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Properties of the Goedecker-Umrigar functional for the many-electron problem and its generalization

A. Holas
Institute of Physical Chemistry of the Polish Academy of Sciences, 44/52 Kasprzaka, 01-224 Warsaw, Poland

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The calculational scheme for an approximate ground-state energy of a many-electron system, recently proposed by Goedecker and Umrigar (GU) [Phys. Rev. Lett. **81**, 866 (1998)], is analyzed in terms of the reduced-density-matrix approach. Its underlying object, the GU density-matrix functional, is generalized, possibly leading to improved energies. Properties of the solutions of the ground-state problem obtained from the original and the generalized GU functionals are established. [S1050-2947(99)08605-9]

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I. INTRODUCTION

Determination of the ground-state (GS) energy of many-fermion systems is a problem frequently encountered in various investigations in atomic, molecular, condensed matter, and nuclear physics. Therefore, reliable and efficient calculational schemes for its solution are of great value and interest. Many such schemes are already available that differ in accuracy and computational complexity, such as the Hartree-Fock approach or the density-functional theory (see, e.g., [1]) with various levels of sophistication for the exchange-correlation energy functional. Nevertheless there is a need for more accurate approaches. A very promising recent calculational scheme of Goedecker and Umrigar (GU) [2] represents a successful step forward in developing the so-called reduced-density-matrix approach to the GS problem (see, e.g., the proceedings [3]). My aim is to provide a better understanding of this scheme within the general density-matrix approach, because the GU paper [2] concentrated mainly on demonstrating the effectiveness of the scheme. The present analysis results also in generalization of the underlying GU density-matrix functional.

To be specific, I am going to consider in this paper, similarly as GU in [2], an N-electron system with one- and two-body interactions, described by the Hamiltonian

$$\hat{H}(\mathbf{x}_1,\ldots,\mathbf{x}_N)=\sum_{i=1}^{N}\hat{h}_1(\mathbf{x}_i)+\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}h_2(\mathbf{x}_i,\mathbf{x}_j), \tag{1.1}$$

where $\mathbf{x}_i\equiv\{\mathbf{r}_i s_i\}\equiv\mathbf{i}$ denotes the space-spin coordinate of ith electron, $h_2(\mathbf{j},\mathbf{i})=h_2(\mathbf{i},\mathbf{j})>0$. In applications,

$$\hat{h}_1(\mathbf{1})=\hat{t}(\mathbf{r}_1)+v_{\mathrm{ext}}(\mathbf{r}_1) \tag{1.2}$$

is a sum of the kinetic energy (differential operator) and the external potential (local operator, e.g., due to Coulombic interactions with fixed nuclei), while

$$h_2(\mathbf{1},\mathbf{2})=\frac{e^2}{\kappa_0\,|\mathbf{r}_1-\mathbf{r}_2|} \tag{1.3}$$

is the electron-electron repulsion energy.

II. REDUCED-DENSITY-MATRIX APPROACH

In the reduced-density-matrix approach, one obtains the GS energy E_{GS} by varying an expression for the energy over reduced density matrices rather than wave functions. At the level of the N-body density matrices (NDM's), these two ways are equivalent, because, according to the variational principle, E_{GS} can be obtained from the following minimizations with respect to $\{C_\lambda,\Psi_\lambda\}$ or with respect to NDM's γ_N, which belong to the set $\mathcal{P}(N,N)$ of the ensemble-N-representable DM's:

$$\begin{aligned}E_{\mathrm{GS}}&=\min_{\{C_\lambda,\Psi_\lambda\}\in\mathrm{Eq.\,(2.5)}}\sum_{\lambda}C_\lambda\langle\Psi_\lambda|\hat{H}|\Psi_\lambda\rangle\\&=\min_{\gamma_N\in\mathcal{P}(N,N)}\{E_1[\check{\gamma}_1[\gamma_N]]+E_2[\check{\gamma}_2[\gamma_N]]\}\\&=\{\ldots\}|_{\gamma_N=\gamma_N^{\mathrm{GS}}}.\end{aligned} \tag{2.1}$$

Here (see, e.g., [1])

$$\begin{aligned}\check{\gamma}_p(\mathbf{1}\ldots\mathbf{p};\mathbf{1}'\ldots\mathbf{p}';[g_N])&=\binom{N}{p}\int d(\mathbf{p}+\mathbf{1})\cdots d\mathbf{N}\\&\quad\times g_N(\mathbf{1}\ldots\mathbf{N};\mathbf{1}'\ldots\mathbf{p}'(\mathbf{p}+\mathbf{1})\ldots\mathbf{N})\end{aligned} \tag{2.2}$$

is the p-body density matrix (pDM) obtained by reduction of an arbitrary NDM g_N, thus $\check{\gamma}_p$ is a functional of g_N,

$$E_1[g_1]=\int d\mathbf{1}\,\hat{h}_1(\mathbf{1})g_1(\mathbf{1};\mathbf{1}')\Big|_{\mathbf{1}'=\mathbf{1}} \tag{2.3}$$

and

$$E_2[g_2]=\int d\mathbf{1}\,d\mathbf{2}\,h_2(\mathbf{12})g_2(\mathbf{12};\mathbf{12}) \tag{2.4}$$

are functionals of g_1 and g_2, involving the one-body and two-body operators of $\hat{H}$, $\int d\mathbf{j}$ means $\Sigma_{s_j}\int d^3r_j$. In the

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present paper, g_1, g_2, g_N denote arbitrary 1DM, 2DM, *N*DM, possibly lacking N representability. The property $\gamma_N \in \mathcal{P}(N,N)$ is defined by

$$\gamma_N(\mathbf{1}\ldots\mathbf{N};\mathbf{1}'\ldots\mathbf{N}')=\sum_{\lambda} C_\lambda \Psi_\lambda(\mathbf{1}\ldots\mathbf{N})\Psi^*_\lambda(\mathbf{1}'\ldots\mathbf{N}'), \tag{2.5a}$$

$$C_\lambda \geqslant 0, \quad \sum_\lambda C_\lambda = 1, \quad \langle \Psi_\lambda | \Psi_\mu \rangle = \delta_{\lambda\mu}, \tag{2.5b}$$

$$\Psi_\lambda(\ldots\mathbf{i}\ldots\mathbf{j}\ldots) = -\Psi_\lambda(\ldots\mathbf{j}\ldots\mathbf{i}\ldots). \tag{2.5c}$$

Obviously, for the minimizer γ_N^{GS} in Eq. (2.1), only the GS wave functions enter Eq. (2.5a). Therefore, if the GS is degenerate, the minimizer is not unique.

Since the expression for the energy involves only 1DM and 2DM, Eq. (2.1) can be rewritten as the following minimization with respect to ensemble-*N*-representable reduced 2DM's:

$$E_{\mathrm{GS}} = \min_{\gamma_2 \in \mathcal{P}(N,2)} \{E_1[\check{\gamma}_1[\gamma_2]] + E_2[\gamma_2]\}, \tag{2.6}$$

where the 1DM $\check{\gamma}_1$, a functional of 2DM g_2, defined as

$$\check{\gamma}_1(\mathbf{1};\mathbf{1}';[g_2]) = \frac{2}{(N-1)}\int d\mathbf{2}\, g_2(\mathbf{12};\mathbf{1}'\mathbf{2}) \tag{2.7}$$

represents a reduction of the 2DM g_2, which is consistent with the general reduction rule, Eq. (2.2). By definition, the relation $\gamma_2 \in \mathcal{P}(N,2)$ means that

$$\gamma_2 = \check{\gamma}_2[\gamma_N] \quad \text{with} \quad \gamma_N \in \mathcal{P}(N,N), \tag{2.8}$$

see Eq. (2.5). Unfortunately, all sufficient conditions to define the set $\mathcal{P}(N,2)$, equivalent to one described in Eq. (2.8) with Eq. (2.5), but solely in terms of constraints imposed on the form of 2DM's, are unknown, as yet.

Nevertheless, if only some selected constraints (among them Hermiticity and proper normalization) are imposed on 2DM's during minimization in Eq. (2.6), then, as observed by Coleman [4] and Garrod and Percus [5], the lower bound to the GS energy is obtained

$$E_{\mathrm{GS}} > E_{\mathrm{GS}}^{\mathcal{A}(N,2)} = \min_{g_2 \in \mathcal{A}(N,2)} \{E_1[\check{\gamma}_1[g_2]] + E_2[g_2]\}. \tag{2.9}$$

Here $\mathcal{A}(N,2)$ denotes the set of 2DM's which satisfy the mentioned constraints, while $\mathcal{A}(N,2) \supset \mathcal{P}(N,2)$ must hold. The last relation justifies the direction of inequality in Eq. (2.9) [compare with Eq. (2.6)]. In order to perform the minimization in Eq. (2.9), one usually expands the trial 2DM g_2 in some basis set of spin orbitals. The expansion coefficients play the role of variational parameters. Various authors define their $\mathcal{A}(N,2)$ by a set of constraints imposed on these parameters (see, e.g., [4–16], and references therein). Tests show that in some cases quite tight lower bounds are generated.

Contrary to the 2DM case, the necessary and sufficient conditions [4] for 1DM to be ensemble-*N*-representable, $\gamma_1 \in \mathcal{P}(N,1)$, i.e., $\gamma_1 = \check{\gamma}_1[\gamma_N]$ with $\gamma_N \in \mathcal{P}(N,N)$, are known, namely that its spectral resolution is in the form

$$\gamma_1(\mathbf{1};\mathbf{1}') = \sum_i n_i\, \phi_i(\mathbf{1})\, \phi_i^*(\mathbf{1}'), \tag{2.10a}$$

$$0 \leqslant n_i \leqslant 1, \tag{2.10b}$$

$$\sum_i n_i = N, \quad \langle \phi_i | \phi_j \rangle = \delta_{ij}, \tag{2.10c}$$

where $n_i, \phi_i(\mathbf{1})$ are called natural occupation numbers and natural spin orbitals. Due to the explicit knowledge of $\mathcal{P}(N,1)$, another reduced-density-matrix approach to the GS problem can be defined (see Levy [17], and references therein for earlier papers) by performing minimization in Eq. (2.6) in two steps, internal over γ_2, external over γ_1:

$$E_{\mathrm{GS}} = \min_{\gamma_1 \in \mathcal{P}(N,1)} \{E_1[\gamma_1] + E_2[\tilde{\gamma}_2^{\min}[\gamma_1]]\}, \tag{2.11}$$

where the functional $\tilde{\gamma}_2^{\min}$ of γ_1 is defined by minimization of E_2 over γ_2:

$$E_2[\tilde{\gamma}_2^{\min}[\gamma_1]] = \min_{\gamma_2 \in \mathcal{P}(N,2) \wedge \check{\gamma}_1[\gamma_2] = \gamma_1} E_2[\gamma_2] \tag{2.12}$$

constrained by the requirement for γ_2 to be reducible [see Eq. (2.7)] to the given γ_1. So this requirement is satisfied also by the minimizer:

$$\check{\gamma}_1[\tilde{\gamma}_2^{\min}[\gamma_1]] = \gamma_1. \tag{2.13}$$

Due to this fact, the argument of the E_1 term in Eq. (2.11) is so simple [compare Eq. (2.6)].

III. EXTENDED GOEDECKER-UMRIGAR APPROACH

Unfortunately, the definition (2.12) does not provide the form of $\tilde{\gamma}_2^{\min}[\gamma_1]$ for computational purposes, because the sufficient conditions for $\gamma_2 \in \mathcal{P}(N,2)$ are unknown. Nevertheless, a useful approach to the GS energy problem can be obtained from Eq. (2.11) if some approximation to the $\tilde{\gamma}_2^{\min}[\gamma_1]$ functional, based on intuition and heuristic arguments, is constructed. This is done by GU [2]. Their approximation, denoted now as $\tilde{\gamma}_2^{\{1/2\}\prime}[\gamma_1]$, may be defined as the orbital-self-interaction-free part ($i \neq j$ terms) of the following (extended here) GU functional:

$$\tilde{\gamma}_2^{\{1/2\}} = \tilde{\gamma}_2^{\{1/2\}\prime} + \tilde{\gamma}_2^{\{1/2\}\prime\prime} \tag{3.1a}$$

written in terms of natural occupations and orbitals of γ_1, Eq. (2.10), as

$$\tilde{\gamma}_2^{\{1/2\}}(\mathbf{12};\mathbf{1}'\mathbf{2}';[\gamma_1])=\tfrac{1}{2}\sum_{ij}\,[n_i n_j \phi_i(\mathbf{1})\phi_i^*(\mathbf{1}')\phi_j(\mathbf{2})\phi_j^*(\mathbf{2}')-n_i^{1/2}n_j^{1/2}\phi_i(\mathbf{1})\phi_i^*(\mathbf{2}')\phi_j(\mathbf{2})\phi_j^*(\mathbf{1}')], \tag{3.1b}$$

where its orbital-self-interaction part ($j=i$ terms) is

$$\tilde{\gamma}_2^{\{1/2\}''}(\mathbf{12};\mathbf{1}'\mathbf{2}';[\gamma_1]) =-\tfrac{1}{2}\sum_i\,[(1-n_i)n_i\phi_i(\mathbf{1})\phi_i(\mathbf{2})\phi_i^*(\mathbf{1}')\phi_i^*(\mathbf{2}')]. \tag{3.1c}$$

In fact, GU defined only the diagonal elements of the 2DM functional, their $\sigma(\mathbf{12})=\tilde{\gamma}_2^{\{1/2\}'}(\mathbf{12};\mathbf{12})$, since that is all that is required to determine E_2 from Eq. (2.4).

The definition (3.1b) of $\tilde{\gamma}_2^{\{1/2\}}$ can be rewritten more compactly in terms of γ_1^{α}—the α power of $\gamma_1 \equiv \gamma_1^1$, for $\alpha>0$:

$$\gamma_1^{\alpha}(\mathbf{1};\mathbf{1}')=\sum_i\, n_i^{\alpha}\,\phi_i(\mathbf{1})\,\phi_i^*(\mathbf{1}'), \tag{3.2a}$$

which, due to the properties shown in Eq. (2.10), satisfies the usual multiplication rule

$$(\gamma_1^{\alpha} *\, \gamma_1^{\beta})(\mathbf{1};\mathbf{1}')\equiv\int d\mathbf{1}''\,\gamma_1^{\alpha}(\mathbf{1};\mathbf{1}'')\gamma_1^{\beta}(\mathbf{1}'';\mathbf{1}')=\gamma_1^{\alpha+\beta}(\mathbf{1};\mathbf{1}'), \tag{3.2b}$$

namely,

$$\tilde{\gamma}_2^{\{1/2\}}(\mathbf{12};\mathbf{1}'\mathbf{2}';[\gamma_1]) =\tfrac{1}{2}[\gamma_1^1(\mathbf{1};\mathbf{1}')\,\gamma_1^1(\mathbf{2};\mathbf{2}')-\gamma_1^{1/2}(\mathbf{1};\mathbf{2}')\,\gamma_1^{1/2}(\mathbf{2};\mathbf{1}')]. \tag{3.3}$$

It is convenient to define the functionals for the norms of 1DM and 2DM as

$$N_1[g_1]=\int d\mathbf{1}\,g_1(\mathbf{1};\mathbf{1}), \tag{3.4}$$

$$N_2[g_2]=\int d\mathbf{1}\,d\mathbf{2}\,g_2(\mathbf{12};\mathbf{12}). \tag{3.5}$$

The norm of the ensemble-*N*-representable γ_1, Eq. (2.10), satisfies obviously

$$N_1[\gamma_1]=N. \tag{3.6}$$

It can be checked immediately from Eq. (3.3), using Eqs. (3.2b) and (3.6), that the result of reducing $\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]$ to 1DM, Eq. (2.7), coincides with the argument γ_1,

$$\check{\gamma}_1[\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]]=\gamma_1. \tag{3.7}$$

This means that $\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]$, the approximation to $\tilde{\gamma}_2^{\min}[\gamma_1]$, obeys the same requirement as $\tilde{\gamma}_2^{\min}[\gamma_1]$ does, Eq. (2.13). Since GU defined only the diagonal elements of $\tilde{\gamma}_2^{\{1/2\}'}$, they were able to recognize this attribute on the diagonal only. From the property shown in Eq. (3.7) follows immediately the normalization of $\tilde{\gamma}_2^{\{1/2\}}$ to the number of pairs in the system [2]:

$$N_2[\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]]=\tfrac{1}{2}(N-1)N \qquad \text{for any} \quad \gamma_1\in\mathcal{P}(N,1). \tag{3.8}$$

GU were aware of this, but they state in their paper that they prefer to use $\tilde{\gamma}_2^{\{1/2\}'}=\tilde{\gamma}_2^{\{1/2\}}-\tilde{\gamma}_2^{\{1/2\}''}$, Eq. (3.1a), which violates Eqs. (3.7) and (3.8), although the numerical error, e.g.,

$$N_2[-\tilde{\gamma}_2^{\{1/2\}''}[\gamma_1]]=\sum_i\,\tfrac{1}{2}(1-n_i)n_i, \tag{3.9}$$

is very small for most systems where the natural occupations n_i are close either to zero or to one. But this may not be true in the case of systems with a degenerate GS.

In my opinion, Eqs. (3.7) and (3.8) are so fundamental that $\tilde{\gamma}_2^{\{1/2\}}$, rather than $\tilde{\gamma}_2^{\{1/2\}'}$, should be preferred as the approximation to $\tilde{\gamma}_2^{\min}$. But the GU opinion is opposite [2], although no arguments are given. By excluding the $\tilde{\gamma}_2^{\{1/2\}''}$ term, they choose to have no orbital self-interactions in their functional. When discussing this problem, GU state that their functional is not perfectly electron self-interaction free, and, therefore, leads to the incorrect value of the calculated GS energy for the hydrogen atom. I propose a different view on this subject. Since the electron self-interactions are excluded from the Hamiltonian (1.1) (summations restricted by $j\neq i$), the exact reduced-density-matrix approach (2.11) to a system described by this Hamiltonian ought to be regarded as electron self-interaction free. The errors of the calculated GS energy for H and other atoms, observed by GU, are due to the approximate nature of the functional $\tilde{\gamma}_2^{\{1/2\}'}[\gamma_1]$, used instead of the exact (but unknown) $\tilde{\gamma}_2^{\min}[\gamma_1]$. It should be noted that this approximate 2DM functional (and also its extension $\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]$) is capable of producing exact results for one-electron systems, provided the spectral resolution of the trial γ_1 in Eq. (2.10) is limited to only one natural orbital. Then both $\tilde{\gamma}_2^{\{1/2\}'}[\gamma_1]$ and $\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]$ behave as the exact $\tilde{\gamma}_2^{\min}$—they vanish (thus showing absence of the electron-electron interaction for $N=1$). But an exact density-matrix approach to any one-electron system is represented by Eq. (2.11) with $\tilde{\gamma}_2^{\min}=0$ inserted (and no limit on the number of natural orbitals). However, if a dissociation of a many-electron molecule into one-electron atoms (ions) is investigated within the approximation based on $\tilde{\gamma}_2^{\{1/2\}'}[\gamma_1]$ or $\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]$, approximate solutions are obtained for $N=1$ fragments (i.e., with nonvanishing 2DM) rather than the abovementioned exact versions. It is worth noting that $\tilde{\gamma}_2^{\min}$ is an implicit function of *N*, because its definition, Eq. (2.12), involves *N*.

IV. GENERALIZATION OF THE GU FUNCTIONAL

The GU choice of the power 1/2 in the definition (3.3) of the approximation to $\tilde{\gamma}_2^{\min}[\gamma_1]$ can be generalized to an arbitrary power $a>0$ by defining the following approximate functional:

$$\begin{aligned}\tilde{\gamma}_2^{\{a\}}&(\mathbf{12};\mathbf{1'2'};[\gamma_1])\\ &=\tfrac{1}{2}\{\gamma_1^1(\mathbf{1};\mathbf{1'})\,\gamma_1^1(\mathbf{2};\mathbf{2'})-\tfrac{1}{2}[\gamma_1^a(\mathbf{1};\mathbf{2'})\,\gamma_1^{1-a}(\mathbf{2};\mathbf{1'})\\ &\quad+\gamma_1^{1-a}(\mathbf{1};\mathbf{2'})\,\gamma_1^a(\mathbf{2};\mathbf{1'})]\}, \qquad \text{for} \quad 0<a\leqslant\tfrac{1}{2}\end{aligned} \tag{4.1}$$

(it is sufficient to take $a\leqslant\frac{1}{2}$ because $\tilde{\gamma}_2^{\{1-a\}}=\tilde{\gamma}_2^{\{a\}}$). Obviously, for $a=\frac{1}{2}$, this definition reduces to that in Eq. (3.3). It is easy to verify that the 2DM functional $\tilde{\gamma}_2^{\{a\}}[\gamma_1]$, Eq. (4.1), obeys the requirement satisfied by $\tilde{\gamma}_2^{\min}[\gamma_1]$ in Eq. (2.13). Actually, the same requirement is satisfied by a linear combination of the $\tilde{\gamma}_2^{\{a\}}$ terms with different powers a:

$$\tilde{\gamma}_2^{\{\mathbf{a}\}}=\sum_{\kappa} a_{1\kappa}\tilde{\gamma}_2^{\{a_{2\kappa}\}} \tag{4.2a}$$

provided its coefficients are related by the equation

$$\sum_{\kappa} a_{1\kappa}=1. \tag{4.2b}$$

It will be convenient to rewrite Eq. (4.2) in terms of $2K$ independent parameters $\mathbf{a}=\{a_{1\kappa},a_{2\kappa}\}_{\kappa=1}^{K}$, namely

$$\tilde{\gamma}_2^{\{\mathbf{a}\}}=\left(1-\sum_{\kappa=1}^{K} a_{1\kappa}\right)\tilde{\gamma}_2^{\{1/2\}}+\sum_{\kappa=1}^{K} a_{1\kappa}\,\tilde{\gamma}_2^{\{a_{2\kappa}\}}, \tag{4.3a}$$

where

$$-\infty<a_{1\kappa}<+\infty, \quad 0<a_{2\kappa}<\tfrac{1}{2}, \tag{4.3b}$$

by choosing $a_{20}=1/2$ and $a_{10}=1-\Sigma_{\kappa=1}^{K}a_{1\kappa}$. At $K=0$ the definition (4.3) reduces to the definition (3.3) of the extended GU functional.

Thus the generalized GU functional $\tilde{\gamma}_2^{\{\mathbf{a}\}}$ satisfies the basic requirement (2.13) imposed on the exact functional $\tilde{\gamma}_2^{\min}[\gamma_1]$, i.e.,

$$\check{\gamma}_1[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1]]=\gamma_1, \tag{4.4}$$

and also satisfies some necessary conditions for $\gamma_2\in\mathcal{P}(N,2)$ [i.e., relations following from Eq. (2.8) with Eq. (2.5)]:

(i) preservation of the homogeneous scaling [2],

$$\tilde{\gamma}_{2,\lambda}^{\{\mathbf{a}\}}[\gamma_1]=\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_{1,\lambda}], \tag{4.5a}$$

where the definition of the scaled pDM, for $\lambda>0$,

$$\begin{aligned}\gamma_{p,\lambda}&(\mathbf{r}_1,s_1,\mathbf{r}_2,s_2,\ldots;\mathbf{r}_1',s_1',\ldots)\\ &=\lambda^{3p}\gamma_p(\lambda\mathbf{r}_1,s_1,\lambda\mathbf{r}_2,s_2,\ldots;\lambda\mathbf{r}_1',s_1',\ldots)\end{aligned} \tag{4.5b}$$

is induced by the scaling $\mathbf{r}\rightarrow\lambda\mathbf{r}$ of the space [the proof of Eq. (4.5a) relies on the identity

$$\gamma_{1,\lambda}^{\alpha}(\mathbf{r}_1,s_1;\mathbf{r}_1',s_1')=\lambda^3\gamma_1^{\alpha}(\lambda\mathbf{r}_1,s_1;\lambda\mathbf{r}_1',s_1'), \tag{4.5c}$$

which stems from Eqs. (3.2a) and (2.10) provided γ_1 scales as in Eq. (4.5b)],

(ii) Hermiticity

$$\gamma_2(\mathbf{12};\mathbf{1'2'})=\gamma_2^{*}(\mathbf{1'2'};\mathbf{12}), \tag{4.6}$$

(iii) normalization

$$N_2[\gamma_2]=\tfrac{1}{2}(N-1)N, \tag{4.7}$$

(iv) symmetry

$$\gamma_2(\mathbf{21};\mathbf{2'1'})=\gamma_2(\mathbf{12};\mathbf{1'2'}). \tag{4.8}$$

But $\tilde{\gamma}_2^{\{\mathbf{a}\}}$ violates the antisymmetry

$$\gamma_2(\mathbf{21};\mathbf{1'2'})=-\gamma_2(\mathbf{12};\mathbf{1'2'}). \tag{4.9}$$

The non-negativity of the diagonal element

$$\gamma_2(\mathbf{12};\mathbf{12})\geqslant 0 \tag{4.10}$$

may be also violated for some arguments **12**. Namely, for $\mathbf{x}_2=\mathbf{x}_1$ one has from Eq. (4.1) for each term of the combination (4.3) the negative value

$$\begin{aligned}\tilde{\gamma}_2^{\{a\}}&(\mathbf{11};\mathbf{11};[\gamma_1])\\ &=\tfrac{1}{2}\{\gamma_1^1(\mathbf{1};\mathbf{1})-[\gamma_1^a(\mathbf{1};\mathbf{1})\,\gamma_1^{1-a}(\mathbf{1};\mathbf{1})]^{1/2}\}\\ &\quad\times\{\gamma_1^1(\mathbf{1};\mathbf{1})+[\gamma_1^a(\mathbf{1};\mathbf{1})\,\gamma_1^{1-a}(\mathbf{1};\mathbf{1})]^{1/2}\}<0,\end{aligned} \tag{4.11}$$

because $\gamma_1^{\beta}(\mathbf{1};\mathbf{1})>\gamma_1^1(\mathbf{1};\mathbf{1})>0$ for $0<\beta<1$ [see Eqs. (3.2a) and (2.10)]. By continuity, this diagonal element should remain negative also for $\mathbf{x}_2$ close to $\mathbf{x}_1$. However, $\tilde{\gamma}_2^{\{a\}}(\mathbf{12};\mathbf{12})$ is positive for most arguments **12**, because it integrates to a positive number, Eq. (4.7) with Eq. (3.5). It should be noted that certain $a_{1\kappa}$ of Eq. (4.3a) may be chosen negative, thus allowing the combination $\tilde{\gamma}_2^{\{\mathbf{a}\}}(\mathbf{11};\mathbf{11};[\gamma_1])$ to become positive in some range of $\mathbf{x}_1$. This would reduce (or even remove) the range of arguments **12** where $\tilde{\gamma}_2^{\{\mathbf{a}\}}$ violates the necessary condition (4.10), as compared with $\tilde{\gamma}_2^{\{1/2\}}$.

V. ENERGIES RESULTING FROM GU SCHEMES

Considering $\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1]$ written explicitly in terms of natural orbitals of γ_1, one can split it similarly as in Eq. (3.1a)

$$\tilde{\gamma}_2^{\{\mathbf{a}\}}=\tilde{\gamma}_2^{\{\mathbf{a}\}\prime}+\tilde{\gamma}_2^{\{\mathbf{a}\}\prime\prime}, \tag{5.1}$$

and find that its orbital-self-interaction part is independent of the collective parameter **a**, namely

$$\tilde{\gamma}_2^{\{\mathbf{a}\}\prime\prime}=\tilde{\gamma}_2^{\{1/2\}\prime\prime}. \tag{5.2}$$

For the energies corresponding to the considered approximations to $\tilde{\gamma}_2^{\min}$ [compare Eq. (2.11)]:

$$\begin{aligned}E_{\mathrm{GS}}\approx E_{\mathrm{GS}}^{\{\mathbf{a}\}}&=\min_{\gamma_1\in\mathcal{P}(N,1)}\{E_1[\gamma_1]+E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1]]\}\\ &=\{\cdots\}\big|_{\gamma_1=\gamma_1^{\{\mathbf{a}\}}},\end{aligned} \tag{5.3}$$

$$E_{\rm GS}\approx E_{\rm GS}^{\{\mathbf{a}\}'}=\min_{\gamma_1\in\mathcal{P}(N,1)}\{E_1[\gamma_1]+E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}'}[\gamma_1]]\}$$
$$=\{\cdots\}|_{\gamma_1=\gamma_1^{\{\mathbf{a}\}'}},\tag{5.4}$$

the following relation holds:

$$E_{\rm GS}^{\{\mathbf{a}\}}<E_{\rm GS}^{\{\mathbf{a}\}'},\qquad \text{for any } \mathbf{a},\tag{5.5}$$

because the above inequality is equivalent to

$$E_1[\gamma_1^{\{\mathbf{a}\}}]+E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1^{\{\mathbf{a}\}}]]\leqslant E_1[\gamma_1^{\{\mathbf{a}\}'}]+E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1^{\{\mathbf{a}\}'}]]$$
$$<E_1[\gamma_1^{\{\mathbf{a}\}'}]+E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}'}[\gamma_1^{\{\mathbf{a}\}'}]].\tag{5.6}$$

Here, the first inequality reflects the fact that $\gamma_1^{\{\mathbf{a}\}}$ is the minimizer in Eq. (5.3), while the second inequality follows from $\tilde{\gamma}_2^{\{\mathbf{a}\}'}=\tilde{\gamma}_2^{\{\mathbf{a}\}}-\tilde{\gamma}_2^{\{1/2\}''}$, Eqs. (5.1) and (5.2), and then from $E_2[-\tilde{\gamma}_2^{\{1/2\}''}]>0$, see Eq. (2.4) with a positive integrand, since $h_2>0$ and $-\tilde{\gamma}_2^{\{1/2\}''}(\mathbf{12};\mathbf{12})>0$ [Eq. (3.1c) with n_i satisfying Eq. (2.10b)].

VI. RELATION WITH THE HARTREE-FOCK APPROXIMATION

The observation made by GU [2], that their functional coincides with the unrestricted Hartree-Fock (UHF) functional if the occupation numbers are constrained to be 1 or 0, will be used now to establish a relation between the GS energies in the generalized GU and the UHF approximations. So, the 1DM $\gamma_1^{\rm UHF}$, derivable from a determinantal wave function of the UHF approach, can be defined by Eq. (2.10) supplemented with the constraints

$$(1-n_i)n_i=0,\quad i=1,2,\ldots\;.\tag{6.1}$$

Such 1DM is idempotent, $\gamma_1^{{\rm UHF},\alpha}=\gamma_1^{\rm UHF,1}$ [compare Eq. (3.2)], therefore Eqs. (4.1) and (4.3) result in $\tilde{\gamma}_2^{\{a\}}[\gamma_1^{\rm UHF}]=\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1^{\rm UHF}]=\gamma_2^{\rm UHF}$—the 2DM derived from the same UHF wave function (see, e.g., [1]). This means that the UHF upper bound to the GS energy can be obtained from the following minimization:

$$E_{\rm GS}<E_{\rm GS}^{\rm UHF}=\min_{\gamma_1\in\mathcal{P}(N,1)\wedge(1-n_i)n_i=0}\{E_1[\gamma_1]+E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}'}[\gamma_1]]\}\tag{6.2}$$

[it is sufficient to involve in Eq. (6.2) the 2DM $\tilde{\gamma}_2^{\{\mathbf{a}\}'}$ rather than $\tilde{\gamma}_2^{\{\mathbf{a}\}}$, because, under the constraints (6.1), $\tilde{\gamma}_2^{\{\mathbf{a}\}''}=0$, see Eqs. (5.2) and (3.1c)]. One sees that both $E_{\rm GS}^{\rm UHF}$ and $E_{\rm GS}^{\{\mathbf{a}\}'}$ result from the minimization of the same functional [Eq. (6.2) and Eq. (5.4)] with respect to γ_1, variations of which being more restricted in Eq. (6.2). Therefore the following inequality holds

$$E_{\rm GS}^{\{\mathbf{a}\}'}<E_{\rm GS}^{\rm UHF},\qquad \text{for any } \mathbf{a}.\tag{6.3}$$

See also Eq. (5.5).

VII. VIRIAL EQUATIONS

An interesting identity can be derived by means of scaling, Eq. (4.5b). Since the scaled minimizer of Eq. (5.3)

$$\gamma_{1,\lambda}^{\{\mathbf{a}\}}(\mathbf{r}_1,s_1;\mathbf{r}_1',s_1')=\lambda^3\gamma_1^{\{\mathbf{a}\}}(\lambda\mathbf{r}_1,s_1;\lambda\mathbf{r}_1',s_1')\tag{7.1}$$

belongs to the set $\mathcal{P}(N,1)$ [Eq. (2.10) with $\phi_{i,\lambda}(\mathbf{r},s)=\lambda^{3/2}\phi_i(\lambda\mathbf{r},s)$, $n_{i,\lambda}=n_i$], and at $\lambda=1$ it coincides with the original minimizer, the resulting $E_{\rm GS}^{\{\mathbf{a}\}}$ can be obtained also from the following minimization:

$$E_{\rm GS}^{\{\mathbf{a}\}}=\min_{0<\lambda<\infty}\{E_1[\gamma_{1,\lambda}^{\{\mathbf{a}\}}]+E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_{1,\lambda}^{\{\mathbf{a}\}}]]\}=\{\cdots\}|_{\lambda=1},\tag{7.2a}$$

and, therefore,

$$\frac{d}{d\lambda}\{\cdots\}|_{\lambda=1}=0\tag{7.2b}$$

must hold. By taking into account Eqs. (2.3), (1.2), and (7.1), the form of the E_1 term of Eq. (7.2a) is found

$$E_1[\gamma_{1,\lambda}^{\{\mathbf{a}\}}]=\lambda^2\,T[\gamma_1^{\{\mathbf{a}\}}]+V[v_{{\rm ext},\lambda},\gamma_1^{\{\mathbf{a}\}}],\tag{7.3a}$$

where

$$v_{{\rm ext},\lambda}(\mathbf{r})=v_{\rm ext}(\lambda^{-1}\mathbf{r}),\tag{7.3b}$$

$$T[g_1]=\int d\mathbf{x}_1\left(-\frac{\hbar^2}{2m}\right)\boldsymbol{\nabla}^2(\mathbf{r}_1)g_1(\mathbf{r}_1,s_1;\mathbf{r}_1',s_1)\bigg|_{\mathbf{r}_1'=\mathbf{r}_1}$$
$$=\int d\mathbf{x}_1\frac{\hbar^2}{2m}\boldsymbol{\nabla}(\mathbf{r}_1)\cdot\boldsymbol{\nabla}(\mathbf{r}_1')g_1(\mathbf{r}_1,s_1;\mathbf{r}_1',s_1)\bigg|_{\mathbf{r}_1'=\mathbf{r}_1},\tag{7.3c}$$

$$V[v,g_1]=\int d\mathbf{x}_1\,v(\mathbf{r}_1)g_1(\mathbf{x}_1;\mathbf{x}_1),\tag{7.3d}$$

and, by taking Eqs. (2.4),(1.3),(4.5a),(4.5b), the form of the electron-electron interaction term is found

$$E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_{1,\lambda}^{\{\mathbf{a}\}}]]=\lambda E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1^{\{\mathbf{a}\}}]].\tag{7.3e}$$

Therefore, the necessary condition (7.2b) for the minimum leads to

$$2\,T[\gamma_1^{\{\mathbf{a}\}}]+V[v_{\rm ext}',\gamma_1^{\{\mathbf{a}\}}]+E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1^{\{\mathbf{a}\}}]]=0,\tag{7.4a}$$

where [see Eq. (7.3b)]

$$v_{\rm ext}'(\mathbf{r})=\frac{\partial}{\partial\lambda}v_{{\rm ext},\lambda}(\mathbf{r})\bigg|_{\lambda=1}=-\mathbf{r}\cdot\boldsymbol{\nabla}v_{\rm ext}(\mathbf{r}),\tag{7.4b}$$

i.e., an identity of the same form as the virial equation (see, e.g., [18]) satisfied by the exact solution, Eq. (2.1),

$$2\,T[\check{\gamma}_1[\gamma_N^{\rm GS}]]+V[v_{\rm ext}',\check{\gamma}_1[\gamma_N^{\rm GS}]]+E_2[\check{\gamma}_2[\gamma_N^{\rm GS}]]=0.\tag{7.5}$$

It should be noted that when the external potential results from the Coulombic interaction of electrons with a single nucleus, $v_{\text{ext}}(\mathbf{r}) = -Ze^2/(\kappa_0 r)$, then $v'_{\text{ext}} = v_{\text{ext}}$, and this should be inserted into Eqs. (7.4a) and (7.5).

If the external potential of Eq. (1.2) is specified as resulting from the Coulombic electron-nuclei interactions,

$$v_{\text{ext}}(\mathbf{r}) = v_{\text{en}}(\mathbf{r};\mathbf{R}) \equiv \sum_{l=1}^{M} \frac{-Z_l e^2}{\kappa_0 |\mathbf{r}-\mathbf{R}_l|},$$

$$\mathbf{R} = (\mathbf{R}_1, \ldots, \mathbf{R}_M) = (R_{11}, R_{12}, \ldots, R_{M3}), \tag{7.6}$$

where Z_l and $\mathbf{R}_l$ are the atomic number and the (fixed) position vector of lth nucleus, then the energies discussed above, like E_{GS}, $E_{\text{GS}}^{\{\mathbf{a}\}}$, $E_{\text{GS}}^{\{\mathbf{a}\}\prime}$, $E_{\text{GS}}^{\text{UHF}}$, and the corresponding DM minimizers γ_N^{GS}, $\gamma_1^{\{\mathbf{a}\}}$, $\gamma_1^{\{\mathbf{a}\}\prime}$, γ_1^{UHF}, all depend on $\mathbf{R}$, e.g., $E_{\text{GS}}^{\{\mathbf{a}\}} = E_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R})$, $\gamma_1^{\{\mathbf{a}\}} = \gamma_1^{\{\mathbf{a}\}}(\mathbf{R})$. In addition to scaling of the electronic coordinates, as in Eq. (4.5b), one can introduce simultaneous scaling of the nuclear coordinates

$$\gamma_{p,\zeta}(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \ldots; \mathbf{r}'_1, s'_1, \ldots; \mathbf{R}) = \zeta^{3p} \gamma_p(\zeta\mathbf{r}_1, s_1, \zeta\mathbf{r}_2, s_2, \ldots; \zeta\mathbf{r}'_1, s'_1, \ldots; \zeta\mathbf{R}). \tag{7.7a}$$

This new scaling, similarly as in Eq. (4.5a), is also preserved by the model 2DM functional $\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1]$:

$$\tilde{\gamma}_{2,\zeta}^{\{\mathbf{a}\}}[\gamma_1] = \tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_{1,\zeta}]. \tag{7.7b}$$

Continuing the analogy with the previous scaling, one can write

$$\begin{aligned} E_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R}) = \min_{0<\zeta<\infty} \{ & T[\gamma_{1,\zeta}^{\{\mathbf{a}\}}] + V[v_{\text{en}}(.;\mathbf{R}), \gamma_{1,\zeta}^{\{\mathbf{a}\}}] \\ & + E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_{1,\zeta}^{\{\mathbf{a}\}}]]\} \\ = \{ & \cdots \}|_{\zeta=1}. \end{aligned} \tag{7.8}$$

Note that the expectation value of the original Hamiltonian is minimized in Eq. (7.8), therefore the nuclear positions in v_{en} are not scaled. After transforming variables of integration in the terms T, V, and E_2 of Eq. (7.8) one obtains

$$\begin{aligned} E_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R}) = \min_{0<\zeta<\infty} \{ & \zeta^2\, T[\gamma_1^{\{\mathbf{a}\}}(\zeta\mathbf{R})] + \zeta\, V[v_{\text{en}}(.;\zeta\mathbf{R}), \gamma_1^{\{\mathbf{a}\}}(\zeta\mathbf{R})] \\ & + \zeta\, E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1^{\{\mathbf{a}\}}(\zeta\mathbf{R})]]\} = \{\cdots\}|_{\zeta=1}, \end{aligned} \tag{7.9a}$$

so the condition, necessary for the minimum,

$$\left. \frac{d}{d\zeta}\{\cdots\} \right|_{\zeta=1} = 0, \tag{7.9b}$$

leads to

$$\begin{aligned} & 2\, T[\gamma_1^{\{\mathbf{a}\}}(\mathbf{R})] + V[v_{\text{en}}(.;\mathbf{R}), \gamma_1^{\{\mathbf{a}\}}(\mathbf{R})] + E_2[\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1^{\{\mathbf{a}\}}(\mathbf{R})]] \\ & \quad + \left. \frac{d}{d\zeta} E_{\text{GS}}^{\{\mathbf{a}\}}(\zeta\mathbf{R}) \right|_{\zeta=1} = 0, \end{aligned} \tag{7.10}$$

or, equivalently,

$$T[\gamma_1^{\{\mathbf{a}\}}(\mathbf{R})] + E_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R}) + \sum_{\alpha} R_\alpha \frac{\partial}{\partial R_\alpha} E_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R}) = 0. \tag{7.11}$$

It should be noted that the summation in Eq. (7.11) involves the independent nuclear coordinates only (e.g., relative to the first atom and allowing for arbitrary rotation of the molecule as a whole). One can consider also the total energy of the molecule

$$W_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R}) = E_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R}) + E_{\text{nn}}(\mathbf{R}), \tag{7.12}$$

which includes the nucleus-nucleus interaction energy

$$E_{\text{nn}}(\mathbf{R}) = \sum_{l<k}^{M} \frac{Z_l Z_k e^2}{\kappa_0 |\mathbf{R}_l - \mathbf{R}_k|}. \tag{7.13}$$

By taking into account that

$$\left. \frac{d}{d\zeta} E_{\text{nn}}(\zeta\mathbf{R}) \right|_{\zeta=1} = -E_{\text{nn}}(\mathbf{R}), \tag{7.14}$$

Eq. (7.11) can be rewritten as

$$T[\gamma_1^{\{\mathbf{a}\}}(\mathbf{R})] + W_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R}) + \sum_{\alpha} R_\alpha \frac{\partial}{\partial R_\alpha} W_{\text{GS}}^{\{\mathbf{a}\}}(\mathbf{R}) = 0. \tag{7.15}$$

This identity is of the same form as another virial equation (see, e.g., [1]) satisfied by the exact solution, Eq. (2.1):

$$T[\check{\gamma}_1[\gamma_N^{\text{GS}}(\mathbf{R})]] + W_{\text{GS}}(\mathbf{R}) + \sum_{\alpha} R_\alpha \frac{\partial}{\partial R_\alpha} W_{\text{GS}}(\mathbf{R}) = 0, \tag{7.16a}$$

where

$$W_{\text{GS}}(\mathbf{R}) = E_{\text{GS}}(\mathbf{R}) + E_{\text{nn}}(\mathbf{R}). \tag{7.16b}$$

It is worth noting that the virial equations (7.4a) and (7.11), satisfied by the solution $\gamma_1^{\{\mathbf{a}\}}$, $E_{\text{GS}}^{\{\mathbf{a}\}}$ of Eq. (5.3) for arbitrary $\mathbf{a}$, are satisfied also by the solutions of Eqs. (5.4) and (6.2), because the scaling properties of the corresponding 2DM's are the same as of $\tilde{\gamma}_2^{\{\mathbf{a}\}}$.

VIII. OPTIMIZATION OF PARAMETERS

As shown in Sec. IV, all important properties, Eqs. (4.4)–(4.8), of the generalized GU functional $\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1]$, which justify its role as an approximation to the exact functional $\tilde{\gamma}_2^{\min}[\gamma_1]$, are satisfied for any $\mathbf{a}$. So, for an approximate solution (5.3) of the GS problem for an arbitrary many-electron system by means of the one-body-density-matrix approach (2.11), a whole family of approximate 2DM functionals parametrized by **a** can be used. In order to apply it to a particular system characterized by v_{ext}, h_2, and N, some optimum collective parameter $\mathbf{a}=\bar{\mathbf{a}}[v_{\text{ext}},h_2,N]$ should be chosen.

There are known identities which are satisfied by the 1DM and 2DM reduced from the exact GS solution γ_N^{GS}, but, in general, are violated by the approximate DM's $\gamma_1^{\{\mathbf{a}\}}$ and $g_2^{\{\mathbf{a}\}}\equiv\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1^{\{\mathbf{a}\}}]$, corresponding to the solution of Eq. (5.3). A requirement to minimize these "violations" can be used to define $\bar{\mathbf{a}}$. I expect that the corresponding energy deviation $|E_{\text{GS}}^{\{\bar{\mathbf{a}}\}}-E_{\text{GS}}|$ will be also close to optimum (minimum with respect to variations of **a**). Of course, this conjecture should be confirmed by tests.

For a given N-electron system, let $Q[g_1,g_2]$ denotes a functional with the following property:

$$Q[g_1,g_2]\geqslant Q[\breve{\gamma}_1[\gamma_N^{\text{GS}}],\breve{\gamma}_2[\gamma_N^{\text{GS}}]]=0 \tag{8.1}$$

(examples will be given). Then the proposed algorithm to obtain, by means of the generalized GU functional, the best approximation to the GS solution for a given system is the following: (i) perform minimizations in Eq. (5.3) for a chosen set of points in the space of the parameters **a**. This defines the DM's $\gamma_1^{\{\mathbf{a}\}}$ and $g_2^{\{\mathbf{a}\}}$ as functions of these **a**; (ii) find in the space of the parameters **a** a point $\bar{\mathbf{a}}$—the minimizer in the following minimization:

$$\min_{\mathbf{a}} Q[\gamma_1^{\{\mathbf{a}\}},g_2^{\{\mathbf{a}\}}]=Q[\gamma_1^{\{\bar{\mathbf{a}}\}},g_2^{\{\bar{\mathbf{a}}\}}] \tag{8.2}$$

[probably some interpolation between the points of the step (i) would be sufficient to determine $\bar{\mathbf{a}}$]; (iii) perform the minimization in Eq. (5.3) for $\mathbf{a}=\bar{\mathbf{a}}$; the obtained $E_{\text{GS}}^{\{\bar{\mathbf{a}}\}}$ is the best approximation to E_{GS}, while the DM's $\gamma_1^{\{\bar{\mathbf{a}}\}}$ and $g_2^{\{\bar{\mathbf{a}}\}}$ are the best approximations to $\breve{\gamma}_1[\gamma_N^{\text{GS}}]$ and $\breve{\gamma}_2[\gamma_N^{\text{GS}}]$.

To be practical, only a few parameters should be involved in this algorithm. For instance, values of a small number K of parameters $a_{2\kappa}$ are chosen and fixed, e.g., $K=2$, $a_{21}=1/6$, $a_{22}=2/6$, [see Eq. (4.3)], and then, K real parameters $a_{1\kappa}$ are to be optimized.

The virial theorems, Eqs. (7.5) and (7.16a), may serve as examples of the above-mentioned identities. Unfortunately, they are useless for constructing $Q[g_1,g_2]$, because they *are satisfied* by $\gamma_1^{\{\mathbf{a}\}}$, $g_2^{\{\mathbf{a}\}}$, Eqs. (7.4a) and (7.15), for arbitrary **a**. However, the virial equation (7.5) is a member of a wide class of identities known as the hypervirial theorems (see, e.g., [19] and [20]). Many of them can be obtained directly from the so-called differential virial theorem (equation)

$$n(\mathbf{r})\,\mathbf{f}(\mathbf{r};[\gamma_1,\gamma_2,v_{\text{ext}},h_2])=0, \tag{8.3}$$

which can be interpreted as a local force balance equation, because among the terms summing to **f** there is $-\boldsymbol{\nabla} v_{\text{ext}}$—the force acting on an electron due to the external potential. This Eq. (8.3), obtained in [21], was shown to be satisfied at any space point **r** by DM's $\gamma_1=\breve{\gamma}_1[\gamma_N]$, $\gamma_2=\breve{\gamma}_2[\gamma_N]$, where the ensemble NDM γ_N is constructed according to Eq. (2.5) from the eigenfunctions Ψ_λ of the Schrödinger equation

$$\hat{H}\Psi_\lambda=E_\lambda\Psi_\lambda \tag{8.4}$$

with $\hat{H}$ given by Eqs. (1.1), (1.2) in terms of the potentials v_{ext},h_2 present also in Eq. (8.3). In particular, the differential virial equation (8.3) is satisfied by the pair $\gamma_1=\breve{\gamma}_1[\gamma_N^{\text{GS}}]$, $\gamma_2=\breve{\gamma}_2[\gamma_N^{\text{GS}}]$, corresponding to the solution of Eq. (2.1). The total force **f**, entering Eq. (8.3), is a sum of the external, internal and kinetic components

$$\mathbf{f}=\mathbf{f}_{\text{ext}}+\mathbf{f}_{\text{int}}+\mathbf{f}_{\text{kin}}, \tag{8.5a}$$

defined as

$$f_{\text{ext},\alpha}(\mathbf{r})=-\nabla_\alpha(\mathbf{r})\,v_{\text{ext}}(\mathbf{r}), \tag{8.5b}$$

$$n(\mathbf{r})\,f_{\text{int},\alpha}(\mathbf{r})=-2\int d^3r'(\nabla_\alpha(\mathbf{r})\,h_2(\mathbf{r},\mathbf{r}'))n_2(\mathbf{r},\mathbf{r}'), \tag{8.5c}$$

$$n(\mathbf{r})\,f_{\text{kin},\alpha}(\mathbf{r})=\sum_\beta\left(\frac{\hbar^2}{4m}\nabla_\alpha(\mathbf{r})\nabla_\beta^2(\mathbf{r})\,n(\mathbf{r})-2\nabla_\beta(\mathbf{r})t_{\alpha\beta}(\mathbf{r})\right), \tag{8.5d}$$

in terms of the following functionals of γ_1 and γ_2—the arguments of **f** in Eq. (8.3):

$$t_{\alpha\beta}(\mathbf{r})=\frac{\hbar^2}{4m}[\nabla_\alpha(\mathbf{r}')\nabla_\beta(\mathbf{r}'')+\nabla_\alpha(\mathbf{r}'')\nabla_\beta(\mathbf{r}')]\times\left(\sum_s\gamma_1(\mathbf{r}+\mathbf{r}',s;\mathbf{r}+\mathbf{r}'',s)\right)\Bigg|_{\mathbf{r}'=\mathbf{r}''=\mathbf{0}} \tag{8.5e}$$

—the kinetic energy density tensor,

$$n(\mathbf{r})=\sum_s\gamma_1(\mathbf{r},s;\mathbf{r},s) \tag{8.5f}$$

—the diagonal spinless 1DM, i.e., the electron number density,

$$n_2(\mathbf{r}_1,\mathbf{r}_2)=\sum_{s_1,s_2}\gamma_2(\mathbf{r}_1,s_1,\mathbf{r}_2,s_2;\mathbf{r}_1,s_1,\mathbf{r}_2,s_2) \tag{8.5g}$$

—the diagonal spinless 2DM, i.e., the electron pair density. Note that the integrated trace of $t_{\alpha\beta}(\mathbf{r})$ gives the total kinetic energy according to Eq. (7.3c), second line.

The virial theorem, Eq. (7.5), can be obtained from Eq. (8.3) by multiplying it by **r** and subsequent integration over the whole space [21]. Other hypervirial theorems can be obtained similarly using $\varphi_i(\mathbf{r})\,\mathbf{r}$ instead of **r** [where $\varphi_i(\mathbf{r})$ are some chosen functions, see discussion by Holas and March in [20]; although noninteracting many-electron systems are considered by them only, their results can be easily extended to the interacting systems by adding the contribution due to $\mathbf{f}_{\rm int}$]. If

$$P_i[\gamma_1,\gamma_2,v_{\rm ext},h_2]=0 \tag{8.6}$$

denotes the ith hypervirial equation, then the ''least-squares'' sum

$$Q[g_1,g_2]=\sum_i p_i(P_i[g_1,g_2,v_{\rm ext},h_2])^2 \tag{8.7}$$

can serve as a particular representation of Q. The role of the weights $p_i>0$ is to make various terms of the sum similarly sensitive to variations of the parameters **a** when used in Eq. (8.2). The property (8.1) is obeyed by this Q, because the hypervirial equations (8.6) are satisfied by $\gamma_1=\breve{\gamma}_1[\gamma_N^{\rm GS}]$, $\gamma_2=\breve{\gamma}_2[\gamma_N^{\rm GS}]$. The number of summed terms in Eq. (8.7) should exceed the number of free parameters in **a**, involved in Eq. (8.2). It is worth noting that, in their recent paper [22], Cioslowski and Lopez-Boada make use of the hypervirial theorem to obtain the electron-electron repulsion energy as an approximate functional of the Hartree-Fock 1DM.

The form (8.7) of Q is ''expensive'' in applications, because the evaluation of each P_i needs accurate numerical integration over the whole space. Therefore I propose another Q which makes an alternative use of the differential virial equation (8.3), namely

$$Q[g_1,g_2]=\int d^3r\, n(\mathbf{r})\{\mathbf{f}(\mathbf{r};[g_1,g_2,v_{\rm ext},h_2])\}^2. \tag{8.8}$$

It shows the property (8.1), because the force $\mathbf{f}(\mathbf{r})$ acting on an electron at any point $\mathbf{r}$ vanishes, Eq. (8.3), when the DM's reduced from $\gamma_N^{\rm GS}$ are used. The electron density plays in Eq. (8.8) the role of the weighting function. Actually, for the use in Eq. (8.2), the integral in Eq. (8.8) need not be evaluated very accurately—approximate numerical integration using a few representative points of space should be sufficient. However, the number of these points should exceed the number of free parameters in **a**.

IX. CONCLUSIONS

In concluding, the main results of the present investigation are summed up:

(i) The GU approach [2] to the GS problem of a many-electron system is analyzed in terms of the reduced-density-matrix approach, as an approximation to Eq. (2.11).
(ii) The GU approximate functional 2DM, when properly extended to $\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]$, shows the property (3.7), i.e., it obeys the requirement imposed on the exact 2DM $\tilde{\gamma}_2^{\rm min}[\gamma_1]$, Eq. (2.13).
(iii) A generalization of the GU functional, $\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1]$, is proposed, Eq. (4.3) with (4.1): the extended GU functional, $\tilde{\gamma}_2^{\{1/2\}}[\gamma_1]$, corresponds to $K=0$ in Eq. (4.3). This $\tilde{\gamma}_2^{\{\mathbf{a}\}}[\gamma_1]$ obeys the properties (4.4)–(4.8). Violation of the property (4.10) can be diminished for some parameters **a**.
(iv) The relations (5.5) and (6.3) between various approximations to the GS energy are established.
(v) The energy and DM's corresponding to the solution of the GS problem with the generalized GU functional, Eq. (5.3), satisfy two virial equations, Eqs. (7.4a) and (7.11), which are also satisfied by the exact solution.
(vi) An algorithm to obtain the best approximation to the GS solution is proposed [below Eq. (8.1)].
(vii) Two versions, Eq. (8.7) and (8.8), of an auxiliary functional $Q[g_1,g_2]$ (used in the algorithm) are proposed.

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