A STUDY OF THE BH MOLECULE

by

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Abstract

Antisymmetrized geminal product wavefunctions with several limited basis sets were calculated for the ground state of BH at R=2.329 atomic units. Extending these wavefunctions to include Kapuy's "one-electron transfer" configurations resulted in a lowering in energy of ~0.01 atomic units. In our case, this improvement accounts for more than 90% of that achieved by a full configuration-interaction wavefunction. A "contracted" double-zeta basis set yielded the best overall energy.

A 13-term, "split core", configuration-interaction wavefunction was developed and yielded an energy of -25.14769 atomic units. This wavefunction was then made to satisfy the virial theorem. Parr and White's method for one-point force constant calculation was applied to the scaled wavefunction with negative results.

A similar wavefunction was partially optimized at three internuclear distances followed by scaling with fixed R. Various parabolic models were used to fit the virial forces and energies corresponding to each R value. The force constants $k_e$ calculated from these models were usually very good and the effect of scaling was shown to be important. Parabolic expansions in 1/R gave better results than
parabolas in R, compared to a quintic model and to experimental values.
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CHAPTER I

INTRODUCTION

The general purpose of this work is to develop and, or, test several methods of seeking information on the electronic representation of molecular systems. All calculations involve the $^1\Sigma^+$ ground state of BH only, and a Born-Oppenheimer spinless Hamiltonian. Three main projects were undertaken: to confirm the usefulness of Kapuy's extended geminal theory [1, 2]; to perform a one-point calculation of $k_e$ (quadratic force constant) according to Parr and White [3]; and to seek a better approach to three-point calculation of $k_e$.

Kapuy applied his extended geminal theory to the π-electrons of trans-butadiene with good results [2]. Our application of extended geminal theory to BH at $R=2.329$ atomic units [4] treats all electrons and several limited basis sets are tried. Full configuration-interaction calculations were within reach and were used for comparison. The results in every case support those of Kapuy. In Chapter II the basic geminal theory is presented, while the extended geminal calculations are described in Chapter III.

Parr and White [3] developed a purely kinetic-energy perturbation at $R_e$ which is used to describe the molecular
potential energy function of diatomic molecules. Using their method and experimental data they calculate the force constants $k_e$ and $l_e$ for many diatomic molecules with excellent results. Since their method requires only the kinetic-energy matrix elements of a given wavefunction at $R_e$, they suggest that actual calculations be carried out using limited basis sets of atomic orbitals. In Chapter IV we begin by seeking a suitable wavefunction on which to apply Parr and White’s theory. Splitting the core orbital on boron into two orbitals for Ohno’s 13-term configuration-interaction wavefunction [5] gives a large improvement in energy. A perturbation scaling procedure is then applied to this “split core” wavefunction before force constants are calculated. The results are very poor and it is concluded that a much larger basis set is required.

In Chapter V a virial scaling procedure, similar to that used on LiH by Thorhallsson and Chong [6], is applied to a configuration-interaction wavefunction for BH at three internuclear distances. Various parabolic models in virial force and energy are investigated and values for the force constant $k_e$ are found to be good. Parabolic fits to scaled data are found to give better results than parabolic fits to unscaled data. Expansion of the diatomic molecular potential-energy function in $1/R$ rather than $R$ led to better results in most cases.
2-1 Concept

The Hartree-Fock energy is usually within about 1 percent of the experimental value. However, total energies are not of much use in themselves, one is usually interested in energy differences, such as the energy difference between two spectroscopic states. Unfortunately, these energy differences are often no larger than about 1 percent of the total energy of either state. Thus, there is a great interest in quantum-mechanical calculations which give better energies than the Hartree-Fock method. Correlation error in the Hartree-Fock method is due to the fact that coulombic interaction between pairs of electrons, especially electrons with antiparallel spins, is not properly accounted for. Electrons of parallel spins are kept apart by the antisymmetry principle and are thus described better than electrons of antiparallel spin. Electronic correlation is found to be of fundamental importance in chemical binding. All one-electron treatments used in molecular quantum mechanics are inherently too inaccurate. Electronic correlation is usually introduced by means of a superposition of configurations.
Although this method can lead to results of any desired accuracy, the wavefunctions become extremely complicated even for relatively simple molecules. Also, as the complexity of the wavefunction increases it becomes more and more difficult to assign any physical significance to the importance of any given configuration.

The electron pair is conceptually attractive to chemists. Molecular electronic structure is usually described in terms of inner shells, bond pairs and lone pairs. It has also been shown that the most important correlation effects are those involving a pair of electrons at a time [7, 8]. Therefore it seems reasonable to construct a method which uses two-electron functions instead of one-electron functions (orbitals). Such electron-pair functions could emphasize intrapair correlation and have little interpair correlation. Correlation can easily be admitted within each pair function. The natural tendency to make the pair functions correspond to distinct bond pairs, etc., allows the pair functions to be relatively separated and highly localized. For example two bonds at opposite ends of a long molecule or the sigma and pi bonds in a double bond, are cases in which, to a very good approximation, the spatial parts of the wavefunction describing different bonds do not overlap.

The high degree of invariance of bond properties from molecule to molecule suggests that pair-functions will be
transferable from one molecule to another to a good approximation [9]. Such transferability would greatly simplify the construction of good wavefunctions for large molecules, because one could use the results obtained from simpler systems. Development of good pair-functions for only a few of the more common bonds, such as C-C or C-H, would allow calculations on large systems to be carried out with much greater accuracy and simplicity than is possible at present.

The idea of pair functions seems to have been originated by Pauling [10]. Usually pair functions are called geminals. Actually, geminal theory (or "separated pair theory") is a particular case of the self-consistent group approach. (See, for example, Refs. [11, 12, 13].) An electron group function would describe a distinct many-electron group in a molecule, such as a \( \pi \)-electron system. In the geminal approach a molecular wavefunction is written as an antisymmetrized product of localized geminals. The separated nature of individual geminals is maintained by the fact that if all geminals are linearly expressed in terms of Slater determinants built from orthogonal one-electron spin orbitals, no spin orbital enters the description of more than one geminal. The effect of one geminal upon another is taken into account in a "self-consistent" manner, using an iterative method analogous to that employed in the standard SCF approach [14].
Computational Procedure

The following treatment is according to Parks and Parr [12].

The molecular wavefunction for a 2n-electron system is written
\[ \Psi = [\psi_a(1,2) \psi_b(3,4) \psi_c(5,6) \ldots \psi_m(2n-1,2n)], \]  
(2-1)
where each geminal \( \psi_i \) is an antisymmetric function of the space and spin coordinates of the two electrons involved. The square brackets represent the normalized partial antisymmetrization operator which generates a completely antisymmetric \( \Psi \) from the simple products of the individual antisymmetric \( \psi_i \).

The geminals are well behaved and normalized to unity:
\[ \int \int |\psi_i(1,2)|^2 d\tau_1 d\tau_2 = 1 \text{ for all } i. \]  
(2-2)

There is a complete set of spin orbitals which can be partitioned into subsets \( \{r_{a1}, r_{a2}, r_{a3}, \ldots; r_{b1}, r_{b2}, r_{b3}, \ldots; r_{i1}, r_{i2}, \ldots \} \) such that the geminal \( \psi_i \) may be expressed in terms of Slater determinants built from the subset i orbitals only, for all i. That is,
\[ \psi_i = C_{i1}\phi_{i1} + C_{i2}\phi_{i2} + \cdots, \]  
(2-3)
where the \( C_{ij} \) are constants and the \( \phi_{ij} \) are Slater determinants built from the spin orbitals in subset i.

Geminals defined in the above manner are mutually orthogonal,
\[ \int \psi_i^*(1,2) \psi_j(1,4) d\tau_1 = 0 \text{ for } i \neq j, \]  
(2-4)
and

\[ \iint \psi_i^*(1,2) \psi_j(1,2) d\tau_1 d\tau_2 = 0 \text{ for } i \neq j. \quad (2-5) \]

These orthogonality relations greatly simplify the calculations. Also, from the orthogonality relations and the normalization of individual geminals, it follows that the total wavefunction \( \Psi \) is normalized. Geminals, as defined so far, satisfy the conditions of separability for electron pairs.

The electronic Hamiltonian of a 2n-electron system of fixed nuclei \( a \) with charges \( Z_a e \) may be written

\[ H(1,2,\ldots,2n) = \sum_{\xi=1}^{2n} H_N(\xi) + 1/2 \sum_{\xi,\eta=1}^{2n} (e^2/r_{\xi\eta}), \quad (2-6) \]

where

\[ H_N(\xi) = T(\xi) + U_N(\xi), \quad (2-7) \]

\[ U_N(\xi) = -\sum_{a} (Z_a e^2/r_{a\xi}). \quad (2-8) \]

\( U_N(\xi) \) gives the potential energy of attraction between electron \( \xi \) and the bare nuclei and \( T(\xi) \) is the kinetic energy operator for electron \( \xi \) if the other electrons were absent.

For a system described by the wavefunction \( \Psi \), discussed earlier, the expectation value for the total electronic energy would be

\[ E = \sum_i I_i + 1/2 \sum_i \sum_{j \neq i} (J_{ij} - K_{ij}), \quad (2-9) \]

where the sums are over the distinct electron pairs \( a, b, \ldots, m \). The quantity \( I_i \) is the electronic energy electron pair \( i \) would have if the other pairs were absent.
The quantity $J_{ij}$ is the total Coulomb repulsion between electron pair $i$ and electron pair $j$:

$$J_{ij} = \iint \psi_i^*(1,2) \psi_j^*(3,4) \times \left[ \frac{e^2}{r_{13}} + \frac{e^2}{r_{14}} + \frac{e^2}{r_{23}} + \frac{e^2}{r_{24}} \right] \psi_i(1,2) \psi_j(3,4) \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4. \quad (2-12)$$

The $K_{ij}$ is a corresponding exchange repulsion:

$$K_{ij} = \iint \psi_i^*(1,2) \psi_j^*(3,4) \times \left[ \frac{e^2}{r_{13}} \psi_i(3,2) \psi_j(1,4) + \frac{e^2}{r_{14}} \psi_i(4,2) \psi_j(3,1) + \frac{e^2}{r_{23}} \psi_i(1,3) \psi_j(2,4) + \frac{e^2}{r_{24}} \psi_i(1,4) \psi_j(3,2) \right] \, d\tau_1 \, d\tau_2 \, d\tau_3 \, d\tau_4. \quad (2-13)$$

There are two methods for minimization of the total electronic energy of a system of geminals.

The first method starts with some specific set of orthonormal one-electron spin orbitals $\psi$ partitioned into nonoverlapping subsets $\psi_a, \psi_b, \ldots \psi_m$, in some specific way, then one seeks the best function $\Psi = [\psi_a \psi_b \ldots \psi_m]$. To do this, one fixes the form of all geminals except one, say $\psi_i$, and then minimizes energy of this geminal. This may be done because Eq. (2-9) can be rewritten

$$E = E_{m-i} + E_i, \quad (2-14)$$

where $E_{m-i}$ is the total electronic energy of all the geminal pairs but $i$, including their interactions. Then one selects
another geminal, and varies the new geminal until its energy is minimized. This procedure is repeated until no further improvements are obtained.

The second method is more general and starts by seeking the best set of one-electron functions and the best partitioning of them.

The first method is used in this work but no iterative procedure is required since there is only one geminal, the bond geminal, which is not of fixed form.

The actual working equations for geminal calculations, as presented by Parks and Parr [12], are in an operator representation. Klessinger and McWeeny [13] give an exactly equivalent treatment of geminal theory; only they use a density matrix approach. Kapuy [1] describes generalized geminal theory and also uses perturbation techniques to develop a method to extend geminal theory.

2-3 Application to BH

Our treatment of BH involved four basis sets, each set containing four orbitals. The orbitals are: \( k \) (1s on boron), \( s \) (2s on boron), \( \sigma (2p\sigma \text{ on boron}) \), and \( h \) (1s on hydrogen). In basis set I, the orbitals on boron are the single-zeta Slater-type orbitals of Clementi and Raimondi [15], but the orbital exponent \( \xi \) of \( h \) (also a single-zeta Slater-type orbital) is optimized to give the lowest energy for the
antisymmetrized geminal product (AGP) wavefunction. Basis set II is like set I, but \( s \) has been Schmidt orthogonalized to \( k \). In set III, \( \xi(h) = 1 \) and the orbitals on boron are "contractions" of the double-zeta set of Clementi \([16, 17]\), that is, with fixed linear coefficients \([17]\). Basis set IV is identical to set III with the exception of \( h \), the exponent of which is optimized as in set I.

Two hybrids were formed from \( s \) and \( a \):

\[
\underline{b} = as + (1-a^2)^{1/2} \underline{a},
\]

\[
\underline{n} = (1-a^2)^{1/2} s - a\underline{a},
\]

where the hybridization parameter \( a \) is also optimized to give the best energy for the AGP wavefunction*. The hybrid \( b \) is bonding and \( n \) is nonbonding.

Next, the orbitals \( k, b, n, \) and \( h \) are symmetrically orthonormalized into \( K, B, N \) and \( H \) respectively.

The geminals for the core and lone pairs are simply

\[
\psi_1 = (KK),
\]

\[
\psi_2 = (NN),
\]

where the symbols represent Slater determinants. The bond pair is described by:

\[
\psi_3 = C_1 (BB) + C_2 [ (BH) + (HB) ] + C_3 (HH).
\]

Now the AGP wavefunction is written

\[
\Psi_{AGP} = [\psi_1 (1,2) \psi_2 (3,4) \psi_3 (5,6)].
\]

* Optimization of \( a \) is carried out following any required optimization of the hydrogen 1s exponent.
The form of geminals $\psi_1$ and $\psi_2$ is already fixed and only geminal $\psi_3$ must be varied to minimize the energy, and therefore no iteration procedure is required. This particular AGP wavefunction is equivalent to a 3-term limited configuration-interaction (CI) wavefunction with the configurations

$$\phi_1 = (KKNNBH) + (KKNNHB),$$  \hspace{1cm} (2-21)

$$\phi_2 = (KKNNBB),$$  \hspace{1cm} (2-22)

$$\phi_3 = (KKNNHH).$$  \hspace{1cm} (2-23)

In order to describe the methods generally used in the actual calculations a sample geminal calculation is presented in Appendix I.

The results of calculations using $\psi_{AGP}$ are presented in Chapter III for comparison with the results of extended geminal and full CI calculations.
3-1 Kapuy's Theory

The best geminal wavefunction $\Psi_{BG}$ can be expressed as a linear combination of antisymmetrized geminal products $\psi_{ij...l}$

$$\Psi_{BG} = \sum_{i,j,...,l} A_{ij...l} \psi_{ij...l} \tag{3-1}$$

where the $A_{ij...l}$ are numerical coefficients and $\psi_{ij...l}$ contains a geminal from each subset, the geminal being designated by a subscript and the subset being designated by the position of the subscript. Our BH ground state wavefunction $\Psi_{AGP}$ could be written as $\Psi_{111}$ and if all of the subscripts were not equal to 1 it would represent some excited configuration of the system.

The wavefunction $\Psi_{BG}$ and the corresponding energy $E_{(BG)}$ could be determined by solving the secular equation

$$|H_{BG} - E_{(BG)}| = 0, \tag{3-2}$$

where $H_{BG}$ is the matrix of the total Hamiltonian operator in the $\psi_{ij...l}$ representation. Fortunately, due to the properties of the geminals, nonvanishing matrix elements occur only between geminal products $\psi_{ij...l}$ and $\psi'_{ij...l'}$ differing in not more than two subscripts.
Kapuy [1] introduces particle number operators $N^K$ in each of the $N$ subspaces (subsets)

$$N^K = \sum_{\alpha=1}^{2N} \sum_{\chi} \int \! d\alpha r_{K\chi}^{\alpha}(\alpha) r_{K\chi}^{\alpha*}(\alpha),$$  \hspace{1cm} (3-3)

where $r_{K\chi}$ is one of the orbitals used in the $K$th geminal. All such operators commute with each other and with the total particle number operator $\mathcal{N} = \sum_i N^K$. It can be shown that all antisymmetrized geminal products and any arbitrary linear combination of them are eigenfunctions of the $N^K$ with eigenvalues $N_1 = N_2 = \ldots = N_N = 2$. Since none of the $N^K$ commutes with the Hamiltonian $H$ which contains one- and two-particle operators, the $N^K$ and $H$ cannot have simultaneous eigenstates. The result is that $\Psi_{BG}$ cannot be the exact eigenstate of the system. It is just the best possible approximate wavefunction with the constraint that it be an eigenfunction of all of the $N^K$ which belong to the eigenvalue 2.

If the set $\{r\}$ is complete the total particle number operator $\mathcal{N}$ commutes with the Hamiltonian and they have simultaneous eigenstates. Any eigenstate of $H$ can be expanded in terms of all linearly independent eigenstates which belong to the eigenvalue $2N$. The set of the $\Psi_{ij \ldots 1}$ comprises only a part of these eigenstates of $\mathcal{N}$ and should be completed with its "orthogonal complement". Since two eigenstates of $\mathcal{N}$ corresponding to different partitions of the occupation numbers $N_1$, $N_2$, ... $N_N$ are automatically
orthogonal, the orthogonal complement can consist of all linearly independent eigenstates of $\mathcal{H}$ which correspond to all possible partitions of the set $N_1, N_2, \ldots, N_N$, $\sum N_K = 2N$, except for which $N_1 = N_2 = \ldots = N_N = 2$. The possible eigenvalues of $N_K$ are $0, 1, 2, \ldots, 2N$, when $n_K > 2N$; or $0, 1, 2, \ldots, n_K$, when $n_K \leq 2N$, where $n_K$ is the number of one-electron functions in subspace $K$. To a given partition there exist $\prod_{K} \binom{n_K}{N_K}$ linearly independent eigenstates of $\mathcal{H}$ which can be orthogonalized.

For suitable building blocks the group functions $\overline{\Psi}_{N_K k}$ are introduced and defined as

$$\overline{\Psi}_{N_K k} = (N_K!)^{-1/2} \sum_{P} (-1)^{P_P} \sum_{\chi, \lambda, \ldots, \nu} a_{\chi, \lambda, \ldots, \nu}^{K K} r_{KX}^{(1)} r_{KL}^{(2)} \ldots r_{K\nu}^{(N_K)}, \quad (3-4)$$

where $N_K = 0, 1, 2, \ldots, n_K$; $k = 1, 2, \ldots, \binom{n_K}{N_K}$; $\chi, \lambda, \ldots, \nu = 1, 2, \ldots, n_K$.

Group functions belonging to different subspaces are orthogonal in the strong sense and within every subspace normalized and mutually orthogonal in the usual sense:

$$\int \overline{\Psi}_{N_K k}^{*} \overline{\Psi}_{N_K l} d_1 d_2 \ldots d_{N_K} = \delta_{kl}. \quad (3-5)$$

The antisymmetrized product functions

$$\Psi_{i_1 j_1 \ldots 1}^{N_1 N_2 \ldots N_N} = \left( \frac{(N_1! N_2! \ldots N_N!}{(2N)!} \right)^{1/2} \sum_{P} (-1)^{P \Psi_{N_1 i_1}^{(1)} \Psi_{N_2 j_1} \ldots \Psi_{N_N l_1}}, \quad (3-6)$$

$i = 1, 2, \ldots, \binom{n_1}{N_1}$, $j = 1, 2, \ldots, \binom{n_2}{N_2}$, \ldots, $l = 1, 2, \ldots, \binom{n_N}{N_N}$, $\sum_{K} N_K = 2N$, containing one group function from each of the $N$ subspaces, form a complete set such that the exact wavefunction of the system $\Psi$ can be expanded in terms of them.
In order that all the states in Eq. (3-6) may be derived from the geminal ground state Kapuy introduces the ideas of "simple excitation" and "electron transfer excitation". Simple excitation substitutes one of the group functions in \( \Psi \) by another belonging to the same subspace: \( \Psi_{N K}^k + \Psi_{N K}^l, k \neq l \). Electron transfer excitation transfers one electron from one of the subspaces to another, changing two group functions simultaneously: \( \Psi_{N K}^k \Psi_{N L}^j + \Psi_{N K-1}^l \Psi_{N L+1}^l \).

Now the exact wavefunction \( \Psi \) can be written as a series of antisymmetrized product functions described in Eq. (3-6) with the terms grouped according to the minimum number of elementary excitations (simple + electron transfer) needed to reach the actual term from the ground state \( \Psi_{11...1} \)

\[
\Psi = c(0)\Psi_{11...1} + \Sigma_c(1)\Psi_{12} + \Sigma_c(2)\Psi_{13} + ... + \Sigma_c(2N-2)\Psi_{2N-2}.
\]

(3-7)

The \( \Psi_{N K}^k, N_K=1 \), and \( N_K>2 \) are still unspecified so far, they may be determined in principle, but for simplicity they are identified with the corresponding \( r_{Kx} \) and \( \psi_{Kk} (1, 2, ..., N_K) \) respectively, where

\[
\psi_{Kk}(1,2,...,N_K) = -(N_K!)^{1/2} \sum_p (-1)^p r_{Kx}(1)r_{Kx}(2)...r_{Kx}(N_K),
\]

(3-8)

and where \( x<\lambda<...<v \) and \( x, \lambda, ..., v=1, 2, ..., n_K \).

In Eq. (3-7) it is the terms of the first and second summations which may have nonvanishing matrix elements with \( \Psi_{11...1} \). A list of them is given below in which only the
factors being changed under excitation are shown. All configurations except those due to one simple excitation may have nonvanishing matrix elements with \( \Psi_{11...1} \).

First summation:

one simple excitation

\[ \Psi_{K}^{1}(1,2) + \Psi_{Kk}^{0}(1,2) \]

for all \( K \) and \( k \) (\( k \neq 1 \));  \( (3-9) \)

one electron transfer excitation

\[ \Psi_{K}^{1}(1,2) \Psi_{L}^{1}(3,4) + r_{KX}(1) \Psi_{L}^{1}(2,3,4), \]

for all \( K, L(K \neq L), X \) and 1;

second summation:

two simple excitations

\[ \Psi_{K}^{1}(1,2) \Psi_{L}^{1}(3,4) + \Psi_{Kk}^{0}(1,2) \Psi_{Ll}^{0}(3,4), \]

for all \( K < L, k \) and 1(\( k, l \neq 1 \));  \( (3-11) \)

one simple + one electron transfer excitations

\[ \Psi_{K}^{1}(1,2) \Psi_{L}^{1}(3,4) \Psi_{M}^{0}(5,6) + r_{KX}(1) \Psi_{L}^{1}(2,3,4) \Psi_{Mm}^{0}(5,6), \]

for all \( K, L, M(K \neq L \neq M), X, 1 \) and \( m(\neq 1) \);  \( (3-12) \)

two electron transfer excitations

\[ \Psi_{K}^{1}(1,2) \Psi_{L}^{1}(3,4) + \Psi_{L}^{1}(1,2,3,4), \]

for all \( K, L(K \neq L) \) and 1;  \( (3-13) \)

\[ \Psi_{K}^{1}(1,2) \Psi_{L}^{1}(3,4) \Psi_{M}^{0}(5,6) + \Psi_{Ll}^{1}(1,3,4) \Psi_{Mm}^{0}(2,5,6), \]

for all \( K, L < M(K \neq L, M), 1 \) and \( m \);  \( (3-14) \)
\[ \psi_{KL}^{(1,2)} \psi_{LM}^{(3,4)} \psi_{M1}^{(5,6)} + r_{KL}^{(1)} r_{LM}^{(3)} \psi_{MM}^{(2,4,5,6)}, \]
for all \( K<L, M(M \neq K, L), X, \lambda \) and \( m \);

\[ \psi_{JL}^{(1,2)} \psi_{K1}^{(3,4)} \psi_{LM}^{(5,6)} \psi_{M1}^{(7,8)} + r_{JL}^{(1)} r_{KL}^{(2,3,4)} r_{LM}^{(5)} \psi_{MM}^{(6,7,8)}, \]
for all \( J<L, K<M(J,L \neq K,M), X, k, \lambda \) and \( m \).

(3-15)

(3-16)

In practical calculations the set \( \{r\} \) obtained by determining the best possible geminal product \( \psi_{11 \ldots 1} \) is a finite one of course, but for systems with \( N \) large it is necessary to terminate the series or use perturbation theory. Kapuy used Rayleigh-Schrödinger perturbation theory up to second order in his work. His results show that the most important corrections to the energy of \( \psi_{11 \ldots 1} \) come from one-electron transfer configurations (Eq. (3-10)).

3-2 Kapuy's Application

Kapuy [2] applied his extended geminal theory to the \( \pi \)-electrons of trans-butadiene. The calculations involved the following approximations: \( \sigma-\pi \) separability, second order perturbation theory and a Goeppert-Mayer and Sklar Hamiltonian. Four SCF orbitals were used as a starting point and the same orbitals were used in a complete CI calculation by Nesbet the result of which is taken as a standard (100%) to which all results are referred. The antisymmetrized geminal product wavefunction accounts for 93.1% of the total correlation energy. The total contribution of all configurations due to two simple excitations is 1.9%. "One-electron
"One-electron transfer" configurations make an important contribution of 6.2% making the total correlation 101.3% of the standard value. The importance of "one-electron transfer" configurations confirms Kapuy's previous estimate [1] of the magnitude of their contribution in the case of the Be atom.

3-3 Application to BH

"One-electron transfer" configurations have three spin orbitals from one subset and one spin orbital from another subset. In our case the subsets are K, Ê; N, Ê; B, H, Ê, Ê. These configurations are included in the extended geminal calculations labelled G+1 (geminals plus one-electron transfer configurations). For our simple example, \( \Psi_{G+1} \) is equivalent to a 7-term limited CI wavefunction with the configurations \( \phi_1 \), \( \phi_2 \) and \( \phi_3 \) (see Eqs. (2-21) to (2-23)) plus

\[
\begin{align*}
\phi_4 &= (KKHHNB) + (KKHHBN), \\
\phi_5 &= (KKBBNH) + (KKBBHN), \\
\phi_6 &= (NBBBKH) + (NBBBHK), \\
\phi_7 &= (NNHHKB) + (NNHHBK).
\end{align*}
\]

Because of the small basis sets used, full CI calculations can be easily performed. In addition to \( \phi_1 \) to \( \phi_7 \), the only other configurations in \( \Psi_{CI} \) are

\[
\begin{align*}
\phi_8 &= (KKBBHH), \\
\phi_9 &= (BBBHHH), \\
\phi_{10} &= (BBHHKN) + (BBHHNK).
\end{align*}
\]
These correspond to "two-electron transfer" configurations in extended geminal terminology. In this case $\psi_{\text{CI}}$ is equivalent to $\psi_{G+1+2}$ (geminals plus one and two-electron transfer configurations).

The results of AGP, G+1 and full CI calculations with the four basis sets are summarized in Table I. The difference $E(\text{AGP}) - E(\text{CI})$ is the maximum improvement we obtain for the particular basis set; and $f$ represents the fraction of this maximum we obtain when we include only "one-electron transfer" configurations. The energies are in atomic units.

Although small basis sets and very little optimization have been used in order to save computer time, the CI energy from basis set IV is quite respectable compared to other calculations on BH. (See compendia by Cade and Huo [18] and by Krauss [19].) However, the main purpose of this work is not to obtain an excellent wavefunction and energy for the system but to support Kapuy's extended geminal theory with a better example. This is achieved by the fact that the fraction $f$ in Table I is over 0.9 with all four basis sets used. This seems to indicate that when one uses more extended basis sets and full CI becomes unmanageable the extended geminal wavefunction $\psi_{G+1}$, including only "one-electron transfer" configurations, may be sufficient.

The results in Table I show that the double-zeta basis set of Clementi [16, 17], even with contraction (fixed linear
TABLE I

GEMINAL CALCULATIONS

All calculations are carried out at an internuclear distance $R$ of 2.329 a.u. Energies are in atomic units.

<table>
<thead>
<tr>
<th>Basis Set</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi$(H)$^a$</td>
<td>1.26</td>
<td>1.31</td>
<td>(1.0)</td>
<td>1.362</td>
</tr>
<tr>
<td>$\alpha^a$</td>
<td>0.47</td>
<td>0.50</td>
<td>0.52</td>
<td>0.507</td>
</tr>
<tr>
<td>$E$(AGP)</td>
<td>-25.07331</td>
<td>-25.07601</td>
<td>-25.06673</td>
<td>-25.10324</td>
</tr>
<tr>
<td>$E$(G+1)</td>
<td>-25.08589</td>
<td>-25.08541</td>
<td>-25.08971</td>
<td>-25.11575</td>
</tr>
<tr>
<td>$E$(CI)</td>
<td>-25.08683</td>
<td>-25.08627</td>
<td>-25.09116</td>
<td>-25.11634</td>
</tr>
<tr>
<td>$f$</td>
<td>0.930</td>
<td>0.916</td>
<td>0.941</td>
<td>0.955</td>
</tr>
</tbody>
</table>

$E$ (Experimental) = -25.29 a.u.$^b$

$^a$ Optimized for minimum $E$(AGP), except the value in parentheses.

$^b$ Ref. [18].
coefficients [17]) and without further exponent optimization, is capable of giving significant improvement over a single-zeta basis set. For example, a full CI with an optimized single-zeta set gives an energy of -25.09034 a.u. for BH [20] compared to our -25.11634 a.u. This means that, for some systems, contracted double-zeta basis sets may be more economical as well as capable of giving lower energies.
CHAPTER IV

ONE-POINT CALCULATION OF \( k_e \)

4-1 Theory

The approach used is that of Parr and White [3] with some of the terms redefined.

The Born-Oppenheimer electronic Hamiltonian for a diatomic molecule may be written in the form

\[
H = R^{-2} \hat{t} + R^{-1} \hat{v}, \tag{4-1}
\]

where \( R \) is the internuclear distance, and \( \hat{t} \) and \( \hat{v} \) are the kinetic-energy and potential-energy operators expressed in confocal elliptic coordinates, for unit \( R \). The terms \( \hat{t} \) and \( \hat{v} \) are independent of \( R \) and the eigenvalue \( W(R) \) of the equation

\[
H\Psi = W(R)\Psi \tag{4-2}
\]

is the conventional potential-energy function for the nuclear motion of the molecule as a function of \( R \). At the equilibrium internuclear separation the Hamiltonian will be

\[
H_e = \hat{T}_e + \hat{V}_e, \tag{4-3}
\]

where \( \hat{T}_e = \hat{t}/R_e^2 \) and \( \hat{V}_e = \hat{v}/R_e \). If we introduce the parameter

\[
\mu = R_e/R = 1 + \beta \tag{4-4}
\]

we may write Eq. (4-1) as

\[
H = \mu^2 \hat{T}_e + \mu \hat{V}_e. \tag{4-5}
\]
Dividing Eq. (4-5) by \( \mu \) we obtain
\[
\frac{H}{\mu} = \mu \hat{T}_e + \hat{V}_e ,
\]
and substituting \( 1 + \beta \) for \( \mu \) gives
\[
\frac{H}{1 + \beta} = \hat{T}_e + \beta \hat{T}_e + \hat{V}_e = H_e + \beta \hat{T}_e .
\]
According to Eq. (4-7) we may write
\[
\frac{W(R)}{1 + \beta} = W(R_e) + \beta \hat{T}_e ,
\]
where \( T_e \) is the matrix of kinetic-energy operator. Taking \( \beta \) as a perturbation parameter we expand \( \psi \) and \( \frac{W(R)}{1 + \beta} \) as a power series in \( \beta \),
\[
\psi = \psi_e + \beta \psi^{(1)} + \beta^2 \psi^{(2)} + \ldots ,
\]
\[
\frac{W(R)}{1 + \beta} = \omega_0 + \omega_1 \beta + \omega_2 \beta^2 + \ldots .
\]
Then
\[
W(R) = \omega_0 + \sum_{k=1}^{\infty} (\omega_{k-1} + \omega_k) \beta^k ,
\]
and
\[
\omega_0 = W(R_e) .
\]
Taking the derivative of \( W(R) \) with respect to \( R \),
\[
W'(R) = \frac{dW(R)}{dR} = \frac{dW(R)}{d\beta} \cdot \frac{d\beta}{dR} = (-R_e/R_e^2) \sum_{k=1}^{\infty} k \beta^{k-1} (\omega_{k-1} + \omega_k) ,
\]
we find that when \( R = R_e \),
\[
W'(R_e) = (-R_e/R_e^2) (\omega_0 + \omega_1) = 0 ,
\]
for any wavefunction satisfying the virial theorem; therefore, \( \omega_0 = -\omega_1 \).

The force constants predicted by this potential are
\[
k_e = \left( \frac{d^2W(R)/dR^2}{R_e^2} \right) = \frac{2(\omega_1 + \omega_2)}{R_e^2} ,
\]
\[ l_e = \left( \frac{d^3W(R)}{dR^3} \right) = \frac{-6(\omega_2+\omega_3) - 12(\omega_1+\omega_2)}{R_e^3}, \]
\[ m_e = \left( \frac{d^4W(R)}{dR^4} \right), \]
\[ = \frac{[24(\omega_3+\omega_4) - 12R_e^3 l_e - 36R_e^2 k_e]}{R_e^4}. \] (4-16)

To calculate these force constants we require the kinetic-energy matrix at \( R_e \) only.

4-2 Scaling Procedure Used to Obtain \( \Psi \) at \( R_e \)

The scaling is performed to make the wavefunction satisfy the virial theorem. In doing so we obtain \( R_e \) and therefore can calculate \( T_e \). Also, when the wavefunction satisfies the virial theorem, Eq. (4-14) is satisfied and it is then possible to calculate the force constants.

Let us represent the unscaled and scaled wavefunction of an \( N \)-electron diatomic molecule by,

\[ \Psi = \Psi(\xi_1, \xi_2, \ldots, \xi_N, R) \] (4-18)

and

\[ \Psi_\eta = \Psi(\eta\xi_1, \eta\xi_2, \ldots, \eta\xi_N, \eta R), \] (4-19)

where \( \xi_i \) is the position vector of the \( i \)th electron, \( R \) is the internuclear distance and \( \eta \) is some arbitrary scale factor.

For diatomic molecules in the Born-Oppenheimer approximation the total energy associated with the scaled wavefunction \( \Psi_\eta \) is [21]

\[ E(\eta, R) = \eta^2 T(1, \eta R) + \eta V(1, \eta R), \] (4-20)
where

\[ T(l, nR) = T(\Sigma_1, \Sigma_2, \ldots, \Sigma_N, nR), \quad (4-21) \]

and

\[ V(l, nR) = V(\Sigma_1, \Sigma_2, \ldots, \Sigma_N, nR). \quad (4-22) \]

If we let our unsealed wavefunction have an internuclear distance \( \rho = nR \), then the unsealed energy is

\[ E = T(l, \rho) + V(l, \rho), \quad (4-23) \]

while the scaled energy is

\[ E^\eta = \eta^2 T(1, \rho) + \eta V(1, \rho). \quad (4-24) \]

Let \( \eta = 1 + \lambda \), then

\[ E_\eta = T(1, \rho) + 2\lambda T(1, \rho) + \lambda^2 T(1, \rho) + V(1, \rho) + \lambda V(1, \rho) \]
\[ = E + \lambda [2T(1, \rho) + V(1, \rho)] + \lambda^2 T(1, \rho) \]
\[ = E + \lambda [E + T(1, \rho) + \lambda^2 T(1, \rho)] \]
\[ = (1+\lambda)E + \lambda (1+\lambda)T(1, \rho). \quad (4-25) \]

Therefore

\[ E_\eta/(1+\lambda) = E + \lambda T(1, \rho). \quad (4-26) \]

Expanding \( E_\eta/(1+\lambda) \) and \( \psi \) as a power series in \( \lambda \),

\[ \psi = \psi(0) + \lambda \psi(1) + \lambda^2 \psi(2) \ldots, \quad (4-27) \]
\[ E_\eta/(1+\lambda) = W_0 + \lambda W_1 + \lambda^2 W_2 \ldots, \quad (4-28) \]

the scaled energy can be written

\[ E_\eta = W_0 + \lambda (W_0 + W_1) + \lambda^2 (W_1 + W_2) + \ldots \quad (4-29) \]

At \( \lambda = 0 \), \( W_0 = E \) so

\[ E_\eta = E + \sum_{k=1}^{\infty} \lambda^k (W_{k-1} + W_k). \quad (4-30) \]

To obtain optimum scaling

\[ \frac{dE_\eta}{d\lambda} = 0. \quad (4-31) \]
Therefore
\[ \sum_{k=1}^{\infty} k \lambda^{k-1} (w_{k-1} + w_k) = 0. \] (4-32)

Optimum \( \lambda \) is obtained by varying \( \lambda \) until Eq. (4-32) is satisfied. Now we can generate the scaled wavefunction and from it the kinetic-energy matrix at \( R_e \).

4-3 Selection of Wavefunction

The extended basis set of Ohno [5] was selected as a starting point. The Slater type orbitals used are: on boron \((1s_B, 2s, 2p_0, 2p_+ \text{ and } 2p_-)\) and on hydrogen \((1s_H)\). All configurations, in which two electrons are retained in the \(1s_B\) orbital, are taken into account to obtain a thirteen-term set of basic functions. (See Table II.) To check computer input a CI calculation identical to Ohno's case (b) [5], except that our \(1s_H\) orbital was not orthogonalized, was performed and the same ground state energy resulted. (See Table III.)

Using the total electronic energy as a criterion, the orbital exponents were optimized through one cycle in the following order: \(1s_B, 2s, 2p_0, (2p_+)\) and \(1s_H\). For resulting orbital exponents and energy see Table IV. The improvement in energy on going from \(E_{(OHNO)}\) to \(E_{(OPT)}\) is not too significant.

Now the \(1s\) orbital on boron was split into two orbitals, \(1s_B'\) and \(1s_B''\). The number of Slater determinants in each term
TABLE II

13-TERM WAVEFUNCTION

The $1s_B^{-1}s_B^{-1}$ core, occurring in all the determinants, is omitted in the following description.

1. \( (2s \overline{2s} p_0 \overline{p_0}) \)
2. \( (2s \overline{2s} 1s_H \overline{1s_H}) \)
3. \( (p_0 \overline{p_0} 1s_H \overline{1s_H}) \)
4. \( (2s \overline{2s} p_0 \overline{1s_H}) + (2s \overline{2s} 1s_H \overline{p_0}) \)
5. \( (p_0 \overline{p_0} 2s \overline{1s_H}) + (p_0 \overline{p_0} 1s_H \overline{2s}) \)
6. \( (2s \overline{p_0} 1s_H \overline{1s_H}) + (p_0 \overline{2s} 1s_H \overline{1s_H}) \)
7. \( (2s \overline{2s} p_+ \overline{p_-}) + (2s \overline{2s} p_- \overline{p_+}) \)
8. \( (p_0 \overline{p_0} p_+ \overline{p_-}) + (p_0 \overline{p_0} p_- \overline{p_+}) \)
9. \( (1s_H \overline{1s_H} p_+ \overline{p_-}) + (1s_H \overline{1s_H} p_- \overline{p_+}) \)
10. \( (2s \overline{p_0} p_+ \overline{p_-}) + (2s \overline{p_0} p_- \overline{p_+}) \)
\hspace{5cm} + (p_0 \overline{2s} p_+ \overline{p_-}) + (p_0 \overline{2s} p_- \overline{p_+}) \)
11. \( (2s \overline{1s_H} p_+ \overline{p_-}) + (2s \overline{1s_H} p_- \overline{p_+}) \)
\hspace{5cm} + (1s_H \overline{2s} p_+ \overline{p_-}) + (1s_H \overline{2s} p_- \overline{p_+}) \)
12. \( (p_0 \overline{1s_H} p_+ \overline{p_-}) + (p_0 \overline{1s_H} p_- \overline{p_+}) \)
\hspace{5cm} + (1s_H \overline{p_0} p_+ \overline{p_-}) + (1s_H \overline{p_0} p_- \overline{p_+}) \)
13. \( (p_+ \overline{p_+} p_- \overline{p_-}) \)
TABLE III

DATA FROM OHNO

<table>
<thead>
<tr>
<th>Orbital Exponents</th>
<th>Boron</th>
<th>Hydrogen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s&lt;sub&gt;B&lt;/sub&gt;</td>
<td>4.70136</td>
<td>1.0038</td>
<td></td>
</tr>
<tr>
<td>2s</td>
<td>1.30092</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2p&lt;sub&gt;0&lt;/sub&gt;</td>
<td>1.30092</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2p&lt;sup&gt;+&lt;/sup&gt;</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2p&lt;sub&gt;-&lt;/sub&gt;</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Internuclear Distance R = 2.32911 a.u.

Total Electronic Energy E<sub>(OHNO) = -25.11045 a.u.</sub>

E (Experimental) = -25.29 a.u.<sup>a</sup>

<sup>a</sup> Ref. [18].
TABLE IV

OPTIMIZED WAVEFUNCTION

<table>
<thead>
<tr>
<th>Orbital Exponents</th>
<th>Boron</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s_B$</td>
<td>4.64915</td>
<td>$1s_H$</td>
</tr>
<tr>
<td>$2s$</td>
<td>1.33334</td>
<td>1.14662</td>
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<td>$2p_0$</td>
<td>1.44977</td>
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<tr>
<td>$2p_+^-$</td>
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<tr>
<td>$2p_-^+$</td>
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<td></td>
</tr>
</tbody>
</table>

Internuclear Distance $R = 2.32911$ a.u.

Total Electronic Energy $E_{(OPT)} = -25.11980$ a.u.

$E$ (Experimental) = $-25.29$ a.u.$^a$

$^a$ Ref. [18].
of the wavefunction in Table II is doubled. In each original determinant the spin orbital $1s_B$ is replaced by the spin orbital $1s'_B$ (or $1s''_B$) while the spin orbital $\bar{1}s_B$ is replaced by the spin orbital $\bar{1}s''_B$ (or $\bar{1}s'_B$). This makes our wavefunction an approximation to a 39-term CI. Starting values of the orbital exponents of the split core orbitals $1s'_B$ and $1s''_B$ were 5.5 and 3.9 respectively. These values are close to those suggested by Silverman, Platas and Matsen [22]. A calculation was carried out using this 13-term split core wavefunction while retaining the original orbital exponents of Ohno (See Table III.) for orbitals other than the split core orbitals. The total electronic energy $E_{SC}$ of this split core wavefunction $\Psi_{SC}$ was -25.13333 a.u. This is quite good. Cade and Huo [18] used an internuclear distance of 2.305 a.u. and an extended basis set of Slater type functions to carry out a SCF Hartree-Fock calculation resulting in an energy of -25.13147 a.u.

The energy improved to -25.134078 a.u. when the orbital exponents of the $1s'_B$ and $1s''_B$ orbitals were optimized to 5.46404 and 3.87451 respectively. Both exponents were optimized together, that is when optimum energy was reached both exponents were changed by the same factor. This new wavefunction $\Psi_{OSC}$ is quite suitable for our purpose but for generality we start at the beginning again using the more
common internuclear distance of 2.329 a.u. and orbital exponents by Slater's rules [23], except for the split core orbitals and $1s_H$, then optimize all exponents. (See Table V.)

The resulting energy, $E_{(TOSC)}$, is very good. Harrison and Allen [18] performed a 13-term VBCI calculation using Gaussian-lobe functions and an internuclear distance of 2.336 a.u. to obtain an energy of $-25.1426$ a.u. Harrison [19] also performed a VB calculation using Gaussian-lobe functions and an internuclear distance of 2.50 a.u. with the resulting energy equal to $-25.1455$ a.u. At present only the calculation of Bender and Davidson [24] yields a ground state energy lower than $E_{(TOSC)}$. Bender and Davidson performed a 1123-term CI calculation using natural orbitals and an internuclear distance of 2.336 a.u. to obtain the value $-25.26214$ a.u. This is lower than the sum of the ground state energies of the individual atoms involved, and thus includes some binding energy of the molecule.

A summary of orbital exponents and energies for the various 13-term wavefunctions is given in Table VI while the corresponding term coefficients are given in Appendix II.

4-4 Scaling and Force Constant Results

The eigenvalue matrix of the wavefunction $\Psi_{(TOSC)}$ was rediagonalized to ensure that the value of any off diagonal elements is negligible, then the new eigenvector matrix was generated. The original ground state energy remained the
TABLE V

WAVEFUNCTION $\psi_{TOSC}$

Order of exponent optimization: $(2p_\pm), 1s_H, 2p_0, 2s, 1s''_B$ and $1s'_B$.

**Orbital Exponents**

<table>
<thead>
<tr>
<th>Starting Values</th>
<th>Optimized Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s'_B$</td>
<td>5.47771</td>
</tr>
<tr>
<td>$1s''_B$</td>
<td>3.84914</td>
</tr>
<tr>
<td>$2s$</td>
<td>1.30378</td>
</tr>
<tr>
<td>$2p_0$</td>
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<tr>
<td>$2p_+$</td>
<td>1.32475</td>
</tr>
<tr>
<td>$2p_-$</td>
<td>&quot;</td>
</tr>
<tr>
<td>$1s_H$</td>
<td>1.1 (arbitrary selection)</td>
</tr>
</tbody>
</table>

Internuclear Distance $R = 2.329$ a.u.

$E$ (Split Core + Total Optimization) = $E_{(TOSC)} = -25.14769$ a.u.

$E$ (Experimental) = $-25.29$ a.u.
### TABLE VI

**ORBITAL EXONENTS FOR 13-TERM WAVEFUNCTIONS**

<table>
<thead>
<tr>
<th></th>
<th>$\Psi_{OHNO}$</th>
<th>$\Psi_{OPT}$</th>
<th>$\Psi_{OSC}$</th>
<th>$\Psi_{TOSC}$</th>
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</thead>
<tbody>
<tr>
<td>$1s_B$</td>
<td>4.70136</td>
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<tr>
<td>$1s_B'$</td>
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<td>$1s_B''$</td>
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<td>1.30378</td>
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<tr>
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<td>1.30092</td>
<td>1.44977</td>
<td>1.30092</td>
<td>1.33424</td>
</tr>
<tr>
<td>$2p_\pm$</td>
<td>1.30092</td>
<td>1.36771</td>
<td>1.30092</td>
<td>1.32475</td>
</tr>
<tr>
<td>$1s_H$</td>
<td>1.00038</td>
<td>1.14662</td>
<td>1.00038</td>
<td>1.21170</td>
</tr>
</tbody>
</table>

-E 25.11045 a.u. 25.11980 a.u. 25.134078 a.u. 25.14769 a.u.

E (Experimental) = -25.29 a.u.
same however. Now the kinetic-energy operator and new eigenvectors were used to calculate the kinetic-energy matrix. The eigenvalues and kinetic-energy matrix were then used in a perturbation computer program to calculate $W_1$ to $W_7$. The results are given in Table VII.

The value of $\eta$ is very close to that obtained by a simpler method [21]

$$\eta = -\frac{V}{2T} = 0.9993749,$$  \hspace{1cm} (4-33)

where $V$ and $T$ are the potential and kinetic-energy of the ground state wavefunction $\Psi_{TOSC}$.

A new Hamiltonian matrix is constructed according to Eq. (4-25). This matrix is diagonalized to obtain the eigenvectors of the scaled wavefunction $\Psi'_{TOSC}$. A check was carried out to see that

$$\frac{dE_\eta}{d\eta} = \hat{C}' (2\eta \hat{T} + \hat{V})C' = 0$$  \hspace{1cm} (4-34)

where $C'$ is the eigenvector of the scaled wavefunction $\Psi_{TOSC}$ corresponding to the lowest energy, while $\hat{T}$ and $\hat{V}$ are, in this case, the usual kinetic and potential-energy matrices.

Now the eigenvectors of $\Psi_{TOSC}'$ are used to obtain the scaled kinetic-energy matrix. Expanding the wavefunction in terms of the parameter $\beta$ we can calculate $\omega_1$ to $\omega_7$. The force constants may be calculated according to Eq. (4-15) to Eq. (4-17). The results are given in Table VIII.
### TABLE VII

**SCALING RESULTS**

<table>
<thead>
<tr>
<th>$k$</th>
<th>$W_k$</th>
<th>$k(W_{k-1} + W_k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.179196</td>
<td>0.0315011</td>
</tr>
<tr>
<td>2</td>
<td>$-1.5153996 \times 10^{-1}$</td>
<td>50.0553121</td>
</tr>
<tr>
<td>3</td>
<td>$1.7958395 \times 10^{-1}$</td>
<td>0.0841320</td>
</tr>
<tr>
<td>4</td>
<td>$-2.2055059 \times 10^{-1}$</td>
<td>$-0.16386656$</td>
</tr>
<tr>
<td>5</td>
<td>$-2.6166944 \times 10^{-1}$</td>
<td>0.2055942</td>
</tr>
<tr>
<td>6</td>
<td>$-2.9812845 \times 10^{-1}$</td>
<td>$-0.2187541$</td>
</tr>
<tr>
<td>7</td>
<td>$3.1521269 \times 10^{-1}$</td>
<td>0.1195897</td>
</tr>
</tbody>
</table>

$\lambda_{OPT}$ (optimized $\lambda$) = $-0.0006293$

$\eta = 0.9993707$

$R_e = R/\eta = 2.3304666$ a.u.
### TABLE VIII

**FORCE CONSTANTS**

<table>
<thead>
<tr>
<th>k</th>
<th>( \omega_k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.147705</td>
</tr>
<tr>
<td>2</td>
<td>(-1.5159298 \times 10^{-1})</td>
</tr>
<tr>
<td>3</td>
<td>(1.7968714 \times 10^{-1})</td>
</tr>
<tr>
<td>4</td>
<td>(-2.2068003 \times 10^{-1})</td>
</tr>
<tr>
<td>5</td>
<td>(2.6180703 \times 10^{-1})</td>
</tr>
<tr>
<td>6</td>
<td>(-2.9820331 \times 10^{-1})</td>
</tr>
<tr>
<td>7</td>
<td>(3.1509448 \times 10^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(k_e)</th>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.204849</td>
<td>0.1958(^a)</td>
<td></td>
</tr>
<tr>
<td>-23.712046</td>
<td>-0.5319(^a)</td>
<td></td>
</tr>
<tr>
<td>61.049772</td>
<td>1.2373(^a)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) From the unpublished results of Mulliken and Ramsy as reported by Cade and Huo [18].
Using experimental data we see that
\[ \omega_1 + \omega_2 = \frac{1}{2} R_e^2 k_e , \]
\[ = (0.5) (2.336 \text{ a.u.})^2 (0.19590) , \]
\[ = 0.5345 . \quad (4-35) \]
The experimental value of \( \omega_2 \) is \(-24.756\). It seems that the calculated values for \( \omega_2 \) and \( \omega_3 \) are far too small. Limited basis set calculations are doomed to fail. Good results might be obtained using a much larger basis set, such as that of Bender and Davidson [24].
5-1 Thorhallsson and Chong's Approach

Thorhallsson and Chong [6] investigated the possibility of expanding the virial force \( F \) in powers of \( R \). The virial force is defined as

\[
F(R) = \frac{dE(R)}{dR} = \frac{-(2T+V)}{R},
\]

(5-1)

where \( V \) and \( T \) are the potential and kinetic energy. This equation holds only for exact wavefunctions, but by applying the virial theorem to an approximate wavefunction one can make \( \frac{dE(R)}{dR} = F(R) \).

Thorhallsson and Chong used a 10-term valence bond configuration-interaction wavefunction for the ground state of LiH. At each of the three \( R \) values the orbital exponents were roughly optimized and scaling was performed. The method of finding the correct value of the scaling parameter \( \eta \) is according to Löwdin [21]

\[
\eta = \frac{[V(1,\rho) + \rho V_{\rho}(1,\rho)]/[2T(1,\rho) + \rho T_{\rho}(1,\rho)]}{\eta R},
\]

(5-2)

where \( \rho = \eta R \), \( V_{\rho} = \partial V(1,\rho)/\partial \rho \) and \( T_{\rho} = \partial T(1,\rho)/\partial \rho \). The derivatives \( V_{\rho} \) and \( T_{\rho} \) are the most difficult to evaluate and were determined from the unscaled wavefunction at \( R_k-x \) and \( R_k+x \).
In this present work we investigate expansions of $E$ and $F$ in $R$ and $1/R$ using scaled and unscaled wavefunctions derived from our wavefunction $\Psi_{\text{TOSC}}$. Since Eq. (5-2) is the expression for $\eta$ derived from the condition that $\partial E(\eta,R)/\partial \eta = 0$, we find it more convenient to perform the scaling at fixed $R$. All orbital exponents were multiplied by three different values of $\eta$, and the resulting energies when fitted to a parabola give a minimum corresponding to the correct value of $\eta$.

5-2 Wavefunctions and Data

Three internuclear distances are selected such that $1/R_1 - 1/R_2 = 1/R_2 - 1/R_3$. The wavefunction $\Psi_{\text{TOSC}}$, described in Table V, is used as a starting point, and the orbital exponents of the split core are optimized once individually at each internuclear distance. Two sets of calculations were carried out, one set involved data from the wavefunctions described above, the other involved taking the mentioned wavefunctions one step further, scaling them. The scaling was performed at each internuclear distance by calculating the energy of the wavefunction as well as the energies given when all of the orbital exponents were multiplied by a factor of $1\pm0.01$. Then a parabolic fit on energy gives the scaled orbital exponents at lowest energy and therefore the scaled wavefunction. Data from the scaled and unscaled wavefunctions is given in Tables IX and X.
TABLE IX

UNSCALED DATA

<table>
<thead>
<tr>
<th></th>
<th>$\Psi_1$</th>
<th>$\Psi_2$</th>
<th>$\Psi_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>2.329 a.u.</td>
<td>2.433688 a.u.</td>
<td>2.548230 a.u.</td>
</tr>
<tr>
<td>$T$</td>
<td>25.196451 a.u.</td>
<td>25.223713 a.u.</td>
<td>25.211669 a.u.</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.252673 a.u.</td>
<td>0.224906 a.u.</td>
<td>0.190736 a.u.</td>
</tr>
<tr>
<td>1s' exponent</td>
<td>5.465763</td>
<td>5.479920</td>
<td>5.479919</td>
</tr>
<tr>
<td>1s'' exponent</td>
<td>3.865785</td>
<td>3.860518</td>
<td>3.860635</td>
</tr>
<tr>
<td>$F(R)$</td>
<td>-0.020936 a.u.</td>
<td>-0.03483 a.u.</td>
<td>-0.024664 a.u.</td>
</tr>
</tbody>
</table>

$E$ (Experimental) = -25.29 a.u.

$\mu$ = dipole moment
### TABLE X

**SCALED DATA**

<table>
<thead>
<tr>
<th></th>
<th>$\psi_1$</th>
<th>$\psi_2$</th>
<th>$\psi_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>2.329 a.u.</td>
<td>2.433688 a.u.</td>
<td>2.548230 a.u.</td>
</tr>
<tr>
<td>Scale Factor</td>
<td>1.00043246</td>
<td>0.99877845</td>
<td>1.00000008</td>
</tr>
<tr>
<td>$T$</td>
<td>25.217952 a.u.</td>
<td>25.162912 a.u.</td>
<td>25.109169 a.u.</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.252367 a.u.</td>
<td>0.225838 a.u.</td>
<td>0.192422 a.u.</td>
</tr>
<tr>
<td>$F$</td>
<td>-0.03016574 a.u.</td>
<td>-0.00548509 a.u.</td>
<td>+0.01560259 a.u.</td>
</tr>
</tbody>
</table>

**Orbital Exponents**

<table>
<thead>
<tr>
<th></th>
<th>1s$_B'$</th>
<th>1s$_B''$</th>
<th>2s</th>
<th>2p$_0$</th>
<th>2p$_+$</th>
<th>2p$_-$</th>
<th>1s$_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.468127</td>
<td>5.473226</td>
<td>5.468635</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.867456</td>
<td>3.855802</td>
<td>3.852686</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2s</td>
<td>1.304343</td>
<td>1.302187</td>
<td>1.301095</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2p$_0$</td>
<td>1.334822</td>
<td>1.3326151</td>
<td>1.331498</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2p$_+$</td>
<td>1.325324</td>
<td>1.323133</td>
<td>1.3220237</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2p$_-$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1s$_H$</td>
<td>1.212213</td>
<td>1.210209</td>
<td>1.209194</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5-3 Numerical Analysis

The three energies and forces from the scaled wavefunctions are fitted to a quintic polynomial. The forces calculated from the unscaled wavefunctions are too irregular to permit the unscaled data to be fitted to a quintic polynomial. Data from the quintic fit is given in Table XI.

Several different parabolic models are used to fit virial forces or energies of both the scaled and unscaled wavefunctions. The various parabolic models are described below.

**Model A**

\[
E(R) = A + BR + CR^2 \quad (5-3)
\]

\[
F(R) = \frac{dE}{dR} = B + 2CR \quad (5-4)
\]

\[
R_e = -\frac{B}{2C} \quad (5-5)
\]

\[
k_e = 2C \quad (5-6)
\]

**Model B**

\[
E(\rho) = A + B(\rho-\rho_0) + C(\rho-\rho_0)^2 , \quad (5-7)
\]

where \( \rho = 1/R \) and \( \rho_0 = 1/R_2 \). Let \( X = E(\rho_0-h) \), \( Y = E(\rho_0) \), and \( Z = E(\rho_0+h) \), where \( h = \rho_2-\rho_1 = \rho_3-\rho_2 \). Then,

\[
A = Y \quad , \quad (5-8)
\]

\[
B = \frac{[Z-X]}{2h} \quad , \quad (5-9)
\]

\[
C = \frac{[X+Z-2Y]}{[2h^2]} \quad , \quad (5-10)
\]

and

\[
F(R) = -\frac{[B+2C(\rho-\rho_0)]}{R^2} . \quad (5-11)
\]

Therefore \( \rho_e-\rho_0 = -B/2C \) and \( k_e = 2C\rho_e^4 \).
TABLE XI

QUINTIC POLYNOMIAL FIT

<table>
<thead>
<tr>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>-25.149634</td>
</tr>
<tr>
<td>-0.934849 x 10^-8</td>
</tr>
<tr>
<td>0.993244 x 10^-1</td>
</tr>
<tr>
<td>-0.131321</td>
</tr>
<tr>
<td>0.129005</td>
</tr>
<tr>
<td>0.255402</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_e</td>
<td>-25.149634 a.u.</td>
</tr>
<tr>
<td>R_e</td>
<td>2.459919 a.u.</td>
</tr>
<tr>
<td>k_e</td>
<td>0.198649 a.u.</td>
</tr>
<tr>
<td>l_e</td>
<td>-0.787925 a.u.</td>
</tr>
</tbody>
</table>

a From the unpublished results of Mulliken and Ramsy as reported by Cade and Huo [18].
Model C

\[ F(R) = A + BR + CR^2 \]  
(5-12)

At \( F=0 \),

\[ R_e = [\frac{-B\pm\sqrt{B^2 - 4AC}}{2C}] \]  
(5-13)
\[ \frac{dF(R)}{dR} = B + 2CR \]  
(5-14)

and

\[ k_e = \frac{[B+2CR_e]}{2} = \frac{[\pm\sqrt{B^2 - 4AC}]}{2} \]  
(5-15)

Therefore, take the positive root.

Model D

\[ F(p) = A + B(p-p_0) + C(p-p_0)^2 \]  
(5-16)

where \( p = 1/R \) and \( p_0 = 1/R_2 \). Let \( X = F(p_0-h) \), \( Y = F(p_0) \) and \( Z = F(p_0+h) \) where \( h = p_2-p_1 = p_3-p_2 \). Then \( A = Y \), \( B = [Z-X]/2h \) and \( C = [X+Z-2Y]/2h^2 \). At \( F(R) = 0 \),

\[ \rho_e - \rho_0 = \frac{[-B\pm\sqrt{B^2 - 4AC}]}{2C} \]  
(5-17)

and

\[ \frac{dF(R)}{dR} = \frac{[-B+2C(p-p_0)]}{R^2} \]  
(5-18)

At \( \rho_e \),

\[ k_e = \frac{-\rho_e^2}{[B+(-B\pm\sqrt{B^2 - 4AC})]} \],  
(5-19)

\[ = \frac{-\rho_e^2}{[\pm\sqrt{B^2 - 4AC}]} \]

therefore, take negative root.

Table XII gives the results of each parabolic model calculation for both scaled and unscaled wavefunctions. The cubic force constant \( l_e \) calculated from the parabolic models, where possible, was very poor except for scaled Model C which gave the value \(-0.471199\).
### TABLE XII

**PARABOLIC MODEL RESULTS**

<table>
<thead>
<tr>
<th>Model</th>
<th>$k_e$</th>
<th>$E_e$ (a.u.)</th>
<th>$R_e$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A unscaled</td>
<td>0.216050</td>
<td>-25.149615</td>
<td>2.462430</td>
</tr>
<tr>
<td>A scaled</td>
<td>0.213184</td>
<td>-25.149667</td>
<td>2.464954</td>
</tr>
<tr>
<td>B unscaled</td>
<td>0.203903</td>
<td>-25.149589</td>
<td>2.458223</td>
</tr>
<tr>
<td>B scaled</td>
<td>0.199896</td>
<td>-25.149639</td>
<td>2.460911</td>
</tr>
<tr>
<td>C unscaled</td>
<td>0.282013</td>
<td></td>
<td>2.669423</td>
</tr>
<tr>
<td>C scaled</td>
<td>0.198469</td>
<td></td>
<td>2.460473</td>
</tr>
<tr>
<td>D unscaled</td>
<td>0.229515</td>
<td></td>
<td>2.689602</td>
</tr>
<tr>
<td>D scaled</td>
<td>0.196769</td>
<td></td>
<td>2.460718</td>
</tr>
<tr>
<td>Quintic</td>
<td>0.198649</td>
<td>-25.149634</td>
<td>2.459919</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.1958</td>
<td>-25.29</td>
<td>2.336</td>
</tr>
</tbody>
</table>
The quintic fit results are used as a standard for comparing the various parabolic models. Table XIII gives energies and virial forces calculated from the quintic polynomial for the different $R_e$ predicted by various models. Table XIII also gives the dipole moments at these different $R_e$. The dipole moments are calculated from simple parabolic fits in $R$ to the scaled and unscaled data.

Virial scaling has resulted in an improved value for $k_e$ in all parabolic models. The importance of scaling confirms the results of Thorhallsson and Chong [6].

Parabolic expansions of energy or virial force in $1/R$ rather than $R$ leads to an improved value for $k_e$, except in the case of going from scaled model C to scaled model D. Thus a Fues potential appears to be better than an harmonic oscillator potential. This supports the approach of Parr and Borkman [25]. Model C scaled gives the best agreement with the quintic polynomial results but the value for $1_e$ seems overly fortunate.

The calculated dipole moments are too small by a factor greater than two, the experimental value given by Thomson and Dalby [26] is $0.4997 \pm 0.08$ a.u.

A summary of energies corresponding to wavefunctions used in this work and wavefunctions from other sources is given in Table XIV.
<table>
<thead>
<tr>
<th>Models</th>
<th>Re predicted by various models</th>
<th>Quintic Polynomial</th>
<th>Parabolic Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (u)</td>
<td>2.462430</td>
<td>-25.149633</td>
<td>0.216710</td>
</tr>
<tr>
<td>A (s)</td>
<td>2.464954</td>
<td>-25.149631</td>
<td>0.217178</td>
</tr>
<tr>
<td>B (u)</td>
<td>2.458223</td>
<td>-25.149634</td>
<td>0.217926</td>
</tr>
<tr>
<td>B (s)</td>
<td>2.460911</td>
<td>-25.149634</td>
<td>0.218318</td>
</tr>
<tr>
<td>C (u)</td>
<td>2.669423</td>
<td>-25.149634</td>
<td>0.150276</td>
</tr>
<tr>
<td>C (s)</td>
<td>2.460473</td>
<td>-25.149634</td>
<td>0.218441</td>
</tr>
<tr>
<td>D (u)</td>
<td>2.689602</td>
<td>-25.149634</td>
<td>0.143108</td>
</tr>
<tr>
<td>D (s)</td>
<td>2.460718</td>
<td>-25.149634</td>
<td>0.218372</td>
</tr>
<tr>
<td>Data Predicted by Quintic Polynomial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.459919</td>
<td>-25.149634</td>
<td>0.0</td>
<td>0.217430</td>
</tr>
</tbody>
</table>

(u) = unscaled
(s) = scaled
μ = dipole moment
TABLE XIV
BH WAVEFUNCTIONS

<table>
<thead>
<tr>
<th>Wavefunction</th>
<th>R (a.u.)</th>
<th>E (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI (Fraga and Ransil [20])</td>
<td>2.329a</td>
<td>-25.09034</td>
</tr>
<tr>
<td>13-term CI (Ohno [5])</td>
<td>2.32911</td>
<td>-25.11018</td>
</tr>
<tr>
<td>10-term CI (Table I:iv)</td>
<td>2.329</td>
<td>-25.11634</td>
</tr>
<tr>
<td>13-term CI (Table IV)</td>
<td>2.32911</td>
<td>-25.11980</td>
</tr>
<tr>
<td>Hartree-Fock (Cade and Huo [18])</td>
<td>2.305*</td>
<td>-25.13147</td>
</tr>
<tr>
<td>VB 'Harrison [19])</td>
<td>2.50*</td>
<td>-25.1455</td>
</tr>
<tr>
<td>13-term split core CI (Table V)</td>
<td>2.329</td>
<td>-25.14769</td>
</tr>
<tr>
<td>13-term split core CI (Table XI)</td>
<td>2.460*</td>
<td>-25.14963</td>
</tr>
<tr>
<td>1123-term CI (Bender and Davidson [24])</td>
<td>2.336</td>
<td>-25.26214</td>
</tr>
<tr>
<td>Experimental</td>
<td>2.336b</td>
<td>-25.29c</td>
</tr>
</tbody>
</table>

* Calculated \( R_e \)

a Experimental value reported by Herzberg [27].
b From the unpublished results of Mulliken and Ramsy as reported by Cade and Huo [18].
c Cade and Huo [18].
BIBLIOGRAPHY


APPENDIX I

SAMPLE GEMINAL CALCULATION

The following description deals with basis set II, (See Table I.) but most of the operations involved also apply to the other basis sets.

The value of $\zeta(H)$ for $\psi_{AGP}$ was determined from a parabolic fit to antisymmetrized geminal product energies calculated at three different values of $\zeta(H)$. In this case the values were 1.26, 1.30 and 1.34. At each of the $\zeta(H)$ the parameter $a$ was optimized. The following procedure was carried out at each of the four $\zeta(H)$ values.

First the four single-zeta Slater-type orbitals, those on boron having the exponents of Clementi and Raimondi [15] while the 1s orbital on hydrogen has some selected value for $\zeta(H)$, were used in a fortran language configuration-interaction computer program called Diatom*. A fictitious wavefunction was used, the only purpose was to calculate all possible overlap, one and two-electron integrals. The 10 different one-electron and the 55 different two-electron integrals were then stored as two and four dimensional arrays respectively.

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The next step was to Schmidt orthogonalize \( s \) to \( k \),

\[
\mathbf{s} = N [\mathbf{s} - \mathbf{S} \mathbf{k}],
\]

where \( N = 1/\sqrt{1-S^2} \) and \( S \) is the overlap integral between \( s \) and \( k \):

\[
S = \int k(l) \bar{s}'(l) d\tau_1.
\]

This orthogonalization was carried out by matrix multiplication,

\[
(k, s, a, h) = (k, s', a', h) A,
\]

where

\[
A = \begin{bmatrix}
1 & (-NS) & 0 & 0 \\
0 & N & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{bmatrix}
\]

\( N = 1.02242, \) and \( S = 0.20827. \)

The required hybridization was performed with matrix \( B \),

\[
(k, b, n, h) = (k, s, a, h) B,
\]

where

\[
B = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 0 & (1-a^2)^{1/2} & 0 \\
0 & (1-a^2)^{1/2} & -a & 0 \\
0 & 0 & 0 & 1 \\
\end{bmatrix}
\]

Symmetric orthogonormalization was carried out using matrix \( C \),

\[
(K, B, N, H) = (k, b, n, h) C,
\]

where \( C \) is the matrix \( \Delta^{-1/2} \) and \( \Delta \) is the matrix of overlap integrals. If \( U \) is the matrix that diagonalizes \( \Delta \),

\[
U^T \Delta U = \lambda,
\]

then

\[
U \lambda^{-1/2} U^T = \Delta^{-1/2}.
\]
By these three transformations we have introduced an alternative basis,

\[ r_i = \sum_j r'_j T_{ji}, \]  

(I-9)

where \( T_{ji} \) is a matrix element of the matrix product \( ABC \). In this new basis the corresponding one and two-electron integrals are related by:

\[ \langle r_i | h | r_j \rangle = \sum_{rs} T^*_r T^*_s \langle r'_r | h | r'_s \rangle T_{sj}, \]  

(I-10)

\[ \langle r_i r_j | g | r_k r_s \rangle = \sum_{rs, tu} T^*_r T^*_s \langle r'_r r'_s | g | r'_t r'_u \rangle T_{tk} T_{ul}, \]  

(I-11)

where the primes designate the original orbitals, and \( h \) and \( g \) are the one and two-electron operators respectively. A short computer program yielded the completely transformed integrals which were then used in the geminal program to obtain the energy. Various sets of integrals, corresponding to different values of the parameter \( \alpha \), were used until optimum \( \alpha \) was obtained. Figure I gives a sample plot of \( E \) versus \( \alpha \) and Figure II gives a plot of \( E \) versus \( \xi(H) \).

The completely transformed integrals corresponding to \( E(AGP) \) were then used in program DIATOM to obtain \( E(G+1) \) and \( E(CI) \). The coefficients of the terms in the bonding geminal of \( \Psi_{AGP} \) along with the coefficients of terms in \( \Psi_{G+1} \) and \( \Psi_{CI} \) are given in Table XV.
FIGURE I

E VERSUS \( \alpha \)

\[ H(\xi) = 1.34 \]

\((-25.075402)\)

\((-25.075560)\)

\((-25.075722)\)

\((-25.075804)\)

\((-25.075857)\)

\((-25.075525)\)
FIGURE II

E VERSUS $\xi(H)$

$E (\text{a.u.})$

-25.0754

-25.0755

-25.0760

$\xi(H)$

1.26 1.30 1.34

$\left( E = -25.075437 \text{ a.u.} \right)$

$\left( \alpha = 0.50 \right)$

$\left( E = -25.075857 \text{ a.u.} \right)$

$\left( \alpha = 0.50 \right)$

$\left( E = -25.075982 \text{ a.u.} \right)$

$\left( \alpha = 0.50 \right)$

$\left( E = -25.076012 \text{ a.u.} \right)$

$\left( \alpha = 0.50 \right)$
TABLE XV
DATA FROM BASIS SET II

<table>
<thead>
<tr>
<th>Orbital Exponents</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1s</td>
</tr>
<tr>
<td></td>
<td>ls</td>
</tr>
<tr>
<td>Boron</td>
<td>4.6795</td>
</tr>
<tr>
<td>ls</td>
<td>4.6795</td>
</tr>
<tr>
<td>2s</td>
<td>1.2881</td>
</tr>
<tr>
<td>2p₀</td>
<td>1.2107</td>
</tr>
</tbody>
</table>

| C₁ 0.48473405     | ψ₁ 0.54252394 | ψ₁ 0.54239176 |
| C₂ 0.766514474    | ψ₂ 0.48625970 | ψ₂ 0.48537033 |
| C₃ 0.42129379     | ψ₃ 0.41595987 | ψ₃ 0.41656740 |
|                   | ψ₄ -0.13886659 x 10⁻¹ | ψ₄ -0.12764533 x 10⁻¹ |
|                   | ψ₅ -0.14870197 x 10⁻¹ | ψ₅ -0.18499101 x 10⁻¹ |
|                   | ψ₆ 0.15156648 x 10⁻¹ | ψ₆ 0.15135885 x 10⁻¹ |
|                   | ψ₇ -0.16986274 x 10⁻¹ | ψ₇ -0.16975390 x 10⁻¹ |
|                   | ψ₈ -0.21502238 x 10⁻¹ | ψ₈ -0.21502238 x 10⁻¹ |
|                   | ψ₉ -0.30078238 x 10⁻³ | ψ₉ -0.30078238 x 10⁻³ |
|                   | 10 0.10816345 x 10⁻² | 10 0.10816345 x 10⁻² |

ψ lure   ΨCI

-25.07601 a.u. -25.08541 a.u. -25.08627

α = 0.50
R = 2.329 a.u.
**APPENDIX II**

**TABLE XVI**

**COEFFICIENTS OF 13-TERM WAVEFUNCTIONS**

<table>
<thead>
<tr>
<th>TERM</th>
<th>$\psi_{OHNO}$</th>
<th>$\psi_{OPT}$</th>
<th>$\psi_{OSC}$</th>
<th>$\psi_{TOSC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0.65160911 \times 10^{-1}$</td>
<td>$0.97622451 \times 10^{-1}$</td>
<td>$0.34391515 \times 10^{-1}$</td>
<td>$0.71924579 \times 10^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>$0.21686080$</td>
<td>$0.23936148$</td>
<td>$0.1097724$</td>
<td>$0.76587498 \times 10^{-1}$</td>
</tr>
<tr>
<td>3</td>
<td>$-0.31982327 \times 10^{-1}$</td>
<td>$-0.14220806 \times 10^{-1}$</td>
<td>$-0.15799579 \times 10^{-1}$</td>
<td>$-0.57602491 \times 10^{-2}$</td>
</tr>
<tr>
<td>4</td>
<td>$0.50163363$</td>
<td>$0.47944053$</td>
<td>$0.25833018$</td>
<td>$0.24332556$</td>
</tr>
<tr>
<td>5</td>
<td>$0.11724651$</td>
<td>$0.11538376$</td>
<td>$0.60380664 \times 10^{-1}$</td>
<td>$0.65463450 \times 10^{-1}$</td>
</tr>
<tr>
<td>6</td>
<td>$-0.59753748 \times 10^{-1}$</td>
<td>$-0.65619440 \times 10^{-1}$</td>
<td>$-0.30337938 \times 10^{-1}$</td>
<td>$-0.26711443 \times 10^{-1}$</td>
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<tr>
<td>7</td>
<td>$0.13112438 \times 10^{-1}$</td>
<td>$0.16147282 \times 10^{-1}$</td>
<td>$0.68367720 \times 10^{-2}$</td>
<td>$0.10012272 \times 10^{-1}$</td>
</tr>
<tr>
<td>8</td>
<td>$0.17893071 \times 10^{-1}$</td>
<td>$0.20531238 \times 10^{-1}$</td>
<td>$0.93060592 \times 10^{-2}$</td>
<td>$0.14028880 \times 10^{-1}$</td>
</tr>
<tr>
<td>9</td>
<td>$0.34097752 \times 10^{-1}$</td>
<td>$0.40209341 \times 10^{-1}$</td>
<td>$0.17170934 \times 10^{-1}$</td>
<td>$0.12314110 \times 10^{-1}$</td>
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<tr>
<td>10</td>
<td>$-0.14793546 \times 10^{-2}$</td>
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<td>$-0.74646173 \times 10^{-2}$</td>
<td>$-0.17865829 \times 10^{-2}$</td>
</tr>
<tr>
<td>11</td>
<td>$0.28422092 \times 10^{-1}$</td>
<td>$0.28109768 \times 10^{-1}$</td>
<td>$0.14850164 \times 10^{-1}$</td>
<td>$0.15692586 \times 10^{-1}$</td>
</tr>
<tr>
<td>12</td>
<td>$0.8804107 \times 10^{-1}$</td>
<td>$0.82458844 \times 10^{-1}$</td>
<td>$0.45148265 \times 10^{-1}$</td>
<td>$0.41494663 \times 10^{-1}$</td>
</tr>
<tr>
<td>13</td>
<td>$-0.99948530 \times 10^{-2}$</td>
<td>$-0.93721254 \times 10^{-2}$</td>
<td>$-0.51528255 \times 10^{-2}$</td>
<td>$-0.50561302 \times 10^{-2}$</td>
</tr>
</tbody>
</table>