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A PHYSICAL INTERPRETATION OF THE HE-HE INTERACTION
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ABSTRACT

The advent of high speed computers allows the quantum chemist to obtain very precise energy calculations by using "good" approximate wavefunctions. These wavefunctions become very complicated which makes the abstraction of much physical information from these wavefunctions quite difficult.

Klaus Ruedenberg has devised a method using two functions: the first and second order density matrices, which gives a physical interpretation of atomic interactions based on "good" mathematical wavefunction approximations. In this analysis, the density matrices are partitioned into various fragments which help one to understand atoms and bonds within a molecule, long range coulombic forces, short range overlap forces, van der Waals forces, and others. The density matrices have parts containing "atomic" densities and terms containing the interactions between these "atomic" densities.

The density matrices are partitioned into four major fragments. The first fragment is promotion energy which causes a rearrangement inside of the separated atom due to these factors: 1) the value of the orbital parameter obtains the same value in the promoted atom state as in the molecule, 2) a hybridization of the atomic orbitals. The quasi-classical energy is the second major fragment. It arises from the electrostatic coulombic interactions between the atoms when they are moved from their separated positions to the inter-

nuclear distances being considered. The third major fragment is called the sharing penetration energy and arises from the sharing of electrons between the atoms in the molecule. Interference energy is the fourth major fragment and is the most important part of the partitioning. The interference energy is caused by an interference among the atomic orbitals which causes a rearrangement in the total density without changing its total population.

This partitioning scheme has been applied to the helium-helium interaction for several different wavefunction approximations and at many different internuclear distances. The He-He interaction is an interesting system to study because although it does not have a strong attractive force as in a chemical bond, there is an attractive force between the two atoms due to the van der Waals forces.

Another aspect that makes this an interesting interaction is the calculations with the $1S-2S-2P\sigma$ and $1S-1S'$ basis sets. The calculations using these basis sets were the most accurate calculations performed over a wide range of internuclear distances, until quite recently, and have a spurious minimum in the van der Waals region as has been shown by the new calculations. It is interesting to study the comparison of the results of the $1S-2S-2P\sigma$ and $1S-1S'$ basis sets and the results of the more accurate calculations by the use of the partitioning method.

The application of the partitioning to the helium-helium interaction has given new insight into the theoretical treatment of

the interaction and in the applicability of Ruedenberg's theory. This theory is useful in giving a good physical interpretation of the He-He interaction and also seems to be able to predict errors that may be occurring in the wavefunction approximations. The partitioning on this interaction has again shown that the kinetic interference energy is the term which determines if bonding or antibonding occurs and also shows the strong relationship between this and the sharing of electrons.

CHAPTER I

THEORETICAL BACKGROUND

The modern day picture of a typical quantum chemist is a person surrounded by hundreds of pages of computer output and punched cards. This picture is quite accurate. In fact, one of the problems confronting quantum chemists is the vast amount of computer output which must be turned into physical ideas for all chemists to understand.

The simple valence bond and molecular orbital models are two well known examples of physical interpretations of the chemical bond. Both of these methods do give nice physical pictures but they are poor approximations to the actual energy. In both of these methods chemical and physical intuition have allowed mathematically unjustified approximations to enter in the calculation.

The recent trend has been to obtain very precise energy calculations by using "good" approximate wavefunctions, but these wavefunctions are so complicated that it is not easy to obtain much physical information from them.

Wavefunctions themselves are not physically observable and hence it may be best to base molecular interpretations on quantities which qualify, at least in principle, as being observable. All observable quantities, including the energy, are completely determined by two functions, which are the first and second order density matrices. This statement is restricted only by the future construction of useful three body operators, in which case the third

order density matrix would be required.

Ruedenberg has devised a method using these first and second order density matrices which gives a physical interpretation of atomic interactions based on "good" mathematical wavefunction approximations. In this analysis, the density matrices are partitioned into various fragments that help one to understand atoms and bonds within a molecule, long range coulombic forces, short range overlap forces, van der Waals forces, etc.¹

An important aspect of this partitioning is the understanding of molecules in terms of atoms and bonds from which molecules are formed. This is achieved by partitioning the density matrices as much as possible into parts containing "atomic" densities and terms containing the interactions between these "atomic" densities.

It has been reported informally that some quantum chemists are critical of Ruedenberg's partitioning for several reasons. One of these reasons is that the partitioning yields some quantities which are not "physical" since they have no direct relationship to specific experimental observations. In a broader sense of the word they are "physical" as these quantities aid in giving a complete understanding of what happens when atoms interact with each other.

A second area in which there has been criticism is due to the arbitrary definitions that must be made at certain times. This

¹K. Ruedenberg, Rev. Mod. Phys., 34, 326 (1962)

should not be a difficult problem when one considers that all mathematics are based on arbitrary definitions. The usefulness of any mathematics is how well it functions in the system in which one is working. The usefulness of Ruedenberg's analysis should be in how successfully it describes the partitioned fragments in different molecules. If the molecules are similar, the partitioned parts should also be similar and exhibit regular and illuminating behavior.

A third area in which there has been disagreement is that Ruedenberg has based his analysis on a model. This model is based on the principle that molecules can be explained in terms of atoms, and the bonds between these atoms. Although it is a model, it is accepted by most theoretical chemists. Ruedenberg has further refined this model in terms of an orbital subdivision which is appropriate for examining atomic interactions. It should also be realized that Quantum Mechanics itself is based on a model and has certain definitions inherent within it which have an arbitrary character.

The product $\Psi^*\Psi$ is identified with the concept of a probability density. That it is a probability density can be disputed through the measure theory language of the general theory of probability.² Nevertheless the traditional dogma centered on $\Psi^*\Psi$ contains a useful picture of the particle distribution in a given system. We accept the traditional interpretation of $\Psi^*\Psi$ in this study.

²B. Rankin, J. Math. Phys. 6, 1657 (1965)

An important point that makes Ruedenberg's analysis very useful is that it is based on density matrices rather than wavefunctions. This fact makes the analysis much more general and is not restricted to certain classes of wavefunctions. It is to be expected that as the wavefunction approximation becomes better, the partitioned fragments will have definite trends while they still retain their character.

A general physical picture emerges from the partitioning which gives an idea of the effects which go into the formation of bonds. This picture is only a conceptual "taking-apart" of the interactions and has nothing to do with the variation of the first and second order density matrices at various internuclear distances.

The first step is promotion which causes a rearrangement inside of each separated atom and causes a rise in the total energy. In the second step the atoms are brought from their separated positions to their actual positions in the molecule causing a quasi-classical electrostatic interaction which causes a slight energy lowering with respect to the promotion energy. The electrons are now shared between the atoms causing two effects. One of these is an increased penetration of the electrons from the different atoms, which will raise the electronic repulsion energy moderately. The other effect is the interference of atomic orbitals which causes the large energy lowering which is crucial for the formation of covalent bonds.

The first and second order spin density matrices are defined

$$\text{as } \Gamma(\bar{X}\bar{S}|XS) = N \int \Psi^*(\bar{X}\bar{S}, \bar{X}_2\bar{S}_2, \dots) \Psi(XS, \bar{X}_2\bar{S}_2, \dots) \frac{d\tau}{d\tau_1}$$

$$\Gamma(\bar{X}, \bar{S}_1, \bar{X}_2\bar{S}_2 | X, S_1, X_2S_2) = N(N-1) \int \Psi^*(X, S_1, X_2S_2, \dots) \Psi(\bar{X}, \bar{S}_1, \bar{X}_2\bar{S}_2, \dots) \frac{d\tau}{d\tau_1 d\tau_2}$$

$$X_i S_i = x_i y_i z_i s_i \quad i=1, 2, \dots, N$$

denotes the space-spin coordinates of the N electrons in a molecule.

$$dV_i = dx_i dy_i dz_i, \quad d\tau_i = dS_i dV_i$$

$$d\tau = d\tau_1 d\tau_2 d\tau_3 \dots d\tau_N$$

denotes the corresponding volume elements.

$$\Psi(X, S_1, X_2 S_2 \dots X_N S_N)$$

denotes the exact electronic wavefunction of the molecular system in question.

$\frac{d\tau}{d\tau_1}$ indicates the integration over all volume elements except $d\tau_1$.

$\frac{d\tau}{d\tau_1 d\tau_2}$ indicates the integration over all volume elements except $d\tau_1$ and $d\tau_2$.

There are higher order density matrices, but the molecular hamiltonian of quantum chemistry depends only upon, at the most, two electron interactions, so that the first and second order density matrices are all that are needed. The hamiltonian does not depend on spin, thus one is able to integrate out the spin to get spinless density matrices.

$$\rho(X'|X) = \int dS \Gamma(\bar{X}\bar{S}|XS)$$

$$\pi(\bar{X}_1, \bar{X}_2|X_1, X_2) = \int dS_1 \int dS_2 \Gamma(\bar{X}_1, \bar{S}_1, \bar{X}_2, \bar{S}_2|X_1, S_1, X_2, S_2)$$

The diagonal elements of the density matrices have the following physical significance

$\rho(X|X) = \rho(X) =$ total probable density of electrons at the space point $X = (x, y, z)$.

$\pi(X_1, X_2|X_1, X_2) = \pi(X_1, X_2) =$ total pair density of the electrons, i.e., the probable number of electron pairs which have one partner at the space point $X_1 = (x_1, y_1, z_1)$ and the other at space point $X_2 = (x_2, y_2, z_2)$.

In terms of atomic orbitals, the first and second order density matrices are expanded as follows: $\rho(X_1|X_2) = \sum_a \sum_b \sum_c \sum_d (A_a)^{(1)} (B_b)^{(2)} P(A_a|B_b)$
The $P(A_a|B_b)$ are the expansion coefficients which form a Hermitian matrix called the bond-order matrix.

$$\pi(X_1, X_2) = \sum_a \sum_{\bar{a}} \sum_b \sum_{\bar{b}} \sum_c \sum_{\bar{c}} (A_a \bar{A}_{\bar{a}})^{(1)} (B_b \bar{B}_{\bar{b}})^{(2)} P(A_a \bar{A}_{\bar{a}}|B_b \bar{B}_{\bar{b}})$$

The $P(A_a \bar{A}_{\bar{a}}|B_b \bar{B}_{\bar{b}})$ elements form a super matrix called the pair bond order matrix.

A, B, C, ... denote atoms

a, b, c, ... are indices numbering the orbitals in the atoms A, B, C respectively.

$\chi_{Aa}(X) = (A_a)$ denotes the a th orbital in atom A

also, $\chi_{Aa}(1) = (A_a)^{(1)}$

$$(A_a \bar{A}_{\bar{a}})^{(1)} = (A_a)^{(1)} (\bar{A}_{\bar{a}})^{(1)}$$

The nonrelativistic energy, assuming the nuclei are held in fixed positions, is given by

$$E = \langle \Psi | H | \Psi \rangle = \sum_{A \neq B} Z_A Z_B R_{AB}^{-1} + \int dV h \rho(x) + \frac{1}{2} \int dV_1 \int dV_2 \pi(x_1, x_2) / r_{12}$$

where A, B denote atoms, Z_A , Z_B denote the respective nuclear charges, X_A , X_B denote the respective nuclear positions, R_{AB} = the various internuclear distances and

$$h = T + V \quad T = -\frac{1}{2} \nabla^2 \quad V = \sum_A Z_A / r_A$$

The requirement in this partitioning scheme is made that all atomic orbitals are normalized and those located on the same atom are mutually orthogonal. The overlap matrix is then $\Delta = I + S$

$$S(A_\alpha, B_\beta) = (1 - \delta_{AB}) \int dV (A_\alpha)(B_\beta)$$

so it can be seen that the matrix S has nonvanishing elements only if the two orbitals belong to different atoms.³

Ruedenberg decided on the partitioning of the first order density matrix by comparing classical electrostatics and wave mechanics. In classical electrostatics, densities are superposed to form new densities. By comparison, in wave mechanics, wavefunctions are superposed to form new wavefunctions which in turn are squared to obtain the new densities. These new densities are different from the sum of the densities of the constituent wavefunctions.

A simple example of this reasoning is obtained by studying the

³K. Ruedenberg, op. cit.

H_2^+ molecule with the wavefunction taken as $\Psi = N_+ (|S_a\rangle + |S_b\rangle)$ where the normalization constant is $N_+ = (2(1 + \langle S_a | S_b \rangle))^{-1/2}$. The densities for the separate constituent atoms are given by $\rho_A(x) = |S_a|^2$, $\rho_B(x) = |S_b|^2$.

In this case the classical electrostatic approach would give a new density $\rho^{\text{cl}} = \frac{1}{2} \rho_A + \frac{1}{2} \rho_B$ ($\frac{1}{2}$ originates from the fact that ρ_A, ρ_B, ρ must all be normalized).

$$\text{The wave mechanics yields } \Psi^* \Psi = N_+^2 (|S_a|S_a + |S_a|S_b + |S_b|S_a + |S_b|S_b)$$

$$\rho = N_+^2 (|S_a|S_a + |S_a|S_b + |S_b|S_a + |S_b|S_b)$$

$$\rho = \rho^{\text{cl}} + \rho^{\text{I}} = \frac{1}{2} |S_a|^2 + \frac{1}{2} |S_b|^2 + \rho^{\text{I}}$$

Therefore from $\rho - \rho^{\text{cl}} = \rho^{\text{I}}$ it follows that

$$\rho^{\text{I}} = (2|S_a|S_b - S(|S_a|^2 + |S_b|^2)) / 2(1+S)$$

$$= 2N_+^2 (|S_a|S_b - \frac{1}{2}(|S_a|^2 + |S_b|^2))$$

where ρ^{I} is the modification of the quasi-classical density due to interference.

By expanding this type of reasoning to the general case one gets

$$\rho^{\text{cl}}(x) = \sum_A \rho_A(x) = \sum_A \left\{ \sum_{a, \bar{a}}' (A_a)(A_{\bar{a}}) P(A_a | A_{\bar{a}}) + \sum_a (A_a^2) q(A_a) \right\}$$

$\sum_{A, \bar{A}}'$ denotes the sum over both quantities but ($A \neq \bar{A}$)

$$\rho^{\text{I}}(x) = \sum_{A, B}' \rho_{AB}(x)$$

$$\sum_{A, B}' \rho_{AB}(x) = \sum_{A, B}' \sum_a \sum_b \langle A_a, B_b \rangle P(A_a, B_b)$$

$$\langle A_a, B_b \rangle = (A_a)(B_b) - \frac{1}{2} S(A_a, B_b) [(A_a^2) + (B_b^2)] (A \neq B)$$

Where for the H_2^+ case the $\sum_{a,\bar{a}}' (A_a)(A_{\bar{a}}) P(A_a/\bar{A}_a) = 0$

$$q(A_a) = \frac{1}{2}$$

$$P(A_a, B_b) = N_+^2$$

$$q(A_a) = P(A_a) + v(A_a)$$

$q(A_a)$ is the populations of the orbitals (A_a) in the quasi-classical density ρ^{cl} , $P(A_a) = P(A_a/A_a) =$ valence-inactive population of (A_a) , $v(A_a) = \sum_{B_b} S(A_a, B_b) P(B_b, A_a) =$ valence-active population of (A_a) .

It would be advantageous to extract hybrid atomic orbitals from the original orbitals which are either valence active or valence inactive. The atomic hybrid orbitals derived from the postulate of maximum or minimum valence activity are called valence atomic orbitals. This postulate requires all intra-atomic parts of the bond-order matrix to be diagonal. This means that the $\sum_{a,\bar{a}} (A_a)(A_{\bar{a}}) P(A_a/A_a)$ term vanishes.

In order to partition the second order density matrix, the interference partitioning, in terms of atomic orbitals, for the first order density matrix is substituted into the general expansion for the second order density matrix. As a result of this partitioning three major fragments are obtained:

$$\pi^{VS} \pi(X_1, X_2) = \pi^{VS}(X_1, X_2) + \pi^I(X_1, X_2) + \pi^{II}(X_1, X_2)$$

π^{VS} is an interference-free pair density,

π^I is a primary interference pair density,

π^{II} is a secondary interference pair density.

π^{VS} is the pair density due to the atoms themselves and is of the

same nature as the ρ^{el} term in our first order partitioning. It contains the intra-atomic electronic repulsions and also the shielding repulsions between the quasi-classical electron densities on different atoms.

$\pi^{\text{I}}(\chi_1, \chi_2)$ and $\pi^{\text{II}}(\chi_1, \chi_2)$ are interactions between the atoms caused by mutual orbital overlap. In previous studies on molecules the energy associated with the π^{I} and ρ^{I} which constitute E^{I} have always been considerably larger than the energy associated with the π^{II} term E^{II} . Ruedenberg considers the interference energy as the major source for covalent binding and antibinding. E^{II} is the only term which contains interactions between different bonds.

The following definitions can be constructed:

$$\begin{aligned} \pi^{\text{VS}} &= \sum_A \sum_B \pi(A, B) \\ &= \sum_A \sum_B \{ \pi^{\text{O}}(A, B) + \pi^{\text{I}}(A, B) + \pi^{\text{II}}(A, B) \} \end{aligned}$$

$$\begin{aligned} \pi^{\text{I}} &= \sum_{A\bar{A}}' \sum_B \pi(A\bar{A}, B) \\ &= \sum_{A\bar{A}}' \sum_B \{ \pi^{\text{I}}(A\bar{A}, B) + \pi^{\text{II}}(A\bar{A}, B) \} (A \neq \bar{A}) \end{aligned}$$

$$\pi^{\text{II}} = \sum_{A\bar{A}}' \sum_{B\bar{B}}' \pi(A\bar{A}, B\bar{B}) \quad (A \neq \bar{A}, B \neq \bar{B})$$

$$\pi^0(A, B) = \sum_a \sum_b g(A_a | B_b) (A_a^2) (B_b^2)$$

$$\pi'(A, B) = \sum_{a, \bar{a}} \sum_b 2P(A_a A_{\bar{a}} | B_b) (A_a A_{\bar{a}}) (B_b^2)$$

$$\pi''(A, B) = \sum_{a, \bar{a}} \sum_{b, \bar{b}} P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) (A_a \bar{A}_{\bar{a}}) (B_b \bar{B}_{\bar{b}})$$

$$\pi'(A\bar{A}, B) = \sum_{a, \bar{a}} \sum_b 2P(A_a \bar{A}_{\bar{a}} | B_b) \langle A_a \bar{A}_{\bar{a}} \rangle (B_b^2) (A \neq \bar{A})$$

$$\pi''(A\bar{A}, B) = \sum_{a, \bar{a}} \sum_{b, \bar{b}} 2P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) \langle A_a \bar{A}_{\bar{a}} \rangle (B_b | B_{\bar{b}}) (A \neq \bar{A})$$

$$\pi''(A\bar{A}, B\bar{B}) = \sum_{a, \bar{a}} \sum_{b, \bar{b}} P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) \langle A_a \bar{A}_{\bar{a}} \rangle \langle B_b \bar{B}_{\bar{b}} \rangle (A \neq \bar{A}, B \neq \bar{B})$$

$$g(A_a, B_b) = \sum_{\bar{A}_{\bar{a}}} \sum_{\bar{B}_{\bar{b}}} \Delta(A_a, \bar{A}_{\bar{a}}) P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) \Delta(B_b, \bar{B}_{\bar{b}})$$

$$P(A_a \bar{A}_{\bar{a}} | B_b) = \sum_{\bar{B}_{\bar{b}}} P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) \Delta(B_b, \bar{B}_{\bar{b}})$$

$$\Delta(A_a, B_b) = \int dV(A_a) (B_b)^4$$

⁴K. Ruedenberg, op. cit.

The ensemble of atoms characterized by the density $\rho^{VS} = \rho^{\text{el}} = \sum_A \rho(A)$ and pair density $\pi^{VS} = \sum_A \sum_B \pi(A, B)$ is called the valence state molecule.

The valence state is only a model to separate the interference free parts of the density and pair density from the interference parts. The valence state is a molecular, rather than an atomic quantity. This is true because it has quantities associated with it that are not purely atomic in nature as will be subsequently shown. The next step in the analysis is to separate the valence state into three quantities: 1) those concerned with the sharing of electrons between atoms called sharing penetration, $\pi^{SP}(X_1, X_2)$ 2) those quantities which are purely atomic called promoted state $\pi^P(X_1, X_2)$ and $\rho^P(X)$, 3) and the quasi-classical interactions between the promoted atoms, π^{QC} and ρ^{QC} .

One can now look into the nature of each of these fragments in greater depth.

Promoted State

The promotion state is considered to be the closest state an atom can get to being a molecule while still remaining as an atom. The density for the promoted state is given by $\rho^P(A) = \sum_a g^P(Aa) Aa^2$ and for the pair density

$$\begin{aligned} \pi^P(A) = & \sum_{a, \bar{a}} \{ g^P(Aa) g^P(A\bar{a}) - g_x^P(Aa|A\bar{a}) \} Aa^2(1) A\bar{a}^2(2) \\ & + \sum'_{a, \bar{a}} \sum'_{a', \bar{a}'} P(AaA\bar{a}|A'a' A'\bar{a}') Aa(1) A\bar{a}(1) A'a'(2) A'\bar{a}'(2) \end{aligned}$$

where $g^P(Aa)$ is the orbital population of the orbital (Aa) for the promoted atom A.⁵

$$\rho^P(A) = \rho^{\text{el}}(A) \quad g^P(Aa) = g(Aa)$$

It would be desirable to have the $g^P(Aa|A\bar{a})$ term derivable directly from the second order density matrix. Unfortunately, this algorithm has not been discovered.

Since the $g_x^P(Aa|A\bar{a})$ is the only term without a suitable direct definition, the following procedure is sufficient for the construction of $g_x^P(Aa|A\bar{a})$.

$$1) g_x^{SP}(Aa|A\bar{a}) = -g^{SP}(Aa|A\bar{a}): \quad \text{The nature of}$$

this term will be discussed under sharing penetration.

$$2) g_x(Aa|A\bar{a}) = g(Aa)g(A\bar{a}) - g(Aa|A\bar{a}). \quad \text{This}$$

is simply part of the valence state term.

$$3) g_x^P(Aa|A\bar{a}) = g_x(Aa|A\bar{a}) - g_x^{SP}(Aa|A\bar{a}).$$

$g_x^P(Aa|A\bar{a})$ is defined as that part of the valence state term $g_x(Aa|A\bar{a})$, which remains after $g_x^{SP}(Aa|A\bar{a})$ has been subtracted from it.

Substituting these results into $\pi^P(A)$ one obtains

$$\pi^P(A) = \sum_{a,\bar{a}} \{ g^P(Aa)g^P(A\bar{a}) - g(Aa)g(A\bar{a}) + g(Aa|A\bar{a}) + g_x^{SP}(Aa|A\bar{a}) \} \\ Aa^2(1)A\bar{a}^2(2) + \sum_{a,\bar{a}} \sum_{a',\bar{a}'} P(AaA\bar{a}|Aa'A\bar{a}') Aa(1)A\bar{a}(1)Aa'(2)A\bar{a}'(2)$$

In simplest form: $\pi^P(A) = \sum_{a,\bar{a}} \{ g(Aa|A\bar{a}) - g^{SP}(Aa|A\bar{a}) \}$

$$Aa^2(1)A\bar{a}^2(2) + \sum_{a,\bar{a}} \sum_{a',\bar{a}'} P(AaA\bar{a}|Aa'A\bar{a}') Aa(1)A\bar{a}(1)Aa'(2)A\bar{a}'(2)$$

⁵C. Edmiston and K. Ruedenberg, J. Phys., Chem. 68, 1628 (1964)

The promotion effects are calculated from the density functions defined by taking the differences between the promoted state densities and the densities of the ground state.

The atoms are considered to be in their ground state at infinite internuclear separation. Under the Hartree-Fock approximation this usually presents a problem, as it tends to preserve electron pairs in the limit of large internuclear separations. This means that the choosing of a proper ground state often can cause difficulties. In the case of the He-He interaction however, He is a closed shell atom and so the wavefunction goes smoothly into a natural separated atom wavefunction.

The density and pair density of the ground state for an atom A is given by $\rho^G(A) = \sum_a g^G(Aa) Aa^2$
and $\pi^G(A) = \rho^G(A) \rho^G(A) - \pi_x^G(A)$
 $= \sum_{a,\bar{a}} \{ g^G(Aa) g^G(A\bar{a}) - \sum_{a,\bar{a}} g_x^G(Aa|A\bar{a}) \} Aa^2(1) A\bar{a}^2(2)$

where $g^G(Aa)$ is the number of electrons in the orbital Aa for the ground state atom A, and $g_x^G(Aa|A\bar{a})$'s are the exchange pair density elements for the ground state. The promotional energy is then given by $E^P(A) = \int dV [T - Z(A)/r_A] [\rho^P(A) - \rho^G(A)]$
 $+ \frac{1}{2} \int dV_1 \int dV_2 [\pi^P(A,A) - \pi^G(A,A)] / r_{12}$

Promotion is just a special type of orbital distortion. It seems physically meaningful to partition this orbital distortion into two types, hybridization promotion and contraction promotion.

Hybridization promotion occurs as a result of the hybridization

of the original Slater type orbitals into valence atomic orbitals, which are the orbitals used in the partitioning. This is calculated as the change in the coefficients of $P^G(Aa, A\bar{a})$ to $P^P(Aa, A\bar{a})$ and $\pi^G(AaA\bar{a}|A\bar{b}A\bar{b})$ to $\pi^P(AaA\bar{a}|A\bar{b}A\bar{b})$.

Contraction promotion arises from changes in the orbital exponents \mathcal{J} in going from the ground state to the promoted state. It arises from the differences of the energy integrals between the ground state and promoted state.⁶

Although at first glance this appears to be a complete separation, unfortunately it is not. Because of the nature of $P^P(Aa, A\bar{a})$ and $\pi^P(AaA\bar{a}|A\bar{b}A\bar{b})$ the overlap integral $S(Aa, B\bar{b})$ is inherent in them. The value of this integral will depend on the value of \mathcal{J} and thus a complete separation cannot result. Despite the difficulty, the separation remains worthwhile.

The hybridization promotional energy (E^{PRH}) for atom A is defined by $E^{PRH} = \sum_{a, \bar{a}} E^{PRH}(Aa, A\bar{a})$

$$E^{PRH}(Aa, A\bar{a}) = \delta P(Aa, A\bar{a}) [Aa|h_A|A\bar{a}] + \frac{1}{2} \sum_{b, \bar{b}} \delta P(AaAb|A\bar{a}A\bar{b}) [AaAb|A\bar{a}A\bar{b}]$$

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

$$\delta P(AaAb|A\bar{a}A\bar{b}) = P^P(AaAb|A\bar{a}A\bar{b}) - P^G(AaAb|A\bar{a}A\bar{b})$$

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

⁶R. R. Rue and K. Ruedenberg, J. Phys. Chem., 68, 1676 (1964)

The contraction promotional energy (E^{PRC}) for atom A is obtained

from
$$E^{PRC} = \sum_{a, \bar{a}} E^{PRC}(A_a, A_{\bar{a}})$$

$$E^{PRC}(A_a, A_{\bar{a}}) = P^P(A_a, A_{\bar{a}}) S[A_a | h_A | A_{\bar{a}}] + \frac{1}{2} \sum_{b, \bar{b}} P^P(A_a A_b | A_{\bar{a}} A_{\bar{b}}) S[A_a A_b | A_{\bar{a}} A_{\bar{b}}]$$

with
$$S[A_a | h_A | A_{\bar{a}}] = [A_a^P | h_A | A_{\bar{a}}^P] - [A_a^G | h_A | A_{\bar{a}}^G]$$

$$S[A_a A_b | A_{\bar{a}} A_{\bar{b}}] = [A_a^P A_b^P | A_{\bar{a}}^P A_{\bar{b}}^P] - [A_a^G A_b^G | A_{\bar{a}}^G A_{\bar{b}}^G]$$

Therefore the total promotional energy is
$$E^P = \sum_A E^P(A) = \sum_A \{E^{PRH} + E^{PRC}\}.$$

Quasi-Classical Interactions

The quasi-classical energy terms arise from the electrostatic coulombic interactions between the atoms when they are moved from their separated positions to the internuclear distances being considered. It consists of four terms: 1) the nuclear repulsions, 2) interaction of the quasi-classical charge distribution on atom B, $\sum_{Bb} q(Bb) Bb^2$ with nucleus A, 3) interaction of the quasi-classical charge distribution on atom A, $\sum_{Aa} q(Aa) Aa^2$, with nucleus B, 4) and the repulsive interaction between these two charge distributions.

$$E^{ac} = Z_A Z_B / R_{AB} + \sum_{Bb} q(Bb) [Bb / -Z_A / R_A | Bb] + \sum_{Aa} q(Aa) [Aa / -Z_B / R_B | Bb] + \sum_{Aa} \sum_{Bb} q(Aa) q(Bb) [Aa^2 / Bb^2]$$

where $q(Aa)$ is the population of the orbitals (Aa).

The energy contribution of E^{ac} to the total energy is usually small and negative, even though it is made up of large individual contributions. Obviously the nuclear and electron repulsion terms

are balanced out by the nuclear attraction terms.

As the quasi-classical energy is partitioned into orbital contributions, it is appropriate to have the orbital pair contributions exhibit the effect of smallness and negativity normally found in the total quasi-classical energy. In order to do this, the nuclear repulsion term $ZAZB/RAB$ must be broken down into orbital pair contributions. Since their magnitude is approximately the same as the electron-nuclear attraction terms, the following definition can be made: $Z(Aa) = q^P(Aa) = q(Aa)$ is that part of the nuclear charge ZA on the nucleus A which is to be associated with orbital Aa .

$$\text{Then } E^{qc} = \sum_{Aa} \sum_{Bb} (Aa, Bb)^{qc} \quad (A \neq B)$$

$$(Aa, Bb)^{qc} = q(Aa)q(Bb) \left\{ \frac{1}{R} + \left[\frac{Bb}{-1/R_A} \middle| Bb \right] + \left[\frac{Aa}{-1/R_B} \middle| Aa \right] + \left[\frac{Aa^2}{Bb^2} \right] \right\}$$

It is seen that the orbital energy consists of a population factor which is the product of two orbital populations and a normalized quasi-classical energy between the orbitals (Aa) and (Bb) . This population factor will vary from zero to four. It will be zero when both orbitals are unoccupied and four when both orbitals are doubly occupied. It will be in between these two extremes for all other cases.⁷

⁷R. R. Rue, Chemical Binding in Homonuclear Diatomic Molecules. (Unpublished thesis in Iowa State University Library)

The normalized quasi-classical energy represents the electrostatic interaction between the nuclear point charges and the electronic charge clouds. In each of these orbital energies the electronic cloud will shield the nucleus to a certain extent, and for this reason $(Aa, Bb)^{ac}$ are called shielded nuclear attraction energy terms.

Sharing Penetration Interactions

The sharing penetration portion arises from the sharing of electrons between the atoms in the molecule. Before the molecule is formed, one charge cloud on one atom repels the charge cloud on the other atom. After electron sharing, part of the charge clouds are now due to the same electron, causing a decrease in the interaction between the charge clouds.

Although there is a decrease in the interatomic electronic repulsion, there is a larger increase in the intra-atomic electronic repulsion because the electrons are much closer to each other and will cause a greater repulsion. The overall effect of sharing penetration is thus a raising of the total energy which is unfavorable for bond formation. Since interference cannot occur without electron sharing, it is evident that it is an important effect in the total energy lowering associated with bond formation.

Since this effect is purely electronic in nature, the sharing penetration energies arise only from the second order density matrix.

In mathematical terms, the part that describes the decrease in interatomic pair density due to interatomic electron sharing is

$$\begin{aligned} \pi^{SP}(A,B) = & \sum_{a,b} g^{SP}(Aa, Bb) [Aa^2 | Bb^2] \\ & + \sum_{a,\bar{a}}' \sum_{b,\bar{b}}' P^{SP}(AaA\bar{a} | BbB\bar{b}) [AaA\bar{a} | BbB\bar{b}] \\ & + \sum_{a,\bar{a}}' \sum_b P^{SP}(AaA\bar{a} | Bb) [AaA\bar{a} | Bb^2] \\ & + \sum_{b,\bar{b}}' \sum_a P^{SP}(BbB\bar{b} | Aa) [BbB\bar{b} | Aa^2] \quad (A \neq B) \end{aligned}$$

where the first term is the major term.

$$g^{SP}(Aa | Bb) = -f_x(Aa | Bb) = g(Aa | Bb) - g(Aa)g(Bb)$$

$$P^{SP}(AaA\bar{a} | Bb) = P(AaA\bar{a} | Bb)$$

$$P^{SP}(BbB\bar{b} | Aa) = P(BbB\bar{b} | Aa)$$

$$P^{SP}(AaA\bar{a} | BbB\bar{b}) = P(AaA\bar{a} | BbB\bar{b})$$

The part that describes the increase in intra-atomic pair density

is given by

$$\begin{aligned} \pi^{SP}(A) = & \sum_{a,\bar{a}} g^{SP}(Aa, A\bar{a}) [Aa^2 | A\bar{a}^2] \\ & + \sum_{a,\bar{a}}' \sum_{a'} P^{SP}(AaA\bar{a} | Aa') [AaA\bar{a} | (Aa')^2] \end{aligned}$$

the first term is the predominant one and is derived from

$$g^{SP}(Aa, A\bar{a}) = g^{SP}(Aa)g^{SP}(A\bar{a}) / \sum_{\bar{a}'} g^{SP}(Aa')$$

$$g^{SP}(Aa) = \sum_b f_x(Aa, Bb) \quad (B \neq A)$$

$$P^{SP}(AaA\bar{a} | Aa') = P(AaA\bar{a} | Aa')$$

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⁸K. Ruedenberg, op. cit.

Interference

The most important part of the partitioning is the interference among the atomic orbitals. It is this interference which causes the stabilization energy required for a chemical bond. The interference density causes a rearrangement in the total density without changing its total population.

Constructive interference rearranges the density so that density is taken from atoms and put in the bond region. Destructive interference does the opposite by taking density out of the bond region and putting it close to the atom.

Most workers up to the time of the publication of Ruedenberg's work felt that the energy lowering required to form a chemical bond came from a lowering of the potential energy. They based this belief on the following reasoning. The virial theorem is known to be true for both the free atom case and also for the molecule in the equilibrium position. The change in the energy in going from the free atom to the molecule will give a binding energy $E^B = \Delta V + \Delta T < 0$ with $\Delta V < 0$ and $\Delta T > 0$ with $|\Delta V| = 2\Delta T$. This shows the energy lowering comes from the drop in potential energy with the kinetic energy increasing.

Ruedenberg however, shows the energy lowering is in fact caused by the large decrease in the kinetic energy when interference occurs and there is usually a slight increase in the potential

energy caused by interference.⁹

There are two types of interference energy, E^{II} and E^I . E^{II} is the only term which contains interactions between different bonds. The integrals that make up this term are large, but there is a considerable amount of internal cancellation within each orbital pair causing each orbital pair and the total E^{II} to be small in comparison to E^I in normal molecules. Ruedenberg feels that since the E^{II} term is small, this gives some theoretical basis for the experimentally established additivity of bond energies.

The interference energy E^I is broken down into orbital contributions via

$$E^I = \sum_{A \neq \bar{A}} E^I(A, \bar{A})$$

$$E^I(A, \bar{A}) = 2 \sum_{a\bar{a}} P(Aa|\bar{A}\bar{a}) E \langle Aa, \bar{A}\bar{a} \rangle \quad (A \neq \bar{A})$$

$$E \langle Aa, \bar{A}\bar{a} \rangle = T \langle Aa, \bar{A}\bar{a} \rangle + U \langle Aa, \bar{A}\bar{a} \rangle$$

$$U \langle Aa, \bar{A}\bar{a} \rangle = \sum_B U_B \langle Aa, \bar{A}\bar{a} \rangle$$

$$U_B \langle Aa, \bar{A}\bar{a} \rangle = [\langle Aa, \bar{A}\bar{a} | B \rangle / N_u B]$$

$$+ \sum_{b, \bar{b}} g^I(Aa, \bar{A}\bar{a} | Bb, \bar{b}) [\langle Aa, \bar{A}\bar{a} | Bb, \bar{b} \rangle]$$

$$g^I(Aa, \bar{A}\bar{a} | Bb, \bar{b}) = P(Aa, \bar{A}\bar{a} | Bb, \bar{b}) / P(Aa, \bar{A}\bar{a})$$

$$g^I(Aa, \bar{A}\bar{a} | Bb, \bar{b}) = P(Aa, \bar{A}\bar{a} | Bb, \bar{b}) / P(Aa, \bar{A}\bar{a}) \quad (b \neq \bar{b})$$

$$T \langle Aa, \bar{A}\bar{a} \rangle = T(Aa, Aa) - \frac{1}{2} S(Aa, \bar{A}\bar{a})$$

$$[T(Aa, Aa) + T(\bar{A}\bar{a}, \bar{A}\bar{a})] \quad (A \neq \bar{A})$$

⁹K. Ruedenberg, op. cit.

The contribution to each orbital pair is made up of two parts; the bond order $P(A_a | \bar{A}\bar{a})$ and the "resonance integral" $E \langle A_a, \bar{A}\bar{a} \rangle$. This illustrates that the bond order concept does have an important place in rigorous calculations and that the resonance integral is more complicated than is considered in semi-empirical approaches.¹⁰

¹⁰K. Ruedenberg, op. cit.

CHAPTER II
THE APPLICATION OF RUEDENBERG'S PARTITIONING ON THE HE-HE
INTERACTION

Ruedenberg and his co-workers have applied the Ruedenberg partitioning method to several cases and have obtained good results. The cases studied thus far have been the water molecule,¹ the hydrogen molecule ion,² some diatomic homonuclear systems³ and some diatomic hydride molecule systems.⁴ In all of this work the partitioning was done at only one internuclear distance, and mainly as a comparison between different molecules of the same family.

In the present investigation of the helium-helium interaction, only one "molecule" will be investigated, but it will be studied thoroughly within the LCAO-MO-SCF model. The partitioning will be done with several different wavefunctions and at several different internuclear distances. The He-He interaction is an interesting system to study because although it does not have a strong attractive force as in a chemical bond, there is an attractive force between the two atoms due to van der Waals forces. Ruedenberg's

¹C. Edmiston and K. Ruedenberg, J. Phys. Chem., 68, 1628 (1964)

²E. Mehler and K. Ruedenberg, (to be published)

³R. R. Rue and K. Ruedenberg, J. Phys. Chem., 68, 1676 (1964)

⁴E. M. Layton and K. Ruedenberg, J. Phys. Chem., 68, 1654 (1964)

method of partitioning would also be expected to be successful on this type of interaction.

Van der Waals forces can be thought of as that force which gives rise to the pressure correction constant, "a", in van der Waals equation. The forces arising in the case of two interacting nonpolar helium atoms were first derived by London and called dispersion forces. Dispersion forces arise from the attraction between the molecules by means of a temporary dipole. Since the electrons in the atom are moving, each atom can have a temporary dipole which is capable of inducing a dipole in another atom parallel to itself. Thus, although the overall dipole may be zero, the tendency for alignment still exists and causes attractive forces.⁵

The calculations of the repulsive energy and van der Waals energy in two helium atoms have been done by a considerable number of persons. Page,⁶ Slater and Kirkwood,⁷ and Karplus and Kolker⁸ have done calculations on van der Waals forces only. Page performed his calculations for helium atoms only, while the other two groups concerned themselves with other atoms and molecules in addition to their calculations on helium atoms. The remaining calculations

⁵H. Margenau, Rev. Mod. Phys., 11, 1 (1939)

⁶C. H. Page, Phys. Rev., 53, 426 (1938)

⁷J. C. Slater and John Kirkwood, Phys. Rev., 37, 682 (1931)

⁸M. Karplus and J. Kolker, J. Chem. Phys., 41, 3955 (1964)

were performed for the interaction of two helium atoms at both the repulsive region and the van der Waals region.⁹⁻²⁶ The early calculations, which were performed by Slater and Rosen, were done by the valence-bond method. Since then, however, the calculations have been of the molecular orbital type.

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- ⁹J. C. Slater, Phys. Rev., 32, 349 (1928)
- ¹⁰P. Rosen, J. Chem. Phys., 18, 1182 (1950)
- ¹¹V. Griffing and J. F. Wehner, J. Chem. Phys., 23, 1024 (1955)
- ¹²M. Sakamoto and E. Ishiguro, Progr. Theoret. Phys. (Kyoto), 15, 37 (1956)
- ¹³S. Huzinaga, Progr. Theoret. Phys. (Kyoto) 18, 131 (1957)
- ¹⁴S. Huzinaga, Progr. Theoret. Phys. (Kyoto) 28, 15 (1958)
- ¹⁵T. Hasino and S. Huzinaga, Progr. Theoret. Phys. (Kyoto), 20, 631 (1958)
- ¹⁶N. Moore, J. Chem. Phys., 33, 471 (1960)
- ¹⁷B. J. Ransil, J. Chem. Phys., 34, 2109 (1961)
- ¹⁸N. Lynn, Proc. Phys. Soc. (London), 72, 201 (1958)
- ¹⁹P. E. Phillipson, Phys. Rev., 125, 1981 (1962)
- ²⁰D. Y. Kim, Zeitschrift fur Physik, 166, 359 (1961)
- ²¹J. S. Dooling and P. Piper, Bull. Am. Phys. Soc., 5, 339 (1960)
- ²²R. Gasper and I. Tamassylentei, Acta Univ. Debrecen. Ludovico Kossuth Nom., Ser. Phys. Chim., 8(4), 103 (1962)
- ²³C. A. Coulson, Rev. Mod. Phys., 32, 170 (1960)
- ²⁴H. S. Taylor and F. E. Harris, Molecular Physics, 7, 287 (1963-1964)
- ²⁵A. C. Wahl (to be published)
- ²⁶N. Kestner (to be published)

The most accurate calculation using just 1S electron orbitals was performed by Phillipson,²⁷ in which the energy was minimized at each internuclear distance by varying the orbital exponents of 1S and 1S'. For this reason 1S,1S' basis set was one of the three chosen on which to do the partitioning. The other two basis sets were the 1S-2S-2P σ performed by Ransil²⁸ and the recent 1S-1S'-2P σ calculation by Wahl.²⁹

The potential energy curves of both Ransil and Phillipson showed a small minimum which appeared to be representing van der Waals forces. The recent results of Wahl and Kestner,³⁰ working independently of each other, have shown that these minimums are merely spurious and not true minimums. In fact, without doing a very accurate calculation, one cannot obtain any true minimum in the potential energy curve because the very small van der Waals forces are part of the electron correlation "forces." Due to the large amount of computer time involved, no one has performed such a calculation to date.

The first step in the actual calculations was to attempt to duplicate the energy values obtained by Phillipson, Ransil and Wahl for their respective basis sets. The values of the internuclear distances, weight factors and orbital parameters used were those

²⁷P. E. Phillipson, op. cit.

²⁸B. J. Ransil, op. cit.

²⁹A. C. Wahl, op. cit.

³⁰N. Kestner, op. cit.

published in their papers. The integrals needed to perform the calculation were obtained from a program adapted from the IBM 7090 to the IBM 7040 by Matule.³¹ The calculated energy values using these integrals were quite close to the published results, but not so accurate as would be expected. The problem seemed to be caused by the fact that enough significant figures could not be attained from the integral program as it then ran on the IBM 7040, yet these were the only integrals available to our group at the time. The partitioning was almost completed using these integrals until new and better integrals were obtained from programs written by Ruedenberg and his students at Iowa State University.³² The calculations were redone using these new integrals for the 1S-1S', 1S-1S'-2P_σ and 1S-2S-2P_σ basis sets.

In order to calculate the energy, a vast amount of tedious and lengthy algebra is involved. Therefore, a general program was written to handle the algebra involved in the expansion of the first and second order density matrices. The output from the General Algebra program has been put on tape and can be used in conjunction with the integrals to calculate the total energy. The General Algebra Program will handle all three basis sets reported here, larger basis sets, as well as other diatomic molecules.

This program is based on finding the first order density matrix

³¹C. Matule, (private communication)

³²D. Silver, (private communication)

in terms of the expansion $\rho(X|X') = \sum_{m=1}^{\infty} P_m(X|X')$

$$P_m(X|X') = N_m \phi_m(X) \phi_m^*(X')$$

n are the number of orbitals involved and N_m are the orbital occupation numbers which vary from zero to two.

For the Hartree-Fock closed shell state the occupation numbers are restricted to $N_m = \begin{cases} 2 & m=1, 2, \dots (N/2) \\ 0, & m > N/2 \end{cases}$

The pair density is then calculated from the first order density matrix via $\pi(X, X_2) = \rho(X_1) \rho(X_2) - \frac{1}{2} \rho(X_1|X_2)^2$

The first step in the actual partitioning is to set up the bond order matrix $P(A_a|B_b)$ and the pair bond order matrix $P(A_a \bar{A}_i | B_b \bar{B}_i)$, which are obtained from the coefficients of the first and second order density matrices.³³

For example, to illustrate what the bond order matrix looks like for a specific case, the 1S-1S' set may be considered. The first order density matrix is

$$\begin{aligned} \rho(X) = & 2N_+^2 1S_a | 1S_a + 2N_+^2 1S_a | 1S_b + 2N_+^2 1S_b | 1S_a + 2N_+^2 1S_b | 1S_b + 2N_-^2 1S_a' | 1S_a' \\ & - 2N_-^2 1S_a' | 1S_b' - 2N_-^2 1S_b' | 1S_a' + 2N_-^2 1S_b' | 1S_b' \end{aligned}$$

The bond order matrix will have the form

$$\begin{array}{l} 1S_a \\ 1S_a' \\ 1S_b \\ 1S_b' \end{array} \begin{pmatrix} 1S_a & 1S_a' & 1S_b & 1S_b' \\ P(1S_a|1S_a) & P(1S_a|1S_a') & P(1S_a|1S_b) & P(1S_a|1S_b') \\ P(1S_a'|1S_a) & P(1S_a'|1S_a') & P(1S_a'|1S_b) & P(1S_a'|1S_b') \\ P(1S_b|1S_a) & P(1S_b|1S_a') & P(1S_b|1S_b) & P(1S_b|1S_b') \\ P(1S_b'|1S_a) & P(1S_b'|1S_a') & P(1S_b'|1S_b) & P(1S_b'|1S_b') \end{pmatrix}$$

³³K. Ruedenberg, Rev. Mod. Phys., 34, 326 (1962)

using the coefficients of the first order density expansion the bond order matrix will appear as follows:

$$\begin{array}{l}
 1Sa \\
 1Sa' \\
 1Sb \\
 1Sb'
 \end{array}
 \begin{pmatrix}
 1Sa & 1Sa' & 1Sb & 1Sb' \\
 2N_+^2 & 0 & 2N_+^2 & 0 \\
 0 & 2N_-^2 & 0 & -2N_-^2 \\
 2N_+^2 & 0 & 2N_+^2 & 0 \\
 0 & -2N_-^2 & 0 & 2N_-^2
 \end{pmatrix}$$

The pair bond matrix can then be attained in a similar way from the coefficients of the second order density matrix, however, it was found that there is an easier way to do this for SCF-MO calculations on closed shell structures. In this special but frequently occurring case the pair bond order matrix can be obtained from

$$P(A_a \bar{A}_a | B_b \bar{B}_b) = P_c(A_a \bar{A}_a | B_b \bar{B}_b) - P_x(A_a \bar{A}_a | B_b \bar{B}_b)$$

$$P_c(A_a \bar{A}_a | B_b \bar{B}_b) = P(A_a | \bar{A}_a) P(B_b | \bar{B}_b)$$

$$P_x(A_a \bar{A}_a | B_b \bar{B}_b) = \frac{1}{4} \{ P(A_a | B_b) P(\bar{A}_a | \bar{B}_b) + P(A_a | \bar{B}_b) P(\bar{A}_a | B_b) \}$$

The total energy can now be expressed in the form

$$E = Z_A Z_B / R + \sum_{A_a} \sum_{B_b} P(A_a, B_b) [A_a | h | B_b]$$

$$+ \frac{1}{2} \sum_{A_a} \sum_{\bar{A}_a} \sum_{B_b} \sum_{\bar{B}_b} P(A_a \bar{A}_a | B_b \bar{B}_b) [A_a \bar{A}_a | B_b \bar{B}_b]$$

where $[A_a | h | B_b]$ are the one-electron energy integrals and

$[A_a \bar{A}_a | B_b \bar{B}_b]$ are the electron interaction integrals. It can

now be easily seen that the total energy for the system under the

SCF-MO closed shell case can be obtained in a more simplified way

than that which uses the General Algebra Program.

The original basis sets are non-orthogonal, but in order to use Ruedenberg's method of partitioning it is necessary to have an orthogonal basis set. This can be accomplished by first obtaining the transformation matrix via the Gram-Schmidt Orthogonalization procedure. This transformation matrix is then used to transform the bond order matrix, the pair bond order matrix and the energy integral matrices associated with them into an orthogonal basis set.

The first order density matrix can be written in the form

$$\rho = X^T P X$$

where P is the bond order matrix. The energy associated with this is $E' = \int dx h P$

$$h = \begin{pmatrix} (X_{ai}|h|X_{aj}) & (X_{ai}|h|X_{bj}) \\ (X_{ai}|h|X_{bj}) & (X_{bi}|h|X_{bj}) \end{pmatrix}$$

The first and second order density matrices are invariant to certain transformations on the basis set so that one can write

$X' = T X$ Therefore $X = T^{-1} X'$ putting this into ρ we get

$$\begin{aligned} \rho &= (T^{-1} X')^T P T^{-1} X' \\ &= X'^T (T^{-1})^T P T^{-1} X' \end{aligned} \quad T = \begin{pmatrix} T_{AA} & 0 \\ 0 & T_{BB} \end{pmatrix}$$

$$P' = (T^{-1})^T P T^{-1}$$

$$T_{AA} = T_{BB}$$

hence $\rho = X'^T P' X'$

It can be seen from above that the matrix is expressed in the new basis set by transforming the bond order matrix P into P' by the transformation \mathbb{T} , where \mathbb{T}_{AA} of \mathbb{T} is the matrix that is obtained from the Gram-Schmidt Orthogonalization.

In order to transform the one-electron energy integrals, it is observed that $E' = \int dx h P = \sum_r \sum_s P(r/s) (X_r' | h | X_s')$

$$h' = ((X_r' | h | X_s')) = ((\sum_i T_{ri} X_i | h | \sum_j T_{sj} X_j))$$

$$\begin{aligned} h' &= (\sum_i \sum_j T_{ri} (X_i | h | X_j) T_{sj}) \\ &= (\vec{T}_r \quad h \quad \vec{T}_s^T) = \mathbb{T} h \mathbb{T}^T \end{aligned}$$

where \vec{T}_r and \vec{T}_s are rows of \mathbb{T} . For the second order density matrix and the energy associated with it, this can be written

$$\mathbb{T}(X_1, X_2) = \sum_{a\bar{a}} \sum_{b\bar{b}} (A_a, \bar{A}_{\bar{a}}), P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) (B_b)_2 (\bar{B}_{\bar{b}})_2$$

$$A' = \mathbb{T} A \quad A'_i = \sum_g t_{ig} A_g$$

$$A = \mathbb{T}^{-1} A' \quad A_g = \sum_i t_{gi}^{-1} A'_i$$

therefore

$$\mathbb{T}(X_1, X_2) = \sum_{m\bar{m}} \sum_{n\bar{n}} \sum_{a\bar{a}} \sum_{b\bar{b}} \tau_{am}^{-1} \tau_{\bar{a}\bar{m}}^{-1}$$

$$P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) \tau_{bn}^{-1} \tau_{\bar{b}\bar{n}}^{-1} A'_m A'_{\bar{m}} B'_n B'_{\bar{n}}$$

$$= \sum_{m\bar{m}} \sum_{n\bar{n}} P(A'_m \bar{A}'_{\bar{m}} | B'_n \bar{B}'_{\bar{n}}) A'_m A'_{\bar{m}} B'_n B'_{\bar{n}}$$

$$P_{m\bar{m}n\bar{n}} = \sum_{a\bar{a}} \sum_{b\bar{b}} \tau_{am}^{-1} \tau_{\bar{a}\bar{m}}^{-1} P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) \tau_{bn}^{-1} \tau_{\bar{b}\bar{n}}^{-1}$$

The π energy contribution to E, E_π is

$$E_\pi = \sum_{a\bar{a}} \sum_{b\bar{b}} P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) [A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}] \\ = \sum_{m\bar{m}} \sum_{n\bar{n}} P(A'_m \bar{A}'_{\bar{m}} | B'_n \bar{B}'_{\bar{n}}) [A'_m \bar{A}'_{\bar{m}} | B'_n \bar{B}'_{\bar{n}}]$$

$$A'_i = \sum_j t_{ij} A_j$$

$$[A'_m \bar{A}'_{\bar{m}} | B'_n \bar{B}'_{\bar{n}}] = \sum_{a\bar{a}} \sum_{b\bar{b}} \tau_{ma} \tau_{\bar{m}\bar{a}} [A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}] \tau_{nb} \tau_{\bar{n}\bar{b}}$$

A second transformation matrix is needed to transform these orthogonal atomic orbitals into valence atomic orbitals (VAO's), the orbitals used in the partitioning. This transformation matrix is obtained by finding the eigenvectors of the intra-atomic terms of the new bond order matrix. In a way similar to obtaining the orthogonal basis set, this new transformation matrix transforms the orthogonal basis set into the basis set consisting of valence atomic orbitals.

At this stage another check on the total energy should be made to find out if the transformation has been performed correctly. These new matrices and energy integrals are used as input to the various partitioning programs.

CHAPTER III
RESULTS AND CONCLUSIONS

The wavefunctions that were used for the different basis sets were as follows:

1S-1S'

$$\begin{aligned}\phi_+ &= N_+ (1S_a + 1S_b) \\ \phi_- &= N_- (1S_{a'} - 1S_{b'})\end{aligned}$$

1S-2S-2P σ

$$\begin{aligned}\phi_+ &= N_+ [(1S_a + 1S_b)C_{11} + (2S_a + 2S_b)C_{12} + (2P_{\sigma a} + 2P_{\sigma b})C_{13}] \\ \phi_- &= N_- [(1S_a - 1S_b)C_{12} + (2S_a - 2S_b)C_{22} + (2P_{\sigma a} - 2P_{\sigma b})C_{23}]\end{aligned}$$

1S-1S'-2P σ

$$\begin{aligned}\phi_+ &= [(1S_a + 1S_b)C_{11} + (1S_{a'} + 1S_{b'})C_{12} + (2P_{\sigma a} + 2P_{\sigma b})C_{13}] / \sqrt{2} \\ \phi_- &= [(1S_a - 1S_b)C_{21} + (1S_{a'} - 1S_{b'})C_{22} + (2P_{\sigma a} - 2P_{\sigma b})C_{23}] / \sqrt{2}\end{aligned}$$

The 1S-1S' basis set generates the two molecular orbitals ϕ_+ and ϕ_- in quite a different manner than the 1S-1S'-2P σ basis set and the 1S-2S-2P σ basis set. If the 1S-1S' basis set was set up like the other two basis sets it would look like:

$$\begin{aligned}\phi_+ &= N_+ [(1S_a + 1S_b)C_{11} + (1S_{a'} + 1S_{b'})C_{12}] \\ \phi_- &= N_- [(1S_a - 1S_b)C_{21} + (1S_{a'} - 1S_{b'})C_{22}]\end{aligned}$$

The ground state for both the 1S-1S' and 1S-2S-2P_σ basis sets is merely a $\phi = 1S_a$ wavefunction with $\zeta = 1.6875$. In this case

$$\rho_A(X) = 2|S_a|S_a \quad \pi_A(X_1, X_2) = 2|S_a(1)|S_a(1)|S_a(2)|S_a(2)$$

$$E\rho_A = \int h\rho(X) dx = -3.90234375 \text{ a. u.}$$

$$E\pi_A = \frac{1}{2} \int dx_1 \int dx_2 \pi(X_1, X_2) / r_{12} = 1.05468750 \text{ a. u.}$$

The total energy for the helium atom is equal to $E\rho_A + E\pi_A$ which is -2.84765625 a. u. The ground state for the 1S-1S'-2P_σ basis set is more complicated. The ground state wavefunction is

$$\phi = (C_{11}|S_a + C_{12}|S_{a'}) / \sqrt{2}$$

$$\rho_A(X) = 2\phi^2 = 2(C_{11}^2|S_a|S_a + C_{11}C_{12}|S_a|S_{a'} + C_{12}C_{11}|S_{a'}|S_a + C_{12}^2|S_{a'}|S_{a'})$$

$$\pi_A(X_1, X_2) = \rho_A(X_1)\rho_A(X_2) - \frac{1}{2}|\rho_A(X_1|X_2)|^2$$

$$C_{11} = .18159$$

$$C_{12} = .84289$$

$$E\rho_A = \int h\rho_A(X) dx = -3.8874331 \text{ a. u.}$$

$$E\pi_A = \frac{1}{2} \int dx_1 \int dx_2 \pi_A(X_1, X_2) / r_{12} = 1.02578755 \text{ a. u.}$$

The total energy for the helium atom for this approximation is -2.86164555 a. u. The exact energy is -2.90372 a. u. so that one

can see the ground state used in the $1S-1S'-2P\sigma$ basis set is a better approximation than the ground state used for the $1S-1S'$ and $1S-2S-2P\sigma$ basis sets.

The He-He interaction presents a very interesting system to study. One of the reasons for the interest in this system was the large discrepancy in the theoretical energy calculations and the experimentally determined energy in the repulsive region for an internuclear distance of 1.0 to 2.0 atomic units. Phillipson performed an extended configuration interaction calculation in this region, but there remained a large discrepancy between the calculated energy and the experimental energy. An extended configuration interaction calculation like Phillipson's should get quite close to the experimental energy, therefore he postulated that the experimental energy was incorrect and that his calculation at the internuclear distances from 1.0 to 2.0 atomic units was much closer to the true energy.¹ This was a unique statement for Phillipson to make since up to this time the accuracy of a calculation was based on how close it came to the experimental energy. The result was that new experimental work has been done on this interaction and it was found that the old experimental results were wrong and the new experimental results were quite close to the calculated results of Phillipson.

¹Phillipson, op. cit.

On the other hand, the calculations of Phillipson with a $1S-1S'$ basis set (different from his configuration interaction calculation)² and that of Ransil with a $1S-2S-2P\sigma$ basis set³ apparently came quite close to the experimental values in the van der Waals region. This is especially true of Ransil's calculation in which the energy minimum and the internuclear distance were very close to the experimental results. These were the most accurate calculations that had been done when this work was started. It was not until quite recently that more extensive calculations were completed on the interaction. These new calculations of Wahl⁴ and Kestner⁵ have shown that the calculations of Ransil and Phillipson gave spurious minimum in the van der Waals region. For this reason the $1S-1S'-2P\sigma$ basis set calculation of Wahl was chosen for Ruedenberg's partitioning along with the $1S-1S'$ of Phillipson and the $1S-2S-2P\sigma$ of Ransil. It was felt that it would form an interesting comparison to look at these different calculations to see how Ruedenberg's partitioning would expose these problems in the wavefunction approximations, if it did at all.

Before I begin a discussion of the partitioned fragments, I will discuss the reasons Kestner believes the $1S-1S'$ and $1S-2S-2P\sigma$ calculations are incorrect. In Ransil's calculation,

²Phillipson, op. cit.

³Ransil, op. cit.

⁴Wahl, op. cit.

⁵Kestner, op. cit.

using a 1S-2S-2P σ basis set, he forced $J_{1s} = J_{2s} = J_{2p\sigma} = J$ and he then varied this orbital parameter. If one compares the energy obtained for the helium atom with a 1S orbital basis set with the energy obtained for the helium atom with a 1S-2S orbital basis set in which $J_{1s} = J_{2s} = J$, the energy obtained for these two basis sets is exactly the same to fourteen significant figures. Therefore this particular 1S-2S orbital basis set is not a better approximation than just the simple 1S basis set which is a poor approximation to the energy for the helium atom. Thus, the 1S-2S-2P σ basis set, using the same orbital parameter values for all three orbitals, describes the atom very poorly but it describes the molecule fairly accurately. In order to have a good description of what is happening, the wavefunction must describe both cases to the same order of error. When one subtracts out the separated atom energies from the total energy a spurious minimum occurs which can be traced back to error accumulation in this poor approximation to the ground state. This ground state is like a "standard state" and if one has a bad "standard state" it can cause all of the results to be inaccurate. The only reason Kestner gives for the spurious minimum in Phillipson's 1S-1S' calculation is that by using very simple wavefunctions, the energy is subject to considerable error.⁶ One thus sees that a complete shift has taken place, since originally the calculations of Ransil and Phillipson were thought

⁶Kestner, op. cit.

to be quite good in the van der Waals region but quite poor in the repulsive region. Now it is felt that just the opposite is true. The wavefunctions are fairly accurate in the repulsive region but not very accurate in the van der Waals region.

In performing the transformations from Slater atomic orbitals into valence atomic orbitals, the transformations progressed very smoothly for the 1S-2S-2P_σ and the 1S-1S'-2P_σ basis sets. The 1S-1S' basis set gave some problems beyond 2.8 a. u., for which the values of \mathcal{J}_{1S} and $\mathcal{J}_{1S'}$ become very close to each other causing the transformation matrices to become unstable. In fact, at the internuclear distances of 3.071834, 10.0 and 20.0 a. u., $\mathcal{J}_{1S} = \mathcal{J}_{1S'}$ and the transformation could not be performed at all. Although the total energy was correct after the transformation, some of the individual fragments of the partitioning gave results that were as much as a factor 10^7 away from the expected results. For this reason, where the 1S-1S' basis set is not discussed in a particular partitioned fragment, assume that meaningful results were not obtained for that particular fragment. Of course, this makes one question whether any of the fragments for the 1S-1S' basis set are correct. One does not know for sure, but the fragments that do not give completely unmeaningful results do show definite trends that are interesting to trace.

Another problem occurs in interpreting the results in the van der Waals regions, in that the total energy and the partitioned fragment energies are so small that the values obtained are right

on the edge of the accuracy of the calculations. For this reason the trends in that region have been considered and not just one isolated internuclear distance.

In calculation of the promoted state energies, Ruedenberg and his students decided to transform from valence atomic orbitals back into the Slater atomic orbitals. The reason they stated for doing so were that since the promoted state was still atomic in nature it was more meaningful to use Slater atomic orbitals.⁷

I have a differing opinion in that the promoted state is still one of the necessary steps in conceptually building up a molecule. The orbital parameters have the same values in the promoted state as in the molecule. The hybridization which occurs in the promoted state for the orbitals is molecular in nature and should best be described in terms of valence atomic orbitals. For these reasons I felt it was more meaningful to perform the partitioning for the promoted state in terms of valence atomic orbitals.

It is now apparent that Ruedenberg and his students had other reasons for transforming the basis sets back to Slater atomic orbitals. The transformation into valence atomic orbitals causes the promoted state partitioning separation into contraction promotion and hybridization promotion to be incorrect. This can easily be seen by looking at the $1S-1S'-2P_{\sigma}$ basis set for which there should be

⁷Rue and Ruedenberg, op. cit.

no contraction promotion because the values of the orbital parameters for all three orbitals do not change their value from the ground state to the promoted state, but the tables do definitely give the contraction promotion energy a large value.

In this case it can easily be resolved, since there is no "real" contraction promotion, by adding together the values given for contraction promotion and hybridization promotion. One can obtain from this the true values of hybridization promotion. In the 1S-1S' and 1S-2S-2P_v cases where there is a change in the orbital parameters from the ground state to the promoted state one cannot obtain contraction promotion or hybridization promotion as completely independent quantities.

It is interesting to speculate on the importance of contraction promotion. Ruedenberg has placed strong emphasis on the connection between contraction promotion and interference.⁸ There may be a strong relationship between the two for a normal chemical bond but this does not seem to be true for the He-He interaction.

The difference between the values obtained by Wahl for the partitioned calculation I have which use the atomic values for the orbital parameters and the calculation in which the orbital parameters are optimized shows a maximum of 6% difference in the energy calculation at 1.0 a. u. and a decreasing difference with increasing internuclear distance. Beyond 4.7 a. u. there is no

⁸Ruedenberg, op. cit.

difference in the energy to the number of significant figures that Wahl calculated.

For the 1S-1S' and 1S-2S-2P σ basis sets no one has calculated the He-He interaction energy curve using the atomic values of the orbital parameters. Therefore one cannot compare the energies resulting from optimized orbital parameters with the energies obtained by using atomic orbital parameters. However, the difference in the values of the orbital parameters in the separated atom case and for two atoms at large internuclear distances is quite small. For the 1S-2S-2P σ basis set at 5.102325 a. u. the $J_{1S} = J_{2S} = J_{2P\sigma} = J = 1.6870$ and for the separated atom case $J = 1.6875$. For the 1S-1S' basis set the values at 6.238185 a. u. are $J_{1S} = 1.6862$, $J_{1S'} = 1.6888$, and for the separated atom case $J_{1S} = J_{1S'} = 1.6875$.

Due to the previously mentioned problems and the apparent smallness of contractive promotion in this particular case, the breakdown of the promotion energy into contraction promotion and hybridization promotion has been abandoned in favor of simply looking at the total promotion energies.

The internuclear distance of approximately 5.12 atomic units is the internuclear distance at which Ransil obtained his minimum energy for the 1S-2S-2P σ basis set and is approximately the experimentally determined point at which the van der Waals minimum occurs. It is therefore interesting to investigate at internuclear distances in the neighborhood of this point what the partitioning

scheme tells us. This will be done in terms of the total energy of each part and also an orbital subdivision of each part. Table I will be of great help in following what is to be said. The specific values can be obtained by looking at Tables III to XIV.

In promotion there are two possible effects that may occur. There is a change in the values of the orbital parameters, which will usually increase from the values they had in the atom. This will cause the valence electrons to contract toward the nucleus and a drop in the potential energy will occur. The electrons will have less room in which to move and this will cause the kinetic energy to increase. The increase in the kinetic energy is greater than the drop in potential energy and thus the total energy will be positive.

Normally, opposed to this effect is the hybridization of the orbitals which will cause an expansion of the orbitals. This expansion will cause the potential energy to increase, the kinetic energy to decrease and usually the total effect is dominated by the potential energy so that the total energy will increase.

In a normal molecule at the equilibrium position the energy associated with a change in the values of the orbital parameters is much greater than the energy due to hybridization. From what was stated previously, this may not be the case for the He-He interaction.

For the $1S-1S'-2P\sigma$ basis set, as stated before, there is no change in the values of the orbital parameters, and so one is left

TABLE I GENERAL VALUES OF THE PARTITIONED FRAGMENTS IN THE
VAN DER WAALS REGION

	<u>1S-2S-2Pσ</u>	<u>1S-1S'</u>	<u>1S-1S'-2Pσ</u>
Kinetic Promotion Energy	-		+
Potential Promotion Energy	+		-
Total Promotion Energy	+		+
Quasi-Classical Energy	-	-	-
Interatomic Sharing Penetration Energy	-	-	+
Intra-atomic Sharing Penetration Energy	+		-
Kinetic Interference Energy	-	-	+
Potential Interference Energy	+	+	-
Total Interference Energy	-	-	-

to consider only hybridization promotion. The $1S-1S'-2P\sigma$ basis set gives a positive kinetic promotional energy and a negative potential promotional energy with the kinetic part being greater to give a positive total promotional energy. This is interesting because it is opposite of what is expected and indicates that instead of expansion occurring there is actually contraction occurring due to hybridization.

The $1S-2S-2P\sigma$ basis set is more complicated because one has both contraction promotion and hybridization promotion involved. In this case the potential promotional energy is positive, the kinetic promotional energy is negative and the total promotional energy is positive. This expansion is due to two factors: 1) There is an expansion occurring due to the hybridization of the orbitals. 2) In contrast to the situation in most molecules there is an expansion due to the change in the value of the orbital parameter. In this case the value of the orbital parameter in the van der Waals region is less than the value of the orbital parameter in the separated atom case for this $1S-2S-2P\sigma$ calculation. Kestner claimed that the problem with the $1S-2S-2P\sigma$ basis set was the separated atom case. This separated atom factor occurs in the promotion energy, so it is here that one would expect the problems to occur. It does seem apparent that this problem is due to the fact that there is an expansion instead of a contraction as would be expected. It must also be said that the $1S-1S'-2P$ basis set does not give normal results because it gives contraction for

hybridization and not the expected expansion. This contraction may be due to the fact that the $1S-1S'-2P_{\sigma}$ basis set is nonbonding. This nonbonding causes the results in most of the fragments to be just the opposite of the results found in a bonding situation.

At very small internuclear distances, the quasi-classical interactions are also repulsive since the nuclear-nuclear term, which is repulsive, becomes much greater than the attractive terms. At larger internuclear distances the quasi-classical energy becomes attractive. It can be seen in Tables III through V that this is precisely what occurs in all three basis sets.

In a typical molecule interatomic electronic repulsion is replaced by additional intra-atomic electronic repulsion as the atoms proceed to share their electrons in forming a molecule. Since the intra-atomic repulsion is much larger than the interatomic repulsion (the electrons being closer to each other) it is evident that this sharing penetration of the pair density will raise the total energy and thus be unfavorable to bond formation. For further discussion on the sharing penetration fragment refer back to Chapter I.

For the case in which no electron sharing occurs as the atoms are brought closer together, the interatomic electronic repulsion will increase and this will cause a compensating decrease in the intra-atomic repulsion.

The $1S-2S-2P_{\sigma}$ basis set gives a negative interatomic sharing penetration energy and a positive intra-atomic sharing penetration

energy with the total energy being positive. This shows that sharing of electrons is occurring which is a good indication that constructive interference is also occurring. One does not know what the intra-atomic energy of the $1S-1S'$ basis set is but the interatomic energy is negative, indicating that constructive interference is also going to occur for this basis set.

The $1S-1S'-2P\sigma$ basis set on the other hand, gives a positive interatomic sharing penetration energy and a negative intra-atomic sharing penetration energy contribution, showing that no sharing of electrons is occurring and implying that there will be destructive interference.

The most important part of interference is the kinetic part. Ruedenberg showed that the reason a chemical bond forms is due to the large decrease in kinetic interference energy for constructive interference. The potential energy will usually increase somewhat although this is not always true. The total interference energy for constructive interference will be negative. Destructive interference will show opposite effects with the kinetic interference energy being positive and the potential interference energy will generally be negative and the kinetic part will again dominate. It is the sign of the kinetic interference energy which shows whether constructive or destructive interference will occur.

The lowering of the kinetic energy for constructive interference is similar to the energy lowering of the electron-in-a-box when the containing box is increased in size. The raising of the

potential energy is due to the fact that the interference effect cannot create new charge between the atoms, but merely transfers charge from the atomic regions into the bond region. Since the electrostatic potential is much lower near the nuclei than at the bond midpoint, the interference process is unfavorable with regards to the potential energy.⁹

The $1S-2S-2P\sigma$ and the $1S-1S'$ basis sets both have a negative kinetic interference energy, a positive potential interference energy, with the total interference energy being negative. This shows that both of these basis sets are giving constructive interference which is consistent with the sharing of electrons that occurred in the sharing penetration part.

The $1S-1S'-2P\sigma$ basis set gives a positive kinetic interference energy, a negative potential interference energy and the total interference potential energy is slightly negative. Thus the $1S-1S'-2P\sigma$ basis set gives destructive interference in accordance with the fact that no sharing of electrons occurred and may also be the explanation of why contraction hybridization occurred instead of expansion hybridization.

One can now look at these various partitioned fragments at these large internuclear distances in terms of an orbital subdivision. The orbital pair energy consists of the energy associated with just the interaction between the two orbitals in that particular orbital

⁹Ruedenberg, op. cit.

pair. For example, the (1Sa,2Sb) orbital pair gives the energy associated with the interaction of the 1Sa orbital with the 2Sb orbital in the fragment being considered. For the case in which the orbitals are exactly the same and on the same atoms, for example the (1Sa,1Sa) this orbital pair is just the energy for the 1Sa orbital alone. In all cases the contribution from all orbital pair interactions involving the 2P σ orbital are negligible, for example (1Sa,2P σ b), and (2P σ a,2P σ a). Table II will be of great help in the following discussion. More explicit values can be found in Tables XV to XLI.

The promotion energy for the 1S-2S-2P σ basis set has the (1Sa,1Sa) orbital pair having a negative kinetic energy, a positive potential energy and a total energy being positive. Therefore, this orbital is undergoing expansion. The (1Sa, 2Sa) and (2Sa, 1Sa) orbital pairs have a positive potential energy, and no contribution from the kinetic part. This indicates that these orbital pairs are also undergoing expansion. The (2Sa, 2Sa) orbital pair has a positive kinetic part, a negative potential part and the total is negative. For this reason this orbital pair is undergoing contraction. These results all seem quite logical when one considers that the ground state is only a 1S atomic orbital with a $\int 1/S = 1.6875$.

The 1S-1S'-2P σ basis set gives some interesting results in comparison to the 1S-2S-2P σ basis set. The (1Sa, 1Sa) orbital pair has a positive promotion kinetic energy, a negative promotion potential energy, and the total promotion energy is negative.

TABLE II GENERAL VALUES OF THE ORBITAL PAIRS FOR THE PARTITIONED
FRAGMENTS IN THE VAN DER WAALS REGION

	<u>1S-2S-2P_σ</u>		
	<u>(1Sa,1Sa)</u> or <u>(1Sa,1Sb)</u>	<u>(1Sa,2Sa)</u> or <u>(1Sa,2Sb)</u>	<u>(2Sa,2Sa)</u> or <u>(2Sa,2Sb)</u>
Kinetic Promotion Energy	-	0.0	+
Potential Promotion Energy	+	+	-
Total Promotion Energy	+	+	-
Quasi-Classical Energy	-	0.0	0.0
Interatomic Sharing Penetration Energy	+	-	0.0
Intra-atomic Sharing Penetration Energy	+	+	0.0
Kinetic Interference Energy	+	-	0.0
Potential Interference Energy			
Total Interference Energy	+	-	0.0

TABLE II (Continued) GENERAL VALUES OF THE ORBITAL PAIRS FOR THE
PARTITIONED FRAGMENTS IN THE VAN DER WAALS REGION

	<u>1S-1S'-2Pσ</u>		
	<u>(1Sa,1Sa)</u> or <u>(1Sa,1Sb)</u>	<u>(1Sa,1Sa')</u> or <u>(1Sa,1Sb')</u>	<u>(1Sa',1Sa')</u> or <u>(1Sa',1Sb')</u>
Kinetic Promotion Energy	+	-	-
Potential Promotion Energy	-	+	+
Total Promotion Energy	-	+	+
Quasi-Classical Energy	-	0.0	0.0
Interatomic Sharing Penetration Energy	+	-	0.0
Intra-atomic Sharing Penetration Energy	+	-	0.0
Kinetic Interference Energy	+	-	0.0
Potential Interference Energy	-	+	0.0
Total Interference Energy	+	-	0.0

There is now a hybridization contraction occurring. The (1Sa,1Sa') and (1Sa',1Sa) orbital pairs have a negative kinetic part, a positive potential part and a positive total energy. In this case, expansion hybridization promotion is occurring. The (1Sa', 1Sa') orbital pair has a negative kinetic energy, a positive potential energy and the total is positive. Again, expansive hybridization promotion is occurring. At first glance these results seem to be the opposite of what one would expect, but if one considers the small weight factor associated with the ground state of the 1S orbital, it seems logical that it would contract and the 1S' orbital would expand due to its larger weight factor.

The quasi-classical energy will be discussed in terms of an orbital subdivision. The (1Sa, 1Sb) orbital pair is negative for all three basis sets. The other orbital pairs are equal to zero for all three basis sets. As in the total quasi-classical energy, the orbital pairs for all three basis sets follow the expected results.

For the 1S-2S-2P σ basis set the sharing penetration energies have the following values: the interatomic sharing penetration energy is positive for the (1Sa, 1Sb) orbital pair, and negative for the (1Sa, 2Sb) and (2Sa, 1Sb) orbital pairs. This tends to indicate that the (1Sa, 1Sb) orbital pair has no sharing of electrons and destructive interference, whereas the (1Sa, 2Sb) and (2Sa, 1Sb) orbital pair allow sharing of electrons and constructive interference can occur. The intra-atomic sharing penetration energy is positive

for the (1Sa, 1Sa) orbital pair, which is just the opposite of the expected results since a positive result was obtained for the interatomic part of the (1Sa, 1Sb) orbital pair. This unexpected result may be due to the fact that the results obtained at these large internuclear distances are close to the accuracy of the calculation. This is felt to be especially important here since for the intra-atomic sharing penetration energies for all three basis sets and for all the orbital pairs, the energies change signs at internuclear distances a little less than 5.0 atomic units. The (1Sa, 2Sa) orbital pair has a positive sign which in this case is the expected result.

The $1S-1S'-2P\sigma$ basis set for the interatomic sharing penetration energies has for the (1Sa, 1Sb) orbital pair a positive value and the (1Sa, 1Sb') and (1Sa', 1Sb) orbital pairs are negative so that like orbitals have the same signs, as they did in the $1S-2S-2P\sigma$ basis set. The difference is then seen to be that in the $1S-2S-2P\sigma$ basis set the (1Sa, 2Sb) and (2Sa, 1Sb) orbital pairs have a greater value than the (1Sa, 1Sb) orbital pair. In the case of the $1S-1S'-2P\sigma$ basis set the opposite occurs with the (1Sa, 1Sb) orbital pair having the larger value and thus predominating over the (1Sa, 1Sb') and (1Sa', 1Sb) orbital pairs. The intra-atomic sharing penetration energy for the $1S-1S'-2P\sigma$ basis set gives a positive value for the (1Sa, 1Sa) orbital pair and negative values for the (1Sa, 1Sa') and (1Sa', 1Sa) orbital pairs, which in all cases is the opposite results of what one would expect by looking at the

interatomic sharing penetration energies. Once again the reason for this is probably that the smallness of the values puts one close to the accuracy of the calculation as discussed under the $1S-2S-2P\sigma$ basis set.

The $1S-1S'$ basis set, for all orbital pairs and for both parts of the sharing penetration energies, gives the same results as the $1S-2S-2P\sigma$ basis set. Again, the close parallelism between these two basis sets is seen.

The orbital partitioning for the interference energy on the $1S-2S-2P\sigma$ basis set has the (1Sa, 1Sb) orbital pair having a positive kinetic interference energy, a negative potential interference energy and the total is positive. This orbital pair is undergoing destructive interference as was expected from the sharing penetration energies. The (1Sa, 2Sb) and (2Sa, 1Sb) orbital pairs have a negative kinetic interference energy, a positive potential interference energy and the total interference energy for this orbital pair is negative. Therefore, these orbitals are undergoing constructive interference, as expected.

The $1S-1S'-2P\sigma$ basis set has the (1Sa, 1Sb) orbital pair having a positive kinetic interference energy, a negative potential interference energy and a positive total interference energy. This orbital pair, as in the $1S-2S-2P\sigma$ basis set, is showing destructive interference. The (1Sa, 1Sb') and (1Sa', 1Sb) orbital pairs have a negative kinetic interference energy, a positive potential interference energy with the total interference energy being negative for this orbital pair. These orbitals show constructive interference

just as they did in the $1S-2S-2P\sigma$ basis set. The difference between the two orbital basis sets for interference is again the same factor as in the interatomic sharing penetration energies. In the $1S-2S-2P\sigma$ basis set the (1Sa, 2Sb) and (2Sa, 1Sb) orbital pairs predominate over the (1Sa, 1Sb) orbital pairs to give constructive interference for the total interaction. In the $1S-1S'-2P\sigma$ basis set the (1Sa, 1Sb) orbital pair dominates over the (1Sa, 1Sb') and (1Sb', 1Sb) orbital pairs to give a total destructive interference.

The $1S-1S'$ basis set again parallels the $1S-2S-2P\sigma$ basis set in all interference parts and for all orbital pairs.

Another interesting aspect of this problem is that for all of the molecules that Ruedenberg and his students have studied the kinetic interference energy was negative except for Be_2 and C_2 , in which cases a positive kinetic interference energy was found. These are the only two molecules studied in which the total energy was nonbonding.¹⁰ This indicates that the kinetic interference energy term may be significant in determining whether a bonding energy will be obtained for a particular wavefunction. In other words, this fragment may be a simpler way of determining which wavefunction approximation will give a lower energy calculation.

It also appears that the Ruedenberg partitioning method may be useful in determining where a wavefunction approximation is in error as it appears as it did for the $1S-2S-2P\sigma$ basis set in

¹⁰Rue and Ruedenberg, op. cit.

indicating that it occurred in the promoted state.

Now that the partitioned fragments have been examined in the van der Waals region an investigation into the nature of these fragments at the close internuclear distances will be undertaken. The results talked about here can be seen in Tables III to XIV.

The promotion energy for the $1S-2S-2P\sigma$ basis set shows the potential promotion energy has a positive value in the van der Waals region, which changes to a negative value at 3.7795 atomic units and then changes back to a positive value near 2.0 atomic units. The kinetic promotion energy which has a negative value at large internuclear distances becomes positive at 4.15745 atomic units and reverses to a negative value in the area of 2.0 atomic units.

These changes in the neighborhood of 4.0 atomic units are due to the contraction of the orbitals as the atoms approach each other. At this internuclear distance the value of the orbital parameter is still less than the value for the separated atom. This could cause an expansion, but the contraction hybridization has a greater value so that the total effect is contraction.

The value of the orbital parameter for the promoted atom does become greater than the value for the ground state, but this does not happen until the internuclear distance of 3.307063 atomic units is reached. This contraction reinforces the contraction due to hybridization. The change from a contraction to an expansion near 2.0 atomic units correlates with the change in the orbital parameter back to a value that is less than the separated atom

value. At these close internuclear distances the orbital parameter varies significantly from the ground state and will cause a considerable expansion that will be greater than the further contraction that is expected from hybridization.

The potential promotion energy for the $1S-1S'-2P\sigma$ basis set, which has a negative value in the van der Waals region, shows a gradually increasing value that becomes positive at 3.0 atomic units, increases to a maximum at 1.75 atomic units and then decreases to attain a negative value at 1.0 atomic units. The kinetic promotion energy which is positive at large internuclear distances remains positive and gradually increases. As in the van der Waals region, the orbital parameter has the same value in the promoted state as in the ground state. Therefore one needs to be concerned with hybridization only. The increasing positive value of the kinetic promotion energy is caused by the electrons having less and less room in which to move as the atoms are brought closer together. The effects talked about under sharing penetration and interference will help to explain the behavior of the potential promotion energy.

The quasi-classical energy which is negative at large internuclear distances for all three basis sets goes through a minimum at 1.36 to 1.70 atomic units and becomes positive from 1.0 to 1.39 atomic units, depending on the basis set. It is interesting that only the quasi-classical energy fragment shows any uniformity in the values for all three basis sets. At close internuclear

distances the nuclear repulsion term becomes very large and causes the increasing positive value for the energy.

The interatomic electron sharing penetration energy is negative for the $1S-2S-2P\sigma$ basis set at large internuclear distances, but it increases and becomes positive at an internuclear distance slightly greater than 2.0 atomic units and increases rapidly thereafter. The $1S-1S'$ basis set shows the same trends in the interatomic electron sharing penetration energy but the numbers become positive at an internuclear distance of approximately 3.75 atomic units. The $1S-1S'-2P\sigma$ basis set yields an interatomic electron sharing penetration energy, which is positive at large internuclear distances, increases until it reaches 1.5 atomic units where it decreases and at 1.25 atomic units it is negative.

The sharing of electrons which occurred for the $1S-1S'$ and $1S-2S-2P\sigma$ basis sets as has been discussed previously in the van der Waals region caused a decrease in the interatomic electron sharing penetration energy, which is due to the decrease in the interatomic repulsion. As the atoms approach each other at internuclear distances closer than the van der Waals separation, the electrons are forced closer and closer together and will repulse each other to a larger and larger extent, and thus cause the interatomic electron sharing penetration energy to increase. The $1S-1S'-2P\sigma$ basis set which had no electron sharing for large internuclear distances also shows the increase in interatomic electron sharing penetration energy which is caused by a further

interatomic repulsion increase as the atoms are brought closer together. The decrease in the interatomic electron sharing penetration energy that occurs within 1.25 to 1.50 atomic units is due to electron sharing that is forced to occur at these close internuclear distances, and this will thus cause a decrease in the interatomic electron repulsion.

The intra-atomic sharing penetration energy for all three basis sets acts just as is expected. That is to say the curves have the opposite sign of what they have in the interatomic sharing penetration part and increase or decrease at the same points as the interatomic sharing penetration energy.

The kinetic interference energy for the $1S-2S-2P\sigma$ basis set is negative in the van der Waals region and reaches a minimum at 3.7715 atomic units. It becomes positive near 2.83 atomic units and increases rapidly thereafter. For the $1S-1S'$ basis set the kinetic interference energy shows a similar behavior. It is negative in the van der Waals region, has its minimum at 4.725898 atomic units, becomes positive at 3.780718 atomic units and increases rapidly after this, except at the very last point where it has a slight decrease in value.

The $1S-2S-2P\sigma$ and $1S-1S'$ basis sets both show minimums in the kinetic interference energy which occurs at the point where the electrons, after having been shared, have the greatest room in which to move. As the atoms get closer together the kinetic interference energy increases and becomes positive showing the electrons then have less room in which to move than they had in the

separated atom. The decrease that occurs for the last point of the $1S-1S'$ basis set is probably due to the effect of the united atom case. The $1S-1S'$ basis set has an unusual united atom limit of a $1S^2 1P^2$ basis set. Kestner also states that calculations below 1.0 atomic units are open to several problems.¹¹

At close internuclear distances, the $1S-1S'-2P\sigma$ basis set gives quite different results from the other two basis sets. The kinetic interference energy, which is positive in the van der Waals region, increases slowly as the nuclear centers get closer together until 1.25 atomic units, at which point a decrease in the energy occurs, and at the closest point 1.0 atomic units the energy becomes negative.

The $1S-1S'-2P\sigma$ basis set has shown destructive interference in the van der Waals region and continues to show a gradually increasing kinetic interference energy until the region of 1.00 to 1.50 atomic units is encountered. In this region the sharing of electrons allows constructive interference to occur and thus allows the electrons more room for movement and causes the kinetic interference to decrease and become negative.

The potential and total interference energies in all three cases back up the results we have just discussed. The increase in the potential interference energy for the $1S-2S-2P\sigma$ and $1S-1S'$ basis

¹¹Kestner, op. cit.

sets is due to the fact that the transfer of charge to bond midpoint becomes less and the electrostatic potential decreases.

An investigation into the nature of the fragments at close internuclear distances will now be undertaken for the orbital pair subdivision. The explicit numbers can be found in Tables XV to XLI.

The promotion energy for the $1S-2S-2P\sigma$ basis set shows that the contraction hybridization that occurs around 4.0 atomic units is due to the (1Sa, 1Sa) orbital pair. Both the kinetic and potential energies change their sign in this region, but for the other orbital pairs no change of sign occurs. At these closer internuclear distances hybridization is causing a transfer from the outer orbitals to the 1S orbital. The expansion that occurs around 2.0 atomic units is again caused by the change in the (1Sa, 1Sa) orbital pair. The 1Sa orbital is affected by the considerable change in the orbital parameter with respect to the ground state.

For the $1S-1S^*-2P\sigma$ basis set the decrease that occurs in the promotion potential energy around 1.75 atomic units is not directly traceable to any specific orbital pair but is caused by the combination of all orbital pairs.

The orbital pair subdivision of the quasi-classical energy shows nothing new. All orbital pairs for all three basis sets are negative until they reach the close internuclear distances where they all become positive.

An examination of the interatomic sharing penetration energy for the $1S-2S-2P\sigma$ basis set reveals the (1Sa, 1Sb) orbital pair is

positive and the (1Sa, 2Sb) orbital pair is negative for all internuclear distances. While at large internuclear distances the (1Sa, 2Sb) orbital pair predominates, at close internuclear distances the (1Sa, 1Sb) orbital pair energy becomes larger. In the 1S-1S' basis set the overall positive value for the interatomic sharing penetration energy is obtained by the (1Sa, 1Sb') orbital pair becoming positive at close internuclear distances. This behavior of the (1Sa, 1Sb') orbital pair is the expected results since the electrons have been shared in the van der Waals region, at close internuclear distances the interatomic repulsion should increase. The negative increasing behavior of the (1Sa, 2Sb) orbital pair in the 1S-2S-2P σ basis set is unexpected and so far unexplainable.

The 1S-1S'-2P σ basis set shows similar results to the 1S-2S-2P σ basis set. The (1Sa, 1Sb) orbital pair is positive and the (1Sa, 1Sb') orbital pair is negative at all internuclear distances. The decrease that occurs in the total interatomic sharing penetration energy at 1.25 atomic units is in fact due to the large decrease in the (1Sa, 1Sb') orbital pair at this point. This decreasing nature of the (1Sa, 1Sb') orbital pair as in the case of the (1Sa, 2Sb) orbital pair in the 1S-2S-2P σ basis set is so far unexplainable. Both of these orbital pairs, at large internuclear distances, had sharing of electrons. At very close internuclear distances these orbital pairs would be expected to become positive because the interatomic repulsion should become greater as these atoms are brought closer together.

In general, the intra-atomic sharing penetration energy for both the $1S-2S-2P\sigma$ and $1S-1S'-2P\sigma$ basis sets give the opposite sign of the interatomic sharing penetration energy for all of the orbital pairs. These are the expected results and although at a few internuclear distances there are some exceptions, they are not thought to be significant.

For the interference energy of the $1S-2S-2P\sigma$ and $1S-1S'$ basis sets both give similar results. The (1Sa, 1Sb) orbital pair has a positive kinetic interference energy in the van der Waals region, which remains positive even at close internuclear distances. The potential interference energy is negative in the van der Waals region and continues to remain negative for close internuclear distances. The (1Sa, 2Sb) and (1Sa, 1Sb') orbital pairs have a negative kinetic interference energy for large internuclear distances which at close internuclear distances eventually become positive. The potential interference energy has just the opposite values, as it is positive at large internuclear distances but becomes negative at close internuclear distances. Orbital pairs that have a negative interference energy at large internuclear distances are showing that they have "overlapped" and that the electrons have more room in which to move than they did in the atom. As the atoms get closer together the room they have in which to move will eventually become smaller and soon the room for movement will become less than in the atom. At this point the kinetic interference energy will become positive. As can be seen this is

exactly what happens in the (1Sa, 1Sb') and (1Sa, 2Sb) orbital pair situations.

The $1S-1S'-2P\sigma$ basis set has the (1Sa, 1Sb) orbital pair showing the same behavior as the (1Sa, 1Sb) orbital pair in the $1S-2S-2P\sigma$ and $1S-1S'$ basis sets. The (1Sa, 1Sb') orbital pair which has a negative kinetic interference energy in the van der Waals region has a decreasing negative value even at very close internuclear distances. The potential interference energy which is positive at large internuclear distances changes to a negative value at closer internuclear distances. These results are quite unusual for two reasons. The kinetic interference energy should become positive at close internuclear distances, which it does not. Also, at close internuclear distances both the kinetic and potential interference energies are negative and usually these two quantities have opposite signs. These results are unusual. I submit the following possible explanation.

It appears that as the atoms are brought closer together the (1Sa, 1Sb') orbital pair is becoming distorted. Overlap between these two orbitals is still occurring, but part of the orbitals are being enlarged away from the bond region, causing the electrons to have more room in which to move. This distortion of the orbitals away from the bond region would also explain the reason the potential energy is negative. The electrostatic potential will be lower at points near the nuclei and away from the bond region and therefore the charge transferred away from the bond region and near the nuclei

will cause the potential energy to become lower. This hypothesis can be checked by the use of plotting programs now available in our group.

In conclusion it can be said that Ruedenberg's partitioning scheme worked very well. It has been shown that this algorithm will work not only for analysis of the chemical bond in molecules in their equilibrium configurations, but it works equally well for other types of interactions between atoms. It gives consistent results over a wide range of internuclear distances. This partitioning method also appears to be able to show where an incorrect wavefunction is in error.

This work has also shown areas in which further research is needed to clarify the partitioning. The general partitioning into a promoted state gives reasonable results, but the further partitioning of this fragment as outlined by Rue and Ruedenberg¹² into contraction promotion and hybridization promotion has certain inherent problems associated with it. The need to transform the valence atomic orbitals back to Slater atomic orbitals for the promoted state makes the partitioning restricted to a specific type of orbital basis set. Even after this transformation has been performed the contraction promotion and hybridization promotion parts are not completely separated. The overlap integrals which should only occur in the contraction promotion part also occur in

¹²Rue and Ruedenberg, *op. cit.*

the hybridization promotion part.

It is also questionable whether the orbital subdivision is worth all of the extra time involved. After a careful investigation into the nature of the major fragments, an insignificant amount of new information was learned by looking at the orbital subdivision. A future area for work is in the investigation of a series of molecules at many different internuclear distances. For such an investigation the orbital subdivision would be even less valuable in that one would have simply too many numbers to interpret. This has been found to be true in this investigation when one molecule was examined for several different basis sets and at many various internuclear distances.

There are two areas in which the He-He interaction investigation can be extended. The first extension would be to take Wahl's calculation, in which the orbital parameters have been optimized, and apply Ruedenberg's partitioning scheme to it. By doing this one will have available a useful way of looking at the promotion fragment. One can compare the results obtained for this new calculation with the results reported here on the $1S-1S'-2P\sigma$ basis set in which the orbital parameters have not been optimized.

The other investigation on the He-He interaction would involve the application of Ruedenberg's partitioning method to an extended calculation beyond the Hartree-Fock Self Consistent Field method. In such a calculation correlation would be taken into consideration. At this time no such investigation can be performed because no one has done the Hartree-Fock method over a wide range of internuclear

distances. In fact, no one has done even such a calculation in the van der Waals region.

Another area for future investigation is the kinetic interference energy fragment. This fragment has consistently shown to be the most important part of the whole partitioning scheme. It has been able to predict in all cases whether constructive or destructive interference will occur. It also appears that it may be able to predict, between a series of wavefunction approximations to a molecule, which wavefunction will give the lowest binding energy curve. This fragment is much easier to calculate than the total energy and it therefore seems like a worthwhile investigation to study this fragment more thoroughly for a series of various approximate wavefunctions for several different molecules.

This project has shown that at least for the He-He interaction the contraction promotion energy and the kinetic interference energy are not significantly related. It has shown that a close connection between the sharing of electrons and constructive interference exists as illustrated by the interatomic sharing penetration energy and the kinetic interference energy respectively.

This research has proven Ruedenberg's analysis is able to handle nonbonding interactions correctly as in the $1S-1S'-2P\sigma$ basis set. In this case the nonbonding is due to the fact that the wavefunction approximation is not accurate enough to obtain the small van der Waals force. In terms of the total energy no minimum is obtained due to the lack of sufficient orbital overlap and the

sharing of electrons. The orbital subdivision shows that a slight overlap and sharing of electrons does occur for one orbital pair but this is small with regards to the strong antibonding occurring in the other orbital pairs.

It is interesting that both the $1S-2S-2P\sigma$ and $1S-1S'$ basis sets in all the fragments except promotion perform precisely as expected of a correct wavefunction that is giving a bonding energy. This makes it appear as if these poorer approximation wavefunctions give a better calculation in the van der Waals region than the $1S-1S'-2P\sigma$ basis set. This cannot be true. While the ground state and the values of the orbital parameters affect the promotion part directly, they will affect the other fragments in an indirect way. The values of the orbital parameters will affect all of the integrals. An important factor is that Ruedenberg's analysis was able to show that there was an error in the $1S-2S-2P\sigma$ basis set and the point at which it occurred.

R	TABLE III ENERGIES OF THE $1S-2S-2P$ PARTITIONED FRAGMENTS					
	CLP E	P E	SP E A,B	SP E A	I E	II E
+ .7559000	+ .4038439	+ .4188674	+ .9089391	- .1083110E+1	+ .1225210E+1	+ .3913719E-1
+ .9448750	+ .8945894E-1	+ .3244209	+ .4656497	- .6104637	+ .9312010	+ .1299234E-1
+ .1133850	- .2053628E-1	+ .2533709	+ .2503939	- .3636213	+ .6796028	- .1522630E-2
+ .1417313E+1	- .5060885E-1	+ .1802702	+ .1005815	- .1752807	+ .3888587	- .9424295E-2
+ .2362188E+1	- .9546794E-2	+ .4424482E-1	- .1690600E-2	+ .5963420E-2	+ .1996389E-1	- .6212259E-2
+ .2834625E+1	- .2917163E-2	+ .2750978E-1	- .3735500E-2	+ .6461250E-2	- .7655970E-2	- .3076438E-2
+ .3307063E+1	- .8122874E-3	+ .1452580E-1	- .2476540E-2	+ .5404464E-2	- .1044480E-1	- .1311262E-2
+ .3779500E+1	+ .5371214E-2	+ .6874800E-2	- .1213100E-2	+ .3164460E-2	- .7017490E-2	- .4764112E-3
+ .4157450E+1	- .6984481E-4	+ .3679000E-2	- .6264500E-3	+ .1827180E-2	- .4267610E-2	- .2148020E-3
+ .4535400E+1	- .2268510E-4	+ .1814300E-2	- .2970500E-3	+ .9603000E-3	- .2326510E-2	- .8830818E-4
+ .4724375E+1	- .1285648E-4	+ .1257200E-2	- .1999600E-3	+ .6782900E-3	- .1669840E-2	- .5575877E-4
+ .4913350E+1	- .7243249E-5	+ .8559000E-3	- .1329900E-3	+ .4726300E-3	- .1175930E-2	- .3492298E-4
+ .5102325E+1	- .4091413E-5	+ .5757200E-3	- .8769000E-4	+ .3258900E-3	- .8183300E-3	- .2169260E-4
+ .5291300E+1	- .2161427E-5	+ .3835600E-3	- .5715000E-4	+ .2217000E-3	- .5613400E-3	- .1339400E-4
+ .5669250E+1	- .7177187E-6	+ .1679800E-3	- .2309000E-4	+ .9669000E-4	- .2549100E-3	- .5002300E-5
+ .6425150E+1	- .4768917E-6	+ .2274000E-4	- .3570000E-5	+ .1716000E-4	- .4631000E-4	- .6563000E-6
+ .7181050E+1	0.0	- .2444000E-4	- .7400000E-6	+ .4518000E-5	- .7740000E-5	- .8300000E-7
+ .7559000E+1	0.0	- .6700000E-5	- .3600000E-6	+ .3010000E-5	- .3120000E-5	- .3000000E-7
+ .8503875E+1	0.0	- .1680000E-4	- .1000000E-6	+ .1100000E-5	- .2800000E-6	0.0
+ .9448750E+1	0.0	- .1340000E-4	- .1000000E-6	+ .1000000E-5	- .2000000E-7	0.0

For definitions of terms used in these Tables refer to Appendix B.

Graphs of the major fragments found in these Tables appear in Appendix C.

TABLE IV ENERGIES OF THE $1s-1s'$ PARTITIONED FRAGMENTS						
R	CLP E	P E	SP E A,B	SP E A	I E	II E
+ .9451800	+ .4229384	+ .8549207	+ .1873674E+	- .2314486	+ .1167670	+ .1701855
+ .1181474E+1	- .5833730E-1	+ .1668770	+ .8702229	- .1319666E+1	+ .9590805	+ .6745024E-1
+ .1417769E+1	- .1082145	- .1151576	+ .4107227	- .7228351	+ .9403446	+ .1585815E-1
+ .1654064E+1	- .7058358E-1	- .1469254	+ .2010003	- .3968498	+ .6727087	- .2234985E-2
+ .1890360E+1	- .3879719E-1	- .1098312	+ .9964904E-1	- .2166823	+ .4294695	- .7771296E-2
+ .2041588E+1	- .2604605E-1	- .8596610E-1	+ .6561342E-1	- .1505623	+ .3180858	- .8227306E-2
+ .2126654E+1	- .2078484E-1	- .6502180E-1	+ .4978588E-1	- .1176674	+ .2557316	- .8120640E-2
+ .2362949E+1	- .1098584E-1	- .3870390E-1	+ .2542520E-1	- .6358380E-1	+ .1505105	- .6679941E-2
+ .2599244E+1	- .5824164E-2	- .4127200E-3	+ .1220689E-1	- .4977692E-1	+ .8135139E-1	- .4633258E-2
+ .2835538E+1	- .3050406E-2	+ .1339042	+ .5943500E-2	- .1577869	+ .4220600E-1	- .2144860E-2
+ .3071834E+1	- .1582145E-2	- .1053827E+1	+ .2334180E-2	+ .1056248E+1	+ .1991960E-1	- .2203009E-2
+ .3038129E+1	- .8069451E-3	+ .2851332E+1	+ .9456000E-3	- .2848911E+1	+ .5975800E-3	+ .2937251E-2
+ .3544423E+1	- .5257092E-3	- .3188989E+1	+ .2453000E-3	+ .3188987E+1	+ .5940690E-2	- .2276189E-2
+ .3780718E+1	- .2104477E-3	+ .2323209E+3	+ .6600000E-5	- .2323175E+3	- .2327830E-2	+ .9248755E-3
+ .4253308E+1	- .5797598E-4	- .2495636	- .9953000E-4	+ .2512849	- .9562400E-3	- .1328734E-3
+ .4725898E+1	- .1779100E-4	+ .1155008E+1	- .6379000E-4	- .1154272E+1	- .3541300E-3	- .2134610E-3
+ .5103970E+1	- .4312772E-5	- .1070339E+1	- .3825000E-4	+ .1070414E+1	- .5761100E-3	+ .5584700E-3
+ .5482042E+1	- .1428757E-5	- .2683012E+1	- .1476000E-4	+ .2683365E+1	- .4484500E-3	+ .8606570E-4
+ .5860113E+1	+ .3919858E-5	- .2153262	- .1164000E-4	+ .2155186	- .1881800E-3	+ .5247600E-5
+ .6238185E+1	+ .6825528E-5	- .1569288E+1	- .3020000E-5	+ .1569369E+1	- .1036600E-3	+ .1649350E-4
+ .6616257E+1	+ .3367488E-3	- .2295427E+2	- .6300000E-6	+ .2295433E+2	- .1238400E-3	+ .5322218E-4
+ .7561437E+1	0.0	- .3392576E+2	0.0	+ .3392577E+2	- .3346000E-4	+ .9654143E-5
+ .1000000E+2	0.0	- .1054689E+1	0.0	+ .1054685E+1	0.0	0.0
+ .2000000E+2	0.0	- .1054691E+1	0.0	+ .1054688E+1	0.0	0.0

R	TABLE V		ENERGIES OF THE $1S-1S'-2P$ PARTITIONED FRAGMENTS				II
	CLP	E	P	$\frac{1S-1S'}{SP}$	SP	I	
	E	E	E A,B	E A	E	E	
+ .1000000E+1	+ .1855594	+ .1129945E+1	- .2768803	+ .3467279	- .3770626	- .2110099E-1	
+ .1250000E+1	+ .1812057E-1	+ .5648516	- .3645554E-1	+ .5987836E-1	+ .9911891E-2	- .1459026E-1	
+ .1500000E+1	- .3033390E-1	+ .2717854	+ .2626869E-1	- .1905498E-2	+ .1082969	- .1269533E-1	
+ .1750000E+1	- .3305221E-1	+ .2209908	+ .3032653E-1	- .9789163E-1	+ .1056787	- .1181925E-1	
+ .2000000E+1	- .2446563E-1	+ .1188860	+ .2210697E-1	- .5947390E-1	+ .7918390E-1	- .1049015E-1	
+ .2250000E+1	- .1579475E-1	+ .6978144E-1	+ .1405411E-1	- .3947620E-1	+ .5334734E-1	- .8687433E-2	
+ .2500000E+1	- .9522550E-2	+ .4173270E-1	+ .8375240E-2	- .2540220E-1	+ .3385830E-1	- .6755450E-2	
+ .3000000E+1	- .3113265E-2	+ .1537412E-1	+ .2666944E-2	- .9642900E-2	+ .1204717E-1	- .3522844E-2	
+ .3500000E+1	- .9428023E-3	+ .5100050E-2	+ .7614490E-3	- .2631000E-2	+ .3688530E-2	- .1591820E-2	
+ .4000000E+1	- .2737849E-3	+ .2202600E-2	+ .1896500E-3	- .1080500E-2	+ .9434300E-3	- .6509455E-3	
+ .4700000E+1	- .4571276E-4	+ .6234000E-3	+ .1670000E-4	- .3125300E-3	+ .5200000E-4	- .1653654E-3	
+ .5000000E+1	- .2128226E-4	- .6509800E-3	+ .2990000E-5	+ .8275800E-3	- .2752000E-4	- .8899809E-4	
+ .5500000E+1	- .5019057E-5	+ .5203000E-4	0.0	+ .2700000E-6	- .2449000E-4	- .3064374E-4	
+ .6000000E+1	- .7167068E-6	+ .6393000E-4	0.0	+ .3820000E-5	- .6533000E-4	- .1018358E-4	
+ .6560000E+1	0.0	+ .1263000E-4	0.0	- .1670000E-4	- .1048200E-4	- .2875083E-5	
+ .7000000E+1	0.0	+ .7630000E-5	0.0	- .1950000E-4	- .5939000E-5	- .1028111E-5	
+ .9000000E+1	0.0	+ .3000000E-5	0.0	- .2350000E-4	- .1000000E-6	- .2029193E-7	

TABLE VI	ENERGIES OF $1S-2S-2P_p$ PROMOTED STATE PARTS		
E^P (A) -- Potential	E (A) Kinetic	$2E^P$ (A)	E (A) Potential
+.5701620	-.2283280	-.2648006	+.4377617
+.4712805	-.2120005	-.1941391	+.3742110
+.3552005	-.1600072	-.1370158	+.2866927
+.2068350	-.7957250E-1	-.7425475E-1	+.1697076
-.2870500E-2	+.3140790E-1	-.1282999E-1	-.9285495E-2
-.9295000E-2	+.2357235E-1	-.1044920E-2	-.9817460E-2
-.4669500E-2	+.1205745E-1	-.2501000E-3	-.4794550E-2
-.6315000E-3	+.4348300E-2	-.5588000E-3	-.9109000E-3
+.9620000E-3	+.1223100E-2	-.6912000E-3	+.6164000E-3
+.1348000E-2	-.1301500E-3	-.6214000E-3	+.1037300E-2
+.1319500E-2	-.4155000E-3	-.5508400E-3	+.1044100E-2
+.1247500E-2	-.5761500E-3	-.4868000E-3	+.1004100E-2
+.9020000E-3	-.4379500E-3	-.3523500E-3	+.7258300E-3
+.7575000E-3	-.4221000E-3	-.2872500E-3	+.6138600E-3
+.3645000E-3	-.2122000E-3	-.1366300E-3	+.2961900E-3
-.1250000E-4	+.2540000E-4	-.3060000E-5	-.1403000E-4
-.2550000E-4	+.2230000E-4	-.1805000E-4	-.3452000E-4
0.0	-.1350000E-5	-.4100000E-5	-.2050000E-5
0.0	-.1800000E-5	-.6600000E-5	-.3300000E-5
0.0	-.1850000E-5	-.4800000E-5	-.2400000E-5

TABLE VII ENERGIES OF THE <u>1S-1S'</u> PROMOTED STATE PARTS			
P	P	P	P
E ρ (A) Potential	E (A) Kinetic	2E ρ (A)	E (A) Potential
+.2040736E+1	-.1041742E+1	-.1143066E+1	+.1469203E+1
+.1427463E+1	-.1059432E+1	-.5691843	+.1142870E+1
+.7967740	-.7190080	-.2706857	+.6614312
+.4099185	-.4215476	-.1236672	+.3480849
+.1804170	-.2112768	-.4811166E-1	+.1563612
+.1071845	-.1368689	-.2659736E-1	+.9388580E-1
+.7698200E-1	-.1006420	-.1770177E-1	+.6813110E-1
+.2117300E-1	-.3847745E-1	-.4094765E-2	+.1912560E-1
+.1822000E-2	-.1084395E-1	+.1763119E-1	+.1063759E-1
-.5525000E-2	+.5932500E-3	+.1437677	+.6635890E-1
-.1000000E-1	+.8441950E-2	-.1060711E+1	-.5403550
-.1074800E-1	+.9900050E-2	+.2853029E+1	+.1415766E+1
-.9042500E-2	+.8960100E-2	-.3188825E+1	-.1602455E+1
-.6845500E-2	+.6938750E-2	+.2323207E+3	+.1161535E+3
-.2464000E-2	+.2835500E-2	-.2503066	-.1276173
-.2206500E-2	+.2240350E-2	+.1154940E+1	+.5752635
-.4935000E-3	+.6212500E-3	+.1070084E+1	+.5345484
-.2400000E-3	+.2977000E-3	-.2683127E+1	-.1341804E+1
+.3775500E-2	-.3115900E-2	-.2166454	-.1045472
-.6500000E-5	+.2715000E-4	-.1569330E+1	-.7846714
-.1000000E-5	+.7250000E-5	-.2295428E+2	-.1147714E+2
0.0	+.1750000E-5	-.3392575E+2	-.1696288E+2
0.0	-.1900000E-5	-.1054685E+1	-.5273424
0.0	-.1900000E-5	-.1054688E+1	-.5273438

TABLE VIII ENERGIES OF $1S-1S'-2P\sigma$ PROMOTED STATE FRAGMENTS

P E ^P (A) Potential	P E (A) Kinetic	$2E\pi^P$ (A)	P E (A) Potential
+ .2787380E-1	+ .6321003	- .1900030	- .6712769E-1
+ .7706030E-1	+ .2679777	- .1252243	+ .1444814E-1
+ .6839880E-1	+ .1247935	- .1145992	+ .1109923E-1
+ .4678030E-1	+ .6522570E-1	- .3021170E-2	+ .4526972E-1
+ .2836980E-1	+ .3768793E-1	- .1322950E-1	+ .2175505E-1
+ .1598130E-1	+ .2335040E-1	- .8881960E-2	+ .1154032E-1
+ .8412800E-2	+ .1507730E-1	- .5245710E-2	+ .5789050E-2
+ .1866800E-2	+ .6625600E-2	- .1610690E-2	+ .1061460E-2
+ .1858000E-3	+ .2917900E-2	- .1107350E-2	- .3678740E-3
- .1432000E-3	+ .1240850E-2	+ .7200000E-5	- .1396000E-3
- .2072000E-3	+ .4008000E-3	+ .2381300E-3	- .8814000E-4
- .9620000E-4	+ .2245500E-3	- .9076700E-3	- .5500400E-3
- .7720000E-4	+ .8975000E-4	+ .2693000E-4	- .6373500E-4
- .3970000E-4	+ .6965000E-4	- .1597000E-4	- .4768500E-4
- .6720000E-4	+ .3985000E-4	+ .6733000E-4	- .3353500E-4
- .6670000E-4	+ .3670000E-4	+ .6763000E-4	- .3288500E-4
- .1087000E-3	+ .5760000E-4	+ .1052000E-3	- .5610000E-4

TABLE IX ENERGIES OF THE $1S-2S-2P_{\sigma}$ SHARING PENETRATION PART

R	$\sum_{\alpha\beta} g^{SP}(A_{\alpha} B_{\beta})$ [$\bar{A}\alpha^2 \bar{B}\beta^2$]	$\sum_{\alpha\bar{\alpha}} \sum_{\beta\bar{\beta}} P^{SP}(A_{\alpha}A_{\bar{\alpha}} B_{\beta}B_{\bar{\beta}})$ [$\bar{A}\alpha A_{\bar{\alpha}} \bar{B}\beta B_{\bar{\beta}}$]	$\sum_{\beta\bar{\beta}} \sum_{\alpha\bar{\alpha}} P^{SP}(B_{\beta}B_{\bar{\beta}} A_{\alpha})$ [$\bar{B}\beta B_{\bar{\beta}} \bar{A}\alpha^2$]	$\sum_{\alpha\bar{\alpha}} \sum_{\beta\bar{\beta}} P^{SP}(A_{\alpha}A_{\bar{\alpha}} B_{\beta}B_{\bar{\beta}})$ [$\bar{A}\alpha A_{\bar{\alpha}} \bar{B}\beta B_{\bar{\beta}}$]	$\sum_{\alpha\bar{\alpha}} \sum_{\beta\bar{\beta}} P^{SP}(A_{\alpha}A_{\bar{\alpha}} A_{\alpha})$ [$\bar{A}\alpha A_{\bar{\alpha}} \bar{A}\alpha^2$]	$\sum_{\alpha\bar{\alpha}} g^{SP}(A_{\alpha}, A_{\bar{\alpha}})$ [$\bar{A}\alpha^2 \bar{A}\alpha^2$]
+0.7559000	+0.6647935	+0.1192127	+0.1192127	+0.5720248E-2	-0.2632431	-0.8198670
+0.9448750	+0.3476105	+0.5998323E-1	+0.5998323E-1	-0.1927317E-2	-0.1377203	-0.4727434
+0.1133850E+1	+0.1895749	+0.3158336E-1	+0.3158336E-1	-0.2347717E-2	-0.7464620E-1	-0.2889751
+0.1417313E+1	+0.7611110E-1	+0.1285888E-1	+0.1285888E-1	-0.1247381E-2	-0.3052200E-1	-0.1447587
+0.2362188E+1	-0.3462000E-2	+0.9370957E-3	+0.9370957E-3	-0.1028109E-3	-0.1365380E-2	+0.7328800E-2
+0.2834625E+1	-0.4276400E-2	+0.2881800E-3	+0.2881800E-3	-0.3544081E-4	-0.1227520E-3	+0.6854000E-2
+0.3307063E+1	-0.2643900E-2	+0.9005516E-4	+0.9005516E-4	-0.1273947E-4	+0.8412400E-3	+0.5320340E-2
+0.3779500E+1	-0.1261900E-2	+0.2659913E-4	+0.2659913E-4	-0.4405670E-5	+0.6886000E-4	+0.3095600E-2
+0.4157450E+1	-0.6471400E-3	+0.1043753E-4	+0.1043753E-4	-0.1863700E-5	+0.4208000E-4	+0.7785096E-2
+0.4535400E+1	-0.3040100E-3	+0.3853500E-5	+0.3853500E-5	-0.7482500E-5	+0.2162000E-4	+0.9386800E-3
+0.4724375E+1	-0.2041400E-3	+0.2322600E-5	+0.2322600E-5	-0.4684000E-6	+0.1504000E-4	+0.6632500E-3
+0.4913350E+1	-0.1354800E-3	+0.1390200E-5	+0.1390200E-5	-0.2899000E-6	+0.1024000E-4	+0.4623900E-3
+0.5102325E+1	-0.8917000E-4	+0.8306000E-6	+0.8306000E-6	-0.1793000E-6	+0.6860000E-5	+0.3190300E-3
+0.5291300E+1	-0.5803000E-4	+0.4933300E-6	+0.4933300E-6	-0.1098000E-6	+0.4540000E-5	+0.2171600E-3
+0.5669250E+1	-0.2343000E-4	+0.1717000E-6	+0.1717000E-6	-0.4036000E-7	+0.1920000E-5	+0.9477000E-4
+0.6425150E+1	-0.3570000E-5	+0.1964000E-7	+0.1964000E-7	0.0	+0.3000000E-6	+0.1686000E-4
+0.7181050E+1	-0.7400000E-6	0.0	0.0	0.0	+0.4000000E-7	+0.4478000E-5
+0.7559000E+1	-0.3900000E-6	0.0	0.0	0.0	0.0	+0.3010000E-5
+0.8503875E+1	-0.1000000E-6	0.0	0.0	0.0	0.0	+0.2100000E-5
+0.9448750E+1	-0.1000000E-6	0.0	0.0	0.0	0.0	+0.1000000E-5

TABLE X ENERGIES OF THE $1S-1S'$ SHARING PENETRATION PART

R	$\sum_{a,b} \rho^{SP}(Aa Bb) / [Aa^2 Bb^2]$	$\sum_{a,b} \rho^{SP}(AaAa Bb) / [AaAa Bb^2]$	$\sum_{a,b} \rho^{SP}(BbBb Aa) / [BbBb Aa^2]$	$\sum_{a,b} \rho^{SP}(AaAa BbBb) / [AaAa BbBb]$	$\sum_{a,b} \rho^{SP}(AaAa Aa) / [AaAa Aa^2]$	$\sum_{a,b} \rho^{SP}(Aa, Aa) / [Aa^2 Aa^2]$
+0.0945180E+1	+1.233429E+1	+2.745545	+2.745545	+9.113570E-1	-.9253935	-.1389092E+1
+1.1181474E+1	+7.177188	+7.553363E-1	+7.553363E-1	+1.436844E-2	-.3802744	-.9393918
+1.1417769E+1	+3.748757	+1.814492E-1	+1.814492E-1	-.4428275E-3	-.1524556	-.5703795
+1.1654064E+1	+1.922633	+4.336709E-2	+4.336709E-2	+6.389790E-4	-.6351078E-1	-.3333390
+1.1890360E+1	+9.752460E-1	+1.028444E-2	+1.028444E-2	+6.764318E-4	-.2697340E-1	-.1897089
+1.2041588E+1	+6.6468710E-1	+4.420747E-3	+4.420747E-3	+4.218222E-4	-.1675290E-1	-.1338094
+1.2126654E+1	+4.927660E-1	+2.427685E-3	+2.427685E-3	+2.374222E-4	-.1132912E-1	-.1063383
+1.2362949E+1	+2.523150E-1	+6.078086E-4	+6.078086E-4	+7.210220E-5	-.5099020E-2	-.5848480E-1
+1.2599244E+1	+1.218030E-1	+1.263527E-4	+1.263527E-4	+1.308045E-5	-.1893990E-2	-.4788293E-1
+1.2835538E+1	+5.938100E-2	+2.598400E-5	+2.598400E-5	+2.361700E-6	-.7089000E-3	-.1570780
+1.3071834E+1	-.3250173	0.0	0.0	+3.273515	0.0	+1.056248E+1
+1.3388129E+1	+9.453000E-3	+1.289960E-6	+1.289960E-6	0.0	+1.1226000E-3	-.2849034E+1
+1.3544423E+1	+2.453000E-3	0.0	0.0	0.0	+1.1626600E-3	+3.188825E+1
+1.3780718E+1	+1.688700E-3	0.0	0.0	0.0	+1.1320500E-3	-.2323177E+3
+1.4253308E+1	-.9953000E-4	0.0	0.0	0.0	+7.224000E-4	+2.512126
+1.4725898E+1	-.6379000E-4	0.0	0.0	0.0	+3.240000E-4	-.1154288E+1
+1.5103970E+1	-.3285000E-4	0.0	0.0	0.0	+1.480000E-4	+1.070399E+1
+1.5482042E+1	-.1476000E-4	0.0	0.0	0.0	+6.400000E-5	+2.683389E+1
+1.5860113E+1	-.1164000E-4	0.0	0.0	0.0	+4.100000E-5	+2.155145
+1.6238185E+1	-.3020000E-5	0.0	0.0	0.0	+1.000000E-5	+1.569368E+1
+1.6616257E+1	-.6300000E-6	0.0	0.0	0.0	+4.100000E-6	+2.295433E+2
+1.7561437E+1	0.0	0.0	0.0	0.0	0.0	+3.392577E+2
+1.1000000E+2	-.9999973E-1	0.0	0.0	+9.999996E-1	0.0	+1.054685E+1
+1.2000000E+2	-.0500000	0.0	0.0	+4.999999E-1	0.0	+1.054688E+1

TABLE XII ENERGIES OF THE $1S-2S-2P_{\sigma}$ INTERFERENCE PARTS

I E Kinetic	I E Potential	I $2E\pi$	I E ρ Potential
+ .2790645E+1	- .1565435E+1	+ .8797254	- .2005298E+1
+ .2013857E+1	- .1082656E+1	+ .5714026	- .1368357E+1
+ .1448110E+1	- .7685067	+ .3685300	- .9527717
+ .8743090	- .4854503	+ .2034303	- .5871655
+ .1142226	- .9425872E-1	+ .3820815E-1	- .1133628
+ .2471728E-1	- .3237325E-1	+ .1216318E-1	- .3845484E-1
- .2342669E-2	- .8101810E-1	+ .1365693E-2	- .8784652E-2
- .6549789E-2	- .4677000E-3	- .1660512E-2	+ .3625524E-3
- .4946240E-2	+ .6786200E-3	- .1635851E-2	+ .1496546E-2
- .3052942E-2	+ .7264300E-3	- .1164230E-2	+ .1308537E-2
- .2285584E-2	+ .6157400E-3	- .9171700E-3	+ .1074324E-2
- .1664114E-2	+ .4881900E-3	- .6969340E-3	+ .8366479E-3
- .1190232E-2	+ .3719000E-3	- .5173470E-3	+ .6305744E-3
- .8351994E-3	+ .2738600E-3	- .3750650E-3	+ .4613907E-3
- .3929749E-3	+ .1350600E-3	- .1864860E-3	+ .2313075E-3
- .7476473E-4	+ .2845000E-4	- .3856270E-4	+ .4773347E-4
- .1288271E-4	+ .5150000E-5	- .7068700E-5	+ .8675768E-5
- .5245363E-5	+ .2120000E-5	- .2957000E-5	+ .3602631E-5
- .4771969E-6	+ .2000000E-6	- .2802300E-6	+ .3399589E-6
- .3822323E-7	+ .1500000E-7	- .2302700E-7	+ .2818835E-7

TABLE XIII ENERGIES OF THE <u>1S-1S'</u> INTERFERENCE FRAGMENTS			
I E Kinetic	I E Potential	I 2E π	I E ρ Potential
+.2971774E+1	-.2855007E+1	+.3006657E+1	-.4358335E+1
+.2982496E+1	-.2023415E+1	+.1702694E+1	-.2874762E+1
+.2192688E+1	-.1252343E+1	+.8313945	-.1668041E+1
+.1443745E+1	-.7710349	+.4153647	-.9787173
+.9008373	-.4713678	+.2252899	-.5840127
+.6691354	-.3510497	+.1657769	-.4339381
+.5397529	-.2840214	+.1303986	-.3492207
+.3231679	-.1726574	+.8228592E-1	-.2138004
+.1809639	-.9961246E-1	+.4809454E-1	-.1236597
+.1016581	-.5945212E-1	+.2552215E-1	-.7221319E-1
+.4856492E-1	-.2864532E-1	+.1582996E-1	-.3656031E-1
+.2413539E-1	-.2353781E-1	-.8525871E-2	-.1927488E-1
+.9703151E-2	-.3762460E-2	+.9912648E-2	-.8718785E-2
+.3350027E-2	-.5677860E-2	-.4033264E-2	-.3661235E-2
-.1029590E-2	+.7335000E-4	-.2360840E-3	+.1913919E-3
-.1177006E-2	+.8228800E-3	+.3048584E-3	+.6704472E-3
-.7517704E-3	+.1756600E-3	-.5636030E-3	+.4574567E-3
-.3954895E-3	-.5296000E-4	-.6190540E-3	+.2565565E-3
-.3143121E-3	+.1261300E-3	-.1834600E-3	+.2178559E-3
-.9467597E-4	-.8980000E-5	-.1399750E-3	+.6100448E-4
-.3709019E-4	-.8675000E-4	-.2246350E-3	+.2555535E-4
-.7791381E-5	-.2567000E-4	-.5626980E-4	+.2458434E-5
0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0

TABLE XIV ENERGIES OF THE $1S-1S'-2P$ INTERFERENCE PARTS

I E Kinetic	I E Potential	I $2 E \pi$	I E ^o Potential
-.1471566	-.2299060	+.6738711E-1	-.2635995
+.4003456	-.3904337	+.1430784	-.4619729
+.4888080	-.3805111	+.1419020	-.4514621
+.4165617	-.3108831	+.1193638	-.3705650
+.3113516	-.2321677	+.9426286E-1	-.2792992
+.2171445	-.1637971	+.7164346E-1	-.1996188
+.1447784	-.1109201	+.5269658E-1	-.1372684
+.0584248	-.4637763E-1	+.2593002E-1	-.0593426
+.0213247	-.1763619E-1	+.1135253E-1	-.0233125
+.7197465E-2	-.6254040E-2	+.4502480E-1	-.8505282E-2
+.1370512E-2	-.1318510E-2	+.1056201E-2	-.1846606E-2
+.6109690E-3	-.6384900E-3	+.5293510E-3	-.9031638E-3
+.1799746E-3	-.2044600E-3	+.1668100E-3	-.2878605E-3
-.6960118E-4	+.4270000E-5	+.7334800E-5	+.6090202E-6
+.4529904E-6	-.0052700E-4	+.6132700E-5	-.1359340E-4
-.5034578E-5	-.9040000E-6	0.0	-.9041809E-6
-.3091668E-6	+.2200000E-6	0.0	+.2175891E-6

TABLE XV ORBITAL ENERGIES: $1S-2S-2P\sigma$ TOTAL PROMOTION PART

$E_A^P(1S_a, 1S_a)$	$E_A^P(1S_a, 2S_a)$	$E_A^P(2S_a, 2S_a)$
+ .1639530	+ .3380605E-1	- .2213143E-1
+ .1293310	+ .2442157E-1	- .1596374E-1
+ .1029328	+ .1694325E-1	- .1013362E-1
+ .7730271E-1	+ .7782400E-2	- .2732260E-2
- .7201430E-2	+ .2521148E-1	- .2106048E-1
+ .4112970E-2	+ .8082610E-2	- .6523230E-2
+ .2884620E-2	+ .3629970E-2	- .2881220E-2
+ .1487200E-2	+ .1598340E-2	- .1246460E-2
+ .8165700E-3	+ .8306000E-3	- .6405600E-3
+ .4063400E-3	+ .4041800E-3	- .3074600E-3
+ .2829100E-3	+ .2779100E-3	- .2103000E-3
+ .1928400E-3	+ .1886000E-3	- .1420000E-3
+ .1291800E-3	+ .1271300E-3	- .9528000E-4
+ .8536000E-4	+ .8485000E-4	- .6334000E-4
+ .3716000E-4	+ .3712000E-4	- .2755000E-4
+ .3270000E-5	+ .6330000E-5	- .4620000E-5
- .1351000E-4	+ .9070000E-6	- .6300000E-6
- .3160000E-5	+ .3200000E-6	- .2300000E-6
- .5100000E-5	0.0	0.0
- .4200000E-5	0.0	0.0

TABLE XVI ORBITAL ENERGIES: 1S-1S' TOTAL PROMOTION PART

$E_A^P(1S_a, 1S_a)$	$E_A^P(1S_a, 1S_a')$	$E_A^P(1S_a', 1S_a')$
+ .5532802	+ .3296075E-1	- .1917418
+ .1165805	- .8488010E-2	- .1616564E-1
- .1312374E-1	- .2735288E-1	+ .1024462E-1
- .3250818E-1	- .2494369E-1	+ .8932950E-2
- .2574055E-1	- .1703988E-1	+ .4859410E-2
- .2005158E-1	- .1362872E-1	+ .3121090E-2
- .1540909E-1	- .9795110E-2	+ .2488410E-2
- .8833070E-2	- .5511080E-2	+ .5034100E-3
- .4028680E-2	- .2407800E-2	+ .8637900E-2
- .1776730E-2	- .1021550E-2	+ .7077199E-1
+ .8934214	+ .2640621	- .1953847E+1
+ .4520400E-3	+ .1550600E-3	+ .1424904E+1
+ .9221300E-3	+ .5601000E-4	- .1595545E+1
+ .1594081E-1	- .1186743E-1	+ .1161693E+3
+ .1530700E-3	+ .3246300E-3	- .1255838
+ .1055900E-3	+ .1468100E-3	+ .5770875
+ .5558000E-4	+ .6866000E-4	- .5351081
+ .2667000E-4	+ .4024000E-4	- .1341613E+1
+ .2012000E-4	+ .2482000E-4	- .1077330
+ .3440000E-5	+ .8950000E-5	- .7846657
- .1100000E-6	- .9300000E-6	- .1147713E+2
- .3700000E-6	+ .1380000E-5	- .1696287E+2
+ .8964854	+ .2636722	- .1951168E+1
+ .8964854	+ .2636719	- .1951173E+1

TABLE XVII ORBITAL ENERGIES: $1S-1S'-2E_r$ TOTAL PROMOTION PART

$E_A^P(1Sa, 1Sa)$	$E_A^P(1Sa, 1Sa')$	$E_A^P(1Sa', 1Sa')$
-.2428456E+1	+.5996971	+.1794034E+1
-.2687865E+1	+.5505363	+.1869221E+1
-.2872194E+1	+.5878844	+.1832260E+1
-.2640674E+1	+.3661463	+.2019872E+1
-.2741954E+1	+.4163472	+.1968724E+1
-.2768183E+1	+.4217442	+.1959585E+1
-.2779990E+1	+.4224200	+.1955992E+1
-.2789373E+1	+.4219742	+.1953109E+1
-.2792391E+1	+.4215986	+.1951726E+1
-.2793470E+1	+.4214238	+.1950726E+1
-.2793820E+1	+.4212338	+.1951666E+1
-.2796365E+1	+.4229136	+.1950211E+1
-.2794363E+1	+.4214989	+.1951392E+1
-.2794329E+1	+.4214532	+.1951443E+1
-.2794310E+1	+.4214362	+.1951438E+1
-.2794311E+1	+.4214359	+.1951485E+1
-.2794321E+1	+.4214354	+.1951455E+1

TABLE XVIII ORBITAL ENERGIES: $1S-2S-2P_{\sigma}$ KINETIC PROMOTION PART

$E_A^P(1S_a, 1S_a)$	$E_A^P(2S_a, 2S_a)$
-.6145249	+.3861968
-.4759806	+.2639801
-.3476795	+.1876723
-.1984581	+.1188857
+.1818150E-2	+.2958984E-1
+.8083018E-2	+.1548941E-1
+.3972440E-2	+.8085015E-2
+.4442000E-3	+.3904086E-2
-.9024000E-3	+.2125603E-2
-.1202270E-2	+.1072200E-2
-.1163780E-2	+.7483169E-3
-.1091010E-2	+.5149505E-3
-.7891600E-3	+.3512536E-3
-.6589800E-3	+.2369196E-3
-.3169100E-3	+.1047300E-3
+.7190000E-5	+.1832600E-4
+.1938000E-4	+.2992000E-5
-.2400000E-5	+.1180000E-5
-.1800000E-5	+.9900000E-7
-.1800000E-5	0.0

TABLE XIX ORBITAL ENERGIES: 1S-1S' KINETIC PROMOTION PART

$E_A^P(\underline{1S_a}, \underline{1S_a})$	$E_A^P(\underline{1S_a'}, \underline{1S_a'})$
-.1861998E+1	+.8202561
-.1089997E+1	+.3056559E-1
-.5561608	-.1628477
-.2647572	-.1567903
-.1023394	-.1089374
-.5332906E-1	-.8353973E-1
-.3700219E-1	-.6363970E-1
-.2217880E-2	-.3625958E-1
+.5462680E-2	-.1630668E-1
+.7699040E-2	-.7105790E-2
-.1401728E+1	+.1428049E+1
+.8430263E-2	+.1469919E-2
+.6639820E-2	+.2320282E-2
+.4896060E-2	+.2043106E-2
+.1508570E-2	+.1326966E-2
+.1567100E-2	+.6733424E-3
+.2668200E-3	+.3539090E-3
+.1314800E-3	+.1662760E-3
-.3234820E-2	+.1190490E-3
-.9210000E-5	+.3646570E-4
-.5500000E-5	+.1285000E-4
+.6000000E-6	+.3590000E-5
-.1423828E+1	+.1423827E+1
-.1423828E+1	+.1438272E+1

TABLE XX ORBITAL ENERGIES: 1S-1S'-2P KINETIC PROMOTION PART

$E_A^P(1S_a, 1S_a)$	$E_A^P(1S_a, 1S_a')$	$E_A^P(1S_a', 1S_a')$
+ .2476051E+1	- .5416203	- .7607105
+ .2420754E+1	- .5416203	- .1069535E+1
+ .2455731E+1	- .5416203	- .1247694E+1
+ .2497395E+1	- .5416203	- .1348917E+1
+ .2529144E+1	- .5416203	- .1408211E+1
+ .2550428E+1	- .5416203	- .1443839E+1
+ .2563836E+1	- .5416203	- .1465534E+1
+ .2576853E+1	- .5416203	- .1486999E+1
+ .2581251E+1	- .5416203	- .1495098E+1
+ .2582664E+1	- .5416203	- .1498163E+1
+ .2583175E+1	- .5416203	- .1499532E+1
+ .2583178E+1	- .5416203	- .1499723E+1
+ .2583207E+1	- .5416203	- .1499871E+1
+ .2583177E+1	- .5416203	- .1499902E+1
+ .2583211E+1	- .5416203	- .1499935E+1
+ .2583211E+1	- .5416203	- .1499932E+1
+ .2583234E+1	- .5416203	- .1499936E+1

TABLE XXI ORBITAL ENERGIES: 1S-2S-2P POTENTIAL PROMOTION PART

$E_A^P(1S_a, 1S_a)$	$E_A^P(1S_a, 2S_a)$	$E_A^P(2S_a, 2S_a)$
+ .7784778	+ .3380605E-1	- .4083282
+ .6053115	+ .2442157E-1	- .2799438
+ .4506123	+ .1694325E-1	- .1978060
+ .2757608	+ .7782400E-2	- .1216180
- .9058230E-1	+ .2521148E-1	- .5065032E-1
- .3970050E-2	+ .8082610E-2	- .2201264E-1
- .1087810E-2	+ .3629970E-2	- .1096637E-1
+ .1043000E-2	+ .1598340E-2	- .5150550E-2
+ .1718960E-2	+ .8312600E-3	- .2766160E-2
+ .1608610E-2	+ .4041800E-3	- .1379660E-2
+ .1446690E-2	+ .2779100E-3	- .9586200E-3
+ .1283850E-2	+ .1886000E-3	- .6569500E-3
+ .9182300E-3	+ .1271300E-3	- .4465300E-3
+ .7443400E-3	+ .8485000E-4	- .3002600E-3
+ .3540700E-3	+ .3712000E-4	- .1322800E-3
- .3930000E-5	+ .6330000E-5	- .2295000E-4
- .3283000E-4	+ .9070000E-6	- .3620000E-5
- .1310000E-5	- .3200000E-6	- .1405500E-5
- .3300000E-5	0.0	0.0
- .2400000E-5	0.0	0.0

TABLE XXII ORBITAL ENERGIES: 1S-1S' POTENTIAL PROMOTION PART

$E_A^P(1S_a, 1S_a)$	$E_A^P(1S_a, 1S_a')$	$E_A^P(1S_a', 1S_a')$
+0.2415278E+1	+0.3296075E-1	-0.1011998E+1
+0.1206578E+1	-0.8488010E-2	-0.4673123E-1
+0.5430371	-0.2735288E-1	+0.1730917
+0.2322490	-0.2484369E-1	+0.1657233
+0.7659884E-1	-0.1703988E-1	+0.1137968
+0.3267745E-1	-0.1302872E-1	+0.8666082E-1
+0.2159309E-1	-0.9795110E-2	+0.6612811E-1
-0.6615190E-2	-0.5511080E-2	+0.3676299E-1
-0.9491360E-2	-0.2407800E-2	+0.2494458E-1
-0.9475770E-2	-0.1021550E-2	+0.7987778E-1
+0.2313029E+1	+0.2640621	-0.3381896E+1
-0.7978220E-2	+0.1550600E-3	+0.1423435E+1
-0.5717690E-2	+0.5601000E-4	-0.1597866E+1
+0.1104476E-1	-0.1186743E-1	+0.1161672E+3
-0.1355500E-2	+0.3246300E-3	-0.1269107
-0.1461610E-2	+0.1468100E-3	+0.5764042
-0.2112800E-3	+0.6866000E-4	-0.5354620
-0.1048200E-3	+0.4024000E-4	-0.1341779E+1
+0.3254940E-2	+0.2482000E-4	-0.1078520
+0.1265000E-4	+0.8950000E-5	-0.7847022
+0.5410000E-5	-0.9300000E-6	-0.1147714E+2
-0.1000000E-5	+0.1380000E-5	-0.1696288E+2
+0.2320313E+1	+0.2636722	-0.3374995E+1
+0.2320313E+1	+0.2636719	-0.3375000E+1

TABLE XXIII ORBITAL ENERGIES: 1S-1S'-2P POTENTIAL PROMOTION PART

$E_A^P(1S_a, 1S_a)$	$E_A^P(1S_a, 1S_a')$	$E_A^P(1S_a', 1S_a')$
-.4904507E+1	+.1141317E+1	+.2554745E+1
-.5108619E+1	+.1092157E+1	+.2938756E+1
-.5327924E+1	+.1129505E+1	+.3079954E+1
-.5138068E+1	+.9077666	+.3367790E+1
-.5271099E+1	+.9579675	+.3376934E+1
-.5318611E+1	+.9633644	+.3403424E+1
-.5343826E+1	+.9640403	+.3421531E+1
-.5366226E+1	+.9635944	+.3440109E+1
-.5373642E+1	+.9632189	+.3447197E+1
-.5376134E+1	+.9630441	+.3449889E+1
-.5376995E+1	+.9628541	+.3451197E+1
-.5379542E+1	+.9645338	+.3449934E+1
-.5377569E+1	+.9631191	+.3451263E+1
-.5377506E+1	+.9630734	+.3451345E+1
-.5377521E+1	+.9630564	+.3451373E+1
-.5377522E+1	+.9630562	+.3451378E+1
-.5377556E+1	+.9630556	+.3451382E+1

TABLE XXIV ORBITAL ENERGIES: $1S-2S-2P_{\sigma}$ QUASI-CLASSICAL PART

$(1S_a, 1S_b)$ QC	$(1S_a, 2S_b)$ QC	$(2S_a, 2S_b)$ QC
+ .3532916	+ .2410647E-1	+ .2339300E-2
+ .7626116E-1	+ .6190091E-2	+ .8175727E-3
- .2131571E-1	+ .2575542E-3	+ .2643196E-3
- .4664087E-1	- .1978904E-2	- .1018055E-4
- .8388285E-2	- .5702772E-3	- .1795447E-4
- .2587980E-2	- .1629728E-3	- .3237126E-5
- .7403950E-3	- .3581851E-4	- .2555087E-6
+ .5368311E-2	+ .1484913E-5	0.0
- .6713957E-4	- .1358831E-5	0.0
- .2215753E-4	- .2654796E-6	0.0
- .1263013E-4	- .1139763E-6	0.0
- .7150218E-5	0.0	0.0
- .4052216E-5	0.0	0.0
- .2145447E-5	0.0	0.0
- .7152089E-6	0.0	0.0
- .4768314E-6	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0

TABLE XXV (<u>1Sa</u> , <u>1Sb</u>) ^{QC}	ORBITAL ENERGIES: $\frac{1S-1S'}{QC}$ (<u>1Sa</u> , <u>1Sb'</u>)	QUASI-CLASSICAL PART (<u>1Sa'</u> , <u>1Sb'</u>) ^{QC}
+ .3480118	+ .3556559E-1	+ .3795381E-2
- .5937269E-1	+ .5149099E-3	+ .5572999E-5
- .1088432	+ .2738629E-3	+ .8093086E-4
- .7329130E-1	+ .1349589E-2	+ .8549497E-5
- .4079912E-1	+ .1008058E-2	- .1418215E-4
- .2742673E-1	+ .6953355E-3	- .9987477E-5
- .2175269E-1	+ .4871443E-3	- .6445589E-5
- .1138556E-1	+ .2033467E-3	- .6977649E-5
- .5941711E-2	+ .6321301E-4	- .8881439E-5
- .3086445E-2	+ .1879943E-4	- .1560390E-5
- .3955362E-3	- .3955362E-3	- .3955360E-3
- .8090586E-3	+ .1087962E-5	0.0
- .4093172E-3	- .8312443E-6	- .1147296E-3
- .2080103E-3	- .1168228E-5	- .1009182E-6
- .5243107E-4	+ .5583435E-6	- .6661592E-5
- .1311031E-4	- .5011588E-6	- .3678382E-5
- .4052688E-5	- .1289641E-6	0.0
- .1192032E-5	- .1181388E-6	0.0
- .4768198E-6	+ .3848178E-6	+ .3627042E-5
- .2384162E-6	0.0	+ .7107111E-5
+ .3371220E-3	- .1866218E-6	0.0
0.0	0.0	0.0
0.0	0.0	0.0
0.0	0.0	0.0

TABLE XXVI ORBITAL ENERGIES: $1S-1S'-2P_{\sigma}$ QUASI-CLASSICAL PART
 QC

$(1S_a, 1S_b)$	$(1S_a, 1S_b')$	$(1S_a', 1S_b')$
+ .1317152	+ .2609852E-1	+ .1647188E-2
+ .1505654E-1	+ .1220167E-2	+ .6236720E-3
- .2739052E-1	- .1545511E-2	+ .1474701E-3
- .3087479E-1	- .1106039E-2	+ .3472864E-4
- .2333849E-1	- .5681429E-3	+ .8897354E-5
- .1527481E-1	- .2611915E-3	+ .2517054E-5
- .9294048E-2	- .1146927E-3	+ .7611708E-6
- .3070601E-2	- .2130338E-4	0.0
- .9346241E-3	- .4082154E-5	0.0
- .2721138E-3	- .8491547E-6	0.0
- .4553108E-4	0.0	0.0
- .2121685E-4	0.0	0.0
- .5006538E-5	0.0	0.0
- .7152221E-6	0.0	0.0
0.0	0.0	0.0
+ .2384137E-6	0.0	0.0
+ .4768363E-6	0.0	0.0

TABLE XXVII ORBITAL ENERGIES: 1S-2S-2P INTRA-ATOMIC PENETRATION:

SP $E\pi$ (<u>1Sa1Sa/1Sa1Sa</u>)	SP $E\pi$ (<u>1Sa1Sa/2Sa2Sa</u>)	SP $E\pi$ (<u>2Sa2Sa/2Sa2Sa</u>)
-.1059100E+1	+.1281599	-.1708661E-1
-.6642561	+.1050152	-.1851777E-1
-.4449505	+.8785522E-1	-.1973508E-1
-.2653476	+.7168627E-1	-.2278364E-1
+.1838216E-1	-.2165555E-1	+.3225774E-1
+.1261416E-4	-.2698684E-3	+.7381119E-2
+.4754548E-3	+.1020861E-2	+.2803284E-2
+.5655707E-3	+.7050466E-3	+.1119935E-2
+.3924591E-3	+.4161371E-3	+.5603626E-3
+.2331072E-3	+.2206030E-3	+.2643643E-3
+.1712709E-3	+.1560653E-3	+.1798435E-3
+.1239345E-3	+.1088502E-3	+.1207604E-3
+.8821426E-4	+.7508528E-4	+.8064821E-4
+.6159383E-4	+.5107923E-4	+.5340521E-4
+.2677037E-4	+.2230366E-4	+.2339056E-4
+.5023639E-5	+.3959949E-5	+.3919941E-5
+.2305048E-5	+.8773330E-6	+.4185583E-6
+.2056664E-5	+.4175333E-6	+.1062760E-6
+.1001997E-5	+.4412388E-7	0.0
+.1005387E-5	0.0	0.0

TABLE XXVIII ORBITAL ENERGIES: 1S-1S' INTRA-ATOMIC PENETRATION

SP $E_{\pi} (1Sa1Sa/1Sa1Sa)$	SP $E_{\pi} (1Sa1Sa/1Sa'1Sa')$	SP $E_{\pi} (1Sa'1Sa'/1Sa'1Sa')$
-.1385877E+1	-.1606575E-2	-.2344211E-5
-.8189070	-.5793513E-1	-.4614469E-2
-.4490297	-.5674511E-1	-.7859629E-2
-.2460236	-.4008237E-1	-.7150661E-2
-.1355015	-.2471688E-1	-.4773684E-2
-.9428012E-1	-.1818350E-1	-.3162250E-2
-.7601523E-1	-.1382314E-1	-.2676789E-2
-.4305928E-1	-.7708736E-2	-.8078076E-5
-.2422556E-1	-.3545343E-2	-.1656669E-1
-.1367865E-1	-.1590018E-2	-.1402193
+.2640626	+.2640621	+.2640616
-.4343044E-2	+.4189103E-3	-.2845529E+1
-.2981776E-2	+.1079840E-2	+.3189647E+1
-.3209989E-1	+.2475343E-1	-.2323351E+3
+.1259845E-5	+.1779776E-4	+.2511769
+.3348452E-4	+.5670913E-4	-.1154405E+1
+.2523336E-4	+.3211996E-4	+.1070310E+1
+.1385654E-4	+.2012042E-4	+.2683335E+1
+.1510904E-4	+.1501497E-4	+.2154694
+.4140667E-5	+.5452450E-5	+.1569353E+1
+.4612869E-6	-.2928233E-6	+.2295433E+2
+.1456576E-6	+.7473512E-6	+.3392577E+2
+.2636718	+.2636712	+.2636707
+.2636719	+.2636719	+.2636719

TABLE XXIX ORBITAL ENERGIES: 1S-1S'-2P_σ INTRA-ATOMIC PENETRATION

SP $E\pi$ (<u>1Sa1Sa/1Sa1Sa</u>)	SP $E\pi$ (<u>1Sa1Sa/1Sa'1Sa'</u>)	SP $E\pi$ (<u>1Sa'1Sa'/1Sa'1Sa'</u>)
+.9304899E-1	+.9493822E-1	+.1155534
+.8005167E-4	-.2836645E-2	+.1171984
+.1810238	-.1887156	+.2299128
-.3309138	+.1936385	-.1327450
-.1344894	+.5884943E-1	-.3017297E-1
-.7663524E-1	+.2823410E-1	-.1217186E-1
-.4602665E-1	+.1528905E-1	-.5932432E-2
-.1700689E-1	+.5242378E-2	-.1883888E-2
-.6310254E-2	+.2061097E-2	-.7871212E-3
-.2447889E-2	+.9557372E-3	-.4419498E-3
-.1145608E-2	+.6559736E-3	-.4626371E-3
+.4061092E-2	-.2813115E-2	+.2445003E-2
+.6995761E-4	-.6954477E-4	+.8323013E-4
+.4112793E-4	-.2070445E-4	+.1205603E-4
-.2891921E-4	+.6341071E-5	-.1995767E-5
-.2210090E-4	+.2123356E-5	-.2933140E-6
-.2450589E-4	-.5201936E-6	0.0

TABLE XXX ORBITAL ENERGIES: 1S-2S-2P INTERATOMIC PENETRATION

SP q (<u>1Sa/1Sb</u>) (<u>1Sa1Sa/1Sb1Sb</u>)	SP q (<u>1Sa/2Sb</u>) (<u>1Sa1Sa/2Sb2Sb</u>)	SP q (<u>2Sa/2Sb</u>) (<u>2Sa2Sa/2Sb2Sb</u>)
+ .8379527	- .8565598E-1	- .1847130E-2
+ .4726642	- .6233555E-1	- .3813027E-3
+ .2811717	- .4578521E-1	- .2687800E-4
+ .1358630	- .2988933E-1	+ .2769840E-4
+ .1282520E-1	- .8143442E-2	+ .6838000E-6
+ .3889980E-2	- .4082538E-2	+ .4643000E-7
+ .1141400E-2	- .1892614E-2	0.0
+ .3041000E-3	- .7825672E-3	0.0
+ .1133700E-3	- .3802268E-3	0.0
+ .3883000E-4	- .1714109E-3	0.0
+ .2275000E-4	- .1134350E-3	0.0
+ .1295000E-4	- .7419247E-4	0.0
+ .7320000E-5	- .4822070E-4	0.0
+ .4120000E-5	- .3105470E-4	0.0
+ .1770000E-5	- .1258540E-4	0.0
+ .2300000E-6	- .1887940E-5	0.0
- .1500000E-6	- .2695920E-6	0.0
- .1900000E-6	- .1016280E-6	0.0
- .6000000E-7	- .1563000E-7	0.0
- .1000000E-6	0.0	0.0

TABLE XXXI ORBITAL ENERGIES: 1S-1S' INTERATOMIC PENETRATION

SP q (<u>1Sa/1Sb</u>) (<u>1Sa1Sa/1Sb1Sb</u>)	SP q (<u>1Sa/1Sb'</u>) (<u>1Sa1Sa/1Sb'1Sb'</u>)	SP q (<u>1Sa'/1Sb'</u>) (<u>1Sa'1Sa'/1Sb'1Sb'</u>)
+ .1212248E+1	+ .2113935	- .2109583E-1
+ .6276430	+ .4508360E-1	- .9222618E-4
+ .2904434	+ .4200402E-1	+ .4234487E-3
+ .1348532	+ .2864611E-1	+ .1185216E-3
+ .6407180E-1	+ .1671523E-1	+ .2311819E-4
+ .4101350E-1	+ .1183267E-1	+ .8437530E-5
+ .3194420E-1	+ .8664455E-2	+ .3643710E-5
+ .1630910E-1	+ .4461610E-2	+ .5169200E-6
+ .8498800E-2	+ .1841345E-2	0.0
+ .4461500E-2	+ .7379740E-3	0.0
+ .16192524	- .5833900E-3	- .1619249
+ .1221400E-2	- .1380864E-3	0.0
+ .6379000E-3	- .1961363E-3	0.0
+ .3317000E-3	- .1628250E-3	0.0
+ .8868000E-4	- .9408540E-4	0.0
+ .2296000E-4	- .4337000E-4	0.0
+ .8140000E-5	- .2048300E-4	0.0
+ .3130000E-5	- .8908600E-5	0.0
+ .9700000E-6	+ .6277000E-5	0.0
+ .2700000E-6	- .1627200E-5	0.0
+ .4500000E-6	- .5700000E-6	0.0
+ .9000000E-7	0.0	0.0
+ .4999992E-1	0.0	- .5000000E-1
+ .2500000E-1	0.0	- .2500000E-1

TABLE XXXII ORBITAL ENERGIES: $1S-1S'-2P_0$ INTERATOMIC PENETRATION

SP q ($1S_a/1S_b$) ($1S_a1S_a/1S_b1S_b$)	SP q ($1S_a/1S_b'$) ($1S_a1S_a/1S_b'1S_b'$)	SP q ($1S_a'/1S_b'$)' ($1S_a'1S_a'/1S_b'1S_b'$)
+ .6919630E-1	- .1932707	+ .2270688E-2
+ .1135473	- .9559276E-1	+ .6077960E-3
+ .9740790E-1	- .4757163E-1	+ .1329745E-3
+ .6676030E-1	- .2422869E-1	+ .2820940E-4
+ .4164340E-1	- .1262939E-1	+ .5951000E-5
+ .2480680E-1	- .6712401E-2	+ .1251000E-5
+ .1439860E-1	- .3633911E-2	+ .2636000E-6
+ .4643700E-2	- .1123151E-2	+ .1170000E-7
+ .1446900E-2	- .3732737E-3	0.0
+ .4411400E-3	- .1344390E-3	0.0
+ .8289000E-4	- .3446540E-4	0.0
+ .4113000E-4	- .1914769E-4	0.0
+ .1331000E-4	- .7844070E-5	0.0
+ .5900000E-5	- .1397920E-5	0.0
+ .3860000E-5	- .1069710E-5	0.0
+ .3030000E-5	- .4378800E-6	0.0
+ .2720000E-5	0.0	0.0

TABLE XXXIII ORBITAL ENERGIES 1S-2S-2P-TOTAL INTERFERENCE PARTS

<u>P(1Sa1Sb)</u> <u>E(1Sa1Sb)</u>	<u>P(1Sa,2Sb)</u> <u>E(1Sa,2Sb)</u>	<u>P(2Sa1Sb)</u> <u>E(2Sa1Sb)</u>	<u>P(2Sa,2Sb)</u> <u>E(2Sa,2Sb)</u>
+ .1098991E+1	- .3474430	- .1082058	- .3073792E-1
+ .7721669	- .2122186	- .8003646E-1	- .1431135E-1
+ .5385287	- .1397732	- .5300327E-1	- .5950810E-2
+ .3105197	- .8226937E-1	- .3238041E-1	- .1440600E-2
+ .4389201E-1	- .1743075E-1	- .1643576E-1	- .4355000E-4
+ .1542800E-1	- .8424830E-2	- .1081354E-1	- .1767000E-4
+ .5166220E-2	- .4092030E-2	- .6290003E-2	- .6390000E-5
+ .1559630E-2	- .1860420E-2	- .3206190E-2	- .1770000E-5
+ .6329900E-3	- .9792900E-3	- .1786930E-2	- .5700000E-6
+ .2372600E-3	- .4794700E-3	- .9208900E-3	- .1600000E-6
+ .1438900E-3	- .3303000E-3	- .6484300E-3	+ .2136870E-7
+ .8682000E-4	- .2246200E-3	- .4501200E-3	+ .1067221E-7
+ .5209000E-4	- .1515100E-3	- .3097300E-3	+ .5186083E-8
+ .3111000E-4	- .1011600E-3	- .2106300E-3	0.0
+ .1098000E-4	- .4390000E-4	- .9453000E-4	0.0
+ .1310000E-5	- .7460000E-5	- .1701000E-4	0.0
+ .1500000E-6	- .1190000E-5	- .2830000E-5	0.0
+ .4000000E-7	- .4700000E-6	- .1150000E-5	0.0
0.0	- .3000000E-7	- .1000000E-6	0.0
0.0	0.0	0.0	0.0

TABLE XXXIV ORBITAL ENERGIES: 1S-1S' TOTAL INTERFERENCE PART

$\frac{P(1S_a, 1S_b)}{E(1S_a, 1S_b)}$	$\frac{P(1S_a, 1S_b')}{E(1S_a, 1S_b')}$	$\frac{P(1S_a', 1S_b)}{E(1S_a', 1S_b)}$	$\frac{P(1S_a, 1S_b)}{E(1S_a', 1S_b')}$
+ .7842902	- .4483117	- .2096750	- .6791995E-1
+ .6612245	+ .9566701E-1	- .2721340	- .5217670E-2
+ .4360990	+ .1659677	- .1318342	- .3317000E-4
+ .2634209	+ .1228022	- .4984840E-1	- .2038000E-4
+ .1544702	+ .7482257E-1	- .1448198E-1	- .7399000E-4
+ .1098861	+ .5472678E-1	- .5508340E-2	- .6178000E-4
+ .9005225E-1	+ .4012965E-1	- .2274700E-2	- .4141000E-4
+ .5247027E-1	+ .2172773E-1	+ .1080000E-2	- .1873000E-4
+ .3038637E-1	+ .9329740E-2	+ .9490000E-3	+ .1059000E-4
+ .1754068E-1	+ .3939970E-2	+ .6498700E-3	+ .9000000E-7
- .5399804E-1	0.0	0.0	+ .6395786E-1
+ .5634850E-2	- .7709500E-3	- .4564210E-2	- .3000000E-7
+ .3148690E-2	- .1071010E-2	+ .8923400E-3	+ .2300000E-6
+ .1745700E-2	- .1022870E-2	- .1886180E-2	- .1500000E-6
+ .5189400E-3	- .6348200E-3	- .3621200E-3	- .1200000E-6
+ .1475800E-3	- .3111200E-3	- .1353000E-4	0.0
+ .5300000E-4	- .1620700E-3	- .1794500E-3	0.0
+ .1866000E-4	- .7507000E-4	- .1112900E-3	0.0
+ .5930000E-5	- .5378000E-4	- .4624000E-4	0.0
+ .2210000E-5	- .2241000E-4	- .3162000E-4	0.0
+ .1300000E-6	- .4050000E-5	- .5723000E-4	0.0
- .3000000E-6	- .1510000E-5	- .1526000E-4	0.0
- .4950000E-5	0.0	0.0	+ .4550000E-5
0.0	0.0	0.0	0.0

TABLE XXXV ORBITAL ENERGIES: 1S-1S'-2P_σ TOTAL INTERFERENCE PARTS

$\frac{P(1S_a, 1S_b)}{E(1S_a, 1S_b)}$	$\frac{P(1S_a, 1S_b')}{E(1S_a, 1S_b')}$	$\frac{P(1S_a' 1S_b)}{E(1S_a', 1S_b)}$	$\frac{P(1S_a', 1S_b')}{E(1S_a', 1S_b')}$
+ .3130061	- .2902463	- .1809562	- .3033469E-1
+ .3291401	- .2097729	- .1069015	- .7509860E-2
+ .2503120	- .1324078	- .6204625E-1	- .1710220E-2
+ .1707126	- .8150996E-1	- .3595838E-1	- .4029600E-3
+ .1106736	- .5001898E-1	- .2096083E-1	- .1041900E-3
+ .6970201E-1	- .3065723E-1	- .1233848E-1	- .3079000E-4
+ .4306019E-1	- .1875553E-1	- .7366590E-2	- .1047000E-4
+ .1577164E-1	- .6961880E-2	- .2776810E-2	- .5243000E-4
+ .5536960E-2	- .2547240E-2	- .1141210E-2	- .2100000E-6
+ .1877680E-2	- .9054400E-3	- .5129200E-3	- .6900000E-7
+ .3939200E-3	- .1930400E-3	- .1749500E-3	0.0
+ .1989100E-3	- .9615000E-4	- .1077600E-3	0.0
+ .6238000E-4	- .2620000E-4	- .5157000E-4	0.0
+ .1964000E-4	- .1546000E-4	- .9580000E-5	0.0
+ .5050000E-5	- .1810000E-5	- .8990000E-5	0.0
+ .1740000E-5	- .7100000E-6	- .4030000E-5	0.0
0.0	0.0	0.0	0.0

TABLE XXXVI ORBITAL ENERGIES: 1S-2S-2P σ POTENTIAL INTERFERENCE PART

<u>P(1Sa1Sb)</u> <u>U(1Sa1Sb)</u>	<u>P(1Sa2Sb)</u> <u>U(1Sa2Sb)</u>	<u>P(2Sa1Sb)</u> <u>U(2Sa1Sb)</u>	<u>P(2Sa2Sb)</u> <u>U(2Sa2Sb)</u>
-.3855738E-1	-.4842151	-.2449779	-.1496764E-1
-.1235431	-.2697767	-.1375946	-.1080221E-1
-.1617240	-.1513688	-.6459891E-1	-.6561598E-2
-.1623927	-.6388663E-1	-.1399767E-1	-.2448162E-2
-.5087403E-1	+.1392916E-2	+.2387914E-2	-.3615527E-4
-.2155011E-1	+.3877101E-2	+.1488385E-2	-.2049997E-5
-.8219830E-2	+.3183067E-2	+.9850711E-3	+.7901478E-6
-.2740448E-2	+.1925993E-2	+.5802220E-3	+.3816521E-6
-.1174952E-2	+.1160875E-2	+.3532441E-3	+.1433075E-6
-.4625750E-3	+.6335817E-3	+.1921625E-3	+.4155409E-7
-.2868238E-3	+.4564005E-3	+.1382709E-3	+.2136870E-7
-.1766231E-3	+.3231011E-3	+.9760247E-4	+.1067221E-7
-.1080776E-3	+.2261188E-3	+.6790384E-4	+.5186083E-8
-.6576709E-4	+.1560849E-3	+.4660884E-4	0.0
-.2400328E-4	+.7183329E-4	+.2120173E-4	0.0
-.3040180E-5	+.1340793E-4	+.3858332E-5	0.0
-.3667142E-6	+.2290792E-5	+.6467042E-6	0.0
-.1254949E-6	+.9329682E-6	+.2546020E-6	0.0
-.8215416E-8	+.8554643E-7	+.2160078E-7	0.0
0.0	+.6696484E-8	+.2085339E-8	0.0

TABLE XXXVII ORBITAL ENERGIES: 1S-1S' POTENTIAL INTERFERENCE PART

<u>P(1Sa1Sb)</u> <u>U(1Sa1Sb)</u>	<u>P(1Sa1Sb')</u> <u>U(1Sa1Sb')</u>	<u>P(1Sa'1Sb)</u> <u>U(1Sa'1Sb)</u>	<u>P(1Sa'1Sb')</u> <u>U(1Sa'1Sb')</u>
-.3327151	-.7661316	-.5274950	+.1988382
-.3753238	-.1797451	-.5475461	+.9090701E-1
-.3061408	-.2583541E-1	-.3236643	+.2946894E-1
-.2186743	-.1284966E-2	-.1739355	+.8377290E-2
-.1464245	-.1063255E-2	-.9036791E-1	+.2173695E-2
-.1119789	-.2157259E-2	-.6239238E-1	+.1003624E-2
-.9555831E-1	-.2277188E-2	-.4468154E-1	+.5063524E-3
-.6096889E-1	-.2418146E-2	-.2306588E-1	+.1282475E-3
-.3833407E-1	-.1564131E-2	-.9944873E-2	+.3685116E-4
-.2364252E-1	-.8853061E-3	-.4175406E-2	+.4785860E-5
+.7765180E-1	0.0	0.0	-.9197444E-1
-.8508588E-2	+.2668219E-3	-.3526443E-2	+.1666855E-6
-.4987029E-2	+.5708337E-3	+.2534178E-2	+.6870293E-6
-.2876289E-2	+.4504382E-3	-.4128702E-3	+.2137406E-6
-.9224664E-3	+.3432041E-3	+.6159042E-3	+.3297277E-7
-.2821088E-3	+.1979552E-3	+.4955529E-3	+.3974992E-7
-.1066219E-3	+.1056830E-3	+.8831321E-4	0.0
-.3940691E-4	+.5282809E-4	+.1661129E-4	0.0
-.1502069E-4	+.3527069E-4	+.4280864E-4	0.0
-.5117266E-5	+.4917287E-5	-.4294901E-5	0.0
-.2419520E-5	+.5103441E-5	-.4667515E-4	0.0
-.1294500E-6	+.5217340E-6	-.1323064E-4	0.0
+.7729959E-5	0.0	0.0	-.8130041E-5
0.0	0.0	0.0	0.0

TABLE XXXVIII ORBITAL ENERGY $1S-1S'-2P_{\sigma}$ POTENTIAL INTERFERENCE PART

$P(1Sa1Sb)$ $U(1Sa1Sb)$	$P(1Sa1Sb')$ $U(1Sa1Sb')$	$P(1Sa'1Sb)$ $U(1Sa'1Sb)$	$P(1Sa'1Sb')$ $U(1Sa'1Sb')$
+ .1377041E-1	- .8386769E-1	+ .2542239E-1	- .7027808E-1
- .1149985	- .7914774E-1	+ .2372364E-1	- .2479398E-1
- .1638527	- .4450116E-1	+ .2586036E-1	- .7760890E-2
- .1550118	- .2178905E-1	+ .2376254E-1	- .2403517E-2
- .1247544	- .9821465E-2	+ .1923669E-1	- .7424183E-3
- .9204977E-1	- .3971020E-2	+ .1434773E-1	- .2272573E-3
- .6426526E-1	- .1256072E-2	+ .1013287E-1	- .6840336E-4
- .2810965E-1	+ .3667875E-3	+ .4551864E-2	- .5642539E-4
- .1114622E-1	+ .4591972E-3	+ .1865229E-2	- .3418531E-6
- .4128074E-2	+ .3108782E-3	+ .7034072E-3	0.0
- .9452433E-3	+ .1339954E-3	+ .1520879E-3	0.0
- .4909269E-3	+ .8827830E-4	+ .7666738E-4	0.0
- .1604770E-3	+ .4366029E-4	+ .1828881E-4	0.0
- .5074143E-4	+ .9053555E-5	+ .1491317E-4	0.0
- .1389917E-4	+ .8150668E-5	+ .9674119E-6	0.0
- .4830009E-5	+ .3732447E-5	+ .4069594E-6	0.0
- .3958000E-7	+ .5315208E-8	+ .1043682E-7	0.0

TABLE XXXIX ORBITAL ENERGIES: 1S-2S-2P KINETIC INTERFERENCE PARTS

P(<u>1Sa, 1Sb</u>) T(<u>1Sa, 1Sb</u>)	P(<u>1Sa, 2Sb</u>) T(<u>1Sa, 2Sb</u>)	P(<u>2Sa, 2Sb</u>) T(<u>2Sa, 2Sb</u>)
+.1137549E+1	+.1367721	-.1577028E-1
+.8953212	+.5755811E-1	-.3509135E-2
+.7002527	+.1159564E-1	+.6107938E-3
+.4729124	-.1838274E-1	+.1007557E-2
+.9476604E-1	-.1882367E-1	-.7389098E-5
+.3697811E-1	-.1230193E-1	-.1561920E-4
+.1338605E-1	-.7275101E-2	-.7179957E-5
+.4300082E-2	-.3786413E-2	-.2151387E-5
+.1807941E-2	-.2140175E-2	-.7105477E-6
+.6998271E-3	-.1113051E-2	-.1954194E-6
+.4307092E-3	-.7867016E-3	0.0
+.2634359E-3	-.5477226E-3	0.0
+.1601673E-3	-.3776302E-3	0.0
+.9688492E-4	-.2572371E-3	0.0
+.3497645E-4	-.1157309E-3	0.0
+.4352534E-5	-.2086741E-4	0.0
+.5158310E-6	-.3478593E-5	0.0
+.1748644E-6	-.1398773E-5	0.0
0.0	-.1249327E-6	0.0
0.0	0.0	0.0

TABLE XL ORBITAL ENERGIES: $1S-1S'$ KINETIC INTERFERENCE PARTS

$P(1S_a, 1S_b)$ $T(1S_a, 1S_b)$	$P(1S_a, 1S_b')$ $T(1S_a, 1S_b')$	$P(1S_a', 1S_b')$ $T(1S_a', 1S_b')$
+0.1117005E+1	+0.3178199	-0.2667582
+0.1036548E+1	+0.2754121	-0.9612468E-1
+0.7422398	+0.1918031	-0.2950211E-1
+0.4820952	+0.1240871	-0.8397670E-2
+0.3008947	+0.7588583E-1	-0.2247676E-2
+0.2218650	+0.5688404E-1	-0.1065401E-2
+0.1856106	+0.4240684E-1	-0.5477604E-3
+0.1134392	+0.2414588E-1	-0.1469822E-3
+0.6872044E-1	+0.1089387E-1	-0.2626313E-4
+0.4118320E-1	+0.4825278E-2	-0.4696784E-5
-0.1316498	0.0	+0.1559323
+0.1414344E-1	-0.1037772E-2	-0.1980403E-6
+0.8135724E-2	-0.1641842E-2	-0.4639074E-6
+0.4621994E-2	-0.1473309E-2	-0.3636204E-6
+0.1441408E-2	-0.9780247E-3	-0.1536599E-6
+0.4296939E-3	-0.5090782E-3	0.0
+0.1596182E-3	-0.2677462E-3	0.0
+0.5806547E-4	-0.1279039E-3	0.0
+0.2094537E-4	-0.8905013E-4	0.0
+0.7325869E-5	-0.2733186E-4	0.0
+0.2549684E-5	-0.1054738E-4	0.0
-0.1736501E-6	-0.2034670E-5	0.0
-0.1268198E-4	0.0	+0.1268211E-4
0.0	0.0	0.0

TABLE XLI ORBITAL ENERGIES: $1S-1S'-2P\sigma$ KINETIC INTERFERENCE PARTS

$P(1S_a, 1S_b)$ $T(1S_a, 1S_b)$	$P(1S_a, 1S_b')$ $T(1S_a, 1S_b')$	$P(1S_a', 1S_b')$ $T(1S_a', 1S_b')$
+ .2992357	- .2063786	+ .3994339E-1
+ .4441386	- .1306252	+ .1728412E-1
+ .4141647	- .8790661E-1	+ .6050673E-2
+ .3257244	- .5972914E-1	+ .2000560E-2
+ .2354280	- .4019752E-1	+ .6382333E-3
+ .1617518	- .2668621E-1	+ .1964738E-3
+ .1073255	- .1749946E-1	+ .5792801E-4
+ .4388129E-1	- .7328666E-2	+ .4004930E-5
+ .1668318E-1	- .3006438E-2	+ .2707886E-7
+ .6005745E-2	- .1216324E-2	0.0
+ .1339162E-2	- .3270392E-3	0.0
+ .6898361E-3	- .1844257E-3	0.0
+ .2228602E-3	- .6985980E-4	0.0
+ .7037529E-4	- .2448670E-4	0.0
+ .1895487E-4	- .9957230E-5	0.0
+ .6569304E-5	- .4444698E-5	0.0
0.0	0.0	0.0

TABLE XLII POTENTIAL CURVE AND ZETAS FOR $1S-2S-2P_{\sigma}$

R	$J_{1S} = J_{2S} = J_{2P_{\sigma}}$	V(R)	Total Energy
0.7559	1.6618	1.9128775	-3.782435
0.994875	1.6409	1.2122575	-4.483055
1.13385	1.6356	0.7976845	-4.897628
1.4173125	1.6465	.4343935	-5.260919
2.362188	1.6898	.0527192	-5.6425933
2.834625	1.6902	.0168533	-5.6784592
3.307063	1.6881	.0048825	-5.6904300
3.7995	1.6868	.0067019	-5.6886106
4.15745	1.6865	.0003177	-5.6949948
4.5354	1.6866	.0000392	-5.6952733
4.724375	1.6867	-.0000042	-5.6953167
4.91335	1.6868	-.0000227	-5.6953352
5.102325	1.6870	-.0000308	-5.6953433
5.2913	1.6871	-.0000304	-5.6953429
5.66925	1.6873	-.0000208	-5.6953333
6.42515	1.6875	-.0000299	-5.6953424
7.18105	1.6875	-.0000099	-5.6953224
7.5590	1.6875	-.0000077	-5.6953207
8.503875	1.6875	-.0000101	-5.6953226
9.44875	1.6875	-.0000080	-5.6953205

TABLE XLIII POTENTIAL CURVE AND ZETAS FOR 1S-1S'

S_{1S}	$S_{1S'}$	V(R)	Total Energy
2.23	0.99	1.1239915	-4.571321
2.04	1.22	.6856125	-5.009700
1.92	1.38	.4207035	-5.274609
1.84	1.49	.2561085	-5.439204
1.79	1.57	.1560355	-5.539277
1.77	1.60	.1128975	-5.582415
1.75	1.62	.9391650E-1	-5.601396
1.73	1.65	.5591650E-1	-5.639396
1.71	1.67	.3189450E-1	-5.663418
1.70	1.68	.1906950E-1	-5.676240
1.69	1.69	.1088650E-1	-5.684426
1.687	1.693	.6092500E-2	-5.689220
1.684	1.695	.3344500E-2	-5.691968
1.683	1.695	.1792800E-2	-5.6935197
1.682	1.694	.4730000E-3	-5.694840
1.683	1.693	.1029000E-3	-5.6952096
1.6838	1.6914	.2230000E-4	-5.6952902
1.6848	1.6903	.2900000E-5	-5.6953096
1.6856	1.6895	.9000000E-6	-5.6953116
1.6862	1.6888	-.3500000E-5	-5.6953160
1.6866	1.6884	-.8500000E-5	-5.6953210
1.6872	1.6878	-.4600000E-5	-5.6953181
1.6875	1.6875	-.4200000E-5	-5.6953167
1.6875	1.6875	-.4000000E-5	-5.6953165

TABLE XLIV POTENTIAL CURVE AND ZETAS FOR 1S-1S'-2P

$$(\mathcal{J}_{1S} = 2.906 \quad \mathcal{J}_{1S'} = 1.453 \quad \mathcal{J}_{2P} = 1.340)$$

R	V(R)	Total Energy
1.0	.987247	-4.736099
1.25	.601763	-5.121583
1.50	.361473	-5.361873
1.75	.214289	-5.509057
2.0	.125796	-5.597550
2.25	.073279	-5.650067
2.50	.042337	-5.681009
3.0	.013874	-5.709472
3.5	.004443	-5.718903
4.0	.001369	-5.721977
4.7	.000224	-5.723122
5.0	.000150	-5.723196
5.5	.000052	-5.723294
6.0	.000066	-5.723280
6.56	.000036	-5.723310
7.0	.000043	-5.723303
9.0	.000013	-5.723333

APPENDIX A

For the calculations performed here the following steps and programs were used. The flow chart, Figure 1, will be helpful in understanding the following discussion. The first order density matrix is determined from the wavefunction by the expansion

$$\rho(X) = \sum_{n=1}^{\infty} \rho_n(X)$$

$$\rho_n(X) = N_n \phi_n(X) \phi_n(X)$$

$$N_n = \begin{cases} 2 & n=1, 2, \dots, (N/2) \\ 0 & n > (N/2) \end{cases}$$

The first order density matrix was then set up in terms of a bond order matrix representation as follows:

$$\rho(X) = \sum_{Aa} \sum_{Bb} (Aa)(Bb) P(Aa|Bb)$$

In this representation the second order density matrix looks like

$$\pi(X_1, X_2) = \sum_{Aa} \sum_{\bar{A}\bar{a}} \sum_{Bb} \sum_{\bar{B}\bar{b}} (Aa \bar{A}\bar{a})' (Bb \bar{B}\bar{b})^2 \times P(Aa \bar{A}\bar{a} | Bb \bar{B}\bar{b})$$

The pair bond order matrix was determined from the bond order matrix by the expansion

$$P(Aa \bar{A}\bar{a} | Bb \bar{B}\bar{b})$$

$$= P_c(Aa \bar{A}\bar{a} | Bb \bar{B}\bar{b}) - P_x(Aa \bar{A}\bar{a} | Bb \bar{B}\bar{b})$$

$$P_c(Aa \bar{A}\bar{a} | Bb \bar{B}\bar{b}) = P(Aa | \bar{A}\bar{a}) P(Bb | \bar{B}\bar{b})$$

$$P_x(Aa \bar{A}\bar{a} | Bb \bar{B}\bar{b}) = \frac{1}{4} \{ P(Aa | Bb) P(\bar{A}\bar{a} | \bar{B}\bar{b})$$

$$+ P(Aa | \bar{B}\bar{b}) P(\bar{A}\bar{a} | Bb) \}$$

This was done automatically by a program called PAIRBOND. In order to determine the energy the integrals involved had to be calculated.

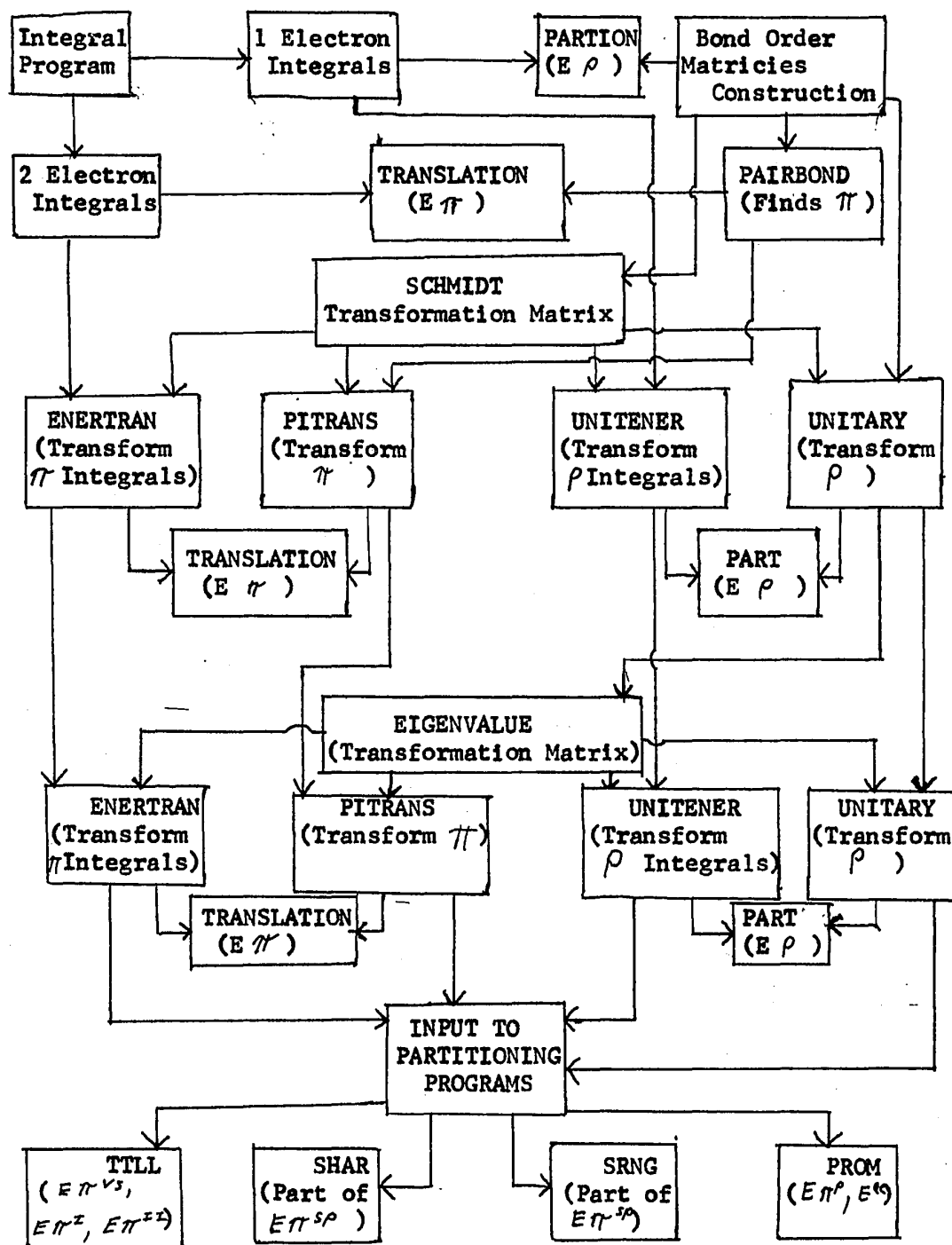


Figure 1. Flow Diagram of Programs Used to Perform Ruedenberg's Partitioning Analysis.

Originally they were obtained from the Diatomic Integral Program but later they were obtained from Ruedenberg's integral program at Iowa State University. The values of these integrals were used in conjunction with the bond order and pair bond order matrices to determine the energy. The energy obtained from the first order density matrix was calculated from a program called PARTION. The energy associated with the second order density matrix was obtained from a program called TRANSLATION. The energies obtained from these programs were used to check the total energy.

The next step was to transform the non-orthogonal basis set into an orthogonal basis set. In order to accomplish this the transformation matrix was required. This was obtained with the Gram-Schmidt Orthogonalization Procedure coded in a program called SCHMIDT. This transformation matrix was then used to transform the bond order matrix, the integrals associated with the bond order matrix, the pair bond order matrix, and the integrals associated with the pair bond order matrix into an orthogonal basis set. Four different programs were used to accomplish the transformation. The program called UNITARY transformed the bond order matrix, UNITENER transformed the one electron integrals associated with the bond order matrix, PITRANS transformed the pair bond order matrix, and ENERTRAN transformed the two electron integrals associated with the pair bond order matrix. A check was then made on the total energy from the first order density matrix and by TRANSLATION for the second order density matrix.

The orthogonal basis set was then transformed into the basis set of valence atomic orbitals. The transformation matrix for this was determined by finding the eigenvectors of the intra-atomic part of the bond order matrix. The program that determined the eigenvectors was called EIGENVALUE. This transformation matrix was then used in the same manner as the Schmidt transformation matrix. I used the same programs as before, which are UNITARY, UNITENER, PITRANS and ENERTRAN. A check on the total energy was again performed with the use of the two programs, PART and TRANSLATION.

The program PART besides checking the total energy also obtained the partitioning needed on the first order density matrix. The partitioning on the second order density matrix was obtained from four programs. The program called TLL partitioned the second order density into the valence state part, the first order interference energy and the second order interference energy. The other three programs called SHAR, SRNG and PROM obtained the sharing penetration fragment and the promoted state fragment. All four of these partitioning programs operate on exactly the same principle. Therefore, only TLL will be discussed, but it will be discussed thoroughly.

The program that obtained the orthogonal transformation was called SCHMIDT. This program was obtained from the Quantum Chemistry Program Exchange.¹ The program that obtained the transformation

¹L. Schadd and H. Joy "Schmidt Orthogonalization" Program 26, Quantum Chemistry Program Exchange, Indiana University (1965).

matrix that transformed the orthogonal basis set into valence atomic orbitals was called EIGENVALUE. This program along with two subroutines were obtained from the University of Hawaii Statistical and Computing Center. These subroutines perform a matrix multiplication and the multiplication of one matrix by the transpose of another.

The first order density matrix is transformed into the new basis set $P' = (\Pi^{-1})^T P \Pi^{-1}$ where P is the bond order matrix and Π is the transformation matrix. After the inverse of Π is determined the calling of the two subroutines that do matrix multiplication and multiplication of one matrix by the transpose of another, the transformation on P' is complete. UNITARY simply has a main program that reads in the necessary data and then calls in these two subroutines. The transformation of the one electron energy integrals is given by $k' = \Pi k \Pi^T$ where k is the matrix of one electron integrals, k' is the matrix of new integrals after transformation and Π is the transformation matrix. The program UNITENER, simply consists of a main program that reads in the data and calls the two subroutines, matrix multiplication and the multiplication of a matrix by the transpose of another matrix.

The transformation on the pair bond order matrix is given by

$$P_{m\bar{m}n\bar{n}} = \sum_{a\bar{a}} \sum_{b\bar{b}} \tau_{am}^{-1} \tau_{a\bar{m}}^{-1} P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}) \tau_{bn}^{-1} \tau_{b\bar{n}}^{-1}$$

where $P_{m\bar{m}n\bar{n}}$ are the elements of the new pair bond order matrix, $P(A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}})$ are the elements of the old pair bond

order matrix and the τ 's are the elements of the transformation matrix \mathbb{T}^{-1} . Thus, all that program PITRANS consists of is a program that reads in the old pair bond order matrix and the transformation matrix. The rest of the program is simply a group of Do loops that do the summations and a statement that multiplies all these terms together. ENERTRAN works on exactly the same principle, except it transforms the two electron integrals for which the algorithm is

$$[A'_m \bar{A}'_{\bar{m}} | B'_n \bar{B}'_{\bar{n}}] = \sum_{a\bar{a}} \sum_{b\bar{b}} \tau_{ma} \tau_{\bar{m}\bar{a}} [A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}] \tau_{nb} \tau_{\bar{n}\bar{b}}$$

where $[A'_m \bar{A}'_{\bar{m}} | B'_n \bar{B}'_{\bar{n}}]$ are elements of the transformed two electron integrals, and $[A_a \bar{A}_{\bar{a}} | B_b \bar{B}_{\bar{b}}]$ are the elements of the untransformed two electron integrals and τ 's are the elements of the transformation matrix \mathbb{T} .

The partitioning and calculation of the energy for the first order density is quite simple in comparison to the calculations required on the second order density. For this reason, both programs PART and PARTION were set up individually for each basis set. This is different from the second order density partitioning programs which are very general. The programs for the second order density partitioning must be general because of the tremendous amount of calculation that must be performed. The programs PART and PARTION consist of the calculation of numbers after the expansions of the first order density was performed by hand. PARTION also takes the one electron integrals as input and puts them out as output in a manner that is more appropriate for input to the

transformation programs. PART takes the one electron integrals after transformation and puts them in a form suitable for the general partitioning programs.

PAIRBOND is an uncomplicated program that has as input the bond order matrix. It then does the necessary expansions and calculations in a series of loops to calculate the pairbond order matrix and write it out on tape. The TRANSLATION program reads in the value of the pairbond order matrix and the integral values. For each element of the pairbond order matrix it searches for the corresponding two electron integral value. After it has found the correct integral value it multiplies that element of the pairbond order matrix by its corresponding integral value. It does this for every element of the pair bond order matrix and then it adds up the total value for all the elements and prints this out as the energy value for the second order density.

In order to illustrate how the partitioning programs work a discussion of the main partitioning program follows. This program does the partitioning of the pair density into the valence state and the first and second order interference parts.

$$\begin{aligned}\pi &= \pi^{VS} + \pi^I + \pi^{II} \\ \pi^{VS} &= \pi^0_{A,B}(A,B) + \pi'^1_{A,B}(A,B) + \pi''_{A,B}(A,B) \\ \pi^I &= \pi'_{A,\bar{A},B}(A\bar{A},B) + \pi''_{A\bar{A},B}(A\bar{A},B) \\ \pi^{II} &= \pi''_{A\bar{A},B\bar{B}}(A\bar{A},B\bar{B})\end{aligned}$$

A, B	subscript indicates	\sum_A	\sum_B
$A \bar{A}, B$	subscript indicates	$\sum_{A, \bar{A}}$	\sum_B
$A \bar{A}, B \bar{B}$	subscript indicates	$\sum_{A, \bar{A}}$	$\sum_{B, \bar{B}}$

Part 1 of this program consists of a main program and seven subroutines. The main program reads in the data and calls the seven subroutines. The first six subroutines and the fragment with which it corresponds are as follows:

<u>Subroutine</u>	<u>Fragment</u>
PAB	$\pi_{A,B}^0(A,B)$
PPAB	$\pi'_{A,B}(A,B)$
PPPAB	$\pi''_{A,B}(A,B)$
PAAB	$\pi'_{A\bar{A},B}(A\bar{A},B)$
PPAAB	$\pi''_{A\bar{A},B}(A\bar{A},B)$
PAABB	$\pi''_{A\bar{A},B\bar{B}}(A\bar{A},B\bar{B})$

Each of the first six subroutines will perform the necessary expansion for the particular fragment with which it is concerned. Each subroutine will thus consist of a summation of many terms. Each of these terms consists of two parts, an element of the pair bond order matrix and one or more integrals. For instance, the PAB subroutine performs the expansion for the term

$$\pi_{A,B}^0(A,B) = \sum_{A,a} \sum_{B,b} \sum_{\bar{A}\bar{a}} \sum_{\bar{B}\bar{b}} \Delta(Aa, \bar{A}\bar{a}) P(Aa\bar{A}\bar{a} | Bb\bar{B}\bar{b}) \Delta(Bb, \bar{B}\bar{b}) [AaAa | BbBb]$$

The $P(A_a \bar{A}_a | B_b \bar{B}_b)$ is an element of the pair bond order matrix. $\Delta(A_a, \bar{A}_a)$, $\Delta(B_b, \bar{B}_b)$ and $[A_a A_a | B_b B_b]$ are all integrals.

For the 1S-1S' basis set the following notation was used:

$$1SA = AA, 1SA' = AB, 1SB = AC, 1SB' = AD$$

The print out of the first term for this expansion in terms of these symbols looks like

$$(S(*, *) + 1.0)P(AAAA|AAAA)(S(*, *) + 1.0)(AAAA|AAAA)$$

This is simply the program notation for

$$P(1S_a 1S_a | 1S_a 1S_a) [1S_a 1S_a | 1S_a 1S_a] / r_{12}$$

where the overlap integrals for $S(1S_a, 1S_a)$ was equal to 1.0.

One obtains many terms similar to this until all of the summations have been performed. All of these terms were written out on tape. After this expansion was completed the program called in the second subroutine. This subroutine will obtain another series of terms that were written out on the same tape, after the previous results. This was done for all six expansions by the six subroutines.

One must realize that these subroutines have done the necessary summation of these various fragments, but the many terms that are obtained for each fragment in symbolic form must be transformed into numeric results. This can be done by a series of comparisons of the expansion terms with the pair bond order matrix and integrals which are read into the computer in a symbolic fashion with the appropriate number.

The subroutine called COMPAR reads in the complete pair bond

order matrix from a different tape. Each element of the pair bond order matrix is read in, in two forms. The first form is the particular element in a notation similar to that used in the previous subroutine. The second form is a numerical value associated with the element of the pair bond order matrix. The first expansion term is then read in and a series of Do loops then makes a comparison of the elements of the pair bond order matrix obtained from the expansion term with each of the elements of the total pair bond order matrix. This is done until the pair bond order element is found that is the same as the pair bond order term of the expansion. The value associated with the pair bond order matrix then replaces the pair bond order part of the expansion term and this number along with the integrals is written out on a third tape. The second expansion term is then read in and the process repeats itself until every expansion term from all six subroutines has had its pair bond order part replaced by the appropriate number. After this is completed at one internuclear distance, COMPAR will repeat this procedure at every internuclear distance. Once this is done, Part 1 of the program is finished.

In general, Part 2 of the program substitutes for every integral in the expansion terms the correct numerical value and then does the necessary calculations to obtain the total values for each fragment and also the total energy.

The main program for Part 2 reads in the input data, and also sends in the integral values obtained from the integral program in

the notation associated with the integral program. Since the notation used in the integral program is different from that used in the program, the main program changes the notation to make it uniform. The program then calls six subroutines, each subroutine corresponding with one of the six fragments that was calculated in Part 1.

Each of the subroutines reads in from tape the expansion elements that were written out on tape from Part 1. The expansion elements now consist of a number and symbols to indicate specific integrals. One is concerned with two types of integrals, overlap integrals and two electron integrals. The subroutine decided which type of integrals it is searching for and calls in one of two subroutines, depending on the type of integral which is needed.

These two subroutines then do the appropriate comparison in looking for the integral value that corresponds with the integral in the expansion term. Once the correct integral is found the value of the integral replaces the symbolic integral in the expansion. This is done for every integral in every expansion term. After this is completed the program does the appropriate numerical calculations in order to get the energy of each major fragment and also the sum of the energy of the major fragments.

APPENDIX B

DEFINITIONS OF TERMS USED IN TABLES

Tables III to XLIV are read vertically as a function of internuclear distance. The internuclear distances appear on Tables III to V and IX to XI, but not on the remaining tables. Let it be understood that the internuclear distances are implied although they do not appear on all the tables, with the exception of Tables I and II.

The orbitals are underlined to indicate that these are valence atom orbitals and not the original non-orthogonal Slater atomic orbitals.

All numbers in the tables are given in terms of atomic units.

R	Internuclear distance
E^{CLP}	Quasi-classical energies
E^{QC}	Quasi-classical energies
E^P	Promotion energies
$E^{SP_{A,B}}$	Total interatomic sharing penetration energy
E^{SP_A}	Total intra-atomic sharing penetration energy
E^I	Interference energies
E^{II}	Secondary interference energy
E^{P^Z}	Z = P, CL, QC or I indicates the contribution to the Z energy fragment by the first order density matrix.
E^{π^Z}	Z = P, CL, QC, SP, I or II indicates the contribution to the Z energy fragment by the second order density matrix.
$E^P_{A(A\bar{a},\bar{A}\bar{a})}$	Indicates the promotion energy of the $(A\bar{a},\bar{A}\bar{a})$ orbital pair

$(Aa, Bb)^{QC}$	Indicates the quasi-classical energy of the (Aa, Bb) orbital pair.
$E\pi^{SP}(AaAa \bar{A}\bar{a}\bar{A}\bar{a})$	Indicates the intra-atomic sharing penetration energy for the (Aa, $\bar{A}\bar{a}$) orbital pair.
$q^{SP}(Aa, Bb) (AaAa BbBb)$	Indicates the interatomic sharing penetration energy to the (Aa, Bb) orbital pair.
$P(Aa, Bb)E(Aa, Bb)$	Indicates the interference energy of the (Aa, Bb) orbital pair.
$P(Aa, Bb)U(Aa, Bb)$	Indicates the potential interference energy of the (Aa, Bb) orbital pair.
$P(Aa, Bb)\dagger(Aa, Bb)$	Indicates the kinetic interference energy of the (Aa, Bb) orbital pair.

APPENDIX C

This Appendix consists of graphs which illustrate the trends of the major energy fragments. The exact numerical results can be found in the Tables in Chapter III.

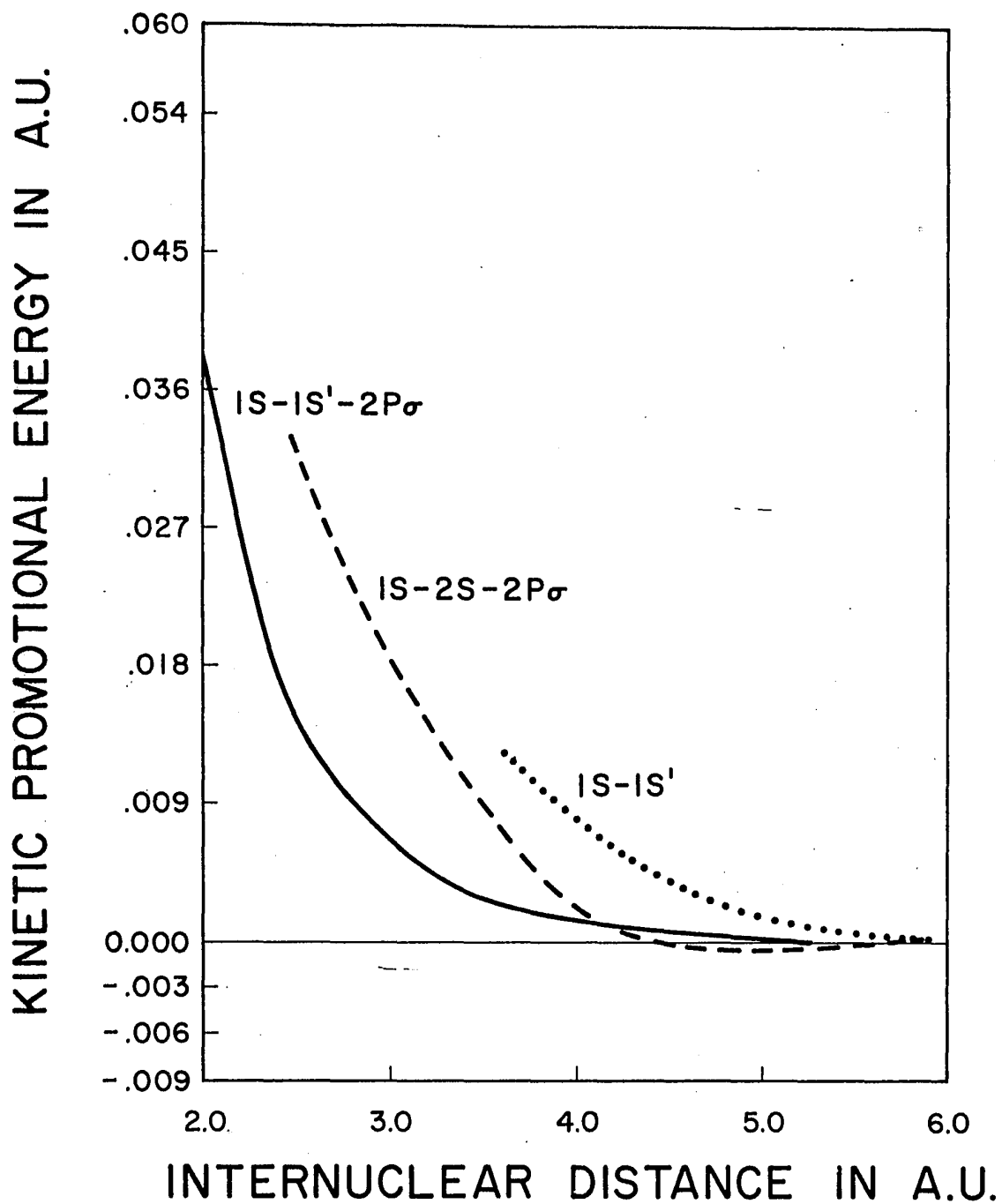


FIGURE 2. KINETIC PROMOTIONAL ENERGY AT LARGE INTERNUCLEAR DISTANCES

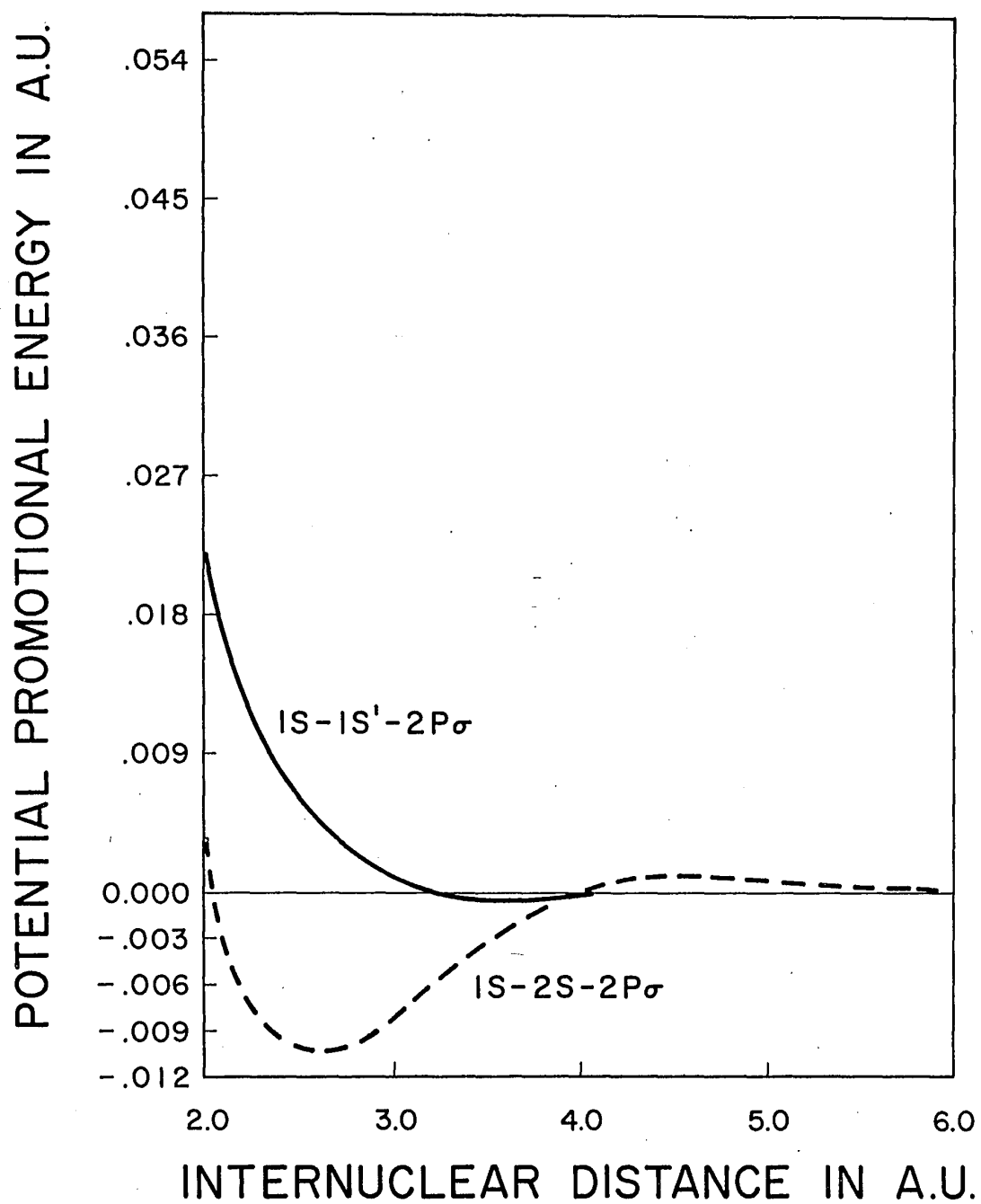


FIGURE 3. POTENTIAL PROMOTIONAL ENERGY AT LARGE INTERNUCLEAR DISTANCES

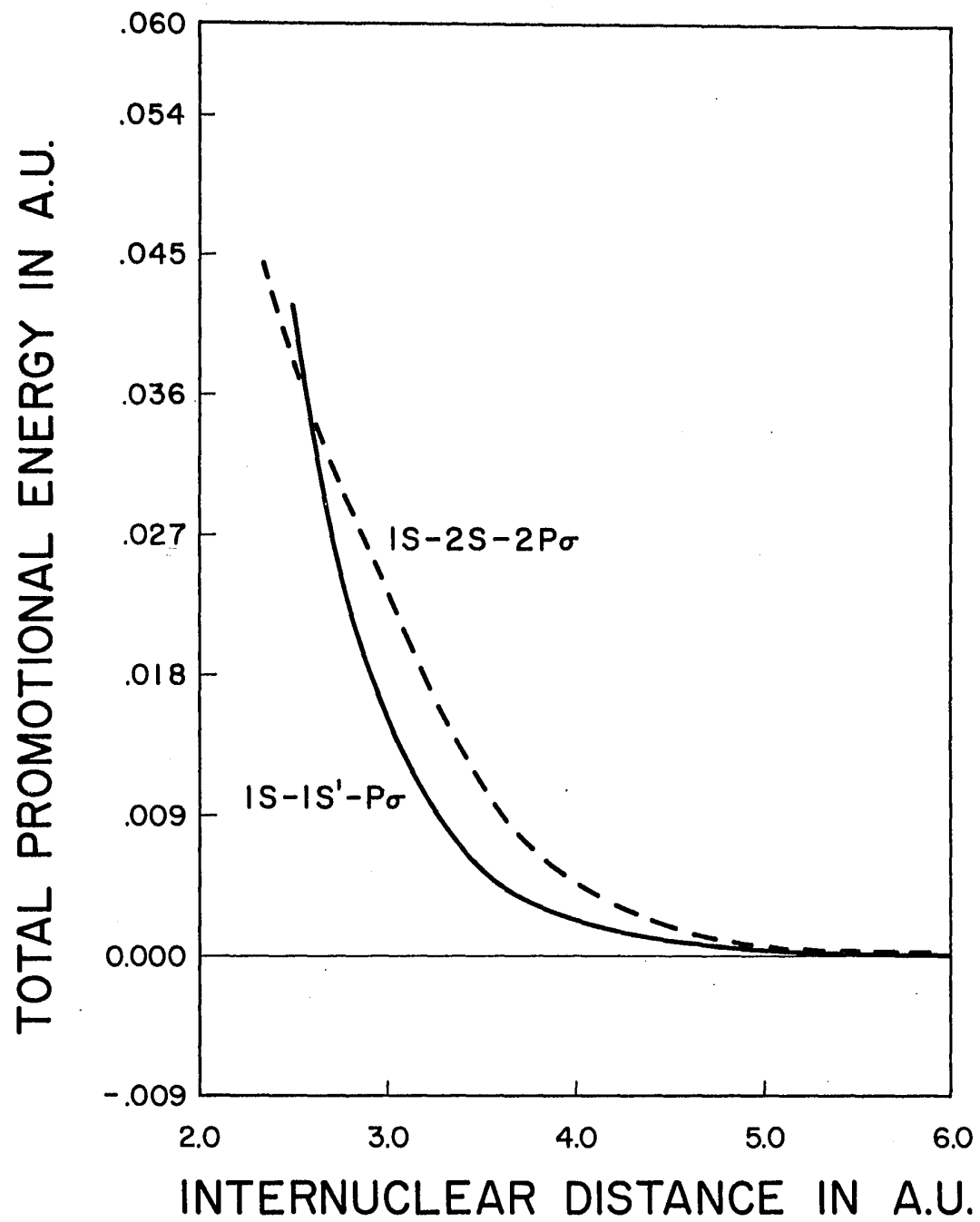


FIGURE 4. TOTAL PROMOTIONAL ENERGY AT LARGE INTERNUCLEAR DISTANCES

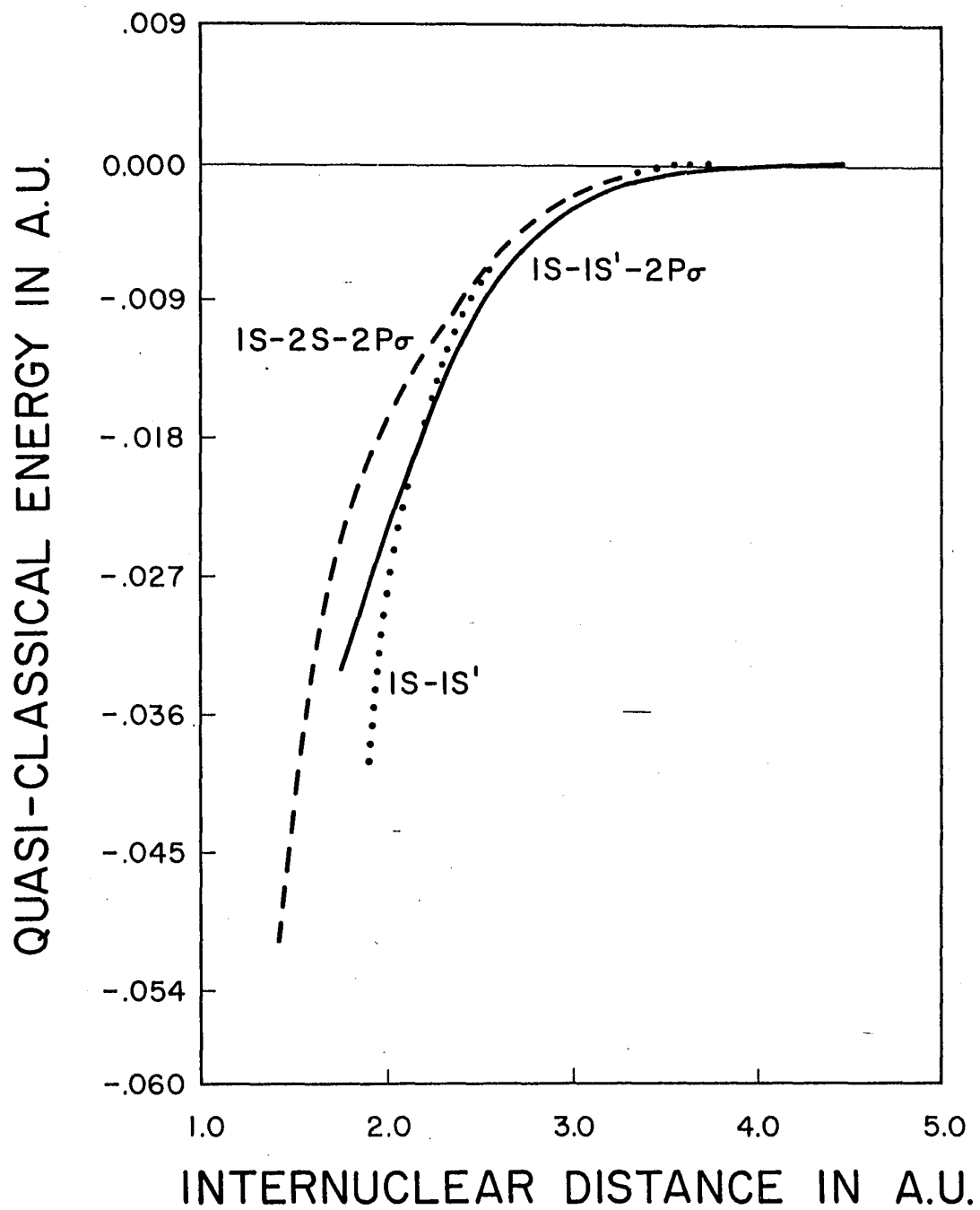


FIGURE 5. QUASI-CLASSICAL ENERGY AT LARGE INTERNUCLEAR DISTANCES

INTERATOMIC SHARING PENETRATION ENERGY IN A.U.

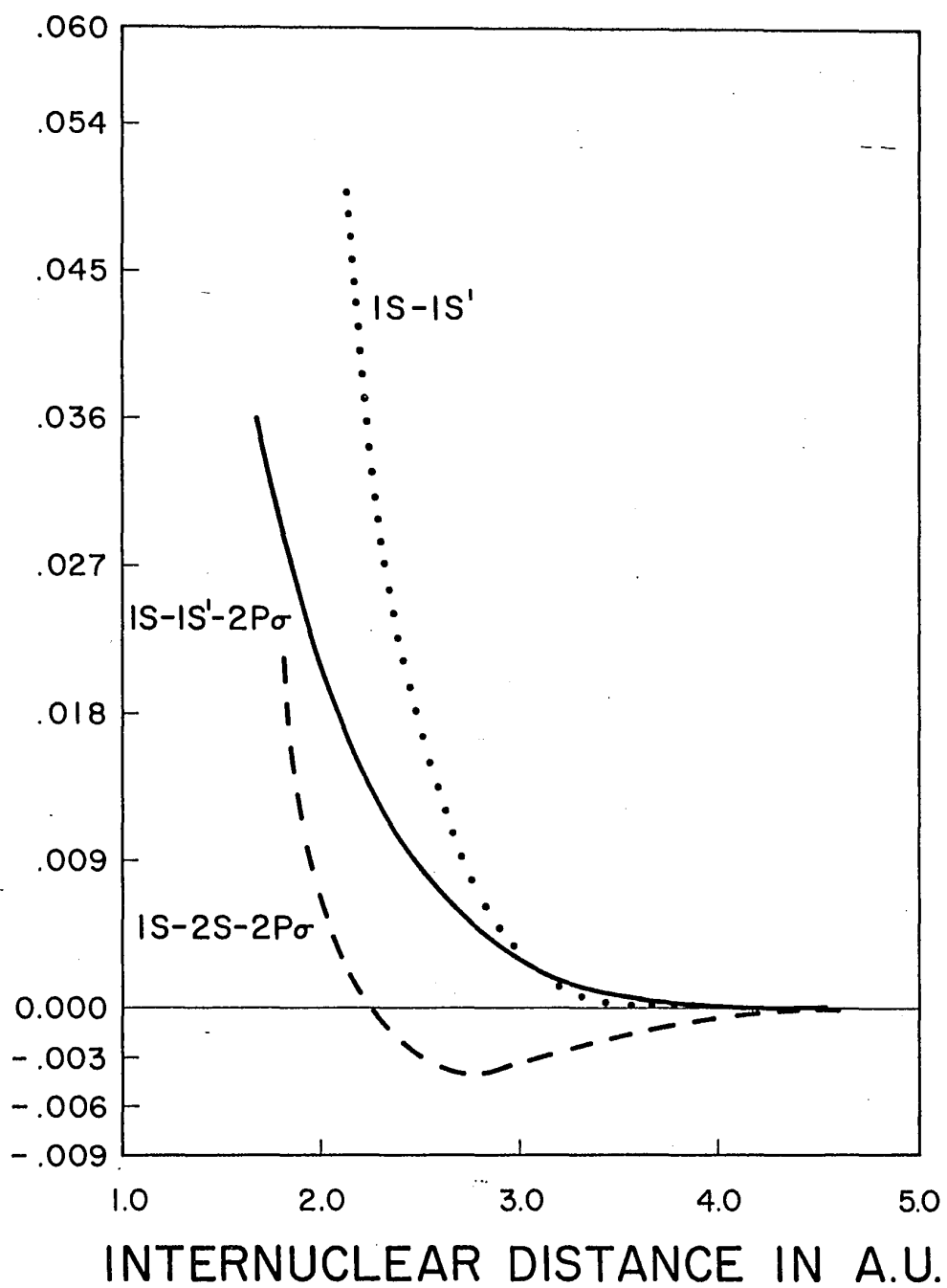


FIGURE 6. INTERATOMIC SHARING PENETRATION ENERGY AT LARGE INTERNUCLEAR DISTANCES

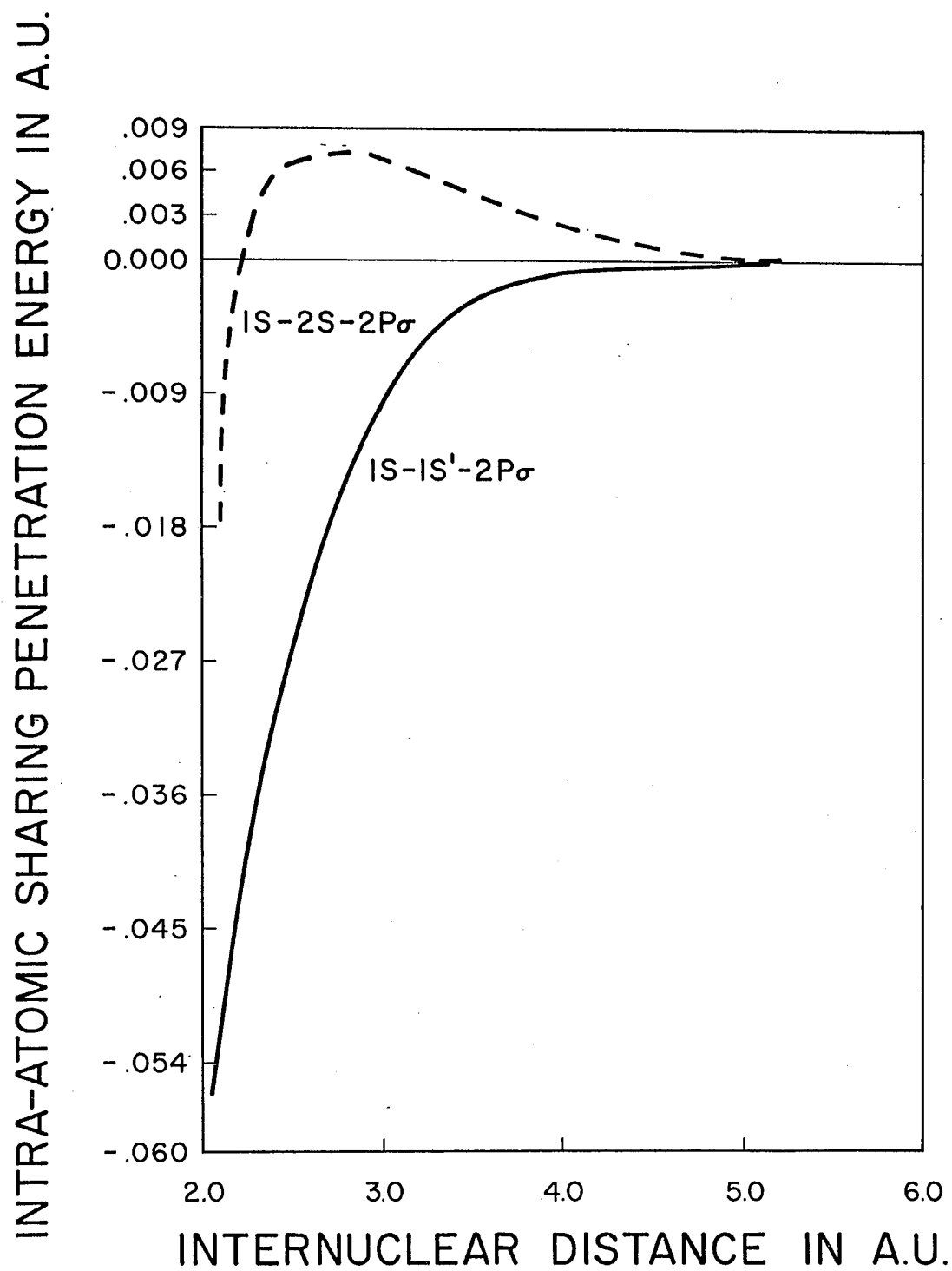


FIGURE 7. INTRA-ATOMIC SHARING PENETRATION ENERGY AT LARGE
INTERNUCLEAR DISTANCES

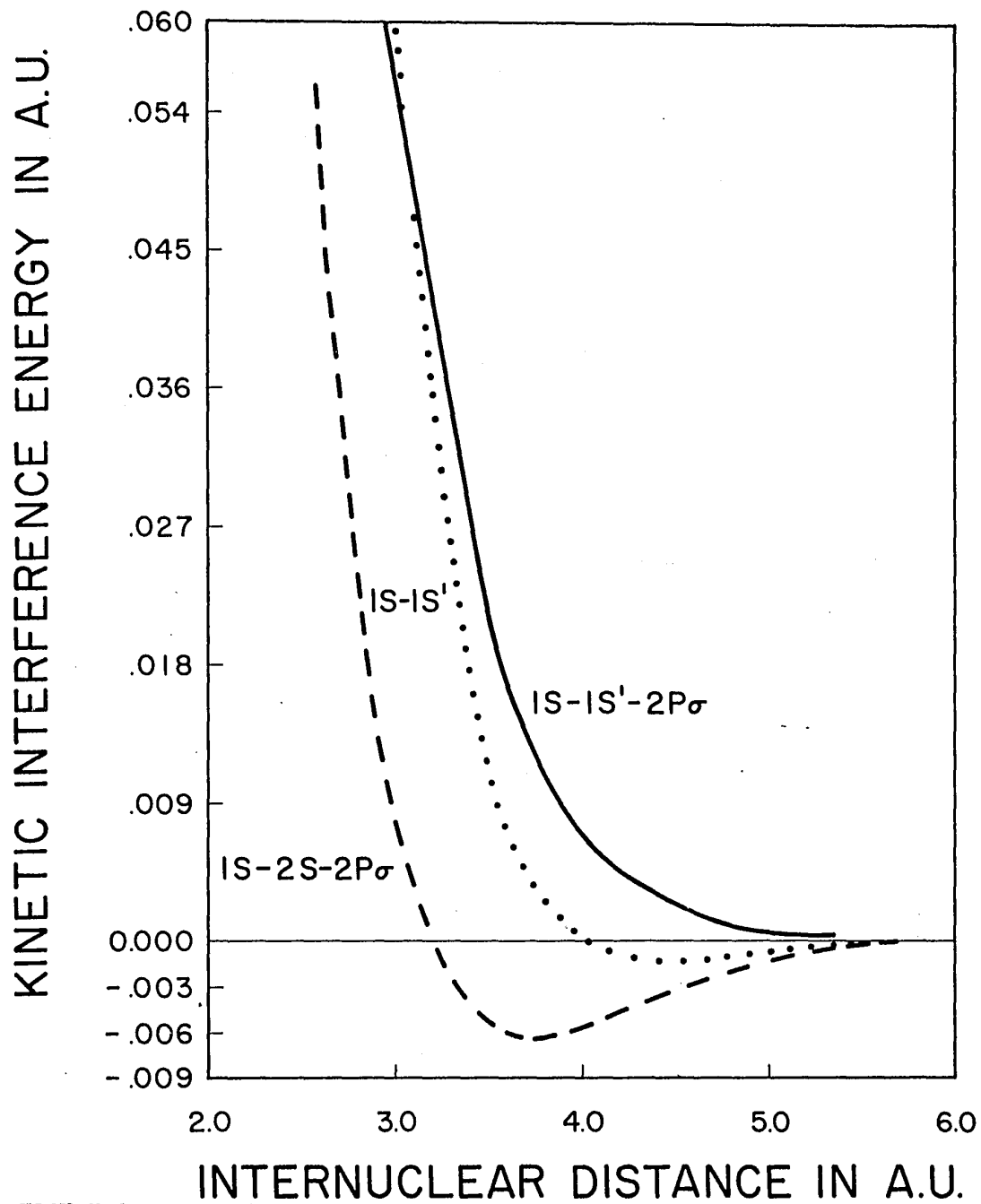


FIGURE 8. KINETIC INTERFERENCE ENERGY AT LARGE INTERNUCLEAR DISTANCES

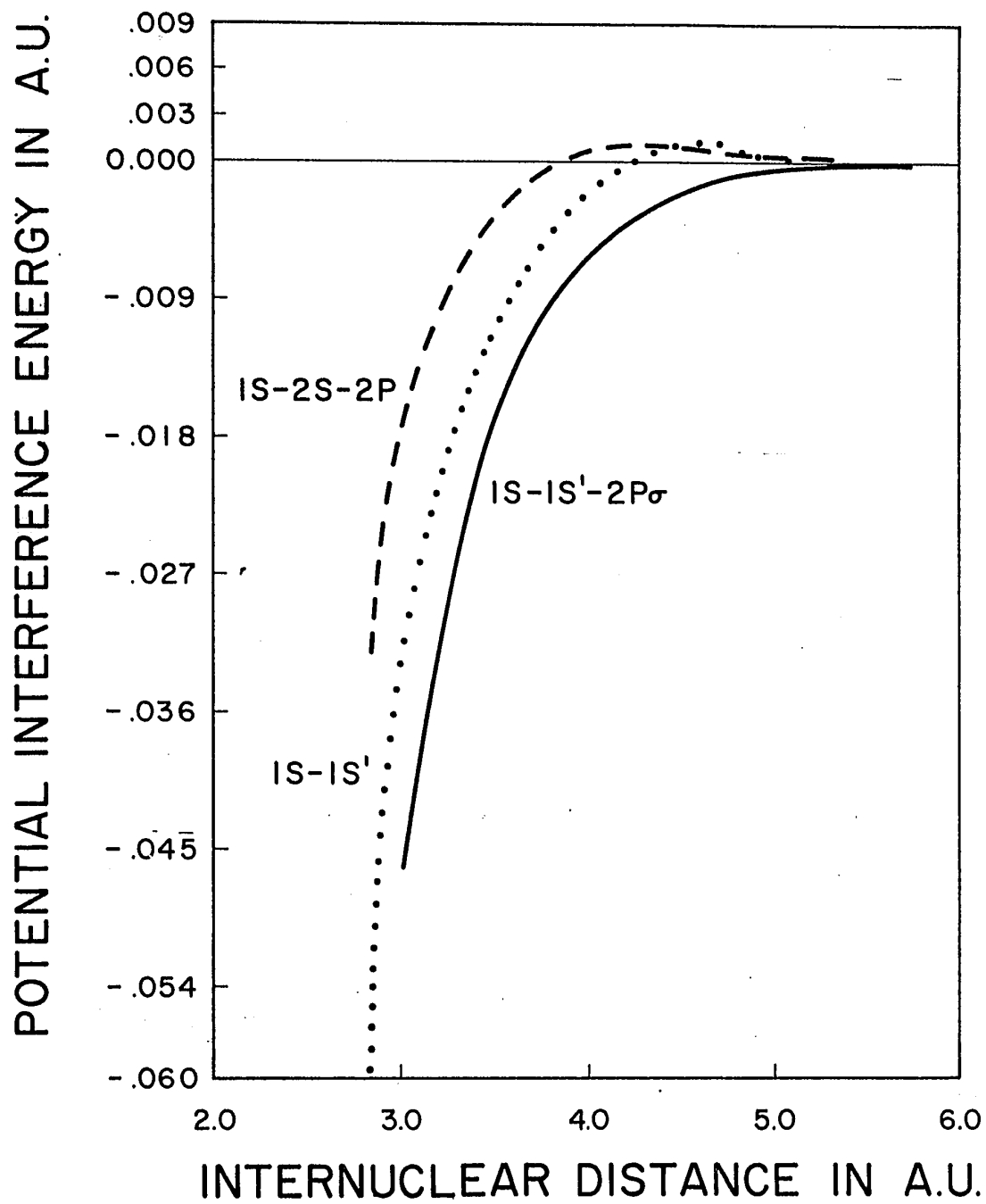


FIGURE 9. POTENTIAL INTERFERENCE ENERGY AT LARGE INTERNUCLEAR DISTANCES

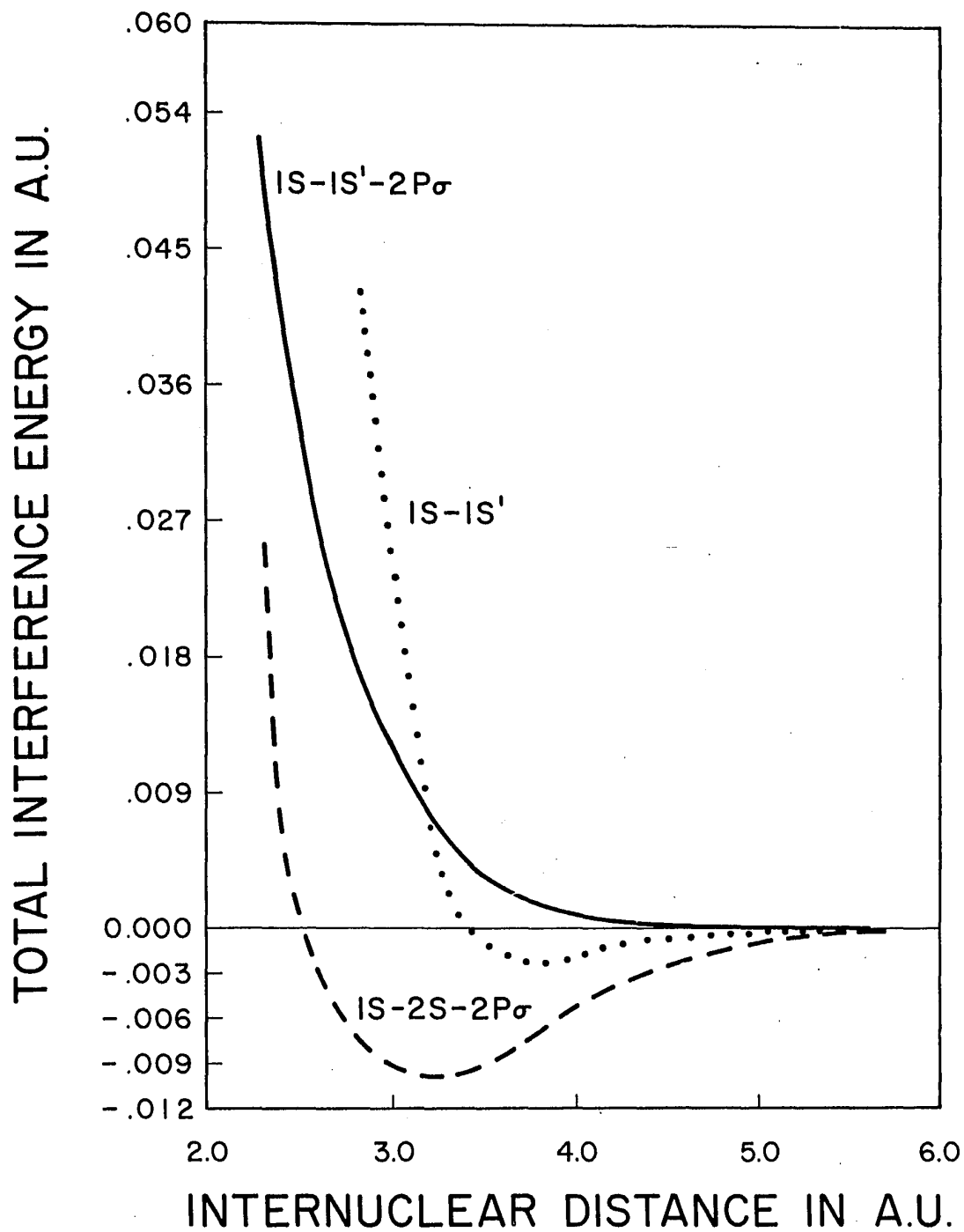


FIGURE 10. TOTAL INTERFERENCE ENERGY AT LARGE INTERNUCLEAR DISTANCES

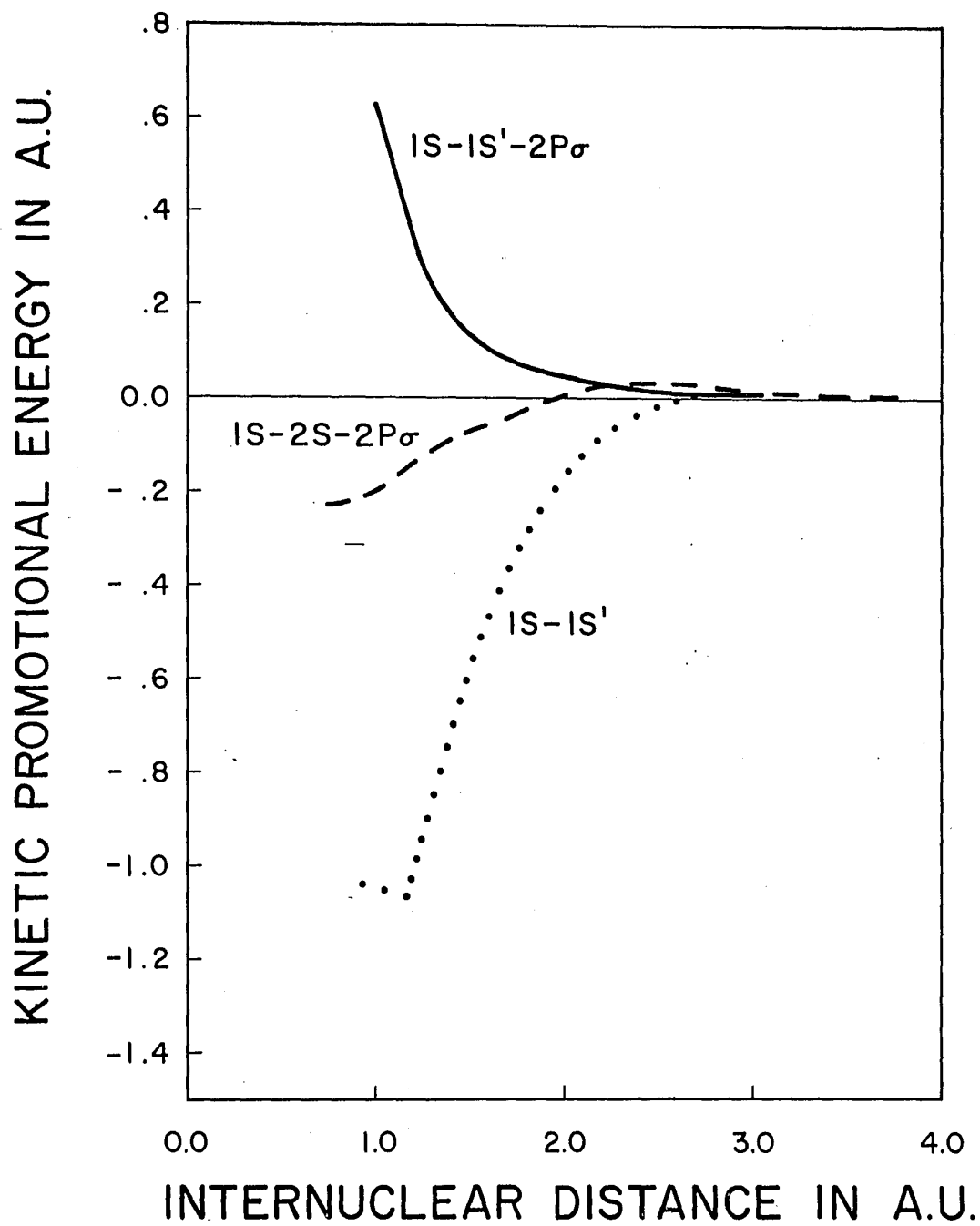


FIGURE 11. KINETIC PROMOTIONAL ENERGY AT CLOSE INTERNUCLEAR DISTANCES

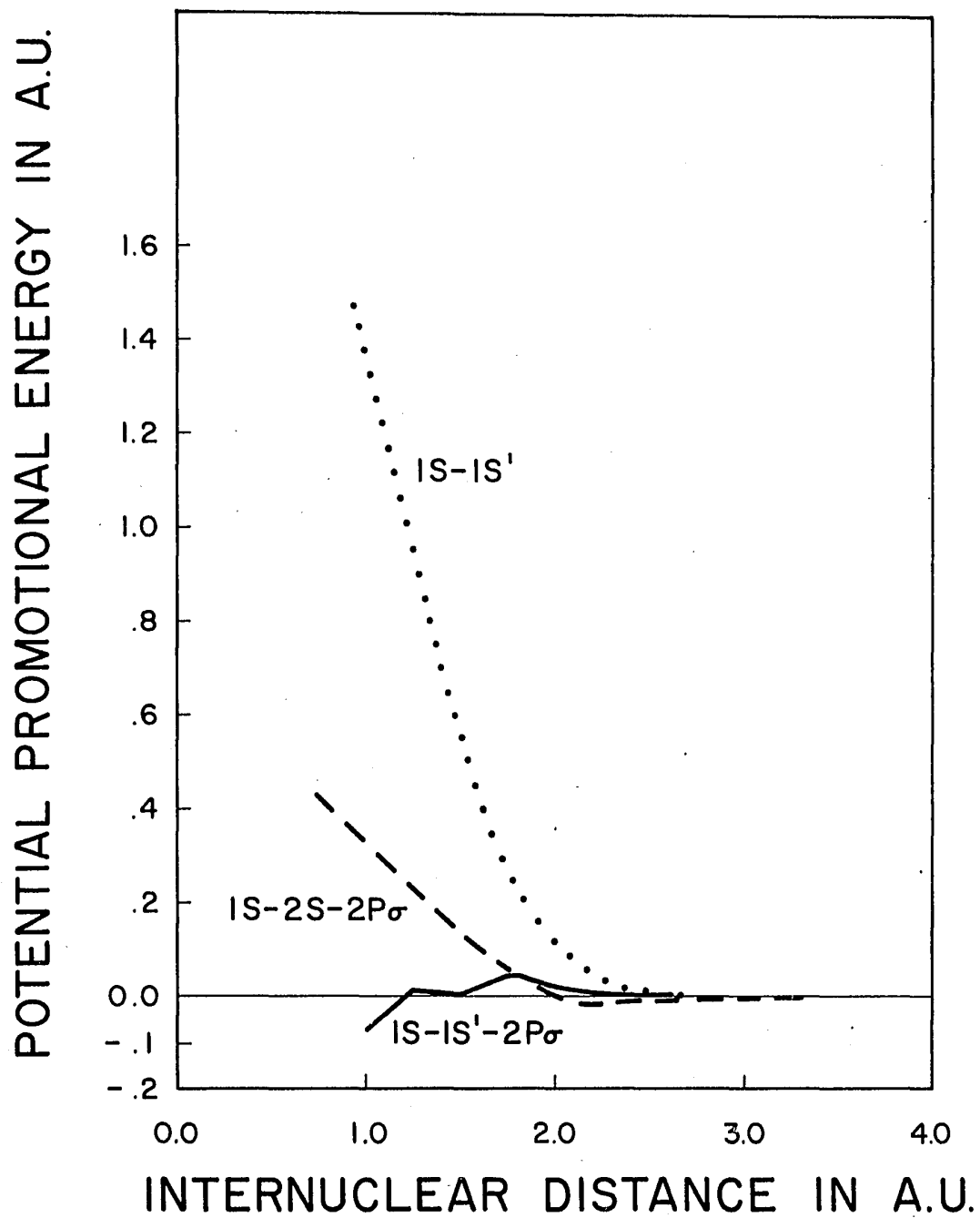


FIGURE 12. POTENTIAL PROMOTIONAL ENERGY AT CLOSE INTERNUCLEAR DISTANCES

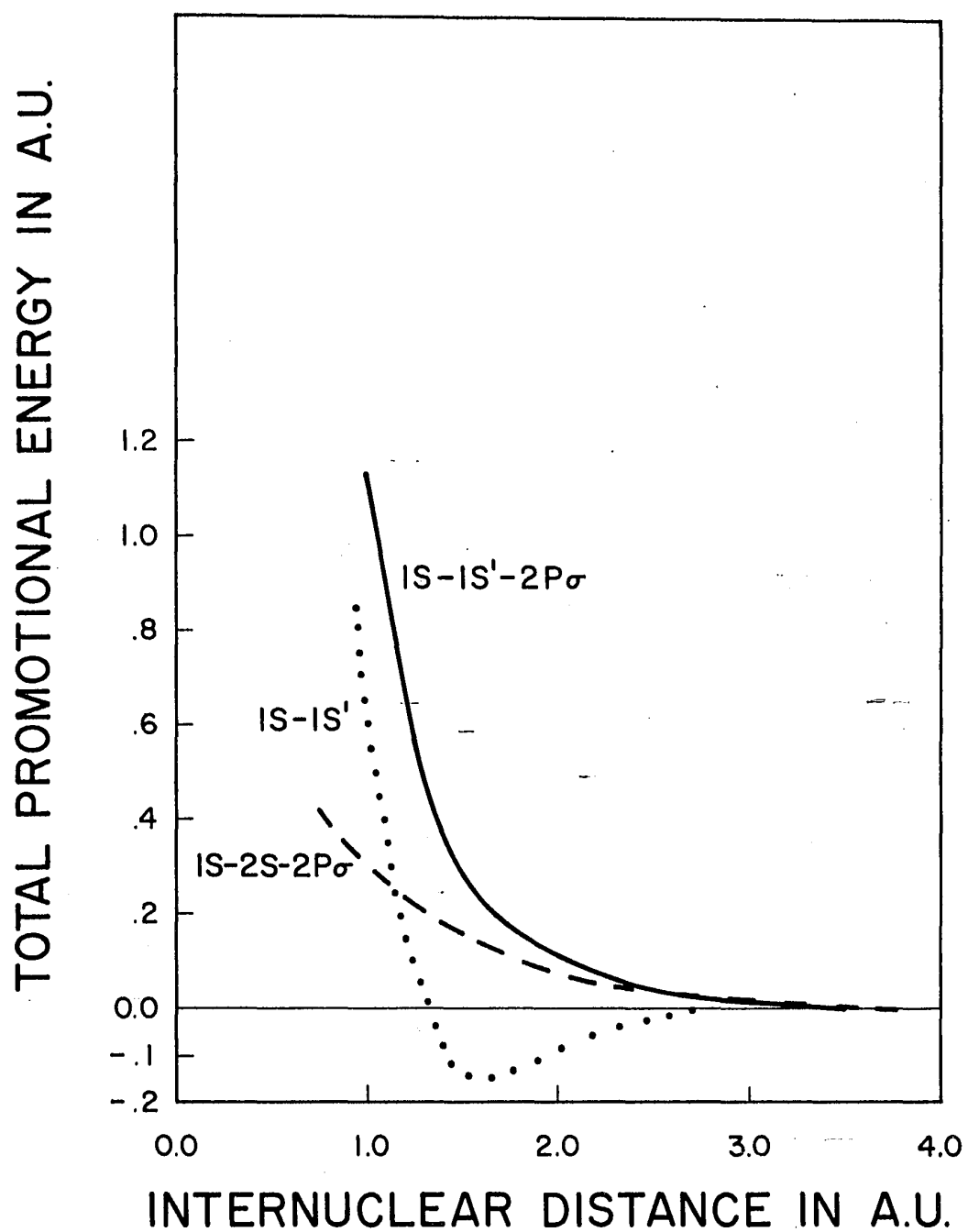


FIGURE 13. TOTAL PROMOTIONAL ENERGY AT CLOSE INTERNUCLEAR DISTANCES

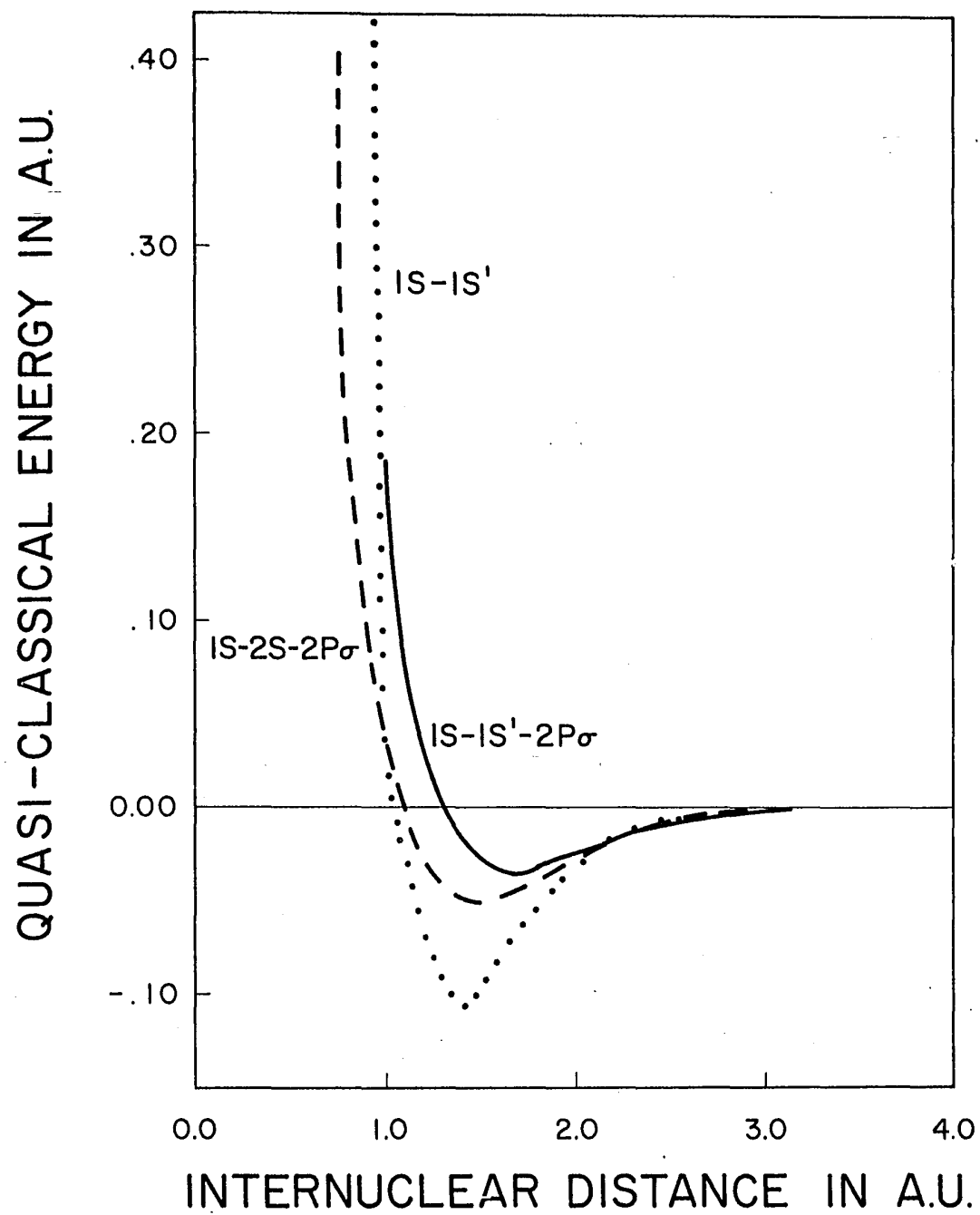


FIGURE 14. QUASI-CLASSICAL ENERGY AT CLOSE INTERNUCLEAR DISTANCES

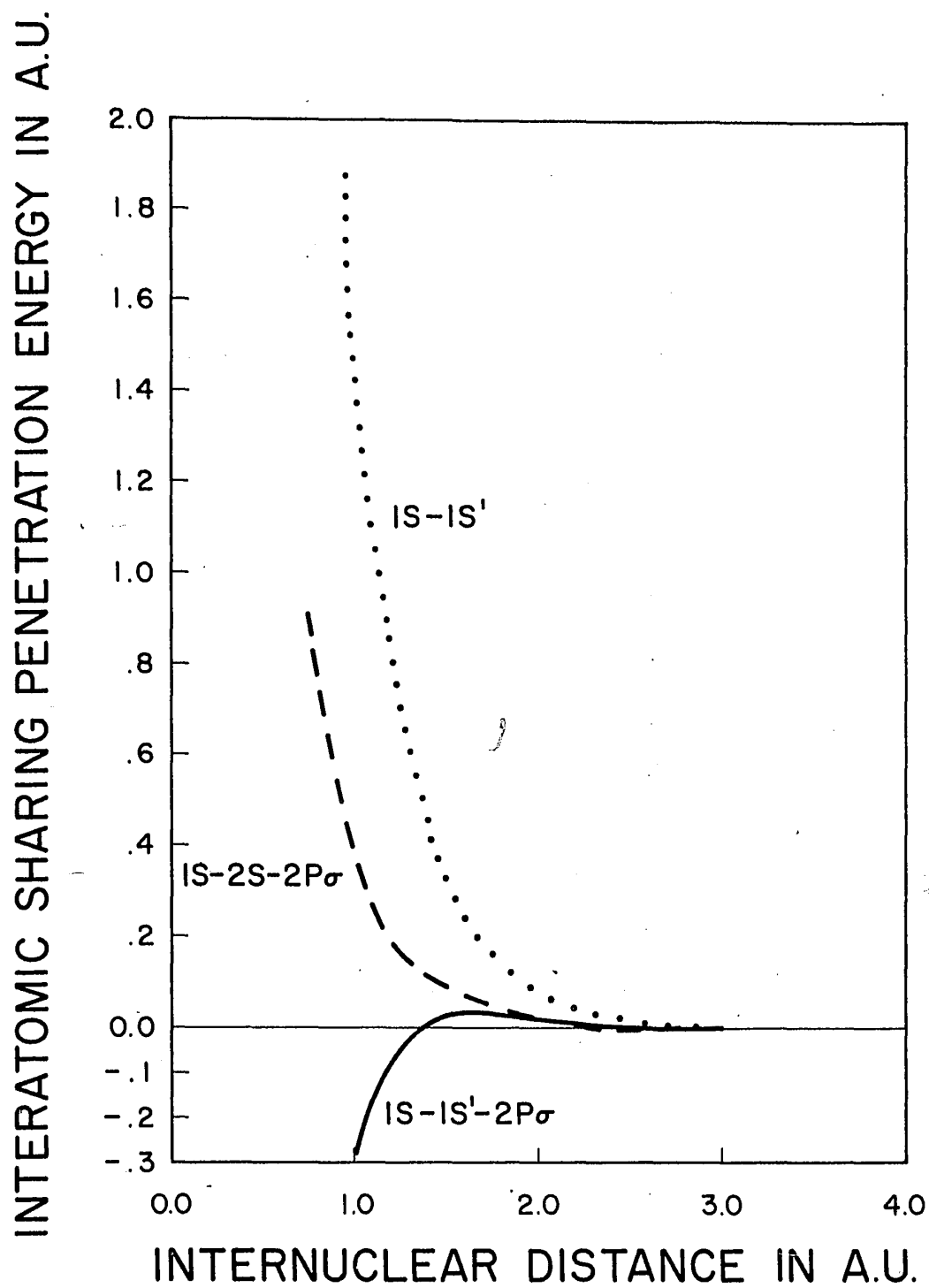


FIGURE 15. INTERATOMIC SHARING PENETRATION ENERGY AT CLOSE INTERNUCLEAR DISTANCES

INTRA-ATOMIC SHARING PENETRATION ENERGY IN A.U.

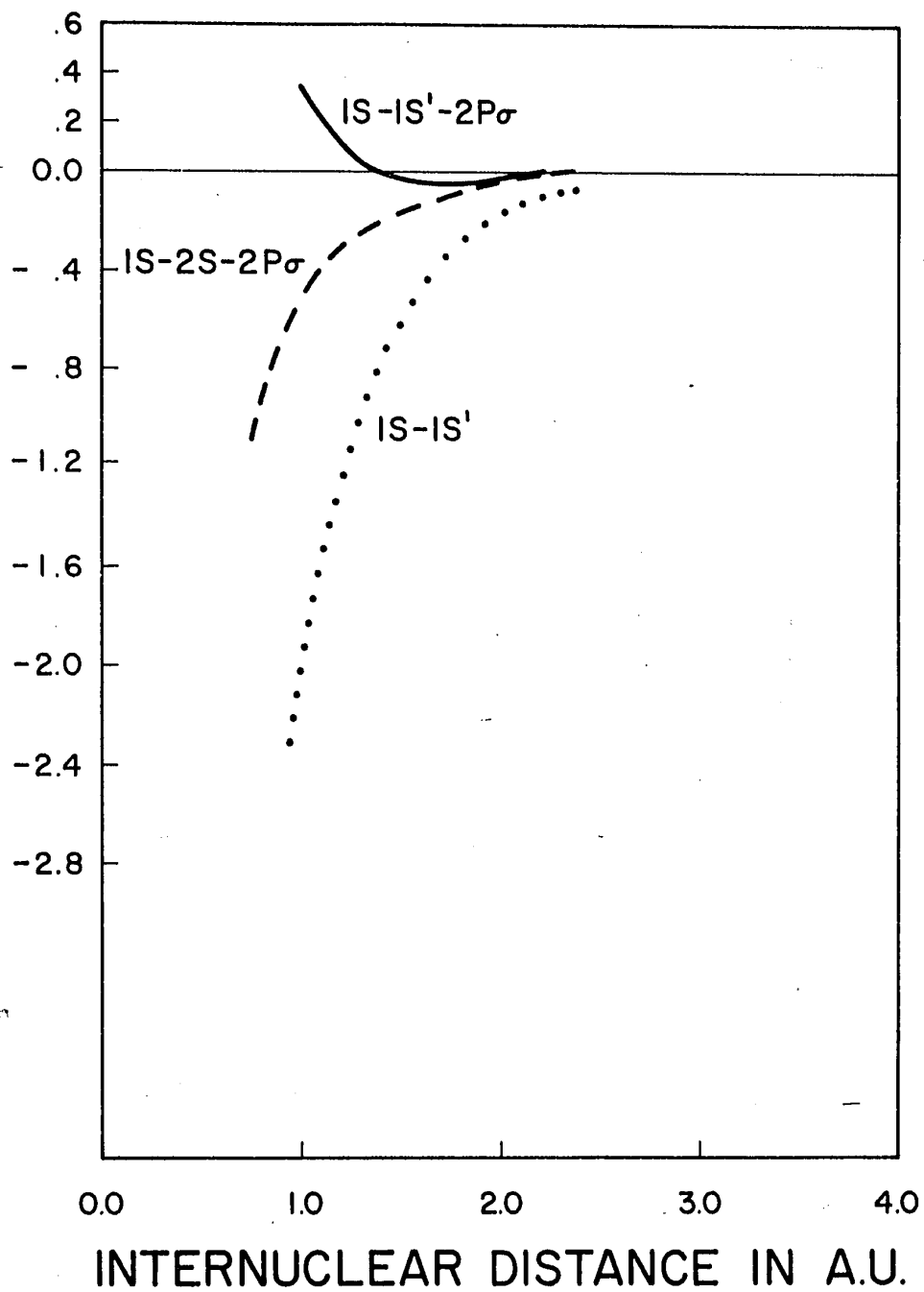


FIGURE 16. INTRA-ATOMIC SHARING PENETRATION ENERGY AT CLOSE INTERNUCLEAR DISTANCES

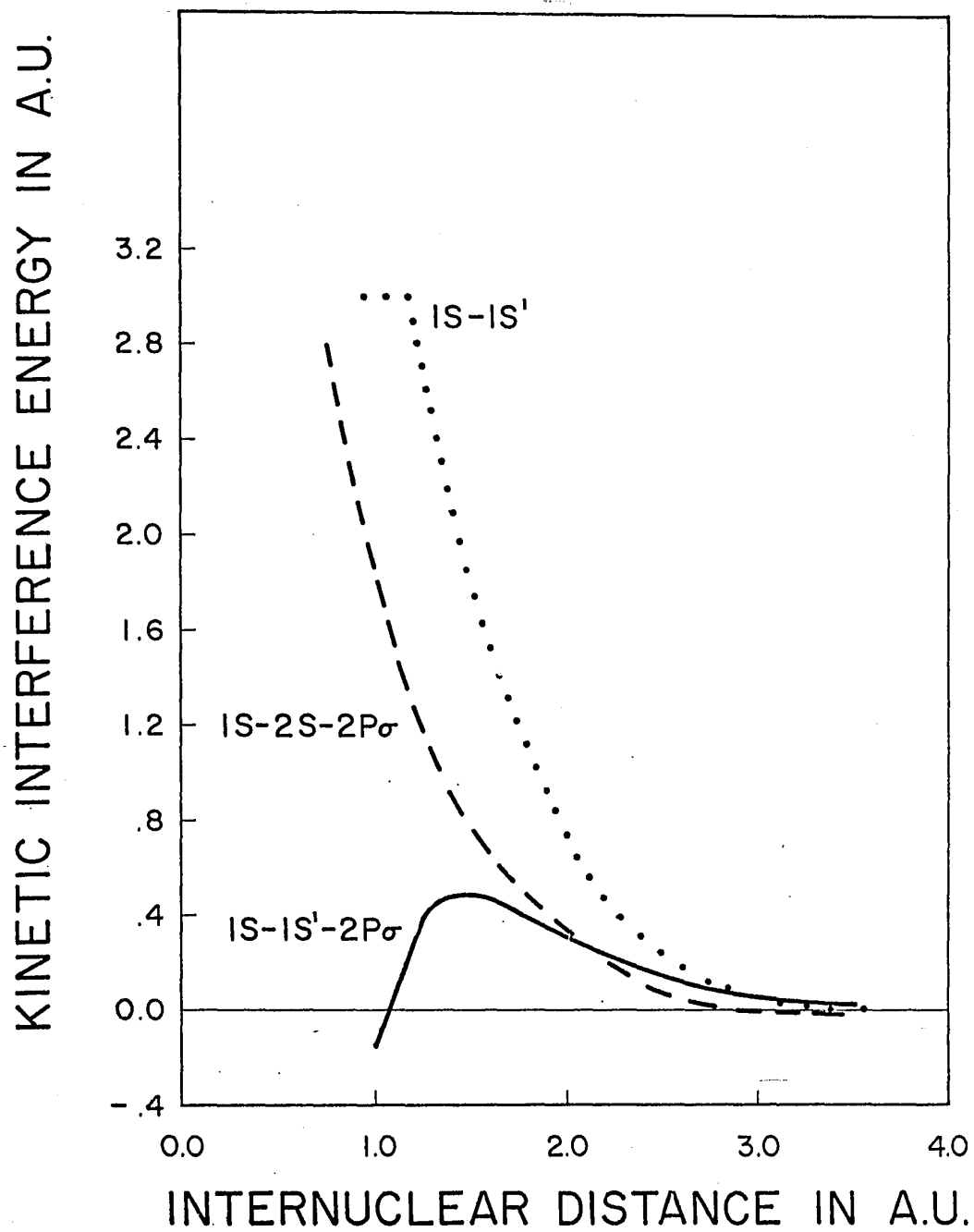


FIGURE 17. KINETIC INTERFERENCE ENERGY AT CLOSE INTERNUCLEAR DISTANCES

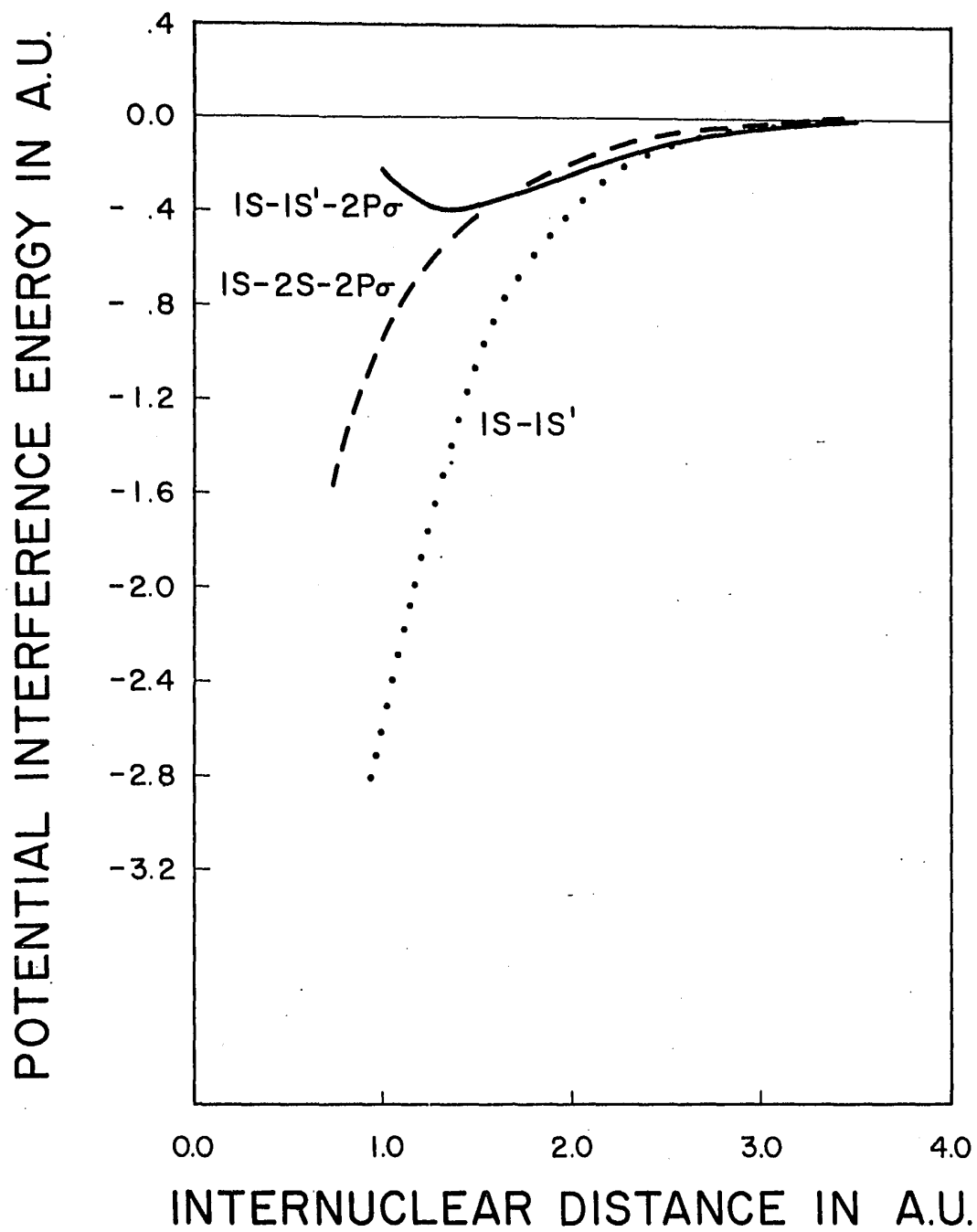


FIGURE 18. POTENTIAL INTERFERENCE ENERGY AT CLOSE INTERNUCLEAR DISTANCES

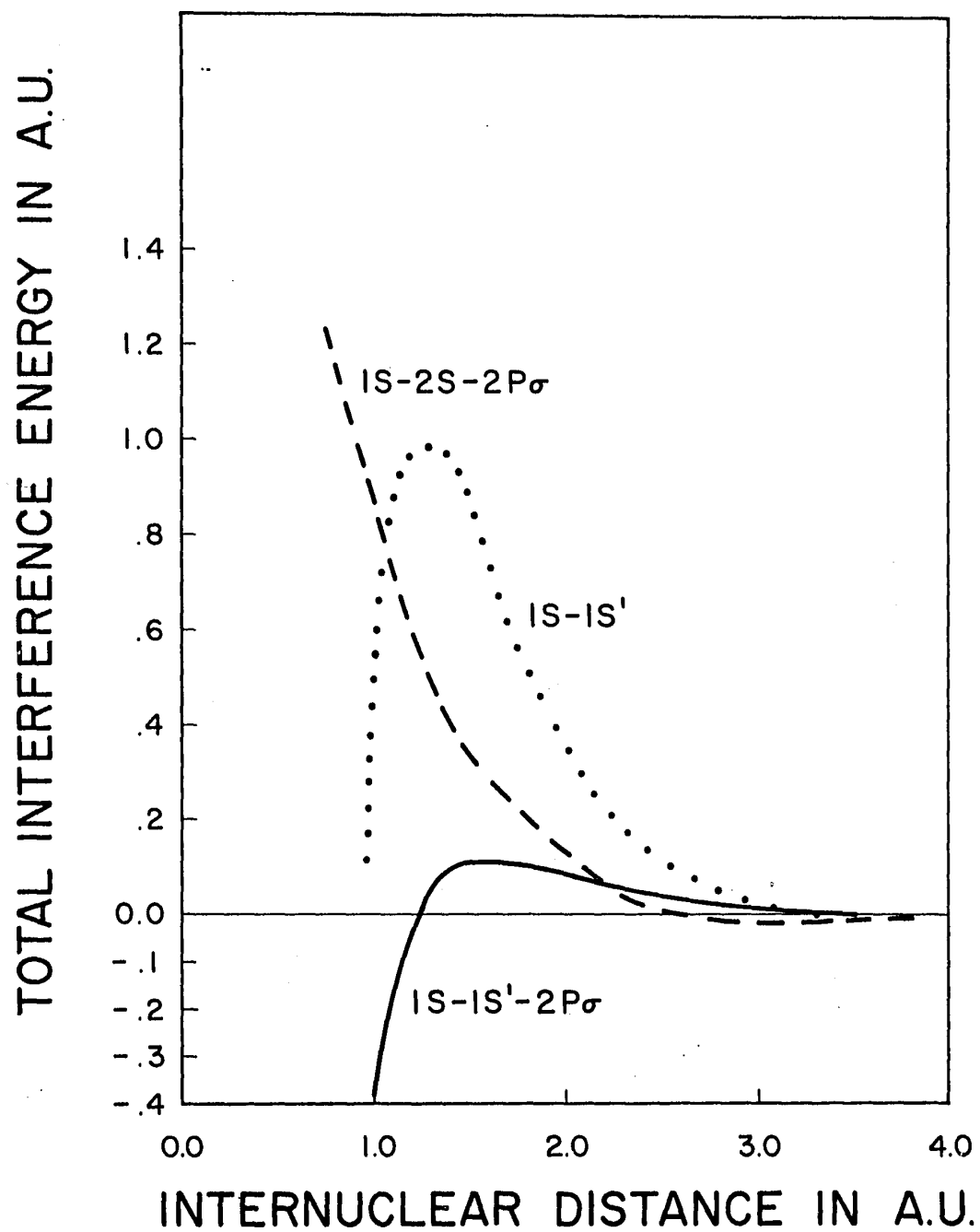


FIGURE 19. TOTAL INTERFERENCE ENERGY AT CLOSE INTERNUCLEAR DISTANCES

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