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Electron correlation energies from scaled exchange-correlation kernels: Importance of spatial versus temporal nonlocality

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Within density functional theory, a coordinate-scaling relation for the coupling-constant dependence of the exchange-correlation kernel $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega)$ is utilized to express the correlation energy of a many-electron system in terms of f_{xc}. As a test of several of the available approximations for the exchange-correlation kernel, or equivalently the local-field factor, we calculate the uniform-gas correlation energy. While the random phase approximation ($f_{\mathrm{xc}}=0$) makes the correlation energy per electron too negative by about 0.5 eV, the adiabatic local-density approximation $[f_{\mathrm{xc}}=f_{\mathrm{xc}}(q=0,\omega=0)]$ makes a comparable error in the opposite direction. The adiabatic nonlocal approximation $[f_{\mathrm{xc}}=f_{\mathrm{xc}}(q,\omega=0)]$ reduces this error to about 0.1 eV, and inclusion of the full frequency dependence $[f_{\mathrm{xc}}=f_{\mathrm{xc}}(q,\omega)]$ in an approximate parametrization reduces it further to less than 0.02 eV. We also report the wave-vector analysis and the imaginary-frequency analysis of the correlation energy for each choice of kernel.

I. INTRODUCTION

The treatment of electron-electron correlations in many-electron systems has been a long-standing problem. It is known that long-range correlations can be described within the framework of the random phase approximation (RPA).[1] Such calculations have been carried out not only for the uniform electron gas[2,3] but also for inhomogeneous systems such as jellium surfaces.[4]

The RPA, however, does not give a good description of short-range correlations. As a result, RPA ground-state energies by themselves are not very accurate. In the uniform electron gas, at least the second-order exchange energy must be added to the RPA correlation energy in order to provide a useful estimate of the total correlation energy. In small finite systems, where short-range contributions are even more important than in extended systems, we cannot expect pure RPA to be a good approximation. This is confirmed by calculations for atoms and molecules[5,6] which treat the short-range contribution to the correlation energy in a density functional framework using generalized gradient approximations. (Interestingly, however, the RPA appears to give accurate atomization energies for molecules.[5,6])

Density functional theory[7,8] (DFT) has proven an extremely successful method in electronic-structure calculations of atoms, molecules, and solids. The central quantity in DFT is the exchange-correlation (xc) energy, which may be split into exchange and correlation terms, and the success of DFT is based on the construction of reliable approximations for the xc energy. A systematic way of finding such approximations is provided by the adiabatic connection formula,[9–11] since for an arbitrary system it exactly expresses the exchange energy in closed form and the correlation energy in terms of the xc kernel f_{xc}, which is defined in the context of time-dependent density functional theory (TDDFT).[12] For the uniform gas, a nice introductory discussion (which ignores the frequency dependence of f_{xc}) is given in Secs. II and IV of Ref. 13. For nonuniform systems, however, very few approximations for f_{xc} are available. Except for the explicitly orbital-dependent formula suggested by Petersilka, Gossmann, and Gross (PGG),[14,15] the only way of constructing f_{xc} is to apply the uniform-gas quantity $f_{\mathrm{xc}}^{\mathrm{hom}}(q,\omega)$ in some way to the inhomogeneous system of interest.

Directly connected to $f_{\mathrm{xc}}^{\mathrm{hom}}(q,\omega)$ is the local-field factor $G(q,\omega)$, which has often been used to express corrections to the RPA in the uniform electron gas:

$$G(q,\omega)=-\frac{q^2}{4\pi e^2}f_{\mathrm{xc}}^{\mathrm{hom}}(q,\omega). \tag{1}$$

In spite of several decades of intensive research, we are still lacking complete knowledge of the local-field factor. Most of the effort[16–22,13,23–28] went into the determination of the static local-field factor $G(q)=G(q,\omega=0)$. Thereby, many exact properties of $G(q)$ have been found, and parametrizations have been given. The most recent work includes the Monte Carlo study by Moroni, Ceperley, and Senatore[27] and the parametrization thereof given by Corradini *et al.*[28] The frequency dependence of the local-field factor has received less attention; some studies have explored the limit of long wavelengths,[29–33] but work has also been done for the full range of arguments (q,ω).[34–38]

For the construction of approximate xc energy functionals on the basis of the adiabatic connection formula, it is of vital interest to assess the quality of the approximations for $f_{\rm xc}$ that enter the construction. The purpose of this article is to test the available parametrizations of $f_{\rm xc}$ by calculating the resulting uniform-gas correlation energies. In particular, we will answer the question: How important are the wave-vector dependence and frequency dependence of the xc kernel? Our answer will support the pioneering studies of Singwi and others,[19,13] which provided realistic estimates for the correlation energy of the uniform electron gas by taking account of the q dependence of $f_{\rm xc}^{\rm hom}$ while ignoring its ω dependence. We believe that our conclusions extend to nonuniform systems as well: The nonzero range of $f_{\rm xc}(\mathbf{r},\mathbf{r}';\omega)$ must be taken into account in any accurate calculation of the xc energy, while its frequency dependence is less important.

The evaluation of the correlation energy requires as input the xc kernel for all values of the Coulomb coupling constant between 0 and 1. This is the motivation for the study of coordinate scaling in Sec. II, which directly relates the dependence on the coupling constant to the density dependence.

II. SCALING OF THE EXCHANGE-CORRELATION KERNEL

In this section, we use time-dependent density functional theory and dynamic scaling to derive Eq. (17), which shows how to find the coupling-constant dependence of the frequency-dependent xc kernel in any system from a knowledge of its density dependence at full coupling strength. For the uniform electron gas, however, we shall need only the simple and readily anticipated Eq. (22).

The Hamiltonian of a many-electron system subject to a time-dependent external potential $v(\mathbf{r},t)$ is given by

$$\hat{H}(t)=\hat{T}+\hat{W}_{\rm Clb}+\int d^3r\,\hat{n}(\mathbf{r})v(\mathbf{r},t), \tag{2}$$

where the operators $\hat{T}$, $\hat{W}_{\rm Clb}$, and $\hat{n}$ represent the kinetic energy, the electron-electron Coulomb interaction, and the electron density. We consider the case that $v(\mathbf{r},t)$ is time-independent for $t\leqslant 0$. At $t=0$, the system is in the initial state Ψ_0 with density $n_0(\mathbf{r})$. For $t>0$, the system evolves with a time-dependent density $n(\mathbf{r},t)$. In TDDFT, the Kohn-Sham (KS) potential $v_{\rm s}(\mathbf{r},t)$ is defined such that the density $n(\mathbf{r},t)$ is reproduced by a system of noninteracting particles moving in the potential $v_{\rm s}$. The KS initial state $\Psi_{\rm s0}$ is chosen such that it reproduces the initial density $n_0(\mathbf{r})$ and the initial time derivative of the density.[39] The Hamiltonian of this KS system reads

$$\hat{H}^{\rm KS}(t)=\hat{T}+\int d^3r\,\hat{n}(\mathbf{r})v_{\rm s}(\mathbf{r},t). \tag{3}$$

The definition of the xc potential $v_{\rm xc}(\mathbf{r},t)$ follows from the decomposition of the KS potential into

$$v_{\rm s}(\mathbf{r},t)=v(\mathbf{r},t)+v_{\rm H}(\mathbf{r},t)+v_{\rm xc}(\mathbf{r},t), \tag{4}$$

where the Hartree potential $v_{\rm H}$ is defined as

$$v_{\rm H}(\mathbf{r},t)=e^2\int d^3r'\,\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}. \tag{5}$$

By virtue of the Runge-Gross theorem,[40] the quantities $v(\mathbf{r},t)$ and $v_{\rm s}(\mathbf{r},t)$ can be considered as functionals of the time-dependent density and the initial state:

$$v(\mathbf{r},t)=v[n,\Psi_0](\mathbf{r},t), \tag{6}$$

$$v_{\rm s}(\mathbf{r},t)=v_{\rm s}[n,\Psi_{\rm s0}](\mathbf{r},t). \tag{7}$$

(The existence of the Kohn-Sham potential can be proved in the case that the system is stationary for $t\leqslant 0$.[39]) It follows from Eqs. (4)–(7) that

$$v_{\rm xc}(\mathbf{r},t)=v_{\rm xc}[n,\Psi_{\rm s0},\Psi_0](\mathbf{r},t). \tag{8}$$

The same formalism can be written down for a system with reduced Coulomb coupling strength λe^2 $(0\leqslant\lambda\leqslant 1)$ and density $n(\mathbf{r},t)$. The external potential and the xc potential of such a system, as functionals of the density and the initial states Ψ_0 and $\Psi_{\rm s0}$, are denoted as $v^{\lambda}[n,\Psi_0](\mathbf{r},t)$ and $v_{\rm xc}^{\lambda}[n,\Psi_0,\Psi_{\rm s0}](\mathbf{r},t)$, respectively. It has been shown[41] that the xc potential at coupling constant λ is related to the xc potential at $\lambda=1$ by the scaling relation (including the dependence on the initial states)

$$v_{\rm xc}^{\lambda}[n,\Psi_0,\Psi_{\rm s0}](\mathbf{r},t)=\lambda^2 v_{\rm xc}[n',\Psi_0',\Psi_{\rm s0}'](\lambda\mathbf{r},\lambda^2 t), \tag{9}$$

with

$$\Psi_{\rm (s)0}'(\{\mathbf{r}_j\})=\lambda^{-3N/2}\Psi_{\rm (s)0}(\{\mathbf{r}_j/\lambda\}), \tag{10}$$

$$n'(\mathbf{r},t)=\lambda^{-3}n(\mathbf{r}/\lambda,t/\lambda^2). \tag{11}$$

To prove Eq. (9), one first shows that

$$v^{\lambda}[n,\Psi_0](\mathbf{r},t)=\lambda^2 v[n',\Psi_0'](\lambda\mathbf{r},\lambda^2 t), \tag{12}$$

$$v_{\rm s}[n,\Psi_{\rm s0}](\mathbf{r},t)=\lambda^2 v_{\rm s}[n',\Psi_{\rm s0}'](\lambda\mathbf{r},\lambda^2 t), \tag{13}$$

and

$$v_{\rm H}^{\lambda}[n](\mathbf{r},t)=\lambda^2 v_{\rm H}[n'](\lambda\mathbf{r},\lambda^2 t). \tag{14}$$

Then, Eq. (9) follows from Eq. (4), taken at coupling constant λ.

Now we specialize to the following case: For times $t\leqslant 0$, the system with coupling constant λ is in its ground state Ψ_0 with density $n(\mathbf{r})$. We assume that the ground state is nondegenerate. We apply the above scaling, Eqs. (10) and (11), and find that the scaled wave function Ψ_0' is the ground state of the system with full coupling ($\lambda = 1$) and scaled ground-state density n'. This can easily be checked by inspection of the stationary Schrödinger equation. Then, according to the Hohenberg-Kohn theorem for ground states,[42] Ψ_0 and Ψ_0' are density functionals. The same is true for $\Psi_{\rm s0}$ and $\Psi_{\rm s0}'$ under the assumption that the density $n(\mathbf{r})$ can be obtained as the ground-state density of a noninteracting system. Thus, the initial-state dependence can now be dropped from Eq. (9).

The xc kernel is defined as the functional derivative of the xc potential:

$$f_{\rm xc}^{\lambda}[n](\mathbf{r},t;\mathbf{r}',t')=\frac{\delta v_{\rm xc}^{\lambda}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}. \tag{15}$$

By taking the functional derivative of Eq. (9), we arrive at the desired scaling relation for the xc kernel:

$$f^{\lambda}_{\rm xc}[n](\mathbf{r},t;\mathbf{r}',t')=\lambda^{4}f_{\rm xc}[n'](\lambda\mathbf{r},\lambda^{2}t;\lambda\mathbf{r}',\lambda^{2}t'). \tag{16}$$

If we further specialize to the situation where the system always remains infinitesimally close to its initial ground state with density $n(\mathbf{r})$, then the xc kernel describes the time-dependent linear response of the density and depends on the difference $(t-t')$ only. Hence we can evaluate the Fourier transform of Eq. (16) with respect to $(t-t')$:

$$f^{\lambda}_{\rm xc}[n](\mathbf{r},\mathbf{r}';\omega)=\lambda^{2}f_{\rm xc}[n'](\lambda\mathbf{r},\lambda\mathbf{r}';\,\omega/\lambda^{2}). \tag{17}$$

In the uniform electron gas, the density is constant in space and the xc kernel depends only on the difference $(\mathbf{r}-\mathbf{r}')$. Then Fourier transformation of Eq. (17) with respect to $(\mathbf{r}-\mathbf{r}')$ yields

$$f^{\lambda}_{\rm xc}[n](q,\omega)=\lambda^{-1}f_{\rm xc}[n/\lambda^{3}](q/\lambda,\,\omega/\lambda^{2}). \tag{18}$$

Finally, we use the relation between local-field factor and xc kernel,

$$G^{\lambda}(q,\omega)=-\frac{q^{2}}{4\pi\lambda e^{2}}f^{\lambda}_{\rm xc}(q,\omega), \tag{19}$$

to obtain the scaling of the local-field factor:

$$G^{\lambda}[n](q,\omega)=G[n/\lambda^{3}](q/\lambda,\omega/\lambda^{2}). \tag{20}$$

Equation (20) shows that the limit $\lambda\to 0$ is closely connected to the high-density limit of $G(q,\omega)$. This becomes even more apparent if we write the local-field factor as a function of r_s, $q/k_{\rm F}$, and $\omega/\omega_{\rm F}$, with

$$\frac{4\pi}{3}(r_s a_0)^{3}=\frac{1}{n},\quad k_{\rm F}^{3}=3\pi^{2}n,\quad \omega_{\rm F}=\frac{\hbar k_{\rm F}^{2}}{2m}, \tag{21}$$

where $a_0=\hbar^{2}/(me^{2})$. Then

$$G^{\lambda}(r_s,q/k_{\rm F},\omega/\omega_{\rm F})=G(\lambda r_s,q/k_{\rm F},\omega/\omega_{\rm F}). \tag{22}$$

Note that Eq. (22) becomes independent of λ in the exchange-only or high-density limit $(r_s\to 0)$, and also in the strong-coupling or low-density limit $(r_s\to\infty)$ if such a limit exists for G.

III. CORRELATION ENERGY FROM APPROXIMATE EXCHANGE-CORRELATION KERNELS

In any many-electron system, the adiabatic connection formula[9,10] allows us to write the correlation energy $E_{\rm c}$ in terms of the xc kernel $f^{\lambda}_{\rm xc}$ and the density-density response function χ^{λ} (see, e.g., Ref. 11):

$$E_{\rm c}=-\frac{\hbar}{2\pi}\int d^{3}r\int d^{3}r'\frac{e^{2}}{|\mathbf{r}-\mathbf{r}'|}\times\int_{0}^{1}d\lambda\int_{0}^{\infty}du[\chi^{\lambda}(\mathbf{r},\mathbf{r}';iu)-\chi^{0}(\mathbf{r},\mathbf{r}';iu)]. \tag{23}$$

In the coupling-constant integration over λ, the density is held fixed at the density $n(\mathbf{r})$ of the fully interacting system. The response function obeys the Dyson-type equation[12]

$$\chi^{\lambda}(\mathbf{r},\mathbf{r}';\omega)-\chi^{0}(\mathbf{r},\mathbf{r}';\omega)=\int d^{3}x\int d^{3}x'\,\chi^{0}(\mathbf{r},\mathbf{x};\omega)f^{\lambda}_{\rm hxc}(\mathbf{x},\mathbf{x}';\omega)\chi^{\lambda}(\mathbf{x}',\mathbf{r}';\omega), \tag{24}$$

with

$$f^{\lambda}_{\rm hxc}(\mathbf{x},\mathbf{x}';\omega)=\frac{\lambda e^{2}}{|\mathbf{x}-\mathbf{x}'|}+f^{\lambda}_{\rm xc}(\mathbf{x},\mathbf{x}';\omega). \tag{25}$$

One way[45] of calculating $E_{\rm c}$ is to approximate χ^{λ} and $f^{\lambda}_{\rm xc}$ independently of each other on the right-hand side of Eq. (24) and then substitute into Eq. (23). In another approach, one chooses a given approximation for $f^{\lambda}_{\rm xc}$ and solves the integral equation (24) for χ^{λ}. While the solution of the Dyson equation is demanding in general, it becomes trivial in the case of the uniform electron gas where we have

$$\chi^{\lambda}(q,\omega)=\frac{\chi^{0}(q,\omega)}{1-\chi^{0}(q,\omega)f^{\lambda}_{\rm hxc}(q,\omega)}, \tag{26}$$

with the well-known Lindhard function $\chi^{0}(q,\omega)$. Thus, the correlation energy per electron $\epsilon_{\rm c}$ follows from Eq. (23) and Eq. (26):

$$\epsilon_{\rm c}=-\frac{\hbar e^{2}}{\pi^{2}n}\int_{0}^{\infty}dq\int_{0}^{1}d\lambda\int_{0}^{\infty}du\,\frac{[\chi^{0}(q,iu)]^{2}f^{\lambda}_{\rm hxc}(q,iu)}{1-\chi^{0}(q,iu)f^{\lambda}_{\rm hxc}(q,iu)}. \tag{27}$$

The Lindhard function at imaginary frequency iu is known exactly:[3]

$$\chi^{0}(q,iu)=\frac{mk_{\rm F}}{2\pi^{2}\hbar^{2}}\left(\frac{Q^{2}-\tilde{u}^{2}-1}{4Q}\ln\frac{\tilde{u}^{2}+(Q+1)^{2}}{\tilde{u}^{2}+(Q-1)^{2}}-1+\tilde{u}\arctan\frac{1+Q}{\tilde{u}}+\tilde{u}\arctan\frac{1-Q}{\tilde{u}}\right), \tag{28}$$

with

$$Q=\frac{q}{2k_{\rm F}},\quad \tilde{u}=\frac{mu}{\hbar qk_{\rm F}}. \tag{29}$$

Therefore, in Eq. (27) only the xc kernel has to be approximated. Owing to Eq. (18), it is sufficient to have the xc kernel at coupling constant $\lambda=1$.

In the following, we give a list of approximations that we have tested.

(a) RPA. $f_{\rm xc}\equiv 0$.

(b) ALDA (Adiabatic local-density approximation). This is the long-wavelength limit of the static xc kernel:

$$f^{\rm ALDA}_{\rm xc}=\lim_{q\to 0}f^{\rm hom}_{\rm xc}(q,\omega=0). \tag{30}$$

It can readily be expressed in terms of the xc energy per electron $\epsilon_{\rm xc}$:

$$f^{\rm ALDA}_{\rm xc}=\frac{d^{2}}{dn^{2}}[n\epsilon_{\rm xc}(n)]. \tag{31}$$

(c) Parametrization by Corradini et al. (Ref. 28) for the static xc kernel. This is a fit to the quantum Monte Carlo data published by Moroni, Ceperley, and Senatore,[27] and it satisfies the known asymptotic small-q and large-q limits. It interpolates between different values of r_s. Therefore it can be evaluated for arbitrary values of the density, in contrast to the original parametrization given in Ref. 27.

(d) Parametrization of Richardson and Ashcroft (RA) for the xc kernel at imaginary frequencies. This approximation is based, not upon Monte Carlo data, but upon results of numerical calculations done by RA.[37] It is constructed to satisfy many known exact conditions. The formula that we use for the xc kernel is related to RA's quantities G_n and spin-symmetric[13] G_s by

$$f_{\mathrm{xc}}^{\mathrm{RA}}(q,iu)=-\frac{4\pi e^2}{q^2}[G_s(Q,iU)+G_n(Q,iU)], \tag{32}$$

with

$$Q=\frac{q}{2k_{\mathrm{F}}},\quad U=\frac{u}{4\omega_{\mathrm{F}}}. \tag{33}$$

We have replaced Eqs. (39) and (40) of RA's article by the following equations, which correct typographical errors there:

$$\lambda_a^{(0)}+\lambda_n^{(0)}=1-\frac{3}{2}\left(\frac{2\pi}{3}\right)^{2/3} r_s\frac{\partial^2}{\partial\zeta^2}\epsilon_c, \tag{RA:39}$$

and

$$\lambda_s^{(\infty)}=\frac{3}{5}-\frac{2\pi\alpha}{5}\left(r_s^2\frac{\partial}{\partial r_s}\epsilon_c+2r_s\epsilon_c\right). \tag{RA:40}$$

[In both equations, ϵ_c is expressed in Rydbergs, as in RA's article. For Eq. (RA:39), compare Eq. (2.21) of Ref. 22 and Eq. (2.13) of Ref. 43. For Eq. (RA:40), see Eqs. (1.1), (2.23), (4.11), and (D9b) of Ref. 23.] The RA formula requires the on-top pair distribution $g(0)$, for which we use the parametrization by Perdew and Wang given in Ref. 44.

We also test the static limit of $f_{\mathrm{xc}}^{\mathrm{RA}}(q,iu)$,

$$f_{\mathrm{xc}}^{\mathrm{static\ RA}}(q)=f_{\mathrm{xc}}^{\mathrm{RA}}(q,0), \tag{34}$$

in order to compare with the static Corradini approximation. (For a comparison of the RA and Monte Carlo f_{xc} in the static limit, see Fig. 3 of Ref. 27.)

As a dynamic but spatially local approximation we may use the long-wavelength limit of $f_{\mathrm{xc}}^{\mathrm{RA}}(q,iu)$,

$$f_{\mathrm{xc}}^{\mathrm{local\ RA}}(iu)=f_{\mathrm{xc}}^{\mathrm{RA}}(0,iu), \tag{35}$$

which we refer to as ''local RA.''

(e) PGG. This formula was derived[14,15] in the context of the time-dependent optimized effective potential method.[46] It is a frequency-independent exchange-only approximation for inhomogeneous systems. Its real-space version reads

$$f_{\mathrm{x}}^{\mathrm{PGG}}(\mathbf{r},\mathbf{r}';\omega)=-\frac{2e^2}{|\mathbf{r}-\mathbf{r}'|}\frac{|\sum_k f_k\phi_k(\mathbf{r})\phi_k^*(\mathbf{r}')|^2}{n(\mathbf{r})n(\mathbf{r}')}, \tag{36}$$

where ϕ_k and f_k are the KS orbitals and their occupation numbers (0 or 1). This approximation, unlike the ones listed above, is readily applicable to any inhomogeneous system. In the uniform gas, transformation to q space yields

$$f_{\mathrm{x}}^{\mathrm{PGG}}(q,\omega)=-\frac{3\pi e^2}{10k_{\mathrm{F}}^2}\left\{\left(\frac{2}{Q}-10Q\right)\ln\frac{1+Q}{|1-Q|}+(2Q^4-10Q^2)\ln\left[\left(1+\frac{1}{Q}\right)\left|1-\frac{1}{Q}\right|\right]+11+2Q^2\right\}, \tag{37}$$

where $Q=q/(2k_{\mathrm{F}})$. Due to its exchange-only nature, the PGG kernel, taken at coupling constant λ, is simply proportional to λ.

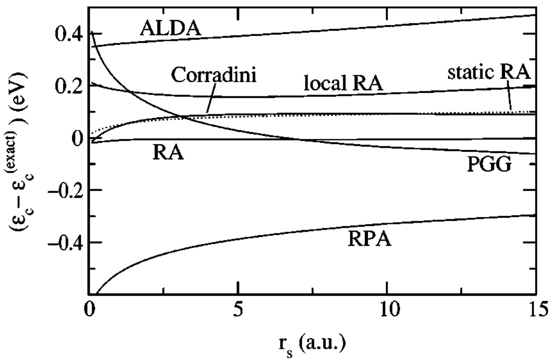

FIG. 1. r_s-dependent deviation of approximate correlation energies from the ''exact'' correlation energy per electron of the uniform electron gas (Ref. 47).

Wherever the xc energy ϵ_{xc} is required as input, we use the parametrization by Perdew and Wang[47] of the Ceperley-Alder[48] diffusion Monte Carlo data.

IV. RESULTS AND DISCUSSION

We expect that RA's parametrization will be close to the exact uniform-gas xc kernel and that the Corradini parametrization will be close to the exact static limit. The ALDA is the exact long-wavelength limit of the static xc kernel. Hence, a comparison between these three cases will clarify the importance of both wave-vector and frequency dependence of the xc kernel.

We calculate the correlation energy ϵ_{c} from Eq. (27) and subtract the ''exact'' correlation energy $\epsilon_{\mathrm{c}}^{(\mathrm{exact})}$ (from the parametrization of Ref. 47). The result for $r_s = 0$–15 is shown in Fig. 1. The RA curve differs from the exact curve by less than 0.02 eV, i.e., it reproduces the exact correlation energy perfectly. With a deviation of less than 0.1 eV, the Corradini approximation gives a good estimate of $\epsilon_{\mathrm{c}}^{(\mathrm{exact})}$ as well. We note that the result of the *static* version of the RA formula lies almost on top of the Corradini curve. From this we infer that the small error produced by the Corradini parametrization is in fact due to its static nature. Thus we are able to conclude that neglecting the frequency dependence causes an error typically smaller than 0.1 eV. (The greatest uncertainty in the ''exact'' correlation energy occurs around $r_s=1$, where the parametrization of Ref. 47 gives -1.63 eV, in good agreement with the older released-node diffusion Monte Carlo value of Ceperley and Alder[48] (-1.62 eV), but not so close to the newer fixed-node value of Ortiz, Harris, and Ballone[49] (-1.53 eV). Although released-node values should be more accurate in principle, the newer fixed-node values are based upon much larger electron numbers. The recent backflow fixed-node result of Kwon, Ceperley, and Martin[50] (-1.64 eV) is, however, very close to our ''exact'' value.)

It is known and also visible in Fig. 1 that in the RPA the correlation energy is too negative. One may hope that a simple approximate xc kernel can roughly fix this deficiency. We recognize, however, that the simplest choice, the ALDA, severely overcorrects ϵ_c, so that the absolute deviation from the exact correlation energy remains about the same as in the RPA. (A similar trend was previously observed for the exchange-only version of the ALDA,[45] and for an approximately scaled ALDA for exchange and correlation,[51] in the uniform gas.) Further, Fig. 1 shows that the local RA (dynamic approximation) performs better than the ALDA, but worse than Corradini or static RA. Therefore, it seems that the wave-vector dependence of the xc kernel must not be neglected, or in other words, that the xc kernel is very nonlocal.

The PGG approximation behaves somewhat differently in that it yields an underestimate for small r_s and an overestimate for large r_s. It is a very good approximation in the range $r_s = 5$–10. Its behavior near $r_s = 0$ indicates that the PGG kernel differs from the exact exchange-only kernel, since exchange should dominate in the high-density limit.

To gain further insight into the effects of the q dependence and the u dependence of f_{xc} in Eq. (27), we analyze the correlation energy into contributions from density fluctuations of different wave vectors q and imaginary frequencies u. Equation (27) naturally defines a wave-vector analysis $\epsilon_c(q)$ if only the q integration is written explicitly while the other integrations are incorporated in $\epsilon_c(q)$:

$$\epsilon_c = \int_0^\infty \epsilon_c(q)\, d\left(\frac{q}{2k_F}\right). \tag{38}$$

The exact wave-vector analysis is essentially given by the Fourier transform of the exact coupling-constant averaged correlation-hole density $n\bar{g}_c(r)$:

$$\epsilon_c^{(\mathrm{exact})}(q) = \frac{2e^2 k_F}{\pi} n\bar{g}_c(q), \tag{39}$$

where

$$\bar{g}_c(q) = \int d^3r\, \bar{g}_c(r) \exp(-i\mathbf{q}\cdot\mathbf{r}). \tag{40}$$

A parametrization of $\bar{g}_c(r)$ has been given by Perdew and Wang.[44] Although this parametrization misses the nonanalytic behavior of $\bar{g}_c(q)$ at $q=2k_F$, it is otherwise almost ''exact.'' A recent comparison [Paola Gori-Giorgi (private communication)] of the Perdew-Wang $g_c^{\lambda=1}(q)$ for $r_s=4$ with that from the diffusion Monte Carlo simulation of Ref. 49 demonstrates full agreement within the numerical noise of the simulation.

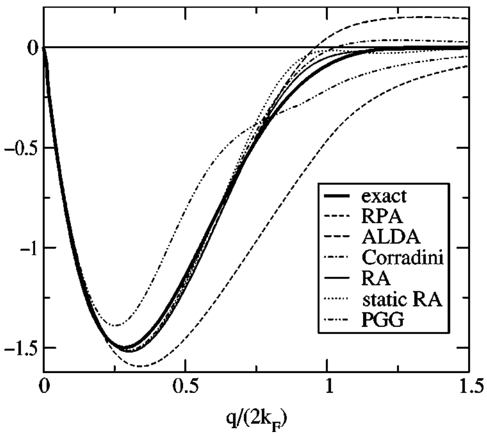

FIG. 2. Wave-vector analysis [Eq. (38)] of the correlation energy per electron of the uniform gas at $r_s=4$. Approximations are compared to the ''exact'' wave-vector analysis of Ref. 44.

In Fig. 2 we compare approximate and ''exact'' wave-vector analyses for $r_s = 4$. While the RPA curve is too negative for all q, we note that the ALDA is quite correct for small q. The ALDA overcorrection to ϵ_c comes from positive contributions at large q. To a much smaller extent, the Corradini curve also exhibits this behavior. In general, however, it is close to the exact wave-vector analysis, as are RA and static RA. In the case of PGG, we note a substantial error cancellation between small and large q values.

As a complement to the wave-vector analysis, we define the imaginary-frequency analysis $\epsilon_c(u)$ of the correlation energy by writing Eq. (27) as an integral over u:

$$\epsilon_c = \int_0^\infty \epsilon_c(u)\, d\left(\frac{u}{\omega_p}\right), \tag{41}$$

with the plasma frequency ω_p given by

$$\omega_p^2 = \frac{4\pi e^2 n}{m}. \tag{42}$$

Since $\epsilon_c(u)$ is not known exactly, we must restrict ourselves to a comparison among different approximations, as displayed in Fig. 3 (low u) and Fig. 4 (high u) for $r_s = 4$. In all

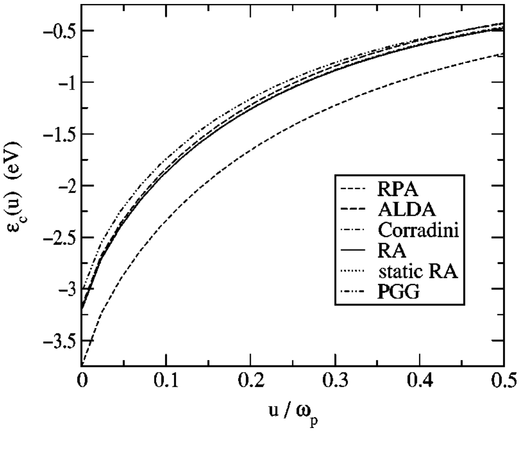

FIG. 3. Imaginary-frequency analysis [Eq. (41)] of the correlation energy per electron of the uniform gas at $r_s=4$ in various approximations (low-u regime).

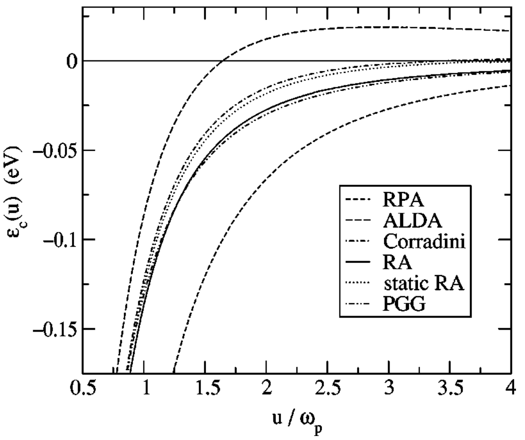

FIG. 4. Imaginary-frequency analysis [Eq. (41)] of the correlation energy per electron of the uniform gas at $r_s = 4$ in various approximations (high-u regime).

cases, $\epsilon_c(u)$ starts with a finite negative value at $u = 0$ and then smoothly approaches zero. As before, the RPA is too negative everywhere. For small frequencies, ALDA, Corradini, and RA results are practically equal; the differences are located at $u \gtrsim \omega_p$. In the ALDA, $\epsilon_c(u)$ becomes positive at $u \approx 1.5\omega_p$. PGG exhibits a slight error cancellation between small and large u, yet it appears to have a very accurate frequency analysis in the high-u regime if we take RA as standard. In consistency with our earlier findings, the Corradini curve is very close to the static RA curve. In a rough estimate, the latter starts to deviate from the dynamic RA at about $u \sim \omega_p$.

Note that an accurate hybrid kernel may be constructed by using the Corradini kernel at small u and the PGG kernel at large u.[52] Then, a generalization to inhomogeneous systems would require modification of only the static Corradini kernel, which has a much simpler analytical structure than the fully frequency-dependent RA kernel.

V. CONCLUSION

In summary, we have demonstrated how to scale available xc kernels for the purpose of calculating correlation energies. In the uniform electron gas, we found that the nonzero spatial range of the kernel $f_{xc}(\mathbf{r},\mathbf{r}';\omega)$ cannot be neglected, while the frequency dependence is less important, as far as the accuracy of the correlation energy is concerned. We therefore expect that the use of a static xc kernel of nonzero spatial range can yield reasonably good energies in nonuniform systems as well. The imaginary-frequency dependence of the xc kernel also appears to be weak in the two-dimensional electron gas; see Fig. 1 of Ref. 53.

By Eq. (15), the xc kernel $f_{xc}(\mathbf{r},t;\mathbf{r}',t')$ describes the linear response of the xc potential v_{xc} at postion $\mathbf{r}$ and time t to an electron-density fluctuation localized at $\mathbf{r}'$ and t'. The spatial range $|\mathbf{r}-\mathbf{r}'|$ of f_{xc} is the range of the xc hole itself, and so cannot be neglected in the calculation of the correlation energy (as it would be in a spatially local approximation). The temporal range $t-t'$ is, however, somewhat shorter than typical time scales that contribute to the correlation energy, making f_{xc} almost local in time (static or adiabatic).

The Richardson-Ashcroft[37] expression for the xc kernel of the uniform electron gas performs well; its imaginary-frequency dependence yields a small but significant improvement in the correlation energy relative to the static RA approximation.

Very accurate ground-state energy calculations for inhomogeneous densities may require a method that is correct not only for slowly varying densities, as are the local spin density (LSDA) and generalized gradient (GGA) approximations, but also at the level of the random phase approximation [$f_{xc}^{\lambda}=0$ in Eqs. (23)–(25)], which treats exchange and long-range correlation exactly. One way to achieve this is to make a RPA Kohn-Sham calculation, treating the short-range correction to the RPA as an extra energy term in the LSDA or GGA.[6] A second possibility, suggested by our present work, is the approximation

$$f_{xc}^{\lambda}(\mathbf{r},\mathbf{r}';\omega) = f_{xc}^{\mathrm{hom},\lambda}([n(\mathbf{r})+n(\mathbf{r}')]/2,|\mathbf{r}-\mathbf{r}'|,\omega), \quad (43)$$

where $f_{xc}^{\mathrm{hom},\lambda}(n,|\mathbf{r}-\mathbf{r}'|,\omega)$ is the kernel of the homogeneous gas. According to Appendix A of Ref. 6, this approximation will correctly make the correlation hole density around an electron integrate to zero. The average density argument in Eq. (43) is chosen as in Ref. 54. Equation (43) may also be useful for the calculation of excitation energies.[14]

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