Density-to-potential map in time-independent excited-state
density-functional theory

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Abstract

In light of the recent work by Sahni et al., Harbola, and Gaudoin and Burke, the question of mapping from an excited-state density of a many-electron interacting system to the potential of the related non-interacting system is analyzed. To do so, we investigate the Levy-Nagy criterion quantitatively for several excited-states. Our work indicates that Levy-Nagy criterion may fix the density to potential map uniquely.

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The question of whether there exists a mapping from an excited-state density \( \rho (r) \) to a potential \( v(r) \) is central to performing density-functional calculations for excited states. The issue has been addressed recently in a series of papers by Sahni et al. [1], Harbola [2], and Gaudoin and Burke [3]. In the work of [1] and [2], it was shown that a given ground- or excited-state density can be generated as a noninteracting-system density by a configuration of one’s choice. Sahni et al. obtained the potentials using the differential virial theorem [4], whereas Harbola did so using the constrained-search approach [5]. It is clear that because of the multiplicity of potentials that could lead to a given density, one needs an additional condition for mapping the density \( \rho (r) \) to a unique potential \( v(r) \). For the ground-state density the Hohenberg-Kohn (HK) theorem [6] fixes the Kohn-Sham (KS) system uniquely - it is that system where the lowest energy orbitals are occupied. For the excited-state density a different criterion is needed. The issue of how to choose a unique potential (KS system) for a given excited-state density has been addressed earlier by Levy and Nagy (LN) [8]. They have proposed a qualitative criterion, discussed below, for doing so. However, it has not been investigated quantitatively.

Furthering the work of [1] and [2], Gaudoin and Burke [3] have shown that even with a fixed configuration, one can reproduce an excited-state density from more than one potentials. They have worked with non-interacting fermions and have generated these potentials using the inverse linear response of a system and have related the multiplicity of these potentials to a property of the linear response kernel. Based on this they have made two observations: (i) that one has to go beyond the HK [6] theorem to understand the multiplicity of potentials with the same density, and (ii) that the mapping \( \rho (r) \rightarrow v(r) \) is not unique. However, as pointed out above, the uniqueness between a density and a potential exists only for the ground-states. Thus the existence of more than one potential for excited-states densities is not excluded by the HK theorem. And precisely for this reason, an additional condition is needed to identify one particular system as the KS system representing an excited-state.

The interesting and thought provoking results of references [1, 2, 3] have prompted us to
pursue the matter of density-to-potential mapping for excited-states further. Our investigations in this direction form the contents of this paper. We show: (i) that the constrained-search approach \[5\] itself is capable of generating all potentials for noninteracting systems giving the same density, thereby establishing once again the importance of this approach \[2, 8, 9, 10\] in excited-state density-functional formalism; (ii) in the examples taken, when the criterion proposed by LN \[8\] is applied to different noninteracting systems corresponding to a given density, it correctly identifies the system that should represent the excited-state density; and (iii) the conclusion of Gaudoin and Burke \[3\] about the “lack of HK theorem for excited-states” has been arrived at by taking into consideration only the excited-state density $\rho(\mathbf{r})$ and therefore do not apply to the Levy-Nagy formalism. In the following, after describing briefly the LN formulation of density-functional theory (DFT) for excited states, we give examples of how its application gives a unique $\rho(\mathbf{r}) \rightarrow v(\mathbf{r})$ map.

Like for the ground-state theory, the LN formulation \[8\] provides a variational DFT approach for the $k$th excited state of an $N$-electron interacting system by defining a unique universal functional $F_k[\rho, \rho_0]$ such that the energy $E_k$ and the density $\rho_k(\mathbf{r})$ of this state are given by

$$E_k = \min_{\rho \rightarrow N} \left\{ \int d^3r v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + F_k[\rho, \rho_0] \right\}$$

$$= \int d^3r v_{\text{ext}}(\mathbf{r}) \rho_k(\mathbf{r}) + F_k[\rho_k, \rho_0]$$

(1)

Here $v_{\text{ext}}(\mathbf{r})$ is the external potential, $\rho_0(\mathbf{r})$ is the ground-state density of this system. Due to the HK \[6\] theorem, $v_{\text{ext}}$ is a unique functional of $\rho_0$. In the definition of the bi-density functional

$$F_k[\rho, \rho_0] = \min_{\Psi \rightarrow \rho, \{\langle \Psi | \Psi_j \rangle = 0, j < k\}} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle,$$

(2)

the $N$-electron trial wave function $\Psi$ belongs to the space which is orthogonal to the space spanned by all lower $j$th-state functions $\Psi_j$ of the system, $j < k$. $\hat{T}$ and $\hat{V}_{\text{ee}}$ are the $N$-electron operators of the kinetic and electron-electron interaction energies. In this formulation, the mapping from the $k$th excited-state density $\rho_k(\mathbf{r})$ to the corresponding wave function $\Psi_k$ of the system follows from Eq. \[2\] after inserting there $\rho = \rho_k$ — the minimizer in Eq. \[1\],
because then $\Psi_k$ is the minimizer in Eq. (2). Since the lower states $\Psi_j$ ($j < k$) in Eq. (2) are determined by $v_{\text{ext}}[\rho_0]$, a functional of $\rho_0$, it is clear that the ground-state density $\rho_0$ plays an important role in this DFT for excited states.

For each original, interacting system, one can introduce a corresponding noninteracting system such that their densities are the same. In the constrained-search approach, this is done by minimizing the expectation value $\langle \Phi | \hat{T} | \Phi \rangle$, where $\Phi$ is now a single Slater determinant of one-electron spin orbitals that gives the density of interest. However, many different noninteracting systems (potentials) can be related with the given excited-state density $\rho_k(r)$ of the interacting system. Of the many $\Phi$'s (many systems) that may give the same density $\rho_k$, a unique one, the KS system, is chosen by comparing the ground-state densities of the corresponding noninteracting systems and the true ground-state density $\rho_0$, and checking if the LN criterion for identifying the Kohn-Sham system for an excited-state is satisfied. Thus, let in a particular noninteracting system [characterized by its potential $v(r)$] the density of its $m$th state, $\rho^v_{m}(r)$, be the same as $\rho_k(r)$. Its ground-state density will be denoted accordingly as $\rho^v_0(r)$. Then the KS system connected with $\rho_k$ is identified among the above noninteracting systems as the one whose $\rho^v_0(r)$ resembles $\rho_0(r)$ most closely in a least-squares sense. The LN criterion intuitively defines the KS system consistent with the adiabatic connection to the $k$th excited-state of the interacting system (characterized in DFT by $F_k[\rho, \rho_0]$). What it means is if the electron-electron interaction in an interacting system is turned off slowly, keeping the excited-state density unchanged, the corresponding ground-state density of the resulting system will remain close to the true ground-state density of the interacting system. Thus of the many noninteracting systems that give the same excited-state density, the one whose ground-state density remains closest to the true ground-state density of a given system is identified as the KS system representing the excited-state of that system. The noninteracting system so chosen should best resemble the true system because, within the constraint of the equality of their excited-state density, their ground-state densities match most closely. This should also make their external potential resemble each other by the HK theorem. We reiterate that in general a particular density can be generated by a multitude
of potentials; and for each potential the associated energy functional is different \cite{1,2} due to the difference in the noninteracting kinetic energy of each system. However, to keep the structure of these functionals and the corresponding potentials simple, it is important that we have a criterion to choose one particular system. In this connection we note that for the ground-state densities of noninteracting electrons too, there exist \cite{1,2} more than one noninteracting systems that give the same density $\rho_0$. However, the one where the lowest energy orbitals are occupied, i.e. $\rho^v_0(r) = \rho_0(r)$, is the chosen KS system, and it is unique due to the HK theorem. For the excited-states the uniqueness should be provided by the LN criterion. But, before applying it in practice, this qualitative LN criterion that “$\rho^v_0(r)$ resembles $\rho_0(r)$ most closely in a least-squares sense” needs to be transformed into some quantitative form.

One of the ways that the difference between two densities $\rho_a$ and $\rho_b$ can be characterized quantitatively is by the squared distance in the functional space

$$\Delta[\rho_a, \rho_b] = \int_\infty d^3 r (\rho_a(r) - \rho_b(r))^2.$$  

We propose to consider the value of $\Delta[\rho^v_0, \rho_0]$ as representing the least-squares deviation of the density $\rho^v_0$ from the density $\rho_0$. Then, applying the LN criterion, the noninteracting system having the smallest $\Delta$ would be chosen as the KS system. We are going to demonstrate on examples that the proposed quantitative version of the LN criterion chooses the KS system in agreement with intuitive expectations in the cases considered. What it means is if the excitation corresponds (i) to a fixed external potential with several configurations\textsuperscript{[1]} and Harbola \textsuperscript{[2]} or (ii) to a particular configuration with different potentials (Gaudoin and Burke \textsuperscript{[3]}), then the minimum deviation occurs only for the true configuration / for the exact potential. It is also shown that if some particular, different quantitative measure of the distance between densities is used in the LN criterion, it may lead to erroneous choice of the KS system. Thus definition of an adequate quantitative form of the criterion is important and needs verification.

We now discuss the case of the excited-state density of a noninteracting Fermionic systems
where the LN criterion is very transparent. This is because in this case the difference between the ground-state density of the KS system representing an excited-state and the true ground-state density will be zero. Thus it is easily shown that the LN criterion fixes the KS system to be the true system: Suppose an excited-state density is produced by two different potentials. Each of these potentials (systems) has a unique ground-state by the HK theorem. Thus only that particular system which has the same ground-state density as the system under consideration can truly represent the original system. In the interacting system, the condition of the ground-state densities being the same is replaced by the condition of the proximity of the densities in the least-square sense. We note that in the work of Gaudoin and Burke who have analyzed non-interacting systems only, this comparison with the ground-state density is not made. Hence they raise a question which potential should be chosen from the many available. It is clear from the discussions above that this should be determined by the comparison of the ground-state densities of the excited-states systems (which are connected with the given \( \rho_k \)) with the true ground-state density of the system under consideration. In the following we show through examples that this gives a KS noninteracting system which is consistent with the original system not only in terms of their ground-states, but also in terms of the configuration of the excited-states.

To construct, for an assumed electronic configuration, the potentials leading to a given density through constrained-search approach, we have employed the procedure of Zhao and Parr. It produces the potential \( v(r) \) of a noninteracting system by making the value of the system kinetic energy \( \sum_{i=1}^{\infty} n_i \langle \psi_i | - \frac{1}{2} \nabla^2 | \psi_i \rangle \) stationary with the constraint that the system density \( \sum_{i=1}^{\infty} n_i | \psi_i(r) |^2 \) equals the given density \( \rho_k(r) \). Here, \( \psi_i(r) \) is the space orbital, \( n_i \) — its occupation number, \( \sum_{i=1}^{\infty} n_i = N; \) any configuration connected with a single Slater determinant can be represented by a proper choice of \( n_i \) from the numbers 0, 1, 2. Depending on the starting potential used to initialize this procedure, various potentials can be generated from the input \( \rho_k \) for each assumed configuration. Thus this procedure is capable of generating all possible systems (potentials) that reproduce the density on hand. Evidently, the determined different potentials give different ground-state densities (by the
Hohenberg-Kohn theorem \cite{6}); the one which is the closest to the true ground-state density singles out the KS potential of the excited-state DFT.

\[ \rho(r) \text{(a.u.)} \]

\[ V(r) \text{(a.u.)} \]

\[ 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \]

\[ 0 \quad 10 \]

\[ -50 \quad -40 \quad -30 \quad -20 \quad -10 \quad 10 \]

FIG. 1: Two potentials (lower panel) yielding the same excited state density (upper panel) for $1s^12s^2$ state of a model Li atom. Note that the x-axis scale in the upper and the lower panel is different.

\[ V_2 \]

\[ V_1 \]

\[ \rho_0 \]

\[ \rho_v \]

\[ \rho \]

\[ 0.01 \quad 0.1 \quad 1 \quad 10 \]

\[ 0.0 \quad 1.0 \quad 2.0 \quad 3.0 \]

\[ 801 \quad 0.1 \quad 1 \quad 10 \]

\[ 0 \quad 0.5 \quad 1.0 \quad 1.5 \quad 2.0 \quad 2.5 \quad 3.0 \quad 3.5 \]

FIG. 2: Shown are the ground-state densities for the two potentials $v_1$ and $v_2$ of Fig. 1.

As the first example we take a model Li atom: $N = 3$ noninteracting electrons moving in the potential $v(r) = -Z/r$, $Z = 3$, resulting in the hydrogen-like orbitals. Atomic units
are used throughout. The $k = 1s^12s^2$ excited-state configuration of the model system is considered. The potential $v_1(r) = v(r)$ and the alternative potential $v_2(r)$ along with the excited-state density $\rho(r) = \rho_k(r)$ are shown in Fig. 1. Both potentials are generated using the Zhao-Parr [11, 12] method with the excited-state density $\rho_k$ as the input. Since the potentials $v_1$ and $v_2$ are different, their ground-state densities can not be the same (by the HK theorem [6]). Whereas the ground-state density corresponding to $v_1 = -Z/r$ is the true ground-state density of the system, that corresponding to $v_2$ should be different — they are shown in Fig. 2. Indeed, the two densities are dissimilar. If $v_2$ also were to represent the KS system connected with the same excited-state density, the difference in the ground-state densities for these two potentials should be zero.

![Graph showing two potentials](image)

**FIG. 3:** Two potentials (lower panel) yielding the same excited state density (upper panel) for the $1s^12s^2 2S$ state of the Li atom. Note that the x-axis scale in the upper and the lower panel is different.

As the second example we take the true Li atom: $N = 3$ interacting electrons moving in the external potential $v_{\text{ext}}(r) = -Z/r$, $Z = 3$, and consider its $k = 1s^12s^2 2S$ excited-state configuration. The density $\rho_k(r)$ of this state is represented by the density calculated self-
FIG. 4: Shown are the noninteracting ground-state densities for the two potentials $v_1$ and $v_2$ of Fig. 3 along with the interacting (exact) one.

consistently using the exchange-only Harbola-Sahni (HS) [13] potential for this configuration. This density is a good approximation to the exact solution and very close [14, 15] to the Hartree-Fock density of this state. Shown in Fig. 3 are the two potentials $v_1(r)$ and $v_2(r)$ reproducing the same density $\rho_k(r)$ as the $1s^22s^2$ excited-state densities of noninteracting systems; $v_1$ coincides with the HS effective potential, $v_1(r) = -Z/r + v_H(r) + v_{\text{HS}}(r)$. The constrained-search procedure, mentioned earlier, was employed to generate both $v_1(r)$ and $v_2(r)$. Although the excited-state densities of the two potentials are the same, the ground-state densities of these potentials are different — that is what discriminates between the two potentials. In Fig. 4 we plot the noninteracting ground-state densities $\rho_{0v}^0(r)$ for potentials $v = v_1$ and $v = v_2$, along with the interacting ground-state density $\rho_0(r)$. The latter is obtained in the same approximation as applied for $\rho_k$, namely with the HS [13] potential, now for the ground-state $1s^22s$ configuration. As expected, the three densities are different. However, the noninteracting ground-state density produced by $v_1$ is quite similar to the “exact” HS ground-state density of Li. On the other hand, that corresponding to $v_2$ is very different from the “exact” one. We introduce also the potential $v_3(r)$ (not shown), which reproduces $\rho_k(r)$ as the ground-state density of a noninteracting system. This $v_3$ is unique according to the HK theorem. Thus the density shown in the upper panel of Fig. 3 can also be labeled with $\rho_{0v}^v$ in analogy with Fig. 4. To apply the LN criterion, the squared distance, Eq. (3), between ground-state densities is evaluated, giving $\Delta[\rho_{0v}^v, \rho_0^0] = 0.111, 1.467, 0.460$.
for \( v = v_1, v_2, v_3 \), respectively. Thus, according to this criterion, the KS system connected with the \( k \)th excited state of the Li atom is given by the potential \( v_1 \). This result confirms our intuitive expectation.

FIG. 5: Two potentials (middle panel) yielding the same excited-state density (upper panel) along with their corresponding ground-state densities (lower panel) for an excited state of the three-electron 1D infinitely deep well model system.

As the third example we take the He atom and consider its \( k = 1s2s \, ^1S \) excited-state, with the density \( \rho_k \) taken from [16]. This example was examined, in fact, in the previous work [2] of one of us. Two potentials were obtained that reproduce the density \( \rho_k \): \( v_1(r) \) as the density of the \( 1s2s \) excited state of a noninteracting system, and \( v_2(r) \) as the density of the \( 1s^2 \) ground state. To make use of the LN criterion, the quantity \( \Delta[\rho_0, \rho_0] = \int_0^\infty dr \{ \rho_0^v(r) - \rho_0(r) \}^2 \) (for
spherical densities) was defined, and evaluated with $\rho_0(r)$, the ground-state density of the true He atom, taken from \cite{17}. On the basis of the results $\bar{\Delta} = 0.273, 0.140$ for $v = v_1, v_2$, respectively, the author concluded that the LN criterion \cite{8} might not be proper for finding the KS potential of the excited-state DFT. However, if the distance between the ground-state densities is evaluated applying the definition \cite{3} (proposed in the present paper), the result $\Delta = 0.086, 0.091$ for $v = v_1, v_2$, respectively, is obtained. Thus on the basis of the LN criterion, we find that indeed the $1s2s^1S$ state of He is properly represented by the KS system with the potential $v_1$ that reproduces $\rho_k$ as the density of its $1s2s$ configuration, in agreement with our intuition.

We note that although the considered examples seem to suggest that comparing $\Delta$ as given by Eq. 3 gives KS system in accordance with the excited-states, Eq. 3 is not the only way of quantifying the LN criterion. Better and more discriminating criteria may exist and should be looked for, particularly because of the limited number of examples considered in this paper and very small difference that is there for the He atom. But the emphasis in this paper is on showing how an additional condition of comparing the ground-state densities may lead to a proper choice of the KS system and that is shown amply by our work. Further work along these lines is in progress and will be reported in the future.

The above arguments apply equally well to the one-dimensional (1D) case considered by Gaudoin and Burke \cite{3}. Using another conventional approach — the van-Leeuwen and Baerends \cite{18} method — for obtaining the noninteracting-system potentials, we have reproduced not only the results of Gaudoin and Burke but have also done many other calculations. The example we give in this paper is for the following 1D model system: $N = 3$ noninteracting electrons in an infinitely deep box of unit length, in the excited state obtained by putting one electron in the lowest-energy state and two electrons in the second-lowest one. The excited-state density ($\rho_e$) and the corresponding two potentials that reproduce this density in the same configuration are shown in Fig. 5. Also shown are the ground state densities $\rho_0^{v_1}$ and $\rho_0^{v_2}$ corresponding to these potentials. Again the ground-state density given by the potential $v_2(x)$ is not the same as that given by $v_1(x)$. Thus $v_2(x)$ can not represent the
excited-state density of the model.

To conclude, we have shown that if the ground-state density is known, then the Levy-Nagy criterion may provide a proper map from an excited-state density to the KS potential, \( \rho(r) \rightarrow u(r) \), provided the closeness of two densities is adequately quantified, e.g., as in Eq. (3). The criterion is exact for systems of non-interacting fermions. For interacting electron systems, on the other hand, there could be other ways of defining this closeness quantitatively, but their effect should be verified (an example of failed definition was discussed). Our focus here is not on various definitions but rather how the proposed measure leads to a map from an excited-state density to the corresponding Kohn-Sham potential that is consistent with the configuration of excitation in the known cases. Thus the excited-state energy can be expressed in terms of the density corresponding to this state and Kohn-Sham calculation can be done following the Levy-Nagy formulation.

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