

## Rigorous formulation of Slater's transition-state theory for excited states

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Slater's transition-state equations, which are used for calculating electronic properties of excited states of atoms, molecules, and solids, are similar to the Kohn-Sham (KS) equations, apart from the fact that the former involve fractional occupation numbers. The subspace density functional theory (SDFT) was introduced by one of us [A. K. Theophilou, *J. Phys. C* **12**, 5419 (1979)] for the development of an excited-state DFT. The lowest-order approximation of SDFT coincides with Slater's transition-state theory. However SDFT shares the mathematical deficiencies of the initial Kohn-Sham DFT for the ground state. In this paper a rigorous derivation of SDFT equations is presented, which lacks these mathematical deficiencies and, in particular, bypasses the  $\nu$ -representability problem. The present formalism makes use of density functionals for subspaces similar to those defined by Levy and Lieb. The procedure followed is along the same lines as the recent developments in the rigorous derivation of the KS theory [N. Hadjisavvas and A. K. Theophilou, *Phys. Rev. A* **30**, 2138 (1984); M. Levy and J. P. Perdew, in *Density Functional Methods in Physics*, edited by R. M. Dreizler and X. da Providencia (Plenum, New York, 1985)].

### I. INTRODUCTION

Many theoretical physics calculations are based on intuition rather than mathematical rigor. The comparison of the experimental data to the theoretical results is the usual criterion applied for their validity. Although some mathematical justification is usually given, the rigorous formulation comes later. A typical case is Slater's transition-state theory.<sup>1-3</sup> This theory was applied for calculating electronic properties of excited states of atoms, molecules, and solids. The equations which resulted from this theory are exactly like those of the Kohn-Sham (KS) equations,<sup>4</sup> where the exchange and correlation energy is expressed as a functional of the density. The difference from the KS theory is that the expression for the density involves fractional occupation numbers. This is a very unusual feature, because in a Slater determinant one cannot have fractionally occupied orbitals. Although Slater gave a statistical interpretation of this unusual feature, not many physicists were convinced.

Slater's transition-state theory found a sound theoretical derivation when it was proved to be the lowest-order approximation of the "subspace theory for excited states" developed by one of us.<sup>5,6</sup> Thus physical intuition proved correct, although mathematical justification lagged far behind. The subspace theory for excited states shares the deficiencies of the original KS theory, the main deficiency being the hypothesis of  $\nu$  representability. As Levy<sup>7</sup> and Lieb<sup>8</sup> have shown, this hypothesis does not always hold. Their proof can be extended to the subspace densities.

The aim of this paper is to present a rigorous derivation of the one-particle equations of the subspace theory, i.e., the equations corresponding to the KS equation for the ground state. The procedure to be followed is similar to that of the KS theory developed independently by Levy and Perdew<sup>9</sup> and the present authors.<sup>10</sup>

### II. THE SUBSPACE THEORY FOR EXCITED STATES

The Hamiltonian of a system of  $N$  electrons in an external potential is

$$H = H_0 + \int \hat{\rho}(\mathbf{r})V(r)d^3r. \quad (1)$$

In the following  $T$  will denote the kinetic-energy operator

$$T = \frac{1}{2} \int \nabla\Psi^\dagger(\mathbf{r})\cdot\nabla\Psi(\mathbf{r})d^3r, \quad (2)$$

while

$$H_0 = T + H_{\text{int}},$$

with

$$H_{\text{int}} = \frac{1}{2} \int \Psi^\dagger(\mathbf{r})\hat{\rho}(\mathbf{r})\Psi(\mathbf{r})d^3r, \quad (3)$$

$\Psi^\dagger(\mathbf{r})$  and  $\Psi(\mathbf{r})$  being the fermion-field operators;  $\rho(\mathbf{r}) = \langle \psi | \hat{\rho}(\mathbf{r}) | \psi \rangle$  is the electron density.

The Hamiltonian considered will be assumed to possess at least  $M$  discrete eigenvalues  $E_i$  lying below the continuous spectrum. The index  $i$  will denote arrangement of the eigenvalues in increasing sequence, i.e.,  $E_i \leq E_{i+1}$ , where each eigenvalue is repeated a number of times equal to its multiplicity. These eigenvalues can be obtained by a Rayleigh-Ritz variational principle.

The subspace theory for excited states relies on the fact that the traces of the various operators representing a physical observable, calculated in a subspace, are functionals of the subspace, i.e., they do not depend on the particular choice of basis. Thus one can define subspace energies and subspace densities. Then the eigenspaces of  $H$  can be obtained by using a principle similar to the Rayleigh-Ritz variational principle. These functionals are defined as follows.

If  $A$  is a self-adjoint operator and  $S$  an  $M$ -dimensional subspace, then

$$G_A(S) = \frac{1}{M} \sum_{i=0}^{M-1} \langle \psi_i | A | \psi_i \rangle, \quad \langle \psi_i | \psi_j \rangle = \delta_{ij} \quad (4)$$

is a functional of  $S$ .<sup>5</sup>

The independence of  $G_A(S)$  on the particular choice of basis can be easily verified by noting that  $G_A(S) = (1/M) \text{Tr}(A E_S)$ ,  $E_S$  being the projection operator on  $S$ . In this way one can define the energy subspace functional  $G_H(S)$  and prove the following<sup>5</sup>

*Lemma 1.* (a) The equality

$$\min_S G_H(S) = \frac{1}{M} \sum_{i=0}^{M-1} E_i$$

holds.

(b) The minimizing  $S$  has a basis of  $M$  orthogonal eigenstates  $|\psi_i\rangle$ , with eigenvalues  $E_i$ ,  $i=0,1,\dots,M-1$ .

One can show that the minimizing subspace  $S$  is uniquely determined apart from the case in which the highest energy level is degenerate and the subspace of degeneracy is not a subspace of  $S$ . When  $S$  is uniquely determined, there is a one-to-one correspondence between the minimizing subspace and its density  $\rho(\mathbf{r}) = G_{\hat{\rho}(\mathbf{r})}(S)$ . Thus all functionals  $G_A(S)$  can be expressed in terms of the density. Then under hypotheses similar to those tacitly assumed in the Hohenberg-Kohn<sup>11</sup> (HK) theory, one can vary the density instead of the subspaces for determining the minimum subspace energy. Unfortunately, as we already pointed out, these hypotheses do not hold. However, the subspace theory can be slightly modified, in the spirit of Levy's modification<sup>12,13</sup> of the HK theory, to be rigorous and to include automatically the case of degenerate energy levels.

Part of this work has already been done by Levy and Perdew,<sup>9</sup> English and English,<sup>14</sup> and Pathak.<sup>15</sup> In the above work the validity of the fundamental theorem of Lieb for the ground state (theorem 3.3 of Ref. 8) was assumed to hold for the subspace density-functional theory (SDFT). This assumption is correct, as we shall now show.

We first introduce some notation. In what follows,  $|\psi\rangle$  will denote an arbitrary  $N$ -fermion state while  $|\phi\rangle$  will be reserved for Slater determinants.  $\psi \Rightarrow \rho$  will mean that  $\rho(\mathbf{r}) = \langle \psi | \hat{\rho}(\mathbf{r}) | \psi \rangle$ . Analogously,  $S$  will denote an arbitrary  $M$ -dimensional subspace,  $R$  a subspace having a basis of  $M$  Slater determinants, and  $S \Rightarrow \rho$  will mean that the subspace density of  $S$  is  $\rho$ , i.e.,  $\rho(\mathbf{r}) = G_{\hat{\rho}(\mathbf{r})}(S)$ .

A further remark is necessary: Since we are interested only in vectors  $|\psi\rangle$  representing physical states, we shall of course require  $\langle \psi | T | \psi \rangle < \infty$ . But then it is known<sup>8</sup> that the corresponding density  $\rho(\mathbf{r}) = \langle \psi | \hat{\rho}(\mathbf{r}) | \psi \rangle$  satisfies  $\int (\nabla \sqrt{\rho})^2 < \infty$ . That is why, in the following, the word "density" will be reserved only for those functions  $\rho(\mathbf{r})$  such that  $\rho(\mathbf{r}) \geq 0$ ,  $\int \rho(\mathbf{r}) = N$ ,  $\int (\nabla \sqrt{\rho})^2 < \infty$ .

The first question we have to consider is the following: Given a density  $\rho$ , does there exist a subspace having this density? The answer is yes, as the following lemma shows:

*Lemma 2.* Let  $\rho(\mathbf{r})$  be a density and  $M$  a positive integer. Then there exists a subspace  $R$  such that  $R \Rightarrow \rho$ .

*Proof.* We simply follow the construction of Harriman.<sup>16</sup> Set  $\mathbf{r} = (x, y, z)$  and define

$$f(x) = \frac{2\pi}{N} \int_{-\infty}^x ds \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} du \rho(s, t, u),$$

$$g^j(\mathbf{r}) = \left[ \frac{\rho(\mathbf{r})}{N} \right]^{1/2} \exp[ij f(x)], \quad j=0, \pm 1, \pm 2, \dots$$

Then  $g^j(\mathbf{r})$  are orthogonal wave functions, each having a finite kinetic energy, such that  $\langle g^j | \hat{\rho}(\mathbf{r}) | g^j \rangle = \rho(\mathbf{r})$ ,  $\forall j$ . (See Ref. 16 for details.) Now arbitrarily choose  $M$  disjoint sets, each containing  $N$  functions  $g^j$ . Each set defines a Slater determinant  $|\phi_k\rangle$ ,  $k=1, \dots, M$ . It is easy to check that the subspace  $R$  generated by  $|\phi_k\rangle$ ,  $k=1, \dots, M$ , satisfies our requirements. ■

Since for any density  $\rho$ , we may find subspaces  $S$  (or  $R$ ) such that  $S \Rightarrow \rho$ , we can also find the infimum of the functional  $G_{H_0}(S)$  under the constraints  $S \Rightarrow \rho$ . The following important theorem guarantees that this infimum is attained and permits us to define functionals of  $\rho$ :

*Theorem 1.* Let  $\rho(\mathbf{r})$  be an arbitrary density and  $M$  a positive integer. Then, (a) the expressions

$$G_T(\rho) \equiv \inf \{ G_T(R) : \dim R = M, R \Rightarrow \rho \}, \quad (5)$$

$$G_{H_0}(\rho) \equiv \inf \{ G_{H_0}(S) : \dim S = M, S \Rightarrow \rho \}, \quad (6)$$

are well defined and finite. (b) The above infima are minima, i.e., they are attained by some subspaces  $R_\rho$  and  $S_\rho$ , respectively. ■

In order to prove Theorem 1, we need some results from functional analysis. For any measurable subset  $\Omega$  of  $\mathbb{R}^{3N}$ ,  $L^2(\Omega)$  is the Hilbert space of square-integrable functions on  $\Omega$ .  $H^1(\mathbb{R}^{3N})$  is the space of all functions  $\psi$  in  $L^2(\mathbb{R}^{3N})$  which possess a generalized first derivative such that

$$\int \sum_{j=1}^{3N} \left| \frac{\partial \psi}{\partial x_j} \right|^2 < \infty.$$

$H^1(\mathbb{R}^{3N})$  is a Hilbert space under the scalar product

$$\langle \psi_1 | \psi_2 \rangle_1 = \int \psi_1^* \psi_2 + \int (\nabla \psi_1)^* \cdot \nabla \psi_2.$$

$H^1(\mathbb{R}^{3N})$  contains exactly those square-integrable functions for which  $\langle \psi | T | \psi \rangle$  and  $\langle \psi | T + H_{\text{int}} | \psi \rangle$  are finite. Details can be found in Ref. 17. [ $\langle | \rangle$  is the usual scalar product in  $L^2(\mathbb{R}^{3N})$ . For simplicity in notation, we omit the spin variables. Of course, only the antisymmetric parts of the spaces  $L^2$  and  $H^1$  are considered.] The proof follows closely the proof of Lieb's<sup>8</sup> Theorem 3.3.

*Proof of Theorem 1.* (a) By Lemma 2 there exists an  $M$ -dimensional subspace  $R \subseteq H^1(\mathbb{R}^{3N})$  such that  $R \Rightarrow \rho$ . For such  $R$ , both  $G_T(R)$  and  $G_{H_0}(R)$  are finite, and thus the infima are well defined. On the other hand, both operators  $T, H_0$  are positive and thus the infima are finite. (b) Let

$$d = \inf \{ MG_{H_0}(S) : S \Rightarrow \rho \}$$

$$= \inf \left\{ \sum_{i=1}^M \langle \psi_i | H_0 | \psi_i \rangle : \langle \psi_i | \psi_j \rangle = \delta_{ij}, \right.$$

$$\left. \frac{1}{M} \sum_i \langle \psi_i | \hat{\rho}(r) | \psi_i \rangle = \rho(r) \right\}.$$

Then one can find a sequence of  $M$ -tuples  $|\psi_1^n\rangle, \dots, |\psi_M^n\rangle$ ,  $n \in \mathbb{N}$ , of antisymmetric elements of  $H^1(\mathbb{R}^{3N})$ , such that

$$\langle \psi_i^n | \psi_j^n \rangle = \delta_{ij},$$

$$\frac{1}{M} \sum_i \langle \psi_i^n | \hat{\rho}(r) \psi_i^n \rangle = \rho(r),$$

$$\lim_{n \rightarrow \infty} \sum_{i=1}^M \langle \psi_i^n | H_0 | \psi_i^n \rangle = d.$$

Since  $|\psi_i^n\rangle$  is bounded, we can select a suitable subsequence  $|\psi_i^n\rangle$  such that  $|\psi_i^n\rangle \xrightarrow{w} |\psi_i\rangle \in H^1(\mathbb{R}^{3N})$  as  $n \rightarrow \infty$  (weak convergence). We shall prove that  $|\psi_i\rangle$  is a minimizing  $M$ -tuple for  $d$ .

Since  $\int \rho = N$ , for any  $\epsilon > 0$  we can find a bounded open set  $A \subseteq \mathbb{R}^3$  with characteristic function  $X_A$ , such that  $\int \rho(1 - X_A) < \epsilon/M$ . If  $B = A^N \subseteq \mathbb{R}^{3N}$ , by the Rellich-Kondrachof imbedding theorem we can find a subsequence of  $M$ -tuples (which we shall denote again by  $|\psi_i^n\rangle$ ) such that  $|\psi_i^n\rangle \rightarrow |\psi_i\rangle$  as  $n \rightarrow \infty$  in  $L^2(B)$ .

If

$$\rho_i^n(r) = \langle \psi_i^n | \hat{\rho}(r) | \psi_i^n \rangle,$$

then

$$\frac{1}{M} \sum_{i=1}^M \rho_i^n = \rho,$$

from which we get  $\rho_i^n(r) \leq M\rho(r)$ , and thus

$$\epsilon > M \int_{\mathbb{R}^3} \rho(1 - X_A) \geq \int_{\mathbb{R}^3} \rho_i^n(1 - X_A)$$

$$= \int_{\mathbb{R}^{3N}} |\psi_i^n|^2 \sum_{j=1}^N |1 - X_A(\mathbf{r}_j)|.$$

But

$$\sum_i |1 - X_A(\mathbf{r}_i)| \geq 1 - X_B$$

and we get

$$\epsilon > \int |\psi_i^n|^2 (1 - X_B) \Rightarrow \int_B |\psi_i^n|^2 \geq 1 - \epsilon, \forall i, \forall n.$$

Since  $|\psi_i^n\rangle \rightarrow |\psi_i\rangle$  as  $n \rightarrow \infty$  in  $L^2(B)$ , we deduce  $\int_B |\psi_i|^2 \geq 1 - \epsilon$ , i.e.,  $\int |\psi_i|^2 \geq 1$ . Since norms do not increase under weak limits, we have  $\int |\psi_i|^2 = 1$ .

But this implies that  $|\psi_i^n\rangle \rightarrow |\psi_i\rangle$  strongly in  $L^2(\mathbb{R}^{3N})$ , and thus  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ . In addition, by the first part of the proof of a theorem of Brezis (cf. Theorem 1.3, Lieb<sup>8</sup>), one has  $(\rho_i^n)^{1/2} \rightarrow \rho_i^{1/2}$  strongly in  $L^2(\mathbb{R}^3)$ , and thus

$$\frac{1}{M} \sum \langle \psi_i | \hat{\rho}(r) | \psi_i \rangle = \rho(r).$$

Finally, since  $|\psi_i^n\rangle, |\psi_i\rangle$  belong to  $H^1(\mathbb{R}^{3N})$  and this space is the domain of  $H_0^{1/2}$  (cf. Simon<sup>18</sup>), it is easy to prove that  $H_0^{1/2} |\psi_i^n\rangle \xrightarrow{w} H_0^{1/2} |\psi_i\rangle$  in  $L^2(\mathbb{R}^{3N})$ . Indeed, for any  $g \in H^1$ ,

$$\lim_n \langle g | H_0^{1/2} |\psi_i^n\rangle = \lim_n \langle H_0^{1/2} g | \psi_i^n \rangle$$

$$= \langle H_0^{1/2} g | \psi_i \rangle = \langle g | H_0^{1/2} |\psi_i\rangle.$$

But  $H^1$  is dense in  $L^2$ , and hence the above holds for any  $g \in L^2$  (cf. Yosida<sup>19</sup>), i.e.,  $H_0^{1/2} |\psi_i^n\rangle \xrightarrow{w} H_0^{1/2} |\psi_i\rangle$ .

But then by the Schwartz inequality,

$$\langle \psi_i | H_0 | \psi_i \rangle = \langle H_0^{1/2} \psi_i | H_0^{1/2} \psi_i \rangle$$

$$= \lim_n \langle H_0^{1/2} \psi_i | H_0^{1/2} \psi_i^n \rangle$$

$$\leq \lim_n (\langle H_0^{1/2} \psi_i^n | H_0^{1/2} \psi_i^n \rangle$$

$$\times \langle H_0^{1/2} \psi_i | H_0^{1/2} \psi_i \rangle)^{1/2}.$$

Hence,

$$\langle \psi_i | H_0 | \psi_i \rangle \leq \lim_n \langle \psi_i^n | H_0 | \psi_i^n \rangle,$$

and from the definition of  $d$  one deduces

$$d = \sum_{i=1}^M \langle \psi_i | H_0 | \psi_i \rangle,$$

and thus  $d$  is a minimum. If  $|\psi_i^n\rangle$  are Slater determinants, then  $|\psi_i\rangle$  are also Slater determinants (cf. proof of Theorem 4.7, Lieb<sup>8</sup>). This means that also the infimum in (5) is a minimum and completes the proof of the theorem. ■

Now the theory can be constructed on the following simple observation: By Lemma 1, we have

$$\frac{1}{M} (E_0 + \dots + E_{M-1}) = \min_S G_H(S).$$

Now the minimum can be calculated by first taking the minimum over the set of subspaces having a given density  $\rho$ , and then minimizing over all  $\rho$ :

$$\min_S G_H(S) = \min_{\rho} [ \min_{S \Rightarrow \rho} G_H(S) ]. \quad (7)$$

But

$$G_H(S) = G_{H_0}(S) + \int \rho(r) V(r) d^3r,$$

and thus

$$\frac{E_0 + \dots + E_{m-1}}{m} = \min_{\rho} \left[ G_{H_0}(\rho) + \int \rho(r) V(r) d^3r \right]. \quad (8)$$

Thus the sum of the first  $M$  eigenvalues can be obtained through variation of a functional of  $\rho$ . In this way, we may calculate this sum from  $M=1, 2, 3, \dots$  and then obtain by subtraction all the eigenvalues of the energy. Of course, for  $M=1$  this theory reduces to the HK theory as modified by Levy.<sup>11, 12</sup>

The variational equation obtained from (8) [assuming that the functional  $G_{H_0}(\rho)$  is derivable], under the condition  $\int \rho = N$ , is

$$\frac{\delta G_{H_0}(\rho)}{\delta \rho(\mathbf{r})} + V(\mathbf{r}) = \mu. \quad (9)$$

Equation (9) may take another form, if we define the kinetic-energy and the exchange and correlation energy functionals by

$$T(\rho) = G_T(S_\rho), \quad (10)$$

$$E_{xc}(\rho) = G_{H_0}(\rho) - T(\rho) - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'. \quad (11)$$

Then (9) becomes

$$\frac{\delta T(\rho)}{\delta \rho(\mathbf{r})} + V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + \frac{\delta E_{xc}(\rho)}{\delta \rho(\mathbf{r})} = \mu, \quad (12)$$

i.e., an equation similar to those of Hohenberg and Kohn. Note that the above formulation has the essential advantage that the functionals are defined for any density  $\rho$ , and not only for  $v$ -representable ones.

### III. RIGOROUS KS THEORY FOR EXCITED STATES

The procedure for the rigorous derivation of the KS equations will be as that followed in Refs. 9 and 10 for the ground state. That is, for the various functionals of the subspace  $S$  we shall define functionals of the subspace  $R$  of the "noninteracting" system. The correspondence will be made in such a way that the densities of the two subspaces will be equal.

This can be made as follows.

For any subspace  $R$ , let  $\rho_R(\mathbf{r}) = G_{\hat{\rho}(\mathbf{r})}(R)$  be the corresponding density. By Theorem 1, there exist subspaces  $R'_R, S_R$  such that

$$G_T(R'_R) = \min \{ G_T(R'): \dim R' = M, R' \Rightarrow \rho_R \}, \quad (13)$$

$$G_{H_0}(S_R) = \min \{ G_{H_0}(S): \dim S = M, S \Rightarrow \rho_R \}. \quad (14)$$

We now define the functionals:

$$\Delta T(R) = G_T(S_R) - G_T(R'_R), \quad (15)$$

$$E_{xc}(R) = G_{H_{int}}(S_R) - \frac{1}{2} \int \frac{\rho_R(\mathbf{r})\rho_R(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r', \quad (16)$$

$$H(R) = G_T(R) + \Delta T(R) + \int V(\mathbf{r})\rho_R(\mathbf{r})d^3r + E_{xc}(R) + \frac{1}{2} \int \frac{\rho_R(\mathbf{r})\rho_R(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'. \quad (17)$$

The physical meaning of these functionals can be seen as follows: Suppose that  $R$  is the eigensubspace corresponding to the first  $M$  eigenvalues of the Hamiltonian of a noninteracting system for some external potential. Suppose further that the corresponding density is also the density of an eigensubspace corresponding to the first  $M$  eigenvalues of an interacting system, for some other external potential. Then it follows easily that the subspaces  $R'_R$  and  $S_R$  defined by relations (13) and (14) are nothing but the subspaces  $R$  and  $S$ , respectively. Thus,  $\Delta T(R)$  is the difference of the kinetic energy of the interacting and the noninteracting system, and  $G_T(R)$  and  $E_{xc}(R)$  are, respectively, the kinetic energy and the exchange and correlation energy of the interacting system, expressed as

functionals of  $R$ . However, the fundamental advantage of the definitions (13)–(17) is that they have a meaning for any  $R$ , eigenspace or not, and no hypothesis on the density of  $R$  is made. We now have the following theorem, which establishes a variational principle for  $H(R)$ .

*Theorem 2.* (a) The following equality holds:

$$\min_R H(R) = \frac{E_0 + E_1 + \cdots + E_{M-1}}{M}.$$

(b) If  $H(R_0) = \min_R H(R)$  for some  $R_0$ , then  $MG_{\hat{\rho}(\mathbf{r})}(R)$  is the sum of densities  $\rho_0 + \cdots + \rho_{M-1}$  corresponding to an orthogonal set of eigenvectors of  $H$ , with eigenvalues  $E_0, E_1, \dots, E_{M-1}$ .

*Proof.* (a) Using definitions (13)–(17) we rewrite  $H(R)$  in the form

$$H(R) = G_T(R) - G_T(R'_R) + G_H(S_R). \quad (18)$$

But, by definition of  $R'_R$ , one has

$$G_T(R) \geq G_T(R'_R) \quad (19)$$

and also, by Lemma 1,

$$G_H(S_R) \geq \frac{E_0 + E_1 + \cdots + E_{M-1}}{M}. \quad (20)$$

Inserting (19) and (20) in (18), we deduce

$$H(R) \geq \frac{E_0 + \cdots + E_{M-1}}{M}. \quad (21)$$

To show that equality can be achieved, consider the subspace  $S_0$  for which, by Lemma 1, we have

$$G_H(S_0) = \frac{E_0 + E_1 + \cdots + E_{M-1}}{M}.$$

If  $S_0 \Rightarrow \rho_0$ , next consider the subspace  $R_{\rho_0}$ , for which, by Theorem 1, we have

$$G_T(R_{\rho_0}) = \min \{ G_T(R): \dim R = M, R \Rightarrow \rho_0 \},$$

and calculate  $H(R_{\rho_0})$ . Then from (18) one easily gets

$$H(R_{\rho_0}) = G_T(R_{\rho_0}) - G_T(R_{\rho_0}) + G_H(S_0) = \frac{E_0 + E_1 + \cdots + E_{M-1}}{M}$$

and part (a) of the theorem is proven. (b) Suppose that

$$H(R_0) = \min_R H(R) = \frac{1}{M}(E_0 + \cdots + E_{M-1}).$$

In order to have an equality in relation (21), relations (19) and (20) should also be equalities. Thus

$$G_H(S_{R_0}) = \frac{1}{M}(E_0 + \cdots + E_{M-1}),$$

from which we get, by Lemma 1, that  $S_{R_0}$  has a basis consisting of orthogonal eigenvectors  $|\psi_i\rangle$ , with  $H|\psi_i\rangle = E_i|\psi_i\rangle$ ,  $i=0, 1, \dots, M-1$ . Consequently,

$$S_{R_0} \Rightarrow \rho = \frac{1}{M} \sum_{i=0}^{M-1} \langle \psi_i | \hat{\rho}(\mathbf{r}) | \psi_i \rangle.$$

Since  $R_0$  and  $S_{R_0}$  have the same density (by definition of

$S_{R_0}$ ), we deduce part (b) of the theorem. ■

We have thus defined a functional  $H(R)$ , by minimization of which we can get the sum of eigenvalues  $E_0 + \dots + E_{M-1}$  of the Hamiltonian of a system of interacting particles, as well as the sum of the densities of the corresponding eigenstates. As we said earlier, in  $E_0 + E_1 + \dots + E_{M-1}$  each eigenvalue is repeated a number of times equal to its multiplicity. Thus, if we calculate this sum for  $M=1, 2, \dots$ , we can also deduce the degeneracy of each energy level. (For instance, if we find that  $E_1 + E_0 = 2E_0$ , but  $E_0 + E_1 + E_2 > 3E_0$ , then the ground state is doubly degenerate.)

In order to find variational equations for  $H(R)$ , consider a basis  $|\phi_1\rangle, \dots, |\phi_M\rangle$  of  $R$ . Then  $H(R)$  can be written in terms of  $\phi = (|\phi_1\rangle, \dots, |\phi_M\rangle)$ . But for such  $\phi$ , a

$$\rho_\phi(\mathbf{r}) = \frac{1}{M} \sum \langle \phi_i | \rho(\mathbf{r}) \phi_i \rangle$$

is defined, and by Eqs. (15) and (16), the functionals  $E_{xc}(\phi), \Delta T(\phi)$  depend only on  $\rho_\phi$ . Thus these functionals can be written as functionals of  $\rho_\phi$  and we have

$$\begin{aligned} H(\phi) = & \sum_{i=1}^M \langle \psi_i | T | \psi_i \rangle + \Delta T(\rho_\phi) + E_{xc}(\rho_\phi) \\ & + \int V(\mathbf{r}) \rho_\phi(\mathbf{r}) d^3r \\ & + \frac{1}{2} \int \frac{\rho_\phi(\mathbf{r}) \rho_\phi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'. \end{aligned}$$

Now performing the variation, we deduce, for the minimizing  $\phi$ ,

$$T | \phi_i \rangle + \int V_{\text{eff}}(\mathbf{r}) \hat{\rho}(\mathbf{r}) d^3r | \phi_i \rangle = E | \phi_i \rangle, \quad (22)$$

where

$$V_{\text{eff}} = V(\mathbf{r}) + V_{\text{xt}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}') d^3r'}{|\mathbf{r} - \mathbf{r}'|} \quad (23)$$

with

$$V_{\text{xt}}(\mathbf{r}) = \frac{\delta}{\delta \rho} [E_{xc}(\rho) + \Delta T(\rho)]. \quad (24)$$

These equations are similar in form to those obtained by Kohn and Sham<sup>4</sup> for the ground state. Their main advantage is that they are exact, due to the existence of a correction term  $\Delta T(\rho)$ , and that they permit calculations of excited-state energies and densities. In addition, the density  $\rho$  which is a solution of these equations involves fractionally occupied orbitals. For a more detailed discussion, we refer the reader to Ref. 5.

#### IV. CONCLUSIONS

Although the equations of the subspace theory for excited states, which are equivalent to those of the KS theory for the ground state, can be rigorously derived, the main problem, as with all functional theories, is the determination with sufficient accuracy of the exchange and correlation energy.<sup>20-22</sup> The correction to the kinetic-energy term is also important. Provided these functionals can be determined with sufficient accuracy, the subspace theory can be used for more efficient numerical calculations, as one may search as a first step to determine the subspace densities and subspace energy, and as a second step one can "diagonalize" the effective Hamiltonian and use the resulting wave functions as starting trial functions for the self-consistent calculation of eigenstate properties.

We believe that the recent developments in energy-density-functional theories and the various aspects from different points of view<sup>9,23-28</sup> will lead to more exact functionals and simpler functional theories.

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