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

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3. Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, Hebrew University of Jerusalem, Israel

Density Functional Theory

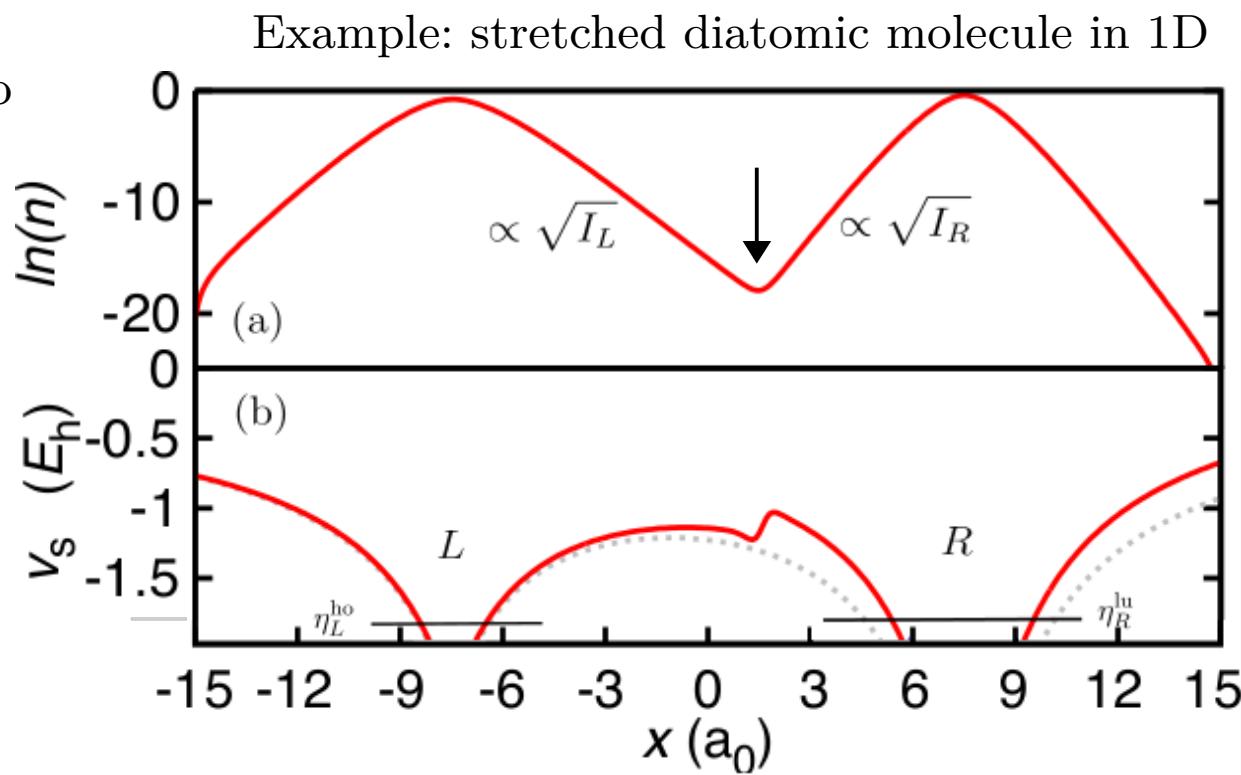
- An exact approach to the many-electron problem
- The exact **exchange-correlation** (xc) potential $v_{\text{xc}}[n](\mathbf{r})$ remains usually unknown and has to be approximated.
$$v_{KS}[n](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r})$$
- 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:

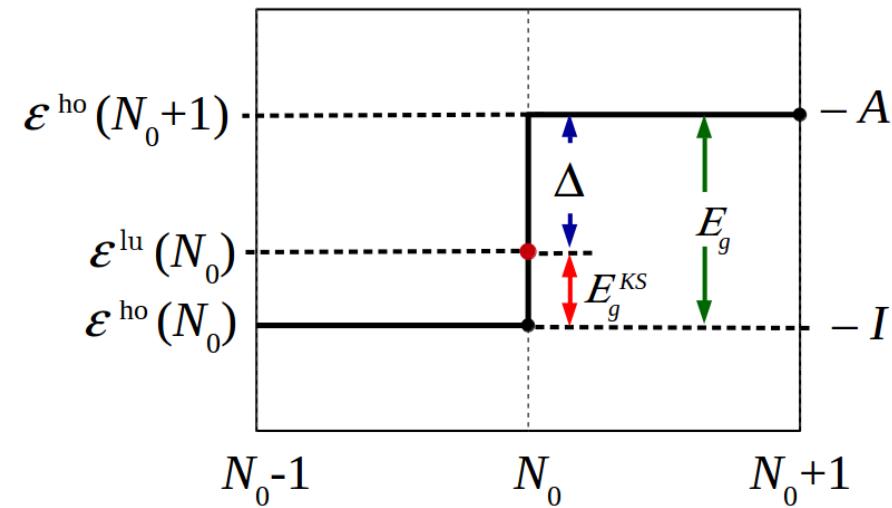
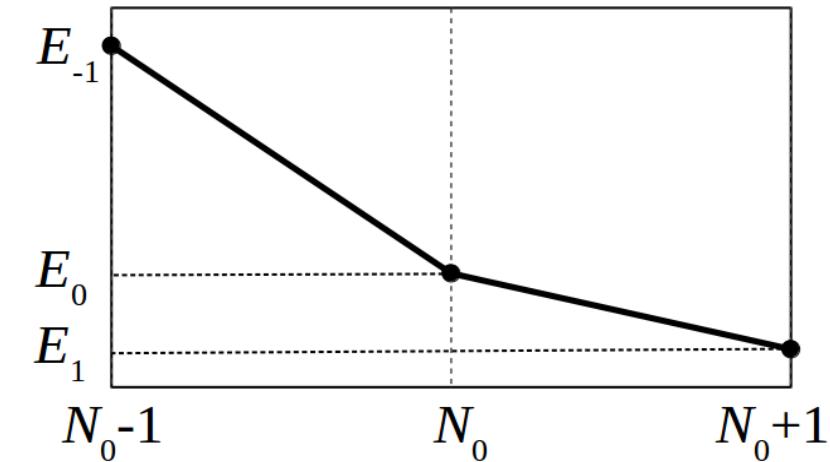
$$S = I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}}$$

- Important for a correct distribution of charge



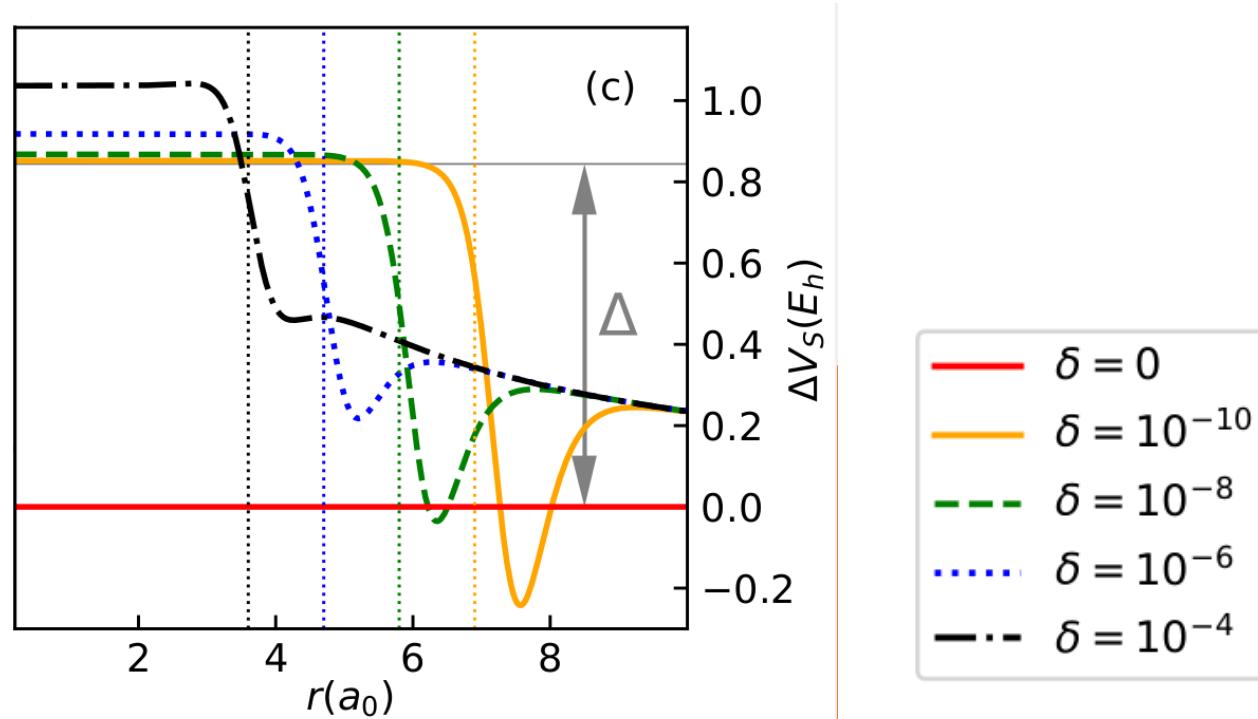
2: derivative discontinuity

- 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



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: $\Delta = I - A + \boldsymbol{\varepsilon}^{\text{ho}} - \boldsymbol{\varepsilon}^{\text{lu}}$
 - ★ Derived from piecewise-linearity
 - ★ Occurs at fractional N
- Step: $S = I_R - I_L + \boldsymbol{\eta}_R^{\text{ho}} - \boldsymbol{\eta}_L^{\text{ho}}$
 - ★ 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

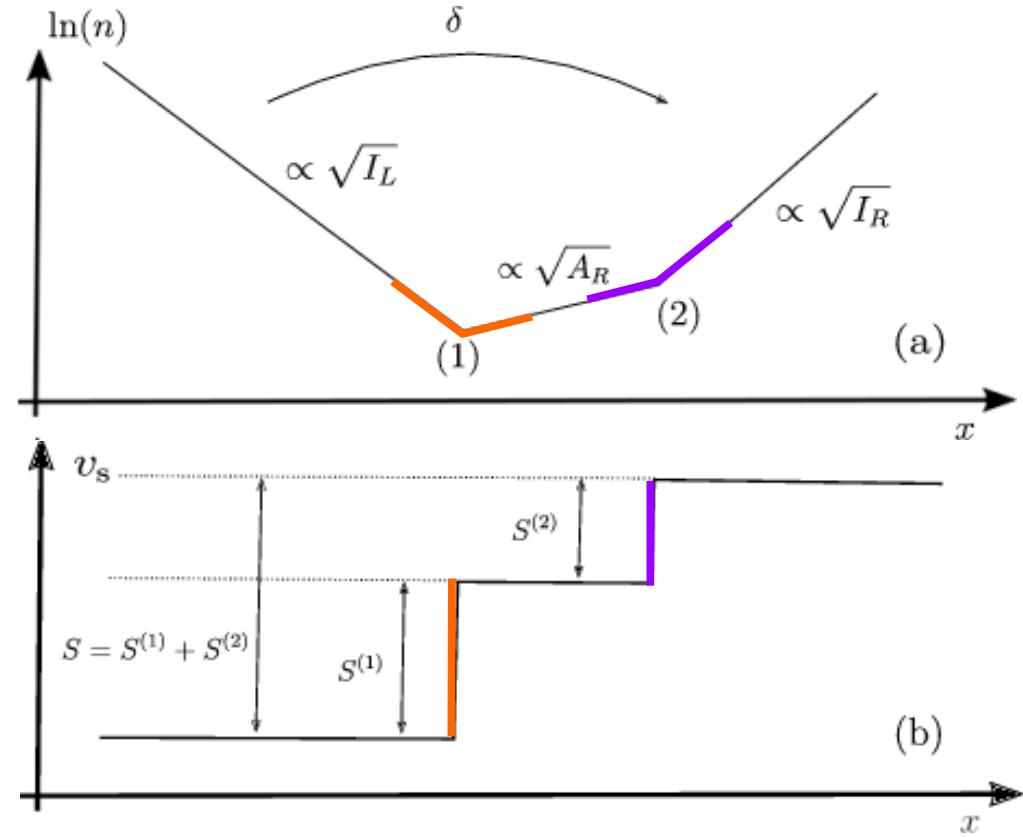
$I_R \rightarrow A_R$: due to e^- addition

$A_R \rightarrow I_L$: the system is one

- 2 intermolecular steps

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

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



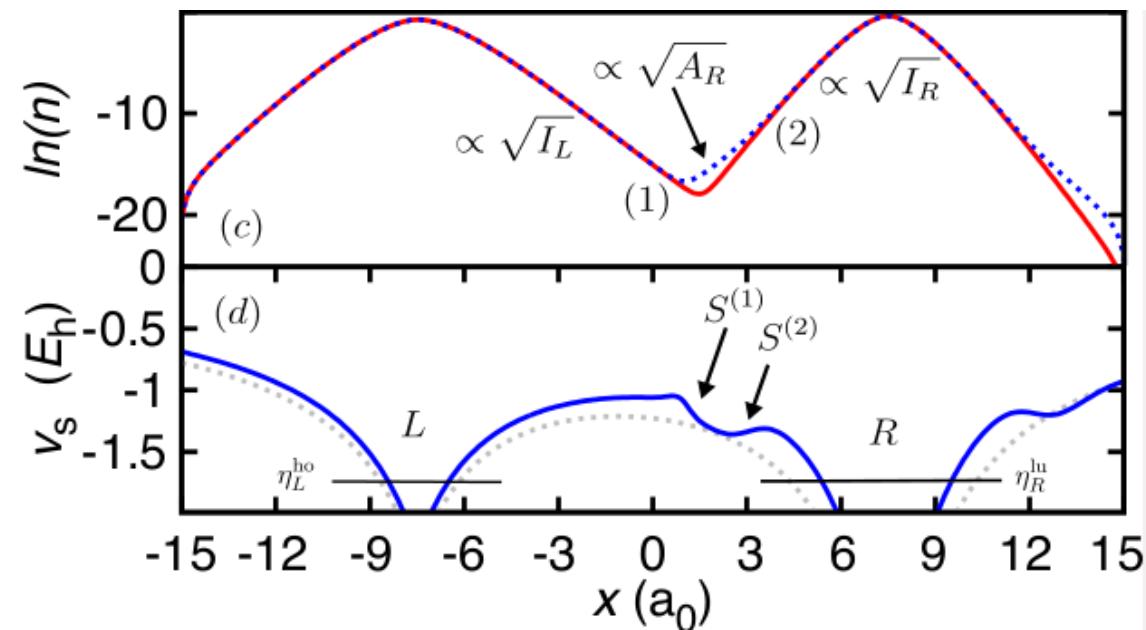
► See also: talk by Matt Hodgson, Monday, 10:45, room HL 001

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

Charge transfer DD

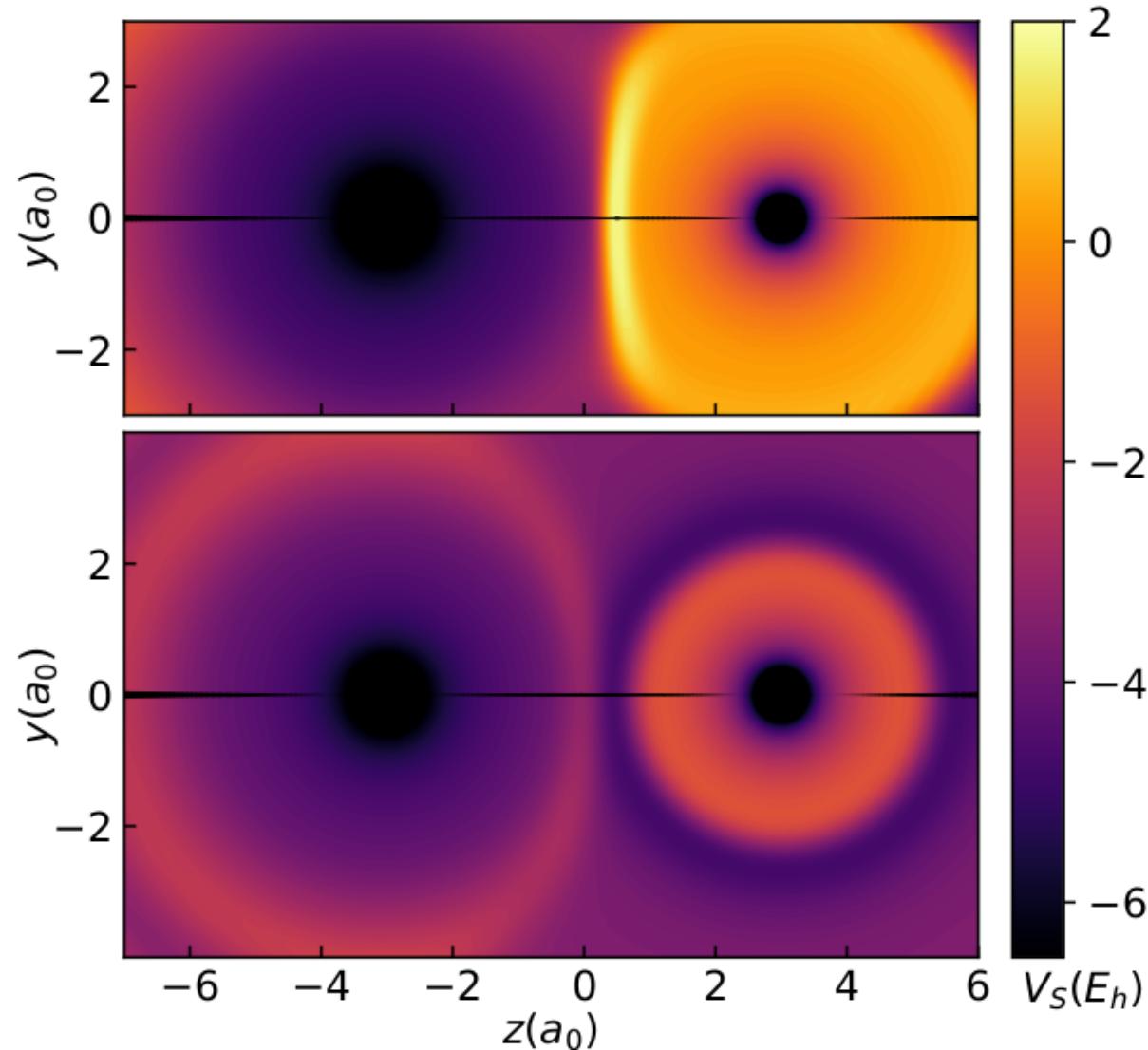
$$\Delta^{\text{CT}}_{L \rightarrow R} = I_L - A_R - (\eta_R^{\text{lu}} - \eta_L^{\text{ho}})$$

- 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.

Steps in the Exact Kohn-Sham Potential of Ensemble Density Functional Theory for Excited States and Their Relation to the Derivative Discontinuity

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¹Max-Planck-Institute für Mikrostrukturphysik, Halle (Saale), Germany,

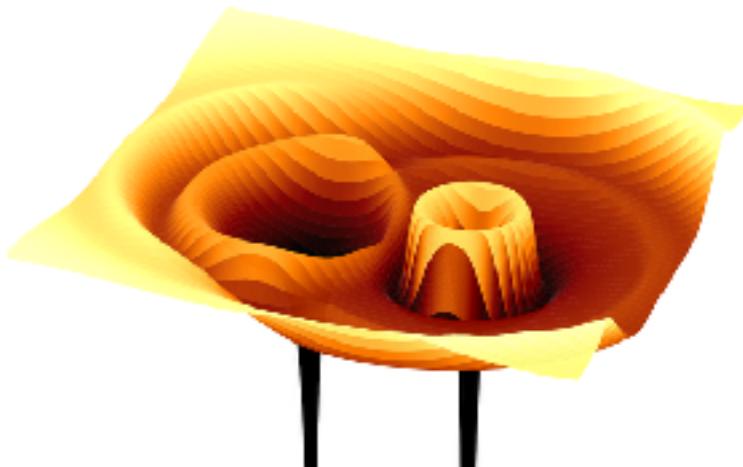
²Department of Physics, University of York, Heslington, York, UK,

³Laboratorium für Physikalische Chemie, ETH Zürich, Zürich, Switzerland,

⁴Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel



MAX-PLANCK-GESELLSCHAFT



Ensemble Density Functional Theory

The electron density of an *excited* system of N interacting electrons is modelled using an auxiliary system of non-interacting electrons:

E. K. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A **37**, 2809 (1988)

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Kohn-Sham
equations:

$$\left(-\frac{1}{2} \nabla^2 + v_s \right) \phi_i(r) = \varepsilon_i \phi_i(r)$$

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Electron
density:

$$n(r) = \delta |\phi_{N+1}(r)|^2 + (1 - \delta) |\phi_N(r)|^2 + \sum_{i=1}^{N-1} |\phi_i(r)|^2$$

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The accuracy of the density relies on the approximation to the exchange-correlation part of v_s .

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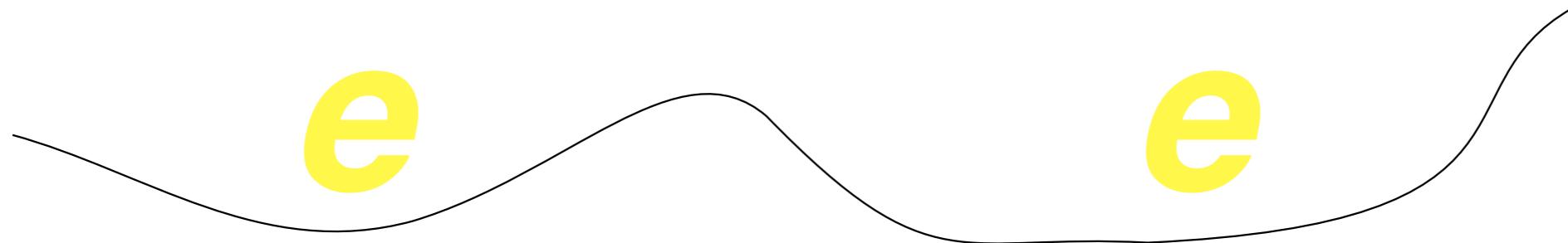
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The iDEA code



Model simple 1D systems consisting of a few electrons

Choose any external potential we like

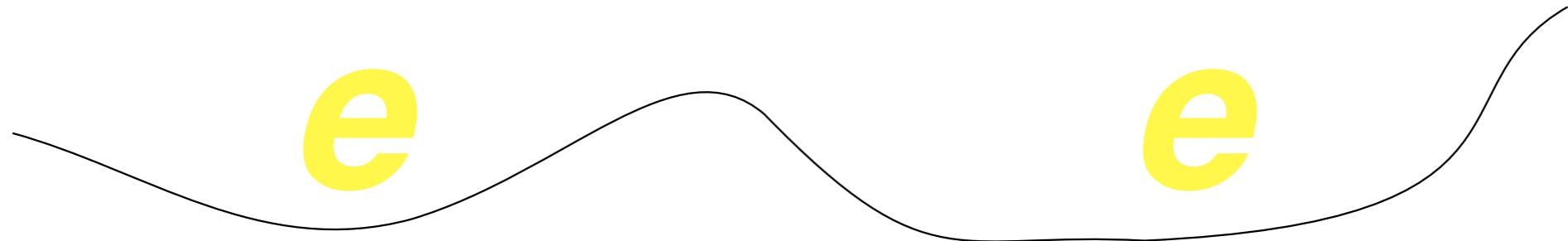


The iDEA code



Model simple 1D systems consisting of a few electrons

Choose any external potential we like



1. Calculate the exact ground-state and **first excited-state** electron density
2. The electron density is a linear combination of these two densities:

$$n(r) = (1 - \delta) \cdot n_0(r) + \delta \cdot n_1(r)$$

3. Next reverse-engineer the exact Kohn-Sham potential

The iDEA code



The ground-state, fully correlated many-electron wavefunction is calculated by propagating a trial wavefunction through imaginary time

The iDEA code



The ground-state, fully correlated many-electron wavefunction is calculated by propagating a trial wavefunction through imaginary time

$$t \rightarrow -i\tau$$

$$\Psi(x, x', \tau) = \Psi_0(x, x')e^{-E_0\tau} + \Psi_1(x, x')e^{-E_1\tau} + \Psi_2(x, x')e^{-E_2\tau} + \dots$$

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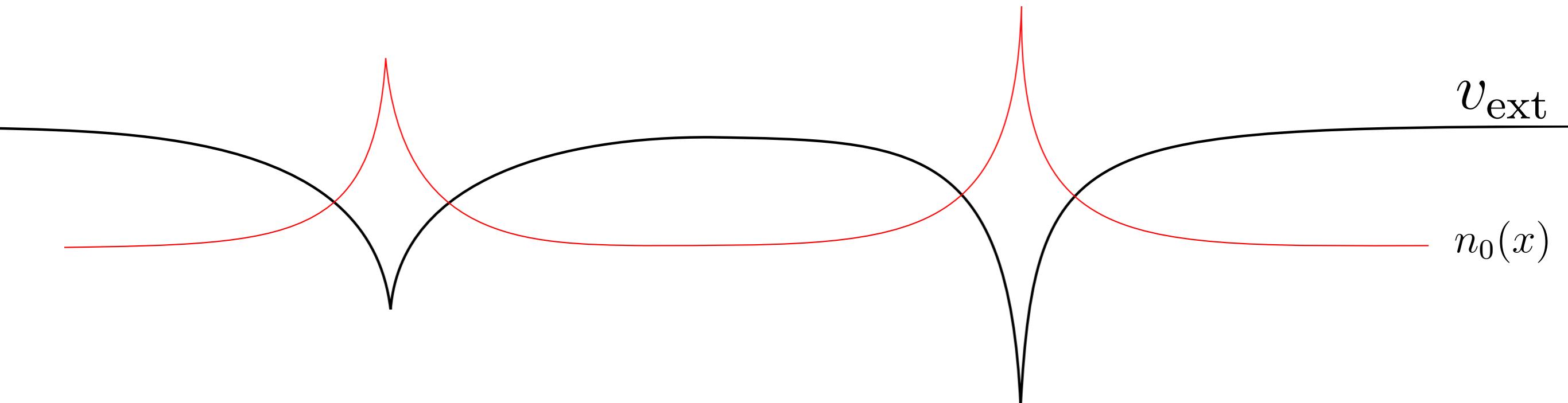
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The first excited-state many-electron wavefunction is calculated by propagating a trail wavefunction through imaginary time while removing the ground-sate solution from the evolving wavefunction

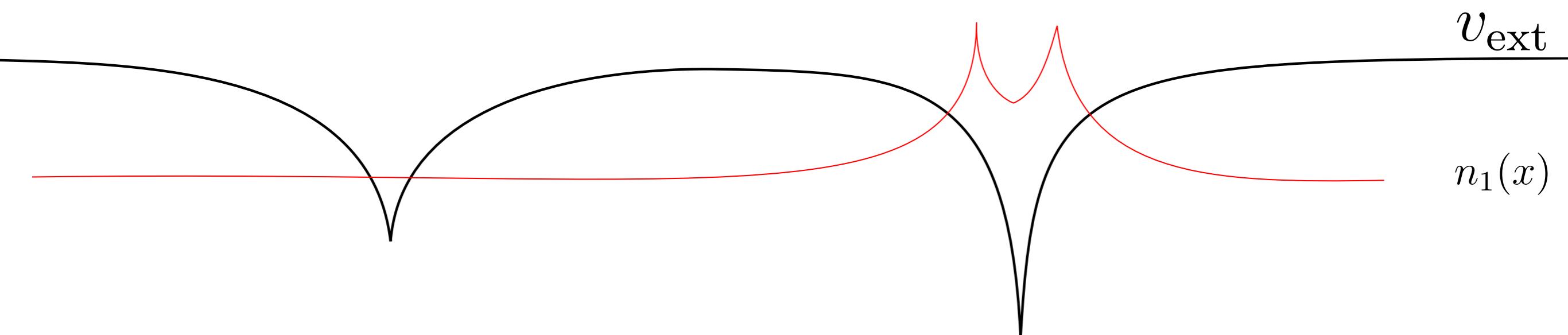
Charge transfer excitation in a 1D molecule

The number of electrons is integer



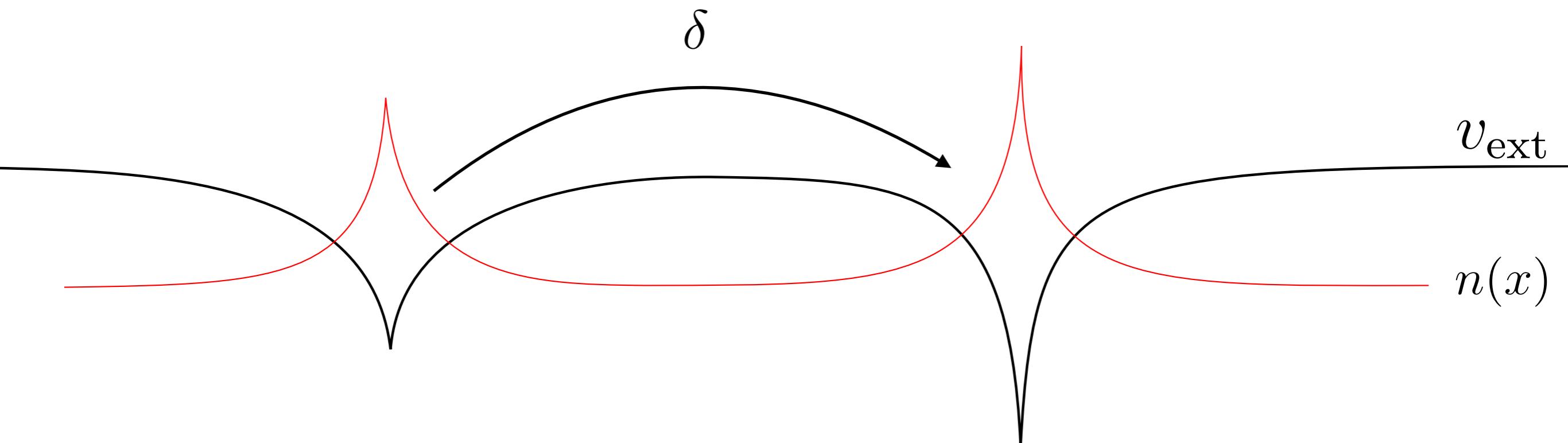
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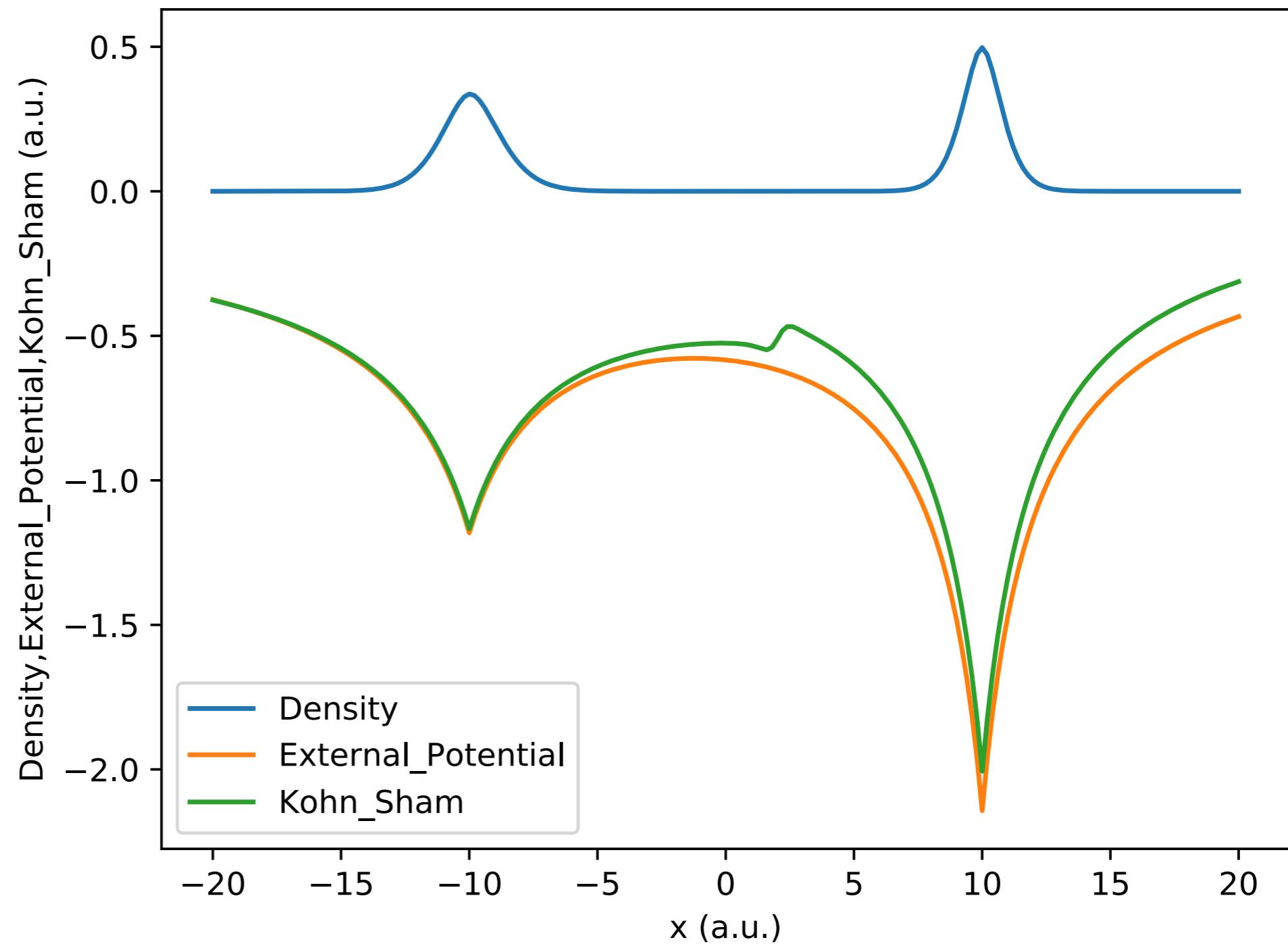
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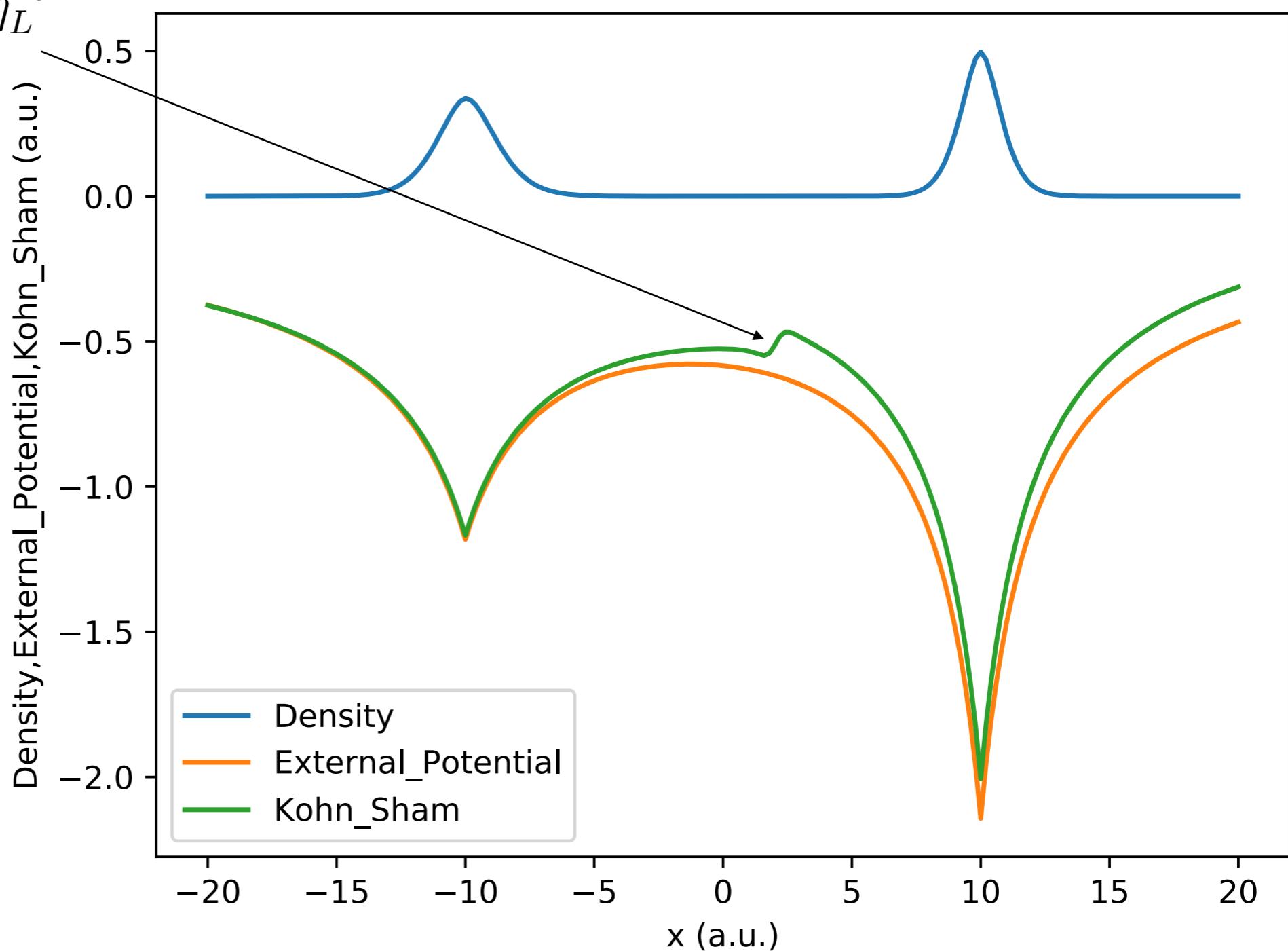
$$0 < \delta \ll 1$$

Ground-state 1D molecule



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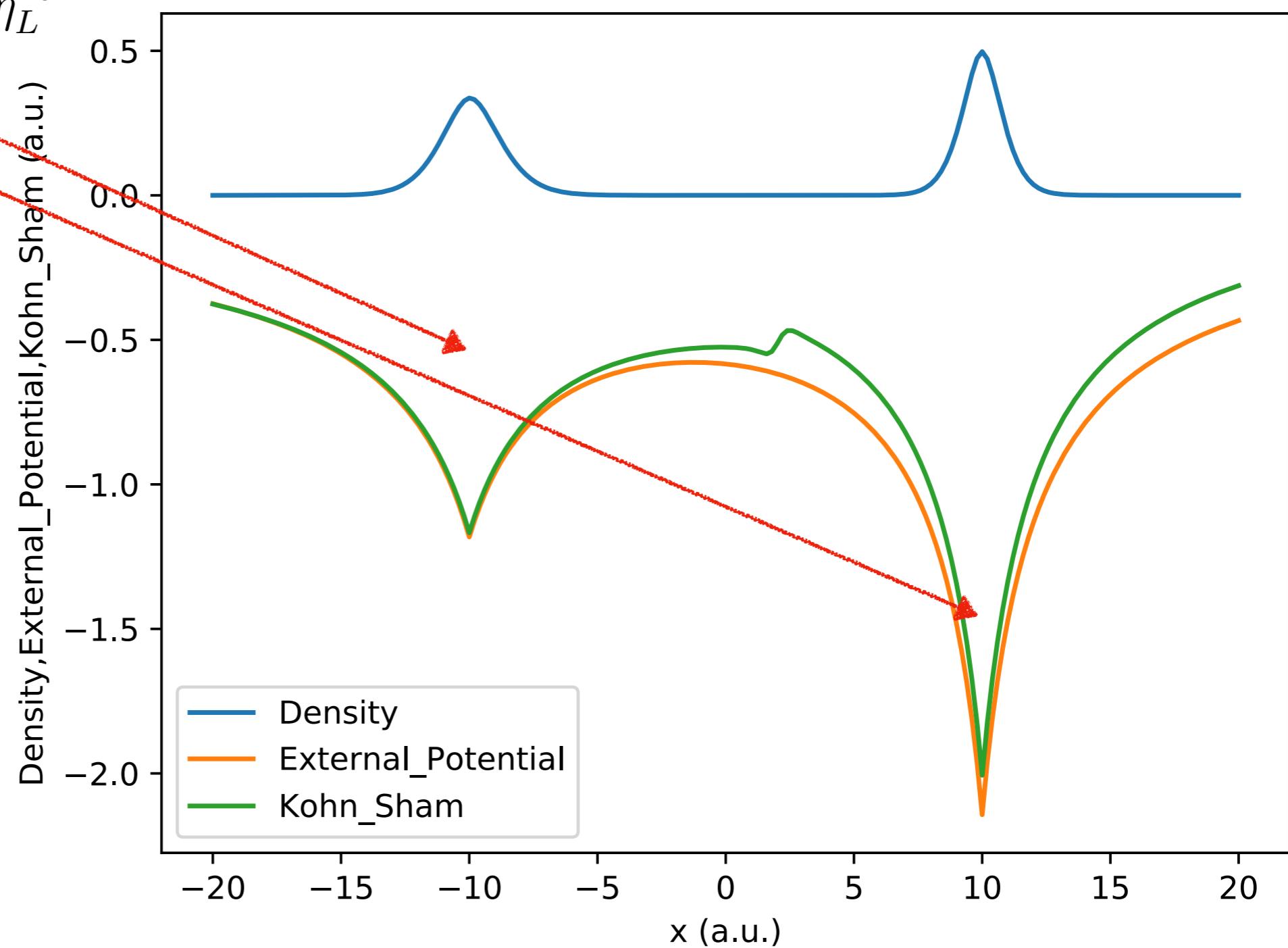
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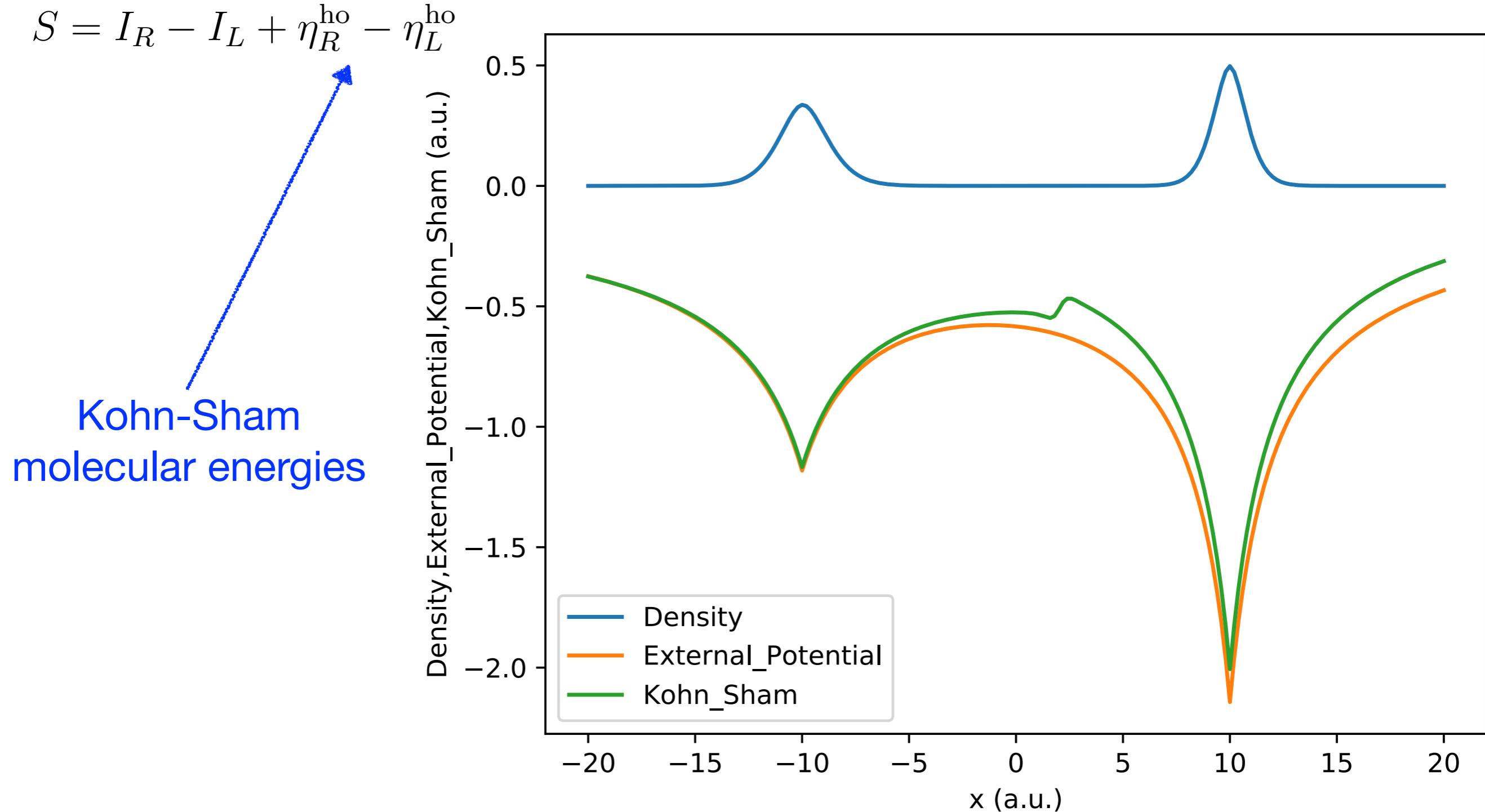
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Ionisation energy



Ground-state 1D molecule

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Ground-state 1D molecule

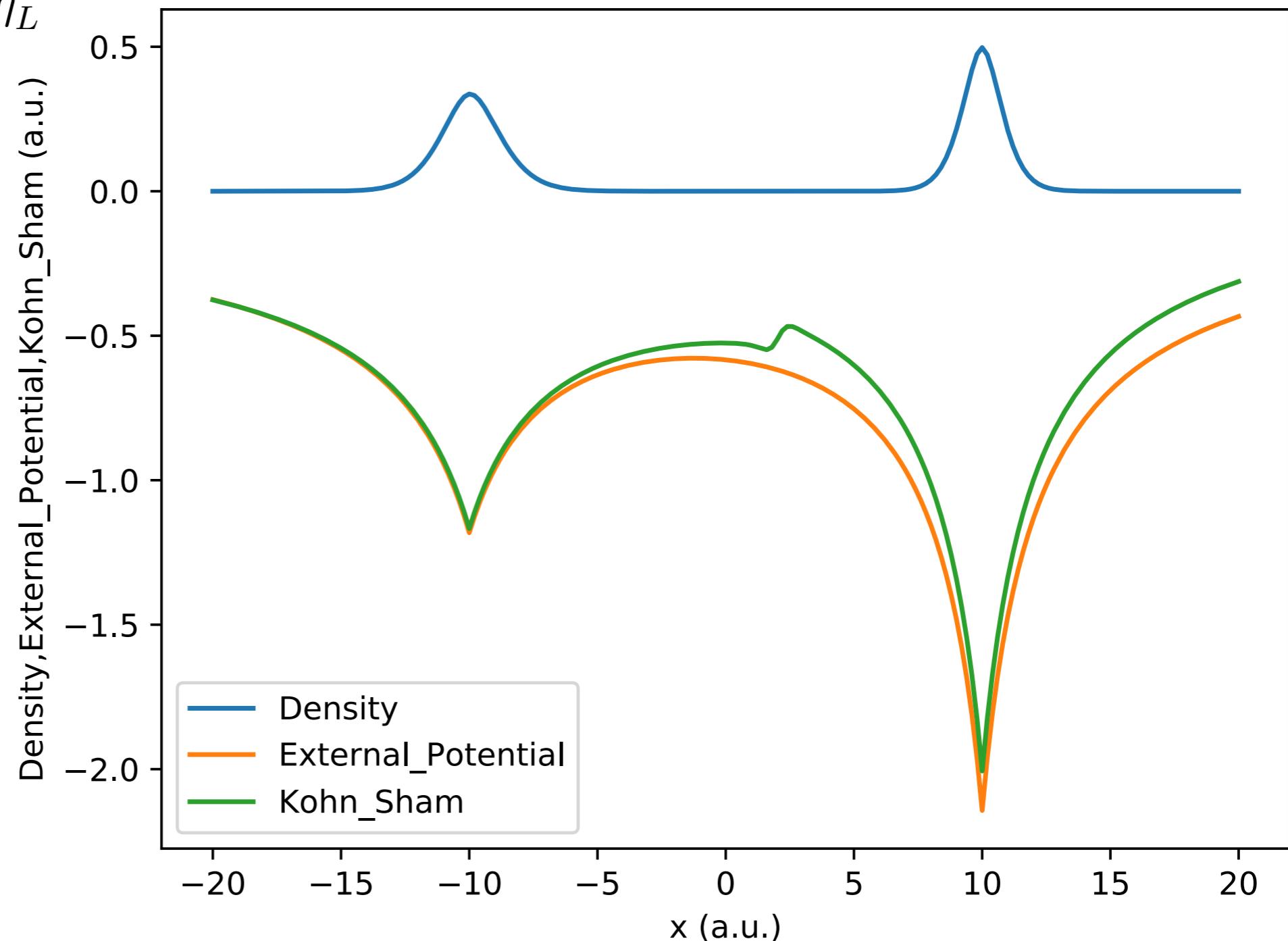
$$S = I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}}$$

Kohn-Sham
molecular energies

Bonded case:

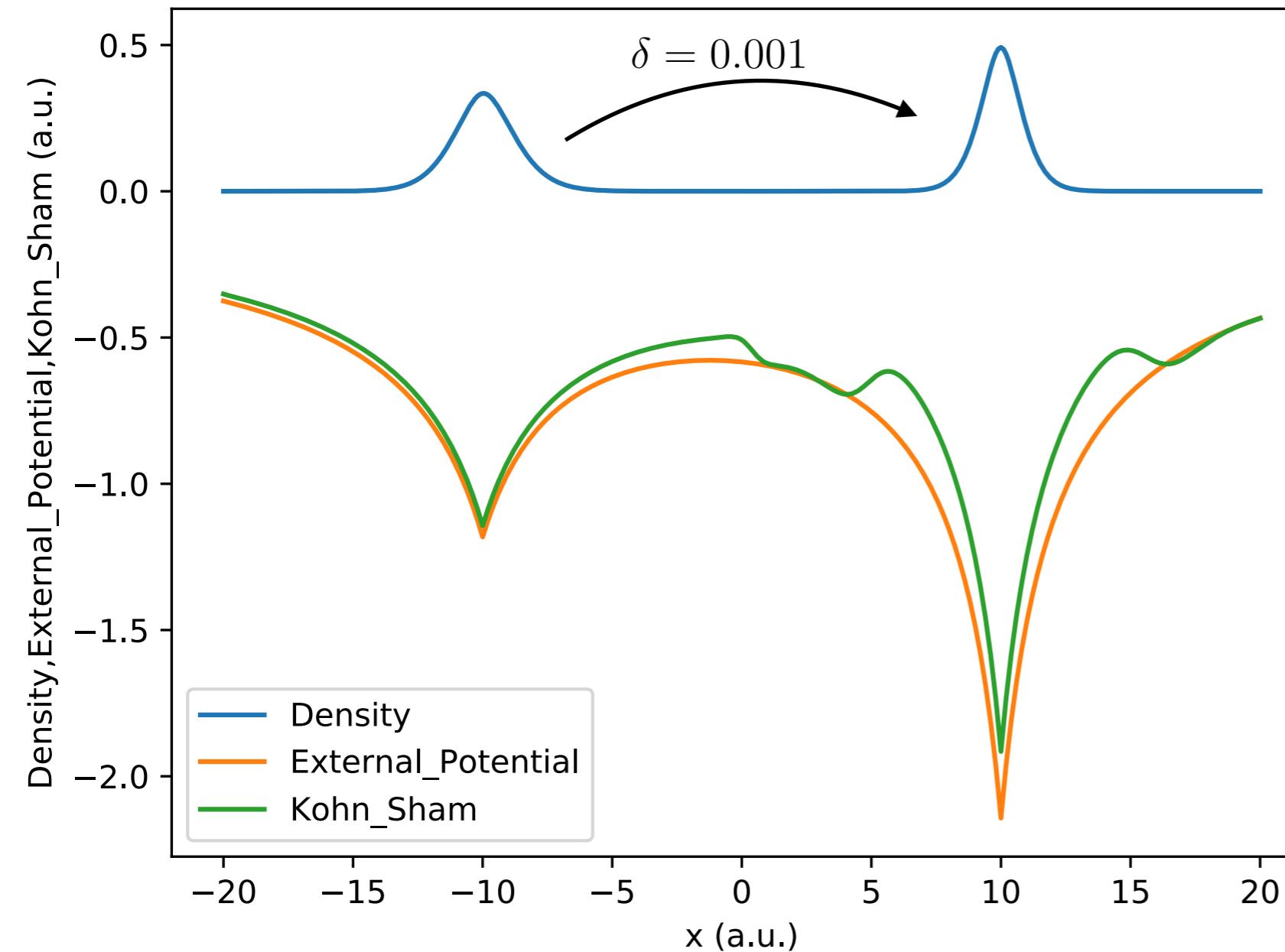
$$\eta_R^{\text{ho}} = \eta_L^{\text{ho}}$$

$$\Rightarrow S = I_R - I_L$$



Charge transfer excitation in a 1D molecule

The number of electrons is integer

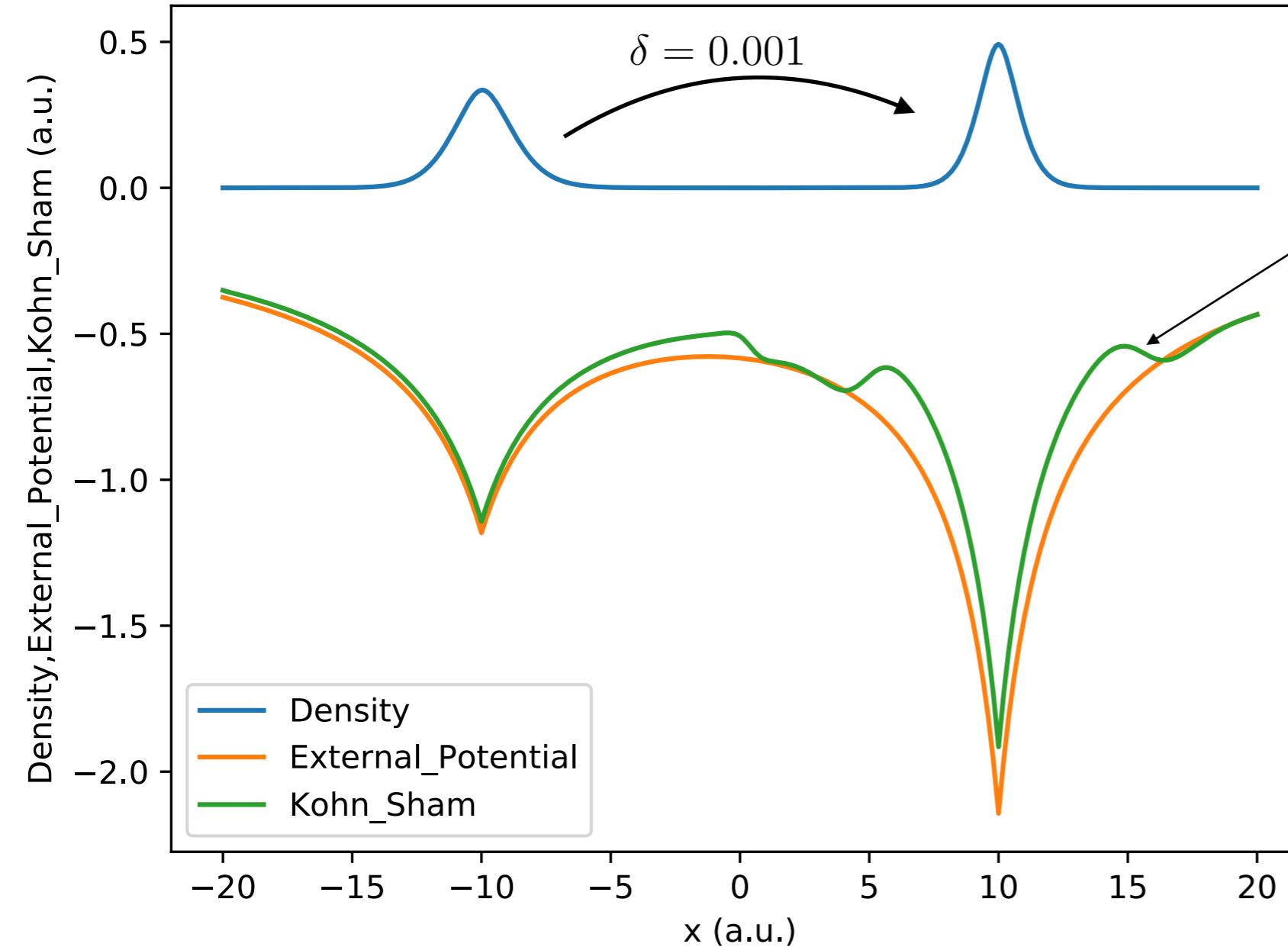


Charge transfer excitation in a 1D molecule

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Derivative discontinuity of Atom R:

$$\Delta_R = I_R - A_R + \varepsilon_R^{\text{ho}} - \varepsilon_R^{\text{lu}}$$



Charge transfer excitation in a 1D molecule

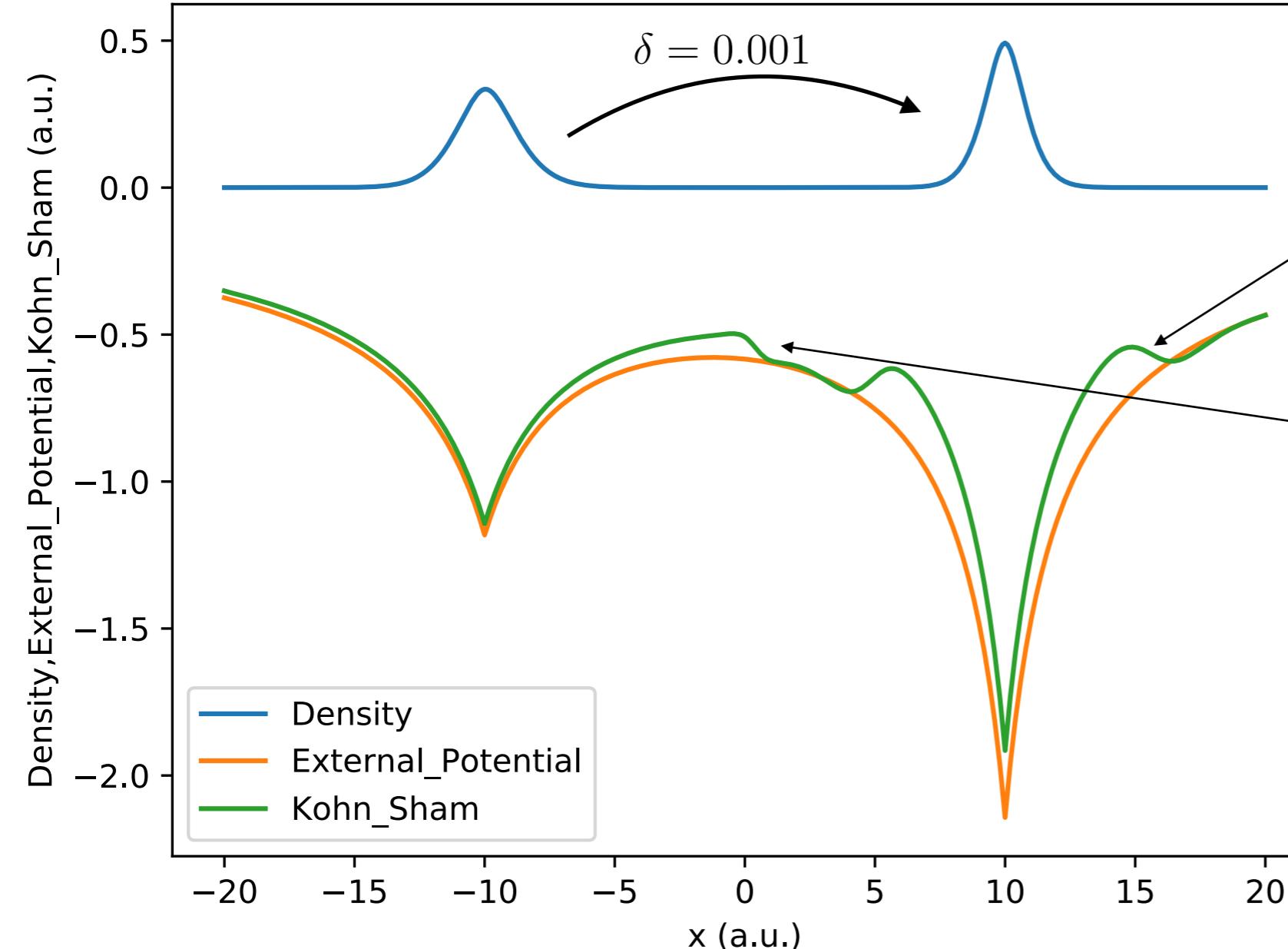
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$$\Delta_{L \rightarrow R}^{\text{CT}} = I_L - A_R + \eta_L^{\text{ho}} - \eta_R^{\text{lu}}$$

What's this?



Charge-transfer derivative discontinuity

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

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Charge-transfer derivative discontinuity

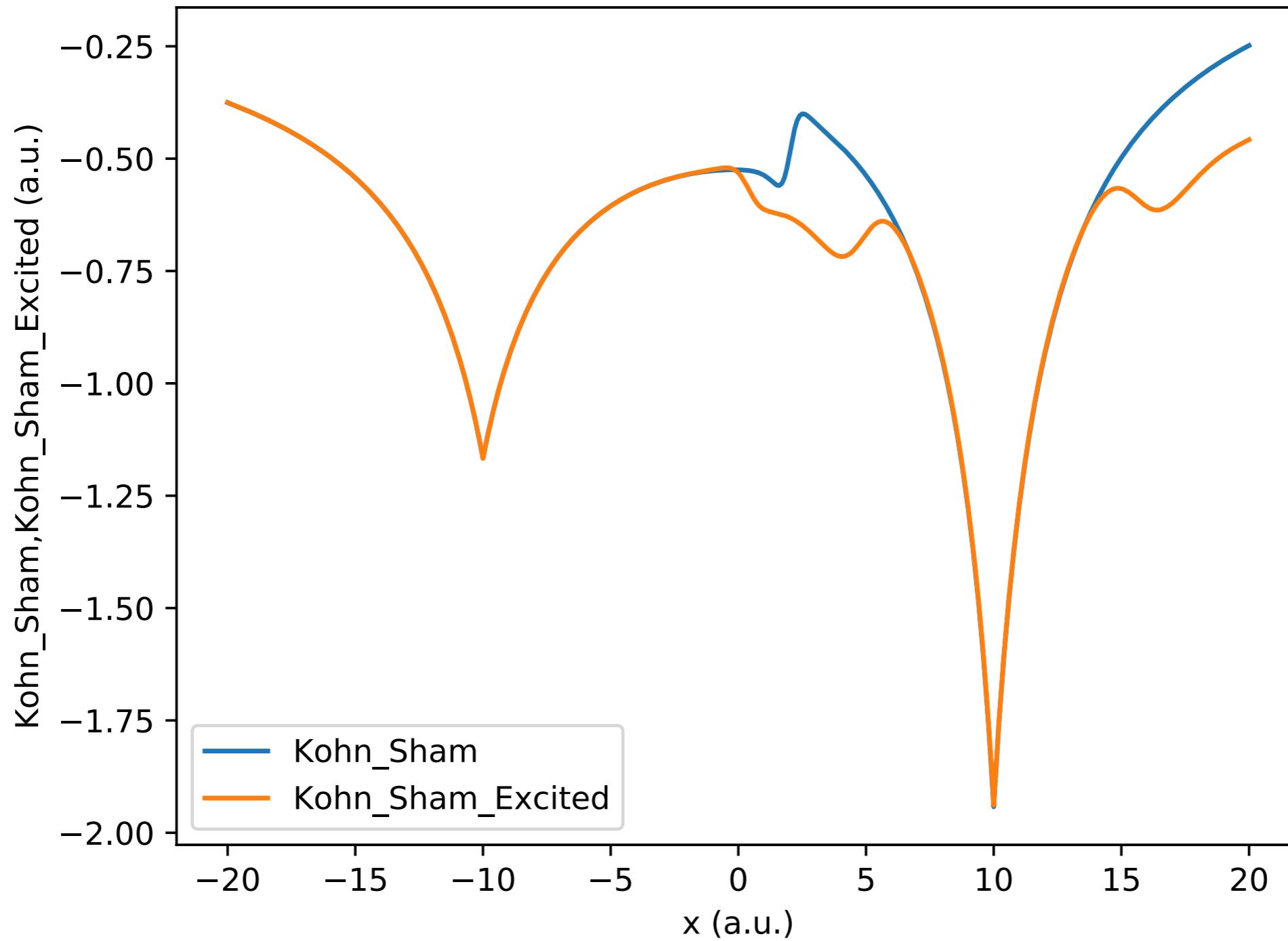
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$$S = S_1 + S_2 = \Delta_R - \Delta_{L \rightarrow R}^{\text{CT}} = I_R - I_L + \eta_R^{\text{ho}} - \eta_L^{\text{ho}}$$

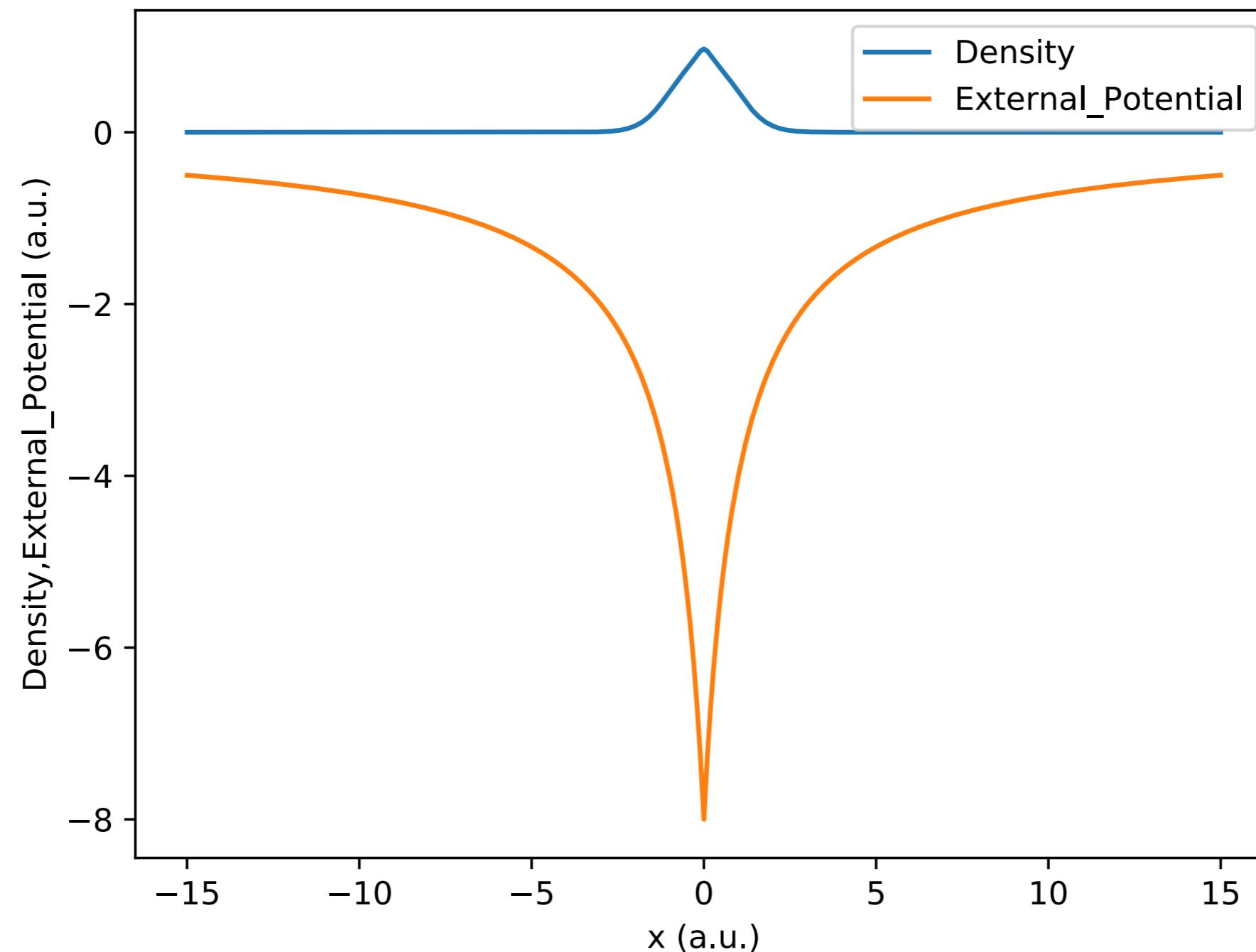
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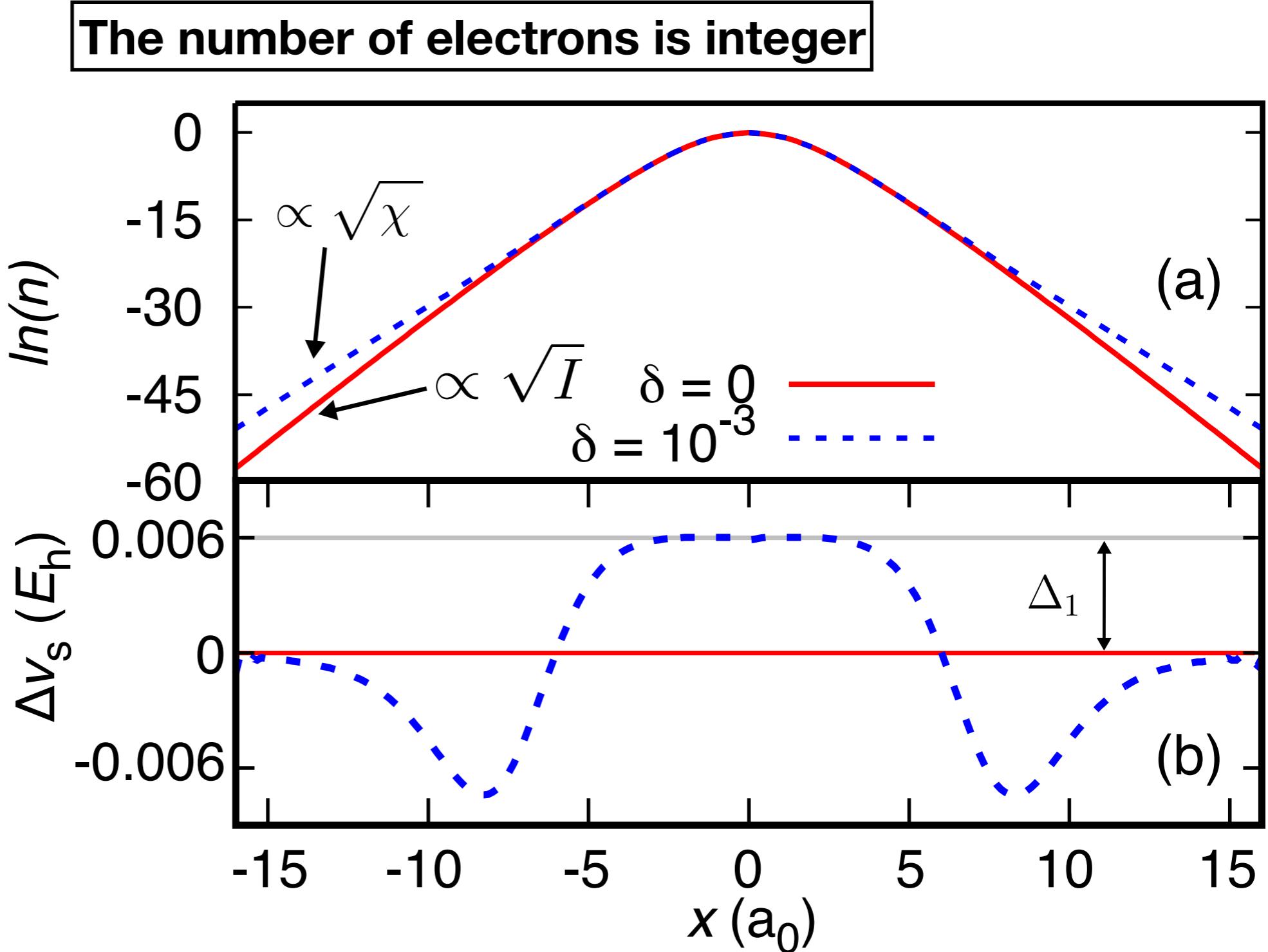
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'Derivative discontinuity' for an excited atom

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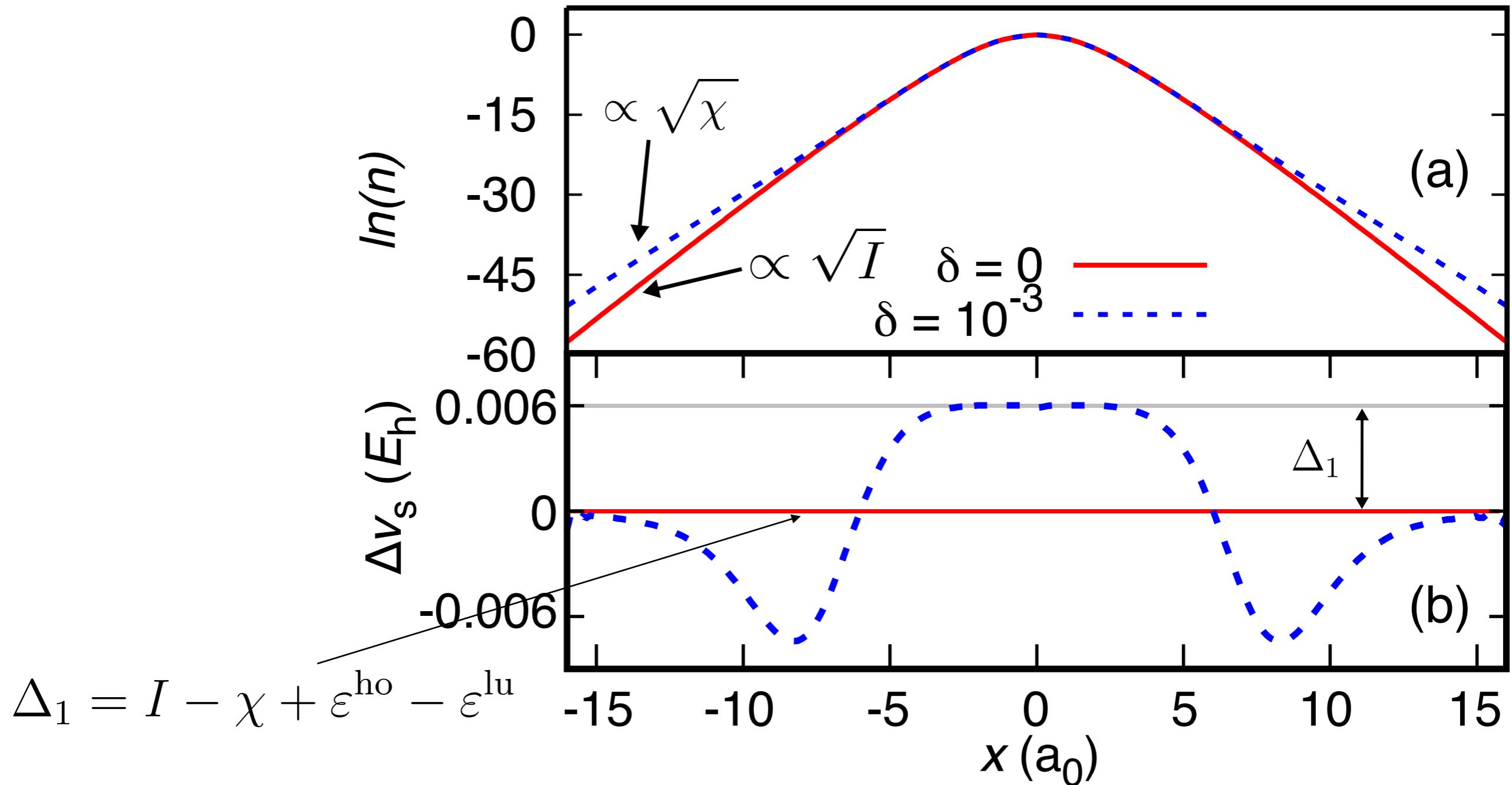


'Derivative discontinuity' for an excited atom



'Derivative discontinuity' for an excited atom

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Conclusions

1. Ensemble density functional theory can be used to model charge transfer
2. Upon charge transfer two plateaus form around the atoms of a diatomic molecule – one corresponds to the derivative discontinuity of the acceptor and the other corresponds to the ‘charge-transfer derivative discontinuity’
3. The steps which correspond to the two derivative discontinuities add together to make the interatomic step which determines the distribution of charge in the molecule

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Thanks for listening!

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