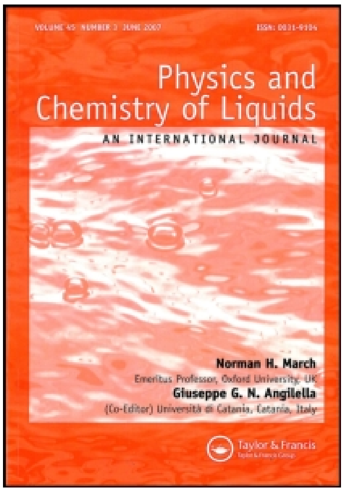

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N. H. March[a]; A. Nagy[b]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, UK [b] Institute for Theoretical Physics, Kossuth Lajos University, Debrecen, Hungary

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THEORY OF THE INHOMOGENEOUS ELECTRON LIQUID, TRANSCENDING HARTREE-FOCK

N. H. MARCH

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

A. NAGY

Institute for Theoretical Physics, Kossuth Lajos University,
Debrecen, H-4010, Hungary

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It is first pointed out that in the jellium model of the homogeneous electron liquid, the correlation energy E_c/N per particle can be directly related to the ratio of the single-particle kinetic energy T_s to the exchange energy A. The relevance of this result to the inhomogeneous electron liquid is then explored for light atoms. Such a relation again obtains, but with a markedly different coefficient of proportionality. With such a form of correlation energy, E_c, the Euler equation of density functional theory has somewhat reduced "coefficients" of $\delta T_s/\delta\rho(\mathbf{r})$ and $\delta A/\delta\rho(\mathbf{r})$. The Hartree–Fock Euler equation is regained by putting $E_c = 0$. Modified Slater–Kohn–Sham equations are obtained, their use being illustrated by an atomic example.

KEY WORDS: Wigner correlation energy, jellium model, effective mass.

1 INTRODUCTION

The very definition of correlation energy E_c, as given by Löwdin[1], relates to Hartree–Fock theory through

$$E_c = E_{\text{exact}} - E_{\text{HF}}. \tag{1.1}$$

Thus it would seem that the most natural generalization of Hartree–Fock (HF) theory to include correlation energy E_c would be to transcend the Euler equation of density functional theory:

$$\mu_{\text{HF}} = \frac{\delta T_s}{\delta\rho(\mathbf{r})} + V_{\text{Hartree}}(\mathbf{r}) + \frac{\delta A}{\delta\rho(\mathbf{r})}, \tag{1.2}$$

where

$$A = \frac{1}{4} e^2 \int \frac{[\rho(\mathbf{r}, \mathbf{r}')]^2}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \tag{1.3}$$

with $\rho(\mathbf{r}, \mathbf{r}')$ the off-diagonal generalization of $\rho_{\mathrm{HF}}(\mathbf{r})$ or the Dirac density matrix[2]. The subscript s in the kinetic energy is to keep track of its single-particle nature in Eq. (1.2).

The aim of the present work is therefore to propose an approximate modification of the Euler Eq. (1.2) for an inhomogeneous electron liquid to include the correlation energy E_c and which reduces to HF theory in the limit $E_c \to 0$. The basic idea underlying this approximate density functional theory is to relate E_c directly, by semi-empirical means eventually, to the single-particle quantities T_s and A in Eqs. (1.2) and (1.3). However, in view of the reliance of current practice in density functional theory[3-6] on the quantitative results of the jellium model of a homogeneous electron liquid, we have provided in Section 2 immediately below some first-principles motivation for the form of E_c to be adopted in the present approximate theory from the above model in the strong correlation limit.

2 RELATION BETWEEN CORRELATION ENERGY E_c AND RATIO T_s/A IN JELLIUM MODEL IN STRONG CORRELATION LIMIT

One of the focal points of density functional theory must be the approximation of the correlation energy E_c as a functional of the electron density. The simplest approximation, that for jellium, where interacting electrons move in a neutralizing non-responsive background of positive charge, is disappointing when applied to atoms[7].

Nevertheless, this model remains interesting as the only one to date in which the ground-state energy is known as a function of density; in this case the constant ρ_0, related to the interelectronic separation r_s measured in units of the Bohr radius a_0:

$$\rho_0 = 3/4\pi r_s^3 a_0^3. \tag{2.1}$$

Let us turn to relate this correlation energy to what is readily calculable, namely single-particle energies.

It is known that, in Rydberg per electron, the groundstate energy E of the jellium model can be quantitatively found. In the Hartree–Fock approximation, E_{HF} is calculated with a single Slater determinant of plane waves, with $\mathbf{k}$ vectors lying inside the Fermi sphere of radius k_f, related to ρ_0 by

$$\rho_0 = \frac{k_f^3}{3\pi^2}. \tag{2.2}$$

Wigner[8] pointed out more than half a century ago that in the extreme low density limit $r_s \to$ infinity, the ground-state energy per electron is quite different from the Hartree–Fock result:

$$\frac{E_{\mathrm{HF}}}{N} = \left(\frac{2.21}{r_s^2} - \frac{0.9}{r_s}\right) \mathrm{Ryd}, \tag{2.3}$$

which is in fact true as r_s tends to zero. In the low density limit Wigner found

$$\frac{E}{N} = -\frac{1.8}{r_s}. \tag{2.4}$$

Hence the correlation energy $E_c = E - E_{\mathrm{HF}}$ is given per electron by

$$\frac{E_c}{N} = -\frac{0.9}{r_s}, \tag{2.5}$$

in the limit of extreme low-density; r_s tends to infinity. One obvious thing to note is that, in this limit, the correlation energy is equal (to a certain numerical accuracy) to the exchange energy. In this strong correlation regime, the question raised by Robles and Kemister[9] as to whether the correlation energy is related to exchange energy can be answered in the affirmative; they are equal in fact in the Wigner electron crystal as r_s tends to infinity.

For reasons connected with the numerical study of atomic correlation energies given in Section 4 below, we shall, in fact, prefer to relate E_c/N to both the single-particle kinetic energy per electron T_s/N which is just the first term in Eq. (2.3), and the exchange energy. Then it is evident that one can write also

$$\frac{E_c}{N} = \text{constant } \frac{T_s}{A}, \tag{2.6}$$

where A/N is the exchange energy per electron given by the second term in Eq. (2.3).

3 CORRELATION ENERGY E_c RELATED TO SINGLE-PARTICLE KINETIC AND EXCHANGE ENERGIES IN LIGHT ATOMS

With the above result (2.6) on the low density limit of the homogeneous jellium model as motivation, the essential idea underlying the approximate density functional theory proposed in the present work is to modify the Hartree–Fock Euler equation (1.2) in the simplest possible manner, without introducing basically new quantities into the theory. As mentioned above, Robles and Kemister[9] have already raised the question as to whether correlation energy can be directly related to exchange energy. Here, with motivation as in Section 2 above, our basic assumption is that the correlation energy E_c can be directly related to a combination of single-particle energy T_s, and exchange energy A; i.e. to quantities already appearing in the Hartree–Fock Euler Eq. (1.2).

For light atoms, our basic assumption is then subsumed into the equation for the correlation energy per electron, E_c/N (See Eq. 2.6 in the low-density jellium model).

$$\frac{E_c}{N} = \text{constant}\ \frac{T_s}{A}. \tag{3.1}$$

While we anticipate, in the future, that refinements of Eq. (3.1) will have to be sought, we shall show that some interesting consequences for density functional theory of light atoms already follow from the simple linear assumption (3.1) between the correlation energy per electron and the ratio T_s/A of single-particle energies. We want to note here, however, that it is essential in utilizing Eq. (3.1) as the basis for transcending Hartree–Fock theory for light atoms, to determine the constant semi-empirically; the strong correlation limit of the jellium model set out above for motivation of Eq. (3.1) must not be used for this purpose. Thus, in Section 4 below, the formula (3.1) will be confronted with known atomic energies. Having thereby estimated the constant in the assumption (3.1) , Section 5 will transcend within the density functional framework the Hartree–Fock Euler Eq. (1.2).

4 CONFRONTATION WITH ATOMIC ENERGIES

In Table 1, we have recorded the correlation energies per electron in the second column, taken from the work of Clementi[10]. In the third column we record the Hartree–Fock exchange energy per electron A/N taken from the study of Lee and Parr[11], and in the fourth column the ratio E_c/A. This ratio has already been determined by Robles and Kemister[9] and found to be approximately $\frac{1}{40}$.

Table 1 Atomic energies, all per electron for neutral atoms, in Rydberg

$Z = N$	$-\frac{E_c}{N}$	$\frac{A}{N}$	$\frac{E_c}{A}$	$-\frac{T_s}{A}$	$\frac{E_c}{N}\Big/\frac{T_s}{A}$
He(2)	0.0425	1.026	0.0414	2.789	0.0152
Li(3)	0.0303	1.187	0.0255	4.173	0.0072
Be(4)	0.0473	1.333	0.0354	5.464	0.0086
B(5)	0.0499	1.498	0.0333	6.552	0.0076
C(6)	0.0522	1.681	0.0310	7.471	0.0070
N(7)	0.0529	1.885	0.0280	8.246	0.0064
O(8)	0.0645	2.044	0.0315	9.151	0.0070
F(9)	0.0716	2.223	0.0322	9.938	0.0072
Ne(10)	0.0780	2.422	0.0322	10.617	0.0073
Na(11)	0.0724	2.549	0.0284	11.547	0.0063
Mg(12)	0.0738	2.666	0.0277	12.481	0.0060
Al(13)	0.0738	2.780	0.0266	13.386	0.0055
Si(14)	0.0744	2.897	0.0257	14.243	0.0052
P(15)	0.0737	3.019	0.0244	15.049	0.0049
S(16)	0.0793	3.125	0.0254	15.899	0.0050
Cl(17)	0.0840	3.237	0.0260	16.701	0.0050
Ar(18)	0.0874	3.354	0.0261	17.453	0.0050

We turn next to the formula in terms of the kinetic energy T_s and the exchange energy A. The kinetic energy T_s is approximated by the negative of the total Hartree–Fock energy. T_s/A is recorded in the fifth column of Table 1 and the ratio of E_c/N to this in the sixth column. The values in the sixth column provide the constant in Eq. (3.1). It is approximately $\frac{1}{200}$ for atoms with $Z \geq 10$.

5 TRANSCENDING THE HF EULER EQUATION (1.2)

The argument below is based on the use of the form (3.1). One therefore writes

$$\frac{\delta E_c}{\delta \rho} = \frac{K}{A}\frac{\delta T_s}{\delta \rho} - \frac{K T_s}{A^2}\frac{\delta A}{\delta \rho}. \tag{5.1}$$

The generalized Euler equation of density functional theory then reads

$$\mu = \frac{\delta T_s}{\delta \rho} + V_{\text{Hartree}}(\mathbf{r}) + \frac{\delta A}{\delta \rho} + \frac{\delta E_c}{\delta \rho} \tag{5.2}$$

and substituting Eq. (5.1) into (5.2) one collects similar terms to obtain

$$\mu = \frac{\delta T_s}{\delta \rho}\left[1 + \frac{E_c}{T_s}\right] + V_{\text{Hartree}}(\mathbf{r}) + \frac{\delta A}{\delta \rho}\left[1 - \frac{E_c}{A}\right]. \tag{5.3}$$

The inclusion of electronic correlation energy is here seen to have the effect of "renormalizing" the single-particle kinetic energy and the exchange energy terms. Evidently, the Hartree–Fock method is regained when one takes the limit $E_c \to 0$. The "renormalization" in Eq. (5.3) is such as to reduce the kinetic* and exchange contributions since E_c and T_s are of opposite signs. If one "renormalized" the exchange term alone, then one would immediately be reminded of Slater's Xα method[4].

6 MODIFIED SLATER–KOHN–SHAM EQUATIONS FOR INHOMOGENEOUS ELECTRON LIQUID

The variation of the total energy functional

$$E = T_s + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + A + E_c \tag{6.1}$$

---

* The change in single-particle kinetic energy is like the introduction of an effective electronic mass $m \neq m_e$ due to electron correlation.

leads to the one-electron equations

$$-\left(1+\frac{K}{A}\right)\nabla^2 u_i + \left[v + 2\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + v_x\left(1 - K\frac{T_s}{A^2}\right)\right]u_i = \varepsilon_i u_i, \tag{6.2}$$

where v is the external potential and

$$v_x = \frac{\delta A}{\delta \rho} \tag{6.3}$$

is the exchange potential. Defining a "renormalized" Slater–Kohn–Sham potential

$$v^*_{SkS} = \frac{1}{1+\frac{K}{A}}\left\{v + 2\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + v_x\left(1 - K\frac{T_s}{A^2}\right)\right\} \tag{6.4}$$

and "renormalized" one-electron energies

$$\varepsilon_i^* = \frac{1}{1+\frac{K}{A}} \tag{6.5}$$

we obtain a set of Slater–Kohn–Sham equations

$$-\nabla^2 u_i + v^*_{SKS} u_i = \varepsilon_i u_i. \tag{6.6}$$

Given knowledge of K and v_x the modified Slater–Kohn–Sham equations can be solved.

7 SOLUTION OF THE MODIFIED SLATER–KOHN–SHAM EQUATIONS FOR LIGHT ATOMS

The exact forms of the exchange energy functional A and hence the exchange energy potential v_x are as yet unknown. There are however several approximate expressions for A and v_x. Here the so-called Xα exchange energy and potential will be adopted. The "renormalized" SKS Eq. (6.6) can be easily solved with appropriate modification of the standard Xα programme. Here, results for light atoms are presented. There are several ways to select the value of the parameter α in the Xα method. In the present context, the best choice seems to be the parameter $\alpha^{12}_{\mathrm{HF}}$, because it provides the Hartree–Fock total energy in the absence of the correlation functional E_c. The values of K can be calculated from Table 1 and are recorded in the second column of Table 2. The third column of Table 2 shows the total energy values obtained with

Table 2 Total energy determined using correlation parameter K compared with exact total energy. Also tabulated is the correlation parameter $\tilde{K}$ providing exact total energy and the exact correlation energy of the conventional theory and the correlation energy of the density functional theory calculated with the present method (in Rydberg)

$Z = N$	K	E	E_{exact}	$\tilde{K}$	E_c	E_c^{DF}
3	0.0218	−15.005	−14.956	0.0142	−0.091	−0.060
4	0.0344	−29.444	−29.335	0.0222	−0.189	−0.121
5	0.0381	−49.453	−49.308	0.0241	−0.249	−0.158
6	0.0419	−75.816	−75.691	0.0314	−0.313	−0.236
7	0.0449	−109.182	−109.172	0.0442	−0.370	−0.372
8	0.0564	−150.343	−150.135	0.0419	−0.516	−0.386
9	0.0648	−199.808	−199.463	0.0423	−0.644	−0.421
10	0.0735	−258.282	−257.875	0.0483	−0.780	−0.515

these parameters K. Comparing them with the exact total energies in the fourth column, we can see that the total energy is somewhat overestimated. The fifth column of Table 2 presents the parameter $\tilde{K}$ that yields the exact total energy.

Besides the correlation and the total energies we can study the electron density obtained from the solution of the "renormalized" SKS Eq. (6.6). Figure 1 presents

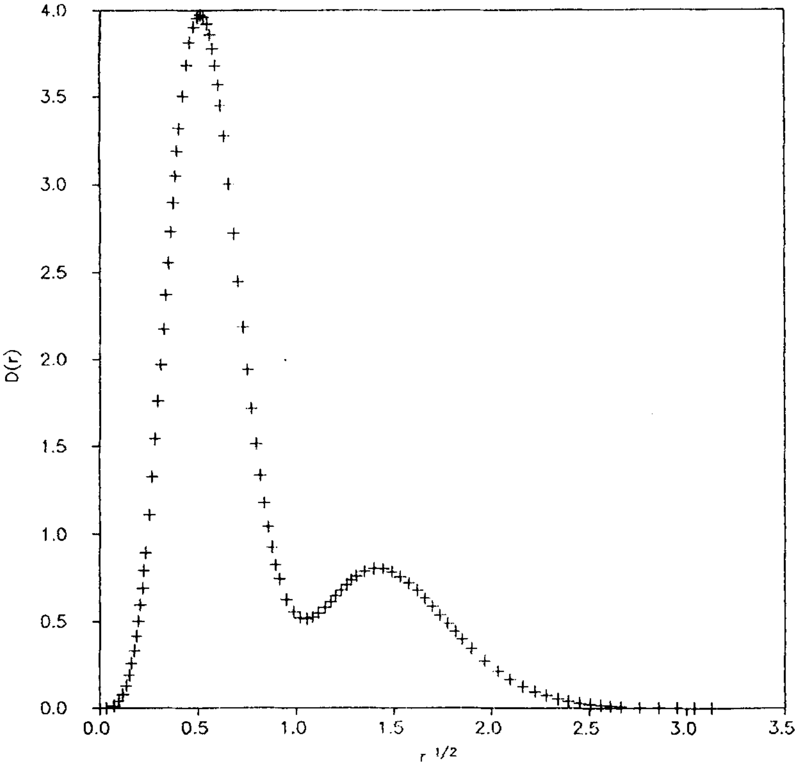

Figure 1 Radial electron density of Be atom with a radial scale which is linear with respect to $r^{1/2}$.

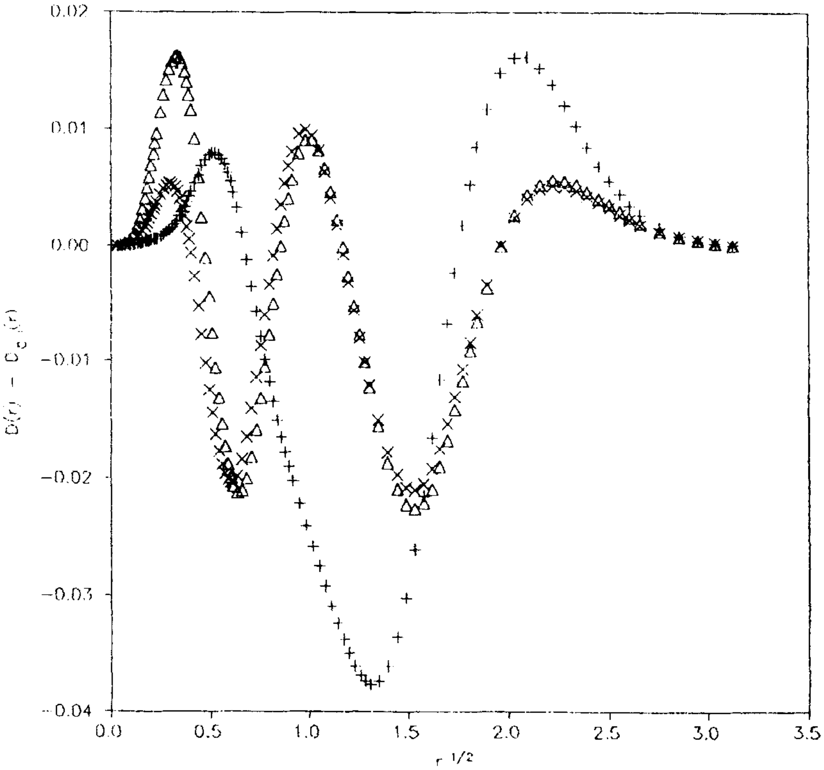

Figure 2 Radial electron density differences for Be atom with a radial scale which in linear with respect to $r^{1/2}$(Δ: $D(r) - D_{\mathrm{CI}}(r)$; $+$: $D_{\mathrm{HF}}(r) - D_{\mathrm{CI}}(r)$; $\times$: $D_{X\alpha_{\mathrm{HF}}} - D_{\mathrm{CI}}$).

the radial density $D(\mathbf{r}) = 4\pi\mathbf{r}^2\varphi(\mathbf{r})$ for the Be atom. Figure 2 shows the difference between radial densities of the present and CI methods $D(r) - D_{\mathrm{CI}}(\mathbf{r})$. For comparison, the deviation of the HF density from the CI density: $D_{\mathrm{HF}}(r) - D_{\mathrm{CI}}(\mathbf{r})$ and the $X\alpha_{HF}$ density from the CI density: $D_{X\alpha_{\mathrm{HF}}}(r) - D_{\mathrm{CI}}(\mathbf{r})$ are also plotted.

A test of radial densities is offered by the expectation values of powers of the radius. $\langle \mathbf{r}^2 \rangle$, $\langle \mathbf{r} \rangle$ and $\langle r^{-1} \rangle$ for the Be atom are presented in Table 3. (Total electron density here is normalized to 1.) For comparison the CI[13-14], HF and $X\alpha_{HF}$ data are also recorded. The present results and the $X\alpha_{HF}$ values are slightly better than the HF data.

Table 3 Expectation values of powers of the radius for Be atom calculated with the Hartree-Fock, CI, $X\alpha_{\mathrm{HF}}$ and the present method

	$\langle r^2 \rangle$	$\langle r \rangle$	$\langle r^{-1} \rangle$
HF	4.3297	1.5322	2.1022
CI	4.0814	1.4970	2.1062
$X\alpha_{\mathrm{HF}}$	4.1793	1.5081	2.1043
present method	4.1860	1.5083	2.1085

8 SUMMARY

The Euler equation of the approximate theory of the inhomogeneous electron liquid proposed in the present work is given in Eq. (5.3). Clearly, it reduces to the HF result (1.2) as the correlation energy E_c tends to zero. In Eq. (5.3), "renormalization" of the exchange term alone has some resemblance to Slater's Xα method. In the method proposed here the single-particle energies and the Slater–Kohn–Sham potential are also subject to some "renormalization" when electronic correlation is introduced.

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