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Concerning the Stability of the Negative Ions H^- and Li^- [*]

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The unrestricted Hartree-Fock (UHF) wave functions for H^- and for 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 term leading to 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 H_2.

INTRODUCTION

A number of negative ions (e. g., H^-, Li^-, C^-, O^-, and F^-) are known to be stable.[1] However, because of the greater importance of electron-electron repulsion for these systems, simple wave functions may not always account for the stability of these ions. For example, for H^-, Li^-, and O^-, the Hartree-Fock wave function leads to a higher energy for the ion than for the neutral atom.[2] In this case it becomes of interest to consider improved wave functions for two reasons. One, if we are to believe the properties predicted by a wave function for a system, we should like for the wave function to be good enough at least to correctly predict the stability of the system And two, it is of theoretical interest to determine and understand physically why the Hartree-Fock and other methods cannot account for stability of negative ions. 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.[3] 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.[3] 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 H^-, Li^-, and 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.

$$\psi^{\mathrm{UHF}}(1,2)=\phi_{1a}(1)\phi_{1b}(2)\alpha(1)\beta(2)-\phi_{1b}(1)\phi_{1a}(2)\beta(1)\alpha(2)$$

$$S^{+}\psi^{\mathrm{UHF}}(1,2)=[\phi_{1a}(1)\phi_{1b}(2)-\phi_{1b}(1)\phi_{1a}(2)]\alpha(1)\alpha(2)\neq 0$$

if $\phi_{1a}\neq\phi_{1b}$.[4]

Hence, if[4] $\phi_{1a}\neq\phi_{1b}$ 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 ϕ_{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.[5,7] We will 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 $Z+1$th 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[8] basis set appropriate for the neutral atom plus one function of variable scale parameter. Thus, for H$^-$, two basis functions were used, a 1*s* with $\zeta_1=1.0$ and another 1*s* with ζ_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 $\zeta_{2s}=0.6687$) and an additional 3*s* function with ζ_5 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

$$H^{a}\phi_{ia}=\epsilon_{ia}\phi_{ia} \tag{1a}$$

$$H^{b}\phi_{ib}=\epsilon_{ib}\phi_{ib}, \tag{1b}$$

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

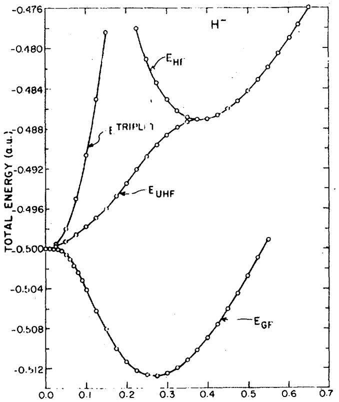

FIG. 1. The total energy from HF, UHF, and GF calculations on H$^-$. The basis set consists of a 1*s* Slater orbital with $\zeta_1=1.0$ and another 1*s* orbital with a variable orbital exponent ζ_2.

state of 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 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.

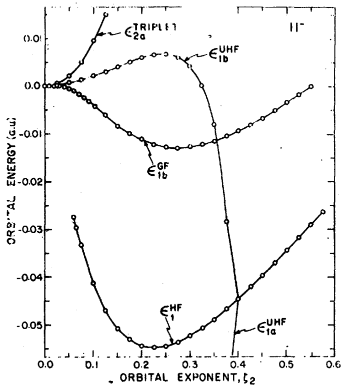

FIG. 2. The orbital energies for the loosely bound electron as found from HF, UHF, and GF calculations on H$^-$.

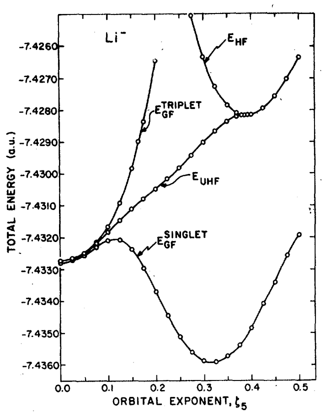

FIG. 3. The total energy from HF, UHF, and GF calculations on Li$^-$. The basis set consists of four Slater orbitals appropriate for Li and another 3s orbital with a variable orbital exponent ζ_5.

From Fig. 1 we see that the UHF wave function for H$^-$ yields a minimum energy for $\zeta_2 = 0$, which corresponds to H + e^-. We also see that the HF wave function never gets an energy even close to that of H + e^-. Note that if we force the UHF wave function to use a large enough ζ_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 ζ_2 which is optimum for the HF wave function. As ζ_2 approaches this value, the overlap between the two UHF orbitals rapidly increases toward 1.0 and ϵ_{1b}^{UHF} and ϵ_{1a}^{UHF} rapidly approach ϵ_1^{HF} (see Fig. 2).

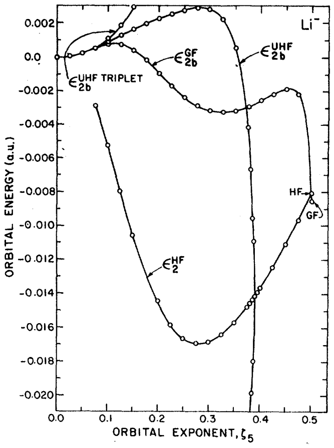

FIG. 4. The orbital energies for the loosely bound electron as found from HF, UHF, and GF calculations on Li$^-$.

The GF method leads to an energy[9] of 0.512809 and thus predicts stability for H$^-$. It is not apparent from the graph, but the GF energy increases for small ζ_2 near 0, reaching a value of -0.499952 at $\zeta_2 = 0.02$. Note that there is a minimum in ϵ_{1b} which occurs almost exactly at the same ζ_2 as the minimum in total energy (see Figs. 1 and 2).

The results for Li$^-$ are quite similar to those for H$^-$. The UHF wave function has a minimum at $\zeta_5 = 0$, which just corresponds to Li + e^-. The HF energy is always far worse than that of Li + e^-. If we force ζ_5 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 ζ_5 for HF. Again the UHF functions change rapidly for ζ_5 slightly less than this critical value.

For Li$^-$ the GF method leads to an energy[9] of -7.43591 which is lower than the energy of Li. Again the GF energy increases for small ζ_5, and again the minimum in the valence orbital energy (ϵ_{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 H$^-$ Negative Ion

For H$^-$ the electronic Hamiltonian is

$$H(1,2) = h(1) + h(2) + g(1,2), \tag{2}$$

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

The HF wave function for H$^-$ is[10]

$$\psi^{HF} = \mathcal{A}(\phi_1\phi_1\alpha\beta) = \tfrac{1}{2}\phi_1\phi_1(\alpha\beta - \beta\alpha), \tag{3}$$

where

$$H^{HF}\phi_1 = \epsilon_1\phi_1,$$

$$H^{HF} = h + U_1^{HF},$$

$$U_1^{HF}(1) = \int d\vec{x}_2 \frac{\phi_1(2)\phi_1(2)}{r_{12}} \tag{4}$$

and

$$E^{\mathrm{HF}} = \langle \phi_1\phi_1 | H | \phi_1\phi_1 \rangle .$$

For H^- the UHF wave function is[10, 11]

$$\psi^{\mathrm{UHF}} = \mathcal{A}(\phi_a\phi_b\alpha\beta) = \tfrac{1}{2}(\phi_a\phi_b\alpha\beta - \phi_b\phi_a\beta\alpha), \quad (5)$$

where

$$H_a^{\mathrm{UHF}}\phi_a = \epsilon_a\phi_a, \quad (6)$$

$$H_a^{\mathrm{UHF}} = h + U_a^{\mathrm{UHF}},$$

$$U_a^{\mathrm{UHF}}(1) = \int d\vec{x}_2 \frac{\phi_b(2)\phi_b(2)}{r_{12}}, \quad (7)$$

and[12]

$$E^{\mathrm{UHF}} = \langle ab | H | ab \rangle .$$

And the GF wave function is[10, 11]

$$\psi^{\mathrm{GF}} = G_f(\phi_a\phi_b\alpha\beta) = \tfrac{1}{4}(\phi_a\phi_b + \phi_b\phi_a)(\alpha\beta - \beta\alpha), \quad (8)$$

where

$$H_a^{\mathrm{GF}}\phi_a = \epsilon_a^{\mathrm{GF}}\phi_a, \quad (9)$$

$$H_a^{\mathrm{GF}} = h + U_a^{\mathrm{GF}},$$

$$U_a^{\mathrm{GF}}(1) = \int d\vec{x}_2 \frac{\phi_b(2)\phi_b(2)}{r_{12}} + \int d\vec{x}_2 \phi_b(2) \langle H(1,2) - E \rangle P_{12}\phi_b(2), \quad (10)$$

and[12]

$$E^{\mathrm{GF}} = \langle ab | H | ab \rangle + \langle ab | H - E | ba \rangle$$

$$= \langle a | h | a \rangle + \epsilon_b .$$

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.[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 $V_b^{\mathrm{UHF}}(r) = U_b^{\mathrm{UHF}}(r) - Z/r$ must be too weak to have a bound state. In the GF method, the potential for the ϕ_b electron is the same as V_b^{UHF} except for an additional term, $U_b^{\mathrm{exch,\,GF}}$, where

$$U_b^{\mathrm{exch,\,GF}}(1) = \int dx_2 \phi_a(2) \times [h(1) + h(2) + 1/r_{12} - E] P_{12}\phi_a(2) .$$

Since the potential

$$V_b^{\mathrm{GF}} = V_b^{\mathrm{UHF}} + U_b^{\mathrm{exch,GF}}$$

does have a bound state, the net effect of $U_b^{\mathrm{exch,\,GF}}$ must be significantly attractive. In fact

$$\langle \phi_b | U_b^{\mathrm{exch,\,GF}} | \phi_b \rangle = 2\langle b | a \rangle \langle a | -\tfrac{1}{2}\nabla^2 | b \rangle + 2\langle b | a \rangle \langle a | -Z/r | b \rangle + \langle ab | g | ba \rangle - E\langle a | b \rangle^2$$

is negative, but all of the components except $2\langle b | a \rangle \langle a | -Z/r | b \rangle$ 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[15,16] (in the sense of Thouless) with respect to the UHF wave function. This is in contrast to the case of He,[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 ($\zeta_2 > 0.4$), 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 ϵ_b and E occur near the same ζ_2 since $E = \langle \phi_a | h | \phi_a \rangle + \epsilon_b$ and ϕ_a is not very dependent on ζ_2 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^{GF} is nonlocal (since it involves permutations); however, after one has solved for the orbitals from (9), we can find the

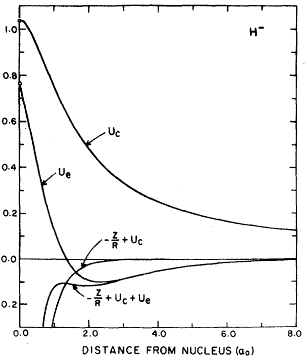

FIG. 5. The local potential seen by the outer electron of H^-.

local potential for which the orbital is a solution.[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 of the $U_b^{\rm GF}$ is negative for $R > 1.33a_0$. This leads to a dramatic difference between $V_b^{\rm UHF} = -Z/r + U_b^{\rm Coul}$ and $V_b^{\rm GF} = -Z/r + U_b^{\rm Coul} + U_b^{\rm exch}$; thus $V^{\rm GF}$ is significantly lower than $V^{\rm UHF}$ for $R > 1.5$. Using this potential and integrating (6) for $\epsilon_b = 0$, we find that $V^{\rm UHF}$ has no bound states: whereas a similar integration of (9) for $V^{\rm GF}$ shows one bound state.

Table I. Expansion coefficients and other results for the GF wave function for H$^-$. (Atomic units are used, thus the unit of energy is the hartree or 27.211 eV.)

Basis function type	ζ	ϕ_{1a}	ϕ_{1b}
1s	1.0	1.04400	0.20402
4s	1.403	−0.03090	0.07695
3s	1.40	−0.03701	0.07014
3s	0.735	0.01191	0.53774
5s	0.4139	−0.01244	−0.69710
4s	0.3647	0.01951	1.03511
orbital energy		−0.26800	−0.01471
cusp		−1.0000	−1.0000
$\phi(0)$		0.58901	0.11511

Total energy	−0.5138393
Kinetic energy	0.5138877
Electron-electron energy	0.2972647
Virial ratio, $V/2E$	1.000047

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$^-$.[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[15,16] with respect to the UHF wave function.[21] For this small basis-set calculation, the HF Roothaan solution is stable for $\zeta_5 > 0.4$ just as occurred for H$^-$.

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 $\hat{L}^2$ 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.

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‡Contribution No. 3634.

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[4] By $\phi_{1a} \neq \phi_{1b}$ we mean not equal within a phase factor.

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[6] W. A. Goddard, III, J. Chem. Phys. 48, 450 (1968), hereafter called III.

[7] W. A. Goddard, III, J. Chem. Phys. 48, 1008 (1968), hereafter called IV.

[8] An *ns* Slater orbital has the form $\chi_{n0} = N_{n0} r^{n-1} e^{-\zeta r}$, where N_{n0} is a normalization factor.

[9] 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 −0.5138392 and for Li$^-$ is −7.443099.

[10] The many-electron wave functions used here are not normalized to one.

[11] When electron numbers are omitted, the orbitals and spin functions are assumed to be ordered according to electron number. Thus $\phi_a\phi_b\alpha\beta \equiv \phi_a(1)\phi_b(2)\alpha(1)\beta(2)$.

[12] For convenience we often denote an orbital by its subscript. Thus $\langle ab|H|ab\rangle \equiv \langle \phi_a\phi_b|H|\phi_a\phi_b\rangle$.

[13] Usually the valence-bond (VB) energy is written

$$E^{\mathrm{VB}} = \frac{\langle ab|H|ab\rangle + \langle ab|H|ba\rangle}{1+|\langle a|b\rangle|^2},$$

but this is equivalent to

$$E^{\mathrm{VB}} = \langle ab|H|ab\rangle + \langle ab|H-E^{\mathrm{VB}}|ba\rangle,$$

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

[14] R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1964), p. 19.

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[16] T. A. Kaplan and W. H. Kleiner [Phys. Rev. 156, 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 B^-, N^-, and O^- must also be unstable. See Ref. 2.

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[18] Even for Z slightly greater than 1.0, the attractive potential is strong enough to lead to a bound state.

[19] W. A. Goddard, III, to be published.

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

$$G_f(\phi_1\phi_{2a}\phi_1\phi_{2b}\alpha\beta\alpha\beta) = c\mathfrak{A}\{\phi_1(1)\phi_1(2)[\phi_{2a}(3)\phi_{2b}(4) + \phi_{2b}(3)\phi_{2a}(4)]\alpha\beta\alpha\beta\}.$$

In this case the UHF and GF energies differ by an exchange energy, exactly the same as for H^-.

[21] Using basis sets appropriate for the HF wave functions 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 ϕ_{2a} and ϕ_{2b} hybridized in opposite directions. Thus even for Be the HF wave function is unstable.

Matrix Elements Between Configurations Having Several Open Shells. I

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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,[3] 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,[5] 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 nth 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.