

Avoiding asymptotic divergence of the potential from orbital- and energy-dependent exchange-correlation functionals

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Abstract

We investigate the asymptotic behavior of the exchange-correlation potentials deriving from orbital- and energy-dependent (OED) functionals potentially able to describe van der Waals interactions. We take some simple functionals based on the adiabatic connection fluctuation-dissipation (ACFD) theorem as examples. Although the potentials deriving from arbitrary OED functionals can be expected to diverge asymptotically, we find that these ACFD potentials are in fact well-behaved. They indeed depend on Kohn-Sham orbitals and energies only through the Kohn-Sham Green function, allowing for complete analytical treatment. However, the dependence on the empty Kohn-Sham orbitals and energies must be treated with care. We discuss some precautions to be taken for practical calculation of these potentials. Last, we introduce approximate potentials, that are much simpler to compute than the exact ones, but are hopefully still quite accurate.

Keywords: Density Functional Theory, Exchange-correlation potentials, van der Waals interactions

I. INTRODUCTION

The Kohn-Sham¹ (KS) implementation of density functional theory^{2,3} (DFT) has now emerged as a powerful tool to calculate the ground-state properties of molecules and solids. The success of DFT results from a long-standing effort to improve the approximations for the exchange-correlation energy $E_{xc}[n]$, a functional of the electronic density $n(\mathbf{r})$. The simplest approximations for $E_{xc}[n]$, such as the local density approximation² (LDA), or the generalized gradients approximations⁴ (GGA's), are *explicit* functionals of the density. As such, they are very easy to compute, while still giving a realistic account of the structural and electronic properties of many materials and molecules. However, the LDA and GGA's have known shortcomings⁵. For example, they do not describe van der Waals interactions between distant subsystems, and do not achieve chemical accuracy in predicting molecular dissociation energies. Moreover, the LDA and GGA's exchange-correlation potentials, $v_{xc}(\mathbf{r}) = \delta E_{xc}[n]/\delta n(\mathbf{r})$, decay exponentially far from a finite system instead of having the expected $-1/r$ behavior⁶. As a consequence, there are only a few bound unoccupied KS states (no Rydberg series in atoms, negative ions not even bound), while the LDA and GGA's ionization energies are consistently too low. This is clearly a bad starting point⁷ for time-dependent DFT (TDDFT)^{8,9} calculations of electronic excitations.

One way to improve over the LDA and GGA's is to make use of the exact exchange functional $E_x[n]$:

$$E_x[n] = - \sum_{j=1}^{N/2} \sum_{k=1}^{N/2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\varphi_j^*(\mathbf{r})\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (1)$$

where N is the number of electrons (we restrict ourselves to spin-compensated systems). The exchange energy is an explicit functional of the occupied KS orbitals $\varphi_i(\mathbf{r})$ and thus only an *implicit* functional of the density. Taking the functional derivative of $E_x[n]$ with respect to the density¹⁰ hence now yields an integral equation for $v_x(\mathbf{r})$, known as the exchange-only optimized effective potential (x-OEP) equation¹⁰⁻¹³. The exchange potential $v_x(\mathbf{r})$ can be shown to have the expected $-1/r$ behavior in finite systems^{10,13}, thus improving the overall quality of the KS spectrum with respect to the LDA and GGA's. However, the exchange-only theory is usually not accurate enough, as it completely misses correlations. Mixing exact exchange with LDA-like exchange and correlation performs better¹⁴, but still not systematically within chemical accuracy.

The obvious step beyond exact exchange is to design approximate E_{xc} 's that are functionals of the occupied as well as empty KS orbitals $\varphi_i(\mathbf{r})$ and energies ε_i [orbital- and energy-dependent (OED) functionals]. There are many ways to achieve this, including standard many-body perturbation theory^{15,16} (MBPT), Görling-Levy perturbation theory¹⁷ (GLPT), or the adiabatic-connection fluctuation-dissipation (ACFD) theorem¹⁸. The latter will be discussed in more detail in section II. An example of such OED functional is the random-phase approximation (RPA) for the correlation energy $E_c[n]$:

$$E_c^{\text{RPA}}[n] = \frac{1}{2} \int \frac{du}{2\pi} \text{Tr} \{ \ln[1 - \chi_0(iu)\nu] + \chi_0(iu)\nu \}, \quad (2)$$

where $\nu(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|$ and $\chi_0(\mathbf{r}, \mathbf{r}'; iu)$ is the imaginary frequency¹⁹ KS density-density response function ($n_j = 2$ for the occupied and $n_j = 0$ for the empty KS states):

$$\chi_0(\mathbf{r}, \mathbf{r}'; iu) = \sum_j \sum_k \frac{n_j - n_k}{iu + \varepsilon_j - \varepsilon_k} \varphi_j^*(\mathbf{r}) \varphi_k(\mathbf{r}) \varphi_k^*(\mathbf{r}') \varphi_j(\mathbf{r}'), \quad (3)$$

The integral over u in Eq. (2) runs over the whole imaginary frequency axis and the symbol Tr stands for the trace $\text{Tr}\{AB\} = \int d^3\mathbf{r} \int d^3\mathbf{r}' A(\mathbf{r}, \mathbf{r}') B(\mathbf{r}', \mathbf{r})$. The RPA is of course much more demanding than the LDA and GGA's, but is within the reach of present computers. The dissociation curves of simple diatomic molecules have indeed been calculated by Furche²⁰, by Fuchs and Gonze^{21,22}, and by Aryasetiawan *et al.*²³, though not self-consistently (using LDA, GGA, or x-OEP orbitals and energies as input). The total energy of bulk Si and Na has also been calculated by T. Miyake *et al.*²⁴ as a function of the lattice constant. The RPA accounts for van der Waals interactions and properly dissociates H_2 for example (without the need for spin polarization), though the dissociation curve still shows an undesirable bump at intermediate distances²².

The RPA $v_{xc}(\mathbf{r})$ also satisfies an integral equation known as the linear-response Sham-Schlüter (LRSS) equation^{15,25}, that will be derived in section III. There has been early calculations of the RPA potential, first in bulk Si by Godby *et al.*²⁶ (again starting from LDA orbitals and energies and not iterating up to self-consistency), then by Eguiluz *et al.*²⁷ for a jellium surface. OED functionals and their potentials have attracted much more attention recently²⁸, following the rapid increase in computational power. However, it has been pointed out that the potentials deriving from *arbitrary* OED functionals could be asymptotically divergent in finite systems²⁹. As a matter of fact, the second-order GLPT potential itself was numerically found to blow up in the He atom³⁰, which raised serious doubts about the

significance of OED functionals. Though, we have analytically investigated the asymptotic behavior of some characteristic OED potentials, such as the RPA^{31,32}, second-order GLPT³², and other ACFD potentials³³. We find, at variance with Ref. 30, that these potentials are well-behaved, and that their asymptotic behavior reveals much physics. However, the dependence on the empty KS orbitals and energies must be treated carefully to avoid any numerical instability.

In this paper, we provide an overview of the results presented in Refs. 32 and 33, and discuss practical implications for both *i*) the calculation of the OED potentials and *ii*) the design of OED approximations for the exchange-correlation energy. We notably focus on avoiding divergent-like behavior in actual calculations. The paper is organized as follows: in section II, we introduce a few OED functionals based on the ACFD theorem. Next, in section III, we derive the associated exchange-correlation potentials, in a way that emphasizes that these OED approximations are explicit functionals of the KS Green function and as such are not *arbitrary* functionals of the KS orbitals and energies. This proves to be a key for the non-divergent behavior of $v_{xc}(\mathbf{r})$ (though this is by no way a necessary nor a sufficient condition). In section IV, we discuss the asymptotic behavior these potentials, treating He as a simple case. Then, in section V, we discuss practical implications of these results, before introducing approximate potentials in section VI.

II. OED FUNCTIONALS WITHIN THE ACFD FRAMEWORK

As pointed out in the introduction, there are many routes towards OED functionals. We will focus here on the adiabatic-connection fluctuation-dissipation framework¹⁸. We will notably introduce a set of four functionals to be compared later on the He atom. Further details on the ACFD functionals can be found in Ref. 32.

The basic idea of the ACFD theorem is to establish a connection between the KS and the true, interacting Hamiltonian of a system. To that end, we adiabatically switch on the interaction $\lambda\nu(\mathbf{r}, \mathbf{r}')$ between electrons, while simultaneously adjusting the local potential $v_\lambda(\mathbf{r})$ so that the density remains unchanged. $v_{\lambda=0}(\mathbf{r})$ is thus the KS potential $v_{KS}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{h}}(\mathbf{r}) + v_{xc}(\mathbf{r})$, while $v_{\lambda=1}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r})$, where $v_{\text{ext}}(\mathbf{r})$ and $v_{\text{h}}(\mathbf{r})$ are respectively the external (ionic) and Hartree potentials. Application of the Hellmann-Feynman and

fluctuation-dissipation theorems along this adiabatic connection path then yields:

$$E_c[n] = -\frac{1}{2} \int_0^1 d\lambda \int \frac{du}{2\pi} \text{Tr} \{ \nu [\chi_\lambda(iu) - \chi_0(iu)] \}, \quad (4)$$

where $\chi_\lambda(\mathbf{r}, \mathbf{r}'; iu)$ is the interacting density-density response function at coupling constant λ . This equation, that formally yields the *exact* correlation energy, will serve as the starting point for various non-local approximations, depending on the assumptions made for $\chi_\lambda(iu)$. One of the simplest approximation is the so-called RPA introduced in section I. Let us indeed consider a perturbation $\delta v_{\text{ext}}(\mathbf{r}; iu)$. We basically want to calculate the linear response of the density $\delta n(iu) = \chi_\lambda(iu) \delta v_{\text{ext}}(iu)$. In the RPA, we assume that the electrons respond (as non-interacting particles) to the bare perturbation $\delta v_{\text{ext}}(\mathbf{r}; iu)$ plus the variation of the Hartree potential $\delta v_{\text{h}}(iu) = \lambda \nu \delta n(iu)$. Hence, $\delta n(iu) = \chi_0(iu) [\delta v_{\text{ext}}(iu) + \lambda \nu \delta n(iu)]$, that is:

$$\chi_\lambda^{\text{RPA}}(iu) = [1 - \lambda \chi_0(iu) \nu]^{-1} \chi_0(iu). \quad (5)$$

The integration over the coupling constant λ can then be done analytically in Eq. (4), which yields Eq. (2) for $E_c[n]$. If needed, further exchange and correlation effects can be included in Eq. (5) with the help of a TDDFT kernel³⁴ $f_{\text{xc},\lambda}(\mathbf{r}, \mathbf{r}'; iu)$ such as the adiabatic LDA³⁵:

$$\chi_\lambda(iu) = \{1 - \chi_0(iu) [\lambda \nu + f_{\text{xc},\lambda}(iu)]\}^{-1} \chi_0(iu). \quad (6)$$

An overview of some available TDDFT kernels as well as scaling relations between $f_{\text{xc},\lambda}(iu)$ and $f_{\text{xc},\lambda=1}(iu)$ can be found in Ref. 36.

In a system with weak screening such as a light atom, we can hopefully get reasonable RPA energies making a second order³⁷ (in ν) approximation for $E_c[n]$, which amounts to replace $\chi_\lambda^{\text{RPA}}(iu)$ with $\chi_\lambda^{\text{RPA}(2)}(iu) = \chi_0(iu) + \lambda \chi_0(iu) \nu \chi_0(iu)$. Integration over the coupling constant and frequency then yields:

$$E_c^{\text{RPA}(2)}[n] = 2 \sum_{i,j=1}^{N/2} \sum_{k,l>N/2} \frac{|\langle \varphi_i \varphi_k^* | \nu | \varphi_j \varphi_l^* \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_k - \varepsilon_l}. \quad (7)$$

This expression, that is much simpler to compute than the full RPA correlation energy, clearly emphasizes the explicit dependence of E_c on the empty KS orbitals and energies.

One of the obvious (but not the only) deficiency of the RPA is that each electron interacts with its own contribution to the variation of the Hartree potential in Eq. (5). As a consequence, the RPA total energies are too negative (too much correlation), though iso-electronic RPA total energy *differences* are believed to be quite accurate³⁸. The deficiencies

of the RPA can be partly circumvented using the exact-exchange approximation for $f_{xc,\lambda}(iu)$ [see Eq. (6)]. Though very complex in general³⁹, the exact-exchange kernel $f_{x,\lambda}(iu)$ assumes a very simple form in two-electron systems such as the He atom we will deal with in section IV. We can recover this X2E (exact eXchange kernel for 2 Electrons) result using the following argument to calculate $\chi_\lambda(iu)$: we now assume that each electron responds to the bare perturbation $\delta v_{\text{ext}}(\mathbf{r}; iu)$ plus the variation $\delta \bar{v}(iu) = \frac{1}{2}\lambda\nu\delta n(iu)$ of the average potential created by the other electron only. We thus get:

$$\chi_\lambda^{\text{X2E}}(iu) = \left[1 - \frac{\lambda}{2}\chi_0(iu)\nu \right]^{-1} \chi_0(iu). \quad (8)$$

Integration over the coupling constant then yields:

$$E_c^{\text{X2E}}[n] = \int \frac{du}{2\pi} \text{Tr} \left\{ \ln \left[1 - \frac{1}{2}\chi_0(iu)\nu \right] + \frac{1}{2}\chi_0(iu)\nu \right\}. \quad (9)$$

If we further make the second-order approximation $\chi_\lambda^{\text{X2E(2)}}(iu) = \chi_0(iu) + \frac{1}{2}\lambda\chi_0(iu)\nu\chi_0(iu)$, we finally end up with:

$$E_c^{\text{X2E(2)}}[n] = \frac{1}{2}E_c^{\text{RPA(2)}}[n]. \quad (10)$$

The RPA, RPA(2), X2E and X2E(2) functionals will be compared on the He atom in section IV. Note that these four functionals can also be obtained by other means such as MBPT [X2E(2) for example is equivalent to the second-order approximation discussed in Ref. 32, though the latter applies to an arbitrary number of electrons]. As a matter of fact, it will later prove convenient to introduce some MBPT quantities such as the KS Green function $G_0(\mathbf{r}, \mathbf{r}'; iu)$ or the self-energy $\Sigma_{xc}(\mathbf{r}, \mathbf{r}'; iu)$. The former is defined on the imaginary frequency axis by:

$$G_0(\mathbf{r}, \mathbf{r}'; iu) = \sum_j \frac{\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r}')}{iu - \varepsilon_j}, \quad (11)$$

the chemical potential $\mu = 0$ being taken as the reference of energies. The point we want to emphasize now is that the four approximations above are not arbitrary functionals of the KS orbitals and energies, but are explicit functionals of the KS density-density response function $\chi_0(iu)$ or KS Green function $G_0(iu)$. Indeed, $\chi_0(iu)$ is itself a functional of $G_0(iu)$ through the relation:

$$\chi_0(\mathbf{r}, \mathbf{r}'; iu) = 2 \int \frac{dv}{2\pi} G_0(\mathbf{r}, \mathbf{r}'; iu + iv)G_0(\mathbf{r}', \mathbf{r}; iv). \quad (12)$$

Furthermore, the exchange energy [Eq. (1)] can also be written as a functional of $G_0(iu)$:

$$E_x[n] = - \int \frac{du}{2\pi} e^{iu\delta} \int \frac{dv}{2\pi} e^{iv\delta'} \int d^3\mathbf{r} \int d^3\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}'; iu) G_0(\mathbf{r}', \mathbf{r}; iv) \nu(\mathbf{r}, \mathbf{r}'), \quad (13)$$

where the limits $\delta \rightarrow 0^+$, $\delta' \rightarrow 0^+$ are implied. In the next section, we will make use of this explicit dependence on $G_0(iu)$ to calculate the exchange-correlation potential.

III. THE EXCHANGE-CORRELATION POTENTIAL

In this section, we derive the exchange-correlation potentials associated with the RPA, RPA(2), X2E and X2E(2) functionals. As stated above, we proceed with the dependence on the KS Green function G_0 rather than (as usual) the dependence on the KS orbitals and energies. Indeed, since G_0 is a functional of the KS potential $v_{\text{KS}}(\mathbf{r})$, we can apply the chain rule twice and write:

$$\begin{aligned} v_{\text{xc}}(\mathbf{r}) &= \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \\ &= \int du \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_3 \frac{\delta E_{\text{xc}}[G_0]}{\delta G_0(\mathbf{r}_1, \mathbf{r}_2; iu)} \times \frac{\delta G_0(\mathbf{r}_1, \mathbf{r}_2; iu)}{\delta v_{\text{KS}}(\mathbf{r}_3)} \times \frac{\delta v_{\text{KS}}(\mathbf{r}_3)}{\delta n(\mathbf{r})}. \end{aligned} \quad (14)$$

The last derivative on the right-hand side of Eq. (14) is just the inverse of the static KS density-density response function⁴⁰, $\chi_0^{-1}(\mathbf{r}_3, \mathbf{r}; iu = 0)$ [since by definition $\chi_0(\mathbf{r}, \mathbf{r}'; iu = 0) = \delta n(\mathbf{r})/\delta v_{\text{KS}}(\mathbf{r}')$]. As for the first derivative, we have (in a compact, matrix notation):

$$\frac{\delta[G_0(iu)G_0^{-1}(iu)]}{\delta v_{\text{KS}}(\mathbf{r})} = 0 \Rightarrow \frac{\delta G_0(iu)}{\delta v_{\text{KS}}(\mathbf{r})} = -G_0(iu) \frac{\delta G_0^{-1}(iu)}{\delta v_{\text{KS}}(\mathbf{r})} G_0(iu). \quad (15)$$

Moreover, the functional derivative of the inverse Green function $G_0^{-1}(iu) = iu - T - v_{\text{KS}}$ (T being the kinetic energy operator) is:

$$\frac{\delta G_0^{-1}(\mathbf{r}_1, \mathbf{r}_2; iu)}{\delta v_{\text{KS}}(\mathbf{r})} = -\delta(\mathbf{r} - \mathbf{r}_1)\delta(\mathbf{r} - \mathbf{r}_2). \quad (16)$$

Backward substitution then yields:

$$v_{\text{xc}}(\mathbf{r}) = \int d^3\mathbf{r}' \chi_0^{-1}(\mathbf{r}, \mathbf{r}'; iu = 0) \rho_{\text{xc}}(\mathbf{r}'), \quad (17)$$

where:

$$\rho_{\text{xc}}(\mathbf{r}) = \int du \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 G_0(\mathbf{r}, \mathbf{r}_1; iu) \frac{\delta E_{\text{xc}}[G_0]}{\delta G_0(\mathbf{r}_1, \mathbf{r}_2; iu)} G_0(\mathbf{r}_2, \mathbf{r}; iu). \quad (18)$$

This result applies to any approximation for the exchange-correlation energy that is an explicit functional of the KS Green function only. We are thus now left with the calculation of the derivative of E_{xc} with respect to G_0 . The derivative of E_x is twice (because of spin) $\tilde{\Sigma}_x(\mathbf{r}, \mathbf{r}')/(2\pi)$, where $\tilde{\Sigma}_x(\mathbf{r}, \mathbf{r}')$ is the exchange-only self-energy:

$$\tilde{\Sigma}_x(\mathbf{r}, \mathbf{r}') = - \int \frac{du}{2\pi} e^{iu\delta} G_0(\mathbf{r}, \mathbf{r}'; iu) \nu(\mathbf{r}, \mathbf{r}') = - \sum_{j=1}^{N/2} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \nu(\mathbf{r}, \mathbf{r}'). \quad (19)$$

As for the RPA, RPA(2), X2E and X2E(2) functionals we get, after a few manipulations [see details in Ref. 33]:

$$\frac{\delta E_c[G_0]}{\delta G_0(\mathbf{r}, \mathbf{r}'; iu)} = \frac{2}{2\pi} \tilde{\Sigma}_c(\mathbf{r}, \mathbf{r}'; iu), \quad (20)$$

where $\tilde{\Sigma}_c(\mathbf{r}, \mathbf{r}'; iu)$ is the correlation part of an effective GW -like self-energy⁴¹:

$$\tilde{\Sigma}_c(\mathbf{r}, \mathbf{r}'; iu) = - \int \frac{dv}{2\pi} G_0(\mathbf{r}, \mathbf{r}'; iu + iv) [\tilde{W}(\mathbf{r}, \mathbf{r}'; iv) - \nu(\mathbf{r}, \mathbf{r}')], \quad (21)$$

and $\tilde{W}(\mathbf{r}, \mathbf{r}'; iu)$ is an effective screened Coulomb interaction. It reads $\tilde{W}(iu) = \nu + \nu \tilde{\chi}(iu) \nu$, with:

$$\tilde{\chi}^{\text{RPA}}(\mathbf{r}, \mathbf{r}'; iu) = \chi_{\lambda=1}^{\text{RPA}}(\mathbf{r}, \mathbf{r}'; iu) \text{ for RPA}, \quad (22a)$$

$$\tilde{\chi}^{\text{RPA(2)}}(\mathbf{r}, \mathbf{r}'; iu) = \chi_0(\mathbf{r}, \mathbf{r}'; iu) \text{ for RPA(2)}, \quad (22b)$$

$$\tilde{\chi}^{\text{X2E}}(\mathbf{r}, \mathbf{r}'; iu) = \frac{1}{2} \chi_{\lambda=1}^{\text{X2E}}(\mathbf{r}, \mathbf{r}'; iu) \text{ for X2E}, \quad (22c)$$

$$\tilde{\chi}^{\text{X2E(2)}}(\mathbf{r}, \mathbf{r}'; iu) = \frac{1}{2} \chi_0(\mathbf{r}, \mathbf{r}'; iu) \text{ for X2E(2)}. \quad (22d)$$

Moreover, the exchange-correlation potential deriving from these functionals can also be cast in a more familiar form, applying $\chi_0(iu = 0)$ on both sides of Eq. (17) then using Eq. (12):

$$0 = \int \frac{du}{2\pi} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 G_0(\mathbf{r}, \mathbf{r}_1; iu) \left\{ \tilde{\Sigma}_{xc}(\mathbf{r}_1, \mathbf{r}_2; iu) - v_{xc}(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \right\} G_0(\mathbf{r}_2, \mathbf{r}; iu), \quad (23)$$

where:

$$\tilde{\Sigma}_{xc}(\mathbf{r}, \mathbf{r}'; iu) = - \int \frac{dv}{2\pi} e^{iv\delta} G_0(\mathbf{r}, \mathbf{r}'; iu + iv) \tilde{W}(\mathbf{r}, \mathbf{r}'; iv). \quad (24)$$

This equation is known as the linear-response Sham-Schlüter equation^{15,25}. Note that the potential is defined by Eqs. (17) and (23) only up to an additive constant, because⁴² $\int d^3\mathbf{r} \chi_0(\mathbf{r}, \mathbf{r}'; iu) = 0$.

In the exchange-only approximation for the self-energy [Eq. (19)], the LRSS equation is equivalent to the x-OEP equation^{10,13} that yields the exchange potential $v_x(\mathbf{r}) =$

$\delta E_x[n]/\delta n(\mathbf{r})$. The *self-consistent* exchange potential however depends on the choice for the correlation functional (since it depends on the actual KS orbitals). The so-called x-OEP potential is the self-consistent solution of the x-OEP equation without any correlation [zero E_c and $v_c(\mathbf{r})$]. In the usual *GW* approximation⁴¹ for the self-energy [Eqs. (22a) and (24)], the LRSS equation yields the RPA exchange-correlation potential. The numerical solution of the LRSS equation is of course quite involved, since both the inverse of $\chi_0(iu = 0)$ and the self-energy have to be calculated (a scheme avoiding the calculation of the inverse of $\chi_0(iu = 0)$ has however been proposed recently by Kümmel and Perdew⁴³). Nonetheless, the RPA potential for example has been calculated in bulk Si by Godby *et al.*²⁶ and for a jellium surface by Eguiluz *et al.*²⁷ In section VI, we will discuss approximate solutions of the LRSS equation, that are much simpler to compute.

IV. ASYMPTOTIC BEHAVIOR OF THE ACFD POTENTIALS

In this section, we discuss the asymptotic behavior of the RPA, RPA(2), X2E and X2E(2) potentials. We consider here the He atom as a test case.

Let us first recall the asymptotic behavior of the *exact* exchange-correlation potential in the He atom⁶:

$$v_{xc}(\mathbf{r}) = -\frac{1}{r} - \frac{\tilde{\alpha}}{2r^4} + \mathcal{O}\left(\frac{1}{r^5}\right), \quad (25)$$

where $\tilde{\alpha} = \alpha_{\text{He}^+} = 9/32$ a.u. is the static polarizability of the He^+ ion. The $-1/r$ term [that comes from $v_x(\mathbf{r})$] is the bare potential felt by an electron dragged away from the He atom, while the $\propto 1/r^4$ term [that comes from $v_c(\mathbf{r})$] arises from the polarization of the resulting ion.

In Ref. 33, we have carefully investigated the asymptotic behavior of the solutions of the LRSS equation. We find, for a *GW*-like self-energy such as Eq. (24), that the asymptotic behavior of the exchange-correlation potential is indeed given by Eq. (25), but with an effective polarizability $\tilde{\alpha}$ now defined by:

$$\tilde{\alpha} = - \int d^3\mathbf{r} \int d^3\mathbf{r}' z z' \tilde{\chi}(\mathbf{r}, \mathbf{r}'; iu = 0), \quad (26)$$

where $\tilde{\chi}(iu)$ is given by Eq. (22) for each of the four functionals.

The RPA, RPA(2), X2E and X2E(2) correlations energies of the He atom, as well as estimates of the corresponding $\tilde{\alpha}$'s are reported in table I. The correlations energies were

evaluated in a plane-wave basis set with the ABINIT package^{21,44}, using x-OEP KS orbitals and energies as input. The $\tilde{\alpha}$'s are borrowed or deduced from Ref. 7, and were calculated in the exact exchange-correlation potential of He⁴⁵. These values for E_c and $\tilde{\alpha}$ should be quite close to the self-consistent ones, the correlation potential of the He atom being one order of magnitude smaller than the exchange potential.

Let us comment on these results. As expected, the RPA and RPA(2) correlation energies are found much too negative, which can be mainly traced back to the self-correlation error made in the calculation of the interacting density-density response function (see section II). Indeed, the X2E and X2E(2) approximations, that are free of this self-correlation error, yield much better results for E_c . $\tilde{\alpha}$ is also improved by X2E and X2E(2), but not as much as E_c . It thus constitutes a more stringent test of the quality of the functionals. $\tilde{\alpha}$ also unveils much physics. $\tilde{\alpha}^{\text{RPA(2)}}$ and $\tilde{\alpha}^{\text{RPA}}$ are respectively the non-interacting KS and interacting RPA polarizabilities of the He atom, which is consistent with these approximations but quite far from the polarizability of He⁺. $\tilde{\chi}^{\text{RPA}}$ and $\tilde{\chi}^{\text{RPA(2)}}$ indeed account for the response of two electrons, whereas one would expect $\tilde{\chi}$ in Eq. (26) to describe the response of only one electron (and to be presumably as close as possible to the density-density response function of the He⁺ ion). $\tilde{\chi}^{\text{X2E}}$ and $\tilde{\chi}^{\text{X2E(2)}}$, that are *half* a two-electron response function and account in that way for the response of only one electron, are a clear step towards the expected result. However, $\tilde{\chi}^{\text{X2E}}$ is still far from the response of the He⁺ ion to a test charge. First, it misses the orbital relaxation upon ionization. Second, the electron still incorrectly interacts with another 1s electron (since we are only cutting a two-electron response function in half). Further inclusion of correlation through Eq. (6) is thus needed to improve $\tilde{\alpha}$.

Other applications of the RPA to small diatomic molecules (such as H₂ or N₂) or solids (Si, Na) can be found in Refs. 20–24 (Ref. 21 also include X2E results for H₂). Results obtained with similar functionals can moreover be found in Ref. 37.

V. PRACTICAL IMPLICATIONS

In this section, we discuss practical aspects of the calculation of OED potentials. We show that the dependence on the empty KS orbitals and energies has to be treated carefully to avoid any numerical instability.

We should first come back to the usual OEP equation to bring the problem into light.

Indeed, the ACFD functionals of section II can be considered as explicit functionals of the KS orbitals $\varphi_i(\mathbf{r})$ and energies ε_i . Using the chain rule for functional derivatives as well as first-order perturbation theory, we can therefore write down the following OEP equation²⁹ for the exchange-correlation potential $v_{xc}(\mathbf{r})$:

$$v_{xc}(\mathbf{r}) = \int d^3\mathbf{r}' \chi_0^{-1}(\mathbf{r}, \mathbf{r}'; iu = 0) \{Q_{xc}^{(a)}(\mathbf{r}') + Q_c^{(b)}(\mathbf{r}')\}, \quad (27)$$

where $Q_{xc}^{(a)}(\mathbf{r})$ involves the functional derivatives of E_{xc} with respect to the KS orbitals, and $Q_c^{(b)}(\mathbf{r})$ those of E_c with respect to the KS energies⁴⁷:

$$Q_{xc}^{(a)}(\mathbf{r}) = \sum_{j=1}^{\infty} \varphi_j(\mathbf{r}) \int d^3\mathbf{r}' G_j(\mathbf{r}', \mathbf{r}) \frac{\delta E_{xc}[\{\varphi_n, \varepsilon_n\}]}{\delta \varphi_j(\mathbf{r}')} + \text{c.c.} \quad (28a)$$

$$Q_c^{(b)}(\mathbf{r}) = \sum_{j=1}^{\infty} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}) \frac{\partial E_c[\{\varphi_n, \varepsilon_n\}]}{\partial \varepsilon_j}. \quad (28b)$$

$G_j(\mathbf{r}, \mathbf{r}')$ is the reduced Green function:

$$G_j(\mathbf{r}, \mathbf{r}') = \sum_{k \neq j} \frac{\varphi_k(\mathbf{r}) \varphi_k^*(\mathbf{r}')}{\varepsilon_j - \varepsilon_k}. \quad (29)$$

We can further define the potentials $v_{xc}^{(a)}(\mathbf{r})$ and $v_c^{(b)}(\mathbf{r})$ that solve Eq. (27) with either $Q_{xc}^{(a)}(\mathbf{r})$ or $Q_c^{(b)}(\mathbf{r})$ as the right-hand side respectively. Yet $v_{xc}^{(a)}(\mathbf{r})$ and $v_c^{(b)}(\mathbf{r})$ can be shown to diverge asymptotically^{32,48} for most OED functionals, including those of section II. Indeed, $Q_{xc}^{(a/b)}(\mathbf{r})$ can be interpreted as the linear response to the perturbation $v_{xc}^{(a/b)}(\mathbf{r})$ [see Eq. (27)]. However, $Q_{xc}^{(a)}(\mathbf{r})$ and $Q_c^{(b)}(\mathbf{r})$ usually decay very slowly due to the presence of the empty KS orbitals in Eqs. (28). Hence $v_{xc}^{(a)}(\mathbf{r})$ and $v_c^{(b)}(\mathbf{r})$ have to blow up to transfer such a slowly decaying charge far away from the system (at least at the linear response level). In the RPA, RPA(2), X2E and X2E(2) approximations for example, $v_{xc}^{(a)}(\mathbf{r})$ and $v_c^{(b)}(\mathbf{r})$ diverge respectively to $+\infty$ and $-\infty$ when $r \rightarrow \infty$, whereas their sum, $v_{xc}(\mathbf{r})$, is finite. We will just give qualitative arguments that point to how cancellations between $v_{xc}^{(a)}(\mathbf{r})$ and $v_c^{(b)}(\mathbf{r})$ arise here (details can be found in Ref. 32). First, as expected, the OEP equation [Eq. (27)] is equivalent to the LRSS equation [Eq. (23)] for these four functionals. $Q_c^{(b)}(\mathbf{r})$ indeed provides the missing pieces of incomplete sum-over-states in $Q_{xc}^{(a)}(\mathbf{r})$, which then allows to recast the problem in terms of the sole KS Green function G_0 . Now comes the key point: these sums over states, once completed, decay really fast due to destructive interference between KS orbitals – the closure relation $\sum_j \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ is at work here, as

usual when dealing with Green functions. Hence $Q_{xc}(\mathbf{r}) = Q_{xc}^{(a)}(\mathbf{r}) + Q_c^{(b)}(\mathbf{r})$ can be shown to decay much faster than $Q_{xc}^{(a)}(\mathbf{r})$ and $Q_c^{(b)}(\mathbf{r})$, thus allowing for a smooth, finite potential.

This, of course, has important consequences for the design of OED functionals. We should first stress that an explicit dependence on the KS Green function G_0 is not a necessary nor a sufficient condition for a smooth exchange-correlation potential. However, it seems hardly possible to design functionals of the empty KS orbitals that are not also functionals of the empty KS energies. Indeed, one has to ensure proper cancellations between $Q_{xc}^{(a)}(\mathbf{r})$ and $Q_c^{(b)}(\mathbf{r})$, that will likely occur through mutual completion of sum-over-states relationships, as is the case for the four functionals at hand here.

We now turn to the practical implications of these results for the calculation of OED potentials in finite basis sets^{17,49}. We expand the KS orbitals $\varphi_i(\mathbf{r})$ in an orthonormal basis set $\{f_i(\mathbf{r})\}$ ($1 \leq i \leq M_f$), $Q_{xc}(\mathbf{r})$ [or $\rho_{xc}(\mathbf{r})$] and $v_{xc}(\mathbf{r})$ in an orthonormal basis set⁵⁰ $\{g_i(\mathbf{r})\}$ ($1 \leq i \leq M_g$). The LRSS or OEP equation turns into a matrix equation $\boldsymbol{\chi} \cdot \mathbf{v} = \mathbf{Q}$, where \mathbf{v} is the vector with M_g components $v_i = \langle g_i | v_{xc} \rangle$, \mathbf{Q} is the vector with M_g components $Q_i = \langle g_i | Q_{xc} \rangle$, and $\boldsymbol{\chi}$ is the $M_g \times M_g$ matrix with elements $\chi_{ij} = \langle g_i | \chi_0(iu = 0) | g_j \rangle$. $\chi_0(iu = 0)$ and $Q_{xc}(\mathbf{r})$ are still defined by Eqs. (3) and (28), but with the various sum over states now restricted to the M_f available KS states. Although the potential can not diverge in a finite basis set, it can show an odd behavior. At least two precautions must be taken to avoid numerical instabilities. First, one should include as many empty states in $\chi_0(iu = 0)$ as in $Q_{xc}(\mathbf{r})$. Second, the basis functions $g_i(\mathbf{r})$ should be chosen with great care. Of course, they must be orthogonal to the constant function for $\boldsymbol{\chi}$ to be invertible (though this can be handled through the diagonalization of $\boldsymbol{\chi}$, see below). This may however not be sufficient⁴⁹. The point is that the Hohenberg-Kohn (HK) theorem² need not hold in a finite basis set, so that *different* KS potentials may in fact yield the *same* density – then the OED approximations are no more functionals of the density and Eq. (27) does not hold. This happens whenever a linear combination of g_i 's turns out to be orthogonal to the $(N/2)[M_f - (N/2)]$ products of an occupied and an empty KS orbital in a given KS potential (which will always occur if $M_g > (N/2)[M_f - (N/2)]$). The perturbation associated with this linear combination of g_i 's indeed leaves the density unchanged (since the occupied KS orbitals only undergo an unitary transformation), which translates into another zero in the matrix $\boldsymbol{\chi}$. $\boldsymbol{\chi}$ may also have very small (but non zero) eigenvalues. These will be responsible for large, unphysical variations of the exchange-correlation potential that, in

turn, yield small variations of the density [and hopefully small (second-order) variations E_{xc} , at least near self-consistency]. These small eigenvalues should be thrown away, making a diagonalization (or singular value decomposition⁵¹) of the matrix χ before solving the linear system $\chi \cdot v = Q$. This method was used by Eguiluz *et al.*²⁷ to calculate the RPA potential for a jellium surface. The discarded eigen- or singular values must however be carefully chosen.

VI. APPROXIMATE POTENTIALS

The calculation of OED potentials is a very intensive task. In this section, we discuss two approximate solutions of the LRSS equation that are much simpler to compute while being likely of reasonable accuracy. Details can be found in Refs. 32 and 33.

The idea of the first approximation is to drop selected contributions to the potential. Indeed, the integration over frequency in Eq. (23) can be performed closing the contour of integration on the left of the imaginary axis. This contour encloses the poles of G_0 related to the occupied KS states, plus some poles of $\tilde{\Sigma}_{xc}$. If we only keep the contributions of the simple poles coming from both G_0 's, we end up with the following equation for $v_{xc}(\mathbf{r}) \equiv v_{xc,pG}(\mathbf{r})$:

$$\sum_{j=1}^{N/2} \int d^3\mathbf{r}' \varphi_j^*(\mathbf{r}') \left[v_{xc,pG}(\mathbf{r}') - u_{xcj}(\mathbf{r}') \right] G_j(\mathbf{r}', \mathbf{r}) \varphi_j(\mathbf{r}) + \text{c.c.} = 0, \quad (30)$$

where $G_j(\mathbf{r}, \mathbf{r}')$ is defined by Eq. (29) and $u_{xcj}(\mathbf{r})$ is the orbital-dependant potential:

$$u_{xcj}(\mathbf{r}) = \frac{1}{\varphi_j^*(\mathbf{r})} \int d^3\mathbf{r}' \tilde{\Sigma}_{xc}(\mathbf{r}', \mathbf{r}; \varepsilon_j) \varphi_j^*(\mathbf{r}') \quad (31)$$

This equation appears as a generalization of the x-OEP equation^{10,13} to the correlated case, in the sense that it only involves a sum over the occupied KS states [the x-OEP equation is indeed recovered using $\tilde{\Sigma}_x(\mathbf{r}', \mathbf{r})$ in Eq. (31)]. It can be shown that the correction arising from the poles we have neglected decays faster than $v_{xc,pG}(\mathbf{r})$ and has no influence on the energy of the KS highest occupied molecular orbital. Hence $v_{xc,pG}(\mathbf{r})$ has the same asymptotic behavior as the exact solution of the LRSS equation. It also has a clear physical interpretation. Indeed, $v_{xc,pG}(\mathbf{r})$ can be obtained from a “quasiparticle (QP) approximation” to the LRSS equation¹⁵. In this QP approximation, the exchange-correlation potential is calculated so that the first-order variation of the density (computed from the quasiparticle amplitudes) is

zero under the perturbation $\tilde{\Sigma}_{xc} - v_{xc}$ that transforms the KS equation into the QP equation with self-energy $\tilde{\Sigma}_{xc}$. This procedure directly yields⁵² Eq. (30).

The second scheme is based on the use of an approximate $\tilde{\Sigma}_{xc}$, whose prototype is the static COHSEX self-energy⁴¹. This frequency-independent approximation to the *GW* self-energy splits into a statically screened exchange part $\tilde{\Sigma}_{ssex}$ and a static Coulomb hole term $\tilde{\Sigma}_{scoh}$:

$$\tilde{\Sigma}_{ssex}(\mathbf{r}, \mathbf{r}') = - \sum_{j=1}^{N/2} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \tilde{W}(\mathbf{r}, \mathbf{r}'; iu = 0) \quad (32a)$$

$$\tilde{\Sigma}_{scoh}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') \tilde{W}_s(\mathbf{r}, \mathbf{r}; iu = 0), \quad (32b)$$

where $\tilde{W}_s(\mathbf{r}, \mathbf{r}'; iu) = \tilde{W}(\mathbf{r}, \mathbf{r}'; iu) - \nu(\mathbf{r}, \mathbf{r}')$. On one hand, $\tilde{\Sigma}_{ssex}(\mathbf{r}, \mathbf{r}')$ has the same functional form as the exchange-only self-energy [Eq. (19)], but with $\nu(\mathbf{r}, \mathbf{r}')$ replaced by $\tilde{W}(\mathbf{r}, \mathbf{r}'; iu = 0)$. $\tilde{\Sigma}_{scoh}(\mathbf{r}, \mathbf{r}')$ on the other hand is just half the potential felt by an electron at \mathbf{r} and due to the Coulomb hole that forms around it (the factor 1/2 comes from the adiabatic building of this Coulomb hole). Accordingly, the solution of Eq. (23) also splits in two parts $v_{xc}(\mathbf{r}) = v_{ssex}(\mathbf{r}) + v_{scoh}(\mathbf{r})$, where $v_{scoh}(\mathbf{r}) = \frac{1}{2} \tilde{W}_s(\mathbf{r}, \mathbf{r}; iu = 0)$, and $v_{ssex}(\mathbf{r})$ satisfies the same equation as the exchange-only potential with $\nu(\mathbf{r}, \mathbf{r}')$ replaced by $\tilde{W}(\mathbf{r}, \mathbf{r}'; iu = 0)$ [i.e., it satisfies Eq. (30) using $\tilde{\Sigma}_{ssex}$ in Eq. (31)]. Therefore, one only needs $\tilde{W}(\mathbf{r}, \mathbf{r}'; iu = 0)$ in order to calculate this approximate potential starting from an existing OEP code. This has been done by Kotani⁵³ for example in some bulk metals [in the RPA approximation for $\tilde{W}(iu = 0)$].

If needed, the OEP equation for $v_{xc,pG}(\mathbf{r})$ and $v_{ssex}(\mathbf{r})$ can also be solved in the Krieger-Li-Iafrate (KLI) approximation¹³, that proved to be very accurate in the exchange-only case (the KLI potentials have the same asymptotic behavior as the exact ones). Note, however, that the KLI approximation can not be used directly on Eqs. (27) and (28), where it systematically leads to a divergence (see discussion in Ref. 32).

VII. CONCLUSION

In this paper, we have investigated the asymptotic behavior of the potentials deriving from orbital- and energy-dependent (OED) approximations for the exchange-correlation energy, taking simple ACFD functionals as examples. Although the potentials deriving from

arbitrary OED functionals will likely diverge asymptotically, these ACFD potentials have the expected $\sim -1/r - \tilde{\alpha}/(2r^4)$ behavior in the He atom, where $\tilde{\alpha}$ is consistent with the underlying physics. The dependence on the empty Kohn-Sham orbitals and energies must however be treated with great care to avoid numerical instabilities. We have thus discussed some precautions to be taken for practical calculation of these potentials. Last, we have introduced two kinds of approximate potentials, that are much simpler to compute while being likely of reasonable accuracy.

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Tables

	RPA(2)	RPA	X2E(2)	X2E	Exact
E_c (mHa)	-93	-78	-47	-44	-43 ⁴⁵
$\tilde{\alpha}$ (a.u.)	1.52 ⁷	1.22 ⁷	0.76 ⁷	0.68 ⁴⁶	0.28 ⁴⁵

TABLE I: Correlation energy E_c and effective polarizability $\tilde{\alpha}$ calculated for the He atom in various approximations.