any estimate of Ω is attempted. It will be noted that the values from virial coefficients (± 6, ± 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 Ω is still more difficult. For the most part they lie below estimates from virial coefficients, although three values are higher.[6,7] The most recent value available to us represents the lowest value yet obtained by calculation.[8] If one were to use our value of Ω to judge the wavefunctions employed in the calculations, then the wavefunctions of Sinai[9] and of Albasiny and Cooper[7] would appear to be the most appropriate.

Our value for the octopole moment of carbon tetrafluoride is $\pm 13.7 \times 10^{-34}$ esu·cm³, somewhat larger than the value of 4.4×10^{-34} esu·cm³ estimated by Parsonage and Scott from phase transition data.[2]

However, the latter value is expected to be small as can be seen by comparing James and Keenan's[3] value for methane, 1.6, with the values obtained from virial coefficients.

It had been our intention to estimate an octopole moment for carbon tetrachloride, but we did not for the following reasons:

(1) The available two sets of viscosity data are over a rather narrow temperature range and even so show discordant temperature dependence.

(2) The available second virial coefficient data are also suspect, primarily because CCl_4 is known to react with mercury[10] and the existing data were taken with apparatus in which mercury was exposed to gaseous CCl_4.

ACKNOWLEDGMENT

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

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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[1] for wavefunctions, which is equivalent

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* Contribution No. 3505.

[1] W. A. Goddard, III, Phys. Rev. **157**, 81 (1967).

to optimizing the orbitals of a Slater determinant wavefunction *after* spin projection. We have shown elsewhere[1] that that GF method yields accurate and consistent wavefunctions for even large internuclear 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

$$\mathcal{Q}\Phi\chi, \qquad (1)$$

where $\mathcal{Q}$ is the antisymmetrizer for N electrons, Φ is a product of N spatial orbitals, and χ is a product of N one-electron spin functions. We then require that the orbitals used in Φ be the best possible ones; i.e., the ones which yield the best possible total energy. The result is a set of N equations

$$H^{\mathrm{HF}}\phi_i = \epsilon_i\phi_i$$

for the best orbitals, where H^{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 $\widehat{S}^2$.

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

$$G_f{}^\gamma\Phi\chi, \qquad (2)$$

where Φ and χ are again products of spatial and spin functions, respectively, and $G_f{}^\gamma$ is an operator defined in terms of permutations of the various spatial and spin coordinates of the electrons. This operator, $G_f{}^\gamma$, has the property that for all Φ and χ, (2) is an eigenfunction of $\widehat{S}^2$ and satisfies Pauli's principle. The $G_f{}^\gamma$ 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 ($N!\,\mathcal{Q}$ is the determinant operator):

$$N=2,\ S=0:\quad G_f{}^\gamma(\phi_{1a}\phi_{1b}\alpha\beta) = \tfrac{1}{2}[\mathcal{Q}(\phi_{1a}\alpha\phi_{1b}\beta)$$
$$+\mathcal{Q}(\phi_{1b}\alpha\phi_{1a}\beta)],$$

$$N=3,\ S=\tfrac{1}{2}:\quad G_f{}^\gamma(\phi_{1a}\phi_{2a}\phi_{1b}\alpha\alpha\beta) = \tfrac{2}{3}[2\mathcal{Q}(\phi_{1a}\alpha\phi_{2a}\alpha\phi_{1b}\beta)$$
$$+\mathcal{Q}(\phi_{1b}\alpha\phi_{2a}\alpha\phi_{1a}\beta)+\mathcal{Q}(\phi_{1a}\alpha\phi_{1b}\alpha\phi_{2a}\beta)],$$

$$N=4,\ S=0:\quad G_f{}^\gamma(\phi_{1a}\phi_{2a}\phi_{1b}\phi_{2b}\alpha\alpha\beta\beta)$$
$$=\tfrac{1}{3}[2\mathcal{Q}(\phi_{1a}\alpha\phi_{2a}\alpha\phi_{1b}\beta\phi_{2b}\beta)+\mathcal{Q}(\phi_{1b}\alpha\phi_{2a}\alpha\phi_{1a}\beta\phi_{2b}\beta)$$
$$+\mathcal{Q}(\phi_{1a}\alpha\phi_{1b}\alpha\phi_{2a}\beta\phi_{2b}\beta)+\mathcal{Q}(\phi_{2b}\alpha\phi_{2a}\alpha\phi_{1b}\beta\phi_{1a}\beta)$$
$$+\mathcal{Q}(\phi_{1a}\alpha\phi_{2b}\alpha\phi_{1a}\beta\phi_{2a}\beta)+2\mathcal{Q}(\phi_{1b}\alpha\phi_{2b}\alpha\phi_{1a}\beta\phi_{2a}\beta)].$$

The notation used here is that

$$\Phi=\phi_{1a}(1)\phi_{2a}(2)\cdots\phi_{na}(n)\phi_{1b}(n+1)\cdots\phi_{mb}(N),$$

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

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.[1,4] 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[1,3]

$$G_f{}^\gamma\Phi\chi = G_f{}^\gamma[\phi_a(1)\phi_b(2)\alpha(1)\beta(2)]$$
$$=\tfrac{1}{4}[\phi_a(1)\phi_b(2)+\phi_b(1)\phi_a(2)]$$
$$\times[\alpha(1)\beta(2)-\beta(1)\alpha(2)]. \quad (3)$$

The orbitals ϕ_a and ϕ_b are variationally chosen to minimize the total energy,

$$E=\langle G_f{}^\gamma\Phi\chi \mid H \mid G_f{}^\gamma\Phi\chi\rangle/\langle G_f{}^\gamma\Phi\chi \mid G_f{}^\gamma\Phi\chi\rangle$$
$$=\langle\Phi\mid H\mid O_{ff}{}^\gamma\Phi\rangle/\langle\Phi\mid O_{ff}{}^\gamma\Phi\rangle$$
$$=[\langle\phi_a\mid h\mid\phi_a\rangle+\langle\phi_a\mid h\mid\phi_b\rangle\langle\phi_b\mid\phi_a\rangle+\langle\phi_b\mid h\mid\phi_b\rangle$$
$$+\langle\phi_b\mid h\mid\phi_a\rangle\langle\phi_a\mid\phi_b\rangle+\langle\phi_a\phi_b\mid g\mid\phi_a\phi_b\rangle$$
$$\langle\phi_a\phi_b\mid g\mid\phi_b\phi_a\rangle]D^{-1},$$

where $H=h(1)+h(2)+g(1,2)$ is the many-electron Hamiltonian, $h=-\tfrac{1}{2}\nabla^2+V$ 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 $D=1+\mid\langle\phi_a\mid\phi_b\rangle\mid^2$.

[2] W. A. Goddard, III, Phys. Rev. **157**, 93 (1967).

[3] W. A. Goodard, III. Phys. Rev. **157**, 73 (1967).

[4] W. A. Goddard, "Improved Quantum Theory of Many-Electron Systems. III. The GF Method," J. Chem. Phys. (to be published); W. A. Goddard, III, thesis, California Institute of Technology, September 1964.

If E is to be stationary under any variation, $\delta\phi$, in ϕ_a or ϕ_b, we have

$$h\phi_a(1) + \langle\phi_b \mid \phi_a\rangle h\phi_b(1) + \langle\phi_b \mid h \mid \phi_a\rangle\phi_b(1) + \left(\int \frac{\phi_b^*(2)\phi_b(2)}{r_{12}} dx_2\right)\phi_a(1)$$

$$+ \left(\int \frac{\phi_b(2)\phi_a(2)}{r_{12}} dx_2\right)\phi_b(1) - E\langle\phi_b \mid \phi_a\rangle\phi_b(1) = \epsilon_a\phi_a(1), \quad (4)$$

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

$$H_a\phi_a(1) \equiv (h+U_a)\phi_a = \epsilon_a\phi_a, \quad (5)$$

where

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

and P_{12} permutes Electrons 1 and 2. The second term of (6) results because the overlap between ϕ_a and ϕ_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 $\langle\phi_a \mid \phi_b\rangle = 1$ (for the ground state). In this case $E\to 2\langle\phi \mid h \mid \phi\rangle$ and thus $U_a\to 0$ as $g\to 0$. Hence U_a, which depends upon ϕ_b but not on ϕ_a, can be interpreted as the average potential acting on the electron in ϕ_a due to an electron in ϕ_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 ϕ_a to place in (3). That is, out of all possible ϕ_a and ϕ_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 ϕ_a and ϕ_b are solutions of (5), we may rather rigorously discuss the two-electron wavefunction in terms of the ϕ_a and ϕ_b separately. That is, we may picture one electron as moving in ϕ_a and the other in ϕ_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 ϕ_a and the other is in ϕ_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 ϕ_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 $G_f{}^\gamma\Phi_\chi$ 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

$$\phi(1)\phi(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)].$$

We require that the ϕ be optimum and obtain

$$U^{HF}(1) = \int \frac{\phi^*(2)\phi(2)}{r_{12}} dx_2,$$

which is similar to what one would expect classically. For more electrons the U^{HF} also contains nonclassical terms like

$$-\int \frac{\phi_i(2) P_{12}\phi_i(2)}{r_{12}} dx_2,$$

called exchange terms, just as does U^{GF}.

One does not in general obtain the semiclassically expected potential

$$U_i{}^{Cl}(1) = \sum_{j\neq i} \int \frac{\phi_j^*(2)\phi_j(2)}{r_{12}} dx_2 \quad (7)$$

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

$$\Psi(1, \cdots, N) = \psi_1(1)\psi_2(2)\cdots\psi_N(N), \quad (8)$$

we do get a U^{Cl} as in (7), where the ψ_i are solutions of

$$(h+U_i{}^{Cl})\psi_i = \epsilon_i\psi_i. \quad (9)$$

But the lowest total energy occurs for

$$\Psi=\psi_1(1)\psi_1(2)\cdots\psi_1(N),$$

where ψ_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 function (8) is not restricted so as to satisfy Pauli's principle. If we arbitrarily choose to select only different orthogonal states for (8), we get more reasonable energies; however, in order to force the Ψ to use orthogonal states, we would have to include new Lagrange multipliers to ensure orthogonality of ψ_i and ψ_j. But the result would be

$$(h+U_i^{\mathrm{Cl}})\psi_i=\sum_j\epsilon_{ij}\psi_j \qquad (10)$$

rather than (9), and in this case it is not possible to remove the nondiagonal ϵ_{ij} by, say, a transformation upon the ψ_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 $h+U_i^{\mathrm{Cl}}$. 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 interpretations 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 H⁻ 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 consistent 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 *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 *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 *not* containing correlation. In addition, the same argument 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 wavefunctions normally contain correlation and, *a fortiori*, so would any electronic wavefunction satisfying Pauli's principle! For this reason the $\pi(1,2)=\rho(1)\rho(2)$ definition 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 wavefunction![5,6] We believe that the thing which has been called correlation has proved to be a useful concept[5,6] 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 correlation 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 *AVERAGE* field due to the other electrons, and thus each orbital is neither determined 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 interpretation (as defined in the previous section) then by definition this wavefunction *does not* contain correlation. 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 *always* leads to a lower energy than the Hartree–Fock wavefunction[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 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 eV higher![5] 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 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

[5] P.-O. Löwdin, Adv. Chem. Phys. **2**, 207 (1959).
[6] E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

TABLE I. Correlation energies[a] for atoms using GF and Hartree–Fock wavefunctions. The Hartree–Fock values are in parentheses. The nuclear charge is Z.

Z	Number of electrons		
	2 $^1S_0$	3 $^2S_{\frac{1}{2}}$	4 $^1S_0$
1	−0.0140 (−0.0398)[b]	...	...
2	−0.0257 (−0.0421)	...	...
3	−0.0285 (−0.0435)	−0.0452 (−0.0453)	−0.0576[c] (−0.0725)[c]
4	−0.0298 (−0.0443)	−0.0473 (−0.0475)	−0.0801 (−0.0944)
5	...	−0.0486 (−0.0489)	−0.0984 (−0.1123)
6	...	...	−0.1131 (−0.1268)

[a] 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.

[c] Based on an estimate of the exact energy for Li⁻ of −7.5007 by A. W. Weiss, Phys. Rev. 122, 1826 (1961).

of the same spin as compared to those of different spin. For this reason Clementi suggests defining correlation with respect to the Hartree energy. However, the Hartree wavefunction does not satisfy Pauli's principle. In this paper, as a result of the above considerations, we define the correlation energy as the difference between the exact energy and the GF energy.

Calculated Correlation Energies

Using the GF energy as the zero for correlation, we obtain the correlation energies, E_{corr}^{GF}, in Table I (atomic units are used[7]). For comparison the correlation energies, E_{corr}^{HF}, based on Hartree–Fock wavefunctions are also given (in parentheses). All of the $|E_{corr}^{GF}|$ are, of course, smaller than $|E_{corr}^{HF}|$, but the most striking difference is that E_{corr}^{GF} is a rather smooth function of the number of electrons while E_{corr}^{HF} is very nearly the same for two and three electrons. For a given number of electrons the $|E_{corr}^{GF}|$ 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 $3\frac{1}{2}$ 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

[7] Atomic units, $e = m_e = \hbar = 1$, are used throughout this paper. Thus the energies are in hartrees (1 h = 27.21 eV).

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 $\Psi(1, 2) = \sum_{i,j} C_{ij}\psi_i(|r_1|)\psi_j(|r_2|)$]. 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_{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 $E_{RL} - E_{GF}$ is the same, 0.0010, for He, Li⁺, and Be⁺⁺.

CALCULATIONS

The GF equations are solved in the same way as are the Hartree–Fock equations except that we must find the eigenfunctions of two different one-electron operators rather than of just one. We expand the unknown set of orbitals in terms of a finite basis set

$$\phi_a = \sum_\mu \chi_\mu C_{\mu 1}{}^a, \qquad \phi_b = \sum_\mu \chi_\mu C_{\mu 1}{}^b$$

and solve for the coefficients iteratively (the equations could, of course, also be solved numerically).

The basis sets used consisted of four to eight functions (Slater-type orbitals, $\chi_{n0} = Nr^{n-1}e^{-\zeta r}$) for the two-electron wavefunctions and six to nine functions for the three- and four-electron systems. The orbital exponents, ζ, for the smaller basis sets were in most cases optimized until the virial ratio, $V/(2E)$, was within 2×10^{-6} of 1.0. The basis sets were then expanded by including orbitals with larger n. For some of the more positively charged ions, the energy is insensitive to such increases in the basis set and smaller sets were used. The matrix GF equations[1,4] have the form $H_A C_A = S C_A \epsilon_A$ and

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

	H⁻	He	Li⁺	Be⁺⁺
HF	−0.4879[a]	−2.8617	−7.2364	−13.6113
GF	−0.5138	−2.8780	−7.2514	−13.6258
Radial limit	−0.5145[d]	−2.8790[b,c]	−7.2524[b]	−13.6268[b]
$\dfrac{E_{GF} - E_{HF}}{E_{RL} - E_{HF}}$	0.977	0.942	0.938	0.935

[a] See Footnote b of Table I.

[b] A. W. Weiss, Phys. Rev. 122, 1826 (1961).

[c] H. Shull and P.-O. Löwdin, J. Chem. Phys. 30, 617 (1959).

[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.

Atom	NBF	E	$\langle \Sigma 1/r_{ij} \rangle$	$V/2E$	$\langle \Sigma_i \delta(\mathbf{r}_i) \rangle$	$\langle \Sigma 1/r_i^2 \rangle$	$\langle \Sigma r_i \rangle$	$\langle \Sigma r_i^2 \rangle$	$\langle \Sigma \delta(\mathbf{r}_i)\hat{s}_{zi} \rangle/S$
H⁻	4	−0.5135930	0.3007160	1.000000	0.32658	2.2005	6.0226	30.534	⋯
	6	−0.5138377	0.2973523	1.000006	0.33124	2.2072	6.2275	34.771	⋯
	8	−0.5138392	0.2972644	1.000002	0.33058	2.2065	6.2341	34.962	⋯
He	4	−2.877984	0.9886161	1.000001	3.6266	12.036	1.8674	2.4136	⋯
	7	−2.877996	0.9885687	0.999998	3.6295	12.038	1.8681	2.4179	⋯
Li⁺	4	−7.251409	1.619428	0.999999	13.722	29.865	1.1472	0.8957	⋯
	6	−7.251415	1.619410	1.000000	13.726	29.866	1.1473	0.8963	⋯
Be⁺⁺	4	−13.62576	2.246644	0.999999	34.430	55.694	0.82913	0.46490	⋯
	6	−13.62577	2.246646	0.999998	34.433	55.695	0.82918	0.46506	⋯
Li	6	−7.432810	2.281232	1.000000	13.826	30.214	5.0149	18.569	0.2394
	8	−7.432813	2.281214	1.000001	13.834	30.216	5.0161	18.592	0.2408
Be⁺	6	−14.27762	3.334591	0.999999	35.111	56.981	3.1085	6.5453	1.008
B⁺⁺	6	−23.37632	4.370407	1.000000	71.493	92.255	2.2858	3.4094	2.521
Li⁻	6	−7.442842	2.726532	1.000005	13.852	30.274	12.391	81.401	⋯
	9	−7.443098	2.721302	1.000005	13.865	30.280	12.646	87.882	⋯
Be	6	−14.58721	4.459035	0.999997	35.447	57.658	6.1274	17.279	⋯
	9	−14.58726	4.459013	1.000004	35.459	57.663	6.1301	17.318	⋯
B⁺	6	−24.25147	6.089144	1.000000	72.716	94.079	4.2468	7.9308	⋯
	9	−24.25149	6.089061	0.999998	72.721	94.082	4.2476	7.9381	⋯
C⁺⁺	6	−36.42220	7.690813	0.999999	129.95	139.51	3.2788	4.6205	⋯

$\mathbf{H}_B\mathbf{C}_B = \mathbf{S}\mathbf{C}_B\epsilon_B$, where the vectors $\mathbf{C}_A$ and $\mathbf{C}_B$ are the GF orbitals and $\mathbf{S}$ is the overlap matrix for the basis functions. These equations were solved by diagonalizing $\mathbf{S}$ and then diagonalizing the transformed H matrix. Thus the $\mathbf{C}$ 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 $\mathbf{S}$ less than 10^{-6}) and in some cases this resulted in a loss of significant figures after transforming the $\mathbf{C}$ 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 3×10^{-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, ϵ; 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[8] and for He, Li⁺, and Be⁺⁺ by Froese.[9] 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⁻ and Li⁻ 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⁻ and the exact orbital for the hydrogen atom are shown in Fig. 1. We immediately arrive at the cogent interpretation of H⁻ 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⁻ which

[8] D. P. Chong, J. Chem. Phys. 45, 3317 (1966).

[9] C. Froese, Phys. Rev. 150, (1966). An extended valence-bond[10] calculation for Be is also reported here.

[10] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1963), Vol. 1, p. 197.

TABLE IV. GF orbitals for two-, three-, and four-electron atoms. ζ is the exponent of the Slater function, ϵ is the energy of the GF orbital, and $\phi(0)$ is the amplitude at the nucleus.

	H⁻			He			Li⁺			Be⁺⁺		
	ζ	ϕ_a	ϕ_b	ζ	ϕ_a	ϕ_b	ζ	ϕ_a	ϕ_b	ζ	ϕ_a	ϕ_b
1s	1.2048	0.78750	−0.00203	3.30	0.43758	−0.13161	5.30	0.34375	−0.14717	7.30	0.29051	−0.14551
2s	1.2048	0.21283	−0.08871	3.30	0.28505	−0.21515	5.30	0.24757	−0.20158	7.30	0.21916	−0.18472
1s	0.3178	0.03924	1.06221	1.433	0.33044	1.29040	2.443	0.44872	1.30844	3.430	0.52757	1.30663
2s	0.3178	−0.00530	0.00255	1.433	0.00087	0.00328	2.443	0.00882	−0.00776	3.430	0.00615	−0.02113
ϵ		−0.2645	−0.0144		1.2151	−0.9038		−3.1964	−2.8147		−6.1743	−5.7326
Cusp		−1.0123	−0.7396		−1.9473	−2.1206		−2.8987	−3.2046		−3.8571	−4.2613
$\phi(0)$		0.5915	0.1058		1.7998	0.8037		3.3330	1.8057		5.1235	3.0638

	Li				Be⁺				B⁺⁺			
	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}
1s	4.33	0.13054	−0.06587	0.12723	6.00	0.09647	−0.06492	0.09508	7.50	0.08101	−0.06190	0.07562
2s	4.33	−0.01390	−0.01805	−0.02139	6.00	−0.00598	−0.01665	−0.01484	7.50	−0.00547	−0.01472	−0.01660
1s	2.41	0.93294	−0.02951	0.92123	3.45	0.93337	−0.05438	0.91662	4.40	0.95834	−0.06263	0.95242
2s	2.41	−0.04692	−0.10313	−0.01935	3.45	−0.02204	−0.09603	0.01164	4.40	−0.03709	−0.08634	−0.00837
1s	0.671	0.00621	−0.01285	0.00534	1.198	0.00700	−0.20004	0.00556	1.709	0.00779	−0.31758	0.00568
2s	0.671	−0.00229	1.04544	−0.00417	1.198	−0.00185	1.20675	−0.00480	1.709	−0.00189	1.30053	−0.00489
ϵ		−2.4987	−0.1965	−2.4638		−5.1835	−0.6666	−5.1113		−8.8762	−1.3905	−8.7687
Cusp		−3.0118	−2.9818	−3.0147		−4.0146	−4.0017	−4.0213		−5.0148	−5.0116	−5.0242
$\phi(0)$		2.6348	−0.4012	2.5930		4.1796	−0.8829	4.1064		5.9388	−1.4437	5.8429

	Li⁻					Be				
	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ϕ_{2b}	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ϕ_{2b}
1s	5.15	0.38525	−0.03948	−0.16133	−0.03417	7.12	0.33566	−0.03826	−0.17072	−0.03388
2s	5.15	0.25958	−0.02393	−0.20942	−0.01395	7.12	0.23882	−0.02340	−0.20158	−0.00771
1s	2.278	0.41213	−0.06965	1.47691	−0.02682	3.213	0.46891	−0.20276	1.50724	−0.11032
2s	2.278	−0.01050	−0.09924	−0.17503	−0.20513	3.213	0.00122	−0.08591	−0.20989	−0.24546
1s	0.287	0.01338	1.04099	−0.01637	1.04828	0.891	0.00118	0.45045	0.01259	0.41432
2s	0.287	0.00187	0.00150	−0.00618	0.01421	0.891	0.02295	0.67049	−0.04022	0.74162
ϵ		−2.7213	−0.1378	−2.3460	−0.1306		−5.2275	−0.4940	−4.8053	−0.4703
Cusp		−2.9457	−2.9505	−3.1115	−2.4467		−3.9001	−4.0472	−4.1870	−3.6649
$\phi(0)$		3.3409	−0.3052	1.7997	−0.1864		5.1220	−0.8552	3.0736	−0.5250

	B⁺					C⁺⁺				
	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ϕ_{2b}	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ϕ_{2b}
1s	9.16	0.29297	−0.02737	−0.16729	−0.03006	11.2	0.26313	−0.01996	−0.16239	−0.02873
2s	9.16	0.21777	−0.01826	−0.18891	−0.00383	11.2	0.20096	−0.01513	−0.17775	−0.00277
1s	4.19	0.52447	−0.27055	1.48043	−0.13376	5.18	0.56412	−0.29578	1.45051	−0.12925
2s	4.19	0.00786	−0.04956	−0.19924	−0.23315	5.18	0.01420	−0.02818	−0.18390	−0.22117
1s	1.419	−0.00676	0.24779	0.02808	0.17765	1.932	−0.01282	0.10916	0.03704	0.01437
2s	1.419	0.03252	0.86386	−0.05287	0.96872	1.932	0.03787	0.98277	−0.05844	1.10736
ϵ		−8.7727	−1.1183	−8.3090	−1.0800		−13.328	−1.997	−12.826	−1.946
Cusp		−4.8452	−5.1011	−5.2659	−4.7354		−5.7968	−6.1287	−6.3295	−5.7486
$\phi(0)$		7.1138	−1.5010	4.5738	−0.9479		9.2973	−2.2241	6.2702	−1.4455

TABLE V. GF orbitals for two-, three-, and four-electron atoms. ζ is the exponent of the Slater function, ϵ is the energy of the GF orbital, and $\phi(0)$ is the amplitude at the nucleus.

	H⁻			He			Li⁺			Be⁺⁺		
	ζ	ϕ_a	ϕ_b	ζ	ϕ_a	ϕ_b	ζ	ϕ_a	ϕ_b	ζ	ϕ_a	ϕ_b
1s	1.2048	0.77629	0.03827	3.30	0.44892	−0.16430	5.30	0.37892	−0.22577	7.30	0.33699	−0.22720
2s	1.2048	0.22584	−0.11265	3.30	0.27487	−0.21108	5.30	0.26856	−0.24823	7.30	0.24585	−0.23167
3s	1.2048	−0.03597	0.09187	⋯	⋯	⋯	5.30	0.01086	−0.02162	7.30	0.01420	−0.02326
4s	1.2048	0.01675	0.02287	3.30	−0.02674	0.04175	⋯	⋯	⋯	⋯	⋯	⋯
1s	0.3178	0.09020	0.86074	1.433	0.29242	1.40411	2.443	0.33647	1.55982	3.430	0.38409	1.55955
2s	0.3178	−0.07890	0.10556	1.433	0.13823	−0.25801	2.443	0.08749	−0.19130	3.430	0.10308	−0.19666
3s	0.3178	0.04559	−0.07684	1.433	−0.11139	0.18230	2.443	−0.02280	0.05642	3.430	−0.02715	0.05121
4s	0.3178	−0.00925	0.12998	1.433	0.03324	−0.04325	⋯	⋯	⋯	⋯	⋯	⋯
ϵ		−0.2680	−0.0147		−1.2152	−0.9039		−3.1965	−2.8149		−6.1746	−5.7330
Cusp		−0.9943	−1.0260		−1.9619	−2.0920		−2.9018	−3.2014		−3.8690	−4.2391
$\phi(0)$		0.5883	0.1156		1.8013	0.8032		3.3333	1.8062		5.1265	3.0611

	Li				Li⁻				
	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ϕ_{2b}
1s	4.33	0.10561	0.03259	0.10847	5.15	0.38561	0.06222	−0.21892	0.11279
2s	4.33	−0.02363	0.01583	−0.02876	5.15	0.26393	0.03172	−0.24881	0.07242
3s	⋯	⋯	⋯	⋯	5.15	−0.01570	0.02244	0.00255	0.02200
1s	2.41	0.99375	−0.28170	0.96686	2.278	0.40591	−0.42338	1.67934	−0.53910
2s	2.41	−0.09058	0.07087	−0.05221	2.278	0.02368	0.20793	−0.37350	0.25531
3s	2.41	0.01602	−0.08928	0.01178	2.278	−0.02287	−0.15555	0.08428	−0.21858
1s	0.671	0.00314	0.08531	0.00399	0.287	0.02248	−0.03622	1.23389	1.24831
2s	0.671	−0.00214	0.95411	−0.00508	0.287	−0.00988	−0.36270	0.01645	−0.35362
3s	0.671	0.00092	0.03261	0.00111	0.287	0.00539	0.23355	−0.00888	0.23299
ϵ		−2.4987	−0.1965	−2.4638		−2.7234	−0.1394	−2.3485	−0.1320
Cusp		−3.0155	−3.0359	−3.0177		−2.8974	−2.8770	−3.2120	−3.0306
$\phi(0)$		2.6355	−0.4025	2.5935		3.3320	−0.3040	1.8109	−0.1938

	Be					B⁺				
	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ϕ_{2b}	ζ	ϕ_{1a}	ϕ_{2a}	ϕ_{1b}	ϕ_{2b}
1s	7.12	0.40222	0.01923	−0.30954	0.09626	9.16	0.40976	−0.02050	−0.35434	0.08196
2s	7.12	0.27797	0.00550	−0.28197	0.06393	9.16	0.28281	−0.01641	−0.29291	0.05539
3s	7.12	0.00790	0.01602	−0.02502	0.01262	9.16	0.02500	0.00989	−0.04132	0.00724
1s	3.213	0.23867	−0.41615	1.98165	−0.57883	4.19	0.12321	−0.31143	2.11932	−0.55599
2s	3.213	0.19521	0.05576	−0.59734	0.14081	4.19	0.30368	−0.06427	−0.67257	0.07913
3s	3.213	−0.09428	−0.09861	0.17768	−0.23065	4.19	−0.14511	−0.01108	0.22765	−0.21741
1s	0.891	0.06004	0.62403	−0.08460	0.66013	1.419	0.11197	0.35425	−0.14454	0.46759
2s	0.891	−0.02116	0.49469	0.02846	0.52357	1.419	−0.04425	0.75873	0.05386	0.75980
3s	0.891	0.01184	0.06794	−0.01653	0.07347	1.419	0.01851	0.03991	−0.02372	0.05799
ϵ		−5.2278	−0.4944	−4.8060	−0.4708		−8.7730	−1.1186	−8.3095	−1.0803
Cusp		−3.8696	−3.8970	−4.2346	−4.1262		−4.8430	−4.8701	−5.2603	−5.1936
$\phi(0)$		5.1154	−0.8500	3.0809	−0.5357		7.1122	−1.4898	4.5751	−0.9625

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

	HF	GF	CI
H⁻	−0.4879[a]	−0.5138	−0.5275[b]
H	−0.5000	−0.5000	−0.5000
Electron affinity	+0.0121	−0.0138	−0.0275
Li⁻	−7.4282[c]	−7.4431	−7.4956[b]
Li	−7.4327[c]	−7.4328	−7.4771[b]
Electron affinity	+0.0045	−0.0103	−0.0185

[a] See Footnote b of Table I.
[b] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).
[c] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

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 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 (ϕ_a exponential for small r, ϕ_b for large r) with the inner orbital much more closely resembling an exponential function.[11] 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 atoms.

The GF wavefunctions for the three-electron atoms are rather similar to the HF orbitals except that the splitting of the 1s orbitals allows the spin density near the nucleus to be properly described.[2] However, this splitting is not very large and we may still speak of the three-electron atom as having two 1s-like states and one 2s state. The four-electron atoms also lead to a shell structure which is qualitatively the same as in the Hartree–Fock method. The 1a and 1b orbitals are 1s-like and the 2a and 2b 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

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[11] H. Shull and P.-O. Löwdin [J. Chem. Phys. **30**, 617 (1959)] have noticed this for $uv+vu$ wavefunctions for He constructed from the first two natural orbitals.

(density at the nucleus, $\langle \sum_i r_i \rangle$ 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 $\langle \sum_i r_i \rangle$ and $\langle \sum_i r_i^2 \rangle$ 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[4] 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
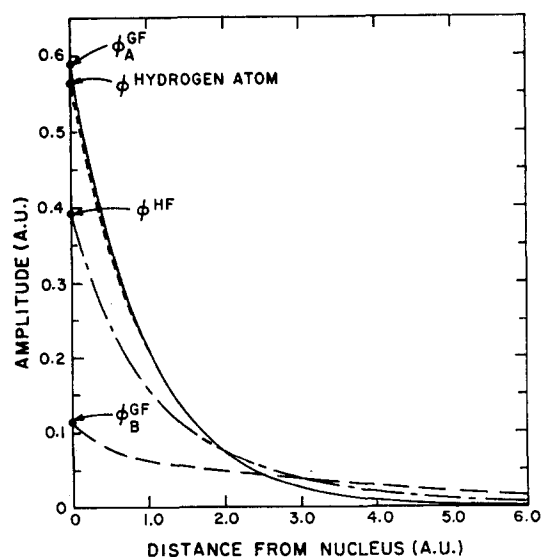

FIG. 1. The GF and Hartree–Fock (HF) orbitals for H⁻ and H.

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 H$^-$. Thus for H$^-$ the outer part of the charge distribution must contract appreciably when the electrons are allowed to correlate angularly.[13] 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 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 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 wave-

TABLE VII. Overlaps for GF orbitals.

Orbital pairs	He	Li	Be
$1b$–$1a$	0.878933	0.9998905	0.953131
$1b$–$2a$	...	0.0036903	0.036849
$2b$–$1a$	...	...	−0.011552
$2b$–$2a$	...	...	0.995474

[12] For a radial configuration interaction wavefunction using $(1s, 2s)$ and $(1s', 2s', 3s')$ basis functions with $\zeta = 1.240$ and $\zeta' = 0.372$, we find $E = -0.51438$ and $\langle \sum r_i^2 \rangle = 34.02$. For $(1s, 2s, 3s)$ and $(1s', 2s', 3s')$ basis functions with $\zeta = 1.43$ and $\zeta' = .346$, we find $E = -0.51446$ and $\langle \sum r_i^2 \rangle = 34.44$. (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 H$^-$, we obtain $E = -0.51321$, $V/(2E) = 1.00779$, and $\langle \sum r_i^2 \rangle = 23.88$. This is to be compared with $E = -0.51438$, $V/(2E) = 1.00000$, and $\langle \sum r_i^2 \rangle = 34.02$ for a separately optimized radial function. Thus the optimum ψ_0 for the exact wavefunction is much more contracted than the ψ_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).

TABLE VIII. Comparison of calculated expectation values for two-electron atoms.

		$\langle \Sigma \delta(\mathbf{r}_i) \rangle$	$\langle \Sigma \mathbf{r}_i \rangle$	$\langle \Sigma \mathbf{r}_i^2 \rangle$
H$^-$	HF[a]	0.3096	5.008	18.82
	GF	0.3306	6.234	34.96
	CI, radial[g]	...	6.207	34.44
	PEK[b]	0.3291	5.420	23.83
He	HF[c]	3.596	1.855	2.370
	GF	3.630	1.868	2.418
	PEK[d]	3.621	1.8589	2.3870
Li$^+$	HF[c]	13.674	1.1447	0.8906
	GF	13.726	1.1473	0.8962
	PEK[e]	13.704	1.1455	0.8926
Be^{++}	HF[c]	34.361	0.8283	0.4637
	GF	34.443	0.8292	0.4651
	PEK[f]	34.396	...	...

[a] See Footnote b of Table I.

[b] C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).

[c] Using 12 basis-function wavefunctions from C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

[d] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).

[e] C. L. Pekeris, Phys. Rev. **126**, 143 (1962).

[f] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[g] See Footnote 12.

functions 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 H$^-$ and 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 H$^-$. The interpretation is that one electron is in a state rather similar to the state for the one-electron atom while the other is for H$^-$ 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.