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How derivative discontinuities in the energy yield interatomic steps in the exact Kohn-Sham potential of Density-Fuctional Theory

Eli Kraisler¹,

Matt Hodgson¹, Axel Schild², E.K.U. Gross^{1,3}

1. Max Planck Institute of Microstructure Physics, Halle (Saale), Germany
2. Laboratorium für Physikalische Chemie, ETH Zürich, Switzerland
3. Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, Hebrew University of Jerusalem, Israel

Density Functional Theory

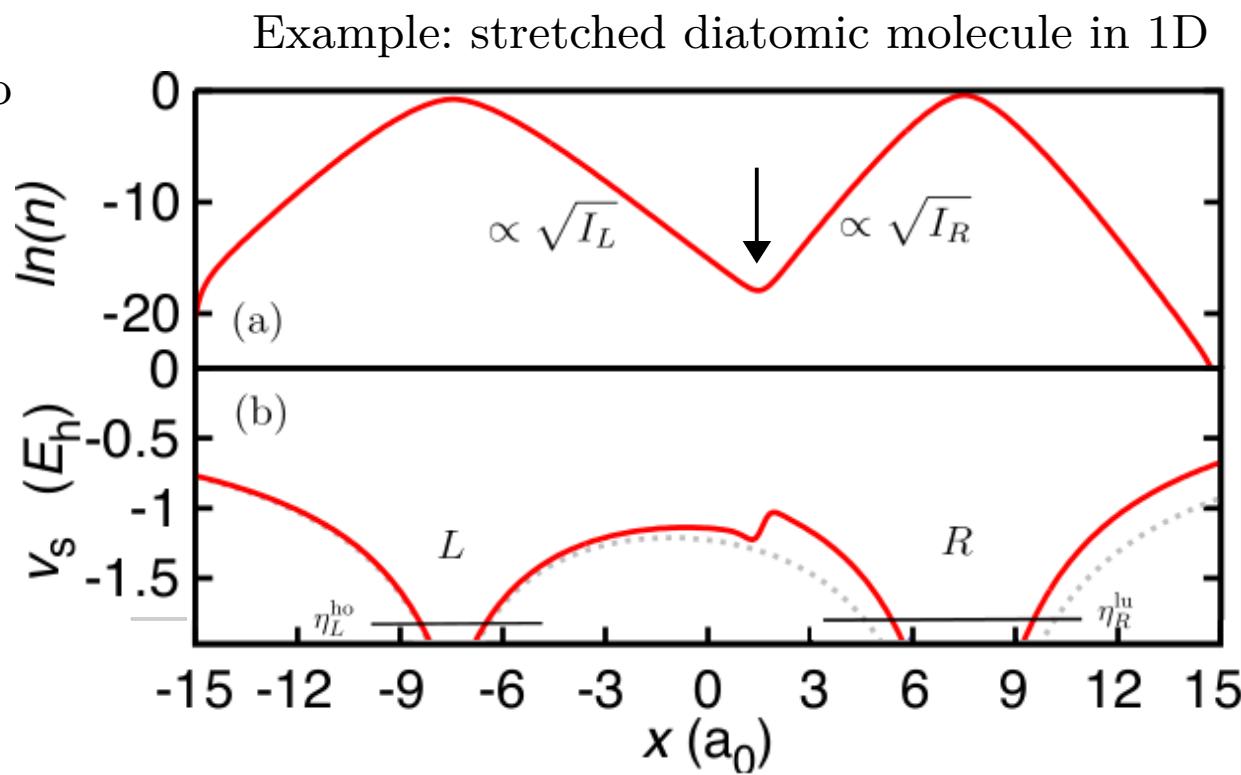
- An exact approach to the many-electron problem
- The exact **exchange-correlation** (xc) potential $v_{\text{xc}}[n](\mathbf{r})$ remains usually unknown and has to be approximated.
$$v_{KS}[n](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r})$$
- Some **properties** of the **exact** $v_{\text{xc}}[n](\mathbf{r})$ can be observed relying on exact solutions of the Schrödinger equation
- Studying these properties is important for the development of improved approximations from first principles

1: interatomic step

- The exact potential, $v_{KS}(\mathbf{r})$, forms a step, S , between isolated fragments of a composite system.
- The step happens where the decay rate of the density $n(\mathbf{r})$ changes
- The step height depends on the atomic ionisation energies and on the molecular energy levels:

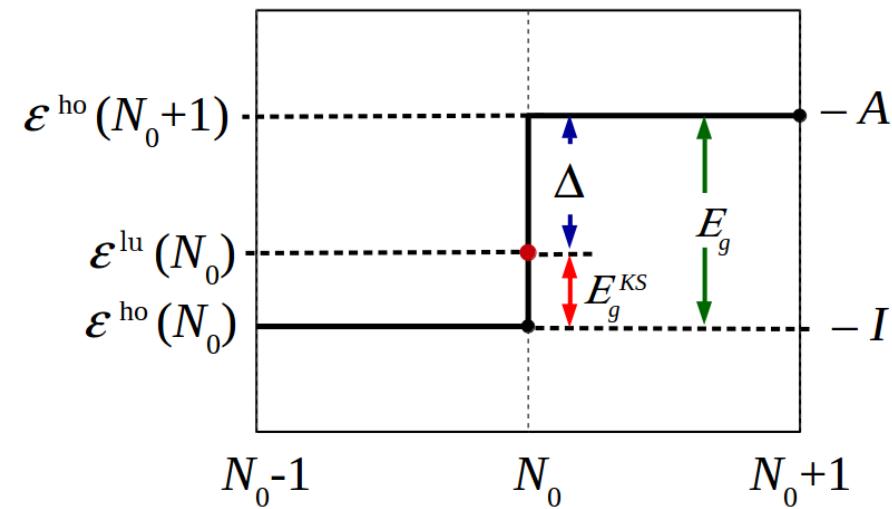
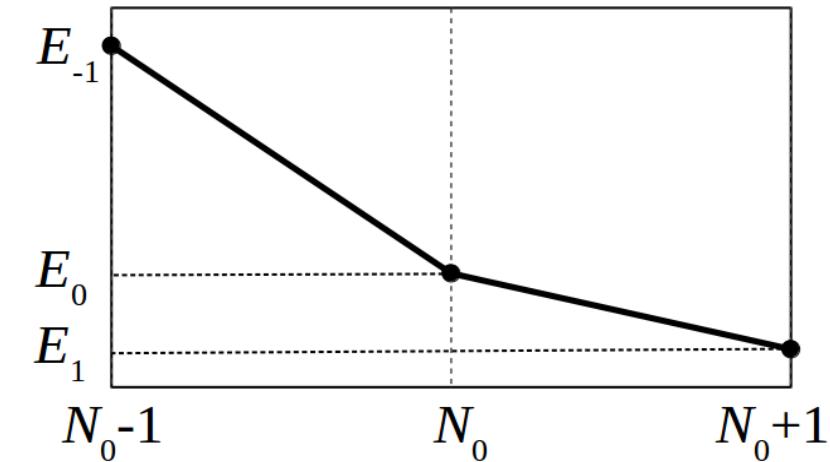
$$S = I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}}$$

- Important for a correct distribution of charge



2: derivative discontinuity

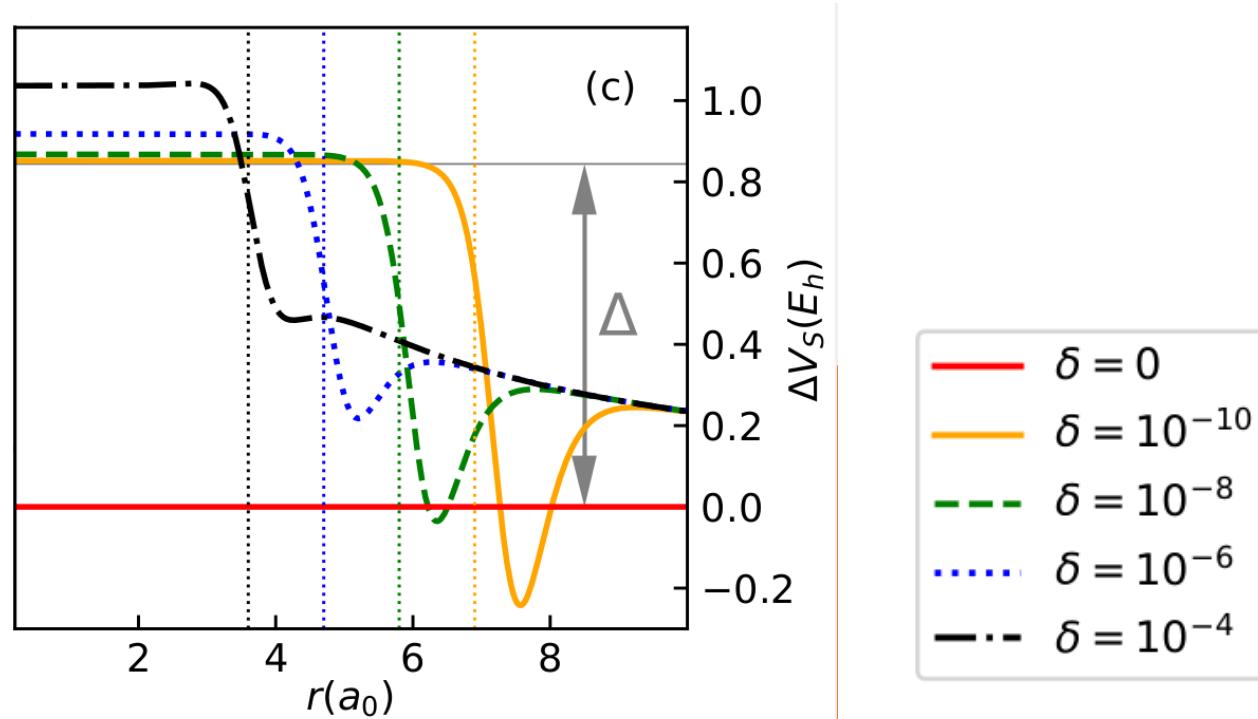
- In a system with a varying N , the exact potential **jumps** by a **constant**, Δ , when N crosses an integer
- The energy, E , is piecewise-linear with N ; its derivative is **discontinuous**
- The highest occupied (ho) energy, $\varepsilon^{\text{ho}} = \partial E / \partial N$, is a stair-step function
- To enforce this, the exact potential jumps by a spatially uniform constant $\Delta = I - A - (\varepsilon^{\text{lu}} - \varepsilon^{\text{ho}})$
- Important for the prediction of the fundamental gap, E_g



- Perdew, Parr, Levy, Balduz, PRL 49, 1691 (1982) ► Almbladh, von Barth, PRB 31, 3231 (1985)
 ► Levy et al., PRA 30, 2745 (1984) ► Perdew, Levy, PRB 56, 16021 (1997) ► Harbola, PRB 60, 4545 (1999)

2: derivative discontinuity

- Example: exact KS potential for the Li atom with $N = 2 + \delta$ obtained from a full-CI calculation
- At any finite δ , there is a **plateau** around the nucleus
- For $\delta \rightarrow 0^+$, the plateau broadens and becomes spatially uniform. The plateau height approaches Δ



Are these two properties related?

- DD: $\Delta = I - A + \varepsilon^{\text{ho}} - \varepsilon^{\text{lu}}$
 - ★ Derived from piecewise-linearity
 - ★ Occurs at fractional N
- Step: $S = I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}}$
 - ★ Derived from density decay
 - ★ Occurs at integer N
- *Contradiction?* From the DD view, transfer of charge $L \rightarrow R$ raises a plateau Δ_R around atom R

Stretched molecule, varying N

- Stretched molecule, $L \dots R$. Increase the number of e^- 's on atom R
 - ★ by charge transfer $L \rightarrow R$
 - ★ by varying the overall number of electrons, $N_{L \dots R}$
- 3 regions of density decay

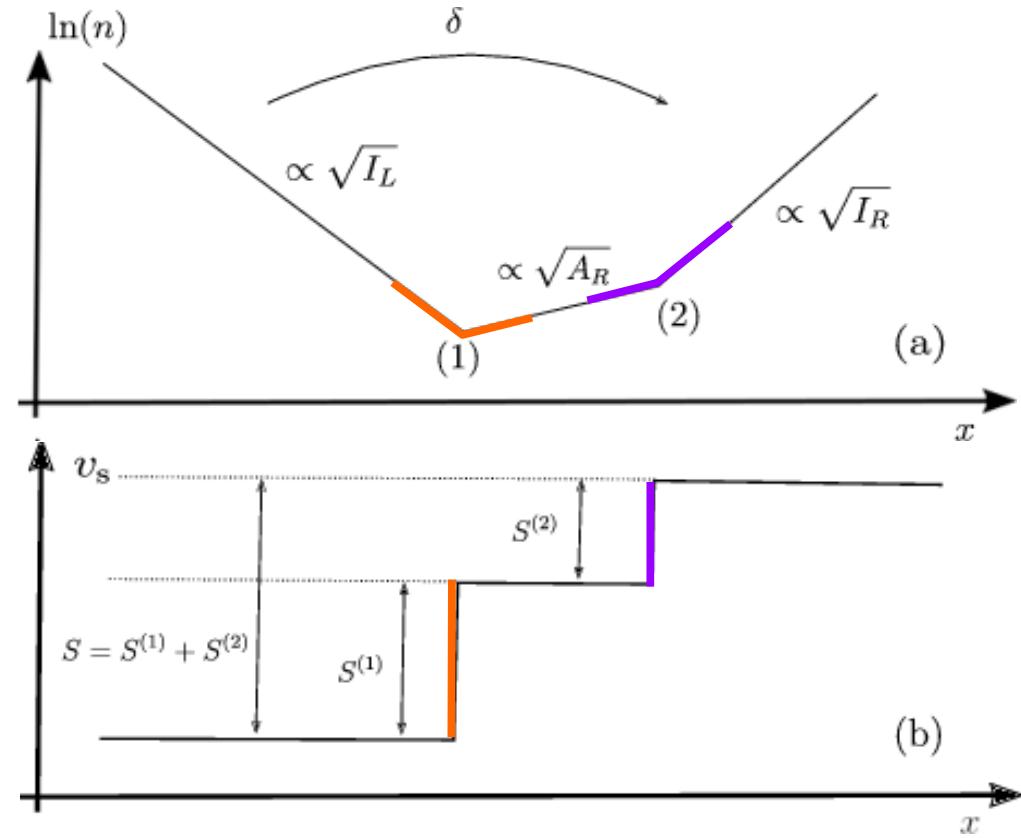
$I_R \rightarrow A_R$: due to e^- addition

$A_R \rightarrow I_L$: the system is one

- 2 intermolecular steps

$$S^{(2)} = \Delta_R$$

$$S^{(1)} = -\Delta_{L \rightarrow R}^{\text{CT}}$$



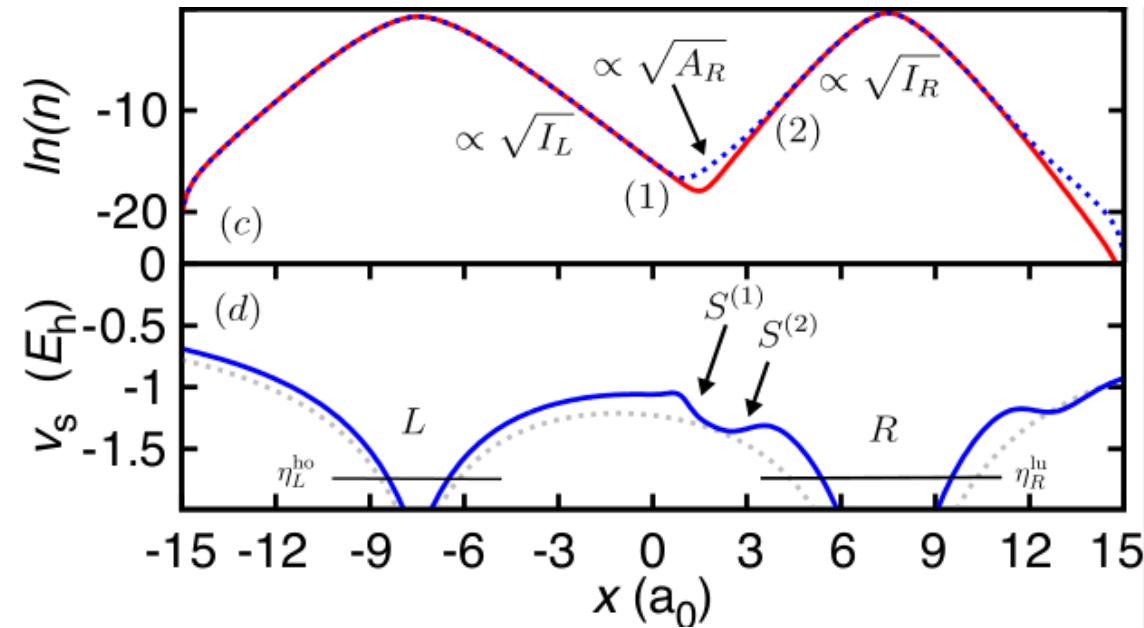
► See also: talk by Matt Hodgson, P02.0004, Wednesday, 15:30, room 150B

► Hodgson*, Kraisler*, Schild, Gross, J. Phys. Chem. Lett. 8, 5974 (2017)

Charge transfer DD

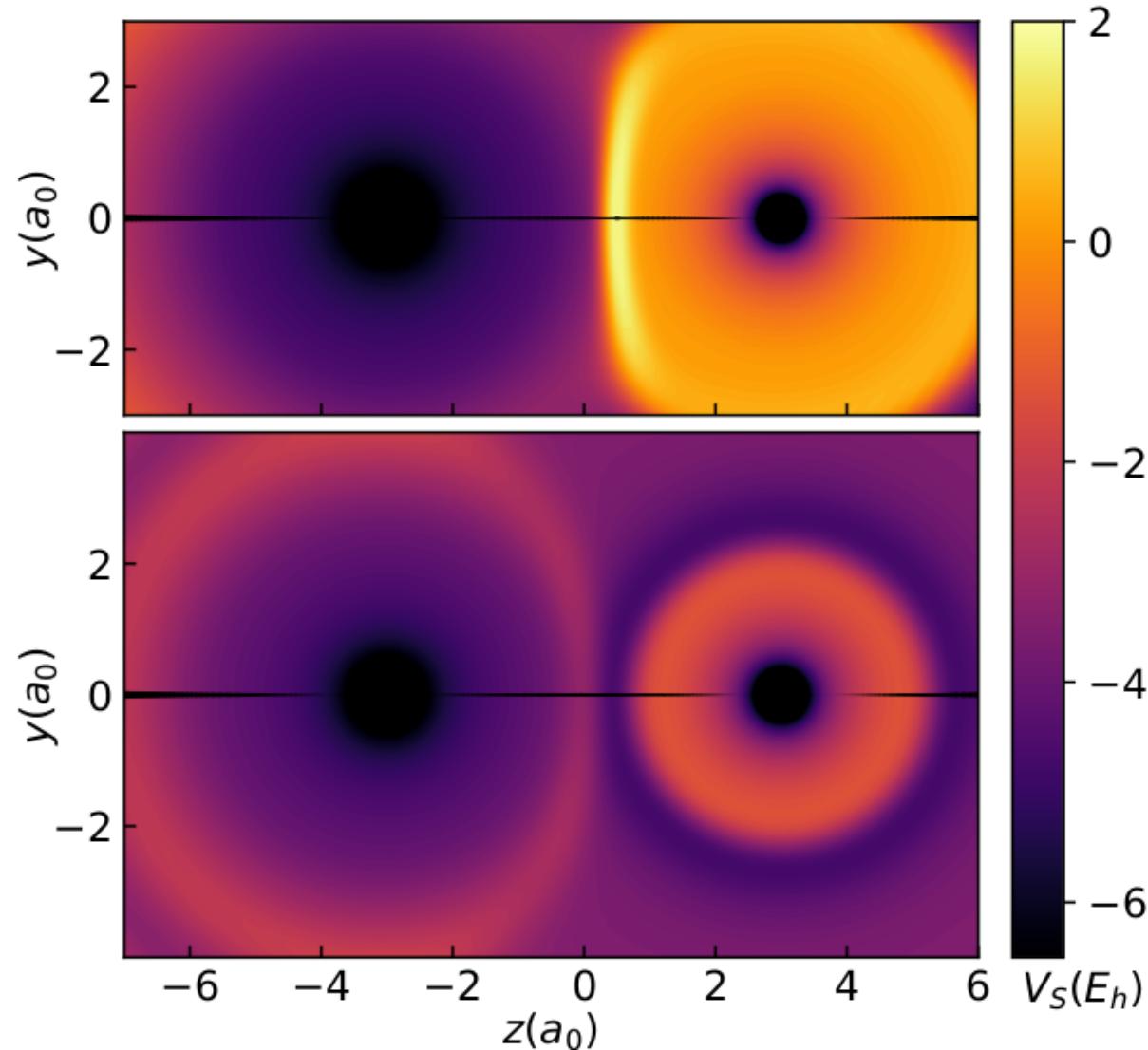
$$\Delta_{L \rightarrow R}^{\text{CT}} = I_L - A_R - (\eta_R^{\text{lu}} - \eta_L^{\text{ho}})$$

- The charge-transfer DD is revealed in an exact 1D model for a diatomic molecule
 - Increase the total N by a very small amount, δ
 - The extra electric charge localizes on R
- Two steps in potential:
 - $S^{(2)}$ is the DD of R
 - $S^{(1)}$ is the charge-transfer DD
- As $\delta \rightarrow 0^+$, $S^{(1)}$ and $S^{(2)}$ coincide to form the step S



Steps and discontinuities in 3D

- Full-CI calculation
- Stretched Li...Be molecule
- v_{KS} for $N = 4$
- ★ platform around Be
- v_{KS} for $N = 4.001$
 - ★ double-step structure:
a halo around Li and
a platform around Be
- Similar results for $(\text{Li} \dots \text{He})^+$
and $(\text{Be} \dots \text{He})^{2+}$



Conclusions

- The relationship between the uniform jump in the exact KS potential, Δ , and the interatomic step, S , has been clarified.
- The step S has an internal structure. This has been found in a 1D model system and a 3D full-CI calculation of a molecule.
- We introduced a new quantity: the charge-transfer derivative discontinuity, Δ^{CT} .
- Advanced xc approximations should account for changes in the decay rate of the density, as this leads to a correct step structure in the potential.

* ***J. Phys. Chem. Lett.* 8, 5974 (2017)** *