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Molecular calculations by the one-center method

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MOLECULAR CALCULATIONS BY THE
ONE-CENTER METHOD

by

Stanley Hagstrom

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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I. INTRODUCTION

The molecular orbital approximation is probably the most important method of general utility for dealing with problems in molecular quantum mechanics. It has found a large measure of success on qualitative and semi-quantitative grounds and, more recently, with the development of the Roothaan SCF procedures and by extensive use of configuration interaction, has yielded semi-quantitative results of considerable interest. Much of the current work is centered on diatomic molecules, where attempts are being made to improve the calculations by an extensive use of configuration interaction. This is being made possible by the use of modern high-speed digital computers, and it seems probable that within the next decade many of the properties of the diatomics will be calculated.

Yet for three and four center problems, even for the very simplest ones, such as H_3^+ and H_3 , the method does not seem capable of providing a truly accurate description of the electronic structure of a molecule. The principal reason for this, of course, lies in the prevailing use of atomic orbitals in building up the molecular wave function, since this leads to major difficulties in evaluation of the molecular integrals. The evaluation of three and four center integrals in particular has proved to be a singularly intractable problem. Although this problem is currently

being vigorously attacked with the aid of large computers, prospects for an early solution do not seem bright. Until more definite progress is made in the evaluation of these integrals, there seems little likelihood that reliable a priori calculations on polyatomic molecules (other than diatomics) will be possible using present techniques.

In this thesis we describe some energy calculations on some simple two-electron molecular systems by a "one-center" method which seeks to avoid some of the difficulties of the conventional molecular orbital method. This one-center method for molecules is aimed primarily at eliminating the calculation of many-center integrals by replacing the usual set of atomic orbitals on the various atoms of a molecule by a more extensive set of basis functions on a single center. Then the only integrals to be evaluated are the one-center integrals and a comparatively simple two-center nuclear attraction integral. Problems of polycentric integrals naturally do not arise. The one-center method is intended only for simple and highly symmetric molecules, such as H_2 , H_3^+ , H_3 , and H_4^{++} . However, these simple two and three electron problems are of such fundamental importance in theoretical chemistry as to warrant the development of specialized techniques for their solution.

It has been the primary objective of this research to examine the relative advantages and disadvantages of the one-center method as a systematic, practical procedure for cal-

culating the electronic properties of simple molecular systems. For this purpose, one-center expansions have been carried out for the hydrogen molecule and triatomic hydrogen molecule ion H_3^+ , two systems of fundamental importance in chemistry.

The hydrogen molecule problem is of little interest per se since it has already been treated with considerable accuracy by James and Coolidge and with lesser accuracy by many others, but it is a very convenient system with which to evaluate the various approaches to an energy calculation (and has been often used for this purpose in the past). The number of simplifying assumptions is here a minimum, and accurate experimental data and the results of many previous calculations are available for evaluation of results.

The H_3^+ system was chosen because it represents the simplest example of an actual molecule containing three centers for which an accurate non-empirical calculation by any of the conventional methods is essentially intractable. This system should provide a more stringent test of the one-center method than the hydrogen molecule problem since the distances from the expansion center to the nuclei are considerably greater. Although no experimental data are available for this case, there are several theoretical calculations with which to compare the results.

All of the calculations described in this thesis were carried out with the aid of the IBM 650 computer at the

Research Computing Center at Indiana University. One of the principal objectives of this investigation has been the development of computer programs which enable the entire one-center calculation to be carried out completely within the 650 (that is, with a minimum dependence on hand computations).

The thesis is divided into four chapters following this introduction. Chapter II comprises a general exposition of the one-center method for molecules as well as a review of previous one-center calculations. In Chapter III we discuss the one-center calculations for the hydrogen molecule. The results of the calculations are presented in both tabular and graphical form and are analyzed in detail. The choice of basis functions, formulas for the basic integrals between these functions, and the construction of the symmetry-adapted wave functions are also discussed in this chapter. In Chapter IV the results of the one-center calculations for H_3^+ are presented, while Chapter V lists the major conclusions of this investigation.

II. THE ONE-CENTER METHOD FOR MOLECULES

It has recently been suggested by several authors that the electronic properties of simple or highly symmetrical molecules can be profitably found by expanding the molecular wave function in terms of a complete set of functions centered at a single point in the molecule. Two essentially different methods have been proposed. In one method the total electronic energy of the molecule is calculated directly. Thus, for instance, Huzinaga (1) has calculated total electronic energies for H_2^+ and H_2 by expanding the ground state wave functions in terms of s and d type Slater orbitals centered at the midpoint of the bond axis. Handler (2) has carried out similar calculations for H_2 and has also used one-center expansions for H_3^+ . A generalized united atom method has been proposed by Chen (3) wherein the electronic wave function of a polyatomic molecule is expanded in terms of the eigenfunctions of the corresponding united atom, the energy then being obtained by a perturbation calculation. Finally, Shull and Löwdin (4) have emphasized that one-center expansions should be particularly feasible for small molecules containing hydrogen atoms and especially feasible for the higher excited Rydberg-like states of such molecules.

On the other hand, Allen and Nesbet (5) and, more recently, Nesbet (6), have developed a one-center method which is quite different in emphasis from the above. These authors take the

view that it is impractical to calculate total energies of molecules directly. Instead, they propose to calculate only certain "localized" molecular quantities, such as the nuclear quadrupole coupling constant ($\sim \langle 1/r^3 \rangle$), which are primarily dependent on the electronic wave function in the neighborhood of a single atom. The wave function used in taking the average values is determined by a one-center energy calculation about the particular atom in question. However, no importance as such is attached to the energy value obtained.

We will consider both of these methods in some detail.

A. Calculation of the Total Energy

The one-center method for molecules is aimed primarily at eliminating the extremely complex integrations that occur in the molecular orbital and valence bond approximations. We recall that in the valence bond approach the molecule is regarded as composed of atoms and that the building blocks for the whole wave function are then necessarily the atomic orbitals centered on the various atoms of the molecule. On the other hand, in the molecular orbital method it is customary, but fortunately not a necessary feature of the method, to express the molecular orbitals as linear combinations of atomic orbitals centered on the various atoms. The major difficulty encountered in using wave functions built up of atomic orbitals is in the evaluation of the molecular integrals,

For two-center problems very complicated methods of integration are required, while in three and four center problems no satisfactory methods of integration are known. There are, of course, good reasons for the prevailing use of atomic orbitals in describing the molecular wave functions. It provides a very good approximation in many cases, especially for those inner electrons which retain their atomic character and partake but little in the chemical binding.

The idea in the one-center method is to replace the usual set of atomic orbitals centered on the various atoms of the molecule by a more extensive set of basis functions centered on a single point. We thus avoid the problems of three and four center integrals entirely, and are left with only the simple one-center integrals of atomic theory (kinetic energy, one-center nuclear attraction, and one-center electron repulsion integrals) plus a comparatively simple two-center nuclear attraction integral. These integrals are all easily evaluated, provided the one-center functions are limited to atomic central field functions, that is, a radial function $f(r)$ multiplied by a spherical harmonic $Y_{lm}(\theta, \phi)$.

Since only a relatively small number of basic orbitals can be considered in any actual calculation, one-center calculations of the total electronic energy will be possible only for simple and highly symmetrical molecules. Inner

shell electrons on centers away from the expansion center will be especially difficult to represent by this method. This effectively limits the molecules that can be treated to those containing only hydrogen atoms off the expansion center. However, it is the outer electrons belonging to the whole molecular frame which play the key role in determining the chemical and physical behavior of the molecule. It is just these electrons, for which the atomic orbitals form less satisfactory building blocks, that are best represented by one-center wave functions. Conceivably, the difficulty concerning the inner shells might be handled empirically, but this seems somewhat dubious in view of the many other limitations of the one-center method. However, see (3). The expansion center, of course, can be chosen anywhere it is physically and mathematically appropriate to do so. It would ordinarily be either the point of maximum electron density or point of highest symmetry or both; it need not necessarily coincide with a nucleus.

It seems not too optimistic then to expect that molecules such as H_2^+ , H_2 , H_3^+ , H_3 , LiH , CH_4 , etc., can all be satisfactorily handled by the one-center approach. It is to be expected that the number of configurations necessary for an adequate description of the molecular wave function will be fairly large, and that the convergence is likely to be slow. This rather obvious disadvantage is mitigated somewhat by the fact that the calculations are sufficiently

systematic and straightforward to enable complete automatic computation on high speed digital computers.

The one-center method has been used to calculate the electronic energy of such simple and highly symmetric molecules as H_2^+ , H_2 , CH_4 , and NH_3 , but with singularly unsuccessful results. Only for H_2^{3+} and H_2 has it been possible to obtain a stable molecule.

Morse and Stueckelburg (7) very early calculated energy levels of H_2^+ by the united-atom treatment. More recently Matsen (8) has extended these calculations to the higher excited states. Using first order perturbation theory on a united-atom model for H_2^+ , Matsen calculated the energies of the $1s\sigma$, $2p\sigma$, $2p\pi$, $3p\pi$, and $3d\delta$ states. The zero order functions were the hydrogen atom functions of charge z centered midway between the nuclei; z ($=2$ for the true united atom He^+) was varied to minimize the energy of each state. The results were surprisingly good for the excited states, but rather poor for the ground state. The reason, probably, that the treatment is better for the excited states is that the electron density is spread far enough away from the two nuclei so that they appear united.

Huzinaga (1) minimized the energy of the ground state of H_2^+ , using for the wave function a three term linear combination of the Slater orbitals $s_1(z)$, $s_4(z')$, and $d_4(z')$ centered at the midpoint of the bond. Here z and z' are variable parameters and

$$s_n(z) = N_n^z r^{n-1} e^{-zr} Y_{00} \quad (2.1)$$

$$d_n(z) = N_n^z r^{n-1} e^{-zr} Y_{20}$$

where N_n^z is a normalization factor and Y_{10} is a normalized axially symmetric spherical harmonic. At the equilibrium distance of 2.0 a.u.*, the best energy obtained for this three term function was -1.0747 a.u. for $z=1$, $z'=3$. This is to be compared with the exact value (9), -1.1026 a.u., and to Matsen's result, -0.967 a.u., for the best single (1s) function.

Huzinaga (1) also attempted a one-center calculation of the total energy of the hydrogen molecule at a fixed internuclear distance of 1.4 a.u. The stages in his calculation are summarized below. The expansion functions are the Slater functions (2.1), the z 's being varied to minimize the energy. As usual, the expansion center is midway between the two nuclei. The experimental energy for H_2 is -1.174 a.u.

(1) The best wave function for H_2 of the type $s_1(z)^2$ gave -0.9879 a.u. for the total energy which means a binding energy of -0.0121 a.u.; that is, the molecule is not stable.

(2) If, instead, the function $\phi(1)\phi(2)$, where $\phi =$

*Atomic units are used throughout this thesis. One atomic unit of length (a.u.) equals one Bohr radius, 0.5292 Å; one atomic unit of energy (a.u.) equals twice the ground state energy of the hydrogen atom, 27.206 electron volts (e.v.).

$c_1 s_1(z) + c_2 s_1(z')$, is used, the molecule does bind and has a total energy of -1.020 a.u. for the optimum values of c_1 , c_2 , z , and z' . It should be noted that this function is still spherically symmetric.

(3) If one of the electrons is assigned to a H_2^+ type orbital, that is, a cigar shaped orbital symmetric about the axis, and the other electron assigned to an atomic $1s$ -type function, a much better energy results. This is to be expected since the wave function now reflects the Σ_g^+ symmetry of the ground state while the use of separate orbitals for the two electrons serves to minimize the energy of repulsion between the two electrons. The calculation gives a total energy of -1.095 a.u.

(4) Addition of a single p^2 configuration to approximation (3) improves the energy by only 0.011 a.u. for a total energy of -1.106 a.u., which is still less than the simple Heitler-London-Sugiura value for H_2 , -1.115 a.u.

(5) In his final approximation, Huzinaga used separate H_2^+ type orbitals for each electron (that is, using s and d orbitals only) and obtained a total energy of -1.1397 . This seems to be an unreasonably good energy for such a simple wave function. We have therefore repeated Huzinaga's work and have reproduced his results up to the final approximation. We believe Huzinaga's final result to be in error and that the actual energy to this approximation is -1.106 a.u.; the details of this calculation are in

Chapter III.

Handler (2) has applied the one-center method to the systems H_2 , linear symmetrical H_3^+ , and equilateral triangular H_3^+ . Using a superposition of six configurations -- three (ss) and three (sd) -- constructed from Slater orbitals with the same orbital exponent for s and d functions, the best energy obtained for H_2 was only -1.088 a.u. for the equilibrium distance 1.4 a.u. We note that this value is less than that given by approximation (3) of Huzinaga, a two configuration wave function, but employing different orbital exponents for the s and d functions. In the calculations on H_3^+ , the expansion center was on the central nucleus for the linear symmetrical configuration and at the center of symmetry of the molecule for the triangular configuration. The best energies obtained were -1.163 a.u. and -1.204 a.u. for the linear ($R=1.55$) and triangular cases ($R_{ab}=1.56$), respectively. Although the energy of H_3^+ is not known, we can compare these results with the corresponding values obtained by Hirschfelder and others (10, 11) using the valence bond method, namely, -1.2476 a.u. for the linear case ($R=1.60$) and -1.2925 a.u. for the triangular case ($R=1.82$). We shall discuss these calculations more fully in Chapter IV.

Buckingham, Massey, and Tibbs (12) carried out a one-center self-consistent field calculation for methane. They treated CH_4 as an eight-electron problem and assumed the

wave function had complete spherical symmetry; that is, they included only the configuration $(2s)^2(2p)^6$, where the s and p functions are Slater orbitals centered on the carbon atom. They also averaged the nuclear field over all orientations about the central nucleus. The calculations indicated the system was stable by ninety per cent of the experimental binding energy. This is a surprisingly large energy when one considers that the spherically symmetric function used does not reflect the tetrahedral character of the molecule, and that ordinary configuration interaction was not included. It should be emphasized that in dealing with a configuration such as $(2s)^2(2p)^6$ for which the charge cloud is spherically symmetric, there is no additional approximation implied in using a Hamiltonian in which the nuclear field is averaged over all orientations. The basic reason for this is that when the charge density is spherical the electron-nuclear interaction energy is solely determined by the first term in the expansion of the nuclear potential in spherical harmonics (13).

Nesbet (6) has repeated and extended this calculation and has established that the value reported by Buckingham, Massey, and Tibbs was in error. The calculated binding energy is actually negative instead of positive as reported. Further calculations by Nesbet indicate that the addition of higher spherical harmonics leads to very slow convergence to the true electronic energy of CH_4 .

Banyard and March (13) used similar methods to obtain one-center wave functions for the ammonia and water molecules. Using one-electron analytical functions centered on the nitrogen and oxygen atoms, they constructed the ten-electron determinantal wave function corresponding to the spherically symmetric configuration $(1s)^2(2s)^2(2p)^6$ and minimized the energy with respect to the parameters in the one-electron functions. The molecular energies thus obtained were quite poor, for example, -75.00 a.u. for water, compared to the experimental value -76.47 a.u. However, when these wave functions were used to calculate X-ray scattering factors, good agreement with the experimental scattering factors was obtained.

We note in passing that one-center calculations of a similar nature have also been carried out by Bernal (14) and by Carter (15) with equally disappointing results.

These results would seem to indicate that one-center calculations of the total electronic energy are in general not at all practical for systems as complex as CH_4 and NH_3 and are only moderately so for simple two and three electron systems, such as H_2 and H_3^+ . It should be noted, however, that all of the above calculations, except that of Nesbet on CH_4 , were carried out by hand with a very limited set of basis functions and only a very few configurations. But if the calculations are done on electronic computers, expansions of thirty and forty terms become

quite feasible, especially for two and three electron systems. From this point of view then, Huzinaga's and Handler's results seem quite encouraging. It seems clear, however, that eight and ten electron problems are at present somewhat beyond the scope of the one-center method.

The one-center calculations described above all make use of "ordinary" configuration interaction; that is, the molecular wave function is expressed as a series of configurations formed from a complete set of analytic one-electron functions which are introduced right from the start. Recently, however, Nesbet (16) has shown that the configuration interaction problem is greatly simplified if the calculations are based on an orthogonal set of self-consistent orbitals satisfying the Hartree-Fock equations (that is, orbitals obtained by the Roothaan procedure)(17). Unfortunately, this simplification did not come to the author's attention until the present investigation was more than half over. Consequently, the configuration interaction method used here is the conventional one described by Condon and Shortley (18) and by Boys (19).

When one-center calculations including the superposition of many configurations are carried out, the question of what basic functions to use is of minor importance. Wave functions of any desired accuracy can in principle be obtained by the superposition of a sufficiently large number of configurations. But when the number of

configurations is limited, as in practice it must be, the choice of basis becomes very important. Unfortunately, there are really no adequate criteria for making the choice. The expansion postulate, of course, requires that the basic orbitals be members of a complete set. Moreover, we require that all integrals between the basic orbitals be readily evaluated. These would appear to be the minimum requirements. The following additional features, although not really necessary, would be most desirable from the point of view of simplifying the numerical work.

1. It is desirable that the basic functions form an orthonormal set and that the basic integrals between these functions be obtained by algebraic rather than numerical methods, thus eliminating the rather laborious transformations of the basic integrals from the non-orthogonal basis to the orthogonal basis. Also, the evaluation of the final energy matrix elements as well as the solution of the secular equation is greatly simplified if the whole calculation is carried out in an orthogonal basis. It should be understood, however, that the use of orthogonal functions is purely a matter of mathematical convenience and has nothing to do with the physical theory.

2. If the number of non-linear parameters is kept to a minimum, the variational problem will be greatly simplified. The problem of simultaneously varying many non-linear parameters is an enormous one and must always be treated by trial

and error methods. The linear parameters, of course, are nicely handled by the mechanics of the variational principle itself.

3. There should be some systematic method for choosing the basic functions. This feature in particular is lacking in most of the conventional approximation methods.

4. Finally, the functions chosen should lead to rapidly converging expansions. Löwdin (20) has investigated this point for two-electron systems and has been able to construct that set of one-electron functions, termed natural spin orbitals (NSO), which when used to form configurations, leads to the most rapidly converging expansion. This analysis is of no help, however, in choosing initial functions, since the construction of the NSO's requires that the variational problem be already solved.

Generally speaking, no known class of functions possesses all these features. However, Shull and Löwdin (21) have recently suggested a set of functions which meets these requirements in many respects, namely, the complete set of orthonormal $(2q+2)$ -order associated Laguerre functions as radial functions multiplied by the spherical harmonics as angular functions:

$$N_{nq}^z (2zr)^q L_{n+q+1}^{2q+2} (2zr) e^{-zr} Y_{qm}(\theta, \phi), \quad (2.2)$$

where the L are the $(2q+2)$ -order Laguerre polynomials, z is an adjustable parameter, and N_{nq}^z is a normalizing factor. The required integrals between these functions are all easily evaluated. The eigenvalue spectrum of the set is entirely discrete, which is apparently of importance for convergence (21). Of great practical advantage is the fact that only a single orbital exponent occurs for all functions with the same angular dependence; this renders a great simplification in the computational work, both in evaluating the integrals and in solving the variational problem. These functions were very early used by Hylleraas (22) in applying configuration interaction to the ground state of the helium atom and, more recently, have been used in similar calculations on helium and helium-like ions by Löwdin and Shull (23), Slater (24), and Holstien (25).

A very general set of functions for which all the integrals occurring in the one-center method can be evaluated in closed form has been given by Chen (26). This is the set

$$N_n^z r^{n-1} e^{-zr^k/k} Y_{qm}(\theta, \phi), \quad (2.3)$$

where k is some prefixed positive number and $z > 0$. For $k=1$ we have the familiar Slater functions, which for fixed z ($n=1, 2, \dots$) form a complete set with discrete eigenvalue spectrum. For $k=2$ we have the complete set of Gaussian

functions. The cases for k other than 1 or 2 have not been investigated, but presumably also form complete sets (for fixed z).

Nesbet (6) has found the Slater functions particularly convenient to use in one-center expansions since they provide a wealth of non-linear parameters, which when properly varied, lead to very rapid initial convergence, although subsequent convergence as more terms are added may be quite slow. However, the many different exponents make the evaluation of the basic integrals correspondingly more difficult. Moreover, the Slater functions with different exponents form an overcomplete set, which, as has been pointed out by Löwdin (27), may occasionally lead to difficulties in solving the secular equation.

In a recent note Parr and Joy (28) have suggested that improved one-center expansion functions might result from dropping the requirement that the principal quantum number n in (2.3) be integral. Although a single configuration constructed from such functions might very well be a superior starting function, it seems very unlikely that the ultimate convergence as more terms are added will be much affected. Moreover, the variation problem has been greatly complicated, since now the principal quantum number, as well as the orbital exponent, is a non-linear parameter to be chosen by trial and error.

Another possible system includes the use of the complete

set of exponential functions, $e^{-nr}Y_{qm}(\theta, \phi)$, n a positive integer, as is currently being used by Boys (29, 30).

As has been shown by Shull and Löwdin (21), the hydrogen-like set of functions, with exponential dependence z/n , is not a suitable system since convergence can be obtained only if account is taken of the rather annoying continuum wave functions, without which this set is not complete.

We have based all our one-center calculations on the complete orthonormal set of associated Laguerre functions (2.2), since for the two electron systems considered here this seems to be the most convenient set to use from the point of view of integral evaluation and solution of the variational problem.

B. Calculation of "Localized" Observables

We have seen that the direct calculation of total electronic energies of molecules by the one-center method is limited to relatively simple hydrogenic systems. Allen and Nesbet (5, 6) have recently developed a modified method which retains all the advantages of the one-center approach but is at the same time applicable to more complicated molecular systems. In particular, systems with inner shell electrons not on the expansion center can be treated. Instead of calculating total energies directly, only those

"localized" quantities are calculated which are primarily dependent on the electronic wave function in the neighborhood of a single atom. The reasoning behind this method is as follows:

Since in any actual one-center calculation only a relatively small number of basic functions can be considered, it will be extremely difficult to approximate the molecular wave function to equal accuracy throughout all regions of the molecule. Hence, except for certain very simple systems, properties such as the total energy or dipole moment, which depend strongly on the value of the wave function over the whole molecule, cannot be calculated with one-center wave functions. But, given a wave function which is sufficiently accurate in the region of a single nucleus, it should be possible to calculate those molecular quantities, such as the electronic coupling with nuclear moments of the force field on the nucleus, which heavily weight the electron density in the vicinity of the nucleus. It is assumed that the "best" wave function in the vicinity of a given nucleus can be obtained by carrying out a one-center configuration interaction calculation about that nucleus of the total electronic energy of the molecule. The wave function obtained cannot be expected to be of practical value beyond the nearest-neighbor nuclei to the expansion center. Moreover, the energy values obtained will in general be very poor and will have significance only insofar as the lowness

of the energy value is an indication of the accuracy of a variationally determined wave function. It is not at all obvious, however, that a wave function which is an admittedly poor approximation to the complete molecular wave function will be a good approximation to the true wave function in the region of a given nucleus simply because it has been obtained by a variational calculation. This point could be easily checked by carrying out calculations on a system such as H_2^+ for which the exact wave function is known, but this does not seem to have been done as yet.

Two molecular observables which can be easily calculated by this method are the force on a given nucleus a , given by the mean value of $-\vec{r}_a/r_a^3$, and the nuclear electric quadrupole coupling constant, which is proportional to the mean value of $1/r^3$.

One feature that makes this method very attractive is that it can be adapted to the indirect calculation of electronic energies of molecules, or rather, to the calculation of the difference of electronic energy between two isoelectronic systems. The procedure depends on the Hellman-Feynman theorem (5)

$$\frac{\partial}{\partial \lambda} \langle H \rangle = \left\langle \frac{\partial}{\partial \lambda} H \right\rangle, \quad (2.4)$$

where the average values are taken over the exact wave functions for the Hamiltonian. For certain parameters λ ,

the derivatives of the Hamiltonian are sums of "localized" operators for which it should be possible to obtain accurate mean values using wave functions obtained from one-center energy calculations about the appropriate nuclei of the molecule. The difference in electronic energy between two isoelectronic systems, characterized by different values of the parameter λ , can then be obtained by integrating the mean values of these derivative operators.

A simple example will illustrate the method. Consider the isoelectronic systems Be, LiH, He₂, and all the intermediate systems with fractional charges on the nuclei such that the sum of the nuclear charges adds up to four. The electronic Hamiltonian for a four electron system may be written

$$H = \sum_{i=1}^4 \left\{ -\frac{1}{2} \nabla_i^2 - Z_a/r_{ai} - Z_b/r_{bi} \right\} + \sum_{i < j} 1/r_{ij} \quad (2.5)$$

where Z_a and Z_b are the charges on nuclei a and b, respectively, and $Z_a + Z_b = 4$. By differentiating with respect to the charge Z_a on nucleus a we get the electronic potential

$$(\partial/\partial Z_a)H = \sum_{i=1}^4 -1/r_{ai}. \quad (2.6)$$

For a fixed internuclear distance, the mean value of this electronic potential must be a smooth function $f(Z_a)$ of the nuclear charge at center a. Similarly, the mean value of

$\sum -1/r_{b1}$ is a smooth function $f(Z_b)$ of the charge at center b. The wave functions used in taking the mean values must be obtained by separate one-center energy calculations about centers a and b respectively. Separate one-center calculations are required for each value of Z_a and Z_b in the range of interest. Since

$$\begin{aligned} d\langle H \rangle &= \partial/\partial Z_a \langle H \rangle dZ_a + \partial/\partial Z_b \langle H \rangle dZ_b \\ &= f(Z_a) dZ_a + f(Z_b) dZ_b, \end{aligned} \quad (2.7)$$

the difference between the electronic energy of LiH and the energy of Be is given by

$$E = \int_3^4 f(Z_a) dZ_a + \int_1^0 f(Z_a) dZ_a, \quad (2.8)$$

since $f(Z_b)$ is clearly equal to $f(Z_a)$ over the range $0 \leq Z_a \leq 1$. Since $f(Z_a)$ is determined only for a few values of Z_a , ΔE must be obtained by graphical integration. Clearly, the one-center calculations about a when Z_a is small will be less accurate than for Z_a large in a case such as LiH, but calculations must be made in both cases.

No detailed calculations using this method have been reported. Preliminary results by Nesbet on the He₂, LiH, and Be systems seem quite encouraging, however. It is too early, however, to judge the ultimate worth of this approach.

III. ONE-CENTER CALCULATION FOR THE HYDROGEN MOLECULE

We now apply the one-center method outlined in the preceding chapter to calculate the total electronic energy of the ground state of the hydrogen molecule. A preliminary report (31) of this investigation was given at the Molecular Quantum Mechanics Conference held in Austin, Texas, December 7-9, 1955.

A. The Configuration Interaction Problem

1. Approximate ground state wave functions

Let ψ_m ($m=1,2, \dots$) be a complete orthonormal basic set of one-particle functions (spin-orbitals) centered at the origin of coordinates. We seek a normalized approximate wave function for the ground state of the hydrogen molecule of the form

$$\bar{\Psi}(x_1, x_2) = \sum_K c_K \bar{\Psi}_K(x_1, x_2), \quad (3.1)$$

where the $\bar{\Psi}_K(x_1, x_2)$ are normalized antisymmetrized product wave functions (Slater determinants) for the various configurations of the molecule, and $x_i = (r_i, s_i)$ is the space-spin coordinate of electron i . (A configuration is here defined as the selection of any two one-electron functions

ψ_m, ψ_n from the complete set $\{\psi_m\}$; in addition, if $m < n$ the configuration is said to be ordered and for convenience is denoted by the abbreviated symbol K).

The best set of coefficients C_K is determined by minimizing the energy $E = \int \Psi(x_1, x_2) H_{op} \Psi(x_1, x_2) dv_1 dv_2$, where H_{op} is the spin-free electronic Hamiltonian for the hydrogen molecule, containing only kinetic and electrostatic terms; namely,

$$H_{op} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} \quad (3.2)$$

(This Hamiltonian is in atomic units) The best coefficients C_K satisfy the equations

$$\sum_K \{ \langle L | H_{op} | K \rangle - E \delta_{KL} \} C_K = 0, \quad L=1, 2, \dots \quad (3.3)$$

while the corresponding best energy E is the lowest root of the secular equation

$$\det \{ \langle L | H_{op} | K \rangle - E \delta_{KL} \} = 0, \quad (3.4)$$

where

$$\langle L | H_{op} | K \rangle = \int \Psi_L H_{op} \Psi_K dv. \quad (3.5)$$

We note that in this secular equation the E 's occur

only on the principal diagonal and with unit coefficients. This form of the secular equation is especially convenient for numerical solution using matrix methods, particularly iterative ones, and is a result of our having chosen the one-electron functions to be orthogonal.

The one-electron functions ψ_m used in the construction of the determinantal wave functions are products of the form

$$\psi_m(x) = \phi_m(r) \begin{cases} \alpha(s) \\ \beta(s) \end{cases}, \quad (3.6)$$

where the $\phi_m(r)$ form a complete orthonormal set of space orbitals depending only on the one-electron space coordinate $r = (r, \theta, \phi)$, and $\alpha(s)$ and $\beta(s)$ are spin functions. Here (r, θ, ϕ) refer to a coordinate system with origin midway between the two nuclei and with the z-axis along the inter-nuclear axis.

The one-electron space orbitals $\phi(r)$ were chosen from the complete orthonormal set of functions

$$\phi_{nqm}^z = R_{nq}(x) Y_{qm}(\theta, \phi) \quad (3.7)$$

$$R_{nq}(x) = (2z)^{3/2} \left\{ \frac{(n-q-1)!}{(n+q+1)!} \right\}^{1/2} x^q L_{n+q+1}^{2q+2}(x) e^{-\frac{1}{2}x}, \quad (3.8)$$

where $x = 2zr$. Here $R_{nq}(x)$ is the associated Laguerre orthogonal function of order $2q+2$ and $L_{n+q+1}^{2q+2}(x)$ is the $(2q+2)$ -order associated Laguerre polynomial of degree

$n-q-1$ defined by

$$L_{n+q+1}^{2q+2}(x) = \sum_{i=0}^{n-q-1} \frac{(n+q+1)!^2}{(n-q-1-i)!(2q+2+i)! i!} (-x)^i \quad (3.9)$$

The quantities n and q are positive integers such that $n \geq q+1$; z is a variable parameter called a scale factor (or effective nuclear charge, although this terminology has little meaning here); and Y_{qm} is the usual normalized spherical harmonic with the particular choice of phases as defined by Condon and Shortley (18, p. 52).

A detailed discussion of the associated Laguerre functions is really unnecessary here, since adequate discussions can usually be found in any book on the special functions of mathematical physics and chemistry, for example (32, 33, 34). However, in Section A of the Appendix, we have summarized a few of the important properties of these functions that have been particularly useful in this investigation.

The associated Laguerre functions of any order are included as a special case in the complete set of Slater orbitals

$$\chi_{nqm}^z(r) = (2z)^{n+\frac{1}{2}} \{(2n)!\}^{-\frac{1}{2}} r^{n-1} e^{-zr} Y_{qm}(\theta, \phi), \quad (3.10)$$

for it is easily shown that if Slater functions all having

the same orbital exponent are made orthogonal by the Schmidt process (27, p. 45), the associated Laguerre functions, or linear combinations thereof, result; consequently

$$\rho_{nqm}^z = \sum_{i=0}^{n-q-1} C_i(nq) \chi_{q+1+i, qm}^z, \quad (3.11)$$

where

$$C_i(nq) = (-1)^i \frac{\{(n-q-1)!(n+q+1)!(2q+2+2i)!\}^{\frac{1}{2}}}{(n-q-1-i)!(2q+2+i)!}. \quad (3.12)$$

Here $C_i(nq) = C_{ni}$ [we drop the q index since both (3.10) and (3.11) are already diagonal in q] is the i th element in the n th row of the Schmidt transformation matrix that transforms the overlap matrix $[S_{i+q+1, j+q+1}]$ for the Slater functions (3.10) into a unit matrix, that is,

$$[C_{ni}] [S_{i+q+1, j+q+1}] [C_{nj}]' = [1]. \quad (3.13)$$

The radial function $R_{nq}(x)$ is similar to the radial eigenfunctions for the bound states of the hydrogen atom, but instead of the orbital exponent varying as $1/n$, the same exponent is used for all R_{nq} . Hence these functions are more concentrated in space, for the high n values, than the hydrogenic functions. On the other hand, the quantum numbers n , q , and m have essentially the same meaning, so that we

may apply to the ϕ_{nqm}^Z the same spectroscopic notation that is employed to describe the bound states of the hydrogen atom. In addition, we shall add subscripts when necessary to indicate the value of the magnetic quantum number. Thus, for example, the functions (3.7) will be denoted in general by ϕ_m , and in particular by $ns = \phi_{n00}$, $np_0 = \phi_{n10}$, $nd_1 = \phi_{n21}$, and so forth. We prefer this notation to the usual spectroscopic notation applicable to one-electron orbitals in a diatomic molecule, namely, ns , $np\sigma$, $np\pi$, $nd\sigma$, $nd\pi$, . . . , since this notation does not distinguish between plus and minus values of m . Furthermore, we shall usually refer to the ϕ_m simply as "Laguerre functions (orbitals)", although this terminology is strictly applicable only to the radial function R_{nq} .

Let us now return to the problem of further specifying the approximate wave function (3.1). Since the ground state of the hydrogen molecule is experimentally known to have the symmetry $^1\Sigma_g^+$, we need consider only those Ψ_K 's which by themselves or in combination with other Ψ_K 's, have this symmetry. Now the most general antisymmetric two-electron wave function that can be constructed from the spin-orbitals ϕ_m^α and ϕ_n^β has the form

$$\Psi(x_1, x_2) = 2^{-\frac{1}{2}} \left\{ \sum_{mn} A_{mn} \det(\phi_m^\alpha, \phi_n^\beta) + B_{mn} \det(\phi_m^\alpha, \phi_n^\alpha) + C_{mn} \det(\phi_m^\beta, \phi_n^\beta) \right\} \quad (3.14)$$

This function is readily seen to be a sum of a singlet term and the three components of a triplet term. We shall be interested only in the singlet component which can be sorted out by applying the projection operator (35) ${}^1_0 = (1 - \frac{1}{2}S^2) = \frac{1}{2}(1 - P_{12}^\sigma)$, where S is the spin angular momentum operator and P_{12}^σ is the operator that permutes the spin coordinates of the two electrons. We obtain

$${}^1\Psi(x_1, x_2) = 2^{-\frac{1}{2}} \sum_m c_{mm} \det(\phi_m^\alpha, \phi_m^\beta) + 2^{-\frac{1}{2}} \sum_{m < n} c_{mn} \{ \det(\phi_m^\alpha, \phi_n^\beta) + \det(\phi_n^\alpha, \phi_m^\beta) \} \quad (3.15)$$

By expanding the determinants, this function can be written as a product of a pure space part and a pure spin part,

$${}^1\Psi(x_1, x_2) = 2^{-\frac{1}{2}} (\alpha_1 \beta_2 - \alpha_2 \beta_1) \Psi(r_1, r_2) \quad (3.16)$$

$$\Psi(r_1, r_2) = \sum_m c_{mm} \phi_m(r_1) \phi_m(r_2) + \sum_{m < n} c_{mn} 2^{-\frac{1}{2}} \{ \phi_m(r_1) \phi_n(r_2) + \phi_n(r_1) \phi_m(r_2) \} \quad (3.17)$$

It is convenient to write (3.17) in the abbreviated form

$$\Psi(r_1, r_2) = \sum_m c_{mm} (\phi_m \phi_m) + \sum_{m < n} c_{mn} (\phi_m \phi_n) \quad (3.18)$$

where by $(\phi_m \phi_n)$ we mean the normalized two-electron space

function symmetric in the coordinates of the two electrons defined by

$$(\phi_m \phi_n) = \phi_m(r_1) \phi_m(r_2) \quad m=n \quad (3.19)$$

$$(\phi_m \phi_n) = 2^{-\frac{1}{2}} \{ \phi_m(r_1) \phi_n(r_2) + \phi_n(r_1) \phi_m(r_2) \}, \quad m < n \quad (3.20)$$

The spin part of (3.16) plays no further part in the calculation and will henceforth be ignored.

In order for $\Psi(r_1, r_2)$ to have Σ_g^+ symmetry, it must have rotational symmetry about the bond axis, be symmetric under inversion at the center of symmetry, and have positive reflection symmetry across any plane containing the bond axis. The same restrictions, however, need not be put on the one-electron functions in terms of which we expand $\Psi(r_1, r_2)$, for as long as the one-electron functions in any configuration are both even or both odd their product will be even; moreover, the requirement of rotational symmetry about the bond axis will be met as long as the m quantum numbers of the two functions sum to zero. The requirement of positive reflection symmetry further restricts the expansion to terms symmetric in the m quantum numbers; that is, not only must the angular coordinates appear as $(\phi_1 - \phi_2)$, they must enter as the cosine of $M(\phi_1 - \phi_2)$, where M is an integer. Expressed analytically, the configuration $(\phi_a \phi_b)$ will have the proper symmetry only if $q_a + q_b$ is even and $m_a + m_b = 0$. For example, the configurations

(msns), (msnd₀), (md₀nd₀), (md₀ni₀), (mp₀mp₀), and (mp₁mp₋₁) all have Σ_g^+ symmetry, while the configurations (msnp₀), (nd₀nd₁), (mp₁np₁) do not.

Note that a configuration of the type (mp₁np₋₁) must be symmetric in both the total and magnetic quantum numbers, that is,

$$\begin{aligned} (mp_1np_{-1}) = & \frac{1}{2} \{ mp_1(1)np_{-1}(2) + mp_1(2)np_{-1}(1) \\ & + mp_{-1}(1)np_1(2) + mp_{-1}(2)np_1(1) \} \end{aligned} \quad (3.21)$$

We have investigated the importance of the following kinds of configurations: ss, sd₀, sg₀, si₀, sl₀, sn₀, p₀p₀, d₀d₀, p₀f₀, and p₁p₋₁. Although not all of these configurations were used at any one time, still a sufficient number of combinations were tried to permit a reasonably full evaluation of the importance of each type.

2. Evaluation of the energy matrix elements

The energy matrix elements $\langle L | H_{op} | K \rangle$, where $\Psi_L = (\phi_k \phi_l)$ and $\Psi_K = (\phi_m \phi_n)$, are given by the formula

$$\begin{aligned} \langle L | H_{op} | K \rangle &= \int (\phi_k \phi_l) H_{op} (\phi_m \phi_n) dv_1 dv_2 \\ &= N \{ (k | H_1 | m) \delta(l, n) + (l | H_1 | n) \delta(k, m) \} \end{aligned}$$

$$+ (k|H_1|m) \delta(1,m) + (1|H_1|m) \delta(k,n) + (km|ln) + (lm|kn) \} \quad (3.22)$$

where $\delta(k,m)$ is the Kronecker delta and

$$(k|H_1|m) = \int \phi_k(1) \left(-\frac{1}{2} \nabla_1^2 - 2/r_{1a} \right) \phi_m(1) dv_1 \quad (3.23)$$

$$(km|ln) = \int \phi_k(1) \phi_m(1) (1/r_{12}) \phi_l(2) \phi_n(2) dv_1 dv_2$$

The factor N has the value $(2)^{-\frac{1}{2}} \{ \delta(m,n) + \delta(k,l) \}$

3. Evaluation of the basic integrals in the Slater representation

In this and the next section we give specific formulas for all the integrals that can occur in molecular calculations by the one-center method. Formulas are given for the integrals in both the Slater and Laguerre representations. The reason we require the integrals in the Slater representation is that for the nuclear attraction and electron repulsion integrals it is usually necessary to calculate the integrals between Laguerre functions in terms of the corresponding integrals between the Slater functions, using the functional relation (3.11) connecting these two functions. The notation is that of (3.10) for the Slater functions and that of (3.7-3.8) for the Laguerre functions.

The integrals are most easily calculated in terms of

certain auxiliary functions. We introduce the following:

$$T(n, q) = \int_0^{\infty} e^{-qr} r^n dr = n! / q^{n+1} \quad (3.24)$$

$$\begin{aligned} D(n, q) &= \int_0^1 e^{-qr} r^n dr \\ &= \frac{e^{-q}}{n+1} {}_1F_1(1, n+2; q) \\ &= \frac{e^{-q}}{n+1} \sum_{r=0}^{\infty} \frac{(n+1)!}{(n+r+1)!} q^r \end{aligned} \quad (3.25)$$

$$\begin{aligned} A(n, q) &= \int_1^{\infty} e^{-qr} r^n dr \quad q > 0 \\ &= \frac{n! e^{-q}}{q^{n+1}} \sum_{k=0}^n q^k / k! \quad \text{all } q \\ &= T(n, q) - D(n, q) \end{aligned} \quad (3.26)$$

$$\begin{aligned} J(m, \alpha; n, \beta) &= \int_0^{\infty} e^{-\alpha x} x^m dx \int_0^x e^{-\beta y} y^n dy \\ &= \frac{m! n!}{\alpha^{m+1} \beta^{n+1}} F_m^n(\alpha/\alpha+\beta) \end{aligned} \quad (3.27)$$

where

$$F_m^n(k) = (1-k)^{n+1} \sum_{r=0}^m \binom{n+r}{n} k^r \quad (3.28)$$

Here ${}_1F_1(1, n+2; q)$ is the confluent hypergeometric function; see Sneddon (34, p. 32) for notation and definitions.

Convenient mathematical relations for generating the A's, D's, and J's by completely inductive methods are given in the Appendix.

The basic integrals in the Slater representation are now easily expressed in terms of these auxiliary functions. The integrations are elementary and involve only well known standard techniques. Hence we give only the final results and refer to (36; 18, p. 175) for the details.

(a) Overlap integral.

$$(\chi_{nqm}^z, \chi_{n'q'm'}^{z'}) = \delta(m, m') \delta(q, q') N_n^z N_{n'}^{z'} T(n+n', z+z') \quad (3.29)$$

where N_n^z is the normalization factor for the Slater functions given by

$$N_n^z = \{T(2n, 2z)\}^{-\frac{1}{2}} \quad (3.30)$$

(b) One-center nuclear attraction integral.

$$(\chi_{nqm}^z | 1/r | \chi_{n'q'm'}^{z'}) = \delta(m, m') \delta(q, q') N_n^z N_{n'}^{z'} T(n+n'-1, z+z') \quad (3.31)$$

(c) Kinetic energy integral.

$$(\chi_{nqm}^z | -\frac{1}{2} \nabla^2 | \chi_{n'q'm'}^{z'}) = \frac{1}{2} \delta(m, m') \delta(q, q') N_n^z N_{n'}^{z'}$$

$$x \left\{ (n-q-1)(n'-q-1)T(n+n'-2, z+z') - [z(n'-q-1) + z'(n-q-1)] T(n+n'-1, z+z') + zz'T(n+n', z+z') \right\} \quad (3.32)$$

(d) Two-center nuclear attraction integral.

$$(\chi_{nqm}^z / 1/r_a | \chi_{n'q'm'}^{z'}) = \delta(m, m') N_n^z N_{n'}^{z'} R^{n+n'} \sum_k c^k(qm, q'm') \\ \times \{ D(n+n'+k, \alpha) + A(n+n'-k, \alpha) \} \quad (3.33)$$

where point a is a distance R from the origin. In evaluating the integral the z -axis is taken to pass through the point a, as is customary. For a given q and q' , k takes on the values $k = q+q', \dots, |q-q'|$. The quantity α is equal to $(z+z')R$. The quantity c^k is defined by

$$c^k(qm, q'm') = \sqrt{\frac{2}{2k+1}} \int_0^\pi \Theta(qm) \Theta(q'm') \Theta(km-m') \sin\theta d\theta \quad (3.34)$$

The c^k 's are tabulated by Condon and Shortley, pp. 178-9, over a wide range of q 's and m 's.

(e) Electron repulsion integral.

$$(a(1)b(2) | 1/r_{12} | c(1)d(2)) = (a(1)c(1) | 1/r_{12} | b(2)d(2)) \\ = N_{n_a}^{z_a} N_{n_b}^{z_b} N_{n_c}^{z_c} N_{n_d}^{z_d} \delta(m_a+m_b, m_c+m_d) \sum_k c^k(q_a m_a, q_c m_c)$$

$$x \ c^k(q_b m_b, q_d m_d) R^k(n_a n_c; n_b n_d) \quad (3.35)$$

where c^k is defined by (3.28) and

$$\begin{aligned} R^k(n_a n_c; n_b n_d) &= \int_0^\infty \int_0^\infty r_1^{n_a+n_c} e^{-\alpha r_1} \frac{r_<^k}{r_>^{k+1}} r_2^{n_b+n_d} e^{-\beta r_2} dr_1 dr_2 \\ &= J(n_a+n_c-k-1, \alpha; n_b+n_d+k, \beta) \\ &\quad + J(n_b+n_d-k-1, \beta; n_a+n_c+k, \alpha) \end{aligned} \quad (3.36)$$

where $r_<$ and $r_>$ are the lesser and greater, respectively, of r_1 and r_2 . Also, $\alpha = z_a + z_c$ and $\beta = z_b + z_d$.

For those c^k 's not given by Condon and Shortley, we have used the following formula for the special case $m = m' = 0$.

$$c^k(q_0, q'_0) = \{(2q+1)(2q'+1)\}^{\frac{1}{2}} \quad (3.37)$$

$$x \frac{(g!)^2 (q+q'-k)! (q'+k-q)! (q+k-q')!}{(2g+1) (g-k)!^2 (g-q)!^2 (g-q')!^2}$$

where $k+q+q'=2g$ and $|q-q'| \leq k \leq q+q'$. This formula is due to Gaunt (37).

4. Evaluation of the basic integrals in the Laguerre representation

The integrals in the Laguerre representation can now obviously be obtained from those in the Slater representation

by means of the defining relation (3.11) connecting these two representations and the integral formulas of the preceding section. Thus,

$$(\phi_a | K | \phi_b) = \sum_{i,j} c_i(a) c_j(b) (\chi_i | K | \chi_j) \quad (3.38)$$

$$(\phi_a \phi_c | 1/r_{12} | \phi_b \phi_d) = \sum_{i,j,k,l} c_i(a) c_j(c) c_k(b) c_l(d) \\ \times (\chi_i \chi_j | 1/r_{12} | \chi_k \chi_l) \quad (3.39)$$

where $c_i(a)$, etc., denote the coefficients in the expansion of the Laguerre functions in terms of the normalized Slater functions χ_i .

The evaluation of the one-electron integrals is simple. The matrix $[\chi_i | K | \chi_j]$ is written in square form and contracted on the right with the column $[c_j(b)]$ to give the matrix $[\chi_i | K | \phi_b]$ which is then contracted on the left with the row $[c_i(a)]$ to give the integral $(\phi_a | K | \phi_b)$. This numerical transformation, however, is required only for the two-center nuclear attraction integrals, since in the case of the kinetic energy and one-center nuclear attraction integrals there exist closed form expressions of quite simple form; see (3.43) and (3.44) below.

The situation is more complicated for the electron repulsion integrals, since here we are dealing with the numerical transformation of a four suffix matrix. The usual

procedure is to write the matrix $[\chi_i \chi_j | 1/r_{12} | \chi_k \chi_l]$ as a two suffix matrix $[s | 1/r_{12} | t]$, that is, one row and column corresponding to each pair of values of i and j . The corresponding vectors

$$C_s(a, c) = \{C_i(a)C_j(c) + C_j(a)C_i(c)\} \{1 - \frac{1}{2}\delta(i, j)\} \quad (3.40)$$

are then formed, and by two contractions of these with $[s | 1/r_{12} | t]$ each of the integrals $(\phi_a \phi_c | 1/r_{12} | \phi_b \phi_d)$ is found. It is this transformation which is one of the most difficult portions of the numerical calculations.

We have used a slight modification of this procedure, however, which reduces the amount of computation necessary by a factor of two or more. The method consists of expanding $\phi_a \phi_c$ not in terms of products of Slater functions, as in (3.40), but instead as a simple polynomial in r multiplied by an exponential term and an angular term, that is,

$$\phi_a \phi_c = \sum_{p=0}^N D_p(a, c) r^{p+q_a+q_c} e^{-(z_a+z_c)r} Y_{q_a m_a} Y_{q_c m_c} \quad (3.41)$$

where $N = n_a + n_c - q_a - q_c - 2$. Equation (3.39) can then be rewritten

$$(\phi_a \phi_c | 1/r_{12} | \phi_b \phi_d) = \sum_{p, q} D_p(a, c) D_q(b, d) (p | 1/r_{12} | q) \quad (3.42)$$

where $(p | 1/r_{12} | q)$ is easily evaluated using (3.35) and (3.36). We observe that the order of the matrix $[p | 1/r_{12} | q]$ is always

less than or equal to that of the matrix $[\chi_i \chi_j | 1/r_{12} | \chi_k \chi_l]$.
A corresponding reduction in the numerical work results.

We summarize below the formulas for the basic integrals between the Laguerre functions. Detailed proofs for formulas (3.43) and (3.44) are to be found in the Appendix, Sections B and C.

(a) Kinetic energy integral.

$$(\phi_{nqm}^z | -\frac{1}{2} \nabla^2 | \phi_{n'q'm'}^{z'}) = z^2 \delta(q, q') \delta(m, m')$$

$$\times \frac{\{4n+2-(2q+3)\delta(n, n')\}}{4q+6} \left\{ \frac{(n'-q-1)!(n+q+1)!}{(n'+q+1)!(n-q-1)!} \right\}^{\frac{1}{2}}, \quad n \leq n' \quad (3.43)$$

(b) One-center nuclear attraction integral.

$$(\phi_{nqm}^z | -1/r | \phi_{n'q'm'}^{z'}) = -z/(q+1) \delta(m, m') \delta(q, q')$$

$$\times \left\{ \frac{(n'-q-1)!(n+q+1)!}{(n'+q+1)!(n-q-1)!} \right\}^{\frac{1}{2}}, \quad n \leq n' \quad (3.44)$$

(c) Two-center nuclear attraction integral. Using (3.33) we write (3.38) in the matrix form

$$(\phi_{nqm}^z | -1/r_a | \phi_{n'q'm'}^{z'}) = -z \delta(m, m') 2 \alpha^{q+\frac{1}{2}} \rho^{q'+3/2}$$

$$\times [C_1(nq)] [B_{ij}] [C_j(n'q')] \quad (3.45)$$

This form differs from (3.38) slightly in that part of the

normalization factor for the Slater orbitals has been incorporated into the transformation matrix so that $C_i(nq)$ is now given by

$$C_i(nq) = (-1)^i \frac{\{(n-q-1)!(n+q+1)!\}^{\frac{1}{2}}}{(n-q-1-i)!(2q+2+i)!i!} \quad (3.46)$$

Here

$$B_{ij} = \alpha^i \beta^j \sum_k c^k(qm, q'm') \left\{ D(i+j+q+q'+2+k, \frac{\alpha+\beta}{2}) \right. \\ \left. + A(i+j+q+q'+1-k, \frac{\alpha+\beta}{2}) \right\} \quad (3.47)$$

with the usual limits on k . Here $\alpha=2zR$ and $\beta=2z'R$. R is the distance from the origin to point a . The z -axis is along the line joining the origin and point a .

(d) Electron repulsion integral. We scale the integrals with respect to z_a , that is, we let $x=2z_a r$. Further, we define $\alpha=(i+v_c)/2$ and $\beta=(v_b+v_d)/2$, where $v_b=z_b/z_a$, $v_c=z_c/z_a$, and $v_d=z_d/z_a$. Then (3.42) may be written

$$[\phi_a \phi_c | 1/r_{12} | \phi_b \phi_d] = z_a \delta(m_a+m_b, m_c+m_d) \\ \times [D_i(a, c)] [B_{ij}] [D_j(b, d)] \quad (3.48)$$

where, from (3.35) and (3.36)

$$\begin{aligned}
B_{ij} = & 2 \sum_k c^k(q_a m_a, q_c m_c) c^k(q_b m_b, q_d m_d) \\
& \times \left\{ J(i+q_a+q_c+1-k, \alpha; j+q_b+q_d+2+k, \beta) \right. \\
& \left. + J(j+q_b+q_d+1-k, \beta; i+q_a+q_c+2+k, \alpha) \right\} \quad (3.49)
\end{aligned}$$

The coefficients in the expansion (3.41) are given by

$$\begin{aligned}
D_i(a, c) &= v_c^{q_c+3/2} \sum_{r=0}^i C_r(a) C_{i-r}(c) v_c^{1-r} \\
D_j(b, d) &= v_b^{q_b+3/2} v_d^{q_d+3/2} \sum_{r=0}^j C_r(b) v_b^r C_{j-r}(d) v_d^{j-r}
\end{aligned} \quad (3.50)$$

where $C_r(a) = C_r(n_a q_a)$, etc. Here $i=0, 1, \dots, n_a+n_c-q_a-q_c-2$ and $j=0, 1, \dots, n_b+n_d+q_b-q_d-2$.

5. Numerical solution of the eigenvalue problem

The IBM 650 computer was programed to carry out all the principal computational processes involved in the one-center configuration interaction calculations on the H_2 and H_3^+ molecules. A description of these routines will now be given. However, a detailed discussion of the inner workings of the routines will not be attempted here. The programs described, with instructions for using them, are available from the author upon request.

The numerical calculations are conveniently divided into three relatively independent stages: (i) evaluation of all required one and two electron integrals over a given set of basis functions, (ii) construction of the configuration interaction matrix elements between the various configurations from these basic integrals, and (iii) diagonalization of the configuration interaction matrix.

Two routines were required for the first stage of calculation, namely, a nuclear attraction integral routine and an electron repulsion integral routine. The kinetic energy integrals are easily calculated by hand. The 650 routine for the nuclear attraction integrals is based directly on equation (3.45). The routine calculates, as a block, all possible integrals between any two given sets $\{\phi_{nq}\}$ ($n=q+1, \dots, n_{\max}$) and $\{\phi_{n'q'}\}$ ($n'=q'+1, \dots, n'_{\max}$) starting with the minimum values of n and n' and proceeding to the maximum values. Therefore, it is not possible to calculate a single integral $(nq|1/r_a|n'q')$ without calculating all the integrals for lesser values of n and n' . In practice this is no limitation since the integrals usually required are those for the small values of n . There is no restriction on q ; n , however, cannot be greater than $q+10$. Furthermore, there are no restrictions on α and β ; in particular, the distance R can be reduced to zero ($\alpha=\beta=0$) without complications, in which case the

routine gives to eight figure accuracy the same result as equation (3.44).

As input the routine requires only the c^k 's, the $C_1(nq)$, the values of α , β , q , q' , and maximum values of n and n' . Although the accuracy depends on the size of the matrix multiplication, it is usually between seven and eight significant figures for all values of the parameters. In typical cases, the time required per integral is about two seconds.

The calculation of electron repulsion integrals is based on equations (3.48-50). Because the process of matrix contraction in (3.48) involves considerable differencing, it is necessary to use double precision floating point arithmetic throughout. This makes the calculations quite lengthy; for instance, more than forty-five minutes are required to calculate the 210 (ss|ss) integrals for the set 1s, . . . , 6s. Here, as in the nuclear attraction integral routine, there are no restrictions on α , β , or the q 's. The matrix $[B_{ij}]$ given by (3.49) cannot exceed 20x20. The n quantum numbers are restricted accordingly. The c^k 's are not computed by the routine. In fact, for large values of q , the calculation of these may prove to be the most difficult part of the whole calculation.

In all cases, the accuracy of the integrals is at least nine significant digits for all values of the parameters.

This, of course, is an accuracy far beyond the immediate requirements of this investigation.

For the second stage of the calculation, a program was constructed which compiled the configuration interaction matrix elements, using formulas (3.22) and (3.23), from the basic one and two electron integrals. This routine can be adapted to one-center calculations on (1) the spherically symmetric component of any two-electron atomic or molecular system, (2) 1S states of atoms, and (3) Σ states of linear two-electron molecules such as H_2 and linear H_3^+ . The one and two electron integrals, along with suitable identification, are loaded into the 650 in table form along with the configuration identification (in terms of the n and q quantum numbers of both functions). To construct a matrix element between any two configurations the program first carries out the various tests indicated in (3.22) and then obtains the required integrals using the Table Look Up feature of the 650. A special subroutine is required for the integral $(k|H_{lm})$. This subroutine, in general, is different for molecules with different nuclear configurations. The output of the routine is the complete configuration interaction matrix in triangular form.

The configuration interaction matrix was solved either for all the roots and vectors or just for the lowest root and vector alone. Routines for carrying out both of these

processes have been written for the 650 by Dr. Keith Howell. The routine for obtaining just the lowest root and vector is based on the well known power method. In this method an arbitrary trial vector x^0 is chosen and a new vector x^1 is computed by means of the matrix multiplication $Hx^0 = x^1$. This process is then repeated to give $Hx^1 = x^2$ and is continued until $x^{p+1} = cx^p$, that is, until the matrix multiplication yields a vector x^{p+1} which differs from the preceding vector x^p by only a constant factor. Then, except for normalization, x^p is the eigenvalue corresponding to the eigenvalue c . It can be proved (38) that such a process converges on the dominant root (i.e., the one with greatest modulus) and corresponding dominant vector. (Note that we can easily make the lowest root of the matrix H the dominant root simply by adding a suitable negative constant to the diagonal elements.) The largest matrix that we have solved by this method is a 39×39 . Starting from an initial trial vector $(1, 0, \dots)$, about two and one-half hours were required to obtain the eigenvalue stable to eight figures. A comparable time for a 20×20 is about 45 minutes.

The routine for obtaining all roots and vectors uses the rotation method. In this method the eigenvalue problem is written in the form $V^{-1}HV = E$, where H is the configuration interaction matrix whose eigenvalues are the elements of the

diagonal matrix E . The vector V_i corresponding to the eigenvalue E_i is the i -th column of the matrix V . The matrix V is obtained as the product of a number of simple unitary transformation (rotation) matrices R_{ij} which successively reduce the i, j elements of the original matrix to zero. It can be shown that if this process is carried far enough, eventually all the off-diagonal elements will be reduced to zero. Moreover, the convergence can be shown to be quadratic.

Throughout our calculations we have mainly used the power method. This is because we have been concerned mostly with large matrices (i.e., greater than 20×20) and in this case the power method is more efficient by a factor of about one and one-half to two. For small matrices, however, the rotation method is more efficient than the power method.

B. Results

The results of the one-center calculations on the hydrogen molecule are summarized in Tables 1-7. The data refer to the observed internuclear distance of 0.7395 \AA or 1.4 a.u. Minimization of the energy with respect to the internuclear distance was not attempted in any case.

All energies given are total energies, that is, the sum

of the electronic and nuclear repulsion energies at the equilibrium distance; no allowance has been made for zero point vibrational energy. Inclusion of this would mean adding about 0.01 a.u. to the total energies given. The data are tabulated with respect to the parameters in the nuclear attraction integrals, that is, $z_q R$, where z_q is the scale factor for the Laguerre functions with azimuthal quantum number q and R is the internuclear distance.

No attempt has been made to give the expansion coefficients for all the various trial functions, since such a tabulation would be quite lengthy and serve little useful purpose. The expansion coefficients have been given for only two functions, namely, the two best expansions obtained in this research (Tables 6 and 7).

We began our calculation by first solving the wave equation in the spherically averaged approximation. The results for configurations up to $6s^2$ are tabulated in Table 1. Columns two to five in the table refer to expansions of 6, 10, 15, and 21 configurations, respectively. The trend in the energy values shows clearly that with 21 configurations we have come very close to the limit to be obtained with s orbitals only. The best energy obtained for a 21 term expansion was -1.04469 a.u. for a scale factor of 2.071429 (parameter value of $z_s R = 2.9$). This is 89.0 per cent of the total energy and 25.7 per cent of the binding energy. Although

this energy is still not as low as even the simple Heitler-London-Sugiura result (-1.1160 a.u.) (See Table 8), it is nevertheless promising that these relatively inappropriate spherical orbitals should provide as much binding as they do.

Table 1. Total energy of the hydrogen molecule in the spherically averaged approximation for various numbers of (ss) configurations. Energy in atomic units.

| $z_s R$ | Terms up to $3s^2$ | Terms up to $4s^2$ | Terms up to $5s^2$ | Terms up to $6s^2$ |
|---------|-----------------------|-----------------------|-----------------------|-----------------------|
| 1.1 | -1.00624 | | -1.03095 | |
| 1.4 | -1.01949 | -1.03384 | -1.04091 | -1.04337 |
| 1.7 | -1.03160 | -1.04116 | -1.04358 | |
| 1.8 | -1.03414 | -1.04234 | | -1.04384 |
| 2.0 | -1.03715 | -1.04349 | -1.04377 | -1.04390 |
| 2.3 | -1.03714 | -1.04328 | -1.04380 | -1.04380 |
| 2.6 | -1.03143 | | -1.04436 | |
| 2.9 | -1.01808 | -1.03668 | -1.04459 | -1.04469 |
| 3.2 | -0.99398 | | -1.04363 | -1.04446 |
| 3.5 | -0.95585 | | -1.04047 | -1.04374 |

We next investigated the effect of adding (sd_0) configurations to the spherically symmetric orbitals. Since

expansions in 21 (ss) configurations do not gain enough in accuracy over expansions in 15 configurations to justify their additional complexity, in all subsequent calculations we limited ourselves to at most 15 (ss) terms (i.e., up to $5s^2$). The results obtained by adding 5 (sd_0) and 15 (sd_0) configurations to the basic 15 (ss) configurations are tabulated in Table 2 for a wide range of values of the s and d scale factors. For 30 configurations, the best energy obtained was -1.12250 a.u. (for $z_s R = z_d R = 2.9$), which is now better than the Heitler-London-Sugiura result but still less than the SCF result (-1.134 a.u.). Thus, using only s and d orbitals, we have accounted for 95.6 per cent of the total energy and 70.4 per cent of the binding energy. Comparison of the results for 5 (sd_0) and 15 (sd_0) terms indicates that the limiting value of the energy that can be obtained with (ss) and (sd_0) terms only is close to this best value.

In Chapter II we reviewed previous calculations by the one-center method and pointed out that Huzinaga (1) and Handler (2) have both carried out one-center expansions for H_2 based on s and d orbitals only. We pointed out further that the best result reported by Huzinaga, -1.1397 a.u. for two s and one d orbital, was no doubt in error. This value is clearly not consistent with the data in Table 2. However, Handler's result, -1.0878 a.u. for three (ss)

Table 2. Total energy of the hydrogen molecule using (ss) and (sd_0) configurations. Energy in atomic units.

| $z_s R$ | $z_d R$ | $15(ss) + 5(sd_0)^a$ | $15(ss) + 15(sd_0)^b$ |
|---------|---------|----------------------|-----------------------|
| 1.7 | 1.7 | -1.06458 | |
| 2.0 | 2.0 | -1.07606 | |
| 2.3 | 2.3 | -1.08771 | |
| 2.6 | 2.6 | -1.09889 | -1.12126 |
| 2.9 | 2.9 | -1.10830 | -1.12250 |
| 3.2 | 3.2 | -1.11459 | |
| 3.5 | 3.5 | -1.11660 | -1.11930 |
| 1.4 | 2.1 | -1.07700 | |
| 1.7 | 2.55 | -1.09634 | |
| 2.0 | 3.0 | -1.10958 | |
| 2.3 | 3.45 | -1.11773 | |
| 2.6 | 3.9 | -1.12116 | -1.12137 |
| 2.9 | 4.35 | -1.12017 | |
| 1.4 | 2.8 | -1.10121 | |
| 1.7 | 3.4 | -1.11676 | -1.12059 |
| 2.0 | 4.0 | -1.12039 | -1.12060 |

^a $1s^2, 1s2s, \dots, 5s^2, 1s3d_0, 2s3d_0, \dots, 5s3d_0.$

^b $1s^2, 1s2s, \dots, 5s^2, 1s3d_0, \dots, 5s3d_0, 1s4d_0, \dots, 5s5d_0.$

Table 2. (Continued)

| $z_s R$ | $z_d R$ | $15(ss) + 5(sd_o)^a$ | $15(ss) + 15(sd_o)^b$ |
|---------|---------|----------------------|-----------------------|
| 2.3 | 4.6 | | -1.12109 |
| 2.6 | 5.2 | -1.10896 | |
| 1.1 | 3.3 | -1.10035 | |
| 1.7 | 5.1 | -1.10953 | -1.12102 |
| 2.0 | 6.0 | -1.09487 | -1.12112 |
| 2.3 | 6.8 | -1.08084 | -1.12024 |
| 1.4 | 5.6 | -1.09790 | -1.12101 |
| 1.7 | 6.8 | -1.08191 | -1.12001 |
| 2.0 | 8.0 | -1.06740 | -1.11776 |
| 2.3 | 9.2 | -1.05787 | -1.11345 |

and three (sd_o) configurations, is in essential agreement with our results, although his energy value is low due to a poor choice of scale factor ($z_s=z_d=1.0714$). In order to remove this discrepancy, and as a further check on our own calculations, we have repeated the final stage of Huzinaga's calculation in its entirety.

For his final approximation, Huzinaga used the three term expansion

$$\Psi(r_1, r_2) = \sum_{i=1}^3 c_i \phi_i(r_1, r_2)$$

$$\phi_1(r_1, r_2) = \{s_1(1) + 0.25s_4(1)\} \{s_1(2) + 0.25s_4(2)\}$$

$$\begin{aligned} \phi_2(r_1, r_2) = & \{s_1(1) + 0.25s_4(1)\} d_4(2) \\ & + d_4(1) \{s_1(2) + 0.25s_4(2)\} \end{aligned}$$

$$\phi_3(r_1, r_2) = d_4(1)d_4(2) \quad (3.51)$$

where the orbitals $s_1 = \chi_{100}^{1.0}$, $s_4 = \chi_{400}^{4.3}$, and $d_4 = \chi_{420}^{4.3}$ are the normalized Slater orbitals (3.10) centered midway between the nuclei. Note that the s_1 and s_4 are not orthogonal and that the secular equation in this case is

$$\det (H_{ij} - ES_{ij}) = 0 \quad (3.52)$$

where $H_{ij} = \int \phi_i^* H \phi_j dv_1 dv_2$ and $S_{ij} = \int \phi_i^* \phi_j dv_1 dv_2$.

Carrying through this calculation, one obtains an energy of -1.106 a.u., which is considerably above the value -1.1397 a.u. reported by Huzinaga. We further checked this result by carrying out the calculation based on the six configurations s_1s_1 , s_1s_4 , s_4s_4 , s_1d_4 , s_4d_4 , and d_4d_4 . This six term expansion must of course give a lower energy value than the three term expansion (3.51). The value obtained was -1.109

a.u. We conclude that Huzinaga's result must be in error.

We next investigated the effect of adding the axially symmetric functions p_0 , f_0 , g_0 , i_0 , l_0 , and n_0 to our s and d_0 basis functions. From these eight types of functions we can construct a total of twenty-four different types of $^1\Sigma_g^+$ configurations. Of these only a few will be important in lowering the energy. We can estimate which ones will be important by comparing the values of the squares of the matrix elements between these states and the (ss) states with the difference in the corresponding diagonal energies. That is, the quantity $(H_{1j})^2/(H_{11}-H_{jj})$ is a rough measure of the importance of the state ϕ_j in lowering the energy. Here ϕ_i may be either a solution of the configuration interaction problem prior to the addition of the state ϕ_j (bordered determinant approximation; see Condon and Shortley, p. 40) or simply the state with lowest diagonal energy. Only if the interaction matrix elements are fairly large, and if the difference between the diagonal energies is not too great, will the added state appreciably lower the energy. For example, states such as (sg_0) , (si_0) , and (sn_0) interact with (ss) states only through the nuclear attraction operator. We expect these states to be important since integrals over the nuclear attraction operator can be made quite large by a proper choice of the g_0 , i_0 , and n_0 scale factors. Of course, the scale factor which maximizes the matrix element H_{1j} may

also raise H_{jj} to a prohibitively large value so that there is a point past which further raises in the scale factor will be detrimental. On the other hand, states such as (d_0d_0) , (d_0g_0) , and (g_0g_0) have small or zero matrix elements with (ss) states since the coupling here is by means of the electron repulsion operator. The integrals for this operator usually have much smaller values than the nuclear attraction integrals and are also less sensitive to scale factor variations. Hence, states of this type are not expected to be very important. An apparent exception is the state (p_0p_0) which turns out to be of major importance; this is no doubt due to the fact that in this case the electron repulsion integrals (sp_0/sp_0) have fairly large values.

We have therefore examined only the following types of configurations: (p_0p_0) , (p_0f_0) , (d_0d_0) , (sg_0) , (si_0) , (sl_0) , and (sn_0) . The relative importance of each of these types in lowering the energy may be seen from Table 3. Each type of state was tested only against the (ss) and (sd_0) configurations. Strictly, a term should be tested in combination with all other terms. It is a general characteristic of variational calculations, however, that the improvement obtainable from any given term becomes progressively less important as the number of other terms is increased. This is especially so if the maximum improvement attainable is small. Moreover, we are justified in

Table 3. Summary of the contributions to the energy for various kinds of configurations when added to an expansion consisting of 15 (ss) and 15 (sd_0) terms.

| $z_s R$ | $z_d R$ | $z_q R$ | $z_{q'} R$ | Number of (qq') added | Energy ^a (a.u.) | E^b (a.u.) |
|---------|---------|---------|------------|------------------------------|----------------------------|--------------|
| 2.9 | 2.9 | 2.9 | 2.9 | 10($p_0 p_0$) ^c | -1.13848x | -0.01598 |
| 3.5 | 3.5 | 3.5 | 3.5 | 6($p_0 p_0$) ^d | -1.13551x | -0.01621 |
| 1.7 | 3.4 | 1.7 | 1.7 | " | -1.13602 | -0.01543 |
| 2.0 | 4.0 | 2.0 | 2.0 | " | -1.13612 | -0.01557 |
| 2.3 | 4.6 | 2.3 | 2.3 | " | -1.13666 | -0.01557 |
| 1.7 | 3.4 | 3.4 | 3.4 | " | -1.13645x | -0.01586 |
| 2.0 | 4.0 | 4.0 | 4.0 | " | -1.13634 | -0.01574 |
| 2.3 | 4.6 | 4.6 | 4.6 | " | -1.13605 | -0.01496 |
| 2.0 | 4.0 | 3.0 | 3.0 | " | -1.13559x | -0.01499 |
| 2.0 | 4.0 | 2.0 | 2.0 | 5(sg_0) ^e | -1.12334 | -0.00274 |

^aTotal energy for an expansion consisting of 15 (ss), 15 (sd_0), and N (qq') configurations. The letter "x" following an entry indicates that the value given is the lowest root of the approximate matrix constructed by considering the solution of the 15(ss)+15(sd_0) problem as a single configuration.

^bDifference between the energy values for the 15(ss)+15(sd_0)+N(qq') and 15(ss)+15(sd_0) problems. The energies for the latter are given in Table 2.

^cAll terms up to $5p^2$.

^dAll terms up to $4p^2$.

^e1s $5g_0$, 2s $5g_0$, . . . , 5s $5g_0$.

Table 3. (Continued)

| $z_s R$ | $z_d R$ | $z_q R$ | $z_{q'} R$ | Number of (qq') added | Energy ^a (a.u.) | E^b (a.u.) |
|---------|---------|---------|------------|-----------------------------|-------------------------------|-----------------|
| 2.0 | 4.0 | 2.0 | 6.0 | 5(sg_0) ^e | -1.12867 | -0.00807 |
| 2.0 | 4.0 | 2.0 | 8.0 | " | -1.13087 | -0.01018 |
| 2.0 | 4.0 | 2.0 | 10.0 | " | -1.12885 | -0.00825 |
| 2.9 | 2.9 | 2.9 | 2.9 | 9(sg_0) ^f | -1.12557x | -0.00307 |
| 2.9 | 2.9 | 2.9 | 8.7 | " | -1.13286x | -0.01036 |
| 3.5 | 3.5 | 3.5 | 3.5 | " | -1.12636x | -0.00706 |
| 3.5 | 3.5 | 3.5 | 10.5 | " | -1.12978x | -0.01048 |
| 2.9 | 2.9 | 2.9 | 5.8 | 9(si_0) ^g | -1.12360x | -0.00110 |
| 2.9 | 2.9 | 2.9 | 8.7 | " | -1.12451x | -0.00201 |
| 2.9 | 2.9 | 2.9 | 11.6 | " | -1.12442x | -0.00192 |
| 2.9 | 2.9 | 2.9 | 14.5 | " | -1.12460x | -0.00210 |
| 2.9 | 2.9 | 2.9 | 8.7 | 9(sl_0) ^h | -1.12285x | -0.00035 |
| 2.9 | 2.9 | 2.9 | 11.6 | " | -1.12309x | -0.00059 |
| 2.9 | 2.9 | 2.9 | 14.5 | " | -1.12309x | -0.00059 |
| 2.9 | 2.9 | 2.9 | 11.6 | 9(sn_0) ⁱ | -1.12264x | -0.00014 |

^f1s5g₀, 2s5g₀, 3s5g₀, 1s6g₀, . . . , 3s7g₀.

^g1s7i₀, 2s7i₀, 3s7i₀, 1s8i₀, . . . , 3s9i₀.

^h1s9l₀, 2s9l₀, 3s9l₀, 1s10l₀, . . . , 3s11l₀.

ⁱ1s11n₀, 2s11n₀, 3s11n₀, 1s12n₀, . . . , 3s13n₀.

Table 3. (Continued)

| z_s^R | z_d^R | z_q^R | $z_{q'}^R$ | Number of (qq') added | Energy ^a (a.u.) | E^b (a.u.) |
|---------|---------|---------|------------|-----------------------------|-------------------------------|-----------------|
| 2.9 | 2.9 | 2.9 | 14.5 | $9(sn_o)^i$ | -1.12273x | -0.00023 |
| 2.9 | 2.9 | 2.9 | 17.4 | " | -1.2273x | -0.00023 |
| 2.0 | 4.0 | 4.0 | 4.0 | $6(d_o d_o)^j$ | -1.12089 | -0.00029 |
| 2.9 | 2.9 | 2.9 | 2.9 | " | -1.12277x | -0.00027 |
| 2.9 | 2.9 | 2.9 | 2.9 | $9(p_o f_o)^k$ | -1.12261x | -0.00011 |
| 3.5 | 3.5 | 3.5 | 3.5 | " | -1.11943x | -0.00014 |

^jTerms up to $5d^2$.

^k $2p_o 4f_o, 3p_o 4f_o, 4p_o 4f_o, 2p_o 5f_o, \dots, 4p_o 6f_o$.

rejecting any terms which at any stage in the building up of our wave function are found to produce a negligible improvement in the energy.

Each of these types of configurations contains a scale factor which should in principle be determined by the configuration interaction. This is too laborious to be feasible, however. The procedure adopted here was to determine the scale factor for each type of state by first taking that set of (ss) and (sd_o) configurations which gives the best energy contribution, freezing the s and d scale factors, and then adding the new set of states and minimizing the energy by

trial and error with respect to the new scale factor. This procedure, of course, neglects any coupling that may exist between the scale factors for the various kinds of states. It assumes that the best s scale factor when only (ss) and (sd_0) terms are present is the same as the best s scale factor when only (ss) terms are used, and that the best s and d scale factor combination obtained using (ss) and (sd_0) terms only will hold when additional states are added, and so on as more types of states are added. That this is in fact the case can be seen from Tables 1 and 2. The maximum (sd_0) contribution occurs for the same s parameter value, that is, $z_s R = z_d R = 2.9$.

Instead of carrying out a complete variation calculation wherein the coefficients of all terms are allowed to vary, we can consider the best (ss) plus (sd_0) expansion as a single state and vary only the coefficients of the added terms. Values in Table 3 followed by the letter "x" were determined by just such an approximate procedure. As can be seen from Table 4, the overall accuracy of this approximation is high. In addition, the reduction in the amount of calculation is considerable.

Two final calculations were carried out. In the first calculation a configuration interaction was set up using as a basis a selected set of 38 axially symmetric configurations shown from the data in Table 3 to be most effective in low-

Table 4. Comparison of energy values obtained using the complete and approximate variational treatments. Energy in atomic units.

| $z_s R$ | $z_d R$ | Energy using 15 (ss) and 5 (sd_0) terms | | |
|---------|---------|---|----------------------|----------|
| | | 20 terms ^a | 6 terms ^b | E^c |
| 2.0 | 2.0 | -1.07606 | -1.07590 | -0.00016 |
| 2.6 | 2.6 | -1.09889 | -1.09833 | -0.00056 |
| 2.9 | 2.9 | -1.10830 | -1.10717 | -0.00113 |
| 3.5 | 3.5 | -1.11660 | -1.11540 | -0.00120 |
| 1.7 | 3.4 | -1.11676 | -1.11553 | -0.00123 |
| 2.0 | 4.0 | -1.12039 | -1.11887 | -0.00152 |
| 2.0 | 6.0 | -1.09487 | -1.09393 | -0.00094 |
| 1.7 | 6.8 | -1.08191 | -1.08133 | -0.00058 |

^a $1s^2, 1s2s, \dots, 5s^2, 1s3d_0, 2s3d_0, \dots, 5s3d_0.$

^b $\phi(1,2), 1s3d_0, 2s3d_0, \dots, 5s3d_0,$ where $\phi(1,2)$ is the result of a calculation based on the 15(ss) terms of footnote a.

^cDifference between the energy values for the 20 term and the 6 term expansions.

ering the energy. In the second calculation, angular dependence was introduced into the wave function in the form of 6 ($p_1 p_{-1}$) configuration. The results of these two calculations are tabulated in Table 5.

As can be seen from Table 3, the maximum contributions

Table 5. Final approximation to the energy and wave function of the hydrogen molecule.

| Terms and parameters | Energy (a.u.) | Terms added | Energy contri- bution (a.u.) |
|--|------------------|-----------------------------------|---------------------------------------|
| 15(ss); $z_s R=2.9$ | -1.04459 | | |
| 15(ss), 15(sd ₀); $z_s R=z_d R=2.9$. | -1.12250 | (sd ₀) | -0.07791 |
| 15(ss), 15(sd ₀), 9(sg ₀); $z_s R=z_d R=2.9, z_g R=8.7$. | -1.13286 | (sg ₀) | -0.01036 |
| 11(ss), 12(sd ₀), 6(sg ₀), 3(si ₀); $z_s R=z_d R=2.9, z_g R=8.7, z_i R=11.6$. | -1.13485 | (si ₀) | -0.00199 |
| 11(ss), 12(sd ₀), 6(sg ₀), 3(si ₀), 6(p ₀ p ₀); $z_s R=z_d R=z_p R=2.9, z_g R=$ 8.7, $z_i R=11.6$. Coefficients in Table 6. | -1.15086 | (p ₀ p ₀) | -0.01601 |
| 11(ss), 12(sd ₀), 6(sg ₀), 3(si ₀), 6(p ₀ p ₀), 6(p ₁ p ₋₁); $z_s R=z_d R=$ $z_p R=2.9, z_g R=8.7, z_i R=11.6$. Coefficients in Table 7. | -1.16141 | (p ₁ p ₋₁) | -0.01055 |
| Experimental energy. | -1.1740 | | |

to the energy for the various types of configurations arranged in order of importance, are: -0.01598 (p₀p₀), -0.01036 (sg₀), -0.00210 (si₀), -0.00059 (sl₀), -0.00027

(d_0d_0), -0.00023 (sn_0), and -0.00011 (p_0f_0). The last four types of states contribute a negligible amount to the energy and may be neglected. The configurations used for the 38-term function were obtained as follows: the best expansion in 15 (ss), 15 (sd_0), and 9 (sg_0) was reduced to a 29-term expansion with a completely negligible effect on the energy, by dropping those configurations entering with very small coefficients. To this 29-term expansion were added first 3 (si) configurations and then 6 (p_0p_0) configurations. The resulting 38-term function, which represents the best function without angular dependence obtained in this investigation, gave an energy of -1.15086 a.u., which is 98.0 of the total energy and 86.7 per cent of the binding energy. The coefficients for this 38-term function are given in Table 6.

This 38-term expansion was then considered as a single state and the 6 (p_1p_{-1}) configurations added. The energy obtained was -1.16141 a.u., which differs from the experimental value by only 0.0126 a.u. Coefficients for this 44-term function are given in Table 7.

C. Discussion

In Table 8 we have listed some of the more important investigations of the hydrogen molecule, with a brief description and reference for each, along with the results

Table 6. Expansion coefficients for 38-term function using axially symmetric configurations only.^a

| Configuration | Coefficient | Configuration | Coefficient |
|-------------------|-------------|---------------------------------|-------------|
| 1s1s | 0.660071 | 4s4d _o | -0.004779 |
| 1s2s | -0.622753 | 1s5d _o | 0.027305 |
| 2s2s | 0.247810 | 2s5d _o | -0.020325 |
| 1s3s | 0.225707 | 3s5d _o | 0.006567 |
| 2s3s | -0.098062 | 1s5g _o | 0.020912 |
| 1s4s | -0.099040 | 2s5g _o | -0.014208 |
| 2s4s | 0.051885 | 3s5g _o | 0.004793 |
| 3s4s | -0.005623 | 1s6g _o | -0.001511 |
| 1s5s | 0.037061 | 1s7g _o | -0.003092 |
| 2s5s | -0.021802 | 2s7g _o | 0.002447 |
| 3s5s | 0.006392 | 2p _o 2p _o | -0.093577 |
| 1s3d _o | 0.133154 | 2p _o 3p _o | 0.031403 |
| 2s3d _o | -0.084880 | 3p _o 3p _o | -0.015316 |
| 3s3d _o | 0.029565 | 2p _o 4p _o | 0.005632 |
| 4s3d _o | -0.013409 | 3p _o 4p _o | 0.002098 |
| 5s3d _o | 0.005040 | 4p _o 4p _o | -0.003245 |
| 1s4d _o | 0.034217 | 1s7i _o | 0.006366 |
| 2s4d _o | -0.027065 | 2s7i _o | 0.004438 |
| 3s4d _o | 0.013578 | 3s7i _o | 0.001610 |

^aSee Table 5 for parameter values.

Table 7. Expansion coefficients for 44-term function with angular dependence.^a

| Configuration | Coefficient |
|----------------|-------------|
| $\phi(1,2)^b$ | 0.997723 |
| $2p_1 2p_{-1}$ | 0.061552 |
| $2p_1 3p_{-1}$ | -0.023301 |
| $3p_1 3p_{-1}$ | 0.014052 |
| $2p_1 4p_{-1}$ | -0.002318 |
| $3p_1 4p_{-1}$ | -0.002494 |
| $4p_1 4p_{-1}$ | 0.003056 |

^aSee Table 5 for parameter values.

^b $\phi(1,2)$ equals the 38-term function given in Table 6.

for our 38-term axially symmetric function and our 44-term function with angular dependence. As can be seen, the energy result for the 44-term function is better than all previous results on hydrogen, except that of James and Coolidge (39). These latter workers, of course, have obtained essentially complete agreement with experiment, using a convergent expansion in elliptical coordinates and the interelectronic distance r_{12} . James and Coolidge also investigated the case in which r_{12} was omitted from the wave function. They found that in this case it was not

Table 8. A number of investigations on the wave function and total energy of the hydrogen molecule.

| Description | Energy (a.u.) | Refer- ence |
|--|------------------|----------------|
| Coulson (one config. MO=LCAO) | -1.1275 | 44 |
| Coulson (one config. SCF) | -1.134 | 45 |
| Heitler-London-Sugiura $a(1)b(2) + a(2)b(1)$ | -1.118 | 46,47 |
| Wang (H-L, scale factor) | -1.139 | 48 |
| Rosen (H-L, scale factor, polarization) | -1.1485 | 49 |
| Weinbaum (H-L, plus ionic, scale factor, polarization) | -1.151 | 50 |
| Gurnee-Magee (H-L, scale factor, polarization using off-center orbitals) | -1.152 | 43 |
| Inui (scale factor, polarization) | -1.148 | 51 |
| Mueller and Eyring (scale factor, polarization; semilocalized) | -1.154 | 52 |
| Callen (variational MO--two config.) | -1.1516 | 53 |
| Wallis and Hulburt (diatomic MO--two config.) | -1.1354 | 54 |
| Callen (variational MO--two config.) | -1.1571 | 53 |
| James and Coolidge (without r_{12}) | -1.1577 | 39 |
| Hagstrom (one-center, 38-term function, no angular dependence) | -1.1509 | |
| Hirschfelder and Linnett (H-L plus ionic, scale factor, angular correlation) | -1.156 | 41 |
| James and Coolidge (with r_{12}) | -1.1735 | 39 |
| Hagstrom (one-center, 44-term function, angular correlation) | -1.161 | |
| Experimental | -1.174 | |

possible to obtain an energy better than -1.1577 a.u. The difference between this value and experiment, -0.0163 a.u., is the angular correlation energy. Angular correlation has to do with the correlation in the spatial positions of the electrons on opposite sides of a plane passing through the bond axis. The use of the r_{12} coordinate is a direct way of bringing angular correlation into the wave function. As has been shown by Green *et al.* (40), however, configurations with angular dependence serve exactly the same function as the r_{12} terms. From Table 5 we see that the energy contribution of the angular terms ($p_{1p_{-1}}$) is -0.01055 a.u. or 64.7 per cent of the total angular correlation energy.

The only other calculation listed in Table 8 which involves angular dependence in the wave function and which may properly be compared with our result using the 44-term function is that of Hirschfelder and Linnett (41). These workers used a wave function of the Heitler-London plus ionic form and in addition included $2p_x$, $2p_y$, and $2p_z$ orbitals on each of the hydrogen nuclei. Our best result, however, is considerably better than the Hirschfelder and Linnett result.

On the other hand, the calculated energy for the 38-term axially symmetric function is inferior to the energy results for several of the calculations listed in Table 8, in particular, the calculations of Weinbaum (50), Gurnee and

Magee (43), Mueller and Eyring (52), Callen (53) (two and three configuration cases), and James and Coolidge without r_{12} (39). All of these calculations are based only on axially symmetric wave functions and involve no angular correlation. The error in our 38-term function is given as the difference between the James and Coolidge without r_{12} value and our value, that is, $-1.1577 - (-1.1509) = -0.0068$ a.u., or 0.250 electron volts.

This amount of energy must then reside in axially symmetric terms which have not been taken into account in our 38-term wave function. It will be recalled, however, that in constructing this function we were careful to include all terms contributing to the energy in the third decimal place and also included many terms contributing only in the fourth decimal place. Individually, the terms neglected are not expected to be important; collectively, however, their effect may be considerable. We can estimate the effect of the terms omitted as follows: Of the various types of configurations in Table 3, only $(s_1)_0$, $(s_n)_0$, $(d_0 d_0)$, and $(p_0 f_0)$ were not taken into account. These contribute a maximum of -0.00059 , -0.00023 , -0.00027 , and -0.00011 , respectively, and if we consider these effects to be additive we can estimate the maximum improvement to be gained by including these functions as -0.00120 a.u., which leads to an estimated energy of -1.1523 a.u. for axially symmetric terms only. Terms such as $(f_0 f_0)$, $(g_0 g_0)$, etc., which were

not investigated here, are expected to contribute at most one or two in the fourth decimal place. Further minor contributions, of course, will come from including more (ss) and (sd_0) configurations.

On the basis of the above, and on other considerations, we have estimated that with an expansion of 50 axially symmetric configurations and with a more judicious choice of the scale factors the best energy obtainable would be about -1.1540 a.u., which means an error of about 0.1 electron volt. The work required to achieve such an accuracy would, however, be considerable.

There is good reason to believe that almost all of the remaining angular correlation could be accounted for by inclusion of angular terms such as (d_1d_{-1}) and (d_2d_{-2}). Convergence problems such as those affecting the axially symmetric part of the wave function are not expected to be important here. It is interesting to note that the angular correlation in hydrogen is almost two-thirds of the angular correlation in the helium atom, which is -0.02474 a.u. according to Löwdin and Shull (23).

The slow convergence which characterizes our one-center expansions is attributable essentially to the fact that it is extremely difficult to represent the wave function accurately in the immediate region of the nuclei with only a limited number of terms in the expansion. The

actual wave function is "peaked" at the nucleus, while the one-center wave function is rounded there. One may attempt to argue that this is not too great an objection since, as has been shown by Eckart (42), if the energy error is small, the error in the wave function itself will be of the order of the square root of the error in the energy. One may further attempt to argue that the portion of configuration space around the nuclei is such a small part of the whole that the error must be negligible. A direct estimate of this effect may be found from the work of Gurnee and Magee (43). These investigators used a wave function of the Heitler-London type, but offset the orbital centers a distance x from the nuclei. Thus, they wrote the wave function (not normalized);

$$\Psi(r_1, r_2) = 1s'_a(1)1s'_b(2) + 1s'_a(2)1s'_b(1), \quad (3.53)$$

where $1s'_a$ represents a $1s$ atomic orbital, not at the nucleus a , but displaced a distance x away from nucleus a toward nucleus b . When the energy was minimized with respect to both the scale factor and the distance, a total energy of -1.152 a.u. was obtained for an internuclear distance of 1.45 a.u. These off-center orbitals, of course, do not "fit" the wave function at the nucleus. Hence, the energy value provided by this calculation represents a lower

limit to the maximum energy attainable using wave functions which do not "fit" at the nucleus. Although the Gurnee-Magee result is remarkably good considering the simple nature of the wave function, the energy error for this function is by no means negligible. We notice that our estimated result for just the axially symmetric terms is slightly better than the Gurnee-Magee result.

Throughout our calculation the internuclear distance was held fixed at 1.4 a.u. It is easy to show that a small change in this distance will not affect the energy appreciably and will in general not account for the observed energy discrepancy. Consider the following qualitative argument. In the region of the equilibrium internuclear distance the potential energy curve is given by $E = \frac{1}{2}kx^2$, where x is the displacement from the equilibrium position and $k = 4\pi^2 m \nu^2$ is the force constant for the vibration of a particle of mass m with a frequency of ν . If we assume that the one-center method is capable of giving the vibrational frequency of hydrogen (4395 cm^{-1}) to within 30 per cent either way of its actual value, then, for a displacement of $x = 0.2$ a.u., for $\nu = 5500 \text{ cm}^{-1}$, $E = 0.0029$, while for $\nu = 3000 \text{ cm}^{-1}$, $E = 0.0008$. Hence we see that even a displacement of 0.2 a.u. would account for at most only fifty per cent of the observed energy discrepancy.

Once we fully realized that an adequate representation

of the axially symmetric part of our one-center function could not be made in terms of (ss) , (sd_0) , (sg_0) , and (p_0p_0) terms only, we decided to investigate the convergence properties of expansions of known wave functions for H_2 in terms of our one-center orbitals. In this way we hoped to gain some idea of the overall rate of convergence of a one-center expansion as well as determine the importance to the final energy of terms occurring in the wave function with only very small coefficients.

The function expanded was the Gurnee and Magee function (3.53). Five s , four p_0 , four d_0 , one f_0 , and one g_0 Laguerre function were used, for which the parameters were $z_sR=z_pR=z_fR=2.0$, $z_dR=4.0$, and $z_gR=8.0$. In order to expand (3.53) we first expanded a single $1s'_a$ orbital with the scale factor $z=1.185$ and located a distance 0.69 a.u. along the bond axis from the expansion center. The internuclear distance was taken as 1.40 a.u. With these values of the parameters, (3.53) gives an energy of -1.151 a.u. according to the data of Gurnee and Magee. The expansion is straightforward. Thus,

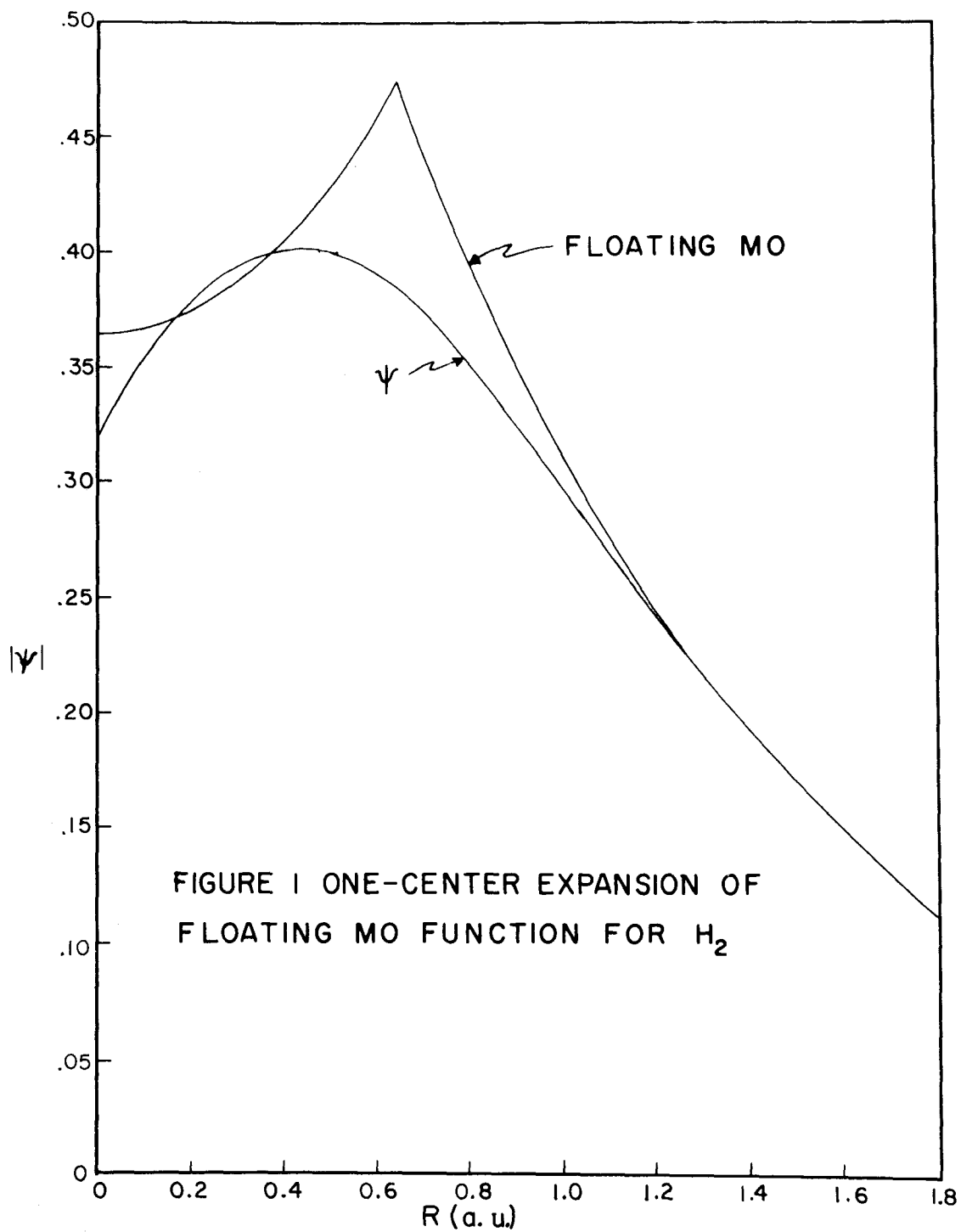
$$1s'_a = \sum_{n,q} S(nq) \phi_{nq0}^z$$

$$S(nq) = \int 1s'_a \phi_{nq0}^z dv = \sum_{i=0}^{n-q-1} C_i(nq) \int 1s'_a \chi_{nq0}^z dv \quad (3.54)$$

where we have expressed ϕ_{nq0}^z in terms of the normalized Slater functions using equation (3.11). The overlap integrals $S(nq)$ were evaluated in elliptical coordinates in the usual way. This expression for $1s'_a$ and a corresponding expression for $1s'_b$, but with the signs of the p_0 and f_0 terms reversed, was then inserted in (3.53) to give the final one-center expansion. In this expansion only the most important terms were retained. In the form finally adopted, the overlap with (3.53) was 0.9989. The calculated energies for this expansion at various stages of truncation were: $15(ss)$, -1.0325 (-1.0438), $15(ss)+15(sd_0)$, -1.1108 (-1.1206), $15(ss)+15(sd_0)+6(p_0p_0)$, -1.1270 (-1.1361), and $15(ss)+15(sd_0)+6(p_0p_0)+5(sg_0)$, -1.1370 (-1.1462). The quantities in parentheses are the energies obtained in a one-center configuration interaction calculation using the same number and kinds of configurations, and also the same parameters. Although the expansion of (3.53) is complete to within 0.1 per cent as measured by the overlap, the computed energy is in error by 1.2 per cent.

The difficulty can be seen from Figure 1, where we compare the values along the bond axis of the floating MO $N(1s'_a+1s'_b)$ with its one-center expansion ψ . A floating MO is here a molecular orbital of the LCAO type but with the atomic orbitals allowed to "float" along the bond axis. With such an orbital Hurley (55) recently obtained essentially

Figure 1. One-center expansion of floating MO function
for H₂



the SCF energy for H_2 . The overlap of Ψ with the floating MO is 0.99982.

Following Shull and Löwdin (56,23) we have also derived the approximate natural spin orbitals for the 38-term function of Table 6. These authors have shown that the total space function

$${}^1\Psi(r_1, r_2) = \sum_{mn} C_{mn} (\phi_m \phi_n) \quad (3.55)$$

for a singlet state of a two electron system is equivalent to a quadratic form having a certain rank r and signature s and that this quadratic form can be reduced to the diagonal form

$${}^1\Psi(r_1, r_2) = \sum_k c_k (\chi_k \chi_k) \quad (3.56)$$

by a suitable nonsingular linear transformation. The rank of the quadratic form is defined as the rank of the determinant of its coefficients, $\det(C_{mn})$. The χ 's, which are given as linear combinations of the ϕ_n 's, are the so-called "natural spin orbitals" which diagonalize the first-order density matrix. The "natural expansion" (3.56) was shown to have certain properties of maximum convergency. First, the natural expansion is characterized by having the most rapid convergence of all superpositions of configurations

describing the same wave function. Second, if the natural expansion is interrupted after r terms, and then renormalized, the resulting function represents the best approximation of rank r , i.e., the function of rank r having the smallest quadratic deviation from ${}^1\Psi(r_1, r_2)$ (this is so whether the expansion (3.55) is exact or only approximate). Numbering the natural orbitals χ_k in order of decreasing values of c_k , the "best" wave function of rank r then has the form

$${}^1\Psi_r(r_1, r_2) = \frac{\sum_{k=1}^r c_k (\chi_k \chi_k)}{(\sum_{k=1}^r c_k^2)^{\frac{1}{2}}} \quad (3.57)$$

where c_k^2 may be interpreted as the "occupation number" n_k of the natural orbitals χ_k . Here "best" must be interpreted as best in the sense of maximum overlap, not in the sense of energy values obtained. It was further shown that the first natural orbital χ_1 should approximate very closely the SCF function, although the two functions cannot be identical since they are obtained by linear and nonlinear processes, respectively. Calculations on He (23) indicate a close correspondence between the two functions, however.

In Table 9 we have listed the occupation numbers and the natural orbitals χ_k ($k=1, \dots, 5$) for the 38-term expansion of Table 6. The method of constructing the natural orbitals is discussed in reference (23) and will

Table 9. Natural spin orbitals for 38-term expansion in Table 6.

| Orbital | Coefficient | Coefficient | Coefficient |
|------------|-------------|-------------|-------------|
| | χ_1 | χ_3 | χ_4 |
| 1s | 0.824278 | 0.477125 | -0.129650 |
| 2s | -0.518421 | 0.517750 | 0.043830 |
| 3s | 0.172041 | -0.672546 | 0.008142 |
| 4s | -0.079177 | 0.202931 | -0.074808 |
| 5s | 0.030995 | -0.026390 | 0.050794 |
| 3d | 0.113986 | 0.036505 | 0.918838 |
| 4d | 0.032010 | 0.090161 | 0.243081 |
| 5d | 0.024336 | 0.022130 | 0.206437 |
| 5g | 0.018108 | 0.006968 | 0.155387 |
| 6g | -0.000887 | 0.008348 | -0.009240 |
| 7g | -0.002718 | 0.002411 | -0.023958 |
| 7i | 0.005573 | 0.003972 | 0.047480 |
| \sqrt{n} | 0.992944 | -0.061083 | -0.014994 |
| n | 0.985938 | 0.003731 | 0.000225 |
| | χ_2 | χ_5 | |
| 2p | 0.966503 | 0.229370 | |
| 3p | -0.254111 | 0.918208 | |
| 4p | -0.036045 | -0.322931 | |
| \sqrt{n} | -0.099564 | -0.010291 | |
| n | 0.009913 | 0.000106 | |

not be given here. Using (3.57), the energies for various combinations of the natural orbitals were then computed. The energy of χ_1^2 was found to be -1.11625 a.u., that of $(\sqrt{n_1}\chi_1^2 - \sqrt{n_2}\chi_2^2)/(n_1+n_2)^{\frac{1}{2}}$, -1.13201 a.u., that of $(\sqrt{n_1}\chi_1^2 - \sqrt{n_3}\chi_3^2)/(n_1+n_3)^{\frac{1}{2}}$, -1.13416 a.u., that of $(\sqrt{n_1}\chi_1^2 - \sqrt{n_2}\chi_2^2 - \sqrt{n_3}\chi_3^2)/(n_1+n_2+n_3)^{\frac{1}{2}}$, -1.14930 a.u. as compared with the exact value -1.15086 a.u.* The rapid convergence of the natural expansion is well illustrated by these results, particularly by the last case where, with only three terms, we have obtained essentially all of the energy. Inclusion of χ_4 and χ_5 in the natural expansion would secure virtually all of the missing energy. The remaining natural orbitals enter with such small occupation numbers as to be of negligible importance as far as the energy is concerned.

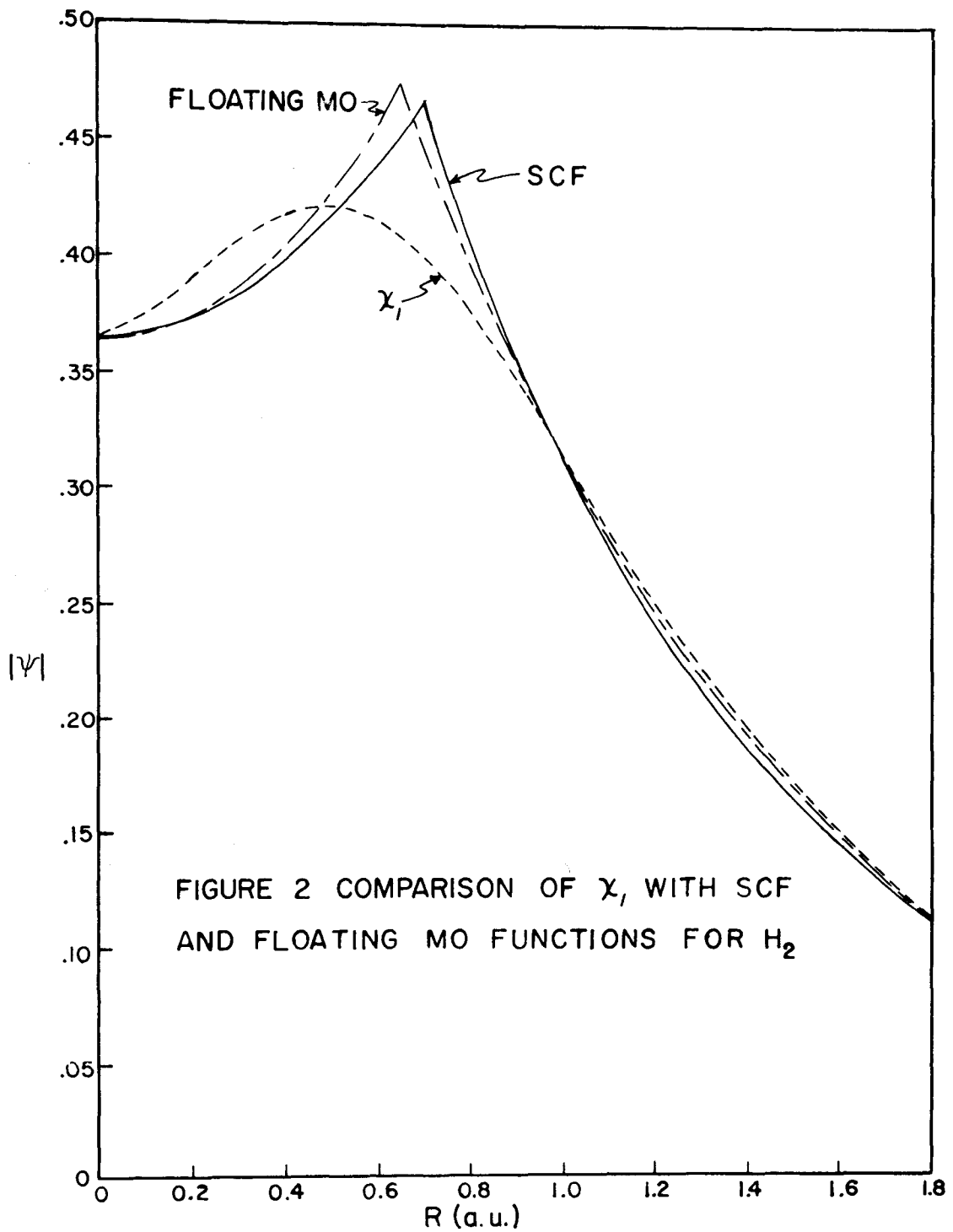
The reduction in the over-all complexity of the 38-term function provided by the natural orbitals is indeed striking. The importance of the orbitals χ_1 , χ_2 , and χ_3 in lowering the energy can be adequately rationalized in terms of electron

*In calculating these energies it was necessary to neglect those states (such as d_0d_0 , d_0g_0 , etc.) which were also neglected in the original configuration interaction, since the integrals arising from these states were not available and to have calculated them would have required a prohibitive amount of additional labor. In any case, these states are not expected to be important and the errors incurred by neglecting them will be small, probably no more than 0.002 a.u. for χ_1^2 and much less for the other expansions. From a computational point of view, then, it appears that the simplifications introduced by the natural orbitals are more apparent than real. This point does not seem to have been adequately emphasized in the literature to date.

correlation effects. A detailed discussion of electron correlation in the hydrogen molecule will not be attempted here, however, since it is a rather involved subject and would, moreover, be beside the point of the present discussion. But see Callen (53) or Lennard-Jones (57) for discussions of the relation between configuration interaction and electron correlation as they apply to the hydrogen molecule.

A comparison of χ_1 and the SCF function of Coulson discloses the essential deficiency in our one-center function. In Figure 2 we have plotted the values along the molecular axis of these two functions. The floating MO function of Figure 1 is also included for comparison sake. Although the agreement between χ_1 and the SCF function is good at large distances from the expansion center, in the region of the nuclei the agreement is especially poor. On the other hand, when the values at points along the perpendicular to the axis at the origin were compared, the agreement was found to be excellent. We note also that the energy of χ_1^2 (-1.116 a.u.) is only a poor approximation to the SCF energy (-1.134 a.u.). This disparity between χ_1 and the SCF function, which is confined predominantly to the region around the nuclei, strongly suggests that a similar discrepancy exists between the 38-term function and the true wave function since, if the one-center expansion were only complete, χ_1 would approximate the SCF function with a much greater accuracy than at present, namely, to at least as high an accuracy as the floating MO

Figure 2. Comparison of χ_1 with SCF and floating MO functions for H_2



function, which may be regarded as the first natural orbital in the reduction of the Gurnee-Magee function (3.53) to natural form.

That the observed error and slow convergence in the energy can be accounted for on this basis can be seen directly from a point by point comparison of our final one-center approximation (the 44-term function with coefficients in Table 7) with the best James and Coolidge wave function (the 13-term function given in the last column of Table II in reference (39)). Table 10 shows values of these two functions for various positions of the electrons along the bond axis (measured from nucleus a towards nucleus b). Since the estimated accuracy of the James and Coolidge function is about three per cent, the discrepancies between the two functions are a rough indication of the

Table 10. Comparison of the best James and Coolidge function with the final 44-term one-center function.

| r_{1a} | r_{2a} | One-center | James and Coolidge |
|----------|----------|------------|--------------------|
| 0.6 | 0.8 | 0.1382 | 0.1131 |
| 0.5 | 0.9 | 0.1925 | 0.1248 |
| 0.4 | 1.0 | 0.2194 | 0.1403 |
| 0.3 | 1.1 | 0.2300 | 0.1600 |
| 0.2 | 1.2 | 0.2096 | 0.1839 |
| 0.1 | 1.3 | 0.1754 | 0.2122 |
| 0.0 | 1.4 | 0.1625 | 0.2452 |

errors in our one-center function. As in the case of the first natural spin orbital, the one-center function is much too contracted, having maxima along the axis at a distance 0.4 a.u. on either side of the origin instead of at the nuclei. A comparison at points other than those on the axis indicates a close correspondence between the two functions everywhere except in the region around and between the nuclei.

Evidently, then, central field functions centered at a single point in the molecule, and in particular the Laguerre functions used in this investigation, do not form a suitable basis for accurately representing the hydrogen molecule wave function throughout all regions of the molecule, particularly in the region of the nuclei. That one-center functions can describe the over-all symmetry of the wave function rather well is shown by the rapid initial convergence. The slow subsequent convergence then simply reflects the failure of the one-center orbitals to fit the detailed form of the wave function, and it is apparently just these details of the wave function which are of importance in securing ultimate convergence in the energy.

It also seems very unlikely that the use of any other set of one-center orbitals, such as the overcomplete set of Slater functions, would secure more rapid and complete convergence in the energy.

We conclude, then, that the one-center method is not a convergent procedure for calculating the total energy of the

ground state of the hydrogen molecule. Although we have obtained an energy value for the hydrogen molecule which is second in accuracy only to that of the convergent James and Coolidge calculation, the error in the energy is still 0.013 a.u., and this is an error which is about one order of magnitude greater than that which can reasonably be tolerated for such a simple system. We further expect that the one-center method will be still less convergent when applied to other more complicated and less tightly bound hydrogenic systems. This point will now be considered more fully, using H_3^+ as an example.

IV. ONE-CENTER CALCULATION FOR THE H_3^+ MOLECULE ION

A. Introduction

The triatomic hydrogen molecule ion, H_3^+ , is known to be a very stable system (when left to itself) and is formed in rather large quantities whenever hydrogen gas is ionized (58,59). Experimentally very little is known about this system. There is reason to believe, however, that the primary process responsible for the formation of H_3^+ is



Experiments tell us no more as to the energy, spectrum, or chemistry of H_3^+ .

The first calculations for this system were made some time ago by Coulson (60) and by Massey (61). Later, Hirschfelder, Eyring, and Rosen (10) applied the valence bond method to the symmetrical linear configuration. Using 1s hydrogen-like atomic orbitals, with screening included, these authors carried out a complete Heitler-London-plus-ionic-terms variational calculation. All integrals were evaluated exactly. The energy values obtained for the various stages in the calculation are given in Table 11. Recent attempts (62) to improve this calculation by introducing off-center Gurnee-Magee orbitals resulted in only

Table 11. Some previous investigations of the wave function and binding energy of H_3^+

| Description of wave function | Binding energy (a.u.) | Reference |
|---|-----------------------|-----------|
| Symmetrical linear. $R=r_{ac}=r_{bc}$ | | |
| H-L, $R=2.0$ | 0.146 | 10 |
| H-L, screening, $R=1.55$ | 0.2086 | 10 |
| H-L, plus ionic, $R=2.0$ | 0.1731 | 10 |
| H-L plus ionic, screening, $R=1.53$ | 0.2477 | 10 |
| H-L plus ionic, Gurnee and Magee orbitals, screening, $R=1.60$ | 0.2528 | 62 |
| MO, one configuration, screening, $R=1.52$ | 0.2180 | 67 |
| Handler, one-center, $R=1.55$ | 0.163 | 2 |
| Hagstrom, one-center, ss, sd_{σ} , sg_{σ} , and $p_{\sigma}p_{\sigma}$ configurations, $R=1.50$ | 0.230 | |
| Unsymmetrical linear | | |
| H-L plus ionic, screening, $r_{ac}=1.55$, $r_{bc}=1.89$ | 0.2406 | 63 |
| H-L plus ionic, screening, $r_{ac}=1.15$, $r_{bc}=1.92$ | 0.2069 | 63 |
| Equilateral triangle | | |
| H-L, screening, $R=1.82$ | 0.2858 | 11 |
| MO, one configuration, screening, $R=1.82$ | 0.2623 | 11 |
| MO, two configurations, screening, $R=1.82$. Equivalent to H-L plus ionic | 0.2929 | 11 |
| Handler, one-center, $R=1.56$ | 0.204 | 2 |
| Hagstrom, one-center, (ss) only, $R=1.6$ | 0.170 | |

negligible improvement, while calculations (63,64) on the unsymmetrical linear configurations indicated that the potential curve for linear H_3^+ has a minimum for the symmetrical configuration.

Calculations have also been carried out by Hirschfelder (11,65) for the ground and excited states of two non-linear configurations of H_3^+ , namely, the equilateral triangle configuration and a right triangular form. In this case it was necessary to resort to a differential analyzer to evaluate the three-center integrals. Only 1s functions were considered. The equilateral triangle configuration was found to be stable by -0.293 a.u. or 184 kcal with respect to dissociation into hydrogen atoms and a proton. Hence we see that the process (4.1) is certainly exothermic by more than 11 kcal (the values for the binding energies of H_2 and H_2^+ are 108.6 kcal and 64.0 kcal respectively) and, allowing for the customary errors in the valence bond treatment, was estimated by Hirschfelder to be exothermic by as much as 38 kcal.

A comparison of the results for the right triangle and equilateral triangle configurations led Hirschfelder to conclude that the equilibrium configuration must lie somewhere in between. Since it was necessary to approximate some of the three-center integrals, the angle could not be reliably determined more closely than this. This result probably should not be taken too seriously, however.

Pearson (66) and recently Walsh, Moore, and Matsen (67) have applied the molecular orbital method to the symmetrical linear configuration of H_3^+ . In general, the results are superior to the simple Heitler-London approximation, but inferior to the Heitler-London-plus-ionic-terms treatment.

As has already been pointed out, Handler (2) used the one-center method to calculate the ground state energies for symmetrical linear and equilateral triangular H_3^+ . The results obtained are given in Table 11.

B. The Variational Problem

One-center calculations were carried out on both the symmetrical linear and equilateral triangular forms of H_3^+ . Except for minor details, calculations proceed much like those for H_2 . The Hamiltonian for H_3^+ is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 1/r_{a1} - 1/r_{b1} - 1/r_{c1} \\ - 1/r_{a2} - 1/r_{b2} - 1/r_{c2} + 1/r_{12} \quad (4.2)$$

where a, b, and c denote the three hydrogen nuclei. For linear symmetrical H_3^+ , the polar axis was located along the bond axis with the central nucleus at the center of coordinates. For the equilateral triangular case, the plane of the molecule was perpendicular to the polar axis, with the

center of symmetry of the molecule at the center of coordinates.

Linear symmetrical H_3^+ belongs to $D_{\infty h}$. The ground state wave function was assumed to have the symmetry $1 \sum_g^+$. Hence, the same kinds of configurations used for H_2 can also be used for H_3^+ . Moreover, the relative importance of the various terms is expected to be approximately the same, since exactly the same kinds of electron correlation effects enter. However, the higher spherical harmonics (i.e., sg_0 , si_0 , etc.) are expected to be more important since in this case the distances of the nuclei from the expansion center are considerably greater than for H_2 .

Equilateral triangular H_3^+ has the symmetry D_{3h} . Symmetry adapted wave functions are easily constructed by group theoretic methods. We shall not discuss these methods here, however, since for this case we have carried out the configuration interaction only in the spherically averaged approximation, that is, with (ss) terms only.

The energy matrix elements are given by equations (3.22) and (3.23) except that H_1 is now given by:

$$\text{For linear } H_3^+, H_1 = -\frac{1}{2} \nabla_1^2 - 2/r_{1a} - 1/r_1$$

$$\text{For triangular } H_3^+, H_1 = -\frac{1}{2} \nabla_1^2 - 1/r_{1a} - 1/r_{1b} - 1/r_{1c}. \quad (4.3)$$

These changes necessitated only a slight modification in the matrix element compiling routine.

The only new integrals required for the calculations on H_3^+ were the nuclear attraction integrals. The electron repulsion integrals used were already available from the H_2 calculations.

C. Results and Discussion

In Table 12 we list in part the results of the calculations for linear symmetrical H_3^+ . Both the internuclear

Table 12. One-center expansion of linear symmetrical H_3^+ .
Parameter values: $z_s=z_p=z_d=z_g=2.086666$.
Internuclear distances: $R_{ac}=R_{bc}=1.5$ a.u.

| Description of Function | Binding Energy (a.u.) |
|---|-----------------------|
| 10(ss) | 0.07389 |
| 10(ss), 9(sd ₀) | 0.18286 |
| 15(ss), 15(sd ₀) | 0.18324 |
| 10(ss), 9(sd ₀), 9(sg ₀) | 0.20929 |
| 10(ss), 9(sd ₀), 6(p ₀ p ₀) | 0.20243 |
| 10(ss), 9(sd ₀), 9(sg ₀), 6(p ₀ p ₀) | 0.230 ^a |

^a Estimated value assuming additivity of (sg₀) and (p₀p₀) contributions.

distances and scale factors were varied to minimize the energy.

Calculations were carried out at internuclear distances of 1.5, 1.525, and 1.55 a.u. using 10 (ss), 9 (sd_0), and 9 (sg_0) configurations. The minimum in the energy was found for an internuclear distance close to 1.5 a.u. The data given in Table 12 are for this distance and for the corresponding best values of the various scale factors as determined by the configuration interaction. The optimum values of these parameters were determined by the usual stepwise procedure, that is, by minimizing first with respect to z_s for 10 (ss) states and then, with z_s held fixed at its optimum value, adding 9 (sd_0) states and minimizing the energy with respect to z_d , and so on for each new type of state added.

The results of these calculations speak pretty much for themselves. We see that with only four types of states we have obtained a binding energy of 0.230 a.u., which is better than all previous results (Table 11) for this system except those of Hirschfelder et al. (10) (0.2477 a.u.) using the Heitler-London method with ionic terms and screening included and Barker et al. (62) (0.2528 a.u.) using the off-center Gurnee-Magee orbitals. This latter calculation represents the best approximation to date for this system. We note that the one-center result of Handler using 3 (ss) and 3 (sd_0) terms

is only 0.163 a.u., while the best result obtained here for terms of this type is 0.18286 a.u.

The convergence of the expansion is manifestly slower than for H_2 as can be seen from a comparison of the energy contributions in H_2 and H_3^+ for corresponding types of terms. Thus in H_3^+ the energy contributions due to (sd_0) , (sg_0) , and (p_0p_0) states are seen to be -0.1095 a.u., -0.0260 a.u., and -0.0196 a.u., respectively. The corresponding best values for these states in H_2 are -0.0779 a.u., -0.0104 a.u., and -0.0160 a.u., respectively. This implies that more configurations will be required to obtain a good energy for H_3^+ than are correspondingly required for H_2 . This slow convergence is due essentially to the fact that in H_3^+ the charge distribution is much more elongated than in H_2 so that in expanding the wave function the axially symmetric terms, especially those involving the higher spherical harmonics (e.g., g_0 , i_0 , l_0 , etc.), assume a correspondingly more important role, that is, enter into the wave function with larger coefficients which in turn implies a greater contribution to the final energy.

These results indicate the necessity of including such states as (si_0) , (sl_0) , etc., as well as the angle-dependent terms (p_1p_{-1}) , (d_1d_{-1}) , etc. We can easily estimate what can be gained in this way, reasoning by analogy from the contributions found for terms of these types in H_2 and assuming anywhere from a two to a four times increase in importance for

the axially symmetric terms. On the other hand, terms with angular dependence such as $(p_1 p_{-1})$ are expected to be less important in H_3^+ than in H_2 . This follows from the fact that the total angular correlation energy steadily decreases as one goes from He to H_2 to H_3^+ (and, in fact, for H_3^+ should approach zero as $R_{ac} = R_{bc}$ approaches infinity). Thus, we estimate the total energy to be gained from adding $(p_1 p_{-1})$, $(d_1 d_{-1})$, etc., terms at about -0.010 a.u., while the contributions due to axially symmetric terms are variously estimated at about -0.008 a.u. for (s_{i_0}) terms, about -0.002 a.u. for (s_{l_0}) terms, and about -0.005 a.u. for miscellaneous terms. Although these estimates are admittedly rather arbitrary, they are certainly not unreasonable. Adding these estimates to the calculated binding energy of 0.230 a.u., and allowing for a spread of 0.005 a.u. either way, leads to an estimated binding energy of 0.255 ± 0.005 a.u. It seems safe to assume, then, that the Hirschfelder et al. (10) result (0.2477 a.u.) can probably be reached with axially symmetric terms only and that inclusion of terms with angular dependence as well will give a result as good as or slightly better than the Barker et al. (62) result (0.2528 a.u.).

Calculations are presently in progress to check this point.

The calculations on the equilateral triangle configuration of H_3^+ were carried out in the spherically averaged approximation only (Table 13). Despite their rather

Table 13. Binding energy of the equilateral triangle configuration of H_3^+ using 6 (ss) configurations. Energies in atomic units.

| R 1.386 a.u. | | R 1.732 a.u. | | R 2.078 a.u. | |
|--------------|--------|--------------|--------|--------------|--------|
| z_s | E | z_s | E | z_s | E |
| 1.5 | 0.1518 | 1.4 | 0.1556 | 1.375 | 0.1112 |
| 1.875 | 0.1567 | 1.8 | 0.1571 | 1.667 | 0.1142 |
| 2.375 | 0.1569 | 2.2 | 0.1590 | 2.083 | 0.1139 |
| 2.875 | 0.1172 | 2.6 | 0.1147 | | |

incomplete form, the results are presented here because of their promising nature. A simple interpolation of this data indicates that the minimum in the energy occurs for an internuclear separation of about 1.6 a.u. A single calculation at this distance using 15 (ss) configurations gave a binding energy of 0.170 a.u. Thus, with (ss) terms alone the system is found to be almost stable with respect to dissociation into a hydrogen molecule and a proton. Although this binding energy is not as high as even the simple Heitler-London without screening result, it is promising that considerable binding is obtained with these relatively inappropriate spherical orbitals. It seems likely that the one center method will be highly successful for the triangular configuration of H_3^+ .

In conclusion, these preliminary results for H_3^+ along with the more detailed results for H_2 , give encouragement that for a very limited class of molecules the one-center method will be a useful and successful procedure capable of giving results comparable in accuracy to those obtained using the conventional approximation methods based on atomic orbitals. On the other hand, the observed slow convergence and, in the case of H_2 , the behavior of the wave function clearly indicates that highly accurate (convergent) calculations of total energies are not at all feasible by this method.

The present calculations, of course, should be regarded as only a rough indication of the realm of applicability of the method. Further calculations on systems with three and four electrons, systems with low symmetry, and systems with larger internuclear separations are needed before the convergence properties of the one-center expansions can be claimed to be completely understood. Nevertheless, it is suggested that the following systems can be successfully handled by this method: H_2^+ , H_2 , H_3^+ , H_3 , and possibly LiH , HeH^+ , and HeH . Extension to more complicated cases (e.g., H_2O , He_2 , etc.) involving inner shell electrons off the expansion center and/or more than four electrons does not seem to be practical.

D. Other Possible Applications

Excited states can be attacked by the same general pro-

cedures outlined above for the ground states. If the excited state is the lowest state of its symmetry type, the calculation is straight forward and proceeds exactly as for the ground state, only now the expansion terms must have the symmetry of the excited state. If the excited state is not the lowest of a given symmetry type, one makes use of the fact that the second lowest root of the secular equation is an upper limit for the energy of the second lowest state of the given symmetry, and so on for the higher roots. Thus, by minimizing the higher roots of the secular equation one may hope to gain approximations to the energies, eigenfunctions, and potential surfaces for the excited states.

Of course, this may demand the use of more terms than are required for the ground state. In addition, the parameters which minimize a particular higher root will in general not be the same as those that minimize the lower roots of the secular equation so that the eigenfunction of the excited state will not be orthogonal to the eigenfunctions for all lower levels as, of course, it should be. This may not be too big an objection, however, if one is interested only in the energies.

Matsen (8) has carried out single configuration one-center calculations for several of the excited states of H_2^+ and has obtained surprisingly good results even for fairly large internuclear separations. In a recent note, Dalgarno, Moiseiwitsch, and Stewart (68) have summarized the main con-

clusions of a series of investigations on H_2^+ and HeH^{++} comparing the one-center (united-atom) approach with the conventional LCAO MO method. Generally speaking, it was found that for excited states the united-atom approximation was remarkably accurate and usually superior to the LCAO MO approximation even for R values as large as 5 a.u., while for the ground states the LCAO MO approximation was superior. In view of these results it would appear that the one-center method will be highly successful for excited states, indeed, probably much more so than for the ground state.

Some preliminary work on excited $^1\Sigma_g^+$ states of H_2 has been done in the course of the present investigation. The results, although generally quite encouraging, are quite incomplete and will therefore not be elaborated on further here.

V. SUMMARY

The use of the one-center method for the direct calculation of total energies of simple molecules has been investigated and application has been made to H_2 and H_3^+ . The results obtained are comparable in accuracy to those obtained with the conventional methods involving the use of atomic orbitals and suggest that extensions to more complex cases (such as H_3 or LiH) are probably possible and well within the reach of computing machines now available. In the case of H_2 the calculated energy is -1.161 a.u. for $R=1.4$ a.u. This is the second best result for this system to date.

Generally speaking, the convergence of the one-center expansion is slow. In view of this slow convergence and from a detailed examination of the calculated wave function in the case of H_2 it is concluded that highly accurate (convergent) calculations are not feasible by this method. Moreover, as shown by the H_3^+ results, the convergence becomes slower as the internuclear separations become larger. The various factors affecting the convergence have been considered in detail.

A one-center calculation on H_2 previously advanced by Huzinaga as support for the one-center approach has been shown to be in error.

The programs constructed for the IBM 650 computer for carrying out the various computational processes in the one-center calculations have been briefly described.

VI. REFERENCES

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VIII. APPENDICES

A. The Associated Laguerre Polynomials

The associated Laguerre polynomial $L_k^n(x)$ is defined by means of the generating function

$$\frac{(-1)^n e^{-xt}/(1-t)}{(1-t)^{n+1}} t^n = \sum_{k=n}^{\infty} L_k^n(x) \frac{t^k}{k!} \quad (8.1)$$

or through the Laguerre polynomials $L_k(x)$

$$L_k^n(x) = \frac{d^n}{dx^n} L_k(x) = \frac{d^n}{dx^n} \left(e^x \frac{d^k}{dx^k} (e^{-x} x^k) \right). \quad (8.2)$$

An explicit series expansion for $L_k^n(x)$ is

$$\begin{aligned} L_k^n(x) &= \frac{(-1)^n (k!)^2}{n! (k-n)!} {}_1F_1(-k+n; n+1; x), \quad k \geq n \\ &= \frac{(-1)^n k!}{(k-n)!} \sum_{i=0}^{k-n} \frac{k! (k-n)!}{(k-n-1)! (n+1)! i!} (-x)^i \end{aligned} \quad (8.3)$$

where ${}_1F_1(m; n; x)$ is the confluent hypergeometric function (see Sneddon (34, p. 32) for notation and definitions).

This series expansion is probably the most convenient way of obtaining the higher order functions. The polynomial

$y=L_k^n(x)$ satisfies the differential equation*

$$xy'' + (n+1-x)y' + (k-n)y = 0 \quad (8.4)$$

and the recurrence relations

$$\frac{d}{dx} L_k^n(x) = L_k^{n+1}(x) \quad (8.5)$$

$$\frac{(k-n+1)}{(k+1)} L_{k+1}^n(x) + (x+n-2k-1) L_k^n(x) + k^2 L_{k-1}^n(x) = 0 \quad (8.6)$$

$$L_k^{n+1}(x) = (1/x) [(k-n) L_k^n(x) - k^2 L_{k-1}^n(x)]. \quad (8.7)$$

Also, the polynomial $L_k^n(x)$ satisfies the orthogonality integral

$$\int_0^\infty e^{-x} x^n L_k^n(x) L_m^n(x) dx = \frac{(k!)^3}{(k-n)!} \delta(k,m) \quad (8.8)$$

*A word of caution is in order here. The definition (8.1) or (8.3) for the associated Laguerre polynomials is the one usually taken in applied mathematics. In pure mathematics the function

$$L_k^n(x) = \frac{(n+k)!}{k!n!} {}_1F_1(-k; n+1; x)$$

which is the solution of the differential equation

$$xy'' + (n+1-x)y' + ky = 0$$

is often taken as the definition of the associated Laguerre polynomial so that care must be taken in reading the literature.

Equation (8.8) is a special case of a more general formula first derived by Schrodinger (69)

$$\int_0^{\infty} x^p e^{-x} L_k^n(x) L_{k'}^{n'}(x) dx = p!k!k'! \sum_{r=0}^b (-1)^{k+k'} \binom{p-n}{k-n-r} \times \binom{p-n'}{k'-n'-r} \binom{p+r}{r} \quad (8.9)$$

Here b is the smaller of the two integers $(k-n)$ and $(k'-n')$, and the parentheses symbols denote binomial coefficients.

B. Derivation of Equation (3.44)

The one-center nuclear attraction integral between the Laguerre functions is given by (for convenience we let $n \leq n'$)

$$(\phi_{nqm}^z | -1/r | \phi_{n'q'm'}^{z'}) = -2z \delta(m, m') \delta(q, q')$$

$$x \left\{ \frac{(n-q-1)!(n'-q-1)!}{(n+q+1)!(n'+q+1)!} \right\}^{\frac{1}{2}} \int_0^{\infty} e^{-x} x^{2q+1} L_{n+q+1}^{2q+2}(x) L_{n'+q+1}^{2q+2}(x) dx \quad (8.10)$$

where we have used the change of variable $2zr=x$. The integral on the right side of (8.10) is easily evaluated using (8.9). We obtain

$$(2q+1)!(n+q+1)!(n'+q+1)! \sum_{r=0}^{n-q-1} (-1)^{n+n'} \binom{-1}{n-q-1-r} \\ \times \binom{-1}{n'-q-1-r} \binom{2q+1+r}{r} \quad (8.11)$$

$$= (n+q+1)!(n'+q+1)! \sum_{r=0}^{n-q-1} (2q+1+r)!/r! \quad (8.12)$$

$$= \frac{(n+q+1)!^2 (n'+q+1)!}{(n-q-1)!(2q+2)} \quad (8.13)$$

where we have used the relation (32, p. 586)

$$\binom{-n}{k} = (-1)^k \binom{n+k-1}{k} \quad (8.14)$$

in going from (8.11) to (8.12). The summation in (8.12) is a particular case of

$$\sum_{r=0}^b (c+r)!/r! = \frac{(c+b+1)!}{b!(c+1)} \quad (8.15)$$

Substituting (8.13) back into (8.10), we obtain (3.44), which is the desired result.

C. Derivation of Equation (3.43)

The kinetic energy integral between the Laguerre functions is given by

$$(\phi_{nqm}^z | -\frac{1}{2} \nabla^2 | \phi_{n'q'm'}^{z'}) = \delta(m, m') \delta(q, q') (1/4z)$$

$$\left\{ \frac{(n-q-1)!(n'-q-1)!}{(n+q+1)!^3(n'+q+1)!^3} \right\}^{\frac{1}{2}} \int_0^\infty dx x^2 e^{-\frac{1}{2}x} x^q L_{n+q+1}^{2q+2}(x) \\ \times \left\{ -\frac{1}{x^2} \frac{d}{dx} x^2 \frac{d}{dx} + \frac{q(q+1)}{x^2} \right\} x^q e^{-\frac{1}{2}x} L_{n'+q+1}^{2q+2}(x) \quad (8.16)$$

where $x=2zr$. Carrying out the differentiation, eliminating the second derivative using (8.4), and regrouping, we get

$$(1/2z) \left\{ \frac{(n-q-1)!(n'-q-1)!}{(n+q+1)!^3(n'+q+1)!^3} \right\}^{\frac{1}{2}} (A + nB - C/4) \quad (8.17)$$

where

$$A = \int_0^\infty e^{-x} x^{2q+1} L_{n+q+1}^{2q+2}(x) L_{n'+q+1}^{2q+3}(x) dx \quad (8.18)$$

$$B = \int_0^\infty e^{-x} x^{2q+1} L_{n+q+1}^{2q+2}(x) L_{n'+q+1}^{2q+2}(x) dx \quad (8.19)$$

$$C = \int_0^\infty e^{-x} x^{2q+2} L_{n+q+1}^{2q+2}(x) L_{n'+q+1}^{2q+2}(x) dx \quad (8.20)$$

The integral C is given by the orthogonality integral (8.8) while B is just the one-center nuclear attraction integral (8.10), except for a constant factor, and is given by (8.13). As before, A is evaluated using (8.9), and is

$$A = -(2q+1)!(n+q+1)!(n'+q+1)! \left[\delta(n, n') \sum_{r=0}^{n-q-2} (n-q-1-r) \right. \\ \left. x \binom{2q+1+r}{r} + \sum_{r=0}^{n-q-1} (n'-q-1-r) \binom{2q+1+r}{r} \right] \quad (8.21)$$

$n \quad n'$

where, in the brackets, the first term is used when $n=n'$ and the second term is used when $n < n'$. The sums are easily evaluated using (8.15) to give

$$A = - \frac{(n+q+1)!(n'+q+1)!}{(n-q-1)!} \left[\frac{(n'-q-1)}{2q+2} - \frac{(n-q-1)}{2q+3} \right], \quad n < n'. \quad (8.22)$$

Substituting the values of A, B, and C into (8.16) and collecting terms, we obtain (3.43), which is the desired result.

D. The Auxiliary Functions

1. The auxiliary functions A(n,q) and D(n,q)

The A(n,q) are defined by

$$A(n, q) = \int_1^{\infty} r^n e^{-qr} dr = n! e^{-q} / q^{n+1} \sum_{k=0}^n q^k / k! \quad (8.23)$$

They are most easily calculated by means of the recursion

relations

$$A(n, q) = q^{-1} (nA(n-1, q) + e^{-q}) \quad (8.24)$$

$$A(0, q) = e^{-q}/q \quad (8.25)$$

Rather extensive tabulations of these functions have been published (70), but these tables are of practical use only in hand calculations since the machine calculation based on (8.24) is an extremely efficient procedure, especially if the $A(n, q)$ for a range $n=0(1)N$ are required. On the other hand, if a particular $A(n, q)$ is required, equation (8.23) should probably be used. In either case, floating point arithmetic must be used because of the wide variation in the value of $A(n, q)$ with n .

The $D(n, q)$ are defined by

$$\begin{aligned} D(n, q) &= \int_0^1 r^n e^{-qr} dr = (n+1)^{-1} e^{-q} {}_1F_1(1; n+2; q) \\ &= (n+1)^{-1} e^{-q} \sum_{r=0}^{\infty} \frac{(n+1)!}{(n+1+r)!} q^r \end{aligned} \quad (8.26)$$

They are related to the $A(n, q)$ by the relation

$$A(n, q) = n!/q^{n+1} - D(n, q) \quad (8.27)$$

but this relation obviously cannot be used to get the $D(n, q)$

since, for $n > q$, $A(n, q)$ behaves like $n!/q^{n+1}$. Rather, given the $D(n, q)$, equation (8.27) is a convenient method for calculating the $A(n, q)$. A recursion scheme for generating these functions is provided by (8.26) followed by repeated application of the downward recursion relation

$$D(n-1, q) = n^{-1}(qD(n, q) + e^{-q}) \quad (8.28)$$

The upward recursion rapidly loses significant figures and cannot be used if n is large (say 10) without carrying a prohibitive number of figures. We observe that $D(n, q) < 1$, and hence fixed point arithmetic can easily be applied with a minimum of scaling difficulties.

For individual computations of $D(n, q)$ with $|q| \leq n \leq 3/4$, ${}_1F_1(1; n+2; q)$ can be evaluated in terms of rapidly converging continued fractions (71, 72). Otherwise, the series development (8.26) should be used. In this case, the magnitude of every term beyond the first is less than one, facilitating the use of fixed point arithmetic.

The $D(n, q)$ occur not only in the two-center nuclear attraction integral, but also can be used to express the Kotani $B_n(q)$ function

$$B_n(q) = \int_{-1}^1 t^n e^{-qt} dt = D(n, q) + (-1)^n D(n, -q) \quad (8.29)$$

This formulation is preferable to the traditional method

of computation which rapidly loses digits. See, however, reference (73) for an alternative convergent method of computing the $B_n(q)$.

2. The auxiliary function $J(m, \alpha; n, \beta)$

The functions $J(m, \alpha; n, \beta)$ defined by (3.27) are most easily calculated by means of the recursion relations

$$J(0, \alpha; n, \beta) = n! / \alpha(\alpha + \beta)^{n+1} \quad (8.30)$$

$$J(0, \alpha; n+1, \beta) = \frac{n+1}{(\alpha + \beta)} J(0, \alpha; n, \beta) \quad (8.31)$$

$$\begin{aligned} J(m, \alpha; n, \beta) &= \frac{m}{\alpha} J(m-1, \alpha; n, \beta) + (m+n)! / (\alpha + \beta)^{n+m+1} \alpha \\ &= \frac{m}{\alpha} J(m-1, \alpha; n, \beta) + J(0, \alpha; n+m, \beta) \end{aligned} \quad (8.32)$$

$$J(m, \alpha; n, \beta) = \frac{n}{\beta} J(m, \alpha; n-1, \beta) - (\alpha/\beta) J(0, \alpha; n+m, \beta) \quad (8.33)$$

With these three relations it is always possible to recur in such a way that all terms enter positively. The most efficient scheme for either hand or machine calculation is as follows:

Suppose we require $J(m, \alpha; n, \beta)$ for all $m_1 \leq m \leq m_2$, $n_1 \leq n \leq n_2$. First, compute $J(0, \alpha; N, \beta)$ for $N=0, 1, \dots, n_2+m_2$ using (8.30) and (8.31). Next, calculate $J(m, \alpha; n_2, \beta)$ ($m=1, 2, \dots$,

m_2) using equation (8.32). Finally, equation (8.33) is used to calculate $J(m, \alpha; n, \beta)$ for $n=n_2, n_2-1, \dots, n_1$ for each value of m in the interval (m_1, m_2) .