

## Calculational scheme for exact exchange and correlation potentials based on the equation of motion for density matrix plus the perturbation theory

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The equation of motion method is used to express the external potential in terms of the first- and second-order interacting density matrices (DMs) for a molecule. By also introducing noninteracting DMs built from the Kohn-Sham (KS) reference system orbitals, the exchange-correlation potential is derived. Applying the perturbation theory of Görling and Levy [Phys. Rev. B **47**, 13 105 (1993)], this potential is separated into the exchange-only potential and various orders of the correlation terms. Each potential term can be determined self-consistently from a specific equation written in terms of both occupied and excited KS orbitals and differences of orbital energies, plus potential terms of lower orders. Naturally, the determination of these orbitals and energies requires a self-consistent solution of KS equations. Explicit expressions for calculation of the exchange potential and the leading term of the correlation potential are obtained and discussed. An approximate exchange potential written directly in terms of noninteracting DMs is also proposed. [S1050-2947(97)05511-X]

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### I. INTRODUCTION

One of the approaches to the many-electron problem of atoms and molecules that is currently of interest is the density-functional method (see, e.g., [1]), having its origins in the statistical theory of Thomas, Fermi, and Dirac (see e.g., [2]). Slater [3] made a major step forward when he recognized that approximations to the (single-particle) kinetic energy made in the Thomas-Fermi-Dirac theory (now called the local-density approximation) were too severe for quantitative work. He therefore proposed a hybrid approach in which one-electron Schrödinger equations were solved with a Hartree-like potential supplemented by a  $n^{1/3}$  exchange potential,  $n(\mathbf{r})$  being the ground-state density. Slater's work was formally completed by Kohn and Sham [4], who showed that such a one-body potential could be constructed as the sum of the external potential  $v(\mathbf{r})$  ( $-Ze^2/r$  in an atom of atomic number  $Z$ ), the electrostatic potential  $v_{\text{es}}(\mathbf{r})$  created by the electronic charge cloud of number density  $n(\mathbf{r})$ , and the exchange-correlation potential  $v_{\text{xc}}(\mathbf{r})$ , which was to be obtained from the exchange-correlation energy functional  $E_{\text{xc}}[n]$  as

$$v_{\text{xc}}(\mathbf{r};[n]) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (1.1)$$

Unfortunately, there is no direct means, within the density-functional theory framework, to derive  $E_{\text{xc}}$  or  $v_{\text{xc}}(\mathbf{r})$  as explicit functionals of the density and therefore, very recently, we have used the differential virial theorem to write  $v_{\text{xc}}(\mathbf{r})$  as a line integral in terms of first- and second-order density matrices (1DMs and 2DMs) [5]. The functional derivative in Eq. (1.1) is thereby bypassed, but the price to be paid, in any final theory, is that the 1DM  $\rho_1$  and 2DM  $\rho_2$  must be, at least implicitly, expressed as functionals of the diagonal 1DM, the

density  $n(\mathbf{r})$ . The present authors noted intimate connection of their result [5] in the exchange-only limit with the work formalism of Harbola and Sahní [6]. Subsequently, Levy and March [7] have expressed the "kinetic" correction to the Harbola-Sahní result, which restores the latter's path independence, giving an exact expression for the exchange potential and correlation potential separately. The perturbation theory applied in [7] had been developed earlier in the work of Görling and Levy [8]. This Görling-Levy (GL) theory involves scaling the electron-electron repulsion  $e^2/r_{ij}$  to the form  $\alpha e^2/r_{ij}$ , together with an  $\alpha$ -dependent one-body potential that constrains the ground-state density at each  $\alpha$  to be the same as in the fully interacting system.

More recently, a second approach to the calculation of  $v_{\text{xc}}(\mathbf{r})$  has been formulated by us [9], in which the line integral appearing in [5] is avoided. This alternative route involves, however, also the third-order DM and gives  $v_{\text{xc}}(\mathbf{r})$  as a solution of an integral equation rather than as a line integral. Holas and Levy [10] have proposed a way in this second approach, based again on the GL theory [8], to separate out  $v_x$ , the exchange only part, from  $v_{\text{xc}}$ . The work in both [7] and [10], due to applied perturbation theory [8], provides also a procedure to calculate self-consistently within the extended Kohn-Sham (KS) approach the exchange potential and various orders of the correlation potential  $v_c$ , expressed via line integrals or integral equations, respectively.

The purpose of the present work is to employ yet a third approach to the calculation of  $v_{\text{xc}}$  in terms of DMs, by constructing and applying the equation of motion for the 1DM, following the work of Dawson and March [11] (see also the work of Ziesche [12]). In addition to the external potential and 1DM, this equation involves only the 2DM coupled with the electron-electron interaction potential. Next, by expressing DMs in the same equation of motion as perturbation

expansions according to GL theory [8], we derive equations determining both  $v_x$  and various orders of the expanded  $v_c$ .

So three works, [7], [10], and the present study, combine the GL perturbation theory [8] with three different equations satisfied by low-order DMs to obtain  $v_x$  and expanded  $v_c$  self-consistently within the extended KS scheme for a given many-electron system. A completely different way to evaluate these potentials, based also on [8], was proposed by Göring and Levy in their subsequent works [13,14]. It involves the inverse of the integral operator of the linear density response, available within the extended KS scheme. All four methods appear somewhat complex in detail: Therefore, it is presently difficult to predict which one will prove most convenient for practical implementation.

## II. EXCHANGE-CORRELATION POTENTIAL IN TERMS OF DENSITY MATRICES

Although the equation of motion for the 1DM  $\rho_1(\mathbf{r}_1; \mathbf{r}_2)$  is already known (see, e.g., [11] and [12]), its derivation is so

simple that we merely give it in Appendix A in order to point out the assumptions and to establish the notation. In this equation [the spinless version of Eq. (A3)]

$$\begin{aligned} & \{[\hat{t}(\mathbf{r}_1) + v(\mathbf{r}_1)] - [\hat{t}(\mathbf{r}'_1) + v(\mathbf{r}'_1)]\} \rho_1(\mathbf{r}_1; \mathbf{r}'_1) \\ & + 2 \int d^3 r_2 \{u(\mathbf{r}_1, \mathbf{r}_2) - u(\mathbf{r}'_1, \mathbf{r}_2)\} \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2) = 0, \end{aligned} \quad (2.1)$$

the 1DM  $\rho_1$  is related to the 2DM  $\rho_2$  via the electron-electron interaction potential  $u(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ . Since the external potential  $v(\mathbf{r})$  is local, one can solve Eq. (2.1) with respect to it,

$$v(\mathbf{r}_1) = v(\mathbf{r}'_1) - W(\mathbf{r}_1, \mathbf{r}'_1; [u, \rho_1, \rho_2]), \quad (2.2a)$$

where

$$W(\mathbf{r}_1, \mathbf{r}'_1; [u, \rho_1, \rho_2]) = \frac{\{\hat{t}(\mathbf{r}_1) - \hat{t}(\mathbf{r}'_1)\} \rho_1(\mathbf{r}_1; \mathbf{r}'_1) + 2 \int d^3 r_2 \{u(\mathbf{r}_1, \mathbf{r}_2) - u(\mathbf{r}'_1, \mathbf{r}_2)\} \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2)}{\rho_1(\mathbf{r}_1; \mathbf{r}'_1)}. \quad (2.2b)$$

The matrix functional  $W$  shows anti-Hermiticity and antisymmetry. Therefore it is real and vanishes on the diagonal. By noting that  $v(\mathbf{r}_1) - v(\mathbf{r}'_1) = \{v(\mathbf{r}_1) - v(\mathbf{r}''_1)\} + \{v(\mathbf{r}''_1) - v(\mathbf{r}'_1)\}$ , one obtains from Eq. (2.2a) a very interesting identity of ‘‘spatial additivity’’ concerning  $\rho_1$ ,  $\rho_2$ , and  $u$ , namely,

$$\begin{aligned} W(\mathbf{r}_1, \mathbf{r}'_1; [u, \rho_1, \rho_2]) &= W(\mathbf{r}_1, \mathbf{r}''_1; [u, \rho_1, \rho_2]) \\ &+ W(\mathbf{r}''_1, \mathbf{r}'_1; [u, \rho_1, \rho_2]). \end{aligned} \quad (2.3)$$

It demonstrates that the sum  $W(\mathbf{r}_1, \mathbf{r}''_1) + W(\mathbf{r}''_1, \mathbf{r}'_1)$  is independent of  $\mathbf{r}''_1$ , even though the separate terms are not.

The presence of  $v(\mathbf{r}'_1)$  on the right-hand side of Eq. (2.2a) reflects the fact that potentials that differ by an additive constant lead to the same wave function and therefore the same DMs. This arbitrary constant of the potential can be fixed here by choosing a value of the potential (e.g., 0) at a chosen reference point  $\mathbf{r}'_1$  (e.g., at  $\infty$ ). Thus Eq. (2.2) demonstrates how the external potential can be reconstructed from given DMs.

As pointed out in Appendix A, the 1DM and 2DM, occurring in Eqs. (2.1) and (2.2), are obtained by means of reducing the pure-state NDM  $\gamma_N = \Psi \Psi^*$ , where  $\Psi$  is any eigenfunction of the system Hamiltonian (A1), or they represent a mixture of such pure-state DMs (A4). Equation (2.2) opens an interesting way of checking the quality of any approximate eigenfunction  $\Psi$  (the ground-state one or excited-state one) resulting from a numerical solution of the Schrödinger equation. In terms of DMs  $\rho_1$  and  $\rho_2$ , generated from this  $\Psi$ , one calculates  $v(\mathbf{r}_1)$  according to Eq. (2.2). The result may be thought of as the actual potential, for which the

given  $\Psi$  is the exact solution of the Schrödinger equation. By comparing this potential with the original one, regions of substantial discrepancy can be determined. This information may be helpful for improvements in calculating  $\Psi$ , e.g., by extending the basis functions set with functions significant for such regions. Taken with a negative sign, the potential  $v(\mathbf{r}_1)$  given by Eq. (2.2) for DMs corresponding to the ground-state (GS) function  $\Psi$  of the system represents also the functional derivative with respect to the density  $n(\mathbf{r}_1)$  of the Hohenberg-Kohn functional  $F[n]$  (see, e.g., [1]).

A similar equation can be obtained for the effective potential  $v_{\text{KS}}(\mathbf{r})$  of the equivalent noninteracting reference KS system having the same GS density  $n(\mathbf{r})$  [1], written in terms of the 1DM  $\rho_1^s$  of this system [the interaction term of Eq. (2.2) being absent now]:

$$v_{\text{KS}}(\mathbf{r}_1) = v_{\text{KS}}(\mathbf{r}'_1) - W_s(\mathbf{r}_1, \mathbf{r}'_1; [\rho_1^s]), \quad (2.4a)$$

where

$$\begin{aligned} W_s(\mathbf{r}_1, \mathbf{r}'_1; [\rho_1^s]) &= W(\mathbf{r}_1, \mathbf{r}'_1; [0, \rho_1^s, 0]) \\ &= \frac{\{\hat{t}(\mathbf{r}_1) - \hat{t}(\mathbf{r}'_1)\} \rho_1^s(\mathbf{r}_1; \mathbf{r}'_1)}{\rho_1^s(\mathbf{r}_1; \mathbf{r}'_1)}. \end{aligned} \quad (2.4b)$$

Obviously, the matrix  $W_s(\mathbf{r}_1, \mathbf{r}'_1)$  exhibits the same properties as the matrix  $W(\mathbf{r}_1, \mathbf{r}'_1)$ . The potential  $v_{\text{KS}}(\mathbf{r})$  is known to be a sum of two potentials: external  $v(\mathbf{r})$  and  $v_{\text{int}}(\mathbf{r})$ , the latter taking account of interactions present in the original electron system

$$v_{\text{KS}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{int}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}), \quad (2.5)$$

$$v_{\text{es}}(\mathbf{r}_1;[n]) = \int d^3r_2 u(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_2), \quad (2.6)$$

while  $v_{\text{xc}}$  is given in Eq. (1.1). After subtracting Eqs. (2.2a) and (2.6) from Eq. (2.4a) we arrive at the result

$$\begin{aligned} v_{\text{xc}}(\mathbf{r}_1) = & v_{\text{xc}}(\mathbf{r}'_1) + \frac{\{\hat{t}(\mathbf{r}_1) - \hat{t}(\mathbf{r}'_1)\} \rho_1(\mathbf{r}_1; \mathbf{r}'_1)}{\rho_1(\mathbf{r}_1; \mathbf{r}'_1)} \\ & - \frac{\{\hat{t}(\mathbf{r}_1) - \hat{t}(\mathbf{r}'_1)\} \rho_1^s(\mathbf{r}_1; \mathbf{r}'_1)}{\rho_1^s(\mathbf{r}_1; \mathbf{r}'_1)} \\ & + \int d^3r_2 \{u(\mathbf{r}_1, \mathbf{r}_2) - u(\mathbf{r}'_1, \mathbf{r}_2)\} \\ & \times \left\{ \frac{2\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2)}{\rho_1(\mathbf{r}_1; \mathbf{r}'_1)} - n(\mathbf{r}_2) \right\}. \end{aligned} \quad (2.7)$$

This form (2.7) is an exact and direct expression for  $v_{\text{xc}}(\mathbf{r})$  in terms of the low-order ground-state DMs  $\rho_1, \rho_2, n$  of the interacting system and  $\rho_1^s$  of the noninteracting system. Analogous exact relations, obtained by us earlier, had given  $v_{\text{xc}}(\mathbf{r})$  indirectly: either in the form of a line integral [5] or as a solution of an integral equation [9].

We expect Eq. (2.7) to be helpful in obtaining new approximations to  $v_{\text{xc}}(\mathbf{r};[n])$  by constructing approximations to the DMs  $\rho_1, \rho_2$ , and  $\rho_1^s$  as functionals of  $n$ . Such approximations to the DMs lead not only to  $v_{\text{xc}}$  but also to the exchange-correlation energy because it can be written in terms of the same DMs:

$$\begin{aligned} E_{\text{xc}}[n] = & \int d^3r_1 \hat{t}(\mathbf{r}_1) \{ \rho_1(\mathbf{r}_1; \mathbf{r}'_1) - \rho_1^s(\mathbf{r}_1; \mathbf{r}'_1) \}_{\mathbf{r}'_1 = \mathbf{r}_1} \\ & + \int d^3r_1 d^3r_2 u(\mathbf{r}_1, \mathbf{r}_2) \{ \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \\ & - \frac{1}{2} n(\mathbf{r}_1) n(\mathbf{r}_2) \}. \end{aligned} \quad (2.8)$$

It should be noted that the equation termed the differential virial theorem, which played the role of the starting point in our route to the exchange-correlation potential in the line-integral form [5], turns out to be the ‘‘diagonal’’ limit of the differentiated equation of motion (2.1). This can be demonstrated directly by acting with the operator  $\frac{1}{2}(\partial/\partial \mathbf{r}_1 - \partial/\partial \mathbf{r}'_1)$  on Eq. (2.1) and subsequently setting  $\mathbf{r}'_1 = \mathbf{r}_1$ .

### III. PERTURBATION-THEORY APPROACH TO EXCHANGE-CORRELATION POTENTIAL

The equation of motion (2.1), which allowed us to obtain the exact expression (2.7) for  $v_{\text{xc}}$  in terms of DMs, can be also useful for setting up a working procedure for evaluation of  $v_{\text{xc}}$  within the extended KS scheme by means of perturbation theory. According to Görling and Levy [8], it is convenient to link the interacting  $N$ -electron system, having the interaction potential  $u(\mathbf{r}_1, \mathbf{r}_2)$  and moving in the external potential  $v(\mathbf{r})$ , with the equivalent noninteracting  $N$ -electron system moving in the effective potential  $v_{\text{KS}}(\mathbf{r};[n])$  [both systems having the same GS density  $n(\mathbf{r})$ ], by introducing an intermediate  $N$ -electron system, having the interaction potential  $\alpha u(\mathbf{r}_1, \mathbf{r}_2)$  (i.e., scaled by a coupling constant  $\alpha$ ) and

moving in the external potential  $v_{\text{ext}}^\alpha(\mathbf{r};[n])$  chosen such that the electron density remains independent of  $\alpha$ ,

$$n^\alpha(\mathbf{r}) = n(\mathbf{r}) \quad \text{for } \alpha \geq 0. \quad (3.1)$$

Obviously, this link demands

$$v_{\text{ext}}^{\alpha=0}(\mathbf{r}) \equiv v_{\text{KS}}(\mathbf{r}), \quad (3.2a)$$

$$v_{\text{ext}}^{\alpha=1}(\mathbf{r}) \equiv v(\mathbf{r}). \quad (3.2b)$$

Denoting the DMs of this family of intermediate systems by  $\rho_i^\alpha$ , we rewrite the equation of motion (2.1) as

$$\begin{aligned} & \{ [\hat{t}(\mathbf{r}_1) + v_{\text{ext}}^\alpha(\mathbf{r}_1)] - [\hat{t}(\mathbf{r}'_1) + v_{\text{ext}}^\alpha(\mathbf{r}'_1)] \} \rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1) \\ & + 2 \int d^3r_2 \{ \alpha u(\mathbf{r}_1, \mathbf{r}_2) - \alpha u(\mathbf{r}'_1, \mathbf{r}_2) \} \rho_2^\alpha(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2) = 0, \end{aligned} \quad (3.3a)$$

so we can obtain  $v_{\text{ext}}^\alpha$  similarly as  $v$  in Eq. (2.2a) from Eq. (2.1):

$$v_{\text{ext}}^\alpha(\mathbf{r}_1) = v_{\text{ext}}^\alpha(\mathbf{r}'_1) - W(\mathbf{r}_1, \mathbf{r}'_1; [\alpha u, \rho_1^\alpha, \rho_2^\alpha]), \quad (3.3b)$$

where  $W$  is defined in Eq. (2.2b).

As shown by Görling and Levy [8], the external potential of an intermediate system depends on the coupling parameter  $\alpha$  as

$$v_{\text{ext}}^\alpha(\mathbf{r};[n]) = v_{\text{KS}}(\mathbf{r};[n]) - \alpha v_{\text{esx}}(\mathbf{r};[n]) - v_{\text{c}}^\alpha(\mathbf{r};[n]), \quad (3.4)$$

where  $v_{\text{esx}}(\mathbf{r}) = v_{\text{es}}(\mathbf{r}) + v_{\text{x}}(\mathbf{r})$  denotes the ‘‘electrostatic-plus-exchange’’ potential [see Eq. (2.6) for  $v_{\text{es}}$ ], while  $v_{\text{x}}(\mathbf{r})$  together with  $v_{\text{c}}(\mathbf{r}) \equiv v_{\text{c}}^{\alpha=1}(\mathbf{r})$  are the exchange and correlation potentials that sum to  $v_{\text{xc}}(\mathbf{r})$  of the KS theory, for the considered electron density  $n(\mathbf{r})$ . It is interesting that the correlation potential  $v_{\text{c}}^\alpha(\mathbf{r})$ , occurring in Eq. (3.4), has an expansion in a power series in  $\alpha$ , commencing at second order:

$$v_{\text{c}}^\alpha(\mathbf{r}) = \sum_{j=2}^{\infty} \alpha^j v_{\text{c}/j}(\mathbf{r}). \quad (3.5)$$

So, combining Eqs. (3.4) and (3.5), the following expansion can be written for the external potential

$$v_{\text{ext}}^\alpha(\mathbf{r}) = \sum_{j=0}^{\infty} \alpha^j v_{\text{ext}/j}(\mathbf{r}), \quad (3.6)$$

which is assumed to be convergent in the range  $0 \leq \alpha \leq 1$ . A similar expansion is taken [8] to hold also for the  $N$ -electron GS wave function  $\Psi^\alpha(\mathbf{x}_1, \dots, \mathbf{x}_N)$  and therefore for the DMs obtained from it (see Appendix B for details):

$$\gamma_i^\alpha = \sum_{j=0}^{\infty} \alpha^j \gamma_{i/j}, \quad \rho_i^\alpha = \sum_{j=0}^{\infty} \alpha^j \rho_{i/j}. \quad (3.7)$$

Similarly to the potential (3.2), the coupling parameter link for DMs demands

$$\rho_i^{\alpha=0} \equiv \rho_{i/0} \equiv \rho_i^s, \quad (3.8a)$$

$$\rho_i^{\alpha=1} \equiv \sum_{j=0}^{\infty} \rho_{i/j} \equiv \rho_i. \quad (3.8b)$$

Since  $\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1)$  occurs in  $W$  in Eq. (3.3b) also in the denominator [see Eq. (2.2b)], we introduce a notation for the expansion of its reciprocal:

$$\theta^\alpha(\mathbf{r}_1; \mathbf{r}'_1) = 1/\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1) = \sum_{j=0}^{\infty} \alpha^j \theta_{1j}; \quad (3.9a)$$

$$\theta_{10} = 1/\rho_{1/0} = 1/\rho_1^s, \quad \theta_{11} = -\rho_{1/1}/(\rho_1^s)^2, \quad (3.9b)$$

$$\theta_{12} = (\rho_{1/1})^2/(\rho_1^s)^3 - \rho_{1/2}/(\rho_1^s)^2, \quad (3.9c)$$

etc. Applying expansions (3.7) and (3.9), we obtain for  $W$  [Eq. (3.3b) with (2.2b)] the expansion

$$\begin{aligned} W(\mathbf{r}_1, \mathbf{r}'_1; [\alpha u, \rho_1^\alpha, \rho_2^\alpha]) &= W_s(\mathbf{r}_1, \mathbf{r}'_1; [\rho_1^s]) \\ &+ \sum_{j=1}^{\infty} \alpha^j W_{1j}(\mathbf{r}_1, \mathbf{r}'_1), \end{aligned} \quad (3.10a)$$

where  $W_s$  is given in Eq. (2.4b) and

$$\begin{aligned} W_{1j}(\mathbf{r}_1, \mathbf{r}'_1; [u, \rho_{1/0}, \dots, \rho_{1/j}, \rho_{2/0}, \dots, \rho_{2/j-1}]) \\ = \sum_{\ell=0}^j \theta_{1/\ell}(\mathbf{r}_1, \mathbf{r}'_1) [\hat{t}(\mathbf{r}_1) - \hat{t}(\mathbf{r}'_1)] \rho_{1/j-\ell}(\mathbf{r}_1; \mathbf{r}'_1) \\ + 2 \sum_{\ell=0}^{j-1} \theta_{1/\ell}(\mathbf{r}_1, \mathbf{r}'_1) \int d^3 r_2 [u(\mathbf{r}_1, \mathbf{r}_2) - u(\mathbf{r}'_1, \mathbf{r}_2)] \\ \times \rho_{2/j-1-\ell}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2). \end{aligned} \quad (3.10b)$$

Since Eq. (3.3b) holds for arbitrary  $\alpha$  (from the range [0,1]), the coefficients at  $\alpha^j$  must be the same for each  $j$  on both sides of this equation written in terms of expansions (3.6) and (3.10a). The  $j=0$  equation, resulting from Eq. (3.3b) is, of course, the same as Eq. (2.4a), while the higher- $j$  equations are

$$v_{\text{ext}/j}(\mathbf{r}_1) = v_{\text{ext}/j}(\mathbf{r}'_1) - W_{1j}(\mathbf{r}_1, \mathbf{r}'_1). \quad (3.11)$$

For further discussion it is convenient to introduce the effective interaction potential  $v_{\text{int}}^\alpha(\mathbf{r})$  [satisfying  $v_{\text{int}}^{\alpha=1}(\mathbf{r}) \equiv v_{\text{int}}(\mathbf{r})$ , Eq. (2.5)] in place of  $v_{\text{ext}}^\alpha(\mathbf{r})$  [Eqs. (3.4)–(3.6)]:

$$v_{\text{int}/1}(\mathbf{r}) = -v_{\text{ext}/1}(\mathbf{r}) = v_{\text{es}}(\mathbf{r}) = v_{\text{es}}(\mathbf{r}) + v_{\text{x}}(\mathbf{r}), \quad (3.12a)$$

$$v_{\text{int}/j}(\mathbf{r}) = -v_{\text{ext}/j}(\mathbf{r}) = v_{\text{c}/j}(\mathbf{r}), \quad j=2,3,\dots, \quad (3.12b)$$

which transforms Eq. (3.11) into

$$\begin{aligned} v_{\text{int}/j}(\mathbf{r}_1) &= v_{\text{int}/j}(\mathbf{r}'_1) \\ &+ W_{1j}(\mathbf{r}_1, \mathbf{r}'_1; [u, \rho_{1/0}, \dots, \rho_{1/j}, \rho_{2/0}, \dots, \rho_{2/j-1}]). \end{aligned} \quad (3.13)$$

Next, we rewrite the first, second, and higher- $j$ th-order potentials explicitly in terms of DMs:

$$\begin{aligned} v_{\text{ess}}(\mathbf{r}_1) &= v_{\text{ess}}(\mathbf{r}'_1) + \theta_{10}(\hat{t} - \hat{t}') \rho_{1/1} + \theta_{11}(\hat{t} - \hat{t}') \rho_{1/0} \\ &+ 2 \theta_{10} f[(u-u) \rho_{2/0}], \end{aligned} \quad (3.14a)$$

$$\begin{aligned} v_{\text{c}/2}(\mathbf{r}_1) &= v_{\text{c}/2}(\mathbf{r}'_1) + \theta_{10}(\hat{t} - \hat{t}') \rho_{1/2} + \theta_{11}(\hat{t} - \hat{t}') \rho_{1/1} \\ &+ \theta_{12}(\hat{t} - \hat{t}') \rho_{1/0} + 2 \theta_{10} f[(u-u) \rho_{2/1}] \\ &+ 2 \theta_{11} f[(u-u) \rho_{2/0}], \end{aligned} \quad (3.14b)$$

$$\begin{aligned} v_{\text{c}/j}(\mathbf{r}_1) &= v_{\text{c}/j}(\mathbf{r}'_1) + \sum_{\ell=0}^j \theta_{1/\ell}(\hat{t} - \hat{t}') \rho_{1/j-\ell} \\ &+ 2 \sum_{\ell=0}^{j-1} \theta_{1/\ell} f[(u-u) \rho_{2/j-1-\ell}]. \end{aligned} \quad (3.14c)$$

Here  $\theta_{1/\ell} = \theta_{1/\ell}(\mathbf{r}_1; \mathbf{r}'_1)$  is a combination of  $\rho_{1/0}(\mathbf{r}_1; \mathbf{r}'_1), \dots, \rho_{1/\ell}(\mathbf{r}_1; \mathbf{r}'_1)$  [see Eq. (3.9)] and the following shorthand notation is introduced:

$$(\hat{t} - \hat{t}') \rho_{1/i} = [\hat{t}(\mathbf{r}_1) - \hat{t}(\mathbf{r}'_1)] \rho_{1/i}(\mathbf{r}_1; \mathbf{r}'_1), \quad (3.14d)$$

$$\begin{aligned} f[(u-u) \rho_{2/i}] &= \int d^3 r_2 [u(\mathbf{r}_1, \mathbf{r}_2) - u(\mathbf{r}'_1, \mathbf{r}_2)] \\ &\times \rho_{2/i}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2). \end{aligned} \quad (3.14e)$$

The above equations allow direct evaluation of the electrostatic-plus-exchange potential and consecutive terms of the correlation potential expansion. The input information consists of the KS reference system objects such as the 1DM  $\rho_1^s = \rho_{1/0}$  and the 2DM  $\rho_2^s = \rho_{2/0}$ , together with perturbation expansion terms of the 1DM and 2DM (which will be shown in following sections to be available within an extended KS approach).

Since  $v_{\text{ext}}^\alpha(\mathbf{r}_1)$  plays a role of the external potential for the intermediate  $N$ -electron system, the matrix  $W(\mathbf{r}_1, \mathbf{r}'_1; [\alpha u, \rho_1^\alpha, \rho_2^\alpha])$ , occurring in Eq. (3.3b), must exhibit the same properties as the matrix  $W(\mathbf{r}_1, \mathbf{r}'_1; [u, \rho_1, \rho_2])$ , occurring in Eq. (2.2a). After expansion, this must remain true for each matrix term  $W_{1j}(\mathbf{r}_1, \mathbf{r}'_1; [u, \rho_{1/0}, \dots, \rho_{1/j}, \rho_{2/0}, \dots, \rho_{2/j-1}])$ .

It is worth noting that an expression, alternative to Eq. (3.11) or (3.13), can be derived also from the equation of motion (3.3a) by (i) inserting there expansions for potentials and DMs, (ii) equating coefficients at  $\alpha^j$  to obtain an equation for  $j$ th order, and (iii) solving the  $j$ th order equation with respect to the highest-order potential term. The result is

$$v_{\text{int}/j}(\mathbf{r}_1) = v_{\text{int}/j}(\mathbf{r}'_1) + \tilde{W}_{1j}(\mathbf{r}_1, \mathbf{r}'_1), \quad (3.15a)$$

where

$$\begin{aligned} \tilde{W}_{1j}(\mathbf{r}_1, \mathbf{r}'_1; [u, v_{\text{KS}}, \rho_{1/0}, \rho_{1/1}, \rho_{2/0}]) \\ = \theta_{10} \{ (\hat{h}_{\text{KS}} - \hat{h}'_{\text{KS}}) \rho_{1/1} + 2f[(u-u) \rho_{2/0}] \}, \end{aligned} \quad (3.15b)$$

$$\begin{aligned}
& \widetilde{W}_{/j}(\mathbf{r}_1, \mathbf{r}'_1; [u, v_{\text{KS}}, v_{\text{int}/1}, \dots, v_{\text{int}/j-1}, \\
& \quad \times \rho_{1/0}, \dots, \rho_{1/j}, \rho_{2/j-1}]) \\
& = \theta_{/0} \left\{ (\hat{h}_{\text{KS}} - \hat{h}_{\text{KS}}) \rho_{1/j} - \sum_{\ell=1}^{j-1} (v_{\text{int}/\ell} - v_{\text{int}/\ell}) \rho_{1/j-\ell} \right. \\
& \quad \left. + 2f[(u-u)\rho_{2/j-1}] \right\}; \quad (3.15c)
\end{aligned}$$

see Eqs. (3.14d) and (3.14e) for notation. Here  $\hat{h}_{\text{KS}}$  denotes the one-body KS Hamiltonian

$$\hat{h}_{\text{KS}}(\mathbf{r}) = \hat{t}(\mathbf{r}) + v_{\text{KS}}(\mathbf{r}). \quad (3.16)$$

Since Eqs. (3.13) and (3.15a) determine the same potential, an identity, which connects expanded DMs and potentials, namely,

$$W_{/j}(\mathbf{r}_1, \mathbf{r}'_1; [u, \rho_{1/0}, \dots]) = \widetilde{W}_{/j}(\mathbf{r}_1, \mathbf{r}'_1; [u, v_{\text{KS}}, \dots]), \quad (3.17)$$

must hold for  $j=1, 2, \dots$  and for any position pair  $\mathbf{r}_1, \mathbf{r}'_1$ .

The main result of this section, Eq. (3.14), hinges on the expansion (3.9) of  $1/\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1)$ . Although there are no general reasons to expect  $\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1)$  to be zero at some positions  $\mathbf{r}_1, \mathbf{r}'_1$  [note that for large  $r$  and large  $r'$  it is real and positive:  $\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1) \approx n^{1/2}(\mathbf{r}_1)n^{1/2}(\mathbf{r}'_1)$ ; see, e.g., [15]], nevertheless, we give below a plausible argument that  $1/\rho_1^\alpha$  is never singular. Equation (3.3b) with Eq. (2.2b) shows that the potential difference  $v_{\text{ext}}^\alpha(\mathbf{r}_1) - v_{\text{ext}}^\alpha(\mathbf{r}'_1)$ , a well-defined object of the intermediate  $N$ -electron system, is expressed in terms of DMs in a form of a fraction  $W$ , having  $\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1)$  as its denominator. The potential is not singular, except at nuclear positions. But  $\rho_1^\alpha$  is not zero at these points because its natural orbitals satisfy there the cusp condition (see, e.g., [16]). So, for the remaining positions, any occurrence of zero of  $\rho_1^\alpha$  would mean a singularity of  $v_{\text{ext}}^\alpha$ , the contradiction. However, may it happen in the numerator of  $W$  that at such zero position the contribution due to  $\rho_1^\alpha$  cancels out that due to  $\rho_2^\alpha$ , allowing thus for a finite limit of the resulting potential? To ascertain if there is a chance for such a situation, let us consider also a completely different representation of  $v_{\text{ext}}^\alpha$ , namely,

$$\begin{aligned}
v_{\text{ext}}^\alpha(\mathbf{r}_1) = & -\{\hat{t}(\mathbf{r}_1)\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1) \\
& + w(\mathbf{r}_1, \mathbf{r}'_1; [v_{\text{ext}}^\alpha, \alpha u, \rho_1^\alpha, \rho_2^\alpha, \rho_3^\alpha])\}/\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1), \quad (3.18)
\end{aligned}$$

which follows directly from Eq. (9) of our paper [9]. The functional  $w$  consists of a sum of two integrals involving indicated potentials and DMs. The denominator in the expression (3.18) is the same as in  $W$ ,  $\rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1)$ , while an expression involving the 3DM  $\rho_3^\alpha$  (absent in  $W$ ) is seen in the numerator. The complete cancellation in this numerator and simultaneously in the  $W$  numerator, exactly at the same position pair  $\mathbf{r}_1, \mathbf{r}'_1$ , must be regarded as improbable.

#### IV. DENSITY-FUNCTIONAL ASPECTS OF THE RESULTS

As is shown in Appendixes B and C, the expanded DMs  $\rho_{\ell/j}$  can be calculated using the KS spin orbitals  $\phi_i$  and corresponding orbital energies  $\epsilon_i$ , for  $i$  running over not only the  $N$  lowest-energy, occupied states, but also an infinite sequence of excited (virtual) states ( $i > N$ ), and using  $j$  potential terms  $v_{\text{int}/1}, v_{\text{int}/2}, \dots, v_{\text{int}/j}$ . Therefore, Eq. (3.14) can be symbolically rewritten as

$$v_{\text{esx}}(\mathbf{r}_1) = v_{\text{esx}}(\mathbf{r}'_1) + w_1(\mathbf{r}_1; \mathbf{r}'_1; [\{\phi_i, \epsilon_i\}, v_{\text{esx}}]), \quad (4.1a)$$

$$v_{c/2}(\mathbf{r}_1) = v_{c/2}(\mathbf{r}'_1) + w_2(\mathbf{r}_1; \mathbf{r}'_1; [\{\phi_i, \epsilon_i\}, v_{\text{esx}}, v_{c/2}]), \quad (4.1b)$$

$$\begin{aligned}
v_{c/j}(\mathbf{r}_1) = & v_{c/j}(\mathbf{r}'_1) \\
& + w_j(\mathbf{r}_1; \mathbf{r}'_1; [\{\phi_i, \epsilon_i\}, v_{\text{esx}}, v_{c/2}, \dots, v_{c/j}]). \quad (4.1c)
\end{aligned}$$

Equation (4.1a) represents a functional (integral) equation determining  $v_{\text{esx}}$  as a functional of  $\{\phi_i, \epsilon_i\}$ . Next, Eq. (4.1b) [with  $v_{\text{esx}}$  considered to be the known solution of Eq. (4.1a)] represents an equation for determining  $v_{c/2}$  as a functional of  $\{\phi_i, \epsilon_i\}$ , and so on for  $v_{c/3}, v_{c/4}, \dots$ .

What is interesting is that the above-mentioned expressions for  $\rho_{\ell/j}$  are insensitive to any shift of potential terms by a constant, i.e., they are invariant with respect to transformations  $v_{\text{int}/j} \rightarrow v_{\text{int}/j} + c_j$ , where  $c_j$  are arbitrary constants. Therefore, the solutions of Eq. (4.1) are determined within an accuracy of additive constants, arbitrary  $v_{\text{int}/j}(\mathbf{r}'_1)$  at arbitrarily chosen reference point  $\mathbf{r}'_1$ . Equations (4.1) can be solved iteratively, provided, of course, that such a method turns out to be convergent (alternatively, an algebraic solution of a system of linear equations can be also applied, as discussed in Sec. V).

Being explicit functionals of  $\{\phi_i, \epsilon_i\}$ , the potentials  $v_{\text{int}/j}$  are implicit functionals of the GS electronic density  $n(\mathbf{r})$ , as follows from the Hohenberg-Kohn theorem (see, e.g. in [1]) applied to the equivalent noninteracting reference system. Therefore, we recognize the functional dependence on  $n$  not only for the exchange potential

$$v_x(\mathbf{r}) = v_{\text{int}/1}(\mathbf{r}; [n]) - v_{\text{es}}(\mathbf{r}; [n]), \quad (4.2)$$

but also for each term separately of the expanded correlation potential ( $j=2, 3, \dots$ )

$$v_{c/j}(\mathbf{r}) = v_{\text{int}/j}(\mathbf{r}; [n]). \quad (4.3)$$

This property just reflects the fact that the perturbation theory expansion for the potential  $v_{\text{ext}}^\alpha$  [Eqs. (3.4) and (3.5)] is obtained by Görling and Levy [8] within the density-functional theory, in which potential terms are defined as functional derivatives of the corresponding terms of the energy expansion

$$\begin{aligned}
v_{\text{esx}}(\mathbf{r}; [n]) = & v_{\text{es}}(\mathbf{r}; [n]) + v_x(\mathbf{r}; [n]) \\
= & \frac{\delta E_{\text{es}}[n]}{\delta n(\mathbf{r})} + \frac{\delta E_x[n]}{\delta n(\mathbf{r})} = \frac{\delta E_{\text{int}/1}[n]}{\delta n(\mathbf{r})}, \quad (4.4a)
\end{aligned}$$

$$v_{c/j}(\mathbf{r};[n]) = \frac{\delta E_{c/j}[n]}{\delta n(\mathbf{r})} = \frac{\delta E_{\text{int}/j}[n]}{\delta n(\mathbf{r})}, \quad j=2,3,\dots \quad (4.4b)$$

and where  $E_{\text{int}/j}$  are terms of the expansion of

$$\begin{aligned} E_{\text{int}}^\alpha[n] &= \langle \Psi^\alpha | \hat{T} + \alpha \hat{U} | \Psi^\alpha \rangle - \langle \Psi^0 | \hat{T} | \Psi^0 \rangle \\ &= \alpha(E_{\text{es}}[n] + E_{\text{x}}[n]) + E_{\text{c}}^\alpha[n] \end{aligned} \quad (4.5)$$

in power series in  $\alpha$

$$E_{\text{int}}^\alpha[n] = \sum_{j=0}^{\infty} \alpha^j E_{\text{int}/j}[n]. \quad (4.6)$$

The energy  $E_{\text{int}}^\alpha[n]$  [Eq. (4.5)] can be next written in terms of DMs obtained from  $\Psi^\alpha$ ,

$$\begin{aligned} E_{\text{int}}^\alpha[n] &= \int d^3 r_1 \hat{t}(\mathbf{r}_1) \{ \rho_1^\alpha(\mathbf{r}_1; \mathbf{r}'_1) - \rho_1^s(\mathbf{r}_1; \mathbf{r}'_1) \}_{|_{\mathbf{r}'_1=\mathbf{r}_1}} \\ &+ \int d^3 r_1 d^3 r_2 \alpha u(\mathbf{r}_1, \mathbf{r}_2) \rho_2^\alpha(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (4.7)$$

After substituting the expansion (3.7) into Eq. (4.7) we obtain the following expressions for the terms of expansion (4.6): for  $j=1$

$$E_{\text{int}/1} = E_{\text{es}} + E_{\text{x}} = \int d^3 r_1 d^3 r_2 u(\mathbf{r}_1, \mathbf{r}_2) \rho_2^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \quad (4.8a)$$

and for  $j \geq 2$

$$\begin{aligned} E_{\text{int}/j} &= E_{c/j} = \int d^3 r_1 \hat{t}(\mathbf{r}_1) \rho_{1/j}(\mathbf{r}_1; \mathbf{r}'_1)_{|_{\mathbf{r}'_1=\mathbf{r}_1}} \\ &+ \int d^3 r_1 d^3 r_2 u(\mathbf{r}_1, \mathbf{r}_2) \rho_{2/j-1}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \\ &= E_{c/j}^{\text{kin}} + E_{c/j}^{\text{pot}}. \end{aligned} \quad (4.8b)$$

It should be noted that the first-order kinetic energy vanishes [8]

$$E_{c/1}^{\text{kin}} = \int [\hat{t} \rho_{1/1}] = 0. \quad (4.8c)$$

Thus Eqs. (4.8) and (3.14) represent explicit formulas for evaluation of the energy terms and their functional derivatives (4.4), all in terms of expanded DMs  $\rho_{i/j}$ .

The above considerations can be summarized as follows. Given the number  $N$  of electrons in the system and the set of eigensolutions  $\{\phi_i(\mathbf{x}), \epsilon_i, i=1,2,\dots\}$  of some single-particle Hamiltonian (to be interpreted as the KS one), we are able, in principle, to evaluate consecutively  $(v_{\text{x}}(\mathbf{r}), E_{\text{x}})$ ,  $(v_{c/2}(\mathbf{r}), E_{c/2})$ ,  $(v_{c/3}(\mathbf{r}), E_{c/3})$ , and so on. These quantities are known to be functionals of the density expressed in terms of the same orbitals as

$$n(\mathbf{r}) = \sum_s \sum_{a=1}^N |\phi_a(\mathbf{r}, s)|^2, \quad (4.9)$$

while their potential terms are related to energy terms via Eq. (4.4).

These facts will allow us to interpret a ‘‘truncated’’ GS problem, in which, because of increasing complexity of  $(v_{c/j}(\mathbf{r}), E_{c/j})$  evaluation, only a finite (and rather small) number of terms can be handled. Consider the total-energy functional truncated after the  $k$ th-order term:

$$E^{(k)}[n] = T_{\text{s}}[n] + \int d^3 r v(\mathbf{r}) n(\mathbf{r}) + \sum_{j=1}^k E_{\text{int}/j}[n], \quad (4.10)$$

which approximates the exact total-energy functional of the considered system [here  $T_{\text{s}} = \langle \Psi^0 | \hat{T} | \Psi^0 \rangle$  and compare Eqs. (4.5) and (4.6) at  $\alpha=1$ ]:

$$\begin{aligned} E[n] &= E^{(\infty)}[n] \\ &= T_{\text{s}}[n] + \int d^3 r v(\mathbf{r}) n(\mathbf{r}) + E_{\text{es}}[n] \\ &+ E_{\text{x}}[n] + E_{\text{c}}[n]. \end{aligned} \quad (4.11)$$

The exact GS energy  $E_{\text{GS}}$  and density  $n_{\text{GS}}(\mathbf{r})$  correspond to

$$E_{\text{GS}} = \min_{n \rightarrow N} E[n] = E[n_{\text{GS}}]. \quad (4.12)$$

Let  $E_{\text{GS}}^{(k)}$  and  $n_{\text{GS}}^{(k)}(\mathbf{r})$  be a solution of

$$E_{\text{GS}}^{(k)} = \min_{n \rightarrow N} E^{(k)}[n] = E^{(k)}[n_{\text{GS}}^{(k)}]. \quad (4.13)$$

But, obviously, these quantities  $E_{\text{GS}}^{(k)}$  and  $n_{\text{GS}}^{(k)}(\mathbf{r})$  can be also obtained, applying our scheme, via a self-consistent solution of KS equations with the truncated effective potential

$$v_{\text{KS}}^{(k)} = v + \sum_{j=1}^k v_{\text{int}/j} = v + v_{\text{es}} + v_{\text{x}} + v_{c/2} + \dots + v_{c/k}. \quad (4.14)$$

The exchange-only approximation ( $k=1$  case) is equivalent to, but expressed in a completely different way from the optimized potential method [17], see our discussion in [18]. The  $k=2$  case may be termed the ‘‘leading-correlation approximation’’ (details of both are given in Sec. V). The accuracy of the above (and, in general,  $k$ th-order) approximation is connected with the speed of convergence of perturbation-theory expansions for energy and potential. By subtracting Eq. (4.13) from Eq. (4.12) we obtain for the GS energy error

$$\begin{aligned} E_{\text{GS}} - E_{\text{GS}}^{(k)} &= O((n_{\text{GS}}^{(k)} - n_{\text{GS}})^2) + E_{c/k+1}[n_{\text{GS}}^{(k)}] \\ &+ E_{c/k+2}[n_{\text{GS}}^{(k)}] + \dots \end{aligned} \quad (4.15)$$

(the functional Taylor expansion of  $E[n]$  for  $n = n_{\text{GS}}^{(k)}$  around  $n_{\text{GS}}$  was applied and minimum property (4.12) used). Anticipating that the term quadratic in density deviation will be small, we need the value of  $E_{c/k+1}[n_{\text{GS}}^{(k)}]$  to estimate the energy error. In fact, this quantity is available within the  $k$ th approximation as

$$E_{c/k+1} = \frac{1}{k+1} \int d^3r_1 d^3r_2 u(\mathbf{r}_1, \mathbf{r}_2) \rho_{2/k}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) \quad (4.16)$$

because  $\rho_{2/k}$  can be calculated within the  $k$ th approximation. Equation (4.16) was obtained from Eq. (4.8b) using the fact that the kinetic-energy term  $E_{c/j}^{\text{kin}}$  of  $E_{c/j}$  is simply related to the accompanying interaction potential-energy term  $E_{c/j}^{\text{pot}}$ , namely,

$$E_{c/j}^{\text{kin}} = -\frac{j-1}{j} E_{c/j}^{\text{pot}}, \quad (4.17)$$

as has been shown in [8] (see also [19]).

A systematic investigation of convergence of the series  $E_{\text{int}} = (E_{\text{es}} + E_x) + E_{c/2} + E_{c/3} + \dots$  and  $v_{\text{int}} = (v_{\text{es}} + v_x) + v_{c/2} + v_{c/3} + \dots$  at  $n = n_{\text{GS}}$  can be performed for systems for which  $E_{\text{GS}}$  and  $n_{\text{GS}}(\mathbf{r})$  are known from configuration-interaction or Hylleraas-type calculations. Having  $n_{\text{GS}}(\mathbf{r})$ , the effective KS potential  $v_{\text{KS}}$  (which leads to this density) can be established numerically by various methods (see, e.g., [20] and references therein). After solving KS equations (with this potential  $v_{\text{KS}}$ ), one can evaluate the separate terms of discussed series in terms of the obtained  $\{\phi_i(\mathbf{x}), \epsilon_i\}$  by applying the methods of the present paper. The truncated sums should be compared with  $(E_{\text{GS}} - T_s[n] - \int [vn])$  and  $(v_{\text{KS}} - v)$ , respectively. On the other hand, it would be interesting also to solve for the same systems the truncated problem (4.13) and compare  $E_{\text{GS}}$  and  $n_{\text{GS}}(\mathbf{r})$  with the resulting  $E_{\text{GS}}^{\{k\}}$  and  $n_{\text{GS}}^{\{k\}}(\mathbf{r})$  to see their accuracy. It is noteworthy that Liu and Parr [19] performed an approximate numerical analysis of the series  $E_c = E_{c/2} + E_{c/3} + \dots$  (in their notation  $E_c = E' + E'' + \dots$ ) for atoms from He to Ar, concluding that the magnitude of  $E_{c/3}$  is roughly 20% of that of  $E_{c/2}$ .

## V. CALCULATIONAL PROCEDURE FOR EXCHANGE AND LEADING-CORRELATION POTENTIALS

### A. Calculation of the exchange potential

The exchange-only potential can be easily separated from Eq. (3.14a) for the electrostatic-plus-exchange potential by taking into account the form of  $\rho_{2/0} = \rho_2^s$  due to the determinantal KS wave function. Since the general spin structure of the reference KS system 1DM [Eq. (C34)] can be written [1] as

$$\begin{aligned} \gamma_1^s(\mathbf{r}_1 s_1; \mathbf{r}'_1 s'_1) &= \rho_{1\uparrow}^s(\mathbf{r}_1; \mathbf{r}'_1) \alpha(s_1) \alpha(s'_1) \\ &+ \rho_{1\downarrow}^s(\mathbf{r}_1; \mathbf{r}'_1) \beta(s_1) \beta(s'_1) \end{aligned} \quad (5.1)$$

and reduced [Eq. (A5)] to

$$\rho_1^s(\mathbf{r}_1; \mathbf{r}'_1) = \rho_{1\uparrow}^s(\mathbf{r}_1; \mathbf{r}'_1) + \rho_{1\downarrow}^s(\mathbf{r}_1; \mathbf{r}'_1), \quad (5.2)$$

the reference system spinless 2DM [Eq. (C35) with Eq. (A5)] can be split as

$$\rho_2^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \rho_{2d}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) + \rho_{2x}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2), \quad (5.3a)$$

where the direct and exchange parts of this DM are

$$\rho_{2d}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \frac{1}{2} \rho_1^s(\mathbf{r}_1; \mathbf{r}'_1) \rho_1^s(\mathbf{r}_2; \mathbf{r}'_2), \quad (5.3b)$$

$$\begin{aligned} \rho_{2x}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) &= -\frac{1}{2} [\rho_{1\uparrow}^s(\mathbf{r}_1; \mathbf{r}'_2) \rho_{1\uparrow}^s(\mathbf{r}_2; \mathbf{r}'_1) \\ &+ \rho_{1\downarrow}^s(\mathbf{r}_1; \mathbf{r}'_2) \rho_{1\downarrow}^s(\mathbf{r}_2; \mathbf{r}'_1)]. \end{aligned} \quad (5.3c)$$

For spin-compensated systems, i.e., satisfying  $\rho_{1\uparrow}^s = \rho_{1\downarrow}^s = \frac{1}{2} \rho_1^s$ , the above expression simplifies to

$$\rho_{2x}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = -\frac{1}{4} \rho_1^s(\mathbf{r}_1; \mathbf{r}'_2) \rho_1^s(\mathbf{r}_2; \mathbf{r}'_1). \quad (5.3d)$$

After inserting the above  $\rho_2^s$  into Eq. (3.14a) we notice cancellation of  $v_{\text{es}}$  contributions, leading to the result

$$\begin{aligned} v_x(\mathbf{r}_1) &= v_x(\mathbf{r}'_1) + \theta_{/0}(\hat{t} - \hat{t}') \rho_{1/1} + \theta_{/1}(\hat{t} - \hat{t}') \rho_{1/0} \\ &+ 2 \theta_{/0} \int [(u - u') \rho_{2x}^s]. \end{aligned} \quad (5.4a)$$

But, from Eq. (2.4) follows  $\theta_{/1}(\hat{t} - \hat{t}') \rho_{1/0} = \theta_{/0}(v_{\text{KS}} - v_{\text{KS}}) \rho_{1/1}$ ; therefore, the above equation can be rewritten finally in terms of the one-body KS Hamiltonian  $\hat{h}_{\text{KS}}$  (3.16) as

$$\begin{aligned} v_x(\mathbf{r}_1) &= v_x(\mathbf{r}'_1) + \left\{ [\hat{h}_{\text{KS}}(\mathbf{r}_1) - \hat{h}_{\text{KS}}(\mathbf{r}'_1)] \rho_{1/1}(\mathbf{r}_1; \mathbf{r}'_1) \right. \\ &+ 2 \int d^3r_2 [u(\mathbf{r}_1, \mathbf{r}_2) - u(\mathbf{r}'_1, \mathbf{r}_2)] \\ &\left. \times \rho_{2x}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) \right\} / \rho_1^s(\mathbf{r}_1; \mathbf{r}'_1), \end{aligned} \quad (5.4b)$$

i.e., in a form resembling Eq. (3.15).

The DM  $\rho_{1/1}$  will be calculated by reduction of  $\gamma_{1/1}$ , using Eqs. (B17b), (B12b), and (C17):

$$\begin{aligned} \gamma_{1/1}(\mathbf{1}; \mathbf{1}') &= \sum_{i,k} \gamma_1^{ki}(\mathbf{1}; \mathbf{1}') \sum_A \{ \langle Y_{/0} | \hat{a}_i^\dagger \hat{a}_k | A \rangle \langle A | Y_{/1} \rangle \\ &+ \langle Y_{/1} | A \rangle \langle A | \hat{a}_i^\dagger \hat{a}_k | Y_{/0} \rangle \}. \end{aligned} \quad (5.5)$$

Due to Eq. (C21), the summation over  $A$  in Eq. (5.5) can be limited to  $A = O_a^r$  only [compare Eqs. (B11) and (C6)] and evaluated, using Eq. (C20), as

$$\begin{aligned} \gamma_{1/1}(\mathbf{1}; \mathbf{1}') &= \sum_a^{\text{occ}} \sum_r^{\text{vir}} \{ \gamma_1^{ra}(\mathbf{1}; \mathbf{1}') \langle O_a^r | Y_{/1} \rangle + \gamma_1^{ar}(\mathbf{1}; \mathbf{1}') \\ &\times \langle Y_{/1} | O_a^r \rangle \}. \end{aligned} \quad (5.6)$$

Next, using Eqs. (C8)–(C14) we evaluate  $\langle O_a^r | Y_{/1} \rangle$  of Eq. (B12b) to be

$$\begin{aligned} \langle O_a^r | Y_{/1} \rangle &= \frac{1}{\omega_{a,r}} \left\{ \frac{1}{4} \sum_{i,j,k,\ell} \langle ij || k\ell \rangle \langle O_a^r | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | O \rangle \right. \\ &\left. - \sum_{i,k} \langle i | v_{\text{ess}} | k \rangle \langle O_a^r | \hat{a}_i^\dagger \hat{a}_k | O \rangle \right\}, \end{aligned} \quad (5.7)$$

where

$$\omega_{a,r} = \mathcal{E}_O - \mathcal{E}_{O_a^r} = \epsilon_a - \epsilon_r \quad (5.8)$$

denotes minus the single-pair excitation energy, and using Eqs. (C26) and (C20),  $\langle O_a^r | Y_{1l} \rangle$  is transformed into

$$\langle O_a^r | Y_{1l} \rangle = \frac{1}{\omega_{a,r}} \left\{ \sum_b^{\text{occ}} \langle rb || ab \rangle - \langle r | v_{\text{esx}} | a \rangle \right\}. \quad (5.9)$$

But, from Eqs. (C13) and (C14) we find

$$\begin{aligned} \sum_b^{\text{occ}} \langle rb || ab \rangle &= \int d\mathbf{1} \phi_r^*(\mathbf{1}) v_{\text{es}}(\mathbf{1}) \phi_a(\mathbf{1}) \\ &+ \int d\mathbf{1} \phi_r^*(\mathbf{1}) \int d\mathbf{2} \tilde{v}_x^{\text{F}}(\mathbf{1}\mathbf{2}) \phi_a(\mathbf{2}) \\ &= \langle r | v_{\text{es}} | a \rangle + \langle r | \hat{v}_x^{\text{F}} | a \rangle, \end{aligned} \quad (5.10)$$

where we have introduced the Fock exchange nonlocal (integral) operator  $\hat{v}_x^{\text{F}}$  [analogous to the exchange operator of the Hartree-Fock (HF) approach, but here in terms of the KS orbitals rather than the HF orbitals]

$$\hat{v}_x^{\text{F}}(\mathbf{1}) \phi(\mathbf{1}) = \int d\mathbf{2} \tilde{v}_x^{\text{F}}(\mathbf{1}\mathbf{2}) \phi(\mathbf{2}), \quad (5.11a)$$

$$\tilde{v}_x^{\text{F}}(\mathbf{1}\mathbf{2}) = -u(\mathbf{1}\mathbf{2}) \gamma_1^s(\mathbf{1}; \mathbf{2}). \quad (5.11b)$$

We note here that  $\hat{v}_x^{\text{F}}$  is a Hermitian operator. So, finally, we have from Eq. (5.9) a simple expression

$$\langle O_a^r | Y_{1l} \rangle = \frac{1}{\omega_{a,r}} \langle r | \hat{v}_x^{\text{F}} - v_x | a \rangle \equiv \frac{1}{\omega_{a,r}} \langle r | x | a \rangle \quad (5.12)$$

because of cancellation of  $v_{\text{es}}$  contributions. The notation  $x(\mathbf{1}) = \hat{v}_x^{\text{F}}(\mathbf{1}) - v_x(\mathbf{1})$  has been introduced.

Equation (5.6) can be thus rewritten as

$$\begin{aligned} \gamma_{1/l}(\mathbf{1}; \mathbf{1}') &= \sum_a^{\text{occ}} \sum_r^{\text{vir}} \frac{1}{\omega_{a,r}} \{ \langle r | x | a \rangle \gamma_1^{ra}(\mathbf{1}; \mathbf{1}') \\ &+ \langle a | x | r \rangle \gamma_1^{ar}(\mathbf{1}; \mathbf{1}') \}. \end{aligned} \quad (5.13)$$

It generalizes for complex orbitals the result of Levy and March [7] obtained for real orbitals.

Note that  $[\hat{h}_{\text{KS}}(\mathbf{1}) - \hat{h}_{\text{KS}}(\mathbf{1}')] \gamma_1^{ij}(\mathbf{1}; \mathbf{1}') = \omega_{i,j} \gamma_1^{ij}(\mathbf{1}; \mathbf{1}')$  follows from Eq. (C2) applied to Eq. (C17b) and the notation (5.8). Therefore, the combination, occurring in Eq. (5.4b), can be found to be

$$\begin{aligned} [\hat{h}_{\text{KS}}(\mathbf{1}) - \hat{h}_{\text{KS}}(\mathbf{1}')] \gamma_{1/l}(\mathbf{1}; \mathbf{1}') &= \sum_a^{\text{occ}} \sum_r^{\text{vir}} \{ -\langle r | x | a \rangle \gamma_1^{ra}(\mathbf{1}; \mathbf{1}') \\ &+ \langle a | x | r \rangle \gamma_1^{ar}(\mathbf{1}; \mathbf{1}') \}. \end{aligned} \quad (5.14)$$

Thus the final equation for  $v_x$  is

$$\begin{aligned} v_x(\mathbf{r}_1) &= v_x(\mathbf{r}'_1) + \left\{ \sum_a^{\text{occ}} \sum_r^{\text{vir}} [ \langle a | \hat{v}_x^{\text{F}} - v_x | r \rangle \rho_1^{ar}(\mathbf{r}_1; \mathbf{r}'_1) \right. \\ &- \langle r | \hat{v}_x^{\text{F}} - v_x | a \rangle \rho_1^{ra}(\mathbf{r}_1; \mathbf{r}'_1) ] + 2 \int d^3 r_2 [ u(\mathbf{r}_1, \mathbf{r}_2) \\ &- u(\mathbf{r}'_1, \mathbf{r}_2) ] \rho_{2x}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2) \left. \right\} / \rho_1^s(\mathbf{r}_1; \mathbf{r}'_1), \end{aligned} \quad (5.15)$$

where [compare Eq. (C17b)]

$$\rho_1^{ki}(\mathbf{r}_1; \mathbf{r}'_1) = \sum_{s_1} \phi_k(\mathbf{r}_1 s_1) \phi_i^*(\mathbf{r}'_1 s_1). \quad (5.16)$$

It should be noted that Eq. (5.15) is free of the energy denominators  $\omega_{a,r}$  [Eq. (5.8)], which are characteristic for perturbation theory expressions such as Eq. (5.13). Because of this, one may expect that Eq. (5.15) will be not too sensitive to (inevitable in practice) truncation in the summation over the virtual orbitals. The alternative approach of Görling and Levy [13,14] is lacking this property. The expression for  $v_x$  [e.g., Eq. (37) of [14]] does contain energy denominators. Their role may be somehow outweighed on average by the presence of the *inverse* response operator  $G^{-1}(\mathbf{r}_2, \mathbf{r}_1)$  in this expression because the *direct* response operator  $G(\mathbf{r}_1, \mathbf{r}_2)$  also contains such energy denominators [e.g., Eq. (35) of [14]].

## B. Solution of the equation for the exchange potential

Let us note that  $v_x$  enters the right-hand side (rhs) of Eq. (5.15) via its off-diagonal, occupied-virtual matrix elements only. Therefore, for a given set of KS orbitals  $\{\phi_i(\mathbf{x}), i = 1, 2, \dots, M\}$  (which, for practical reasons, must be finite and its dimension  $M$  should satisfy  $M \gg N$  for accurate results) and for some fixed  $\mathbf{r}'_1$ , one can solve Eq. (5.15) by finding the values of  $N \times (M - N)$  complex matrix elements  $X_{bs} = \langle b | v_x | s \rangle$  for  $b = 1, \dots, N$  and  $s = N + 1, \dots, M$ . From Eq. (5.15) the following set of equations can be deduced:

$$\begin{aligned} X_{bs} &= \sum_a^{\text{occ}} \sum_r^{\text{vir}} \{ A_{bs,ar} (X_{ar}^{\text{F}} - X_{ar}) - B_{bs,ar} (X_{ar}^{\text{F}} - X_{ar})^* \} \\ &+ C_{bs}, \end{aligned} \quad (5.17)$$

where [see Eq. (5.11)]

$$X_{ar}^{\text{F}} = \langle a | \hat{v}_x^{\text{F}} | r \rangle, \quad (5.18)$$

$$A_{bs,ar} = \int d\mathbf{1} \phi_b^*(\mathbf{1}) \frac{\rho_1^{ar}(\mathbf{1}; \mathbf{1}')}{\rho_1^s(\mathbf{1}; \mathbf{1}')} \phi_s(\mathbf{1}), \quad (5.19)$$

$$B_{bs,ar} = \int d\mathbf{1} \phi_b^*(\mathbf{1}) \frac{\rho_1^{ra}(\mathbf{1}; \mathbf{1}')}{\rho_1^s(\mathbf{1}; \mathbf{1}')} \phi_s(\mathbf{1}), \quad (5.20)$$

$$C_{bs} = \int d\mathbf{1} \phi_b^*(\mathbf{1}) R(\mathbf{1}; \mathbf{1}') \phi_s(\mathbf{1}), \quad (5.21a)$$

with



$$R(1;1') = \left\{ 2 \int d2 [u(12) - u(1'2)] \rho_{2x}^s(12;1'2) \right\} / \rho_1^s(1;1'). \quad (5.21b)$$

The constant  $v_x(\mathbf{r}'_1)$  of Eq. (5.15) does not enter Eq. (5.17) because  $\langle b|v_x(\mathbf{r}'_1)|s\rangle = v_x(\mathbf{r}'_1)\delta_{bs} = 0$ . Equation (5.17) represents a set of  $N \times (M-N)$  complex linear equations for the same number of complex unknowns  $X_{bs}$ . Its form is suitable for iterative solution. For the initial step one may insert on the rhs for the value of  $X_{ar}$  the matrix element of some approximation for  $v_x(\mathbf{r})$  or even just neglect  $(X_{ar}^F - X_{ar})$ . Provided the iterative process converges, it may turn out to be more efficient than the alternative, algebraic method of solution. This linear algebra problem, in a large,  $[2 \times N \times (M-N)]$ -dimensional space, may be written in a block matrix form as

$$\begin{bmatrix} \mathbb{1} + A' - B' & -A'' - B'' \\ A'' - B'' & \mathbb{1} + A' + B' \end{bmatrix} \begin{bmatrix} X' \\ X'' \end{bmatrix} = \begin{bmatrix} C' \\ C'' \end{bmatrix} + \begin{bmatrix} A' - B' & -A'' - B'' \\ A'' - B'' & A' + B' \end{bmatrix} \begin{bmatrix} (X^F)' \\ (X^F)'' \end{bmatrix}, \quad (5.22)$$

where  $X_{ar} = X'_{ar} + iX''_{ar}$ , etc., and  $(\mathbb{1} + A' - B')_{bs,ar} = \delta_{ba}\delta_{sr} + A'_{bs,ar} - B'_{bs,ar}$ , etc. It should be noted that by using only real orbitals we halve the dimensionality of this linear algebra problem.

Since the matrices  $A$ ,  $B$ , and  $C$  [Eqs. (5.19)–(5.21)] depend on  $\mathbf{r}'_1$ , the solution  $X_{bs}$  of Eq. (5.17) or (5.22) depends on  $\mathbf{r}'_1$  too. However, this dependence should be rather weak, diminishing with the increase of  $M$ , because in the limit of  $M \rightarrow \infty$  the solution represents the matrix element  $\langle b|v_x|s\rangle$  of the exact  $v_x(\mathbf{r}_1)$ , which is independent of  $\mathbf{r}'_1$ .

With  $\langle b|v_x|s\rangle$  determined, Eq. (5.15) gives  $v_x(\mathbf{r}_1)$  directly at arbitrary point  $\mathbf{r}_1$  at the cost of summations over  $a, r$  and space integration over  $\mathbf{r}_2$ . This equation provides the exact exchange potential for the density  $n(\mathbf{r})$  given by Eq. (4.9) in terms of the same orbitals as those used in Eq. (5.15).

### C. Calculation of the leading-correlation potential

The leading term  $v_{c/2}(\mathbf{r})$  of the expanded correlation potential  $v_c(\mathbf{r})$  [Eq. (3.5) for  $\alpha=1$ ] is given by Eq. (3.14b). Of various DMs entering this equation, we already have determined  $\rho_{1/0} = \rho_1^s$  and  $\rho_{1/1}$ , the spin reduced forms of  $\gamma_1^s$ , [Eq. (C34)] and  $\gamma_{1/1}$  [Eq. (5.13)] and also  $\rho_{2/0} = \rho_2^s$  [Eq. (5.3)]. Below we obtain  $\gamma_{1/2}$  and  $\gamma_{2/1}$ , from which  $\rho_{1/2}$  and  $\rho_{2/1}$  follow immediately by spin reduction.

By combining Eqs. (B17b), (B12b), and (C8) we arrive at

$$\gamma_{2/1} = \left\{ \sum_a^{\text{occ}} \sum_r^{\text{vir}} \langle O|\hat{\gamma}_2|O_a^r\rangle \langle O_a^r|Y_{11}\rangle + \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} \langle O|\hat{\gamma}_2|O_{ab}^{rs}\rangle \frac{1}{\omega_{ab,rs}} \langle O_{ab}^{rs}|\hat{U}|O\rangle \right\} + \text{H.c.}, \quad (5.23)$$

where

$$\omega_{ab,rs} = \mathcal{E}_O - \mathcal{E}_{O_{ab}^{rs}} = \epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s \quad (5.24)$$

denotes minus the two-pair excitation energy. We used the fact that  $\langle O|\hat{\gamma}_2|A\rangle$  vanishes for triple- and higher-excited  $A$  [see Eqs. (C18) and (C28)] and that  $\langle O_{ab}^{rs}|\hat{V}_{\text{esx}}|O\rangle = 0$ . Next, using Eqs. (C26) and (C27) for evaluation of matrix elements of  $\hat{\gamma}_2$  and  $\hat{U}$ , and also the result (5.12), we arrive at the final result

$$\begin{aligned} \gamma_{2/1}(\mathbf{12};\mathbf{1}'\mathbf{2}') = & \left\{ \sum_a^{\text{occ}} \sum_r^{\text{vir}} \frac{\langle r|\hat{v}_x^F - v_x|a\rangle}{2\omega_{a,r}} [\gamma_1^s(\mathbf{1};\mathbf{1}')\gamma_1^{ra}(\mathbf{2};\mathbf{2}') \right. \\ & - \gamma_1^s(\mathbf{1};\mathbf{2}')\gamma_1^{ra}(\mathbf{2};\mathbf{1}') + \gamma_1^s(\mathbf{2};\mathbf{2}')\gamma_1^{ra}(\mathbf{1};\mathbf{1}') \\ & - \gamma_1^s(\mathbf{2};\mathbf{1}')\gamma_1^{ra}(\mathbf{1};\mathbf{2}')] \\ & \left. + \sum_{a,b}^{\text{occ}} \sum_{r,s}^{\text{vir}} \frac{\langle rs||ab\rangle}{2\omega_{ab,rs}} \gamma_1^{ra}(\mathbf{1};\mathbf{1}')\gamma_1^{sb}(\mathbf{2};\mathbf{2}') \right\} \\ & + \text{H.c.} \end{aligned} \quad (5.25)$$

[note that the Hermitian conjugate (H.c.) of  $A(\mathbf{12};\mathbf{1}'\mathbf{2}')$  is  $A^*(\mathbf{1}'\mathbf{2}';\mathbf{12})$ ].

In order to evaluate  $\gamma_{1/2}$  we rewrite Eq. (B17c) as

$$\gamma_{1/2}(\mathbf{1};\mathbf{1}') = \gamma_{1/2}^{(02)}(\mathbf{1};\mathbf{1}') + [\gamma_{1/2}^{(02)}(\mathbf{1}';\mathbf{1})]^* + \gamma_{1/2}^{(11)}(\mathbf{1};\mathbf{1}'), \quad (5.26a)$$

with

$$\begin{aligned} \gamma_{1/2}^{(02)} &= \langle Y_{10}|\hat{\gamma}_1|Y_{12}\rangle = \sum_a^{\text{occ}} \sum_r^{\text{vir}} \langle O|\hat{\gamma}_1|O_a^r\rangle \langle O_a^r|Y_{12}\rangle \\ &= \sum_a^{\text{occ}} \sum_r^{\text{vir}} \gamma_1^{ra} \langle O_a^r|Y_{12}\rangle, \end{aligned} \quad (5.26b)$$

$$\gamma_{1/2}^{(11)} = \langle Y_{11}|\hat{\gamma}_1|Y_{11}\rangle - \langle Y_{11}|Y_{11}\rangle \gamma_1^s. \quad (5.26c)$$

According to Eq. (B13) with Eq. (B12) and taking into account that  $\langle A|\hat{\mathcal{H}}_{11}|O\rangle$  vanishes for triple- and higher-excited  $A$ , we find

$$\begin{aligned} \langle O_a^r|Y_{12}\rangle &= \frac{1}{\omega_{a,r}} \left\{ \langle O_a^r|\hat{\mathcal{H}}_{12}|O\rangle - \langle O|\hat{\mathcal{H}}_{11}|O\rangle \frac{1}{\omega_{a,r}} \langle O_a^r|\hat{\mathcal{H}}_{11}|O\rangle \right. \\ &+ \sum_b^{\text{occ}} \sum_s^{\text{vir}} \langle O_a^r|\hat{\mathcal{H}}_{11}|O_b^s\rangle \frac{1}{\omega_{b,s}} \langle O_b^s|\hat{\mathcal{H}}_{11}|O\rangle \\ &\left. + \frac{1}{4} \sum_{b,c}^{\text{occ}} \sum_{s,t}^{\text{vir}} \langle O_a^r|\hat{\mathcal{H}}_{11}|O_{bc}^{st}\rangle \frac{1}{\omega_{bc,st}} \langle O_{bc}^{st}|\hat{\mathcal{H}}_{11}|O\rangle \right\}. \end{aligned} \quad (5.27)$$

After evaluation of all matrix elements using Eqs. (C19)–(C30), we arrive at

$$\begin{aligned} \omega_{a,r} \langle O_a^r|Y_{12}\rangle &= -\langle r|v_{c/2}|a\rangle + \sum_b^{\text{occ}} \sum_s^{\text{vir}} \frac{\langle rb||as\rangle \langle s|x|b\rangle}{\omega_{b,s}} \\ &+ \sum_s^{\text{vir}} \frac{\langle r|x|s\rangle \langle s|x|a\rangle}{\omega_{a,s}} - \sum_b^{\text{occ}} \frac{\langle r|x|b\rangle \langle b|x|a\rangle}{\omega_{b,r}} \end{aligned}$$

$$\begin{aligned}
& + \sum_{b < c}^{\text{occ}} \sum_s^{\text{vir}} \frac{\langle sr || bc \rangle \langle bc || as \rangle}{\omega_{bc, sr}} \\
& - \sum_b^{\text{occ}} \sum_{s < t}^{\text{vir}} \frac{\langle br || st \rangle \langle st || ab \rangle}{\omega_{ab, st}} \\
& - \sum_b^{\text{occ}} \sum_s^{\text{vir}} \frac{\langle sr || ab \rangle \langle b | x | s \rangle}{\omega_{ab, st}}. \quad (5.28)
\end{aligned}$$

Evaluation of  $\gamma_{1/2}^{(11)}$  [Eq. (5.26c)] is quite straightforward, although tedious, and can be performed using the matrix elements (C19)–(C30). The term  $\langle Y_{/1} | Y_{/1} \rangle \gamma_1^s$  cancels out exactly one of the terms obtained from  $\langle Y_{/1} | \hat{\gamma}_1 | Y_{/1} \rangle$ . The final result is then

$$\begin{aligned}
\gamma_{1/2}^{(11)} = & \sum_{t,r}^{\text{vir}} \left\{ \sum_a^{\text{occ}} \frac{\langle t | x | a \rangle \langle a | x | r \rangle}{\omega_{a,t} \omega_{a,r}} \right. \\
& + \sum_{a < b}^{\text{occ}} \sum_s^{\text{vir}} \frac{\langle ts || ab \rangle \langle ba || sr \rangle}{\omega_{ab, ts} \omega_{ab, sr}} \left. \right\} \gamma_1^{tr} \\
& - \sum_{a,c}^{\text{occ}} \left\{ \sum_r^{\text{vir}} \frac{\langle a | x | r \rangle \langle r | x | c \rangle}{\omega_{a,r} \omega_{c,r}} \right. \\
& + \sum_{r < s}^{\text{vir}} \sum_b^{\text{occ}} \frac{\langle ab || rs \rangle \langle sr || bc \rangle}{\omega_{ab, rs} \omega_{bc, rs}} \left. \right\} \gamma_1^{ac} \\
& + \sum_{a,c}^{\text{occ}} \sum_{r,t}^{\text{vir}} \left\{ \frac{\langle a | x | r \rangle \langle tr || ca \rangle}{\omega_{a,r} \omega_{ac, tr}} \gamma_1^{tc} \right. \\
& \left. + \frac{\langle ac || rt \rangle \langle r | x | a \rangle}{\omega_{ac, rt} \omega_{a,r}} \gamma_1^{ct} \right\}. \quad (5.29)
\end{aligned}$$

The arguments  $(\mathbf{1}; \mathbf{1}')$  of  $\hat{\gamma}_1$ ,  $\gamma_{1/2}^{(02)}$ ,  $\gamma_{1/2}^{(11)}$ , and  $\gamma_1^{ij}$  have been omitted for brevity.

The exchange potential, determined in previous subsections, enters the expression for  $\gamma_{1/2}$  not only in a form of matrix elements of occupied-virtual type, but also occupied-occupied and virtual-virtual types. Its diagonal elements occur in Eq. (5.28) for  $s=r$  and  $b=a$  only in a combination  $(\langle r | x | r \rangle - \langle a | x | a \rangle) / \omega_{a,r}$ , which is independent of the constant  $v_x(\mathbf{r}'_1)$ .

When determining  $v_{c/2}$  from Eq. (3.14b) we meet this  $v_{c/2}$  also on the rhs as off-diagonal, occupied-virtual matrix elements; see Eq. (5.26) with (5.28). Similarly to the case of the exchange potential, we fix  $\mathbf{r}'_1$  (the same as previously), and then calculate the values of  $N \times (M - N)$  complex matrix elements  $Y_{bs} = \langle b | v_{c/2} | s \rangle$ , integrating expression (3.14b) between  $\langle b |$  and  $| s \rangle$  functions [a null contribution due to the constant  $v_{c/2}(\mathbf{r}'_1)$ ]. This leads to an algebraic problem

$$Y_{bs} = \sum_a^{\text{occ}} \sum_r^{\text{vir}} \{ -A_{bs, ar} Y_{ar} + B_{bs, ar} Y_{ar}^* \} + D_{bs}, \quad (5.30)$$

with the same  $A$  and  $B$  as in Eqs. (5.19) and (5.20). The matrix  $D$  combines all terms independent of  $v_{c/2}$ . Again, Eq. (5.30) can be solved iteratively or algebraically. In the last case, since the equation for  $Y$  is similar to Eq. (5.22) for  $X$

(having, however, a different rhs), the matrix inverted for solution of Eq. (5.22) can be utilized again.

With  $\langle b | v_{c/2} | s \rangle$  determined, Eq. (3.14b) gives  $v_{c/2}(\mathbf{r}_1)$  at arbitrary  $\mathbf{r}_1$  at the cost of spatial integration over  $\mathbf{r}_2$ . The contribution  $v_{c/2}(\mathbf{r}_1)$  thereby obtained provides the leading term of the expanded  $v_c(\mathbf{r}_1)$ , for the actual density  $n(\mathbf{r})$ , corresponding to occupied KS orbitals used in the calculation (4.9).

## VI. DISCUSSION AND CONCLUSIONS

### A. Approximate exchange potential

Observing that the expression for  $E_x[n]$  in terms of DMs can be obtained from that for  $E_{xc}[n]$  [Eq. (2.8)] by means of replacing the interacting DMs  $\rho_i$  with the noninteracting ones  $\rho_i^s$ , we applied previously the same replacement in our works [5] and [9] to obtain approximate expressions for  $v_x(\mathbf{r})$  from those for  $v_{xc}(\mathbf{r})$ . In particular, for  $v_{xc}$  in a line-integral form [5], this replacement has led us to an expression that is equivalent to the Harbola-Sahni [6] approximation for  $v_x$  in their work formalism.

Applying again this replacement to the present Eq. (2.7) for  $v_{xc}(\mathbf{r})$ , we obtain an expression for the approximate exchange potential, in which there are no terms containing kinetic-energy operators, while the DM  $\rho_2$  of the interaction term is replaced by  $\rho_2^s$  in the form (5.3). Although the exact  $v_{xc}(\mathbf{r})$  [Eq. (2.7)] is obviously real (because  $W$  and  $W_s$  are real), the approximation constructed above may happen to be complex valued; therefore, we should take its real part. So, finally,

$$\begin{aligned}
v_x^{\text{app}}(\mathbf{r}_1) = & v_x^{\text{app}}(\mathbf{r}'_1) + \int d^3 r_2 \{ u(\mathbf{r}_1, \mathbf{r}_2) - u(\mathbf{r}'_1, \mathbf{r}_2) \} \\
& \times \left\{ \frac{\rho_{2x}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2)}{\rho_1^s(\mathbf{r}_1; \mathbf{r}'_1)} + \frac{\rho_{2x}^s(\mathbf{r}'_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)}{\rho_1^s(\mathbf{r}'_1; \mathbf{r}_1)} \right\}, \quad (6.1a)
\end{aligned}$$

where

$$\begin{aligned}
v_x^{\text{app}}(\mathbf{r}'_1) = & \int d^3 r_2 u(\mathbf{r}'_1, \mathbf{r}_2) \lim_{r_1 \rightarrow \infty} \left\{ \frac{\rho_{2x}^s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}_2)}{\rho_1^s(\mathbf{r}_1; \mathbf{r}'_1)} \right. \\
& \left. + \frac{\rho_{2x}^s(\mathbf{r}'_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)}{\rho_1^s(\mathbf{r}'_1; \mathbf{r}_1)} \right\} \quad (6.1b)
\end{aligned}$$

is chosen to provide  $v_x^{\text{app}}(\mathbf{r}_1) \rightarrow 0$  when  $r_1 \rightarrow \infty$ , for any fixed  $\mathbf{r}'_1$ . With  $u(\mathbf{r}_1, \mathbf{r}_2) = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ , the large- $r_1$  behavior of the approximate exchange potential

$$v_x^{\text{app}}(\mathbf{r}_1) = -\frac{1}{r_1} + O\left(\frac{1}{r_1^2}\right) \quad (6.2)$$

is the same as the behavior of the exact  $v_x(\mathbf{r}_1)$ ; see, e.g., our discussion in [18]. The idempotency property

$$\int d^3 r_2 \rho_{1\sigma}^s(\mathbf{r}_1; \mathbf{r}_2) \rho_{1\sigma}^s(\mathbf{r}_2; \mathbf{r}'_1) = \rho_{1\sigma}^s(\mathbf{r}_1; \mathbf{r}'_1) \quad (6.3)$$

was used to derive the result (6.2) from Eq. (6.1).

While the shape of the exchange-correlation potential  $v_{xc}(\mathbf{r}_1)$ , given by the exact Eq. (2.7), is independent of the reference point  $\mathbf{r}'_1$  choice [due to Eq. (2.3) for  $W$  and its analogue for  $W_s$ ], the approximate exchange potential  $v_x^{\text{app}}(\mathbf{r}_1)$  [Eq. (6.1)] depends, in general, on  $\mathbf{r}'_1$  (except maybe in the case of some high-symmetry systems). This  $\mathbf{r}'_1$  dependence is an analog of the path dependence of the approximate exchange potential in a line-integral form [5], equivalent to the Harbola-Sahni potential. Therefore, for practical applications, it may be useful to average the right-hand side of Eq. (6.1) over some set of  $\mathbf{r}'_1$  points.

Since, as discussed above, our approximation (6.1) is an analog of the Harbola-Sahni approximation [6], one may expect it to lead to a similarly promising result as theirs (see, e.g., Sahni's review [21]), while being simpler in evaluation. Let us notice, finally, that the exact exchange potential (5.4b) differs from the approximate one (6.1) in the term involving  $\rho_{1/1}$ . What is crucial for applications is that  $v_x^{\text{app}}(\mathbf{r}_1)$  is expressed entirely in terms of the noninteracting 1DMs  $\rho_{1\uparrow}^s$  and  $\rho_{1\downarrow}^s$  [see Eqs. (5.2) and (5.3c)] or, for spin-compensated systems, just  $\rho_1^s$  [see Eq. (5.3d)]. Therefore, it can be calculated self-consistently within the traditional KS scheme. Its form removes also the problem of the self-interaction correction at the level of the exchange. We expect that this form of an approximate exchange potential is suitable for application to extended systems too.

In general, approximate exchange potentials are obtained in two ways: either by functional differentiation of an approximate expression for the energy  $E_x$  as a functional of the density or by simplification of some exact expression or equation for the potential  $v_x$  or  $v_{xc}$ . The first way is the most popular one because it leads to inexpensive (in calculational costs) expressions, which are local in the density and density gradients. In its simplest form it is known therefore as the local-density approximation (LDA), while various improved versions are known as generalized gradient approximations (GGAs) (see, e.g., [22–25] and references therein). Although some modern GGAs give highly accurate  $E_x$ , they lead typically to less satisfactory potentials after differentiation. The second way of approximating circumvents this difficulty. It is represented, first of all, by the Krieger-Li-Iafrate (KLI) approximation [26,27]. The exact integral equation for  $v_x$  of the optimized effective potential method [17] is simplified there and an expression in terms of KS orbitals is obtained, which is similar to the Slater construction of  $v_x$ . Application of this the KLI approximation to self-consistent calculations of atomic properties [28] demonstrates its high accuracy. Gritsenko *et al.* [29] propose and develop a family of approximate exchange potentials, the form of which is based on the KLI approximation, while their evaluation involves, to various extents, some elements of the GGA to the exchange energy. Reduced calculational costs accompany reasonably accurate results. It is interesting that the KLI approximation can be derived alternatively, as shown by Nagy [30], by introducing approximations to the effective local potential of the Hartree-Fock method posed as a density-functional theory. Our three approximations to  $v_x$ , discussed earlier in this section, belong also to the second way of approximating because they represent simplifications of the exact results for  $v_{xc}$  in terms of DMs, stemming from three

equations satisfied by DMs: the differential virial equation, the integral equation, and the equation of motion for the 1DM. The approximate  $v_x$  based on virial equation happens to be equivalent to the Harbola-Sahni [6] approximation, derived within their work formalism.

## B. Sum rules for checking accuracy

Any implementation of the, exact in principle, present method of solution of the ground-state problem leads inevitably to inaccuracies due to various limitations. Among them, the most basic one is connected with the chosen order  $k$  of the perturbation theory. It causes the exact GS problem (4.12) to be replaced by the truncated one (4.13). Complete formulas are given for  $k=1$  and 2 and ways are indicated to handle other  $k$ . Remaining computational inaccuracies arise due to a finite number of virtual KS orbitals taken into account, an approximate representation of each KS orbital (by its values on some grid or when expanded in some incomplete basis set of molecular orbitals), and terminations in iterative approaching to self-consistency during solution of KS equations, equations for  $v_x$ ,  $v_{c/2}$ , and so on. Therefore, it is important to have, during the computational process, some criteria allowing estimation of inaccuracies. We propose for this purpose to check how well the ‘‘sum rules,’’ the exact relations of the theory, are satisfied.

A distinctive feature of the GL perturbation theory is presented by Eq. (3.1). Since the density is the diagonal element of the 1DM  $\rho_1^\alpha$ , which is represented as expansion (3.7), therefore (3.1) is equivalent to the following pointwise identities for each perturbational order:

$$n_{1j}(\mathbf{r}) \equiv \rho_{1j}(\mathbf{r}; \mathbf{r}) = 0 \quad \text{for } j = 1, \dots, k. \quad (6.4)$$

It should be noted that this equation serves Görling and Levy [14] as a basis for determining  $v_x$ , at  $j=1$ , and  $v_{c/j}$ , at  $j \geq 2$ , with the help of the inverted operator of the linear density response.

As an indicator of calculational accuracy, one can take, for example, the smallness of either the maximum (over  $\mathbf{r}$ ) of  $|n_{1j}(\mathbf{r})|/n(\mathbf{r})$  or its average value. It is interesting that calculational defects, causing violation of the sum rule (6.4), do not lead to errors in the total number of electrons. Namely, we find from Eqs. (5.13) and (5.26) that the identity

$$\int d^3r n_{1j}(\mathbf{r}) = \int d\mathbf{1} \gamma_{1j}(\mathbf{1}; \mathbf{1}) = 0 \quad (6.5)$$

is satisfied for  $j=1$  and 2 despite truncated summations over virtual KS orbitals and inaccurate matrix elements of the exchange potential. What really matters is the orthogonality of virtual orbitals with respect to occupied ones.

Other sum rules originate in equivalence of two methods applied for the calculation of the GS energy  $E^\alpha$  of the interpolating system, the solution of Eq. (B1). Corresponding expansion coefficients [see Eq. (B7)] can be evaluated either from the perturbation theory (PT) expressions (B12a), (B13a), and (B14a), to be denoted in this section as  $E_{ij}^{\text{PT}}$ , or from the Hamiltonian  $\hat{\mathcal{H}}^\alpha$  [Eqs. (B2), (C1), (C8), and (C9)] expectation value, expressed next in terms of DMs [compare Eqs. (4.5) and (4.7)] as

$$\begin{aligned}
E^\alpha &= \langle \Psi^\alpha | \hat{T} + \alpha \hat{U} + \hat{V}_{\text{ext}}^\alpha | \Psi^\alpha \rangle \\
&= \int [\hat{t} \gamma_1^\alpha] + \int \int [\alpha u \gamma_2^\alpha] + \int [v_{\text{ext}}^\alpha n^\alpha] = \sum_{j=0}^{\infty} \alpha^j E_{ij}^{\text{DM}},
\end{aligned} \tag{6.6}$$

where the property (3.1) and expansions (3.7) and (3.6) should be used to obtain the last form. The resulting sum rules

$$E_{ij}^{\text{PT}} = E_{ij}^{\text{DM}} \quad \text{for } j=1, \dots, k \tag{6.7}$$

can be satisfied only approximately because of computational inaccuracies. At first order we find

$$\begin{aligned}
E_{/1}^{\text{DM}} - E_{/1}^{\text{PT}} &= \left( \int [\hat{t} \gamma_{1/1}] + \int \int [u \gamma_{2/0}] + \int [v_{\text{ext}/1} n] \right) \\
&\quad - \left( \int \int [u \gamma_{2/0}] + \int [v_{\text{ext}/1} n] \right).
\end{aligned} \tag{6.8}$$

This difference vanishes when Eq. (6.4) is accurately satisfied because we find for it, with the help of Eqs. (3.16), (5.13) and (C2), that

$$\int [\hat{t} \gamma_{1/1}] = \int [(\hat{h}_{\text{KS}} - v_{\text{KS}}) \gamma_{1/1}] = - \int [v_{\text{KS}} n_{/1}]. \tag{6.9}$$

So,  $|\int [v_{\text{KS}} n_{/1}] / E_{/1}^{\text{PT}}| \ll 1$  may serve as a criterion of calculational accuracy. Similarly, at the second order, after tedious algebra involving, among other equations, Eqs. (5.12), (C27), (5.29), and (5.25), we find

$$E_{/2}^{\text{DM}} - E_{/2}^{\text{PT}} = \int [v_{\text{esx}} n_{/1}] - \int [v_{\text{KS}} n_{/2}]; \tag{6.10}$$

so again this difference vanishes when Eq. (6.4) is satisfied for  $j=1$  and 2. On the way leading to the result (6.10), the identity (4.17) for  $j=2$  is being proven in terms of explicit expressions such as Eq. (5.29) [note that the same identity for  $j=1$  means vanishing of the left-hand side of Eq. (6.9)]. Altogether, obtaining the result (6.10) provides a nontrivial cross-check of the whole collection of second-order formulas given in our paper. Similarly, numerical satisfaction of Eq. (6.10) may serve as a sensitive confirmation of error-free coding of applied formulas.

We should also point out the sum rules connected with basic properties of potentials, namely vanishing of  $\text{Im}W$  and the identity (2.3), which must be satisfied by each  $W_{ij}(\mathbf{r}_1, \mathbf{r}'_1)$  separately, for  $j=1, \dots, k$ , the terms of the expanded  $W(\mathbf{r}_1, \mathbf{r}'_1)$  [Eq. (3.10)]. Similarly, identities (3.17) for  $j=1, \dots, k$  can also serve as sum rules checking expanded potential and expanded DMs terms.

Finally, the accuracy of evaluated potentials can be estimated in the following way. Equations (3.14) and (3.15) and similar ones depend on two positions  $\mathbf{r}_1$  and  $\mathbf{r}'_1$ , of which  $\mathbf{r}'_1$ , the reference point, is chosen arbitrarily at the beginning and then kept fixed during all calculations. Potentials  $v_{\text{esx}}, v_{c/j}$ , determined according to the mentioned equations as functions of the independent variable  $\mathbf{r}_1$ , should be the same (up to additive constants) for various choices of  $\mathbf{r}'_1$ , provided computational inaccuracies are avoided. But they are present in practice: In order to estimate the resulting inaccuracies of evaluated potentials, one should repeat all calculations with a new (significantly different) choice of  $\mathbf{r}'_1$  and

decide if the discrepancies between the new and previous potentials are acceptable. When they are not, the calculational procedure needs improvements (e.g., by increasing the number of the virtual orbitals involved or by more accurate representing each orbital).

### C. Upper bound to the ground-state energy

In the process of self-consistent determination of  $v_x, v_{c/2}, \dots$ , by means of our method, the expanded many-electron wave function is obtained as a by-product. Therefore, regardless of all computational deficiencies, an exact upper bound (UB) to the system GS energy can be obtained

$$E_{\text{GS}} < E_{\text{UB}}^{\{k\}} = \frac{\langle Y^{\{k\}} | \hat{\mathcal{H}} | Y^{\{k\}} \rangle}{\langle Y^{\{k\}} | Y^{\{k\}} \rangle}, \tag{6.11a}$$

where [compare Eqs. (B3) and (B5) for  $\alpha=1$ ]

$$|Y^{\{k\}}\rangle = \sum_{j=0}^k |Y_{ij}\rangle \tag{6.11b}$$

and  $\hat{\mathcal{H}}$  is given in Eq. (A1). By using  $|Y_{ij}\rangle$  expanded in a form (B11), an explicit expression can be derived for  $E_{\text{UB}}^{\{k\}}$  with the help of methods described in Appendixes B and C. However, it involves terms that are formally of higher order than those in perturbational expansions. For example, for  $k=2$ , one meets the third-order terms such as  $\langle Y_{/1} | \hat{\mathcal{H}} | Y_{/2} \rangle$  and  $\langle Y_{/1} | Y_{/2} \rangle$  and fourth-order terms  $\langle Y_{/2} | \hat{\mathcal{H}} | Y_{/2} \rangle$  and  $\langle Y_{/2} | Y_{/2} \rangle$ . For their determination the list of matrix elements (C19)–(C30) must be enlarged significantly. A recent paper by Gotoh *et al.* [31] demonstrates that evaluation of such matrix elements can be automated by methods of computer algebraic calculation. This method may prove to be helpful also in extending our perturbation theory formulas to  $k>2$  cases.

### D. Summary

The main achievements of the present paper are to (i) establish the exchange-correlation potential in terms of first- and second-order density matrices: both fully interacting and “reference” KS system quantities, in Eq. (2.7) [it should be noted that the exchange-correlation energy can be also written in terms of the same input information, Eq. (2.8)]; (ii) obtain an approximate exchange potential in terms of first-order density matrix of the KS system, in Eq. (6.1); (iii) derive an equation for the exact exchange potential, in terms of the KS orbitals, in Eq. (5.15); (iv) derive an equation for the leading contribution to the correlation potential, in terms of the KS orbitals, in Eq. (3.14b) with details in Eqs. (5.23)–(5.30); and (v) indicate ways to obtain higher contributions to the correlation potential, in Eq. (3.14c). Of course, in (iii)–(v) one needs not only the Kohn-Sham orbitals required to calculate the (in principle) exact ground-state density  $n(\mathbf{r})$  but also excited (virtual) orbitals generated by the same one-body potential  $v_{\text{KS}}$  used to construct  $n(\mathbf{r})$ . Naturally, it will require numerical calculations on specific systems to demonstrate whether the present approach, with currently available computing power, can be competitive among known high-accuracy but costly approaches, such as configuration-interaction (CI) one. While the present scheme involves the

same two-electron integrals as in these *ab initio* approaches, thus being similarly expensive in calculation, its perturbation expansion may be faster converging because  $n(\mathbf{r})$  is kept fixed during the perturbation [in opposition to changing  $n(\mathbf{r})$  in the CI approach] and because the orbitals (especially virtuals) may be of better quality. Of course, all such schemes based on perturbation theory are not able to compete in cost not only with the LDA but also with the most sophisticated GGA approaches.

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### APPENDIX A: MANY-ELECTRON SYSTEM AND ITS DENSITY MATRICES

The  $N$ -electron finite system under consideration (such as an atom, a molecule, or a cluster) is characterized by the Hamiltonian

$$\hat{\mathcal{H}} = \hat{T} + \hat{U} + \hat{V}, \quad (\text{A1})$$

representing the kinetic-energy, electron-electron repulsion and electron-nuclear attraction (external potential) energy operators (for their definitions and also conventions concerning DMs and remaining notation see [5,9]). Atomic units are used throughout. From an obvious identity

$$N \int d\mathbf{2} \cdots d\mathbf{N} \{ [\hat{\mathcal{H}}\Psi(\mathbf{1}\mathbf{2}\dots\mathbf{N})] \Psi^*(\mathbf{1}'\mathbf{2}'\dots\mathbf{N}') - \Psi(\mathbf{1}\mathbf{2}\dots\mathbf{N}) [\hat{\mathcal{H}}\Psi(\mathbf{1}'\mathbf{2}'\dots\mathbf{N}')]^* \} = 0, \quad (\text{A2})$$

satisfied by any normalized eigenfunction  $\Psi$  of the Hamiltonian  $\hat{\mathcal{H}}$  (A1), follows immediately the so-called equation of motion for the 1DM (see, e.g., [11,12])

$$\{ [\hat{t}(1) + v(1)] - [\hat{t}(1') + v(1')] \} \gamma_1(\mathbf{1}; \mathbf{1}') + 2 \int d\mathbf{2} \{ u(12) - u(1'2) \} \gamma_2(\mathbf{1}\mathbf{2}; \mathbf{1}'\mathbf{2}') = 0. \quad (\text{A3})$$

Here  $\mathbf{1} = \mathbf{x}_1 = \{\mathbf{r}_1, s_1\}$  means the first space and spin coordinate,  $\int d\mathbf{2} f(\mathbf{2})$  means  $\sum_{s_2} \int d^3 r_2 f(\mathbf{r}_2, s_2)$ ,  $\hat{t}(1) = -\frac{1}{2} \nabla_1^2 = -\frac{1}{2} (\partial/\partial \mathbf{r}_1)^2$  is the kinetic-energy operator, and  $u(12) = u(\mathbf{r}_1, \mathbf{r}_2)$  and  $v(1) = v(\mathbf{r}_1)$  denote electron-electron interaction and external potential, respectively.

Equation (A3) represents an exact relation at  $\mathbf{1}, \mathbf{1}'$ , involving potentials  $u, v$  and DMs  $\gamma_1$  and  $\gamma_2$  [generated from an arbitrary eigenfunction  $\Psi$  of the Hamiltonian  $\hat{\mathcal{H}}$  (A1)]. Since Eq. (A3) is linear in DMs, it remains true if DMs  $\gamma_1$  and  $\gamma_2$  are replaced by a ‘‘mixture’’ of pure-state matrices  $\gamma_{\Lambda i}$ :

$$\gamma_i = \sum_{\Lambda} p_{\Lambda} \gamma_{\Lambda i}, \quad (\text{A4a})$$

where the probabilities  $p_{\Lambda}$  satisfy conditions

$$p_{\Lambda} \geq 0, \quad \sum_{\Lambda} p_{\Lambda} = 1, \quad (\text{A4b})$$

and the  $i$ DM  $\gamma_{\Lambda i}$  is obtained by reduction of  $\gamma_{\Lambda N} = \Psi_{\Lambda}(\mathbf{1}\dots\mathbf{N}) \Psi_{\Lambda}^*(\mathbf{1}'\dots\mathbf{N}')$ , where  $\Psi_{\Lambda}$  is an eigenfunction of  $\hat{\mathcal{H}}$ , labeled with the quantum number  $\Lambda$ . Thus Eq. (A3) is valid not only for pure-state DMs, but also for ensemble-state DMs of the system under consideration. Since Eq. (A3) is independent of the number  $N$  of electrons in the system, the above-mentioned ensemble can contain systems with different numbers of electrons too. For many applications it suffices to use spinless DMs, defined as

$$\begin{aligned} \rho_i(12\dots i; 1'2'\dots i') \\ = \sum_{s_1, s_2, \dots, s_i} \gamma_i(1s_1 2s_2 \dots i s_i; 1's_1 2's_2 \dots i' s_i). \end{aligned} \quad (\text{A5})$$

### APPENDIX B: DENSITY MATRICES VIA PERTURBATION THEORY

The GS energy  $E^{\alpha}$  and wave function  $\Psi^{\alpha}$  of the ‘‘interpolating’’  $N$ -electron system introduced by Görling and Levy [8], which is used in Sec. III to obtain the exchange potential and expanded correlation potential, satisfy the Schrödinger equation

$$(\hat{\mathcal{H}}^{\alpha} - E^{\alpha}) \Psi^{\alpha} = 0, \quad (\text{B1})$$

where the Hamiltonian is given as an expansion in powers of the coupling parameter  $\alpha$ ,

$$\hat{\mathcal{H}}^{\alpha} = \sum_{j=0}^{\infty} \alpha^j \hat{\mathcal{H}}_{ij} \quad (\text{B2})$$

(see Appendix C for details). Considering its leading term to be the unperturbed Hamiltonian and all remaining terms to be the perturbation, we shall proceed to solve Eq. (B1) by means of the perturbation theory. Following [8], we apply a modified form (because of the presence in the perturbation terms higher than linear) of Rayleigh-Schrödinger perturbation theory and also assume that the GS is nondegenerate for  $\alpha$  in the range  $[0, 1]$ . Owing to this assumption, the simplest method of solution of Eq. (B1) can be used. In general, this restriction may have to be lifted in the future when a degenerate-state perturbation theory will be elaborated. In particular, its version formulated for an ensemble of pure systems, leading to ensemble DMs, would be of special interest because, as shown in Appendix A, the equation of motion for the 1DM, the basis of the present paper, is valid for ensemble DMs.

While the GS function  $\Psi^{\alpha}(\mathbf{1}\dots\mathbf{N})$  normalized as  $\langle \Psi^{\alpha} | \Psi^{\alpha} \rangle = 1$  is necessary for construction of DMs  $\gamma_i^{\alpha}$ , the function  $Y^{\alpha}(\mathbf{1}\dots\mathbf{N})$ , proportional to it,

$$\Psi^{\alpha}(\mathbf{1}\dots\mathbf{N}) = C^{\alpha} Y^{\alpha}(\mathbf{1}\dots\mathbf{N}), \quad (\text{B3})$$

having the so-called intermediate normalization

$$\langle Y^0 | Y^{\alpha} \rangle = 1 \quad \text{for } \alpha \geq 0, \quad (\text{B4})$$

is more convenient for perturbation expansion (see, e.g., [32]). Due to this normalization, the coefficient functions of the expansion

$$Y^\alpha = \sum_{j=0}^{\infty} \alpha^j Y_{lj} \quad (\text{B5})$$

are orthogonal to the unperturbed function

$$\langle Y_{l0} | Y_{lj} \rangle = 0 \quad \text{for } j \geq 1. \quad (\text{B6})$$

After inserting the expanded GS eigenfunction  $\Psi^\alpha$  [Eq. (B3) with Eq. (B5)], the Hamiltonian (B2), and the GS eigenvalue

$$E^\alpha = \sum_{j=0}^{\infty} \alpha^j E_{lj} \quad (\text{B7})$$

into the Schrödinger equation (B1), a set of equations is obtained

$$\sum_{\ell=0}^j (\hat{\mathcal{H}}_{l\ell} - E_{l\ell}) Y_{lj-\ell} = 0, \quad \text{for } j=0,1,2,\dots \quad (\text{B8})$$

Its solution can be readily written [32] in terms of a set  $\{\mathcal{E}_A\}$  of eigenvalues and a complete set  $\{\Phi_A \equiv |A\rangle\}$  of orthonormal eigenfunctions  $\langle A|B\rangle = \delta_{AB}$  of the unperturbed Hamiltonian

$$(\hat{\mathcal{H}}_{l0} - \mathcal{E}_A) \Phi_A = 0, \quad (\text{B9})$$

among them its GS energy  $\mathcal{E}_O \equiv E^0 \equiv E_{l0}$  and the wave function

$$\Phi_O \equiv |O\rangle \equiv |Y_{l0}\rangle \equiv \Psi^0. \quad (\text{B10})$$

After inserting the expansion

$$Y_{lj} \equiv |Y_{lj}\rangle = \sum_A' |A\rangle \langle A|Y_{lj}\rangle \quad \text{for } j=1,2,\dots \quad (\text{B11})$$

[the prime means  $A \neq O$  because of condition (B6) with Eq. (B10)], the following solutions are found from Eq. (B8): for first order

$$E_{l1} = \langle O | \hat{\mathcal{H}}_{l1} | O \rangle, \quad (\text{B12a})$$

$$\langle A | Y_{l1} \rangle = \frac{\langle A | \hat{\mathcal{H}}_{l1} | O \rangle}{\mathcal{E}_O - \mathcal{E}_A}; \quad (\text{B12b})$$

for second order

$$E_{l2} = \langle O | \hat{\mathcal{H}}_{l2} | O \rangle + \sum_B' \langle O | \hat{\mathcal{H}}_{l1} | B \rangle \langle B | Y_{l1} \rangle, \quad (\text{B13a})$$

$$\langle A | Y_{l2} \rangle = \frac{1}{\mathcal{E}_O - \mathcal{E}_A} \left\{ \langle A | \hat{\mathcal{H}}_{l2} | O \rangle - \left[ E_{l1} \langle A | Y_{l1} \rangle - \sum_B' \langle A | \hat{\mathcal{H}}_{l1} | B \rangle \langle B | Y_{l1} \rangle \right] \right\}; \quad (\text{B13b})$$

and for  $j$ th order,  $j \geq 2$ , which is written using  $\hat{\mathcal{H}}_{lj}$  and previous,  $(j-1)$ - and lower-order solutions,

$$E_{lj} = \langle O | \hat{\mathcal{H}}_{lj} | O \rangle + \sum_{\ell=1}^{j-1} \sum_B' \langle O | \hat{\mathcal{H}}_{l,j-\ell} | B \rangle \langle B | Y_{l\ell} \rangle, \quad (\text{B14a})$$

$$\langle A | Y_{lj} \rangle = \frac{1}{\mathcal{E}_O - \mathcal{E}_A} \left\{ \langle A | \hat{\mathcal{H}}_{lj} | O \rangle - \sum_{\ell=1}^{j-1} \left[ E_{l,j-\ell} \langle A | Y_{l\ell} \rangle - \sum_B' \langle A | \hat{\mathcal{H}}_{l,j-\ell} | B \rangle \langle B | Y_{l\ell} \rangle \right] \right\}. \quad (\text{B14b})$$

The spinless DMs  $\rho_i^\alpha$  are found by spin reduction [Eq. (A5)] of the corresponding full DMs  $\gamma_i^\alpha$ , which can be obtained as expectation values of  $\hat{\gamma}_i$  [we omit, for brevity, the arguments  $(\mathbf{x}_1, \dots, \mathbf{x}_i; \mathbf{x}'_1, \dots, \mathbf{x}'_i)$  of  $\gamma_i^\alpha$ ,  $\hat{\gamma}_i$ , and  $\gamma_{ij}$ ], namely,

$$\gamma_i^\alpha = \langle \Psi^\alpha | \hat{\gamma}_i | \Psi^\alpha \rangle = \frac{\langle Y^\alpha | \hat{\gamma}_i | Y^\alpha \rangle}{\langle Y^\alpha | Y^\alpha \rangle} \quad (\text{B15})$$

[see Eq. (B3)]. After inserting the expansion (B5) with the condition (B6) into Eq. (B15) we arrive at a ratio of series

$$\gamma_i^\alpha = \frac{\sum_{j=0}^{\infty} \alpha^j \sum_{\ell=0}^j \langle Y_{l\ell} | \hat{\gamma}_i | Y_{lj-\ell} \rangle}{1 + \sum_{j=2}^{\infty} \alpha^j \sum_{\ell=1}^j \langle Y_{l\ell} | Y_{lj-\ell} \rangle}, \quad (\text{B16})$$

which allows for immediate calculation of the coefficients  $\gamma_{ij}$  in the expansion (3.7) as

$$\gamma_{i0} = \langle Y_{l0} | \hat{\gamma}_i | Y_{l0} \rangle \equiv \gamma_i^s, \quad (\text{B17a})$$

$$\gamma_{i1} = \langle Y_{l0} | \hat{\gamma}_i | Y_{l1} \rangle + \langle Y_{l1} | \hat{\gamma}_i | Y_{l0} \rangle, \quad (\text{B17b})$$

$$\gamma_{i2} = \left[ \sum_{\ell=0}^2 \langle Y_{l\ell} | \hat{\gamma}_i | Y_{l2-\ell} \rangle \right] - \langle Y_{l1} | Y_{l1} \rangle \gamma_{i0}, \quad (\text{B17c})$$

$$\gamma_{i3} = \left[ \sum_{\ell=0}^3 \langle Y_{l\ell} | \hat{\gamma}_i | Y_{l3-\ell} \rangle \right] - \langle Y_{l1} | Y_{l1} \rangle \gamma_{i1} - [\langle Y_{l1} | Y_{l2} \rangle + \langle Y_{l2} | Y_{l1} \rangle] \gamma_{i0}, \quad (\text{B17d})$$

and so on.

### APPENDIX C: EVALUATION OF MATRIX ELEMENTS

The unperturbed ( $\alpha=0$ ) Hamiltonian  $\hat{\mathcal{H}}^0 \equiv \hat{\mathcal{H}}_{l0}$  (B2) coincides with the noninteracting  $N$ -electron reference system Hamiltonian, which in terms of the KS potential [see Eqs. (3.2a) and (3.16)] equals

$$\hat{\mathcal{H}}_{l0} = \sum_{i=1}^N \hat{h}_{\text{KS}}(\mathbf{r}_i). \quad (\text{C1})$$

Therefore, any solution  $\Phi_A$  of the Schrödinger equation (B9) can be written in a form of a Slater determinant constructed out of  $\phi_j$  (the KS spin orbitals), the solutions of the KS equation

$$\hat{h}_{\text{KS}}(\mathbf{r})\phi_j(\mathbf{r}s) = \epsilon_j\phi_j(\mathbf{r}s), \quad j = 1, 2, \dots, \quad (\text{C2})$$

with its eigenvalues ordered as

$$\epsilon_1 \leq \epsilon_2 \leq \dots \leq \epsilon_N < \epsilon_{N+1} \leq \epsilon_{N+2} \leq \dots. \quad (\text{C3})$$

The nondegenerate (by assumption) GS energy and function are given by

$$\mathcal{E}_O = E_{/0} = \sum_{i=1}^N \epsilon_i, \quad (\text{C4a})$$

$$\Phi_O = (N!)^{-1/2} \det\{\phi_j(\mathbf{r}_i s_i)\}_{j,i=1}^N \equiv |O\rangle = \hat{a}_1^\dagger \hat{a}_2^\dagger \dots \hat{a}_N^\dagger | \rangle. \quad (\text{C4b})$$

The last form of  $\Phi_O$  is expressed in terms of the creation operators  $\hat{a}_j^\dagger$  acting on the vacuum state  $| \rangle$ , having, together with the annihilation operators  $\hat{a}_j = (\hat{a}_j^\dagger)^\dagger$ , the properties

$$\langle | \rangle = 1, \quad \hat{a}_j | \rangle = 0 = \langle | \hat{a}_j^\dagger, \quad (\text{C5a})$$

$$[\hat{a}_j, \hat{a}_k^\dagger]_+ = \delta_{jk}, \quad [\hat{a}_j, \hat{a}_k]_+ = 0 = [\hat{a}_j^\dagger, \hat{a}_k^\dagger]_+. \quad (\text{C5b})$$

We follow closely the notation and relations developed by Szabo and Ostlund [32], but apply them to KS orbitals rather than the Hartree-Fock ones.

The expansion (B11) in a complete set of eigenfunctions of  $\hat{\mathcal{H}}_{/0}$  can be specified [32] as

$$\begin{aligned} |Y_{/j}\rangle &= \sum_a^{\text{occ}} \sum_r^{\text{vir}} |O_a^r\rangle \langle O_a^r | Y_{/j}\rangle + \sum_{a<b}^{\text{occ}} \sum_{r<s}^{\text{vir}} |O_{ab}^{rs}\rangle \langle O_{ab}^{rs} | Y_{/j}\rangle \\ &+ \sum_{a<b<c}^{\text{occ}} \sum_{r<s<t}^{\text{vir}} |O_{abc}^{rst}\rangle \langle O_{abc}^{rst} | Y_{/j}\rangle + \dots, \quad (\text{C6}) \end{aligned}$$

i.e., in terms of singly, doubly, up to  $N$ -tuply excited determinants:

$$|O_a^r\rangle = \hat{a}_r^\dagger \hat{a}_a |O\rangle, \quad |O_{ab}^{rs}\rangle = \hat{a}_s^\dagger \hat{a}_b \hat{a}_r^\dagger \hat{a}_a |O\rangle, \dots \quad (\text{C7})$$

A convention is adopted that indices  $a, b, c, d$  belong to occupied orbitals (e.g.,  $1 \leq a \leq N$ ),  $r, s, t, u$  to virtual orbitals (e.g.,  $N < r$ ), and  $i, j, k, l$  to orbitals of unspecified type (e.g.,  $1 \leq i$ ).

According to Görling and Levy [8], perturbing terms of the expanded Hamiltonian  $\hat{\mathcal{H}}^\alpha$  (B2) consist of two-body and one-body contributions in the first order,

$$\hat{\mathcal{H}}_{/1} = \hat{U} + \hat{V}_{\text{ext}/1} = \hat{U} - \hat{V}_{\text{esx}}, \quad (\text{C8})$$

and only one-body contributions in higher orders,

$$\hat{\mathcal{H}}_{/j} = \hat{V}_{\text{ext}/j} = -\hat{V}_{c/j}, \quad j = 2, 3, \dots \quad (\text{C9})$$

These can be written in terms of the creation and annihilation operators as

$$\hat{V}_{\text{ext}/j} = \sum_{i,k} \langle i | v_{\text{ext}/j} | k \rangle \hat{a}_i^\dagger \hat{a}_k, \quad (\text{C10})$$

$$\hat{U} = \frac{1}{4} \sum_{i,j,k,\ell} \langle ij || k\ell \rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k, \quad (\text{C11})$$

where

$$\langle i | v_{\text{ext}/j} | k \rangle = \int d\mathbf{x} \phi_i^*(\mathbf{x}) v_{\text{ext}/j}(\mathbf{r}) \phi_k(\mathbf{x}), \quad (\text{C12})$$

$$\langle ij || k\ell \rangle = \langle ij | k\ell \rangle - \langle ij | \ell k \rangle, \quad (\text{C13})$$

with

$$\begin{aligned} \langle ij | k\ell \rangle &\equiv \langle ij | u | k\ell \rangle \\ &= \int d\mathbf{x}_1 d\mathbf{x}_2 \phi_i^*(\mathbf{x}_1) \phi_j^*(\mathbf{x}_2) u(\mathbf{r}_1, \mathbf{r}_2) \phi_k(\mathbf{x}_1) \phi_\ell(\mathbf{x}_2), \quad (\text{C14}) \end{aligned}$$

having properties

$$\langle i | v_{\text{ext}/j} | k \rangle = (\langle k | v_{\text{ext}/j} | i \rangle)^*, \quad (\text{C15})$$

$$\langle ij || k\ell \rangle = -\langle ij || \ell k \rangle = -\langle ji || k\ell \rangle = (\langle \ell k || ji \rangle)^*. \quad (\text{C16})$$

The 1DM and 2DM operators, used in Eqs. (B15)–(B17), are defined as

$$\hat{\gamma}_1(\mathbf{x}_1; \mathbf{x}'_1) = \sum_{i,k} \gamma_1^{ki}(\mathbf{x}_1; \mathbf{x}'_1) \hat{a}_i^\dagger \hat{a}_k, \quad (\text{C17a})$$

with

$$\gamma_1^{ki}(\mathbf{x}_1; \mathbf{x}'_1) = \phi_k(\mathbf{x}_1) \phi_i^*(\mathbf{x}'_1), \quad (\text{C17b})$$

$$\begin{aligned} \hat{\gamma}_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) &= \frac{1}{2} \sum_{i,j,k,\ell} \phi_k(\mathbf{x}_1) \phi_\ell(\mathbf{x}_2) \\ &\times \phi_i^*(\mathbf{x}'_1) \phi_j^*(\mathbf{x}'_2) \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k. \quad (\text{C18}) \end{aligned}$$

We see that all quantities of interest in perturbation theory can be written in terms of matrix elements  $\langle A | \hat{a}_i^\dagger \hat{a}_k | B \rangle$  and  $\langle A | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | B \rangle$ , where  $|A\rangle$  and  $|B\rangle$  are Slater determinants. Nonzero values arise when  $|A\rangle$  and  $|B\rangle$  are identical or differ only slightly. Here we give a collection of results necessary for the evaluation of  $v_x$  and  $v_{c/2}$  in Sec. V:

$$\langle O | \hat{a}_i^\dagger \hat{a}_k | O \rangle = \tilde{\delta}_{ik}, \quad (\text{C19})$$

$$\langle O_a^r | \hat{a}_i^\dagger \hat{a}_k | O \rangle = \delta_{ir} \delta_{ka}, \quad (\text{C20})$$

$$\langle O_{ab}^{rs} | \hat{a}_i^\dagger \hat{a}_k | O \rangle = \langle O_{ab \dots c}^{rs \dots t} | \hat{a}_i^\dagger \hat{a}_k | O \rangle = 0, \quad (\text{C21})$$

$$\langle O_a^r | \hat{a}_i^\dagger \hat{a}_k | O_b^s \rangle = \delta_{ab} \delta_{rs} \bar{\delta}_{ik} + \delta_{ab} \delta_{ri} \delta_{sk} - \delta_{rs} \delta_{bi} \delta_{ak}, \quad (C22)$$

$$\langle O_{ab}^{rs} | \hat{a}_i^\dagger \hat{a}_k | O_c^t \rangle = (\delta_{ir} \delta_{st} - \delta_{is} \delta_{rt}) (\delta_{ka} \delta_{bc} - \delta_{kb} \delta_{ac}), \quad (C23)$$

$$\begin{aligned} \langle O_{ab}^{rs} | \hat{a}_i^\dagger \hat{a}_k | O_{cd}^{tu} \rangle &= (\delta_{ac} \delta_{bd} - \delta_{ad} \delta_{bc}) (\delta_{rt} \delta_{su} - \delta_{ru} \delta_{st}) \bar{\delta}_{ik} + (\delta_{ac} \delta_{bd} - \delta_{ad} \delta_{bc}) [\delta_{ir} (\delta_{kt} \delta_{su} - \delta_{ku} \delta_{st}) - \delta_{is} (\delta_{kt} \delta_{ru} - \delta_{ku} \delta_{rt})] \\ &+ (\delta_{rt} \delta_{su} - \delta_{ru} \delta_{st}) [\delta_{id} (\delta_{ka} \delta_{bc} - \delta_{kb} \delta_{ac}) - \delta_{ic} (\delta_{ka} \delta_{bd} - \delta_{kb} \delta_{ad})], \end{aligned} \quad (C24)$$

$$\langle O | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | O \rangle = \bar{\delta}_{ik} \bar{\delta}_{j\ell} - \bar{\delta}_{i\ell} \bar{\delta}_{jk}, \quad (C25)$$

$$\langle O_a^r | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | O \rangle = \delta_{rj} (\delta_{a\ell} \bar{\delta}_{ik} - \delta_{ak} \bar{\delta}_{i\ell}) - \delta_{ri} (\delta_{a\ell} \bar{\delta}_{jk} - \delta_{ak} \bar{\delta}_{j\ell}), \quad (C26)$$

$$\langle O_{ab}^{rs} | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | O \rangle = (\delta_{ak} \delta_{b\ell} - \delta_{a\ell} \delta_{bk}) (\delta_{ri} \delta_{sj} - \delta_{rj} \delta_{si}), \quad (C27)$$

$$\langle O_{abc}^{rst} | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | O \rangle = \langle O_{abc\dots d}^{rst\dots tu} | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | O \rangle = 0, \quad (C28)$$

$$\begin{aligned} \langle O_a^r | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | O_b^s \rangle &= \delta_{ab} \delta_{rs} (\bar{\delta}_{ik} \bar{\delta}_{j\ell} - \bar{\delta}_{i\ell} \bar{\delta}_{jk}) + \delta_{ab} [\delta_{ri} (\delta_{sk} \bar{\delta}_{j\ell} - \delta_{s\ell} \bar{\delta}_{jk}) - \delta_{rj} (\delta_{sk} \bar{\delta}_{i\ell} - \delta_{s\ell} \bar{\delta}_{ik})] + \delta_{rs} [\delta_{a\ell} (\delta_{bi} \bar{\delta}_{kj} - \delta_{bj} \bar{\delta}_{ki}) \\ &- \delta_{ak} (\delta_{bi} \bar{\delta}_{j\ell} - \delta_{bj} \bar{\delta}_{i\ell})] + (\delta_{bi} \delta_{rj} - \delta_{ri} \delta_{bj}) (\delta_{a\ell} \delta_{sk} - \delta_{s\ell} \delta_{ak}), \end{aligned} \quad (C29)$$

$$\begin{aligned} \langle O_a^r | \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k | O_{bc}^{st} \rangle &= + \delta_{ab} \delta_{rs} [\delta_{ci} (\delta_{tk} \bar{\delta}_{j\ell} - \delta_{t\ell} \bar{\delta}_{jk}) - \delta_{cj} (\delta_{tk} \bar{\delta}_{i\ell} - \delta_{t\ell} \bar{\delta}_{ik})] - \delta_{ab} \delta_{ri} [\delta_{ci} (\delta_{sk} \bar{\delta}_{j\ell} - \delta_{s\ell} \bar{\delta}_{jk}) - \delta_{cj} (\delta_{sk} \bar{\delta}_{i\ell} \\ &- \delta_{s\ell} \bar{\delta}_{ik})] - \delta_{ac} \delta_{rs} [\delta_{bi} (\delta_{tk} \bar{\delta}_{j\ell} - \delta_{t\ell} \bar{\delta}_{jk}) - \delta_{bj} (\delta_{tk} \bar{\delta}_{i\ell} - \delta_{t\ell} \bar{\delta}_{ik})] + \delta_{ac} \delta_{ri} [\delta_{bi} (\delta_{sk} \bar{\delta}_{j\ell} - \delta_{s\ell} \bar{\delta}_{jk}) \\ &- \delta_{bj} (\delta_{sk} \bar{\delta}_{i\ell} - \delta_{s\ell} \bar{\delta}_{ik})] + (\delta_{bi} \delta_{cj} - \delta_{bj} \delta_{ci}) [\delta_{rs} (\delta_{a\ell} \delta_{tk} - \delta_{t\ell} \delta_{ak}) - \delta_{ri} (\delta_{a\ell} \delta_{sk} - \delta_{s\ell} \delta_{ak})] + (\delta_{s\ell} \delta_{tk} \\ &- \delta_{sk} \delta_{t\ell}) [\delta_{ab} (\delta_{ci} \delta_{rj} - \delta_{ri} \delta_{cj}) - \delta_{ac} (\delta_{bi} \delta_{rj} - \delta_{ri} \delta_{bj})], \end{aligned} \quad (C30)$$

where

$$\bar{\delta}_{ik} = \sum_a^{\text{occ}} \delta_{ai} \delta_{ak}. \quad (C31)$$

The strategy to obtain such results is to move operators, using relations (C5b), and to apply properties

$$\langle O | O \rangle = 1, \quad \hat{a}_r | O \rangle = 0 = \langle O | \hat{a}_r^\dagger, \quad \hat{a}_a^\dagger | O \rangle = 0 = \langle O | \hat{a}_a, \quad (C32)$$

which follow from Eqs. (C4) and (C5a); e.g., in

$$\langle O_a^r | \hat{a}_i^\dagger \hat{a}_k | O_b^s \rangle = \langle O | \hat{a}_a^\dagger \hat{a}_r \hat{a}_i^\dagger \hat{a}_k \hat{a}_s^\dagger \hat{a}_b | O \rangle \quad (C33)$$

the operators  $\hat{a}_s^\dagger \hat{a}_b$  are moved to the left, while operators  $\hat{a}_a^\dagger \hat{a}_r$  moved to the right. The well-known results (C19) and (C25) [32] lead immediately to the KS reference system DMs

$$\gamma_1^s(\mathbf{x}_1; \mathbf{x}'_1) = \sum_a^{\text{occ}} \phi_a(\mathbf{x}_1) \phi_a^*(\mathbf{x}'_1), \quad (C34)$$

$$\begin{aligned} \gamma_2^s(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) &= \frac{1}{2} \{ \gamma_1^s(\mathbf{x}_1; \mathbf{x}'_1) \gamma_1^s(\mathbf{x}_2; \mathbf{x}'_2) \\ &- \gamma_1^s(\mathbf{x}_1; \mathbf{x}'_2) \gamma_1^s(\mathbf{x}_2; \mathbf{x}'_1) \}. \end{aligned} \quad (C35)$$

Let us note finally that the one-body potential operator (C10) can be written in terms of the diagonal 1DM operator (C17) as

$$\hat{v}_{\text{ex}U_j} = \int d\mathbf{1} v_{\text{ex}U_j}(\mathbf{1}) \hat{\gamma}_1(\mathbf{1}; \mathbf{1}); \quad (C36)$$

the one-body kinetic-energy operator

$$\hat{T} = \sum_{i,k} \langle i | \hat{t} | k \rangle \hat{a}_i^\dagger \hat{a}_k \quad (C37)$$

where  $\langle i | \hat{t} | k \rangle$  is defined analogously to  $\langle i | v_{\text{ex}U_j} | k \rangle$  in Eq. (C12), can be written in terms of the ‘‘close to diagonal’’ 1DM operator

$$\hat{T} = \int d\mathbf{1} \hat{t}(\mathbf{1}) \hat{\gamma}_1(\mathbf{1}; \mathbf{1}')|_{\mathbf{1}'=\mathbf{1}}; \quad (C38)$$

and the two-body operator (C11), can be written as

$$\hat{U} = \int d\mathbf{1} d\mathbf{2} u(\mathbf{1}, \mathbf{2}) \hat{\gamma}_2(\mathbf{1}, \mathbf{2}; \mathbf{1}, \mathbf{2}), \quad (C39)$$

which all can be verified directly.



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