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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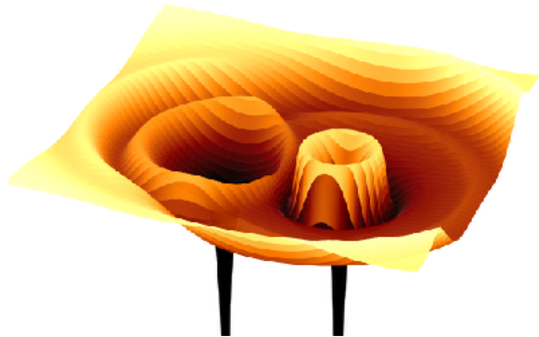
MARCH MEETING 2018
LOS ANGELES MARCH 5-9



Ensemble Density Functional Theory

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Electron density:

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

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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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The iDEA code

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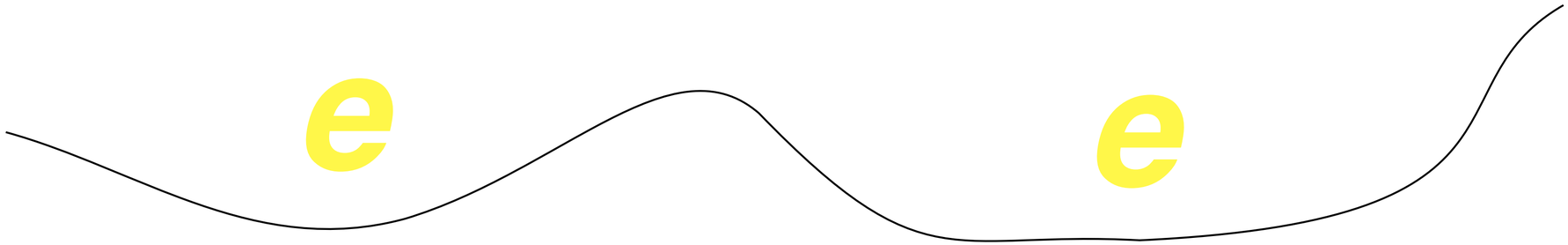
Model simple 1D systems consisting of a few electrons

Choose any external potential we like



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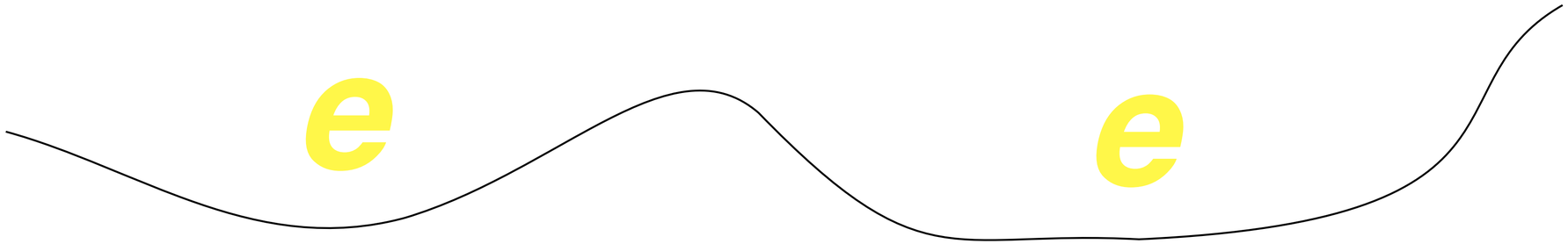
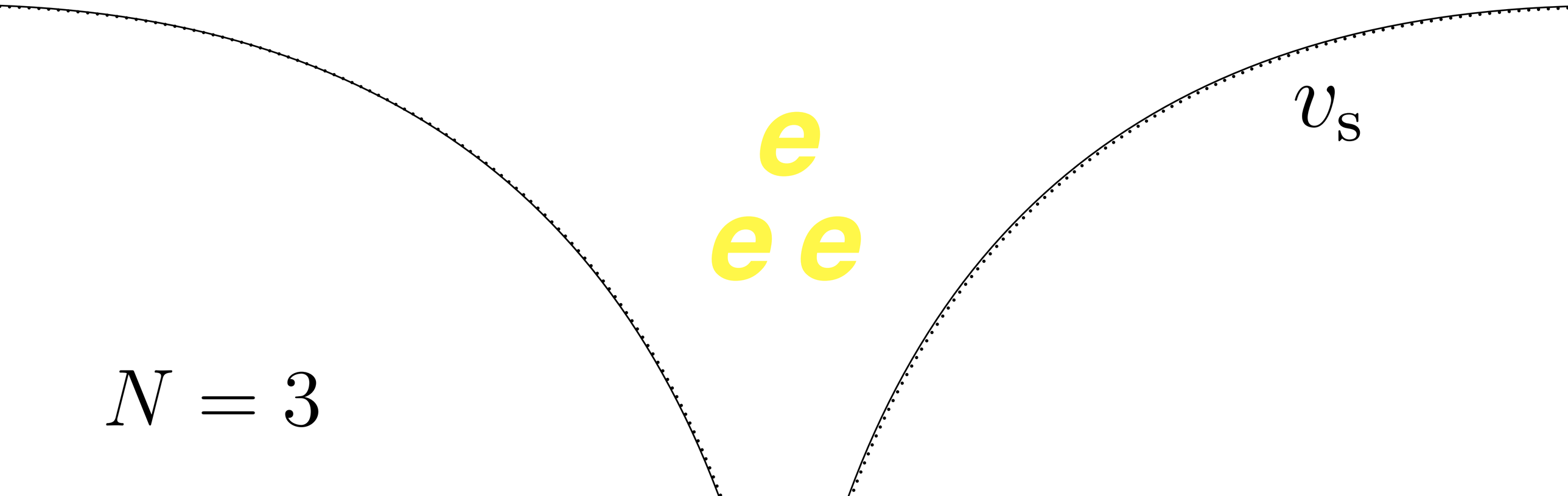


1. Calculate the exact ground-state and **first excited-state** electron density
2. The electron density is a linear combination of these two densities:

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

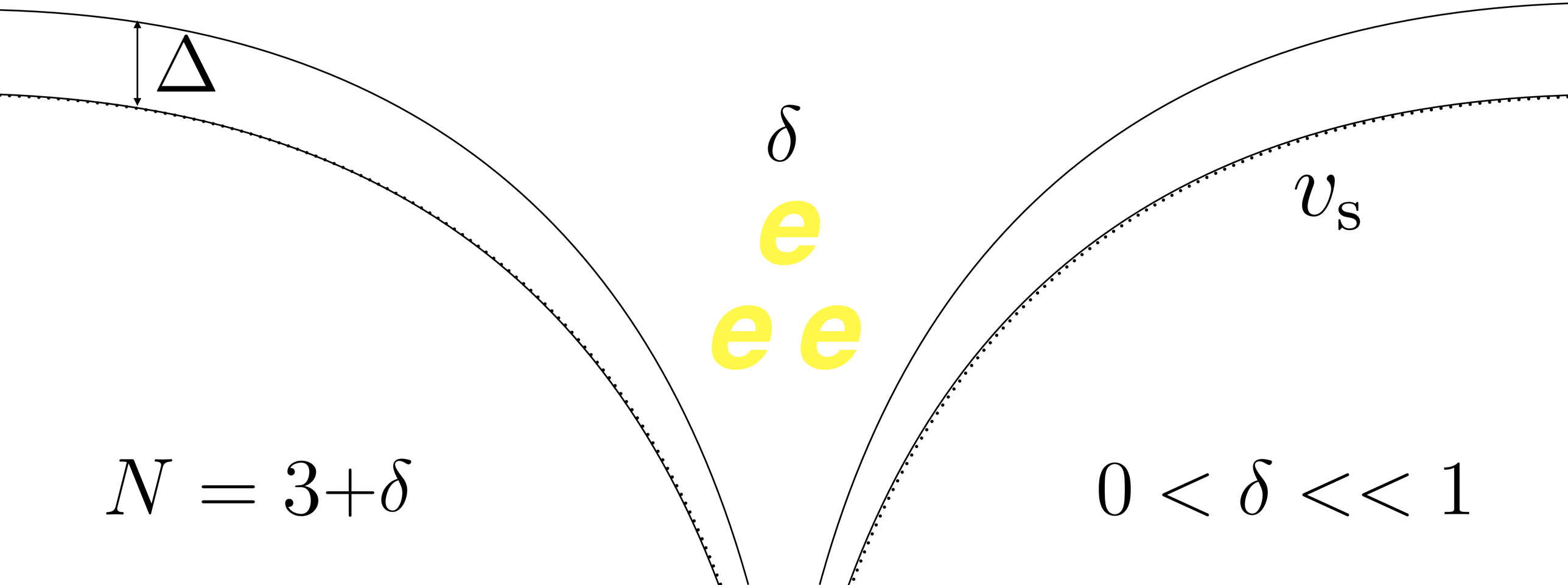
3. Next reverse-engineer the exact Kohn-Sham potential

Derivative discontinuity of an atom

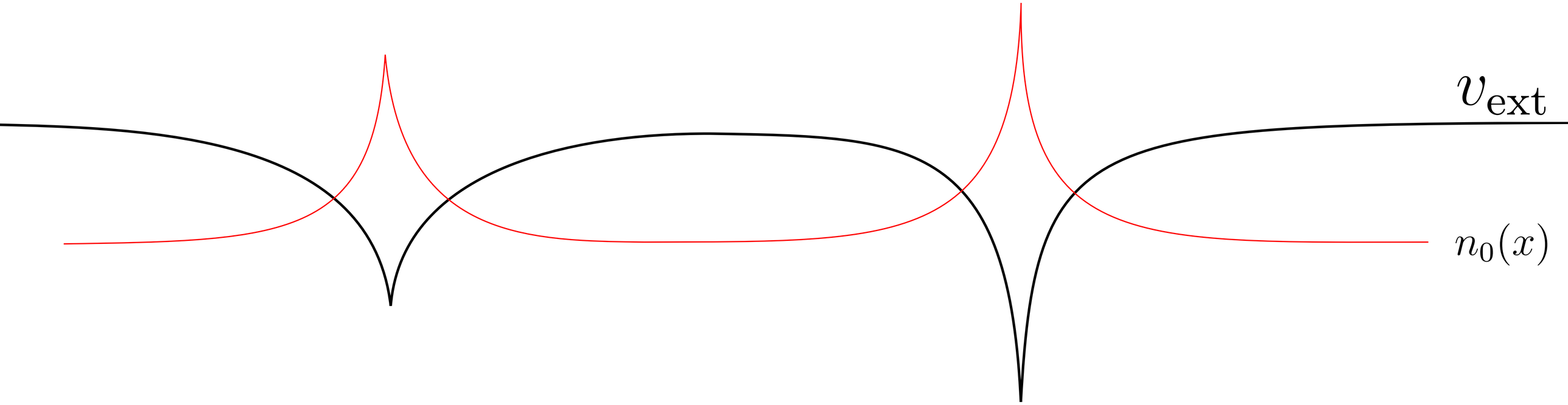


Derivative discontinuity of an atom

$$\Delta = I - A + \varepsilon^{\mathrm{ho}} - \varepsilon^{\mathrm{lu}}$$



Charge transfer excitation in a 1D molecule



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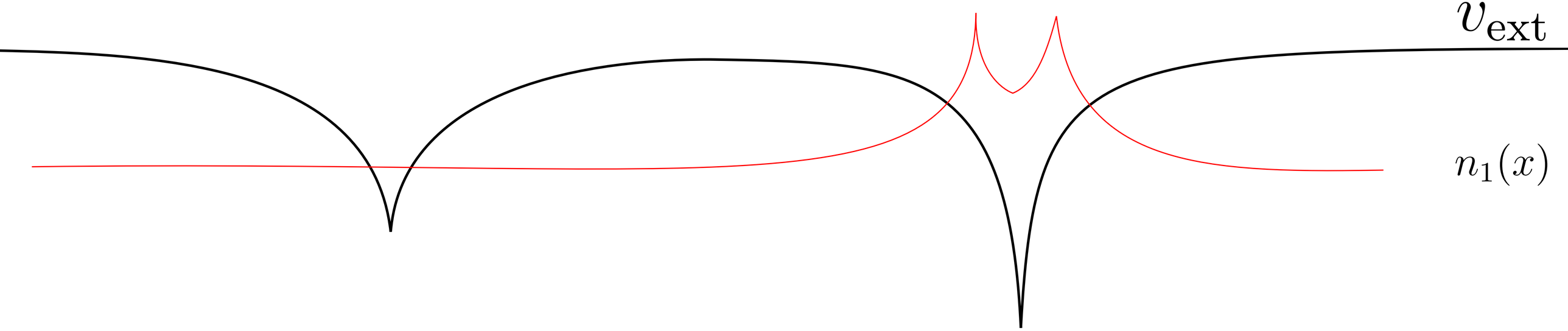

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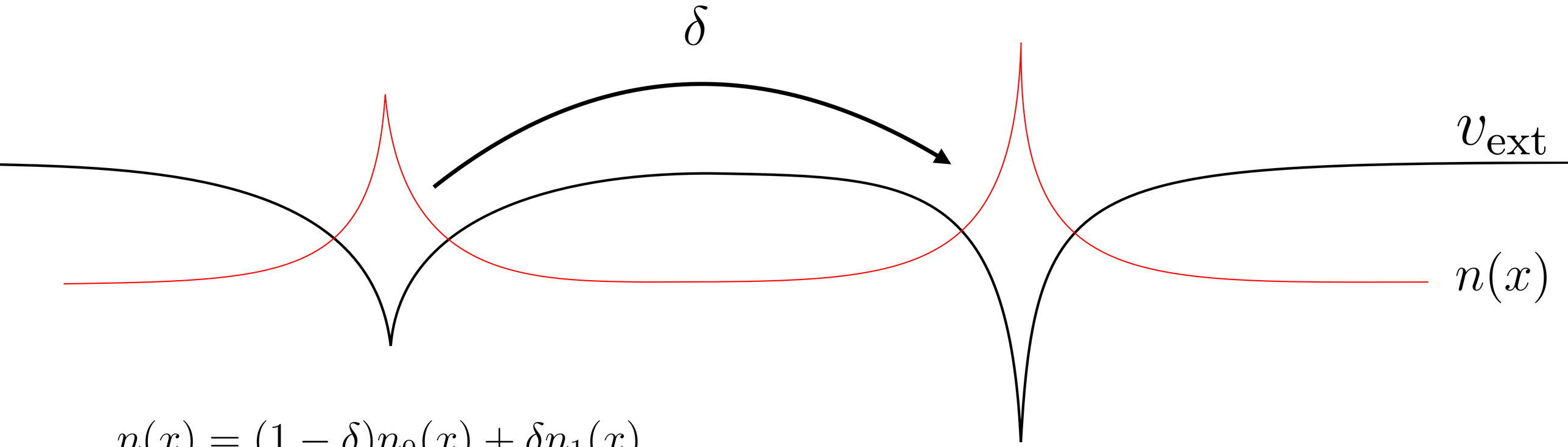
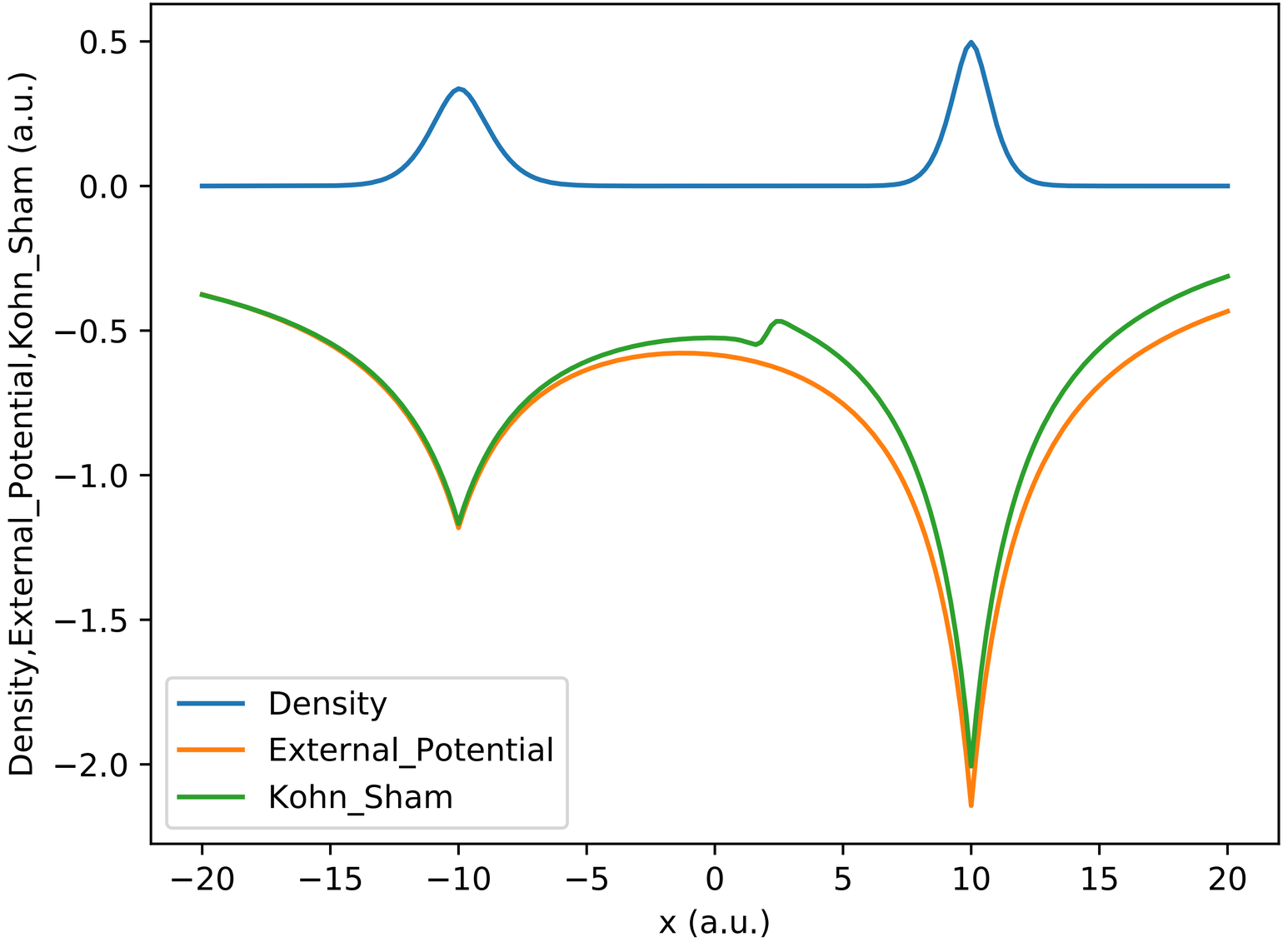


$$n(x) = (1-\delta)n_0(x) + \delta n_1(x)$$

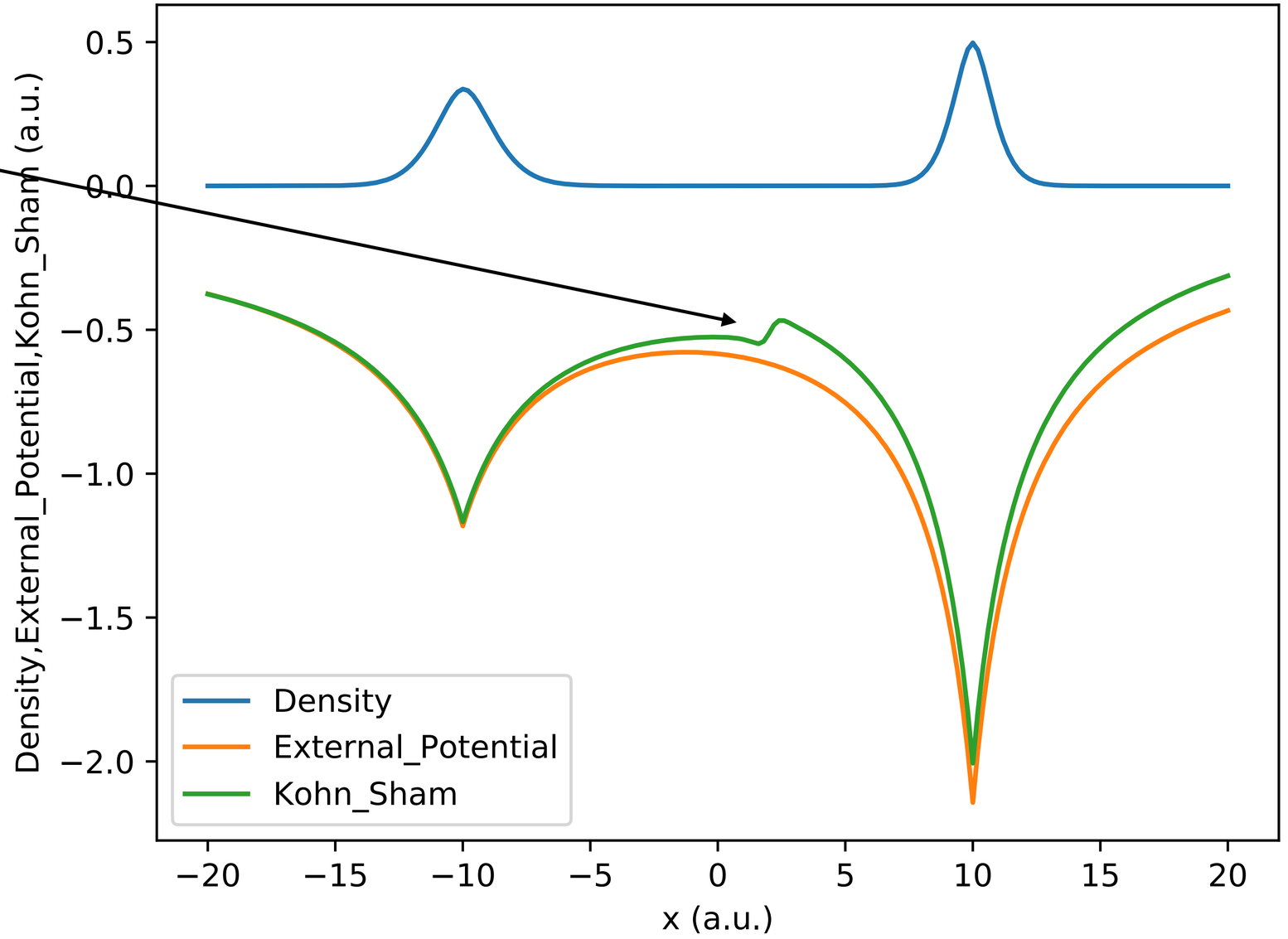
$$0 < \delta << 1$$

Ground-state 1D molecule



Ground-state 1D molecule

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



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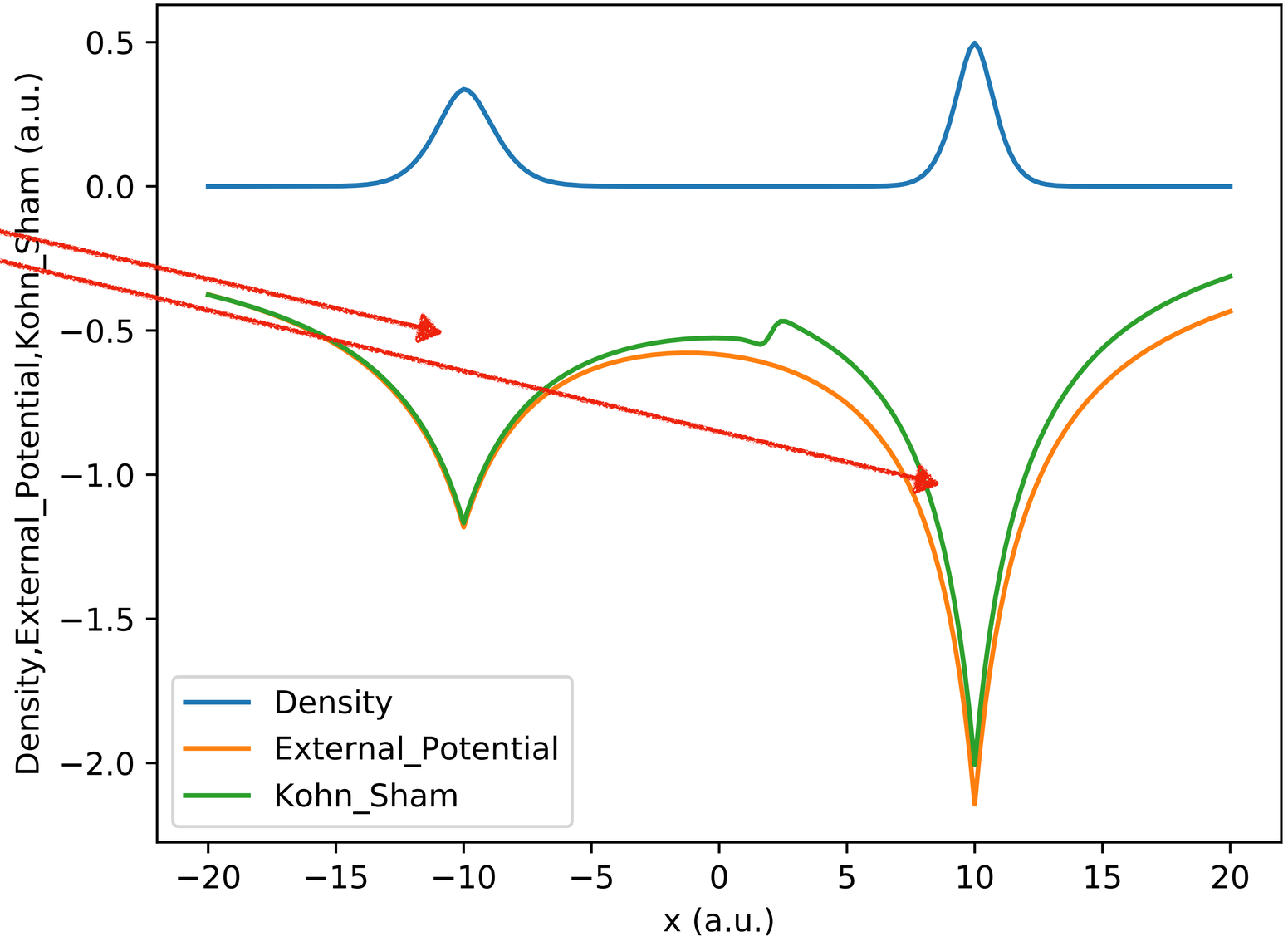
Ionisation energy



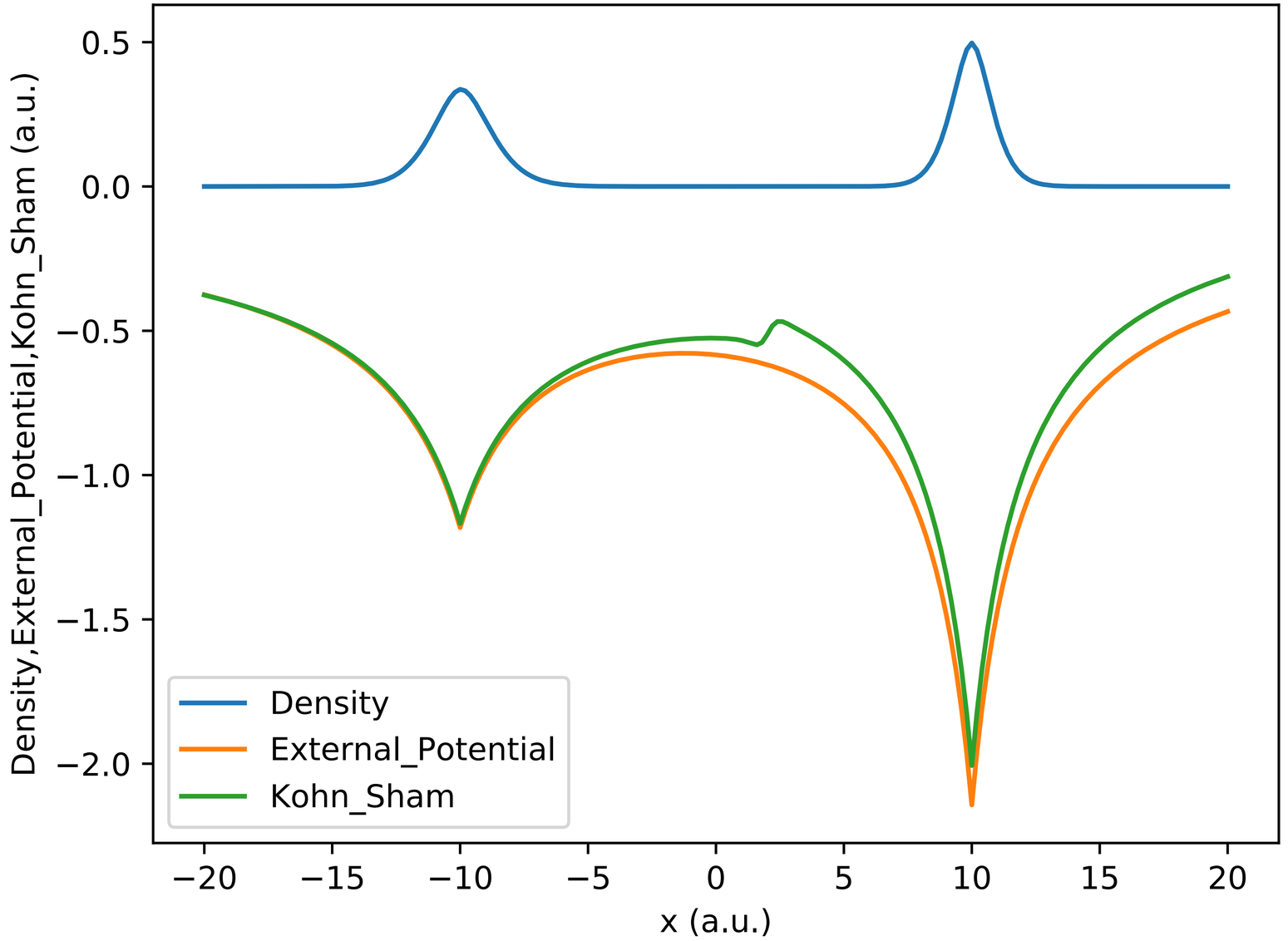
Ground-state 1D molecule

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

Kohn-Sham molecular energies

Bonded case: $\eta_R^{\mathrm{ho}} = \eta_L^{\mathrm{ho}}$

$$\Rightarrow S = I_R - I_L$$



Almbladh, C. O.; von Barth, U. In Density Functional Methods in Physics; Dreizler, R. M., da Providência, J., Eds.; NATO ASI Series; Plenum Press, 1985; Vol. 123, pp 209–231.

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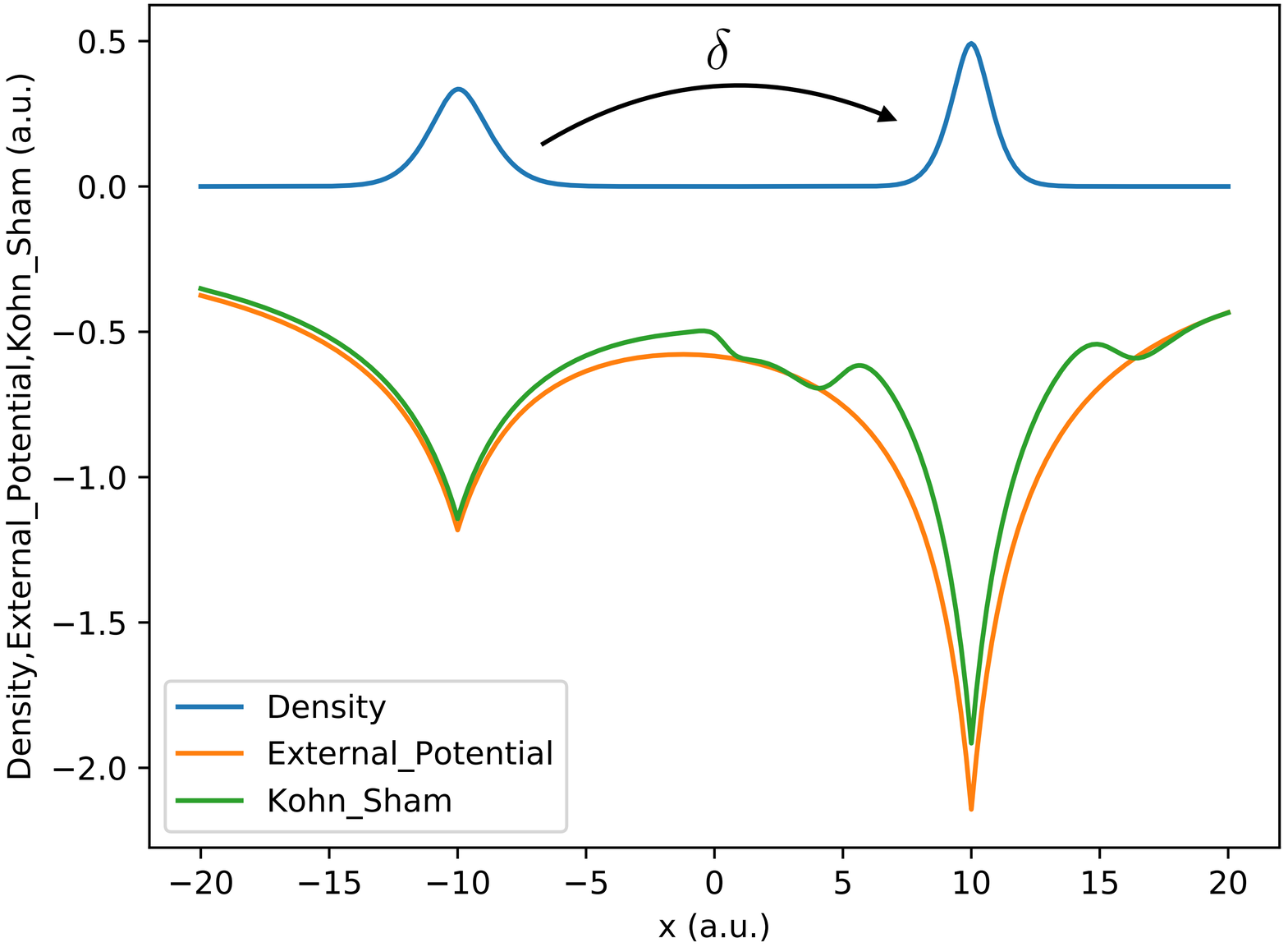

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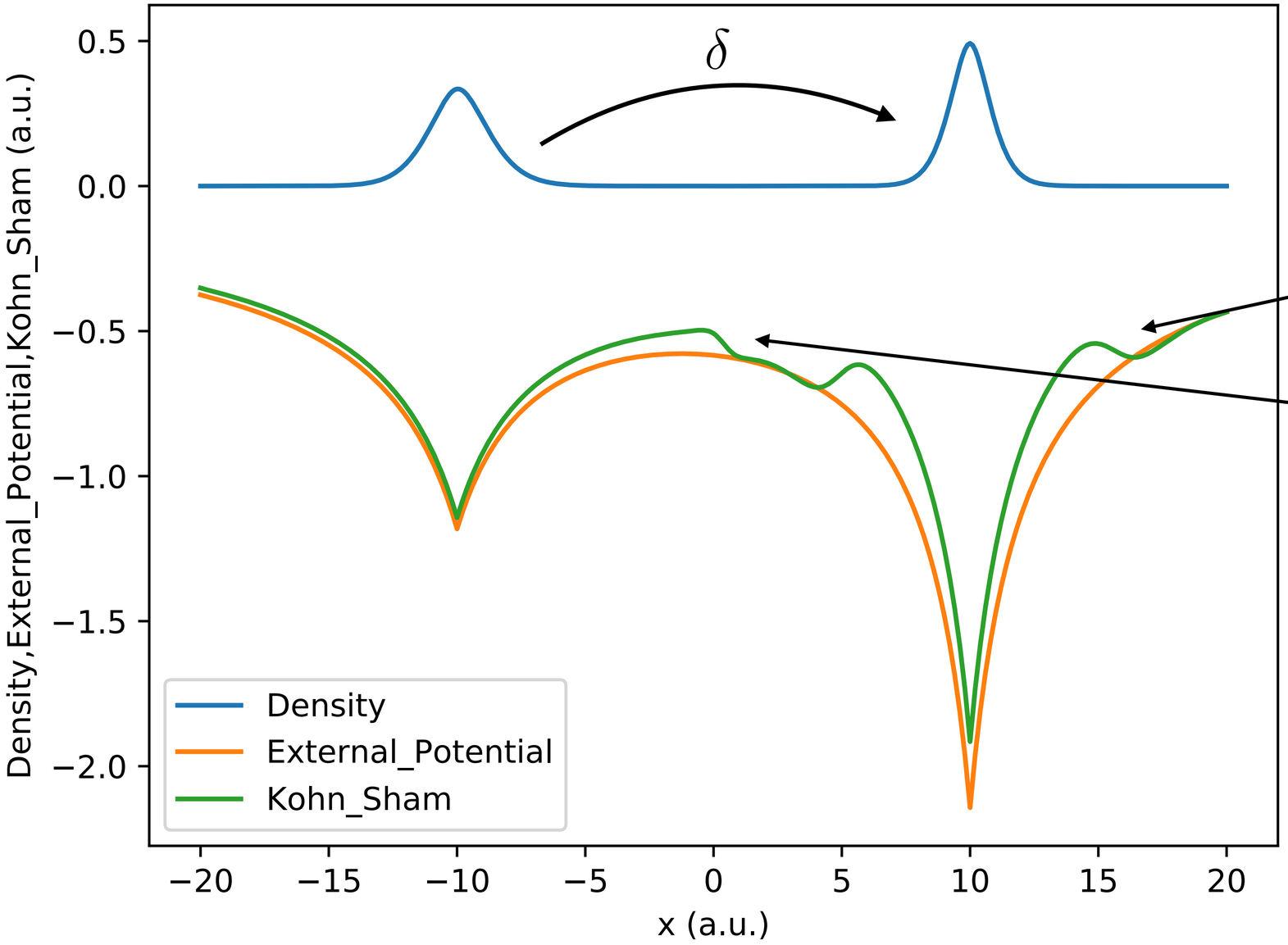

Derivative discontinuity of Atom R:

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

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

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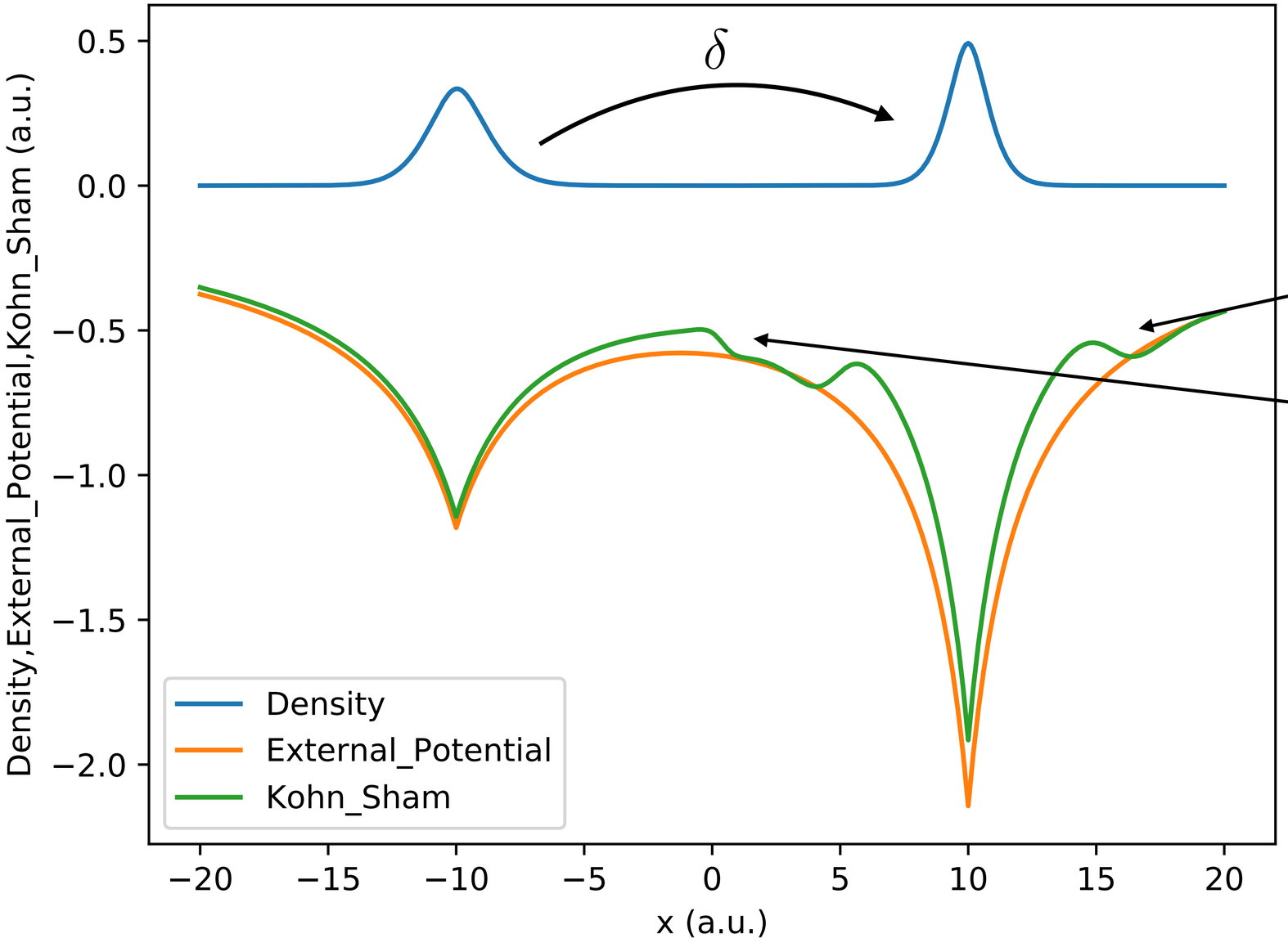

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What's this?

Charge-transfer derivative discontinuity

$$\Delta^{\mathrm{CT}}_{L\to R} = I_L - A_R + \eta^{\mathrm{ho}}_L - \eta^{\mathrm{lu}}_R$$

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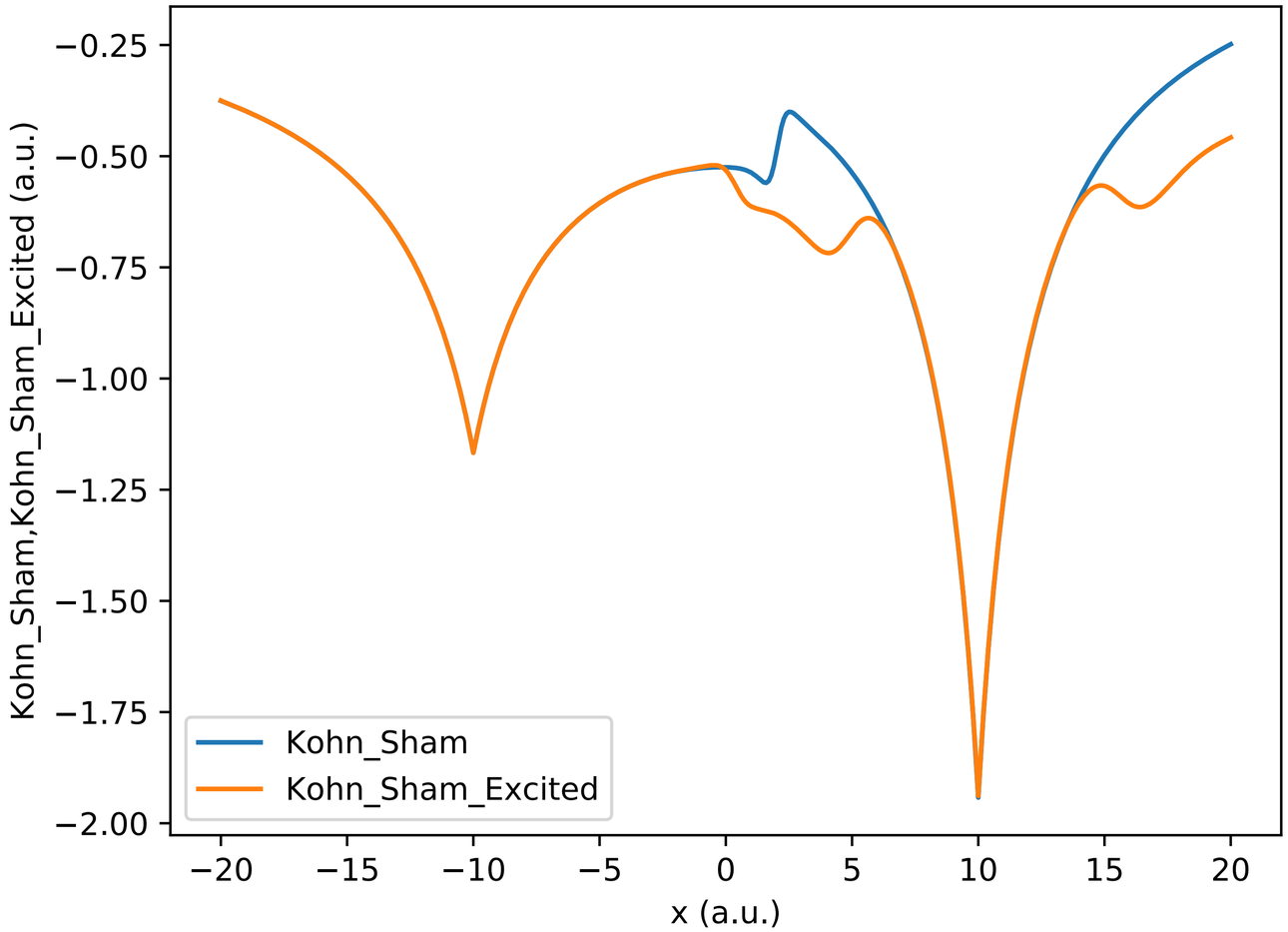
$$S = S_1 + S_2 = \Delta_R - \Delta^{\mathrm{CT}}_{L\to R} = I_R - I_L + \eta^{\mathrm{ho}}_R - \eta^{\mathrm{ho}}_L$$

Charge-transfer derivative discontinuity



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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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