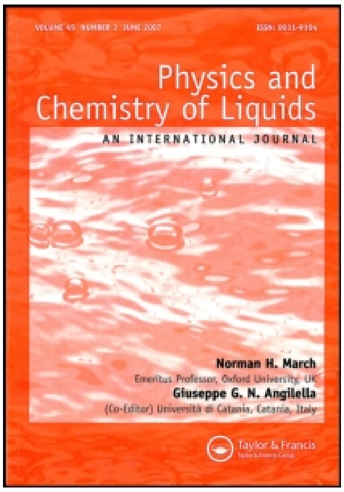

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The importance of fully quantitative non-local treatments of exchange energy in Density Functional Theory of atoms, molecules and clusters, characterised by strongly inhomogeneous electron liquids

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LETTER

The importance of fully quantitative non-local treatments of exchange energy in Density Functional Theory of atoms, molecules and clusters, characterised by strongly inhomogeneous electron liquids

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After a brief summary of some recent work on non-local approximations to the exchange energy and potential in density functional theory, a table is presented for atoms from Be to Ar, with an even number of electrons, having large electron density gradients, which highlights the importance of exchange. Until non-local exchange energy is truly quantitative, refinements of correlation energy may be submerged through 'noisy' exchange.

Keywords: inhomogeneous electron liquid; exchange and correlation energies

Recently, a good deal of attention has been given to non-local treatments of the exchange energy E_x for the ground states of atoms, molecules and clusters. We might note especially the work of Della Sala and Görling [1] and Howard and March [2–4]. Although the studies of Baerends and coworkers [5,6] seem different in philosophy from that in [1], their (somewhat drastic) denominator approximation leads back to the same approximate integral equation as that in [1]. Especially in [4], the Howard–March [2] formally exact integral equation is related to the valuable approximation of Krieger, *et al.* [7,8].

However, what we want to emphasise by atomic examples from Be to Ar, is the great importance for density functional theory (DFT) of correct non-local treatments of exchange, such as discussed especially in the early pioneering work of Talman and Shadwick [9,10] by the so-called optimised effective potential method.

To make the above statement fully quantitative, we present in Table 1 a summary of existing results [11,12] on the ground-states of atoms Be to Ar inclusive, atoms with an even number of electrons. What is immediately clear from the final two columns of this table is that (i) both the HF exchange energy and the (semiempirical) correlation energy E_{corr} are closely connected with the Dirac–Slater exchange energy

$$E_x^{\text{DS}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{(1/3)} \int n(r)^{(4/3)} \mathrm{d}\vec{r}, \tag{1}$$

and (ii) the correlation energy is only 3 or 4% of the exchange energy in these relatively light atoms with large electron density gradients. To attempt to gain insight into the data presented in the first two columns of Table 1, we have constructed Figures 1 and 2.

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Table 1. Atomic exchange and correlation energies scaled with the LDA result (Equation (1)). All values in au.

Element	Hartree–Fock exchange energy [11]	Dirac–Slater LDA [11]	Exact correlation energies [12]	Ratio $E_x^{\mathrm{HF}}/E_x^{\mathrm{DS}}$	Ratio $E_{\mathrm{corr}}/E_x^{\mathrm{DS}}$
Be	−2.667	−2.312	−0.094	1.15	0.040
C	−5.045	−4.459	−0.157	1.13	0.035
O	−8.174	−7.342	−0.258	1.11	0.035
Ne	−12.11	−11.03	−0.390	1.09	0.035
Mg	−15.99	−14.61	−0.444	1.09	0.030
Si	−20.28	−18.59	−0.520	1.09	0.028
S	−25.00	−23.00	−0.634	1.09	0.028
Ar	−30.19	−27.86	−0.787	1.08	0.028

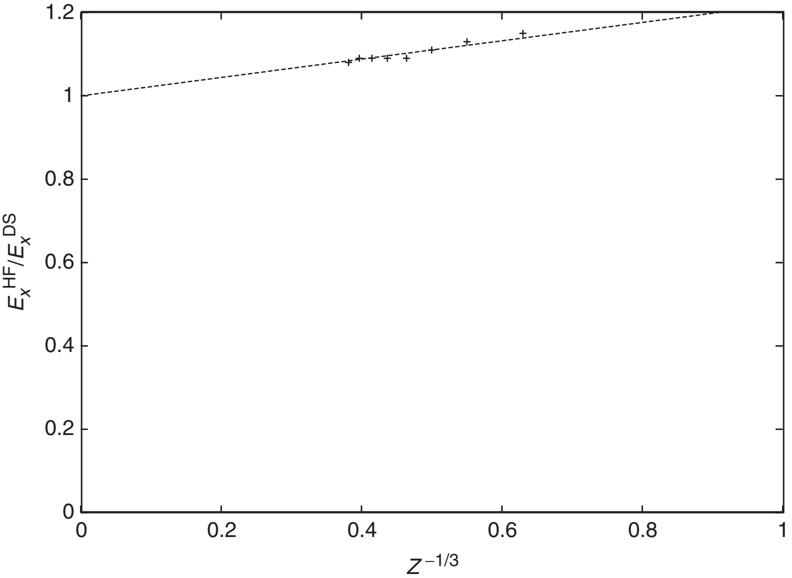

Figure 1. Plot of the non-relativistic ratio $E_x^{\mathrm{HF}}/E_x^{\mathrm{LDA}}$ given in Table 1 *vs.* $Z^{-1/3}$. The straight line drawn through the point '1' at $Z^{-1/3}=0$ is to suggest that the Dirac–Slater exchange energy becomes exact in this limit.

There we have utilised the knowledge that, for heavy non-relativistic atomic energies, with atomic number Z, the energy $E(Z)$ has an expansion parameter $Z^{-1/3}$ [13]. Thus, Figure 1 plots the dimensionless ratio $E_x^{\mathrm{HF}}/E_x^{\mathrm{DS}}$ recorded in Table 1 against $Z^{-1/3}$. The points shown, of course, are the reliable data, but as a guide to the eye a straight line is drawn assuming that E_x^{DS}, coming from the Thomas–Fermi–Dirac statistical theory [13], a forerunner of DFT [14], will be the exact exchange energy as Z tends to infinity. Less, of course, is known about the correlation energy ratio $E_{\mathrm{corr}}/E_x^{\mathrm{DS}}$ in the final column of the table. Therefore, in Figure 2(a), we have multiplied the above ratio by $Z^{1/3}$ and then have plotted *versus* $Z^{-1/3}$ again. It seems possible, but not, of course, decisive, that the ratio plotted in Figure 2(a) will have a non-zero limit as Z tends to infinity. In contrast, Figure 2(b) is directly comparable with Figure 1 in that it simply plots the last column of

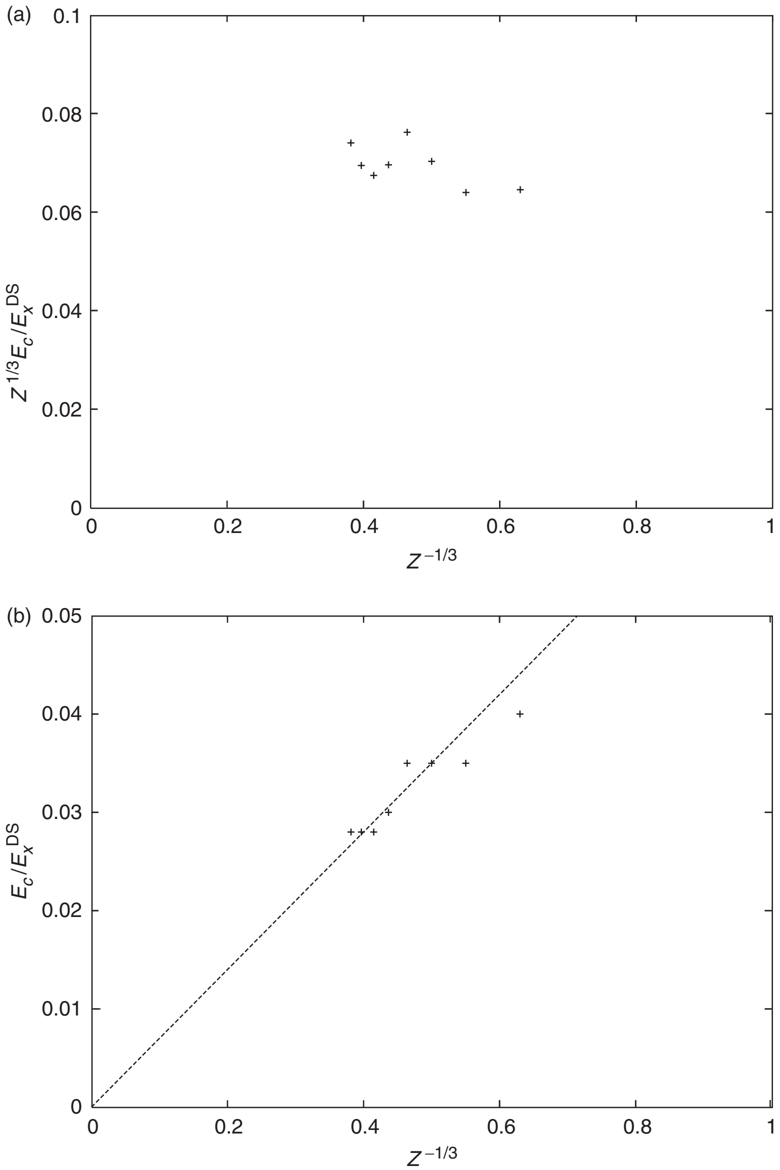

Figure 2. (a): Plot of the non-relativistic ratio $Z^{(1/3)}$ E_c/E_x^{LDA} given in the final column of Table 1 *versus* $Z^{-1/3}$. In this form, though the 'scatter' is large, it seems possible that the ratio plotted tends to a non-zero limit as $Z^{-1/3}$ tends to zero. (b): Plot of the non-relativistic ratio E_c/E_x^{LDA} given in the final column of Table 1 *versus* $Z^{-1/3}$. This form of plot is directly comparable with that for the exchange shown in Figure 1.

the Table *versus* $Z^{-1/3}$. We expect with such a plot, that the ratio will eventually go to zero as Z tends to infinity, of course, non-relativistic theory based on the many-electron Schrödinger equation.

It is obvious then that the relatively recent movement recorded in [1–6] towards fundamental non-local treatments of exchange reflect the need in DFT for such careful non-local treatments. Of course, if the optimised effective potential [9] can be economically incorporated in DFT programmes, that is, approaching the 'exact exchange' of HF theory. Until that is achieved, too much first-principles attention to the correlation energy in atoms, molecules and clusters may seem somewhat premature.

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