

# Exact high-density limit of correlation potential for two-electron density

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Present approximations to the correlation energy,  $E_c[n]$ , in density functional theory yield poor results for the corresponding correlation potential,  $v_c([n];\mathbf{r}) = \delta E_c[n] / \delta n(\mathbf{r})$ . Improvements in  $v_c([n];\mathbf{r})$ , are especially needed for high-quality Kohn–Sham calculations. For a two-electron density, the exact form of  $v_c([n];\mathbf{r})$  in its high-density limit is derived in terms of the density of the system and the first-order wave function from the adiabatic perturbation theory. Our expression leads to a formula for the difference  $2E_c[n] - \int v_c([n];\mathbf{r})n(\mathbf{r})d\mathbf{r}$ , valid for any two-electron density in the high-density limit, thus generalizes previous results. Numerical results (both exact and approximate) are presented for both  $E_c[n]$  and  $\int v_c([n];\mathbf{r})n(\mathbf{r})d\mathbf{r}$  in this limit for two electrons in a harmonic oscillator external potential (Hooke's atom). © 1999 American Institute of Physics. [S0021-9606(99)30319-6]

## INTRODUCTION AND DEFINITIONS

Density functional theory (DFT) has provided an effective machinery for quantum chemistry calculations on large molecules.<sup>1–5</sup> This state-of-the-art theory enables one to replace the complicated conventional wave function approach with the simpler density functional formalism. In density functional calculations an energy functional must be employed. The form of the exact exchange–correlation component,  $E_{xc}[n]$ , of this functional must be approximated.<sup>1–8</sup> For convenience,  $E_{xc}[n]$  is further partitioned into exchange  $E_x[n]$  and correlation  $E_c[n]$  contributions, i.e.,  $E_{xc}[n] = E_x[n] + E_c[n]$ .<sup>8</sup>

The most widely used implementation of DFT is the Kohn–Sham (KS) theory.<sup>2–5</sup> In this approach, the interacting system of interest is replaced by a model noninteracting system with the same ground-state density in a new effective multiplicative potential (the KS potential) incorporating all effects associated with the electron–electron interactions. The ground-state properties of the system under investigation are then obtained by means of the density and the noninteracting ground-state wave function that yields this density.

The KS potential  $v_s([n];\mathbf{r})$  is a unique functional of the density  $n(\mathbf{r})$ , and is usually written as

$$v_s([n];\mathbf{r}) = v(\mathbf{r}) + u([n];\mathbf{r}) + v_x([n];\mathbf{r}) + v_c([n];\mathbf{r}), \quad (1)$$

where  $v(\mathbf{r})$  is the physical external potential of the system. The Hartree potential  $u([n];\mathbf{r})$  is

$$u([n];\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \quad (2)$$

which is the functional derivative of the Hartree electron–electron repulsion energy  $U[n]$  given explicitly in terms of the density by

$$U[n] = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (3)$$

In Eq. (1), the exchange potential  $v_x([n];\mathbf{r})$  is the functional derivative of  $E_x[n]$ , i.e.,  $v_x([n];\mathbf{r}) = \delta E_x[n] / \delta n(\mathbf{r})$ . The exchange energy  $E_x[n]$  is known exactly in terms of the noninteracting KS wave function, and is defined as

$$E_x[n] = \langle \Phi_0[n] | \hat{V}_{ee} | \Phi_0[n] \rangle - U[n], \quad (4)$$

where  $\hat{V}_{ee}$  is the operator for the electron–electron repulsion, and  $\Phi_0[n]$  is the KS wave function, i.e., the wave function that minimizes the expectation value of the kinetic energy operator only, and yields the same density  $n(\mathbf{r})$ . Except for certain degenerate cases, the KS wave function is a single determinant.<sup>9</sup> In practice,  $E_x[n]$  is usually approximated as an explicit functional of the density. The exact density dependence of  $E_x[n]$  is known only for two-electron diamagnetic densities because  $E_x[n] = -\frac{1}{2}U[n]$ .

The last term on the right-hand side of Eq. (1) is the correlation potential  $v_c([n];\mathbf{r})$ , which is the functional derivative of  $E_c[n]$ , i.e.,  $v_c([n];\mathbf{r}) = \delta E_c[n] / \delta n(\mathbf{r})$ . The correlation energy functional,  $E_c[n]$ , is formally defined as

$$E_c[n] = \langle \Psi[n] | \hat{T} + \hat{V}_{ee} | \Psi[n] \rangle - \langle \Phi_0[n] | \hat{T} + \hat{V}_{ee} | \Phi_0[n] \rangle. \quad (5)$$

In Eq. (5),  $\hat{T}$  is the kinetic energy operator and  $\Psi[n]$  is that antisymmetric wave function that minimizes  $\langle \hat{T} + \hat{V}_{ee} \rangle$  and yields the density  $n(\mathbf{r})$ .

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In order to arrive at very the best approximations to  $E_c[n]$  and  $E_x[n]$ , knowledge of their exact properties is needed. While many exact conditions on  $E_c[n]$  are known to guide the construction of approximations; relatively few exist for  $v_c([n];\mathbf{r})$ . The purpose of this work is to present new constraints for  $v_c([n];\mathbf{r})$  in its high-density scaling limit for two-electron diamagnetic densities. The correlation potential  $v_c([n];\mathbf{r})$  is very difficult to mimic because of its pointwise nature in contrast to  $E_c[n]$ , which is just a number. Many accurate approximations to  $E_c[n]$  yield poor approximations to  $v_c([n];\mathbf{r})$ . In addition, properties like ionization and excitation energies, polarizabilities, and hyperpolarizabilities, are very sensitive to the quality of the approximations used to generate the KS potential. Designing new functionals with improved properties of their functional derivatives is crucial for high-quality KS calculations.

An important technique for deriving the properties of the unknown density functionals is the scaling of the electron density  $n(\mathbf{r})$ . Coordinate scaling provides key requirements for the exact dimensional properties of  $E_x[n]$  and  $E_c[n]$ . When the density is scaled uniformly along each direction in space, i.e.,

$$n_\lambda(x,y,z) \equiv \lambda^3 n(\lambda x, \lambda y, \lambda z), \quad (6)$$

the following simple scaling occurs with  $U[n]$  and  $E_x[n]$ :<sup>8</sup>

$$U[n_\lambda] = \lambda U[n] \quad (7)$$

and

$$E_x[n_\lambda] = \lambda E_x[n]. \quad (8)$$

Upon uniform scaling of the electron density,  $E_c[n]$  does not scale homogeneously. Instead,  $E_c[n]$  has the following expansion for large  $\lambda$ :

$$\begin{aligned} E_c[n_\lambda] &= E_c^{(2)}[n] + \lambda^{-1} E_c^{(3)}[n] + \lambda^{-2} E_c^{(4)}[n] \cdots \\ &= \sum_{j=2}^{\infty} \lambda^{2-j} E_c^{(j)}[n]. \end{aligned} \quad (9)$$

In other words,  $E_c[n_\lambda]$  is bounded, as  $\lambda \rightarrow \infty$ , and is equal to a second-order energy,<sup>10–14</sup> i.e.,

$$\lim_{\lambda \rightarrow \infty} E_c[n_\lambda] = E_c^{(2)}[n]. \quad (10)$$

The quantity  $2E_c^{(2)}[n]$  is particularly important because it is the initial slope in the adiabatic connection method (coupling-constant formula) for  $E_c[n]$ .<sup>10,11,15–19</sup> It is also believed that  $E_c[n]$  is relatively insensitive to coordinate scaling,<sup>11</sup> i.e.,  $E_c^{(2)}[n] \approx E_c[n]$  for small atoms. As a result, knowledge of  $E_c^{(2)}[n]$  can be used for constructing accurate approximations to  $E_c[n]$ .

The link between uniform scaling of the electron density and scaling of the electron–electron interaction has been developed by Görling and Levy in a series of papers.<sup>11,20</sup> The effective potential and the electron–electron interaction along the coupling constant path, which connects a noninteracting and a fully interacting system with the same electron density, have been used by them to construct a DFT perturbation theory, yielding

$$\begin{aligned} E_c^{(2)}[n] &= \frac{1}{2} \{ \langle \Phi_0[n] | \hat{H}^{(1)}[n] | \Psi^{(1)}[n] \rangle \\ &\quad + \langle \Psi^{(1)}[n] | \hat{H}^{(1)}[n] | \Phi_0[n] \rangle \}, \end{aligned} \quad (11)$$

with

$$\begin{aligned} \hat{H}^{(1)}[n] &= \hat{V}_{ee} - \sum_{i=1}^N \{ u([n];\mathbf{r}_i) + v_x([n];\mathbf{r}_i) \} \\ &\equiv \hat{V}_{ee} - \sum_{i=1}^N v_{xu}([n];\mathbf{r}_i), \end{aligned} \quad (12)$$

and  $\Psi^{(1)}[n]$  being the solution to

$$\{ \hat{H}_0[n] - E_0 \} \Psi^{(1)}[n] = \{ E^{(1)} - \hat{H}^{(1)}[n] \} \Phi_0[n]. \quad (13)$$

In Eq. (13),  $E^{(1)}$  is the first-order correction to the energy due to  $\hat{H}^{(1)}[n]$  from the standard Rayleigh–Schrodinger perturbation theory. In the above equation,  $u([n];\mathbf{r})$  and  $v_x([n];\mathbf{r})$  are the functional derivatives of  $U[n]$  and  $E_x[n]$  with respect to the density, and  $v_{xu}([n];\mathbf{r}) = v_x([n];\mathbf{r}) + u([n];\mathbf{r})$ .

In Eq. (11), the KS wave function  $\Phi_0$  is the ground-state solution to the noninteracting Schrödinger equation,

$$\begin{aligned} \hat{H}_0[n] \Phi_k &= \left\{ \hat{T} + \sum_{i=1}^N v_s([n];\mathbf{r}_i) \right\} \Phi_k = E_k^0 \Phi_k; \\ E_0 &< E_1^0 \leq \cdots \leq E_k^0 \leq \cdots, \end{aligned} \quad (14)$$

where we shall assume that  $E_0$  ( $\equiv E_0^0$ ) is nondegenerate. The energies  $E_0$  and  $E_k^0$  are the eigenvalues corresponding to  $\Phi_0$  and  $\Phi_k$ , respectively.

Since most of the present approximations to  $E_c[n]$  give relatively good results for  $E_c[n]$ , but the shapes of the corresponding correlation potentials are not quite satisfactory, we shall derive an expression for the exact form of  $v_c^{(2)}([n];\mathbf{r})$  for two-electron diamagnetic densities. This expression should prove useful in the process of obtaining new improved approximations to  $v_c([n];\mathbf{r})$ . By taking the functional derivative of  $E_c^{(2)}[n]$ , we arrive at a formal expression for  $v_c^{(2)}([n];\mathbf{r})$  featuring the density of the system of interest,  $n(\mathbf{r})$ , and the first-order wave function from Görling–Levy (GL) adiabatic perturbation theory, associated with  $n(\mathbf{r})$ . Our pointwise identity for  $v_c^{(2)}([n];\mathbf{r})$  leads to a generalization of a previous result obtained by Görling and Levy<sup>20</sup> with the caveat that all components of the KS potential vanish at infinity.

## DIFFERENT EXPRESSIONS FOR $E_c^{(2)}[n]$

Before approaching the subtle subject of taking the functional derivative of  $E_c^{(2)}[n]$ , we introduce two different forms of the GL expression for the high-density scaling limit of  $E_c[n]$ .

First, as has been pointed out by Görling and Levy,<sup>11,20</sup>

$$\langle \Psi^{(1)}[n] | \hat{\rho} | \Phi_0[n] \rangle + \langle \Phi_0[n] | \hat{\rho} | \Psi^{(1)}[n] \rangle = 0, \quad (15)$$

because the density is held fixed along the adiabatic path. In Eq. (15),  $\hat{\rho}$  is the density operator. Formula (15) implies that

$$\left\langle \Psi^{(1)}[n] \left| \sum_{i=1}^N A(\mathbf{r}_i) \right| \Phi_0[n] \right\rangle + \left\langle \Phi_0[n] \left| \sum_{i=1}^N A(\mathbf{r}_i) \right| \Psi^{(1)}[n] \right\rangle = 0, \quad (16)$$

where  $A(\mathbf{r})$  is any one-body multiplicative operator. By means of Eq. (16), along with  $A(\mathbf{r}) = v_{xu}([n]; \mathbf{r})$ , Eq. (11) simplifies to

$$E_c^{(2)}[n] = \frac{1}{2} \{ \langle \Phi_0[n] | \hat{V}_{ee} | \Psi^{(1)}[n] \rangle + \langle \Psi^{(1)}[n] | \hat{V}_{ee} | \Phi_0[n] \rangle \}. \quad (17)$$

Another form of Eq. (17), which can be readily developed, considers  $\hat{V}_{ee}$  alone as the perturbation. We introduce  $\tilde{\Psi}^{(1)}[n] (\neq \Psi^{(1)}[n])$  as the solution to

$$\{ \hat{H}_0[n] - E_0 \} \tilde{\Psi}^{(1)}[n] = \{ \tilde{E}^{(1)} - \hat{V}_{ee} \} \Phi_0[n], \quad (18)$$

where  $\tilde{E}^{(1)}$  and  $\tilde{\Psi}^{(1)}[n]$  are the first-order energy and wave function respectively, when the perturbation is  $\hat{V}_{ee}$  only.

By making use of Eqs. (13) and (18), Eq. (17) can be equivalently expressed as

$$E_c^{(2)}[n] = \frac{1}{2} \{ \langle \Phi_0[n] | \hat{H}^{(1)}[n] | \tilde{\Psi}^{(1)}[n] \rangle + \langle \tilde{\Psi}^{(1)}[n] | \hat{H}^{(1)}[n] | \Phi_0[n] \rangle \}. \quad (19)$$

A comparison of Eqs. (17) and (19) shows that  $E_c^{(2)}[n]$  can be expressed either in terms of  $\hat{V}_{ee}$  acting on  $\Psi^{(1)}$ , the response to  $\hat{H}^{(1)}[n]$ , or in terms of  $\hat{H}^{(1)}[n]$  acting on  $\tilde{\Psi}^{(1)}[n]$ , the response to  $\hat{V}_{ee}$ .

## DERIVATIONS

To obtain an expression for  $v_c^{(2)}([n]; \mathbf{r})$ , we start with the second-order energy from GL perturbation theory, Eq. (17), and calculate

$$v_c^{(2)}([n]; \mathbf{r}) = \left. \frac{\delta E_c^{(2)}[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=n}. \quad (20)$$

In the special case of a spin-unpolarized two-electron density, there is only one quantity in Eq. (17) whose density dependence cannot be expressed in terms of the density explicitly. This quantity is the first-order wave function,  $\Psi^{(1)}[n]$ . Note that  $\hat{V}_{ee}$  is independent of the density for fixed particle number, and  $\Psi_0[n]$  is given in terms of the density  $n(\mathbf{r})$  (the spin part is omitted for simplicity of the notation) by

$$\Phi_0([n]; \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} n^{1/2}(\mathbf{r}_1) n^{1/2}(\mathbf{r}_2). \quad (21)$$

To find the functional derivative of  $E_c^{(2)}[n]$ , we rewrite Eq. (17) as

$$E_c^{(2)}[n] = \frac{1}{2} \{ \langle \Phi_0[n] | \hat{V}_{ee} - \tilde{E}^{(1)} | \Psi^{(1)}[n] \rangle + \frac{1}{2} \langle \Psi^{(1)}[n] | \hat{V}_{ee} - \tilde{E}^{(1)} | \Phi_0[n] \rangle \}. \quad (22)$$

By using the differential equation (18), we arrive at

$$E_c^{(2)}[n] = \frac{1}{2} \langle \tilde{\Psi}^{(1)}[n] | E_0 - \hat{H}_0[n] | \Psi^{(1)}[n] \rangle + \frac{1}{2} \langle \Psi^{(1)}[n] | E_0 - \hat{H}_0[n] | \tilde{\Psi}^{(1)}[n] \rangle. \quad (23)$$

We shall take the functional derivative of  $E_c^{(2)}[n]$  given by Eq. (23). Note that in the above formula  $\Psi^{(1)}[n]$ ,  $\tilde{\Psi}^{(1)}[n]$ ,  $E_0$ , and  $\hat{H}_0[n]$  depend on the density. If either  $\Psi^{(1)}[n]$  or  $\tilde{\Psi}^{(1)}[n]$  is known exactly, the other one is uniquely determined as well.

In order to obtain the form of  $v_c^{(2)}([n]; \mathbf{r})$ , we will make use of the following expression:

$$\left. \frac{\partial G[n + \sigma g]}{\partial \sigma} \right|_{\sigma=0} = \int d\mathbf{r} \left. \frac{\delta G[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=n} g(\mathbf{r}), \quad (24)$$

for all  $g(\mathbf{r})$ , such that  $\int g(\mathbf{r}) d\mathbf{r} = 0$ , keeping the particle number fixed through a small variation of the density. With this in mind, a variation of the density leads to

$$\begin{aligned} \left. \frac{\partial E_c^{(2)}[n + \sigma g]}{\partial \sigma} \right|_{\sigma=0} &= \frac{1}{2} \{ \langle (\tilde{\Psi}^{(1)}[n] | E_0 - \hat{H}_0[n])' | \Psi^{(1)}[n] \rangle \\ &\quad \times [n] \rangle + \langle \tilde{\Psi}^{(1)}[n] | (E_0 - \hat{H}_0[n] | \Psi^{(1)}[n])' \rangle \} - \frac{1}{2} \{ \langle \tilde{\Psi}^{(1)}[n] \\ &\quad \times [n] | (E_0 - \hat{H}_0[n])' | \Psi^{(1)}[n] \rangle \} \\ &\quad + \frac{1}{2} \{ \langle \Psi^{(1)}[n] | E_0 - \hat{H}_0[n] \rangle' | \tilde{\Psi}^{(1)}[n] \rangle \\ &\quad \times [n] \rangle + \langle \Psi^{(1)}[n] | (E_0 - \hat{H}_0[n] | \tilde{\Psi}^{(1)}[n])' \rangle \} - \frac{1}{2} \{ \langle \Psi^{(1)}[n] \\ &\quad \times [n] | (E_0 - \hat{H}_0[n])' | \tilde{\Psi}^{(1)}[n] \rangle \}. \end{aligned} \quad (25)$$

Here primes indicate density variations of the terms in the parentheses. In order to find the effect of changing the density upon the terms involving the first-order wave functions,  $\Psi^{(1)}[n]$  and  $\tilde{\Psi}^{(1)}[n]$ , we use the corresponding differential equations, Eqs. (13) and (18), and their complex conjugate counterparts. In general, the left-hand sides of Eqs. (13) and (18) are very convenient for density variations because everything is expressed in terms of the density  $n(\mathbf{r})$  only. Also, note that when one varies the left-hand sides of Eqs. (13) and (18), the first-order energies  $E^{(1)}$  and  $\tilde{E}^{(1)}$  could be conveniently eliminated. It follows from the fact that the expressions for  $E_c^{(2)}[n]$ , Eqs. (11), (17), and (19) are determined within a constant in the perturbation because of the normalization conditions, i.e.,

$$\langle \tilde{\Psi}^{(1)}[n] | \Phi_0[n] \rangle + \langle \Phi_0[n] | \tilde{\Psi}^{(1)}[n] \rangle = 0. \quad (26)$$

When  $\Psi^{(1)}[n]$  is considered, a more severe normalization constraint for the density, Eq. (16), applies.

The last term that deserves special attention is

$$-\frac{1}{2} \langle \tilde{\Psi}^{(1)}[n] | (E_0 - \hat{H}_0[n])' | \Psi^{(1)}[n] \rangle - \frac{1}{2} \langle \Psi^{(1)}[n] | (E_0 - \hat{H}_0[n])' | \tilde{\Psi}^{(1)}[n] \rangle. \quad (27)$$

To find the result coming from varying  $(E_0 - \hat{H}_0[n])$  with respect to the density, we use the exact form of  $\hat{H}_0[n]$ . In terms of  $n(\mathbf{r})$ ,  $\hat{H}_0[n]$  is given by

$$\hat{H}_0[n] = \sum_{i=1}^2 \left\{ -\frac{1}{2} \nabla_i^2 + v_0([n]; \mathbf{r}_i) \right\}, \quad (28)$$

where

$$v_0([n]; \mathbf{r}) = \epsilon_0 + \frac{1}{2} \frac{\nabla^2 n^{1/2}(\mathbf{r})}{n^{1/2}(\mathbf{r})}. \quad (29)$$

The potential,  $v_0([n]; \mathbf{r})$ , is obtained by inverting the corresponding one-particle equation. In Eq. (29),  $\epsilon_0$  is the orbital energy of the doubly occupied KS orbital, and

$$E_0[n] = 2\epsilon_0. \quad (30)$$

By integrating by parts, we obtain

$$\begin{aligned} \left. \frac{\partial E_c^{(2)}[n + \sigma g]}{\partial \sigma} \right|_{\sigma=0} &= \frac{1}{4} \langle g(\mathbf{r}_1) n^{-1/2}(\mathbf{r}_1) n^{1/2}(\mathbf{r}_2) | \hat{V}_{ee} | \Psi^{(1)}[n] \rangle \\ &+ \frac{1}{4} \langle g(\mathbf{r}_1) n^{-1/2}(\mathbf{r}_1) n^{1/2}(\mathbf{r}_2) | \\ &\times \hat{H}^{(1)}[n] | \tilde{\Psi}^{(1)}[n] \rangle \\ &- \frac{1}{2} \int \int \frac{g(\mathbf{r}_1) s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &+ \frac{1}{4} \int g(\mathbf{r}) \left( \frac{\nabla^2 t(\mathbf{r})}{n(\mathbf{r})} - \frac{(\nabla t) \cdot (\nabla n)}{n^2(\mathbf{r})} \right. \\ &\left. + \frac{t |\nabla n|^2}{n^3(\mathbf{r})} - \frac{t \nabla^2 n}{n^2(\mathbf{r})} \right) d\mathbf{r} + \text{c.c.} \end{aligned} \quad (31)$$

In formula (31),  $s(\mathbf{r})$  and  $t(\mathbf{r})$  are defined as follows:

$$s(\mathbf{r}) = \int [\Phi_0(\mathbf{r}, \mathbf{r}')]^* \tilde{\Psi}^{(1)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' \quad (32)$$

and

$$t(\mathbf{r}) = \int [\Psi^{(1)}(\mathbf{r}, \mathbf{r}')]^* \tilde{\Psi}^{(1)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}'. \quad (33)$$

In the above equations,  $\Psi^{(1)}(\mathbf{r}, \mathbf{r}')$ ,  $\tilde{\Psi}^{(1)}(\mathbf{r}, \mathbf{r}')$ , and  $\Phi_0(\mathbf{r}, \mathbf{r}')$  are functionals of the density.

The form of the potential,  $v_c^{(2)}([n]; \mathbf{r})$ , is easily obtained from Eq. (31), and it is

$$\begin{aligned} v_c^{(2)}([n]; \mathbf{r}) &= \frac{1}{4} n^{-1/2}(\mathbf{r}) \int \frac{n^{1/2}(\mathbf{r}') \Psi^{(1)}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &+ \frac{1}{4} n^{-1/2}(\mathbf{r}) \int n^{1/2}(\mathbf{r}') \left\{ \frac{1}{|\mathbf{r} - \mathbf{r}'|} - v_{xu}([n]; \mathbf{r}') \right. \\ &\left. - v_{xu}([n]; \mathbf{r}) \right\} \tilde{\Psi}^{(1)}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' - \frac{1}{2} \int \frac{s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &+ \frac{1}{4} \left\{ \frac{\nabla^2 t(\mathbf{r})}{n(\mathbf{r})} - \frac{(\nabla t) \cdot (\nabla n)}{n^2(\mathbf{r})} \right. \\ &\left. + \frac{t |\nabla n|^2}{n^3(\mathbf{r})} - \frac{t \nabla^2 n}{n^2(\mathbf{r})} \right\} + \text{c.c.} \end{aligned} \quad (34)$$

Formula (34), our key result, features the density of the system under investigation and the first-order wave functions from adiabatic perturbation theory,  $\Psi^{(1)}[n]$ , and from perturbation theory when electron-electron repulsion is the per-

turbation,  $\tilde{\Psi}^{(1)}[n]$ . Very good approximations to either one can be found by using the variation-perturbation approach of Hylleraas.<sup>21</sup> Once, for example,  $\Psi^{(1)}[n]$  is determined, then  $\tilde{\Psi}^{(1)}[n]$  can be easily obtained because<sup>22</sup>

$$\begin{aligned} \tilde{\Psi}^{(1)}[n] - \Psi^{(1)}[n] \\ = \left\{ f(\mathbf{r}_1) - \frac{1}{2} \int f(\mathbf{r}_1) n(\mathbf{r}_1) d\mathbf{r}_1 \right\} n^{1/2}(\mathbf{r}_1) n^{1/2}(\mathbf{r}_2), \end{aligned} \quad (35)$$

where  $f(\mathbf{r})$  is the solution to

$$\begin{aligned} \nabla \cdot [n(\mathbf{r}) \nabla f(\mathbf{r})] \\ = n(\mathbf{r}) \left[ u([n]; \mathbf{r}) - \frac{1}{2} \int n(\mathbf{r}) u([n]; \mathbf{r}) d\mathbf{r} \right]. \end{aligned} \quad (36)$$

When an appropriate transformation exists, such that the three-dimensional one-particle problem is reduced to three one-dimensional ones (i.e., the separation of variables is possible), then the analytic solution to Eq. (36) exists<sup>22</sup> and can be obtained by two consecutive integrations over each of the coordinates.

If we multiply both sides of Eq. (34) by  $n(\mathbf{r})$  and integrate over all space, we arrive at an identity previously obtained by Görling and Levy<sup>20</sup> and recently expressed in a closed form by Ivanov *et al.*<sup>22</sup> Namely,

$$\begin{aligned} 2E_c^{(2)}[n] - \int v_c^{(2)}([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ = \frac{1}{2} \left\{ \int f(\mathbf{r}) n(\mathbf{r}) u([n]; \mathbf{r}) d\mathbf{r} - 2\epsilon^{(1)} \int f(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\}, \end{aligned} \quad (37)$$

where  $f(\mathbf{r})$  is the solution to Eq. (36), and  $\epsilon^{(1)}$  is given by

$$\epsilon^{(1)} = \frac{1}{4} \int n(\mathbf{r}) u([n]; \mathbf{r}) d\mathbf{r}. \quad (38)$$

By integrating by parts, it can be shown that

$$\frac{1}{4} \int n(\mathbf{r}) \left\{ \frac{\nabla^2 t(\mathbf{r})}{n(\mathbf{r})} - \frac{(\nabla t) \cdot (\nabla n)}{n^2(\mathbf{r})} + \frac{t |\nabla n|^2}{n^3(\mathbf{r})} - \frac{t \nabla^2 n}{n^2(\mathbf{r})} \right\} d\mathbf{r} = 0. \quad (39)$$

### EXAMPLE: HARMONIC OSCILLATOR EXTERNAL POTENTIAL

To illustrate the fact that our results apply to any external potential, we test them on a simple model system, the Hooke's atom, which consists of two electrons repelling each other via a Coulomb repulsion, but bound to an attractive center by a simple oscillator potential of frequency  $\omega$ . This model has been treated by many authors before,<sup>23</sup> often to illustrate concepts in DFT.<sup>24-27</sup> Recently, an analytic solution was discovered at  $\omega = \frac{1}{2}$ .<sup>28</sup> Later, an infinite set of such discrete values were found, at lower frequencies.<sup>29</sup>

Since formula (37) is true for a density associated with any kind of external potential, we calculate the difference  $E_c^{(2)}[n] - \int v_c^{(2)}([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r}$  for density  $n(\mathbf{r}) = 2(2a/\pi)^{3/2} \exp(-2ar^2)$ ;  $a > 0$  by applying some recent

identities of Ivanov *et al.*<sup>22</sup> This density corresponds to the external potential  $v_0(\mathbf{r}) = a^{1/2} r^2$ , which approaches infinity as  $|\mathbf{r}|$  goes to infinity. (The exact values of  $E_c^{(2)}[n]$  and  $\int d\mathbf{r} v_c^{(2)}([n]; \mathbf{r}) n(\mathbf{r})$ , corresponding to density  $n(\mathbf{r}) = (2a^3/\pi) \exp(-2ar)$  have been obtained in Ref. 22.)

First, note that

$$\epsilon^{(1)} = \sqrt{\frac{4a}{\pi}}. \quad (40)$$

Then, the radial component of the operator  $f(r)$  reads as

$$f(r) = \frac{1}{\sqrt{4a}} \left\{ -\frac{2I_A}{r} e^{r^2/2} + \frac{4}{\sqrt{2\pi}} (1 - e^{-r^2/2}) - \frac{r^2}{\sqrt{\pi}} \right\} + \frac{1}{\sqrt{4a}} \frac{4}{\sqrt{2\pi}} \int_0^r e^{r^2/2} \Gamma\left(\frac{3}{2}, \frac{r^2}{2}, r^2\right) dr, \quad (41)$$

with

$$I_A = \frac{2}{\sqrt{2\pi}} \Gamma\left(\frac{3}{2}, \frac{r^2}{2}, r^2\right) - \frac{2}{\sqrt{\pi}} e^{-r^2/2} \Gamma\left(\frac{3}{2}, 0, r^2\right). \quad (42)$$

In Eqs. (41) and (42),  $\Gamma(k, z_1, z_2)$  is the generalized incomplete Gamma function:

$$\Gamma(k, z_1, z_2) = \int_{z_1}^{z_2} t^{k-1} e^{-t} dt. \quad (43)$$

[A similar expression for  $f(r)$  has been developed by White and Brown.<sup>30</sup>]

By means of expressions (40)–(43), we calculate the integrals on the right-hand side of Eq. (37) to obtain

$$2E_c^{(2)}[n] - \int v_c^{(2)}([n]; \mathbf{r}) n(\mathbf{r}) d\mathbf{r} = -0.028188. \quad (44)$$

To test this result, we employ a numerical method to solve Hooke's atom for any  $\omega$ .

The Hamiltonian may be written as

$$\hat{H} = -\frac{1}{2} \{\nabla_1^2 + \nabla_2^2\} + \frac{\omega^2}{2} (r_1^2 + r_2^2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (45)$$

This is more conveniently expressed in terms of the center of mass  $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$  and difference  $\mathbf{u} = \mathbf{r}_2 - \mathbf{r}_1$  coordinates:

$$\hat{H} = -\frac{1}{4} \nabla_{\mathbf{R}}^2 - \nabla_{\mathbf{u}}^2 + \omega^2 \left( R^2 + \frac{u^2}{4} \right) + \frac{1}{u}. \quad (46)$$

The advantage of the harmonic oscillator potential is now clear. The center of mass and difference variables may be separated:

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \Phi_0(\mathbf{R}) \phi_0(\mathbf{u}), \quad (47)$$

yielding a simple three-dimensional oscillator equation in  $\mathbf{R}$ , with mass 2 and force constant  $2\omega^2$ , and ground-state solution:

$$\Phi_0(\mathbf{R}) = \exp(-R^2/2R_0^2) / (\pi^{3/4} R_0^{3/2}), \quad (48)$$

where  $R_0 = 1/\sqrt{2\omega}$ . The equation in  $\mathbf{u}$  is especially interesting:

TABLE I. First three analytic solutions to Hooke's atom.

Solution	$\omega$	$u_0 = \sqrt{2/\omega}$	$\{c_j/c_0\}$	$\epsilon_0/\omega$
0	$\infty$	0	$\{1, 0, \dots\}$	$\frac{3}{2}$
1	$\frac{1}{2}$	2	$\{1, 1/2, 0, \dots\}$	$\frac{5}{2}$
2	$\frac{1}{10}$	$\sqrt{20}$	$\{1, 1/2, 1/20, 0, \dots\}$	$\frac{7}{2}$

$$\left\{ -\nabla_{\mathbf{u}}^2 + \frac{\omega^2 \mathbf{u}^2}{4} + \frac{1}{u} \right\} \phi(\mathbf{u}) = \epsilon_u \phi(\mathbf{u}). \quad (49)$$

It looks like a three-dimensional oscillator of mass  $\frac{1}{2}$ , except for the Coulomb repulsion term  $1/u$ .

The ground state of the eigenvalue, Eq. (49), is spherically symmetric, and will decay as a Gaussian for large  $u$ . We expand the wave function in the basis set,

$$\phi(\mathbf{u}) = \sum_{j=0}^{\infty} c_j u^j \exp(-u^2/2u_0^2), \quad (50)$$

where  $u_0 = \sqrt{2/\omega}$  is the (noninteracting) length scale of the  $u$  oscillator. Note that this set is not orthonormal. This expansion becomes exact for those values of  $\omega$  at which analytic solutions exist, as given in the examples of Table I.

We now use dimensionless functions to capture the scale-independent features of the solution. We write the scaled wave function as

$$\tilde{\phi}(u_0; x) = u_0^{3/2} \phi_0(u_0; u) = \sum_{j=0}^{\infty} \tilde{c}_j \tilde{\phi}_j(x), \quad (51)$$

where  $x = u/u_0$  and

$$\tilde{\phi}_j(x) = \frac{x^j}{\pi^{3/4}} e^{-x^2/2}, \quad (52)$$

so that  $\tilde{c}_j = \delta_{j0}$  for  $\omega \rightarrow \infty$ . For values of  $\omega$  other than those at which analytic solutions exist, we truncate the series in Eq. (51) at large but finite  $N$ , and find the lowest-energy level by diagonalizing the Hamiltonian within the truncated basis set. The overlap matrix elements are

$$S_{ij} = 4\pi \int_0^{\infty} \tilde{\phi}_i(x) \tilde{\phi}_j(x) x^2 dx = f(i+j+2), \quad (53)$$

where  $f(k) = \Gamma[(k+1)/2]/\Gamma(\frac{3}{2})$ , and  $\Gamma$  is the Gamma function, while the  $u$ -component Hamiltonian matrix elements are

$$H_{ij} = \frac{f(i+j)}{u_0^2} \left( ij + \frac{3}{2}(i+j+1) \right) + \frac{f(i+j+1)}{u_0}. \quad (54)$$

This procedure is numerically unstable, in that a small denominator occurs in the generalized eigenvalue solution. However, using 32-digit accuracy, we find that inversion works reliably for  $N \leq 26$ . We find that  $N=26$  allows us to solve the problem for all frequencies down to about  $10^{-4}$ . We find that the virial relation for the Hooke's atom,

$$2T = 2V_{\text{ext}} - V_{ee}, \quad (55)$$

is satisfied more and more accurately as  $N$  is increased, being good to about 30 digits when  $N=26$ . We also find that, for

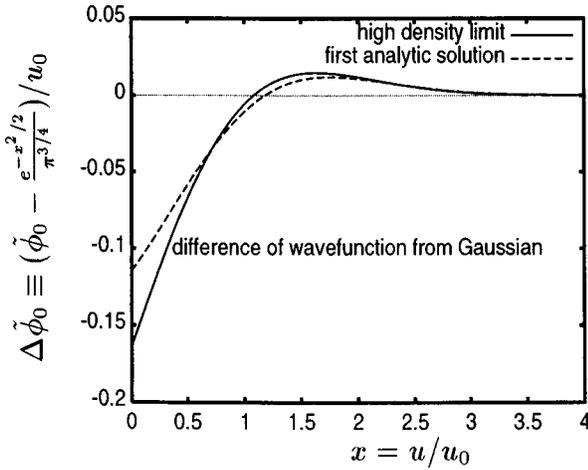


FIG. 1. The difference between a dimensionless wave function and a simple Gaussian for  $\omega \rightarrow \infty$  and for  $\omega = \frac{1}{2}$ .

large  $\omega$ , the energy converges rapidly with  $N$ , but the much tougher test, satisfaction of the electron–electron cusp condition, ( $c_1/c_0 = \frac{1}{2}$ ), requires large  $N$ . For example, for  $\omega = 3200$  and  $N = 26$ , this condition is only satisfied to the first 11 digits.

We use this numerical solution to explore the high-density (noninteracting) limit. As  $\omega \rightarrow \infty$ ,  $\Phi(u)$  tends to a simple Gaussian. The approach to the noninteracting limit is then characterized by the difference of the wave function from this Gaussian as  $u \rightarrow 0$ :

$$\Delta\tilde{\phi}(u_0;x) = \frac{1}{u_0} [\tilde{\phi}(u_0;x) - \tilde{\phi}(0;x)]. \quad (56)$$

The function  $\Delta\tilde{\phi}(u_0 \rightarrow 0;x)$  is plotted in Fig. 1, and is clearly finite and well behaved. We also plot  $\Delta\tilde{\phi}(u_0 = 2;x)$ . We see that the first analytic solution is close to the high-density limit. For the correlation energy, we find the expansion about  $u_0 = 0$  to be

$$E_c \approx -0.0497 + 0.0062u_0 + O(u_0^2). \quad (57)$$

The exact value at  $u_0 = 2$  is  $-0.0385$  a.u.<sup>31</sup> In the high-density limit,  $T_c \rightarrow -E_c$ , and we find

$$E_c + T_c \approx -0.007u_0 + 0.0013u_0^2. \quad (58)$$

The exact value at  $u_0 = 2$  is  $-0.0093$  a.u.<sup>31</sup> In Fig. 2, we plot the correlation potential in this limit. Note that the virial of the correlation potential is

$$E_c + T_c = - \int [n(\mathbf{r})\mathbf{r} \cdot \nabla v_c([n];\mathbf{r})] d\mathbf{r}, \quad (59)$$

which therefore vanishes for  $v_c^{(2)}([n];\mathbf{r})$ . The integral involving the correlation potential is found to be

$$\int v_c([n];\mathbf{r})n(\mathbf{r})d\mathbf{r} \approx -0.0712 + 0.0105u_0 + O(u_0^2). \quad (60)$$

The exact value at  $u_0 = 2$  is  $-0.0536$  a.u. Several of these results were later confirmed by Huang and Umrigar.<sup>32</sup> For all these energies, the high-density expansion, extrapolated to realistic densities ( $u_0 = 2$ ), yields an excellent estimate (to

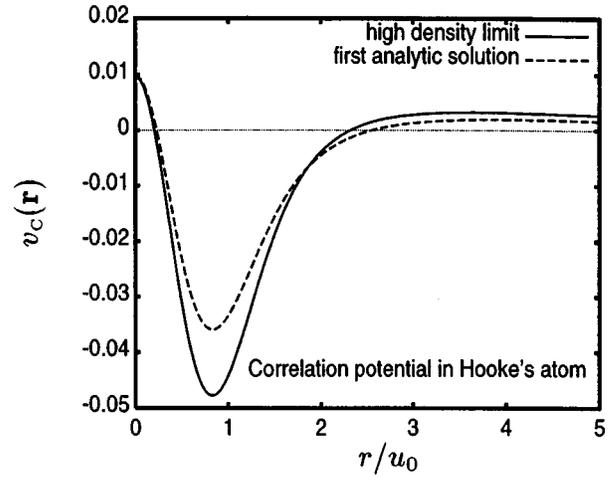


FIG. 2. The correlation potential for Hooke's atom for  $\omega \rightarrow \infty (v_c^{(2)})$  and for  $\omega = \frac{1}{2}$ .

within 10%) of the exact values, thereby demonstrating the usefulness of studying these limits. By making use of Eqs. (57) and (60), we obtain an excellent agreement for the difference  $2E_c^{(2)}[n] - \int v_c^{(2)}([n];\mathbf{r})n(\mathbf{r})d\mathbf{r}$ , with the exact value in Eq. (44).

Last but not least, in Table II, we compare the exact values for  $E_c^{(2)}[n]$  and  $\int v_c^{(2)}([n];\mathbf{r})n(\mathbf{r})d\mathbf{r}$  against the respective values obtained from three different approximations to  $E_c[n]$ , respectively, to  $E_c^{(2)}[n]$ , the one by Lee, Yang, and Parr (LYP),<sup>33</sup> the one by Wilson and Levy (WL),<sup>34</sup> and the recently derived GGA by Perdew, Burke, and Ernzerhof (PBE).<sup>35</sup> In Table II, the density depends on the strength of the harmonic oscillator  $a$ , but  $E_c^{(2)}[n]$  and  $\int v_c^{(2)}([n];\mathbf{r})n(\mathbf{r})d\mathbf{r}$  are independent of  $a$ .

## CONCLUDING REMARKS

Formula (34) is the first known expression for the correlation potential in the high-density limit. As a consequence of this pointwise identity for  $v_c^{(2)}([n];\mathbf{r})$ , we have shown that the closed-form expression, Eq. (37), is valid for *any* two-electron density. Our general approach of taking a functional derivative of the energy functional given by perturbation theory can be extended to more than two electrons. For more than two electrons, taking the functional derivative with respect to each occupied orbital rather than to the whole density, leads to an orbital-dependent correlation potential.

TABLE II. A comparison of the exact values for  $E_c^{(2)}[n]$  and  $\int v_c^{(2)}([n];\mathbf{r})n(\mathbf{r})d\mathbf{r}$  for density  $n(\mathbf{r}) = 2(2a/\pi)^{3/2}e^{-2ar^2}$ , with those obtained from different approximations.

	$E_c^{(2)}[n]$	$\int v_c^{(2)}([n];\mathbf{r})n(\mathbf{r})d\mathbf{r}$
Exact value	-0.0497	-0.0712
$E_c^{\text{LYP}}[n]$	-0.0355	-0.1023
$E_c^{\text{WL}}[n]$	-0.0782	-0.1061
$E_c^{\text{PBE}}[n]$	-0.0813	-0.1096

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