Concerning the Stability of the Negative Ions $\text{H}^-$ and $\text{Li}^-$

William A. Goddard, III

Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109
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The unrestricted Hartree-Fock (UHF) wave functions for $\text{H}^-$ and for $\text{Li}^-$ have the $Z+1$th electron at infinity, and thus have the same energy as the neutral atoms. That is, the stability of these negative ions is not accounted for by Slater determinant wave functions, not even if the orbitals are allowed to split. We show that the difficulty here is that the UHF wave functions do not have the proper spin symmetry. If the Slater determinant is spin-projected and the orbitals optimized after projection (to obtain what is called the GF wave function), these negative ions are predicted correctly to be stable. Since the GF wave function leads to an independent particle interpretation, we see that instantaneous polarization of the neutral-atom orbitals by the $Z+1$th electron is not crucial to the stability of these negative ions.

From an analysis of the differences between the UHF and GF wave functions, we find that the key leading term to the stability of the negative ions is an exchange term (particularly the nuclear attraction part of this term), just like the exchange term important in the valence-bond wave function of $\text{H}_2$.

This can be approached by examining better types of wave functions until we obtain a type which can correctly predict stability.

The negative ion has more electrons than protons; thus we expect one electron to be very loosely bound and to be in a rather diffuse state. Hence it is possible that the average potential due to the other $Z$ electrons and the nucleus of charge $Z$ might not be strong enough to bind the $Z+1$th electron. In this case it would be the instantaneous polarization of the other electrons which is primarily responsible for allowing a deep enough potential to bind the $Z+1$th electron. We will denote this possibility as explanation I. In the HF method each orbital is adjusted only for the average potential due to the other electrons. Thus explanation I could account for the incorrect description by the HF method of such ions as $\text{H}^-$, $\text{Li}^-$, and $\text{O}^-$.

However, the HF method has an additional
constraint. For singlet systems such as H\(^-\) and Li\(^-\), besides assuming that the wave function can be written as a Slater determinant, we also take each orbital to describe two electrons (one of each spin). This seems to be an especially bad assumption for negative ions, where on physical grounds we would expect one electron to be in an orbital which is far more diffuse than the others. Thus we should consider determinant wave functions in which all orbitals are allowed to be different; such wave functions are called unrestricted Hartree-Fock (UHF) wave functions. If the UHF method correctly predicts the stability of negative ions, then it is not explanation I but rather the double-occupation assumption (explanation II) which causes the bad description of negative ions by the HF method.

However, we will show that the UHF method also leads to a prediction of instability for H\(^-\) and Li\(^-\). Nevertheless, this does not yet mean that explanation I is correct, because the UHF wave function is not the best independent-particle wave function. That is, there are still better wave functions which describe each electron as moving in the average field due to the other electrons.

If the orbitals in the UHF wave function for H\(^-\) or Li\(^-\) are not doubly occupied, then the UHF wave function is not an eigenfunction of \(\hat{S}^2\). Thus for the ground state of H\(^-\), the UHF wave function is a mixture of singlet and triplet components.

\[
\psi_{\text{UHF}}(1, 2) = \phi_{1a}(1)\phi_{1b}(2)\alpha(1)\beta(2) - \phi_{1b}(1)\phi_{1a}(2)\beta(1)\alpha(2)
\]

\[
S^2\psi_{\text{UHF}}(1, 2) = [\phi_{1a}(1)\phi_{1b}(2) - \phi_{1b}(1)\phi_{1a}(2)]\alpha(1)\alpha(2) \neq 0
\]

if \(\phi_{1a} \neq \phi_{1b}\).

Hence, if \(\phi_{1a} \neq \phi_{1b}\) the UHF energy must be a compromise between the energy of a singlet state and the energy of a triplet state. As we shall see later, the UHF method resolves this conflict by putting \(\phi_{1b}\) at infinity, which is just the case for which the singlet and triplet energies are the same. That is, according to the UHF method, H\(^-\) is not stable; the energy is lowered by putting the second electron at infinity.

It could be that the problem with using the UHF method for describing negative ions is that the wave function is not an eigenfunction of \(\hat{S}^2\) (explanation III) or it could still be that explanation I is correct. The reasonable way to test this is to spin-project the UHF wave function to obtain a singlet wave function and then to optimize all the orbitals. This corresponds to a previously developed method,\(^5,6\) called the GF method, which has already been shown to remove some deficiencies present in the HF method (such as improper dissociation of molecules\(^5,7\)) but which still leads to an independent particle interpretation.\(^5,6\) We shall show below that for both H\(^-\) and Li\(^-\) the GF wave function does predict stability of the negative ion. Thus it is possible to describe correctly negative ions with wave functions which adjust the electron orbitals only for the average potentials due to the other electrons. That is, instantaneous polarization by the Z + 1th electron of the other Z electrons is not crucial to the stability of these negative ions.

For both H\(^-\) and Li\(^-\), the GF many-electron wave functions are purely radial, that is, no sort of angular correlation is present. Thus it is the static or nondynamic radial correlation energy accounted for by the GF method and not accounted for by the UHF method which is responsible for the stability of the negative ions. We shall see that this difference is primarily due to an exchange term similar to the exchange term of H\(_2\) in the valence-bond method.

**CALCULATIONS**

For both H\(^-\) and Li\(^-\), the basis set consisted of a Slater orbital\(^6\) basis set appropriate for the neutral atom plus one function of variable scale parameter. Thus, for H\(^-\), two basis functions were used, a 1s with \(\zeta_1 = 1.0\) and another 1s with \(\zeta_2\) varied from 0.0 to 0.6. For Li\(^-\) the basis set consisted of a basis set of four functions for Li\(^{7+}\) (\(\zeta_{1s} = 2.128, \zeta_{1s} = 4.279, \zeta_{3s} = 2.59,\) and \(\zeta_{3s} = 0.6679\)) and an additional 3s function with \(\zeta_3\) varied from 0.0 to 0.5. For each set of orbital exponents a self-consistent-field calculation was performed with each of the three methods, HF, UHF, and GF.

In the UHF and GF methods there are two self-consistent-field equations to be solved

\[H^a\phi_{ia} = \epsilon_{ia}\phi_{ia}\]

\[H^b\phi_{ib} = \epsilon_{ib}\phi_{ib}\]

where for H\(^-\) we use the first solution of both Eqs. (1a) and (1b), and for Li\(^-\) we use the two lowest solutions of each equation. For the HF method there is just one equation, and we take the first or the first two solutions for H\(^-\) or Li\(^-\), respectively.

In Fig. 1 the energies are plotted for the ground

![FIG. 1. The total energy from HF, UHF, and GF calculations on H\(^-\). The basis set consists of a 1s Slater orbital with \(\zeta_1 = 1.0\) and another 1s orbital with a variable orbital exponent \(\zeta_2\).](image-url)
state of \( \text{H}^- \) as calculated by the HF, UHF, and GF methods. In addition, the energy of the triplet state is plotted as calculated by the GF method. [For the triplet state we choose the first two solutions of Eq. (1a).] The orbital energies for the loosely bound orbitals as obtained from these calculations are plotted in Fig. 2. The total energies and orbital energies for \( \text{Li}^- \) are shown in Figs. 3 and 4, respectively. Again, only the orbital energy of the most diffuse orbital is shown, and the GF results for the triplet state are also given.

![Figure 2](image1.png)

**FIG. 2.** The orbital energies for the loosely bound electron as found from HF, UHF, and GF calculations on \( \text{H}^- \).

![Figure 3](image2.png)

**FIG. 3.** The total energy from HF, UHF, and GF calculations on \( \text{Li}^- \). The basis set consists of four Slater orbitals appropriate for \( \text{Li}^- \) and another \( 3s \) orbital with a variable orbital exponent \( \xi_2 \).

From Fig. 1 we see that the UHF wave function for \( \text{H}^- \) yields a minimum energy for \( \xi_2 = 0 \), which corresponds to \( \text{H} + \text{e}^- \). We also see that the HF wave function never gets an energy even close to that of \( \text{H} + \text{e}^- \). Note that if we force the UHF wave function to use a large enough \( \xi_2 \), the orbitals do not split, and the HF and UHF results are the same. For the basis set used here this occurs near (slightly larger than) the \( \xi_2 \) which is optimum for the HF wave function. As \( \xi_2 \) approaches this value, the overlap between the two UHF orbitals rapidly increases toward 1.0 and \( \epsilon_{1b} \) rapidly approach \( \epsilon_{1F} \) (see Fig. 2).

The GF method leads to an energy of 0.512809 and thus predicts stability for \( \text{H}^- \). It is not ap-

![Figure 4](image3.png)

**FIG. 4.** The orbital energies for the loosely bound electron as found from HF, UHF, and GF calculations on \( \text{Li}^- \).

parent from the graph, but the GF energy increases for small \( \xi_2 \) near 0, reaching a value of -0.499952 at \( \xi_2 = 0.02 \). Note that there is a minimum in \( \epsilon_{1b} \) which occurs almost exactly at the same \( \xi_2 \) as the minimum in total energy (see Figs. 1 and 2).

The results for \( \text{Li}^- \) are quite similar to those for \( \text{H}^- \). The UHF wave function has a minimum at \( \xi_2 = 0 \), which just corresponds to \( \text{Li} + \text{e}^- \). The HF energy is always far worse than that of \( \text{Li} + \text{e}^- \). If we force \( \xi_2 \) to be large enough, the HF and UHF results are the same. For the basis set used here this occurs near (slightly less than) the optimum \( \xi_2 \) for HF. Again the UHF functions change rapidly for \( \xi_2 \) slightly less than this critical value.

For \( \text{Li}^- \) the GF method leads to an energy of -7.43591 which is lower than the energy of \( \text{Li}^- \). Again the GF energy increases for small \( \xi_2 \), and again the minimum in the valence orbital energy (\( \epsilon_{2b} \)) occurs very near the minimum in the total energy.

The significance of these results will now be analyzed in a little more detail.

**DISCUSSION**

**A. The \( \text{H}^- \) Negative Ion**

For \( \text{H}^- \) the electronic Hamiltonian is

\[
H(1, 2) = h(1) + h(2) + g(1, 2),
\]

where \( h = -\frac{1}{2} \nabla^2 - Z/r \) and \( g = 1/r_{12} \).

The HF wave function for \( \text{H}^- \) is

\[
\psi_{\text{HF}} = \alpha(\phi_1 \phi_1 \alpha \beta) = \frac{1}{2} \phi_1 \phi_1 (\alpha \beta - \beta \alpha),
\]

where

\[
\begin{align*}
\phi_{\text{HF}} &= \epsilon_1 \phi_1, \\
H_{\text{HF}}^H &= h + U_{1 \text{HF}}^H, \\
U_{1 \text{HF}}^H(1) &= \int d\xi_2 \frac{\phi_1(2) \phi_1(2)}{r_{12}}
\end{align*}
\]
and
\[ E^{\text{HF}} = \langle \phi_1 \phi_2 | H | \phi_1 \phi_2 \rangle. \]

For \( H^- \) the UHF wave function is\textsuperscript{10, 11}
\[ \psi_{\text{UHF}} = a(\phi_a \phi_b \alpha \beta) = \frac{1}{2} (\phi_a \phi_a \alpha \beta - \phi_b \phi_b \alpha \beta), \]
(5)
where
\[ H_a^{\text{UHF}} \phi_a = \epsilon_a \phi_a, \]
(6)
\[ H_a^{\text{UHF}} = h + U_a^{\text{UHF}}, \]
\[ U_a^{\text{UHF}}(1) = \int d\vec{x}_2 \frac{\phi_b(2)\phi_b(2)}{r_{12}}, \]
(7)
and\textsuperscript{12}
\[ E^{\text{UHF}} = \langle ab | H | ab \rangle. \]
And the GF wave function is\textsuperscript{10, 11}
\[ \psi_{\text{GF}} = G_F(\phi_a \phi_b \alpha \beta) = \frac{1}{2} (\phi_a \phi_a \alpha \beta + \phi_b \phi_b \alpha \beta)(\alpha \beta - \beta \alpha), \]
(8)
where
\[ H_a^{\text{GF}} \phi_a = \epsilon_a^{\text{GF}} \phi_a, \]
(9)
\[ H_a^{\text{GF}} = h + U_a^{\text{GF}}, \]
\[ U_a^{\text{GF}}(1) = \int d\vec{x}_2 \frac{\phi_b(2)\phi_b(2)}{r_{12}} + \int d\vec{x}_2 \phi_b(2) \langle H(1, 2) - H \rangle P^{12} \phi_b(2), \]
(10)
and\textsuperscript{12}
\[ E^{\text{GF}} = \langle ab | H | ab \rangle + \langle ab | H - E | ba \rangle \\
= \langle ab | H | ab \rangle + \epsilon_b. \]

The main difference in the various expressions for \( E \) and \( U \) is that in the GF case there is an extra exchange term which does not occur in the others. This term results from the spin symmetry of the wave function but becomes zero for the case where \( \phi_a = \phi_b \) (since then \( E = \langle aa | H | aa \rangle \) or \( \langle aa | H - E | aa \rangle = 0 \)). This exchange energy, \( \langle ab | H - E | ba \rangle \), is exactly the same type of term which leads to the binding of \( H_2 \) in the valence-bond wave method.\textsuperscript{13, 14} We will see next that it is also this exchange term which is essentially responsible for the stability of \( H^- \) and \( Li^- \).

Since the UHF wave function does not lead to stability for \( H^- \), the potential \( V_b^{\text{UHF}}(r) = U_b^{\text{UHF}}(r) - Z/r \) must be too weak to have a bound state.

In the GF method, the potential for the \( \phi_b \) electron is the same as \( V_b^{\text{GF}} \) except for an additional term, \( U_b^{\text{exch, GF}} \), where
\[ U_b^{\text{exch, GF}}(1) = \int d\vec{x}_2 \phi_b(2) \]
\[ \times \left[ \frac{\hbar(1) + \hbar(2) + 1/r_{12} - E}{12} \right] \phi_a(2). \]

Since the potential
\[ V_b^{\text{GF}} = V_b^{\text{UHF}} + U_b^{\text{exch, GF}} \]
does have a bound state, the net effect of \( U_b^{\text{exch, GF}} \) must be significantly attractive.

In fact
\[ \langle \phi_b | V_b^{\text{exch, GF}} | \phi_b \rangle = 2 \langle b | a \rangle < a | -\frac{1}{2} Z^2 | b \rangle + \langle b | a \rangle < a | Z/r | b \rangle + \langle ab | g | ba \rangle - E \langle a | b \rangle^2 \]
is negative, but all of the components except \( 2 \langle b | a \rangle < a | Z/r | b \rangle \) are positive. Thus the binding in \( H^- \) arises from the nuclear-attraction part of the exchange term, in spite of energy increases due to the kinetic energy and electron repulsion terms.

The HF wave function for \( H^- \) never gets as low an energy as the \( H \) atom. This is because both electrons are forced to be in the same orbital which prevents us from allowing one electron to go to infinity while the other stays with the \( H \) nucleus. Hence the HF wave function for \( H^- \) is unstable\textsuperscript{15, 16} (in the sense of Thouless) with respect to the UHF wave function. This is in contrast to the case of \( He \),\textsuperscript{17, 18} where the HF wave function is stable (i.e., if we solve the UHF equations allowing the orbitals to be different, we find that the optimum orbitals are, in fact, identical). It is interesting that when one uses a small basis set and restricts the orbital exponents (\( \xi_x > 0.4 \)), the solutions to the UHF Roothaan equations are the same as the HF solutions. However, this need not occur if larger basis sets are used.

The minimum in \( \epsilon_b \) and \( E \) occur near the same \( \xi_x \) since \( E = \langle \phi_a | H | \phi_a \rangle + \epsilon_b \) and \( \phi_a \) is not very dependent on \( \xi_x \) in this region.

In order to obtain a clearer picture of the hydrogen ion, we show in Fig. 5 the potential in which an electron in the outer orbital moves. Actually the potential in \( U_b^{\text{GF}} \) is nonlocal (since it involves permutations); however, after one has solved for the orbitals from (9), we can find the

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**FIG. 5.** The local potential seen by the outer electron of \( H^- \).
Concerning Stability of Negative Ions

local potential for which the orbital is a solution.\textsuperscript{19} Thus the local potential of Fig. 5 is equivalent to the actual nonlocal potential of (10). In order for this local potential to be well defined, we have used a larger basis set which is given in Table I along with the orbital expansion coefficients. In Fig. 5 we see that the exchange part

<table>
<thead>
<tr>
<th>Basis function type</th>
<th>$\zeta$</th>
<th>$\phi_{1a}$</th>
<th>$\phi_{1b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1s$</td>
<td>1.0</td>
<td>1.04400</td>
<td>0.20402</td>
</tr>
<tr>
<td>$4s$</td>
<td>1.403</td>
<td>-0.03090</td>
<td>0.07695</td>
</tr>
<tr>
<td>$3s$</td>
<td>1.40</td>
<td>-0.00701</td>
<td>0.07014</td>
</tr>
<tr>
<td>$3s$</td>
<td>0.735</td>
<td>0.01191</td>
<td>0.53774</td>
</tr>
<tr>
<td>$5s$</td>
<td>0.4339</td>
<td>-0.01244</td>
<td>-0.69710</td>
</tr>
<tr>
<td>$4s$</td>
<td>0.3647</td>
<td>0.01951</td>
<td>1.05311</td>
</tr>
<tr>
<td>orbital energy</td>
<td>0.26800</td>
<td>-0.01471</td>
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</tr>
<tr>
<td>cuup</td>
<td>-1.0000</td>
<td>-1.0000</td>
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</tr>
<tr>
<td>$\phi(0)$</td>
<td>0.58901</td>
<td>0.11511</td>
<td></td>
</tr>
</tbody>
</table>

Total energy $-0.513893$, Kinetic energy 0.513897, Electron-electron energy 0.297264, Virial ratio, $V/2E$ 1.000047

of the $U_{G}^{GF}$ is negative for $R > 1.33a_o$. This leads to a dramatic difference between $V_{G}^{UHF} = -Z/r + U_{0}^{Coul}$ and $V_{G}^{GF} = -Z/r + U_{0}^{Coul} + U_{exch}^{G}$, thus $V_{G}^{GF}$ is significantly lower than $V_{UHF}$ for $R > 1.5$. Using this potential and integrating (6) for $\epsilon_b = 0$, we find that $V_{UHF}$ has no bound states; whereas a similar integration of (9) for $V_{G}^{GF}$ shows one bound state.

B. The Li$^-$ Negative Ion

Since the energy curves for Li$^-$ are very similar to those for the H$^-$ case, the basic reasons for the stability of Li$^-$ are apparently the same as for H$^-$.\textsuperscript{20} That is, the stability of the negative ion is due to an exchange-type term, particularly the nuclear attraction part of this term.

In this case also, the HF wave function leads to a worse energy for Li$^-$ than for Li. As in the case of H$^-$, this is due to the double occupation restriction on the orbitals. The HF wave function for Li$^-$ can have an even number of electrons near the Li nucleus, but not an odd number. Thus the HF wave function for Li$^-$ is unstable.\textsuperscript{15,16}

\textsuperscript{15}This research was partially supported by a grant (GP-4965) from the National Science Foundation.
\textsuperscript{16}Contribution No. 3634.
\textsuperscript{17}B. L. Moiseiwitsch [Adv. Atomic and Molec. Phys. 3, 62 (1960)] suggests that this is always the case.
\textsuperscript{18}By $\phi_{1a} \neq \phi_{1b}$ we mean not equal within a phase factor.
\textsuperscript{19}W. A. Goddard, III, Phys. Rev. 157, 81 (1967), hereafter called III.
\textsuperscript{20}For small basis set calculations, the HF Roothaan solution is stable for $\epsilon_b > 0.4$ just as occurred for H$^-$.\textsuperscript{19}
\textsuperscript{21}C. Other Systems

For a system such as B$^-$ there are two p orbitals, of which one should be similar to the p orbital of B whereas the other should be much more diffuse. Since these orbitals will not transform into each other under spatial rotations, it will be necessary to project the Slater determinant onto an eigenstate of $L^2$ in order to obtain the proper spatial symmetry. Since spin projection of the wave function is crucial for describing the negative ions H$^-$ and Li$^-$, it is likely that spin projection and orbital angular-momentum projection will both be important for ions such as B$^-$, C$^-$, and N$^-.$

**SUMMARY**

For both H$^-$ and Li$^-$, an HF wave function leads to a higher energy than for the neutral atom. Allowing the orbitals to split leads to the UHF wave function, but the lowest energy with this method is just the energy of the neutral atom. Thus again, stability of the negative ion is not obtained. However, if the Slater determinant is spin-projected and the orbitals optimized after projection (to obtain the GF wave function), the resulting wave function leads to stability of the negative ion. The stability of these negative ions arises from an exchange interaction term and, in particular, from the nuclear attraction portion of this exchange term.

**CONCLUSIONS**

In order to describe weakly bound negative ions, it is important that the $Z - 1$th electron be allowed to be in a much more diffuse orbital than the other electrons. However, this is not sufficient; it is also important that the many-electron wave function have the proper spin (and spatial) symmetry. Thus it is not enough to use a single Slater determinant; rather we must consider symmetry-projected wave functions.

**ACKNOWLEDGMENTS**

I thank John Armstrong and Len Doborne for some assistance with the calculations.

\textsuperscript{21}W. A. Goddard, III, J. Chem. Phys. 48, 150 (1968), hereafter called III.
\textsuperscript{20}W. A. Goddard, III, J. Chem. Phys. 48, 1008 (1968), hereafter called IV.
\textsuperscript{19}An ns Slater orbital has the form $\chi_{n0} = N_{n0} r^n e^{-\kappa r}$, where $N_{n0}$ is a normalization factor.
\textsuperscript{18}This result is for the small basis set considered here without reoptimizing the neutral-atom basis functions. In a larger, completely optimized basis set (See W. A. Goddard, III, J. Chem. Phys. 48, 1008 (1968), the GF energy for H$^-$ is $-0.513892$ and for Li$^-$ is $-0.443099$.}
The many-electron wave functions used here are not normalized to one. When electron numbers are omitted, the orbitals and spin functions are assumed to be ordered according to electron number. Thus \( \phi_a \phi_b \phi_c = \phi_a(1) \phi_b(2) \phi_c(3) \).

For convenience we often denote an orbital by its subscript. Thus \( \langle ab | H | ab \rangle = \langle \phi_a \phi_b | H | \phi_a \phi_b \rangle \).

Usually the valence-bond (VB) energy is written

\[
E_{VB} = \frac{\langle ab | H | ab \rangle + \langle ab | H | ba \rangle}{1 + |\langle ab \rangle|^2},
\]

but this is equivalent to

\[
E_{VB} = \langle ab | H | ab \rangle + \langle ab | H - E_{VB} | ba \rangle,
\]

which more clearly shows the influence of the exchange term. Of course, in the VB method, \( \phi_a \) and \( \phi_b \) are atomic orbitals, whereas in the GF method there is no restriction upon the form of \( \phi_a \) and \( \phi_b \).


T. A. Kaplan and W. H. Klein, Phys. Rev. 155, 1 (1967) have shown that whenever the HF energy for an \((N+1)\)-electron system is greater than the HF energy for an \(N\)-electron system, then the HF wave function for \((N+1)\)-electron system is unstable. Thus the HF wave functions for the ground states of \(^1B^-\), \(^1N^-\), and \(^1D^-\) must also be unstable. See Ref. 2.

V. Heine, Czech J. Phys. B13, 619 (1963). We have used larger basis sets and started with GF orbitals as trial functions, and yet the orbitals of the UHF wave function have always converged to the HF results.

Even for \(Z\) slightly greater than 1.0, the attractive potential is strong enough to lead to a bound state.

W. A. Goddard, III, to be published.

The \( \phi_{1a} \) and \( \phi_{1b} \) orbitals (essentially Li inner-shell orbitals) are nearly identical. If \( \phi_{1a} = \phi_{1b} \), then the GF wave function for \( \text{Li}^- \) can be written as

\[
G \{ \phi_{1a} \phi_{2a} \phi_{1b} \phi_{2b} \alpha \beta \alpha \beta \} = c \alpha \beta \phi_{1a} \phi_{2a} \phi_{1b} \phi_{2b} \phi_{2a} \phi_{2b} (2) \phi_{1a} \phi_{1b} (4)
\]

In this case the UHF and GF energies differ by an exchange energy, exactly the same as for \( \text{H}^- \).

Using basis sets appropriate for the UHF wavefunctions and for the GF wave functions and using GF orbitals as trial functions, the UHF orbitals converged to the HF results if only \( s \) basis functions are allowed. However, if \( p \) basis functions are allowed, the UHF and GF orbitals have nonzero coefficients for the \( p \) orbitals, with \( \phi_{2a} \) and \( \phi_{2b} \) hybridized in opposite directions. Thus even for Be the HF wave function is unstable.

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**Matrix Elements Between Configurations Having Several Open Shells. I**

Lloyd Armstrong, Jr.

*Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235* (Received 9 October 1967)

The formalism of second quantization is used to calculate matrix elements of the Coulomb operator between configurations having several open shells. Antisymmetric many-particle states are formed by products of creation operators acting on the vacuum state, and the Coulomb interaction is written as a product of creation and destruction operators. Manipulation of all of these operators leads to results equivalent to those obtained by Fano.

**I. INTRODUCTION**

The calculation of matrix elements between states of an atom having many open shells is a subject which has recently been considered by several authors.1-4 Fano,5 in particular, has made a detailed analysis of the evaluation of the Coulomb operator in such cases. His method entails construction of the antisymmetric states involved by a series of permutations on unsymmetrized wave functions, followed by the use of a procedure, described in an earlier paper,6 which involves the inclusion in the wave function of an imaginary particle, the orbiton. This method allows the entire calculation to be made without recoupling the wave functions at any intermediate point.

A very large portion of Fano's paper was devoted to defining the antisymmetrized wave function, and separating off from this wave function the \( n \)th and \((n-1)\)th particles so that the matrix element could be evaluated. Much of this effort can be bypassed, however, by dealing not with wave functions but rather with the creation operators of the second quantization formalism which produce the wave functions.

In Sec. II we shall consider the pertinent parts of the second quantization formalism, and in Sec. III we shall use this formalism to derive the results obtained by Fano.