

# How interatomic steps in the exact Kohn-Sham potential relate to the derivative discontinuity



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## Kohn-Sham DFT

Kohn-Sham (KS) density functional theory (DFT) is the most widely used method for calculating the properties of materials. However, the commonly used approximations to its exchange-correlation (xc) potential are inadequate when used to describe properties such as charge transfer effects and the fundamental gap.

In order to develop advanced approximations which accurately describe challenging phenomena, features of the *exact* xc potential must be deduced and studied.

## Interatomic step

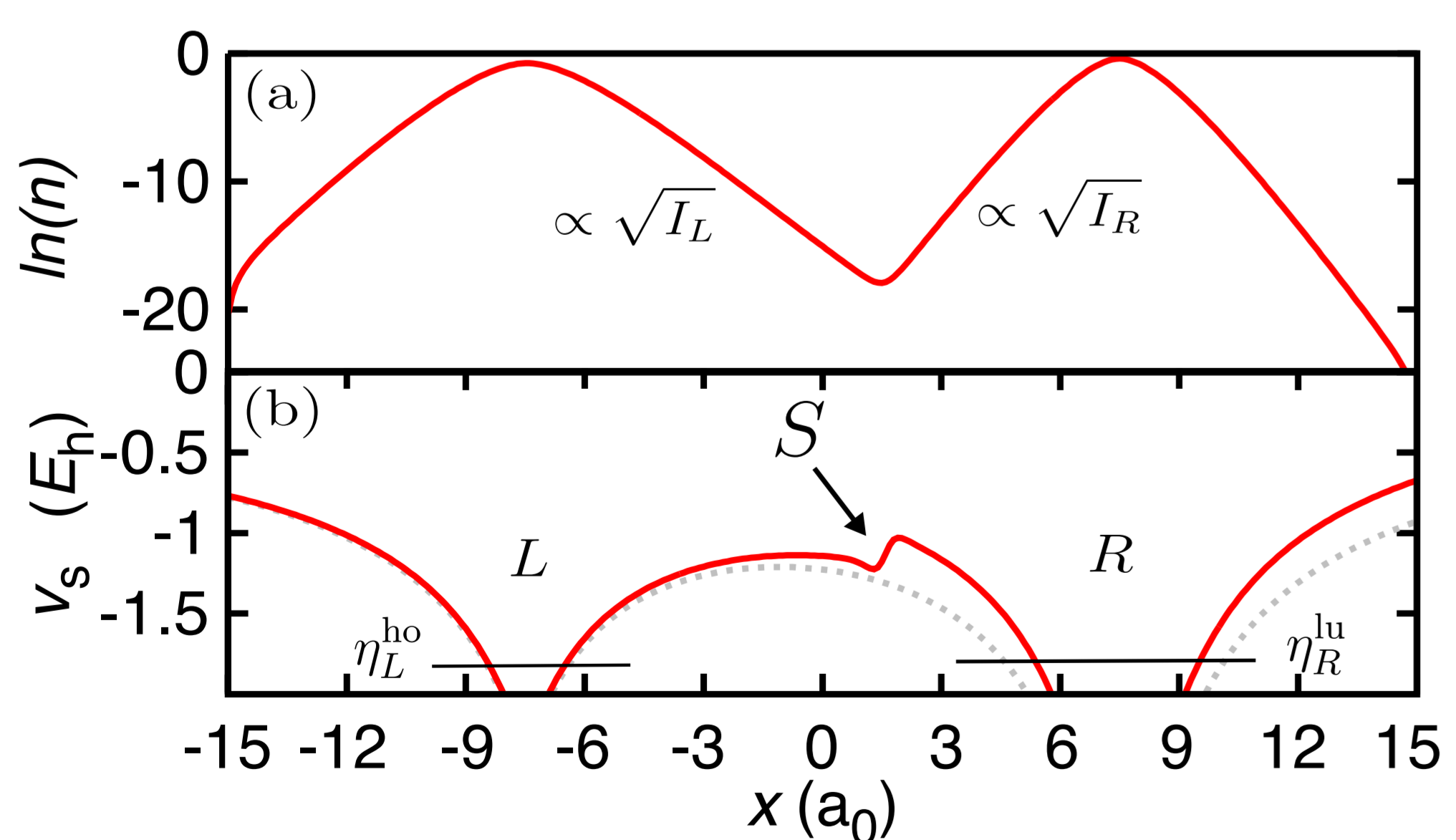
For systems which consist of localised electrons that form “subsystems” – e.g., a stretched diatomic molecule ( $L \cdots R$ ) – a spatial step between the subsystems forms in the exact xc potential to ensure the correct distribution of charge throughout the system [1,2].

The height of the step,  $S$ , is related to the ionisation potential ( $I$ ) and the highest occupied (ho) KS *molecular* energy level localised on each subsystem, as follows

$$S = I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}}$$

The step forms at the point where the exponential decay of the electron density changes; see Figure below.

It is usually assumed that this sharp change in the KS potential is unrelated to the “derivative discontinuity”.



**One-dimensional diatomic molecule. (a) The nat. log of the exact electron density ( $N = 2$ ). (b) The exact KS potential: a step forms where the density decay changes.**

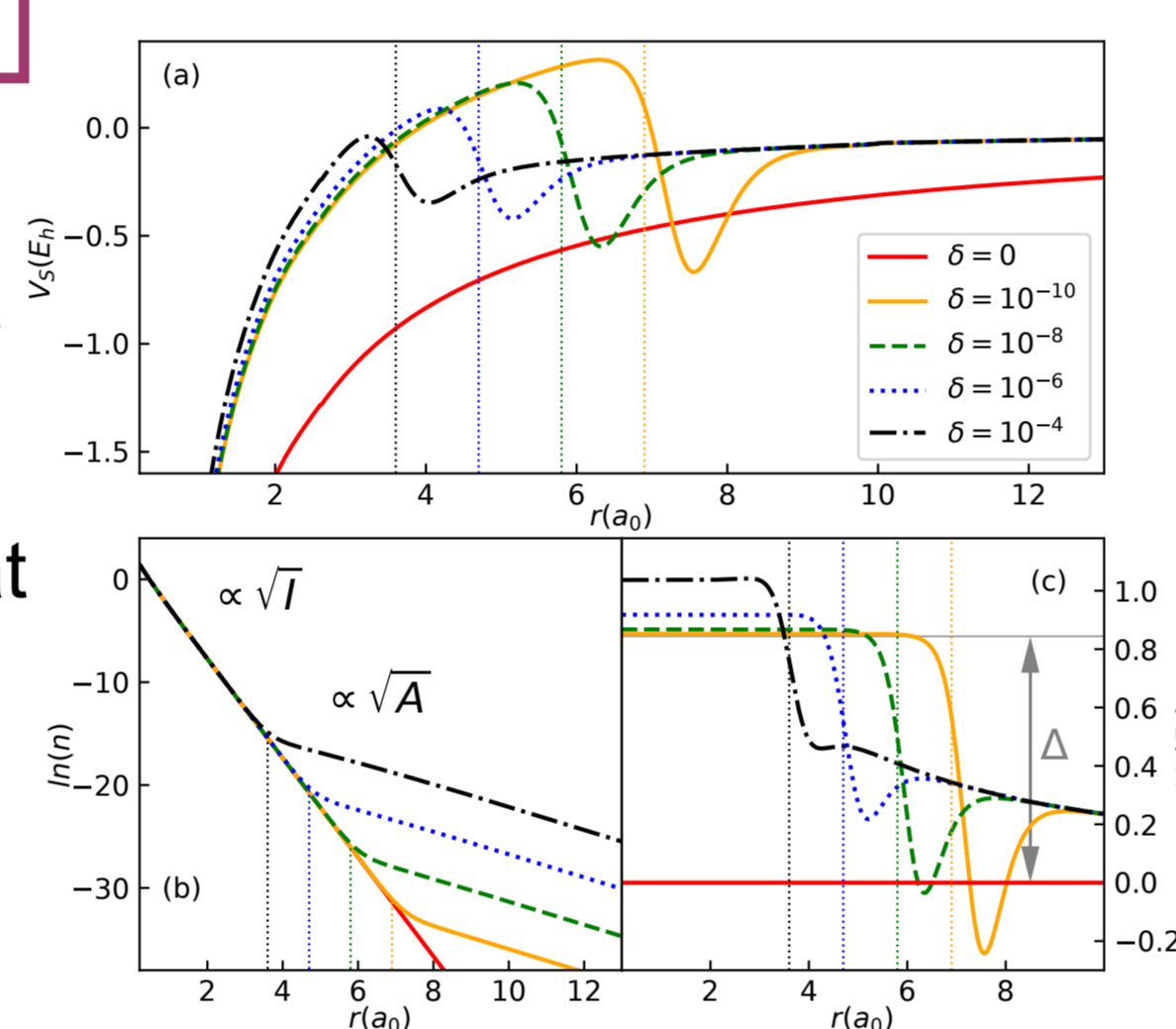
## Derivative discontinuity

The exact xc potential “jumps” discontinuously by a constant shift ( $\Delta$ ) as the electron number ( $N$ ) infinitesimally surpasses an integer. This is known as the “derivative discontinuity” [3]. This feature of the xc potential is crucial for predicting the fundamental gap [4].

$\Delta$  is related to the ionisation potential ( $I$ ), electron affinity ( $A$ ) and the KS atomic highest occupied (ho) and lowest unoccupied (lu) energy levels, as follows

$$\Delta = I - A + \epsilon^{\text{ho}} - \epsilon^{\text{lu}}$$

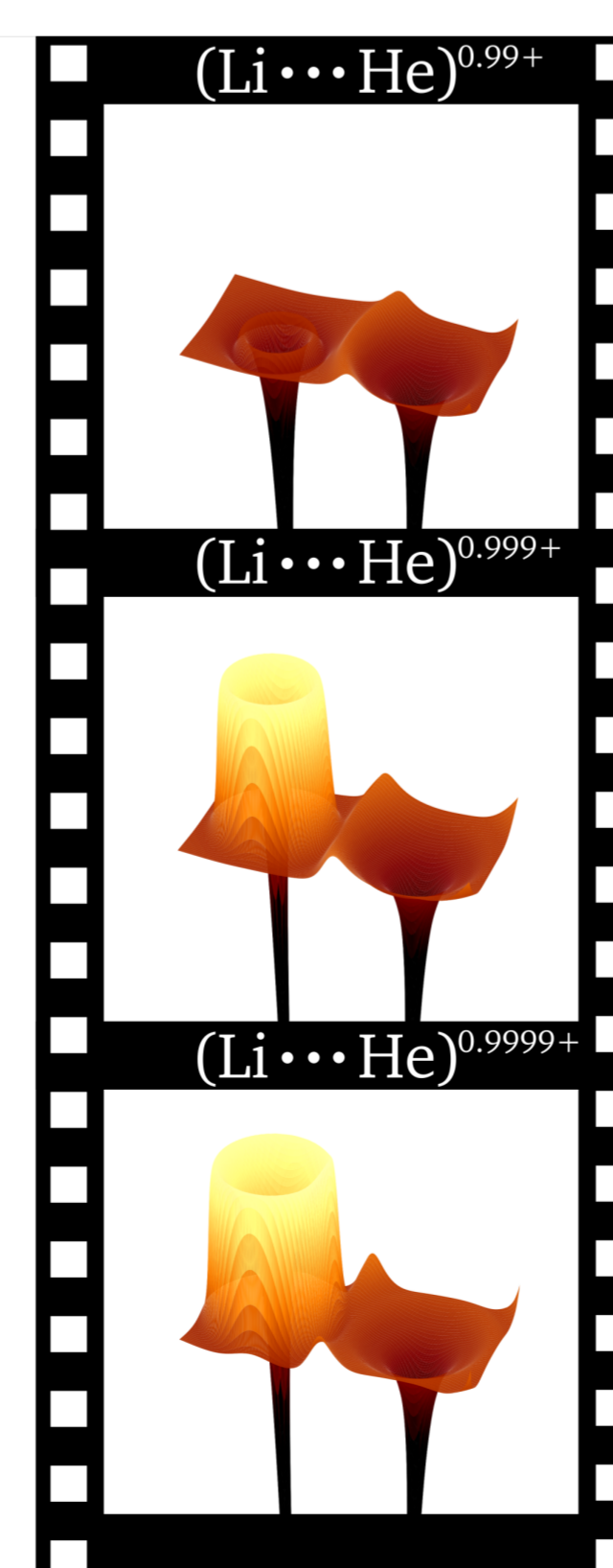
For any finite addition of charge ( $\delta$ ), the shift of the whole potential,  $\Delta$ , is a plateau owing to the requirement that the KS potential goes to zero as  $r \rightarrow \infty$ ; see Figure to the right – the plateau is centred around the nucleus.



**Three-dimensional Li atom. (a) Exact KS potential for Li with  $2 + \delta$  electrons; steps occur for  $\delta > 0$ . (b) Nat. log of the density: two decay regions for  $\delta > 0$  are apparent. (c) The potential is elevated by  $\Delta$  for  $\delta > 0$ .**

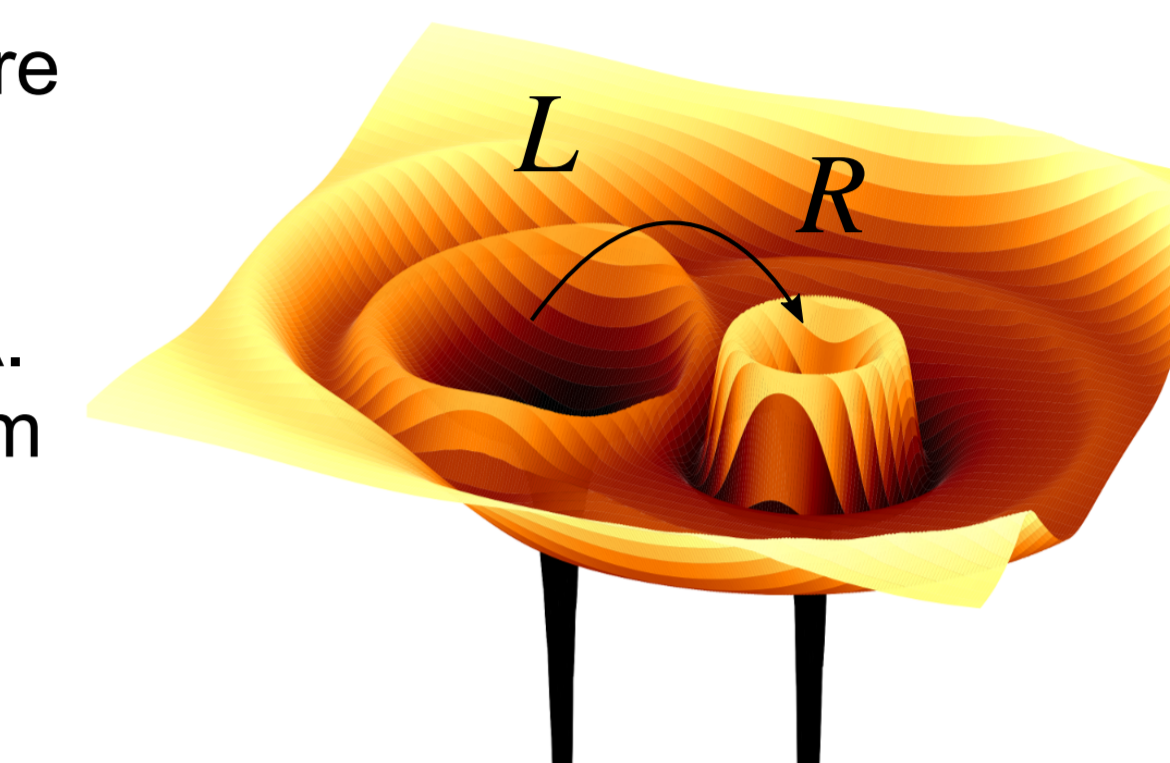
## Conclusions

1. We have clarified the relationship between the uniform jump in the exact KS potential,  $\Delta$ , and the interatomic step,  $S$ .
2. The step  $S$  has an internal structure which has been numerically demonstrated in a 1D model system and a 3D full-CI calculation of a molecule.
3. We introduced a new quantity: the charge-transfer derivative discontinuity,  $\Delta^{\text{CT}}$ .
4. To yield a correct step structure in the KS potential, approximations should account for changes in the decay rate of the density.



## Is the interatomic step related to the derivative discontinuity?

Naively, it seems as though the interatomic step and the derivative discontinuity are contradictory: if one adds charge to, say, the right atom of a stretched diatomic molecule ( $L \cdots R$ ), by either adding charge to the overall molecule or by charge transfer, the xc potential in the region of the acceptor atom must be elevated by  $\Delta$ . However, the overall difference between the xc potential in the region of each atom must remain  $S$  – how can these features of the exact xc potential be concurrent?

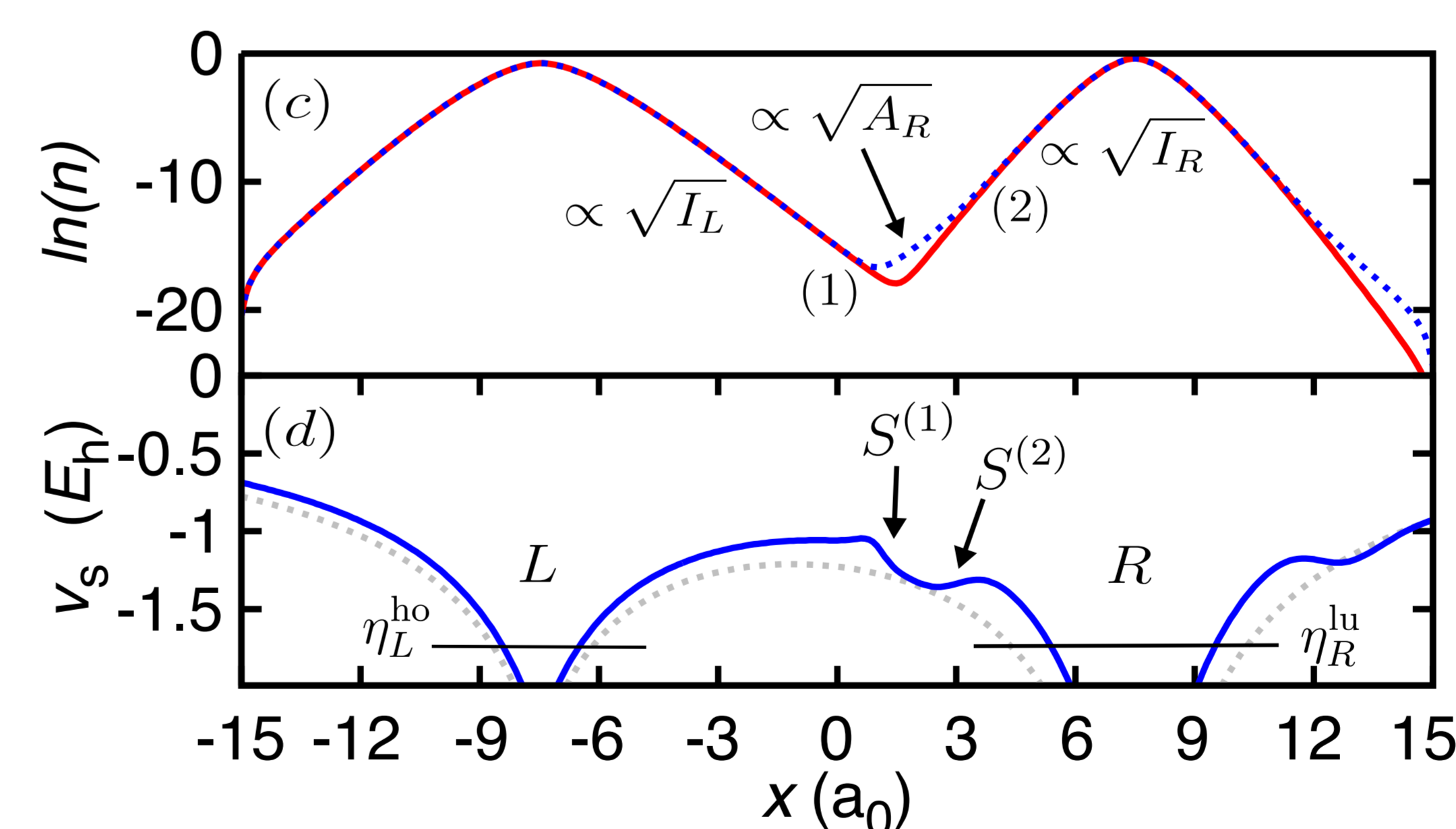


## Charge-transfer derivative discontinuity

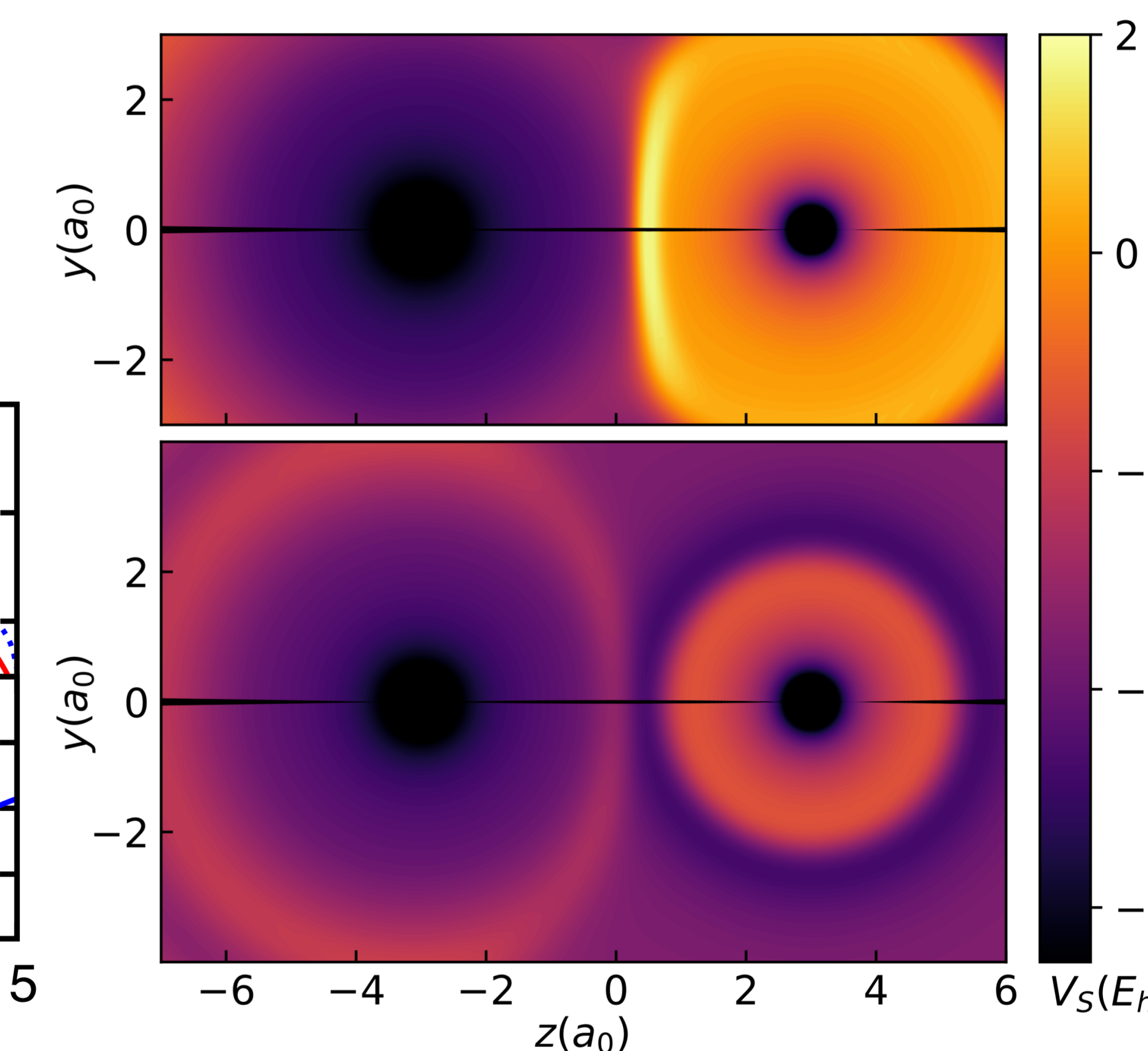
Consider a small amount of charge added to the right atom: the rate of density decay changes in two places between the atoms; see Fig. (c) below. At points (1) and (2) steps form in the exact KS potential (Fig. (d) below): Step 2 corresponds to the derivative discontinuity of atom  $R$  ( $\Delta_R$ ). Step 1 corresponds to a previously unknown quantity which equals the difference between the energy required to transfer an electron from the left to the right in the many-electron system ( $I_L - A_R$ ) and the corresponding quantity in the KS system ( $\eta_R^{\text{lu}} - \eta_L^{\text{ho}}$ ):

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

We term this the “charge-transfer derivative discontinuity” [5]. The sum of these two steps equals the interatomic step  $S$ . Thus,  $S$  has an internal structure consisting of two derivative discontinuities. On the right we present a 3D example of this effect: stretched  $(\text{LiBe})^{3+}$  calculated via full-configuration interaction. Two “platforms” are present – the 3D analog of the plateaus seen in the 1D examples.



**One-dimensional diatomic molecule. (c) The nat. log of the exact electron density ( $N = 2.0005$ ). (d) The exact KS potential: there are two steps: one which corresponds to  $\Delta_R$  and the other  $-\Delta_{L \rightarrow R}^{\text{CT}}$ :  $S = \Delta_R - \Delta_{L \rightarrow R}^{\text{CT}}$ .**



**Three-dimensional  $(\text{Li} \cdots \text{Be})^{3+}$ . (Top) The exact KS potential ( $N = 4$ ): a “platform” gives rise to the interatomic step  $S$ . (Bottom) The exact KS potential ( $N = 4.001$ ): the  $\Delta_{\text{Be}}$  and  $-\Delta_{\text{Li} \rightarrow \text{Be}}^{\text{CT}}$  platforms are now present:  $S = \Delta_{\text{Be}} - \Delta_{\text{Li} \rightarrow \text{Be}}^{\text{CT}}$ .**

## References

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