Prediction of the Derivative Discontinuity in Density Functional Theory from an Electrostatic Description of the Exchange and Correlation Potential

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Prediction of the derivative discontinuity in density functional theory from an electrostatic description of the exchange and correlation potential

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We propose an approach to approximate the exchange and correlation (XC) term in density functional theory. The XC potential is considered as an electrostatic potential, generated by a fictitious XC density, which is in turn a functional of the electronic density. We apply the approach to develop a correction scheme that fixes the asymptotic behavior of any approximated XC potential for finite systems. Additionally, the correction procedure gives the value of the XC derivative discontinuity; therefore it can directly predict the fundamental gap as a ground-state property.

An important and long standing topic in density functional theory (DFT) [1] is the prediction of the fundamental gap [2, 3] $E_{\rm g}$, which is defined as the difference of the ionization energy and the electron affinity. In DFT, the gap is not simply the difference between the Kohn-Sham (KS) eigenvalues of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Instead, it is given by [4]

$$E_{\rm g} = \epsilon_{\rm LUMO} - \epsilon_{\rm HOMO} + \Delta_{\rm xc} \ , \qquad (1)$$

where $\epsilon_{\rm HOMO}$ and $\epsilon_{\rm LUMO}$ are the HOMO and LUMO KS eigenvalues, respectively, and $\Delta_{\rm xc}$ is the derivative discontinuity (DD) of the XC energy with respect to the particle number N,

$$\Delta_{\rm xc} = V_{\rm xc}(N^+) - V_{\rm xc}(N^-) \ . \qquad (2)$$

For the local density approximation (LDA) and many generalized gradient approximations (GGA), the DD is zero [5]. In these approximations the predicted gap is effectively the KS gap, which severely underestimates the experimental value. Even for

XC energy functionals that are discontinuous with the particle number, the DD is not simple to calculate [3, 6–8]. Alternatively, XC approximations have been proposed where the KS gap is directly used to predict the gap [9] avoiding the calculation of the DD.

In this article, we present an XC potential for finite systems that, with similar computational cost as a LDA or GGA calculation, has the right asymptotic limit for low density regions and directly provides the value of the DD. Hence, the proposed XC approximation can predict the fundamental gap for an atom or molecule as a ground state property.

The approach that we advocate,
related to an early proposal by Görling [10], is not based on increasing the number of functional variables, but on changing the way that the XC potential is described: we consider the XC potential as an electrostatic potential, generated by a fictitious XC charge density. In

contrast to directly modelling the potential, the XC density becomes the quantity to approximate as a functional of the electronic density n.

Given a XC potential $V_{\rm xc}$, we define the XC density $n_{\rm xc}$ by the Poisson equation (atomic units are used throughout)

$$\nabla^2 V_{\rm xc}(\boldsymbol{r}) = -4\pi\, n_{\rm xc}(\boldsymbol{r}) \ , \qquad (3)$$

with the boundary condition $V_{\rm xc}(\boldsymbol{r} \to \infty) = 0$.

This establishes a one to one correspondence between the XC potential and the XC density. Therefore, Eq. (3) does not impose any condition over the XC potential.

A physical interpretation to XC density as a polarization charge density has been given by Tokatly [11].

The
motivation for the XC density approach comes from an important property of the XC potential: the so-called asymptotic limit [12, 13],

$$V_{\rm xc}(\boldsymbol{r}) \approx -\frac{1}{|\boldsymbol{r}|} \quad (|\boldsymbol{r}| \to \infty) \ , \qquad (4)$$

The LDA and most GGAs do not obey the asymptotic limit condition. In part, this common deficiency can be explained simply. In regions that are spatially far away from the system, the density and its derivatives decay exponentially to zero [13]. It is difficult to use local values of the density and its derivatives to reproduce a field that decays to zero much more slowly.

For the XC density the asymptotic limit implies two simple conditions: normalization and localization. Formally,

$$n_{\rm xc}(\boldsymbol{r}) = 0 \quad (|\boldsymbol{r}| \to \infty) \ , \qquad (5a)$$

$$\int \mathrm{d}\boldsymbol{r}\, n_{\rm xc}(\boldsymbol{r}) = -1 \ , \qquad (5b)$$

(proof in supp. mat. [14]). These constraints are similar to the ones for the electronic density. So, in principle, it is simple to construct a local or semi-local density functional $n_{\rm xc}[n]$ with the proper asymptotic limit. In
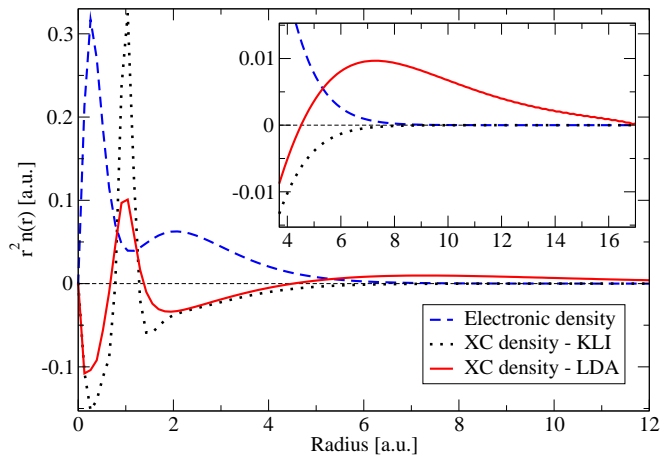
FIG. 1. KLI electronic density and KLI and LDA XC densities for the beryllium atom. The inset details the asymptotic region, where the KLI XC density shows the correct behavior. The LDA XC density is incorrect in this region, with a positive part that screens the charge in the central region.

fact, a direct example of this XC density based approach is the functional $n_{\mathrm{xc}}[n](\boldsymbol{r}) = -n(\boldsymbol{r})/N$, which yields the Fermi-Amaldi XC potential [15] and provides an accurate approximation of V_{xc} in the asymptotic regime [16, 17].

It is illustrative to see what the XC density looks like for standard DFT approximations. For a given XC potential, n_{xc} can be calculated analytically (see supp. mat. [14]), but in practice it is simpler to evaluate Eq. (3) numerically. In Fig. 1, we compare n_{xc} for LDA and exact exchange in the Krieger-Li-Iafrate (KLI) [18] approximation. As can be seen from the figure, for large radius the KLI XC density correctly goes to zero faster than the electronic density. On the other hand, the LDA XC density becomes positive. This positive XC charge screens the XC charge in the central region making the total XC charge zero and therefore causing the potential to decay exponentially.

As a first application of our approach, we propose a correction method to enforce the proper asymptotic limit for XC approximations that do not have it by construction. Given a certain potential $\bar{V}_{\mathrm{xc}}$, we calculate the associated $\bar{n}_{\mathrm{xc}}$ from Eq. (3). To this XC density we apply the correction procedure, that generates a corrected XC density n^c_{xc}. In turn, the corrected XC density is used to reconstruct the corrected XC potential V^c_{xc} by solving Eq. (3).

The correction procedure for $\bar{n}_{\mathrm{xc}}$ enforces it to be localized by setting it to zero when the local value of electronic density is below a certain threshold η. This simple procedure can be written as a correction term Δn_{xc} to be added to the XC density of the original potential,

$$\Delta n_{\mathrm{xc}}[n](\boldsymbol{r},\eta) = \begin{cases} 0 & \text{if } n(\boldsymbol{r}) \geq \eta \\ -\bar{n}_{\mathrm{xc}}[n](\boldsymbol{r}) & \text{if } n(\boldsymbol{r}) < \eta \end{cases} . \quad (6)$$

To determine the parameter η, for each density we ob-

tain an optimized value η_0 that tries to enforce Eq. (5b). First, we define the total XC charge as a function of η

$$q_{\mathrm{xc}}(\eta) = \int \mathrm{d}\boldsymbol{r} \left\{ \bar{n}_{\mathrm{xc}}[n](\boldsymbol{r}) + \Delta n_{\mathrm{xc}}[n](\boldsymbol{r},\eta) \right\} . \quad (7)$$

Ideally, from Eq. (5b), we need to find η_0 such that $q_{\mathrm{xc}}(\eta_0) = -1$. However, there is no guarantee about the existence or uniqueness of η_0. So we choose η_0 such that $q_{\mathrm{xc}}(\eta_0)$ has the closest value to -1, with η_0 restricted to be smaller than the first minimum of $q_{\mathrm{xc}}(\eta)$.

This unambiguously determines η_0 for each system. (See supp. mat. [14].)

When $q_{\mathrm{xc}}(\eta_0) \neq -1$, Eq. (5b) is still not satisfied, so we rescale the correction by $|q_{\mathrm{xc}}(\eta_0)|^{-1}$. The final expression for the XC density of the corrected potential is

$$n^c_{\mathrm{xc}}(\boldsymbol{r}) = \bar{n}_{\mathrm{xc}}(\boldsymbol{r}) + \frac{1}{|q_{\mathrm{xc}}(\eta_0)|} \Delta n_{\mathrm{xc}}(\boldsymbol{r},\eta_0) . \quad (8)$$

This rescaling form guarantees that Eq. (5b) is satisfied, and that the original XC potential is changed as little as possible in the central region (the region where $n \geq \eta_0$).

In theory, it is only the exchange term that is responsible for the long range behavior, due to the much faster decay of the correlation term [13], therefore, the correction can be applied either to the exchange potential or the full XC potential. In this work, we apply it to the exchange part of the LDA, and we call the combination of the corrected LDA exchange and LDA correlation (in the Perdew-Wang form [19]) the corrected exchange density LDA (CXD-LDA).

In all calculations the corrected potential is used self-consistently. For spin-polarized systems, the correction is calculated for the spin-unpolarized potential using the total density. Then the difference between the corrected potential and the original one is added to the XC potential for each spin component.

To test the CXD-LDA potential, we performed calculations for atoms and for a set of small molecules. We implemented the correction procedure in the APE [20] and Octopus [21] codes. We find that the optimized value of η_o changes significantly for different systems. For most atoms $q_{\mathrm{xc}}(\eta_0) \neq -1$ while for all the tested molecules $q_{\mathrm{xc}}(\eta_0) = -1$ (see supp. mat. [14]). The numerical cost of a self-consistent solution using the correction is similar to the LDA calculation (see supp. mat. for details [14]).

In Fig. 2, we show the CXD-LDA potential for Ne compared with an accurate approximation to the exact potential [16], the LDA and two approximations that have the correct asymptotic behavior: the van Leeuwen-Baerends (LB) GGA [13] and the Räsänen-Pittalis-Proetto (RPP) meta-GGA [22].

For atoms it is simple to understand the effect of the correction procedure. Due to the spherical symmetry and the monotonically-decreasing density, the correction XC charge Δn_{xc} is a spherical shell. By Newton's shell
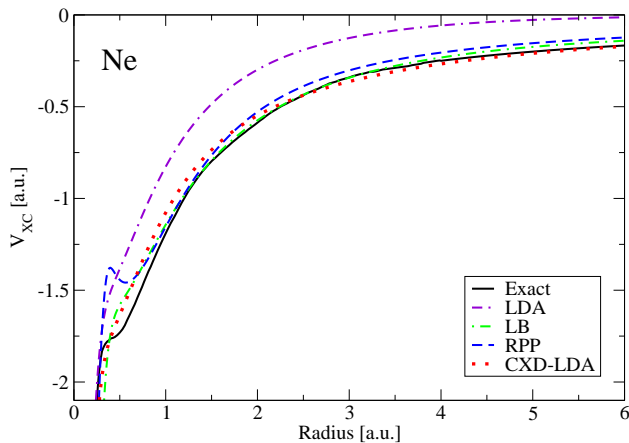
FIG. 2. CXD-LDA potential for neon. Comparison with the LDA, LB [13], RPP [22] and the exact [16] potentials.

theorem, the correction potential will be constant in the central region. Outside, the correction will decay close to $-1/r$. We can expect this behavior to be similar for more complex systems if the $n(\boldsymbol{r}) = \eta_0$ surface is close to a sphere (see supp. mat. [14]).

The shape of the correction is similar to the one proposed by Casida and Salahub [23, 24], who argument that a shift of the XC potential in the central region is necessary to fix the asymptotic limit of the LDA potential[25]. Moreover, they show that the shift is related to the DD of the energy with respect to the particle number. As in our method the shift appears naturally from imposing the asymptotic limit, we can obtain the value of the DD.

To obtain the relation between the DD and the shift, we assume that a potential $\bar{V}_{\mathrm{xc}}$, which lacks the DD, approximates the XC potential averaged over the discontinuity [5, 7]. This is

$$\bar{V}_{\mathrm{xc}} = \frac{1}{2} \left[V_{\mathrm{xc}}(N^+) + V_{\mathrm{xc}}(N^-) \right] . \tag{9}$$

Using Eq. (2), immediately follows that

$$V_{\mathrm{xc}}(N^-) = \bar{V}_{\mathrm{xc}} - \frac{1}{2}\Delta_{\mathrm{xc}} . \tag{10}$$

By imposing the asymptotic limit of Eq. 4, our corrected potential is approximating $V_{\mathrm{xc}}(N^-)$ [26]. Therefore, we can obtain the value of the DD from Eq. (10). For practical calculations we average the change of the XC potential due to the correction over the central region

$$\Delta_{\mathrm{xc}} = -\frac{2}{\Omega} \int_{n(\boldsymbol{r}) \geq \eta} \mathrm{d}\boldsymbol{r} \left[V_{\mathrm{xc}}^c(\boldsymbol{r}) - \bar{V}_{\mathrm{xc}}(\boldsymbol{r}) \right] , \tag{11}$$

where Ω is the volume of the central region. This expression for the DD can be calculated directly from the correction process as a ground-state property. An alternative, but less practical, method for the calculation of the DD is detailed in supp. mat. [14].

TABLE I. Comparison of the calculated derivative discontinuity with theoretical and experimental results. [a] Experimental gap values from Ref. [27]. [b] Ensemble spin DFT results by Chan [6]. Values in atomic units.

Atom	Experimental[a]	ESDFT[b]	CXD-LDA
B	0.295	0.270	0.284
C	0.367	0.342	0.337
O	0.447	0.404	0.435
F	0.515	0.478	0.467

TABLE II. Mean absolute error in the ionization energy for atoms (He to Ar). Comparison of CXD-LDA with LDA, LB [13], RPP [22] and KLI-CS [18, 30] potentials. [a]Results from Ref. [31]. [b]Results from Ref. [32] given in Ref. [31]. (Data in supp. mat. [14].)

LDA	LB[a]	RPP[a]	KLI-CS[b]	CXD-LDA
41%	3.7%	7.4%	5.7%	4.1%

In Table I, we compare the DD obtained with Eq. (11) with the values reported by Chan [6] from ensemble DFT (with XC potentials obtained from wave-function methods). We also compare it with the experimental value of the gap, that for these open-shell atoms is equal to the DD since the KS gap is zero. The three sets present a remarkable agreement, with our results being smaller that the experimental values by less than 10%.

To investigate further the quality of corrected potential and the predicted DD, we compare the calculated gap with the LDA KS gap and the experimental gap, for our set of atoms and molecules. The results are plotted in Fig. 3. The KS gap of the corrected potential is close to the LDA one [28] and far from the experimental value. Once we add the DD, however, the results are closer to the experiment, with an average error of 11% for atoms and 7% for molecules.

While the correction has little effect on the KS gap, it changes the KS eigenvalues. This can be seen in the ionization energy (I), which in DFT is given by $-\epsilon_{\mathrm{HOMO}}$ [12]. In Fig. 4, we plot I for the LDA and CXD-LDA as a function of the experimental value. In Table II, we compare the deviation from experimental results for atoms with other XC approximations that have the proper asymptotic limit: LB, RPP, and KLI with Colle-Salvetti correlation [30] (KLI-CS). The correction procedure improves considerably the LDA results, with similar accuracy to other long range XC potentials.

The XC density approach directly provides an approximation to the XC potential and not to the XC energy functional. In principle, the XC energy can be obtained by a path integration [33], or in the particular case of an exchange potential by the Levy-Perdew virial relation [34]. However, not all potentials are functional derivatives of an energy functional. For those who are
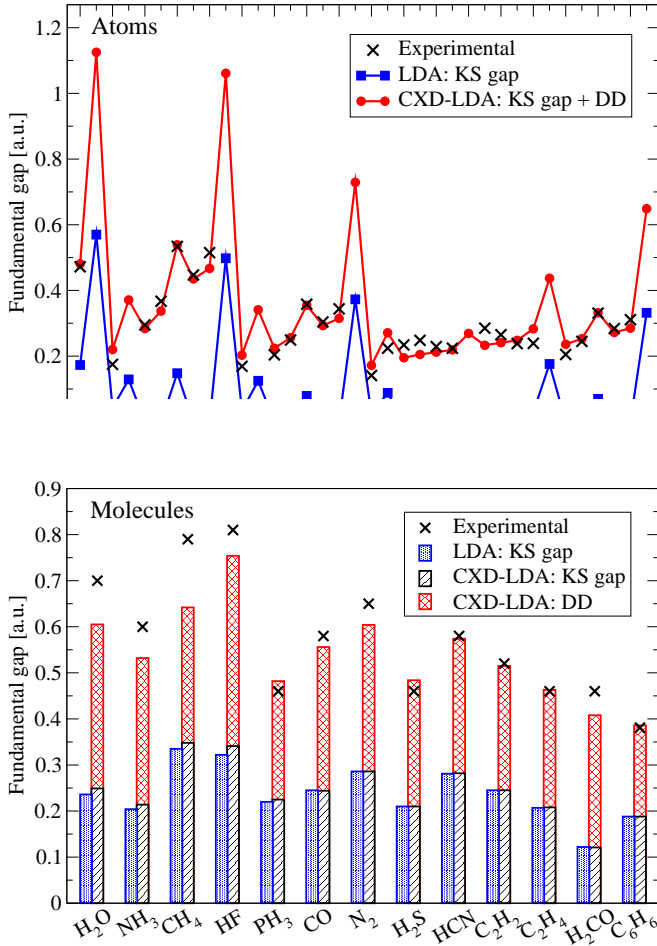
FIG. 3. Comparison of the CXD-LDA gap with LDA and available experimental results. The CXD-LDA gap has contributions from the Kohn-Sham (KS) gap and the derivative discontinuity (DD). Result for atoms (top) from H to Kr, experimental values from Ref. [27], and a set of molecules (bottom), experimental values compiled in Ref. [7], except for C_6H_6 [27, 29]. (Data in supp. mat. [14].)

FIG. 4. LDA and CXD-LDA ionization energy as a function of the experimental value. Atoms from H to Sr. (Data in supp. mat. [14].)

not, sometimes called *stray* potentials, the XC energy is not properly defined as it depends on the integration path.

Some numerical tests have been proposed to detect when a potential is stray [35]. We have applied one of this tests to our corrected LDA potential and it appears to indicate that it is not a functional derivative (see supp. mat. [14]). This issue will be addressed in detail in future work. Even when a potential is stray, it can be used useful to predict physical properties, especially properties that are total energy differences. For example, the KLI, LB and RPP potentials used in this article for comparison are stray potentials [35].

In summary, we have introduced a new auxiliary quantity, the XC density, to construct approximations for the XC potential. Based on an exact condition that the XC potential must fulfill and basic notions of electrostatics, we have presented a correction method for any previously proposed XC potential.
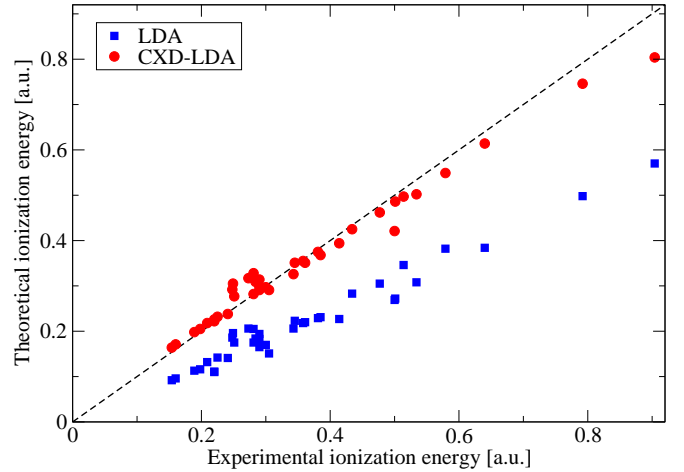
Additionally, the correction procedure allows for the direct calculation of the DD of the XC energy, which can be used to directly predict the fundamental gap as a ground-state property. Moreover, our approach allows for a routine computation of the DD as a practical method for the prediction of the gap.

The proposed potential is a pure functional of the electronic density with a certain degree of non-locality included by the optimization of η_0 and by the Poisson equation. The correction procedure does not depend on any empirical or globally adjusted parameter.

Since the basis for our method is the correction of the XC potential in the asymptotic region, it is not directly applicable to crystalline systems. However, the concepts of the XC density and the DD as a potential shift are still valid. Therefore, it might be possible to generalize the method to solids, where the determination of accurate gaps is one of the main challenges for DFT.

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