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Density-functional theory for ensembles of fractionally occupied states. I. Basic formalism

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A density-functional theory for ensembles of unequally weighted states is formulated on the basis of the generalized Rayleigh-Ritz principle of the preceding paper. From this formalism, two alternative approaches to the computation of excitation energies are derived, one equivalent to the equiensemble method proposed by Theophilou [J. Phys. C **12**, 5419 (1979)], the other grounded on an expression relating the excitation energies to the Kohn-Sham single-particle eigenvalues.

I. INTRODUCTION

Density-functional theory was originally developed[1,2] as a ground-state formalism. For excited states, a straightforward extension on the basis of the Rayleigh-Ritz principle is possible only for the lowest-energy state in each symmetry class.[3,4] A more general approach, applicable to arbitrary excited states, has been proposed by Theophilou,[5] who extended the theory to *equiensembles* of the lowest M eigenstates, equally weighted. Using a variational principle for the ensemble energy, he demonstrated that the ensemble density uniquely determines the external potential and that the correct density of a given system can be obtained by solving self-consistently a set of Kohn-Sham (KS) -like equations. The exchange-correlation functional $E_{\mathrm{xc}}^{M}[\rho]$ arising in this formalism has recently been investigated,[6] a quasilocal-density approximation for E_{xc}^{M} having been derived by identifying the equiensemble with a thermal ensemble.

In this paper, we shall develop a density-functional theory for ensembles of fractionally occupied states. In these ensembles, the M states are weighted unequally. The extended Rayleigh-Ritz principle presented in the preceding paper,[7] hereafter referred to as I, enables us to generalize Theophilou's ensemble, different weights $w_1, w_2, \ldots, w_M$ being assigned to the lowest M eigenstates. A density-functional formalism for such an ensemble, parametrized by M distinct weights, can be constructed. For practical applications, however, it is more convenient to define the weights as functions of a single, real parameter w. Thus, for example, in the case of a nondegenerate spectrum, we assign to the highest-energy state in the ensemble the weight w (i.e., choose $w_M = w$) and assign to each other state the weight $(1-w)/(M-1)$ [i.e., choose $w_1 = w_2 = \cdots = w_{M-1} = (1-w)/(M-1)$]. The condition $w_1 \geq w_2 \geq \cdots \geq w_M$, required by the variational principle in paper I, implies that $0 \leq w \leq 1/M$.

For $w = 1/M$, this definition of the weights ensures that Theophilou's formalism[5] for an equiensemble of M states be recovered, all weights being equal to $1/M$. Similarly, for $w=0$, the formalism for an equiensemble of $M-1$ states is obtained, all weights being equal to $1/(M-1)$. In these two limits, therefore, Ref. 6 provides an approximation for the exchange-correlation energy functional.

Our analysis leads to an exact expression relating the excitation energies to the KS energies. In a subsequent paper,[8] hereafter referred to as III, we shall show that, with a simple approximation, the expression for E_{xc}^{M} in Ref. 6 turns the formal relation into a practical, accurate calculational device. In this context, we shall compare our expression with Slater's transition state formula.[9] Here, however, we concentrate on deriving the exact relation.

The paper is organized as follows. Section II develops the density-functional formalism for $M=2$, i.e., for ensembles comprising only the ground state and the first excited state, both assumed nondegenerate, with weights $1-w$ and w, respectively. Section III addresses the calculation of the first excitation energy. Section IV extends the basic formalism to larger ensembles, including degenerate states. Section V discusses the calculation of the corresponding excitation energies. The density functionals considered in Secs. II–V are defined for ensemble v-representable densities; Sec. VI extends the domain of these functionals to arbitrary non-negative functions, using the constrained search formulation of Levy[10] and Lieb.[11]

II. DENSITY-FUNCTIONAL FORMALISM FOR NONDEGENERATE TWO-STATE ENSEMBLES

Consider a many-electron system with Hamiltonian

$$\hat{H} = \hat{T} + \hat{U} + \hat{V} \ , \tag{1}$$

where

$$\hat{T} = \tfrac{1}{2}\int \nabla\hat{\psi}^{\dagger}(r)\cdot\nabla\hat{\psi}(r)\,d^3r \ , \tag{2a}$$

$$\hat{U} = \tfrac{1}{2}\int\int \frac{\hat{\psi}^{\dagger}(r)\hat{\psi}^{\dagger}(r')\hat{\psi}(r')\hat{\psi}(r)}{|r-r'|}\,d^3r\,d^3r' \ , \tag{2b}$$

$$\hat{V} = \int \hat{\rho}(r)v(r)\,d^3r \ , \tag{2c}$$

and

$$\hat{\rho}(r) = \hat{\psi}^{\dagger}(r)\hat{\psi}(r) \ . \tag{2d}$$

Here, $v(r)$ denotes the external potential, and $\hat{\psi}(r)$ is the usual fermion field operator. Atomic units are used throughout this paper.

For notational convenience, the ground state,

$$\hat{H}\,|1\rangle = E_1\,|1\rangle \;,$$

and the first excited state,

$$\hat{H}\,|2\rangle = E_2\,|2\rangle \;,$$

are assumed nondegenerate. This restriction is by no means essential, however; degeneracies will be discussed in Sec. IV.

We consider the ensemble density

$$\rho(r) = (1-w)\langle 1|\hat{\rho}(r)|1\rangle + w\langle 2|\hat{\rho}(r)|2\rangle \;, \tag{3}$$

where w is any real number in the interval

$$0 \le w \le \tfrac{1}{2} \;. \tag{4}$$

The coefficients on the right-hand side of Eq. (3) ensure that

$$\int \rho(r)\,d^3r = N \;, \tag{5}$$

provided that both states, $|1\rangle$ and $|2\rangle$, contain N particles.

If now

$$\rho'(r) = (1-w)\langle 1'|\hat{\rho}(r)|1'\rangle + w\langle 2'|\hat{\rho}(r)|2'\rangle \tag{6}$$

is calculated with the ground state $|1'\rangle$ and the first excited state $|2'\rangle$ (both assumed nondegenerate) of the Hamiltonian $\hat{H}' = \hat{T} + \hat{U} + \hat{V}'$, then

$$\rho'(r) \ne \rho(r) \;,$$

provided that $\hat{V}$ and $\hat{V}'$ differ by more than a constant.

The proof of this statement follows the original argument of Hohenberg and Kohn[1] (HK). For notational brevity, we define a density matrix

$$\hat{D} = (1-w)\,|1\rangle\langle 1| + w\,|2\rangle\langle 2| \;.$$

The ensemble expectation value of any operator $\hat{A}$ is then the trace

$$\mathrm{tr}\{\hat{D}\,\hat{A}\} = (1-w)\langle 1|\,\hat{A}\,|1\rangle + w\langle 2|\,\hat{A}\,|2\rangle \;.$$

Now, consider the density matrix

$$\hat{D}' = (1-w)\,|1'\rangle\langle 1'| + w\,|2'\rangle\langle 2'| \;.$$

The variational theorem of paper I then shows that

$$\mathrm{tr}\{\hat{D}\hat{H}\} < \mathrm{tr}\{\hat{D}'\hat{H}\} \;.$$

Since $|1'\rangle$ is different from $|1\rangle$, we have a strict inequality here [this follows from part (b) of the variational principle; cf. Eq. (14) of paper I].[12]

In the trace on the right-hand side, we rewrite $\hat{H}$ as $\hat{H}' + \hat{V} - \hat{V}'$. The definition (2c) of $\hat{V}$ and the analogous definition of $\hat{V}'$ then yield

$$\mathrm{tr}\{\hat{D}\,\hat{H}\} < \mathrm{tr}\{\hat{D}'\hat{H}'\} + \int \rho'(r)[v(r) - v'(r)]\,d^3r \;. \tag{7}$$

The primed and unprimed variables interchanged, we find

$$\mathrm{tr}\{\hat{D}'\hat{H}'\} < \mathrm{tr}\{\hat{D}\,\hat{H}\} + \int \rho(r)[v'(r) - v(r)]\,d^3r \;. \tag{8}$$

By adding (7) to (8) and assuming $\rho'(r) = \rho(r)$, we are led to the contradiction

$$\mathrm{tr}\{\hat{D}'\hat{H}'\} + \mathrm{tr}\{\hat{D}\,\hat{H}\} < \mathrm{tr}\{\hat{D}\,\hat{H}\rangle + \mathrm{tr}\{\hat{D}'\hat{H}'\} \;,$$

which proves the desired statement.

For fixed w, therefore, the potential $\hat{V}'$ and hence its eigenstates $|1'\rangle$ and $|2'\rangle$ are uniquely determined by $\rho'(r)$, so that the ensemble expectation value of $\hat{T} + \hat{U}$ is a functional of the density,

$$F[w;\rho'] \equiv (1-w)\langle 1'|\,\hat{T} + \hat{U}\,|1'\rangle + w\langle 2'|\,\hat{T} + \hat{U}\,|2'\rangle \;. \tag{9}$$

It follows from the variational principle derived in paper I that the functional

$$E_v[w;\rho'] \equiv \int \rho'(r)v(r)\,d^3r + F[w;\rho'] \tag{10}$$

has the following properties:

$$E_v[w;\rho'] > (1-w)E_1 + wE_2 \quad \text{for } \rho'(r) \ne \rho(r) \tag{11a}$$

and

$$E_v[w;\rho] = (1-w)E_1 + wE_2 \;, \tag{11b}$$

where $\rho(r)$ is the ensemble density associated with $v(r)$.

In the following, the variational principle (11) will be used to generate a KS scheme. This end in mind, we define a density functional for the exchange-correlation energy by

$$E_{\mathrm{xc}}[w;\rho'] \equiv F[w;\rho'] - T_s[w;\rho'] - \tfrac{1}{2}\int\int \frac{\rho'(r)\rho'(r')}{|r-r'|}\,d^3r\,d^3r' \;, \tag{12}$$

where

$$T_s[w;\rho'] \equiv (1-w)\langle 1_s'|\,\hat{T}\,|1_s'\rangle + w\langle 2_s'|\,\hat{T}\,|2_s'\rangle \tag{13}$$

denotes the kinetic energy of a noninteracting ensemble subject to the external potential

$$\hat{V}_s' = \int v_s'(r)\hat{\rho}(r)\,d^3r \;. \tag{14}$$

This potential is chosen to make the noninteracting ensemble density equal to ρ', i.e.,

$$\rho'(r) = (1-w)\langle 1_s'|\hat{\rho}(r)|1_s'\rangle + w\langle 2_s'|\hat{\rho}(r)|2_s'\rangle \;, \tag{15}$$

where $|1_s'\rangle$ and $|2_s'\rangle$ are the ground state and the first excited state of the noninteracting system in the potential $\hat{V}_s'$. Existence of the potential, i.e., noninteracting-ensemble v representability, is assumed.

With the definition (12) of the exchange-correlation functional, the total-energy functional (10) can be written as

$$E_v[w;\rho'] = T_s[w;\rho'] + \int \rho'(r)v(r)\,d^3r + \tfrac{1}{2}\int\int \frac{\rho'(r)\rho'(r')}{|r-r'|}\,d^3r\,d^3r' + E_{\mathrm{xc}}[w;\rho'] \;. \tag{16}$$

According to the HK theorem proved above, the density $\rho'(r)$ determines $v_s'(r)$ uniquely, so that a unique potential $v_s(r)$ is associated with the density $\rho(r)$ minimizing $E_v[w;\rho']$. The following analysis determines v_s.

The noninteracting N-particle functions $|1_s'\rangle$ and $|2_s'\rangle$ are Slater determinants comprising single-particle orbitals obeying the Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2+v_s'(r)]\varphi_i(r)=\varepsilon_i\varphi_i(r);\quad \varepsilon_1\le\varepsilon_2\le\cdots\ . \tag{17}$$

In terms of these orbitals, the ensemble density, Eq. (15), is given by

$$\rho'(r)=\sum_{i=1}^{N-1}|\varphi_i(r)|^2+(1-w)|\varphi_N(r)|^2 +w\,|\varphi_{N+1}(r)|^2\ . \tag{18}$$

Similarly, the noninteracting kinetic energy can be expressed as

$$T_s[w;\rho']=\sum_{i=1}^{N-1}t_i+(1-w)t_N+wt_{N+1}\ , \tag{19}$$

with

$$t_j=\int\varphi_j^*(r)(-\tfrac{1}{2}\nabla^2)\varphi_j(r)d^3r\ . \tag{20}$$

According to the variational property, Eq. (11), $E_v[w;\rho']$ must be invariant under small changes $\delta\rho$ around the correct density $\rho(r)$, i.e.,

$$\delta E_v=\delta T_s+\int\delta\rho(r)v(r)d^3r+\int\int\frac{\delta\rho(r)\rho(r')}{|r-r'|}d^3r\,d^3r' +\int\delta\rho(r)v_{\rm xc}[w;\rho](r)d^3r=0\ , \tag{21}$$

where

$$v_{\rm xc}[w;\rho](r)=\delta E_{\rm xc}[w;\rho]/\delta\rho(r)\ . \tag{22}$$

For fixed w, the change in the noninteracting kinetic energy is given by

$$\delta T_s=\sum_{j=1}^{N-1}\delta t_j+(1-w)\delta t_N+w\,\delta t_{N+1}\ ,$$

where, in view of Green's theorem,

$$\delta t_j=\int\delta\varphi_j^*(r)(-\tfrac{1}{2}\nabla^2)\varphi_j(r)d^3r +\int\delta\varphi_j(r)(-\tfrac{1}{2}\nabla^2)\varphi_j^*(r)d^3r\ .$$

Since the orbitals $\varphi_j(r)$ solve Eq. (17) for $v_s'(r)=v_s(r)$, it follows that

$$\delta t_j=\int\delta\varphi_j^*(r)[\varepsilon_j-v_s(r)]\varphi_j(r)d^3r +\int\delta\varphi_j(r)[\varepsilon_j-v_s(r)]\varphi_j^*(r)d^3r\ ,$$

and hence that

$$\delta t_j=\varepsilon_j\delta\int|\varphi_j(r)|^2d^3r-\int v_s(r)\delta|\varphi_j(r)|^2d^3r\ .$$

The φ_j being normalized, the first term on the right-hand side vanishes, so that

$$\delta t_j=-\int v_s(r)\delta|\varphi_j(r)|^2d^3r\ . \tag{23}$$

The change in the total kinetic energy is therefore

$$\delta T_s=-\int v_s(r)\delta\rho(r)d^3r\ ,$$

and Eq. (21) reduces to

$$\delta E_v=\int\delta\rho(r)\left[-v_s(r)+v(r)+\int\frac{\rho(r')}{|r-r'|}d^3r' +v_{\rm xc}[w;\rho](r)\right]d^3r=0\ , \tag{24}$$

leading to the final result

$$v_s(r)=v(r)+\int\frac{\rho(r')}{|r-r'|}d^3r'+v_{\rm xc}[w;\rho](r)\ . \tag{25}$$

With this potential, Eq. (17) becomes the usual KS equation, here to be solved self-consistently with Eq. (18).

III. CALCULATION OF THE FIRST EXCITATION ENERGY

For $M=2$, the ensemble energy, defined in analogy with Eq. (3), is

$$\mathcal{E}(w)=(1-w)E_1+wE_2\ . \tag{26}$$

If this quantity were known for $w=0$ and for some other $w\le\frac{1}{2}$, the first excitation energy could be obtained by straightforward subtraction:

$$E_2-E_1=[\mathcal{E}(w)-\mathcal{E}(0)]/w\ . \tag{27}$$

Alternatively, if $\mathcal{E}(w)$ were known for a range of w, the first excitation energy could be computed by differentiation

$$E_2-E_1=d\mathcal{E}(w)/dw\ . \tag{28}$$

The ensemble energy $\mathcal{E}(w)$ is the minimum of the functional $E_v[w;\rho']$, Eq. (16). Explicit expressions for the right-hand side of both Eqs. (27) and (28) can therefore be obtained by solving self-consistently the KS equations, w fixed, and then substituting the resulting density $\rho_w(r)$ for $\rho'(r)$ in Eq. (16).

For Eq. (28), in particular, this program leads to considerable simplification, as we now show. The single-particle energies ε_i, Eq. (17), are given by

$$\varepsilon_i=t_i+\int|\varphi_i(r)|^2v_s'(r)d^3r\ . \tag{29}$$

The noninteracting kinetic energy, Eq. (19), can therefore be expressed as

$$T_s[w;\rho']=\sum_{i=1}^{N-1}\varepsilon_i+(1-w)\varepsilon_N+w\varepsilon_{N+1} -\int\rho'(r)v_s'(r)d^3r\ . \tag{30}$$

For $\rho'=\rho_w$ and $v_s'=v_s$, one then finds, from Eq. (25),

$$
\begin{aligned}
\mathcal{E}(w)&=E_v[w;\rho_w]\\
&=\sum_{i=1}^{N-1}\varepsilon_i+(1-w)\varepsilon_N+w\varepsilon_{N+1}\\
&\quad-\tfrac{1}{2}\int\int\frac{\rho_w(r)\rho_w(r')}{|r-r'|}d^3r\,d^3r'\\
&\quad-\int\rho_w(r)v_{\mathrm{xc}}[w;\rho_w](r)d^3r+E_{\mathrm{xc}}[w;\rho_w]\;. \qquad (31)
\end{aligned}
$$

Since the derivative of $\mathcal{E}(w)$ is needed in Eq. (28), we now compute the change $\delta\mathcal{E}(w)$ resulting from a small change δw:

$$
\begin{aligned}
\delta\mathcal{E}(w)=\delta T_s[w;\rho_w]&+\int v(r)\delta\rho_w(r)d^3r\\
&+\int\int\frac{\rho_w(r')\delta\rho_w(r)}{|r-r'|}d^3r\,d^3r'\\
&+\delta E_{\mathrm{xc}}[w;\rho_w]\;. \qquad (32)
\end{aligned}
$$

The last term on the right-hand side is

$$
\delta E_{\mathrm{xc}}[w;\rho_w]=\int v_{\mathrm{xc}}[w;\rho_w]\delta\rho_w(r)d^3r+\left.\frac{\partial E_{\mathrm{xc}}[w;\rho]}{\partial w}\right|_{\rho=\rho_w}\delta w\;,
$$

where the partial derivative of E_{xc} with respect to w is to be evaluated at fixed density $\rho(r)=\rho_w(r)$.

The first term on the right-hand side of Eq. (32),

$$
\delta T_s[w;\rho_w]=\sum_{i=1}^{N}\delta t_i+w(\delta t_{N+1}-\delta t_N)+(t_{N+1}-t_N)\delta w\;,
$$

is easily evaluated from Eqs. (23) and (29):

$$
\begin{aligned}
\delta T_s[w;\rho_w]=&-\int v_s(r)\left[\sum_{i=1}^{N}\delta|\varphi_i(r)|^2+w[\delta|\varphi_{N+1}(r)|^2-\delta|\varphi_N(r)|^2]\right]d^3r\\
&-\int v_s(r)[\,|\varphi_{N+1}(r)|^2-|\varphi_N(r)|^2]\delta w\,d^3r+(\varepsilon_{N+1}-\varepsilon_N)\delta w\;.
\end{aligned}
$$

Equation (18) then shows that

$$
\delta T_s[w;\rho_w]=(\varepsilon_{N+1}-\varepsilon_N)\delta w-\int v_s(r)\delta\rho_w(r)d^3r\;. \qquad (33)
$$

With these transformations, Eq. (32) becomes

$$
\delta\mathcal{E}(w)=\left[\varepsilon_{N+1}-\varepsilon_N+\left.\frac{\partial E_{\mathrm{xc}}[w;\rho]}{\partial w}\right|_{\rho=\rho_w}\right]\delta w\;,
$$

and the right-hand side of Eq. (28) can finally be computed, yielding

$$
E_2-E_1=\varepsilon_{N+1}-\varepsilon_N+\left.\frac{\partial E_{\mathrm{xc}}[w;\rho]}{\partial w}\right|_{\rho=\rho_w}\;. \qquad (34)
$$

Were the exact exchange-correlation energy known, then, for any w in the interval $0\leq w\leq\frac{1}{2}$, Eqs. (27) and (34) would yield exactly the same excitation energy. Since in practice we must rely on approximate forms for $E_{\mathrm{xc}}[w;\rho]$, the value of E_2-E_1 resulting from Eq. (27) is different from that resulting from Eq. (34). Accordingly, considerations of calculational accuracy dictate the choice of w and of the computational formula. Since the KS eigenvalues ε_{N+1} and ε_N are associated with the same density $\rho_w(r)$, while the equiensemble energies $\mathcal{E}(w)$ and $\mathcal{E}(0)$ are associated with the different densities $\rho_w(r)$ and $\rho_0(r)$, respectively, and since the KS eigenvalues are smaller in absolute value than the ensemble energies, the difference $\varepsilon_{N+1}-\varepsilon_N$ can be computed more accurately than $\mathcal{E}(w)-\mathcal{E}(0)$. Equation (34) will therefore produce more accurate results than Eq. (27), provided that a reliable approximation for $\partial E_{\mathrm{xc}}[w;\rho]/\partial w$ be available. One simple expression for this derivative, obtained from the quasi-local-density approximation[6] for the equiensemble exchange-correlation potential, is presented in paper III. Deferring to that paper a more extensive discussion of Eq. (34) and of its relation to the formally similar Slater transition state expression[9] for the excitation energy, we turn our attention to degenerate ensembles.

IV. DENSITY-FUNCTIONAL FORMALISM FOR ARBITRARILY LARGE ENSEMBLES, INCLUDING DEGENERATE STATES

In this section we shall consider ensembles consisting of the lowest M eigenstates of the Hamiltonian $\hat{H}=\hat{T}+\hat{U}+\hat{V}$,

$$
\hat{H}\,|\,m\,\rangle=E_m\,|\,m\,\rangle\quad(m=1,2,\ldots,M)\;, \qquad (35)
$$

the energies, generally degenerate, being labeled such that

$$
E_1\leq E_2\leq\cdots\;. \qquad (36)
$$

The density matrix defining our ensemble,

$$
\hat{D}^{M,g}(w)=\sum_{m=1}^{M}w_m\,|\,m\,\rangle\langle\,m\,|\;, \qquad (37)
$$

is characterized by three parameters, M, g, and w, which enter the occupation numbers w_m as follows:

$$
w_1=w_2=\cdots=w_{M-g}\equiv\frac{1-wg}{M-g} \qquad (38a)
$$

and

$$
w_{M-g+1}=w_{M-g+2}=\cdots=w_M\equiv w\;. \qquad (38b)
$$

g is an integer satisfying $1 \le g \le M-1$ while w is a real parameter in the range $0 \le w \le 1/M$. The case $w=0$ corresponds to the equiensemble of $M-g$ states, $w_1 = w_2 = \cdots = w_{M-g} = 1/(M-g)$, $w_{j>M-g}=0$. The other limit, $w=1/M$, yields the equiensemble of M states: $w_1 = w_2 = \cdots = w_M = 1/M$. The parameter w thus interpolates linearly between these equiensembles. This fact becomes most evident when the density matrix (37) with occupation numbers (38) is written in the equivalent form

$$\hat{D}^{M,g}(w) = (1-wM)\left[\frac{1}{M-g}\sum_{m=1}^{M-g} |\,m\,\rangle\langle\, m\,|\right] + (wM)\left[\frac{1}{M}\sum_{m=1}^{M} |\,m\,\rangle\langle\, m\,|\right]. \tag{39}$$

Now consider the density matrix

$$\hat{D}^{M,g}(w)' = (1-wM)\left[\frac{1}{M-g}\sum_{m=1}^{M-g} |\,m'\rangle\langle m'\,|\right] + (wM)\left[\frac{1}{M}\sum_{m=1}^{M} |\,m'\rangle\langle m'\,|\right], \tag{40}$$

constructed from the lowest M eigenstates of the Hamiltonian $\hat{H}' = \hat{T} + \hat{U} + \hat{V}'$,

$$\hat{H}'\,|\,m'\rangle = E'_m\,|\,m'\rangle \quad (m=1,2,\ldots,M)\,, \tag{41}$$

with energy eigenvalues satisfying

$$E'_1 \le E'_2 \le \cdots\,. \tag{42}$$

Then, for fixed M, g, and w, the densities

$$\rho(r) = \mathrm{tr}\{\hat{D}^{M,g}(w)\hat{\rho}(r)\} \tag{43}$$

and

$$\rho'(r) = \mathrm{tr}\{\hat{D}^{M,g}(w)'\hat{\rho}(r)\} \tag{44}$$

are different,

$$\rho(r) \ne \rho'(r)\,, \tag{45}$$

provided the potentials $\hat{V}$ and $\hat{V}'$ differ by more than a constant.

To prove this statement we first establish the strict inequality

$$\sum_{m=1}^{M} w_m \langle\, m\,|\,\hat{T}+\hat{U}+\hat{V}\,|\,m\,\rangle < \sum_{m=1}^{M} w_m \langle\, m'\,|\,\hat{T}+\hat{U}+\hat{V}\,|\,m'\rangle\,, \tag{46}$$

with the occupation numbers w_m given by Eqs. (38). This relation follows from the variational principle of paper I. In order to demonstrate that (46) is in fact a *strict* inequality we assume the opposite, i.e., equality of the left-hand and right-hand expressions in (46). Then part (b) of the variational theorem of paper I implies that, for $q=M-g$ and $q=M$,

$$[\,|\,1\rangle, |\,2\rangle, \ldots, |\,r\rangle] \subset [\,|\,1'\rangle, |\,2'\rangle, \ldots, |\,q'\rangle] \subset [\,|\,1\rangle, |\,2\rangle, \ldots, |\,s\rangle]\,. \tag{47}$$

Here, $[\,|\,\psi_1\rangle, \ldots, |\,\psi_k\rangle]$ denotes the subspace spanned by the states $|\,\psi_1\rangle, \ldots, |\,\psi_k\rangle$, and the labels r and s $(r < q \le s)$ characterize the multiplet of energy E_q:

$$E_1 \le E_2 \le \cdots \le E_r < E_{r+1} = \cdots = E_q = \cdots = E_s < E_{s+1} \le E_{s+2} \le \cdots\,.$$

The relation (47) allows us to expand the states $|\,1\rangle, |\,2\rangle, \ldots, |\,r\rangle$ as

$$|\,j\,\rangle = \sum_{m=1}^{q} \alpha_{jm}\,|\,m'\rangle \quad (j=1,2,\ldots,r)\,, \tag{48}$$

and, similarly, the states $|\,1'\rangle, |\,2'\rangle, \ldots, |\,q'\rangle$ as

$$|\,k'\rangle = \sum_{j=1}^{s} \beta_{kj}\,|\,j\,\rangle \quad (k=1,2,..,q)\,. \tag{49}$$

Writing the Hamiltonian $\hat{H}'$ as $\hat{H} - (\hat{V} - \hat{V}')$, the Schrödinger equation (41) reads

$$[\hat{H} - (\hat{V} - \hat{V}')]\,|\,k'\rangle = E'_k\,|\,k'\rangle\,,$$

so that

$$(\hat{V} - \hat{V}')\,|\,k'\rangle = (\hat{H} - E'_k)\,|\,k'\rangle \quad (k=1,2,\ldots,q)\,, \tag{50}$$

Substituting the expansion (49) for $|\,k'\rangle$ on the right-hand side of Eq. (50) and employing the Schrödinger Eq. (35), we obtain

$$(\hat{V} - \hat{V}')\,|\,k'\rangle = \sum_{j=1}^{s} (E_j - E'_k)\beta_{kj}\,|\,j\,\rangle \quad (k=1,2,\ldots,q)\,.$$

Singling out the contribution of the multiplet with energy E_q, we have

$$(\hat{V} - \hat{V}')\,|\,k'\rangle = \sum_{j=1}^{r} (E_j - E'_k)\beta_{kj}\,|\,j\,\rangle + (E_q - E'_k)\sum_{j=r+1}^{s} \beta_{kj}\,|\,j\,\rangle\,,$$

which, by Eq. (49), leads to

$$\begin{aligned}(\hat{V} - \hat{V}')\,|\,k'\rangle &= \sum_{j=1}^{r} (E_j - E'_k)\beta_{kj}\,|\,j\,\rangle + (E_q - E'_k)\left[\,|\,k'\rangle - \sum_{j=1}^{r} \beta_{kj}\,|\,j\,\rangle\right] \\ &= (E_q - E'_k)\,|\,k'\rangle + \sum_{j=1}^{r} (E_j - E_q)\beta_{kj}\,|\,j\,\rangle\,.\end{aligned}$$

Finally, by Eq. (48), the states $|\,1\rangle, |\,2\rangle, \ldots, |\,r\rangle$ are reexpressed in terms of the states $|\,1'\rangle, |\,2'\rangle, \ldots, |\,q'\rangle$, so that

$$(\hat{V}-\hat{V}')\,|\,k'\rangle=\sum_{m=1}^{q}\left[\delta_{mk}(E_q-E'_k)+\sum_{j=1}^{r}(E_j-E_q)\beta_{kj}\alpha_{jm}\right]|\,m'\rangle \qquad (k=1,2,\dots,q)\;. \tag{51}$$

Equation (51) implies that the subspace $[\,|\,1'\rangle,|\,2'\rangle,\dots,|\,q'\rangle]$ is invariant under the action of the operator $(\hat{V}-\hat{V}')$. Therefore, according to a theorem of linear algebra, $(\hat{V}-\hat{V}')$ has eigenstates in $[\,|\,1'\rangle,|\,2'\rangle,\dots,|\,q'\rangle]$. This is a contradiction to $\hat{V}-\hat{V}'\neq\text{const}$, since $\hat{V}$ and $\hat{V}'$ are multiplicative operators.
tors.

This establishes the strict inequality (46), which, more compactly, is written as

$$\mathrm{tr}\{\hat{D}^{M,g}(w)\hat{H}\}<\mathrm{tr}\{\hat{D}^{M,g}(w)'\hat{H}\}\;. \tag{52}$$

A similar chain of arguments leads to

$$\mathrm{tr}\{\hat{D}^{M,g}(w)'\hat{H}'\}<\mathrm{tr}\{\hat{D}^{M,g}(w)\hat{H}'\}\;. \tag{53}$$

Based on these two inequalities, the proof of the HK statement, $\rho\neq\rho'$ for $V\neq V'+\text{const}$, proceeds exactly as in Sec. II. Thus, for fixed M, g, and w, the external potential is uniquely determined by the ensemble density.

In the case of nondegenerate systems, the potential yields a unique set of lowest eigenstates $|\,1\rangle,|\,2\rangle,\dots,|\,M\rangle$, so that the ensemble expectation value of an arbitrary operator $\hat{A}$,

$$\mathrm{tr}\{\hat{D}^{M,g}(w)\hat{A}\}=\frac{1-wg}{M-g}\sum_{m=1}^{M-g}\langle m\,|\,\hat{A}\,|\,m\rangle+w\sum_{m=M-g+1}^{M}\langle m\,|\,\hat{A}\,|\,m\rangle\;, \tag{54}$$

is a unique functional of the ensemble density.

In the presence of degeneracies, the situation is more complicated. First of all, the "lowest M eigenstates" of a given Hamiltonian are determined only up to unitary transformations within the multiplets of degenerate eigenstates. The expectation value (54) therefore generally depends on the choice of the eigenstates.[13] In particular, there are in general many different densities associated with a given external potential. Conversely, however, as demonstrated above, the potential producing a given density is uniquely determined (up to within a constant). The intermediate density matrix generated by the (unique) potential to reproduce the given density, however, need not be unique; i.e., we can encounter the following situation:[14]

$$\rho(r)\rightarrow\hat{V}\rightarrow\left\{\begin{array}{l}\hat{D}=\sum_{m=1}^{M}w_m\,|\,m\rangle\langle m\,|\\[2ex] \hat{\hat{D}}=\sum_{m=1}^{M}w_m\,|\,\bar{m}\rangle\langle\bar{m}\,|\end{array}\right\}\rightarrow\rho(r)\;, \tag{55}$$

the sets of eigenstates $\{\,|\,m\rangle,m=1,2,\dots,M\}$ and $\{\,|\,\bar{m}\rangle,m=1,2,\dots,M\}$ differing by a unitary transformation within the multiplets of degenerate states. As a consequence of this, the ensemble expectation value (54) of an operator $\hat{A}$ is in general *not* a unique functional of the ensemble density.

The derivation of a variational principle for the ensemble density requires a unique and universal analog to the functional $F[w;\rho]=\mathrm{tr}\{\hat{D}(\hat{T}+\hat{U})\}$, described in Sec. II. The construction of this functional for degenerate ensembles follows the extension of the traditional HK theorem to degenerate ground states:[15] we first observe that the ensemble energy $\mathscr{E}=\sum_{m=1}^{M}w_mE_m$ is independent of the choice of eigenstates, since unitary transformations within a multiplet do not affect the energy eigenvalues. In other words, if the potential $\hat{V}$ corresponding to a given density $\rho(r)$ generates different density matrices $\hat{D}$ and $\hat{\hat{D}}$, as indicated in diagram (55), then these density matrices yield the same ensemble energy

$$\mathrm{tr}\{\hat{D}(\hat{T}+\hat{U}+\hat{V})\}=\mathrm{tr}\{\hat{\hat{D}}(\hat{T}+\hat{U}+\hat{V})\}=\mathscr{E}\;. \tag{56}$$

The value of the ensemble energy (56) is therefore fixed by the density *up to within a constant.* Consequently, the quantity

$$F^{M,g}[w;\rho]\equiv\mathscr{E}-\int\rho(r)v[\rho](r)d^3r \tag{57}$$

is a *unique* functional of the density; the ambiguity with respect to the additive constant in the external potential cancels out. The functional $F^{M,g}[w;\rho]$ may now be written as

$$F^{M,g}[w;\rho]=\mathrm{tr}\{\hat{D}^{M,g}(w)(\hat{T}+\hat{U})\}\;, \tag{58}$$

where $\hat{D}^{M,g}(w)$ is any of possibly many density matrices generated by the unique potential $\hat{V}$ that corresponds to the given density $\rho(r)$.

The variational principle of paper I then ensures that the functional

$$E_v^{M,g}[w;\rho']\equiv\int\rho'(r)v(r)d^3r+F^{M,g}[w;\rho'] \tag{59}$$

has the following properties:

$$E_v^{M,g}[w;\rho']>\frac{M-wg}{M-g}\sum_{m=1}^{M-g}E_m+w\sum_{m=M-g+1}^{M}E_m \quad \text{for } \rho'(r)\neq\rho(r) \tag{60a}$$

and

$$E_v^{M,g}[w;\rho]=\frac{M-wg}{M-g}\sum_{m=1}^{M-g}E_m+w\sum_{m=M-g+1}^{M}E_m\;, \tag{60b}$$

where $\rho(r)$ is an ensemble density associated with the potential $v(r)$. [In the presence of degeneracies, the relations (60) are valid for *any* ensemble density $\rho(r)$ corresponding to the potential $v(r)$].

Next, we shall derive a Kohn-Sham scheme. For this purpose, we define a density functional for the exchange-correlation energy as

$$E_{\mathrm{xc}}^{M,g}[w;\rho] \equiv F^{M,g}[w;\rho] - T_s^{M,g}[w;\rho] - \frac{1}{2}\int\int \frac{\rho(r)\rho(r')}{|r-r'|}d^3r\,d^3r' \; . \tag{61}$$

The noninteracting kinetic energy functional $T_s^{M,g}[w;\rho]$ is constructed as follows: given the interacting ensemble density $\rho(r)$, we postulate existence of a local single-particle potential $\hat{V}_s$ such that

$$\rho(r) = \mathrm{tr}\{\hat{D}_s^{M,g}(w)\hat{\rho}(r)\} \tag{62}$$

is satisfied with a density matrix

$$\hat{D}_s^{M,g}(w) = \frac{1-wg}{M-g}\sum_{m=1}^{M-g} |m,s\rangle\langle m,s| + w\sum_{m=M-g+1}^{M} |m,s\rangle\langle m,s| \; , \tag{63}$$

constructed from the lowest M determinantal[16] solutions $|m,s\rangle$ of the Schrödinger equation

$$(\hat{T}+\hat{V}_s)\,|m,s\rangle = E_{m,s}\,|m,s\rangle \tag{64}$$

with

$$E_{1,s} \le E_{2,s} \le E_{3,s} \le \cdots \; . \tag{65}$$

Once the *existence* of a noninteracting Hamiltonian $(\hat{T}+\hat{V}_s)$ reproducing a given interacting density $\rho(r)$ is assumed, *uniqueness* of $\hat{V}_s$ follows from the HK theorem proven above. However, as before, the intermediate density matrix generated by the (unique) potential $\hat{V}_s$ to reproduce the given density need not be unique, i.e., we can encounter the following situation

$$\rho(r) \rightarrow \hat{V}_s \rightarrow \left\{ \begin{array}{l} \hat{D}_s = \displaystyle\sum_{m=1}^{M} w_m\,|m,s\rangle\langle m,s| \\ \hat{\overline{D}}_s = \displaystyle\sum_{m=1}^{M} w_m\,|\overline{m,s}\rangle\langle \overline{m,s}| \end{array} \right\} \rightarrow \rho(r) \; , \tag{66}$$

where the sets of eigenstates $\{\,|m,s\rangle, m=1,2,\ldots,M\}$ and $\{\,|\overline{m,s}\rangle, m=1,2,\ldots,M\}$ differ by a unitary transformation within the multiplets of degenerate states.

To define a unique functional $T_s^{M,g}[w;\rho]$, we follow the construction of the functional $F^{M,g}[w;\rho]$: being invariant under unitary transformations among the eigenstates of a multiplet, the noninteracting ensemble energy $\mathcal{E}_s = \sum_{m=1}^{M} w_m E_{m,s}$ is fixed by the density up to within a constant, so that

$$T_s^{M,g}[w;\rho] \equiv \mathcal{E}_s - \int \rho(r)v_s[\rho](r)d^3r \tag{67}$$

is a unique functional of the density.

In terms of this functional and the exchange-correlation functional, Eq. (61), the total interacting ensemble energy, Eq. (59), is given by

$$E_v^{M,g}[w;\rho'] = T_s^{M,g}[w;\rho'] + \int \rho'(r)v(r)d^3r + \frac{1}{2}\int\int \frac{\rho'(r)\rho'(r')}{|r-r'|}d^3r\,d^3r' + E_{\mathrm{xc}}^{M,g}[w;\rho'] \; . \tag{68}$$

According to the variational property, Eq. (60), $E_v^{M,g}[w;\rho']$ must be invariant under small changes $\delta\rho$ around any of the correct minimizing densities $\rho(r)$ corresponding to $v(r)$, i.e.,

$$\delta E_v^{M,g} = \delta T_s^{M,g} + \int \delta\rho(r)v(r)d^3r + \int\int \frac{\delta\rho(r)\rho(r')}{|r-r'|}d^3r\,d^3r' + \int \delta\rho(r)v_{\mathrm{xc}}^{M,g}[w;\rho](r)d^3r = 0 \; , \tag{69}$$

where

$$v_{\mathrm{xc}}^{M,g}[w;\rho](r) = \delta E_{\mathrm{xc}}^{M,g}[w;\rho]/\delta\rho(r) \; . \tag{70}$$

By Eq. (67), the change in the noninteracting kinetic energy is

$$\delta T_s^{M,g} = \delta\mathcal{E}_s - \int \delta\rho(r)v_s[\rho](r)d^3r - \int \rho(r)\delta v_s(r)d^3r \; . \tag{71}$$

The variation of the noninteracting ensemble energy,

$$\delta\mathcal{E}_s = \sum_{m=1}^{M} w_m\,\delta E_{m,s} \; , \tag{72}$$

is then computed using first-order perturbation theory,

$$\delta\mathcal{E}_s = \sum_{m=1}^{M} w_m\langle m,s\,|\,\delta\hat{V}_s\,|\,m,s\rangle = \int \rho(r)\delta v_s(r)d^3r \; , \tag{73}$$

so that

$$\delta T_s^{M,g} = -\int \delta\rho(r)v_s[\rho](r)d^3r \; . \tag{74}$$

Equation (69) then reduces to

$$\delta E_v^{M,g} = \int \delta\rho(r)\left[-v_s(r) + v(r) + \int \frac{\rho(r')}{|r-r'|}d^3r' + v_{\mathrm{xc}}^{M,g}[w;\rho](r)\right] d^3r = 0 \; , \tag{75}$$

leading to the final result

$$v_s(r) = v(r) + \int \frac{\rho(r')}{|r-r'|}d^3r' + v_{\mathrm{xc}}^{M,g}[w;\rho](r) \; . \tag{76}$$

With this potential, Eq. (64) yields a generalized KS scheme, to be solved self-consistently with the density (62), i.e.,

$$\rho(r)=\frac{1-wg}{M-g}\sum_{m=1}^{M-g}\langle m,s\,|\hat{\rho}(r)\,|\,m,s\rangle + w\sum_{m=M-g+1}^{M}\langle m,s\,|\hat{\rho}(r)\,|\,m,s\rangle\ . \tag{77}$$

V. CALCULATION OF EXCITATION ENERGIES

In this section, we shall describe the computation of excitation energies of a given interacting system with specified external potential. The corresponding energy spectrum, generally degenerate, will be divided in multiplets,

$$\hat{H}\,|\,i,k\rangle=\bar{E}_i\,|\,i,k\rangle,\quad k=1,2,\dots,g_i\ ,\qquad i=1,2,3,\dots, \tag{78}$$

an energy $\bar{E}_i$ and a degeneracy g_i associated with the ith multiplet. The labeling is chosen such that

$$\bar{E}_1<\bar{E}_2<\bar{E}_3<\cdots\ . \tag{79}$$

At this point, we have to take a definite choice for the ensemble parameters, M and g, introduced in the general formalism of the last section. Since the objective is to calculate the multiplet energies $\bar{E}_1,\bar{E}_2,\dots,$ it is most convenient to choose M and g in such a way that both the M-state and the $(M-g)$-state ensembles contain only *complete* multiplets. This guarantees a unique minimizing density for the variational principle (60) and thus a unique solution of the KS equations (cf. Ref. 13). The values to be taken for M are therefore

$$M_I\equiv\sum_{i=1}^{I}g_i\ , \tag{80}$$

where I is the total number of multiplets included in the M_I-state ensemble. Given M_I, the most natural choice for g is g_I, i.e., the degeneracy of the highest multiplet in the ensemble.[17] The parameter w in the density matrix then interpolates between the equiensembles of M_I and $(M_I-g_I)=M_{I-1}$ states:

$$\hat{D}^{\,I}(w)\equiv\hat{D}^{\,M_I,g_I}(w) =\frac{1-wg_I}{M_{I-1}}\sum_{i=1}^{I-1}\sum_{k=1}^{g_i}|\,i,k\rangle\langle i,k\,| + w\sum_{k=1}^{g_I}|\,I,k\rangle\langle I,k\,|\ . \tag{81}$$

The corresponding ensemble density is given by

$$\rho_w^I(r)=\mathrm{tr}\{\hat{D}^{\,I}(w)\hat{\rho}(r)\} =\frac{1-wg_I}{M_{I-1}}\sum_{i=1}^{I-1}\sum_{k=1}^{g_i}\langle i,k\,|\hat{\rho}(r)\,|\,i,k\rangle + w\sum_{k=1}^{g_I}\langle I,k\,|\hat{\rho}(r)\,|\,I,k\rangle\ , \tag{82}$$

and the ensemble energy amounts to

$$\mathcal{E}^I(w)=\mathrm{tr}\{\hat{D}^{\,I}(w)\hat{H}\} =\frac{1-wg_I}{M_{I-1}}(g_1\bar{E}_1+g_2\bar{E}_2+\cdots+g_{I-1}\bar{E}_{I-1}) + wg_I\bar{E}_I\ . \tag{83}$$

For nondegenerate two-state ensembles, this expression reduces to Eq. (26). We now wish to show that relations analogous to Eqs. (27) and (28), allowing us to compute excitation energies from $\mathcal{E}^I(w)$ or from $d\mathcal{E}^I(w)/dw$, respectively, can be derived from Eq. (83). To this end, we first consider the special choice $w=1/M_I$, which reduces $\mathcal{E}^I(w)$ to the equiensemble energy

$$\varepsilon^I(1/M_I)=(g_1\bar{E}_1+g_2\bar{E}_2+\cdots+g_I\bar{E}_I)/M_I\ . \tag{84}$$

This equation and its analog for $I-1$ lead to an expression for the excited-state energy $\bar{E}_I$:

$$\bar{E}_I=(M_I/g_I)[\mathcal{E}^I(1/M_I)-\mathcal{E}^{I-1}(1/M_{I-1})] + \mathcal{E}^{I-1}(1/M_{I-1})\ . \tag{85}$$

Once the lowest I equiensemble energies are calculated, therefore, the lowest I eigenvalues can be easily obtained. Equation (85), a generalization of Eq. (27), is of course implicit in Theophilou's formalism,[5] which provides formal expressions for the equiensemble energies $\varepsilon^I(1/M_I)$.

The more general approach described in Sec. III establishes an important alternative to the calculation of excitation energies. To show this, we differentiate Eq. (83) with respect to w:

$$d\mathcal{E}^I(w)/dw =g_I[\bar{E}_I-(g_1\bar{E}_1+g_2\bar{E}_2+\cdots+g_{I-1}\bar{E}_{I-1})/M_{I-1}]\ . \tag{86}$$

Noticing that the second term within the square brackets on the right-hand side is the equiensemble energy $\mathcal{E}^{I-1}(1/M_{I-1})$, and substituting Eq. (85) for the first term in the square brackets, we are led to

$$\mathcal{E}^I(1/M_I)-\mathcal{E}^{I-1}(1/M_{I-1})=(1/M_I)d\mathcal{E}^I(w)/dw\ . \tag{87}$$

This shows that if, for $i=1,2,\dots,I$, each $d\mathcal{E}^i(w)/dw\,|_{w=w_i}$ is calculated for some w_i in the interval $0\le w_i\le 1/M_i$, then the equiensemble energies $\mathcal{E}^i(1/M_i)$—reckoned from the ground-state energy $\bar{E}_1=\mathcal{E}^{I=1}(1/g_1)$—can be easily computed:

$$\mathcal{E}^I(1/M_I)-\bar{E}_1=\sum_{i=2}^{I}(1/M_i)d\mathcal{E}^i(w)/dw\,\big|_{w=w_i}\ , \tag{88}$$

and Eqs. (85) and (87) determine the excitation energies measured from the ground state:

$$\bar{E}_I-\bar{E}_1=\frac{1}{g_I}\frac{d\mathcal{E}^I(w)}{dw}\bigg|_{w=w_I}+\sum_{i=2}^{I-1}\frac{1}{M_i}\frac{d\mathcal{E}^i(w)}{dw}\bigg|_{w=w_i}\ . \tag{89}$$

This is the desired generalization of Eq. (28). If $\mathcal{E}^I(w)$ were known exactly, Eqs. (85) and (89) would yield exactly the same excitation energies. In practice, however, $\mathcal{E}^I(1/M_I)$ and $d\mathcal{E}^I(w)/dw$ can be calculated only approximately. The difference between equiensemble energies on the right-hand side of Eq. (85), a small quantity found by subtracting two large energies, introduces large relative errors. Since, as we show next, each derivative $d\mathcal{E}^i(w)/dw\,|_{w=w_i}$ can be determined with the same relative accuracy as $\mathcal{E}^i(w)$, Eq. (89) produces significantly more accurate excitation energies than Eq. (85).

Explicit expressions for $\mathcal{E}^I(w)$ and $d\mathcal{E}^I(w)/dw$ are found by evaluating the functional

$$E_v^I[w;\rho]=T_s^I[w;\rho]+\int\rho(r)v(r)d^3r+\frac{1}{2}\int\int\frac{\rho(r)\rho(r')}{|r-r'|}d^3r\,d^3r'+E_{\rm xc}^I[w;\rho] \qquad (90)$$

at the solution $\rho_w^I(r)$ of the KS equations and differentiating it with respect to w. In Eq. (90), we have introduced the abbreviations $E_v^I\equiv E_v^{M_I,g_I}$, $T_s^I\equiv T_s^{M_I,g_I}$, and $E_{\rm xc}^I\equiv E_{\rm xc}^{M_I,g_I}$.

We first compute the kinetic contribution, $T_s^I[w;\rho_w^I]$, to the ensemble energy: in terms of the N-particle functions $|m,s\rangle$ obtained from the KS equation (64), the exact ensemble density is given by

$$\rho_w^I(r)=\frac{1-wg_I}{M_{I-1}}\sum_{m=1}^{M_{I-1}}\langle m,s\,|\hat{\rho}(r)|\,m,s\rangle+w\sum_{m=M_{I-1}+1}^{M_I}\langle m,s\,|\hat{\rho}(r)|\,m,s\rangle\ . \qquad (91)$$

By assumption, the states $|m,s\rangle$ are Slater determinants (cf. Ref. 16), the single-particle orbitals being computed from

$$\left[-\frac{\nabla^2}{2}+v_s(r)\right]\varphi_j(r)=\varepsilon_j\varphi_j(r),\quad \varepsilon_1\le\varepsilon_2\le\cdots \qquad (92)$$

and Eqs. (76) and (91) in self-consistent fashion.

In terms of these orbitals, the density of the Slater determinant $|m,s\rangle$ is

$$\langle m,s\,|\hat{\rho}(r)|\,m,s\rangle=\sum_{j=1}^{\infty}f_{mj}\,|\varphi_j(r)|^2\ , \qquad (93)$$

where $f_{mj}=0$ or 1 denotes the occupation number of orbital $\varphi_j(r)$ in the N-particle state $|m,s\rangle$. Similarly, the noninteracting N-particle energies are given by

$$E_{m,s}=\sum_{j=1}^{\infty}f_{mj}\varepsilon_j\ . \qquad (94)$$

This allows us to rewrite the total density, Eq. (91), and the kinetic energy, Eq. (67), in terms of the single-particle orbitals as

$$\rho_w^I(r)=\sum_{j=1}^{\infty}\left[\frac{1-wg_I}{M_{I-1}}a_j+wb_j\right]|\varphi_j(r)|^2 \qquad (95)$$

and

$$T_s^I[w;\rho_w^I]=\sum_{j=1}^{\infty}\left[\frac{1-wg_I}{M_{I-1}}a_j+wb_j\right]\varepsilon_j-\int\rho_w^I(r)v_s(r)d^3r\ , \qquad (96)$$

with

$$a_j=\sum_{m=1}^{M_{I-1}}f_{mj} \qquad (97)$$

and

$$b_j=\sum_{m=M_{I-1}+1}^{M_I}f_{mj}\ . \qquad (98)$$

Next, we insert Eq. (96), along with the definition of $v_s(r)$, Eq. (76), in Eq. (90), to find

$$\mathcal{E}^I(w)=\sum_{j=1}^{\infty}\left[\frac{1-wg_I}{M_{I-1}}a_j+wb_j\right]\varepsilon_j-\frac{1}{2}\int\int\frac{\rho_w^I(r)\rho_w^I(r')}{|r-r'|}d^3r\,d^3r'-\int\rho_w^I(r)v_{\rm xc}^I[w;\rho_w^I](r)d^3r+E_{\rm xc}^I[w;\rho_w^I]\ . \qquad (99)$$

For nondegenerate two-state ensembles, this expression reduces to Eq. (31). The analysis leading to Eq. (34) finally yields in the general case

$$\frac{d\mathcal{E}^I(w)}{dw}=\sum_{j=1}^{\infty}\left[b_j-\frac{g_I}{M_{I-1}}a_j\right]\varepsilon_j+\left.\frac{\partial E_{\rm xc}^I[w;\rho]}{\partial w}\right|_{\rho=\rho_w^I}\ . \qquad (100)$$

Equation (100) involves only KS single-particle states and a functional of the density. Provided that an accurate expression for $\partial E_{\rm xc}^I/\partial w$ be employed, $d\mathcal{E}^I(w)/dw$ can be computed as easily and as accurately as the equiensemble energies. To underscore this point, paper III proposes a simple approximation for $\partial E_{\rm xc}^I/\partial w$ and computes the excitation spectrum of the He atom, comparing the results of Eq. (85) with those of Eq. (100).

To conclude this section, we illustrate the computation of a particularly simple spectrum where the M_I lowest KS N-particle states correspond to excitations of *one* particle from the highest single-particle level ε_N occupied in the noninteracting ground state. The total KS energies then take the form

$$E_{m,s}=\sum_{j=1}^{N-1}\varepsilon_j+\varepsilon_{N-1+m}\quad (m=1,2,\ldots,M_I)\ , \qquad (101)$$

and the corresponding N-particle states are given by

$$|m,s\rangle=\frac{1}{\sqrt{N!}}\det\{\varphi_1,\varphi_2,\ldots,\varphi_{N-1},\varphi_{N-1+m}\}\quad (m=1,2,\ldots,M_I)\ . \qquad (102)$$

The occupation number f_{mj} for orbital φ_j in state $|m,s\rangle$ then takes the form

$$f_{mj}=\begin{cases}1, \quad 1\le j\le N-1 & \text{(103a)}\\ \delta_{j,(N-1+m)}, \quad j\ge N & \text{(103b)}\end{cases}$$

and the coefficients a_i and b_i entering the general expressions (99) and (100) for the ensemble energy and its derivative are readily computed

$$a_j=\sum_{m=1}^{M_{I-1}} f_{mj}=\begin{cases}M_{I-1}, \quad 1\le j\le N-1 & \text{(104a)}\\ 1, \quad N\le j\le N-1+M_{I-1} & \text{(104b)}\\ 0, \quad j\ge N+M_{I-1} & \text{(104c)}\end{cases}$$

$$b_j=\sum_{m=M_{I-1}+1}^{M_I} f_{mj}=\begin{cases}g_I, \quad 1\le j\le N-1 & \text{(105a)}\\ 0, \quad N\le j\le N-1+M_{I-1} & \text{(105b)}\\ 1, \quad N+M_{I-1}\le j\le N-1+M_I & \text{(105c)}\\ 0, \quad j\ge N+M_I\,. & \text{(105d)}\end{cases}$$

The ensemble density, Eq. (95), then reads

$$\rho_w^I(r)=\sum_{j=1}^{N-1}|\varphi_j(r)|^2+\frac{1-wg_I}{M_{I-1}}\sum_{j=N}^{N-1+M_{I-1}}|\varphi_j(r)|^2 +w\sum_{j=N+M_{I-1}}^{N-1+M_I}|\varphi_j(r)|^2\,, \tag{106}$$

and the ensemble energy (99) and its derivative (100) are given by

$$\mathcal{E}^I(\omega)=\sum_{j=1}^{N-1}\varepsilon_j+\frac{1-wg_I}{M_{I-1}}\sum_{j=N}^{N-1+M_{I-1}}\varepsilon_j+w\sum_{j=N+M_{I-1}}^{N-1+M_I}\varepsilon_j -\frac{1}{2}\int\int\frac{\rho_w^I(r)\rho_w^I(r')}{|r-r'|}d^3r\,d^3r' -\int\rho_w^I(r)v_{\text{xc}}^I[w;\rho_w^I](r)d^3r+E_{\text{xc}}^I[w;\rho_w^I] \tag{107}$$

and

$$\frac{d\mathcal{E}^I(w)}{dw}=\sum_{j=N+M_{I-1}}^{N-1+M_I}\varepsilon_j-\frac{g_I}{M_{I-1}}\sum_{j=N}^{N-1+M_{I-1}}\varepsilon_j +\left.\frac{\partial E_{\text{xc}}^I[w;\rho]}{\partial w}\right|_{\rho=\rho_w^I}\,. \tag{108}$$

VI. CONSTRAINED-SEARCH FORMULATION

So far, the density functionals considered were defined only for (ensemble) v-representable densities. In this section, we shall extend the domain to arbitrary non-negative functions. For the equiensemble case, a detailed mathematical analysis, including also a rigorous derivation of the Kohn-Sham scheme, has been presented by Hadjisavvas and Theophilou.[18] Here, we consider the unequally weighted ensemble defined by Eqs. (38). For fixed M, g, and w, the extension of the functional $F^{M,g}[w;\rho]$ is then defined as

$$\tilde{F}^{M,g}[w;\rho]\equiv\min_{D^{M,g}(w)\to\rho}\text{tr}\{\hat{D}^{M,g}(w)(\hat{T}+\hat{U})\}\,. \tag{109}$$

The notation $D^{M,g}(w)\to\rho$ indicates that the minimum is searched over the set of all density matrices

$$\hat{D}^{M,g}(w)=\frac{1-wg}{M-g}\sum_{m=1}^{M-g}|\phi_m\rangle\langle\phi_m| +w\sum_{m=M-g+1}^{M}|\phi_m\rangle\langle\phi_m| \tag{110}$$

(constructed from arbitrary orthonormal N-particle functions $|\phi_1\rangle, |\phi_2\rangle, \ldots, |\phi_M\rangle$) yielding the prescribed function $\rho(r)$ as expectation value of the density operator, i.e.,

$$\rho(r)=\text{tr}\{\hat{D}^{M,g}(w)\hat{\rho}(r)\}\,. \tag{111}$$

Similarly, the extension of the noninteracting kinetic energy functional is given by

$$\tilde{T}_s^{M,g}[w;\rho]\equiv\min_{D_s^{M,g}(w)\to\rho}\text{tr}\{\hat{D}_s^{M,g}(w)\hat{T}\}\,. \tag{112}$$

Here, the search is to be carried through over the set of density matrices

$$\hat{D}_s^{M,g}(w)=\frac{1-wg}{M-g}\sum_{m=1}^{M-g}|\phi_{m,s}\rangle\langle\phi_{m,s}| +w\sum_{m=M-g+1}^{M}|\phi_{m,s}\rangle\langle\phi_{m,s}| \tag{113}$$

(constructed from orthornormal Slater determinants $|\phi_{1,s}\rangle, \ldots, |\phi_{M,s}\rangle$) yielding the prescribed function $\rho(r)$ as ensemble expectation value, i.e.,

$$\rho(r)=\text{tr}\{\hat{D}_s^{M,g}(w)\hat{\rho}(r)\}\,. \tag{114}$$

In order to show that $\tilde{F}^{M,g}[w;\rho]$ and $\tilde{T}_s^{M,g}[w;\rho]$ are well defined by Eqs. (109) and (112), one has to demonstrate that, for an arbitrary non-negative function $\rho(r)$, the set of density matrices yielding $\rho(r)$ is not empty. To show this, we refer to the work of Zumbach and Maschke,[19] who constructed a complete set of Slater determinants, each with a density equal to a prescribed non-negative function $\rho(r)$. Inserting these determinants in Eqs. (110) or (113), one immediately obtains an infinite set of density matrices, each of which yields an ensemble density equal to the prescribed function $\rho(r)$.

With Eqs. (109) and (112), the extensions of the total energy functional and the exchange-correlation energy functional are given by

$$\tilde{E}_v^{M,g}[w;\rho]=\int\rho(r)v(r)d^3r+\tilde{F}^{M,g}[w;\rho] \tag{115}$$

and

$$\tilde{E}_{\mathrm{xc}}^{M,g}[w;\rho]=\tilde{F}^{M,g}[w;\rho]-\tilde{T}_s^{M,g}[w;\rho] -\tfrac{1}{2}\int\int \frac{\rho(r)\rho(r')}{|r-r'|}d^3r\,d^3r' \ . \tag{116}$$

Finally, one has to assure that the functional $\tilde{E}^{M,g}[w;\rho]$ provides a variational principle giving the same minimum as $E_v^{M,g}[w;\rho]$. This is easily demonstrated using the variational statement of paper I:

$$\frac{1-wg}{M-g}\sum_{m=1}^{M-g}E_m+w\sum_{m=M-g+1}^{M}E_m=\min_{\substack{\{|\phi_1\rangle,|\phi_2\rangle,\ldots,|\phi_M\rangle\} \\ \text{orthonormal}}}\left[\frac{1-wg}{M-g}\sum_{m=1}^{M-g}\langle\phi_m|\hat{H}|\phi_m\rangle+w\sum_{m=M-g+1}^{M}\langle\phi_m|\hat{H}|\phi_m\rangle\right], \tag{117}$$

or

$$\frac{1-wg}{M-g}\sum_{m=1}^{M-g}E_m+w\sum_{m=M-g+1}^{M}E_m =\min_{D^{M,g}(w)}\mathrm{tr}\{\hat{D}^{M,g}(w)\hat{H}\}\ ,$$

which, alternatively, can be written as

$$\frac{1-wg}{M-g}\sum_{m=1}^{M-g}E_m+w\sum_{m=M-g+1}^{M}E_m =\min_{\{\rho(r)\}}\left[\min_{D^{M,g}(w)\to\rho(r)}\mathrm{tr}\{\hat{D}^{M,g}(w)\hat{H}\}\right].$$

The definition of the Hamiltonian then enables us to write

$$\frac{1-wg}{M-g}\sum_{m=1}^{M-g}E_m+w\sum_{m=M-g+1}^{M}E_m =\min_{\{\rho(r)\}}\left[\min_{D^{M,g}(w)\to\rho(r)}\mathrm{tr}\{\hat{D}^{M,g}(w)(\hat{T}+\hat{U})\} +\int\rho(r)v(r)d^3r\right].$$

Equations (109) and (115) finally lead to

$$\frac{1-wg}{M-g}\sum_{m=1}^{M-g}E_m+w\sum_{m=M-g+1}^{M}E_m=\min_{\{\rho(r)\}}\tilde{E}_v^{M,g}[w;\rho]\ ,$$

thus proving that $\tilde{E}_v^{M,g}[w;\rho]$ and $E_v^{M,g}[w;\rho]$ have the same minimum.

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[12] To ensure a strict inequality for $w=\frac{1}{2}$, i.e., the equiensemble, it is necessary to show that the space spanned by $\{|1'\rangle,|2'\rangle\}$ is different from the space spanned by $\{|1\rangle,|2\rangle\}$. This is proved in Ref. 5.

[13] It should be noted, however, that the expectation value (54) is *uniquely* determined if both the relations $E_{M-g}<E_{M-g+1}$ and $E_M<E_{M+1}$ are satisfied. In that case, both the $(M-g)$- and the M-state ensembles contain only *fully* occupied multiplets, so that the two summations in Eq. (54) comprise only *complete* traces over the multiplets involved. Since these traces are invariant under the unitary transformations described, the expectation value (54) is unique in this case.

[14] As an example, consider a noninteracting He atom with ground-state configuration $(1s)^2$, and the degenerate excited states $(1s)(2s)$, $(1s)(2p^+)$, $(1s)(2p^0)$, and $(1s)(2p^-)$. For an equiensemble of two states, the density matrices $\hat{D}=\frac{1}{2}[\,|(1s)^2\rangle\langle(1s)^2|+|(1s)(2p^+)\rangle\langle(1s)(2p^+)|\,]$ and $\hat{\bar{D}}=\frac{1}{2}[\,|(1s)^2\rangle\langle(1s)^2|+|(1s)(2p^-)\rangle\langle(1s)(2p^-)|\,]$ lead to the densities $\rho=\frac{3}{2}\rho_{1s}+\frac{1}{2}\rho_{2p^+}$ and $\bar{\rho}=\frac{3}{2}\rho_{1s}+\frac{1}{2}\rho_{2p^-}$. Since $\rho_{2p^+}=\rho_{2p^-}$, the ensemble densities ρ and $\bar{\rho}$ are identical.

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[16] The requirement that $\rho(r)$ be representable by an ensemble of *Slater determinants* is more restrictive, in the presence of de-

generacies, than the mere assumption of noninteracting ensemble v-representability.

[17] Other choices for g are possible. The value $g \equiv M_I - g_1$, for example, yields a set of occupation numbers interpolating between the ground-state equiensemble and the M_I-state equiensemble. Our choice, $g \equiv g_I$, is motivated by numerical considerations: for this value, the finite-difference approximation introduced in paper III for the derivative $\partial E_{\mathrm{xc}}^{M,g}/\partial w$ becomes most accurate.

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