PHYSICAL REVIEW A **66**, 022505 (2002)

Density-matrix functional theory

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(Received 18 March 2002; published 27 August 2002)

An auxiliary system is defined by adiabatic connection. In the ground state the diagonal of the spin-independent second-order density matrix n can be determined by solving a single auxiliary equation of a two-particle problem. Thus the problem of an arbitrary system with even electrons can be reduced to a two-particle problem. The effective potential of the two-particle equation contains a term of completely kinetic origin.

DOI: 10.1103/PhysRevA.66.022505 PACS number(s): 31.15.Ew

I. INTRODUCTION

Recently there has been growing interest in the theory of density matrices. The theory goes back to the pioneering works of Husimi [1] and Löwdin [2]. The problem of N representability [3] turned out to be a serious difficulty that hindered the theory from becoming a powerful tool for treating many-electron systems. A breakthrough has come with the recent research of Nakatsuji and Yasuda [4], Valdemoro and co-workers [5], and Mazziotti [6] (NVM). The NVM theory presents an alternative to traditional many-body quantum calculations through solving the contracted Schrödinger equation.

In this paper another approach is presented. In the next section recent results of Gonis *et al.* [7] are reviewed and generalized. They extended the Hohenberg-Kohn theorems [9] showing that the total energy is a functional of the "hyperspace density" that is the diagonal of the spin-independent reduced second-order density matrix. Another approach based on the pair density, i.e., a pair density functional theory, was proposed by Ziesche [8].

The main results of this paper are presented in Sec. III. Auxiliary equations are derived through adiabatic connection. It is shown that in the ground state the diagonal of the spin-independent second-order density matrix n can be determined by solving a single auxiliary equation of a two-particle problem. Thus the problem of an arbitrary system with even electrons can be reduced to a two-particle problem.

II. DENSITY MATRIX FUNCTIONAL THEORY

Consider the Hamiltonian of interest

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

where $\hat{T}$ is the kinetic energy operator, $\hat{V}_{ee}$ is the electron-electron repulsion energy operator, and $v(\mathbf{r})$ is a local external potential. The kinetic energy and the electron-electron energy operators have the form

$$\hat{T}=\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2\right) \tag{2}$$

and

$$\hat{V}_{ee}=\sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}. \tag{3}$$

The ground-state energy is given by the variational principle

$$E=\min_{\Psi}\langle\Psi|\hat{H}|\Psi\rangle. \tag{4}$$

The constraint search principle [10] yields

$$E=\min_{\varrho}\min_{\Psi\to\varrho}\langle\Psi|\hat{H}|\Psi\rangle. \tag{5}$$

With the universal functional F,

$$F[\varrho]=\min_{\Psi\to\varrho}\langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle, \tag{6}$$

the ground-state energy takes the form

$$E=\min_{\varrho}\left\{\int v(\mathbf{r})\varrho(\mathbf{r})d\mathbf{r}+F[\varrho]\right\}. \tag{7}$$

The second-order reduced density matrix is defined as

$$n_2(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')=\frac{N(N-1)}{2}\int\Psi(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N)\times\Psi^*(\mathbf{x}_1',\mathbf{x}_2',\mathbf{x}_3,\ldots,\mathbf{x}_N)d\mathbf{x}_3\cdots d\mathbf{x}_N, \tag{8}$$

where $\mathbf{x}_i$ stands for the spatial and the spin coordinates $\mathbf{r}_i$ and σ_i. In the following the diagonal of the spin-independent second-order density matrix

$$n(\mathbf{r}_1,\mathbf{r}_2)=\int n_2(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1,\mathbf{x}_2)d\sigma_1 d\sigma_2 \tag{9}$$

will play the fundamental role.

Now the constrained search method is applied again with the density matrix n:

$$E=\min_{n}\min_{\Psi\to n}\langle\Psi|\hat{H}|\Psi\rangle. \tag{10}$$

We can define the universal functional Q as

$$Q[n]=\min_{\Psi\to n}\langle\Psi|\hat{K}+\hat{W}|\Psi\rangle. \tag{11}$$

$Q[n]$ searches all antisymmetric wave functions Ψ which yield the given n. Consequently, the ground-state energy can also be written as

$$E=\min_{n}\left\{\frac{1}{N-1}\int u(\mathbf{r}_1,\mathbf{r}_2)n(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2+Q[n]\right\}. \tag{12}$$

The factor $1/(N-1)$ comes from the normalization of n. In Eqs. (11) and (12) the total Hamiltonian is partitioned as

$$\hat{H}=\hat{K}+\hat{W}+\hat{U}. \tag{13}$$

Following Gonis *et al.* [7] we consider the Hamiltonian (1) but as a sum of distinct, nonoverlapping pairs of particles. (A particle belongs to only one pair.) As Gonis *et al.* proposed, it is convenient to introduce six-dimensional coordinate forms combining the two particles as a single one:

$$\mathbf{q}=(\mathbf{r}_i,\mathbf{r}_j)=(x_i,y_i,z_i,x_j,y_j,z_j)=(q_1,q_2,q_3,q_4,q_5,q_6). \tag{14}$$

Then the "internal" potential for the particles in a pair $J=jj'$ is given by

$$\tilde{v}(\mathbf{r}_j,\mathbf{r}_{j'})=\frac{1}{|\mathbf{r}_j-\mathbf{r}_{j'}|}. \tag{15}$$

The interaction potential between the pairs has the form

$$\begin{aligned}W_{IJ}&=W(\mathbf{q}_I,\mathbf{q}_J)=W(\mathbf{r}_i,\mathbf{r}_{i'};\mathbf{r}_j,\mathbf{r}_{j'})\\&=\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}+\frac{1}{|\mathbf{r}_i-\mathbf{r}_{j'}|}+\frac{1}{|\mathbf{r}_{i'}-\mathbf{r}_j|}+\frac{1}{|\mathbf{r}_{i'}-\mathbf{r}_{j'}|}.\end{aligned} \tag{16}$$

The "external" potential for the pair of particles is

$$\hat{U}=\sum_I u_I=\sum_{i\neq j}^{N} u(\mathbf{r}_i,\mathbf{r}_j)=v(\mathbf{r}_i)+v(\mathbf{r}_j). \tag{17}$$

The operators $\hat{K}$ and $\hat{W}$ in the Hamiltonian (13) are defined as

$$\hat{K}=\sum_{I=1}\left(-\frac{1}{2}\nabla_I^2+\tilde{v}(\mathbf{q})\right), \tag{18}$$

$$\hat{W}=\frac{1}{2}\sum_{I\neq I} W_{IJ}. \tag{19}$$

Although this Hamiltonian H is the same as before, it is now expressed in terms of pairs of particles. The Laplacian in the kinetic energy operator can also be written as

$$\nabla_I^2=\nabla_{\mathbf{q}}^2=\nabla_i^2+\nabla_{i'}^2=\sum_{\alpha=1}^{6}\frac{\partial^2}{\partial q_{i\alpha}^2}. \tag{20}$$

$M=N/2$, that is, the number of particles is supposed to be even. The density in the six-dimensional hyperspace is defined as

$$\begin{aligned}n(\mathbf{q})&=\frac{1}{2}N(N-1)\\&\times\int|\Psi(\mathbf{r},\sigma,\mathbf{r}',\sigma',\mathbf{r}_3,\sigma_3,\ldots,\mathbf{r}_N,\sigma_N)|^2\\&\times d\sigma d\sigma' d\mathbf{r}_3,d\sigma_3,\ldots,d\mathbf{r}_N,d\sigma_N.\end{aligned} \tag{21}$$

We note that the density in the six-dimensional hyperspace is the same as the diagonal form of the spin-independent second-order reduced density matrix in the original space.

The following two theorems can be proved.

Theorem 1.

$$\frac{1}{N-1}\int n(\mathbf{q})u(\mathbf{q})+Q[n]\geqslant E_0. \tag{22}$$

Theorem 2.

$$\frac{1}{N-1}\int n_0(\mathbf{q})u(\mathbf{q})+Q[n_0]=E_0. \tag{23}$$

where E_0 and n_0 are the ground-state energy and the diagonal of the spin-independent second-order density matrix, respectively.

Proof of Theorem 1. From the definition of $Q(n)$ [Eq. (11)] we obtain

$$\begin{aligned}&\frac{1}{N-1}\int n(\mathbf{q})u(\mathbf{q})+Q[n]\\&=\min_{\Psi\to n}\langle\Psi|\hat{K}+\hat{W}|\Psi\rangle+\frac{1}{N-1}\int n(\mathbf{q})u(\mathbf{q})\\&=\min_{\Psi\to n}\langle\Psi|\hat{K}+\hat{W}+\hat{U}|\Psi\rangle.\end{aligned} \tag{24}$$

From the variational principle

$$\langle\Psi_{min}^{n}|\hat{T}+\hat{W}+\hat{U}|\Psi_{min}^{n}\rangle\geqslant E_0. \tag{25}$$

Equations (24) and (25) give Eq. (22), which completes the proof of Theorem 1.

Proof of Theorem 2. The ground-state energy can be given by the variational principle

$$E=\min_{\Psi}\langle\Psi|\tilde{H}|\Psi\rangle. \tag{26}$$

The constraint search principle [10] leads to the expression

$$E=\min_{n}\min_{\Psi\to n}\langle\Psi|\tilde{H}|\Psi\rangle. \tag{27}$$

We can define the universal functional Q as

$$Q[n]=\min_{\Psi\to n}\langle\Psi|\tilde{H}|\Psi\rangle. \tag{28}$$

$Q[n]$ searches all antisymmetric wave functions Ψ that yield the hyperspace density n. Then the ground-state energy has the form

$$E=\min_{n}\left\{\frac{1}{N-1}\int V(\mathbf{q})n(\mathbf{q})d\mathbf{q}+Q[n]\right\}. \tag{29}$$

Theorems 1 and 2 can be considered the generalized Hohenberg-Kohn theorems [9]. In Sec. III the "generalized Kohn-Sham equations" will be obtained. The derivation and the results are different from those of Gonis *et al.* Here the spirit of the adiabatic connection derivation of the Kohn-Sham equations is utilized.

III. AUXILIARY EQUATIONS THROUGH ADIABATIC CONNECTION

In the density functional theory we construct the Hamiltonian

$$\hat{H}_{v}^{\alpha}=\hat{T}+\alpha\hat{V}_{ee}+\sum_{i=1}^{N}v^{\alpha}(\mathbf{r}_i), \tag{30}$$

where $v^{\alpha}(\mathbf{r})$ is defined such that the density $\varrho(\mathbf{r})$ remains independent of α. This adiabatic connection leads to the noninteracting system, for which $\alpha=0$,

$$\hat{H}_{v}^{\alpha=0}=\hat{T}+\sum_{i=1}^{N}v^{\alpha=0}(\mathbf{r}_i). \tag{31}$$

It is well known that for a nondegenerate ground state the noninteracting wave function is a Slater determinant constructed from one-particle functions ϕ_i satisfying the Kohn-Sham equations [11]

$$\left[-\frac{1}{2}\nabla^2+v^0(\varrho;\mathbf{r})\right]\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r}). \tag{32}$$

The one-particle electron density is given by

$$\varrho(\mathbf{r})=\sum_{i=1}^{N}\sum_{\sigma}|\phi_i(\mathbf{x})|^2. \tag{33}$$

The Kohn-Sham equations can be derived by the minimization principle for the noninteracting kinetic energy

$$T_s=\min_{\Phi\to\varrho}\langle\Phi|\hat{T}|\Phi\rangle. \tag{34}$$

Adiabatic connection can also be performed in the hyperspace. Define the Hamiltonian

$$\hat{H}^{\alpha}=\hat{K}+\alpha\hat{W}+\hat{U}^{\alpha}, \tag{35}$$

where $\hat{U}^{\alpha}=\Sigma_I u_I^{\alpha}(\mathbf{q})$ is defined such that the hyperspace density $n(\mathbf{q})$ remains independent of α. For $\alpha=0$ the noninteracting Hamiltonian

$$\hat{H}^{\alpha=0}=\hat{K}+\hat{U}^{\alpha=0}=\sum_{I=1}h_I^{\alpha=0} \tag{36}$$

is obtained, where

$$h_I^{\alpha=0}=-\frac{1}{2}\nabla_I^2+\tilde{v}(\mathbf{q}_I)+u^{\alpha=0}. \tag{37}$$

The hyperspace "Kohn-Sham like equation" has the form

$$\hat{H}^0\Psi^0=E^0\Psi^0, \tag{38}$$

where

$$\Psi^0(\mathbf{x}_1,\ldots,\mathbf{x}_N)=\hat{S}(\chi_1(\mathbf{x}_1,\mathbf{x}_2)\cdots\chi_M(\mathbf{x}_{N-1},\mathbf{x}_N)). \tag{39}$$

$\hat{S}$ is the symmetrizer operator and the antisymmetric functions χ_I satisfy the equations

$$\begin{aligned}h^0(\mathbf{q})\chi_I(\mathbf{x}_1,\mathbf{x}_2)&=\left[-\frac{1}{2}\nabla_{\mathbf{q}}^2+\tilde{v}(\mathbf{q})+u^0(\mathbf{q})\right]\chi_I(\mathbf{x}_1,\mathbf{x}_2)\\&=\varepsilon_I\chi_I(\mathbf{x}_1,\mathbf{x}_2).\end{aligned} \tag{40}$$

One can easily see from the definition of the Hamiltonian $\hat{H}^0$ that $\hat{H}^0$ is invariant with respect to the exchange of the coordinates of electrons within one pair but it is not invariant if the coordinates of electrons in different pairs are exchanged. Consider for example the simplest nontrivial case, that is, the case of four electrons. Then the "noninteracting" Hamiltonian has the form

$$\begin{aligned}\hat{H}^0&=\sum_{I=1}^{2}\left[-\frac{1}{2}\nabla_{\mathbf{q}_I}^2+\tilde{v}(\mathbf{q}_I)+u^0(\mathbf{q}_I)\right]\\&=\sum_{i=1}^{4}\left[-\frac{1}{2}\nabla_i^2\right]+u^0(\mathbf{r}_1,\mathbf{r}_2)+u^0(\mathbf{r}_3,\mathbf{r}_4)+\frac{1}{r_{12}}+\frac{1}{r_{34}}.\end{aligned} \tag{41}$$

$\hat{H}_0$ is invariant with respect to the exchange of the coordinates of electrons 1 and 2 or 3 and 4 but it is not invariant if the coordinates of electrons 1 and 3 or 2 and 4 are exchanged. The "noninteracting" wave function takes the form

$$\begin{aligned}\Psi^0(\mathbf{x}_1,\ldots,\mathbf{x}_4)=2^{-1/2}[&\chi_1(\mathbf{x}_1,\mathbf{x}_2)\chi_2(\mathbf{x}_3,\mathbf{x}_4)\\&+\chi_2(\mathbf{x}_1,\mathbf{x}_2)\chi_1(\mathbf{x}_3,\mathbf{x}_4)].\end{aligned} \tag{42}$$

The "hyperspace Kohn-Sham equations" can be derived by constrained search. In the derivation of the original Kohn-Sham equations of the density functional theory the kinetic energy is minimized with the constraint that the electron density is fixed,

$$T_s=\min_{\Phi\to\varrho}\langle\Phi|\hat{T}|\Phi\rangle=\langle\Phi[\varrho]|\hat{T}|\Phi[\varrho]\rangle. \tag{43}$$

To obtain the "hyperspace Kohn-Sham equations" one just has to write $\hat{K}$ instead of $\hat{T}$. Then we have to minimize the expectation value

$$\langle \Psi^0|\hat{K}|\Psi^0\rangle \tag{44}$$

with the constraint that n is fixed. Substituting the "noninteracting" wave function (39) into the diagonal form of the spin-independent second-order reduced density matrix [Eq. (21)] we are led to

$$n(\mathbf{q})=(N-1)\sum_{I=1}^{M}\sum_{\sigma}|\chi_I(\mathbf{x}_1,\mathbf{x}_2)|^2. \tag{45}$$

Then the minimization of

$$\langle \Psi^0|\hat{K}|\Psi^0\rangle+\sum_I\int|\chi_I|^2u(\mathbf{q})-\sum_{I,J}\tilde{\varepsilon}_{I,J}\int\chi_I^*\chi_J \tag{46}$$

with respect to the antisymmetric functions χ_I leads to the Kohn-Sham like equations (40) after a unitary transformation.

The minimum energy is obtained if all two-particle functions χ_I are the same: $\chi_I=\chi_0$. Then

$$n(\mathbf{q})=\frac{N(N-1)}{2}\sum_{\sigma}|\chi_0(\mathbf{x}_1,\mathbf{x}_2)|^2=\frac{N(N-1)}{2}|\tilde{\chi}_0(\mathbf{q})|^2. \tag{47}$$

It means that the calculation of n is reduced to the solution of a two-particle equation

$$h^0(\mathbf{q})\tilde{\chi}_0(\mathbf{q})=\left[-\frac{1}{2}\nabla^2_{\mathbf{q}}+v_{eff}(\mathbf{q})\right]\tilde{\chi}_0(\mathbf{q})=\varepsilon_0\tilde{\chi}_0(\mathbf{q}), \tag{48}$$

where

$$v_{eff}(\mathbf{q})=\tilde{v}(\mathbf{q})+u^0(\mathbf{q}), \tag{49}$$

that is, the N-body problem can be reduced to a two-body problem.

Theorem 3. The auxiliary potential v_{eff} is uniquely determined by the diagonal form of the spin-independent second-order density matrix.

Proof of Theorem 3. The auxiliary potential v_{eff} can easily be constructed. From Eq. (47) the two-particle function $\tilde{\chi}_0$ is given by

$$\tilde{\chi}_0(\mathbf{q})=\left(\frac{2}{N(N-1)}n(\mathbf{q})\right)^{1/2} \tag{50}$$

up to a phase factor. Then from Eq. (48) we arrive at the expression

$$v_{eff}(\mathbf{q})=\varepsilon_0+\frac{1}{2\tilde{\chi}_0(\mathbf{q})}\nabla^2_{\mathbf{q}}\tilde{\chi}_0(\mathbf{q}). \tag{51}$$

So the auxiliary potential v_{eff} is obtained up to an additive constant.

Although the potential v_{eff} can be exactly determined if n is known, it does not mean that v_{eff} is known as a functional of n. (v_{eff} can only be obtained as a function of $\mathbf{q}$. One should find an approximation for v_{eff} in order to perform calculations.)

Theorem 4. The auxiliary potential has the form $v_{eff}=v(\mathbf{r}_1)+v(\mathbf{r}_2)+(N-1)/r_{12}+v_k(\mathbf{q})$ where $v_k(\mathbf{q})$ is of completely kinetic origin.

Proof of Theorem 4. E^α can be written as

$$\begin{aligned}E^\alpha&=\langle\Psi^\alpha|\hat{H}^\alpha|\Psi^\alpha\rangle\\&=\hat{K}^\alpha+\alpha\langle\Psi^\alpha|\hat{W}|\Psi^\alpha\rangle+\frac{1}{N-1}\int n(\mathbf{q})u^\alpha(\mathbf{q}).\end{aligned} \tag{52}$$

Writing

$$u^\alpha(\mathbf{q})=u^{\alpha=1}(\mathbf{q})+\tilde{u}^\alpha(\mathbf{q})=v(\mathbf{r}_1)+v(\mathbf{r}_2)+\tilde{u}^\alpha \tag{53}$$

and using Eqs. (18) and (19) we obtain

$$\begin{aligned}E^\alpha&=T^\alpha+\frac{1}{N-1}\int\left[v(\mathbf{r}_1)+v(\mathbf{r}_2)+\frac{1}{r_{12}}\right]n(\mathbf{q})d\mathbf{q}+\frac{1}{N-1}\int\tilde{u}^\alpha(\mathbf{q})n(\mathbf{q})d\mathbf{q}+\alpha\frac{N-2}{N-1}\int\frac{n(\mathbf{q})}{r_{12}}d\mathbf{q}\\&=T^\alpha+\frac{1}{N-1}\int[v(\mathbf{r}_1)+v(\mathbf{r}_2)]n(\mathbf{q})d\mathbf{q}+\frac{1}{N-1}\int\tilde{u}^\alpha(\mathbf{q})n(\mathbf{q})d\mathbf{q}+\frac{1}{N-1}[1+\alpha(N-2)]\int\frac{n(\mathbf{q})}{r_{12}}d\mathbf{q}.\end{aligned} \tag{54}$$

For the auxiliary system with $\alpha=0$, Eq. (54) leads to

$$\begin{aligned}E^0=T^0&+\frac{1}{N-1}\int[v(\mathbf{r}_1)+v(\mathbf{r}_2)]n(\mathbf{q})d\mathbf{q}\\&+\frac{1}{N-1}\int\tilde{u}^0(\mathbf{q})n(\mathbf{q})d\mathbf{q}+\frac{1}{N-1}\int\frac{n(\mathbf{q})}{r_{12}}d\mathbf{q}.\end{aligned} \tag{55}$$

The total energy of the real system [Eq. (54)] has the form

$$E=T+\frac{1}{N-1}\int[v(\mathbf{r}_1)+v(\mathbf{r}_2)]n(\mathbf{q})d\mathbf{q}+\int\frac{n(\mathbf{q})}{r_{12}}d\mathbf{q}. \tag{56}$$

E can also be written in a form that contains the kinetic energy of the auxiliary system:

$$E=T^0+T_c+\frac{1}{N-1}\int[v(\mathbf{r}_1)+v(\mathbf{r}_2)]n(\mathbf{q})d\mathbf{q}+\int\frac{n(\mathbf{q})}{r_{12}}d\mathbf{q}, \tag{57}$$

where

$$T_c=T-T^0 \tag{58}$$

is the difference between the kinetic energies of the real and the auxiliary systems. Using Eq. (39) we arrive at

$$T^0=\sum_{I=1}^{M}\int \chi_I^*(\mathbf{x}_1,\mathbf{x}_2)\left[-\frac{1}{2}\nabla_{\mathbf{q}}^2\right]\chi_I(\mathbf{x}_1,\mathbf{x}_2). \tag{59}$$

Variation of E [Eq. (57)] with respect to the χ_I's leads to the set of auxiliary equations

$$\left[-\frac{1}{2}\nabla_{\mathbf{q}}^2+v_{eff}(\mathbf{q})\right]\chi_I(\mathbf{x}_1,\mathbf{x}_2)=\varepsilon_I^0\chi_I(\mathbf{x}_1,\mathbf{x}_2), \tag{60}$$

where the effective potential has the form

$$\begin{aligned}v_{eff}(\mathbf{q})&=v(\mathbf{r}_1)+v(\mathbf{r}_2)+\frac{1}{r_{12}}+\frac{N-2}{r_{12}}+(N-1)\frac{\delta T_c}{\delta n}\\&=v(\mathbf{r}_1)+v(\mathbf{r}_2)+\frac{N-1}{r_{12}}+v_k,\end{aligned} \tag{61}$$

where

$$v_k=(N-1)\frac{\delta T_c}{\delta n}. \tag{62}$$

So the term v_k in the effective potential is of completely kinetic origin.

IV. DISCUSSION

In this paper an auxiliary system is defined. The diagonal of the spin-independent second-order reduced density matrix n is the same in both the real and the auxiliary systems. In the ground state n can be determined by solving a single auxiliary equation of a two-particle problem. The fact that the problem of an arbitrary system with even electrons can be reduced to a two-particle problem means enormous simplification. A very important property of the effective potential has been explored. It contains a term of completely kinetic origin. An adequate enough approximation of this term would lead to a very simple treatment of an electron system. To study the further properties of this term and to find an approximation to it should be the subject of further research. While in the original density functional theory T_c is a rather small quantity, here T_c is expected to be much larger, increasing roughly linearly with the number of electrons.

It is important to emphasize that this auxiliary system is just an imagined system. The particles in it are neither fermions nor bosons. The wave function is neither antisymmetric nor symmetric. It is just a symmetrized expression of antisymmetric two-particle functions. There is some similarity in spirit to the antisymmetrized geminal wave function advocated by Coleman [3]. Of course, the latter is related to the real system, while the former corresponds to the auxiliary system. It should also be noted that the idea of constructing wave functions as products of geminals is well established [12].

One of the fundamental problems in density-matrix theory is the N-representability problem. In the present theory, there exists a wave function for any value of the coupling constant α. If we have the exact n, then it follows from Theorem 3 that the noninteracting N representability is also valid. We can see from Eq. (50) that the noninteracting N representability is also valid for an approximate n. However, an approximate n does not generally satisfy N representability [13]. So the form of the approximate functional will be crucial from the point of view of N representability.

ACKNOWLEDGMENT

OTKA Grant No. T 029469 is gratefully acknowledged.

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