

## Exact expressions for the height of the interatomic step in the exchange-correlation potential from the derivative discontinuity of the energy

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Popular approximations to the exchange-correlation (xc) energy of density-functional theory do not yield the spatial “step” structures in the exact xc potential which are necessary to describe dissociation and electron excitation with the Kohn-Sham (KS) system. Via the discontinuity in the derivative of the xc energy as a function of electron number I derive exact analytic expressions in terms of the KS single-particle energies for the height of the step in the xc potential between a variety of open- and closed-shell atoms within stretched molecules.

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### I. INTRODUCTION

The unparalleled success of Kohn-Sham (KS) [1] density-functional theory (DFT) [2] within solid-state physics [3–5] is not experienced within quantum chemistry. DFT’s popularity stems from the accuracy and computational efficiency of commonly used approximations to the exchange-correlation (xc) energy, such as the local density [1] and the generalized gradient [6] approximation. However, these popular approximations are unreliable for molecules with strong electron localization [7–9].

An accurate ground-state KS potential is required for determining ground-state properties, such as the total energy [10], as well as the optical absorption spectra [11,12], charge-transfer energies [13–16], and electron real-time dynamics [17]. As existing approximations within KS theory are unreliable, computationally demanding hybrid density functionals [18,19] are employed to calculate these properties [5,20–28].

The exact xc potential has a strong dependence on the electron density *everywhere* in the system, which is challenging to capture within an approximation. In the KS system, the KS potential ensures that the noninteracting single-particle electron density equals the many-body density. For systems in which there is a large distance  $d$  between its subsystems, e.g., the disassociated atoms of a molecule or a donor-acceptor pair, the exact xc potential can consist of continuous, but sharp, features, termed spatial “steps.” They occur at points in the density where the “local effective ionization potential” (LEIP) [29] changes, for example, at the intersection of two subsystems. The step can be present in the xc potential in the limit that the subsystems are infinitely separated [29–31] and can depend on properties of each subsystem [see Eq. (1)].

For diatomic molecules the step that occurs *between* the atoms can be crucial to obtain the correct electron

occupation on each atom throughout the ground- and excited-state KS system [15,29]. Common approximations based on the local density that omit this “interatomic” step yield spurious fractional electron numbers on the disassociated atoms [7,32–36], termed the delocalization error [37,38], which leads to an unreliable prediction of the bonding length and dissociation energy [39]. Despite employing a spatially non-local potential, the *exact* multiplicative potential of hybrid density functionals [19] can also require an interatomic step to accurately describe atomic dissociation [40].

In order to calculate accurate excitation energies within ensemble and time-dependent DFT a reliable xc approximation must capture steps in the ground-state KS potential [13,15].

For a system that consists of two separated open-shell atoms the interatomic step height  $S$  is given by Almladh and von Barth’s expression [30]

$$S = I_L - I_R, \quad (1)$$

where  $I_L$  is the ionization energy of the left atom and  $I_R$  is that of the right atom. An analytic expression for the step height in terms of the atomic KS quantities has not been formally derived for a system that contains any closed-shell atoms.

In this article I study the addition of an electron to various stretched diatomic molecules (composed of a variety of open- and closed-shell atoms) that each initially consists of an arbitrary *integer* number of electrons  $N_0$  in order to deduce the height of the interatomic step in the KS potential of the  $(N_0 + 1)$ -electron molecule. I study the evolution of the exact KS potential as the amount of additional electron goes smoothly from 0 to 1 via an ensemble of the two integer systems. This insight could aid the development of advanced density-functional approximations aiming to model electron excitation or within ground-state approximations that yield step structures in the xc potential but require exact conditions for practical use (e.g., Ref. [41]).

The electron number of a finite system can vary continuously if it is in contact with an electron reservoir, the chemical potential of which can be adjusted. In this case the exact total energy of the finite system is a linear function of the electron

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number  $N$  between integer values [42]. At an integer value  $N_0$ , the derivative of the energy with respect to  $N$  is discontinuous. The magnitude of this derivative discontinuity is the fundamental gap of the  $N_0$ -electron system—its ionization energy minus its electron affinity ( $I^{N_0} - A^{N_0}$ ). Within the KS system, Janak’s theorem [43] ensures that the highest occupied molecular orbital (HOMO) energy is also discontinuous at integer values of  $N$  and is equal to minus the ionization energy (the “IP theorem” of DFT). Therefore, when the system consists of infinitesimally *less* than  $N_0$  electrons, the HOMO energy  $\lim_{\delta \rightarrow 0} \varepsilon_{N_0}^{N_0 - \delta} = -I^{N_0}$ . When  $N$  is infinitesimally *more* than  $N_0$ ,  $\lim_{\delta \rightarrow 0} \varepsilon_{N_0+1}^{N_0 + \delta} = -I^{N_0+1} = -A^{N_0}$ . In order to ensure that these two KS orbital energies yield the required ionization energies, the exact xc potential  $v_{xc}(x)$  experiences a discontinuous *uniform* shift by a constant,  $\Delta^{N_0}$ , when the number of electrons  $N$  within the system infinitesimally surpasses an integer [42]:  $\Delta^{N_0} = \lim_{\delta \rightarrow 0} [v_{xc}(x)|_{N=N_0+\delta} - v_{xc}(x)|_{N=N_0-\delta}]$ . The magnitude of the shift is thus

$$\begin{aligned} \Delta^{N_0} &= \lim_{\delta \rightarrow 0} [I^{N_0} + \varepsilon_{N_0}^{N_0 - \delta} - (A^{N_0} + \varepsilon_{N_0+1}^{N_0 + \delta})] \\ &= I^{N_0} - A^{N_0} - (\varepsilon_{N_0+1}^{N_0} - \varepsilon_{N_0}^{N_0}), \end{aligned} \quad (2)$$

where  $\varepsilon_{N_0}^{N_0}$  is the KS energy of the HOMO and  $\varepsilon_{N_0+1}^{N_0}$  is the KS energy of the lowest unoccupied molecular orbital (LUMO), both of the  $N_0$ -electron system. Owing to the IP theorem,  $I^{N_0} = -\varepsilon_{N_0}^{N_0}$  (where the exact KS potential of the  $N_0$ -electron system asymptotically approaches zero; if a nodal plane is present in the HOMO orbital, this may not be the case [44]), and thus, Eq. (2) can be simplified to  $\Delta^{N_0} = -A^{N_0} - \varepsilon_{N_0+1}^{N_0}$ .

For clarity I present my arguments in one dimension. It is straightforward to generalize my arguments to three-dimensional (3D) systems without altering my conclusions. However, one must be mindful of nodal planes in the HOMO on which the exact KS potential can exhibit divergent behavior [44].

In principle  $\Delta^{N_0}$  yields the fundamental gap from the KS system [42,45,46]; in practice, common density-functional approximations do not capture this xc derivative discontinuity [32,47–51].

In Refs. [15,52] the relationship between the interatomic step and the discontinuity in the derivative of the xc energy was demonstrated in the context of charge transfer within a diatomic molecule. In this article I show analytically that the height of the interatomic step in the exact KS potential of any stretched molecule consisting of an arbitrary  $N_0 + 1$  number of electrons is equal to the xc derivative discontinuity of the  $N_0$ -electron system.

## II. COMPUTATIONAL DETAILS

I employ the iDEA code [53] to verify my analytic results via exactly solvable model systems. The code models few-electron systems exactly by solving the many-body Schrödinger equation on a real-space grid in one dimension. The code employs the softened Coulomb interaction  $(|x - x'| + 1)^{-1}$  as appropriate [54]. From the exact fully correlated, ground-state many-body wave function I obtain the exact ground-state many-body density  $n(x)$ . I reverse engineer the KS equations so that the KS density is equal to the many-body

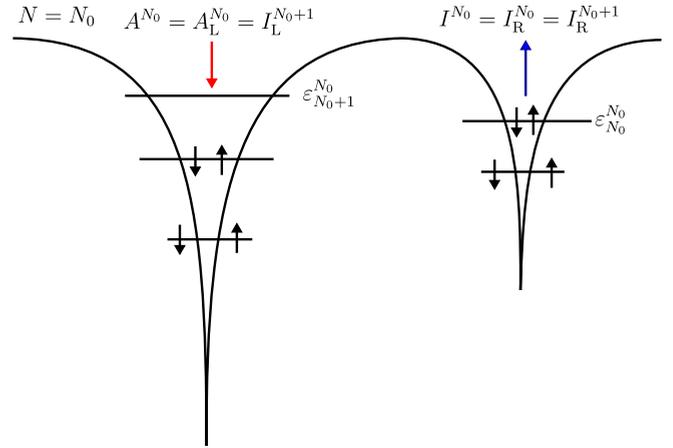


FIG. 1. Diagram of an  $N_0$ -electron stretched diatomic molecule. Both atoms are closed shell within the exact KS description. The lowest unoccupied KS orbital is localized to the left atom, and the highest occupied KS orbital is localized to the right atom.

density to find the corresponding *exact* KS potential, orbitals, and energies; details of the reverse-engineering procedure are given in Ref. [53].

## III. ADDING AN INFINITESIMAL AMOUNT OF AN ELECTRON TO A DIATOMIC MOLECULE

Consider the exact KS description of an  $N_0$ -electron stretched diatomic molecule. The external potential generated by the left nucleus (L) corresponds to a deeper potential well than that of the right (R), and both atoms are closed shell (see Fig. 1). The HOMO is localized to the right atom, and the LUMO is localized to the left atom. The atoms are so separated that adding or subtracting electrons from either atom has a negligible effect on the electron density localized to the other atom.

An electron added to this  $N_0$ -electron system localizes to the left atom, and ionization causes an electron localized to the right atom to escape. Hence, the ionization energy of the *whole* system corresponds to the ionization energy of the isolated right atom ( $I^{N_0} = I_R^{N_0}$ ), and the whole system’s electron affinity is that of the isolated left atom ( $A^{N_0} = A_L^{N_0}$ ); see Fig. 1.

The interatomic step in the KS potential is usually discussed in the context of “reordering” the KS single-particle energy levels of one atom relative to the other [15]. The role of the step in this case is to ensure that the additional KS electron localizes to the “correct” atom, i.e., that which matches the many-body system; for more details see Sec. V. For the  $N_0$ -electron system described above, without any adjustments to its exact KS potential, the additional KS electron localizes to the left atom just like the many-body system. Thus, the reordering of KS single-particle energy states is *not* required—does this mean there is no interatomic step in the  $(N_0 + 1)$ -electron system’s xc potential?

According to Eq. (2) the xc derivative discontinuity of the *whole*  $N_0$ -electron system (left and right atoms) is  $\Delta^{N_0} = I_R^{N_0} - A_L^{N_0} - (\varepsilon_{N_0+1}^{N_0} - \varepsilon_{N_0}^{N_0})$ . As the right atom’s ionization energy is that of the whole molecule, the IP theorem states  $I_R^{N_0} = -\varepsilon_{N_0}^{N_0}$ . Thus,  $\Delta^{N_0} = A_L^{N_0} - \varepsilon_{N_0+1}^{N_0}$ .

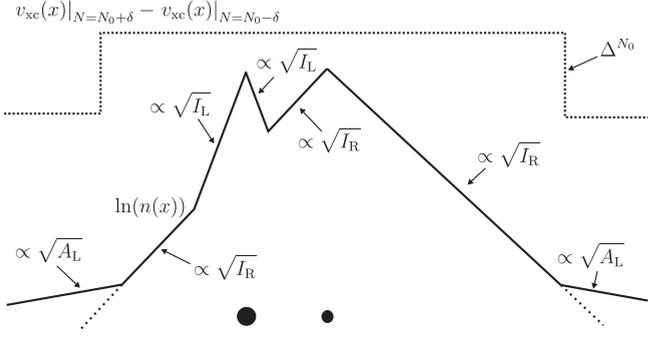


FIG. 2. Diagram of the natural logarithm of the density of an  $(N_0 + \delta)$ -electron system with a vanishingly small  $\delta$ . Black dots indicate the left and right nuclei. On the periphery of the system the exponential decay of the density changes from  $\propto \sqrt{I_R^{N_0}}$  to  $\propto \sqrt{A_L^{N_0}}$ , which yields a step in the xc potential of height  $\Delta^{N_0}$  (see text).

For this system the LUMO is also the left atom's (the atom to which the additional electron localizes) lowest unoccupied KS *atomic* orbital. Thus, the xc derivative discontinuity of the isolated left atom  $\Delta_L = -A_L^{N_0} - \varepsilon_{N_0+1}^{N_0}$ , which is *equal* to  $\Delta^{N_0}$  for this molecule.

Figure 2 demonstrates the change in the xc potential and the natural log of the electron density when a vanishingly small amount of an electron is added to this  $N_0$ -electron system. The exact many-body total density of the  $(N_0 + \delta)$ -electron system is an ensemble of the  $N_0$ -electron and  $(N_0 + 1)$ -electron systems, as such

$$n^{N_0+\delta}(x) = (1 - \delta)n^{N_0}(x) + \delta n^{N_0+1}(x). \quad (3)$$

Far from any system the many-body density decays exponentially  $\propto e^{-2\sqrt{2I}|x|}$  [55,56], where  $I$  is the ionization energy of the system. Thus, far from the center of my stretched molecule the density decays  $\propto e^{-2\sqrt{2I_R^{N_0}}|x|}$  ( $I_R^{N_0}$  is the whole system's ionization energy). Even when  $\delta$  is vanishingly small, eventually, the total density decay is dominated by the decay  $e^{-2\sqrt{2A_L^{N_0}}|x|}$  ( $A_L^{N_0}$  is the whole system's electron affinity):

$$n^{N_0+\delta}(|x| \rightarrow \infty) = (1 - \delta)Be^{-2\sqrt{2I_R^{N_0}}|x - \frac{1}{2}d|} + \delta Ce^{-2\sqrt{2A_L^{N_0}}|x + \frac{1}{2}d|}, \quad (4)$$

where  $B$  and  $C$  are normalization constants. In order for the KS density to decay at the *same rate* as the many-body density, on the periphery of the system, at the point in the density where the LEIP changes, steps must form in the xc potential, yielding a finite "plateau" which raises the xc potential by a constant,  $v_p$ , in the vicinity of *only the molecule* (see Fig. 2) [57]. Hence, the KS density is

$$n^{N_0+\delta}(|x| \rightarrow \infty) = (1 - \delta)Be^{-2\sqrt{-2(\varepsilon_{N_0}^{N_0+\delta} - v_p)}|x - \frac{1}{2}d|} + \delta Ce^{-2\sqrt{-2\varepsilon_{N_0+1}^{N_0+\delta}}|x + \frac{1}{2}d|}, \quad (5)$$

where  $v_{xc}(|x| \rightarrow \infty) = 0$ ,  $\lim_{\delta \rightarrow 0} \varepsilon_{N_0+1}^{N_0+\delta} = \varepsilon_{N_0+1}^{N_0} + v_p$ , and  $\lim_{\delta \rightarrow 0} \varepsilon_{N_0}^{N_0+\delta} = \varepsilon_{N_0}^{N_0} + v_p$ . For the KS density to decay at the same rate as the many-body density,  $\varepsilon_{N_0}^{N_0+\delta} - v_p = \varepsilon_{N_0}^{N_0} + v_p -$

$v_p = \varepsilon_{N_0}^{N_0} = -I_R^{N_0}$ , and  $\varepsilon_{N_0+1}^{N_0+\delta} = \varepsilon_{N_0+1}^{N_0} + v_p = -A_L^{N_0}$ . Thus, the height of the plateau  $v_p = -A_L^{N_0} - \varepsilon_{N_0+1}^{N_0}$ , which is  $\Delta^{N_0}$ . These steps are drawn infinitely far from the system's center as  $\delta \rightarrow 0$  and the plateau becomes a uniform shift in the xc potential, a numerical demonstration of which is in Ref. [52].

#### IV. INCREASING THE AMOUNT OF ADDITIONAL ELECTRON TO 1

On the periphery of any *subsystem* within a larger system the electron density decays in accordance with that subsystem's ionization energy. The decay can abruptly change, for example, when the decay of two subsystems meet. This change in the density corresponds to a change in the LEIP which in turn can yield an abrupt spatial step in the xc potential at that point [29].

For my stretched molecule, as  $\delta$  is increased slightly, the additional electron completely localizes to the left atom. Hence, the left atom's local number of electrons surpasses an integer, and consequently, its xc potential experiences a *local* shift (spatially uniform just for the left atom) by  $\Delta_L$ , as depicted in Fig. 3.

When an atom's local number of electrons increases by a small amount, the exponential decay of the atom's density (in my case the left atom) changes from  $\propto e^{-2\sqrt{2I_L^{N_0}}|x|}$  to  $\propto e^{-2\sqrt{2A_L^{N_0}}|x|}$  far from *that atom*, e.g., in Fig. 3. This causes a step to form in the xc potential around the atom [58], the height of which is given by that atom's xc derivative discontinuity [15,52], giving rise to the plateau in the atom's xc potential. For my stretched molecule this happens for the left atom such that the KS density decays  $\propto e^{-2\sqrt{-2\varepsilon_{N_0+1}^{N_0+\delta}}|x|} = e^{-2\sqrt{-2(\varepsilon_{N_0+1}^{N_0} + \Delta_L)}|x|} = e^{-2\sqrt{2A_L^{N_0}}|x|}$ . This  $\sqrt{A_L^{N_0}}$  decay then meets the decay of the right atom, which is  $\propto e^{-2\sqrt{2I_R^{N_0}}|x|}$ , causing a second change in the LEIP and a second step in the xc potential between the atoms (see Fig. 3).

In principle, when the atoms are far apart, the *right* plateau's height does not affect the KS decay in any region which is  $\propto e^{-2\sqrt{-2\varepsilon_{N_0+1}^{N_0+\delta}}|x|}$  because the highest (partially) occupied KS orbital is localized to the *left* atom. Thus, the height of the right plateau (within a range [29]) has no effect on the corresponding KS single-particle energy  $\varepsilon_{N_0+1}^{N_0+\delta}$ . This may lead one to assume that the height of the right plateau cannot be determined from the decay of the density. However, recall that the atoms are so far apart that the introduction of an electron to the left atom has a negligible effect on the right atom's density, so the decays  $\propto e^{-2\sqrt{2I_R^{N_0}}|x|}$  and  $e^{-2\sqrt{2A_L^{N_0}}|x|}$  are both *independent* of  $\delta$ . Hence, the density to the right of the right atom, given by Eq. (4), *does not change* its spatial structure as  $\delta$  is increased [59]. As the KS potential is uniquely determined by the spatial structure of the density [2], the height of the corresponding step in the xc potential at the point where the  $\sqrt{I_R^{N_0}}$  decay becomes the  $\sqrt{A_L^{N_0}}$  decay must remain fixed as a function of  $\delta$ . The step height is  $\Delta^{N_0}$  in the limit that  $\delta \rightarrow 0$ ; therefore, the plateau localized to the right atom has a height of  $\Delta^{N_0}$  for  $0 < \delta \leq 1$ . It follows that the plateau's other step—located *between* the atoms—has a height of  $\Delta^{N_0}$  also, as shown in Fig. 3.

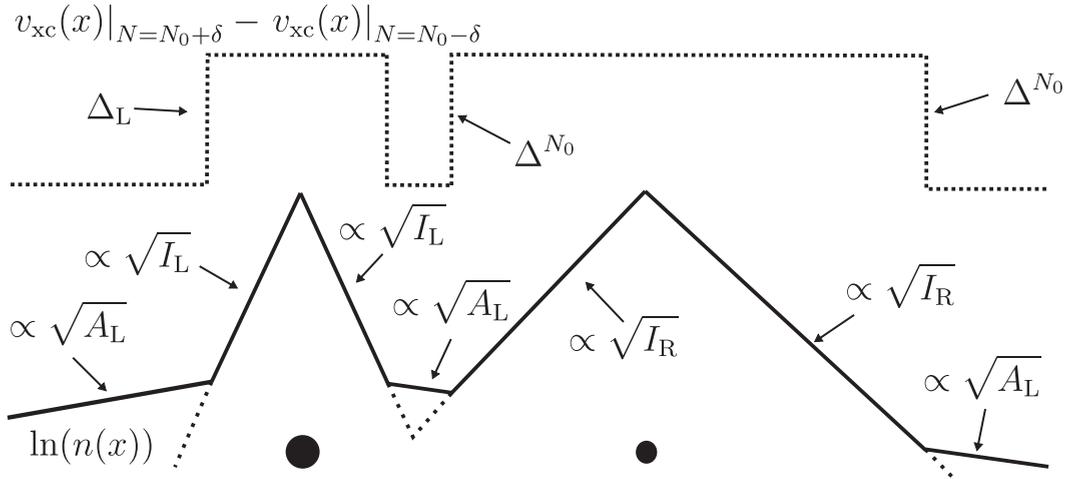


FIG. 3. Diagram of the natural logarithm of the density of an  $(N_0 + \delta)$ -electron system;  $\delta$  is finite, but small. Black dots indicate the left and right nuclei. For the stretched molecule the LEIP changes on the periphery of the left atom, resulting in a plateau with a height corresponding to the left atom’s xc derivative discontinuity  $\Delta_L$ . The decay of the left atom then meets the decay of the right atom, yielding a second step *between* the atoms. A final change in the LEIP occurs far to the right of the system. The height of the right plateau is the xc derivative discontinuity of the whole molecule  $\Delta^{N_0}$  in the limit that the atoms are infinitely separated (see text).

In Ref. [52] the double-step structure between two separated atoms was demonstrated to occur for a 3D stretched diatomic molecule whose KS potential possesses an interatomic step *before* the addition of any fraction of an electron. I have shown that, in general, when a small amount of an electron is added to *any* stretched molecule the atom to which the additional electron localizes experiences a shift by its own xc derivative discontinuity and the other atom’s xc potential also shifts but by the xc derivative discontinuity of the *whole* system [60].

As  $\delta \rightarrow 1$ , the width of the plateau localized to the *left* atom (with height  $\Delta_L$ ) shrinks as the LEIP in left atom’s density moves closer to the center of the atom (see Fig. 5). The height of the plateau localized to the right atom is unaffected owing to the large separation of the atoms.

In summary, for small  $\delta$  there are *two* steps between the atoms: an interatomic step with height  $\Delta^{N_0}$  and an “intra-atomic step” (related to the left atom) of height  $-\Delta_L$  (minus indicates a step “down”; see Figs. 3 and 5, bottom). For this system  $\Delta^{N_0} = \Delta_L$ , thus, there is no *overall* step between the atoms for small  $\delta$ . When  $\delta = 1$ , only the interatomic step remains in the KS potential, yielding an overall step in the  $(N_0 + 1)$ -electron system of height  $\Delta^{N_0}$ :

$$\lim_{d \rightarrow \infty} S^{N_0+1} = \Delta^{N_0}$$

(see Fig. 4, bottom).

I model a one-dimensional (1D) two-electron stretched diatomic molecule ( $N_0 = 2$ ), where the external potential is  $v_{\text{ext}}(x) = -2/(|x - \frac{d}{2}| + 1) - 3/(|x + \frac{d}{2}| + 1)$  and  $d = 30$  a.u. (see Fig. 4, top). All electrons have the *same spin*, so that each atom is closed shell. This achieves the maximum richness of exchange and correlation for a given computational effort; for example, three KS orbitals are occupied in the three-electron system.

The system is designed such that the LUMO is localized to the left well and the HOMO is localized the right one (see

Fig. 4, middle, and compare it with Fig. 1). Within the three-electron many-body system the additional electron localizes to the left well (see Fig. 4, bottom).

Via Eq. (3) I combine the two-electron density and the three-electron density in an ensemble to obtain the exact many-body density as a function of  $\delta$ . I reverse

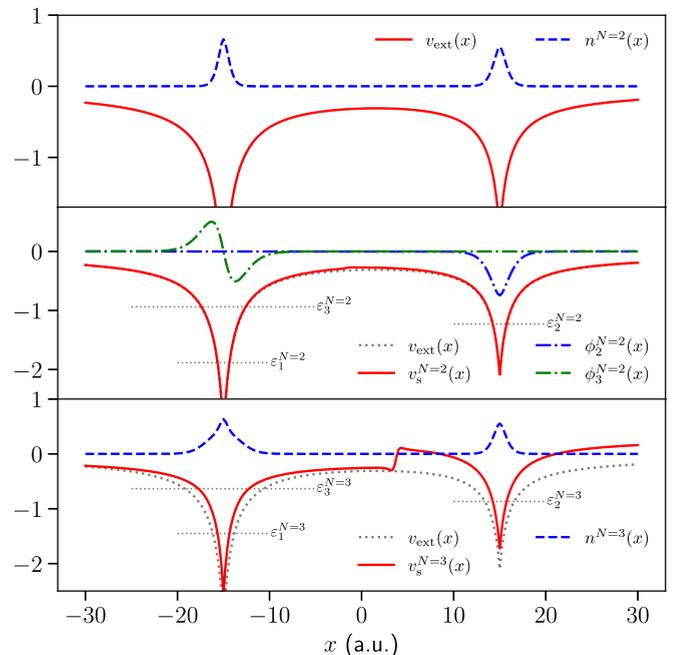


FIG. 4. Top: The two-electron density and external potential. Middle: The lowest unoccupied KS orbital,  $\phi_2^{N=2}(x)$ , and the highest occupied KS orbital,  $\phi_3^{N=2}(x)$ , of the two-electron system. The corresponding single-particle energy levels are shown in gray. Bottom: The many-body density of three same-spin electrons and the corresponding exact KS potential. A step is present which elevates the potential in the vicinity of the right well, the height of which is given by the xc derivative discontinuity of the two-electron molecule.

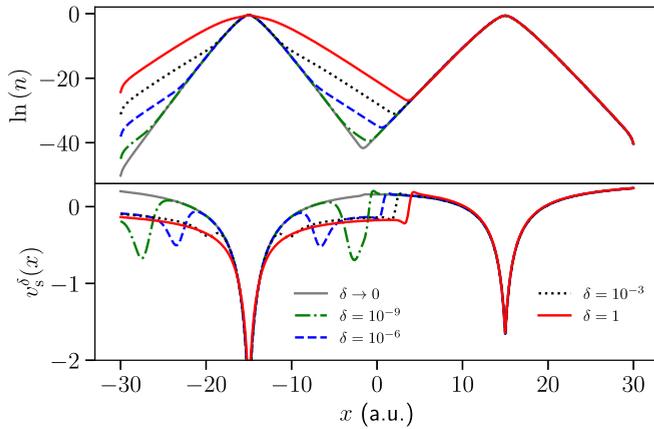


FIG. 5. Top: The natural log of the density with  $2 + \delta$  same-spin electrons. Bottom: The corresponding exact KS potential. As  $\delta \rightarrow 1$ , the additional fraction of an electron localizes to the left atom, giving rise to a plateau localized to the left atom which corresponds to the left atom's xc derivative discontinuity  $\Delta_L$ . Simultaneously, a separate plateau localizes to the right atom with height  $\Delta^{N=2}$  (the xc derivative discontinuity of the whole molecule). When  $\delta = 1$ , only the right plateau remains, giving rise to an interatomic step in the three-electron system of height  $\Delta^{N_0}$ .

engineer the KS equations with fractional occupation of the (now) HOMO, such that  $n^{N=2+\delta}(x) = |\phi_1^{N=2+\delta}(x)|^2 + |\phi_2^{N=2+\delta}(x)|^2 + \delta|\phi_3^{N=2+\delta}(x)|^2$ , to find the corresponding exact KS potential as a function of  $\delta$  (see Fig. 5).

For small  $\delta$  the density in the region of the left atom is unchanged; there is a change in the LEIP on either side of the left atom as expected (compare Fig. 5 with Fig. 3). The corresponding steps in the xc potential give rise to the plateau which elevates the left atom's xc potential by the xc derivative discontinuity of the left atom [15,52]  $\Delta_L$  (Fig. 5, bottom). (For this system  $\Delta_L = 0.349$  a.u.) This plateau in the xc potential shrinks as  $\delta \rightarrow 1$ ; the steps move towards the left atom until the plateau has zero width and the xc potential corresponds to the left atom with an additional electron ( $\delta = 1$ ).

Towards the right atom, at the point where the left atom's density meets the right's, there is a second change in the LEIP (see Fig. 5, top). As predicted above, a plateau which elevates the xc potential in the region of the *right atom* with magnitude  $\Delta^{N=2}$  is present as  $\delta \rightarrow 1$  (see Figs. 5, bottom, and 4, bottom).

In summary, when a finite, but small, fraction of an electron is added to this stretched molecule, there are *two* plateaus in the exact xc potential—one localized to the left atom with height  $\Delta_L$  and one localized to the right atom with height  $\Delta^{N_0}$ . At the edge of each plateau between the atoms there is a step. For this molecule  $\Delta_L = \Delta^{N_0}$ ; below I investigate the effect on the exact xc potential when the heights of these two plateaus are *not* equal. As the amount of additional electron tends to 1, the left plateau (in the vicinity of the atom to which the additional electron localizes) is removed from the xc potential, while the right plateau remains at a height of  $\Delta^{N_0}$ . Thus, within the  $(N_0 + 1)$ -electron system the right atom's xc potential is elevated by  $\Delta^{N_0}$ , yielding the interatomic step (see Fig. 4, bottom). Therefore, although the interatomic step in the KS potential for this type of system is *not* needed to reorder the KS single-particle energies, the requirement that

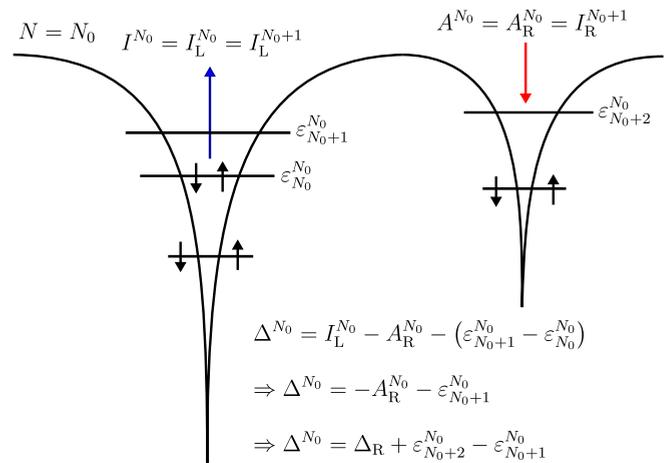


FIG. 6. Diagram of an  $N_0$ -electron stretched diatomic molecule where both atoms are closed shell *and* the lowest unoccupied and highest occupied molecular orbitals are localized to the left atom.

the KS potential yield the correct electron density *at all* points in space means an interatomic step is present.

## V. AN INTERATOMIC STEP TO CORRECTLY DISTRIBUTE ELECTRONS

Imagine an  $N_0$ -electron stretched diatomic molecule where the system is asymmetric (as above) and both atoms are closed shell (see Fig. 6).

Consider the atoms to be so separated that the ionization energy of the molecule corresponds to the ionization energy of the isolated *left* atom ( $I^{N_0} = I_L^{N_0}$ ) and the electron affinity of the whole molecule corresponds to the affinity of the isolated *right* atom ( $A^{N_0} = A_R^{N_0}$ ). Hence, for this system  $\Delta^{N_0} = I_L^{N_0} - A_R^{N_0} - (\epsilon_{N_0+1}^{N_0} - \epsilon_{N_0}^{N_0}) = -A_R^{N_0} - \epsilon_{N_0+1}^{N_0}$ . The HOMO and the LUMO are *both* localized to the left atom (see Fig. 6). When an electron is added to this system, it localizes to the right atom owing to the Coulomb and Pauli interaction which would be experienced if it were to localize to the left atom. Within the exact KS description, if an electron were to be added to the exact KS potential of the  $N_0$ -electron system, it would spuriously localize to the left atom (within the many-body system it would localize in the right atom). Therefore, an interatomic step in the  $(N_0 + 1)$  electron is required to ensure that the KS single-particle density is equal to the many-body density by reordering the KS energies. When an infinitesimal amount of an electron is added to this  $N_0$ -electron system, the xc potential of the *whole* system jumps by  $\Delta^{N_0}$  (demonstrated above).

For small  $\delta$ , the additional electron completely localizes to the right atom, which gives rise to a plateau in its xc potential, the height of which corresponds to the xc derivative discontinuity of the right atom  $\Delta_R$  (see Fig. 7). Like for the system above, the left atom's xc potential is elevated by  $\Delta^{N_0}$  (for  $0 < \delta \leq 1$ ; see Sec. IV). Thus, the overall height of the interatomic step within the  $(N_0 + \delta)$ -electron system is  $\Delta^{N_0} - \Delta_R = -A_R^{N_0} - \epsilon_{N_0+1}^{N_0} - \Delta_R$ . For this system  $\Delta_R = -A_R^{N_0} - \epsilon_{N_0+2}^{N_0}$  as  $\epsilon_{N_0+2}^{N_0}$  is the lowest unoccupied *atomic* KS energy of the right atom. Therefore,  $\Delta^{N_0} - \Delta_R = \epsilon_{N_0+2}^{N_0} -$

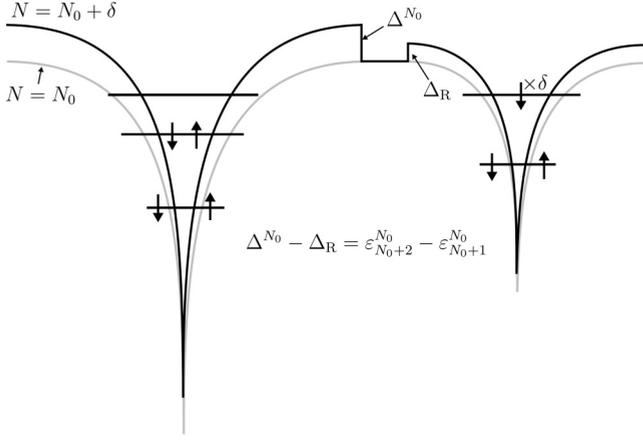


FIG. 7. Diagram of an  $(N_0 + \delta)$ -electron stretched diatomic molecule with a closed-shell left atom and a partially occupied open-shell right atom within the exact KS description ( $\delta \neq 1$ ). The double-step structure occurs between the atoms because the left and right atoms' xc potentials are elevated by two plateaus (see Fig. 5, bottom).

$\epsilon_{N_0+1}^{N_0}$ . The highest (partially) occupied KS energy of the right atom is aligned with the lowest *unoccupied* KS energy of the left atom via a double-step structure between the atoms (see Fig. 7). These two steps occur because each atom has been elevated locally by a plateau (like for the system above; see Sec. IV, specifically Fig. 5, bottom). This case differs from that shown in Fig. 5 (bottom) because the magnitudes of the two step heights are not equal [61].

When  $\delta \rightarrow 1$ , the right plateau is removed from the xc potential, and the left plateau remains, the mechanism for which is described in Sec. IV. Hence, within the  $(N_0 + 1)$ -electron system the right atom is elevated by the plateau of height  $\Delta^{N_0}$ , and thus, there is an interatomic step in the xc potential with height  $S = \Delta^{N_0}$ .

For this system, as  $A_R^{N_0} = I_R^{N_0+1}$ ,  $\Delta^{N_0} = -I_R^{N_0+1} - \epsilon_{N_0+1}^{N_0}$ . Within the  $(N_0 + 1)$ -electron system  $I_R^{N_0+1} = -\epsilon_{N_0+1}^{N_0+1}$  owing to the IP theorem. Therefore,  $\Delta^{N_0} = \epsilon_{N_0+1}^{N_0+1} - \epsilon_{N_0+1}^{N_0}$  (see Fig. 8, bottom). Thus,

$$\lim_{d \rightarrow \infty} S^{N_0+1} = \Delta^{N_0} = \epsilon_{N_0+1}^{N_0+1} - \epsilon_{N_0+1}^{N_0}. \quad (6)$$

I model a 1D stretched diatomic molecule which initially consists of one electron ( $N_0 = 1$ ). The additional electron has the same spin as the initial electron so that the atoms are closed shell.  $v_{\text{ext}}(x) = -1/(|x - \frac{d}{2}| + 1) - 3/(|x + \frac{d}{2}| + 1)$ , and  $d = 15$  a.u. (see Fig. 8, top). The left external potential well is deep enough that two same-spin fully noninteracting electrons in *this external potential* both occupy the left well (see Fig. 8, middle). However, within the triplet two-electron many-body system one electron localizes in the left well, and the other electron localizes in the opposite well owing to the Coulomb and Pauli interaction they would experience if they were to occupy the same well (see Fig. 8, bottom).

Equation (6) implies that the role of the step is to ensure that as the atoms are separated, the difference between the highest occupied atomic KS energy of the right atom and the lowest unoccupied atomic KS energy of the left atom tends to

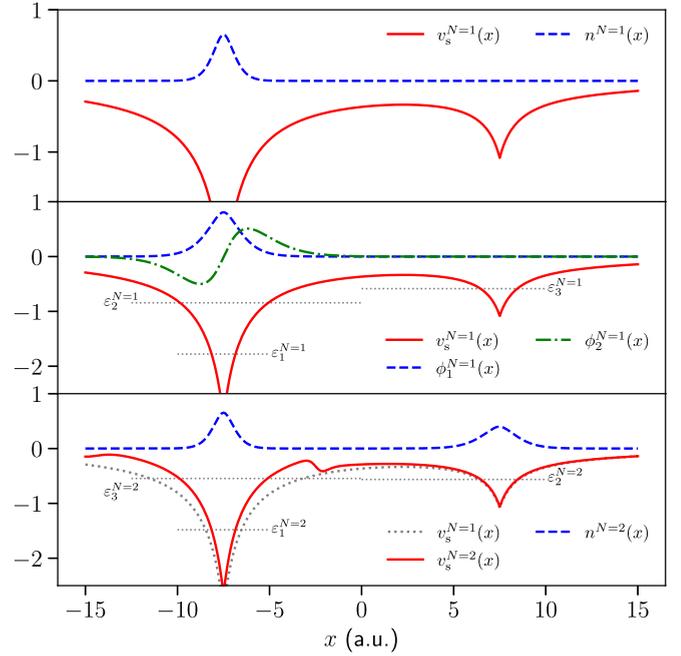


FIG. 8. Top: The one-electron density and the external potential. Middle: The lowest unoccupied KS orbital  $\phi_2^{N=1}(x)$  and the highest occupied KS orbital  $\phi_1^{N=1}(x)$  of the one-electron system. The corresponding single-particle energy levels are shown in gray. Bottom: The many-body density of two same-spin electrons and the corresponding exact KS potential. The step elevates the xc potential in the vicinity of the left well in order to reorder the occupation of the KS states.

zero. For any large, but finite, separation the highest occupied atomic KS energy of the right atom is slightly lower than the lowest unoccupied atomic KS energy of the left atom because the additional electron localized to the right atom has a small effect on the left atom's density. In practice this avoids the spurious occupation of the LUMO (for finite separations the inequality of Ref. [29] must be obeyed by the step height; see Fig. 8, bottom). As I increase the separation of the external potential wells, I find that this difference tends to zero as predicted by Eq. (6).

#### A. Almladh and von Barth case

The Almladh and von Barth case is similar to that above, but the left atom is open shell. Thus,  $\epsilon_{N_0}^{N_0} = \epsilon_{N_0+1}^{N_0}$ , and  $\Delta^{N_0} = I_L^{N_0} - A_R^{N_0}$  [see Eq. (2)].

When an electron with the *opposite* spin to the unpaired electron is added to this system within the many-body description, the additional electron localizes to the *right* atom owing to the Coulomb interaction which it would experience if it tried to localize to the left atom. Note that within the exact KS system, despite the LUMO being localized to the left atom within the  $N_0$ -electron system, the additional KS electron must localize to the right atom in order for the single-particle KS density to equal the exact many-body electron density. As such the highest occupied *atomic* energies must be aligned within the  $(N_0 + 1)$ -electron KS system, which is ensured within the exact system by the interatomic step [see Eq. (1)].

Within the  $(N_0 + \delta)$ -electron system, the localization of the additional electron within the exact KS system is the same as described above; a plateau of height  $\Delta_R$  forms for the right atom (the atom to which the additional electron localizes), while a plateau of height  $\Delta^{N_0}$  forms in the vicinity of the left atom.  $\Delta^{N_0} - \Delta_R = \varepsilon_{N_0+2}^{N_0} - \varepsilon_{N_0+1}^{N_0}$ , so in this case the step acts to align the highest (partially) occupied KS energy of the right atom with the highest occupied KS energy of the left atom, as required by Almladh and von Barth's argument [30].

When  $\delta = 1$ , the right plateau has gone, and the left plateau is still present. For this stretched molecule  $A_R^{N_0} = I_R^{N_0+1}$ , and because the additional electron localizes to the right atom,  $I_L^{N_0} = I_L^{N_0+1}$ , where  $I_L^{N_0+1}$  is the ionization energy of the left atom and  $I_R^{N_0+1}$  is the ionization energy of the right atom within the  $(N_0 + 1)$ -electron system. Therefore,  $\Delta^{N_0} = I_L^{N_0+1} - I_R^{N_0+1}$ . Thus, in accordance with Eq. (1), the step height is given by the difference between the left and right atoms' ionization energies:

$$\lim_{d \rightarrow \infty} S^{N_0+1} = \Delta^{N_0} = I_L^{N_0+1} - I_R^{N_0+1}. \quad (7)$$

## VI. CONCLUSION

I demonstrated analytically that the height of the spatial step that forms in the exact exchange-correlation potential between a variety of open- and closed-shell atoms within any stretched diatomic molecule composed of an arbitrary  $N_0 + 1$  number of electrons, where  $N_0$  is an integer, is equal to the xc derivative discontinuity [42] of the  $N_0$ -electron system. I verified my results with exactly solvable 1D model systems.

I considered the addition of an electron to an  $N_0$ -electron diatomic molecule in order to find an expression for the interatomic step in the  $(N_0 + 1)$ -electron system: When the amount of additional electrons is infinitesimal, the *whole* system's xc potential shifts discontinuously by a constant,  $\Delta^{N_0}$  (the xc derivative discontinuity of the  $N_0$ -electron system). For sufficiently large separation between the atoms of this molecule, the additional electron completely localizes to one of the atoms, say the left. This left atom experiences a local shift (a plateau) by its xc derivative discontinuity  $\Delta_L$ , which may differ from that of the whole molecule  $\Delta^{N_0}$ . In conjunction a

plateau with height  $\Delta^{N_0}$  localizes to the right atom, as depicted in Fig. 3 in Sec. IV.

As the amount of additional electron is increased to 1, the plateau localized to the left atom, to which the additional electron localizes, shrinks, while the plateau localized to the right atom has a fixed height of  $\Delta^{N_0}$ , as shown in Sec. IV. As a result, within the  $(N_0 + 1)$ -electron system the right atom's xc potential is elevated by  $\Delta^{N_0}$ , which means a step with height  $\Delta^{N_0}$  is present in the xc potential *between* the atoms.

I presented three distinct example diatomic molecules that consist of a variety of open- and closed-shell atoms. In each case the height of the interatomic step  $S = \Delta^{N_0}$ . Two of my example systems require a step in the xc potential to reorder the KS single-particle energies so that the KS density equals the many-body density (one of which is the well-known thought experiment of Almladh and von Barth [30]; see Sec. V). Without the step, the KS electron density would experience a large delocalization error [38]. I demonstrated that the required reordering of the KS single-particle states is achieved completely by the interatomic step of height  $\Delta^{N_0}$  [see Eq. (6)], which is verified numerically in Fig. 8 (bottom). I showed that in the case of two open-shell atoms  $S = \Delta^{N_0}$  is consistent with Almladh and von Barth's result [see Eq. (7)].

An accurate description of the step structures in the xc potential is needed to correctly distribute electron density throughout a molecular structure and describe the dissociation of atoms, bonding lengths, ground-state energies, and excitation energies [15,16]. For example, existing approximate functionals that omit these step features cannot be employed to reliably calculate optical absorption properties for charge-transfer donor-acceptors [15,38,62,63]. The insights offered in this paper could aid the development of advanced approximations to the xc energy and corresponding xc potential in order to yield more reliable KS calculations and offer a path to the computationally efficient calculation of excitation energies within quantum chemistry, alleviating the reliance on hybrid density functionals that carry a large computational cost.

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