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# Variational density-functional theory for degenerate excited states

Á. Nagy[1] and M. Levy[2]
[1]Department of Theoretical Physics, University of Debrecen, H-4010 Debrecen, Hungary
[2]Department of Chemistry and Quantum Chemistry Group, Tulane University, New Orleans, Louisiana 70118

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The variational time-independent density-functional theory for an individual excited state introduced recently [M. Levy and Á. Nagy, Phys. Rev. Lett. **83**, 4361 (1999)] is extended to degenerate states.

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## I. INTRODUCTION

In a recent paper [1], one of the authors introduced a theory for excited states. It is a nonvariational theory that is based on Kato's theorem [2], and valid for a Coulomb external potential. It has the advantage that one can handle an individual excited state. In a more recent paper [3], the present authors put forth a *variational* Kohn-Sham theory for an individual excited state. Here this latter theory is enlarged to include degenerate excited states. For ground states, the original nondegenerate Hohenberg-Kohn theorem [4] was extended, through the constrained-search approach, to include degeneracies by Levy [5], who followed earlier work by Percus [6]. Recent key developments and formulations involving degeneracies and symmetries for ground states include those of Görling [7] and Nagy [8]. The nonvariational theory mentioned above was also formulated for degenerate excited states [1].

## II. VARIATIONAL DENSITY-FUNCTIONAL THEORY FOR DEGENERATE EXCITED STATES

Consider the solutions of the Schrödinger equation

$$\hat{H}|\Psi^i_\gamma\rangle = E^i|\Psi^i_\gamma\rangle \quad (\gamma=1,2,\ldots,g_i), \tag{1}$$

where $g_i$ is the degeneracy. For the sake of simplicity, only one index is used to denote the symmetry both in spin and ordinary space. The $N$-electron Hamiltonian has the form

$$\hat{H}_v = \hat{T} + \hat{V}_{ee} + \sum_{k=1}^{N} v(\mathbf{r}_k), \tag{2}$$

where $\hat{T}$, $\hat{V}_{ee}$, and $v$ are the kinetic-energy operator, the electron-electron repulsion energy operator, and the external (electron-nucleon) potential, respectively.

Instead of treating one wave function, the subspace $S_i$, spanned by a set of wave functions $\Psi^i_\gamma$, will be considered. We can define the density matrix in subspace $S_i$ as

$$\hat{D}^i = \sum_{\gamma=1}^{g_i} \eta^i_\gamma |\Psi^i_\gamma\rangle\langle\Psi^i_\gamma|, \tag{3}$$

where the weighting factors $\eta^i_\gamma$ satisfy the conditions

$$1 = \sum_{\gamma=1}^{g_i} \eta^i_\gamma \tag{4}$$

and

$$\eta^i_\gamma \geqslant 0. \tag{5}$$

In principle, any set of weighting factors $\eta^i_\gamma$ satisfying conditions (4) and (5) can be used. The subspace density is defined as

$$n_i = N \sum_{\gamma=1}^{g_i} \eta^i_\gamma \int |\Psi^i_\gamma|^2 ds_1 d\mathbf{x_2} \ldots d\mathbf{x_N}, \tag{6}$$

where $\mathbf{x}$ stands for a space-spin coordinate. The superscript $i$ in $n_i$ and the subspace density matrix denotes that they are constructed from wave functions that belong to the subspace $S_i$. One is free to select the values of the weighting factors $\eta^i_\gamma$: they only need to satisfy conditions (4) and (5). If the weighting factors $\eta^i_\gamma$ are all equal, the density has the property of transforming according to the totally symmetric irreducible representation [7,8]. So, for instance, for atoms the subspace density will be spherically symmetric. However, it is possible to select other values for the weighting factors $\eta^i_\gamma$.

This approach has the advantage that with equal weighting factors, the subspace density has the symmetry of the external potential. We emphasize that this procedure can be done for both ground and excited states.

Define the universal functional

$$F[n_i,n_0] = \min_{S\to n_i} \sum_{\gamma=1}^{g_i} \eta_\gamma \langle\Psi_\gamma|\hat{T}+\hat{V}_{ee}|\Psi_\gamma\rangle. \tag{7}$$

Using the density matrix, this can also be written as

$$F[n_i,n_0] = \min_{S\to n_i} \mathrm{tr}\{\hat{D}(\hat{T}+\hat{V}_{ee})\}, \tag{8}$$

where $n_i$ and $n_0$ are arbitrary densities. $n_0$ is a ground-subspace density, while $n_i$ is a trial excited subspace density we are considering. All the subspaces corresponding to the first $i-1$ states of a Hamiltonian $\hat{H}_v = \hat{T} + \hat{V}_{ee} + \Sigma_{k=1}^{N} v(\mathbf{r}_k)$, for which $n_0$ is the ground-state subspace density, are supposed to be orthogonal to the subspace considered. Thus the total energy of the $i$th excited state has the form

$$\begin{aligned} E_i &= \min_{S_i} \sum_{\gamma=1}^{g_i} \eta_\gamma \langle \Psi^i_\gamma | \hat{H}_v | \Psi^i_\gamma \rangle \\ &= \min_{n_i} \left\{ \min_{S_i \to n} \sum_{\gamma=1}^{g_i} \eta_\gamma \langle \Psi^i_\gamma | \hat{H} | \Psi^i_\gamma \rangle \right\} \\ &= \min_{n_i} \left\{ F[n_i, n_0] + \int n_i(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \right\}. \end{aligned} \tag{9}$$

$E_i$ can also be expressed with the density matrix:

$$E_i = \min_{S_i} \operatorname{tr}\{\hat{D}^i \hat{H}\} = \min_{n_i} \{ \min_{S_i \to n_i} \operatorname{tr}\{\hat{D}^i \hat{H}\}\}. \tag{10}$$

For purposes of approximating $F[n_i, n_0]$, let us construct the Hamiltonian

$$\hat{H}^{i,\alpha} = \hat{T} + \alpha \hat{V}_{ee} + \sum_{k=1}^{N} v^i_\alpha(\mathbf{r}_k), \tag{11}$$

where $v^i_\alpha(\mathbf{r};[n_i, n_0])$ is defined such that the subspace density $n_i$ remains independent of $\alpha$, and that makes the ground state of $\hat{H}^{i,\alpha}$ closest to $n_0$ in a least squares sense. This adiabatic connection leads to the noninteracting system, for which $\alpha = 0$.

The noninteracting Kohn-Sham Hamiltonian is defined as

$$\hat{H}^i_w = \hat{H}^{i,\alpha=0} = \hat{T} + \sum_{j=1}^{N} w^i([n_i, n_0]; \mathbf{r}_j). \tag{12}$$

Both the noninteracting Hamiltonian $\hat{H}^i_w$ and the Kohn-Sham-like potential $w^i([n_i, n_0]; \mathbf{r}) = v^i_0(\mathbf{r})$ depend on *i*. That is, they are different for different excited states. The Kohn-Sham-like equations have the form

$$\hat{H}^{i,0} | \Psi^{i,0}_\gamma \rangle = E^{i,0} | \Psi^{i,0}_\gamma \rangle \quad (\gamma = 1, 2, \ldots, g_i), \tag{13}$$

where the noninteracting density matrix can be constructed from the wave functions $\Psi^{i,0}_\gamma$ as

$$\hat{D}^i_s = \sum_{\gamma=1}^{g_i} \eta_\gamma | \Psi^{i,0}_\gamma \rangle \langle \Psi^{i,0}_\gamma |, \tag{14}$$

while the noninteracting kinetic energy has the form

$$T_s[n_i, n_0] = \operatorname{tr}\{\hat{D}^i_s \hat{T}\}. \tag{15}$$

$T_s$ can also be given variationally as

$$T_s[n_i, n_0] = \min_{S_i \to n_i} \operatorname{tr}\{\hat{D}^i \hat{T}\} = \operatorname{tr}\{\hat{D}^i_s[n_i, n_0] \hat{T}\}, \tag{16}$$

where each $S_i$ is orthogonal to all subspaces corresponding to the first $m-1$ states of $\hat{H}^i_w$, and $n_i$ is the subspace density of the $m$th excited state of $\hat{H}^i_w$. $\hat{D}^i_s[n_i, n_0]$ is that noninteracting excited-state density matrix of $\hat{H}^i_w$, whose subspace density is $n_i$. The minimum principle for noninteracting kinetic energy is

$$\begin{aligned} &T_s[n_i, n_0] + \int n_i(\mathbf{r}) w^i([n_i, n_0]; \mathbf{r}) d\mathbf{r} \\ &\quad = \min_{n_i} \left\{ T_s[n_i, n_0] + \int n_i(\mathbf{r}) w^i([n_i, n_0]; \mathbf{r}) d\mathbf{r} \right\}, \end{aligned} \tag{17}$$

leading to the Euler equation

$$w^i([n_i, n_0]; \mathbf{r}) + \left. \frac{\delta T_s[n_i, n_0]}{\delta n} \right|_{n = n_i} = \mu_i, \tag{18}$$

where $\mu_i$ is a Lagrange parameter.

The Kohn-Sham potential has the form

$$w^i(\mathbf{r}) = v(\mathbf{r}) + \left. \frac{\delta G[n_i, n_0]}{\delta n} \right|_{n = n_i}, \tag{19}$$

where the functional $G[n_i, n_0]$ is defined by the partition

$$F[n_i, n_0] = T_s[n_i, n_0] + G[n_i, n_0]. \tag{20}$$

Further, it is convenient to partition $G[n_i, n_0]$ into

$$G[n_i, n_0] = J[n_i] + E_x[n_i, n_0] + E_c[n_i, n_0], \tag{21}$$

where $J$, $E_x$, and $E_c$ are the Coulomb, exchange, and correlation components of $G$. That is,

$$J[n_i] + E_x[n_i, n_0] = \operatorname{tr}\{\hat{D}^i \hat{V}_{ee}\}, \tag{22}$$

$$E_c[n_i, n_0] = \operatorname{tr}\{\hat{D}^i \hat{V}_{ee}\} - \operatorname{tr}\{\hat{D}^i_s \hat{V}_{ee}\}. \tag{23}$$

Thus the Kohn-Sham potential has the form

$$w^i(\mathbf{r}) = v(\mathbf{r}) + v^i_J(\mathbf{r}) + v^i_{xc}(\mathbf{r}), \tag{24}$$

where $v(\mathbf{r})$, $v^i_J$, and $v^i_{xc}(\mathbf{r})$ are the external, Coulomb, and exchange-correlation potentials, respectively.

## III. KOHN-SHAM EQUATIONS FOR DEGENERATE EXCITED STATES IN SPHERICALLY SYMMETRIC SYSTEMS

The noninteracting wave functions can be constructed as a linear combination of Slater determinants. They cannot generally be given as a single Slater determinant. Now the Kohn-Sham equations can be obtained from a minimalization of the noninteracting kinetic energy after expressing it with one-electron orbitals. Because of the fact that $\Psi^{i,0}_\gamma$ is a linear combination of several Slater determinants, the form of the Kohn-Sham equations is rather complicated for an arbitrarily selected set of weighting factors $\eta_\gamma$, and have to be derived separately for each desired case. For a spherically symmetric case and equal weighting factors, however, the

Kohn-Sham equations have a very simple form, as shown in Ref. [9]. In this case the noninteracting kinetic energy is given by

$$T_s=\sum_{j=1}^{N}\lambda_j^i\int P_j^i\left[-\frac{1}{2}(P_j^i)''+\frac{l_j^i(l_j^i+1)}{2r^2}P_j^i\right]dr, \tag{25}$$

where $P_j^i$ and $\lambda_j^i$ are the radial wave functions and the occupation numbers corresponding to the given configuration, respectively. '' denotes a second derivative with respect to $r$. The radial subspace density

$$\varrho_i=\sum_{j=1}^{N}\lambda_j^i(P_j^i)^2 \tag{26}$$

in this particular case is spherically symmetric. The minimization of the noninteracting kinetic energy leads to the radial Kohn-Sham equations

$$-\frac{1}{2}(P_j^i)''+\frac{l_j(l_j+1)}{2r^2}P_j^i+w^iP_j^i=\varepsilon_j^iP_j^i. \tag{27}$$

## IV. OPTIMIZED POTENTIAL METHOD FOR DEGENERATE EXCITED STATES

The optimized potential method [10] can be applied when the total energy $E_i$ is given as a functional of the one-electron orbitals $u_k^i$. The one-electron orbitals $u_k^i$ are eigenfunctions of a local effective potential $V^i$,

$$\hat{h}^iu_k^i=(-\tfrac{1}{2}\nabla^2+V^i)u_k^i=\varepsilon_k^iu_k^i, \tag{28}$$

with $V^i$ determined by requiring that $E_i$ is minimized for all $u_k^i$ obtained from Eq. (28). This results in

$$\frac{\delta E_i}{\delta V^i}=\sum_i\int\frac{\delta E^i}{\delta u_k^{i*}(\mathbf{r}')}\frac{\delta u_k^{i*}(\mathbf{r}')}{\delta V^i(\mathbf{r})}d\mathbf{r}'+\text{c.c.}=0. \tag{29}$$

The functional derivative of the one-electron orbitals $u_k^i$ with respect to the local effective potential $V^i$ can be calculated with the help of the Green's functions

$$\frac{\delta u_k^{i*}(\mathbf{r}')}{\delta V^i(\mathbf{r})}=-G_k^i(\mathbf{r}',\mathbf{r})u_k^i(\mathbf{r}), \tag{30}$$

$$(\hat{h}^i-\varepsilon_k^i)G_k^i(\mathbf{r}',\mathbf{r})=\delta(\mathbf{r}-\mathbf{r}')-u_k^i(\mathbf{r})u_k^{i*}(\mathbf{r}'). \tag{31}$$

Using Eqs. (28)–(31), integral equations for the effective exchange-correlation potential $V_{xc}^i$ follow:

$$\int H^i(\mathbf{r},\mathbf{r}')V_{xc}^i(\mathbf{r}')d\mathbf{r}'=Q^i(\mathbf{r}), \tag{32}$$

$$H({}^i\mathbf{r},\mathbf{r}')=\sum_k u_k^{i*}(\mathbf{r})G_k^i(\mathbf{r},\mathbf{r}')u_k^i(\mathbf{r}'), \tag{33}$$

$$Q^i(\mathbf{r})=\sum_k\int d\mathbf{r}'u_k^{i*}(\mathbf{r})G_k^i(\mathbf{r},\mathbf{r}')v_{xc,k}^i(\mathbf{r}')u_k^i(\mathbf{r}'). \tag{34}$$

The orbital-dependent potential $v_{xc,k}^i$ is given by

$$v_{xc,k}^i(\mathbf{r})=\frac{\delta E_{xc}^i[u_k^i]}{u_k^i\delta u_k^{i*}}. \tag{35}$$

The effective exchange-correlation potential $V_{xc}^i$ can be determined from the effective potential $V^i$,

$$V_{xc}^i(\mathbf{r})=V^i-v-v_J^i, \tag{36}$$

where $v$ is the external potential. The classical Coulomb potential $v_J^i$ depends slightly on $i$, as the density $n^i$ is somewhat different for different excited states.

Now we turn to the exchange-only case. To obtain the effective potential $V^i$, the total energy $E^i[u_k^i]$ as a functional of the orbitals $u_k^i$ is needed. In the ground-state theory for nondegenerate states, the exchange-only total energy is given by the well-known Hartree-Fock energy expression with Kohn-Sham orbitals. However, in a degenerate case, this will not be appropriate, as we cannot approximate the wave function as a single Slater determinant. In this situation, one can proceed as follows: In case of a given electron configuration, there exist several Slater determinants: $\Phi_k^i$. Constructing appropriate linear combination of these Slater determinants, one can obtain the wave functions $\tilde{\Psi}_\gamma^i$:

$$\tilde{\Psi}_\gamma^i=\sum_j c_{\gamma,j}^i\Phi_j^i\quad(\gamma=1,2,\ldots,g_i). \tag{37}$$

The way to calculate the coefficients $c_{\gamma,j}^i$ is not detailed here as several methods (e.g., step-up and step-down operators, and projections) are available and discussed in textbooks (see, e.g., Ref. [11]).

In the nondegenerate exchange-only case, the energy is taken as the average of the total Hamiltonian $\hat{H}$ with a single Slater determinant (with Kohn-Sham orbitals, of course). Generalizing this idea, the following energy expression is now proposed for the degenerate state:

$$E^i=\langle\tilde{\Psi}_\gamma^i|\hat{H}|\tilde{\Psi}_\gamma^i\rangle. \tag{38}$$

As is well known from group theory, $E^i$ is independent of $\gamma$. Using Eq. (37), $E^i$ is a functional of the one-electron orbitals $u_j^i$:

$$E^i=E^i[u_j^i]. \tag{39}$$

For the special case of atomic multiplets, it is a functional of the radial wave functions $P_j^i$:

$$E^i=E^i[P_j^i]. \tag{40}$$

It can also be written as

$$E^i = E_{av} + \sum_m C_m^i B_m^i , \tag{41}$$

where $E_{av}$ is the average energy of the different multiplets corresponding to a given configuration. The second term in the right-hand side of Eq. (41) is responsible for the multiplet separation. The explicit form of Eq. (41) has to be given for the multiplet considered before by performing an optimized potential method (OPM) calculation. Expressions for several atomic multiplets have already been derived. For example, in the case $nsmp^3$, the energies of the multiplets have the forms [11]

$$E(^5S) = E_{av} - \tfrac{9}{25} F^2(pp) - \tfrac{1}{2} G^1(sp), \tag{42}$$

$$E(^3S) = E_{av} - \tfrac{9}{25} F^2(pp) + \tfrac{5}{6} G^1(sp), \tag{43}$$

$$E(^3D) = E_{av} - \tfrac{1}{6} G^1(sp). \tag{44}$$

$$E(^1D) = E_{av} + \tfrac{1}{2} G^1(sp). \tag{45}$$

$$E(^3P) = E_{av} + \tfrac{9}{25} F^2(pp) - \tfrac{1}{6} G^1(sp), \tag{46}$$

$$E(^1P) = E_{av} - \tfrac{6}{25} F^2(pp) + \tfrac{1}{2} G^1(sp), \tag{47}$$

where $F^2(pp)$ and $G^1(sp)$ are the Slater integrals:

$$F^2(pp) = \int \int R_p^2(r_1) R_p^2(r_2) \frac{r_<^2}{r_>^3} dr_1 dr_2 \tag{48}$$

and

$$G^1(sp) = \int \int R_s(r_1) R_p(r_2) R_p(r_1) R_s(r_2) \frac{r_<}{r_>^2} dr_1 dr_2 , \tag{49}$$

where $R_s$ and $R_p$ are the radial wave functions of the $ns$ and $mp$ electrons, respectively. $r_<$ means $r_1$ if it is smaller than $r_2$, and $r_2$ if it is smaller than $r_1$. Now, in the knowledge of total-energy expression, the OPM calculations can be performed solving Eqs. (32)–(35).

One can also obtain Hartree-Fock-like equations by taking the functional derivative of Eq. (41). For spherically symmetric systems, we obtain the radial equations

$$\left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l_j(l_j+1)}{r^2} + v + v_J^i + v_{x,j}^i + q_j^i \right) P_j^i = \varepsilon_j^i P_j^i , \tag{50}$$

where $P = rR$;

$$v_{x,j}^i(\mathbf{r}) = \frac{\delta E_{av,x}^i [P_j^i]}{P_j^i \delta P_j^{i*}} \tag{51}$$

is the Hartree-Fock exchange potential corresponding to the average of energies; and

$$q_j^i = \sum_m C_m^i \frac{1}{P_j^i} \frac{dB_m^i}{dP_j^i} \tag{52}$$

is responsible for the separation between the different multiplets. The difference between the optimized potential method for degenerate excited states and the conventional OPM is in the different form of the exchange energy. In the conventional OPM the exchange energy is the well-known Hartree-Fock exchange energy expression, with Kohn-Sham orbitals. In the optimized potential method for degenerate excited states presented here, the exchange energy is given by the second term in Eq. (41). The procedure is exactly the same in both cases.

## V. GENERALIZED KLI METHOD FOR A DEGENERATE EXCITED STATE

It is very difficult to calculate the effective potential $V^i$ because of the vast numerical problems. Krieger, Li, and Iafrate (KLI) [12] proposed an accurate approximate approach to the OPM for the ground state. Recently one of the authors [13] proposed an alternative derivation of the KLI approximation. Using this method, a generalization of the KLI approach for excited states can also be obtained.

The total radial electron subspace density $\varrho^i$ can be expressed with the radial wave functions $P_j^i$:

$$\varrho^i(r) = \sum_j \lambda_j^i (P_j^i)^2. \tag{53}$$

The functions $K_j^i$ are introduced with the following definition:

$$P_j^i = (\varrho^i / \lambda_j^i)^{1/2} K_j^i . \tag{54}$$

The functions $K_j^i$ are not all independent:

$$1 = \sum_j (K_j^i)^2. \tag{55}$$

Substituting Eq. (54) into Eq. (50), multiplying it by $K_j^i$, summing for all orbitals, and using the derivative of Eq. (55), we arrive at the equation

$$\begin{aligned} -\frac{1}{8} \left( \frac{(\varrho^i)'}{\varrho^i} \right)^2 + \frac{1}{4} \frac{(\varrho^i)''}{\varrho^i} + \sum_j \frac{l_j(l_j+1)(K_j^i)^2}{r^2} \\ + \frac{1}{2} \sum_j ((K_j^i)')^2 + v + v_J^i + v_S^i + \sum_j K_j^i (v_{x,j}^i + q_j^i) K_j^i \\ = \sum_j \varepsilon_j^i (K_j^i)^2, \end{aligned} \tag{56}$$

where $v_{x,j}^i$ is a Hartree-Fock-like exchange potential [Eq. (36)], and $v_S^i$ is the Slater potential:

$$v_S^i(\mathbf{r}) = \sum_j K_j^i v_{x,j}^i K_j^i . \tag{57}$$

The Kohn-Sham equations

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l_j(l_j+1)}{r^2}+v^i_{KS}\right)\overline{P^i_j}=\epsilon^i_j\overline{P^i_j} \qquad (58)$$

can be rewritten in a similar way. The Kohn-Sham potential has the form

$$v^i_{KS}=v+v^i_J+v^i_x+q^i, \qquad (59)$$

where $v^i_x$ is the exchange potential and $q^i$ is a potential which is responsible for the multiplet separation. Introducing functions $k^i_j$, with the definition

$$\overline{P^i_j}=(\varrho^i/\lambda^i_j)^{1/2}k^i_j, \qquad (60)$$

with $k_i$ satisfying an equation similar to Eq. (55), substituting Eq. (60) into Eq. (58), multiplying Eq. (60) by $k^i_j$, and summing for all orbitals, the Kohn-Sham equations (58) take the form

$$-\frac{1}{8}\left(\frac{(\varrho^i)'}{\varrho^i}\right)^2+\frac{1}{4}\frac{(\varrho^i)''}{\varrho^i}+\sum_j\frac{l_j(l_j+1)(k^i_j)^2}{r^2}$$
$$+\frac{1}{2}\sum_j((k^i_j)')^2+v+v^i_J+v^i_x+q^i=\sum_j\epsilon^i_j(k^i_j)^2. \qquad (61)$$

Now, comparing the Hartree-Fock- [Eq. (56)] and Kohn-Sham-type [Eq. (61)] equations in the case when both equations provide the same density, we obtain

$$v^i_x=v^i_S+\sum_j(\epsilon^i_j-\varepsilon^i_j)(k^i_j)^2-\sum_j\varepsilon^i_j((K^i_j)^2-(k^i_j)^2)$$
$$-\frac{1}{2}\sum_j[|\nabla k^i_j|^2-|\nabla K^i_j|^2]+\sum_j\frac{l_j(l_j+1)}{r^2}((k^i_j)^2$$
$$-(K^i_j)^2) \qquad (62)$$

and

$$w^i=\sum_j K^i_i q^i_j K^i_j. \qquad (63)$$

By supposing that the Hartree-Fock -like wave functions $K^i_j$ are very close to the orbitals $k^i_j$, satisfying the Kohn-Sham type equations, we obtain

$$v^i_x=v^i_S+\sum_j(\epsilon^i_j-\varepsilon^i_j)|k^i_j|^2 \qquad (64)$$

and

$$q^i=\sum_j(k^i_j)^2q^i_j=\sum_j(k^i_j)^2\sum_m C^i_m\frac{1}{P^i_j}\frac{dB^i_m}{dP^i_j}. \qquad (65)$$

Expressions (64) and (65) provide accurate approximations for the exact OPM potential in the exchange-only case.

## VI. KOOPMANS' THEOREM FOR THE EXCITED STATE

From previous studies, we know that the asymptotic decay of $n^{\alpha}_i=n_i$ is governed by $|E^{i,\alpha}-E^{i,\alpha}_{0,N-1}|$, where $E^{i,\alpha}$ is the $i$th excited-state energy of $\hat{H}^{i,\alpha}$. $E^{i,\alpha}_{0,N-1}$ on the other hand, is the ''ground-state'' energy of $\hat{H}^{i,\alpha}$ with one electron removed. As $n_i$ is independent of $\alpha$, $|E^{i,\alpha}-E^{i,\alpha}_{0,N-1}|$ is also independent of $\alpha$. Consequently,

$$\frac{\partial}{\partial\alpha}|E^{i,\alpha}-E^{i,\alpha}_{0,N-1}|_{\alpha=0}=0. \qquad (66)$$

It is supposed that we have a single excitation, and an electron from the highest occupied level is excited.

From Eqs. (11) and (66), we obtain

$$\mathrm{tr}\{\hat{D}^i_s\hat{V}_{ee}\}+\int d\mathbf{r}n_i\frac{\partial v^i_{\alpha}}{\partial\alpha}\bigg|_{\alpha=0}=\mathrm{tr}\{\hat{D}^{i,N-1}_s\hat{V}_{ee}\}$$
$$+\int d\mathbf{r}n^{N-1}_0\frac{\partial v^i_{\alpha}}{\partial\alpha}\bigg|_{\alpha=0}. \qquad (67)$$

Using Eq. (11),

$$\mathrm{tr}\{\hat{D}^i_s\hat{H}\}-\mathrm{tr}\{\hat{D}^{i,N-1}_s\hat{H}^{N-1}\}$$
$$=\mathrm{tr}\left\{\hat{D}^i_s\left(\hat{T}+\sum_{k=1}^{N}v(\mathbf{r}_k)\right)\right\}$$
$$-\mathrm{tr}\left\{\hat{D}^{i,N-1}_s\left(\hat{T}^{N-1}+\sum_{k=1}^{N-1}v(\mathbf{r}_k)\right)\right\}$$
$$+\int d\mathbf{r}n^{N-1}_0\frac{\partial v^i_{\alpha}}{\partial\alpha}\bigg|_{\alpha=0}-\int d\mathbf{r}n_i\frac{\partial v^i_{\alpha}}{\partial\alpha}\bigg|_{\alpha=0}, \qquad (68)$$

where $n^{N-1}_0$, $\hat{H}^{N-1}$, and $\hat{T}^{N-1}$ are the ground-state subspace density, the total Hamiltonian, and the kinetic-energy opera-

TABLE I. Ionization energy (in Ry) obtained from the orbital energies.

| Atom | Configuration | Generalized KLI | HF | Expt. |
|---|---|---|---|---|
| He | $1s2p\ ^3P$ | 0.270 | 0.263 | 0.266 |
| | $1s2p\ ^1P$ | 0.255 | 0.245 | 0.248 |
| Be | $[\mathrm{He}]2s2p\ ^3P$ | 0.550 | 0.483 | 0.485 |
| | $[\mathrm{He}]2s2p\ ^1P$ | 0.287 | 0.235 | 0.297 |
| Ne | $[\mathrm{He}]2p^53s\ ^3P$ | 0.357 | 0.350 | 0.361 |
| | $[\mathrm{He}]2p^53s\ ^1P$ | 0.346 | 0.337 | 0.349 |
| Mg | $[\mathrm{Ne}]3s3p\ ^3P$ | 0.405 | 0.359 | 0.363 |
| | $[\mathrm{Ne}]3s3p\ ^1\mathrm{P}$ | 0.235 | 0.199 | 0.243 |
| N | $[\mathrm{He}]2s^22p^23s\ ^4P$ | 0.393 | | 0.310 |
| | $[\mathrm{He}]2s^22p^23s\ ^2P$ | 0.347 | | 0.284 |
| O | $[\mathrm{He}]2s^22p^33s\ ^5S$ | 0.605 | | 0.329 |
| | $[\mathrm{He}]2s^22p^33s\ ^3S$ | 0.515 | | 0.301 |

tor with one electron removed, respectively. Note that, in Eq. (68), $v$ is the external potential. This is an exact relation that is analogous to the ground-state exchange-only Koopmans' relation.

Now, following Görling and Levy [14] and Nagy [1], $v^i_\alpha$ can be expanded as

$$v^i_\alpha([n_0,n_i];\mathbf{r}) = v^i_0 - \alpha(u([n_0,n_i];\mathbf{r}) + v^i_x([n_0,n_i];\mathbf{r})) + \cdots, \tag{69}$$

where $u$ and $v^i_x$ are the Coulomb and exchange potentials, respectively. From Eqs. (68) and (69), it follows that

$$\mathrm{tr}\{\hat{D}^i_s \hat{H}\} - \mathrm{tr}\{\hat{D}^{i,N-1}_s \hat{H}^{N-1}\} = \varepsilon_i . \tag{70}$$

Thus we have obtained a ''Koopmans' theorem'' for excited states.

We mention that Koopmans' theorem is valid for an average of the multiplets corresponding to a given configuration. Contrary to the nondegenerate case, in the degenerate generalized KLI as formulated here, ''Koopmans' theorem'' is not quite valid. Using Eqs. (41), (50)–(52), we instead obtain:

$$\Delta E = \varepsilon_N - \int q^i (P^i_N)^2 + \tfrac{1}{2}\int \varrho^i q^i - \tfrac{1}{2}\int \varrho^i_{N-1} q^i_{N-1} \tag{71}$$

for the total energy difference. The last three terms in Eq. (71) give a small correction to the highest orbital energy $\varepsilon_N$. Nevertheless, it would be worthwhile, in the future, to generalize the KLI for degenerate excited states, so that the effective potential satisfies Koopmans' theorem, as derived here.

Table I contains the calculated and the experimental values [15]. In those cases, where the Hartree-Fock (HF) one-electron energies of the excited state are known, Hartree-Fock results are also presented. The one-electron Hartree-Fock orbital energies were calculated by Tatewaki *et al.* [16]. These numerical Hartree-Fock calculations were performed with MCHF72 [17]. Koopmans' theorem is valid in the single-determinant Hartree-Fock theory. When we have several determinants, there is no Koopmans' theorem. Observe that in certain cases there is a good agreement between the calculated and experimental results, suggesting that the last three terms in Eq. (71) are small. Also note that correlation is not included in the present calculations, so the good results might come from a cancellation of errors.

In closing, we note the recent comprehensive review of excited-state theory by Singh and Deb [18]. Contained within is a discussion of the use of the work-function potential [19] as a time-independent method for an individual excited state [20].

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