any estimate of $\Omega$ is attempted. It will be noted that the values from virial coefficients ($\pm 6$, $\pm 5$) are appreciably larger than our value and may reflect the fact that in selecting parameters for the 12-6 core potential, the dispersion forces were underestimated leading to a corresponding overestimate of the effect of an octopole moment.

An evaluation of the quantum-mechanical estimates of $\Omega$ is still more difficult. For the most part they lie below estimates from virial coefficients, although three values are higher. If one were to use our value of $\Omega$ to judge the wavefunctions employed in the calculations, then the wavefunctions of Sinai and Albasiny and Cooper would appear to be the most appropriate.

Our value for the octopole moment of carbon tetrafluoride is $\pm 13.7 \times 10^{-34}$ esu cm$^3$, somewhat larger than the value of $4.4 \times 10^{-34}$ esu cm$^3$ estimated by Parsonage and Scott from phase transition data.

**ACKNOWLEDGMENT**

The computer time was supported by National Aeronautics and Space Administration Grant NsG-398 to the Computer Science Center of the University of Maryland.


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**Wavefunctions and Correlation Energies for Two-, Three-, and Four-Electron Atoms**

**William A. Goddard III**

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

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A recently developed method (the GF method) which is equivalent to optimizing the orbitals of a Slater determinant after spin projection has been applied to H-, He, Li+, Be++, Li, Be+, B++, Li-, Be-, B-, and C++. These wavefunctions, which can be given an independent particle interpretation, yield better energies than those of the Hartree–Fock method. For example, H– and Li– are correctly predicted to be stable in contradistinction with the Hartree–Fock results. The new correlation energies are tabulated and compared to the Hartree–Fock values. In the case of the two-electron systems the new wavefunctions are nearly at the radial limit, accounting for 93% to 97% of the radial correlation error present in the Hartree–Fock description.

**INTRODUCTION**

Numerous different methods have been used to calculate the nonrelativistic wavefunctions for atoms. Probably the method which has been most important conceptually has been the Hartree–Fock method. The independent particle interpretation of the many-electron wavefunction afforded by this method leads to a persuasive and cogent interpretation of the ground and excited states of the various atoms and ions that forms the basis of practically every discussion of such systems. Other methods such as configuration interaction have led to more accurate results on the smaller atoms but are usually interpreted in terms of concepts based on the Hartree–Fock method. In addition, the Hartree–Fock method forms a useful, although much more imperfect, conceptual foundation for molecules and solids. Here, for example, the description of changes in energies and wavefunctions as a function of internuclear distance usually become patently incorrect for large distances (e.g., the Hartree–Fock wavefunction for LiH dissociates to Li+ and H– rather than to Li and H). This problem and others have been overcome by the GF method for wavefunctions, which is equivalent to optimizing the orbitals of a Slater determinant after spin projection.

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* Contribution No. 3505.
to optimizing the orbitals of a Slater determinant wavefunction after spin projection. We have shown elsewhere\(^1\) that GF method yields accurate and consistent wavefunctions for even large intermolecular distances and that the many-electron wavefunctions can be interpreted in an independent particle scheme. In addition, we have shown that the GF method, which always leads to energies lower than the Hartree–Fock energy, can yield drastically improved values for such properties as the spin density\(^2\) at the nucleus.

The GF method is a special case of the general GI method described in Ref. 1. This special case is of particular interest because it leads to wavefunctions equivalent to those from the spin-polarized extended Hartree–Fock method (optimization of the orbitals of a Slater determinant after spin projection), because the general GF equations are particularly simple to develop and program, and because this method does remove the above-mentioned deficiencies present in the Hartree–Fock method. The GF method is applied here to a series of two-, three-, and four-electron atoms and ions in order to continue the examination of the efficacy and usefulness of this method for atoms.

THE GF EQUATIONS

In the Hartree–Fock method we consider wavefunctions of the form

\[ \alpha \Phi \chi, \]

where \( \alpha \) is the antisymmetrizer for \( N \) electrons, \( \Phi \) is a product of \( N \) spatial orbitals, and \( \chi \) is a product of \( N \) one-electron spin functions. We then require that the orbitals used in \( \Phi \) be the best possible ones; i.e., the ones which yield the best possible total energy. The result is a set of \( N \) equations

\[ H_{\text{HF}} \Phi_i = \epsilon_i \Phi_i, \]

for the best orbitals, where \( H_{\text{HF}} \) consists of the one-electron operator for an electron and a sum over Coulomb and exchange operators depending on the other orbitals occupied. The antisymmetrizer ensures that the many-electron wavefunction in (1) satisfies Pauli’s principle; however, it does not ensure that the function be an eigenfunction of \( S^2 \).

In the GF method we consider many-electron wavefunctions of the form

\[ G_\gamma \Phi \chi, \]

where \( \Phi \) and \( \chi \) are again products of spatial and spin functions, respectively, and \( G_\gamma \) is an operator defined in terms of permutations of the various spatial and spin coordinates of the electrons. This operator, \( G_\gamma \), has the property that for all \( \Phi \) and \( \chi \), (2) is an eigenfunction of \( S^2 \) and satisfies Pauli’s principle. The \( G_\gamma \) operator is discussed in Refs. 1 and 3, but for convenience we include an expansion of (2) in terms of Slater determinants for the two-, three-, and four-electron systems discussed here (\( N! \) \( \alpha \) is the determinant operator):

\[ N = 2, \ S = 0: \ G_\gamma(\phi_{1\alpha}\phi_{1\beta}) = \frac{1}{2} [\alpha(\phi_{1\alpha}\phi_{1\beta}) \]

\[ + \alpha(\phi_{1\beta}\phi_{1\alpha})], \]

\[ N = 3, \ S = \frac{1}{2} : \ G_\gamma(\phi_{1\alpha}\phi_{2\beta}\phi_{3\gamma}) = \frac{3}{2} [2(\alpha(\phi_{1\alpha}\phi_{2\beta}\phi_{3\gamma}) \]

\[ + \alpha(\phi_{1\alpha}\phi_{2\beta}\phi_{3\gamma}) + \alpha(\phi_{1\beta}\phi_{2\alpha}\phi_{3\gamma}) + \alpha(\phi_{1\beta}\phi_{2\alpha}\phi_{3\gamma}) + \alpha(\phi_{1\beta}\phi_{2\alpha}\phi_{3\gamma}) + \alpha(\phi_{1\beta}\phi_{2\alpha}\phi_{3\gamma})], \]

\[ N = 4, \ S = 0: \ G_\gamma(\phi_{1\alpha}\phi_{2\beta}\phi_{3\gamma}\phi_{4\delta}) = \frac{3}{2} [2(\alpha(\phi_{1\alpha}\phi_{2\beta}\phi_{3\gamma}\phi_{4\delta}) \]

\[ + \alpha(\phi_{1\alpha}\phi_{2\beta}\phi_{3\gamma}\phi_{4\delta}) + \alpha(\phi_{1\beta}\phi_{2\alpha}\phi_{3\gamma}\phi_{4\delta}) + \alpha(\phi_{1\beta}\phi_{2\alpha}\phi_{3\gamma}\phi_{4\delta}) + \alpha(\phi_{1\beta}\phi_{2\alpha}\phi_{3\gamma}\phi_{4\delta}) + \alpha(\phi_{1\beta}\phi_{2\alpha}\phi_{3\gamma}\phi_{4\delta})]. \]

The notation used here is that

\[ \Phi = \phi_{1\alpha}(1) \phi_{2\beta}(2) \cdots \phi_{n\alpha}(n) \phi_{n+1\beta}(n+1) \cdots \phi_{m\delta}(N), \]

\[ \chi = \alpha(1)\alpha(2)\cdots\alpha(n)\beta(n+1)\cdots\beta(N), \]

where \( n + m = N \), the number of electrons; and \( (n - m)/2 = S \), the total spin. The GF method consists of using the variational principle to obtain the optimum orbitals for (2). The resulting equations for the optimum orbitals (the GF orbitals) for general \( N \) have been derived elsewhere.\(^3\) However, in order to clarify the ideas involved in the GF method and the significance of the independent particle interpretation, we consider the case of a two-electron singlet state in detail. In this case the GF wavefunction is\(^3\)

\[ G_\gamma \Phi \chi \]

\[ = \frac{1}{2} [\phi_{1\alpha}(1)\phi_{2\beta}(2) + \phi_{1\beta}(1)\phi_{2\alpha}(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]. \]

The orbitals \( \phi_{1\alpha} \) and \( \phi_{2\beta} \) are variationally chosen to minimize the total energy,

\[ E = \langle G_\gamma \Phi \chi | H | G_\gamma \Phi \chi \rangle / \langle G_\gamma \Phi \chi | G_\gamma \Phi \chi \rangle \]

\[ = \langle \Phi | H | O_{1/2} \Phi \rangle / \langle \Phi | O_{1/2} \Phi \rangle \]

\[ = \frac{1}{2} [\langle \phi_{1\alpha} | h | \phi_{1\alpha} \rangle + \langle \phi_{1\beta} | h | \phi_{1\beta} \rangle + \langle \phi_{1\beta} | h | \phi_{1\alpha} \rangle + \langle \phi_{1\alpha} | h | \phi_{1\beta} \rangle + \langle \phi_{2\alpha} | h | \phi_{2\alpha} \rangle + \langle \phi_{2\beta} | h | \phi_{2\beta} \rangle + \langle \phi_{2\beta} | h | \phi_{2\alpha} \rangle + \langle \phi_{2\alpha} | h | \phi_{2\beta} \rangle] \]

\[ = \frac{1}{2} [\langle \phi_{1\alpha} | h | \phi_{1\alpha} \rangle + \langle \phi_{1\beta} | h | \phi_{1\beta} \rangle + \langle \phi_{2\alpha} | h | \phi_{2\alpha} \rangle + \langle \phi_{2\beta} | h | \phi_{2\beta} \rangle] D^{-1}, \]

where \( H = h(1,2) + g(1,2) \) is the many-electron Hamiltonian, \( h = -\frac{1}{2} \nabla^2 + V \) is the sum of the kinetic energy and nuclear attraction terms for an electron, \( g(1,2) = 1/\|r_{12} \| \) is the electron repulsion term, and \( D = 1 + \langle \phi_{1\alpha} | \phi_{1\alpha} \rangle \).

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\(^1\) W. A. Goddard, III, Phys. Rev. 157, 93 (1967).
If \( E \) is to be stationary under any variation, \( \delta \phi', \) in \( \phi_a \) or \( \phi_b, \) we have

\[
\hbar \delta \phi_a(1) + \langle \phi_b | \phi_a \rangle \hbar \delta \phi_b(1) + \langle \phi_b | \hat{h} \phi_a \rangle \phi_b(1) + \left( \int \frac{\phi_b^* (2) \phi_b (2)}{r_{12}} \; dx_2 \right) \phi_a (1)
\]

\[+ \left( \int \frac{\phi_b (2) \phi_b (2)}{r_{12}} \; dx_2 \right) \phi_b (1) - E \langle \phi_b | \phi_b \rangle \phi_b (1) = \epsilon_a \phi_a (1), \tag{4} \]

where we have imposed the constraints that both \( \phi_a \) and the total wavefunction remain normalized under the variation. Replacing each \( a \) by \( b \) and vice versa we obtain a similar equation involving \( \epsilon_b. \) We write (4) as

\[
H_{\phi_a} (1) = (\hbar + U_a) \phi_a = \epsilon_a \phi_a, \tag{5} \]

where

\[
U_a (1) = \left( \int dx_2 \frac{\phi_b^* (2) \phi_b (2)}{r_{12}} \right) + \left( \int dx_2 \phi_b^* (2) [h(1) + h(2) + r_{12}^{-1} - E] \phi_b (2) \right) \tag{6} \]

and \( P_{12} \) permutes Electrons 1 and 2. The second term of (6) results because the overlap between \( \phi_b \) and \( \phi_b \) is not fixed; such terms need not be kept in the Hartree–Fock method since the orbital overlaps are 0 or 1. On the other hand, if the Hamiltonian had no inter-electronic repulsions, it would be separable and the exact wavefunction could be written in the form (3), where the \( \langle \phi_a | \phi_b \rangle = 1 \) (for the ground state). In this case \( E \rightarrow 2 \langle \phi | \hat{h} | \phi \rangle \) and thus \( U_a = 0 \) as \( g \rightarrow 0. \) Hence \( U_a, \) which depends upon \( \phi_b \), but not on \( \phi_b, \) can be interpreted as the average potential acting on the electron in \( \phi_a \) due to an electron in \( \phi_b \). The form of this potential is not at all arbitrarily chosen [say, e.g., on classical grounds which might have yielded only the first term in (6)] but rather is just exactly the form for which the eigenfunction of \( h + U_a \) is the best possible orbital \( \phi_a \) to place in (3). That is, out of all possible \( \phi_a, \) and \( \phi_b, \) the ones which are the optimum for moving in the fields \( U_a \) and \( U_b \) are just the ones which yield the best possible energy [for wavefunctions of form (3)]. Thus, by use of the variational principle we have determined what one might consider to be the proper quantum mechanical potential for an electron moving in the field of one other electron [for the case where the many-electron wavefunction is a singlet; for a triplet state the second term in (6) would be multiplied by \(-1\)]. Hence, if the \( \phi_a, \) and \( \phi_b, \) are solutions of (5), we may rather rigorously discuss the two-electron wavefunction in terms of the \( \phi_a, \) and \( \phi_b, \) separately. That is, we may picture one electron as moving in \( \phi_a, \) and the other in \( \phi_b, \) with each one experiencing a time average of the potential due to the other one. It must be emphasized that we do not imply that we can actually distinguish between the real electrons, and we do not say that one electron is in \( \phi_a, \) and the other is in \( \phi_b. \) Rather we say that if we had a system with a potential distribution \( V + U_a, \) where \( V \) is the potential due to the nuclei, then the eigenstate for an electron moving in this potential is just \( \phi_a. \) Thus, it is the states which are discussed independently in the independent particle scheme, and we discuss an electron moving in each state only by making a correspondence to a hypothetical system with all of the other electrons replaced by \( U_a. \) (One could, of course, picture this hypothetical system as just our real one with time averages over the other electrons, providing one remembers that the electrons cannot really be so assigned to orbitals.)

The same arguments apply to the case with more than two electrons where we also obtain equations like (5) which lead to the independent particle interpretation for \( G_r^o \phi_X \) wavefunctions as discussed in Ref. 1. Similarly, the same arguments can be used to show that the Hartree–Fock wavefunction can also be given an independent particle interpretation. In this case the wavefunction is approximated by (1) which for the case of a two-electron singlet becomes

\[
\psi (1) \psi (2) \left[ \alpha (1) \beta (2) - \beta (1) \alpha (2) \right].
\]

We require that the \( \phi \) be optimum and obtain

\[
U_{HF} (1) = \int \frac{\phi_b^* (2) \phi_b (2)}{r_{12}} \; dx_2,
\]

which is similar to what one would expect classically. For more electrons the \( U_{HF} \) also contains nonclassical terms like

\[
- \int \frac{\phi_b (2) P_{r} \phi_b (2)}{r_{12}} \; dx_2,
\]

called exchange terms, just as does \( U_{GF}. \)

One does not in general obtain the semiclassically expected potential

\[
U_{cl} (1) = \sum_{j=1}^{N} \int \frac{\phi_j^* (2) \phi_j (2)}{r_{12}} \; dx_2 \tag{7}
\]

for either of these independent particle schemes. However, by taking the many-electron wavefunction as a product of spin orbitals,

\[
\Psi (1, \cdots, N) = \psi_1 (1) \psi_2 (2) \cdots \psi_N (N), \tag{8}
\]

do we get a \( U_{cl} \) as in (7), where the \( \psi_i, \) are solutions of

\[
(h + U_{cl}) \psi_i = \epsilon_i \psi_i. \tag{9}
\]
But the lowest total energy occurs for

\[ \Psi = \psi_1(1)\psi_1(2) \cdots \psi_1(N), \]

where \( \psi_1 \) is the lowest eigenfunction of (9) (but having
either spin). Such a state is not allowed for electrons if
\( N > 2 \), of course, and results because our general func-
tion (8) is not restricted so as to satisfy Pauli’s prin-
ciple! If we arbitrarily choose to select only different
orthogonal states for (8), we get more reasonable
energies; however, in order to force the \( \Psi \) to use ortho-
gonal states, we would have to include new Lagrange
multipliers to ensure orthogonality of \( \psi_i \) and \( \psi_j \). But
the result would be

\[ (\hbar + U_r \ell) \psi_i = \sum_j \epsilon_j \psi_j \]

rather than (9), and in this case it is not possible to
remove the nondiagonal \( \epsilon_{ij} \) by, say, a transformation
upon the \( \psi_j \), as is done in the Hartree–Fock method.
Even if we did solve (10), the resulting orbitals could
not be given an independent particle interpretation
since they would not be eigenfunctions of \( \hbar + U_r \ell \).
Thus this whole approach must be considered as a
method for approximate solutions to the Hartree–Fock
or GF equations (in which terms in \( U \) are neglected).
This procedure with certain additional restrictions is
referred to as the Hartree method.

Our conclusion is that both the Hartree–Fock and
GF methods yield valid independent particle inter-
pretations of the many-electron wavefunctions. Since
the GF energy is always the lower and since the GF
orbitals sometimes give rise to a far more compelling
interpretation of the atom (e.g., the picture of \( ^2 \) as
given in the Discussion) the GF method might often be
preferred. In addition, we have previously shown\(^1\)
that the GF wavefunction changes continuously from
the molecular form to the atomic form as the atoms
are pulled apart (e.g., the GF wavefunction for LiH goes
continuously to that for separated Li and H atoms).
Thus of the two only the GF method affords a con-
sistent interpretation of both molecular and atomic
systems (and solids).

### Correlation

In the GF method each orbital is determined self-
consistently as the best orbital for an electron moving in the
\textit{average} field due to all of the other electrons. Each
best orbital is neither determined by nor a function of
the instantaneous positions of the other electrons, and
the interelectronic coordinates, \( r_{ij} \), are \textit{not}
involved in the resulting many-electron wavefunction.
Thus the GF wavefunctions do not depend on the instantaneous
positions of the electrons and can be properly termed as
\textit{not} containing correlation. In addition, the same argu-
ment which is used to show that GF wavefunctions can
be termed as not containing correlation may also be
used to show that the Hartree–Fock wavefunctions can
also be so termed.

One might have considered defining correlation such
that a wavefunction contains correlation only if the pair
probability of having an electron at \( r_1 \) simultaneous with
having another electron at \( r_2 \) is just the probability of
having an electron at \( r_1 \), times the probability of having
an electron at \( r_2 \), i.e., \( \pi(1, 2) = \rho(1)\rho(2) \). By such a
definition both the Hartree–Fock and the GF wave-
functions normally contain correlation and, \textit{a fortiori},
so would any electronic wavefunction satisfying Pauli’s
principle! For this reason the \( \pi(1, 2) = \rho(1)\rho(2) \) defini-
tion has generally not been used to define correlation,
and in fact correlation seems often to be defined as
whatever is not contained in the Hartree–Fock wave-
function.\(^6\)\(^8\) We believe that the thing which has been
called correlation has proved to be a useful concept\(^6\)
and that the physical idea which corresponds to the
way this concept has been used is just as follows: A
many-electron wavefunction does not contain correla-
tion if it can be interpreted in terms of a set of one-
electron states each of which is the optimum state for
an electron moving in the \textit{average} field due to the
other electrons, and thus each orbital is neither deter-
mined by nor a function of the instantaneous positions
of the other electrons. That is, we would say that if a
wavefunction can be given an independent particle inter-
pretation (as defined in the previous section) then
by definition this wavefunction does \textit{not} contain correla-
tion. In order to finish the definition we must specify
which of these types of functions not containing
correlation is to be taken as defining correlation. The
obvious criterion is to use the one yielding the best
energy. For ground states the GF wavefunction \textit{always}
leads to a lower energy than the Hartree–Fock wave-
function\(^1\) which in turn generally leads to a lower
energy than the Hartree wavefunction; hence the GF
energy would appear to be a more appropriate zero for
correlation energy than either the Hartree or Hartree–
Fock energies. This becomes manifest when we consider
molecules. For example, as the internuclear distance for
\( \text{H}_2 \) is infinitely increased, the GF energy goes to the
energy of two separated hydrogen atoms whereas the
Hartree–Fock energy is \( 7.74 \text{ eV} \) higher.\(^5\)\(^6\) Thus using the
Hartree–Fock wavefunction as the zero for correlation,
we would say that two separated hydrogen atoms
infinitely far apart have a correlation energy of \( 7.74 \text{ eV} \! \)!
This is, of course, quite contrary to what we wish to
mean by correlation since electrons infinitely far apart
should be quite oblivious to the motions of each other.
Since for the majority of molecules the Hartree–Fock
wavefunction has a similar nonphysical error in energy
at large internuclear distances, we see that use of the
Hartree–Fock energy as a zero for correlation is at best
ambiguous. In addition, the use of Hartree–Fock
energy for defining correlation has been criticized by
Clementi\(^6\) because of the imbalance in treating electrons

This Hartree-Fock calculation used eight basis functions, Roothaan, L. M. Sachs, and A. with orbital exponents of 1.215 and .4623, the total energy is Hartree wavefunction does not satisfy Pauli’s principle. Fock correlation energies of Clementi (Ref. 6) are used. Of the same spin as compared to those of different spin. For this reason Clementi suggests defining correlation energy as the difference between the exact energy and the GF energy. In this paper, as a result of the above considerations, we obtain the correlation energies, $E_{\text{corr}}$, in Table I for the two- and four-electron systems. This Hartree-Fock wavefunctions. The Hartree-Fock values are in parentheses. The nuclear charge is $Z$.

### Table I. Correlation energies* for atoms using GF and Hartree-Fock correlation energies of Clementi (Ref. 6) are used.

<table>
<thead>
<tr>
<th>Number of electrons</th>
<th>$Z$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 $^1S^0$</td>
<td>-0.0140 ($-0.0398$)</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>2</td>
<td>3 $^3S^0$</td>
<td>-0.0257 ($-0.0421$)</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>3</td>
<td>4 $^1S^0$</td>
<td>-0.0285 ($-0.0435$)</td>
<td>-0.0452 ($-0.0453$)</td>
<td>-0.0576 ($-0.0725$)</td>
<td>...</td>
</tr>
<tr>
<td>4</td>
<td>...</td>
<td>-0.0298 ($-0.0443$)</td>
<td>-0.0473 ($-0.0475$)</td>
<td>-0.0801 ($-0.0944$)</td>
<td>...</td>
</tr>
<tr>
<td>5</td>
<td>...</td>
<td>...</td>
<td>-0.0486 ($-0.0489$)</td>
<td>-0.0984 ($-0.1123$)</td>
<td>...</td>
</tr>
<tr>
<td>6</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>-0.1131 ($-0.1268$)</td>
<td>...</td>
</tr>
</tbody>
</table>

* Except for $H^-$ and $Li^+$ the nonrelativistic “exact” energies and Hartree-Fock correlation energies of Clementi (Ref. 6) are used.

b Based on the “exact” energy from C. L. Pekeris, Phys. Rev. 126, 1470 (1962) and a Hartree-Fock calculation similar to C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960). This Hartree-Fock calculation used eight basis functions, 1s, 2s, 3s, and 4s, with orbital exponents of 1.215 and .4623, the total energy is -0.4879297.

Calculated Correlation Energies

Using the GF energy as the zero for correlation, we obtain the correlation energies, $E_{\text{corr}}$, in Table I (atomic units are used7). For comparison the correlation energies, $E_{\text{corr}}$, based on Hartree-Fock wavefunctions are also given (in parentheses). All of the $|E_{\text{corr}}|$ are, of course, smaller than $|E_{\text{corr}}|$, but the most striking difference is that $E_{\text{corr}}$ is a rather smooth function of the number of electrons while $E_{\text{corr}}$ is nearly the same for two and three electrons. For a given number of electrons the $|E_{\text{corr}}|$ is a gradually increasing function of nuclear charge except for the negatively charged ions, which have relatively lower correlation energy. For three-electron atoms the GF energies are only slightly better than the Hartree-Fock energies. Although these energy improvements are 3½ and 2 times greater than those obtained by the unrestricted Hartree-Fock (UHF) and spin-projected UHF methods, they are small compared to the improvements obtained for the two- and four-electron systems. This apparent difference in the treatment of singlets and doublets may mean that the GF correlation energies of the three-electron atoms are not strictly comparable with those of the two- and four-electron atoms.

Of particular interest are the results for the two-electron atoms. In this case the GF energy approaches the radial limit [the limiting energy for configuration interaction wavefunctions of type $\psi(1,2) = \sum \psi_1 \psi_2 | r_1 \rangle | r_2 \rangle$]. Thus for He the GF energy is 99.96% of the radial limit and accounts for 94.2% of the radial correlation energy as defined with respect to $E_{\text{HF}}$. Since the GF wavefunction does not involve the instantaneous correlation of the electrons, we conclude that instantaneous radial correlation is of very little importance in two-electron atoms and that all that is important, radially speaking, is to allow the electrons to move in different radial regions. The GF energy and radial limit are compared in Table II for the various two-electron atoms. Note that $E_{\text{RF}} - E_{\text{HF}}$ is the same, 0.0010, for He, $Li^+$, and $Be^+$.

### Table II. Comparison of Hartree-Fock and GF energies with the radial limit for two-electron atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$E_{\text{HF}}$</th>
<th>$E_{\text{GF}}$</th>
<th>$E_{\text{RF}}$</th>
<th>$E_{\text{RF}} - E_{\text{HF}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-0.4879</td>
<td>-0.4879</td>
<td>-0.5138</td>
<td>-0.0259</td>
</tr>
<tr>
<td>He</td>
<td>-2.8617</td>
<td>-2.8790</td>
<td>-2.8780</td>
<td>-0.0070</td>
</tr>
<tr>
<td>Li+</td>
<td>-7.2364</td>
<td>-7.2524</td>
<td>-7.5007</td>
<td>-0.2400</td>
</tr>
</tbody>
</table>

a See Footnote b of Table I.
d See Footnote 12.
Table III. Energies and expectation values for GF wavefunctions of atoms. NBF is the number of basis functions, $V$ is the total potential energy, and $E$ is the total energy.

<table>
<thead>
<tr>
<th>Atom</th>
<th>NBF</th>
<th>$E$</th>
<th>$\langle \Sigma V(r_i) \rangle$</th>
<th>$V/2E$</th>
<th>$\langle \Sigma \delta(r_i) \rangle$</th>
<th>$\langle \Sigma 1/r_i \rangle$</th>
<th>$\langle \Sigma r_i \rangle$</th>
<th>$\langle \Sigma r_i^2 \rangle$</th>
<th>$\langle \Sigma (r_i)^3 \rangle/S$</th>
</tr>
</thead>
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$H_2C_B = SC_BH_2$, where the vectors $C_A$ and $C_B$ are the GF orbitals and $S$ is the overlap matrix for the basis functions. These equations were solved by diagonalizing $S$ and then diagonalizing the transformed $H$ matrix. Thus the $C$ were solved for in terms of an orthogonal basis set and then transformed back to the Slater basis set. Most of the expanded basis sets were nearly linearly dependent (eigenvalues of $S$ less than $10^{-6}$) and in some cases this resulted in a loss of significant figures after transforming the $C$ matrix back to the Slater basis set. The orbital exponents for the expanded basis sets were not reoptimized since in most cases the virial ratio remained within $3 \times 10^{-6}$ of 1.0.

The energies from the calculations with the larger basis sets were used in Tables I and II. The energies and several other properties are given in Table III for both basis sets. The GF orbitals (i.e., the coefficients for the expansion in terms of the basis functions) are given in Tables IV and V along with the orbital energy, $\epsilon_i$; the cusp at the nucleus; and the amplitude at the nucleus for each orbital.

Recently, different methods have been used to obtain wavefunctions related to the GF wavefunctions for He by Chong and for He, Li\textsuperscript{+}, and Be\textsuperscript{++} by Froese. The energies for He are $-2.877995$ by Chong, $-2.87799$ by Froese, and $-2.877996$ here.

DISCUSSION

From Table III we see that the GF energies for H\textsuperscript{-} and Li\textsuperscript{-} are lower than for the neutral atom. That is we predict correctly that these negative ions are stable. This is in marked contrast to the results from the Hartree–Fock calculations which in both cases yield a higher energy for the negative ion than for the neutral atom. The energies for these calculations are summarized in Table VI. Actually this superiority of the GF method for negative ions is expected since the electron repulsion energy is more important for anions, and thus the driving force for splitting the Hartree–Fock orbitals is greater. As the nuclear charge increases the driving force becomes relatively smaller and the splitting is less.

The two GF orbitals for H\textsuperscript{-} and the exact orbital for the hydrogen atom are shown in Fig. 1. We immediately arrive at the cogent interpretation of H\textsuperscript{-} as having one electron in a state very similar to the ground state of the hydrogen atom and a loosely bound electron in a rather diffuse state. In contrast, the Hartree–Fock wavefunction has both electrons in the same orbital (which is somewhat more spread out than a hydrogen atom orbital). Thus the GF wavefunction, but not the Hartree–Fock wavefunction, yields directly from quantum mechanics an interpretation of H\textsuperscript{-} which
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Table IV. GF orbitals for two-, three-, and four-electron atoms. $\xi$ is the exponent of the Slater function, $\epsilon$ is the energy of the GF orbital, and $\phi(0)$ is the amplitude at the nucleus.
Table V. GF orbitals for two-, three-, and four-electron atoms. \( \xi \) is the exponent of the Slater function, \( \epsilon \) is the energy of the GF orbital, and \( \phi(0) \) is the amplitude at the nucleus.

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TABLE VI. Electron affinities for H- and Li- as predicted by the Hartree-Fock, GF, and configuration-interaction methods.

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a See Footnote b of Table I.


 coincides with the intuitive picture based on physical reasoning.

For He, Li++, and Be++ both orbitals are tightly bound (orbital energies: -1.2152 and -0.9039 for He; -0.2680 and -0.0147 for H- and H-); and have high overlaps (0.8789 for He, 0.5657 for H-). Each orbital is approximately exponential in the region where it is larger than the other orbital ($\phi_a$, exponential for small $r$, $\phi_b$ for large $r$) with the inner orbital much more closely resembling an exponential function. Thus, as the nuclear charge, $Z$, increases, the electron repulsion becomes relatively much less important than the one-electron terms and the orbitals become more similar to each other and to the Hartree-Fock orbitals.

For both the Hartree-Fock and GF methods one can show that the orbital energy for the most loosely bound electron should approximate the first ionization energy. Both methods give about equally reliable predictions of the ionization energy for the two- and three-electron systems but the GF value is much worse for the four-electron atom. The four-electron atom is qualitatively the same as in the Hartree-Fock method. The $1s$ and $2s$ orbitals are $1s$-like and the $2s$ and $2p$ orbitals are $2s$-like. The $1s$ orbitals are split most for the two-electron systems and least for the three-electron systems while the $2s$ orbitals of the four-electron systems are split less than the $1s$ orbitals (see Table VII for the orbital overlaps for He, Li, and Be).

Pekeris has reported a series of calculations on two-electron atoms obtaining very accurate energies. In Table VIII we compare the values of several properties (density at the nucleus, $\langle \sum r_i \rangle$ and $\langle \sum r_i^2 \rangle$ for H-, He, Li++, and Be++, + as calculated by the HF, GF, and Pekeris methods. The GF method yields a density at the nucleus of 0.2% to 0.5% too high while the HF method yields values of 0.1% to 0.6% too low. The HF and GF methods yield similarly good values for $\langle \sum r_i \rangle$ and $\langle \sum r_i^2 \rangle$ for He and Li++ but not for H-.

From Table VIII we see that the GF method leads to expectation values of $\langle \sum r_i \rangle$ and $\langle \sum r_i^2 \rangle$ which are consistently too large. This is, of course, what we expect since inclusion of angular correlation should decrease these quantities. (Inclusion of angular correlation allows the electrons to get closer to the nucleus without becoming correspondingly closer to each other.) On the other hand, the Hartree-Fock values are too small. This is because in addition to not including angular correlation the HF forces both electrons to be in one orbital, and the resulting orbital is tightly bound. Thus in place of the diffuse orbital we have another compact orbital and hence we should obtain values of $\langle \sum r_i \rangle$ and $\langle \sum r_i^2 \rangle$ which are too low as compared to the correct values for the radial limit. This effect is so strong that the resulting $\langle \sum r_i \rangle$ and $\langle \sum r_i^2 \rangle$ are actually less than the exact values.

It is well known that Brillouin’s theorem holds for the Hartree-Fock wavefunction and thus that expectation values for spinless one-electron operators should be correct through the first order in adding excited configurations. In fact such properties are usually predicted accurately as we see in Table VIII, but H- is definitely an exception. The Brillouin theorem also holds for the GF wavefunction and again we see from Table VIII that the properties are predicted accurately except for H-. Since the GF functions are nearly at the radial limit and since good configuration interaction radial

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\[ 11 \text{H. Shull and P.-O. L"owdin [J. Chem. Phys. 30, 617 (1959)] have noticed this for } \psi_{\text{HF}} \text{ wavefunctions for He constructed from the first two natural orbitals.} \]
wavefunctions yield a similar \( \langle \sum_i r_i^2 \rangle \),\(^{12}\) we must presume that all accurate purely radial functions will lead to very poor values of \( \langle \sum_i r_i^2 \rangle \) for \( \text{H}^- \). Thus for \( \text{H}^- \) the outer part of the charge distribution must contract appreciably when the electrons are allowed to correlate angularly.\(^{12}\) For this reason it would be interesting to examine the convergence of \( \langle \sum_i r_i^2 \rangle \) as a function of the successive limits for higher and higher \( l \)-terms in

\[
\Psi(1, 2) = \sum_{l=0}^{\infty} P_l(\cos\theta_{12}) \psi_l(|r_1|, |r_2|).
\]

Similarly, we would expect poor values of electric polarizability for \( \text{H}^- \) when using purely radial functions. Since the polarizability is probably mainly due to the loosely bound electron, the GF method should yield too high a value (the diffuse orbital being too diffuse) and the Hartree–Fock method should yield a value much too small (both orbitals are forced to be the same and hence there is no diffuse orbital to polarize easily). These expectations seem to be borne out\(^{14}\) and thus one would expect good results for such properties for \( \text{H}^- \) only if angular terms are included in the wavefunction.

**SUMMARY**

The GF wavefunctions for several two-, three-, and four-electron ions have been reported. These wavefunctions can be given an independent particle interpretation and their energies can be defined as the zero for correlation. This is made reasonable since with the GF method the negative ions \( \text{H}^- \) and \( \text{Li}^- \) are correctly predicted to be stable (the Hartree–Fock wavefunctions would lead to the opposite prediction). Thus the GF method seems especially useful for negative ions.

We find that the GF energy for the two-electron atoms is nearly at the radial limit; hence radial correlation energy over and above letting one electron move near the nucleus and the other move in a more distant region is very small. In addition, the GF orbitals lead to a perspicuous interpretation of the two-electron atoms which is especially compelling for \( \text{H}^- \). The interpretation is that one electron is in a state rather loosely bound.

The wavefunctions for the three- and four-electron atoms lead to an interpretation in terms of shells (although each shell is now split) just as does the Hartree–Fock wavefunctions.

The GF correlation energies for the three-electron atoms may not be strictly comparable with those of the two- and four-electron atoms.

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\(^{12}\) For a radial configuration interaction wavefunction using \((1s, 2s)\) and \((1\ell', 2\ell', 3\ell')\) basis functions with \(\ell=1.240\) and \(r'=0.372\), we find \(E=-0.51438\) and \(\langle \Sigma r_i^2 \rangle=34.02\). For \((1s, 2s, 3s)\) and \((1\ell', 2\ell', 3\ell')\) basis functions with \(\ell=1.43\) and \(r'=0.346\), we find \(E=-0.51446\) and \(\langle \Sigma r_i^2 \rangle=34.44\). (The orbital exponents have been optimized in each case.)

\(^{13}\) As an example, using the radial part, \(\psi_0(r_1, r_2)\), from Weiss' best CI wavefunction for \( \text{H}^- \), we obtain \(E=-0.51321, V(2E)=1.00779, \) and \(\langle \Sigma r_i^2 \rangle=23.88\). This is to be compared with \(E=-0.51438, V(2E)=1.00000, \) and \(\langle \Sigma r_i^2 \rangle=34.02\) for a separately optimized radial function. Thus the optimum \(\phi_0\) for the exact wavefunction is much more contracted than the \(\psi_0\) optimized for a purely radial wavefunction. That is, adding angular correlation allows the radial parts to shrink appreciably.

\(^{14}\) (a) H. D. Cohen, J. Chem. Phys. 43, 3558 (1965); (b) an approximate calculation using a GF wavefunction by N. R. Kestner and W. J. Deal (private communication).