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# The intermolecular potential and vibrational relaxation of the Ar-CO system

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# THE INTERMOLECULAR POTENTIAL AND VIBRATIONAL RELAXATION OF THE Ar-CO SYSTEM

A Dissertation
Presented to the
Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Gregory Allen Parker
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This dissertation, by Gregory A. Parker, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the dissertation requirement for the degree of Doctor of Philosophy.

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# I. INTRODUCTION

This dissertation consists of a study of the interactions of CO with Ar. The Ar-CO system is of particular interest since Ar is often used as a buffer gas in the CO laser. Theoretical calculations are essential in understanding the detailed mechanisms which produce the population inversion and subsequent lasing. Calculations of rate constants can be very useful in understanding the experimental rates, i.e., what are the effects of rotational transitions, energy defects, and anharmonicities. Theoretical rates can also be calculated for temperature ranges and transitions which are difficult to obtain experimentally. The results of the present study represent the most extensive calculations ever to be performed on the Ar-CO system.

In order to study the interactions of CO with Ar theoretically, one must first determine the distance, angle, and vibration dependence of the potential energy surface. Because of the large number of electrons in the Ar-CO system, construction of the potential energy surface using conventional self consistant field (SCF) and configuration interaction (CI) methods is extremely time consuming and not feasible using present-day computers. However, the electron gas method developed by Gaydaenkó and Nikulin [1] and Gordon and Kim [2] has been very successful in predicting the short range interactions of other closed shell systems. Modifications suggested by Cohen and Pack [3] and Gordon and Kim [4] to give the correct long range behavior have resulted in potential energy surfaces which are smooth and reasonable everywhere, and it is believed that this model should work reasonably well for the Ar-CO system. Thus, we have programmed the method for atom-molecule [5] and molecule-molecule [6] (Appendix C) interactions and used it to calculate an Ar-CO potential energy surface. Secondly, in the study of the interactions of the Ar-CO system one must perform detailed scattering calculations. Since CO has a small rotational constant, many states are strongly coupled together by the collision, and it is not possible to include enough states in the usual close coupling method [7] to obtain convergence except at very low energies. However, the infinite order sudden approximation (which decouples the rotations) has been shown [8-12] (ref. 9 is Appendix A) to be an excellent approximation when the reduced mass of the system is large, at high relative kinetic energies, small total angular momentum and when the rotational constant of the molecule is small. Hence, it should be very accurate for rotational transitions in the Ar-CO system allowing a much smaller number of vibrationally coupled scattering equations to be solved numerically.

In chapter II we use the electron gas model to calculate the distance, angle, and vibration dependence of the Ar-CO potential energy surface. The electron gas potentials are quite reasonable in the repulsive region but fail to give the correct long range van der Waals behavior. However, modifications suggested by Cohen and Pack[3] and Gordon and Kim [4] to include the long range behavior are used to get potentials which are smooth and reasonable everywhere. To implement the modifications suggested by Cohen and Pack [3] requires one to know the van der Waals interaction coefficients. By using available experimental refractive index data, one can obtain accurate values and error bounds for the van der Waals interaction coefficients using the Padé approximant methods of Langhoff and Karplus [13]. In addition to calculating the Ar-CO interaction, we have used this procedure to calculate the van der Waals interactions of $CO_2$ [14], CO [15] (Appendix E), and NO [16] (Appendix F) with He, Ne, Ar, Kr, Xe, H, Li, Na, K, Rb, Cs, $H_2$, $N_2$, $O_2$, $CO_2$, CO, and NO. Molecules (such as NO) in $\Pi$-electronic states are very interesting since the interaction with an S-state atom breaks the degeneracy of the $\Pi$-state and two potential energy surfaces arise; one for which the electronic wavefunction is symmetric and one for which it is antisymmetric under reflection in the triatomic plane.

In chapter III a simple and yet transparent derivation of the infinite order sudden [8-12] (ref. 9 is Appendix A) approximation is presented. We then obtain simplified expressions for the scattering amplitude and differential cross section in the infinite order sudden [8-12] (ref. 9 is Appendix A) approximation. These expressions should be very useful in determing angle dependent potentials which reproduce differential cross sections obtained from molecular beam experiments.

Even though the sudden approximation is used, the numerical solution of the coupled differential scattering equations involved can be very time consuming. However, by using a combination of the two most popular methods (integral equations [17] and Airy function expansion [18]) we were able to propagate the solution 5 times as fast as either method alone. We used this combination of the two methods to determine the vibrational transition probabilities at several energies and then determined vibrational relaxation rates. Since vibrational relaxation mechanisms are very important (as in theoretical modeling of gas lasers) in molecular energy transfer studies, numerous experimental techniques (such as: relaxation behind shock waves [19], acoustic absorbtion [20], relaxation behind wave expansion [21,22], and laser fluorescence [23]) have been exploited and experimental vibrational relaxation rates are known for many systems. These experimental values are compared with our calculated rates.

In chapter IV we conclude with some remarks on the validity of this approach.

# II. THE Ar-CO INTERMOLECULAR POTENTIAL

In the first section of this chapter we define the coordinate system used and briefly describe the calculation of the short range potential via the electron gas model. In section B this potential is fit to an analytic form. The van der Waals interaction coefficients are determined in section C. Then, in section D the short and long range potentials are joined to give a potential which is smooth and reasonable everywhere. We then make necessary adjustments and compare with available experimental data in section E.

## A. Calculations

We summarize the electron gas model only briefly here, since a detailed description of the model [6,24,25] and our particular method of computation are given in Appendices B, C and D. For the interaction of a vibrating diatomic molecule BC (in this case CO) with an atom A (in this case Ar) the interaction potential using the coordinates of Fig. 1 can be defined as,

$$V(r,\theta,R) = E(r,\theta,R) - E(\infty,\text{any }\theta,R), \tag{2-1}$$

where E is the electronic energy.

To calculate V using the electron gas model one approximates the electron density $\rho$ of the combined system as,

$$\rho = \rho_A + \rho_{BC} \tag{2-2}$$

then calculates the potential energy from functionals of the unperturbed electron densities $\rho_A$ and $\rho_{BC}$. These functionals are the coulombic interaction energy and integrals over the kinetic, exchange, and correlation energy densities of a uniform free electron gas. For the

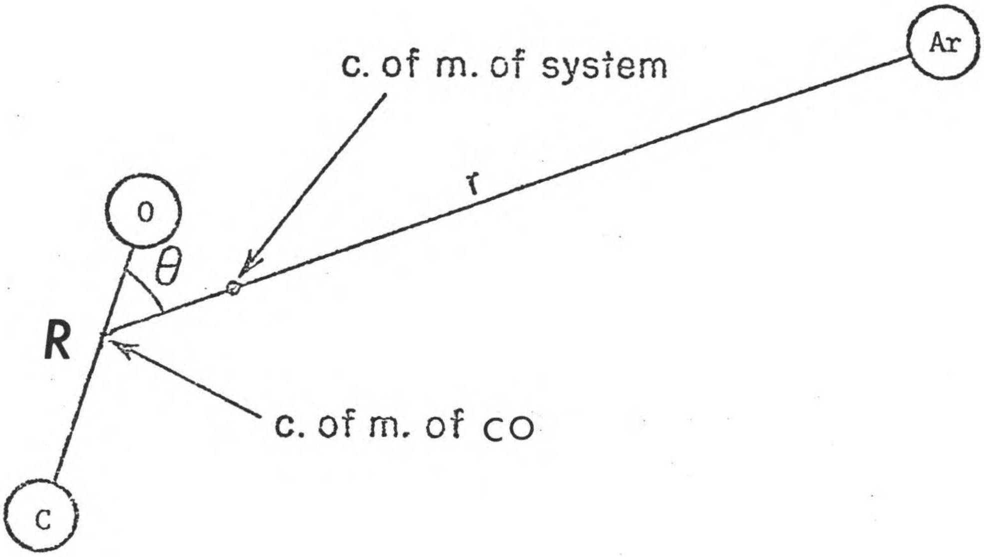

Fig. 1. -- Center-of-mass coordinates used in the Ar-CO potential.

calculation reported herein we have used Rae's [26] exchange energy correction. This self exchange energy correction is simply a multiplicative constant times the exchange energy term (see Appendix B) and is similar to the $\alpha$ in $X\alpha$ [27] calculations.

For subsequent fitting, the resulting interaction potential is written in terms of the electron gas estimates of the Hartree-Fock and correlation energy contributions,

$$V(r,\theta,R) = V_{HF}(r,\theta,R) + V_{COR}(r,\theta,R) \qquad (2\text{-}3)$$

as defined in Appendices B and D.

To calculate the electron densities $\rho_A$ and $\rho_{BC}$ needed we used the Ar SCF wavefunctions of Clementi [28] and the CO SCF wavefunctions of Mclean and Yoshimine [29] (their wavefunctions were calculated at 6 equally spaced values of the vibrational coordinate R ranging from 1.898 a.u. to 2.483 a.u.). The potential energy surface was calculated at 14 equally spaced values of the Ar-CO distance r from r=2.5 a.u. to r=9.0 a.u., the six equally spaced values of R, and 12 values of $x=\cos\theta$, which are the zeros [30] of the 12th Legendre polynomial $P_{12}(x)$, (These points are optimum [31] for expansion of the potential in Legendre polynomials.) for a total of 1008 points. The computational time required was roughly 5.5 hrs. on the CDC 7600 computer or about 20 sec./point on the potential energy surface. Conventional configuration interaction programs would require 10-15 min./point or a total of 170-250 hrs. of CDC 7600 computer time.

Subsequent to the completion of the calculations reported herein, we have found and reported elsewhere [24] (Appendix B) a much faster (~2 sec./point) and more accurate procedure for doing the calculation. Also, since the computational time requirement for the electron gas model is completely independent of the number of electrons in the system, it is possible to calculate the potential between interacting systems with a large number of electrons.

## B. Fitting of the Short Range Potential

Rather than give a large table of all the calculated points on the surface, (1008 points for each of the potential energy contributions $V_{HF}$ and $V_{COR}$) only the parameters that are necessary to accurately fit the potential will be given.

An attempt was made to fit the $V_i$ (i = HF or COR) to the following form,

$$V_i(r,\theta,R) = \sum_{n=0}^{11} \sum_{m=0}^{2} \bar{v}^i_{nm}(r) P_n(x)(R - R_e)^m , \tag{2-4}$$

where $R_e$ is the equilibrium internuclear distance of the CO molecule (2.132 a.u.), but this resulted in oscillations in the $\bar{v}^i_{nm}(r)$ for $n \neq 0$, $m \neq 0$. Consequently, we were unable to find a simple analytic function with a few adjustable parameters to accurately fit the $\bar{v}^i_{nm}(r)$. However, for each of the vibrational separations of CO a fit was obtained using,

$$\begin{aligned} V_i(r,\theta,R_m) &= \sum_{n=0}^{8} \bar{v}^{mi}_n(r)\; P_n(x) \\ &= \sum_{n=0}^{8} \bar{a}^{mi}_n \; e^{-\bar{\alpha}^{mi}_n r - \beta^{mi}_n r^2} \; P_n(x). \end{aligned} \tag{2-5}$$

The parameters used in fitting the surface at the equilibrium position of CO are given in Table 1. This fit resulted in a standard fractional deviation of 2%.

As discussed in the next chapter our main interest was in calculating the vibrational relaxation of CO interacting with Ar, treating the rotations in the Infinite Order Sudden approximation [8-12] (IOS) and using the close-coupling method (CC) for the vibrations. For this one needs only to have an analytic fit of the potential at each angle. The following form was chosen to separately fit the correlation and Hartree-Fock energy contributions,

TABLE 1. -- Parameters used in Eq. (2-5) for fitting the short range Ar-CO electron gas intermolecular potential

i=HARTREE FOCK

| | n=0 | n=1 | n=2 | n=3 | n=4 | n=5 | n=6 |
|---|---|---|---|---|---|---|---|
| $\bar{a}^{mi}_n$ | 15.973 | -.4009 | 31.726 | -4.815 | 17.358 | -1.984 | .930 |
| $\bar{\alpha}^{mi}_n$ | .7536 | .1433 | 1.0909 | 1.0862 | 1.5357 | 1.3922 | 1.3951 |
| $\bar{\beta}^{mi}_n$ | .0910 | .1019 | .0468 | .0277 | 0.0 | 0.0 | 0.0 |

i=CORRELATION

| | n=0 | n=1 | n=2 | n=3 | n=4 | n=5 | n=6 |
|---|---|---|---|---|---|---|---|
| $\bar{a}^{mi}_n$ | -.1826 | .0192 | -.0570 | .0028 | -.0143 | .0022 | .0008 |
| $\bar{\alpha}^{mi}_n$ | .6513 | .6444 | .4865 | .0710 | .7925 | .7684 | .7213 |
| $\bar{\beta}^{mi}_n$ | .0326 | 0.0 | .0354 | .0575 | .0076 | 0.0 | 0.0 |

$$V_i(r,\theta_k,R) = \sum_{m=0}^{2} V_m^{ki}(r)(R - R_e)^m$$

$$= \sum_{m=0}^{2} \left(a_m^{ki}+b_m^{ki}r+c_m^{ki}r^2+d_m^{ki}r^3\right) e^{-\alpha_m^{ki}r} (R - R_e)^m , \qquad (2\text{-}6)$$

for each of the 12 angles. A linear least squares algorithm was used for determining the linear coefficients and a nonlinear search for the nonlinear parameter to minimize the percent deviation rather than the standard deviation. This resulted in a deviation of 1.8%. The results of this fitting procedure are given in Tables 2 and 3.

## C. The Long Range Potential

As noted elsewhere [3] , if one attempts to construct the potential energy surface by simply adding together the $V_{HF}$ and $V_{COR}$ contributions he obtains a potential which does not have the correct long range behavior. This is due to the fact that the electron gas model does not allow for any rearrangement of the electron densities; hence, it does not have induction and dispersion contributions. As is well known [32], the correct long range behavior of the intermolecular potential can be expressed in terms of van der Waals coefficients as,

$$V_{L.R}(r,x) = - C_6/r^6 - C_7/r^7 - C_8/r^8 - \dots$$

$$= - \frac{1}{r^6}\left[C_6(0)+C_6(2)P_2(x)\right] - \frac{1}{r^7}\left[C_7(1)P_1(x)+C_7(3)P_3(x)\right]$$

$$- \frac{1}{r^8}\left[C_8(0)+C_8(2)P_2(x) + C_8(4)P_4(x)\right] - \dots \qquad (2\text{-}7)$$

We have determined and reported elsewhere [15] (Appendix E) the $C_6$ coefficients of CO interacting with several atoms and molecules including Ar, and, for completeness, the resulting $C_6$ coefficients for the interactions of CO are given in Table 4 along with higher order coefficients determined in the following subsections. The notation and method

TABLE 2. -- Parameters used in Eq. (2-6) for fitting the Ar-CO electron gas Hartree-Fock contribution at each angle (k labels the angle)

m = 0 i = HARTREE-FOCK

| | k = 1 | k = 2 | k = 3 | k = 4 | k = 5 | k = 6 | k = 7 | k = 8 | k = 9 | k = 10 | k = 11 | k = 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\alpha_m^{ki}$ | 1.875 | 1.788 | 1.775 | 1.774 | 1.235 | 1.207 | 1.211 | 1.365 | 1.443 | 1.903 | 1.947 | 2.002 |
| $a_m^{ki}$ | 3865 | 1736 | 785.6 | 308.9 | 30.75 | 32.77 | 37.78 | 38.95 | 37.21 | 195.8 | 629.9 | 1408 |
| $b_m^{ki}$ | -2539 | -1132 | -517.3 | -199.9 | 1.965 | -6.269 | -8.524 | 2.201 | 18.37 | -92.90 | -390.9 | -952.6 |
| $c_m^{ki}$ | 577.6 | 272.3 | 136.7 | 62.24 | -.6521 | .1716 | .4807 | -1.924 | -5.231 | 57.41 | 141.2 | 289.6 |
| $d_m^{ki}$ | -34.80 | -17.88 | -9.539 | -4.770 | .0548 | .0134 | 0 | .1333 | .3043 | -5.476 | -11.57 | -21.80 |

m = 1 i = HARTREE-FOCK

| | k = 1 | k = 2 | k = 3 | k = 4 | k = 5 | k = 6 | k = 7 | k = 8 | k = 9 | k = 10 | k = 11 | k = 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\alpha_m^{ki}$ | 1.984 | 1.941 | 1.944 | 1.309 | 1.383 | 1.287 | 1.275 | 1.717 | 1.768 | 1.836 | 1.916 | 2.012 |
| $a_m^{ki}$ | 7480 | 3126 | 993.3 | -17.35 | -27.39 | -21.51 | -22.44 | 14.19 | 72.40 | 304.6 | 1023 | 2554 |
| $b_m^{ki}$ | 1709 | -2042 | -717.5 | 12.55 | 13.06 | 9.398 | 10.67 | -31.53 | -73.72 | -225.3 | -686.2 | -1694 |
| $c_m^{ki}$ | 986.3 | 454.7 | 177.9 | -2.118 | -1.886 | -1.279 | -1.491 | 12.24 | 25.29 | 65.96 | 175.2 | 405.1 |
| $d_m^{ki}$ | -57.00 | -27.79 | -11.55 | .1047 | .0860 | .0557 | .0648 | -.9870 | -2.036 | -4.838 | -11.97 | -26.08 |

TABLE 2. -- Continued

|  |  |  |  |  | m = 2 | i = HARTREE-FOCK |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | k = 1 | k = 2 | k = 3 | k = 4 | k = 5 | k = 6 | k = 7 | k = 8 | k = 9 | k = 10 | k = 11 | k = 12 |
| $\alpha_m^{ki}$ | 2.257 | 2.387 | 2.328 | 1.146 | .7817 | 1.477 | 1.513 | 1.492 | 1.046 | 1.607 | 1.853 | 2.031 |
| $a_m^{ki}$ | -2798 | -14739 | -4641 | -5.769 | -1.921 | 15.56 | 17.10 | 9.639 | -5.159 | 24.62 | 478.7 | 1855 |
| $b_m^{ki}$ | 5124 | 14023 | 4135 | 1.657 | .7289 | -11.66 | -12.95 | -9.244 | 2.326 | -21.60 | -307.9 | 1142 |
| $c_m^{ki}$ | -1921 | -4214 | -1205 | -.1112 | -.0906 | 2.285 | 2.569 | 2.073 | -.3166 | 6.052 | 67.03 | 232.4 |
| $d_m^{ki}$ | 218.2 | 417.9 | 116.4 | 0 | .0037 | -.1309 | -.1480 | -.1275 | .0136 | -.4219 | -4.071 | -12.69 |

TABLE 3. -- Parameters used in Eq. (2-6) for fitting the Ar-CO electron gas correlation energy contribution at each angle (k labels the angle)

m = 0 i = CORRELATION

| | k = 1 | k = 2 | k = 3 | k = 4 | k = 5 | k = 6 | k = 7 | k = 8 | k = 9 | k = 10 | k = 11 | k = 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\alpha_m^{ki}$ | .9676 | .9450 | .9441 | .9485 | .9646 | .9086 | .8898 | 1.036 | 1.038 | 1.040 | 1.044 | 1.051 |
| $a_m^{ki}$ | .1452 | .0637 | -.0010 | -.0687 | -.1138 | -.1517 | -.1793 | -.1540 | -.1691 | -.1845 | -.2013 | -.2107 |
| $b_m^{ki}$ | -.3248 | -.2508 | -.1865 | -.1270 | -.0911 | -.0555 | -.0384 | -.1015 | -.1176 | -.1409 | -.1653 | -.1866 |
| $c_m^{ki}$ | .0245 | .0208 | .0163 | .1192 | .0094 | .0108 | .0099 | .0107 | .0122 | .0142 | .0164 | .0180 |
| $d_m^{ki}$ | 0 | 0 | 0 | 0 | 0 | -.0004 | -.0005 | 0 | 0 | 0 | 0 | 0 |

m = 1 i = CORRELATION

| | k = 1 | k = 2 | k = 3 | k = 4 | k = 5 | k = 6 | k = 7 | k = 8 | k = 9 | k = 10 | k = 11 | k = 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\alpha_m^{ki}$ | 1.584 | 1.347 | 1.334 | 1.306 | 1.195 | .9167 | .8707 | .8763 | .9094 | .9487 | .9841 | 1.015 |
| $a_m^{ki}$ | .2476 | -.5230 | -.2970 | -.0885 | .0419 | .0610 | .0538 | .0530 | .0540 | .0504 | .0409 | .0343 |
| $b_m^{ki}$ | 2967 | .6258 | .3922 | .1694 | .0188 | -.0269 | -.0281 | -.0360 | -.0506 | -.0702 | -.0916 | -.1114 |
| $c_m^{ki}$ | .1977 | -.2346 | -.1477 | -.0680 | -.0151 | .0020 | .0021 | .0028 | .0040 | .0056 | .0073 | .0085 |
| $d_m^{ki}$ | -.0850 | .0139 | .0099 | .0050 | .0012 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

TABLE 3. -- Continued

m = 2 i = CORRELATION

| | k = 1 | k = 2 | k = 3 | k = 4 | k = 5 | k = 6 | k = 7 | k = 8 | k = 9 | k = 10 | k = 11 | k = 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\alpha_m^{ki}$ | 1.431 | 1.464 | .9621 | .9013 | .8867 | .8871 | .9350 | 1.016 | 1.291 | 1.384 | 1.433 | 1.438 |
| $a_m^{ki}$ | 1.821 | 1.088 | -.0255 | -.0214 | -.0229 | -.0166 | -.0148 | -.0131 | .0106 | .1497 | .3244 | .5018 |
| $b_m^{ki}$ | -1.508 | -.9964 | .0470 | .0320 | .0279 | .0221 | .0221 | .0245 | .0076 | -.1105 | -.2715 | -.4127 |
| $c_m^{ki}$ | .4490 | .3443 | -.0130 | -.0078 | -.0063 | -.0050 | -.0050 | -.0057 | .0038 | .0388 | .0843 | .1162 |
| $d_m^{ki}$ | -.0513 | -.0428 | .0008 | .0005 | .0004 | .0003 | .0003 | .0003 | -.0015 | -.0060 | -.0119 | -.0151 |

TABLE 4. -- van der Waals interaction coefficients through $C_8$ for the interactions of CO with various partners

| Coefficient | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| $C_6(0)$ | 11.2 ± .8 | 23.8 ± 2.5 | 78.2 ± 7.6 | 111 ± 12 | 192 ± 25 |
| $C_6(2)$ | .94 ± .27 | 1.99 ± .65 | 6.55 ± 2.06 | 7.3 ± 3.0 | 16.1 ± 5.7 |
| $C_7(1,\mathrm{ind})$ | .41 ± .06 | .79 ± .12 | 3.28 ± .48 | 4.95 ± .73 | 8.1 ± 1.2 |
| $C_7(1,\mathrm{dis})$ | 2.1 ± 1.6 | 4.4 ± 3.7 | 14. ± 12 | 20. ± 17. | 35 ± 31 |
| $C_7(1)$ | 2.5 ± 1.7 | 5.1 ± 3.8 | 18 ± 12 | 25. ± 18 | 42 ± 32 |
| $C_7(3,\mathrm{ind})$ | .27 ± .04 | .53 ± .08 | 2.19 ± .32 | 3.30 ± .48 | 5.38 ± .79 |
| $C_7(3,\mathrm{dis})$ | .13 ± .15 | .29 ± .35 | .94 ± 1.1 | 1.33 ± 1.6 | 2.30 ± 2.9 |
| $C_7(3)$ | .41 ± .19 | .81 ± .42 | 3.12 ± 1.4 | 4.63 ± 2.1 | 7.69 ± 3.7 |
| $\Delta_{44}(0,2,\mathrm{ind})$ | 5.8 ± 1.2 | 11. ± 2 | 46 ± 10 | 70 ± 15 | 114 ± 24 |
| $\Delta_{44}(0,1,\mathrm{dis})$ | 54. ± 5.0 | 128 ± 21 | 688 ± 105 | 1060 ± 174 | 2402 ± 448 |
| $\Delta_{44}(0,2,\mathrm{dis})$ | 101 ± 25 | 215 ± 62 | 708 ± 197 | 1004 ± 293 | 1738 ± 552 |
| $\Delta_{44}(0,1,\mathrm{ind})$ | .015 ± .001 | .039 ± .004 | .292 ± .031 | .477 ± .049 | .776 ± .076 |
| $C_8(0)$ | 161.4 ± 31 | 354 ± 85 | 1442 ± 312 | 2135 ± 482 | 4254 ± 1025 |
| $\Delta_{44}(2,2,\mathrm{ind})$ | 6.6 ± 1.4 | 12.7 ± 2.7 | 53 ± 11 | 80 ± 17 | 130 ± 28 |
| $\Delta_{44}(2,1,\mathrm{dis})$ | 3.6 ± 1.1 | 8.5 ± 3.3 | 46 ± 18 | 71 ± 28 | 160 ± 68 |
| $\Delta_{44}(2,2,\mathrm{dis})$ | 10.4 ± 4.4 | 22. ± 10 | 72 ± 34 | 103 ± 49 | 178 ± 90 |
| $2\Delta_{35}(2,\mathrm{dis})$ | 40.0 ± 21.4 | 85 ± 49 | 279 ± 159 | 397 ± 232 | 686 ± 424 |
| $2\Delta_{35}(2,\mathrm{ind})$ | 1.4 ± .4 | 2.8 ± .8 | 12 ± 3 | 17 ± 5 | 28 ± 8 |
| $\Delta_{44}(2,1,\mathrm{ind})$ | .012 ± .001 | .031 ± .003 | .23 ± .02 | .38 ± .04 | .62 ± .06 |
| $C_8(2)$ | 62 ± 28 | 131 ± 67 | 462 ± 225 | 668 ± 332 | 1183 ± 618 |
| $\Delta_{44}(4,2,\mathrm{ind})$ | 5.0 ± 1.1 | 9.5 ± 2.0 | 39.7 ± 8.5 | 60.0 ± 12.8 | 98 ± 21 |
| $\Delta_{44}(4,2,\mathrm{dis})$ | .49 ± .30 | 1.0 ± .71 | 3.4 ± 2.3 | 4.9 ± 3.3 | 8 ± 6 |
| $2\Delta_{35}(4,\mathrm{dis})$ | 2.4 ± 1.8 | 5.2 ± 4.2 | 17.0 ± 13 | 24.1 ± 20 | 42 ± 35 |

TABLE 4. -- Continued

| Coefficient | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| $2\Delta_{35}(4,\mathrm{ind})$ | .80 ± .23 | 1.5 ± .4 | 6.4 ± 1.8 | 9.7 ± 2.8 | 15.8 ± 4.5 |
| $C_8(4)$ | 8.7 ± 3 | 17 ± 7 | 67 ± 26 | 99 ± 39 | 164 ± 67 |

is that of Pack [32] in his studies of van der Waals coefficients for atom-linear molecule systems, except that we denote the atom by A and the molecule by BC.

### i. The $C_7$ Coefficient

As shown elsewhere [32] the $C_7$ coefficients can be written in terms of induction and dispersion contributions,

$$C_7(n) = C_7(n,\mathrm{ind}) + C_7(n,\mathrm{dis}), \quad n = 1 \text{ or } 3. \tag{2-8}$$

The induction contributions are

$$C_7(1,\mathrm{ind}) = \frac{18}{5}\,\mu(BC)\,\theta(BC)\,\alpha(A) \tag{2-9}$$

and

$$C_7(3,\mathrm{ind}) = \frac{12}{5}\,\mu(BC)\,\theta(BC)\,\alpha(A), \tag{2-10}$$

where $\alpha(A)$ is the polarizability of the atom A, and $\mu(BC)$ and $\theta(BC)$ are the permanent dipole and quadrupole moments of the molecule BC.

Using the labels n and $\nu$ to identify the electronic states of A and BC, respectively, the dispersion contributions can be written in terms of the generalized oscillator strengths,

$$f^{\mu}_{0\nu}(\ell,\ell') = 2\,\varepsilon_\nu \langle\nu|Q^{\mu}_{\ell}|0\rangle^{*} \langle\nu|Q^{\mu}_{\ell'}|0\rangle \tag{2-11}$$

as

$$C_7(1,\mathrm{dis}) = \frac{9}{5}\sum_{\nu,n} \frac{f^{0}_{0n}(1,1)}{\varepsilon_n\varepsilon_\nu(\varepsilon_n+\varepsilon_\nu)} \left[f^{0}_{0\nu}(1,2) + \sqrt{3}\, f^{1}_{0\nu}(1,2)\right] \tag{2-12}$$

and

$$C_7(3,\mathrm{dis}) = \frac{6}{5} \sum_{\nu,n}{}'' \frac{f^o_{on}(1,1)}{\varepsilon_n \varepsilon_\nu (\varepsilon_n + \varepsilon_\nu)} \left[ f^o_{o\nu}(1,2) - \frac{2}{\sqrt{3}} f^1_{o\nu}(1,2) \right] \tag{2-13}$$

where $\varepsilon_\nu$ are the electronic excitation energies, and the double prime on the sum implies omission of all the terms with either $n = 0$ or $\nu = 0$. The multipole moment operators in Eq. (2-11) are given by,

$$Q^m_\ell(BC) = [4\pi/(2\ell+1)]^{1/2} \sum_{i \varepsilon BC} Z_i \, r_i^\ell \, Y^m_\ell(\theta_i, \phi_i), \tag{2-14}$$

where the summation is over all the electrons and nuclei belonging to BC, the coordinates are measured from the center of mass of BC, and the z-axis is taken to be along the diatomic $\underset{\sim}{R}$ axis. Similar formulas hold for atom A. Upon replacing the arithmetic mean $(\varepsilon_\nu + \varepsilon_n)/2$ by the geometric mean $(\varepsilon_\nu \varepsilon_n)^{1/2}$ in Eqs. (2-12) and (2-13), one obtains good approximations to the van der Waals coefficients,

$$C_7(1,\mathrm{dis}) \approx \frac{9}{10} S_A\left(1,1,-\tfrac{3}{2}\right) \left[ S^o_{BC}\left(1,2,-\tfrac{3}{2}\right) + \sqrt{3}\, S^1_{BC}\left(1,2,-\tfrac{3}{2}\right) \right] \tag{2-15}$$

and

$$C_7(3,\mathrm{dis}) \approx \frac{6}{10} S_A\left(1,1,-\tfrac{3}{2}\right) \left[ S^o_{BC}\left(1,2,-\tfrac{3}{2}\right) - \frac{2}{\sqrt{3}} S^1_{BC}\left(1,2,-\tfrac{3}{2}\right) \right] \tag{2-16}$$

in terms of the generalized oscillator strength sums,

$$S^\mu_{BC}(\ell,\ell',k) = \sum_\nu{}' f^\mu_{o\nu}(\ell,\ell')\,\varepsilon^k_\nu, \tag{2-17}$$

where the prime on the sum implies omission of the $\nu = 0$ term. For the spherical atom the $S^\mu_A$ are independent of $\mu$. Using an oscillator model in which the center of charge is displaced by a distance of $z_o$ from the center of mass, one obtains an expression for the $S^{\mu}_{BC}(1,2,k)$ in terms of $S^{\mu}_{BC}(1,1,k)$ as [32],

$$S^{o}_{BC}(1,2,k) = 2\ z_o S^{o}_{BC}(1,1,k) \tag{2-18}$$

and

$$S^{1}_{BC}(1,2,k) = \sqrt{3}\ z_o S^{1}_{BC}(1,1,k). \tag{2-19}$$

Since the $C_6$ coefficients are expressed in these same quantities [32]

$$C_6(0,\text{dis}) \approx \frac{1}{4} S_A\left(1,1,-\frac{3}{2}\right) \left[S^{o}_{BC}\left(1,1,-\frac{3}{2}\right) + 2\, S^{1}_{BC}\left(1,1,-\frac{3}{2}\right)\right] \tag{2-20}$$

and

$$C_6(2,\text{dis}) \approx \frac{1}{4} S_A\left(1,1,-\frac{3}{2}\right) \left[S^{o}_{BC}\left(1,1,-\frac{3}{2}\right) - S^{1}_{BC}\left(1,1,-\frac{3}{2}\right)\right] \tag{2-21}$$

the $C_7$ coefficients can be written in terms of the $C_6$ coefficients as,

$$C_7(1,\text{dis}) \approx 6\ z_o\left[C_6(0,\text{dis}) + \frac{1}{5}\, C_6(2,\text{dis})\right] \tag{2-22}$$

and

$$C_7(3,\text{dis}) \approx \frac{24\ z_o}{5}\ C_6(2,\text{dis}). \tag{2-23}$$

### ii. The $C_8$ Coefficients

The procedure used in determining the $C_8$ coefficient

$$C_8 = C_8(0) + C_8(2)\ P_2(x) + C_8(4)\ P_4(x) \tag{2-24}$$

is the same as that given by Pack [32], and it is recommended that the reader refer to that paper for details. We only give the formulas that are necessary in its construction. Again each of the coefficients in Eq. (2-24) can be written in terms of induction and dispersion contributions,

$$C_8(L) = C_8(L,\mathrm{ind}) + C_8(L,\mathrm{dis}). \tag{2-25}$$

It is convenient to express the induction and dispersion contributions as

$$C_8(L,\mathrm{ind}) = 2\,\Delta_{35}(L,\mathrm{ind}) + \sum_{\ell=1}^{2} \Delta_{44}(L,\ell,\mathrm{ind}) \tag{2-26}$$

and

$$C_8(L,\mathrm{dis}) = 2\,\Delta_{35}(L,\mathrm{dis}) + \sum_{\ell=1}^{2} \Delta_{44}(L,\ell,\mathrm{dis}). \tag{2-27}$$

The induction terms are,

$$\Delta_{35}(0,\mathrm{ind}) = 0, \tag{2-28}$$

$$\Delta_{35}(2,\mathrm{ind}) = \frac{18}{7}\,\mu(BC)\overline{Q}_3(BC)\alpha(A), \tag{2-29}$$

$$\Delta_{35}(4,\mathrm{ind}) = \frac{10}{7}\,\mu(BC)\overline{Q}_3(BC)\alpha(A), \tag{2-30}$$

$$\Delta_{44}(0,1,\mathrm{ind}) = \frac{5}{2}\,\mu^2(BC)q(A), \tag{2-31}$$

$$\Delta_{44}(0,1,\mathrm{ind}) = 2\,\mu^2(BC)q(A), \tag{2-32}$$

$$\Delta_{44}(4,1,\mathrm{ind}) = 0\,, \tag{2-33}$$

$$\Delta_{44}(0,2,\mathrm{ind}) = \frac{3}{2}\,\theta^2(\mathrm{BC})\alpha(\mathrm{A}), \tag{2-34}$$

$$\Delta_{44}(2,2,\mathrm{ind}) = \frac{12}{7}\,\theta^2(\mathrm{BC})\alpha(\mathrm{A}), \tag{2-35}$$

and

$$\Delta_{44}(4,2,\mathrm{ind}) = \frac{9}{7}\,\theta^2(\mathrm{BC})\alpha(\mathrm{A}), \tag{2-36}$$

where $\overline{Q}_3(\mathrm{BC})$ is the permanent octupole moment of the molecule and $q(\mathrm{A})$ is the quadrupole polarizability of A. By replacing the arithmetic by the geometric mean, Pack [32] was able to express the dispersion contributions as

$$\Delta_{35}(2,\mathrm{dis}) \approx \frac{12}{7}\,a\left(-\frac{3}{2}\right)\,\Delta_{44}(0,2,\mathrm{dis}), \tag{2-37}$$

$$\Delta_{35}(4,\mathrm{dis}) \approx \frac{20}{21}\,b\left(-\frac{3}{2}\right)\,\Delta_{44}(0,2,\mathrm{dis}), \tag{2-38}$$

$$\Delta_{44}(0,1,\mathrm{dis}) \approx \frac{1}{2}\,C_6(0,\mathrm{dis},\mathrm{A},\mathrm{B})\;C_8(\mathrm{A},\mathrm{A})/C_6(\mathrm{A},\mathrm{A}), \tag{2-39}$$

$$\Delta_{44}(2,1,\mathrm{dis}) \approx \frac{4}{5}\,d\left(-\frac{3}{2}\right)\Delta_{44}(0,1,\mathrm{dis}), \tag{2-40}$$

$$\Delta_{44}(0,2,\mathrm{dis}) \approx \frac{1}{2}\,C_6(0,\mathrm{dis},\mathrm{A},\mathrm{B})\;C_8(0,\mathrm{dis},\mathrm{B},\mathrm{B})/C_6(0,\mathrm{dis},\mathrm{B},\mathrm{B}), \tag{2-41}$$

$$\Delta_{44}(2,2,\mathrm{dis}) \approx \frac{8}{7}\,e\left(-\frac{3}{2}\right)\,\Delta_{44}(0,2,\mathrm{dis}), \tag{2-42}$$

$$\Delta_{44}(4,2,\mathrm{dis}) \approx \frac{6}{7}\,g\left(-\frac{3}{2}\right)\,\Delta_{44}(0,2,\mathrm{dis}). \tag{2-43}$$

Here,

$$a(k) = \left[S^{\mathrm{o}}_{\mathrm{BC}}(1,1,k) - S^{1}_{\mathrm{BC}}(1,1,k)\right] / \left[S^{\mathrm{o}}_{\mathrm{BC}}(1,1,k) + 2\,S^{1}_{\mathrm{BC}}(1,1,k)\right], \tag{2-44}$$

$$b(k) = \left[S^{o}_{BC}(2,2,k)+S^{1}_{BC}(2,2,k)-2\ S^{2}_{BC}(2,2,k)\right] /$$

$$\left[S^{o}_{BC}(2,2,k)+2\ S^{1}_{BC}(2,2,k)+2\ S^{2}_{BC}(2,2,k)\right], \tag{2-45}$$

$$d(k) = \left[S^{o}_{BC}(2,2,k)-\frac{4}{3}\ S^{1}_{BC}(2,2,k)+\frac{1}{3}\ S^{2}_{BC}(2,2,k)\right] /$$

$$\left[S^{o}_{BC}(2,2,k)+2\ S^{1}_{BC}(2,2,k)+2\ S^{2}_{BC}(2,2,k)\right], \tag{2-46}$$

$$e(k) = \left[S^{o}_{BC}(1,3,k)+2\left(\frac{2}{3}\right)^{1/2}\ S_{BC}(1,3,k)\right] /$$

$$\left[S^{o}_{BC}(2,2,k)+2\ S^{1}_{BC}(2,2,k)+2\ S^{2}_{BC}(2,2,k)\right], \tag{2-47}$$

and

$$g(k) = \left[S^{o}_{BC}(1,3,k)-\left(\frac{3}{2}\right)^{1/2}\ S_{BC}(1,3,k)\right] /$$

$$\left[S^{o}_{BC}(2,2,k)+2\ S^{1}_{BC}(2,2,k)+2\ S^{2}_{BC}(2,2,k)\right]. \tag{2-48}$$

Pack [32] obtains values for the quantities in these equations by use of the oscillator model. The results for the interactions of CO with several atoms are given in Table 4. The error estimates may be small, but we feel that they are reasonable.

### D. Addition of the van der Waals Tail

We can obtain a potential which has the correct behavior at both short and long range by using a simple generalization of the method used by Cohen and Pack [3] for atoms. This can easily be done by letting,

$$V^{kCOR}_{m}(r) = \begin{cases} V^{kCOR}_{m}(r) & , r \leqslant r^{k}_{m} \\ V_{L.R.}(r,x_{k})A_{m} + B^{k}_{m}V^{kCOR}_{m}(r) & , r > r^{k}_{m} \end{cases} \tag{2-49}$$

where the $r_m^k$ are the points where the logarithmic derivatives (with respect to r) of the two forms are equal (this insures that the first derivative is continuous). The $B_m^k$ were chosen to make the potential continuous at $r_m^k$ and hence continuous everywhere. In order to get a rough estimate of the vibrational dependence of the long range interaction the $A_m$ were chosen to be the angle average of the vibrational dependence of the short range potential at the point where the logarithmic derivative of the short and long range potentials are equal, i.e.,

$$A_m = \sum_{k=1}^{12} w_k V_m^{kcor}(r_m^k) / \sum_{k=1}^{12} w_k V_o^{kcor}(r_o^k) \tag{2-50}$$

where the $w_k$ are the weights [30] associated with a 12-point Gauss-Legendre quadrature. We could have obtained a more accurate long range vibrational dependence of the induction terms by using expansions of the dipole, quadrupole, and octupole moments in powers of $(R-R_e)$ but did not because the exact long range vibrational dependence should have little effect on the vibrational relaxation of CO for reasons discussed in the next chapter. Also the largest contributions are usually the dispersion terms, whose vibrational dependence would have been difficult to obtain accurately. The results of the above procedure are given in Table 5.

### E. Results and Comparison with Experiment

In this section we compare the second interaction virial coefficients obtained from our calculated potential with the experimental values of Brewer [33] and also compare our spherically averaged potential with a spherical potential of Jordan et al. [34] which was inferred from their high energy scattering data. Vibrational relaxation data will be used to further test the potential in chapter III.

We determined the interaction second virial coefficients of the Ar-CO system at the equilibrium position of CO using [35]

$$B(T) = \pi \int_0^\infty r^2 dr \int_{-1}^{1} dx \{1-\exp[-V(r,x,R_e)/kT]\} \tag{2-51}$$

TABLE 5. -- Parameters used in Eq. (2-49) for smoothly joining the short range electron gas correlation estimate to the long range van der Waals tail

|  | $r_m^k$ |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m k | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| 0 | 6.819 | 6.729 | 6.626 | 6.484 | 6.297 | 6.113 | 6.008 | 5.995 | 6.029 | 6.072 | 6.107 | 6.129 |
| 1 | 6.347 | 6.294 | 6.193 | 6.117 | 6.427 | 6.982 | 7.060 | 6.972 | 6.848 | 6.725 | 6.626 | 6.574 |
| 2 | 7.636 | 7.553 | 7.844 | 8.136 | 8.266 | 8.337 | 8.416 | 8.340 | 8.018 | 7.548 | 7.273 | 7.203 |

|  | $B_m^k$ |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m k | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| 0 | .6137 | .5628 | .4625 | .2997 | .0763 | -.1411 | -.2444 | -.2113 | -.1045 | .0006 | .0759 | .1165 |
| 1 | .8863 | .8476 | .7386 | .4541 | .1050 | .3874 | .6443 | .7586 | .8132 | .8416 | .8566 | .8638 |
| 2 | .9881 | .9830 | .9730 | .9584 | .9426 | .9252 | .9110 | .9183 | .9398 | .9577 | .9672 | .9715 |

| $A_m$ |  |  |
|---|---|---|
| m = 0 | m = 1 | m = 2 |
| 1.0 | .3084 | .0763 |

where k is Boltzmann's constant and T is the absolute temperature. Vibrational averaging of the virial coefficients should be unnecessary for the temperature range (T=100-300$^\circ$K) of concern to us because the CO vibrational motion contributes little at these temperatures. In evaluation of Eq. (2-51), we used a 48-point Gauss-laguerre quadrature for the r integration and a 48-point Gauss-Legendre quadrature for the x=cosθ integration. The results (in cc/mole) are shown in Fig. 2, where one sees that our virial coefficients (--- dashed line) are too large. This implies that our short range potential is too repulsive or the long range potential is not attractive enough. Had Rae's [26] self exchange energy correction not been used, we may have obtained better agreement. For some systems this correction seems to improve the agreement but not for others. We now believe that this self exchange energy correction (which is similar to the α in Xα [27] calculations) should be varied as an empirical parameter to fit the experimental second virial coefficients or other data. Since we determined only the Hartree-Fock estimate which is the sum of the exchange, kinetic, and coulombic energies

$$V_{HF} = V_{EX} + V_{KIN} + V_{COUL} \tag{2-52}$$

we had no way of doing this, so that it was necessary to scale the Hartree-Fock and short range correlation electron gas estimates to fit the experimental virial coefficients. An excellent agreement (percent deviation of 0.2%) was obtained using scaling factors of 0.77 and 2.62, respectively for the Hartree-Fock and short range correlation energies. Our new potential is now given by

$$V_{(r,\theta,R)} = 0.77\ V_{HF}(r,\theta,k) + \overline{V}_{COR}(r,\theta,R) \tag{2-53}$$

where

$$V_{COR}(r,\theta_R,R) = \sum_{m=0}^{2} \overline{V}_m^{kCOR}(r)\ (R-R_e)^m \tag{2-54}$$

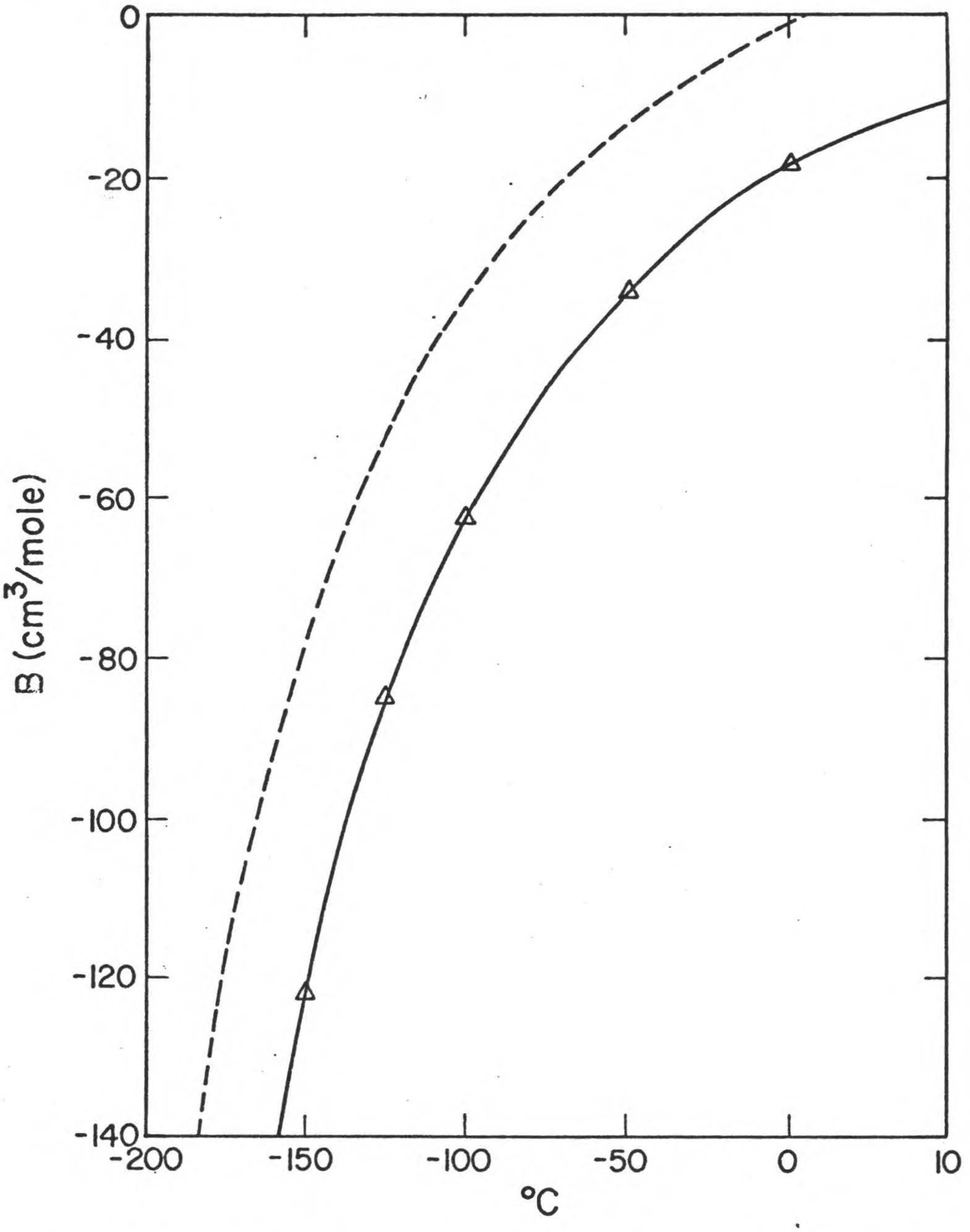

Fig. 2. -- Comparison of calculated and experimental interaction second virial coefficients. Dashed line --- before adjustment, Solid line —— after adjustment. Triangles Δ are the experimental values of Brewer ref. 14.

and

$$\bar{V}_m^{kCOR} = \begin{cases} 2.62\ \bar{V}_m^{kCOR}(r) & r \leq r_m^k \\ V_{L.R.}(r,\theta_k)A_m + (1.62 + B_m^k)V_m^{kCOR}(r) & r \geq r_m^k \end{cases} \qquad (2\text{-}55)$$

A plot of our new virial coefficients (— solid line) is also shown in Fig. 2 and, as can be seen, they are in excellent agreement (within experimental error) with the experimental values of Brewer.

In Fig. 3 we compare our spherically averaged potential with a spherical potential of Jordan et al. [34] . Their potential was obtained from fitting their high energy Ar-CO scattering data to a spherical potential of the form

$$V(r) = A/r^{\gamma} \qquad 2.09\ \text{Å} < r < 2.68\ \text{Å}. \qquad (2\text{-}56)$$

They obtained $A = 551$ and $\gamma = 6.99$ with the potential given in e.v. The agreement is excellent considering that a spherical potential fit to scattering data need not be the spherical average of the true potential.

The contour plot in Fig. 4 is that of the Ar-CO intermolecular potential at the vibrational equilibrium position of CO $V(r,\theta,R_e)$. The values of the contours are given in Table 6. As can be seen the potential has a minimum of roughly -.0004 a.u. (130°K) deep. The -.0004 a.u. contour extends almost completely around the CO molecule which indicates that the minimum is very flat.

The contours shown in Fig. 5 are of the vibrational derivative of the potential at the equilibrium position of CO,

$$\frac{\partial}{\partial R} V(r,\theta,R)\Big|_{R=R_e} \qquad (2\text{-}57)$$

where the value of the labeled contours are given in Table 7.

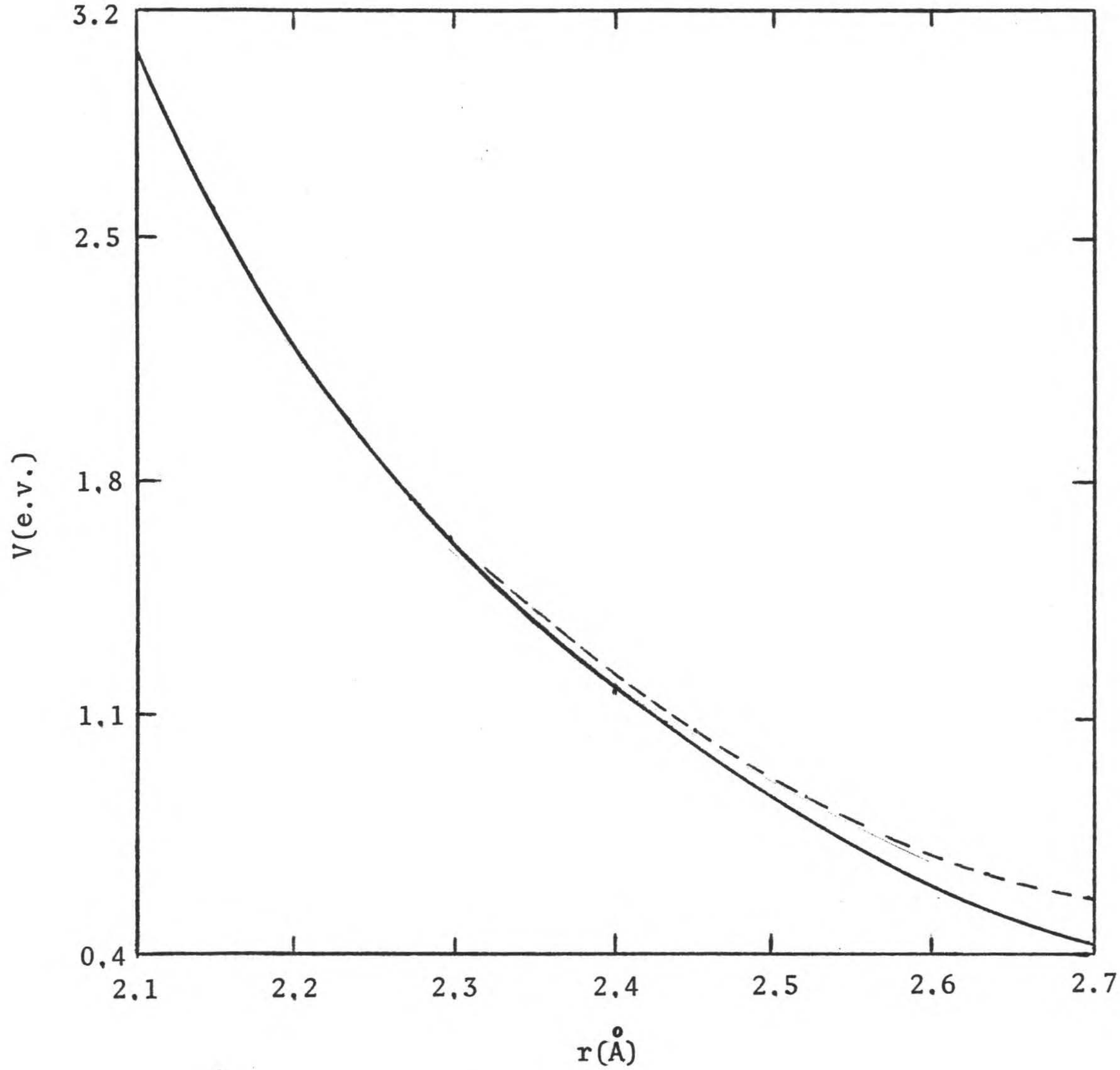

Fig. 3. -- Comparison of our spherically averaged potential with a spherical potential fit to high energy scattering data. Solid line —— result of present calculations. Dashed line --- the spherical potential of Jordan et. al. ref.

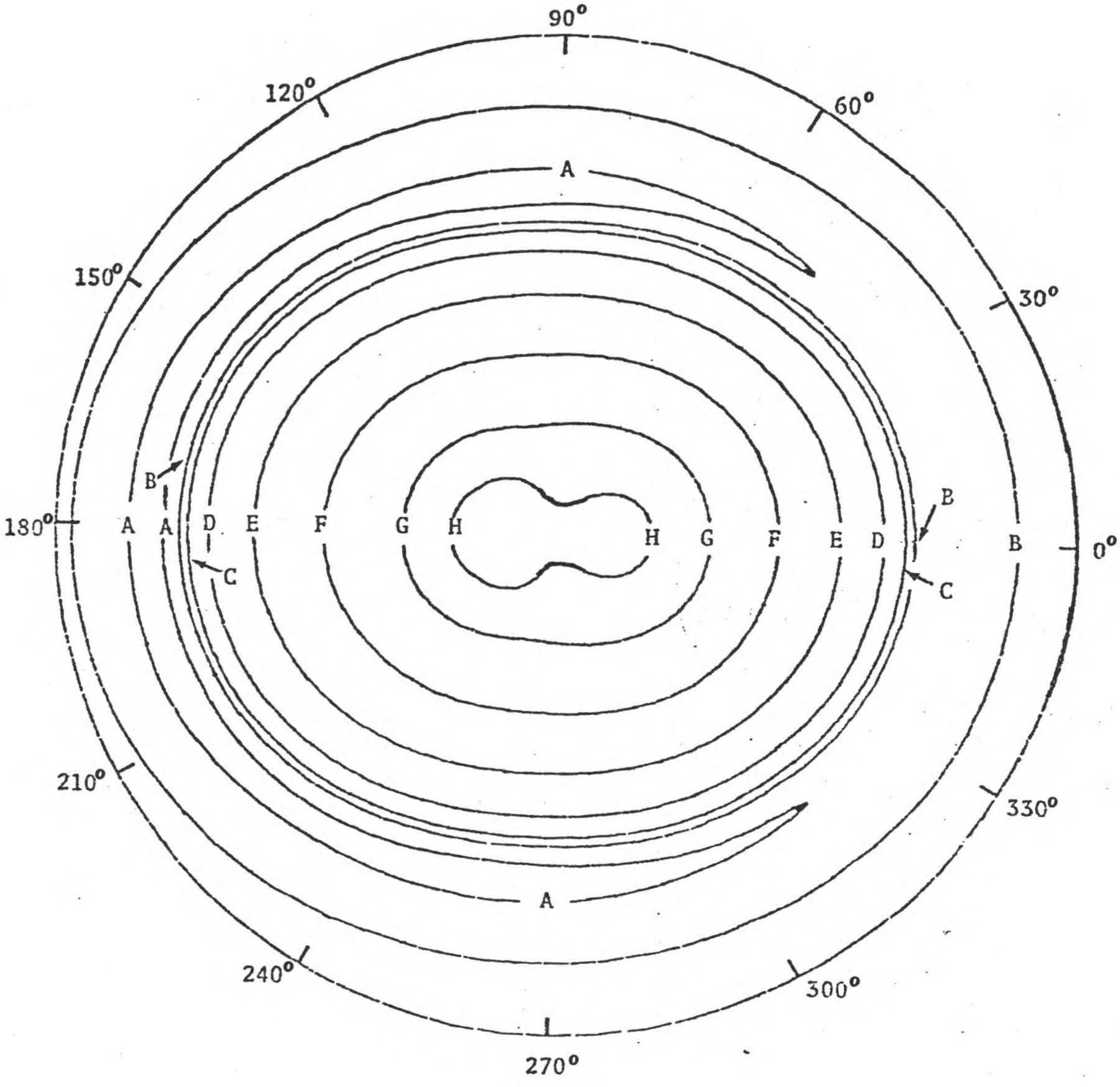

Fig. 4. -- Contour plot of the Ar-CO potential at the vibrational equilibrium position of CO. Values of the contours are given in Table 6.

TABLE 6. -- Values of the contours used in Fig. 4

| Identifaction | Contour Value (a.u.) |
|---|---|
| A - A - A - A | -.0004 |
| B - B - B - B | -.0002 |
| C - C - C - C | .0000 |
| D - D - D - D | .0010 |
| E - E - E - E | .0100 |
| F - F - F - F | .1000 |
| G - G - G - G | 1.0000 |
| H - H - H - H | 10.0000 |

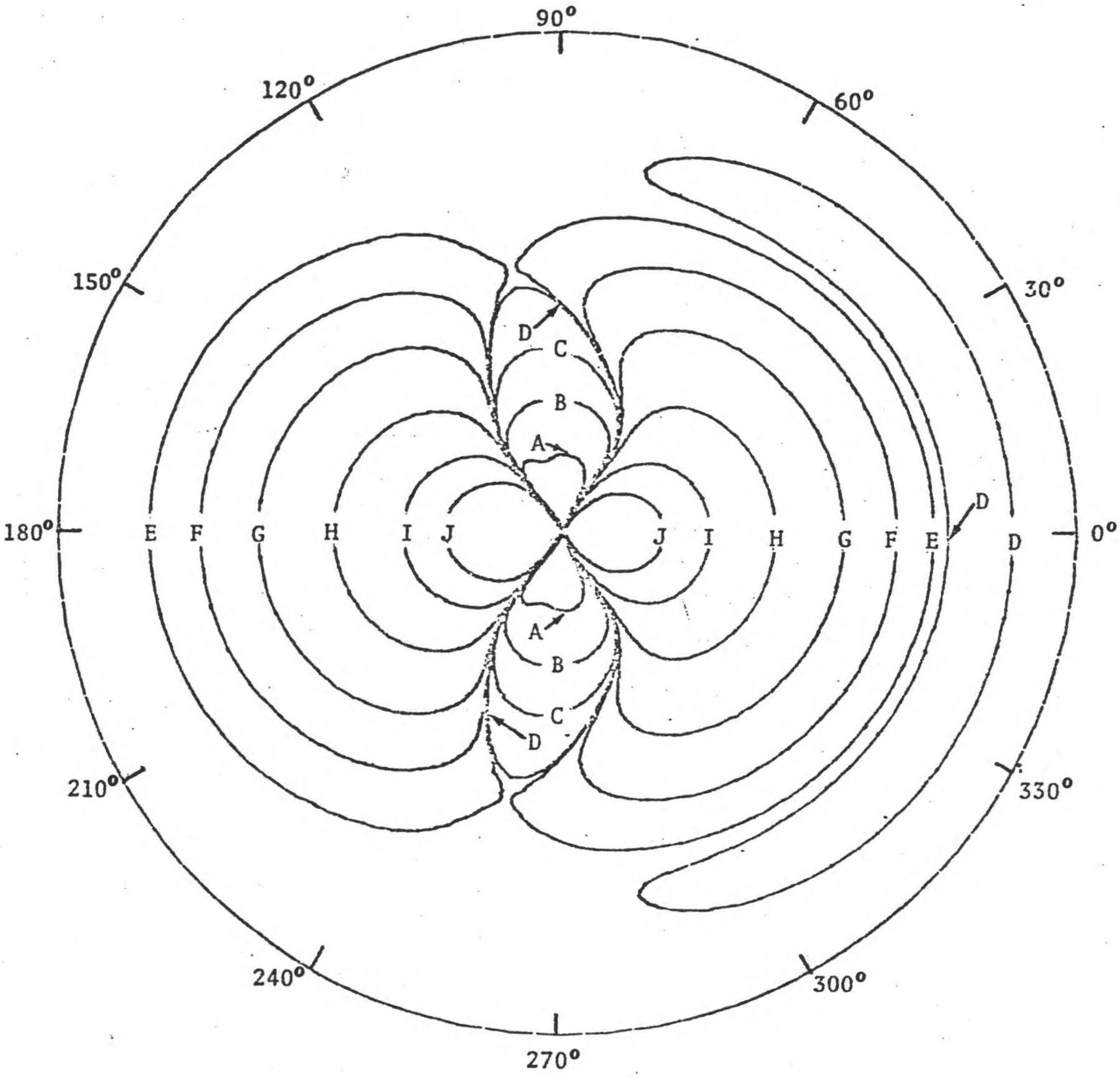

Fig. 5. -- Contour plot of the vibrational derivative of the Ar-CO potential at the equilibrium position of CO. Values of the contours are given in table 7.

TABLE 7. -- Values of the contours used in Fig. 5

| Identifaction | Contour Value (a.u.) |
|---|---|
| A - A - A - A | -1.0000 |
| B - B - B - B | -.1000 |
| C - C - C - C | -.0100 |
| D - D - D - D | -.0001 |
| E - E - E - E | .0000 |
| F - F - F - F | .0010 |
| G - G - G - G | .0100 |
| H - H - H - H | .1000 |
| I - I - I - I | 1.0000 |
| J - J - J - J | 10.0000 |

Between the nuclei there is a deep well region as should be expected since in this expansion the vibrational derivative should approach a negative infinity at the nuclei from the inside and a positive infinity from the outside which also causes the cliff region.

The contours of Table 8 were used in plotting the vibrational curvature,

$$\frac{\partial^2}{\partial R^2} V(r,\theta,R)\Big|_{R=R_e} \tag{2-58}$$

of the Ar-CO potential shown in Fig. 6. It has the same qualitative behavior as the vibrational derivative in Fig. 5 but is somewhat smoother.

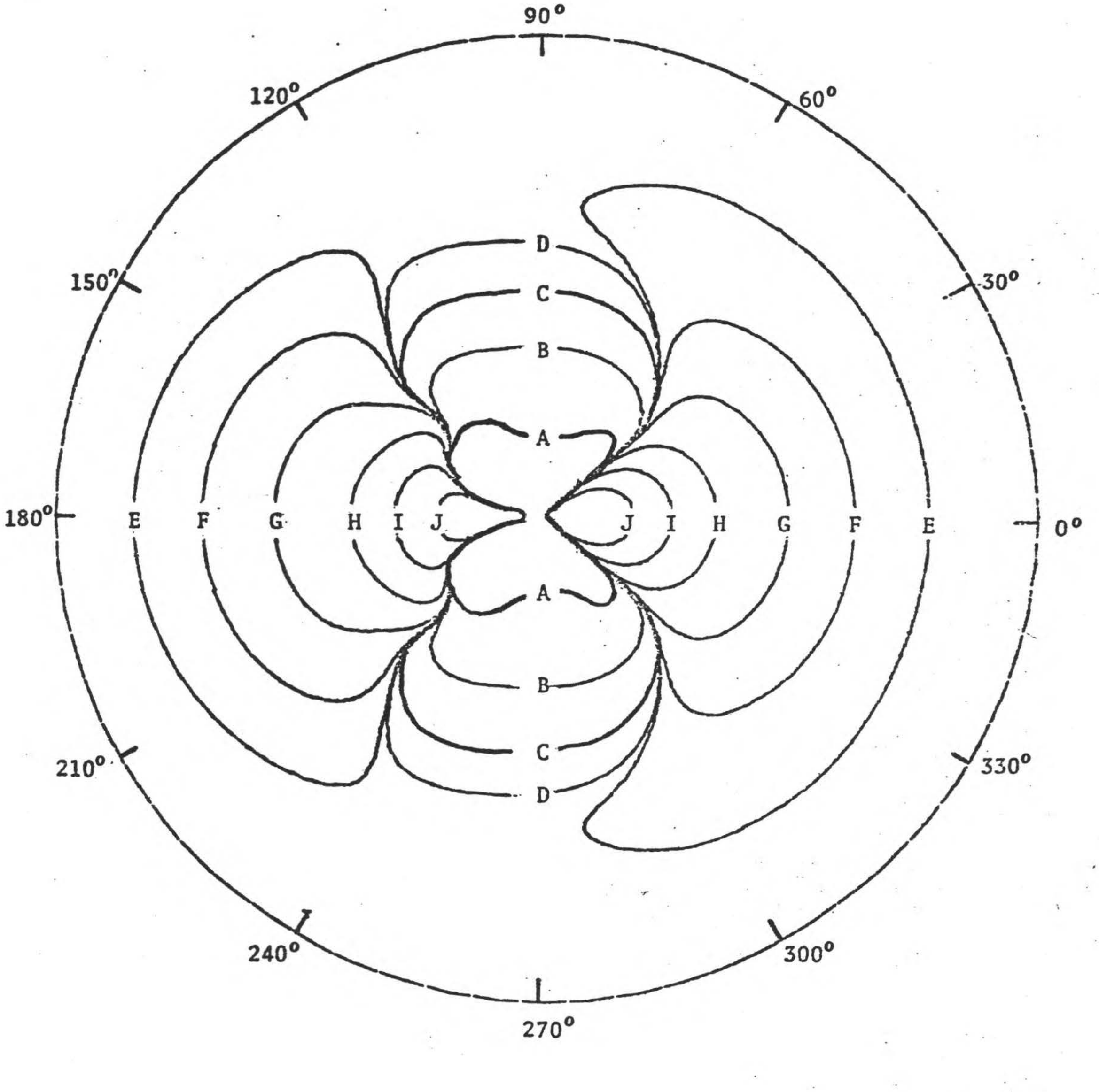

Fig. 6. -- Contour plot of the vibrational curvature of the Ar-CO potential at the equilibrium position of CO. Values of the contours are given in Table 8.

TABLE 8. -- Values of the contours used in Fig. 6

| Identifaction | Contour Value (a.u.) |
|---|---|
| A - A - A - A | -.1000 |
| B - B - B - B | -.0100 |
| C - C - C - C | -.0010 |
| D - D - D - D | -.0001 |
| E - E - E - E | .0000 |
| F - F - F - F | .0010 |
| G - G - G - G | .0100 |
| H - H - H - H | .1000 |
| I - I - I - I | 1.0000 |
| J - J - J - J | 10.0000 |

# III. Ar-CO V-T-R ENERGY TRANSFER

In the first section of this chapter the theory of molecular collisions in the Infinite Order Sudden (IOS) approximation is described. In section B we describe the calculation of V-T-R (Vibrational-Translational-Rotational) energy transfer, total cross sections, and vibrational relaxation rates, treating the rotations in the IOS approximation and using close-coupling for the vibrations. These calculations use the Ar-CO potential previously described in chapter II. Then our calculated vibrational relaxation rates will be compared with experiment in section C.

## A. Theory

The formal theory of the Infinite Order Sudden (IOS) approximation has been derived using both space-fixed [8] and body-fixed [10] coordinates. Both approaches are enlightening and give very valuable insights into the validity range of the approximation. In this section we present a derivation of the IOS approximation which is equivalent to that given by Secrest [11] but is more straightforward and clearly shows its relation to the semi-classical sudden [36] approximation. After separation of the center of mass motion, the Hamiltonian [using either the space-fixed (primed) axes or body-fixed (unprimed) axes shown in Fig. 7] for an atom A interacting with a $\Sigma$-state diatomic molecule BC can be written in the form,

$$\underset{\sim}{H} = \frac{-\hbar^2}{2\mu} r^{-1} \frac{\partial^2}{\partial r^2} r + \frac{\underset{\sim}{L}^2}{2\mu r^2} + \underset{\sim}{H}_{BC} + V(r,\theta,R), \tag{3-1}$$

where $\underset{\sim}{L}$ and $\mu$ are, respectively, the angular momentum operator [37] and reduced mass,

$$\mu = m_A m_{BC} / \left(m_A + m_{BC}\right), \tag{3-2}$$

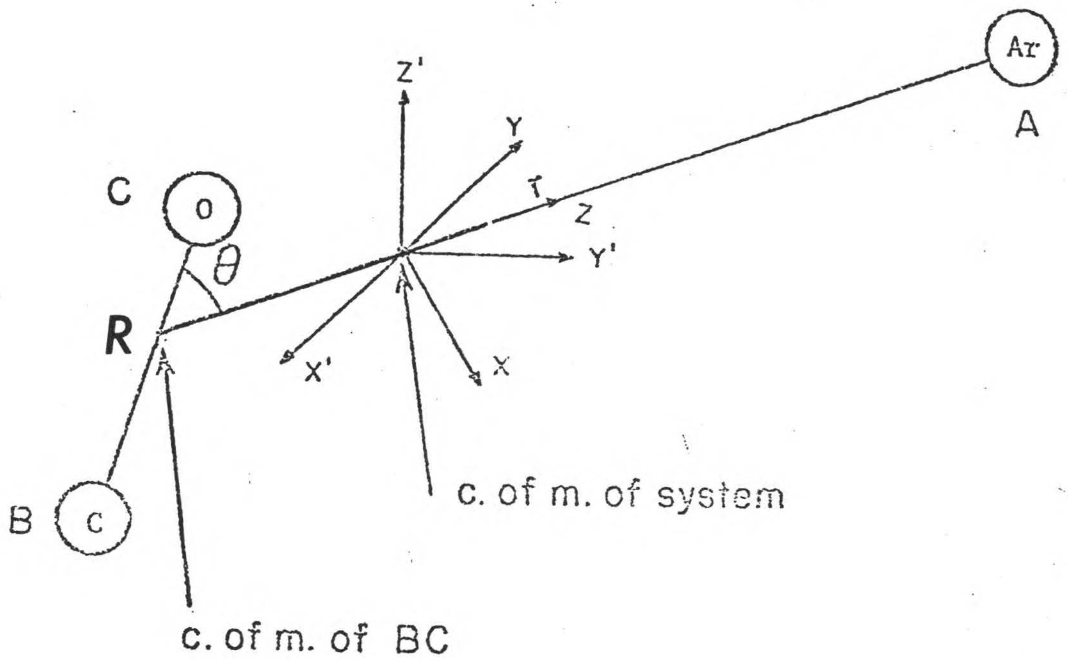

Fig. 7. -- Center-of-mass coordinates used herein for A + BC collisions. The primed axes are the space-fixed coordinates, the unprimed axes are the body-fixed coordinates.

of A relative to BC and $V(r,\theta,R)$ is the Born-Oppenheimer intermolecular potential. The internal Hamiltonian $H_{BC}$ in Eq. (3-1) governs the nuclear motion of the diatomic molecule BC,

$$\underset{\sim}{H}_{BC} = -\frac{\hbar^2}{2\mu_{BC}} R^{-2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\underset{\sim}{J}_R^2}{2\mu_{BC}R^2} + V_{BC}(R), \tag{3-3}$$

where $\mu_{BC}$ is the reduced mass,

$$\mu_{BC} = m_B\, m_C/\left(m_B + m_C\right), \tag{3-4}$$

$\underset{\sim}{J}_R$ is the angular momentum operator [38] of the diatomic molecule, and $V_{BC}$ is the Born-Oppenheimer interatomic potential. In the IOS approximation the following replacements of operators by constants are made [39],

$$\underset{\sim}{L}^2 \rightarrow \hbar^2\, \lambda(\lambda + 1), \tag{3-5}$$

in Eq. (3-1) and

$$\underset{\sim}{J}_R^2 \rightarrow \hbar^2\, \bar{j}(\bar{j} + 1), \tag{3-6}$$

in Eq. (3-3) to give,

$$\left[-\frac{\hbar^2}{2\mu} r^{-1} \frac{\partial^2}{\partial r^2} r + \frac{\hbar^2\, \lambda(\lambda + 1)}{2\mu r^2} + V(r,\theta,R) - \frac{\hbar^2}{2\mu_{BC}} R^{-2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \right.$$

$$\left. + \frac{\hbar^2 \bar{j}(\bar{j} + 1)}{2\mu_{BC}R^2} + V_{BC}(R)\right] \psi_\nu^{\lambda\bar{j}}(r,R;\theta) = E\, \psi_\nu^{\lambda\bar{j}}(r,k;\theta) \tag{3-7}$$

Where the notation on the wavefunction $\psi_{\nu}^{\lambda \bar{j}}(r,R;\theta)$ is used to indicate that it now has only a parametric dependence upon the angle $\theta$. The numbers $\lambda$ and $\bar{j}$ in Eq. (3-7) are arbitrary constants. The wavefunction $\psi_{\nu}^{\lambda \bar{j}}(r,R;\theta)$ can be expanded in a complete set of vibrational wavefunctions $\chi_{\bar{j}\nu''}(R)$

$$\psi_{\nu}^{\lambda \bar{j}}(r,R;\theta) = \sum_{\nu''} r^{-1} g_{\nu''}^{\nu}(r;\theta) \chi_{\bar{j}\nu''}(R) \qquad (3\text{-}8)$$

where

$$\left[ -\frac{\hbar^2}{2\mu_{BC}} R^{-2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\hbar^2 \bar{j}(\bar{j}+1)}{2\mu_{BC} R^2} + V_{BC}(R) \right] \chi_{\bar{j}\nu}(R) = \varepsilon_{\bar{j}\nu} \chi_{\bar{j}\nu}(R) \qquad (3\text{-}9)$$

and $\varepsilon_{\bar{j}\nu}$ are the rotation-vibration energy levels. Substitution of Eq. (3-8) into Eq. (3-7), multiplication by $\frac{-2\mu}{\hbar^2} \chi^*_{\bar{j}\nu'}(R)$ on the left and integration over R gives the following set of second order coupled differential equations,

$$\left[ \frac{d^2}{dr^2} + k_{\bar{j}\nu}^2 - \frac{\lambda(\lambda+1)}{r^2} \right] g_{\nu'}^{\nu}(r;\theta) = \sum_{\nu''} U_{\nu''}^{\nu}(r,\theta)\, g_{\nu''}^{\nu}(r;\theta) \qquad (3\text{-}10)$$

where

$$k_{\bar{j}}^2 = \frac{2\mu}{\hbar^2} \left[ E - \varepsilon_{\bar{j}\nu} \right] \qquad (3\text{-}11)$$

and

$$U_{\nu''}^{\nu}(r,\theta) = \frac{2\mu}{\hbar^2} \int_0^\infty R^2 \chi^*_{\nu''}(R)\, V(r,\theta,R)\, \chi_{\nu}(R)\, dR \qquad (3\text{-}12)$$

These equations are solved subject to the boundary conditions,

$$g_{\nu'}^{\nu}(0;\theta) = 0 \qquad (3\text{-}13)$$

and

$$g^{\nu}_{\nu'}(r;\theta) \xrightarrow[r\to\infty]{} k_{\bar{j}\nu'}^{-1/2}\left\{\delta_{\nu\nu'}\exp\left[-i\left(k_{\bar{j}\nu}r-\frac{\lambda\pi}{2}\right)\right]-S^{\bar{j}\lambda}_{\nu\nu'}(\theta)\exp\left[i\left(k_{\bar{j}\nu}r-\frac{\lambda\pi}{2}\right)\right]\right\} \tag{3-14}$$

These are not the usual IOS solutions [10] but the usual scattering solutions can be obtained by projection. The body-fixed solutions are

$$G^{\bar{J}j\Omega\nu'}_{j'\Omega'\nu'}(r) = \langle j'\Omega' \,|\, g^{\nu}_{\nu'}(r;\theta) \,|\, j\,\Omega\rangle \exp\left[i\,\frac{\pi}{2}\,(J+j-\lambda)\right] \tag{3-15}$$

where

$$|j\Omega\rangle = Y_{j\Omega}(\hat{R}) \tag{3-16}$$

and $Y_{j\Omega}(\hat{R})$ is a spherical harmonic with angles $\hat{R} = (\theta,\phi)$ in the body-fixed system. That these are indeed the solutions of the usual IOS scattering equations can be shown by multiplying $\langle j'\Omega'|$ on the left and $|j\Omega\rangle\exp\left[\frac{i\pi}{2}\left(J-j+\lambda\right)\right]$ on the right of Eq. (3-10) to give

$$\left[\frac{d^2}{dr^2}+k^2_{\bar{j}\nu'}-\frac{\lambda(\lambda+1)}{r^2}\right]G^{Jj\Omega\nu}_{j'\Omega'\nu'}(r)$$

$$=\sum_{\nu''}\langle j'\Omega' \,|\, U^{\nu}_{\nu''}(r,\theta)\,g^{\nu}_{\nu''}(r;\theta)|\, j\Omega\rangle\exp\left[\frac{i\pi}{2}\,(J+j-\lambda)\right]. \tag{3-17}$$

Then inserting the completeness relation [40],

$$1=\sum_{j''}\sum_{\Omega''}|j''\Omega''\rangle\langle j''\Omega''| \tag{3-18}$$

on the right hand side of Eq. (3-17) gives the usual IOS scattering equations [10]

$$\left[\frac{d^2}{dr^2} + k^2_{j\nu} - \frac{\lambda(\lambda+1)}{r^2}\right] G^{Jjr\nu}_{j'\Omega'\nu'}(r)$$

$$= \sum_{j''} \sum_{\nu''} \langle j\,\Omega' \,|U^{\nu}_{\nu''}\,(r,\theta)|\, j''\Omega'\rangle\, G^{Jj\Omega\nu}_{j''\Omega'\nu''} \tag{3-19}$$

in the body-fixed formulation, where we have used [41]

$$\langle j'\Omega'|U^{\nu}_{\nu''}\,(r,\theta)|\,j''\Omega''\rangle$$

$$= \delta_{\Omega'\Omega''}\langle j'\Omega'|\,U^{\nu}_{\nu''}(r,\theta)\,\,|j''\Omega'\rangle \tag{3-20}$$

in obtaining this result. The solutions $G^{Jj\Omega\nu}_{j'\Omega'\nu'}(r)$ are subject to the boundary conditions,

$$G^{Jj\Omega\nu}_{j'\Omega'\nu'}(0) = 0 \tag{3-21}$$

and

$$G^{Jj\Omega\nu}_{j'\Omega'\nu'}(r) \xrightarrow[r\to\infty]{} k^{-1/2}_{\bar{j}\nu'}\left\{\delta_{jj'}\delta_{\Omega\Omega'}\delta_{\nu\nu'}\,\exp\left[-i\left(k_{\bar{j}\nu}r-(J+j)\,\frac{\pi}{2}\right)\right]\right.$$

$$\left.- S^J(j'\Omega'\nu'|j,-\Omega,\nu)\,\exp\left[i\left(k_{\bar{j}\nu'}r - \frac{(J+j')\pi}{2}\right)\right]\right\} \tag{3-22}$$

where $\underset{\sim}{S}^J$ is the scattering matrix. Multiplication of Eqs. (3-13) and (3-14) by $\langle j'\Omega'|$ and $\exp\frac{i\pi}{2}(J+j-\lambda)|j\Omega\rangle$ on the left and right, respectively, gives

$$G^{Jj\Omega\nu}_{j'\Omega'\nu'}(0) = 0 \tag{3-23}$$

and

$$G^{Jj\Omega\nu}_{j'\Omega'\nu'}(r) \xrightarrow[r\to\infty]{} k^{-1/2}_{\bar{j}\nu'}\Big\{\delta_{jj'}\delta_{\Omega\Omega'}\delta_{\nu\nu'} \exp\Big[-i\Big(k_{\bar{j}\nu}\, r - \frac{(J+j)\pi}{2}\Big)\Big]$$

$$-(-1)^{J-\lambda}\, i^{j'+j} \langle j'\Omega' \mid S^{\bar{j}\lambda}_{\nu\nu'}(\theta) \mid j\Omega\rangle \exp\Big[i\Big(k_{\bar{j}\nu'} r - \frac{(J+j')\pi}{2}\Big)\Big]\Big\} \qquad (3\text{-}24)$$

which proves that these are the usual IOS scattering solutions. Also from the comparison of Eq. (3-23) with Eq. (3-22) one obtains an expression for the scattering matrix $\underset{\sim}{S}^J$,

$$S^J(j'\Omega'\nu' \mid j,-\Omega,\nu,) = \langle j\Omega \mid S^{\bar{j}\lambda}_{\nu\nu'}(\theta) \mid j'\Omega'\rangle (-1)^{J-\lambda} (i)^{j'+j} \; . \qquad (3\text{-}25)$$

The space-fixed IOS solutions [10] can also be constructed by projection [39]

$$G^{Jj\ell\nu}_{j'\ell'\nu'}(r) = \langle JMj\ell \mid g^{\nu}_{\nu'}(r;\theta) \mid JMj'\ell'\rangle \qquad (3\text{-}26)$$

where the brackets imply integration with

$$\langle JMj\ell| = \sum_{m_j=-j}^{j} \sum_{m_\ell=-\ell}^{\ell} C(j\ell J; m_j m_\ell m)\, Y_{j_{m_j}}(\hat{R}')\, Y_{\ell_{m_\ell}}(\hat{r}') \qquad (3\text{-}27)$$

with angles $\hat{R}' = (\theta', \phi')$ and $\hat{r}' = (\theta_r', \phi_r')$ in the space-fixed system. That these are the usual IOS space-fixed solutions is easily proved as before giving the $\underset{\sim}{S}^J$ matrix as,

$$S^J(j'\ell'\nu' \mid j\ell\nu) = \langle JMj\ell \mid S^{j\lambda}_{\nu\nu'}(\theta) \mid JMj'\ell'\rangle \, . \qquad (3\text{-}28)$$

Using any physically reasonable choice for $\bar{j}$ and $\lambda$ which are independent of the total angular momentum J, the J sum in the scattering amplitude formula can be done analytically to give simplified expressions for the scattering amplitude and differential cross sections. In the body-fixed formulation the scattering amplitude is [10]

$$f(j'm_{j'}\nu' \leftarrow jm_j\nu|\hat{r}') = \sum_J \sum_{\Omega'} \sum_{\ell'} (i)^{j-j'+1} (-1)^{m_{j'}-m_j} (2J+1)\, \pi^{1/2}$$

$$\left[(2\ell'+1) k_{j\nu} k_{j'\nu'}\right]^{-1/2} T^J(j'\Omega'\nu'|jm_j\,\nu)$$

$$C(Jj'\ell';\Omega',-\Omega',\ ) \; C(Jj'\ell';m_j,-m_{j'},m_j-m_{j'}) \tag{3-29}$$

$$Y_{\ell',m_j-m_{j'}}(r')$$

where the $C(Jj'\ell;m_j,-m_{j'},m_j-m_{j'})$ are the Clebsch-Gordan coefficients[42] and $\hat{r}' = (\theta_r',\phi_r')$ are the angles associated with the space-fixed coordinate system. The transition matrix $\underset{\sim}{T}^J$ in Eq. (3-30) is defined as,

$$T^J(j'\Omega'\nu' \,|\, j\text{-}\Omega\nu) = \delta_{\nu\nu'}\delta_{jj'}\delta_{\Omega',-\Omega} - S^J(j'\Omega'\nu'|j\text{-}\Omega\nu) \tag{3-30}$$

$$= \delta_{\nu\nu'}\delta_{jj'}\delta_{\Omega',-\Omega} - \langle j'\Omega'|S^{\bar{j}\lambda}_{\nu\nu'}(\theta)|j\Omega\rangle (-1)^{J-\lambda} i^{j'+j}$$

Substitution of Eq. (3-30) into the scattering amplitude Eq.(3-29) and using the properties [43] of the Clebsch-Gordan coefficients the sum over the total angular momentum J can be done analytically to give,

$$f(j'm_j\nu' \leftarrow jm_j\nu|\hat{r}') = \frac{(-1)^{j+j'+1}}{2i\left[k_{j\nu}k_{j'\nu'}\right]^{1/2}} \left\{ \sum_{\ell'} (2\ell'+1)\; P_{\ell'}(\cos\theta_r') \right.$$

$$\left. \left[\delta_{\nu\nu'}\delta_{jj'} - \langle j'\text{-}m_j|S^{\bar{j}\lambda}_{\nu\nu'}(\theta)|j\text{-}m_j\rangle (-1)^{\ell'-\lambda}\right] \right\} \delta_{m_j m_{j'}} \tag{3-31}$$

$$= (-1)^{j+j'+1} \langle jm_j|f^{\bar{j}\lambda}(\nu'\leftarrow\nu|\; \hat{r}';\theta)|j'm_{j'}\rangle$$

where the central field scattering amplitude (which parametrically depends upon the angle θ) is

$$f^{\bar{j}\lambda}(\nu'\leftarrow\nu|\hat{r}';\theta) = \frac{1}{2i\left[k_{j'\nu'}k_{j\nu}\right]^{1/2}} \sum_{\ell'} (2\ell'+1)P_{\ell'}(\cos\theta_r')T^{\bar{j}\lambda}_{\nu\nu'}(\theta) \qquad (3\text{-}32)$$

and

$$T^{\bar{j}\lambda}_{\nu\nu'}(\theta) = \delta_{\nu\nu'} - (-1)^{\ell'-\lambda}\, S^{\bar{j}\ell'}_{\nu\nu'}(\theta) \qquad (3\text{-}33)$$

are the elements of the transition matrix $T^{\bar{j}\lambda}(\theta)$.

The degeneracy averaged differential cross section (scattering intensity) is [10]

$$\begin{aligned} I(j'\nu'\leftarrow j\nu|\hat{r}) &= \frac{1}{2j+1}\frac{k_{j'\nu'}}{k_{j\nu}}\sum_{m_j}\sum_{m_{j'}}\left|f(j'm_{j'}\nu'\leftarrow jm_j\nu|\hat{r}')\right|^2 \\ &= \frac{1}{2j+1}\frac{k_{j'\nu'}}{k_{j\nu}}\sum_{m_j}\left|\langle jm_j|f^{\bar{j}\lambda}\,(\nu'\leftarrow\nu|\hat{r}';\theta)\,|j'm_j\rangle\right|^2 \end{aligned} \qquad (3\text{-}34)$$

If we also assume that $\bar{j}$ and $\lambda$ are independent of $j'$ we can sum the degeneracy averaged differential cross section over the final rotational states using the completeness relation [40]

$$1 = \sum_{j'}\sum_{m_{j'}}|j'm_{j'}\rangle\langle j'm_{j'}| \qquad (3\text{-}35)$$

to give

$$I(\nu'\leftarrow j\nu|\hat{r}) = \frac{1}{(2j+1)}\sum_{m_j}\langle jm_j|\frac{1}{4k^2_{j\nu}}\left|\sum_{\ell'}(2\ell'+1)P_{\ell'}(\cos\theta_r')T^{\bar{j}\lambda}_{\nu\nu'}(\theta)\right|^2|jm_j\rangle \qquad (3\text{-}36)$$

This can be further simplified by use of the spherical harmonic addition theorem [44],

$$\left(\frac{2j+1}{4\pi}\right)^{1/2} Y_{j0}(\theta,0) = \sum_{m_j} Y^*_{jm_j}(\theta_1,\phi_1)Y_{jm_j}(\theta_2,\phi_2), \qquad (3\text{-}37)$$

[where $\theta$ is the angle between the vectors $\hat{r}_1$ and $\hat{r}_2$ defined by the angles $(\theta_1,\phi_1)$ and $(\theta_2,\phi_2)$, respectively, (for the present case $\theta_1 = \theta_2$ and $\phi_1 = \phi_2$ and hence $\theta = 0$)] giving

$$I(\nu' \leftarrow j\nu|\hat{r}) = \frac{1}{8k_{j\nu}^2} \int_0^{\pi} \left| \sum_{\ell'} (2\ell'+1) P_{\ell'}(\cos\theta_r') T_{\nu\nu'}^{\bar{j}\lambda}(\theta) \right|^2 \sin\theta \, d\theta \quad (3\text{-}38)$$

where we have used [45]

$$Y_{j0}(0,0) = \left(\frac{2j+1}{4\pi}\right)^{1/2} \quad (3\text{-}39)$$

in deriving Eq. (3-38). The following equations and Eq. (3-38) are independent of j if $\bar{j}$ and $\lambda$ are taken to be independent of j.

The differential cross section in Eq. (3-38) can be written as an average over the central field differential cross section which also parametrically depends upon the angle $\theta$,

$$I(\nu' \leftarrow j\nu|\hat{r}) = \frac{1}{2} \int_0^{\pi} I(\nu' \leftarrow j\nu|\hat{r}';\theta) \sin\theta \, d\theta \quad (3\text{-}40)$$

with the central field differential cross section defined as,

$$I(\nu' \leftarrow j\nu|\hat{r};\theta) = \frac{1}{4k_{j\nu}^2} \left| \sum_{\ell'} (2\ell'+1) P_{\ell'}(\cos\theta_r') T_{\nu\nu'}^{\bar{j}\lambda}(\theta) \right|^2 . \quad (3\text{-}41)$$

The total cross section can also be written as an average over the central field total cross sections as,

$$\sigma(\nu' \leftarrow j\nu) = \frac{1}{2} \int_0^{\pi} \sigma(\nu' \leftarrow j\nu;\theta) \sin\theta \, d\theta \quad (3\text{-}42)$$

where

$$\sigma(\nu' \leftarrow j\nu;\theta) = \int_0^{2\pi} \int_0^{\pi} I(\nu' \leftarrow j\nu|\hat{r}';\theta) \sin\theta_r' \, d\theta_r' \, d\phi_r' \quad (3\text{-}43)$$

with substitution of Eq. (3-41) into Eq. (3-43) and using the orthogonality [46] of the Legendre polynomials gives the usual central field expression for the total cross section,

$$\sigma(\nu' \leftarrow j\nu;\theta) = \frac{\pi}{k_{j\nu}^2} \sum_{\ell'} (2\ell'+1) |T_{\nu\nu'}^{\bar{j}\lambda}(\theta)|^2. \tag{3-44}$$

As seen from the simplified expressions given above a physically reasonable choice of $\lambda$ is

$$\lambda = \ell'. \tag{3-45}$$

Also since $\bar{j}$ mainly affects the energy levels in Eq. (3-10) a physically reasonable choice for $\bar{j}$ is

$$\bar{j} = (j + j')/2 \tag{3-46}$$

but for molecules with a small rotational constant the $\underset{\sim}{S}^{\bar{j}\lambda}(\theta)$ matrix will almost be independent of $\bar{j}$ and we can choose $\bar{j}$ as a constant independent of j and j'.

After obtaining the total cross sections $\sigma(\nu' \leftarrow j\nu)$ the vibrational relaxation rate constants $k_{\nu'\leftarrow\nu}(T)$ are evaluated using [47],

$$k_{\nu'\leftarrow\nu}(T) = \left(\frac{8}{\pi\mu k_B^3 T^3}\right)^{1/2} \sum_j p_j(T) \int_0^\infty \sigma(\nu' \leftarrow j\nu) E e^{-E/k_B T} dE \tag{3-47}$$

where $p_j(T)$ is the probability of being in the j'th rotational state at a temperature T, E is the incident relative kinetic energy and $k_B$ is Boltzmann constant. From the detailed balance relation [48],

$$k_{\nu\leftarrow\nu'}(T) = e^{-(E_{o\nu}-E_{o\nu'})/k_B T} k_{\nu'\leftarrow\nu}(T) \tag{3-48}$$

the corresponding excitation rates can then be obtained.

## B. Calculations

There have been several methods proposed for numerical solution of the coupled scattering equations. The two most promising methods known are the Sams and Kouri [17] integral equations method, and the Gordon [18] piecewise analytic function method. All of the close-coupling calculations reported herein have used a combination of both methods in order to utilize the advantages of each.

It was found that for large values of the angular momentum ($\lambda = \ell' > 200$) and small kinetic energies [$E < 25{,}000°K$ (relative to the ground state vibrational line of CO)] that the Distorted Wave [49] approximation correctly predicted the elements of the S-matrix, $\underset{\sim}{S}^{j\lambda}(\theta)$, to within 5%. We therefore used it for the scattering calculations in this range. Close-coupling was used for all values of the angular momentum at high energies ($E \geqslant 25{,}000°K$) and also for all of the energies when the angular momentum was small ($\lambda = \ell' \leqslant 200$).

### i. Integral Equations

The Sams and Kouri [17] integral equations method will be presented for the single channel case to keep the notation simple. Generalization to the multi-channel problem is straightforward.

The single channel scattering solution $g_\ell(r)$, where

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2}\right] g_\ell(r) = U(r)\ g_\ell(r) \tag{3-49}$$

is subject to the usual scattering boundary conditions,

$$g_\ell(0) = 0 \tag{3-50}$$

and

$$g_\ell(r) \xrightarrow[r\to\infty]{} e^{-i(kr - \frac{\ell\pi}{2})} - S^\ell e^{i(kr - \frac{\ell\pi}{2})} \tag{3-51}$$

where $S^\ell$ is the scattering matrix,

$$S^{\ell} = e^{2i\eta_{\ell}}, \tag{3-52}$$

and the $\eta_{\ell}$ are the phase shifts. The solution $g_{\ell}(r)$ of Eq. (3-49) can then be written as a sum of a homogeneous $g_{\ell}^{h}(r)$, and a particular $g_{\ell}^{p}(r)$ solution,

$$g_{\ell}(r) = g_{\ell}^{h}(r) + g_{\ell}^{p}(r) \tag{3-53}$$

where the homogeneous solution satisfies,

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2}\right] g_{\ell}^{h}(r) = 0 \tag{3-54}$$

and the particular solution is any nontrivial solution of Eq. (3-49). The homogeneous solution can be written in terms of the Riccatti-Bessel function $\hat{j}_{\ell}(r)$ and the Riccatti-Hankel [30] function of the first kind $h_{\ell}^{(1)}(r)$ as,

$$g_{\ell}^{h}(r) = C_1 \hat{j}_{\ell}(kr) + C_2 \hat{h}_{\ell}^{(1)}(kr) \tag{3-55}$$

where the constants $C_1$ and $C_2$ are determined from the boundary conditions on $g_{\ell}(r)$. The particular solution of Eq. (3-49) can be obtained using Green's functions [50] or equivalently by the method of variation of parameters [50]. Using the method of variation of parameters gives,

$$g_{\ell}^{p}(r) = \int_0^r \frac{\hat{j}_{\ell}(kr)\ \hat{h}_{\ell}^{(1)}(kr) - \hat{j}_{\ell}(kr')\ \hat{h}_{\ell}^{(1)}(kr)}{W\left[\hat{h}_{\ell}^{(1)}(kr),\ \hat{j}_{\ell}(kr)\right]} \times U(r')\ g_{\ell}^{p}(r')\ dr' \tag{3-56}$$

for the particular solution, where W is the Wronskian,

$$W\left[\hat{h}_{\ell}^{(1)}(kr),\ \hat{j}_{\ell}(kr)\right] = \hat{h}_{\ell}^{(1)}(kr)\frac{d}{dr}\hat{j}_{\ell}(kr) - \hat{j}_{\ell}(kr)\frac{d}{dr}\hat{h}_{\ell}^{(1)}(kr) \tag{3-57}$$

which can be easily evaluated to give,

$$W\left[\hat{j}_\ell(kr),\ \hat{h}_\ell^{(1)}(kr)\right] = -ik. \tag{3-58}$$

Since $\frac{i}{k}g_\ell(r)$ is also a particular solution of Eq. (3-49) the solution $g_\ell(r)$ can be written as,

$$g_\ell(r) = g_\ell^h(r) + \hat{j}_\ell(kr)\int_0^r \hat{h}_\ell^{(1)}(kr') \quad U(r')\ g_\ell(r')dr'$$

$$- \hat{h}_\ell^{(1)}(kr')\int_0^r \hat{j}_\ell(kr')\ U(r')\ g_\ell(r')\ dr'\ . \tag{3-59}$$

The boundary condition at $r = 0$, Eq. (3-50), then gives

$$C_2 = 0. \tag{3-60}$$

Since the solution is zero at $r = 0$, the asymptotic boundary condition simply scales the solution; hence,

$$\overline{g}_\ell(r) = \hat{j}_\ell(kr) + \hat{j}_\ell(kr)\int_0^r \hat{h}_\ell^{(1)}(kr')\ U(r')\ \overline{g}_\ell(r')\ dr'$$

$$- \hat{h}_\ell^{(1)}(kr)\int_0^r \hat{j}_\ell(kr')\ U(r')\ \overline{g}_\ell(r')\ dr \tag{3-61}$$

where,

$$\overline{g}_\ell(r) = C\ g_\ell(r). \tag{3-62}$$

A formal expression for the constant C in Eq. (3-62) can be obtained by using the asymptotic boundary condition to give

$$C = 2i/\left\{1 + \int_0^\infty \left[\hat{h}_\ell^{(1)}(kr') + 2\ \hat{j}_\ell(kr')\right]U(r')\overline{g}_\ell(r')\ dr'\right\}. \tag{3-63}$$

where we have used the asymptotic behavior of the Riccatti-Bessel [30],

$$\hat{j}_\ell(kr) \xrightarrow[r\to\infty]{} \sin\left(kr - \frac{\ell\pi}{2}\right) \tag{3-64}$$

and the Riccatti-Hankel [30],

$$\hat{h}_\ell^{(1)}(kr) \xrightarrow[r\to\infty]{} -i\; e^{i\left(kr - \frac{\ell\pi}{2}\right)} \tag{3-65}$$

functions. In practice the constant C is never determined using Eq. (3-63), but by directly scaling the solution $\bar{g}_\ell(r)$ at some large distance to match the asymptotic boundary condition.

At first glance it looks as though Eq. (3-61) would have to be solved iteratively since $\bar{g}_\ell(r)$ is on both sides of the equation. However, replacing the integrals by a numerical quadrature gives,

$$\begin{aligned}\bar{g}_\ell(r_i) = j_\ell(kr_i) &+ \hat{j}_\ell(kr_i)\sum_{j=1}^{i} \hat{h}_\ell^{(1)}(kr_j)\; U(r_j)\; \bar{g}_\ell(r_j)\; W_j \\ &- \hat{h}_\ell^{(1)}(kr_i)\sum_{j=1}^{i} \hat{j}_\ell(kr_j)\; U(r_j)\; \bar{g}_\ell(r_j)\; W_j\end{aligned} \tag{3-66}$$

and one sees that the i'th term on the right-hand side cancels exactly giving,

$$\begin{aligned}\bar{g}_\ell(r_i) = \hat{j}_\ell(kr_i) &+ \hat{j}_\ell(kr_i)\sum_{j=1}^{i-1} \hat{h}_\ell^{(1)}(kr_j)\; U(r_j)\; \bar{g}_\ell(r_j)\; W_j \\ &- \hat{h}_\ell^{(1)}(kr_i)\sum_{j=1}^{i-1} \hat{j}_\ell(kr_j)\; U(r_j)\; \bar{g}_\ell(r_j)\; W_j\end{aligned} \tag{3-67}$$

The weights $w_j$ in Eqs. (3-66) and (3-67) are the weights associated with a particular quadrature (i.e., Trapezoidal [30], Simpson [30], etc.). The integral equations method has the advantage that it requires little computational time per step, however the method integrates an oscillatory solution and hence requires a large number of steps. It also has a disadvantage for high $\ell$-values since it must calculate the Riccatti-Bessel [30] and Riccatii-Hankel [30] functions which are usually obtained by recursion. For coupled channels with the same $\ell$ values the last disadvantage can be essentially eliminated if one numerically integrates the homogeneous equation Eq. (3-54) to obtain the Riccatti-Bessel [30] and Riccatti-Hankel [30] functions.

### ii. Piecewise Analytic Functions

In Gordon's [18] piecewise analytic functions method what one does is replace the effective potential

$$U_\ell^{eff}(r) = U(r) + \frac{\ell(\ell+1)}{r^2} \tag{3-68}$$

by a reference potential $U_\ell^i(r)$ in a piecewise fashion

$$U_\ell^{eff}(r) \rightarrow U_\ell^i(r) \quad r_i < r < r_{i+1} \ . \tag{3-69}$$

The reference potential is chosen such that it accurately fits the effective potential in the given region $r_i < r < r_{i+1}$, and the solutions $g_\ell^i$

$$\left[\frac{d^2}{dr^2} + k^2 - U_\ell^i(r)\right] g_\ell^i(r) = 0 \tag{3-70}$$

are known analytically. Then the scattering solution $g_\ell(r)$ is formed by matching the reference solution and its derivative across the boundaries of the regions

$$g_\ell^i(r_i) = g_\ell^{i+1}(r_i) \tag{3-71}$$

and

$$\frac{d}{dr} g_\ell^i(r)\bigg|_{r=r_i} = \frac{d}{dr} g_\ell^{i+1}(r)\bigg|_{r=r_i} \tag{3-72}$$

The $r_i$ are determined by a perturbative procedure [18] resulting in unequal step sizes which is a major advantage of the method as discussed in iii. The method is simply generalized to the many channel case by the diagonalizing of the matrix $\underset{\sim}{W}$ whose elements are,

$$W_{\nu\nu'} = k^2 - \frac{\ell(\ell+1)}{r^2} - U_{\nu\nu'}(r) \tag{3-73}$$

in the region of interest and then fitting the eigenvalues with the reference potential and hence obtaining the reference solutions $\underset{\sim}{g}_\ell^i$ and then transforming back to get the scattering solution. This is a disadvantage since the diagonalization of a matrix is a time consuming process.

### iii. Joining of Both Methods

Since the Gordon piecewise linear program [18] can take large step sizes when the potential is varying slowly (large r) it is very efficient in that region. In the Sams and Kouri [17] method however, one is limited by the De Broglie wavelength and not the smoothness of the potential hence it is inefficient where the potential varies slowly. However, when the potential is varying rapidly (small r) the Gordon Program [18] requires a large number of steps and hence is less efficient than the Sams and Kouri [17] procedure. This is why we chose to use the Sams and Kouri [17] method at short distances and then switch over to Gordon Program [18] at large distances. Using this procedure we were able to solve the coupled scattering equations 5 times as fast as either method alone.

For distances less than 14.0 a.u. the Sams and Kouri [17] method was used with a step size of .005 a.u. which required about 3000 steps. For distances greater than 14.0 a.u. the Gordon Program [18] was used with all of the tolerance parameters set to $1.0 \times 10^{-12}$ except for TOLHI which was set at $5.0 \times 10^{-7}$. TOLHI governs the step size and hence the accuracy. Using these parameters we were able to calculate $|S_{\nu\nu'}^{\ell}|^2$ within a few percent when they had magnitudes as low as $10^{-11}$. Since the Sams and Kouri [17] algorithm does not use the first derivative of the scattering solution whereas the Gordon Program does it was necessary to calculate the first derivative of the solution at the switch over point 14.0 a.u. The first derivative could be propagated along with the solution in the Sams and Kouri [17] procedure with little additional computational effort. Also the derivative could be calculated very accurately using the Sloan formula [51],

$$\begin{aligned}\frac{d}{dr}\bar{g}_\ell(r_i) &= \frac{1}{2h}\left[9\,\bar{g}_\ell(r_i) - 16\,\bar{g}_\ell(r_{i-1}) + 7\,\bar{g}_\ell(r_{i-2})\right] \\ &\quad - \frac{h}{3}\left[8\,\bar{g}_\ell(r_{i-1})\left(\frac{\ell(\ell+1)}{r_{i-1}^2} + U(r_{i-1}) + k^2\right)\right. \\ &\quad \left. + \bar{g}_\ell(r_{i-1})\left(\frac{\ell(\ell+1)}{r_{i-2}^2} + U(r_{i-2}) + k^2\right)\right]\end{aligned} \qquad (3\text{-}74)$$

where h is the step size. Since the derivative is needed only at the switchover point, we chose this latter procedure since it is slightly faster numerically.

### iv. Vibrational Wavefunctions

The vibrational wavefunctions $\chi_{\bar{j}v}(R)$ [solutions of Eq. (3-9) with the Simons-Parr-Finlan [52] interatomic potential V(R)] of CO were obtained using the variational principle with the first 20 harmonic oscillators as a basis set. The harmonic oscillators have their origin at

$$R_o = (R_{max} + R_{min})/2 = 1.183\ \text{Å} \qquad (3\text{-}75)$$

where $R_{min}$ and $R_{max}$ are the inner and outer Rydberg-Klein-Reese [53] (RKR) turning points for the 9th vibrational level of CO. The force constant is chosen so that the eigenvalue of the 9th harmonic oscillator is equal to the experimental energy of the 9th vibrational level of CO. We obtained the first 10 vibrational energies accurate to within .0004%. Since the intermolecular potential was expanded in a power series about the equilibrium position Re, of CO it was necessary to calculate the coupling constants.

$$C^{n}_{\bar{j}\nu'\bar{j}\nu} = \langle \bar{j}\nu | (R-R_e)^m | \bar{j}\nu' \rangle \quad m = 0,1,2 \tag{3-76}$$

These constants were calculated using a 50 point Gauss-Hermite quadrature and are accurate to at least 5 significant figures.

## C. Results and Comparison with Experiment

Because the final rate constants involve averaging cross sections calculated at many energies and each cross section involves summing transition probabilities calculated at many values of the angular momentum $\ell'$ we will only give a few representative detailed results here. In Fig. 8 a plot is made of the opacity function $[(2\ell+1)|S^{\ell}_{01}|^2]$ (after averaging over the angle $\theta$) verses the angular momentum $\ell$ for the $0 \leftarrow 1$ transition at a relative incident energy $E/k_B = 1,915\ ^{\circ}K$. Opacity plots are very interesting since the area under the curve is proportional to the cross section and the impact parameter $(b=(\ell+1/2)/k$, where $k^2=2\mu E/h^2$ and E is the relative incident energy) is a measure of the closeness of the collision, i.e., small impact parameters imply a close collision. The maximum on the opacity curve corresponds to an impact parameter of 4.1 a.u. This indicates that at this relative kinetic energy the main contribution is due to the long range attractive part of the potential. The dependence upon the angular momentum is quite smooth and this plot is typical for all of the low energy scattering.

The opacity plot in Fig. 9 is at a relative incident kinetic energy $E/k_B$ of 20,915 $^{\circ}K$ for the $0 \leftarrow 1$ transition. The dependence upon the angular momentum $\ell$ is very smooth. This plot is typical for all scattering energies above 8,000 $^{\circ}K$. The maximum occurs at an impact parameter b of 1.1 a.u. which implies close collisions. The transition probability is totally dominated by the repulsive wall of the potential.

In Figs. 10 and 11 we have made opacity plots for the $1 \leftarrow 2$ and $0 \leftarrow 2$ transitions respectively at a relative incident $(\nu=2)$ $E/k_B$ of 17,869 $^{\circ}K$. It is seen that these plots are very similiar to the $0 \leftarrow 1$ transition given in Fig. 9, but the transition probabilities are smaller because the relative kinetic energy has decreased. The $0 \leftarrow 2$ transition in Fig. 11 has a very small cross section and is down by a factor of $10^5$

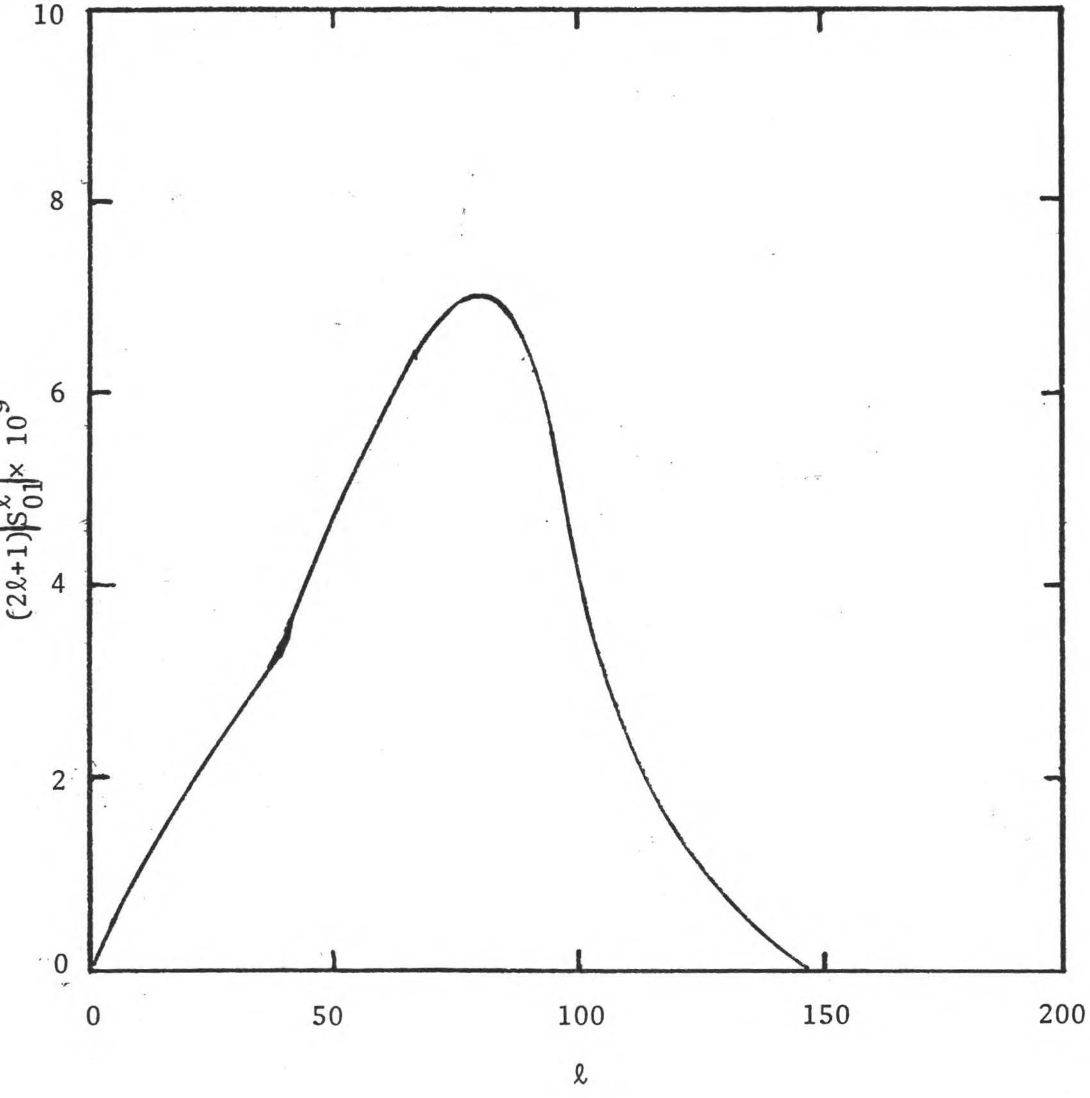

Fig. 8. -- Opacity function for the $0\leftarrow1$ transition at $E/k_B$ = 1,915 °K

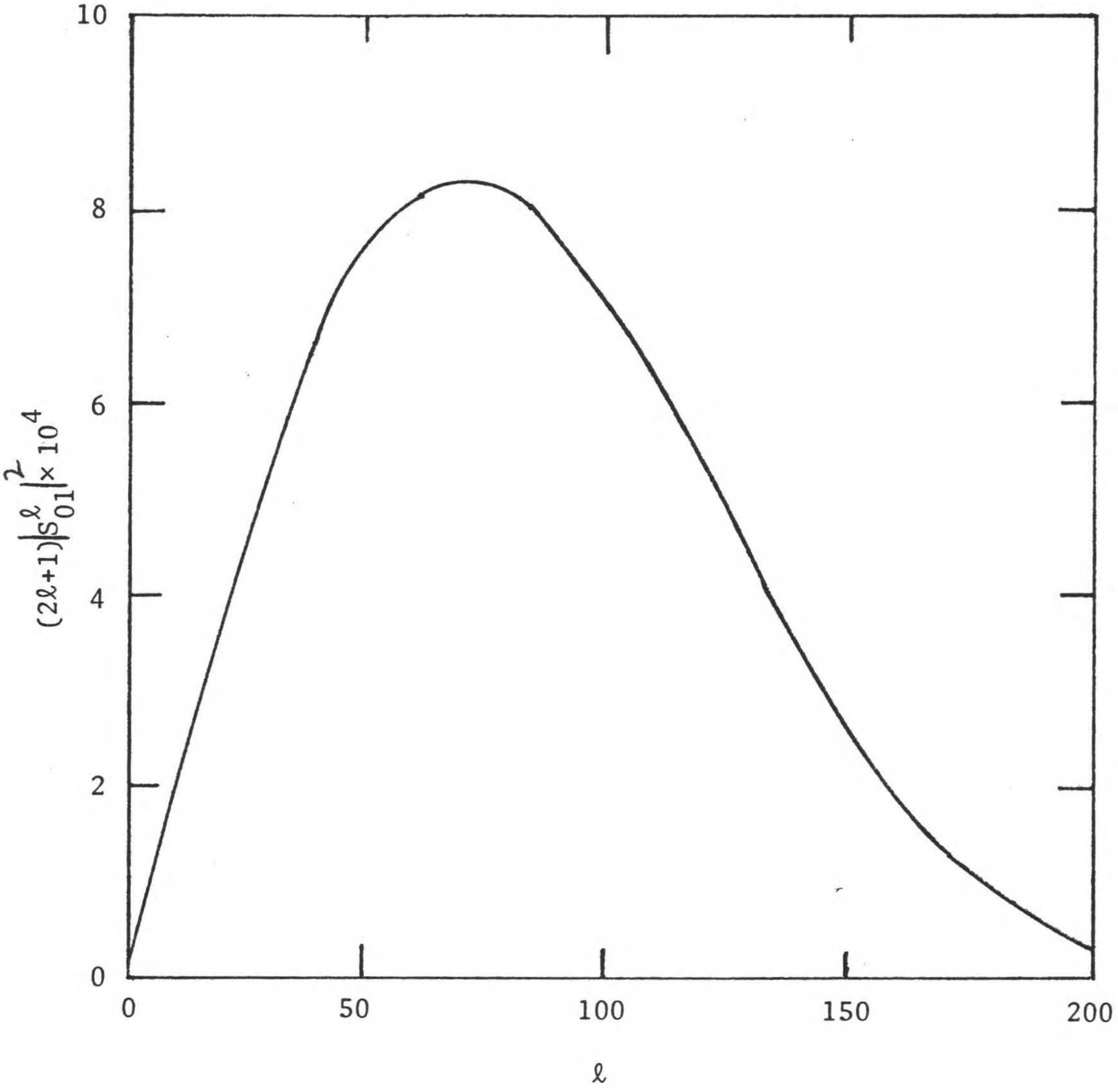

Fig. 9. -- Opacity function for the 0←1 transition at $E/k_B$ = 20,915 °K

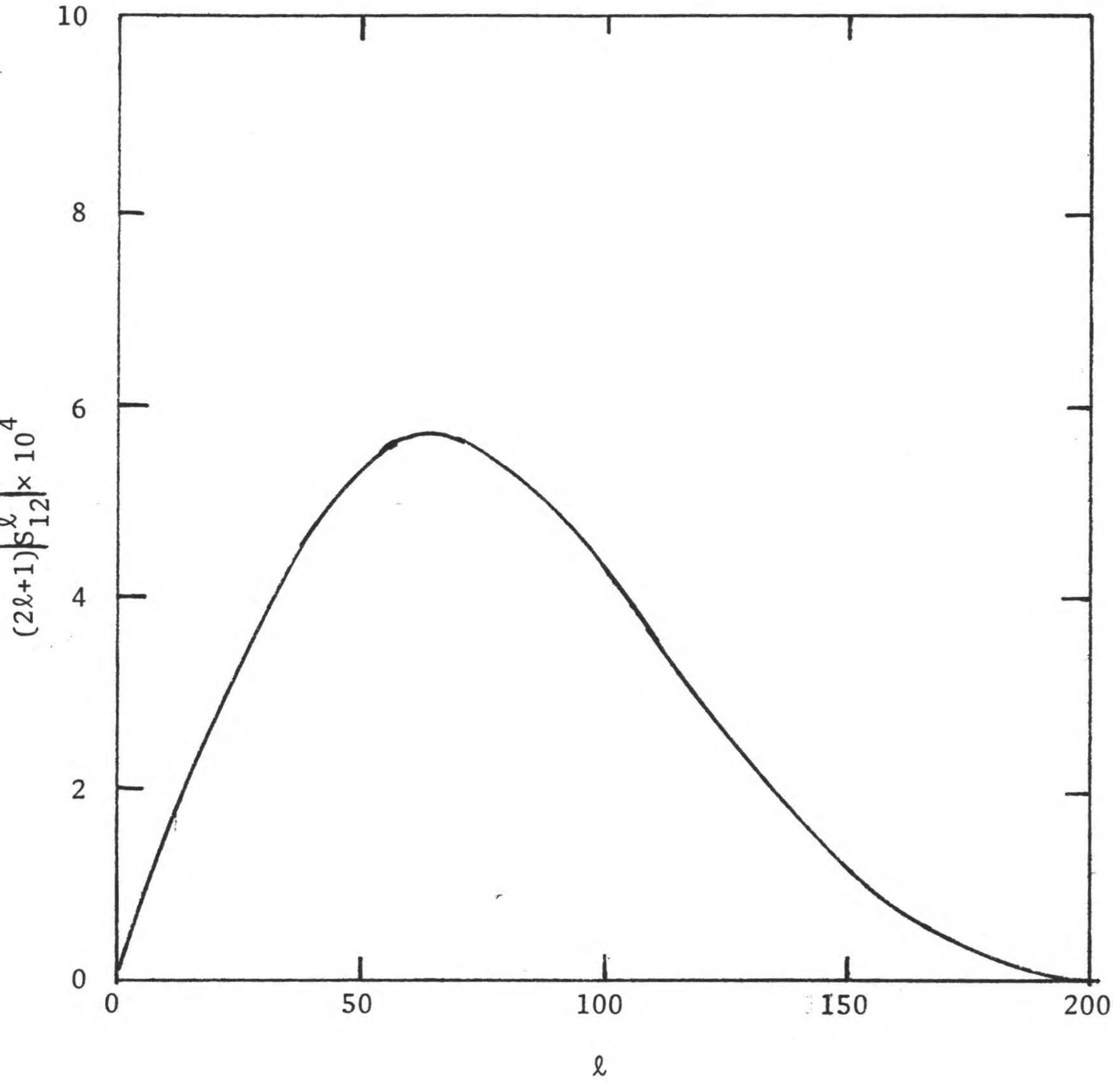

Fig. 10. -- Opacity function for the 1←2 transition at $E/k_B$ = 17,869 °K

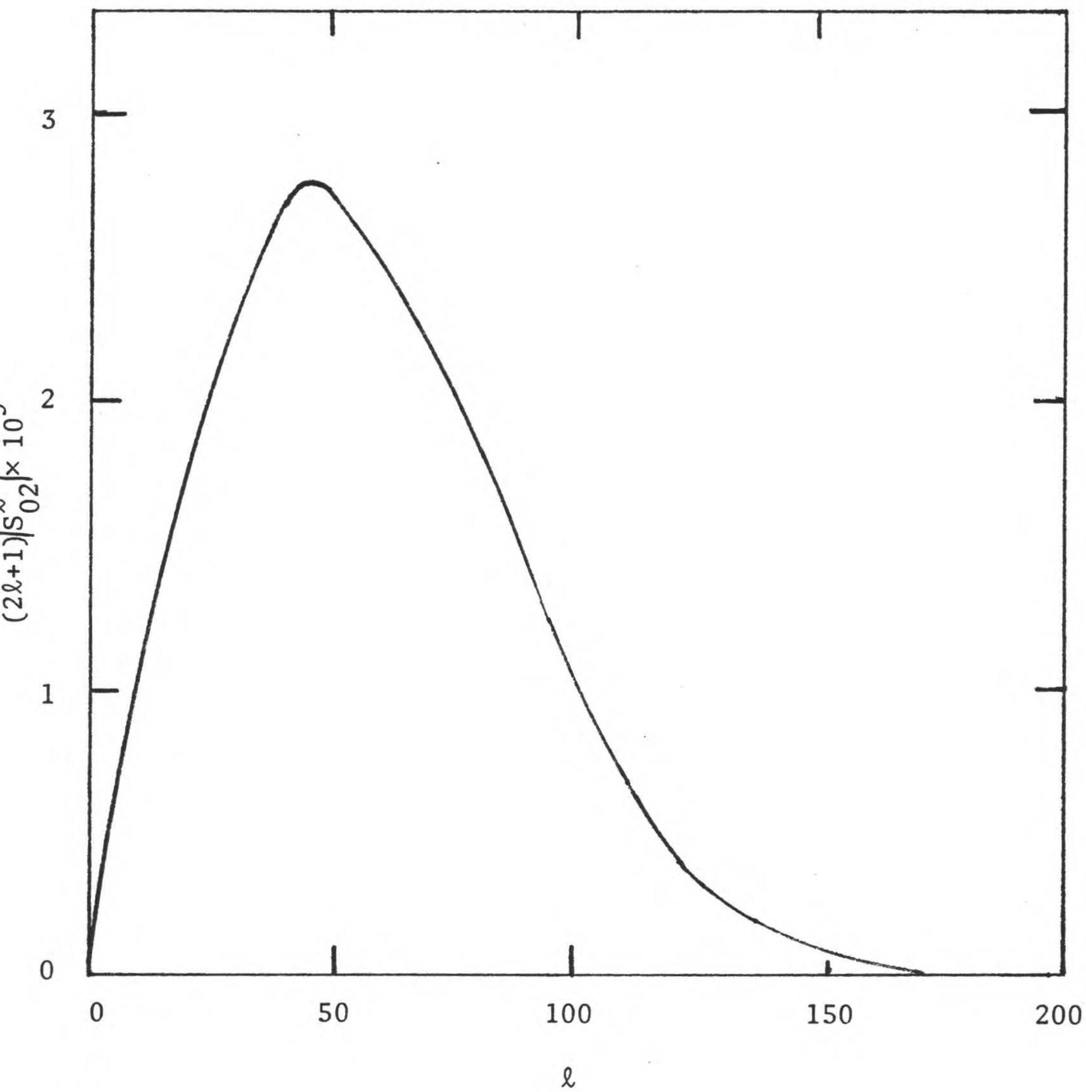

Fig. 11. -- Opacity function for the 0←2 transition at $E/k_B$ = 17,869 °K

when compared to the 0←1 transition. Also, the 0←2 transition has its maximum at a smaller impact parameter (b=0.77) than the 1←2 transition which implies that closer collisions are required for the 0←2 transition as would be expected.

In Figs. 12-15 plots are made of the total cross section $\sigma(0\leftarrow 1;\theta)$ (which parametrically depends upon the angle $\theta$) for the 0←1 transition at 4 different energies as a function of the angle $\theta$. It is seen that the angular dependence is quite smooth especially for the higher energies. For the higher energies it is noticed that the plots are all very similiar and that the maximum transition probability is near $90^{o}$ which clearly shows that the major contribution comes from perpendicular collisions. Thus, the well-known simple models which assume that vibrational transitions are predominately caused by collinear collisions are simply not valid for this system. These results are typical of all scattering energies. As the energy is decreased the maximum shifts off $90^{o}$ but never to a collinear configuration.

Since this angle dependence is somewhat surprising let us consider why it occurs. In Figs. 16-18 the coefficients, $V_m(r,\theta)$ (m=0, 1 or 2), in the expansion of the potential

$$V(r,\theta,R) = \sum_{m=0}^{2} V_m(r,\theta)(R-R_e)^m \quad , \tag{3-77}$$

in powers of the vibrational coordinate, have been plotted as a function of the distance r for 3 different angles. It is seen that for $\theta=97.2^{o}$ the m=1 and m=2 contributions are negative. That makes this the most favorable angle for vibrational transitions for the following reasons: First, it decreases the slope and hence allows more penetration into the barrier. Secondly, since the diagonal vibrational coupling matrix element [Eq. (3-76)] is larger for the higher vibrational state, the slope and magnitude of the diagonal potential matrix element [Eq. (3-12)] is smaller for the upper vibrational state causing the classical turning points to be closer together, giving more overlap and a greater transition probability. These explanations can also be shown [54] to be correct by using the distorted wave [49] approximation (which

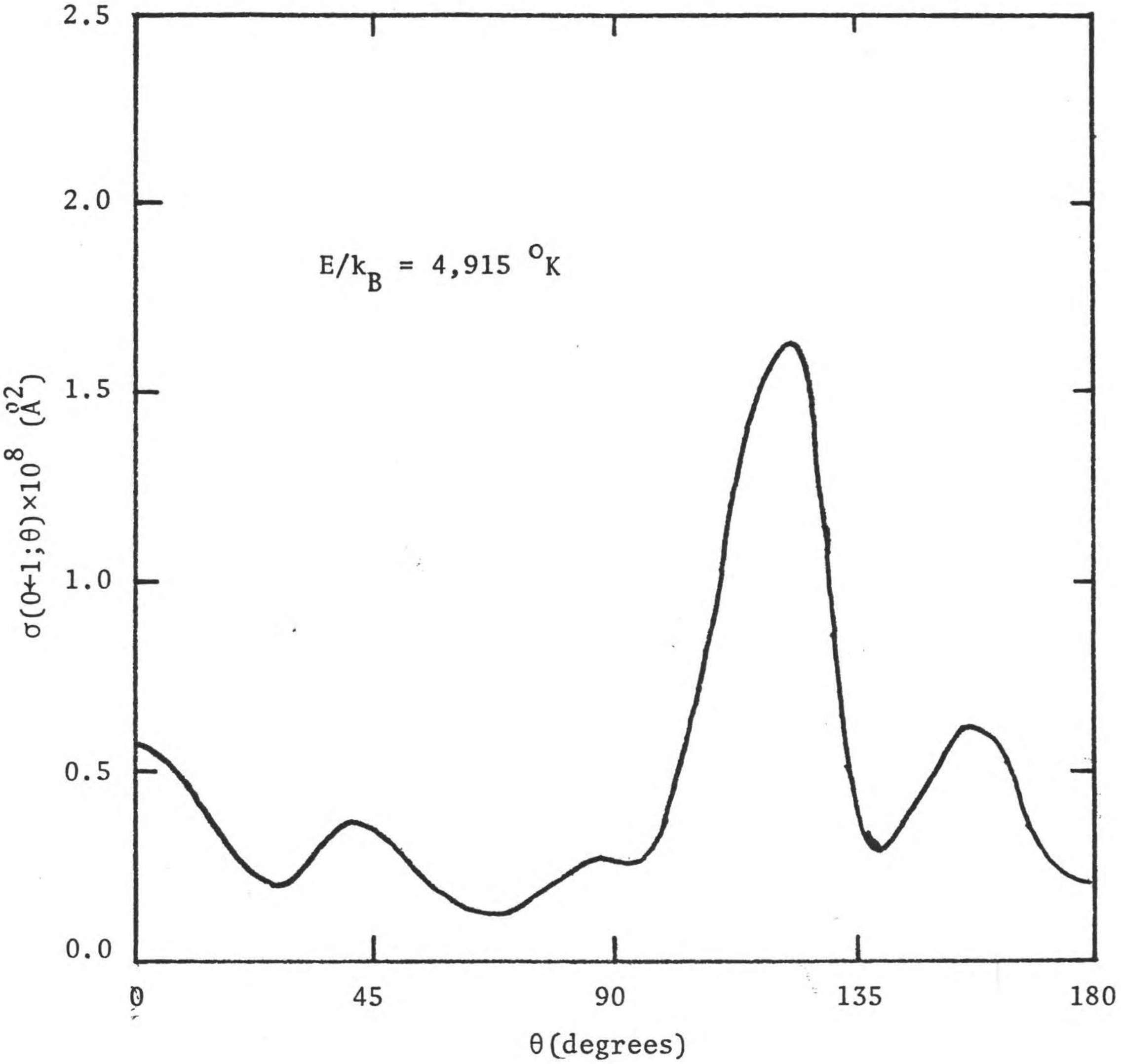

Fig. 12. -- The parametric θ dependence of the IOS total cross section for the $0\leftarrow 1$ transition at $E/k_B$ = 4,915 °K

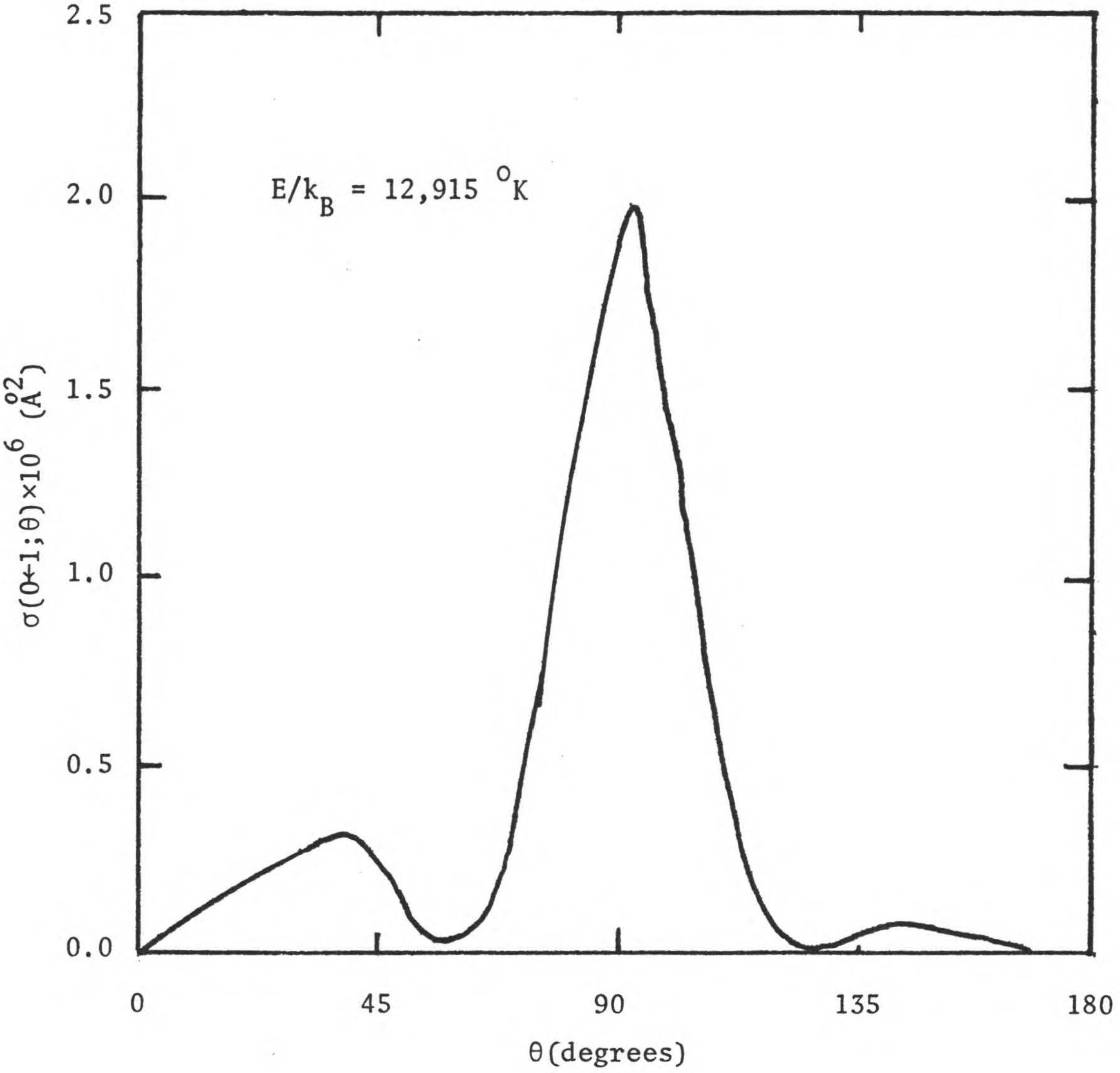

Fig. 13. -- The parametric θ dependence of the IOS total cross section for the 0←1 transition at $E/k_B$ = 12,915 °K

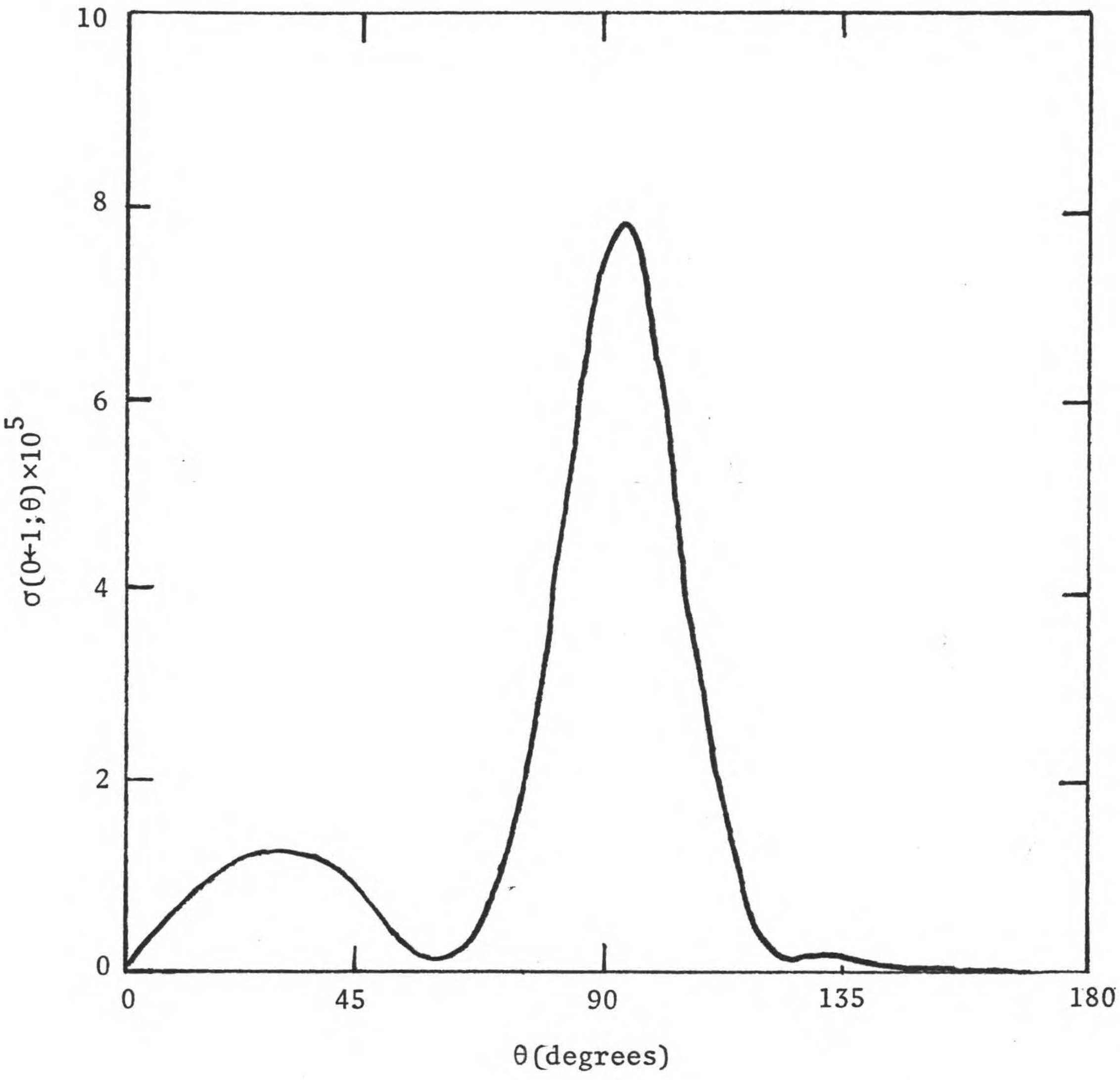

Fig. 14. -- The parametric θ dependence of the IOS total cross section for the $0\leftarrow1$ transition at $E/k_B$ = 20,915 °K

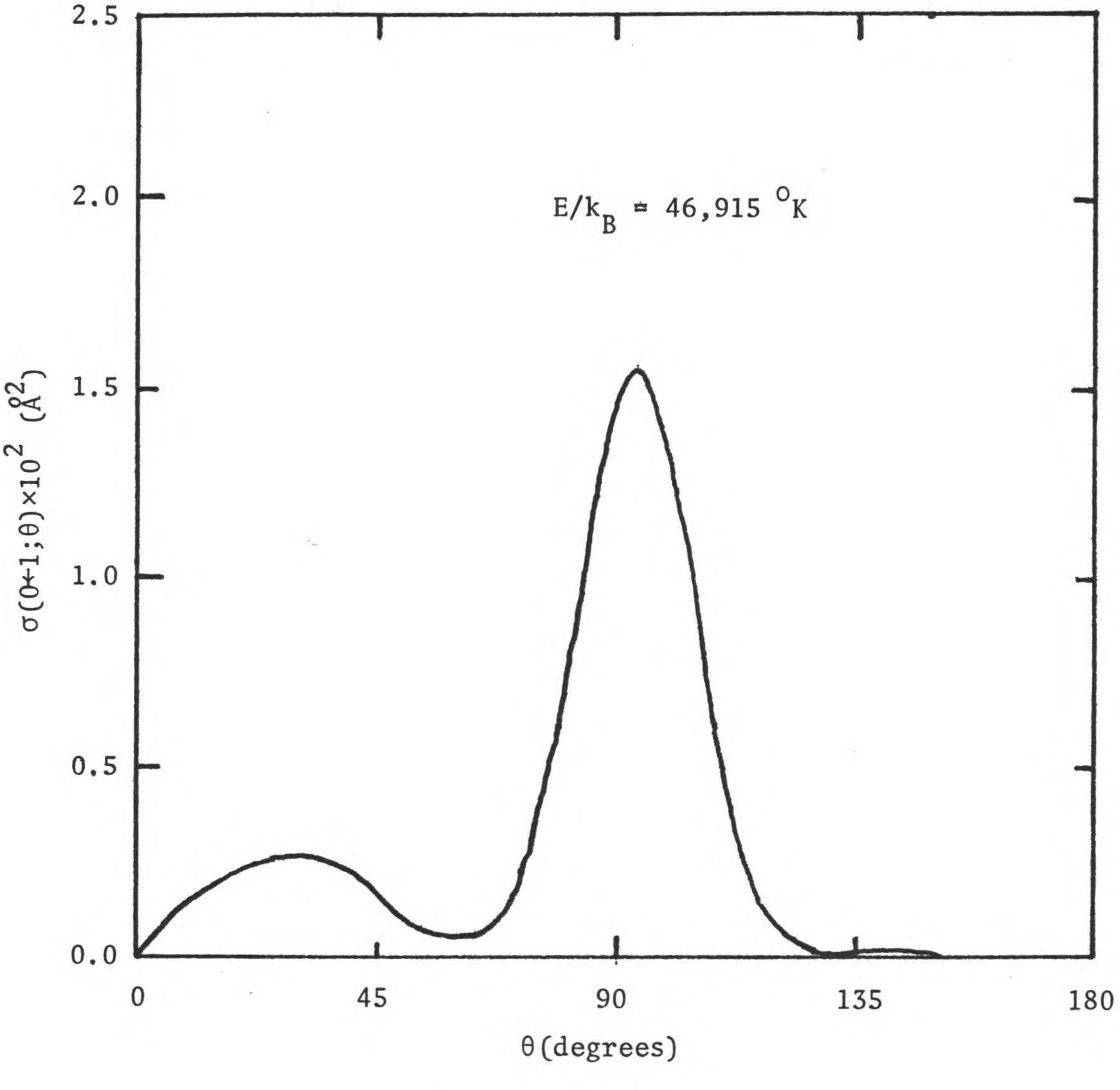

Fig. 15. -- The parametric θ dependence of the IOS total cross section for the $0\leftarrow 1$ transition at $E/k_B$ = 46,915 °K

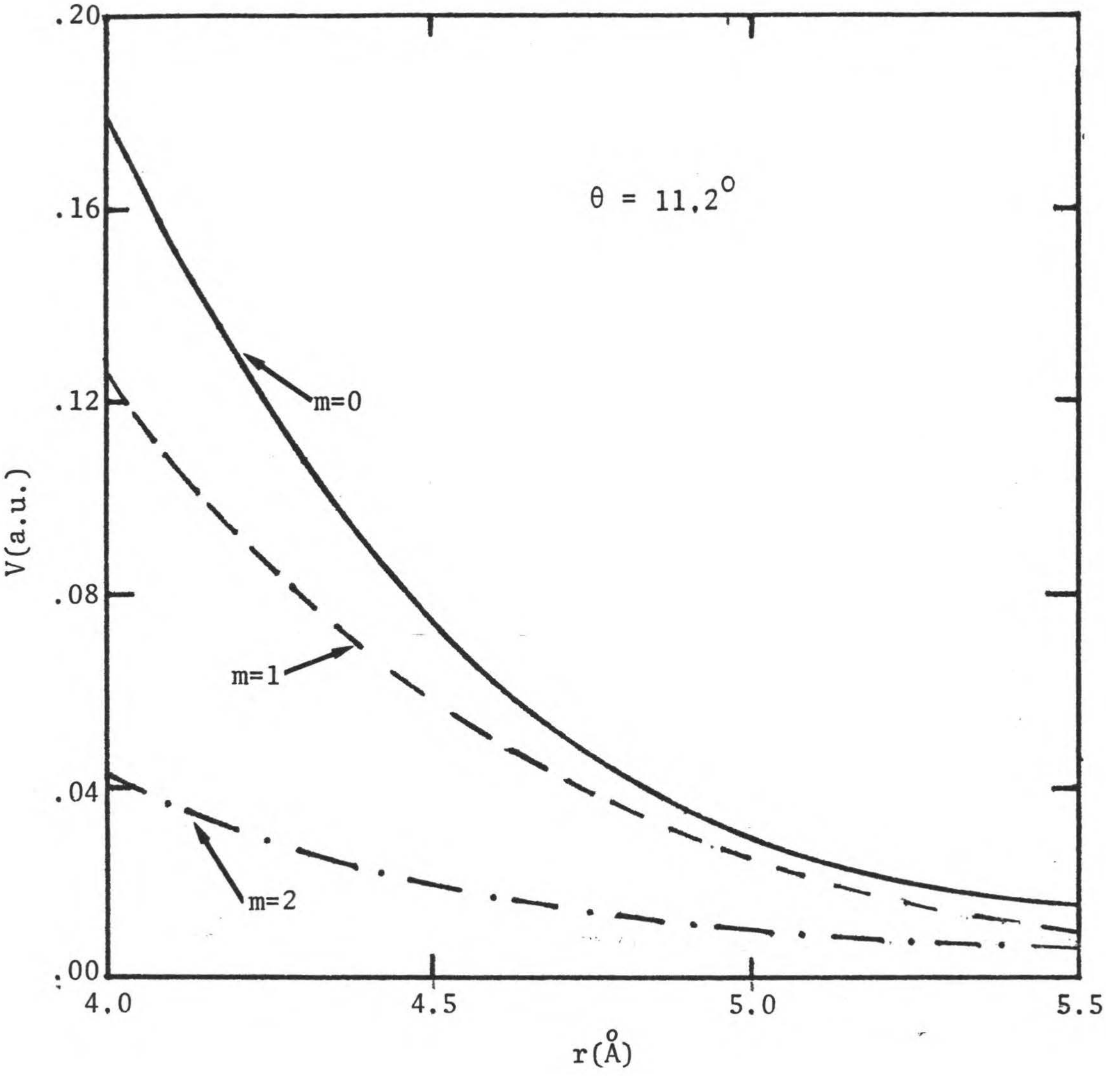

Fig. 16. -- The vibrational expansion coefficients of the Ar-CO potential at θ = 11.2°

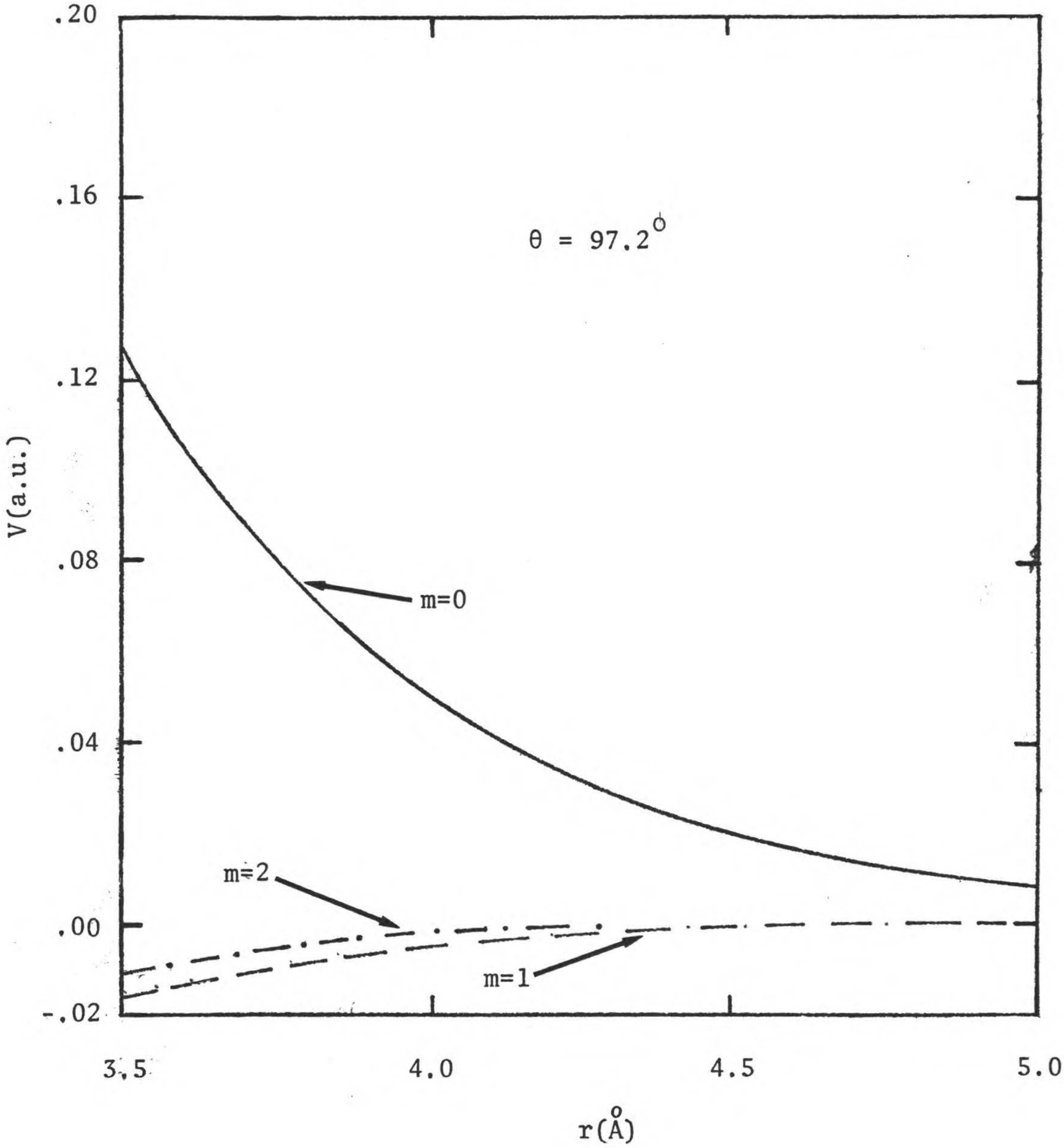

Fig. 17. -- The vibrational expansion coefficients of the Ar-CO potential at θ = 97.2°

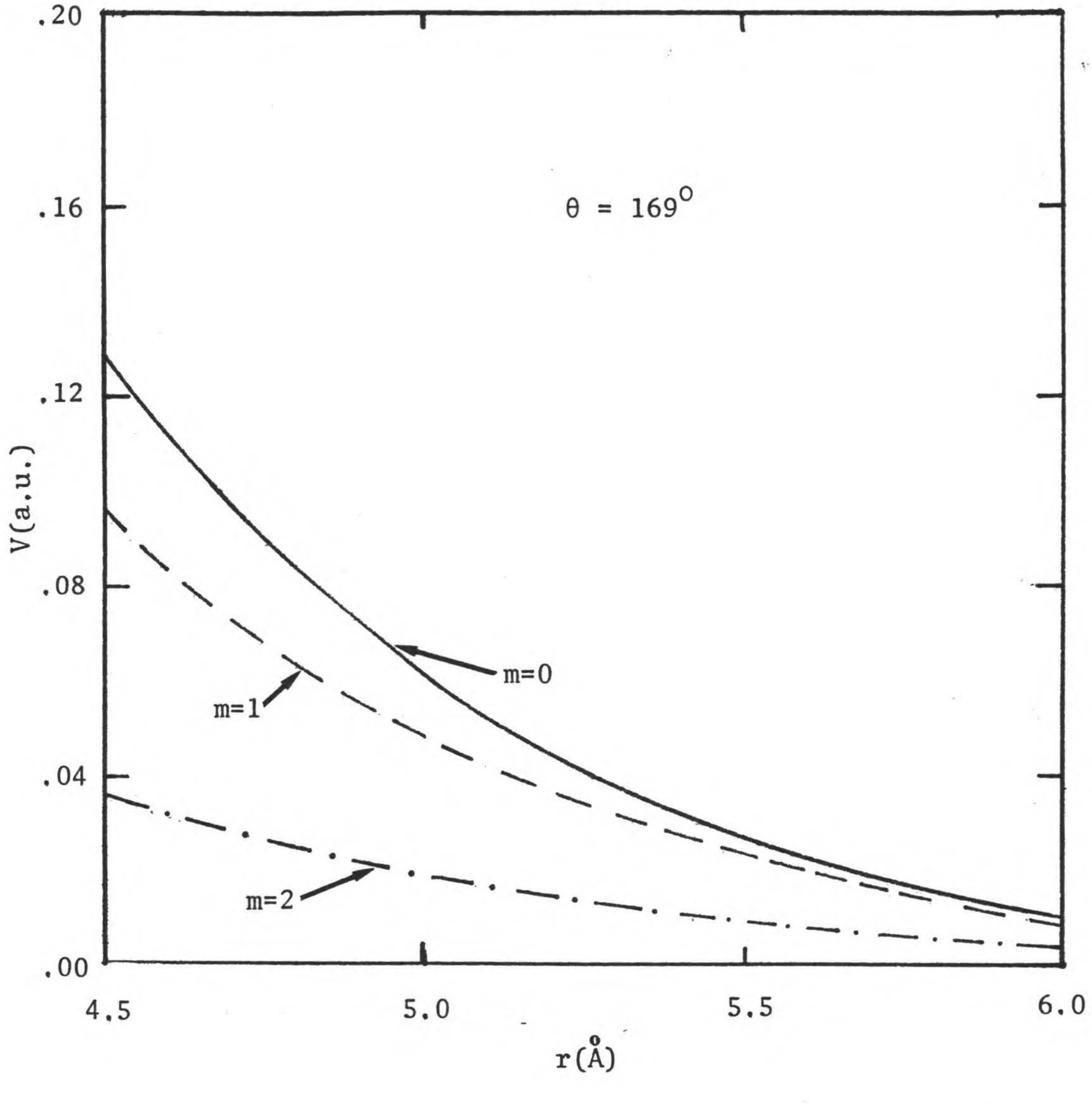

Fig. 18. -- The vibrational expansion coefficients of the Ar-CO potential at θ = 168.2°

correctly but qualitatively gives the same results) and evaluating the transition matrix elements using the saddle point method [55]. This also shows that the transition probabilities are not only very sensitive to the sign of the perturbing potentials ($V_m(r,\theta)$, m=1 or 2), through their diagonal matrix elements, but also to the ratio of the slope of the perturbing potential to its magnitude ($|V'_m(r,\theta)/V_m(r,\theta)|$, m=1 or 2) where the larger this ratio the larger the transition probability. This ratio is also largest at 97.2°. Thus, we see why the vibrational transition probabilities are very sensitive to the potential in this region.

Plotted in Fig. 19 are the total angle averaged cross sections (for $\Delta\nu=1$ transitions) versus the relative incident kinetic energy. The cross sections increase more rapidly with $\nu$ than one would expect from simple harmonic models. The additional increase is attributed to the closer spacing of the CO vibrational levels at higher vibrational quanta. Even at the highest scattering energies the cross sections have not reached a maximum and are well below the gas kinetic cross section in magnitude.

In Fig. 20 a comparison is made of our calculated vibrational relaxation rates (—— solid line) with the experimental values. The dashed line through the experimental values is a fit to the experiments using the Landau-Teller theory which predicts that $\ln k_{\nu\nu'}(T)$ vs. $T^{-1/3}$ should be a straight line. It is clear from the figure that our cross sections are considerably too small. This discrepancy can be caused by one of two reasons or a combination of both. First, in using the infinite order sudden approximation for the rotations we neglected the differences in the rotational energies, and large rotational transitions could reduce the effective energy gap between the vibrational channels; hence, larger transition probabilities would be expected. If this were the sole cause our relaxation rates would be better at low temperatures (since at higher temperatures the larger j states are more highly populated and the difference in rotational energies for the same $\Delta j$ transition would be larger causing a smaller effective vibrational energy gap) which is opposite to what is observed in our calculated rates. Although we do not believe this to be the case further calculations in which the vibrational energy gap has been reduced to test this possibility are necessary. The second and we feel most likely reason for the discrepancy could come from inaccuracies in the short range electron gas potential. As mentioned earlier our transition probabilities are very sensitive to the potential and self consistant field calculations are currently being performed to test the short range electron gas potential and hence this hypothesis.

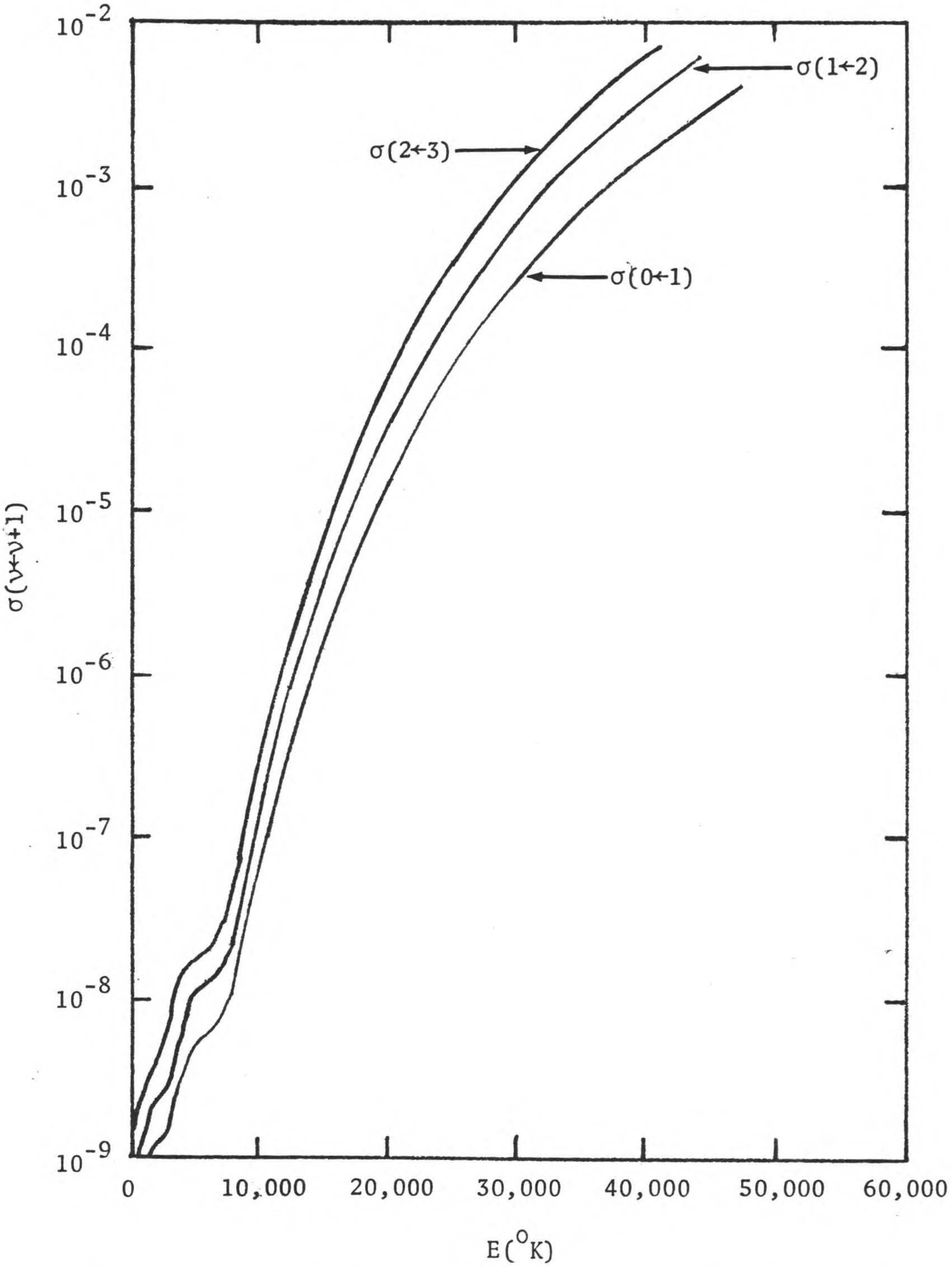

Fig. 19. -- Energy dependence of the total cross sections for the $\Delta\nu = \pm 1$ transitions

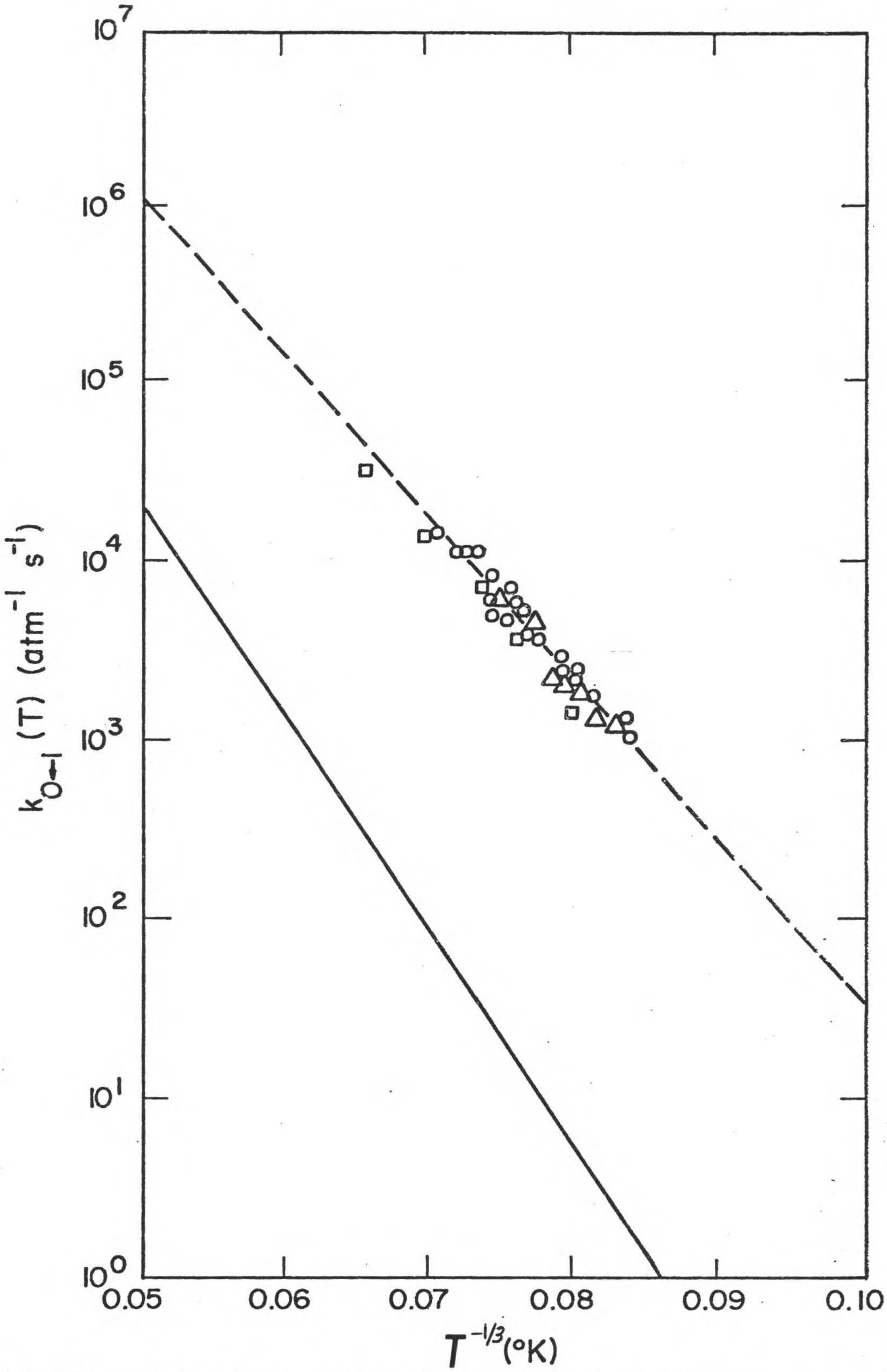

Fig. 20. -- Comparison of the calculated and experimental vibrational relaxation rates.

# IV. SUMMARY AND CONCLUSIONS

We have determined the angle, distance and vibration dependence of the Ar-CO intermolecular potential using a modification [3] of the electron gas model [1-4]. The long range behavior of the potential was determined from accurate van der Waals coefficients which were calculated from experimental refractive index data using the Padé approximant methods of Langhoff and Karplus [13]. These are presently the most accurate van der Waals coefficients for the interactions of CO.

We have obtained simplified expressions for the scattering amplitude and differential cross section within the infinite order sudden approximation. Then using the infinite order sudden approximation for the rotations in the Ar-CO system we solved the coupled vibrational scattering equations using a combination of the Sams and Kouri [17] algorithm (for short distances) and the Gordon [18] Airy function expansion method (for large distances) at a number of energies. and angular momentum values. Total cross sections were then calculated at several energies in order to determine the vibrational relaxation rates. It was found that our calculated rates are very sensitive to the short range potential and that they were much smaller that the experimental values. Indicating that extreme care should be taken in the classical turning point region, where a limited amount of configuration interaction or self consistant field calculations should be performed and used to obtain an $\alpha$-type parameter with which to scale the electron gas exchange energy, which will also be a very useful test of the accuracy of the potential.

In conclusion we beleive that this type of approach should be very useful in determining interactions of systems similiar to the Ar-CO system, i.e., systems in which the molecule has a small rotational constant and the reduced mass is large.

## LIST OF REFERENCES

1. V. L. Gaydaenko and V. K. Nikulin, Chem. Phys. Lett. 7, 360 (1970); V. K. Nikulin, Zh. Tekh. Fiz. 41, 41 (1971) [Sov. Phys. Tech. Phys. 16, 28 (1971)]. For a history of the method see V. K. Nikulin and Yu. N. Tsarev, Chem. Phys. 10, 433 (1975).

2. R. G. Gordon and Y. S. Kim, J. Chem. Phys. 56, 3122 (1972); Y. S. Kim and R. G. Gordon, J. Chem. Phys. 60, 1842 (1974).

3. J. S. Cohen and R. T Pack, J. Chem. Phys. 61, 2372 (1974).

4. Y. S. Kim and R. G. Gordon, J. Chem. Phys. 61, 1 (1974).

5. G. A. Parker, R. L. Snow, and R. T Pack (unpublished).

6. G. A. Parker, R. L. Snow, and R. T Pack, Program No. 305 (1976), Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana 47401.

7. A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc. Lond. A 256, 540 (1960).

8. T. P. Tsien and R. T Pack, Chem. Phys. Lett. 6, 54 (1970); 8, 579 (1971).

9. T. P. Tsien, G. A. Parker, and R. T Pack, J. Chem. Phys. 59, 5373 (1973).

10. R. T Pack, J. Chem. Phys. 60, 633 (1974).

11. D. Secrest, J. Chem. Phys. 62, 710 (1975).

12. L. W. Hunter, J. Chem. Phys. 62, 2855 (1975).

13. P. W. Langhoff and M. Karplus, J. Opt. Soc. Am. 59, 863 (1969); P. W. Langhoff, J. Chem. Phys. 57, 2604 (1972).

14. R. T Pack, J. Chem. Phys. 61, 2091 (1974).

15. G. A. Parker and R. T Pack, J. Chem. Phys. 64, 2010 (1976).

16. G. C. Nielson, G. A. Parker, and R. T Pack, J. Chem. Phys. 64, 2055 (1976).

17. W. N. Sams and D. J. Kouri, J. Chem. Phys. 51, 4809 (1969); W. N. Sams and D. J. Kouri, J. Chem. Phys. 51, 4815 (1969).

18. R. G. Gordon, J. Chem. Phys. 51, 14 (1969); R. G. Gordon, Methods in Computat. Phys. 10, 81 (1971); Program 187, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana 47401.

19. W. J. Hooker and R. C. Millikan, J. Chem. Phys. 38, 214 (1963).

20. K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press, New York, 1959).

21. A. L. Russo, J. Chem. Phys. 47, 5201 (1967).

22. T. Just and P. Roth, J. Chem. Phys. 55, 2395 (1971).

23. W. H. Green and J. K. Hancock, J. Chem. Phys. 59, 4326 (1973).

24. G. A. Parker, R. L. Snow, and R. T Pack, Chem. Phys. Lett. 33, 399 (1975).

25. G. A. Parker, R. L. Snow, and R. T Pack, J. Chem. Phys. 64, 1668 (1975).

26. A. I. M. Rae, Chem. Phys. Lett. 18, 574 (1973).

27. J. C. Slater and K. H. Johnson, Phys. B 5, 844 (1972); J. C. Slater, Phys. Rev. 81, 385 (1851); 82, 538 (1951).

28. E. Clementi, IBM J. Res. Dev. Suppl. 9, 2 (1965).

29. A. D. Mclean and M. Yoshimine, IBM J. Res. Dev. 12, 206 (1968).

30. M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1968).

31. A. H. Stroud and D. Secrest, *Gaussian Quadrature Formulas* (Prentice-Hall, Englewood Cliffs, N. J., 1966).

32. R. T Pack, J. Chem. Phys. 64, 1659 (1976), references therein, and subsequent unpublished work.

33. J. Brewer, Tech. Rept. AD 663448 (1967). Available from the Clearinghouse for Federal Scientific and Technical Information.

34. J. E. Jordan, S. O. Colgate, I. Amdur, and E. A. Mason, J. Chem. Phys. 52, 1143 (1970).

35. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967).

17. W. N. Sams and D. J. Kouri, J. Chem. Phys. 51, 4809 (1969); W. N. Sams and D. J. Kouri, J. Chem. Phys. 51, 4815 (1969).

18. R. G. Gordon, J. Chem. Phys. 51, 14 (1969); R. G. Gordon, Methods in Computat. Phys. 10, 81 (1971); Program 187, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana 47401.

19. W. J. Hooker and R. C. Millikan, J. Chem. Phys. 38, 214 (1963).

20. K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic Press, New York, 1959).

21. A. L. Russo, J. Chem. Phys. 47, 5201 (1967).

22. T. Just and P. Roth, J. Chem. Phys. 55, 2395 (1971).

23. W. H. Green and J. K. Hancock, J. Chem. Phys. 59, 4326 (1973).

24. G. A. Parker, R. L. Snow, and R. T Pack, Chem. Phys. Lett. 33, 399 (1975).

25. G. A. Parker, R. L. Snow, and R. T Pack, J. Chem. Phys. 64, 1668 (1975).

26. A. I. M. Rae, Chem. Phys. Lett. 18, 574 (1973).

27. J. C. Slater and K. H. Johnson, Phys. B 5, 844 (1972); J. C. Slater, Phys. Rev. 81, 385 (1851); 82, 538 (1951).

28. E. Clementi, IBM J. Res. Dev. Suppl. 9, 2 (1965).

29. A. D. Mclean and M. Yoshimine, IBM J. Res. Dev. 12, 206 (1968).

30. M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions (Dover, New York, 1968).

31. A. H. Stroud and D. Secrest, Gaussian Quadrature Formulas (Prentice-Hall, Englewood Cliffs, N. J., 1966).

32. R. T Pack, J. Chem. Phys. 64, 1659 (1976), references therein, and subsequent unpublished work.

33. J. Brewer, Tech. Rept. AD 663448 (1967). Available from the Clearinghouse for Federal Scientific and Technical Information.

34. J. E. Jordan, S. O. Colgate, I. Amdur, and E. A. Mason, J. Chem. Phys. 52, 1143 (1970).

35. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1967).

54. R. T Pack (private communication).

55. R. T Pack and J. S. Dahler, J. Chem. Phys. 50, 2397 (1969).

# APPENDIX A

## ROTATIONALLY INELASTIC MOLECULAR SCATTERING. COMPUTATIONAL TESTS OF SOME SIMPLE SOLUTIONS OF THE STRONG COUPLING PROBLEM.

(A reprint. See Thomas P. Tsien, Gregory A. Parker and Russell T Pack, J. Chem. Phys. 59, 5373 (1973).)

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# Rotationally inelastic molecular scattering. Computational tests of some simple solutions of the strong coupling problem*

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(Received 13 August 1973)

Partial cross sections (opacity functions) for rotational transitions in atom–diatom collisions are computed in the infinite-order sudden (IOS) approximation and compared with accurate close-coupling (CC) calculations. Agreement is good in the dominant coupling (small total angular momentum $J$) region. Simple methods for calculating integral inelastic cross sections are discussed, and it is found that accurate cross sections can often be computed very simply, even when large numbers of channels are coupled together, by using IOS or first-order sudden (FOS) approximations for small $J$ and CC or exponential Born (EBDW) methods for large $J$.

## I. INTRODUCTION

A major problem in the quantum theory of molecular scattering is that (for small total angular momentum $J$ and any molecules except hydrides) the collision causes large numbers of rotational states to be strongly coupled together. This gives rise to a large set of coupled radial Schrödinger equations which must be solved simultaneously. Although truly significant advances[1,2] have been made in recent years in the accurate, close-coupled (CC) numerical solution of these equations, the CC computation of the large numbers of cross sections needed in the description of relaxation and reactive processes is still exceedingly expensive. Hence, there remains a real need for approximate methods which give accurate results and yet are computationally simple.

Most simple approximations (such as the ordinary distorted wave approximation) fail miserably in the dominant coupling (small $J$) region. Besides the sudden approximations used herein, the only other computationally simple method that we know of that may be useful here is the statistical approximation.[3] But it cannot be used unless one knows from some other source how many channels are strongly coupled together,[4] and it does not give the phase oscillations observed in the figures presented in Sec. III. Hence, it was not used in this work.

In this paper we report calculations comparing some sudden approximations with accurate CC results for several atom–diatom rotationally inelastic collisons using empirical intermolecular potentials. In Sec. II the problem and methods used are outlined; then, in Sec. III, results are presented and comparisons made. We conclude in Sec. IV that simple but adequate approximate solutions of the rotationally inelastic scattering problem are now known.

## II. THEORY AND CALCULATIONS

Since the approximations used in this paper have all been discussed elsewhere, only a sketch of their derivations is given.

The objective here is to solve the Schrödinger equation for the collision of an atom A with a diatomic molecule BC. To get at the essential difficulty of treating rotational states, we use the rigid rotor model and formulation of Arthurs and Dalgarno[5] with empirical intermolecular potentials $U$ of the form

$$U(r', \theta) = V(r') + W(r')\, P_2(\cos\theta), \tag{1}$$

where the coordinates are those shown in Fig. 1 and the primes stand for cgs units. In reduced units ($r = r'/\sigma$, where $\sigma$ is the point at which $V$ is zero), the coupled equations which must be solved can be written in the form[5]

$$[\mathbf{1}d^2/dr^2 + \mathbf{E} - V(r)\,\mathbf{1} - W(r)\,\mathbf{F}]\,\mathbf{G}(r) = 0, \tag{2}$$

where $\mathbf{G} = \{G_n(r)\}$ is a column vector of radial channel wavefunctions, $\mathbf{F}$ is a matrix of Percival–Seaton[3,5,6] coefficients, $\mathbf{1}$ is the unit matrix, and the elements of $\mathbf{E}$ are

$$E_{mn} = \delta_{mn}[k_n^2 - l_n(l_n + 1)/r^2], \tag{3}$$

where the $l_n$ are relative orbital angular momenta. In these reduced units the channel wavenumbers $k_n$ and energies $k_n^2$ are given by

$$k_n^2 = 2\mu\sigma^2 E/\hbar^2 - Bj_n(j_n + 1), \tag{4}$$

where $\mu$ is the atom–diatom reduced mass, $E$ is the total energy (in cgs units), and the $j_n$ are the rotor angular momentum quantum numbers. The rotational constant $B$ of the diatomic molecule is given in these units by

$$B = \mu\sigma^2/I_{BC} = \mu_{A-BC}\,\sigma^2/\mu_{BC}R'^2 \tag{5}$$

where $R'$ is the average BC internuclear distance,

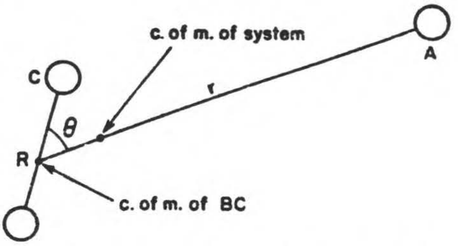

FIG. 1. Center of mass coordinates used herein for A + BC collisions.

and $\mu_{BC}$ is the reduced mass of BC. The potentials used herein are (in reduced units)

$$V = 4D(r^{-12} - r^{-6}), \tag{6}$$

and

$$W = 4D(a_{12}\, r^{-12} - a_6\, r^{-6}), \tag{7}$$

where $D = 2\mu_{A-BC}\sigma^2\epsilon/\hbar^2$. Here $\epsilon$ is the (cgs) depth of the intermolecular potential and $a_{12}$ and $a_6$ are asymmetry parameters.

For each value of the total angular momentum $J$, one must solve the set of coupled equations (2) subject to the boundary conditions

$$G_n \underset{r\to\infty}{\simeq} k_n^{-1/2}\{\delta_{ni}\exp[-i(k_i r - \tfrac{1}{2}l_i\pi)] - S_{ni}^J \exp[i(k_n r - \tfrac{1}{2}l_n\pi)]\} \tag{8}$$

to obtain the elements $S_{ni}^J$ of the scattering matrix. Once this is done the degeneracy-averaged integral cross sections needed can be written in the form[5]

$$\sigma(j_m \to j_n) = (\pi/k_n^2)\sum_{J=0}^{\infty}(2J+1)\,\mathcal{P}_J(j_m, j_n), \tag{9}$$

where the opacity functions (average transition probabilities) $\mathcal{P}_J(j_m, j_n)$ are given by[7]

$$\mathcal{P}_J(j_m, j_n) = (2j_n+1)^{-1}\sum_{l_n=|J-j_n|}^{J+j_n}\ \sum_{l_m=|J-j_m|}^{J+j_m} |\delta_{mn} - S_{mn}^J|^2. \tag{10}$$

To compute "exact" cross sections, one truncates the infinite set of coupled equations by restricting the number of rotational states $j_n$ included, solves the resulting finite set of equations numerically using some CC method and then adds additional rotor states $j_n$ (and their associated $l_n$) and repeats the CC calculations until the desired opacity functions converge to within some specified accuracy. The CC computations reported here were performed using Gordon's method[1] and program.[8] The results are accurate but expensive.

Many simple approximate solutions of (2), such as the ordinary distorted-wave (DW) methods, often give ridiculous results for the systems considered here. For example, the DW $\sigma(2-0)$ for the Ar + TlF example in Sec. III is over ten times too large, and the DW $\sigma(4-0)$ is identically zero. At the very least, one must have a many-state, probability-conserving approximation. One such approximation which we have previously discussed[9,10] is the strong coupling or infinite-order sudden (IOS) approximation, appropriate for the small $J$ regions where the elements of $WF$ dominate the differences in the elements of $\mathbf{E}$ and strongly couple the equations together. In the IOS approximation one sets $k_n = k$ and $l_n = l$ for all the strongly coupled channels. Then, the resulting equations can be solved exactly: Let $\mathbf{G} = \mathbf{U}\mathbf{g}$, where $\mathbf{U}$ is the $r$-independent unitary transformation which makes $\mathbf{U}^\dagger\mathbf{F}\mathbf{U} = \Lambda$ diagonal. Then, the elements of $\mathbf{g}$ satisfy uncoupled equations and the resulting $S$ matrix is[9,10]

$$\mathbf{S}^J = \mathbf{U}\mathbf{B}\mathbf{U}^\dagger = \exp(2i\mathbf{U}\eta\mathbf{U}^\dagger), \tag{11}$$

where

$$B_{mn} = \delta_{mn}\exp(2i\eta_n^{sc}), \tag{12}$$

and

$$(\eta)_{mn} = \delta_{mn}\eta_n^{sc} \tag{13}$$

The WKB approximation for the phase shifts $\eta_n^{sc}$ is

$$\eta_n^{sc} = \int_{r_n}^{\infty}\{[k^2 - (l+\tfrac{1}{2})^2/r^2 - V - W\Lambda_n]^{1/2} - k\}\,dr - kr_n + \tfrac{1}{2}(l+\tfrac{1}{2})\pi, \tag{14}$$

where $r_n$ is the turning point and $\Lambda_n$ an element of the diagonal matrix $\Lambda$. Thus, an $N$ state IOS calculation at a given $J$ simply requires the diagonalization of one $N\times N$ matrix $\mathbf{F}$ and evaluation of $N$ WKB phase shifts. In the IOS computations reported here, the Jacobi method was used for the diagonalization and a Simpson's rule numerical integration with increasing step size was used for the phase shifts.

As we have noted previously,[10] if one expands (14) in powers of $\Lambda_n$ and keeps only the terms through $\mathcal{O}(\Lambda_n)$, the resulting scattering matrix,

$$\mathbf{S}^J = \exp[2i(\eta^{(0)}\mathbf{1} + \eta^{(1)}\mathbf{F})], \tag{15}$$

is precisely that of the familiar semiclassical first-order sudden (FOS) approximation.[11] Here

$$\eta^{(0)} = \int_{r_0}^{\infty}\{[k^2 - (l+\tfrac{1}{2})^2/r^2 - V]^{1/2} - k\}\,dr - kr_0 + \tfrac{1}{2}(l+\tfrac{1}{2})\pi, \tag{16}$$

and

$$\eta^{(1)} = -\frac{1}{2}\int_{r_0}^{\infty}\frac{W(r)}{[k^2 - (l+\tfrac{1}{2})^2/r^2 - V]^{1/2}}\,dr. \tag{17}$$

Thus, $N$ state FOS calculations require evaluation of just two phase integrals and expansion of the

TABLE I. Parameters used herein. $\mu_{A-BC}$ is the reduced mass of A + BC in atomic mass units; $\sigma$ is the size parameter of the 12–6 potential in angstroms; $a_{12}$ and $a_6$ are the repulsive and attractive asymmetry parameters, respectively; $\epsilon/k_B$ is the depth of the potential well in °K; $B'$ is the rotational constant of the diatomic molecule in $\mathrm{cm}^{-1}$; $E/k_B$ is the total relative energy available in °K; $D$ is the reduced well depth; $B$ the reduced rotational constant; and $k^2(j=0)$ the reduced total energy.

| System | $\mu_{A-BC}$(amu) | $\sigma$(Å) | $a_{12}$ | $a_6$ | $\epsilon/k_B$(°K) | $B'$ ($\mathrm{cm}^{-1}$) | $E/k_B$(°K) | $D$ | $B$ | $k^2(j=0)$ | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ar–TlF | 33.89 | 4.62 | 0.50 | 0.30 | 132.5 | 0.22246 | 1344 | 3947.8 | 9.541 | 40,071 | 13,a |
| Ar–$N_2$ | 16.47 | 3.50 | 0.50 | 0.13 | 119.5 | 2.010 | 300 | 994.2 | 24.06 | 2495.9 | 16 |
| Ar–$F_2$ | 19.48 | 3.550 | 0.200 | 0.200 | 115.9 | 0.862 | 300 | 1173. | 12.55 | 3036 | 18,b |
| Ar–$Cl_2$ | 25.55 | 3.831 | 0.200 | 0.200 | 190.7 | 0.2438 | 300 | 2948. | 5.423 | 4638 | 18,b |
| Ar–$Br_2$ | 31.96 | 3.837 | 0.200 | 0.200 | 249.8 | 0.08091 | 300 | 4846. | 2.258 | 5820 | 18,b |
| Ar–$I_2$ | 34.52 | 4.146 | 0.200 | 0.200 | 256.9 | 0.03736 | 300 | 6285. | 1.315 | 7339 | 18,b |

[a] R. K. Ritchie and H. Lew, Can. J. Phys. 43, 1701 (1965).

[b] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950), 2nd edition.

exponential of a matrix. In this work direct expansion of (15) was found to require as many as 30 terms for convergence. To decrease this number and avoid roundoff error, a Chebyshev polynomial contraction of the expansion was made.

For the moderate- and weak-coupling region (large $J$) the sudden approximations are not accurate. However, the number of channels ($N$) required in this region is quite small, so that one can often afford to do the CC calculations. Also, one could use the exponential distorted wave approximations (EDW) discussed by Levine.[12] These start with Eq. (2) and treat $WF$ as the perturbation in an exponential perturbation method to get a unitary $S$ matrix. If one uses the Born approximation as zeroth order, the resulting EBDW calculations[13] are easily performed. If one uses a distorted-wave approximation as zeroth order, the resulting EDWD approximation gives better results but is *much* more expensive computationally, except in those cases in which one can evaluate the necessary integrals using asymptotic methods.[10,14]

The calculations reported herein were carried out using the Brigham Young University IBM 360/50 and 7030 STRETCH computers. For typical many-state calculations the relative running times of the FOS : IOS : CC programs were 1 : 2 : 90.

## III. RESULTS

In this section numerical results for some model problems are presented.

TABLE II. Convergence of partial cross sections as the number of channels ($N$) is increased. The numbers are the values of $(2J+1)\,\mathcal{P}_J(2-0)$ for Ar + TlF calculated in the infinite order sudden (IOS) and close-coupling (CC) approximations. $J$ is the total angular momentum and $j_{max}$ the largest rotor $j$ kept.

| $j_{max}$ | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | |
|---|---|---|---|---|---|---|---|---|---|
| $J$ | $N$ 9 | 16 | 25 | 36 | 49 | 64 | 81 | 100 | Method |
| 0 | 0.433 | 0.209 | 0.182 | 0.040 | 0.085 | 0.079 | 0.078 | 0.078 | IOS |
| | 0.428 | 0.217 | 0.199 | 0.045 | 0.090 | 0.086 | 0.085 | 0.085 | CC |
| 20 | 16.1 | 8.78 | 7.18 | 1.65 | 3.43 | 3.11 | 3.11 | | IOS |
| | 16.0 | 9.11 | 7.49 | 1.81 | 3.55 | | | | CC |
| 40 | 22.5 | 17.9 | 12.0 | 2.88 | 5.54 | 5.31 | 5.25 | | IOS |
| | 23.0 | 18.4 | 13.6 | 3.40 | 6.10 | | | | CC |
| 80 | 0.28 | 26.4 | 3.37 | 0.89 | 1.60 | 1.42 | 1.42 | | IOS |
| | 1.13 | 26.6 | 5.30 | 0.91 | 1.91 | | | | CC |
| 120 | 102.5 | 51.8 | 26.0 | 34.1 | 33.5 | 33.3 | | | IOS |
| | 99.7 | 48.1 | 23.0 | 31.0 | 30.4 | | | | CC |
| 160 | 33.7 | 21.5 | 25.6 | 25.5 | 25.5 | 25.5 | | | IOS |
| | 14.2 | 1.84 | 3.40 | 3.17 | 3.16 | | | | CC |
| 200 | 2.09 | 2.10 | 2.10 | 2.10 | | | | | IOS |
| | 125.5 | 123.8 | 123.7 | | | | | | CC |

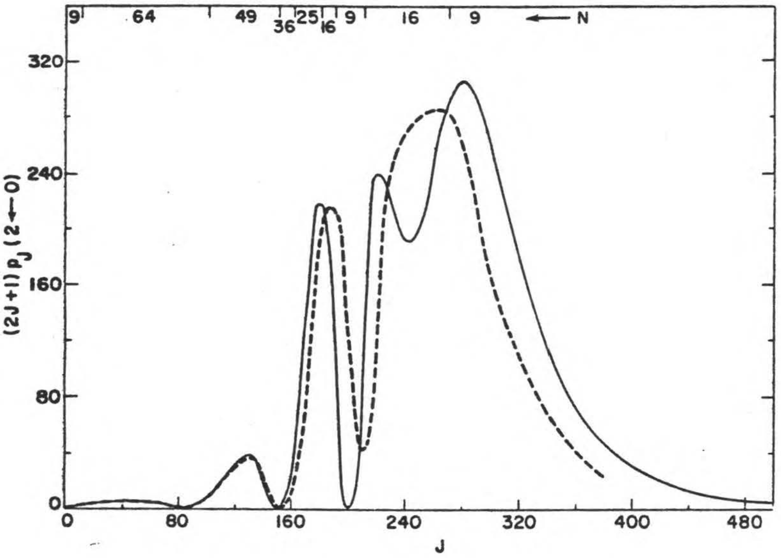

FIG. 2. Behavior of the dimensionless partial cross sections $[(2J+1)$ times the opacity function $\mathcal{P}_J]$ as a function of the total angular momentum $J$ for the $j=0$ to $j=2$ transition in an Ar–TlF collision. At the top of the figure is the number of channels $N$ required to obtain convergence. Solid line, IOS results; dashed line, CC results.

### A. Ar+TlF

The intermolecular potential used in the calculations on Ar–TlF rotationally inelastic scattering is that of Balint-Kurti and Levine,[13] who studied the large $J$ (weak and moderate coupling) opacity functions for this system. This potential (its parameters are listed in Table I) treats TlF as a "homonuclear" diatomic and is thus a crude[15] model for this particular system, but its behavior is typical of an atom–heavy homonuclear diatom collision.

In this work we calculated cross sections for the $0-2$ and $0-4$ rotationally inelastic collisions using the CC, IOS, and FOS approximations. Particular emphasis was placed on determining the dependence of the opacity functions on the number of channels ($N$) included and on the total angular momentum $J$. The rotational states with $j=0, 2, \ldots, j_{\max}$ were

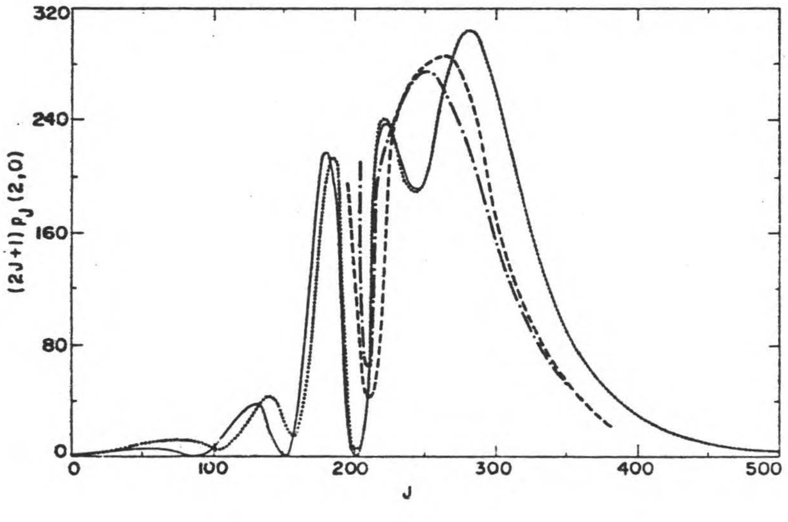

FIG. 3. Comparison of the IOS (solid line), FOS (dotted line), CC (dashed line), and EBDW (dot-dash line) dimensionless partial cross sections $(2J+1)\,\mathcal{P}_J$ $(2 \leftarrow 0)$ for Ar+TlF.

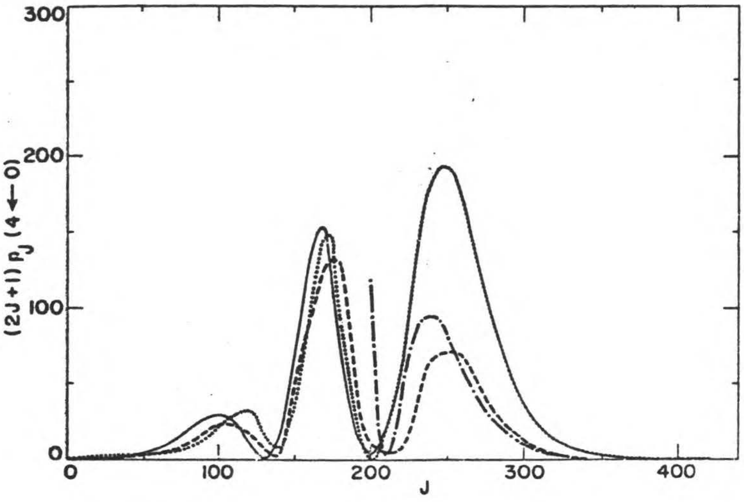

FIG. 4. Dimensionless partial cross sections $(2J+1)\mathcal{P}_J(4\leftarrow 0)$ for Ar + TlF. The notation is the same as in Fig. 3.

included and $j_{\max}$ was increased until the desired opacity functions converged to a value stable to within about 5%. For a given $j_{\max}$ and $J \geq j_{\max}$, the total number of channels ($j, l$ combinations) is

$$N = \sum_{j=0,2,\ldots}^{j_{\max}} (j+1) = \tfrac{1}{4}(j_{\max}+2)^2 . \tag{18}$$

For very small $J$ ($J < j_{\max}$), $N$ is less than this decreasing to $N = \tfrac{1}{2}(j_{\max}+2)$ at $J = 0$.

The convergence of the opacity functions as $N$ is increased was found to be very similar for the FOS, IOS, and CC methods and is illustrated by Table II in which the IOS and CC values for $(2J+1)\mathcal{P}_J(2\leftarrow 0)$ are given for a few $J$ values as a function of $N$. One sees immediately that in the small $J$ ($J \lesssim 180$ in this case) region, convergence is neither rapid nor monotonic, and as many as 64 channels are required to obtain satisfactory convergence.

In Fig. 2 the converged $(2J+1)\mathcal{P}_J(2\leftarrow 0)$ obtained from the IOS and CC methods are plotted vs $J$ for all $J$ to allow easy comparison. At the top of the

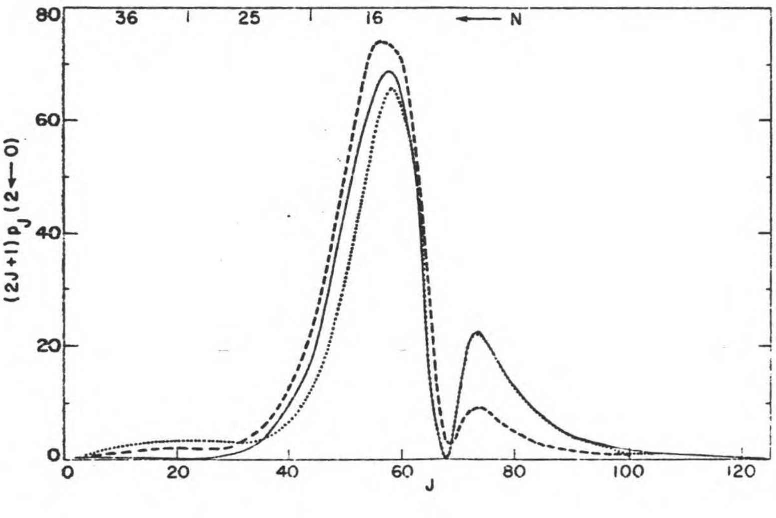

FIG. 5. Dimensionless partial cross sections $(2J+1)\mathcal{P}_J(2\leftarrow 0)$ for Ar + $N_2$. The notation is the same as in Fig. 3.

TABLE III. Rotationally inelastic integral cross sections $\sigma(j_f \leftarrow j_i)$ for Ar + TlF collisions at total energy $E/k_B = 1344\,^\circ$K. The units are Å$^2$. Also listed are the percent deviations from the accurate CC value. In the mixed methods the change from small $J$ method to large $J$ method was made at $J = 210$.

| Method | $\sigma(2\leftarrow 0)$ | % | $\sigma(4\leftarrow 0)$ | % |
|---|---|---|---|---|
| CC | 58.9 | ... | 16.4 | ... |
| IOS | 69.6 | 18.4 | 29.1 | 77.4 |
| FOS | 69.3 | 17.9 | 28.3 | 72.6 |
| IOS + CC | 59.0 | 0.3 | 16.5 | 0.6 |
| FOS + CC | 59.0 | 0.3 | 15.5 | −5.5 |
| IOS + EBDW | 59.5 | 1.2 | 18.6 | 13.4 |
| FOS + EBDW | 59.5 | 1.2 | 17.5 | 6.7 |

figure is listed the $N$ required for convergence. One sees that the IOS results are a very good approximation to the exact CC results for small $J$. As $J$ increases the IOS results slowly get out of phase and become, as one might expect, considerably too large in the large $J$, weak-coupling region. It may be noted that the minimum near $J = 200$ is due to cancellation between the short and long range potentials. Scattering for $J > 200$ is dominated by the long range tail of the potential, and scattering for $J < 200$ is dominated by the short range repulsive potential. In the small $J$ region competition between many strongly coupled channels markedly damps the probability of a transition to any one channel.

In Fig. 3 the FOS results are compared with the IOS results for this same $0\rightarrow 2$ transition; they become identical to the IOS results at larger $J$. At small $J$ the FOS approximation gets out of phase but has about the right magnitude. Since the integral inelastic cross section $\sigma(2\leftarrow 0)$ is proportional to the area under the curve, it is clear that the IOS and FOS cross sections are nearly equal. Also plotted for large $J$ on Fig. 3 are the CC results and the exponential Born (EBDW) results of Balint-Kurti and Levine.[12] The EBDW approximation is better than the sudden approximations for large $J$ but is known to fail completely for small $J$ in this case.[13]

In Fig. 4 the converged FOS, IOS, EBDW, and CC values of $(2J+1)\mathcal{P}_J$ are plotted for the $0\rightarrow 4$ transition. The behavior is similar.

The availability of different simple approximations valid in different $J$ regions immediately suggests calculation of integral inelastic cross sections using one approximation for small $J$ and another for large $J$. Accordingly, in Table III we present the integral inelastic cross sections calculated in the CC, IOS, FOS approximations and several combinations in which one approximation is used for $J < 210$ and another for $J \geqslant 210$. Several of the simple methods are seen to give integral cross sections accurate to within a few percent.

It is also worth noting that because of the damping and associated small contribution of the dominant coupling (small $J$) region, the integral cross sections converge much more rapidly with $N$ than did the small $J$ opacity functions (partial cross sections). This is illustrated by Table IV, which gives the integral cross sections as functions of $N$.

### B. Ar + $N_2$

Calculations of the $0\rightarrow 2$ and $0\rightarrow 4$ cross sections were also carried out for room temperature Ar-$N_2$ collisions using the potential parameters of

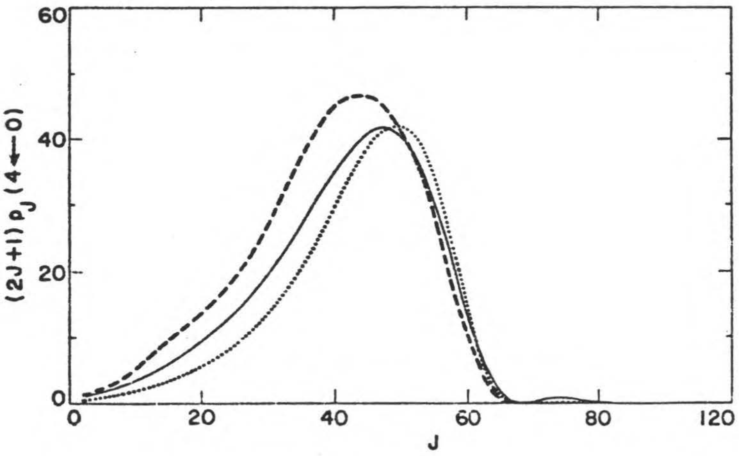

FIG. 6. Dimensionless partial cross sections $(2J+1)\mathcal{P}_J(4\leftarrow 0)$ for Ar + $N_2$. The notation is that of Fig. 3.

TABLE IV. Convergence of integral inelastic cross sections $\sigma(j_f \leftarrow j_i)$ for Ar + TlF as the number of channels ($N$) is increased. The units are Å$^2$.

| | | $N$ | | | | | |
|---|---|---|---|---|---|---|---|
| Cross section | Method | 9 | 16 | 25 | 36 | 49 | 64 |
| | CC | 65.2 | 62.8 | 57.3 | 58.8 | 58.9 | ··· |
| $\sigma(2 \leftarrow 0)$ | IOS | 74.7 | 73.3 | 69.7 | 69.4 | 69.6 | 69.6 |
| | FOS | 76.6 | 73.7 | 68.7 | 69.9 | 69.3 | 69.4 |
| | CC | 33.7 | 24.1 | 20.2 | 16.3 | 16.4 | ··· |
| $\sigma(4 \leftarrow 0)$ | IOS | 45.2 | 38.2 | 32.2 | 28.3 | 29.1 | 29.0 |
| | FOS | 43.0 | 39.5 | 29.7 | 28.6 | 28.3 | 28.2 |

Pattengill, LaBudde, Bernstein, and Curtiss.[16] The resulting IOS, FOS, and CC opacity functions are compared in Figs. 5 and 6. From the number of channels required for convergence [listed at the top of Fig. 5] one sees that this system is not so strongly coupled as the previous one. However, the depression of the partial cross sections for $J \leq 40$ is a strong coupling effect.

Although the sudden approximations are not quite as well justified in this system as in the previous one, they still work quite well in the small $J$ ($J \leq 68$ here) region. It is interesting that for $J < 35$, the FOS results for the $0 \rightarrow 2$ transition are better than those of the IOS approximation, which gives too much dominant coupling.

The large $J$ region where the sudden approximations are poor contributes only a very small fraction of the integral cross sections (given in Table V) for this system, and nothing is gained by using one approximation for small $J$ and another for large $J$. However, the IOS and FOS integral cross sections are still accurate enough to be useful.

The existence and extent of the dominant coupling region in this problem depends very strongly on the repulsive asymmetry parameter $a_{12}$ whose value is still uncertain. It is interesting to note that if $a_{12}$ were decreased from 0.5 to an earlier estimate[17] of 0.375 with the other parameters fixed, the dominant coupling region disappears, and no more than 16 channels are required for convergence at any $J$. This is illustrated in Fig. 7, where the FOS values of $(2J+1)\mathcal{P}_J(2,0)$ obtained with the two values of $a_{12}$ are compared.

### C. Ar+$F_2$, $Cl_2$, $Br_2$, and $I_2$

To check further the observation that in the two previous examples the well-known FOS approximation gives reasonable results for small $J$, even in dominant coupling regions, and to see how the

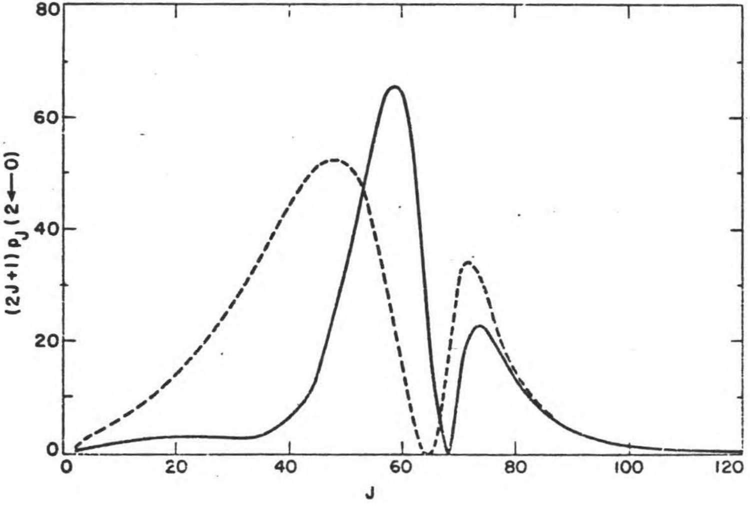

FIG. 7. Effect of the size of the repulsive asymmetry parameter $a_{12}$ on the FOS dimensionless partial cross sections $(2J+1)\mathcal{P}_J(2 \leftarrow 0)$ for Ar + $N_2$. The solid line is with $a_{12} = 0.5$; the dotted line is with $a_{12} = 0.375$.

TABLE V. Rotationally inelastic integral cross sections $\sigma(j_f \leftarrow j_i)$ for Ar + $N_2$ collisions at total energy $E/k_B = 300$ °K. The units are Å². Also listed are the percent deviations from the accurate CC value.

| Method | $\sigma(2 \leftarrow 0)$ | % | $\sigma(4 \leftarrow 0)$ | % |
|---|---|---|---|---|
| CC | 22.5 | ··· | 22.4 | ··· |
| IOS | 22.3 | −0.9 | 18.8 | −16 |
| FOS | 21.1 | −6.2 | 16.7 | −25 |

TABLE VI. Integral inelastic cross sections $\sigma(j_f \leftarrow j_i)$ (in Å²) for room temperature collisions of Ar with $F_2$. $Cl_2$, $Br_2$, and $I_2$.

| System | Approx. | $N$ | $\sigma(2 \leftarrow 0)$ | $\sigma(4 \leftarrow 0)$ |
|---|---|---|---|---|
| Ar + $F_2$ | FOS | 25 | 55.72 | 17.23 |
| Ar + $F_2$ | IOS | | 51.29 | 17.03 |
| Ar + $Cl_2$ | FOS | 36 | 55.15 | 36.38 |
| Ar + $Cl_2$ | IOS | | 55.72 | 36.39 |
| Ar + $Br_2$ | FOS | 36 | 44.38 | 35.26 |
| Ar + $Br_2$ | IOS | | 46.40 | 34.15 |
| Ar + $I_2$ | FOS | 64 | 51.91 | 34.14 |
| Ar + $I_2$ | IOS | | 51.44 | 31.93 |

number $N$ of coupled channels required increases with increasing reduced mass, we calculated the FOS and IOS values of some inelastic cross sections on a series of model problems intended to represent scattering of Ar atoms by $F_2$, $Cl_2$, $Br_2$, and $I_2$, respectively. The parameters of the spherical part of each intermolecular potential (see Table I) were obtained using the parameters and combining rules of Hirschfelder, Curtiss, and Bird[18] and should be fairly reasonable estimates; however, the asymmetry parameters were arbitrarily kept fixed at 0.20.

The resulting integral inelastic cross sections (in units of Å²) are presented in Table VI along with the maximum number of channels required to obtain convergence of all partial cross sections to within 5%. Again, the FOS results are good approximations to the IOS results regardless of the number of channels involved.

## IV. DISCUSSION AND CONCLUSIONS

From the results of this paper, we conclude that the rotationally inelastic scattering problem is much less difficult than the large number of coupled rotational states would make it appear to be. This is due to the fact that the region where large numbers of states are strongly coupled and competing makes a small contribution to the inelastic cross sections and can hence be safely treated with rather simple approximations. In particular, the IOS and the well-known FOS approximation provide computationally easy ways of obtaining rather good small $J$ partial cross sections for rotationally inelastic collisions of heavy diatomic molecules. For systems in which the large $J$ (weak-coupling long-range) region gives a large contribution to the integral cross section, one can calculate reliable cross sections economically using a sudden approximation at small $J$ and a CC or EBDW method in the large $J$ region where only a few channels are needed.

The major reason for our present interest in the FOS approximation, since the IOS method is already computationally very simple, is that the FOS method is easily applied to potentials more general than that used here. For example, the FOS approximation can be applied to potentials of the form

$$U(r', \theta) = \sum_{n=0}^{\infty} U_n(r') P_n(\cos\theta) \tag{19}$$

by direct generalization of Eqs. (15) and (17). As formulated herein, the IOS approximation cannot be used for such a potential unless $U_n(r') \propto U_m(r')$ for all $n$, $m > 0$. However, as this work was being completed, it was discovered[19] that by using body-fixed coordinate axes a drastic simplification can *always* be achieved via an IOS approximation, regardless of the form of the potential. Furthermore, this approach will also produce a marked increase in the computation speed of both the sudden approximations. Research along this line will be reported in a subsequent paper.[19]

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[1] R. G. Gordon, J. Chem. Phys. **51**, 14 (1969).

[2] W. N. Sams and D. J. Kouri, J. Chem. Phys. **51**, 4809 (1969); J. Chem. Phys. **51**, 4815 (1969); J. Chem. Phys. **52**, 4144 (1970); and J. Chem. Phys. **53**, 496 (1970).

[3] R. B. Bernstein, A. Dalgarno, H. S. W. Massey, and I. C. Percival, Proc. Roy. Soc. (London) A **274**, 427 (1963).

[4] W. A. Lester, Jr. and R. B. Bernstein, J. Chem. Phys. **53**, 11 (1970).

[5] A. M. Arthurs and A. Dalgarno, Proc. R. Soc. A **256**, 540

(1960).

[6] I. C. Percival and M. J. Seaton, Proc. Camb. Phil. Soc. 53, 654 (1957).

[7] R. D. Levine and R. B. Bernstein, J. Chem. Phys. 53, 686 (1970).

[8] R. G. Gordon, Program 187, Quantum Chemistry Program Exchange, Indiana University, 1969. We thank W. A. Lester, Jr. and D. G. Truhlar for a list of the errors in the QCPE version of this program.

[9] T. P. Tsien and R. T Pack, Chem. Phys. Lett. 6, 54 (1970); J. Chem. Phys. 6, 400 (1970); and J. Chem. Phys. 8, 579 (1971).

[10] R. T Pack, Chem. Phys. Lett. 14, 393 (1972).

[11] See, for example, R. J. Cross, Jr., J. Chem. Phys. 51, 5163 (1969); R. W. Fenstermaker, C. F. Curtiss, and R. B. Bernstein, J. Chem. Phys. 51, 2439 (1969).

[12] R. D. Levine, Mol. Phys. 22, 497 (1971), and references therein.

[13] G. G. Balint-Kurti and R. D. Levine, Chem. Phys. Lett. 7, 107 (1970).

[14] R. T Pack and J. S. Dahler, J. Chem. Phys. 50, 2397 (1969); W. D. Smith and R. T Pack, J. Chem. Phys. 52, 1381 (1970).

[15] A more realistic $Ar + TlF$ potential has been given by J. van de Ree and J. G. R. Okel, J. Chem. Phys. 54, 589 (1971).

[16] M. D. Pattengill, R. A. LaBudde, R. B. Bernstein, and C. F. Curtiss, J. Chem. Phys. 55, 5517 (1971).

[17] W. Erlewein, M. von Seggern, and J. P. Toennies, Z. Phys. 211, 35 (1968).

[18] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).

[19] R. T Pack, J. Chem. Phys. (to be published).

# APPENDIX B

# CALCULATION OF MOLECULE-MOLECULE INTERMOLECULAR POTENTIALS USING ELECTRON GAS METHODS.

(A reprint. See Gregory A. Parker, Richard L. Snow and Russell T Pack Chem. Phys. Lett. 33, 399 (1975).)

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# CALCULATION OF MOLECULE–MOLECULE INTERMOLECULAR POTENTIALS USING ELECTRON GAS METHODS*

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A procedure for extending electron gas calculations to *molecule–molecule* interactions is presented which allows rapid determination of the dependence of intermolecular potentials on all vibration and rotation coordinates. Results for HF–HF agree well with accurate SCF calculations.

## 1. Introduction

There is currently much interest in the calculation of intermolecular potentials between closed shell systems using the electron gas methods developed by Gaydaenko and Nikulin [1], and Gordon and Kim [2], and modified by Rae [3], and Cohen and Pack [4]. These methods have been used successfully to calculate the interaction energies of many pairs [1–5] of closed shell atoms or atomic ions. The method has also been applied to *atom–molecule* interactions by Kim [6] and by Green and Gordon, whose computer program is available through QCPE [7]. They have used it to determine the angle and distance dependence of the Ar–$N_2$ [6], Ar–HCl [8], He–HCN [9], He–CO [10], and He–$H_2CO$ [11] interactions. We [12] have also programmed the method and used it to calculate the angle and distance dependence of He–$H_2$, He–$CO_2$, Ar–$CO_2$, noble-gas–CO, and noble-gas–HF interactions and the angle, vibrational coordinate, and distance dependence of the Ar–CO and Ar–HF interactions. All results to date are very encouraging, and the agreement with available experimental and ab initio data is very good, considering the simplicity of the method.

In this letter we show how to extend the calculation of electron gas intermolecular potentials to *molecule–molecule* interactions without loss of speed or accuracy. We apply it to HF · HF interactions as an example and compare results with the accurate SCF calculations of Yarkony et al. [13].

## 2. Method of calculation

We now sketch the method used to calculate molecule–molecule interactions; details are given elsewhere [12].

In the electron gas model the intermolecular potential energy is the sum of Coulomb, kinetic, exchange and correlation contributions [2,4]. The kinetic, exchange, and correlation terms are expressed as three-dimensional integrals over functions of the electron density, and the Coulomb energy is a six-dimensional integral over the electron densities of the two molecules. When one of the species is an atom whose wavefunction is written in terms of a basis set of Slater orbitals, the electrostatic potential due to the atom can be evaluated analytically. This reduces the Coulomb integral to three dimensions, so that in the atom–molecule programs [7,12] all the terms are obtained via a three-dimensional numerical integration. However, in the molecule–molecule case, the electrostatic potential due to a molecule cannot be evaluated analytically.

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and the direct extension of the atom–molecule method leads either to a six-dimensional numerical integration, or, if the charge densities are expanded in orbitals, to all the multicenter Coulomb integrals encountered in the usual ab initio methods. Either of these approaches makes the method so much more expensive computationally as to leave it little advantage over the more accurate rigorous ab initio methods.

Our solution to this problem is to expand the charge density, $\rho_B$, of one of the molecules (B), *not* in terms of products of molecular orbitals which are then expanded in basis functions, but directly in a basis of Slater orbitals*,

$$\rho_B \doteq \tilde{\rho}_B = \sum_i^{n_B} a_i \chi_i . \tag{1}$$

The $a_i$ are determined by an ordinary linear least squares method except that $(\tilde{\rho}_B - \rho_B)^2/\rho_B^2 = (\tilde{\rho}_B/\rho_B - 1)^2$ rather than $(\tilde{\rho}_B - \rho_B)^2$ is minimized to provide a good fit to the tail of the charge distribution (important in calculating interactions at large intermolecular distances). The fit is improved by taking Slater orbitals, $\chi$, centered between, as well as on the nuclei of molecule B. If the charge densities of both molecules (A and B) are thus expanded, one can rapidly evaluate the Coulomb energy by doing only $n_A n_B$ *two*-center type integrals all of which can be done using standard integral programs [14]. However, one can also now evaluate the electrostatic potential ($\Phi_B$) due to B analytically, via

$$\Phi_B(r_1) = \int \tilde{\rho}_B(r_2) r_{12}^{-1}\, dr_2 . \tag{2}$$

Then, in atomic units the Coulomb interaction energy takes the form

$$V_c = \int dr_1\, \rho_A(r_1) \Big[ \Phi_B(r_1) + \sum_\alpha \sum_\beta \frac{Z_\beta f_\alpha}{r_{\alpha\beta}} - \sum_\beta \frac{Z_\beta}{r_{1\beta}} - \sum_\alpha f_\alpha \Phi_B(r_\alpha) \Big], \tag{3}$$

where the sums are over the nuclei $\alpha$ in A and $\beta$ in B. Here $f_\alpha = Z_\alpha / N_A$, where $N_A$ is given by

$$N_A = \int \rho_A(r_1)\, dr_1 . \tag{4}$$

The second and fourth terms in the bracket in (3) are constant; they are kept there in that form to achieve maximum cancellation of quadrature errors. Since a three-dimensional quadrature was already required for the exchange, etc., energies, it turned out to be faster in practice to use (2) and (3) and get the Coulomb energy together with the other energies than to evaluate it using a standard two-center integral program [14].

A FORTRAN program to carry out the above calculation has been written [12] and will be submitted to QCPE; some of the procedures in it are as follows: All integration points lying outside a large ellipsoid containing both molecules are bypassed. Integration over the half-ellipsoid closest to A (B) is done using spherical-polar coordinates centered on A (B). Use of two coordinate systems allows the quadrature points to be chosen to handle accurately the peaking of $\rho_A$ and $\Phi_B$ near the nuclei of A and B, respectively. Each of the two coordinate systems rotates with its molecule, so that $\Phi_B$, $\rho_B^{1/3}$ and $\rho_A^{1/3}$ can be calculated and tabulated at each of the quadrature points before the integration begins and used to construct the whole potential energy surface, being changed only when vibrational coordinates are changed. The two half-space quadratures are done simultaneously, and at each step of the quadrature on A (B) the functions of $\rho_A$ ($\rho_B$) needed are obtained directly from the tables while those of $\rho_B$($\rho_A$) are obtained from low order Lagrange interpolation. Although the truncation of each of the two quadratures at the boundary between the half-ellipsoids is not an optimum procedure, the errors in the two halves seem to cancel each other, and the procedure is much faster and more accurate than any of several other approaches that were tried. In practice all the energy terms (Coulomb, exchange, etc.) were obtained accurate to within about 1% at all intermolecular distances using 24 to 40 point Gauss–Legendre quadratures for the $\phi_1$ and $x = \cos\theta_1$ integrations and a total of 32 to 40 points for the radial integration which was split up into several small, piecewice Gauss Legendre quadratures with the first few intervals ending at the nuclei of A (B).

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* Gaussian basis functions were also tried, but that required a large number of functions with small orbital exponents to fit the tail of distribution. This is also a problem when gaussian basis SCF wavefunctions are used for input.

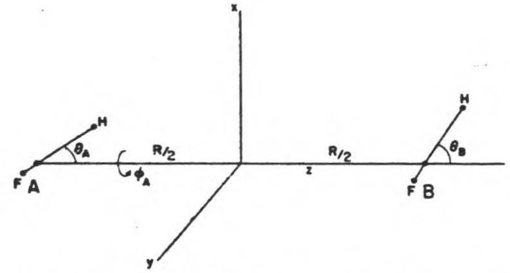

Fig. 1. The coordinates $R, \theta_A, \phi_A, \theta_B$ for the interaction between two linear molecules.

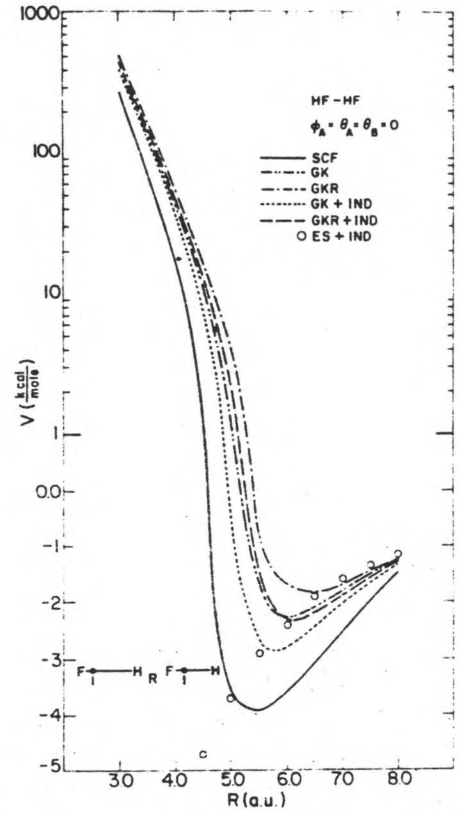

Fig. 2. Comparison of SCF and electron gas results for the interaction energy (in kcal/mole) of two HF molecules with $\phi_A = \theta_A = \theta_B = 0$. The solid line gives the SCF results of ref. [13]; the dash–double dot line is the unmodified electron gas (GK) SCF estimate; the dash-dot line is the (GKR) modified SCF estimate; the dotted line is GK plus induction; the dashed line is GKR plus induction; and the circled dots are the long-range electrostatic plus induction energy.

## 3. Results and discussion for HF–HF interactions

As an example, the interaction energy of two hydrogen fluoride (HF) molecules was calculated at a number of intermolecular distances and angles. Although HF is a closed-shell molecule, this system has strong hydrogen bonding interactions and is not an ideal system for use of the electron gas model, which allows no adjustment of the charge densities due to the interaction. It was chosen simply because accurate SCF calculations [13] were available for comparison. The calculations were carried out as described above using the SCF wavefunctions for HF of McLean and Yoshimine [15]; each point on the potential energy surface required only 1–2 minutes using an IBM 7030 computer. (This is about 1–2 min/point on an IBM 360/65 or 2–4 s/point on a CDC 7600.) A few representative results are presented in figs. 2–5 using the usual [16] intermolecular coordinates shown in fig. 1 rather than the highly redundant coordinates used by Yarkony et al. [13]. Because true SCF results contain induction but not dispersion effects a rough estimate of the leading terms of the long range induction (IND) energy [17] was added to the "SCF" part (i.e., omitting the correlation terms) of the electron gas results to provide comparable quantities. One sees that for most distances and angles the results are just as good as for atom–atom interactions [2,4] and certainly good enough to encourage use of the method for larger systems where SCF results are expensive and unavailable. Electron gas results both with (GKR) and without (GK) use of the Rae [3] exchange correction are given; for this system results *without* the correction, i.e., allowing more exchange interaction, are clearly superior and truly remarkably good for most angles. This behavior is opposite that observed in the isoelectronic Ne–Ne interaction [4]. Also plotted in the figures are the estimates of the long range $R^{-1}$ expansion [17] of the electrostatic (ES) plus induction (IND) energies; one sees that the other energies are slowly converging toward the asymptotic results at the largest distances shown on the plots.

The electron gas model does not contain all the in-

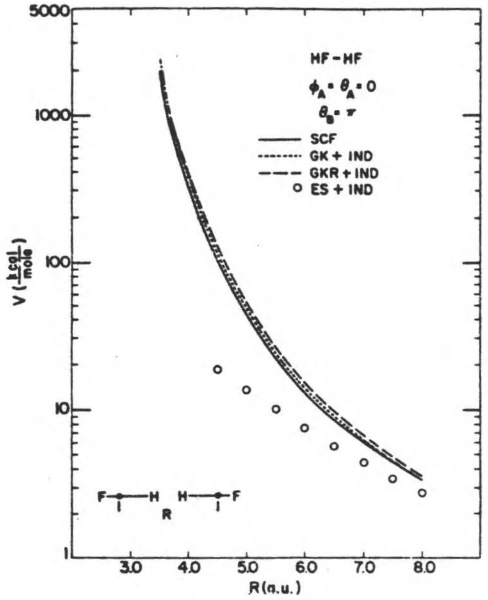

Fig. 3. HF–HF interaction with $\phi_A = \theta_A = 0$, $\theta_B = \pi$. The notation is that of fig. 2.

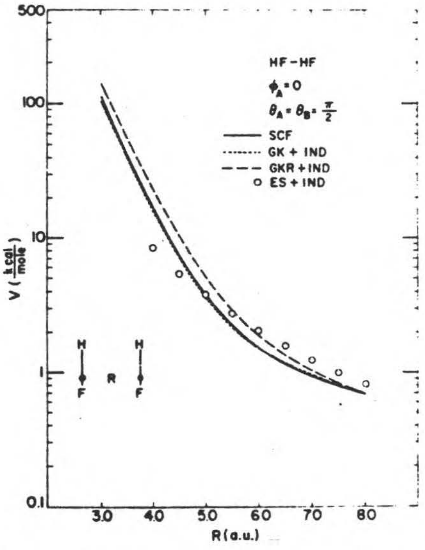

Fig. 4. HF–HF interaction with $\phi_A = 0$, $\theta_A = \theta_B = \pi/2$. The notation is that of fig. 2.

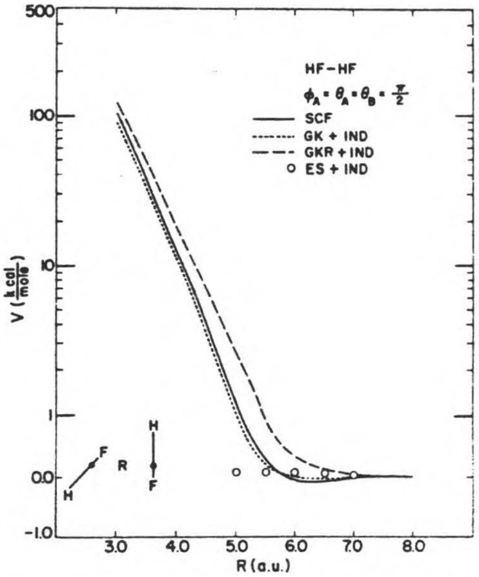

Fig. 5. HF–HF interaction with $\phi_A = \theta_A = \theta_B = \pi/2$. The notation is that of fig. 2.

duction and charge transfer effects present in the SCF calculation and thus fails to accurately describe the hydrogen bonding region shown in fig. 2. Results in fig. 2 with and without the addition of the leading terms of the long-range induction energy show that it helps considerably; inclusion of more long-range induction terms [18] would make agreement a little better, so that one can thus get most but not all of the attractive well.

Thus, we conclude that the present method, which is directly applicable to polyatomic–polyatomic systems as well, allows rapid construction of a good representation of the repulsive wall of intermolecular potentials. We expect that upon inclusion of van der Waals or correlation contributions [4] one can readily produce whole potential energy surfaces accurate enough to be extremely useful in calculations of V,T,R ⟷ V,T,R energy transfer in molecular collisions. Calculations of potential energy surfaces containing vibrational as well as rotational coordinate dependence are in progress for HF–HF, CO–CO, and other systems [12].

## References

[1] V.I. Gaydaenko and V.K. Nikulin, Chem. Phys. Letters 7 (1970) 360;
V.K. Nikulin, Zh. Tekh. Fiz. 41 (1970) 41 [English transl. Soviet Phys. Tech. Phys. 16 (1971) 28].

[2] R.G. Gordon and Y.S. Kim, J. Chem. Phys. 56 (1972) 3122;
Y.S. Kim and R.G. Gordon, J. Chem. Phys. 60 (1974) 1842, 4323, 4332; 61 (1974) 1.

[3] A.I.M. Rae, Chem. Phys. Letters 18 (1973) 574.

[4] J.S. Cohen and R.T Pack, J. Chem. Phys. 61 (1974) 2372.

[5] B. Schneider, J. Chem. Phys. 58 (1973) 4447.

[6] Y.S. Kim, Thesis, Harvard University (1973).

[7] S. Green and R.G. Gordon, Program No. 251 (1974), Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana 47401, USA.

[8] S. Green, J. Chem. Phys. 60 (1974) 2654.

[9] S. Green and P. Thaddeus, Astrophys. J. 191 (1974) 653.

[10] S. Green and P. Thaddeus, Astrophys. J., to be published.

[11] S. Green, private communication (1974).

[12] G.A. Parker, R.L. Snow and R. T Pack, to be published.

[13] D.R. Yarkony, S.V. O'Neil, H.F. Schaefer, C.P. Baskin and C.F. Bender, J. Chem. Phys. 60 (1974) 855.

[14] S. Hagstrom, Program No. 252, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana 47401, USA.

[15] A.D. McLean and M. Yoshimine, IBM J. Res. Develop. Suppl. (1967).

[16] J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, Molecular theory of gases and liquids (Wiley, New York, 1954) p. 848.

[17] A.D. Buckingham, Advan. Chem. Phys. 12 (1967) 107.

[18] A.D. Buckingham, J. Chem. Phys. 48 (1968) 3827.

# APPENDIX C

## MOLMOL: POTENTIAL ENERGY SURFACES FOR THE INTERACTION OF TWO LINEAR MOLECULES.

(Description of program MOLMOL. See Gregory A. Parker, Richard L. Snow and Russell T Pack, Program No. 305 (1976), Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana 47401.)

# MOLMOL

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Provo, Utah 84602

QCPE - - -

## MOLMOL: POTENTIAL ENERGY SURFACES FOR THE INTERACTION OF TWO LINEAR MOLECULES.

| | |
|---|---|
| Main Entries: | LMOLMO (Calculates the intermolecular potential)<br>SLAFIT (Fits the electron density with a linear combination of Slater basis functions) |
| Other Entries: | None |
| Abstract: | SLAFIT uses a linear least squares method to fit the electron density of a linear molecule with a linear combination of Slater orbitals. LMOLMO uses the output of SLAFIT and rapidly calculates the interaction energy between two closed shell linear molecules using the electron gas model. The numerical methods and notation used are those of G. A. Parker, R. L. Snow, and R. T Pack, Chem. Phys. Lett. 33, 399 (1975). The electron gas method is that of V. I. Gaydaekno and V. K. Nikulin, Chem. Phys. Lett. <u>2</u> 360 (1970); R. G. Gordon and Y. S. Kim, J. Chem. Phys. <u>56</u>, 3122 (1972); A. I. M. Rae, Chem. Phys. Lett. <u>18</u>, 574 (1973); and J. S. Cohen and R. T Pack, J. Chem. Phys. <u>61</u>, 2372 (1974). The present program can be extended in a straightforward way to the calculation of polyatomic-polyatomic interactions with little loss of speed. Such an extension is planned and will be sent to QCPE when complete. |
| Language: | FORTRAN IV |
| Hardware: | IBM 7030 STRETCH, CDC 7600, PDP-15 |
| Library Routines: | ALOG, ARCOS, COS, DATE, EXP, SECOND, SIN, SQRT, TIME |
| Common Storage: | BASE, BLK1-BLK11 |
| Accuracy: | Single precision floating point operations are used throughout. About 3 significant figures are usually obtained when the number of $r$, $\theta$, and $\phi$ integration points used are, respectively, NRA = 32-40, NTA = 24-40, and NPA = 24-40. However, convergence with increasing numbers of integration points should be carefully checked at several distances and angles for each new pair of molecules. |
| Input Parameters: | The input parameters are described in the comment cards in subroutines LMOLMO, ELCPOT, SLATE, RHOMOL. |

**Example:** Sample test data sets and a sample main program which runs LMOLMO and SLAFIT independently are included. The results can be compared with the sample output.

**Running time:** SLAFIT requires about 100 sec of CDC 7600 CP time. LMOLMO requires only about 2.5 sec of CDC 7600 time per point on the potential energy surface.

**Subroutines:** Subroutines EG, ELCPOT, PFUNC, MOMENT, PN, QUAD3, SELFX, and SLATE are used only by LMOLMO. Subroutines DOT, F, LINEQ, LSTSQ, and VECSUM are used only by SLAFIT. Subroutines GLEGEN, RHOMOL, PLM, and REP are used by both. LMOLMO and SLAFIT and their associated subroutines can be compiled and run as separate programs or overlaid if one wishes to decrease core storage required.

**Authors:** G. A. Parker*, R. L. Snow and R. T Pack*, Department of Chemistry, Brigham Young University, Provo, Utah, 84602. (*Present address (1975): Group T-6, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545) Additional information, flow charts, etc. can be obtained from G. A. Parker.

**Acknowledgment:** Work supported in part by the USERDA.

Subroutine Page

Test calculation

Listing of LMOLMO and the subroutine that are only used by LMOLMO: EG, ELCPOT, PFUNC, MOMENT, PN, QUAD3, SELFX, and SLATE.

```
RUN-107    0                        76/04/09     20.13.03     PARKERZ2UR    PAGE NO. 1
          SUBROUTINE LMOLMO                                                    LMO          2
      C                                                                        LMO          3
      C                                                                        LMO          4
1         DIMENSION COSPA(96)        ,COSTA(96)        ,POTENB(51,40)   ,      LMO          5
         1          COSTB(96)        ,COSP1(96)        ,COST1(96)       ,      LMO          6
         2          COST2(96)        ,DIST(20)         ,FLDENA(51,40)   ,      LMO          7
         3          EDENB(96,96)     ,NRIJ(20)         ,POTNB(96,96)    ,      LMO          8
         4          RADA(96)         ,RADB(96)         ,RE(20)          ,      LMO          9
         5          SINPA(96)        ,SINTA(96)        ,SINTB(96)       ,      LMO         10
         6          WP(96)           ,WR(96)           ,WT(96)          ,      LMO         11
         7          ZNUCA(5)         ,ZNUCB(5)         ,ZPOSA(5)        ,      LMO         12
         8          ZPOSB(5)         ,COSTP(5)         ,RPOS(5)         ,      LMO         13
         9          ELDENB(51,40)    ,EDENA(96,96)                             LMO         14
      C                                                                        LMO         15
      C                                                                        LMO         16
      C   PURPOSE                                                              LMO         17
      C      CALCULATE THE INTERMOLECULAR POTENTIAL BETWEEN TWO CLOSED-        LMO         18
      C      SHELL LINEAR MOLECULES.                                           LMO         19
      C   DATA TO BE READ IN                                                   LMO         20
      C      TITLE (A 1 IN COLUMN 1 FOLLOWED BY THE TITLE)                     LMO         21
      C   CARD 2                                                               LMO         22
      C      NDIST-NUMBER OF DISTANCES                                         LMO         23
      C      NPHI1-NUMBER OF PHI1 ANGLES                                       LMO         24
      C      NTHET1-NUMBER OF THET1 ANGLES                                     LMO         25
      C      NTHET2-NUMBER OF THET2 ANGLES                                     LMO         26
      C      IDENT=1 IF THE MOLECULES ARE IDENTICAL                            LMO         27
      C           ***NOTE- IF THE MOLECULES ARE IDENTICAL  REMOVE THE          LMO         28
      C                    COMMENT ON LMOL0068 AND LMOL0069 IF                 LMO         29
      C                    SAVINGS IN CORE STORAGE IS DESIRED***               LMO         30
      C      KASE=1 IF THE COSINE OF THE ANGLES PHI1,THET1,THET2 ARE TO        LMO         31
      C      KASE=1 BE READ IN.                                                LMO         32
      C      NCASE=1 IF THE WAVE FUNCTION BASIS SET IS TO BE USED FOR          LMO         33
      C              MOLECULE A.                                               LMO         34
      C   CARD 3                                                               LMO         35
      C      DIST-DISTANCES AT WHICH THE POTENTIAL IS TO BE CALCULATED AT      LMO         36
      C   CARD 4                                                               LMO         37
      C      NRB-NUMBER OF RADIAL INTERPOLATION POINTS.                        LMO         38
      C      NTB-NUMBER OF ANGULAR INTERPOLATION POINTS                        LMO         39
      C      RMAX-MAXIMUM DISTANCE FOR INTERPOLATION                           LMO         40
      C      B-SEMI MAJOR AXIS OF THE ELLIPSE                                  LMO         41
      C      REEGN-FIRST RADIAL POINT FOR EQUIDISTANT INTERPOLATION            LMO         42
      C   CARD 5                                                               LMO         43
      C      NTA-NUMBER OF THETA INTEGRATION POINTS                            LMO         44
      C      NPA-NUMBER OF PHI INTEGRATION POINTS                              LMO         45
      C      NRIS-NUMBER OF SECTIONS FOR THE RADIAL INTEGRATIONS               LMO         46
      C   CARD 6                                                               LMO         47
      C      NRIJ-NUMBER OF RADIAL INTEGRATION POINTS IN EACH SECTION          LMO         48
      C   CARD 7                                                               LMO         49
      C      RE-ENDING POINTS FOR THE RADIAL INTEGRATION                       LMO         50
      C   CARD 8                                                               LMO         51
      C      ISTD-STARTING PARAMETER FOR THE DISTANCES                         LMO         52
      C      ISP1-STARTING PARAMETER FOR THE PHI1 ANGLES                       LMO         53
      C      IST1-STARTING PARAMETER FOR THE THET1 ANGLES                      LMO         54
      C      IST2-STARTING PARAMETER FOR THE THET2 ANGLES                      LMO         55
      C   CARD 9                                                               LMO         56
```

```
      C          NELECA-NUMBER OF ELECTRONS IN MOLECULE-A
      C          NELECB-NUMBER OF ELECTRONS IN MOLECULE-B
      C       CARD 10 (OPTIONAL)
      C          COSP1-COSINE OF THE PHI1 ANGLES
      C       CARD 11 (OPTIONAL)
      C          COST1-COSINE OF THE THET1 ANGLES
      C       CARD 12 (OPTIONAL)
      C          COST2-COSINE OF THE THET2 ANGLES
      C
    1         COMMON /BASE/CA(5,35),LA(5,35),NA(5,35),NBFA(5),NCENB,ZETA(5,35)
      C
      C
    1         EQUIVALENCE (ELDENA(1,1),ELDENB(1,1))
    1         EQUIVALENCE (EDENA(1,1),EDENB(1,1))
      C
      C
              DATA TWOPI/6.2831853071896/
              DATA PI/3.1415926535898/
              DATA PI2/1.5707963267949/
      C
      C
      C       A SYSTEM CLOCK SUBROUTINE
      C
    1         STOT=0.0
    2         CALL SECOND(SEC1)
      C
      C
    4         READ(5,240)
   10         READ(5,370)NDIST,NPHI1,NTHET1,NTHET2,IDENT,KASE,NCASE
   32         READ(5,190)(DIST(NR),NR=1,NDIST)
   41         READ(5,430)NRB,NTB,RMAX,B,RBEGN
   57         READ(5,370)NTA,NPA,NRIS
   71         READ(5,370)(NRIJ(J),J=1,NRIS)
  100         READ(5,190)(RE(J),J=1,NRIS)
  107         READ(5,370)ISTD,ISP1,IST1,IST2
  123         READ(5,370)NELECA,NELECB
      C
      C
      C                            DETERMINE THE ANGLES AT WHICH THE
      C                            INTERMOLECULAR POTENTIAL WILL BE
      C                            CALCULATED AT.
      C
      C
  133         CALL GLEGEN(NTHET2,COST2,WT,-1.0,1.0)
  137         CALL GLEGEN(NPHI1 ,COSP1,WT,-1.0,1.0)
  143         CALL GLEGEN(NTHET1,COST1,WT,-1.0,1.0)
  147         IF(KASE.NE.1)GO TO 10
  151         READ(5,190)(COSP1(J),J=1,NPHI1)
  160         READ(5,190)(COST1(K),K=1,NTHET1)
  167         READ(5,190)(COST2(L),L=1,NTHET2)
      C
      C
      C                            CALCULATE THE ANGLES AND THE RADIAL
      C                            DISTANCES FOR THE EQUIDISTANT
      C                            TABULATION OF THE ELECTRON
```

```
      C                           DENSTIIES AND THE ELECTROSTATIC POTENTIAL.
      C
      C
176       10 DELTAT=2.0/FLOAT(NTB-1)
202          DO 20 NT=1,NTB
203          COSTB(NT)=FLOAT(NT-1)*DELTAT-1.0
207       20 SINTB(NT)=SQRT(1.0-COSTB(NT)*COSTB(NT))
220          RLAST=SQRT(RMAX*RMAX/4.0+B*B)
226          RE(NRIS)=RLAST
226          REND=RMAX+B
226          DELTAR=(REND-RBEGN)/FLOAT(NRB-3)
236          DO 30 NR=1,NRB
244       30 RADB(NR)=DELTAR*FLOAT(NR-2)+RBEGN
      C
      C
      C                           FORM THE INTEGRATION POINTS.
      C
      C
247          NRA=0
247          R1E=0.0
250          DO 40 J=1,NRIS
253          NRIP1=NRA+1
253          NRA=NRA+NRIJ(J)
256          CALL GLEGEN(NRIJ(J),RADA(NRIP1),WR(NRIP1),R1E,RE(J))
262       40 R1E=RE(J)
266          DO 50 NR=1,NRA
274       50 WR(NR)=WR(NR)*RADA(NR)*RADA(NR)
276          CALL GLEGEN(NTA,COSTA,WT,-1.0,1.0)
302          DO 60 NT=1.NTA
304       60 SINTA(NT)=SQRT(1.0-COSTA(NT)*COSTA(NT))
316          CALL GLEGEN(NPA,COSPA,WP,0.0,TWOPI)
321          DO 70 NP=1,NPA
323          SINPA(NP)=SIN(COSPA(NP))
327       70 COSPA(NP)=COS(COSPA(NP))
      C
      C
      C                           STORE THE ELECTRON DENSITIES OF
      C                           THE MOLECULES AND THE ELECTROSTATIC
      C                           POTENTIAL OF MOLECULE-B.
      C
336          IF(IDENT.EQ.1)GO TO 100
340          IF(NCASE.EQ.1)GO TO 80
341          CALL SLATE(COSTA.ELDENA,NNUCA,NRA,NTA,RADA,SINTA,ZNUCA,ZPOSA,1)
353          CALL SLATE(COSTB,EDENA ,NNUCA,NRB,NTB,RADB,SINTB,ZNUCA,ZPOSA,1)
365          GO TO 90
366       80 CALL RHOMOL(COSTA,ELDENA,NNUCA,NRA,NTA,RADA,SINTA,ZNUCA,ZPOSA,1)
401          CALL RHOMOL(COSTB, EDENA,NNUCA,NRB,NTB,RADB,SINTB,ZNUCA,ZPOSA,0)
413       90 CALL MOMENT(COSTA ,ELDENA,NELECA,NNUCA ,NRA    ,NTA    ,RADA  ,
           1            SINTA ,WR    ,WT    ,ZPOSA ,ZNUCA )
430      100 CALL ELCPOT(COSTA ,COSTP ,ELDENB,ELDENA,NNUCB ,NRA    ,NTA    ,
           1            POTENB,RADA  ,RPOS  ,SINTA ,ZNUCB ,ZPOSB ,1      ,
           2            IDENT )
450          CALL ELCPOT(COSTB ,COSTP ,EDENB ,EDENA ,NNUCB ,NRB    ,NTB    ,
           1            POTNB ,RADB  ,RPOS  ,SINTB ,ZNUCB ,ZPOSB ,0      ,
           2            IDENT )
```

```
 467          IF(IDENT.NE.1)GO TO 120
 471          NNUCA=NNUCB
 473          DO 110 IA=1,NCENB
 501          ZNUCA(IA)=ZNUCB(IA)
 501      110 ZPOSA(IA)=ZPOSB(IA)
 504      120 CALL MOMENT(COSTA ,ELDENB,NELECB,NNUCB ,NRA    ,NTA    ,RADA   ,
             1            SINTA ,WR     ,WT     ,ZPOSB ,ZNUCB )
        C
        C
        C                                CALCULATE THE SELF EXCHANGE
        C                                ENERGY CORRECTION
        C
        C
 521          NELECT=NELECA+NELECB
 523          CALL SELFX(NELECT,SELF)
        C
        C     A SYSTEM CLOCK SUBROUTINE
        C
 525          CALL SECOND(SEC)
 530          SFC=SEC-SEC1
 530          STOT=STOT+SEC
        C
        C
 533          CALL DATE(TODAY)
 534          CALL TIME(TYME)
 536          WRITE(6,240)
 542          WRITE(6,250)TODAY
 550          WRITE(6,260)TYME
 556          IF(IDENT.EQ.1)WRITE(6,380)
 564          WRITE(6,510)NDIST
 572          WRITE(6,290)(DIST(NR),NR=1,NDIST)
 601          WRITE(6,520)NPHI1
 607          WRITE(6,290)(COSP1(NT),NT=1,NPHI1)
 616          WRITE(6,530)NTHET1
 624          WRITE(6,290)(COST1(NT),NT=1,NTHET2)
 633          WRITE(6,540)NTHET2
 641          WRITE(6,290)(COST2(NT),NT=1,NTHET2)
 650          WRITE(6,240)
 654          WRITE(6,250)TODAY
 662          WRITE(6,260)TYME
 670          WRITE(6,560)NRB
 676          WRITE(6,290)(RADB(NR),NR=1,NRB)
 705          WRITE(6,550)NTB
 713          WRITE(6,290)(COSTB(NT),NT=1,NTB)
 722          WRITE(6,570)NRIS
 730          ZERO=0.0
 731          WRITE(6,190)ZERO
 737          WRITE(6,200)(NRIJ(J),RE(J),J=1,NRIS)
 755          WRITE(6,580)NRA
 763          WRITE(6,290)(RADA(NR),NR=1,NRA)
 772          WRITE(6,590)NTA
1000          WRITE(6,290)(COSTA(NT),NT=1,NTA)
1007          WRITE(6,600)NPA
1015          WRITE(6,290)(COSPA(NP),NP=1,NPA)
1024          WRITE(6,610)NELECA
```

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        RUN-107    0        LMOLMO          76/04/09     20.13.03    PARKERZZUR   PAGE NO. 5
 1032         WRITE(6,620)NELECB                                                  LMO       222
 1040         WRITE(6,210)SEC                                                     LMO       223
 1046         WRITE(6,180)                                                        LMO       224
        C                                                                         LMO       225
        C                                                                         LMO       226
        C                          A DO LOOP FOR THE RADIAL DISTANCES             LMO       227
        C                                                                         LMO       228
 1052         DO 170 I=ISTD,NDIST                                                 LMO       229
 1054         R=DIST(I)                                                           LMO       230
        C                                                                         LMO       231
        C                          A DO LOOP FOR THE PHI1 ANGLES                  LMO       232
        C                                                                         LMO       233
 1056         DO 160 J=ISP1,NPHI1                                                 LMO       234
 1060         CPHI1=COSP1(J)                                                      LMO       235
 1061         PHI1=ARCOS(CPHI1)                                                   LMO       236
 1063         SPHI1=SQRT(1.0-CPHI1*CPHI1)                                         LMO       237
        C                                                                         LMO       238
        C                          A DO LOOP FOR THE THET1 ANGLES                 LMO       239
        C                                                                         LMO       240
 1071         DO 150 K=IST1,NTHET1                                                LMO       241
 1073         CTHET1=COST1(K)                                                     LMO       242
 1074         THET1=ARCOS(CTHET1)                                                 LMO       243
 1076         STHET1=SQRT(1.0-CTHET1*CTHET1)                                      LMO       244
        C                                                                         LMO       245
        C                          A DO LOOP FOR THE THET2 ANGLES                 LMO       246
        C                                                                         LMO       247
 1104         DO 140 L=IST2,NTHET2                                                LMO       248
 1106         CTHET2=COST2(L)                                                     LMO       249
 1107         THET2=ARCOS(CTHET2)                                                 LMO       250
 1111         STHET2=SQRT(1.0-CTHET2*CTHET2)                                      LMO       251
        C     A SYSTEM CLOCK SUBROUTINE                                           LMO       252
        C                                                                         LMO       253
 1117         CALL SECOND(SEC1)                                                   LMO       254
        C                                                                         LMO       255
        C                                                                         LMO       256
        C                          DO A THREE DIMENSIONAL NUMERICAL               LMO       257
        C                          QUADRATURE TO CALCULATE THE                    LMO       258
        C                          INTERACTION POTENTIAL BETWEEN                  LMO       259
        C                          THE MOLECULES.                                 LMO       260
        C                                                                         LMO       261
        C                                                                         LMO       262
 1120         CALL QUAD3( POTNB,COSPA ,COSTA ,COSTB ,COSTP ,CPHI1 ,CTHET1         LMO       263
             1          ,CTHET2,DELTAR,DELTAT,EDENA ,EDENB ,ECORR ,ECOUL          LMO       264
             2          ,EKIN  ,ELDENA,ELDENB,EXCH  ,NELECA,NELECB,NNUCA          LMO       265
             3          ,NNUCB ,NPA   ,NRA   ,NRB   ,NTA   ,NTB   ,POTENB          LMO       266
             4          ,R     ,RPOS  ,RADA  ,RADB  ,SELF  ,SINPA ,SINTA          LMO       267
             5          ,SPHI1 ,STHET1,STHET2,WP    ,WR    ,WT    ,ZPOSA          LMO       268
             6          ,ZPOSB ,ZNUCA ,ZNUCB ,RBEGN ,IDENT ,B     )               LMO       269
        C                                                                         LMO       270
        C                                                                         LMO       271
 1200         CALL SECOND(SEC)                                                    LMO       272
 1205         SEC=SEC-SEC1                                                        LMO       273
 1205         STOT=STOT+SEC                                                       LMO       274
 1205         GKSCF=EXCH/SELF+EKIN+ECOUL                                          LMO       275
 1205         GKRSCF=EXCH+EKIN+ECOUL                                              LMO       276
```

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      RUN-107     0          LMOLMO          76/04/09     20.13.03     PARKERZZUR   PAGE NO. 6
1205           GK=GKSCF+ECORR
1205           GKR=GKRSCF+ECORR
          C
          C
1217           IF(ICOUNT.NE.0)GO TO 130
1220           CALL DATE(TODAY)
1222           CALL TIME(TYME)
1224           WRITE(6,240)
1230           WRITE(6,250)TODAY
1236           WRITE(6,260)TYME
1244       130 ICOUNT=ICOUNT+1
1246           IF(ICOUNT.EQ.8)ICOUNT=0
1250           WRITE(6,490)SELF,SFC,R,PHI1,THET1,THET2,ECORR,ECOUL,EXCH,EKIN
             1            ,GKSCF,GKRSCF,GK,GKR
1310           WRITE(7,500)THET2,ECORR,EXCH,EKIN,ECOUL,GKSCF,GKRSCF,GK,GKR
1336       140 CONTINUE
          C
          C
          C                             RESET THE STARTING PARAMETERS
          C                             TO ONE.
          C
          C
1341       150 IST2=1
1344       160 IST1=1
1350       170 ISP1=1
1353           ISTD=1
          C
          C
1354           WRITE(6,270)STOT
1362           RETURN
          C
          C
           180 FORMAT(1H1)
           190 FORMAT(8F10.7)
           200 FORMAT(15X,I5/F10.5)
           210 FORMAT(1H0,42HTIME REQUIREMENT FOR THIS CALCULATION WAS ,F10.5
             1       ,9H SECONDS./)
           220 FORMAT(1H ,10I8)
           230 FORMAT(1H0,8H   NDIST,8H  NTHET2,8H  NPHI1 ,8H  NTHET1,8H    KASE)
           240 FORMAT(40H                                        ,
             1        40H                                        )
           250 FORMAT(1H ,60X,5HDATE ,A8)
           260 FORMAT(1H ,60X,5HTIME ,A8)
           270 FORMAT(1H0,20HTOTAL TIME REQUIRED=,E14.7,8HSECONDS./1H1)
           280 FORMAT(1H0,10A8)
           290 FORMAT(2X,5F12.5)
           300 FORMAT(1H0,17HTHE THETA2 ANGLES)
           310 FORMAT(1H0,17HTHE PHI1   ANGLES)
           320 FORMAT(1H0,16HTHE THET1 ANGLES)
           330 FORMAT(1H0,20HTHE RADIAL DISTANCES)
           340 FORMAT(1H0,29HTHE RADIAL INTEGRATION POINTS)
           350 FORMAT(1H0,28HTHE THETA INTEGRATION POINTS)
           360 FORMAT(1H0,26HTHE PHI INTEGRATION POINTS)
           370 FORMAT(16I5)
           380 FORMAT(1H0,42HTHIS POTENTIAL SURFACE CALCULATION IS FOR ,
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RUN-107     0         LMOLMO          76/04/09     20.13.03     PARKERZ2UR   PAGE NO. 7

     1         19HIDENTICAL MOLECULES)                                        LMO        332
   390 FORMAT(1H0,15H        R1E       ,15H        R2E       )                LMO        333
   400 FORMAT(1H0,5H NTI ,5H NPI ,5H NRIS)                                    LMO        334
   410 FORMAT(1H0,10H    NELECA,10H    NELECB)                                LMO        335
   420 FORMAT(1H ,2I10)                                                       LMO        336
   430 FORMAT(2I5,5F10.5,E14.7)                                               LMO        337
   440 FORMAT(1H0,2I5,5X,F10.5,E14.7)                                         LMO        338
   450 FORMAT(1H0,3HXT2)                                                      LMO        339
   460 FORMAT(1H0,3HXR2)                                                      LMO        340
   470 FORMAT(1H0,4HZETA)                                                     LMO        341
   480 FORMAT(1H0,2HAN)                                                       LMO        342
   490 FORMAT(1H0,7X,5HSELF=,E14.7,3X,8HSECONDS=,E14.7/1H ,10X,2HR=,E14.7 LMO        343
     1        ,6X,5HPHI1=,E14.7,3X,7HTHETA1=,E14.7,2X,7HTHETA2=,E14.7/1H      LMO        344
     2        ,12HCORRELATION=,E14.7,11H COULOMBIC=,E14.7,10H EXCHANGE=       LMO        345
     3        ,E14.7,9H KINETIC=,E14.7/1H ,6X,6HGKSCF=,E14.7,4X,7HGKRSCF=     LMO        346
     4        ,E14.7,7X,3HGK=,E14.7,5X,4HGKR=,E14.7)                          LMO        347
   500 FORMAT(F10.5,4E14.7/4E14.7)                                            LMO        348
   510 FORMAT(1H0,43HTHE POTENTIAL SURFACE WILL BE CALCULATED AT,I3,          LMO        349
     1         17H RADIAL DISTANCES/)                                         LMO        350
   520 FORMAT(1H0,43HTHE POTENTIAL SURFACE WILL BE CALCULATED AT,I3,          LMO        351
     1         13H PHI1 ANGLES./35H THE COSINES OF THE PHI1 ANGLES ARE/)      MOL1         1
   530 FORMAT(1H0,43HTHE POTENTIAL SURFACE WILL BE CALCULATED AT,I3,          LMO        353
     1         15H THETA1 ANGLES./37H THE COSINES OF THE THETA1 ANGLES ARE MOL1         2
     2         /)                                                             LMO        355
   540 FORMAT(1H0,43HTHE POTENTIAL SURFACE WILL BE CALCULATED AT,I3,          LMO        356
     1         15H THETA2 ANGLES./37H THE COSINES OF THE THETA2 ANGLES ARE MOL1         3
     2         /)                                                             LMO        358
   550 FORMAT(1H0,18HTHE COSINES OF THE,I3,20H THETA INTERPOLATION,           MOL1         4
     1         11H POINTS ARE/)                                               LMO        360
   560 FORMAT(1H0,3HTHE,I3,32H RADIAL INTERPOLATION POINTS ARE/)              LMO        361
   570 FORMAT(1H1,41HTHE RADIAL INTEGRATION WILL BE SPLIT INTO,I3,            LMO        362
     1         10H SECTIONS./32H THE SECTIONS AND THE NUMBER OF               MOL1         5
     2         26HPOINTS IN EACH SECTION ARE/)                                MOL1         6
   580 FORMAT(1H0,3HTHE,I3,26H RADIAL INTEGRATION POINTS/)                    LMO        365
   590 FORMAT(1H0,3HTHE,I3,25H THETA INTEGRATION POINTS/)                     LMO        366
   600 FORMAT(1H0,3HTHE,I3,23H PHI INTEGRATION POINTS/)                       LMO        367
   610 FORMAT(1H0,14HMOLECULE A HAS,I3,10H ELECTRONS)                         LMO        368
   620 FORMAT(1H0,14HMOLECULE B HAS,I3,10H ELECTRONS)                         LMO        369
C                                                                             LMO        370
C                                                                             LMO        371
1363        END                                                               LMO        372
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RUN-107    0                        76/04/09    20.13.03    PARKERZ2UR   PAGE NO. 1
              FUNCTION EG(CUBRDN)                                                LMO       373
        C                                                                        LMO       374
        C                                                                        LMO       375
        C     PURPOSE                                                            LMO       376
        C        CORRELATION ENERGY DENSITY.                                     LMO       377
        C                                                                        LMO       378
        C     DESCRIPTION OF PARAMETERS                                          LMO       379
        C        CUBRDN     CUBE ROOT OF THE ELECTRON DENSITY                    LMO       380
        C                                                                        LMO       381
        C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                      LMO       382
        C        NONE.                                                           LMO       383
        C                                                                        LMO       384
        C     METHOD                                                             LMO       385
        C        USING THE UNIFORM FREE ELECTRON GAS APPROXIMATION.              LMO       386
        C                                                                        LMO       387
   3          REAL LNRS                                                          LMO       388
        C                                                                        LMO       389
              DATA PI34/0.6203504908/                                            LMO       390
   3          RS=PI34/CUBRDN                                                     LMO       391
   4          IF(RS.GT.10.0)GO TO 10                                             LMO       392
  10          LNRS=ALOG(RS)                                                      LMO       393
  11          IF(RS.LT..7)GO TO 20                                               LMO       394
        C                                                                        LMO       395
        C        INTERPOLATIVE FUNCTION FOR INTERMEDIATE DENSITIES               LMO       396
        C                                                                        LMO       397
  15          EG=0.01898*LNRS-0.06156                                            LMO       398
  20          RETURN                                                             LMO       399
        C                                                                        LMO       400
        C        LOW ENERGY DENSITY                                              LMO       401
        C                                                                        LMO       402
  21       10 RS2=SQRT(RS)                                                       LMO       403
  23          EG=((-0.4/RS2-1.47)/RS+1.325/RS2-0.438)/RS                         LMO       404
  32          RETURN                                                             LMO       405
        C                                                                        LMO       406
        C        HIGH ENERGY DENSITY                                             LMO       407
        C                                                                        LMO       408
  33       20 EG=(0.0311+0.009*RS)*LNRS-0.01*RS-0.048                            LMO       409
  41          RETURN                                                             LMO       410
  42          END                                                                LMO       411
```

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RUN=107    0                      76/04/09     20.13.03    PARKERZ2UR    PAGE NO. 1
         SUBROUTINE ELCPOT(COSTA ,COSTP ,ELDENB,ELDENA,NNUCA ,NRA   ,
        1                  NTA   ,POTENA,RADA  ,RPOS  ,SINTA ,ZNUCA ,
        2                  ZPOSA ,IREAD ,IDENT )
      C
      C
27       DIMENSION COSTA(1)       ,COSTP(1)        ,ELDENA(NRA,NTA),
        1          POTENA(NRA,NTA),RADA(1)         ,RPOS(1)        ,
        2          SINTA(1)       ,ZNUCA(1)        ,ZPOSA(1)       ,
        3          ELDENB(NRA,NTA)
      C
      C
27       COMMON /BASE/CA(5,35),LA(5,35),NA(5,35),NBFA(5),NCENA,ZETA(5,35)
      C
      C
      C  PURPOSE
      C     CALCULATES THE ELECTROSTATIC POTENTIAL AND THE CUBE ROOT OF
      C     THE ELECTRON DENSITY
      C  DESCRIPTION OF PARAMETERS
      C     COSTA-COSINE OF THE THETA ANGLES
      C     COSTP-WORK ARRAY
      C     ELDENB-CUBE ROOT OF THE ELECTRON DENSITY FOR MOLECULE-B
      C     ELDENA-CUBE ROOT OF THE ELECTRON DENSITY FOR MOLECULE-A
      C     NNUCA-NUMBER OF NUCLEI
      C     NRA-NUMBER OF RADIAL DISTANCES
      C     NTA-NUMBER OF THETA ANGLES
      C     POTENA-ELECTROSTATIC POTENTIAL
      C     RADA-RADIAL DISTANCES
      C     RPOS-WORK ARRAY
      C     SINTA-SINE OF THE THETA ANGLES
      C     ZNUCA-NUCLEAR CHARGES
      C     ZPOSA-NUCLEAR POSITIONS
      C     IREAD=0  IF IT IS NOT NECESSARY TO READ IN NEW DATA
      C     IDENT=1 IF MOLECULES- AND AND B ARE IDENTICAL
      C     SUBROUTINE USED
      C     PFUNC
      C
      C  PARAMETERS TO BE READ IN IF IREAD IS NOT EQUAL TO 0
      C  CARD 1
      C     TITLE (COLUMN 1 CONTAINS A 1 FOLLOWED BY THE TITLE)
      C  CARD 2
      C     NUMBER OF NUCLEI AND THE NUMBER OF BASIS SET CENTERS (I5)
      C  CARD 3
      C     NUCLEAR CHARGES (F10.5)
      C  CARD 4
      C     NUMBER OF BASIS FUNCTIONS FOR EACH CENTER (I5)
      C  CARD 5
      C     CENTERS FOR THE BASIS SET WITH THE FIRST PART OF THE ARRAY
      C  CARD 6----
      C     PRINCIPAL QUANTUM NUMBER,SUBSIDARY QUANTUM NUMBER,
      C     RADIAL EXPONENT, AND THE COEFFICIENT (2I5,2F10.5)
      C
      C
27       IF(IREAD.EQ.0)GO TO 20
      C
30       READ(5,60)
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        RUN=107    0        ELCPOT         76/04/09    20.13.03    PARKERZ2UR    PAGE NO. 2
  34           READ(5,80)NNUCA,NCENA                                    LMO        467
  47           READ(5,90)(ZNUCA(IA),IA=1,NNUCA)                         LMO        468
  64           READ(5,90)(ZPOSA(IA),IA=1,NCENA)                         LMO        469
  76           READ(5,80)(NBFA(IA),IA=1,NCENA)                          LMO        470
        C                                                               LMO        471
        C                                                               LMO        472
 110           WRITE(6,60)                                              LMO        473
        C                                                               LMO        474
        C                                                               LMO        475
 117           ICOUNT=0                                                 LMO        476
 120           DO 10 IA=1,NCENA                                         LMO        477
 125           ICOUNT=ICOUNT+3                                          LMO        478
 125           NBF=NBFA(IA)                                             LMO        479
 131           WRITE(6,150)NBF,ZPOSA(IA),ZNUCA(IA)                      LMO        480
 144           WRITE(6,140)                                             LMO        481
 153           DO 10 K=1,NBF                                            LMO        482
 160           ICOUNT=ICOUNT+1                                          LMO        483
 161           IF(ICOUNT.GT.50)WRITE(6,70)                              LMO        484
 173           IF(ICOUNT.GT.50)ICOUNT=1                                 LMO        485
 177           READ(5,50)NA(IA,K),LA(IA,K),ZETA(IA,K),CA(IA,K)          LMO        486
 225        10 WRITE(6,50)NA(IA,K),LA(IA,K),ZETA(IA,K),CA(IA,K)         LMO        487
        C                                                               LMO        488
        C                                                               LMO        489
        C                            TABULATE THE CHARGE DENSITY AND THE LMO        490
        C                            ELECTROSTATIC POTENTIAL OF MOLECULE-B LMO      491
        C                            IN ELDENA AND POTENA RESPECTIVELY. LMO         492
        C                                                               LMO        493
        C                                                               LMO        494
 257        20 DO 40 NR=1,NRA                                           LMO        495
 261           RA=RADA(NR)                                              LMO        496
 263           DO 40 NT=1,NTA                                           LMO        497
 265           DENA=0.0                                                 LMO        498
 265           X=RA*SINTA(NT)                                           LMO        499
 265           Z=RA*COSTA(NT)                                           LMO        500
 272           DO 30 IA=1,NCENA                                         LMO        501
 273           ZC=Z-ZPOSA(IA)                                           LMO        502
 276           RPOS(IA)=SQRT(X*X+ZC*ZC)                                 LMO        503
 310           COSTP(IA)=ZC/RPOS(IA)                                    LMO        504
 310           NBF=NBFA(IA)                                             LMO        505
 314           DO 30 K=1,NBF                                            LMO        506
 316           FF=1.0                                                   LMO        507
 317           IF(NA(IA,K).GT.1)FF=RPOS(IA)**(NA(IA,K)-1)               LMO        508
 334           IF(LA(IA,K).GT.0)FF=FF*PN(LA(IA,K),COSTP(IA))            LMO        509
 354        30 DENA=DENA+FF*EXP(-ZETA(IA,K)*RPOS(IA))*CA(IA,K)          LMO        510
 402           ELDENA(NR,NT)=DENA**.33333333333333                      LMO        511
 410           IF(IDENT.EQ.1)ELDENB(NR,NT)=ELDENA(NR,NT)                LMO        512
 421           CALL PFUNC(RPOS,COSTP,ZNUCA,POTL,NNUCA)                  LMO        513
 431        40 POTENA(NR,NT)=POTL                                       LMO        514
        C                                                               LMO        515
        C                                                               LMO        516
 442           RETURN                                                   LMO        517
        C                                                               LMO        518
        C                                                               LMO        519
            50 FORMAT(2I5,F10.5,E14.7)                                  LMO        520
            60 FORMAT(40H                                               LMO        521
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RUN=107     0          ELCPOT          76/04/09     20.13.03     PARKERZ2UR    PAGE NO. 3

          1         40H                                         )              LMO       522
         70 FORMAT(1H1)                                                         LMO       523
         60 FORMAT(16I5)                                                        LMO       524
         90 FORMAT(8F10.5)                                                      LMO       525
        100 FORMAT(16I5)                                                        LMO       526
        110 FORMAT(3F10.5)                                                      LMO       527
        120 FORMAT(F10.5,3I5,F10.5)                                             LMO       528
        130 FORMAT(1H ,2I5,2F10.5)                                              LMO       529
        140 FORMAT(1H0,3X,1HN,4X,1HL,4X,4HZETA,7X,5HCOEFF)                      LMO       530
        150 FORMAT(1H0,I3,16H BASIS FUNCTIONS,15H,Z=COORDINATE =,F10.5,         LMO       531
          1         17H,NUCLEAR CHARGE =,F5.1)                                  MOL1        7
      C                                                                         LMO       533
      C                                                                         LMO       534
443           END                                                               LMO       535
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     RUN-107     0                          76/04/09     20.13.03     PARKERZ2UR    PAGE NO. 1

             SUBROUTINE MOMENT(COSTA ,ELDENA,NELECA,NNUCA ,NRA    ,NTA    ,         MOL       1946
            1                    RADA  ,SINTA ,WR     ,WT     ,ZPOSA ,ZNUCA )       MOL       1947
          C                                                                         MOL       1948
          C                                                                         MOL       1949
24           DIMENSION COSTA(1)        ,ELDENA(NRA,NTA),ELMOM(5)        ,           MOL       1950
            1          SINTA(1)        ,RADA(1)        ,WR(1)           ,           MOL       1951
            2          WT(1)           ,ZPOSA(1)       ,ZNUCA(1)                    MOL       1952
          C                                                                         MOL       1953
          C                                                                         MOL       1954
             DATA TWOPI/6.2831853071896/                                            MOL       1955
          C                                                                         MOL       1956
          C                                                                         MOL       1957
          C  PURPOSE                                                                MOL       1958
          C     CALCULATES THE MOMENTS OF THE MOLECULE FROM THE MONOPOLE            MOL       1959
          C     TO THE HEXADECAPOLE.                                                MOL       1960
          C  DESCRIPTION OF PARAMETERS                                              MOL       1961
          C     COSTA-ARRAY CONTAINING THE COSINE OF THE THETA ANGLES.              MOL       1962
          C     ELCDENA-THE TABULATED ELECTRON DENSITY                              MOL       1963
          C     NELECA-NUMBER OF ELECTRONS                                          MOL       1964
          C     NRA-NUMBER OF RADIAL DISTANCES                                      MOL       1965
          C     NTA-NUMBER OF THETA ANGLES                                          MOL       1966
          C     SINTA-ARRAY CONTAINING THE SINE OF THE THETA ANGLES                 MOL       1967
          C     WR-RADIAL INTEGRATION WEIGHTS                                       MOL       1968
          C     WT-THETA INTEGRATION WEIGHTS                                        MOL       1969
          C     ZPOSA-NUCLEAR POSITIONS                                             MOL       1970
          C     ZNUCA-NUCLEAR CHARGES                                               MOL       1971
          C  SUBROUTINES USED                                                       MOL       1972
          C     NONE                                                                MOL       1973
          C                                                                         MOL       1974
          C                                                                         MOL       1975
24           DO 10 IM=1,5                                                           MOL       1976
30        10 ELMOM(IM)=0.0                                                          MOL       1977
          C                                                                         MOL       1978
          C                                                                         MOL       1979
          C                            FIND THE MOMENTS DO TO THE ELECTRONIC        MOL       1980
          C                            DISTRIBUTION.                                MOL       1981
          C                                                                         MOL       1982
          C                                                                         MOL       1983
32           DO 20 NR=1,NRA                                                         MOL       1984
37           RA=RADA(NR)                                                            MOL       1985
37           WEIGHR=WR(NR)                                                          MOL       1986
43           DO 20 NT=1,NTA                                                         MOL       1987
53           COST=COSTA(NT)                                                         MOL       1988
53           COSTS=COST*COST                                                        MOL       1989
53           CUBRHA=ELDENA(NR,NT)                                                   MOL       1990
53           RHOA=CUBRHA*CUBRHA*CUBRHA                                              MOL       1991
53           WEIGHT=WEIGHR*WT(NT)                                                   MOL       1992
53           ELMOM(1)=ELMOM(1)+RHOA*WEIGHT                                          MOL       1993
53           ELMOM(2)=ELMOM(2)+RHOA*WEIGHT*RA*COST                                  MOL       1994
53           RAL=RA*RA                                                              MOL       1995
53           ELMOM(3)=ELMOM(3)+RHOA*WEIGHT*(3.0*COSTS-1.0)*0.5*RAL                  MOL       1996
53           RAL=RAL*RA                                                             MOL       1997
53           ELMOM(4)=ELMOM(4)+RHOA*COST*(5.0*COSTS-3.0)*0.5*RAL*WEIGHT             MOL       1998
53           RAL=RAL*RA                                                             MOL       1999
53        20 ELMOM(5)=ELMOM(5)+RHOA*WEIGHT*(3.+COSTS*(-30.0+35.*COSTS))*0.125       MOL       2000
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      RUN-107    O        MOMENT          76/04/09     20.13.03     PARKERZ2UR    PAGE NO. 2

               1 *RAL                                                            MOL        2001
130              DO 30 IM=1,5                                                    MOL        2002
134           30 ELMOM(IM)=ELMOM(IM)*TWOPI                                       MOL        2003
          C                                                                      MOL        2004
          C                                                                      MOL        2005
          C                              SUBSTRACT THE MOMENTS DO TO THE NUCLEAR MOL        2006
          C                              CHARGES.                                MOL        2007
          C                                                                      MOL        2008
          C                                                                      MOL        2009
136              ZCHARG=0.0                                                      MOL        2010
137              DO 40 IA=1,NNUCA                                                MOL        2011
147           40 ZCHARG=ZCHARG+ZNUCA(IA)                                         MOL        2012
152              ELMOM(1)=ELMOM(1)-ZCHARG                                        MOL        2013
154              DO 60 IM=2,5                                                    MOL        2014
161              N=IM-1                                                          MOL        2015
161              ELMOM(IM)=ELMOM(IM)                                             MOL        2016
161              ELNM=0.0                                                        MOL        2017
165              DO 50 IA=1,NNUCA                                                MOL        2018
172           50 ELNM=ELNM+ZNUCA(IA)*ZPOSA(IA)**N                                MOL        2019
204           60 ELMOM(IM)=ELNM-ELMOM(IM)                                        MOL        2020
          C                                                                      MOL        2021
          C                                                                      MOL        2022
          C                              WRITE OUT THE ELECTRIC MOMENTS IN ATOMIC MOL       2023
          C                              UNITS.                                  MOL        2024
          C                                                                      MOL        2025
          C                                                                      MOL        2026
211              WRITE(6,70)                                                     MOL        2027
214              WRITE(6,80)                                                     MOL        2028
223              WRITE(6,90)(ELMOM(IM),IM=1,5)                                   MOL        2029
234              WRITE(6,100)                                                    MOL        2030
          C                                                                      MOL        2031
          C                                                                      MOL        2032
243              RETURN                                                          MOL        2033
          C                                                                      MOL        2034
          C                                                                      MOL        2035
              70 FORMAT(1H0,23HMOMENTS IN ATOMIC UNITS)                          MOL        2036
              80 FORMAT(1H0,3X,8HMONOPOLE,7X,6HDIPOLE,6X,10HQUADRUPOLE,5X,       MOL        2037
             1         8HOCTAPOLE,4X,12HHEXADECAPOLE)                            MOL        2038
              90 FORMAT(1H0,5E14.7)                                              MOL        2039
             100 FORMAT(1H1)                                                     MOL        2040
244              END                                                             MOL        2041
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      RUN-107      0                                 76/04/09     20.13.03     PARKERZZUR    PAGE NO. 1

                 SUBROUTINE PFUNC(RPOS,COSTP,ZNUCA,POTL,NNUCA)                   LMO          536
          C                                                                      LMO          537
          C                                                                      LMO          538
          C      PURPOSE                                                         LMO          539
          C         CALCULATES THE POTENTIAL                                     LMO          540
          C      DESCRIPTION OF PARAMETERS                                       LMO          541
          C         RPOS-ARRAY CONTAINING THE RADIAL DISTANCES FROM THE NUCLEI   LMO          542
          C         COSTP-ARRAY CONTAINING THE COSINE OF THE ANGLES FROM THE     LMO          543
          C              NUCLEI.                                                 LMO          544
          C         ZNUCA-NUCLEAR CHARGES                                        LMO          545
          C         POTL-RESULTANT POTENTIAL                                     LMO          546
          C         NNUCA-NUMBER OF NUCLEI                                       LMO          547
          C                                                                      LMO          548
          C                                                                      LMO          549
       14        DIMENSION COSTP(1),FACT(10),RPOS(1),ZNUCA(1)                    LMO          550
          C                                                                      LMO          551
          C                                                                      LMO          552
       14        COMMON /BASE/CA(5,35),LA(5,35),NA(5,35),NBFA(5),NCENA,ZETA(5,35) LMO         553
          C                                                                      LMO          554
          C                                                                      LMO          555
                 DATA FACT(1)/1.0/                                               LMO          556
                 DATA FACT(2)/2.0/                                               LMO          557
                 DATA FACT(3)/6.0/                                               LMO          558
                 DATA FACT(4)/24.0/                                              LMO          559
                 DATA FACT(5)/120.0/                                             LMO          560
                 DATA FACT(6)/720.0/                                             LMO          561
                 DATA FACT(7)/5040.0/                                            LMO          562
                 DATA FACT(8)/40320.0/                                           LMO          563
                 DATA FACT(9)/362880.0/                                          LMO          564
                 DATA FACT(10)/3628800.0/                                        LMO          565
          C                                                                      LMO          566
                 DATA FOURPI/12.5663706/                                         LMO          567
          C                                                                      LMO          568
          C                                                                      LMO          569
          C                               CALCULATE THE ELECTROSTATIC POTENTIAL  LMO          570
          C                               OF THE ELECTRON CLOUD.                 LMO          571
          C                                                                      LMO          572
          C                                                                      LMO          573
       14        POTL=0.0                                                        LMO          574
       14        DO 40 IA=1,NCENA                                                LMO          575
       17        NBF=NBFA(IA)                                                    LMO          576
       17        RALFBT=RPOS(IA)                                                 LMO          577
       17        CALFBT=COSTP(IA)                                                LMO          578
       22        DO 40 K=1,NBF                                                   LMO          579
       26        NK=NA(IA,K)                                                     LMO          580
       26        LK=LA(IA,K)                                                     LMO          581
       26        LKP1=LK                                                         LMO          582
       26        RZET=RALFBT*ZETA(IA,K)                                          LMO          583
       34        COEF=RALFBT**(NK+1)*PN(LKP1,CALFBT)*CA(IA,K)/FLOAT(2*LK+1)      LMO          584
       56        RZETI=1.0/RZET                                                  LMO          585
       56        NK1=NK+LK+1                                                     LMO          586
       56        NKMLK=NK-LK                                                     LMO          587
       56        TERM1=FACT(NK1)*RZETI**(NK+LK+2)                                LMO          588
       56        TERM2=RZETI**(NK-LK+1)                                          LMO          589
       56        NKLK=NK-LK-1                                                    LMO          590
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     RUN-107     0          PFUNC            76/04/09     20.13.03     PARKERZ2UR    PAGE NO. 2

100         IF(NKLK.LE.0)GO TO 20                                                 LMO         591
105         DO 10 M=1,NKLK                                                        LMO         592
114         NKM=NKMLK-M                                                           LMO         593
114      10 TERM2=TERM2+RZETI**(M+1)/FACT(NKM)                                    LMO         594
132      20 TERM2=TERM2*FACT(NKMLK)                                               LMO         595
132         TERM3=RZETI**(NK+LK+2)                                                LMO         596
132         NKLK=NK+LK                                                            LMO         597
143         DO 30 M=1,NKLK                                                        LMO         598
152         NKM=NK1-M                                                             LMO         599
152      30 TERM3=TERM3+RZETI**(M+1)/FACT(NKM)                                    LMO         600
163         TERM3=TERM3*FACT(NK1)                                                 LMO         601
170      40 POTL=POTL+COEF*(TERM1+EXP(-RZET)*(TERM2-TERM3))                       LMO         602
211      50 POTL=POTL*FOURPI                                                      LMO         603
      C                                                                           LMO         604
      C                                                                           LMO         605
      C                              INCLUDE THE ELECTROSTATIC POTENTIAL          LMO         606
      C                              DO TO THE NUCLEI OF MOLECULE-A.              LMO         607
      C                                                                           LMO         608
      C                                                                           LMO         609
213         DO 60 IA=1,NNUCA                                                      LMO         610
216      60 POTL=POTL-ZNUCA(IA)/RPOS(IA)                                          LMO         611
221         RETURN                                                                LMO         612
222         END                                                                   LMO         613
```

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     RUN-107    0                    76/04/09    20.13.03    PARKERZZUR   PAGE NO. 1

                FUNCTION PN(N,COST)                                        LMO        614
     C    CALCULATES THE N-TH LEGENDRE POLYNOMIAL AT COST                  LMO        615
  6             DIMENSION P(96)                                            LMO        616
  6             NP1=N+1                                                    LMO        617
  6             P(1)=1.0                                                   LMO        618
  6             P(2)=COST                                                  LMO        619
 11             IF(N-1)30,30,10                                            LMO        620
 13          10 DO 20 I=3,NP1                                              LMO        621
 23             IM1=I-1                                                    LMO        622
 23             IM2=I-2                                                    LMO        623
 23             COSTP=COST*P(IM1)                                          LMO        624
 23          20 P(I)=COSTP-P(IM2)+COSTP-(COSTP-P(IM2))/FLOAT(IM1)          LMO        625
 40          30 PN=P(NP1)                                                  LMO        626
 42             RETURN                                                     LMO        627
 43             END                                                        LMO        628
```

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RUN=107    0                    76/04/09    20.13.03    PARKERZ2UR   PAGE NO. 1

      SUBROUTINE QUAD3( POTNB,COSPA ,COSTA ,COSTB ,COSTP ,CPHI1 ,CTHET1  LMO
     1                ,CTHET2,DELTAR,DELTAT,EDENA ,EDENB ,ECORR ,ECOUL   LMO
     2                ,EKIN  ,ELDENA,ELDENB,EXCH  ,NELECA,NELECB,NNUCA   LMO
     3                ,NNUCB ,NPA   ,NRA   ,NRB   ,NTA   ,NTB   ,POTENB  LMO
     4                ,R     ,RPOS  ,RADA  ,RADB  ,SELF  ,SINPA ,SINTA   LMO
     5                ,SPHI1 ,STHET1,STHET2,WP    ,WR    ,WT    ,ZPOSA   LMO
     6                ,ZPOSB ,ZNUCA ,ZNUCB ,RBEGN ,IDENT ,B     )        LMO
C                                                                        LMO
C         POTNB=POTENTIAL MATRIX OF MOLECULE=B                           LMO
C         COSPA=COSINE OF THE PHI INTEGRATION ANGLES                     LMO
C         COSTA=COSTINE OF THE THETA INTEGRATION ANGLES                  LMO
C         COSTP=WORK ARRAY                                               LMO
C         CPHI1=COSINE OF PHI1                                           LMO
C         CTHET1=COSINE OF THETA1                                        LMO
C         CTHET2=COSINE OF THETA 2                                       LMO
C         DELTAR RADIAL INCREMENT                                        LMO
C         DELTAT=THETA INCREMENT                                         LMO
C         EDENA=CUBE ROOT OF THE ELECTRON DENSITY OF MOLECULE=A TABULATED LMO
C               EQUIDISANTLY                                             LMO
C         EDENB=CUBE ROOT OF THE ELECTRON DENSITY OF MOLECULE=B TABULATED LMO
C               EQUIDISANTLY                                             LMO
C         ECORR=CORRELATION ENERGY                                       LMO
C         COULOMBIC ENERGY                                               LMO
C         EKIN=KINETIC ENERGY                                            LMO
C         ELDENA=CUBE ROOT OF THE ELECTRON DENSITY FOR MOLECULE=A        LMO
C                AT THE INTEGRATION POINTS                               LMO
C         ELDENB=CUBE ROOT OF THE ELECTRON DENSITY FOR MOLECULE=B        LMO
C                AT THE INTEGRATION POINTS                               LMO
C         EXCH=EXCHANGE ENERGY                                           LMO
C         NELECA=NUMBER OF ELECTRONS ON MOLECULE=A                       LMO
C         NELECB=NUMBER OF ELECTRONS ON MOLECULE=B                       LMO
C         NNUCA=NUMBER OF NUCLEI IN MOLECULE=A                           LMO
C         NUMBER OF NUCLEI IN MOLECULE=B                                 LMO
C         NPA=NUMBER OF PHI INTEGRATION POINTS                           LMO
C         NRA=NUMBER OF RADIAL INTEGRATION POINTS                        LMO
C         NRB=NUMBER OF EQUIDISTANT RADIAL POINTS                        LMO
C         NTB=NUMBER OF EQUIDISTANT THETA POINTS                         LMO
C         POTENB=POTENTIAL OF MOLECULE=B TABULATED AT THE                LMO
C                INTEGRATION POINTS                                      LMO
C         R=DISTANCE BETWEEN THE CENTER OF MASSES                        LMO
C         RADA=RADIAL INTEGRATION POINTS                                 LMO
C         SELF=SELF ENERGY CORRECTION                                    LMO
C         SINPA=SINE OF THE PHI INTEGRATION POINTS                       LMO
C         SINTA=SINE OF THE THETA INTEGRATION POINTS                     LMO
C         SPHO1=SINE OF PHI1                                             LMO
C         STHET1=SINE OF THETA 1                                         LMO
C         STHET2=SINE OF THEAT 2                                         LMO
C         WP=RADIAL INTEGRATION WEIGHTS                                  LMO
C         WP=PHI INTEGRATION WEIGHTS                                     LMO
C         WT=THETA INTEGRATION WEIGHTS                                   LMO
C         ZPOSA=NUCLEAR POSITIONS OF MOLECULE=A                          LMO
C         ZPOSB=NUCLEAR POSITIONS OF MOLECULE=B                          LMO
C         ZNUCA=NUCLEAR CHARGES OF MOLECULE=A                            LMO
C         ZNUCB=NUCLEAR CHARGES OF MOLECULE=B                            LMO
C         IDENT=1 IF THE MOLECULE ARE IDENTICAL                          LMO
```

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    C          B-LENGHT OF THE SEMI-MAJOR AXIS OF THE ELLIPSE
    C
70          DIMENSION COSPA(1)          ,COSTA(1)          ,POTENB(NRA,NTA),
           1         COSTB(1)          ,COSTP(1)          ,ELDENA(NRA,NTA),
           2         ELDENB(NRA,NTA),POTNB(NRB,NTB) ,RADA(1)          ,
           3         RADB(1)           ,RPOS(1)           ,SINPA(1)         ,
           4         SINTA(1)          ,WP(1)             ,WR(1)            ,
           5         WT(1)             ,ZPOSA(1)          ,ZPOSB(1)         ,
           6         ZNUCA(1)          ,ZNUCB(1)          ,EDENA(NRB,NTB) ,
           7         EDENB(NRB,NTB)
    C
    C
70          COMMON /BASE/CA(5,35),LA(5,35),NA(5,35),NBFA(5),NCENB,ZETA(5,35)
    C
    C
70          LOGICAL TEST
    C
    C
            DATA PI/3.1415926535898/
            DATA TWOPI/6.2831853071796/
            DATA CE/-.73855870636202/
            DATA CK/2.6712340001881/
    C
    C
70          NRAM1=NRA-1
70          NTAM1=NTA-1
70          ODR=1.0/DELTAR
70          ODT=1.0/DELTAT
    C
    C
    C                                    THESE ARE CONSTANTS THAT ARE
    C                                    NECESSARY IN THE TRANFORMATION
    C                                    FROM A COORDINATE SYSTEM CENTERED
    C                                    ON MOLECULE-A TO A COORDINATE
    C                                    SYSTEM CENTERED ON MOLECULE-B.
    C                                    MOLECULE-A HAS BEEN ROTATED BY
    C                                    THE THREE EULER ANGLES (PHI1,THET1,PI)
    C                                    AND MOLECULE-B HAS BEEN ROTATED
    C                                    BY (0,THET2,0). THE EULER ANGLES
    C                                    USED ARE DEFINED IN M. E. ROSE,
    C                                    ELEMENTARY THEORY OF ANGULAR
    C                                    MOMENTUM, JOHN WILEY AND SONS,
    C                                    1957.
    C
    C
70          CC=-CPHI1*CTHET1
70          CS= CPHI1*STHET1
70          SC=-SPHI1*CTHET1
70          SS= SPHI1*STHET1
70          A1=CTHET2*CC-STHET2*STHET1
70          B1=CTHET2*SPHI1
70          C1=CTHET2*CS-STHET2*CTHET1
70          D1=R*STHET2
70          A3=STHET2*CC+CTHET2*STHET1
70          B3=STHET2*SPHI1
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      RUN-107     0          QUAD3           76/04/09      20.13.03     PARKERZ2UR     PAGE NO. 3

 70          C3=STHET2*CS+CTHET2*CTHET1                                                LMO        739
 70          D3=-R*CTHET2                                                              LMO        740
      C                                                                                LMO        741
      C                                                                                LMO        742
      C                              CALCULATE THE PART OF THE COULOMBIC               LMO        743
      C                              ENERGY WHICH IS CONSTANT RELATIVE TO              LMO        744
      C                              THIS NUMERICAL INTEGRATION.                       LMO        745
      C                                                                                LMO        746
      C                                                                                LMO        747
 70          CONST=0.0                                                                 LMO        748
131          DO 20 IA=1,NNUCA                                                          LMO        749
133          FA=ZNUCA(IA)/FLOAT(NELECA)                                                LMO        750
133          ZP=ZPOSA(IA)                                                              LMO        751
140          DO 10 IB=1,NCENB                                                          LMO        752
142          XBETA=ZP*C1+D1                                                            LMO        753
142          YBETA=ZP*SS                                                               LMO        754
142          ZBETA=ZP*C3+D3-ZPOSB(IB)                                                  LMO        755
153          RPOS(IB)=SQRT(XBETA*XBETA+YBETA*YBETA+ZBETA*ZBETA)                        LMO        756
164       10 COSTP(IB)=ZBETA/RPOS(IB)                                                  LMO        757
171          CALL PFUNC(RPOS,COSTP,ZNUCB,POTL,NNUCB)                                   LMO        758
201       20 CONST=CONST-FA*POTL                                                       LMO        759
      C                                                                                LMO        760
      C                                                                                LMO        761
206          CONST2=0.0                                                                LMO        762
207          DO 40 IA=1,NNUCA                                                          LMO        763
210          FA=ZNUCA(IA)/FLOAT(NELECA)                                                LMO        764
210          ZP=ZPOSA(IA)                                                              LMO        765
215          DO 30 IB=1,NCENB                                                          LMO        766
217          XBETA=ZP*(-CC*STHET2-STHET1*CTHET2)-R*STHET1                              LMO        767
217          YBETA=-ZP*SPHI1*STHET2                                                    LMO        768
217          ZBETA=ZP*(CS*STHET2+CTHET1*CTHET2)+R*CTHET1-ZPOSB(IB)                     LMO        769
241          RPOS(IB)=SQRT(XBETA*XBETA+YBETA*YBETA+ZBETA*ZBETA)                        LMO        770
252       30 COSTP(IB)=ZBETA/RPOS(IB)                                                  LMO        771
257          CALL PFUNC(RPOS,COSTP,ZNUCB,POTL,NNUCB)                                   LMO        772
267       40 CONST2=CONST2-FB*POTL                                                     LMO        773
      C                                                                                LMO        774
      C                                                                                LMO        775
      C                              INITILIZATIONS.                                   LMO        776
      C                                                                                LMO        777
      C                                                                                LMO        778
276          EXCH=0.0                                                                  LMO        779
276          EKIN=0.0                                                                  LMO        780
276          ECORR=0.0                                                                 LMO        781
276          ECOUL=0.0                                                                 LMO        782
276          DENA=0.0                                                                  LMO        783
276          DENB=0.0                                                                  LMO        784
276          A=R/2.0+B                                                                 LMO        785
276          OBSQ=1.0/(B*B)                                                            LMO        786
276          OASQ=1.0/(A*A)                                                            LMO        787
276          RHALF=R/2.0                                                               LMO        788
312          RMAX=SQRT(R*R/4.0+B*B)                                                    LMO        789
320          NPI=NPA                                                                   LMO        790
320          SWP=WP(1)                                                                 LMO        791
323          IF(ABS(CTHET1).EQ.1.0.AND.ABS(CTHET2).EQ.1.0)GO TO 50                     LMO        792
340          GO TO 60                                                                  LMO        793
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      RUN-107     0          QUAD3            76/04/09     20.13.03     PARKERZ2UR   PAGE NO. 4
340         50 NPI=1                                                               LMO          794
340            WP(1)=TWOPI                                                         LMO          795
343         60 CONTINUE                                                            LMO          796
       C                                                                           LMO          797
       C                                                                           LMO          798
       C                           RADIAL INTEGRATION LOOP.                        LMO          799
       C                                                                           LMO          800
       C                                                                           LMO          801
343            DO 230 NR=1,NRA                                                     LMO          802
345            RA=RADA(NR)                                                         LMO          803
347            IF(RA.GT.RMAX)GO TO 240                                             LMO          804
353            WEIGHR=WR(NR)                                                       LMO          805
       C                                                                           LMO          806
       C                                                                           LMO          807
       C                           THETA INTEGRATION LOOP.                         LMO          808
       C                                                                           LMO          809
       C                                                                           LMO          810
355            DO 230 NT=1,NTA                                                     LMO          811
363            CUBRHA=FLDENA(NR,NT)                                                LMO          812
363            RAST=RA*SINTA(NT)                                                   LMO          813
363            ZA=RA*COSTA(NT)                                                     LMO          814
363            POTLN=POTENB(NR,NT)                                                 LMO          815
363            RHOA=CUBRHA*CUBRHA*CUBRHA                                           LMO          816
363            WEIGHT=WEIGHR*WT(NT)                                                LMO          817
374            EGRHOA=RHOA*EG(CUBRHA)                                              LMO          818
400            RHOA43=RHOA*CUBRHA                                                  LMO          819
400            RHOA53=RHOA43*CUBRHA                                                LMO          820
401            IF(IDENT.EQ.1)GO TO 70                                              LMO          821
414            CBRHOB=FLDENB(NR,NT)                                                LMO          822
414            RHOBN=CBRHOB*CBRHOB*CBRHOB                                          LMO          823
416            ERHOB=RHOBN*EG(CBRHOB)                                              LMO          824
422            ROB43=RHOBN*CBRHOB                                                  LMO          825
422            ROB53=ROB43*CBRHOB                                                  LMO          826
424            GO TO 80                                                            LMO          827
430         70 CBRHOB=CUBRHA                                                       LMO          828
430            RHOBN=RHOA                                                          LMO          829
430            ERHOB=EGRHOA                                                        LMO          830
430            ROB43=RHOA43                                                        LMO          831
430            ROB53=RHOA53                                                        LMO          832
       C                                                                           LMO          833
      .C                                                                           LMO          834
       C                           PHI INTEGRATION LOOP.                           LMO          835
       C                                                                           LMO          836
       C                                                                           LMO          837
437         80 DO 220 NP=1,NPI                                                     LMO          838
441            WEIGHP=WEIGHT*WP(NP)                                                LMO          839
       C                                                                           LMO          840
       C                                                                           LMO          841
       C                           CALCULATE THE CARTESIAN COORDINATE              LMO          842
       C                           FOR THE INTEGRATION POINT RELATIVE              LMO          843
       C                           TO MOLECULE-A                                   LMO          844
       C                                                                           LMO          845
       C                                                                           LMO          846
441            XA=RAST*COSPA(NP)                                                   LMO          847
441            YA=RAST*SINPA(NP)                                                   LMO          848
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     RUN=107    0         QUAD3          76/04/29    20.13.03    PARKERZ2UR    PAGE NO. 5
441        X=XA*CC+YA*SPHI1+ZA*CS
441        Y=XA*SC-YA*CPHI1+ZA*SS
441        Z=XA*STHET1+ZA*CTHET1-RHALF
465        IF(Z.GT.0.0)GO TO 150
467        YSQ=Y*Y
467        IF(((X*X+YSQ)*OBSQ+Z*Z*OASQ).GT.1.0)GO TO 150
      C                             WITHIN REGION I
      C
      C
      C                             TRANSFORM TO COORDINATES RELATIVE
      C                             TO MOLECULE-B.
      C
      C
477        XB=X*CTHET2+(RHALF-Z)*STHET2
477        ZB=X*STHET2+(Z-RHALF)*CTHET2
510        RB=SQRT(XB*XB+YSQ+ZB*ZB)
515        CTHETB=ZB/RB
517        IF(RB.LT.RBEGN)GO TO 90
      C
      C
      C                             DO A TWO DIMENSIONAL STERLINGS
      C                             INTERPOLATION FOR THE ELECTRON
      C                             DENSITY AND POTENTIAL OF MOLECULE-B
      C                             TYPE INTERPOLATION FOR THE ELECTRON
      C                             DENSITY OF MOLECULE-B
      C
      C
526        MR=(RB-RBEGN)*ODR+2.5
526        MT=(CTHETB+DELTAT+1.0)*ODT+0.5
526        MRP1=MR+1
526        MRM1=MR-1
526        RB=(RB-RADB(MR))*ODR
526        CTHETB=(CTHETB-COSTB(MT))*ODT
526        MTP1=MT+1
526        MTM1=MT-1
526        TF00=EDENB(MR,MT)*2.0
526        TP00=POTNB(MR,MT)*2.0
526        F10=EDENB(MRP1,MT)
526        P10=POTNB(MRP1,MT)
526        FM10=EDENB(MRM1,MT)
526        PM10=POTNB(MRM1,MT)
601        IF(MTP1.GT.NTB)MTP1=NTB
604        IF(MTM1.LT.1)MTM1=1
615        F01=EDENB(MR,MTP1)
615        P01=POTNB(MR,MTP1)
615        F0M1=EDENB(MR,MTM1)
615        P0M1=POTNB(MR,MTM1)
615        CUBRHB=0.5*(TF00+RB*(F10-FM10+RB*(F10+FM10-TF00))
          1          +CTHETB*(F01-F0M1+CTHETB*(F01+F0M1-TF00)))
615        POTL=0.5*(TP00+RB*(P10-PM10+RB*(P10+PM10-TP00))
          1          +CTHETB*(P01-P0M1+CTHETB*(P01+P0M1-TP00)))
615        RHOB=CUBRHB*CUBRHB*CUBRHB
664        GO TO 140
      C
      C
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      RUN-107     0          QUADS            76/04/09     20.13.03    PARKERZ2UR   PAGE NO. 6

          C                            DO A LINEAR INTERPOLATION                      LMO        904
          C                            ON THE COSINE OF THETA AND AN                  LMO        905
          C                            EXPONENTIAL INTERPOLATION ON R.                LMO        906
          C                                                                           LMO        907
          C                                                                           LMO        908
   670         90 DO 100 MNR=1,NRAM1                                                  LMO        909
   672            MR=NRA-MNR                                                          LMO        910
   673        100 IF(RADA(MR).LT.RB)GO TO 110                                         LMO        911
   702        110 DO 120 MNT=1,NTAM1                                                  LMO        912
   704            MT=NTA-MNT                                                          LMO        913
   705        120 IF(COSTA(MT).LT.CTHETB)GO TO 130                                    LMO        914
   723        130 MRP1=MR+1                                                           LMO        915
   723            MTP1=MT+1                                                           LMO        916
   723            ZETMT=(COSTA(MT)-CTHETB)/(COSTA(MTP1)-COSTA(MT))                    LMO        917
   723            ZETMR=(RADA(MR)-RB)/(RADA(MRP1)-RADA(MR))                           LMO        918
   723            RHRMT=ELDENB(MR,MT)+ZETMT*(ELDENB(MR,MT)-ELDENB(MR,MTP1))           LMO        919
   723            PORMT=POTENB(MR,MT)+ZETMT*(POTENB(MR,MT)-POTENB(MR,MTP1))           LMO        920
   723            RHRM1T=ELDENB(MRP1,MT)+ZETMT*(ELDENB(MRP1,MT)-ELDENB(MRP1,MTP1))    LMO        921
   723            PORM1T=POTENB(MRP1,MT)+ZETMT*(POTENB(MRP1,MT)-POTENB(MRP1,MTP1))    LMO        922
   774            CUBRHB=RHRMT*EXP(ZETHR*ALOG(RHRMT/RHRM1T))                          LMO        923
  1005            POTL=PORMT+ZETMR*(PORMT-PORM1T)                                     LMO        924
  1005            RHOB=CUBRHB*CUBRHB*CUBRHB                                           LMO        925
          C                                                                           LMO        926
          C                                                                           LMO        927
          C                            END OF INTERPOLATION SCHEME IN                 LMO        928
          C                            REGION I.                                      LMO        929
          C                                                                           LMO        930
          C                                                                           LMO        931
  1015        140 RHOSUM=RHOA+RHOB                                                    LMO        932
  1015            CUBSUM=RHOSUM**.33333333333333                                      LMO        933
  1015            ECOUL=ECOUL+(POTL+CONST)*RHOA*WEIGHP                                LMO        934
  1015            RHOB43=CUBRHB*RHOB                                                  LMO        935
  1015            RHOS43=CUBSUM*RHOSUM                                                LMO        936
  1015            EKIN=(CUBSUM*RHOS43-RHOA53-CUBRHB*RHOB43)*WEIGHP+EKIN               LMO        937
  1041            ECORR=(RHOSUM*EG(CUBSUM)-EGRHOA-RHOB*EG(CUBRHB))*WEIGHP+ECORR       LMO        938
  1052            EXCH=(RHOS43-RHOA43-RHOB43)*WEIGHP+EXCH                             LMO        939
  1063        150 X=XA*CTHET2+ZA*STHET2                                               LMO        940
  1063            Y=YA                                                                LMO        941
  1063            Z=-XA*STHET2+ZA*CTHET2+RHALF                                        LMO        942
  1074            IF(Z.LT.0.0)GO TO 220                                               LMO        943
  1075            IF(((X*X+Y*Y)*OBSQ+Z*Z*OASQ).GT.1.0)GO TO 220                       LMO        944
          C                                                                           LMO        945
          C                                                                           LMO        946
          C                            WITHIN REGION I                                LMO        947
          C                                                                           LMO        948
          C                                                                           LMO        949
  1106            XB=X*CC+Y*SC+(Z+RHALF)*STHET1                                       LMO        950
  1106            YB=X*SPHI1-Y*CPHI1                                                  LMO        951
  1106            ZB=X*CS+Y*SS+(Z+RHALF)*CTHET1                                       LMO        952
  1124            RB=SQRT(XB*XB+YB*YB+ZB*ZB)                                          LMO        953
  1131            CTHETB=ZB/RB                                                        LMO        954
  1133            IF(RB.LT.RBEGN)GO TO 160                                            LMO        955
          C                                                                           LMO        956
          C                                                                           LMO        957
          C                            DO A TWO DIMENSIONAL STERLINGS                 LMO        958
```

```
         C                          INTERPOLATION FOR THE ELECTRON DENSITY
         C                          OF MOLECULE-A.
         C
         C
1142           MR=(RB-RBEGN)*ODR+2.5
1142           MT=(CTHETB+DELTAT+1.0)*ODT+0.5
1142           MRP1=MR+1
1142           MRM1=MR-1
1142           RB=(RB-RADB(MR))*ODR
1142           CTHETB=(CTHETB-COSTB(MT))*ODT
1142           MTP1=MT+1
1142           MTM1=MT-1
1142           TF00=EDENA(MR,MT)*2.0
1142           F10=EDENA(MRP1,MT)
1142           FM10=EDENA(MRM1,MT)
1205           IF(MTP1.GT.NTB)MTP1=NTB
1210           IF(MTM1.LT.1)MTM1=1
1221           F01=EDENA(MR,MTP1)
1221           F0M1=EDENA(MR,MTM1)
1221           CBRHOA=0.5*(TF00+RB*(F10-FM10+RB*(F10+FM10-TF00))
              1       +CTHETB*(F01-F0M1+CTHETB*(F01+F0M1-TF00)))
1221           RHOAN=CBRHOA*CBRHOA*CBRHOA
1244           GO TO 210
         C
         C
         C                          DO A LINEAR INTERPOLATION
         C                          ON THE COSINE OF THETA AND AN
         C                          EXPONENTIAL INTERPOLATION ON R.
         C
         C
1244       160 DO 170 MNR=1,NRAM1
1246           MR=NRA-MNR
1247       170 IF(RADA(MR).LT.RB)GO TO 180
1256       180 DO 190 MNT=1,NTAM1
1260           MT=NTA-MNT
1261       190 IF(COSTA(MT).LT.CTHETB)GO TO 200
1277       200 MRP1=MR+1
1277           MTP1=MT+1
1277           ZETMT=(COSTA(MT)-CTHETB)/(COSTA(MTP1)-COSTA(MT))
1277           ZETMR=(RADA(MR)-RB)/(RADA(MRP1)-RADA(MR))
1277           RHRMT=ELDENA(MR,MT)+ZETMT*(ELDENA(MR,MT)-ELDENA(MR,MTP1))
1277           RHRM1T=ELDENA(MRP1,MT)+ZETMT*(ELDENA(MRP1,MT)-ELDENA(MRP1,MTP1))
1332           CBRHOA=RHRMT*EXP(ZETMR*ALOG(RHRMT/RHRM1T))
1341           RHOAN=CBRHOA*CBRHOA*CBRHOA
         C
         C
         C                          END OF INTERPOLATION SCHEME IN
         C                          REGION II.
         C
         C
1346       210 RHOSUM=RHOAN+RHOBN
1346           CUBSUM=RHOSUM**.33333333333333
1346           ECOUL=ECOUL+(POTLN+CONST2)*RHOAN*WEIGHP
1346           RHO43=CBRHOA*RHOAN
1346           RHOS43=CUBSUM*RHOSUM
```

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      RUN=107     0          QUAD3            76/04/09     20.13.03     PARKERZZUR    PAGE NO. 8

1346        EKIN=(CUBSUM*RHOS43- ROB53-CBRHOA*RHO43)*WEIGHP+EKIN
1370        ECORR=(RHOSUM*EG(CUBSUM)- ERHOB-RHOAN*EG(CBRHOA))*WEIGHP+ECORR
1402        EXCH=(RHOS43-RHO43- ROB43)*WEIGHP+EXCH
1413    220 CONTINUE
1416    230 CONTINUE
      C
      C
      C                              END OF THE NUMERICAL INTEGRATION.
      C
      C
1424    240 EKIN=EKIN*CK
1424        EXCH=CE*SELF*EXCH
1424        WP(1)=SWP
1433        RETURN
1434        END
```

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RUN-107     0                     76/04/09     20.13.03    PARKERZ2UR   PAGE NO. 1

           SUBROUTINE SELFX(N,SELF)                                     LMO       1029
     C                                                                  LMO       1030
     C                                                                  LMO       1031
     C     PURPOSE                                                      LMO       1032
     C     COMPUTES SELF EXCHANGE CORRECTION                            LMO       1033
     C                                                                  LMO       1034
     C     DESCRIPTION OF PARAMETERS                                    LMO       1035
     C        N-NUMBER OF ELECTRONS.                                    LMO       1036
     C        SELF THIS IS THE SELF ENERGY CORRECTION ON RETURN.        LMO       1037
     C                                                                  LMO       1038
     C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                LMO       1039
     C        NONE.                                                     LMO       1040
     C                                                                  LMO       1041
     C     METHOD                                                       LMO       1042
     C     BY METHOD OF A.I.M. RAE, CHEM. PHYS. LETT. 18,574 (1973).    LMO       1043
     C     WRITTEN BY SHELDON GREEN                                     LMO       1044
     C                                                                  LMO       1045
     C     STATEMENT FUNCTION DEFINITIONS                               LMO       1046
     C                                                                  LMO       1047
 6         F(X)=((.25E0*X*X-1.125E0)*X+1.0)*X*X*X-XN                    LMO       1048
20         F1(X)=((1.5E0*X*X-4.5E0)*X+3.0)*X*X                          LMO       1049
     C                                                                  LMO       1050
31         ONE3=1.E0/3.E0                                               LMO       1051
31         XN=.25E0/FLOAT(N)                                            LMO       1052
31         XO=XN**ONE3                                                  LMO       1053
40      10 DX=F(XO)/F1(XO)                                              LMO       1054
44         XO=XO-DX                                                     LMO       1055
46         IF(ABS(DX).GT.1.E-8) GO TO 10                                LMO       1056
52         SELF=((-ONE3*XO*XO+2.E0)*XO-8.E0*ONE3)*XO+1.E0               LMO       1057
60         RETURN                                                       LMO       1058
61         END                                                          LMO       1059
```

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     RUN-107    0                      76/04/09     20.13.03     PARKERZZUR    PAGE NO. 1
            SUBROUTINE SLATE(COSTB ,ELDENB,NNUCB ,NRB   ,NTB   ,RADB  ,          LMO       1060
           1                    SINTB ,ZNUCB ,ZPOSB ,IREAD )                     LMO       1061
        C                                                                        LMC       1062
        C                                                                        LMO       1063
  22        DIMENSION COSTB(1)        ,ELDENB(NRB,NTB),RADB(1)         ,         LMO       1064
           1          SINTB(1)        ,ZNUCB(1)       ,ZPOSB(1)                  LMO       1065
        C                                                                        LMO       1066
        C                                                                        LMO       1067
  22        COMMON /BASE/CB(5,35),LB(5,35),NB(5,35),NBFB(5),NCENB,ZETB(5,35)     LMO       1068
        C                                                                        LMO       1069
        C                                                                        LMO       1070
        C   PURPOSE                                                              LMO       1071
        C      CALCULATES THE CUBE ROOT OF THE ELECTRON DENSITY                  LMO       1072
        C   DESCRIPTION OF PARAMETERS                                            LMO       1073
        C      COSTB-COSINE OF THE THETA ANGLES                                  LMO       1074
        C      ELDENB-CUBE ROOT OF THE ELECTRON DENSITY FOR MOLECULE-B           LMO       1075
        C      NNUCB-NUMBER OF NUCLEI                                            LMO       1076
        C      NRB-NUMBER OF RADIAL DISTANCES                                    LMO       1077
        C      NTB-NUMBER OF THETA ANGLES                                        LMO       1078
        C      RADB-RADIAL DISTANCES                                             LMO       1079
        C      SINTB-SINE OF THE THETA ANGLES                                    LMO       1080
        C      ZNUCB-NUCLEAR CHARGES                                             LMO       1081
        C      ZPOSB-NUCLEAR POSITIONS                                           LMO       1082
        C      IREAD=0  IF IT IS NOT NECESSARY TO READ IN NEW DATA               LMO       1083
        C      SUBROUTINE USED                                                   LMO       1084
        C      NONE                                                              LMO       1085
        C   PARAMETERS TO BE READ IN IF IREAD IS NOT EQUAL TO 0                  LMC       1086
        C   CARD1                                                                LMO       1087
        C      TITLE (COLUMN 1 CONTAINS A 1 FOLLOWED BY THE TITLE)               LMO       1088
        C   CARD 2                                                               LMO       1089
        C      NUMBER OF NUCLEI AND THE NUMBER OF BASIS SET CENTERS (I5)         LMO       1090
        C   CARD 3                                                               LMO       1091
        C      NUCLEAR CHARGES (F10.5)                                           LMO       1092
        C   CARD 4                                                               LMO       1093
        C      CENTERS FOR THE BASIS SET WITH THE FIRST PART OF THE ARRAY        LMO       1094
        C      HAVING THE CENTERS AT THE NUCLEI, (F10.5)                         LMO       1095
        C   CARD 5                                                               LMO       1096
        C      NUMBER OF BASIS FUNCTIONS FOR EACH CENTER (I5)                    LMO       1097
        C   CARD 6----                                                           LMO       1098
        C      PRINCIPAL QUANTUM NUMBER,SUBSIDARY QUANTUM NUMBER,                LMO       1099
        C      RADIAL EXPONENT, AND THE COEFFICIENT (2I5,2F10.5)                 LMO       1100
        C                                                                        LMO       1101
        C                                                                        LMO       1102
  22        IF(IREAD.EQ.0)GO TO 20                                               LMO       1103
        C                                                                        LMO       1104
        C                                                                        LMO       1105
  23        READ(5,60)                                                           LMO       1106
  27        READ(5,80)NNUCB,NCENB                                                LMO       1107
  42        READ(5,90)(ZNUCB(IB),IB=1,NNUCB)                                     LMO       1108
  57        READ(5,90)(ZPOSB(IB),IB=1,NCENB)                                     LMC       1109
  71        READ(5,80)(NBFB(IB),IB=1,NCENB)                                      LMO       1110
        C                                                                        LMC       1111
        C                                                                        LMO       1112
 103        WRITE(6,60)                                                          LMO       1113
 112        WRITE(6,80)(NBFB(IB),IB=1,NCENB)                                     LMC       1114
```

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      RUN-107     0          SLATE           76/04/09      20.13.03     PARKERZ2UR    PAGE NO. 2
          C                                                                    LMO        1115
          C                                                                    LMO        1116
124             ICOUNT=0                                                       LMO        1117
125             DO 10 IB=1,NCENB                                               LMO        1118
132             ICOUNT=ICOUNT+3                                                LMO        1119
132             NBF=NBFB(IB)                                                   LMO        1120
136             WRITE(6,150)NBF,ZPOSB(IB),ZNUCB(IB)                            LMO        1121
151             WRITE(6,140)                                                   LMO        1122
160             DO 10 K=1,NBF                                                  LMO        1123
165             ICOUNT=ICOUNT+1                                                LMO        1124
166             IF(ICOUNT.GT.50)WRITE(6,70)                                    LMO        1125
200             IF(ICOUNT.GT.50)ICOUNT=1                                       LMO        1126
204             READ(5,50)NB(IB,K),LB(IB,K),ZETB(IB,K),CB(IB,K)                LMO        1127
232          10 WRITE(6,50)NB(IB,K),LB(IB,K),ZETB(IB,K),CB(IB,K)               LMO        1128
          C                                                                    LMO        1129
          C                                                                    LMO        1130
          C                           TABULATE THE ELECTRON DENSITY            LMO        1131
          C                           FOR MOLECULE-B.                          LMO        1132
          C                                                                    LMO        1133
          C                                                                    LMO        1134
264          20 DO 40 NR=1,NRB                                                 LMO        1135
266             DO 40 NT=1,NTB                                                 LMO        1136
271             XC=RADB(NR)*SINTB(NT)                                          LMO        1137
271             ZC=RADB(NR)*COSTB(NT)                                          LMO        1138
271             XSQ=XC*XC                                                      LMO        1139
271             DENB=0.0                                                       LMO        1140
277             DO 30 IB=1,NCENB                                               LMO        1141
300             NBF=NBFB(IB)                                                   LMO        1142
302             DO 30 K=1,NBF                                                  LMO        1143
304             Z=ZC-ZPOSB(IB)                                                 LMO        1144
307             RB=SQRT(XSQ+Z*Z)                                               LMO        1145
314             CTHETB=Z/RB                                                    LMO        1146
314             FF=1.0                                                         LMO        1147
316             IF(NB(IB,K).GT.1)FF=RB**(NB(IB,K)-1)                           LMO        1148
336             IF(LB(IB,K).GT.0)FF=FF*PN(LB(IB,K),CTHETB)                     LMO        1149
354          30 DENB=DENB+FF*EXP(-ZETB(IB,K)*RB)*CB(IB,K)                      LMO        1150
401          40 ELDENB(NR,NT)=DENB**.33333333333333                            LMO        1151
          C                                                                    LMO        1152
          C                                                                    LMO        1153
414             RETURN                                                         LMO        1154
          C                                                                    LMO        1155
          C                                                                    LMO        1156
             50 FORMAT(2I5,F10.5,E14.7)                                        LMO        1157
             60 FORMAT(40H                                         ,           LMO        1158
               1         40H                                       )           LMO        1159
             70 FORMAT(1H1)                                                    LMO        1160
             80 FORMAT(16I5)                                                   LMO        1161
             90 FORMAT(8F10.5)                                                 LMO        1162
            100 FORMAT(1H ,2I5,2F10.5)                                         LMO        1163
            110 FORMAT(16I5)                                                   LMO        1164
            120 FORMAT(3F10.5)                                                 LMO        1165
            130 FORMAT(F10.5,3I5,F10.5)                                        LMO        1166
            140 FORMAT(1H0,3X,1HN,4X,1HL,4X,4HZETA,7X,5HCOEFF)                 LMO        1167
            150 FORMAT(1H0,I3,16H BASIS FUNCTIONS,15H,Z-COORDINATE =,F10.5,    LMO        1168
               1         17H,NUCLEAR CHARGE =,F5.1)                            MOL1          8
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     RUN-107    0        SLATE          76/04/09    20.13.03    PARKERZ2UR   PAGE NO. 3

     C                                                                       LMO      1170
     C                                                                       LMO      1171
415        END                                                               LMO      1172
```

Listing of SLAFIT and the subroutines that are used only by SLAFIT: DOT, F, LINEQ, LSTSQ, and VECSUM.

```
RUN-107     0                         76/04/09     20.36.32    PARKERZ3PT   PAGE NO. 1
          SUBROUTINE SLAFIT
      C
      C
      C      USES A LINEAR LEAST SQUARES METHOD TO FIT THE ELECTRON DENSITY
      C      DIRECTLY IN A LINEAR COMBINATION OF SLATER BASIS FUNCTIONS.
      C      GIVES THE NECESSARY PUNCHED OUTPUT  FOR LMOLMO.
      C
      C
      C   INPUT DATA
      C   CARD 1
      C      TITLE (A 1 IN COLUMN 1 FOLLWOED BY THE TITLE)
      C   CARD 2
      C      NRE-NUMBER OF EQUIDISTANT RADIAL POINTS
      C      RLAST-LAST RADIAL DISTANCE
      C   CARD 3
      C      NRIS-NUMBER OF RADIAL INTEGRATION SEGMENTS
      C      NTI-NUMBER OF THETA INTEGRATION POINTS
      C      IREL=1 IF A RELATIVE  LEAST SQUARES METHOD IS TO BE USED
      C   CARD 4
      C      NRIJ-NUMBER OF POINTS IN EACH RADIAL SEGMENT
      C   CARD 5
      C      RE-ENDING POINTS FOR THE RADIAL INTEGRATION
      C   CARD 6
      C      NNUC-NUMBER OF NUCLEI
      C      NCEN-NUMBER OF BASIS SET CENTERS
      C   CARD 7
      C      ZPOS-BASIS SET CENTERS NOT ON THE NUCLEI
      C   CARD 8
      C      NBFB-NUMBER OF BASIS SET FUNCTIONS FOR EACH CENTER
      C   CARD 9---
      C      ZETA-ORBITAL EXPONENT
      C      LZ-POWER OF Z
      C      LXSQ-POWER OF X**2+Y**2
      C      LR-POWER OF R
      C
      C
1         DIMENSION WT(96)   ,WR(100) ,NRIJ(20),RE(20)   ,C(50)    ,
         1          R(100)   ,SINT(96),COST(96),ZNUC(50),B(50),A(50,50)
      C
      C
1         COMMON /BLK1/XSQ(4000)
1         COMMON /BLK2/Z(4000)
1         COMMON /BLK3/LZ(50)
1         COMMON /BLK4/LXSQ(50)
1         COMMON /BLK5/LR(50)
1         COMMON /BLK6/ZETA(50)
1         COMMON /BLK7/M,NCEN
1         COMMON /BLK8/RHO(4000)
1         COMMON /BLK9/NPOINT
1         COMMON /BLK10/NBFB(5)
1         COMMON /BLK11/ZPOS(50)
      C
          DATA TOL/1.E-10/
      C
      C
```

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       RUN-107    D          SLAFIT          76/04/09     20.36.32     PARKERZ3PT   PAGE NO. 2
       C                                READ IN BASIS SET                            FIT          57
       C                                                                             FIT          58
       C                                                                             FIT          59
   1         CALL DATE(TODAY)                                                        FIT          60
   3         CALL TIME(TYME)                                                         FIT          61
   5         READ(5,300)                                                             FIT          62
  11         READ(5,230)NRE,RLAST                                                    FIT          63
  21         READ(5,160)NRIS,NTI,IREL                                                FIT          64
  33         READ(5,160)(NRIJ(J),J=1,NRIS)                                           FIT          65
  42         READ(5,170)(RE(J),J=1,NRIS)                                             FIT          66
  51         READ(5,210)NNUC,NCEN                                                    FIT          67
  61         NP1=NNUC+1                                                              FIT          68
  63         IF(NP1.GT.NCEN)GO TO 10                                                 FIT          69
  66         READ(5,170)(ZPOS(J),J=NP1,NCEN)                                         FIT          70
  75      10 READ(5,210)(NBFB(I),I=1,NCEN)                                           FIT          71
 104         M=0                                                                     FIT          72
 105         DO 20 I=1,NCEN                                                          FIT          73
 113      20 M=M+NBFB(I)                                                             FIT          74
 115         MP1=M+1                                                                 FIT          75
 117         WRITE(6,300)                                                            FIT          76
 123         WRITE(6,240)TODAY                                                       FIT          77
 131         WRITE(6,250)TYME                                                        FIT          78
 137         WRITE(6,180)                                                            FIT          79
 143         DO 30 I=1,M                                                             FIT          80
 145         READ(5,200)ZETA(I),LZ(I),LXSQ(I),LR(I)                                  FIT          81
 164      30 WRITE(6,200)ZETA(I),LZ(I),LXSQ(I),LR(I)                                 FIT          82
       C                                                                             FIT          83
       C                                                                             FIT          84
       C                                SET UP THE POINTS AT WHICH THE               FIT          85
       C                                ELECTRON DENSITY WILL BE CALCULATED          FIT          86
       C                                                                             FIT          87
       C                                                                             FIT          88
 207         NRI=0                                                                   FIT          89
 207         R1E=0.0                                                                 FIT          90
 210         DO 40 J=1,NRIS                                                          FIT          91
 213         NRIP1=NRI+1                                                             FIT          92
 213         NRI=NRI+NRIJ(J)                                                         FIT          93
 216         CALL GLEGEN(NRIJ(J),R(NRIP1),WR(NRIP1),R1E,RE(J))                       FIT          94
 222      40 R1E=RE(J)                                                               FIT          95
 226         NR=NRI+1                                                                FIT          96
 226         NRI=NRI+NRE                                                             FIT          97
 226         DELTAR=(RLAST-RE(NRIS))/FLOAT(NRE)                                      FIT          98
 234         DO 50 J=NR,NRI                                                          FIT          99
 245      50 R(J)=RE(NRIS)+FLOAT(J-NR+1)*DELTAR                                      FIT         100
 251         CALL GLEGEN(NTI,COST,WT,-1.0,1.0)                                       FIT         101
 254         DO 60 NT=1,NTI                                                          FIT         102
 256      60 SINT(NT)=SQRT(1.0-COST(NT)*COST(NT))                                    FIT         103
       C                                                                             FIT         104
       C                                                                             FIT         105
       C                                CALCULATE ELECTRON DENSITY OF THE MOLECULE   FIT         106
       C                                                                             FIT         107
       C                                                                             FIT         108
 270         CALL RHOMCL(COST,RHO,NNUC,NRI,NTI,R,SINT,ZNUC,ZPOS,1)                   FIT         109
       C                                                                             FIT         110
       C                                                                             FIT         111
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        RUN-107    0          SLAFIT          76/04/09     20.36.32     PARKERZ3PT     PAGE NO. 3
        C                                CALCULATE XSQ AND Z                           FIT       112
        C                                                                              FIT       113
        C                                                                              FIT       114
302           I=0                                                                      FIT       115
303           DO 70 NT=1,NTI                                                           FIT       116
305           DO 70 NR=1,NRI                                                           FIT       117
317           I=I+1                                                                    FIT       118
317           X=R(NR)*SINT(NT)                                                         FIT       119
317           Z(I)=R(NR)*COST(NT)                                                      FIT       120
317        70 XSQ(I)=X*X                                                               FIT       121
327           N=NRI*NTI                                                                FIT       122
327           ICOUNT=0                                                                 FIT       123
332           DO 80 J=1,NCEN                                                           FIT       124
334           KK=NCEN+1-J                                                              FIT       125
334           NBF=NBFB(KK)                                                             FIT       126
340           DO 80 I=1,NBF                                                            FIT       127
347           K=M-ICOUNT                                                               FIT       128
347           ICOUNT=ICOUNT+1                                                          FIT       129
347        80 ZPOS(K)=ZPOS(KK)                                                         FIT       130
        C                                                                              FIT       131
        C                                                                              FIT       132
356           WRITE(6,300)                                                             FIT       133
362           WRITE(6,240)TODAY                                                        FIT       134
370           WRITE(6,250)TYME                                                         FIT       135
376           WRITE(6,270)NRIS,NRI                                                     FIT       136
406           WRITE(6,260)(R(I),I=1,NRI)                                               FIT       137
415           WRITE(6,280)NTI                                                          FIT       138
423           WRITE(6,260)(COST(I),I=1,NTI)                                            FIT       139
        C                                                                              FIT       140
        C                                                                              FIT       141
        C                                DO A LEAST SQUARES FIT                        FIT       142
        C                                                                              FIT       143
        C                                                                              FIT       144
432           CALL LSTSQ(A,C,M,RHO,N,IREL,DEV,RDEV,TOL,IER)                            FIT       145
        C                                                                              FIT       146
        C                                                                              FIT       147
        C                                WRITE OUT STANDARD DEVIATION AND              FIT       148
        C                                THE RELATIVE DEVIATION                        FIT       149
        C                                                                              FIT       150
        C                                                                              FIT       151
444           WRITE(6,290)DEV,RDEV                                                     FIT       152
        C                                                                              FIT       153
        C                                                                              FIT       154
        C                                OUTPUT BASIS IN TERMS OF LEGENDRE             FIT       155
        C                                POLYNOMIALS                                   FIT       156
        C                                                                              FIT       157
        C                                                                              FIT       158
454           K=1                                                                      FIT       159
455           DO 90 I=1,NCEN                                                           FIT       160
457           IM1=I-1                                                                  FIT       161
460           IF(I.GT.1)K=K+NBFB(IM1)                                                  FIT       162
464        90 ZPOS(I)=ZPOS(K)                                                          FIT       163
471           WRITE(6,300)                                                             FIT       164
474           WRITE(6,240)TODAY                                                        FIT       165
502           WRITE(6,250)TYME                                                         FIT       166
```

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      RUN-107     0          SLAFIT            76/04/09     20.36.32     PARKERZ3PT    PAGE NO. 4
 510          WRITF(7,300)                                                              FIT        167
 514          WRITE(7,160)NNUC,NCEN                                                     FIT        168
 524          WRITE(6,160)NNUC,NCEN                                                     FIT        169
 534          WRITE(7,170)(ZNUC(I),I=1,NNUC)                                            FIT        170
 543          WRITE(6,170)(ZNUC(I),I=1,NNUC)                                            FIT        171
 552          WRITE(7,170)(ZPOS(I),I=1,NCEN)                                            FIT        172
 561          WRITE(6,170)(ZPOS(I),I=1,NCEN)                                            FIT        173
        C                                                                               FIT        174
        C                                                                               FIT        175
 570          WRITE(6,220)                                                              FIT        176
 574          DO 130 I=1,M                                                              FIT        177
 576          IF(LXSQ(I).GT.0)GO TO 100                                                 FIT        178
 601          IF(LZ(I).GT.1)GO TO 110                                                   FIT        179
 604          N=LR(I)+1                                                                 FIT        180
 604          IF(LZ(I).EQ.1)N=N+1                                                       FIT        181
 610          L=LZ(I)                                                                   FIT        182
 610          COEFF=C(I)                                                                FIT        183
 610          ZET=ZETA(I)                                                               FIT        184
 615          WRITE(6,140)N,L,ZET,COEFF                                                 FIT        185
 630          WRITE(7,140)N,L,ZET,COEFF                                                 FIT        186
 644          GO TO 120                                                                 FIT        187
 646      100 N=3                                                                       FIT        188
 646          L=0                                                                       FIT        189
 646          COEFF=2.0*C(I)/3.0                                                        FIT        190
 646          ZET=ZETA(I)                                                               FIT        191
 654          WRITE(6,140)N,L,ZET,COEFF                                                 FIT        192
 670          WRITE(7,140)N,L,ZET,COEFF                                                 FIT        193
 705          N=3                                                                       FIT        194
 705          L=2                                                                       FIT        195
 705          COEFF=-2.0*C(I)/3.0                                                       FIT        196
 705          ZET=ZETA(I)                                                               FIT        197
 714          WRITE(6,140)N,L,ZET,COEFF                                                 FIT        198
 727          WRITE(7,140)N,L,ZET,COEFF                                                 FIT        199
 743          GO TO 120                                                                 FIT        200
 745      110 N=3                                                                       FIT        201
 745          L=0                                                                       FIT        202
 745          COEFF=C(I)/3.0                                                            FIT        203
 745          ZET=ZETA(I)                                                               FIT        204
 753          WRITE(6,140)N,L,ZET,COEFF                                                 FIT        205
 766          WRITE(7,140)N,L,ZET,COEFF                                                 FIT        206
1003          N=3                                                                       FIT        207
1003          L=2                                                                       FIT        208
1003          COEFF=2.0*C(I)/3.0                                                        FIT        209
1003          ZET=ZETA(I)                                                               FIT        210
1012          WRITE(6,140)N,L,ZET,COEFF                                                 FIT        211
1025          WRITE(7,140)N,L,ZET,COEFF                                                 FIT        212
1041      120 CONTINUE                                                                  FIT        213
1041      130 CONTINUE                                                                  FIT        214
          140 FORMAT(2I5,F10.5,E14.7)                                                   FIT        215
          150 FORMAT(F10.5,3I5,F10.5)                                                   FIT        216
1044          RETURN                                                                    FIT        217
          160 FORMAT(16I5)                                                              FIT        218
          170 FORMAT(8F10.5)                                                            FIT        219
          180 FORMAT(14X,8HPOWER OF/4X,4HZETA,6X,1HZ,3X,3HXSQ,3X,1HR)                   FIT        220
          190 FORMAT(F10.5,3I5,F10.5)                                                   FIT        221
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RUN-107     0          SLAFIT           76/04/09     20.36.32     PARKERZ3PT    PAGE NO. 5

      200 FORMAT(F10.5,3I5)                                                      FIT       222
      210 FORMAT(16I5)                                                           FIT       223
      220 FORMAT(1H0,3X,1HN,4X,1HL,4X,4HZFTA,7X,5HCOEFF)                         FIT       224
      230 FORMAT(I5,F10.5)                                                       FIT       225
      240 FORMAT(1H ,60X,5HDATE ,A10)                                            FIT       226
      250 FORMAT(1H ,60X,5HTIME ,A10)                                            FIT       227
      260 FORMAT(5F12.5)                                                         FIT       228
      270 FORMAT(1H0,5HNRIS=,I5,10X,4HNRI=,I5)                                   FIT       229
      280 FORMAT(1H0,4HNTI=,I5)                                                  FIT       230
      290 FORMAT(1H0,19HSTANDARD DEVIATION=,E14.7/                               FIT       231
         1        1H0,28HRELATIVE STANDARD DEVIATION=,E14.7)                     FIT       232
      300 FORMAT(40H                                               ,             FIT       233
         1        40H                                              )             FIT       234
1045          END                                                                FIT       235
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RUN=107    0                    76/04/09     20.36.32    PARKERZ3PT   PAGE NO. 1

            DOUBLE PRECISION FUNCTION DOT(A,B)                               FIT       499
        C  FORMS THE DOT PRODUCT OF VECTORS A AND B                          FIT       500
        C  THE LENGTH OF THE VECTORS IS TRANSMITTED BY THE COMMON STATEMENT  FIT       501
  6         DIMENSION A(1),B(1)                                              FIT       502
  6         COMMON /VECTOR/ LIMIT,FACTOR                                     FIT       503
  6         DOT=0.0D0                                                        FIT       504
  6         ITOP = LIMIT + 1                                                 FIT       505
 12         IF(ITOP.LT.1)ITOP=1                                              FIT       506
 15         DO 10 I=1,ITOP                                                   FIT       507
 22      10 DOT = DOT + A(I)*B(I)                                            FIT       508
 33         RETURN                                                           FIT       509
 35         END                                                              FIT       510
```

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RUN-107    0                        76/04/09    20.36.32    PARKERZ3PT    PAGE NO. 1

          FUNCTION F(I,J)                                                FIT       479
   6      COMMON /BLK1/XSQ(4000)                                         FIT       480
   6      COMMON /BLK2/Z(4000)                                           FIT       481
   6      COMMON /BLK3/LZ(50)                                            FIT       482
   6      COMMON /BLK4/LXSQ(50)                                          FIT       483
   6      COMMON /BLK5/LR(50)                                            FIT       484
   6      COMMON /BLK6/C(50)                                             FIT       485
   6      COMMON /BLK7/M,NNUC                                            FIT       486
   6      COMMON /BLK10/N1(5)                                            FIT       487
   6      COMMON /BLK11/ZN(5)                                            FIT       488
   7      ZC=Z(J)-ZN(I)                                                  FIT       489
   7      XS=XSQ(J)                                                      FIT       490
  13      R=SQRT(ZC*ZC+XS)                                               FIT       491
  16      F=1.0                                                          FIT       492
  20      IF(LZ(I).GT.0)F=ZC**LZ(I)                                      FIT       493
  27      IF(LXSQ(I).GT.0)F=F*XS**LXSQ(I)                                FIT       494
  36      IF(LR(I).GT.0)F=F*R**LR(I)                                     FIT       495
  45      F=F*EXP(-C(I)*R)                                               FIT       496
  53      RETURN                                                         FIT       497
  53      END                                                            FIT       498
```

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RUN-107    0                      76/04/09    20.36.32    PARKERZ3PT   PAGE NO. 1
            SUBROUTINE  LINEQ(R,C,N,M,TOL,IER)                             FIT         236
      C   SOLVES SIMULTANEOUS LINEAR EQUATIONS BY NUMERICALLY STABLE UNITARY   FIT         237
      C    TRIANGULARIZATION.                                              FIT         238
      C   THIS VERSION FOR REAL EQUATIONS                                  FIT         239
      C     C IS THE N BY N COEFFICIENT MATRIX                             FIT         240
      C    R IS THE MATRIX OF RIGHT HAND SIDES, WITH N ROWS AND M COLUMNS.   FIT         241
      C   ON RETURN, R CONTAINS THE SOLUTIONS X,   CX = R                  FIT         242
      C    THE ELEMENTS OF C SHOULD BE SCALED IN EACH ROW SO THAT          FIT         243
      C    THE MAXIMUM ELEMENT IN EACH ROW IS ABOUT UNITY                  FIT         244
      C    EACH ROW OF THE RIGHT HAND SIDES SHOULD BE MULTIPLIED BY THE    FIT         245
      C    THE SAME FACTOR AS THE CORRESPONDING ROW OF THE COEFFICIENTS    FIT         246
      C    TOL IS A TOLERANCE, ELEMENTS LESS THAN TOL IN MAGNITUDE MAY BE  FIT         247
      C   NEGLECTED SOMETIMES.                                             FIT         248
      C   IER IS AN ERROR PARAMETER,  ON RETURN, IF IER=0, NO ERROR,       FIT         249
      C         IF IER = -1, NO RESULT BECAUSE M OR N IS NOT POSITIVE      FIT         250
      C          IF IER = K, WARNING. POSSIBLE LOSS OF SIGNIFICANCE IN THE   FIT         251
      C          K-TH COMPONENTS OF THE SOLUTIONS,  ERRORS LARGER THAN TOL   FIT         252
      C          MAY HAVE BEEN INTRODUCED.                                 FIT         253
 16         DIMENSION C(1), R(1)                                           FIT         254
 16         DOUBLE PRECISION DOT,SSQ,SMAG,DIAG,S,SCALE                     FIT         255
 16         COMMON /VECTOR/LIMIT,FACTOR                                    FIT         256
 16         IF(M.LT.1) GO TO 10                                            FIT         257
 20         IER = 0                                                        FIT         258
      C   SET TOLERANCE FOR POSSIBLE LOSS OF SOME ACCURACY IN RESULTS      FIT         259
      C    THE SINGLE PRECISION ROUNDOFF ERROR FOR THE IBM 360 IS ABOUT 5.E-7   FIT         260
 20         DTOL = 5.E-14/(TOL*FLOAT(N))                                   FIT         261
 20         NSQ = N*N                                                      FIT         262
 20         NM1 = N - 1                                                    FIT         263
 20         NMM1 = N*(M-1)                                                 FIT         264
 20         NP1 = N + 1                                                    FIT         265
 20         NM = N*M                                                       FIT         266
 32         IF(NM1)10,90,20                                                FIT         267
 34       10 IER = -1                                                      FIT         268
 35         RETURN                                                         FIT         269
      C   NELEM POINTS TO THE TOP OF THE COLUMN IN THE COEFFICIENT MATRIX  FIT         270
      C   WHOSE SUPER-DIAGONAL ELEMENTS ARE BEING ELIMINATED BY THIS TRANS-   FIT         271
      C   FORMATION.                                                       FIT         272
 36       20 NELEM = NSQ - NM1                                             FIT         273
 36         NSHIFT = NSQ - N                                               FIT         274
      C   THIS LOOP IS OVER THE COLUMNS OF THE COEFFICIENT MATRIX C        FIT         275
 41         DO 80 I=1,NM1                                                  FIT         276
 43         NSHIFT = NSHIFT - N                                            FIT         277
 43         LIMHI = NELEM + NM1 - I                                        FIT         278
      C   THIS LOOP SEARCHES FOR THE FIRST SIGNIFICANT ELEMENT TO BE REMOVED   FIT         279
 47         DO 30 J=NELEM,LIMHI                                            FIT         280
 50         IF(ABS(C(J)).LE.TOL) GO TO 30                                  FIT         281
      C   THIS IS REACHED FOR THE FIRST SIGNIFICANT ELEMENT TO BE ELIMINATED   FIT         282
 54         NSTART = J                                                     FIT         283
 55         GO TO 40                                                       FIT         284
 56       30 CONTINUE                                                      FIT         285
      C   THIS IS REACHED ONLY IF ALL SUPER-DIAGONAL ELEMENTS IN THIS COLUMN   FIT         286
      C   ARE ALREADY NEGLIGIBLE.                                          FIT         287
 61         GO TO 80                                                       FIT         288
      C   FORM THE NORMALIZATION FOR THE UNITARY TRIANGULARIZATION         FIT         289
 61       40 LIMHI = LIMHI + 1                                             FIT         290
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     RUN-107    0         LINEQ           76/04/09    20.36.32    PARKERZ3PT   PAGE NO. 2
 61           LIMIT = LIMHI - NSTART                                          FIT          291
 64           SSQ = DOT(C(NSTART),C(NSTART))                                  FIT          292
 77           SMAG =DSQRT(SSQ)                                                FIT          293
101           DIAG = C(LIMHI)                                                 FIT          294
       C  FIX A PHASE FOR S, WHICH WILL GUARANTEE NON-VANISHING DENOMINATOR.  FIT          295
110           S =DSIGN(SMAG,DIAG)                                             FIT          296
117           SCALE = -1.0D0/(SSQ+DIAG*S)                                     FIT          297
117           C(LIMHI) = S + DIAG                                             FIT          298
       C  TRANSFORM THE RIGHT HAND SIDES R BY MULTIPLYING ON THE LEFT         FIT          299
       C  BY THE UNITARY MATRIX 1 - 2W WH                                     FIT          300
154        50 NR = NSTART - NELEM + 1                                         FIT          301
154           NLAST = NR + NMM1                                               FIT          302
160           DO 60 J=NR,NLAST,N                                              FIT          303
162           FACTOR = SCALE*DOT(C(NSTART),R(J))                              FIT          304
202        60 CALL VECSUM(R(J),C(NSTART))                                     FIT          305
       C   TRANSFORM THE COEFFICIENT MATRIX                                   FIT          306
217           NLAST = NR + NSHIFT                                             FIT          307
221           DO 70 J=NR,NLAST,N                                              FIT          308
222           FACTOR = SCALE*DOT(C(NSTART),C(J))                              FIT          309
242        70 CALL VECSUM(C(J),C(NSTART))                                     FIT          310
       C  FIX UP DIAGONAL ELEMENT                                             FIT          311
257           C(LIMHI) = -S                                                   FIT          312
       C  FIND NEW POINTER TO ELEMENT AT TOP OF COLUMN                        FIT          313
262        80 NELEM = NELEM - N                                               FIT          314
       C  SOLVE THE TRANSFORMED LINEAR EQUATIONS WITH LOWER TRIANGULAR        FIT          315
       C  COEFFICIENT MATRIX C.                                               FIT          316
266        90 LCOL= NM1                                                       FIT          317
265           NDIAG = 1                                                       FIT          318
266           NBCOL = N                                                       FIT          319
       C   THIS LOOP IS OVER THE ROWS OF COMPONENTS                           FIT          320
272           DO 220 I=1,N                                                    FIT          321
       C  FIND THE LARGEST ELEMENT IN THIS ROW OF THE RIGHT HAND SIDES        FIT          322
273           NLAST = I + NMM1                                                FIT          323
273           RMAX=0.0                                                        FIT          324
275           DO 100 J=I,NLAST,N                                              FIT          325
277           RMAG=ABS(R(J))                                                  FIT          326
301           IF(RMAG.GT.RMAX) RMAX=RMAG                                      FIT          327
305       100 CONTINUE                                                        FIT          328
       C  SET TOLERANCE FOR LOSS OF ACCURACY                                  FIT          329
310           RTOL=DTOL*AMIN1(RMAX,1.0)                                       FIT          330
       C   TEST FOR SINGULAR MATRIX                                           FIT          331
310           TEST = ABS(C(NDIAG))                                            FIT          332
316           IF(TEST.GT.0.0) GO TO 130                                       FIT          333
       C  THIS IS REACHED IF THE COEFFICIENT MATRIX IS SINGULAR.              FIT          334
321       110 WRITE(6,120)                                                    FIT          335
          120 FORMAT(18H SINGULAR MATRIX  )                                   FIT          336
331           DINV = 1.0E+07                                                  FIT          337
331           IFR = I                                                         FIT          338
333           GO TO 160                                                       FIT          339
334       130 IF(TEST.GT.RTOL)GO TO 150                                       FIT          340
340           WRITE(6,140)I                                                   FIT          341
          140 FORMAT(43H WARNING. POSSIBLE LOSS OF SIGNIFICANCE IN  ,I4,      FIT          342
            1   32H-TH COMPONENTS OF THE SOLUTIONS.   )                       FIT          343
351           IER = I                                                         FIT          344
       C  INVERT THE DIAGONAL ELEMENT                                         FIT          345
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      RUN-107     0        LINEQ          76/04/09     20.36.32     PARKERZ3PT    PAGE NO. 3

352      150 DINV = 1.0/C(NDIAG)
       C  FIND THE LAST SIGNIFICANT ELEMENT IN THIS COLUMN OF THE COEFFICIENT
       C  MATRIX C.
355      160 NR = NBCOL
355          NLCOL=LCOL
357          IF(LCOL.LE.0)NLCOL=1
362          DO 170 J=1,NLCOL
364          IF(ABS(C(NR)).LE.TOL) GO TO 170
       C  THIS IS REACHED FOR THE LAST SIGNIFICANT ELEMENT IN THIS COLUMN
370          LIMIT = LCOL - J
372          GO TO 180
372      170 NR = NR - 1
       C  THIS IS REACHED ONLY IF THERE ARE NO SIGNIFICANT SUBDIAGONAL ELEMENTS
376          LIMIT = -1
       C
       C  THIS LOOP IS OVER THE COLUMNS OF THE SOLUTION
377      180 NLAST = I + NMM1
401          DO 210 J=I,NLAST,N
       C  SOLVE FOR A COMPONENT
402          R(J) = R(J)*DINV
       C  ELIMINATE THIS COMPONENT FROM THE REMAINING EQUATIONS.
404          IF(LIMIT)210,190,200
406      190 R(J+1) = R(J+1) - R(J)*C(NDIAG+1)
413          GO TO 210
414      200 FACTOR = -R(J)
416          CALL VECSUM(R(J+1),C(NDIAG+1))
431      210 CONTINUE
430          NDIAG = NDIAG + NP1
434          NBCOL = NBCOL + N
436      220 LCOL = LCOL - 1
       C  SOLUTION NOW COMPLETE
442          RETURN
443          END
```

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RUN-107    0                        76/04/09    20.36.32    PARKERZ3PT   PAGE NO. 1

          SUBROUTINE LSTSQ(A,B,M,Y,N,IREL,DEV,RDEV,TOL,IER)                    FIT        379
      C                                                                        FIT        380
      C                                                                        FIT        381
      C   PURPOSE                                                              FIT        382
      C      A LINEAR LEAST SQUARES SUBROUTINE,                                FIT        383
      C   DESCRIPTION OF PARAMETERS                                            FIT        384
      C      A-MATRIX TO SET UP THE LEAST SQUARES EQUATIONS                    FIT        385
      C      B-VECTOR FOR THE LEAST SQUARES EQUATIONS ON RETURN B              FIT        386
      C        CONTATINS THE LINEAR COEFFICIENTS,                              FIT        387
      C      M-NUMBER OF BASIS FUNCTIONS                                       FIT        388
      C      Y-ARRAY CONTAINING THE FUNCTIONAL VALUES TO BE FIT.               FIT        389
      C      N-NUMBER OF POINTS TO BE FIT.                                     FIT        390
      C      IREL=1 IF THE LEAST SQUARES METHOD WILL BE PREFORMED WITH         FIT        391
      C              RELATIVE WEIGHTING                                        FIT        392
      C      DEV-RESULTANT STANDARD DEVIATION                                  FIT        393
      C      RDEV-RESULTANT RELATIVE STANDARD DEVIATION                        FIT        394
      C      TOL-THE DESIRED ACCURACY WANTED,                                  FIT        395
      C      IER-RESULTANT ERROR PARAMETER FOR A DESCRIPTION SEE LINEQ.        FIT        396
      C   FUNCTION AND SUBROUTINE REQUIRED                                     FIT        397
      C      FUNCTION F(I,J) WHICH CONTAINS THE I-TH FUNCTION AT THE           FIT        398
      C                      J-TH POINT.                                       FIT        399
      C      LINEQ                                                             FIT        400
      C                                                                        FIT        401
      C                                                                        FIT        402
 22       DIMENSION A(M,M),B(1),Y(1)                                           FIT        403
      C                                                                        FIT        404
 22       LOGICAL TEST                                                         FIT        405
      C                                                                        FIT        406
 22       TEST=IREL.EQ.1                                                       FIT        407
      C                                                                        FIT        408
      C                                                                        FIT        409
      C                             INITIALIZE A AND B TO ZEO.                 FIT        410
      C                                                                        FIT        411
      C                                                                        FIT        412
 25       DO 10 I=1,M                                                          FIT        413
 27       B(I)=0.0                                                             FIT        414
 30       DO 10 K=1,M                                                          FIT        415
 37    10 A(K,I)=0.0                                                           FIT        416
      C                                                                        FIT        417
      C                                                                        FIT        418
      C                             FORM THE LEAST SQUARES SYSTEMS OF          FIT        419
      C                             EQUATIONS                                  FIT        420
      C                                                                        FIT        421
      C                                                                        FIT        422
 47       DO 20 J=1,N                                                          FIT        423
 50       YJ=Y(J)                                                              FIT        424
 51       IF(TEST)ODYJ=1.0/YJ                                                  FIT        425
 55       IF(TEST)YJ=1.0                                                       FIT        426
 60       DO 20 I=1,M                                                          FIT        427
 62       FIJ=F(I,J)                                                           FIT        428
 64       IF(TEST)FIJ=FIJ*ODYJ                                                 FIT        429
 73       B(I)=B(I)+FIJ*YJ                                                     FIT        430
 77       DO 20 K=1,I                                                          FIT        431
100       FKJ=F(K,J)                                                           FIT        432
102       IF(TEST)FKJ=FKJ*ODYJ                                                 FIT        433
```

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     RUN-107    0        LSTSQ          76/04/09    20.36.32    PARKERZ3PT   PAGE NO. 2

111          A(K,I)=A(K,I)+FKJ*FIJ                                        FIT       434
117       20 A(I,K)=A(K,I)                                                FIT       435
      C                                                                   FIT       436
      C                                                                   FIT       437
      C                            MAKE THE MAXIMUM OF EACH ROW EQUAL TO  FIT       438
      C                            UNITY IN ABSOLUTE VALUE.               FIT       439
      C                                                                   FIT       440
      C                                                                   FIT       441
133          DO 40 I=1,M                                                  FIT       442
134          AMAX=0.0                                                     FIT       443
135          DO 30 J=1,M                                                  FIT       444
143       30 AMAX=AMAX1(AMAX,ABS(A(I,J)))                                 FIT       445
151          B(I)=B(I)/AMAX                                               FIT       446
157          DO 40 J=1,M                                                  FIT       447
167       40 A(I,J)=A(I,J)/AMAX                                           FIT       448
      C                                                                   FIT       449
      C                                                                   FIT       450
      C                            SOLVE THE LINEAR SYSTEM OF EQUATIONS   FIT       451
      C                                                                   FIT       452
      C                                                                   FIT       453
177          CALL LINEQ(B,A,M,1,TOL,IER)                                  FIT       454
      C                                                                   FIT       455
      C                                                                   FIT       456
      C                            CALCULATE THE STANDARD DEVIATION AND   FIT       457
      C                            THE RELATIVE DEVATION                  FIT       458
      C                                                                   FIT       459
      C                                                                   FIT       460
203          DEV=0.0                                                      FIT       461
203          RDEV=0.0                                                     FIT       462
205          DO 60 J=1,N                                                  FIT       463
212          YJ=Y(J)                                                      FIT       464
212          ODYJSQ=1.0/(YJ*YJ)                                           FIT       465
212          SUM=0.0                                                      FIT       466
216          DO 50 I=1,M                                                  FIT       467
220       50 SUM=SUM+B(I)*F(I,J)                                          FIT       468
233          DIFSQ=(SUM-YJ)**2                                            FIT       469
233          DEV=DEV+DIFSQ                                                FIT       470
237       60 RDEV=RDEV+DIFSQ*ODYJSQ                                       FIT       471
244          ODXN=1.0/FLOAT(N-1)                                          FIT       472
246          DEV=SQRT(DEV*ODXN)                                           FIT       473
252          RDEV=SQRT(RDEV*ODXN)                                         FIT       474
      C                                                                   FIT       475
      C                                                                   FIT       476
260          RETURN                                                       FIT       477
261          END                                                          FIT       478
```

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    RUN-107    0                          76/04/09    20.36.32    PARKERZ3PT    PAGE NO. 1
            SUBROUTINE VECSUM(A,B)                                                FIT        511
       C  ADDS FACTOR*B TO A, WHERE A AND B ARE VECTORS OF LENGTH LIMIT + 1       FIT        512
  6         COMMON /VECTOR/ LIMIT,FACTOR                                          FIT        513
  6         DIMENSION A(1),B(1)                                                   FIT        514
  6         ITOP = LIMIT + 1                                                      FIT        515
  7         IF(ITOP.LT.1)ITOP=1                                                   FIT        516
 12         DO 10 I=1,ITOP                                                        FIT        517
 17      10 A(I) = A(I) + FACTOR*B(I)                                             FIT        518
 22         RETURN                                                                FIT        519
 23         END                                                                   FIT        520
```

Listing of subroutines that are used by both LMOLMO and SLAFIT; GLEGEN, RHOMOL, PLM, and REP.

```
RUN-107    0                         76/04/09    20.13.03    PARKERZ2UR    PAGE NO. 1
             SUBROUTINE GLEGEN(NPT,XPT,WHT,A,B)
        C
        C
        C    PURPOSE
        C       SUPPLIES THE GAUSS LEGENDRE ZEROS AND WEIGHTS
        C
        C    DESCRIPTION OF PARAMETERS
        C       NPT-THE  NUMBER OF POINTS DESIRED
        C       XPT-RESULTANT ARRAY CONTAINING THE GAUSS LEGENDRE ZEROS
        C       WHT-RESULTANT ARRAY CONTAINING THE GAUSS LEGENDRE WEIGHTS
        C       A-LOWER LIMIT OF THE INTEGRATION
        C       B-THE UPPER LIMIT OF THE INTEGRATION
        C
        C    SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
        C       NONE
        C
        C    METHOD
        C       WRITTEN BY SHELDON GREEN MODIFIED BY G. A. PARKER
        C       ALL ZEROS AND WEIGHTS WHERE CALCULATED ON THE IBM 7030
        C       STRETCH USING DOUBLE PRECISION (128 BITS)
        C
        C
   14        DIMENSION XPT(1),WHT(1)
   14        DIMENSION X(1144),W(1144)
   14        DIMENSION X2(1),W2(1)
   14        DIMENSION X3(2),W3(2)
   14        DIMENSION X4(2),W4(2)
   14        DIMENSION X5(3),W5(3)
   14        DIMENSION X6(3),W6(3)
   14        DIMENSION X7(4),W7(4)
   14        DIMENSION X8(4),W8(4)
   14        DIMENSION X9(5),W9(5)
   14        DIMENSION X10(5),W10(5)
   14        DIMENSION X11(6),W11(6)
   14        DIMENSION X12(6),W12(6)
   14        DIMENSION X13(7),W13(7)
   14        DIMENSION X14(7),W14(7)
   14        DIMENSION X15(8),W15(8)
   14        DIMENSION X16(8),W16(8)
   14        DIMENSION X17(9),W17(9)
   14        DIMENSION X18(9),W18(9)
   14        DIMENSION X19(10),W19(10)
   14        DIMENSION X20(10),W20(10)
   14        DIMENSION X21(11),W21(11)
   14        DIMENSION X22(11),W22(11)
   14        DIMENSION X23(12),W23(12)
   14        DIMENSION X24(12),W24(12)
   14        DIMENSION X25(13),W25(13)
   14        DIMENSION X26(13),W26(13)
   14        DIMENSION X27(14),W27(14)
   14        DIMENSION X28(14),W28(14)
   14        DIMENSION X29(15),W29(15)
   14        DIMENSION X30(15),W30(15)
   14        DIMENSION X31(16),W31(16)
   14        DIMENSION X32(16),W32(16)
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    RUN-107    C          GLEGEN            76/04/09      20.13.03    PARKERZ2UR   PAGE NO. 2

14          DIMENSION X33(17),W33(17)                                                 MOL         66
14          DIMENSION X34(17),W34(17)                                                 MOL         67
14          DIMENSION X35(18),W35(18)                                                 MOL         68
14          DIMENSION X36(18),W36(18)                                                 MOL         69
14          DIMENSION X37(19),W37(19)                                                 MOL         70
14          DIMENSION X38(19),W38(19)                                                 MOL         71
14          DIMENSION X39(20),W39(20)                                                 MOL         72
14          DIMENSION X40(20),W40(20)                                                 MOL         73
14          DIMENSION X41(21),W41(21)                                                 MOL         74
14          DIMENSION X42(21),W42(21)                                                 MOL         75
14          DIMENSION X43(22),W43(22)                                                 MOL         76
14          DIMENSION X44(22),W44(22)                                                 MOL         77
14          DIMENSION X45(23),W45(23)                                                 MOL         78
14          DIMENSION X46(23),W46(23)                                                 MOL         79
14          DIMENSION X47(24),W47(24)                                                 MOL         80
14          DIMENSION X48(24),W48(24)                                                 MOL         81
14          DIMENSION X49(25),W49(25)                                                 MOL         82
14          DIMENSION X50(25),W50(25)                                                 MOL         83
14          DIMENSION X51(26),W51(26)                                                 MOL         84
14          DIMENSION X52(26),W52(26)                                                 MOL         85
14          DIMENSION X53(27),W53(27)                                                 MOL         86
14          DIMENSION X54(27),W54(27)                                                 MOL         87
14          DIMENSION X55(28),W55(28)                                                 MOL         88
14          DIMENSION X56(28),W56(28)                                                 MOL         89
14          DIMENSION X57(29),W57(29)                                                 MOL         90
14          DIMENSION X58(29),W58(29)                                                 MOL         91
14          DIMENSION X59(30),W59(30)                                                 MOL         92
14          DIMENSION X60(30),W60(30)                                                 MOL         93
14          DIMENSION X61(31),W61(31)                                                 MOL         94
14          DIMENSION X62(31),W62(31)                                                 MOL         95
14          DIMENSION X63(32),W63(32)                                                 MOL         96
14          DIMENSION X64(32),W64(32)                                                 MOL         97
14          DIMENSION X80(40),W80(40)                                                 MOL         98
14          DIMENSION X96(48),W96(48)                                                 MOL         99
      C                                                                               MOL        100
      C                                                                               MOL        101
14          EQUIVALENCE(X2(1),X(  1)),(W2(1),W(  1))                                  MOL        102
14          EQUIVALENCE(X3(1),X(  2)),(W3(1),W(  2))                                  MOL        103
14          EQUIVALENCE(X4(1),X(  4)),(W4(1),W(  4))                                  MOL        104
14          EQUIVALENCE(X5(1),X(  6)),(W5(1),W(  6))                                  MOL        105
14          EQUIVALENCE(X6(1),X(  9)),(W6(1),W(  9))                                  MOL        106
14          EQUIVALENCE(X7(1),X( 12)),(W7(1),W( 12))                                  MOL        107
14          EQUIVALENCE(X8(1),X( 16)),(W8(1),W( 16))                                  MOL        108
14          EQUIVALENCE(X9(1),X( 20)),(W9(1),W( 20))                                  MOL        109
14          EQUIVALENCE(X10(1),X( 25)),(W10(1),W( 25))                                MOL        110
14          EQUIVALENCE(X11(1),X( 30)),(W11(1),W( 30))                                MOL        111
14          EQUIVALENCE(X12(1),X( 36)),(W12(1),W( 36))                                MOL        112
14          EQUIVALENCE(X13(1),X( 42)),(W13(1),W( 42))                                MOL        113
14          EQUIVALENCE(X14(1),X( 49)),(W14(1),W( 49))                                MOL        114
14          EQUIVALENCE(X15(1),X( 56)),(W15(1),W( 56))                                MOL        115
14          EQUIVALENCE(X16(1),X( 64)),(W16(1),W( 64))                                MOL        116
14          EQUIVALENCE(X17(1),X( 72)),(W17(1),W( 72))                                MOL        117
14          EQUIVALENCE(X18(1),X( 81)),(W18(1),W( 81))                                MOL        118
14          EQUIVALENCE(X19(1),X( 90)),(W19(1),W( 90))                                MOL        119
14          EQUIVALENCE(X20(1),X(100)),(W20(1),W(100))                                MOL        120
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14        EQUIVALENCE(X21(1),X(110)),(W21(1),W(110))                          MOL      121
14        EQUIVALENCE(X22(1),X(121)),(W22(1),W(121))                          MOL      122
14        EQUIVALENCE(X23(1),X(132)),(W23(1),W(132))                          MOL      123
14        EQUIVALENCE(X24(1),X(144)),(W24(1),W(144))                          MOL      124
14        EQUIVALENCE(X25(1),X(156)),(W25(1),W(156))                          MOL      125
14        EQUIVALENCE(X26(1),X(169)),(W26(1),W(169))                          MOL      126
14        EQUIVALENCE(X27(1),X(182)),(W27(1),W(182))                          MOL      127
14        EQUIVALENCE(X28(1),X(196)),(W28(1),W(196))                          MOL      128
14        EQUIVALENCE(X29(1),X(210)),(W29(1),W(210))                          MOL      129
14        EQUIVALENCE(X30(1),X(225)),(W30(1),W(225))                          MOL      130
14        EQUIVALENCE(X31(1),X(240)),(W31(1),W(240))                          MOL      131
14        EQUIVALENCE(X32(1),X(256)),(W32(1),W(256))                          MOL      132
14        EQUIVALENCE(X33(1),X(272)),(W33(1),W(272))                          MOL      133
14        EQUIVALENCE(X34(1),X(289)),(W34(1),W(289))                          MOL      134
14        EQUIVALENCE(X35(1),X(306)),(W35(1),W(306))                          MOL      135
14        EQUIVALENCE(X36(1),X(342)),(W36(1),W(324))                          MOL      136
14        EQUIVALENCE(X37(1),X(342)),(W37(1),W(342))                          MOL      137
14        EQUIVALENCE(X38(1),X(361)),(W38(1),W(361))                          MOL      138
14        EQUIVALENCE(X39(1),X(380)),(W39(1),W(380))                          MOL      139
14        EQUIVALENCE(X40(1),X(400)),(W40(1),W(400))                          MOL      140
14        EQUIVALENCE(X41(1),X(420)),(W41(1),W(420))                          MOL      141
14        EQUIVALENCE(X42(1),X(441)),(W42(1),W(441))                          MOL      142
14        EQUIVALENCE(X43(1),X(462)),(W43(1),W(462))                          MOL      143
14        EQUIVALENCE(X44(1),Y(484)),(W44(1),W(484))                          MOL      144
14        EQUIVALENCE(X45(1),X(506)),(W45(1),W(506))                          MOL      145
14        EQUIVALENCE(X46(1),X(529)),(W46(1),W(529))                          MOL      146
14        EQUIVALENCE(X47(1),X(552)),(W47(1),W(552))                          MOL      147
14        EQUIVALENCE(X48(1),X(576)),(W48(1),W(576))                          MOL      148
14        EQUIVALENCE(X49(1),X(600)),(W49(1),W(600))                          MOL      149
14        EQUIVALENCE(X50(1),X(625)),(W50(1),W(625))                          MOL      150
14        EQUIVALENCE(X51(1),X(650)),(W51(1),W(650))                          MOL      151
14        EQUIVALENCE(X52(1),X(676)),(W52(1),W(676))                          MOL      152
14        EQUIVALENCE(X53(1),X(702)),(W53(1),W(702))                          MOL      153
14        EQUIVALENCE(X54(1),X(729)),(W54(1),W(729))                          MOL      154
14        EQUIVALENCE(X55(1),X(756)),(W55(1),W(756))                          MOL      155
14        EQUIVALENCE(X56(1),X(784)),(W56(1),W(784))                          MOL      156
14        EQUIVALENCE(X57(1),X(812)),(W57(1),W(812))                          MOL      157
14        EQUIVALENCE(X58(1),X(841)),(W58(1),W(841))                          MOL      158
14        EQUIVALENCE(X59(1),X(870)),(W59(1),W(870))                          MOL      159
14        EQUIVALENCE(X60(1),X(900)),(W60(1),W(900))                          MOL      160
14        EQUIVALENCE(X61(1),X(930)),(W61(1),W(930))                          MOL      161
14        EQUIVALENCE(X62(1),X(961)),(W62(1),W(961))                          MOL      162
14        EQUIVALENCE(Y63(1),X(992)),(W63(1),W(992))                          MOL      163
14        EQUIVALENCE(X64(1),X(1024)),(W64(1),W(1024))                        MOL      164
14        EQUIVALENCE(X80(1),X(1056)),(W80(1),W(1056))                        MOL      165
14        EQUIVALENCE(X96(1),X(1096)),(W96(1),W(1096))                        MOL      166
     C.....                                                                   MOL      167
     C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=2   MOL      168
     C.....                                                                   MOL      169
          DATA  X2( 1)/0.5773502691696E 00/, W2( 1)/0.10000000000000E 01/     MOL      170
     C.....                                                                   MOL      171
     C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=3   MOL      172
     C.....                                                                   MOL      173
           DATA X3(1)/.00000000000000E 00/,W3(1)/.88888888888888E+00/         MOL      174
           DATA X3(2)/.77459666924148E+00/,W3(2)/.55555555555555E+00/         MOL      175
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C.....                                                                  MOL
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=4  MOL
C.....                                                                  MOL
      DATA X4(1)/.33998104358485E-00/,W4(1)/.65214515486254E+00/        MOL
      DATA X4(2)/.86113631159405E+00/,W4(2)/.34785484513745E-00/        MOL
C.....                                                                  MOL
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=5  MOL
C.....                                                                  MOL
      DATA X5(1)/.00000000000000E 00/,W5(1)/.56888888888888E+00/        MOL
      DATA X5(2)/.53846931010568E+00/,W5(2)/.47862867049936E-00/        MOL
      DATA X5(3)/.90617984593866E+00/,W5(3)/.23692688505619E-00/        MOL
C.....                                                                  MOL
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=6  MOL
C.....                                                                  MOL
      DATA X6(1)/.23861918608320E-00/,W6(1)/.46791393457269E-00/        MOL
      DATA X6(2)/.66120938646626E+00/,W6(2)/.36076157304814E-00/        MOL
      DATA X6(3)/.93246951420315E+00/,W6(3)/.17132449237917E-00/        MOL
C.....                                                                  MOL
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=7  MOL
C.....                                                                  MOL
      DATA X7(1)/.00000000000000E 00/,W7(1)/.41795918367347E-00/        MOL
      DATA X7(2)/.40584515137740E-00/,W7(2)/.38183005050512E-00/        MOL
      DATA X7(3)/.74153118559939E+00/,W7(3)/.27970539148928E-00/        MOL
      DATA X7(4)/.94910791234276E+00/,W7(4)/.12948496616887E-00/        MOL
C.....                                                                  MOL
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=8  MOL
C.....                                                                  MOL
      DATA X8(1)/.18343464249565E-00/,W8(1)/.36268378337836E-00/        MOL
      DATA X8(2)/.52553240991633E+00/,W8(2)/.31370664587788E-00/        MOL
      DATA X8(3)/.79666647741362E+00/,W8(3)/.22238103445337E-00/        MOL
      DATA X8(4)/.96028985649753E+00/,W8(4)/.10122853629038E-00/        MOL
C.....                                                                  MOL
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=9  MOL
C.....                                                                  MOL
      DATA X9(1)/.00000000000000E 00/,W9(1)/.33023935500126E-00/        MOL
      DATA X9(2)/.32425342340381E-00/,W9(2)/.31234707704000E-00/        MOL
      DATA X9(3)/.61337143270059E+00/,W9(3)/.26061069640293E-00/        MOL
      DATA X9(4)/.83603110732663E+00/,W9(4)/.18064816069486E-00/        MOL
      DATA X9(5)/.96816023950762E+00/,W9(5)/.81274388361574E-01/        MOL
C.....                                                                  MOL
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=10 MOL
C.....                                                                  MOL
      DATA X10( 1)/.14887433898163E-00/,W10( 1)/.29552422471475E-00/    MOL
      DATA X10( 2)/.43339539412924E-00/,W10( 2)/.26926671930999E-00/    MOL
      DATA X10( 3)/.67940956829902E+00/,W10( 3)/.21908636251598E-00/    MOL
      DATA X10( 4)/.86506336668898E+00/,W10( 4)/.14945134915058E-00/    MOL
      DATA X10( 5)/.97390652851717E+00/,W10( 5)/.66671344308688E-01/    MOL
C.....                                                                  MOL
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=11 MOL
C.....                                                                  MOL
      DATA X11( 1)/.00000000000000E 00/,W11( 1)/.27292508677790E-00/    MOL
      DATA X11( 2)/.26954315595234E-00/,W11( 2)/.26280454451025E-00/    MOL
      DATA X11( 3)/.51909612920681E+00/,W11( 3)/.23319376459199E-00/    MOL
      DATA X11( 4)/.73015200557405E+00/,W11( 4)/.18629021092773E-00/    MOL
      DATA X11( 5)/.88706259976809E+00/,W11( 5)/.12558036946490E-00/    MOL
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      DATA X11( 6)/.97822865814605E+00/,W11( 6)/.55668567116174E-01/     MOL         231
C.....                                                                  MOL         232
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=12 MOL         233
C.....                                                                  MOL         234
      DATA X12( 1)/.12523340851147E-00/,W12( 1)/.24914704581340E-00/     MOL         235
      DATA X12( 2)/.36783149899818E-00/,W12( 2)/.23349253653835E-00/     MOL         236
      DATA X12( 3)/.58731795428661E+00/,W12( 3)/.20316742672307E-00/     MOL         237
      DATA X12( 4)/.76990267419430E+00/,W12( 4)/.16007832854335E-00/     MOL         238
      DATA X12( 5)/.90411725637047E+00/,W12( 5)/.10693932599532E-00/     MOL         239
      DATA X12( 6)/.98156063424672E+00/,W12( 6)/.47175336386512E-01/     MOL         240
C.....                                                                  MOL         241
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=13 MOL         242
C.....                                                                  MOL         243
      DATA X13( 1)/.00000000000000E 00/,W13( 1)/.23255155323087E-00/     MOL         244
      DATA X13( 2)/.23045831595513E-00/,W13( 2)/.22628318026290E-00/     MOL         245
      DATA X13( 3)/.44849275103644E-00/,W13( 3)/.20781604753689E-00/     MOL         246
      DATA X13( 4)/.64234933944034E+00/,W13( 4)/.17814598076194E-00/     MOL         247
      DATA X13( 5)/.80157809073331E+00/,W13( 5)/.13887351021979E-00/     MOL         248
      DATA X13( 6)/.91759839922297E+00/,W13( 6)/.92121499837728E-01/     MOL         249
      DATA X13( 7)/.98418305471858E+00/,W13( 7)/.40484004765316E-01/     MOL         250
C.....                                                                  MOL         251
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=14 MOL         252
C.....                                                                  MOL         253
      DATA X14( 1)/.10805494870734E-00/,W14( 1)/.21526385346316E-00/     MOL         254
      DATA X14( 2)/.31911236892789E-00/,W14( 2)/.20519846372129E-00/     MOL         255
      DATA X14( 3)/.51524863635815E+00/,W14( 3)/.18553839747794E-00/     MOL         256
      DATA X14( 4)/.68729290481168E+00/,W14( 4)/.15720316715819E-00/     MOL         257
      DATA X14( 5)/.82720131506976E+00/,W14( 5)/.12151857068790E-00/     MOL         258
      DATA X14( 6)/.92843488366356E+00/,W14( 6)/.80158087159759E-01/     MOL         259
      DATA X14( 7)/.98628380869681E+00/,W14( 7)/.35119460331752E-01/     MOL         260
C.....                                                                  MOL         261
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=15 MOL         262
C.....                                                                  MOL         263
      DATA X15( 1)/.00000000000000E 00/,W15( 1)/.20257824192556E-00/     MOL         264
      DATA X15( 2)/.20119409399743E-00/,W15( 2)/.19843148532711E-00/     MOL         265
      DATA X15( 3)/.39415134707756E-00/,W15( 3)/.18616100001556E-00/     MOL         266
      DATA X15( 4)/.57097217260854E+00/,W15( 4)/.16626920581699E-00/     MOL         267
      DATA X15( 5)/.72441773136017E+00/,W15( 5)/.13957067792615E-00/     MOL         268
      DATA X15( 6)/.84820658341043E+00/,W15( 6)/.10715922046717E-00/     MOL         269
      DATA X15( 7)/.93727339240070E+00/,W15( 7)/.70366047488108E-01/     MOL         270
      DATA X15( 8)/.98799251802048E+00/,W15( 8)/.30753241996117E-01/     MOL         271
C.....                                                                  MOL         272
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=16 MOL         273
C.....                                                                  MOL         274
      DATA X16( 1)/.95012509837636E-01/,W16( 1)/.18945061045507E-00/     MOL         275
      DATA X16( 2)/.28160355077926E-00/,W16( 2)/.18260341504492E-00/     MOL         276
      DATA X16( 3)/.45801677765723E-00/,W16( 3)/.16915651939500E-00/     MOL         277
      DATA X16( 4)/.61787624440264E+00/,W16( 4)/.14959598881658E-00/     MOL         278
      DATA X16( 5)/.75540440835500E+00/,W16( 5)/.12462897125553E-00/     MOL         279
      DATA X16( 6)/.86563120238783E+00/,W16( 6)/.95158511682492E-01/     MOL         280
      DATA X16( 7)/.94457502307323E+00/,W16( 7)/.62253523938647E-01/     MOL         281
      DATA X16( 8)/.98940093499164E+00/,W16( 8)/.27152459411754E-01/     MOL         282
C.....                                                                  MOL         283
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=17 MOL         284
      DATA X17( 1)/.00000000000000E 00/,W17( 1)/.17944647035621E-00/     MOL         285
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RUN-107    0        CLEGEN          76/04/09     20.13.03     PARKERZ2UR    PAGE NO. 6
      DATA X17( 2)/.17848418149585E-00/,W17( 2)/.17656270536699E-00/    MOL       286
      DATA X17( 3)/.35123176345387E-00/,W17( 3)/.16800410215645E-00/    MOL       287
      DATA X17( 4)/.51269053708647E+00/,W17( 4)/.15404576107681E-00/    MOL       288
      DATA X17( 5)/.65767115921669E+00/,W17( 5)/.13513636846852E-00/    MOL       289
      DATA X17( 6)/.78151400389680E+00/,W17( 6)/.11188384719340E-00/    MOL       290
      DATA X17( 7)/.88023915372698E+00/,W17( 7)/.85036148317179E-01/    MOL       291
      DATA X17( 8)/.95067552176876E+00/,W17( 8)/.55459529373987E-01/    MOL       292
      DATA X17( 9)/.99057547531441E+00/,W17( 9)/.24148302868548E-01/    MOL       293
C.....                                                                  MOL       294
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=18  MOL       295
C.....                                                                  MOL       296
      DATA X18( 1)/.84775013041735E-01/,W18( 1)/.16914238296314E-00/    MOL       297
      DATA X18( 2)/.25188622569150E-00/,W18( 2)/.16427648374583E-00/    MOL       298
      DATA X18( 3)/.41175116146284E-00/,W18( 3)/.15468467512626E-00/    MOL       299
      DATA X18( 4)/.55977083107394E+00/,W18( 4)/.14064291467065E-00/    MOL       300
      DATA X18( 5)/.69168704306035E+00/,W18( 5)/.12255520671148E-00/    MOL       301
      DATA X18( 6)/.80370495897252E+00/,W18( 6)/.10094204410629E-00/    MOL       302
      DATA X18( 7)/.89260246649755E+00/,W18( 7)/.76425730254889E-01/    MOL       303
      DATA X18( 8)/.95582394957140E+00/,W18( 8)/.49714548894970E-01/    MOL       304
      DATA X18( 9)/.99156516842093E+00/,W18( 9)/.21616013526483E-01/    MOL       305
C.....                                                                  MOL       306
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=19  MOL       307
C.....                                                                  MOL       308
      DATA X19( 1)/.00000000000000E 00/,W19( 1)/.16105444984878E-00/    MOL       309
      DATA X19( 2)/.16035864564022E-00/,W19( 2)/.15896884339395E-00/    MOL       310
      DATA X19( 3)/.31656409996363E-00/,W19( 3)/.15276604206586E-00/    MOL       311
      DATA X19( 4)/.46457074137596E-00/,W19( 4)/.14260670217361E-00/    MOL       312
      DATA X19( 5)/.60054530466168E+00/,W19( 5)/.12875396253934E-00/    MOL       313
      DATA X19( 6)/.72096617733523E+00/,W19( 6)/.11156664554733E-00/    MOL       314
      DATA X19( 7)/.82271465653714E+00/,W19( 7)/.91490021622449E-01/    MOL       315
      DATA X19( 8)/.90315590361481E+00/,W19( 8)/.69044542737640E-01/    MOL       316
      DATA X19( 9)/.96020815213483E+00/,W19( 9)/.44814226765699E-01/    MOL       317
      DATA X19(10)/.99240684384358E+00/,W19(10)/.19461788229726E-01/    MOL       318
C.....                                                                  MOL       319
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=20  MOL       320
C.....                                                                  MOL       321
      DATA X20( 1)/.76526521133497E-01/,W20( 1)/.15275338713072E-00/    MOL       322
      DATA X20( 2)/.22778585114164E-00/,W20( 2)/.14917298647260E-00/    MOL       323
      DATA X20( 3)/.37370608871542E-00/,W20( 3)/.14209610931838E-00/    MOL       324
      DATA X20( 4)/.51086700195082E+00/,W20( 4)/.13168863844918E-00/    MOL       325
      DATA X20( 5)/.63605368072651E+00/,W20( 5)/.11819453196152E-00/    MOL       326
      DATA X20( 6)/.74633190646015E+00/,W20( 6)/.10193011981724E-00/    MOL       327
      DATA X20( 7)/.83911697182222E+00/,W20( 7)/.83276741576704E-01/    MOL       328
      DATA X20( 8)/.91223442825132E+00/,W20( 8)/.62672048334108E-01/    MOL       329
      DATA X20( 9)/.96397192727791E+00/,W20( 9)/.40601429800387E-01/    MOL       330
      DATA X20(10)/.99312859918509E+00/,W20(10)/.17614007139152E-01/    MOL       331
C.....                                                                  MOL       332
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=21  MOL       333
C.....                                                                  MOL       334
      DATA X21( 1)/.00000000000000E 00/,X21( 1)/.14608113364969E-00/    MOL       335
      DATA X21( 2)/.14556185416089E-00/,W21( 2)/.14452440398997E-00/    MOL       336
      DATA X21( 3)/.28802131680240E-00/,W21( 3)/.13988739479107E-00/    MOL       337
      DATA X21( 4)/.42434212020744E-00/,W21( 4)/.13226893863334E-00/    MOL       338
      DATA X21( 5)/.55161883588722E+00/,W21( 5)/.12183141605373E-00/    MOL       339
      DATA X21( 6)/.66713880419741E+00/,W21( 6)/.10879729916715E-00/    MOL       340
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RUN-107    0         GLEGEN          76/04/09     20.13.03    PARKER22UR   PAGE NO. 7
      DATA X21( 7)/.76843996347567E+00/,W21( 7)/.93444423456033E-01/    MOL        341
      DATA X21( 8)/.85336336458331E+00/,W21( 8)/.76100113628378E-01/    MOL        342
      DATA X21( 9)/.92200993341504E+00/,W21( 9)/.57134425426857E-01/    MOL        343
      DATA X21(10)/.96722683856630E+00/,W21(10)/.36953789770852E-01/    MOL        344
      DATA X21(11)/.99375217062038E+00/,W21(11)/.16017228257774E-01/    MOL        345
C.....                                                                  MOL        346
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=22  MOL        347
C.....                                                                  MOL        348
      DATA X22( 1)/.69739273319722E-01/,W22( 1)/.13925187285563E-00/    MOL        349
      DATA X22( 2)/.20786042668822E-00/,W22( 2)/.13654149834601E-00/    MOL        350
      DATA X22( 3)/.34193582089208E-00/,W22( 3)/.13117350478706E-00/    MOL        351
      DATA X22( 4)/.46935583798676E-00/,W22( 4)/.12325237681051E-00/    MOL        352
      DATA X22( 5)/.58764040350691E+00/,W22( 5)/.11293229608054E-00/    MOL        353
      DATA X22( 6)/.69448726318668E+00/,W22( 6)/.10041414444288E-00/    MOL        354
      DATA X22( 7)/.78781680597921E+00/,W22( 7)/.85941606217068E-01/    MOL        355
      DATA X22( 8)/.86581257772030E+00/,W22( 8)/.69796468424520E-01/    MOL        356
      DATA X22( 9)/.92695677218717E+00/,W22( 9)/.52293335152683E-01/    MOL        357
      DATA X22(10)/.97006049783542E+00/,W22(10)/.33774901584814E-01/    MOL        358
      DATA X22(11)/.99429458548239E+00/,W22(11)/.14627995298272E-01/    MOL        359
C.....                                                                  MOL        360
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=23  MOL        361
C.....                                                                  MOL        362
      DATA X23( 1)/.00000000000000E 00/,W23( 1)/.13365457218611E-00/    MOL        363
      DATA X23( 2)/.13325682429846E-00/,W23( 2)/.13246203940470E-00/    MOL        364
      DATA X23( 3)/.26413568097034E-00/,W23( 3)/.12890572218808E-00/    MOL        365
      DATA X23( 4)/.39032103803029E-00/,W23( 4)/.12304908430673E-00/    MOL        366
      DATA X23( 5)/.50950147784600E+00/,W23( 5)/.11499664022241E-00/    MOL        367
      DATA X23( 6)/.61960987576364E+00/,W23( 6)/.10489209146454E-00/    MOL        368
      DATA X23( 7)/.71866136313195E+00/,W23( 7)/.92915766060034E-01/    MOL        369
      DATA X23( 8)/.80488840161884E+00/,W23( 8)/.79281411776718E-01/    MOL        370
      DATA X23( 9)/.87675235827044E+00/,W23( 9)/.64232421408525E-01/    MOL        371
      DATA X23(10)/.93297108682601E+00/,W23(10)/.48237671731084E-01/    MOL        372
      DATA X23(11)/.97254247121811E+00/,W23(11)/.30988005856979E-01/    MOL        373
      DATA X23(12)/.99476933499755E+00/,W23(12)/.13411859487142E-01/    MOL        374
C.....                                                                  MOL        375
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=24  MOL        376
C.....                                                                  MOL        377
      DATA X24( 1)/.64056892862605E-01/,W24( 1)/.12793819534675E-00/    MOL        378
      DATA X24( 2)/.19111886747362E-00/,W24( 2)/.12583745634683E-00/    MOL        379
      DATA X24( 3)/.31504267969616E-00/,W24( 3)/.12167047292780E-00/    MOL        380
      DATA X24( 4)/.43379350762604E-00/,W24( 4)/.11550566805373E-00/    MOL        381
      DATA X24( 5)/.54542147138884E+00/,W24( 5)/.10744427011596E-00/    MOL        382
      DATA X24( 6)/.64809365193697E+00/,W24( 6)/.97618652104113E-01/    MOL        383
      DATA X24( 7)/.74012419157855E+00/,W24( 7)/.86190161531953E-01/    MOL        384
      DATA X24( 8)/.82000198597390E+00/,W24( 8)/.73346481411080E-01/    MOL        385
      DATA X24( 9)/.88641552700440E+00/,W24( 9)/.59298584915437E-01/    MOL        386
      DATA X24(10)/.93827455200273E+00/,W24(10)/.44277438817419E-01/    MOL        387
      DATA X24(11)/.97472855597130E+00/,W24(11)/.28531388628933E-01/    MOL        388
      DATA X24(12)/.99518721999702E+00/,W24(12)/.12341229799987E-01/    MOL        389
C.....                                                                  MOL        390
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=25  MOL        391
C.....                                                                  MOL        392
      DATA X25( 1)/.00000000000000E 00/,W25( 1)/.12317605372671E-00/    MOL        393
      DATA X25( 2)/.12286469261071E-00/,W25( 2)/.12222424429903E-00/    MOL        394
      DATA X25( 3)/.24386688372098E-00/,W25( 3)/.11945576353578E-00/    MOL        395
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      DATA X25( 4)/.36117230580939E-00/,W25( 4)/.11485825914571E-00/    MOL      396
      DATA X25( 5)/.47300273144571E-00/,W25( 5)/.10851962447426E-00/    MOL      397
      DATA X25( 6)/.57766293024122E+00/,W25( 6)/.10053594906705E-00/    MOL      398
      DATA X25( 7)/.67356636847346E+00/,W25( 7)/.91028261982962E-01/    MOL      399
      DATA X25( 8)/.75925926303735E+00/,W25( 8)/.80140700335000E-01/    MOL      400
      DATA X25( 9)/.83344262876083E+00/,W25( 9)/.68038333812356E-01/    MOL      401
      DATA X25(10)/.89499199787827E+00/,W25(10)/.54904695975834E-01/    MOL      402
      DATA X25(11)/.94297457122897E+00/,W25(11)/.40939156701306E-01/    MOL      403
      DATA X25(12)/.97666392145951E+00/,W25(12)/.26354986615032E-01/    MOL      404
      DATA X25(13)/.99555696979049E+00/,W25(13)/.11393798501026E-01/    MOL      405
C.....                                                                   MOL      406
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=26  MOL      407
C.....                                                                   MOL      408
      DATA X26( 1)/.59230093429313E-01/,W26( 1)/.11832141527926E-00/    MOL      409
      DATA X26( 2)/.17685882035689E-00/,W26( 2)/.11666044348530E-00/    MOL      410
      DATA X26( 3)/.29200483948596E-00/,W26( 3)/.11336181654632E-00/    MOL      411
      DATA X26( 4)/.40305175512349E-00/,W26( 4)/.10847184052857E-00/    MOL      412
      DATA X26( 5)/.50844071482451E+00/,W26( 5)/.10205916109442E-00/    MOL      413
      DATA X26( 6)/.60669229301761E+00/,W26( 6)/.94213800355913E-01/    MOL      414
      DATA X26( 7)/.69642726041995E+00/,W26( 7)/.85045894313484E-01/    MOL      415
      DATA X26( 8)/.77638594882065E+00/,W26( 8)/.74684149765658E-01/    MOL      416
      DATA X26( 9)/.84544594278857E+00/,W26( 9)/.63274046329574E-01/    MOL      417
      DATA X26(10)/.90263786198430E+00/,W26(10)/.50975825297147E-01/    MOL      418
      DATA X26(11)/.94715906666171E+00/,W26(11)/.37962383294363E-01/    MOL      419
      DATA X26(12)/.97838544595647E+00/,W26(12)/.24417851092632E-01/    MOL      420
      DATA X26(13)/.99588570114561E+00/,W26(13)/.10551372617343E-01/    MOL      421
C.....                                                                   MOL      422
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=27  MOL      423
C.....                                                                   MOL      424
      DATA X27( 1)/.00000000000000E 00/,W27( 1)/.11422086737896E-00/    MOL      425
      DATA X27( 2)/.11397258560953E-00/,W27( 2)/.11347634610896E-00/    MOL      426
      DATA X27( 3)/.22645936543954E-00/,W27( 3)/.11125248835684E-00/    MOL      427
      DATA X27( 4)/.33599390363851E-00/,W27( 4)/.10757828578853E-00/    MOL      428
      DATA X27( 5)/.44114825175002E-00/,W27( 5)/.10250163781774E-00/    MOL      429
      DATA X27( 6)/.54055156457945E+00/,W27( 6)/.96088727370027E-01/    MOL      430
      DATA X27( 7)/.63290797194649E+00/,W27( 7)/.88423158543755E-01/    MOL      431
      DATA X27( 8)/.71701347373942E+00/,W27( 8)/.79604867773057E-01/    MOL      432
      DATA X27( 9)/.79177163907051E+00/,W27( 9)/.69748823766244E-01/    MOL      433
      DATA X27(10)/.85620790801829E+00/,W27(10)/.58983536859833E-01/    MOL      434
      DATA X27(11)/.90948232067749E+00/,W27(11)/.47449412520615E-01/    MOL      435
      DATA X27(12)/.95090055781470E+00/,W27(12)/.35297053757419E-01/    MOL      436
      DATA X27(13)/.97992347596150E+00/,W27(13)/.22686231596180E-01/    MOL      437
      DATA X27(14)/.99617926288898E+00/,W27(14)/.97989960512943E-02/    MOL      438
C.....                                                                   MOL      439
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=28  MOL      440
C.....                                                                   MOL      441
      DATA X28( 1)/.55079289884034E-01/,W28( 1)/.11004701301647E-00/    MOL      442
      DATA X28( 2)/.16456928213338E-00/,W28( 2)/.10871119225829E-00/    MOL      443
      DATA X28( 3)/.27206162763518E-00/,W28( 3)/.10605576592284E-00/    MOL      444
      DATA X28( 4)/.37625151608908E-00/,W28( 4)/.10211296757806E-00/    MOL      445
      DATA X28( 5)/.47587422495511E-00/,W28( 5)/.96930657997928E-01/    MOL      446
      DATA X28( 6)/.56972047181140E+00/,W28( 6)/.90571744393031E-01/    MOL      447
      DATA X28( 7)/.65665109403886E+00/,W28( 7)/.83113417228899E-01/    MOL      448
      DATA X28( 8)/.73561087801363E+00/,W28( 8)/.74646214234568E-01/    MOL      449
      DATA X28( 9)/.80564137091718E+00/,W28( 9)/.65272923966998E-01/    MOL      450
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RUN-107    0        GLEGEN          76/04/09     20.13.03     PARKERZZUR    PAGE NO. 9
      DATA X28(10)/.86589252257439E+00/,W28(10)/.55107345675716E-01/    MOL         451
      DATA X28(11)/.91563302639212E+00/,W28(11)/.44272934759004E-01/    MOL         452
      DATA X28(12)/.95425928062893E+00/,W28(12)/.32901427782304E-01/    MOL         453
      DATA X28(13)/.98130316537087E+00/,W28(13)/.21132112592771E-01/    MOL         454
      DATA X28(14)/.99644249757395E+00/,W28(14)/.91242625930944E-02/    MOL         455
C.....                                                                  MOL         456
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=29 MOL         457
C.....                                                                  MOL         458
      DATA X29( 1)/.00000000000000E 00/,W29( 1)/.10647938171831E-00/    MOL         459
      DATA X29( 2)/.10627823013268E-00/,W29( 2)/.10587615509732E-00/    MOL         460
      DATA X29( 3)/.21135228616600E-00/,W29( 3)/.10407331007773E-00/    MOL         461
      DATA X29( 4)/.31403163786764E-00/,W29( 4)/.10109127375991E-00/    MOL         462
      DATA X29( 5)/.41315288817401E-00/,W29( 5)/.96963834094408E-01/    MOL         463
      DATA X29( 6)/.50759295512423E+00/,W29( 6)/.91737757139257E-01/    MOL         464
      DATA X29( 7)/.59628179713822E+00/,W29( 7)/.85472257366171E-01/    MOL         465
      DATA X29( 8)/.67821453760268E+00/,W29( 8)/.78238327135763E-01/    MOL         466
      DATA X29( 9)/.75246285173447E+00/,W29( 9)/.70117933255050E-01/    MOL         467
      DATA X29(10)/.81818548761525E+00/,W29(10)/.61203090657078E-01/    MOL         468
      DATA X29(11)/.87463780492010E+00/,W29(11)/.51594826902497E-01/    MOL         469
      DATA X29(12)/.92116023295305E+00/,W29(12)/.41402062518682E-01/    MOL         470
      DATA X29(13)/.95728559577806E+00/,W29(13)/.30740492202093E-01/    MOL         471
      DATA X29(14)/.98254550526141E+00/,W29(14)/.19732085056123E-01/    MOL         472
      DATA X29(15)/.99667944226059E+00/,W29(15)/.85169038787463E-02/    MOL         473
C.....                                                                  MOL         474
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=30 MOL         475
C.....                                                                  MOL         476
      DATA X30( 1)/.51471842555317E-01/,W30( 1)/.10285265289356E-00/    MOL         477
      DATA X30( 2)/.15386991360858E-00/,W30( 2)/.10176238974840E-00/    MOL         478
      DATA X30( 3)/.25463692616789E-00/,W30( 3)/.99593420586793E-01/    MOL         479
      DATA X30( 4)/.35270472553088E-00/,W30( 4)/.96368737174643E-01/    MOL         480
      DATA X30( 5)/.44703376953809E-00/,W30( 5)/.92122522237784E-01/    MOL         481
      DATA X30( 6)/.53662414814201E+00/,W30( 6)/.86899787201081E-01/    MOL         482
      DATA X30( 7)/.62052618298924E+00/,W30( 7)/.80755895229419E-01/    MOL         483
      DATA X30( 8)/.69785049479331E+00/,W30( 8)/.73755974737704E-01/    MOL         484
      DATA X30( 9)/.76777743210482E+00/,W30( 9)/.65974229882179E-01/    MOL         485
      DATA X30(10)/.82956576238276E+00/,W30(10)/.57493156217618E-01/    MOL         486
      DATA X30(11)/.88256053579205E+00/,W30(11)/.48402672830593E-01/    MOL         487
      DATA X30(12)/.92620004742927E+00/,W30(12)/.38799192569627E-01/    MOL         488
      DATA X30(13)/.96002186496830E+00/,W30(13)/.28784707883323E-01/    MOL         489
      DATA X30(14)/.98366812327974E+00/,W30(14)/.18466468311091E-01/    MOL         490
      DATA X30(15)/.99689348407465E+00/,W30(15)/.79681924961665E-02/    MOL         491
C.....                                                                  MOL         492
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=31 MOL         493
C.....                                                                  MOL         494
      DATA X31( 1)/.00000000000000E 00/,W31( 1)/.99720544793426E-01/    MOL         495
      DATA X31( 2)/.99555312152341E-01/,W31( 2)/.99225011226670E-01/    MOL         496
      DATA X31( 3)/.19812119933557E-00/,W31( 3)/.97743335386326E-01/    MOL         497
      DATA X31( 4)/.29471806998170E-00/,W31( 4)/.95290242912318E-01/    MOL         498
      DATA X31( 5)/.38838590160823E-00/,W31( 5)/.91892113893639E-01/    MOL         499
      DATA X31( 6)/.47819378204490E-00/,W31( 6)/.87576740608476E-01/    MOL         500
      DATA X31( 7)/.56324916140714E+00/,W31( 7)/.82392991761588E-01/    MOL         501
      DATA X31( 8)/.64278672292426E+00/,W31( 8)/.76390386598775E-01/    MOL         502
      DATA X31( 9)/.71577678458685E+00/,W31( 9)/.69628583235409E-01/    MOL         503
      DATA X31(10)/.78173314841662E+00/,W31(10)/.62174786561028E-01/    MOL         504
      DATA X31(11)/.83992032014626E+00/,W31(11)/.54103082424916E-01/    MOL         505
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      DATA X31(12)/.84976062994827E+00/,W31(12)/.45493707527200E-01/     MOL          506
      DATA X31(13)/.93075699789664E+00/,W31(13)/.36432273912385E-01/     MOL          507
      DATA X31(14)/.96250392509294E+00/,W31(14)/.27009019184979E-01/     MOL          508
      DATA X31(15)/.98468590966515E+00/,W31(15)/.17318620790310E-01/     MOL          509
      DATA X31(16)/.99708748181947E+00/,W31(16)/.74708315792487E-02/     MOL          510
C.....                                                                   MOL          511
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=32  MOL          512
C.....                                                                   MOL          513
      DATA X32( 1)/.48307665687738E-01/,W32( 1)/.96540088514726E-01/     MOL          514
      DATA X32( 2)/.14447196158280E-00/,W32( 2)/.95638720079273E-01/     MOL          515
      DATA X32( 3)/.23928736225214E-00/,W32( 3)/.93844399080803E-01/     MOL          516
      DATA X32( 4)/.33186860228213E-00/,W32( 4)/.91173878695762E-01/     MOL          517
      DATA X32( 5)/.42135127613063E-00/,W32( 5)/.87652093004402E-01/     MOL          518
      DATA X32( 6)/.50689990893223E+00/,W32( 6)/.83311924226945E-01/     MOL          519
      DATA X32( 7)/.58771575724076E+00/,W32( 7)/.78193895787069E-01/     MOL          520
      DATA X32( 8)/.66304426693021E+00/,W32( 8)/.72345794108847E-01/     MOL          521
      DATA X32( 9)/.73218211874028E+00/,W32( 9)/.65822222776361E-01/     MOL          522
      DATA X32(10)/.79448379596794E+00/,W32(10)/.58684093478535E-01/     MOL          523
      DATA X32(11)/.84936761373256E+00/,W32(11)/.50998059262375E-01/     MOL          524
      DATA X32(12)/.89632115576605E+00/,W32(12)/.42835898022226E-01/     MOL          525
      DATA X32(13)/.93490607593774E+00/,W32(13)/.34273862913021E-01/     MOL          526
      DATA X32(14)/.96476225558750E+00/,W32(14)/.25392065309262E-01/     MOL          527
      DATA X32(15)/.98561151154526E+00/,W32(15)/.16274394730905E-01/     MOL          528
      DATA X32(16)/.99726386184947E+00/,W32(16)/.70186100094701E-02/     MOL          529
C.....                                                                   MOL          530
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=33  MOL          531
C.....                                                                   MOL          532
      DATA X33( 1)/.00000000000000E 00/,W33( 1)/.93768446160209E-01/     MOL          533
      DATA X33( 2)/.93631065854733E-01/,W33( 2)/.93356426065595E-01/     MOL          534
      DATA X33( 3)/.18643929882799E-00/,W33( 3)/.92123986643314E-01/     MOL          535
      DATA X33( 4)/.27760909715250E-00/,W33( 4)/.90381958660637E-01/     MOL          536
      DATA X33( 5)/.36633925774807E-00/,W33( 5)/.87248287618843E-01/     MOL          537
      DATA X33( 6)/.45165001727245E-00/,W33( 6)/.83647876067039E-01/     MOL          538
      DATA X33( 7)/.53338990478635E+00/,W33( 7)/.79312364794885E-01/     MOL          539
      DATA X33( 8)/.61024234583637E+00/,W33( 8)/.74279854843953E-01/     MOL          540
      DATA X33( 9)/.68173195996974E+00/,W33( 9)/.68594572818655E-01/     MOL          541
      DATA X33(10)/.74723049644956E+00/,W33(10)/.62306482530317E-01/     MOL          542
      DATA X33(11)/.80616235627416E+00/,W33(11)/.55470846631663E-01/     MOL          543
      DATA X33(12)/.85800965267650E+00/,W33(12)/.48147742818711E-01/     MOL          544
      DATA X33(13)/.90231676774343E+00/,W33(13)/.40401541331669E-01/     MOL          545
      DATA X33(14)/.93869437261116E+00/,W33(14)/.32300358632328E-01/     MOL          546
      DATA X33(15)/.96682290968999E+00/,W33(15)/.23915548101749E-01/     MOL          547
      DATA X33(16)/.98645572623064E+00/,W33(16)/.15321701512935E-01/     MOL          548
      DATA X33(17)/.99742469424645E+00/,W33(17)/.66062278475873E-02/     MOL          549
C.....                                                                   MOL          550
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=34  MOL          551
C.....                                                                   MOL          552
      DATA X34( 1)/.45509821953102E-01/,W34( 1)/.90956740330258E-01/     MOL          553
      DATA X34( 2)/.13615235725918E-00/,W34( 2)/.90203044370639E-01/     MOL          554
      DATA X34( 3)/.22566669161645E-00/,W34( 3)/.88701897835692E-01/     MOL          555
      DATA X34( 4)/.31331108133946E-00/,W34( 4)/.86465739747034E-01/     MOL          556
      DATA X34( 5)/.39835927775865E-00/,W34( 5)/.83513099699844E-01/     MOL          557
      DATA X34( 6)/.48310654519032E-00/,W34( 6)/.79568444339771E-01/     MOL          558
      DATA X34( 7)/.55787550066974E+00/,W34( 7)/.75551974660030E-01/     MOL          559
      DATA X34( 8)/.63102172708052E+00/,W34( 8)/.70629375814254E-01/     MOL          560
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      DATA X34( 9)/.69893911321626E+00/,W34( 9)/.65111521554075E-01/     MOL      561
      DATA X34(10)/.76106487662987E+00/,W34(10)/.59054135827524E-01/     MOL      562
      DATA X34(11)/.81668422790093E+00/,W34(11)/.52527014572677E-01/     MOL      563
      DATA X34(12)/.86593463813056E+00/,W34(12)/.45525611523353E-01/     MOL      564
      DATA X34(13)/.90780967771832E+00/,W34(13)/.38166593796387E-01/     MOL      565
      DATA X34(14)/.94216239740510E+00/,W34(14)/.30491380638446E-01/     MOL      566
      DATA X34(15)/.96872826253334E+00/,W34(15)/.22563721985495E-01/     MOL      567
      DATA X34(16)/.98722761640631E+00/,W34(16)/.14450162748595E-01/     MOL      568
      DATA X34(17)/.99757175379083E+00/,W34(17)/.62291405559087E-02/     MOL      569
C.....                                                                   MOL      570
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=35   MOL      571
C.....                                                                   MOL      572
      DATA X35( 1)/.00000000000000E 00/,W35( 1)/.88486794907104E-01/     MOL      573
      DATA X35( 2)/.88371343275659E-01/,W35( 2)/.88140530430273E-01/     MOL      574
      DATA X35( 3)/.17605106116599E-00/,W35( 3)/.87104446997182E-01/     MOL      575
      DATA X35( 4)/.26235294120929E-00/,W35( 4)/.85386653392097E-01/     MOL      576
      DATA X35( 5)/.34660155443081E-00/,W35( 5)/.83000593728855E-01/     MOL      577
      DATA X35( 6)/.42813754151781E-00/,W35( 6)/.79964942242323E-01/     MOL      578
      DATA X35( 7)/.50632277324148E+00/,W35( 7)/.76303457155441E-01/     MOL      579
      DATA X35( 8)/.58054534474976E+00/,W35( 8)/.72044794772559E-01/     MOL      580
      DATA X35( 9)/.65022436466589E+00/,W35( 9)/.67222285269085E-01/     MOL      581
      DATA X35(10)/.71481450155663E+00/,W35(10)/.61873671966079E-01/     MOL      582
      DATA X35(11)/.77381025228691E+00/,W35(11)/.56040816212369E-01/     MOL      583
      DATA X35(12)/.82674989909222E+00/,W35(12)/.49769370401353E-01/     MOL      584
      DATA X35(13)/.87321912502522E+00/,W35(13)/.43108422326170E-01/     MOL      585
      DATA X35(14)/.91265426135932E+00/,W35(14)/.36110115863463E-01/     MOL      586
      DATA X35(15)/.94534514820782E+00/,W35(15)/.28629260108894E-01/     MOL      587
      DATA X35(16)/.97043761603922E+00/,W35(16)/.21322979911483E-01/     MOL      588
      DATA X35(17)/.98793576444385E+00/,W35(17)/.13650828348361E-01/     MOL      589
      DATA X35(18)/.99770656909960E+00/,W35(18)/.58834334204430E-02/     MOL      590
C.....                                                                   MOL      591
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=36   MOL      592
C.....                                                                   MOL      593
      DATA X36( 1)/.43018198473708E-01/,W36( 1)/.85983275670393E-01/     MOL      594
      DATA X36( 2)/.12873610380938E-00/,W36( 2)/.85346685739337E-01/     MOL      595
      DATA X36( 3)/.21350089231686E-00/,W36( 3)/.84078218979660E-01/     MOL      596
      DATA X36( 4)/.29668499534403E-00/,W36( 4)/.82187266704338E-01/     MOL      597
      DATA X36( 5)/.37767254711969E-00/,W36( 5)/.79687828912070E-01/     MOL      598
      DATA X36( 6)/.45586394443342E-00/,W36( 6)/.76598410645868E-01/     MOL      599
      DATA X36( 7)/.53068028592624E+00/,W36( 7)/.72941885005651E-01/     MOL      600
      DATA X36( 8)/.60156765813598E+00/,W36( 8)/.68745323835735E-01/     MOL      601
      DATA X36( 9)/.66800123658552E+00/,W36( 9)/.64039797355014E-01/     MOL      602
      DATA X36(10)/.72948917159355E+00/,W36(10)/.58860144245324E-01/     MOL      603
      DATA X36(11)/.78557623013220E+00/,W36(11)/.53244713977759E-01/     MOL      604
      DATA X36(12)/.83584716699247E+00/,W36(12)/.47235083490265E-01/     MOL      605
      DATA X36(13)/.87992980089039E+00/,W36(13)/.40875750923644E-01/     MOL      606
      DATA X36(14)/.91749777451566E+00/,W36(14)/.34213810770307E-01/     MOL      607
      DATA X36(15)/.94827298439950E+00/,W36(15)/.27298621498569E-01/     MOL      608
      DATA X36(16)/.97202769104969E+00/,W36(16)/.20181515297735E-01/     MOL      609
      DATA X36(17)/.98858647890221E+00/,W36(17)/.12915947284065E-01/     MOL      610
      DATA X36(18)/.99783046248409E+00/,W36(18)/.55657196642450E-02/     MOL      611
C.....                                                                   MOL      612
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=37   MOL      613
C.....                                                                   MOL      614
      DATA X37( 1)/.00000000000000E 00/,W37( 1)/.83768360993138E-01/     MOL      615
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RUN=107    0         GLEGEN          76/04/09     20.13.03     PARKERZ2UR    PAGE NO. 12
          DATA X37( 2)/.83670408954769E-01/,W37( 2)/.83474573625861E-01/     MOL           616
          DATA X37( 3)/.16675393023985E-00/,W37( 3)/.82595272236435E-01/     MOL           617
          DATA X37( 4)/.24866779279136E-00/,W37( 4)/.81136624580463E-01/     MOL           618
          DATA X37( 5)/.32653742988371E-00/,W37( 5)/.79108661837528E-01/     MOL           619
          DATA X37( 6)/.40670050931832E-00/,W37( 6)/.76526207570528E-01/     MOL           620
          DATA X37( 7)/.48171067780320E-00/,W37( 7)/.73406777248487E-01/     MOL           621
          DATA X37( 8)/.55334239186158E+00/,W37( 8)/.69772451555699E-01/     MOL           622
          DATA X37( 9)/.62109260840892E+00/,W37( 9)/.65648722872750E-01/     MOL           623
          DATA X37(10)/.68448630913096E+00/,W37(10)/.61064516523225E-01/     MOL           624
          DATA X37(11)/.74307883398196E+00/,W37(11)/.56051987998274E-01/     MOL           625
          DATA X37(12)/.79645920050900E+00/,W37(12)/.50646297654824E-01/     MOL           626
          DATA X37(13)/.84425298734055E+00/,W37(13)/.44885364662436E-01/     MOL           627
          DATA X37(14)/.88612496215548E+00/,W37(14)/.38809602501934E-01/     MOL           628
          DATA X37(15)/.92178143741246E+00/,W37(15)/.32461639847521E-01/     MOL           629
          DATA X37(16)/.95097234326209E+00/,W37(16)/.25886036990559E-01/     MOL           630
          DATA X37(17)/.97349303005648E+00/,W37(17)/.19129044489084E-01/     MOL           631
          DATA X37(18)/.98918596321432E+00/,W37(18)/.12238780100307E-01/     MOL           632
          DATA X37(19)/.99794458247791E+00/,W37(19)/.52730572794979E-02/     MOL           633
C.....                                                                       MOL           634
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=38      MOL           635
C.....                                                                       MOL           636
          DATA X38( 1)/.40785147904578E-01/,W38( 1)/.81525029280384E-01/     MOL           637
          DATA X38( 2)/.12208402533787E-00/,W38( 2)/.80982493770596E-01/     MOL           638
          DATA X38( 3)/.20257045389212E-00/,W38( 3)/.79901033243526E-01/     MOL           639
          DATA X38( 4)/.28170680979016E-00/,W38( 4)/.78287844658210E-01/     MOL           640
          DATA X38( 5)/.35897244047943E-00/,W38( 5)/.76153663548444E-01/     MOL           641
          DATA X38( 6)/.43384716943237E-00/,W38( 6)/.73512692584742E-01/     MOL           642
          DATA X38( 7)/.50583471792793E+00/,W38( 7)/.70382507066898E-01/     MOL           643
          DATA X38( 8)/.57445602104760E+00/,W38( 8)/.66783937979139E-01/     MOL           644
          DATA X38( 9)/.63925441582968E+00/,W38( 9)/.62740933392132E-01/     MOL           645
          DATA X38(10)/.69979868037918E+00/,W38(10)/.58280399146996E-01/     MOL           646
          DATA X38(11)/.75568590375397E+00/,W38(11)/.53432019910331E-01/     MOL           647
          DATA X38(12)/.80654416760531E+00/,W38(12)/.48228061860758E-01/     MOL           648
          DATA X38(13)/.85203502193235E+00/,W38(13)/.42703158504674E-01/     MOL           649
          DATA X38(14)/.89185573900462E+00/,W38(14)/.36894081594024E-01/     MOL           650
          DATA X38(15)/.92574133204858E+00/,W38(15)/.30839500545175E-01/     MOL           651
          DATA X38(16)/.95346633093352E+00/,W38(16)/.24579739738232E-01/     MOL           652
          DATA X38(17)/.97484632859015E+00/,W38(17)/.18156577709613E-01/     MOL           653
          DATA X38(18)/.98973945426638E+00/,W38(18)/.11613444716469E-01/     MOL           654
          DATA X38(19)/.99804993053566E+00/,W38(19)/.50028807496393E-02/     MOL           655
C.....                                                                       MOL           656
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=39      MOL           657
C.....                                                                       MOL           658
          DATA X39( 1)/.00000000000000E 00/,W39( 1)/.79527622139443E-01/     MOL           659
          DATA X39( 2)/.79443580460875E-01/,W39( 2)/.79276222568367E-01/     MOL           660
          DATA X39( 3)/.15838533999784E-00/,W39( 3)/.78523613287369E-01/     MOL           661
          DATA X39( 4)/.23632551246183E-00/,W39( 4)/.77274552544680E-01/     MOL           662
          DATA X39( 5)/.31277155924819E-00/,W39( 5)/.75536937322834E-01/     MOL           663
          DATA X39( 6)/.38724016397156E-00/,W39( 6)/.73321753414267E-01/     MOL           664
          DATA X39( 7)/.45926051230913E-00/,W39( 7)/.70643005970607E-01/     MOL           665
          DATA X39( 8)/.52837726866043E+00/,W39( 8)/.67517630966230E-01/     MOL           666
          DATA X39( 9)/.59415345495727E+00/,W39( 9)/.63965381386681E-01/     MOL           667
          DATA X39(10)/.65617321343281E+00/,W39(10)/.60008736086595E-01/     MOL           668
          DATA X39(11)/.71408444589453E+00/,W39(11)/.55672690340915E-01/     MOL           669
          DATA X39(12)/.76740124293106E+00/,W39(12)/.50984665292129E-01/     MOL           670
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      DATA X39(13)/.81590629743014E+00/,W39(13)/.45974321108916E-01/    MOL       671
      DATA X39(14)/.85925293799946E+00/,W39(14)/.40673276847933E-01/    MOL       672
      DATA X39(15)/.89716711929299E+00/,W39(15)/.35115111498131E-01/    MOL       673
      DATA X39(16)/.92940314808673E+00/,W39(16)/.29334955983903E-01/    MOL       674
      DATA X39(17)/.95577521232465E+00/,W39(17)/.23369384832178E-01/    MOL       675
      DATA X39(18)/.97609873933347E+00/,W39(18)/.17256229093725E-01/    MOL       676
      DATA X39(19)/.99025153685468E+00/,W39(19)/.11034788939164E-01/    MOL       677
      DATA X39(20)/.99814738306643E+00/,W39(20)/.47529446916351E-02/    MOL       678
C.....                                                                  MOL       679
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=40  MOL       680
C.....                                                                  MOL       681
      DATA X40( 1)/.38772417506051E-01/,W40( 1)/.77505947978423E-01/    MOL       682
      DATA X40( 2)/.11608407067525E-00/,W40( 2)/.77039818164247E-01/    MOL       683
      DATA X40( 3)/.19269758070137E-00/,W40( 3)/.76110361900625E-01/    MOL       684
      DATA X40( 4)/.26815218500725E-00/,W40( 4)/.74723169057966E-01/    MOL       685
      DATA X40( 5)/.34199409082576E-00/,W40( 5)/.72886582395803E-01/    MOL       686
      DATA X40( 6)/.41377920437160E-00/,W40( 6)/.70611607391285E-01/    MOL       687
      DATA X40( 7)/.48307580168618E-00/,W40( 7)/.67912045815233E-01/    MOL       688
      DATA X40( 8)/.54946712509512E+00/,W40( 8)/.64804013456599E-01/    MOL       689
      DATA X40( 9)/.61255388966798E+00/,W40( 9)/.61306242492928E-01/    MOL       690
      DATA X40(10)/.67195668461418E+00/,W40(10)/.57439769099391E-01/    MOL       691
      DATA X40(11)/.72731825518992E+00/,W40(11)/.53227846983936E-01/    MOL       692
      DATA X40(12)/.77830565142652E+00/,W40(12)/.48695807635071E-01/    MOL       693
      DATA X40(13)/.82461223083331E+00/,W40(13)/.43870908185672E-01/    MOL       694
      DATA X40(14)/.86595950321225E+00/,W40(14)/.38782167974472E-01/    MOL       695
      DATA X40(15)/.90209880696887E+00/,W40(15)/.33460195282548E-01/    MOL       696
      DATA X40(16)/.93281280827867E+00/,W40(16)/.27937006980023E-01/    MOL       697
      DATA X40(17)/.95791681921378E+00/,W40(17)/.22245849194167E-01/    MOL       698
      DATA X40(18)/.97725994998377E+00/,W40(18)/.16421058381908E-01/    MOL       699
      DATA X40(19)/.99072623869946E+00/,W40(19)/.10498284531153E-01/    MOL       700
      DATA X40(20)/.99823770971055E+00/,W40(20)/.45212770985331E-02/    MOL       701
C.....                                                                  MOL       702
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=41  MOL       703
C.....                                                                  MOL       704
      DATA X41( 1)/.00000000000000E 00/,W41( 1)/.75695535647298E-01/    MOL       705
      DATA X41( 2)/.75623258989162E-01/,W41( 2)/.75478747092714E-01/    MOL       706
      DATA X41( 3)/.15081335986399E-00/,W41( 3)/.74829623176220E-01/    MOL       707
      DATA X41( 4)/.22513960563342E-00/,W41( 4)/.73751882027222E-01/    MOL       708
      DATA X41( 5)/.29817627734182E-00/,W41( 5)/.72251696861022E-01/    MOL       709
      DATA X41( 6)/.36950502264048E-00/,W41( 6)/.70337660620816E-01/    MOL       710
      DATA X41( 7)/.43871727705140E-00/,W41( 7)/.68020736760875E-01/    MOL       711
      DATA X41( 8)/.50541659919940E+00/,W41( 8)/.65314196453526E-01/    MOL       712
      DATA X41( 9)/.56922094161021E+00/,W41( 9)/.62233554260965E-01/    MOL       713
      DATA X41(10)/.62976483907219E+00/,W41(10)/.58796420949671E-01/    MOL       714
      DATA X41(11)/.68670150203695E+00/,W41(11)/.55022519242578E-01/    MOL       715
      DATA X41(12)/.73970480306992E+00/,W41(12)/.50933454294617E-01/    MOL       716
      DATA X41(13)/.78847114504740E+00/,W41(13)/.46552648369014E-01/    MOL       717
      DATA X41(14)/.83272120040135E+00/,W41(14)/.41905195195909E-01/    MOL       718
      DATA X41(15)/.87220151169244E+00/,W41(15)/.37017716703507E-01/    MOL       719
      DATA X41(16)/.90668594475309E+00/,W41(16)/.31918211731699E-01/    MOL       720
      DATA X41(17)/.93597698749705E+00/,W41(17)/.26635899207110E-01/    MOL       721
      DATA X41(18)/.95990689173034E+00/,W41(18)/.21201063368779E-01/    MOL       722
      DATA X41(19)/.97833867356108E+00/,W41(19)/.15644938407818E-01/    MOL       723
      DATA X41(20)/.99116710969901E+00/,W41(20)/.99999387739958E-02/    MOL       724
      DATA X41(21)/.99832158857476E+00/,W41(21)/.43061403581648E-02/    MOL       725
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C.....                                                                  MOL        726
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=42  MOL        727
C.....                                                                  MOL        728
      DATA X42( 1)/.36948943165352E-01/,W42( 1)/.73864234232171E-01/   MOL        729
      DATA X42( 2)/.11064502720852E-00/,W42( 2)/.73460813453466E-01/   MOL        730
      DATA X42( 3)/.18373680656485E-00/,W42( 3)/.72656175243802E-01/   MOL        731
      DATA X42( 4)/.25582507934288E-00/,W42( 4)/.71454714265169E-01/   MOL        732
      DATA X42( 5)/.32651612446541E-00/,W42( 5)/.69862992492592E-01/   MOL        733
      DATA X42( 6)/.39542385204297E-00/,W42( 6)/.67889703376521E-01/   MOL        734
      DATA X42( 7)/.46217191207042E-00/,W42( 7)/.65545624364907E-01/   MOL        735
      DATA X42( 8)/.52639574993119E+00/,W42( 8)/.62843558045001E-01/   MOL        736
      DATA X42( 9)/.58774459748511E+00/,W42( 9)/.59798262227586E-01/   MOL        737
      DATA X42(10)/.64588338886925E+00/,W42(10)/.56426369358018E-01/   MOL        738
      DATA X42(11)/.70049459055617E+00/,W42(11)/.52746295699173E-01/   MOL        739
      DATA X42(12)/.75127993568948E+00/,W42(12)/.48778140792802E-01/   MOL        740
      DATA X42(13)/.79796205325548E+00/,W42(13)/.44543577771965E-01/   MOL        741
      DATA X42(14)/.84028598326181E+00/,W42(14)/.40065735180692E-01/   MOL        742
      DATA X42(15)/.87802056981217E+00/,W42(15)/.35369071097592E-01/   MOL        743
      DATA X42(16)/.91095972490412E+00/,W42(16)/.30479240699603E-01/   MOL        744
      DATA X42(17)/.93892355735498E+00/,W42(17)/.25422959526113E-01/   MOL        745
      DATA X42(18)/.96175936533820E+00/,W42(18)/.20227869569052E-01/   MOL        746
      DATA X42(19)/.97934250806374E+00/,W42(19)/.14922443697357E-01/   MOL        747
      DATA X42(20)/.99157728834066E+00/,W42(20)/.95362203017484E-02/   MOL        748
      DATA X42(21)/.99839961899006E+00/,W42(21)/.41059986046490E-02/   MOL        749
C.....                                                                  MOL        750
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=43  MOL        751
C.....                                                                  MOL        752
      DATA X43( 1)/.00000000000000E 00/,W43( 1)/.72215751693798E-01/   MOL        753
      DATA X43( 2)/.72152990674586E-01/,W43( 2)/.72027501971421E-01/   MOL        754
      DATA X43( 3)/.14392980951071E-00/,W43( 3)/.71463734252513E-01/   MOL        755
      DATA X43( 4)/.21495624486052E-00/,W43( 4)/.70527387765084E-01/   MOL        756
      DATA X43( 5)/.28486199803291E-00/,W43( 5)/.69223344193655E-01/   MOL        757
      DATA X43( 6)/.35328261286430E-00/,W43( 6)/.67558402229363E-01/   MOL        758
      DATA X43( 7)/.41986137602927E-00/,W43( 7)/.65541242126322E-01/   MOL        759
      DATA X43( 8)/.48425117678573E-00/,W43( 8)/.63182380449395E-01/   MOL        760
      DATA X43( 9)/.54611631666008E+00/,W43( 9)/.60494115249990E-01/   MOL        761
      DATA X43(10)/.60513425963960E+00/,W43(10)/.57490461956910E-01/   MOL        762
      DATA X43(11)/.66099731375150E+00/,W43(11)/.54187080316881E-01/   MOL        763
      DATA X43(12)/.71341423526896E+00/,W43(12)/.50601192784389E-01/   MOL        764
      DATA X43(13)/.76211174719495E+00/,W43(13)/.46751494754346E-01/   MOL        765
      DATA X43(14)/.80683596413693E+00/,W43(14)/.42658057197981E-01/   MOL        766
      DATA X43(15)/.84735371620931E+00/,W43(15)/.38342222194132E-01/   MOL        767
      DATA X43(16)/.88345376521861E+00/,W43(16)/.33826492086860E-01/   MOL        768
      DATA X43(17)/.91494790720614E+00/,W43(17)/.29134413261498E-01/   MOL        769
      DATA X43(18)/.94167195684763E+00/,W43(18)/.24290456613838E-01/   MOL        770
      DATA X43(19)/.96348661301407E+00/,W43(19)/.19319901423684E-01/   MOL        771
      DATA X43(20)/.98027822098025E+00/,W43(20)/.14248756431576E-01/   MOL        772
      DATA X43(21)/.99195955759324E+00/,W43(21)/.91039966374013E-02/   MOL        773
      DATA X43(22)/.99847233224250E+00/,W43(22)/.39194902538441E-02/   MOL        774
C.....                                                                  MOL        775
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=44  MOL        776
C.....                                                                  MOL        777
      DATA X44( 1)/.35289236964135E-01/,W44( 1)/.70549157789352E-01/   MOL        778
      DATA X44( 2)/.10569190170865E-00/,W44( 2)/.70197685473557E-01/   MOL        779
      DATA X44( 3)/.17556801477552E-00/,W44( 3)/.69496491861572E-01/   MOL        780
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          DATA X44( 4)/,24056945692820E-00/,W44( 4)/,68449070269365E-01/     MOL        781
          DATA X44( 5)/,31235246657278E-00/,W44( 5)/,67067538926293E-01/     MOL        782
          DATA X44( 6)/,37257535201471E-00/,W44( 6)/,65338114879180E-01/     MOL        783
          DATA X44( 7)/,44297017452541E-00/,W44( 7)/,63290797332033E-01/     MOL        784
          DATA X44( 8)/,52505439136620E-00/,W44( 8)/,60920736701561E-01/     MOL        785
          DATA X44( 9)/,56467245318507E+00/,W44( 9)/,58259859877594E-01/     MOL        786
          DATA X44(10)/,62147734590357E+00/,W44(10)/,55302735563727E-01/     MOL        787
          DATA X44(11)/,67516607066612E+00/,W44(11)/,52270096291704E-01/     MOL        788
          DATA X44(12)/,72553105366072E+00/,W44(12)/,48578046448351E-01/     MOL        789
          DATA X44(13)/,77226147924073E+00/,W44(13)/,44843984081969E-01/     MOL        790
          DATA X44(14)/,81514453964513E+00/,W44(14)/,40886512310346E-01/     MOL        791
          DATA X44(15)/,85396659500471E+00/,W44(15)/,36725347813808E-01/     MOL        792
          DATA X44(16)/,88853423828604E+00/,W44(16)/,32381222812069E-01/     MOL        793
          DATA X44(17)/,9186752599034.7E+00/,W44(17)/,27875782821281E-01/     MOL        794
          DATA X44(18)/,94423950911619E+00/,W44(18)/,23231481902019E-01/     MOL        795
          DATA X44(19)/,96509965042247E+00/,W44(19)/,18471481735815E-01/     MOL        796
          DATA X44(20)/,98115183307791E+00/,W44(20)/,13617586755580E-01/     MOL        797
          DATA X44(21)/,99231639213651E+00/,W44(21)/,87004813675247E-02/     MOL        798
          DATA X44(22)/,99856020063677E+00/,W44(22)/,37454048031127E-02/     MOL        799
C.....                                                                       MOL        800
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=45       MOL        801
C.....                                                                       MOL        802
          DATA X45( 1)/,00000000000020E 00/,W45( 1)/,69041824829232E-01/     MOL        803
          DATA X45( 2)/,68985980163143E-01/,W45( 2)/,68877316977660E-01/     MOL        804
          DATA X45( 3)/,13764520598325E-00/,W45( 3)/,68384577378668E-01/     MOL        805
          DATA X45( 4)/,20560748978326E-00/,W45( 4)/,67565954163606E-01/     MOL        806
          DATA X45( 5)/,27266976975237E-00/,W45( 5)/,66425348449840E-01/     MOL        807
          DATA X45( 6)/,33839265425060E-00/,W45( 6)/,64968195750722E-01/     MOL        808
          DATA X45( 7)/,40259294385854E-00/,W45( 7)/,63201440073618E-01/     MOL        809
          DATA X45( 8)/,46469512391963E-00/,W45( 8)/,61133508831065E-01/     MOL        810
          DATA X45( 9)/,52467282046291E+00/,W45( 9)/,58774232718841E-01/     MOL        811
          DATA X45(10)/,58215021256935E+00/,W45(10)/,56134678759785E-01/     MOL        812
          DATA X45(11)/,63685339445322E+00/,W45(11)/,53226016731268E-01/     MOL        813
          DATA X45(12)/,68852163077120E+00/,W45(12)/,50067499237951E-01/     MOL        814
          DATA X45(13)/,73690884694549E+00/,W45(13)/,46668387718372E-01/     MOL        815
          DATA X45(14)/,78178431259390E+00/,W45(14)/,43045680709164E-01/     MOL        816
          DATA X45(15)/,82293422050208E+00/,W45(15)/,39220236729302E-01/     MOL        817
          DATA X45(16)/,86016247596066E+00/,W45(16)/,35206692201609E-01/     MOL        818
          DATA X45(17)/,89329167175324E+00/,W45(17)/,31025374934515E-01/     MOL        819
          DATA X45(18)/,92216393671900E+00/,W45(18)/,26696213967577E-01/     MOL        820
          DATA X45(19)/,94664169099563E+00/,W45(19)/,22239847550578E-01/     MOL        821
          DATA X45(20)/,96660831039689E+00/,W45(20)/,17677535257937E-01/     MOL        822
          DATA X45(21)/,98196871503454E+00/,W45(21)/,13031104991583E-01/     MOL        823
          DATA X45(22)/,99264999844720E+00/,W45(22)/,85231892962181E-02/     MOL        824
          DATA X45(23)/,99860364518193E+00/,W45(23)/,35826631552835E-02/     MOL        825
C.....                                                                       MOL        826
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=46       MOL        827
C.....                                                                       MOL        828
          DATA X46( 1)/,33772190016052E-01/,W46( 1)/,67518685849035E-01/     MOL        829
          DATA X46( 2)/,10116247530558E-00/,W46( 2)/,67210613600677E-01/     MOL        830
          DATA X46( 3)/,16809117946710E-00/,W46( 3)/,66595874763453E-01/     MOL        831
          DATA X46( 4)/,23425292220627E-00/,W46( 4)/,65677274267779E-01/     MOL        832
          DATA X46( 5)/,29934582270167E-00/,W46( 5)/,64459003457137E-01/     MOL        833
          DATA X46( 6)/,36307287702099E-00/,W46( 6)/,62946621064393E-01/     MOL        834
          DATA X46( 7)/,42514331328283E-00/,W46( 7)/,61147027724650E-01/     MOL        835
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      DATA X46( 8)/,.40527391838816E-00/,W46( 8)/,.59068434595545E-01/      MOL      836
      DATA X46( 9)/,.54319033026180E+00/,W46( 9)/,.56720325843990E-01/      MOL      837
      DATA X46(10)/,.59962825971271E+00/,W46(10)/,.54113415385856E-01/      MOL      838
      DATA X46(11)/,.65133450620200E+00/,W46(11)/.51259598007142E-01/       MOL      839
      DATA X46(12)/,.70106951202090E+00/,W46(12)/,.48171695101711E-01/      MOL      840
      DATA X46(13)/,.74760535961506E+00/,W46(13)/,.44864395277317E-01/      MOL      841
      DATA X46(14)/,.79073005707527E+00/,W46(14)/,.41352190109678E-01/      MOL      842
      DATA X46(15)/,.83024633706606E-00/,W46(15)/,.37651305357335E-01/      MOL      843
      DATA X46(16)/,.86597539408685E+00/,W46(16)/.33778627999106E-01/       MOL      844
      DATA X46(17)/,.89775271153394E+00/,W46(17)/,.27751829552202E-01/      MOL      845
      DATA X46(18)/,.92543379580675E+00/,W46(18)/,.25589286397130E-01/      MOL      846
      DATA X46(19)/,.94889230344609E+00/,W46(19)/,.21309998754136E-01/      MOL      847
      DATA X46(20)/,.96802139185399E+00/,W46(20)/,.16933514007836E-01/      MOL      848
      DATA X46(21)/,.98273369804416E+00/,W46(21)/,.12479883770989E-01/      MOL      849
      DATA X46(22)/,.99296234690617E-00/,W46(22)/,.79698982297245E-02/      MOL      850
      DATA X46(23)/,.99866304213381E+00/,W46(23)/,.34303008681070E-02/      MOL      851
C.....                                                                      MOL      852
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=47     MOL      853
C.....                                                                      MOL      854
      DATA X47( 1)/,.00000000000000E 00/,W47( 1)/,.66135129623655E-01/      MOL      855
      DATA X47( 2)/,.66086923916355E-01/,W47( 2)/,.65990533588809E-01/      MOL      856
      DATA X47( 3)/,.13188486655451E-00/,W47( 3)/,.65557377766548E-01/      MOL      857
      DATA X47( 4)/,.19710611027911E-00/,W47( 4)/,.64837556235944E-01/      MOL      858
      DATA X47( 5)/,.26146545921497E-00/,W47( 5)/,.63834216605716E-01/      MOL      859
      DATA X47( 6)/,.32468148633773E-00/,W47( 6)/,.62551746220920E-01/      MOL      860
      DATA X47( 7)/,.38647776408467E-00/,W47( 7)/,.60995753708739E-01/      MOL      861
      DATA X47( 8)/,.44658407310485E-00/,W47( 8)/,.59173040942338E-01/      MOL      862
      DATA X47( 9)/,.50473756386358E+00/,W47( 9)/,.57091580293230E-01/      MOL      863
      DATA X47(10)/,.56068400593466E+00/,W47(10)/,.54760472781529E-01/      MOL      864
      DATA X47(11)/,.61417869995637E+00/,W47(11)/,.52180911780056E-01/      MOL      865
      DATA X47(12)/,.66498774739033E+00/,W47(12)/,.49391137747360E-01/      MOL      866
      DATA X47(13)/,.71288697340906E+00/,W47(13)/,.46376389086505E-01/      MOL      867
      DATA X47(14)/,.75767291844543E+00/,W47(14)/,.43158848648479E-01/      MOL      868
      DATA X47(15)/,.79914375416774E+00/,W47(15)/,.39752586122530E-01/      MOL      869
      DATA X47(16)/,.83712013989990E+00/,W47(16)/,.36172496584175E-01/      MOL      870
      DATA X47(17)/,.87143601579689E+00/,W47(17)/,.32434235515184E-01/      MOL      871
      DATA X47(18)/,.90194132943852E+00/,W47(18)/,.28554150708643E-01/      MOL      872
      DATA X47(19)/,.92850269301236E+00/,W47(19)/,.24549211659659E-01/      MOL      873
      DATA X47(20)/,.95100396925770E+00/,W47(20)/,.20436938147668E-01/      MOL      874
      DATA X47(21)/,.96934678732656E+00/,W47(21)/,.16235333146433E-01/      MOL      875
      DATA X47(22)/,.98345100307162E+00/,W47(22)/.11962848464312E-01/       MOL      876
      DATA X47(23)/,.99325521098776E+00/,W47(23)/,.76386162958488E-02/      MOL      877
      DATA X47(24)/,.99871872658421E+00/,W47(24)/,.32874538425280E-02/      MOL      878
C.....                                                                      MOL      879
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=48     MOL      880
C.....                                                                      MOL      881
      DATA X48( 1)/.32380170962869E-01/,W48( 1)/,.64737696812682E-01/       MOL      882
      DATA X48( 2)/,.97004699209462E-01/,W48( 2)/,.64466164435949E-01/      MOL      883
      DATA X48( 3)/,.16122235606889E-00/,W48( 3)/,.63924238584647E-01/      MOL      884
      DATA X48( 4)/,.22476379039469E-00/,W48( 4)/,.63114192286253E-01/      MOL      885
      DATA X48( 5)/,.28736248735546E-00/,W48( 5)/,.62039423159892E-01/      MOL      886
      DATA X48( 6)/,.34875588629216E-00/,W48( 6)/,.60704439165893E-01/      MOL      887
      DATA X48( 7)/,.40868648199071E-00/,W48( 7)/,.59114839698394E-01/      MOL      888
      DATA X48( 8)/,.46690290475096E-00/,W48( 8)/,.57277292100402E-01/      MOL      889
      DATA X48( 9)/,.52316097472223E+00/,W48( 9)/,.55199503699983E-01/      MOL      890
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      DATA X48(10)/.57722472608397E+00/,W48(10)/.52890189485193E-01/    MOL        891
      DATA X48(11)/.62886739677651E+00/,W48(11)/.50359035553854E-01/    MOL        892
      DATA X48(12)/.67787237963266E+00/,W48(12)/.47616658492490E-01/    MOL        893
      DATA X48(13)/.72403413092381E+00/,W48(13)/.44674560856693E-01/    MOL        894
      DATA X48(14)/.76715903251574E+00/,W48(14)/.41545082943464E-01/    MOL        895
      DATA X48(15)/.80706620402944E+00/,W48(15)/.38261351065830E-01/    MOL        896
      DATA X48(16)/.84358826162438E+00/,W48(16)/.34777222564770E-01/    MOL        897
      DATA X48(17)/.87657202027424E+00/,W48(17)/.31167227832798E-01/    MOL        898
      DATA X48(18)/.90587913671557E+00/,W48(18)/.27026509708357E-01/    MOL        899
      DATA X48(19)/.93138669070655E+00/,W48(19)/.23570760839324E-01/    MOL        900
      DATA X48(20)/.95298770316042E+00/,W48(20)/.19616160457355E-01/    MOL        901
      DATA X48(21)/.97059159254624E+00/,W48(21)/.15579315722944E-01/    MOL        902
      DATA X48(22)/.98412458372282E+00/,W48(22)/.11477234579234E-01/    MOL        903
      DATA X48(23)/.99353017226635E+00/,W48(23)/.73275539012762E-02/    MOL        904
      DATA X48(24)/.99877100725242E+00/,W48(24)/.31533460523058E-02/    MOL        905
C.....                                                                  MOL        906
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=49  MOL        907
C.....                                                                  MOL        908
      DATA X49( 1)/.00000000000000E 00/,W49( 1)/.63463281404790E-01/    MOL        909
      DATA X49( 2)/.63420684982686E-01/,W49( 2)/.63335509296491E-01/    MOL        910
      DATA X49( 3)/.12658599726967E-00/,W49( 3)/.62952707465194E-01/    MOL        911
      DATA X49( 4)/.18924159246181E-00/,W49( 4)/.62316417320056E-01/    MOL        912
      DATA X49( 5)/.25113517861254E-00/,W49( 5)/.61429200979192E-01/    MOL        913
      DATA X49( 6)/.31201753211975E-00/,W49( 6)/.60294630953151E-01/    MOL        914
      DATA X49( 7)/.37164350126228E-00/,W49( 7)/.58917275760026E-01/    MOL        915
      DATA X49( 8)/.42977299334157E-00/,W49( 8)/.57302681530186E-01/    MOL        916
      DATA X49( 9)/.48617194145249E-00/,W49( 9)/.55457349674802E-01/    MOL        917
      DATA X49(10)/.54061324699172E+00/,W49(10)/.53388710708258E-01/    MOL        918
      DATA X49(11)/.59287759410690E+00/,W49(11)/.51125094332144E-01/    MOL        919
      DATA X49(12)/.64275483241924E+00/,W49(12)/.48615695887828E-01/    MOL        920
      DATA X49(13)/.69004382442513E+00/,W49(13)/.45930539355595E-01/    MOL        921
      DATA X49(14)/.73455425423740E+00/,W49(14)/.43060436981259E-01/    MOL        922
      DATA X49(15)/.77610689434544E+00/,W49(15)/.40016945766372E-01/    MOL        923
      DATA X49(16)/.81453442735985E+00/,W49(16)/.36812320963000E-01/    MOL        924
      DATA X49(17)/.84968211984416E+00/,W49(17)/.33459466791622E-01/    MOL        925
      DATA X49(18)/.88140084557300E+00/,W49(18)/.29971884620583E-01/    MOL        926
      DATA X49(19)/.90958565582807E+00/,W49(19)/.26363618927066E-01/    MOL        927
      DATA X49(20)/.93410029475581E+00/,W49(20)/.22549201587446E-01/    MOL        928
      DATA X49(21)/.95485365867413E+00/,W49(21)/.18843595853089E-01/    MOL        929
      DATA X49(22)/.97176220090155E+00/,W49(22)/.14962144935625E-01/    MOL        930
      DATA X49(23)/.98475789591421E+00/,W49(23)/.11020551031593E-01/    MOL        931
      DATA X49(24)/.99378866194416E+00/,W49(24)/.70350995900864E-02/    MOL        932
      DATA X49(25)/.99882015060663E+00/,W49(25)/.30272789889229E-02/    MOL        933
C.....                                                                  MOL        934
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=50  MOL        935
C.....                                                                  MOL        936
      DATA X50( 1)/.31098338327189E-01/,W50( 1)/.62176616655346E-01/    MOL        937
      DATA X50( 2)/.93174701560086E-01/,W50( 2)/.61936067420682E-01/    MOL        938
      DATA X50( 3)/.15489058999815E-00/,W50( 3)/.61455899590316E-01/    MOL        939
      DATA X50( 4)/.21600723687604E-00/,W50( 4)/.60737970841769E-01/    MOL        940
      DATA X50( 5)/.27628819377953E-00/,W50( 5)/.59785058704254E-01/    MOL        941
      DATA X50( 6)/.33550024541944E-00/,W50( 6)/.58600849813221E-01/    MOL        942
      DATA X50( 7)/.39341431189756E-00/,W50( 7)/.57199925647727E-01/    MOL        943
      DATA X50( 8)/.44980633497404E-00/,W50( 8)/.55557744806212E-01/    MOL        944
      DATA X50( 9)/.50445814490746E+00/,W50( 9)/.53710621868996E-01/    MOL        945
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         DATA X50(10)/.55715830451465E+00/,W50(10)/.51655703069580E-01/     MOL          946
         DATA X50(11)/.60770292718495E+00/,W50(11)/.49470938494466E-01/     MOL          947
         DATA X50(12)/.65589646568544E+00/,W50(12)/.46955051303948E-01/     MOL          948
         DATA X50(13)/.70155246870682E+00/,W50(13)/.44327574335803E-01/     MOL          949
         DATA X50(14)/.74449430222606E+00/,W50(14)/.41528463090147E-01/     MOL          950
         DATA X50(15)/.78455583290040E+00/,W50(15)/.38563755612587E-01/     MOL          951
         DATA X50(16)/.82215820708593E+00/,W50(16)/.35459835615146E-01/     MOL          952
         DATA X50(17)/.85542976942994E+00/,W50(17)/.32213728223578E-01/     MOL          953
         DATA X50(18)/.85596797952761E+00/,W50(18)/.28842993580535E-01/     MOL          954
         DATA X50(19)/.91307855665579E+00/,W50(19)/.25367673570012E-01/     MOL          955
         DATA X50(20)/.93665661894488E+00/,W50(20)/.21782203170125E-01/     MOL          956
         DATA X50(21)/.95661095524280E+00/,W50(21)/.18115560713489E-01/     MOL          957
         DATA X50(22)/.97286438510669E+00/,W50(22)/.14380822761485E-01/     MOL          958
         DATA X50(23)/.98535408404602E+00/,W50(23)/.10590548383651E-01/     MOL          959
         DATA X50(24)/.99403196943208E+00/,W50(24)/.67597991957453E-02/     MOL          960
         DATA X50(25)/.99886640442007E+00/,W50(25)/.29086225531551E-02/     MOL          961
C.....                                                                      MOL          962
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=51      MOL          963
C.....                                                                      MOL          964
         DATA X51( 1)/.00000000000000E 00/,W51( 1)/.60998924841206E-01/     MOL          965
         DATA X51( 2)/.60961102150578E-01/,W51( 2)/.60885464844855E-01/     MOL          966
         DATA X51( 3)/.12169542101889E+00/,W51( 3)/.60545506934736E-01/     MOL          967
         DATA X51( 4)/.18197702695708E+00/,W51( 4)/.59988315777502E-01/     MOL          968
         DATA X51( 5)/.24158166644782E+00/,W51( 5)/.59171993922960E-01/     MOL          969
         DATA X51( 6)/.30028767633533E+00/,W51( 6)/.58183473982591E-01/     MOL          970
         DATA X51( 7)/.35787645668841E+00/,W51( 7)/.56958507722257E-01/     MOL          971
         DATA X51( 8)/.41413398322630E+00/,W51( 8)/.55521652095736E-01/     MOL          972
         DATA X51( 9)/.46885090428604E+00/,W51( 9)/.53878252313045E-01/     MOL          973
         DATA X51(10)/.52182366930618E+00/,W51(10)/.52034421936696E-01/     MOL          974
         DATA X51(11)/.57285521635130E+00/,W51(11)/.49997020150056E-01/     MOL          975
         DATA X51(12)/.62175572460072E+00/,W51(12)/.47773626240622E-01/     MOL          976
         DATA X51(13)/.66834322117537E+00/,W51(13)/.45372511407649E-01/     MOL          977
         DATA X51(14)/.71244045757704E+00/,W51(14)/.42802607997879E-01/     MOL          978
         DATA X51(15)/.75389535442537E+00/,W51(15)/.40073476285496E-01/     MOL          979
         DATA X51(16)/.79254171200938E+00/,W51(16)/.37195268923260E-01/     MOL          980
         DATA X51(17)/.82823976382306E+00/,W51(17)/.34178693204188E-01/     MOL          981
         DATA X51(18)/.86085671118229E+00/,W51(18)/.31034971290159E-01/     MOL          982
         DATA X51(19)/.89027121002952E+00/,W51(19)/.27775798594162E-01/     MOL          983
         DATA X51(20)/.91637386230976E+00/,W51(20)/.24413300573781E-01/     MOL          984
         DATA X51(21)/.93906754400296E+00/,W51(21)/.26959958401703E-01/     MOL          985
         DATA X51(22)/.95826784861390E+00/,W51(22)/.17428714723401E-01/     MOL          986
         DATA X51(23)/.97390334601932E+00/,W51(23)/.13832634006478E-01/     MOL          987
         DATA X51(24)/.98591599173590E+00/,W51(24)/.10185191297622E-01/     MOL          988
         DATA X51(25)/.99426126043675E+00/,W51(25)/.65003377632526E-02/     MOL          989
         DATA X51(26)/.99890999084890E+00/,W51(26)/.27968071710899E-02/     MOL          990
C.....                                                                      MOL          991
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDEF=52      MOL          992
C.....                                                                      MOL          993
         DATA X52( 1)/.29914109797339E-01/,W52( 1)/.59812365745291E-01/     MOL          994
         DATA X52( 2)/.89635244648899E-01/,W52( 2)/.59556260171247E-01/     MOL          995
         DATA X52( 3)/.14903550852695E+00/,W52( 3)/.59166815466042E-01/     MOL          996
         DATA X52( 4)/.20790226415637E+00/,W52( 4)/.58529561771813E-01/     MOL          997
         DATA X52( 5)/.26602473360500E+00/,W52( 5)/.57660787452526E-01/     MOL          998
         DATA X52( 6)/.32319500343481E+00/,W52( 6)/.56625533902367E-01/     MOL          999
         DATA X52( 7)/.37920826911609E+00/,W52( 7)/.55367569669301E-01/     MOL         1000
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RUN=107     0          GLEGEN          76/04/09     20.13.03     PARKEPZZUR     PAGE NO. 19
      DATA X52( 8)/.43386406771876E-00/,W52( 8)/.53911406932756E-01/   MOL      1001
      DATA X52( 9)/.48696674569807E-00/,W52( 9)/.52262255383906E-01/   MOL      1002
      DATA X52(10)/.53832620928583E+00/,W52(10)/.50426018566341E-01/   MOL      1003
      DATA X52(11)/.58775860497958E+00/,W52(11)/.48409269744074E-01/   MOL      1004
      DATA X52(12)/.63508697769524E+00/,W52(12)/.46219228372784E-01/   MOL      1005
      DATA X52(13)/.68014190422716E+00/,W52(13)/.43863734259000E-01/   MOL      1006
      DATA X52(14)/.72276209974998E+00/,W52(14)/.41351219502559E-01/   MOL      1007
      DATA X52(15)/.76270499519374E+00/,W52(15)/.38690678310423E-01/   MOL      1008
      DATA X52(16)/.80009728343047E+00/,W52(16)/.35891634835097E-01/   MOL      1009
      DATA X52(17)/.83453543232673E+00/,W52(17)/.32964109089718E-01/   MOL      1010
      DATA X52(18)/.86598616284696E+00/,W52(18)/.29918581147144E-01/   MOL      1011
      DATA X52(19)/.89433689053449E+00/,W52(19)/.26765953746504E-01/   MOL      1012
      DATA X52(20)/.91948612691642E+00/,W52(20)/.23517513553984E-01/   MOL      1013
      DATA X52(21)/.94134385364135E+00/,W52(21)/.20184891507981E-01/   MOL      1014
      DATA X52(22)/.95983182693308E+00/,W52(22)/.16780023396301E-01/   MOL      1015
      DATA X52(23)/.97488388422174E+00/,W52(23)/.13315114982341E-01/   MOL      1016
      DATA X52(24)/.98644619565154E+00/,W52(24)/.98026345794626E-02/   MOL      1017
      DATA X52(25)/.99447759092921E+00/,W52(25)/.62555239629732E-02/   MOL      1018
      DATA X52(26)/.99695111110394E+00/,W52(26)/.26913169500471E-02/   MOL      1019
C.....                                                                 MOL      1020
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=53 MOL      1021
C.....                                                                 MOL      1022
      DATA X53( 1)/.00000000000000E 00/,W53( 1)/.58718794151164E-01/   MOL      1023
      DATA X53( 2)/.58685054300259E-01/,W53( 2)/.58617586232719E-01/   MOL      1024
      DATA X53( 3)/.11716780907195E-00/,W53( 3)/.58314311362254E-01/   MOL      1025
      DATA X53( 4)/.17524666215533E-00/,W53( 4)/.57810014991712E-01/   MOL      1026
      DATA X53( 5)/.23272140372427E-00/,W53( 5)/.57106435536266E-01/   MOL      1027
      DATA X53( 6)/.28939390645162E-00/,W53( 6)/.56205996381739E-01/   MOL      1028
      DATA X53( 7)/.34506880849572E-00/,W53( 7)/.55111807523932E-01/   MOL      1029
      DATA X53( 8)/.39955418695395E-00/,W53( 8)/.53827634866730E-01/   MOL      1030
      DATA X53( 9)/.45266221946184E-00/,W53( 9)/.52357907229872E-01/   MOL      1031
      DATA X53(10)/.50420983165713E+00/,W53(10)/.50707691069292E-01/   MOL      1032
      DATA X53(11)/.55401932227736E+00/,W53(11)/.48882675432698E-01/   MOL      1033
      DATA X53(12)/.60191920571377E+00/,W53(12)/.46889150340750E-01/   MOL      1034
      DATA X53(13)/.64774374391650E+00/,W53(13)/.44733989103672E-01/   MOL      1035
      DATA X53(14)/.69133557560136E+00/,W53(14)/.42424620634519E-01/   MOL      1036
      DATA X53(15)/.73254423080751E+00/,W53(15)/.39969005843540E-01/   MOL      1037
      DATA X53(16)/.77122765492553E+00/,W53(16)/.37375609803482E-01/   MOL      1038
      DATA X53(17)/.80725249841689E+00/,W53(17)/.34653372583533E-01/   MOL      1039
      DATA X53(18)/.84049457654580E+00/,W53(18)/.31811678459219E-01/   MOL      1040
      DATA X53(19)/.87083929755824E+00/,W53(19)/.28260323617823E-01/   MOL      1041
      DATA X53(20)/.89818205787542E+00/,W53(20)/.25809482510757E-01/   MOL      1042
      DATA X53(21)/.92242860504281E+00/,W53(21)/.22669673057070E-01/   MOL      1043
      DATA X53(22)/.94349535346443E+00/,W53(22)/.19451721107637E-01/   MOL      1044
      DATA X53(23)/.96130969462313E+00/,W53(23)/.16166725256687E-01/   MOL      1045
      DATA X53(24)/.97581023371498E+00/,W53(24)/.12826026144240E-01/   MOL      1046
      DATA X53(25)/.98694703502337E+00/,W53(25)/.94412022849403E-02/   MOL      1047
      DATA X53(26)/.99468191930602E+00/,W53(26)/.60242762269486E-02/   MOL      1048
      DATA X53(27)/.99898994777632E+00/,W53(27)/.25916837205670E-02/   MOL      1049
C.....                                                                 MOL      1050
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=54 MOL      1051
C.....                                                                 MOL      1052
      DATA X54( 1)/.28816748199342E-01/,W54( 1)/.57617536707146E-01/   MOL      1053
      DATA X54( 2)/.86354518263248E-01/,W54( 2)/.57426137054111E-01/   MOL      1054
      DATA X54( 3)/.14360542731626E-00/,W54( 3)/.57043973558794E-01/   MOL      1055
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      DATA X54( 4)/.20037229540621E-00/,W54( 4)/.56472315737625E-01/    MOL     1056
      DATA X54( 5)/.25648752807800E-00/,W54( 5)/.55713762557529E-01/    MOL     1057
      DATA X54( 6)/.31174572483447E-00/,W54( 6)/.54768736213057E-01/    MOL     1058
      DATA X54( 7)/.36596434037219E-00/,W54( 7)/.53642473647553E-01/    MOL     1059
      DATA X54( 8)/.41896926325520E-00/,W54( 8)/.52338216398290E-01/    MOL     1060
      DATA X54( 9)/.47036241248139E-00/,W54( 9)/.50659697146187E-01/    MOL     1061
      DATA X54(10)/.527632354385593E+00/,W54(10)/.49212927324528E-01/    MOL     1062
      DATA X54(11)/.56895276619552E+00/,W54(11)/.47901678006444E-01/    MOL     1063
      DATA X54(12)/.61538319833112E+00/,W54(12)/.45433466729276E-01/    MOL     1064
      DATA X54(13)/.65976432763198E-00/,W54(13)/.43314329309597E-01/    MOL     1065
      DATA X54(14)/.70196380971917E+00/,W54(14)/.41251306136644E-01/    MOL     1066
      DATA X54(15)/.74182653880918E+00/,W54(15)/.38651914782102E-01/    MOL     1067
      DATA X54(16)/.77922491534625E+00/,W54(16)/.36124125840383E-01/    MOL     1068
      DATA X54(17)/.81403407591357E+00/,W54(17)/.33476336064372E-01/    MOL     1069
      DATA X54(18)/.84614051597070E+00/,W54(18)/.30717342497870E-01/    MOL     1070
      DATA X54(19)/.87543545426556E+00/,W54(19)/.27656329312595E-01/    MOL     1071
      DATA X54(20)/.90182228628470E+00/,W54(20)/.24922741467208E-01/    MOL     1072
      DATA X54(21)/.92521435986665E+00/,W54(21)/.21560451422853E-01/    MOL     1073
      DATA X54(22)/.94553097516499E+00/,W54(22)/.18757527621469E-01/    MOL     1074
      DATA X54(23)/.96270764578592E-00/,W54(23)/.15586303035924E-01/    MOL     1075
      DATA X54(24)/.97668632885790E+00/,W54(24)/.12363328128847E-01/    MOL     1076
      DATA X54(25)/.98742063739730E+00/,W54(25)/.90973694555293E-02/    MOL     1077
      DATA X54(26)/.99497511701834E+00/,W54(26)/.58055110152399E-02/    MOL     1078
      DATA X54(27)/.99902606036734E+00/,W54(27)/.24974618357616E-02/    MOL     1079
C.....                                                                   MOL     1080
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=55  MOL     1081
C.....                                                                   MOL     1082
      DATA X55( 1)/.00000000000000E 00/,W55( 1)/.56602976444560E-01/    MOL     1083
      DATA X55( 2)/.56572753510337E-01/,W55( 2)/.56512318249771E-01/    MOL     1084
      DATA X55( 3)/.11296042868593E-00/,W55( 3)/.56240634071083E-01/    MOL     1085
      DATA X55( 4)/.16899396364687E-00/,W55( 4)/.55788794195283E-01/    MOL     1086
      DATA X55( 5)/.22448230867645E-00/,W55( 5)/.55158246002508E-01/    MOL     1087
      DATA X55( 6)/.27925155320881E-00/,W55( 6)/.54351209325910E-01/    MOL     1088
      DATA X55( 7)/.33312627889202E-00/,W55( 7)/.53369670801605E-01/    MOL     1089
      DATA X55( 8)/.38593392374298E-00/,W55( 8)/.52217371945631E-01/    MOL     1090
      DATA X55( 9)/.43750524003717E-00/,W55( 9)/.50897805124493E-01/    MOL     1091
      DATA X55(10)/.48767515816747E+00/,W55(10)/.49015197711551E-01/    MOL     1092
      DATA X55(11)/.53628285590834E+00/,W55(11)/.47774298551200E-01/    MOL     1093
      DATA X55(12)/.58317273802603E+00/,W55(12)/.45950363946283E-01/    MOL     1094
      DATA X55(13)/.62819451222993E+00/,W55(13)/.44239140421646E-01/    MOL     1095
      DATA X55(14)/.67120399031982E+00/,W55(14)/.41956846317718E-01/    MOL     1096
      DATA X55(15)/.71206339998663E+00/,W55(15)/.39740151874337E-01/    MOL     1097
      DATA X55(16)/.75064155634822E+00/,W55(16)/.37396157867965E-01/    MOL     1098
      DATA X55(17)/.78681578112762E+00/,W55(17)/.34932372873589E-01/    MOL     1099
      DATA X55(18)/.82046929855932E+00/,W55(18)/.32355689226185E-01/    MOL     1100
      DATA X55(19)/.85149460661715E+00/,W55(19)/.29677357765161E-01/    MOL     1101
      DATA X55(20)/.87979232241989E+00/,W55(20)/.26902961456396E-01/    MOL     1102
      DATA X55(21)/.90521168074080E+00/,W55(21)/.24042388039725E-01/    MOL     1103
      DATA X55(22)/.92785142472078E+00/,W55(22)/.21104531658016E-01/    MOL     1104
      DATA X55(23)/.94745886804121E+00/,W55(23)/.18099614527729E-01/    MOL     1105
      DATA X55(24)/.96403132859313E+00/,W55(24)/.15236456333512E-01/    MOL     1106
      DATA X55(25)/.97751573558398E+00/,W55(25)/.11925160719848E-01/    MOL     1107
      DATA X55(26)/.98786954119888E+00/,W55(26)/.87757061072584E-02/    MOL     1108
      DATA X55(27)/.99505787784741E+00/,W55(27)/.55950322665607E-02/    MOL     1109
      DATA X55(28)/.99906141956482E+00/,W55(28)/.24083236199798E-02/    MOL     1110
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C.....                                                               MOL        1111
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=56  MOL        1112
C.....                                                               MOL        1113
      DATA X56( 1)/.27797035287275E-01/,W56( 1)/.55579746306513E-01/  MOL        1114
      DATA X56( 2)/.83305186822435E-01/,W56( 2)/.55407952503244E-01/  MOL        1115
      DATA X56( 3)/.13855584681038E-00/,W56( 3)/.55064895901761E-01/  MOL        1116
      DATA X56( 4)/.19337623863527E-00/,W56( 4)/.54551636870886E-01/  MOL        1117
      DATA X56( 5)/.24760290943434E-00/,W56( 5)/.53869761865714E-01/  MOL        1118
      DATA X56( 6)/.30106225386722E-00/,W56( 6)/.53021378524009E-01/  MOL        1119
      DATA X56( 7)/.35359103217495E-00/,W56( 7)/.52009109151741E-01/  MOL        1120
      DATA X56( 8)/.40502680692709E-00/,W56( 8)/.50836082617797E-01/  MOL        1121
      DATA X56( 9)/.45521081487846E-00/,W56( 9)/.49505924683046E-01/  MOL        1122
      DATA X56(10)/.50398771838438E+00/,W56(10)/.48022746793599E-01/  MOL        1123
      DATA X56(11)/.55120682485553E+00/,W56(11)/.46391133373001E-01/  MOL        1124
      DATA X56(12)/.59672218277066E+00/,W56(12)/.44616127652692E-01/  MOL        1125
      DATA X56(13)/.64039310680700E+00/,W56(13)/.42703216084666E-01/  MOL        1126
      DATA X56(14)/.68208461269447E+00/,W56(14)/.40658311384744E-01/  MOL        1127
      DATA X56(15)/.72166783445019E+00/,W56(15)/.38487734259247E-01/  MOL        1128
      DATA X56(16)/.75902042270513E+00/,W56(16)/.36198193872315E-01/  MOL        1129
      DATA X56(17)/.79402692289386E+00/,W56(17)/.33796767115611E-01/  MOL        1130
      DATA X56(18)/.82657913214288E+00/,W56(18)/.31290876747310E-01/  MOL        1131
      DATA X56(19)/.85657643376275E+00/,W56(19)/.28688268473822E-01/  MOL        1132
      DATA X56(20)/.88392610832782E+00/,W56(20)/.25996987058392E-01/  MOL        1133
      DATA X56(21)/.90854362042065E+00/,W56(21)/.23225351562565E-01/  MOL        1134
      DATA X56(22)/.93035288024749E+00/,W56(22)/.20381929882402E-01/  MOL        1135
      DATA X56(23)/.94928647956196E+00/,W56(23)/.17475512911401E-01/  MOL        1136
      DATA X56(24)/.96528590190549E+00/,W56(24)/.14515089278021E-01/  MOL        1137
      DATA X56(25)/.97830172914025E+00/,W56(25)/.11509824340383E-01/  MOL        1138
      DATA X56(26)/.98829371554016E+00/,W56(26)/.84690631633078E-02/  MOL        1139
      DATA X56(27)/.99523122608106E+00/,W56(27)/.54025222460153E-02/  MOL        1140
      DATA X56(28)/.99909434380146E+00/,W56(28)/.23238553757732E-02/  MOL        1141
C.....                                                               MOL        1142
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=57  MOL        1143
C.....                                                               MOL        1144
      DATA X57( 1)/.00000000000000E 00/,W57( 1)/.54634328756584E-01/  MOL        1145
      DATA X57( 2)/.54607151001647E-01/,W57( 2)/.54552803604761E-01/  MOL        1146
      DATA X57( 3)/.10905133280879E-00/,W57( 3)/.54308471452497E-01/  MOL        1147
      DATA X57( 4)/.16317006259126E-00/,W57( 4)/.53902061483298E-01/  MOL        1148
      DATA X57( 5)/.21680162879612E-00/,W57( 5)/.53334786584818E-01/  MOL        1149
      DATA X57( 6)/.26978657316184E-00/,W57( 6)/.52608339729176E-01/  MOL        1150
      DATA X57( 7)/.32196616539536E-00/,W57( 7)/.51724868970517E-01/  MOL        1151
      DATA X57( 8)/.37318489008659E-00/,W57( 8)/.50687070724927E-01/  MOL        1152
      DATA X57( 9)/.42323938145155E-00/,W57( 9)/.49497982402019E-01/  MOL        1153
      DATA X57(10)/.47213160951797E-00/,W57(10)/.48161172661687E-01/  MOL        1154
      DATA X57(11)/.51956431139119E+00/,W57(11)/.46680631073641E-01/  MOL        1155
      DATA X57(12)/.56544642926923E+00/,W57(12)/.45060775161380E-01/  MOL        1156
      DATA X57(13)/.60964103292871E+00/,W57(13)/.43306442216214E-01/  MOL        1157
      DATA X57(14)/.65201622628097E+00/,W57(14)/.41422864870600E-01/  MOL        1158
      DATA X57(15)/.69244555119952E+00/,W57(15)/.39415665475479E-01/  MOL        1159
      DATA X57(16)/.73080634474452E+00/,W57(16)/.37290834324417E-01/  MOL        1160
      DATA X57(17)/.76699011935945E+00/,W57(17)/.35054712782312E-01/  MOL        1161
      DATA X57(18)/.80088267454722E+00/,W57(18)/.32713974366371E-01/  MOL        1162
      DATA X57(19)/.83238552115944E+00/,W57(19)/.30275604842694E-01/  MOL        1163
      DATA X57(20)/.86140393326204E+00/,W57(20)/.27746881402130E-01/  MOL        1164
      DATA X57(21)/.88785167868222E+00/,W57(21)/.25135350990916E-01/  MOL        1165
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      DATA X57(22)/.91164967852139E+00/,W57(22)/.22440807890776E-01/    MOL       1166
      DATA X57(23)/.93272696106710E+00/,W57(23)/.19695270699488E-01/    MOL       1167
      DATA X57(24)/.95102062644787E+00/,W57(24)/.16882959023441E-01/    MOL       1168
      DATA X57(25)/.96647608517188E+00/,W57(25)/.14020270790753E-01/    MOL       1169
      DATA X57(26)/.97904722670947E+00/,W57(26)/.11115763732336E-01/    MOL       1170
      DATA X57(27)/.98869657765022E+00/,W57(27)/.81761600678211E-02/    MOL       1171
      DATA X57(28)/.99539552367842E+00/,W57(28)/.52165334747187E-02/    MOL       1172
      DATA X57(29)/.99912556562526E+00/,W57(29)/.22437538722506E-02/    MOL       1173
C.....                                                                  MOL       1174
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=58  MOL       1175
C.....                                                                  MOL       1176
      DATA X58( 1)/.26847012365942E-01/,W58( 1)/.53681119863333E-01/    MOL       1177
      DATA X58( 2)/.80463630214143E-01/,W58( 2)/.53526343304057E-01/    MOL       1178
      DATA X58( 3)/.13384825059547E-00/,W58( 3)/.53217236446578E-01/    MOL       1179
      DATA X58( 4)/.18684695183576E-00/,W58( 4)/.52754690526370E-01/    MOL       1180
      DATA X58( 5)/.23930692496615E-00/,W58( 5)/.52140039183669E-01/    MOL       1181
      DATA X58( 6)/.29107691431111E-00/,W58( 6)/.51375054618284E-01/    MOL       1182
      DATA X58( 7)/.34200765359799E-00/,W58( 7)/.50461942479952E-01/    MOL       1183
      DATA X58( 8)/.39195229633075E-00/,W58( 8)/.49403335508961E-01/    MOL       1184
      DATA X58( 9)/.44076683918684E-00/,W58( 9)/.48202285945417E-01/    MOL       1185
      DATA X58(10)/.48831053721672E-00/,W58(10)/.46862256729025E-01/    MOL       1186
      DATA X58(11)/.53444630964884E+00/,W58(11)/.45387115514819E-01/    MOL       1187
      DATA X58(12)/.57904113513022E+00/,W58(12)/.43781103533639E-01/    MOL       1188
      DATA X58(13)/.62196643526307E+00/,W58(13)/.42048863329582E-01/    MOL       1189
      DATA X58(14)/.66309844533212E+00/,W58(14)/.40195385409867E-01/    MOL       1190
      DATA X58(15)/.70231857115391E+00/,W58(15)/.38226013845858E-01/    MOL       1191
      DATA X58(16)/.73951373102004E+00/,W58(16)/.36146426867087E-01/    MOL       1192
      DATA X58(17)/.77457668174965E+00/,W58(17)/.33962620493415E-01/    MOL       1193
      DATA X58(18)/.80740632791308E+00/,W58(18)/.31680891253809E-01/    MOL       1194
      DATA X58(19)/.83790801333937E+00/,W58(19)/.29307818044160E-01/    MOL       1195
      DATA X58(20)/.86599379407481E+00/,W58(20)/.26850243181981E-01/    MOL       1196
      DATA X58(21)/.89158269202202E+00/,W58(21)/.24315252724964E-01/    MOL       1197
      DATA X58(22)/.91460092856435E+00/,W58(22)/.21710156140146E-01/    MOL       1198
      DATA X58(23)/.93498213758825E+00/,W58(23)/.19042465461893E-01/    MOL       1199
      DATA X58(24)/.95266755751887E+00/,W58(24)/.16319874234971E-01/    MOL       1200
      DATA X58(25)/.96760620250292E+00/,W58(25)/.13550237112989E-01/    MOL       1201
      DATA X58(26)/.97975501469434E+00/,W58(26)/.10741553532879E-01/    MOL       1202
      DATA X58(27)/.98907900624844E+00/,W58(27)/.79019738499986E-02/    MOL       1203
      DATA X58(28)/.99555147659729E+00/,W58(28)/.50399816126502E-02/    MOL       1204
      DATA X58(29)/.99915520040738E+00/,W58(29)/.21677232496274E-02/    MOL       1205
C.....                                                                  MOL       1206
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=59  MOL       1207
C.....                                                                  MOL       1208
      DATA X59( 1)/.00000000000000E 00/,W59( 1)/.52798012621990E-01/    MOL       1209
      DATA X59( 2)/.52773484088310E-01/,W59( 2)/.52724433859127E-01/    MOL       1210
      DATA X59( 3)/.10539983901634E-00/,W59( 3)/.52503902647828E-01/    MOL       1211
      DATA X59( 4)/.15773250550786E-00/,W59( 4)/.52137033646375E-01/    MOL       1212
      DATA X59( 5)/.20962557339204E-00/,W59( 5)/.51624849390890E-01/    MOL       1213
      DATA X59( 6)/.26093423734281E-00/,W59( 6)/.50960777425393E-01/    MOL       1214
      DATA X59( 7)/.31151570060301E-00/,W59( 7)/.50170646342996E-01/    MOL       1215
      DATA X59( 8)/.36122891416979E-00/,W59( 8)/.49232680679361E-01/    MOL       1216
      DATA X59( 9)/.40993531781042E-00/,W59( 9)/.48157494714605E-01/    MOL       1217
      DATA X59(10)/.45749915825326E-00/,W59(10)/.46946085186961E-01/    MOL       1218
      DATA X59(11)/.50378796655771E+00/,W59(11)/.45607822940509E-01/    MOL       1219
      DATA X59(12)/.54867242780839E+00/,W59(12)/.44140443530296E-01/    MOL       1220
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RUN=197    0         GLEGEN         76/04/09     20.13.03    PARKERZZUR    PAGE NO. 23
         DATA X59(13)/.59202774870403E+00/,W59(13)/.42550036811067E-01/     MOL        1221
         DATA X59(14)/.63373295623885E+00/,W59(14)/.40841035535686E-01/     MOL        1222
         DATA X59(15)/.67367186450493E+00/,W59(15)/.39218203016159E-01/     MOL        1223
         DATA X59(16)/.71173311607719E+00/,W59(16)/.37086619816870E-01/     MOL        1224
         DATA X59(17)/.74781064527664E+00/,W59(17)/.35051669636399E-01/     MOL        1225
         DATA X59(18)/.78150368786236E+00/,W59(18)/.32919024271045E-01/     MOL        1226
         DATA X59(19)/.81361818728821E+00/,W59(19)/.30694627236111E-01/     MOL        1227
         DATA X59(20)/.84316462581687E+00/,W59(20)/.28384680200534E-01/     MOL        1228
         DATA X59(21)/.87236109229286E+00/,W59(21)/.25995619731298E-01/     MOL        1229
         DATA X59(22)/.89513171174347E+00/,W59(22)/.23534105393713E-01/     MOL        1230
         DATA X59(23)/.91740743878815E+00/,W59(23)/.21006998288437E-01/     MOL        1231
         DATA X59(24)/.93712619235305E+00/,W59(24)/.18421342753610E-01/     MOL        1232
         DATA X59(25)/.95423300437695E+00/,W59(25)/.15784347313081E-01/     MOL        1233
         DATA X59(26)/.96868022168177E+00/,W59(26)/.13103366306345E-01/     MOL        1234
         DATA X59(27)/.98042757395671E+00/,W59(27)/.10385885500996E-01/     MOL        1235
         DATA X59(28)/.98944236513373E+00/,W59(28)/.76395294534875E-02/     MOL        1236
         DATA X59(29)/.99569964038324E+00/,W59(29)/.48722391682652E-02/     MOL        1237
         DATA X59(30)/.99918335390929E+00/,W59(30)/.20954922845412E-02/     MOL        1238
C.....                                                                      MOL        1239
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=60      MOL        1240
C.....                                                                      MOL        1241
         DATA X60( 1)/.25959772301248E-01/,W60( 1)/.51907877631220E-01/     MOL        1242
         DATA X60( 2)/.77809333949536E-01/,W60( 2)/.51767943174909E-01/     MOL        1243
         DATA X60( 3)/.12944913539694E+00/,W60( 3)/.51488451500980E-01/     MOL        1244
         DATA X60( 4)/.18073996487342E+00/,W60( 4)/.51070156069855E-01/     MOL        1245
         DATA X60( 5)/.23154355137603E+00/,W60( 5)/.50514184532508E-01/     MOL        1246
         DATA X60( 6)/.28172293742326E+00/,W60( 6)/.49822035690550E-01/     MOL        1247
         DATA X60( 7)/.33114284826845E+00/,W60( 7)/.48995575455756E-01/     MOL        1248
         DATA X60( 8)/.37967005657680E+00/,W60( 8)/.48037031819970E-01/     MOL        1249
         DATA X60( 9)/.42717374158305E+00/,W60( 9)/.46948988848912E-01/     MOL        1250
         DATA X60(10)/.47352584176170E+00/,W60(10)/.45734379716114E-01/     MOL        1251
         DATA X60(11)/.51860140005857E+00/,W60(11)/.44396478795786E-01/     MOL        1252
         DATA X60(12)/.56227890075394E+00/,W60(12)/.42936892835935E-01/     MOL        1253
         DATA X60(13)/.60444059704851E+00/,W60(13)/.41365551235584E-01/     MOL        1254
         DATA X60(14)/.64497282848946E+00/,W60(14)/.39620695452380E-01/     MOL        1255
         DATA X60(15)/.68376632738135E+00/,W60(15)/.37800067569243E-01/     MOL        1256
         DATA X60(16)/.72071651335573E+00/,W60(16)/.35974898051084E-01/     MOL        1257
         DATA X60(17)/.75572377530658E+00/,W60(17)/.34003892724946E-01/     MOL        1258
         DATA X60(18)/.78869373993226E+00/,W60(18)/.31921219019296E-01/     MOL        1259
         DATA X60(19)/.81953752616214E+00/,W60(19)/.29752491500789E-01/     MOL        1260
         DATA X60(20)/.84817198478592E+00/,W60(20)/.27503556749924E-01/     MOL        1261
         DATA X60(21)/.87451992264689E+00/,W60(21)/.25180477621521E-01/     MOL        1262
         DATA X60(22)/.89851031081004E+00/,W60(22)/.22789516943997E-01/     MOL        1263
         DATA X60(23)/.92007847617762E+00/,W60(23)/.20337120729457E-01/     MOL        1264
         DATA X60(24)/.93916627611642E+00/,W60(24)/.17829901014207E-01/     MOL        1265
         DATA X60(25)/.95572225583999E+00/,W60(25)/.15274618596785E-01/     MOL        1266
         DATA X60(26)/.96970178876505E+00/,W60(26)/.12678166476816E-01/     MOL        1267
         DATA X60(27)/.98106720175259E+00/,W60(27)/.10047557182288E-01/     MOL        1268
         DATA X60(28)/.98978789522222E+00/,W60(28)/.73899311633454E-02/     MOL        1269
         DATA X60(29)/.99584052511883E+00/,W60(29)/.47127299269535E-02/     MOL        1270
         DATA X60(30)/.99921012322743E+00/,W60(30)/.20268119688737E-02/     MOL        1271
C.....                                                                      MOL        1272
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=61      MOL        1273
C.....                                                                      MOL        1274
         DATA X61( 1)/.00000000000000E 00/,W61( 1)/.51081119440786E-01/     MOL        1275
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RUN=107    0         GLEGEN         76/04/09    20.13.03    PARKERZ2UR    PAGE NO. 24
          DATA X61( 2)/.51056906707974E-01/,W61( 2)/.51014487038697E-01/    MOL    1276
          DATA X61( 3)/.10198460656227E-00/,W61( 3)/.50814763668817E-01/    MOL    1277
          DATA X61( 4)/.15264424023092E-00/,W61( 4)/.50482470386797E-01/    MOL    1278
          DATA X61( 5)/.20290564251806E-00/,W61( 5)/.50018474108177E-01/    MOL    1279
          DATA X61( 6)/.25263768716905E-00/,W61( 6)/.49423985346734E-01/    MOL    1280
          DATA X61( 7)/.30171062096303E-00/,W61( 7)/.48700555056410E-01/    MOL    1281
          DATA X61( 8)/.34999644220406E-00/,W61( 8)/.47850870585095E-01/    MOL    1282
          DATA X61( 9)/.39736915472575E-00/,W61( 9)/.46874750750808E-01/    MOL    1283
          DATA X61(10)/.44370517653853E-00/,W61(10)/.45777140053145E-01/    MOL    1284
          DATA X61(11)/.48880362226225E-00/,W61(11)/.44560102035083E-01/    MOL    1285
          DATA X61(12)/.53278662650292E+00/,W61(12)/.43226811812495E-01/    MOL    1286
          DATA X61(13)/.57529965135083E+00/,W61(13)/.41780747790886E-01/    MOL    1287
          DATA X61(14)/.61631178519792E+00/,W61(14)/.40225682590998E-01/    MOL    1288
          DATA X61(15)/.65571603209507E+00/,W61(15)/.38565673207007E-01/    MOL    1289
          DATA X61(16)/.69340959089449E+00/,W61(16)/.36805050423154E-01/    MOL    1290
          DATA X61(17)/.72929412344946E+00/,W61(17)/.34948407516533E-01/    MOL    1291
          DATA X61(18)/.76327601117231E+00/,W61(18)/.33000588275907E-01/    MOL    1292
          DATA X61(19)/.79526659920235E+00/,W61(19)/.30966674368397E-01/    MOL    1293
          DATA X61(20)/.82518242810866E+00/,W61(20)/.28851972088183E-01/    MOL    1294
          DATA X61(21)/.85294545084766E+00/,W61(21)/.26661998524151E-01/    MOL    1295
          DATA X61(22)/.87848323721488E+00/,W61(22)/.24402467187544E-01/    MOL    1296
          DATA X61(23)/.90172916247399E+00/,W61(23)/.22079273148319E-01/    MOL    1297
          DATA X61(24)/.92262250138295E+00/,W61(24)/.19698477746101E-01/    MOL    1298
          DATA X61(25)/.94110898068136E+00/,W61(25)/.17266292987613E-01/    MOL    1299
          DATA X61(26)/.95714215191298E+00/,W61(26)/.14789065584938E-01/    MOL    1300
          DATA X61(27)/.97067425863318E+00/,W61(27)/.12273263507512E-01/    MOL    1301
          DATA X61(28)/.98167601128403E+00/,W61(28)/.97254618303560E-02/    MOL    1302
          DATA X61(29)/.99011674523251E+00/,W61(29)/.71523549917490E-02/    MOL    1303
          DATA X61(30)/.99597459981511E+00/,W61(30)/.45609240060124E-02/    MOL    1304
          DATA X61(31)/.99923559763136E+00/,W61(31)/.19614533616703E-02/    MOL    1305
C.....                                                                      MOL    1306
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=62      MOL    1307
C.....                                                                      MOL    1308
          DATA X62( 1)/.25129291421820E-01/,W62( 1)/.50248000375255E-01/    MOL    1309
          DATA X62( 2)/.75324395496234E-01/,W62( 2)/.50121069569042E-01/    MOL    1310
          DATA X62( 3)/.12532922361590E-00/,W62( 3)/.49867528594951E-01/    MOL    1311
          DATA X62( 4)/.17531745924901E-00/,W62( 4)/.49488017919698E-01/    MOL    1312
          DATA X62( 5)/.22426358560416E-00/,W62( 5)/.48983496220517E-01/    MOL    1313
          DATA X62( 6)/.27294320269672E-00/,W62( 6)/.48355237963477E-01/    MOL    1314
          DATA X62( 7)/.32093334159419E-00/,W62( 7)/.47604830184100E-01/    MOL    1315
          DATA X62( 8)/.36811277504656E-00/,W62( 8)/.46734168478414E-01/    MOL    1316
          DATA X62( 9)/.41436232371712E-00/,W62( 9)/.45745452214569E-01/    MOL    1317
          DATA X62(10)/.45956515724011E-00/,W62(10)/.44641178977124E-01/    MOL    1318
          DATA X62(11)/.50360708934475E+00/,W62(11)/.43424138250047E-01/    MOL    1319
          DATA X62(12)/.54637686630025E+00/,W62(12)/.42097404410384E-01/    MOL    1320
          DATA X62(13)/.58776644795309E+00/,W62(13)/.40664328682417E-01/    MOL    1321
          DATA X62(14)/.62767128064688E+00/,W62(14)/.39128531751962E-01/    MOL    1322
          DATA X62(15)/.66579256133548E+00/,W62(15)/.37493892562279E-01/    MOL    1323
          DATA X62(16)/.70262709222229E+00/,W62(16)/.35764540622768E-01/    MOL    1324
          DATA X62(17)/.73748952528315E+00/,W62(17)/.33944844379410E-01/    MOL    1325
          DATA X62(18)/.77038859685542E+00/,W62(18)/.32039400581624E-01/    MOL    1326
          DATA X62(19)/.80154134610397E+00/,W62(19)/.30053022573989E-01/    MOL    1327
          DATA X62(20)/.83056933360407E+00/,W62(20)/.27990728163314E-01/    MOL    1328
          DATA X62(21)/.85749923151206E+00/,W62(21)/.25857726954024E-01/    MOL    1329
          DATA X62(22)/.88226301283189E+00/,W62(22)/.23659407208683E-01/    MOL    1330
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RUN=107    0          GLEGEN           76/04/09      20,13,03     PARKERZ2UR    PAGE NO, 25
          DATA X62(23)/,904798122752109E+00/,W62(23)/,21401322277670E-01/     MOL          1331
          DATA X62(24)/,925304763563629E+00/,W62(24)/,19289176658573E-01/     MOL          1332
          DATA X62(25)/,942960840139235E+00/,W62(25)/,16728811790177E-01/     MOL          1333
          DATA X62(26)/,958491172973928E+00/,W62(26)/,14326191023696E-01/     MOL          1334
          DATA X62(27)/,97160072337165E+00/,W62(27)/,11887390117810E-01/      MOL          1335
          DATA X62(28)/,98225594929723E+00/,W62(28)/,94165794284203E-02/      MOL          1336
          DATA X62(29)/,99042997118922E+00/,W62(29)/,69250419010309E-02/      MOL          1337
          DATA X62(30)/,99610227631626E+00/,W62(30)/,44163334569308E-02/      MOL          1338
          DATA X62(31)/,99925985930876E+00/,W62(31)/,18992056795137E-02/      MOL          1339
C.....                                                                        MOL          1340
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=63       MOL          1341
C.....                                                                        MOL          1342
          DATA X63( 1)/,000000000000000E 00/,W63( 1)/,49472366623931E-01/     MOL          1343
          DATA X63( 2)/,49452187116159E-01/,W63( 2)/,49411033039917E-01/     MOL          1344
          DATA X63( 3)/,98783356446944E-01/,W63( 3)/,49230380423747E-01/     MOL          1345
          DATA X63( 4)/,14787278635787E+00/,W63( 4)/,48928452820511E-01/     MOL          1346
          DATA X63( 5)/,19660034679151E+00/,W63( 5)/,48506789097883E-01/     MOL          1347
          DATA X63( 6)/,24484674324595E+00/,W63( 6)/,47966421137994E-01/     MOL          1348
          DATA X63( 7)/,29249405859625E+00/,W63( 7)/,47328671312268E-01/     MOL          1349
          DATA X63( 8)/,33942554197458E+00/,W63( 8)/,46535149245383E-01/     MOL          1350
          DATA X63( 9)/,38552639421225E+00/,W63( 9)/,45647747876292E-01/     MOL          1351
          DATA X63(10)/,43068379879511E+00/,W63(10)/,44648635825941E-01/     MOL          1352
          DATA X63(11)/,47478724799480E+00/,W63(11)/,43549267083027E-01/     MOL          1353
          DATA X63(12)/,51772861329003E+00/,W63(12)/,42325345020815E-01/     MOL          1354
          DATA X63(13)/,55940340946628E+00/,W63(13)/,41006845759666E-01/     MOL          1355
          DATA X63(14)/,59970985187762E+00/,W63(14)/,39587995891544E-01/     MOL          1356
          DATA X63(15)/,63854710582136E+00/,W63(15)/,38072267584349E-01/     MOL          1357
          DATA X63(16)/,67582252811498E+00/,W63(16)/,36463370085457E-01/     MOL          1358
          DATA X63(17)/,71144403958458E+00/,W63(17)/,34765240645355E-01/     MOL          1359
          DATA X63(18)/,74532464831784E+00/,W63(18)/,32962034883779E-01/     MOL          1360
          DATA X63(19)/,77738126299037E+00/,W63(19)/,31118166222219E-01/     MOL          1361
          DATA X63(20)/,80753549577345E+00/,W63(20)/,29176047208280E-01/     MOL          1362
          DATA X63(21)/,83571355431949E+00/,W63(21)/,27165574359097E-01/     MOL          1363
          DATA X63(22)/,86184462364412E+00/,W63(22)/,25088620553345E-01/     MOL          1364
          DATA X63(23)/,88587032850785E+00/,W63(23)/,22949271004890E-01/     MOL          1365
          DATA X63(24)/,90772630277853E+00/,W63(24)/,20753761258039E-01/     MOL          1366
          DATA X63(25)/,92736092062184E+00/,W63(25)/,18507464467161E-01/     MOL          1367
          DATA X63(26)/,94472613404100E+00/,W63(26)/,16215878410338E-01/     MOL          1368
          DATA X63(27)/,95977944975843E+00/,W63(27)/,13884612616115E-01/     MOL          1369
          DATA X63(28)/,97248403469757E+00/,W63(28)/,11519376076880E-01/     MOL          1370
          DATA X63(29)/,98280881059372E+00/,W63(29)/,91259686763265E-02/     MOL          1371
          DATA X63(30)/,99072854689219E+00/,W63(30)/,67102917659601E-02/     MOL          1372
          DATA X63(31)/,99622401277797E+00/,W63(31)/,42785083468637E-02/     MOL          1373
          DATA X63(32)/,99928298402912E+00/,W63(32)/,18398745955771E-02/     MOL          1374
C.....                                                                        MOL          1375
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=64       MOL          1376
C.....                                                                        MOL          1377
          DATA X64( 1)/,24350292663424E-01/,W64( 1)/,48690957009139E-01/     MOL          1378
          DATA X64( 2)/,72993121787799E-01/,W64( 2)/,48575467441502E-01/     MOL          1379
          DATA X64( 3)/,12146281929612E+00/,W64( 3)/,48344762234802E-01/     MOL          1380
          DATA X64( 4)/,16964442042399E+00/,W64( 4)/,47999388596457E-01/     MOL          1381
          DATA X64( 5)/,21742364374001E+00/,W64( 5)/,47540165714829E-01/     MOL          1382
          DATA X64( 6)/,26468716220877E+00/,W64( 6)/,46968182816209E-01/     MOL          1383
          DATA X64( 7)/,31132287199021E+00/,W64( 7)/,46284796581314E-01/     MOL          1384
          DATA X64( 8)/,35722015833767E+00/,W64( 8)/,45491627927417E-01/     MOL          1385
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RUN-107     0          GLFGEN          76/04/09      20.13.03      PARKERZ2UR    PAGE NO. 26
          DATA X64( 9)/.40227015796399E-00/,W64( 9)/.44590558163755E-01/      MOL        1386
          DATA X64(10)/.44636601725346E-00/,W64(10)/.43583724529323E-01/      MOL        1387
          DATA X64(11)/.48940314570705E-00/,W64(11)/.42473515123653E-01/      MOL        1388
          DATA X64(12)/.53127946401989E+00/,W64(12)/.41262563242623E-01/      MOL        1389
          DATA X64(13)/.57189564620263E+00/,W64(13)/.39953741132720E-01/      MOL        1390
          DATA X64(14)/.61115535517239E+00/,W64(14)/.38550153178615E-01/      MOL        1391
          DATA X64(15)/.64896547125465E+00/,W64(15)/.37055128540239E-01/      MOL        1392
          DATA X64(16)/.68523631305423E+00/,W64(16)/.35472213256882E-01/      MOL        1393
          DATA X64(17)/.71988185017161E+00/,W64(17)/.33805161837141E-01/      MOL        1394
          DATA X64(18)/.75281990726053E+00/,W64(18)/.32057928354851E-01/      MOL        1395
          DATA X64(19)/.78397235894334E+00/,W64(19)/.30234657072402E-01/      MOL        1396
          DATA X64(20)/.81326531512279E+00/,W64(20)/.28339672614259E-01/      MOL        1397
          DATA X64(21)/.84062929625257E+00/,W64(21)/.26377469715054E-01/      MOL        1398
          DATA X64(22)/.86599939815409E+00/,W64(22)/.24352702568711E-01/      MOL        1399
          DATA X64(23)/.88931544599511E+00/,W64(23)/.22270173808383E-01/      MOL        1400
          DATA X64(24)/.91052213707850E+00/,W64(24)/.20134823153530E-01/      MOL        1401
          DATA X64(25)/.92956917213193E+00/,W64(25)/.17951715775697E-01/      MOL        1402
          DATA X64(26)/.94641137485839E+00/,W64(26)/.15726030476024E-01/      MOL        1403
          DATA X64(27)/.96100879965205E+00/,W64(27)/.13463047896718E-01/      MOL        1404
          DATA X64(28)/.97332682778991E+00/,W64(28)/.11168139460131E-01/      MOL        1405
          DATA X64(29)/.98333625388462E+00/,W64(29)/.88467598263638E-02/      MOL        1406
          DATA X64(30)/.99101337147674E+00/,W64(30)/.65044579689783E-02/      MOL        1407
          DATA X64(31)/.99634011677195E+00/,W64(31)/.41470332605624E-02/      MOL        1408
          DATA X64(32)/.99930504173576E+00/,W64(32)/.17832807216964E-02/      MOL        1409
C.....                                                                        MOL        1410
C,....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=80       MOL        1411
C.....                                                                        MOL        1412
          DATA X80( 1)/.19511383256794E-01/,W80( 1)/.39017813656306E-01/      MOL        1413
          DATA X80( 2)/.58504437152421E-01/,W80( 2)/.38958395962769E-01/      MOL        1414
          DATA X80( 3)/.97408398441584E-01/,W80( 3)/.38839651059051E-01/      MOL        1415
          DATA X80( 4)/.13616402280914E-00/,W80( 4)/.38661759774076E-01/      MOL        1416
          DATA X80( 5)/.17471229183265E-00/,W80( 5)/.38424993006959E-01/      MOL        1417
          DATA X80( 6)/.21299450285767E-00/,W80( 6)/.38129711314477E-01/      MOL        1418
          DATA X80( 7)/.25095235839227E-00/,W80( 7)/.37776364362001E-01/      MOL        1419
          DATA X80( 8)/.28852805488451E-00/,W80( 8)/.37365490238730E-01/      MOL        1420
          DATA X80( 9)/.32566437074770E-00/,W80( 9)/.36897714638276E-01/      MOL        1421
          DATA X80(10)/.36230475349949E-00/,W80(10)/.36373749905835E-01/      MOL        1422
          DATA X80(11)/.39839340588197E-00/,W80(11)/.35794393953415E-01/      MOL        1423
          DATA X80(12)/.43387537083175E-00/,W80(12)/.35160529044747E-01/      MOL        1424
          DATA X80(13)/.46869661517054E-00/,W80(13)/.34473120451753E-01/      MOL        1425
          DATA X80(14)/.50280411188878E+00/,W80(14)/.33733214984611E-01/      MOL        1426
          DATA X80(15)/.53614592089713E+00/,W80(15)/.32941939397645E-01/      MOL        1427
          DATA X80(16)/.56867126812270E+00/,W80(16)/.32100498673487E-01/      MOL        1428
          DATA X80(17)/.60033062282975E+00/,W80(17)/.31210174188114E-01/      MOL        1429
          DATA X80(18)/.63107577304687E+00/,W80(18)/.30272321759557E-01/      MOL        1430
          DATA X80(19)/.66085989898612E+00/,W80(19)/.29288369583267E-01/      MOL        1431
          DATA X80(20)/.68963764434202E+00/,W80(20)/.28259816057276E-01/      MOL        1432
          DATA X80(21)/.71736518536210E+00/,W80(21)/.27186227500486E-01/      MOL        1433
          DATA X80(22)/.74400029758360E+00/,W80(22)/.26075235767565E-01/      MOL        1434
          DATA X80(23)/.76950242013504E+00/,W80(23)/.24922535764115E-01/      MOL        1435
          DATA X80(24)/.79383271750460E+00/,W80(24)/.23731882865930E-01/      MOL        1436
          DATA X80(25)/.81695413868146E+00/,W80(25)/.22505090246332E-01/      MOL        1437
          DATA X80(26)/.83883147358025E+00/,W80(26)/.21244026115782E-01/      MOL        1438
          DATA X80(27)/.85943140666311E+00/,W80(27)/.19950610878142E-01/      MOL        1439
          DATA X80(28)/.87872256767821E+00/,W80(28)/.18626814208299E-01/      MOL        1440
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RUN-107    0        GLEGEN          76/04/09     20.13.03    PARKERZ2UR    PAGE NO. 27

      DATA X80(29)/.89667557943877E+00/,W80(29)/.17274652036269E-01/      MOL       1441
      DATA X80(30)/.91326310257175E+00/,W80(30)/.15896183583725E-01/      MOL       1442
      DATA X80(31)/.92845987717244E+00/,W80(31)/.14493508040509E-01/      MOL       1443
      DATA X80(32)/.94224276130987E+00/,W80(32)/.13068761592401E-01/      MOL       1444
      DATA X80(33)/.95459276634363E+00/,W80(33)/.11624114120798E-01/      MOL       1445
      DATA X80(34)/.96548508904380E+00/,W80(34)/.10161766041103E-01/      MOL       1446
      DATA X80(35)/.97490914058572E+00/,W80(35)/.86839452692607E-02/      MOL       1447
      DATA X80(36)/.98284857273863E+00/,W80(36)/.71929047681172E-02/      MOL       1448
      DATA X80(37)/.98929130249975E+00/,W80(37)/.56909224514031E-02/      MOL       1449
      DATA X80(38)/.99422754096568E+00/,W80(38)/.41803131246948E-02/      MOL       1450
      DATA X80(39)/.99764986439823E+00/,W80(39)/.26635335895127E-02/      MOL       1451
      DATA X80(40)/.99955382265162E+00/,W80(40)/.11449500031869E-02/      MOL       1452
C.....                                                                    MOL       1453
C.....ABSCISSAS AND WEIGHTS FOR THE GAUSS LEGENDRE INTEGRATION ORDER=96   MOL       1454
C.....                                                                    MOL       1455
      DATA X96( 1)/.16276744849603E-01/,W96( 1)/.32550614492362E-01/      MOL       1456
      DATA X96( 2)/.48812985136050E-01/,W96( 2)/.32516118713868E-01/      MOL       1457
      DATA X96( 3)/.81297495464425E-01/,W96( 3)/.32447163714064E-01/      MOL       1458
      DATA X96( 4)/.11369585011067E-00/,W96( 4)/.32343822568575E-01/      MOL       1459
      DATA X96( 5)/.14597371465490E-00/,W96( 5)/.32206204794030E-01/      MOL       1460
      DATA X96( 6)/.17809688236762E-00/,W96( 6)/.32034456231992E-01/      MOL       1461
      DATA X96( 7)/.21003131046057E-00/,W96( 7)/.31828758894410E-01/      MOL       1462
      DATA X96( 8)/.24174315616384E-00/,W96( 8)/.31589330770726E-01/      MOL       1463
      DATA X96( 9)/.27319881259105E-00/,W96( 9)/.31316425596861E-01/      MOL       1464
      DATA X96(10)/.30436494435449E-00/,W96(10)/.31010332586313E-01/      MOL       1465
      DATA X96(11)/.33520852289262E-00/,W96(11)/.30671376123669E-01/      MOL       1466
      DATA X96(12)/.36569686147231E-00/,W96(12)/.30299915420827E-01/      MOL       1467
      DATA X96(13)/.39579764982891E-00/,W96(13)/.29896344136328E-01/      MOL       1468
      DATA X96(14)/.42547898840730E-00/,W96(14)/.29461089958167E-01/      MOL       1469
      DATA X96(15)/.45470942216774E-00/,W96(15)/.28994614150555E-01/      MOL       1470
      DATA X96(16)/.48345797392059E-00/,W96(16)/.28497411065085E-01/      MOL       1471
      DATA X96(17)/.51169417715466E+00/,W96(17)/.27970007616848E-01/      MOL       1472
      DAYA X96(18)/.53938810832436E+00/,W96(18)/.27412962726029E-01/      MOL       1473
      DATA X96(19)/.56651041856139E+00/,W96(19)/.26826866725591E-01/      MOL       1474
      DATA X96(20)/.59303236477757E+00/,W96(20)/.26212340735672E-01/      MOL       1475
      DATA X96(21)/.61892584012547E+00/,W96(21)/.25570036005349E-01/      MOL       1476
      DATA X96(22)/.64416340378496E+00/,W96(22)/.24900633222483E-01/      MOL       1477
      DATA X96(23)/.66871831004391E+00/,W96(23)/.24204841792364E-01/      MOL       1478
      DATA X96(24)/.69256453664217E+00/,W96(24)/.23483399085926E-01/      MOL       1479
      DATA X96(25)/.71567681234897E+00/,W96(25)/.22737069658329E-01/      MOL       1480
      DATA X96(26)/.73803064374440E+00/,W96(26)/.21966644438744E-01/      MOL       1481
      DATA X96(27)/.75960234117665E+00/,W96(27)/.21172939892191E-01/      MOL       1482
      DATA X96(28)/.78036904386743E+00/,W96(28)/.20356797154333E-01/      MOL       1483
      DATA X96(29)/.80030874413914E+00/,W96(29)/.19519081140145E-01/      MOL       1484
      DATA X96(30)/.81940031073792E+00/,W96(30)/.18660679627411E-01/      MOL       1485
      DATA X96(31)/.83762351122818E+00/,W96(31)/.17782502316045E-01/      MOL       1486
      DATA X96(32)/.85495903343460E+00/,W96(32)/.16885479864245E-01/      MOL       1487
      DATA X96(33)/.87138850590929E+00/,W96(33)/.15970562902562E-01/      MOL       1488
      DATA X96(34)/.88689451740241E+00/,W96(34)/.15038721026995E-01/      MOL       1489
      DATA X96(35)/.90146063531585E+00/,W96(35)/.14090941772315E-01/      MOL       1490
      DATA X96(36)/.91507142312090E+00/,W96(35)/.13128229566961E-01/      MOL       1491
      DATA X96(37)/.92771245672231E+00/,W96(37)/.12151604671088E-01/      MOL       1492
      DATA X96(38)/.93937033975275E+00/,W96(38)/.11162102099838E-01/      MOL       1493
      DATA X96(39)/.95003271778443E+00/,W96(39)/.10160770535008E-01/      MOL       1494
      DATA X96(40)/.95968829144874E+00/,W96(40)/.91486712307833E-02/      MOL       1495
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RUN-107   0        CLEGEN         76/04/09     20.13.03    PARKERZZUR   PAGE NO. 28
             DATA X96(41)/.96532682846326E+00/,W96(41)/.81268769256987E-02/   MOL       1496
             DATA X96(42)/.97593917458513E+00/,W96(42)/.70964707911538E-02/   MOL       1497
             DATA X96(43)/.98251726356301E+00/,W96(43)/.60595455042359E-02/   MOL       1498
             DATA X96(44)/.98805412632962E+00/,W96(44)/.50142027429275E-02/   MOL       1499
             DATA X96(45)/.99254390032376E+00/,W96(45)/.39645543384446E-02/   MOL       1500
             DATA X96(46)/.99598184298720E+00/,W96(46)/.29107318179349E-02/   MOL       1501
             DATA X96(47)/.99836437586318E+00/,W96(47)/.18539607889469E-02/   MOL       1502
             DATA X96(48)/.99968950388323E+00/,W96(48)/.79679206555201E-03/   MOL       1503
      C.....                                                                  MOL       1504
      C.....                                                                  MOL       1505
 14          T1=(B-A)/2.0                                                     MOL       1506
 14          T2=(B+A)/2.0                                                     MOL       1507
 17          IF(NPT-1)50,70,10                                                MOL       1508
 22       10 IF(NPT.GT.64)GO TO 20                                            MOL       1509
 26          IC=NPT*NPT/4+(NPT+1)/2-1                                         MOL       1510
 32          GO TO 30                                                         MOL       1511
 33       20 IF(NPT.NE.80.AND.NPT.NE.96)GO TO 50                              MOL       1512
 43          IC=1095                                                          MOL       1513
 43          IF(NPT.EQ.96)IC=1143                                             MOL       1514
 46       30 N2=(NPT+1)/2                                                     MOL       1515
 46          I1=1                                                             MOL       1516
 46          I2=NPT                                                           MOL       1517
 52          DO 40 I=1,N2                                                     MOL       1518
 62          XPT(I1)=-X(IC)*T1+T2                                             MOL       1519
 62          XPT(I2)=X(IC)*T1+T2                                              MOL       1520
 62          WHT(I1)=W(IC)*T1                                                 MOL       1521
 62          WHT(I2)=WHT(I1)                                                  MOL       1522
 62          I1=I1+1                                                          MOL       1523
 62          I2=I2-1                                                          MOL       1524
 62       40 IC=IC-1                                                          MOL       1525
100          RETURN                                                           MOL       1526
101       50 WRITE(6,60)NPT                                                   MOL       1527
          60 FORMAT(1H0,50H***** WARNING, GAUSS-LEGENDRE REQUESTED WITH NPT= ,  MOL       1528
            1 I6)                                                             MOL       1529
112          NPT=1                                                            MOL       1530
113       70 XPT(1)=T2                                                        MOL       1531
113          WHT(1)=2.0*T1                                                    MOL       1532
117          RETURN                                                           MOL       1533
117          END                                                              MOL       1534
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    RUN-107     0                   76/04/09     20.11.03     PARKERZZUR    PAGE NO. 1

              FUNCTION PLM(L,MM,X)                                         MOL       1535
      C                                                                    MOL       1536
      C                                                                    MOL       1537
      C       PURPOSE                                                      MOL       1538
      C       COMPUTES NORMALIZED ASSOCIATED LEGENDRE POLYNOMIALS BY RECURSION.  MOL   1539
      C                                                                    MOL       1540
      C       DESCRIPTION OF PARAMETERS                                    MOL       1541
      C          MM-MAGNETIC QUANTUM NUMBER.                               MOL       1542
      C          L-SUBSIDIARY QUANTUM NUMBER.                              MOL       1543
      C          X-COSINE OF THETA.                                        MOL       1544
      C                                                                    MOL       1545
      C       SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                MOL       1546
      C          NONE.                                                     MOL       1547
      C                                                                    MOL       1548
      C       METHOD                                                       MOL       1549
      C       IN ACCORD WITH MCLEAN AND YOSHEMINE CONVENTION.              MOL       1550
      C       EACH PLN IS NORMALIZED TO 1.0 ON (-1.,1.).                   MOL       1551
      C       PROGRAM OF R. NERF MODIFIED BY S. GREEN.                     MOL       1552
      C                                                                    MOL       1553
 10           M=IABS(MM)                                                   MOL       1554
      C                                                                    MOL       1555
      C       COMPUTE GENERAL CASE BY RECURSION UPWARDS IN L AND ACROSS IN M.  MOL     1556
      C                                                                    MOL       1557
           10 FORMAT(1H0,42H**** ERROR, ARGUMENT OUT OF RANGE FOR PLM(,2I6  MOL      1558
             1       ,E21.14,3H ).)                                        MOL       1559
      C                                                                    MOL       1560
 11        20 XL=FLOAT(L)                                                  MOL       1561
 12           IF(M.GT.L.OR.L.LT.0)GO TO 90                                 MOL       1562
 21           P1=1.E0                                                      MOL       1563
 21           P2=X                                                         MOL       1564
 23           IF(L.EQ.0)GO TO 60                                           MOL       1565
 24           DO 30 I=1,L                                                  MOL       1566
 31           XI=FLOAT(I)                                                  MOL       1567
 31           P3=((2.E0*XI+1.E0)*X*P2-XI*P1)/(XI+1.E0)                     MOL       1568
 31           P1=P2                                                        MOL       1569
 31        30 P2=P3                                                        MOL       1570
 43           IF(M.EQ.0)GO TO 60                                           MOL       1571
      C                                                                    MOL       1572
      C       AT END OF LOOP P1=P(L,0,X)                                   MOL       1573
      C                                                                    MOL       1574
 46           IF(ABS(X).GT.1.0)WRITE(6,10)L,MM,X                           MOL       1575
 65           Z=SQRT(ABS(1.E0-X*X))                                        MOL       1576
 70           IF(Z.GT.1.E-6)GO TO 40                                       MOL       1577
      C                                                                    MOL       1578
      C       IF Z=0, THEN X=1 AND PLM(1.)=0 FOR M.GT.0.                   MOL       1579
      C                                                                    MOL       1580
100           PLM=0.E0                                                     MOL       1581
100           RETURN                                                       MOL       1582
101        40 P2=(XL+1.E0)*(P2-X*P1)/Z                                     MOL       1583
107           DO 50 I=1,M                                                  MOL       1584
120           XI=FLOAT(I)                                                  MOL       1585
120           P3=-2.E0*X/Z*P2*XI-(XL+XI)*(XL-XI+1.E0)*P1                   MOL       1586
120           P1=P2                                                        MOL       1587
120        50 P2=P3                                                        MOL       1588
      C                                                                    MOL       1589
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       C      NORMALIZATION.....                                                  MOL       1590
       C                                                                          MOL       1591
134        60 XNORM=(2.E0*XL+1.E0)/2.E0                                           MOL       1592
140           IF(M.LE.0)GO TO 80                                                  MOL       1593
142           XLM=XL+1.E0                                                         MOL       1594
142           XLP=XL                                                              MOL       1595
144           DO 70 I=1,M                                                         MOL       1596
152           XLM=XLM-1.E0                                                        MOL       1597
152           XLP=XLP+1.E0                                                        MOL       1598
152        70 XNORM=XNORM/(XLM*XLP)                                               MOL       1599
161        80 PLM=P1*SQRT(XNORM)                                                  MOL       1600
165           RETURN                                                              MOL       1601
165        90 WRITE(6,10)L,MM,X                                                   MOL       1602
177           PLM=0.E0                                                            MOL       1603
200           RETURN                                                              MOL       1604
201           END                                                                 MOL       1605
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          FUNCTION REP(N,L,M,ZETA,R,COSX)                               MOL     1606
      C                                                                 MOL     1607
      C                                                                 MOL     1608
      C   PURPOSE                                                       MOL     1609
      C      EVALUATION OF NORMALIZED SLATER TYPE BASIS FUNCTIONS       MOL     1610
      C                                                                 MOL     1611
      C   DESCRIPTION OF PARAMETERS                                     MOL     1612
      C      N-PRINCIPAL QUANTUM NUMBER                                 MOL     1613
      C      L-SUBSIDIARY QUANTUM NUMBER                                MOL     1614
      C      ZETA-ORBITAL EXPONENT                                      MOL     1615
      C      R-RADIAL DISTANCE                                          MOL     1616
      C      COSX-COSINE OF THE ANGLE THETA                             MOL     1617
      C                                                                 MOL     1618
      C   SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                 MOL     1619
      C      PLM                                                        MOL     1620
      C                                                                 MOL     1621
      C                                                                 MOL     1622
16        REAL NORM                                                     MOL     1623
16        DIMENSION FACT(8)                                             MOL     1624
          DATA FACT(1)/0.2E1/                                           MOL     1625
          DATA FACT(2)/0.24E2/                                          MOL     1626
          DATA FACT(3)/0.72E3/                                          MOL     1627
          DATA FACT(4)/0.4032E5/                                        MOL     1628
          DATA FACT(5)/0.36288E7/                                       MOL     1629
          DATA FACT(6)/0.4790016E9/                                     MOL     1630
          DATA FACT(7)/0.871782912E11/                                  MOL     1631
          DATA FACT(8)/0.20922789888E14/                                MOL     1632
      C                                                                 MOL     1633
16        K=2*N+1                                                       MOL     1634
16        NORM=1.0                                                      MOL     1635
      C                                                                 MOL     1636
      C      CALCULATE THE NORMALIZATION CONSTANT                       MOL     1637
      C                                                                 MOL     1638
21        DO 10 J=1,K                                                   MOL     1639
30     10 NORM=NORM*2.0*ZETA                                            MOL     1640
32        NORM=NORM/FACT(N)                                             MOL     1641
37        NORM=SQRT(NORM)                                               MOL     1642
      C                                                                 MOL     1643
      C      MULTIPLY BY THE ASSOCIATED LEGENDRE POLYNOMIAL             MOL     1644
      C                                                                 MOL     1645
41        REP=NORM*EXP(-ZETA*R)*PLM(L,M,COSX)                           MOL     1646
60        IF(N.GT.1)REP=REP*R**(N-1)                                    MOL     1647
70        RETURN                                                        MOL     1648
76        END                                                           MOL     1649
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      SUBROUTINE RHOMOL(COST  ,ELCDEN,NNUC  ,NRINT ,NTI   ,XR    ,          MOL      1650
     1                  SINT  ,ZNUC  ,ZN    ,IREAD )                        MOL      1651
C                                                                           MOL      1652
C                                                                           MOL      1653
C     PURPOSE                                                               MOL      1654
C        THE CHARGE DENSITY FOR LINEAR CLOSED SHELL MOLECULES.              MOL      1655
C                                                                           MOL      1656
C     DESCRIPTION OF PARAMETERS                                             MOL      1657
C        COST=COSINE OF THE THETA ANGLES                                    MOL      1658
C        ELCDEN=MATRIX OF THE ELECTRON DENSITY                              MOL      1659
C        NNUC=NUMBER OF NUCLEI                                              MOL      1660
C        NRINT=NUMBER OF RADIAL DISTANCES                                   MOL      1661
C        NTI=NUMBER OF THETA ANGLES                                         MOL      1662
C        XR=RADIAL DISTANCES                                                MOL      1663
C        SINT=SINE OF THE THETA ANGLES                                      MOL      1664
C        ZNUC=NUCLEAR CHARGES                                               MOL      1665
C        ZN=NUCLEAR POSITIONS                                               MOL      1666
C        IREAD=0 IF IT IS NOT NECESSARY TO READ IN NEW DATA                 MOL      1667
C                                                                           MOL      1668
C     SUBROUTINES AND FUNCTION SUSPROGRAMS REQUIRED                         MOL      1669
C        REP                                                                MOL      1670
C                                                                           MOL      1671
C     METHOD                                                                MOL      1672
C        THE ELECTRON DENSITY IS STORED IN ELCDEN                           MOL      1673
C                                                                           MOL      1674
C     DATA TO BE READ IN IF IREAD IS NOT EQUAL TO 0                         MOL      1675
C     CARD 1                                                                MOL      1676
C        TITLE (A 1 IN COLUMN 1 FOLLOWED BY THE TITLE)                      MOL      1677
C     CARD 2                                                                MOL      1678
C        NUMBER OF NUCLEI                                                   MOL      1679
C     CARD 3                                                                MOL      1680
C        NUCLEAR MASSES                                                     MOL      1681
C     CARD 4                                                                MOL      1682
C        THE DISTANCES BETWEEE THE NUCLEI                                   MOL      1683
C        THE DISTANCES BETWEEENTHE NUCLEI                                   MOL      1684
C        THE DISTANCES BETWEEN THE NUCLEI                                   MOL      1685
C     CARD 5                                                                MOL      1686
C        THE CHEMICAL SYMBOLS                                               MOL      1687
C     CARD 6                                                                MOL      1688
C        THE NUCLEAR CHARGES                                                MOL      1689
C     CARD 7---                                                             MOL      1690
C        PRINCIPAL QUANTUM NUMBER,SUBSIDARY QUANTUM NUMBER,ATOM,SIGN,       MOL      1691
C        ATOM,ORBITAL EXPONENT,COEFFICIENT (I1,A1,I1,A1,2X,I1,3X,           MOL      1692
C        F13.6,7F10.5)                                                      MOL      1693
22    DIMENSION XR(1),SINT(1),COST(1),ZN(1),ZNUC(1),ELCDEN(NRINT,NTI)       MOL      1694
22    DIMENSION RR(20),CTHET(20)                                            MOL      1695
22    DIMENSION NS(40),LS(40),KS(40),ZETAS(40),CS(40,7)                     MOL      1696
22    DIMENSION NU(40),LU(40),KU(40),ZETAU(40),CU(40,7)                     MOL      1697
22    DIMENSION NP(20),LP(20),KP(20),ZETAP(20),CP(20,5)                     MOL      1698
22    DIMENSION NA(20),LA(20),KA(20),ZETAA(20),CA(20,5)                     MOL      1699
22    DIMENSION JS(40),IS(40)                                               MOL      1700
22    DIMENSION JU(40),IU(40)                                               MOL      1701
22    DIMENSION JP(20),IP(20)                                               MOL      1702
22    DIMENSION JA(20),IA(20)                                               MOL      1703
22    DIMENSION LTYP(4)                                                     MOL      1704
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 22          DIMENSION SYMBOL(20)                                                  MOL        1705
 22          DIMENSION ZMAS(20)                                                    MOL        1706
       C                                                                           MOL        1707
       C                                                                           MOL        1708
       C                                                                           MOL        1709
             DATA PI/3,1415926535898/                                              MOL        1710
             DATA PI2/1,5707963267949/                                             MOL        1711
             DATA IPLUS/1H+/                                                       MOL        1712
             DATA INEG/1H-/                                                        MOL        1713
             DATA IBLNK/1H /                                                       MOL        1714
             DATA LTYP(1)/1HS/                                                     MOL        1715
             DATA LTYP(2)/1HP/                                                     MOL        1716
             DATA LTYP(3)/1HD/                                                     MOL        1717
             DATA LTYP(4)/1HF/                                                     MOL        1718
             DATA TWOPI/6,2831853071796/                                           MOL        1719
 22          IF(IREAD,EQ,0)GO TO 190                                               MOL        1720
       C                                                                           MOL        1721
       C        READ IN THE NUMBER OF NUCLEI                                       MOL        1722
       C                                                                           MOL        1723
 23          READ(5,370)                                                           MOL        1724
 27          WRITE(6,370)                                                          MOL        1725
 36          READ(5,410)NNUC                                                       MOL        1726
 47          WRITE(6,400)NNUC                                                      MOL        1727
       C                                                                           MOL        1728
       C        READ IN THE NUCLEAR POSITIONS AND CHARGES,                         MOL        1729
       C                                                                           MOL        1730
 60          READ(5,450)(ZMAS(KN),KN=1,NNUC)                                       MOL        1731
 75          READ(5,450)(ZNUC(KN),KN=1,NNUC)                                       MOL        1732
112          READ(5,470)(SYMBOL(I),I=1,NNUC)                                       MOL        1733
127          WRITE(6,500)                                                          MOL        1734
136          WRITE(6,480)(SYMBOL(I),I=1,NNUC)                                      MOL        1735
153          READ(5,450)(ZN(I),I=2,NNUC)                                           MOL        1736
171          WRITE(6,490)(ZN(I),I=2,NNUC)                                          MOL        1737
207          ZCM=0,0                                                               MOL        1738
207          ZN(1)=0.0                                                             MOL        1739
207          Z=0,0                                                                 MOL        1740
207          AMASS=0.0                                                             MOL        1741
213          DO 10 I=1,NNUC                                                        MOL        1742
225          Z=Z+ZN(I)                                                             MOL        1743
225          AMASS=AMASS+ZMAS(I)                                                   MOL        1744
225       10 ZCM=ZCM+ZMAS(I)*Z                                                     MOL        1745
233          ZCM=ZCM/AMASS                                                         MOL        1746
233          Z=0,0                                                                 MOL        1747
235          DO 20 I=1,NNUC                                                        MOL        1748
245          Z=Z+ZN(I)                                                             MOL        1749
245       20 ZN(I)=Z-ZCM                                                           MOL        1750
251          WRITE(6,380)                                                          MOL        1751
260          DO 30 I=1,NNUC                                                        MOL        1752
265       30 WRITE(6,390)I,ZN(I),ZMAS(I),ZNUC(I)                                   MOL        1753
       C                                                                           MOL        1754
       C        READ IN THE NUMBER OF SIGMA TYPE ORBITALS, NUMBER OF               MOL        1755
       C        SIGMA TYPE BASIS FUNCTIONS, NUMBER OF PI TYPE ORBITALS             MOL        1756
       C        AND THE NUMBER OF PI TYPE BASIS FUNCTIONS,                         MOL        1757
311          READ(5,410)NSIG,NBSIG,NPI,NBPI,NSIU,NBSIU,NPU,NBPU                    MOL        1758
334          WRITE(6,550)NSIG,NBSIG,NPI,NBPI,NSIU,NBSIU,NPU,NBPU                   MOL        1759
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       RUN-107     0          RHOMOL            76/04/09      20.13.03     PARKERZ2UR    PAGE NO. 3

       C                                                                         MOL        1760
       C          READ IN THE I-TH BASIS FUNCTION                                MOL        1761
       C                                                                         MOL        1762
 363              WRITE(6,510)                                                   MOL        1763
 372              WRITE(6,570)(IO,IO=1,NSIG)                                     MOL        1764
 407              DO 60 I=1,NBSIG                                                MOL        1765
 414              READ(5,420)NS(I),LTYPE,KS(I),ISIGS,JS(I),ZETAS(I),(CS(I,J),J=1,NSI MOL        1766
                 1G)                                                             MOL        1767
 453              IF(ISIGS.EQ.IPLUS)IS(I)=1                                      MOL        1768
 463              IF(ISIGS.EQ.INEG)IS(I)=-1                                      MOL        1769
 467              IF(ISIGS.EQ.IBLNK)IS(I)=0                                      MOL        1770
 473              DO 40 LT=1,4                                                   MOL        1771
 475           40 IF(LTYPE.EQ.LTYP(LT))LS(I)=LT-1                                MOL        1772
 505              IF(ISIGS.EQ.IBLNK)GO TO 50                                     MOL        1773
 507              WRITE(6,430)NS(I),LTYPE,KS(I),ISIGS,NS(I),LTYPE,JS(I),ZETAS(I),    MOL        1774
                 1  (CS(I,J),J=1,NSIG)                                           MOL        1775
 554              GO TO 60                                                       MOL        1776
 560           50 WRITE(6,560)NS(I),LTYPE,KS(I),ZETAS(I),(CS(I,J),J=1,NSIG)       MOL        1777
 617           60 CONTINUE                                                       MOL        1778
 622              IF(NBSIU.EQ.0)GO TO 100                                        MOL        1779
 623              WRITE(6,520)                                                   MOL        1780
 626              WRITE(6,570)(IO,IO=1,NSIU)                                     MOL        1781
 643              DO 90 I=1,NBSIU                                                MOL        1782
 650              READ(5,420)NU(I),LTYPE,KS(I),ISIGS,JS(I),ZETAU(I),(CU(I,J),J=1,NSI MOL        1783
                 1U)                                                             MOL        1784
 707              IF(ISIGS.EQ.IPLUS)IU(I)=1                                      MOL        1785
 717              IF(ISIGS.EQ.INEG)IU(I)=-1                                      MOL        1786
 723              IF(ISIGS.EQ.IBLNK)IU(I)=0                                      MOL        1787
 727              DO 70 LT=1,4                                                   MOL        1788
 731           70 IF(LTYPE.EQ.LTYP(LT))LU(I)=LT-1                                MOL        1789
 741              IF(ISIGS.EQ.IBLNK)GO TO 80                                     MOL        1790
 743              WRITE(6,430)NU(I),LTYPE,KU(I),ISIGS,NS(I),LTYPE,JU(I),ZETAU(I),    MOL        1791
                 1  (CU(I,J),J=1,NSIU)                                           MOL        1792
1010              GO TO 90                                                       MOL        1793
1014           80 WRITE(6,560)NU(I),LTYPE,KU(I),ZETAU(I),(CU(I,J),J=1,NSIU)       MOL        1794
1053           90 CONTINUE                                                       MOL        1795
1056          100 CONTINUE                                                       MOL        1796
1056              IF(NPO.EQ.0)GO TO 140                                          MOL        1797
1060              WRITE(6,530)                                                   MOL        1798
1063              WRITE(6,570)(IO,IO=1,NPO)                                      MOL        1799
1100              DO 130 I=1,NBPI                                                MOL        1800
1105              READ(5,420)NP(I),LTYPE,KP(I),ISIGS,JP(I),ZETAP(I),(CP(I,J),J=1,NPO MOL        1801
                 1)                                                              MOL        1802
1144              IF(ISIGS.EQ.IPLUS)IP(I)=1                                      MOL        1803
1154              IF(ISIGS.EQ.INEG)IP(I)=-1                                      MOL        1804
1160              IF(ISIGS.EQ.IBLNK)IP(I)=0                                      MOL        1805
1164              DO 110 LT=1,4                                                  MOL        1806
1166          110 IF(LTYPE.EQ.LTYP(LT))LP(I)=LT-1                                MOL        1807
1176              IF(ISIGS.EQ.IBLNK)GO TO 120                                    MOL        1808
1200              WRITE(6,430)NP(I),LTYPE,KP(I),ISIGS,NP(I),LTYPE,JP(I),ZETAP(I),    MOL        1809
                 1  (CP(I,J),J=1,NPO)                                            MOL        1810
1251          120 WRITE(6,560)NP(I),LTYPE,KP(I),ZETAP(I),(CP(I,J),J=1,NPO)        MOL        1811
1310          130 CONTINUE                                                       MOL        1812
1312          140 CONTINUE                                                       MOL        1813
1312              IF(NBPU.EQ.0)GO TO 180                                         MOL        1814
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        RUN=107     0          RHOMOL           76/04/09      20.13.03     PARKERZZUR    PAGE NO. 4

1314            WRITE(6,540)
1317            WRITE(6,570)(IO,IO=1,NPU)
1334            DO 170 I=1,NBPU
1341            READ(5,420)NA(I),LTYPE,KA(I),ISIGS,JA(I),ZETAA(I),(CA(I,J),J=1,NPU
               1)
1400            IF(ISIGS.EQ.IPLUS)IA(I)=1
1410            IF(ISIGS.EQ.INEG)IA(I)=-1
1414            IF(ISIGS.EQ.IBLNK)IA(I)=0
1420            DO 150 LT=1,4
1422        150 IF(LTYPE.EQ.LTYP(LT))LA(I)=LT-1
1432            IF(ISIGS.EQ.IBLNK)GO TO 160
1434            WRITE(6,430)NA(I),LTYPE,KA(I),ISIGS,NA(I),LTYPE,JP(I),ZETAP(I),
               1  (CA(I,J),J=1,NPU)
1501            GO TO 170
1505        160 WRITE(6,560)NA(I),LTYPE,KA(I),ZETAA(I),(CA(I,J),J=1,NPU)
1544        170 CONTINUE
1547        180 CONTINUE
1547        190 DO 360 JTH=1,NTI
1551            STHETA=SINT(JTH)
1551            CTHETA=COST(JTH)
1554            DO 340 IKR=1,NRINT
1556            R1=XR(IKR)
1556            YO=R1*STHETA
1555            ZO=R1*CTHETA
1563            DO 200 NN=1,NNUC
1564            RR(NN)=SQRT(ABS(YO*YO+(ZO-ZN(NN))*(ZO-ZN(NN))))
1574            CTHET(NN)=(ZO-ZN(NN))/RR(NN)
1606        200 CONTINUE
1610            RHO=0.0
          C
          C         SUM OVER THE SIGMA ORBITALS
          C
1611            DO 230 J=1,NSIG
1612            ORB=0.0
          C
          C         SUM OVER THE SIGMA BASIS FUNCTIONS
          C
1613            DO 220 I=1,NBSIG
1614            IF(IS(I).EQ.0)GO TO 210
1616            KJ=JS(I)
1620            ORB=ORB+REP(NS(I),LS(I),0,ZETAS(I),RR(KJ  ),CTHET(KJ  ))*CS(I,J)*
               1FLOAT(IS(I))
1650        210 CONTINUE
1650            KI=KS(I)
1652        220 ORB=ORB+REP(NS(I),LS(I),0,ZETAS(I),RR(KI  ),CTHET(KI  ))*CS(I,J)
          C
          C         SQUARE THE ORBITALS AND MULTIPLY BY THE OCCUPATION NUMBER
          C
1704        230 RHO=RHO+ORB*ORB*2.0
1712            IF(NSIU.EQ.0)GO TO 270
1713            DO 260 J=1,NSIU
1714            ORB=0.0
1715            DO 250 I=1,NBSIU
1716            IF(IU(I).EQ.0)GO TO 240
1720            KJ=JU(I)
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1722          ORB=ORB+REP(NU(I),LU(I),0,ZETAU(I),RR(KJ  ),CTHET(KJ   ))*CU(I,J)*  MOL
             1FLOAT(IS(I))                                                          MOL
1754      240 CONTINUE                                                              MOL
1755          KI=KU(I)                                                              MOL
1756      250 ORB=ORB+REP(NU(I),LU(I),0,ZETAU(I),RR(KI  ),CTHET(KI   ))*CU(I,J)   MOL
2010      260 RHO=RHO+ORB*ORB*2.0                                                   MOL
2015      270 CONTINUE                                                              MOL
        C                                                                           MOL
        C          SUM OVER THE PI ORBITALS                                         MOL
        C                                                                           MOL
2015          IF(NPO.EQ.0)GO TO 310                                                 MOL
2017          DO 300 J=1,NPO                                                        MOL
2020          ORB=0.0                                                               MOL
        C                                                                           MOL
        C          SUM OVER THE PI BASIS FUNCTIONS                                  MOL
        C                                                                           MOL
2021          DO 290 I=1,NBPI                                                       MOL
2022          IF(IP(I).EQ.0)GO TO 280                                               MOL
2024          KJ=JP(I)                                                              MOL
2026          ORB=ORB+REP(NP(I),LP(I),1,ZETAP(I),RR(KJ  ),CTHET(KJ   ))*CP(I,J)*  MOL
             1FLOAT(IP(I))                                                          MOL
2056      280 CONTINUE                                                              MOL
2056          KI=KP(I)                                                              MOL
2060      290 ORB=ORB+REP(NP(I),LP(I),1,ZETAP(I),RR(KI  ),CTHET(KI   ))*CP(I,J)   MOL
        C                                                                           MOL
        C          SQUARE THE ORBITALS AND MULTIPLY BY THE OCCUPATION NUMBER        MOL
        C                                                                           MOL
2112      300 RHO=RHO+ORB*ORB*4.0                                                   MOL
2117      310 IF(NPU.EQ.0)GO TO 350                                                 MOL
2121          DO 340 J=1,NPU                                                        MOL
2122          ORB=0.0                                                               MOL
2123          DO 330 I=1,NBPU                                                       MOL
2124          IF(IA(I).EQ.0)GO TO 320                                               MOL
2126          KJ=JA(I)                                                              MOL
2130          ORB=ORB+REP(NA(I),LA(I),1,ZETAA(I),RR(KJ  ),CTHET(KJ   ))*CA(I,J)*  MOL
             1FLOAT(IA(I))                                                          MOL
2160      320 CONTINUE                                                              MOL
2160          KI=KA(I)                                                              MOL
2162      330 ORB=ORB+REP(NA(I),LA(I),1,ZETAA(I),RR(KI  ),CTHET(KI   ))*CA(I,J)   MOL
2214      340 RHO=RHO+ORB*ORB*4.0                                                   MOL
2221      350 CONTINUE                                                              MOL
2221      360 ELCDEN(IKR,JTH)=RHO/TWOPI                                             MOL
2232          RETURN                                                                MOL
        C                                                                           MOL
        C                                                                           MOL
          370 FORMAT(40H                                                            MOL
             1 40H                                                                  MOL
          380 FORMAT(1H0,3X,4HATOM,5X,12HZ-COORDINATE,5X,13HATOMIC WEIGHT,          MOL
             15X,14HNUCLEAR CHARGE)                                                 MOL
          390 FORMAT(1H ,2X,I2,7X,3F14.9)                                           MOL
          400 FORMAT(1H0,21HTHE NUMBER OF NUCLEI  ,3X,I5)                           MOL
          410 FORMAT(8I5)                                                           MOL
          420 FORMAT(I1,A1,I1,A1,2X,I1,3X,F10.6,7F10.5)                             MOL
          430 FORMAT(1H ,I1,A1,I1,A1,I1,A1,I1,3X,7F10.5)                            MOL
          440 FORMAT(1H ,4I5)                                                       MOL
```

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        RUN-107    0        RHOMOL          76/04/09     20.13.03     PARKER22UR    PAGE NO. 6

          450 FORMAT(4F10.5)                                                        MOL         1925
          460 FORMAT(1H ,4F10.5)                                                    MOL         1926
          470 FORMAT(20A2)                                                          MOL         1927
          480 FORMAT(1H ,9(6X,A2,6X))                                               MOL         1928
          490 FORMAT(1H ,7X,8(1H*,1X,F10.5,2X))                                     MOL         1929
          500 FORMAT(1H0,8HGEOMETRY)                                                MOL         1930
          510 FORMAT(1H0,14HSIGMA SYMMETRY ,/)                                      MOL         1931
          520 FORMAT(1H0,23HSIGMA UNGERADE SYMMETRY ,/)                             MOL         1932
          530 FORMAT(1H0,11HPI SYMMETRY ,/)                                         MOL         1933
          540 FORMAT(1H0,20HPI UNGERADE SYMMETRY ,/)                                MOL         1934
          550 FORMAT(/,25H NUMBER OF SIGMA ORBITALS,I5,                             MOL         1935
             1/45H NUMBER OF BASIS FUNCTIONS FOR SIGMA ORBITALS,I5,                 MOL         1936
             2 /22H NUMBER OF PI ORBITALS,I5,                                       MOL         1937
             3 /42H NUMBER OF BASIS FUNCTIONS FOR PI ORBITALS,I5,                   MOL         1938
             4 /34H NUMBER OF SIGMA UNGERADE ORBITALS,I5,                           MOL         1939
             5/54H NUMBER OF BASIS FUNCTIONS FOR SIGMA UNGERADE ORBITALS,I5,        MOL         1940
             6 /31H NUMBER OF PI UNGERADE ORBITALS,I5,                              MOL         1941
             7 /51H NUMBER OF BASIS FUNCTIONS FOR PI UNGERADE ORBITALS,I5)          MOL         1942
          560  FORMAT(1H ,I1,A1,I1,7X,10F10.6)                                      MOL         1943
          570 FORMAT(4H NLK,9X,8HEXPONENT,I8,6I10)                                  MOL         1944
 2233         END                                                                   MOL         1945
```

Sample output using LMOLMO. This sample run calculates the electron gas potential between two HF molecules.

```
HYDROGEN FLUORIDE

28 BASIS FUNCTIONS,Z-COORDINATE =    -.08729,NUCLEAR CHARGE =  9.0

  N     L     ZETA         COEFF
  3     0  11.20007 -.1408299E+04
  3     0   9.87840  .1158758E+04
  4     0  17.86914  .4023174E+04
  3     0   5.68544 -.4870859E+02
  3     2   5.68544 -.9741719E+02
  3     0   8.55686 -.5221206E+02
  3     2   8.55686 -.1044240E+03
  1     0  15.88748  .2833941E+03
  1     0  22.05320  .1680531E+03
  3     0   5.19098  .2451414E+02
  3     0   6.51266 -.4606536E+01
  3     0   2.81402  .1161248E+00
  3     2   2.81402  .2322495E+00
  3     0   3.78026  .3600384E+01
  3     2   3.78026  .7200769E+01
  3     0   4.74650 -.1784759E+02
  3     2   4.74650 -.3569519E+02
  3     0   6.65168  .7649703E+02
  3     2   6.65168  .1529941E+03
  3     0   2.71672  .2278555E+00
  3     2   2.71672 -.2278556E+00
  3     0   3.68748  .8843553E+01
  3     2   3.68748 -.8843553E+01
  3     0   4.65824 -.4113930E+02
  3     2   4.65824  .4113930E+02
  2     1   4.30790 -.5530379E+02
  2     1   5.62958  .7416267E+02
  3     1   3.34166 -.1008724E+01

 9 BASIS FUNCTIONS,Z-COORDINATE =    1.64551,NUCLEAR CHARGE =  1.0

  N     L     ZETA         COEFF
  1     0   2.74538  .1900348E+00
  2     0   3.83317  .4533139E+00
  3     0   3.00000  .2125173E-01
  3     2   3.00000 -.2125173E-01
  3     0   3.57122 -.8331737E-01
  3     2   3.57122  .8331737E-01
  2     1   4.29531 -.1099739E+01
  2     1   5.38310  .1046355E+01
  3     1   5.38409  .5379890E+00

 6 BASIS FUNCTIONS,Z-COORDINATE =   -0.00000,NUCLEAR CHARGE =  0.0

  N     L     ZETA         COEFF
  2     1   3.74594  .1357075E+02
  2     1   2.77970  .6535777E+00
  2     1   5.65112 -.5056750E+01
  2     0   4.62902  .1397906E+03
```

```
  2     0    3.30734 -.7293302E+01
  2     0    5.71681 -.1652621E+03

 6 BASIS FUNCTIONS,Z-COORDINATE =    1.04000,NUCLEAR CHARGE =  0.0

  N     L     ZETA         COEFF
  3     0    7.00000   .6048218E+01
  3     0    7.00000   .2143273E+01
  3     2    7.00000   .4286546E+01
  3     0    4.00000 -.7519484E-01
  3     2    4.00000 -.1503897E+00
  3     0    4.00000   .8562901E+00

MOMENTS IN ATOMIC UNITS

   MONOPOLE          DIPOLE        QUADRUPOLE       OCTAPOLE     HEXADECAPOLE

 -.7569298E-02  .7547643E+00  .1735125E+01  .2583110E+01  .4926913E+01
```

```
 HYDROGEN FLUORIDE HYDROGEN FLUORIDE POTENTIAL
                                                                     DATE 050376
                                                                     TIME

THIS POTENTIAL SURFACE CALCULATION IS FOR IDENTICAL MOLECULES

THE POTENTIAL SURFACE WILL BE CALCULATED AT  6 RADIAL DISTANCES

      8.00000      7.00000      6.00000      5.00000      4.00000
      3.00000

THE POTENTIAL SURFACE WILL BE CALCULATED AT  1 PHI1 ANGLES.
THE COSINES OF THE PHI1 ANGLES ARE

      1.00000

THE POTENTIAL SURFACE WILL BE CALCULATED AT  2 THETA1 ANGLES.
THE COSINES OF THE THETA1 ANGLES ARE

      1.00000      0.00000

THE POTENTIAL SURFACE WILL BE CALCULATED AT  2 THETA2 ANGLES.
THE COSINES OF THE THETA2 ANGLES ARE

      1.00000      0.00000
```

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 HYDROGEN FLUORIDE HYDROGEN FLUORIDE POTENTIAL
                                                                 DATE 050376
                                                                 TIME

THE 96 RADIAL INTERPOLATION POINTS ARE

      1.88172      2.00000      2.11828      2.23656      2.35484
      2.47312      2.59140      2.70968      2.82796      2.94624
      3.06452      3.18280      3.30108      3.41935      3.53763
      3.65591      3.77419      3.89247      4.01075      4.12903
      4.24731      4.36559      4.48387      4.60215      4.72043
      4.83871      4.95699      5.07527      5.19355      5.31183
      5.43011      5.54839      5.66667      5.78495      5.90323
      6.02151      6.13978      6.25806      6.37634      6.49462
      6.61290      6.73118      6.84946      6.96774      7.08602
      7.20430      7.32258      7.44086      7.55914      7.67742
      7.79570      7.91398      8.03226      8.15054      8.26882
      8.38710      8.50538      8.62366      8.74194      8.86022
      8.97849      9.09677      9.21505      9.33333      9.45161
      9.56989      9.68817      9.80645      9.92473     10.04301
     10.16129     10.27957     10.39785     10.51613     10.63441
     10.75269     10.87097     10.98925     11.10753     11.22581
     11.34409     11.46237     11.58065     11.69892     11.81720
     11.93548     12.05376     12.17204     12.29032     12.40860
     12.52688     12.64516     12.76344     12.88172     13.00000
     13.11828

THE COSINES OF THE 96 THETA INTERPOLATION POINTS ARE

     -1.00000     -.97895      -.95789      -.93684      -.91579
      -.89474     -.87368      -.85263      -.83158      -.81053
      -.78947     -.76842      -.74737      -.72632      -.70526
      -.68421     -.66316      -.64211      -.62105      -.60000
      -.57895     -.55789      -.53684      -.51579      -.49474
      -.47368     -.45263      -.43158      -.41053      -.38947
      -.36842     -.34737      -.32632      -.30526      -.28421
      -.26316     -.24211      -.22105      -.20000      -.17895
      -.15789     -.13684      -.11579      -.09474      -.07368
      -.05263     -.03158      -.01053       .01053       .03158
       .05263      .07368       .09474       .11579       .13684
       .15789      .17895       .20000       .22105       .24211
       .26316      .28421       .30526       .32632       .34737
       .36842      .38947       .41053       .43158       .45263
       .47368      .49474       .51579       .53684       .55789
       .57895      .60000       .62105       .64211       .66316
       .68421      .70526       .72632       .74737       .76842
       .78947      .81053       .83158       .85263       .87368
       .89474      .91579       .93684       .95789       .97895
      1.00000
```

```
THE RADIAL INTEGRATION WILL BE SPLIT INTO 11 SECTIONS.
THE SECTIONS AND THE NUMBER OF POINTS IN EACH SECTION ARE

0.0000000
                    3
   .08729
                    9
  1.50000
                    4
  1.64551
                    2
  2.00000
                    2
  2.50000
                    2
  3.00000
                    2
  3.50000
                    2
  4.00000
                    4
  5.00000
                    4
  6.00000
                    2
  6.40312

THE 36 RADIAL INTEGRATION POINTS

          .00984      .04365      .07745      .10976      .20311
          .36039      .56461      .79365     1.02266     1.22690
         1.38418     1.47751     1.51010     1.54802     1.59749
         1.63541     1.72042     1.92509     2.10566     2.39434
         2.60566     2.89434     3.10566     3.39434     3.60566
         3.89434     4.06943     4.33001     4.66999     4.93057
         5.06943     5.33001     5.66999     5.93057     6.08519
         6.31793

THE 24 THETA INTEGRATION POINTS

         -.99519     -.97473     -.93827     -.88642     -.82000
         -.74012     -.64809     -.54542     -.43379     -.31504
         -.19112     -.06406      .06406      .19112      .31504
          .43379      .54542      .64809      .74012      .82000
          .88642      .93827      .97473      .99519

THE 24 PHI INTEGRATION POINTS

          .99989      .99685      .98126      .93701      .84433
          .68483      .44865      .14221     -.20650     -.54891
         -.82510     -.97982     -.97982     -.82510     -.54891
         -.20650      .14221      .44865      .68483      .84433
          .93701      .98126      .99685      .99989

MOLECULE A HAS 10 ELECTRONS

MOLECULE B HAS 10 ELECTRONS

TIME REQUIREMENT FOR THIS CALCULATION WAS   39.38567 SECONDS.
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```
HYDROGEN FLUORIDE HYDROGEN FLUORIDE POTENTIAL
                                                                 DATE 050376
                                                                 TIME

       SELF=  .4405045E+00   SECONDS=  .1384605E+00
          R=  .8000000E+01      PHI1= 0.              THETA1= 0.              THETA2= 0.
CORRELATION= -.1815626E-04 COULOMBIC= -.1955372E-02 EXCHANGE= -.2623662E-04 KINETIC=  .3328929E-04
      GKSCF= -.1981643E-02    GKRSCF= -.1948319E-02       GK= -.1999799E-02     GKR= -.1966475F-02

       SELF=  .4405045E+00   SECONDS=  .2699019E+01
          R=  .8000000E+01      PHI1= 0.              THETA1= 0.              THETA2=  .1570796E+01
CORRELATION= -.2377256E-04 COULOMBIC= -.7087754E-03 EXCHANGE= -.3486082E-04 KINETIC=  .4673089E-04
      GKSCF= -.7411829E-03    GKRSCF= -.6969053E-03       GK= -.7649554E-03     GKR= -.7206779E-03

       SELF=  .4405045E+00   SECONDS=  .2670205E+01
          R=  .8000000E+01      PHI1= 0.              THETA1=  .1570796E+01 THETA2= 0.
CORRELATION= -.1119356E-04 COULOMBIC=  .2969551E-03 EXCHANGE= -.1601794E-04 KINETIC=  .1771620E-04
      GKSCF=  .2783085E-03    GKRSCF=  .2986533E-03       GK=  .2671150E-03     GKR=  .2874598E-03

       SELF=  .4405045E+00   SECONDS=  .2686051E+01
          R=  .8000000E+01      PHI1= 0.              THETA1=  .1570796E+01 THETA2=  .1570796E+01
CORRELATION= -.1459551E-04 COULOMBIC=  .1127493E-02 EXCHANGE= -.2119317E-04 KINETIC=  .2454196E-04
      GKSCF=  .1103924E-02    GKRSCF=  .1130842E-02       GK=  .1089328E-02     GKR=  .1116246E-02

       SELF=  .4405045E+00   SECONDS=  .1340806E+00
          R=  .7000000E+01      PHI1= 0.              THETA1= 0.              THETA2= 0.
CORRELATION= -.7816781E-04 COULOMBIC= -.2881706E-02 EXCHANGE= -.1311088E-03 KINETIC=  .2533619E-03
      GKSCF= -.2925978E-02    GKRSCF= -.2759453E-02       GK= -.3004146E-02     GKR= -.2837621E-02

       SELF=  .4405045E+00   SECONDS=  .2620062E+01
          R=  .7000000E+01      PHI1= 0.              THETA1= 0.              THETA2=  .1570796E+01
CORRELATION= -.9556989E-04 COULOMBIC= -.1369962E-02 EXCHANGE= -.1651074E-03 KINETIC=  .3315924E-03
      GKSCF= -.1413184E-02    GKRSCF= -.1203477E-02       GK= -.1508754E-02     GKR= -.1299047E-02

       SELF=  .4405045E+00   SECONDS=  .2619672E+01
          R=  .7000000E+01      PHI1= 0.              THETA1=  .1570796E+01 THETA2= 0.
CORRELATION= -.4843840E-04 COULOMBIC=  .4381756E-03 EXCHANGE= -.7522733E-04 KINETIC=  .1256257E-03
      GKSCF=  .3930259E-03    GKRSCF=  .4885739E-03       GK=  .3445875E-03     GKR=  .4401355E-03

       SELF=  .4405045E+00   SECONDS=  .2663308E+01
          R=  .7000000E+01      PHI1= 0.              THETA1=  .1570796E+01 THETA2=  .1570796E+01
CORRELATION= -.6019310E-04 COULOMBIC=  .1675973E-02 EXCHANGE= -.9531888E-04 KINETIC=  .1651234E-03
      GKSCF=  .1624711E-02    GKRSCF=  .1745778E-02       GK=  .1564518E-02     GKR=  .1685584E-02
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HYDROGEN FLUORIDE HYDROGEN FLUORIDE POTENTIAL
                                                                DATE 050376
                                                                TIME

          SELF=  .4405045E+00   SECONDS=  .1315535E+00
             R=  .6000000E+01     PHI1= 0.             THETA1= 0.                THETA2= 0.
   CORRELATION= -.2869982E-03 COULOMBIC= -.4513557E-02 EXCHANGE= -.6557910E-03 KINETIC=  .1944065E-02
         GKSCF= -.4058219E-02    GKRSCF= -.3225283E-02       GK= -.4345217E-02     GKR= -.3512281E-02

          SELF=  .4405045E+00   SECONDS=  .2556407E+01
             R=  .6000000E+01     PHI1= 0.             THETA1= 0.                THETA2=  .1570796E+01
   CORRELATION= -.3327341E-03 COULOMBIC= -.3031722E-02 EXCHANGE= -.7807180E-03 KINETIC=  .2357090E-02
         GKSCF= -.2446959E-02    GKRSCF= -.1455350E-02       GK= -.2779693E-02     GKR= -.1788085E-02

          SELF=  .4405045E+00   SECONDS=  .2552889E+01
             R=  .6000000E+01     PHI1= 0.             THETA1=  .1570796E+01 THETA2= 0.
   CORRELATION= -.1814894E-03 COULOMBIC=  .6161017E-03 EXCHANGE= -.3563781E-03 KINETIC=  .8986678E-03
         GKSCF=  .7057470E-03    GKRSCF=  .1158391E-02       GK=  .5242576E-03     GKR=  .9769020E-03

          SELF=  .4405045E+00   SECONDS=  .2579054E+01
             R=  .6000000E+01     PHI1= 0.             THETA1=  .1570796E+01 THETA2=  .1570796E+01
   CORRELATION= -.2143069E-03 COULOMBIC=  .2554210E-02 EXCHANGE= -.4329906E-03 KINETIC=  .1119962E-02
         GKSCF=  .2691229E-02    GKRSCF=  .3241181E-02       GK=  .2476922E-02     GKR=  .3026874E-02

          SELF=  .4405045E+00   SECONDS=  .1273407E+00
             R=  .5000000E+01     PHI1= 0.             THETA1= 0.                THETA2= 0.
   CORRELATION= -.9737384E-03 COULOMBIC= -.8273797E-02 EXCHANGE= -.3310273E-02 KINETIC=  .1497530E-01
         GKSCF= -.8132231E-03    GKRSCF=  .3391235E-02       GK= -.1786961E-02     GKR=  .2417496E-02

          SELF=  .4405045E+00   SECONDS=  .2482100E+01
             R=  .5000000E+01     PHI1= 0.             THETA1= 0.                THETA2=  .1570796E+01
   CORRELATION= -.1079566E-02 COULOMBIC= -.8537275E-02 EXCHANGE= -.3680704E-02 KINETIC=  .1658237E-01
         GKSCF= -.3105605E-03    GKRSCF=  .4364390E-02       GK= -.1390126E-02     GKR=  .3284824E-02

          SELF=  .4405045E+00   SECONDS=  .2483352E+01
             R=  .5000000E+01     PHI1= 0.             THETA1=  .1570796E+01 THETA2= 0.
   CORRELATION= -.6197121E-03 COULOMBIC=  .2662628E-03 EXCHANGE= -.1726163E-02 KINETIC=  .6519114E-02
         GKSCF=  .2866772E-02    GKRSCF=  .5059214E-02       GK=  .2247060E-02     GKR=  .4439502E-02

          SELF=  .4405045E+00   SECONDS=  .2506695E+01
             R=  .5000000E+01     PHI1= 0.             THETA1=  .1570796E+01 THETA2=  .1570796E+01
   CORRELATION= -.7061766E-03 COULOMBIC=  .3370652E-02 EXCHANGE= -.1996154E-02 KINETIC=  .7626935E-02
         GKSCF=  .6466069E-02    GKRSCF=  .9001433E-02       GK=  .5759892E-02     GKR=  .8295256E-02
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 HYDROGEN FLUORIDE HYDROGEN FLUORIDE POTENTIAL
                                                            DATE 050376
                                                            TIME

       SELF=  .4405045E+00   SECONDS=  .1243775E+00
          R=  .4000000E+01     PHI1= 0.              THETA1= 0.                 THETA2= 0.
CORRELATION= -.3313797E-02 COULOMBIC= -.2107258E-01 EXCHANGE= -.1687929E-01 KINETIC=  .1136705E+00
      GKSCF=  .5427989E-01    GKRSCF=  .7571867E-01       GK=  .5096609E-01    GKR=  .7240488E-01

       SELF=  .4405045E+00   SECONDS=  .2414344E+01
          R=  .4000000E+01     PHI1= 0.              THETA1= 0.                 THETA2=  .1570796E+01
CORRELATION= -.3430521E-02 COULOMBIC= -.3134211E-01 EXCHANGE= -.1731155E-01 KINETIC=  .1149199E+00
      GKSCF=  .4427845E-01    GKRSCF=  .6626627E-01       GK=  .4064793E-01    GKR=  .6283575E-01

       SELF=  .4405045E+00   SECONDS=  .2409448E+01
          R=  .4000000E+01     PHI1= 0.              THETA1=  .1570796E+01  THETA2= 0.
CORRELATION= -.2093551E-02 COULOMBIC= -.7049265E-02 EXCHANGE= -.8683907E-02 KINETIC=  .4857899E-01
      GKSCF=  .2181618E-01    GKRSCF=  .3284582E-01       GK=  .1972263E-01    GKR=  .3075227E-01

       SELF=  .4405045E+00   SECONDS=  .2427753E+01
          R=  .4000000E+01     PHI1= 0.              THETA1=  .1570796E+01  THETA2=  .1570796E+01
CORRELATION= -.2227423E-02 COULOMBIC= -.2657496E-02 EXCHANGE= -.9290768E-02 KINETIC=  .5232281E-01
      GKSCF=  .2857411E-01    GKRSCF=  .4037454E-01       GK=  .2634669E-01    GKR=  .3814712E-01

       SELF=  .4405045E+00   SECONDS=  .1233205E+00
          R=  .3000000E+01     PHI1= 0.              THETA1= 0.                 THETA2= 0.
CORRELATION= -.9747657E-02 COULOMBIC=  .6294975E-01 EXCHANGE= -.7348273E-01 KINETIC=  .7371701E+00
      GKSCF=  .6333050E+00    GKRSCF=  .7266371E+00       GK=  .6235573E+00    GKR=  .7168895E+00

       SELF=  .4405045E+00   SECONDS=  .2386296E+01
          R=  .3000000E+01     PHI1= 0.              THETA1= 0.                 THETA2=  .1570796E+01
CORRELATION= -.9874032E-02 COULOMBIC= -.3562013E-01 EXCHANGE= -.7275364E-01 KINETIC=  .7093341E+00
      GKSCF=  .5085541E+00    GKRSCF=  .6009603E+00       GK=  .4986801E+00    GKR=  .5910863E+00

       SELF=  .4405045E+00   SECONDS=  .2400238E+01
          R=  .3000000E+01     PHI1= 0.              THETA1=  .1570796E+01  THETA2= 0.
CORRELATION= -.6567649E-02 COULOMBIC= -.8788867E-01 EXCHANGE= -.4144088E-01 KINETIC=  .3481034E+00
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TOTAL TIME REQUIRED=  .8572641E+02SECONDS.
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Sample output using SLAFIT. This sample run fits the electron density of a HF molecule to a linear combination of Slater type basis functions. Data is punched for use in LMOLMO.

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                                                                    DATE 050376
                                                                    TIME

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A. D. MCLEAN AND M. YOSHIMINE PAGE 1, HYDROGEN FLUORIDE

THE NUMBER OF NUCLEI          2

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NUMBER OF BASIS FUNCTIONS FOR SIGMA ORBITALS    18
NUMBER OF PI ORBITALS      1
NUMBER OF BASIS FUNCTIONS FOR PI ORBITALS    10
NUMBER OF SIGMA UNGERADE ORBITALS     -0
NUMBER OF BASIS FUNCTIONS FOR SIGMA UNGERADE ORBITALS     -0
NUMBER OF PI UNGERADE ORBITALS     -0
NUMBER OF BASIS FUNCTIONS FOR PI UNGERADE ORBITALS     -0

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PI SYMMETRY

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                                                                                  TIME

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```

# APPENDIX D

# INTERMOLECULAR POTENTIAL SURFACES FROM ELECTRON GAS METHODS. I. ANGLE AND DISTANCE DEPENDENCE OF THE $He-CO_2$ AND $Ar-CO_2$ INTERACTIONS

(A reprint. See Gregory A. Parker, Richard L. Snow and Russell T Pack J. Chem. Phys. 64, 1668 (1976).)

# Intermolecular potential surfaces from electron gas methods. I. Angle and distance dependence of the He–$CO_2$ and Ar–$CO_2$ interactions*

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(Received 12 September 1975)

Angle dependent intermolecular potential energy surfaces suitable for use in studies of rotationally inelastic collisions of rigid linear $CO_2$ with Ar and He are calculated using the electron gas model to obtain the short range interactions and joining them smoothly to the long range van der Waals tails of the preceding paper. Smooth analytic fits to the potentials, convenient for use in scattering calculations, are given. The surfaces are very strongly nonspherical. Virial coefficients calculated using the *a priori* He–$CO_2$ potential are in excellent agreement with experiment, and a simple adjustment of the Ar–$CO_2$ potential gives excellent agreement with both virial coefficients and a potential inferred from high energy scattering data.

## I. INTRODUCTION

Until recently, little has been known about the angle dependence of the interaction energies of molecules with other atoms or molecules. Use of *ab initio* SCF and CI methods to generate the whole potential energy surface is slow and expensive, so that results are available for very few systems, while analysis of experiments gives information mostly about the spherical average of the intermolecular potential. However, renewed interest in calculating interaction energies between closed shell systems has recently been generated by the successes of a simple electron gas model developed by Gaydaenko and Nikulin[1] and Gordon and Kim.[2] A modification to avoid overcounting of self-exchange energy has been suggested by Rae,[3] and ways to introduce correct van der Waals long range behavior have been given by Cohen and Pack[4] and Kim and Gordon.[5] The surprisingly good results of the method for the interactions of closed shell atoms[2–6] and ions,[7] collisional polarizabilities,[8] three-body interactions,[9] atom–surface interactions,[10] and the spherical part of molecular interactions[11] have led to its being programmed for atom–molecule[12] and molecule–molecule interactions.[13] The atom–molecule program of Green and Gordon[12] is available from QCPE and our[13] molecule–molecule program will also be sent there. The method has been used by others to determine the distance and angle dependence of the Ar–$N_2$,[14] Ar–HCl,[15] He–HCN,[16] He–CO,[17] and He–$H_2CO$[16] interactions, and the distance, angle, and vibrational coordinate dependence of the $Li^+$–$H_2$[18] interactions. We[19] have calculated the angle and distance dependence of the He–$H_2$, He–$CO_2$, Ar–$CO_2$, noble gas–CO, Ar–NO,[20] noble gas–HF, HF–HF,[13] and CO–CO interactions and the angle, vibrational coordinate, and distance dependence of the Ar–CO and Ar–HF interactions.

In this paper we report the He–$CO_2$ and Ar–$CO_2$ surfaces. Most previous potentials for these systems have been crude empirical forms which assume either spherical or pairwise additive forces. However, a minimal basis set SCF calculation of the Ar–$CO_2$ surface, including some vibrational coordinate dependence has recently been done by Suzukawa,[21] and we compare our results with his.

In Sec. II of this paper we briefly review the equations of the electron gas model and our particular version and computational method. In Sec. III we give the results of the calculations, fit the potential surfaces with a convenient analytic form and attach previously determined[22,23] van der Waals potentials to give smooth intermolecular potentials which behave properly at both large and small distances. Then, in the last section we make a comparison with available experimental data, adjust the results to improve agreement, and discuss the accuracy and usefulness of the resulting potential energy surfaces.

## II. METHOD OF CALCULATION

We consider the interaction of a neutral closed shell linear molecule A (in this case $CO_2$ with the nuclei fixed in their equilibrium positions) with a neutral closed shell atom B (in this case He or Ar). For such a system the interaction potential in the electron gas model using the coordinates of Fig. 1 is[2,4]

$$V(r,\theta)=E(r,\theta)-E(\infty,\ \text{any }\theta)\ , \tag{1}$$

$$=V_{HF}(r,\theta)+V_{COR}(r,\theta)\ , \tag{2}$$

and

$$V_{HF}=V_{COUL}+V_{KIN}+V_{EXC}\ , \tag{3}$$

where the various terms represent the electron gas estimates of the Hartree–Fock, correlation, Coulomb, kinetic, and exchange contributions to the interaction energy. To calculate these, one approximates the charge density $\rho_{AB}$ of the combined system as[1,2]

$$\rho_{AB}\approx\rho_A+\rho_B\ . \tag{4}$$

Then, the Coulombic interaction is given simply (in atomic units) by the electrostatic expression,

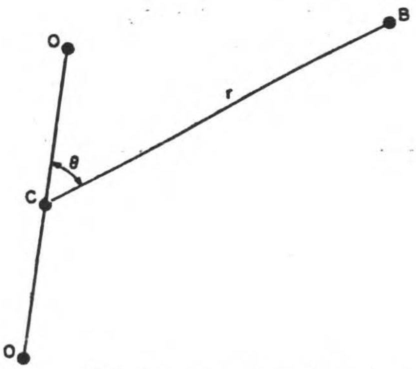

FIG. 1. The coordinates $r$ and $\theta$ for the interaction of rigid linear $CO_2$ with atom B (He or Ar).

$$V_{\text{COUL}} = \int\int \rho_A(\mathbf{r}_1)\rho_B(\mathbf{r}_2)\Big[\frac{1}{r_{12}} - \frac{1}{r_{1B}} + \sum_\alpha f_\alpha\Big(\frac{1}{r_{\alpha B}} - \frac{1}{r_{2\alpha}}\Big)\Big]\, d\mathbf{r}_1\, d\mathbf{r}_2\ , \tag{5}$$

where the sums are over the nuclei $\alpha$ in A, and $f_\alpha = Z_\alpha / N_A$, where $Z_\alpha$ is the charge of nucleus $\alpha$ and $N_A$ is the number of electrons in molecule A,

$$N_A = \int \rho_A(\mathbf{r}_1)\, d\mathbf{r}_1\ . \tag{6}$$

The other terms $V_i$ ($i$ = KIN, EXC, or COR) in $V$ are obtained using the energy density functionals of a uniform electron gas; that is,

$$V_i = \int d\mathbf{r}\,[\rho_{AB}\epsilon_i(\rho_{AB}) - \rho_A\epsilon_i(\rho_A) - \rho_B\epsilon_i(\rho_B)]\ , \tag{7}$$

where

$$\epsilon_{\text{KIN}}(\rho) = \tfrac{3}{10}(3\pi^2)^{2/3}\rho^{2/3}\ , \tag{8}$$

$$\epsilon_{\text{EXC}}(\rho) = -\tfrac{3}{4}(3/\pi)^{1/3}\rho^{1/3}\ , \tag{9}$$

and

$$\epsilon_{\text{COR}}(\rho) = -0.0311\ln r_s - 0.048 + 0.009\, r_s \ln r_s - 0.01\, r_s\ , \quad r_s \leq 0.7\ , \tag{10a}$$

$$= -0.06156 + 0.01898\ln r_s\ , \quad 0.7 < r_s < 10\ , \tag{10b}$$

$$= -0.438\, r_s^{-1} + 1.325\, r_s^{-3/2} - 1.47\, r_s^{-2} - 0.4\, r_s^{-5/2}\ , \quad 10 \leq r_s\ , \tag{10c}$$

with $r_s(4\pi\rho/3)^{-1/3}$. Equations (10a) and (10c) are the high and low density expansions. respectively, of the electron gas correlation energy density, and (10b) is an interpolation formula.

In the present calculations, for reasons discussed in detail elsewhere,[4] we used Rae's[3] correction to the exchange energy to avoid self-exchange contributions. This changes $V_{\text{EXC}}$ of Eq. (7) into

$$V_{\text{EXC}}(\text{Rae}) = C(N)\, V_{\text{EXC}}\ , \tag{11}$$

where $C(N)$ is the correction factor

$$C(N) = 1 - 8\delta/3 + 2\delta^2 - \delta^4/3\ , \tag{12}$$

$\delta$ is the solution of

$$(4N)^{-1} = \delta^3(1 - 9\delta/8 + \delta^3/4)\ , \tag{13}$$

and $N$ is the total number of electrons in the system. $C(N) = 0.5454$ for Ar–$CO_2$, and $C(N) = 0.4699$ for He–$CO_2$. In addition, $V_{\text{COR}}$ is known to be quite inaccurate, and we thus feel free to scale it to match the long range van der Waals correlation energy as described in the next section and elsewhere.[4]

Use of the above formulas and the available Hartree–Fock wavefunctions of McLean and Yoshimine[24] for $CO_2$ and Clementi[25] for Ar and He to construct $\rho_A$ and $\rho_B$ reduces the determination of $V$ to evaluation of the quadratures, Eqs. (5) and (7). To do them, we note that B is a spherical atom and the Hartree–Fock atomic wavefunctions[25] used are expressed in Slater orbitals, so that the electrostatic potential due to B can be evaluated analytically,

$$\Phi_B(\mathbf{r}_1) = \int \rho_B(\mathbf{r}_2)\, r_{12}^{-1}\, d\mathbf{r}_2\ , \tag{14}$$

which reduces Eq. (5) to the three dimensional quadrature,

$$V_{\text{COUL}} = \int d\mathbf{r}_1\, \rho_A(\mathbf{r}_1)\Big\{\Phi_B(\mathbf{r}_1) - \frac{Z_B}{r_{1B}} + \sum_\alpha f_\alpha\Big[\frac{Z_B}{r_{\alpha B}} - \Phi_B(\mathbf{r}_\alpha)\Big]\Big\}\ . \tag{15}$$

Equations (7) and (15) are then evaluated by three-dimensional quadrature. In this connection, it is important to note that although some of the terms in Eq. (15) are constants and could be integrated over analytically, keeping them in the integrand increases cancellation of quadrature errors. It is also convenient to tabulate $\Phi_B$ and $\rho_B$, which are spherically symmetric about B, at a large number of distances and then obtain them at each point needed by low order Sterling interpolation. In programming the quadrature we used spherical polar coordinates centered on the center of mass of A (the carbon atom in this case). This is different from the QCPE program of Green and Gordon[12] which uses prolate spheroidal coordinates. Our approach requires more integration points but saves on interpolation time as $\rho_A$ can be tabulated at each of the integration points once and for all and the complete potential energy surface $V(r, \theta)$ calculated at all $r$ and $\theta$ without further calculation or interpolation of $\rho_A$. In the present calculations Gauss–Legendre quadrature formulas were used typically with 32 points for the $\phi_1$ integration, 40 points for the $\theta_1$ integration, and two quadratures for the radial integration: a 16-point quadrature extending from the C atom (at the origin) to the O atoms (at 2.1944 $a_0$) and a 48-point quadrature extending from the O atoms to 13 $a_0$. This sufficed to give all the terms except $V_{\text{COUL}}$ converged to within 1% everywhere; it gave $V_{\text{COUL}}$ converged to about 1% at the smaller $r$ values with the error increasing to about 10% at the largest (9.5 $a_0$) distances used. Since the total interaction is dominated by the van der Waals potential at the large distances, we believe that the quadrature errors in the

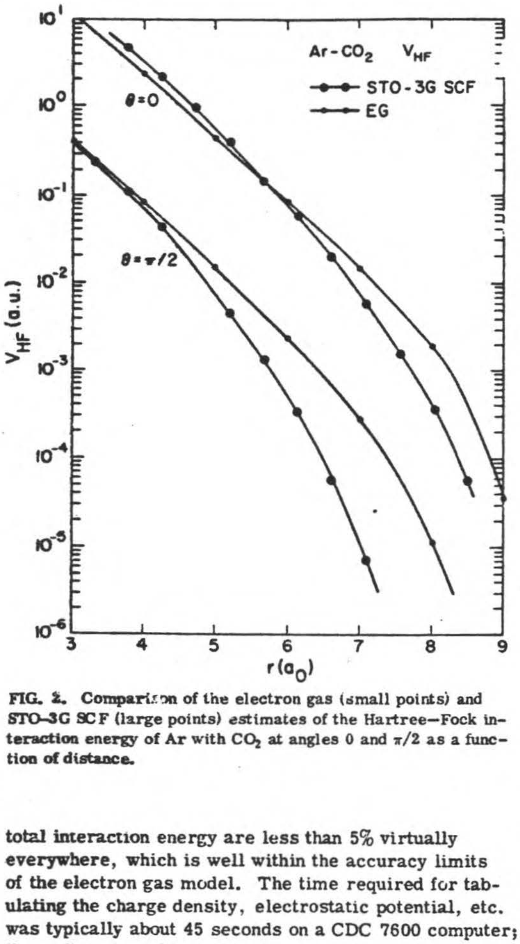

FIG. 2. Comparison of the electron gas (small points) and STO-3G SCF (large points) estimates of the Hartree–Fock interaction energy of Ar with CO$_2$ at angles 0 and $\pi/2$ as a function of distance.

total interaction energy are less than 5% virtually everywhere, which is well within the accuracy limits of the electron gas model. The time required for tabulating the charge density, electrostatic potential, etc. was typically about 45 seconds on a CDC 7600 computer; thereafter about 20 seconds was required for each point on the potential energy surface $V(r,\theta)$.

Subsequent to the completion of the calculations reported herein, we have found and reported elsewhere[13] a much faster and more accurate way to do this quadrature.

## III. RESULTS AND FITTING

### A. Results

The results of the calculations described in the previous section are given in Tables I and II for the He–CO$_2$ interaction and Tables III and IV for the Ar–CO$_2$ interaction. Tables I and III are the electron gas model estimates (including the Rae correction) of $V_{HF}$, and Tables II and IV are the electron gas estimates of $V_{COR}$. These tables are given so that the reader who does not wish to use the procedure which follows to fit $V$ with analytic functions is free to use the results directly. Also, $V_{HF}$ is plotted at two angles in Fig. 2 for comparison with the minimal basis set (STO-3G) SCF calculations of Suzukawa.[21] Considering the approximations involved in both methods, we consider the agreement at small distances to be adequate, but at the larger distances the present results should be the more accurate ones. The SCF results die too rapidly at large $r$ because minimal basis set orbitals are too small at large distances making the integrals involving exchange and overlap energies fall off much too rapidly.

### B. Fitting of short range potential

The results of Tables I–IV were first expanded in Legendre polynomials at each $r$,

$$V_i(r,\theta)=\sum_{n=0,2,\dots} v_n^i(r)\,P_n(\cos\theta)\ , \tag{16}$$

where only even $n$ occur because of the $D_{\infty h}$ symmetry of CO$_2$. Since the angles at which the Ar–CO$_2$ calculations were done were exactly those of a 15-point Gauss–Legendre quadrature (the symmetry of CO$_2$ makes the results independent of the sign of $x=\cos\theta$), the $v_n^i$ for that system were obtained directly from quadrature of

$$v_n^i=\left(n+\frac{1}{2}\right)\int_{-1}^{1} P_n(x)\,V_i(r,x)\,dx\ . \tag{17}$$

However, the He–CO$_2$ calculations were first done at the angles of a seven point Gauss–Legendre quadrature

TABLE I. $V_{HF}$ for the He–CO$_2$ interaction as a function of distance and angle. The angles are in radians; $V$ and $r$ are in Hartree atomic units.

| $x=\cos\theta$ | 1.0000 | 0.9491 | 0.8500 | 0.7415 | 0.6000 | 0.4058 | 0.2000 | 0.0000 |
|---|---|---|---|---|---|---|---|---|
| $r$ \ $\theta$ | 0.0000 | 0.3204 | 0.5548 | 0.7355 | 0.9273 | 1.1529 | 1.3694 | 1.5708 |
| 3.5 | 0.1322E+01 | 0.7943E+00 | 0.3725E+00 | 0.1927E+00 | 0.9753E−01 | 0.4767E−01 | 0.2875E−01 | 0.2410E−01 |
| 4.0 | 0.5111E+00 | 0.3383E+00 | 0.1690E+00 | 0.8806E−01 | 0.4362E−01 | 0.2020E−01 | 0.1146E−01 | 0.9335E−02 |
| 4.5 | 0.2011E+00 | 0.1386E+00 | 0.7124E−01 | 0.3753E−01 | 0.1838E−01 | 0.8146E−02 | 0.4368E−02 | 0.3462E−02 |
| 5.0 | 0.7706E−01 | 0.5437E−01 | 0.2848E−01 | 0.1526E−01 | 0.7364E−02 | 0.3136E−02 | 0.1592E−02 | 0.1225E−02 |
| 5.5 | 0.2860E−01 | 0.2053E−01 | 0.1098E−01 | 0.5907E−02 | 0.2819E−02 | 0.1153E−02 | 0.5516E−03 | 0.4102E−03 |
| 6.0 | 0.1028E−01 | 0.7486E−02 | 0.4038E−02 | 0.2184E−02 | 0.1029E−02 | 0.4019E−03 | 0.1784E−03 | 0.1266E−03 |
| 6.5 | 0.3598E−02 | 0.2637E−02 | 0.1437E−02 | 0.7704E−03 | 0.3552E−03 | 0.1300E−03 | 0.5151E−04 | 0.3374E−04 |
| 7.0 | 0.1213E−02 | 0.8921E−03 | 0.4856E−03 | 0.2565E−03 | 0.1136E−03 | 0.3719E−04 | 0.1160E−04 | 0.6033E−05 |
| 7.5 | 0.3885E−03 | 0.2863E−03 | 0.1526E−03 | 0.7857E−04 | 0.3193E−04 | 0.8014E−05 | 0.6293E−06 | −0.8474E−06 |
| 8.0 | 0.1167E−03 | 0.8478E−04 | 0.4365E−04 | 0.2055E−04 | 0.6662E−05 | 0.1182E−06 | −0.1515E−05 | −0.1759E−05 |
| 8.5 | 0.3100E−04 | 0.2159E−04 | 0.9839E−05 | 0.3441E−05 | −0.3102E−07 | −0.1307E−05 | −0.1378E−05 | −0.1322E−05 |
| 9.0 | 0.6038E−05 | 0.3608E−05 | 0.7286E−06 | −0.6348E−06 | −0.1159E−05 | −0.1101E−05 | −0.8842E−06 | −0.7980E−06 |
| 9.5 | −0.1055E−06 | −0.5704E−06 | −0.1009E−05 | −0.1075E−05 | −0.9316E−06 | −0.6786E−06 | −0.4951E−06 | −0.4360E−06 |

TABLE II. $V_{\mathrm{COR}}$ for the He–$CO_2$ interaction as a function of distance and angle. Hartree atomic units.

| $x = \cos\theta$ | 1.0000 | 0.9491 | 0.8500 | 0.7415 | 0.6000 | 0.4058 | 0.2000 | 0.0000 |
|---|---|---|---|---|---|---|---|---|
| $r \backslash \theta$ | 0.0000 | 0.3204 | 0.5548 | 0.7355 | 0.9273 | 1.1529 | 1.3694 | 1.5708 |
| 3.5 | −0.1663E−01 | −0.1290E−01 | −0.8676E−02 | −0.6092E−02 | −0.4179E−02 | −0.2823E−02 | −0.2171E−02 | −0.1989E−02 |
| 4.0 | −0.1008E−01 | −0.8038E−02 | −0.5490E−02 | −0.3841E−02 | −0.2595E−02 | −0.1703E−02 | −0.1274E−02 | −0.1154E−02 |
| 4.5 | −0.5924E−02 | −0.4809E−02 | −0.3329E−02 | −0.2334E−02 | −0.1562E−02 | −0.1002E−02 | −0.7320E−03 | −0.6561E−03 |
| 5.0 | −0.3406E−02 | −0.2796E−02 | −0.1960E−02 | −0.1379E−02 | −0.9174E−03 | −0.5775E−03 | −0.4115E−03 | −0.3650E−03 |
| 5.5 | −0.1924E−02 | −0.1593E−02 | −0.1129E−02 | −0.7964E−03 | −0.5272E−03 | −0.3255E−03 | −0.2263E−03 | −0.1984E−03 |
| 6.0 | −0.1070E−02 | −0.8933E−03 | −0.6378E−03 | −0.4506E−03 | −0.2963E−03 | −0.1790E−03 | −0.1207E−03 | −0.1043E−03 |
| 6.5 | −0.5883E−03 | −0.4941E−03 | −0.3543E−03 | −0.2502E−03 | −0.1627E−03 | −0.9565E−04 | −0.6188E−04 | −0.5232E−04 |
| 7.0 | −0.3199E−03 | −0.2687E−03 | −0.1928E−03 | −0.1352E−03 | −0.8660E−04 | −0.4907E−04 | −0.3037E−04 | −0.2507E−04 |
| 7.5 | −0.1693E−03 | −0.1425E−03 | −0.1020E−03 | −0.7084E−04 | −0.4437E−04 | −0.2410E−04 | −0.1429E−04 | −0.1163E−04 |
| 8.0 | −0.8696E−04 | −0.7317E−04 | −0.5185E−04 | −0.3548E−04 | −0.2154E−04 | −0.1139E−04 | −0.6735E−05 | −0.5511E−05 |
| 8.5 | −0.4301E−04 | −0.3590E−04 | −0.2506E−04 | −0.1681E−04 | −0.1012E−04 | −0.5401E−05 | −0.3227E−05 | −0.2640E−05 |
| 9.0 | −0.2019E−04 | −0.1678E−04 | −0.1159E−04 | −0.7827E−05 | −0.4799E−05 | −0.2597E−05 | −0.1556E−05 | −0.1272E−05 |
| 9.5 | −0.9222E−05 | −0.7686E−05 | −0.5416E−05 | −0.3708E−05 | −0.2299E−05 | −0.1255E−05 | −0.7539E−06 | −0.6151E−06 |

TABLE III. $V_{\mathrm{HF}}$ for the Ar–$CO_2$ interaction as a function of distance and angle. The angles are in radians; $V$ and $r$ are in Hartree atomic units.

| $x = \cos\theta$ | 0.9880 | 0.9373 | 0.8482 | 0.7244 | 0.5710 | 0.3942 | 0.2012 | 0.0000 |
|---|---|---|---|---|---|---|---|---|
| $r \backslash \theta$ | 0.1551 | 0.3561 | 0.5582 | 0.7606 | 0.9631 | 1.1657 | 1.3682 | 1.5708 |
| 3.0 | 0.1951E+02 | 0.8586E+01 | 0.3411E+01 | 0.1622E+01 | 0.9152E+00 | 0.5948E+00 | 0.4511E+00 | 0.4103E+00 |
| 4.0 | 0.2090E+01 | 0.1422E+01 | 0.8333E+00 | 0.4603E+00 | 0.2519E+00 | 0.1463E+00 | 0.9910E−01 | 0.8590E−01 |
| 5.0 | 0.4197E+00 | 0.3124E+00 | 0.1949E+00 | 0.1075E+00 | 0.5621E−01 | 0.3013E−01 | 0.1863E−01 | 0.1544E−01 |
| 6.0 | 0.8060E−01 | 0.6075E−01 | 0.3807E−01 | 0.2073E−01 | 0.1044E−01 | 0.5237E−02 | 0.2971E−02 | 0.2349E−02 |
| 7.0 | 0.1330E−01 | 0.1008E−01 | 0.6310E−02 | 0.3370E−02 | 0.1621E−02 | 0.7500E−03 | 0.3799E−03 | 0.2801E−03 |
| 8.0 | 0.1859E−02 | 0.1404E−02 | 0.8598E−03 | 0.4364E−03 | 0.1890E−03 | 0.7137E−04 | 0.2409E−04 | 0.1166E−04 |
| 9.0 | 0.3151E−04 | 0.4026E−05 | −0.2334E−04 | −0.3742E−04 | −0.3253E−04 | −0.2529E−04 | −0.1847E−04 | −0.1618E−04 |

TABLE IV. $V_{\mathrm{COR}}$ for the Ar–$CO_2$ interaction as a function of distance and angle. Hartree atomic units.

| $x = \cos\theta$ | 0.9880 | 0.9373 | 0.8482 | 0.7244 | 0.5710 | 0.3942 | 0.2012 | 0.0000 |
|---|---|---|---|---|---|---|---|---|
| $r \backslash \theta$ | 0.1551 | 0.3561 | 0.5582 | 0.7606 | 0.9631 | 1.1657 | 1.3682 | 1.5708 |
| 3.0 | −0.7168E−01 | −0.5866E−01 | −0.4395E−01 | −0.3199E−01 | −0.2381E−01 | −0.1863E−01 | −0.1580E−01 | −0.1490E−01 |
| 4.0 | −0.3271E−01 | −0.2715E−01 | −0.2043E−01 | −0.1462E−01 | −0.1040E−01 | −0.7710E−02 | −0.6252E−02 | −0.5794E−02 |
| 5.0 | −0.1296E−01 | −0.1093E−01 | −0.8287E−02 | −0.5881E−02 | −0.4088E−02 | −0.2929E−02 | −0.2299E−02 | −0.2101E−02 |
| 6.0 | −0.4735E−02 | −0.4028E−01 | −0.3079E−02 | −0.2186E−02 | −0.1501E−02 | −0.1048E−02 | −0.7991E−03 | −0.7204E−03 |
| 7.0 | −0.1639E−02 | −0.1405E−02 | −0.1082E−02 | −0.7683E−03 | −0.5205E−03 | −0.3535E−03 | −0.2603E−03 | −0.2305E−03 |
| 8.0 | −0.5429E−03 | −0.4670E−03 | −0.3602E−03 | −0.2539E−03 | −0.1683E−03 | −0.1096E−03 | −0.7637E−04 | −0.6572E−04 |
| 9.0 | −0.1688E−03 | −0.1449E−03 | −0.1108E−03 | −0.7639E−04 | −0.4859E−04 | −0.2981E−04 | −0.1959E−04 | −0.1649E−04 |

before we realized how anisotropic these intermolecular potentials are. When it was found that more terms were required to get the expansion of Eq. (16) to converge, calculations were performed at the additional angles in Tables I and II and the $v_n^i$ determined from a weighted linear least-squares fit in which the points in the tables were given the approximate Gauss weights of 0.02, 0.06, 0.10, 0.14, 0.17, 0.19, 0.21, and 0.22, respectively. The reason this was done is that a least-squares fit using Gaussian points and weights gives the same optimum fit as the quadrature.

The results of the above procedure are in Tables V–VIII. The fact that $v_2^{HF}$ and $v_4^{HF}$ are consistently larger than $v_0^{HF}$ and the lack of convergence of Eq. (16) at the smallest $r$ values underscore the strong anisotropy of the potential energy surfaces. For the Ar–$CO_2$ system keeping terms through $v_{10}^i$ gives Eq. (16) converged to within 2 or 3% everywhere except at the smallest $r$ shown. However, the procedure used for He–$CO_2$ gave stable coefficients only through $v_8^i$ and convergence of Eq. (16) to within about 10% (and worse at the smallest $r$ shown).

Over most of their ranges the $v_n^i$ in Tables V–VIII die smoothly and slightly faster than exponentially with $r$. At large $r$ it is seen that some of the $v_n^{HF}$ become slightly negative as did the $V_{\mathrm{HF}}$ of Tables I and III. (Had we not used Rae's correction they would have been much more negative.) A true Hartree–Fock potential would go slightly negative here only because of induction effects that are not included in the electron gas model. Hence, these negative points were considered to be an artifact of the model and omitted in fitting the

TABLE V. The coefficients $v_n^{HF}(r)$ in the Legendre expansion of $V_{HF}$ for the He–$CO_2$ interaction. Hartree atomic units.

| $r$ \ $n$ | 0 | 2 | 4 | 6 | 8 |
|---|---|---|---|---|---|
| 3.5 | 0.1817E+00 | 0.4997E+00 | 0.3510E+00 | 0.1768E+00 | 0.8034E−01 |
| 4.0 | 0.7838E−01 | 0.2133E+00 | 0.1371E+00 | 0.5764E−01 | 0.1947E−01 |
| 4.5 | 0.3231E−01 | 0.8787E−01 | 0.5373E−01 | 0.2051E−01 | 0.5816E−02 |
| 5.0 | 0.1274E−01 | 0.3469E−01 | 0.2039E−01 | 0.7247E−02 | 0.1891E−02 |
| 5.5 | 0.4829E−02 | 0.1320E−01 | 0.7510E−02 | 0.2477E−02 | 0.5759E−03 |
| 6.0 | 0.1755E−02 | 0.4839E−02 | 0.2690E−02 | 0.8409E−03 | 0.1788E−03 |
| 6.5 | 0.6125E−03 | 0.1718E−02 | 0.9425E−03 | 0.2780E−03 | 0.5295E−04 |
| 7.0 | 0.2024E−03 | 0.5854E−03 | 0.3212E−03 | 0.9042E−04 | 0.1564E−04 |
| 7.5 | 0.6166E−04 | 0.1890E−03 | 0.1059E−03 | 0.2894E−04 | 0.4771E−05 |
| 8.0 | 0.1636E−04 | 0.5672E−04 | 0.3379E−04 | 0.8895E−05 | 0.1278E−05 |
| 8.5 | 0.2979E−05 | 0.1475E−04 | 0.1020E−04 | 0.2740E−05 | 0.3831E−06 |
| 9.0 | −0.2991E−06 | 0.2638E−05 | 0.2780E−05 | 0.8167E−06 | 0.1215E−06 |
| 9.5 | −0.7251E−06 | −0.2504E−06 | 0.6017E−06 | 0.2319E−06 | 0.4110E−07 |

TABLE VI. $v_n^{COR}(r)$ for He–$CO_2$. Hartree atomic units.

| $r$ \ $n$ | 0 | 2 | 4 | 6 | 8 |
|---|---|---|---|---|---|
| 3.5 | −0.4873E−02 | −0.7504E−02 | −0.2919E−02 | −0.9281E−03 | −0.3068E−03 |
| 4.0 | −0.3008E−02 | −0.4757E−02 | −0.1713E−02 | −0.4580E−03 | −0.1141E−03 |
| 4.5 | −0.1796E−02 | −0.2885E−02 | −0.9677E−03 | −0.2250E−03 | −0.4446E−04 |
| 5.0 | −0.1045E−02 | −0.1698E−02 | −0.5323E−03 | −0.1103E−03 | −0.1844E−04 |
| 5.5 | −0.5949E−03 | −0.9793E−03 | −0.2877E−03 | −0.5316E−04 | −0.7775E−05 |
| 6.0 | −0.3319E−03 | −0.5561E−03 | −0.1537E−03 | −0.2529E−04 | −0.2721E−05 |
| 6.5 | −0.1814E−03 | −0.3123E−03 | −0.8176E−04 | −0.1213E−04 | −0.8436E−05 |
| 7.0 | −0.9662E−04 | −0.1728E−03 | −0.4417E−04 | −0.5820E−05 | −0.4180E−06 |
| 7.5 | −0.4990E−04 | −0.9299E−04 | −0.2379E−04 | −0.2408E−05 | −0.1781E−06 |
| 8.0 | −0.2488E−04 | −0.4803E−04 | −0.1319E−04 | −0.9094E−06 | +0.3021E−07 |
| 8.5 | −0.1196E−04 | −0.2344E−04 | −0.7035E−05 | −0.6809E−06 | +0.1226E−06 |
| 9.0 | −0.5617E−05 | −0.1087E−04 | −0.3284E−05 | −0.4664E−06 | +0.7783E−08 |
| 9.5 | −0.2641E−05 | −0.4995E−05 | −0.1402E−05 | −0.1753E−06 | −0.3894E−08 |

TABLE VII. $v_n^{HF}(r)$ for Ar–$CO_2$. Hartree atomic units.

| $r$ \ $n$ | 0 | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|
| 3.0 | 0.2190E+01 | 0.6290E+01 | 0.5973E+01 | 0.4410E+01 | 0.2803E+01 | 0.1572E+01 |
| 4.0 | 0.4153E+00 | 0.9661E+00 | 0.5519E+00 | 0.2315E+00 | 0.9499E−01 | 0.3846E−01 |
| 5.0 | 0.9100E−01 | 0.2141E+00 | 0.1052E+00 | 0.3091E−01 | 0.7562E−02 | 0.2075E−02 |
| 6.0 | 0.1726E−01 | 0.4211E−01 | 0.2019E−01 | 0.5386E−02 | 0.1063E−02 | 0.2345E−03 |
| 7.0 | 0.2778E−02 | 0.7069E−02 | 0.3367E−02 | 0.8293E−03 | 0.1371E−03 | 0.2365E−04 |
| 8.0 | 0.3597E−03 | 0.1001E−02 | 0.4931E−03 | 0.1161E−03 | 0.1544E−04 | 0.1757E−05 |
| 9.0 | −0.2189E−04 | 0.9817E−05 | 0.3823E−04 | 0.1317E−04 | 0.4996E−06 | −0.1639E−05 |

TABLE VIII. $v_n^{COR}(r)$ for Ar–$CO_2$. Hartree atomic units.

| $r$ \ $n$ | 0 | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|
| 3.0 | −0.2758E−01 | −0.3205E−01 | −0.1121E−01 | −0.3398E−02 | −0.9135E−03 | −0.2542E−03 |
| 4.0 | −0.1214E−01 | −0.1573E−01 | −0.4856E−02 | −0.1173E−02 | −0.2973E−03 | −0.8660E−04 |
| 5.0 | −0.4770E−02 | −0.6517E−02 | −0.1821E−02 | −0.3423E−03 | −0.5455E−04 | −0.8626E−05 |
| 6.0 | −0.1740E−02 | −0.2450E−02 | −0.6209E−03 | −0.9945E−04 | −0.1285E−04 | −0.1419E−05 |
| 7.0 | −0.5998E−03 | −0.8725E−03 | −0.1994E−03 | −0.2687E−04 | −0.2764E−05 | −0.3638E−06 |
| 8.0 | −0.1938E−03 | −0.2988E−03 | −0.6259E−04 | −0.7160E−05 | −0.3754E−06 | +0.1509E−07 |
| 9.0 | −0.5711E−04 | −0.9583E−04 | −0.2050E−04 | −0.1474E−05 | −0.1484E−06 | +0.7528E−07 |

TABLE IX. Parameters $A_{ni}$ and $B_{ni}$ for He–CO$_2$ obtained directly by fitting the electron gas estimates of $v_n^{HF}$ and $v_n^{COR}$. Hartree atomic units.

| $n=$ | 0 | 2 | 4 | 6 | 8 |
|---|---|---|---|---|---|
| $A_{n1}$ | 0.172995E+02 | 0.655752E+02 | 0.105137E+03 | 0.178531E+03 | 0.314919E+03 |
| $A_{n2}$ | −0.982289E+00 | −0.112538E+01 | −0.144877E+01 | −0.190354E+01 | −0.240207E+01 |
| $A_{n3}$ | −0.917494E−01 | −0.766468E−01 | −0.522417E−01 | −0.239120E−01 | 0.0 E+00 |
| $B_{n1}$ | 0.784153E−01 | 0.126468E+00 | 0.118507E+00 | 0.761871E−01 | 0.298293E+00 |
| $B_{n2}$ | −0.628088E+00 | −0.663263E+00 | −0.976097E+00 | −0.116525E+01 | −0.188254E+01 |
| $B_{n3}$ | −0.470607E−01 | −0.399192E−01 | −0.215588E−01 | −0.280915E−01 | 0.0 E+00 |

$v_n^i$, so that a better estimate of the induction effects could be included as in the next section. Also, due to the fact that the He or Ar atom gets very close to the O atoms at some of the smallest $r$ values, some of the $v_n^i$ kink upward at small $r$; such values were also omitted. Then, the $v_n^i$ were fit to the forms

$$v_n^{HF}(r) = A_{n1}\exp(A_{n2}r + A_{n3}r^2) , \tag{18a}$$

and

$$v_n^{COR}(r) = -B_{n1}\exp(B_{n2}r + B_{n3}r^2) , \tag{18b}$$

by ordinary least-squares fitting of $\ln|v_n^i|$. The forms shown are sufficient to fit the $\ln|v_n^i|$ of the larger $v_n^i$ with a standard deviation of about 1% which corresponds to an error of about 5% in the $v_n^i$ themselves. The expansions in Eq. (18) were truncated to a linear term in the exponential whenever addition of the quadratic term decreased the standard deviation by less than 20%. The results are in Tables IX and X.

As a test of the overall fit we note that when these parameters were used in Eqs. (16) and (18), the parameters for Ar–CO$_2$ gave back all the original points with $4 \le r \le 8$ in Table III with a standard fractional deviation of 3.4%, and the parameters for He–CO$_2$ gave back the original points with $3.5 \le r \le 7$ in Table I with a standard fractional deviation of about 8%.

### C. Addition of van der Waals tail

If one attempts to construct a complete potential energy surface by simply adding together the $V_{HF}$ and $V_{COR}$ of the previous subsection, he gets, as we noted elsewhere,[4] an attractive well that is much too shallow and lacks proper van der Waals behavior at large distances. To remedy this deficiency and give a potential which is smooth and behaves reasonably everywhere, we use a simple generalization of our method for atoms;[4] namely, we note that $V_{COR}$ is only qualitatively correct[2] and also small compared to $V_{HF}$ at small distances, so that we are free to scale it without loss of accuracy in the method. Then, we let

$$v_n^{COR}(r) = \begin{cases} -B'_{n1}\exp(B_{n2}r + B_{n3}r^2) , & r \le r_n \quad (19a) \\ -C_6(n)r^{-6} - C_8(n)r^{-8} , & r \ge r_n \quad (19b) \end{cases}$$

where the van der Waals $C_6$ and $C_8$ coefficients are taken from the preceding paper,[22,23] $r_n$ is the point at which the logarithmic derivatives of the two forms are equal, and $B'_{n1}$ is chosen to make $v_n^{COR}$ continuous at $r_n$, for $n \le 4$. For $n > 4$, $B_{n1}$ was scaled by the same factor as was $B_{41}$. The resulting parameters are in Tables XI and XII. They constitute our best present *a priori* estimates of the potential energy surfaces.

### D. Comparison with experiment and adjustment

Results from a number of experiments capable of giving information about the He–CO$_2$ and Ar–CO$_2$ interactions are available. However, to use line broadening,[26] rotational relaxation,[27] or molecular beam[28–30] data to make a meaningful test of intermolecular potentials as anisotropic as these requires treatment of the rotationally inelastic collision problem; this is in progress and will be reported later. Thus, except for comparison in the next section with the results of Amdur and Mason,[30] the only experimental data that we now consider are the virial coefficients measured by Brewer[31] and Cottrell *et al.*[32] The interaction second virial coefficient (in atomic units) for our angle-dependent potentials is given by[33]

$$B(T) = \pi\int_0^\infty r^2\,dr\int_{-1}^{1} dx\{1 - \exp[-V(r,x)/kT]\} , \tag{20}$$

where $x = \cos\theta$, $k$ is Boltzmann's constant, and $T$ is the absolute temperature. In evaluating Eq. (20) using the

TABLE X. Parameters $A_{ni}$ and $B_{ni}$ for Ar–CO$_2$ obtained directly from fitting electron gas estimates. Hartree atomic units.

| $n=$ | 0 | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|
| $A_{n1}$ | 0.290852E+02 | 0.824571E+02 | 0.128551E+03 | 0.413298E+03 | 0.431680E+03 | 0.565288E+03 |
| $A_{n2}$ | −0.716288E+00 | −0.811806E+00 | −0.117577E+01 | −0.188135E+01 | −0.214596E+01 | −0.244616E+01 |
| $A_{n3}$ | −0.869136E−01 | −0.753131E−01 | −0.477138E−01 | 0.0 E+00 | 0.0 E+00 | 0.0 E+00 |
| $B_{n1}$ | 0.273733E+00 | 0.311774E+00 | 0.148938E+00 | 0.106688E+00 | 0.390843E−01 | 0.308072E+00 |
| $B_{n2}$ | −0.650479E+00 | −0.620877E+00 | −0.735340E+00 | −0.105547E+01 | −0.183942E+01 | −0.204765E+01 |
| $B_{n3}$ | −0.320299E−01 | −0.310717E−01 | −0.296750E−01 | −0.182219E−01 | −0.494781E−01 | 0.0 E+00 |

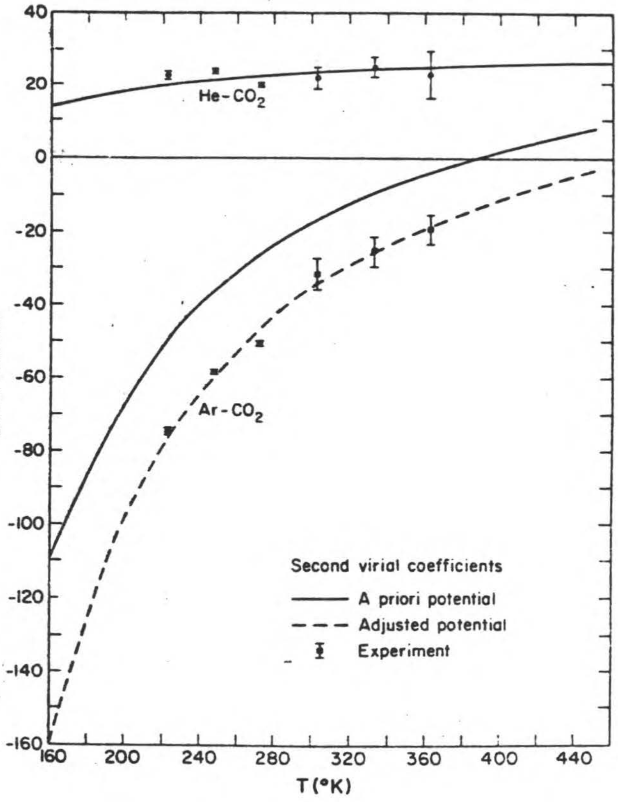

FIG. 3. Interaction second virial coefficients (in cc/mole) vs temperature for He–CO$_2$ and Ar–CO$_2$. The points and error bars are experimental results; the solid lines are calculated from the *a priori* intermolecular potentials; and the dashed line is calculated from the adjusted Ar–CO$_2$ potential.

parameters of Tables XI and XII, the integrations over very small and very large $r$ were done analytically, and that over moderate $r$ was done by two dimensional Gauss–Legendre quadrature using 32 points in each coordinate. The results (in units of cc/mole) are the solid lines in Fig. 3, where one sees that the agreement for He–CO$_2$ is excellent and limited only by the scatter in the experimental results. However, this agreement is clearly fortuitous as the calculated Ar–CO$_2$ $B(T)$ lies parallel to but above the experimental results and indicates that our Ar–CO$_2$ potential is too repulsive. This was surprising to us, and we have no explanation for it; on the basis of our atom–atom results[4] we expected He–CO$_2$ to be too repulsive and Ar–CO$_2$ to be accurate. To improve agreement, one can increase the magnitude of the attractive $V_{\mathrm{COR}}$ or decrease the repulsive $V_{\mathrm{HF}}$. To know which is appropriate would require more information; we arbitrarily chose to do the latter by scaling down all the Ar–CO$_2$ $A_{n1}$ uniformly so that the slope and anisotropy of $V_{\mathrm{HF}}$ are still those given by the electron gas model. Use of $A'_{n1} = 0.771\, A_{n1}$ was found to minimize the standard deviation from experi-

TABLE XI. Parameters of the best *a priori* He–CO$_2$ intermolecular potential obtained by the present method. Includes the van der Waals potential. Hartree atomic units.

| $n =$ | 0 | 2 | 4 | 6 | 8 |
|---|---|---|---|---|---|
| $A_{n1}$ | 0.172995E+02 | 0.655752E+02 | 0.105137E+03 | 0.178531E+03 | 0.314919E+03 |
| $A_{n2}$ | −0.982289E+00 | −0.112538E+01 | −0.144877E+01 | −0.190354E+01 | −0.240207E+01 |
| $A_{n3}$ | −0.917494E−01 | −0.766468E−01 | −0.522417E−01 | −0.239120E−01 | 0.0 E+00 |
| $B'_{n1}$ | 0.122126E+00 | 0.569431E−01 | 0.252919E−01 | 0.162599E−01 | 0.636620E−01 |
| $B_{n2}$ | −0.628082E+00 | −0.663263E+00 | −0.976097E+00 | −0.116525E+01 | −0.188254E+01 |
| $B_{n3}$ | −0.470607E−01 | −0.399192E−01 | −0.215588E−01 | −0.280915E−01 | 0.0 E+00 |
| $r_n$ | 5.72050 | 6.27735 | 6.39141 | ∞ | ∞ |
| $C_6(n)$ | 16.75 | 3.88 | 0.0 | 0.0 | 0.0 |
| $C_8(n)$ | 278. | 290. | 57. | 0.0 | 0.0 |

TABLE XII. Parameters of the best present *a priori* Ar–$CO_2$ interaction including the van der Waals potential. Hartree atomic units.

| $n =$ | 0 | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|
| $A_{n1}$ | 0.290852E+02 | 0.824571E+02 | 0.128551E+03 | 0.413298E+03 | 0.431680E+03 | 0.565288E+03 |
| $A_{n2}$ | −0.716288E+00 | −0.811806E+00 | −0.117577E+01 | −0.188135E+01 | −0.214596E+01 | −0.244616E+01 |
| $A_{n3}$ | −0.869136E−01 | −0.753131E−01 | −0.477138E−01 | 0.0 E+00 | 0.0 E+00 | 0.0 E+00 |
| $B'_{n1}$ | 0.599056E+00 | 0.207391E+00 | 0.523497E−01 | 0.374994E−01 | 0.137376E−01 | 0.108283E+00 |
| $B_{n2}$ | −0.650479E+00 | −0.620877E+00 | −0.735340E+00 | −0.105547E+01 | −0.103942E+01 | −0.204765E+01 |
| $B_{n3}$ | −0.320299E−01 | −0.310717E−01 | −0.296750E−01 | −0.182219E−01 | −0.494781E−01 | 0.0 E+00 |
| $r_n$ | 6.32925 | 6.90026 | 6.96450 | ∞ | ∞ | ∞ |
| $C_6(n)$ | 114.5 | 26.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| $C_8(n)$ | 2380. | 2080. | 410. | 0.0 | 0.0 | 0.0 |

ment and gives the excellent agreement of the dashed line in Fig. 3. For convenience, the parameters of the resulting Ar–$CO_2$ potential are all given in Table XIII. (It should perhaps be noted that the standard deviation is already a minimum for He–$CO_2$; variation of the $A_{n1}$ by even 1% makes agreement worse!)

## IV. DISCUSSION AND CONCLUSIONS

The total $v_n$ of the final potentials for He–$CO_2$ (Table XI) and Ar–$CO_2$ (Table XIII) are plotted in Figs. 4 and 5. Note from them that $v_0$ and $v_2$ are the only $v_n$ with appreciable attractive wells and that they emphasize the dominance of the nonspherical parts of the potential at short range. Because of this the $v_0$ for He–$CO_2$ obtained by fitting integral scattering cross sections with a simple almost spherical model[29] and the $v_0$ for Ar–$CO_2$ obtained from fitting the virial coefficient data with a spherical model potential[34] bear little similarity to the present $v_0$. However, also plotted on Fig. 5 as a dashed line is the $v_0$ inferred by Mason[30] from Amdur's high energy scattering data. Considering the approximations involved in using a spherical model to analyze the scattering data, the fact that our $v_0$ and theirs cross and have slopes no more different than they are is surprising and must be considered to be excellent agreement.

A contour map of the final Ar–$CO_2$ surface is given in Fig. 6 which shows clearly the shape of the surface and

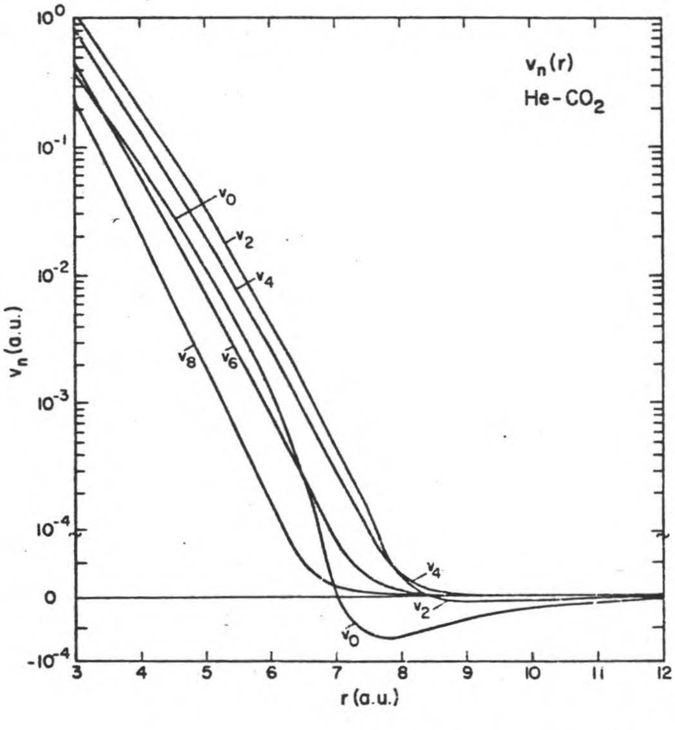

FIG. 4. Lengendre coefficients $v_n$ of the final He–$CO_2$ intermolecular potential vs distance. Atomic units.

**TABLE XIII.** Parameters for the final Ar–$CO_2$ interaction after inclusion of the van der Waals potential and adjustment to fit virial coefficient data. Hartree atomic units.

| $n$ = | 0 | 2 | 4 | 6 | 8 | 10 |
|---|---|---|---|---|---|---|
| $A'_{n1}$ | 0.224247E+02 | 0.635744E+02 | 0.991128E+02 | 0.318652E+03 | 0.332826E+03 | 0.435837E+03 |
| $A_{n2}$ | −0.716288E+00 | −0.811806E+00 | −0.117577E+01 | −0.188135E+01 | −0.214596E+01 | −0.244616E+01 |
| $A_{n3}$ | −0.869136E−01 | −0.753131E−01 | −0.477138E−01 | 0.0 E+00 | 0.0 E+00 | 0.0 E+00 |
| $B'_{n1}$ | 0.599056E+00 | 0.207391E+00 | 0.523497E−01 | 0.374994E−01 | 0.137376E−01 | 0.108283E+00 |
| $B_{n2}$ | −0.650479E+00 | −0.620877E+00 | −0.735340E+00 | −0.105547E+01 | −0.103942E+01 | −0.204765E+01 |
| $B_{n3}$ | −0.320299E−01 | −0.310717E−01 | −0.296750E−01 | −0.182219E−01 | −0.494781E−01 | 0.0 E+00 |
| $r_n$ | 6.32925 | 6.90026 | 6.96450 | ∞ | ∞ | ∞ |
| $C_6(n)$ | 114.5 | 26.6 | 0.0 | 0.0 | 0.0 | 0.0 |
| $C_8(n)$ | 2380. | 2080. | 410. | 0.0 | 0.0 | 0.0 |

location of the minimum. The He–$CO_2$ surface (not shown) is qualitatively similar, with a minimum 3.05 $\times 10^{-4}$ a.u. deep occurring at $r = 5.7\ a_0$ and $\theta = \pi/2$. These surfaces are probably reasonably accurate in the repulsive region up to the 0.1 a.u. contour; however, the nonphysical behavior of the 1 a.u. contour is due to divergence of the Legendre polynomial expansion and analytic fit of the $v_n$. It was not present in the original

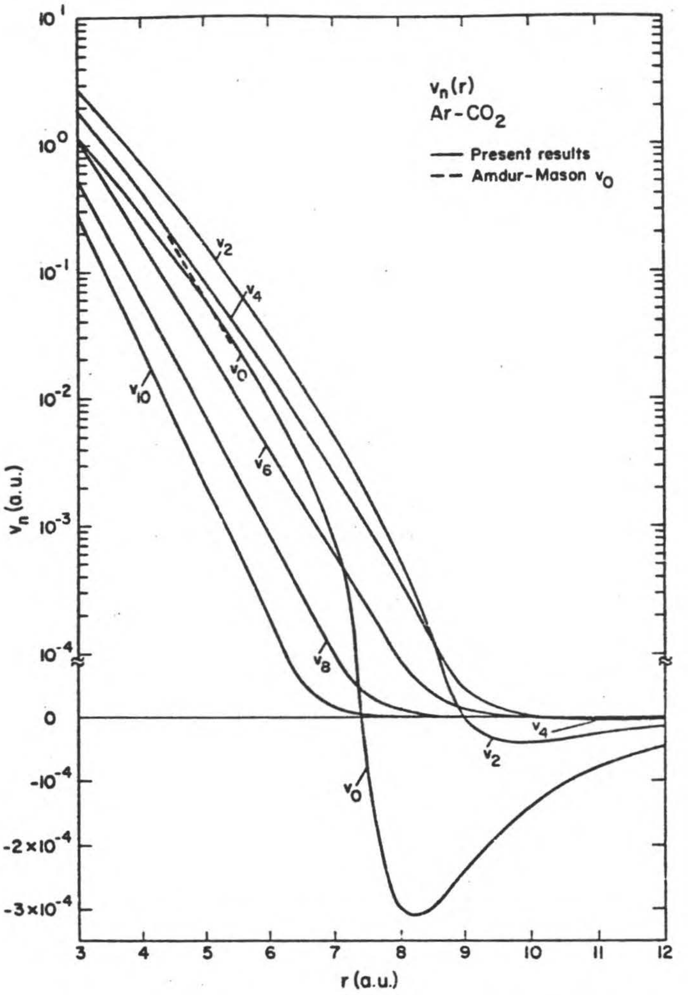

FIG. 5. Legendre coefficients $v_n$ of the final Ar–$CO_2$ intermolecular potential vs distance. The dashed line is the $v_0$ of Ref. 30. Atomic units.

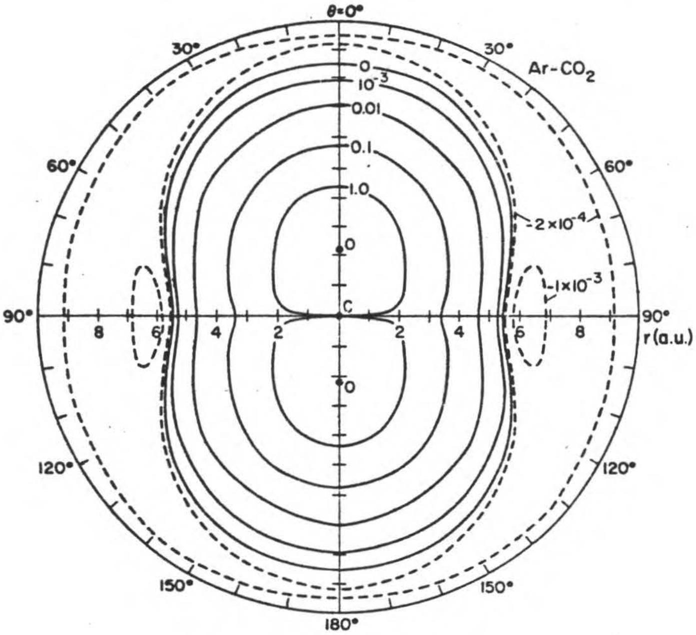

FIG. 6. Contour plot of the Ar–CO$_2$ potential energy surface. The positions of the carbon and oxygen atoms are noted. The contours in the plane give the potential energy felt by an argon atom at that point in atomic units.

results of Table II. Thus, the present analytic fits to these surfaces should not be used for the calculation of properties at energies or temperatures high enough that there is appreciable penetration inside the 0.1 a.u. contour. For such properties or for a study of vibrationally inelastic collisions, use of the potential surface of Suzukawa[21] would probably be more appropriate.

Before ending this discussion we point out some of the limitations and weaknesses of the present method and results. First, the comparisons with virial and scattering results indicate that the present surfaces are much better than one might have expected from such a crude model as the electron gas model, but many more studies are needed to see just what the limits of reliability of the model are. In this connection an improvement to the Rae[3] exchange correction is needed; had we not used it our *a priori* Ar–CO$_2$ surface would probably have given better virial coefficients, but our He–CO$_2$ surface would have been too attractive. Second, there is some arbitrariness in our fit of the surfaces. For a molecule as asymmetric as CO$_2$, use of prolate spheroidal coordinates and expansion in spheroidal harmonics would probably have given better convergence at small distances than the present expansion, and the van der Waals potential would also be valid to smaller distances.[35] (In the present expansion the distances $r_n$ in to which the van der Waals potential is used are appropriate at angles near $\pi/2$ but too small for angles near 0.) For the present, rigid rotor model scattering calculations could be done in spheroidal coordinates, but if vibrational motion were allowed, it would cause difficulty as the vibrational and spheroidal coordinates are not orthogonal. Third, our scaling of $V_{\mathrm{COR}}$ to match the van der Waals potential makes it much less anisotropic everywhere, and there should really be some short-ranged anisotropic correlation contributions, but we do not presently know how important they are or how to include them in a less than arbitrary way. Finally, because of the way they are constructed, these intermolecular potentials are expected to be rather good in the long range and moderately short range regions but weakest near the bottom of the attractive well. As a result, we expect them to give rather good estimates of the magnitudes of thermal scattering cross sections but not to reproduce accurately any structure that is very sensitive to the well region.

In conclusion, we believe that, notwithstanding their limitations, the present surfaces for these systems are the first to have both realistic long and short range behavior. We are very encouraged by the success of the electron gas–van der Waals potentials in describing the few experimental properties used herein and believe the surfaces are accurate enough to be useful in predicting and understanding many He–CO$_2$ and Ar–CO$_2$ collision phenomena. Scattering calculations to test this hypothesis are in progress.

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# APPENDIX E

# van der Waals INTERACTIONS OF CARBON MONOXIDE

(A reprint. See Gregory A. Parker and Russell T Pack, J. Chem. Phys. 64, 2010 (1976).)

# van der Waals interactions of carbon monoxide*

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(Received 9 September 1975)

Padé approximant methods and experimental frequency dependent polarizabilities are used to calculate reliable van der Waals $C_6$ coefficients for the interaction of CO with He, Ne, Ar, Kr, Xe, H, Li, Na, K, Rb, Cs, $H_2$, $N_2$, $O_2$, $CO_2$, and CO. Error bounds are given for the $C_6$ coefficients and for the CO oscillator strength sums.

## I. INTRODUCTION AND THEORY

In a recent paper[1] (hereinafter called I), one of us calculated van der Waals coefficients for $CO_2$ interactions using the Padé approximant methods of Langhoff and Karplus[2] to get the contribution to the polarizability from the ultraviolet part of its spectrum and the method of Nir, Adams, and Rein,[3] which views molecular bands as lines of finite width, to get the infrared contribution. In this paper we use this method to calculate the first reliable van der Waals $C_6$ coefficients for interactions involving carbon monoxide, CO.

As is well known,[4] the van der Waals $C_6$ coefficient for the interaction of a $\Sigma$-state diatomic molecule such as CO with an $S$-state atom takes the form

$$C_6 = C_6(0) + C_6(2)\, P_2(\cos\theta), \tag{1}$$

where $\theta$ is the angle between the molecular axis and the vector from the center of mass of the molecule to the atom, and $P_2$ is a Legendre polynomial. Here each coefficient includes both induction and dispersion contributions:

$$C_6(L) = C_6^{\text{ind}}(L) + C_6^{\text{dis}}(L). \tag{2}$$

The induction terms are simply given (in atomic units) by[4]

$$C_6^{\text{ind}}(0) = C_6^{\text{ind}}(2) = \alpha(A)\mu^2, \tag{3}$$

where $\mu$ is the permanent dipole moment of the molecule and $\alpha(A)$ is the static dipole polarizability of the atom. Using the experimental value[5] $\mu(\text{CO}) = -0.112$ D $= -0.0441$ a.u. consistent with the use of experimental polarizabilities, so that the resulting van der Waals potential has been averaged over the ground state vibrational motion, one obtains the $C_6^{\text{ind}}(L)$ directly.

If the polarizability anisotropy ratio, $\kappa = (\alpha_\parallel - \alpha_\perp)/(\alpha_\parallel + 2\alpha_\perp)$, is known as a function of frequency, $C_6^{\text{dis}}(2)$ can be calculated accurately.[6] Unfortunately, for CO values of $\kappa$ have been reported at only two frequencies ($\kappa = 0.089$, at[7] $\omega = 0.0720$ a.u. and 0.100 at[8] 0.0934 a.u.), and their difference is opposite that necessitated by the spectrum of CO and thus wrong. We assume that the average of the two is the correct value and negligibly different from that at zero frequency. Then, as we have shown elsewhere,[4] one can obtain reasonable bounds on $C_6^{\text{dis}}(2)$ from

$$C_6^{\text{dis}}(2) = a_6 C_6^{\text{dis}}(0), \tag{4}$$

with

$$\frac{\alpha_\parallel^{3/4} - \alpha_\perp^{3/4}}{\alpha_\parallel^{3/4} + 2\alpha_\perp^{3/4}} \lesssim a_6 \lesssim \kappa, \tag{5}$$

which gives the estimate

$$a_6 = 0.083 \pm 0.017 \tag{6}$$

for CO interactions.

The remaining part of $C_6$, $C_6^{\text{dis}}(0)$, is determined in the following section using, with minor modifications, the method of Paper I, which briefly stated is as follows: The experimental frequency dependent polarizability is obtained from refractive index data using the Lorenz–Lorentz equation; then, it is fit using a finite linewidth dispersion term for the ir part and a Cauchy expansion for the uv part. Then, the resulting sum rules (coefficients of the Cauchy expansion) are used to construct upper and lower Padé bounds to the polarizability. From these, effective oscillator strengths and excitation frequencies are obtained from which upper and lower bounds to $C_6^{\text{dis}}(0)$ are obtained.

## II. CALCULATIONS AND RESULTS

As input data we used values of the refractive index $\eta$ of CO at 94 wavelengths ranging from 237.9–13 000 nm reported by Landolt and Bornstein[9] and the International Critical Tables.[10] We were unable to find any newer measurements. The frequency-dependent average polarizability $[\alpha = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)]$ was obtained at each frequency from the Lorenz–Lorentz equation[3]

$$\alpha(\omega) = \frac{3}{4\pi n}\left(\frac{\eta^2 - 1}{\eta^2 + 2}\right), \tag{7}$$

where $n$ is the number density of CO molecules. The Benedict–Webb–Rubin equation of state for CO of

TABLE I. Oscillator strength sums for CO. The ultraviolet contributions were obtained directly from fitting Eq. (9) and the infrared contributions from expansion of the first term in Eq. (9) after fitting: $S(0)$ is from the Reiche–Thomas–Kuhn sum rule. All are in Hartree atomic units.

| $k$ | $S^{\text{uv}}(k)$ | $S^{\text{ir}}(k)$ | $S^{\text{tot}}(k)$ |
|---|---|---|---|
| 0 | 14.0000 | $1.37 \times 10^{-5}$ | 14.0000 |
| −2 | 13.0891 ± 0.0002 | 0.142 ± 0.003 | 13.231 ± 0.003 |
| −4 | 47.842 ± 0.055 | $1.48 \times 10^3$ | $1.53 \times 10^3$ |
| −6 | 318.6 ± 5.7 | $1.51 \times 10^7$ | $1.51 \times 10^7$ |
| −8 | 2800 ± 230 | $1.53 \times 10^{11}$ | $1.53 \times 10^{11}$ |
| −10 | 26500 ± 3000 | $1.59 \times 10^{15}$ | $1.59 \times 10^{15}$ |

TABLE II. Effective oscillator strengths $f_n$, frequencies $\omega_n$, and widths $\gamma_n$ for CO. Here $A_n = f_n/\omega_n^2$. The parameters for $n=1$ were obtained from Eq. (9). On the others $u$ and $l$ label parameters from the upper and lower bounding Padé approximants. Hartree atomic units.

| $n$ | $f_n$ | $A_n$ | $\omega_n$ | $\gamma_n$ |
|---|---|---|---|---|
| 1 | 1.36874 $E$−5 | 0.1415644 | 9.832942 $E$−3 | 3.040752 $E$−4 |
| 2$u$ | 13.13886 | 6.919783 | 1.377947 | 0.0 |
| 2$l$ | 5.539610 | 9.959741 | 0.7457883 | 0.0 |
| 3$u$ | 0.8611361 | 6.169317 | 0.3736090 | 0.0 |
| 3$l$ | 0.3271316 | 3.129359 | 0.3233207 | 0.0 |

Schiller and Canjar[11] gives as the conversion factor from measurements at STP to $\alpha(\omega)$ in atomic units

$$3/(4\pi n) = 59926.98\ a_0^3\ . \tag{8}$$

$\alpha(0)$ can also be obtained from dielectric constant measurements[12] via the Clausius–Mosotti equation,[13] and the value $\alpha(0) = 13.21 \pm 0.13\ a_0^3$ thus obtained is consistent with the $\alpha(0) = S(-2)$ determined below from refractive index data but sufficiently uncertain that it could not be used to improve accuracy.

The experimental $\alpha(\omega)$ were then fit by the formula (see Paper I)

$$\mathrm{Re}\,\alpha(\omega) = \frac{A_1[1-(\omega/\omega_1)^2]}{[1-(\omega/\omega_1)^2]^2 + (\gamma_1\omega/\omega_1^2)^2} + \sum_{k=0}^{4} S^{uv}(-2k-2)\omega^{2k}, \tag{9}$$

where the first term is the contribution of the ir spectrum of CO, and the uv contribution has been expanded in a Cauchy series. The parameters in (9) were determined by an iterative procedure in which the three parameters in the ir term and $S(-10)$ were calculated using a nonlinear flexible tolerance minimization program[14] which included the Stieltjes constraints,[2] and $S(-2)$ through $S(-8)$ were calculated using a linear least squares method. This procedure gave a root mean square deviation of 0.041 $a_0^3$, which is half that of the 2 term fit of Nir, Adams, and Rein.[3]

The resulting oscillator strength sums $S^{uv}(k)$ are given in Table I. These were used to calculate the [2, 1] Padé approximants[2] from which the effective oscillator strengths and effective frequencies of Table II and upper and lower bounds to the $C_6^{\mathrm{dis}}(0)$ could be obtained as in Paper I. However, the Padé methods treat the $S^{uv}(k)$ as though they were exact and had been determined with an infinite number of terms in the summation in Eq. (9). To get an estimate of the additional error thus introduced, we varied $S^{uv}(-10)$, which is not needed by the [2, 1] Padé approximants, over the entire range allowed by the Stieltjes constraints to see what values of the other $S(k)$ and of $C_6^{\mathrm{dis}}(0)$ that would generate. That gave the error limits shown in Table I, but because the original data were quite smooth and the uncertainties in the $S(k)$ are quite small, it only widened the error bounds on the $C_6^{\mathrm{dis}}(0)$ slightly.

The resulting $C_6^{\mathrm{dis}}(0)$ for the interaction of CO with a number of partners (using the sum rules from Refs. 1 and 2 for the other atoms and molecules) are given in Table III. The numbers shown are the means of the best Padé bounds, but the uncertainties include the range of values generated by the uncertainties in the $S(k)$. Also in Table II are the induction and angle-dependent parts of $C_6$ for the partners for which Eq. (1)–(3) are adequate. The induction terms are very small because the dipole moment of CO is so small.

Before concluding we note that the $C_6$ coefficients discussed herein are only defined within the Born–Oppenheimer approximation, and only the *electronic* polarizability should be used in calculating $C_6^{\mathrm{dis}}(0)$. In a future publication,[4] we discuss the vibrational coordinate dependence of $C_6$ in detail and show that, to a good approximation, the experimental quantities needed in calculating $C_6$ are the $S^{uv}(k)$ rather than the $S^{\mathrm{tot}}(k)$. In the present case the ir spectrum of CO contributes only about 1% of the static polarizability, and inclusion of the ir contribution ($n = 1$ term of Table II) would change the $C_6^{\mathrm{dis}}$ of Table III by a completely negligible amount (less than 0.1%). In our previous paper on $CO_2$ $C_6$ coef-

TABLE III. Van der Waals $C_6$ coefficients for the interaction of CO with various partners. All are in Hartree atomic units ($e^2a_0^5$).

| Partner | $C_6^{\mathrm{dis}}(0)$ | $C_6^{\mathrm{ind}}(0)$ | $C_6^{\mathrm{tot}}(0)$ | $C_6^{\mathrm{dis}}(2)$ | $C_6^{\mathrm{ind}}(2)$ | $C_6^{\mathrm{tot}}(2)$ |
|---|---|---|---|---|---|---|
| H | 23.0 ± 0.9 | 8.74 $E$−3 | 23.0 ± 0.9 | 1.92 ± 0.47 | 8.74 $E$−3 | 1.92 ± 0.47 |
| Li | 201.9 ± 4.1 | 3.18 $E$−1 | 202.2 ± 4.1 | 16.8 ± 3.8 | 3.18 $E$−1 | 17.1 ± 3.8 |
| Na | 246 ± 16 | 3.25 $E$−1 | 247 ± 16 | 20.5 ± 5.7 | 3.25 $E$−1 | 20.8 ± 5.7 |
| K | 363 ± 24 | 5.59 $E$−1 | 364 ± 24 | 30.3 ± 8.4 | 5.59 $E$−1 | 30.8 ± 8.5 |
| Rb | 412 ± 28 | 6.13 $E$−1 | 412 ± 28 | 34.3 ± 9.7 | 6.13 $E$−1 | 34.9 ± 9.7 |
| Cs | 355 ± 16 | 6.92 $E$−1 | 356 ± 16 | 29.6 ± 7.5 | 6.92 $E$−1 | 30.3 ± 7.6 |
| He | 11.2 ± 0.8 | 2.69 $E$−3 | 11.2 ± 0.8 | 0.93 ± 0.27 | 2.69 $E$−3 | 0.93 ± 0.27 |
| Ne | 23.8 ± 2.5 | 5.18 $E$−3 | 23.8 ± 2.5 | 1.98 ± 0.65 | 5.18 $E$−3 | 1.98 ± 0.65 |
| Ar | 78.2 ± 7.6 | 2.15 $E$−2 | 78.2 ± 7.6 | 6.5 ± 2.1 | 2.15 $E$−2 | 6.5 ± 2.1 |
| Kr | 111 ± 12 | 3.25 $E$−2 | 111 ± 12 | 9.3 ± 3.0 | 3.25 $E$−2 | 9.3 ± 3.1 |
| Xe | 192 ± 25 | 5.31 $E$−2 | 192 ± 25 | 16.0 ± 5.7 | 5.31 $E$−2 | 16.0 ± 5.7 |
| $H_2$ | 32.1 ± 1.5 | | | | | |
| $N_2$ | 80.7 ± 6.9 | | | | | |
| $O_2$ | 62.8 ± 3.3 | | | | | |
| $CO_2$ | 128.6 ± 8.7 | | | | | |
| CO | 88.4 ± 9.7 | | | | | |

ficients,[1] this ir contribution was inadvertently included, and the $C_6$ coefficients obtained there should be revised downward by about 1% (which is still well within the stated uncertainity).

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*Work performed in part under the auspices of the USERDA and supported in part at Brigham Young University by the USERDA and the University of California Los Alamos Scientific Laboratory through Subcontract No. XP5-72554.

†Present address of both authors.

[1] R. T Pack, J. Chem. Phys. 61, 2091 (1974).

[2] P. W. Langhoff and M. Karplus, J. Chem. Phys. 53, 233 (1970); P. W. Langhoff and M. Karplus, J. Opt. Soc. Am. 59, 363 (1969); P. W. Langhoff, J. Chem. Phys. 57, 2604 (1972).

[3] (a) S. Nir, S. Adams, and R. Rein, J. Chem. Phys. 59, 3341 (1973); (b) S. Nir, S. Adams, and R. Rein, Int. J. Quantum Chem. Symp. 6, 295 (1972).

[4] See, for example, R. T Pack, J. Chem. Phys. 64, 1257 (1976).

[5] See references in F. P. Billingsley II and M. Krauss, J. Chem. Phys. 60, 4130 (1974).

[6] P. W. Langhoff, R. G. Gordon, and M. Karplus, J. Chem. Phys. 55, 2126 (1971).

[7] N. J. Bridge and A. D. Buckingham, Proc. R. Soc. London Ser. A 295, 334 (1966).

[8] R. L. Rowell and G. M. Aval, J. Chem. Phys. 54, 1960 (1971).

[9] Ländolt-Bornstein, *Zahlenwerte und Functionen* (Springer, Berlin, 1962), 6 Auflage, II Band, 8 Teil, pp. 871–889.

[10] *International Critical Tables*, edited by E. W. Washburn (McGraw-Hill, New York, 1930), Vol. VII, pp. 6–11.

[11] F. C. Schiller and L. N. Canjar, Chem. Eng. Proc. Symp. Ser. 49, 67 (1953).

[12] Hans-Joachim v. Braunmühl, Phys. Z. 28, 141 (1927).

[13] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964), pp. 858–861.

[14] D. M. Himmelblau, *Applied Nonlinear Programming* (McGraw-Hill, New York, 1972), pp. 458–468.

# APPENDIX F

# van der Waals INTERACTIONS OF $\Pi$-STATE LINEAR MOLECULES WITH ATOMS. $C_6$ FOR NO($X^2\Pi$) INTERACTIONS.

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# van der Waals interactions of Π-state linear molecules with atoms. $C_6$ for NO($X^2\Pi$) interactions*

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Formulas are derived for the van der Waals $C_n$ coefficients for the interaction of a diatomic molecule in a Π electronic state with an $S$-state atom. Two triatomic states arise from the degenerate Π state. The average of the two energies has the usual Legendre polynomial ($P_L$) angular dependence, but the difference in energies of the two states is shown to have associated Legendre polynomial ($P_L^M$ with $M = 2$) angular dependence. Procedures for including spin orbit coupling are included, and the extension to interactions of Δ- and Φ-state molecules is discussed. Values of the spherical part of the $C_6$ coefficients for the interaction of NO with He, Ne, Ar, Kr, Xe, H, Li, Na, K, Rb, Cs, $H_2$, $N_2$, $O_2$, CO, $CO_2$, and NO are obtained from frequency-dependent polarizability data using Padé approximants. In addition, estimates of all the induction and angle-dependent parts of $C_6$ are given for the NO–atom interactions.

## I. INTRODUCTION

When a diatomic molecule in Π electronic state interacts with an $S$-state atom, the interaction breaks the degeneracy of the Π state and two potential energy surfaces arise, one for which the electronic wavefunction is symmetric under reflection in the triatomic plane and one for which it is antisymmetric. In connection with our calculation of these two surfaces for the Ar–NO system[1] using the electron gas model, we became interested in also determining the van der Waals potentials for such systems. This paper presents the results of our study.

In the next section we derive the formula for the general second order van der Waals $C_n$ coefficient for the nonrelativistic interaction of a Π state diatomic with an $S$-state atom using the notation of our recent paper on those interactions for Σ-state molecules.[2] Two surfaces are obtained. Others[3,4] have combined these two surfaces by introducing dependence on an azimuthal angle; however, when one does that he must remember that the additional coordinate is an *electronic* coordinate and cannot be treated as a nuclear coordinate in collision studies. To avoid confusion, we stay strictly within the Born–Oppenheimer approximation and keep two surfaces.

In Sec. II we also look in detail at the $C_6$ coefficient and discuss ways to estimate the parts of it. In Sec. III we apply these methods to the interactions of NO ($X^2\Pi$), obtaining the spherical part of $C_6$ from frequency-dependent polarizability data using the Padé approximant methods of Langhoff and Karplus[5] and estimating the angle-dependent parts of $C_6$ from available data. Then, in Sec. IV we show how to include spin–orbit coupling and also discuss the results.

## II. THEORY

### A. Derivation of general formulas

We consider a neutral molecule A in a Π electronic state and a neutral $S$-state atom B interacting at a distance large enough that electron exchange and overlap are negligible. In this section a completely nonrelativistic, spin-free Hamiltonian is used; spin–orbit effects can be included afterward as discussed in Sec. IV. Thus, were it not for the interaction, the correct zeroth-order electronic states for the molecule, regardless of total spin $S$, would be denoted by $|\Lambda, M_s\rangle = |\pm 1, M_s\rangle$, where $\Lambda$ is the component of electronic orbital angular momentum along the molecular axis and $M_s$ is the component of electronic spin angular momentum $S$ along the same axis. Since $M_s$ is being treated as a good quantum number at present, we will suppress it and write $|\Lambda\rangle$ for $|\Lambda, M_s\rangle$. Now, when the atom is present, the only symmetry remaining, in general, is reflection in the plane of the three atoms, so that the degeneracy of $|1\rangle$ and $|-1\rangle$ is removed. If the $x$ axis is kept perpendicular to the triatomic plane (Fig. 1), the proper zeroth-order molecular wavefunctions $|\sigma\rangle$ are those which have definite parity $\sigma$ under the operation $\sigma$ which reflects $x$ into $-x$ (but leaves spin space alone[6]); that is,

$$\sigma|\sigma\rangle = (-1)^{\sigma}|\sigma\rangle, \tag{1}$$

where $\sigma = 0$ and 1 give the even (+) and odd (−) states, respectively. However, as we have discussed elsewhere,[6] one has

$$\sigma|\Lambda\rangle = (-1)^{s\Lambda}|-\Lambda\rangle, \tag{2}$$

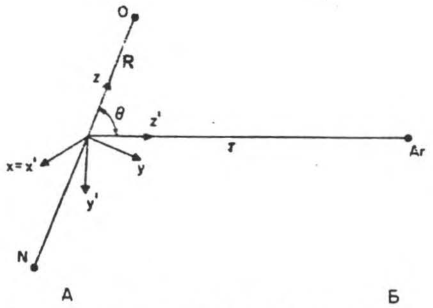

FIG. 1. Coordinate axes systems used for the interaction of a Π-state molecule A (in this case NO) with an $S$-state atom B (such as Ar). The $x$ axis of both systems is perpendicular to the plane of the three atoms.

where $s_A$ is a natural parity dependent on phase conventions. (For our NO example, $s_A = 0$.) Similarly, if $|0\rangle$ is the ground ($S$) state wavefunction of atom B, it will automatically have some parity $s_B$ under $\sigma$,

$$\sigma|0\rangle = (-1)^{s_B}|0\rangle. \tag{3}$$

(It happens that $s_B = 0$ for all the atoms used as examples in this paper.) With projection techniques one easily shows that the proper products to take as the two zeroth-order solutions of the triatomic problem are

$$|\sigma, 0\rangle = |\sigma\rangle|0\rangle = 2^{-1/2}[|1\rangle + (-1)^{s_A+s_B+\sigma}|-1\rangle]|0\rangle. \tag{4}$$

The long range potential is obtained by solving the electronic Schrödinger equation in the usual perturbative fashion.[7] The Born–Oppenheimer electronic Hamiltonian is written in the form,

$$H_e = H_A + H_B + V, \tag{5}$$

where $H_A$ and $H_B$ are the electronic Hamiltonians of molecule A and atom B, and $V$ is the electrostatic interaction. Because atom B has no permanent multipole moments, the first order interaction energy vanishes at large distances,

$$E^{(1)} = \langle 0, \sigma|V|\sigma, 0\rangle = 0. \tag{6}$$

The second order energy can be written, in general, in terms of a Green's function as

$$E^{(2)} = -\langle 0, \sigma|(V - E^{(1)})[H_A + H_B - E_0(A) - E_0(B)]^{-1} \times (V - E^{(1)})|\sigma, 0\rangle. \tag{7}$$

In evaluating this, one is free to use any spectral representation of the Green's function he wishes. For convenience we choose to use the complete set of functions $|\nu, n\rangle = |\nu\rangle|n\rangle$, where $|\nu\rangle$ and $|n\rangle$ are the eigenfunctions of A and B, respectively, which have definite $\Lambda$ and $M_L(B)$ rather than definite reflection parity $\sigma$. Then, because of the symmetry of B, Eq. (7) becomes

$$E^{(2)} = -\sum_\nu \sum_n{}' \frac{\langle 0, \sigma|V|\nu, n\rangle\langle n, \nu|V|\sigma, 0\rangle}{\epsilon_\nu + \epsilon_n}, \tag{8}$$

where $\epsilon_\nu = E_\nu(A) - E_0(A)$, etc., and the prime implies omission of the $n = 0$ term. However, the $\nu = |\pm 1\rangle$ induction terms are included.

When the multipole expansion for $V$ is substituted into Eq. (8), $E^{(2)}$ takes on the usual van der Waals form,

$$E^{(2)} = -\sum_{k=6} r^{-k} C_k, \tag{9}$$

where $r$ is the distance from the center of mass of the nuclei of A to the nucleus of B, and in the notation of our recent work[2] on $\Sigma$-state interactions, $C_k$ is given by

$$C_k = \sum_{j=3}^{k-3} \Delta_{j,k-j}, \tag{10}$$

where

$$\Delta_{jj'} = \frac{1}{2}\sum_{l=1}^{j-2}\sum_m F(j, l, m)F(j', j'-j+l, -m)(-1)^{-m} \times \sum_\nu \sum_n{}' \frac{\langle\sigma|Q_l^m(A)|\nu\rangle\langle\nu|Q_{j'-j+l}^{-m}(A)|\sigma\rangle}{\epsilon_n(\epsilon_\nu + \epsilon_n)} \times f_{0n}(j-1-l, j-1-l; B). \tag{11}$$

Here $F(j, l, m)$ is a known coefficient,[2,7,8] the $f_{0n}$ are the usual[9] $2^{j-1-l}$-pole oscillator strengths of atom B, and the $Q_l^m(A)$ are the multipole moment operators of A (in atomic units),

$$Q_l^m(A) = [4\pi/(2l+1)]^{1/2}\sum_{i\in A} Z_i r_{iA}^l Y_l^m(\theta_i, \phi_i). \tag{12}$$

The sum in Eq. (12) is over all nuclei and electrons belonging to molecule A with coordinates measured from the center of mass of the nuclei of A and the $z'$ axis taken to point along $\mathbf{r}$ as in Fig. 1.

To simplify evaluation of the matrix elements in Eq. (11) we transform from the present coordinates (the primed set in Fig. 1) to a new set (unprimed in Fig. 1) in which the $z$ axis points along the molecular axis R. In doing so, the $x$ axis is kept perpendicular to the plane of the three atoms so that reflection in the triatomic plane will be the same ($x \rightarrow -x$) in both systems. To achieve this rotation through angle $\theta$ about $x$ using Euler angles, we rotate the axes by $\alpha = 3\pi/2$ around $z'$, then by $\beta = \theta$ around the resulting $y''$ axis, and then by $\gamma = \pi/2$ about the new $z$ axis. The effect of this rotation on the multipole moment operators is

$$Q_l^m(\hat{r} = \hat{z}) = \sum_{\mu=-l}^{l} D_{\mu m}^l(3\pi/2, \theta, \pi/2) Q_l^\mu(\hat{R} = \hat{z}), \tag{13}$$

where the Wigner $D$ functions are the representations of of the rotation group.[10,11] This gives

$$\Delta_{jj'} = \frac{1}{2}\sum_{l=1}^{j-2}\sum_m F(j, l, m)F(j', j'-j+l, -m)(-1)^{-m}\sum_\mu\sum_{\mu'} D_{\mu m}^l D_{\mu', -m}^{j'-j+l}\sum_\nu\sum_n{}' \frac{\langle\sigma|Q_l^\mu|\nu\rangle\langle\nu|Q_{j'-j+l}^{\mu'}|\sigma\rangle}{\epsilon_n(\epsilon_\nu + \epsilon_n)} f_{0n}(j-1-l, j-1-l), \tag{14}$$

where we have surpressed the arguments of the $D$ functions and also the A and B labels where $\nu$ and $n$ make them clear. Coupling the two Wigner $D$ functions together via the Clebsch–Gordan theorem[10,12] gives

$$\Delta_{jj'} = \frac{1}{2}\sum_{l=1}^{j-2}\sum_L \alpha(L, l, j, j')\sum_\mu\sum_{\mu'} C(l, j'-j+l, L; \mu, \mu', \mu+\mu') D_{\mu+\mu', 0}^L \sum_\nu\sum_n{}' \frac{\langle\sigma|Q_l^\mu|\nu\rangle\langle\nu|Q_{j'-j+l}^{\mu'}|\sigma\rangle}{\epsilon_n(\epsilon_\nu + \epsilon_n)} f_{0n}(j-1-l, j-1-l), \tag{15}$$

where[2]

$$\alpha(L, l, j, j') = \sum_m (-1)^{-m} F(j, l, m)F(j', j'-j+l, -m)C(l, j'-j+l; L, m, -m, 0), \tag{16}$$

$$= \frac{(-1)^{j'-l+1+L}}{(2j-2l-2)!}\left[\frac{(2j-1)!(2j'-1)!}{(2l)!(2j'-2j+2l)!}\right]^{1/2} C(j-1, j'-1, L; 000)\, W(j-l-1, l, j'-1, L; j-1, j'-j+l), \tag{17}$$

and $W$ is a Racah coefficient.[13] For those values of the parameters for which $\alpha$ is nonzero, it reduces to

$$\alpha(L,l,j,j')=\frac{(-1)^{(j-j'+L)/2-l}(j+j'-L-2)!\left(\frac{j+j'+L-2}{2}\right)!}{(2j-2l-2)!\left(\frac{j+j'-L-2}{2}\right)!\left(\frac{j-j'+L}{2}\right)!\left(\frac{j'-j+L}{2}\right)!}\left[\frac{(2L+1)(j-j'+L)!(j'-j+L)!}{(j'-j+2l+1+L)!(j'-j+2l-L)!}\right]^{1/2}. \tag{18}$$

Use of the definition [Eq. (4)] for $|\sigma\rangle$, the $m$-type selection rule, and the fact that state $|\nu\rangle$ has a well-defined angular momentum projection $\Lambda_\nu$ along the molecular axis allows the sums over $\mu$ and $\mu'$ in Eq. (15) to be done and gives

$$\begin{aligned}\Delta_{jj'}=\frac{1}{4}\sum_{l=1}^{j-2}\sum_{L}\alpha(L,l,j,j')\sum_{\nu}\sum_{n}{}'\frac{f_{0n}(j-1-l,j-1-l)}{\epsilon_n(\epsilon_\nu+\epsilon_n)}&[D^L_{0,0}C(l,j'-j+l,L;1-\Lambda_\nu,\Lambda_\nu-1,0)\langle 1|Q_l^{1-\Lambda_\nu}|\nu\rangle\langle\nu|Q^{\Lambda_\nu-1}_{j'-j+l}|1\rangle\\ &+D^L_{0,0}C(l,j'-j+l,L;-1-\Lambda_\nu,\Lambda_\nu+1,0)\langle -1|Q_l^{-1-\Lambda_\nu}|\nu\rangle\langle\nu|Q^{\Lambda_\nu+1}_{j'-j+l}|-1\rangle+(-1)^{s_A+s_B+\sigma}D^L_{2,0}C(l,j'-j+l,L;1-\Lambda_\nu,\Lambda_\nu\\ &+1,2)\langle 1|Q_l^{1-\Lambda_\nu}|\nu\rangle\langle\nu|Q^{\Lambda_\nu+1}_{j'-j+l}|-1\rangle+(-1)^{s_A+s_B+\sigma}D^L_{-2,0}C(l,j'-j+l,L;-1-\Lambda_\nu,\Lambda_\nu-1,-2)\langle -1|Q_l^{-1-\Lambda_\nu}|\nu\rangle\\ &\times\langle\nu|Q^{\Lambda_\nu-1}_{j'-j+l}|1\rangle].\end{aligned} \tag{19}$$

The $D$ functions here reduce[10,14] to spherical harmonics or to associated Legendre polynomials,[15]

$$D^L_{M,0}(3\pi/2,\theta,\pi/2)=[4\pi/(2L+1)]^{1/2}Y_L^{M*}(-\theta,-\pi/2), \tag{20}$$

$$=\left[\frac{(L-M)!}{(L+M)!}\right]^{1/2}P_L^M(\cos\theta)\,e^{iM\pi/2}. \tag{21}$$

Using this and the relation

$$Y_L^{-M}=(-1)^M Y_L^{M*}, \tag{22}$$

to avoid dealing with $P_L^{-2}$, we have

$$\begin{aligned}\Delta_{jj'}=\frac{1}{4}\sum_{l=1}^{j-2}\sum_{L}\alpha(L,l,j,j')\sum_{\nu}\sum_{n}{}'\frac{f_{0n}(j-1-l,j-1-l)}{\epsilon_n(\epsilon_\nu+\epsilon_n)}&\{P_L^0(\cos\theta)[C(l,j'-j+l,L;1-\Lambda_\nu,\Lambda_\nu-1,0)\langle 1|Q_l^{1-\Lambda_\nu}|\nu\rangle\\ &\times\langle\nu|Q^{\Lambda_\nu-1}_{j'-j+l}|1\rangle+C(l,j'-j+l,L;-1-\Lambda_\nu,\Lambda_\nu+1,0)\langle -1|Q_l^{-1-\Lambda_\nu}|\nu\rangle\langle\nu|Q^{\Lambda_\nu+1}_{j'-j+l}|-1\rangle]-(-1)^{s_A+s_B+\sigma}\left(\frac{(L-2)!}{(L+2)!}\right)^{1/2}\\ &\times P_L^2(\cos\theta)[C(l,j'-j+1,L;1-\Lambda_\nu,\Lambda_\nu+1,2)\langle 1|Q_l^{1-\Lambda_\nu}|\nu\rangle\langle\nu|Q^{\Lambda_\nu+1}_{j'-j+l}|-1\rangle+C(l,j'-j+l,L;-1-\Lambda_\nu,\Lambda_\nu-1,-2)\\ &\times\langle -1|Q_l^{-1-\Lambda_\nu}|\nu\rangle\langle\nu|Q^{\Lambda_\nu-1}_{j'-j+l}|1\rangle]\}.\end{aligned} \tag{23}$$

Thus, it is seen that in addition to the ordinary Legendre polynomial $P_L^0$ angle-dependent terms which are essentially the same as those obtained for the interactions of $\Sigma$-state molecules,[2] the natural expression for the $C_n$ for $\Pi$-state molecules also involves the associated Legendre polynomials $P_L^2$. Since the $P_L^0=P_L$ form a complete set, one could express the $P_L^2$ as linear combinations of the $P_L$, but, as we will show in a future paper[1] on collisions in these systems, it is convenient to keep the $P_L^2$ in there. Also, the fact that $P_L^2=0$ when $\theta=0$ or $\pi$ makes it clear that the difference in energies of the two states with different $\sigma$ vanishes, as it should, when the triatomic system is linear.

From Eq. (23) one could generate explicit expressions for any $C_n$ coefficient desired as we recently did in getting coefficients through $C_6$ for $\Sigma$-state molecules.[2] However, there is presently not enough information available for most $\Pi$-state molecules to calculate anything past $C_6$ with any reliability; hence, we only consider $C_6$ in the next subsection. Before doing so, we note in passing that the procedure just presented can be extended very simply to treat van der Waals interactions of molecules in $\Delta$, $\Phi$, etc. ($\Lambda=2,3$, etc.) states. Everything goes through as before except that in Eq. (4) one has

$$|\sigma\rangle=2^{-1/2}[|\Lambda\rangle+(-1)^{s_A+s_B+\sigma}|-\Lambda\rangle]. \tag{24}$$

Equation (15) is obtained as at present, but Eqs. (19) and (23) are generalized, and the angle dependence obtained involves the $P_L^{|2\Lambda|}$ in addition to the usual $P_L^0$.

### B. The $C_6$ coefficient

Let us now construct simpler explicit formulas for $C_6$. We start from Eq. (10),

$$C_6=\Delta_{33}, \tag{25}$$

and from Eq. (15), rather than Eq. (23), to make comparison with the usual formulas easier. Thus, $C_6$ is given by

$$\begin{aligned}C_6=\frac{1}{2}\sum_{L=0}^{2}\alpha(L,1,3,3)\sum_{\mu}\sum_{\mu'}C(1,1,L;\mu,\mu',\mu+\mu')\\ \times D^L_{\mu+\mu',0}\sum_{\nu}\sum_{n}{}'\frac{\langle\sigma|Q_1^{\mu}|\nu\rangle\langle\nu|Q_1^{\mu'}|\sigma\rangle}{\epsilon_n(\epsilon_\nu+\epsilon_n)}f_{0n}(1,1).\end{aligned} \tag{26}$$

We break this up into induction and dispersion contributions,

$$C_6 = C_6(\mathrm{ind}) + C_6(\mathrm{dis}), \tag{27}$$

and consider each separately.

### *1. Induction terms*

The induction contributions come from the terms with $|\nu\rangle = |1\rangle$ and $|-1\rangle$. Noting that $-1 \leq \mu, \mu' \leq 1$, one sees that all matrix elements like $\langle -1|Q_1^{\mu}|1\rangle$ are zero due to the $m$-type selection rule, and all that survive are the $\mu = \mu' = 0$ terms, so that $C_6(\mathrm{ind})$ becomes

$$C_6(\mathrm{ind}) = \frac{1}{4}\sum_{L=0}^{2} \alpha(L,1,3,3)C(1,1,L;0,0,0)D_{0,0}^{L}\,\alpha(\mathrm{B}) \times[\langle 1|Q_1^0|1\rangle\langle 1|Q_1^0|1\rangle + \langle -1|Q_1^0|-1\rangle \times\langle -1|Q_1^0|-1\rangle], \tag{28}$$

where $\alpha(\mathrm{B})$, given by

$$\alpha(\mathrm{B}) = \sum_n{}' f_{0n}\epsilon_n^{-2}, \tag{29}$$

is the usual static dipole polarizability of atom B. The matrix elements left here are all equal to the ordinary dipole moment of A, due to

$$\mu(\mathrm{A}) = \langle 1|Q_1^0|1\rangle = (-1)^{s_\mathrm{A}}\langle\sigma(-1)|Q_1^0|1\rangle = (-1)^{s_\mathrm{A}}\langle -1|\sigma Q_1^0|1\rangle = (-1)^{s_\mathrm{A}}\langle -1|Q_1^0\sigma|1\rangle = \langle -1|Q_1^0|-1\rangle. \tag{30}$$

Here $\sigma$ only need reflect the molecular coordinates, and we have used the commutation relation[6]

$$\sigma Q_l^m = Q_l^{-m}\sigma. \tag{31}$$

Use of Eq. (21) and evaluation of the coefficients in Eq. (28) gives

$$C_6(\mathrm{ind}) = C_6(0,\mathrm{ind}) + C_6(2,\mathrm{ind})P_2^0(\cos\theta), \tag{32a}$$

where

$$C_6(0,\mathrm{ind}) = C_6(2,\mathrm{ind}) = \alpha(\mathrm{B})\mu^2(\mathrm{A}), \tag{32b}$$

which is exactly the formula obtained for $\Sigma$-state molecules, so that nothing new is needed for this term for $\Pi$ states.

### *2. Dispersion terms*

The dispersion contribution is given by the terms in Eq. (26) for which $|\nu\rangle \neq |\pm 1\rangle$ and $n \neq 0$. The matrix elements involved are

$$\langle\sigma|Q_1^{\mu}|\nu\rangle\langle\nu|Q_1^{\mu'}|\sigma\rangle = \tfrac{1}{2}\{[\langle 1|Q_1^{\mu}|\nu\rangle\langle\nu|Q_1^{\mu'}|1\rangle + \langle -1|Q_1^{\mu}|\nu\rangle \times\langle\nu|Q_1^{\mu'}|-1\rangle] + (-1)^{s_\mathrm{A}+s_\mathrm{B}+\sigma}[\langle 1|Q_1^{\mu}|\nu\rangle \times\langle\nu|Q_1^{\mu'}|-1\rangle + \langle -1|Q_1^{\mu}|\nu\rangle\langle\nu|Q_1^{\mu'}|1\rangle]\}. \tag{33}$$

We assert that the first two terms here give equal contributions to the sum, and the last two do likewise. To prove this we represent $|\nu\rangle$ by $|\Lambda_\nu\rangle$ for clarity and use manipulations such as those in Eq. (30) to show that

$$\langle -1|Q_1^{\mu}|\Lambda_\nu\rangle\langle\Lambda_\nu|Q_1^{\mu'}|-1\rangle = \langle 1|Q_1^{-\mu}|-\Lambda_\nu\rangle\langle -\Lambda_\nu|Q_1^{-\mu'}|1\rangle, \tag{34}$$

and

$$\langle -1|Q_1^{\mu}|\Lambda_\nu\rangle\langle\Lambda_\nu|Q_1^{\mu'}|1\rangle = \langle 1|Q_1^{-\mu}|-\Lambda_\nu\rangle\langle -\Lambda_\nu|Q_1^{-\mu'}|-1\rangle, \tag{35}$$

where $\sigma|\Lambda_\nu\rangle = (-1)^{s_\nu}|-\Lambda_\nu\rangle$. Now, the $\mu$-type sums run symmetrically over positive and negative values, $\alpha(L,1,3,3)$ is only nonzero for even $L$, for which the Clebsch–Gordan coefficient is symmetric[12] under change of sign of $\mu$ and $\mu'$, and in the present case $D_{-\mu-\mu',0}^{L} = D_{\mu+\mu',0}^{L}$, so that we can change the signs of $\mu$ and $\mu'$ in the right hand sides of Eqs. (34) and (35). That proves the assertion for all states $\nu$ for which $\Lambda_\nu = 0$. For any state with $\Lambda_\nu \neq 0$, there is always another state with the same energy and $-\Lambda_\nu$ in the sum, so that the total contributions are equal. Furthermore, we note that the $m$-type selection rule is only satisfied if $\mu' = -\mu$ in the first term and $\mu' = 2-\mu$ in the third term of Eq. (33). Using these simplifications, we can write

$$C_6(\mathrm{dis}) = C_6(0,\mathrm{dis}) + C_6(2,\mathrm{dis})P_2^0(\cos\theta) + (-1)^{\gamma}D_6P_2^2(\cos\theta), \tag{36}$$

where

$$C_6(L,\mathrm{dis}) = \tfrac{1}{2}\alpha(L,1,3,3)\sum_{\mu} C(1,1,L;\mu,-\mu,0) \times\sum_{\nu}{}'\sum_{n}{}'\frac{\langle 1|Q_1^{\mu}|\nu\rangle\langle\nu|Q_1^{-\mu}|1\rangle}{\epsilon_n(\epsilon_\nu+\epsilon_n)}f_{0n}(1,1), \tag{37}$$

and

$$D_6 = \tfrac{1}{2}(-1)^{s_\mathrm{A}+s_\mathrm{B}+1}\alpha(2,1,3,3)\sum_{\mu} C(1,1,2;\mu,2-\mu,2)(4!)^{-1/2} \times\sum_{\nu}{}'\sum_{n}{}'\frac{\langle 1|Q_1^{\mu}|\nu\rangle\langle\nu|Q_1^{2-\mu}|-1\rangle}{\epsilon_n(\epsilon_\nu+\epsilon_n)}f_{0n}(1,1). \tag{38}$$

In the $C_6(L,\mathrm{dis})$ we note that

$$\langle 1|Q_1^{\mu}|\nu\rangle\langle\nu|Q_1^{-\mu}|1\rangle = (-1)^{\mu}|\langle\nu|Q_1^{-\mu}|1\rangle|^2, \tag{39}$$

and define $\mu$-dependent oscillator strengths[2] by

$$f_{0\nu}^{-\mu}(1,1) = 2\epsilon_\nu|\langle\nu|Q_1^{-\mu}|1\rangle|^2. \tag{40}$$

With this it is clear that the $C_6(L,\mathrm{dis})$, in which $\Lambda = 1$ is conserved, are exactly the well-known terms that appear in $\Sigma$-state interactions. Evaluating the coefficients in Eq. (37) gives the usual formulas

$$C_6(0,\mathrm{dis}) = \frac{3}{2}\sum_{\nu,n}{}''\frac{\bar{f}_{0\nu}f_{0n}}{\epsilon_n\epsilon_\nu(\epsilon_n+\epsilon_\nu)}, \tag{41}$$

and

$$C_6(2,\mathrm{dis}) = \frac{1}{2}\sum_{\nu,n}{}''\frac{f_{0n}}{\epsilon_n\epsilon_\nu(\epsilon_n+\epsilon_\nu)}(f_{0\nu}^{0} - \tfrac{1}{2}f_{0\nu}^{1} - \tfrac{1}{2}f_{0\nu}^{-1}), \tag{42}$$

where

$$\bar{f}_{0\nu} = \frac{1}{3}\sum_{\mu} f_{0\nu}^{-\mu},$$

and for the atom $f_{0n} = \bar{f}_{0n}$.

To simplify the equation for the new coefficient, $D_6$, we note that the operators $Q_1^{\mu}$ and $Q_1^{2-\mu}$ are both nonzero only if $-1 \leq \mu \leq 1$ and $-1 \leq 2-\mu \leq 1$ which is true only for $\mu = 1$. This means also that the only states $\nu$ that contribute to Eq. (38) are those with $\Lambda_\nu = 0$; i.e., $\Sigma$ states. Using that, reflection symmetry, and Eqs. (39) and (40), one has

$$\langle \nu | Q_1^1 | -1 \rangle = (-1)^{s_A + s_\nu} \langle \nu | Q_1^{-1} | 1 \rangle, \tag{43}$$

and

$$D_6 = \tfrac{1}{4}(4!)^{-1/2}(-1)^{s_B}\alpha(2,1,3,3)C(1,1,2;1,1,2)$$

$$\times \sum_{\nu,n}{}'' (-1)^{s_\nu} f_{0\nu}^{-1}(1,1) f_{0n}(1,1)/\epsilon_n \epsilon_\nu(\epsilon_n + \epsilon_\nu), \tag{44}$$

or

$$D_6 = \frac{1}{8}\sum_{\nu,n}{}'' \frac{(-1)^{s_\nu + s_B} f_{0\nu}^{-1}(1,1) f_{0n}(1,1)}{\epsilon_n \epsilon_\nu (\epsilon_n + \epsilon_\nu)}. \tag{45}$$

### C. Evaluation of $C_6$

Now let us consider ways to calculate or estimate the values of the exact formulas [Eqs. (32), (41), (42), and (45)]. Accurate theoretical or experimental values of $\alpha(B)$ and $\mu(A)$ are often available, so that the $C_6(L, \text{ind})$ are easily obtained for many systems. $C_6(0, \text{dis})$ can be obtained accurately from experimental frequency-dependent polarizability data using Padé approximants,[5,16] Eq. (41), and

$$C_6(0, \text{dis}) = 3(2\pi)^{-1}\int_{-\infty}^{\infty} \bar{\alpha}_A(iy)\alpha_B(iy)\,dy, \tag{46}$$

where $\bar{\alpha}_A(iy)$ is the average polarizability of molecule A at the imaginary frequency $iy$. If the frequency dependence of the polarizability anisotropy is known, then $C_6(2, \text{dis})$ can be obtained the same way.[17] However, if the polarizability anisotropy $\kappa$ of A is known at only one frequency, then, as we have shown elsewhere,[2] reasonably good bounds on $C_6(2, \text{dis})$ can often still be obtained from

$$C_6(2, \text{dis}) = a_6 C_6(0, \text{dis}), \tag{47}$$

where

$$(\alpha_\parallel^{3/4} - \alpha_\perp^{3/4})/(\alpha_\parallel^{3/4} + 2\alpha_\perp^{3/4}) \lesssim a_6 \lesssim \kappa = (\alpha_\parallel - \alpha_\perp)/(\alpha_\parallel + 2\alpha_\perp), \tag{48}$$

and $\alpha_\parallel$ and $\alpha_\perp$ are the parallel and perpendicular polarizabilities of A, respectively.

Evaluation of Eq. (45) to get $D_6$ appears to be much more difficult. One might think of relating it to the similar parts of $C_6(2, \text{dis})$ but, in contrast to $\Sigma$ states, $f_{0\nu}^1 \neq f_{0\nu}^{-1}$ in Eq. (42), and it should also be noted that the contributions of the excited $\Sigma^+$ and $\Sigma^-$ states in Eq. (45) have opposite signs. About all that can be said at the moment is that $D_6$ should be small compared to $C_6(0, \text{dis})$. The only experiments[3,4] that we know of, that do not involve the $\sigma = 0$ and $\sigma = 1$ states in equal numbers and give averages in which all information about $D_6$ cancels out, require detailed analysis of collisions and will be discussed in a future paper.[1] It is now possible (but not easy) to obtain $D_6$ from accurate *ab initio* calculations, and such calculations are to be encouraged. The equivalent calculations for interactions of $P$-state atoms have been carried out for some systems, and in the next section we use atomic results to get a rough estimate of $D_6$ for NO interactions.

## III. CALCULATIONS AND RESULTS

The van der Waals coefficients of the previous section are functions of the internuclear distance of the molecule. However, since we use experimental data in the present calculations, the results represent an average over the ground state vibration of the molecule.

Using the experimental dipole moment[18] of NO, $\mu(\text{NO}) = -0.158$ D $= -0.062$ a.u. and the sum rules $S(-2) = \alpha(B)$ of Langhoff and Karplus,[5,19] we obtain the values of $C_6(L, \text{ind})$ shown in Table II.

The frequency-dependent polarizability was obtained from refractive index data using the Lorenz–Lorentz equation,[20]

$$\bar{\alpha}(\omega) = \frac{3}{4\pi n}\frac{(\eta^2 - 1)}{(\eta^2 + 2)}, \tag{49}$$

where $\eta$ is the refractive index at frequency $\omega$, and $n$ is the number density of molecules. The Benedict–Webb–Rubin equation of state[21] for NO gives $3/4\pi n = 60\,035\ a_0^3$ at STP. Refractive index values were found at 22 visible and ultraviolet wavelengths ranging from 224.7 to 670.9 nm.[22,23] No infrared data were found; however, only the electronic (essentially the uv) part of $\bar{\alpha}(\omega)$ goes into Eq. (46), and NO has a small dipole moment, so that it is clear from our work[24] on CO that the ir spectrum of NO contributes negligibly to the available $\bar{\alpha}(\omega)$. A rough value of the zero frequency polarizability of NO, $\bar{\alpha}(0) = 11.70 \pm 0.27\ a_0^3$, was obtained from available dielectric constant data[25] and the Clausius–Mosotti equation[20]; it is consistent with the value of $\bar{\alpha}(0) = S(-2)$ obtained below but not accurate enough to add any information.

Because there is much less data available in this case than there was for CO[24] or $CO_2$,[16] nothing could be gained by using the finite linewidth formulas employed there, and the Langhoff–Karplus[5] procedure was followed directly. Briefly summarized, the frequency-dependent polarizability,

$$\bar{\alpha}(\omega) = \sum_\nu{}' \frac{\bar{f}_{0\nu}}{\epsilon_\nu^2 - \omega^2}, \tag{50}$$

is expanded in the Cauchy series,

$$\bar{\alpha}(\omega) = \sum_k S(-2k-2)\,\omega^{2k}, \tag{51}$$

and the sum rules $S(j)$ are determined by fitting the experimental data. Then, these sum rules are used to construct upper and lower bounding Padé approximants to $\bar{\alpha}(\omega)$ which can be put in the form of Eq. (50) with a finite sum, and used in Eq. (46) to obtain bounds to $C_6(0, \text{dis})$. In fitting the limited available data with Eq. (51), five coefficients were kept and determined by an iterative procedure in which the first three coefficients were obtained from a linear least-squares method and $S(-8)$ and $S(-10)$ were determined by a nonlinear method[26] which assured satisfaction of the Stieltjes constraints.[5] The resulting sum rules, which fit the data with a standard deviation of $0.0068\ a_0^3$, are in Table I. The $S(0)$ in this table was obtained from the Reiche–Thomas–Kuhn[9] theorem. To obtain reasonable uncertainty limits for the $S(j)$, which reflect the effects of omitting the higher terms in Eq. (51), $S(-10)$ (which is not needed in the [2, 1] Padé approximants used) was varied within the range allowed by the Stieltjes constraints and the induced fluctuations in the $S(j)$ were

TABLE I. Oscillator strength sums for NO. Hartree atomic units.

| $j$ | $S(j)$ |
|---|---|
| 0 | 15.0000 |
| −2 | 11.518 ± 0.013 |
| −4 | 39.05 ± 0.22 |
| −6 | 246 ± 12 |
| −8 | $(4.19 \pm 0.10) \times 10^3$ |
| −10 | $(1.0 \pm 0.1) \times 10^5$ |

found. Because of the limited data available, these $S(j)$ are considerably less accurate than those obtained recently for other molecules.[16,24]

The $C_6(0, \text{dis})$ for the interaction of NO with a number of partners (using the sum rules of Refs. 5, 16, and 24) are in Table II. The values given are the means of the best Padé bounds, but the error bounds have been extended to include the effects of the uncertainties in the sum rules.

Using the experimental value[27] of the polarizability anisotropy of NO, $\kappa = 0.161_7$, and Eq. (48), we obtain

$$a_6 = 0.141 \pm 0.021, \qquad (52)$$

and use this and Eq. (47) to generate the $C_6(2, \text{dis})$ shown in Table II.

To get a rough estimate of $D_6$ we note that the contribution to $s_B$ in Eq. (45) of closed shells is always zero, and all the atoms in Table II are either closed shell or have one $s$-type electron outside a closed shell, so that $s_B = 0$. Also, since all the low-lying excited states[28] of NO that occur in Eq. (45) are $\Sigma^+$ states ($s_\nu = 0$), we expect $D_6$ to be positive and from Eq. (36) $C_6$ for the $+ (\sigma = 0)$ state to be larger than that of the − state. This is consistent with the observation that the electronic structure of NO is basically that of closed-shell $N_2(^1\Sigma_g^+)$ plus one extra electron in a $\pi$ orbital. The − state corresponds to a $\pi_x$ orbital (see Fig. 1), and the + state to a $\pi_y$ orbital which sticks out in the plane of the atom and is more strongly polarized by it. This interpretation in terms of orbital directions also predicts correctly the relative values of all the $\Sigma$- and $\Pi$-state polarizabilities calculated for $P$-state atoms by Stevens and Billingsley.[29] Assuming that NO is like the O atom, that is, that the ratio of the two $C_6$ coefficients in the direction perpendicular to the NO axis is equal to the ratio of O polarizabilities,[29] we have

$$\frac{C_6^-(\text{dis}, \theta = \pi/2)}{C_6^+(\text{dis}, \theta = \pi/2)} \approx \frac{\alpha_0(\Pi)}{\alpha_0(\Sigma)} = \frac{0.66}{0.74}. \qquad (53)$$

Letting $D_6 = \delta C_6(0, \text{dis})$ and using Eq. (36) we have

$$\frac{1 - \frac{1}{2}a_6 - 3\delta}{1 - \frac{1}{2}a_6 + 3\delta} = \frac{0.66}{0.74}, \qquad (54)$$

and with Eq. (52) we have

$$\delta = 0.018 \pm 0.010, \qquad (55)$$

which was used to generate the last column of Table II. The uncertainty in Eq. (55) is a guesstimate based on the following: the polarizability of NO is nearer that of C than O; use of the ratio[28] for C would give $\delta = 0.035$. But NO has more electrons than O, so that changing the direction of one electron should have a proportionately smaller effect and give a smaller $\delta$ than that from O. This uncertainty makes it clear that the present rough estimate of $D_6$ is mostly an illustrative example calculation.

## IV. CONCLUSION

### A. Spin-orbit effects

In the preceding sections we have assumed a completely nonrelativistic model with spin and orbital angular momentum completely uncoupled. For $^1\Pi$ molecules interacting with $^1S$ atoms this is adequate. However, NO is a $^2\Pi$-state molecule with spin–orbit splitting constant[28] $\bar{A} = 124.2\ \text{cm}^{-1} = 5.66 \times 10^{-4}$ a.u. For the interaction of NO with the $^1S$ atoms in Table II, the $r$-dependent relativistic corrections are negligible,[30] so

TABLE II. Contributions to the van der Waals $C_6$ coefficients for the interaction of NO($^2\Pi$) with several partners. The angle-dependent terms are omitted for the molecular partners as the formulas in the paper are not appropriate for them. Hartree atomic units ($e^2a_0^5$).

| Partner | $C_6(0, \text{ind}) = C_6(2, \text{ind})$ | $C_6(0, \text{dis})$ | $C_6(2, \text{dis})$ | $C_6(0, \text{tot})$ | $C_6(2, \text{tot})$ | $D_6$ |
|---|---|---|---|---|---|---|
| He | 0.00535 | 9.8 ± 1.3 | 1.41 ± 0.39 | 9.8 ± 1.3 | 1.41 ± 0.39 | 0.18 ± 0.11 |
| Ne | 0.0103 | 21.0 ± 3.6 | 3.00 ± 0.95 | 21.0 ± 3.6 | 3.01 ± 0.95 | 0.38 ± 0.25 |
| Ar | 0.0429 | 69 ± 10 | 9.9 ± 2.9 | 69 ± 10 | 9.9 ± 2.9 | 1.24 ± 0.79 |
| Kr | 0.0647 | 98 ± 15 | 14.0 ± 4.3 | 98 ± 15 | 14.1 ± 4.3 | 1.8 ± 1.1 |
| Xe | 0.106 | 170 ± 31 | 24.3 ± 8.0 | 170 ± 31 | 24.4 ± 8.0 | 3.1 ± 2.0 |
| H | 0.0174 | 20.2 ± 1.4 | 2.89 ± 0.63 | 20.2 ± 1.4 | 2.91 ± 0.63 | 0.36 ± 0.21 |
| Li | 0.633 | 177.8 ± 4.6 | 25.4 ± 4.4 | 178.4 ± 4.6 | 26.1 ± 4.4 | 3.2 ± 1.9 |
| Na | 0.647 | 217 ± 16 | 31.1 ± 6.9 | 218 ± 16 | 31.7 ± 6.9 | 3.9 ± 2.3 |
| K | 1.11 | 321 ± 25 | 46 ± 10 | 322 ± 25 | 47 ± 10 | 5.8 ± 3.5 |
| Rb | 1.22 | 364 ± 30 | 52 ± 12 | 365 ± 30 | 53 ± 12 | 6.6 ± 3.9 |
| Cs | 1.38 | 314 ± 16 | 44.8 ± 8.9 | 315 ± 16 | 46.2 ± 8.9 | 5.7 ± 3.3 |
| $H_2$ | ··· | 28.2 ± 2.4 | ··· | ··· | ··· | ··· |
| $N_2$ | ··· | 71.1 ± 9.3 | ··· | ··· | ··· | ··· |
| $O_2$ | ··· | 55.2 ± 4.9 | ··· | ··· | ··· | ··· |
| $CO_2$ | ··· | 113 ± 14 | ··· | ··· | ··· | ··· |
| CO | ··· | 78 ± 12 | ··· | ··· | ··· | ··· |
| NO | ··· | 69 ± 13 | ··· | ··· | ··· | ··· |

that all that need be added is the spin–orbit splitting of the NO. This can be done by using the phenomenological Hamiltonian,

$$H = H_e + \bar{A} L_z(A) S_z(A), \tag{56}$$

instead of Eq. (5). The two terms in this $H$ are not simultaneously diagonable, so that if we use the eigenfunctions of $H_e$ obtained in the previous sections (denoted by $|\sigma, 0\rangle \equiv |\sigma, M_s, 0\rangle = |\pm, M_s, 0\rangle$ with eigenvalues $E^{\pm}$) as a basis, a two by two secular equation results (only $2\times 2$ as $M_s$ stays a good quantum number here) which has the simple form

$$\begin{vmatrix} E^{+} - E & \bar{A}M_s \\ \bar{A}M_s & E^{-} - E \end{vmatrix} = 0. \tag{57}$$

This has the eigenvalues

$$E = (E^{+} + E^{-})/2 \pm \{[(E^{+} - E^{-})/2]^2 + (\bar{A}/2)^2\}^{1/2}. \tag{58}$$

For small $r$ with $\theta$ not near 0 or $\pi$ the $E^{+} - E^{-}$ term dominates and the present basis is appropriate. For large $r$ or $\theta$ near 0 or $\pi$ and the LS coupling dominates and the appropriate basis is the set $|\Lambda, M_s, 0\rangle$, which describes the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states. In the present examples, the spin-orbit coupling dominates in most of the van der Waals region, and the appropriate potentials are easily generated using Eq. (58).

The above approach can also be used for the interaction of NO($^2\Pi$) with the $^2S$-state atoms of Table II unless very high accuracy is desired in which case one would need to include the small ($\lesssim 0.05$ cm$^{-1}$) magnetic dipole-dipole interaction.[30]

## B. Discussion

In this paper we have rigorously shown that the van der Waals potential between a $\Pi$-state molecule and an $S$-state atom does have the associated Legendre polynomial dependence which others have assumed[3] or argued[4] that it should have. The accuracy of the present $C_6(0, \text{dis})$ for NO interactions is the best obtainable using the present data; other methods[17] would give the same results from the same data. However, it might be possible to obtain improved accuracy by using the method of Starkschall and Gordon[31] which allows one to also use other types of data. A better determination of the new $D_6$ coefficients than the present rough estimate is likely to be difficult experimentally and best accomplished by accurate *ab initio* calculations.

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[†] Present address of GAP and RTP.

[1] G. C. Nielson, G. A. Parker, and R. T Pack, to be published.

[2] R. T Pack, J. Chem. Phys. 64, 1257 (1976).

[3] K. Bergmann, H. Klar, and W. Schlecht, Chem. Phys. Lett. 12, 522 (1972).

[4] S. Green and R. N. Zare, Chem. Phys. 7, 62 (1975).

[5] P. W. Langhoff and M. Karplus, J. Chem. Phys. 53, 233 (1970); J. Opt. Soc. Am. 59, 863 (1969).

[6] R. T Pack and J. O. Hirschfelder, J. Chem. Phys. 49, 4009 (1968); 52, 521 and 4198 (1970).

[7] J. O. Hirschfelder and W. J. Meath, Adv. Chem. Phys. 12, 1 (1967).

[8] M. E. Rose, J. Math. and Phys. (Cambridge, Mass.) 37, 215 (1958).

[9] J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Adv. Quantum Chem. 1, 255 (1964).

[10] The $D$ used here are those of Ref. 6. If one remembers that $D$ (here) $= D^{\dagger}$ (Ref. 11) he can use the formulas of Ref. 11.

[11] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957), p. 52.

[12] Reference 11, p. 58.

[13] Reference 11, p. 110.

[14] Reference 11, pp. 54 and 60. Because of the difference in conventions (Ref. 10) this is different from the usual reduction.

[15] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1965).

[16] R. T Pack, J. Chem. Phys. 61, 2091 (1974).

[17] P. W. Langhoff, R. G. Gordon, and M. Karplus, J. Chem. Phys. 55, 2126 (1971).

[18] See F. P. Billingsley II, J. Chem. Phys. 62, 864 (1975) and references therein.

[19] Better values of some of these polarizabilities are in R. R. Teachout and R. T Pack, At. Data 3, 195 (1971), but the induction contribution is so small here anyway that they make no difference and the $S(j)$ of Ref. 5 are all kept for the dispersion calculations because they form consistent sets.

[20] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), pp. 861 and 883.

[21] D. N. Seshadri, D. S. Viswanath, and N. R. Kuloor, J. Chem. Eng. Data 12, 70 (1967).

[22] Landolt-Börnstein, *Zahlenwerte und Functionen* (Springer-Berlin, 1962), 6th ed., Vol. II, Chap. 8, pp. 871–901.

[23] *International Critical Tables*, edited by E. W. Washburn (McGraw–Hill, New York, 1930), Vol. VII, pp. 6–11.

[24] G. A. Parker and R. T Pack, J. Chem. Phys. 64, 2010 (1976).

[25] C. P. Smith and K. B. McAlpine, J. Chem. Phys. 1, 60 (1933).

[26] D. M. Himmelblau, *Applied Nonlinear Programming* (McGraw–Hill, New York, 1972), p. 458.

[27] N. J. Bridge and A. D. Buckingham, Proc. R. Soc. London Ser. A 295, 334 (1966).

[28] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1950), 2nd ed., p. 558.

[29] W. J. Stevens and F. P. Billingsley II, Phys. Rev. A 8, 2236 (1973).

[30] W. J. Meath, J. Chem. Phys. 45, 4519 (1966).

[31] G. Starkschall and R. G. Gordon, J. Chem. Phys. 54, 663 (1971).

# THE INTERMOLECULAR POTENTIAL AND VIBRATIONAL RELAXATION OF THE Ar-CO SYSTEM

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## ABSTRACT

The angle, distance and vibration dependence of the Ar-CO intermolecular potential is calculated using the electron gas model to obtain the short range interaction which is smoothly joined onto the long range van der Waals tail which is obtained from accurate $C_6$, $C_7$, and $C_8$ coefficients. Our calculated second interaction virial coefficients are compared with experiment and with a simple adjustment of the Ar-CO potential an excellent agreement is obtained. Our spherically averaged potential is also in excellent agreement with a spherical potential inferred from high energy scattering data.

Simplified expressions for the scattering amplitude and differential cross section are obtained in the infinite order sudden approximation. Then, treating the rotations and vibrations in the infinite order sudden and close coupling approximations respectively, vibrational transition probabilities and relaxation rates are calculated using the Ar-CO intermolecular potential. Our calculated vibrational relaxation rates are much smaller than the experimental values.