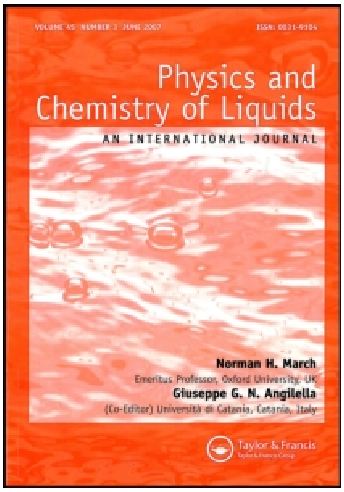

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Relation between single-particle kinetic energy and exchange energy in DFT for the inhomogeneous electron liquid in the Be atom

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In a recent study, the authors have used the semi empirical fine-tuned Hartree–Fock ground-state electron density $n(r)$ of Cordero *et al.* [Phys. Rev. A **75**, 052502 (2007)] for the Be atom to calculate the phase $\theta(r)$ from a non-linear pendulum-like equation. Since the density amplitude $n(r)^{1/2}$ plus $\theta(r)$ determine, in turn, the idempotent Dirac density matrix $\gamma(r, r')$, we use $n(r)$ and $\theta(r)$ first of all to calculate the exchange energy density $e_X(r)$ of the density functional theory (DFT). This enables us to obtain the Slater (Sl) approximation $V_X^{Sl}(r)$ to the exchange-only potential. A comparison can then be made, by integrating the earlier predicted exchange-correlation force $-\partial V_{XC}(r)/\partial r$, of $V_{XC}(r)$ with $V_X^{Sl}(r)$. Relationship to the Becke semiempirical density gradient approximation for exchange is also established. Some brief discussion of the Perdew–Burke–Ernzerhof density functional is added.

Keywords: kinetic energy density; Slater's potential; exchange-correlation potential; beryllium atom; exact Kohn–Sham potential

1. Background and outline

As was known already to Møller and Plesset [1] in their pioneering work on perturbation theory with the non-relativistic Hartree–Fock (HF) method as the unperturbed solution, the HF ground-state electron density of atoms, molecules and clusters is of high accuracy. Indeed, as pointed out already in [1], this density is correct to second-order in the difference between the Fock operator and the exact non-relativistic Hamiltonian.

Recently, Cordero *et al.* [2] have proposed a method to bypass such perturbation theory [1] by invoking semiempirical tuning of the HF electron density. Their experimental input was the measured ionisation potential. Here, we first set out largely analytic theory which allows the Cordero *et al.* fine-tuned density, denoted simply by $n(\mathbf{r})$ below, for the case of the non-relativistic Be atomic ions for arbitrary atomic number to be utilised within density functional theory (DFT) [3] to obtain

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rather directly the single-particle kinetic energy density $t_s(\mathbf{r})$. Then, a generalisation beyond the two-level occupancy of the Be series is presented, again based on the semiempirical fine-tuned HF ground-state electron density.

Starting with the Be-like series of atomic ions, we draw on the early study of Dawson and March [4]. For a given one-body potential $V(\mathbf{r})$, chosen below to be the sum of a symmetrised Hartree contribution plus the exchange-correlation potential $V_{XC}(\mathbf{r})$ of DFT [3], the Dirac [5] single-particle idempotent density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ can be expressed [4] as

$$\gamma_s(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})^{1/2} n(\mathbf{r}')^{1/2} \cos[\theta(\mathbf{r}) - \theta(\mathbf{r}')]. \tag{1}$$

In Equation (1), $n(\mathbf{r})^{1/2}$ is the so-called density amplitude, determined at the quantum Monte Carlo level of accuracy by Cordero *et al.* [2], while $\theta(\mathbf{r})$ is a phase factor. From [4], this is determined, for the given ground-state density $n(\mathbf{r})$, by solving the non-linear pendulum-like equation

$$\nabla^2\theta(\mathbf{r}) + \frac{\nabla n(\mathbf{r})}{n(\mathbf{r})} \nabla\theta(\mathbf{r}) + \lambda \sin 2\theta(\mathbf{r}) = 0 \tag{2}$$

for the eigenvalue λ, and for the phase factor $\theta(\mathbf{r})$ entering Equation (1). Then the important single-particle kinetic energy density $t_s(\mathbf{r})$ already referred to is given by

$$t_s(\mathbf{r}) = \frac{1}{8}\frac{[\nabla n(\mathbf{r})]^2}{n(\mathbf{r})} + \frac{1}{2} n(\mathbf{r})[\nabla\theta(\mathbf{r})]^2. \tag{3}$$

With this background, the outline of what follows is related to our previous study of the Be atom [6] in which $\theta(\mathbf{r})$ is obtained, essentially by solution of Equation (2), by inserting the Cordero *et al.* density for $n(\mathbf{r})$. Thus in Section 2, $\theta(\mathbf{r})$ and $n(\mathbf{r})$ are utilised for the Be atom to plot the single-particle kinetic energy density $t_s(\mathbf{r})$ given in Equation (3) and calculate the exchange energy density $e_X(\mathbf{r})$, which is defined, following Dirac [5] in terms of γ_s as

$$e_X(\mathbf{r}) = -\frac{1}{4}\int \frac{\gamma_s^2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'. \tag{4}$$

From Equations (1)–(4), it is then evident, as stressed for example by March and Santamaria [7] that $e_X(\mathbf{r})$ and $t_s(\mathbf{r})$ are closely related: for Be, in particular, both being determined by $n(\mathbf{r})$ and the phase factor $\theta(\mathbf{r})$.

Section 3 is then concerned first with the exchange potential of Slater [8] determined essentially by $e_X(\mathbf{r})$ in Equation (4) and the Cordero *et al.* density $n(\mathbf{r})$ and secondly with Becke's gradient-corrected exchange potential. Section 4 summarises results for the Perdew–Burke–Ernzerhof (PBE) density functional, shown in a recent contribution of Amovilli *et al.* [9] to have considerable merit over three other widely used functionals.

A brief summary is then given in Section 5, which also considers for further study the relaxing of the two-level occupancy constraint which allows the Be γ_s to be written in terms of $n(\mathbf{r})$ and $\theta(\mathbf{r})$.

2. Single-particle kinetic energy in relation to exchange energy density in the Be atom

Using the phase factor $\theta(\mathbf{r})$ calculated by Bogár *et al.* [6] and displayed in their Figure 2, plus the Cordero ground-state electron density $n(\mathbf{r})$, we depict in Figure 1a our present results for the single-particle kinetic energy per particle $\tau_s(\mathbf{r}) = t_s(\mathbf{r})/n(\mathbf{r})$ given in Equation (3) above. The value at the Be nucleus, namely $\tau_s(\mathbf{0})$, can be related

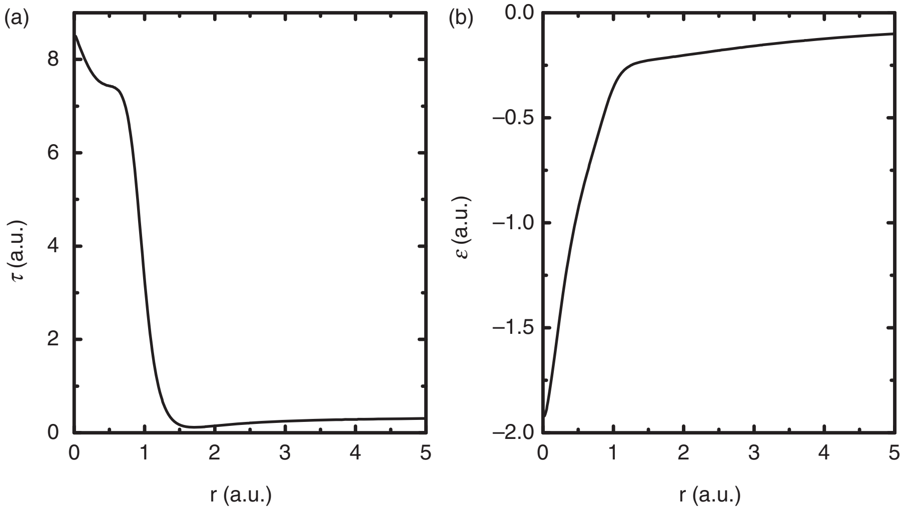

Figure 1. (a) The single-particle kinetic energy and (b) Slater's exchange energy per particle for the Be atom calculated from the exact KS solution corresponding to the Cordero *et al.* [2] density.

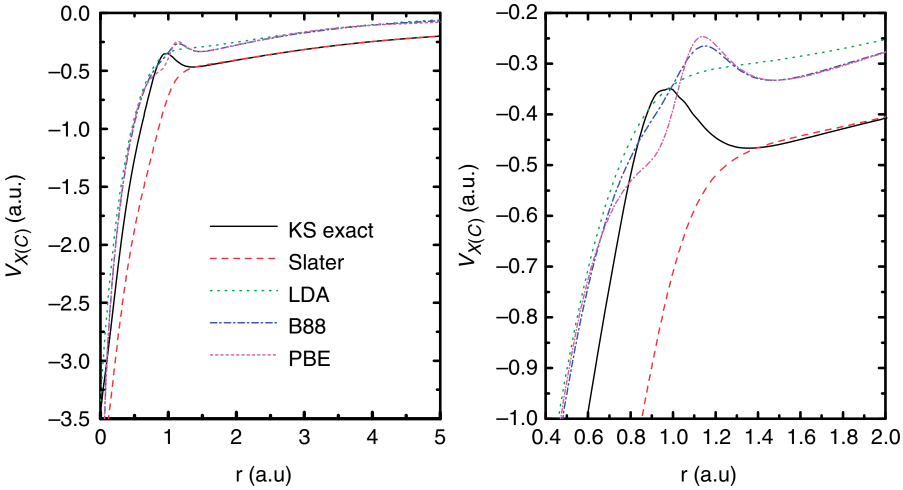

Figure 2. The exact KS exchange-correlation potential $V_{XC}(r)$ and several approximate exchange potentials (LDA, Slater, Becke88 and PBE) as derived from the Cordero *et al.* [2] density for the Be atom. The right panel is a closer view of the potentials around the shell region.

to the singularity at the nucleus. The Kohn-Sham (KS) orbitals are the bounded solutions of the

$$-\frac{1}{2}\nabla^2\varphi(\mathbf{r}) - \frac{Z}{r}\varphi(\mathbf{r}) + v_{eff}(\mathbf{r})\varphi(\mathbf{r}) = \varepsilon\varphi(\mathbf{r}) \tag{5}$$

KS eigenvalue equation. Provided that the singularity of the potential at the nucleus is properly represented by Z/r (thus Z is the Kato effective charge), the eigenfunctions satisfy the 'cusp' condition

$$[\nabla\varphi]_{\mathbf{0}}^{av} + Z\,\varphi(\mathbf{0}) = 0\ , \tag{6}$$

where $[\nabla\varphi]_{\mathbf{0}}^{av}$ is the spherical average

$$[\nabla\varphi]_{\mathbf{0}}^{av} = \lim_{R\to 0}\frac{1}{4\pi R^2}\int_{G(R)}\nabla\varphi\ \mathrm{d}\mathbf{f}, \tag{7}$$

(G is a ball of radius R around the nucleus). It follows from Equation (6), that

$$\left.\frac{\mathrm{d}}{\mathrm{d}r}\theta(r)\right|_{r=0} = 0, \quad \tau_s(\mathbf{0}) = \frac{1}{2}Z^2. \tag{8}$$

The asymptotic value,

$$\tau_s \to \frac{1}{4}\sqrt{2I}, \quad r\to\infty, \tag{9}$$

is determined by the ionisation potential. The Cordero density corresponds to $Z = 4.127$ and $I = 0.344$, which is reflected in our figure.

With the same input of $n(\mathbf{r})$ and $\theta(\mathbf{r})$, but now via Equations (1) and (4), the exchange energy per particle $\varepsilon_X(\mathbf{r}) = e_x(\mathbf{r})/n(\mathbf{r})$ is displayed for the Be atom in Figure 1b.

Having stressed the intimate connection between kinetic and exchange energy densities in this section, we turn to treat the more difficult problem of the exchange-only potential $V_X(\mathbf{r})$ of DFT in the following section.

3. Exchange-only potentials for Be: especially the Slater (Sl) approximation $V_X^{Sl}(\mathbf{r})$ and the Becke result

On physical grounds, Slater [8] proposed to write the total exchange energy E_X given by

$$E_X = \int e_X(\mathbf{r})\,\mathrm{d}\mathbf{r}\ , \tag{10}$$

by analogy with electrostatics in the form

$$E_X = \frac{1}{2}\int n(\mathbf{r})V_X^{Sl}(\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{11}$$

Then a 'differential equation' yields Slater's approximation

$$V_X^{Sl}(\mathbf{r}) = \frac{2e_X(\mathbf{r})}{n(\mathbf{r})}. \tag{12}$$

Since one of us (March) showed in early work, using Equation (4) as **r** tends to infinity, plus the idempotency of γ_s, that

$$e_X(r) \to -\frac{1}{2r}n(r), \quad r \to \infty, \tag{13}$$

it follows from Equation (12) that $V_X^{Sl}(r) \to -1/r$ far from all nuclei yields the correct self-interaction correction. The form of $V_X^{Sl}(\mathbf{r})$ is shown in Figure 2.

Slater's potential can be obtained via numerical integration of the terms

$$V_X^{Sl}(\mathbf{r}) = -\frac{1}{2}\sum_{i,j} f_i(\mathbf{r})f_j(\mathbf{r})\int \frac{n(\mathbf{r}')f_i(\mathbf{r}')f_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}', \quad i,j = 1,2, \tag{14}$$

where $f_1(\mathbf{r}) = \sin\theta(\mathbf{r})$ and $f_2(\mathbf{r}) = \cos\theta\,(\mathbf{r})$. Utilising the spherical symmetry the volume integrals can be calculated using Gauss' theorem:

$$\int \frac{\rho(r')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}' = 4\pi\left(\frac{1}{r}\int_0^r s^2\rho(s)\,\mathrm{d}s - \int_0^r s\rho(s)\,\mathrm{d}s + C\right), \quad C = \int_0^\infty s\rho(s)\,\mathrm{d}s. \tag{15}$$

In Figure 2, the exact V_{XC} KS potential is displayed and can be compared to the approximate exchange potentials discussed in this article. The Slater's potential approaches the exact one far from the nucleus, however, for $r \lessapprox 1.5$ a.u. it behaves differently and does not show the shell structure.

Becke's [10] gradient corrected potential can be evaluated solely from the density (and its derivatives, but $\theta(r)$ is not needed). The exchange energy density for spin compensated systems is

$$e_{88}[n, \nabla n] = e_{LDA}[n] - b_{88}[n, \nabla n], \tag{16}$$

where $e_{LDA}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{4/3}$ and

$$b_{88}[n, \nabla n] = 2\beta\left(\frac{n}{2}\right)^{4/3} f(x), \quad f(x) = \frac{x^2}{1 + 6\beta x \sinh^{-1}(x)} \tag{17}$$

and $x = 2^{1/3} n^{-4/3} |\nabla n|$, $\beta = 0.0042$. The exchange potential is the functional derivative:

$$V_X^{88}(\mathbf{r}) = \frac{\partial e}{\partial n} - \nabla\frac{\partial e}{\partial \nabla n} = V_X^{LDA} - \left(\frac{\partial b_{88}}{\partial n} - \nabla\frac{\partial b_{88}}{\partial \nabla n}\right) \tag{18}$$

with $V_X^{LDA} = -\left(\frac{3}{\pi}\right)^{1/3} n^{1/3}$. For the spherically symmetric atomic density the potential can be written explicitly as

$$V_X^{88} = V_X^{LDA} - \left[\frac{4}{3}2^{-1/3}n^{1/3}\left(f - x\frac{\partial f}{\partial x}\right) - \frac{\mathrm{d}n/\mathrm{d}r}{|\mathrm{d}n/\mathrm{d}r|}\left(\frac{\mathrm{d}}{\mathrm{d}r}\frac{\partial f}{\partial x} + \frac{2}{r}\frac{\partial f}{\partial x}\right)\right]. \tag{19}$$

Figure 2 shows that Becke's correction adds a shell structure to LDA, although this is displaced when compared to the exact potential.

4. PBE functional

The PBE [11] exchange energy density is usually written in terms of

$$s[n, \nabla n] = \frac{1}{2(3\pi^2)^{1/3}}\frac{|\nabla n|}{n^{4/3}}, \tag{20}$$

and is defined as

$$e_{PBE} = e_{LDA} \cdot F, \quad F = 1 + \kappa\left(1 - \frac{\kappa}{\kappa + \mu s^2}\right), \tag{21}$$

with $\kappa = 0.804$ and $\mu \simeq 0.21951$. The corresponding potential is

$$V_X^{PBE} = V_X^{LDA} \cdot \left(F - s\frac{\mathrm{d}F}{\mathrm{d}s}\right) - \nabla\left(\frac{3n}{4} \cdot v_{LDA} \cdot \frac{\mathrm{d}F}{\mathrm{d}s} \cdot \frac{\nabla n}{|\nabla n|}\frac{s}{|\nabla n|}\right), \tag{22}$$

which is again simplified as in Equation (19) for the spherical atomic density and plotted in Figure 2.

5. Summary and future directions

Using the density amplitude $n^{1/2}(\mathbf{r})$ from the fine-tuned HF method of Cordero *et al.* [2], and the phase $\theta(\mathbf{r})$ thereby determined by the pendulum-like Equation (2), we have calculated both the single-particle kinetic energy density of DFT from Equation (3), and the exchange energy density from Equation (4). For the latter quantity, the Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ was obtained using Equation (1). The intimate connection between $t_s(\mathbf{r})$ and $e_X(\mathbf{r})$ has been stressed here: both being determined via $n(\mathbf{r})$ and $\theta(\mathbf{r})$.

Contact between an approximate exchange potential due to Slater, determined solely by $e_X(\mathbf{r})$ and $n(\mathbf{r})$ and the Becke gradient approximation has been established. Also, reference is made to the important PBE functional, discussed also by Amovilli *et al.* [9].

As to future directions, we make proposals below to relax the two-level occupancy restriction for Be, which allows the Dirac matrix to be constructed from $n(\mathbf{r})$ and $\theta(\mathbf{r})$ as in Equation (1). Then, we refer to the force equation set out in Equation (1) of Bogár *et al.* [6]. This is an equation for $-\partial V/\partial r$, where $V(r)$ of DFT [3] determine $\gamma_s(\mathbf{r}, \mathbf{r}')$ through the equation of motion [12]

$$\nabla_{\mathbf{r}}^2 \gamma_s(\mathbf{r}, \mathbf{r}') - \nabla_{\mathbf{r}'}^2 \gamma_s(\mathbf{r}, \mathbf{r}') = 2[V(\mathbf{r}) - V(\mathbf{r}')]\gamma_s(\mathbf{r}, \mathbf{r}'). \tag{23}$$

To treat the case of general level occupancy, but still retaining spherical symmetry (e.g. Ne and Ar atoms) one must now combine Equation (23) with the force equation (1) of Bogár *et al.*

By dividing Equation (23) throughout by γ_s, and then differentiating with respect to r to remove $V(\mathbf{r}')$, one can utilise the force equation given in Bogár *et al.* [6]. This relates $-\partial V/\partial r$ solely to $\gamma_s(\mathbf{r}, \mathbf{r}')$ with its diagonal Cordero density $n(\mathbf{r})$. Of course, unlike the two-level Be example, one must then solve numerically the resulting partial differential equation arising from Equation (23) above, but now with input $n(\mathbf{r})$. And, naturally, one has to have finally an idempoten γ_s. Though numerically exacting, grid methods for solution of such a partial differential equation are now in use. The main new point to be confronted is that an idempotent $\gamma_s(\mathbf{r}, \mathbf{r}')$ must be the final product of such a multilevel occupancy generalisation.

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References

[1] C. Møller and M.S. Plesset, Phys. Rev. **46**, 618 (1934).
[2] N.A. Cordero, N.H. March, and J.A. Alonso, Phys. Rev. A **75**, 052502 (2007).
[3] R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[4] K.A. Dawson and N.H. March, J. Chem. Phys. **81**, 5850 (1984).
[5] P.A.M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930).
[6] F. Bogár, F. Bartha, and N.H. March, Phys. Rev. A **79**, 014501 (2009).
[7] N.H. March and R. Santamaria, Int. J. Quantum Chem. **39**, 585 (1991).
[8] J.C. Slater, Phys. Rev. **81**, 385 (1951).
[9] C. Amovilli, N.H. March, F. Bogár, and T. Gál, Phys. Lett. A **373**, 3158 (2009).
[10] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
[11] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[12] N.H. March and W.H. Young, Nucl. Phys. **12**, 237 (1959).