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Density-functional theory of the correlation energy in atoms and ions: A simple analytic model and a challenge

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A simple and accurate analytic model is derived for the correlation energy of any atom or ion within three density-functional approximations based on the uniform electron gas: the local-spin-density approximation (LSD), the self-interaction corrected (SIC) version of LSD, and the antiparallel-spin LSD of Stoll *et al*. The last two approximations give good results for the correlation energies of neutral atoms, in contrast to LSD which overestimates these energies by a factor of 2. However, all three approximations show an incorrect $\ln Z$ leading behavior when the nuclear charge Z tends to infinity at fixed electron number N. It is hard to see how any *a priori* electron-gas approximation can reproduce the exact leading behavior, which is constant or linear in Z according to the value of N.

I. INTRODUCTION

One of the long-standing problems in the physics of many-electron atoms and ions has been the calculation of the correlation energy (Ref. 1) E_c, defined as the difference between the exact nonrelativistic total energy and the Hartree-Fock approximation to it. While many different sophisticated computational techniques have been applied to study the correlation energy in *individual* atoms or ions (ranging from configuration interaction[2] to various diagrammatic techniques[3]), theoretical formulations of the *trends* [i.e., atomic number Z and electron number N dependence of $E_c(Z,N)$] have rarely been attempted. If one considers only $Z \leq 36$, and allows one negative-ion state and $Z-1$ positive-ion states per atomic number, there are 702 distinct values for $E_c(Z,N)$. Thus a formidable computational effort would be required if standard quantum-chemical techniques were used. However, density-functional approximations[4,5] provide an alternative which is simple and amenable to analytic modeling over the whole Z,N plane.

The simplest approximation for the correlation energy of a many-electron system is the local spin density (LSD)[4,5]

$$E_c^{\text{LSD}} = \int d^3r\, n(\vec{r})\epsilon_c(n_\uparrow(\vec{r}), n_\downarrow(\vec{r})), \tag{1}$$

where $n(\vec{r}) = n_\uparrow(\vec{r}) + n_\downarrow(\vec{r})$ is the electron density and $\epsilon_c(n_\uparrow, n_\downarrow)$ is the correlation energy per particle of an electron gas with uniform spin densities $n_\uparrow$ and $n_\downarrow$. Although an early application to atoms[6] led to the disappointing result that E_c^{LSD} is about twice the exact correlation energy, more recent work has shown that self-consistent LSD gives a useful account of correlation effects on valence-shell interconfigurational energies and multiplet splittings,[7] as well as other important properties of atoms, molecules, and solids.[5]

It has recently been shown[8-10] that the factor-of-two error of Eq. (1) is largely due to a spurious orbital self-correlation. This can be removed by a simple scheme of self-interaction correction (SIC)[8-10]

$$E_c^{\text{SIC}} = E_c^{\text{LSD}}[n_\uparrow, n_\downarrow] - \sum_{\alpha\sigma} E_c^{\text{LSD}}[n_{\alpha\sigma}, 0], \tag{2}$$

where $n_{\alpha\sigma}(\vec{r}) = |\psi_{\alpha\sigma}(\vec{r})|^2$ is the density of occupied orbital $\alpha\sigma$. Self-consistent SIC calculations for atoms,[9,10] including corrections for self-exchange as well as self-correlation, show a dramatic improvement over LSD in the total energy, the separate exchange and correlation energies, the orbital energy eigenvalues (which now closely approximate physical removal energies), and the predicted stability and binding energy of negative ions. Some other properties, such as interconfigurational energies, are essentially the same in SIC as in LSD.[10-11]

Stoll and co-workers[12,13] have argued that LSD exaggerates the correlation between parallel-spin electrons in atoms and small molecules, where the long-range correlations present in the electron gas cannot occur. They proposed using LSD only for antiparallel-spin correlation

$$E_c^{\text{anti-}\|} = E_c^{\text{LSD}}[n_\uparrow, n_\downarrow] - E_c^{\text{LSD}}[n_\uparrow, 0] - E_c^{\text{LSD}}[n_\downarrow, 0]\,, \tag{3}$$

a scheme which also effectively subtracts out the self-correlation.[13]

Both the SIC and antiparallel-spin approximations give accurate (within 20%) correlation energies for neutral atoms with $Z \leq 18$.[9,10,12] In order to predict the results for larger atoms and for ions, we have constructed a simple analytic model for the correlation energy as a function of nuclear charge Z and electron number N. The model shows that all three electron-gas approximations for the correlation energy are qualitatively wrong when $Z \to \infty$ for fixed N, a result that was also observed independently for $N=2$ in the numerical calculations of Stoll *et al.*,[13] using the LSD and antiparallel-spin approximations. This fact is not a *practical* obstacle, since correlation is not qualitatively important in strongly positive ions; correlation is more important in neutral systems and negative ions[8-10,14,15] where it is well described by, e.g., SIC. However, it will appear that *no a priori* electron-gas approximation is likely to succeed for the correlation energies of strongly positive ions. This problem thus poses an intellectual challenge to density-functional theory, and a stringent test of new density-functional approximations.[16]

II. THE MODEL AND RESULTS

The basic ingredient of all three approximations is the electron-gas correlation energy $\epsilon_c(n_\uparrow, n_\downarrow)$, for which we use the recent and accurate results of Ceperley and Alder,[17] matched smoothly onto the exact high-density limit.[10] The densities of greatest importance in atoms are the high and metallic densities $0<r_s<5$ where $n=(4\pi r_s^3/3)^{-1}$ in atomic units ($\hbar = m = e^2 = 1$). In this density range, the Ceperley-Alder correlation energies can be fitted with an error of 1% by the simple expressions (in atomic units)

$$\epsilon_c(n/2, n/2) = 0.0311\ln r_s - 0.048 + 0.0034 r_s \ln r_s - 0.0116 r_s\,, \tag{4}$$

$$\epsilon_c(n, 0) = 0.015\,55\ln r_s - 0.0269 + 0.0013 r_s \ln r_s - 0.0048 r_s\,. \tag{5}$$

The first two constants in each of Eqs. (4) and (5) reproduce the exact high-density limit, while the next two were found by fitting at $r_s=1$ and 5. More elaborate parametrizations, valid at all r_s, have been given elsewhere.[10,18]

At typical atomic densities, the first two terms in each of Eqs. (4) and (5) are dominant. These terms depend so weakly on the density that we may use a rather crude model for the density profile,

$$n(r) = N\frac{Z_e^3}{\pi}\,e^{-2Z_e r}\,, \tag{6}$$

where Z_e is an "effective nuclear charge." We will also take $n_\uparrow(\vec{r}) = n_\downarrow(\vec{r}) = n(\vec{r})/2$, which is only a mild approximation for all $N \geq 2$, and in the SIC calculation we will replace each orbital density $n_{\alpha\sigma}(\vec{r})$ by the average orbital density $n(\vec{r})/N$. Then the integrals of Eqs. (1)–(3) can be evaluated analytically, with the results for the correlation energy per electron (in atomic units)

$$\frac{E_c^{\text{LSD}}}{N} = 0.0311\ln s - 0.048 + 0.0043 s\ln s - 0.0123 s\,, \tag{7}$$

$$\frac{E_c^{\text{SIC}}}{N} = 0.015\,55\ln s - (0.0211 + 0.015\,55\ln N^{1/3}) + (0.0043 - 0.0016 N^{1/3}) s\ln s - (0.0123 - 0.0052 N^{1/3} + 0.0016 N^{1/3}\ln N^{1/3}) s\,, \tag{8}$$

$$\frac{E_c^{\text{anti-}\|}}{N} = 0.015\,55\ln s - 0.0247 + 0.0023 s\ln s - 0.0062 s\,, \tag{9}$$

where

$$s = e\left(\frac{3}{4}\frac{1}{NZ_e^3}\right)^{1/3} \tag{10}$$

evidently plays the role of an "effective r_s value for the atom" and e is the base of natural logarithms. Finally, for the effective nuclear charge Z_e we use

$$Z_e = (Z - \tfrac{5}{32}N)\,\frac{(N/2)^{2/3} + 1.105}{2.105(N/2)^{4/3}}\,. \tag{11}$$

Equation (11) was chosen to have the following properties: (1) When $N=2$, $Z_e = Z - \frac{5}{16}$ is the value of Z_e which minimizes the Hartree-Fock energy using the exponential orbitals, $(Z_e^3/\pi)^{1/2} e^{-Z_e r}$.[19] Thus our model of the density is realistic for

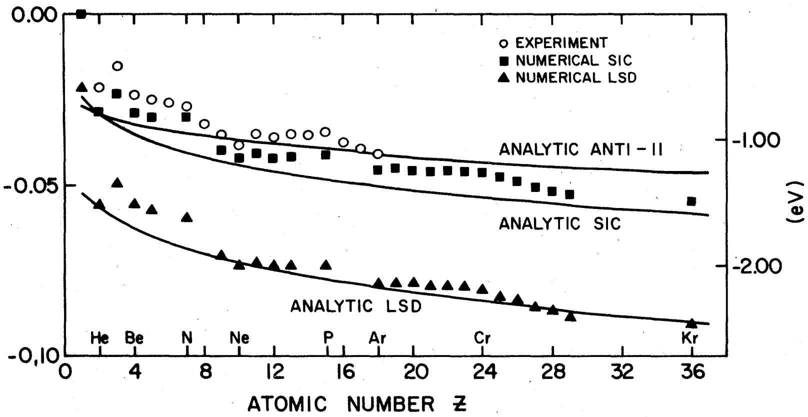

FIG. 1. Correlation energies per electron for neutral atoms of atomic number Z. Solid curves show the analytic results (7)–(9) for the LSD, SIC, and antiparallel spin approximations. Triangles and squares show the results of numerical calculations using accurate self-consistent orbitals and expressions for $\epsilon_c(n_\uparrow, n_\downarrow)$ valid at all densities, for the LSD and SIC approximations, respectively. Open circles show the experimental correlation energies (from Ref. 20). The Lamb correction (Ref. 20) has been neglected in the experimental correlation energies, which for $10 \leq Z \leq 18$ have an uncertainty of 10 or 20%.

$N = 2$. (2) In the opposite limit $N \to \infty$, the leading terms $(0.0311 \ln s - 0.048)$ in the LSD expression (7) are the same as those found in the Thomas-Fermi calculation of Appendix A. In this limit, the Thomas-Fermi density is a qualitatively correct description of the core.

Figure 1 compares the analytic expressions (7)–(9) with experimental correlation energies[20] for neutral atoms. The results of numerical calculations[10] in the LSD and SIC approximations using accurate self-consistent orbitals are also shown for comparison. The analytic LSD expression (7) is evidently very close to its numerical counterpart, the largest deviations occuring for the strongly spin-polarized atoms like Li, N, P, and Cr because spin polarization was neglected in the analytic calculation. The analytic antiparallel-spin expression (9) would probably also be close to its numerical counterpart, if the latter were known for Ceperley-Alder $\epsilon_c(n_\uparrow, n_\downarrow)$. However, the analytic SIC expression (8) is somewhat more negative than its numerical counterpart because the orbital densities were so crudely approximated in the analytic calculation. In comparison with experimental correlation energies[20] for $Z \leq 18$, both the numerical SIC and the analytic antiparallel-spin correlation energies are found to be highly accurate. Note that the SIC and antiparallel-spin expressions are identical for $N = 2$, but gradually start to differ as N increases. Note further that the antiparallel-spin expression (9) is always about half of the LSD expression (7).

Figures 2 and 3 show similar comparisons for

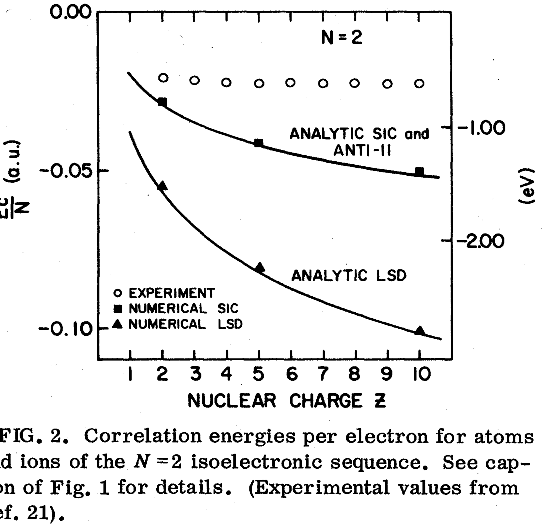

FIG. 2. Correlation energies per electron for atoms and ions of the $N = 2$ isoelectronic sequence. See caption of Fig. 1 for details. (Experimental values from Ref. 21).

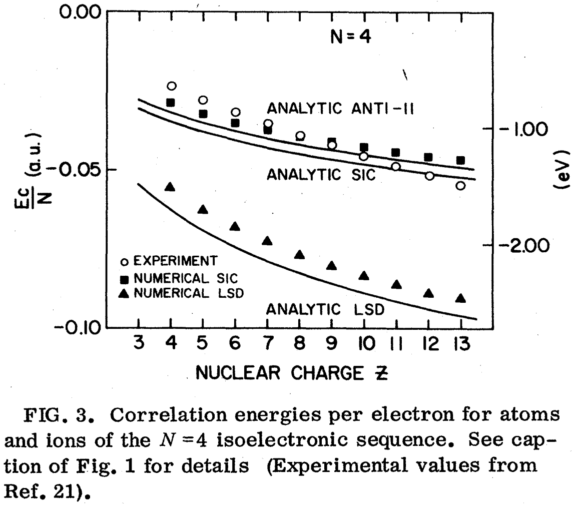

FIG. 3. Correlation energies per electron for atoms and ions of the $N = 4$ isoelectronic sequence. See caption of Fig. 1 for details (Experimental values from Ref. 21).

the atoms and ions of the $N=2$ and $N=4$ isoelectronic sequences. Once again the analytic expressions agree very well with their numerical counterparts, especially for $N=2$, where the approximations used to derive the analytic expressions are least severe. However, the calculated behavior of E_c as Z increases for fixed N is not in agreement with experiment[21]: All the electron-gas approximations fail for strongly positive ions.

III. DISCUSSION

Equations (7)–(11) show that, for all three electron-gas approximations, the correlation energy behaves as $\ln Z$ when $Z\rightarrow\infty$ for fixed N. This behavior is also evident in Figs. 2 and 3. However, the experimental atomic correlation energy behaves either as a constant or as Z in this limit, depending on N; the former behavior is found for $N=2$ and the latter for $N=4$. Linderberg and Shull[22] have explained this as follows: The electron-electron repulsion can be regarded as a perturbation of order Z^{-1} on a "zero-order atom". Both the exact and the Hartree-Fock total energies have a Z^{-1} expansion, and the difference of these two energies (the correlation energy) can begin at order Z^1 or Z^0, depending on whether or not other orbital configurations of the same symmetry become degenerate with the ground-state configuration in the limit $Z^{-1}\rightarrow 0$. This happens for $N=4$, where $(2s)^2\,{}^1S$ and $(2p)^2\,{}^1S$ become degenerate as $Z^{-1}\rightarrow 0$, but not for $N=2$.

The uniform electron gas cannot discriminate between these two cases, and settles on $\ln Z$ as a compromise between Z^0 and Z^1. In the context of a different problem (correlation in open shell neutrals like Ni), Kleinman[23] has also observed that electron-gas approximations cannot be simultaneously correct for nondegenerate and degenerate configurations. Of course one might try to account for degeneracy effects by postulating different density functionals for different N, as Stoll *et al.*[13] have done for $N=2$. However, it is a difficult intellectual challenge to density-functional theory to find an *a priori*, *universal* density-functional approximation which correctly describes the correlation energy of strongly positive ions. Unlike LSD and related schemes, such an approximation would have to be accurate even when the density varies quite rapidly on the scale of the local Thomas-Fermi screening length, i.e., when $|\nabla n|/n \gg 2\pi^{-1/2}(3\pi^2 n)^{1/6}$ atomic units.

Note added in proof. Our simple analytic models for the correlation energy, tested here for $Z\leqslant 36$, are comparably accurate at much larger Z. For Au ($Z=N=79$) the analytic models predict $E_c^{\mathrm{LSD}}/N=-2.80$ eV and $E_c^{\mathrm{SIC}}/N=-1.92$ eV, while the corresponding self-consistent numerical values are -2.83 and -1.76 eV (L. Cole, private communication).

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APPENDIX A: THOMAS-FERMI VARIATIONAL CALCULATION FOR AN ATOM OR ION

The Thomas-Fermi density profile[19] for a neutral atom of atomic number $Z=N$ is (in atomic units)

$$n(r)=\frac{N}{b^3}\frac{1}{4\pi}\left(\frac{\phi(r/b)}{(r/b)}\right)^{3/2}, \tag{A1}$$

where $b=\frac{1}{4}(9\pi^2/2Z)^{1/3}$ and[24]

$$\phi^{-1}(x)\approx 1+0.027\,47x^{1/2}+1.243x-0.1486x^{3/2} +0.2302x^2+0.007\,298x^{5/2}+x^3/144\,. \tag{A2}$$

To describe an arbitrary ion, let us use (A1) as a trial density profile and adjust b to minimize the Thomas-Fermi total energy E^{TF}. We then find (in atomic units) that the effective radius of the ion is

$$b=0.7588\,\frac{N^{2/3}}{(Z-\frac{1}{7}N)}, \tag{A3}$$

and its energy is

$$E^{\mathrm{TF}}=-1.0463N^{1/3}(Z-\tfrac{1}{7}N)^2\,. \tag{A4}$$

Equation (A4) reduces for neutral atoms to the exact Thomas-Fermi.[19] For ions the error in (A4) is of order $[(Z-N)/Z]^2$, but even in the limit $N/Z\rightarrow 0$ the variational estimate (A4) lies only 9% above the exact Thomas-Fermi value.[25] An approximate energy expression similar to (A4) (but slightly more complicated) was derived by Parr, Gadre, and Bartolotti.[26]

The Thomas-Fermi energy itself becomes relatively exact in the limit $N=Z\rightarrow\infty$,[27] and we suppose the same may be true of the Thomas-Fermi core density. Inserting (A1)–(A3) into Eq. (1), and retaining only the two leading terms of Eq. (4), we find

$$E_c^{\mathrm{LSD}}=0.0311\ln\left(\frac{N^{1/3}}{Z-\frac{1}{7}N}\right)-0.0106\,. \tag{A5}$$

Equation (A5) is almost the same as the leading terms of Eq. (7) when we take the limit $N\rightarrow\infty$ in Eq. (11). It is *exactly* the same when we take $N=Z\rightarrow\infty$.

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