Submitted to Phys. Rev. A.

Local correlation energies of two-electron atoms and model systems

Chien-Jung Huang

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853

C. J. Umrigar

Cornell Theory Center and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853

We present nearly-local definitions of the correlation energy density, and its potential and kinetic components, and evaluate them for several two-electron systems. This information should provide valuable guidance in constructing better correlation functionals than those in common use. In addition, we demonstrate that the quantum chemistry and the density functional definitions of the correlation energy rapidly approach one anther with increasing atomic number.

I. INTRODUCTION

The total energy of an N-electron system in an external potential, $v_{\rm ext}$, is

$$\begin{aligned} E = &-\frac{1}{2}\int d^{3N}\mathbf{r}\ \Psi^*(\mathbf{r}_1,...,\mathbf{r}_N)\ \sum_{i=1}^{N}\nabla_i^2\,\Psi(\mathbf{r}_1,...,\mathbf{r}_N) \\ &+\int d^{3N}\mathbf{r}\ \Psi^*(\mathbf{r}_1,...,\mathbf{r}_N)\sum_{i=1}^{N} v_{\rm ext}(\mathbf{r}_i)\Psi(\mathbf{r}_1,...,\mathbf{r}_N) \\ &+\int d^{3N}\mathbf{r}\ \Psi^*(\mathbf{r}_1,...,\mathbf{r}_N)\sum_{i<j}\frac{1}{r_{ij}}\Psi(\mathbf{r}_1,...,\mathbf{r}_N) \\ \equiv\, & T + E_{\rm en} + E_{\rm ee}, \end{aligned} \tag{1}$$

where $\Psi(\mathbf{r}_1,...,\mathbf{r}_N)$ is the many-body wave function, T is the kinetic energy, $E_{\rm en}$ is the potential energy of the electrons interacting with the external (usually nuclear) potential and $E_{\rm ee}$ is the electron-electron potential energy. Here, and throughout the paper, we use Hartree atomic units ($\hbar = e = m = 1$). On the other hand, in Kohn-Sham density functional theory (DFT) [1,2], the ground state energy of an interacting system of electrons in an external potential is written as a functional of the ground state electronic density [1]:

$$\begin{aligned} E = &-\frac{1}{2}\sum_i\int d\mathbf{r}\ \psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r}) + v_{\rm ext}(\mathbf{r})\rho(\mathbf{r}) \\ &+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\ \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\rm xc}[\rho] \\ \equiv\, & T_s + E_{\rm en} + E_{\rm H} + E_{\rm xc}. \end{aligned} \tag{2}$$

Here $\psi_i(\mathbf{r})$ is Kohn-Sham orbital i, $\rho(\mathbf{r})$ is the electronic density, T_s is the kinetic energy of a system of non-interacting electrons that has the same density as the interacting system of interest, $E_{\rm en}$ is the potential energy of the electrons interacting with the external potential, and $E_{\rm H}$ is the classical Hartree approximation to the potential energy of the electrons interacting with each other. Note that although T_s is expressed in terms of the orbitals $\psi_i(\mathbf{r})$, it can be viewed as a functional of the density since the orbitals are themselves functionals of the density. The exchange-correlation energy $E_{\rm xc}$ is by definition the part of the total energy not contained in the first three terms.

Various approximate expressions for $E_{\rm xc}$ have been employed in the literature. The exchange-correlation energy $E_{\rm xc}$ is the sum of the exchange energy $E_{\rm x}$ and the correlation energy $E_{\rm c}$. The exact $E_{\rm x}$ is defined in terms of the single-particle orbitals

$$E_{\rm x}\left[\rho\right] = -\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\delta_{m_{s_i},m_{s_j}}\int\!\!\int \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}', \tag{3}$$

where the δ-function is over the spin quantum numbers of the i-th and j-th spin-orbitals. Hence, although in most density functional calculations both exchange and correlation energies are approximated, it is in fact necessary to approximate only the correlation energy $E_{\rm c}$, which, usually, is just a small fraction of $E_{\rm xc}$. From Eqs. 1 and 2, we obtain

$$E_{\rm c} = V_{\rm c} + T_{\rm c}, \tag{4}$$

where

$$V_{\rm c} = E_{\rm ee} - E_{\rm H} - E_{\rm x} \quad \text{and} \quad T_{\rm c} = T - T_s. \tag{5}$$

$E_{\rm c}$ contains a negative contribution coming from the fact that the interaction energy of the electrons is smaller than that given by $E_{\rm H}+E_{\rm x}$ and a smaller positive contribution from the difference of the true many-body kinetic energy T and the single-particle kinetic energy T_s.

Usually local or semi-local approximations are made for $E_{\rm c}$:

$$E_{\rm c}\left[\rho\right] = \int e_{\rm c}\,\mathrm{d}\mathbf{r} = \int \rho(\mathbf{r})\,\epsilon_{\rm c}\,\mathrm{d}\mathbf{r}, \tag{6}$$

where $e_{\rm c}$ is the correlation energy density and $\epsilon_{\rm c}$ is the local correlation energy per electron. In the local density approximation (LDA), $e_{\rm c}$ is a function of the local density at $\mathbf{r}$, $e_{\rm c} = e_{\rm c}(\rho(\mathbf{r}))$, while in the generalized gradient approximations (GGAs) it depends also on the $\nabla\rho(\mathbf{r})$ and possibly also on higher derivatives of $\rho(\mathbf{r})$, $e_{\rm c} = e_{\rm c}\left(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), ...\right)$.

In order to invent better approximate functionals, it is useful to know what the true $e_{\rm c}$ is. It is apparent that there is not a unique definition of $e_{\rm c}$ since we are always free to add any function that integrates to zero. However, since the approximate functionals are written as integrals of functions that depend on the local density and its derivatives, it is reasonable to seek a definition that is as nearly local as possible. In this spirit, a natural definition for the exchange energy density, which is consistent with the expression for $E_{\rm x}$ in Eq. 3, is

$$e_{\rm x}(\mathbf{r}) = -\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\delta_{m_{s_i},m_{s_j}}\,\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\int \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}'. \tag{7}$$

This definition results in a local exchange energy per electron, $\epsilon_{\rm x} = e_x/\rho$, that at large distances goes as $-1/2r$ [3], a fact that was used by Becke in constructing his successful exchange GGA [4].

In order to provide guidance for the construction of better approximate correlation functionals, we present a natural and nearly local definition of the correlation energy density for all systems and evaluate it for several two-electron systems. To do this, we write each of the energies in Eqs. 5 as a 3-d integral over an integrand which we define to be the corresponding energy density.

$$\begin{aligned} T &= -\frac{1}{2}\int d^{3N}\mathbf{r}\;\Psi^*(\mathbf{r}_1,...,\mathbf{r}_N)\;\sum_{i=1}^{N}\nabla_i^2\,\Psi(\mathbf{r}_1,...,\mathbf{r}_N) \\ &= \int d^3\mathbf{r}_1\;\left(-\frac{N}{2}\right)\int d^3\mathbf{r}_2...d^3\mathbf{r}_N\;\Psi^*(\mathbf{r}_1,...,\mathbf{r}_N)\;\nabla_1^2\Psi(\mathbf{r}_1,...,\mathbf{r}_N) \\ &\equiv \int d^3\mathbf{r}_1\;\;t(\mathbf{r_1}) \equiv \int d^3\mathbf{r}_1\;\;\rho(\mathbf{r_1})\tau(\mathbf{r_1}) \end{aligned} \tag{8}$$

$$
\begin{aligned}
E_{\rm ee} &= \int d^{3N}\mathbf{r}\ \Psi^*(\mathbf{r}_1,...,\mathbf{r}_N) \sum_{i<j}^{N} \frac{1}{r_{ij}} \Psi(\mathbf{r}_1,...,\mathbf{r}_N) \\
&= \int d^3\mathbf{r}_1\ \frac{N}{2} \int d^3\mathbf{r}_2...d^3\mathbf{r}_N\ \Psi^*(\mathbf{r}_1,...,\mathbf{r}_N) \sum_{i=2}^{N} \frac{1}{r_{1i}} \Psi(\mathbf{r}_1,...,\mathbf{r}_N) \\
&\equiv \int d^3\mathbf{r}_1\ e_{\rm ee}(\mathbf{r_1}) \equiv \int d^3\mathbf{r}_1\ \rho(\mathbf{r_1})\,\epsilon_{\rm ee}(\mathbf{r_1}) \qquad (9)
\end{aligned}
$$

$$
T_s = \int d^3\mathbf{r}_1\ \left(-\frac{1}{2}\right) \sum_{i=1}^{N} \psi_i^*(\mathbf{r_1})\ \nabla_1^2\, \psi_i(\mathbf{r_1}) \equiv \int d^3\mathbf{r}_1\ t_s(\mathbf{r_1}) \equiv \int d^3\mathbf{r}_1\ \rho(\mathbf{r_1})\tau_s(\mathbf{r_1}) \qquad (10)
$$

$$
\begin{aligned}
E_{\rm H} &= \int d^3\mathbf{r}_1\ \frac{1}{2} \int d^3\mathbf{r_2}\ \rho(\mathbf{r}_1)\frac{1}{r_{12}}\rho(\mathbf{r_2}) \\
&= \frac{1}{2} \int d^3\mathbf{r}_1\ \rho(\mathbf{r}_1) v_{\rm H}(\mathbf{r_1}) \equiv \int d^3\mathbf{r}_1\ e_{\rm H}(\mathbf{r_1}) \equiv \int d^3\mathbf{r}_1\ \rho(\mathbf{r_1})\,\epsilon_{\rm H}(\mathbf{r_1}) \qquad (11)
\end{aligned}
$$

$$
\begin{aligned}
E_{\rm x} &= \int d^3\mathbf{r}_1\ \left(-\frac{1}{2}\right) \sum_{i=1}^{N}\sum_{j=1}^{N} \delta_{m_{s_i},m_{s_j}} \psi_i^*(\mathbf{r_1})\psi_j(\mathbf{r_1}) \int d^3\mathbf{r_2} \frac{\psi_j^*(\mathbf{r_2})\psi_i(\mathbf{r_2})}{|\mathbf{r_1}-\mathbf{r_2}|} \\
&\equiv \int d^3\mathbf{r}_1\ e_{\rm x}(\mathbf{r_1}) \equiv \int d^3\mathbf{r}_1\ \rho(\mathbf{r_1})\,\epsilon_{\rm x}(\mathbf{r_1}) \qquad (12)
\end{aligned}
$$

$$
E_{\rm c} = \int d^3\mathbf{r}_1\ e_{\rm c}(\mathbf{r_1}) \equiv \int d^3\mathbf{r}_1\ \rho(\mathbf{r_1})\,\epsilon_{\rm c}(\mathbf{r_1}) \qquad (13)
$$

Then $e_{\rm c}$ and $\epsilon_{\rm c}$ can be evaluated as,

$$
e_{\rm c} = v_{\rm c} + t_{\rm c}, \qquad \epsilon_{\rm c} = \nu_{\rm c} + \tau_{\rm c}, \qquad (14)
$$

where

$$
\begin{aligned}
v_{\rm c} &= e_{\rm ee} - e_{\rm H} - e_{\rm x}. \quad & \nu_{\rm c} &= \epsilon_{\rm ee} - \epsilon_{\rm H} - \epsilon_{\rm x}, \\
t_{\rm c} &= t - t_s, & \tau_{\rm c} &= \tau - \tau_s.
\end{aligned}
$$

We have consistently used capital Roman characters for energies, small Roman characters for energy densities and Greek characters for the local energies per electron. Note that $V_{\rm c}$ or $v_{\rm c}$ should not be confused with the correlation potential, which is the functional derivative of $E_{\rm c}$ with respect to ρ.

We now discuss another interesting, but not very useful, definition of the correlation energy density. Instead of Eqs. 8 and 9 another possible choice for t and $e_{\rm ee}$ is

$$
T = \int d^3\mathbf{r}_1\ \left(-\frac{1}{2}\right) \int d^3\mathbf{r}_2...d^3\mathbf{r}_N\ \Psi^*(\mathbf{r}_1,...,\mathbf{r}_N) \sum_{i=1}^{N} \nabla_i^2\, \Psi(\mathbf{r}_1,...,\mathbf{r}_N) \equiv \int d^3\mathbf{r}_1\ t(\mathbf{r_1}) \qquad (15)
$$

$$
E_{\rm ee} = \int d^3\mathbf{r}_1\ \int d^3\mathbf{r}_2...d^3\mathbf{r}_N\ \Psi^*(\mathbf{r}_1,...,\mathbf{r}_N) \sum_{i<j}^{N} \frac{1}{r_{ij}} \Psi(\mathbf{r}_1,...,\mathbf{r}_N) \equiv \int d^3\mathbf{r}_1\ e_{\rm ee}(\mathbf{r_1}), \qquad (16)
$$

which has the intersting feature that it yields a constant local energy per electron, $\epsilon = E/N$, over all space. This follows from

$$
\begin{aligned}
E &= \int d^{3N}\mathbf{r}\ |\Psi(\mathbf{r}_1,...,\mathbf{r}_N)|^2\ \frac{\mathcal{H}\Psi(\mathbf{r}_1,...,\mathbf{r}_N)}{\Psi(\mathbf{r}_1,...,\mathbf{r}_N)} \\
&= \int d^3\mathbf{r}_1\ \int d^3\mathbf{r}_2...d^3\mathbf{r}_N\ |\Psi(\mathbf{r}_1,...,\mathbf{r}_N)|^2\ \frac{\mathcal{H}\Psi(\mathbf{r}_1,...,\mathbf{r}_N)}{\Psi(\mathbf{r}_1,...,\mathbf{r}_N)} \\
&= \int d^3\mathbf{r}_1\ \rho(\mathbf{r}_1)\ \frac{E}{N} \equiv \int d^3\mathbf{r}_1\ \rho(\mathbf{r_1})\epsilon(\mathbf{r_1}) \qquad (17)
\end{aligned}
$$

$$
(18)
$$

This has the advantage that one could test approximate correlation energy functionals by checking to see if they yield a constant local total energy per electron ϵ. However, note that $t(\mathbf{r_1})$ in Eq. 15, assigns to the position of the first electron contributions from the Laplacian acting not only on the first electron but also on all the other electrons. Similarly, $e_{\rm ee}(\mathbf{r_1})$ contains contributions from all pairs of electrons. Hence, in contrast to our earlier definitions, the definitions in Eqs. 15 and 16 have the disadvantage that t and $e_{\rm ee}$ are very non-local, and so any approximate correlation energy functional, that mimics this definition of $e_{\rm c}$, would also have to be very non-local. Hence, this is not a suitable definition of the correlation energy density for our purpose.

In Eqs. 8 and 10 we have written the kinetic energy in terms of the Laplacian. Of course one could instead write the kinetic energy in terms of the square of the gradient. It is interesting to note that the kinetic contribution to the correlation energy density, $t_{\rm c}$, does not depend on which expression is used provided that it is used consistently for both the many-particle kinetic energy and for the single-particle Kohn-Sham kinetic energy, as was pointed out to us by Robert van Leeuwen. This follows simply from equating the many-particle and the Kohn-Sham expressions for the single-particle density and taking the Laplacian.

II. TWO-ELECTRON SYSTEMS

We have studied the two-electron helium iso-electronic series and a model system (referred to in the literature as harmonium or Hooke's law atom) in which the nuclear $-Z/r$ potential is replaced by an harmonic potential $(\omega r)^2/2$. This model was first introduced by Kestner and Sinanoğlu [5] and has since then been studied by various authors [6–10].

In order to calculate accurate density functional quantities for these systems it is necessary to have accurate wave functions. For the ions we use exceedingly accurate 477-term wave functions of the form used by Freund, Huxtable and Morgan [11]. For harmonium, Kestner and Sinanoğlu [5] wrote down a series solution, with a 3-term recursion, which is rapidly convergent at small interparticle distances and slowly convergent at large interparticle distances. They also give an asymptotic series that is accurate at large interparticle distances. Kais [8] showed that the former series terminates for a particular value of the spring constant, $\omega^2 = 1/4$, thereby obtaining an exact closed-form wave function. Taut [9] showed that it is possible to find such wave functions for an infinite discrete set of spring constants, the largest of which is $\omega^2 = 1/4$. To obtain solutions for arbitrary ω, we employ the two series solutions of [5], using 300 terms in the convergent series. The relative normalization constant of the two series is obtained by matching them in the overlap region where they are both accurate. The number of terms kept in the asymptotic series is such that the last term is the smallest in magnitude term at the matching radius. For special values of ω both series reduce to the exact solutions of Taut.

III. RESULTS

A. Energies

In Tables I and II we give the total energy and its components for ions and harmonium respectively. Some of these data have been presented earlier [10,12]. Of particular interest are the correlation energies $E_{\rm c}$ and their potential and kinetic components, $V_{\rm c}, T_{\rm c}$. Each of these quantities tends to a constant in the high-density (large Z, ω) limit. Interestingly, the limiting values for the ions and harmonium differ by only 6%. From Figs. 1 and 2 we observe that, at small $1/Z$, $E_{\rm c}, V_{\rm c}$ and $T_{\rm c}$ are very nearly linear and the same is true at small $1/\sqrt{\omega}$ but to a lesser degree. The behavior is monotonic. In earlier work by other authors [7] it was found that $E_{\rm c}$ has a minimum at a finite ω but we attribute this to a lack of accuracy in their calculations at large ω.

In Tables I and II, we also show the quantum chemistry definition of the correlation energy $E_{\rm c}^{\rm QC}$ which is defined to be

$$E_{\rm c}^{\rm QC} = \langle \Psi | \mathcal{H} | \Psi \rangle - \langle \Psi^{\rm HF} | \mathcal{H} | \Psi^{\rm HF} \rangle, \tag{19}$$

where Ψ is the true many-body wave function, $\Psi^{\rm HF}$ is the Hartree-Fock wave function and $\mathcal{H}$ is the Hamiltonian.

According to Levy's constrained-search formulation of density functional theory [13], the density functional definition of the correlation energy is

$$E_{\rm c} = \langle \Psi | \mathcal{H} | \Psi \rangle - \langle \Phi | \mathcal{H} | \Phi \rangle , \tag{20}$$

where Φ is the Kohn-Sham wave function, i.e. the wave function that yields the same density as the true wave function and minimizes the expectation value of the kinetic energy operator. Hence, as first pointed out by Sahni and Levy [14], it follows from the variational principle that $E_{\rm c} \lesssim E_{\rm c}^{\rm QC}$. We observe from Table I that this is in fact the case and, further, that the two definitions rapidly approach each other, the leading term in the difference going as $1/Z^3$. This convergence of $E_{\rm c}$ and $E_{\rm c}^{\rm QC}$, at large Z, has strong implications for the terms in the $1/Z$ perturbation expansion discussed later. The $Z = \infty$ value of $E_{\rm c}$ and $E_{\rm c}^{\rm QC}$ agrees to all digits with that in Ref. [15] for $E_{\rm c}^{\rm QC}$.

It is known [16] that the quantum chemistry definition of the correlation energy $E_{\rm c}^{\rm QC}$ of two-electron ions in their ^1S ground states goes to a constant with increasing Z. The proof is based on perturbation theory. Similarly, the linearly convergent behavior of $E_{\rm c}, V_{\rm c}$ and $T_{\rm c}$ can be explained as follows. As observed by Hylleraas [17], the scaling transformation $\mathbf{r} \to \mathbf{r}/Z$ applied to the Schrödinger equation

$$\left(-\frac{1}{2} \left(\nabla_1^2 + \nabla_2^2 \right) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Psi(\mathbf{r_1}, \mathbf{r_2}) = E \Psi(\mathbf{r_1}, \mathbf{r_2}) \tag{21}$$

yields the scaled Schrödinger equation

$$\left(\tilde{\mathcal{H}}_0 + \tilde{\mathcal{H}}_1 \right) \tilde{\Psi}(\mathbf{r_1}, \mathbf{r_2}) = \tilde{E} \tilde{\Psi}(\mathbf{r_1}, \mathbf{r_2}) \tag{22}$$

where

$$\begin{aligned} \tilde{\mathcal{H}}_0 &= -\frac{1}{2} \left(\nabla_1^2 + \nabla_2^2 \right) - \frac{1}{r_1} - \frac{1}{r_2} \\ \tilde{\mathcal{H}}_1 &= \frac{1}{Z r_{12}} \\ \tilde{\Psi}(\mathbf{r_1}, \mathbf{r_2}) &= \Psi(\frac{\mathbf{r_1}}{Z}, \frac{\mathbf{r_2}}{Z}) \\ \tilde{E} &= \frac{E}{Z^2}. \end{aligned} \tag{23}$$

The eigenvector $\tilde{\Psi}$ and eigenvalue $\tilde{E}$ of the scaled Hamiltonian can be expressed as a power series in the perturbation parameter $1/Z$:

$$\begin{aligned} \tilde{\Psi} &= \Psi_0 + \Psi_1/Z + O(Z^{-2}) \\ \tilde{E} &= E_0 + E_1/Z + E_2/Z^2 + E_3/Z^3 + O(Z^{-4}). \end{aligned} \tag{24}$$

Similarly a $1/Z$ expansion can also be performed for the Hartree-Fock and Kohn-Sham wave functions and energies:

$$\begin{aligned} \tilde{\Psi}^{\rm HF} &= \Psi_0^{\rm HF} + \Psi_1^{\rm HF}/Z + O(Z^{-2}) \\ \tilde{E}^{\rm HF} &= E_0^{\rm HF} + E_1^{\rm HF}/Z + E_2^{\rm HF}/Z^2 + E_3^{\rm HF}/Z^3 + O(Z^{-4}) \\ \tilde{\Phi} &= \Phi_0 + \Phi_1/Z + O(Z^{-2}) \\ \tilde{E}^{\rm KS} &= E_0^{\rm KS} + E_1^{\rm KS}/Z + E_2^{\rm KS}/Z^2 + E_3^{\rm KS}/Z^3 + O(Z^{-4}) \end{aligned} \tag{25}$$

For the ground states of two-electron ions, the unperturbed ground state is non-degenerate, so $\Psi_0 = \Psi_0^{\rm HF} = \Phi_0$. As a consequence, from perturbation theory, we have

$$\begin{aligned} E_0 &= Z^2 < \Psi_0 | \tilde{\mathcal{H}}_0 | \Psi_0 > = E_0^{\rm HF} = E_0^{\rm KS} \\ E_1 &= Z < \Psi_0 | r_{12}^{-1} | \Psi_0 > = E_1^{\rm HF} = E_1^{\rm KS} \end{aligned} \tag{26}$$

and it follows from Eqs. 19, 20, 25, 26, and 23 that

$$\begin{aligned} E_c^{\rm QC} &= (E_2 - E_2^{\rm HF}) + 1/Z(E_3 - E_3^{\rm HF}) + O(Z^{-2}) \\ E_{\rm c} &= (E_2 - E_2^{\rm KS}) + 1/Z(E_3 - E_3^{\rm KS}) + O(Z^{-2}). \end{aligned} \tag{27}$$

Therefore, at large Z, both $E_c^{\rm QC}$ and $E_{\rm c}$ go to a constant, linearly in $1/Z$, as shown in Fig 1. If the non-interacting ground state is degenerate, E_1 differs from $E_1^{\rm HF}$ and $E_1^{\rm KS}$, and $E_{\rm c} \sim Z$ as $Z \to \infty$ [16]. As observed by Perdew, McMullen and Zunger [18], it is a difficult challenge to find an a priori, universal density functional approximation that correctly describes both of the $Z \to \infty$ limiting behaviors.

The observed behavior $E_{\rm c} - E_c^{\rm QC} \sim 1/Z^3$ in Table I implies that $E_2^{\rm HF} = E_2^{\rm KS}$, $E_3^{\rm HF} = E_3^{\rm KS}$ and $E_4^{\rm HF} = E_4^{\rm KS}$, though of course it is impossible to tell from the numerical data if these equalities hold strictly or only approximately.

The argument given above that $E_{\rm c}$ is finite in the $Z \to \infty$ limit applies to any system for which the non-interacting ground state is non-degenerate. In particular, it applies to harmonium with the expansion parameter $1/Z$ replaced by $1/\sqrt{\omega}$. In the remainder of this paper, we use an expansion parameter $\alpha = 1/Z$ for ions and $\alpha = 1/\sqrt{\omega}$ for harmonium. The argument that the correlation energy $E_{\rm c}$ converges to a constant in the $Z, \sqrt{\omega} \to \infty$ limit can be easily extended to its potential and kinetic components $T_{\rm c}, V_{\rm c}$ but we have not shown that $E_{\rm c} = -T_{\rm c} = V_{\rm c}/2$ in this limit. However, Levy and Perdew [19] have shown that

$$E_{\rm c}[\rho_\lambda]{+}T_{\rm c}[\rho_\lambda] = \lambda \frac{\partial E_{\rm c}[\rho_\lambda]}{\partial \lambda}. \tag{28}$$

where $\rho_\lambda(\mathbf{r})$ is a uniformly scaled density that integrates to the same number of electrons as $\rho(\mathbf{r})$, *i.e.* $\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r})$. Combining this with the fact, shown by Levy [20], that $E_{\rm c}[\rho_\lambda]$ goes to a constant linearly in λ^{-1} at large λ, we have $\lambda \frac{\partial E_{\rm c}[\rho_\lambda]}{\partial \lambda} \to 0$ as $\lambda \to \infty$. It follows that $E_{\rm c} = -T_{\rm c} = V_{\rm c}/2$ in that limit. Although they do not provide a rigorous proof, Levy and Perdew [19] argue that $E_{\rm c} = -T_{\rm c} = V_{\rm c}/2$ in the $Z \to \infty$ limit. We note in passing that the difference between the $\lambda \to \infty$ and the $Z \to \infty$ limits can be important, *e.g.* the correlation energy of a uniformly-scaled Be atom, in its ground state, tends to a constant in the $\lambda \to \infty$ limit but the correlation energy of 4-electron ions tends to negative infinity in the $Z \to \infty$ limit because in the latter case the 2s and 2p orbital energies are degenerate whereas in the former case they are not.

TABLE I. Energies of two-electron ions in Hartree atomic units.

Z	E	$T_{\rm s}$	$E_{\rm en}$	$E_{\rm H}$	$E_{\rm x}$	$E_{\rm c}$	$V_{\rm c}$	$T_{\rm c}$	$E_c^{\rm QC}$	$E_c^{\rm LDA}$
1	-0.527751	0.499869	-1.366524	0.761796	-0.380898	-0.041994	-0.069876	0.027882		-0.071816
2	-2.903724	2.867082	-6.753267	2.049137	-1.024568	-0.042107	-0.078750	0.036643	-0.042044	-0.112372
3	-7.279913	7.240085	-16.127546	3.302126	-1.651063	-0.043515	-0.083343	0.039828	-0.043498	-0.134582
4	-13.655566	13.614084	-29.502003	4.553255	-2.276628	-0.044274	-0.085757	0.041483	-0.044267	-0.150419
6	-32.406247	32.363072	-68.251384	7.054244	-3.527122	-0.045056	-0.088231	0.043175	-0.045054	-0.173013
10	-93.906807	93.862252	-193.750849	12.054968	-6.027484	-0.045694	-0.090248	0.044555	-0.045693	-0.202032
20	-387.657234	387.611630	-787.500430	24.555485	-12.277743	-0.046177	-0.091780	0.045603	-0.046177	-0.242379
∞	$-\infty$	∞	$-\infty$	∞	$-\infty$	-0.046663	-0.093327	0.046663	-0.046663	$-\infty$

TABLE II. Energies of harmonium in Hartree atomic units.

ω	E	T_s	E_{en}	E_H	E_x	E_c	V_c	T_c	E_c^{LDA}
0.1	0.500000	0.109603	0.208676	0.421927	-0.210964	-0.029242	-0.045668	0.016426	-0.055025
1	3.730121	1.327580	1.697210	1.493431	-0.746716	-0.041385	-0.075315	0.033930	-0.101335
4	13.523219	5.628842	6.397678	3.083973	-1.541986	-0.045287	-0.086259	0.040972	-0.134190
10	32.448685	14.397196	15.629951	4.936774	-2.468387	-0.046848	-0.090819	0.043971	-0.157546
100	307.902068	148.033430	151.994436	15.845959	-7.922979	-0.048777	-0.096586	0.047809	-0.220763
400	1215.880360	596.038744	603.989284	31.803138	-15.901569	-0.049237	-0.097983	0.048746	-0.261076
1000	3025.153789	1493.720344	1506.307743	50.350219	-25.175110	-0.049407	-0.098503	0.049096	-0.288334
∞	∞	∞	∞	∞	$-\infty$	-0.049702	-0.099404	0.049702	$-\infty$

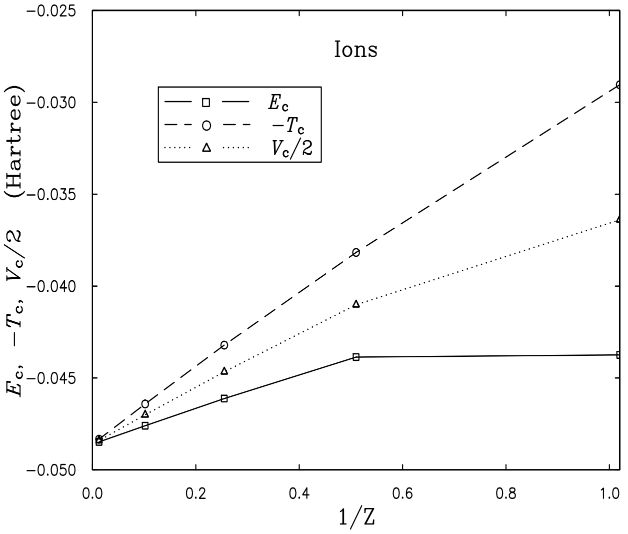

FIG. 1. $E_c, -T_c, V_c/2$ for 2-electron ions as a function of $1/Z$. The data points are for $Z = 1, 2, 4, 10, 80$.

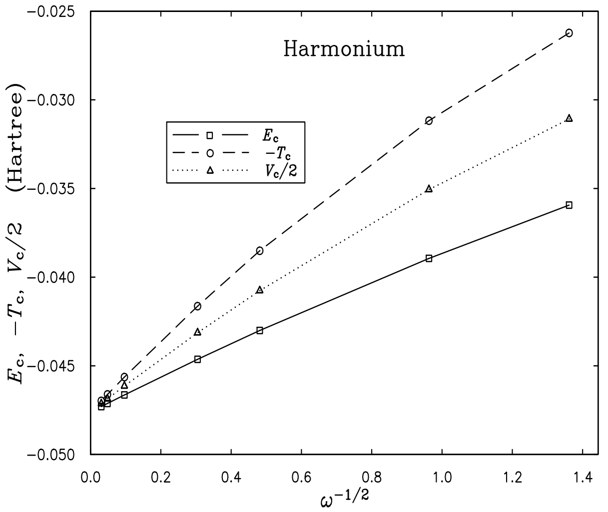

FIG. 2. $E_c, -T_c, V_c/2$ for harmonium as a function of $1/\sqrt{\omega}$. The data points are for $\omega = 1, 4, 10, 100, 400, 1000$.

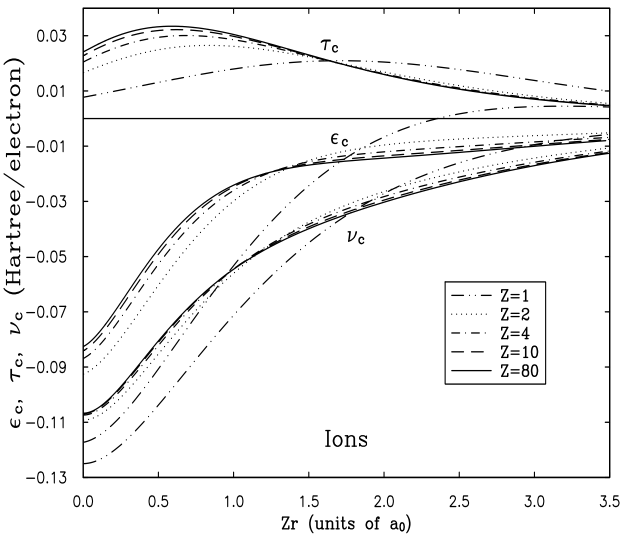

FIG. 3. Local correlation energy per electron ϵ_c and its potential and kinetic components ν_c, τ_c versus Zr for 2-electron ions. Each of these quantities is plotted for $Z = 1, 2, 4, 10, 80$. At $Zr \approx 1.6$ the top five curves are for τ_c, the middle five are for ϵ_c and the bottom five are for ν_c. The curves for each of the three quantities $\epsilon_c, \nu_c, \tau_c$ tend to a limiting curve in the high Z limit.

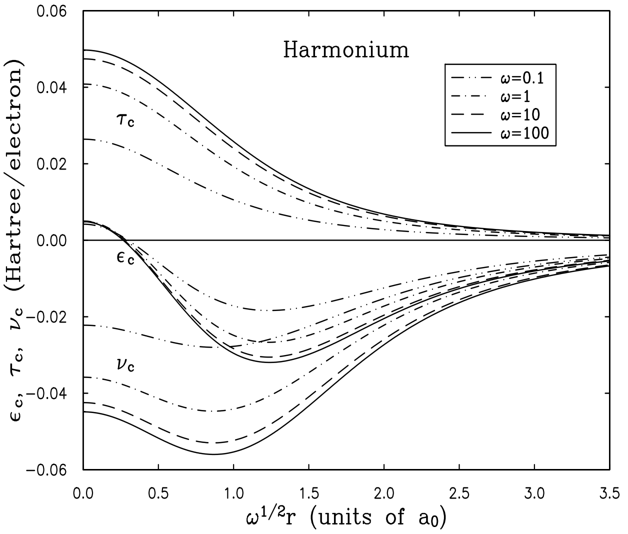

FIG. 4. Local correlation energy per electron ϵ_c and its potential and kinetic components ν_c, τ_c versus $\sqrt{\omega}r$ for harmonium. Each of these quantities is plotted for $\omega = 0.1, 1, 10, 100$. At $r = 0$ the top four curves are for τ_c, the middle four are for ϵ_c and the bottom four are for ν_c. The curves for each of the three quantities $\epsilon_c, \nu_c, \tau_c$ tend to a limiting curve in the high ω limit.

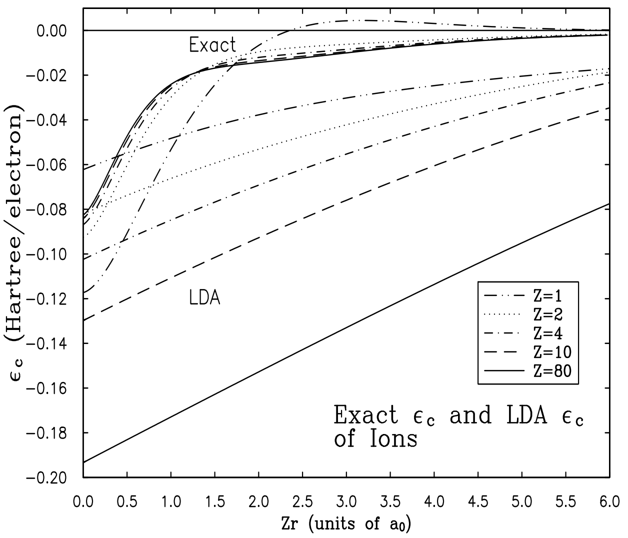

FIG. 5. Comparison of the true local correlation energy per electron ϵ_c and the LDA approximation to it $\epsilon_c^{\rm LDA}$ for 2-electron ions. Each of these quantities is plotted for $Z = 1, 2, 4, 10, 80$. The LDA curves have less structure than the true curves and become much too deep at large Z.

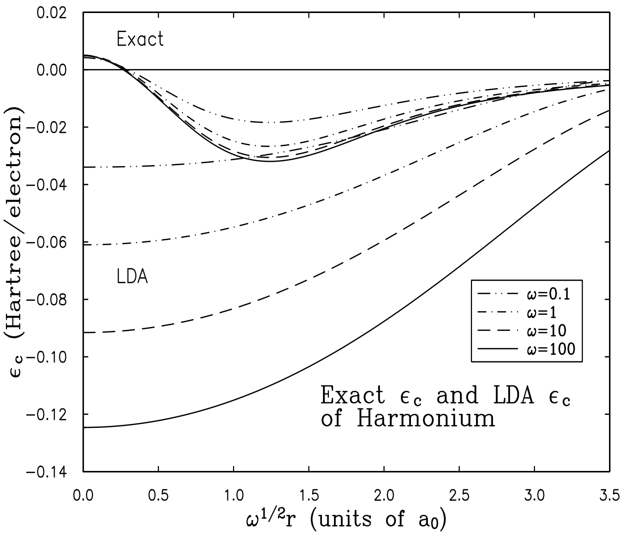

FIG. 6. Comparison of the true local correlation energy per electron ϵ_c and the LDA approximation to it $\epsilon_c^{\rm LDA}$ for harmonium. Each of these quantities is plotted for $\omega = 0.1, 1, 10, 100$. The LDA curves have less structure than the true curves and become much too deep at large ω.

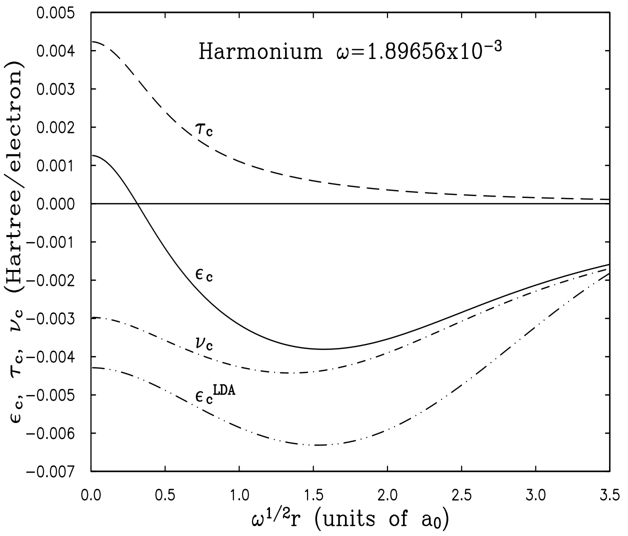

FIG. 7. Local correlation energy per electron ϵ_c and its potential and kinetic components ν_c, τ_c versus $\sqrt{\omega}r$ for the harmonium $n = 10$ (high-correlation, low spring-constant) state. The $\epsilon_c^{\mathrm{LDA}}$ curve is also shown for comparison.

B. Local Energies per Electron

In Figs. 3 and 4 we show the local correlation energy per electron ϵ_c and its kinetic and potential components, τ_c, ν_c. As the expansion parameter α ($1/Z$ for two-electron ion and $1/\sqrt{\omega}$ for harmonium) approaches zero, each of $\epsilon_c, \tau_c, \nu_c$ tends to a limiting curve. Since the integrated quantities E_c, V_c and T_c have α expansions, it is plausible that there are similar expansions for $\epsilon_c, \tau_c, \nu_c$. With a scaled variable $\mathbf{x} = \mathbf{r}/\alpha$, we have

$$\epsilon_c(\mathbf{x},\alpha) \approx \epsilon_c^*(\mathbf{x}) + \alpha\epsilon_c'(\mathbf{x}), \qquad \tau_c(\mathbf{x},\alpha) \approx \tau_c^*(\mathbf{x}) + \alpha\tau_c'(\mathbf{x}), \qquad \nu_c(\mathbf{x},\alpha) \approx \nu_c^*(\mathbf{x}) + \alpha\nu_c'(\mathbf{x}), \qquad \alpha \ll 1 \tag{29}$$

Namely, these curves converge linearly in α to the limiting curves ϵ_c^*,τ_c^*, and ν_c^*.

Except for small Z or ω, the three families of curves ϵ_c, τ_c, and ν_c are characterized by functions ϵ_c^*, τ_c^*, ν_c^*, ϵ_c', τ_c', and ν_c'. Despite the fact that the integrated E_c, T_c, V_c differ by only 6% in the high Z,ω limit, the limiting curves τ_c^*, ν_c^*, and ϵ_c^* for two-electron ions are quite different from those for harmonium. For harmonium both ν_c and τ_c are quadratic at $r = 0$ whereas for the ions ν_c is quadratic and τ_c is linear. Similarly it has been observed before [10,12,21] that the correlation potentials (*i.e.* the functional derivatives, $\frac{\delta E_c}{\delta\rho}$) for all the 2-electron ions are closely related and tend to a limiting curve and the same is true for the correlation potentials for harmonium, but the two sets of systems have qualitatively different potentials. In fact for the ions the correlation potential is negative at short and long distances, and positive at intermediate distances, while the opposite is true for harmonium.

In Figs. 5 and 6 we compare ϵ_c with the LDA approximation to it, $\epsilon_c^{\mathrm{LDA}}$. The LDA curves have less structure than the true curves and for increasing Z,ω rapidly become much too negative everywhere except in the far tails of the density. We have used the Perdew-Wang [22] parametrization of the LDA correlation energy since it is probably the most accurate one, but any of the other commonly used parametrizations would give very similar curves. The LDA curves do not tend to a limiting curve in the large Z,ω limits, reflecting the fact that E_c^{LDA} diverges to $-\infty$ as $Z,\omega \to \infty$. We have also compared ϵ_c to $\epsilon_c^{\mathrm{GGA}}$ for all the commonly used GGAs and in no case do we find a good agreement, despite the fact that the integrated energies E_c^{GGA} are in considerably better agreement with E_c than are LDA energies [12]. However, we wish to emphasize that the failure of the $\epsilon_c^{\mathrm{GGA}}$ to agree with ϵ_c does not necessarily imply a deficiency in the GGA functionals since, as mentioned before, ϵ_c is not uniquely defined. For this reason we do not present the GGA curves. On the other hand, the failure of the GGA correlation potentials to reproduce the true correlation potentials [10,12,21] does imply a deficiency in the GGAs.

For harmonium, at very small spring constants, the electron-electron repulsion dominates the interaction of the electrons with the external potential and the maximum of the charge density occurs not at the minimum of the external potential but at a finite distance from it [10,21]. As shown in Fig. 7, even in this extreme situation where we expect the linear scaling rule of Eq. 29 to break down, the curves for ϵ_c, ν_c and τ_c still have the same shape as for the other harmonium systems, although the magnitudes are quite different.

It is somewhat surprising that although the ions have a maximum in the charge density at the nucleus, τ_c does not have its maximum there. Also, for harmonium, the minimum of ν_c does not occur at $r = 0$ both for spring constants for which the density has a peak at the nucleus and those for which the density has a peak at $r > 0$. Yet another surprise is that, for ions, the range of values of ϵ_c and ν_c is smaller at high Z than at low Z. Again, the same behavior for the correlation potential has been observed earlier [12] and is equally surprising.

IV. DISCUSSION

Our purpose in defining and evaluating a correlation energy density and its potential energy and kinetic energy components, was to provide guidance for the construction of improved approximate correlation functionals. To this purpose, we are continuing this work by using quantum Monte Carlo methods to evaluate these quantities for atoms, ions and model systems with a larger number of electrons. The goal is to have a sufficient body of data to be able to identify correlations of $\epsilon_c^{\rm LDA} - \epsilon_c$ with $\nabla\rho$ and $\nabla^2\rho$. We have in fact observed that a strong correlation of this nature exists for the exchange energy density. However, in many respects correlation appears to be subtler than exchange and we suspect that it will be a good deal more difficult to make such a connection in the case of the correlation energy density.

ACKNOWLEDGMENTS

We thank John Morgan and Jonathan Baker for making available their program for calculating very accurate wave functions for the He iso-electronic series, and Mel Levy, Robert van Leeuwen and Claudia Filippi for useful discussions. The calculations were performed on the IBM SP2 computer at the Cornell Theory Center. This work is supported by the Office of Naval Research.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[3] N. H. March, Phys. Rev. A **36**, 5077 (1987).
[4] A. D. Becke, Phys. Rev. A **33**, 3098 (1988).
[5] N. R. Kestner and O. Sinanoglu, Phys. Rev. **128**, 2687 (1962)
[6] P. M. Laufer and J. B. Krieger, Phys. Rev. A **33**, 1480 (1986)
[7] S.K. Ghosh and A. Samantha, J. Chem. Phys. **94**, 517 (1991).
[8] S. Kais, D. R. Herschbach, N.C. Handy, C. W. Murray and G. J. Laming, J. Chem. Phys. **99**, 417 (1993).
[9] M. Taut, Phys. Rev. A **48**, 3561 (1993).
[10] C. Filippi, C. J. Umrigar and M. Taut, J. Chem. Phys. **100**, 1290 (1994).
[11] The wave function used is a minor modification of that in D. E. Freund, B. D. Huxtable and J. D. Morgan, Phys. Rev. A **29**, 980 (1984). The wave function used in this paper is the 491-term wave function described in Ref. [12] except that the 14 terms, that have zero coefficients in the infinite series limit, have been omitted.
[12] C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).
[13] M. Levy, Proc. Natl. Acad. Sci. (U.S.A.) **76**, 6062 (1979); Phys. Rev. A **26**, 1200 (1982).
[14] V. Sahni and M. Levy, Phys. Rev. B **33**, 3869 (1986).
[15] S. J. Chakravorty and E. R. Davidson, J. Phys. Chem., **100**, 6167 (1996).
[16] J. Linderberg and H. Shull, J. Mol. Spect., **5**, 1, (1960).
[17] E.A. Hylleraas, Z. Phys., **65**, 209 (1930).
[18] J.P. Perdew, E. R. McMullen and A. Zunger, Phys. Rev. A **23**, 13105 (1981).
[19] M. Levy, J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).
[20] M. Levy, Phys. Rev. A **43**, 4637 (1991).

[21] C. Filippi, X. Gonze and C. J. Umrigar, to be published in: *Recent Developments and Applications of Density Functional Theory*, ed. J. M. Seminario, (Elsevier, Amsterdam, 1996).
[22] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).