ONE-CENTER EXPANSION WAVE FUNCTIONS AND THE HELLMANN-FEYNMAN THEOREM

JAMES JOSEPH EBERHARDT

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ONE-CENTER EXPANSION WAVE FUNCTIONS AND THE HELLMANN-FEYNMAN THEOREM

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ONE-CENTER EXPANSION WAVE FUNCTIONS
AND THE HELLMANN-FEYNMAN THEOREM

by

JAMES JOSEPH EBERHARDT
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A THESIS

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[Signature]

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ABSTRACT

ONE-CENTER EXPANSION WAVE FUNCTIONS
AND THE HELLMANN-FEYNMAN THEOREM

by

JAMES JOSEPH EBERHARDT

One-center expansion wave functions (OCE-WF's) of multiconfigurational type are used to compute internuclear forces for the hydrogen molecule. A comparison is made between the force values computed from the slope of the total energy curve and those forces predicted by the Hellmann-Feynman electrostatic theorem (HFET) in order to ascertain the reliability of the forces computed from the latter when an approximate wave function of the OCE type is used.

In general, the HFET cannot be expected to provide quantitatively or even qualitatively correct behavior for internuclear forces when approximate wave functions are used unless infinitesimal changes in nuclear positions (in the case of a diatomic molecule, an infinitesimal change in the internuclear distance) produce no change in the approximate wave function. Such approximate wave functions are characterized as "floating" or "stable" wave functions. Since OCE-WF's have no provision for the inclusion of parameters to allow
them to "float", they would not be expected to satisfy the theorem.

The results show that OCE-WF's do indeed satisfy the HFET without need of floating parameters if the following three restrictions are observed.

1) The coordinate system must be chosen such that the kinetic energy part of the Hamiltonian is independent of nuclear coordinates (internuclear distance).

2) The OCE approximate wave function must be fully optimized with respect to all of the basis function parameters included in the wave function.

3) The basis functions used to construct the wave function must exhibit no explicit dependence upon nuclear coordinates (internuclear distance), although an implicit or parametric dependence is allowable if condition (2) is fulfilled.

OCE functions satisfying the above three criteria are referred to as being stable with respect to changes in nuclear coordinates and hence the HFET is satisfied.

From an analysis of the OCE results it is inferred that most approximate wave functions do not satisfy the theorem because they are of multicenter type. Use of such approximate wave functions leads to the introduction of explicit dependence of the wave function on nuclear coordinates when the basis functions are transformed from their nuclear centers to a point coincident with the origin of a volume element of integration. Without such coordinate transformations the basic
multicenter integrals could not be evaluated. It is pointed out that the introduction of additional variational parameters which allow the basis functions to "float" or move from their fixed nuclear centers removes the explicit dependence of the multicenter integrals (and hence, the wave function) on nuclear coordinates which would ordinarily be introduced by the basis transformation.

Correlation effects, as expected, are shown to have no part in the satisfaction or negation of the theorem.

Comparison of the forces computed by either method with experimentally determined values shows that the results obtained from comparable OCE-WF's in a Gaussian, a Slater or a generalized exponential type basis all become progressively worse as the internuclear distance is increased from the equilibrium internuclear separation. However, the energetically inferior Gaussian basis trial functions are shown to lead to predictions of equilibrium internuclear separations in better agreement with the experimentally determined value of 1.40 au than both of the comparable wave functions in the other two bases.

Finally, forces computed with a seven configuration wave function are compared to experimentally determined values in order to demonstrate that OCE-WF's have the capability, for certain centrosymmetric systems, of predicting internuclear forces approaching the experimental values in accuracy, at least in the region of the equilibrium internuclear separation.
SECTION I

INTRODUCTION

This thesis is concerned with an investigation of the forces predicted by the Hellmann-Feynman electrostatic theorem (HFET) when one kind of approximate wave function viz. a one-center expansion wave function (OCE-WF), which does not contain a so-called 'floating' variational parameter, is used. The single center approach has the computational advantage that no multicenter electron repulsion molecular integrals need be evaluated and hence, all integrals can be expressed in closed analytical form.

The hydrogen molecule was chosen as the simplest case of general applicability, and a multiconfiguration variational rather than Hartree-Fock approach was taken in building up the wave function in order to ascertain the effect of introducing some electron correlation. Moreover, Stanton, and Kern and Karplus have already shown that fully optimized wave functions such as the Hartree-Fock satisfy the theorem.

Despite the apparent simplicity of the derivation of the generalized Hellmann-Feynman theorem (GHFT), there has been some confusion concerning its validity and consequences. In particular, misinterpretations of the conditions under which the GHFT reduces to the HFET for approximate wave functions have been common.

In general, when an approximate instead of exact wave function is used to compute internuclear forces from the HFET, the results are no longer quantitatively or even qualitatively reliable. Since the
exact wave function is not known for most systems of chemical interest, it is of some importance to determine the conditions under which approximate wave functions will satisfy the theorem. Hurley\(^3\) and Hall\(^10\) have specified general conditions for satisfaction of the theorem when approximate wave functions are used. However, even though the theorem may be satisfied by certain types of approximate wave functions, such satisfaction does not imply that the forces so computed will agree quantitatively with the experimentally determined exact forces\(^11\) (or those forces which would have been predicted by the theorem had the exact wave function been known). Rather, it only allows one to specify conditions under which internuclear forces can be computed with confidence from approximate wave functions by means of the computationally simple HFET instead of by the more difficult task of calculating the slope of the total energy curve. The final criterion for the "goodness" of the forces calculated by either method must be, as always, agreement with experiment.

In this thesis, internuclear force curves for the hydrogen molecule were constructed using an OCE-WF both by application of the HFET and by taking the slope (first derivative of the total energy with respect to internuclear distance) of the total energy curve. From a comparison of the forces computed by each method with each other and an analysis of the OCE-WF used, one may ascertain the degree of reliability of the forces predicted when one uses this type of wave function in the HFET as compared to the forces computed from the alternative method of taking the slope of the total energy curve. The experimental force curve is also presented for comparison.
SECTION II

HISTORY

1. THE HELLMANN-FEYNMAN THEOREM

The theorem was first formulated by Hellmann and followed shortly thereafter by an alternative derivation by Feynman. An attack on the validity of the theorem was mounted by Coulson and Bell but was subsequently refuted in a paper by Berlin.

Investigations of some of the types of approximate wave functions which satisfy the theorem have been carried out by Hurley, Hirschfelder and Coulson, and Coulson and Hurley. Such an analysis by Hurley has shown that in order for an approximate wave function to satisfy the HFET it is necessary, when one uses the variational approach to building an approximate wave function, to include a variational floating parameter in the wave function. More recently, Hall has introduced the more general concept of "stable" wave functions but Hurley has demonstrated the equivalence of his floating wave function to the former.

Although the OCE-WF used in the thesis does not contain, as such, a floating parameter and hence cannot be expected to yield good forces from the HFET, it is to be expected that as the wave function becomes more flexible (more configurations are added or a better basis set is used) that the force curve from the theorem will approach that obtained from the slope of the total energy curve.

2. ONE-CENTER EXPANSION WAVE FUNCTIONS

The single center or one-center expansion (OCE) method has long
been used as a means of constructing approximate wave functions for certain centrosymmetric molecules. The main reason for the popularity of the approach lies in its computationally significant advantage of avoiding the evaluation of the difficult multicenter electron repulsion integrals. However, early results for molecules\textsuperscript{16} were not promising and the method was in danger of being abandoned. Significant contributions to the resurrection of the OCE method may be attributed to Joy and Parr\textsuperscript{2} who showed that the initially discouraging results obtained by some investigators were due to an inappropriate choice of basis functions rather than any inherent fault of the method. Furthermore, Moccia\textsuperscript{17} applied the method of the self-consistent field (SCF) to obtain startlingly good results for a single center wave function. The thesis follows the variational approach used by the former authors with the incidental innovation of the quite flexible basis functions of Carrier and Pilar.\textsuperscript{15} Comparisons were made with results obtained from wave functions constructed from Slater type functions (STF's) and Gaussian type functions (GTF's) in order to determine any advantage which might be gained by a change in basis.

Since it is not the purpose of this thesis to provide yet another hydrogen molecule wave function for the literature, but rather to test the efficacy of such OCE-WF's for computing internuclear forces through the HFET, the reader will be referred to the very recent reviews and comprehensive bibliographies on OCE-WF's given by Joshi\textsuperscript{18}, Bishop\textsuperscript{19}, and Hayes and Parr.\textsuperscript{20}
SECTION III

METHOD

1. THE WAVE FUNCTION

The wave functions considered in this thesis are of the multiconfigurational type similar to those employed by Joy and Parr. Each wave function is expressed as a linear combination of split shell configurations, viz.

\[ \psi = \sum_{i} c_i \phi_i \]  

(1-1)

For the \( \sum_g^+ \) ground state of the hydrogen molecule, each split shell configuration is composed of a linear combination of two Slater determinants of the form

\[ \phi_i = \frac{N_i}{\sqrt{a!}} \left( \begin{array}{c} X_{s_1}^{(1)} \ X_{s_2}^{(1)} \\ X_{l_1}^{(2)} \ X_{l_2}^{(2)} \end{array} \right) \left( \begin{array}{c} X_{s_1}^{(1)} \ X_{s_2}^{(1)} \\ X_{l_1}^{(2)} \ X_{l_2}^{(2)} \end{array} \right) \]  

(1-2)

\( N_i \) is the configuration normalization constant given by

\[ N_i = \left[ 2a(l + S_{l_1, l_2}) \right]^{-\frac{1}{2}} \]  

(1-3)

and the \( \chi^\alpha \) are the basis functions used to construct the wave function. The subscripts \( l_1, l_2 \) on \( \chi \) refer to the basis functions of angular quantum number \( l_1 \) and \( l_2 \) respectively, while the numbers in parentheses denote specific electron coordinates. Absence or presence of a bar over \( \chi \) indicates \( \alpha \) or \( \beta \) spin functions, respectively. Split shell configurations were used rather than the alternative closed shell (single determinant) configurations in order to utilize
more variational parameters and hence, introduce more flexibility into the wave function. One can readily show, however, that the former reduces to the latter if the variational parameters of $\chi_{1}$ and $\chi_{2}$ are equal.

The basis set employed in the present calculations is due to Carrier and Pilar. These generalized exponential type functions (GETF's) have the form

$$\chi_{\ell} = A_{\ell}(n_{\ell}, \alpha_{\ell}, p) r^{n_{\ell}-1} e^{-\alpha_{\ell} r^{p}} Y_{\ell,m}(\theta, \phi)$$

(1-4)

where $n_{\ell}$ is the principal quantum number (in this case a variational parameter and, in general, non-integral). $\alpha_{\ell}$ is the orbital exponent variational parameter and $p$ is the exponential power parameter. $A_{\ell}(n_{\ell}, \alpha_{\ell}, p)$ is the radial normalization constant of the form

$$A_{\ell}(n_{\ell}, \alpha_{\ell}, p) = \frac{\left[p (2\alpha_{\ell})^{2(n_{\ell}+1)/p}\right]}{\Gamma[(2n_{\ell}+1)/p]}^{1/2}$$

(1-5)

$Y_{\ell,m}(\theta, \phi)$ is the usual normalized spherical harmonic. One can immediately see that when $p = 1$ and $p = 2$ the GETF's reduce to the familiar Slater type functions (STF's) and Gaussian type functions (GTF's), respectively.

A variational solution to the time-independent Schrödinger wave equation

$$\mathcal{H}_{0} \Psi = E \Psi$$

(1-6)

is obtained by minimization of the expectation value of the
Hamiltonian operator with respect to all of the variational parameters, \( u_r \), in the trial wave function. That is,

\[
\frac{\partial \langle H_{op} \rangle}{\partial u_r} = 0 \quad r = 1, 2, 3 \ldots
\]  

(1-7a)

Where \( H_{op} \) is the system Hamiltonian and \( \langle H_{op} \rangle \) is its expectation value, the total energy of the system. Here \( u_r \) represents any of the variational parameter \( C_i, n, \alpha, p \).

If one wishes to find the optimal internuclear separation for the trial wave function employed, then the internuclear distance also becomes a variational parameter

\[
\frac{\partial \langle H_{op} \rangle}{\partial R} = 0
\]  

(1-7b)

In the above equations

\[
\langle H_{op} \rangle = \langle \Psi | H_{op} | \Psi \rangle
\]  

(1-8)

and it is assumed that \( \Psi \) is normalized, viz.

\[
\langle \Psi | \Psi \rangle = 1
\]  

(1-9)

Solution of the linear variational equations (i.e. when \( u_r = C_i \)) leads to the usual matrix* eigenvalue problem^21

\[
(H - E_i \Delta) C_i = 0
\]  

(1-10)

---

* Matrices are denoted herein by the presence of \( \sim \) below upper case alphabetical symbols, for example, \( \Delta \).
from which arises the secular determinant

$$\det(H - E_i \Delta) = 0$$  \hspace{1cm} (1-11)

The matrix elements between configurations $\Phi_i$, $\Phi_j$ of the Hamiltonian and unit operators are denoted by $H_{ij}$ and $\Delta_{ij}$, respectively, and have the form

$$H_{ij} = \langle \Phi_i \vert H_\text{op} \vert \Phi_j \rangle$$  \hspace{1cm} (1-12a)

$$\Delta_{ij} = \langle \Phi_i \vert \Phi_j \rangle$$  \hspace{1cm} (1-12b)

where the configurations are normalized to unity (but not necessarily orthogonal).

$$\langle \Phi_i \vert \Phi_i \rangle = 1$$  \hspace{1cm} (1-13)

$E_i$ represents the set of eigenvalues which come from solution of the secular determinant (1-11); the lowest eigenvalue corresponds to the desired ground state total energy.

A much more difficult problem is that of optimizing the non-linear parameters ($n_k$, $a_k$, $p$) and much effort has been expended to determine the most efficient method of optimization. The pattern search technique of Hook and Jeeves$^{22}$ was the method employed herein. A description of the computer programs and flow charts is given in Appendix 3.

The coordinate system was set up as shown in Figure 1 with the origin taken at the molecular midpoint. For the hydrogen molecule the exact non-relativistic Hamiltonian, $H_\text{op}$, may be written (in atomic units)
Figure 1

The Coordinate System
where $V_1^2$ and $V_2^2$ are the kinetic energy operators for electrons 1 and 2; $r_{1A}^*, r_{1B}^*, r_{2A}^*, r_{2B}^*$ are the distances from electrons 1 and 2 and nuclei A and B, respectively; $r_{12}$ is the inter-electronic distance and $R$ is the internuclear distance.

Expansion of the general matrix elements $H_{ij}$ and $\Delta_{ij}$ after application of the appropriate operator leads to expressions composed of four types of integrals over the basis functions (1-4).

\[
H_{ij} = (1 + S_{x_i z_i})^{-1/2} (1 + S_{x_j z_j})^{-1/2} \left[ S_{x_i z_i} (T_{x_2 z_2} + V_{x_2 z_2}) + S_{x_j z_j} (T_{x_3 z_3} + V_{x_3 z_3}) + S_{x_k z_k} (T_{x_4 z_4} + V_{x_4 z_4}) + S_{x_l z_l} (T_{x_5 z_5} + V_{x_5 z_5}) \right] / R \]  

(1-15)

\[
\Delta_{ij} = (1 + S_{x_i z_i})^{-1/2} (1 + S_{x_j z_j})^{-1/2} \left[ S_{x_i z_i} S_{x_j z_j} + S_{x_k z_k} S_{x_l z_l} \right] / R \]  

(1-16)

Appendix 1 gives in detail the method for expanding matrix elements between non-orthogonal configurations in terms of the basis functions.

The basic integrals are

Overlap integrals:

\[
S_{x_i z_i} = \int \chi_{x_i}^*(i) \chi_{x_i} (i) \, d\nu_i  
\]  

(1-17)

Kinetic energy integrals:

\[
T_{x_i z_i} = \int \chi_{x_i}^*(i) \left[ -i \hbar \nabla^2 \right] \chi_{x_i} (i) \, d\nu_i  
\]  

(1-18)

Nuclear-electron attraction integrals:

\[
V_{x_i z_i} = \int \chi_{x_i}^*(i) \left[ \sum N \, \hbar \nabla^2 \right] \chi_{x_i} (i) \, d\nu_i  
\]  

(1-19)
where \( N \) represents either nucleus A or B

Electron-electron repulsion integrals:

\[
J_{r_1, r_2, r_3, r_4} = \int \chi_{r_1}^*(r_1) \chi_{r_2}^*(r_2) \frac{1}{r_{12}} \chi_{r_3}^*(r_3) \chi_{r_4}(r_4) \, d\rho_1 \, d\rho_2 \tag{1-20}
\]

\[
K_{r_1, r_2, r_3, r_4} = \int \chi_{r_1}^*(r_1) \chi_{r_2}^*(r_2) \frac{1}{r_{12}} \chi_{r_3}(r_3) \chi_{r_4}(r_4) \, d\rho_1 \, d\rho_2 \tag{1-21}
\]

The basic integrals of Eqs. (1-17) - (1-21) were evaluated in terms of a number of auxiliary functions such as the gamma function, incomplete gamma function and the incomplete beta function. Thus, the overlap integral is written:

\[
S_{l_1, l_2} = \delta_{m_1, m_2} \delta_{l_1, l_2} A_F(n_{l_1}, \alpha_{l_1}, p) A_F(n_{l_2}, \alpha_{l_2}, p) \frac{\Gamma[(n_{l_1} + n_{l_2} + 1)/p]}{\rho \, \Gamma[\alpha_{l_1} + \alpha_{l_2}][(n_{l_1} + n_{l_2} + 1)/p]} \tag{1-22}
\]

where \( \delta_{m_1, m_2}, \delta_{l_1, l_2} \) are Kronecker deltas and \( \Gamma[(n_{l_1} + n_{l_2} + 1)/p] \) is the gamma function defined by

\[
\Gamma(x) = \int_0^\infty e^{-t} t^{x-1} \, dt \tag{1-23}
\]

The kinetic energy integral is:

\[
T_{l_1, l_2} = \frac{1}{2} \delta_{m_1, m_2} \delta_{l_1, l_2} A_F(n_{l_1}, \alpha_{l_1}, p) A_F(n_{l_2}, \alpha_{l_2}, p) \frac{\Gamma(x) \rho(\alpha_{l_1} + \alpha_{l_2})}{\Gamma[\alpha_{l_1} + \alpha_{l_2}]}
\]

\[
\cdot \left[ \frac{n_{l_1}(n_{l_1} - 1) - \lambda_1 (\lambda_1 + 1) - \alpha_{l_1}(2n_{l_1} + p - 1)(n_{l_1} + n_{l_2} - 1)/(\alpha_{l_1} + \alpha_{l_2})}{\alpha_{l_1}^2} + \frac{n_{l_2}(n_{l_2} - 1) + p(n_{l_2} + n_{l_2} - 1)(\alpha_{l_2} + \alpha_{l_2})}{\alpha_{l_2}^2} \right] \tag{1-24}
\]

where here \( x = (n_{l_1} + n_{l_2} - 1)/p \) and it is required that the principal quantum numbers be such that \( (n_{l_1} + n_{l_2}) > 1 \).

The nuclear-electron attraction integral has the form:
\[ v_{x, z} = - \delta(m, m - m_2) A_r(n_{x, z}, \alpha_{r, z}, \rho) \sum_{k=0}^{l_{x, z} + l_{z, z}} \left[ \frac{4\pi}{2k + 1} \right]^{l_{x, z} + l_{z, z}} \]

\[ \cdot \sum_{N} Y_{l_{x, z}, m_{l_{x, z}}}(\Theta_{CN}, \Phi_{CN}) C^k(l, m_{l_{x, z}}, m_{l_{z, z}}) \]

\[ \cdot \left( \frac{\gamma(a, x)}{R_{CN}^l a^{l + 1} \rho (\alpha_{l_{x, z}} + \alpha_{l_{z, z}})} + \frac{\Gamma(b, x)}{\rho (\alpha_{l_{x, z}} + \alpha_{l_{z, z}})} \right) \]

(1-25)

Where in (1-25) \( R_{CN} \) is the distance from the origin of the coordinate system (C) to nucleus N (i.e. either A or B), \( Y_{l, m}(\Theta_{CN}, \Phi_{CN}) \) is a geometrical spherical harmonic which depends upon the angular coordinates of nucleus N. \( \gamma(a, x) \) and \( \Gamma(b, x) \) are the small and large incomplete gamma functions respectively, defined by:

\[ \gamma(a, x) = \int_0^x e^{-t} t^{a - 1} \, dt \]

(1-26)

\[ \Gamma(a, x) = \int_x^\infty e^{-t} t^{a - 1} \, dt \]

(1-27)

\( C^k(l_{x, z}, l_{z, z}) \) is the integral over a product of three spherical harmonics given by Condon and Shortley\(^{26}\) and

\[ x = (\alpha_{l_{x, z}} + \alpha_{l_{z, z}}) R_{CN} \]  

(1-28a)

\[ a = (n_{x, z} + n_{l_{x, z}} + \rho + 1)/\rho \]  

(1-28b)

\[ b = (n_{z, z} + n_{l_{z, z}} - \rho)/\rho \]  

(1-28c)
The repulsion integrals are given by:
\[
\begin{align*}
\mathcal{J}_{\ell_1, \ell_2, \ell_3, \ell_4} &= \delta(m, m_1 - m_3) \delta(m, m_2 - m_5) A_{\ell_1}(\ell_1) A_{\ell_2}(\ell_2) A_{\ell_3}(\ell_3) A_{\ell_4}(\ell_4) \\
&\quad \times \sum_{A = 1}^{(\ell_1, \ell_2)} C^A(\ell_1, m_1, \ell_2, m_2) C^A(\ell_3, m_3, \ell_4, m_4) \\
&\quad \cdot \left( \frac{\Gamma(s) \Gamma(t) \Gamma(1-s, t)}{\Gamma(1, t)} \int_0^1 t^{s-1} (1-t)^{\nu-1} dt + \frac{\Gamma(u) \Gamma(v) \Gamma(1-u, v)}{\Gamma(1, v)} \int_0^1 t^{u-1} (1-t)^{\nu-1} dt \right)
\end{align*}
\]
(1-29)

here
\[
\begin{align*}
S &= (n_{\ell_1} + n_{\ell_2} - \lambda) / \rho \quad (1-30a) \\
T &= (n_{\ell_2} + n_{\ell_3} + \lambda + 1) / \rho \quad (1-30b) \\
U &= (n_{\ell_3} + n_{\ell_4} - \lambda) / \rho \quad (1-30c) \\
\nu &= (n_{\ell_1} + n_{\ell_3} + \lambda + 1) / \rho \quad (1-30d) \\
A &= \frac{\alpha_{\ell_1} + \alpha_{\ell_2}}{\alpha_{\ell_1} + \alpha_{\ell_2} + \alpha_{\ell_3} + \alpha_{\ell_4}} \quad (1-30e)
\end{align*}
\]

The incomplete beta function is defined:
\[
\begin{align*}
\mathcal{I}_x(p, q) &= \mathcal{B}_x(p, q) / \mathcal{B}(p, q) \\
&= \int_0^1 t^{x-1} (1-t)^{p-1} dt \\
&= \frac{\Gamma(p) \Gamma(q)}{\Gamma(p+q)}
\end{align*}
\]
(1-31)

and the complete beta function is given by
\[
\mathcal{B}_x(p, q) = \int_0^1 t^{x-1} (1-t)^{p-1} dt
\]
(1-32)

Also
\[
\mathcal{I}_{1-x}(y, p) = 1 - \mathcal{I}_x(p, q)
\]
(1-33)
Similarly, the expression for the repulsion integral
\[ K_{\ell_1 \ell_2 l_3 l_4} \]
may be written down simply by interchanging the
\( l_3 \) with the \( l_4 \) parameters in (1-29).

Appendix 2 gives detailed procedures for obtaining
the above integral expressions.

2. FORCES

The force on any nucleus, \( N \), in a molecule is defined
as the negative gradient of the total energy with respect
to some nuclear coordinate(s) contained in the Hamiltonian
of the system. For a diatomic molecule one may choose
to use the internuclear distance, \( R \), since this automatically
fixes the nuclear positions with respect to each other.

Then,
\[ F^N(R) = -\frac{\partial E(R)}{\partial R} \quad (2-1) \]
where \( E(R) \), the total energy, is a function of the internuclear
distance, \( R \). Since \( E(R) \) corresponds to the expectation
value of the Hamiltonian, we have (neglecting the
negative sign for the moment)
\[ \frac{\partial E(R)}{\partial R} = \frac{\partial \langle H_0 \rangle}{\partial R} \quad (2-2) \]

\[ = \langle \Psi | \partial H_0 / \partial R | \Psi \rangle + \langle \partial \Psi / \partial R | H_0 | \Psi \rangle \]
\[ + \langle \Psi | H_0 | \partial \Psi / \partial R \rangle \]
By the hermitian nature of \( H_0 \) and use of the turnover
rule \(^{21}\)
\[ \langle \Psi | H_0 | \partial \Psi / \partial R \rangle = \langle \partial \Psi / \partial R | H_0 | \Psi \rangle \quad (2-3) \]

For the exact stationary state eigenfunction of \( H_0 \), (1-6)
applies, so that the last two terms in (2-2) cancel since their sum is

\[ E(R) \frac{\partial}{\partial R} \int \psi^* \psi \, d\nu = E(R) \frac{\partial}{\partial R} (1) = 0 \]  

(2-4)

where \( \psi \) is assumed to be normalized. One has then arrived at a statement of the generalized Hellmann-Feynman theorem (GHFT).

\[ \partial \langle H_{op} \rangle / \partial R = \langle \partial H_{op} / \partial R \rangle = \langle \psi \partial H_{op} / \partial R | \psi \rangle \]  

(2-5)

In the above derivation the tacit assumption has been made that nuclear and electronic motions are essentially independent of each other; this is known as the Born-Oppenheimer approximation.\(^{28,29}\)

Since the Hamiltonian operator may be partitioned into kinetic and potential energy parts, respectively,

\[ H_{op} = T_{op} + V_{op} \]  

(2-6)

then if

\[ T_{op} \neq T_{op} (R) \]  

(2-7)

that is, if \( T_{op} \) is independent of \( R \), it follows that

\[ \partial E(R) / \partial R = \langle \partial V_{op} / \partial R \rangle = \langle \psi \partial V_{op} / \partial R | \psi \rangle \]  

(2-8)

which is a statement of the Hellmann-Feynman electrostatic theorem (HFET).
However, Coulson and Hurley\textsuperscript{9} have pointed out that for approximate wave functions condition (2-7) depends upon the coordinate system employed to construct the wave function and to express the Hamiltonian. Indeed, spheroidal coordinates, used in many two center computations, are one such example of a coordinate system which leads to an $R$-dependent kinetic energy operator, $T_{op}(R)$. The spherical polar coordinate system fixed in space\textsuperscript{30} employed throughout this thesis satisfies requirement (2-7) and hence, (2-8) could be used to compute forces rather than (2-5). The derivation of the theorem (2-8) given above holds only for the exact eigenfunction of $H_{op}$. Additional specifications must be set down if one desires to compute forces from (2-8) with the use of approximate wave functions.

Following Hurley,\textsuperscript{3} consider the case of an approximate wave function for a diatomic molecule

\[ \varphi = \varphi (u_1, u_2, \ldots, u_n) \quad (2-9) \]

where

\[ u_r = u_r(R) \quad (2-10) \]

that is, $\varphi$ is specified by some set of parameters, $u_r$, which themselves depend upon $R$. In the present case of a variational trial wave function, the $u_r$ correspond to the $C_1$, $n_\ell$, $a_\ell$ and $p$ of the limited basis set used to construct the desired approximation.

The internuclear forces computed by the use of such a wave function are given by (neglecting the negative sign)

\[ \frac{dE}{dR} = \left[ \frac{\partial E}{\partial u_r} \right]_{u_r} + \sum_r \left[ \frac{\partial E}{\partial u_r} \right]_{u_r} \frac{du_r}{dR} \quad (2-11) \]
where \( r \neq s \) and \( \{ u_r \} \) denotes the (finite) subset of parameters, \( u_r \), in the basis making up the wave function.

At optimization the summation term in (2-11) drops out since by definition of variational optimization

\[
\left[ \frac{\partial E}{\partial u_r} \right]_{R, \{ u_s \}} = 0
\]  

(2-12)

for all \( u_r \) in the trial wave function. In lieu of condition (2-12), the summation term may become zero if the parameters are made independent of \( R \), that is if

\[
\frac{du_r}{dR} = 0
\]  

(2-13)

It is not clear how this condition (2-13) might be accomplished, if at all, for a trial wave function composed of a finite number of parameters. For the exact wave function, of course, the quantities \( u_r \) are no longer dependent upon \( R \) since the exact wave function may be expanded in a complete set of basis functions. (Recall from the exact solution of the hydrogen atom, for example, that \( n \) is the principal quantum number of the complete set of H-like functions and a constant.) However, we shall assume optimization of the approximate wave function and hence we need not be concerned further with (2-13). Assuming optimization, the expression for computation of forces becomes

\[
\frac{dE}{dR} = \left[ \frac{\partial E}{\partial R} \right]_{u_r^{\text{opt}}} = \left[ \frac{\partial T}{\partial R} \right]_{u_r^{\text{opt}}} + \left[ \frac{\partial V}{\partial R} \right]_{u_r^{\text{opt}}}
\]  

(2-14)

where we have made use of the fact that the total energy is the sum of the kinetic and potential energies.
Extension of the above equations to polyatomic molecules may easily be made by taking the partial(s) with respect to the desired nuclear coordinate(s) while holding other nuclear positions fixed. By so doing the total differential on the left hand side of (2-14) becomes equivalent to the partial(s) on the right hand side.

Continuing, each term in (2-14) may be written

\[ \left( \frac{\partial T}{\partial R} \right)_{\psi_{\text{opt}}} = \left( \frac{\partial \langle T_{\text{opt}} \rangle}{\partial R} \right)_{\psi_{\text{opt}}} \]  

\[ = \langle \psi_{\text{opt}} | \frac{\partial T_{\text{opt}}}{\partial R} | \psi_{\text{opt}} \rangle + \langle \psi_{\text{opt}} | \frac{\partial T_{\text{opt}}}{\partial R} | \psi_{\text{opt}} \rangle \]

\[ + \langle \psi_{\text{opt}} | \frac{\partial T_{\text{opt}}}{\partial R} | \psi_{\text{opt}} \rangle \]

\[ = \langle \psi_{\text{opt}} | \frac{\partial V_{\text{opt}}}{\partial R} | \psi_{\text{opt}} \rangle + \langle \psi_{\text{opt}} | \frac{\partial V_{\text{opt}}}{\partial R} | \psi_{\text{opt}} \rangle \]

\[ + \langle \psi_{\text{opt}} | \frac{\partial V_{\text{opt}}}{\partial R} | \psi_{\text{opt}} \rangle \]

\[ \psi_{\text{opt}} \] denotes the wave function composed of the variationally determined optimum parameters, \( \psi_{\text{opt}} \).

Assuming that the coordinate system is chosen such that (2-7) is fulfilled, then the middle term of (2-15) drops out. Furthermore, in order that (2-14) reduce to (2-8), a statement of the HFET, it is necessary that

\[ \frac{\partial \psi_{\text{opt}}}{\partial R} = 0 \]  

(2-17)

that is, the parametrically optimized trial wave function must exhibit no explicit R-dependence. Berlin\(^7\) has shown that, for the case of the exact wave function, the potential
energy and kinetic energy contributions to the ∂Ψ/∂R terms of (2-15) and (2-16) cancel. Such cancellation does not generally occur for approximate wave functions and the ∂Ψ/∂R terms must be eliminated by requirement (2-17).

Assuming (2-17) and substituting (2-15) and (2-16) into (2-14) one obtains (with insertion of the negative signs)

\[
F_{HFET}^N (R) = -\left[ \frac{\partial E}{\partial R} \right]_{\Psi_{opt}^N} = -\left[ \frac{\partial V_{opt}}{\partial R} \right]_{\Psi_{opt}^N} = -\langle \Psi_{opt}^N | \frac{\partial V_{opt}}{\partial R} |\Psi_{opt}^N \rangle
\]

which is a statement of the HFET for a variationally optimized wave function explicitly independent of the internuclear distance, R. In general (2-17) does not hold for approximate wave functions and it is this failure to meet such a condition which negates the HFET for such wave functions.

Forces were computed from (2-18) for various values of the internuclear distance by the use of a number of OCE trial wave functions.

For the hydrogen molecule

\[
V_{opt} = -(1/r_{1A} + 1/r_{1B}) - (1/r_{2A} + 1/r_{2B}) + 1/r_{12} + 1/R
\]

(2-19)

However, the two electron operator, 1/r_{12}, is independent of R so that the force on nucleus N (either A or B) along the internuclear axis is

\[
F_{HFET}^N (R) = -\langle \Psi_{opt}^N | \frac{\partial V_{opt}}{\partial R} |\Psi_{opt}^N \rangle
+ \langle \Psi_{opt}^N |\frac{\partial}{\partial R}[\gamma_{1a} + \gamma_{1b} + \gamma_{2a} + \gamma_{2b}] |\Psi_{opt}^N \rangle
\]

(2-20)
Noting that the R-dependent part of $V_{op}$ is essentially a one-electron operator, one may integrate out the coordinates of all electrons, save one, to obtain the quantum mechanical charge density

$$\rho = \sum_{\mu=1}^{3} \rho_{\mu}$$

(2-21)

where the summation is over electron coordinates, $\mu$, and

$$\rho_{\mu} = \int \psi^*_{(1,2)} \psi_{(1,2)} \, dn_{\mu}$$

(2-22)

where $\mu = 1$ or 2.

For a multiconfiguration wave function

$$\rho_{\mu} = \sum_{i,j} \rho_{ij}$$

(2-23)

where the matrix elements over configurations, $\rho_{ij}$, are given by

$$\rho_{ij} = c_i^* c_j \int \Phi_i^* \Phi_j \, dn_{\mu}$$

(2-24)

If the configurations $\Phi_i$ and $\Phi_j$ were orthonormal, $\rho_{\mu}$ would reduce to a sum of the diagonal elements (the trace), $\rho_{i1}$. However, the basis (1-4) is not orthogonal and hence, neither are the configurations so that the general matrix element, $\rho_{ij}$, expanded in terms of the basis functions is given by

$$\rho_{ij} = c_i^* c_j \left[ 2(1 + S_{x_1 s_1}) \right]^{-\lambda_a} \left[ 2(1 + S_{x_2 s_2}) \right]^{-\lambda_b}$$

$$\cdot \left[ S_{s_1 s_4} X^{(i)}_{x_1} X^{(i)}_{x_2} + S_{s_2 s_3} X^{(i)}_{x_2} X^{(i)}_{x_3} \right.$$  

$$\left. + S_{s_3 s_4} X^{(i)}_{x_3} X^{(i)}_{x_4} + S_{s_1 s_2} X^{(i)}_{x_1} X^{(i)}_{x_4} \right]$$

(2-25)
The HFET then becomes

\[ F_{\text{HFET}}^N(R) = 1/R^2 + \int \rho \left[ \alpha (1/r_a + 1/r_b)/\varepsilon R \right] \, d\varepsilon \]  

(2-26)

Substitution of equations (2-21) through (2-25) into (2-26) and integration over coordinates \( dv_1 \) leads to

\[ F_{\text{HFET}}^N(R) = 1/R^2 + \sum_{i,j} F_{ij} \]  

(2-27)

where in an obvious notation

\[ F_{ij} = C_i^* C_j (1+ S_i t_a^2)^{-v_a} (1+ S_j t_b^2)^{-v_b} \cdot \left[ S_k t_a F_{k} t_a + S_k t_b F_{k} t_b + S_k t_a t_b F_{k} t_a t_b \right] \]  

(2-28)

and the force integrals over basis functions are given by

\[ F_{i,a} = \delta (m_i, m_i - m_a) A_r (\ell_1) A_r (\ell_2) \sum_{\varepsilon = \ell_1 - \ell_2} \left( \frac{4\pi}{2 \varepsilon + 1} \right)^{v_a} \]  

\[ \cdot \sum_{\ell} Y_{\ell,1m_1} (\theta_{CN}, \phi_{CN}) C_i^* (\ell_i, m_i, \ell_2 m_a) [2(n)/(PR)] \]  

\[ \cdot \left( \frac{-b(x) \gamma(\alpha, x)}{[R_{CN}^{\alpha+1} (\alpha+\alpha_2)]^\alpha} + \frac{I_{CN} \Gamma_{PB} (b, x)}{(\alpha_1+\alpha_2)^{b/\alpha}} \right) \]  

(2-29)

Here

\[ x = (\alpha_1+\alpha_2) R_{CN}^\alpha \]  

\[ a = (n_1 + n_2 + \alpha_1 + \alpha_2)/p \]  

\[ b = (n_1 + n_2 - \alpha_1)/p \]

Equation (2-29) may be derived by differentiating (1-25) with respect to \( R \).

For purposes of comparison, forces were also computed from the slope of the total energy curve.

\[ F_{\text{slope}}^N(R) = -\partial E/\partial R = (2T + V)/R \]  

(2-30)
or since \( E = T + V \)

\[
F_{\text{slope}}^N (R) = (T + E)/R \tag{2-31}
\]

The experimental force curve was computed by differentiating of the Hulburt-Hirschfelder potential function.

\[
F_{\text{exper}}''(R) = -\left[ \frac{1}{2} \frac{\omega_e}{\sqrt{\omega_e^2 R_e}} \right] \left[ \frac{\hbar c_o e^2/a_o^2}{2} \exp(-x) \left( 1 - \exp(-x) \right) \right]
+ C x^2 \exp(-2x) \left( 3 - 2x \left( 1 - b(1 - x) \right) \right) \tag{2-32}
\]

where

\[
x = \left[ \frac{\omega_e}{2 \sqrt{\omega_e D}} \right] \frac{(R - R_e)}{R} \tag{2-33}
\]

and \( h \) is Planck's constant, \( c_o \) is the speed of light, \( e \) and \( a_o \) are the charge on the electron and the first Bohr radius, respectively, all in cgs units. Definitions and numerical values for the spectroscopic constants are given in reference 11. The quantity \( \hbar c_o e^2/a_o^2 \) was needed to convert the forces to atomic units. Equations (2-27) and (2-31) also compute force values in atomic units.
SECTION IV

RESULTS

A preliminary calculation was performed using a simple single closed shell configuration wave function in a 1s GTF basis. The parameter values, forces from the theorem and the slope as a function of internuclear distance are presented in Table I. The forces computed from the theorem agree numerically with those computed from the slope to two or three figures. This agreement suggests that the forces computed in either manner should be identical, at least for this simple function. That this is indeed so may easily be shown analytically. Figure 2 is a graphical comparison of the data in Table I with the experimental forces of Table II and since the forces from the slope are equivalent to those from the theorem, only the former values were plotted. As is to be expected for such a simple function, agreement with experiment is poor although extrapolation of the theoretically computed curve to zero force predicts a surprisingly good, if somewhat large, value of 1.45 au as the equilibrium internuclear distance (that internuclear distance at which the net forces are zero) compared to the experimental value of 1.40 au.

As expected, there is no effect upon the satisfaction of the theorem due to the introduction of angular and radial correlation. Forces computed from 2 configuration wave
Table I

Optimized Non-linear Parameter, Total Molecular Energy, Kinetic Energy and Forces as a Function of Internuclear Distance for a Single Closed Shell Configuration OCE-WF of the Hydrogen Molecule In a 1s GTF Basis

<table>
<thead>
<tr>
<th>R</th>
<th>1.20</th>
<th>1.30</th>
<th>1.40</th>
<th>1.50</th>
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<tr>
<td>α_s</td>
<td>0.38383025</td>
<td>0.35796642</td>
<td>0.33461988</td>
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</tr>
<tr>
<td>E</td>
<td>-0.93469906</td>
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<td>-0.95468807</td>
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<tr>
<td>T</td>
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<td>1.0738993</td>
<td>1.0038595</td>
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</tr>
<tr>
<td>F_slope</td>
<td>+0.18065989</td>
<td>+0.09663255</td>
<td>+0.035122637</td>
<td>-0.010143973</td>
</tr>
<tr>
<td>F_HFET</td>
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<td>+0.096078694</td>
<td>+0.034842554</td>
<td>-0.010927960</td>
</tr>
</tbody>
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<th>1.70</th>
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<th>1.90</th>
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<tr>
<td>α_s</td>
<td>0.29376292</td>
<td>0.27619243</td>
<td>0.26005006</td>
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<tr>
<td>E</td>
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<td>F_HFET</td>
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<td>α_s</td>
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<td>E</td>
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Table I continued

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<th>3.00</th>
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<table>
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<th>3.40</th>
<th>3.50</th>
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<td>-0.11402476</td>
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Figure 2

Plot of Force vs. Internuclear Distance for a Single Closed Shell Configuration OCE-WF in a 1s GTF Basis

(1) $F_{\text{exper}}$ (Table II)
(2) $F_{\text{slope}}$ (Table I)
Table II

Experimental Forces as a Function of Internuclear Distance for The Hydrogen Molecule from the Hulbert-Hirschfelder Potential Function

<table>
<thead>
<tr>
<th>$R$</th>
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<th>$R$</th>
<th>$F_{\text{exper}}$</th>
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functions in GTF, STF and GETF bases are given in Tables III, IV, V and displayed graphically in Figures 3, 4 and 5, respectively. One may readily see from the latter that the change in basis from GTF to STF to GETF also has no effect upon satisfaction of the theorem (since the two curves are essentially superposed one on the other) so long as the respective wave function parameters are fully optimized. The importance of optimization is illustrated by the divergence of the slope and HFET curves in Figure 4 (for the STF wave function) where optimization was artificially constrained for large values of the internuclear distance. This suggests that comparison of the forces computed from the slope to those computed from the HFET is a highly sensitive test of wave function optimization.

Agreement with experiment for all three functions becomes progressively worse as R increases, although agreement is good in the region of the equilibrium internuclear distance and in fact, the GTF basis wave function predicts (perhaps fortuitously) the experimental equilibrium internuclear distance, 1.40 au. Both the STF and GETF wave functions predict somewhat shorter equilibrium values of 1.34 and 1.33 au, respectively.

The best of the three wave functions energetically is that in the GETF basis with a total energy of -1.1154604 au compared to -1.1125317 and -1.0987644 au for the respective comparable STF and GTF functions (all at the experimental internuclear distance of 1.40 au). The experimental total energy is given as -1.17 au at 1.40 au of distance.
### Table III

Optimized Non-linear and Linear Parameters, Total Molecular Energy, Kinetic Energy and Forces as a Function of Internuclear Distance for a Two Configuration OCE-GTF-WF of the Hydrogen Molecule

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Figure 3

Plot of Force vs. Internuclear Distance for a Two Split Shell Configuration OCE-GTF-WF

(1) \( F_{\text{exper}} \) (Table II)
(2) \( F_{\text{slope}} \) (Table III)
(3) \( F_{\text{HFET}} \) (Table III)
Table IV

Optimized Non-linear and Linear Parameters, Total Molecular
Energy, Kinetic Energy and Forces as a Function of Internuclear
Distance for a Two Configuration OCE-STF-WF of the Hydrogen
Molecule

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Plot of Force vs. Internuclear Distance for a Two Split Shell Configuration OCE-STF-WF. Divergence of Curves (2) and (3) with Increasing $R$ Indicates Lack of Optimization of the Trial Wave Function.

(1) $F_{\text{exper}}$ (Table II)
(2) $F_{\text{slope}}$ (Table IV)
(3) $F_{\text{HFET}}$ (Table IV)
Table V

Optimized Non-linear and Linear Parameters, Total Molecular Energy, Kinetic Energy and Forces as a Function of Internuclear Distance for a Two Configuration OCE-GEFF-WF of the Hydrogen Molecule

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Figure 5

Plot of Force vs. Internuclear Distance for a Two Split Shell Configuration OCE-GETF-WF

(1) $F_{\text{exper}}$ (Table II)
(2) $F_{\text{slope}}$ (Table V)
(3) $F_{\text{HFET}}$ (Table V)
However, on the basis of forces, the three functions are quite comparable except for the fact that the energetically most inferior function constructed from Gaussians leads to the best prediction of the equilibrium internuclear separation.

Table VI reproduces the parameters and energies from Bishop's\textsuperscript{32} seven configuration STF wave function. The forces computed from this wave function are given at the bottom of the same table. Again the theorem is shown to be satisfied since the slope forces agree quantitatively with those computed from the HFET. Perhaps more significant is the good agreement between the forces computed from this function and the experimental results of Table II. Although the relative errors are large because of the smallness of the forces in the region near the equilibrium point, the absolute magnitudes compare well. Thus, it appears that single center wave functions composed of a computationally tractable number of configurations have the capability of predicting quantitatively good force values, at least in the region of the equilibrium internuclear distance.
Table VI

Optimized Non-linear and Linear Parameters, Total Molecular Energy, Kinetic Energy and Forces as a Function of Internuclear Distance for a Seven Configuration OCE-STF-WF of the Hydrogen Molecule

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Parameter values, total and kinetic energies are taken from Bishop (reference 32) and reproduced here for convenience.
SECTION V

DISCUSSION

The results presented in the foregoing show that, contrary to original expectations, one-center expansion wave functions do indeed satisfy the Hellmann-Feynman electrostatic theorem, without need of a floating parameter, if the following three conditions are fulfilled:

1) The coordinate system must be chosen such that the kinetic energy operator is independent of $R$.

2) The wave function must be optimized with respect to all parameters used in the construction of the trial function.

3) The basis functions must have no explicit dependence upon the internuclear distance, although a parametric (implicit) dependence is allowable if condition (2) is subsequently fulfilled.

In retrospect, the above conclusions might easily have been seen from a consideration of the basic types of integrals [equations (1-17) through (1-21)] which arise in the expectation value of the Hamiltonian for both single center and multicenter trial wave functions. Such a comparison (most easily done when the basis functions are Gaussian) shows that all of the basic integrals of multicenter type contain explicit $R$-dependencies. This arises from the necessity of transforming each basis function, usually centered on a nucleus, from that nucleus to a point in common with the origin of the volume element of integration.
Without such a transformation, the integrals could not be evaluated. Hence, for multicenter trial wave functions, overlap, kinetic energy, nuclear-electron attraction and even electron-electron repulsion integrals contain an explicit $R$-dependence introduced by this transformation. Integral formulae for simple $1s$ Gaussians on fixed nuclear centers have been given by Shavitt$^{37}$ and Boys.$^{38}$

On the other hand, in the case of a single center function, only the nuclear-electron attraction integrals (1-19), (1-25) exhibit explicit $R$-dependence since these are the only type of single center basic integrals which require a coordinate transformation which makes them explicit functions of $R$. Moreover, the $R$-dependence is introduced by a transformation of the nuclear-electron part of the Hamiltonian and not by a transformation of the basis functions. Since any trial wave function which is composed of a linear combination of Slater determinants may ultimately be seen to expand into a superposition of the basis functions [by expanding the determinants as sums and differences of products of basis functions as in (1-15)], one may readily see that when differentiation with respect to $R$ of the respective types of wave functions is accomplished, the former wave function will lead to many terms explicitly containing powers of $R$. The latter single center function will exhibit no such explicit $R$ dependence and hence the derivatives will be zero (for the optimized wave function).
These non-zero derivatives of the wave function for the multiconfigurational case will lead to contributions to the force from the kinetic energy (2-15) which, of course, immediately negates the theorem. Similar terms arise in the potential energy (2-16) and there is no guarantee that the contribution from the kinetic energy is exactly offset by the comparable terms in the potential energy as is the case for the exact wave function. Hurley's introduction of a variational floating parameter seeks to eliminate the explicit dependence of \( \Psi \) on \( R \) and change it to a parametric dependence (2-11). If this is done the HFET may be satisfied by the multiconfigurational approximate wave function (provided the kinetic energy operator is also independent of \( R \)). Integral formulae for 1s Gaussians containing such floating parameters have been given by Preuss. The lack of explicit \( R \)-dependence is readily apparent. For optimized single center approximate wave functions \( \partial \Psi / \partial R = 0 \) so that the above mentioned kinetic energy and potential energy terms immediately drop out and the theorem is satisfied directly.

Introduction of angular correlation through the use of the \( d_0 \) function and radial correlation through the use of one or more split shell configurations shows no apparent effect on satisfaction of the theorem for OCE-WF's. That this should be so is readily understandable in light of the conditions laid down above for satisfaction of the theorem for this type of function.
An extension of this work could be undertaken to investigate the general usefulness of OCE-GTF-WF's for predicting internuclear distances. Although it is known that energetically, one for one, Gaussians are inferior to STF's (and now also GETF's) this work has shown that, at least for the simple system of a homonuclear diatomic molecule, OCE-GTF-WF's predict internuclear distances in better agreement with experiment than comparable OCE-WF's in either an STF or GETF basis. A more demanding test of an OCE-GTF-WF to predict bond lengths would be a study of a simple heteronuclear diatomic molecule such as LiH.

Another extension of interest would be a study to determine to what extent the kinetic energy and potential energy contributions to the computation of forces arising from the terms containing the derivative of the wave function with respect to \( R \), (2-15) and (2-16), for a multicenter wave function cancel each other. This could lead one to an estimate of the extent of the difference between forces computed from the slope of the energy curve and the HFET for multicenter wave functions not containing a floating parameter.

The importance of the present work is that it shows that optimized single center approximate wave functions by their very nature of being explicitly independent of nuclear positions automatically satisfy the GHFT (2-5) and that they may easily be made to satisfy the HFET (2-18) if the coordinate system is chosen with care such that (2-7) obtains. Furthermore, this implies that the inclusion of
a variational floating parameter in order to satisfy the theorem is necessary only in the case of multicenter trial wave functions so as to remove the explicit R-dependence introduced by the transformations necessary for integral evaluation. Hence, we have demonstrated yet another advantage of the single center approach to the construction of approximate wave functions. Finally, the encouraging agreement of the seven term wave function with experimentally determined forces provides additional support for the use of OCE-WF's to compute various molecular properties.
SECTION VI

SUMMARY

Simple one and two configuration single center wave functions in GTF, STF and GETF bases were used to compute internuclear forces for the hydrogen molecule by taking the slope of the total energy curve and by computation from the Hellmann-Feynman electrostatic theorem.

Contrary to expectations, the forces computed by these alternative methods were the same, indicating satisfaction of the HFET, if the wave function was variationally optimized. Such satisfaction of the theorem was attributable to the fact that single center wave functions were not explicitly functions of the nuclear coordinates but rather implicitly dependent through parameters.

The results showed that satisfaction of the theorem was basis independent so long as the basis functions themselves were not explicit functions of R.

The introduction of angular correlation through the use of the $d_{\theta}$ function and radial correlation by including one or more split shell configurations also had no bearing on the satisfaction of the theorem since OCE-WF's with and without $l$ values greater than zero and of one or more closed or split shell configurations all satisfied the theorem.

The OCE-WF results implied that variational optimization did not lead to the satisfaction of the HFET
for most approximate wave functions because they were of
the multicenter type which led to the introduction of an
explicit R-dependence when the basis functions were transformed
to a center of integration. Hence, an approximate multicenter
wave function without the floating feature to make the basic
integrals independent of R, would be expected to approach
satisfaction of the theorem only if a very large basis set
were used i.e. in the limit as the trial wave function began
to approach the exact wave function.

The use of Gaussian functions led to predictions of
the internuclear distance which were much closer to the
experimental equilibrium value than those of the other two
bases. This suggested that Gaussians may be especially good
for predicting bond lengths. Moreover, although the GTF-WF's
were energetically far inferior to either the STF or GETF
wave functions, the forces predicted were quantitatively and
qualitatively comparable for all three cases.

Finally, the use of Bishop's seven term STF wave
function showed promise that OCE-WF's have the capability
of predicting values for internuclear forces approaching
the experimental values in accuracy.
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APPENDIX 1

MATRIX ELEMENTS OF OPERATORS FOR DETERMINANTAL WAVE FUNCTIONS

COMPOSED OF NON-ORTHOGONAL BASIS FUNCTIONS

Solution of the secular determinant (1-11) for the energy eigenvalues, $E_1$, and the associated eigenvectors, $C_1$, computation of the quantum mechanical charge density matrix elements (2-24) and calculation of forces from the HFET require expansion of matrix elements over configurations (1-2), where the split shell configurations used herein are a linear combination of two Slater determinants, for a specified operator, $\Omega_{\text{op}}$, in terms of the basis functions. If the basis functions employed are orthonormal, standard formulae are available to give the desired expansions. However, basis functions (1-4) used in the present work are non-orthogonal, although they are normalized.

Prior to expansion, the determinants constituting the configuration(s) are put into maximum coincidence (reference 33 p. 24), i.e. columns are interchanged until as many as possible in one determinant have the same spin as the corresponding column in the other. For the $^1\Sigma_g^+$ ground state split shell configuration of the hydrogen molecule, one interchange of columns is required in the second determinant, which, since it is an odd number of interchanges, alters the sign preceeding this latter determinant. One may
write
\[ \Phi_i = \frac{N_i}{\sqrt{2^i}} \left( \begin{vmatrix} X_{i1}'(1) & \bar{X}_{j2}'(1) \\ X_{i1}(2) & \bar{X}_{j2}(2) \end{vmatrix} + \begin{vmatrix} X_{i3}'(1) & \bar{X}_{j3}'(1) \\ X_{i3}(2) & \bar{X}_{j3}(2) \end{vmatrix} \right) \] (Al-1)

Determination of the configuration normalization constant, \( N_1 \), and the overlap matrix elements between configurations, \( A_{ij} \), are examples of expansions in which the operator is a constant, the unit operator \( \Omega_{op} = 1 \). The former will be illustrated in detail, while the latter follows by analogy.

The normalization condition requires that
\[ \langle \Phi_i | \Omega_{op} | \Phi_i \rangle = \langle \Phi_i | \Phi_i \rangle = 1 \] (Al-2)

where \( \Omega_{op} = 1 \). Upon substitution of (Al-1) into (Al-2) and expansion, one has
\[ N_i^2 \left[ \frac{1}{2^i} \left( \begin{vmatrix} X_{i1}'(1) & \bar{X}_{j2}'(1) \\ X_{i1}(2) & \bar{X}_{j2}(2) \end{vmatrix} \Omega_{op} \begin{vmatrix} X_{i1}'(1) & \bar{X}_{j2}'(1) \\ X_{i1}(2) & \bar{X}_{j2}(2) \end{vmatrix} + \begin{vmatrix} X_{i3}'(1) & \bar{X}_{j3}'(1) \\ X_{i3}(2) & \bar{X}_{j3}(2) \end{vmatrix} \Omega_{op} \begin{vmatrix} X_{i3}'(1) & \bar{X}_{j3}'(1) \\ X_{i3}(2) & \bar{X}_{j3}(2) \end{vmatrix} + \frac{1}{2^i} \left( \begin{vmatrix} X_{i3}'(1) & \bar{X}_{j3}'(1) \\ X_{i3}(2) & \bar{X}_{j3}(2) \end{vmatrix} \Omega_{op} \begin{vmatrix} X_{i3}'(1) & \bar{X}_{j3}'(1) \\ X_{i3}(2) & \bar{X}_{j3}(2) \end{vmatrix} \right) = 1 \] (Al-3)

For the simple 2x2 case one could proceed to fully expand each set of two determinants; however, this quickly becomes impractical for larger determinants. Following Slater (reference 29 Appendix 9) one may show that each term in (Al-3) may be simplified. For example, rewriting the first term we have

\[ \frac{N_i}{\sqrt{2}} \left( \langle X_{i1}'(1) | X_{j2}(2) \rangle + \langle X_{i1}'(1) | X_{j2}(2) \rangle \right) = \frac{N_i}{\sqrt{2}} \left( \langle X_{i1}'(1) | \bar{X}_{j3}(2) \rangle + \langle X_{i1}'(1) | \bar{X}_{j3}(2) \rangle \right) = 1 \]
\[
\frac{2!}{2!} \left\langle \begin{array}{cc}
\chi_{e_{i}}^{(i)} & 0 \\
0 & \overline{\chi}_{e_{a}}^{(a)}
\end{array} \right| \Omega_{op} \left| \begin{array}{cc}
\chi_{e_{i}}^{(i)} & \overline{\chi}_{e_{a}}^{(i)} \\
\chi_{e_{a}}^{(a)} & \overline{\chi}_{e_{a}}^{(a)}
\end{array} \right\rangle \tag{A1-4}
\]

where the 2! in the numerator comes from the fact that if another set of elements other than those of the principal diagonal were chosen for the expansion of the first determinant, another term identical to (A1-4) would be produced (without the 2! in the numerator). In general, for the N x N case there would arise N! identical expressions of the type (A1-4) (without the N! in the numerator preceding the integral). The other two terms of (A1-3) may similarly be condensed to form (A1-4). Use of the rule for determinant or matrix multiplication (row x column) on (A1-4) leads to a determinant of overlap integrals over the basis set.

\[
\begin{vmatrix}
\langle \chi_{e_{i}}^{(i)} | \chi_{e_{i}}^{(i)} \rangle & \langle \chi_{e_{i}}^{(i)} | \overline{\chi}_{e_{a}}^{(i)} \rangle \\
\langle \overline{\chi}_{e_{a}}^{(a)} | \chi_{e_{i}}^{(a)} \rangle & \langle \overline{\chi}_{e_{a}}^{(a)} | \overline{\chi}_{e_{a}}^{(a)} \rangle
\end{vmatrix} = 1 \tag{A1-5a}
\]

Similarly,

\[
\begin{vmatrix}
\langle \chi_{e_{i}}^{(i)} | \chi_{e_{i}}^{(i)} \rangle & \langle \chi_{e_{i}}^{(i)} | \overline{\chi}_{e_{a}}^{(i)} \rangle \\
\langle \overline{\chi}_{e_{a}}^{(a)} | \chi_{e_{i}}^{(a)} \rangle & \langle \overline{\chi}_{e_{a}}^{(a)} | \overline{\chi}_{e_{a}}^{(a)} \rangle
\end{vmatrix} = 2 S_{e_{i}e_{a}} \tag{A1-5b}
\]

\[
\begin{vmatrix}
\langle \chi_{e_{a}}^{(i)} | \chi_{e_{a}}^{(i)} \rangle & \langle \chi_{e_{a}}^{(i)} | \overline{\chi}_{e_{i}}^{(i)} \rangle \\
\langle \overline{\chi}_{e_{i}}^{(a)} | \chi_{e_{a}}^{(a)} \rangle & \langle \overline{\chi}_{e_{i}}^{(a)} | \overline{\chi}_{e_{i}}^{(a)} \rangle
\end{vmatrix} = 1 \tag{A1-5c}
\]

where, in the above, the determinants were expanded in the usual manner and integration over the electron coordinates
includes summation over spin, so that many overlaps are zero due to spin orthogonality; the basis functions are assumed normalized.

Substitution of equations (Al-5) into (Al-3) and solving for \( N_i \) leads to the normalization expression (1-3).

The expression (1-16) for the overlap matrix elements, \( A_{ij} \), may readily be obtained using the method of expansion illustrated above.

The Hamiltonian operator (1-14) may be considered to be composed of three types of operators, a constant operator, \( \Omega_{op} \), a one electron part, \( \Omega_{op}(1) \), and a two electron part, \( \Omega_{op}(1,2) \).

Explicitly

\[
\begin{align*}
\Omega_{op} &= \frac{1}{R} \\
\Omega_{op}(1) &= -\frac{1}{2} \nabla_i^2 - \left( \frac{1}{r_{1a}} + \frac{1}{r_{1b}} \right) \\
\Omega_{op}(1,2) &= \frac{1}{r_{1a}}
\end{align*}
\]

where the numbers in the brackets indicate the electronic coordinates on which the operator acts. The case of the constant operator (Al-6a) has already been treated above since it is analogous to the treatment given the unit operator. Application of the one electron operator \( \Omega_{op}(1) \) to configurations (1-2) leads to an expression similar to (Al-3) except that the operator is now \( \Omega_{op}(1) \) rather than a constant, \( \Omega_{op} \), and the expression, in general, is not equal to unity. Continuing, simplification (Al-4) may be applied so that by multiplying the determinants and bearing in mind that \( \Omega_{op}(1) \) operates only on coordinates of electron (1), that is, only on the first row of the combined determinant,
one obtains

\[
\begin{vmatrix}
\langle \chi_2^{(1)} | \Omega_{\text{op}}^{(1)} | \chi_2^{(1)} \rangle & \langle \chi_2^{(1)} | \Omega_{\text{op}}^{(1)} | \chi_{2\alpha}^{(1)} \rangle \\
\langle \chi_{2\alpha}^{(2)} | \chi_2^{(1)} \rangle & \langle \chi_{2\alpha}^{(2)} | \chi_{2\alpha}^{(1)} \rangle 
\end{vmatrix} = T_{2\alpha,2\alpha} + V_{2\alpha,2\alpha} S_{2\alpha,2\alpha} \quad (A1-8)
\]

Expansion of the determinant in the usual manner and application of the operator leads to the result

\[
\langle \chi_2^{(1)} | \Omega_{\text{op}}^{(1)} | \chi_2^{(1)} \rangle \langle \chi_{2\alpha}^{(2)} | \chi_{2\alpha}^{(1)} \rangle = \left[ T_{2\alpha,2\alpha} + V_{2\alpha,2\alpha} \right] S_{2\alpha,2\alpha}
\]

where, again some terms drop out because of spin orthogonality. Likewise the operator for electron (2) coordinates, \( \Omega_{\text{op}}^{(2)} \), is applied to the second row of the combined determinant to obtain expressions analogous to \( (A1-7) \) and \( (A1-8) \).

The other determinants of \( (A1-3) \) are expanded in like manner and collecting the resulting expressions \( (A1-8) \) leads to the total one electron contribution to the matrix element from the \( n \) electrons, where in the present case \( n = 2 \).

The two electron part, \( \Omega_{\text{op}}^{(1,2)} \), of the Hamiltonian also leads to expressions of the type \( (A1-3) \) and simplifications \( (A1-4) \). Expanding an expression like \( (A1-4) \) in the usual manner and bearing in mind that \( \Omega_{\text{op}}^{(1,2)} \) acts on electron coordinates \( (1) \) and \( (2) \), that is on rows \( (1) \) and \( (2) \), one obtains

\[
\left\langle \Omega_{\text{op}}^{(1,2)} \left| \begin{bmatrix} \chi_2^{(1)} & \chi_2^{(1)} \\ \chi_{2\alpha}^{(2)} & \chi_{2\alpha}^{(2)} \end{bmatrix} \right| \begin{bmatrix} \chi_2^{(1)} \\ \chi_{2\alpha}^{(2)} \end{bmatrix} \right\rangle = J_{2\alpha,2\alpha,2\alpha,2\alpha} \quad (A1-9)
\]

\[
\langle \chi_2^{(1)} | \Omega_{\text{op}}^{(1,2)} | \chi_{2\alpha}^{(2)} \rangle \langle \chi_{2\alpha}^{(2)} | \chi_2^{(1)} \rangle = J_{2\alpha,2\alpha,2\alpha,2\alpha}
\]
where once again some terms drop out because of spin orthogonality.

Collecting all parts of the matrix element together leads to a final expression of the form (1-15).
APPENDIX 2

THE INTEGRATIONS

Since single center integrals over GETF's have not previously appeared in the literature in any great detail, it is useful to indicate here some of the techniques required for the evaluation of the types of integrals which one encounters in carrying out molecular OCE calculations using this new basis set. The methods and substitutions used are essentially those employed in the evaluation of the less general OCE-STF's with non-integral principal quantum numbers.\textsuperscript{34}

Overlap integrals:

Substituting the orbital functions (1-4) into (1-17) and the spherical polar coordinate volume element

\[ d\nu_{ic} = r_{ic}^2 dr_{ic} \sin \theta_{ic} d\theta_{ic} d\phi_{ic} \]  

(A2-1)

where C is the expansion center (Figure 1)

\[ S_{\ell_{1}\ell_{2}} = A_{r}(\ell_{1})A_{r}(\ell_{2}) \int_{0}^{\infty} r_{ic}^{n_{\ell_{1}}+n_{\ell_{2}}} e^{-(\alpha_{\ell_{1}}+\alpha_{\ell_{2}})r_{ic}} d\nu_{ic} \]  

(A2-2)

\[ \cdot \int_{0}^{\pi} \int_{0}^{2\pi} Y_{\ell_{1}m_{1}}^{*}(\theta_{ic},\phi_{ic}) Y_{\ell_{2}m_{2}}(\theta_{ic},\phi_{ic}) \sin \theta_{ic} d\theta_{ic} d\phi_{ic} \]

Since the spherical harmonics are orthonormal

\[ S_{\ell_{1}\ell_{2}} = \delta_{m_{1}m_{2}} \delta_{\ell_{1}\ell_{2}} A_{r}(\ell_{1})A_{r}(\ell_{2}) \int_{0}^{\infty} r_{ic}^{n_{\ell_{1}}+n_{\ell_{2}}} e^{-(\alpha_{\ell_{1}}+\alpha_{\ell_{2}})r_{ic}} d\nu_{ic} \]  

(A2-3)
where $\delta_{m_1 m_2}$ and $\delta_{l_1 l_2}$ are the Kronecker deltas and we have simplified notation for the normalization constants by setting $A_r(n, \alpha, p) \equiv A_r(k)$.

With the substitutions
\begin{align*}
t & = (\alpha_{s_1} + \alpha_{s_2}) r_{ic}^p, \\
Dt & = (\alpha_{s_1} + \alpha_{s_2}) \rho r_{ic}^{p-1} dr_{ie}, \\
x & = (n_{s_1} + n_{s_2} + 1)/\rho
\end{align*}

and noting that the limits of integration are unchanged since $t \to 0$ as $r_{1c} \to 0$ and $t \to \infty$ as $r_{1c} \to \infty$, one has

$$S_\delta_{s_1 s_2} = \delta_{m_1 m_2} \delta_{s_1 s_2} A_r(k) A_r(k) [\rho(\alpha_{s_1} + \alpha_{s_2})]^{x-1} \int_0^\infty t^{x-1} e^{-t} dt \tag{A2-5}$$

The integral of (A2-5) is now recognized as that of the gamma function (1-23) which leads directly to (1-22).

**Kinetic energy integrals:**

The Laplacian operator in spherical polar coordinates

$$\nabla^2 = (1/r^2) \partial/\partial r (r^2 \partial/\partial r) + 1/(r^2 \sin \theta) \left[ \partial/\partial \theta (\sin \theta \partial/\partial \theta + (1/\sin \theta) \partial^2/\partial \phi^2 \right] \tag{A2-6}$$

may be partitioned into radial and angular parts

$$\nabla^2 = (1/r^2) \partial/\partial r (r^2 \partial/\partial r) - L^2/r \tag{A2-7}$$

where $L^2$ is the square of the total angular momentum operator (reference 21 p. 133) defined by

$$L^2 = -(1/\sin \theta) \left[ \partial/\partial \theta (\sin \theta \partial/\partial \theta + (1/\sin \theta) \partial^2/\partial \phi^2 \right] \tag{A2-8}$$
Application of (A2-7) to the basis functions (1-4) results in the radial part of the operator acting only on the radial part of the function and the angular part operating only on the spherical harmonic. Partitioning the basis functions into radial and angular parts

\[ \chi_{l_a}(r_{ic}, \theta_{ic}, \phi_{ic}) = \omega_{l_a}(r_{ic}) \gamma_{l_a, m_a}(\theta_{ic}, \phi_{ic}) \]  

(A2-9)

where

\[ \omega_{l_a}(r_{ic}) = \lambda_{l_a}(l_a) r_{ic}^{n_{l_a}-1} e^{-\alpha_{l_a} r_{ic}} \]  

(A2-10)

and applying the respective operators, one obtains

\[ \nabla_{ic}^2 \omega_{l_a}(r_{ic}) = (1/r_{ic})^2 \left[ n_{l_a}(n_{l_a}-1) - \alpha_{l_a} \rho r_{ic}^2 (2n_{l_a} + \rho - 1) \right. 

\left. + \alpha_{l_a} \rho r_{ic}^2 \right] \omega_{l_a}(r_{ic}) \]  

(A2-11)

\[ \int r_{ic}^2 \gamma_{l_a, m_a}(\theta_{ic}, \phi_{ic}) = l_a(l_a + 1) \gamma_{l_a, m_a}(\theta_{ic}, \phi_{ic}) \]  

(A2-12)

So that application of the full operator leads to

\[ -\frac{1}{2} \nabla_{ic}^2 \chi_{l_a}(r_{ic}, \theta_{ic}, \phi_{ic}) = \left[ \frac{1}{2r_{ic}} \right] \left[ l_a(l_a+1) - n_{l_a}(n_{l_a}-1) \right. 

\left. + \alpha_{l_a} \rho r_{ic}^2 (2n_{l_a} + \rho - 1 - \alpha_{l_a} \rho r_{ic}^2) \right] \chi_{l_a}(r_{ic}, \theta_{ic}, \phi_{ic}) \]  

(A2-13)

Substitution of (A2-13) into (1-18) and integration over angles, keeping in mind the orthogonality of spherical harmonics, leads to

\[ T_{l_a, l_a} = \frac{1}{2} \delta_{m_m} \delta_{l_a, l_a} \lambda_{l_a}(l_a) \lambda_{l_a}(l_a) \left[ l_a(l_a+1) - n_{l_a}(n_{l_a}-1) \right. 

\left. + \alpha_{l_a} \rho r_{ic}^2 (2n_{l_a} + \rho - 1 - \alpha_{l_a} \rho r_{ic}^2) \right] \]  

(A2-14)
Using substitutions (A2-4) each of the above three integrals may be put into the form recognizable as that of the gamma function (1-23). Integration then leads to result (1-24).

**Nuclear-electron attraction integrals:**

In order to evaluate the nuclear-electron attraction integrals, it is necessary to transform the nuclear-electron attraction one-electron part of the Hamiltonian to the expansion center, $C$, since the volume element originates from this center. The formula for this transformation is derived from the law of cosines (reference 36 Appendix V)

$$\sum_{N=1}^{Q} \int_{r_1}^{r_2} \int_{h_0}^{h+1} \sum_{m=-h}^{h} \sum_{N=1}^{Q} \frac{2\pi}{r_{1C}^{h+1}} \int_{r_1}^{r_2} \left( \frac{r_1}{r_2} \right) \gamma_{n_{m_{m}}^{*}} (\phi_{CN}, \phi_{CN}) \gamma_{n_{m_{m}}^{*}} (\phi_{CN}, \phi_{CN})$$

(A2-15)

$r_1$ and $r_2$ represent the ranges of integration of the center to which transformation is desired, viz. $r_{1C}$, of which there are two cases: I. $r_{1C} < R_{CN}$ and II. $r_{1C} > R_{CN}$. In the present case of the hydrogen molecule $R_{CN} = R/2$, $\theta_{CA} = 0^\circ$, $\theta_{CB} = 180^\circ$, $\phi_{CA} = \phi_{CB} = 0^\circ$, $Q = 2$, $Z_N = +1$, and it is obvious that $N = 1$ implies nucleus $A$ and $N = 2$ implies nucleus $B$. (A2-15) is general for any number of nuclei of charge $Z_N$. (1-19) may now be written

$$V_{i, i} = -\lambda_r (\lambda_r) A_i (\lambda_i) \sum_{h=0}^{\alpha} \int_{r_1}^{r_2} \int_{h_0}^{h+1} \sum_{m=-h}^{h} \sum_{N=1}^{Q} \gamma_{n_{m_{m}}^{*}} (\phi_{CN}, \phi_{CN})$$

(A2-16)
$Y_{k,|m|}^{\left(\Theta_{CN},\phi_{CN}\right)}$ is a geometrical spherical harmonic for the nuclear framework. Following Condon and Shortley for the angular part, one may define the integral of a product of three spherical harmonics as

$$C^k(\ell_1 m_1, \ell_2 m_2) = \frac{4\pi}{2k+1} \int_0^{2\pi} \int_0^{\pi} Y_{\ell_1 m_1}^* Y_{\ell_2 m_2}^* \sin \theta_c \, d\theta_c \, d\phi_c.$$  \hspace{1cm} (A2-17)

The infinite sum over $k$ reduces to the sum of a very few terms because of a number of limiting conditions. Firstly, the only non-zero $C^k$ in the sum over $m$ for each $k$ is that for which

$$m = m_1 - m_2$$ \hspace{1cm} (A2-18)

Secondly, the apparently infinite summation over $k$ is limited by the so-called triangle condition

$$|\ell_1 - \ell_2| \leq k \leq \ell_1 + \ell_2$$ \hspace{1cm} (A2-19)

Moreover,

$$\left\{ k + \ell_1 + \ell_2 \right\}/2 = g$$ \hspace{1cm} (A2-20)

where $g$ must be integral otherwise $C^k$ is identically zero. Substituting (A2-17) into (A2-16) and applying limitations (A2-18) through (A2-20)

$$V_{\ell_1,\ell_2} = -\mathcal{A}(\ell_1) \mathcal{A}(\ell_2) \delta(m, m_1 - m_2) \sum_{k = |\ell_1 - \ell_2|}^{\ell_1 + \ell_2} \left( \frac{4\pi}{2k+1} \right)^{1/2}$$

$$\cdot \sum_{N=1}^{2k} \sum_{m_1} \sum_{m_2} \left( \Theta_{CN}, \phi_{CN} \right) C^k(\ell_1 m_1, \ell_2 m_2)$$

$$\cdot \int_0^{n_{\ell_1} + n_{\ell_2}} \int_0^{n_{\ell_1} + n_{\ell_2}} \frac{1}{r_{ic}^{\alpha_{\ell_1} + \alpha_{\ell_2}}} r_{ic}^\alpha \, d\theta_c \, d\phi_c$$

$$\hspace{1cm} (A2-21)$$
The integral in (A2-21) is broken into two parts: I. $r_{1c} < R_{CN}$ and II. $r_{1c} > R_{CN}$

$$
\frac{1}{R_{CN}} \int_{r_{1c} = 0}^{R_{CN}} r_{1c}^{n_{2}, n_{2} + \lambda_{2}} e^{-(\alpha_{21} + \alpha_{22}) r_{1c}^{\rho}} \, dr_{1c}
$$

(A2-22)

$$
+ R_{CN} \int_{r_{1c} = R_{CN}}^{\infty} r_{1c}^{n_{2}, n_{2} + \lambda_{2} - 1} e^{-(\alpha_{21} + \alpha_{22}) r_{1c}^{\rho}} \, dr_{1c}
$$

Substitutions (A2-4a) and (A2-4b) along with definitions (1-28a, b, c) put the integrals (A2-22) into the form of the small and large incomplete gamma functions (1-26) and (1-27), respectively, which leads directly to (1-25).

A final note concerning the nuclear-electron attraction integrals - if a nucleus is situated at the expansion center, a special case arises in which $R_{CN} = 0$. In this case the nuclear-electron attraction integral is given by

$$
\nu_{1, 2} = -Z_{n} \delta_{m_{1}, m_{2}} \delta_{\ell_{1}, \ell_{2}} \delta_{\lambda_{1}, \lambda_{2}} \delta_{\alpha_{1}, \alpha_{2}} \frac{1}{[\rho(\alpha_{1} + \alpha_{2})]} \nu_{\alpha_{1} \alpha_{2}}
$$

(A2-23)

where here $a = (n_{1} + n_{2})/p$.

**Electron-electron repulsion integrals:**

The expansion for the two electron operator of the Hamiltonian is given by Eyring, Walter and Kimball

$$
1/r_{ij} = \sum_{k, l} \sum_{m = -k}^{k} \frac{4\pi}{2k + 1} \left| \frac{r_{i}}{r_{j}^{k+1}} \right| Y_{k}^{j} (\theta_{i j}, \phi_{i j}) Y_{k}^{j} (\theta_{i j}, \phi_{i j})
$$

(A2-24)
where in the present case \( i = 1 \) and \( j = 2 \). Substituting (A2-24) into (1-20) along with the explicit expressions for the functions leads to

\[
\mathcal{J}_e \mathcal{e}_a \mathcal{e}_b \mathcal{e}_c = A_\nu(l_1)A_\nu(l_2)A_\nu(l_3)A_\nu(l_4) \sum_{k=0}^{\infty} \sum_{m=-\infty}^{\infty} C^k \left( l_1, m_1, l_2, m_2 \right) C^k \left( l_3, m_3, l_4, m_4 \right)
\]

\[
\cdot \int \int r_i^{n_{A}+n_{B}} C^{-\left( \alpha_{A} + \alpha_{B} \right)} \left[ \frac{r_i^k}{r_{A+B+1}} \right] r_c^{n_{B}+n_{C}} C^{-\left( \alpha_{B} + \alpha_{C} \right)} dr_i dr_c
\]

(A2-25)

Again the angular parts are seen to reduce to \( C^k \) coefficients (A2-17) with the restrictions on the summations

\[
m = m_1 - m_3 = m_4 - m_2
\]

\[
|l_1 - l_3| \leq l_2 = (l_1 + l_3) \quad \text{(A2-27a)} \quad \text{or} \quad |l_2 - l_4| \leq l_5 = (l_2 + l_4) \quad \text{(A2-27b)}
\]

whichever is the lesser \(|l_1 - l_3|\) or \(|l_2 - l_4|\). Also, depending on (A2-27a) or (A2-27b) either

\[
(k + l_1 + l_3)/2 = g \quad \text{(A2-28a)} \quad \text{or} \quad (k + l_2 + l_4)/2 = g \quad \text{(A2-28b)}
\]

where \( g \) is an integer, must be satisfied if \( C^k \) is to be non-zero. Assuming that \(|l_1 - l_3| \leq |l_2 - l_4|\) one may write

\[
\mathcal{J}_e \mathcal{e}_a \mathcal{e}_b \mathcal{e}_c = \delta(m_1, m_2, m_3, m_4) A_\nu(l_1)A_\nu(l_2)A_\nu(l_3)A_\nu(l_4)
\]

\[
\cdot \sum_{k=0}^{\infty} \sum_{m=-\infty}^{\infty} C^k \left( l_1, m_1, l_2, m_2 \right) C^k \left( l_3, m_3, l_4, m_4 \right)
\]

\[
\cdot \int \int r_i^{n_{A}+n_{B}} C^{-\left( \alpha_{A} + \alpha_{B} \right)} \left[ \frac{r_i^k}{r_{A+B+1}} \right] r_c^{n_{B}+n_{C}} C^{-\left( \alpha_{B} + \alpha_{C} \right)} dr_i dr_c
da
\]

(A2-29)
The above radial double integrals may be broken into two double integrals with ranges of integration

\[ \int \int = \int \int + \int \int = J_i + J_a \quad (A2-30) \]

\[ J_i = \int \int \int_{r_{ac} = 0}^{\infty} r_{ac}^{n_{a}+n_{b}+n_{c}} e^{-(\alpha_{a} + \alpha_{b}) r_{ac}^{p}} \quad (A2-31) \]

\[ J_a = \int \int \int_{r_{ic} = r_{ac}}^{\infty} r_{ac}^{n_{a}+n_{b}+n_{c}} e^{-(\alpha_{a} + \alpha_{b}) r_{ac}^{p}} \quad (A2-32) \]

To separate variables, use is made of the trigonometric substitutions

\[ (\alpha_{a} + \alpha_{b}) r_{ac}^{p} = r^2 \sin^2 \theta = f(r, \theta) \quad (A2-33) \]

\[ (\alpha_{a} + \alpha_{b}) r_{ac}^{p} = r^2 \cos^2 \theta = g(r, \theta) \]

Recalling that the Jacobian (reference 21 p. 133) must be used in making coordinate transformations, use is made of

\[ \begin{vmatrix} \frac{d \theta}{d \rho} & \frac{d \rho}{d \theta} \\ \frac{d \phi}{d \rho} & \frac{d \rho}{d \phi} \end{vmatrix} = \]

\[ \begin{vmatrix} \frac{d \theta}{d \rho} & \frac{d \rho}{d \theta} \\ \frac{d \phi}{d \rho} & \frac{d \rho}{d \phi} \end{vmatrix} = \]

\[ \begin{vmatrix} \frac{d \theta}{d r_{ic}} & \frac{d r_{ic}}{d \theta} \\ \frac{d \phi}{d r_{ic}} & \frac{d r_{ic}}{d \phi} \end{vmatrix} = \]

\[ \begin{vmatrix} \frac{d \theta}{d r_{ac}} & \frac{d r_{ac}}{d \theta} \\ \frac{d \phi}{d r_{ac}} & \frac{d r_{ac}}{d \phi} \end{vmatrix} = \]

\[ \begin{vmatrix} \frac{d \theta}{d r_{ac}} & \frac{d r_{ac}}{d \theta} \\ \frac{d \phi}{d r_{ac}} & \frac{d r_{ac}}{d \phi} \end{vmatrix} = \]
Upon expanding (A2-34), solving for $dr_1c$ $dr_2c$ and substituting into (A2-31)

$$J_1 = \frac{\pi}{\left[ p^2(\alpha_{x_2^2} + \alpha_{x_4^2})^2(\alpha_{x_1^2} + \alpha_{x_3^2})^2 \right] \int_0^\infty e^{-r^2} \left[ r^2 \left( \sin^2 \theta + \cos^2 \theta \right) \sin^{-1} \theta \cos^{-1} \theta \right] d\theta} \cdot \int_0^\pi (\cos^2 \theta)^t (\sin^2 \theta)^s \sin^{-1} \theta \cos^{-1} \theta \, d\theta$$

(A2-35)

$s$ and $t$ were defined by (1-30a) and (1-30b), respectively.

The limits on the $\theta$ integral are arrived at by consideration of the fact that as

$$r_1c \rightarrow r_2c \text{ then } [(r^2 \sin^2 \theta)/(\alpha_{x_1^2} + \alpha_{x_3^2})]^{1/p} \rightarrow [(r^2 \cos^2 \theta)/(\alpha_{x_2^2} + \alpha_{x_4^2})]^{1/p}$$

or as $r_1c \rightarrow r_2c$ then $\tan \theta \rightarrow [(\alpha_{x_2^2} + \alpha_{x_4^2})/(\alpha_{x_1^2} + \alpha_{x_3^2})]^{1/a}$. Solving for $\theta$

$$\theta = \arctan \left[ (\alpha_{x_2^2} + \alpha_{x_4^2})/(\alpha_{x_1^2} + \alpha_{x_3^2}) \right]^{1/a} \text{ with an upper limit of } \theta = \pi/2.$$ Also, as $r_2c \rightarrow 0$, $r \rightarrow 0$ and $r_2c \rightarrow \infty$, $r \rightarrow \infty$. The $r$ integral may easily be recognized as a gamma function by making the substitution

$$x = r^2$$

(A2-36)

and noting that as $r \rightarrow 0$, $x \rightarrow 0$ and $r \rightarrow \infty$, $x \rightarrow \infty$. So that

$$\frac{2 \int_0^\infty x^{\theta-1} e^{-x} \, dx}{\left[ p^2(\alpha_{x_2^2} + \alpha_{x_4^2})^t(\alpha_{x_1^2} + \alpha_{x_3^2})^s \right]} = \frac{2 \left[ \Gamma(\theta) \right]}{p^2(\alpha_{x_2^2} + \alpha_{x_4^2})^t(\alpha_{x_1^2} + \alpha_{x_3^2})^s}$$

(A2-37)

where $t$ and $s$ have been previously defined and

$$q = (n_{\lambda_2} + n_{\lambda_4} + n_{\lambda_1} + n_{\lambda_3} + 1)/p$$

(A2-38)
Further substitutions in the $\theta$ integral are

$$a = \sin^2 \theta$$  \hspace{1cm} (A2-39a)

$$1-a = \cos^2 \theta$$  \hspace{1cm} (A2-39b)

$$\text{da} = 2 \sin \theta \cos \theta \, d\theta$$  \hspace{1cm} (A2-39c)

with limits of integration following from the fact that

$$\tan^2 \theta = \frac{\sin^2 \theta}{\cos^2 \theta} = \frac{\alpha_2^2 + \alpha_3^2}{\alpha_2^2 + \alpha_3^2} \Rightarrow a/(1-a) \quad \text{(A2-40)}$$

which upon solving for "$a$" leads to

$$a = \frac{(\alpha_2^2 + \alpha_3^2)}{(\alpha_2^2 + \alpha_3^2 + \alpha_4^2 + \alpha_5^2)} \Rightarrow \theta = \arctan \left[ \frac{\alpha_2^2 + \alpha_3^2}{(\alpha_2^2 + \alpha_3^2 + \alpha_4^2 + \alpha_5^2)} \right]^\frac{1}{2} \quad \text{(A2-41)}$$

$$a = 1 \quad \Rightarrow \quad \theta = \pi/2$$

Use of substitutions (A2-39) and limits (A2-41) in (A2-35)

$$J_1 = \frac{\Gamma(g)}{\rho^2 (\alpha_2^2 + \alpha_3^2)^{\frac{5}{2}} (\alpha_2^2 + \alpha_3^2)^{\frac{5}{2}}} \int_{\alpha = 0}^{1} (1-a)^{t-1} (1-a)^{\delta-1} \, da \quad \text{(A2-42)}$$

or rewriting (A2-42)

$$J_1 = \frac{\Gamma(g)}{\rho^2 (\alpha_2^2 + \alpha_3^2)^{\frac{5}{2}} (\alpha_2^2 + \alpha_3^2)^{\frac{5}{2}}} \left\{ \int_{a=0}^{1} (1-a)^{t-1} a^{\delta-1} \, da ight. \bigg| \begin{array}{c}
\alpha = 0 \\
(\alpha_2^2 + \alpha_3^2)/(\alpha_2^2 + \alpha_3^2 + \alpha_4^2 + \alpha_5^2)
\end{array} \\
- \int_{a=0}^{1} (1-a)^{t-1} a^{\delta-1} \, da \bigg\} \quad \text{(A2-43)}$$

Multiplying and dividing (A2-43) by the complete beta function (1-32), use of the expression for the incomplete beta function (1-31) as well as relation (1-33) and combining some of the gamma functions leads to

$$J_1 = \frac{\Gamma(s)}{\Gamma(t)} \left[ \frac{\rho^2 (\alpha_2^2 + \alpha_3^2)^{t} (\alpha_2^2 + \alpha_3^2)^{s}}{\left[ \rho^2 (\alpha_2^2 + \alpha_3^2)^{t} (\alpha_2^2 + \alpha_3^2)^{s} \right]^{t}} \right] \quad \text{(A2-44)}$$

A similar series of steps leads to an analogous expression for $J_2$. Substitution of the expressions for $J_1$ and $J_2$
into (A2-29) then leads to the final expression for the repulsion integral (1-29).
APPENDIX 3

THE PROGRAMS

The computer programs for performing the required computations were written in the FORTRAN IV (G) compiler language for an IBM 360/44 computer. A modular (SUBROUTINE) approach was taken in order to facilitate the writing, debugging, combining and assembling of the many routines required for the various computing JOBS.

OCE-WF Routines: The following is a listing of the names along with a brief description of the major routines needed for constructing the optimized trial wave functions of multiconfigurational type.

MAIN - The main program handles input of data, output of results and calls routines to compute and store for later use quantities such as factorials and the nuclear geometrical factors, $Y_{k|m}^{(}\Theta_N,\phi_N)$. MAIN also calls the optimization routine MINIMUM and computes $F^N_{\text{slope}}(R)$ from (2-31).

SUBROUTINE FACGAM - Computes factorials and loads them into a one dimensional array. Requires the use of FUNCTION FACT.

FUNCTION FACT - A table look up of previously computed factorials.

SUBROUTINE GEOFAC - Computes nuclear geometrical factors and loads them into a two dimensional array. Requires the use of SUBROUTINE SPHERE, SUBROUTINE ALEGEN and FUNCTION PNMX.
SUBROUTINE SPHERE - Evaluates normalized Spherical Harmonics. Requires the use of SUBROUTINE ALEGEN and FUNCTION PNMX.

SUBROUTINE ALEGEN - Evaluates the associated Legendre functions. Requires the use of FUNCTION PNMX.

FUNCTION PNMX - Table look up of previously computed associated Legendre functions.

SUBROUTINE MINMUM - MINMUM is a modification of SUBROUTINE STEPIT obtained from the Quantum Chemistry Program Exchange (QCPE). The routine varies the non-linear parameters \(n, \alpha\) and \(p\) in a systematic pattern search until any further change in the parameters produces no decrease in the energy eigenvalue. These are taken to be the optimum parameter values for the wave function.

SUBROUTINE FUNK - Computes an energy value with the parameters furnished from SUBROUTINE MINMUM.

SUBROUTINE MATRIX - Computes values for the matrix elements \(H_{ij}\) (l-15) and \(\Delta_{ij}\) (l-16) using the current values for the parameters \(n, \alpha\) and \(p\) furnished from SUBROUTINE MINMUM.

SUBROUTINE NORMAL - Computes basis function radial normalization constants (1-5).

SUBROUTINE OVERLP - Computes overlap integrals (1-22).

SUBROUTINE KINETK - Computes kinetic energy integrals (1-24).
SUBROUTINE ATTRAK - Computes nuclear-electron attraction integrals (1-25). Requires the use of SUBROUTINE CSUBK and SUBROUTINE GAMIN.

SUBROUTINE CSUBK - Computes $C^k$ coefficients (A2-17).

SUBROUTINE GAMIN - Evaluates the small and large incomplete gamma functions (1-26) and (1-27).

SUBROUTINE COULMB - Computes repulsion integral (1-29).

SUBROUTINE BETIN - Evaluates the incomplete beta function (1-31).

SUBROUTINE EXCHNG - Computes repulsion integral (1-21).

SUBROUTINE CEIG - Routine to solve the secular determinant (1-11). Requires the use of diagonalization routine SUBROUTINE NESBET.

SUBROUTINE NESBET - Diagonalization routine to solve matrix eigenvalue problem for the eigenvectors, $C_1$, and the energy eigenvalues, $E_1$.

A flow chart illustrating the linkage among the above subprograms is given at the conclusion of this appendix.

**Force Routines:** As stated above, the forces from the slope of the total energy curve were computed in the latter part of the main program used to construct the wave function. The energy had been suitably partitioned into kinetic and potential energy parts in anticipation of the calculation of these forces.
The experimental forces were calculated simply by programming expression (2-32) and using the values for the spectroscopic constants given by Hulburt and Hirschfelder.\textsuperscript{11}

The following routines were needed to compute $F_{HFET}^N(R)$ from (2-27).

**MAIN** - The main program read in the wave function parameters $n_k, \alpha_k$, $p$ and $C_1$ at various internuclear distances. Output consisted of punched cards listing $F_{HFET}^N(R)$ at internuclear distance $R$. These were used as input for a plotting routine which would graph the forces as a function of internuclear distance.

**SUBROUTINE FODM** - Computes the force matrix elements $F_{ij}$ (2-28). Requires the use of SUBROUTINE OVERLP and SUBROUTINE FINT.

**SUBROUTINE FINT** - Computes the basic force integrals $F_{1,\ell^1,\ell^2}$ (2-29). Requires the use of SUBROUTINE GEOFAC, SUBROUTINE CSUBK and SUBROUTINE GAMIN.

**PLOT Routine** - A separate program was written using the computer library routines PLOT and CHAR to plot the computed forces as a function of internuclear distance. The calculations were performed on the 360 computer because of its superior computing speed but the actual plotting was done on the 1620-1627 plotter.

Any of the programs used herein, if not available from QCPE, may be obtained by addressing requests to Professor Frank L. Pilar, Chemistry Department, Parsons Hall,
Flow Chart Illustrating Linkages Among Major Subprograms
Needed to Construct Optimized Multiconfigurational OCE
Trial Wave Functions.