PHYSICAL REVIEW A **84**, 032506 (2011)

Density and pair-density scaling for deriving the Euler equation in density-functional and pair-density-functional theory

Á. Nagy
Department of Theoretical Physics, University of Debrecen, H-4010 Debrecen, Hungary

(Received 6 June 2011; published 14 September 2011)

A link between density and pair density functional theories is presented. Density and pair density scaling are used to derive the Euler equation in both theories. Density scaling provides a constructive way of obtaining approximations for the Pauli potential. The Pauli potential (energy) of the density functional theory is expressed as the difference of the scaled and original exchange-correlation potentials (energies).

DOI: 10.1103/PhysRevA.84.032506 PACS number(s): 31.15.−p

I. INTRODUCTION

Nowadays, studies on electronic and spectroscopic properties of atoms, molecules, and clusters are generally based on density functional theory. In addition to the Kohn-Sham approach there is a growing role of the orbital-free theory. The fact that only the Euler equation has to be solved instead of the Kohn-Sham equations, might lead to an enourmous simplification provided that a good approximation for the unknown kinetic energy functional is found.

Therefore, the Euler equation is a fundamental equation of the density functional theory [1]. There exist several derivations of the Euler equation [2–4]. The Euler equation of the noninteracting system has the form

$$\frac{\delta T_s}{\delta \varrho} + v_{\mathrm{KS}} = \mu, \tag{1}$$

where T_s is the noninteracting kinetic energy, v_{KS} is the Kohn-Sham potential, and μ is the chemical potential.

Here we present a derivation using density scaling. Density scaling was proposed by Chan and Handy [5]. In density scaling the density $\varrho(\mathbf{r})$ is changed to $\zeta\varrho(\mathbf{r})$. Earlier we used density scaling to treat electron correlation [6,7] and generalized to multiplets [8] and excited states [9]. Density scaling provides an extension of the original density functional theory. The Euler equation is derived here in the enlarged theory.

We now extend density scaling to pair density and derive the two-particle equation that can be considered the "Euler equation" of the pair density functional theory. The method provides a link between the two theories. Moreover, it is found that the Pauli potential (energy) of the density functional theory is expressed as the difference of the scaled and original exchange-correlation potentials (energies). This relation gives a constructive way of obtaining approximations for the Pauli potential.

II. DERIVATION OF EULER EQUATION OF DENSITY FUNCTIONAL THEORY VIA DENSITY SCALING

Consider the ground state of the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ee}, \tag{2}$$

where

$$\hat{T} = \sum_{j=1}^{N}\left(-\frac{1}{2}\nabla_j^2\right), \tag{3}$$

$$\hat{V}_{ee} = \sum_{k=1}^{N-1}\sum_{j=k+1}^{N}\frac{1}{|\mathbf{r}_k - \mathbf{r}_j|}, \tag{4}$$

and

$$\hat{V} = \sum_{k=1}^{N}\sum_{J=1}^{N_n}\frac{-Z_J}{|\mathbf{r}_k - \mathbf{R}_J|} \tag{5}$$

are the kinetic energy, the electron-electron energy, and the electron-nuclear energy operators, respectively. N and N_n are the number of electrons and nuclei. The density ϱ is defined as

$$\varrho(\mathbf{r}) = \langle\Psi|\hat{\varrho}(\mathbf{r})|\rangle\Psi = N\int|\Psi(\mathbf{r},\sigma_1,\mathbf{r}_2,\sigma_2,\ldots,\mathbf{r}_N,\sigma_N)|^2 \times d\sigma_1 d\mathbf{r}_2 d\sigma_2 \ldots d\mathbf{r}_N d\sigma_N, \tag{6}$$

where $\mathbf{r}_i,\sigma_i$ stand for the spatial and the spin coordinates and the integral symbol when referred to spin denotes summation and $\hat{\varrho}$ is the density operator. The density ϱ has the properties that $\varrho \geqslant 0$, $\int\varrho(\mathbf{r})d\mathbf{r} = N$ and $\int(\nabla\varrho^{1/2})^2 d\mathbf{r}$ is finite [10,11]. The noninteracting system is usually defined via adiabatic connection [12,13] considering a Hamiltonian

$$\hat{H}_{\mathrm{KS}} = \hat{T} + \hat{V}_{\mathrm{KS}}, \tag{7}$$

where

$$\hat{H}_{\mathrm{KS}} = \sum_{j=1}^{N} v_{\mathrm{KS}}(\mathbf{r}_j). \tag{8}$$

The effective potential v_{KS} is constructed by keeping the ground-state density $\varrho(\mathbf{r})$ fixed.

In density scaling we construct another noninteracting system with a scaled density $\varrho_\zeta(\mathbf{r}) = \varrho(\mathbf{r})/\zeta$, where $\zeta = N/N_\zeta$ is a positive number. If $\zeta = 1$ we get back the original noninteracting (Kohn-Sham) system. If the original real system has N electrons the Kohn-Sham system with the scaled density ϱ_ζ has N_ζ electrons:

$$\int\varrho_\zeta(\mathbf{r})d\mathbf{r} = N_\zeta. \tag{9}$$

N is always an integer, but N_ζ is generally a noninteger. To extend the formalism to a noninteger electron number, Chan and Handy [5] considered the grand canonical ensemble [14,15]. Let Γ denote a zero temperature grand canonical density matrix. It is defined in the Fock space

$$\Gamma = \sum_N \sum_i f_{Ni} |\Psi_{Ni}\rangle\langle\Psi_{Ni}|, \tag{10}$$

where Ψ_{Ni} is the ith N-particle eigenfunction of the Hamiltonian. The occupation numbers f_{Ni} should satisfy the conditions $0 \leqslant f_{Ni} \leqslant 1$ and $\sum_N \sum_i f_{Ni} = 1$. The Kohn-Sham system with a scaled density then is constructed by the constrained search over the density matrices Γ that lead to density ϱ_ζ

$$\varrho_\zeta = \mathrm{Tr}[\hat{\Gamma}\hat{\varrho}]. \tag{11}$$

The functional $T_\zeta[\varrho]$ is defined as

$$T_\zeta[\varrho] = \zeta \min_{\Gamma\to\varrho_\zeta} \mathrm{Tr}[\hat{\Gamma}\hat{T}]. \tag{12}$$

Chan and Handy [5] proved that $T_\zeta[\varrho]$ is a convex functional. For convex functionals the functional derivative exists [11,16].

In this section we take $N_\zeta = 2$ and denote this value of ζ as $\zeta_d = N/2$. It means that we have a noninteracting system with two electrons. We then apply the constrained search [10,17] and minimize the scaled kinetic energy

$$-2\frac{1}{2}\int \phi^*(\mathbf{r})\nabla^2\phi(\mathbf{r})d\mathbf{r} \tag{13}$$

with a fixed scaled density

$$\varrho_{\zeta_d} = 2|\phi|^2 : \tag{14}$$

$$\mathrm{Min}\left[-\int \phi^*(\mathbf{r})\nabla^2\phi(\mathbf{r})d\mathbf{r} + \int \varrho_{\zeta_d}(\mathbf{r})v_{\zeta_d}(\mathbf{r})d\mathbf{r} + \mu\int \varrho_{\zeta_d}(\mathbf{r})d\mathbf{r}\right]. \tag{15}$$

The constraints of the minimization include fixing the density ϱ_{ζ_d} and its norm [Eq. (9)] with the Lagrange multipliers $v_{\zeta_d}(\mathbf{r})$ and μ, respectively. The minimization leads to the equation

$$-\frac{1}{2}\nabla^2\phi + v_{\zeta_d}\phi = \mu\phi. \tag{16}$$

This equation can also be written as

$$\left(-\frac{1}{2}\nabla^2 + v_{\zeta_d}\right)\varrho_{\zeta_d}^{1/2} = \mu\varrho_{\zeta_d}^{1/2} \tag{17}$$

or

$$\left(-\frac{1}{2}\nabla^2 + v_{\zeta_d}\right)\varrho^{1/2} = \mu\varrho^{1/2}. \tag{18}$$

Equations (17) and (18) can be transcripted as

$$-\frac{1}{2\varrho^{1/2}}\nabla^2\varrho^{1/2} + v_{\zeta_d} = \mu. \tag{19}$$

From Eqs. (17), (18), and (19) we can see that v_{ζ_d} exists and unique up to a constant (μ):

$$v_{\zeta_d} = \mu + \frac{1}{2\varrho^{1/2}}\nabla^2\varrho^{1/2}. \tag{20}$$

Taking into account that the first term in Eq. (19) is the functional derivative of the Weizsäcker kinetic energy [18]

$$T_w = \frac{1}{8}\int \frac{|\nabla\varrho|^2}{\varrho}d\mathbf{r} \tag{21}$$

$$\frac{\delta T_w}{\delta\varrho} = -\frac{1}{2\varrho^{1/2}}\nabla^2\varrho^{1/2}, \tag{22}$$

Eq. (19) has the form

$$\frac{\delta T_w}{\delta\varrho} + v_{\zeta_d} = \mu. \tag{23}$$

Define the potential v_p as

$$v_p = v_{\zeta_d} - v_{\mathrm{KS}}. \tag{24}$$

From the existence of v_{ζ_d} [Eq. (20)] and v_{KS} [Eq. (8)] follows the existence of the potential v_p. Equations (23) and (24) lead to

$$v_p = \mu - \frac{\delta T_w}{\delta\varrho} - v_{\mathrm{KS}}. \tag{25}$$

It is customary to partition the original noninteracting kinetic energy as

$$T_s = T_w + T_p, \tag{26}$$

where T_p is the Pauli energy. Writing Eq. (25) in the form

$$\frac{\delta T_w}{\delta\varrho} + v_p + v_{\mathrm{KS}} = \mu \tag{27}$$

we immediately see that this equation is the Euler equation (1) and v_p is the Pauli potential [2,19,20], that is, the functional derivative of the Pauli energy

$$v_p = \frac{\delta T_p}{\delta\varrho}. \tag{28}$$

From the existence of v_p [Eq. (24)] follows that the functional derivative of the Pauli energy [Eq. (28)] exists.

III. DERIVATION OF PAIR DENSITY FUNCTIONAL THEORY VIA PAIR DENSITY SCALING

The pair density n can be calculated from the wave function by integrating $|\Phi|^2$ for all coordinates except $\mathbf{r}_1$ and $\mathbf{r}_2$:

$$n(\mathbf{r}_1,\mathbf{r}_2) = \frac{N(N-1)}{2}\int |\Phi(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2\mathbf{r}_3,\sigma_3,\ldots,\mathbf{r}_N,\sigma_N)|^2 \times d\sigma_1 d\sigma_2 d\mathbf{r}_3 d\sigma_3 \ldots d\mathbf{r}_N d\sigma_N. \tag{29}$$

There is a simple relation between the density and the pair density

$$\varrho(\mathbf{r}_1) = \frac{2}{N-1}\int n(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2. \tag{30}$$

It has been shown [21–23] that in the ground state the pair density can be determined by solving a single auxiliary equation of a two-particle problem,

$$\left[-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2+v_p^{\rm pdft}(\mathbf{r}_1,\mathbf{r}_2)+v_{\rm eff}(\mathbf{r}_1,\mathbf{r}_2)\right]n^{1/2}(\mathbf{r}_1,\mathbf{r}_2) = \mu_p n^{1/2}(\mathbf{r}_1,\mathbf{r}_2)\,, \tag{31}$$

$$v_{\rm eff}(\mathbf{r}_1,\mathbf{r}_2)=v(\mathbf{r}_1)+v(\mathbf{r}_2)+\frac{N-1}{r}, \tag{32}$$

where v is the external potential and the notation $r=|\mathbf{r}_1-\mathbf{r}_2|$ is used. μ_p is the energy needed to remove two electrons from the N-electron system. The meaning of the potential $v_p^{\rm pdft}$ will be detailed below.

Consider an auxiliary system with a scaled pair density $n_\zeta(\mathbf{r})=n(\mathbf{r})/\zeta$, where ζ is a positive number. We have to extend the formalism to noninteger electron number as N_ζ is generally noninteger. Therefore, we consider again the grand canonical ensemble and construct the zero temperature grand canonical density matrix Γ [Eq. (10)].

In this section we take $\zeta=\zeta_p=N(N-1)/2$. It means that we have an auxiliary system with two electrons and $n_\zeta(\mathbf{r})$ is normalized to 1

$$\int n_{\zeta_p}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2=1. \tag{33}$$

We then apply the constrained search: minimize the scaled kinetic energy

$$-\frac{1}{2}\int\chi_{\zeta_p}^*(\mathbf{r}_1,\mathbf{r}_2)\left(\nabla_1^2+\nabla_2^2\right)\chi_{\zeta_p}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \tag{34}$$

with a fixed scaled pair density

$$n_{\zeta_p}=|\chi_{\zeta_p}|^2: \tag{35}$$

$$\begin{aligned}\mathrm{Min}\Bigg[&-\frac{1}{2}\int\chi_{\zeta_p}^*(\mathbf{r}_1,\mathbf{r}_2)\left(\nabla_1^2+\nabla_2^2\right)\chi_{\zeta_p}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2\\&+\int n_{\zeta_p}(\mathbf{r}_1,\mathbf{r}_2)v_{\zeta_p,\rm eff}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2\\&+\mu_p\int n_{\zeta_p}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2\Bigg].\end{aligned} \tag{36}$$

Note that the function χ_{ζ_p} is defined up to a phase factor. The minimization leads to the equation

$$\left[-\frac{1}{2}\left(\nabla_1^2+\nabla_2^2\right)+v_{\zeta_p,\rm eff}\right]\chi_{\zeta_p}=\mu_p\chi_{\zeta_p}. \tag{37}$$

This equation can also be written as

$$\left[-\frac{1}{2}\left(\nabla_1^2+\nabla_2^2\right)+v_{\zeta_p,\rm eff}\right]n_{\zeta_p}^{1/2}=\mu_p n_{\zeta_p}^{1/2} \tag{38}$$

or

$$\left[-\frac{1}{2}\left(\nabla_1^2+\nabla_2^2\right)+v_{\zeta_p,\rm eff}\right]n^{1/2}=\mu_p n^{1/2}. \tag{39}$$

Equations (38) and (39) can be transcripted as

$$-\frac{1}{2n^{1/2}}\left(\nabla_1^2+\nabla_2^2\right)n^{1/2}+v_{\zeta_p,\rm eff}=\mu_p. \tag{40}$$

Note that the potential $v_{\zeta_p,\rm eff}$ exists and unique up to a constant (μ_p) as it can be expressed from Eq. (40)

$$v_{\zeta_p,\rm eff}=\mu_p+\frac{1}{2n^{1/2}}\left(\nabla_1^2+\nabla_2^2\right)n^{1/2}. \tag{41}$$

Earlier we defined [21,24] (see also Refs. [25,26]) the Weizsäcker kinetic energy with the pair density

$$T_w^{\rm pdft}=\int n^{1/2}(\mathbf{r}_1,\mathbf{r}_2)\left(-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2\right)n^{1/2}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \tag{42}$$

[Note that for convenience there is a different (from Refs. [21,24]) factor here in the definition of the Weizsäcker kinetic energy.] The functional derivative with respect to the pair density has the form

$$\frac{\delta T_w^{\rm pdft}}{\delta n}=-\frac{1}{2n^{1/2}}\left(\nabla_1^2+\nabla_2^2\right)n^{1/2}. \tag{43}$$

Therefore Eq. (40) can be rewritten as

$$\frac{\delta T_w^{\rm pdft}}{\delta n}+v_{\zeta_p,\rm eff}=\mu_p. \tag{44}$$

Define the potential $v_p^{\rm pdft}$ as

$$v_p^{\rm pdft}=v_{\zeta_p,\rm eff}-v_{\rm eff}. \tag{45}$$

From the existence of $v_{\zeta_p,\rm eff}$ [Eq. (41)] and $v_{\rm eff}$ [Eq. (32)] follows the existence of the potential $v_p^{\rm pdft}$. Equations (44) and (45) lead to

$$v_p^{\rm pdft}=\mu_p-\frac{\delta T_w^{\rm pdft}}{\delta n}-v_{\rm eff}. \tag{46}$$

Partition now the kinetic energy as

$$T=T_w^{\rm pdft}+T_p^{\rm pdft}, \tag{47}$$

where $T_p^{\rm pdft}$ is the Pauli energy of the pair density functional theory. Writing Eq. (46) in the form

$$\frac{\delta T_w^{\rm pdft}}{\delta n}+v_p^{\rm pdft}+v_{\rm eff}=\mu_p, \tag{48}$$

we immediately see that this equation is the two-particle equation (31) and $v_p^{\rm pdft}$ is the functional derivative of the Pauli energy with respect to the pair density functional

$$v_p^{\rm pdft}=\frac{\delta T_p^{\rm pdft}}{\delta n}. \tag{49}$$

From the existence of the Pauli potential $v_p^{\rm pdft}$ follows that the functional derivative of the Pauli energy with respect to the pair density functional exists.

IV. DISCUSSION

The Euler equations derived above in the density and pair density functional theories are very similar. They have a similar form. Both equations include a Pauli potential. The kinetic energy functionals (as functionals of the density or the pair density) are unknown. Separating from them the known Weizsäcker term, the unknown part is incorporated into the Pauli term in both theories.

The forms of Euler equations obtained via density scaling [Eqs. (19) and (39)] are of importance. These are very simple, exact equations of the many-body problem. However, the potentials v_{ζ_d} and $v_{\zeta_p,\mathrm{eff}}$ include unknown terms. Density and pair density scaling might give a practical way of construction of these potentials. Finding an adequate approximation for the Pauli potential is a very hard problem. Density scaling induces a hope of constructing good approximate Pauli potentials. It should be the subject of further research.

Beyond the similarity there are differences between the density and pair density functional theories. The main difference, we have to emphasize here, comes from the fact that we considered noninteracting kinetic energy in the density functional theory. In the pair density functional theory, on the other hand, the true interacting kinetic energy was treated. We discuss now an important consequence of using T_s. As it was presented earlier [5–7], there is a relation between the original noninteracting kinetic (T_s) and exchange-correlation (E_{xc}) and the scaled noninteracting kinetic (T_ζ) and exchange-correlation ($E_{\zeta\mathrm{xc}}$) energies:

$$T_s + E_{\mathrm{xc}} = T_\zeta + E_{\zeta\mathrm{xc}}. \tag{50}$$

The functional derivation leads to an expression containing the original and scaled exchange-correlation potentials:

$$\frac{\delta T_s}{\delta \varrho} + v_{\mathrm{xc}} = \frac{\delta T_\zeta}{\delta \varrho} + v_{\zeta\mathrm{xc}}. \tag{51}$$

Taking the case $\zeta = \zeta_d$ and the separation $T_s = T_w + T_p$ we arrive at

$$T_w + T_p + E_{\mathrm{xc}} = T_w + E_{\zeta_d\mathrm{xc}} \tag{52}$$

or

$$T_p = E_{\zeta_d\mathrm{xc}} - E_{\mathrm{xc}}. \tag{53}$$

Use of Eq. (28) leads to the corresponding equation for the functional derivatives:

$$v_p = v_{\zeta_d\mathrm{xc}} - v_{\mathrm{xc}}. \tag{54}$$

Equations (53) and (54) are expressions for the Pauli energy and potential. What is remarkable here is the fact that the kinetic terms T_p and v_p are expressed as the difference of the scaled and original exchange-correlation energies and potentials. It is, of course, the consequence of Eq. (50) that shows how the density scaling mixes the kinetic and exchange-correlation terms. Expressions (53) and (54) make it possible to seek alternative approximations for the Pauli energy and potential.

The noninteracting kinetic energy functional T_s has been in the center of interest [4,11,27–37]. The key issue is the existence and uniqueness of its functional derivative with respect to the electron density.

Density scaling makes it possible to find an alternative derivation. It concerns, however, not the original density functional theory but an extended one. As density scaling changes the number of electrons the formalism includes density matrices. Therefore, the Euler equation is derived in this enlarged theory. Recently, there has been a growing interest in orbital-free density functional theory. The present derivation of the Euler equation might give fresh insight into the problem and the expression for the Pauli potential and energy might help the search for better approximations.

The enlarged theory obtained via density scaling might have practical importance, too. In large systems with a lot of electrons we have to solve only one equation instead of many Kohn-Sham equations. After a good approximation is found, it will be possible to treat huge systems that cannot be calculated with the Kohn-Sham equations. Therefore, the present approach is relevant to real electronic systems.

The pair density functional theory can be an alternative approach of the density functional theory provided that an adequate approximation for the Pauli potential of the pair density functional theory is found. The problem is much more difficult than in the density functional theory because of the N-representability problem [38–54]. It is hoped that the present derivation of the two-particle effective equation of the pair density functional theory will turn to be useful in seeking approximate approaches for the Pauli potential.

ACKNOWLEDGMENTS

The work is supported by the TAMOP 4.2.1/B-09/1/KONV-2010-0007 project. The project is cofinanced by the European Union and the European Social Fund. Grant OTKA No. K 67923 is also gratefully acknowledged.

[1] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).
[2] M. Levy, J. P. Perdew and V. Sahni, Phys. Rev. A **30**, 2745 (1984).
[3] M. Levy and Hui Ou-Yang, Phys. Rev. A **38**, 625 (1988).
[4] S. Liu and P. W. Ayers, Phys. Rev. A **70**, 022501 (2004).
[5] Garnet Kin-Lic Chan and N. C. Handy, Phys. Rev. A **59**, 2670 (1999).
[6] Á. Nagy, Chem. Phys. Lett. **411**, 492 (2005).
[7] Á. Nagy, J. Chem. Phys. **123**, 044105 (2005).
[8] Á. Nagy, J. Phys. B **44**, 035001 (2011).
[9] Á. Nagy, in *Progress in Theoretical Chemistry and Physics*, edited by P. Hoggan, (Springer, Berlin, in press).
[10] E. H. Lieb, Int. J. Quantum. Chem. **24**, 243 (1983).
[11] R. van Leeuwen, Adv. Quantum. Chem. **43**, 24 (2003).
[12] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976); O. Gunnarsson, M. Jonson, and B. I. Lundqvist, *ibid.* **20**, 3136 (1979).
[13] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977); J. Harris and R. O. Jones, J. Phys. F **4**, 1170 (1974); J. Harris, Phys. Rev. A **29**, 1648 (1984).
[14] J. P. Perdew, R. G. Parr, M. Levy, J. L. Balduz Jr., Phys. Rev. Lett. **49**, 1691 (1982).
[15] R. G. Parr and W. Yang, *Density–Functional Theory of Atoms and Molecules* (Oxford, University Press, New York, 1989).
[16] I. Ekeland and R. Teman, *Convex Analysis and Variational Problems* (North-Holland, Amsterdam, 1976).

[17] M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979).
[18] C. F. Weizsäcker, Z. Phys. **96**, 341 (1935).
[19] N. H. March, Phys. Lett. A **113**, 66 (1986); **113**, 476 (1986); Int. J. Quantum Chem. Symp **13**, 3 (1986).
[20] S. B. Liu, J. Chem. Phys. **126**, 244103 (2007).
[21] Á. Nagy, Phys. Rev. A **66**, 022505 (2002).
[22] Á. Nagy, in *The Fundamentals of Electron Density, Density Matrices and Density Functional Theory in Atoms, Molecules and Solid State*, edited by N. I. Gidopoulos and S. Wilson (Kluwer, Dordrecht, 2003), p. 79.
[23] F. Furche, Phys. Rev. A **70**, 022514 (2004).
[24] Á. Nagy and C. Amovilli, J. Chem. Phys. **121**, 6640 (2004).
[25] Á. Nagy and C. Amovilli, J. Chem. Phys. **128**, 11411 (2008).
[26] Á. Nagy and C. Amovilli, Chem. Phys. Lett. **469**, 353 (2009).
[27] H. English and R. English, Phys. Status Solidi A **123**, 711 (1984); **124**, 373 (1984).
[28] R. K. Nesbet, Phys. Rev. A **58**, R12 (1998).
[29] R. K. Nesbet and R. Colle, Phys. Rev. A **61**, 012503 (1999).
[30] R. K. Nesbet, Phys. Rev. A **65**, 010502 (2001).
[31] R. K. Nesbet, Int. J. Quantum Chem. **90**, 262 (2002).
[32] T. Gal, Phys. Rev. A **62**, 044501 (2000).
[33] A. Holas and N. H. March, Phys. Rev. A **64**, 016501 (2001).
[34] A. Holas and N. H. March, Phys. Rev. A **66**, 066501 (2002).
[35] I. Lindgren and S. Salomonson, Phys. Rev. A **67**, 056501 (2003).
[36] I. Lindgren and S. Salomonson, Adv. Quantum Chem. **43**, 95 (2003).
[37] I. Lindgren and S. Salomonson, Phys. Rev. A **70**, 032509 (2004).
[38] P. W. Ayers, J. Math. Phys. **46**, 062107 (2005).
[39] E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976).
[40] P. Ziesche, Phys. Lett. A **195**, 213 (1994); Int. J. Quantum. Chem. **60**, 149 (1996).
[41] M. Levy and P. Ziesche, J. Chem. Phys. **115**, 9110 (2001).
[42] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963); A. J. Coleman and V. I. Yukalov, *Reduced Density Matrices: Coulson's Challange* (Sringer-Verlag, New York, 2000); J. Cioslowski, *Many-Electron Densities and Reduced Density Matrices* (Kluwer/Plenum, New York, 2000).
[43] K. Husimi, Proc. Phys. Math. Soc. Jpn. **22**, 264 (1940).
[44] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).
[45] E. R. Davidson, Chem. Phys. Lett. **246**, 209 (1995);
[46] E. R. Davidson, Phys. Rev. A **1**, 30 (1970).
[47] F. Sasaki, Phys. Rev. **138**, B1338 (1965).
[48] J. K. Percus, J. Chem. Phys. **122**, 234103 (2005); B. Liu and J. K. Percus, Phys. Rev. A **74**, 012508 (2006).
[49] M. E. Pistol, Chem. Phys. Lett. **400**, 548 (2004);
[50] M. E. Pistol, Chem. Phys. Lett. **417**, 521 (2006).
[51] P. W. Ayers and E. R. Davidson, Int. J. Quantum. Chem. **106**, 1487 (2006).
[52] P. W. Ayers, S. Gordon, and M. Levy, J. Chem. Phys. **124**, 054101 (2006).
[53] P. W. Ayers and M. Levy, J. Chem. Sci. **117**, 507 (2006).
[54] C. Garnod and J. K. Percus, J. Math. Phys. **5**, 1756 (1964).