

Exchange-correlation energy densities and response potentials: Connection between two definitions and analytical model for the strong-coupling limit of a stretched bond

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Abstract

We analyze in depth two widely used definitions (from the theory of conditional probability amplitudes and from the adiabatic connection formalism) of the exchange-correlation energy density and of the response potential of Kohn-Sham density functional theory. We introduce a local form of the coupling-constant-dependent Hohenberg-Kohn functional, showing that the difference between the two definitions is due to a corresponding local first-order term in the coupling constant, which disappears globally (when integrated over all space), but not locally. We also design an analytic representation for the response potential in the strong-coupling limit of density functional theory for a model single stretched bond.

1 Introduction

In Kohn-Sham (KS) Density Functional Theory (DFT), the ground-state energy of a given chemical system is computed via an exact mapping onto a system of non-interacting electrons, the KS system, having the same one-electron density $n(\mathbf{r})$. The particles in the KS system feel the one-body KS potential, which forces them to have the prescribed density $n(\mathbf{r})$. The KS potential is built from parts that are exactly known (the external potential due to the nuclei and the Hartree potential, which gives a mean-field approximation for the effects of the electron-electron interaction), plus a part that needs to be approximated, the so-called exchange-correlation (XC) potential $v_{xc}(\mathbf{r})$, given by the functional derivative with respect to $n(\mathbf{r})$ of the unknown XC energy $E_{xc}[n]$.

Exact properties¹⁻²⁰ of the XC potential have played, and continue to play, a central role in building new approximations. In particular, it has become clear over the years that standard approximations miss certain non-intuitive features of the XC potential, such as “peaks” and “steps”, which are crucial to predict static electric polarizabilities and band gaps, and to describe bond breaking and strongly-correlated systems.^{1,2,4,6-20}

Using the theory of conditional probability amplitudes,^{21,22} Levy, Perdew and Sahni²³ have introduced in the DFT context a Schrödinger-type equation for $\sqrt{n(\mathbf{r})}$, which was later used by Baerends and coworkers^{2,4,6-8,24} to derive an insightful and exact decomposition of the XC potential into so-called kinetic, response, and XC-hole terms. They also showed that standard approximations typically reproduce quite well only the XC hole part of the XC potential, and that features such as “peaks” and “steps” are due, respectively, to the kinetic and response parts. A slightly different, but related, decomposition of the XC potential arises when we write $E_{xc}[n]$ in terms of an integration along the adiabatic connection at fixed density:²⁵⁻²⁷ in this case we have a coupling-constant averaged (CCA) XC-hole potential and a CCA response part,²⁸ due to the functional derivative of the

pair-correlation function with respect to the density. Also in this case, standard approximate functionals capture rather well the CCA XC-hole part, while missing completely the features of the response part.²⁸

The purpose of this work is twofold: on the one hand, we further investigate the relationship between the two different decompositions, using a local form of the Hohenberg-Kohn functional along the adiabatic connection. On the other hand, we construct a simple analytic representation for the response potential in the strong-coupling limit of DFT for the case of a model stretched heteronuclear bond.

2 Decompositions of the XC potential

We start by reviewing the two different definitions of response potential. The first one arises by using the theory of conditional probability amplitudes first developed by Hunter.^{21,22} Following the work in Refs. 2,23, we partition the hamiltonian for N electrons bound by the external (nuclear) potential $v(\mathbf{r})$ in three parts: the hamiltonian for $N - 1$ electrons (with $i = 2, \dots, N$), the one-body terms acting on electron 1, and the remaining interaction between electron 1 (taken as the reference) and all the others

$$\hat{H}^N(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) = \hat{H}^{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N) - \frac{\nabla_{\mathbf{r}}^2}{2} + v(\mathbf{r}) + \sum_{i=2}^N \frac{1}{|\mathbf{r} - \mathbf{r}_i|}. \quad (2.1)$$

In the same spirit, we factorize the N -particle wavefunction

$$\Psi^N(\mathbf{r}\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N) = \sqrt{\frac{n(\mathbf{r})}{N}} \Phi(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r}) \quad (2.2)$$

into the so-called *marginal* and *conditional (probability) amplitudes*, represented respectively by the square root of the density as a function of coordinates of electron 1 divided by the number of electrons N and a function of the other $N - 1$ electronic positions,

$\Phi(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r})$, which depends on electron 1 in a parametric way. We consider here the case that the wavefunction Ψ is real. Physically speaking, $\Phi(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r})$ is a sort of $(N - 1)$ -particle wavefunction that describes how the electronic cloud of $N - 1$ electrons readjusts as a function of the position of electron 1. Indeed, its modulus square integrates to one for any value of the position vector of the reference electron

$$\int |\Phi(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r})|^2 d\sigma d\mathbf{x}_2 \cdots d\mathbf{x}_N = 1 \quad \forall \mathbf{r}. \quad (2.3)$$

By applying eq (2.1) to eq (2.2), and by multiplying to the left both members by $\Phi(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r})$ and integrating over the spin variable of the reference electron and on the spatial and spin variables of electrons $2, \dots, N$, we obtain a Schrödinger-like equation for $\sqrt{n(\mathbf{r})}$,

$$-\frac{\nabla^2}{2} \sqrt{n(\mathbf{r})} + v_{\text{eff}}(\mathbf{r}) \sqrt{n(\mathbf{r})} = -I \sqrt{n(\mathbf{r})}, \quad (2.4)$$

where $I = E_0^{N-1} - E_0^N$ is the ionization potential. The resulting effective potential $v_{\text{eff}}(\mathbf{r})$ is equal to

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{cond}}(\mathbf{r}) + v_{\text{kin}}(\mathbf{r}) + v_{N-1}(\mathbf{r}), \quad (2.5)$$

with

$$v_{\text{cond}}(\mathbf{r}) = \int \frac{P_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (2.6)$$

where we have used the definition of the pair density, $P_2(\mathbf{r}, \mathbf{r}')$,

$$P_2(\mathbf{r}, \mathbf{r}') = N(N - 1) \int |\Psi(\mathbf{r}\sigma, \mathbf{r}'\sigma', \dots, \mathbf{x}_N)|^2 d\sigma d\sigma' d\mathbf{x}_3 \cdots d\mathbf{x}_N. \quad (2.7)$$

This potential is usually split into $v_{cond}(\mathbf{r}) = v_H(\mathbf{r}) + v_{xc,hole}(\mathbf{r})$, where $v_H(\mathbf{r})$ is the Hartree potential. We also define the exchange-correlation pair-distribution function, $g_{xc}(\mathbf{r}, \mathbf{r}')$,

$$g_{xc}(\mathbf{r}, \mathbf{r}') = \frac{P_2(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})n(\mathbf{r}')} - 1, \quad (2.8)$$

and write $v_{xc,hole}(\mathbf{r})$ as

$$v_{xc,hole}(\mathbf{r}) = \int n(\mathbf{r}') \frac{g_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2.9)$$

The term that comes from the kinetic energy operator acting on the conditional amplitude can be written, when we take into account eq (2.3), as

$$v_{kin}(\mathbf{r}) = \frac{1}{2} \int |\nabla_{\mathbf{r}} \Phi(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r})|^2 d\sigma d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (2.10)$$

and it is called kinetic potential. Finally, the term coming from the $N - 1$ hamiltonian is equal to

$$v_{N-1}(\mathbf{r}) = \int \Phi^*(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r}) \hat{H}^{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N) \Phi(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r}) d\sigma d\mathbf{x}_2 \dots d\mathbf{x}_N - E_0^{N-1}, \quad (2.11)$$

where the shift E_0^{N-1} makes this potential vanish when $|\mathbf{r}| \rightarrow \infty$ (with the possible exception in certain directions, if there are nodal planes that extend to infinity²⁹⁻³¹). It is evident that these three potentials are always positive, as in eqs (2.6) and (2.10) the integrands are squared quantities, and the right-hand-side of eq (2.11) must be positive by virtue of the variational principle.

Baerends and coworkers^{2,4,6-8,24} have then repeated the same procedure for the KS

hamiltonian \hat{H}_s^N with KS potential $v_s(\mathbf{r})$,

$$\hat{H}_s^N = - \sum_i^N \frac{\nabla_{\mathbf{r}_i}^2}{2} + \sum_{i=1}^N v_s(\mathbf{r}_i), \quad (2.12)$$

which has the same one-electron density of the physical interacting system, obtaining

$$v_{s,kin}(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^H \left| \nabla \frac{\psi_i(\mathbf{r})}{\sqrt{n(\mathbf{r})}} \right|^2 = \frac{1}{2n(\mathbf{r})} \sum_{i=1}^H |\nabla \psi_i(\mathbf{r})|^2 - \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})^2}, \quad (2.13)$$

where $\psi_i(\mathbf{r})$ are the H occupied KS orbitals, and

$$v_{s,N-1}(\mathbf{r}) = \sum_{i=1}^H (\epsilon_H - \epsilon_i) \frac{|\psi_i(\mathbf{r})|^2}{n(\mathbf{r})}, \quad (2.14)$$

where ϵ_H is the energy of the KS highest occupied molecular orbital (HOMO). The effective KS potential for the square root of the density is nothing but the sum of the foreshown potentials plus the KS potential itself (the conditional potential being absent as there is no Coulomb repulsion between the particles),

$$v_{\text{eff}}(\mathbf{r}) = v_s(\mathbf{r}) + v_{s,kin}(\mathbf{r}) + v_{s,N-1}(\mathbf{r}). \quad (2.15)$$

Since the one-electron density is the same for the physical and the KS syetm, then the right-hand sides of eqs (2.5) and (2.15) are also the same, providing an expression for v_{xc}

$$v_{xc}(\mathbf{r}) = v_{c,kin}(\mathbf{r}) + v_{resp}(\mathbf{r}) + v_{xc-hole}(\mathbf{r}). \quad (2.16)$$

with the correlation kinetic potential $v_{c,kin}(\mathbf{r})$ given by

$$v_{c,kin}(\mathbf{r}) = v_{kin}(\mathbf{r}) - v_{s,kin}(\mathbf{r}) \quad (2.17)$$

and the response potential $v_{resp}(\mathbf{r})$ equal to

$$v_{resp}(\mathbf{r}) = v_{N-1}(\mathbf{r}) - v_{s,N-1}(\mathbf{r}). \quad (2.18)$$

2.1 Response potential with kinetic and interaction components

The reason why (2.18) is called response potential is that from the definition of the XC energy,

$$E_{xc}[n] = \underbrace{\langle \Psi | \hat{T} | \Psi \rangle - T_s[n]}_{T_c[n]} + \underbrace{\langle \Psi | \hat{V}_{ee} | \Psi \rangle - U[\rho]}_{W_1[n]}, \quad (2.19)$$

where Ψ is the exact many-body wavefunction of the system under study, $T_s[n]$ is the KS kinetic energy, and $U[n]$ is the Hartree energy, we also have the exact equation

$$E_{xc}[n] = \int n(\mathbf{r}) v_{c,kin}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int n(\mathbf{r}) v_{xc-hole}(\mathbf{r}) d\mathbf{r}. \quad (2.20)$$

By taking the functional derivative with respect to the density of both sides of (2.20) we obtain

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = v_{c,kin}(\mathbf{r}) + v_{xc,hole}(\mathbf{r}) + v_{c,kin}^{resp}(\mathbf{r}) + v_{xc,hole}^{resp}(\mathbf{r}), \quad (2.21)$$

with

$$v_{c,kin}^{resp}(\mathbf{r}) = \int n(\mathbf{r}') \frac{\delta v_{c,kin}(\mathbf{r}')}{\delta n(\mathbf{r})} d\mathbf{r}' \quad (2.22)$$

and

$$v_{xc,hole}^{resp}(\mathbf{r}) = \frac{1}{2} \int \frac{n(\mathbf{r}') n(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \frac{\delta g_{xc}(\mathbf{r}', \mathbf{r}'')}{\delta n(\mathbf{r})} d\mathbf{r}' d\mathbf{r}'' \quad (2.23)$$

By comparing eqs (2.16) and (2.21) we see that

$$v_{resp}(\mathbf{r}) = v_{c,kin}^{resp}(\mathbf{r}) + v_{xc,hole}^{resp}(\mathbf{r}). \quad (2.24)$$

It has been shown that “peaks” in the KS potential come from $v_{c,kin}(\mathbf{r})$,^{2,10,17,32,33} while “steps” come from $v_{resp}(\mathbf{r})$.^{8,9,15,34} Also, notice that $v_{xc,hole}(|\mathbf{r}| \rightarrow \infty) \sim -\frac{1}{|\mathbf{r}|}$, implying that all the other terms are shorter ranged.

2.2 Response potential from the coupling-constant integration

Another exact equation for $E_{xc}[n]$ can be obtained by considering the λ -dependent Hohenberg-Kohn (HK) functional in the Levy constrained-search formulation,³⁵ where the interaction is scaled by a real and positive coupling parameter λ , namely

$$F_\lambda[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle, \quad (2.25)$$

with $F_1[n]$ the universal HK functional of the physical system and $F_0[n]$ equal to the KS kinetic energy $T_s[n]$. By simply plugging the wavefunction $\Psi_\lambda[n]$ that minimizes (2.25) in eqs (2.7) and (2.8), we define the pair-density $P_2^\lambda(\mathbf{r}, \mathbf{r}')$ and the corresponding $g_{xc}^\lambda(\mathbf{r}, \mathbf{r}')$. The CCA pair-correlation function $\bar{g}_{xc}(\mathbf{r}, \mathbf{r}')$ is then defined as

$$\bar{g}_{xc}(\mathbf{r}, \mathbf{r}') = \int_0^1 g_{xc}^\lambda(\mathbf{r}, \mathbf{r}') d\lambda. \quad (2.26)$$

The XC energy can be written in terms of the CCA $\bar{g}_{xc}(\mathbf{r}, \mathbf{r}')$,

$$E_{xc}[n] = \frac{1}{2} \iint n(\mathbf{r})n(\mathbf{r}') \frac{\bar{g}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (2.27)$$

as the integration over λ allows to recover the kinetic contribution to $E_{xc}[n]$.^{25–27} Taking the functional derivative of eq (2.27) we obtain two terms²⁸

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \bar{v}_{xc,hole}(\mathbf{r}) + \bar{v}_{resp}(\mathbf{r}), \quad (2.28)$$

where

$$\bar{v}_{xc,hole}(\mathbf{r}) = \int n(\mathbf{r}') \frac{\bar{g}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (2.29)$$

and

$$\bar{v}_{resp}(\mathbf{r}) = \frac{1}{2} \iint \frac{n(\mathbf{r}')n(\mathbf{r}'') \delta\bar{g}_{xc}(\mathbf{r}', \mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''| \delta n(\mathbf{r})} d\mathbf{r}' d\mathbf{r}''. \quad (2.30)$$

Again, also in this case $\bar{v}_{xc,hole}(\mathbf{r})$ has the full asymptotic behavior $-\frac{1}{|\mathbf{r}|}$ at large $|\mathbf{r}|$ and the response part $\bar{v}_{resp}(\mathbf{r})$ is shorter ranged. A decomposition in which the response part also contains $\frac{1}{2}\bar{v}_{xc,hole}(\mathbf{r})$, has been proposed in Ref. 36. Comparing eqs (2.21) and (2.28), we have

$$\begin{aligned} \bar{v}_{xc,hole}(\mathbf{r}) + \bar{v}_{resp}(\mathbf{r}) = \\ v_{c,kin}(\mathbf{r}) + v_{xc,hole}(\mathbf{r}) + v_{c,kin}^{resp}(\mathbf{r}) + v_{xc,hole}^{resp}(\mathbf{r}). \end{aligned} \quad (2.31)$$

One would naively expect that the response part in the left-hand side equals the sum of the response parts in the right-hand sides. However, this is not true, and in general we have

$$v_{c,kin}^{resp}(\mathbf{r}) + v_{xc,hole}^{resp}(\mathbf{r}) \neq \bar{v}_{resp}(\mathbf{r}), \quad (2.32)$$

$$v_{c,kin}(\mathbf{r}) + v_{xc,hole}(\mathbf{r}) \neq \bar{v}_{xc,hole}(\mathbf{r}). \quad (2.33)$$

It is one of the purpose of this work to further investigate and analyse the difference between these two response potentials. Notice that if we split the potential into its exchange (X) and correlation (C) components, for the X part the two definitions become equivalent, as there is no kinetic and no λ dependence in exchange, $\bar{v}_{x,hole} = v_{x,hole}$.

3 Analysis of energy densities and response potentials within the two definitions

The two ways to write the XC energy reviewed in the previous section, from the conditional amplitude formalism and from the adiabatic connection, stem from the two different energy densities (sometimes called gauges)

$$\epsilon_{kin+hole}(\mathbf{r}) = v_{c,kin}(\mathbf{r}) + \frac{1}{2}v_{xc,hole}(\mathbf{r}) \quad (3.1)$$

$$\epsilon_{xc}(\mathbf{r}) = \frac{1}{2}\bar{v}_{xc,hole}(\mathbf{r}), \quad (3.2)$$

which both yield the same $E_{xc}[n]$ when multiplied by the density and integrated over all space. The second definition, $\epsilon_{xc}(\mathbf{r})$, is the one most commonly used in DFT, also called the XC-hole potential gauge. By rewriting it as

$$\epsilon_{xc}(\mathbf{r}) = \frac{1}{2}v_{xc,hole}(\mathbf{r}) + \left(\frac{1}{2}\bar{v}_{c,hole}(\mathbf{r}) - \frac{1}{2}v_{c,hole}(\mathbf{r}) \right), \quad (3.3)$$

we see that the difference between the two definitions stem from how they describe the correlation kinetic energy density, as both $v_{c,kin}(\mathbf{r})$ and $\frac{1}{2}\bar{v}_{c,hole}(\mathbf{r}) - \frac{1}{2}v_{c,hole}(\mathbf{r})$ integrate to $T_c[n]$ when multiplied by $n(\mathbf{r})$. These two kinetic energy densities are in general rather different, as shown, for example, in fig 1 for the H⁻ anion, or in fig 14 of Ref 37 for the Hooke's atom series. An exception is the uniform electron gas case (including the finite ones^{38,39}), in which the kinetic energy density is a constant and thus the same in both definitions. The local-density approximation (LDA) can then be interpreted, in each point of space, as an approximation for either of the two gauges.

Both energy density definitions of eqs (3.1) and (3.2) go like $-\frac{1}{2|\mathbf{r}|}$ at large $|\mathbf{r}|$. The total functional derivative is obviously the same, as in (2.31), and has the well known large- $|\mathbf{r}|$

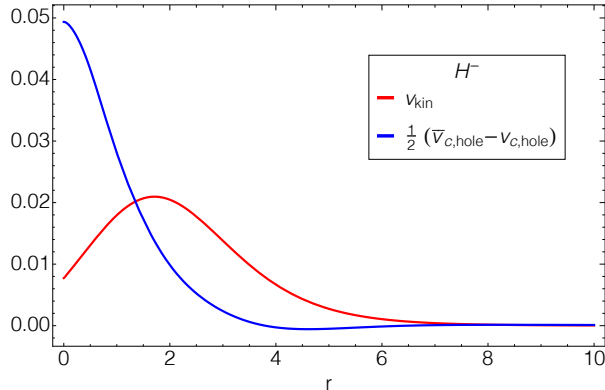


Figure 1: Two possible kinetic correlation energy densities, from the conditional amplitude formalism and from the coupling-constant average of the interaction part. Notice that in this case, as $N = 2$ we have $v_{c,kin} = v_{kin}$. Accurate data are obtained from Refs. 40–46

behavior $-\frac{1}{|r|}$, thus two times the one of the energy density. Semilocal approximate functionals typically miss both asymptotic behaviors. It is possible to fix the energy density long-range behavior in a semilocal functional for a specific density decay (e.g., Ref 47 for exponentially decaying density), but then the factor 2 in the functional derivative will be missing. It is also possible to fix, instead, the behavior of the XC potential, but in this case the asymptotics of the energy density will be spoiled.^{36,48} An exception, besides the exact exchange case, is the strictly-correlated electrons (SCE) functional, corresponding to the $\lambda \rightarrow \infty$ limit of the adiabatic connection, which is able to capture both asymptotic behaviors.⁴⁹ However, existing approximations inspired to the SCE mathematical structure, which use integrals of the density as basic ingredient,^{50–52} are, again, only able to capture the exact energy density asymptotics but not the one of the XC potential, missing the factor 2.

Here we want to further analyze the difference between the two possible definitions of the energy densities and of the response part of the XC potential. Let us first introduce

the new quantity $\mathfrak{f}_\lambda[n](\mathbf{r})$

$$\mathfrak{f}_\lambda[n](\mathbf{r}) = \int \Phi_\lambda^*(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r}) \left(-\frac{\nabla_{\mathbf{r}}^2}{2} + \frac{\sum_{i=2}^N \lambda}{2 r_{1i}} \right) \Phi_\lambda(\sigma, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{r}) d\sigma d\mathbf{r}_2 \cdots \mathbf{r}_N \quad (3.4)$$

which defines an energy density for the λ -dependent HK functional in the Levy constrained formulation of eq (2.25), because it holds

$$\int n(\mathbf{r}) \mathfrak{f}_\lambda[n](\mathbf{r}) d\mathbf{r} = F_\lambda[n]. \quad (3.5)$$

The conditional amplitude Φ_λ is obtained by plugging the wavefunction Ψ_λ that minimizes eq. (2.25) into eq (2.2). However, Φ_λ will not be in general the minimizer of $\hat{h}_\lambda = -\frac{\nabla_{\mathbf{r}}^2}{2} + \frac{\sum_{i=2}^N \lambda}{2 r_{1i}}$ at a given \mathbf{r} . By differentiating with respect to λ both sides of eq (3.4) we then obtain

$$\frac{\partial}{\partial \lambda} \mathfrak{f}_\lambda(\mathbf{r}) = \left(\langle \Phi_\lambda | \frac{\partial \hat{h}_\lambda}{\partial \lambda} | \Phi_\lambda \rangle_{2\dots N} + \langle \frac{\partial \Phi_\lambda}{\partial \lambda} | \hat{h}_\lambda | \Phi_\lambda \rangle_{2\dots N} + \langle \Phi_\lambda | \hat{h}_\lambda | \frac{\partial \Phi_\lambda}{\partial \lambda} \rangle_{2\dots N} \right) (\mathbf{r}) \quad (3.6)$$

where the Dirac brackets $\langle \dots | \dots \rangle_{2\dots N}$ stand for $\int d\sigma d\mathbf{x}_2 \cdots \mathbf{x}_N$.

We set $\langle \frac{\partial \Phi_\lambda}{\partial \lambda} | \hat{h}_\lambda | \Phi_\lambda \rangle_{2\dots N} + \langle \Phi_\lambda | \hat{h}_\lambda | \frac{\partial \Phi_\lambda}{\partial \lambda} \rangle_{2\dots N} = 2 \langle \Phi_\lambda | \hat{h}_\lambda | \frac{\partial \Phi_\lambda}{\partial \lambda} \rangle_{2\dots N}$ as we assumed Φ_λ to be real. We then simply write

$$\mathfrak{f}_1(\mathbf{r}) - \mathfrak{f}_0(\mathbf{r}) = \int_0^1 d\lambda \left(\frac{\partial}{\partial \lambda} \mathfrak{f}_\lambda(\mathbf{r}) \right). \quad (3.7)$$

Evaluating the left hand side, we immediately get

$$\mathfrak{f}_1(\mathbf{r}) - \mathfrak{f}_0(\mathbf{r}) = v_{c,kin}(\mathbf{r}) + \frac{1}{2} v_{cond}(\mathbf{r}). \quad (3.8)$$

But we also have

$$\langle \Phi_\lambda | \frac{\partial \hat{h}_\lambda}{\partial \lambda} | \Phi_\lambda \rangle_{2\dots N}(\mathbf{r}) = \frac{1}{2} \int \frac{n(\mathbf{r}') (g_{xc}^\lambda(\mathbf{r}, \mathbf{r}') + 1)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (3.9)$$

so that combining eqs (3.6), (3.8) and (3.9) and subtracting the Hartree potential from both sides we find the relation

$$\frac{1}{2} \bar{v}_{xc-hole} = v_{c,kin} + \frac{1}{2} v_{xc-hole} - 2 \int_0^1 d\lambda \langle \Phi_\lambda | \hat{h}_\lambda | \frac{\partial \Phi_\lambda}{\partial \lambda} \rangle_{2\dots N}. \quad (3.10)$$

We then see that the difference between the two energy densities of eq (3.1) and (3.2) is given by the term

$$\epsilon_{kin+hole} - \epsilon_{xc} = 2 \int_0^1 d\lambda \langle \Phi_\lambda | \hat{h}_\lambda | \frac{\partial \Phi_\lambda}{\partial \lambda} \rangle_{2\dots N}. \quad (3.11)$$

When multiplied by the density and integrated over all space, the right-hand side of eq (3.11) integrates to zero by virtue of the Hellmann-Feynman theorem, as Ψ_λ is the minimizer of eq (2.25). The two energy densities are then different because the first-order term in λ does not disappear locally, but only globally. We see that they are also equal, as it should, for exchange-only, as in that case the conditional amplitude Φ does not depend on λ . By combining eqs (3.10) and (2.31), we can also find a relation between the two response potentials

$$\bar{v}_{resp} = v_{resp} - v_{c,kin} + 4 \int_0^1 d\lambda \langle \Phi_\lambda | \hat{h}_\lambda | \frac{\partial \Phi_\lambda}{\partial \lambda} \rangle_{2\dots N}. \quad (3.12)$$

We can then analyze what happens in some prototypical cases, like the one of a two-electron system dissociating into two one-electron fragments, which is often used to test and understand the problems of approximate DFT in describing bond breaking.^{2,9,10,16,18}

In that case we have $\hat{h}_\lambda \sim -\frac{\nabla^2 r_2^2}{2}$, and then

$$\int_0^1 d\lambda \langle \Phi_\lambda | \hat{h}_\lambda | \frac{\partial \Phi_\lambda}{\partial \lambda} \rangle_{2\dots N} \sim \frac{1}{2} v_{c,kin}, \quad (3.13)$$

which plugged into eqs (3.10) and (3.12) gives

$$v_{xc,hole} \sim \bar{v}_{xc,hole} \quad (3.14)$$

$$\bar{v}_{resp}(x) \sim v_{c,kin}(x) + v_{resp}(x), \quad (3.15)$$

as we had already conjectured in eq (83) of Ref. 46.

4 Analytical 1D model for v_{Hxc}^{SCE} and v_{resp}^{SCE} in the dissociation limit

We now consider the strictly-correlated electron (SCE) XC functional, which is given by

$$W_{SCE}[n] = \lim_{\lambda \rightarrow \infty} \lambda^{-1} F_\lambda[n] - U[\rho], \quad (4.1)$$

and provides an extreme approximation for the XC energy, which becomes asymptotically exact when the system is driven to low density.^{53,54} We focus on a prototypical model, often used to understand, test and improve approximations in DFT,^{9,10,16,18,46} consisting of a one-dimensional (1D) system of $N = 2$ electrons dissociating into two one-electron fragments, mimicking the breaking of a single bond. The response potential v_{resp}^{SCE} for the SCE functional was analyzed in Ref. 46, where it was found that, although v_{resp}^{SCE} does not saturate as the exact response potential, it behaves very differently from semilocal functionals, with qualitative features much closer to the exact ones. Here we go one step

further with respect to Ref. 46 and build a simple analytic model for v_{resp}^{SCE} which works extremely well. This could be of interest, for example, in transport calculations for model systems,⁵⁵ but also as a starting point for new approximations.

We thus consider the following model for a heteronuclear diatomic molecule

$$n(x) = n_a \left(x - \frac{R}{2} \right) + n_b \left(x + \frac{R}{2} \right) = \frac{a}{2} e^{-a|x-\frac{R}{2}|} + \frac{b}{2} e^{-b|x+\frac{R}{2}|}, \quad (4.2)$$

where a and b mimic the different ionization potentials of the “atoms” (pseudopotentials or frozen cores) and the density is normalized to 2. We have chosen $a > b$, therefore the more electronegative atom will be found to the right side of the origin (at a distance $+\frac{R}{2}$ from it) and the less electronegative to the left. The SCE functional of eq (4.1) for a two-electron system is given by^{56–58}

$$W_{\text{SCE}}[n] = \frac{1}{2} \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{f}(\mathbf{r}, [n])|} d\mathbf{r} - U[n], \quad (4.3)$$

where the co-motion function $\mathbf{f}(\mathbf{r}, [n])$ determines the position of the second electron as a function of the position \mathbf{r} of the first one and it is a non-local functional of the density. Despite this extreme non-locality, its functional derivative

$$v_{Hxc}^{\text{SCE}}(\mathbf{r}) = \frac{\delta W_{\text{SCE}}[n]}{\delta n(\mathbf{r})} + v_{\text{H}}(\mathbf{r}) \quad (4.4)$$

can be computed from the exact force equation^{57,59}

$$\nabla v_{Hxc}^{\text{SCE}}(\mathbf{r}) = -\frac{\mathbf{r} - \mathbf{f}(\mathbf{r})}{|\mathbf{r} - \mathbf{f}(\mathbf{r})|^3}. \quad (4.5)$$

And for the response potential, we have⁴⁶

$$v_{resp}^{\text{SCE}}(\mathbf{r}) = v_{Hxc}^{\text{SCE}}(\mathbf{r}) - \frac{1}{|\mathbf{r} - \mathbf{f}(\mathbf{r})|}. \quad (4.6)$$

Notice that in the SCE limit there is no difference between \bar{v}_{resp} and v_{resp} , as SCE has the same scaling of exchange⁶⁰ or, equivalently, there is no kinetic correlation component to leading order in the $\lambda \rightarrow \infty$ limit. By defining

$$a_R : \int_{-\infty}^{a_R} n(x) dx = 1 \quad (4.7)$$

the exact 1D co-motion function is given by^{56,61}

$$f(x) = \begin{cases} N_e^{-1}[N_e(x) + 1] & x < a_R \\ N_e^{-1}[N_e(x) - 1] & x > a_R. \end{cases} \quad (4.8)$$

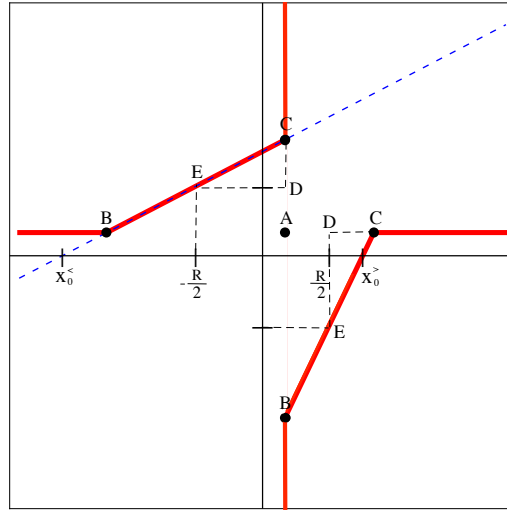


Figure 2: Asymptotic co-motion function of eq 4.9.

In Ref. 46, it has been shown that the shape of the co-motion function for the density of eq (4.2) becomes asymptotically the same at any internuclear distance (“saturation” phenomenon), behaving, in particular, as a constant in the asymptotic regions $x \ll 1$ and

$x \gg 1$ and as a linear curve with coefficients, $m^< = \frac{b}{a}$ and $m^> = \frac{a}{b}$ close to a_R . If we now approximate the small regions where the co-motion function switches from the constant to the linear behaviour and those where it diverges (it is sufficient to know each one of such regions, only for one branch as the co-motion is symmetric w.r.t. the axis $y = x$) with sharp angles, we can determine the asymptotic ($R \rightarrow \infty$) co-motion function

$$f_{\text{mod}}(y) = \begin{cases} a_R & y \leq x_T^< \\ m^< y + c^< & x_T^< < y < a_R \\ \infty & y = a_R^1 \\ m^> y + c^> & a_R < y \leq x_T^> \\ a_R & y > x_T^> \end{cases} \quad (4.9)$$

where $x_T^<$ ($x_T^>$) is the distance at which the co-motion function switches from constant (linear) to linear (constant), while $c^<$ ($c^>$) is the constant shifting the zero of the linear region to the negative (positive) x - axis.

Assuming that eq 2 is a good model for the co-motion function, we need very few considerations to determine all the quantities needed to calculate the SCE potential and its response part from it. In particular, considering the two identical right triangles ABC plotted in fig 2, where the point A is $A = \{a_R, a_R\}$, we can determine their catheti \overline{AB} and \overline{AC} from

$$\begin{cases} \overline{AB} (\overline{AC})^{-1} & = \frac{a}{b} \\ \overline{AB} + \overline{AC} & = 2R \end{cases} \quad (4.10)$$

where the first equation follows directly from eq (78) of Ref. 46, while the second is an

¹We can arbitrarily pick a side, namely if $f_{\text{mod}}(a_R) = \infty$ or $f_{\text{mod}}(a_R) = -\infty$; just as well as, with the inequalities, we can arbitrarily decide whether $f_{\text{mod}}(x_T^<) = a_R$ or $f_{\text{mod}}(x_T^<) = m^< y + c^<$. Such single points choices do not affect the SCE Hartree XC potential as it is obtained from an integral expression containing f_{mod} and neither they affect the SCE response potential, as long as $f_{\text{mod}}(a_R)$ diverges.

extension of the discussion contained in section 5.2 of the same work, but it takes a bit more of details to support it.

When the reference electron is situated slightly off $-\frac{R}{2}$, say $-\frac{R}{2} + \epsilon$ the second electron will be displaced by an amount $\frac{b}{a}\epsilon$ by the property of the right triangles.

Let us now consider the displacement from $-\frac{R}{2}$ to a_R , corresponding to the \overline{DE} segment in fig 2.

The co-motion then increases by an amount $\frac{b}{a} \left(\frac{R}{2} + a_R \right)$ (the \overline{DC} segment in the figure). On the other hand, because of its symmetry, the displacement of the co-motion on one branch corresponds to the displacement of the variable of the reference electron on the other branch. Furthermore, what happens from $-\frac{R}{2}$ “*onward*” must be mirrored by what happens from $-\frac{R}{2}$ “*backward*” bringing us to the conclusion that the segment $\overline{AB} + \overline{AC} = 2 \left(\left(1 + \frac{b}{a}\right) \frac{R}{2} + \left(1 + \frac{b}{a}\right) a_R \right) = 2R$.

Once \overline{AB} and \overline{AC} are known, evaluating all the quantities specifying the asymptotic co-motion in eq 4.9 is just a matter of basic trigonometry, providing

$$\begin{aligned}
x_T^< &= -(\overline{AB} - a_R) \\
x_T^> &= a_R + \overline{AC} \\
x_0^< &= x_T^< - \frac{a}{b} a_R \\
x_0^> &= x_T^> - \frac{b}{a} a_R \\
c^< &= -m^< x_0^< \\
c^> &= -m^> x_0^>
\end{aligned} \tag{4.11}$$

where $x_0^<$ ($x_0^>$) is the zero of the function $m^<x + c^<$ ($m^>x + c^>$), see fig 2.

Table 1: Values of the maximum of v_{Hxc}^{SCE} for the density in eq 4.2 and the parameters $a = 2, b = 1$ at different internuclear distance, R .

R	$v_{Hxc}^{\text{SCE}}(a_R)$	
	numerical	modelled
3	0.684	0.75
8	0.278	0.281
11	0.203	0.205
14	0.160	0.161
17	0.132	0.132
20	0.113	0.113

The modelled Hartree XC SCE potential, $v_{Hxc,\text{mod}}^{\text{SCE}}$, obtained from

$$v_{Hxc,\text{mod}}^{\text{SCE}}(x) = - \int_{-\infty}^x (f_{\text{mod}}(y) - y)^{-2} dy \quad (4.12)$$

(see eq 4.5), compares nicely with the numerically exact one as shown in the right column of fig 3. In addition to the profile of the modelled potential, we report in table 1, the values obtained for the maximum, which is the most delicate point.

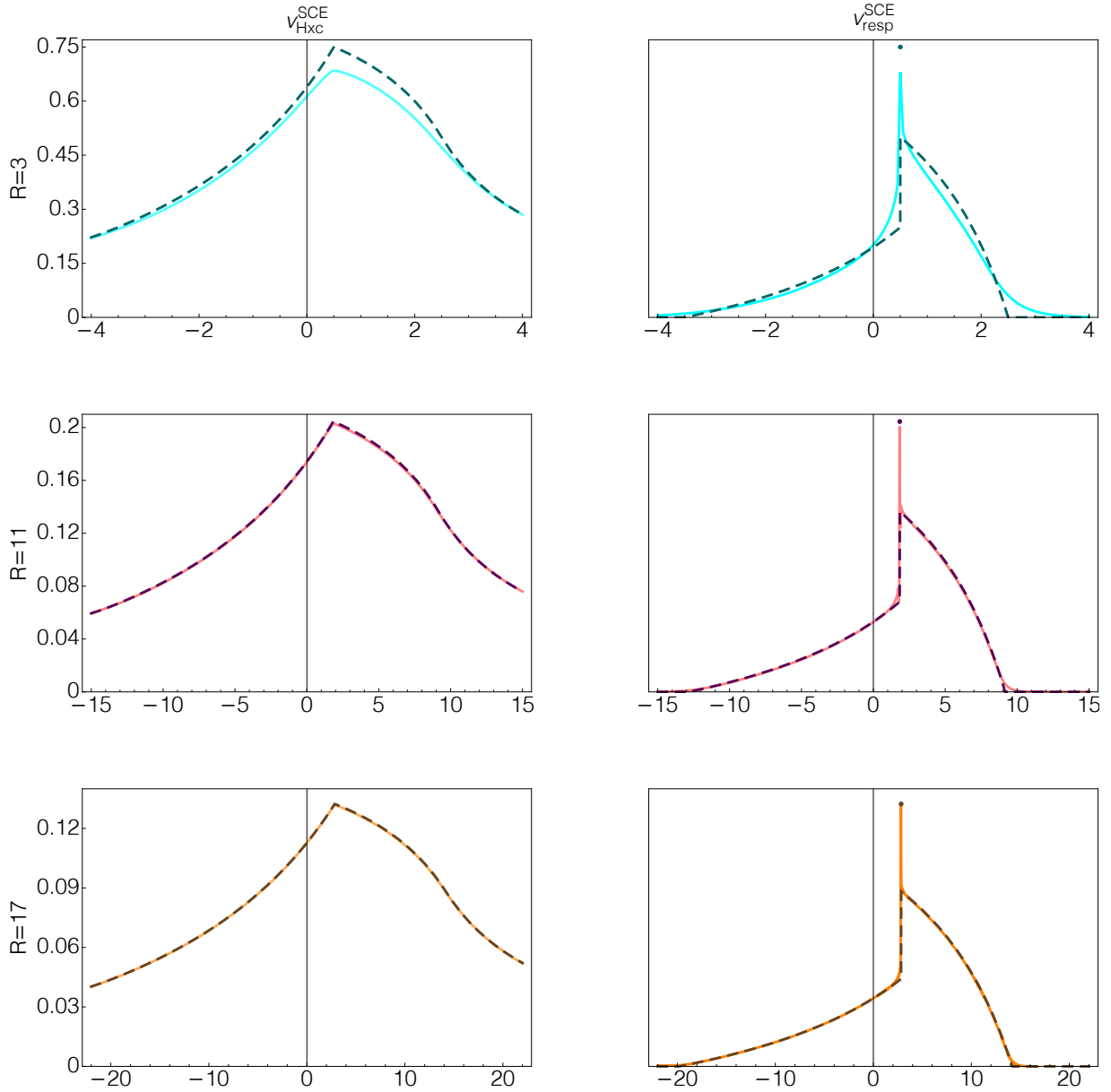


Figure 3: Comparison of between the numerical (thick) and the modelled (dashed) v_{Hxc}^{SCE} (right) and the numerical (thick) and the modelled (dashed) v_{resp}^{SCE} at different internuclear distances. Notice that, because within the model the local behaviour of the co-motion around the divergence is not treated, the response potential $v_{resp}^{\text{SCE}}(x)$ shows a pointwise jump in $x = a_R$.

The analytical expression for the dependence of the maximum of the Hartree XC SCE

we obtain is

$$v_{Hxc}^{\text{SCE}}(a_R) = \frac{(a+b)^2}{2abR} \quad (4.13)$$

Equation (4.13) shows that when the two fragment densities are equal, the maximum value decreases like $\frac{2}{R}$, thus missing the exact behavior in which this value should saturate and become R -independent at large R . Note that when $a > b$, the maximum value decreases like $\frac{2}{R}\varsigma$, where ς is a factor greater than one. In this sense, the repulsion is minimum when the two densities are identical.

In the right column of fig 3, we report the comparison between the modelled and the numerical SCE response potentials, obtained using the exact relation⁴⁶

$$v_{resp}^{\text{SCE}}(x) = -v^{\text{SCE}}(f(x)) + v^{\text{SCE}}(a_R), \quad (4.14)$$

It is quite interesting to notice that the SCE response potential resulting from our model co-motion (eq 4.9) shows a pointwise jump in $x = a_R$. It is evident that, in order to correctly describe how this potential behaves around its maximum, we need to include also the knowledge of how the co-motion function diverges, while this information is not needed in the case of the maximum of the SCE Hartree XC potential. Nonetheless, our modelled SCE response potential correctly integrates to exactly one as it should, fulfilling a recently derived sum-rule.⁶² Moreover, excluding for a moment the point $f_{\text{mod}}(a_r) = \infty$ from our model co-motion function, we can evaluate the analytical behaviour of the step structure of the modelled SCE response potential, $v_{resp,\text{mod}}^{\text{SCE}}$, i.e. the difference from its left and right limits towards a_R , getting

$$\left| \lim_{x \rightarrow a_R^+} v_{resp,\text{mod}}^{\text{SCE}}(x) - \lim_{x \rightarrow a_R^-} v_{resp,\text{mod}}^{\text{SCE}}(x) \right| = \frac{a^2 - b^2}{2abR} \quad (4.15)$$

which differs from the exact step height in the model $\left(\frac{a^2}{8} - \frac{b^2}{8}\right)$ by the factor $\frac{a}{2} \frac{b}{2} R$.

5 Conclusions and perspectives

We have identified a fundamental difference between two definitions of the XC energy densities and two different decompositions of the XC potential in the fact that, differently than what happens with the global (integrated over all space) expectation values, the conditional amplitude is not stationary for the local hamiltonian \hat{h}_λ , preserving first-order terms in the coupling constant, eqs (3.4)-(3.12). This allows us to connect the two different response potentials in the case of a stretched bond [eq (3.15)]. Future works will include the derivation for the case in which the wavefunction is complex, an analysis of approximate functionals,²⁸ and the investigation of the relation with response properties of DFT for the understanding of chemistry.⁶³

In addition, we have proposed a working model for the XC and response potential in the strong-coupling limit of DFT for a two-electron stretched dimer, which is very accurate in the dissociation limit. Although restricted to the 1D case, it could prove useful, e.g., to model quantum transport calculations⁵⁵ and systems out of equilibrium in hybrid approaches,⁶⁴ but also as a starting point to build new approximations that would also include the missing kinetic correlation component.

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