

Electron gas exchange for atoms

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Current use of electron gas theory for exchange allows calculations of Hartree-Fock (HF) energies through the use of local potentials. A recent proposal of Gopinathan, Whitehead, and Bogdanović to use a realistic pair correlation function $f_{\uparrow\uparrow}(1,2)$ that incorporates the boundary conditions of Kutzelnigg, Del Re, and Berthier, which consider the finite number of electrons of a given spin, showed much better agreement with atomic HF calculations. This paper explores the use of an improved $f_{\uparrow\uparrow}(1,2)$ either with the electron cloud form (exponential) or with a modified Wigner form. The total energies obtained from this method are in excellent agreement with HF total energies. The calculated total energies lie above the HF values; we interpret this as an open possibility for the inclusion of refinements such as the inhomogeneity corrections.

I. INTRODUCTION

The solution of the Hartree-Fock equations, especially for larger atoms, is complicated by the nonlocal nature of the exchange potential. A simplifying assumption, due to Slater,¹ consisted in averaging the exchange terms in the total (Hartree-Fock) energy expression over all occupied one-electron states; in a further approximation, these averaged terms were replaced by the interaction of the spin-up (\uparrow) and spin-down (\downarrow) electronic charge densities, ρ_{\uparrow} and ρ_{\downarrow} , with two total exchange potential functions U_{\uparrow} and U_{\downarrow} according to

$$E_{\text{exch}} = \frac{1}{2} \int [\rho_{\uparrow}(1)U_{\uparrow}(1) + \rho_{\downarrow}(1)U_{\downarrow}(1)] dv_1. \quad (1)$$

The expressions for U_{\uparrow} and U_{\downarrow} were derived by assuming that the local behavior of the ρ 's was that of a uniform free electron gas.

Hohenberg, Kohn, Sham, and Tong² and Gaspar³ have shown that the exchange potentials appearing in the one-electron Schrödinger equations that are variationally derived from the approximate total-energy expression are not U_{\uparrow} and U_{\downarrow} , but these functions multiplied by a constant factor $C_{\text{GKS}} = \frac{2}{3}$ (GKS stands for Gaspar-Kohn-Sham). The study, by many people in different fields of computational physics, employing different values for C_{GKS} led to the development of the so-called X_{α} method⁴ in which the total exchange potential is given in rydberg units by

$$U_{\uparrow}(1) = -9\alpha[(3/4\pi)\rho_{\uparrow}(1)]^{1/3}. \quad (2)$$

with a similar expression for U_{\downarrow} .

Several methods have been proposed to determine empirically or theoretically the parameter α that should replace C_{GKS} for atomic, molecular, and solid-state computations^{5,6}; it was found that

the α values should change from atom to atom if Hartree-Fock accuracy is desired. For isolated atoms, Schwarz⁶ determined the α values (α_{HF}) using the *ad hoc* theoretical criterion that the total energy in the X_{α} method should equal the Hartree-Fock energy; he found a smooth variation of α with Z (atomic number). Berrondo and Gosciniski⁶ proposed the use of the virial theorem to determine α (α_{VT}), and found that $\alpha_{\text{VT}} \approx \alpha_{\text{HF}}$. Unfortunately there is no unique way to extend these criteria to molecular calculations.

Herman *et al.*⁷ proposed the use of $\alpha = \frac{2}{3}$ (Gaspar-Kohn-Sham) always, and included terms in U depending on the gradients of the charge density to account for the inhomogeneity. This was also intended to avoid the problem of using different values of α in different regions of a molecule or solid. Nevertheless, the use of the inhomogeneity terms remains a heuristic approach.

Recently however, Gopinathan, Whitehead, and Bogdanović⁸ (GWB) have demonstrated that the parametrization of Schwarz can be correlated with the finite number of electrons in an atom. These authors assumed a functional variation of the Fermi hole density, with the proper boundary values [following the statistical analysis of Kutzelnigg, Del Re, and Berthier⁹ (KDRB)].

Here, we consider the relation between the functional form of the Fermi hole density and the electron gas exchange for atoms.

II. THE FERMI HOLE

In terms of the one- and two-particle density matrices

$$\rho(1) = n \int |\psi(1, 2, \dots, n)|^2 d\tau_2 \dots d\tau_n dS_1 dS_2 \dots dS_n, \quad (3)$$

$$\pi(1,2) = n(n-1) \times \int |\psi(1,2,\dots,n)|^2 d\tau_3 \dots d\tau_n dS_1 dS_2 \dots dS_n, \quad (4)$$

where $d\tau_i$ represents the volume element of the i th electron and dS_i the spin coordinate, n is the total number of electrons, and ψ is the electronic wave function. $\rho(1)$, the charge density at point 1, is the probability of finding any of the n electrons at this point. $\pi(1,2)$ is the pair density and gives the probability of finding any of the n electrons at point 1 and simultaneously another at point 2. The total electron-electron interaction energy is given by

$$\left\langle \sum_{i < j} r_{ij}^{-1} \right\rangle = \frac{1}{2} \int r_{12}^{-1} \pi(1,2) d\tau_1 d\tau_2. \quad (5)$$

The one- and two-particle density matrices may be written in terms of their spin components as

$$\rho(1) = \rho_{\uparrow}(1) + \rho_{\downarrow}(1), \quad (6)$$

and

$$\pi(1,2) = \pi_{\uparrow\uparrow}(1,2) + \pi_{\uparrow\downarrow}(1,2) + \pi_{\downarrow\uparrow}(1,2) + \pi_{\downarrow\downarrow}(1,2). \quad (7)$$

When the electronic motion is correlated, the pair-density distribution $\pi(1,2)$ may be expressed as

$$\pi_{\uparrow\uparrow}(1,2) = \rho_{\uparrow}(1)\rho_{\uparrow}(2) + \rho_{\uparrow}(1)\rho_{\uparrow}(2)f_{\uparrow\uparrow}(1,2) \quad (8)$$

and

$$\pi_{\uparrow\downarrow}(1,2) = \rho_{\uparrow}(1)\rho_{\downarrow}(2) + \rho_{\uparrow}(1)\rho_{\downarrow}(2)f_{\uparrow\downarrow}(1,2), \quad (9)$$

with similar expressions for $\pi_{\downarrow\downarrow}(1,2)$ and $\pi_{\downarrow\uparrow}(1,2)$. The f 's are the correlation factors.

In Hartree-Fock theory it is assumed that $f_{\uparrow\uparrow}(1,2) = f_{\downarrow\downarrow}(1,2) = 0$, and one obtains, by substituting Eqs. (7) and (8) into Eq. (5), the exchange potential for spin-up electrons:

$$U_{\uparrow}(1) = \int r_{12}^{-1} \rho_{\uparrow}(2) f_{\uparrow\uparrow}(1,2) d\tau_2, \quad (10)$$

with a similar expression for spin-down electrons. This corresponds to the potential set up by an exchange charge ρ^{ex} at position 2, given by

$$\rho_{\uparrow}^{\text{ex}}(2) = \rho_{\uparrow}(2) f_{\uparrow\uparrow}(1,2), \quad (11)$$

with the following properties:

$$\int \rho_{\uparrow}^{\text{ex}}(2) d\tau_2 = -1, \quad (12)$$

$$\rho_{\uparrow}^{\text{ex}}(1) = -\rho_{\uparrow}(1), \quad (13)$$

$$\rho_{\uparrow}^{\text{ex}}(2) \rightarrow -\rho_{\uparrow}(2)/n_{\uparrow}, \quad (14)$$

for large r_{12} when it may be assumed that the elec-

trons move independently. Therefore,

$$\pi^{\text{ind}}(1,2) = \rho(1)\rho(2) - \rho(1)\rho(2)/n, \quad (15)$$

to preserve the correct normalization in finite systems (as pointed out by KDRB).

One may assume that near position 1, $\rho(2)$ may be replaced by $\rho(1)$; thus, the exchange density changes because $f_{\uparrow\uparrow}$ changes. This was the starting point of GWB.

Now, assuming that the Fermi hole centered at position 1 is spherically symmetric and has the finite radius r_0 , Eq. (12) becomes

$$4\pi \int_0^{r_0} \rho_{\uparrow}^{\text{ex}}(r) r^2 dr = -1, \quad (16)$$

and the potential at the center of the sphere due to the exchange density is (rydberg units)

$$U_{\uparrow}(1) = 8\pi \int_0^{r_0} \rho_{\uparrow}^{\text{ex}}(r) r dr. \quad (17)$$

Even though an exact form of $\rho^{\text{ex}}(r)$ as a function of $\rho_{\uparrow}(1)$ is not known for an atom or a molecule, one may assume some functional variation with distance and impose the boundary conditions of KDRB. That is,

$$\rho_{\uparrow}^{\text{ex}}(r) = ag(r) + b, \quad (18)$$

with a and b determined so that it satisfies Eqs. (13) and (14).

GWB found that assuming $g(r)$ to be a straight line from zero to r_0 leads to z -dependent values of α proportional to the α_{HF} or α_{VT} . Their results are plotted in Fig. 1. The agreement with α_{HF} or α_{VT} was closer when the obtained values were multiplied by a constant factor of 0.972, but this does not satisfy the boundary conditions. Also, it may be pointed out that the chosen linear variation forces $f_{\uparrow\uparrow}(1,2)$ to the asymptotic value at small distances from the first electron.

Now, in the electron gas approximation one may assume that since the total amount of exchange charge removed from the distribution as far as electron 1 is concerned is -1 , the exchange charge the electron carries in its movement should not be very different from a hydrogenlike distribution; such a Fermi hole density with exponential behavior is given by

$$\rho_{\uparrow}^{\text{ex}}(1) = -\rho_{\uparrow}(1) [(1 - 1/n_{\uparrow}) e^{-br/r_0} + 1/n_{\uparrow}]. \quad (19)$$

The last term in the square bracket conforms to the KDRB boundary conditions for $f_{\uparrow\uparrow}$, and the parameter b may be determined by requiring that the exchange approach the free-electron gas value as the number of electrons becomes infinite. Replacing Eq. (19) in Eq. (16) and Eq. (17) gives for the

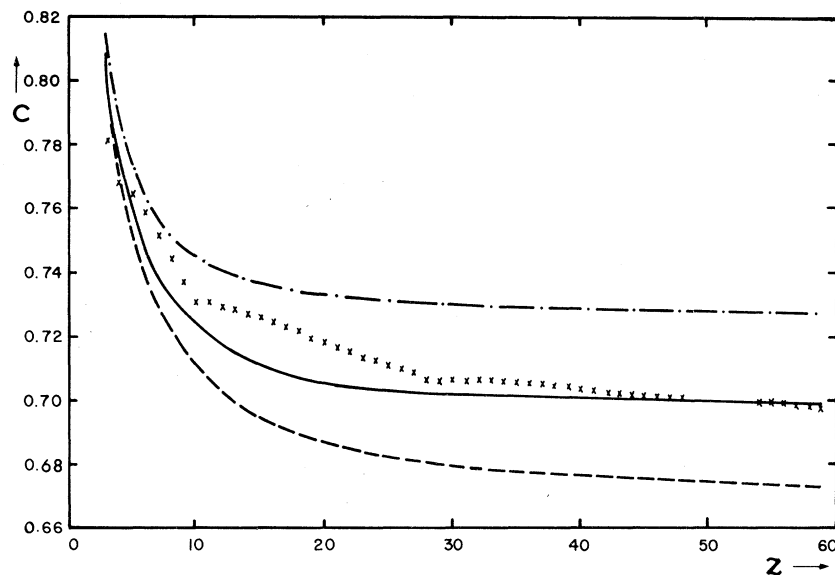


FIG. 1. Plot of different exchange approximations versus atomic number. $C = (n_{\uparrow} C_{\uparrow} + n_{\downarrow} C_{\downarrow}) / (n_{\uparrow} + n_{\downarrow})$. The dash-dot line represents C_{GWB} ; dashed line, C , Eq. (21); solid line, C , Eq. (23); \times corresponds to α_{HF} .

electron gas exchange potential

$$\begin{aligned}
 U_{\uparrow}(1) &= -2(4\pi)^{1/3} \rho_{\uparrow}^{1/3}(1) \\
 &\times \left\{ \left(1 - \frac{1}{n_{\uparrow}}\right) \frac{1}{b} \left[\frac{1}{b} - e^{-b} \left(1 + \frac{1}{b}\right) \right] + \frac{1}{2n_{\uparrow}} \right\} \\
 &\times \left\{ \left(1 - \frac{1}{n_{\uparrow}}\right) \frac{1}{b} \left[\frac{2}{b^2} - e^{-b} \left(1 + \frac{2}{b} + \frac{2}{b^2}\right) \right] + \frac{1}{3n_{\uparrow}} \right\}^{-2/3} \\
 &= C_{\uparrow} U_{\uparrow \text{Slater}}(1). \quad (20)
 \end{aligned}$$

Comparing with Eq. (2), this is equivalent to using an exchange constant factor

$$C_{\uparrow} = \frac{2}{3} \frac{1 + 2.2321/n_{\uparrow}}{(1 + 2.9212/n_{\uparrow})^{2/3}}, \quad (21)$$

where $b = 1.925$ was used. The values of C obtained with this equation are plotted in Fig. 1.

We now explore the use of a modified Wigner approximation¹⁰ to the pair correlation function of free electrons with parallel spin, in a seemingly more realistic form,

$$\begin{aligned}
 \rho_{\uparrow}^{\text{ex}}(1) &= -\rho_{\uparrow}(1) \left\{ \left(1 - \frac{1}{n_{\uparrow}}\right) \right. \\
 &\times \left. \left(e^{-br/r_0} \left[1 + \frac{br}{r_0} + b \left(\frac{r}{r_0} \right)^2 \right] \right) + \frac{1}{n_{\uparrow}} \right\}, \quad (22)
 \end{aligned}$$

including in the last term of the curly brackets the KDRB boundary condition for $f_{\uparrow\uparrow}$. Determining b by requiring the free-electron-gas limit when the number of electrons goes to infinity, we find that C_{\uparrow} has a minimum value, lower than $\frac{2}{3}$, around $n = 10$. This may be avoided by determining b so that the minimum of C_{\uparrow} occurs for $n_{\uparrow} \rightarrow \infty$,

the final expression being

$$C_{\uparrow} = 0.6985 \frac{1 + 2.5148/n_{\uparrow}}{(1 + 3.7723/n_{\uparrow})^{2/3}}, \quad (23)$$

with $b = 5.029$. Values obtained with this expression are also plotted in Fig. 1. They are, in general, very close to α_{HF} .

In Fig. 2 we have drawn schematically the different approximations to the Fermi hole.

In order to assess the usefulness of the different approximations to $f_{\uparrow\uparrow}$, we have done self-consistent-field calculations on several closed-shell atoms and ions with the different electron gas exchange potentials.

The self-consistent equations to be solved are (in rydberg units):

$$[-\nabla^2 + \phi(\vec{r}) + V_x(\vec{r})] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \quad (24)$$

where the electrostatic potential $\phi(\vec{r})$ for a nucleus with charge Z , including self-Coulomb terms, is given by

$$\phi(\vec{r}) = -\frac{2Z}{r} + \int \frac{2\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'; \quad (25)$$

the electron density for an atom with N electrons (closed shell) is

$$\rho(\vec{r}) = \sum_{i=1}^{N/2} n_i |\psi_i(\vec{r})|^2; \quad (26)$$

and the exchange potential for the spin-restricted case (closed shell) is

$$V_x(\vec{r}) = \frac{2}{3} U(\vec{r}) = -6C[(3/8\pi)\rho(\vec{r})]^{1/3}. \quad (27)$$

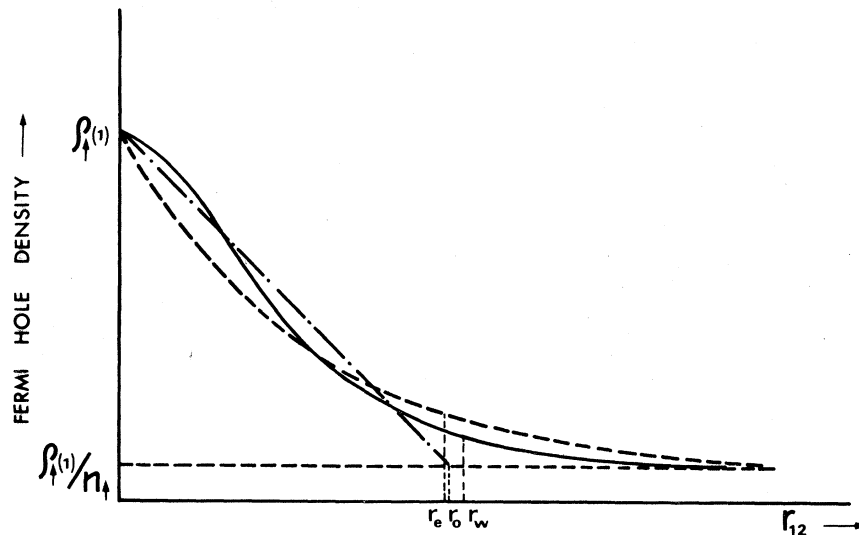


FIG. 2. Approximations to the Fermi-hole density distribution (schematic). The local approximation forces $\rho(2)f_{\uparrow\uparrow}^{(1,2)} = 0$ after r_0 , r_e , or r_w , neglecting the tails of $\rho(2)$. The dash-dot line represents GWB; dotted line, exponential; solid line, modified Wigner's form. r_0 (GWB), r_e , and r_w are the radii of the Fermi sphere in the different approximations.

The total energy is given by

$$E = \sum_{i=1}^{N/2} n_i \epsilon_i - \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + \int \rho(\vec{r}) \left[\frac{1}{2} U(\vec{r}) - \dot{V}_x(\vec{r}) \right] d\vec{r}. \quad (28)$$

Total energies for the different electron gas exchange approximations are reported together with Hartree-Fock values in Table I.

III. DISCUSSION

α_{HF} was determined to make the approximate total energy of Eq. (28) equal to the Hartree-Fock energy, and in general $\alpha > \alpha_{\text{HF}}$ results in lower total energies as in the case of the GWB values. On the other hand, the exponential form $f_{\uparrow\uparrow}$, and, in general, the modified Wigner-form electron gas total energies are above the HF limit. This situa-

tion is good since, in principle, we still have to include the effect of the inhomogeneity corrections which tend to lower the total energy. At present, we do not prefer one form over the other since the gradient corrections are uncertain.¹¹

The results for He show a relatively large error, E_T being below the experimental value. However, even if convenient for programming, one- and two-electron systems should be treated in a different way. For one-electron systems the potential should, of course, include only the electron-nuclear attraction; thus in any computer program, one should declare explicitly neither exchange nor self-Coulomb contributions in the one-electron Schrödinger equation.

For He $1s^2$ the Hartree and Hartree-Fock theories are the same; that is, the exchange term cancels exactly with part of the Coulombic interaction. Thus, making the exchange exactly equal to zero

TABLE I. Total energies for different electron gas exchange approximations (in rydberg units). For a closed-shell system, $C_{\uparrow} = C_{\downarrow} = C$.

Atom	α_{HF}^a	C_{GWB}	C , Eq. (21)	C , Eq. (23)	Hartree-Fock ^b
He	-5.6974	-5.9489	-5.9489	-5.9489	-5.7233
Ne	-257.0681	-257.521	-256.3567	-256.763	-257.0939
Ar	-1053.614	-1054.634	-1050.715	-1052.437	-1053.634
Kr	-5504.068	-5510.378	-5496.597	-5502.871	-5504.108
Li ⁺	-14.4359	-14.8384	-14.8384	-14.8384	-14.474
Na ⁺	-323.335	-323.857	-322.517	-322.985	-323.4
K ⁺	-1198.079	-1199.186	-1194.946	-1196.807	-1198.0
Rb ⁺	-5876.464	-5883.041	-5868.690	-5875.215	-5876.44

^a Values of α_{HF} taken from Schwarz, Ref. 6.

^b Hartree-Fock values taken from B. Y. Tong and L. J. Sham, Phys. Rev. **144**, 1 (1966); and Y. S. Kim and R. G. Gordon, J. Chem. Phys. **60**, 1842 (1974).

in the computer program will result, solving the Hartree problem, in an energy of $-5.723\,55$ Ry which is practically equal to the Hartree-Fock energy.

From the results on positive ions, it may be seen that the total number of electrons is not the only determining factor for the exchange to be used—it appears to depend also on the atomic num-

ber. The atomic number is otherwise related to the gradients in the charge density. The effect of neglecting the exponential tails in $\rho(2)$ will have to be reconsidered for molecules. This, together with the possible improvements introduced by different exchange values for spin-up and for spin-down electrons (spin-polarized calculations), is at present under investigation in this laboratory.

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