## Kinetic and Exchange Energy Densities of an Inhomogenous Electron Liquid Related in Hartree—Fock Theory and Other Models

A. Holas[a]; N. H. March[b]

[a] Institute of Physical Chemistry of Polish Academy of Sciences, Warsaw, Poland [b] Theoretical Chemistry Department, University of Oxford, Oxford, UK

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# KINETIC AND EXCHANGE ENERGY DENSITIES OF AN INHOMOGENOUS ELECTRON LIQUID RELATED IN HARTREE–FOCK THEORY AND OTHER MODELS

A. HOLAS

*Institute of Physical Chemistry of Polish Academy of Sciences,
Kasprzaka 44, 01-224 Warsaw, Poland*

and

N. H. MARCH

*Theoretical Chemistry Department, University of Oxford,
5 South Parks Road, Oxford OX1 3UB, UK*

March and Santamaria have recently proposed non-local generalizations of kinetic and exchange energy densities of an inhomogeneous electron liquid and have related these through restricted Hartree–Fock theory. Prompted further by the work of Lee, Lee and Parr, the above results are generalized to include the unrestricted Hartree–Fock theory. Finally, approximations of the type required to relate to the work of Lee *et. al.* are referred to.

KEY WORDS: Kinetic energy density, Hartree–Fock theory, idempotency.

## 1  BACKGROUND

Non-local generalizations of kinetic and exchange energy densities of an inhomogeneous electron liquid have recently been defined by March and Santamaria[1] (referred to as MS below) and these have then been related through Hartree–Fock (HF) theory. Since this work, the related approximate study of Lee, Lee and Parr[2] (LLP) has appeared. This has prompted us to (i) effect generalizations of the work of Ref. 1, (ii) study these generalizations variationally and (iii) relate Refs. 1 and 2.

It has been known for a long time that restricted Hartree–Fock (RHF) theory can be characterized by its idempotent first-order density matrix (Dirac density matrix). For even numbers of electrons $N$, with $N/2$ doubly occupied spatial orbitals $\varphi_j(\mathbf{r})$, $j = 1, \ldots, N/2$, this matrix has the form

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = 2 \sum_{j=1}^{N/2} \phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2) \tag{1}$$

which satisfies the idempotency relation

$$\tfrac{1}{2}\rho(\mathbf{r}_1, \mathbf{r}_3) = \int d^3 r_2 \; \tfrac{1}{2}\rho(\mathbf{r}_1, \mathbf{r}_2) \; \tfrac{1}{2}\rho(\mathbf{r}_2, \mathbf{r}_3). \tag{2}$$

## 2  KINETIC AND EXCHANGE ENERGY DENSITIES

A general, complex form of the matrix $\rho(\mathbf{r}_1, \mathbf{r}_2)$ in Eq. (1) will first be used. However, for some final steps it will prove necessary to specialize by assuming a real matrix. Following MS, the total kinetic energy $T$ is written as an integral through space of the kinetic energy density $\tau(\mathbf{r})$:

$$T = \int d^3 r \tau(\mathbf{r}) \tag{3}$$

where $\tau(\mathbf{r})$ is then expressed by the non-local kernel $K(\mathbf{r}, \mathbf{r}')$ through

$$\tau(\mathbf{r}) = \int d^3 r' K(\mathbf{r}, \mathbf{r}'). \tag{4}$$

In terms of the Dirac density matrix $\rho(\mathbf{r}, \mathbf{r}')$ this kernel $K$ takes the form[4]

$$K(\mathbf{r}, \mathbf{r}') = \tfrac{1}{4}[\nabla_r \rho(\mathbf{r}, \mathbf{r}')] \cdot [\nabla_r \rho(\mathbf{r}', \mathbf{r})] = \tfrac{1}{4}|\nabla_r \rho(\mathbf{r}, \mathbf{r}')|^2. \tag{5}$$

The following definition of the kinetic energy:

$$\tau(\mathbf{r}) = \lim_{\mathbf{r}_1 \to \mathbf{r}} \lim_{\mathbf{r}_2 \to \mathbf{r}} \tfrac{1}{2} \nabla_{r_1} \nabla_{r_2} \rho(\mathbf{r}_1, \mathbf{r}_2) \tag{6}$$

and the idempotency property (2) have been used to obtain the result (5). The kinetic energy density defined by Eq. (6) possesses a unique property

$$\tau(\mathbf{r}) \geq 0. \tag{7}$$

Turning to the restricted HF exchange energy $A$, MS[1] again write this in terms of an energy density, $\varepsilon_x(\mathbf{r})$ say, where

$$A = \int d^3 r \varepsilon_x(\mathbf{r}) \tag{8}$$

with $\varepsilon_x(\mathbf{r})$ given by the non-local expression

$$\varepsilon_x(\mathbf{r}) = \int d^3 r' X(\mathbf{r}, \mathbf{r}'). \tag{9}$$

Here the kernel can again by written in terms of the Dirac density matrix as

$$X(\mathbf{r}, \mathbf{r}') = -\frac{1}{4} \frac{\rho(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} = -\frac{1}{4} \frac{|\rho(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \qquad (10)$$

which evidently reduces to Eq. (11) of Ref. 1 when $\rho(\mathbf{r}, \mathbf{r}')$ is real.

In order to express both $K$ and $X$ in terms of some common function, $F(\mathbf{r}, \mathbf{r}')$ say, we must restrict ourselves subsequently to those RHF systems for which the Dirac matrix is real:

$$\rho(\mathbf{r}, \mathbf{r}') = \rho^*(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}', \mathbf{r}). \qquad (11)$$

Given this assumption (11), one again follows Ref. 1 by introducing

$$F(\mathbf{r}_1, \mathbf{r}_2) = [\rho(\mathbf{r}_1, \mathbf{r}_2)]^2 = F(\mathbf{r}_2, \mathbf{r}_1) \qquad (12)$$

which is evidently also real and symmetrical. Then the kinetic energy kernel $K$ in Eq. (5) can be rewritten as

$$K(\mathbf{r}, \mathbf{r}') = \frac{1}{16} \frac{[\nabla_r F(\mathbf{r}, \mathbf{r}')]^2}{F(\mathbf{r}, \mathbf{r}')} \qquad (13)$$

to be compared[5] with Eq. (14) of Ref. 1. The exchange energy kernel (10) likewise becomes

$$X(\mathbf{r}, \mathbf{r}') = -\frac{1}{4} \frac{F(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \qquad (14)$$

Since Eqs. (13) and (14) are written in terms of $F(\mathbf{r}, \mathbf{r}')$ rather than the Dirac matrix, it is worth recording that the electron density $\rho(\mathbf{r})$ is also expressible in terms of $F$. Thus, taking into account Eqs. (1), (2), (11) and (12) we find

$$\rho(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}) = F^{1/2}(\mathbf{r}, \mathbf{r}) = \tfrac{1}{2} \int d^3 r' F(\mathbf{r}, \mathbf{r}'). \qquad (15)$$

Therefore the classical parts of the potential energy in RHF theory can be considered as functionals of $F(\mathbf{r}, \mathbf{r}')$, just as with the kinetic and exchange energies given through Eqs. (13) and (14) respectively.

## 3 VARIATIONAL APPROACH

From the above, it might seem attractive to minimize the RHF total energy with respect to $F(\mathbf{r}, \mathbf{r}')$ for systems where $\rho(\mathbf{r}, \mathbf{r}')$ is real. Of course, some constraints are

necessary. As usual, one of these is the normalization condition, which from Eq. (15) can evidently be written as

$$\tfrac{1}{2} \int d^3r d^3r' F(\mathbf{r}, \mathbf{r}') = N. \tag{16}$$

In addition the diagonal part of the idempotency condition (2) (see also Eq. (15)) implies the constraint

$$F^{1/2}(\mathbf{r}, \mathbf{r}) = \tfrac{1}{2} \int d^3r' F(\mathbf{r}, \mathbf{r}'), \tag{17}$$

but it has not, so far, proved possible to write the off-diagonal part in terms of $F$.

In order to explore the variational approach with the above constraints, let us consider independent electrons moving in an external potential $v(\mathbf{r})$, rather than the RHF problem. The result obtained is then

$$-\frac{1}{4} \frac{\nabla_r^2 F(\mathbf{r}, \mathbf{r}')}{F(\mathbf{r}, \mathbf{r}')} + \frac{1}{8}\left[\frac{\nabla_r F(\mathbf{r}, \mathbf{r}')}{F(\mathbf{r}, \mathbf{r}')}\right]^2 + v(\mathbf{r}) - \lambda - \Lambda(\mathbf{r})\left[\frac{\delta(\mathbf{r} - \mathbf{r}')}{F^{1/2}(\mathbf{r}, \mathbf{r}')} - 1\right] = 0. \tag{18}$$

The Lagrange multipliers $\lambda$ and $\Lambda(\mathbf{r})$ are introduced to take care of the constraints (16) and (17) respectively.

But now this non-interacting problem can be solved alternatively via the one-electron Schrödinger equation with the potential $v(\mathbf{r})$. The quantities $\rho(\mathbf{r}, \mathbf{r}')$ and $F(\mathbf{r}, \mathbf{r}')$ can be constructed then from the eigenfunctions according to Eqs. (1) and (12). It turns out that Eq. (18) is only exactly satisfied by the $F(\mathbf{r}, \mathbf{r}')$ thus constructed when all the one-electron eigenvalues are degenerate; an uninteresting case. Presumably therefore, calculating from Eq. (18) would then, in general, lead to a ground-state energy lower than the correct value, since some constraints are still neglected. However, it may well be that a modification of Eq. (18) to include, besides exchange and classical repulsion, some electron correlation, will find its place in an eventual approximate many-electron theory, since there is no such idempotency condition when the one-electron approximation is relaxed.

## 4 UNRESTRICTED HARTREE–FOCK THEORY

The results above can be readily generalized to unrestricted HF (UHF) theory, because both the kinetic energy and exchange energy can be written in this theory again in terms of first-order density matrices, separately for subsystems of spin-up and spin-down electrons. Of $N$ spin orbitals $\psi_j(\mathbf{r}, s)$, let those having $j = 1, 2, \ldots, N_\uparrow$ be connected with "up" spinors, $\psi_j = \varphi_j(\mathbf{r})\alpha(s)$ and those having $j = N_\uparrow + 1, \ldots, N$ with ("down") spinors, $\psi_j(\mathbf{r}, s) = \varphi_j(\mathbf{r}) \beta(s)$. Evidently

$$N_\uparrow + N_\downarrow = N. \tag{19}$$

Let us define Dirac matrices for the subsystems as

$$\rho_\uparrow(\mathbf{r}_1, \mathbf{r}_2) = \sum_{j=1}^{N_\uparrow} \phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2) \tag{20}$$

and

$$\rho_\downarrow(\mathbf{r}_1, \mathbf{r}_2) = \sum_{j=N_\uparrow+1}^{N_\uparrow+N_\downarrow} \phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2). \tag{21}$$

If $N_\uparrow = N_\downarrow$ and the set of all functions involved in Eq. (20) is the same as the set in Eq. (21), then $\rho_\uparrow = \rho_\downarrow$ and by denoting $\rho(\mathbf{r}_1, \mathbf{r}_2) = 2\,\rho_\uparrow(\mathbf{r}_1, \mathbf{r}_2)$ we regain the case of restricted HF theory.

In UHF theory, either $N_\uparrow \neq N_\downarrow$ or the sets differ by one, two or more functions. The matrices $\rho_\uparrow$ and $\rho_\downarrow$ are again idempotent.

$$\rho_\sigma(\mathbf{r}_1, \mathbf{r}_3) = \int d^3r_2 \rho_\sigma(\mathbf{r}_1, \mathbf{r}_2)\rho_\sigma(\mathbf{r}_2, \mathbf{r}_3) \tag{22}$$

and the total density is given by the sum of subsystem diagonal contributions:

$$\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r}) = \rho_\uparrow(\mathbf{r}, \mathbf{r}) + \rho_\downarrow(\mathbf{r}, \mathbf{r}) \tag{23}$$

which are such that

$$\int d^3r \rho_\sigma(\mathbf{r}) = N_\sigma. \tag{24}$$

The kinetic energy $\tau_\sigma(\mathbf{r})$ is obtained by applying the definition (6) acting on $\rho_\sigma(\mathbf{r}_1, \mathbf{r}_2)$ so the total value is

$$\tau(\mathbf{r}) = \tau_\uparrow(\mathbf{r}) + \tau_\downarrow(\mathbf{r}) \tag{25}$$

and

$$T = T_\uparrow + T_\downarrow. \tag{26}$$

The exchange energy is also additive:

$$A = A_\uparrow + A_\downarrow, \tag{27}$$

where

$$A_\sigma = -\frac{1}{2} \iint d^3r_1\, d^3r_2\, \frac{\rho_\sigma(\mathbf{r}_1, \mathbf{r}_2)\rho_\sigma(\mathbf{r}_2, \mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{28}$$

The different numerical factor as compared with Eqs. (8)–(10) should be noted. All derivations given above in Eqs. (4)–(14) can now be applied to each subsystem separately, with minor modifications.

If, as previously, we restrict attention to configurations for which the matrices $\rho_\sigma(\mathbf{r}_1, \mathbf{r}_2)$ are real, then the results of March and Santamaria[1] are generalized for UHF theory to

$$F_\sigma(\mathbf{r}_1, \mathbf{r}_2) = [\rho_\sigma(\mathbf{r}_1, \mathbf{r}_2)]^2 \tag{29}$$

$$K_\sigma(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{16} \frac{[\nabla_{\mathbf{r}_1} F_\sigma(\mathbf{r}_1, \mathbf{r}_2)]^2}{F_\sigma(\mathbf{r}_1, \mathbf{r}_2)} \tag{30}$$

and

$$X_\sigma(\mathbf{r}_1, \mathbf{r}_2) = -\tfrac{1}{2} F_\sigma(\mathbf{r}_1, \mathbf{r}_2)/|\mathbf{r}_1 - \mathbf{r}_2|. \tag{31}$$

## 5  APPROXIMATE MODELS

At this point, let us return to the approximate formulation of Lee, Lee and Parr[2], based on the earlier work of Becke[6]. We no longer are within Hartree–Fock; we are entering the province of models. Using the approximate results for $T$ and $A$ set out by LLP, we have

$$\tau = c_k \{\rho(\mathbf{r})\}^{5/3}(1 + \alpha G(\tilde{x})); \quad c_k = \frac{3h^2}{10m}(3/8\pi)^{2/3} \tag{32}$$

and

$$\varepsilon_x = -c_e\{\rho(\mathbf{r})\}^{4/3}(1 + \beta G(\tilde{x})); \quad c_e = \tfrac{3}{4}e^2(3/\pi)^{1/3} \tag{33}$$

where $\tilde{x}$ is a density gradient variable $\tilde{x} = 2^{1/3}\nabla\rho/\rho^{4/3}$. Returning to the non-local kernels $K$ and $X$ of March and Santamaria, we hence have the approximate results

$$\int K(\mathbf{r}, \mathbf{r}')d^3r' = c_k\{\rho(\mathbf{r})\}^{5/3}[1 + \alpha G(\tilde{x})] \tag{34}$$

and

$$\int X(\mathbf{r}, \mathbf{r}')d^3r' = -c_e\{\rho(\mathbf{r})\}^{4/3}[1 + \beta G(\tilde{x})]. \tag{35}$$

We now proceed to eliminate the function $G(x)$ between Eqs. (34) and (35) to obtain, after the somewhat drastic step of equating integrands[7], with the choice, for

simplicity, $\alpha = \beta$ recommended by LLP for some purposes:

$$\frac{K(\mathbf{r}, \mathbf{r}')}{X(\mathbf{r}, \mathbf{r}')} + \frac{c_k}{c_e}\{\rho(\mathbf{r})\}^{1/3} = 0. \tag{36}$$

Accepting Eq. (36) as the basis for a model, one can satisfy it by writing

$$|\mathbf{r} - \mathbf{r}'|K(\mathbf{r}, \mathbf{r}') = c(\mathbf{r}')k(\mathbf{r}) \tag{37}$$

and

$$|\mathbf{r} - \mathbf{r}'|X(\mathbf{r}, \mathbf{r}') = c(\mathbf{r}')x(\mathbf{r}) \tag{38}$$

to find

$$k(\mathbf{r}) = -\left(\frac{c_k}{c_e}\right)\{\rho(\mathbf{r})\}^{1/3}x(\mathbf{r}). \tag{39}$$

All this is equivalent to the choice (compare Eqs. (14) and (38))

$$F(\mathbf{r}, \mathbf{r}') = -4c(\mathbf{r}')x(\mathbf{r}) \tag{40}$$

with the simplicity, but no doubt the severe limitation, of a separable assumption. One can escape from this by symmetrizing to write

$$F_{\text{model}}(\mathbf{r}, \mathbf{r}') = -2[c(\mathbf{r}')x(\mathbf{r}) + c(\mathbf{r})x(\mathbf{r}')]. \tag{41}$$

Of course, once such a model for $F$ as in Eq. (41) is established, then for example $K$ is to be found from Eq. (13). But it should be cautioned, as with the variational result (18), that constraints are not fully incorporated and there is no longer an upper bound assured for the total energy.

## 6  SUMMARY

In summary, RHF and UHF theories of an inhomogeneous electron liquid can be written in a form in which an intimate relation between kinetic and exchange energies emerges. But, so far, to exploit this relation variationally, some part of the idempotency constraint on the Dirac density matrix has to be relaxed. However, it has been pointed out that, once correlation is incorporated, the strict idempotency of the first-order Dirac density matrix is replaced by a weaker (Pauli) condition on the correlated first-order density matrix, $\gamma(\mathbf{r}, \mathbf{r}')$, namely $\gamma^2 < \gamma$. Thus some of the present study, when modified to include an approximate form of correlation energy, may have interest beyond RHF or UHF.

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2. H. Lee, C. Lee and R. G. Parr, *Phys. Rev.* **A44**, 768 (1991).
3. See, for example, R. McWeeny, Molecular quantum mechanics (Academic: London), (1987).
4. Eq. (7) of Ref. 1 should have a factor $\frac{1}{4}$ rather than $\frac{1}{2}$ multiplying the density matrix gradients.
5. Eq. (14) of Ref. 1 is modified as a consequence of Ref. 4 above to have a factor $\frac{1}{16}$ rather than $\frac{1}{8}$.
6. A. D. Becke, *Phys. Rev.* **A38**, 3098 (1988).
7. Of course, one can add functions that integrate to zero.