Time-independent (static) density-functional theories for pure excited states: Extensions and unification

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(Received 28 March 2009; published 16 July 2009)

Time-independent density-functional theoretic approaches to pure excited states are considered, with special emphasis on the extensions of the constrained search to excited states. Links between the Levy-Nagy and Görling formulations are revealed. The excited-state analog of the Legendre-transform functional for ground states is constructed. Powerful results for Coulombic systems may facilitate the construction of an excited-state density functional with a simple and universal form.

I. INTRODUCTION

The intent of the present work is to extend, clarify, organize, and systematize previous results on the time-independent theory of pure excited states and to form a coherent theoretical underpinning for excited-state density-functional theory (DFT), where the theoretical foundations are presently less well established than for ground states. Further, for the purpose of approximating the time-independent excited-state functionals, several of their properties are derived. The scope of the present paper does not include the common time-dependent density-functional theory [1–7], nor does it encompass "ensemble mixing" methods for computing excited states [8–14].

Within the confines of excited-state density-functional theories that use a "pure state" and "time-independent" formulation [15], there are several outstanding theoretical issues. Some relate to problems in, or extensions to, existing work along these lines. For instance, Lemma II of the important 1999 paper of Görling [16] on excited-state density-functional theory does not apply for certain special densities, and so the proof provided for this theorem needs to be modified a little. More severe, however, is the somewhat disorganized state of the general theory: what is the relationship between the Levy-Nagy [17,18] and Görling [16] functionals? For ground states, an important complement to the constrained-search formulation is provided by the Legendre-transform formulation [19,20]. Is there a similar functional for excited states? These issues form the heart of the present paper, and will be addressed in Sec. III. Foreshadowing our results, we formulate an analog to Lemma II of Görling [16]. We observe that the Görling functional can be viewed as a special case of the Levy-Nagy bifunctional and, through stationary principles, we generalize the Legendre-transform functional to excited states. In addition, we derive a stationary property and some bounds for the Levy-Nagy functional and, finally, remark on the simplifications that occur when we restrict ourselves to Coulombic systems.

II. VARIATIONAL PRINCIPLES FOR EXCITED-STATE WAVE FUNCTIONS

A necessary foreward to any density-functional theoretic treatment for pure excited states is a brief exploration of the wave-functional analog. To this end, we present a number of different formulations for excited-state energies. First among them:

(i) A wave function Ψ_k is a stationary state of the N-electron system with external potential $v(\mathbf{r})$ if and only if the energy is stationary:

$$\frac{\delta E_{N,v(\mathbf{r})}[\Psi_k]}{\delta \Psi} \equiv \frac{\delta \frac{\langle \Psi_k | \hat{H}[v;N] | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle}}{\delta \Psi} = 0. \tag{1}$$

The kth excited state is the $(k+1)$th stationary point, counting from the lowest-energy state Ψ_0.

The notation $\frac{\delta E_{N,v(\mathbf{r})}[\Psi_k]}{\delta \Psi}$ indicates that the functional derivatives are evaluated for $\Psi = \Psi_k$. Equation (1) is the basis for the Görling excited-state density functional [16].

There are also a number of methods for determining excited states in which an excited state's energy is an extremum of some functional. The most fundamental one states the following:

(ii) Ψ_k is the kth-excited-state wave function of a system if and only if among all wave functions orthogonal to the lower excited states, it minimizes the energy. Thus

$$E_k[v;N] \equiv \underbrace{\min}_{\{\Psi | \langle \Psi | \Psi_j[v;N] \rangle = 0; 0 \leq j < k\}} \frac{\langle \Psi | H[v;N] | \Psi \rangle}{\langle \Psi | \Psi \rangle},$$

$$\Psi_k[v;N] \equiv \underbrace{\arg\min}_{\{\Psi | \langle \Psi | \Psi_j[v;N] \rangle = 0; 0 \leq j < k\}} \frac{\langle \Psi | H[v;N] | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{2}$$

where the minimization is subject to the constraint that the wave function is orthogonal to the lower-energy eigenfunctions $\{\Psi_j[v;N]\}_{j=0}^{k-1}$ of the system in question.

This second principle is more directly analogous to the ground-state variational principle (since it reduces to this principle when $k=0$) and is the basis for the Levy-Nagy excited-state density functional [17,18].

An aspect of (ii) is that it, in principle, requires one to "precompute" all the lower-lying eigenstates of the system.

One way around this is to use the Courant max-min principle:

(iii) *Courant max-min principle* [21,22]—Let $\mathbb{C}_k$ be a k-dimensional subspace of the space of all wave functions. [For concreteness, we may take this to be the appropriately antisymmetric elements of the first Sobolev space $\mathbb{H}_a^1(\mathbb{R}^{3N})$.] Then

$$E_k[v;N] \equiv \underbrace{\max}_{\mathbb{C}_k} \ \underbrace{\min}_{\{\Psi|\Psi \perp \mathbb{C}_k\}} \frac{\langle\Psi|H[v;N]|\Psi\rangle}{\langle\Psi|\Psi\rangle},$$

$$\Psi_k[v;N] \equiv \arg_\Psi \underbrace{\max}_{\mathbb{C}_k} \ \underbrace{\min}_{\{\Psi|\Psi \perp \mathbb{C}_k\}} \frac{\langle\Psi|H[v;N]|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (3)$$

The inner minimization is over all wave functions that are not in the subspace $\mathbb{C}_k$, while the outer maximization is over the subspace $\mathbb{C}_k$ (and could be carried out, for instance, by varying the basis set of this space).

Equation (3) may be rephrased as a minimization of the energy subject to the constraint that the wave function is in the complement of $\mathbb{C}_k$, $\bar{\mathbb{C}}_k$. This yields what may be termed the "Courant complement," namely:

(iv) *Courant complement*—Let $\bar{\mathbb{C}}_k$ be a subspace with codimension k. Then

$$E_k[v;N] \equiv \underbrace{\max}_{\bar{\mathbb{C}}_k} \ \underbrace{\min}_{\{\Psi|\Psi \in \bar{\mathbb{C}}_k\}} \frac{\langle\Psi|H[v;N]|\Psi\rangle}{\langle\Psi|\Psi\rangle},$$

$$\Psi_k[v;N] \equiv \arg_\Psi \underbrace{\max}_{\bar{\mathbb{C}}_k} \ \underbrace{\min}_{\{\Psi|\Psi \in \bar{\mathbb{C}}_k\}} \frac{\langle\Psi|H[v;N]|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (4)$$

Yet another principle may be derived from Eq. (4). Note that if the space of wave functions under consideration is finite dimensional with dimension m, then Eq. (4) is a method for determining the $(m-k)$th highest eigenvalue. By analogy, we may determine the $(k+1)$th eigenvalue by the following procedure:

(v) *Poincaré-Fischer-Pólya-Schiffer* (PFPS) *min-max principle* [22–24]—Let $\mathbb{P}_{k+1}$ be a $(k+1)$-dimensional subspace of the set of all electronic wave functions. Then

$$E_k[v;N] \equiv \underbrace{\min}_{\mathbb{P}_{k+1}} \ \underbrace{\max}_{\{\Psi|\Psi \in \mathbb{P}_{k+1}\}} \frac{\langle\Psi|H[v;N]|\Psi\rangle}{\langle\Psi|\Psi\rangle},$$

$$\Psi_k[v;N] \equiv \arg_\Psi \underbrace{\min}_{\mathbb{P}_{k+1}} \ \underbrace{\max}_{\{\Psi|\Psi \in \mathbb{P}_{k+1}\}} \frac{\langle\Psi|H[v;N]|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (5)$$

Though Eq. (5) does not seem to have been used previously in the context of the electronic Schrödinger equation, this result has appeared in the mathematics literature. In particular, as noted by Pólya and Schiffer [22], the theorem is a corollary to the theorem of Poincaré [24] on the interlacing of eigenvalues (i.e., the notes of the characteristic equation of

the associated matrix) as the size of the basis set is increased. (For the Schrödinger equation, this interlacing theorem is credited to Hylleraas, Undheim, [25] and MacDonald [26].) In the present form, Eq. (5) may be credited to Fischer [23], who derived the analogous result for quadratic forms in 1905.

There is also a complement to the PFPS principle, namely:

(vi) *PFPS complement*—Let $\bar{\mathbb{P}}_{k+1}$ be a subspace of the set of all electronic wave functions with codimension $(k+1)$. Then

$$E_k[v;N] \equiv \underbrace{\min}_{\bar{\mathbb{P}}_{k+1}} \ \underbrace{\max}_{\{\Psi|\Psi \perp \bar{\mathbb{P}}_{k+1}\}} \frac{\langle\Psi|H[v;N]|\Psi\rangle}{\langle\Psi|\Psi\rangle},$$

$$\Psi_k[v;N] \equiv \arg_\Psi \underbrace{\min}_{\bar{\mathbb{P}}_{k+1}} \ \underbrace{\max}_{\{\Psi|\Psi \perp \bar{\mathbb{P}}_{k+1}\}} \frac{\langle\Psi|H[v;N]|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (6)$$

Unlike (i) and (ii), which are directly associated with exact density functionals for excited states, (iii)–(vi) give density functionals that are bounds to the exact excited-state density functionals. Some of these bounds are related to those derived by Lieb [27].

III. VARIATIONAL PRINCIPLES FOR EXCITED-STATE DENSITIES

A. Ground-state constrained-search functional

Perdew and Levy [29] note that the ground-state constrained-search functional [28],

$$\begin{aligned} E_v^{\text{CS}}[\rho] &\equiv \underbrace{\min}_{\{\Psi|\Psi \to \rho(r)\}} \frac{\langle\Psi|\hat{T} + \hat{V}_{ee} + \sum\limits_{i=1}^{N} v(\boldsymbol{r}_i)|\Psi\rangle}{\langle\Psi|\Psi\rangle} \\ &= \underbrace{\min}_{\{\Psi|\Psi \to \rho(r)\}} \left(\frac{\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle}{\langle\Psi|\Psi\rangle} + \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r} \right) \\ &= F^{\text{CS}}[\rho] + \int \rho(\boldsymbol{r})v(\boldsymbol{r})d\boldsymbol{r}, \end{aligned} \quad (7)$$

is actually stationary for certain excited states [29]. In Eq. (7), $\hat{T}$ denotes the kinetic-energy operator, $\hat{V}_{ee}$ denotes the electron-electron repulsion energy operator, and the minimum is over all antisymmetric N-electron wave functions with electron density $\rho(\boldsymbol{r})$. We denote the wave function that minimizes Eq. (7) as

$$\Psi^{\text{CS}}[\rho] \equiv \arg \underbrace{\min}_{\{\Psi|\Psi \to \rho(r)\}} \frac{\langle\Psi|\hat{T} + \hat{V}_{ee}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad (8)$$

and so

$$F^{\text{CS}}[\rho] \equiv \langle\Psi^{\text{CS}}[\rho]|\hat{F}|\Psi^{\text{CS}}[\rho]\rangle / \langle\Psi^{\text{CS}}[\rho]|\Psi^{\text{CS}}[\rho]\rangle, \quad (9)$$

where we have introduced the notation

$$\hat{F} \equiv \hat{T} + \hat{V}_{ee}. \tag{10}$$

The constrained-search functional is actually stationary for certain excited states. The key equation is the chain rule for functional derivatives

$$\left(\frac{\delta E_v^{CS}[\rho]}{\delta \rho(\boldsymbol{r})} \right)_N = \int \frac{\delta E_{v,N}[\Psi^{CS}[\rho]]}{\delta \Psi^{CS}(\boldsymbol{\tau})} \frac{\delta \Psi^{CS}(\boldsymbol{\tau})}{\delta \rho(\boldsymbol{r})} d\boldsymbol{\tau}, \tag{11}$$

where $E_{v,N}[\Psi]$ denotes the Rayleigh quotient,

$$E_{v,N}[\Psi] \equiv \frac{\langle \Psi | \hat{H}[v;N] | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{12}$$

Because Eq. (11) is only valid for number-conserving variations in the density (unless the Fock-space wave function is considered), Eq. (11) only determines $(\frac{\delta E_v^{CS}[\rho]}{\delta \rho(\boldsymbol{r})})_N$ up to an arbitrary constant, which we denote μ [30]. When $\Psi^{CS}[\rho]$ is an eigenstate of $\hat{H}[v;N]$, $\frac{\delta E_{v,N}[\Psi^{CS}[\rho]]}{\delta \Psi} = 0$, and so $(\frac{\delta E_v^{CS}[\rho]}{\delta \rho(\boldsymbol{r})})_N = \mu$. It follows that $(\frac{\delta E_v^{CS}[\rho]}{\delta \rho(\boldsymbol{r})})_N = \mu$ if and only if

$$\Psi^{CS}[\rho_k[v;N]] = \Psi_k[v;N], \tag{13}$$

where $\rho_k[v;N,\boldsymbol{r}]$ is the kth-excited-state density for the system with N electrons in external potential $v(\boldsymbol{r})$ and $\Psi_k[v;N]$ is the kth-excited-state wave function for this system. The $k=0$ case is just the standard "ground-state" constrained-search result.

The key result,

$$\left(\frac{\delta E_v^{CS}[\rho_k]}{\delta \rho(\boldsymbol{r})} \right)_N = \mu, \tag{14}$$

indicates that the constrained-search energy functional is stationary with respect to number-conserving variations in the density about $\rho_k(\boldsymbol{r})$, which is similar to the result for the stationary states of wave functions [Eq. (1)]. Unfortunately, Eq. (14) does not hold for many excited-state electron densities: electron densities that are "excited-state densities" for one system are frequently ground-state densities for other systems, and in this case $E_v^{CS}[\rho_k] = E_{v;N}[\Psi^{CS}[\rho_k]]$ is a lower bound to the excited-state energy $E_{v;N}[\Psi_k]$ [28]. Even if there is no ground state with the electron density $\rho_k[v;N,\boldsymbol{r}]$, this could be the density of the lth excited state of some other N-electron system, $\Psi_l[w;N]$ [31–34]. In this case, the constrained search will converge to whichever state has a smaller value for

$$F[\Psi] \equiv \frac{\langle \Psi | \hat{F} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \tag{15}$$

which may or may not correspond to the state with the lowest excitation level or total energy [28].

We summarize the preceding results in a theorem:

Theorem 1 (Perdew and Levy [29]). Let $\rho_k[v;N,\boldsymbol{r}]$ denote the kth-excited-state density ($k \geq 0$) for the system with N electrons bound by external potential $v(\boldsymbol{r})$. Let $\Psi_k[v;N]$ denote one of the eigenfunctions for this state. The constrained-search functional $E_v^{CS}[\rho]$ is stationary with respect to number-conserving variations about $\rho_k(\boldsymbol{r})$ if and only if $\Psi^{CS}[\rho_k] \equiv \Psi_k[v;N]$, and if this result holds, then $E_v^{CS}[\rho_k]$

gives the eigenvalue for this state, $E_k[v;N]$. However, this favorable result can occur only when every other electronic eigenstate with the same density, $\Psi_l[w;N]$, satisfies

$$F[\Psi_l[w;N]] \geq F[\Psi_k[v;N]] \tag{16}$$

or, equivalently,

$$E_k[v;N] - E_l[w;N] \leq \int \rho_k(\boldsymbol{r})[w(\boldsymbol{r}) - v(\boldsymbol{r})] d\boldsymbol{r}. \tag{17}$$

B. Görling excited-state functional

The early work of Perdew and Levy [29] suggests seeking a way to adapt the conventional constrained-search functional so that it is stationary for any excited state, rather than just a few special choices of excited states. To this end, decompose the energy into two parts,

$$E_{v;N}[\Psi_k] \equiv F[\Psi_k] + \int \rho[\Psi_k;\boldsymbol{r}] v(\boldsymbol{r}) d\boldsymbol{r}, \tag{18}$$

where $\rho[\Psi_k;\boldsymbol{r}]$ denotes that the electron density is a functional of the wave function Ψ_k,

$$\rho[\Psi_k;\boldsymbol{r}] \equiv \frac{\langle \Psi_k | \sum_{i=1}^{N} \delta(\boldsymbol{r}_i - \boldsymbol{r}) | \Psi_k \rangle}{\langle \Psi_k | \Psi_k \rangle}, \tag{19}$$

and a function of the position in space, $\boldsymbol{r}$. Substituting Eq. (18) into the stationary principle for the energy [Eq. (1)], we find that

$$\frac{\delta F[\Psi_k]}{\delta \Psi} = - \frac{\delta \int \rho[\Psi_k;\boldsymbol{r}] v(\boldsymbol{r}) d\boldsymbol{r}}{\delta \Psi}. \tag{20}$$

The right-hand side of Eq. (20) is unchanged as long as the variation in the wave function does not change the electron density, leading to the conclusion that [16,35,36]

$$\left(\frac{\delta F[\Psi_k]}{\delta \Psi} \right)_{\rho[\Psi_k]} = 0, \tag{21}$$

where the notation indicates that the electron density of the wave function is held constant during the variation. This leads to the excited-state energy density functional proposed by Görling [16,35],

$$F_v^G[\rho] \equiv \underset{\{\Psi | \Psi \to \rho\}}{\text{stat}} F[\Psi], \tag{22}$$

where the notation indicates that among all the wave functions with the electron density of interest, one locates those for which $F[\Psi]$ is stationary with respect to variations in the wave function that conserve the electron density. The resulting stationary points and their associated eigenfunctions,

$$\Psi_v^G[\rho] \equiv \underset{\nu}{\arg} \underset{\{\Psi | \Psi \to \rho\}}{\text{stat}} F[\Psi], \tag{23}$$

are labeled with the index ν, which could, in general, be any index set. As yet, we have no reason to suspect that the

number of stationary points is countable, and so it is impermissible to assume that ν is an integer [16].

The preceding analysis yields "Lemma 1" of Görling [16], which in the present notation, is as follows:

Theorem 2 (Görling [16]). Suppose Ψ_k to be the eigenfunction of the kth excited state for the some electronic system. Then $F[\Psi]$ is stationary with respect to density-conserving variations about Ψ_k, and so there exists some value of ν such that the argument of the Görling functional Ψ_ν^G is equal to Ψ_k. In general, $\nu \neq k$.

Görling [16] supplemented the preceding result with his "Lemma 2," which suggests that to every stationary point of the Görling function there corresponds an electronic system, with external potential

$$v_\nu(\mathbf{r}) = -\frac{\delta F_\nu^G[\rho]}{\delta \rho(\mathbf{r})}, \tag{24}$$

for which Ψ_ν^G is a stationary state. [We neglect the arbitrary constant in the functional derivative of Eq. (24) because shifting the external potential by a constant has no effect for changes in density that preserve electron number.]

Despite the well-known v-representability problem in ground-state density-functional theory, one might suspect that the above result is correct. For example, many of the electron densities that are not ground-state v-representable are electron densities for some excited state of the system and indeed, it is precisely such excited states for which the conventional ground-state constrained-search functional suffices [29]. However, the examples of non-v-representable constructed by Englisch and Englisch [37] are not stationary-state densities for any external potential, as is clear from the fact these counterexamples are designed to render the Hamiltonian noninvertible. We call such densities *totally non-v*-representable, since they are not a stationary-state density for any electronic system. Moreover, such densities are not ensemble v representable [37,38]: one cannot form these densities through convex linear combinations of the electron densities from a degenerate stationary state of an electronic system.

Recalling that the ground-state constrained search has a minimum for any N-representable density [19,28], and observing that the $F^{CS}[\rho]$ is just the special case of the Görling functional where the stationary point is forced to be a minimum, we deduce that the Görling function will be stationary even for totally non-v-representable densities, which contradicts the assertion that every stationary point of Eq. (22) corresponds to a real electronic system. We recall, however, that totally non-v-representable densities can be viewed as the ground-state densities for systems with external potentials that are generalized functions [30]. This leads to the following theorem:

Theorem 3 (extension of Lemma 2 of Görling [16]). Let $\Psi_\nu^G[\rho]$ denote the wave function associated with a stationary value of the Görling functional [Eq. (22)] for the electron density $\rho(\mathbf{r})$. Then there exists a generalized function $d(\mathbf{r})$ so that $\Psi_\nu^G[\rho]$ is an eigenfunction of the Hamiltonian with this "generalized external potential,"

$$\left(\hat{F} + \sum_{i=1}^N d(\mathbf{r})\right)\Psi_\nu^G[\rho] = E\Psi_\nu^G[\rho],, \tag{25}$$

and therefore the "energy" of this system,

$$E_{d;N}[\Psi] \equiv \frac{\langle\Psi|\hat{F} + \sum_{i=1}^N d(\mathbf{r}_i)|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \tag{26}$$

is stationary with respect to variations in the wave function about $\Psi = \Psi_\nu^G[\rho]$.

Proof. Define

$$D(\mathbf{r}_1, \ldots, \mathbf{r}_N) \equiv \frac{\hat{T}\Psi_\nu^G(\mathbf{r}_1, \ldots, \mathbf{r}_N) + \hat{V}_{ee}\Psi_\nu^G(\mathbf{r}_1, \ldots, \mathbf{r}_N)}{\Psi_\nu^G(\mathbf{r}_1, \ldots, \mathbf{r}_N)}. \tag{27}$$

Note that, because $\Psi_\nu^G(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ will have nodes in it, $D(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is generally not a function, but a "generalized function" or distribution. By this, we connote that while $D(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is not a function, it can be written as the limit as a sequence of functions, each of which is in the function space appropriate to the potentials for electronic systems. (Following Lieb [19], we can take this space to be $\mathbb{L}^{3/2}(\mathbb{R}^{3N}) + \mathbb{L}^\infty(\mathbb{R}^{3N})$, but the precise identity of the space depends on the space of densities under consideration [39], and will not be of consequence in the following analysis.)

Define a ρ_k-stationary variation $\delta\Psi$ about Ψ_ν^G as any variation for which

$$0 = \int \int \int \cdots \int \delta\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)\Psi_\nu^G(\mathbf{r}_1, \ldots, \mathbf{r}_N)d\mathbf{r}_{k+1} \cdots d\mathbf{r}_N. \tag{28}$$

A ρ_k-stationary variation does not change the k-electron distribution function of the system to first order, which we denote $\left(\frac{\delta\rho_k[\Psi_\nu^G]}{\delta\Psi}\right)_{\rho_k[\Psi_\nu^G]}=0$, in similitude to the notation in Eq. (21).

Denote the set of all ρ_k-stationary variations about Ψ_ν^G as $S_k[\Psi_\nu^G]$. It is clear that every ρ_j-stationary variation is also ρ_k stationary if $k<j$ ($S_k[\Psi_\nu^G] \supset S_{j>k}[\Psi_\nu^G]$) and that, moreover, there are more ρ_k-stationary variations than there are ρ_j-stationary variations ($S_k[\Psi_\nu^G]\backslash S_{j>k}[\Psi_\nu^G] \neq \varnothing$). In addition, if $\delta\Psi_1$ and $\delta\Psi_2$ are in $S_k[\Psi_\nu^G]$, then $\delta\Psi_1+\delta\Psi_2$ and $\kappa\cdot\delta\Psi_1$ are also in $S_k[\Psi_\nu^G]$ (where κ is a constant). So the set of ρ_k-stationary variations, $S_k[\Psi_\nu^G]$, being a subspace of a Hilbert space, is also a Hilbert space.

Referring back to Eq. (27), we decompose $D(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ as a sum of q-body terms,

$$D(\mathbf{r}_1, \ldots, \mathbf{r}_N) \equiv \sum_{i_q=i_{q-1}+1}^N \cdots \sum_{i_2=i_1+1}^N \sum_{i_1=1}^N d(\mathbf{r}_{i_1}, \ldots, \mathbf{r}_{i_q}). \tag{29}$$

It is exceptional that $q<N$. However, in the special case of interest, $F[\Psi]$ is ρ_1 stationary about Ψ_ν^G, and so for all $\delta\Psi \in S_1[\Psi_\nu^G]$,

$$F[\Psi_\nu^G + \delta\Psi] - F[\Psi_\nu^G] = 0 \qquad (30)$$

(to within terms of order $\|\delta\Psi\|^2$). Using definition (15), we simplify Eq. (30) to find that, except for terms of $\mathbb{O}(\|\delta\Psi\|^2)$,

$$\frac{\langle \Psi_\nu^G + \delta\Psi | \hat{F} | \Psi_\nu^G + \delta\Psi \rangle}{\langle \Psi_\nu^G + \delta\Psi | \Psi_\nu^G + \delta\Psi \rangle} - \frac{\langle \Psi_\nu^G | \hat{F} | \Psi_\nu^G \rangle}{\langle \Psi_\nu^G | \Psi_\nu^G \rangle}$$

$$= \frac{\langle \Psi_\nu^G | \hat{F} | \Psi_\nu^G \rangle}{\langle \Psi_\nu^G | \Psi_\nu^G \rangle} \left(1 - \frac{\langle \delta\Psi | \Psi_\nu^G \rangle}{\langle \Psi_\nu^G | \Psi_\nu^G \rangle} - \frac{\langle \Psi_\nu^G | \delta\Psi \rangle}{\langle \Psi_\nu^G | \Psi_\nu^G \rangle} \right)$$

$$+ \frac{\langle \delta\Psi | \hat{F} | \Psi_\nu^G \rangle + \langle \Psi_\nu^G | \hat{F} | \delta\Psi \rangle}{\langle \Psi_\nu^G | \Psi_\nu^G \rangle} - \frac{\langle \Psi_\nu^G | \hat{F} | \Psi_\nu^G \rangle}{\langle \Psi_\nu^G | \Psi_\nu^G \rangle}$$

$$= \frac{\langle \delta\Psi | \hat{F} | \Psi_\nu^G \rangle + \langle \Psi_\nu^G | \hat{F} | \delta\Psi \rangle}{\langle \Psi_\nu^G | \Psi_\nu^G \rangle}. \qquad (31)$$

The second two terms on the first line vanishes because every ρ_1-stationary variation is also ρ_0 stationary. Because $\hat{F}$ is a Hermitian operator, we deduce from Eqs. (31) and (30) that

$$\langle \Psi_\nu^G | \hat{F} | \delta\Psi \rangle + \langle \delta\Psi | \hat{F} | \Psi_\nu^G \rangle = 2 \, \mathrm{Re}(\langle \delta\Psi | \hat{F} | \Psi_\nu^G \rangle) = 0. \quad (32)$$

Substituting Eqs. (27) and (29), we have

$$\mathrm{Re}\left(\langle \delta\Psi | \sum_{i_q=i_{q-1}+1}^{N} \cdots \sum_{i_2=i_1+1}^{N} \sum_{i_1=1}^{N} d(\boldsymbol{r}_{i_1}, \ldots, \boldsymbol{r}_{i_q}) | \Psi_\nu^G \rangle \right) = 0. \quad (33)$$

Because electrons are identical particles, we conclude that for every $\delta\Psi \in S_1[\Psi_\nu^G]$,

$$\mathrm{Re}[\langle \delta\Psi | d(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_q) | \Psi_\nu^G \rangle] = 0. \qquad (34)$$

Now, if $q > 1$, we will be able to choose a variation $\delta\Psi$ that is in $S_1[\Psi_\nu^G]$ but not in $S_q[\Psi_\nu^G]$ for which Eq. (34) is invalid. [This follows from the fact a Hilbert space has enough elements to "separate points" or, more specifically, from the fact that Eq. (34) can be used to define a subspace of $S_1[\Psi_\nu^G]$ with codimension 1 for which Eq. (34) does not hold.] The fact that Eq. (34) must be true for all $\delta\Psi$ in $S_1[\Psi_\nu^G]$ implies that $q = 1$ in Eq. (29); i.e.,

$$D(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \equiv \sum_{i=1}^{N} d(\boldsymbol{r}_i). \qquad (35)$$

Substituting this expression into Eq. (27) and rearranging yields Eq. (25). ∎

It is important to recognize that the Hohenberg-Kohn theorem does not hold in any meaningful way for generalized external potentials—two different generalized external potentials can have the same ground-state density [30,39] and, indeed, it is possible (even likely) that several different distributions will satisfy Eq. (27), although, by the above analysis, all of them will have one-particle form (35).

This ambiguity is best illustrated with an example. Consider the following two sequences of external potentials:

$$v_H(\boldsymbol{r}) = \begin{cases} 0 & \text{if } r < 1 \\ H & \text{if } r > 1, \end{cases} \qquad (36)$$

and

$$w_H(\boldsymbol{r}) = \begin{cases} 0 & \text{if } r < 1 \\ W & \text{if } |\boldsymbol{r} - [2,0,0]| < 1 \\ H & \text{otherwise.} \end{cases} \qquad (37)$$

Each of these potentials is in $\mathbb{L}^\infty(\mathbb{R}^3)$, and is thus permissible according to any reasonable conditions imposed on potentials. However, forming the generalized external potentials by sequence in which H increases to infinity, $v_H(\boldsymbol{r})$ becomes a simple "electrons-in-a-sphere" system, while $w_H(\boldsymbol{r})$ consists of two "spheres," with different potentials, separated by an infinite barrier. If W is chosen to be sufficiently large, the electrons will be localized in the sphere centered at the origin, so that the ground state-electron density (and, if W is large enough, some of the excited states too) of the two different generalized external potentials will be the same [39,40]. Thus, evaluating the functional derivative of $F_\nu^G[\rho]$ with respect to the electron density gives

$$\frac{\delta F_\nu^G[\rho]}{\delta \rho(\boldsymbol{r})} = -d(\boldsymbol{r}) + \mu. \qquad (38)$$

However, if $d(\boldsymbol{r})$ is not a potential, but instead a generalized function, then it must be recognized that there are many different generalized functions that may serve to describe the same functional derivative. In a proper mathematical sense, then, we may consider the functional derivative to be an "equivalence class" of all the generalized external potentials consistent with Eq. (38), with the understanding that the equivalence class will have only one element when functional differentiation yields an appropriate external potential. (Though they did not describe it in these terms, this is the phenomenon that underlies the assertion of Englisch and Englisch [41,42] that the functional derivative of the ground-state Legendre-transform functional does not exist for totally non-v-representable densities.)

We conclude this section by reiterating that when viewed in the appropriately generalized form of Theorem 2, Lemma 2 of Görling [16] is essentially correct: there are "electronic systems," in a generalized sense, that correspond to each and every stationary point of the Görling functional [16]. Recent numerical applications based on the approach of Görling [16] have given promising results, which reinforces the fact that there are no essential theoretical problems with this formulation [35,43–45].

C. Levy-Nagy excited-state functional

Perusal of the preceding argument reveals that the Görling functional can be regarded as the natural generalization of the stationary principle for the wave function [Eq. (1)] to density-functional theory. An alternative approach, due to

Levy and Nagy [17,18], is based on the constrained minimization approach to excited states [Eq. (2)]. Specifically, one replaces the minimization over wave functions Ψ that are orthogonal to the lower-energy eigenfunctions of the system,

$\{\Psi_j[v;N]\}_{j=0}^{k-1}$ with a nested minimization, the inner minimization over all wave functions that are orthogonal to the lower excited states that give a desired density $\rho(\mathbf{r})$, and the outer minimization over all densities:

$$E_k[v;N] \equiv \underbrace{\min}_{\rho}\left(\left[\underbrace{\min}_{\left\{\Psi \middle| \begin{smallmatrix}\Psi \to \rho\\\langle\Psi|\Psi_j[v;N]\rangle=0;0\leq j<k\end{smallmatrix}\right\}} \frac{\langle\Psi|\hat{F}|\Psi\rangle}{\langle\Psi|\Psi\rangle}\right] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}\right).$$

(39)

In analogy to the ground-state constrained-search functional [Eq. (7)], the inner minimization defines the Levy-Nagy excited-state density functional [17,18],

$$F_k^{LN}[\rho,v] \equiv \underbrace{\min}_{\left\{\Psi \middle| \begin{smallmatrix}\Psi \to \rho\\\langle\Psi|\Psi_j[v;N]\rangle=0;0\leq j<k\end{smallmatrix}\right\}} \frac{\langle\Psi|\hat{F}|\Psi\rangle}{\langle\Psi|\Psi\rangle},$$

(40)

and the minimizing wave function is denoted

$$\Psi_k^{LN}[\rho,v] \equiv \arg \underbrace{\min}_{\left\{\Psi \middle| \begin{smallmatrix}\Psi \to \rho\\\langle\Psi|\Psi_j[v;N]\rangle=0;0\leq j<k\end{smallmatrix}\right\}} \frac{\langle\Psi|\hat{F}|\Psi\rangle}{\langle\Psi|\Psi\rangle}.$$

(41)

Note that, unlike the Görling functional $F_v^G[\rho]$, the index labeling the different states in the Levy-Nagy function $F_k^{LN}[\rho,v]$ has direct relevance to the excitation level of the state of interest. The trade-off is that the Levy-Nagy functional is not a simple functional of the electron density, but, as written here, a bifunctional of the electron density and the external potential.

We here observe, by the way, that the Levy-Nagy functional can be nicely made convex by simply replacing the pure state Ψ in Eqs. (40) and (41) with ensembles, where each element of an ensemble is constructed from wave functions orthogonal to the lower excited states, $\{\Psi_j[v,N]\}$.

Referring to Eq. (40), it is clear that we can substitute for the external potential any quantity that determines the electronic Hamiltonian of the system of interest, thence determining the identity of the k states of the system to which the wave function is constrained to be orthogonal. In particular, based on the Hohenberg-Kohn theorem, one could choose to use the ground-state electron density instead of the external potential in defining the orthogonality constraint as, in fact, was done by Levy and Nagy [17] in their original paper. Unfortunately, if one takes this approach the resulting functional, $F_k^{LN}[\rho,\rho_{gs}]$, is not unambiguously defined except when the reference density is v representable. This, however, is primarily a "formal" difficulty: practical computational studies have been performed using the Levy-Nagy criterion [18,46–50] or an alternative criterion (based on minimizing

the error in the Kohn-Sham kinetic energy of the noninteracting system) proposed by Samal and Harbola [51,52]. Samal and Harbola [53] also developed a local-density approximation that is effective for the Levy-Nagy approach. Tasnadi and Nagy [46,54] developed orbital-based exchange formulations.

As noted by Levy and Nagy [17], $\rho_{gs}(\mathbf{r})$ can be replaced by the external potential. This choice has important practical benefits. For example, while the ground-state density for a system of interest is generally unknown, the usual input to quantum chemistry calculations (e.g., the types and positions of molecules composing atoms) define the external potential for the system of interest. Indeed, the variational principle

$$E_k[v;N] \equiv \underbrace{\min}_{\rho(\mathbf{r})} F_k[\rho,v] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}$$

(42)

for the energy and electron density of the excited state already depends on the external potential, and so adding a dependence on the external potential to the excited-state analog of the Hohenberg-Kohn functional is relatively unproblematic. Finally, it is possible that the external potential will be useful in deriving improved approximations to $F_k^{LN}[\rho]$, even for the $k=0$ case. Note, for example, that many functionals for inhomogeneous densities in the classical theory of fluids depend explicitly on the external potential, as this is useful for describing the dependence of the hole-correlation function on the external potential [55,56]. The exchange-correlation hole in molecules is similarly strongly influenced by the shape of the external potential [57]. Thus it is reasonable to expect that including an explicit dependence on the external potential in our functionals may facilitate modeling electron correlation and, in particular, allow one to treat angular and radial correlation effects separately. Finally, we note that potential-based DFT seems to be a useful alternative to the conventional density-focused approach, with the directly available information about the potential being particular important for materials exhibiting noncollinear magnetism [58–60].

Based on the similarities of both the Levy-Nagy and Görling functionals to the original ground-state constrained-search formalism, one might suppose that the two functionals

are related. To investigate further, we prove results that are analogous to Theorems 2 and 3.

Theorem 4. $F_k^{LN}[\rho,w]$ is stationary with respect to variations in external potential about $w(\boldsymbol{r})$ if and only if $\rho(\boldsymbol{r})$ is the eigendensity associated with the nondegenerate kth excited state of the N-electron system with external potential $w(\boldsymbol{r})$.

Proof. Suppose $\rho(\boldsymbol{r})$ is an eigendensity associated with the kth excited state of the N-electron system. Then, by definition,

$$E_k[w;N] = F_k^{LN}[\rho,w] + \int \rho(\boldsymbol{r})w(\boldsymbol{r})d\boldsymbol{r}. \tag{43}$$

Suppose that the kth excited state is not degenerate. Then, from the Hellmann-Feynman theorem, $E[w+\delta w;N] - E[w;N] = \int \rho(\boldsymbol{r})\delta w(\boldsymbol{r})d\boldsymbol{r}$. [We omit terms of order $\|\delta w(\boldsymbol{r})\|^2$.] Then, from Eq. (43),

$$F_k^{LN}[\rho,w+\delta w] - F_k^{LN}[\rho,w] = 0 \tag{44}$$

for a nondegenerate state. That is, $F_k^{LN}[\rho,w]$ is stationary with respect to variations in external potential about $w(\boldsymbol{r})$.

The converse of this result is proved in a similar manner to Theorem 3, and reveals the link between the Levy-Nagy and Görling formulations of excited-state density-functional theory. In particular, since $F_k^{LN}[\rho,w]$ is stationary with respect to variations in external potential about $w(\boldsymbol{r})$,

$$\begin{aligned}
0 &= F_k^{LN}[\rho,w+\delta w] - F_k^{LN}[\rho,w] \\
&= \frac{\langle \Psi_k^{LN}[\rho,w+\delta w]|\hat{F}|\Psi_k^{LN}[\rho,w+\delta w]\rangle}{\langle \Psi_k^{LN}[\rho,w+\delta w]|\Psi_k^{LN}[\rho,w+\delta w]\rangle} \\
&\quad - \frac{\langle \Psi_k^{LN}[\rho,w]|\hat{F}|\Psi_k^{LN}[\rho,w]\rangle}{\langle \Psi_k^{LN}[\rho,w]|\Psi_k^{LN}[\rho,w]\rangle} \\
&= \frac{\langle \Psi_k^{LN}[\rho,w]+\delta\Psi_{\delta w}|\hat{F}|\Psi_k^{LN}[\rho,w]+\delta\Psi_{\delta w}\rangle}{\langle \Psi_k^{LN}[\rho,w]+\delta\Psi_{\delta w}|\Psi_k^{LN}[\rho,w]+\delta\Psi_{\delta w}\rangle} \\
&\quad - \frac{\langle \Psi_k^{LN}[\rho,w]|\hat{F}|\Psi_k^{LN}[\rho,w]\rangle}{\langle \Psi_k^{LN}[\rho,w]|\Psi_k^{LN}[\rho,w]\rangle} = 2\,\mathrm{Re}(\langle \delta\Psi_{\delta w}|\hat{F}|\Psi_k^{LN}[\rho,w]\rangle),
\end{aligned} \tag{45}$$

where we have defined

$$\delta\Psi_{\delta w} \equiv \Psi_k^{LN}[\rho,w+\delta w] - \Psi_k^{LN}[\rho,w]. \tag{46}$$

By the definition of the Levy-Nagy functional [Eq. (40)], it is evident that the two wave functions of interest, $\Psi_k^{LN}[\rho,w]+\delta\Psi_{\delta w}$ and $\Psi_k^{LN}[\rho,w]$, have the same electron density. So $\delta\Psi_{\delta w}$ is a ρ_1-stationary variation of $\Psi_k^{LN}[\rho,w]$. By having different choices for the change in external potential, $\delta w(\boldsymbol{r})$, we can span the space of all ρ_1-stationary variations, $S_1[\Psi_k^{LN}[\rho,w]]$. Using the same argument as in the proof of Theorem 3 [cf. Eqs. (32)–(35)], we conclude from Eq. (45) that there exists a generalized function, $d(r)$, for which

$$\hat{F}\Psi_k^{LN}[\rho,w] = \left(E - \sum_{i=1}^{N} d(\boldsymbol{r}_i)\right)\Psi_k^{LN}[\rho,w]. \tag{47}$$

From the definition of the Levy-Nagy functional, $\Psi_k^{LN}[\rho,w]$ is orthogonal to the first k eigenfunctions of the system with external potential $w(\boldsymbol{r})$, $\{\Psi_i[w;N]\}_{i=0}^{k-1}$. Suppose $d(\boldsymbol{r}) \neq w(\boldsymbol{r})$; then $\Psi_k^{LN}[w,\rho] \neq \Psi_k[w;N]$ [19]. This, however, indicates that one can construct a ρ_1-stationary variation about $\Psi_k^{LN}[\rho,w]$, $\delta\Psi_d$, that is orthogonal to the first k eigenfunctions of the system and lowers the energy. That is,

$$\begin{aligned}
&\frac{\langle \Psi_k^{LN}[\rho,w]+\delta\Psi_d|\hat{F}|\Psi_k^{LN}[\rho,w]+\delta\Psi_d\rangle}{\langle \Psi_k^{LN}[\rho,w]+\delta\Psi_d|\Psi_k^{LN}[\rho,w]+\delta\Psi_d\rangle} + \int \rho(\boldsymbol{r})w(\boldsymbol{r})d\boldsymbol{r} \\
&< \frac{\langle \Psi_k^{LN}[\rho,w]|\hat{F}|\Psi_k^{LN}[\rho,w]\rangle}{\langle \Psi_k^{LN}[\rho,w]|\Psi_k^{LN}[\rho,w]\rangle} + \int \rho(\boldsymbol{r})w(\boldsymbol{r})d\boldsymbol{r}. \tag{48}
\end{aligned}$$

(To construct such a variation, use a variation that is dominated by the desired eigenstate, $\Psi_k[w,N]$ and use small portions of higher-energy eigenstates to fulfill the requirement of ρ_1 stationarity.)

Equation (48) implies that $F[\Psi_k^{LN}+\delta\Psi_d] < F[\Psi_k^{LN}]$, contradicting the definition of $\Psi_k^{LN}[\rho,w]$ [Eq. (41)]. We conclude that $d(\boldsymbol{r}) = w(\boldsymbol{r})$. Thus, if $F_k^{LN}[\rho,w]$ is stationary with respect to variations in external potential about $w(\boldsymbol{r})$, then $\rho(\boldsymbol{r})$ is an eigendensity of the kth excited state of the system with this external potential. ∎

The generalization of Theorem 4 to degenerate excited states is that $F_k^{LN}[\rho,w]$ is stationary with respect to a space of variations in the external potential, $\mathbb{V}_k[v]$, with codimension $\frac{g(g+1)}{2} - 1$, where g is the multiplicity of the degeneracy. We will not prove this extension here, because it requires only a small adaptation of a proof we will present later (cf. Theorem 8). The key idea is that the $F_k^{LN}[\rho,w]$ is stationary with respect to the set of perturbations that do not break the degeneracy.

Referring back to Eq. (45) in the proof of Theorem 4, we have the following:

Theorem 5. If $F_k^{LN}[\rho,w]$ is stationary with respect to variations in external potential $w(\boldsymbol{r})$, then $F[\Psi_k^{LN}]$ is ρ_1 stationary with respect to variations in the wave function Ψ_k^{LN}.

Comparing this result to Eq. (32) in the proof of Theorem 3, we recognize that the Görling functional $F_v^G[\rho]$ is the restriction of the Levy-Nagy functional to generalized external potentials for which $F_k^{LN}[\rho,v]$ is stationary. To see this more explicitly, label the stationary points of the Görling function in a revised manner, using two indices: k to specify the excitation level of the wave function and λ to "count" the number of different kth excited states with the same electron density. With this revised notation, $F_v^G[\rho] \rightarrow F_{k,\lambda}^G[\rho]$. Similarly, we label the generalized external potentials for which the Levy-Nagy functional is stationary with $d_\lambda(\boldsymbol{r})$, so $F_k^{LN}[\rho,d] \rightarrow F_k^{LN}[\rho,d_\lambda]$. From Theorem 5, the fact $F_k^{LN}[\rho,v_\lambda]$ is stationary with respect to variations in the external potential implies that $F[\Psi_k^{LN}[\rho,v_\lambda]]$ is ρ_1 stationary with respect to variations about $\Psi_k^{LN}[\rho,v_\lambda]$, leading to the conclusion that $\rho(\boldsymbol{r})$ is an eigendensity for the kth excited state of the N-electron system with external potential $d_\lambda(\boldsymbol{r})$. Similarly, from Theorem 3, we conclude that because $F[\Psi_{k,\lambda}^G[\rho]]$ is ρ_1 stationary with respect to variations about $\Psi_{k,\lambda}^G[\rho]$, $\rho(\boldsymbol{r})$ is an eigendensity for the kth excited state of the N-electron sys-

tem with external potential $d_\lambda(\boldsymbol{r})$. This establishes the following:

Theorem 6. The Görling functional $F_\nu^G[\rho]$ is equivalent to the restriction of the Levy-Nagy functional $F_k^{LN}[\rho, w]$ to external potentials for which it is stationary with respect to further variation.

From the reverse perspective, the Levy-Nagy functional can be viewed as a generalization of the Görling functional. Samal and Harbola [51] already observed that the Levy-Nagy functional is a generalization of the Görling functional. Their argument is based on the version of the Levy-Nagy functional that employs the ground-state electron density, $F_k^{LN}[\rho, \rho_{gs}]$ [51].

One advantage of the Levy-Nagy functional [17,18] is that because of its explicit dependence on the external potential, one can avoid consideration of generalized external potentials. As is clear from Theorem 3, however, there is no way to avoid considering generalized external potentials in the analysis of the Görling formulation [16]. One disadvantage of the Levy-Nagy formulation is that it may be difficult to design approximate functionals for which $F_k[\rho, v]$ is stationary.

For the ground state, $k=0$, the Hohenberg-Kohn theorem [61] indicates that for any given electron density $\rho(\boldsymbol{r})$, there is at most one external potential $v(\boldsymbol{r})$. It is not known whether the corresponding result for excited states is true. To account for the possibility that there may be more than one external potential with the same kth-excited-state eigendensity, we label the external potentials for which $F_k^{LN}[\rho, v]$ with the additional index λ, which labels "which external potential" we are referring to. We can show, however, the following:

Theorem 7. If $\rho(\boldsymbol{r})$ is the kth-excited-state eigendensity for two external potentials $v_1(\boldsymbol{r})$ and $v_2(\boldsymbol{r})$, then the distance between the external potentials is greater than zero. This implies that the external potentials for which $\rho(\boldsymbol{r})$ is the kth-excited-state density are isolated points in the space of all permissible external potentials.

Proof. Suppose this was not the case. Then for some external potential $v_1(\boldsymbol{r})$, there would exist a small perturbation, $\Delta v(\boldsymbol{r}) = v_2(\boldsymbol{r}) - v_1(\boldsymbol{r})$, which did not change the electron density to any order. Writing the change in wave function due to $\Delta v(\boldsymbol{r})$ as a perturbation series, where $\Delta \Psi^{(k)}$ is proportional to the size of the perturbation to the kth power, we have

$$
\begin{aligned}
0 &= \Delta\rho(\boldsymbol{r}) \\
&= \frac{\langle \Psi[v_1, N] + \Delta\Psi^{(1)} + \Delta\Psi^{(2)} + \cdots | \hat{\rho}(\boldsymbol{r}) | \Psi[v_1, N] + \Delta\Psi^{(1)} + \Delta\Psi^{(2)} + \cdots \rangle}{\langle \Psi[v_1, N] + \Delta\Psi^{(1)} + \Delta\Psi^{(2)} + \cdots | \Psi[v_1, N] + \Delta\Psi^{(1)} + \Delta\Psi^{(2)} + \cdots \rangle} - \langle \Psi[v_1, N] | \hat{\rho}(\boldsymbol{r}) | \Psi[v_1, N] \rangle \\
&= 2\,\mathrm{Re}(\langle \Delta\Psi^{(1)} | \hat{\rho}(\boldsymbol{r}) | \Psi[v_1, N] \rangle) + \langle \Delta\Psi^{(1)} | \hat{\rho}(\boldsymbol{r}) | \Delta\Psi^{(1)} \rangle + \langle \Delta\Psi^{(2)} | \hat{\rho}(\boldsymbol{r}) | \Psi[v_1, N] \rangle \\
&\quad - (\langle \Delta\Psi^{(1)} | \Delta\Psi^{(1)} \rangle + 2\,\mathrm{Re}(\langle \Delta\Psi^{(2)} | \Psi[v_1, N] \rangle)) \langle \Psi[v_1, N] | \hat{\rho}(\boldsymbol{r}) | \Psi[v_1, N] \rangle + \cdots,
\end{aligned}
\tag{49}
$$

from which it is clear that the requirement that the electron density do not change imposes extremely restrictive constraints on the nature of the perturbation $\Delta v(\boldsymbol{r})$. Let us suppose, however, that these constraints were satisfied for some perturbation. Then, in general, they would not be satisfied when the size of the perturbation was halved, as the delicate cancellation of terms would no longer occur. From this general type of argument, we deduce that given two external potentials with the same kth-excited-state density, there will be no constant-density path connecting the two external potentials. The absence of such a path, however, indicates that every external potential with a given kth-excited-state density $\rho(\boldsymbol{r})$ is isolated in the space of permissible external potentials. ∎

Theorem 7 is important because any set of isolated points in a separable function space is necessarily countable. That is, if the external potentials under consideration has a countable dense set, then Theorem 7 indicates that the number of external potentials that share a given kth-excited-state density will always be countable, allowing us to choose the indices labeling these external potentials as integers. As a consequence, the state index for the Görling functional $F_\nu^G[\rho]$ could be chosen to be integers.

Unfortunately, the spaces of external potentials usually considered, e.g., $\mathbb{L}^{3/2}(\mathbb{R}^3) + \mathbb{L}^\infty(\mathbb{R}^3)$, are not separable because $\mathbb{L}^\infty(\mathbb{R}^3)$ has no countable dense subset. However, if we restrict ourselves to the type of external potentials considered further in Sec. IV [e.g., external potentials that can be written as a sum of a function in $\mathbb{L}^{3/2}(\mathbb{R}^3)$ and a bounded and continuous function], then the set of external potentials will have a countable dense set.

A recent computational study by Gaudoin and Burke [62,63] (and later work by Samal and co-workers [51,64]) suggests that the first Hohenberg-Kohn theorem cannot be extended to excited states. In particular, these studies provide strong numerical evidence that it is possible for the same electron density $\rho_k(\boldsymbol{r})$ to be the kth-excited-state density for several external potentials [62]. These studies are suggestive and plausible but not decisive [65]. The essential problem is that the density-potential mapping is very ill conditioned: giant changes in potential can give rise to tiny change in density. (This is true even for ground states.) Because of this, it is impossible to provide decisive numerical evidence for the absence of the excited-state Hohenberg-Kohn theorem. (Mathematically, the problem is that the spectrum of the linear response kernel has an accumulation point at zero, and so

its inverse has an infinite number of arbitrarily large eigen-values. These eigenvalues befuddle numerical applications [66,67].) Still, the result of Gaudoin and Burke [62,63] is enough to suggest that there is no way to reduce the Görling functional to a single index form. So it is generally impossible to choose the label ν in $F_\nu^G[\rho]$ to be equal to the excitation level.

D. Legendre-transform functional to excited states

For the ground state, the Legendre-transform functional [19,20,68–71],

$$F^{\text{Leg}}[\rho] = \underbrace{\sup}_{v(r)} E[v;N] - \int \rho(r)v(r)dr, \qquad (50)$$

provides an alternative to the constrained-search formalism. The Legendre-transform functional in Eq. (50) originates with Lieb [19]. (Though many other researchers had discussed the DFT from a Legendre-transform perspective, by and large they did not consider the Legendre transform as an alternative to the constrained search [68–71].)

Based on the similarity of $F_\nu^G[\rho]$ and $F_k^{LN}[\rho,v]$ to the Levy ground-state constrained-search density functional, we expect that there is also a Legendre-transform functional for excited states. To this end, we have the following:

Theorem 8. Suppose the kth excited state of the system with external potential $v(r)$ is g-fold degenerate. If $\rho_k(r)$ is one of the eigendensities of this state, then

$$\Gamma_k[\rho_k,v] \equiv E_k[v,N] - \int \rho_k(r)v(r)dr \qquad (51)$$

is stationary with respect to a space of variations in the external potential, $\mathbb{V}_k[v]$, with codimension $\frac{g(g+1)}{2}-1$. The converse is also true.

Proof. Suppose that $\rho_k(r)$ is an eigendensity for a g-fold degenerate state with external potential $v(r)$. Denote a set of degenerate eigenfunctions spanning the degenerate subspace of the kth excited state with $\{\psi_i\}_{i=1}^g$. Changes in external potential, $\delta v(r)$, have two effects. First of all, changes in external potential will split the degeneracy if the eigenvalues of the perturbation matrix,

$$V_{mn} \equiv \langle \psi_m | \sum_{i=1}^N \delta v(r_i) | \psi_n \rangle, \qquad (52)$$

are not all identical. Equivalently we have that the energy shift $\Delta[\delta v(r)]$ is independent of the coefficients $\{k_n\}_{n=1}^g$ of the degenerate basis functions:

$$\Delta[\delta v(r)] = \left\langle \sum_{n=1}^g k_m \psi_m \left| \sum_{i=1}^N \delta v(r_i) \right| \sum_{n=1}^g k_n \psi_n \right\rangle. \qquad (53)$$

Defining the transition densities according to

$$\rho_{mn}(r) = \langle \psi_m | \sum_{i=1}^N \delta(r_i - r) | \psi_n \rangle = [\rho_{nm}(r)]^*, \qquad (54)$$

the condition in Eq. (53) can be re-expressed as

$$\Delta[\delta v(r)] = \sum_{m=1}^g \sum_{n=1}^g k_m k_n \int \rho_{mn}(r)\delta v(r)dr. \qquad (55)$$

$\Delta[\delta v(r)]=0$ for all choices of $\{k_m\}_{m=1}^g$ if and only if

$$\int \rho_{mn}(r)\delta v(r)dr = 0 \qquad (56)$$

for all $1 \leq m, n \leq g$. Equation (56) defines $\frac{g(g+1)}{2}$ constraints. One constraint can be relaxed because it is not necessary that $\Delta[\delta v(r)]=0$: $\Delta[\delta v(r)]$ can be any number, as long as that number is independent of the particular choice of the coefficients $\{k_m\}_{m=1}^g$. That is, one can choose one of the integrals $\int \rho_{mm}(r)\delta v(r)dr$ to have any value one likes, but then one must have that

$$\int \rho_{nn}(r)\delta v(r)dr = \int \rho_{mm}(r)\delta v(r)dr \qquad (57)$$

and

$$\int \rho_{ij}(r)\delta v(r)dr = 0, \quad 0 \leq i < j \leq g, \qquad (58)$$

or otherwise the degeneracy will be lifted [72]. These constraints define $\frac{g(g+1)}{2}-1$ hyperplanes in the space of external potentials, and so there is a subspace of external potentials, $\mathbb{V}_k[v]$, with codimension $\frac{g(g+1)}{2}-1$, such that any external potential in this space will preserve the level of the degeneracy. For any $\delta v(r) \in \mathbb{V}_k[v]$, we have that

$$E_k[v + \delta v;N] - E_k[v] = \int \rho_k(r)\delta v(r)dr, \qquad (59)$$

where $\rho_k(r)$ is the electron density of *any* of the degenerate eigenstates. From Eq. (59) we deduce that $\Gamma_k[\rho_k,v]$, as defined in Eq. (51), is stationary with respect to changes in external potential in a space with codimension $\frac{g(g+1)}{2}-1$, as asserted in the theorem.

To prove the converse, note that if $\tilde{\rho}(r)$ is not an eigendensity for the kth excited state of this system, then

$$E_k[v + \delta v;N] - E_k[v] - \int \rho_k(r)\delta v(r)dr$$

$$= \int [\rho_k(r) - \tilde{\rho}(r)]\delta v(r)dr, \qquad (60)$$

where $\rho_k(r)$ is any eigendensity of this system and $\delta v(r) \in V_k[v]$. In order for $\Gamma_k[\rho,v]$ to be stationary, then we must have that

$$\int [\rho_k(r) - \tilde{\rho}(r)]\delta v(r)dr = 0 \qquad (61)$$

when $\rho_k(r)$ is any degenerate state of the system. This, however, requires that Eqs. (57), (58), and (61) be satisfied, which defines a subspace with codimension $\frac{g(g+1)}{2}$, which is smaller than the subspace we asserted in Theorem 8. $\Gamma_k[\rho,v]$ can only be stationary with respect to a subspace with codimension $\frac{g(g+1)}{2}-1$ if $\tilde{\rho}(r)$ is one of the kth-excited-state

eigendensities. Otherwise there exists a choice of $\delta v(r)$ $\in \mathbb{V}_k$ for which Eq. (61) is untrue. ∎

$\Gamma_k[\rho,v]$ is related to the Levy-Nagy excited-state functional insofar as it is a bifunctional, and depends on both the electron density and the external potential. We can also derive a pure density functional for excited states, which is related to the Görling functional in the same way that the Legendre-transform functional is related to constrained-search functional for ground states. Namely, we have the following:

Theorem 9. Define

$$\Gamma_k^\lambda[\rho] \equiv \underbrace{\mathrm{stat}}_{d(r)}\, E_k[d;N] - \int \rho(r)d(r)dr, \qquad (62)$$

where $d(r)$ is any distribution and λ labels the distributions for which Eq. (62) is stationary. It is understood that by stationary, we imply only that $E_k[d,N] - \int \rho(r)d(r)dr$ is stationary with respect to a set of variations with codimension $\frac{g(g+1)}{2} - 1$ for some positive integer g. Then

$$E_v^{(k,\lambda)}[\rho] = \Gamma_k^\lambda[\rho] + \int \rho(r)v(r)dr \qquad (63)$$

is stationary if and only if $\rho(r)$ is an eigendensity of the kth excited state of the system with external potential $v(r)$.

Before proving Theorem 9, we should mention that since distributions are not included in the space of potentials under consideration, finding a stationary subspace of the allowable potentials is somewhat complicated. Just as the Legendre functional for ground states uses a generalized maximum principle over the external potentials, the supremum [cf. Eq. (50)] does so also. We can define the excited-state functional in terms of a generalized stationary principle over a subspace of external potentials with codimension $\frac{g(g+1)}{2} - 1$,

$$\Gamma_k^\lambda[\rho] \equiv \underbrace{\mathrm{gstat}}_{v(r) \in \mathbb{V}_k}\, E_k[v;N] - \int \rho(r)v(r)dr. \qquad (64)$$

We say that a functional has a generalized stationary point if there is a nonconvergent sequence of potentials $v_\mu(r)$ for which the size of the variation in the functional with respect to $v_\mu(r)$ nonetheless, approaches zero as $\mu \to \infty$. For the ground state, one obtains a supremum in this fashion, but for an excited state one encounters true generalized stationary points. The mathematically precise statement of the theorem using Eq. (64) is related to the conceptually simpler Eq. (62) by recognizing that

$$d(r) = \underbrace{\lim}_{\mu \to \infty} v_\mu(r)$$

is, in general, a generalized function.

To demonstrate the concept, recall that supremum of $f(x) = \tanh(x)$ for $x \in \mathbb{R}$ is 1, corresponding to $x \to \infty$. The generalized stationary point is a similar concept: the generalized stationary point of $g(x,y) = (y-1)^2 + \tanh(x)$ for

$(x,y) \in \mathbb{R}^2$ is 1, corresponding to $y = 1$ and $x \to \infty$. Neither $f(x)$ nor $g(x,y)$ has any "true" maxima or stationary points, however.

To prove Theorem 9, let $\rho(r)$ be a density associated with the kth-excited-state density of the external potential $w(r)$; $w(r)$ might be a generalized function. Then, from Theorem 9 and the definition of $\Gamma_k^\lambda[\rho]$ [cf. Eq. (62)], there exists some λ for which $\Gamma_k^\lambda[\rho] = \Gamma_k[\rho,w]$. Substitution of the definition of $\Gamma_k[\rho,w]$ [Eq. (51)] into variational energy expression [Eq. (63)] then gives

$$E_v^{(k,\lambda)}[\rho] = E_k[w,N] - \int \rho(r)[w(r) - v(r)]dr. \qquad (65)$$

Consider a small change in the electron density, from $\rho(r)$ to $\rho(r) + \delta\rho(r)$. We assume that this new electron density is the kth-excited-state density for either an external potential or a generalized function, which we denote $w(r) + \Delta(r)$ [73]. By the same argument used to derive Eq. (65),

$$E_v^{(k,\lambda)}[\rho + \delta\rho] = E_k[w + \Delta, N] - \int [\rho(r) + \delta\rho(r)][w(r) + \Delta(r) \\ - v(r)]dr. \qquad (66)$$

Subtracting Eq. (65) from Eq. (66), we have

$$E_v^{(k,\lambda)}[\rho + \delta\rho] - E_v^{(k,\lambda)}[\rho] = E_k[w + \Delta;N] - E_k[w;N] \\ - \int \delta\rho(r)\Delta(r)dr - \int \rho(r)\Delta(r)dr \\ + \int \delta\rho(r)[w(r) - v(r)]dr. \qquad (67)$$

If the kth excited state is nondegenerate then, from the Hellmann-Feynman theorem [74,75],

$$E_k[w + \Delta;N] - E_k[w;N] = \int \rho(r)\Delta(r)dr \qquad (68)$$

and so

$$E_v^{(k,\lambda)}[\rho + \delta\rho] - E_v^{(k,\lambda)}[\rho] = \int \delta\rho(r)[w(r) - v(r)]dr \\ - \int \delta\rho(r)\Delta(r)dr \qquad (69)$$

is stationary if and only if $w(r) = v(r)$. That is, the energy is stationary with respect to variations in the electron density, $\delta\rho(r)$, if and only if the electron density in question is actually the kth-excited-state density for the external potential $v(r)$.

For a degenerate ground state, the argument is slightly more complex. Upon applying the perturbation $\Delta(r)$, the degeneracy may be removed. However, $\rho(r) + \delta\rho(r)$ is actually the kth excited state of the system with external potential $w(r) + \Delta(r)$. Moreover because $\delta\rho(r)$ is small, after diagonalizing the perturbation matrix for the excited state, we must observe that the kth perturbed energy level has electron density $\rho(r)$. [For this to not be true would contradict the assumption that $\delta\rho(r)$ is an infinitesimal perturbation of the

electron density $\rho(\boldsymbol{r})$.] Consequently, first-order perturbation theory for the energy of the kth excited state gives Eq. (68), and so the change in the energy of a degenerate-state density is stationary only if the electron density is actually the kth-excited-state density for the external potential $v(\boldsymbol{r})$ entering Eq. (63). This completes the proof of Theorem 9.

The authors are aware of unpublished work by Perez-Jorda *et al.* [76], in which they considered a functional similar to that in Theorem 8 as an intermediate step in another argument.

E. Bounds on excited-state functionals

From the preceding analysis, it should be clear for any method of finding the wave functions and energies of a stationary state, there is a corresponding density functional. Thus, corresponding to the constraint minimum principle for excited states [Eq. (2)], we have the Levy-Nagy functional [Eq. (40)] [with the corresponding density-functional variational principle, Eq. (39)] and the Legendre-transform analog to the Levy-Nagy functional. The stationary principle for the wave function [Eq. (1)] is associated with the Görling functional [Eq. (22)] or, in the Legendre-transformed representation, the excited-state generalization of the Legendre-transform functional [Eqs. (51) and (62)]. The other excited-state variational principles in Sec. II [Eqs. (3)–(6)] are similarly associated with excited-state density functionals. Taking, for simplicity, the Courant [Eq. (3)] and Poincaré-Fischer-Pólya-Schiffer [Eq. (5)] forms, we have, in analogy to the Levy-Nagy functional [cf. Eq. (40)],

$$
\begin{aligned}
E_{v,k}^{C}[\rho] &= \underbrace{\max}_{\mathbb{C}_k} \underbrace{\min}_{\left\{\Psi \left| \begin{smallmatrix} \Psi \perp \mathbb{C}_k \\ \Psi \to \rho \end{smallmatrix} \right.\right\}} \left(\frac{\langle \Psi | \hat{F} | \Psi \rangle}{\langle \Psi | \Psi \rangle} + \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} \right) \\
&\equiv F_k^C[\rho] + \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r},
\end{aligned}
\tag{70}
$$

$$
\begin{aligned}
E_{v,k}^{PFPS}[\rho] &\equiv \underbrace{\min}_{\mathbb{P}_{k+1}} \underbrace{\max}_{\left\{\Psi \left| \begin{smallmatrix} \Psi \in \mathbb{P}_{k+1} \\ \Psi \to \rho \end{smallmatrix} \right.\right\}} \left(\frac{\langle \Psi | \hat{F} | \Psi \rangle}{\langle \Psi | \Psi \rangle} + \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} \right) \\
&\equiv F_k^{PFPS}[\rho] + \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r}.
\end{aligned}
\tag{71}
$$

Lieb [27] constructed analogs to these functionals for the external potential search. Note that since the subspace in the Poincaré-Fischer-Pólya-Schiffer (PFPS) variational principle is not infinite dimensional, there are only a very limited number of subspaces, $\mathbb{P}_{k+1}$, for which there exists a $\psi \in \mathbb{P}_{k+1}$ that satisfies the density constraint $\langle \Psi | \hat{\rho}(\boldsymbol{r}) | \Psi \rangle = \rho(\boldsymbol{r})$.

Unlike the Levy-Nagy functional, $F_k^C[\rho]$ and $F_k^{PFPS}[\rho]$ are universal functionals of the density, with no dependence on the external potential. In addition, the index on which the functionals depend is merely the excitation level k, which is an advantage over the Görling functional and its Legendre transform [Eq. (62)]. Unfortunately, and also unlike the aforementioned alternatives, $F_k^C[\rho]$ and $F_k^{PFPS}[\rho]$ are *not* ex-

act density functionals for the electronic energy. This is because the Courant and PFPS variational principles feature nested extrema in opposing directions.

Following the discussion of Lieb [27], we recognize that Eqs. (70) and (71) provide useful bounds for the exact density functional. In particular, for any trial density $\rho(\boldsymbol{r})$,

$$
E_{v,k}^{PFPS}[\rho] \le E_{v,k}^{LN}[\rho] \le E_{v,k}^{C}[\rho].
\tag{72}
$$

For the exact density of the kth excited state, the Levy-Nagy functional is exact and the PFPS and Courant functionals are lower and upper bounds to the exact energy, respectively.

To deduce the lower bound, pick $\mathbb{P}_{k+1}$ to include (i) the minimizing wave function from the ground-state constrained wave function search [Eq. (8)] and (ii) k other wave functions chosen such that the only wave function in $\mathbb{P}_{k+1}$ with the requisite electron density is $\Psi^{Levy}[\rho] = \Psi_{k=0}^{LN}[\rho, v]$. (This is an optimal choice for $\mathbb{P}_{k+1}$.) Hence

$$
E_{v,k}^{PFPS}[\rho] = E_v^{Levy}[\rho] = E_{v,k=0}^{LN}[\rho] \le E_{v,k}^{LN}[\rho],
\tag{73}
$$

and the lower bound is exact only when the ground-state Levy-constrained search is exact for the excited state, as discussed in Sec. III A.

To deduce the upper bound, suppose that the kth excited state has a certain symmetry $\mathcal{G}$. Also suppose that the electron density of interest, $\rho(\boldsymbol{r})$, is consistent with this symmetry requirement. Hence the constrained search need only proceed over wave functions with appropriate symmetry [77]. Suppose that among the k lowest eigenfunctions of the system, $l \le k$ have this symmetry. Choose the "trial" space $\widetilde{\mathbb{C}}_k$ to consist of (i) the eigenfunctions with symmetry $\mathcal{G}$, and (ii) if $l < k$, then also the minimizing wave function from the Levy-Nagy variational principle. Perform the inner minimization in Eq. (70) using $\widetilde{\mathbb{C}}_k$ as the k-dimensional subspace and denote the result as $\widetilde{E}_{v,k}^C[\rho]$. Then

$$
E_k[v;N] \le E_{v,k}^{LN}[\rho] \le \widetilde{E}_{v,k}^{C}[\rho] \le E_{v,k}^{C}[\rho].
\tag{74}
$$

For excited states ($k>0$), the equalities in Eqs. (73) and (74) rarely hold. Nonetheless, the Courant and PFPS bounds on the excited-state density functionals are useful theoretical tools [27].

The reader may well ask whether there is any exact excited-state density functional that satisfies a minimum principle [such as the Levy-Nagy functional; cf. Eq. (42)] but can still be written as the sum of a "universal" excited-state Hohenberg-Kohn functional $F_k^{univ}[\rho]$ and the interaction with the external potential (such as the Courant and PFPS functionals),

$$
E_k[v;N] \equiv \underbrace{\min}_{\rho(\boldsymbol{r})} \left[F_k^{univ}[\rho] + \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} \right].
\tag{75}
$$

Lieb [27] demonstrated that, because $E_k[v;N]$ is not concave with respect to $v(\boldsymbol{r})$, no functional of this form exists. Clearly, however, stationary functionals with this general form (such as the Görling functional) do exist.

IV. ON EXCITED STATES OF COULOMBIC SYSTEMS

All of the theories presented here require consideration of some quantity beyond the density, such as an index reflecting the "level of excitation." One may speculate whether one can ever construct a theory of excited states in density-functional theory that does not depend on an auxiliary variable (such as the time or external potential) or index (such as an index reflecting the level of excitation.) As is clear from the conclusion of Sec. III, in general one cannot. Specifically, there are indubitably excited-state densities that are also stationary-state densities (even ground-state densities) for other systems. This was observed by Perdew and Levy [29] in their early work, when they noted the rarity with which the constrained-search functional coincides with the excitation energy of Coulombic systems. For example, the complex square of the $2p$ wave function for hydrogen, $\psi_{2p}^*(r)\psi_{2p}(r)$, is an excited-state wave function for the hydrogen-atom external potential $[v(r) = -\frac{1}{r}]$ but is the ground-state density for $w(r) = -\frac{Z}{r} + \frac{l(l+1)}{2r^2}$, with $l=1$. Though this example is admittedly contrived (one may reasonably argue that certain highly singular potentials should be exempted from consideration), it underscores the basic problem and indicates the path to a possible solution. Find a set of external potentials, encompassing as many as possible of the external potentials of "chemical" interest, and construct a density-functional theory on this limited set of potentials. For example, the above-cited example suggests that one must exclude highly singular potentials, but we will surely have to exclude many other, otherwise reasonable, potentials also.

The first research along these lines was done by Nagy [54], who recognized that molecular systems are characterized by a very special sort of external potentials: Coulombic potentials,

$$v_{Coul}(r) \equiv \sum_{\alpha=1}^{K} \frac{-Z_\alpha}{|r_1 - R_\alpha|}, \qquad (76)$$

consisting of the electrostatic potential due to discrete point charges, $\{Z_\alpha\}$, placed at the positions $\{R_\alpha\}$. Moreover, it was recognized that the electron densities of the stationary states of these systems could be used to determine the position of the point charges and their magnitude directly, through either the conventional cusp conditions [78–80] or, in cases where there is no electron density at the position of the point charge, generalizations thereof [81–83]. Summarizing these results is the following:

Theorem 10. Let $\rho(r)$ be the electron density of a Coulombic system, that is, a system whose external potential can be written in the form of Eq. (76). Then $\rho(r)$ is not a stationary-state density for any other Coulombic external potential.

Theorem 10 is, by itself, not enough to construct an excited-state density-functional theory for Coulombic systems, because it does not exclude the possibility that two different excited states of the same system might have the same electron density. However, because the asymptotic decay of the electron density in a Coulombic system is given by [84–91]

$$\lim_{r \to \infty} \frac{\partial \ln \bar{\rho}_k(r)}{\partial r} = -\sqrt{8(E_0^{(N-1)} - E_k^{(N)})}, \qquad (77)$$

where $\bar{\rho}_k(r)$ is the spherically average density for the kth excited state of the N-electron system, $E_0^{(N-1)}$ is the ground-state energy of the $N-1$ electron system, and $E_k^{(N)}$ is the energy of the excited state of the N-electron system. Because the external potential is known from Theorem 10, and because the number of electrons N is known from direct integration of $\rho_k(r)$, we can determine the energy associated with any eigendensity of any Coulombic system directly from Eq. (77) [83]. With this information, we can then compute the Hohenberg-Kohn functional for this system directly from the definition

$$F^{Coul}[\rho] \equiv E_k[\rho] - \int \rho(r)v[\rho;r]dr. \qquad (78)$$

Equation (78) is valid for *any* stationary state of *any* system with a Coulombic external potential.

Given the potential importance of this result, it seems prudent to provide an explicit algorithm for generating Eq. (78), as the key pieces of this algorithm have been, to this point, scattered throughout the literature.

(1) To construct the external potential:

(a) Locate cusps in the electron density. These are the positions of charges, R_α.

(b) Locate places where the electron density is zero, r_0. Evaluate, using l'Hôpital's rule [81–83],

$$\lim_{r \to r_0} \frac{\rho(r)}{|r - r_0|^{2\lambda}} \qquad (79)$$

for $\lambda = 1, 2, \ldots$. If the electron density is observed to have a cusp in these locations, there is also a point charge in these positions. The $\lambda=0$ case corresponds to the usual circumstance (case a), while the $\lambda = 1, 2, \ldots$ cases correspond to excited states wherein the node of the excited-state density coincides with the nuclear position, e.g., the $2p$ state of a one-electron atom.

(c) For each charge located in steps a and b, the charge may be computed using the generalized cusp relation [81–83],

$$Z_\alpha = -\frac{\lambda_\alpha + 1}{2}\left[|r - R_\alpha|^{2\lambda_\alpha}\frac{\partial \ln\left(\frac{\bar{\rho}(r)}{|r - R_\alpha|^{2\lambda_\alpha}}\right)}{\partial|r - R_\alpha|}\right]_{|r - R_\alpha|=0}. \qquad (80)$$

The notation in this formula indicates that the derivative is to be evaluated with respect to the distance from the position of the charge, and evaluated at the position of the charge.

(d) Construct the external potential

$$v(r) \equiv \sum_{\alpha=1}^{K} -\frac{Z_\alpha}{|r - R_\alpha|}. \qquad (81)$$

(2) Determine the number of electrons by direct integration of the electron density, $N[\rho] = \int \rho(r)dr$.

(3) Determine the energy of the cation by solving the Schrödinger equation for the $N-1$ electrons confined by the external potential constructed in Eq. (81).

(4) Using Eq. (77), evaluate the energy of $\rho(\mathbf{r})$.

(5) Using Eq. (78), evaluate $F^{Coul}[\rho]$.

It is critical to emphasize that this entire analysis is predicated on the fact that the given density $\rho(\mathbf{r})$ is known to be Coulombic. Given an arbitrary density, this method will fail, since there is no known way to determine whether the given density is Coulombic without constructing the predicted external potential from step 1 of the above algorithm, solving the Schrödinger equation for this system, and then explicitly testing whether or not the given density is an eigendensity. In particular, there are many densities possessing the sorts of cusps and asymptotic decay that typify a Coulombic density that are not Coulombic. For example, given an atomic density $\rho_{atom}(\mathbf{r})$, the electron density

$$\widetilde{\rho}(\mathbf{r}) = \rho_{atom}(\mathbf{r}) + \varepsilon r^2(r^2-1)e^{-(3/2)r^2} \qquad (82)$$

[ε is any number for which $\widetilde{\rho}(\mathbf{r})$ remains positive] has the same number of electrons, the same cusps, and the same asymptotic decay as $\rho_{atom}(\mathbf{r})$. Yet the revised density is not Coulombic.

To motivate a method by which to proceed, we review the situation for the ground-state density functional. The ground-state functional is easily defined for v-representable densities, and this was the nature of the original Hohenberg-Kohn function $F^{HK}[\rho]$ [61]. To extend the ground-state functional to all N-representable densities, one can first require that exact functional be convex, which completely specifies the value of the functional for ensemble-v-representable densities, leading to usual ensemble functional $F^{ens}[\rho]$ [19,27]. As pointed out by Englisch and Englisch [37,41,42], there are still other densities that are not ensemble v representable, but the ensemble-v-representable densities for a dense subset of the set of all N-representable densities. Moreover, for any two ensemble-v-representable densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ separated by a distance $\varepsilon > 0$, there exists a $\delta(\varepsilon) > 0$ such that

$$\|\rho_1 - \rho_2\| < \delta(\varepsilon) \rightarrow |F^{ens}[\rho_1] - F^{ens}[\rho_2]| < \varepsilon. \qquad (83)$$

This suggests that we define $F[\rho]$ as the continuous extension of the ensemble functional and, because the ensemble-v-representable densities are dense, this totally and completely specifies the form of the density functional [40]. (In fact, because the Legendre-transform functional is coincident with the ensemble-v-representable functional and is also continuous, the functional that results from this procedure is just the Legendre-transform functional.) [40]

We would like to form a functional for Coulombic systems based on these ideas. We have an explicit formulation for the functional $F^{Coul}[\rho]$ for Coulombic systems; cf. Eq. (78). Indeed, as it is presently formulated, $F^{Coul}[\rho]$ is valid not only for Coulombic systems, but also for convex sums of the degenerate states of Coulombic systems, a set we may call the ensemble-Coulomb-representable densities.

The set of ensemble-Coulomb-representable densities is a dense subset of the set of all N-representable densities. To see why this is the case, consider that many (if not all) external potentials of interest can be viewed as being generated by some distribution of electric charge, $\mathcal{P}(\mathbf{r})$ [92]:

$$v(\mathbf{r}) = \int \frac{\mathcal{P}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \qquad (84)$$

We call these external potentials "generalized Coulombic potentials" to distinguish them from the special case where $\mathcal{P}(\mathbf{r}')$ is an assemblage of point charges [Eq. (76)].

Evaluating Eq. (84) using a K-point quadrature formula, we have

$$v(\mathbf{r}) = \sum_{i=1}^{K} w_i \frac{\mathcal{P}(\mathbf{r}'_i)}{|\mathbf{r}-\mathbf{r}'_i|} = \sum_{i=1}^{K} \frac{q_i}{|\mathbf{r}-\mathbf{r}'_i|}, \qquad (85)$$

where we have identified the charge q_i with $w_i\mathcal{P}(\mathbf{r}'_i)$. It follows from Eq. (85) that one may, by choosing an appropriately large value of K, approximate any generalized Coulombic potential to any desired accuracy with a system of point charges [93]. In the limit $K \rightarrow \infty$, the quadrature points in Eq. (85) become a dense subset of $\mathbb{R}^3$. (This does not contradict the assertion that the number of charges must be countable: recall, for example, that the set of all ordered pairs of rational numbers is a dense subset of $\mathbb{R}^3$, even though the set of rational numbers is countable but the set of real numbers is not.) From Eq. (85), then, we conclude that the set of Coulombic external potentials is a subset of measure zero lying dense in the space of generalized Coulombic external potentials [94].

Suppose $\rho(\mathbf{r})$ is an ensemble-v-representable density corresponding to a stationary state of the N-electron system with generalized Coulombic external potential $v(\mathbf{r})$, as per Eq. (84). Using the density of the Coulomb external potentials, we can construct a sequence of Coulomb potentials $v_k^{Coul}(\mathbf{r})$ for which

$$\lim_{k \rightarrow \infty} v_k^{Coul}(\mathbf{r}) \rightarrow v(\mathbf{r}) \qquad (86)$$

because the electron density is a continuous function of the external potential,

$$\lim_{k \rightarrow \infty} \rho[v_k^{Coul};\mathbf{r}] \rightarrow \rho(\mathbf{r}). \qquad (87)$$

[For any bound state, the electron density is a continuous functional of the external potential because the wave function is a continuous functional of the external potential. This follows, most generally, from perturbative arguments, resting on the assurance that the class of external potentials under consideration is generally nonsingular enough so that if $v(\mathbf{r})$ binds N electrons, then $v(\mathbf{r}) + \delta v(\mathbf{r})$ will also bind N electrons. In particular, it is important that the external potential be bound at infinity, as is the case for the usually considered spaces of external potentials.]

From Eq. (87), we deduce that since the ensemble-v-representable densities are dense in the set of N-representable densities, and so is the set of Coulombic densities. The only fine point that bears mention is the restriction to external potentials that satisfy Eq. (84). This space does not lie dense in the set of essentially bound functions, $\mathbb{L}^\infty(\mathbb{R}^3)$, as immediately apparent from the fact the Coulomb potentials comprise a countable dense subset of the

generalized Coulomb potentials, while there exists no countable dense subset of $\mathbb{L}^{\infty}(\mathbb{R}^3)$. The problem is that $\mathbb{L}^{\infty}(\mathbb{R}^3)$ includes a number of very irregular functions, notably functions with an uncountable number of points of discontinuity. However, the nonzero de Broglie wavelength of the electrons renders the electron density insensitive to rapid variations in external potential. Thus the "excessive roughness" of the more discontinuous functions in $\mathbb{L}^{\infty}(\mathbb{R}^3)$ has very little effect on the electron density. We deduce that the set of ensemble-v-representable densities corresponding to functions that can be written as a sum of a function in $\mathbb{L}^{3/2}(\mathbb{R}^3)$ and a not-too-discontinuous [95] function will, in fact, be a dense subset in the set of N-representable densities. Such potentials can be written either as a generalized Coulomb potential, as in Eq. (84), or as the limit of a sequence of generalized Coulomb potentials. Each generalized Coulomb potential can, in turn be written as a sequence of Coulomb potentials, as in Eq. (86). Consequently, we have the following:

Theorem 11. The set of ensemble-Coulomb-representable electron densities is a dense subset of the set of N-representable electron densities.

It follows from Theorem 11 that $F^{Coul}[\rho]$, as defined in Eq. (78), is defined on a dense subset of the set of N-representable densities. Given a density $\tilde{\rho}(\mathbf{r})$ that is not Coulombic, however, how should we define $F^{Coul}[\rho]$? Based on Theorem 11, select a sequence of ensemble-Coulombic-representable densities $\rho_k^{Coul}(\mathbf{r})$ such that

$$\lim_{k\to\infty} \rho_k^{Coul}(\mathbf{r}) \to \tilde{\rho}(\mathbf{r}). \tag{88}$$

We might then define

$$F^{Coul}[\tilde{\rho}] \equiv \lim_{k\to\infty} F^{Coul}[\rho_k^{Coul}], \tag{89}$$

which is the direct analog of the technique we used for extending the ground-state density functionals from the ensemble-v-representable densities to the full set of N-representable densities [40]. However, we can only use Eq. (89) if the limit exists. Moreover, if different choices of sequences in Eq. (88) lead to different limits, the value of $F^{Coul}[\tilde{\rho}]$ will be ambiguous. A sufficient condition for the limit in Eq. (89) to exist and be unique is that $F^{Coul}[\rho]$ be continuous on the set of Coulomb densities. That is, for any $\varepsilon > 0$, there exists a $\delta(\varepsilon) > 0$ such that if two Coulomb densities $\rho_1^{Coul}(\mathbf{r})$ and $\rho_2^{Coul}(\mathbf{r})$ satisfy

$$\|\rho_1^{Coul}(\mathbf{r}) - \rho_2^{Coul}(\mathbf{r})\| < \delta(\varepsilon), \tag{90}$$

then

$$|F^{Coul}[\rho_1^{Coul}] - F^{Coul}[\rho_2^{Coul}]| < \varepsilon. \tag{91}$$

Whether $F^{Coul}[\rho]$ is continuous is unknown. Continuity cannot be deduced directly from definition (78), because the cusp and asymptotic decay conditions only restrict the values of the electron density on sets of measure zero. This implies that given a Coulombic electron density $\rho^{Coul}(\mathbf{r})$, one can construct a density $\tilde{\rho}(\mathbf{r})$ with very different cusps and asymptotic decay which is still arbitrarily close to $\rho^{Coul}(\mathbf{r})$. The mere existence of such densities does not prove that $F^{Coul}[\rho]$ is not continuous. However, because, even if $\tilde{\rho}(\mathbf{r})$ is Coulombic, Coulombic densities with every different cusps and asymptotic decay can have similar values of $F^{Coul}[\rho]$. [For example, suppose the nuclear charges from $\tilde{\rho}(\mathbf{r})$ were much larger than those in $\rho^{Coul}(\mathbf{r})$. The large difference in the external potential term in Eq. (78) may be compensated for by a large change in the energy of the system.] Further studies of the mathematical properties of $F^{Coul}[\rho]$ are clearly warranted.

To conclude this section, we note that many of the fundamental theorems presented here have already been introduced in the context of shape-functional theory [83,96,97], wherein the fundamental variable is not the electron density, but the density per particle, $\sigma(\mathbf{r}) = \frac{\rho(\mathbf{r})}{N}$ [83,98]. Indeed, the shape function satisfies all of the preceding results: because both the cusp conditions [Eq. (80)] and the asymptotic condition [Eq. (77)] depend only on the logarithmic derivative of the density, these properties are unaffected by the number of electrons. However, the density-functional analog of these results is to be preferred. If the Hohenberg-Kohn functional for the shape function, $F^{Coul}[\sigma]$, is continuous, then the Hohenberg-Kohn functional for the electron density will also be continuous. However, the converse is not true. Insofar as practical application of these results will depend on the ability to construct good approximations to $F^{Coul}[\rho]$ or $F^{Coul}[\sigma]$, it is advisable to focus efforts, at least initially, on the density-functional, as it is more likely to be continuous.

V. SUMMARY

With the theoretical foundations made firmer through the work in this paper and the essential structure and relationships between the various functionals established, the important quest for time-independent excited-state density functionals can proceed with greater insight and, hopefully, greater success. Just as importantly, the present systematic treatment has opened several frontiers for further theoretical work, notably with regard to the Legendre-transform functionals for excited states (Sec. III D), with regards to discovered properties of the constrained-search functionals, and with regards to excited-state density functionals specifically for Coulombic systems (Sec. V). It would also be possible (and interesting) to extend these results to density matrices and many-electron distribution functions, perhaps using the recently developed generalized constrained-search and generalized Legendre-transform formulations [99–101].

One of the specific issues addressed is Lemma II of Görling [16], which he proved in his original exposition of the stationary principle for excited-state density-functional theory. From the work of Englisch and Englisch [37], it is clear that this lemma needed to be modified slightly in order to be valid in the most general context. For this purpose, Lemma II was extended to generalized external potentials (Theorem 3), which places the Görling density functional for excited states, $F_\nu^G[\rho]$, on a firm theoretical foundation. It is important to note that if one considers the results of Görling [16] to implicitly include this extension, then all his results follow.

A different constrained-search-based approach to excited states was put forth by Levy and Nagy [17,18]. Using our

result that $F_k^{LN}[\rho, w]$ is stationary with respect to variations in the external potential when $\rho(\mathbf{r})$ is a kth-excited-state density for the system (Theorem 4) allows us to deduce that the Görling functional can be viewed as a restriction of the Levy-Nagy functional to those external potentials for which it is stationary (Theorem 6). Samal and Harbola [51] also discussed the relationship between the Görling functional and the density-based Levy-Nagy functional $F_k^{LN}[\rho, \rho_{gs}]$.

One of the unanswered fundamental questions in excited-state density-functional theory is whether or not there is an excited-state Hohenberg-Kohn theorem. That is, is it possible that a single electron density can be the kth-excited-state density for two different external potentials? Numerical studies indicate that an excited-state Hohenberg-Kohn theorem is unlikely to exist [62,64], but those studies are subject to numerical ill conditioning. While we are unable to resolve this issue theoretically, Theorem 7 allows us to argue that under reasonable assumptions, the number of external potentials that share the same electron density is countable.

Theorems 8 and 9 extend the Legendre-transform formalism to excited states. While we do not fully investigate the properties of these functionals, it may be anticipated that these functionals will have formal properties that are similarly useful to their ground-state analog [19,20].

After deriving some bounds for the density functionals, we conclude by asking the following question: can we restrict the range of external potentials so that there is a functional $F[\rho]$ that is exact for both ground-state electron densities and excited-state electron densities? The analysis in Sec. IV indicates, somewhat surprisingly, that the answer is yes. Moreover, the class of external potentials, contains every molecular system and, more generally, every system whose external potential results from a finite assemblage of point charges. Since the Coulomb densities so obtained lie dense in the set of N-representable densities, one can uniquely define a universal functional $F[\rho]$ by extension of the "Coulombic" functional $F^{Coul}[\rho]$ [cf. Eq. (78)] if this functional is continuous. Establishing the continuity of the Hohenberg-Kohn functional for Coulombic systems is a priority for future work.

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