

Investigation of the Correlation Potential from Kohn-Sham Perturbation Theory

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Perturbation theory on the basis of the Kohn-Sham Hamiltonian leads to an implicit density functional for the correlation energy E_c . In this contribution we investigate the corresponding correlation potential v_c . It is shown that for finite systems the v_c obtained by direct application of the optimized potential method diverges in the asymptotic region. The presence of unoccupied states, inherent in any perturbative form of E_c , is identified as the origin of this unphysical behavior. An approximate variational procedure is developed in order to avoid this difficulty. The potential resulting from this method qualitatively reproduces the shell structure of the exact atomic v_c .

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In recent years a new class of implicit density functionals for the exchange-correlation (xc) energy E_{xc} , the central quantity of density functional theory (DFT) [1], has attracted considerable interest [2,3]—for an overview, see [4]. Unlike conventional density functionals such as generalized gradient approximations (GGAs) [5], implicit forms do not directly depend on the density n of the system, but rather on the Kohn-Sham (KS) orbitals ϕ_k (which are themselves functionals of n). This concept immediately provides an exact representation for the exchange energy E_x . The most obvious advantage resulting from use of the exact E_x is the possibility to describe negative ions [6]: This is due to the asymptotic $-e^2/r$ dependence of the exact exchange potential of finite systems, reflecting the complete cancellation of the self-interaction inherent in the Hartree potential. The failure of GGAs for negative ions, on the other hand, directly originates from their inability to reproduce the $-e^2/r$ behavior [7], a fact which emphasizes the importance of the xc potential $v_{xc} = \delta E_{xc}/\delta n$.

It is not yet clear which approximation for the correlation component E_c of E_{xc} should be used with the exact E_x . Initially the semiempirical functional of Colle and Salvetti (CS) [8] was put forward as a possible candidate [9]. In the meantime KS perturbation theory (KSPT) [10,11] appears to be the most promising method for the derivation of a first-principle approximation of E_c . In particular, it has been shown that the lowest order correlation contribution $E_c^{(2)}$ obtained by KSPT allows a semiquantitative description of van der Waals forces [11,12] (in contrast to GGAs [13]). In this contribution we examine the corresponding potential $v_c^{(2)}$ of atoms, for which exact reference results are available [14].

In KSPT an expansion of E_{xc} in powers of the interaction strength e^2 , $E_{xc}[n] = e^2 E_x[n] + \sum_{i=2}^{\infty} e^{2i} E_c^{(i)}[n]$, is generated by using the KS auxiliary Hamiltonian as a starting point [4]. The lowest order term, i.e., the Fock expression, represents the exact E_x of DFT,

$$E_x = -\frac{1}{2} \sum_{\epsilon_i, \epsilon_j \leq \epsilon_F} (ij||ji), \quad (1)$$

where ϵ_F is the Fermi energy and the Slater integral

$$(ij||kl) = \int d^3 r_1 \int d^3 r_2 \frac{\phi_i^\dagger(\mathbf{r}_1)\phi_k(\mathbf{r}_1)\phi_j^\dagger(\mathbf{r}_2)\phi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

is evaluated with KS orbitals. The lowest order correlation contribution $E_c^{(2)}$ consists of two components, $E_c^{(2)} = E_c^{\text{MP2}} + E_c^{\Delta\text{HF}}$. The dominant term is given by (for details, see [11])

$$E_c^{\text{MP2}} = \frac{1}{2} \sum_{\epsilon_i, \epsilon_j \leq \epsilon_F < \epsilon_k, \epsilon_l} \frac{(ij||kl)[(lk||ji) - (lk||ij)]}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l}, \quad (2)$$

where the summations over the excited states k, l include all discrete and continuum states. E_c^{MP2} has the same functional form as the well-known second order Møller-Plesset term [15], obtained by a perturbation expansion on the basis of the Hartree-Fock (HF) approach. $E_c^{\Delta\text{HF}}$, on the other hand, is roughly 2 orders of magnitude smaller than E_c^{MP2} for all systems considered so far [4,12]. This suggests the neglect of $E_c^{\Delta\text{HF}}$, although $|E_c^{\Delta\text{HF}}| \ll |E_c^{\text{MP2}}|$ does not automatically imply that $|v_c^{\Delta\text{HF}}| \ll |v_c^{\text{MP2}}|$ for all r . It must be emphasized, however, that $E_c^{\Delta\text{HF}}$, and thus also $v_c^{\Delta\text{HF}}$, vanish identically for He-like atoms [4]. Focusing on this class of systems, we disregard $E_c^{\Delta\text{HF}}$ in the following analysis.

Given the approximation $E_{xc} \approx e^2 E_x + e^4 E_c^{\text{MP2}}$ any self-consistent application requires the determination of the corresponding $v_{xc} \approx e^2 v_x + e^4 v_c^{\text{MP2}}$ which, in the case of implicit functionals, is obtained via the optimized potential method (OPM) [16]. For spherical systems, to which we restrict the discussion, the KS orbitals can be separated as $\phi_k(\mathbf{r}) = \varphi_{nl}(r)Y_{lm}(\Omega)/r$ and the OPM integral equation for v_{xc} reduces to

$$\int_0^\infty dr' K(r, r') v_{xc}(r') = Q_{xc}(r). \quad (3)$$

Here $K = \delta(4\pi r^2 n)/\delta v_{\text{KS}}$ is the static, radial KS response function and $Q_{xc} = Q_x + Q_c^{\text{MP2}}$,

$$Q_x(r) = \sum_{\epsilon_k \leq \epsilon_F} \int dr' \frac{\delta E_x}{\delta \varphi_k(r')} \Big|_{\text{expl}} \frac{\delta \varphi_k(r')}{\delta v_{\text{KS}}(r)}, \quad (4)$$

$$Q_c^{\text{MP2}}(r) = \sum_{\epsilon_k} \int dr' \frac{\delta E_c^{\text{MP2}}}{\delta \varphi_k(r')} \Big|_{\text{expl}} \frac{\delta \varphi_k(r')}{\delta v_{\text{KS}}(r)} + \sum_{\epsilon_k} \frac{\partial E_c^{\text{MP2}}}{\partial \epsilon_k} \Big|_{\text{expl}} \frac{\delta \epsilon_k}{\delta v_{\text{KS}}(r)} \quad (5)$$

(for details, see Appendix A of Ref. [11]). Equations (2), (3), and (5) establish a complete scheme for the determination of v_c^{MP2} .

We now show that for finite systems, v_c^{MP2} exhibits an exponential divergence in the large r regime, rather than approaching a constant. This contradicts the standard physical boundary condition $v_{xc} \xrightarrow{r \rightarrow \infty} 0$. In order to prove this by *reductio ad absurdum*, let us assume that v_c^{MP2} satisfies the physical boundary condition (as is the case for v_x). Then the left-hand side of Eq. (3) is dominated by (compare Appendix B of Ref. [11])

$$\int dr' K(r, r') v_{x/c}(r') \xrightarrow{r \rightarrow \infty} 2\Theta_F |\varphi_F(r)|^2 \times \int_0^r dr' \varphi_F(r') \chi_F(r') \int_0^\infty dr'' \times |\varphi_F(r'')|^2 v_{x/c}(r''), \quad (6)$$

where the index F denotes the highest occupied KS state, Θ_F is the occupation number of this state, and χ_F is the nonnormalizable solution of the radial KS equation corresponding to the same eigenvalue as φ_F . We now compare this asymptotic behavior with that of the right-hand side of (3). Separating the individual asymptotic forms of exchange and correlation one is lead to

$$\lim_{r \rightarrow \infty} \frac{Q_c^{\text{MP2}}(r)}{Q_x(r)} = \lim_{r \rightarrow \infty} \frac{\int_0^\infty dr' K(r, r') v_c^{\text{MP2}}(r')}{\int_0^\infty dr'' K(r, r'') v_x(r'')} = \frac{\int_0^\infty dr' |\varphi_F(r')|^2 v_c^{\text{MP2}}(r')}{\int_0^\infty dr'' |\varphi_F(r'')|^2 v_x(r'')} = C. \quad (7)$$

$$v_c^{\text{KLI}}(r) = \frac{1}{4\pi n(r)} \left\{ \frac{1}{2} \sum_{\epsilon_k} \varphi_k(r) \frac{\delta E_c^{\text{MP2}}}{\delta \varphi_k(r)} - \frac{1}{2} \sum_{\epsilon_k} |\varphi_k(r)|^2 \int dr' \varphi_k(r') \frac{\delta E_c^{\text{MP2}}}{\delta \varphi_k(r')} + \sum_{\epsilon_k \leq \epsilon_F} \Theta_k |\varphi_k(r)|^2 \int dr' |\varphi_k(r')|^2 v_c^{\text{KLI}}(r') \right\}. \quad (8)$$

For v_x the KLI approximation is known to accurately reproduce the full OPM potential [4] and to be exact in the limit $r \rightarrow \infty$ [17], so that one expects that at least the qualitative features of v_c^{MP2} should be correctly given by v_c^{KLI} . In Fig. 2 v_c^{KLI} is plotted for the He-isoelectronic series. All potentials displayed show a clear asymptotic divergence, whose onset shifts to smaller r values with increasing Z , i.e., with increasing localization of the density in the

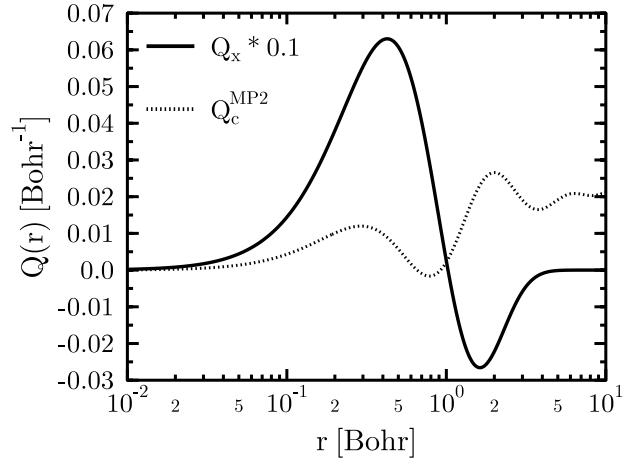


FIG. 1. Comparison of Q_x and Q_c^{MP2} for He.

Thus, as long as the numerator of the right-hand side of (7) is finite, C must also be a finite number (as the denominator is known to be nonzero [17]). The left-hand side of (7) can be evaluated numerically. In Fig. 1 we compare Q_x and Q_c^{MP2} for the He-atom (Fig. 1 has been generated with the exact x -only orbitals). While the exponential decay of Q_x is evident for $r \geq 2$ bohr, Q_c^{MP2} does not approach zero in the physically relevant part of the asymptotic regime. As a consequence, Q_c^{MP2}/Q_x diverges exponentially. We emphasize that numerical convergence for Q_c^{MP2} has been achieved: Using a finite differences code, discrete excited states were explicitly summed up to $n = 10$ and $l = 6$, while for the integration over the continuous spectrum with $l \leq 6$ a logarithmic energy mesh with 100 points was used, ranging from 1 mhartree to 50 hartree. This representation of the excited states gives 99% of the exact E_c^{MP2} of 48.2 mhartree. As the numerical result contradicts the right-hand side of Eq. (7) the assumption $v_c^{\text{MP2}}(r \rightarrow \infty) = 0$ has been proven to be incorrect.

The divergence of v_c^{MP2} originates from the presence of unoccupied states in E_c^{MP2} . This can be directly illustrated by consideration of the Krieger-Li-Iafate (KLI) approximation [11,17] to v_c^{MP2} ,

denominator of Eq. (8): By contrast, the r dependence of the numerator is dominated by the more delocalized unoccupied states. A closer analysis of Eq. (8) shows that v_c^{KLI} diverges nearly as strongly as $\exp[\sqrt{-2\epsilon_F}r]$.

The two previous examples either rely on a (necessarily incomplete) numerical evaluation or on the assumption of the accuracy of the KLI approximation. A rigorous statement, however, can be made for the model functional

$$E_c^{(CA)} = \frac{e^4}{2} \left\{ \sum_{\epsilon_i, \epsilon_j, \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{(ij||kl)[(kl||ji) - (kl||ij)]}{\epsilon_F - \epsilon_{F+1}} \right. \\ \left. + \sum_{\epsilon_i, \epsilon_j \leq \epsilon_F} \frac{(ij||ij) - (ij||ji)}{\epsilon_F - \epsilon_{F+1}} \right\}, \\ (ij||kl) = \int d^3 r_1 \int d^3 r_2 \frac{\phi_i^\dagger(\mathbf{r}_1) \phi_k(\mathbf{r}_1) \phi_j^\dagger(\mathbf{r}_2) \phi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|^2}. \quad (9)$$

$E_c^{(CA)}$ is obtained from E_c^{MP2} by a closure approximation (CA) and represents the most simple strict bound to E_c^{MP2} , $|E_c^{MP2}| < |E_c^{(CA)}|$. $E_c^{(CA)}$ only depends on the occupied states plus the eigenvalues of the highest occupied (F) and the lowest unoccupied state ($F + 1$). For a spherical sys-

tem with a discrete spectrum, Eq. (9) leads to an inhomogeneity, which falls off asymptotically as

$$\lim_{r \rightarrow \infty} Q_c^{(CA)}(r) = |\varphi_{F+1}(r)|^2 \frac{\partial E_c^{(CA)}}{\partial \epsilon_{F+1}}. \quad (10)$$

This behavior clearly does not agree with the $|\varphi_F|^2$ decay of the left-hand side of the OPM equation, Eq. (6). Consequently, $v_c^{(CA)}$ must diverge. This model functional thus demonstrates explicitly that for functionals which depend on excited states the OPM does not necessarily lead to a physically meaningful potential.

The problematic character of v_c^{MP2} is underscored by an analytical result for He-like systems, which has been obtained by Levy *et al.* [18],

$$v_c^{MP2}(\mathbf{r}) = \frac{1}{2n(\mathbf{r})} \left\{ \int d^3 r' \Psi_1^*(\mathbf{r}', \mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \Phi_0(\mathbf{r}', \mathbf{r}) + \int d^3 r' \tilde{\Psi}_1^*(\mathbf{r}', \mathbf{r}) [\hat{H}_1(\mathbf{r}', \mathbf{r}) - E_1] \Phi_0(\mathbf{r}', \mathbf{r}) \right\} \\ - \frac{1}{2} \int d^3 r' \int d^3 r'' \frac{\tilde{\Psi}_1^*(\mathbf{r}', \mathbf{r}'') \Phi_0(\mathbf{r}', \mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} - \frac{1}{4n} \nabla \cdot \left\{ \nabla t - t \frac{\nabla n}{n} \right\} + \text{c.c.}, \quad (11)$$

$$t(\mathbf{r}) = \int d^3 r' \tilde{\Psi}_1^*(\mathbf{r}, \mathbf{r}') \Phi_0(\mathbf{r}, \mathbf{r}').$$

Here Φ_0 represents the ground state of the auxiliary non-interacting KS system and

$$\Psi_1(\mathbf{r}, \mathbf{r}') = \sum_{0 < k < l} \Phi_{kl}(\mathbf{r}, \mathbf{r}') \frac{\langle kl | \hat{H}_1 | \Phi_0 \rangle}{2\epsilon_0 - \epsilon_k - \epsilon_l} \quad (12)$$

is the first order correction to Φ_0 with respect to the Hamiltonian $\hat{H}_1 = e^2/|\mathbf{r}_1 - \mathbf{r}_2| - \sum_{i=1}^2 [v_{KS}(\mathbf{r}_i) - v_{ext}(\mathbf{r}_i)]$, which connects the KS system to the full interacting many-body problem. Φ_{kl} denotes the two-particle basis states built from the KS orbitals and $E_1 = \langle \Phi_0 | \hat{H}_1 | \Phi_0 \rangle$. $\tilde{\Psi}_1$ is obtained from Eq. (12) after replacement of \hat{H}_1 by $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ only. As occupied states are more localized than excited levels, the density in the denominator of (11)

decays faster than the numerator which depends on the Ψ_1 and $\tilde{\Psi}_1$. Thus inspection of Eq. (11) confirms the result of an exponentially diverging v_c^{MP2} .

We now recast (2) in an alternative form in order to circumvent the difficulties encountered with the rigorous solution of (3) for E_c^{MP2} , starting from the individual pair-correlation energies

$$e_{ij}^{MP2} = \frac{1}{2} \sum_{\epsilon_F < \epsilon_k, \epsilon_l} \frac{(ij||kl)[(kl||ij) - (kl||ji)]}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l}. \quad (13)$$

The excited states in e_{ij}^{MP2} can be eliminated by a closure approximation, in which the energy denominator is replaced by a suitable, yet unspecified mean value $\Delta\epsilon$,

$$e_{ij}^{CA} = \frac{1}{2} \frac{1}{\Delta\epsilon} \left\{ (ij||ij) - (ij||ji) \right. \\ \left. + \sum_{\epsilon_k, \epsilon_l \leq \epsilon_F} (ij||kl)[(kl||ji) - (kl||ij)] \right\}. \quad (14)$$

With the help of e_{ij}^{CA} , E_c^{MP2} can be rewritten as

$$E_c^{MP2} = \sum_{\epsilon_i, \epsilon_j \leq \epsilon_F} w_{ij} e_{ij}^{CA}; \quad w_{ij} = e_{ij}^{MP2} / e_{ij}^{CA}. \quad (15)$$

Note that the arbitrary constant $\Delta\epsilon$ drops out, so that no approximation is made for the energy. For the calculation of an approximate v_c , however, the weights w_{ij} may be understood as numbers, rather than as functionals of the ϕ_k and ϵ_k . The potential $v_c^{(CA)}$ resulting from solution of (3) with fixed w_{ij} for the He and Ne atoms is displayed in Figs. 3 and 4. Also shown are the exact v_c [14], the

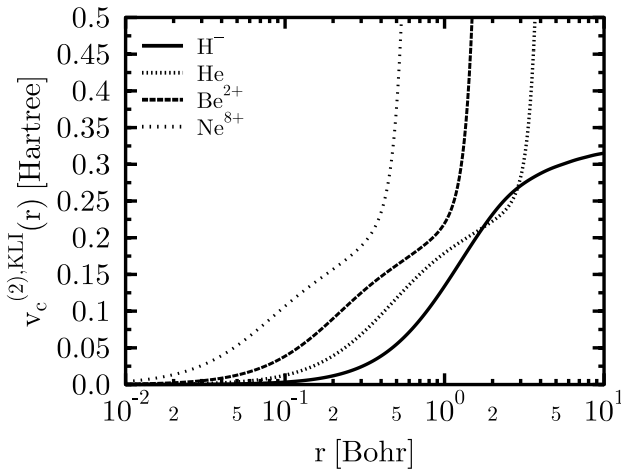


FIG. 2. v_c^{KLI} , Eq. (8), for selected $2e$ systems.

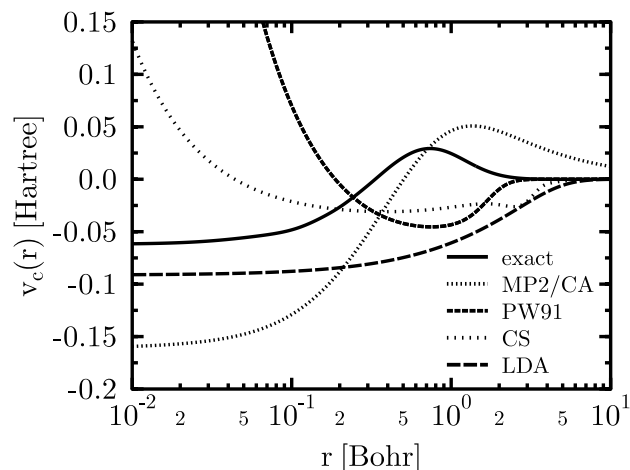


FIG. 3. Correlation potential of He: Exact v_c [14] versus LDA, PW91-GGA [5], and CS [8] results as well as $v_c^{(CA)}$ (MP2-CA).

local density approximation (LDA), the PW91-GGA [5] and CS [8] approximation (all v_c have been evaluated with the eigenfunctions corresponding the exact xc potential [14]). It is immediately obvious that neither the LDA, nor the GGA or the CS potentials reproduce the shell structure of the exact v_c . On the other hand, $v_c^{(CA)}$ appears to be the first DFT potential, which at least qualitatively follows the exact v_c . Figures 3 and 4 can thus be interpreted as an encouraging result, reflecting the systematic origin of E_c^{MP2} . However, it is also obvious that $v_c^{(CA)}$ overestimates the shell structure. In addition, $v_c^{(CA)}$ asymptotically decays as a/r with $0 < a < 1$, which is much slower than the $\sim 1/r^4$ behavior of the exact v_c [19] and thus leads to an unphysical repulsion in the bond region.

In summary, we have shown in a variety of ways that the correlation potential corresponding to E_c^{MP2} diverges for finite systems. Consequently, a direct self-consistent application of E_c^{MP2} is not possible even for systems with a sizable gap at the Fermi surface, for which second order perturbation theory gives reasonable values for E_c . This failure has been traced to the occurrence of unoccupied KS states in E_c^{MP2} . In view of this fact it appears questionable whether higher order perturbation theory or semiempirical resummations of the perturbation series based on E_c^{MP2} [3] can remedy this problem. On the other hand, an approximate evaluation of v_c^{MP2} , which eliminates the explicit presence of the unoccupied states, yields promising results in the innershell region. This situation is reminiscent of the failure of the second order gradient expansion (GE) for E_x to produce a finite v_x in the asymptotic regime, which suggests a modification of v_c^{MP2} in analogy to the transition from the GE to the GGA. Such a procedure could start from $v_c^{(CA)}$, using Slater integrals as the main building blocks. In any case, the present study emphasizes the importance of analyzing v_c , which is a much more sensitive quantity than the aggregate energy.

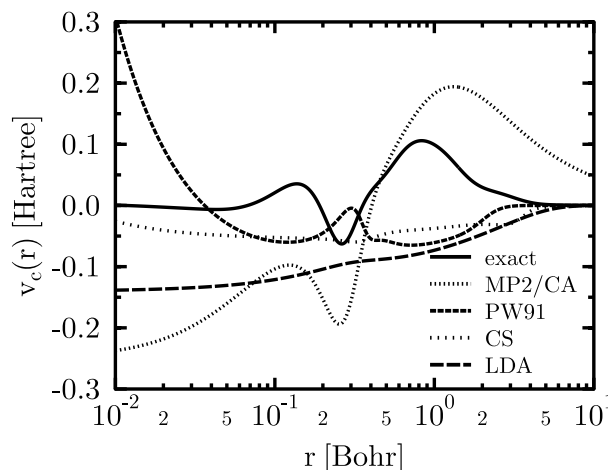


FIG. 4. Same as in Fig. 3 for Ne.

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