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Density-functional approach to the calculation of correlation energies of two-electron atoms and ions

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The correlation-energy density functional is studied here through an exact solution of a two-electron system bound by a harmonic-oscillator external potential. Since the correlation energy is a universal functional of density in density-functional theory, the same functional form is valid for two-electron atoms and ions as well. Using this fact we have proposed here density-functional schemes, within a local-density approximation as well as nonlocal considerations, for the study of correlation energies of two-electron atomic and ionic systems. The nonlocal scheme leads to significant improvement over the local ones, yielding results that show good agreement with the standard values.

Density-functional theory[1-5] provides a conceptually simple and physically appealing approach to the calculation of electronic structure and properties of many-electron systems. As proposed by Hohenberg and Kohn,[1] the energy of an N-electron system characterized by an external potential $v(\mathbf{r})$ is written in this theory as a unique functional of the single-particle electron density $\rho(\mathbf{r})$, viz.,

$$E_v[\rho]=\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}+F[\rho]\ , \tag{1}$$

where $F[\rho]$ is a universal functional

$$F[\rho]=T[\rho]+V_{ee}[\rho] \tag{2}$$

consisting of the kinetic-energy functional $T[\rho]$ and the electron-electron interaction energy functional $V_{ee}[\rho]$. The latter can be partitioned[2] into the classical electrostatic interaction energy and the exchange-correlation energy density functionals as

$$V_{ee}[\rho]=\frac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+U_{\mathrm{xc}}[\rho]\ . \tag{3}$$

Exact forms of the density functionals $T[\rho]$ and $U_{\mathrm{xc}}[\rho]$ are, however, unknown, and therefore approximate schemes[6] are needed for practical calculations using the density-functional formalism. The fact that these functionals are universal implies that the corresponding functional forms in terms of density are independent of the external potential characterizing the system and can thus provide a means for obtaining the forms of these energy functionals. Thus, if one can obtain the functional forms of $T[\rho]$ and $U_{\mathrm{xc}}[\rho]$ in terms of density for an N-electron system bound by any suitable external potential, one can evaluate these functionals for any atomic and molecular system with the help of the same expressions but using the actual densities of the concerned systems.

In this paper, we exploit this fact to calculate the correlation energies of simple atomic systems. The exact correlation energy density is first determined for a two-electron system where the electrons are bound by a central harmonic-oscillator potential,[7-10] for which an exact solution is possible.[11] By studying this exact correlation energy density $u_c(r)$ we have attempted to obtain its functional dependence on density, which is then employed to calculate the correlation energy of two-electron atoms and ions, by evaluating this expression using the densities of these systems.

The solvable model system that we consider here consists of two electrons attracted to a common center by harmonic forces, for which the Hamiltonian is given by (in atomic units)

$$H=-\frac{1}{2}(\nabla_1^2+\nabla_2^2)+\frac{1}{2}k(r_1^2+r_2^2)+1/r_{12}\ , \tag{4}$$

where k is the force constant. Using the center-of-mass coordinate $\mathbf{R}$ $[=(\mathbf{r}_1+\mathbf{r}_2)/2]$ and the relative coordinate $\mathbf{r}$ $[=(\mathbf{r}_1-\mathbf{r}_2)]$, and separating the variables, one obtains the pair of decoupled equations

$$(-\tfrac{1}{4}\nabla_R^2+kR^2)\chi(\mathbf{R})=E_R\chi(\mathbf{R})\ , \tag{5}$$

$$[-\nabla_r^2+\tfrac{1}{4}kr^2+1/r]\phi(\mathbf{r})=E_r\phi(\mathbf{r})\ . \tag{6}$$

The total energy is given by the sum $E=E_R+E_r$ and the ground-state wave function of the system is given by the product

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\chi(\mathbf{R})\phi(\mathbf{r})\ , \tag{7}$$

where $\chi(\mathbf{R})$ is the ground-state solution of the spherical harmonic oscillator given by

$$\chi(R)=(2\alpha/\pi)^{3/4}\exp(-\alpha R^2)\ , \tag{8}$$

with $\alpha=k^{1/2}$ and the energy $E_R=\frac{3}{2}\alpha$. The function $\phi(r)$ is, however, to be obtained from numerical solution of Eq. (6). The density can then be calculated from

$$\rho(r_1)=2\int\psi^*(\mathbf{r}_1,\mathbf{r}_2)\psi(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 \tag{9}$$

which gives, on using Eqs. (7) and (8), the result

$$\rho(r_1)=8(2\alpha/\pi)^{1/2}(1/r_1)\exp(-2\alpha r_1^2)\times\int_0^\infty dr\,r\phi^2(r)\exp(-\alpha r^2/2)\sinh(2\alpha r r_1)\ . \tag{10}$$

The correlation energy density $u_c(r_1)$ is obtained by subtracting the classical electrostatic interaction energy of the charge distribution and the exchange energy from the total exact interaction energy, viz.,

$$u_c(\mathbf{r}_1)=\int d\mathbf{r}_2\frac{\psi^*(\mathbf{r}_1,\mathbf{r}_2)\psi(\mathbf{r}_1,\mathbf{r}_2)}{r_{12}}-\tfrac{1}{4}\rho(r_1)\int d\mathbf{r}_2\rho(\mathbf{r}_2)\frac{1}{r_{12}}\ . \tag{11}$$

Substitution of the wave function of Eq. (7) in Eq. (11) leads to the final expression

$$\begin{aligned}u_c(r_1)=&4(2\alpha/\pi)^{1/2}(1/r_1)\exp(-2\alpha r_1^2)\\&\times\int_0^\infty dr\,\phi^2(r)\exp(-\alpha r^2/2)\sinh(2\alpha r r_1)\\&-\tfrac{1}{4}\rho(r_1)\int d\mathbf{r}_2\rho(\mathbf{r}_2)/r_{12}\ .\end{aligned} \tag{12}$$

Thus, both the density $\rho(r)$ and the correlation energy density $u_c(r)$ can be calculated for the system for any value of the force constant k using Eqs. (10) and (12), respectively. Although both these quantities are thus exactly known as a function of the radial distance r, the crux of the problem, however, lies in obtaining the correlation energy density functional, i.e., expressing u_c in terms of the density.

If the correlation energy $U_c[\rho]$ $(=\int d\mathbf{r}\,u_c(r))$ were a local functional of density alone, the plot of u_c versus ρ would have been independent of the parameter α. The plots of u_c versus ρ for two different values of α shown in Fig. 1 reveal clearly that this is not the case and hence $U_c[\rho]$ is actually a nonlocal functional of density. Although the knowledge of the exact analytic form of this functional would be of much importance, it is difficult to guess this form from only the numerical values of the exact correlation energy density as obtained here. Nevertheless, these results can still be useful for obtaining information about correlation in other systems since the functional is a universal one. Our objective here is to use these results for the calculation of the correlation energies of two-electron atomic and ionic systems, for which we now propose approximate schemes.

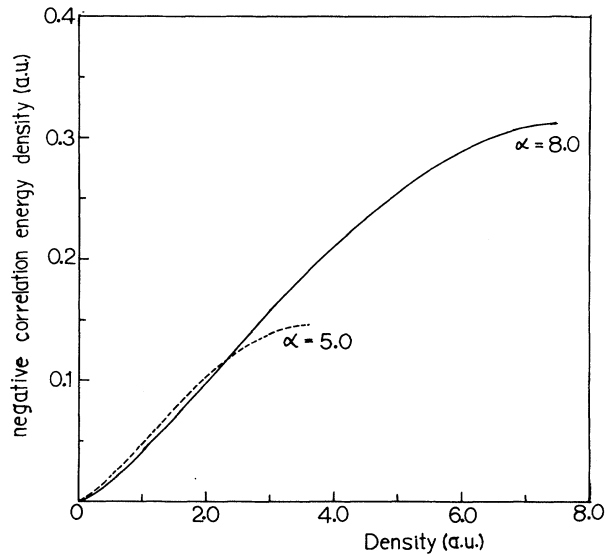

FIG. 1. Plot of the negative of the correlation-energy density $u_c(r)$ against the density $\rho(r)$ for the model two-electron system.

If one could find a value of the parameter α for which the resulting density distribution for the present model is identical to that of an atom of interest, the correlation energy of the two systems would have been the same and could thus easily be calculated by integrating the function $u_c(r)$ obtained for the particular value of α. However, the density distribution of the atomic system cannot be identical to that of the model system since two different potentials can never correspond to the same density as has been proved by Hohenberg and Kohn.[1] It may, however, be possible that for some value of α the resulting density for the model system is close to that of the atom concerned. In this regard, we propose to select a suitable value of α which yields, for the model system, a density whose value at the origin $(r=0)$ is the same as that of the actual density of the atom or ion at the nucleus. The correlation energy for the model system corresponding to this value of α would thus yield an approximate estimate of the correlation energy of the atom. Although the two densities are same at the origin and also have a crossing at some intermediate value of r, they differ significantly in most of the other regions. An improvement of this scheme (scheme A) is possible if one uses the actual density and employs a local-density approximation (LDA) after setting the above-mentioned value of α, i.e., one uses the values of u_c versus ρ obtained for the model system with this α for the calculation of $u_c(r)$ from $\rho(r)$ of the actual system (atom or ion) of interest. The integrated value of $u_c(r)$ generated in this manner (scheme B) yields an estimate of the correlation energy U_c. While scheme B is based on the LDA, although different values of the parameter α are used for a different atom or ion, we propose a third scheme (scheme C) for further improvement by incorporating partly the effects of nonlocality through the kinetic-energy density $t(r;\rho)$, which itself is a nonlocal functional of density $\rho(r)$, depending essentially on density gradients.

Inspired by our recent observation[10] that an approximate proportionality of the two-particle interaction energy density to the square root of the kinetic-energy density holds, in scheme C, we propose the relation

$$u_c(r)=-A_\alpha\rho(r)t(r;\rho)^{1/2}f_\alpha(r)\ , \tag{13}$$

with $A_\alpha=u_c(0)\rho(0)^{-1}t(0)^{-1/2}$. The function $f_\alpha(r)$, determined from Eq. (13) using exact $u_c(r)$ of Eq. (12) for the model system, is unity at $r=0$ and is found to be a slowly varying function of density except in the regions of very low density far away from the center. Motivated by this weak density dependence, we assume $f_\alpha(r)$ to be a local-density functional. The correlation energy density for the atomic and/or ionic system of interest is then calculated from Eq. (13) with the actual density and kinetic-energy density of the system but using the same value of A_α and the same local-density dependence of $f_\alpha(r)$ as

TABLE I. Calculated correlation energies for the two-electron atoms and ions.

Z	α	E_{corr}[a]	E_{corr}[b]	E_{corr}[c]	E_{corr}[d]
2	5.0092	−0.0875	−0.0628	−0.0339	−0.0421
3	11.892	−0.0915	−0.0678	−0.0386	−0.0435
4	21.706	−0.0935	−0.0702	−0.0412	−0.0443
5	34.440	−0.0947	−0.0717	−0.0429	−0.0448
6	50.100	−0.0955	−0.0727	−0.0441	−0.0451
7	68.684	−0.0961	−0.0734	−0.0449	−0.0453
8	90.212	−0.0965	−0.0740	−0.0456	−0.0455
9	114.64	−0.0969	−0.0744	−0.0460	
10	142.00	−0.0972	−0.0747	−0.0464	

[a] Correlation energies calculated using scheme A.

[b] Correlation energies calculated using scheme B.

[c] Correlation energies calculated using scheme C.

[d] Standard correlation energies reported in the literature (Ref. 13).

that of the model system corresponding to the chosen value of α.

For the present calculation of correlation energies of two-electron atoms and ions using schemes B and C, we have employed the Hartree-Fock density of Clementi and Roetti.[12] The calculated values of U_c for the He atom and several two-electron ions corresponding to schemes A, B, and C are reported in Table I, where the values of the parameter α are also indicated. The results show an overall good agreement with values reported in the literature which are also included in the table for comparison. The better prediction from scheme C reflects the importance of corrections due to nonlocality. These results also reflect the interesting trend of improved predictions with an increase in Z. This might be a consequence of the fact that a higher Z corresponds to a larger value of α for the model system for which the function $f_\alpha(r)$ becomes very close to unity at all values of r where the magnitude of density is significant.

While the new schemes proposed here for calculating the correlation energies for atomic or ionic systems from the knowledge of the correlation energy density of a model system are only illustrative, further attempts to obtain an exact analytic expression for this energy-density functional for the model system would be of much importance. Also the possibility of generalization of these results to the case of many-electron systems can be investigated.

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