Self-consistent-field electron-gas local-spin-density model including correlation for atoms

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The model previously derived for the electron-gas exchange in atoms is extended to include Coulomb correlation effects. Exchange, Coulomb-correlation, and total energies for the atoms He through Ar, calculated within this spin-density model, are found to correspond closely to the exact values.

A proposal by Gopinathan, Whitehead, and Bogdanovič[1] based on the properties of the one- and two-particle density matrices and on the Kutzelnigg–del Re–Berthier analysis of the boundary conditions[2] for a system with a finite number of electrons, showed a possible way to derive the Z dependence of the α parameter in the $X\alpha$ theory.[3] They assumed the pair-correlation function for electrons with parallel spin $f_{\uparrow\uparrow}(1,2)$ to be linear in r_{12}. We have shown[4] that the use of more realistic forms for $f_{\uparrow\uparrow}(1,2)$, leads to local exchange potentials for atoms which give total energies very close to the Hartree-Fock limit.

The purpose of the present work is to extend the theory developed in Ref. 4 to include the full electron-gas pair-correlation effects in these local potentials. A large amount of work has been done in this direction since Wigner[5] proposed a local correlation potential for an electron gas of low density. The relative novelty of the present approach is that we work directly in real space.

The correlation potential for the interaction between antiparallel-spin electrons is given by (using the notation and the equations developed in Ref. 4)

$$U_{\uparrow}^{Cou}(1) = \int f_{\uparrow\downarrow}(1,2)\rho_{\downarrow}(2)\,d\tau_2 ,\tag{1}$$

with a similar expression for $U_{\downarrow}^{Cou}(1)$. This corresponds to the potential set up by a Coulomb charge $\rho_{\uparrow}^{Cou}$ at position 2, given by

$$\rho_{\uparrow}^{Cou}(2) = \rho_{\downarrow}(2)f_{\uparrow\downarrow}(1,2) ,\tag{2}$$

with the following properties:

$$\int \rho_{\uparrow}^{Cou}(2)\,d\tau_2 = 0 ,\tag{3}$$

since the Coulomb correlation induces only density modulations

$$\rho_{\uparrow}^{Cou}(1) = -\rho_{\downarrow}(1) ,\tag{4}$$

as in the case of a fixed negative charge-electron interaction,[6] and

$$\rho_{\uparrow}^{Cou}(2) \rightarrow 0\tag{5}$$

for large r_{12} where it may be assumed that the electrons move independently. Equation (3) and (5) are derived from the relations[4]

$$\pi_{\uparrow\downarrow}(1,2) = \rho_{\uparrow}(1)\rho_{\downarrow}(2) + \rho_{\uparrow}(1)\rho_{\downarrow}(2)f_{\uparrow\downarrow}(1,2)\tag{6}$$

and

$$\pi_{\uparrow\downarrow}^{ind}(1,2) = \rho_{\uparrow}(1)\rho_{\downarrow}(2) .\tag{7}$$

In accordance with the electron-gas theory ideas, we need a functional form obeying these conditions that is able to describe the $f_{\uparrow\downarrow}(1,2)$ obtained with the theoretical formalism of the Fermi gas. This can be done with the functional form

$$\rho_{\uparrow}^{Cou}(2) = -\rho_{\downarrow}(1)\exp\!\left(\frac{-cr_{12}}{r_a}\right)\cos\!\left(\frac{3\pi r_{12}}{2r_a}\right) .\tag{8}$$

The standard approximation $\rho_{\downarrow}(2) \approx \rho_{\downarrow}(1)$ near the center of the Coulombic hole has been made in Eq. (8). The Coulombic hole is assumed to be spherically symmetric and centered at 1. In order to satisfy Eq. (3), we define C and a finite r_a such that

$$4\pi \int_0^{r_a} \rho_{\uparrow}^{Cou}(r)r^2\,dr = 0 .\tag{9}$$

The last factor in Eq. (8) has been introduced to approximately reproduce the typical form of $f_{\uparrow\downarrow}(1,2)$ (compare Fig. 1 with, for example, Fig. 2 of Lobo, Singwi, and Tosi[7]). At the same time we make use of their numerical result, that their $f_{\uparrow\uparrow}(1,2)$ and $f_{\uparrow\downarrow}(1,2)$ tend to zero at approximately the same r_{12}. Next in making the finite-size hole approximation for $\rho_{\uparrow}^{ex}(r)$ and $\rho_{\uparrow}^{Cou}(r)$ we shall assume $r_a = r_0$, where r_0 is the Fermi hole radius,
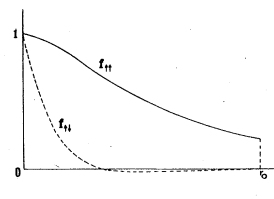

FIG. 1. Approximations to the parallel pair-correlation function (solid line) and the antiparallel pair correlation function (dotted line). r_0 is the radius of both the Fermi and the Coulomb spheres.

that for a modified Wigner form is given by[4]

$$r_0 = \left\{ 4\pi\rho_\uparrow(1) \left[\left(1 - \frac{1}{n_\uparrow}\right) 0.0698 + \frac{1}{3n_\uparrow} \right] \right\}^{-1/3}, \quad (10)$$

where $n_\uparrow$ is the number of spin-up electrons.
This should be regarded as a plausible useful approximation. Its value will be assessed from the good correlation between the numerical results presented here and the correct values of the total energies for the atomic systems we have studied so far. The value of r_a could also be chosen from physical considerations, such as minimizing the total energy by requiring that the absolute value of the correlation energy be a maximum.

Then the only unknown parameter in Eq. (8) is C which can be determined by requiring that Eq. (9) be satisfied; it is found that $C = 8.216$. Finally, from Eqs. (1), (8), and (10) one obtains for the Coulomb hole potential of spin-up electrons (in Rydbergs)

$$U_\uparrow^{C\,ou}(1) = -C_\uparrow^{C\,ou}\rho_\downarrow(1)\rho_\uparrow^{-2/3}(1)$$
$$= -0.1538(1 + 3.7723/n_\uparrow)^{-2/3}\rho_\downarrow(1)\rho_\uparrow^{-2/3}(1), \quad (11)$$

that is to be added to the exchange potential

$$U_\uparrow^{ex}(1) = -C_\uparrow^{ex}\rho_\uparrow^{1/3}(1) = -3.90(1 + 2.5148/n_\uparrow)$$
$$\times (1 + 3.7723/n_\uparrow)^{-2/3}\rho_\uparrow^{1/3}(1), \quad (12)$$

with similar expressions for spin-down electrons.

The variational procedure leads to the set of one-electron Schrödinger equations for spin-up electrons

$$[-\nabla^2 + \phi(\vec{r}) + V_\uparrow^{ex}(\vec{r}) + V_\uparrow^{C\,ou}(\vec{r})]\psi_{\uparrow i}(\vec{r}) = \epsilon_{\uparrow i}\psi_{\uparrow i}(\vec{r}), \quad (13)$$

where $\phi(\vec{r})$ is the electrostatic potential including nuclear and self-Coulomb terms

$$V_\uparrow^{ex}(\vec{r}) = \tfrac{2}{3}U_\uparrow^{ex}(\vec{r}), \quad (14)$$

$$V_\uparrow^{C\,ou}(\vec{r}) = -\tfrac{1}{2}C_\uparrow^{C\,ou}\rho_\downarrow(\vec{r})\rho_\uparrow^{-2/3}(\vec{r})$$
$$\times \left[\frac{1}{3} + \frac{C_\uparrow^{Cou}}{C_\uparrow^{Cou}}\left(\frac{\rho_\downarrow(\vec{r})}{\rho_\downarrow(\vec{r})}\right)^{2/3}\right], \quad (15)$$

and

$$\rho_\uparrow(\vec{r}) = \sum_i n_i \psi_{\uparrow i}^*(\vec{r})\psi_{\uparrow i}(\vec{r}), \quad (16)$$

with similar expressions for spin-down electrons.

To solve Eq. (13) we have modified the original Herman-Skillman program[8] to handle spin-polar-

TABLE I. Antiparallel-spin pair-correlation energy, total pair-correlation energy, and total energy for several atoms (Rydbergs).

Atom	Z	Correlation[a] energy	Exact total pair correlation energy[b]	This work	% difference[c]	Exact nonrelativistic total energy[d]	This work	% difference[c]
He	2	0.010(0.084)	2.119	2.066[e]	2.52	5.807	5.744	1.09
Li	3	0.051(0.091)	3.491	3.863	10.65	14.956	15.134	1.19
Be	4	0.095(0.188)	5.379	5.512	2.47	29.334	29.306	0.10
B	5	0.143(0.248)	7.655	7.627	0.37	49.306	49.185	0.25
C	6	0.198(0.310)	10.381	10.203	1.71	75.687	75.525	0.21
N	7	0.259(0.372)	13.655	13.394	1.91	109.174	108.999	0.16
O	8	0.371(0.468)	16.775	16.502	1.62	150.087	149.772	0.21
F	9	0.494(0.632)	20.435	20.209	1.11	199.451	199.029	0.21
Ne	10	0.627(0.762)	24.635	24.509	0.51	257.855	257.416	0.17
Na	11	0.742(0.772)	28.534	28.336	0.70	324.491	324.011	0.14
Mg	12	0.874(0.856)	32.557	32.297	0.80	400.085	399.514	0.14
Al	13	1.005(0.918)	36.781	36.465	0.86	484.671	484.049	0.13
Si	14	1.142(0.988)	41.283	40.940	0.83	578.696	578.050	0.11
P	15	1.284(1.042)	46.084	45.722	0.79	682.479	681.835	0.09
S	16	1.459(1.190)	50.845	50.492	0.69	796.199	795.446	0.09
Cl	17	1.639(1.334)	55.848	55.602	0.44	920.297	919.477	0.09
Ar	18	1.826(1.464)	61.243	61.050	0.31	1055.098	1054.245	0.08

[a] Values in parentheses correspond to the correlation energies defined and reported in Ref. 9 for a comparison. However, the present values are obtained from a spin-polarized calculation and therefore should be compared with the correlation energy defined from an unrestricted Hartree-Fock calculation.

[b] These values were obtained by adding the values in parentheses to the Hartree-Fock exchange energy which was obtained by subtracting from the total potential energy reported in Ref. 13 the Coulombic energy obtained from a spin-restricted calculation following the present approach.

[c] $(|E(\text{true}) - E(\text{this work})|/E(\text{true})) \times 100$.

[d] Hartree-Fock plus correlation as defined in Ref. 9.

[e] Obtained from a Hartree-type calculation including the correlation potential described in the text.

ized calculations. The results obtained for the ground states of He through Ar are reported in Table I. The total pair-correlation energies (exchange plus correlation) agree very well with the exact values (Hartree-Fock exchange plus correlation[9]), and are comparable to the values obtained with the more sophisticated approach of Gunnarson, Jonson, and Lundqvist.[10] The pair correlation energies for antiparallel spin electrons are in much better agreement with the correct values than are those given by most of the electron-gas theories[11] which tend to overestimate the energies by a factor of 2 or 3. [This is true of the model of Gunnarson and Lundqvist[12] (GL) which predicts the total pair correlation with an $X\alpha$ exchange corresponding to $\alpha = \frac{2}{3}$. This is not good for atoms,[1] so the GL correlation potential must be compensating for this.] The total energies are in agreement with the known values.

It is interesting to note that the equations derived for the correlation energy between antiparallel spin electrons take, for the spin restricted case, a form similar to the one empirically proposed by Clementi.[13]

ACKNOWLEDGMENTS

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