

## Local correlation energies of two-electron atoms and model systems

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We present nearly local definitions of 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 another as the atomic number increases. [S1050-2947(97)06607-9]

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### I. INTRODUCTION

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

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

where  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is the many-body wave function,  $T$  is the kinetic energy,  $E_{\text{en}}$  is the potential energy of the electrons interacting with the external (usually nuclear) potential, and  $E_{\text{ee}}$  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]

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

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 noninteracting electrons that has the same density as the interacting system of interest,  $E_{\text{en}}$  is the potential energy of the electrons interacting with the external potential, and  $E_{\text{H}}$  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  $E_{\text{xc}}$  is by definition the part of the total energy not contained in the first three terms.

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

$$\begin{aligned} E_{\text{x}}[\rho] &= -\frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \delta_{m_{s_i}, m_{s_j}} \\ &\times \int \int \frac{\psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}) \psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \end{aligned} \quad (3)$$

where the  $\delta$  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  $E_{\text{c}}$ , which, usually, is just a small fraction of  $E_{\text{xc}}$ . From Eqs. (1) and (2), we obtain

$$E_{\text{c}} = V_{\text{c}} + T_{\text{c}}, \quad (4)$$

where

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

$E_{\text{c}}$  contains a negative contribution coming from the fact that the interaction energy of the electrons is smaller than that given by  $E_{\text{H}} + E_{\text{x}}$  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 semilocal approximations are made for  $E_{\text{c}}$

$$E_{\text{c}}[\rho] = \int e_{\text{c}} d\mathbf{r} = \int \rho(\mathbf{r}) \epsilon_{\text{c}} d\mathbf{r}, \quad (6)$$

where  $e_{\text{c}}$  is the correlation energy density and  $\epsilon_{\text{c}}$  is the local correlation energy per electron. In the local-density approxi-

mation (LDA),  $e_c$  is a function of the local density at  $\mathbf{r}$ ,  $e_c = e_c(\rho(\mathbf{r}))$ , while in the generalized gradient approximations (GGAs) it depends also on the  $\nabla\rho(\mathbf{r})$ , and possibly also on higher derivatives of  $\rho(\mathbf{r})$ ,  $e_c = e_c(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \dots)$ .

In order to invent better approximate functionals, it is useful to know what the true  $e_c$  is. It is apparent that there is not a unique definition of  $e_c$  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  $E_x$  in Eq. (3), is

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

This definition results in a local exchange energy per electron,  $\epsilon_x = e_x/\rho$ , 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.

$$T = -\frac{1}{2} \int d^3\mathbf{r}_1 \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_{i=1}^N \nabla_i^2 \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ = \int d^3\mathbf{r}_1 \left( -\frac{N}{2} \right) \\ \times \int d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \nabla_1^2 \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ \equiv \int d^3\mathbf{r}_1 t(\mathbf{r}_1) \equiv \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \tau(\mathbf{r}_1), \quad (8)$$

$$E_{ee} = \int d^3\mathbf{r}_1 \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_{i < j}^N \frac{1}{\mathbf{r}_{ij}} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ = \int d^3\mathbf{r}_1 \frac{N}{2} \int d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ \times \sum_{i=2}^N \frac{1}{\mathbf{r}_{1i}} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ \equiv \int d^3\mathbf{r}_1 e_{ee}(\mathbf{r}_1) \equiv \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \epsilon_{ee}(\mathbf{r}_1), \quad (9)$$

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

$$E_H = \int d^3\mathbf{r}_1 \frac{1}{2} \int d^3\mathbf{r}_2 \rho(\mathbf{r}_1) \frac{1}{r_{12}} \rho(\mathbf{r}_2) \\ = \frac{1}{2} \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) v_H(\mathbf{r}_1) \\ \equiv \int d^3\mathbf{r}_1 e_H(\mathbf{r}_1) \equiv \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \epsilon_H(\mathbf{r}_1), \quad (11)$$

$$E_x = \int d^3\mathbf{r}_1 \left( -\frac{1}{2} \right) \sum_{i=1}^N \sum_{j=1}^N \delta_{m_{s_i}, m_{s_j}} \psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1) \\ \times \int d^3\mathbf{r}_2 \frac{\psi_j^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ \equiv \int d^3\mathbf{r}_1 e_x(\mathbf{r}_1) \equiv \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \epsilon_x(\mathbf{r}_1), \quad (12)$$

$$E_c = \int d^3\mathbf{r}_1 e_c(\mathbf{r}_1) \equiv \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \epsilon_c(\mathbf{r}_1). \quad (13)$$

Then  $e_c$  and  $\epsilon_c$  can be evaluated as

$$e_c = v_c + t_c, \quad \epsilon_c = v_c + \tau_c, \quad (14)$$

where

$$v_c = e_{ee} - e_H - e_x, \quad v_c = \epsilon_{ee} - \epsilon_H - \epsilon_x, \\ t_c = t - t_s, \quad \tau_c = \tau - \tau_s.$$

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  $V_c$  or  $v_c$  should not be confused with the correlation potential, which is the functional derivative of  $E_c$  with respect to  $\rho$ .

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  $e_{ee}$  is

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

$$E_{ee} = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ \times \sum_{i < j}^N \frac{1}{\mathbf{r}_{ij}} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \equiv \int d^3\mathbf{r}_1 e_{ee}(\mathbf{r}_1), \quad (16)$$

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

$Z$	$E$	$T_S$	$E_{en}$	$E_H$	$E_X$	$E_C$	$V_C$	$T_C$	$E_c^{QC}$	$E_c^{LDA}$
1	-0.527 751	0.499 869	-1.366 524	0.761 796	-0.380 898	-0.041 994	-0.069 876	0.027 882		-0.071 816
2	-2.903 724	2.867 082	-6.753 267	2.049 137	-1.024 568	-0.042 107	-0.078 750	0.036 643	-0.042 044	-0.112 372
3	-7.279 913	7.240 085	-16.127 546	3.302 126	-1.651 063	-0.043 515	-0.083 343	0.039 828	-0.043 498	-0.134 582
4	-13.655 566	13.614 084	-29.502 003	4.553 255	-2.276 628	-0.044 274	-0.085 757	0.041 483	-0.044 267	-0.150 419
6	-32.406 247	32.363 072	-68.251 384	7.054 244	-3.527 122	-0.045 056	-0.088 231	0.043 175	-0.045 054	-0.173 013
10	-93.906 807	93.862 252	-193.750 849	12.054 968	-6.027 484	-0.045 694	-0.090 248	0.044 555	-0.045 693	-0.202 032
20	-387.657 234	387.611 630	-787.500 430	24.555 485	-12.277 743	-0.046 177	-0.091 780	0.045 603	-0.046 177	-0.242 379
$\infty$	$-\infty$	$\infty$	$-\infty$	$\infty$	$-\infty$	-0.046 663	-0.093 327	0.046 663	-0.046 663	$-\infty$

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

$$E = \int d^3\mathbf{r} |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 \frac{\mathcal{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}$$

$$= \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 \frac{\mathcal{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}, \quad (17)$$

$$= \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \frac{E}{N} \equiv \int d^3\mathbf{r}_1 \rho(\mathbf{r}_1) \epsilon(\mathbf{r}_1). \quad (18)$$

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  $\epsilon$ . 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,  $e_{ee}(\mathbf{r}_1)$  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  $e_{ee}$  are very nonlocal, and so any approximate correlation energy functional, that mimics this definition of  $e_c$ , would also have to be very nonlocal. 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  $t_c$  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. 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 three-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 *et al.* [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  $\omega^2 = 1/4$ . Ivanov and Burke [23] solved this system numerically for arbitrary values of  $\omega$  by expanding the interelectronic wave function in powers of the interelectronic distances. To obtain solutions for arbitrary  $\omega$ , 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  $\omega$  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]. The results in Table II, including the values at  $\omega = \infty$ , were previously calculated [23] by a different method, yielding the same results within a few microhartree. Of particular interest are the correlation energies  $E_c$  and their potential and kinetic components  $V_c$ ,  $T_c$ . Each of these quantities tends to a constant in the high-density (large  $Z, \omega$ ) limit. Interestingly, the limiting values for the ions and harmonium differ by only 6%. From Figs. 1 and 2 we observe that, at small  $1/Z$ ,  $E_c$ ,  $V_c$ , and  $T_c$  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  $E_c$  has a minimum at a finite  $\omega$  but we attribute this to a lack of accuracy in their calculations at large  $\omega$ .

TABLE II. Energies of harmonium in Hartree atomic units.

$\omega$	$E$	$T_s$	$E_{\text{en}}$	$E_{\text{H}}$	$E_x$	$E_c$	$V_c$	$T_c$	$E_c^{\text{LDA}}$
0.1	0.500 000	0.109 603	0.208 676	0.421 927	-0.210 964	-0.029 242	-0.045 668	0.016 426	-0.055 025
1	3.730 121	1.327 580	1.697 210	1.493 431	-0.746 716	-0.041 385	-0.075 315	0.033 930	-0.101 335
4	13.523 219	5.628 842	6.397 678	3.083 973	-1.541 986	-0.045 287	-0.086 259	0.040 972	-0.134 190
10	32.448 685	14.397 196	15.629 951	4.936 774	-2.468 387	-0.046 848	-0.090 819	0.043 971	-0.157 546
100	307.902 068	148.033 430	151.994 436	15.845 959	-7.922 979	-0.048 777	-0.096 586	0.047 809	-0.220 763
400	1215.880 360	596.038 744	603.989 284	31.803 138	-15.901 569	-0.049 237	-0.097 983	0.048 746	-0.261 076
1000	3025.153 789	1493.720 344	1506.307 743	50.350 219	-25.175 110	-0.049 407	-0.098 503	0.049 096	-0.288 334
$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	$-\infty$	-0.049 702	-0.099 404	0.049 702	$-\infty$

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

$$E_c^{\text{QC}} = \langle \Psi | \mathcal{H} | \Psi \rangle - \langle \Psi^{\text{HF}} | \mathcal{H} | \Psi^{\text{HF}} \rangle, \quad (19)$$

where  $\Psi$  is the true many-body wave function,  $\Psi^{\text{HF}}$  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

$$E_c = \langle \Psi | \mathcal{H} | \Psi \rangle - \langle \Phi | \mathcal{H} | \Phi \rangle, \quad (20)$$

where  $\Phi$  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  $E_c \leq E_c^{\text{QC}}$ . 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  $E_c$  and  $E_c^{\text{QC}}$ , at large  $Z$ , has strong implications for the terms in the  $1/Z$  perturbation expansion discussed later. The  $Z = \infty$  value of  $E_c$  and  $E_c^{\text{QC}}$  agrees to all digits with that in Ref. [15] for  $E_c^{\text{QC}}$ .

It is known [16] that the quantum chemistry definition of the correlation energy  $E_c^{\text{QC}}$  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  $E_c$ ,  $V_c$ , and  $T_c$  can be explained as follows. As observed by Hylleraas [17], the scaling transformation  $\mathbf{r} \rightarrow \mathbf{r}/Z$  applied to the Schrödinger equation

$$\left( -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) = E \Psi(\mathbf{r}_1, \mathbf{r}_2) \quad (21)$$

yields the scaled Schrödinger equation

$$(\tilde{\mathcal{H}}_0 + \tilde{\mathcal{H}}_1) \tilde{\Psi}(\mathbf{r}_1, \mathbf{r}_2) = \tilde{E} \tilde{\Psi}(\mathbf{r}_1, \mathbf{r}_2), \quad (22)$$

where

$$\tilde{\mathcal{H}}_0 = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2},$$

$$\tilde{\mathcal{H}}_1 = \frac{1}{Zr_{12}},$$

$$\tilde{\Psi}(\mathbf{r}_1, \mathbf{r}_2) = \Psi\left(\frac{\mathbf{r}_1}{Z}, \frac{\mathbf{r}_2}{Z}\right),$$

$$\tilde{E} = \frac{E}{Z^2}. \quad (23)$$

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

$$\tilde{\Psi} = \Psi_0 + \Psi_1/Z + O(Z^{-2}),$$

$$\tilde{E} = E_0 + E_1/Z + E_2/Z^2 + E_3/Z^3 + O(Z^{-4}). \quad (24)$$

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

$$\tilde{\Psi}^{\text{HF}} = \Psi_0^{\text{HF}} + \Psi_1^{\text{HF}}/Z + O(Z^{-2}),$$

$$\tilde{E}^{\text{HF}} = E_0^{\text{HF}} + E_1^{\text{HF}}/Z + E_2^{\text{HF}}/Z^2 + E_3^{\text{HF}}/Z^3 + O(Z^{-4}),$$

$$\tilde{\Phi} = \Phi_0 + \Phi_1/Z + O(Z^{-2}),$$

$$\tilde{E}^{\text{KS}} = E_0^{\text{KS}} + E_1^{\text{KS}}/Z + E_2^{\text{KS}}/Z^2 + E_3^{\text{KS}}/Z^3 + O(Z^{-4}). \quad (25)$$

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

$$E_0 = \langle \Psi_0 | \tilde{\mathcal{H}}_0 | \Psi_0 \rangle = E_0^{\text{HF}} = E_0^{\text{KS}},$$

$$E_1 = \langle \Psi_0 | r_{12}^{-1} | \Psi_0 \rangle = E_1^{\text{HF}} = E_1^{\text{KS}} \quad (26)$$

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

$$E_c^{\text{QC}} = (E_2 - E_2^{\text{HF}}) + 1/Z(E_3 - E_3^{\text{HF}}) + O(Z^{-2}),$$

$$E_c = (E_2 - E_2^{\text{KS}}) + 1/Z(E_3 - E_3^{\text{KS}}) + O(Z^{-2}). \quad (27)$$

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

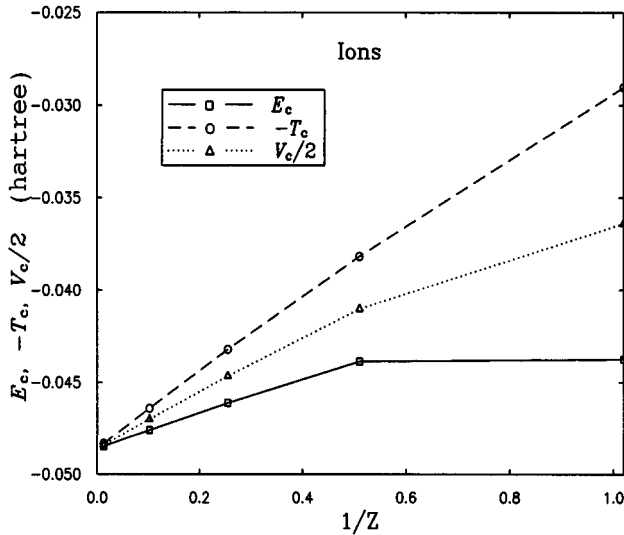


FIG. 1.  $E_c$ ,  $-T_c$ ,  $V_c/2$  for two-electron ions as a function of  $1/Z$ . The data points are for  $Z=1, 2, 4, 10$ , and  $80$ .

The observed behavior  $E_c - E_c^{\text{QC}} \sim 1/Z^3$  in Table I implies that  $E_2^{\text{HF}} = E_2^{\text{KS}}$ ,  $E_3^{\text{HF}} = E_3^{\text{KS}}$ , and  $E_4^{\text{HF}} = E_4^{\text{KS}}$ , 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  $E_c$  is finite in the  $Z \rightarrow \infty$  limit applies to any system for which the noninteracting ground state is nondegenerate. 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  $E_c$  converges to a constant in the  $Z, \sqrt{\omega} \rightarrow \infty$  limit can be easily extended to its potential and kinetic components  $T_c, V_c$  but we have not shown that  $E_c = -T_c = V_c/2$  in this limit. However, Levy and Perdew [19] have shown that

$$E_c[\rho_\lambda] + T_c[\rho_\lambda] = \lambda \frac{\partial E_c[\rho_\lambda]}{\partial \lambda}, \quad (28)$$

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  $E_c[\rho_\lambda]$  goes to a constant linearly in  $\lambda^{-1}$  at large  $\lambda$ , we have  $\lambda \{(\partial E_c[\rho_\lambda]) / \partial \lambda\} \rightarrow 0$  as  $\lambda \rightarrow \infty$ . It follows that  $E_c = -T_c = V_c/2$  in that limit. Although they do not provide a rigorous proof, Levy and Perdew [19] argue that  $E_c = -T_c = V_c/2$  in the  $Z \rightarrow \infty$  limit. We note in passing that the difference between the  $\lambda \rightarrow \infty$  and the  $Z \rightarrow \infty$  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  $\lambda \rightarrow \infty$  limit but the correlation energy of four-electron ions tends to negative infinity in the  $Z \rightarrow \infty$  limit because in the latter case the  $2s$  and  $2p$  orbital energies are degenerate, whereas in the former case they are not.

### B. Local energies per electron

In Figs. 3 and 4 we show the local correlation energy per electron  $\epsilon_c$  and its kinetic and potential components  $\tau_c$  and  $\nu_c$ . As the expansion parameter  $\alpha$  ( $1/Z$  for two-electron ion

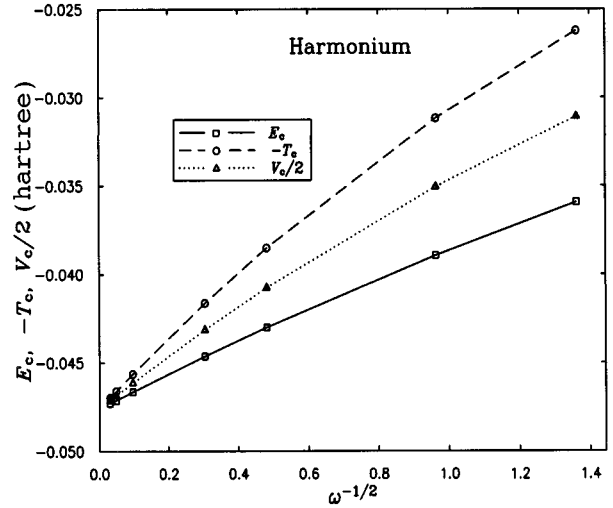


FIG. 2.  $E_c$ ,  $-T_c$ ,  $V_c/2$  for harmonium as a function of  $1/\sqrt{\omega}$ . The data points are for  $\omega=1, 4, 10, 100, 400$ , and  $1000$ .

and  $1/\sqrt{\omega}$  for harmonium) approaches zero, each of  $\epsilon_c$ ,  $\tau_c$ , and  $\nu_c$  tends to a limiting curve. Since the integrated quantities  $E_c$ ,  $V_c$ , and  $T_c$  have  $\alpha$  expansions, it is plausible that there are similar expansions for  $\epsilon_c$ ,  $\tau_c$ , and  $\nu_c$ . With a scaled variable  $\mathbf{x} = \mathbf{r}/\alpha$ , we have

$$\begin{aligned} \epsilon_c(\mathbf{x}, \alpha) &\approx \epsilon_c^*(\mathbf{x}) + \alpha \epsilon_c'(\mathbf{x}), & \tau_c(\mathbf{x}, \alpha) &\approx \tau_c^*(\mathbf{x}) + \alpha \tau_c'(\mathbf{x}), \\ \nu_c(\mathbf{x}, \alpha) &\approx \nu_c^*(\mathbf{x}) + \alpha \nu_c'(\mathbf{x}), & \alpha &\ll 1. \end{aligned} \quad (29)$$

Namely, these curves converge linearly in  $\alpha$  to the limiting curves  $\epsilon_c^*$ ,  $\tau_c^*$ , and  $\nu_c^*$ .

Except for small  $Z$  or  $\omega$ , the three families of curves  $\epsilon_c$ ,  $\tau_c$ , and  $\nu_c$  are characterized by functions  $\epsilon_c^*$ ,  $\tau_c^*$ ,  $\nu_c^*$ ,  $\epsilon_c'$ ,  $\tau_c'$ , and  $\nu_c'$ . Despite the fact that the integrated  $E_c$ ,  $T_c$ , and

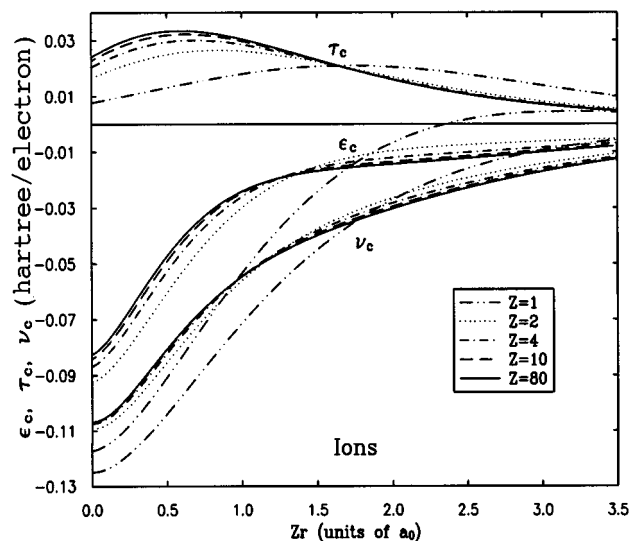


FIG. 3. Local correlation energy per electron  $\epsilon_c$  and its potential and kinetic components  $\nu_c$ ,  $\tau_c$  vs  $Zr$  for two-electron ions. Each of these quantities is plotted for  $Z=1, 2, 4, 10$ , and  $80$ . At  $Zr \approx 1.6$  the top five curves are for  $\tau_c$ , the middle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

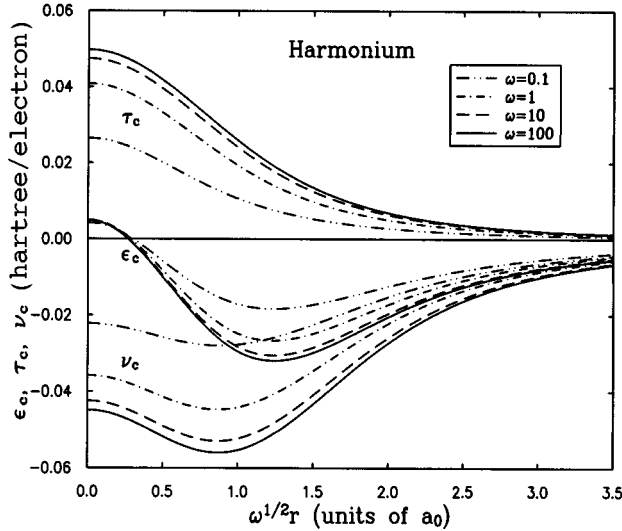


FIG. 4. Local correlation energy per electron  $\epsilon_c$  and its potential and kinetic components  $\nu_c$ ,  $\tau_c$  vs  $\sqrt{\omega}r$  for harmonium. Each of these quantities is plotted for  $\omega=0.1, 1, 10$ , and  $100$ . At  $r=0$  the top four curves are for  $\tau_c$ , the middle four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

$V_c$  differ by only 6% in the high  $Z, \omega$  limit, the limiting curves  $\tau_c^*$ ,  $\nu_c^*$ , and  $\epsilon_c^*$  for two-electron ions are quite different from those for harmonium. For harmonium both  $\nu_c$  and  $\tau_c$  are quadratic at  $r=0$  whereas for the ions  $\nu_c$  is quadratic and  $\tau_c$  is linear. Similarly it has been observed before [10,12,21] that the correlation potentials (i.e., the functional derivatives,  $[\delta E_c/\delta\rho]$ ) for all the two-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

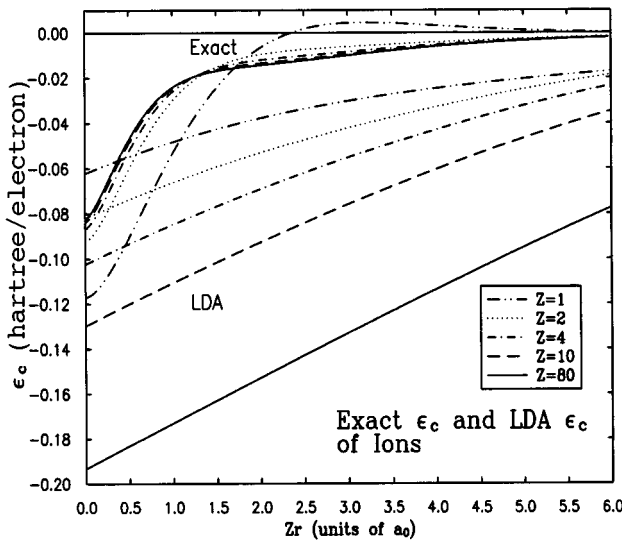


FIG. 5. Comparison of the true local correlation energy per electron  $\epsilon_c$  and the LDA approximation to it  $\epsilon_c^{\text{LDA}}$  for two-electron ions. Each of these quantities is plotted for  $Z=1, 2, 4, 10$ , and  $80$ . The LDA curves have less structure than the true curves and become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

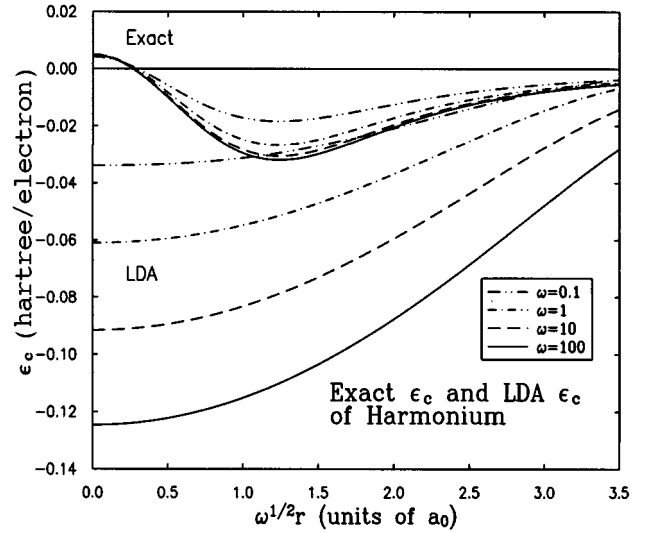


FIG. 6. Comparison of the true local correlation energy per electron  $\epsilon_c$  and the LDA approximation to it  $\epsilon_c^{\text{LDA}}$  for harmonium. Each of these quantities is plotted for  $\omega=0.1, 1, 10$ , and  $100$ . The LDA curves have less structure than the true curves and become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

long distances, and positive at intermediate distances, while the opposite is true for harmonium.

In Figs. 5 and 6 we compare  $\epsilon_c$  with the LDA approximation to it,  $\epsilon_c^{\text{LDA}}$ . The LDA curves have less structure than the true curves and for increasing  $Z, \omega$  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  $Z, \omega$  limits, reflecting the fact that  $E_c^{\text{LDA}}$  diverges to  $-\infty$  as  $Z, \omega \rightarrow \infty$ . We have also compared  $\epsilon_c$  to  $\epsilon_c^{\text{GGA}}$  for all the commonly used GGAs and

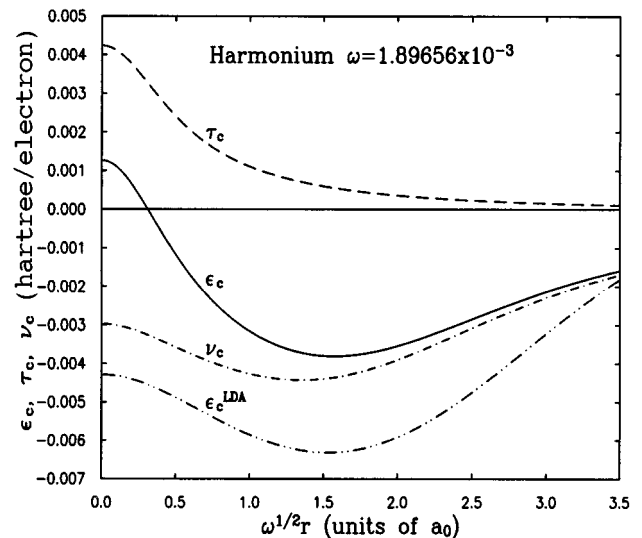


FIG. 7. Local correlation energy per electron  $\epsilon_c$  and its potential and kinetic components  $\nu_c$ ,  $\tau_c$  vs  $\sqrt{\omega}r$  for the harmonium  $n=10$  (high-correlation, low spring-constant) state. The  $\epsilon_c^{\text{LDA}}$  curve is also shown for comparison.

in no case do we find a good agreement, despite the fact that the integrated energies  $E_c^{\text{GGA}}$  are in considerably better agreement with  $E_c$  than are LDA energies [12]. However, we wish to emphasize that the failure of the  $\epsilon_c^{\text{GGA}}$  to agree with  $\epsilon_c$  does not necessarily imply a deficiency in the GGA functionals since, as mentioned before,  $\epsilon_c$  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  $\epsilon_c$ ,  $\nu_c$ , and  $\tau_c$  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,  $\tau_c$  does not have its maximum there. Also, for harmonium, the minimum of  $\nu_c$  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  $\epsilon_c$  and  $\nu_c$  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  $\epsilon_c^{\text{LDA}} - \epsilon_c$  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.

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