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Improved approximate representation of the Hartree-Fock potential in atoms

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A new method is proposed to approximate the exchange-correlation potential in the Hartree-Fock equations for a many-electron atom. The exchange-correlation potential is separated into a self-interaction term and a characteristic exchange term. The self-interaction term is evaluated exactly, while the exchange term is approximated in a manner similar to Slater's statistical average method using a previously obtained theoretical exchange parameter α. In the present method different potentials are used for different spin orbitals instead of the average potential used in the Hartree-Fock-Slater (HFS) scheme. The separation of the exchange-correlation potential into a self-interaction plus exchange terms removes all the major defects of the HFS potential, such as the wrong asymptotic behavior at large r values and the underestimation of the self-interaction. The accuracy of the present method is demonstrated by calculations on the first-row transition-metal ions Cu^+ and Mn^{+2}. The results for exchange potentials, one-electron eigenvalues, spin density distribution, and contact hyperfine interaction agree excellently with Hartree-Fock values. The relative importance of the self-interaction and exchange terms for various electron shells are discussed. Computationally, the method is as simple as the Hartree-Fock-Slater scheme.

I. INTRODUCTION

The practical need to simplify the exchange potential in the Hartree-Fock equations has been recognised for a long time. The major step in this direction was taken by Slater[1] in 1951, by introducing the statistical exchange approximation following the work of Dirac.[2] Since then, this approximation has been extensively used in atomic, molecular, and solid-state calculations. In this section we briefly discuss Slater's method and point out its major defects. In Sec. II, we introduce a new approximation for the exchange potential which is free of all the major defects of the Slater method but is equally simple to apply. The method is demonstrated in Sec. III by calculations on the first-row transition metal ions, Cu^+ and Mn^{+2} and the results are compared with those from the Hartree-Fock (HF) and Hartree-Fock-Slater (HFS) methods.

The Hartree-Fock equations for a many-electron atom may be written (in Rydberg units) as[3a],

$$[f_1 + V_c(r) + V_{\mathrm{XHF}i}(r)]u_i(r) = \epsilon_i u_i(r)\,, \tag{1}$$

where the u_i's are the spin orbitals with occupancy n_i; $f_1 = -\nabla^2 - 2Z/r$, and $V_c(r)$ is the Coulomb potential

$$V_c(r) = \sum_j n_j \int u_j^*(r')u_j(r')g_{rr'}\,dr' \tag{2}$$

with $g_{rr'} = 2/|r-r'|$. $V_{\mathrm{XHF}i}$ is the exchange-correlation potential[3b] for the electron in the ith spin orbital and is given by

$$V_{\mathrm{XHF}i}(r) = -\sum_j{}' \left(n_j \int u_i^*(r)u_j^*(r')u_j(r) \times u_i(r')g_{rr'}\,dr' \right) \Big/ u_i^*(r)u_i(r)\,, \tag{3}$$

where $\sum'$ is only over spin orbitals of the same spin as u_i.

It is advantageous to rewrite Eq. (3) with the exchange-correlation potential separated into a self-interaction and the true exchange potential

$$V_{\mathrm{XHF}i}(r) = V^{\mathrm{s}}_{\mathrm{HF}i}(r) + V^{\mathrm{ex}}_{\mathrm{HF}i}(r)\,, \tag{4}$$

with

$$V^{\mathrm{s}}_{\mathrm{HF}i}(r) = -n_i \int u_i^*(r')u_i(r')g_{rr'}\,dr' \tag{5}$$

$$V^{\mathrm{ex}}_{\mathrm{HF}i}(r) = -\sum_{j\neq i}{}' \left(n_j \int u_i^*(r)u_j^*(r') \times u_j(r)u_i(r')g_{rr'}\,dr' \right) \Big/ u_i^*(r)u_i(r)\,. \tag{6}$$

Here $V^{\mathrm{s}}_{\mathrm{HF}i}(r)$ is the self-interaction potential which is incorrectly included in the Coulomb term in Eq. (2); $V^{\mathrm{ex}}_{\mathrm{HF}i}(r)$ is the actual exchange potential.

In the HFS method, Eq. (1) is greatly simplified by replacing the various $V_{\mathrm{XHF}i}$ potentials by a single average potential; for up-spin electrons this is

$$V_{\mathrm{XS}\uparrow}(r) = -6C\alpha\rho_\uparrow^{1/3}(r)\,, \tag{7}$$

with a similar expression for the down-spin electrons.

In Eq. (7),

$$C = (3/4\pi)^{1/3}\,, \qquad \rho_\uparrow(r) = \sum_{i\uparrow} n_i u_i^*(r)u_i(r)\,, \tag{8}$$

and α is an exchange scaling parameter, usually determined empirically for each atom or ion.

The author and colleagues[4] have recently shown that this empirical nature of the V_{XS} potential can be easily removed. Using the properties of the Fermi hole, it was shown that this parameter for an up-spin electron is

$$\alpha_{\uparrow} = \frac{8}{2\pi}\left(\frac{4\pi^2}{3}\right)^{1/3} \frac{1/n_{\uparrow} + \frac{1}{2}}{(1/n_{\uparrow} + \frac{1}{3})^{2/3}}\,, \tag{9}$$

where $n_{\uparrow}$ is the number of up-spin electrons. A similar expression holds for $\alpha_{\downarrow}$. If desired, an average α may also be obtained as

$$\alpha = (n_{\uparrow}\alpha_{\uparrow} + n_{\downarrow}\alpha_{\downarrow})/(n_{\uparrow} + n_{\downarrow})\,. \tag{10}$$

These average α values were computed for all atoms in the periodic table and were shown to be in close agreement with the available empirical values.

The exchange-correlation potential of Eq. (7) has more serious defects. The value of the potential $V_{\mathrm{XHF}i}$ of Eq. (4) usually varies by a factor of 2 for various spin orbitals i at a fixed value of r. Therefore, its replacement by an average as in Eq. (7) is only a very approximate treatment of the exchange effects in atoms. This has been shown quantitatively for the Cu^{+} ion by Hartree.[5] For a given spin orbital, Eq. (7) gives an exchange-correlation potential which is too large at some r values and too small at others.

Another major defect of the average potential $V_{\mathrm{XS}}(r)$ is its incorrect behavior at large r values. In the Hartree-Fock method, the exchange-correlation potential has the property

$$rV_{\mathrm{XHF}i}(r) \to -2 \quad \text{as} \quad r \to \infty\,, \tag{11}$$

because for the self-interaction term we have

$$rV^{s}_{\mathrm{HF}i}(r) \to -2 \tag{12}$$

and for the exchange,

$$rV^{\mathrm{ex}}_{\mathrm{HF}i}(r) \to 0 \quad \text{as} \quad r \to \infty\,. \tag{13}$$

In contrast, in the HFS scheme,

$$rV_{\mathrm{XS}}(r) \to 0 \quad \text{as} \quad r \to \infty \tag{14}$$

That is, V_{XS} fails to correct for the electron self-interaction at large r values.

To overcome this defect, an empirical correction due to Latter[6] is usually made to the total potential V_{HFS}

$$rV_{\mathrm{HFS}}(r) = -2(Z - N + 1) \quad \text{for } r \geq r_c\,, \tag{15}$$

where r_c is determined by the condition

$$r_c V_{\mathrm{HFS}}(r_c) = -2(Z - N + 1)\,. \tag{16}$$

In Eqs. (15) and (16), N is the total number of electrons. Results using the Latter correction are generally poorer than those obtained without this correction.[7,8] This is to be expected for the following reasons, pointed out by Coulson and Sharma.[9] First, the Latter potential has a discontinuous slope at r_c and consequently produces a nonvanishing surface-charge density on the sphere separating the two regions $r \geq r_c$ and $r < r_c$. This is distinctly unphysical. Secondly, the potential is uncorrected for $r < r_c$. Further, the Latter potential is not variationally derivable from the expression for the total energy of the system, as pointed out by Wilson *et al.*[7] Finally, there is another flaw in introducing the Latter correction to the HFS potential. As will be shown in Sec. III, $V_{\mathrm{HFS}}(r)$ underestimates self-interaction *not only* at large r values, but also at intermediate values. Consequently $V_{\mathrm{HFS}}(r)$ is generally smaller than the correct potential. Therefore, the Eqs. (15) and (16) introduce an r^{-1} potential at too small an r value (r_c). From the Poisson equation it follows that the charge due to $(N - 1)$ electrons outside r_c is zero. Thus the use of the Latter potential in the HFS scheme leads to an unphysical shrinkage of the atom.

II. DERIVATION OF THE NEW ONE-ELECTRON EQUATIONS

The present approximation to the HF potential will be designated HFG.

The total energy of the atom or ion can be written exactly as

$$\begin{aligned}\langle E\rangle = \sum_i n_i \quad & u_i^*(r) f_1 u_i(r)\, dr \\ & + \tfrac{1}{2}\int \rho(r)\rho(r')g_{rr'}\, dr\, dr' \\ & - \tfrac{1}{2}\int \rho_{\uparrow}(r) U^{\mathrm{exc}}_{\uparrow}(r)\, dr \\ & - \tfrac{1}{2}\int \rho_{\downarrow}(r) U^{\mathrm{exc}}_{\downarrow}(r)\, dr\,,\end{aligned} \tag{17}$$

where $U^{\mathrm{exc}}_{\uparrow}(r)$ is the exchange correlation potential at point r for up-spin electrons and similarly for $U^{\mathrm{exc}}_{\downarrow}(r)$. As in Eq. (4) $U^{\mathrm{exc}}_{\uparrow}$ can be separated into the self-interaction and exchange parts

$$U^{\mathrm{exc}}_{\uparrow}(r) = U^{s}_{\uparrow}(r) + U^{\mathrm{ex}}_{\uparrow}(r)\,. \tag{18}$$

The self-interaction term is given exactly by

$$\begin{aligned}U^{s}_{\uparrow}(r) = -\sum_{i\uparrow}\Big(& n_i u_i^*(r) u_i(r) \\ & \times \int n_i u_i^*(r') u_i(r') g_{rr'}\, dr'\Big)\Big/\rho_{\uparrow}(r)\,.\end{aligned} \tag{19}$$

In the present HFG scheme, this term is evaluated without any approximation.

However, the HFS scheme corresponds to approximating $U^{\mathrm{exc}}_{\uparrow}$ as,

$$U^{\mathrm{exc}}_{\uparrow}(r) = -9C\alpha\rho_{\uparrow}^{1/3}(r)\,. \tag{20}$$

A similar approximation can be introduced in the HFG scheme for the $U^{\mathrm{ex}}_{\uparrow}(r)$ part of the exchange-correlation potential in Eq. (18). For this purpose we define

$$\rho_{i'\uparrow}(r)=\sum_{j\neq i\uparrow} n_j u_j^*(r)u_j(r) \tag{21}$$

as the density of electrons of up-spin at point r, excluding the density of the electron in spin orbital $u_{i\uparrow}$. Now, as in Ref. 4, consider a Fermi sphere centered at r, its radius being determined by the total density $\rho_\uparrow(r)$ and the condition that the Fermi sphere contains a unit electron charge. It follows that the exchange-correlation potential (which includes the self-interaction) at the center of the sphere is proportional to $\rho_\uparrow^{1/3}(r)$, whereas the exchange potential (without self-interaction) is proportional to $\rho_{i'\uparrow}(r)\rho_\uparrow^{-2/3}(r)$. Accordingly, we set

$$U_\uparrow^{\text{ex}}(r)=\Big(-9C\alpha_\uparrow\sum_{i\uparrow}\rho_{i'\uparrow}(r)\rho_\uparrow^{-2/3}(r)\times n_i u_i^*(r)u_i(r)\Big)\Big/\rho_\uparrow(r). \tag{22}$$

Here α is given by Eq. (9). Use of Eqs. (18), (19), and (22) in Eq. (17) gives, for the total energy in the HFG scheme

$$\begin{aligned}\langle\text{EHFG}\rangle=&\sum_i n_i\int u_i^*(r)f_1u_i(r)\,dr+\frac{1}{2}\int\rho(r)\rho(r')g_{rr'}\,dr\,dr'-\frac{1}{2}\int\sum_{i\uparrow}n_iu_i^*(r)u_i(r)\,n_iu_i^*(r')u_i(r')g_{rr'}\,dr\,dr'\\&-\frac{9C\alpha_\uparrow}{2}\int\sum_{i\uparrow}\rho_{i'\uparrow}(r)\rho_\uparrow^{-2/3}(r)n_iu_i^*(r)u_i(r)\,dr\\&-\frac{1}{2}\int\sum_{j\downarrow}n_ju_j^*(r)u_j(r)n_ju_j^*(r')u_j(r')g_{rr'}\,dr\,dr'-\frac{9C\alpha_\downarrow}{2}\int\sum_{j\downarrow}\rho_{j'\downarrow}(r)\rho_\downarrow^{-2/3}(r)n_ju_j^*(r)u_j(r)\,dr.\end{aligned} \tag{23}$$

The variational procedure making the total energy EHFG stationary with respect to arbitrary variations in each of the spin orbitals subject to the orthonormality constraints on the u_i's, leads to the following set of one-electron Schrödinger equations for the u_i's and corresponding eigenvalues ϵ_i's:

$$[f_1+V_c(r)+V_{\text{HFG}i\uparrow}^s(r)+V_{\text{HFG}i\uparrow}^{\text{ex}}(r)]u_{i\uparrow}(r)=\epsilon_iu_{i\uparrow}(r), \tag{24}$$

with a similar equation for down-spin orbitals.

Here $V_c(r)$ is the Coulomb potential of Eq. (2). $V_{\text{HFG}i\uparrow}^s(r)$ is the self-interaction potential for the ith-spin orbital given by

$$V_{\text{HFG}i\uparrow}^s(r)=n_i\int u_{i\uparrow}^*(r')u_{i\uparrow}(r')g_{rr'}\,dr' \tag{25}$$

and $V_{\text{HFG}i\uparrow}^{\text{ex}}(r)$ is the exchange potential given by

$$\begin{aligned}V_{\text{HFG}i\uparrow}^{\text{ex}}(r)&\\=\frac{-9C\alpha_\uparrow}{2}&\Big(2\rho_{i'\uparrow}(r)\rho_\uparrow^{-2/3}(r)\\&-\tfrac{2}{3}\rho_\uparrow^{-5/3}(r)\sum_{i\uparrow}n_iu_i^*(r)u_i(r)\rho_{i'\uparrow}(r)\Big).\end{aligned} \tag{26}$$

The terms on the right-hand side of Eq. (26) arise from the differentiation of the fourth term on the right-hand side of Eq. (23) with respect to u_i. Note that in regions where $\rho_{i'}\simeq\rho_\uparrow$, where self-interaction is not dominant, the assumption that ρ_i has the same value for all spin orbitals of the same spin, reduces Eq. (26) to the same form as Eq. (7) of the HFS method. Such assumptions are unnecessary, since the terms in Eq. (26) can be easily evaluated.

Equation (25) represents the one-electron equations of the present HFG method. Note that the electron in each spin orbital has a characteristic exchange-correlation potential, as in the HF method and unlike the HFS method. All the disadvantages of the Slater averaging procedure are thus avoided, while the simplicity of the HFS scheme is retained. Further, since $rV_{\text{HFG}i}^s(r)\to-2$ and $rV_{\text{HFG}i}^{\text{ex}}(r)\to0$ as $r\to\infty$, the correct asymptotic behavior of the potential at large r values is ensured and there is no need for Latter correction. Computationally, Eq. (24) is as simple to solve as the corresponding HFS equation, and we have no new integrals to evaluate.

The correct asymptotic form for the exchange-correlation potential at large values of r is also obtained in a modification of the HFS scheme proposed by Liberman.[10] In this method, the atom is arbitrarily divided into two regions of high and low densities and the free-electron gas exchange-correlation is treated differently in these regions. Apart from the arbitrary nature of this division and the lack of explicit consideration of self-interaction in the high-density regions, this method has the additional defect that the potential is discontinuous at the boundary between the two regions. Cowan,[11] on the other hand, has proposed a potential in which the self-interaction is explicitly evaluated as in the present HFG scheme. But the exchange part is approximated by an empirical function of the density containing a few arbitrary constants. A more serious defect of Cowan's potential is that it is not variationally derived from the total energy expression. The approximation suggested by Lindgren[12] also evaluates the self-interaction exactly, but the exchange part is expressed by

$$V^{\mathrm{ex}}(r)=-2(6/\pi)^{1/3}\{[\rho_{\uparrow}(r)^{1/3}-[\rho_{\uparrow}(r)-\rho_{i',\uparrow}(r)]^{1/3}\} \tag{27}$$

in the units and notation we are using. This is an approximate expression for the exchange potential for a free-electron gas.[12a] Note that Eq. (27) is quite different from the corresponding expression $V^{\mathrm{ex}}_{\mathrm{HFG}i}$, Eq. (26) of the present method. The latter has been derived not from the free-electron model but by considering the potential produced at the center of the Fermi-hole by the charge distribution from which the electron under consideration has been removed, together with the necessary condition that the total exchange-correlation density is equal to unity. Another significant difference between the two exchange potentials is that in $V^{\mathrm{ex}}_{\mathrm{HFG}}$ we have incorporated the theoretical exchange parameter α. This is desirable since the free-electron gas exchange is not strictly applicable to atoms.[3c] Thus Eq. (26) may be thought of as combining the virtues of these various approximations to the exchange potential while avoiding their shortcomings.

In the HFS method, if it is assumed that the total energy is a continuous function of n_i, then the eigenvalues are related to the total energy by,[3d]

$$\frac{\partial\langle \mathrm{EHFS}\rangle}{\partial n_i}=\epsilon_{\mathrm{HFS}\,i}\,. \tag{28}$$

In the HFG scheme also, under the same assumptions,

$$\frac{\partial\langle \mathrm{EHFG}\rangle}{\partial n_i}=\epsilon_{\mathrm{HFG}i}\,. \tag{29}$$

This is easily shown by differentiating Eq. (23) with respect to n_i and comparing the result to that of multiplying Eq. (24) by $u^*_{i\uparrow}(r)$ on the left-hand side and integrating. Such a relation does not hold the Hartree-Fock energy and eigenvalues. This is often stated[3d] to be the reason for the large difference obtained between the eigenvalues in the HF and HFS methods. This is not true. In the HFG scheme, relation (29) holds and at the same time eigenvalues obtained are in good agreement with HF values (see Sec. III). The reason for the disagreement between HF and HFS eigenvalues is that eigenvalues of the Schrödinger equation are determined mainly by the depth of the potential well. It can be shown (Sec. III) that in the HFS method the exchange-correlation potential is too positive due to underestimation of electron self-interaction. This leads to too positive eigenvalues. On the other hand, in the HFG method, the exchange-correlation potential is very close to the HF value and hence the good agreement between $\epsilon_{\mathrm{HFG}i}$ and $\epsilon_{\mathrm{HF}i}$ values. These facts are quantitatively discussed in Sec. III.

A word of caution about Eqs. (28), (29), or their equivalent in the hyper-Hartree-Fock method[3e] is in order. These equations are obviously derived assuming that the total energy is a differentiable function of n_i. However, it can be shown[13] that the admittance of non-integral n_i values leads to serious errors in total energy, eigenvalues and other properties due to an incorrect counting of the number of pair-wise electron-electron interactions in the expression for the total energy. The correct expression to be used for nonintegral n_i values and the consequences of using the incorrect one will be discussed in a forthcoming communication.[13]

III. APPLICATION TO FIRST-ROW TRANSITION ELEMENTS

The computer program to solve Eq. (24) was written by the author by extensively modifying the original Herman-Skillman program.[14] The program performs spin-polarized HFG calculations. The time required per run is of the same order as the Herman-Skillman program.

The HFG results for the first-row transition elements, Cu^+ and Mn^{+2} for which extensive HFS and HF results are available for comparison are discussed below.

A. Eigenvalues and potentials for Cu^+ ion

For both HFG and HFS calculations reported here, the theoretical α value obtained from Eq. (9) was used.[4] The eigenvalues obtained are given in Table I. The HFG values are in close agreement with the HF values, while the HFS results are much too positive; the largest deviation being for the core levels. The reason for these differences is clear from Fig. 1 where the exchange correlation potentials for the various orbitals in the HF and HFG methods are compared with the average potential used in the HFS method. For the sake of clarity, only the 1s, 3s and 3d potentials are shown in Fig. 1. The HFG potentials are generally close to the HF potentials, except for the 3d orbital for which the HFG potential is somewhat more negative. The reason for this will be discussed under the Mn^{+2} ion. In contrast, the HFS method grossly underestimates the exchange-correlation potential for all states except 3d. Further, the HFS potential has the wrong behavior for large r values (not shown in the figure), whereas the HFG and HF potential become identical in this region. These features of the potentials are quite general and will be discussed below.

TABLE I. Comparison of eigenvalues for Cu$^+$, by HF, HFG, and HFS methods. Energies are in Ry. Theoretical value of α [Eq. (9)] used is 0.7305. HF values are taken from J. C. Slater, Intern. J. Quantum Chem. IIIS, 727 (1970).

Orbital i	$-\epsilon_{HFi}$	$-\epsilon_{HFGi}$	Diff.	$-\epsilon_{HFSi}$	Diff.
1s	658.22	656.18	2.04	643.61	14.61
2s	82.26	81.66	0.60	77.15	5.11
2p	71.86	73.08	−1.22	67.86	4.00
3s	10.65	10.07	0.58	8.75	1.90
3p	7.28	7.11	0.17	5.85	1.43
3d	1.62	2.06	−0.44	1.01	0.61

B. Eigenvalues, potentials and contact hyperfine interaction for Mn^{+2} ion

The ground-state configuration of Mn^{+2} is taken to be (Ar)3d^5. Spin-polarized calculations were made in the HFS and HFG methods using theoretical α values. The spin-polarized HF results are taken from Ref. 7.

TABLE II. Eigenvalues for Mn^{+2} by spin-polarized HF, HFG, and HFS methods. Energies are in Ry. Theoretical spin-dependent α values used. $\alpha_\uparrow = 0.7305$, $\alpha_\downarrow = 0.7340$ [Eq. (9)]. HF values are from Ref. 7.

Orbital i	$-\epsilon_{HFi}$	$-\epsilon_{HFGi}$	Diff.	$-\epsilon_{HFSi}$	Diff.
1$s\uparrow$	482.369	480.774	1.595	469.594	12.775
1$s\downarrow$	482.374	480.797	1.577	469.595	12.779
2$s\uparrow$	59.663	59.359	0.304	55.203	4.460
2$s\downarrow$	59.633	59.094	0.539	54.997	4.636
2$p\uparrow$	51.044	52.303	−1.259	47.600	3.444
2$p\downarrow$	50.781	52.144	−1.363	47.444	3.337
3$s\uparrow$	9.323	8.991	0.332	7.600	1.723
3$s\downarrow$	8.494	8.320	0.174	7.127	1.367
3$p\uparrow$	6.753	6.749	0.004	5.423	1.330
3$p\downarrow$	5.745	6.099	−0.354	4.958	0.787
3$d\uparrow$	2.576	3.093	−0.517	1.929	0.647

The eigenvalues are given in Table II. As in the case of Cu$^+$, the HFG results are generally very close to the HF results and the HFS values are too positive, indicating that the HFS method underestimates the exchange correlation potential. Consider the self-interaction part, Eq. (25), and the exchange part, Eq. (26), of the HFG potential for the 1s (Fig. 2) and the 3d (Fig. 3) orbitals, which represent, respectively, the lowest (most negative) and highest potentials in Mn^{+2}. Figure 2

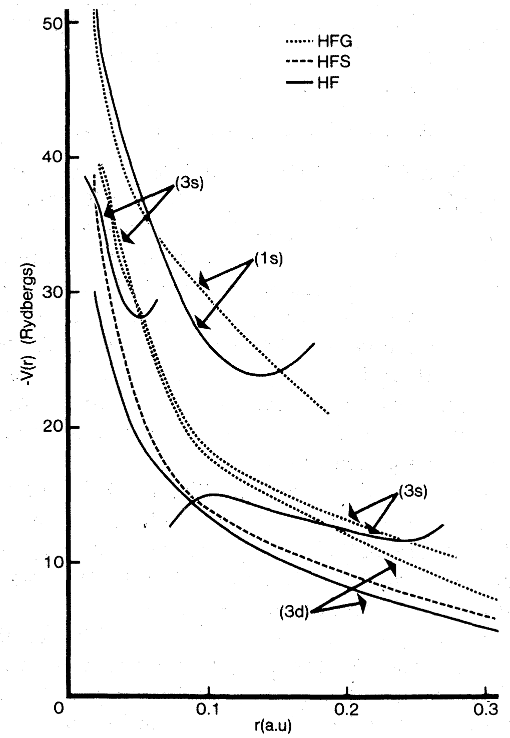

FIG. 1. Comparison of HF, HFS, and HFG exchange-correlation potentials for 1s, 3s, and 3d orbitals in Cu$^+$. HF results are taken from Ref. 5. For HFS and HFG calculations, theoretical α value of 0.7305 from Eq. (9) was used.

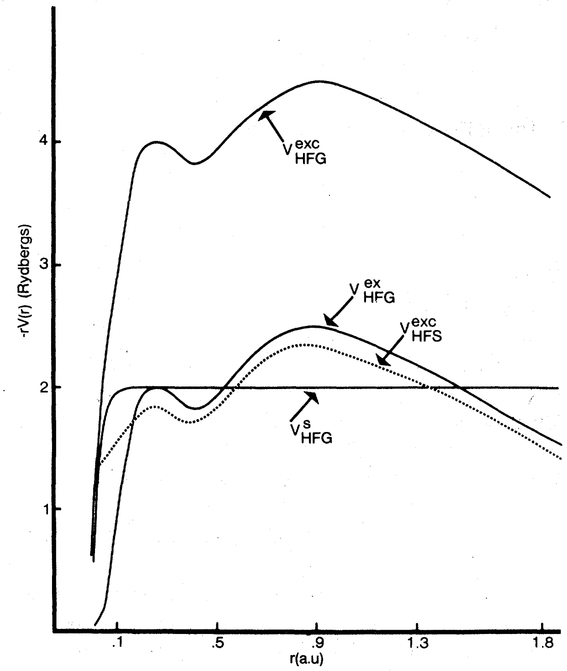

FIG. 2. Self-interaction potential V^s_{HFG}, exchange potential V^{ex}_{HFG} and the total exchange-correlation potential V^{exc}_{HFG} for 1$s\uparrow$ orbital in Mn^{+2} ion, calculated by the present method. V^{exc}_{HFS} is the average exchange-correlation potential by the HFS method. Note that $rV(r)$ is plotted in the figure.

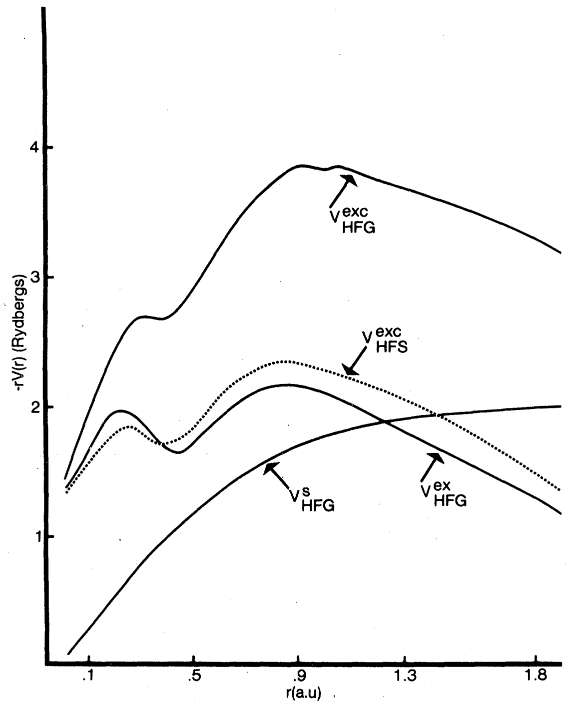

FIG. 3. Self-interaction potential $V^{s}_{\rm HFG}$, exchange potential $V^{\rm ex}_{\rm HFG}$ and the total exchange-correlation potential $V^{\rm exc}_{\rm HFG}$ for $3d\uparrow$ orbital in $\rm Mn^{+2}$ ion, calculated by the present method. $V^{\rm exc}_{\rm HFS}$ is the average exchange-correlation potential by the HFS method. Notice that $rV(r)$ is plotted in the figure.

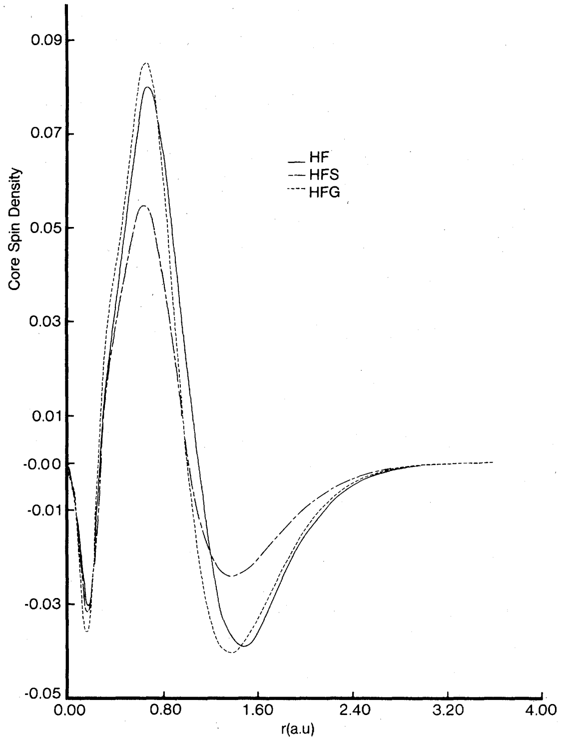

FIG. 4. Comparison of the argon core spin-density distribution in $\rm Mn^{+2}$ ion by the spin-polarized HF, HFS, and the present HFG methods. The HF curve is taken from Ref. 7. Average theoretical α value used is 0.7319 [Eq. (10)]. Spin-dependent α values Eq. (9) lead to essentially the same curves as in this figure for HFG and HFS methods, respectively.

shows that for the 1*s* orbital, the dominant contribution comes from the self-interaction term rather than from the exchange term for r values <0.1 a.u. Since the 1*s* electron has little density outside this region, the eigenvalue is mainly determined by the potential for $r<0.1$. In this region, the HFS exchange-correlation potential is ever smaller than the self-interaction term, except very close to the nucleus, showing that the HFS scheme fails to account for self-interaction at intermediate r values in addition to its complete failure to do so at large r values. This is the reason why the HFS eigenvalues are too positive.

Moving from the nucleus towards orbitals of higher *nl* values, the self-interaction becomes progressively less important in determining the deep regions of the potential well. Comparison of the 3*d* potential terms (Fig. 3) with the 1*s* potentials (Fig. 2) shows this clearly. Thus the error in the HFS eigenvalues progressively diminish for higher *nl* values, as may be seen from Table I (for $\rm Cu^{+}$) and II (for $\rm Mn^{+2}$). In the HFG scheme, even though the eigenvalues are generally close to the HF values, the maximum relative error occurs for the 3*d* orbital, again due to the importance of the exchange term for this orbital which is treated only approximately by Eq. (26) in contrast to the self-interaction term of Eq. (25) which is exactly evaluated.

We now turn to a discussion of the spin-density distribution and the contact hyperfine interaction in $\rm Mn^{+2}$. The spins of the electrons in the argon core of $\rm Mn^{+2}$ are polarized by the five unpaired (taken to be up-spin) 3*d* electrons. This gives a nonvanishing spin density at the nucleus as well as at other r values. The distribution of this core-spin density as a function of r is a very stringent test of the approximations to the exchange-correlation potential. This has been studied for $\rm Mn^{+2}$ by the HF method,[15] as well as by various forms of the HFS method.[7] The general result is that the HFS method fails to describe spin polarization adequately. Figure 4 is a comparison of the HF, HFS and HFG results for the core-spin density distribution. The HFS results are poor for $r>0.4$ a.u., due to the underestimation of self-interaction at large r values. Latter correction to the HFS potential not only does not improve the spin-density distribution at large r, but gives results appreciably worse for all r values.[16] This is due to the defects of the Latter correction procedure discussed in Sec. I. On the other hand, the HFG method describes the spin-density distribution remarkably well (Fig. 4) proving that the HFG exchange-correlation potential is a very good approximation to the corresponding HF potential.

The magnitudes of the spin density at the nucleus of Mn^{+2} given by the three methods could be compared. Only the s orbitals have a nonvanishing density at the nucleus, and the individual contributions of the s-orbitals are given in Table III, in terms of the quantity χ defined by[15]

$$\chi = \frac{4\pi}{n_\uparrow - n_\downarrow} \sum_n \left[\rho_{ns}^{\uparrow}(0) - \rho_{ns}^{\downarrow}(0)\right] = \sum_n \chi_n \,. \tag{30}$$

The HF result is in agreement with the experimental measurement of the contact hyperfine interaction. The major contribution to χ comes from $2s$ and $3s$ potentials and we see that the HFS method underestimates this. This failure of the HFS method to describe spin-polarization has been discussed by Slater.[3f] In contrast, the HFG method gives results in much closer agreement with the HF values. In Table III, we have given HFG results for the spin-dependent α values of Eq. (9) as well as for the average α value of Eq. (10). While the core spin-density distribution is not very sensitive to this difference in α values, the $1s$ contribution to χ is sensitive to it.

One form of the HFS method, in which the free-electron exchange-correlation potential is used according to a suggestion by Liberman,[17] gives eigenvalues for Mn^{+2} in very good agreement with HF values. This method does not use the Slater averaging procedure for the potential. But this approach totally breaks down for the spin-polarization effects, as shown by Wilson *et al.*[7] These authors have also pointed out the sensitiveness of the χ values to the choice of basis set in the HF method. Of course, the HFS and HFG schemes are numerical methods and therefore do not have this problem.

TABLE III. Fermi contact term[a] χ in Mn^{+2}, by HF, HFG, and HFS methods.

	HF[b]	HFS[c]	HFG[d]	HFG[e]
χ_{1s}	−0.191	−0.158	−0.081	+0.300
χ_{2s}	−7.154	−5.376	−7.683	−8.046
χ_{3s}	+3.218	+2.004	+3.364	+3.209
χ	−4.127	−3.530	−4.400	−4.537

[a] See Eq. (30).
[b] Reference 15.
[c] Reference 7.
[d] Using average theoretical $\alpha = 0.7319$, see Eq. (10).
[e] Using spin-dependent theoretical α values. $\alpha_\uparrow = 0.7305$, $\alpha_\downarrow = 0.7340$. See Eq. (9).

IV. CONCLUSIONS

The present method of treating the exchange-correlation potential in atoms is based on the separation of the potential into an electron self-interaction term and the characteristic exchange terms. The self-interaction term is evaluated exactly while the exchange term is approximated by a procedure similar to the $\rho^{1/3}$ approximation due to Dirac and Slater. Electrons in different spin-orbitals have different exchange potentials in our scheme. We thus avoid the major defects of the HFS method, namely, the use of a single average potential for all the electrons, as well as the underestimation of the self-interaction. The HFG eigenvalues are shown to be in close agreement with the HF eigenvalues, in contrast to the inaccurate eigenvalues from the HFS scheme. Spin polarization in the first-row transition ions, which depends critically on the exchange-correlation potentials and its variation with r for the various shells, is described very well by the present method, whereas the HFS scheme and its many modifications have all failed in this respect.

Since the method proposed here is computationally as simple as the HFS method, and much superior to it in performance, it should prove useful in molecular and solid state calculations. However, Slater and Wood[18] have pointed out certain difficulties in extending to polyatomic systems schemes in which the self-interaction is separated from the total exchange correlation. Their argument is that the single-determinantal wave function, the Coulomb energy and the total exchange-correlation energy are invariant under a unitary transformation of the spin orbitals; the self-interaction term is not invariant under such a transformation and hence this term is not uniquely defined. For example, for well-localized spin orbitals the self-interaction is large, whereas if these spin orbitals are transformed into delocalized orbitals it becomes negligibly small. In this connection, we note that when the self-interaction is small we have $\rho_{i,\uparrow} \approx \rho_\uparrow$ and hence the exchange potential of the present HFG scheme $V_{\mathrm{HFG}}^{\mathrm{ex}}$ of Eq. (26) reduces to the exchange potential V_{XS}, Eq. (7) of the HFS method, so that the two methods become identical. This fact aside, the author believes that the lack of invariance of the self-interaction can be profitably taken advantage of in extending the HFG scheme to polyatomic systems. Several methods have now been developed[19] to transform (in a unitary fashion) the delocalized spin orbitals in such systems to well-localized orbitals. Instead of transforming the delocalized orbitals into localized ones in this way, one may equivalently introduce[20] a localizing potential to obtain modified HF operators with localized eigenfunctions. As remarked by Gilbert,[20] these modified equations may be easier to solve and interpret than the standard HF equations, especially for large molecules and crystals. One of the most efficient and practical methods of determining the localization potential (or equivalently the transformation matrix discussed above) is that of maximizing the self-repulsion energy as proposed originally by Lennard-Jones[21] and developed by Edmiston and Ruedenberg.[22] Maximization of the self-repulsion energy means also the simultaneous minimization of the pure-exchange energy because of the invariance of the total exchange-correlation energy. Orbitals obtained by this procedure are called energy-localized orbitals. Obviously, the present HFG scheme is best suited to obtain accurate energy-localized orbitals for large polyatomic systems. For these orbitals, the self-repulsion part which is a maximum would be evaluated exactly in the HFG procedure, and only the pure exchange part, which is a minimum, would be approximated. Consequently the HFG scheme can be expected to reduce the errors to a minimum and to yield much more accurate orbitals than schemes like the HFS in which the total exchange-correlation energy is approximated. Another theoretically attractive feature of the energy-localized orbitals is worth mentioning. An assumption fundamental to both the HFS and HFG schemes is that the spin-orbitals u_i are close approximations to the natural spin orbitals of the system. As discussed by Edmiston and Ruedenberg,[22] there are reasons to believe that this would be nearly so for the energy-localized orbitals.

Admittedly this is only an optimistic account of the possible application of the HFG scheme to obtain accurate wave functions for polyatomic systems. Certain limitations should be borne in mind. Firstly, the localization scheme is applicable only to localizable electrons such as core electrons, electrons in rare gas and ionic crystals and not, for example, to electrons in the conduction band of metals, which are not very localizable. Secondly, the computational problems involved in solving the HFG equation with the localizing potential remain to be worked out. Work along these lines is now in progress.

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[1] J. C. Slater, Phys. Rev. 81, 385 (1951).

[2] P. A. M. Dirac, Proc. Cambridge Philos. Soc. 26, 376 (1930).

[3] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4, (a) p. 17, (b) p. 15, (c) p. 21, (d) p. 26, (e) p. 39, (f) p. 65.

[4] M. S. Gopinathan, M. A. Whitehead, and R. Bogdanovic, Phys. Rev. A 14, 1 (1976).

[5] D. R. Hartree, Phys. Rev. 109, 840 (1958).

[6] R. Latter, Phys. Rev. 99, 510 (1955).

[7] T. H. Wilson, J. H. Wood, and J. C. Slater, Phys. Rev. A 2, 620 (1970).

[8] D. J. McNaughton and V. H. Smith, Jr., Intern. J. Quantum. Chem. 3S, 775 (1970).

[9] C. A. Coulson and C. S. Sharma, Proc. Phys. Soc. Lond. 79, 920 (1962).

[10] D. A. Liberman, Phys. Rev. B 2, 244 (1970).

[11] R. D. Cowan, Phys. Rev. 163, 54 (1967).

[12] I. Lindgren, Intern. J. Quantum Chem. 5S, 411 (1971); (a) see also A. I. M. Rae [Chem. Phys. Lett. 18, 574 (1973)] for a similar treatment of the free-electron exchange.

[13] M. S. Gopinathan and M. A. Whitehead (unpublished).

[14] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[15] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 2027 (1961).

[16] P. E. Desmier, M. A. Whitehead, R. Bogdanovic, and M. S. Gopinathan, Mol. Phys. (to be published).

[17] D. A. Liberman, Phys. Rev. 171, 1 (1968).

[18] J. C. Slater and J. H. Wood, Intern. J. Quantum Chem. 4S, 3 (1974).

[19] H. Weinstein, R. Pauncz, and M. Cohen, in *Advances in Atomic and Molecular Physics* (Academic, New York, 1971), Vol. 7, p. 40; W. England, L. S. Salmon, and K. Ruedenberg, Topics Curr. Chem. 23, 31 (1971).

[20] T. L. Gilbert, in *Molecular Orbitals in Physics and Chemistry* (Academic, New York, 1964), p. 405.

[21] J. E. Lennard-Jones, Proc. R. Soc. Lond. A 198, 14 (1949).

[22] C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. 35, 457 (1963).