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Theoretical analysis of chemical binding in homonuclear diatomic molecules

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THEORETICAL ANALYSIS OF CHEMICAL BINDING
IN HOMONUCLEAR DIATOMIC MOLECULES

by

Rolland Ray Rue

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INTRODUCTION

The last decade has witnessed the emergence of the so-called ab initio calculations for molecules other than hydrogen¹. This somewhat weighty label refers to the fact that, by overcoming a series of mathematical difficulties (4, 5, 6, 7 and 8), it has been possible to solve the electronic Schroedinger equation of such systems by sequences of successive approximations which are completely and unambiguously characterized as regards 1) the mathematical nature of the process of solution, 2) the mathematical validity of all approximations involved, and 3) the mathematical accuracy of the resulting wave functions and energies.

This emphasis contrasts with the majority of previous approaches in which physical and chemical arguments were extensively used to postulate and substitute simple over-all results for the more complicated parts of the quantum mechanical calculations². While it might be intriguing to speculate over the psychological reasons for this shift in attitude, it cannot be denied that the advent of high-speed computers has been a conditio sine qua non for the success of the more mathematically oriented work. For this reason, it can be expected to

¹See, for example, papers presented at the Conference on Molecular Quantum Mechanics held at the University of Colorado in June, 1959 (1). See also the bibliographies (2) and (3).

²The indicated differences in philosophy of the two approaches are reflected in some remarks by Coulson (9).

grow in quantity as well as quality.

It would be a mistake to draw from this development the conclusion that intuitive concepts must be sacrificed. But the progress does make it likely that previously available intuitive interpretations may not have been adequate to cope with the full complexity of the problem. Starting from this premise, Ruedenberg (10) has recently suggested that a suitable analysis of the more mathematically reliable solutions may lead to an improved and more complete set of interpretative concepts which, in fact, may be closer to molecular reality. As a first step towards the implementation of such a program, he has proposed an analysis based upon a partitioning of the molecular binding energy which is derived from a partitioning of the electronic density and pairdensity.

Execution of the proposed analysis for specific molecules and, preferably, series of molecules, is required in order to assess the efficacy of the scheme. It is hoped that, at least in part, such applications will be successful in crystallizing conceptual interpretations which correctly reflect those features of the actual electronic distributions which are pertinent to the binding process. On the other hand, it is expected that they will also expose deficiencies and indicate necessary improvements in the formulation of the method.

An analysis of the hydrogen molecule ion (11) has led to the conclusion that chemical binding is the result of a little-noticed interplay between the kinetic and potential energy

which can be formulated in terms of inter-atomic constructive interference and intra-atomic contractive promotion.

The same energetic interpretation appears in an investigation of the hydrogen molecule (10). Here it was found, moreover, that in an electron-pair bond, interference resulting from the sharing of electrons between atoms is partially offset by an increase in electron repulsion associated with electron sharing, an effect which was called sharing penetration.

An application to the water molecule (12) yielded additional information as regards the relation between destructive interference and anti-binding and non-bonded repulsions, as well as the effects of charge transfer.

The usefulness of the analysis, for the comparison within a series of similarly treated molecules, was tested (13) on a set of diatomic hydride calculations (14). In contrast to the water case, they also included the effect of contractive promotion which was found to be as important here as it had been for the hydrogen molecule and the hydrogen molecule ion. The increase in electronegativity was found to be reflected in charge transfer as well as in the interference energy, the latter accounting for the increase in binding energy.

The present investigation applies the analysis to the homonuclear diatomic systems Li_2 , Be_2 , C_2 , N_2 and F_2 . These molecules are simpler than the hydrides by the absence of

charge transfer, but more complicated in having two heavy atoms generating a more diverse variety of orbital interactions. For this reason, the members of the group show greater individualities which the analysis does, in fact, bring out. The calculations analyzed (14) are similar in kind to those for the hydrides and, in particular, also include contraction promotion. As in the case of the hydrides, the advantage of analyzing such a set of analogous wave functions was considered to outweigh the limitations inherent in the approximations.

The observations made in the preceding investigations are largely confirmed in the present study. The major complications arise from having the possibility of hybridization on both centers. Classifications and trends are found, but it may be that improvements in the sharing penetration part would clarify the analysis. The present approach shows that the wave functions for the homonuclear molecules leave much more to be desired than those for the hydrides and it pin-points hidden deficiencies in these wave functions.

In conclusion, it is felt that the present sequence of investigations, in answering some questions and raising others, indicates the merit of further efforts towards reconciling intuitive thinking with the information embodied in bona fide molecular wave functions.

SUMMARY OF THEORY

Basis of Analysis

The present summary of the analysis is given in order to facilitate the understanding of the discussion and interpretation of the results in the subsequent sections. The detailed theory of the analysis can be found in the original article by K. Ruedenberg (10). Further discussions and qualitative interpretations of the theory as well as the results obtained from the application to some molecular systems have been given in other reports (11, 12 and 13). The present investigation adds further interpretative details for discussing the results obtained from the analysis. In this summary, all formulas, definitions, and derivations are restricted to those which are pertinent to a SCF wave function for a homonuclear diatomic system. (See also the terminology used in Reference 15.)

The basis of the analysis is a partitioning of the electron-density-operator, ρ , and of the electron-pairdensity-operator, π , for the molecular system under consideration. Both ρ and π are calculable functions of the molecular wave function. Definitions, properties, and methods of calculation of ρ and π have been discussed in numerous articles (16, 17 and 18). In general, ρ and π are mathematical constructs found to be helpful in extracting useful information from complicated wave functions which are assumed to be suitably well defined. Methods for calculating ρ and π by an iteration

procedure rather than by first determining the wave function have also been given (19, 20 and 21) and the results are entirely equivalent.

All physically observable quantities, including the total molecular energy, are completely determined by ρ and π . Naturally, approximate wave functions can only give approximate functions for ρ and π and thus an approximate value for any calculated quantity. In the present context we are mainly concerned with the energy effects associated with the various components of ρ and π , since our objective is the analysis of the calculated molecular binding energy. This binding energy is defined to be the difference between the computed total molecular energy and the computed ground state energies of the separated atoms.

In the basis of a set of atomic orbitals $Aa(x)$, the electron density, ρ , and the electron pair density, π , can be represented by the expansion

$$\rho(x, x') = \sum_{Aa, Bb} p(Aa, Bb) Aa(x) Bb(x')$$

$$\pi(x_1, x_2) = \sum_{Aa, \bar{A}\bar{a}} \sum_{Bb, \bar{B}\bar{b}} p(Aa\bar{A}\bar{a} | Bb\bar{B}\bar{b}) Aa(x_1) \bar{A}\bar{a}(x_1) Bb(x_2) \bar{B}\bar{b}(x_2)$$

The coefficient matrices, $p(Aa, Bb)$ and $p(Aa\bar{A}\bar{a} | Bb\bar{B}\bar{b})$, are termed the bond-order matrix and the pair-bond-order matrix respectively. The total molecular energy E , which is defined by

$$E = Z_A Z_B / R + \int dV h(x) \rho(x, x') + \frac{1}{2} \int dV_1 \int dV_2 1/r_{12} \pi(x_1, x_2),$$

with

$$h(x) = -\frac{1}{2}\nabla^2(x) - Z_A/r_{Ax} - Z_B/r_{Bx} ; r_{Ax} = |x_A - x| ,$$

can therefore be expressed in the matrix form

$$E = Z_A Z_B / R + \sum_{Aa, Bb} p(Aa, Bb) [Aa|h|Bb] \\ + \frac{1}{2} \sum_{Aa, \bar{A}\bar{a}} \sum_{Bb, \bar{B}\bar{b}} p(Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b}) [Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b}]$$

where, $[Aa|h|Bb]$ are the one-electron energy integrals and $[Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b}]$ are the electron interaction integrals.

ρ and π are now partitioned into the various components which are specifically defined and discussed in the theoretical derivation of the analysis (10). They are

$$\rho(x, x') = \rho^{QC}(x, x') + \rho^I(x, x')$$

$$\pi(x_1, x_2) = \pi^{VS}(x_1, x_2) + \pi^I(x_1, x_2) \\ = \pi^{PS}(x_1, x_2) + \pi^{SP}(x_1, x_2) + \pi^I(x_1, x_2)$$

In the homonuclear case, the quasi-classical density (ρ^{QC}) is identical with the valence state density (ρ^{VS}) and the promoted state density (ρ^{PS}), and is expressible in terms of separate atomic contributions. The valence state pairdensity (π^{VS}) consists of a promoted state part (π^{PS}) and a sharing penetration part (π^{SP}).

From this partitioning of ρ and π , the following decomposition of the total molecular energy is obtained

$$E = \left[\frac{E_S}{L} + \frac{E^P}{A} + \frac{E_S}{B} + \frac{E^P}{B} + \frac{E^{QC}}{AB} \right] + \left[\frac{E^{SP}}{A} + \frac{E^{SP}}{B} + \frac{E^{SP}}{AB} \right] + \frac{E^I}{AB}$$

The energy terms in the first bracket are obtained from ρ^{PS} and π^{PS} . They include the ground state energies of the atoms (E_A^{G} and E_B^{G}), the promotion energy effects (E_A^{P} and E_B^{P}), and the quasi-classical interaction energy between the two atoms when in their promoted states ($E_{\text{AB}}^{\text{QC}}$). The remaining terms arise from the sharing of electrons between the atoms A and B. The energy terms in the second bracket are obtained from π^{SP} . They include the intra-atomic sharing penetration energies (E_A^{SP} and E_B^{SP}) and the inter-atomic sharing penetration energy ($E_{\text{AB}}^{\text{SP}}$). The last term (E_{AB}^{I}) is the interference energy which is obtained from ρ^{I} and π^{I} . For a homonuclear diatomic molecule, all intra-atomic terms are identical for the two atoms A and B. From the preceding equation results the following decomposition for the molecular binding energy

$$\Delta E = E - 2E_A^{\text{G}} = E^{\text{P}} + E^{\text{QC}} + E^{\text{SP}} + E^{\text{I}}$$

with

$$E^{\text{P}} = 2E_A^{\text{P}}$$

$$E^{\text{QC}} = E_{\text{AB}}^{\text{QC}}$$

$$E^{\text{SP}} = 2E_A^{\text{SP}} + E_{\text{AB}}^{\text{SP}}$$

$$E^{\text{I}} = E_{\text{AB}}^{\text{I}}$$

Promotion Energy

Since the detailed breakdown of the promotion energy was left open in the original exposition, we give here the specific method adopted in the present analysis for this purpose.

Because it is of interest to compare atomic promotion effects occurring in different molecules, it appears desirable to carry out the interpretative partitioning of the promotion energy in terms of orthogonal spherical atomic orbitals, i.e., in the present case, orthogonalized Slater-type orbitals. On the other hand, the promotion state density and pairdensity, as extracted from the molecule, are expressed in terms of valence atomic orbitals, i.e., certain hybrid orbitals which are determined by the requirement that the promotion state density matrix have a diagonal intra-atomic structure. It is therefore necessary to transform the promotion state matrices into the basis of spherical orbitals and, thereby, the density matrix acquires off-diagonal terms. Hence, promotion state density and pairdensity are of the form

$$\rho^P(x, x') = \sum_{a, \bar{a}}^P (Aa, A\bar{a}) Aa(x) A\bar{a}(x')$$

$$\pi^P(1, 2) = \sum_{a, \bar{a}}^P \sum_{b, \bar{b}}^P (AaA\bar{a} | AbA\bar{b}) Aa(1) A\bar{a}(1) Ab(2) A\bar{b}(2)$$

The ground state comes naturally expressed in terms of the spherical atomic orbitals, viz.,

$$\rho^{\mathcal{G}}(x, x') = \sum_{a, \bar{a}} p^{\mathcal{G}}(Aa, A\bar{a}) Aa^{\mathcal{G}}(x) A\bar{a}^{\mathcal{G}}(x')$$

$$\pi^{\mathcal{G}}(1, 2) = \sum_{a, \bar{a}} \sum_{b, \bar{b}} p^{\mathcal{G}}(AaA\bar{a} | AbA\bar{b}) Aa^{\mathcal{G}}(1) A\bar{a}^{\mathcal{G}}(1) Ab^{\mathcal{G}}(2) A\bar{b}^{\mathcal{G}}(2).$$

Promotion, i.e., the passage from $\rho^{\mathcal{G}}$, $\pi^{\mathcal{G}}$ to $\rho^{\mathcal{P}}$, $\pi^{\mathcal{P}}$ consists of two changes: first, the change in the coefficients from $p^{\mathcal{G}}(Aa, A\bar{a})$, $p^{\mathcal{G}}(AaA\bar{a} | AbA\bar{b})$ to $p^{\mathcal{P}}(Aa, A\bar{a})$, $p^{\mathcal{P}}(AaA\bar{a} | AbA\bar{b})$ and second, the change in the spherical atomic orbitals from $A\bar{a}^{\mathcal{G}}(x)$ to $Aa^{\mathcal{P}}(x)$ because the orbital exponents change from $\zeta^{\mathcal{G}}$ to $\zeta^{\mathcal{P}}$. Consequently, the promotion energy is divided into two parts. The first corresponds to the change in the coefficients p , while leaving the orbital exponents at their ground state values, and this is called hybridization promotion. The second corresponds to the changes in the orbital exponents ζ , while leaving the coefficients in their promotion state values $p^{\mathcal{P}}$. It is called contraction promotion, expansion being considered as a negative contraction. The hybridization promotion energy (E^{PRH}) and the contraction promotion energy (E^{PRC}) are defined by the following equations:

$$E_A^{\text{PRH}} = \sum_{a, \bar{a}} \delta p(Aa, A\bar{a}) [Aa | h_A | A\bar{a}] + \sum_{a, \bar{a}} \sum_{b, \bar{b}} \delta p(AaA\bar{a} | AbA\bar{b}) [AaA\bar{a} | AbA\bar{b}]$$

with $\delta p(Aa, A\bar{a}) = p^{\mathcal{P}}(Aa, A\bar{a}) - p^{\mathcal{G}}(Aa, A\bar{a})$

$$\delta p(AaA\bar{a} | AbA\bar{b}) = p^{\mathcal{P}}(AaA\bar{a} | AbA\bar{b}) - p^{\mathcal{G}}(AaA\bar{a} | AbA\bar{b})$$

$$h_A = -\frac{1}{2} \nabla^2 - Z_A / r_A$$

and

$$E_A^{\text{PRC}} = \sum_{a, \bar{a}} p^{\text{P}}(Aa, A\bar{a}) \delta [Aa | h_A | A\bar{a}] \\ + \sum_{a, \bar{a}} \sum_{b, \bar{b}} p^{\text{P}}(AaA\bar{a} | AbA\bar{b}) \delta [AaA\bar{a} | AbA\bar{b}]$$

$$\text{with } \delta [Aa | h_A | A\bar{a}] = [Aa^{\text{P}} | h_A^{\text{P}} | A\bar{a}^{\text{P}}] - [A\bar{a}^{\text{g}} | h_A^{\text{g}} | A\bar{a}^{\text{g}}] \\ \delta [AaA\bar{a} | AbA\bar{b}] = [AaA\bar{a}^{\text{P}} | AbA\bar{b}^{\text{P}}] - [AaA\bar{a}^{\text{g}} | AbA\bar{b}^{\text{g}}]$$

$$\text{where } [f | g] = \int dV_1 \int dV_2 f(1)g(2)/r_{12}.$$

There remains the problem of apportioning the promotion energy to the individual orbitals. Such a prorating is necessarily arbitrary but, if carried out with reason, it can nevertheless be instructive.

The first step is the reduction of the quadruple electronic interaction sum to a double sum. This was achieved according to the formulas:

$$\sum_{a, b} \sum_{\bar{a}, \bar{b}} \delta p(AaAb | A\bar{a}A\bar{b}) [AaAb | A\bar{a}A\bar{b}] = \sum_{a, \bar{a}} \epsilon^{\text{PRH}}(Aa, A\bar{a})$$

$$\text{with } \epsilon^{\text{PRH}}(Aa, A\bar{a}) = \sum_{b, \bar{b}} \delta p(AaAb | A\bar{a}A\bar{b}) [AaAb | A\bar{a}A\bar{b}].$$

The second step consists in apportioning the orbital pair contributions to the individual orbitals. This was done differently for the electron interaction terms than for the first-order terms. For the hybridization promotion, the following prorating was used:

$$E_A^{\text{PRH}} = \sum_a E^{\text{PRH}}(Aa)$$

where

$$E^{\text{PRH}}(\text{Aa}) = \sum_{\bar{a}} \left[\frac{2 \delta p(\text{Aa}, \text{Aa})}{\delta p(\text{Aa}, \text{Aa}) + \delta p(\text{A}\bar{a}, \text{A}\bar{a})} \right] \delta p(\text{Aa}, \text{A}\bar{a}) [\text{Aa} | h_A | \text{A}\bar{a}]$$

$$+ \sum_{\bar{a}} \left[\frac{2 \delta p(\text{Aa}, \text{Aa}) p_m(\text{A}\bar{a})}{\delta p(\text{Aa}, \text{Aa}) p_m(\text{A}\bar{a}) + \delta p(\text{A}\bar{a}, \text{A}\bar{a}) p_m(\text{Aa})} \right] \epsilon^{\text{PRH}}(\text{Aa}, \text{A}\bar{a})$$

with $2 p_m(\text{Aa}) = p^{\text{P}}(\text{Aa}, \text{Aa}) + p^{\text{G}}(\text{Aa}, \text{Aa})$.

For the contraction promotion, the following prorating was used:

$$E_A^{\text{PRC}} = \sum_a E^{\text{PRC}}(\text{Aa})$$

where

$$E^{\text{PRC}}(\text{Aa}) = \sum_{\bar{a}} \left[\frac{2 \delta [\text{Aa} | h_A | \text{Aa}]}{\delta [\text{Aa} | h_A | \text{Aa}] + \delta [\text{A}\bar{a} | h_A | \text{A}\bar{a}]} \right] p^{\text{P}}(\text{Aa}, \text{A}\bar{a}) \delta [\text{Aa} | h_A | \text{A}\bar{a}]$$

$$+ \sum_{\bar{a}} \left[\frac{2 \delta(\text{NA}; \text{Aa})(\text{NA}; \text{A}\bar{a})_m}{\delta(\text{NA}; \text{Aa})(\text{NA}; \text{A}\bar{a})_m + \delta(\text{NA}; \text{A}\bar{a})(\text{NA}; \text{Aa})_m} \right] \epsilon^{\text{PRC}}(\text{Aa}, \text{A}\bar{a})$$

with

$$\delta(\text{NA}; \text{Aa}) = [\text{Aa}^{\text{P}} | 1/r_A | \text{Aa}^{\text{P}}] - [\text{A}\bar{a}^{\text{G}} | 1/r_A | \text{A}\bar{a}^{\text{G}}]$$

and

$$2(\text{NA}; \text{Aa})_m = [\text{Aa}^{\text{P}} | 1/r_A | \text{Aa}^{\text{P}}] + [\text{A}\bar{a}^{\text{G}} | 1/r_A | \text{A}\bar{a}^{\text{G}}] .$$

Quasi-classical Interactions

The quasi-classical energy terms are the purely electrostatic coulombic interactions between the two atoms A and B. That is, they are interactions between charge distributions where one also considers the nuclei as point charge distribu-

tions. This includes the nuclear repulsion, the attraction of the quasi-classical electronic charge on B to the nucleus A, the attraction of the quasi-classical electronic charge on A to the nucleus B, and the repulsive interaction of these two electronic charge clouds. There are no charge transfer terms involved in the homonuclear diatomic systems.

In terms of the VAO's, Aa , the quasi-classical density is expressed as

$$\rho^{QC} = \sum_A \rho(A) = \sum_{Aa} q(Aa) Aa^2,$$

where $\rho(A)$ is the quasi-classical density attributable to atom A and $q(Aa)$, the orbital population, is the amount of electronic charge contained in the charge distribution represented by Aa^2 . The expressions for the quasi-classical energy terms now follow directly from the density formalism presented earlier. The attraction of the electronic charge on B to the nucleus A is given by:

$$\begin{aligned} \int (-Z_A/r_A) \rho(B) dV &= \int (-Z_A/r_A) \left[\sum_{Bb} q(Bb) Bb^2 \right] dV \\ &= \sum_{Bb} q(Bb) \left[Bb \left| -Z_A/r_A \right| Bb \right]. \end{aligned}$$

Likewise, the attraction of the electronic charge on A to the nucleus B is given by:

$$\int (-Z_B/r_B) \rho(A) dV = \sum_{Aa} q(Aa) \left[Aa \left| -Z_B/r_B \right| Aa \right].$$

The interaction of the electronic charge on A with the one on B is given by:

$$\int dV_1 \int dV_2 (1/r_{12}) \rho(A) \rho(B) = \sum_{Aa} \sum_{Bb} q(Aa)q(Bb) [Aa^2 | Bb^2] .$$

The total quasi-classical energy contribution to the binding energy of the molecule is thus given by:

$$E^{QC} = Z_A Z_B / R + \sum_{Bb} q(Bb) [Bb | -Z_A / r_A | Bb] \\ + \sum_{Aa} q(Aa) [Aa | -Z_B / r_B | Aa] + \sum_{Aa} \sum_{Bb} q(Aa)q(Bb) [Aa^2 | Bb^2] .$$

The total quasi-classical energy is now divided into orbital pair contributions, $(Aa, Bb)^{QC}$. E^{QC} , which is usually quite small and negative, is the sum of relatively large contributions of opposite sign. That is, the nuclear repulsion (and the smaller electronic repulsion) is balanced off by the nuclear attraction terms. It seems desirable that the orbital pair contributions should exhibit this same effect. This is achieved by dividing the large nuclear repulsion term into orbital pair contributions. These contributions, furthermore, are of about the same magnitude as the corresponding electron-nuclear attraction contribution. Thus, we define

$$Z(Aa) = q^P(Aa) = q(Aa)$$

as that part of the nuclear charge Z_A on nucleus A which is to be associated with orbital Aa. Upon introducing this partitioning of the nuclear charge Z_A , one obtains:

$$E^{QC} = \sum_{Aa} \sum_{Bb} (Aa, Bb)^{QC} ; (A \neq B) ,$$

where the pair contributions are defined by:

$$(Aa, Bb)^{QC} = q(Aa)q(Bb)/Z_A Z_B \left\{ Z_A Z_B / R + Z_B [Bb | -Z_A / r_A | Bb] \right. \\ \left. + Z_A [Aa | -Z_B / r_B | Aa] + Z_A Z_B [Aa^2 | Bb^2] \right\} .$$

The orbital pair contributions, $(Aa, Bb)^{QC}$, are called shielded nuclear attraction (SNA) energy terms. (Note that in this usage of the term, we have included nuclear repulsions.)

In order to facilitate the discussion of the orbital pair contributions in the various molecular systems, it is convenient to express $(Aa, Bb)^{QC}$ in the form:

$$(Aa, Bb)^{QC} = q(Aa)q(Bb) \left\{ 1/R + [Bb | -1/r_A | Bb] \right. \\ \left. + [Aa | -1/r_B | Aa] + [Aa^2 | Bb^2] \right\} .$$

The expression in the curly brackets represents the quasi-classical interaction between two unit nuclear point charges at an internuclear distance of R and two unit electronic charge clouds represented by the charge distributions, Aa^2 and Bb^2 . The orbital populations act simply as proportionality factors as far as the interpretation of the results are concerned. The expression in the bracket is called the normalized quasi-classical energy between the orbitals (Aa) and (Bb) .

Sharing Interference Interactions

The interference energy terms arise because, as a consequence of electron sharing, the actual density $\rho(x)$ differs from the quasi-classical density $\rho^{QC}(x)$ by the inter-atomic

interference density $\rho^I(x)$. The latter can be decomposed into orbital pair contributions as follows:

$$I(x) = \sum_{Aa} \sum_{Bb} p(Aa, Bb) \left\{ Aa(x) Bb(x) - \frac{1}{2} S(Aa, Bb) [Aa^2(x) + Bb^2(x)] \right\}$$

where the $p(Aa, Bb)$ are the aforementioned bond-orders. Each orbital pair contribution represents a shift of electronic charge from one part of the molecule to another. The basic shifts are from the atoms into the bond region or vice versa. But in the sequel, more intricate redistributions will be found. For the pair density a similar interference effect exists.

Similar to the quasi-classical interactions, the sharing interference can therefore be written as a sum of orbital pair contributions:

$$E^I = \sum_{Aa} \sum_{Bb} (Aa, Bb)^I ; (A \neq B) ,$$

and each pair consists of a kinetic and a potential part. The kinetic interference energy arises since addition of the interference density ρ^I to ρ^{QC} modifies the gradient of the electronic distribution. The potential part can again be subdivided into two parts. The major term describes the interaction between the density term ρ^I and the two shielded nuclei, i.e., the attraction by the two nuclei and the repulsion by the respective shielding electrons. The minor part arises from additional other electronic interactions.

If the bond-order $p(Aa, Bb)$ is non-vanishing, the orbital pair contribution can be written as the product,

$$(Aa, Bb)^I = p(Aa, Bb) \langle Aa, Bb \rangle ,$$

where $\langle Aa, Bb \rangle$ is the resonance integral between the two orbitals. It represents the interference energy between the two orbitals for unit bond-order. If the bond-order vanishes, the interference energy has no kinetic part and the potential parts are both relatively small.

Sharing Penetration Interactions

The sharing penetration energies arise from the exchange part of the pairdensity and hence contain only electronic interaction terms. They describe the changes in the electronic interaction resulting from the fact that, in the molecule, the electrons are shared between the atoms.

Electron sharing materially changes the probability of finding two electrons on the same atom, as well as the probability of finding simultaneously one electron on A and the other on B. The latter change is essentially described by the inter-atomic sharing penetration pairdensity,

$$\pi_{AB}^{SP} \doteq \sum_{a,b} q^S(Aa, Bb) Aa^2(x_1) Bb^2(x_2);$$

the former by the intra-atomic sharing penetration pairdensity,

$$\pi_A^{SP} \doteq \sum_{a,\bar{a}} q^S(Aa, A\bar{a}) Aa^2(x_1) A\bar{a}^2(x_2).$$

In these formulas, the

$$q^S(Aa, Bb) = -q_x(Aa, Bb),$$

are the negative inter-atomic exchange pairpopulations derived from

$$\pi_x(x_1, x_2) = \rho(x_1)\rho(x_2) - \pi(x_1, x_2).$$

The intra-atomic coefficients are derived from these inter-atomic coefficients by:

$$q^S(Aa, A\bar{a}) = q^S(Aa)q^S(A\bar{a}) / \sum_{\bar{a}} q^S(A\bar{a})$$

with

$$q^S(Aa) = \sum_b q_x(Aa, Bb), \quad (B \neq A).$$

Actually, π_{AB}^{SP} as well as π_A^{SP} contain additional smaller terms.

In view of the foregoing, the corresponding electronic interaction energies, i.e., the sharing penetration energies, can be decomposed by orbital pairs:

$$E_{AB}^{SP} = \int dV_1 \int dV_2 \frac{1}{r_{12}} \pi_{AB}^{SP} = \sum_{a,b} (Aa, Bb)^{SP}, \quad (A \neq B);$$

$$E_A^{SP} = \frac{1}{2} \int dV_1 \int dV_2 \frac{1}{r_{12}} \pi_A^{SP} = \sum_{a, \bar{a}} (Aa, A\bar{a})^{SP}.$$

If the intra-atomic cross terms ($a \neq \bar{a}$) are attributed equally to both partners, one obtains the decomposition into orbitals:

$$E_A^{SP} = \sum_a (Aa)^{SP}$$

with

$$(Aa)^{SP} = \frac{1}{2} \sum_{\bar{a}} (Aa, A\bar{a})^{SP}.$$

OUTLINE OF CALCULATIONS

General Remarks

The starting data for the analyses were the wave functions described above which were obtained from Dr. B. J. Ransil at Chicago. This data was given in the form of the coefficients which determined the occupied MO's as LCAO-MO's and all of the corresponding one- and two-center, one- and two-electron integrals. These integrals included all of the overlap, kinetic, nuclear attraction, and electron interaction integrals. All data was obtained in terms of the nonorthogonal STO basis set of atomic orbitals and atomic units (a.u.) were used throughout¹.

All arithmetical calculations and manipulations used in the analysis were done on the Cyclone computer. This computer is a high-speed digital computer with a random-access static core memory and paper tape input-output. It was built by the Electrical Engineering department at ISU and is a modified version of the Illiac at the University of Illinois. The programming of the analysis was done in basic machine language and was generalized for any diatomic molecule, including the heteronuclear cases. Most of the arithmetical operations used in

¹The a.u. are: length, 1 a.u. = $0.5293\overset{\circ}{\text{A}}$
energy, 1 a.u. = 1 Hartree = 27.2052eV
Atomic units were used throughout the analysis except for the reporting of the final results. The energy decomposition presented by the figures and tables contained in this report are in units of eV's unless specifically noted as being otherwise.

the analysis were standard matrix operations and much of the programing consisted of writing subroutines for these operations.

Because of limited memory capacity of the computer, all matrix manipulations were executed with the submatrices rather than with the total matrices. This also allowed one to take advantage of the symmetry properties of these matrices. As a means of checking for computational errors, the total molecular electronic energy was recalculated after each major step in the analysis. Although not foolproof, it is believed that all computational errors have been detected and corrected by this procedure. One reason for believing so is the high consistency in the numerical accuracy of the results which was maintained throughout the analysis. Another is the highly improbable occurrence of two or more simultaneous errors which would tend to exactly cancel themselves.

Transformation to Valence Atomic Orbitals

The first step in the analysis was the calculation of the bond-order matrix, $p(Aa, Bb)$, and the pair-bond-order matrix, $p(AaAa | BbBb)$, for which the definitions have been given in an earlier report (10). These matrices, calculated in terms of the nonorthogonal atomic orbital basis set, and the corresponding energy integral matrices were then transformed into an orthogonal atomic orbital set. after the transformation matrix had been determined by Schmidt's orthogonalization pro-

cedure.

The next step involved the calculation of a basis set of hybrid "valence atomic orbitals, VAO". These were determined by locally diagonalizing the intra-atomic submatrices of the bond-order matrix (10). The eigenvectors thus obtained were used to construct a second orthogonal transformation matrix which was used for transforming all matrices into this new basis set of VAO's. It was in terms of these VAO's that the partitioning of the densities (and molecular energy) was performed. Only the promotion effects, which are reported in terms of the orthogonal STO basis set, do not involve the VAO's.

Partitioning into Interference Terms and Interference-Free Terms

The separation of the interference effects was the next step in the analysis and the first step in the actual partitioning of the densities and the corresponding energies. It involved the calculation of the interference energy integrals and new coefficient matrices, as well as the corresponding interference energy terms. Also obtained at this time were the "orbital population numbers", $q(Aa)$, which correspond to Mulliken's "gross atomic populations", and the division of $q(Aa)$ into a valence-inactive part, $p(Aa)$, and a valence-active part, $v(Aa)$. At this stage of the analysis, the first- and second-order densities (and corresponding energies) have

been divided into an interference part and an interference free ("valence state") part.

Sharing Penetration and Quasi-classical Terms

After the isolation of the interference effects, the sharing penetration effects were next separated out according to the formulas prescribed in the theoretical derivation of the analysis (10). Since sharing penetration involves only the electron-pairdensity, this corresponds to the separation of the valence state pairdensity into a sharing penetration part and a promoted state part. For the first-order density, the promoted state is equivalent to the valence state and no distinction exists between the two. The calculation of the sharing penetration effects was accomplished by calculating new coefficient matrices, i.e., by separating the valence state pairdensity coefficient matrix into the two parts mentioned. Following this, the quasi-classical energy effect arising from the interactions between the atoms in their promoted state densities was calculated. This, as well as all of the other energy effects mentioned previously, was calculated in terms of orbital pair contributions which, when summed together, give the total.

Promotional Terms

The next step in the analysis was the calculation of the promotion effects, i.e., the energy effects associated with

the differences between the ground state and the promoted state densities of the separated atoms. The ground state densities and energies of the atoms were first calculated as well as the promoted state energies. In the SAO cases, the Slater orbital exponents were also used in the ground state wave functions. In the BAO and BMAO cases, the ground state wave functions were assumed to have the BAO orbital exponents, since they give the lowest ground state energies. The only promotion effect in the SAO and BAO calculations is that due to the hybridization of the orbitals, i.e., "hybridization promotion". It is calculated as the difference between the ground state and promoted state energies in these cases. In the BMAO calculations, there are, in addition to hybridization promotion, promotion effects arising from the changes in the orbital exponents, i.e., "contractive promotion". They result from the differences in the energy integrals used in calculating the ground and promoted state energies.

Preparation of Tables

The final step of the analysis was the accumulation and sorting of the final energetic results in a more suitable tabular form similar to that used in the figures contained in this report. At this time the results were also converted into the units of electron volts, eV. All of the final and intermediate results of the analysis have been punched out on paper tape and most of them have also been printed. Some

plots of the interference densities were made and were found to be quite useful in the interpretation and understanding of the interference energy effects. Figures which show the overall general trends of the various energy components in the different molecules and for the different approximations were also made.

DESCRIPTION OF MOLECULAR SYSTEMS AND WAVE FUNCTIONS

The molecular systems analysed are the homonuclear diatomic molecules, Li_2 , Be_2 , C_2 , N_2 and F_2 . All of the molecular ground state wave functions, as well as the corresponding integrals needed for computing the molecular energy, for these systems were obtained from Dr. B. J. Ransil at the Laboratory of Molecular Structure and Spectra, University of Chicago, Chicago, Illinois (14). This data formed the starting point for the present investigation. The wave functions were calculated as a single-determinant limited SCF LCAO-MO approximation to the accurate ground state wave functions, based on a minimal set of Slater AO's. The terminology used here follows that of Mulliken (15) and Ransil (14). That is, on both atoms there were used at most the $1S$, $2S$, $2P\sigma$, $2P\pi$ and $2P\bar{\pi}$ orbitals.

For each molecular system, three different wave functions were computed which differed only in the manner in which the orbital exponents of the basis atomic orbitals are determined (14). In the first case, the ζ 's are determined by Slater's rules ("Slater orbitals"). This wave function and the analysis associated with it will be referred to as the "SAO case". In the second case, the ζ 's are determined by minimizing the separate atomic ground state energies ("best atom atomic orbitals (BAO)"). This case will be referred to as the "BAO case". In the third case, the ζ 's are determined by minimiz-

ing the total molecular energy ("best molecular orbital atomic orbitals (BMAO)"). This case will be referred to as the "BMAO case". Thus, three analyses are carried out for each molecular system, and the results are given in the appendix. Since it was found, however, that in general there is little difference between the SAO and the BAO cases, the discussion will be concerned mainly with the SAO and the BMAO cases.

The calculations for each molecule were not made at the theoretically determined equilibrium distance, but at the experimentally observed equilibrium internuclear distance. In the unknown Be_2 , this distance was chosen arbitrarily. Consequently, the results obtained do not satisfy the virial theorem. In all cases, the absolute error in the total molecular energy was greater than the computed dissociation energy. In spite of these limitations, it is believed that the following discussion will exhibit some significant physical aspects of chemical binding in these molecular systems and will allow a certain amount of comparison between them.

GROSS ENERGY BALANCE

The basis for the analysis is a decomposition of the molecular binding energy into four parts ascribed to promotional, quasi-classical, sharing penetration and sharing interference interactions. Each of these parts is further examined according to intra- and inter-atomic contributions from orbitals and orbital pairs and also according to their energetic origin, i.e., kinetic, nuclear-electronic or inter-electronic. This complete breakdown is given in the appendix for all molecular calculations. Thus, there are three analyses for each molecule corresponding to the SAO, BAO and BMAO approximations.

Before discussing these molecular analyses in detail, it is of interest to consider the over-all behavior of the four basic interactions mentioned above. A comparative graphical representation is given in Figure 1, which information is extracted from the first table of each of the analyses in the appendix. Since the BAO results closely parallel the SAO results, they are omitted from the plot. Each curve represents a running total.

The curves show a satisfying similarity to each other and to similar plots obtained in the previous investigations (11, 12 and 13). In spite of this apparent similarity, a profound difference exists, however, between the systems Li_2 , N_2 and F_2 on one hand and Be_2 and C_2 on the other hand. For this

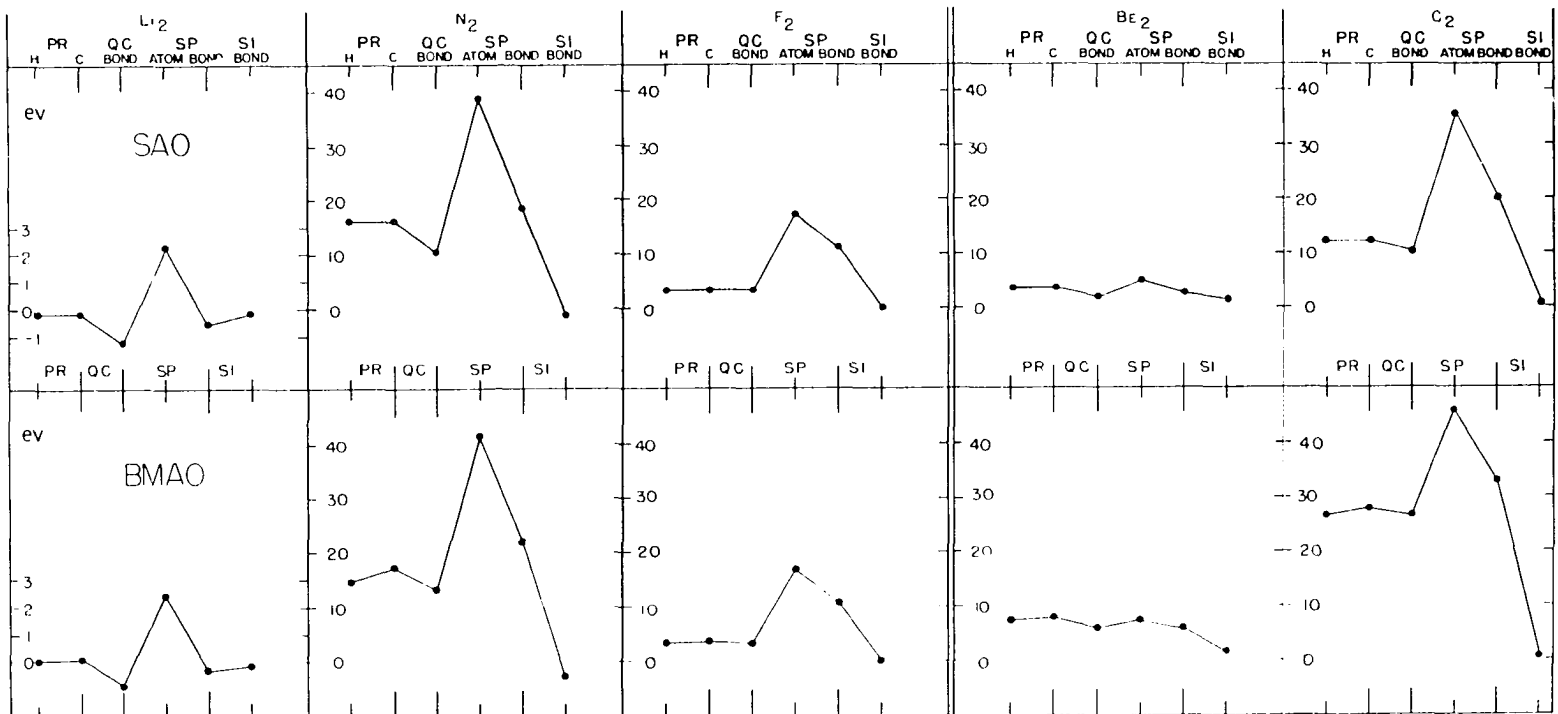


Figure 1. Theoretical molecular binding energy decomposition

reason these groups are distinguished in the figure. The former group has an odd number of electrons per atom while the latter has an even number. The experimental molecular ground state is a singlet for the members of the former group, a triplet for C_2 and unobserved for Be_2 (if existing, a triplet would be expected). The present singlet wave functions for the latter two molecules must be regarded with caution. It is not clear whether, or how close, they approach an actual physical situation. The theoretically predicted equilibrium distance may be far from that used for C_2 and it may be non-existent for Be_2 . Note also that binding is not obtained for either of them. It is rather surprising that the Be_2 and C_2 plots in Figure 1 do conform to the general pattern, since the detailed examination will indeed reveal considerable peculiarities in their wave functions.

In each curve, the first two points correspond to the combined promotion effects of the atoms. Hybridization promotion is labelled H and contraction promotion is labelled C. The former is quite large in C_2 and N_2 and small in Li_2 , Be_2 , and F_2 . The explanation of these values are given in a subsequent section. In all cases, the contraction promotion appears to be very small but it is consistently the result of a considerable drop in potential energy and a compensating increase in kinetic energy indicating an average contraction in agreement with previous conclusions (11, 12 and 13).

The next point on the curve represents the quasi-classical interactions, i.e., the electrostatic potential energy arising when the atomic charge clouds, including the nuclei, are moved from infinity to their equilibrium positions. In all cases it is attractive and less than 5 eV.

The last three points describe the energy contributions from electron sharing. The first two show the characteristic increase in electron repulsion due to sharing penetration. The positive intra-atomic contributions (first point) always outweigh the negative inter-atomic contribution (second point). The final point furnishes the energy effects arising from the interference between the orbitals of the two atoms. According to all previous experience, this interaction is the crucial element in chemical binding. In the present study, two types of anomalous behavior are found. First, the aforementioned peculiarity of the Be_2 and C_2 molecules finds expression in the fact that the kinetic part of the interference energy is positive and the potential part is larger and negative, in complete contradiction to all other cases so far analyzed. In view of the uncertainty connected with these wave functions, it is difficult to assess the meaning of this as well as the other aberrations in Be_2 and C_2 . Second, the present Li_2 calculations yield the unique examples of a positive total interference effect, although the signs of the kinetic and potential parts show normal behavior. The meaning

of this deviation is also uncertain since the violation of the virial theorem appears to indicate that the calculation has been performed at a distance markedly shorter than the theoretically predicted equilibrium position.

ELECTRONIC DISTRIBUTION

The five molecules studied separate into two categories with quite different characteristics. The first group is formed by Li_2 , N_2 and F_2 , where each atom contributes an odd number of electrons to the MO's. The second group, Be_2 and C_2 , is characterized by each atom contributing an even number of σ electrons.

Within the first group, there is a notable difference in the composition of the bonding and lone-pair valence hybrids depending upon the occupation of the lone-pair orbital. Exactly the same observation was made and explained in the study of the hydride molecules. For Li_2 , with no lone-pair electrons, the bonding orbital is predominantly 2S and the lone-pair is predominantly 2P σ . The actual weighting of the 2S contribution to the bonding orbital is smaller in LiH (60%) than it is in Li_2 (94%), but the latter fraction may not be too reliable because there is some question with regard to the present Li_2 calculation since it has not been executed at the theoretically determined equilibrium distance. This leads to a rather large relative deviation from the virial theorem and also is suspected of producing unreasonable interference energy values. In N_2 and F_2 , the lone-pair orbital is doubly occupied and therefore preempts the available 2S orbital so that the dominant part of the bonding orbital becomes 2P σ . In this respect, the N_2 molecule differs from the particular

state of the NH molecule treated in the hydride series. Rather, the σ valence orbitals in N_2 are similar in character to those of the boron atom found in the BH calculation. For both cases, the $2P\sigma$ character of the bonding orbital is about 83%. The 2S character is 17% in BH and 16% in N_2 . The σ valence orbitals in F_2 are very similar to those in HF, about 90% $2P\sigma$ character in the bonding orbital. (In HF it is 88%.)

The systems of the second group, Be_2 and C_2 , have doubly filled $2\sigma_g$ and $2\sigma_u$ MO's. Since S-P hybridization appears to be too costly, both MO's have only a minor $2P\sigma$ admixture. If this mixture were zero, then one would have the situation of two doubly filled lone-pair orbitals with non-bonded repulsions. Actually, the lone-pair valence orbital, possessing more than 96% 2S character, is found to have the approximate population of 1.7 whereas the bonding orbital, with more than 98% $2P\sigma$ character, is populated by approximately 0.3 to 0.4 electrons. The exact values are given in Table 1.

Table 1. Populations of lone-pair orbital and bonding orbital in Be_2 and C_2

Orbital	SAO		BMAO	
	Be_2	C_2	Be_2	C_2
b	0.323	0.411	0.253	0.323
l	1.686	1.586	1.761	1.699

PROMOTION

Hybridization

In order to find the effect of hybridization promotion, suitable ground state wave functions must be chosen.

For lithium, this function is the determinant for the $(1S^2 2S) 2S$ configuration. Promotion therefore consists in changing the 2S orbital into a bonding hybrid involving a shift of charge of about 0.05 electron from the 2S to the $2P\sigma$ orbital.

The nitrogen ground state is a $(1S^2 2S^2 2P\sigma 2P\pi 2P\bar{\pi}) 4S$ determinant. The fluorine ground state is a $(1S^2 2S^2 2P\sigma 2P\pi^2 2P\bar{\pi}^2) 2P$ determinant. In both of these, promotion consists in adulterating the 2S lone-pair by some $2P\sigma$ admixture and transforming the singly occupied $2P\sigma$ orbital into a bonding hybrid by adding some 2S character. The net effect is the loss of 2S and the gain of $2P\sigma$ character by one electron. Thus, in nitrogen, with the aforementioned strong hybridization, there is a considerable charge shift (0.20 electrons in the SAO approximation, 0.13 electrons in the BMAO approximation) from the 2S to the $2P\sigma$ orbitals. In fluorine, the charge shift is only 0.03 electrons because of the minute hybridization.

The ground state of beryllium is the $(1S^2 2S^2) 1S$ determinant. For carbon it is a $(1S^2 2S^2 2P\pi 2P\bar{\pi}) 3P$ determinant. In both cases, promotion consists in removing part of an

electron from the 2S (which essentially remains a lone-pair orbital) and placing this charge into the $2P\sigma$ orbital, the bonding orbital. The amounts of charge shifted are identical with those given in Figure 2.

The promotion energies resulting from these hybridizations in the SAO and BMAO approximations are summarized, by orbitals, in the first two sections of Figure 2. Also included, as the first column for each atom, are the corresponding population changes (Δp) which have just been discussed. They are the changes of the diagonal elements of the bond-order matrix. While it is true that the listed energy values also contain contributions from off-diagonal elements, especially from electronic interaction, these are generally minor. Only in Be_2 and C_2 do the 1S-2S cross terms gain some influence on the total.

In all cases, removal of charge from an orbital decreases the kinetic and increases the potential energy of that orbital. Addition of charge generates opposite changes. Nearly always the change in potential energy dominates. In view of the foregoing, the over-all energy increase due to hybridization, is basically due to the decrease in nuclear attraction in moving charge from the 2S to the $2P\sigma$ orbital. In Li_2 and N_2 , this effect also dominates over the not negligible drop in energy associated with the slight charge shift into the 1S orbital. Since the present definition of promotion densities is

SUMMARY OF PROMOTION ENERGIES

Orbital	I			II			III			IV			V		
	ΔE	EP	IOI	ΔE	EP	IOI	ΔE	EP	IOI	ΔE	EP	IOI	ΔE	EP	IOI
1	0.000	0.0	0.00	0.000	1.0	2.51	1.78	0.000	0.0	0.01	0.02	0.000	0.0	0.01	0.02
2	0.004	0.21	0.12	0.004	11.0	27.13	11.28	0.004	0.21	0.12	0.1	0.004	0.21	0.12	0.1
3	0.015	0.78	0.41	0.017	13.15	31.22	13.21	0.017	0.81	0.41	0.34	0.017	0.81	0.41	0.34
4	0.03	1.78	0.91	0.04	27.04	70.04	27.04	0.04	1.78	0.91	0.91	0.04	1.78	0.91	0.91
101	0.01	0.21	0.07	0.01	0.21	0.52	0.14	0.000	0.0	0.01	0.02	0.000	0.0	0.01	0.02
102	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.000	0.0	0.01	0.02	0.000	0.0	0.01	0.02
103	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
104	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
105	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
106	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
107	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
108	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
109	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
110	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
111	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
112	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
113	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
114	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
115	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
116	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
117	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
118	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
119	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02
120	0.001	0.01	0.01	0.001	0.01	0.25	0.13	0.001	0.01	0.01	0.02	0.001	0.01	0.01	0.02

ΔE = energy difference between orbitals in eV; EP = energy of promotion in eV; IOI = orbital ionization potential in eV.

Figure 2. Summary of orbital promotion energy decompositions

not derived from atomic wave functions, the 1S population can increase beyond two, a fact which accounts for the slightly negative promotion energy in the SAO calculation of Li_2 . In Be_2 and C_2 , the 1S promotion has the opposite sign and, in the BMAO case, is quite substantial.

Contraction and Expansion

The third section of Figure 2 gives the promotion energies arising from the contraction and expansion of the AO's in the BMAO calculation, with reference to the BAO calculation. The energy differences are the results of the changes in the various orbital exponents calculated for the hybridized promotion state. The orbital exponent modifications ($\Delta\zeta$), in going from the BAO to the BMAO case, are also listed in the first column for each molecule.

The magnitude of the energy values can be understood from the changes in orbital exponents and the population of the orbitals in the promoted state. For example, the kinetic contribution to the contractive promotion is approximately reproduced by:

$$\frac{1}{2}p [\zeta^2(\text{BMAO}) - \zeta^2(\text{BAO})] \doteq p(\zeta \Delta\zeta) \doteq p(\zeta \Delta\zeta)(27.2) \text{ eV},$$

where p is the orbital population. Thus, for example, the very large effect in N_2 is the result of the large population (1.20) and the large $\Delta\zeta$. F_2 has a large population (1.03) but a small $\Delta\zeta$, while C_2 has a large $\Delta\zeta$ but a smaller population (0.43), both factors are even smaller in Be_2 and very

small in Li_2 . The really large changes in the orbital exponents are the increases in the $2p\sigma$ orbitals. This is in agreement with the repeatedly expressed idea that contractive promotion is linked to constructive interference. The changes in the other orbital exponents seem to be determined by a more complicated chain of cross influences. We consider it, however, very significant that in all cases the total molecular contractive promotion shows the following characteristics: the kinetic energy increases, the potential energy decreases, and the total energy change is positive, but small compared to its kinetic or potential parts. In short, contractive promotion essentially shifts energy from the potential to the kinetic category and this shift is at least of the order of magnitude of the calculated binding energy. Except for C_2 , this behavior of the contractive promotion also determines the signs of the kinetic and potential parts of the total BMAO molecular promotion energy.

QUASI-CLASSICAL INTERACTION

Factors Influencing Quasi-classical Energies

A great variety is observed in the orbital pair contributions to the quasi-classical energy in the various molecular systems. It indicates that many factors are involved.

First, there is the weighting factor for each orbital pair, which indicates how many times the orbital interaction occurs in the total. Thus, a pair involving two analogous orbitals, such as (b, b') , has a weighting factor of one, whereas, pairs involving two different orbitals (cross terms) have a weighting factor of two since either orbital can be on either atom, e.g., one has (l, b') and (b, l') . Finally, all pairs involving a π orbital are subject to an additional doubling to account for the equivalent $\bar{\pi}$ contribution. Thus, for examples, the (l, b') and (π, π') terms have a weighting factor of two, and so has the $(\pi, \bar{\pi}')$ term, but the (l, π') term has a weighting factor of four.

Secondly, there is the population factor, i.e., the product of the two orbital populations. Each orbital pair contribution is the product of the population factor and a "normalized" quasi-classical interaction energy between the two orbitals. The latter is the sum of the quasi-classical interactions arising between two unit nuclear point charges and the two unit electronic charge distributions represented by the densities of the specific orbitals involved. The population

factors vary from zero, when one or both of the orbitals are unoccupied, to about four which is common between doubly occupied i or l orbitals.

The normalized quasi-classical energy ("Coulomb Integral") of an orbital pair represents the electrostatic interaction between two neutral units. In each unit, the electronic cloud can be considered as "shielding" the nucleus. The effectiveness of this shielding depends upon the relative diffuseness of the electron cloud as well as its polarization. By "relative diffuseness" is meant the average diameter of the orbital cloud as compared to the internuclear distance. A relatively diffuse distribution tends to have a poorer shielding effect and a larger interaction energy than a contracted distribution which, otherwise, has the same polarization characteristics. Thus, the inner orbitals generally exhibit a high shielding effect. The overlap integral, S , gives a rough indication of shielding for fixed polarization. A large S indicates little shielding, while a very small S indicates almost complete shielding.

On the other hand, the polarization of the orbital cloud is of paramount importance. For example, a cloud will have a larger interaction with the other atom, if it is concentrated between that atom and its own nucleus. One can say that its nucleus is better shielded by such a polarized cloud. But the picture becomes less apt at the point where, as frequently

occurs, the interaction of the polarized electron cloud with the other atom, in particular its nucleus, becomes the dominant effect. It stands to reason that the electron-nuclear attraction terms are much more sensitive to the polarization effects than to variations in the diffuseness of the electron cloud. But for the electron-electron repulsion terms, both effects are consequential. The influence of polarization in simple interactions is shown in the comparative calculations by Fraga and Mulliken for various charge distributions in some valence bond structures, especially for H_2 (22). (They used the term "coulomb energy" for the interaction effects which, here, are referred to as quasi-classical.) Their results form a good introductory review to the quasi-classical effects associated with various spatial arrangements of charge distributions.

A given charge distribution can be contracted by an increase in the orbital exponent, ζ , but also by a change in hybridization, such as 1S and 2S mixing, and frequently both changes occur together. The polarization of the orbitals is largely due to hybridization, as given by the VAO decomposition in the appendix. But polarization of hybrid orbitals can also be influenced by changes in the ζ values, especially the $2p\sigma$ ζ value.

The final factor to be considered is the internuclear distance. At very small distances, the quasi-classical inter-

actions are always repulsive since the nuclear-nuclear term is overwhelming. In the case of the π - π interaction, this remains so for all distances. The σ interaction terms become attractive in the range of actual interest. At very large distances, i.e., for small overlap values, the S-S interaction remains attractive, whereas the P σ -P σ interactions become repulsive due to quadrupole interactions. As a general rule, the smaller the internuclear distance, the larger the quasi-classical interaction will be and vice versa. This is so, since the electronic repulsion (shielding) increases less than the nuclear-electronic attractions as charge clouds approach and interpenetrate each other.

Discussion of Principal Contributions

Many of the orbital pairs, such as those involving an inner orbital, make an insignificant contribution to the total quasi-classical energy. On the other hand, a relatively few of the orbital pairs invariably contribute most of the total energy. In Table 2 the principal orbital pair contributions are summarized for the various molecular systems. Only the results of the BMAO and the SAO calculations are given since the BAO calculation shows only minor variations from the SAO case. In order to facilitate the discussion, the table contains the following pertinent information: the internuclear distances, the weighting factor for each contribution (given in parenthesis under the orbital pair designation), the

Table 2. Comparison of main quasi-classical contributions

		Li ₂	N ₂	SAO F ₂	Be ₂	C ₂	Li ₂	N ₂	BMAO F ₂	Be ₂	C ₂
R (a.u.)		5.05	2.07	2.68	3.78	2.35	5.05	2.07	2.68	3.78	2.35
Binding Orbital Pairs											
b, b' (1)	Norm E	-1.02	-2.60	0.35	-1.83	-2.84	-0.94	-1.27	0.33	-1.09	-1.24
	Popul.	0.99	0.91	0.99	0.10	0.17	0.99	0.92	0.99	0.06	0.10
	Ov'lap	0.77	0.72	0.22	0.37	0.42	0.75	0.62	0.25	0.37	0.39
l, b' (2)	Norm E	--	-2.43	-0.29	-1.08	-1.75	--	-2.19	-0.32	-0.90	-1.26
	Popul.	0.00	1.95	1.99	0.54	0.65	0.00	1.95	1.99	0.45	0.55
	Ov'lap	0.36	0.30	0.12	0.45	0.46	0.32	0.30	0.14	0.41	0.34
b, π' (4)	Norm E	--	-1.98	-0.20	--	-1.43	--	-1.72	-0.22	--	-1.08
	Popul.	--	0.95	1.99	--	0.41	--	0.96	1.99	--	0.32
Antibinding Orbital Pairs											
l, l' (1)	Norm E	--	1.42	0.11	-0.12	0.02	--	1.18	0.11	-0.22	-0.25
	Popul.	0.00	4.18	4.02	2.84	2.51	0.00	4.18	4.03	3.10	2.88
	Ov'lap	0.03	0.05	0.06	0.40	0.37	0.15	0.17	0.06	0.47	0.38
l, π' (4)	Norm E	--	0.73	0.06	--	0.24	--	0.68	0.07	--	0.09
	Popul.	--	2.04	4.01	--	1.58	--	2.04	4.01	--	1.70
π, π' (2)	Norm E	--	0.62	0.08	--	0.63	--	0.65	0.09	--	0.64
	Popul.	--	1.00	4.00	--	1.00	--	1.00	4.00	--	1.00
	Ov'lap	--	0.28	0.05	--	0.32	--	0.29	0.05	--	0.32
π, π' (2)	Norm E	--	0.28	0.03	--	0.30	--	0.30	0.03	--	0.31
	Popul.	--	1.00	4.00	--	1.00	--	1.00	4.00	--	1.00

normalized energy effects (Norm E), the population product factors (Popul.), and the overlap integrals (Overlap) when different from zero.

Binding are, in general, the (b,b') , (l,b') and (b,π') contributions. (See first section of Table 2.)

The usual attraction of the (b,b') term is associated with the localization of the electrons between the two nuclei whereby the electronic nuclear attraction becomes the overwhelming effect. This is accomplished by b orbitals which are mainly $2p\sigma$ character or are strongly polarized S orbitals. The former usually has a more favorable effect, although this depends upon the diffuseness of the orbitals and the internuclear distance. A strongly polarized S orbital, while very favorable, is somewhat handicapped by the increase in the electronic repulsion arising from having the majority of its charge in the bond region. The population factor, which is always one or less, as well as the weighting factor of unity place a definite limit on the total affect of the (b,b') contribution.

In many instances the (l,b') interaction becomes the predominant attractive contribution, because it has the weighting factor two and a larger population factor which, in some cases, gets as large as three. Moreover, its normalized energy, too, is relatively large and attractive because of the nature of the l and b orbitals. The l orbitals are usually of

2S character, somewhat polarized away from the other nucleus and quite diffuse. The interpenetration of the orbitals, as indicated by the relatively large (ℓ, b') overlap, does not increase the electronic repulsion too much since it arises from rather diffuse distributions. Thus they counteract little the large nuclear attraction for the b orbital distribution (largely located in the bond region) which is the predominant effect. The more strongly polarized both orbitals are, the larger the normalized energy is.

The total (b, π') contribution is quite large because of the large weighting factor of four. The reasons for the large attractive nature of the (b, π') interaction are much the same as those noted for (ℓ, b') interaction. Again, the normalized energy effect increases with increased polarization of the b orbitals.

The remaining interactions, namely (ℓ, ℓ') , (ℓ, π') , (π, π') and $(\pi, \bar{\pi})$, are usually repulsive. The (ℓ, ℓ') interaction is repulsive when the lone-pair orbital is sufficiently polarized away from its nucleus since, thus, the nuclear-nuclear repulsion is domineering. This is the more common case and the repulsion can be substantial. If, on the other hand, the lone-pair becomes close to being pure 2S, then the (ℓ, ℓ') interaction can become somewhat attractive, e.g., in Be_2 and C_2 . In any case, this contribution is important since it usually has a large population factor (between three

and four, unless it is zero).

The (ℓ, π') interaction is similar to the (b, π') interaction except that it is now repulsive since the ℓ orbital is always at least somewhat polarized away from the other nucleus. Here, the nuclear attractions for the ℓ and π charge distributions are not enough to overcome the nuclear repulsion, i. e., the shielding is not great enough, mainly because of the polarization. The normalized energy for the (ℓ, π') interaction is much smaller than that of the (b, π') interaction, but the larger population factor tends to reduce this difference somewhat. The large weighting factor of four also makes the (ℓ, π') interaction of considerable importance.

The (π, π') interaction is repulsive because of weak shielding, and also because of the strong electronic repulsion for two similar π distributions. For geometric reasons, this repulsion is much weaker for the $(\pi, \bar{\pi}')$ interactions which, therefore, are only about half as large. There is a weighting factor of two in both cases. The effects of the internuclear distance and the orbital exponent values (diffuseness) on these interactions can be easily seen from the results in the table.

From the preceding discussion, it can be seen that polarization is the most influential and the most predominant factor in the quasi-classical interactions. It occurs to some extent in practically all b orbitals and is very favorable for

the (b, π') and (ℓ, b') interactions. However, because of orthogonalization, polarization of the b orbitals induces some complementary polarization of the ℓ orbitals and the resulting (ℓ, π') and (ℓ, ℓ') interactions will usually be repulsive. Shielding is important in that it can affect the relative magnitudes of these two opposing effects. It must be remembered, of course, that the other energetic interactions, such as interference and promotion, are essential factors in the determination of the electronic distributions from which the quasi-classical effects are calculated.

It is of interest to note that the net effect of the π electrons, i.e., the sum of the (b, π') , (ℓ, π') , (i, π') , (π, π') and $(\pi, \bar{\pi}')$ contributions, is always repulsive. In $C_2(\text{SAO})$, this effect is 1.02 eV, about twice as large as it is in $N_2(\text{SAO})$.

Comparison of Different Approximations

The differences between the SAO and the BMAO calculations show a great regularity for all systems. In all, except F_2 , there is a general decrease in the polarization of the orbitals in going from the SAO to the BMAO case. This decrease almost invariably gives a decrease in the individual orbital pair contributions, and thus also the total. The only exception to this in Table 2 is the attractive (ℓ, ℓ') interaction in Be_2 and C_2 which, in agreement with the foregoing discussion of this case, is enhanced by the decrease in polarization of the

l orbital. There is very little change in the π orbitals, only a slight expansion due to a slight decrease in the ζ values. Usually, the decrease in polarization of the b orbital is due partly to a change in hybridization and partly to an increase in the $2p\sigma$ ζ value. The latter also causes a contraction which further reduces the energy contributions, in particular for the (b,b') interactions.

Examination of Specific Contributions

Interactions in F_2

The results for F_2 are sufficiently different from those of the other molecular systems to warrant special consideration. The total quasi-classical interaction for $F_2(\text{SAO})$ is zero and it is only slightly attractive for $F_2(\text{BMAO})$. The smallness of these interactions, as compared to the other systems, is due to the large internuclear distance in comparison with the diameter of the atomic orbitals, as indicated by the large values of (ζR) and the correspondingly small overlap integrals. This situation is caused by non-bonded repulsion of the π electrons, which are essentially lone-pair electrons. The distance is, in fact, so large that the (b,b') interaction is now repulsive, in agreement with the earlier discussion. The unique increase of the interactions in the BMAO case, as compared to the SAO case, is due to an increase in the polarization and expansion of the b orbital. It is

caused by the decrease in the $2P\sigma$ ζ value since the hybridization remains essentially the same. Most of the differences between the SAO and the BMAO calculations are however, very small compared to those in the other systems.

(b,b') interactions

The normalized (b,b') interaction in Be_2 and C_2 is quite high because of the $2P\sigma$ character of the b orbital. Be_2 is the lower of the two because of the larger internuclear distance. It is also quite high in N_2 . Here, the strong polarization of the b orbital is less helpful, but the shorter internuclear distance makes the result for C_2 and N_2 quite similar. It is smaller in Li_2 , because the b orbital has only slightly polarized 2S character. However, since it is quite diffuse (as noted by the large overlap), the electronic repulsion is small, and hence the total interaction is quite remarkable considering the large internuclear distance. The (b,b') contribution is almost the entire quasi-classical effect in Li_2 since the ℓ orbitals are unoccupied. For Be_2 and C_2 , however, the small population factors make the (b,b') contribution quite unimportant.

(ℓ ,b') interactions

The normalized (ℓ ,b') interaction is very large in N_2 because of the strong polarization of both the b and ℓ orbitals. It is much smaller for Be_2 and C_2 because of the decrease in

polarization as well as larger internuclear distances. The lack of polarization of the ℓ orbitals is especially effective. Be_2 is the smaller of the two for the same reasons. The decrease in the BMAO case for C_2 is also larger than usual because of the contraction of the ℓ orbital as well as the decreased polarization of the b and ℓ orbitals. The decrease for $\text{Be}_2(\text{BMAO})$ is somewhat reduced by the expansion of the ℓ orbital. Again, the population factors for Be_2 and C_2 are quite small. The (ℓ, b') interaction in F_2 is small for the reasons discussed previously.

(ℓ, ℓ') interactions

The (ℓ, ℓ') interaction obeys the general behavior in N_2 and F_2 . Be_2 and C_2 , however, are exceptions which have already been discussed. The increased attraction in $\text{C}_2(\text{BMAO})$ is much larger than in $\text{Be}_2(\text{BMAO})$ because of the changes in the ℓ orbitals as mentioned above.

Interactions involving π orbitals

The (b, π') interaction is much larger in N_2 than in C_2 because of the increased polarization. It is much smaller in F_2 . The (ℓ, π') , (π, π') and $(\pi, \bar{\pi}')$ interactions follow the discussion given above in all cases. In spite of a population product which is four times larger, the results for F_2 are only about half as large as for N_2 and C_2 . The (ℓ, π') interaction shows a quite large decrease in the $\text{C}_2(\text{BMAO})$ case

which is due to the changes in the ℓ orbital as already indicated. The (ℓ, π') interaction is also much larger in N_2 because of the strong polarization of the ℓ orbital.

Inner orbital interactions

Almost all contributions involving the inner orbitals are practically zero as is expected, with a few exceptions to be considered. There is an exception in the N_2 (SAO) case where the ℓ orbital is so strongly polarized away from the nucleus that there is a substantial repulsive energy (0.26 eV) with the inner orbital of the other atom. This interaction becomes almost negligible in the BMAO case because of the decreased polarization. However, the (i, ℓ') contribution in the BMAO cases of C_2 and Be_2 is slightly attractive (-0.07 eV and -0.10 eV respectively) since the ℓ orbital is almost pure 2S character. Note the similarity to the behavior of the (ℓ, ℓ') contributions. Another surprisingly large contribution is the attractive (i, b') interaction in N_2 (-0.34 eV in the SAO case and -0.17 eV in the BMAO case). This is due mainly to the polarized nature of the b orbital.

INTERFERENCE

Factors Affecting the Interference Energies

As has been discussed elsewhere, the interference energy arises from the fact that the actual density differs from the quasi-classical density by certain orbital pair contributions which represent either constructive or destructive interference effects. For atomic orbitals which have somewhat complicated contours the difference between the two types may not always be immediately obvious from the geometry. Constructive interference exists if there is an over-all smoothing of the density, destructive interference takes place if the opposite occurs. More specifically, we speak of constructive interference if the kinetic interference energy is negative and of destructive interference if the kinetic interference energy is positive.

In general, constructive interference is also associated with a positive potential interference energy, and destructive interference with a negative potential contribution. To this, there are, however, quite a few exceptions, in particular if the interference affects only little the electron density near the nuclei. The total interference energy is almost always determined by the kinetic part, so that constructive interference implies a binding effect, whereas destructive interference implies an antibinding effect.

Each orbital pair interaction is the product of two

factors, bond-order and resonance integral. This is similar to the quasi-classical energies, being products of populations and normalized orbital interactions (coulomb integrals). In fact the relative size of a given bond-order appears to be closely related to the populations of the orbitals involved.

Note the smallness of $p(b, b')$ in Be_2 and C_2 . Also, the various pair contributions have the same weighting factors which were discussed for the quasi-classical effects; two for cross terms, an additional two for π contributions except $(\pi, \bar{\pi}')$.

The situation is somewhat different if the bond-order vanishes, e.g., for the σ - π and π - $\bar{\pi}$ cross terms. Although here the kinetic interference energy vanishes, there is in general a small potential contribution from the electron interaction terms. Such cases will be discussed further below. Their influence on the total interference effect is, however, small.

A notable difference to the quasi-classical interaction is the fact, that an arbitrary change of sign (or a more general phase change) in the definition of one of the atomic orbitals in a pair will simultaneously change the sign of the bond-order and of the resonance integral while leaving the total interference energy invariant. However, in almost all cases at hand it was found that the resonance integral between two valence atomic orbitals corresponded to constructive

interference, i.e., had a negative kinetic resonance integral. Consequently, a positive bond-order usually corresponds to constructive interference and a binding effect in the interference energy, whereas a negative bond-order goes hand in hand with destructive interference and an antibinding effect.

For a given orbital pair, a large positive bond-order implies that the orbitals are mainly involved only in a bonding MO [see $p(\pi, \pi')$ in N_2 and C_2 and $p(b, b')$ in F_2]. Similarly, a large negative bond-order implies that the orbitals are mainly involved only in antibonding MO's [see $p(l, l')$ in C_2 and Be_2]. When one or both of the orbitals are involved in both types, the bond-order will be smaller and most often negative [see $p(\pi, \pi')$ in F_2 as well as the bond-orders involving the inner orbitals]. These results are quite similar to those which occur in valence bond structures where the individual antibonding effects are larger than the bonding effect.

Discussion of Principal Types

Similar to the quasi-classical effects, the interference energies are functions of many variables, such as; the internuclear distance, shielding (by all electrons), the orbital exponents (relative contraction or expansion), and the spatial orientation of the interacting orbitals (includes type of orbital as well as degree of polarization). Thus,

considerable variations occur in the results. They are best understood by considering the interference densities from which they originate. (These densities are meant to contain the bond-orders as well as the orbital densities in the resonance integrals.) It emerges that, in practically all cases, the interference density belongs to one of a small number of general basic types. In discussing them, the following terminology will be used. Since the interference density is a density modification, it can be regarded as a "shift" of electronic charge from one region of space into another, due to the interference between two orbitals. The "recipient region" for the orbital pair, (Aa,Bb), will be that region where there is an increase in the electronic charge as compared with the quasi-classical density. The "dative region" is that region where there is a decrease in the electronic charge. The change in the electronic interaction part of the shielded nuclear attraction terms, due to the charge shift, is referred to as a change in the shielding effect.

The type I+ interference density is the "normal" constructive type, such as found in H₂. The recipient region is the bond region while the dative regions lie more or less symmetrically about the nuclei. There is a large drop in kinetic energy and a smaller rise in the shielded nuclear attraction, the total being quite favorable for binding. Usually, there is a substantial decrease in the shielding effect

which aids in keeping the rise in the shielded nuclear attraction small. Analogously, the type I- represents the "normal" destructive interference and is just the reverse of type I+. There is now a rise in kinetic energy and a smaller drop in shielded nuclear attraction, the total being unfavorable for binding. There are cases where types I+ and I- differ mainly in the sign of the bond-order, but little in the resonance integrals.

Type II+ is a less frequent constructive type which differs from type I+ in that the dative regions lie strictly on the far sides of the nuclei (away from the other nucleus), while the recipient region still lies in the bond region. The consequence is that the drop in kinetic energy is not nearly as great as in the first case (type I+) and the rise in the shielded nuclear attraction is very small (the decrease in the shielding effect is also very small). In some more extreme cases, there is actually a decrease in the shielded nuclear attraction since the potential attraction is greater in the recipient region, where it arises from two shielded nuclei, than in the dative region where it comes from one shielded nucleus. This peculiar case is rather close to what used to be considered by earlier workers as the essential effect of overlap in chemical bonding. In fact, it corresponds, however, to rather untypical special situations. The destructive counterpart of type II+ is type II-. The recipient regions

lie rather toward the far sides of the nuclei, and the dative region lies in the bond region. This shift of charge is accompanied by a smaller than normal rise in kinetic energy, but only a minor drop in shielded nuclear attraction. In extreme cases, there will actually be a considerable rise in the shielded nuclear attraction [see the (i,b') interaction in N_2].

Another constructive type which, however, occurs rather rarely, may be called type III+. In this case, the charge is shifted from the bond region side near the nuclei, i.e., the side closest to the opposite nucleus, into the center bond region in a quite diffuse, spread out manner. The drop in kinetic energy is smaller than in the normal case (type I+), and the rise in shielded nuclear attraction is much larger so that the two effects tend to cancel each other [see the (ℓ ,b') interactions in Be_2 (SAO) and C_2 (BMAO)]. The destructive counterpart, type III-, occurs mainly with the inner orbitals. The recipient regions are small, centrally located regions about the nuclei while the dative regions are a little farther away from the nuclei on the bond side. There is now a considerable rise in kinetic energy and, in general, a smaller but quite large drop in shielded nuclear attraction, leaving a slightly repulsive net effect. In an extreme form of this case, the potential energy may actually overcome the kinetic, leading to a binding effect [see (i, ℓ') in N_2].

The variations within these types are the result of dif-

ferences in internuclear distances, bond-orders and orbital hybridization. The latter largely determines how the recipient and dative regions are distributed in space and to which basic type a given interaction will belong.

Comparison of Different Approximations

In going from the SAO to the BAO calculations, there is a general expansion of the orbitals and very little change in the hybridization. The changes which occur are quite small but they follow a general pattern. Because of the expansion, there is a decrease in the attractive contributions and an increase in the repulsive ones. This is usually so for the separate parts of each contribution as well as the net result. These changes are largely caused by an increase in the antibonding bond-orders, due to the increase in overlap. The inner orbital contributions and the results of Be_2 and C_2 show the largest deviations from these general trends, since here hybridization changes are no longer insignificant.

Much stronger hybridization changes occur in the BMAO calculation and result in much larger and more erratic changes. In general, however, all contributions are increased by the decrease in polarization. The changes in the bonding orbital contributions are usually more predominant because of the $2p\sigma$ contraction and thus the total interference result becomes more binding. On the whole, the modifications are due to the fact that the interference interactions occur closer to

the nuclei.

These differences can be seen in Table 3, which summarizes the principal orbital pair contributions for all molecules in the SAO and BMAO approximations. For each orbital pair, there is given the kinetic and potential (and total) energy effect as well as the bond-order (p).

Examination of Specific Contributions

π contributions

We consider the (π, π') contributions first, since their interference effects are simplest. In N_2 and C_2 they are of type I+ and are very similar to the constructive interference found in H_2 . In F_2 this contribution is of type I- and corresponds to a closed shell repulsion. It is mainly this repulsive (non-bonded) interaction of the π electrons that is the reason for the relatively large internuclear distance and, thus, the small overlapping in F_2 .

σ contributions in Li_2 , N_2 and F_2

The contributions from the σ electrons show a basic difference between the molecular systems of Li_2 , N_2 and F_2 , where there is an odd number of electrons per atom, and Be_2 and C_2 , where there is an even number of electrons per atom. This difference is most obvious in the (ℓ, b') contributions, being repulsive in N_2 and F_2 and attractive in C_2 and Be_2 .

The (b, b') contribution is "normal", type I+, in both Li_2

Table 3. Comparison of main sharing interference contributions

		Li ₂	N ₂	SAO F ₂	Be ₂	C ₂	Li ₂	N ₂	BMAO F ₂	Be ₂	C ₂
b, b' (1)	KIN	-3.61	-20.73	-30.66	-0.04	-0.45	-2.97	-28.86	-29.83	-0.17	-1.17
	POT	2.68	8.32	16.23	-0.28	-0.58	1.98	10.99	15.67	-0.15	-0.06
	TOT	-0.93	-12.41	-14.43	-0.32	-1.03	-0.99	-17.87	-14.16	-0.32	-1.23
	p	0.56	0.59	0.82	0.05	0.08	0.57	0.63	0.80	0.04	0.06
q, q' (1)	KIN	--	0.70	1.60	20.72	21.62	--	3.80	1.48	3.22	70.48
	POT	--	-0.32	-0.82	-20.42	-16.08	--	-0.73	-0.73	-2.71	-79.44
	TOT	--	0.38	0.78	0.30	5.54	--	3.07	0.75	0.51	-8.96
	p	0.00	-0.16	-0.14	-0.84	-0.75	0.00	-0.43	-0.14	-1.10	-0.83
q, b' (2)	KIN	--	8.40	4.29	-6.68	-12.34	--	8.88	4.61	-1.86	-21.43
	POT	--	-0.57	-3.07	6.00	7.37	--	-2.30	-3.21	-0.40	21.57
	TOT	--	7.84	1.22	-0.69	-4.96	--	6.58	1.40	-2.26	0.14
	p	0.00	-0.35	-0.19	0.40	0.47	0.00	-0.34	-0.21	0.35	0.44
π, π' (2)	KIN	--	-15.61	0.84	--	-11.24	--	-15.19	0.91	--	-11.07
	POT	--	6.80	-0.49	--	4.96	--	6.61	-0.54	--	4.93
	TOT	--	-8.80	0.35	--	-6.28	--	-8.58	0.37	--	-6.14
	p	--	0.78	-0.09	--	0.76	--	0.77	-0.10	--	0.76
i, b' (2)	KIN	0.95	0.02	0.00	-1.00	1.86	0.70	0.23	0.00	-0.81	-5.39
	POT	-0.34	1.12	0.01	0.49	-0.62	-0.14	1.21	0.01	3.23	4.15
	TOT	0.61	1.15	0.01	-0.51	1.24	0.56	1.44	0.01	2.42	-1.24
	p	-0.10	-0.01	-0.00	0.03	-0.04	-0.09	-0.02	-0.00	-0.13	0.08
i, q' (2)	KIN	0.07	0.51	0.00	5.83	2.20	0.00	0.55	0.01	3.20	21.75
	POT	-0.02	-0.82	-0.02	-5.14	-0.68	0.00	-1.38	-0.03	-5.67	-22.36
	TOT	0.05	-0.31	-0.02	0.69	1.52	0.00	-0.83	-0.02	-2.47	-0.61
	p	-0.01	0.04	0.00	-0.25	-0.10	-0.00	0.04	0.00	0.19	-0.32

and F_2 , and of type II+ in N_2 (because of the extreme polarization). It is fairly large in F_2 and N_2 but is quite small in Li_2 because of the relatively small ζ values and large internuclear distance.

The (ℓ, ℓ') and (ℓ, b') contributions, which are absent in Li_2 , are antibinding due to destructive interference in both F_2 and N_2 . The (ℓ, ℓ') contribution in both, as well as the (ℓ, b') contribution in F_2 , are normal, type I-, and quite small, compared to the (b, b') contributions. They are typical non-bonded repulsions. The (ℓ, b') contribution in N_2 is, however, of type II- and shows an unusually large repulsion because of the polarized nature of the ℓ and b orbitals. In the $N_2(BMAO)$ case, polarization is less pronounced and the repulsion decreases accordingly.

Because of small overlapping, there are no significant contributions in F_2 arising from the inner shells. In Li_2 and N_2 , however, there exists a comparatively large antibinding (i, b') contribution. It is normal, type I-, in Li_2 , but in N_2 the polarization of the b orbital leads to an extreme case of type II-, with a surprisingly large rise in the shielded nuclear attraction. In N_2 there is also a smaller, but quite significant, binding (i, ℓ') contribution which is an extreme case of type III- (here, the dative regions lie also on the far sides of the nuclei and there is a large drop in the shielded nuclear attraction).

The total σ contribution to the interference energy in Li_2 and N_2 is antibinding in all cases except one [$\text{Li}_2(\text{SAO})$, 0.39 eV; $\text{Li}_2(\text{BMAO})$, 0.13 eV; $\text{N}_2(\text{SAO})$, 5.32 eV; $\text{N}_2(\text{BMAO})$, -0.37 eV]. In Li_2 , this is due to the strong inner shell interaction, (i, b') ; in N_2 , it arises largely from the non-bonded repulsion of the (l, b') interaction.

Since there are no other interference terms in Li_2 , the result is that here the binding energy is entirely furnished by the quasi-classical effects, a consequence which is in complete contradiction to previous qualitative understanding and was already noted by Mulliken and Fraga. In N_2 , the similar behavior of the σ contribution is concealed by the strongly binding π interference.

Whether or not this result for Li_2 is characteristic for the actual molecular situation is, however, rather questionable. It may be an artifact since the deviations of Ransil's calculations from the virial theorem are larger than the interference energies in the case of Li_2 . It may well be that a more accurate calculation will find a negative interference contribution in Li_2 . The same may be true in N_2 . In fact, the BMAO approximation gives here a slightly attractive interference energy as well as a better approximation to the virial theorem. It may also be noted that, in Li_2 , the negative kinetic interference energy is clearly responsible for the contractive promotion which is seen to furnish a large part of

the potential energy drop.

On the other hand, it may be that in N_2 the strong π bonds pull the nuclei so close together that the σ orbitals are forced into non-binding or antibinding. In F_2 , where the antibinding repulsion of π lone pair contributions prevent a too close approach, the total σ contribution is binding.

σ contributions in Be_2 and C_2

The results for Be_2 and C_2 are quite different because of the large and peculiar influence of the ℓ and i orbitals. Also, the variations between the SAO and BMAO calculations are much greater. Due to the small population of the b orbitals, the negative $p(\ell, \ell')$ bond-orders are larger than all others. Furthermore, the $p(\ell, b')$ bond-orders are now positive, in contrast to the situation in N_2 and F_2 , so that the (ℓ, b') interference is binding; except in C_2 (BMAO), where it is almost zero.

The total σ interference energy is binding in all cases except one [Be_2 (SAO), -1.01 eV; Be_2 (BMAO), -4.54 eV; C_2 (SAO), +0.11 eV; C_2 (BMAO), -14.10 eV]. This binding effect is now due to the negative shielded nuclear attraction contributions being larger than the positive kinetic energy terms. This unusual situation is related to the 1S-2S hybridization and is paid for by opposing promotion effects associated with the expansion of the 1S orbital by hybridization.

The (b, b') contribution in both Be_2 and C_2 is an extreme

case of type II+ in which there is a decrease in shielded nuclear attraction as well as in kinetic energy. The energies are very small, however, because of the small bond-orders.

The (ℓ, ℓ') contribution in Be_2 and the SAO case of C_2 is normal (type I-), but because of the contracted nature of the ℓ orbitals, due to 1S admixture, the rise in kinetic energy and drop in shielded nuclear attraction are very large effects. In the BMAO case of Be_2 , where the ℓ orbitals are somewhat expanded, these effects are much smaller. In the BMAO calculation of C_2 , the (ℓ, ℓ') contribution is an extreme case of type III- and is strongly binding.

The (ℓ, b') contribution, for the SAO calculations, is of type III+ (binding) in Be_2 and of type I+ in C_2 . For the BMAO calculations, it is an extreme case of type II+ in Be_2 [similar to the (b, b') contribution] and is close to type III+ in C_2 . For the latter, the drop in kinetic energy and rise in shielded nuclear attraction are large effects while the total effect is only slightly antibinding.

The (i, b') contribution, for the SAO calculations, is of type I+ in Be_2 and of type I- in C_2 . For the BMAO calculations, it is similar to type III+ in Be_2 (and antibinding) while in C_2 it is of type I+.

The (i, ℓ') contribution is an extreme case of type III- (and therefore is binding) in $\text{Be}_2(\text{SAO})$, $\text{Be}_2(\text{BMAO})$ and in $\text{C}_2(\text{BMAO})$. It is of type I- in $\text{C}_2(\text{SAO})$.

These peculiar energy relationships in Be_2 and C_2 are very different from those obtained in the cases where the calculated wave function yields binding and describes a molecule near the equilibrium position. This is certainly not at all the case for the present Be_2 and C_2 calculations, and it is questionable whether the calculated wave functions could correspond to any stable physical situation.

Second-order contributions

For orbital pairs of different symmetry species, the bond-orders vanish and the interference energies arise solely from the exchange part of the electronic interactions. Such energy contributions are found for (i, π') , (ℓ, π') , (b, π') and $(\pi, \bar{\pi}')$ and occur only in C_2 , N_2 and F_2 . In all cases, they are negative, i.e., binding, in agreement with similar findings in other molecular analyses (12 and 13). [The only exception is the (ℓ, π') contribution in F_2 , but this term, like the others in F_2 , is insignificantly small.] In C_2 and N_2 , the combined effect of these terms is far from insignificant (-6.90 eV for C_2 and -7.48 eV for N_2 in the SAO approximation and only slightly smaller in the BMAO approximation). These interactions appear to be similar to the inter-atomic sharing penetration terms which will be discussed in the subsequent section. The specific nature of this decrease in electronic interaction is difficult to ascertain without a detailed study.

SHARING PENETRATION

The most striking feature of the sharing penetration energies is the parallelism existing between them and the interference effects. It confirms the idea that this part of the electronic repulsion energy is intimately related to the sharing of electrons. Also confirmed is the view that the over-all effect of these contributions is, in general, bond-opposing.

The parallelism mentioned arises from the fact that the exchange contributions to the inter-atomic pairpopulations reflect, to some degree, the behavior of the bond-orders for the various orbital pairs. For, each inter-atomic sharing penetration energy is essentially the negative product of such an exchange pairpopulation and the corresponding inter-orbital coulomb integral.

Table 4 collects the significant orbital and orbital-pair sharing penetration energies for all molecules in the SAO and BMAO approximations. For the inter-atomic terms there are also listed the corresponding exchange pairpopulations and bond-orders.

In every instance, the exchange pairpopulation has the same sign as the corresponding bond-order. Thus, the constructive interference of all (b,b') pairs is associated with a negative sharing penetration energy; much weaker for Be₂ and C₂ where these orbitals are poorly populated than in Li₂, F₂

Table 4. Comparison of main sharing penetration contributions

		Li ₂	N ₂	SAO F ₂	Be ₂	C ₂	Li ₂	N ₂	BMAO F ₂	Be ₂	C ₂
Inter-atomic Contributions											
b, b' (1)	E	-2.89	-10.70	-6.48	-0.14	-0.43	-2.81	-10.56	-6.55	-0.12	-0.34
	q _x	0.501	0.514	0.502	0.003	0.010	0.501	0.512	0.503	0.002	0.006
	p	0.564	0.587	0.817	0.054	0.075	0.570	0.627	0.799	0.046	0.065
q, q' (1)	E	---	0.04	0.04	1.13	1.69	---	0.40	0.04	1.74	1.96
	q _x	---	-0.004	-0.005	-0.138	-0.095	---	-0.037	-0.004	-0.228	-0.120
	p	---	-0.160	-0.138	-0.838	-0.751	---	-0.430	-0.135	-1.099	-0.827
q, b' (2)	E	---	0.96	0.20	-1.78	-3.66	---	0.90	0.22	-1.43	-2.84
	q _x	---	-0.062	-0.010	0.272	0.326	---	-0.059	-0.012	0.222	0.254
	p	---	-0.352	-0.194	0.405	0.469	---	-0.337	-0.206	0.351	0.437
π π' (2)	E	---	-5.72	0.02	---	-4.94	---	-5.64	0.02	---	-4.86
	q _x	---	0.500	-0.002	---	0.500	---	0.500	-0.002	---	0.500
	p	---	0.780	-0.094	---	0.760	---	0.772	-0.100	---	0.756
Intra-atomic Contributions											
b	E	1.67	4.74	7.07	1.46	2.69	1.63	5.03	6.78	1.45	2.51
q	E	---	-0.30	-0.04	0.43	1.94	---	-0.56	-0.05	-0.26	0.35
π	E	---	4.83	-0.03	---	4.02	---	4.83	-0.03	---	4.08
i	E	0.09	-0.02	0.00	-0.35	0.06	0.07	-0.02	0.00	-0.55	-1.18

and N_2 , with filled bonding orbitals. The destructive interference of the (l, l') pairs is associated with a positive sharing penetration energy, very weak in F_2 and N_2 , having small bond-orders, but rather substantial in Be_2 and C_2 , with large negative bond-orders. Most striking is the correlation for the (l, b') pair. The F_2 and N_2 molecules, with a moderate destructive interference, have a moderate positive sharing penetration contribution while, on the contrary, Be_2 and C_2 have substantial negative sharing penetration terms corresponding to marked constructive interference (the different behavior of Be_2 and C_2 has been discussed in the preceding section). Finally, the (π, π') orbital pair shows large negative sharing penetration energies for N_2 and C_2 where there exists a strong constructive interference, but only a very slight positive sharing penetration energy for F_2 where destructive interference generates non-bonded π repulsions. As a general rule, the sharing penetration terms are larger in magnitude in the case of constructive interference than for a comparable case of destructive interference.

These features of the inter-atomic sharing penetration energies also provide the key for understanding the intra-atomic sharing penetration energies. For, a change in the amount of inter-atomic sharing is always accompanied by compensating intra-atomic effects of opposite sign. Thus, the intra-atomic π contributions are large and positive in N_2

and C_2 while small and negative in F_2 . The positive sharing penetration energies for the bonding orbitals become intelligible if one appreciates that they compensate the inter-atomic contributions of the (b, b') pair and one of the two (l, b') pairs. This explains their positive sign and correlates with their magnitudes. Similarly, the intra-atomic sharing penetration energies for the l orbitals must be considered as compensation for the inter-atomic (l, l') pair and the remaining (l, b') term. In this way, one can see why F_2 and N_2 have negative contributions whereas C_2 and Be_2 have positive contributions, all relatively weak.

These arguments gloss over the inner shell and the other cross term contributions. While they are generally unimportant, they are not altogether negligible as can be seen by the intra-atomic contributions included in the summary table.

There is a remarkable consistency between the results derived from the SAO and BMAO approximations so that the differences hardly merit elaboration except maybe for the change in sign of the intra-atomic lone-pair contribution in Be_2 . This value is, however, consistent in that it compensates for the corresponding inter-atomic effects.

In general, but not always, the sum of compensating intra- and inter-atomic contributions will be positive. The molecular sums of all sharing penetration terms are always positive, i.e., bond opposing, as mentioned before.

CONCLUSIONS

There exists a significant difference between the present study and that of the hydrides. All members of the latter series exhibited qualitative similarities, the differences in their energy partitionings were of a quantitative nature and conformed to simple trends. In contrast, the members of the homonuclear series have far greater individualities so that the energy partitioning yields not only differences in degree but also in kind. The pattern of individual terms is much more varied, cross-interactions more complicated, occasional erratic behavior more common.

The execution of the analysis has yielded new information regarding the behavior of the various energy terms, such as the quasi-classical and interference interactions, under more complicated conditions. It has shed light on the deeper differences between the five molecules treated, particularly as regards the differences between the group of Be_2 and C_2 and the rest of the molecules. The difficulties encountered in the analysis may in part suggest a need for improvements in the method but they reveal, at least to an equal degree, serious deficiencies in the wave functions analyzed. A similar analysis of analogous, but better, wave functions would therefore be very instructive, in particular if carried out as a function of the internuclear distance.

Even under the present handicaps, many general ground

rules are always obeyed by the individual energy fragments defined in the present partitioning; such as, for example the instrumental role of contractive promotion in the lowering of the potential energy upon molecular formation.

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APPENDIX: PRESENTATION OF NUMERICAL RESULTS

Each of the figures, 3 through 17, represents the complete molecular analysis for one of the fifteen calculations. The molecules are arranged in order of increasing molecular weight. For each molecule, the approximations are listed in the order: SAO, BAO, BMAO.

Within each molecular analysis, the first section, labelled "Binding Energy Partitioning", gives a summary of the binding energy totals for the various energetic effects: promotion (both hybridization and contraction), quasi-classical, sharing penetration, sharing interference and the total. It lists the binding energy fragments by atom and bond (and for the molecule), decomposed in terms of kinetic interactions (KIN) and potential interactions. For the intra-atomic promotion contributions, the latter are subdivided into nuclear attraction (NA) and other electronic interactions (OEI). For all other intra- and inter-atomic contributions, the potential contributions are decomposed into shielded nuclear attraction (SNA) and other electronic interactions (OEI). Non-zero contraction promotion occurs for the BMAO cases only.

The second section, labelled "Valence Atomic Orbitals", gives the VAO decompositions in terms of orthogonal Slater-type-orbital basis functions. It also lists the inter-atomic overlap integrals of the VAO's. In this section, as well as in the following sections, the $\overline{\pi}$ terms are not included

since they are identical to the π terms.

The third section, labelled "Density Contributions", gives the populations and inter-atomic bond-orders of the VAO's. The valence inactive (p), the valence active (v), and the total (q) electronic populations are given for each orbital.

The fourth section, entitled "Exchange Contributions to Pairpopulations", gives the decomposition of the interference-free intra- and inter-atomic orbital pair coefficients of the exchange pair-density, $\pi_x(x_1, x_2)$, in terms of promotion state and sharing penetration contributions. The latter is subdivided into intra- and inter-atomic orbital pair fragments.

The last two tables give the detailed partitioning, according to orbitals and orbital pairs, of the intra- and inter-atomic summary presented in the first table ("Binding Energy Partitioning") discussed above. The intra-atomic promotion effects are given in terms of the orthogonal spherical atomic orbitals while the intra-atomic sharing penetration as well as all inter-atomic effects are given in terms of the VAO's. In the SNA rows of the inter-atomic sharing interference column, the left entry gives the potential interaction of the interference density, arising from the orbital pair (Aa, Bb), with the neutral atom A while the right entry gives that interaction with the neutral atom B. Equivalent orbital pair con-

tributions to the inter-atomic energies are given only once, e.g., the (b,i') contribution is not included since it is equivalent to the (i,b') contribution which is given. (See the discussion about the weighting factor in the chapter on the quasi-classical interactions.) All energy terms in these tables are in units of electron volts.

BINDING ENERGY PARTITIONING

		Promotion		Quasi-Classical	Sharing		Total
		PRH	PRC		Penetration	Interference	
Li	KIN	0.53	0.00				0.53
	NA	-0.92	0.00				-0.92
	OBI	0.31	0.00		1.76		2.07
	TOT	-0.07	0.00		1.76		1.69
BOND	KIN					-1.57	-1.57
	SNA			-1.08		0.99 0.99	0.90
	OBI				-2.82	-0.02	-2.84
	TOT			-1.08	-2.82	0.39	-3.51
Li ₂	KIN	1.06	0.00			-1.57	-0.51
	SNA	-1.84	0.00	-1.08		0.99 0.99	-0.94
	OBI	0.62	0.00		0.69	-0.02	1.27
	TOT	-0.14	0.00	-1.08	0.69	0.39	-0.14

VALENCE ATOMIC ORBITALS

Orbital	VAO Expansion			Overlap Integrals		
	1S	2S	2P _z	i	b	l
1	0.999797	-0.001960	0.001150	0.000086	0.090536	0.094319
b	0.001652	0.974527	0.224262	0.090536	0.773882	0.360853
1	-0.001560	-0.224260	0.974528	0.094319	0.360853	0.030649

DENSITY CONTRIBUTIONS

Orbital	VAO Populations			Inter-Atomic Bond-Orders		
	p	v	q	i	b	l
1	2.014623	-0.009862	2.004761	-0.004360	-0.100996	-0.007613
b	0.568954	0.427112	0.996066	-0.100996	0.563902	-0.000361
1	0.000029	-0.000856	-0.000826	-0.007613	-0.000361	0.001000

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State			Sharing Penetration					
	(Intra-Atomic)			(Intra-Atomic)			(Inter-Atomic)		
	i	b	l	i	b	l	i	b	l
1	2.012	-0.007	0.000	-0.000	0.006	-0.000	0.000	-0.005	-0.001
b	-0.007	1.004	-0.001	0.006	-0.503	0.001	-0.005	0.501	-0.000
1	0.000	-0.001	0.000	-0.000	0.001	-0.000	-0.001	-0.000	0.000

Figure 3. Binding energy decomposition and description of electron distribution for Li₂, SAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion				Total	Orbital	Sharing Penetration	
	1S	2S	2P _z					
1S	KIN	0.47	0.05	0.00	0.46	1	KIN	
	NA	-1.05	-0.05	0.00	-1.04		SNA	
	OEI	0.21	-0.38	0.44	0.24		OEI	0.09
	TOT	-0.37	-0.39	0.44	-0.33		TOT	0.09
2S	KIN	0.05	-0.31	0.00	-0.21	b	KIN	
	NA	-0.05	1.53	0.00	1.42		SNA	
	OEI	-0.38	0.01	-0.00	-0.79		OEI	1.67
	TOT	-0.39	1.23	-0.00	0.42		TOT	1.67
2P _z	KIN	0.00	0.00	0.28	0.28	1	KIN	
	NA	0.00	0.00	-1.31	-1.31		SNA	
	OEI	0.44	-0.00	-0.00	0.87		OEI	-0.00
	TOT	0.44	-0.00	-1.03	-0.16		TOT	-0.00
Li	KIN				0.53	Li	KIN	
	NA				-0.92		SNA	
	OEI				0.31		OEI	1.76
	TOT				-0.07		TOT	1.76

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

Li	Li	Quasi- Classical	Sharing			Total
			Penetration	Interference		
1	1	KIN				
		SNA	.00			
		OEI				
		TOT	.00			
1	b	KIN				
		SNA	-.04			
		OEI		.03		
		TOT	-.04	.03		
1	1	KIN				
		SNA	.00			
		OEI		.00		
		TOT	.00	.00		
b	b	KIN				
		SNA	-1.01			
		OEI				
		TOT	-1.01			
b	1	KIN				
		SNA	.00			
		OEI		.00		
		TOT	.00	.00		
1	1	KIN				
		SNA	.00			
		OEI		.00		
		TOT	.00	.00		
Li ₂	2	KIN				
		SNA	-1.03			
		OEI				
		TOT	-1.03			

Figure 3. (Continued)

BINDING ENERGY DECOMPOSITION

		Promotion		Quasi- Classical	Sharing		Total
		PHH	IRC		Penetration	Interference	
E ₁	KIN	0.66	0.00				0.66
	NA	-1.04	0.00				-1.04
	Li1	0.32	0.00		1.72		2.04
	Li2	-0.17	0.00		1.72		1.65
E ₂	KIN					-1.34	-1.34
	SMA			-1.15		0.00	-1.15
	Li1				-2.81	-0.03	-2.84
	Li2				-2.81	0.02	-2.79
E ₃	KIN	1.32	0.00			-1.34	-0.02
	SMA	-2.00	0.00	-1.15		0.00	-3.15
	Li1	0.60	0.00		0.65	-0.03	1.22
	Li2	-0.18	0.00	-1.15	0.65	0.52	-0.14

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals		
	1s	2s	2p	i	b	l
1	0.999984	-0.005612	-0.000127	-0.000697	0.090091	0.093992
b	0.005554	0.972244	0.233904	0.090091	0.793147	0.350569
l	-0.001205	-0.233901	0.972260	0.093992	0.350569	0.013164

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders		
	s	v	p	i	b	l
1	2.014166	-0.009577	2.004610	-0.002742	-0.099788	-0.006262
b	0.562744	0.433824	0.996368	-0.099788	0.557506	-0.000310
l	0.000020	-0.000697	-0.000677	-0.006262	-0.000310	0.000000

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State			Sharing Penetration					
	(Intra-Atomic)			(Intra-Atomic)			(Inter-Atomic)		
	i	b	l	i	b	l	i	b	l
1	2.012	-0.007	0.000	-0.000	0.006	-0.000	0.000	-0.005	-0.001
b	-0.007	1.004	-0.001	0.006	-0.502	0.001	-0.005	0.501	-0.000
l	0.000	-0.001	0.000	-0.000	0.001	-0.000	-0.001	-0.000	0.000

Figure 4. Binding energy decomposition and description of electron distribution for Li₂, BAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion				Total	Orbital	Sharing Penetration	
	1S	2S	2P _a					
1s	KIN	0.45	0.11	0.00	0.43	i	KIN	
	NA	-1.00	-0.13	0.00	-0.98		SNA	
	OEI	0.21	-0.41	0.47	0.24		OEI	0.08
	TOT	-0.35	-0.43	0.47	-0.31		TOT	0.08
2s	KIN	0.11	-0.32	0.00	-0.07	b	KIN	
	NA	-0.13	1.62	0.00	1.34		SNA	
	OEI	-0.41	0.01	-0.00	-0.85		OEI	1.64
	TOT	-0.43	1.31	-0.00	0.42		TOT	1.64
2P _a	KIN	0.00	0.00	0.30	0.30	i	KIN	
	NA	0.00	0.00	-1.40	-1.40		SNA	
	OEI	0.47	-0.00	-0.00	0.93		OEI	-0.00
	TOT	0.47	-0.00	-1.10	-0.18		TOT	-0.00
Li	KIN				0.66	Li	KIN	
	NA				-1.04		SNA	
	OEI				0.32		OEI	1.72
	TOT				-0.07		TOT	1.72

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

Li	Li	Quasi-Classical	Sharing		Total	
			Penetration	Interference		
i	i	KIN			-0.22	-0.22
		SNA	.22		.22	.22
		OEI		-0.22	.22	-0.22
		TOT	.22	-0.22	-0.22	-0.22
i	b	KIN			.92	.92
		SNA	-0.24		-0.23	-0.31
		OEI		.23	-0.22	.22
		TOT	-0.24	.23	.63	.62
i	i	KIN			.26	.26
		SNA	.22		-0.21	-0.21
		OEI		.22	-0.22	.22
		TOT	.22	.22	.24	.25
b	b	KIN			-3.29	-3.29
		SNA	-1.27		1.23	1.39
		OEI		-2.83	.21	-2.87
		TOT	-1.27	-2.83	-0.23	-4.75
b	i	KIN			.22	.22
		SNA	.22		.22	.22
		OEI		.22	.22	.22
		TOT	.22	.22	.22	.22
i	i	KIN			.22	.22
		SNA	.22		.22	.22
		OEI		.22	.22	.22
		TOT	.22	.22	.22	.22
Li ₂	2	KIN			-1.34	-1.34
		SNA	-1.15		.94	.73
		OEI		-2.81	-0.23	-2.84
		TOT	-1.15	-2.81	.52	-3.45

Figure 4. (Continued)

BINDING ENERGY PARTITIONING

		Promotion		Quasi-	Sharing		Total
		PRH	PRC	Classical	Penetration	Interference	
Li	KIN	0.76	0.83				1.19
	SNA	-1.01	-0.52				-1.52
	CEI	0.27	0.10		1.69		2.07
	TOT	0.03	0.02		1.69		1.74
BOND	KIN					-1.56	-1.56
	SNA			-1.01		0.86 0.86	-0.71
	CEI				-2.76	-0.02	-2.79
	TOT			-1.01	-2.76	0.13	-3.64
Li ₂	KIN	1.52	0.86			-1.56	0.82
	SNA	-2.02	-1.04	-1.01		0.86 0.86	-2.33
	CEI	0.54	0.20		0.63	-0.02	1.35
	TOT	0.06	0.04	-1.01	0.63	0.13	-0.15

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals		
	1s	2s	2p _z	i	b	l
i	0.999893	-0.013662	-0.005154	-0.002624	0.076846	0.075849
b	0.014447	0.976858	0.213401	0.076846	0.754394	0.315428
l	0.002119	-0.213452	0.976951	0.075849	0.315428	0.146538

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders		
	p	v	q	i	b	l
i	2.009760	-0.006810	2.002950	0.002354	-0.088041	-0.000505
b	0.573862	0.423232	0.997095	-0.088041	0.570001	-0.000022
l	0.000000	-0.000045	-0.000045	-0.000505	-0.000022	0.000000

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State			Sharing Penetration					
	(Intra-Atomic)			(Intra-Atomic)			(Inter-Atomic)		
	i	b	l	i	b	l	i	b	l
i	2.008	-0.005	0.000	-0.000	0.004	0.000	0.000	-0.004	-0.000
b	-0.005	1.002	-0.000	0.004	-0.501	0.000	-0.004	0.501	0.000
l	0.000	-0.000	0.000	0.000	0.000	0.000	-0.000	0.000	0.000

Figure 5. Binding energy decomposition and description of electron distribution for Li₂, BMAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion									Orbital	Sharing Penetration	
	1S		2S		2P _z		Total		TOT			
	PRH	PRC	PRH	PRC	PRH	PRC	PRH	PRC	TOT			
1S	KIN	0.27	0.42	0.25	-0.00	0.00	0.00	0.24	0.42	0.65	KIN	
	NA	-0.60	-0.47	-0.28	0.00	0.00	0.00	-0.57	-0.44	-1.01	SNA	
	OEI	0.15	0.05	-0.34	-0.05	0.39	0.07	0.17	0.07	0.24	OEI	0.07
	TOT	-0.18	0.00	-0.37	-0.05	0.39	0.07	-0.16	0.04	-0.12	TOT	0.07
2S	KIN	0.25	-0.00	-0.26	-0.09	0.00	0.00	0.27	-0.09	0.18	KIN	
	NA	-0.28	0.00	1.34	0.18	0.00	0.00	0.74	0.16	0.90	SNA	
	OEI	-0.34	-0.05	0.02	0.00	-0.00	-0.00	-0.68	-0.11	-0.79	OEI	1.63
	TOT	-0.37	-0.05	1.09	0.09	-0.00	-0.00	0.33	-0.04	0.29	TOT	1.63
2P _z	KIN	0.00	0.00	0.00	0.00	0.25	0.11	0.25	0.11	0.36	KIN	
	NA	0.00	0.00	0.00	0.00	-1.18	-0.23	-1.18	-0.23	-1.41	SNA	
	OEI	0.39	0.07	-0.00	-0.00	-0.00	-0.00	0.78	0.15	0.93	OEI	-0.00
	TOT	0.39	0.07	-0.00	-0.00	-0.93	-0.12	-0.15	0.02	-0.12	TOT	-0.00
Li	KIN							0.76	0.43	1.19	KIN	
	NA							-1.01	-0.52	-1.52	SNA	
	OEI							0.27	0.10	0.38	OEI	1.69
	TOT							0.03	0.02	0.05	TOT	1.69

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

Li	Li	Quasi-Classical	Sharing			Total
			Penetration	Interference		
1	1	KIN				.20
		SNA	-.20		-.20	-.20
		OEI		.20	-.20	-.20
		TOT	-.20	.20	-.20	-.20
1	b	KIN			.70	.70
		SNA	-.24		-.29	-.16
		OEI		.22	-.22	.21
		TOT	-.24	.22	.56	.54
1	1	KIN			.20	.20
		SNA	.20		-.20	-.20
		OEI		.20	.20	.20
		TOT	.20	.20	.20	.20
b	b	KIN			-2.97	-2.97
		SNA	-.94		.98	1.23
		OEI		-2.31	.01	-2.30
		TOT	-.94	-2.31	-.99	-4.74
b	1	KIN			.20	.20
		SNA	.20		.20	.20
		OEI		.20	-.20	.20
		TOT	.20	.20	.20	.20
1	1	KIN			.20	.20
		SNA	.20		.20	.20
		OEI		.20	.20	.20
		TOT	.20	.20	.20	.20
Li ₂		KIN			-1.56	-1.56
		SNA	-1.21		.86	.71
		OEI		-2.76	-.22	-2.79
		TOT	-1.21	-2.76	.13	-3.84

Figure 5. (Continued)

BINDING ENERGY PARTITIONING

		Promotion		Quasi- Classical	Sharing		Total
		FRH	FRC		Penetration	Interference	
Be	MIN	-7.46	0.00				-7.46
	SHA	11.90	0.00				11.90
	CEI	-2.55	0.00		1.54		-1.01
	TOT	1.90	0.00		1.54		3.44
Be ₂	MIN					17.55	17.55
	SHA			-1.87		-0.03	-1.90
	CEI				-2.40	-0.50	-2.90
	TOT			-1.87	-2.40	-1.01	-5.28
Be ₂	MIN	-14.92	0.00			17.55	2.63
	SHA	23.90	0.00	-1.87		-0.03	3.07
	CEI	-5.10	0.00		0.80	-0.50	-5.00
	TOT	3.90	0.00	-1.87	0.80	-1.01	1.52

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals		
	1s	2s	2p _z	i	l	b
i	0.986516	0.162752	-0.017240	0.026658	0.115866	0.177652
l	-0.163621	0.983154	-0.081465	0.115866	0.402467	0.450900
b	0.003691	0.083187	0.996527	0.177652	0.450900	0.369155

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders		
	d	v	g	i	l	b
i	2.016319	-0.025264	1.891055	-0.064077	-0.252653	0.032190
l	1.869701	-0.183275	1.655826	-0.252653	-0.838421	0.405489
b	0.114658	0.208462	0.323120	0.032190	0.405489	0.053928

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State			Sharing Penetration					
	(Intra-Atomic)			(Intra-Atomic)			(Inter-Atomic)		
	i	l	b	i	l	b	i	l	b
i	1.997	-0.001	-0.005	-0.000	0.002	0.004	-0.001	-0.013	0.008
l	-0.001	1.514	0.072	0.002	-0.036	-0.086	-0.013	-0.138	0.272
b	-0.005	0.072	0.256	0.004	-0.086	-0.201	0.008	0.272	0.003

Figure 6. Binding energy decomposition and description of electron distribution for Be₂, SAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion				Total	Orbital	Sharing Penetration	
	1S	2S	2P _v					
1S	KIN	-3.19	-2.07	0.00	-3.40	1	KIN	
	NA	6.90	2.24	0.00	7.13		SNA	
	OEI	-2.24	-4.51	4.37	-2.71		OEI	-0.35
	TOT	1.47	-4.34	4.37	1.02		TOT	-0.35
2S	KIN	-2.07	-4.43	0.00	-8.35	1	KIN	
	NA	2.24	18.17	0.00	22.42		SNA	
	OEI	-4.51	-3.67	2.23	-12.67		OEI	0.43
	TOT	-4.34	10.07	2.23	1.39		TOT	0.43
2P _v	KIN	0.00	0.00	4.30	4.30	b	KIN	
	NA	0.00	0.00	-17.65	-17.65		SNA	
	OEI	4.37	2.23	-0.81	12.84		OEI	1.46
	TOT	4.37	2.23	-14.16	-0.51		TOT	1.46
Be	KIN				-7.46	Be	KIN	
	NA				11.90		SNA	
	OEI				-2.55		OEI	1.54
	TOT				1.90		TOT	1.54

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

Be Be		Quasi-Classical	Sharing			Total
			Penetration	Interference		
1 1	KIN			.57		.57
	SNA	-.22			-.28	-.55
	OEI		.21		-.21	-.21
	TOT	-.22	.21		.21	.21
1 1	KIN			5.83		5.83
	SNA	-.23			-4.17	-5.27
	OEI		.12		-.12	.21
	TOT	-.23	.12		.69	.76
1 b	KIN			-1.22		-1.22
	SNA	-.25			.48	.46
	OEI		-.26		-.21	-.27
	TOT	-.25	-.26		-.51	-.61
1 1	KIN			22.72		22.72
	SNA	-.34			-12.28	-22.49
	OEI		1.13		-.26	.86
	TOT	-.34	1.13		.32	1.29
1 b	KIN			-6.68		-6.68
	SNA	-.59			5.47	5.42
	OEI		-1.78		.21	-1.73
	TOT	-.59	-1.73		-.69	-3.66
b b	KIN			-.24		-.24
	SNA	-.19			-.13	-.45
	OEI		-.14		-.22	-.17
	TOT	-.19	-.14		-.32	-.66
Be ₂	KIN				17.55	17.55
	SNA	-1.87			-9.23	-19.93
	OEI		-2.43		-.51	-2.98
	TOT	-1.87	-2.43		-1.21	-5.36

Figure 6. (Continued)

BINDING ENERGY PARTITIONING

		Promotion		Quasi- Classical	Sharing		Total
		PRH	PRC		Penetration	Interference	
Be	KIN	-11.14	0.00				-11.14
	NA	10.46	0.00				10.46
	CEI	-4.19	0.00		1.01		-3.18
	TOT	3.16	0.00		1.01		4.17
BOND	KIN					25.56	25.56
	SNA			-2.02		-13.64	-29.30
	CEI				-2.37	-0.70	-3.07
	TOT			-2.02	-2.37	-2.40	-6.79
Be ₂	KIN	-22.26	0.00			25.56	3.30
	SNA	36.96	0.00	-2.02		-13.64	7.66
	CEI	-8.38	0.00		-0.34	-0.70	-9.43
	TOT	6.32	0.00	-2.02	-0.34	-2.40	1.55

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals		
	1s	2S	2P _z	i	l	b
i	0.974432	0.223560	-0.022222	0.043624	0.143376	0.208619
l	-0.224621	0.971664	-0.073320	0.143376	0.402898	0.444780
b	0.005200	0.076436	0.997061	0.208619	0.444780	0.355059

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders		
	p	v	o	i	l	b
i	2.018503	-0.037185	1.981319	-0.102796	-0.314162	0.059165
l	1.903619	-0.207965	1.692654	-0.314162	-0.247936	0.401794
b	0.114871	0.210956	0.325827	0.059165	0.401794	0.056056

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State			Sharing Penetration					
	(Intra-Atomic)			(Intra-Atomic)			(Inter-Atomic)		
	i	l	b	i	l	b	i	l	b
i	1.987	0.000	-0.006	-0.000	0.001	0.003	-0.002	-0.020	0.017
l	0.000	1.628	0.064	0.001	-0.029	-0.079	-0.020	-0.140	0.267
b	-0.006	0.064	0.267	0.003	-0.079	-0.212	0.017	0.267	0.003

Figure 7. Binding energy decomposition and description of electron distribution for Be₂, BA0 approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion				Total	Orbital	Sharing Penetration	
	1S	2S	2P _σ					
1s	KIN	-6.15	-2.57	0.00	-6.66	1	KIN	
	NA	13.34	2.79	0.00	13.90		SNA	
	OEI	-3.99	-4.44	4.26	-4.89		OEI	-0.62
	TOT	3.21	-4.22	4.26	2.35		TOT	-0.62
2s	KIN	-2.57	-4.01	0.00	-8.63	1	KIN	
	NA	2.79	16.94	0.00	21.96		SNA	
	OEI	-4.44	-3.53	2.27	-11.98		OEI	0.18
	TOT	-4.22	9.41	2.27	1.35		TOT	0.18
2P _σ	KIN	0.00	0.00	4.15	4.15	b	KIN	
	NA	0.00	0.00	-17.38	-17.38		SNA	
	OEI	4.26	2.27	-0.85	12.68		OEI	1.45
	TOT	4.26	2.27	-14.07	-0.54		TOT	1.45
Be	KIN				-11.14	Be	KIN	
	NA				18.48		SNA	
	OEI				-4.19		OEI	1.01
	TOT				3.16		TOT	1.01

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

Be Be		Quasi-Classical	Sharing			Total
			Penetration	Interference		
i i	KIN			1.42		1.42
	SNA	-.00		-.72	-.72	-1.45
	OEI		.02	-.04		-.02
	TOT	-.00	.02	-.07		-.05
i l	KIN			8.84		8.84
	SNA	-.05		-6.61	-1.78	-8.43
	OEI		.16	-.15		.01
	TOT	-.05	.16	.30		.41
i b	KIN			-2.03		-2.03
	SNA	-.07		1.30	.26	1.29
	OEI		-.12	-.01		-.13
	TOT	-.07	-.12	-.69		-.87
l l	KIN			26.14		26.14
	SNA	-.39		-13.74	-13.74	-27.86
	OEI		1.14	-.27		.87
	TOT	-.39	1.14	-1.61		-.85
l b	KIN			-7.79		-7.79
	SNA	-.60		7.51	.48	7.39
	OEI		-1.73	-.02		-1.75
	TOT	-.60	-1.73	.16		-2.15
b b	KIN			-.01		-.01
	SNA	-.21		-.14	-.14	-.49
	OEI		-.14	-.02		-.17
	TOT	-.21	-.14	-.32		-.67
Be ₂	KIN				25.58	25.58
	SNA	-2.02		-13.64	-13.64	-29.30
	OEI		-2.37	-.70		-3.07
	TOT	-2.02	-2.37	-2.46		-6.79

Figure 7. (Continued)

BINDING ENERGY PARTITIONING

		Promotion		Quasi- Classical	Sharing		Total
		PRM	PRC		Penetration	Interference	
Be	KIN	-0.69	1.33				0.65
	SEA	6.75	-2.56				4.19
	OBI	-2.22	1.35		0.63		-0.24
	TOT	3.84	0.12		0.63		4.60
Be	KIN			-1.98		4.19	4.19
	SEA				-1.28	-3.61	-7.10
	OBI				-1.28	-1.50	-2.78
	TOT			-1.98	-1.28	-4.54	-7.70
Be ₂	KIN	-1.38	2.66			4.19	5.47
	SEA	13.50	-5.12	-1.98		-3.61	-0.72
	OBI	-4.44	2.70		-0.01	-1.50	-3.25
	TOT	7.58	0.24	-1.98	-0.01	-4.54	1.50

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals		
	1s	2s	2p _z	i	l	b
i	0.958675	-0.284454	0.005251	0.008697	-0.087194	-0.035734
l	0.284400	0.957672	-0.044513	-0.087194	0.474305	0.456030
b	0.007633	0.044167	0.998995	-0.035734	0.406030	0.366489

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders		
	p	v	q	i	l	b
i	1.998169	-0.012324	1.985845	-0.019420	0.191204	-0.126391
l	2.156202	-0.395455	1.760748	0.191204	-1.099352	0.351316
b	0.087414	0.163993	0.253408	-0.126391	0.351316	0.045928

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State			Sharing Penetration					
	(Intra-Atomic)			(Intra-Atomic)			(Inter-Atomic)		
	i	l	b	i	l	b	i	l	b
i	1.980	0.001	0.005	-0.000	0.000	-0.005	-0.000	-0.007	0.012
l	0.001	1.789	-0.029	0.000	-0.001	0.013	-0.007	-0.228	0.222
b	0.005	-0.029	0.278	-0.005	0.013	-0.244	0.012	0.222	0.002

Figure 8. Binding energy decomposition and description of electron distribution for Be₂, BMAC approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion									Orbital	Sharing Penetration	
	1S		2S		2P _a		Total		TOT			
	PRH	PRC	PRH	PRC	PRH	PRC	PRH	PRC	TOT			
1s	KIN	-6.00	-0.04	2.55	0.01	0.00	0.00	-5.35	-0.05	-5.40	KIN	
	NA	13.02	0.04	-2.77	-0.01	0.00	0.00	12.32	0.05	12.36	SNA	
	OEI	-3.44	-0.01	-2.65	0.03	3.25	0.57	-4.13	-0.01	-4.14	OEI	-0.55
	TOT	3.59	-0.00	-2.87	0.03	3.25	0.57	2.83	-0.01	2.83	TOT	-0.55
2s	KIN	2.55	0.01	-2.98	0.11	0.00	0.00	1.47	0.13	1.60	KIN	
	NA	-2.77	-0.01	12.62	-0.19	0.00	0.00	7.78	-0.20	7.58	SNA	
	OEI	-2.65	0.03	-3.22	0.01	2.19	0.17	-8.16	0.08	-8.08	OEI	-0.26
	TOT	-2.87	0.03	6.41	-0.07	2.19	0.17	1.09	0.00	1.10	TOT	-0.26
2P _a	KIN	0.00	0.00	0.00	0.00	3.19	1.25	3.19	1.25	4.44	KIN	
	NA	0.00	0.00	0.00	0.00	-13.34	-2.41	-13.34	-2.41	-15.75	SNA	
	OEI	3.25	0.57	2.19	0.17	-1.13	-0.20	10.07	1.28	11.35	OEI	1.45
	TOT	3.25	0.57	2.19	0.17	-11.28	-1.35	-0.09	0.13	0.04	TOT	1.45
Be	KIN							-0.69	1.33	0.65	KIN	
	NA							6.75	-2.56	4.19	SNA	
	OEI							-2.22	1.35	-0.87	OEI	0.63
	TOT							3.84	0.12	3.96	TOT	0.63

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

Be Be		Quasi-Classical	Sharing			Total
			Penetration	Interference		
i i	KIN			.46		.46
	SNA	-.01		-.07	-.07	-.15
	OEI		.02	-.04		-.03
	TOT	-.01	.02	-.11		-.12
i l	KIN			3.22		3.22
	SNA	-.10		-5.21	.12	-5.21
	OEI		.26	-.57		-.32
	TOT	-.12	.26	-2.47		-2.32
i b	KIN			3.29		3.29
	SNA	-.05		-.04	-.04	-.13
	OEI		-.03	-.02		-.05
	TOT	-.05	-.08	-.06		-.19
l l	KIN			3.22		3.22
	SNA	-.70		-1.23	-1.23	-2.15
	OEI		1.74	-.26		1.49
	TOT	-.70	1.74	.51		1.55
l b	KIN			-1.86		-1.86
	SNA	-.40		-1.12	.72	-.80
	OEI		-1.43	.02		-1.43
	TOT	-.40	-1.43	-2.26		-4.09
b b	KIN			-.17		-.17
	SNA	-.07		-.26	-.06	-.39
	OEI		-.12	-.02		-.14
	TOT	-.07	-.12	-.32		-.52
Be ₂	KIN			4.15		4.15
	SNA	-1.38		-3.61	-3.61	-4.99
	OEI		-1.28	-1.56		-2.84
	TOT	-1.38	-1.28	-4.54		-7.20

Figure 8. (Continued)

BINDING ENERGY PARTITIONING

		Promotion		Quasi-	Sharing		Total
		PRH	PHC	Classical	Penetration	Interference	
C	KIN	-1.31	0.00				-1.31
	NA	3.61	0.00				3.61
	OEI	3.81	0.00		12.73		16.54
	TOT	6.12	0.00		12.73		18.85
Bond	KIN					-17.08	-17.08
	SNA			-1.85		-0.05	-1.90
	OEI				-15.78	-1.38	-17.17
	TOT			-1.85	-15.78	-19.37	-37.00
C ₂	KIN	-2.62	0.00			-17.88	-20.50
	SNA	7.22	0.00	-1.85		-0.05	5.27
	OEI	7.62	0.00		9.69	-1.38	15.93
	TOT	12.23	0.00	-1.85	9.69	-19.37	0.70

VALENCE ATOMIC ORBITALS

Orbital	VAO Expansion			Overlap Integrals			
	1S	2S	2P _z	i	l	b	π
i	0.999963	0.002605	-0.008241	-0.001224	0.045482	0.106141	0
l	-0.003638	0.991772	-0.127968	0.045482	0.368105	0.458548	0
b	0.007839	0.127993	0.991744	0.106141	0.458548	0.423028	0
π	(Unhybridized)			0	0	0	0.316034

DENSITY CONTRIBUTIONS

Orbital	VAO Populations			Inter-Atomic Bond-Orders			
	p	v	q	i	l	b	π
i	2.011353	-0.008422	2.002931	-0.001270	-0.098251	-0.037259	0
l	1.651663	-0.066011	1.585653	-0.098251	-0.751039	0.468696	0
b	0.168513	0.242903	0.411416	-0.037259	0.468696	0.075499	0
π	0.759858	0.240141	1.000000	0	0	0	0.759858

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	i	l	b	π	i	l	b	π	i	l	b	π
i	2.008	-0.001	-0.002	-0.002	0.000	0.001	0.001	0.002	0.000	-0.002	-0.003	0
l	-0.001	1.398	0.041	0.074	0.001	-0.034	-0.049	-0.074	-0.002	-0.095	0.326	0
b	-0.002	0.041	0.158	0.107	0.001	-0.049	-0.071	-0.107	-0.003	0.326	0.010	0
π	-0.002	0.074	0.107	0.660	0.002	-0.074	-0.107	-0.160	0	0	0	0.500
$\bar{\pi}$	-0.002	0.074	0.107	0.160	0.002	-0.074	-0.107	-0.160	0	0	0	0

Figure 9. Binding energy decomposition and description of electron distribution for C₂, SAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

		Promotion							Sharing Penetration	
Orbital		1S	2S	2P σ	2P π	2P $\bar{\pi}$	Total	Orbital		
1s	KIN	1.25	0.01	0.00	0.00	0.00	1.25	1	KIN	
	NA	-2.63	-0.01	0.00	0.00	0.00	-2.63		SNA	
	OEI	0.29	-9.38	9.47	0.08	0.08	0.72		OEI	0.06
	TOT	-1.09	-9.38	9.47	0.08	0.08	-0.66		TOT	0.06
2s	KIN	0.01	-18.05	0.00	0.00	0.00	-18.03	1	KIN	
	NA	-0.01	63.40	0.00	0.00	0.00	63.37		SNA	
	OEI	-9.38	-6.43	4.75	-3.69	-3.69	-41.39		OEI	1.94
	TOT	-9.38	38.91	4.75	-3.69	-3.69	3.95		TOT	1.94
2P σ	KIN	0.00	0.00	15.47	0.00	0.00	15.47	b	KIN	
	NA	0.00	0.00	-57.13	0.00	0.00	-57.13		SNA	
	OEI	9.47	4.75	0.06	2.49	2.49	39.75		OEI	2.69
	TOT	9.47	4.75	-41.60	2.49	2.49	-1.91		TOT	2.69
2P π	KIN	0.00	0.00	0.00	0.00	0.00	0.00	π	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	0.08	-3.69	2.49	3.44	-1.07	2.37		OEI	4.02
	TOT	0.08	-3.69	2.49	3.44	-1.07	2.37		TOT	4.02
2P $\bar{\pi}$	KIN	0.00	0.00	0.00	0.00	0.00	0.00	$\bar{\pi}$	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	0.08	-3.69	2.49	-1.07	3.44	2.37		OEI	4.02
	TOT	0.08	-3.69	2.49	-1.07	3.44	2.37		TOT	4.02
c	KIN						-1.31	c	KIN	
	NA						3.61		SNA	
	OEI						3.81		OEI	12.73
	TOT						6.12		TOT	12.73

Figure 9. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

C C		Quasi- Classical	Sharing			Total
			Penetration		Interference	
1 1	KIN				-.00	-.00
	SNA	.00		.00	.00	.00
	OEI		-.00		-.00	-.00
	TOT	.00	-.00		-.00	-.00
1 1	KIN				2.20	2.20
	SNA	-.03		-.48	-.16	-.67
	OEI		.03		-.04	-.01
	TOT	-.03	.03		1.52	1.51
1 b	KIN				1.86	1.86
	SNA	-.05		-.53	-.08	-.66
	OEI		.04		-.01	.03
	TOT	-.05	.04		1.24	1.23
1 π	KIN				.00	.00
	SNA	.00		-.04	.00	-.03
	OEI		.00		-.00	.00
	TOT	.00	.00		-.04	-.03
1 1	KIN				21.62	21.62
	SNA	.06		-7.73	-7.73	-15.40
	OEI		1.69		-.61	1.08
	TOT	.06	1.69		5.54	7.29
1 b	KIN				-12.34	-12.34
	SNA	-1.14		4.85	2.26	5.98
	OEI		-3.66		.26	-3.40
	TOT	-1.14	-3.66		-4.96	-9.76
1 π	KIN				.00	.00
	SNA	.38		-.94	.41	-.15
	OEI		.08		-.23	-.14
	TOT	.38	.08		-.75	-.29
b b	KIN				-.45	-.45
	SNA	-.43		-.30	-.30	-1.07
	OEI		-.43		.01	-.42
	TOT	-.43	-.43		-1.03	-1.94
b π	KIN				.00	.00
	SNA	-.59		-.27	-.58	-1.24
	OEI		-.07		-.17	-.23
	TOT	-.59	-.07		-.81	-1.47
$\pi \pi$	KIN				-11.24	-11.24
	SNA	.63		2.37	2.37	5.36
	OEI		-4.94		.23	-4.72
	TOT	.63	-4.94		-6.28	-12.60
$\pi \bar{\pi}$	KIN				.00	.00
	SNA	.30		-.12	-.10	.09
	OEI		-.02		-.04	-.07
	TOT	.30	-.02		-.25	.02
C ₂	KIN				-17.88	-17.88
	SNA	-1.85		-.05	-.05	-1.95
	OEI		-15.78		-1.38	-17.17
	TOT	-1.85	-15.78		-19.37	-37.00

Figure 9. (Continued)

BINDING ENERGY PARTITIONING

		Promotion		Quasi- Classical	Sharing		Total
		PRH	PRC		Penetration	Interference	
C	KIN	-0.92	0.00				-0.92
	NA	3.88	0.00				3.88
	OEI	3.25	0.00		12.50		15.75
	TOT	6.21	0.00		12.50		18.71
Bond	KIN					-17.12	-17.12
	SNA			-1.99		0.14 0.14	-1.71
	OEI				-15.86	-1.47	-17.33
	TOT			-1.99	-15.86	-18.31	-36.16
C ₂	KIN	-1.84	0.00			-17.12	-18.96
	SNA	7.76	0.00	-1.99		0.14 0.14	6.05
	OEI	6.50	0.00		9.14	-1.47	14.17
	TOT	12.42	0.00	-1.99	9.14	-18.31	1.26

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals			
	1S	2S	2P _z	i	l	b	π
1	0.999934	-0.007727	-0.008449	-0.002516	0.041364	0.105742	0
1	0.006582	0.991756	-0.127973	0.041364	0.371707	0.476079	0
b	0.009368	0.127909	0.991742	0.105742	0.476079	0.412981	0
π	(Unhybridized)			0	0	0	0.338306

DENSITY CONTRIBUTIONS

Orbital	VAO Populations			Inter-Atomic Bond-Orders			
	d	v	g	i	l	b	π
1	2.011271	-0.008080	2.003190	0.001457	-0.090255	-0.041078	0
1	1.629865	-0.059478	1.570387	-0.090255	-0.753142	0.470938	0
b	0.173896	0.252526	0.426422	-0.041078	0.470938	0.079098	0
π	0.747213	0.252787	1.000000	0	0	0	0.747213

EXCHANGE CONTRIBUTIONS TO PAIR POPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	i	l	b	π	i	l	b	π	i	l	b	π
1	2.009	-0.001	-0.001	-0.002	0.000	0.001	0.001	0.002	0.000	-0.002	-0.003	0
1	-0.001	1.377	0.043	0.076	0.001	-0.036	-0.052	-0.076	-0.002	-0.095	0.335	0
b	-0.001	0.043	0.166	0.109	0.001	-0.052	-0.074	-0.109	-0.003	0.335	0.010	0
π	-0.002	0.076	0.109	0.659	0.002	-0.076	-0.109	-0.159	0	0	0	0.500
$\bar{\pi}$	-0.002	0.076	0.109	0.159	0.002	-0.076	-0.109	-0.159	0	0	0	0

Figure 10. Binding energy decomposition and description of electron distribution for C₂, BAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

		Promotion							Sharing Penetration	
Orbital		1S	2S	2P σ	2P π	2P $\bar{\pi}$	Total	Orbital		
1S	KIN	1.33	0.53	0.00	0.00	0.00	1.32	i	KIN	
	NA	-2.81	-0.56	0.00	0.00	0.00	-2.80		SNA	
	OEI	0.37	-9.57	9.45	0.08	0.08	0.80		OEI	0.07
	TOT	-1.11	-9.60	9.45	0.08	0.08	-0.68		TOT	0.07
2S	KIN	0.53	-18.20	0.00	0.00	0.00	-17.13	l	KIN	
	NA	-0.56	64.80	0.00	0.00	0.00	63.67		SNA	
	OEI	-9.57	-6.54	4.76	-3.72	-3.72	-42.07		OEI	1.98
	TOT	-9.60	40.06	4.76	-3.72	-3.72	4.47		TOT	1.98
2P σ	KIN	0.00	0.00	14.89	0.00	0.00	14.89	b	KIN	
	NA	0.00	0.00	-56.98	0.00	0.00	-56.98		SNA	
	OEI	9.45	4.76	0.08	2.49	2.49	39.83		OEI	2.68
	TOT	9.45	4.76	-42.01	2.49	2.49	-2.26		TOT	2.68
2P π	KIN	0.00	0.00	0.00	0.00	0.00	0.00	π	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	0.08	-3.72	2.49	3.36	-1.02	2.34		OEI	3.88
	TOT	0.08	-3.72	2.49	3.36	-1.02	2.34		TOT	3.88
2P $\bar{\pi}$	KIN	0.00	0.00	0.00	0.00	0.00	0.00	$\bar{\pi}$	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	0.08	-3.72	2.49	-1.02	3.36	2.34		OEI	3.88
	TOT	0.08	-3.72	2.49	-1.02	3.36	2.34		TOT	3.88
c	KIN						-0.92	c	KIN	
	NA						3.88		SNA	
	OEI						3.25		OEI	12.50
	TOT						6.21		TOT	12.50

Figure 10. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

C C		Quasi- Classical	Penetration	Sharing	Interference	Total
i i	KIN				.00	.00
	SNA	-.00		-.00	-.00	-.00
	OEI		-.00		-.00	-.00
	TOT	-.00	-.00		-.00	-.00
i l	KIN				1.82	1.82
	SNA	-.23		-.13	-.13	-.34
	OEI		.22		-.04	-.02
	TOT	-.03	.02		1.47	1.46
i b	KIN				2.02	2.02
	SNA	-.06		-.44	-.49	-.58
	OEI		.04		-.21	.03
	TOT	-.06	.04		1.48	1.47
i π	KIN				.00	.00
	SNA	.00		-.03	-.00	-.03
	OEI		.00		-.00	.00
	TOT	.00	.00		-.03	-.03
l l	KIN				20.04	20.04
	SNA	.08		-6.86	-6.86	-13.65
	OEI		1.71		-.61	1.10
	TOT	.08	1.71		5.70	7.49
l b	KIN				-11.62	-11.62
	SNA	-1.21		4.23	2.16	5.18
	OEI		-3.74		.25	-3.49
	TOT	-1.21	-3.74		-4.97	-9.93
l π	KIN				.00	.00
	SNA	.41		-.95	.41	-.13
	OEI		.08		-.23	-.15
	TOT	.41	.08		-.77	-.28
b b	KIN				-.30	-.30
	SNA	-.57		-.38	-.38	-1.32
	OEI		-.44		.01	-.43
	TOT	-.57	-.44		-1.04	-2.05
b π	KIN				.00	.00
	SNA	-.65		-.08	-.59	-1.31
	OEI		-.07		-.18	-.24
	TOT	-.65	-.07		-.84	-1.56
$\pi \pi$	KIN				-10.65	-10.65
	SNA	.69		2.25	2.25	5.19
	OEI		-4.90		.22	-4.68
	TOT	.69	-4.90		-5.92	-10.13
$\pi \bar{\pi}$	KIN				.00	.00
	SNA	.33		-.10	-.10	.13
	OEI		-.02		-.25	-.07
	TOT	.33	-.02		-.26	.05
C ₂	KIN				-17.12	-17.12
	SNA	-1.99		.14	.14	-1.71
	OEI		-15.86		-1.47	-17.33
	TOT	-1.99	-15.86		-10.31	-35.16

Figure 10. (Continued)

BINDING ENERGY PARTITIONING

		Promotion		Quasi- Classical	Sharing		Total
		PRH	PRC		Penetration	Interference	
C	KIN	-31.37	13.02				-18.35
	NA	49.80	-22.15				27.65
	OEI	-5.11	9.75		9.82		14.46
	TOT	13.32	0.61		9.82		23.75
Bond	KIN					40.55	40.55
	SNA			-1.28		-35.39	-72.07
	OEI				-13.27	-2.15	-15.41
	TOT			-1.28	-13.27	-32.38	-46.93
C ₂	KIN	-62.74	26.04			40.55	3.85
	SNA	99.60	-44.30	-1.28		-35.39	-16.77
	OEI	-10.22	19.50		6.38	-2.15	13.51
	TOT	26.64	1.22	-1.28	6.38	-32.38	0.58

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals			
	1S	2S	2P _x	i	l	b	π
i	0.971602	0.234768	-0.029554	0.045591	0.143532	0.160455	0
l	-0.236228	0.969018	-0.071786	0.143532	0.379011	0.340976	0
b	0.011786	0.076732	0.996982	0.160455	0.340976	0.359155	0
π	(Unhybridized)			0	0	0	0.322570

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders			
	p	v	d	i	l	b	π
i	2.015397	-0.037306	1.978090	-0.106236	-0.318238	0.082356	0
l	1.909059	-0.210281	1.698778	-0.318238	-0.827285	0.436824	0
b	0.135546	0.187586	0.323132	0.082356	0.436824	0.065335	0
π	0.756104	0.243896	1.000000	0	0	0	0.756104

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	i	l	b	π	i	l	b	π	i	l	b	π
i	1.980	0.002	-0.002	-0.000	0.000	0.000	0.000	0.000	-0.002	-0.019	0.019	0
l	0.002	1.600	0.015	0.041	0.000	-0.010	-0.023	-0.041	-0.019	-0.120	0.254	0
b	-0.002	0.015	0.110	0.100	0.000	-0.023	-0.056	-0.100	0.019	0.254	0.006	0
π	-0.000	0.041	0.100	0.679	0.000	-0.041	-0.100	-0.179	0	0	0	0.500
$\bar{\pi}$	-0.000	0.041	0.100	0.179	0.000	-0.041	-0.100	-0.179	0	0	0	0

Figure 11. Binding energy decomposition and description of electron distribution for C₂, BMAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion												Total PRC	TOT	Orbital	Sharing Penetration	
	1S		2S		2P σ		2P π		2P $\bar{\pi}$		PRH	PRC					
1s	KIN	-16.52	0.36	-7.01	-0.17	0.00	0.00	0.00	0.00	0.00	0.00	-18.11	0.33	-17.78	1	KIN	
	NA	34.94	-0.38	7.41	0.18	0.00	0.00	0.00	0.00	0.00	0.00	36.63	-0.36	36.27		SNA	
	OEI	-6.72	-0.06	-7.40	0.53	6.89	1.72	-0.40	0.51	-0.40	0.51	-10.05	-0.03	-10.07		OEI	-1.18
	TOT	11.70	-0.08	-7.00	0.53	6.89	1.72	-0.40	0.51	-0.40	0.51	8.47	-0.06	8.41		TOT	-1.18
2s	KIN	-7.01	-0.17	-11.93	3.06	0.00	0.00	0.00	0.00	0.00	0.00	-24.35	2.75	-21.60	1	KIN	
	NA	7.41	0.18	42.48	-4.62	0.00	0.00	0.00	0.00	0.00	0.00	55.62	-4.30	51.32		SNA	
	OEI	-7.40	0.53	-5.09	0.09	4.10	0.48	-2.35	0.24	-2.35	0.24	-28.42	1.62	-26.80		OEI	0.35
	TOT	-7.00	0.53	25.47	-1.47	4.10	0.48	-2.35	0.24	-2.35	0.24	2.85	0.08	2.93		TOT	0.35
2P σ	KIN	0.00	0.00	0.00	0.00	11.09	6.48	0.00	0.00	0.00	0.00	11.09	6.48	17.57	b	KIN	
	NA	0.00	0.00	0.00	0.00	-42.45	-10.98	0.00	0.00	0.00	0.00	-42.45	-10.98	-53.42		SNA	
	OEI	6.89	1.72	4.10	0.48	-0.14	-0.02	1.71	0.21	1.71	0.21	29.54	5.07	34.61		OEI	2.51
	TOT	6.89	1.72	4.10	0.48	-31.50	-4.52	1.71	0.21	1.71	0.21	-1.82	0.57	1.24		TOT	2.51
2P π	KIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.73	0.00	0.00	0.00	1.73	1.73	π	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-3.26	0.00	0.00	0.00	-3.26	-3.26		SNA	
	OEI	-0.40	0.51	-2.35	0.24	1.71	0.21	3.08	0.05	-1.18	0.15	1.91	1.54	3.45		OEI	4.08
	TOT	-0.40	0.51	-2.35	0.24	1.71	0.21	3.08	-1.49	-1.18	0.15	1.91	0.00	1.91		TOT	4.08
2P $\bar{\pi}$	KIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.73	0.00	1.73	1.73	$\bar{\pi}$	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-3.26	0.00	-3.26	-3.26		SNA	
	OEI	-0.40	0.51	-2.35	0.24	1.71	0.21	-1.18	0.15	3.08	0.05	1.91	1.54	3.45		OEI	4.08
	TOT	-0.40	0.51	-2.35	0.24	1.71	0.21	-1.18	0.15	3.08	-1.49	1.91	0.01	1.91		TOT	4.08
c	KIN											-31.37	13.02	-18.35	c	KIN	
	NA											49.80	-22.15	27.65		SNA	
	OEI											-5.11	9.75	4.63		OEI	9.82
	TOT											13.32	0.61	13.93		TOT	9.82

Figure 11. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

C C		Quasi- Classical	Penetration	Sharing	Interference	Total
i i	KIN				3.52	3.52
	SNA	-.02		-1.97	-1.97	-3.95
	OEI		.03		-.06	-.03
	TOT	-.02	.03		-.49	-.46
i l	KIN				21.75	21.75
	SNA	-.07		-16.51	-5.53	-22.17
	OEI		.32		-.26	.04
	TOT	-.07	.32		-.61	-.38
i b	KIN				-5.39	-5.39
	SNA	-.08		3.31	.34	4.08
	OEI		-.22		-.01	-.23
	TOT	-.08	-.22		-1.24	-1.54
i π	KIN				.00	.00
	SNA	.04		-.15	.06	-.06
	OEI		.02		-.01	.01
	TOT	.04	.02		-.11	-.05
l l	KIN				72.43	72.43
	SNA	-.73		-39.32	-39.32	-79.37
	OEI		1.96		-.79	1.17
	TOT	-.73	1.96		-2.96	-7.73
l b	KIN				-21.43	-21.43
	SNA	-.69		18.99	2.37	20.67
	OEI		-2.84		.21	-2.63
	TOT	-.69	-2.84		.14	-3.39
l π	KIN				.00	.00
	SNA	.15		-1.07	.59	-.33
	OEI		.13		-.24	-.12
	TOT	.15	.13		-.73	-.45
b b	KIN				-1.17	-1.17
	SNA	-.13		-.03	-.03	-.19
	OEI		-.34		.01	-.33
	TOT	-.13	-.34		-1.23	-1.69
b π	KIN				.00	.00
	SNA	-.35		-.04	-.42	-.79
	OEI		-.05		-.11	-.16
	TOT	-.35	-.05		-.55	-.95
$\pi \pi$	KIN				-11.07	-11.07
	SNA	.64		2.37	2.37	5.39
	OEI		-4.86		.18	-4.68
	TOT	.64	-4.26		-6.14	-10.36
$\pi \bar{\pi}$	KIN				.00	.00
	SNA	.31		-.10	-.10	.10
	OEI		-.02		-.04	-.07
	TOT	.31	-.02		-.25	.03
C ₂	KIN				40.55	40.55
	SNA	-1.23		-35.39	-35.39	-72.27
	OEI		-13.27		-2.15	-15.41
	TOT	-1.23	-13.27		-32.33	-46.83

Figure 11. (Continued)

BINDING ENERGY DECOMPOSITION

		Promotion		Quasi-Classical	Sharing		Total
		PRH	PRC		Penetration	Interference	
N	KIN	0.62	0.00				0.62
	NA	0.17	0.00				0.17
	OBI	7.35	0.00		14.08		21.43
	TOT	8.14	0.00		14.08		22.22
Bond	KIN					-33.39	-33.39
	SEA			-5.62		7.81	9.99
	OBI				-20.24	-1.98	-22.22
	TOT			-5.62	-20.24	-19.75	-45.62
N ₂	KIN	1.24	0.00			-33.39	-32.15
	SEA	0.34	0.00	-5.62		7.81	10.34
	OBI	14.70	0.00		7.93	-1.98	20.65
	TOT	16.28	0.00	-5.62	7.93	-19.75	-1.16

VALENCE ATOMIC ORBITALS

Orbital	VAO Expansion			Overlap Integrals			
	1S	2S	2P _z	1	1	b	π
1	0.962047	-0.251559	0.105749	0.001108	-0.019294	0.002251	0
1	0.271464	0.842797	-0.464759	-0.019294	0.052811	0.302377	0
b	0.027789	0.475828	0.879099	0.002251	0.302377	0.716894	0
π	(Unhybridized)			0	0	0	0.282041

DENSITY CONTRIBUTIONS

Orbital	VAO Populations			Inter-Atomic Bond Orders			
	s	v	p	1	1	b	π
1	2.000744	-0.000784	1.999961	-0.002177	0.039370	-0.009554	0
1	2.161576	-0.115817	2.045759	0.039370	-0.159915	-0.352581	0
b	0.640336	0.313944	0.954280	-0.009554	-0.352581	0.586667	0
π	0.780006	0.219994	1.000000	0	0	0	0.780006

EXCHANGE CONTRIBUTIONS TO PAIR POPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	1	1	b	π	1	1	b	π	1	1	b	π
1	2.000	0.000	-0.000	-0.000	0.000	0.000	0.000	0.000	0.000	-0.000	0.000	0
1	0.000	2.128	-0.034	-0.024	0.000	-0.003	0.022	0.024	-0.000	-0.004	-0.062	0
b	-0.000	-0.034	0.662	0.163	0.000	0.022	-0.147	-0.163	0.000	-0.062	0.514	0
π	-0.000	-0.024	0.163	0.681	0.000	0.024	-0.163	-0.181	0	0	0	0.500
$\bar{\pi}$	-0.000	-0.024	0.163	0.181	0.000	0.024	-0.163	-0.181	0	0	0	0

Figure 12. Binding energy decomposition and description of electron distribution for N₂; SAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

		Promotion							Sharing Penetration	
Orbital		1S	2S	2P σ	2P π	2P $\bar{\pi}$	Total	Orbital		
1s	KIN	1.54	0.55	0.00	0.00	0.00	1.53	1	KIN	
	NA	-3.23	-0.57	0.00	0.00	0.00	-3.21		SNA	
	OEI	-0.24	-5.00	5.41	0.09	0.09	0.30		OEI	-0.02
	TOT	-1.92	-5.02	5.41	0.09	0.09	-1.38		TOT	-0.02
2s	KIN	0.55	-12.45	0.00	0.00	0.00	-11.35	1	KIN	
	NA	-0.57	41.99	0.00	0.00	0.00	40.84		SNA	
	OEI	-5.00	-2.07	-0.45	-1.83	-1.83	-18.21		OEI	-0.30
	TOT	-5.02	27.48	-0.45	-1.83	-1.83	11.28		TOT	-0.30
2P σ	KIN	0.00	0.00	10.43	0.00	0.00	10.43	b	KIN	
	NA	0.00	0.00	-37.46	0.00	0.00	-37.46		SNA	
	OEI	5.41	-0.45	7.91	0.92	0.92	20.19		OEI	4.74
	TOT	5.41	-0.45	-19.11	0.92	0.92	-6.83		TOT	4.74
2P π	KIN	0.00	0.00	0.00	0.00	0.00	0.00	π	KIN	
	NA	0.00	0.00	0.00	-0.00	0.00	0.00		SNA	
	OEI	0.09	-1.83	0.92	4.01	-1.48	2.54		OEI	4.83
	TOT	0.09	-1.83	0.92	4.01	-1.48	2.54		TOT	4.83
2P $\bar{\pi}$	KIN	0.00	0.00	0.00	0.00	0.00	0.00	$\bar{\pi}$	KIN	
	NA	0.00	0.00	0.00	0.00	-0.00	0.00		SNA	
	OEI	0.09	-1.83	0.92	-1.48	4.01	2.54		OEI	4.83
	TOT	0.09	-1.83	0.92	-1.48	4.01	2.54		TOT	4.83
N	KIN						0.62	N	KIN	
	NA						0.17		SNA	
	OEI						7.35		OEI	14.08
	TOT						8.14		TOT	14.08

Figure 12. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

N N		Quasi- Classical	Sharing			Total
			Penetration	Interference		
i i	KIN			.20		.20
	SNA	.01		-.01	-.01	-.01
	OEI		.00	-.00		-.00
	TOT	.01	.00	-.01		-.00
i l	KIN			.51		.51
	SNA	.26		-.79	.01	-.52
	OEI		.01	-.03		-.02
	TOT	.26	.01	-.31		-.04
i b	KIN			.02		.02
	SNA	-.34		1.33	-.01	.98
	OEI		.00	-.20		-.20
	TOT	-.34	.00	1.15		.80
i π	KIN			.00		.00
	SNA	.06		-.04	.00	.02
	OEI		.00	-.01		-.01
	TOT	.06	.00	-.05		.01
l l	KIN			.70		.70
	SNA	5.96		-.14	-.14	5.69
	OEI		.04	-.05		-.01
	TOT	5.96	.04	.38		6.39
l b	KIN			8.40		8.40
	SNA	-4.75		2.90	-3.34	-5.19
	OEI		.96	-.13		.83
	TOT	-4.75	.96	7.84		4.05
l π	KIN			.00		.00
	SNA	1.49		-.58	.09	1.00
	OEI		.07	-.01		.06
	TOT	1.49	.07	-.52		1.06
b b	KIN			-20.73		-20.73
	SNA	-2.37		3.98	3.98	5.59
	OEI		-10.70	.36		-10.34
	TOT	-2.37	-10.70	-12.41		-25.48
b π	KIN			.00		.00
	SNA	-1.89		-.51	-.19	-2.59
	OEI		-.07	-.49		-.56
	TOT	-1.89	-.07	-1.19		-3.15
π π	KIN			-15.61		-15.61
	SNA	.62		3.27	3.27	7.16
	OEI		-5.72	.26		-5.46
	TOT	.62	-5.72	-8.30		-13.91
π π̄	KIN			.00		.00
	SNA	.28		-.11	-.11	.06
	OEI		-.03	-.04		-.07
	TOT	.28	-.03	-.26		-.01
N ₂	KIN			-33.39		-33.39
	SNA	-5.62		7.81	7.81	9.99
	OEI		-20.24	-1.98		-22.22
	TOT	-5.62	-20.24	-13.75		-45.62

Figure 12. (Continued)

BINDING ENERGY PARTITIONING

		Promotion		Quasi-Classical	Sharing		Total
		PRF	PRC		Penetration	Interference	
N	KIN	0.97	0.00				0.97
	NA	-0.11	0.00				-0.11
	OBI	7.14	0.00		13.78		20.92
	TOT	8.00	0.00		13.78		21.78
Bond	KIN					-30.54	-30.54
	SNA			-5.72		7.09	8.45
	OBI				-19.93	-2.09	-22.02
	TOT			-5.72	-19.93	-18.45	-44.11
N ₂	KIN	1.94	0.00			-30.54	-28.60
	SNA	-0.22	0.00	-5.72		7.09	8.23
	OBI	14.28	0.00		7.62	-2.09	19.82
	TOT	16.00	0.00	-5.72	7.62	-18.45	-0.55

VALENCE ATOMIC ORBITALS

Orbital	VAO Expansion			Overlap Integrals			
	1S	2S	2P _z	i	l	b	π
i	0.964526	-0.245545	0.096936	0.000744	-0.020722	0.002355	0
l	0.262105	0.846988	-0.462507	-0.020722	0.055738	0.314232	0
b	0.031463	0.471508	0.881300	0.002354	0.314232	0.718822	0
π		(Unhybridized)		0	0	0	0.292380

DENSITY CONTRIBUTIONS

Orbital	VAO Populations			Inter-Atomic Bond-Orders			
	p	v	q	i	l	b	π
i	2.000854	-0.000904	1.999951	-0.001439	0.042365	-0.010485	0
l	2.175132	-0.125560	2.049573	0.042366	-0.170810	-0.366484	0
b	0.644000	0.306477	0.950477	-0.010483	-0.366484	0.586602	0
π	0.773766	0.226234	1.000000	0	0	0	0.773766

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	i	l	b	π	i	l	b	π	i	l	b	π
i	2.000	0.000	-0.000	-0.000	0.000	0.000	0.000	0.000	0.000	-0.000	0.000	0
l	0.000	2.139	-0.037	-0.026	0.000	-0.004	0.024	0.026	-0.000	-0.004	-0.068	0
b	-0.000	-0.037	0.662	0.163	0.000	0.024	-0.145	-0.163	0.000	-0.068	0.515	0
π	-0.000	-0.026	0.163	0.682	0.000	0.026	-0.163	-0.182	0	0	0	0.500
$\bar{\pi}$	-0.000	-0.026	0.163	0.182	0.000	0.026	-0.163	-0.182	0	0	0	0

Figure 13. Binding energy decomposition and description of electron distribution for N₂, BAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

-----Promotion-----							Sharing Penetration			
Orbital	1S	2S	2P σ	2P π	2P $\bar{\pi}$	Total	Orbital			
1S	KIN	1.40	0.72	0.00	0.00	0.00	1.39	i	KIN	
	NA	-2.95	-0.76	0.00	0.00	0.00	-2.93		SNA	
	OEI	-0.26	-4.76	5.15	0.08	0.08	0.25		OEI	-0.02
	TOT	-1.81	-4.79	5.15	0.08	0.08	-1.30		TOT	-0.02
2S	KIN	0.72	-11.65	0.00	0.00	0.00	-10.19	l	KIN	
	NA	-0.76	40.04	0.00	0.00	0.00	38.50		SNA	
	OEI	-4.76	-2.00	-0.41	-1.71	-1.71	-17.32		OEI	-0.34
	TOT	-4.79	26.38	-0.41	-1.71	-1.71	10.99		TOT	-0.34
2P σ	KIN	0.00	0.00	9.77	0.00	0.00	9.77	b	KIN	
	NA	0.00	0.00	-35.68	0.00	0.00	-35.68		SNA	
	OEI	5.15	-0.41	7.63	0.85	0.85	19.27		OEI	4.63
	TOT	5.15	-0.41	-18.28	0.85	0.85	-6.63		TOT	4.63
2P π	KIN	0.00	0.00	0.00	0.00	0.00	0.00	π	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	0.08	-1.71	0.85	3.93	-1.46	2.47		OEI	4.75
	TOT	0.08	-1.71	0.85	3.93	-1.46	2.47		TOT	4.75
2P $\bar{\pi}$	KIN	0.00	0.00	0.00	0.00	0.00	0.00	$\bar{\pi}$	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	0.08	-1.71	0.85	-1.46	3.93	2.47		OEI	4.75
	TOT	0.08	-1.71	0.85	-1.46	3.93	2.47		TOT	4.75
N	KIN						0.97	N	KIN	
	NA						-0.11		SNA	
	OEI						7.14		OEI	13.78
	TOT						8.00		TOT	13.78

Figure 13. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

N N		Quasi- Classical	Sharing			Total
			Penetration	Interference		
1 1	KIN			.00		.00
	SNA	.01		-.00	-.00	.00
	OEI		-.00	-.00		-.00
	TOT	.01	-.00	-.01		.00
1 1	KIN			.58		.58
	SNA	.24		-.91	.01	-.66
	OEI		.01	-.03		-.03
	TOT	.24	.01	-.36		-.11
1 b	KIN			.02		.02
	SNA	-.34		1.42	-.01	1.07
	OEI		.00	-.21		-.21
	TOT	-.34	.00	1.23		.89
1 π	KIN			.00		.00
	SNA	.06		-.04	.00	.02
	OEI		.00	-.01		-.01
	TOT	.06	.00	-.05		.01
1 1	KIN			.76		.76
	SNA	6.12		-.13	-.13	5.86
	OEI		.04	-.05		-.01
	TOT	6.12	.04	.45		6.61
1 b	KIN			8.55		8.55
	SNA	-4.82		3.10	-3.44	-5.15
	OEI		1.03	-.13		.90
	TOT	-4.82	1.03	8.08		4.30
1 π	KIN			.00		.00
	SNA	1.56		-.61	.10	1.05
	OEI		.07	-.01		.06
	TOT	1.56	.07	-.52		1.11
b b	KIN			-19.05		-19.05
	SNA	-2.57		3.31	3.31	4.05
	OEI		-10.62		.37	-10.26
	TOT	-2.57	-10.62	-12.06		-25.26
b π	KIN			.00		.00
	SNA	-1.95		-.52	-.17	-2.63
	OEI		-.07	-.50		-.57
	TOT	-1.95	-.07	-1.19		-3.20
$\pi \pi$	KIN			-15.27		-15.27
	SNA	.64		3.21	3.21	7.07
	OEI		-5.69		.26	-5.43
	TOT	.64	-5.69	-3.59		-13.64
$\pi \bar{\pi}$	KIN			.00		.00
	SNA	.30		-.11	-.11	.07
	OEI		-.23	-.04		-.27
	TOT	.30	-.03	-.27		-.00
N ₂	KIN			-30.54		-30.54
	SNA	-5.72		7.09	7.09	8.45
	OEI		-19.93		-2.09	-22.02
	TOT	-5.72	-10.80	-18.45		-44.11

Figure 13. (Continued)

BINDING ENERGY DECOMPOSITION

		Promotion		Quasi- Classical	Sharing		Total
		PRH	PRC		Penetration	Interference	
N	KIN	0.27	20.40				20.67
	NA	0.55	-33.82				-33.27
	OBI	6.52	14.81		14.11		35.44
	TOT	7.34	1.38		14.11		22.84
Bond	KIN					-36.11	-36.11
	SNA			-4.15		6.83 6.83	4.51
	OBI				-19.49	-2.19	-21.67
	TOT			-4.15	-19.49	-24.63	-48.27
N ₂	KIN	0.54	40.80			-36.11	5.23
	SNA	1.10	-67.64	-4.15		6.83 6.83	-57.03
	OBI	13.04	29.62		8.72	-2.19	49.19
	TOT	14.68	2.76	-4.15	8.72	-24.63	-2.61

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals			
	1S	2S	2P _z	i	l	b	π
i	0.979978	-0.190980	0.056307	-0.002912	-0.000331	0.011779	0
l	0.197542	0.697226	-0.394920	-0.020341	0.004484	0.004484	0
b	0.024006	0.398136	0.916988	0.011779	0.004484	0.620728	0
π	(Unhybridized)			0	0	0	0.294928

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders			
	p	v	q	i	l	b	π
i	2.001121	-0.001102	2.000019	0.005809	0.040510	-0.022196	0
l	2.221433	-0.178223	2.043210	0.040510	-0.429885	-0.336870	0
b	0.670319	0.286452	0.956771	-0.022196	-0.336870	0.627142	0
π	0.772244	0.227756	1.000000	0	0	0	0.772244

EXCHANGE CONTRIBUTIONS TO PAIR-POPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	i	l	b	π	i	l	b	π	i	l	b	π
i	2.000	0.000	-0.000	-0.000	0.000	-0.000	0.000	0.000	0.000	-0.000	-0.000	0
l	0.000	2.159	-0.044	-0.036	-0.000	-0.007	0.032	0.036	-0.000	-0.037	-0.059	0
b	-0.000	-0.044	0.666	0.167	0.000	0.032	-0.151	-0.167	-0.000	-0.059	0.512	0
π	-0.000	-0.036	0.167	0.684	0.000	0.036	-0.167	-0.184	0	0	0	0.500
π̄	-0.000	-0.036	0.167	0.184	0.000	0.036	-0.167	-0.184	0	0	0	0

Figure 14. Binding energy decomposition and description of electron distribution for N₂, BMAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion												Total PRC	TOT	Orbital	Sharing Penetration	
	1s		2s		2P _σ		2P _π		2P _{π̄}		PRH	PRC					
1s	KIN	0.64	0.83	0.43	-0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.63	0.85	1.48	1	KIN	
	NA	-1.34	-0.88	-0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-1.33	-0.88	-2.22		SNA	
	OEI	-0.26	-0.04	-3.09	-0.16	3.41	4.90	0.06	-0.10	0.06	-0.10	0.07	0.04	0.11		OEI	-0.02
	TOT	-0.96	-0.09	-3.11	-0.16	3.41	4.90	0.06	-0.10	0.06	-0.10	-0.63	0.01	-0.63		TOT	-0.02
2s	KIN	0.43	-0.00	-7.69	-1.09	0.00	0.00	0.00	0.00	0.00	0.00	-6.83	-1.10	-7.94	1	KIN	
	NA	-0.45	0.00	26.43	1.60	0.00	0.00	0.00	0.00	0.00	0.00	25.53	1.61	27.14		SNA	
	OEI	-3.09	-0.16	-1.54	-0.06	-0.15	1.29	-0.96	-0.06	-0.96	-0.06	-11.23	-0.59	-11.82		OEI	-0.56
	TOT	-3.11	-0.16	17.20	0.45	-0.15	1.29	-0.96	-0.06	-0.96	-0.06	7.47	-0.09	7.38		TOT	-0.56
2P _σ	KIN	0.00	0.00	0.00	0.00	6.47	21.49	0.00	0.00	0.00	0.00	6.47	21.49	27.96	b	KIN	
	NA	0.00	0.00	0.00	0.00	-23.64	-36.07	0.00	0.00	0.00	0.00	-23.64	-36.07	-59.71		SHA	
	OEI	3.41	4.90	-0.15	1.29	6.30	0.89	0.13	0.67	0.13	0.67	12.93	16.10	29.03		OEI	5.03
	TOT	3.41	4.90	-0.15	1.29	-10.87	-13.70	0.13	0.67	0.13	0.67	-4.24	1.51	-2.73		TOT	5.03
2P _π	KIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.42	0.00	0.00	0.00	-0.42	-0.42	π	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.76	0.00	0.00	0.00	0.76	0.76		SHA	
	OEI	0.06	-0.10	-0.96	-0.06	0.13	0.67	3.86	-0.01	-1.49	-0.03	2.37	-0.37	2.01		OEI	4.83
	TOT	0.06	-0.10	-0.96	-0.06	0.13	0.67	3.86	0.33	-1.49	-0.03	2.37	-0.02	2.35		TOT	4.83
2P _{π̄}	KIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.42	0.00	-0.42	-0.42	-0.42	π̄	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.76	0.00	0.76	0.76	0.76		SNA	
	OEI	0.06	-0.10	-0.96	-0.06	0.13	0.67	-1.49	-0.03	3.86	-0.01	2.37	-0.37	2.01		OEI	4.83
	TOT	0.06	-0.10	-0.96	-0.06	0.13	0.67	-1.49	-0.03	3.86	0.33	2.37	-0.02	2.35		TOT	4.83
N	KIN											0.27	20.40	20.67	N	KIN	
	NA											0.55	-33.82	-33.27		SNA	
	OEI											6.52	14.81	21.33		OEI	14.11
	TOT											7.34	1.38	8.73		TOT	14.11

Figure 14. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

N N		Quasi- Classical	Sharing			Total
			Penetration		Interference	
i i	KIN				.02	.02
	SNA	-.00		.01	.01	.03
	OEI		.00		-.00	-.00
	TOT	-.00	.00		.05	.04
i l	KIN				.55	.55
	SNA	.05		-1.29	.03	-1.21
	OEI		.01		-.11	-.11
	TOT	.05	.01		-.83	-.78
i b	KIN				.23	.23
	SNA	-.17		1.39	-.04	1.18
	OEI		.00		-.13	-.12
	TOT	-.17	.00		1.44	1.28
i π	KIN				.00	.00
	SNA	.01		-.04	.00	-.02
	OEI		.00		-.01	-.01
	TOT	.01	.00		-.04	-.03
l l	KIN				3.80	3.80
	SNA	4.94		-.24	-.24	4.46
	OEI		.40		-.26	.14
	TOT	4.94	.40		3.07	8.40
l b	KIN				8.88	8.88
	SNA	-4.29		.97	-3.09	-6.41
	OEI		.90		-.18	.72
	TOT	-4.29	.90		6.58	3.19
l π	KIN				.00	.00
	SNA	1.39		-.85	.29	.82
	OEI		.11		-.07	.04
	TOT	1.39	.11		-.64	.86
b b	KIN				-28.86	-28.86
	SNA	-1.16		5.31	5.31	9.47
	OEI		-10.56		.36	-10.21
	TOT	-1.16	-10.56		-17.87	-29.60
b π	KIN				.00	.00
	SNA	-1.65		-.44	-.15	-2.25
	OEI		-.06		-.37	-.43
	TOT	-1.65	-.06		-.96	-2.68
$\pi \pi$	KIN				-15.19	-15.19
	SNA	.65		3.20	3.20	7.04
	OEI		-5.64		.22	-5.42
	TOT	.65	-5.64		-8.58	-13.57
$\pi \bar{\pi}$	KIN				.00	.00
	SNA	.30		-.11	-.11	.07
	OEI		-.03		-.05	-.07
	TOT	.30	-.03		-.27	.00
N ₂	KIN				-36.11	-36.11
	SNA	-4.15		6.83	6.83	9.51
	OEI		-19.49		-2.19	-21.67
	TOT	-4.15	-19.49		-24.63	-48.27

Figure 14. (Continued)

BINDING ENERGY DECOMPOSITION

		Promotion		Quasi- Classical	Sharing		Total
		PRH	PRC		Penetration	Interference	
n	KIN	-0.42	0.00				-0.42
	NA	0.93	0.00				0.93
	OEI	1.17	0.00		6.98		8.15
	TOT	1.68	0.00		6.98		8.66
Bond	KIN					-18.79	-18.79
	SNA			0.00		4.09	4.09
	OEI				-6.01	-0.53	-6.54
	TOT			0.00	-6.01	-11.14	-17.14
n_2	KIN	-0.84	0.00			-18.79	-19.63
	SNA	1.86	0.00	0.00		4.09	10.05
	OEI	2.34	0.00		7.94	-0.53	9.75
	TOT	3.36	0.00	0.00	7.94	-11.14	0.18

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals			
	1s	2s	2p _z	i	l	b	π
i	0.997550	-0.069237	0.009987	-0.000205	-0.001263	0.000653	0
l	0.069879	0.979674	-0.188030	-0.001263	0.064967	0.124860	0
b	0.003235	0.188267	0.982113	0.000653	0.124860	0.225604	0
π	(Unhybridized)			0	0	0	0.047024

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders			
	s	v	a	i	l	b	π
i	2.000004	-0.000004	2.000000	0.000410	0.002527	-0.001323	0
l	2.038565	-0.033145	2.005420	0.002527	-0.137860	-0.193669	0
b	0.834408	0.160172	0.994580	-0.001323	-0.193669	0.817174	0
π	2.004432	-0.004432	2.000000	0	0	0	-0.094256

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	i	l	b	π	i	l	b	π	i	l	b	π
i	2.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
l	0.000	2.022	-0.017	0.000	0.000	-0.000	0.015	-0.000	0.000	-0.005	-0.010	0
b	0.000	-0.017	1.016	-0.002	0.000	0.015	-0.512	0.002	0.000	-0.010	0.502	0
π	0.000	0.000	-0.002	2.002	0.000	-0.000	0.002	-0.000	0	0	0	-0.002
$\bar{\pi}$	0.000	0.000	-0.002	0.000	0.000	-0.000	0.002	-0.000	0	0	0	0

Figure 15. Binding energy decomposition and description of electron distribution for F_2 , SAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

		Promotion							Sharing Penetration	
Orbital		1S	2S	2P _σ	2P _π	2P _{π̄}	Total	Orbital		
1S	KIN	0.02	0.07	0.00	0.00	0.00	0.02	i	KIN	
	NA	-0.03	-0.07	0.00	0.00	0.00	-0.03		SNA	
	OEI	0.04	-1.05	1.10	-0.00	-0.00	0.04		OEI	0.00
	TOT	0.02	-1.05	1.10	-0.00	-0.00	0.02		TOT	0.00
2S	KIN	0.07	-3.37	0.00	0.00	0.00	-3.23	l	KIN	
	NA	-0.07	10.79	0.00	0.00	0.00	10.65		SNA	
	OEI	-1.05	-0.58	0.16	-0.77	-0.77	-6.10		OEI	-0.04
	TOT	-1.05	6.84	0.16	-0.77	-0.77	1.31		TOT	-0.04
2P _σ	KIN	0.00	0.00	2.80	0.00	0.00	2.80	b	KIN	
	NA	0.00	0.00	-9.68	0.00	0.00	-9.68		SNA	
	OEI	1.10	0.16	1.08	0.82	0.82	7.22		OEI	7.07
	TOT	1.10	0.16	-5.81	0.82	0.82	0.34		TOT	7.07
2P _π	KIN	0.00	0.00	0.00	0.00	0.00	0.00	π	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	-0.00	-0.77	0.82	0.01	-0.00	0.01		OEI	-0.03
	TOT	-0.00	-0.77	0.82	0.01	-0.00	0.01		TOT	-0.03
2P _{π̄}	KIN	0.00	0.00	0.00	0.00	0.00	0.00	π̄	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	-0.00	-0.77	0.82	-0.00	0.01	0.01		OEI	-0.03
	TOT	-0.00	-0.77	0.82	-0.00	0.01	0.01		TOT	-0.03
F	KIN						-0.42	F	KIN	
	NA						0.93		SNA	
	OEI						1.17		OEI	6.98
	TOT						1.68		TOT	6.98

Figure 15. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

F	F		Quasi- Classical	Sharing			Total
				Penetration		Interference	
i	i	KIN				.00	.00
		SNA	.00		.00	.00	.00
		OEI		.00	-.00		-.00
		TOT	.00	.00	.00		.00
i	l	KIN				.00	.00
		SNA	-.00		-.02	.00	-.02
		OEI		.00	-.00		-.00
		TOT	-.00	.00	-.02		-.02
i	b	KIN				.00	.00
		SNA	-.00		.01	-.00	.01
		OEI		.00	-.00		-.00
		TOT	-.00	.00	.01		.01
i	π	KIN				.00	.00
		SNA	-.00		.00	.00	-.00
		OEI		.00	-.00		-.00
		TOT	-.00	.00	.00		-.00
l	l	KIN				1.60	1.60
		SNA	.43		-.38	-.38	-.34
		OEI		.04	-.06		-.02
		TOT	.43	.04	.78		1.24
l	b	KIN				4.29	4.29
		SNA	-.57		-1.75	-1.23	-3.56
		OEI		.20	-.09		.11
		TOT	-.57	.20	1.22		.84
l	π	KIN				.00	.00
		SNA	.26		.02	.08	.36
		OEI		-.00	-.03		-.03
		TOT	.26	-.00	.07		.33
b	b	KIN				-30.66	-30.66
		SNA	.35		8.08	8.08	16.51
		OEI		-6.48	.08		-6.40
		TOT	.35	-6.48	-14.43		-20.56
b	π	KIN				.00	.00
		SNA	-.39		.01	-.18	-.57
		OEI		.00	-.05		-.05
		TOT	-.39	.00	-.22		-.61
π	π	KIN				.84	.84
		SNA	.33		-.23	-.23	-.13
		OEI		.02	-.03		-.01
		TOT	.33	.02	.35		.70
π	$\bar{\pi}$	KIN				.00	.00
		SNA	.11		.00	.00	.12
		OEI		-.00	-.00		-.00
		TOT	.11	-.00	.00		.12
F	2	KIN				-18.79	-18.79
		SNA	.00		4.09	4.09	8.19
		OEI		-6.01	-.53		-6.54
		TOT	.00	-6.01	-11.14		-17.14

Figure 15. (Continued)

BINDING ENERGY PARTITIONING

	Promotion		Quasi- Classical	Sharing		Total
	PRi	PRC		Penetration	Interference	
s	KIN	-0.32	0.00			-0.32
	NA	0.83	0.00			0.83
	CEI	1.10	0.00	6.81		7.91
	TOT	1.61	0.00	6.81		8.42
Bond	KIN				-17.50	-17.50
	SNA		-0.06		3.79	3.79
	CEI			-5.98	-0.60	-6.59
	TOT		-0.06	-5.98	-10.53	-16.56
F ₂	KIN	-0.61	0.00			-17.50
	SNA	1.66	0.00	-0.06	3.79	3.79
	CEI	2.29	0.00		7.64	-0.60
	TOT	3.22	0.00	-0.06	7.64	-10.53

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals			
	1S	2S	2P _z	i	l	b	π
i	0.997548	-0.069430	0.308830	-0.000224	-0.001442	0.000737	0
l	0.069856	0.979920	-0.186752	-0.001442	0.068368	0.132658	0
b	0.004313	0.186911	0.982367	0.000737	0.132658	0.238521	0
π	(Unhybridized)			0	0	0	0.051470

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders			
	s	p	d	i	l	b	π
i	2.000005	-0.000005	2.000000	0.000449	0.002886	-0.001500	0
l	2.043240	-0.036943	2.006297	0.002886	-0.145988	-0.203217	0
b	0.827731	0.165972	0.993703	-0.001500	-0.203217	0.808866	0
π	2.005312	-0.005312	2.000000	0	0	0	-0.103214

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	i	l	b	π	i	l	b	π	i	l	b	π
i	2.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
l	0.000	2.025	-0.019	0.000	0.000	-0.001	0.017	-0.000	0.000	-0.005	-0.011	0
b	0.000	-0.019	1.018	-0.003	0.000	0.017	-0.514	0.003	0.000	-0.011	0.503	0
π	0.000	0.000	-0.003	2.003	0.000	-0.000	0.003	0.000	0	0	0	-0.003
$\bar{\pi}$	0.000	0.000	-0.003	0.000	0.000	-0.000	0.003	0.000	0	0	0	0

Figure 16. Binding energy decomposition and description of electron distribution for F₂, BAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion						Total	Orbital	Sharing Penetration	
	1S	2S	2R _r	2P _π	2P _{π̄}					
1s	KIN	0.01	0.11	0.00	0.00	0.00	0.01	i	KIN	
	NA	-0.03	-0.11	0.00	0.00	0.00	-0.03		SNA	
	OEI	0.04	-0.99	1.03	-0.00	-0.00	0.03		OEI	0.00
	TOT	0.02	-0.99	1.03	-0.00	-0.00	0.02		TOT	0.00
2s	KIN	0.11	-3.11	0.00	0.00	0.00	-2.90	l	KIN	
	NA	-0.11	10.16	0.00	0.00	0.00	9.94		SNA	
	OEI	-0.99	-0.57	0.18	-0.73	-0.73	-5.85		OEI	-0.05
	TOT	-0.99	6.48	0.18	-0.73	-0.73	1.19		TOT	-0.05
2R _r	KIN	0.00	0.00	2.57	0.00	0.00	2.57	b	KIN	
	NA	0.00	0.00	-9.08	0.00	0.00	-9.08		SNA	
	OEI	1.03	0.18	1.00	0.78	0.78	6.93		OEI	6.93
	TOT	1.03	0.18	-5.51	0.78	0.78	0.42		TOT	6.93
2P _r	KIN	0.00	0.00	0.00	0.00	0.00	0.00	π	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	-0.00	-0.73	0.78	-0.00	-0.00	-0.01		OEI	-0.03
	TOT	-0.00	-0.73	0.78	-0.00	-0.00	-0.01		TOT	-0.03
2P _{r̄}	KIN	0.00	0.00	0.00	0.00	0.00	0.00	π̄	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00		SNA	
	OEI	-0.00	-0.73	0.78	-0.00	-0.00	-0.01		OEI	-0.03
	TOT	-0.00	-0.73	0.78	-0.00	-0.00	-0.01		TOT	-0.03
F	KIN						-0.32	F	KIN	
	NA						0.83		SNA	
	OEI						1.10		OEI	6.81
	TOT						1.61		TOT	6.81

Figure 16. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

F	F		Quasi- Classical	Sharing			Total
				Penetration	Interference		
i	i	KIN			.00		.00
		SNA	-.00		.00	.00	.00
		OEI		.00	-.00		-.00
		TOT	-.00	.00	.00		.00
i	i	KIN			.00		.00
		SNA	-.00		-.02	.00	-.03
		OEI		.00	-.00		-.00
		TOT	-.00	.00	-.22		-.22
i	b	KIN			.00		.00
		SNA	-.00		.01	-.00	.01
		OEI		.00	-.00		-.00
		TOT	-.00	.00	.01		.01
i	π	KIN			.00		.00
		SNA	-.00		.00	.00	.00
		OEI		.00	-.00		-.00
		TOT	-.00	.00	.00		-.00
l	l	KIN				1.71	1.71
		SNA	.43		-.41	-.41	-.39
		OEI		.04	-.07		-.03
		TOT	.43	.04	.83		1.30
l	b	KIN				4.55	4.55
		SNA	-.60		-1.82	-1.33	-3.75
		OEI		.21	-.09		.12
		TOT	-.60	.21	1.31		.92
l	π	KIN			.00		.00
		SNA	.28		.02	.09	.39
		OEI		-.00	-.03		-.03
		TOT	.28	-.00	.02		.35
b	b	KIN				-30.26	-30.26
		SNA	.34		8.02	8.02	16.37
		OEI		-6.50	.07		-6.43
		TOT	.34	-6.52	-14.15		-20.31
b	π	KIN			.00		.00
		SNA	-.42		.01	-.18	-.59
		OEI		.00	-.05		-.05
		TOT	-.42	.00	-.23		-.65
π	π	KIN				.96	.96
		SNA	.36		-.27	-.27	-.18
		OEI		.03	-.03		-.00
		TOT	.36	.03	.39		.77
π	$\bar{\pi}$	KIN			.00		.00
		SNA	.12		.01	.01	.13
		OEI		-.00	-.01		-.01
		TOT	.12	-.00	.01		.13
F	2	KIN				-17.50	-17.50
		SNA	-.06		3.79	3.79	7.53
		OEI		-5.98	-.60		-6.59
		TOT	-.06	-5.98	-10.53		-16.56

Figure 16. (Continued)

BINDING ENERGY PARTITIONING

	Promotion		Quasi-Classical	Sharing		Total
	FRH	PRC		Penetration	Interference	
F	KIN	-0.30	4.60			4.29
	MA	0.83	-5.32			-5.98
	OBI	1.20	2.27	6.68		10.15
	TOT	1.73	0.05	6.68		8.46
Bond	KIN				-17.27	-17.27
	SMA		-0.15		3.67	3.67
	OBI			-6.03	-0.60	-6.62
	TOT		-0.15	-6.03	-10.53	-16.71
F ₂	KIN	-0.60	9.20		-17.27	-8.69
	SMA	1.66	-13.34	-0.15	3.67	3.67
	OBI	2.40	4.54		-0.60	13.68
	TOT	3.46	0.10	-0.15	7.32	10.53

VALENCE ATOMIC ORBITALS

Orbital	VAC Expansion			Overlap Integrals			
	1s	2s	2p	i	l	b	π
i	0.997285	-0.003047	0.000042	-0.000197	-0.001720	0.000790	0
l	0.003486	0.978916	-0.190584	-0.001720	0.062994	0.135494	0
b	0.004776	0.190753	0.981626	0.000790	0.135494	0.253180	0
π	(Unhybridized)			0	0	0	0.049744

DENSITY CONTRIBUTIONS

Orbital	VAC Populations			Inter-Atomic Bond-Orders			
	s	v	d	i	l	b	π
i	2.000007	-0.000007	2.000000	0.000395	0.003446	-0.001634	0
l	2.0043164	-0.006483	2.006681	0.003446	-0.135389	-0.206271	0
b	0.818587	0.174431	0.993319	-0.001634	-0.206271	0.799355	0
π	2.004961	-0.004961	2.000000	0	0	0	-0.099734

EXCHANGE CONTRIBUTIONS TO PAIRPOPULATIONS

Orbital	Promotion State				Sharing Penetration							
	(Intra-Atomic)				(Intra-Atomic)				(Inter-Atomic)			
	i	l	b	π	i	l	b	π	i	l	b	π
i	2.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0
l	0.000	2.025	-0.019	0.000	0.000	-0.001	0.017	-0.000	0.000	-0.004	-0.012	0
b	0.000	-0.019	1.017	-0.003	0.000	0.017	-0.513	0.003	0.000	-0.012	0.503	0
π	0.000	0.000	-0.003	2.002	0.000	-0.000	0.003	-0.000	0	0	0	-0.002
$\bar{\pi}$	0.000	0.000	-0.003	0.000	0.000	-0.000	0.003	-0.000	0	0	0	0

Figure 17. Binding energy decomposition and description of electron distribution for F₂, BMAO approximation

INTRA-ATOMIC CONTRIBUTION TO BINDING ENERGY

Orbital	Promotion												Total PRC	TOT	Orbital	Sharing Penetration	
	1S		2S		2P _σ		2P _π		2P _{π'}		PRH	PRC					
1s	KIN	0.01	0.14	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.14	0.15	1	KIN	
	NA	-0.03	-0.15	-0.13	-0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.03	-0.15	-0.17		SNA	
	OEI	0.04	-0.02	-1.02	0.35	1.07	-0.76	-0.00	0.49	-0.00	0.49	0.04	-0.00	0.03		OEI	0.00
	TOT	0.03	-0.02	-1.03	0.35	1.07	-0.76	-0.00	0.49	-0.00	0.49	0.02	-0.01	0.01		TOT	0.00
2s	KIN	0.12	0.00	-3.23	3.15	0.00	0.00	0.00	0.00	0.00	0.00	-2.99	3.15	0.16	1	KIN	
	NA	-0.13	-0.00	10.55	-4.48	0.00	0.00	0.00	0.00	0.00	0.00	10.29	-4.48	5.81		SNA	
	OEI	-1.02	0.35	-0.56	0.08	0.17	-0.20	-0.76	0.29	-0.76	0.29	-5.99	1.47	-4.52		OEI	-0.05
	TOT	-1.03	0.35	6.75	-1.25	0.17	-0.20	-0.76	0.29	-0.76	0.29	1.32	0.14	1.45		TOT	-0.05
2P _σ	KIN	0.00	0.00	0.00	0.00	2.67	-3.99	0.00	0.00	0.00	0.00	2.67	-3.99	-1.31	b	KIN	
	NA	0.00	0.00	0.00	0.00	-9.43	7.11	0.00	0.00	0.00	0.00	-9.43	7.11	-2.32		SNA	
	OEI	1.07	-0.76	0.17	-0.20	1.08	0.01	0.81	-0.19	0.81	-0.19	7.15	-3.20	3.94		OEI	6.78
	TOT	1.07	-0.76	0.17	-0.20	-5.68	3.14	0.81	-0.19	0.81	-0.19	0.39	-0.07	0.31		TOT	6.78
2P _π	KIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.65	0.00	0.00	0.00	2.65	2.65	π	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-4.65	0.00	0.00	0.00	-4.65	-4.65		SNA	
	OEI	-0.00	0.49	-0.76	0.29	0.81	-0.19	0.01	0.18	-0.00	0.36	0.00	2.00	2.01		OEI	-0.03
	TOT	-0.00	0.49	-0.76	0.29	0.81	-0.19	0.01	-1.83	-0.00	0.36	0.00	-0.00	-0.00		TOT	-0.03
2P _{π'}	KIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.65	0.00	2.65	2.65	2.65	π'	KIN	
	NA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-4.65	0.00	-4.65	-4.65	-4.65		SNA	
	OEI	-0.00	0.49	-0.76	0.29	0.81	-0.19	-0.00	0.36	0.01	0.18	0.00	2.00	2.01		OEI	-0.03
	TOT	-0.00	0.49	-0.76	0.29	0.81	-0.19	-0.00	0.36	0.01	-1.83	0.00	-0.00	-0.00		TOT	-0.03
F	KIN											-0.30	4.60	4.29	F	KIN	
	NA											0.83	-6.82	-5.98		SNA	
	OEI											1.20	2.27	3.47		OEI	6.68
	TOT											1.73	0.05	1.78		TOT	6.68

Figure 17. (Continued)

INTER-ATOMIC CONTRIBUTIONS TO BINDING ENERGY

F F		Quasi- Classical	Sharing		Total
			Penetration	Interference	
1 i	KIN			.00	.00
	SNA	-.00		.00	.00
	OEI		.00	-.00	-.00
	TOT	-.00	.00	.00	.00
1 l	KIN			.01	.01
	SNA	-.00		-.03	-.03
	OEI		.00	-.00	-.00
	TOT	-.00	.00	-.02	-.03
1 b	KIN			.00	.00
	SNA	-.00		.02	.01
	OEI		.00	-.01	-.01
	TOT	-.00	.00	.01	.01
1 π	KIN			.00	.00
	SNA	-.00		.00	.00
	OEI		.00	-.00	-.00
	TOT	-.00	.00	.00	-.00
1 l	KIN			1.43	1.43
	SNA	.46		-.34	-.21
	OEI		.24	-.06	-.03
	TOT	.46	.24	.75	1.24
1 b	KIN			4.61	4.61
	SNA	-.63		-1.79	-3.75
	OEI		.22	-.09	.13
	TOT	-.63	.22	1.40	.99
1 π	KIN			.00	.00
	SNA	.28		.02	.38
	OEI		-.00	-.03	-.03
	TOT	.28	-.00	.07	.35
b b	KIN			-29.83	-29.83
	SNA	.33		7.79	15.92
	OEI		-6.55	.08	-6.47
	TOT	.33	-6.55	-14.16	-22.38
b π	KIN			.00	.00
	SNA	-.43		.01	-.61
	OEI		.00	-.06	-.06
	TOT	-.43	.00	-.23	-.67
π π	KIN			.91	.91
	SNA	.35		-.26	-.17
	OEI		.00	-.03	-.03
	TOT	.35	.00	.37	.74
π π̄	KIN			.00	.00
	SNA	.12		.00	.13
	OEI		-.00	-.00	-.00
	TOT	.12	-.00	.00	.12
F ₂	KIN			-17.27	-17.27
	SNA	-.15		3.67	7.18
	OEI		-6.03	-.00	-8.62
	TOT	-.15	-6.03	-10.53	-16.71

Figure 17. (Continued)