On the relationship between the Kohn-Sham potential, the Pauli potential, and the Exact Electron Factorization

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Abstract

The one-electron density of a many-electron system corresponds to the ground state of a one-electron Schrödinger equation with an effective potential $v$. This potential can be constructed in two ways: In Orbital-Free Density Functional Theory, it is the sum of the Kohn-Sham (KS) potential and the Pauli potential, where the latter can be expressed in terms of the KS system of non-interacting electrons. In the Exact Electron Factorization (EEF), it is the sum of terms which are invariant with respect to a gauge freedom in the theory. The two formalisms also differ in that that KS potential is not explicitly known even when the many-electron wavefunction is available, while the EEF potential is. We compare the two constructions of the potential and provide a physical interpretation of contributions to $v$ in the EEF, which are illustrated with numerical studies of one-dimensional two- and three-electron systems. We find that features of $v$ can be explained with the conditional wavefunction that shows how the electron in the one-electron theory is entangled with the other electrons implicitly present in $v$. Our work thus sheds a different light on the mapping of a many-electron system to a one-electron system and provides a construction of $v$ which does not rely on KS quantities.

1 Introduction

The quantum-mechanical solution of the many-electron problem in molecular systems is difficult but important for a variety of applications. Thus, in the last decades many clever theoretical developments have been made to solve this problem. One such development, Density Functional Theory (DFT), has been immensely successful in describing static and time-dependent properties of molecules and solids [1-2].

The central idea of the most widely used variant of DFT, KS-DFT [3], is to map an interacting many-electron system to a fictitious system of non-interacting electrons, the Kohn-Sham (KS) system, such that both systems have the same one-electron density $\rho(r)$. As the electrons in the KS system are non-interacting, the many-electron problem is effectively reduced to a one-electron problem. To determine the KS system, the one-electron KS potential $v_{KS}(r)$ is needed, which is typically treated as a functional of $\rho(r)$ or of the KS orbitals, i.e., of the eigenfunctions of $v_{KS}(r)$. The functional dependence of $v_{KS}(r)$ is not completely known but suitable approximations allow to describe systems with a number of electrons accurately enough to answer many questions of physical and chemical relevance.

A related approach is orbital-free DFT (OF-DFT), where the many-electron problem is also mapped to a one-electron problem, but in a different way [4-5]. OF-DFT is based on the observation that $\sqrt{\rho(r)}$ is a wavefunction which can be obtained as eigenstate of a one-electron Schrödinger equation with an effective potential $v(r)$ [6-9]. Compared to KS-DFT, where the Schrödinger equation for many KS orbitals needs to be solved, OF-DFT avoids the need to calculate excited states of the one-electron Schrödinger equation and hence promises to be computationally very efficient and applicable for large systems. Thus, there has been recent interest in understanding the properties of $v(r)$, or, alternatively, of the Pauli potential

$$v^P(r) = v(r) - v_{KS}(r) \quad (1)$$

as the difference potential between the potentials used in OF-DFT and KS-DFT [10-21].

Although the usual approach in OF-DFT is to view the effective potential $v(r)$ as functional of the one-electron density, OF-DFT has an interesting advantage: In contrast to the KS potential $v_{KS}(r)$, a general equation for the potential $v(r)$ in terms of quantities derived from the many-electron wavefunction can be given explicitly. To obtain this equation, the $N$-electron wavefunction is written as a product of a marginal wavefunction ($\sqrt{\rho(r)}$ up to a possibly $r$-dependent phase) and a conditional wavefunction. The marginal wavefunction depends only on the coordinate of one electron and is an eigenstate of the
same one-electron Schrödinger equation that is the basic equation of OF-DFT \[22\]. The conditional wavefunction is an \((N - 1)\)-electron wavefunction which depends on the coordinates of \(N - 1\) electrons, and, also, parametrically on the coordinates of the remaining electron of the \(N\)-electron system. From the conditional wavefunction, the potential \(v(r)\) can be obtained which appears in the one-electron Schrödinger equation of OF-DFT \[23, 24\]. The separation of a wavefunction into a marginal and a conditional part has recently been reconsidered in the Exact Factorization formalism for electron-nuclear systems \[25–27\] and has been transferred to the many electron problem as Exact Electron Factorization (EEF) \[28,29\], with a focus on time-dependent problems.

While OF-DFT and the EEF are both based on a one-electron Schrödinger equation with the same potential \(v(r)\), the way how this potential is constructed is different: OF-DFT focuses on the construction of \(v(r)\) given in (1) as a sum of the well-studied KS-potential and the Pauli potential, where the latter can be explicitly expressed in terms of the eigensystem of the KS-potential. Thus, this construction is based on a fictitious system of non-interacting electrons, the KS system. In the EEF, \(v(r)\) is a functional of the conditional wavefunction and is obtained naturally as a sum of terms that are gauge-invariant with respect to a gauge freedom of the theory. Hence, \(v(r)\) is constructed from quantities of the full interacting system of electrons. With our article, we want to illuminate the relation between the two constructions of \(v(r)\). For this purpose, we first briefly review the relevant notions of KS-DFT, the EEF, and OF-DFT in Section 2. Then, in Section 3 a model of an atom and of a diatomic is studied and the features of the contributions to \(v(r)\) are analyzed and explained in terms of KS and EEF quantities, respectively. Finally, in Section 4 we discuss aspects of the model studies and their implications.

2 Theory

2.1 KS-DFT

For simplicity, we use atomic units and we consider the ground state of a system of \(N\) non-relativistic spinless electrons (fermions). To be precise, we consider the solution \(\psi(r_1, \ldots, r_N)\) of a non-relativistic many-electron Hamiltonian for some external potential. This solution is antisymmetric w.r.t. exchange of any two electronic coordinates \(r_j\) and has the lowest possible energy. The generalization to include electron spin and excited states is straightforward but complicates the equations, hence it will not be discussed here. For brevity, we abbreviate the electronic coordinates sometimes with numbers, e.g. \(\psi(r_1, \ldots, r_N) \equiv \psi(1, \ldots, N)\). The considered Schrödinger equation is

\[
\left( -\sum_{j=1}^{N} \nabla_{j}^{2} + V(1,\ldots,N) \right) \psi(1,\ldots,N) = E\psi(1,\ldots,N) \tag{2}
\]

with scalar potential

\[
V(1,\ldots,N) = \sum_{j=1}^{N} V^{\text{ext}}(j) + \sum_{j=1}^{N} \sum_{k=j+1}^{N} V^{\text{ee}}(j,k) \tag{3}
\]

that is the sum of single-electron (external) potentials \(V^{\text{ext}}(r)\) and the electron-electron interaction \(V^{\text{ee}}(r_j, r_k)\).

In KS-DFT, the interacting many electron system is replaced by a non-interacting many-electron system, the KS system, with the same one-electron density as the interacting problem. The wavefunction of the KS system is

\[
\psi^{\text{KS}}(1,\ldots,N) = \hat{A} \left( \prod_{j=1}^{N} \phi_{j}^{\text{KS}}(j) \right) \tag{4}
\]

where \(\hat{A}\) is an anti-symmetrization operator defined such that \(\langle \psi^{\text{KS}} \mid \psi^{\text{KS}} \rangle = 1\). The KS orbitals \(\phi_{j}^{\text{KS}}(r)\) are obtained by solving the single-electron Schrödinger equation

\[
\left( -\nabla_{r}^{2} / 2 + v^{\text{KS}}(r) \right) \phi_{j}^{\text{KS}}(r) = \epsilon_{j}^{\text{KS}} \phi_{j}^{\text{KS}}(r). \tag{5}
\]

with KS potential

\[
v^{\text{KS}}(r) = v^{\text{HXC}}(r) + V^{\text{ext}}(r). \tag{6}
\]
The potential \( v^{\text{HXC}} \) is usually written as a sum of the Hartree potential and the exchange-correlation potential. The one-electron density of the interacting system is given by

\[
\rho(r) := \langle \psi(r, 2, \ldots, N) | \psi(r, 2, \ldots, N) \rangle_{2 \ldots N} \equiv \frac{1}{N} \sum_{j=1}^{N} |\varphi_j^{\text{KS}}(r)|^2, \tag{7}
\]

where \( \langle \cdot \rangle_{2 \ldots N} \) denotes the scalar product w.r.t. coordinates \( r_2, \ldots, r_N \). In contrast to the usual convention of normalizing the one-electron density to the number of electrons, we assume that \( \langle \psi | \psi \rangle = \langle \rho(r) \rangle = \langle |\varphi_j^{\text{KS}}(r)|^2 \rangle = 1 \), i.e., the many-electron wavefunction, the one-electron density, and the Kohn-Sham orbitals are all normalized to 1. While the KS system exists and is unique \([30]\), the KS potential \( v^{\text{KS}}(r) \) cannot be directly obtained from the many-electron wavefunction \( \psi(r) \) and/or the one-electron density. Different numerical methods exist to find the exact \( v^{\text{KS}}(r) \) for a given one-electron density, and some recent discussions and applications of this inverted KS problem can be found in \([31–34]\).

### 2.2 EEF

The EEF is another exact one-electron theory that describes the interacting many-electron system. It is based on the ansatz

\[
\psi(1, \ldots, N) = \chi(1) \phi(2, \ldots, N; 1) \tag{8}
\]

where

\[
|\chi(r)|^2 := \langle \psi(r, 2, \ldots, N) | \psi(r, 2, \ldots, N) \rangle_{2 \ldots N} \equiv \rho(r) \tag{9}
\]

is the one-electron density. As the one-electron density is the marginal density of finding an electron at \( r \) independent of the location of the other electrons, \( \chi(r) \) is called the marginal amplitude. The function

\[
\phi(2, \ldots, N; r) := \frac{\psi(r, 2, \ldots, N)}{\chi(r)} \tag{10}
\]

is the conditional amplitude whose squared magnitude, \( |\phi(2, \ldots, N; r)|^2 \), represents the conditional probability of finding electrons at \( r_2, \ldots, r_N \), given an electron is at \( r \). Thus, it has to obey the partial normalization condition

\[
\langle \phi(2, \ldots, N; r) | \phi(2, \ldots, N; r) \rangle_{2 \ldots N} = 1 \tag{11}
\]

for all values of \( r \). The conditional amplitude \( \phi(2, \ldots, N; r) \) is the wavefunction of the electrons at \( r_2, \ldots, r_N \) under the condition that another electron is at \( r \), hence we call those electrons the conditioned electrons. From the ansatz \([8]\) follows that \( \chi(r) \) obeys a one-electron Schrödinger equation \([25–28]\)

\[
\left( \frac{(-i\nabla_r + A(r))^2}{2} + v(r) \right) \chi(r) = E\chi(r) \tag{12}
\]

with vector potential

\[
A(r) = \langle \phi(2, \ldots, N; r) | -i\nabla_r \phi(2, \ldots, N; r) \rangle_{2 \ldots N} \tag{13}
\]

and with scalar potential

\[
v(r) = v^T(r) + v^V(r) + v^G(r) + V^{\text{ext}}(r) \tag{14}
\]

that contains the terms

\[
v^T(r) = \left\langle \phi(2, \ldots, N; r) \right| - \sum_{j=2}^{N} \frac{\nabla_j^2}{2} \phi(2, \ldots, N; r) \right\rangle_{2 \ldots N} \tag{15}
\]

\[
v^V(r) = \left\langle \phi(2, \ldots, N; r) \right| V(1, 2, \ldots, N) \left| \phi(2, \ldots, N; r) \right\rangle_{2 \ldots N} - V^{\text{ext}}(r) \tag{16}
\]

\[
v^G(r) = \frac{1}{2} \left( \langle \nabla_r \phi(2, \ldots, N; r) | \nabla_r \phi(2, \ldots, N; r) \rangle - A^2 \right) \tag{17}
\]

It will be useful for the discussion below to define the sums

\[
v^H(r) = v^T(r) + v^V(r) \tag{18}
\]

\[
v^{\text{EEF}}(r) = v^H(r) + v^G(r). \tag{19}
\]
The term $\psi^T(r)$ is the average kinetic energy of the $N - 1$ conditioned electrons and $\psi^V(r)$ is the corresponding average potential energy, hence $\psi^H(r)$ can be thought of as average energy of the conditioned electrons given one additional electron is at $r$. The geometric potential $v^G(r)$ measures how much the conditional wavefunction $\phi$ changes with respect to $r$. Together with $A(r)$, it describes the reaction of the conditioned electrons on an infinitesimal position change of the additional electron at $r$, and it is related to the Pubini-Study metric as well as to the quantum geometric tensor [35]. We note that we call both potentials $v(r)$ and $v^{\text{EEF}}(r)$ the EEF potential below, as they only differ by the external potential $V^{\text{ext}}(r)$.

From the ansatz (5) the one-electron wavefunction $\chi(r)$ is defined only up to a phase, because using

$$\tilde{\chi}(r) := e^{-iS(r)}\chi(r)$$  
(20)

$$\tilde{\phi}(2, \ldots, N; r) := e^{-iS(r)}\phi(2, \ldots, N; r)$$  
(21)

with $S(r) \in \mathbb{R}$ instead of $\chi(r)$ and $\phi(2, \ldots, N; r)$ leaves the many-electron wavefunction $\psi(1, \ldots, N)$ as well as the determining equations for $\chi$ (equation (12)) and $\tilde{\phi}$ (see the Supplemental Material of [28]) invariant if $A(r)$ is replaced with $\tilde{A}(r) = A(r) + \nabla_r S(r)$. The choice of $S(r)$ is arbitrary, it is a gauge freedom of the theory. Hence, the important quantities of the theory need to be gauge invariant, i.e., they cannot depend on the choice of $S(r)$. The potentials $v^T(r)$, $v^V(r)$, and $v^G(r)$ have this property. Also, $-i\nabla_r + A(r)$ is the gauge-invariant canonical momentum and $\frac{1}{2}(-i\nabla_r + A(r))^2 + v^G(r)$ is the gauge-invariant kinetic energy of an electron in the interacting $N$-electron system.

The EEF can be useful because the many-electron problem is replaced by the one-electron problem [12] for the one-electron wavefunction $\chi(r)$. If the (components of the) potentials $v(r)$ and $A(r)$ were known, one-electron observables of the many-electron system (like dipole or momentum) could directly be calculated from the knowledge of $\chi(r)$, and the energy of the many-electron system $E$ could be obtained. In contrast to DFT, in the EEF formalism an expression for the needed one-electron potentials is known explicitly in terms of the conditional wavefunction $\phi$ (or in terms of the full many-electron wavefunction $\psi$). However, the equation for $\phi$ is difficult to solve [36], hence the explicit equations for the one-electron potentials are not immediately useful and suitable approximations need to be found.

### 2.3 OF-DFT

The EEF equation (12) is equivalent to the central equation of OF-DFT,

$$\left(-\nabla_r^2 + v^{\text{KS}}(r) + v^P(r)\right)\sqrt{\rho(r)} = \mu \sqrt{\rho(r)}$$  
(22)

where $\mu = \epsilon^\text{KS}_N$ is the chemical potential (the eigenvalue of the highest occupied KS orbital) and $v^P(r)$ is the Pauli potential. From (1) we see that (22) is identical to the EEF equation (12) if we fix the gauge as $A(r) = 0$ and if $\chi(r) = \sqrt{\rho(r)}$, i.e., if $\chi(r)$ is real-valued. This gauge choice cannot always be made [37,38] but is possible for the ground state of the many-electron system with zero total angular momentum and possibly also for other states without total angular momentum. Then, the EEF potential is related to KS and Pauli potential via

$$v(r) - E = v^{\text{KS}}(r) + v^P(r) - \mu$$  
(23)

or

$$v^{\text{EEF}}(r) - E = v^{\text{HXC}}(r) + v^P(r) - \mu.$$  
(24)

As $E$ and $\mu$ are constants, we write

$$v(r) \simeq v^{\text{KS}}(r) + v^P(r)$$  
(25)

$$v^{\text{EEF}}(r) \simeq v^{\text{HXC}}(r) + v^P(r)$$  
(26)

where $f(x) \simeq g(x)$ means that $f(x) = g(x) + c$ for some constant $c$.

The Pauli potential can be written in terms of the KS system as [9,21]

$$v^P(r) = v^{\text{PH}}(r) + v^{\text{PG}}(r)$$  
(27)

\(^1\)The gauge $A(r) = 0$ implies that the vector potential is curl-free in any gauge. This condition may be violated even if the total angular momentum vanishes, hence we cannot make a definite statement here.
\[ v_{PH}(r) = \sum_{n=1}^{N} (\epsilon_{n}^{KS} - \epsilon_{n}^{KS})(\phi_{n}^{KS}(r))^{2} \]  
\[ v_{PG}(r) = \frac{1}{2} \sum_{n=1}^{N} |\nabla_{r}\phi_{n}^{KS}(r)|^{2} \]

where we defined the scaled KS orbitals

\[ \phi_{n}^{KS}(r) = \frac{\phi_{n}(r)}{\sqrt{\rho(r)}}. \]  

We chose to denote these functions as \( \phi_{n}^{KS} \) because they are similar to the conditional wavefunction \( \phi \) of the EEF. We could also use the conditional wavefunction \( \phi_{n}^{KS}(2, \ldots, N; r) = \psi_{KS}(r, 2, \ldots, N) \sqrt{\rho(r)} \).

When we interpret the EEF potentials \( v_{H} = v^{T} + v^{V} \) and \( v_{G} \) defined in (15), (16) and (17), respectively, as functionals \( v_{H}[\phi] \) and \( v_{G}[\phi] \) of the conditional wavefunction \( \phi \), we can write

\[ v_{PH}(r) = v_{H}[\phi^{KS}](r) \]  
\[ v_{PG}(r) = v_{G}[\phi^{KS}](r). \]

This illustrates the similarity of the two parts of the Pauli potential with the corresponding parts of the EEF potential. The reason why we can work with the scaled KS orbitals \( \phi_{n}^{KS}(r) \) instead of the full conditional KS-wavefunction \( \phi_{n}^{KS}(r) \) is the orthogonality of the KS-orbitals \( \phi_{n}^{KS}(r) \) which simplifies the functional dependencies in expressions for the potentials.

Consequently, we can relate \( v_{PH}(r) \) and \( v_{PG}(r) \) to the terms appearing in the EEF potential (14) by comparison to a non-interacting many-electron system. For such a system, \( v_{H}^{X}(r) \simeq 0 \) and \( v_{ext}^{X}(r) \simeq v_{KS}(r) \). We chose \( V_{ext}^{X}(r) = v_{KS}(r) + \sum_{n=1}^{N-1} \epsilon_{n}^{KS} \). Then, parts of the EEF potential become the corresponding terms of the Pauli potential in (27),

\[ v_{H}(r) \to v_{PH}(r) \]  
\[ v_{G}(r) \to v_{PG}(r). \]

Hence, there is an exact correspondence between the gauge-invariant parts of the EEF potential, which are defined in terms of the exact conditional wavefunction, and the parts of the Pauli potential expressed in terms of the KS orbitals, for the limiting case of a non-interacting wavefunction.

3 Models

All model systems described in the following were solved numerically with the program package QMstunftì, which is based on the sparse-matrix functionality of Scipy, which in turn uses partially the ARPACK library. The KS potentials were obtained from the inversion procedure used in [42], see also [43]. We chose the gauge of zero vector potential, which is always possible for one-dimensional finite systems.

3.1 One-dimensional atom

As the EEF scalar potential \( v_{EEF}(r) \) is the sum of \( v_{H}^{X}(r) \) and the Pauli potential \( v_{P}(r) \), the question is relevant how \( v_{PH}(r) \) and \( v_{PG}(r) \) for the non-interacting KS system differ from their counterparts \( v_{H}(r) \) and \( v_{G}(r) \) for the interacting system. This is investigated in the following with the help of simple numerically solvable model systems.

The first investigated system is a one-dimensional model of an \( N \)-electron atom with Hamiltonian

\[ H_{a}^{(N)} = \sum_{j=1}^{N} \left( -\frac{\partial^{2}}{2} + V_{ex}(x_{j}) + \lambda \sum_{k=j+1}^{N} V_{ex}(x_{j}, x_{k}) \right), \]  

where we defined the scaled KS orbitals
Figure 1: (a) EEF/OF-DFT potential $v$ with one-electron density $\rho$ (shifted to its energy $E$) and (b) KS potential $v^{KS}$ with the two occupied KS orbitals $\phi_{KS}^{j}$ (shifted to their eigenvalues $\varepsilon_{j}^{KS}$) for (c) the wavefunction $\psi(x_1, x_2)$ of the one-dimensional two-electron atom ($\lambda = 1$) shown as contour plot (color indicates the sign). (d) The corresponding conditional wavefunction $\phi(x_2; x_1)$ is shown as similar contour plot. Panels (e) and (f) depict the contributions to $v$ in OF-DFT (Hartree-exchange-correlation potential $v^{HXC}$ and the two parts of the Pauli potential $v^{PH}$ and $v^{PG}$) and in the EEF (average potential $v^{H}$ and geometric potential $v^{G}$) for a non-interacting ($\lambda = 0$, (e)) and an interacting ($\lambda = 1$, (f)) system, together with the external potential $V^{ext}$. 
where the interactions between nuclei and electrons is described with the soft-Coulomb potential

\[ V^\text{ext}(x) \equiv V_{\text{en}}(x) = \frac{-N}{\sqrt{x^2 + c_{\text{en}}}} \]  

and the interactions between the electrons is described with the soft-Coulomb potential

\[ V_{\text{ee}}(x_1, x_2) = \frac{1}{\sqrt{(x_1 - x_2)^2 + c_{\text{ee}}}}. \]  

The parameter \( \lambda \) modifies the strength of the electron-electron interaction. We considered an \( N = 2 \) electron atom with parameters \( c_{\text{en}} = c_{\text{ee}} = 0.5a_0^2 \) and an \( N = 3 \) electron atom with parameters \( c_{\text{en}} = c_{\text{ee}} = 0.25a_0^2 \). As stated above, we discuss here and in the following the ground states of a system of spinless electrons, i.e. the lowest totally antisymmetric eigenstates of \( H_{\text{EE}}^N \). Additionally, for the 3-electron system we also considered the energetically lowest doublet state. However, we found that the results do not differ qualitatively for all these states and systems, hence only the 2-electron system is discussed here. Some information about the 3-electron system can be found in the appendix.

Panel (c) of Figure 1 shows a contour plot of the state of interest, i.e., the energetically lowest antisymmetric eigenfunction \( \psi \) of \( H_{\text{EE}}^{(2)} \) for \( \lambda = 1 \). Panels (a), (b), and (d) of that figure show quantities of that state which appear in KS-DFT and in the EEF/OF-DFT. The conditional wavefunction \( \rho \) shown in panel (d) looks qualitatively similar to \( \psi \) in the region close to the nucleus \( x_1 = 0 \) but differs for larger \( |x_1| \). In particular, the limit \( |x_1| \to \infty \) of \( \rho(x_2; x_1) \) is the lowest eigenstate of the singly-ionized system. The EEF potential \( v \) is shown in panel (a), together with the one-electron density \( \rho(x_1) = |\chi(x_1)|^2 \) of the state \( \psi(x_1, x_2) \), where \( \chi \) is also the energetically lowest eigenstate of \( v \). Local maxima at \( |x| \approx 1a_0 \) are visible in \( v \) which reflect the electronic structure. In contrast, the KS potential \( v_{\text{KS}} \) (shown in panel (b) together with the relevant KS orbitals) looks like a soft-Coulomb potential, although it can also have additional structure like local maxima for other states of the two-electron system \([44]\). The figures illustrate that the EEF potential with its eigenfunction \( \chi \) describe the electronic structure in a different (but not too different) way than the KS potential with its KS orbitals, even though both yield the same one-electron density.

In panels (e) and (f) of Figure 1 the different contributions to the potential \( v \) in the EEF and in OF-DFT are shown for the non-interacting system \( \lambda = 0 \) and for the interacting system \( \lambda = 1 \). While there is a repulsive contribution from the Hartree-exchange-correlation potential \( v_{\text{HXC}} \) around the nucleus for interacting electrons, this contribution is zero for non-interacting electrons which only feel the external potential but not the presence of each other. As discussed above, for \( \lambda = 0 \) we have the identities \( v_{\text{PG}} \simeq v^G \) and \( v_{\text{PH}} \simeq v^H \) between the parts of the Pauli potential and the parts of the EEF potential, which is illustrated in panel (e). Interestingly, similar equalities seem also to hold for the interacting system if \( 0 < \lambda < 1.6 \) and if \( v_{\text{HXC}} \) is taken into account. A larger \( \lambda \) was not used for numerical reasons, as the wavefunction becomes very delocalized and a large grid would be necessary to describe it correctly. Closer inspection reveals that there are small difference of maximally 0.03 \( E_0 \) between the quantities for \( \lambda > 0 \), i.e.,

\[ v_{\text{PG}} \sim v^G \]

\[ v_{\text{PH}} + v_{\text{HXC}} \sim v^H \]  

where \( f(x) \sim g(x) \) means \( f(x) \approx g(x) + c \) for some constant \( c \). The similarities (39) can be found also for the other studied models, as discussed below.

We note that the Pauli potential \( v_{\text{PH}}(x_1) + v_{\text{PG}}(x_1) \) is essentially a repulsive bell-shaped function centered at \( x_1 = 0 \). This additional potential in the region of the nucleus is the reason why the EEF potential \( v(x_1) \) has local maxima at \( |x_1| \approx 1a_0 \) while the KS potential \( v_{\text{KS}} \) has not such maxima. The single peak of \( v_{\text{PG}} \) and of the geometric potential \( v^G \) itself also splits into two peaks for ca. \( \lambda > 1.4 \) due to delocalization of the electronic wavefunction.

### 3.2 One-dimensional homonuclear diatomic molecule

As a second example, we consider a one-dimensional model of a diatomic molecule with two electrons. The Hamiltonian is

\[ H_{\text{m}}^{(Z)}(R) = \sum_{j=1}^{2} \left( -\frac{\partial^2}{2} + V_{\text{en}}(x_j; R, Z) + \sum_{k=j+1}^{N} V_{\text{ee}}(x_j, x_k) \right) + V_{\text{nn}}(R, Z), \]  

(40)
where the electron-nuclear interaction is given by

\[
V_{en}(x; R, Z) = -\frac{Z}{\sqrt{(x + R/2)^2 + c_{en}}} - \frac{1}{\sqrt{(x - R/2)^2 + c_{en}}},
\]

the electron interaction is given by (38), and the nuclear interaction is given by

\[
V_{nn}(R, Z) = \frac{Z}{\sqrt{R^2 + c_{nn}}}.
\]

The external potential for this model is

\[
V^{\text{ext}}(x) = V_{en}(x; R, Z) + V_{nn}(R, Z).
\]

The parameters are \(c_{en} = c_{ee} = 0.5a_0^2\) and \(c_{nn} = 0.1a_0^2\). The two nuclei are located at \(\pm R/2\) and thus have an internuclear distance of \(R\). We first consider the homonuclear (symmetric) case where one nucleus at \(+ R/2\) has a charge \(+1\) and the other nucleus at \(- R/2\) also has charge \(Z = +1\).

Figure 2: (top) KS potential \(v^{KS}\) and occupied KS orbitals \(\phi^{KS}_j\) (shifted to their corresponding eigenvalues \(\varepsilon^{KS}_j\)) as well as (bottom) EEF/OF-DFT potential \(v\) and one-electron density \(\rho\) (shifted to its energy) for the homonuclear two-electron diatomic molecule with internuclear distance \(R = 5a_0\).

Figure 2 shows the EEF potential together with the one-electron density as well as the KS potential together with the two lowest KS-orbitals for an internuclear distance of \(R = 5a_0\). The KS-orbitals are almost degenerate and look like typical tunneling states of a double well potential, with the wavefunction of the energetically lower state having the same sign in both wells, while the wavefunction of the energetically higher state switches the sign at \(x_1 = 0\). The EEF potential and the KS potential look similar, but the EEF potential has a higher barrier at \(x_1 = 0\).

The components of the EEF potential \(v\) are depicted in panels (a), (b), and (c) Figure 3 for the internuclear distances \(R = 2a_0\), \(R = 5a_0\), and \(R = 8a_0\), respectively. For \(R = 2a_0\) the two electrons are relatively close to each other which is reflected in the contributions to \(v\): All parts of \(v\) except the external potential \(V^{\text{ext}}\) are repulsive bell-shaped potentials centered around \(x_1 = 0\).

Like for the atomic model, the parts which \(v\) is composed of in OF-DFT and in the EEF are similar, i.e., (39) is valid. However, some differences of up to 0.08 \(E_h\) exists, with \(v^{PG}\) being slightly smaller than \(v^G\) and \(v^{PH} + v^{\text{HXC}} - \varepsilon^{KS}_1\) being slightly larger than \(v^H - E\).

If the interatomic distance \(R\) is increased, the system becomes that of two separated one-electron atoms and the two electrons do not interact with each other anymore. Consequently, \(v^{\text{HXC}}\) quickly becomes zero with increasing \(R\) and \(v^{PH} \sim v^H\) like for a non-interacting system. The average energy \(v^H\) (or \(v^{PH}\)) becomes more and more a constant shift to the potential: It is the energetic contribution of the conditioned electron at \(x_2\) to the potential felt by the electron at \(x_1\), and the wavefunction \(\phi(x_2; x_1)\) of
the conditioned electron is approximately the ground state of one of the separated atoms. This is visible in \( \phi(x_2; x_1) \), shown in panels (d), (e), and (f) of Figure 3. As \( \phi(x_2; x_1) \) is the wavefunction of one electron at \( x_2 \) given there is another one at \( x_1 \), we have that for a large internuclear distance \( R \) the electron at \( x_2 \) is either located at one nucleus or at the other. For \( R = 8 \ a_0 \), given one electron of the two-electron system is e.g. found at \( x_1 < -2 \), it is likely to “originate” from the nucleus at \( x_1 = -4 \ a_0 \). The other electron is thus most likely found at the other nucleus centered around \( x_2 = +4 \ a_0 \) and \( \phi(x_2; x_1) \) corresponds to the ground state of that electron at that nucleus. Similarly, if one electron of the two-electron system is found at \( x_1 > +2 \), the conditional wavefunction \( \phi(x_2; x_1) \) of the other electron is that of the ground state centered around \( x_2 = -4 \ a_0 \).

The peak of the geometric potential \( v^G \) (or \( v^PG \)) becomes somewhat more localized at \( x_1 = 0 \) and also slightly higher with increasing internuclear distance. This potential describes how strong the conditional wavefunction \( \phi(x_2; x_1) \) of the conditioned electron changes if the other electron is moved along \( x_1 \). There is a large change in the conditional wavefunction only at \( x_1 \approx 0 \) which is reflected in \( v^G \) as peak in this region. If the internuclear distance is increased, the system becomes more and more that of two separated atoms and the change of the conditional wavefunction at \( x_1 \approx 0 \) becomes sharper. We emphasize that this effect has nothing to do with the sign change of \( \phi(x_2; x_1) \) along \( x_1 \) as can been seen from the definition \(^{(1)}_{17}\) of \( v^G \). It is for example also present in the symmetric ground state of \( H^{(1)}_{in} \) for which no sign change happens in \( \phi(x_2; x_1) \).

### 3.3 One-dimensional heteronuclear diatomic molecule

The third considered system is a model of a heteronuclear (asymmetric) diatomic molecule. For this purpose, we use \( Z = 2 \) in the Hamiltonian \(^{[40]}\), such that there is one nucleus at \(+R/2\) with charge +1 and one nucleus at \(-R/2\) with charge +2.

Figure 4 shows the KS potential together with the relevant KS orbitals as well as the EEF potential together with the one-electron density for an internuclear distance of \( R = 5 \ a_0 \). The lowest KS orbital \( \varphi^1_{KS} \) is localized around \( x_1 = -2.5 \ a_0 \) (where the nucleus with charge +2 is) while the highest occupied KS orbital \( \varphi^0_{KS} \) is localized around \( x_1 = +2.5 \ a_0 \) (where the nucleus with charge +1 is). Like for the homonuclear diatomic, the EEF potential and the KS potential look somewhat similar. In particular, there is a barrier between the potential wells at the location of the nuclei and there is an additional
quantities and the OF-DFT quantities are once more visible. The geometric potential \( v \) the case of the homonuclear diatomic, with a bell-shaped maximum centered at \( x \). Those contributions are depicted in panels (a), (b), and (c) of Figure 5 for the internuclear distances individual contributions to the potentials.

\[
\begin{align*}
R & \quad \phi
\end{align*}
\]

For \( \phi \) qualitative change of the conditional wavefunction \( \phi(x_2; x_1) \) along \( x_1 \). For \( R = 5 a_0 \) this second change is at \( x_1 \approx -8 a_0 \). If an electron is found somewhere in \(-8 < x_1 < 0 a_0\), we see from \( \phi(x_2; x_1) \) that the second electron is most probably found around \( x_2 = 2.5 a_0 \), corresponding to the location of the nucleus with charge +1. In contrast, if an electron is found at \( x_1 < -8 a_0 \), the second electron is found around \( x_2 = -2.5 a_0 \) which corresponds to the nucleus with charge +2. The larger the internuclear distance \( R \) becomes, the more does this transition move to smaller values of \( x_1 \). Mechanistically, this transition is a kind of charge transfer where the electron at \( x_2 \) switches from the energetically higher potential well to the lower well depending on where the other electron at \( x_1 \) is located. A close look at the potentials for \( R = 5 a_0 \) reveals that this charge transfer, which is a qualitative change in the conditional wavefunction \( \phi(x_2; x_1) \), is visible in the \( v^G \), albeit barely: The change happens over a rather large interval along \( x_1 \) compared to the change at \( x_1 \approx 0 \) and thus leads only to a comparably small but broad local increase in \( v^G \).

The average energy \( v^H \) of the conditioned electron, or, equivalently, \( v^{\text{HXC}} + v^{\text{PH}} \), shows also an interesting behavior: While it constitutes an asymmetric barrier between the nuclei for small internuclear distances, a plateau emerges for larger internuclear distances with a step at \( x_1 \approx 0 \) and a second step at smaller and larger \( x_1 \) the larger \( R \) becomes. This behavior was recently discussed for the KS potential and for the Pauli potential \( 21 \) in terms of the KS quantities. Like all features of the EEF and KS potentials, it can be seen as result of a change in the behavior of the density. In the KS picture, the density in the left potential well is dominated by \( \psi^0 \). However, \( \psi^1 \) is more delocalized, hence at some point around \( x_1 \approx -8 a_0 \) the dominant contribution to the density switches from \( \psi^0 \) (for \( x > -8 a_0 \)) to \( \psi^1 \) (for \( x < -8 a_0 \)). This switch can easily be seen in a logarithmic plot of the density, see panels (g), (h), and (i) of Figure 5 and it is also the reason why the density is asymptotically always dominated by the highest occupied KS orbital.

Another interpretation of the steps and plateaus can be given with the help of the EEF, as these features are related to the change of the conditional wavefunction. As just discussed, the wavefunction \( \phi(x_2; x_1) \) of the electron at \( x_2 \) depends on at which value of \( x_1 \) the other electron is found: It is either localized at the nucleus with charge +1 or at the nucleus with charge +2. These two situations correspond to
Figure 5: Panels (a), (b), (c): Contributions to $v$ in the EEF and in OF-DFT for different internuclear distances $R$ of the heteronuclear two-electron diatomic molecule. Panels (d), (e), (f): Conditional wavefunctions $\phi(x_2; x_1)$ corresponding to the panels above, shown as contour plots (color indicates the sign). Panels (g), (h), (i): Logarithmic plot of the one-electron density $\rho$ and the density of the KS orbitals corresponding to the panels above.
different average energies $v^H(x_1)$ of the conditioned electron at $x_2$, which each cause essentially a constant shift of $v$. Hence, there is a step in $v(x_1)$ along $x_1$ whenever the electron transfer between the two nuclei occurs.

4 Discussion

When OF-DFT and KS-DFT are compared, a typical point of discussion is how the two theories treat the fermionic antisymmetry of a many-electron system. The symmetry constraints for the many-electron wavefunction $\psi(1, \ldots , N)$ are included in an elegant way in KS-DFT via the construction of the non-interacting KS system, which has the same one-electron density like the interacting system, but which also corresponds to an antisymmetric many-electron wavefunction $\psi^{KS}(1, \ldots, N)$. OF-DFT, in contrast, is sometimes interpreted as mapping to a non-interacting bosonic system with the same one-body density. The Pauli potential may thus be viewed as the difference potential between the non-interacting fermionic and bosonic systems.

While the construction of the non-interacting bosonic system is technically correct, the EEF provides a rather different interpretation: It splits the joint $N$-electron wavefunction into a product of a one-electron wavefunction $\chi$ experiencing a potential due to the implicit presence of the other electrons (the marginal wavefunction) and and $(N-1)$-electron wavefunction $\phi$ which depends conditionally on the location of the remaining electron. The fermionic antisymmetry constraints are unbroken: The wavefunction $\phi$ of the $N-1$ conditioned electrons fulfills antisymmetry constraints with respect to exchange of the electronic (spin- & spatial) coordinates. The antisymmetry constraints with respect to the additional electron, however, are found in the product $\chi(1)\phi(2, \ldots, N; 1)$ but are otherwise only implicitly contained in the EEF formalism.

In the EEF picture, there is thus no Pauli potential which turns a (non-interacting) fermionic system into a bosonic system, but the interacting fermionic system itself is considered. The central quantity which determines the features of the effective one-electron potential $v$ in the EEF is thus the conditional wavefunction $\phi(2, \ldots, N; 1)$, which represents the spatial entanglement of the conditioned electrons on the electron at $r_1$. As demonstrated with the model systems, this function is a useful tool for the interpretation of the features of the EEF/OF-DFT potential $v(r)$ because it provides a direct physical picture of the behavior of the conditioned system, which in turn provides the relevant potential in the one-electron picture. In particular, the origin of the charge-transfer step discussed previously for the KS-potential [42] becomes immediately obvious: If the system can be described as being composed of subsystems (e.g. atoms in a molecule), there can be a qualitative change of the (conditional) wavefunction depending on where one electron is localized. Our example model of a diatomic molecule showed this clearly when $\phi(x_2; x_1)$ changes depending on whether the electron at $x_1$ is associated with one nucleus or the other. This effect of the electron repulsion is thus truly a charge transfer process, although meant in a conditional sense without any additional external time parameter. Nevertheless, $\phi$ is in principle also an $N$-dimensional function. It is thus difficult to obtain and to analyze for a many-electron system, and much more still needs to be learned about its behavior.

On the level of the potentials, we found for our models the interesting correspondence between the quantities $v^G$ and $v^H$ of the interacting system and the quantities $v^{PG}$ and $v^{PH} + v^{HXC}$ constructed from the non-interacting KS system. In particular, $v^G \sim v^{PG}$ corresponds to

$$
\frac{1}{2} \sum_{n=1}^{N} (\nabla_r \phi^{KS}_n(r))^2 \sim \frac{1}{2} (\nabla_r \psi(r, 2, \ldots, N))^2_{2 \ldots N}
$$

where the left-hand side of (44) is the kinetic energy density of the KS system and the right-hand side of (44) is the kinetic energy density of the exact system. Thus, we conclude that for our models that the Hartree-exchange-correlation term $v^{HXC}$ describes the different average energies of the conditioned non-interacting and interacting systems. However, the wavefunctions of our model are well described within the Hartree-Fock approximation and hence can be represented accurately by a system of non-interacting electrons. It remains to be seen how the comparison changes in situations where the Hartree-Fock approximation fails.

In summary, we have investigated the construction of the one-electron potential $v$ that yields the exact one-electron density of a many-electron system from the perspective of OF-DFT and of the EEF. Correspondence of the components of $v$ in the two theories was found, it was shown that there is a clear interpretation of the EEF quantities, and features of $v$ could be explained mechanistically as a conditional charge transfer by considering the conditional wavefunction of the studied few-electron models. Our work
thus offers a new perspective on the reduction of the many-electron problem to a one-electron problem and is laying the foundation for further investigations of the involved potentials beyond low-dimensional model systems.

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A Additional information for the atomic model

In the discussion of the one-dimensional model of an atom in section 3 it was mentioned that we also studied two states of the three-electron Hamiltonian $H^{(3)}_a$. Those states are the energetically lowest doublet state and the lowest fully antisymmetric eigenstate.

![Figure 6: Contributions to the potential $v$ in the EEF and in OF-DFT for the energetically lowest antisymmetric eigenstate of the model of a three-electron atom, for two values of the electron-electron interaction parameter $\lambda$.](image)

The contributions to $v$ for these states are very similar to the contributions for the lowest antisymmetric eigenstate of the two-electron. Figure 6 illustrates this for the lowest fully antisymmetric eigenstate of $H^{(3)}_a$, for two different values of the parameter $\lambda$ which controls the electron-electron interaction.