How is the derivative discontinuity related to steps in the exact Kohn-Sham potential?

Matt Hodgson, Eli Kraisler, Axel Schild, and Hardy Gross

Max Planck Institute of Microstructure physics

YRM 2017

MAX-PLANCK-GESELLSCHAFT

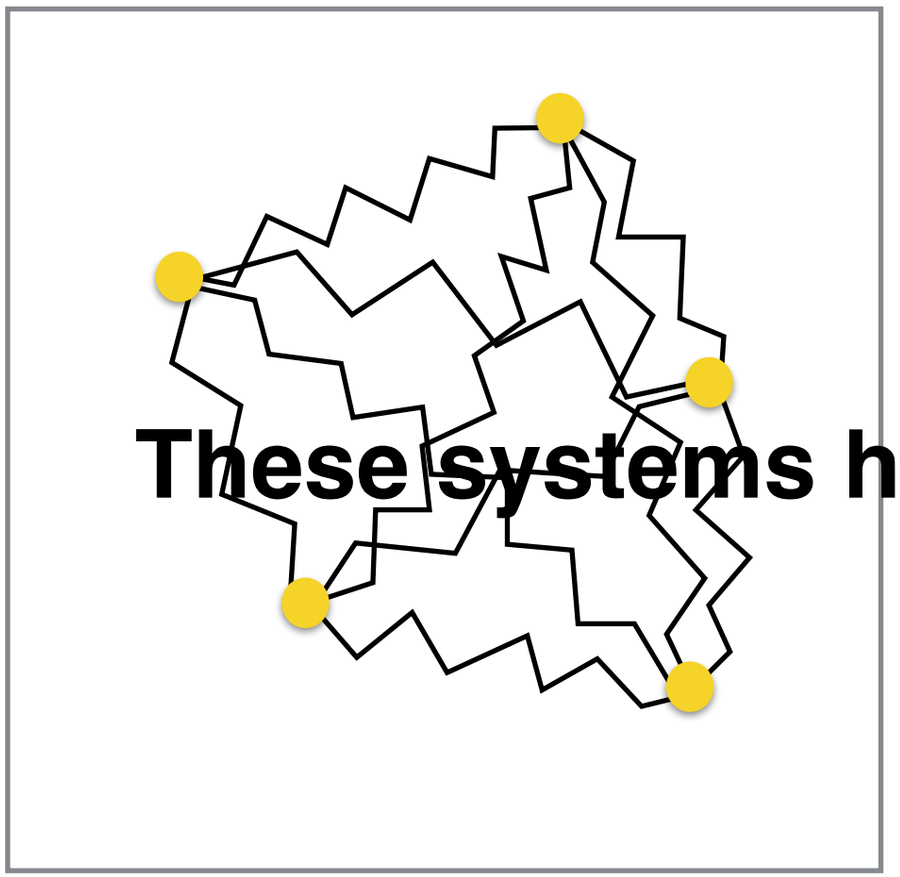
ETSF
European Theoretical Spectroscopy Facility

Outline

- What is Kohn-Sham density-functional theory?
- What is the derivative discontinuity?
- Why do steps form in the exact Kohn-Sham potential?
- How are these two features of the exact potential related?
- Conclusions

Many-body quantum mechanics

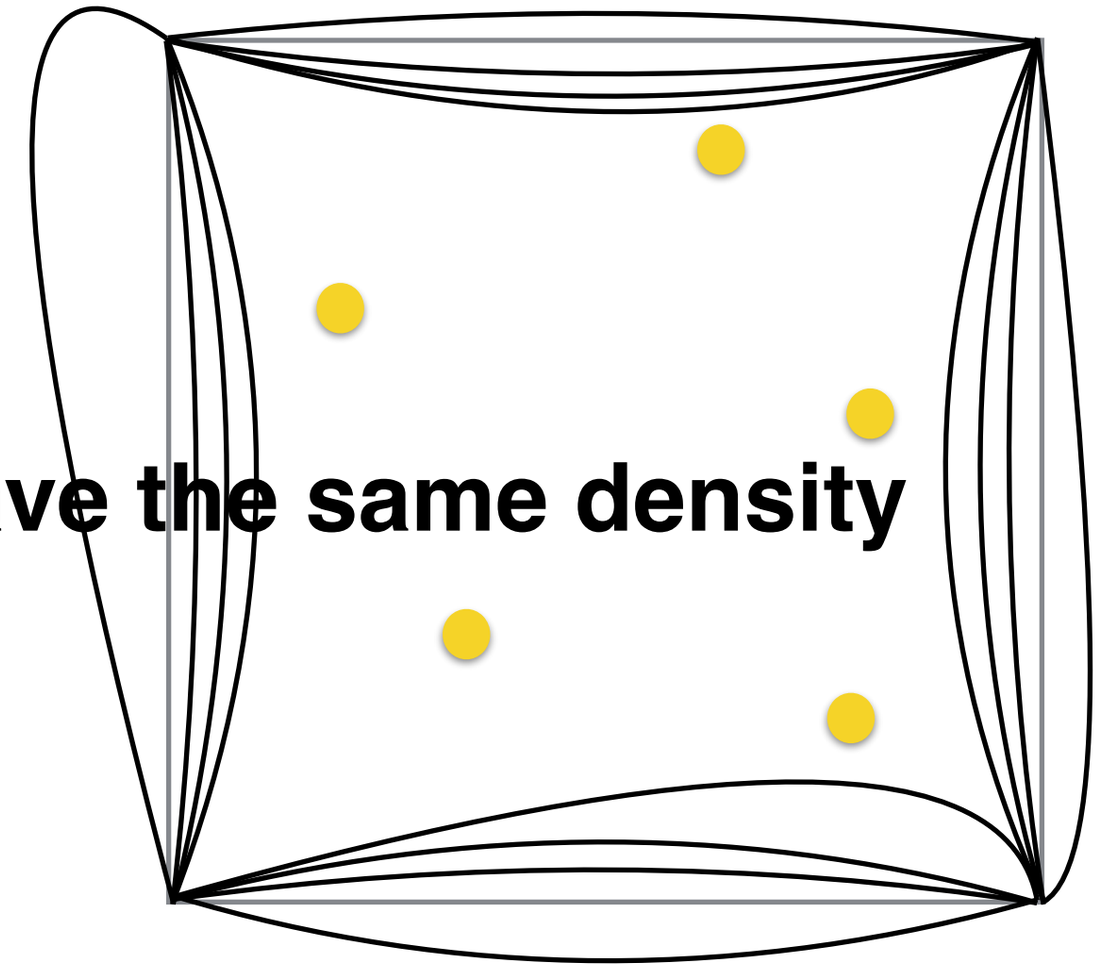
No. interactions = 10



Computational Scaling = k^4

Density-functional theory

No. interactions = 0



Computational Scaling = k^3

These systems have the same density

Kohn and Sham

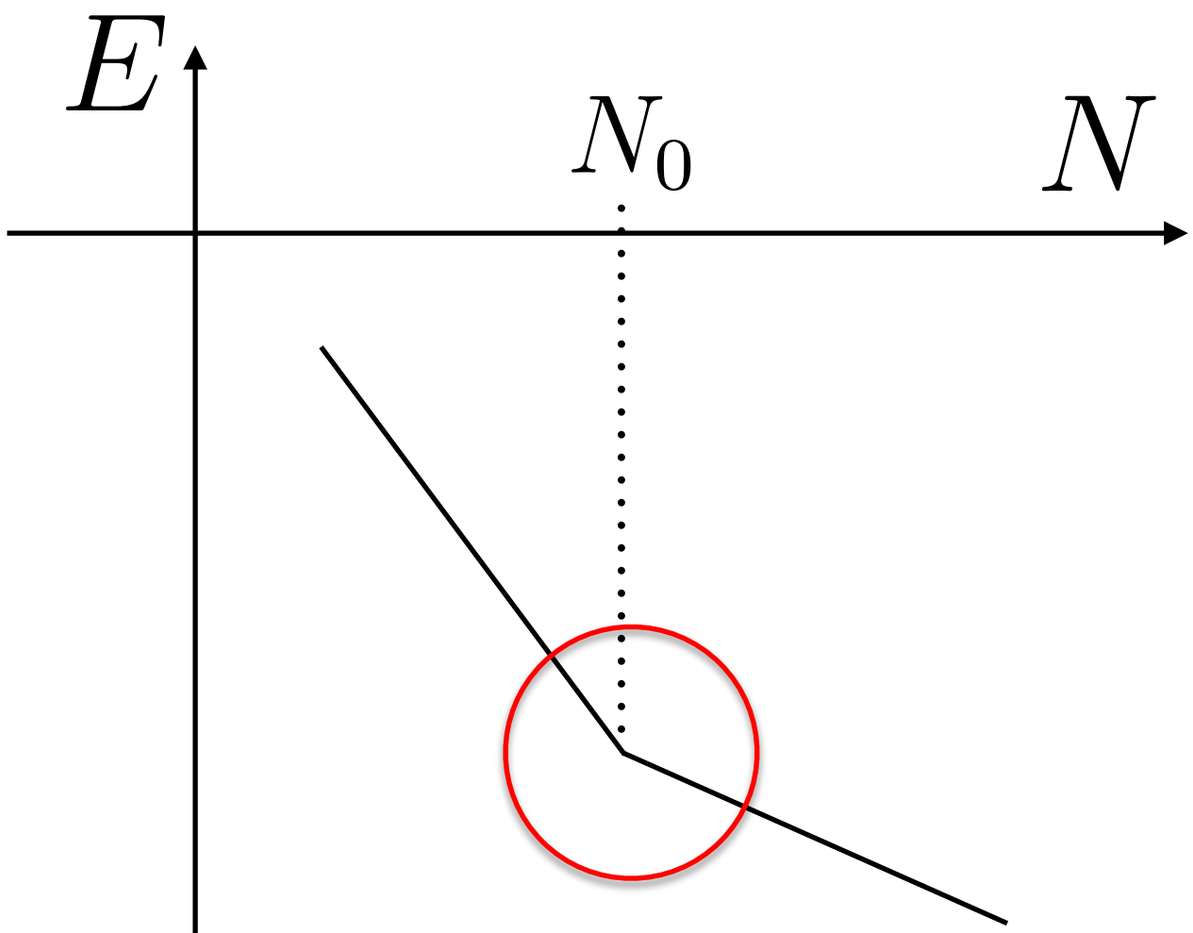
Kohn-Sham equations:

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{s}}[n](\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

Kohn-Sham density:

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

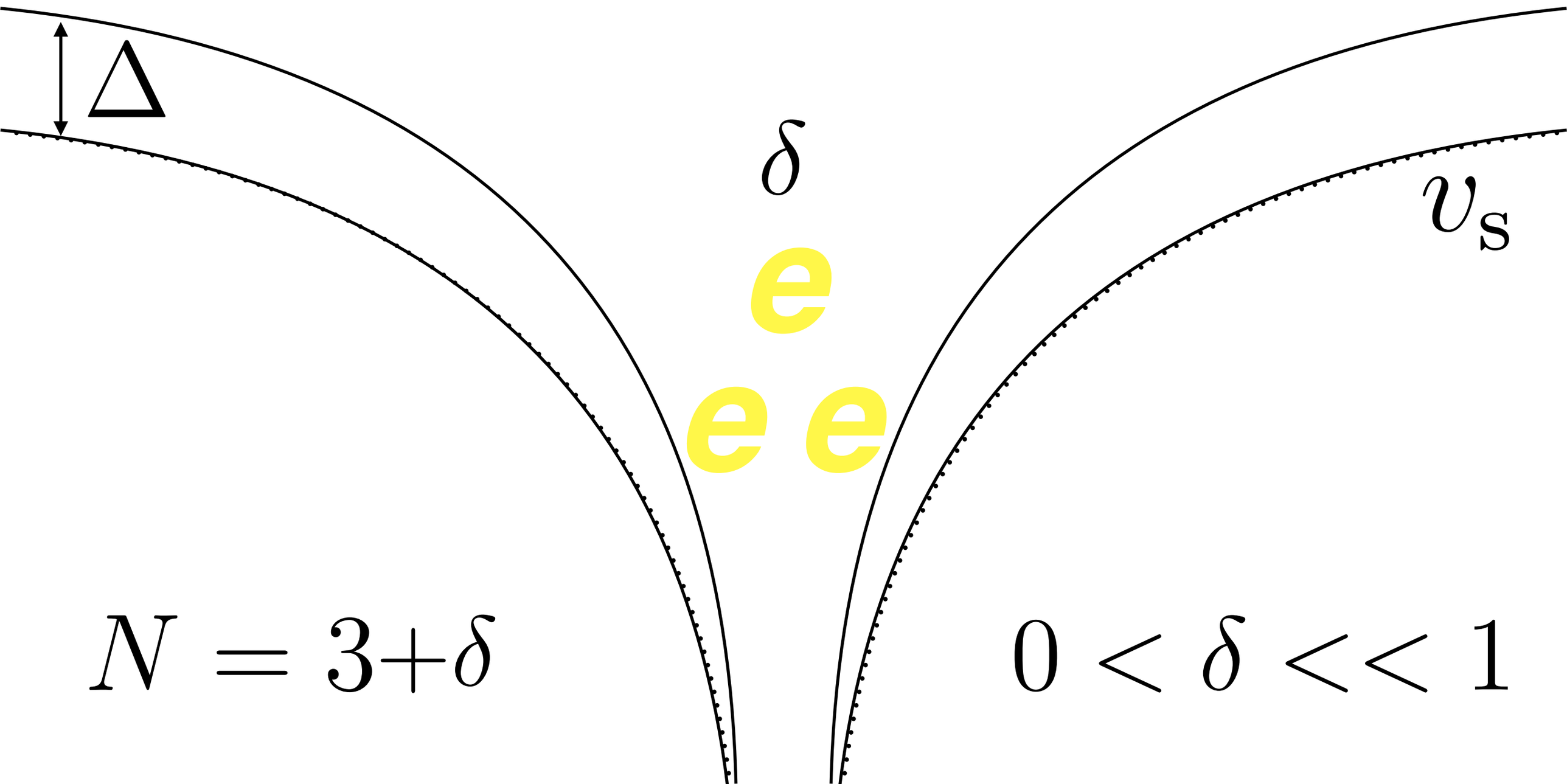
What is the derivative discontinuity?



$$E_g = \left(\frac{\partial E}{\partial N}\right)_{N=N_0+\delta} - \left(\frac{\partial E}{\partial N}\right)_{N=N_0-\delta} = \varepsilon_g + \Delta$$

Single atom

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



iDEA

interacting Dynamic Electrons Approach

1) We calculate the fully correlated many-body wavefunction for two or three electrons for any system we choose

2) We compute the exact electron density, then reverse engineer it to get the exact Kohn-Sham potential

Please note:

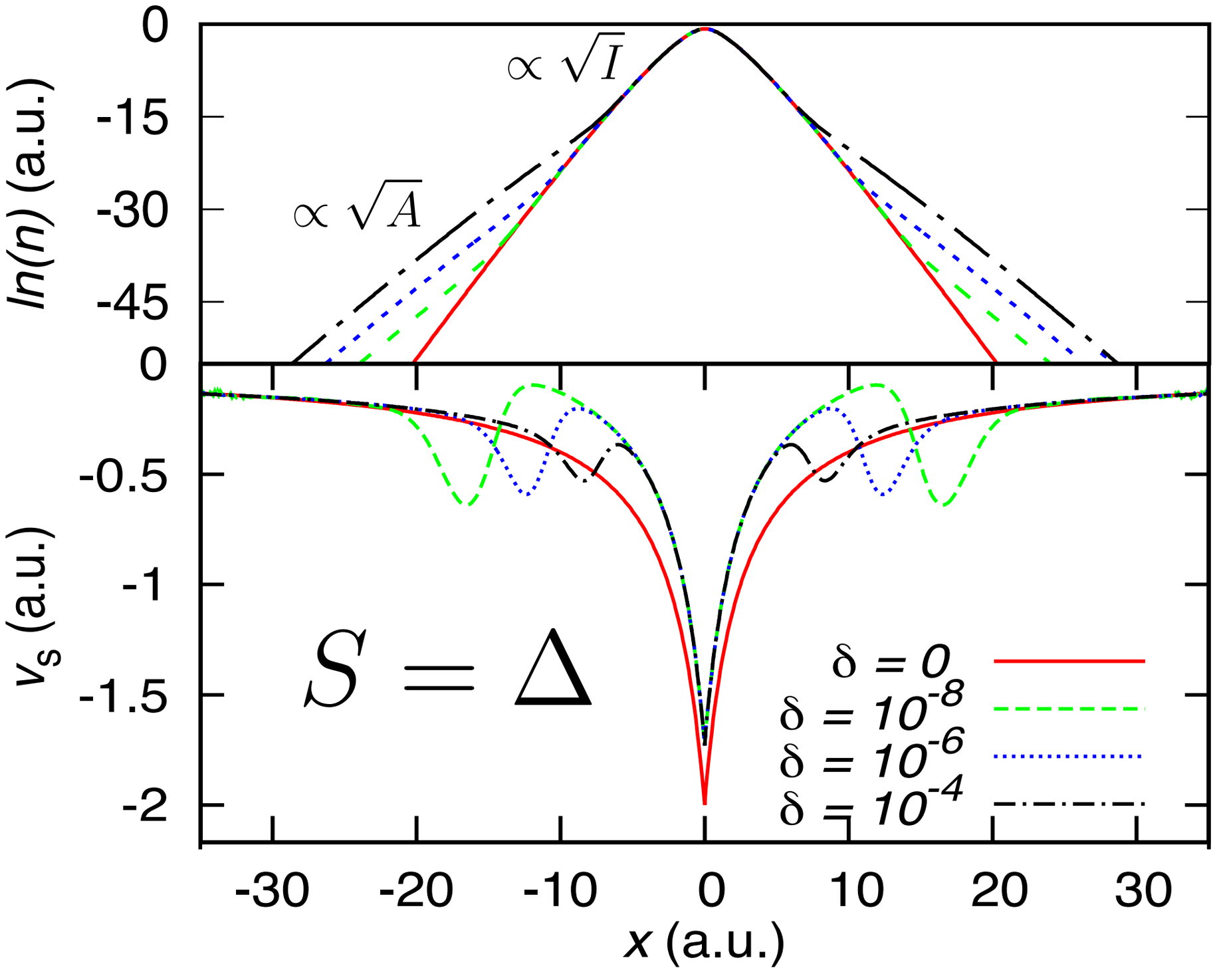
Results are numerically very accurate for the import low density regions

Our electrons are spinless, hence each electron occupies a distinct Kohn-Sham orbital

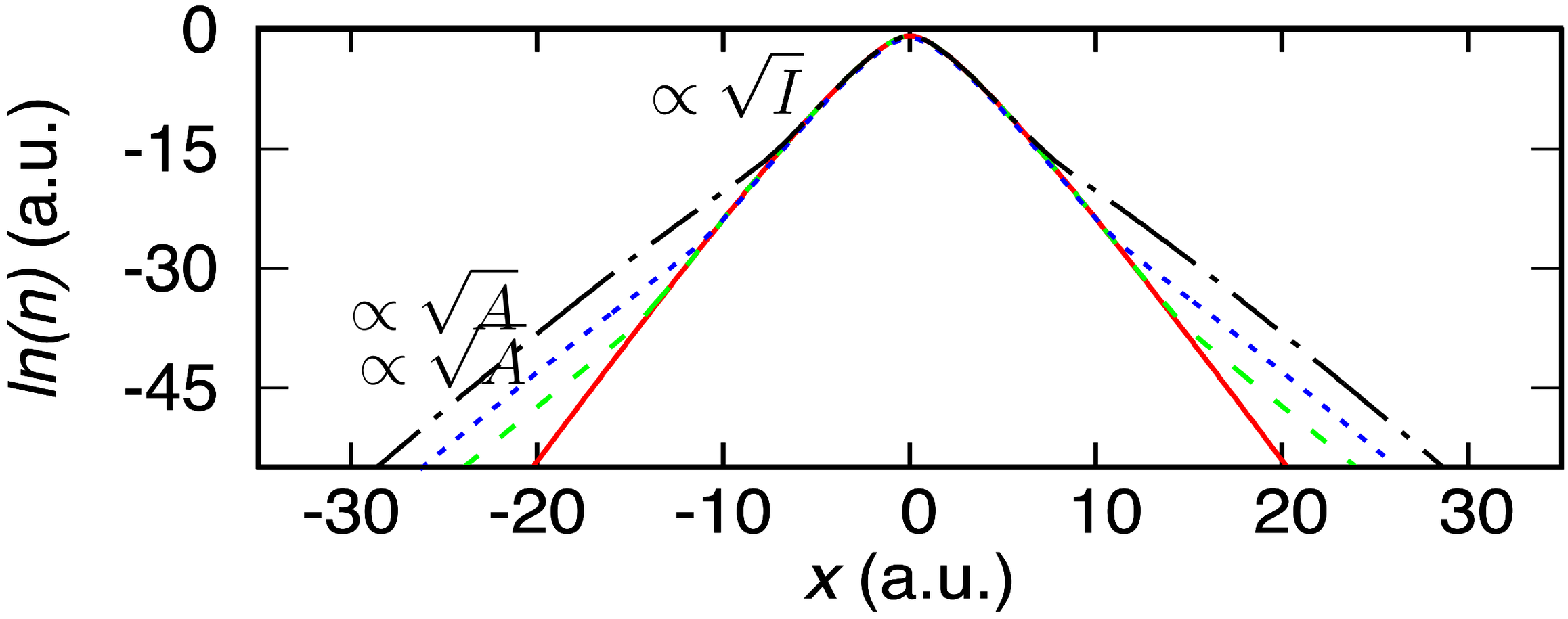
Our systems are one-dimensional

We are currently running CI calculations of 'real', 3D atoms/molecules; the results agree with our model systems using iDEA. Although, the CI calculations are far more computationally taxing

Exact Kohn-Sham potential



Numerical example



$$N = 1 + \delta$$

$\delta = 0$

$\delta = 10^{-8}$

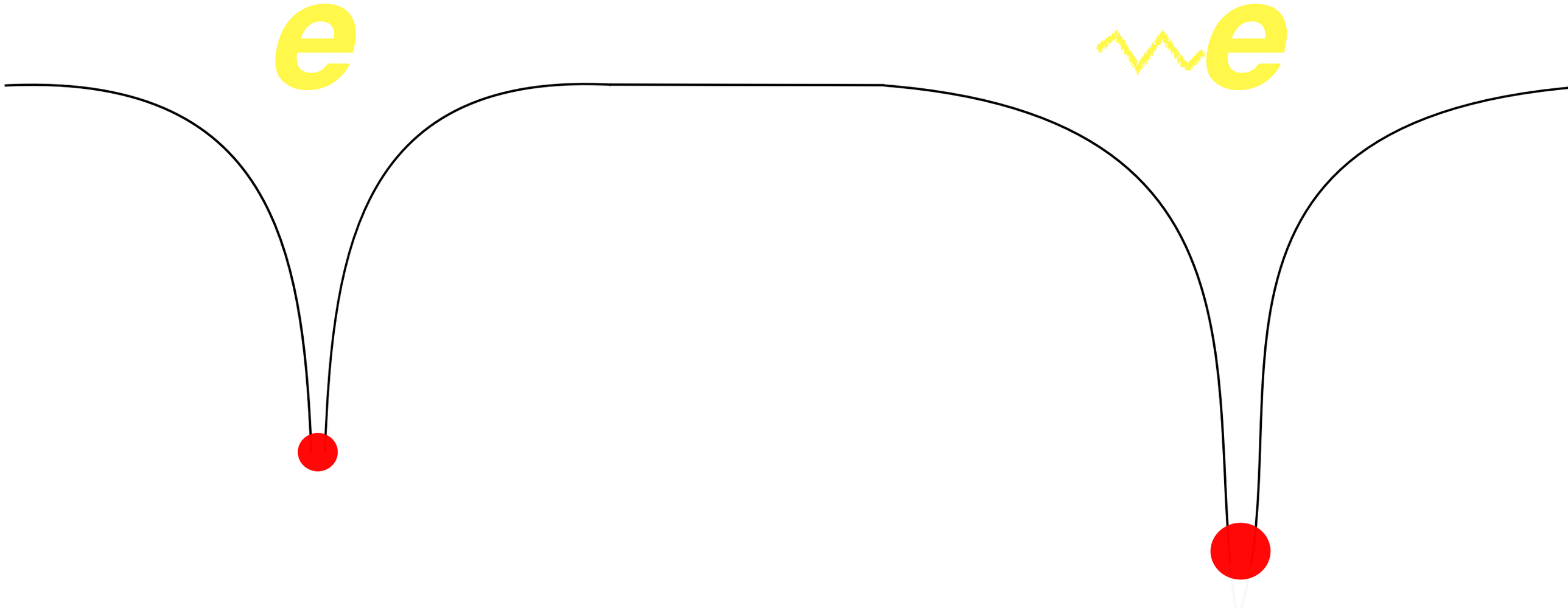
$\delta = 10^{-6}$

$\delta = 10^{-4}$

Why do steps form in the Kohn-Sham potential?

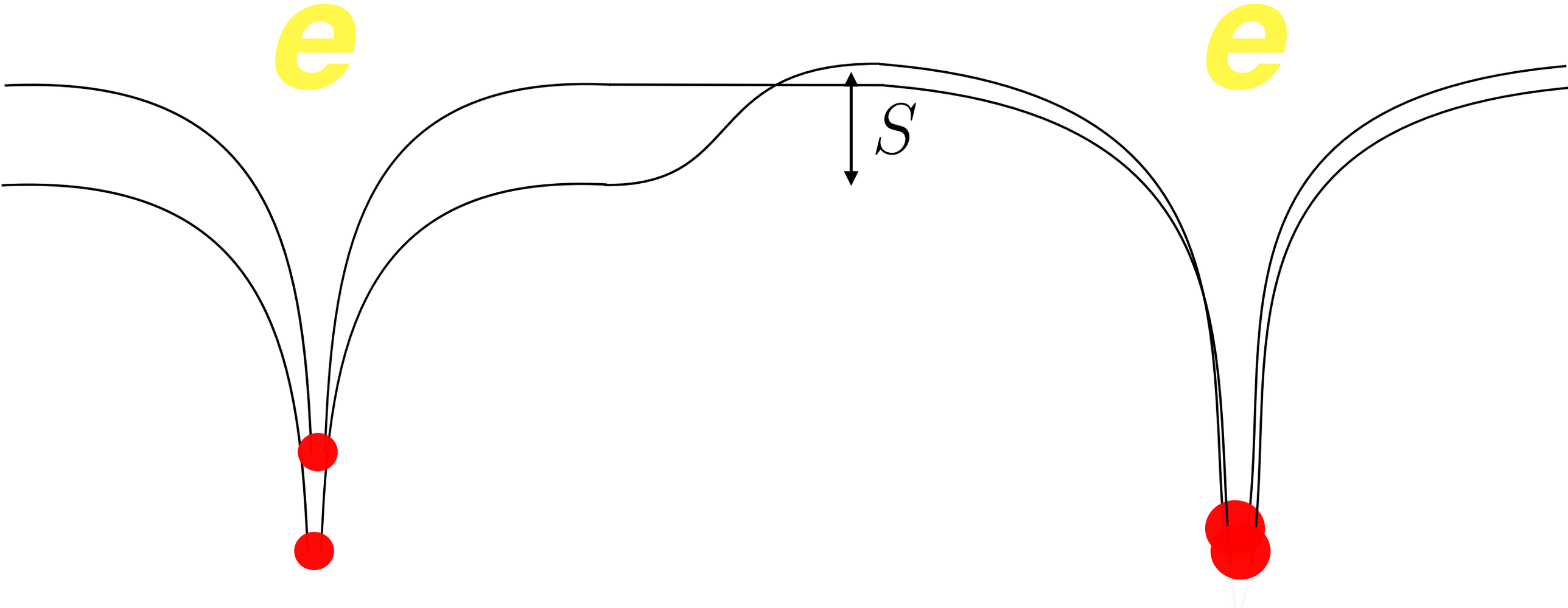
Diatomic molecule

Many-electron scenario



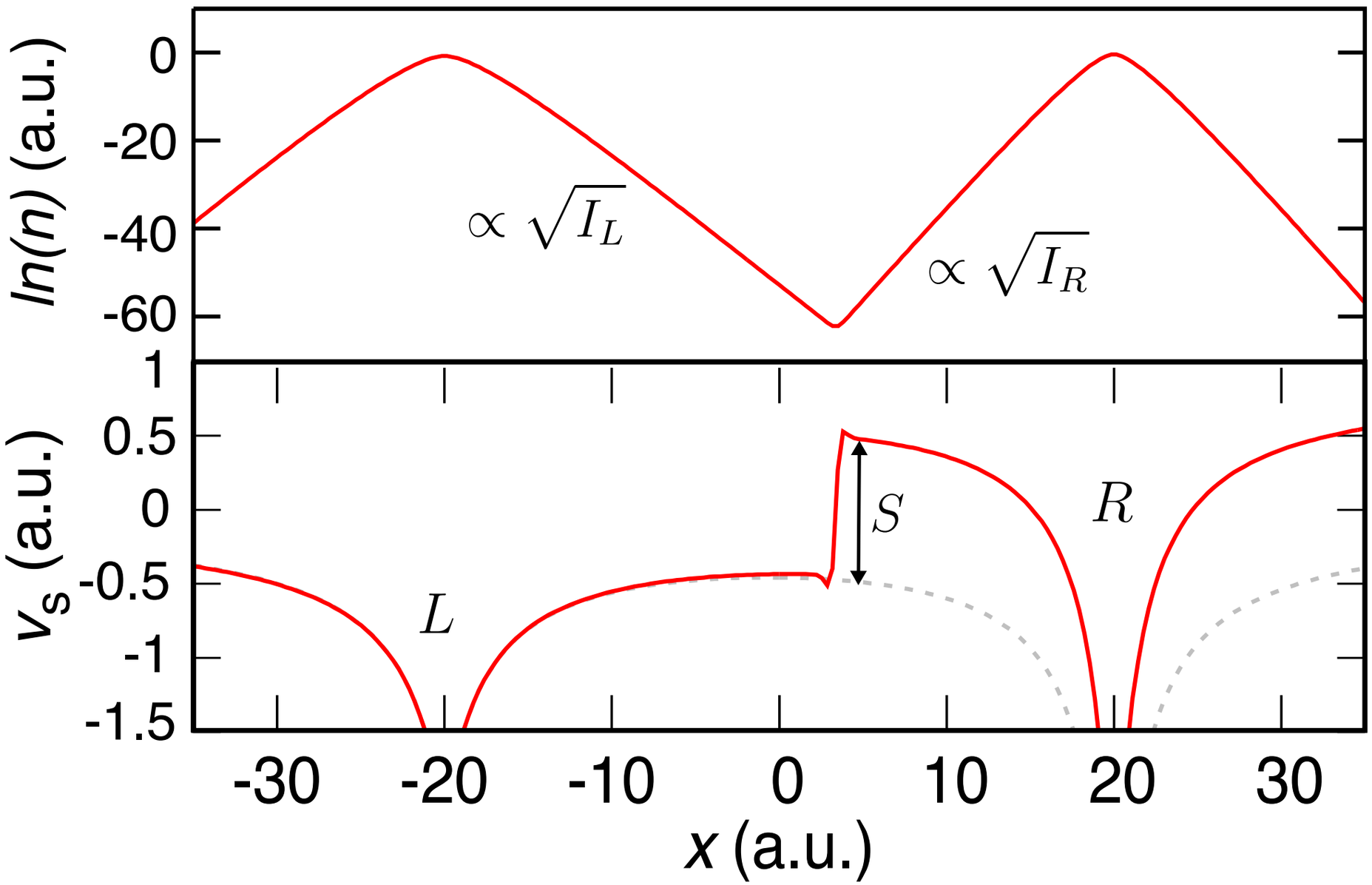
Diatomic molecule

Kohn-Sham scenario



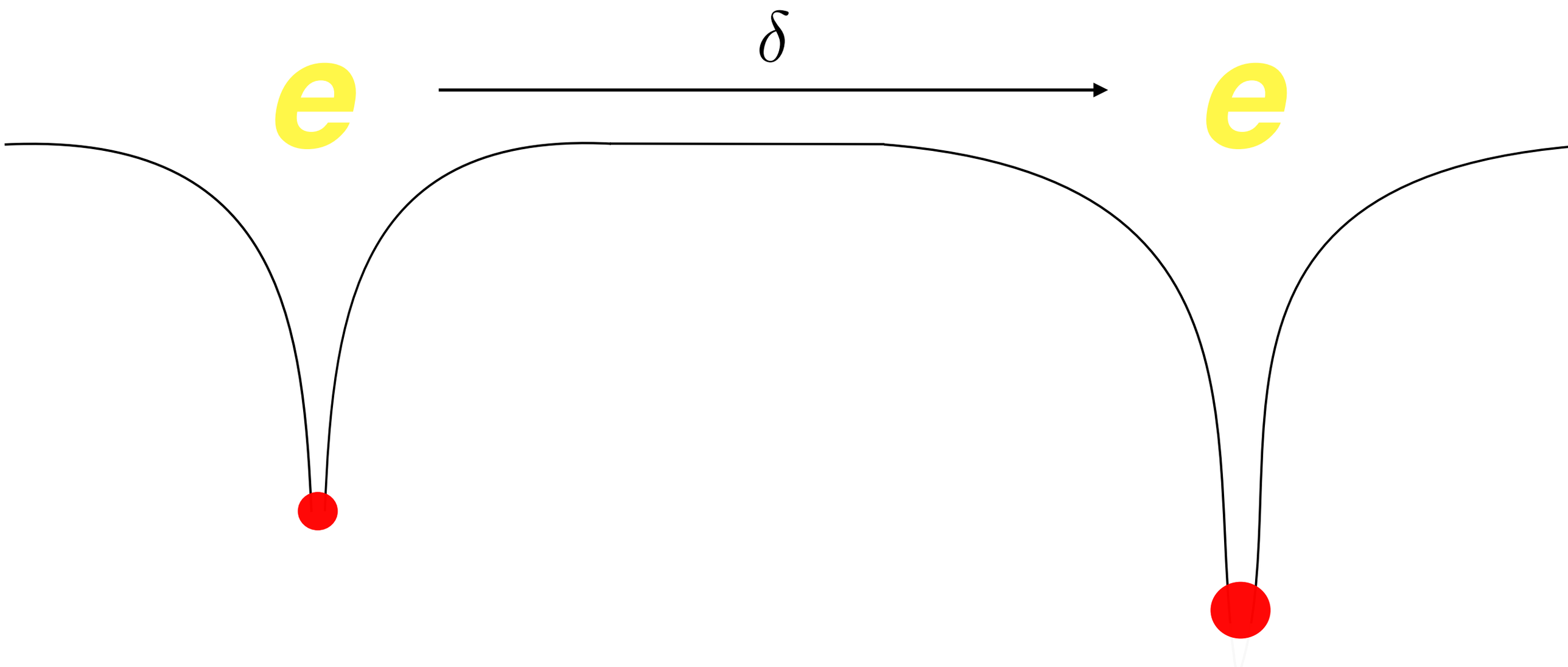
Numerical example

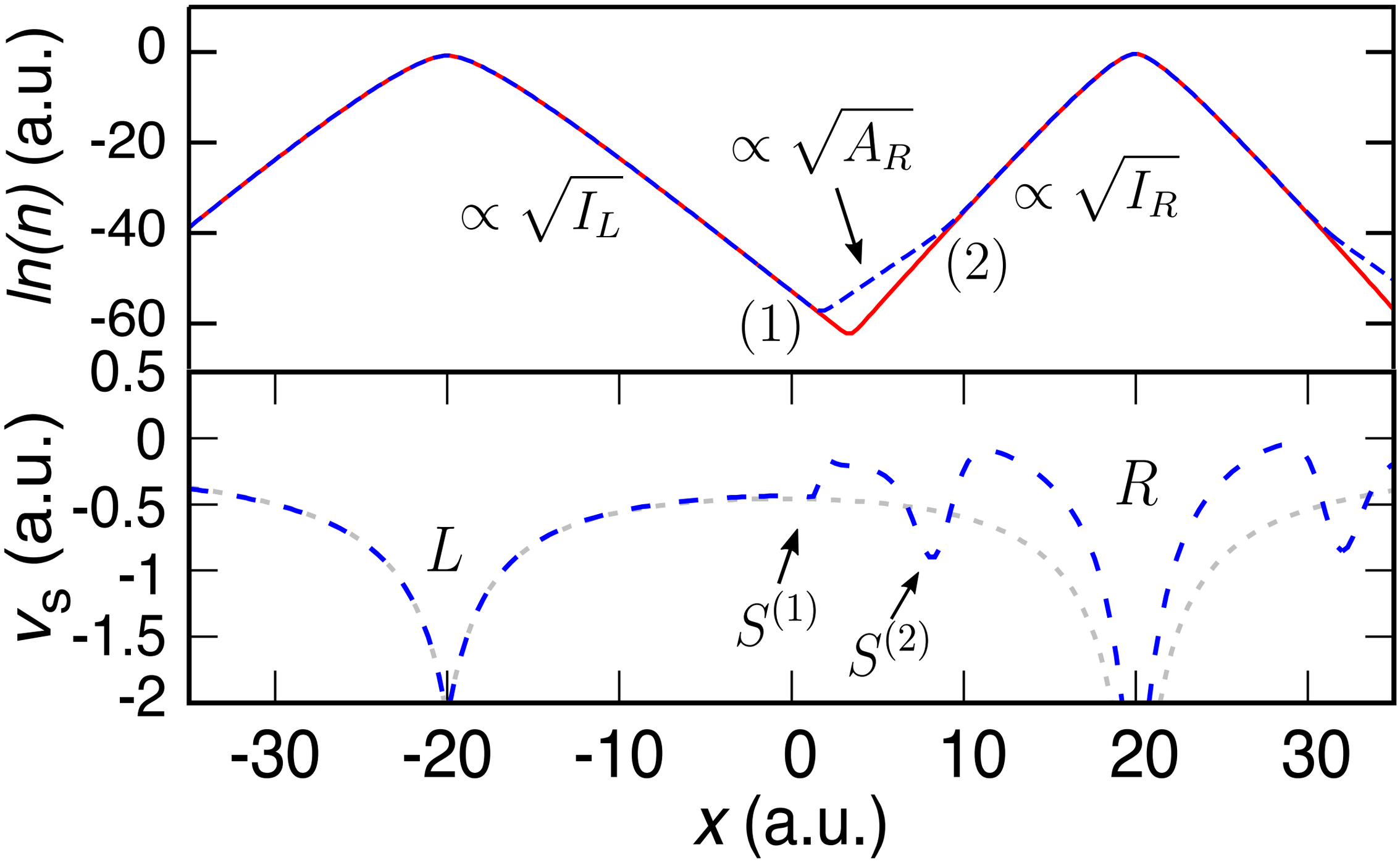
$$S = I_R - I_L + \varepsilon_R^{\mathrm{ho}} - \varepsilon_L^{\mathrm{ho}}$$



Charge transfer

Question: what happens when we transfer a very small amount of charge from one atom to the other?





$$S^{(2)} = I_R - A_R + \varepsilon_R^{\mathrm{ho}} - \varepsilon_R^{\mathrm{lu}} = \Delta_R$$

$$S^{(1)} = -(I_L - A_R + \varepsilon_L^{\mathrm{ho}} - \varepsilon_R^{\mathrm{lu}}) = -\Delta_{L\to R}$$

$$S^{(2)} = I_R - A_R + \varepsilon_R^{\mathrm{ho}} - \varepsilon_R^{\mathrm{lu}} = \Delta_R$$

$$S^{(1)} = -(I_L - A_R + \varepsilon_L^{\mathrm{ho}} - \varepsilon_R^{\mathrm{lu}}) = -\Delta_{L\to R}$$

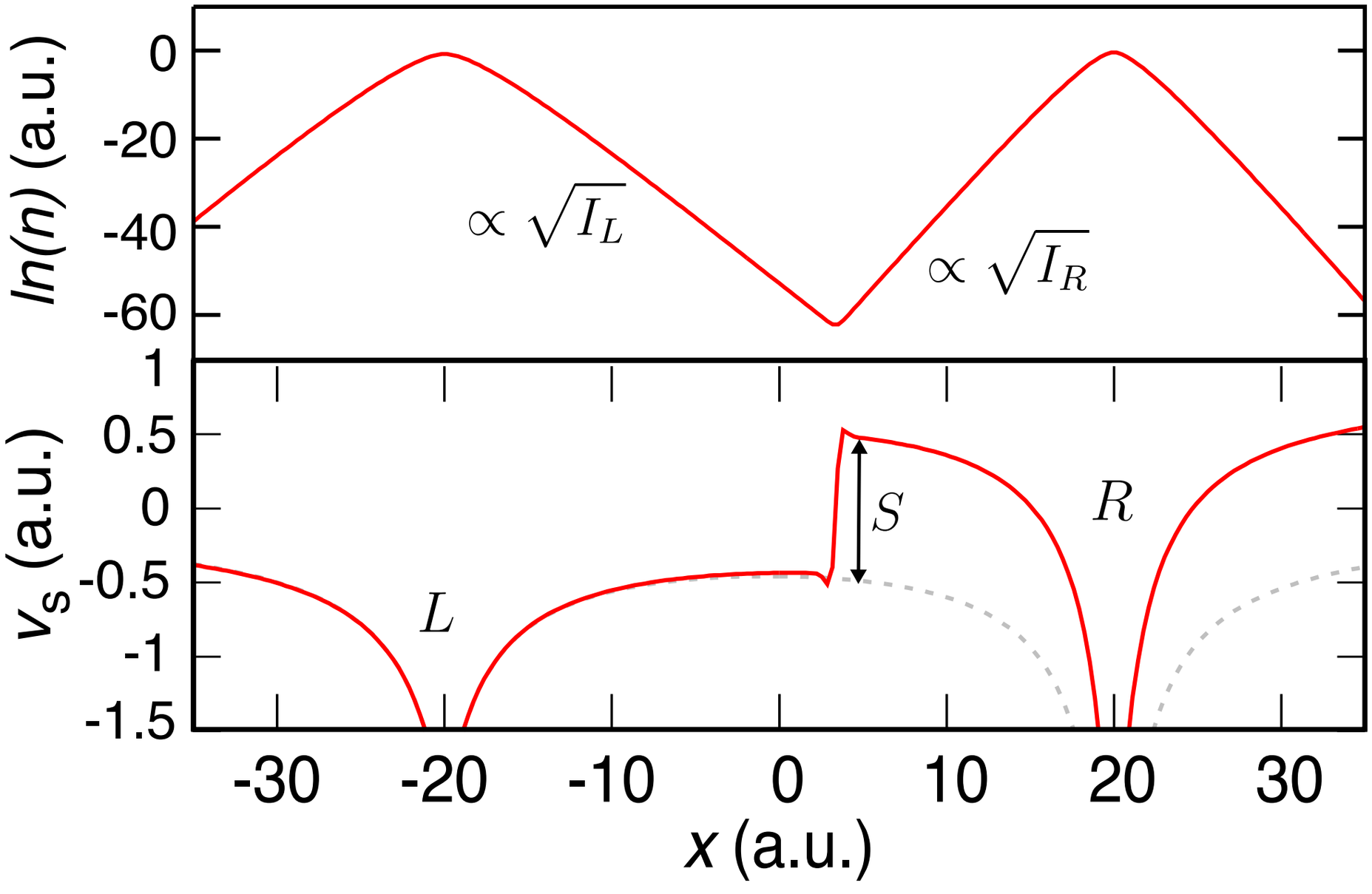
‘Charge transfer derivative discontinuity’

$$S^{(1)} + S^{(2)} = \Delta_R - \Delta_{L\to R} = I_R - I_L + \varepsilon_R^{\mathrm{ho}} - \varepsilon_L^{\mathrm{ho}}$$

$$S = I_R - I_L + \varepsilon_R^{\mathrm{ho}} - \varepsilon_L^{\mathrm{ho}}$$

Equilibrium

- The two steps from before form at the same point in the electron density, hence only one step is present

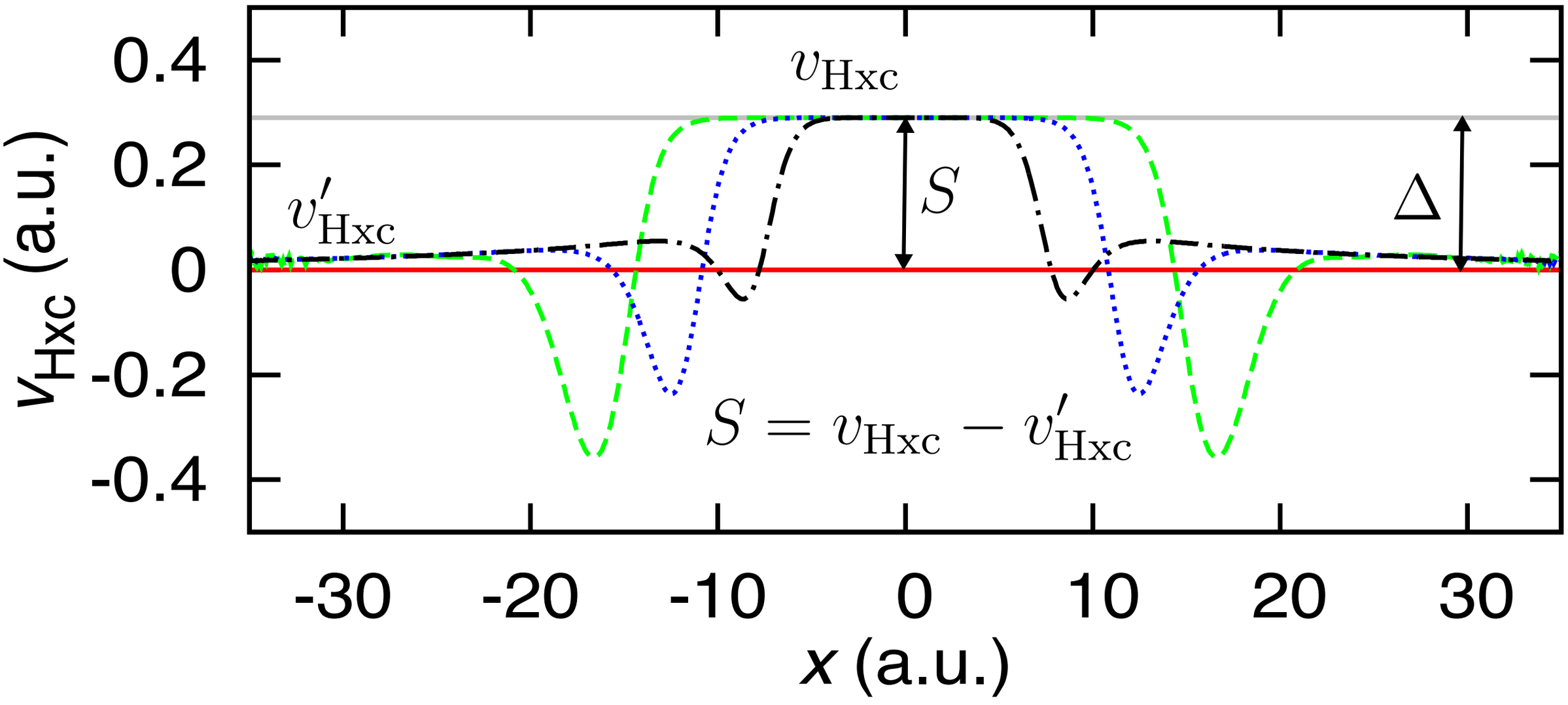


Conclusions

- These two features of the exact Kohn-Sham potential (derivative discontinuity and steps) are related
- We have a new quantity: the charge-transfer derivative discontinuity
- If the charge transfer derivative discontinuity is present in the Kohn-Sham potential, then the atoms are bonded

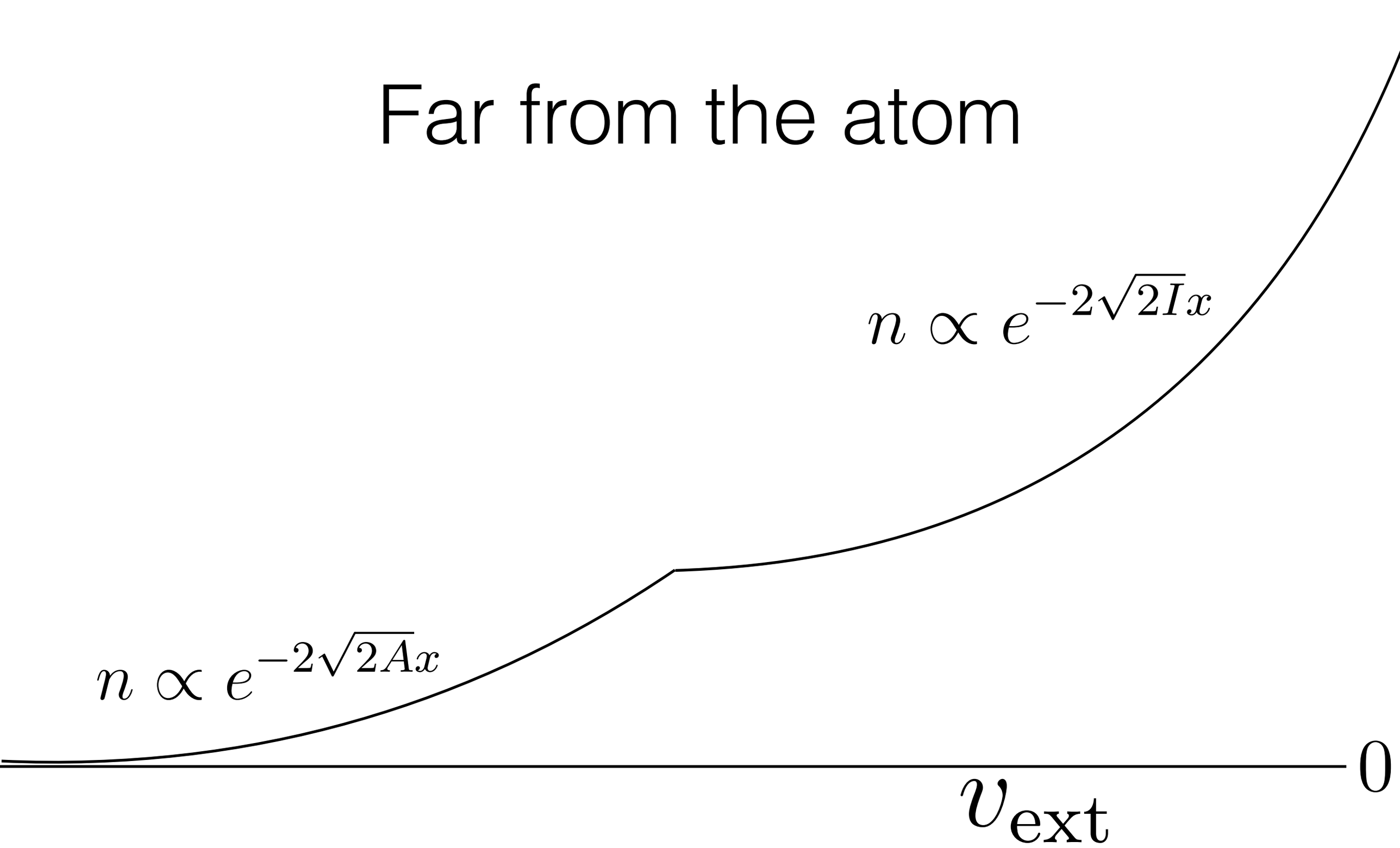
Extra slides

Exact Hartree-exchange-correlation potential



$$S = \Delta$$

Far from the atom



Kohn-Sham perspective

$$n \propto e^{-2\sqrt{2(v-\varepsilon^{\mathrm{ho}})}x} = e^{-2\sqrt{2I}x}$$

$$n \propto e^{-2\sqrt{2(v'-\varepsilon^{\mathrm{lu}})}x} = e^{-2\sqrt{2A}x}$$

0

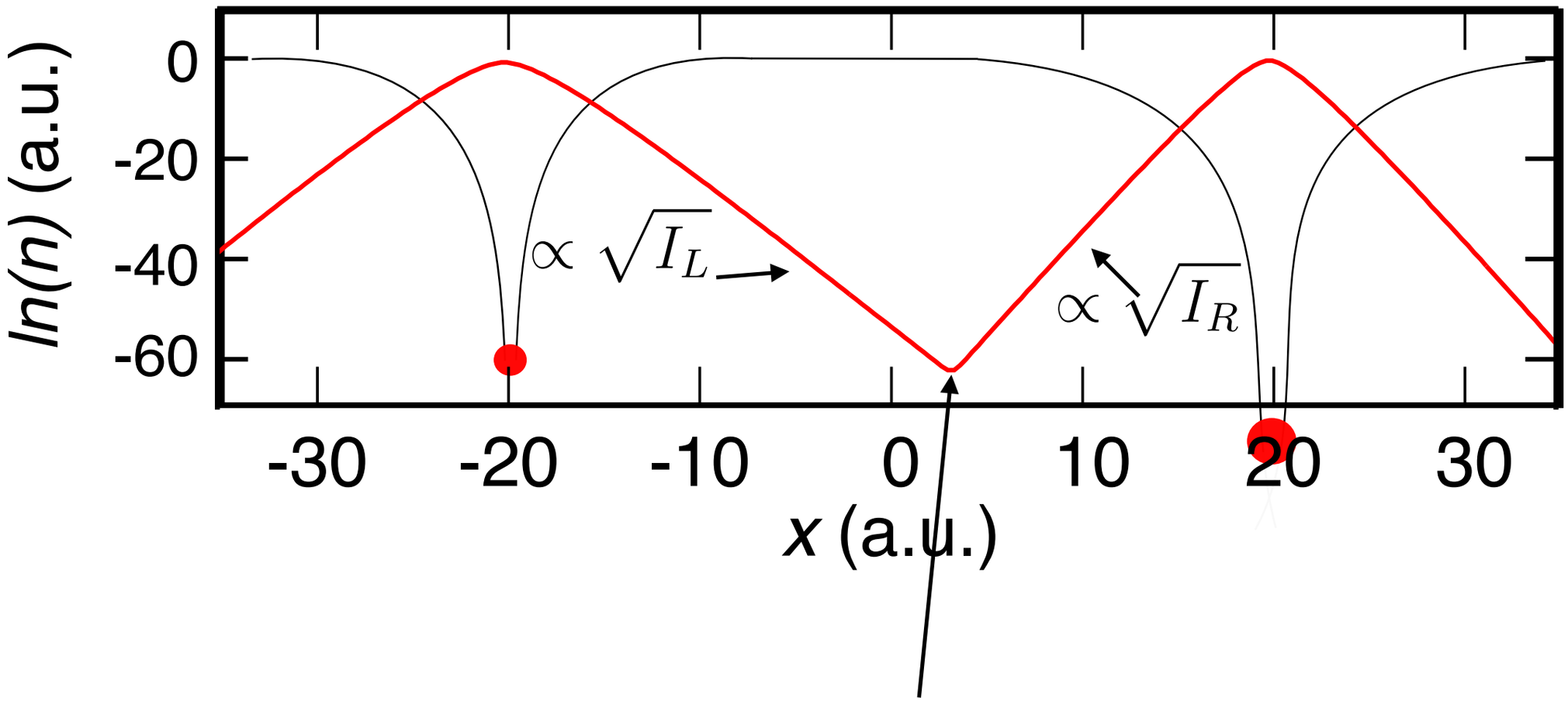
$v = I + \varepsilon^{\mathrm{ho}}$

$v' = A + \varepsilon^{\mathrm{lu}}$

$S = v - v' = I - A - (\varepsilon^{\mathrm{lu}} - \varepsilon^{\mathrm{ho}}) = \Delta$

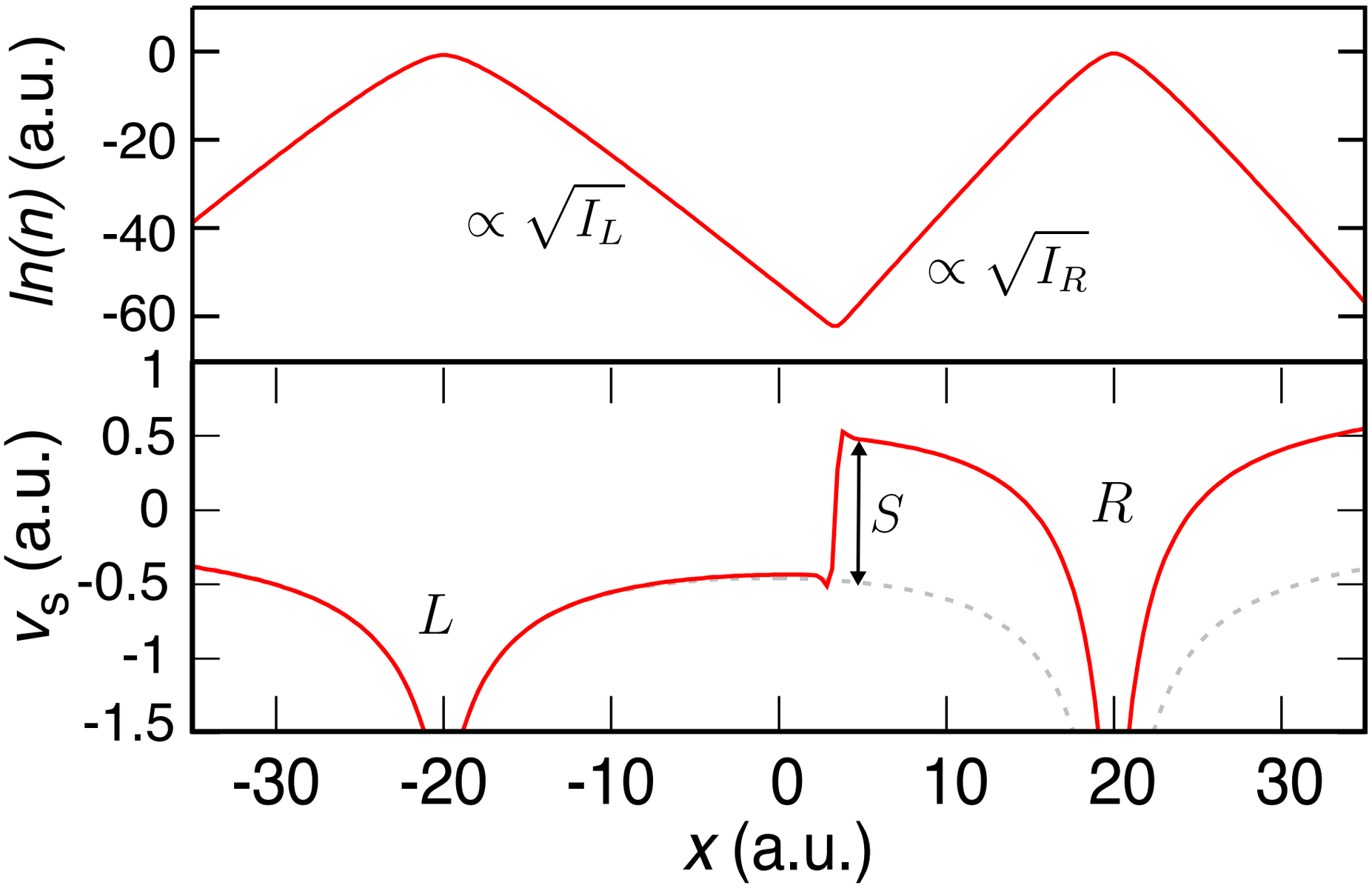
- Far from any atom the many-electron density decays as

$$n \sim e^{-2\sqrt{2I}x}$$



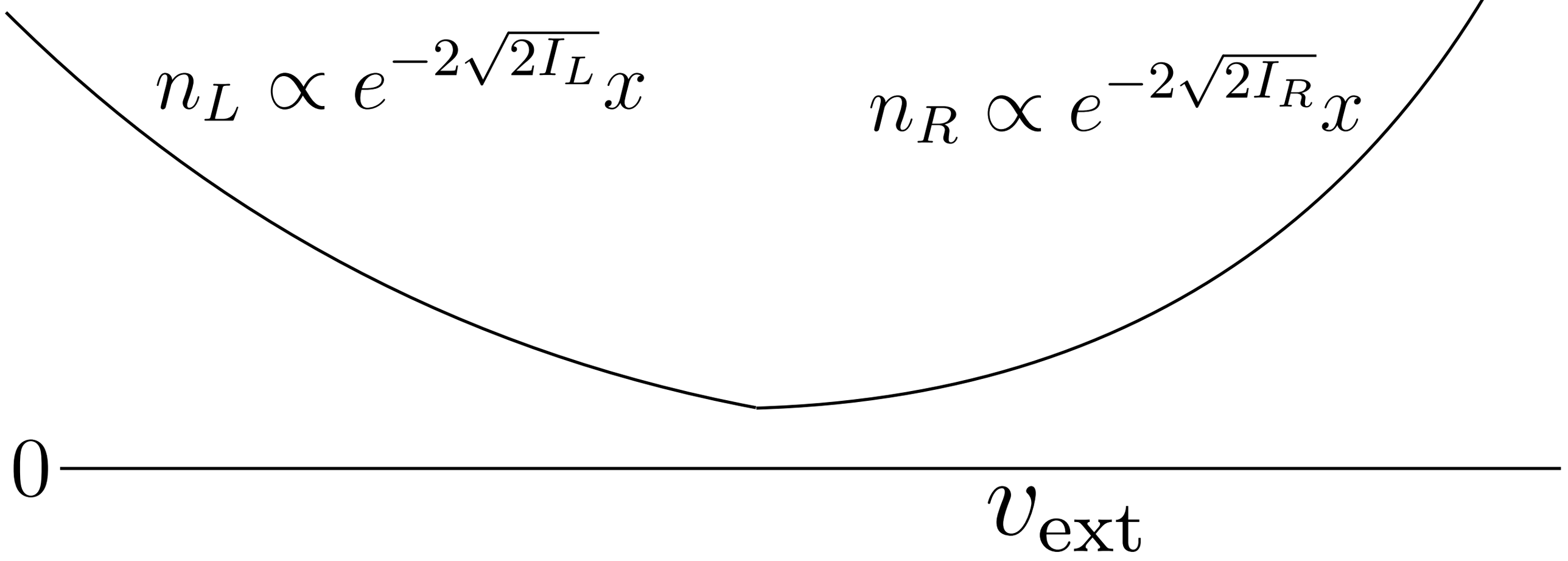
- Where the asymptotic decay rate changes…

- …a step forms in the Kohn-Sham potential



$$S = I_R - I_L + \varepsilon_R - \varepsilon_L$$

Far from and between the two atoms



Kohn-Sham perspective