

Communication: Kohn-Sham theory for excited states of Coulomb systems

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For obtaining individual excited-state energies and densities of Coulomb electronic systems, by means of an energy stationary principle, it was shown previously that there exists a universal functional of the density, $F^{Coul}[\varrho]$, for the kinetic plus electron-electron repulsion part of the total energy. Here, we make knowledge of the existence of $F^{Coul}[\varrho]$ practical for calculation by identifying $T_s^{Coul}[\varrho]$, the non-interacting kinetic energy component of $F^{Coul}[\varrho]$, and by showing that $T_s^{Coul}[\varrho]$ may be computed exactly by means of orbitals that are obtained through a set of single-particle Kohn-Sham equations. Constraints for obtaining accurate approximations to the remaining unknown component of $F^{Coul}[\varrho]$ are presented. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4934963>]

Coulomb systems are common and special. Common because atoms, molecules, and solids are all Coulomb systems and special because the Coulomb density has very special properties. Computation of the spectrum of energy levels is of great importance in interpreting or predicting experimental phenomena. Practical computational approaches are frequently based on the electron density. The very special properties of the Coulomb density make it possible to formulate an exact time-independent density functional theory of ground and excited states of Coulomb systems.¹ The Kohn-Sham version of that theory is put forward now. As with ground states, the Kohn-Sham approach² is particularly useful for computational implementation and desirable in order to obtain an accurate non-interacting kinetic energy component of the total energy.

Presently, most excited-state calculations are performed with time-dependent DFT (e.g., Refs. 3–5), although several time-independent approaches have also been given to treat excited states within DFT.^{6–18} The subspace theory of Theophilou⁶ and its generalization by Gross, Oliveira, and Kohn⁷ are complicated by the requirement that a whole ensemble of states has to be considered. Individual excited-states can be targeted using time-independent approaches based on the adiabatic connection¹⁹ or the constrained search.²⁰ The Levy-Nagy⁸ constrained-search functional is complicated by the fact that it requires a bifunctional that utilizes not only the density of the given state but also the external potential (or the ground-state density). (Nevertheless, approximate functionals for this bifunctional approach and the ensemble theory have been developed for and applied to atomic and molecular systems.^{9–11,17,18}) The time-independent Kohn-Sham theory that we give in this communication has the advantage that it employs a unifunctional.

The ground-state total energy functional^{20,21} can be written as

$$E[\varrho_1] = F[\varrho_1] + \int \varrho_1(\mathbf{r})v(\mathbf{r})d\mathbf{r}, \quad (1)$$

where $\varrho_1(\mathbf{r})$ is the ground-state density, $v(\mathbf{r})$ is the external potential, and $F[\varrho]$ is a universal functional of the electron density $\varrho(\mathbf{r})$. There are special cases where the ground-state constrained search F gives exact excited-state energies.²² However, there exists no general $F[\varrho]$, with a minimum principle for excited states.²³ Therefore, Görling²⁴ proposed a theory of excited states based on a stationary principle instead of a minimization. His approach has influenced our theory. However, in his functional F_k , the index k does not necessarily correspond to the level of excitation. The Görling functional is one of the several functionals that can be derived from the Levy-Nagy functional.²⁵ (This and other key developments in time-independent excited-state DFT are reviewed in Ref. 26 and explained in the systematic paper.²⁵)

For Coulomb systems, we showed¹ that there exists an excited-state functional $F^{Coul}[\varrho]$. For such calculations, we shall show that there exists a non-interacting kinetic energy functional $T_s^{Coul}[\varrho]$. Consequently, we are able to derive the following excited-state Kohn-Sham equations for the k th state of a Coulomb system:

$$\left[-\frac{1}{2}\nabla^2 + w([\varrho_k], \mathbf{r}) \right] \phi_i = \varepsilon_i \phi_i, \quad (2)$$

with the Kohn-Sham potential $w([\varrho], \mathbf{r})$ satisfying the Euler equation

$$w([\varrho], \mathbf{r}) = -\frac{\delta T_s^{Coul}[\varrho]}{\delta \varrho}. \quad (3)$$

The excited-state density ϱ_k is given by

$$\varrho_k = \sum_{i=1}^m \lambda_i |\phi_i|^2. \quad (4)$$

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The occupation numbers λ_i are 0, 1, or 2 for a non-degenerate system, and m denotes the orbital having the highest orbital energy with non-zero occupation number.

For our derivation, consider the Coulomb Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N v^{Coul}(\mathbf{r}_i), \quad (5)$$

where \hat{T} and \hat{V}_{ee} are the kinetic energy and the electron-electron energy operators, respectively. Here, $v^{Coul}(\mathbf{r}) = \sum_{\beta=1}^M -Z_{\beta}/|\mathbf{r} - \mathbf{R}_{\beta}|$, where \mathbf{R}_{β} gives the position of the nucleus β with charge Z_{β} and M is the number of nuclei. It was Wilson who observed that the ground-state electron density of the Coulomb system is sufficient in principle to determine all molecular properties: the cusps of the density^{27,28} tell us where the nuclei are and what their corresponding atomic numbers are, and the integral of the density yields the number of electrons. Later Nagy^{29,30} formulated an excited-state theory for Coulomb systems utilizing cusp conditions generalized to excited-state Coulomb densities.^{31–43} In our recent paper, we generalized this theory¹ by proving that the electron density of a Coulomb system cannot be a stationary state density for any other Coulomb external potential, and two different Coulomb excited states cannot have the same electron density. Furthermore, we proved the existence of a universal excited-state $F^{Coul}[\varrho]$, and we derived the Euler equation

$$v^{Coul}([\varrho], \mathbf{r}) = -\frac{\delta F^{Coul}[\varrho]}{\delta \varrho} \quad (6)$$

up to a constant.

To derive the non-interacting excited-state kinetic energy for an interacting Coulomb density, consider

$$\hat{H}^0 \Phi_j = (\hat{T} + \sum_{i=1}^N v^0(\mathbf{r}_i)) \Phi_j = E_j^0 \Phi_j. \quad (7)$$

The non-interacting Hamiltonian \hat{H}^0 is defined so that the density of its l th state, Φ_l , is the same as the given Coulomb density ϱ_k^{Coul} of an interacting system. Φ_l is orthogonal to all states Φ_j , $1 \leq j < l$. Though the requirement that the excited-state densities of the interacting and the non-interacting systems be the same is a strong one, there may be several non-interacting Hamiltonians that fulfil this demand. To define a unique non-interacting system, we require that the ground-state density ϱ_1^0 of the non-interacting system be as close as possible to the ground-state density ϱ_1^{Coul} of the interacting Coulomb system. That is, $\|\varrho_1^{Coul} - \varrho_1^0\| \leq \delta_{min}$. Then, the non-interacting kinetic energy for Coulomb densities can be defined as

$$T_s^{Coul}[\varrho_k^{Coul}] = \min_{\substack{\Phi \rightarrow \varrho_k^{Coul} \\ \{ \langle \Phi | \Phi_j | \varrho_k^{Coul} \rangle = 0 \}_{j=1}^{l-1} \\ \|\varrho_1^{Coul} - \varrho_1^0\| \leq \delta_{min}}} \langle \Phi | \hat{T} | \Phi \rangle. \quad (8)$$

Note that l can be different from k , that is, ϱ_k^{Coul} does not necessarily correspond to the k th excited state of the non-interacting system.

Define now the non-interacting kinetic energy for any density (not necessarily Coulomb). This general definition is needed in order to take the functional derivative of $T_s^{Coul}[\varrho]$.

Consider first the definition of T_s as a functional of any trial density ϱ and a Coulomb density ϱ_k^{Coul} corresponding to the k th state of some Coulomb Hamiltonian,

$$T_s^{Coul}[\varrho, \varrho_k^{Coul}] = \min_{\substack{\Phi \rightarrow \varrho \\ \{ \langle \Phi | \Phi_j | \varrho_k^{Coul} \rangle = 0 \}_{j=1}^{l-1} \\ \|\varrho_1^{Coul} - \varrho_1^0\| \leq \delta_{min}}} \langle \Phi | \hat{T} | \Phi \rangle. \quad (9)$$

That is, the minimization is done with the constraints that the density of Φ is the given ϱ , where Φ is orthogonal to all states Φ_j , $1 \leq j < l$, and ϱ_1^0 is as close as possible to ϱ_1^{Coul} . (We mention in passing that $T_s^{Coul}[\varrho, \varrho_k^{Coul}]$ is a bifunctional that is similar to the Levy-Nagy⁸ non-interacting kinetic energy bifunctional.)

Construct then a functional $T_s[\varrho]$ assuming that there exists a unique Coulomb density that is closest to the (possible non-Coulomb) density ϱ , by first forming

$$T_{s,\epsilon}^{Coul}[\varrho] = \min_{\varrho_k^{Coul}} T_s^{Coul}[\varrho, \varrho_k^{Coul}], \quad \text{where } \|\varrho_k^{Coul} - \varrho\| \leq \epsilon \quad (10)$$

and where ϵ is supposed to be large enough to ensure the existence of at least one stationary state Coulomb density in the distance smaller than ϵ . Then denoting ϵ_{min} as the smallest possible value of ϵ , we obtain

$$T_s^{Coul}[\varrho] = T_{s,\epsilon_{min}}^{Coul}[\varrho]. \quad (11)$$

If there are several Coulomb densities with the same distance from ϱ , the one leading to the smallest T_s is selected. With knowledge of the non-interacting kinetic energy functional, the variational principle leads immediately to the identification of $w[\varrho_k]$ in Equation (2), as we shall now show. Further, by introducing the orbitals ϕ_i , Kohn-Sham equations (2) are obtained.

The “complicated” procedure applied in the definition of the non-interacting Hamiltonian and the non-interacting kinetic energy functional does not mean that one has to actually find total wave functions in a density functional calculation. It is similar to the ground-state theory, where the wave functions are applied in the definition of the functional $F[\varrho]$ (see Refs. 20, 21, and 23), but we use only the density in the calculations.

Now use Eq. (6) to obtain the Kohn-Sham potential. That is,

$$\begin{aligned} v^{Coul}[\varrho_k] &= -\left(\frac{\delta F^{Coul}[\varrho]}{\delta \varrho} \right)_{\varrho=\varrho_k} \\ &= \left(-\frac{\delta T_s^{Coul}[\varrho]}{\delta \varrho} - \frac{\delta J_{xc}^{Coul}[\varrho]}{\delta \varrho} - \frac{\delta E_{xc}^{Coul}[\varrho]}{\delta \varrho} \right)_{\varrho=\varrho_k} \end{aligned} \quad (12)$$

or

$$v^{Coul}[\varrho_k] = w[\varrho_k] - v_J^{Coul}[\varrho_k] - v_{xc}^{Coul}[\varrho_k], \quad (13)$$

where J^{Coul} , v_J^{Coul} and E_{xc}^{Coul} , v_{xc}^{Coul} are the classical Coulomb and the exchange-correlation energies and potentials. Therefore, the Kohn-Sham potential in Eq. (2),

$$w[\varrho_k] = v^{Coul}[\varrho_k] + v_J^{Coul}[\varrho_k] + v_{xc}^{Coul}[\varrho_k], \quad (14)$$

and total energy,

$$E^{Coul}[\varrho_k] = T_s^{Coul}[\varrho_k] + J^{Coul}[\varrho_k] + E_{xc}^{Coul}[\varrho_k] + \int \varrho_k(\mathbf{r}) v^{Coul}([\varrho_k]; \mathbf{r}) d\mathbf{r}, \quad (15)$$

have the same form as in the ground-state Kohn-Sham theory. The exchange-correlation energy $E_{xc}^{Coul}[\varrho_k]$ is defined by the above equation and the exchange-correlation potential is

$$v_{xc}^{Coul}[\varrho; \mathbf{r}] = \frac{\delta E_{xc}^{Coul}[\varrho]}{\delta \varrho}. \quad (16)$$

Practical applications of the theory presented above are expected when appropriate approximations are made. To construct approximate functionals exact relations can be very useful. With this in mind, we present a severe constraint for the first excited state as a simple example. As the asymptotic decay of the excited-state density ϱ_2 is governed by the highest-occupied orbital energy ε_m ,^{44–51}

$$I_2 = E_1^{(N-1)} - E_2 = -\varepsilon_m. \quad (17)$$

This constraint has recently been applied to test approximate excited-state density functionals.⁵²

In the Kohn-Sham scheme, the exchange-correlation functional $E_{xc}^{Coul}[\varrho_2]$ must be approximated. Important constraints between the exchange and the exchange-correlation energies and the corresponding potentials are

$$\begin{aligned} E_x^{Coul}[\varrho_2] - E_x^{Coul}[\varrho_2 - |\phi_m|^2] \\ = \int |\phi_m(\mathbf{r})|^2 v_x^{Coul}([\varrho_2]; \mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \int \frac{|\phi_m(\mathbf{r}_1)|^2 |\phi_m(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (18)$$

and

$$\begin{aligned} E_{xc}^{Coul}[\varrho_2] - E_{xc}^{Coul}[\varrho_2 - |\phi_m|^2] \\ \leq \int |\phi_m(\mathbf{r})|^2 v_{xc}^{Coul}([\varrho_2]; \mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \int \frac{|\phi_m(\mathbf{r}_1)|^2 |\phi_m(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (19)$$

where $|\phi_m|^2$ is the eigendensity of the highest occupied Kohn-Sham orbital. As the exchange energy is known as a functional of the orbitals, one can use the optimized potential method⁵³ to generate the exchange potential and approximate only the correlation energy. A crucial constraint for the correlation energy is

$$E_c^{Coul}[\varrho_2] - E_c^{Coul}[\varrho_2 - |\phi_m|^2] \leq \int |\phi_m(\mathbf{r})|^2 v_c^{Coul}([\varrho_2]; \mathbf{r}) d\mathbf{r}. \quad (20)$$

To derive relations (18)–(20), it is useful to introduce the adiabatic connection with the Hamiltonian $\hat{H}_\alpha = \hat{T} + \alpha \hat{V}_{ee} + \sum_{i=1}^N v_\alpha(\mathbf{r}_i)$, where α is the coupling constant. The potential v_α is the Coulomb external potential if $\alpha = 1$ (that is, for the true interacting case) and the Kohn-Sham potential w if $\alpha = 0$ (that is, for the non-interacting case). For values $0 < \alpha < 1$, the Hamiltonian \hat{H}^α is defined so that the density of the 2nd state Φ_2^α is the same as the given Coulomb density ϱ_2 of the true interacting system, Φ_2^α is orthogonal to the ground state

Φ_1^α , and the ground-state density ϱ_1^α of the Hamiltonian \hat{H}^α is as close as possible to the ground-state density ϱ_1^{Coul} of the interacting Coulomb system. The asymptotic decay of the excited-state density is governed by the ionization energy. As the excited-state density is the same for any α , the ionization energy is independent of α and constraint (17) follows. To prove relations (18)–(20), the derivation presented in Ref. 54 is followed.

It is well known that an excited state density of one Hamiltonian can be a ground-state density of another Hamiltonian. It has been recently shown⁵⁵ that a given density associated with the k th state might be an eigendensity of several different external potentials. Our construction within provides a procedure to select the most appropriate potential. (Note that the functional we have proposed uses the Coulomb density to specify the excitation-level but it should be clear, as in Ref. 1, that there is an alternative version of the theory where the excitation level is explicitly included as a parameter in the functional, and this parameter may be employed with approximate functionals.)

In summary, we showed previously that there exists an energy functional of the density for obtaining individual excited-state energies and densities of Coulomb systems through a stationary principle. Here, we made use of the knowledge of the existence of this functional practical for calculation by identifying its non-interacting component and deriving the single particle Kohn-Sham equations.

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