Correlation energies of inhomogeneous many-electron systems

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Using ideas from general density-functional theory, we generalize the uniform-gas correlation-energy formalism of Singwi, Tosi, Land, and Sjölander to the case of an arbitrary inhomogeneous many-particle system. For jellium slabs of finite thickness with a self-consistent local-density approximation ground-state Kohn-Sham potential as input, our numerical results for the correlation energy agree well with diffusion Monte Carlo results. For a helium atom we also obtain a good correlation energy.

Despite 80 years of study, the accurate calculation of the correlation energy of interacting quantal many-electron systems is still a challenge, even for some systems not regarded as "strongly correlated." For realistic many-electrons systems the current state of the art includes diffusion/Green-function quantum Monte Carlo (DMC), variational formalisms and quantum chemical methods such as the configuration-interaction (CI) approach. These all have stringent practical limitations to relatively small and/or not-too-complex systems. Approximate density functionals of the local-density (LDA) and generalized gradient (GGA) class[1] are, in principle, less accurate than the above approaches, but they remain feasible even for very large, complex systems, and often provide useful accuracy. They fail completely, however, to describe long-ranged correlations in cases where these differ qualitatively from those of the homogeneous electron gas. A case in point is the van der Waals (vdW) or dispersion interaction: all LDA/GGA approaches miss its long-ranged part completely,[2–4] and give at best patchy results at short range.[5] Thus DMC, CI, and standard DFT methods are all likely to be problematic for large complex vdW systems of practical interest, including many soft-matter cases.

Here we present a general approximation method (ISTLS) for the correlation energy of *inhomogeneous* electronic systems, which we believe will be appropriate for vdW problems among others. It employs a self-consistent scheme for the pair distribution based on the surprisingly accurate *homogeneous*-gas correlation-energy method of Singwi, Tosi, Land, and Sjolander (STLS).[6] We take as input an approximate Kohn-Sham (KS) potential $v_{KS}(\vec{r})$ of the inhomogeneous system, and produce the correlation energy E_c as output. Tractable input theories such as the LDA or exchange-only Krieger-Li-Iafrate (KLI) theory,[7] by themselves, make large correlation-energy errors of order +100% and −100%, respectively, yet starting from their KS potentials our ISTLS theory yields correlation energies accurate to a few percent. In its numerical complexity, and also in its accuracy for E_c of large systems, ISTLS appears to be intermediate between LDA/GGA and the more microscopic approaches mentioned above.

Our original motivation for deriving ISTLS was primarily to address soft-matter problems such as polymer cohesion or the energetics of graphite and its intercalates. For such vdW systems, the random-phase-approximation (RPA)-like[3] nature of the method, together with its uniquely self-consistent local-field correction, suggests it will accurately describe vdW interactions[2] while also correctly treating other kinds of bonding.[4] The method is by no means restricted to vdW problems, however, and should provide a useful alternative approach both for soft and for hard matter. In particular, it appears to be highly competitive with recently proposed correlation-energy theories based on the GW method;[8] it gives a more accurate correlation energy in the homogeneous gas at large r_s, for example. Being intrinsically approximate, ISTLS needs to be tested. Therefore, in the present paper, we benchmark our method against state-of-the-art results for two simple but highly inhomogeneous situations: finite-thickness jellium slabs and the He atom. The results suggest that our scheme, while based on approximations known to work well in uniform electron gases, also gives a good treatment of strong inhomogeneity in one to three space dimensions. Details follow.

The ground-state energy of an inhomogeneous many-electron system with external potential $v^{ext}(\vec{r})$ and ground-state electron density $n(\vec{r})$ is given exactly by the constant-density adiabatic connection formula of the formal Kohn-Sham density-functional theory,[9]

$$E_0 = T_s[n] + \int n(\vec{r})v^{ext}(\vec{r})d\vec{r}$$
$$+ \frac{1}{2}\int \frac{e^2}{|\vec{r}-\vec{r}'|}n(\vec{r})n(\vec{r}')d\vec{r}d\vec{r}' + E_{xc}[n], \quad (1)$$

$$E_{xc}[n] = \frac{1}{2}\int_0^1 d\lambda \int \frac{e^2}{|\vec{r}-\vec{r}'|}(n_{2\lambda}(\vec{r},\vec{r}') - n(\vec{r})n(\vec{r}'))d\vec{r}d\vec{r}'. \quad (2)$$

Here $T_s[n] = \hbar^2(2m)^{-1}\Sigma_{k\,occ}\int|\vec{\nabla}\phi_k(\vec{r})|^2 d\vec{r}$ is the KS kinetic energy, and $\{\phi_k\}$ are the occupied KS orbitals, eigenfunctions of the one-electron KS potential $v_{KS}(\vec{r})$. v_{KS} is defined to be such that *independent* electrons moving in v_{KS} yield the true ground-state density,

$$v_{KS} \Rightarrow \{\phi_k(\vec{r})\} : n(\vec{r}) = \sum_{k\,occ} |\phi_k(\vec{r})|^2. \quad (3)$$

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The λ integration in Eq. (2) accounts for the kinetic part of the KS correlation energy. The ground-state pair distribution $n_{2\lambda}(\vec{r},r')$ is that of a λ *system* defined to have a reduced electron-electron interaction $\lambda e^2/r_{12}$, and a modified external potential $v_\lambda^{ext}(\vec{r})$ chosen to maintain the true ($\lambda=1$) ground-state density at any $\lambda : n_\lambda(\vec{r}) = n_{\lambda=1}(\vec{r}) \equiv n(\vec{r})$. Remarkably,[9] only the true external potential $v^{ext} \equiv v_{\lambda=1}^{ext}$ appears in Eq. (1). Note that from Eq. (3) the KS potential of each λ system is the same as that of the true ($\lambda=1$) system, because the density is the same,

$$v_{KS,\lambda} \equiv v_{KS}. \qquad (4)$$

The ground-state pair distribution $n_{2\lambda}$ in Eq. (2) can be related to the Kubo density-density response function χ_λ of the λ system by the $T=0$ K fluctuation-dissipation theorem,[10]

$$n(\vec{r})n(\vec{r}')[g_\lambda(\vec{r},\vec{r}')-1] \equiv n_{2\lambda}(\vec{r},\vec{r}')-n(\vec{r})n(\vec{r}')$$

$$= -\frac{\hbar}{\pi}\int_0^\infty \chi_\lambda(\vec{r},\vec{r}',\omega=iu)$$

$$\times du - n(\vec{r})\delta(\vec{r}-\vec{r}'). \qquad (5)$$

Equation (5) also introduces the equilibrium pair correlation factor $g_\lambda(\vec{r},\vec{r}')$.

The Kohn-Sham density-density response χ_{KS}[11] is defined to be that of *independent* electrons moving in the KS potential v_{KS}. Note that, by Eq. (4),

$$\chi_{KS,\lambda} \equiv \chi_{KS} \equiv \chi_{\lambda=0}. \qquad (6)$$

χ_{KS} is exactly expressible[11] by perturbation theory in terms of KS orbitals $\{\phi_k\}$. From this expression it is readily shown that, when χ_λ is replaced by $\chi_{\lambda=0} \equiv \chi_{KS}$, Eq. (5) gives the "exact density-functional theory (DFT) exchange" energy, i.e., it gives the Hartree-Fock energy integral in which the self-consistent Hartree-Fock orbitals are replaced by the KS orbitals ϕ_k. Thus this formalism easily deals with the exchange. Subtracting this DFT exchange energy from Eq. (2) we obtain the exact DFT correlation energy

$$E_c = \frac{-\hbar}{2\pi}\int d\vec{r}d\vec{r}'\frac{e^2}{|\vec{r}-\vec{r}'|}\int_0^1 d\lambda \int_0^\infty du[\chi_\lambda(\vec{r},\vec{r}',\omega=iu)$$

$$-\chi_{\lambda=0}(\vec{r},\vec{r}',\omega=iu)]. \qquad (7)$$

At each λ value the interacting and KS responses are related exactly by a Dyson-like screening integral equation[11] $\chi_\lambda = \chi_{\lambda=0} + \chi_{\lambda=0} * (\lambda V_{coulomb} + f_{xc\lambda}) * \chi_\lambda$, where the spatial convolution is represented by asterisks. The xc kernel $f_{xc\lambda}$ contains the many-body xc effects and has traditionally been treated by a local-density approximation.[11,12] At finite frequency the local approximation actually requires a tensor current-current version of the screening theory.[13] Here, however, instead of using a local uniform-gas-based approximation we effectively generate a nonlocal, nonscalar f_{xc} self-consistently for the particular inhomogeneous system. To do this we extend the semiclassical approach of STLS to non-

uniform systems. Thus we relate the independent-electron and interacting responses by solving the time-evolution equation (first Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy equation[14]) for the one-electron distribution function $f(\vec{r},\vec{p},t)$ of the classical λ system,

$$\left(\frac{\partial}{\partial t}+m^{-1}\vec{p}\cdot\frac{\partial}{\partial\vec{r}}+\vec{F}_\lambda^{ext}(\vec{r},t)\cdot\frac{\partial}{\partial\vec{p}}\right)f(\vec{r},\vec{p},t)$$

$$=\int\left(\frac{\partial}{\partial\vec{r}}\frac{\lambda e^2}{|\vec{r}-\vec{r}'|}\right)\cdot\frac{\partial}{\partial\vec{p}}f_\lambda^{(2)}(\vec{r},\vec{p};\vec{r}',\vec{p}',t)d\vec{r}'d\vec{p}'. \qquad (8)$$

This equation is exact but requires the dynamic pair distribution $f_\lambda^{(2)}$. The essential contribution of STLS was to use the equilibrium pair-density factor $g_\lambda(\vec{r},\vec{r}')$ of Eq. (5) in a semiclassical truncation scheme

$$f_\lambda^{(2)}(\vec{r},\vec{p};\vec{r}',\vec{p}',t) \approx g_\lambda(\vec{r},\vec{r}')f(\vec{r},\vec{p},t)f(\vec{r}',\vec{p}',t), \qquad (9)$$

where the true dynamic correlation factor g_λ should depend on both the momenta and the time, but this dependence is ignored and g_λ is taken to be the static, momentum-independent equilibrium density correlating factor from Eq. (5). Using Eqs. (9) in (8) and linearizing about the equilibrium distribution, $f=f_0(\vec{r},\vec{p})+\delta f(\vec{r},\vec{p},t)$, we obtain a closed one-body kinetic equation

$$\left(\frac{\partial}{\partial t}+m^{-1}\vec{p}\cdot\frac{\partial}{\partial\vec{r}}+\vec{F}^{(0)}(\vec{r})\cdot\frac{\partial}{\partial\vec{p}}\right)\delta f(\vec{r},\vec{p},t)$$

$$=-\delta\vec{F}^{eff}(\vec{r},t)\cdot\frac{\partial f_0(\vec{r},\vec{p})}{\partial\vec{p}}. \qquad (10)$$

Here

$$\vec{F}^{(0)}(\vec{r})=\vec{F}_{0\lambda}^{ext}(\vec{r})-\int\left(\frac{\partial}{\partial\vec{r}}\frac{\lambda e^2}{|\vec{r}-\vec{r}'|}\right)g_\lambda(\vec{r},\vec{r}')n_0(\vec{r}')d\vec{r}'$$

corresponds to the gradient of the KS potential in the quantal case, and is independent of λ by choice of $F_{0\lambda}^{ext}(\vec{r})$. Further,

$$\delta\vec{F}^{eff}(\vec{r},t)=\delta\vec{F}^{ext}(\vec{r},t)+\int\vec{W}_\lambda(\vec{r},\vec{r}')\delta n(\vec{r}',t)d\vec{r}', \qquad (11)$$

$$\vec{W}_\lambda(\vec{r},\vec{r}')=g_\lambda(\vec{r},\vec{r}')\frac{-\partial}{\partial\vec{r}}\frac{\lambda e^2}{|\vec{r}-\vec{r}'|}. \qquad (12)$$

Because Eq. (10) is linear and time invariant, its solution $\delta n(\vec{r},t) \equiv \int \delta f(\vec{r},\vec{p},t)d\vec{p}$ can be expressed in the form

$$\delta n(\vec{r},t)=\int\vec{\nu}_0(\vec{r},\vec{r}',t-t')\cdot\delta\vec{F}^{eff}(\vec{r}',t')d\vec{r}'dt', \qquad (13)$$

where a $\vec{\nu}_0$ is a λ-independent classical vector response func-

tion giving the independent-electron density response to an applied force, with $(\partial/\partial\vec{r}') \cdot \vec{\nu}_0 = \chi_{\lambda=0}$.

In the case of *homogeneous* electron gases, $\vec{F}_0$ is zero and g_λ is a function only of the separation $R \equiv |\vec{r}-\vec{r}'|$, and then $\vec{\nabla}\times\vec{W}=\vec{0}$ so that the effective pair force $\vec{W}_\lambda$ is irrotational and can be expressed as a gradient of a scalar potential, $\vec{W}_\lambda(\vec{R}) = -(\partial/\partial\vec{R})w_\lambda(R)$. Then, assuming $\delta\vec{F}^{ext}$ comes from a potential δV^{ext} we can use integration by parts (Green's theorem) followed by space Fourier transformation to write Eq. (13) in q space as $\delta n = \chi_{\lambda=0}\delta V^{eff} = \chi_{\lambda=0}(\delta V^{ext}+w_\lambda\delta n)$. This yields $\chi_\lambda(q,\omega) = \chi_{\lambda=0}(q,\omega) \times(1-w_\lambda(q)\chi_{\lambda=0}(q,\omega))^{-1}$. This equation resembles a classical RPA, with $w_\lambda(q)$ replacing the bare coulomb pair potential $4\pi\lambda e^2/q^2$. This response χ_λ depends on g_λ via w_λ, and g_λ is determined by χ_λ using Eq. (5), giving a closed self-consistent scheme. STLS applied this theory to the degenerate electron gas by replacing the classical Boltzmann equation density response $\chi_{\lambda=0}$ with the quantal Lindhard response. Despite the crudeness of the factorization (9), the STLS formalism gives excellent correlation energies for both three-dimensional (3D) and 2D homogeneous electron gases, up to relatively large values of the interelectron spacing parameter r_s. For example, in 3D E_c^{STLS} is within about 1% of the 3D diffusion Monte Carlo results[15] for $2<r_s\le 5$. The error is still under 4% at $r_s=20$ and under 7% at $r_s=50$, a regime including gases generally regarded as significantly correlated. These results are significantly better than recent GW-based many-body methods,[8] which give 20% error at $r_s=20$. The homogeneous STLS scheme has a number of shortcomings, including unphysical negative values of the on-top pair factor $g(\vec{r},\vec{r})$ and failure to satisfy the compressibility sum rule. Further work addressing these difficulties[16] did not, however, significantly improve the predicted uniform gas correlation energy. Therefore, in the present work we have concentrated on generalizing the original semiclassical STLS scheme to inhomogeneous systems. This does not appear to have been attempted previously: bilayered electron gases have certainly been treated,[17] but these are isomorphic to a two-species *homogeneous* 2D electron gas. We will show that the formalism is tractable for cases of genuine inhomogeneity.

In an *inhomogeneous* system we have $\vec{\nabla}\times\vec{W}_\lambda = -\vec{\nabla}g_\lambda(\vec{r},\vec{r}')\times\vec{\nabla}(\lambda e^2/|\vec{r}-\vec{r}'|)\ne\vec{0}$ so that there is no scalar potential corresponding to $\vec{W}_\lambda$, and the *vector* bare response $\vec{\nu}_0$ from Eq. (13) must be used: the scalar version χ_0 is not sufficient. This is an essential difference between the inhomogeneous case and the homogeneous one. As in the homogeneous case, we postulate that a degenerate Fermi system can be treated within the above semiclassical analysis by using the quantal Fermi independent-electron response for $\vec{\nu}_0$: this also amounts to using the quantal KS potential in place of its classical counterpart $\vec{F}_0$. By perturbation of the occupied independent-electron (KS) orbitals $\phi_j(\vec{r})$, we obtained for the inhomogeneous quantal response at imaginary frequency iu

$$\vec{\nu}_0(\vec{r},\vec{r}',\omega=iu) = \frac{1}{u}\mathrm{Re}\left[\frac{i\hbar}{m}\sum_j f_j\phi_j^*(\vec{r})\right.$$
$$\times[G(\vec{r},\vec{r}',E=\hbar\omega_j+i\hbar u)\vec{\nabla}'\phi_j(\vec{r}')$$
$$\left.-\phi_j(\vec{r}')\vec{\nabla}'G(\vec{r},\vec{r}',E=\hbar\omega_j+i\hbar u)],\right.$$

(14)

where f_j is the Fermi occupation factor and G is the Green function for a single electron moving in the ground-state Kohn-Sham potential $v_{KS}(r)$. The Coulomb screening conditions(11, 12, 13) for the inhomogeneous case can be written as a Dyson-like "screening" integral equation for the interacting response $\chi_\lambda(\vec{r},\vec{r}',\omega)$,

$$\chi_\lambda = \chi_{KS} + \int Q_\lambda(\vec{r},\vec{r}'',\omega)\chi_\lambda(\vec{r}'',\vec{r}',\omega)dr'', \quad (15)$$

$$Q_\lambda = \int \vec{\nu}_0(\vec{r},\vec{r}'''\omega)\cdot\vec{W}_\lambda(\vec{r}''',\vec{r}'')d\vec{r}''', \chi_{KS}=\vec{\nabla}'\cdot\vec{\nu}_0. \quad (16)$$

We term this the "inhomogeneous STLS" (ISTLS) scheme. To demonstrate its feasibility and accuracy we have carried it out numerically for two highly inhomogeneous but spatially symmetric cases, namely (i) charge-neutral jellium slabs and (ii) a helium atom.

The jellium slabs were first solved in the ground-state PW91-LDA[18] to give $v_{KS}^{LDA}(z)$ and density $n(z)$, where z is the space coordinate in the thin dimension of the slab. Our ISTLS formalism was applied as a "postfunctional" giving the correlation energy starting from the fixed $v_{KS}^{LDA}(z)$, though, of course, ideally one would choose a $v(z)$ to minimize the total energy including the STLS corrections. [This OPM method would also give an improved density $n(\vec{r})$]. We then implemented Eqs. (5), (12), (14)–(16), and (7), starting the iterations from an exchange-only g factor.

Figure 1 gives the jellium slab correlation energy per electron for a number of positive background densities n_{0+}, parametrized by the dimensionless interelectron spacing $r_s = me^2\hbar^{-2}(3n_{0+}/4\pi)^{1/3}$. We show results from ISTLS (solid line), DMC[19] (dotted line), RPA (diamonds), Perdew-Burke-Ernzerhof (PBE)[20] correlation-only GGA (long dashes), and LDA (pluses) schemes. The thickness of the positive background in each slab is $L=7.21r_s a_B$, to match the available DMC results. Uniform-gas results are also shown (filled symbols). ISTLS gives the best agreement with the slab DMC data, within 3%. This is comparable to the agreement of STLS with DMC for the uniform 3D gas with $2\le r_s \le 20$. We have also checked that ISTLS recovers 2D results in the thin-slab limit, in contrast to, e.g., GGA.

For small finite systems, such as atoms, one needs a self-interaction correction in the starting KS potential and density. Otherwise (as, for example, when one uses the simple LDA) unrealistic response functions are obtained because the asymptotic $-e^2/r$ potential is missing in v^{KS}. We solved helium using the Krieger-Li-Iafrate exchange-only description[7] of the atomic ground state. This has the advantage of a common potential $v^{KLI}\equiv v^{KS}$ for all orbitals. The
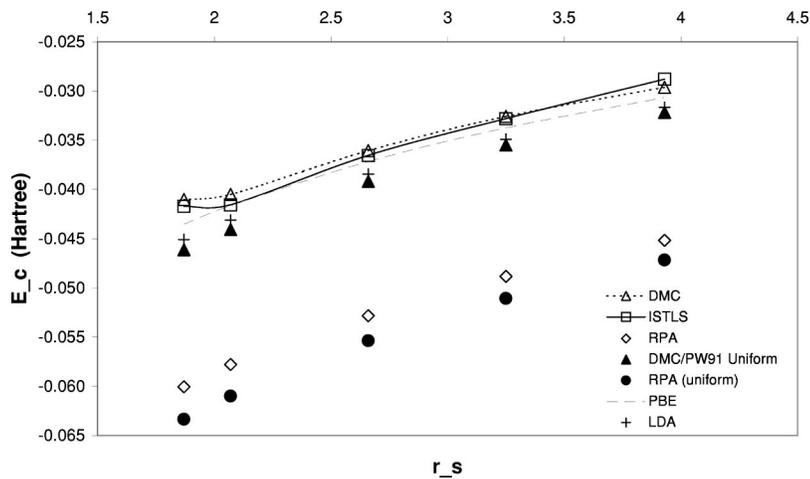
FIG. 1. Correlation energy of neutral jellium slabs (Hartree/electron).

explicit spherical form of Eqs. (14)–(16) involves spherical harmonics but is somewhat cumbersome because of the vector character of $\vec{\nu}_0$. We obtained a total ISTLS He correlation energy of -40.0 milliHartree, within 5% of the "exact" nonrelativistic value[21] of -42.0 mH. Our result is of "chemical accuracy," but does not improve on the PBE GGA[20] value of -43 mH. The KLI starting potential is adequate: we re-ran our method starting from the numerically exact He KS potential,[22] obtaining $\ll 1\%$ change in E_c.

In summary, we have derived an inhomogeneous generalization (ISTLS) of the rather successful STLS uniform-gas correlation-energy formalism: see Eqs. (12), (14), (16), (15), (5), and (7). We have shown that ISTLS gives good ground-state correlation energies in some highly inhomogeneous electronic systems. The scheme can also encompass finite temperatures, and plasmon calculations. An advantage of the ISTLS scheme is that it gives pair correlation physics that is "self-tailored" to the system at hand, rather than "stolen" from the uniform gas. Our tests suggest that ISTLS will be tractable numerically wherever the RPA correlation energy is,[3,23] but evaluation will take 5–20 times as long. We speculate that interesting density functionals for the correlation energy might be derived by using the ISTLS scheme with semi-local-density approximations for the bare response $\vec{\nu}_0$, somewhat as in Ref. 3.

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