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A QUANTUM MECHANICAL CALCULATION
OF THE HELIUM-HELIUM INTERACTION POTENTIAL

by

Howard Davis Thames, Jr.

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[Signature]

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1. INTRODUCTION

The estimated depth of the He₂ ground state potential well (approximately .00004 a.u.) and the total electronic energy (-5.8 a.u.) suggest that a highly refined calculation would be necessary to accurately determine the potential curve. Besides the correlation energy, there are other corrections of the same or greater order of magnitude when compared with the depth of the well. For the ¹S He atom ground state the mass polarization correction is approximately 10⁻⁵ a.u., the relativistic correction approximately -10⁻³ a.u., and magnetic interactions approximately -10⁻⁴ a.u. Finally, a Born-Oppenheimer correction of .001% of the total energy would be of the same magnitude as the depth of the well. The only justification for any non-relativistic, Born-Oppenheimer variational approach to this problem is the assumption that these effects are not strong functions of the internuclear distance in the Van der Waals region.

The single-configuration LCAO-MO-SCF results of Ransil (minimum -5.7 a.u.) suggest a correlation energy of -.06 to .1 a.u.; completely open-shell variational calculations resulted in minima of roughly -5.751 a.u.; finally the 64-configuration CI treatment of Phillipson gave a minimum of
roughly $-5.753$ a.u. In any case, the correlation error is at least 1000 times as great as the depth of the well, indication that a calculation accurate to at least six significant figures will be necessary for an idea of the depth of the well, and that at least seven figures' accuracy will be necessary for an idea of the shape of the curve in the vicinity of the well.

The only calculations which have achieved such accuracy for any system have involved use of the "correlated wave-function", which has explicit functional dependence on the interelectronic coordinates $r_{ij}$ (see for example Hylleraas$^7$, James and Coolidge$^8$, Kolos and Wolniewicz$^9$). Unfortunately, attempts to apply this method to diatomics with more electrons than $\text{H}_2$ have met seemingly insuperable mathematical difficulties. At the heart of these difficulties is the evaluation of integrals whose integrands possess factors of the form $f(r_{ij}) r_{ik}^{-1}$.

The use of coordinates appearing in the potential terms of the Hamiltonian allows such factors to be integrated directly, all $r_{ij}$ being independent coordinates. This procedure is limited to problems involving six or less electrons since $\frac{1}{2}N(N-1)\geq 3N$ for $N\geq 7$. Once again, however, the mathematics involved in the transformation to these coordinates appears to produce unconscionable difficulties.
Thus this research was restricted to studying potential curves known to be in error by approximately .05 a.u. in the neighborhood of the Van der Waals region. The amount of error in the repulsive region is a point of some uncertainty, since a large (1 a.u.) difference between experimental\textsuperscript{10} and theoretical\textsuperscript{3} results has been reported. This research confirms Barnett's results\textsuperscript{3} in the repulsive region (-4.8 a.u. at R = 1 a.u.).

The open-shell functions used by Taylor and Harris\textsuperscript{4} and Barnett\textsuperscript{3} were designed to study the repulsive region, and in general will not dissociate correctly to a product of $^1S$ He-atom functions. This research compares the results of calculations using functions designed as in References 3 and 4 for the repulsive region with the results obtained from a function forced to dissociate to a product of $^1S$ He atomic functions of the form $1s(1)1s'(2) + 1s(2)1s'(1)$. The salient result is that the function which dissociates correctly possesses no minimum, whereas the function not dissociating correctly exhibits a (spurious) minimum due to the (too) high asymptotic (internuclear separation→∞) energy. The lack of a minimum is in direct contrast to the results of Ransil\textsuperscript{5}, whose single-configuration Hartree-Fock calculation managed a minimum of .00003 a.u. at approximately 5 a.u.
See discussion in Section 5.

Another result of this research is the suggestion of limiting the number of scaling parameters, yet achieving results comparable to the completely open-shell calculations. Harris' two-center completely open-shell function\(^2\) allows for independent variation of a parameter for each coordinate of each configuration! Thus an M-electron, N-configuration problem might require non-linear optimization of the energy in 3MN dimensions. The one-term function of Taylor and Harris\(^4\) has eight parameters, which group (after optimization of the energy with respect to these parameters) into four pairs, two parameters nearly equal in each pair. This pairing occurs from the Van der Waals region to dissociation, and reflects the asymptotic form of the dissociating state, namely a product of \(^1\)S functions. It is interesting that this pairing occurs whether or not the actual ground state wave-function dissociates correctly to a product of \(^1\)S atomic functions.

The Van Vleck-Serber-Yamanouchi representation matrix method\(^11\) was used for handling the spin. A somewhat different way of looking at these matrices (henceforth referred to as spin-permutation matrices) is provided in which the collection of N-electron spin functions (excluding \(S_Z\) degeneracy) defines a unitary transformation.
of regular (reducible) representations of $S_N$ to block diagonal form, each block being one of the spin permutation matrices which are an irreducible representation of $S_N$. The irreducibility of the spin permutation matrices pertaining to the $\text{He}_2$ problem is proved using Schur's lemma. In this four-electron case, the regular representations are isomorphic to the group of permutations of the vertices, edges, faces, of the regular tetrahedron, according to whether the eigenvalue of $S_z$ is 1, 0, or -1. $M_S = 2$ defines a one by one representation of the permutations of the "center" of the tetrahedron with itself, and $M_S = -2$ defines a representation of the exchange of the tetrahedron with itself. For all $N$, an isomorphism between the symmetry group $S_N$ and the $(N-1)$-simplex is indicated.

Non-linear optimization was handled by assuming that the energy is a quadratic form on the parameter vector $\omega$ in some neighborhood of its minimum: $E = (\omega, A\omega) + E_0$. $A$ is determined by computing $E$ on a 15-point lattice in $\omega$-space. The lattice must have special geometry to insure non-singularity in the determination of $A$. After differentiation, an optimum $\omega^*$ is found, and the corresponding $E(\omega^*) = (\omega^*, A\omega^*) + E_0$ computed. Convergence is quadratic. Difficulties with the method were encountered.
when the energy was a rapidly varying function of the parameters; the surface contains many local maxima and minima. This effect was evident in the repulsive region only, and the curvature of the energy with respect to each of the parameters was a monotone decreasing function of the internuclear distance. A rational fit to the parameters as functions of $R$ was found to be very good, possessing correct asymptotic behavior.

The energy was computed for an approximate Hamiltonian in the sense that the reciprocal interelectronic distances $r_{ij}^{-1}$ were approximated by a Neumann sum with finite number of terms $M$. The energy was found to converge best in terms of $M$ in the Van der Waals region, the convergence getting worse as separation of the atoms increased. These results cast doubt on the effectiveness of the Neumann sum approximation as the atoms are separated well beyond the Van der Waals region.
2. WAVEFUNCTIONS

2.1. Spin and Space Components of the Wavefunction.

Construction of spin functions for the four-electron singlet spin space proceeds as outlined in Kotani, by the repeated application of the lowering operator $S_-$ to spin functions $\Theta_{S,M}$ for states of multiplicity $2S + 1$ and $z$-component of spin angular momentum $M$:

$$S_- \Theta_{S,M} = \left[(S+M)(S-M+1)\right]^{\frac{1}{2}} \Theta_{S,M-1}.$$

The four-electron singlet spin subspace is spanned by the functions:

$$\begin{align*}
\Theta_1 &= \frac{1}{\sqrt{3}} \left[ \alpha \beta \alpha \beta - \alpha \beta \beta \alpha - \beta \alpha \alpha \beta + \beta \alpha \beta \alpha \right] \\
\Theta_2 &= \left[ \alpha \beta \alpha \beta + \beta \alpha \beta \alpha - \frac{1}{2} (\alpha \beta \alpha \beta + \alpha \beta \beta \alpha + \beta \alpha \alpha \beta + \beta \alpha \beta \alpha) \right]/\sqrt{3}
\end{align*}$$

(2.1.1)

$\Theta_1$ is a product of two atomic singlet functions $\alpha \beta - \beta \alpha$;

$\Theta_2$ is a singlet projection of two atomic triplets.

The space parts of wavefunctions used in this research are of two types. First define $\psi(1,2)$ to be a symmetric function of the coordinates of electrons 1 and 2 of the form

$$\psi_a(1,2) = 1s_\alpha(1)ls_\alpha(2) + 1s_\alpha(2)ls_\alpha(1)$$

$$= \exp \left[-\delta (r_{1\alpha} + r_{2\alpha})\right] \cosh \mathcal{E} (r_{1\alpha} - r_{2\alpha})$$

(2.1.2)
where the subscript "a" labels the nucleus. Let
\[ \omega = (\omega_1, \omega_2, \omega_3, \omega_4) \] such that \( \omega_k > 0 \) for \( k = 1,2 \) and \( \omega_k \geq 0 \) for \( k = 3,4 \). Define the two-center elliptic coordinates \( \xi, \eta, \) and \( \varphi \) as
\[
\xi_k = \frac{r_{ka} + r_{kb}}{R}, \quad \eta_k = \frac{r_{ka} - r_{kb}}{R},
\]
and \( \varphi_k \) is the angle of rotation about the axis joining the two nuclei, for electron \( k \). Surfaces of constant \( \xi \) are confocal ellipsoids with the nuclei as foci. Surfaces of constant \( \eta \) are confocal hyperboloids, orthogonal to the ellipsoids with the same foci. \( \xi \) ranges from 1 to \( \infty \), \( \eta \) from -1 to 1, and \( \varphi \) from 0 to \( 2\pi \).

In terms of these quantities, the two space functions used have the form (where \( \sigma_1, \sigma_2 = (\delta - \varepsilon)R/2, \Delta_1, \Delta_2 = (\delta + \varepsilon)R/2 \))
\[
\psi_1 = e^{\exp[-\omega_1(\xi_1 + \xi_2) - \omega_2(\xi_3 + \xi_4) - \exp[\omega_3(\eta_1 - \eta_2) - \omega_4(\eta_3 - \eta_4)]}, \quad (2.1.3a)
\]
\[
\psi_2 = \psi_a \psi_b
\]
\[
= e^{\exp(-\sigma_1 \xi_1 - \sigma_2 \eta_1 - \Delta_1 \xi_2 - \Delta_2 \eta_2 - \sigma_1 \xi_3 + \sigma_2 \eta_3 - \Delta_1 \xi_4 + \Delta_2 \eta_4)}
\]
\[
+ e^{\exp(-\sigma_1 \xi_1 - \sigma_2 \eta_1 - \Delta_1 \xi_2 - \Delta_2 \eta_2 - \sigma_1 \xi_3 + \sigma_2 \eta_3 - \Delta_1 \xi_4 + \sigma_2 \eta_4)}
\]
\[
+ e^{\exp(-\Delta_1 \xi_1 - \Delta_2 \eta_1 - \sigma_1 \xi_2 - \sigma_2 \eta_2 - \sigma_1 \xi_3 + \sigma_2 \eta_3 - \Delta_1 \xi_4 + \Delta_2 \eta_4)}
\]
\[ + \exp(-\Delta_1 \xi_1 - 4_2 \eta_1 - \sigma_1 \xi_2 - \tau_2 \eta_2 - \Delta_1 \xi_3 + \Delta_2 \eta_3 - \sigma_1 \xi_4 + \sigma_2 \eta_4). \quad (2.1.3b) \]

\( \psi_2 \) is thus symmetric to exchange of electrons 1 and 2 or 3 and 4. \( \psi_1 \) is simply one term selected from a product of the form \( \psi_a \psi_b \).

\( \psi_1 \) is intended to serve as the base configuration of a two-configuration treatment of the repulsive and Van der Waals regions. Its antisymmetric component does not dissociate into a product of \( ^1S \) Helium atomic functions, as demonstrated in Appendix 1. By comparison, \( \psi_2 \) does dissociate correctly. \( \psi_2 \) is used in a single-configuration calculation in the Van der Waals region, and compared with the antisymmetric component of the two-term function

\[ (\xi_1 \xi_2 + \eta_1 \eta_2) \psi_1 \]

in the repulsive region.

The parameter vector \( \omega \) for \( \psi_2 \) is defined

\[ \omega = (\sigma_1, \Delta_1, \sigma_2, \Delta_2). \]

In the limit \( R \to \infty \), the optimum \( \omega(R) \) will behave as \( \omega_1 \to \omega_3 \) and \( \omega_2 \to \omega_4 \) (see Section 4.2) because of the form of \( \psi_2 \) (2.1.3b). See Appendix 1. Thus in terms of the parameters \( \delta \) and \( \varepsilon \) of (2.1.2) we have

\[ \sigma = (\delta - \varepsilon)c, \quad \Delta = (\sigma + \varepsilon)c \]

and \( \omega_1, \omega_3 \to \sigma \) and \( \omega_2, \omega_4 \to \Delta \) as \( R \to \infty \) \( (c = \frac{1}{2}R) \). Using four independent parameters instead of two corresponds simply to increasing the flexibility of the function in the regions of strong overlap by "splitting" atomic parameters \( \sigma \) and \( \Delta \) such that \( \omega_1 > \sigma > \omega_3 \) and \( \omega_4 > \Delta > \omega_2 \), these relations valid.
for optimized parameter vector $\omega(R)$ for $R > 6$ a.u. See Table 7.

2.2. **Construction of an Anti-Symmetric Spin-Space Combination.**

Let $\psi_0$ refer to either $\psi_1$ or $\psi_2$. To select the component of $\psi_0 \Theta_1$ transforming as the $\Gamma_1$ irreducible representation of $S_4$ (i.e., the antisymmetric component) the projection operator

$$A=4!^{\frac{1}{2}} \sum_{P \in S_4} \varepsilon_P P$$

is applied to the product. The question of what effect a permutation $P$ has on $\Theta_1$ is settled by the following theorem:

The vectors $\Theta_1$ and $\Theta_2$ span a closed subspace under operators $P \in S_4$ such that

$$P \Theta_k = \sum_{j=1}^{2} v_{jk} \Theta_j$$

or in matrix notation

$$P \Theta = V(P)^T \Theta$$  \hspace{1cm} (2.2.1)$$

where $$\Theta = (\Theta_1, \Theta_2)$$.

$\Theta$ is a carrier for the irreducible $2 \times 2$ matrix representation $V(P)$ of $S_4$. 

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Proof. Since $S^2$ and $S_z$ are symmetric in the four electrons, they commute with each $P \in S_4$. Thus $P \Theta_k$ is also a simultaneous eigenfunction of $S^2$ and $S_z$ for $k = 1,2$. $P \Theta_1$ and $P \Theta_2$ therefore span the four-electron singlet spin subspace, and must be linear combinations of $\Theta_1$ and $\Theta_2$. This proves (2.2.1); the proof is taken from Kotani.\textsuperscript{11}

Next suppose that $P,Q,R \in S_4$ and $P = QR$. Then

$$P \Theta = V(P)^T \Theta$$

$$= QR \Theta$$

$$= Q \left[ V(R)^T \Theta \right]$$

$$= V(R)^T Q \Theta$$

$$= V(R)^T V(Q)^T \Theta$$

or $V(P) = V(Q)V(R)$. Thus $\Theta$ is a carrier for the representation $V$ of $S_4$.

Finally suppose that the representation $V$ is reducible. Then by Schur's lemma there exists an Hermitean matrix\textsuperscript{12} $M$ which satisfies

$$V(P)M = MV(P) \quad (2.2.2)$$

for every $P \in S_4$, and which is not a multiple of the unit.
matrix under the transform \( U^{-1}MU = \text{diag}(\lambda_1) = D \); since \( M \) is 2x2, we have \( \lambda_1 \neq \lambda_2 \). Let \( V'(P) = U^{-1}V(P)U \); then
\[
(2.2.1) \Rightarrow PU(\Theta) = (UV(P)^T U^{-1})U(\Theta) \text{ or } P\Theta' = V'(P)^T \Theta'.
\]
The set of matrices \( V' \) is also a representation of \( S_4 \). (2.2.2) \( \Rightarrow V'D = DV' \) for each \( P \in S_4 \). The \((j,k)\)th element of this product is \( V'_{jk}\lambda_k = V'_{jk}\lambda_j \), or
\[
V'_{jk}(\lambda_k - \lambda_j) = 0.
\]
Let \( j = 1, k = 2 \) (the argument is the same for \( j = 2, k = 1 \)). Then for every \( P \in S_4 \), \( V'_{12} = 0 \). This implies that \( \Theta'_2 \) (the second element of the vector \( U\Theta \)) is invariant under each \( P \), or
\[
\Theta'_2 = \text{const} x \sum_{k=1}^{6} \mathcal{N}_k. \tag{2.2.3}
\]
The \( \mathcal{N}_k \)'s (simple products of \( \alpha \)'s and \( \beta \)'s) are listed in Table 1.

Now examine \( \Theta'_2 \), the second element of the product \( U\Theta \), in detail:
\[
\Theta'_2 = \frac{1}{2} (U_{21} - U_{22}/\sqrt{3}) \mathcal{N}_1 - \frac{1}{2} (U_{21} + U_{22}/\sqrt{3}) \mathcal{N}_2 + \text{etc.}
\]
In order that (2.2.3) be satisfied, it is clear that \( U_{21} \) and \( U_{22} \) must satisfy an inconsistent set of linear equations. But \( M \) was Hermitean and thus diagonalizable. Thus the assumption that \( \lambda_1 \neq \lambda_2 \) (i.e., that \( V \) is reducible)
leads to a contradiction, and $V$ is irreducible. This completes the proof of the theorem.

Definition. $U(P) = \mathcal{E}_p V(P)$. Remark that $U(P)$ is an irreducible representation of $S_4$. We can now show that the function

$$\Phi = 4!^{-\frac{3}{2}} \sum_{P \in S_4} U(P)^T \Theta P \psi_0$$

(2.2.4)

is antisymmetric. For $Q \in S_4$ we have

$$4!^{\frac{3}{2}} Q \Phi = \sum_{P \in S_4} \mathcal{E}_P V(P)^T Q \Theta QP \psi_0$$

$$= \sum_{P \in S_4} \mathcal{E}_P (QP) \psi_0 V(P)^T V(Q)^T \Theta$$

$$= \sum_{R \in S_4} \mathcal{E}_Q^{-1} R \psi_0 V(Q^{-1} R)^T V(Q)^T \Theta$$

$$= \mathcal{E}_Q \sum_{R \in S_4} \mathcal{E}_R R \psi_0 (V(Q^{-1} V(R))^T V(Q)^T \Theta$$

$$= \mathcal{E}_Q \sum_{R \in S_4} \mathcal{E}_R R \psi_0 V(R)^T V(Q^{-1} V(R)^T \Theta$$

$$= \mathcal{E}_Q \sum_{R \in S_4} U(R)^T \Theta R \psi_0$$

$$= 4!^{\frac{3}{2}} \mathcal{E}_Q \Phi.$$

Remark that $\Phi = (\Phi_1, \Phi_2)$; thus for each configuration $\psi_0$ in the trial function a 2x2 block in the Hamiltonian and overlap matrices results.

2.3. Construction of the Spin Permutation Matrices.

The two four-electron singlet spin functions $\Theta_1$
and $\Theta_2$ are linear combinations of $M_3 = 0$ products of one-electron spin functions $\alpha$ and $\beta$. For convenience these products are labeled in Table 1.

$$
\begin{align*}
\Lambda_1 & \quad \alpha\beta \alpha\beta \\
\Lambda_2 & \quad \alpha\beta\beta\alpha \\
\Lambda_3 & \quad \beta\alpha\beta\alpha \\
\Lambda_4 & \quad \beta\alpha\beta\alpha \\
\Lambda_5 & \quad \alpha\alpha\beta\beta \\
\Lambda_6 & \quad \beta\beta\alpha\alpha
\end{align*}
$$

**TABLE 1**

Thus from definitions (2.1.1)

$$
\begin{align*}
\Theta_1 & = \frac{1}{2} (\Lambda_1 - \Lambda_2 - \Lambda_3 + \Lambda_4), \\
\Theta_2 & = (\frac{1}{2} \Lambda_1 - \frac{1}{2} \Lambda_2 - \frac{1}{2} \Lambda_3 - \frac{1}{2} \Lambda_4 + \Lambda_5 + \Lambda_6) / 3^{\frac{1}{2}}.
\end{align*}
$$

The matrix $C$ is defined row-wise by the coefficients of the $\Lambda$'s for $\Theta_1$ (row 1) and $\Theta_2$ (row 2):

$$
C = \frac{1}{2} \left(\begin{array}{ccccccc}
1 & 1 & 1 & 1 & 0 & 0 \\
-3^{-\frac{1}{2}} & -3^{-\frac{1}{2}} & -3^{-\frac{1}{2}} & -3^{-\frac{1}{2}} & 2 \cdot 3^{-\frac{1}{2}} & 2 \cdot 3^{-\frac{1}{2}}
\end{array}\right).
$$

Let $\mathcal{N} = (\Lambda_1, \Lambda_2, \ldots, \Lambda_6)$. Define $P \cdot \mathcal{N} = (P \cdot \Lambda_1, \ldots, P \cdot \Lambda_6)$. Table 2 lists the 24 permutations of $S_4$ and the mappings $P_j \cdot \Lambda_k \rightarrow \Lambda_m$ for $1 \leq j \leq 24$; $1 \leq k, m \leq 6$. 

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By definition, \( \Theta = C \mathcal{N} \). (2.2.1) \( V(P)^T \Theta = C P \mathcal{N} \)
or \( C(P \mathcal{N}) \Theta^T = V(P)^T \Theta \Theta^T = C(P \mathcal{N}) \mathcal{N} C^T \). But

\[
\Theta \Theta^T = \begin{pmatrix}
\Theta_1^2 & \Theta_1 \Theta_2 \\
\Theta_1 \Theta_2 & \Theta_2^2
\end{pmatrix}
\] (2.3.1)

so that \( \int \Theta \Theta^T d\sigma = \) unit matrix \( I \), since the \( \Theta \)'s are linearly independent. Define

\[
\Pi(P) = \int (P \mathcal{N}) \mathcal{N}^T d\sigma ,
\] (2.3.2)

so that \( \Pi(P)_{j,k} = 1 \) if \( P \mathcal{N}_j = \mathcal{N}_k, 0 \) otherwise. Thus \( \Pi(P) \)
can be constructed for each permutation \( P \) by inspection of Table 2, and

\[
V(P)^T = C \Pi(P) C^T .
\] (2.3.3)

All \( V(P)^T \) are listed in Table 3. Remark that the \( \Pi(P) \) are symmetric for the classes \( 1^4, 1^2 2, \) and \( 2^2 \) and unsymmetric for the classes \( 1, 3 \) and \( 4 \). Also note that the \( V^T \) are given in terms of a quasi-similarity transformation of the \( \Pi(P) \). In section 2.4 it will be shown that the \( \Pi(P) \) for each triple \( (N,S,M) \) are a set of regular representations of certain group operations of \( S_N \). Thus the result follows that

The spin eigenfunctions for a triple \( (N,S,M) \) define a similarity transform which reduces the regular representations \( \Pi(P) \) of \( S_N \) to the irreducible
representations $V(P)$ of $S_N$:

$$V(P) = C^T \Pi(P)^T C.$$ 

Harris\(^2\) gives a method essentially identical to that presented above for computing $V(P)$, except that the matrix $\Pi(P)$ is not introduced, its ones and zeros having already been taken into account. It is felt that, although Harris' prescription is computationally preferable when many electrons come into a calculation, the matrix $\Pi(P)$ is of enough interest in itself to deserve some discussion.

2.4. Characterization of the Regular Representations.

After the fashion of Kotani\(^11\) monomial products of $N$ one-electron spin functions are classified according to eigenvalue of $S_z$, or $M$, in Table 4. In general, there are \( {N \choose \frac{1}{2}N + M} \) = $g(N,M)$ independent functions for a given $M$. To the eigenvalue $S(S + 1)$ of $S^2$ and $M$ of $S_z$ belong the $f(N,S)$ functions\(^11\) $\Theta_{S,M,k}, 1 \leq k \leq f(N,S)$, where

$$f(N,S) = \frac{(2S+1)N!}{(N/2+S+1)!(N/2-S)!}.$$ 

Given a triple $(N,S,M)$, the $g(N,M)$ products from Table 4 corresponding to eigenvalue $M$ of $S_z$ are labeled $\{\Omega_1, \Omega_2, \ldots, \Omega_{g(N,M)}\} = \Omega$. The $f(N,S)$ spin functions which are eigenfunctions of $S^2$ with eigenvalue $S(S+1)$ and of $S_z$ with eigenvalue $M$ are then linear combinations
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**TABLE 2**

-17-
<table>
<thead>
<tr>
<th>P</th>
<th>$U(P)^T$</th>
</tr>
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<tbody>
<tr>
<td>1, 22, 23, 24</td>
<td>$(1, 0)$</td>
</tr>
<tr>
<td>2, 7, 17, 21</td>
<td>$(1, 0)$</td>
</tr>
<tr>
<td>3, 6, 16, 18</td>
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</tr>
<tr>
<td>4, 5, 19, 20</td>
<td>$\frac{1}{2}\begin{pmatrix} -1 &amp; -\sqrt{3} \ -\sqrt{3} &amp; 1 \end{pmatrix}$</td>
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<tr>
<td>8, 10, 12, 14</td>
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</tr>
<tr>
<td>9, 11, 13, 15</td>
<td>$\frac{1}{2}\begin{pmatrix} -1 &amp; \sqrt{3} \ -\sqrt{3} &amp; -1 \end{pmatrix}$</td>
</tr>
</tbody>
</table>

**TABLE 3**

Spin Permutation Matrices
of the $\Omega$'s:

$$\Theta_{S,M,j} = \sum_{k=1}^{g(N,M)} c_{j,k} \Omega_k, \quad 1 \leq j \leq f(N,S)$$

thus defining the $f(N,S) \times g(N,M)$ matrix $C$.

<table>
<thead>
<tr>
<th>$M$</th>
<th>Number of Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/2</td>
<td>$\alpha \alpha \alpha \cdots \alpha$</td>
</tr>
<tr>
<td>N/2-1</td>
<td>$\beta \alpha \cdots \alpha, \alpha \beta \alpha \cdots \alpha, \cdots, \alpha \alpha \alpha \cdots \beta$</td>
</tr>
<tr>
<td>N/2-2</td>
<td>$\beta \beta \alpha \cdots \alpha, \beta \alpha \beta \cdots \alpha, \cdots, \alpha \alpha \alpha \cdots \beta$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>-N/2</td>
<td>$\beta \beta \cdots \beta$</td>
</tr>
</tbody>
</table>

**TABLE 4**

Classification of $\alpha \beta$ Products According to $M^{11}$

The set of all $C$'s for a given $N$ block together to form a square super-matrix $C$ dimension

$$\sum_{S=0 \text{ or } \frac{1}{2}}^{N/2} f(N,S) = \left(\begin{array}{c} N \\ N/2 \end{array}\right) \text{ or } \left(\begin{array}{c} N \\ \frac{1}{2}(N+1) \end{array}\right)$$

= $g(N,0)$.

The irreducible representations $V$ then appear as the diagonal blocks of the generalization of (2.3.3):

$$V_N(P)^T = C_N \Pi_{N,0}(P) C_N^T.$$
The isomorphism between the full tetrahedral group $T_d$ and $S_4$ serves as a geometrical illustration of the manner in which $\Pi_{N,M}^{\ast}$ serves as a regular representation. For $M=0$, the 6x6 matrix $\Pi_{4,0}^{\ast}$ is a regular representation of the group of permutations of the edges of a regular tetrahedron.

![Diagram of a tetrahedron]

Fig. 1

The Regular Tetrahedron

Thus corresponding to $P_3$ of Table 2 (2,4 exchange) is the mapping of sides $a\rightarrow a$, $b\rightarrow e$, $c\rightarrow f$, $d\rightarrow d$, $e\rightarrow b$, $f\rightarrow c$ which is seen to be represented by the matrix $\Pi(P_3)$.

In the same manner, $\Pi_{4,1}^{\ast}$ is the regular representation for the group of interchanges of the vertices $(1,2,3,4)$. The $\Pi_{4,1}^{\ast}$ are 4x4 matrices, and of course are a representation of $S_4$ itself. $\Pi_{4,2}^{\ast}$ may be thought of as a representation of the exchange of the center of the tetrahedron with itself under any of the permutations of $S_4$, and $\Pi_{4,-1}^{\ast}$ as a representation of the exchange of the four faces (labeled by the vertices)
under permutations of $S_4$. Finally $\Pi_{4,-2}$ represents the exchange of the tetrahedron with itself. Table 5 summarizes these results. Note that $\Pi$ is independent of $S$, so that these results hold for singlet, triplet, or quintet states of $\text{He}_2$ given the restriction $|M| \leq S$.

<table>
<thead>
<tr>
<th>$M$</th>
<th>Exchange</th>
<th>Dimensionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&quot;Center&quot;</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>Vertices</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>Edges</td>
<td>1</td>
</tr>
<tr>
<td>-1</td>
<td>Faces</td>
<td>2</td>
</tr>
<tr>
<td>-2</td>
<td>Tetrahedron</td>
<td>3</td>
</tr>
</tbody>
</table>

**TABLE 5**

The argument for arbitrary $N$ goes in the same way. $\Pi_{N,N/2}$ is a representation of the exchange of the set (1 2 3 \ldots N) with itself; $\Pi_{N,N/2-1}$ is a representation of the exchange of single elements of the set (1 2 3 \ldots N) among themselves (in this case a regular representation of $S_N$); $\Pi_{N,N/2-2}$ is a representation of the exchange of the $\frac{1}{2}N(N-1)$ pairs of elements from the set (1 2 3 \ldots N) among themselves, etc. Note that $\Pi_{N,N/2-2}$ is a representation of permutations in $S_N$, not permutations in $S_{\frac{1}{2}N(N-1)}$. Thus in the example illustrated by Fig. 1 (see Table 2) we have
\[ P_3 (a \ b \ c \ d \ e \ f) = P_3 \left( (13)(23)(12)(24)(34)(14) \right) \]
\[ = \left( (13)(34)(14)(24)(23)(12) \right) \]
\[ = (a \ e \ f \ d \ b \ c). \]

The generalization of Table 5 to \( N > 4 \) affords a geometrical analogue of the permutation group \( S_N \). Namely, \( S_N \) is isomorphic to the exchange of vertices of the \((N-1)\)-simplex.
3. MATRIX ELEMENTS

3.1. **Derivation of Matrix Elements.**

The Hamiltonian and Overlap matrices, H and D respectively, are matrix representations of the Hamiltonian and identity operators in the basis supplied by the trial wavefunction

\[ \Psi = \sum_k x_k \Phi_k = (x, \Phi). \]

The \( x_k \)'s are coefficients determined in the solution of the secular equation to minimize the computed energy eigenvalue. The \( \Phi \)'s have the form (2.2.4). For the angle-independent functions used in this research the condition

\[ \psi^0_k(\xi, \eta) = \psi^0_k(\xi, -\eta) \quad (3.1.1) \]

fulfills the \( \sum^+ \) symmetry requirement.

Each \( \Phi_k \) is a vector \((\Phi^1_k, \Phi^2_k)\). For notational simplicity, omit the subscript \( k \) and put \( \Phi = (\Phi^1, \Phi^2) \).

Following Kotani\(^{11}\)

\[ \tilde{H}_{mn} = \left< \Phi_m, H \Phi_n \right> \]

\[ = \frac{1}{4!} \sum_{P, Q \in S_4} \sum_{k=1} U_{km}(P)U_{kn}(Q) \left< P \psi_0, HQ \psi_0 \right>. \]

The integral operator \( \left< \cdot \right> \) is invariant to any permutation
of indices among its arguments, as is \( H \). Thus for each \( Q \) in \( S_4 \)

\[
Q^{-1} \langle p \psi_0, HQ \psi_0 \rangle = \langle (Q^{-1}p \psi_0), (Q^{-1}H)Q^{-1}Q \psi_0 \rangle
= \langle Q^{-1}p \psi_0, H \psi_0 \rangle.
\]

Thus \( H_{mn} = \frac{1}{4!} \sum_{P,Q} \sum_k U_{km}(P)U_{nk}(Q^{-1}) \langle Q^{-1}p \psi_0, H \psi_0 \rangle \)

\[
= \frac{1}{4!} \sum_{P,Q} U_{nm}(Q^{-1}P) \langle Q^{-1}p \psi_0, H \psi_0 \rangle
= \sum_R U_{nm}(R)^T \langle R \psi_0, H \psi_0 \rangle.
\]

Thus the 2x2 block of the Hamiltonian matrix associated with \( \psi_j^0 \) and \( \psi_k^0 \) is

\[
H_{jk} = \sum_{P \in S_4} U(P)^T \langle P \psi_j^0, H \psi_k^0 \rangle \quad (3.1.2)
\]

and the corresponding block of \( D \) is

\[
D_{jk} = \sum_{P \in S_4} U(P)^T \langle P \psi_j^0, \psi_k^0 \rangle.
\]

The complete Hamiltonian matrix is

\[
H = \begin{pmatrix}
H_{11} & H_{12} & \cdots & H_{1N} \\
H_{21} & \ddots & \cdots & \vdots \\
\vdots & \ddots & \ddots & \vdots \\
H_{N1} & \cdots & \cdots & H_{NN}
\end{pmatrix}
\]

with a similar result for \( D \).
Concerning the computation of the integral 
\[ \langle p \psi_0, H \psi_0 \rangle \], it would seem that if \( \Phi \) is antisymmetric, then

\[ \langle \Phi, \sum_{i<j} r_{ij}^{*-1} \Phi \rangle = 6 \langle \Phi, r_{12}^{*-1} \Phi \rangle, \]

with similar simplifications for other terms in the Hamiltonian. This simplification can be extended to the integral \( \langle p \psi_0, H \psi_0 \rangle \), but since none of the terms of \( H \) is symmetric to permutations in \( S_4 \), a double summation over \( S_4 \ (4!)^2 \) terms would be required. Thus the simplification really amounts to a complication by approximately squaring the number of terms to be summed over.

The computational approach adopted for 
\( \langle p \psi_0, H \psi_0 \rangle \) differs somewhat from previous treatments\(^2,^3\) in that no one- and two-electron integrals (in the usual sense\(^2\)) were tabulated. Instead, programs which assembled matrix elements for various terms of the Hamiltonian were defined directly on the table of basic primitive integrals (see Appendix 2). This procedure entails some repetitious computing (as is always the case when fetches from tables are replaced by recursive evaluation of functions), but has the advantage that one step in the logic between basic primitive integral combination and matrix element has been removed. The procedure is clearly limited to few-configura-
tion calculations.

A final remark concerning computation is in order for the evaluation of integrals over $r_{ij}^{-1}$. The Neumann sum must be terminated at a finite number of terms, so that in effect the true Hamiltonian $H$ has been replaced by a model Hamiltonian $H_N$ where $H$ and $H_N$ differ in that the latter approximates $r_{ij}^{-1}$ to $N + 1$ terms in the Neumann sum. The rate of convergence of the Neumann sum is a function of the internuclear distance. Practicality specified $N = 8$ as an upper bound for Neumann sums in this research; the reasons are discussed in Appendix 2. The dependence of the energy on the length of the Neumann sum is described in Table 6. Optimization of the parameters in each case occurred at $N = 8$; slightly different optima are obtained for other values of $N$.

Table 6 demonstrates that $E_8$ is apparently correct to five significant figures at $R = 5$ a.u., but that the fourth figure is still in doubt by as much as $\pm 2$ at $R = 12$ a.u. This result suggests that the use of the Neumann sum approximation will not be valid at large internuclear distances. The use of a wavefunction which dissociates properly allows the asymptotic energy to be computed as simply twice the atomic energy computed with $\psi(1,2)$ (see Section 2.1). Reference 16 gives this
<table>
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<tr>
<th>Length of Neumann Sum</th>
<th>Internuclear Distance (a.u.)</th>
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<tr>
<td>N</td>
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<tr>
<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>-5.7534</td>
</tr>
<tr>
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<td>-5.75113</td>
</tr>
<tr>
<td>7</td>
<td>-5.75181</td>
</tr>
<tr>
<td>8</td>
<td>-5.75112</td>
</tr>
</tbody>
</table>

**TABLE 6**

Convergence of the Neumann Sum \((N + 1 \text{ terms})\) for \(\psi_2\)

(Energies (a.u.) computed for optimum parameters at \(N = 8\))
this energy as -5.751 337 at $\varepsilon = 1.188$ 531, $\sigma = 2.183$ 171. The integrals over $r^{-1}_{12}$ are exact for the atomic case, so that a strict comparison is not possible. The figure does suggest that $E_8$ at $R = 12$ a.u. is off by 0.001 a.u., whereas $E_8$ at 6.0 a.u. is off by 0.0001 a.u.

$E_8$ at $R = 5.0$ a.u. has converged to five figures, but disagrees in the fifth figure with -5.751 337. Assuming that the minimum occurs at 6.0 a.u., this discrepancy is probably due to the fact that $\psi_2$ is not correct for the $(1s)^2 (2s)^2$ Be configuration as $R \to 0$.

3.2. **Evaluation of Matrix Elements**

As an illustration of the evaluation of $\langle \Phi, H \Phi \rangle$, we take $\Phi$ to be constructed from the space function $\psi_2(2.1.3b)$.

First, from the Theorem on symmetry of $\psi_2$ (Kotani, p.18) we note that $\Phi^{(2)}$ vanishes identically, and thus that the secular equation is one dimensional. Second, let $\langle P \psi_2, H \psi_2 \rangle$ be labeled $H(P)$. Then the (1,2) and (3,4) exchange symmetry of $\psi_2$ condenses the sum over 24 permutations to a sum over six permutations, each selected from a coset of the subgroup $\{P_1, P_{22}, P_{23}, P_{24}\}$ (see Table 2) of $S_4$. The spin factor $U(P)_{11}$ is multiplied by 4 to account for the other members of the coset. Finally, the antisymmetrizing operator also projects a component of
+g symmetry to satisfy (3.1.1), because for example
\[ \psi_2(\bar{\xi}, \eta) + p_{24}\psi_2(\bar{\xi}, \eta) = \psi_2(\bar{\xi}, \eta) + \psi_2(\bar{\xi}, -\eta), \]
and \( S_4 \) can be decomposed into 12 pairs which effect this
projection, each with the same spin factor. Thus, (3.1.2)
becomes
\[ \langle H \rangle = \langle \left[ 4(\psi_2 + p_{24}\psi_2) - 2(p_3\psi_2 + p_4\psi_2 + p_5\psi_2 + p_6\psi_2) \right], H\psi_2 \rangle. \]

The integral \( \langle p\psi_2, H\psi_2 \rangle \) remains to be evaluated.
Under permutations in \( S_4 \), the \( \sigma, \Delta \) factors in \( \psi_2 \) permute
into six basic orderings. These are numbered in the same
way as the \( \alpha/\beta \) products in Table 1, with the correspondence
\( \sigma \leftrightarrow \alpha, \Delta \leftrightarrow \beta \). After an ordering has been specified, a
term of \( \psi_2 \) is unique when negative \( \gamma \)-coefficients are
specified. Let \( T_{j}^{k1} \) denote the term specified by the \( j \)th
ordering of \( \sigma \)'s and \( \Delta \)'s, with the \( k \)th and \( l \)th \( \gamma \)-coefficients
negative. Then \( \psi_2 = T_{1}^{12} + T_{2}^{12} + T_{3}^{12} + T_{4}^{12} \).

Let integer matrices \( A \) and \( B \) be constructed,
such that \( B_{k1} \) specifies the ordering resulting from
\( p_{k}T_{1} \), and the \( k \)th row of \( A \) specifies resulting negative
\( \gamma \)-coefficients when \( p_{k} \) acts on \( T_{1}^{12} \). Then
\[ (p_{k}\psi_2)\psi_2 = \sum_{j=1}^{4} T_{B_{k1}}^{A_{k}} T_{j}^{12}. \]
and  
\[ \langle H \rangle = \sum_{j=1}^{6} \varepsilon_j \sum_{k,\ell=1}^{4} \langle T^{A}_{B}^{j},HT^{12}_{k} \rangle, \quad (3.1.3) \]

where  
\[ \varepsilon_1 = \varepsilon_2 = 4, \quad \varepsilon_3 = \ldots = \varepsilon_6 = -2. \]

The integrals \[ \langle T,HT \rangle \] are evaluated in the usual way, and coded for the computer as functions of \[ j, k, \text{ and } \ell. \]
4. NON-LINEAR OPTIMIZATION

4.1. Method.

The minimization of the energy with respect to the four parameters \( \omega = (\omega_1, \omega_2, \omega_3, \omega_4) \) proceeds on the assumption that the energy is a quadratic form on \( \omega \) in some neighborhood of the minimum: \( E(\omega) = E_0 + (\omega, A\omega) \) plus higher order terms. The vector \( \omega^* \) is defined such that \( E(\omega^*) \leq E(\omega) \) in the appropriate neighborhood of the minimum for a given internuclear distance \( R \). \( \omega^* \) is determined by differentiation and setting partial derivatives equal to zero in the usual way. Thus determination of the matrix \( A \) at a given \( R \) completely determines the solution of the optimization problem for a given grid size, \( h \).

In practice, the energy \( E_8 \) (see Section 3.1 and Table 6) is computed on a lattice of 15 points in \( \omega \)-space. Successive parameter values differ by \( h \). Fifteen versions of the equation

\[
E = a_1 \omega_1^2 + a_2 \omega_2^2 + a_3 \omega_3^2 + a_4 \omega_4^2 + a_5 \omega_1 \omega_2 \\
+ a_6 \omega_1 \omega_3 + a_7 \omega_1 \omega_4 + a_8 \omega_2 \omega_3 + a_9 \omega_2 \omega_4 + a_{10} \omega_3 \omega_4 \\
+ a_{11} \omega_1 + a_{12} \omega_2 + a_{13} \omega_3 + a_{14} \omega_4 + a_{15}
\]

are produced. The resulting linear set is solved for the
coefficients \( a \), determining the matrix \( A \). Non-singularity in the determination of \( A \) was found to be assured by a certain geometry of the lattice. This geometry is illustrated for the coupling between three of the four components of \( \omega \):

![Diagram showing coupling between \( \omega \) components]

Variation of \( \omega \) and of the energy with internuclear distance is discussed in Section 4.2.

A curvature \( K \) was computed by diagonalizing the matrix

\[
\frac{1}{2} \begin{pmatrix}
2a_1 & a_5 & a_6 & a_7 \\
a_5 & 2a_2 & a_8 & a_9 \\
a_6 & a_8 & 2a_3 & a_{10} \\
a_7 & a_9 & a_{10} & 2a_4
\end{pmatrix}
\]

These curvatures are the second partial of the energy with respect to parameter in the diagonalized version of the parameter space. Variation of the curvature with internuclear distance is discussed in Section 4.3.

An indication of how the procedure works in practice is given by the optimization of parameters \( \sigma \) and
for the function \( \psi_a (1,2) (2.1.2) \) for decreasing grid size \( h \). The results are given below.

<table>
<thead>
<tr>
<th>( h )</th>
<th>( \delta )</th>
<th>( \xi )</th>
<th>( K_\delta )</th>
<th>( K_\xi )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.05</td>
<td>2.180 72</td>
<td>1.191 49</td>
<td>.706</td>
<td>.746</td>
<td>-2.875 660</td>
</tr>
<tr>
<td>.005</td>
<td>2.183 16</td>
<td>1.188 533</td>
<td>.680</td>
<td>.783</td>
<td>-2.875 661</td>
</tr>
<tr>
<td>.0005</td>
<td>2.183 171</td>
<td>1.188 531</td>
<td>.680</td>
<td>.792</td>
<td>-2.875 661</td>
</tr>
<tr>
<td>.00005</td>
<td>2.183 171</td>
<td>1.188 531</td>
<td>.680</td>
<td>.796</td>
<td>-2.875 661</td>
</tr>
</tbody>
</table>

The energy, quadratic in the parameters, converges quickly to a stable value (13 figures when \( h = .00005 \)). The curvatures (second derivatives) settle most slowly to a stable value.

4.2. **Energy and Parameters as Functions of \( R \).**

Table 7 details the variation of the energy \( E \), the parameter vector \( \omega \), and the curvature \( K \) with internuclear distance \( R \) for the wavefunction \( \psi_2 (2.1.3b) \), grid size \( h = .005 \). \( \frac{dE}{dR} \) and \( \frac{V}{T} \) are computed to check the results against the virial theorem. The underlined figures in the energies are believed not to be significant in the sense of non-convergence of the Neumann sum.

Table 8 shows these quantities for the function \((\xi_1 \xi_2 + \eta_1 \eta_2) \psi_1 \) at \( R = 1.0 \) a.u. and for the function \((1 + \prod \xi_k \eta_k^2) \psi_1 \) for other \( R \), with grid size \( h = .01 \).

The components of the parameter vector \( \omega \) were
<table>
<thead>
<tr>
<th>R</th>
<th>w1</th>
<th>w2</th>
<th>w3</th>
<th>w4</th>
<th>K1</th>
<th>K2</th>
<th>K3</th>
<th>K4</th>
<th>dR/</th>
<th>-E</th>
<th>-V/T</th>
</tr>
</thead>
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**Table 7**

Energy and Parameters(\(w\)) and Curvatures(\(K\)) for \(\psi_2\) as Functions of \(R\)

(Atomic Units throughout; grid size \(h = .005\))

*The underlined figures are considered not significant in the sense of non-convergence of the Neumann sum. **Computation using the \(w\) predicted by (cubic/quadratic) rational fit.
<table>
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<tr>
<th>R</th>
<th>( \omega_1 )</th>
<th>( \omega_2 )</th>
<th>( \omega_3 )</th>
<th>( \omega_4 )</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
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<td>5.733</td>
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</tbody>
</table>

**TABLE 8**

(Atomic Units; grid size \( h = 0.01 \))

At \( R = 1.0 \): \( (\xi_1 \xi_2 + \eta_1 \eta_2) \psi_1 \)

Otherwise: \( (1 + \pi \xi_k \xi_k^2) \psi_1 \)
fitted to rational functions of $R$ such that degree
(numerator) = degree (denominator) + 1. This insured
correct behavior of $\omega$ for $R \to \infty$ (i.e., proportional to
$R$). The optima $(\delta, \varepsilon)$ for $\psi_a(1,2)$ (2.1.2) are
$(2.183\, 171, 1.188\, 531)$. From Table 7, at $R = 12$ a.u.
($c = 6$), $\omega_1/c = 1.19$, $\omega_2/c = 2.18$, $\omega_3/c = 1.19$, and
$\omega_4/c = 2.18$, whereas the rational fit predicts the
limiting ($c \to \infty$) behavior $\omega_1/c = 1.19$, $\omega_2/c = 2.18$,
$\omega_3/c = 1.19$, $\omega_4/c = 2.18$. These values are remarkably
stable, from the Van der Waals region to larger $R$. The
vector $\omega/c$ does not behave as would have been predicted
from the derivation of $\psi_2(2.1.3b)$, namely $\omega_1, \omega_3 \sim
(\delta - \varepsilon), \omega_2, \omega_4 \sim c(\delta + \varepsilon)$. It is possible that as
$R \to \infty$ this behavior would be eventually observed.

The rational fit provided excellent predictions
about optimum values of the parameters at points exterior
to the domain of the fit. For example, a (quadratic/
linear) fit at the points $R = 5, 5.5, 6, \text{ and } 6.5$ for
$\psi_2$ predicted an optimum $\omega = (7.15, 13.1, 7.12, 13.4)$ at
$R = 12$. Optimization of $\psi_2$ at $R = 12$ yielded $\omega =
(7.1487, 13.094, 7.1334, 13.098)$.

Unfortunately, no meaningful conclusions can
be accepted from these figures about the core width, or
the location or depth of the well. $\psi_2$ yields a curve
with no minimum, and \( \psi_1 \) a curve with a (spurious) minimum at approximately 4.7 a.u., spurious because the potential curve rises too fast in the Van der Waals region (for reasons discussed in Appendix 1).

Barnett obtained\(^3\) an energy of \(-4.8\) a.u. at \( R = 1 \) a.u., in contrast to the experimental result\(^{10}\) \(-5.5\) a.u. The function \( (\xi_1 \xi_2 + \eta_1 \eta_2) \psi_1 \) gave an energy \(-4.75\) a.u. at \( R = 1 \) a.u., while \( \psi_2 \) gave an energy of \(-4.3\) a.u. It is noteworthy that although the completely open-shell treatment is only superficially better than functions discussed in this research in the Van der Waals region (at \( R = 5 \) a.u., Barnett obtained \(-5.7510\) a.u. with his one-term, eight-parameter function, which agrees with the result for \( \psi_1 \)), the improvement is clear in the core, where there is no pairing of parameter values.

4.3 Curvature of the Energy in Parameter Space

We have seen how the scaled parameter vector \( \omega/c \) is asymptotically correct for the optimum atomic parameters \( \delta \) and \( \varepsilon \) of (2.1.2). To correctly scale the curvatures, note that

\[
\frac{\partial^2 E}{\partial \omega_k^2} = \frac{\delta^2 E}{\delta (c \delta)^2}
\]
where $\lambda$ is one of the atomic parameters. Thus molecular curvatures are to be scaled by the factor $(R/2)^2$.

Table 9 displays the scaled curvatures as functions of $R$, in the diagonalized parameter space. The atomic curvature $K_\alpha$ is .68, and $K_\beta$ is .80 (see Section 4.1). It can be seen that the trends are correct.
<table>
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<th>$K_3'$</th>
<th>$K_4'$</th>
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<td>.61</td>
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</table>

**TABLE 9**

Scaled Curvatures $K_k' = (R/2)^2 \frac{\partial^2 E}{\partial \omega_k^2}$
5. SUMMARY

A comparison between the completely open-shell results of Taylor and Harris\(^4\) and Barnett\(^3\) with the restricted open-shell results of this research indicates: (a) the restricted method gives essentially the same results whenever as many scaling parameters are used as there are pairs of nearly equal parameters in the completely open-shell treatment; (b) the pairing structure of the parameter space can be predicted by asymptotic analysis of the wavefunction if it dissociates correctly; (c) results are not as good in the restricted method when pairing breaks down, in the case of He\(_2\) in the strong-interaction core region; (d) pairing of parameters is reflected in the curvature of the energy on the parameter space; (e) optimum parameters and curvatures go smoothly in the limit \(R \to \infty\) to the appropriate atomic values for correctly dissociating wavefunctions.

The Neumann sum approximation to the reciprocal inter-electronic distances \(r_{ij}^{-1}\) in two-centers breaks down numerically for large inter-nuclear distances, probably due to the unbounded increase of the arguments of the pertinent integrals (asymptotically proportional
to R). For He$_2$, the nine-term Neumann sum had converged to five figures at R = 5 a.u., but to only three figures at R = 12 a.u.

The assumption that the energy is a quadratic form on the scaling parameter vector was found to give a convergent method for the non-linear minimization of the energy from the Van der Waals region to larger R, getting better as R increased due to the monotone decreasing dependence on R of the second derivatives of the energy with respect to components of the parameter vector. In the repulsive region, the method broke down at times, due to the highly-convoluted nature of the energy hyper-surface there.

The representation matrix method of Serber-Van Vleck-Yamanouchi for handling the spin was shown to give rise to a new prescription for N-electron spin eigenfunctions. The representation matrices are completely reduced regular representations of S$_N$, whereby the unitary transformation effecting the reduction for each P in S$_N$ defines the spin eigenfunctions of S$^2$ and S$_z$.

The first extension to be suggested for this work is a configuration-interaction treatment with $\psi_2$ as the first term. For example, $(1 + \xi_1 \xi_2 + \eta_1 \eta_2 + \eta_1^2 + \eta_2^2) \psi_2$, a function correct at the limits R→0 and R→∞.
In particular, it would be interesting if a CI basis set of this type could be found which would exhibit a minimum in its potential curve. Care must be taken that the set of functions chosen for the CI set would admit an interpretation at the limit $R \to \infty$, so that an appropriate atomic calculation may be done; otherwise the worsening of the Neumann sum approximation at large $R$ will leave the asymptotic value of the energy in doubt, which will in turn leave the core radius and the well depth in doubt.

Ransil$^5$ seems to have avoided these difficulties by not using as atomic functions the asymptotic form of the molecular function. A 1s Slater Type Orbital (STO) was used for the atom; a negative energy region is then found by the expedient of matching this function with molecular functions using 1s, 2s, and 2p STO's in the LCAO-MO-SCF treatment. There is doubt about the value of the results. Kestner and Sinanoglu$^{15}$ termed the minimum that Ransil found "fortuitous"; meaningless would perhaps be a better suited term.

Another possible extension of this research consists of using the interpretation of N-electron spin eigenfunctions given to eliminate the necessity for producing these functions before obtaining the spin permutation matrices as in the procedure outlined by Harris$^2$, an extremely
laborious task when $N$ exceeds 6. The suggested pro-
cedure: (1) Consult Table 2 to set up the regular
representations as described in Section 2.3; these may
be stored in the computer in very abbreviated form.
(2) For $P$ not equal to the identity, diagonalize the
regular representation of $P$, which was also chosen
to be in a "symmetric" class (the regular representations
are symmetric or not by class in the group). (3) Apply
the diagonalizing transform to each of the other
regular representations in the group. If all are not
simultaneously reduced to diagonal or block-diagonal
form, pick a new $P$ from a symmetric class and repeat
step (2).

If a unitary transform does show up which simul-
taneously diagonalizes all the regular representations,
we have arrived at the spin permutation matrices with-
out prior knowledge of the $N$-electron spin eigenfunc-
tions. It is probable that these irreducible represent-
ations will be only unitarily equivalent to the spin
permutation matrices arrived at when spin eigenfunctions
are constructed by the genealogical\textsuperscript{11} method, a circum-
stance having of course no bearing on the results.
APPENDIX 1: Asymptotic Behavior of Wavefunctions

The antisymmetric component of the function \((\xi_1 \xi_2 + \eta_1 \eta_2) \psi_1\) (2.1.3a) is asymptotically correct for the \((1s)^2(2s)^2\) configuration of Beryllium as \(R \to 0\), as is easily verified. This is not true of the antisymmetric component of \(\psi_2\) (2.1.3b); see the discussion in Section 4.2. The antisymmetric component is of course correct asymptotically as \(R \to \infty\), for a product of two \(^1S\) He atom functions of the form \(1s(1)1s'(2)+1s(2)1s'(1)\).

We now show that the antisymmetric component of \(\psi_1\) is not asymptotically correct for a product of \(^1S\) He atom functions of any kind.

\(S_4\) is partitioned according to permutations having the same \(V(P)^T\) (Table 3). Thus let \(A_1 = \{P \in S_4: V(P)^T = V(P_1)^T\}\); \(A_2 = \{P \in S_4: V(P)^T = V(P_2)^T\}\); \(A_3 = \{P \in S_4: V(P)^T = V(P_4)^T\}\); \(A_4 = \{P \in S_4: V(P)^T = V(P_9)^T\}\); \(A_5 = \{P \in S_4: V(P)^T = V(P_3)^T\}\); \(A_6 = \{P \in S_4: V(P)^T = V(P_8)^T\}\).

A considerable amount of algebra shows that

\[
\sum_{P \in A_1} P \psi_1 = (P_1 + P_{22} + P_{23} + P_{24}) \psi_1
\]

\[
= 4 \left\{ \exp \left[ -\delta(r_{1a} + r_{4a} + r_{2b} + r_{3b}) \cosh [\xi(r_{1a} - r_{4a}) + \xi(r_{2b} - r_{3b})] \right] + \exp \left[ -\delta(r_{1b} + r_{4b} + r_{2a} + r_{3a}) \cosh [\xi(r_{1b} - r_{4b}) + \xi(r_{2a} - r_{3a})] \right] \right\}
\]
\[ \equiv g(1423) \]

with the substitutions \( \omega_1 = \omega_3 = c \sigma; \omega_2 = \omega_4 = c \Delta \)
and \( c \sigma = \delta - \varepsilon, c \Delta = \delta + \varepsilon \). Similarly

\[ \sum_{P \in A_3} P \psi_1 = \]

\[ 4 \left\{ \exp\left[ -\delta (r_{1a} + r_{4a} + r_{2b} + r_{3b}) \right] \cosh\left[ \varepsilon (r_{1a} - r_{4a}) - \varepsilon (r_{2b} - r_{3b}) \right] ight. \]

\[ + \exp\left[ -\delta (r_{1b} + r_{4b} + r_{2a} + r_{3a}) \right] \cosh\left[ \varepsilon (r_{1b} - r_{4b}) - \varepsilon (r_{2a} - r_{3a}) \right] \right\} \]

\[ \equiv h(1423). \]

In the same way,

\[ \sum_{P \in A_2 \cup A_6} P \psi_1 = g(1342) + h(1342) \]

and

\[ \sum_{P \in A_4 \cup A_5} P \psi_1 = g(1234) + h(1234). \]

Now let \( R \to \infty \), and electrons 1 and 2 be associated with
nucleus a and 3 and 4 with nucleus b. \( r_{1b}, r_{2b}, r_{3a}, \)
and \( r_{4a} \sim R \) as \( R \to \infty \), so terms from \( g(1324), h(1324), \)
g(1423), and h(1423) go to zero as \( e^{-4R} \). Attaching the
proper spin factors from Table 3, we find that

\[ \Phi^{(1)} = \frac{1}{\sqrt{4!}} \sum_{P \in S_4} \sum_{k=1}^{2} U_{k,1}(P) \Theta_k P \psi_1 \]

\[ \longrightarrow - \frac{2}{\sqrt{6}} [\psi_a(1,2) \psi_b(3,4) \theta_1 + \psi_a(3,4) \psi_b(1,2) \theta_1] \]
\[ + \sqrt{3}(e^{-\delta(r_{1a}+r_{2a})}\sinh\varepsilon(r_{1a}-r_{2a})}e^{-\delta(r_{3b}+r_{4b})}\sinh\varepsilon(r_{3b}-r_{4b}) \]
\[ e^{-\delta(r_{1b}+r_{2b})}\sinh\varepsilon(r_{1b}-r_{2b})}e^{-\delta(r_{3a}+r_{4a})}\sinh\varepsilon(r_{3a}-r_{4a}))\Theta_2 \]
as \( R \to \infty \). One part has the correct form, but the terms
with sinh factors have antisymmetric space parts, indicat-
ing a mixture of \( ^1S \) and \( ^3S \) He atom states. Since
\( \psi_2 \) is symmetric to \( (1,2) \) and \( (3,4) \) exchange, it is
clear that a necessary and sufficient condition that the
antisymmetric component of a primitive space function
should dissociate correctly is that the space coefficient
of \( \Theta_2 \) must vanish in the limit \( R \to \infty \). This condition
is automatically satisfied by space functions symmetric
to \( (1,2) \) and \( (3,4) \) exchange, as Kotani's results\textsuperscript{11}
(Theorem, page 18) demonstrate.
APPENDIX 2: Basic Integrals

Four basic integrals were used in this research. Of these,

\[ A_n(x) = \int_{-\infty}^{\infty} t^n e^{-xt} \, dt \]

and

\[ B_n(x) = \int_{-\infty}^{\infty} t^n e^{xt} \, dt \]

were computed by standard methods. The integral

\[ R_n(m,x) = \int_{-\infty}^{\infty} t^m P_n(t) e^{xt} \, dt, \]

where \( P_n(t) \) is the (unnormalized) Legendre Polynomial, was computed by noting that

\[ R_n(m,x) = \left( \frac{d}{dx} \right)^m R_n(0,x), \]

where

\[ R_n(0,x) = 2 \sqrt{x} x^{-\frac{3}{2}} I_{n+\frac{1}{2}}(x) \]

and

\[ R_n(m,-x) = (-1)^{n+m} R_n(m,x). \]

\( I_{n+\frac{1}{2}}(x) \) is the modified Spherical Bessel function of purely imaginary argument. Finally,

\[
\overline{F}_n(\alpha, \beta, \gamma_1, \gamma_2) = \\
\int_{-\infty}^{\infty} x^\alpha e^{-\gamma_1 x} Q_n(x) \, dx \int_{-\infty}^{\infty} y^\beta e^{-\gamma_2 y} P_n(y) \, dy \\
+ \int_{-\infty}^{\infty} x^\alpha e^{-\gamma_2 x} Q_n(x) \, dx \int_{-\infty}^{\infty} y^\beta e^{-\gamma_1 y} P_n(y) \, dy
\]
was computed as described by James and Coolidge. In their method, \( \Phi_n \) is given as a linear combination of the \( \Phi_k \), for \( k = 0, 1, \ldots, n-1 \). Numerically, the errors in \( \Phi_n \) for small \( n \) are rapidly compounded as \( n \) increases, as a snowballing effect. Using double-precision (94 bits on the Rice Computer) arithmetic, it was found that the \( \Phi_n \) could not be computed reliably for \( n \geq 8 \). In fact, when the argument \( \gamma < 1 \), the \( \Phi_n \) could not be computed reliably for \( n \geq 6 \).
APPENDIX 3: Solution of the Secular Equation

For the symmetric matrix $H$ and the positive definite matrix $D$ the solution of the linear problem

$$(H - \varepsilon D)X = 0$$

is desired. $\varepsilon$ is a scaler, and $X$ a vector. The following method is discussed in Wilkinson. Let $U$ be orthogonal such that

$$U^{-1}DU = \text{diag}(d_i) = d.$$

Then $HX = \varepsilon DX$ when multiplied from the left by $U^{-1}$ is

$$(U^{-1}HU)(U^{-1}X) = \varepsilon(U^{-1}DU)(U^{-1}X).$$

This when multiplied from the left by $d^{-\frac{1}{2}}$ is

$$d^{-\frac{1}{2}}(U^{-1}HU)d^{-\frac{1}{2}}(d^{\frac{1}{2}}U^{-1}X) = \varepsilon(d^{-\frac{1}{2}}U^{-1}X). \quad (1)$$

Now (1) defines the classical eigenvalue problem

$$\det(H' - \varepsilon I) = 0 \quad (2)$$

where

$$H' = d^{-\frac{1}{2}}(U^{-1}HU)d^{-\frac{1}{2}}.$$

The solution $\varepsilon$ of (2) gives the desired energy eigenvalue as the lowest root, and the eigenvector $X$ is related to the solution $X'$ by $X = Ud^\frac{1}{2}X'$. 

-49-
2. F. E. Harris, J. Chem. Phys. 32, 1, 3 (1960)
15. N. R. Kestner and O. Sinanoglu, J. Chem. Phys. 45, 1, -50-
194 (1966)