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Exchange energy density and some approximate exchange potentials obtained from Hartree–Fock theory of the ground state of the Be atom

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Abstract

Hartree–Fock (HF) theory of the ground state of the Be atom is used to calculate first the exchange energy density $\epsilon_x(r)$ from the Dirac density matrix. Beyond $r = 2a_0$, with $a_0 = \hbar^2/me^2$, $\epsilon_x(r)$ rapidly approaches the general asymptotic form $-\frac{1}{2}e^2\rho(r)/r$, with $\rho(r)$ the HF electronic density. The nuclear cusp condition

$$\left. \frac{1}{\epsilon_x(r)} \frac{\partial \epsilon_x}{\partial r} \right|_{r \rightarrow 0} = -\frac{2Z}{a_0}$$

with atomic number $Z = 4$, is also accurately satisfied by the present numerical data. Since a quantum Monte Carlo (QMC) exchange-correlation potential exists for the Be atom, we have compared this with (a) the Slater potential $V_{\text{SL}}(r) = 2\epsilon_x(r)/\rho(r)$ and (b) the Harbola–Sahni form. Both have the main features of the QMC exchange-correlation potential, though the magnitude of $V_{\text{SL}}(r)$ at $r = 0$ is too large by some 16%. We have also studied how well these two approximate HF exchange potentials fare when inserted into the Levy–Perdew relation between the total exchange energy and the ‘virial-like’ form involving the gradient of the exchange potential. © 2001 Elsevier Science B.V. All rights reserved.

Density functional theory (DFT) is presently widely used for electronic structure calculations on atoms, molecules and clusters [1,2]. However, in many current programmes, there are still uncontrolled approximations made in the exchange-correlation potential $V_{\text{xc}}(r)$, typically LDA or GGA. It is clearly important to refine existing treatments of $V_{\text{xc}}(r)$, especially bearing in mind

that current approximations can occasionally violate the variational basis of DFT by going below the exact ground-state energy.

That exchange is often important compared to correlation is clear from examining an approximate form of the ground-state energy $E(Z)$ of a neutral atom with atomic number Z . This has the expansion for large Z given by [3]

$$E(Z)/(e^2/a_0) = -0.77Z^{7/3} + \frac{1}{2}Z^2 - 0.26Z^{5/3} + \dots \quad (1)$$

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In Eq. (1), exchange enters at $O(Z^{5/3})$. Various workers have discussed the Z -dependence of the correlation energy $E_c(Z)$ to be added to Eq. (1). All current theories agree that $E_c(Z)$ depends more weakly on Z than the exchange energy, and though estimates range from $Z^{4/3}$ [4] through $Z \ln Z$ [5] to Z [6,7], it is clear that eventually, with increasing Z , exchange will dominate correlation.

Returning briefly to $V_{xc}(r)$, we note that in light atoms and molecules with rather few electrons, quantum Monte Carlo studies are now becoming available for the exchange-correlation potential. We may cite the recent work of Al-Sharif et al. [8], who compare quantum defect ideas with V_{xc}^{QMC} for Be and for Ne. We shall restrict discussion here to ‘exact exchange’, i.e., to Hartree–Fock (HF) theory, and we have chosen to focus on the Be atom. Here, the total exchange energy, estimated from the last displayed term in the expansion (1), is of the order $\sim 2.6(e^2/a_0)$. In the computations reported here, we shall use the approach to HF theory as set out by Holas et al. [9]. It is relevant to note here also the work of Görling and Ernzerhof [10] and of Krieger et al. [11].

We start from Eqs. (A1) and (A2) of [9] for the lowest occupied orbital ψ_1 (of eigenvalue ϵ_1) and the highest occupied orbital ψ_2 (of eigenvalue ϵ_2) in the Be atom:

$$-\frac{1}{2}\psi_1\nabla^2\psi_1 + [V_{en}(r) + V_{es}(r)]\psi_1^2 - \int d\mathbf{r}' k(r, r')\psi_1(r')\psi_1(r) = \epsilon_1\psi_1^2, \quad (2)$$

$$-\frac{1}{2}\psi_2\nabla^2\psi_2 + [V_{en}(r) + V_{es}(r)]\psi_2^2 - \int d\mathbf{r}' k(r, r')\psi_2(r')\psi_2(r) = \epsilon_2\psi_2^2, \quad (3)$$

where $V_{en}(r)$ and $V_{es}(r)$ represent the usual electron–nuclear potential and the classical electrostatic potential of the electronic cloud. The expression for $k(r, r')$ is [9]

$$k(r, r') = \frac{[\psi_1(r')\psi_1(r) + \psi_2(r')\psi_2(r)]}{|\mathbf{r} - \mathbf{r}'|}.$$

Adding (2) and (3), and introducing the definition of the HF kinetic energy density $t(r)$ as

$$t(r) = 2\left[-\frac{1}{2}\psi_1\nabla^2\psi_1 - \frac{1}{2}\psi_2\nabla^2\psi_2\right],$$

we find

$$\begin{aligned} \frac{t(r)}{2} + [V_{en}(r) + V_{es}(r)]\frac{\rho(r)}{2} \\ - \int d\mathbf{r}' k(r, r')[\psi_1(r')\psi_1(r) + \psi_2(r')\psi_2(r)] \\ = \frac{1}{2}\rho[\epsilon_1 + \lambda \sin^2\theta], \end{aligned} \quad (4)$$

where $\lambda \equiv \epsilon_2 - \epsilon_1$ and $\psi_1 \equiv (\rho/2)^{1/2} \cos\theta$, $\psi_2 \equiv (\rho/2)^{1/2} \sin\theta$. Substituting $k(r, r')$ and using the (HF) first-order density matrix

$$\gamma(r, r') = 2[\psi_1(r')\psi_1(r) + \psi_2(r')\psi_2(r)], \quad (5)$$

we then have

$$\begin{aligned} \frac{t(r)}{2} + [V_{en}(r) + V_{es}(r)]\frac{\rho(r)}{2} + \epsilon_x(r) \\ = \frac{\epsilon_1}{2}\rho(r) + \frac{\lambda}{2}\rho(r)\sin^2\theta. \end{aligned} \quad (6)$$

Integrating left- and right-hand sides of Eq. (6) over all space then yields, with $T_{HF} = \int t(r) d\mathbf{r}$,

$$\frac{T_{HF}}{2} + \frac{1}{2}U_{en} + U_{ee} + E_x = 2\epsilon_1 + \lambda = \epsilon_1 + \epsilon_2, \quad (7)$$

where U_{en} and U_{ee} represent the electron–nuclear and the electrostatic electron–electron potential energies of the atom, respectively.

Below, we shall focus most attention on the Dirac exchange energy density [12] $\epsilon_x(r)$ entering Eq. (6). We define this in terms of the Dirac density matrix $\gamma(r, r')$ in Eq. (5) as

$$\epsilon_x(r) = -\frac{e^2}{4} \int \frac{\gamma^2(r, r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (8)$$

As shown by one of us elsewhere [13], for large r the idempotency of γ can be used to obtain

$$\epsilon_x^{\text{asym}}(r) = -\frac{1}{2} \frac{e^2}{r} \rho(r) : r \rightarrow \infty. \quad (9)$$

Fig. 1 shows $\epsilon_x(r)$ for the ground state of the Be atom, together with the large r form (9), calculated of course with the HF electron density $\rho(r)$. We have used the optimized HF wave functions of Clementi and Roetti [14] for the occupied orbitals ψ_1 and ψ_2 of the neutral Be atom in all the

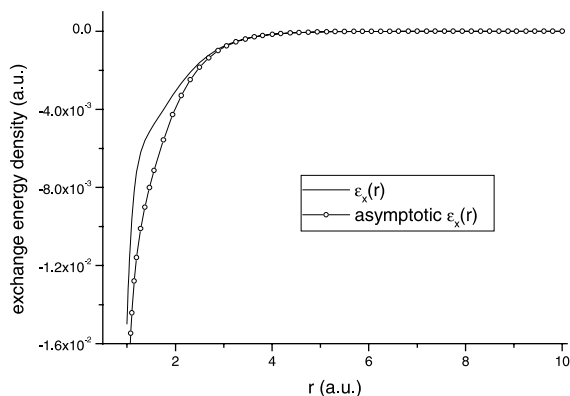


Fig. 1. Exchange energy density $\epsilon_x(r)$ of Eq. (8), determined from the HF wave functions for the Be atom (solid curve); and asymptotic exchange energy density of Eq. (9) for the same case (circles).

calculations that follow. It can be seen that for $r \gtrsim 2a_0$, the asymptotic result (9) reproduces $\epsilon_x(r)$ to graphical accuracy.

A further point we have checked is the nuclear cusp condition [15]. This reads

$$\frac{1}{\epsilon_x(r)} \frac{\partial \epsilon_x}{\partial r} \bigg|_{r \rightarrow 0} = -\frac{2Z}{a_0}. \quad (10)$$

To our numerical accuracy, $\partial \epsilon_x / \partial r$ tends to ~ 530 (e^2/a_0^2) as the origin is approached, while $\epsilon_x(r)$ tends to $\sim -66(e^2/a_0)$; thus the ratio is $\sim -8/a_0$, which is in accord with the exact result (10) for $Z = 4$.

In the rest of this Letter, we shall be concerned with how one might usefully approximate the exchange potential using either the $\epsilon_x(r)$ in Fig. 1 plus $\rho(r)$, or the input information $\gamma(r, r')$ from which $\epsilon_x(r)$ is calculated via Eq. (8). Slater [16], in early work (see also [17,18]), proposed that an approximate exchange potential, denoted below by $V_{SL}(r)$, be constructed directly from $\epsilon_x(r)$ and $\rho(r)$ as

$$V_{SL}(r) = \frac{2\epsilon_x(r)}{\rho(r)}. \quad (11)$$

This potential is shown in Fig. 2, where it is compared with the $V_{xc}^{QMC}(r)$ already referred to. The QMC potential is seen to be reproduced relatively well, including a quasi-linear region and a slight ‘bump’ around 1 a.u. But the Slater potential

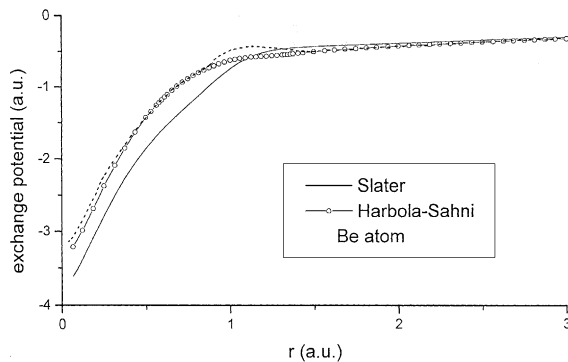


Fig. 2. Quantum Monte Carlo potential (dashed curve) taken from Fig. 6 of [8], compared with the Slater potential $V_{SL}(r) = 2\epsilon_x(r)/\rho(r)$ (solid line) and the Harbola-Sahni potential $V_{HS}(r)$ (circles). The approximate exchange potentials V_{SL} and V_{HS} are calculated using the HF density and the first-order density matrix.

(11) becomes somewhat more negative than $V_{xc}^{QMC}(r)$ near the nucleus, $V_{SL}(0)$ being ~ -3.75 a.u. while $V_{xc}^{QMC}(0) \sim -3.25$ a.u. Also shown in Fig. 2 is the Harbola-Sahni [19] approximation $V_{HS}(r)$ to the exchange potential for the Be atom, calculated numerically; the value of $V_{HS}(r)$ at the nucleus is very nearly the value given by $V_{xc}^{QMC}(0)$, although the quasi-linear region and the bump near 1 a.u. are less distinct than for $V_{SL}(r)$.

Some further progress results if we evaluate with the two approximate exchange potentials the Levy-Perdew virial-like expression [20] $\langle \mathbf{r} \cdot \mathbf{F}_x \rangle$, with $\mathbf{F}_x(r) = -\nabla V_x$:

$$\langle \mathbf{r} \cdot \mathbf{F}_x \rangle = - \int \rho(r) \mathbf{r} \cdot \nabla V_x(r) d\mathbf{r}. \quad (12)$$

Although we do not know the exact ‘exchange-only’ energy required in the Levy-Perdew relation, if we evaluate $E_x^{HF} = \int \epsilon_x(r) d\mathbf{r}$ we find $E_x^{HF} = -2.664$ a.u. for the Be atom. If we use the Slater potential $V_{SL}(r)$ in the right-hand side of Eq. (12), we get $\langle \mathbf{r} \cdot \mathbf{F}_x \rangle = -3.007$ a.u. Use of the Harbola-Sahni potential $V_{HS}(r)$ instead results in a value of $\langle \mathbf{r} \cdot \mathbf{F}_x \rangle = -2.837$ a.u. We can interpret the Harbola-Sahni discrepancy physically by quoting the phase equation of HF theory [18],

$$\theta''(r) + \left(\frac{\rho'}{\rho} + \frac{2}{r} \right) \theta' - F(r) + \lambda \sin(2\theta) = 0, \quad (13)$$

where the term written $F(r)$ is the integral (Fock operator) term

$$F(r) = \frac{1}{2} \int d^3r' \frac{\rho(r') \sin(2\theta(r) - 2\theta(r'))}{|\mathbf{r} - \mathbf{r}'|}. \quad (14)$$

Here, $\psi_1(r) = (\rho(r)/2)^{1/2} \cos \theta$ and $\psi_2(r) = (\rho(r)/2)^{1/2} \sin \theta$ are the HF wave functions for Be, yielding

$$\tan \theta(r) = \frac{\psi_2(r)}{\psi_1(r)}. \quad (15)$$

Then, as shown by Holas and March [18],

$$V_x(r) = V_{\text{SL}}(r) + \frac{1}{2}(\theta^2 - \theta_s^2) - \lambda \sin^2 \theta(r) + \lambda_s \sin^2 \theta_s(r). \quad (16)$$

Here θ_s is to be derived from the HF density $\rho(r)$, but using a local potential, and not the non-local HF potential. This phase θ_s was shown in [9,18] to satisfy Eq. (13), with corresponding eigenvalue λ_s , when $F(r)$ is set equal to zero. After some manipulation of the HF results, one can demonstrate that

$$\frac{\partial}{\partial r} [V_{\text{HS}}(r) - V_{\text{SL}}(r)] = -\theta'(r)F(r), \quad (17)$$

which shows that if $F(r)$ is put to zero, then (to within an additive constant) $V_{\text{HS}}(r) = V_{\text{SL}}(r)$, and also, from Eq. (16), $V_x(r) = V_{\text{SL}}(r) = V_{\text{HS}}(r)$, again to within a constant. We should note here the earlier study of Nagy and March [21] on the difference of the HF exchange energy and the approximate exchange energy obtained from the Slater potential only.

When $F(r)$ is included exactly in the HF theory of Be, then it follows that:

$$\frac{\partial}{\partial r} [V_x(r) - V_{\text{HS}}(r)] = \frac{\partial}{\partial r} (\theta^2 - \theta_s^2) + \left(\frac{\rho'}{\rho} + \frac{2}{r} \right) (\theta^2 - \theta_s^2). \quad (18)$$

The conclusion from Eq. (18) agrees with that of Levy and March [22], reached via the exact density-matrix theory of the exchange-correlation potential $V_{\text{xc}}(r)$ of Holas and March [23]; namely, that there are ‘kinetic corrections’ to be made to the Harbola–Sahni approximate exchange potential.

One can now integrate Eq. (18) for $(\theta^2 - \theta_s^2)$ by means of an integrating factor, to obtain first of all

$$\frac{\partial}{\partial r} [V_x(r) - V_{\text{HS}}(r)] = \frac{1}{r^2 \rho(r)} \frac{\partial}{\partial r} (r^2 \rho(r) \{ \theta^2 - \theta_s^2 \}). \quad (19)$$

Using the Levy–Perdew relation (12) once again, it is now straightforward to prove that the total exchange only energy is

$$E_x = - \int \rho(r) r \frac{\partial}{\partial r} V_{\text{HS}} d\mathbf{r} + \int \rho(r) (\theta^2 - \theta_s^2) d\mathbf{r} \quad (20)$$

and the ‘correction’ to the Harbola–Sahni virial-like term is readily shown to be just twice the kinetic energy difference between the HF value and the Slater–Kohn–Sham (slightly lower) kinetic energy. From the above numbers, one finds the kinetic energy difference to be rather small, namely $(2.837 - 2.664)/2 = 0.087$ a.u.

This has prompted us to go somewhat further and to integrate Eq. (19) to obtain

$$\begin{aligned} \theta^2(r) - \theta_s^2(r) &= (V_x(r) - V_{\text{HS}}(r)) - \frac{1}{r^2 \rho(r)} \\ &\times \int_{\infty}^r [V_x(r) - V_{\text{HS}}(r)] [2r\rho + r^2\rho'] dr. \end{aligned} \quad (21)$$

From Eq. (15), $\theta(r)$ is known, while $V_{\text{HS}}(r)$ has already been calculated. Thus, if we approximate $V_x(r)$ by $V_{\text{QMC}}(r)$, θ_s^2 can be calculated from Eq. (21), and hence a first approximation to $\theta_s(r)$ can be obtained.

In summary, in a light atom such as Be the expansion (1) suggests that while exchange should exceed correlation, the latter might still be appreciable. However, the present results show that $V_{\text{xc}}^{\text{QMC}}(r)$ is already usefully approximated by the Slater form (11). As to $\epsilon_x(r)$ itself, we have shown that two limiting features are important: (i) the asymptotic form (9) takes over at $r \simeq 2a_0$, and (ii) the nuclear cusp condition (10) is satisfied. We note from [15] that Eq. (10) remains exact when $\epsilon_x(r)$ is replaced by the (as yet unknown) exact exchange-correlation energy density $\epsilon_{\text{xc}}(r)$.

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