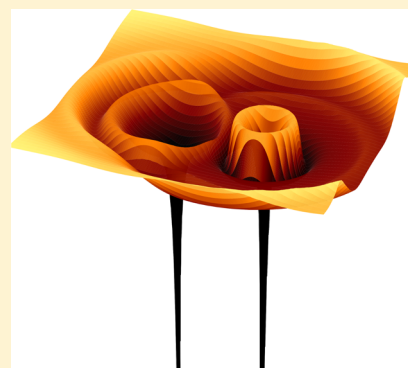


## How Interatomic Steps in the Exact Kohn–Sham Potential Relate to Derivative Discontinuities of the Energy

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## Supporting Information

**ABSTRACT:** Accurate density functional calculations hinge on reliable approximations to the unknown exchange–correlation (xc) potential. The most popular approximations usually lack features of the exact xc potential that are important for an accurate prediction of the fundamental gap and the distribution of charge in complex systems. Two principal features in this regard are the spatially uniform shift in the potential, as the number of electrons infinitesimally surpasses an integer, and the spatial steps that form, for example, between the atoms of stretched molecules. Although both aforementioned concepts are well known, the exact relationship between them remained unclear. Here we establish this relationship via an analytical derivation. We support our result by numerically solving the many-electron Schrödinger equation to extract the exact Kohn–Sham potential and directly observe its features. Spatial steps in the exact xc potential of a full configuration–interaction (FCI) calculation of a molecule are presented in three dimensions.



Density functional theory (DFT),<sup>1</sup> in the Kohn–Sham (KS) approach,<sup>2</sup> is widely used for simulating many-electron systems.<sup>3–12</sup> The accuracy of density functional calculations hinges on approximating the unknown exchange–correlation (xc) energy term,  $E_{xc}[n]$ . Whereas numerous successful approximations exist,<sup>13–24</sup> they often lack the discontinuous nature of the derivative of  $E_{xc}[n]$  with respect to electron number,  $N$ , at integer  $N$  (derivative discontinuity (DD))<sup>25–30</sup>.

The DD is essential for exactly describing the fundamental gap,  $E_g = I - A$ , being the difference between  $I$ , the ionization potential (IP), and  $A$ , the electron affinity (EA).  $E_g$  is equivalent to twice the chemical hardness and is of central importance for any material. Approximate functionals devoid of the DD (e.g., refs 13–16) underestimate  $E_g$  by ~50%<sup>19,31–35</sup> when relying solely on the KS eigenvalues. Furthermore, these functionals may qualitatively fail for charge transfer in molecules and materials, of which an accurate description is crucial for the understanding of chemical processes.<sup>36–44</sup> For example, (semi)local functionals may predict spurious fractional charges on the atoms of a stretched diatomic molecule,<sup>25,45–53</sup> violating the principle of integer preference.<sup>54</sup>

One manifestation of the DD is the emergence of a spatially uniform shift,  $\Delta$ , in the level of the KS potential,  $v_s(\mathbf{r})$ , as  $N$  infinitesimally surpasses an integer value,  $N_0$ , by  $\delta$ <sup>55–68</sup>

$$\Delta = \lim_{\delta \rightarrow 0^+} v_s(\mathbf{r}; N_0 + \delta) - v_s(\mathbf{r}; N_0 - \delta)$$

$\Delta$  originates from the piecewise-linearity of the total energy,  $E(N)$ ,<sup>25,69–76</sup> which leads to a stair-step structure of the highest

occupied (ho) KS eigenvalue,  $\epsilon^{\text{ho}}(N)$ , with discontinuities at integer  $N$ . In particular, for a neutral system of  $N_0$  electrons, infinitesimally below  $N_0$ ,  $\epsilon^{\text{ho}}(N_0^-) = -I$ , and infinitesimally above  $N_0$ ,  $\epsilon^{\text{ho}}(N_0^+) = -A$ .<sup>25,66,77–80</sup> To enforce this behavior, the exact  $v_s(\mathbf{r})$  experiences a discontinuous shift<sup>55,56</sup>

$$\Delta = I - A - (\epsilon^{\text{lu}} - \epsilon^{\text{ho}}) \quad (1)$$

where  $\epsilon^{\text{ho}}$  and  $\epsilon^{\text{lu}}$  are the ho and the lowest unoccupied (lu) KS eigenvalues at  $N_0^-$  (from here on, the argument  $N_0^-$  is suppressed for brevity). While this overall shift in  $v_s(\mathbf{r})$  does not affect the electron density,  $n(\mathbf{r})$ , it is vital to accurately predict the fundamental gap:<sup>31,32,34,55,73–76,81–96</sup> Even for the exact KS potential,  $\epsilon^{\text{lu}} \neq -A$ , and thus  $\Delta$  must be added to the KS gap,  $\epsilon^{\text{lu}} - \epsilon^{\text{ho}}$ , to obtain  $E_g$ .

The shift is spatially uniform only for  $\delta \rightarrow 0^+$ . In a finite system, such as an atom or molecule, for any small, but finite  $\delta$ ,  $v_s(\mathbf{r})$  forms a “plateau” that elevates the level of the potential in the vicinity of the nuclei. At the edge of the plateau, the level of  $v_s(\mathbf{r})$  must drop to 0, forming a sharp spatial step. As  $\delta$  vanishes, the plateau extends over all space, becoming spatially uniform, and its height approaches the value  $\Delta$ .<sup>97</sup>

A plateau in the exact  $v_s(\mathbf{r})$  is also observed for a different physical scenario: a stretched diatomic molecule with an integer number of electrons,  $L \cdots R$ , which is one system consisting of Atom  $L$  and Atom  $R$  with a large separation,  $d$ . The plateau

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forms around one of the atoms, introducing an interatomic step<sup>98–103</sup> and ensuring the correct distribution of charge throughout the system.<sup>42,54,64,104–115</sup> In the general case, the step height,  $S$ , is related to  $I_R$  and  $I_L$ , the IPs of atoms  $R$  and  $L$ , respectively, in the following way<sup>116</sup>

$$S = I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}} \quad (2)$$

where  $\eta_R^{\text{ho}}$  refers to the energy of the ho molecular KS orbital localized around  $R$  and likewise for  $\eta_L^{\text{ho}}$ . (The molecular orbital energies,  $\eta$ , are obtained at integer number of electrons for the overall system.) The energies  $\eta_L^{\text{ho}}$  and  $\eta_R^{\text{ho}}$  may or may not be equal. The latter is true when  $L$  and/or  $R$  are closed-shell atoms. In the specific, yet important, case that  $L$  and  $R$  are bonded, both the bonding and the antibonding molecular orbitals delocalize over both atoms, and in the limit  $d = |\mathbf{d}| \rightarrow \infty$  the bonding orbital can equally be described by two half-filled orbitals of the same energy, one localized on  $L$  and one on  $R$ . Hence, in the bonded case,  $\eta_R^{\text{ho}} = \eta_L^{\text{ho}}$  and eq 2 reduces to the famous result  $S = I_R - I_L$  by Almbladh and von Barth.<sup>98</sup> Throughout this Letter, we consider eq 2 in its general form.

Depending on the atoms  $L$  and  $R$ , either  $I_L$  or  $I_R$  is the overall IP of the molecule; let it be  $I_L$ . In this case, the overall ho molecular orbital is  $\eta_L^{\text{ho}}$  and equal to the atomic orbital associated with the isolated Atom  $L$ ,  $\epsilon_L^{\text{ho}}$ . Furthermore, because of the IP theorem,  $\eta_L^{\text{ho}} = -I_L$ . It then follows that eq 2 reduces to  $S = I_R + \eta_R^{\text{ho}}$ , which does not necessarily equal zero. The fact that  $S$  may be nonzero stems from the inclusion of the molecular energy,  $\eta_R^{\text{ho}}$ , and not the atomic energy,  $\epsilon_R^{\text{ho}}$ , in eq 2.  $\epsilon_R^{\text{ho}}$  equals  $-I_R$ , whereas the molecular energy does not as it is elevated relative to the atomic energy by the step height  $S$ :  $\eta_R^{\text{ho}} = \epsilon_R^{\text{ho}} + S$ . Hence, in general  $S$  is nonzero. For a system with at least one closed-shell atom, in the limit  $d \rightarrow \infty$ ,  $S$  has a range of values that yield an exact electron density, discussed in ref 116.

The two aforementioned phenomena,  $\Delta$  and  $S$ , are usually treated as unrelated properties of the exact KS potential. Indeed, there are differences between the two:  $\Delta$  depends on quantities that describe the system as a whole, whereas  $S$  is related to quantities corresponding to fragments of the system (atoms  $L$  and  $R$  in our case). Moreover, the EA and the lu energy, which contribute to  $\Delta$ , are absent from  $S$ . Finally, the shift  $\Delta$  occurs when a small amount of charge is added to the system, whereas  $S$  occurs at a fixed, integer number of electrons; the behavior of  $S$  when  $N$  is varied has thus far remained unexplored. However, it has been understood for a long time<sup>98,117</sup> that both the interatomic step  $S$  and the steps that form as a function of  $N$ , which are attributed to the DD as described above, occur for a finite system when the decay rate of the electron density abruptly changes. This suggests a relation between  $\Delta$  and  $S$ .

In this Letter, we establish the relationship between the interatomic step,  $S$ , and the DD,  $\Delta$ . We explore the properties of steps in the exact KS potential as a function of  $N$  for a single atom and a diatomic molecule. This is done first via an analytical derivation by analyzing the changes in the exponential decay rate of the density. We then support our findings by numerically solving the many-electron Schrödinger equation for the Li atom and the stretched Li··Be molecule to extract the exact KS potential and directly observe the steps. For the first time, the 3D spatial structure of the steps in the exact xc potential of a full configuration-interaction (FCI) calculation of a molecule is displayed.

To illustrate how  $\Delta$  arises for a finite system with varying  $N$ , we consider a single atom with  $N = N_0 + \delta$ . The density is piecewise-linear<sup>25</sup>

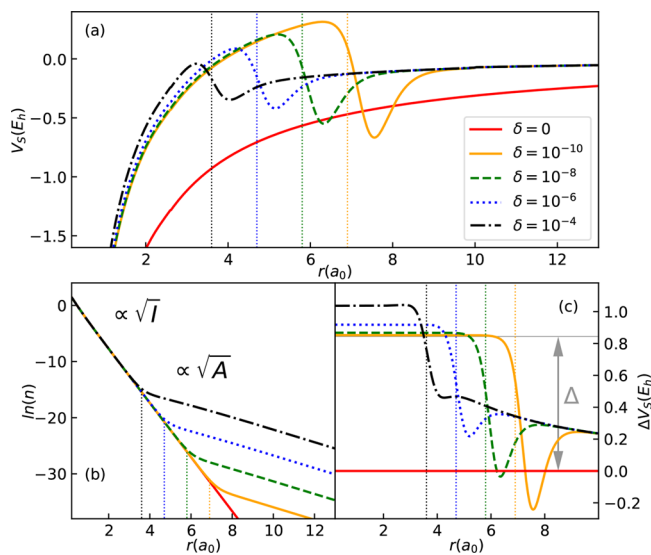
$$n(\mathbf{r}; N) = (1 - \delta) \cdot n(\mathbf{r}; N_0) + \delta \cdot n(\mathbf{r}; N_0 + 1) \quad (3)$$

being a combination of the density of a neutral atom and an anion ( $N_0$  and  $N_0 + 1$  electrons, respectively). When  $\delta$  is small and positive, the density has two regions of exponential decay: as  $|\mathbf{r}| \rightarrow \infty$ ,  $n(\mathbf{r}; N) \propto n(\mathbf{r}; N_0 + 1) \propto e^{-2\sqrt{2A}|\mathbf{r}|}$ <sup>25,78</sup> (the decay rate is governed by the IP of the anion, which equals the EA of the neutral). We term this the region of “A-decay”. However, for small  $\delta$ ,  $n(\mathbf{r}; N_0) \propto e^{-2\sqrt{2I}|\mathbf{r}|}$  starts to dominate the density at some point approaching the nucleus (“I-decay”).<sup>97</sup>

From the KS perspective, in the A-decay region  $v_s(\mathbf{r})$  reaches the asymptotic value  $v'$ , whereas in the I-decay region it tends to the value  $v$ . In general,  $v$  and  $v'$  may differ, forming the atomic step,  $v - v'$ . In the limit  $\delta \rightarrow 0^+$ , in the A-decay region,  $n(\mathbf{r}; N) \propto |\varphi^{\text{lu}}(\mathbf{r})|^2 \propto e^{-2\sqrt{2(v'-\epsilon^{\text{lu}})}|\mathbf{r}|}$ , where  $\{\varphi^i(\mathbf{r})\}$  are the atomic KS orbitals. In the I-decay region, the density  $n(\mathbf{r}; N) \propto |\varphi^{\text{ho}}(\mathbf{r})|^2 \propto e^{-2\sqrt{2(v-\epsilon^{\text{ho}})}|\mathbf{r}|}$ . Therefore,  $A = v' - \epsilon^{\text{lu}}$  and  $I = v - \epsilon^{\text{ho}}$ . Thus  $v - v' = I + \epsilon^{\text{ho}} - (A + \epsilon^{\text{lu}}) = \Delta$ , exactly as in eq 1.

To demonstrate the above numerically, we calculate the Li atom with  $2 \leq N \leq 3$ . We solve the many-electron problem for  $\text{Li}^+$  ( $N = 2$ ) and Li ( $N = 3$ ) using the FCI method in Molpro<sup>118</sup> with the Universal Gaussian Basis Set,<sup>119</sup> employing the approach suggested in ref 120. We calculate the densities  $n(\mathbf{r}; N)$  with ORBKIT<sup>121</sup> and use eq 3. Finally, we employ the inversion procedure of ref 122 to obtain  $v_s(\mathbf{r}; N)$ ; see the Supporting Information for technical details.

Figure 1b shows the natural log of the density,  $\ln[n(r)]$ , as a function of the radial distance  $r = |\mathbf{r}|$ , for  $\delta = 0, 10^{-10}, 10^{-8}, 10^{-6}$ , and  $10^{-4}$  (atomic units are used throughout). Plotting the log helps to recognize the regions of exponential decay. For  $\delta =$



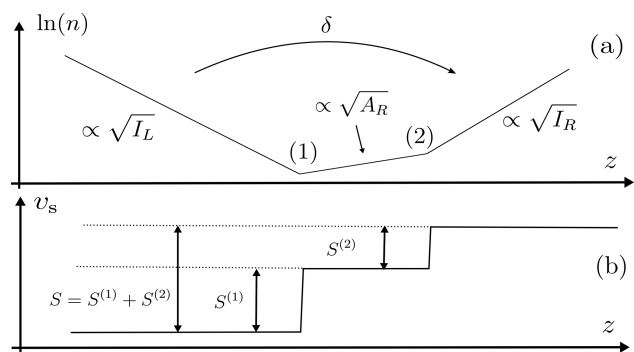
**Figure 1.** (a) The exact KS potential for Li with  $2 + \delta$  electrons; steps occur for  $\delta > 0$ . (b)  $\ln[n(r)]$ : the I- and A-decay regions for  $\delta > 0$  are apparent. (c) The plateau elevates the potential by  $\Delta$ , for  $\delta > 0$ . The vertical lines on all panels correspond to the position of decay change in  $n(r)$ .

0, there is only one such region (*I*-decay). For  $\delta > 0$ , we clearly recognize the *I*- and the *A*-decay regions. The above analysis indicates that the point where the decay rate changes is also the point where the step in  $v_s(r)$  occurs. This is demonstrated numerically in Figure 1a for  $v_s(r)$  and Figure 1c for  $\Delta v_s(r; \delta) = v_s(r; N_0 + \delta) - v_s(r; N_0)$ : For all finite values of  $\delta$ , the exact  $v_s(r)$  has a spatial step, which approaches  $\Delta$  calculated via eq 1. The step acts to elevate the level of the KS potential for the central region, where most of the electron density resides. The positions of the step vary with  $\delta$ ; the smaller  $\delta$  is, the further from the atom the step forms. Therefore, as  $\delta \rightarrow 0^+$ , the plateau becomes a spatially uniform shift in the potential, as required.

We now consider the stretched diatomic molecule  $L \cdots R$ . For this system, at the interface between the atoms, the decay of the density from Atom *L*,  $e^{-2\sqrt{2I_L}|r+\frac{1}{2}d|}$ , meets the decay of the density from Atom *R*,  $e^{-2\sqrt{2I_R}|r-\frac{1}{2}d|}$ , giving rise to an interatomic step, *S*, in the exact KS potential. Following ref 116, we can derive the step height, *S*, as given by eq 2, from considerations similar to those used for the atomic case above. Notably, the form of eq 2 does not depend on the magnitude of  $n(r)$  at the point where it forms; therefore, the step is expected to appear at any large *d*, as long as the atoms may be considered one system. (This situation is qualitatively different from the case of a dissociated molecule, originally introduced in ref 25 and recently discussed in ref 53, where one considers two completely separated atoms with varying number of electrons  $N_L$  and  $N_R$  at constant  $N_{L+R}$ . Although  $N_L$  and  $N_R$  are varied in a concerted manner, strictly speaking this is no longer one molecule.)

To understand how this step relates to the DDs of the individual atoms in the molecule ( $\Delta_L$  and  $\Delta_R$ ), one may slightly increase the charge on one of the atoms. This can be done by either transferring charge, say, from *L* to *R*, or by increasing the overall charge of  $L \cdots R$ . First, we consider the charge-transfer scenario. Relying on the atomic case described above, provided the atoms are very far apart and  $\delta$  is sufficiently small, we expect a plateau of height  $\Delta_R = I_R - A_R - \epsilon_R^{\text{lu}} + \epsilon_R^{\text{ho}}$  to form around the acceptor, Atom *R*. However, this seems to contradict eq 2, which states that the interatomic step height must always be  $I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}}$ . (Here and below, the formulas are expressed in terms of the molecular energies before the charge transfer occurred, which is valid in the limit that  $\delta \rightarrow 0^+$ .)

To resolve this apparent contradiction, we imagine the density of the molecule after the charge transfer. Figure 2



**Figure 2.** (a) Diagram of  $\ln(n)$  far from, and between, the atoms of a molecule  $L \cdots R$ , showing a transition from the  $I_R$ - to the  $A_R$ -decay region (point (2)) and from the  $A_R$ - to the  $I_L$ -decay region (point (1)). The changes in the density give rise to steps in the KS potential (b).

sketches the changes in the exponential decay of the density, which occur between the atoms. We note three regions of exponential decay:  $I_R$ -,  $A_R$ -, and  $I_L$ -decay. Upon every change of the decay rate we expect a step in the KS potential. At point (2) of Figure 2a the density changes from the  $I_R$ - to  $A_R$ -decay. Hence, the corresponding step is  $S^{(2)} = I_R - A_R - \eta_R^{\text{lu}} + \eta_R^{\text{ho}}$ .  $S^{(2)}$  may also be written in terms of the atomic energies,  $S^{(2)} = I_R - A_R - \epsilon_R^{\text{lu}} + \epsilon_R^{\text{ho}} = \Delta_R$ , because, as  $d \rightarrow \infty$ , the difference between the ho and lu energies of the molecular orbitals localized on Atom *R* ( $\eta_R^{\text{lu}} - \eta_R^{\text{ho}}$ ) is equal to the corresponding difference in the atomic energies ( $\epsilon_R^{\text{lu}} - \epsilon_R^{\text{ho}}$ ). Therefore, upon receiving a small amount of charge, the plateau height that forms around Atom *R* indeed equals  $\Delta_R$ , as required by eq 1. Additionally, at point (1) the density changes from the  $A_R$ - to  $I_L$ -decay. This occurs because  $L \cdots R$  is one system. The additional step that arises at this point is derived to be  $S^{(1)} = A_R - I_L + \eta_R^{\text{lu}} - \eta_L^{\text{ho}}$ , using considerations of the exponential decay of the density as before. The overall step between *L* and *R*,  $S^{(1)} + S^{(2)} = I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}}$  equals *S*, as in eq 2. Therefore, there is no contradiction, but the overall step *S* has an internal structure consisting of  $S^{(1)}$  and  $S^{(2)}$ .

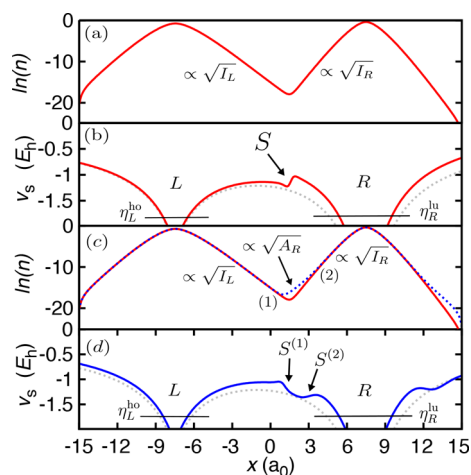
The new quantity that emerges from this analysis,  $S^{(1)}$ , appears to be (the negative of) the energy required to move an electron from *L* to *R*,  $I_L - A_R$ , minus the corresponding quantity in the KS system,  $-\eta_L^{\text{ho}} + \eta_R^{\text{lu}}$ . Because of the formal similarity of  $S^{(1)}$  to eq 1, we term this new quantity the charge transfer DD

$$\Delta_{L \rightarrow R}^{\text{CT}} = I_L - A_R + \eta_L^{\text{ho}} - \eta_R^{\text{lu}} \quad (4)$$

Furthermore,  $\Delta_{L \rightarrow R}^{\text{CT}}$  can be derived from the discontinuity in the slope of the total energy of  $L \cdots R$  as a function of  $\delta$ ,  $E_{L \cdots R}(\delta)$ , around  $\delta = 0$ , justifying the term charge transfer DD. In the bonded case, where  $\eta_L^{\text{ho}} = \eta_R^{\text{ho}}$ ,  $\Delta_{L \rightarrow R}^{\text{CT}} = I_L - A_R + \eta_R^{\text{ho}} - \eta_R^{\text{lu}}$ . (Assuming that the transferred charge localizes on Atom *R* and after such a transfer the molecule is still bonded.) Moreover, as the difference in the molecular energies localized on Atom *R* is equal to the difference in atomic energies,  $\Delta_{L \rightarrow R}^{\text{CT}} = I_L - A_R + \epsilon_R^{\text{ho}} - \epsilon_R^{\text{lu}}$ .

To illustrate the internal step structure derived above, we model  $L \cdots R$  with a simple, yet instructive 1D calculation with two spinless electrons, subsequently adding a small charge  $\delta$  to Atom *R*. For this we employ the iDEA code.<sup>122</sup> Spinless electrons allow for convenient modeling of two closed-shell atoms for a given computational cost, as each electron occupies a distinct KS orbital. No significant qualitative effect is expected when using two spinful electrons per atom instead of one spinless electron. Moreover, modeling in 1D allows us, at moderate numerical cost, to achieve high accuracy for  $n(x)$  and  $v_s(x)$ , especially in the regions where  $n(x)$  is extremely low, and thus consider large separation values, *d*. In our model,  $v_{\text{ext}}(x)$  is chosen so that two interacting electrons occupying this potential localize such that there is one electron worth of charge in each well; see Figure 3a. For such a scenario, to reproduce the density in the KS system,  $v_s(x)$  must form a spatial step between the atoms.<sup>98,104,116</sup> In the absence of the step,  $\eta_L^{\text{lu}}$  would be lower than  $\eta_L^{\text{ho}}$ , which would cause both electrons to artificially localize on Atom *R*. Figure 3b shows a clear step in  $v_s(x)$ , where the decay rate of  $n(x)$  changes (cf. Figure 3a,b) and whose height is given by eq 2. To the far right of Atom *R* there is another change in the decay rate of  $n(x)$ , which causes a step down (not shown). We correctly observe





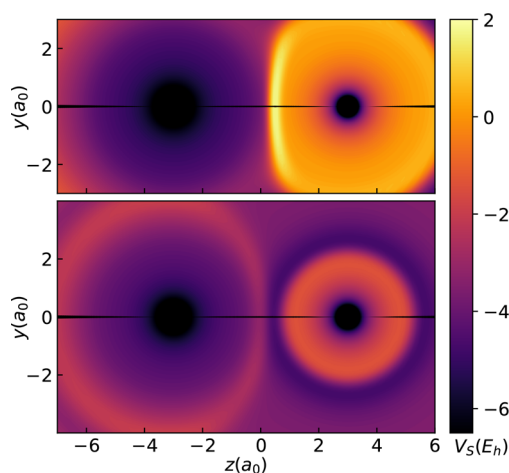
**Figure 3.** (a)  $\ln[n(x)]$  for two electrons in a stretched 1D molecule. (b) The exact  $v_s(x)$  (solid red) forms a step  $S$  between atoms  $L$  and  $R$ .  $v_{\text{ext}}(x)$  (dotted gray),  $\eta_L^{\text{ho}}$  and  $\eta_R^{\text{lu}}$  are shown for comparison.  $\eta_R^{\text{ho}} = -2.87$  and  $\eta_L^{\text{lu}} = -1.37$  hartree (not shown). (c)  $\ln[n(x)]$  for  $2 + 5 \times 10^{-4}$  electrons (dashed blue) for the same  $v_{\text{ext}}(x)$  as panel a. The two-electron density of panel a is shown for comparison (solid red). (d) Exact  $v_s(x)$  corresponding to panel c (dashed blue) forms two steps between the atoms.  $v_{\text{ext}}(x)$  (dotted gray),  $\eta_L^{\text{ho}}$  and  $\eta_R^{\text{lu}}$  (using the nomenclature of panel b) are shown for comparison.  $\eta_R^{\text{ho}} = -2.81$  and  $\eta_L^{\text{lu}} = -1.34$  hartree (not shown).

no regions of  $A$ -decay, as none of the higher states of  $L$  or  $R$  are occupied.

We now slightly increase  $N_{L \cdots R}$  to  $2 + \delta$ . For this we additionally calculate a three-electron system with the same  $v_{\text{ext}}(x)$  and use eq 3. In the three-electron case, one electron is localized on  $L$  and two on  $R$ . Even for  $\delta = 5 \times 10^{-4}$ , in Figure 3c we recognize three regions of exponential density decay, in accordance with Figure 2. In Figure 3d we see two distinct steps in  $v_s(x)$  between the atoms:  $S^{(2)}$  forms the plateau around  $R$ , which is indicative of  $\Delta_R$  and  $S^{(1)}$  corresponds to the charge transfer DD. Far to the left of  $L$  the  $A_R$ -decay prevails over  $I_L$  (not shown) and a step of height  $-S^{(1)}$  in  $v_s(x)$  occurs. Therefore, while  $R$  resides on a plateau  $\Delta_R$ ,  $L$  resides on a plateau  $-\Delta_{L \rightarrow R}^{\text{CT}}$ .

As  $\delta$  decreases, points (1) and (2) travel toward each other until they meet; see the Supporting Information for technical details. Likewise, steps (1) and (2) coincide and form the overall step  $S$  at the meeting point; its internal structure is no longer apparent. This point can be thought of as the boundary between atoms  $L$  and  $R$  (cf. ref 116).

Finally, we consider the exact solution for  $\text{Li} \cdots \text{Be}$ , with  $4 \leq N_{\text{Li} \cdots \text{Be}} \leq 5$  to investigate whether the aforementioned features of the exact KS potential for the stretched 1D molecule are also apparent for a molecule in 3D. The KS potentials for  $\text{Li} \cdots \text{Be}$  were obtained with the same methods as those of  $\text{Li}$ . Figure 4 (top) shows the molecular  $v_s(\mathbf{r})$  for  $N_{\text{Li} \cdots \text{Be}} = 4$ . We recognize a “platform”, being the analogue of the 1D plateau, around  $\text{Be}^{2+}$ , and hence an interatomic step between  $\text{Li}^+$  and  $\text{Be}^{2+}$  whose height is given by eq 2. Figure 4 (bottom) corresponds to the same molecule with  $10^{-3}$  electrons added. When going from  $\text{Li}^+$  to  $\text{Be}^{2+}$ , we recognize, by analogy to Figure 3d, a double-step structure: First, we see a raise in  $v_s(\mathbf{r})$ , as a halo at  $\sim 3a_0$  around  $\text{Li}^+$ , which corresponds to the outer edge of the platform  $-\Delta_{\text{Li}^+ \rightarrow \text{Be}^{2+}}^{\text{CT}}$ , then a drop, followed by a raise to the platform of radius  $\sim 2a_0$  around  $\text{Be}^{2+}$ , which corresponds to  $\Delta_{\text{Be}^{2+}}$ . We stress that the interatomic step height is still given by eq 2. Therefore,



**Figure 4.** Exact KS potential for the  $\text{Li} \cdots \text{Be}$  molecule,  $d = 6 a_0$ , with 4 electrons (top) and 4.001 electrons (bottom).

we conclude that steps occur and possess an internal structure also for realistic systems.

We now imagine that  $\delta \rightarrow 0^+$ . The platform around  $\text{Li}^+$ , corresponding to  $-\Delta_{\text{Li}^+ \rightarrow \text{Be}^{2+}}^{\text{CT}}$ , increases in radius until it reaches further than  $\text{Be}^{2+}$ , enclosing both atoms. At this point the interatomic step between  $\text{Li}^+$  and  $\text{Be}^{2+}$  is  $S = \Delta_{\text{Be}^{2+}} - \Delta_{\text{Li}^+ \rightarrow \text{Be}^{2+}}^{\text{CT}}$ , equivalent to eq 2. In this scenario, far from both atoms  $-\Delta_{\text{Li}^+ \rightarrow \text{Be}^{2+}}^{\text{CT}}$  is recognizable as the step corresponding to the DD of the whole molecule,  $\Delta_{\text{Li}^+ \cdots \text{Be}^{2+}}$ . Thus, as  $\delta \rightarrow 0^+$ ,  $-\Delta_{\text{Li}^+ \rightarrow \text{Be}^{2+}}^{\text{CT}}$  changes the level of  $v_s(\mathbf{r})$  everywhere, as required by the DD of the molecule, and the interatomic step, given by eq 2, is a combination of the atomic and the charge-transfer DDs.

To conclude, in this Letter, we clarified the relationship between the jump  $\Delta$  experienced by the Kohn–Sham (KS) potential as the number of electrons in the system infinitesimally surpasses an integer and the interatomic spatial step,  $S$ , that forms in the KS potential for stretched molecular systems. The step  $S$  was shown to have an internal structure that is revealed when a small amount of charge is added to one of the atoms of a stretched diatomic molecule:  $S$  consists of the atomic derivative discontinuity and the charge-transfer derivative discontinuity,  $\Delta^{\text{CT}}$ , a new quantity that has been introduced in this work.  $\Delta^{\text{CT}}$  corresponds to the difference between the energy required to move an electron from one atom in a diatomic molecule to the other and the corresponding quantity in the KS system. This internal structure of  $S$  has been demonstrated both in a 1D model and in a 3D full configuration-interaction (FCI) calculation for the  $\text{Li} \cdots \text{Be}$  molecule. We observe platforms in the exact KS potential—the analogue of the 1D plateaus—for a molecule in three dimensions. This work also highlights the importance of approximate exchange–correlation potentials accurately accounting for changes in the decay rate of the density, as this leads to a correct step structure in the potential. In turn, steps are crucial to predict the fundamental gap and provide a correct distribution of the electronic charge in complex systems. Suggestions made, for example, in refs 28, 94, 99, and 123, are relevant in this context.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b02615.

Technical details of calculations performed. (PDF)

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### Notes

The authors declare no competing financial interest.

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