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Uniform electron gas limit of an exact expression for the Kohn–Sham exchange–correlation potential

Viktor N. Staroverov¹

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Abstract Previously, we derived an exact formula for the Kohn–Sham exchange–correlation potential corresponding, in the basis-set limit, to the Hartree–Fock electron density of a given system. This formula expresses the potential in terms of the occupied Hartree–Fock and Kohn–Sham orbitals and orbital energies. Here we show that, when applied to the Hartree–Fock description of a uniform electron gas, the formula correctly reduces to the exchange-only local density approximation.

Keywords Uniform electron gas · Local density approximation · Exchange–correlation potential · Hartree–Fock self-consistent field

1 Introduction

Some time ago, we devised a method for constructing the Kohn–Sham (KS) exchange–correlation (XC) potential corresponding, in the basis-set limit, to the electron density generated by a ground-state Hartree–Fock (HF) wave function [1, 2]. Here we will denote this potential by $v_{XC}^{HF}(\mathbf{r})$ and call it “HFXC potential” for short. The method is based on an exact expression for $v_{XC}^{HF}(\mathbf{r})$ in terms of the occupied HF and KS orbitals and orbital energies of the system. (An equivalent expression had been also derived by Nagy [3] and Miao [4].) Using this method we showed that HFXC potentials obtained from finite-basis-set HF wave functions of atoms and molecules at equilibrium geometries can serve

as excellent approximations to the corresponding basis-set-limit exchange-only optimized effective potentials (OEPs) [1, 2]. (Hollins *et al.* [5] later suggested that HFXC potentials might differ from exchange-only OEPs for strongly correlated systems.) Subsequently, we generalized our approach to correlated wave functions, which made it possible to generate accurate atomic and molecular exchange–correlation potentials at various level of *ab initio* theory [6–12].

The purpose of this work is to demonstrate an anticipated but non-obvious result: that the somewhat intricate expression for $v_{XC}^{HF}(\mathbf{r})$ derived in Ref. 1 reduces to the local density approximation (LDA) exchange-only potential when the HFXC formula is applied to a uniform electron gas (UEG) described at the HF level of theory. All equations below are written using atomic units.

2 HFXC potential

Consider a spin-unpolarized ground-state N -electron system. In the notation of Ref. 11, its HFXC potential is given by

$$v_{XC}^{HF}(\mathbf{r}) = v_S^{HF}(\mathbf{r}) + \bar{\epsilon}^{KS}(\mathbf{r}) - \bar{\epsilon}^{HF}(\mathbf{r}) + \frac{\tau_P^{HF}(\mathbf{r})}{\rho^{HF}(\mathbf{r})} - \frac{\tau_P^{KS}(\mathbf{r})}{\rho^{KS}(\mathbf{r})}, \quad (1)$$

where

$$v_S^{HF}(\mathbf{r}) = -\frac{1}{2\rho^{HF}(\mathbf{r})} \int \frac{|\rho^{HF}(\mathbf{r}; \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2)$$

is the Slater exchange–hole charge potential [13], in which $\rho^{HF}(\mathbf{r}; \mathbf{r}')$ is the HF one-electron spin-free reduced density matrix,

$$\bar{\epsilon}^{KS}(\mathbf{r}) = \frac{2}{\rho^{KS}(\mathbf{r})} \sum_{i=1}^{N/2} \epsilon_i^{KS} |\phi_i^{KS}(\mathbf{r})|^2 \quad (3)$$

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is the average local KS orbital energy, and

$$\bar{\varepsilon}^{\text{HF}}(\mathbf{r}) = \frac{2}{\rho^{\text{HF}}(\mathbf{r})} \sum_{i=1}^{N/2} \varepsilon_i^{\text{HF}} |\phi_i^{\text{HF}}(\mathbf{r})|^2 \quad (4)$$

is the average local HF orbital energy; $\rho^{\text{KS}}(\mathbf{r})$ and $\rho^{\text{HF}}(\mathbf{r})$ are, respectively, the usual KS and HF expressions for the same total electron density,

$$\rho^{\text{KS}}(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\phi_i^{\text{KS}}(\mathbf{r})|^2 \quad (5)$$

and

$$\rho^{\text{HF}}(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\phi_i^{\text{HF}}(\mathbf{r})|^2. \quad (6)$$

The quantities

$$\tau_P^{\text{HF}}(\mathbf{r}) = \frac{2}{\rho^{\text{HF}}(\mathbf{r})} \sum_{i < j}^{N/2} |\phi_i^{\text{HF}}(\mathbf{r}) \nabla \phi_j^{\text{HF}}(\mathbf{r}) - \phi_j^{\text{HF}}(\mathbf{r}) \nabla \phi_i^{\text{HF}}(\mathbf{r})|^2 \quad (7)$$

and

$$\tau_P^{\text{KS}}(\mathbf{r}) = \frac{2}{\rho^{\text{KS}}(\mathbf{r})} \sum_{i < j}^{N/2} |\phi_i^{\text{KS}}(\mathbf{r}) \nabla \phi_j^{\text{KS}}(\mathbf{r}) - \phi_j^{\text{KS}}(\mathbf{r}) \nabla \phi_i^{\text{KS}}(\mathbf{r})|^2 \quad (8)$$

are the HF and KS Pauli kinetic energy densities. Note that the upper summation limit in Eqs. (3)–(8) is $N/2$ rather than N ; this accounts for the different prefactors compared to the corresponding equations of Ref. 11.

The KS orbitals and their eigenvalues appearing in Eq. (1) are initially unknown and are determined by solving the KS equations with $v_{\text{XC}}^{\text{HF}}(\mathbf{r})$ using the usual self-consistent-field procedure with convergence acceleration [14]: we treat Eq. (1) as a formula for a model KS potential (cf Refs. 15–17), start with some initial guess for $\phi_i^{\text{KS}}(\mathbf{r})$ and $\varepsilon_i^{\text{KS}}$, and iterate the KS eigenvalue problem until self-consistency.

As explained in Refs. 10 and 18, if Eq. (1) were implemented using a complete (infinite) basis set, then $\rho^{\text{HF}}(\mathbf{r})$ and $\rho^{\text{KS}}(\mathbf{r})$ would automatically satisfy the KS condition at convergence,

$$\rho^{\text{KS}}(\mathbf{r}) = \rho^{\text{HF}}(\mathbf{r}). \quad (9)$$

In a finite basis set, Eq. (9) is weakly violated even at convergence. The discrepancy between $\rho^{\text{HF}}(\mathbf{r})$ and the final $\rho^{\text{KS}}(\mathbf{r})$ depends on the basis set and tends to zero in the basis-set limit [10]. This fact is of no consequence here because the present work concerns exact analytic expressions rather than their practical implementation.

3 Uniform electron gas limit of the HFXC potential

The UEG is an infinitely extended system with a constant electron density. Usually, the UEG is considered to be the same as jellium—an infinitely extended system of interacting electrons with a constant neutralizing background potential, but no uniformity constraint on the electron density. Lewin and co-workers [19, 20] recently suggested that those two systems are not necessarily identical. Here we follow the traditional approach [21, 22], in which the UEG is assumed to have a constant background potential.

Equation (1) is exact in the HF limit for any system. Therefore, it should reduce to the LDA exchange potential when applied to the HF description of a UEG. That is, if $\rho^{\text{KS}}(\mathbf{r}) = \rho^{\text{HF}}(\mathbf{r}) = \rho(\mathbf{r}) = \text{const}$, then one should have

$$v_{\text{XC}}^{\text{HF}}(\mathbf{r}) = v_{\text{X}}^{\text{LDA}}(\mathbf{r}), \quad (10)$$

where

$$v_{\text{X}}^{\text{LDA}}(\mathbf{r}) = -\frac{k_F(\mathbf{r})}{\pi} \quad (11)$$

and

$$k_F(\mathbf{r}) = [3\pi^2 \rho(\mathbf{r})]^{1/3} \quad (12)$$

is the Fermi momentum. This can be shown as follows.

Method 1. Consider a paramagnetic (spin-unpolarized) UEG in a cube of volume V . In the standard treatment of a UEG [21, 22], where the UEG is identified with jellium, the sum of the electron-electron and background-background electrostatic repulsion potentials is canceled by the electron-background attraction, so the HF equations become

$$\left[-\frac{1}{2} \nabla^2 + \hat{K} \right] \phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}^{\text{HF}} \phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r}), \quad (13)$$

where \hat{K} is the Fock exchange operator and \mathbf{k} is the wavevector of the state $\phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r})$. The solutions to Eq. (13) are plane waves

$$\phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (14)$$

with the eigenvalues [21, 22]

$$\varepsilon_{\mathbf{k}}^{\text{HF}} = \frac{k^2}{2} - \frac{k_F}{\pi} f(k), \quad (15)$$

where

$$f(k) = 1 + \frac{k_F^2 - k^2}{2kk_F} \ln \left| \frac{k_F + k}{k_F - k} \right|. \quad (16)$$

It is interesting to note that the spin-restricted HF wave function of jellium is unstable with respect to spin-polarization and symmetry breaking [22–24]. However, only the spin-restricted solution is characterized by a uniform density, so it is the one of relevance here.

The KS description of the UEG is formally simpler: the exchange-only KS equations are [25]

$$\left[-\frac{1}{2}\nabla^2 + v_X^{\text{LDA}}(\mathbf{r}) \right] \phi_{\mathbf{k}}^{\text{KS}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}^{\text{KS}} \phi_{\mathbf{k}}^{\text{KS}}(\mathbf{r}), \quad (17)$$

where the orbitals are also plane waves

$$\phi_{\mathbf{k}}^{\text{KS}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (18)$$

but the eigenvalues are different:

$$\varepsilon_{\mathbf{k}}^{\text{KS}} = \frac{k^2}{2} - \frac{k_F}{\pi}. \quad (19)$$

To evaluate the UEG limit of Eq. (1), we proceed term by term. The Slater potential of a UEG is given by [25, 26]

$$v_S^{\text{HF}}(\mathbf{r}) = -\frac{3}{2} \frac{k_F(\mathbf{r})}{\pi}. \quad (20)$$

The HF and KS Pauli kinetic energies of the UEG are equal because $\phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r}) = \phi_{\mathbf{k}}^{\text{KS}}(\mathbf{r})$. Therefore,

$$\frac{\tau_P^{\text{HF}}(\mathbf{r})}{\rho(\mathbf{r})} - \frac{\tau_P^{\text{KS}}(\mathbf{r})}{\rho(\mathbf{r})} = 0. \quad (21)$$

To evaluate the contribution of the average local orbital energies, we note that

$$|\phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r})|^2 = |\phi_{\mathbf{k}}^{\text{KS}}(\mathbf{r})|^2 = \frac{1}{V}. \quad (22)$$

This implies that $\bar{\varepsilon}^{\text{KS}}$ and $\bar{\varepsilon}^{\text{HF}}$ are constant functions for a UEG, just like ρ and k_F . From Eqs. (3) and (4),

$$\bar{\varepsilon}^{\text{KS}} - \bar{\varepsilon}^{\text{HF}} = \frac{2}{\rho V} \sum_{|\mathbf{k}| \leq k_F} (\varepsilon_{\mathbf{k}}^{\text{KS}} - \varepsilon_{\mathbf{k}}^{\text{HF}}). \quad (23)$$

Replacing the sum over \mathbf{k} with an integral and considering that the number of states lying within a volume element $d\mathbf{k}$ of \mathbf{k} -space is $(V/8\pi^3)d\mathbf{k}$, we obtain

$$\bar{\varepsilon}^{\text{KS}} - \bar{\varepsilon}^{\text{HF}} = \frac{2}{\rho V} \frac{V}{8\pi^3} \int_{|\mathbf{k}| \leq k_F} (\varepsilon_{\mathbf{k}}^{\text{KS}} - \varepsilon_{\mathbf{k}}^{\text{HF}}) d\mathbf{k}. \quad (24)$$

Next we substitute Eqs. (15) and (19) into Eq. (24) and switch to spherical polar coordinates. This gives

$$\bar{\varepsilon}^{\text{KS}} - \bar{\varepsilon}^{\text{HF}} = \frac{1}{\pi^2 \rho} \frac{k_F}{\pi} \int_0^{k_F} k^2 [f(k) - 1] dk, \quad (25)$$

where $f(k)$ is defined by Eq. (16). Evaluating the integral, substituting $\rho = k_F^3/3\pi^2$, and reintroducing the \mathbf{r} -dependence of ρ (i.e., by making the transition to the LDA), we have

$$\bar{\varepsilon}^{\text{KS}}(\mathbf{r}) - \bar{\varepsilon}^{\text{HF}}(\mathbf{r}) = \frac{1}{2} \frac{k_F(\mathbf{r})}{\pi}. \quad (26)$$

Finally, by combining Eqs. (20), (21), and (26) we arrive at

$$v_{\text{XC}}^{\text{HF}}(\mathbf{r}) = -\frac{k_F(\mathbf{r})}{\pi}. \quad (27)$$

Method 2. Let us multiply Eq. (13) by $2\phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r})^*$, sum over \mathbf{k} , and divide the sum by $\rho(\mathbf{r}) = 2\sum_{|\mathbf{k}| \leq k_F} |\phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r})|^2$. The result of these manipulations is

$$\bar{\varepsilon}^{\text{HF}}(\mathbf{r}) = \frac{\tau_L^{\text{HF}}(\mathbf{r})}{\rho(\mathbf{r})} + v_S^{\text{HF}}(\mathbf{r}), \quad (28)$$

where we have introduced the quantity

$$\tau_L^{\text{HF}}(\mathbf{r}) = - \sum_{|\mathbf{k}| \leq k_F} \phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r})^* \nabla^2 \phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r}) \quad (29)$$

and used the fact that, by definition [13],

$$v_S^{\text{HF}}(\mathbf{r}) = \frac{2}{\rho(\mathbf{r})} \sum_{|\mathbf{k}| \leq k_F} \phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r})^* \hat{K} \phi_{\mathbf{k}}^{\text{HF}}(\mathbf{r}). \quad (30)$$

Similarly, from Eq. (17) we have

$$\bar{\varepsilon}^{\text{KS}}(\mathbf{r}) = \frac{\tau_L^{\text{KS}}(\mathbf{r})}{\rho(\mathbf{r})} + v_X^{\text{LDA}}(\mathbf{r}), \quad (31)$$

where

$$\tau_L^{\text{KS}}(\mathbf{r}) = - \sum_{|\mathbf{k}| \leq k_F} \phi_{\mathbf{k}}^{\text{KS}}(\mathbf{r})^* \nabla^2 \phi_{\mathbf{k}}^{\text{KS}}(\mathbf{r}). \quad (32)$$

Given that $\tau_L^{\text{HF}}(\mathbf{r}) = \tau_L^{\text{KS}}(\mathbf{r})$, subtraction of Eq. (28) from Eq. (31) produces

$$\bar{\varepsilon}^{\text{KS}}(\mathbf{r}) - \bar{\varepsilon}^{\text{HF}}(\mathbf{r}) = v_X^{\text{LDA}}(\mathbf{r}) - v_S^{\text{HF}}(\mathbf{r}). \quad (33)$$

Substituting this result into Eq. (1) and using Eq. (21) we arrive directly at Eq. (10). Although this method appears simpler than the first, it is actually less constructive because it merely retraces the general derivation [1] of Eq. (1) for a particular system—the UEG.

4 Concluding remarks

Generalization of the HFXC method to spin-unrestricted HF wave functions is straightforward [1]. Using the above approach it would be easy to show that the spin-up and spin-down HFXC potentials also reduce to the respective local spin-density approximation potentials in the UEG limit.

Apart from the UEG, Eq. (1) can also be simplified for one- and singlet two-electron systems such as ground-state He, Li⁺, H₂, H₃⁺, etc. The KS description of such systems involves only one occupied KS orbital, so the KS quantities in Eq. (1) either drop out or become constants and it becomes possible to write the exchange-correlation potential in terms of interacting wave-function quantities alone (see Refs. 11 and Ref. 27 for details). For $N = 2$, the resulting formulas provide direct access to the exact KS correlation potential and as such they can be very useful for studying correlation effects in real and model two-electron systems [28–32].

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