# Lack of Hohenberg-Kohn Theorem for Excited States

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(Received 11 April 2004; published 18 October 2004; corrected 13 January 2005)

For a given excited state there exist densities that arise from more than one external potential. This is due to a qualitatively different energy-density relationship from that of the ground state and is related to positive eigenvalues in the nonlocal susceptibility for excited states. Resulting problems with the generalization of the density functional methodology to excited states are discussed.

DOI: 10.1103/PhysRevLett.93.173001 PACS numbers: 31.15.Ew, 71.15.Qe

Kohn-Sham density functional theory (DFT) [1] now enjoys enormous popularity as an electronic structure method in solid-state physics, quantum chemistry, and materials science. A cornerstone of its rigorous foundation is the first part of the Hohenberg-Kohn (HK) theorem [2] that demonstrates that, for given interparticle statistics and interaction, a ground-state density can be produced by at most *one* external one-body potential. This one-to-one correspondence implies that all properties of an electronic system and, in particular, its ground-state energy are functionals of the ground-state density. Application of the same logic to fictitious noninteracting electrons produces the Kohn-Sham (KS) equations, whose solution is typically very much faster than traditional wave function approaches. One path to excited-state properties that has become popular [3] recently is time-dependent DFT (TDDFT) [4]. By studying the frequency-dependent response of the ground state within TDDFT, one finds corrections to the transition frequencies of the Kohn-Sham ground-state potential [5]. Variational alternatives include ensemble DFT [6,7], variation of bifunctionals [8], change in self consistent field [9], and others [10,11] which we briefly discuss later. Such approaches do not suffer from a tremendous sensitivity to the orbital positions of the underlying ground-state KS potential [12] and should provide a valuable alternative to TDDFT in situations where the excited-state density differs substantially from its KS analog, such as in charge-transfer excitations [13].

A naive and appealing idea is to imagine an excited-state energy functional of the excited-state density. Then an excited-state calculation could proceed analogously to a ground-state calculation, which would be convenient for mapping excited-state energy surfaces.

In the present Letter, we address the relationship between energy and density for excited states, about which little is known, in contrast to the ground-state problem. We consider only Hamiltonians with local one-body potentials. For example, is the excited-state energy a functional of the excited-state density? (It is a functional of the *ground-state* density, by virtue of the potential being unique.) To answer this simple question, the lower panel of Fig. 1 shows the density of two same-spin particles, noninteracting, in a one-dimensional box. This is a textbook problem, with the lowest and third-lowest energy levels occupied. In the upper panel, the dashed line is that of a *different* potential for which this density is *also* the first excited-state density (how these potentials were found is described below). The corresponding wave functions are not degenerate or unusual in any way, and there are many such examples. Clearly, the potential is not unique, and so the excited-state energy is not a functional of the excited-state density, even for a given level of excitation (In contrast to others [14], our analysis remains within a fixed level of excitation or orbital occupation.) The rest of this Letter explains how and why this happens. We analyze the relationship between energies and densities for excited states. This is qualitatively different to the ground-state case and implies difficulties with the extension of formal constructions, such as the adiabatic connection, to excited states.

To understand how more than one potential can yield a given excited-state density, and more importantly, how the number of such potentials varies as the density is altered, we first prove an elementary theorem concerning the linear susceptibility of the system. Consider any finite number $N$ of electrons in a large box with Hamiltonian $H$. The susceptibility of the $j$-th state is

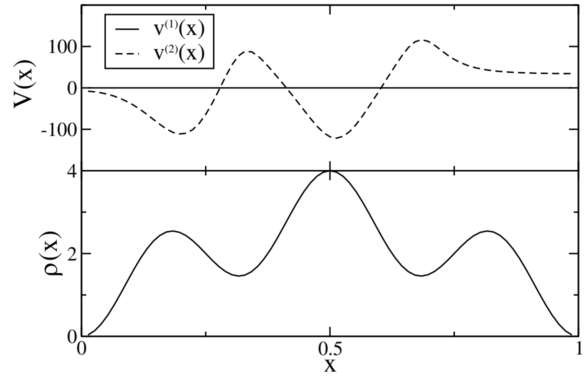

FIG. 1. Two potentials (upper panel) yielding the same first excited-state density (lower panel).

$$\chi_j(\mathbf{r},\mathbf{r}') = \frac{\delta\rho_j(\mathbf{r})}{\delta V(\mathbf{r}')} = 2\Re\sum_{i\neq j}\frac{\langle\Psi_j|\hat{\rho}(\mathbf{r})|\Psi_i\rangle\langle\Psi_i|\hat{\rho}(\mathbf{r}')|\Psi_j\rangle}{E_j - E_i} \quad (1)$$

where $H|\Psi_j\rangle = E_j|\Psi_j\rangle$, $\hat{\rho}(\mathbf{r})$ is the density operator, and $V(\mathbf{r})$ is the one-body potential. For convenience we choose the states $|\Psi_i\rangle$ to be real. Also, at this point these states may be one-particle orbitals or many particle states. We ignore possible degeneracies: $E_j > E_i \forall j > i$. For ensembles $\chi(\mathbf{r}, \mathbf{r}') = \sum_j n_j \chi_j(\mathbf{r}, \mathbf{r}')$, where the weights $n_j \geq 0$ are nonzero for finitely many eigenstates:

$$\chi(\mathbf{r}, \mathbf{r}') = 2\sum_{i\langle j}\langle\Psi_j|\hat{\rho}(\mathbf{r})|\Psi_i\rangle\langle\Psi_i|\hat{\rho}(\mathbf{r}')|\Psi_j\rangle\frac{n_j - n_i}{E_j - E_i} \quad (2)$$

Define real eigenvectors and eigenvalues of $\chi(\mathbf{r}, \mathbf{r}')$ by

$$\int d^3r'\chi(\mathbf{r}, \mathbf{r}')\xi_\alpha(\mathbf{r}') = \lambda_\alpha\xi_\alpha(\mathbf{r}) \quad (3)$$

choosing their normalization $\int d^3r'[\xi_\alpha(\mathbf{r}')]^2 = 1$. The index $\alpha = 1, 2, 3, \ldots,$ labels eigenstates in nonincreasing order of eigenvalue. Let $M$ denote the number of non-negative eigenvalues $\lambda_\alpha$ and $L$ the number of terms for which $\sigma_{ij} = -\mathrm{sgn}(\frac{n_j - n_i}{E_j - E_i}) < 0$. A constant shift in the external potential, or potential changes having support only where the density is zero, are both eigenvectors of $\chi(\mathbf{r}, \mathbf{r}')$ with eigenvalue zero. We denote these eigenvalues as trivial and do not include them in $M$.

Theorem: Discounting trivial eigenvectors, the number of non-negative eigenvalues $M$ cannot exceed $L$.

Proof: Begin by defining $\hat{\xi}_\alpha = \int d^3r\xi_\alpha(\mathbf{r})\hat{\rho}(\mathbf{r})$ and for all $i \neq j$ the set of numbers $v_\alpha^{ij} = \langle\Psi_i|\hat{\xi}_\alpha|\Psi_j\rangle\sqrt{|\frac{n_j - n_i}{E_j - E_i}|}$. Then Eqs. (2) and (3) yield

$$\lambda_\alpha\delta_{\alpha\beta} = +2\sum_{\sigma_{ij}<0} v_\alpha^{ij}v_\beta^{ij} - 2\sum_{\sigma_{ij}\geq 0} v_\alpha^{ij}v_\beta^{ij} \quad (4)$$

Now consider the vectors $\{v_\alpha^{ij}, ij|\sigma_{ij} < 0\}$, one for each $\alpha$ and $1 \leq \alpha \leq M$. We show below that they are linearly independent. Since they are $L$-dimensional, there can at most be $L$ of them, so that $M \leq L$.

To show linear independence, imagine a set of numbers $c_\alpha$ such that $\sum_{\alpha=1}^M c_\alpha v_\alpha^{ij} = 0$ for all $i, j$ with $\sigma_{ij} < 0$. By multiplying Eq. (4) by $c_\alpha^* c_\beta$ and summing over $\alpha$ and $\beta$

$$\sum_{\alpha=1}^M |c_\alpha|^2\lambda_\alpha = \sum_{\alpha,\beta=1}^M c_\alpha^* c_\beta\lambda_\alpha\delta_{\alpha\beta} = -2\sum_{\sigma_{ij}\geq 0}|\sum_{\alpha=1}^M c_\alpha v_\alpha^{ij}|^2 \quad (5)$$

Since the first expression is non-negative, while the last expression is nonpositive, both must vanish. If, however the last term is zero, then for all $i \neq j$, $\sum_{\alpha=1}^M c_\alpha v_\alpha^{ij} = 0$. Hence whenever $n_j \neq n_i$, $\langle\Psi_i|\sum_{\alpha=1}^M c_\alpha\hat{\xi}_\alpha|\Psi_j\rangle = 0$. For all $j$ such that $n_j \neq 0$ it follows $\sum_{\alpha=1}^M c_\alpha\hat{\xi}_\alpha|\Psi_j\rangle = c^{jj}|\Psi_j\rangle + \sum_{i\neq j; n_i = n_j} c^{ij}|\Psi_i\rangle$, or in short $\sum_{\alpha=1}^M c_\alpha\hat{\xi}_\alpha|\boldsymbol{\Psi}\rangle = C|\boldsymbol{\Psi}\rangle$. The matrix $C$ is Hermitian and *not* a function of $\mathbf{r}$. Diagonalizing $C$ leads to $\sum_{\alpha=1}^M c_\alpha\hat{\xi}_\alpha|\tilde{\Psi}_j\rangle = \tilde{c}^j|\tilde{\Psi}_j\rangle$. In real space the eigenvectors of $\chi(\mathbf{r}, \mathbf{r}')$ are multiplicative functions and, therefore, for all $j$, $\sum_{\alpha=1}^M c_\alpha\hat{\xi}_\alpha = \tilde{c}^j$ plus possible terms with support only where the density of the $j$'th state is zero. Such an equation exists for all $j$, so except for pathological cases (e.g., all $n_i = 1$ for systems with finite dimension), $\sum_{\alpha=1}^M c_\alpha\hat{\xi}_\alpha = c$ plus terms with support only where the total density is zero. In other words, a sum of eigenvectors is equal to a sum of the trivial eigenvectors of $\chi(\mathbf{r}, \mathbf{r}')$. Since eigenvectors are linearly independent, this is only possible if all $c_\alpha = 0$, which in turn proves the linear independence of the vectors $\{v_\alpha^{ij}, ij|\sigma_{ij} < 0\}$.

Applying this theorem to the ground state, we find no eigenvalue can be non-negative except for the trivial ones. This result is *not* implied by the Hohenberg-Kohn theorem (e.g., Ref. [15]) because HK does not exclude the possibility of a nontrivial zero eigenvalue, with uniqueness being produced by a higher-order response. Additional analysis as presented here is needed (see also [16]).

Although our illustrations are for two noninteracting electrons in one dimension, the proof applies to any quantum system, including interacting electrons in three dimensions. In particular, for Slater determinants the response function becomes that of an ensemble of one-electron orbitals with weights $\{n_j\} = 1$ for occupied single-particle orbitals, and zero, otherwise. A prominent use of ensembles is to find approximations to excited-state energies. The proof of the validity of a HK theorem for a weighted ensemble of ground and excited states requires that the weights must be monotonically decreasing [6]. In that case, $\sigma_{ij}$ is positive for every pair $i$ and $j$, and $\chi$ has only negative eigenvalues. This is not true anymore for nonmonotonically decreasing weights. Our examples of excited states of two noninteracting same-spin particles are ensembles of a one-particle problem whose weights violate the rule of monotonically decreasing weights. Thus our examples show that ensemble theory cannot be formulated for such extreme cases.

To show that nonuniqueness of excited-state potentials is common and not an artifact of one-dimensional particles in a box, we have also studied the $1s^1 2s^2$ configuration of hydrogen atom orbitals. The density is shown in the upper panel of Fig. 2. Below it, we show three potentials for which this density is generated by the same occupation of single-particle orbitals. The potentials are very similar, and when viewed as a nonground state KS scheme, it is far from obvious which of these should be considered the "true" one. We believe such demonstrations are possible for most electronic densities.

Next we discuss how this theorem allows us to understand the origin of Fig. 1, whose density we denote as $\rho_A(x)$. To find a potential for which it is a specific excited-state density we choose a smooth starting potential and calculate its density $\rho_R(x)$. We also calculate its susceptibility. We apply the inverse susceptibility to

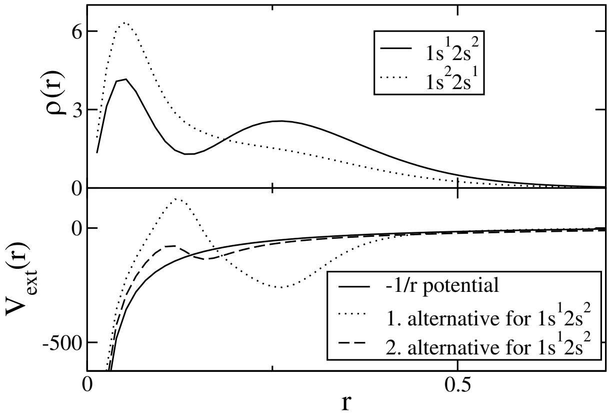

FIG. 2. Lithium-like occupations of a $-1/r$ potential and similar alternatives yield the $1s^12s^2$ density shown above.

$\rho_A(x) - \rho_R(x)$ to estimate the change in potential needed to produce the target density $\rho_A(x)$. We repeat this procedure with the new potential, and iterate to convergence. Since a shift in the constant in the potential is always a zero eigenvector of $\chi$, the constant contribution has to be disregarded when inverting the susceptibility. In this way, by varying the starting potential, we found *three* potentials, denoted $v_A^{(1)}(x)$, $v_A^{(2)}(x)$, and its mirror image, $v_A^{(3)}(x)$ for each of which $\rho_A(x)$ is a first excited-state density. The three susceptibilities corresponding to these three potentials have only negative eigenvalues except one, $\chi_A^{(1)}$, that has one positive eigenvalue. Then consider the linear combination of $v_A^{(1)}(x)$ with $v_A^{(2)}(x)$:

$$v_{A,\alpha}(x) = (1-\alpha)v_A^{(1)}(x) + \alpha v_A^{(2)}(x). \qquad (6)$$

Assuming continuity of the eigenvalues of $\chi$ as a function of $\alpha$, there exists some value of $\alpha$ for which the potential and the $\chi$ of its corresponding first excited state has a zero eigenvalue. Label this potential and its first excited-state density by $B$. We show below that this corresponds to a fold in the relationship between energies and densities. Such folds exist only for excited-state configurations and divide the space of densities into regions labeled by the number of potentials that can represent that density. In general, when interpolating between two systems with the same density, one only crosses a fold if the number of positive eigenvectors changes.

Similarly, we can repeat this process for $v_A^{(1)}(x)$ and $v_A^{(3)}(x)$ to find another fold point $E$, where $\rho_E(x)$ is the mirror image of $\rho_B(x)$. We then define a line in density space between the two fold points:

$$\rho_\zeta(x) = (1-\zeta)\rho_E(x)/2 + (1+\zeta)\rho_B(x)/2. \qquad (7)$$

In Fig. 3, we plot the transition frequency, i.e., the energy difference between the first excited state (levels one and three occupied) and the ground state (levels one and two occupied) for the potentials we have found for each density (there may yet be more). To understand this curve, begin in the top left hand corner, for $\zeta < -1$ [point $A$ in Fig. (3)]. For such a density, there is only one potential, whose $\chi$ has no positive eigenvalues. Follow this curve to $\zeta = 1$ (point $B$), where an eigenvalue passes through zero, producing one positive eigenvalue. The curve runs back to point $C$ at $\zeta = -0.9$, where there is another fold, and the maximum eigenvalue becomes negative once more, in accordance with our theorem. This curve runs until $\zeta = 0$, and the whole process reverses itself (points $D$, $E$, and $F$). In Fig. 4, we plot the densities at several values of $\zeta$ to emphasize that there is nothing unusual about them. Their orbitals and eigenvalues are equally innocuous.

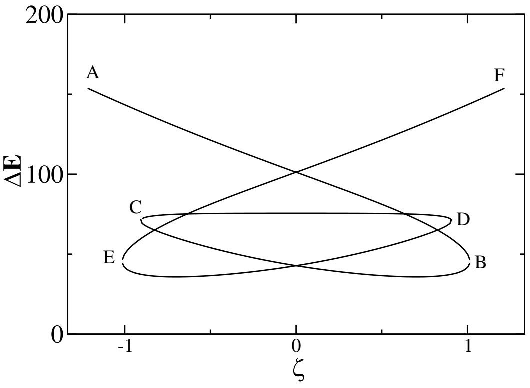

FIG. 3. Transition energies $E_1 - E_0$ as a function of the first excited-state density parameterized by $\zeta$ (see text).

In the middle section of the curves, $|\zeta| < 0.9$, each density has (at least) five corresponding potentials. At $\zeta = 0$, these consist of one symmetric potential, two distinct nonsymmetric potentials, and their mirror images. As the first fold is approached, the (originally) symmetric potential merges with one of the others, and for $0.9 \leq |\zeta| < 1$, only three potentials remain. As $|\zeta| \to 1$, two more merge and vanish, so that for $|\zeta| \geq 1$, there is only one potential.

What happens at a fold point in density space? Are there discontinuous jumps in quantities as two potentials merge? In Fig. 5, we plot the individual kinetic and potential contributions to the energy. Since a constant shift of the potential has no effect on the energy-density relationship we choose the potentials such that the

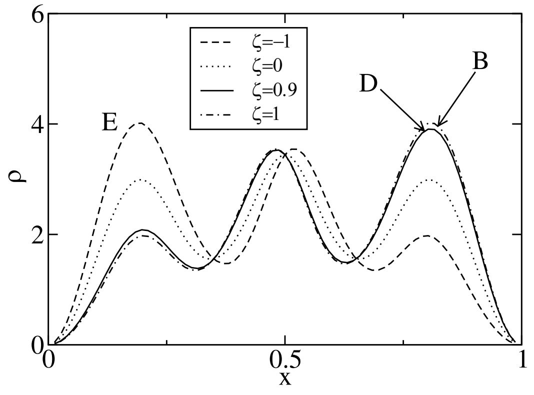

FIG. 4. Densities at different values of $\zeta$ [see Fig. (3)].

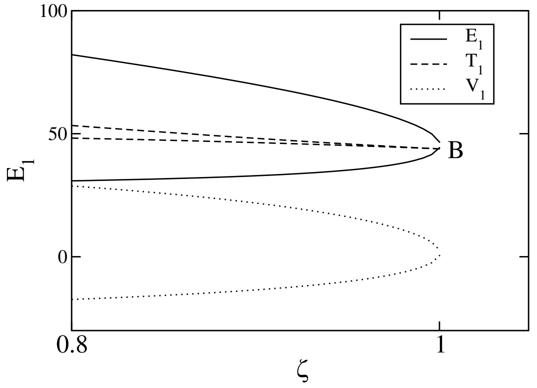

FIG. 5. $E_1$, $V_1 = \int d^3r v(\mathbf{r})\rho_1(\mathbf{r})$ and $T_1$ as a function of $\zeta$ as in Fig. (3).

ground-state energy is zero. Therefore in this gauge, $E_1$ is equal to the transition frequency. The figure shows that the kinetic contributions for the two distinct potentials merge at the fold point, having the same value and slope there. On the other hand, the potential contributions each have slope of infinite magnitude, producing a smooth curve. If $\chi$ is invertible (i.e., has no zero eigenvectors) the energy-density relationship is locally one-to-one and $\delta V/\delta\rho(\mathbf{r})$ is well defined. So for the potential energy and the total energy we get $\delta V/\delta\rho(\mathbf{r}) =$

$$\frac{\delta}{\delta\rho(\mathbf{r})}\int d^3r' v(\mathbf{r}')\rho(\mathbf{r}') = v(\mathbf{r}) + \int \rho(\mathbf{r}')\chi^{-1}(\mathbf{r},\mathbf{r}')d^3r' \quad (8)$$

$$\frac{\delta E}{\delta\rho(\mathbf{r})} = \int d^3r' \frac{\delta E}{\delta v(\mathbf{r}')}\frac{\delta v(\mathbf{r}')}{\delta\rho(\mathbf{r})} = \int \rho(\mathbf{r}')\chi^{-1}(\mathbf{r},\mathbf{r}')d^3r' \quad (9)$$

plus terms due to the gauge of the external potential. Since $\chi(\mathbf{r},\mathbf{r}')$ has a zero eigenvalue at the fold point, $\frac{\delta V}{\delta\rho(\mathbf{r})}$ and $\frac{\delta E}{\delta\rho(\mathbf{r})}$ will diverge at $\zeta = 1$. However, $\delta F/\delta\rho(\mathbf{r}) = -v(\mathbf{r})$, where $F = E - V$. Despite the absence of a density functional, and Eqs. (8) and (9) do not imply one, this result is identical to the ground-state DFT case. Curves for $E_1$ and $V_1$ vs. $\zeta$ are continuous and exhibit folds, Fig. (3), provided some universal gauge condition to define arbitrary constants of potentials is chosen, e.g., $E_0 = 0$ in this case. At the folds two different branches merge continuously, and beyond $\zeta = 1$ the only existing potential is discontinuously different, producing discontinuities in the density-potential relationship. Therefore, even along a specific branch, a limited excited-state density functional cannot be defined.

We have discussed the problems due to nonuniqueness of the excited-state potentials [Fig. (1)] and its implications for ensembles [Eq. (2)]. We close with the implications due to folding for various treatments of excited states within density functional theory.

An important tool in DFT has been the adiabatic connection [17,18], in which a coupling constant $\lambda$ is inserted in front of the electron-electron repulsion, and the one-body potential is made $\lambda$-dependent so as to keep the ground-state density fixed. This procedure therefore also defines all the excited-state energies and densities at each value for $\lambda$, and is used, for example, in defining the $\lambda$-dependent susceptibility used in expressing the exchange-correlation energy in terms of the fluctuations of the ground state, a common starting point for random-phase approximation treatments within DFT [19]. Difficulties can arise when the first excited-state energy crosses that of the ground state, and it has been suggested [10] that these can be avoided by remaining on a continuous curve, i.e., following the energy of what is now an excited state. Our results show a danger inherent in such a procedure. If a fold is encountered, both the potential generating this density as an excited state and its corresponding energy will change discontinuously as the fold is traversed.

Related problems appear with an excited-state variant of the adiabatic connection (called the generalized adiabatic connection) proposed by Görling [11], in which the density of an excited state is held fixed while $\lambda$ varies. If the folds in density space occur at different densities for different values of $\lambda$, and there is no reason to think otherwise, again a discontinuous change in potential and energy occurs when a fold is reached.

This work was supported by DOE under Grant No. DE-FG02-01ER45928.

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