

Exchange energy density definitions from the optimized exchange-force, exemplified for non-relativistic Ne- and Ar-like atomic ions in the limit of large nuclear charge

N. H. March · A. Krishtal · C. Van Alsenoy ·
J. D. Talman

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Abstract An alternative exchange energy density (eed) in DFT is first proposed, depending on the optimized exchange force (OEF). It is evaluated using a numerical form of OEF for the non-relativistic Ne-like atomic ion series for atomic number $Z = 92$. Comparison is made with the Dirac form of eed available analytically. Related results are also presented for Ar-like atomic ions.

Keywords Inhomogeneous electron liquid · Exchange potential and exchange energy densities

In atoms, molecules and clusters, it is becoming increasingly clear that since exchange energy is usually considerably larger than the correlation contribution, it is essential to improve exchange-only DFT. In this spirit, the approximate work of Della Sala and Görling [1] is notable. It led to an integral equation for the exchange-only potential $V_x(r)$ [2] based on the assumption, drastic as it may appear, that the Hartree-Fock single determinant was set equal to that built from Slater-Kohn-Sham orbitals [2].

N. H. March
Abdus Salam International Centre for Theoretical Physics, Trieste, Belgium

N. H. March
Physics Department, University of Antwerp, Universiteitsplein 1, 2610 Antwerp, Belgium

N. H. March
Oxford University, Oxford, England

A. Krishtal (✉) · C. Van Alsenoy
Chemistry Department, University of Antwerp, Universiteitsplein 1, 2610 Antwerp, Belgium
e-mail: alisa.krishtal@ua.ac.be

J. D. Talman
Department of Applied Mathematics, University of Western Ontario, London, ON, Canada

Independently, Baerends and co-workers [3,4] reached the same result as in [1] by a denominator approximation which again appeared drastic. Approximations were formally removed from the integral equation theory in [1] by Howard and March [5,6] but at the expense of the introduction of a function $P(\mathbf{r})$ shown to satisfy the sum rule $\int P(\mathbf{r})d\mathbf{r} = 0$. Subsequent first principles work on $P(\mathbf{r})$ has recently been reported by Joubert [7].

The essential input into this integral equation theory of $V_x(r)$ is the single-particle idempotent Dirac (D) [8] matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$. In turn, this matrix determines the exchange energy density $\epsilon_x^D(r)$, as [8]

$$\epsilon_x^D(r) = -\frac{e^2}{4} \int \frac{\gamma_s^2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (1)$$

This definition is difficult to work with analytically, but below, by way of an example, we shall consider non-relativistic Ne-like atomic ions in the limit of large nuclear charge Ze .

Following earlier analytical work by Howard et al. [9] on this exchange energy density $\epsilon_x^D(r)$ of non-relativistic Ne-like atomic ions in the limit of large nuclear charge Ze , Howard et al. [10] have presented a numerical optimized exchange potential $V_x(r)$ for $Z = 92$ in this system. Additionally, these authors have also studied the Ar-like atomic ions in the large Z limit, to which we shall also return below.

Let us next employ the Levy-Perdew (LP) virial-like relation [11] between the total exchange energy E_x and the optimized exchange force $-\partial V_x/\partial\mathbf{r}$, namely

$$E_x = - \int n(r) \mathbf{r} \frac{\partial V_x(r)}{\partial \mathbf{r}} d\mathbf{r} \quad (2)$$

but now in the limit of spherical symmetry, to define a ‘virial-like’ exchange energy density, denoted below by $\epsilon_x^{\text{virial}}(r)$, as

$$\epsilon_x^{\text{virial}}(r) = -n(r) \mathbf{r} \frac{\partial V_x(r)}{\partial \mathbf{r}} \equiv n(r) \mathbf{r} F_x(r) \quad (3)$$

Here the optimized exchange force $F_x(r) = -\partial V_x(r)/\partial\mathbf{r}$.

However, for reasons that will emerge when treating the example of Ne-like atomic ions at large Z , we find it important to define what we term an alternative $\epsilon_x^{\text{alt}}(r)$ to the Dirac form $\epsilon_x^D(r)$ in Eq. 1. This is done almost immediately below. We then utilise the Coulombic ground-state density for the 10-electron atomic ions to evaluate $\epsilon_x^{\text{alt}}(r)$, plotted for $Z = 92$, for the Ne-like series of atomic ions, from the optimized exchange potential given in [10], following the work of Shadwick and Talman [12] and Talman [13]. A summary, plus some suggestions for future work which should prove fruitful will conclude this Brief Report.

Instead of the ‘natural’ definition of $\epsilon_x^{\text{virial}}(r)$ in Eq. 2 from the LP integral relation (Eq. 2) a focal point of the present study is to propose as an alternative to the Dirac form (1) an alternative exchange density $\epsilon_x^{\text{alt}}(r)$, but restricted, as throughout the remainder of this article, to the case of spherical symmetry, already utilized in

writing Eq. 3. What we shall do below is first to give a quite explicit definition for the quantity $\epsilon_x^{alt}(r)$ above, again in terms of the optimized exchange force (OEF), namely $-\partial V_x(r)/\partial \mathbf{r}$. This definition we chose to take as a line integral, namely

$$\epsilon_x^{alt}(r) = -3 \int_r^\infty n(s) \frac{\partial V_x(s)}{\partial s} ds \quad (4)$$

Of course, any definition of exchange energy density must integrate to E_x in the LP relation (2): that is we must next prove that the proposal (4) does indeed satisfy

$$E_x = \int \epsilon_x^{alt}(r) d\mathbf{r}, \quad (5)$$

and will therefore give precisely the same exchange energy as with the Dirac form $\epsilon_x^D(r)$ in Eq. 1.

Introducing, for compactness, ϵ_x^{virial} into Eq. 5 using Eqs. 3 and 4, we have the result

$$E_x = 3 \int d\mathbf{r} \int_r^\infty \frac{\epsilon_x^{virial}(s)}{s} ds \quad (6)$$

Interchanging the order of integration after introducing the Heaviside function $H(\mathbf{r}, s)$ into Eq. 6 readily yields

$$E_x = -3 \int_0^\infty 4\pi \mathbf{r}^2 dr \int_0^\infty H(r, s) \frac{\epsilon_x^{virial}(s)}{s} ds \quad (7)$$

Performing the \mathbf{r} integration then gives after a short calculation

$$E_x = \int_0^\infty \epsilon_x^{virial}(s) 4\pi s^2 ds \quad (8)$$

which is indeed the definition of E_x in spherical symmetry from the exchange energy density.

Immediately below, we shall evaluate numerically the quantity $\epsilon_x^{alt}(r)$ in Eq. 4 for the Ne-like atomic ions already referred to above, using the OEF given in [10]

Since the Dirac density matrix $\gamma_s(\mathbf{r}, \mathbf{r}')$ entering Eq. 1 becomes Coulombic in this Ne-like example for sufficiently large Z , one can utilize the Coulombic wave functions to evaluate γ_s . This was done by Howard et al. [9] who wrote thereby an analytical form of $\epsilon_x^D(r)$ for this example. For $Z = 92$, we have plotted their result in Fig. 1, curve (a). Though the OEF $-\frac{\partial V_x}{\partial \mathbf{r}}$ is only known numerically, we have utilized the results of [10] to evaluate Eq. 4, with the density $n(r)$ taken from the Coulombic limit set out in

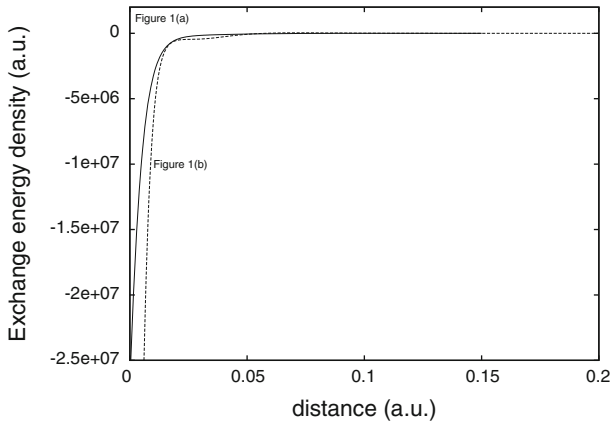


Fig. 1 Plot of the Dirac exchange energy density $\epsilon_x^D(r)$, represented by the *full line*, and the alternative exchange energy density $\epsilon_x^{alt}(r)$ defined in Eq. 4 versus r , represented by the *dashed line*, in atomic units, for Ne-like ions having large nuclear charge 92e

the early study of March and Santamaria [14] who also gave γ_s corresponding to this same density. This electron density $n(r)$ is explicitly

$$n(r) = \frac{2}{\pi} \left(\frac{Z}{a_0} \right)^3 \exp(-2Zr/a_0) + \frac{1}{4\pi} \left(\frac{Z}{a_0} \right)^3 \exp(-Zr/a_0) \times \left[1 - Zr/a_0 + \frac{1}{2}(Zr/a_0)^2 \right] \quad (9)$$

We show the result of such numerical evaluation of $\epsilon_x^{alt}(r)$ in Eq. 4 in curve (b) of Fig. 1, for comparison with the Dirac form ϵ_x^D in curve (a). We have verified to our numerical accuracy that the volume integrals of both these exchange energy densities integrate to the same total exchange energy, as indeed was proved analytically above. Similar plots for the radial exchange energy density $4\pi r^2 \epsilon_x(r)$ are shown in Fig. 2, curves (a) and (b), for $\epsilon_x^D(r)$ and $\epsilon_x^{alt}(r)$ respectively.

As a second example, we consider the non relativistic Ar-like series of atomic ions in the large Z limit. The electron density $n(r)$ is in this case explicitly

$$n(r) = n_{MS}(r) + \frac{Z^3}{486\pi a_0^3} \left(6 - \frac{4Zr}{a_0} + \frac{4Z^2 r^2}{9a_0^2} \right)^2 \exp(-2Zr/3a_0) + n_{3p}(r) \quad (10)$$

where $n_{MS}(r)$ is given in Eq. 12 while $n_{3p}(r)$ is quoted immediately below

$$n_{3p}(r) = \frac{1}{96\pi} \left(\frac{2Z}{a_0} \right)^2 \rho^2 (\rho - 4)^2 \exp(-\rho) \quad (11)$$

where ρ in Eq. 11 is simply $2Zr/3a_0$. Since we do not have results for $\epsilon_x^D(r)$ for the Ar-like series, we have utilized the OEF give in [10], again for $Z = 92$, plus the elec-

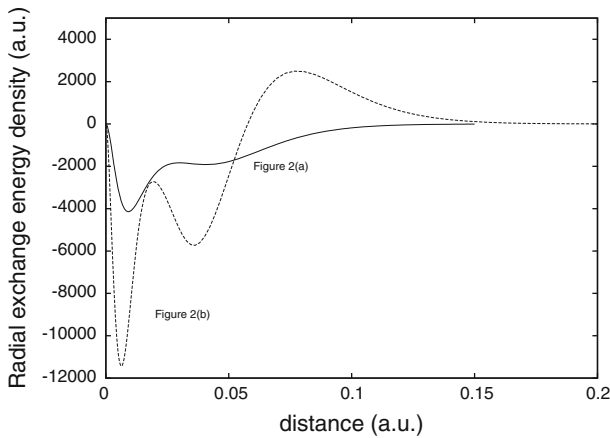


Fig. 2 Plot of the radial Dirac exchange energy density $4\pi r^2 \epsilon_x^D(r)$, represented by the *full line*, and the radial alternative exchange energy density $4\pi r^2 \epsilon_x^{alt}(r)$, represented by the *dashed line*, in atomic units, for Ne-like ions having large nuclear charge $92e$

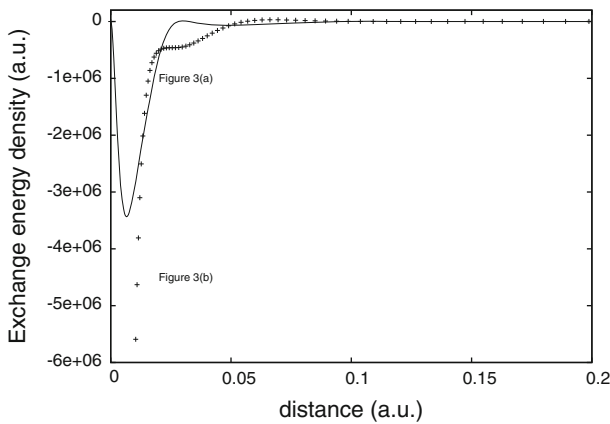


Fig. 3 Plot of the virial exchange energy density $\epsilon_x^{virial}(r)$, represented by the *full line*, and the alternative exchange energy density $\epsilon_x^{alt}(r)$ defined in Eq. 4 versus r , represented by the *crosses*, in atomic units, for Ar-like ions having large nuclear charge $92e$

tron density $n(r)$ in Eq. 13, to plot $\epsilon_x^{alt}(r)$ in Fig. 3b. For purposes of comparison, this time we show $\epsilon_x^{virial}(r)$ from Eq. 3, with of course the same input data in Fig. 3a. The equivalent radial exchange densities are shown in Fig. 4. The total exchange energies E_x agree to satisfactory numerical accuracy, the value for $Z = 92$ being $-179.6(05)$ atomic units.

In summary, for Ne-like atomic ions at large Z , we have exhibited in Figs. 1 and 2 the results of the two definitions of $\epsilon_x^D(r)$ and $\epsilon_x^{alt}(r)$ in Eqs. 1 and 4 respectively for $Z = 92$. Of course, both lead to identical values of E_x . Since ϵ_x^D is not available analytically for the Ar series, in Figs. 3 and 4 we have compared $\epsilon_x^{alt}(r)$ and $\epsilon_x^{virial}(r)$, again for $Z = 92$. To conclude, let us add some suggestions for further work that

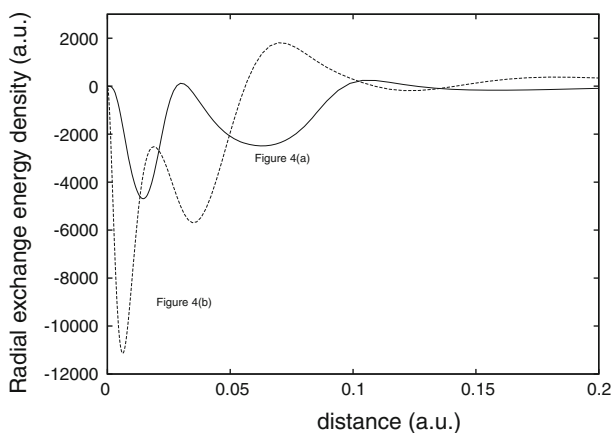


Fig. 4 Plot of the radial virial exchange energy density $4\pi r^2 \epsilon_x^{virial}(r)$, represented by the *full line*, and the radial alternative exchange energy density $4\pi r^2 \epsilon_x^{alt}(r)$, represented by the *dashed line*, in atomic units, for Ar-like ions having large nuclear charge $92e$

should prove fruitful. It is all connected with performing the functional derivative $\frac{\partial E_x}{\partial n(r)}$ to obtain the DFT exchange potential. This route was already pursued in the work of Howard and March [15], who focussed, after integrating Eq. 1 above to find E_x , on the functional derivative of the Dirac matrix $\gamma(\mathbf{r}, \mathbf{r})$ with respect to the electron density. To date, this is only available in approximate forms discussed in [15]. In some sense, the line integral in the definition of $\epsilon_x^{alt}(r)$ in Eq. 4 relates, at least indirectly, to the above functional derivatives. This is an area worth pursuing for the future, we believe and therefore our final step here along this path is to deduce from Eq. 4 that

$$\frac{\partial \epsilon_x^{alt}(r)}{\partial r} = 3n(r) \frac{\partial V_x(r)}{\partial r} \quad (12)$$

which leads immediately to a functional derivative relation, namely

$$\frac{\partial}{\partial r} \left[\frac{\partial E_x}{\partial n(r)} \right] = \frac{1}{3n(r)} \frac{\partial \epsilon_x^{alt}(r)}{\partial r} \quad (13)$$

It is instructive in the context of Eq. 13 to return to the integral equation theory of $V_x(r)$ in [1–5] above. The zeroth-order approximation in the Slater (SI) exchange potential [16], given by

$$V_x^{SI} = \frac{2\epsilon_x^D(r)}{n(r)} \quad (14)$$

with $\epsilon_x^D(r)$ as in Eq. 1. Since $\frac{\partial E_x}{\partial n(r)}$ in Eq. 13 is $V_x(r)$, Eq. 13 is a formally exact generalization of Eq. 14, but now involving $\epsilon_x^{alt}(r)$. Thus, it is of interest for the future to study the function $\epsilon_x^{alt}[n]$. A start can in fact be made from Eq. 12, since $V_x(r)$ as

$r \rightarrow \infty$ yields the self-interaction tail $-\frac{e^2}{r}$. Hence $\epsilon_x^{alt}[n]$ tends, in the above asymptotic limit, to a term proportional to $\int_r^\infty \left(\frac{n(s)}{s^2}\right) ds$. No doubt, more can be learnt about this alternative form $\epsilon_x^{alt}[n]$ by further study.

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