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Physical interpretation of density-functional theory and of its representation of the Hartree-Fock and Hartree theories

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In this paper we provide a rigorous physical interpretation of the Kohn-Sham (KS) density-functional theory electron-interaction energy functional $E_{ee}^{\mathrm{KS}}[\rho]$ and its functional derivative $v_{ee}^{\mathrm{KS}}(\mathbf{r})=\delta E_{ee}^{\mathrm{KS}}[\rho]/\delta\rho(\mathbf{r})$ based on the original ideas of Harbola and Sahni, and of their extension by Holas and March. The functional, and hence the derivative, incorporate electron correlations due to the Pauli exclusion principle and Coulomb repulsion as well as those of the correlation contribution to the kinetic energy. The interpretation is in terms of a field $\boldsymbol{\mathcal{F}}(\mathbf{r})$, which is the sum of two fields whose source distributions are expectations of Hermitian operators. The first of these fields $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ accounts for Pauli and Coulomb correlations. Its source is the pair-correlation density and it is determined by Coulomb's law. The second $\mathbf{Z}_{t_c}(\mathbf{r})$ accounts for the correlation-kinetic contribution, and its source is the difference between the kinetic-energy-density tensor for the noninteracting and interacting systems. The corresponding field is the derivative of this tensor. The functional derivative $v_{ee}^{\mathrm{KS}}(\mathbf{r})$ is the work done to move an electron in the field $\boldsymbol{\mathcal{F}}(\mathbf{r})$. Since the field $\boldsymbol{\mathcal{F}}(\mathbf{r})$ is conservative, this work done is path independent. The quantum-mechanical electron-interaction energy $E_{ee}[\rho]$ and correlation-kinetic energy $T_c[\rho]$ components of $E_{ee}^{\mathrm{KS}}[\rho]$ can also be expressed in virial form in terms of the respective fields $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and $\mathbf{Z}_{t_c}(\mathbf{r})$, which give rise to them. A similar rigorous physical interpretation of the Kohn-Sham theory representation of the Hartree-Fock and Hartree approximations is also given. If in these representations, the correlation kinetic energy is neglected the equations reduce to the corresponding approximations of the work formalism of electronic structure. Finally, it is argued on physical grounds that the interpretation provided for the ground state is equally valid for excited states. [S1050-2947(97)04703-3]

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I. INTRODUCTION

Hohenberg-Kohn-Sham [1,2] density-functional theory [3–5] is founded in Schrödinger [6] theory. Thus, according to the first theorem of Hohenberg and Kohn, the ground-state wave function Ψ is a functional of the exact ground-state electronic density $\rho(\mathbf{r})$ so that the expectation value of any observable is a unique functional of the density. The ground-state energy $E[\rho]$ is, therefore, such a functional. The density itself in turn is the expectation of a Hermitian operator. Since the ground-state density does not discriminate between interacting and noninteracting electronic systems, the basic assumption in the Kohn-Sham version of the theory is that there exists a model-system of *noninteracting* fermions possessing the true density. To account for the distinction between the interacting Schrödinger and noninteracting Kohn-Sham systems, one therefore defines within the latter an electron-interaction energy functional that represents correlations due to the Pauli exclusion principle and Coulomb repulsion as well as those of the correlation contribution to the kinetic energy. Further, since the model fermions are noninteracting, the electron-interaction operator representative of these correlations in the corresponding Schrödinger (Kohn-Sham) equation is *local* or multiplicative. As a consequence of the second theorem of Hohenberg and Kohn, which establishes the variational character of the ground-state energy functional, this local operator has a *rigorous mathematical* definition: it is the *functional derivative* with respect to arbitrary norm-conserving variations of the density of the electron-interaction energy functional. From the wave function of the model system, which is a *single* Slater determinant of the solutions of the Kohn-Sham equation, the ground-state density $\rho(\mathbf{r})$ and therefore the energy $E[\rho]$ are then determined. It is in this mathematical framework that Kohn-Sham density-functional theory is generally understood.

In this paper we provide a *rigorous physical* understanding of Kohn-Sham theory via a quantum-mechanical interpretation of the electron-interaction energy functional and its functional derivative (potential). The interpretation is in terms of fields arising from source distributions that are quantum-mechanical expectations of Hermitian operators. Thereby the relationship between Kohn-Sham theory and Schrödinger theory via the system wave function Ψ [rather than through the density $\rho(\mathbf{r})$] is also made explicit. The interpretation further distinguishes between the Pauli-Coulomb correlation and the correlation-kinetic-energy components of the energy functional and potential, each component arising from a separate field and source distribution. The physical interpretation in terms of fields and their sources is arrived at by combining the original ideas of Harbola and Sahni [7] with that of the recent work of Holas and March [8]. In this manner we present a simple physical picture of that model system of noninteracting fermions that has the same electronic density and energy as that of Schrödinger theory.

The constrained search formulation [9], which generalizes the proofs of the Hohenberg-Kohn theorems thereby eliminating the v-representability constraint further shows that there exists [9–11] a density-functional theory representation of the Hartree-Fock [12] and Hartree [13] theory approximations. The same conclusion is arrived [14] at via many-body perturbation theory. This means that in each case there exists a Kohn-Sham theory electron-interaction energy functional and derivative, which lead to the same ground-state density and energy as those of these approximations. In a hierarchical manner, a rigorous physical interpretation entirely similar to that for the fully correlated case can be provided for these energy functionals and local potentials. Once again, the interpretation is in terms of fields and their source distributions, which are expectations of the *same* Hermitian operators as for the fully correlated case, but taken with respect to the Hartree-Fock and Hartree theory wave functions instead. Again, the purely quantum-mechanical electron-interaction and correlation-kinetic-energy components can be distinguished. If in the Kohn-Sham theory representation of the Hartree-Fock and Hartree approximations, the correlation-kinetic-energy component is neglected, the equations then reduce to those of the work formalism [15,16] for these approximations.

For the quantum-mechanical description of density-functional theory, we begin with the definitions of requisite properties within Schrödinger and Kohn-Sham theories. We then provide a description and proof of the physical interpretation of the electron-interaction energy functional and functional derivative of Kohn-Sham theory. Following this we describe the interpretation for the Kohn-Sham representation of Hartree-Fock and Hartree theories, from which the equations of the work formalism then emerge. Finally, based on the physical picture of Kohn-Sham theory (a ground-state theory), we present in the concluding section a plausible argument that a similar description is equally valid for excited states.

II. SCHRÖDINGER AND KOHN-SHAM THEORIES

We define in this section properties within the context of Schrödinger theory relevant to the physical interpretation of Kohn-Sham density-functional theory. We also give a brief description of Kohn-Sham theory in order to define the local potential representing electron correlations as well as other properties derived within its context.

A. Definitions within Schrödinger theory

The Schrödinger equation for a system of N electrons in an external potential of local single particle form $v(\mathbf{r})$ is

$$\hat{H}\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)=E\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N), \tag{1}$$

where the Hamiltonian $\hat{H}$ in atomic units is

$$\hat{H}=\sum_i -\frac{1}{2}\nabla_i^2+\sum_i v(\mathbf{r}_i)+\frac{1}{2}\sum_{ij}{}' \frac{1}{|(\mathbf{r}_i-\mathbf{r}_j)|}, \tag{2}$$

and where Ψ and E are the normalized system wave function and energy, respectively. The energy is the expectation $E=\langle\Psi|\hat{H}|\Psi\rangle$. (Here $\mathbf{x}=\mathbf{r}\sigma$, where $\mathbf{r}$ is the spatial and σ the spin coordinate of the electron. The integral $\int d\mathbf{x}\equiv\Sigma_\sigma\int d\mathbf{r}$).

The first property of interest is the spinless single-particle density matrix $\gamma(\mathbf{r},\mathbf{r}')$ defined as

$$\begin{aligned}\gamma(\mathbf{r},\mathbf{r}')&=N\sum_\sigma\int\Psi^*(\mathbf{r}\sigma,\mathbf{x}_2,\ldots,\mathbf{x}_N)\\&\quad\times\Psi(\mathbf{r}'\sigma,\mathbf{x}_2,\ldots,\mathbf{x}_N)d\mathbf{x}_2,\ldots,d\mathbf{x}_N\\&=\langle\Psi|\hat{X}|\Psi\rangle,\end{aligned} \tag{3}$$

where the Hermitian operator [17]

$$\hat{X}=\hat{A}+i\hat{B},$$

$$\hat{A}=(1/2)\Sigma_j[\delta(\mathbf{r}_j-\mathbf{r})T_j(\mathbf{a})+\delta(\mathbf{r}_j-\mathbf{r}')T_j(-\mathbf{a})],$$

$$\hat{B}=-(i/2)\Sigma_j[\delta(\mathbf{r}_j-\mathbf{r})T_j(\mathbf{a})-\delta(\mathbf{r}_j-\mathbf{r}')T_j(-\mathbf{a})],$$

$T_j(\mathbf{a})$ is a translation operator such that

$$T_j(\mathbf{a})\Psi(\cdots\mathbf{r}_j\cdots)=\Psi(\cdots\mathbf{r}_j+\mathbf{a}\cdots),$$

and $\mathbf{a}=\mathbf{r}'-\mathbf{r}$. The single-particle density matrix constructed from the wave function Ψ is not idempotent. The diagonal matrix element of the density matrix is the density $\rho(\mathbf{r})$. Equivalently, it is the expectation value of the density operator $\hat{\rho}(\mathbf{r})=\Sigma_i\delta(\mathbf{r}_i-\mathbf{r})$, so that

$$\rho(\mathbf{r})=\gamma(\mathbf{r},\mathbf{r})=\langle\Psi|\hat{\rho}|\Psi\rangle. \tag{4}$$

The property associated [7] with the purely electron-interaction component of the Kohn-Sham theory many-body potential as well as the electron-interaction energy is the pair-correlation density $g(\mathbf{r},\mathbf{r}')$. It is defined in terms of the Hermitian pair-correlation operator $\hat{P}(\mathbf{r},\mathbf{r}')=\Sigma_{i,j}'\delta(\mathbf{r}_i-\mathbf{r})\delta(\mathbf{r}_j-\mathbf{r}')$ as

$$g(\mathbf{r},\mathbf{r}')=\langle\Psi|\hat{P}(\mathbf{r},\mathbf{r}')|\Psi\rangle/\rho(\mathbf{r}). \tag{5}$$

Note that in the definition of the pair-correlation density there is no self-interaction. In physical terms, the pair-correlation density is the *density* at $\mathbf{r}'$ for an electron at $\mathbf{r}$. Its total charge for arbitrary electron position is thus $\int g(\mathbf{r},\mathbf{r}')d\mathbf{r}'=N-1$. The pair-correlation density is a property that arises due to the Pauli and Coulomb correlations between electrons. Thus, it can also be interpreted as the density $\rho(\mathbf{r}')$ at $\mathbf{r}'$ plus the reduction in this density at $\mathbf{r}'$ due to the electron correlations. The reduction in density about an electron that occurs as a result of the Pauli exclusion principle and Coulomb repulsion is the quantum-mechanical Fermi-Coulomb hole charge distribution $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$. Thus, we may write the pair-correlation density as

$$g(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')+\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}'), \tag{6}$$

and consequently the total charge of the Fermi-Coulomb hole for arbitrary electron position is $\int\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')d\mathbf{r}'=-1$. Note that the self-interaction contribution to the Fermi-Coulomb hole charge is canceled by the density, so that the pair-correlation density as defined by Eq. (6) is self-interaction free.

The electron-interaction energy E_{ee} can be afforded a physical interpretation in terms of the pair-correlation density as the energy of interaction between it and the electronic density:

$$E_{ee}=\langle\Psi|\frac{1}{2}\sum_{ij}{}'\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}|\Psi\rangle$$
$$=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})g(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'. \quad (7)$$

Using the form of $g(\mathbf{r},\mathbf{r}')$ as given by Eq. (6), the electron-interaction energy can be split further as

$$E_{ee}=E_H+E_{\mathrm{xc}}, \quad (8)$$

where E_H is the Coulomb self-energy,

$$E_H=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}', \quad (9)$$

and E_{xc} is the quantum-mechanical exchange-correlation energy,

$$E_{\mathrm{xc}}=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}', \quad (10)$$

which is the energy of interaction between the density and the Fermi-Coulomb hole charge distribution.

The property associated [8] with the correlation-kinetic-energy component of the Kohn-Sham potential is the kinetic-energy-density tensor $t_{\alpha\beta}(\mathbf{r})$. This is a real, symmetric tensor defined in terms of the single-particle density matrix $\gamma(\mathbf{r},\mathbf{r}')$ as

$$t_{\alpha\beta}(\mathbf{r};[\gamma])=\frac{1}{4}\left(\frac{\partial^2}{\partial r'_\alpha\partial r''_\beta}+\frac{\partial^2}{\partial r'_\beta\partial r''_\alpha}\right)\gamma(\mathbf{r}',\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \quad (11)$$

The trace of the kinetic-energy-density tensor is the scalar kinetic energy density $t(\mathbf{r})=\Sigma_\alpha t_{\alpha\alpha}(\mathbf{r})\geqslant 0$. The kinetic energy T is then

$$T=\langle\Psi|-\sum_i\frac{1}{2}\nabla_i^2|\Psi\rangle=\int d\mathbf{r}\;t(\mathbf{r}). \quad (12)$$

Finally, the total energy E can thus be written as

$$E=T+\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}+E_{ee}, \quad (13)$$

with T and E_{ee} as defined above.

B. Definitions within Kohn-Sham theory

The basic idea underlying Kohn-Sham theory [2] is the construction of a model system of noninteracting fermions for which the density is the same as that of the interacting system. As such the ground-state energy functional $E[\rho]$ is partitioned as

$$E[\rho]=T_s[\rho]+\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}+E_{ee}^{\mathrm{KS}}[\rho], \quad (14)$$

where $T_s[\rho]$ is the corresponding kinetic energy of the noninteracting system. This equation defines the Kohn-Sham theory electron-interaction energy functional $E_{ee}^{\mathrm{KS}}[\rho]$, which can then be further partitioned as

$$E_{ee}^{\mathrm{KS}}[\rho]=E_H[\rho]+E_{\mathrm{xc}}^{\mathrm{KS}}[\rho], \quad (15)$$

where $E_H[\rho]$ is the Coulomb self-energy defined previously. Comparison with Eq. (13) for the energy expression in Schrödinger theory then defines the Kohn-Sham theory exchange-correlation energy functional $E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]$ as the sum of the quantum-mechanical exchange-correlation energy E_{xc} and the correlation-kinetic energy $T_c[\rho]$:

$$E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]=E_{\mathrm{xc}}[\rho]+T_c[\rho], \quad (16)$$

where in turn

$$T_c[\rho]=T[\rho]-T_s[\rho]. \quad (17)$$

The application of the variational principle to the ground-state energy functional of Eq. (14) for arbitrary norm-conserving variations of the density leads to the Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2+v(\mathbf{r})+v_{ee}^{\mathrm{KS}}(\mathbf{r})\right]\phi_i(\mathbf{x})=\epsilon_i\phi_i(\mathbf{x}),\quad i=1,\ldots,N, \quad (18)$$

where $v_{ee}^{\mathrm{KS}}(\mathbf{r})$ is the local potential in which *all* the electron correlations are incorporated. As a result of the variational principle, this potential is derived to be the functional derivative of $E_{ee}^{\mathrm{KS}}[\rho]$:

$$v_{ee}^{\mathrm{KS}}(\mathbf{r})=\delta E_{ee}^{\mathrm{KS}}[\rho]/\delta\rho(\mathbf{r}). \quad (19)$$

With the partition of $E_{ee}^{\mathrm{KS}}[\rho]$ according to Eq. (15), the potential can be written as the sum

$$v_{ee}^{\mathrm{KS}}(\mathbf{r})=v_H(\mathbf{r})+v_{\mathrm{xc}}^{\mathrm{KS}}(\mathbf{r}), \quad (20)$$

which defines the density-functional theory Hartree potential $v_H(\mathbf{r})$ as the functional derivative

$$v_H(\mathbf{r})=\frac{\delta E_H[\rho]}{\delta\rho(r)}=\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \quad (21)$$

and the Kohn-Sham theory ‘‘exchange-correlation’’ potential $v_{\mathrm{xc}}^{\mathrm{KS}}(\mathbf{r})$ as the functional derivative

$$v_{\mathrm{xc}}^{\mathrm{KS}}(\mathbf{r})=\delta E_{\mathrm{xc}}^{\mathrm{KS}}[\rho]/\delta\rho(\mathbf{r}). \quad (22)$$

The ground-state ‘‘wave function’’ corresponding to this noninteracting system is then a *single* Slater determinant $\Phi_s\{\phi_i(\mathbf{x})\}$ of the lowest occupied orbitals $\phi_i(\mathbf{x})$ of the Kohn-Sham differential equation. The Dirac [18] single-particle density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ that results from this Slater determinant is

$$\gamma_s(\mathbf{r},\mathbf{r}')=\langle\Phi_s|\hat{X}|\Phi_s\rangle=\sum_i\sum_\sigma\phi_i^*(\mathbf{r}\sigma)\phi_i(\mathbf{r}'\sigma), \quad (23)$$

and it is idempotent. The exact ground-state density $\rho(\mathbf{r})$ and the noninteracting kinetic energy $T_s[\rho]$ are also obtained from this Slater determinant as

$$\rho(\mathbf{r}) = \langle \Phi_s | \hat{\rho} | \Phi_s \rangle = \sum_i \sum_\sigma |\phi_i(\mathbf{r}\sigma)|^2, \tag{24}$$

and

$$T_s[\rho] = \sum_i \int \phi_i^*(\mathbf{x}) \left[-\frac{1}{2} \nabla^2 \right] \phi_i(\mathbf{x}) d\mathbf{r}, \tag{25}$$

respectively. The ground-state energy is then determined by the energy functional of Eq. (14). Finally, in addition to generating the orbitals from which the exact ground-state density and energy of the interacting system are determined, the highest occupied eigenvalue of the Kohn-Sham differential equation Eq. (18) has the physical interpretation [19] of being the removal energy. Thus, in principle, its solution can lead to the determination of properties such as the ionization potential, electron affinity, and work function.

III. PHYSICAL INTERPRETATION OF ELECTRON-INTERACTION POTENTIAL OF KOHN-SHAM THEORY

Since the electron-interaction energy functional $E_{ee}^{\mathrm{KS}}[\rho]$ of Kohn-Sham theory is representative of Pauli and Coulomb correlations as well as the correlation contribution to the kinetic energy, so is the corresponding local potential $v_{ee}^{\mathrm{KS}}(\mathbf{r})$ obtained from it through functional differentiation. In the physical interpretation of the potential $v_{ee}^{\mathrm{KS}}(\mathbf{r})$, however, it is possible to distinguish between the *purely* quantum-mechanical (Pauli and Coulomb) electron-correlation component $W_{ee}(\mathbf{r})$, and the correlation-kinetic-energy component $W_{t_c}(\mathbf{r})$. We begin this section with a description of the physical interpretation of $v_{ee}^{\mathrm{KS}}(\mathbf{r})$, and then discuss its components $W_{ee}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ more fully.

The electron-interaction potential $v_{ee}^{\mathrm{KS}}(\mathbf{r})$ of Kohn-Sham theory is the work done to bring an electron from infinity to its position at $\mathbf{r}$ against a field $\boldsymbol{\mathcal{F}}(\mathbf{r})$:

$$v_{ee}^{\mathrm{KS}}(\mathbf{r}) = \frac{\delta E_{ee}^{\mathrm{KS}}[\rho]}{\delta \rho(\mathbf{r})} = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{F}}(\mathbf{r}') \cdot d\boldsymbol{l}'. \tag{26}$$

The field $\boldsymbol{\mathcal{F}}(\mathbf{r})$ is the sum of two fields:

$$\boldsymbol{\mathcal{F}}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) + Z_{t_c}(\mathbf{r}). \tag{27}$$

The field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ is strictly representative of Pauli and Coulomb correlations since its quantum-mechanical source charge distribution is the pair-correlation density $g(\mathbf{r},\mathbf{r}')$. On the other hand, the field $\mathbf{Z}_{t_c}(\mathbf{r})$ arises from the kinetic-energy-density tensor $t_{\alpha\beta}(\mathbf{r})$. It is the difference of the fields derived from the tensor for the interacting and Kohn-Sham noninteracting systems, and is thereby representative of the correlation-kinetic contribution.

Thus, the potential $v_{ee}^{\mathrm{KS}}(\mathbf{r})$ may be expressed as the sum

$$v_{ee}^{\mathrm{KS}}(\mathbf{r}) = W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r}), \tag{28}$$

where

$$W_{ee}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}') \cdot d\boldsymbol{l}', \tag{29}$$

and

$$W_{t_c}(\mathbf{r}) = -\int_\infty^{\mathbf{r}} \mathbf{Z}_{t_c}(\mathbf{r}') \cdot d\boldsymbol{l}'. \tag{30}$$

The interpretation of the functional derivative $v_{ee}^{\mathrm{KS}}(\mathbf{r})$ as the work done is due to the fact that it can be written as

$$\boldsymbol{\nabla} v_{ee}^{\mathrm{KS}}(\mathbf{r}) = -\boldsymbol{\mathcal{F}}(\mathbf{r}), \tag{31}$$

so that the sum of the work $W_{ee}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ is path independent. The path independence of the work is, of course, rigorously valid provided the field $\boldsymbol{\mathcal{F}}(\mathbf{r})$ is smooth, i.e., it is continuous, differentiable, and has continuous first derivatives. Equation (31) also implies that the curl of the field $\boldsymbol{\mathcal{F}}(\mathbf{r})$ vanishes:

$$\boldsymbol{\nabla} \times \boldsymbol{\mathcal{F}}(\mathbf{r}) = \mathbf{0}. \tag{32}$$

For systems of a certain symmetry such as closed-shell atoms, jellium metal clusters, jellium metal surfaces, open-shell atoms in the central-field approximation, etc., the work $W_{ee}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ are, however, separately path independent since $\boldsymbol{\nabla} \times \boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = \boldsymbol{\nabla} \times \mathbf{Z}_{t_c}(\mathbf{r}) = \mathbf{0}$.

A. The quantum-mechanical electron-interaction component $W_{ee}(\mathbf{r})$

The physical interpretation of the electron-interaction component $W_{ee}(\mathbf{r})$ was originally proposed by Harbola and Sahni [7], and derived by them via Coulomb's law. It is based on the observation that the pair-correlation density $g(\mathbf{r},\mathbf{r}')$ is not a static but rather a *dynamic* charge distribution whose structure changes as a function of electron position. The dynamic nature of this charge then must be accounted for in the description of the potential. Thus, in order to obtain the local potential in which the electron moves, the force field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ due to this charge distribution must first be determined. According to Coulomb's law this field is

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = \int \frac{g(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} d\mathbf{r}'. \tag{33}$$

The component $W_{ee}(\mathbf{r})$ is then the work done to bring an electron from infinity to its position at $\mathbf{r}$ in this force field as defined by Eq. (29).

The component $W_{ee}(\mathbf{r})$ can be further simplified by employing the expression for $g(\mathbf{r}, \mathbf{r}')$ [see Eq. (6)] in terms of the density $\rho(\mathbf{r}')$ and the Fermi-Coulomb hole charge density $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$. The field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ is then the sum of the Hartree $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$ and exchange-correlation $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$ fields:

$$\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) = \boldsymbol{\mathcal{E}}_H(\mathbf{r}) + \boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}), \tag{34}$$

where

$$\boldsymbol{\mathcal{E}}_H(\mathbf{r})=\int\frac{\rho(\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,d\mathbf{r}',$$

$$\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})=\int\frac{\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,d\mathbf{r}'. \tag{35}$$

The component $W_{ee}(\mathbf{r})$ is in turn the sum of the work done $W_H(\mathbf{r})$ and $W_{\mathrm{xc}}(\mathbf{r})$ to move an electron in the Hartree and exchange-correlation fields, respectively,

$$W_{ee}(\mathbf{r})=W_H(\mathbf{r})+W_{\mathrm{xc}}(\mathbf{r}), \tag{36}$$

where

$$W_H(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{E}}_H(\mathbf{r}')\cdot d\boldsymbol{l}',\quad W_{\mathrm{xc}}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}')\cdot d\boldsymbol{l}'. \tag{37}$$

Now, the electronic density $\rho(\mathbf{r})$ is a *static* charge distribution whose structure does not change as a function of electron position. Thus, the Hartree field can be written as $\boldsymbol{\mathcal{E}}_H(\mathbf{r})=-\nabla W_H(\mathbf{r})$, where

$$W_H(\mathbf{r})=\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'. \tag{38}$$

The work $W_H(\mathbf{r})$ is path independent and $\boldsymbol{\nabla}\times\boldsymbol{\mathcal{E}}_H(\mathbf{r})=0$. Furthermore, the scalar potential $W_H(\mathbf{r})$ is recognized to be the density-functional theory Hartree potential $v_H(\mathbf{r})$ of Eq. (21). Thus, the functional derivative of the Coulomb self-energy functional $E_H[\rho]$ has the physical interpretation of being the work done in the field of the electronic density. The component $W_{ee}(\mathbf{r})$ is then the sum of the Hartree potential and the work done to move an electron in the field of the quantum-mechanical Fermi-Coulomb hole charge distribution: $W_{ee}(\mathbf{r})=v_H(\mathbf{r})+W_{\mathrm{xc}}(\mathbf{r})$. The work $W_{\mathrm{xc}}(\mathbf{r})$ is path independent for the symmetrical density systems noted previously since the $\boldsymbol{\nabla}\times\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})=0$ for these cases. It is important to note, however, that the corresponding Fermi-Coulomb hole charge distribution $\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$, which gives rise to the field $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$ need not possess the same symmetry for arbitrary electron position. For example, in either closed-shell atoms or open-shell atoms in the central-field approximation for which the density is spherically symmetric, the Fermi-Coulomb hole is not, the only exception being when the electron is at the nucleus.

B. The correlation-kinetic energy component $W_{t_c}(\mathbf{r})$

The correlation-kinetic energy component $W_{t_c}(\mathbf{r})$ is the work done to move an electron in the field $\mathbf{Z}_{t_c}(\mathbf{r})$ as expressed by Eq. (30). The field $\mathbf{Z}_{t_c}(\mathbf{r})$ is given in terms of a field $\mathbf{z}(\mathbf{r};[\gamma])$ whose component $z_\alpha(\mathbf{r})$ is derived from the kinetic-energy-density tensor $t_{\alpha\beta}(\mathbf{r};[\gamma])$ as [8]

$$z_\alpha(\mathbf{r};[\gamma])=2\sum_{\beta=1}^{3}\frac{\partial}{\partial r_\beta}t_{\alpha\beta}(\mathbf{r};[\gamma]). \tag{39}$$

The field $\mathbf{z}(\mathbf{r};[\gamma])$ thus defined is for the interacting system since the tensor involves the density matrix $\gamma(\mathbf{r},\mathbf{r}')$ of Eq. (3). With the field $z(\mathbf{r};[\gamma_s])$ derived similarly from the tensor $t_{\alpha\beta}(\mathbf{r};[\gamma_s])$ written in terms of the idempotent Dirac density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ of Kohn-Sham theory, the field $\mathbf{Z}_{t_c}(\mathbf{r})$ is then defined as

$$\mathbf{Z}_{t_c}(\mathbf{r})=\frac{1}{\rho(\mathbf{r})}\{\mathbf{z}(\mathbf{r};[\gamma_s])-\mathbf{z}(\mathbf{r};[\gamma])\}. \tag{40}$$

Note that the determination of this field thus requires knowledge of the Kohn-Sham orbitals and system wave function.

C. Proof via the differential virial theorem

The electron-interaction component $W_{ee}(\mathbf{r})$ was originally derived, as noted previously, by Harbola and Sahni [7] via Coulomb's law. Since this component does not contain any correlation-kinetic-energy contributions, it does not [7,20,21] satisfy the Kohn-Sham theory sum rule relating the corresponding electron-interaction energy $E_{ee}^{\mathrm{KS}}[\rho]$ to its functional derivative (potential) $v_{ee}^{\mathrm{KS}}(\mathbf{r})$. The sum rule, which is derived [22,23] from the virial theorem, and in which the correlation-kinetic energy $T_c[\rho]$ contribution is made explicit, is

$$E_{ee}^{\mathrm{KS}}[\rho]+\int d\mathbf{r}\;\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}v_{ee}^{\mathrm{KS}}(\mathbf{r})=-T_c\leqslant 0. \tag{41}$$

Consequently, Harbola and Sahni [7,21] proposed that a term that accounts for the correlation-kinetic energy contribution be added to $W_{ee}(\mathbf{r})$ in order to obtain the Kohn-Sham potential $v_{ee}^{\mathrm{KS}}(\mathbf{r})$. As such they suggested adding a term proportional to $\delta T_c[\rho]/\delta\rho(\mathbf{r})$. The term to add to $W_{ee}(\mathbf{r})$ is the work $W_{t_c}(\mathbf{r})$. Both the components $W_{ee}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ can, however, be derived from the virial theorem and we give here for completeness the proof according to Holas and March [8].

The integral form of the quantum-mechanical virial theorem, which is

$$2T+E_{ee}=\int d\mathbf{r}\;\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}v(\mathbf{r}), \tag{42}$$

can be written in differential form [8] as

$$\boldsymbol{\nabla}v(\mathbf{r})=-\mathbf{F}(\mathbf{r}), \tag{43}$$

where

$$\mathbf{F}(\mathbf{r})=-\boldsymbol{\mathcal{E}}_{ee}+\frac{1}{\rho(\mathbf{r})}\left[-\frac{1}{4}\boldsymbol{\nabla}\nabla^2\rho(\mathbf{r})+\mathbf{z}(\mathbf{r};[\gamma])\right]. \tag{44}$$

Note that the field $\mathbf{F}(\mathbf{r})$ depends upon the density $\rho(\mathbf{r})$, as well as the single-particle density matrix $\gamma(\mathbf{r},\mathbf{r}')$ and the pair-correlation density $g(\mathbf{r},\mathbf{r}')$ through the fields $\mathbf{z}(\mathbf{r})$ and $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$, respectively. The corresponding differential form of the virial theorem for the noninteracting Kohn-Sham system is

$$\boldsymbol{\nabla}v(\mathbf{r})=-\mathbf{F}^{\mathrm{KS}}(\mathbf{r}), \tag{45}$$

where

$$\mathbf{F}^{\mathrm{KS}}(\mathbf{r})=\boldsymbol{\nabla}v_{ee}^{\mathrm{KS}}(\mathbf{r})+\frac{1}{\rho(\mathbf{r})}\left[-\frac{1}{4}\boldsymbol{\nabla}\nabla^2\rho(\mathbf{r})+\mathbf{z}(\mathbf{r};[\gamma_s])\right]. \tag{46}$$

The field $\mathbf{F}^{\mathrm{KS}}(\mathbf{r})$ depends on the density $\rho(\mathbf{r})$, and the idempotent density matrix $\gamma_s(\mathbf{r},\mathbf{r}')$ through the field $\mathbf{z}(\mathbf{r};[\gamma_s])$, and instead of the field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ it is the gradient of the Kohn-Sham potential $v_{ee}^{\mathrm{KS}}(\mathbf{r})$ that appears. On equating Eqs. (43) and (45), one obtains

$$\begin{aligned}\boldsymbol{\nabla} v_{ee}^{\mathrm{KS}}(\mathbf{r}) &= -\left\{\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) + \frac{1}{\rho(\mathbf{r})}\left[\mathbf{z}(\mathbf{r};[\gamma_s]) - \mathbf{z}(\mathbf{r};[\gamma])\right]\right\} \\ &= -\boldsymbol{\mathcal{F}}(\mathbf{r}), \end{aligned} \tag{47}$$

which in turn leads to the interpretation of $v_{ee}^{\mathrm{KS}}(\mathbf{r})$ as the work done to move an electron in the field $\boldsymbol{\mathcal{F}}(\mathbf{r})$, and shows that this field is conservative.

IV. ELECTRON-INTERACTION ENERGY OF KOHN-SHAM THEORY

As is the case for the electron-interaction potential $v_{ee}^{\mathrm{KS}}(\mathbf{r})$, the Kohn-Sham electron-interaction energy $E_{ee}^{\mathrm{KS}}[\rho]$ of Eq. (15) can also be expressed in terms of fields (and thus source distributions) corresponding to the quantum-mechanical electron-interaction and correlation-kinetic energy components. The quantum-mechanical electron-interaction energy component Eq. (7) is

$$E_{ee}[\rho] = \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}), \tag{48}$$

which can be reduced further to its Coulomb self-energy [Eq. (9)] and exchange-correlation [Eq. (10)] components as

$$E_H[\rho] = \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_H(\mathbf{r}) \tag{49}$$

and

$$E_{\mathrm{xc}}[\rho] = \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r}), \tag{50}$$

respectively. The correlation-kinetic-energy component of Eq. (17) is

$$T_c[\rho] = \frac{1}{2}\int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\mathbf{Z}_{t_c}(\mathbf{r}). \tag{51}$$

The fields $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_H(\mathbf{r})$, $\boldsymbol{\mathcal{E}}_{\mathrm{xc}}(\mathbf{r})$, and $\mathbf{Z}_{t_c}(\mathbf{r})$ are as defined in the previous section.

The proof of Eq. (48) for $E_{ee}[\rho]$ follows [7] trivially from the symmetry in an interchange of $\mathbf{r}$ and $\mathbf{r}'$ of the pair-correlation *function* $h(\mathbf{r},\mathbf{r}')=g(\mathbf{r},\mathbf{r}')/\rho(\mathbf{r}')$. We provide here the proof of Eq. (51) for $T_c[\rho]$ via the virial theorem.

Proof via integral virial theorem

The virial theorem [Eq. (42)] can also be written as [4,23]

$$\begin{aligned}E_{ee}[\rho] &+ \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta E_{ee}[\rho]}{\delta\rho(\mathbf{r})}\right) \\ &= -2T - \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta T[\rho]}{\delta\rho(\mathbf{r})}\right). \end{aligned} \tag{52}$$

Since $E_{ee}^{\mathrm{KS}}[\rho] = E_{ee}[\rho] + T_c[\rho]$, we have

$$v_{ee}^{\mathrm{KS}}(\mathbf{r}) = \frac{\delta E_{ee}[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta T_c[\rho]}{\delta\rho(\mathbf{r})} = W_{ee}(\mathbf{r}) + W_{t_c}(\mathbf{r}), \tag{53}$$

and thus

$$\boldsymbol{\nabla} v_{ee}^{\mathrm{KS}}(\mathbf{r}) = \boldsymbol{\nabla}\left(\frac{\delta E_{ee}[\rho]}{\delta\rho(\mathbf{r})}\right) + \boldsymbol{\nabla}\left(\frac{\delta T_c[\rho]}{\delta\rho(\mathbf{r})}\right) = -\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) - \mathbf{Z}_{t_c}(\mathbf{r}). \tag{54}$$

On substituting for $\boldsymbol{\nabla}(\delta E_{ee}/\delta\rho)$ from Eq. (54) into Eq. (52) we obtain

$$\begin{aligned}E_{ee}[\rho] &- \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r}) - \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\mathbf{Z}_{t_c}(\mathbf{r}) \\ &= -2T_s[\rho] - 2T_c[\rho] - \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla}\left(\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})}\right). \end{aligned} \tag{55}$$

Using the relation of Eq. (48) and those of [4,23]

$$\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} = -v_s(\mathbf{r}) + \mathrm{const} \tag{56}$$

and

$$2T_s[\rho] = \int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\nabla} v_s \tag{57}$$

in Eq. (55) leads to Eq. (51) for $T_c[\rho]$. It is interesting to note that in deriving the expression for $T_c[\rho]$, the question whether $\boldsymbol{\nabla}\times\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ and $\boldsymbol{\nabla}\times\mathbf{Z}_{t_c}(\mathbf{r})$ vanishes or not is of no consequence. What is important is that the curl of the sum of these fields vanishes. We also note that Eq. (51) for $T_c[\rho]$ can equally well be derived [24] from the density-functional theory virial theorem Eq. (41).

V. PHYSICAL INTERPRETATION OF DENSITY-FUNCTIONAL THEORY REPRESENTATION OF THE HARTREE-FOCK AND HARTREE APPROXIMATIONS

As a consequence of the constrained search formulation [9] as well as a Green's-function analysis [14] of density-functional theory, there exists [9–11] an energy functional $E^{\mathrm{HF}}[\rho]$ that has a minimum corresponding to the Hartree-Fock [12] (HF) ground-state energy at the HF ground-state density $\rho(\mathbf{r})$. In the context of Kohn-Sham theory, this means that it is possible to define an electron-interaction energy functional $E_{ee}^{\mathrm{KSHF}}[\rho]$ whose functional derivative $v_{ee}^{\mathrm{KSHF}}(\mathbf{r})$ leads to the HF density and thereby the energy. [Similar remarks are valid for the Hartree [13] (H) approximation.] In the following subsection we provide the *rigorous physical* interpretation of the local potentials and energies in terms of the fields and source distributions which give rise to them. [The symbol $\rho(\mathbf{r})$ here indicates either the HF or H density, as the case may be.]

A. Hartree-Fock approximation

In the HF approximation, the wave function Ψ is assumed to be a single Slater determinant $\Phi\{\phi_i^{\mathrm{HF}}\}$ of spin orbitals $\phi_i^{\mathrm{HF}}(\mathbf{r})$. The pair-correlation density $g^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$ corresponding to this wave function [see Eq. (5)] is

$$g^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')+\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}'), \tag{58}$$

where $\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$ is the HF theory Fermi hole charge defined in terms of the HF spinless idempotent Dirac density matrix $\gamma^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$ as $\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')=-|\gamma^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')|^2/[2\rho(\mathbf{r})]$. (This expression is valid for spin-compensated systems of a certain symmetry such as closed-shell atoms, open-shell atoms in the central field approximation, jellium metal surfaces, etc.) The Fermi hole satisfies the constraints of charge neutrality, negativity, and value at electron position: $\int\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')d\mathbf{r}'=-1$, $\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r})\leqslant 0$, $\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r})=-\rho(\mathbf{r})/2$. The electron-interaction energy E_{ee}^{HF} is then

$$\begin{aligned}E_{ee}^{\mathrm{HF}}[\rho;\gamma^{\mathrm{HF}}]&=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})g^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'\\&=E_H[\rho]+E_x[\rho;\gamma^{\mathrm{HF}}],\end{aligned} \tag{59}$$

where the exchange energy $E_x[\rho;\gamma^{\mathrm{HF}}]$ is the energy of interaction between the electronic and Fermi hole charge densities:

$$E_x[\rho;\gamma^{\mathrm{HF}}]=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'. \tag{60}$$

Thus, the ground-state energy is

$$\begin{aligned}E^{\mathrm{HF}}[\rho;\gamma^{\mathrm{HF}}]=T^{\mathrm{HF}}[\rho]+\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}+E_H[\rho]\\+E_x[\rho;\gamma^{\mathrm{HF}}].\end{aligned} \tag{61}$$

The HF theory differential equation, obtained by variational minimization of this energy for arbitrary variations of the space orbitals, is then

$$\left[-\frac{1}{2}\nabla^2+v(\mathbf{r})+v_H(\mathbf{r})+v_{x,i}(\mathbf{r})\right]\phi_i^{\mathrm{HF}}(\mathbf{r})=\epsilon_i\phi_i^{\mathrm{HF}}(\mathbf{r}), \tag{62}$$

where $v_{x,i}(\mathbf{r})$ is an orbital-dependent potential defined as

$$v_{x,i}(\mathbf{r})=\int\frac{\rho_{x,i}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}', \tag{63}$$

due to the orbital-dependent Fermi hole $\rho_{x,i}(\mathbf{r},\mathbf{r}')$ which in turn is defined as

$$\rho_{x,i}(\mathbf{r},\mathbf{r}')=\tfrac{1}{2}\gamma^{\mathrm{HF}}(\vec{\mathbf{r}},\vec{\mathbf{r}}')\phi_i^{\mathrm{HF}}(\vec{\mathbf{r}}')/\phi_i^{\mathrm{HF}}(\vec{\mathbf{r}}). \tag{64}$$

Thus, as described by Slater [25], Hartree-Fock theory can be viewed as one in which each electron moves in a local effective potential of its own. (Of course, when the HF theory differential equation is written [3] in terms of the Hermitian nonlocal integral exchange operator, the effective potential is identical for all orbitals).

In the Kohn-Sham representation of the HF approximation, the corresponding energy functional and differential equation are

$$E^{\mathrm{HF}}[\rho]=T_s[\rho]+\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}+E_{ee}^{\mathrm{KSHF}}[\rho] \tag{65}$$

and

$$\left[-\frac{1}{2}\nabla^2+v(\mathbf{r})+v_{ee}^{\mathrm{KSHF}}(\mathbf{r})\right]\phi_i(\mathbf{x})=\epsilon_i\phi_i(\mathbf{x}), \tag{66}$$

respectively. Here $E_{ee}^{\mathrm{KSHF}}[\rho]$ is the energy functional, and

$$v_{ee}^{\mathrm{KSHF}}(\mathbf{r})=\frac{\delta E_{ee}^{\mathrm{KSHF}}[\rho]}{\delta\rho(\mathbf{r})}, \tag{67}$$

the local potential representing electron correlations, which lead to the HF density

$$\rho(\mathbf{r})=\sum_i\sum_\sigma|\phi_i(\mathbf{r}\sigma)|^2=2\sum_i|\phi_i^{\mathrm{HF}}(\vec{\mathbf{r}})|^2, \tag{68}$$

and thereby to the HF ground-state energy.

The physical interpretation of the local potential $v_{ee}^{\mathrm{KSHF}}(\mathbf{r})$ is that it is the work done to move an electron in the field $\boldsymbol{\mathcal{F}}^{\mathrm{HF}}(\mathbf{r})$:

$$v_{ee}^{\mathrm{KSHF}}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{F}}^{\mathrm{HF}}(\mathbf{r}')\cdot d\boldsymbol{l}', \tag{69}$$

where

$$\boldsymbol{\mathcal{F}}^{\mathrm{HF}}(\mathbf{r})=\boldsymbol{\mathcal{E}}_{ee}^{\mathrm{HF}}(\mathbf{r})+\mathbf{Z}_{t_c}^{\mathrm{HF}}(\mathbf{r}). \tag{70}$$

Here $\boldsymbol{\mathcal{E}}_{ee}^{\mathrm{HF}}(\mathbf{r})$ is the field due to the pair-correlation density $g^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$ obtained via Coulomb's law, and $\mathbf{Z}_{t_c}^{\mathrm{HF}}(\mathbf{r})$ the difference of the fields $\mathbf{z}(\mathbf{r})$ obtained from the Kohn-Sham and Hartree-Fock kinetic-energy-density tensors:

$$\boldsymbol{\mathcal{E}}_{ee}^{\mathrm{HF}}(\mathbf{r})=\int\frac{g^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,d\mathbf{r}',$$

$$\mathbf{Z}_{t_c}^{\mathrm{HF}}(\mathbf{r})=\frac{1}{\rho(\mathbf{r})}\{\mathbf{z}(\mathbf{r};[\gamma_s])-\mathbf{z}(\mathbf{r};[\gamma^{\mathrm{HF}}])\}. \tag{71}$$

Thus, the potential $v_{ee}^{\mathrm{KSHF}}(\mathbf{r})$ may be written as

$$v_{ee}^{\mathrm{KSHF}}(\mathbf{r})=W_{ee}^{\mathrm{HF}}(\mathbf{r})+W_{t_c}^{\mathrm{HF}}(\mathbf{r}), \tag{72}$$

where

$$W_{ee}^{\mathrm{HF}}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{E}}_{ee}^{\mathrm{HF}}(\mathbf{r}')\cdot d\boldsymbol{l}',\quad W_{t_c}^{\mathrm{HF}}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\mathbf{Z}_{t_c}^{\mathrm{HF}}(\mathbf{r}')\cdot d\boldsymbol{l}'. \tag{73}$$

Furthermore, since $\boldsymbol{\nabla}v_{ee}^{\mathrm{KSHF}}(\mathbf{r})=-\boldsymbol{\mathcal{F}}^{\mathrm{HF}}(\mathbf{r})$, the sum of the work $W_{ee}^{\mathrm{KSHF}}(\mathbf{r})$ and $W_{t_c}^{\mathrm{HF}}(\mathbf{r})$ is path independent. The work

$W_{ee}^{\mathrm{HF}}(\mathbf{r})$ can be further split into its Hartree $W_H(\mathbf{r})$ and exchange $W_x^{\mathrm{HF}}(\mathbf{r})$ components, where

$$W_x^{\mathrm{HF}}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{E}}_x^{\mathrm{HF}}(\mathbf{r}')\cdot d\boldsymbol{l}',$$

$$\boldsymbol{\mathcal{E}}_x^{\mathrm{HF}}(\mathbf{r})=\int\frac{\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,d\boldsymbol{l}'. \tag{74}$$

Note that $W_x^{\mathrm{HF}}(\mathbf{r})$ is the work done in the field $\boldsymbol{\mathcal{E}}_x^{\mathrm{HF}}(\mathbf{r})$ due to the HF theory Fermi hole charge $\rho_x^{\mathrm{HF}}(\mathbf{r},\mathbf{r}')$.

A comparison of Eqs. (61) and (65) shows that the Kohn-Sham theory functional $E_{ee}^{\mathrm{KSHF}}[\rho]$ can also be separated into the quantum-mechanical electron-interaction and correlation-kinetic-energy components as

$$E_{ee}^{\mathrm{KSHF}}[\rho]=E_{ee}^{\mathrm{HF}}[\rho;\gamma^{\mathrm{HF}}]+T_c^{\mathrm{HF}}[\rho], \tag{75}$$

where

$$T_c^{\mathrm{HF}}[\rho]=T^{\mathrm{HF}}[\rho]-T_s[\rho]. \tag{76}$$

The quantum-mechanical exchange $E_x[\rho;\gamma^{\mathrm{HF}}]$ component of $E_{ee}^{\mathrm{HF}}[\rho;\gamma^{\mathrm{HF}}]$, and $T_c^{\mathrm{HF}}[\rho]$ can also be written in terms of the fields which give rise to them as

$$E_x[\rho;\gamma^{\mathrm{HF}}]=\int d\mathbf{r}\;\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_x^{\mathrm{HF}}(\mathbf{r}) \tag{77}$$

and

$$T_c^{\mathrm{HF}}[\rho]=\frac{1}{2}\int d\mathbf{r}\rho(\mathbf{r})\mathbf{r}\cdot\mathbf{Z}_{t_c}^{\mathrm{HF}}(\mathbf{r}), \tag{78}$$

respectively.

The equations of the physical interpretation of the density-functional theory representation of the HF approximation are derived by replacing the system wave function Ψ in the expectations of Secs. III and IV by the HF wave function $\Phi\{\phi_i^{\mathrm{HF}}\}$. The proof of this statement lies in the fact that in the Hartree-Fock approximation the virial theorem in integral form is satisfied and the differential form of the virial theorem Eq. (43) remains unchanged [26].

Finally, we note that provided the HF theory density is known, it is possible [27] to determine a local effective potential whose orbitals generate the same density. However, the total ground-state energy as determined by these orbitals via the HF energy functional Eq. (61) must be greater than that of HF theory. In principle these energies should also be greater than those of the optimized potential method [28]. The Kohn-Sham theory electron-interaction energy functional and potential that give the HF theory density and energy are given in Eqs. (75) and (72), respectively.

B. Hartree approximation

In the Hartree approximation [13] in which the system wave function is assumed to be a product of spin orbitals $\Psi=\Pi_j\phi_i^H(\mathbf{r}\sigma)$, each electron also moves in a local effective potential of its own given by $[v(\mathbf{r})+v_H(\mathbf{r})+v_i^{\mathrm{SIC}}(\mathbf{r})]$, where the potential

$$v_i^{\mathrm{SIC}}(\mathbf{r})=\int\frac{q_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' \tag{79}$$

is due to the static self-interaction-correction (SIC) charge $q_i=-\Sigma_\sigma\phi_i^H(\mathbf{r}\sigma)\phi_i^H(\mathbf{r}\sigma)$. The pair-correlation density $g^H(\mathbf{r},\mathbf{r}')$ in this case is

$$g^H(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r}')+\rho_{\mathrm{SIC}}^H(\mathbf{r},\mathbf{r}'), \tag{80}$$

where $\rho_{\mathrm{SIC}}^H(\mathbf{r},\mathbf{r}')=-\Sigma_i q_i(\mathbf{r})q_i(\mathbf{r}')/\rho(\mathbf{r})$, with $\int\rho_{\mathrm{SIC}}(\mathbf{r},\mathbf{r}')d\mathbf{r}'=-1$. Thus, the electron-interaction energy E_{ee}^H is

$$E_{ee}^H[\rho;\phi_i^H]=E_H[\rho]+E_{\mathrm{SIC}}^H[\rho;\phi_i^H], \tag{81}$$

where the SIC energy $E_{\mathrm{SIC}}^H[\rho;\phi_i^H]$ is

$$E_{\mathrm{SIC}}^H[\rho;\phi_i^H]=\frac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho_{\mathrm{SIC}}^H(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'. \tag{82}$$

In a manner similar to that previously described, a rigorous physical interpretation can be derived for the Kohn-Sham theory electron-interaction energy functional $E_{ee}^{\mathrm{KS}\text{-}H}[\rho]$ and local potential $v_{ee}^{\mathrm{KS}\text{-}H}(\mathbf{r})=\delta E_{ee}^{\mathrm{KS}\text{-}H}[\rho]/\delta\rho(\mathbf{r})$ that lead to the Hartree approximation ground-state density and energy. Note that once again the differential form of the virial theorem Eq. (43) remains unchanged in this approximation and that the virial theorem in integral form is satisfied. Thus, the potential $v_{ee}^{\mathrm{KS}\text{-}H}(\mathbf{r})$ is the work done in the field $\boldsymbol{\mathcal{F}}^H(\mathbf{r})$:

$$v_{ee}^{\mathrm{KS}\text{-}H}(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{F}}^H(\mathbf{r}')\cdot d\boldsymbol{l}'=W_{ee}^H(\mathbf{r})+W_{t_c}^H(\mathbf{r}), \tag{83}$$

where $\boldsymbol{\mathcal{F}}^H(\mathbf{r})$ is the sum of the fields $\boldsymbol{\mathcal{E}}_{ee}^H(\mathbf{r})$ due to the pair-correlation density $g^H(\mathbf{r},\mathbf{r}')$ obtained by Coulomb's law, and $\mathbf{Z}_{t_c}^H(\mathbf{r})$ the difference of the fields $\mathbf{z}(\mathbf{r})$ obtained from the Kohn-Sham and Hartree kinetic-energy-density tensors. The work $W_{ee}^H(\mathbf{r})$ done in the field $\boldsymbol{\mathcal{E}}_{ee}^H(\mathbf{r})$ can be split into a Hartree $W_H(\mathbf{r})$ and a SIC component $W_{\mathrm{SIC}}^H(\mathbf{r})$, where

$$W_{\mathrm{SIC}}^H(\mathbf{r})=-\int_\infty^{\mathbf{r}}\boldsymbol{\mathcal{E}}_{\mathrm{SIC}}^H(\mathbf{r}')\cdot d\boldsymbol{l}',$$

$$\boldsymbol{\mathcal{E}}_{\mathrm{SIC}}^H(\mathbf{r})=\int\frac{\rho_{\mathrm{SIC}}^H(\mathbf{r},\mathbf{r}')(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3}\,d\mathbf{r}'. \tag{84}$$

The work $W_{t_c}^H(\mathbf{r})$ is that done in the field $\mathbf{Z}_{t_c}^H(\mathbf{r})$. The sum of the work $[W_{\mathrm{SIC}}^H(\mathbf{r})+W_{t_c}^H(\mathbf{r})]$ is path independent.

The Kohn-Sham electron-interaction energy functional $E_{ee}^{\mathrm{KS}\text{-}H}[\rho]$ is then

$$E_{ee}^{\mathrm{KS}\text{-}H}[\rho]=E_{ee}^H[\rho;\phi_i^H]+T_c^H[\rho], \tag{85}$$

where the SIC $E_{\mathrm{SIC}}^H[\rho;\phi_i^H]$ component of $E_{ee}^H[\rho;\phi_i^H]$ [see Eq. (81)], and $T_c^H[\rho]$ can be written in terms of the fields that give rise to them as

$$E_{\mathrm{SIC}}^H[\rho;\phi_i^H]=\int d\mathbf{r}\;\rho(\mathbf{r})\mathbf{r}\cdot\boldsymbol{\mathcal{E}}_{\mathrm{SIC}}^H(\mathbf{r}), \tag{86}$$

and

$$T_c^H[\rho] = \frac{1}{2}\int d\mathbf{r}\ \rho(\mathbf{r})\mathbf{r}\cdot\mathbf{Z}_{t_c}^H(\mathbf{r}), \tag{87}$$

respectively.

VI. WORK FORMALISM HARTREE-FOCK AND HARTREE APPROXIMATIONS

The work formalism [15,16] Hartree-Fock approximation is obtained from the density-functional theory representation of the HF approximation by neglecting the correlation-kinetic-energy contribution, i.e., by setting $W_{t_c}^{\mathrm{HF}}$ and $T_c^{\mathrm{HF}}[\rho]$ in Eqs. (72) and (75) to zero. (This implies that the pair-correlation density and Fermi hole are modified and not the same as those of Hartree-Fock theory.) The resulting Kohn-Sham differential equation Eq. (66) then becomes

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + W_x(\mathbf{r})\right]\psi_i(\mathbf{x}) = \epsilon_i\psi_i(\mathbf{x}), \tag{88}$$

where $W_x(\mathbf{r})$ is the work done in the field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ due to the Fermi hole $\rho_x(\mathbf{r},\mathbf{r}')$ constructed from the solutions of this equation. Additionally [see Eq. (75)], the corresponding electron-interaction energy is the same as the Hartree-Fock theory expression, but determined with the orbitals $\psi_i(\mathbf{x})$ of Eq. (88). The resulting ground-state energy is then a rigorous upper bound to the HF theory value.

The work formalism approximation leads to results [15,16,29,30] for atoms and atomic ions that are essentially the same as those of Hartree-Fock theory [15]. Thus, for example, the ground-state energies of atoms lie within [31] 50 ppm of those of Hartree-Fock theory [32], the difference for ^{35}Br-^{86}Rn being less than 10 ppm. These results also indicate that the correlation-kinetic-energy contribution at the exchange-only level is negligible for atoms. In all probability, this is also the case for molecules.

On neglect of the correlation-kinetic-energy contribution, the path independence [33] of the work $W_x(\mathbf{r})$ of Eq. (88) must be ensured for systems such as open-shell atoms and molecules. This is achieved either within the central field approximation [31] or by considering [7,34] only the irrotational component of the field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ in constructing the potential. In the latter case, the local exchange potential $W_x^{\mathrm{eff}}(\mathbf{r})$ is due to a *static* effective exchange charge distribution $\rho_x^{\mathrm{eff}}(\mathbf{r}) = \boldsymbol{\nabla}\cdot\boldsymbol{\mathcal{E}}_x(\mathbf{r})/4\pi$ so that

$$W_x^{\mathrm{eff}}(\mathbf{r}) = \int \frac{\rho_x^{\mathrm{eff}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'. \tag{89}$$

For atoms, the solenoidal component of the field $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$ is negligible [34] in comparison to its irrotational component. The reason for this is that the correlation-kinetic-energy work $W_{t_c}^{\mathrm{HF}}(\mathbf{r})$ is negligible. Recall that it is the sum $[W_x^{\mathrm{HF}}(\mathbf{r}) + W_{t_c}^{\mathrm{HF}}(\mathbf{r})]$ that is path independent. For negligible $W_{t_c}^{\mathrm{HF}}(\mathbf{r})$, the corresponding work $W_x(\mathbf{r})$ is then essentially path independent. Thus, the path-independent potential $W_x^{\mathrm{eff}}(\mathbf{r})$, constructed from the irrotational component of $\boldsymbol{\mathcal{E}}_x(\mathbf{r})$, is an accurate representation of Pauli correlations.

Once again, with the correlation-kinetic-energy contributions $W_{t_c}^H(\mathbf{r})$ and $T_c^H[\rho]$ neglected in the equations of the density-functional theory representation of the Hartree approximation, one obtains the work formalism [15,16] Hartree approximation. The resulting differential equation is

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + W_{\mathrm{SIC}}(\mathbf{r})\right]\psi_i(\mathbf{x}) = \epsilon_i\psi_i(\mathbf{x}), \tag{90}$$

with the ground-state energy expression being the same as that of the Hartree approximation but determined with the orbitals $\psi_i(\mathbf{x})$ of Eq. (90) instead. Again, the ground-state energy in this approximation is an upper bound to that of Hartree theory. For atoms these energies are [35] within 50 ppm of the results of the latter. Further, remarks similar to those on the path dependence of $W_x(\mathbf{r})$ are equally valid for the work $W_{\mathrm{SIC}}(\mathbf{r})$.

VII. CONCLUSION

In this paper we have provided a rigorous physical interpretation of the electron-interaction energy functional and functional derivative (potential) of Kohn-Sham density-functional theory. The interpretation is in terms of a sum of two fields whose source distributions are expectations of Hermitian operators. The first of these fields accounts for the purely quantum-mechanical electron correlations due to the Pauli exclusion principle and Coulomb repulsion. Its source is the pair-correlation density and it is determined by Coulomb's law. The second accounts for the correlation contribution to the kinetic energy, and its source is the difference between the kinetic-energy-density tensor for the noninteracting and interacting systems. The corresponding field is the derivative of this tensor. The sum of the electron-interaction and correlation-kinetic-energy fields is conservative. Thus, the Kohn-Sham theory potential representing *all* electron correlations is the work done in the sum of these fields. The Kohn-Sham electron-interaction energy functional in turn can also be expressed in virial form in terms of these fields. This then is the explanation of Kohn-Sham theory from the physical perspective of fields (and sources) representative of the different correlations present.

The physical description in terms of fields and their sources provides many insights into density-functional theory. These insights can then be used to construct accurate energy functionals and their derivatives. For example it leads to an *a priori* understanding of the structure of the components of the Kohn-Sham potential. Thus, we know that the (quantum-mechanical) exchange-correlation component $W_{\mathrm{xc}}(\mathbf{r})$ must approach the nucleus of an atom quadratically having zero slope there. This is because for an electron at the nucleus, the Fermi-Coulomb hole charge distribution is spherically symmetric. Thus, the field due to it at the electron position vanishes, which in turn implies that the potential there must have zero slope. In the interior of atoms and molecules, this potential must exhibit shell structure but be monotonic throughout since positive work must be done to remove an electron against the force of the field. Any non-monotonicity of the Kohn-Sham potential can then be attributed to correlation-kinetic-energy effects. Asymptotically, in the classically forbidden region, the potential $W_{\mathrm{xc}}(\mathbf{r})$ must vanish as $-1/r$ since the total charge of the Fermi-Coulomb hole is negative unity. Precisely the same reasoning applies to the corresponding exchange $W_x^{\mathrm{HF}}(\mathbf{r})$ and SIC $W_{\mathrm{SIC}}^H(\mathbf{r})$ potentials respectively of the density-functional representation of the Hartree-Fock and Hartree approximations.

Thus, together with previous quantitative work [7,15,29–31,36], there is considerable understanding of the structure of the exchange $W_x(\mathbf{r})$ and exchange-correlation $W_{\mathrm{xc}}(\mathbf{r})$ components for finite systems. Recently, methods [27,37] have been developed whereby given a ground- or excited-state wave function and corresponding density, it is possible to determine the Kohn-Sham orbitals that lead to the same density. As such it is now possible to also study the structure of the correlation-kinetic-energy field $\mathbf{Z}_{t_c}(\mathbf{r})$ and the component $W_{t_c}(\mathbf{r})$ of the Kohn-Sham potential. Preliminary studies indicate [24] the field $\mathbf{Z}_{t_c}(\mathbf{r})$ for atoms to be oscillatory, so that $W_{t_c}(\mathbf{r})$ is not monotonic as expected. Furthermore, the maximum values of $\mathbf{Z}_{t_c}(\mathbf{r})$ and $W_{t_c}(\mathbf{r})$ are an order of magnitude smaller than the corresponding exchange-correlation terms.

As another example, the physical interpretation leads to an understanding of electron correlations in approximate Kohn-Sham theory. When an approximate electron-interaction energy functional and its functional derivative are *both* derived via the *same* field and source distribution, correlations beyond those assumed in the construction of the energy functional itself then appear. This in turn leads to a better understanding of the approximation and of its results. For a discussion of electron correlations within the density-functional theory Hartree, local density, and gradient expansion approximations, we refer the reader to the literature [38–41].

Finally, as is known, there is no equivalent Hohenberg-Kohn-Sham variational principle for the excited-state energy in terms of the excited-state density. The physical interpretation for the ground state, however, leads to a plausible argument for the existence [7] of a local potential for excited states that incorporates all correlation effects. The argument is as follows: (i) A system in an excited state has a well defined wave function. Therefore, the electron-interaction field $\boldsymbol{\mathcal{E}}_{ee}(\mathbf{r})$ due to the corresponding pair-correlation density exists. (ii) If a system of noninteracting fermions with the true excited-state density exists, then the kinetic energies of the noninteracting and interacting systems must differ. The corresponding kinetic-energy-density tensors differ, and therefore a correlation-kinetic field $\mathbf{Z}_{t_c}(\mathbf{r})$ exists. (The assumption of the existence of a local potential leading to the excited state density, i.e., simultaneous v-representability of the interacting and noninteracting densities, is the same as that made in the excited-state Kohn-Sham scheme for ensembles, [4,42]). (iii) The proof of the physical interpretation for the ground state is based on the virial theorem. Both the integral and differential forms of the theorem are also valid for bound excited states. Thus, it seems reasonable to assume that excited states can be described by the same physical interpretation as for the ground state. The question of which noninteracting excited state of a given density to associate with the interacting excited state of the same density is related to the existence of an energy functional and variational principle for such states. Provided such an energy functional exists, one would choose that noninteracting excited state which leads to the same energy as that of the interacting system. Such a functional has been determined [43] for the lowest state of a given symmetry whereby orthogonality to the lower lying states is ensured. However, since a general energy functional for excited states is unknown, another way to determine the energy would be to strip the electrons and sum the removal energies, i.e., sum the highest occupied eigenvalues of the neutral and ionized systems.

There is also recent numerical evidence to support the physical description of excited states. These calculations are for [44] the excited states of Be and Na, the [24,45] $2\,{}^3S$ He isoelectronic sequence, and several [46] doubly excited autoionizing states of He. There are also calculations [47] for various multiplets of the ground, and singly and doubly excited states of carbon and silicon which also support the existence of a local potential for excited states.

In conclusion, the principal contribution of this work has been to combine the original ideas of Harbola and Sahni with their formal extension by Holas and March to provide a simple description of the physics underlying Kohn-Sham density-functional theory. In other words, we have explained the physics whereby the electron-interaction operator and wave function of Schrödinger theory can be replaced by a local potential and single Slater determinant, respectively, such that the same density and energy are obtained for the ground state. Harbola and Sahni arrived at their interpretation of the electron-interaction field through the physical consideration of the dynamic nature of the pair-correlation density, and proposed *ad hoc* the addition of a correlation-kinetic potential. On the other hand, Holas and March derived an expression for the Kohn-Sham exchange-correlation potential in terms of density matrices from the differential form of the virial theorem. It is from this expression that the electron-interaction and correlation-kinetic fields, and thereby the connection to the work of Harbola and Sahni, then emerges. The physical description of the Kohn-Sham theory electron-interaction potential is then unified with that of the corresponding energy functional by deriving via the integral virial theorem an expression for the energy in terms of these fields. We have in addition shown that the physics of the Kohn-Sham representation of the Hartree-Fock and Hartree theories is the same as that of its representation of Schrödinger theory. That is, it is the expectation of the same Hermitian operators but taken with respect to the Hartree-Fock and Hartree theory wave functions, respectively, that are the source distributions for the electron-interaction and correlation-kinetic fields of these representations. We have furthermore shown that if in these representations, the correlation-kinetic-energy component is neglected, the equations then reduce to those of the work formalism Hartree-Fock and Hartree approximations. Finally, we have provided a plausible argument extending the physical picture of ground-state Kohn-Sham theory to excited states.

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