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EXCHANGE-ONLY THEORY: RELATION BETWEEN EXCHANGE ENERGY, ITS FUNCTIONAL DERIVATIVE AND EIGENVALUE SUMS IN AN INHOMOGENEOUS ELECTRON LIQUID

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In earlier work (*Phys. Rev. A*, **55**, 3465, 1997) one of us (A.N.) has related the exchange-only potential designed to reproduce the Hartree–Fock density to the sum of the Slater potential and a term involving the difference between the eigenvalues of the Hartree–Fock (HF) and Kohn–Sham (KS) wave functions. Here, a consequence of this approximate theory is derived that relates the total exchange energy to its functional derivative and to the difference ΔE_s between the eigenvalue sums of the HF and KS schemes.

Keywords: Inhomogeneous electron liquid; exchange-only theory

In a recent paper [1], one of us (A.N.) has derived an approximate expression for the exchange potential $v_x(\mathbf{r})$ designed to reproduce the Hartree–Fock (HF) density. This result takes the form (see Eq. (35) of Ref. [1]):

$$v_x(\mathbf{r}) = v_s(\mathbf{r}) + \sum (\varepsilon_i^{\text{KS}} - \varepsilon_i^{\text{HF}}) |k_i(\mathbf{r})|^2, \quad (1)$$

where $v_s(\mathbf{r})$ is the so-called Slater potential, $\varepsilon_i^{\text{KS}}$ and $\varepsilon_i^{\text{HF}}$ are the KS and HF eigenvalues. The potential $v_x(\mathbf{r})$ is designed to reproduce exactly the

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Hartree-Fock ground-state density $\varrho_{\text{HF}}(\mathbf{r})$. Finally in Eq. (1) $\varrho(\mathbf{r})^{1/2}k_i = \psi_i$ is the KS wave function.

The exchange energy, A say, is given by

$$A = \frac{1}{2} \int v_S(\mathbf{r}) \varrho(\mathbf{r}) d\mathbf{r}. \quad (2)$$

Substituting for $v_S(\mathbf{r})$ in Eq. (2) using Eq. (1), the following expression is obtained, since

$$v_x(\mathbf{r}) = \frac{\delta A}{\delta \varrho(\mathbf{r})}; \quad (3)$$

$$\begin{aligned} A - \frac{1}{2} \int \varrho(\mathbf{r}) \frac{\delta A}{\delta \varrho(\mathbf{r})} d\mathbf{r} &= \frac{1}{2} \int \varrho(\mathbf{r}) \sum (\varepsilon_i^{\text{HF}} - \varepsilon_i^{\text{KS}}) |k_i(\mathbf{r})|^2 \\ &= \frac{1}{2} \int \sum (\varepsilon_i^{\text{HF}} - \varepsilon_i^{\text{KS}}) |\psi_i(\mathbf{r})|^2. \end{aligned} \quad (4)$$

The normalization of the KS wave functions ψ_i yields then

$$\begin{aligned} A - \frac{1}{2} \int \varrho(\mathbf{r}) \frac{\delta A}{\delta \varrho(\mathbf{r})} d\mathbf{r} \\ = \frac{1}{2} [E_S^{\text{HF}} - E_S^{\text{KS}}] = \frac{1}{2} \Delta E_S, \end{aligned} \quad (5)$$

where E_S^{HF} and E_S^{KS} are the eigenvalue sums over occupied states of the HF and KS energy levels respectively, while ΔE_S denotes the difference of the two sums. Of course, the result (5) evidently rests on the approximation (1) of Ref. [1].

Let us apply the result (5), first of all, to the Thomas–Fermi–Dirac statistical theory [2]. There,

$$A_{\text{Dirac-Slater}} = -c_x \int \varrho^{4/3} d\mathbf{r}; \quad (6)$$

where

$$c_x = \frac{3}{4} e^2 \left(\frac{3}{\pi} \right)^{1/3} \quad (7)$$

and hence

$$\frac{\delta A}{\delta \varrho(\mathbf{r})} = -\frac{4}{3} c_x \varrho^{1/3} : \quad (8)$$

and evidently

$$\int \varrho(\mathbf{r}) \frac{\delta A}{\delta \varrho(\mathbf{r})} d\mathbf{r} = \frac{4}{3} A. \quad (9)$$

Substituting this result (9) for a large number N of electrons into Eq. (5) yields

$$A_{\text{Dirac-Slater}} = \frac{3}{2} \Delta E_s. \quad (10)$$

We next note that the Levy-Perdew relation [3] relating A and $v_x(\mathbf{r})$ reads

$$\begin{aligned} A &= - \int \varrho(\mathbf{r}) \mathbf{r} \cdot \nabla \frac{\delta A}{\delta \varrho(\mathbf{r})} d\mathbf{r} \\ &= \int \varrho(\mathbf{r}) \frac{\delta A}{\delta \varrho(\mathbf{r})} \left(3 + \mathbf{r} \cdot \frac{\nabla \varrho}{\varrho} \right) d\mathbf{r}, \end{aligned} \quad (11)$$

where in the last step of Eq. (11) an integration by parts has been performed and the resulting contribution from the limits has been put equal to zero on physical grounds. Using Eqs. (5) and (11), one readily finds

$$\Delta E_s = \int \varrho(\mathbf{r}) \frac{\delta A}{\delta \varrho(\mathbf{r})} \left(5 + \mathbf{r} \cdot \frac{\nabla \varrho}{\varrho} \right) d\mathbf{r}, \quad (12)$$

which permits an estimate of ΔE_s in terms of the density and the functional derivative of the exchange energy with respect to the density.

It is well known that the exchange-only KS and the HF orbitals are very close (see [4, 5]). However, the orbital energies are different with the exception of the highest occupied orbital energy. The sum of these differences is given by Eq. (12). While the HF orbital energies provide an estimate for the ionization energies, the KS orbital energies approximate poorly the ionization energies. Slater [6] introduced the

transition-state method to obtain an adequate way of approximating the ionization energies with the help of the orbital energies.

Equation (12) gives the difference of the HF and KS orbital energy sum explicitly as a functional of the density. We know from an earlier work of Holas and March [4] that the Hartree-Fock total energy can be considered as the functional of the electron density. This is also true for the orbital energy sum.

The Dirac–Slater exchange energy is a homogeneous functional of degree $4/3$ in the density. Q is a homogeneous functional of degree k in the density if and only if

$$\int \varrho(\mathbf{r}) \frac{\delta Q}{\delta \varrho(\mathbf{r})} d\mathbf{r} = kQ. \quad (13)$$

Table I addresses the homogeneity issue. We calculate an effective homogeneity parameter

$$k_{\text{eff}}^x = \frac{1}{A} \int \varrho(\mathbf{r}) \frac{\delta A}{\delta \varrho(\mathbf{r})} d\mathbf{r}. \quad (14)$$

Using Eq. (5) the effective homogeneity parameter is given by

$$k_{\text{eff}}^x = 2 - \frac{\Delta E_s}{A}. \quad (15)$$

Very accurate exchange-only calculations have been performed using the method described earlier [7]. Hartree-Fock values were taken from [8]. The effective homogeneity parameter has been already determined for the exchange-correlation energy [9]. Equation (9) shows that the effective homogeneity parameter for exchange tends to $4/3$ for large number of electrons. As we can see from Table I. the effective homogeneity parameter still deviates from the statistical limit

TABLE I Hartree-Fock and exchange-only density functional orbital energy sums, their difference, exchange energy and the effective homogeneity parameter for exchange for neutral atoms (in Ry)

	E_s^{HF}	E_s^{DF}	ΔE_s	A	k_{eff}^x
Be	-20.17	-17.74	-2.43	-5.33	1.54
Ne	-149.02	-140.36	-8.67	-24.22	1.64
Ar	-650.08	-618.78	-31.30	-60.36	1.48
Kr	-3347.2	-3237.4	-109.8	-187.8	1.42

4/3 by some 6% for Kr with $N = 36$. Rewriting Eq. (15)

$$\Delta E_s = A(2 - k_{\text{eff}}^x). \quad (16)$$

we emphasize that the shift of the eigenvalue sum ΔE_s arises from the exchange and can be characterized by the exchange energy A and an effective homogeneity parameter k_{eff}^x .

A final comment concerns the relation to single-particle kinetic energy T_s . This can be established *via* the Euler equation [10] in the exchange-only approximation.

$$\mu = \frac{\delta T_s}{\delta \varrho(\mathbf{r})} + V_n + V_e + \frac{\delta A}{\delta \varrho(\mathbf{r})}, \quad (17)$$

where V_n denotes the potential due to the nuclei and V_e the classical electrostatic potential. Multiplying both sides of Eq. (17) by $\varrho(\mathbf{r})$ and integrating through the whole space yields

$$N\mu - \int \varrho(\mathbf{r}) \frac{\delta T_s}{\delta \varrho(\mathbf{r})} d\mathbf{r} = U_{en} + 2U_{ee} + \int \varrho(\mathbf{r}) \frac{\delta A}{\delta \varrho(\mathbf{r})} d\mathbf{r}, \quad (18)$$

where U_{en} is the electron-electron potential energy and U_{ee} is the classical electrostatic energy of $\varrho(\mathbf{r})$. Use of Eq. (5) in Eq. (18) leads to

$$N\mu - \int \varrho(\mathbf{r}) \frac{\delta T_s}{\delta \varrho(\mathbf{r})} d\mathbf{r} = U_{en} + 2U_{ee} + 2A - \Delta E_s. \quad (19)$$

To estimate $\int \varrho(\mathbf{r})(\partial T_s/\partial \varrho(\mathbf{r}))d\mathbf{r}$ from the known quantities on the RHS of Eq. (19), one has to approximate the chemical potential μ : for example by (the negative of) the electronegativity using Mulliken or Pauling forms.

In summary, a number of consequences flow from the approximate formula (1) in [1]. These are embodied in Eq. (5), in its large N limit in Eq. (10), the effective homogeneity parameter for exchange in Eq. (15) and in Eq. (19).

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Finally, we acknowledge the stimulation provided by work of Parr and Liu [11], who were concerned, however, with homogeneity scaling in density and the way assumptions about the degree of homogeneity affect the relations of T_s and potential energy contributions to their respective functional derivatives.

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