Treatments of the exchange energy in density-functional theory

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Abstract: Following a recent work [Gál, Phys. Rev. A 64, 062503 (2001)], a simple derivation of the density-functional correction of the Hartree-Fock equations, the Hartree-Fock-Kohn-Sham equations, is presented, completing an integrated view of quantum mechanical theories, in which the Kohn-Sham equations, the Hartree-Fock-Kohn-Sham equations and the ground-state Schrödinger equation formally stem from a common ground: density-functional theory, through its Euler equation for the ground-state density. Along similar lines, the Kohn-Sham formulation of the Hartree-Fock approach is also considered. Further, it is pointed out that the exchange energy of density-functional theory built from the Kohn-Sham orbitals can be given by degree-two homogeneous $N$-particle density functionals ($N=1,2,...$), forming a sequence of degree-two homogeneous exchange-energy density functionals, the first element of which is minus the classical Coulomb-repulsion energy functional.

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I. Introduction

Density-functional theory (DFT) [1,2] forms the exact theoretical background for particle-density based approaches to the quantum mechanical many-body problem, such as theories of the Thomas-Fermi kind [3-7] and of the Slater kind [8-10]. The main idea behind DFT is to replace the quantum mechanical wave-function with the particle density as basic variable from which all properties of a quantum system can be gained, which means the use of density functionals instead of wave-function functionals. This idea is justified for ground states formally by the Hohenberg-Kohn theorems [11], but in practical applications DFT appears as an approximative theory because of the lack of knowledge of an exact expression for the ground-state energy density functional

\[ E_v[\rho] = F[\rho] + \int \rho(\vec{r})v(\vec{r})d\vec{r}, \quad (1) \]

the minimum position of which gives the ground-state density for a given external potential \( v(\vec{r}) \) and particle number

\[ N = \int \rho(\vec{r})d\vec{r}, \quad (2) \]

yielding the Euler equation

\[ \frac{\delta E_v[\rho]}{\delta N \rho(\vec{r})} = 0, \quad (3a) \]

or

\[ \frac{\delta F[\rho]}{\delta \rho(\vec{r})} + v(\vec{r}) = \mu \]  

(with \( \mu \) being the Lagrange multiplier corresponding to the \( N \)-conserving constraint on \( \rho(\vec{r}), \) Eq.(2)), for the determination of the ground-state density. In Eq.(1), \( F[\rho], \) characteristic to the interaction between the (identical) Fermions of the considered system, is a universal functional of the density \( \rho(\vec{r}) \) [not depending on the external potential, \( v(\vec{r}) \)], which represents the unknown in \( E_v[\rho]. \)

To treat a major part of \( F[\rho] \) exactly, the Kohn-Sham (KS) method [12] introduces single-particle orbitals \([ u_i(\vec{r}) ]\) into DFT, separating in \( F \) the kinetic energy
\[ T_s = \int \sum_{i=1}^{N} u_i^*(\vec{r}) \left( -\frac{1}{2} \nabla^2 \right) u_i(\vec{r}) \, d\vec{r} \]  

(4)

of a ground-state system of noninteracting fermions with the density \( \rho(\vec{r}) \) of the given interacting fermion system, getting a set of single-particle equations,

\[ -\frac{1}{2} \nabla^2 u_i(\vec{r}) + v_{KS}(\vec{r}) u_i(\vec{r}) = \varepsilon_{KS}^i u_i(\vec{r}) \quad i=1,\ldots,N \]  

(5)

with

\[ v_{KS}(\vec{r}) = \frac{\delta(F[\rho] - T_s[\rho])}{\delta \rho(\vec{r})} + \nu(\vec{r}) , \]  

(6)

for the determination of the (ground-state) density

\[ \rho(\vec{r}) = \sum_{i=1}^{N} u_i^*(\vec{r}) u_i(\vec{r}) , \]  

(7)

instead of using Eq.(3) directly. With the subtraction of the classical Coulomb repulsion

\[ J[\rho] = \frac{1}{2} \int \rho(\vec{r}) \rho(\vec{r}') \frac{d\vec{r}d\vec{r}'}{|\vec{r} - \vec{r}'|} \]  

(8)

from \( F[\rho] - T_s[\rho] \),

\[ F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] , \]  

(9)

then only the relatively small exchange-correlation (xc) part of the energy remains to be approximated. The exchange part of \( E_{xc} \) is usually defined by

\[ E_x = -\frac{1}{2} \int \sum_{i,j=1}^{N} \frac{u_i^*(\vec{r}) u_j(\vec{r}) u_j^*(\vec{r}') u_i(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}d\vec{r}' . \]  

(10)

A further reduction of need for approximation can be achieved by utilizing the definition Eq.(10) of the exchange energy by single-particle orbitals, and setting up the single-particle equations

\[ -\frac{1}{2} \nabla^2 u_i(\vec{r}) - \sum_{j=1}^{N} \frac{u_j(\vec{r}) u_j^*(\vec{r}') u_i(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' + v_{HFKS}(\vec{r}) u_i(\vec{r}) = \varepsilon_{HFKS}^i u_i(\vec{r}) \quad i=1,\ldots,N , \]  

(11)

with the local (multiplicative) potential

\[ v_{HFKS}(\vec{r}) = \frac{\delta(F[\rho] - T_{s,\text{HFKS}}[\rho] - E_{s,\text{HFKS}}[\rho])}{\delta \rho(\vec{r})} + \nu(\vec{r}) = \frac{\delta J[\rho]}{\delta \rho(\vec{r})} + \frac{\delta E_{xc,\text{HFKS}}[\rho]}{\delta \rho(\vec{r})} + \nu(\vec{r}) , \]  

(12)

which gives a density-functional correction of the Hartree-Fock (HF) equations, yielding the Hartree-Fock-Kohn-Sham method [12,13]. The solutions \( \{u_i(\vec{r})\}_{i=1}^{N} \) of the
different sets of single-particle equations, Eqs.(5) and (11), corresponding to the same \( \rho(\vec{r}) \), are different. Note that though with the HFKS approach a higher degree of exactness of practical calculations can be reached, it means another step of backing away from a pure density-functional theory; in addition to the introduction of orbitals, now a nonlocal potential appearing. (The next step would be to ”introduce” many-particle wave-functions to treat correlation exactly as well, regaining the Schrödinger equation itself.)

Following the spirit of a recent work by the author [14], in this article a simple derivation of the HFKS equations will be presented, placing them in a unified scheme of quantum mechanical theories in which the Kohn-Sham equations, the Hartree-Fock-Kohn-Sham equations and the ground-state Schrödinger equation originate from one root: the Hohenberg-Kohn theorems, through the Euler equation Eq.(3). Beside the HFKS scheme, another mixture of DFT and the Hartree-Fock theory, the Kohn-Sham formulation of the Hartree-Fock scheme, will also be considered. In the second part of the paper, the concept of \( N \)-particle exchange-energy density functionals will be introduced, following also [14] (see also [15]), and it will be shown that they emerge naturally as second-degree homogeneous functionals, for every particle number \( N \). For simplicity, spin is not considered throughout the paper.

II. The Hartree-Fock-Kohn-Sham scheme, and the Kohn-Sham formulation of the Hartree-Fock theory

Building on the idea of the constrained search definition of density functionals [16-18], the exact incorporation of correlation into the Hartree-Fock method in the form of a multiplicative, density-dependent potential (which is a density-functional derivative), that is, the so-called Hartree-Fock-Kohn-Sham method, can be derived directly from density-functional theory in a simple way.

The starting point is the definition of the functional [17]
\[
F_D[\rho] = \min_{\psi_D \rightarrow \rho} \{ T[\psi_D] + V[\psi_D] \} ,
\]
(13)
which, for a \( \rho(\vec{r}) \), gives the minimum of the sum \( T[\psi] + V[\psi] \) of wave-function functionals

\[
T[\psi] = \left\langle \psi \left| \sum_{i=1}^{N} -\frac{1}{2} \nabla_{i}^{2} \right| \psi \right\rangle
\]  

(14)

and

\[
V[\psi] = \left\langle \psi \left| \sum_{i,j}^{N} \frac{1}{|\vec{r}_{i} - \vec{r}_{j}|} \right| \psi \right\rangle
\]  

(15)

over the set of normalized Slater determinants \( (\psi_{D}) \) that yield \( \rho(\vec{r}) \), that is, \( \left\langle \psi_{D} | \hat{\rho}(\vec{r}) | \psi_{D} \right\rangle = \rho(\vec{r}) \) —while \( F[\rho] \), defined by

\[
F[\rho] = \min_{\psi \rightarrow \rho} \{ T[\psi] + V[\psi] \} ,
\]  

(16)

searches over the space of normalized (antisymmetric) wave-functions not restricted to be determinants. Similar to the case of the noninteracting kinetic-energy density functional

\[
T_{s}[\rho] = \min_{\psi_{D} \rightarrow \rho} T[\psi_{D}] ,
\]  

(17)

Eq.(13), by the mapping

\[
\rho \rightarrow \psi_{D} : \quad \rho(\psi_{D}) = \rho, \quad T[\psi_{D}] + V[\psi_{D}] = F_{D}[\rho] ,
\]  

(18)

associates every \( \rho(\vec{r}) \) with a fictive noninteracting system of density \( \rho(\vec{r}) \), composed of single-particle orbitals \( u_{i}(\vec{r}) \) of number \( N = \int \rho(\vec{r}) d\vec{r} \). Writing Eq.(13) explicitly with the orbitals,

\[
F_{D}[\rho] = \min_{\{ u_{i} \} \rightarrow \rho} \left\{ T_{s}[u_{1}, u_{2}, \ldots, u_{N}, u_{N}^{*}] + E_{s}[u_{1}, u_{2}, \ldots, u_{N}, u_{N}^{*}] \right\} + J[\rho] ,
\]  

(19)

with \( T_{s}[u_{1}, u_{2}, \ldots, u_{N}, u_{N}^{*}] \) being defined by Eq.(4) and \( E_{s}[u_{1}, u_{2}, \ldots, u_{N}, u_{N}^{*}] \) by Eq.(10).

The orbitals \( u_{i}(\vec{r}) \) corresponding to a density \( \rho(\vec{r}) \) can be determined through an Euler-Lagrange minimization procedure [16,19,20] (see also p. 151 and p. 187 of [1]), with the constraints of fixed density, and orthonormalization,

\[
\int u_{i}^{*}(\vec{r}) u_{j}(\vec{r}) d\vec{r} = \delta_{ij} ,
\]  

(20)

yielding the Euler-Lagrange equations

\[
-\frac{1}{2} \nabla^{2} u_{i}(\vec{r}) - \sum_{j=1}^{N} \frac{u_{j}(\vec{r}) u_{j}^{*}(\vec{r}')}{|\vec{r} - \vec{r}'|} u_{i}(\vec{r}') d\vec{r}' + \lambda_{\rho}(\vec{r}) u_{i}(\vec{r}) = \varepsilon_{i} u_{i}(\vec{r}) \quad i = 1, \ldots, N
\]  

(21)
(in canonical form), with the Lagrange multipliers $\varepsilon_i$ securing the normalization of $u_i(\vec{r})$ and $\lambda_i(\vec{r})$ securing the fulfilment of Eq.(7) (with $\rho(\vec{r})$ fixed). This approach of the minimization problem posed by Eq.(19), however, tells nothing more about $\lambda_i(\vec{r})$, about its connection to $\rho(\vec{r})$, and hence to $v_{HFKS}(\vec{r})$; this is because, as has been pointed out in [14], it does not utilize the definition Eq.(19), the implicit definition of the $u_i(\vec{r})$’s corresponding to a given $\rho(\vec{r})$, fully.

With a different approach, namely, minimizing the difference
\[
\Delta_{F_D}[u_1,u_1^*,...,u_N,u_N^*] := T_s[u_1,u_1^*,...,u_N,u_N^*] + E_x[u_1,u_1^*,...,u_N,u_N^*] - (F_D - J)[\rho[u_1,u_1^*,...,u_N,u_N^*]]
\]
under the orthonormalization constraint only (instead of the above minimization of $T_s[u_1,u_1^*,...,u_N,u_N^*] + E_x[u_1,u_1^*,...,u_N,u_N^*]$), the $\rho$-dependence of the multiplier that forces the orbitals $u_i(\vec{r})$ to yield a given $\rho(\vec{r})$ can be identified: the Euler-Lagrange equations resulting from the minimization of $\Delta_{F_D}[u_1,u_1^*,...,u_N,u_N^*]$, under normalization constraint on $u_i(\vec{r})$’s, are
\[
-\frac{1}{2} \nabla^2 u_i(\vec{r}) - \int \sum_{j=1}^{N} \frac{u_j(\vec{r})u_j^*(\vec{r}')}{|\vec{r} - \vec{r}'|} u_i(\vec{r}') d\vec{r}' - \frac{\delta(F_D[\rho] - J[\rho])}{\delta \rho(\vec{r})} u_i(\vec{r}) = \varepsilon_i u_i(\vec{r}) \quad i=1,...,N.
\]
The basis for this minimization is that, following from the definition of $F_D[\rho]$, \[
\Delta_{F_D}[u_1,u_1^*,...,u_N,u_N^*] \geq 0
\]
for any normalized $u_i(\vec{r})$’s, the equality holding for the orbitals $\{u_i(\vec{r})\}_{i=1}^{N}$ associated to $\rho(\vec{r})$ by Eq.(18); thus only the normalization of $u_i(\vec{r})$’s has to be reckoned with as external constraint. With Eq.(23) then the equations Eq.(11) of the HFKS method arise immediately through the Hohenberg-Kohn Euler equation, Eq.(3), that is, \[
\frac{\delta(F_D[\rho] - J[\rho])}{\delta \rho(\vec{r})} + v_{HFKS}(\vec{r}) = \mu
\]
with
\[
v_{HFKS}(\vec{r}) = \frac{\delta\{F[\rho] - (F_D[\rho] - J[\rho])\}}{\delta \rho(\vec{r})} + v(\vec{r})
\]
[Eq.(12)], which brings the external potential $v(\vec{r})$ into the equations, fixing $\rho(\vec{r})$ (as that corresponding to $v(\vec{r})$).
It is important to underline that the correlation energy functional of the HFKS scheme is not the same as that of the Kohn-Sham theory, since it is defined by

$$E^{\text{HFKS}}_c[\rho] = F[\rho] - F_D[\rho],$$  \hfill (27)

while in the Kohn-Sham scheme

$$E_c[\rho] = F[\rho] - T[\rho] - J[\rho] - E_s[\rho],$$  \hfill (28)

but

$$F_D[\rho] \leq T[\rho] + J[\rho] + E_s[\rho]$$  \hfill (29)

[$E_s[\rho]$ is defined through Eq.(10) with $u_i(\vec{r})$’s being the ($\rho$-dependent) orbitals of the Kohn-Sham scheme]. In particular, since $F_D[\rho]$ minimizes

$$T_s[u_1,u_1^*,...,u_N,u_N^*] + E_s[u_1,u_1^*,...,u_N,u_N^*]$$ in total [under Eq.(7)],

$$F_D[\rho] \leq T[\rho] + J[\rho] + E_s[\rho],$$ \hfill (30)

from which

$$E^{\text{HFKS}}_c[\rho] \geq E_s[\rho],$$ \hfill (31)

which means that, besides the need for approximation of $E_s[\rho]$, in the Kohn-Sham method, there is also a greater correlation part in the energy density functional to be approximated. (Note that both kinds of correlation energies are always negative or zero [13].)

Beside the density-functional amplification of Hartree-Fock theory, discussed so far, there is another mixture of DFT and Hartree-Fock theory: the Kohn-Sham formulation of the Hartree-Fock scheme [19,17,21,13] (the Kohn-Sham-Hartree-Fock scheme), where the nonlocal exchange operator of the Hartree-Fock equations is replaced by a local potential which is a density-functional derivative. This theory gives the sound justification of early attempts in that direction. As the Hartree-Fock method is an approximative theory by definition, neglecting correlation completely by narrowing the space of wave-functions to Slater determinants, its Kohn-Sham formulation is not exact either. Here, the density functional $F[\rho]$ of exact DFT is replaced by $F_D[\rho]$, and the energy functional

$$E^{\text{HF}}_c[\rho] = F_D[\rho] + \int \rho(\vec{r})\nu(\vec{r})d\vec{r}$$ \hfill (32)
is minimized, under the $N$-conservation constraint, giving the Hartree-Fock groundstate energy, and density. This yields the Euler equation

$$\frac{\delta F_D[\rho]}{\delta \rho(\bar{r})} + \nu(\bar{r}) = \mu_{\text{HF}}$$

for the determination of the Hartree-Fock ground-state density. Note that, with $E_{v,\text{HF}}[\rho]$, $E_{v}[\rho]$ arises as

$$E_{v}[\rho] = E_{v,\text{HF}}[\rho] + E_{v,\text{HFKS}}[\rho].$$

Separating $T_{v}[\rho]$ in $E_{v,\text{HF}}[\rho]$, analogously to exact DFT, a major part of the unknown $F_{v}[\rho]$ can be treated exactly, obtaining the single-particle Schrödinger equations

$$-\frac{1}{2} \nabla^2 u_i(\bar{r}) + v_{v,\text{KS}}(\bar{r}) u_i(\bar{r}) = \epsilon_{v,\text{KS}} u_i(\bar{r})$$

with Eq.(7), for the determination of the density, where

$$v_{v,\text{KS}}(\bar{r}) = \frac{\delta (F_{v}[\rho] - T_{v}[\rho])}{\delta \rho(\bar{r})} + \nu(\bar{r}).$$

These equations can be obtained in a simple manner, utilizing the idea described above in connection with the HFKS method; namely, minimizing the difference

$$\Delta_{T_{v}}[u_1, u_1^*, \ldots, u_N, u_N^*] = T_{v}[u_1, u_1^*, \ldots, u_N, u_N^*] - T_{v}[\rho[u_1, u_1^*, \ldots, u_N, u_N^*]]$$

under orthonormalization constraint on $u_i(\bar{r})$’s (just as in the case of the derivation of the Kohn-Sham equations given in [14]), then using the pure density-functional Euler equation Eq.(33) to substitute for $-\frac{\delta T_{v}[\rho]}{\delta \rho(\bar{r})}$ in the obtained Euler-Lagrange equations, hereby fixing $\rho(\bar{r})$ by the external potential. The traditional quantum mechanical equations of the Hartree-Fock approach, the Hartree-Fock equations themselves, can be recovered as well from Eq.(33), following the above procedure, but now

$$\Delta_{\epsilon_{v}}[u_1, u_1^*, \ldots, u_N, u_N^*] = T_{\epsilon}[u_1, u_1^*, \ldots, u_N, u_N^*] + E_{\epsilon}[u_1, u_1^*, \ldots, u_N, u_N^*] - (F_{\epsilon} - J)[\rho[u_1, u_1^*, \ldots, u_N, u_N^*]]$$

has to be minimized (followed by the insertion of Eq.(33)); just as can the (groundstate) Schrödinger equation of exact quantum mechanics be derived from the Hohenberg-Kohn Euler equation [Eq.(3)] [14]. Note that the difference functionals Eq.(22) and Eq.(38) are the same; the difference between the single-particle equations of the HFKS and the HF theories arises from the different [exact, or approximate
(HF)] physics behind the equations, that is, different DFT backgrounds, characterized by the density-functional Euler equations Eq.(3) and Eq.(33), respectively.

Regarding the derivations of Schrödinger equations from DFT, some words need to be said about the density-functional derivatives (local potentials) appearing in these equations since the density functionals defined through wave-functions are defined only for densities of integer norm \( N \). This problem can be eliminated with the help of the concept of \( N \)-particle density functionals and \( N \)-conserving functional differentiation [22] (for a discussion of its mathematics, see [23]). In [14], it has been pointed out that the Euler-Lagrange minimization procedure proposed there, and used above as well, to determine the corresponding orbitals for a density \( \rho(\vec{r}) \), can be carried out by using an \( N \)-particle density functional \( A_N[\rho] \) instead of the given density functional \( A[\rho] \), defining the difference functional \( \Delta \) with \( A_N[\rho] \),

\[
\Delta_{A_N}[u_1, u_1^*, \ldots, u_N, u_N^*] = A_N[u_1, u_1^*, \ldots, u_N, u_N^*] - A_N[\rho_{\{u_1, u_1^*, \ldots, u_N, u_N^*\}],
\]

since the normalization of the orbitals and the fixation of their number conserve the norm \( N \) of \( \rho(\vec{r}) \). An \( A_N[\rho] \) defined for every \( \rho(\vec{r}) \) can then be chosen; the trivial constant shifting [22] (or other homogeneous extension) of \( A[\rho_N] \), e.g., is one proper choice, being (unconstrained) differentiable if \( A[\rho] \) is differentiable over the space of \( \rho(\vec{r})'s \) of the given norm \( N \). In the orbital equations resulting from the minimization of \( \Delta_{A_N}[u_1, u_1^*, \ldots, u_N, u_N^*] \), adding \( \frac{1}{N} \int \rho(\vec{r}') \frac{\delta A_N[\rho]}{\delta \rho(\vec{r}')} d\vec{r}' u_i(\vec{r}) \) to both sides of the equations [22], the unconstrained derivative of \( A_N[\rho] \) is replaced by the \( N \)-conserving functional derivative, \( \frac{\delta A_N[\rho]}{\delta_N \rho(\vec{r})} \), for which [22]

\[
\frac{\delta A_N[\rho_N]}{\delta_N \rho(\vec{r})} = \frac{\delta A[\rho_N]}{\delta \rho(\vec{r})}.
\]

After using Eq.(39), finally, the replacement of the unconstrained derivative by the corresponding \( N \)-conserving derivative (of \( A[\rho] \)) is achieved in the orbital equations (for \( \rho_N(\vec{r})'s \), thereby restricting the differentiation to the allowed domain of \( \rho(\vec{r})'s \).

Note that similar considerations hold also if \( A[\rho] \) comes from a wave-function
functional $A[\psi]$ that is not an orbital functional. With $N$-conserving density-functional derivatives, the derivations of Schrödinger equations from DFT thus look like: from

$$-\frac{1}{2} \nabla^2 u_i(\bar{r}) - \int_{|\bar{r} - \bar{r}'|} \sum_{j=1}^{N'} u_j(\bar{r}) u_j^*(\bar{r}') u_i(\bar{r}') d\bar{r}' - \frac{\delta[F_D[\rho_N] - J[\rho_N]]}{\delta \rho(\bar{r})} u_i(\bar{r}) = \varepsilon_i^* u_i(\bar{r})$$

(e.g.), using

$$\frac{\delta F[\rho]}{\delta \rho(\bar{r})} + \nu(\bar{r}) = \mu^* ,$$

$$-\frac{1}{2} \nabla^2 u_i(\bar{r}) - \int_{|\bar{r} - \bar{r}'|} \sum_{j=1}^{N'} u_j(\bar{r}) u_j^*(\bar{r}') u_i(\bar{r}') d\bar{r}' + \left[ \frac{\delta J[\rho_N]}{\delta \rho(\bar{r})} + \frac{\delta F_{vKS}[\rho_N]}{\delta \rho(\bar{r})} + \nu(\bar{r}) \right] u_i(\bar{r}) = \varepsilon_i^{vKS} u_i(\bar{r}) .$$

Another way of treating the problem of $A[\rho]$ (= $T_x[\rho]$, $F_D[\rho]$, or $F[\rho]$) being defined only for integer $N$'s is to utilize that a chain rule, namely,

$$\frac{\delta A[\rho(g)]}{\delta g(x)} = \int \frac{\delta A[\rho]}{\delta \rho(x')} \frac{\delta \rho(x')}{\delta g(x)} dx' ,$$

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$$\frac{\delta A[\rho(g)]}{\delta g(x)} = \int \frac{\delta A[\rho]}{\delta \rho(x')} \frac{\delta \rho(x')}{\delta g(x)} dx' ,$$

still holds (as proved in the Appendix of [23]) for cases $A[\rho(g)]$ where the functional $\rho[g]$ is such that $\rho(x)[g]$ satisfies the given $K$-conservation constraint –here $\int \rho(\bar{r}) d\bar{r} = N$ – for any (allowed) $g(x')$. In the present cases, $g = (u_1, u_1^*, ..., u_N, u_N^*)$ or $g = (\psi, \psi^*)$, and the normalization of $u_i(\bar{r})$'s ensures the fulfilment of $\int \rho(\bar{r}) d\bar{r} = N$. Thus,

$$\left. \frac{\delta F_D[\rho_N[u_j, u_j^*]]}{\delta u_i(\bar{r})} \right|_{u_i^*(\bar{r}) \neq u_i(\bar{r}) d\bar{r} = 1} = \int \left. \frac{\delta F_D[\rho_N]}{\delta \rho(\bar{r})} \right|_{u_i^*(\bar{r}) \neq u_i(\bar{r}) d\bar{r} = 1} \frac{\delta \rho(\bar{r}^*)}{\delta u_i(\bar{r})} |_{u_i^*(\bar{r}) \neq u_i(\bar{r}) d\bar{r} = 1} d\bar{r}' ,$$

or

$$\left. \frac{\delta F_D[\rho_N[u_j, u_j^*]]}{\delta u_i(\bar{r})} \right|_{u_i^*(\bar{r}) \neq u_i(\bar{r}) d\bar{r} = 1} = \int \left. \frac{\delta F_D[\rho_N]}{\delta \rho(\bar{r})} \right|_{u_i^*(\bar{r}) \neq u_i(\bar{r}) d\bar{r} = 1} \frac{\delta \rho(\bar{r}^*)}{\delta u_i(\bar{r})} |_{u_i^*(\bar{r}) \neq u_i(\bar{r}) d\bar{r} = 1} d\bar{r}' .$$

Note that this chain rule is essential also for the variational derivation of the Kohn-Sham equations themselves.
It is important to note here finally that, having the $N$-conserving derivatives (as potentials) in the derived wave-function equations, the fractional-particle-number generalization [24] of density functionals can be substituted for the original density functionals, obtaining the possibility of relaxing the constraint of $N$-conservation on the functional differentiation and using the unconstrained (left or right) derivatives of density functionals.

### III. Second-degree homogeneous $N$-particle exchange-energy density functionals

To construct approximations for density functionals, knowledge about the structure of the functionals is essential. In this section, a natural formal construction of the exchange-energy density functional $E_x[\rho]$ of Kohn-Sham DFT, via second-degree homogeneous $N$-particle exchange-energy density functionals, will be proposed.

It is known that $E_x[\rho]$, defined through Eq.(10) with $u_i(\vec{r})$ as the ($\rho$-dependent) Kohn-Sham orbitals, scales homogeneously of degree one with coordinate scaling [25], that is,

$$E_x[\lambda^3 \rho(\lambda \vec{r})] = \lambda E_x[\rho(\vec{r})] \ ,$$

from which

$$E_x[\rho] = -\int \rho(\vec{r})\vec{r} \nabla \frac{\delta E_x[\rho]}{\delta \rho(\vec{r})} d\vec{r}$$

emerges [26]. Beside this property, the question of homogeneity of $E_x[\rho]$ in $\rho$ itself may also arise, considering that the classical Coulomb repulsion functional $J[\rho]$, the negative of which is an exact expression for $E_x$ for one-particle densities, is homogeneous of degree two, i.e.

$$J[\lambda \rho] = \lambda^2 J[\rho] \ .$$

The question of homogeneity with respect to the density, and related, or affinitative, properties of the various components of the energy, has been addressed in several works recently [27-39], homogeneity being a very attractive (strong) analytical property for functionals. For the noninteracting kinetic-energy density functional
$T_s[\rho]$, the first-degree homogeneity in $\rho$ [33] has been shown to be an incorrect proposal [37,38], though the Weizsäcker (one-particle kinetic-energy) functional,

$$T_w[\rho] = \frac{1}{8} \int \frac{[\nabla \rho(\vec{r})]^2}{\rho(\vec{r})} \, d\vec{r}$$  \hspace{1cm} (47)

(which is an exact expression for $T_s[\rho]$ for one-particle densities), is homogeneous of degree one (in $\rho$). In the case of $E_x[\rho]$, the invalidity of homogeneity (of second, or any other, degree) in $\rho$ can be proven in a simple way, as for $T_s[\rho]$ [37]; since if homogeneity of a degree $k$ held then

$$\left( \frac{1}{N} \right)^k E_x[\rho] = E_x\left[ \frac{\rho}{N} \right] = -J\left[ \frac{\rho}{N} \right] = \left( \frac{1}{N} \right)^2 J[\rho] \, ,$$ \hspace{1cm} (48)

that is, $E_x[\rho]$ would be $-N^{k-2} J[\rho]$. Note that from the second-degree homogeneity of $E_x[\rho]$ (in $\rho$), Eq.(15) of [39], derived from the result of [32] for the full electron-electron-interaction energy density functional, would also follow. (Chan and Handy [37] having shown that the homogeneity results of [32-34] are incorrect in the case of the kinetic energy, Joubert [39] has also shown that for the correlation energy functional after, in [38], it was pointed out that an essential question was not treated properly in [32-34], therefore their results cannot be considered to be valid.)

With the introduction of the concept of $N$-particle density functionals, that is, functionals that are valid expressions for a given density functional for $N$-particle densities, however, it can be shown that the exchange energy can be given by density functionals homogeneous of degree two, as in the case of $T_s$, which can be given by first-degree homogeneous $N$-particle density functionals, for all particle numbers $N$ [14]. By utilizing the result in [14] that the KS orbitals arise most naturally as degree-$\frac{1}{2}$ homogeneous functionals of the density, that is,

$$\left( u_1(\vec{r}),...,u_N(\vec{r}) \right)[k\rho] = \sqrt{k} \left( u_1(\vec{r}),...,u_N(\vec{r}) \right)[\rho] \, ,$$ \hspace{1cm} (49)

$E_x$ arises as a second-degree homogeneous functional of the density, through Eq.(10). The resultant density functional is an $N$-particle density functional, $E_x^N[\rho]$, since its form depends on the number $N$ of orbitals used in its construction. This $E_x^N[\rho]$ thus satisfies
\[ E_x^N[\lambda\rho] = \lambda^2 E_x^N[\rho] , \quad (50) \]

that is,

\[ E_x^N[\rho] = \frac{1}{2} \int \rho(\vec{r}) \frac{\delta E_x^N[\rho]}{\delta \rho(\vec{r})} d\vec{r} . \quad (51) \]

Note that an \( N \)-particle exchange-energy density functional (as any other \( N \)-particle density functional) can be considered as a two-variable functional, \( E_x[N, \rho] \), and the general exchange-energy density functional emerges as

\[ E_x[\rho] = E_x[\int \rho, \rho] , \quad (52) \]

for which thus the homogeneity Eq.(50) yields the property

\[ E_x[\rho] = \frac{1}{\lambda^2} E_x[\int \rho, \lambda\rho] . \quad (53) \]

Beside Eq.(51), also the analogue of Eq.(45) can be written for \( E_x^N[\rho] \), for \( N \)-particle densities \( \rho_N(\vec{r}) \),

\[ E_x^N[\rho_N] = -\int \rho_N(\vec{r}) \vec{r} \nabla \frac{\delta E_x^N[\rho_N]}{\delta \rho_N(\vec{r})} d\vec{r} , \quad (54) \]

since the difference between the derivatives \( \frac{\delta E_x[\rho_N]}{\delta \rho_N(\vec{r})} \) and \( \frac{\delta E_x^N[\rho_N]}{\delta \rho_N(\vec{r})} \) is \( \vec{r} \)-independent [22,23]. Eq.(54) is in accordance with the fact that coordinate scaling conserves the normalization of the density, with the use of which

\[ E_x^N[\lambda^3 \rho_N(\lambda\vec{r})] = \lambda E_x[\hat{x}^3 \rho_N(\lambda\vec{r})] = \lambda E_x[\rho_N(\vec{r})] = \lambda E_x^N[\rho_N(\vec{r})] \quad (55) \]

[giving also Eq.(54)]; see the Appendix for the proof for a general \( \rho(\vec{r}) \).

It is worth noting that requiring \( N \)-particle density functionals to be homogeneous of some degree eliminates the ambiguity present in their definition [15], meaning that the only possible \( N \)-particle noninteracting kinetic-energy and exchange-energy density functionals homogeneous of degree one and two, respectively, are those constructed in [14] and here (see also the Appendix).

The simplest exchange energy density functional arising from the conditions of homogeneity of degree two in density scaling [Eq.(50)] and homogeneity of degree one in coordinate scaling [Eq.(55), see also Eq.(A6)] is minus the Coulomb functional \( J[\rho] \) [which is just (the degree-two homogeneous) \( E_x^1[\rho] \), \( E_x^1[\rho] = -J[\rho] \); just as the
Weizsäcker functional is the simplest expression for a kinetic energy density functional satisfying the two homogeneity scaling-conditions for $T_\rho$ [14] (see also [40]). That $-J[\rho]$ is the simplest exchange energy functional satisfying the homogeneity conditions is of course stated from a physical point of view: a "real" exchange-energy density functional, on one hand, has to be a two-particle functional (regarding its structure), and on the other hand, a term $\frac{1}{|\vec{r} - \vec{r}'|}$, characterizing the interaction, has to appear explicitly beside the density-functional part, since the exchange energy is obtained via Eq.(10), the orbitals $u_i(\vec{r})$ forming the $\rho$-dependent part in the functional; thus, it has to have a form (or a combination of forms like)

$$\int \int \frac{f[\rho(\vec{r})] f[\rho(\vec{r}')] d\vec{r} d\vec{r}'}{|\vec{r} - \vec{r}'|}.$$  \hspace{1cm} (56)

Note that with the separation of a factor $\frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$ in the integrand,

$$\int \int g[\rho(\vec{r})] g[\rho(\vec{r}')] \rho(\vec{r}) \rho(\vec{r}') d\vec{r} d\vec{r}'.$$  \hspace{1cm} (57)

the remaining part $g[\rho(\vec{r})] g[\rho(\vec{r}')]$ (or, simply $g[\rho(\vec{r})]$) has to be homogeneous of degree zero in $\rho(\vec{r})$ for Eq.(57) to satisfy the scaling conditions.

Finally, the question of separability [41] for $N$-particle density functionals may be worth taking a look at, referring also to a recent work [42], which investigates the separability problem of (explicitly) $N$-dependent density functionals. It can be seen easily that $N$-particle density functionals $A_N[\rho]$ corresponding to a separable density functional $A[\rho]$ are separable for $N$-particle densities (only for which they have physical relevance):

$$A_N[\rho_{N_1} + \rho_{N_2}] = A[\rho_{N_1}] + A[\rho_{N_2}] = A[\rho_{N_1}] + A[\rho_{N_2}] = A_N[\rho_{N_1} + \rho_{N_2}],$$ \hspace{1cm} (58)

where $N_1 + N_2 = N$.

**IV. Summary**

Various treatments of exchange in the framework of density-functional theory have been investigated. First, the so-called Hartree-Fock-Kohn-Sham method, which is
the density-functional amplification of the Hartree-Fock approach, has been considered. In Sec.II, a simple derivation of the Hartree-Fock-Kohn-Sham equations has been presented, following the spirit of [14], showing how these equations, together with the Kohn-Sham equations and the ground-state Schrödinger equation [14], formally originate from one common root: density-functional theory, through its Hohenberg-Kohn Euler equation. Beside the Hartree-Fock-Kohn-Sham scheme, along the same lines, in Sec.II another mixture of density-functional theory and Hartree-Fock theory, the Kohn-Sham formulation of the Hartree-Fock approach (with the Kohn-Sham-Hartree-Fock equations), has also been considered.

In Sec.III, it has been pointed out that the exchange energy of ground-state systems of \( N \) identical fermions naturally emerges as a second-degree homogeneous \( N \)-particle density functional \( E^N_x[\rho] \), for any particle number \( N \), yielding a construction \( E_x[\rho] = E^F_x[\rho] \) of the exchange-energy density functional, for which Eq.(53) holds. The first element of the arising sequence (that is, \( N=1,2,\ldots \)) of degree-two homogeneous \( N \)-particle exchange-energy density functionals \( E^N_x[\rho] \) is just minus the classical Coulomb-repulsion energy functional. It has further been shown that \( E^N_x[\rho] \) (homogeneous in \( \rho \)) retains the coordinate scaling property of the general exchange-energy density functional, \( E_x[\rho] \), and generally, any \( N \)-particle density functional homogeneous in the density has the same coordinate scaling behaviour as the general density functional to which it corresponds. Thus, the scaling properties of \( E^N_x[\rho] \) proposed in Sec.III are just the reverse of those of \( T^N_x[\rho] \) of [14], which is first-degree homogeneous in \( \rho \) and second-degree homogeneous with respect to coordinate scaling.

**Appendix: Uniqueness of homogeneous \( N \)-particle density functionals, and their coordinate scaling**

Given a density functional \( A[\rho] \), \( N \)-particle density functionals \( A_N[\rho] \) can be defined, for which

\[
A_N[\rho_N] = A[\rho_N] \quad (A1)
\]
(with $\int \rho_N(\vec{r}) d\vec{r} = N$), giving the value of $A$ for $N$-particle densities $\rho_N$. The definition Eq.(A1) is of course ambiguous. E.g., the free choice of generalization of normalization represents the ambiguity in the case of $N$-particle noninteracting kinetic-energy density functionals constructed as described in [14]. Requiring an $A_N[\rho]$ to be homogeneous of some degree $k$, which means

$$A_N[\lambda \rho] = \lambda^k A_N[\rho],$$

(A2)

however, leads to a unique definition for this $A_N[\rho]$. For, utilizing Eqs.(A1) and (A2),

$$\left(\frac{N}{\int \rho}\right)^k A_N[\rho] = A_N\left[N \frac{\rho}{\int \rho}\right] = A\left[N \frac{\rho}{\int \rho}\right],$$

(A3)

making use of that the norm of $N \frac{\rho}{\int \rho}$ is $N$ [15]. From Eq.(A3) then

$$A_N[\rho] = \left(\frac{\int \rho}{N}\right)^k A\left[N \frac{\rho}{\int \rho}\right],$$

(A4)

which shows that the fixation of $N$ (on the right) leads to the $N$-particle nature.

Eq.(A4) is the unique expression for a degree-$k$ homogeneous $N$-particle density functional corresponding to an $A[\rho]$. This uniqueness, in the case of the density functionals $T_s[\rho]$ and $E_s[\rho]$, means that the homogeneous $N$-particle density functionals $T_s^N[\rho]$ and $E_s^N[\rho]$ constructed in [14] and Sec.III of the present article are the only first-degree homogeneous $N$-particle noninteracting kinetic-energy and second-degree homogeneous $N$-particle exchange-energy density functionals, respectively. Thus, e.g., $T_N[\rho]$ and $-J[\rho]$ are the only possible first-degree homogeneous and second-degree homogeneous density functionals that give the exact noninteracting kinetic energy and the exact exchange energy, respectively, for one-electron systems.

With Eq.(A4), the validity of Eq.(54) [and Eq.(55)] for arbitrary $\rho(\vec{r})$ (not just for $\rho(\vec{r})$’s of norm $N$), i.e.

$$E_s^N[\rho] = -\int \rho(\vec{r}) \nabla \cdot \frac{\partial E_s^N[\rho]}{\partial \rho(\vec{r})} d\vec{r},$$

(A5)
can be justified easily. Utilizing \( \int \lambda \rho(\lambda \vec{r}) d\vec{r} = \int \rho(\vec{r}) d\vec{r} \) and the homogeneity of degree one of \( E_i[\rho] \) in coordinate scaling,

\[
E^N_i[\lambda \rho(\lambda \vec{r})] = \left( \frac{\int \rho}{N} \right)^2 E_i \left[ \lambda \frac{N}{\int \rho} \rho(\lambda \vec{r}) \right] = \left( \frac{\int \rho}{N} \right)^2 \lambda E_i \left[ \frac{N}{\int \rho} \rho(\vec{r}) \right] = \lambda E^N_i[\rho(\vec{r})], \tag{A6}
\]

which means that \( E^N_i[\rho] \) itself, too, is homogeneous of degree one in coordinate scaling, yielding Eq.(A5). A similar proof applies for \( T^N_i[\rho] \) of [14] as well, meaning that \( T^N_i[\rho] \) has the same coordinate scaling property as \( T_i[\rho] \), that is, homogeneity of degree two.

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Appendix B. Summary of the connections between the density-functional Euler equation and the various wave-function equations, indicating the functional the constrained-search definition of which is utilized to get to the given wave-function equation(s)

Exact quantum mechanics:

\[ T_s[\rho] \]

\[ \frac{\delta F[\rho]}{\delta \rho(\vec{r})} + \nu(\vec{r}) = \mu \]

Hartree-Fock-Kohn-Sham eqs.

\[ F[\rho] \]

Schrödinger equation

Hartree-Fock approximation:

\[ T_s[\rho] \]

\[ \frac{\delta F_D[\rho]}{\delta \rho(\vec{r})} + \nu(\vec{r}) = \mu^{\text{HF}} \]

Hartree-Fock equations