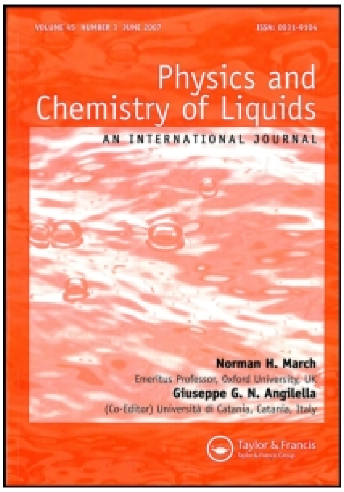

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Kinetic and exchange energy related non-locally in Hartree–Fock theory of an inhomogeneous electron liquid

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Using a non-local exchange kernel $X(\vec{r},\vec{r}')$ defined earlier by March and Santamaria, Hartree–Fock theory is shown to yield an exact relation for the kinetic energy density $t(\vec{r})$. This involves $X(\vec{r},\vec{r}')$ and its low-order gradients with respect to $\vec{r}$. Explicit limiting results then emerge for t at large $\vec{r}$. A two-level example applicable to either the Be atom or the diatomic heteronuclear molecule LiH confirms the general relation between $t(\vec{r})$ and $X(\vec{r},\vec{r}')$ presented here.

Keywords: Inhomogeneous electron liquid; Hartree–Fock theory; Kinetic and exchange properties

1. Introduction

It is of considerable interest for density functional theory (DFT) to relate the single-particle kinetic energy density to the exchange energy counterpart in the ground state of atoms and molecules. The exchange energy density has been usefully approximated by adding a term involving density gradients to a local density approximation (LDA) but orbital-free kinetic energy density theory is presently of much poorer quality.

Therefore, in the present article the authors have worked out from Hartree–Fock (HF) theory for finite closed shell molecules and clusters, an expression for the kinetic energy density in terms of a non-local exchange energy kernel introduced in the early work of March and Santamaria [1,2]. An illustration of this relation between kinetic and exchange contributions is then presented for two-level systems such as the Be atom or LiH.

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Though the earliest form of DFT proposed by Thomas [3], Fermi [4] and Dirac [5], now known as the LDA to current DFT, yielded explicit functionals for kinetic energy density $t[\varrho]$ and exchange energy density $\varepsilon_x[\varrho]$, namely

$$t^{TFD}[\varrho] = c_k\{\varrho(\vec{r})\}^{5/3}:\ c_k = \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3} \tag{1}$$

and

$$\epsilon_x^{TFD}[\varrho] = -c_x\{\varrho(\vec{r})\}^{4/3}:\ c_x = \frac{3}{4}e^2\left(\frac{3}{\pi}\right)^{1/3}, \tag{2}$$

it is the latter that has proved much more useful for recent quantitative versions of DFT, when corrected for density gradients [6,7]. Therefore, in the Kohn–Sham procedure [8] the single-particle kinetic energy problem is bypassed by returning, as in Hartree self-consistent field theory but without self-interaction correction, to one-electron Schrödinger equations. Nevertheless, a number of workers in DFT continue to study the orbital-free approximations to the single-particle kinetic energy. The present study is a contribution to the latter area, and directly connects the exchange and kinetic contributions. However, to do so explicitly, one can appeal to restricted HF theory for closed shell systems. This theory is attractive as a result of Möller and Plesset confirms the high quality of its ground-state-electron density $\varrho(\vec{r})$, the central tool of DFT.

2. Non-local generalizations of kinetic and exchange energy densities

In HF theory, the natural starting point for the direct calculation of kinetic energy density, $t(\vec{r})$ say, is the idempotent Dirac density matrix $\gamma(\vec{r},\vec{r}')$ defined by

$$\gamma(\vec{r},\vec{r}') = \sum_{\text{occupied } i} \Psi_i(\vec{r})\Psi_i^*(\vec{r}'), \tag{3}$$

where $\Psi_i(\vec{r})$ denotes the ith HF orbital. Defining the quantity $F(\vec{r},\vec{r}')$ by

$$F(\vec{r},\vec{r}') = \gamma(\vec{r},\vec{r}')^2, \tag{4}$$

Dawson and March [9] pointed out that the kinetic energy density $t(\vec{r})$ can be written as

$$t(\vec{r}) \sim \frac{\hbar^2}{8m}\int \frac{(\nabla_{\vec{r}}F)^2}{F}\,\mathrm{d}\vec{r}', \tag{5}$$

which is somewhat reminiscent of the 'inhomogeneity' kinetic energy density proposed by von Weizsäcker [10], namely

$$t_w(\vec{r}) = \frac{\hbar^2}{8m}\frac{\left(\nabla_{\vec{r}}\varrho(\vec{r})\right)^2}{\varrho(\vec{r})}, \tag{6}$$

to which quantity referred again later in equation (22).

Having written $t(\vec{r})$ in terms of $F=\gamma^2$ in equation (5), one can similarly express the exchange energy density $\epsilon_x(\vec{r})$ in HF theory. To do so, the Dirac [5] total exchange energy E_x in terms of $\gamma(\vec{r},\vec{r}')$ is the natural starting point, namely

$$E_x = -\frac{e^2}{4}\int \frac{\gamma(\vec{r},\vec{r}')^2}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}'. \tag{7}$$

Though it is not unique, the definition of the exchange energy density $\epsilon_x(\vec{r})$ which is adopted throughout this study follows, naturally enough, from equation (7) as

$$E_x = \int \epsilon_x(\vec{r})\mathrm{d}\vec{r} \tag{8}$$

where

$$\begin{aligned}\epsilon_x(\vec{r}) &= -\frac{e^2}{4}\int \frac{\gamma(\vec{r},\vec{r}')^2}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}' \\ &= -\frac{e^2}{4}\int \frac{F(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}',\end{aligned} \tag{9}$$

the latter step utilizing the definition (4).

March and Santamaria [1,2] proposed to define non-local kinetic and exchange energy kernels which they denoted respectively by $K(\vec{r},\vec{r}')$ and $X(\vec{r},\vec{r}')$ such that

$$\tau(\vec{r}) = \int K(\vec{r},\vec{r}')\mathrm{d}\vec{r}', \tag{10}$$

where $\tau(\vec{r})$ differs from $t(\vec{r})$ by an N-dependent-constant only and

$$\epsilon_x(\vec{r}) = \int X(\vec{r},\vec{r}')\mathrm{d}\vec{r}'. \tag{11}$$

Then the simplest explicit forms for K and X, which the authors adopt as definitions below, follow respectively from equations (5) and (9) as

$$K(\vec{r},\vec{r}') = \frac{\hbar^2}{8m}\frac{(\nabla_{\vec{r}}F)^2}{F} \tag{12}$$

and

$$X(\vec{r},\vec{r}') = -\frac{e^2}{4}\frac{F(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}. \tag{13}$$

Given equations (12) and (13), it is a straightforward matter by using

$$F(\vec{r},\vec{r}') = -\left(\frac{4}{e^2}\right)X(\vec{r},\vec{r}')|\vec{r}-\vec{r}'| \tag{14}$$

in equation (12), to write the kinetic energy non-local kernel $K(\vec{r},\vec{r}')$ solely in terms of its exchange energy counterpart $X(\vec{r},\vec{r}')$. Then after some straightforward manipulation, the authors obtain, now using atomic units in what follows,

$$K(\vec{r},\vec{r}') = -\frac{1}{2}|\vec{r}-\vec{r}'|\frac{(\nabla_{\vec{r}}X)^2}{X} - \nabla_{\vec{r}}X\,\nabla_{\vec{r}}|\vec{r}-\vec{r}'| - \frac{X}{2|\vec{r}-\vec{r}'|}(\nabla_{\vec{r}}|\vec{r}-\vec{r}'|)^2. \tag{15}$$

Integrating equation (15) with respect to $\vec{r}'$ we find the HF (normalized) kinetic energy density $\tau(\vec{r})$ in terms of the non-local exchange kernel $X(\vec{r},\vec{r}')$ as

$$\tau(\vec{r}) = \int K(\vec{r},\vec{r}')\mathrm{d}\vec{r}' = -\frac{1}{2}\int |\vec{r}-\vec{r}'|\frac{(\nabla_{\vec{r}}X)^2}{X}\mathrm{d}\vec{r}' - \int \nabla_{\vec{r}}X\,\nabla_{\vec{r}}|\vec{r}-\vec{r}'|\mathrm{d}\vec{r}'$$
$$-\frac{1}{2}\int \frac{(\nabla_{\vec{r}}|\vec{r}-\vec{r}'|)^2}{|\vec{r}-\vec{r}'|}X(\vec{r},\vec{r}')\mathrm{d}\vec{r}'. \tag{16}$$

In the penultimate section 4, it will be shown that the idempotency of the Dirac density matrix $\gamma(\vec{r},\vec{r}')$ can be utilized to rewrite the second term appearing in equation (16), a Laplacian term $\nabla^2_{\vec{r}}\varrho(\vec{r})$ is then being introduced into the kinetic energy density.

Section 3 applies equation (16), valid for an arbitrary number of doubly filled spin-compensated levels in HF theory, to a two-level system such as the Be atom or the diatomic molecule LiH.

3. Calculation of kinetic energy density for a two-level system: e.g. LiH or Be atom

To illustrate the utility of equation (16), let one calculate $t(r)$ for the Be atom. Then, using the 1s and 2s wave functions in terms of the density amplitude $\varrho^{1/2}(r)$ and the phase $\Theta(r)$ one have [9]

$$\Psi_{1\mathrm{s}} = \left(\frac{\varrho}{2}\right)^{1/2}\cos\Theta \tag{17}$$

and

$$\Psi_{2\mathrm{s}} = \left(\frac{\varrho}{2}\right)^{1/2}\sin\Theta \tag{18}$$

Evidently, the Dirac density matrix is given by substituting these wave functions into equation (3), when the known result

$$\gamma(r,\ r') = \varrho^{1/2}(r)\varrho^{1/2}(r')\cos(\Theta(r)-\Theta(r')) \tag{19}$$

is obtained or from equation (4):

$$F(r,\ r') = \varrho(r)\varrho(r')\cos^2(\Theta(r)-\Theta(r')). \tag{20}$$

Therefore, substituting equation (20) into equation (13), one can find the non-local exchange kernel to be

$$X(\vec{r},\vec{r}') = -\frac{e^2}{4}\frac{\varrho(r)\varrho(r')\cos^2(\Theta(r)-\Theta(r'))}{|\vec{r}-\vec{r}'|}. \tag{21}$$

Inserting equation (21) into equation (16) one must find the result already in the literature that the total kinetic energy T is given by

$$T = \frac{\hbar^2}{8m}\int\frac{(\nabla\varrho)^2}{\varrho}\mathrm{d}\vec{r} + \frac{1}{2}\int\varrho(\nabla\Theta)^2\mathrm{d}\vec{r}. \tag{22}$$

Though the most direct way, still, of reaching equation (22) is from $(1/2)(\partial^2/\partial\vec{r}'\partial\vec{r})\gamma(\vec{r},\vec{r}')|_{\vec{r}'=\vec{r}}$ using equation (19), from equation (16) and after allowing for the N-dependent normalization constant relating $\tau(\vec{r})$ and $t(\vec{r})$ plus idempotency and the pendulum equation (9), the two-level result (22) must emerge.

4. Further relations resulting from idempotency of HF Dirac density matrix $\gamma(\vec{r},\vec{r}')$ defined in equation (3)

Already, in reaching equations (5) and (16), Dawson and March [9] had employed the idempotency of the Dirac density matrix defined in equation (3). For doubly occupied levels considered throughout this article, this idempotency condition reads

$$\int \frac{\gamma(\vec{r},\vec{r}'')}{2}\frac{\gamma(\vec{r}'',\vec{r}')}{2}\mathrm{d}\vec{r}'' = \frac{\gamma(\vec{r},\vec{r}')}{2}. \tag{23}$$

Putting $\vec{r}' = \vec{r}$, and using the definition (4) readily yields

$$\int F(\vec{r},\vec{r}')\mathrm{d}\vec{r}' = 2\varrho(\vec{r}). \tag{24}$$

Inserting equation (14) into equation (24),

$$\int |\vec{r}-\vec{r}'|X(\vec{r},\vec{r}')\mathrm{d}\vec{r}' = -\frac{e^2}{2}\varrho(\vec{r}). \tag{25}$$

Taking the gradient with respect to $\vec{r}$ of equation (25) yields

$$\int \nabla_{\vec{r}}|\vec{r}-\vec{r}'|X(\vec{r},\vec{r}')\mathrm{d}\vec{r}' + \int |\vec{r}-\vec{r}'|\nabla_{\vec{r}}X(\vec{r},\vec{r}')\mathrm{d}\vec{r}' = -\frac{e^2}{2}\nabla_{\vec{r}}\varrho(\vec{r}). \tag{26}$$

A further gradient operation on equation (26) then leads to the result

$$\begin{aligned}\int \nabla^2_{\vec{r}}|\vec{r}-\vec{r}'|X(\vec{r},\vec{r}')\mathrm{d}\vec{r}' + 2\int \nabla_{\vec{r}}|\vec{r}-\vec{r}'|\nabla_{\vec{r}}X(\vec{r},\vec{r}')\mathrm{d}\vec{r}' \\ + \int |\vec{r}-\vec{r}'|\nabla^2_{\vec{r}}X(\vec{r},\vec{r}')\mathrm{d}\vec{r}' = -\frac{e^2}{2}\nabla^2_{\vec{r}}\varrho(\vec{r}).\end{aligned} \tag{27}$$

This identity (27) can be used to remove the scalar product term $\nabla_{\vec{r}}X\,\nabla_{\vec{r}}|\vec{r}-\vec{r}'|$ from equation (16), which may be helpful in subsequent practical applications.

5. Summary

Equation (16), when combined with equation (11), sums up the main achievement of this study. The kinetic energy density $\tau(\vec{r})$ in equation (16) is determined solely by the exchange energy kernel $X(\vec{r},\vec{r}')$, which in turn is related to the exchange energy density $\epsilon_x(\vec{r})$ by equation (11). The relation between $t(\vec{r})$ and the exchange kernel $X(\vec{r},\vec{r}')$ is fundamentally non-local, in contrast to that in the Thomas–Fermi–Dirac statistical theory valid for large numbers of electrons N, the essential functional content of which has been displayed in equations (1) and (2). Naturally, one can rewrite equations (1) and (2) through the elementary local relation between kinetic energy density $t(\vec{r})$ its exchange counterpart $\epsilon_x(\vec{r})$ as

$$t^{TFD}(\vec{r}) = \text{const}\left\{|\epsilon_x^{TFD}(\vec{r})|\right\}^{5/4}. \tag{28}$$

this relation (28) is valid only in LDA and must be replaced in HF theory by equation (16). This must then lead to the correct two-level result (22), but the authors reiterate that the relation (16) between $\tau(\vec{r})$ and the non-local exchange kernel $X(\vec{r}, \vec{r}')$ is valid for an arbitrary number of spin-compensated occupied levels. Finally, in the appendix, the asymptotic behaviour of $\tau(\vec{r})$ large r in equation (16) is discussed.

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Appendix: asymptotic large $\vec{r}$ behaviour of the kinetic energy density in equation (16)

As sufficiently large $\vec{r}$ equation (16) can be simplified considerably. It reads then

$$\lim_{\vec{r}\to\infty} \tau(\vec{r}) = -\frac{1}{2}r\int \frac{(\nabla_{\vec{r}}X(\vec{r}, \vec{r}'))^2}{X(\vec{r}, \vec{r}')}\mathrm{d}\vec{r}' - \frac{1}{2r}\int X(\vec{r}, \vec{r}')\mathrm{d}\vec{r}'$$

$$-\int \nabla_{\vec{r}}|\vec{r}-\vec{r}'|\,\nabla_{\vec{r}}X(\vec{r}, \vec{r}')\mathrm{d}\vec{r}' \tag{A1}$$

The term $-(1/2r)\int X(\vec{r},\vec{r}')\mathrm{d}\vec{r}'$, using equation (11) becomes simply $-(1/2r)\epsilon_x(\vec{r})$ and therefore in this asymptotic regime depends only on $\epsilon_x(\vec{r})$ rather than on the non-local kernel $X(\vec{r},\vec{r}')$. To discuss the final term in equation (A1) as $r \to \infty$, one can employ equation (27) which comes from the idempotency of the Dirac density matrix. The result is readily found to be expressible solely in terms of the Laplacian $\nabla_r^2\varrho(\vec{r})$ already appearing in equation (27), again the exchange energy density $\epsilon_x(\vec{r})$ from the first term in that equation, while the final term on the LHS of equation (27) involves $\nabla^2\epsilon_x(\vec{r})$ times r at sufficiently large r. The authors anticipate that the first term on the RHS of equation (A1) will dominate $\tau(\vec{r})$ at sufficiently large $\vec{r}$ and will be of Weizsäcker's form. However, the first term can be written asymptotically in this limit as $-(r/4)((\nabla_{\vec{r}}\epsilon_x(\vec{r}))^2/\epsilon_x(\vec{r}))$: that is in terms of $\epsilon_x[\vec{r}]$ and its gradient.