

## Bound excited states in density-functional theory

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Using recent modifications of the original Hohenberg-Kohn theorem due to Levy [Proc. Natl. Acad. Sci. USA **76**, 6062 (1979)] and Valone [J. Chem. Phys. **73**, 1344 (1980)] and the modified Ritz variational principles [J.K.L. MacDonald, Phys. Rev. **46**, 828 (1934)] alternative density functionals are exhibited which respect the bounds of the modified principles. Excited-state energies and electron densities may be calculated by direct minimization of the new functionals. The density functional  $R_2[\rho, U]$  obeys the bound  $R_2[\rho, U] \geq (E_b - U)^2$ , where  $U$  is a fixed constant energy and  $E_b$  is the bound-state energy of the system closest to  $U$ . At present, it appears that the functional depends nontrivially on the external potential. Some properties of reduced density-matrix functionals are presented. The nature of the 2 matrix functional,  $R_2[\rho, U]$ , provides clues to the nature of the density functional. The evident dependence of  $R_2[\rho, U]$  on the external potential indicates that the presence of excited states in the Levy density functional is very unlikely. The point of view in this paper is found to complement the recently proposed Theophilou density functional for excited states.

### I. INTRODUCTION

#### A. Prior history of excited-state density-functional theory

In an immediate sense, the Hohenberg-Kohn (HK) theorem,<sup>1</sup> valid for variationally determining ground-state density, may not be extended to excited states. Previously, Epstein and Rosenthal<sup>2</sup> demonstrated by counterexample that the external potential is not uniquely determined by an excited-state density. Recently, Theophilou<sup>3</sup> produced a functional of "composite" densities with excited-state components which satisfy an HK-type theorem, using Schrödinger-type functionals. However, the excited-state density must be calculated from the difference of two composite densities. In the precipitant analysis of Katriel,<sup>4</sup> the Theophilou approach was shown to be a variant of the original HK theorem applied to a composite Hamiltonian. Of further interest is the fact that each composite state requires a new (composite) density functional, and each composite density contains the ground-state density, which determines the external potential. Because of this situation, the relationship between the external potential and the excited states remains unclear in details, but it is apparent that a different functional must be constructed for each external potential.

To continue the elucidation of this relationship, we examine density functionals based on MacDonald-type functionals,<sup>5</sup> i. e., expectation values of various powers of the Hamiltonian. These functionals are not a consequence of the original HK theorem and prior knowledge of other states is not required as in the Theophilou approach.<sup>3,4</sup> The role of the external potential appears explicitly in the resulting map between densities and ensembles, necessitating a different functional for each external potential.

#### B. The conventional variational principle and Hohenberg-Kohn theorem elucidated by the Levy functional

The Ritz variational principle states that the Schrödinger energy functional  $E_s[\Psi]$  is bounded below by some finite constant, the ground-state energy

$$E_s[\Psi] \equiv \langle \Psi, H\Psi \rangle \geq E_0, \quad (1)$$

for all normalized, antisymmetric wave functions  $\Psi$  and for a fixed, molecular Hamiltonian  $H$ . The original HK theorem demonstrates the existence of a universal energy functional  $E_{\text{HK}}[\rho]$  for a fixed Hamiltonian, depending only on the total, 1-particle density  $\rho$ , which respects the bound in Eq. (1), for all  $\rho$  which are representable by a wave function of appropriate symmetry which is also the normalized, nondegenerate ground state for some local, external potential:

$$E_{\text{HK}}[\rho] \geq E_0, \quad (2)$$

for representable<sup>6</sup> and normalized  $\rho$ . A density  $\rho$  is representable by a wave function if

$$\rho(x) = \int dx_{N-1} \Psi(x, x_{N-1}) \Psi^*(x, x_{N-1}), \quad (3)$$

where  $x_K = (x_1, \dots, x_N)$  is a vector of spin-space coordinates. By universal, we mean that the dependence on  $\rho$  does not change when the local, external potential changes.<sup>7</sup>

This definition of universal is different than the one used by HK in Ref. 1 and by Levy.<sup>7</sup> In Ref. 1 for instance,  $E_{\text{HK}}[\rho]$  is decomposed as

$$E_{\text{HK}}[\rho] = F[\rho] + \int dr v(r)\rho(r),$$

where  $F[\rho]$  is a functional only of the density  $\rho$  and not of the external potential  $v$ . Thus,  $F[\rho]$  is "universal" in the sense that it need be computed only once for all times. A part of  $E_{\text{HK}}[\rho]$  is universal in this sense. The concept to be used in this paper is most naturally referred to as a type of universality and so we have not introduced new vocabulary. In addition, the excited-state density functionals to be discussed do not submit to such a helpful decomposition. Therefore, we have chosen to shift the definition of universal, in order to aid the comparison of ground- and excited-state functionals.

The original theorem has been extended by Levy<sup>7</sup> and modified by Valone<sup>8</sup> to establish the existence of a universal energy functional of the total one-particle density which is defined for any density, representable by an  $n$ -particle density matrix. A density matrix  $D(N, N')$  (or an ensemble) may be defined as

$$D(N, N') = \sum_k w_k \Psi_k(N) \Psi_k^*(N'), \quad (4)$$

where  $N$  stands for a vector of spin-space coordinates  $(x_1, \dots, x_n)$ ,  $\{\Psi_k(N)\}$  is some set of orthonormal, antisymmetric  $n$ -particle wave functions and  $\sum_k w_k = 1$ , with all  $w_k \geq 0$ . The set of all such density matrices we denote by  $\mathcal{E}_n$ . The one-particle density is obtained from some  $n$ -particle density matrix by integrating all but one coordinate

$$\rho_D(s) \equiv \int dx_{N-1} D(x, x_{N-1}; x, x_{N-1}). \quad (5)$$

We call the set of all  $n$ -particle density matrices which produce the same one-particle density  $L_\rho(n)$ <sup>9</sup>:

$$L_\rho(n) \equiv \left\{ D \in \mathcal{E}_n : \int dx_{N-1} D(x, x_{N-1}; x, x_{N-1}) = \rho(x) \right\}, \quad (6)$$

for one fixed  $\rho(x)$ . As Gilbert has shown,<sup>6</sup> none of the  $L_\rho(n)$  is empty. Then the one-particle density function as  $E_\rho[\rho]$  may be defined by<sup>7,8</sup>

$$E_\rho[\rho] \equiv \min\{\langle H, D \rangle : D \in L_\rho(n)\}. \quad (7)$$

The inner product notation,  $\langle A, B \rangle$ , for matrices  $A$  and  $B$ , is adapted.

Recently it has been shown that there is a well-defined method for selecting one energy-minimizing ensemble from  $L_\rho(n)$  which one may uniquely associate with  $\rho$ .<sup>10</sup> Consequently, there is a parametrization of a set of ensembles by the densities,

$$D(\rho) \equiv D(N, N'; \rho), \quad (8)$$

such that

$$E_\rho[\rho] = \langle H, D(\rho) \rangle, \quad (9)$$

for all normalized  $\rho$ . We call this the Levy representation of the energy-density functional. The result is that grouping the  $n$ -particle densities together according to which one-particle density is produced preserves the bound in Eq. (1)

$$E_\rho[\rho] \geq E_0, \quad (10)$$

for all  $\rho$  with unit norm. Further, there is a density  $\rho_0$ , representable by the (assumed nondegenerate) ground-state wave functions,  $\Psi_0$  which attains this bound

$$E_\rho[\rho_0] = E_0, \quad (11)$$

and

$$\int dx_{N-1} \Psi_0(x, x_{N-1}) \Psi_0^*(x, x_{N-1}) = \rho_0(x). \quad (12)$$

Therefore, a direct minimization of  $E_\rho[\rho]$  would yield the ground-state energy  $E_0$  and the ground-state density  $\rho_0$ .<sup>1</sup> We may identify  $E_{\text{HK}}$  with  $E_\rho$ .

One wonders whether analogous results hold for excited states. Is there a method for calculating excited-state energies and one-particle densities, representable by excited-state wave functions, by direct minimization of a functional? We will show that such a method exists but first we must ask how to do this for wave functions (or  $n$ -particle density matrices).

### C. Modified Ritz variational principle

MacDonald<sup>5</sup> long ago gave an answer for the  $n$ -particle case which does not require prior knowledge of other states.<sup>3,4</sup> He defines functionals

$$I_m[\Psi, U] \equiv \langle \Psi, (H - U)^m \Psi \rangle, \quad (13)$$

where  $U$  is an arbitrary, fixed real constant and  $m$  is an integer  $\geq 1$ . The Euler equation from Eq. (13) is

$$[(H - U)^m - \lambda^{(m)}] \Psi^{(m)} = 0, \quad (14)$$

where  $\lambda^{(m)}$  is the Lagrange multiplier associated with the normalization constraint. MacDonald then shows that the solutions to Eq. (14) are  $\Psi^{(m)} = \Psi_E$  and  $\lambda^{(m)} = (E - U)^m$  where

$$[H - E] \Psi_E = 0, \quad (15)$$

where  $E$  is some discrete eigenvalue of  $H$ . The critical fact is that if  $E_b$  is the bound-state eigenvalue of  $H$  which minimizes  $(E - U)^m$ , then

$$I_m[\Psi, U] \geq (E_b - U)^m, \quad (16)$$

for all normalized  $\Psi$  of appropriate symmetry.

For even  $m$ , these equations allow excited-state energies and wave functions to be calculated by direct minimization of the functional  $I_m$ . Apart from the problem of computational attractiveness, this is a possibility which is available in principle and provides an analytical scheme which may be examined for general physical principles and used for approximation purposes. These provide the starting point for a density-functional theory of excited states.

In Sec. II, the new density functionals analogous to the Levy functional are defined. The preservation of the variational bound and the representability of various extremal eigendensities by excited-state  $n$  matrices are proved. In Sec. III the generalization of these functionals for reduced-density matrices suggests easier evaluation of the functionals, but for matrices of order two or higher, the  $N$ -representability problems prevent their immediate use.<sup>6,7,8</sup> In Sec. IV, speculation concerning the nature of the density functional is based upon the corresponding 2 matrix functional. The possibility of excited states in the Levy functional are also considered.

## II. A DENSITY-FUNCTIONAL THEORY OF BOUND, EXCITED STATES

### A. Definitions of density functionals

We first note that the MacDonald functionals of Eq. (13) may be defined on ensembles without violation of the associated variational bound in Eq. (16). Now define the functionals  $R'_m[\rho, U]$  by

$$\begin{aligned} R'_m[\rho, U] &\equiv \min\{\langle (H - U)^m, D \rangle : D \in L_\rho(n)\} \\ &= \min\{I_m[D, U] : D \in L_\rho(n)\}, \end{aligned} \quad (17)$$

for  $H$  with a local external potential  $v$  and  $U$  as above. Using the arguments of Ref. 10, one ensemble of those minimizing  $I_m[D, U]$  over  $L_\rho(n)$  may be uniquely selected to associate with  $\rho$ . The resulting parametrization of ensembles is denoted as

$$D_m(\rho, v) \equiv D_m(N, N'; \rho, v), \quad (18)$$

allowing definition of the functionals

$$\begin{aligned} R_m[\rho, U] &\equiv \langle (H - U)^m, D_m(\rho, v) \rangle \\ &= I_m[D_m(\rho, v), U]. \end{aligned} \quad (19)$$

These are the density functionals which we will exploit in describing excited states. At this time, we assume that, for  $m \geq 2$ ,  $D_m(\rho, v)$  depends on  $v$ . A long-range goal is to verify whether or not this is indeed the case. (See Sec. IV.) Note that, for a local  $v$ ,  $D_1(\rho, v) = D(\rho)$  of Eq. (8) and

$$R_1[\rho, U] = E_\rho[\rho] - U. \quad (20)$$

This approach to density-functional theory emphasizes the parametrization implicit in the theories of HK<sup>1</sup> and of Levy.<sup>7</sup> It also provides for the construction of a density-functional theory for nonlocal potentials and arbitrary powers of the Hamiltonian, even though the functionals may not be universal. Nothing of this type is available from the HK approach, which relies on a proof by contradiction and is not defined for all densities. The approach advocated by Levy is seen to be essential. Note also that knowledge of states other than the one resulting from minimization of Eq. (19) over  $\rho$  is not required to produce an excited-state density, as will be demonstrated in the next subsection.<sup>3,4</sup> The advantages of this are in part counterbalanced by the fact that  $D_2(\rho, v)$  apparently depends on the external potential  $v$ .

Since excited states appear as absolute minima in the MacDonald functionals  $I_2[D, U]$ , we may concern ourselves with the corresponding  $m=2$  functionals  $R_2[\rho, U]$ . In spite of the apparent lack of universality, we fix the external potential and proceed with the incumbent restriction.

### B. Variational principle

#### 1. Theorem

Assume that  $U$  and the known external potential are fixed. We wish to prove that  $R_2[\rho, U]$  respects the lower bound  $(E_b - U)^2$ , with  $E_b$  as in Eq. (16)

$$R_2[\rho, U] \geq (E_b - U)^2, \quad (21)$$

for all normalized  $\rho$ .<sup>6</sup> Further the bound is attained at the density  $\rho^*$ , if and only if  $\rho^*$  is representable by  $D_b$ , where  $(H - E_b)D_b = 0$ .

#### 2. Proof

To arrive at Eq. (21), note that the evaluation of  $R_2[\rho, U]$  for any normalized  $\rho$  requires only expectation values already appearing in the original  $n$ -particle theory.

The second assertion is proved in two parts. First, assume  $\rho = \rho_b$  so that  $D_b \in L_{\rho_b}(n)$ . Then

$$I_2[D_b, U] = (E_b - U)^2 \geq R_2[\rho_b, U] \geq (E_b - U)^2. \quad (22)$$

The left inequality follows from the definition of  $R_2$  [Eq. (19)] and the right inequality follows from Eq. (21).

For the second part, let

$$R_2[\rho^*, U] = \min_{\rho} R_2[\rho, U] \equiv S^*. \quad (23)$$

Assume that

$$S^* = [E_b(U) - U]^2 = I_2[D_2(\rho^*, v), U]. \quad (24)$$

To proceed, we must prove that  $D_2(\rho^*, v) = D^*$  and

$E_b(U)$  are independent of  $U$  for sufficiently small changes in  $U$ . For sufficiently small changes in  $U$ , the minimizing ensembles of  $I_2[D, U]$  remains the same. (We are dealing with a discrete portion of the spectrum.) Therefore minimization of  $R_2[\rho, U']$  over  $\rho$  must yield the same minimizing ensemble  $D^\#$ , if  $U'$  is sufficiently close to  $U$ . This implies that  $R_2[\rho^\#, U'] = \min_\rho R_2[\rho, U']$  for such  $U'$ , further implying the assertion that  $D_2(\rho^\#, v)$  and  $E_b(U) = E_b$  are independent of small changes in  $U$ .

This result is necessary so that we may define the differentiable function

$$S^\#(U') = (E_b - U')^2 = I_2[D^\#, U'], \quad (25)$$

for all  $U'$  sufficiently close to  $U$  (which determines  $E_b$ ). Now, by optimization with respect to  $U$ ,

$$0 = \left. \frac{\partial S^\#}{\partial U'} \right|_{U=U_b} = -2 \langle H - U_b, D^\# \rangle. \quad (26)$$

This implies

$$U_b = E_b = \langle H, D_2(\rho^\#, v) \rangle \quad (27)$$

and

$$S^\#(E_b) = 0 = \langle H - E_b, D^\# \rangle. \quad (28)$$

Following Gilbert,<sup>6</sup> we conclude from the diagonalization of  $D^\#$  that  $D^\#$  must be some particular convex combination<sup>11</sup> of degenerate wave functions belonging to  $E_b$ . Thus  $\rho^\# = \rho_b$  is represented by  $D_b$ , where  $(H - E_b)D_b = 0$ , completing the proof.

Now we turn to analogous functionals for reduced matrices.<sup>9</sup>

### III. FUNCTIONALS FOR REDUCED MATRICES

Defining reduced density matrices by the formula

$$\Gamma_D^{(p)}(X_p; X_p') \equiv \int dX_{N-p} D(X_p, X_{N-p}; X_p', X_{N-p}'), \quad (29)$$

for  $1 \leq p \leq n$ , functionals analogous to those in Eq. (19) may be easily formulated. Denoting the parametrization of  $n$  matrices by  $p$  matrices as  $D_m(\Gamma^{(p)}, v)$ , we define the functionals

$$R_m[\Gamma^{(p)}, U] = \langle (H - U)^m, D_m(\Gamma^{(p)}, v) \rangle, \quad (30)$$

for  $1 \leq p \leq n$ . These have the same basic properties as the density functionals  $R_m[\rho, U]$ , although  $N$  representability problems arise for  $2 \leq p \leq n - 2$ .<sup>6,7,8</sup> The functions  $D_m(\Gamma^{(p)}, v)$  have different properties for different values of  $p$  and  $m$ . For example questions of differentiability and the presence of excited states may change as  $p$  and  $m$  change.

As a specific example, define  $L(n, \Gamma^{(p)})$  as the set of all  $n$  matrices which represent a given  $p$  matrix,  $\Gamma^{(p)}$ . Then, for reduced matrices of order 4 or greater, minimization over  $L(n, \Gamma^{(p)})$  is not necessary, as may be seen in the expression for  $(H - U)^2$  in the second quantized notation

$$\langle (H - U)^2, D \rangle = \left\langle \left( \sum_{i,j} \langle j|h|i \rangle a_j^\dagger a_i + \frac{1}{2} \sum_{q,r,s,t} \langle q,r|V|s,t \rangle a_r^\dagger a_q^\dagger a_s a_t - U \right)^2, D \right\rangle, \quad (31)$$

where  $h$  is a 1 particle operator and  $V$  is a 2 particle operator. The terms that will contribute to  $\langle H^2 \rangle$  alone are

$$\begin{aligned} \langle H^2, D \rangle = & \left\langle \sum_{i,j,k,l} \langle j|h|i \rangle \langle l|h|k \rangle a_j^\dagger a_i^\dagger a_k + \frac{1}{2} \sum_{i,j} \sum_{m,n,o,p} \langle j|h|i \rangle \langle m,n|V|o,p \rangle a_j^\dagger a_i^\dagger a_n^\dagger a_m^\dagger a_o a_p \right. \\ & + \frac{1}{2} \sum_{k,j} \sum_{q,r,s,t} \langle q,r|V|s,t \rangle \langle j|h|k \rangle a_r^\dagger a_q^\dagger a_s a_t a_j^\dagger a_k \\ & \left. + \frac{1}{4} \sum_{m,n,o,p} \sum_{q,r,s,t} \langle q,r|V|s,t \rangle \langle m,n|V|o,p \rangle a_r^\dagger a_q^\dagger a_s a_t a_n^\dagger a_m^\dagger a_o a_p, D \right\rangle. \quad (32) \end{aligned}$$

Hence, the expectation value of  $\langle (H - U)^2, D \rangle$  is determined by  $\Gamma_D^{(4)}$ .

As discussed by Erdahl and Grudzinski<sup>12</sup> if the  $N$ -representability conditions for  $\Gamma^{(4)}$  were known, a direct minimization of Eq. (31) would be possible yielding some eigen-4 matrix. To this effect, it is interesting to note that Eq. (31) contains some necessary  $N$ -representability conditions. One such condition is the non-negativity of the first term of the right side of Eq. (32), which may be rewritten as

$$\langle h^2 \rangle = \sum_{i,j} \sum_{k,l} \langle j|h|i \rangle \langle l|h|k \rangle [\delta_{i,l} \gamma(k|j) - \Gamma(i,k|l,j)] \geq 0. \quad (33)$$

This equation is the  $G$  condition of Garrod and Percus.<sup>13</sup> Similarly, the last term on the right side of Eq. (32) can be rewritten as

$$\begin{aligned} \langle V^2 \rangle = & \frac{1}{4} \sum_{m, n, o, p} \sum_{q, r, s, t} \langle q, r | V | s, t \rangle \langle m, n | V | o, p \rangle \\ & + [\delta_{n, t} \delta_{s, m} \Gamma(o, p | q, r) - \delta_{m, t} \delta_{s, n} \Gamma(o, p | q, r) - \delta_{s, m} \Gamma(t, o, p | n, q, r) \\ & - \delta_{n, t} \Gamma(s, o, p | m, q, r) + \delta_{m, t} \Gamma(s, o, p | n, q, r) + \delta_{s, n} \Gamma(t, o, p | m, q, r) + \Gamma(s, t, o, p | m, n, q, r)] \geq 0. \end{aligned} \quad (34)$$

This equation is also a hyperplane constraint, a necessary  $N$ -representability condition, on  $\Gamma^{(4)}$ . Should Eq. (31) be minimized subject to incomplete  $N$ -representability conditions, then the equation itself partially selects the approximate  $N$ -representable cone for the search. Other comments in Ref. 12 lead to the additional conclusion that if  $\Gamma_D^{(4)}$  is some eigen-4 matrix, Eq. (31) is equivalent to the Nakatsuji density equation.<sup>14</sup> Other differences in the behavior of the functionals  $R_m[\Gamma^{(p)}, U]$  will be noted in the ensuing discussion.

#### IV. SPECULATION ON THE STRUCTURE OF $D_2(\rho, v)$

##### A. Background

A central concern with  $D_2(\rho, v)$  is its dependence on the local external potential  $v$ . How does  $D_2(\rho, v)$  change with changes in  $v$ ? Changes in  $v$  may be broken into two categories. One category consists of constant shifts in  $v$ . In the functional  $R_2[\rho, U]$ , constant shifts are nontrivial, as these changes may result in the density corresponding to the absolute minimum to change. Such is not the case for  $R_1[\rho, U] = E_\rho[\rho] - U$ . In a second category are nonconstant changes of the potential.

For small constant changes of the potential,  $D_2(\rho, v)$  has been seen to be independent of  $U$ . However, results for other  $\rho$ 's are not available. The presence of excited states may not be demonstrated currently. As a potential probe of  $D_2(\rho, v)$  and as a further example of how properties of  $D_2(\Gamma^{(p)}, v)$  may change with  $p$ , we examine  $D_2(\Gamma^{(2)}, v)$ .

Without question,  $D_2(\Gamma^{(2)}, v)$  represents all the excited states independent of  $U$ , which we now prove. Suppose  $E_j$  and  $\Gamma_j^{(2)}$  are the  $j$ th excited-state energy and eigen-2 matrix of  $H$ , respectively.<sup>14</sup> By definition of  $R_2[\Gamma^{(2)}, U]$ ,

$$(E_j - U)^2 \geq R_2[\Gamma_j^{(2)}, U] = \langle (H - U)^2, D_2(\Gamma_j^{(2)}, v) \rangle. \quad (35)$$

From the Schwartz inequality,<sup>15</sup> modified for ensembles,<sup>16</sup> we have

$$\langle (H - U)^2, D_2(\Gamma_j^{(2)}, v) \rangle \geq \langle H - U, D_2(\Gamma_j^{(2)}, v) \rangle^2. \quad (36)$$

However,

$$\begin{aligned} \langle H - U, D_2(\Gamma_j^{(2)}, v) \rangle &= \langle (H^{(2)} - U), \Gamma_j^{(2)} \rangle \\ &= E_j - U. \end{aligned} \quad (37)$$

Again using the properties of the Schwartz inequality, Eqs. (35)–(37) imply that  $D_2(\Gamma_j^{(2)}, v)$  is an ensemble (with minimum  $L_2$  norm by definition) composed of degenerate pure states. The quantity  $U$  has been arbitrary. Since Eq. (37) is not known to be true for  $D_2(\rho, v)$ , we may not as yet conclude that  $D_2(\rho, v) = D_j$ .

As for nonconstant changes in  $v$ , the evidence from other sources, such as the Green-function theory<sup>17</sup> and other density-functional theories,<sup>3,4</sup> gives little hope for  $D_2(\Gamma^{(2)}, v)$  to be independent of  $v$ . However, it may be possible to elucidate the nature of the  $v$  dependence.

##### B. Speculation on the presence of excited states in $D_1(\rho)$ and $D_2(\rho, v)$

Here we consider the possibility that  $D_1(\rho_j)$  is an excited-state ensemble, if  $\rho_j$  is an excited-state density of some Hamiltonian. One approach is to examine the relationship between  $D_1(\rho)$  and  $D_2(\rho, v)$ . Again, we turn to the 2-matrix situation for inspiration. Since it seems likely that  $D_2(\Gamma^{(2)}, v)$  depends on  $v$ , it is doubtful that  $D_1(\Gamma^{(2)})$  and  $D_2(\Gamma^{(2)}, v)$  agree even at eigenmatrices (except, for the ground-state  $\Gamma^{(2)}$  corresponding to  $v$ ). If this holds,  $D_1(\rho)$  would not represent the excited states. In fact, the presence of excited states in  $D_1(\rho)$  openly contradicts the stronger likelihood of  $v$  dependence in  $D_2(\rho, v)$ .

To see this, again consider  $D_1(\Gamma^{(2)}, v)$ . Assume that  $(H' - E')D_1(\Gamma^{(2)}) = 0$  and  $D_1(\Gamma^{(2)}) = D_2(\Gamma^{(2)}, v)$  for all  $v$ . From Eq. (19), for Hamiltonian  $H$ ,

$$\begin{aligned} \langle (H - E')^2, D_1(\Gamma^{(2)}) \rangle \\ = \min\{\langle (H - E')^2, D \rangle : D \in L(n, \Gamma^{(2)})\}. \end{aligned} \quad (38)$$

A simple calculation shows that our assumption leads to

$$\begin{aligned} 0 = \min\{\langle (H' - E')^2 \\ + 2(H' - E')(v - v'), D \rangle : D \in L(n, \Gamma^{(2)})\}, \end{aligned} \quad (39)$$

independent of  $v$ . This is very unlikely.

From a somewhat different point of view, Nakatsuji has shown that not all  $D \in L(n, \Gamma_j^{(2)})$  are solu-

tions to the Schrödinger equation, even if  $\Gamma_j^{(2)}$  is an eigen-2 matrix.<sup>14</sup> On the other hand,  $D_2(\Gamma_j^{(2)}, v)$  is an eigen- $n$  matrix, as demonstrated in Eqs. (35) through (37). Therefore, in general,  $D_1(\Gamma_j^{(2)}) \neq D_2(\Gamma_j^{(2)}, v)$ .

The physical significance of this conclusion is that nonground-state solutions to the Euler equation for the Levy functional contain no known physical meaning.

### C. Euler equations for $R_2[\rho, U]$

Suppose that  $D_2(\rho, v)$  is differentiable and is independent of constant shifts in  $v$  at  $\rho = \rho_b$ . It would then be worthwhile to examine an Euler equation. First, note the expansion of  $I_2[D_2(\rho, v), U]$ :

$$I_2[D_2(\rho, v), U] = \langle H^2(n), D_2(\rho, v) \rangle - 2U \langle H(n), D_2(\rho, v) \rangle + U^2 \equiv E_2[\rho, v] - 2UE_1[\rho, v] + U^2. \quad (40)$$

Now there are two ways to proceed. The first is to leave  $n$  fixed in  $H(n)$  and in Eq. (19). Let  $N[\rho] = 1$  be the normalization constraint with Lagrange multiplier  $\lambda^{(2)}$ . Construct the auxiliary functional  $\Omega_2[\rho, U]$ :

$$\Omega_2[\rho, U] \equiv I_2[D_2(\rho, v), U] - \lambda^{(2)} N[\rho]. \quad (41)$$

Take variations with respect to  $\rho$  and  $U$  to obtain

$$\left. \frac{\partial E_2}{\partial \rho} - 2U \frac{\partial E_1}{\partial \rho} \right|_{\rho_b} = \lambda^{(2)}, \quad (42)$$

and

$$-2 \langle H - U, D_2(\rho, v) \rangle + \left\langle (H - U)^2, \frac{\partial D_2}{\partial U} \right\rangle \Big|_{\rho_b} = 0. \quad (43)$$

The second term in Eq. (43) is zero because  $D_2(\rho_b, v)$  is assumed to be independent of  $U$ . This allows the elimination of  $U$  from Eq. (42):

$$\left. \frac{\partial E_2}{\partial \rho} - \frac{\partial (E_1)^2}{\partial \rho} \right|_{\rho_{\text{ext}}} = \lambda^{(2)}. \quad (44)$$

In this case,  $\lambda^{(2)}$  would be related to an energy density.<sup>18</sup> Motivated by the analysis of  $D_2(\Gamma_j^{(2)}, v)$ . One hopes that Eq. (42) also contains excited-state solutions.

The second procedure consists of replacing all  $n$  in  $H(n)$  and  $D_2$  by  $n \times N[\rho]$ . One may wish to introduce a second quantization formulation of Eqs. (6), (18), and (19) at this point. The Lagrange multiplier would then have a different physical significance, presumably related to the chemical potential,  $\mu$ . A similar situation arises in the case of  $E_g[\rho]$  (see Ref. 18) and one must decide which procedure to use. They need not be equivalent.

### D. Comparison between $R_2[\rho, U]$ and other constructions of density functionals

We emphasize that the nature of the present theory of density functionals rests upon the parametrization of a set of ensembles according to the density each produces. The parametrization results from strict adherence to the variational principle. To derive a description of excited states, the external potential is shifted by constant values; the mapping between densities and ensembles appears to depend on the nonconstant portion of the external potential. In another theory of excited states, developed by Theophilou,<sup>3,4</sup> in order to variationally calculate nonground-state eigendensities, one must possess knowledge of the next lowest composite state. This seems to replace the information contained in the  $v$  dependence of  $D_2(\rho, v)$ .

Concerning gradient expansion techniques for constructing density functionals, they are very different in character than the present theory.<sup>1,19</sup> It has not been shown that they adhere to the variational principle, or to the minimum-energy characterization of a set of ensembles. Hence, the present approach provides no justification for their pursuit.

On the other hand, any density functional acting as lower bound to the true functional may be regarded as a partial characterization of an exact procedure. An example of this is available in the work of Lieb<sup>20</sup> and Lieb and Thirring.<sup>21</sup> This example is not completely satisfactory, since two different approximations were used to derive their functionals, and it is difficult to see what parametrization of ensembles is being suggested in this case. Their approach seems closer to an approximation of the action of the Hamiltonian, rather than an approximation to minimum-energy ensembles. The pseudo-potential method is certainly an example of one which approximates the action of the Hamiltonian.<sup>22</sup> Consequently, no approximations to density functionals incorporating the prescription of Eq. (19) exist at present.

### V. SUMMARY

In Eqs. (17) through (19), we have constructed functionals of the one-particle density which respect the bounds associated with the analogous modified Ritz variational principles. The functional  $R_2[\rho, v, U]$  was shown to possess absolute minima acquired by one-particle densities representable by excited-state  $n$ -particle density matrices or ensembles. Thus, it has been established in principle, that all bound states may be calculated by direct minimization of an energy-related, density functional, provided the external

potential is known. This contrasts with the Theophilou approach to excited-state density functionals, in which one must know a certain additional composite state in order to calculate an excited-state energy and density of interest.

The reduced 2 matrix functional,  $R_2[\Gamma^{(2)}, U]$  has been shown to contain all the excited states for a fixed (apart from constant shifts), local external potential. We speculated that the same holds for  $R_2[\rho, U]$ . The  $v$  dependence of  $D_2(\rho, v)$

leads to the conclusion that  $D_1(\rho)$  does not represent the excited states.

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