

# Origin of static and dynamic steps in exact Kohn-Sham potentials

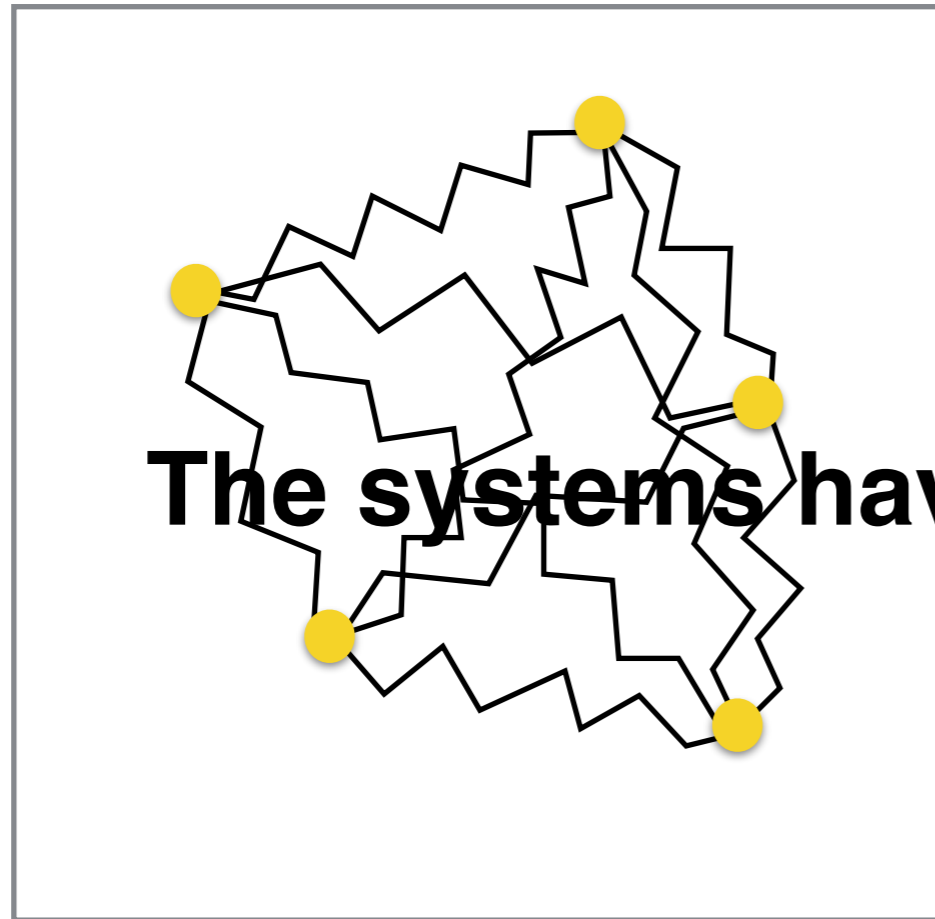
Matt Hodgson, James Ramsden and Rex Godby

UNIVERSITY *of York*



# Many-body quantum mechanics

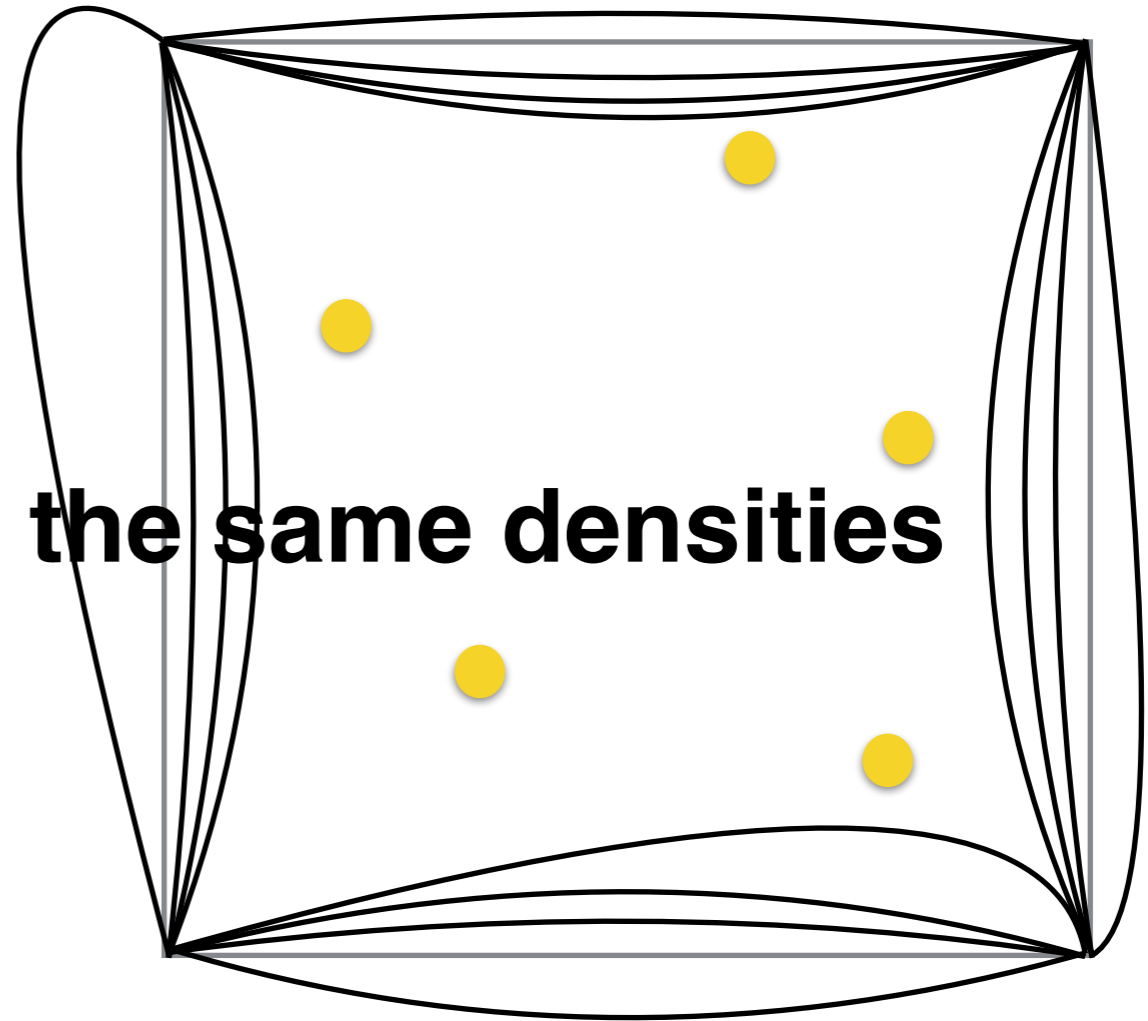
No. interactions = ~~10~~



Computational Scaling =  $k^{\frac{3}{2}}$

# Density functional theory

No. interactions = 0



Computational Scaling =  $k$

**The systems have the same densities**

# Time-dependent density functional theory

The auxiliary system of non-interacting electrons now obey

$$i \frac{\partial}{\partial t} \phi(x, t) = \left( -\frac{1}{2} \frac{\partial^2}{\partial x^2} + v_s(x, t) \right) \phi(x, t)$$

The accuracy of the approach hinges on knowledge of the **time-dependent Kohn-Sham potential**  $v_s(x, t)$

TDDFT can be applied to many physical systems, e.g. molecular junctions

However, in that case, the currents predicted can be quite wrong

**Why?**

# iDEA

interacting Dynamic Electrons Approach

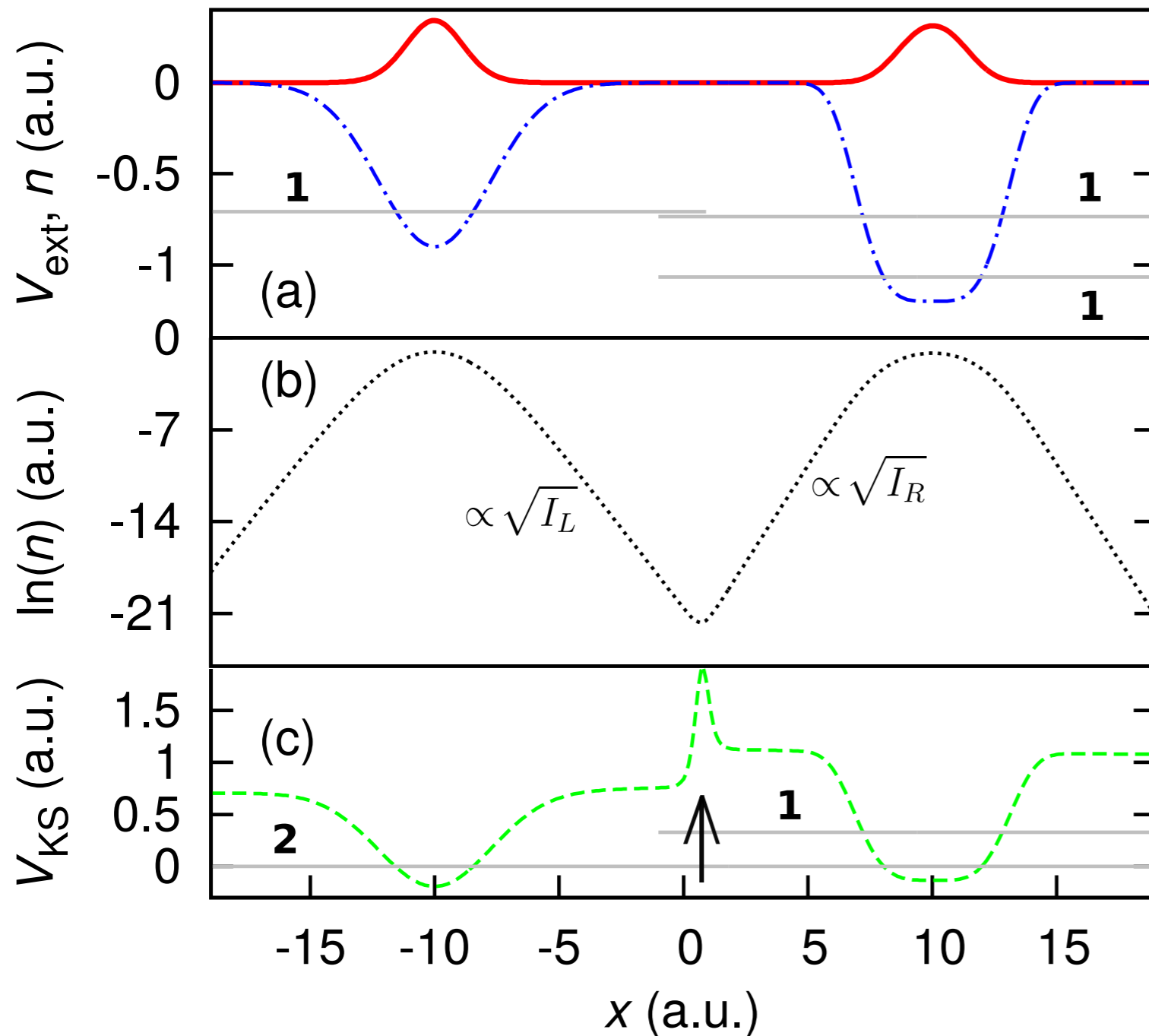
- 1) We calculate the fully correlated many-body wavefunction for two or three electrons
- 2) We perturb the system and time-evolve the wavefunction
- 3) We compute the exact electron density, then reverse engineer it to get the exact time-dependent Kohn-Sham potential

## **Note**

*Our electrons are spinless, hence each electron occupies one Kohn-Sham orbital  
Our systems are one-dimensional – we look at nano-wires*

Static and dynamic  
**steps** in the Kohn-  
Sham potential

# Almbadh-von Barth thought experiment (ground state)



Two *spin-half* electrons in an asymmetric external potential

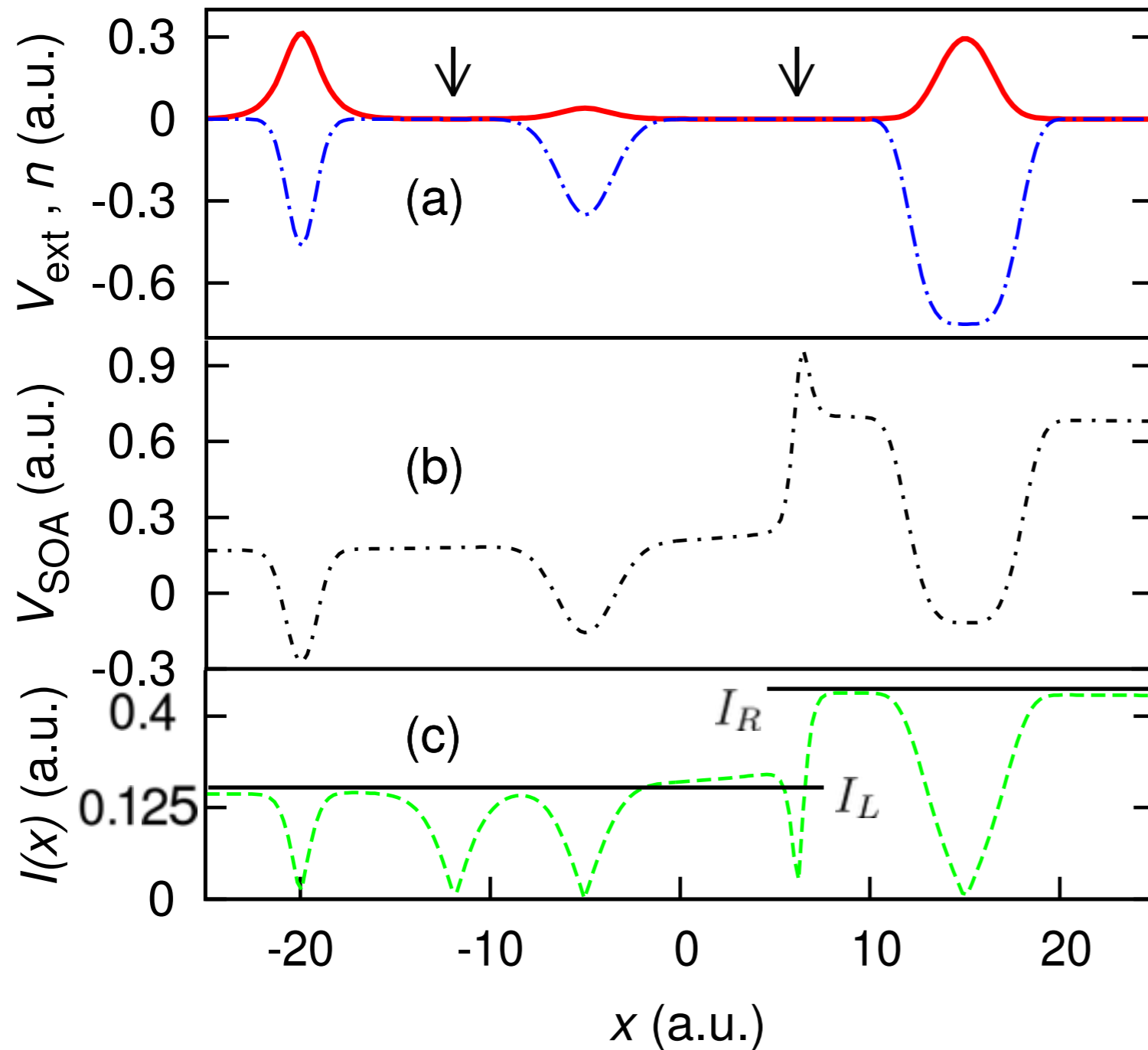
Far from an atom the electron density decays asymptotically

$$n(x) \propto e^{-2\sqrt{2I}x}$$

The Kohn-Sham (KS) potential has a *step in the region of the density minimum* (arrow)

$$S_{\text{xc}}^I = I_R - I_L$$

# Change in 'local effective ionisation energy'



Two *spinless* electrons, with two minima in the density (arrows)

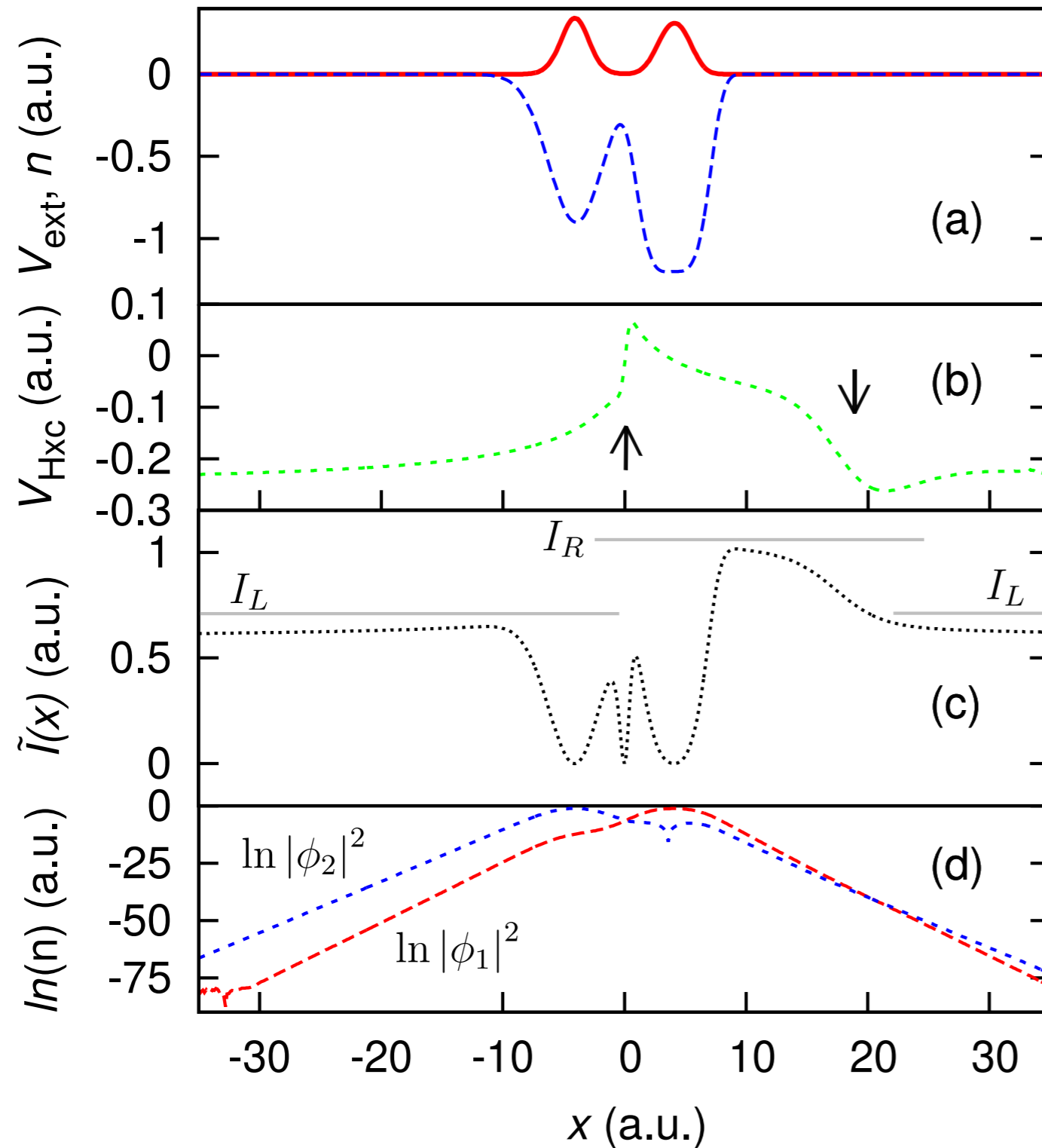
Only one of the density minima has a step

The local effective ionisation energy –

$$\tilde{I}(x) = \frac{1}{8n^2} \left( \frac{\partial n}{\partial x} \right)^2$$

– step only forms when there is a change!

# Origin of steps



Two *spinless* electrons in an asymmetric double-well

The step which forms at the density minimum has magnitude

$$S_{\text{xc}} = \underbrace{(I_R - I_L)} + \underbrace{(\epsilon_R - \epsilon_L)}$$

Both these steps correspond to the changes in the local effective ionisation energy

Two KS orbitals are occupied, they cross at two points which also correspond to the steps



# The superposition of steps

The change in ionisation energy in the many-body system gives rise to a step with magnitude

$$S_{\text{xc}}^I = I_R - I_L$$

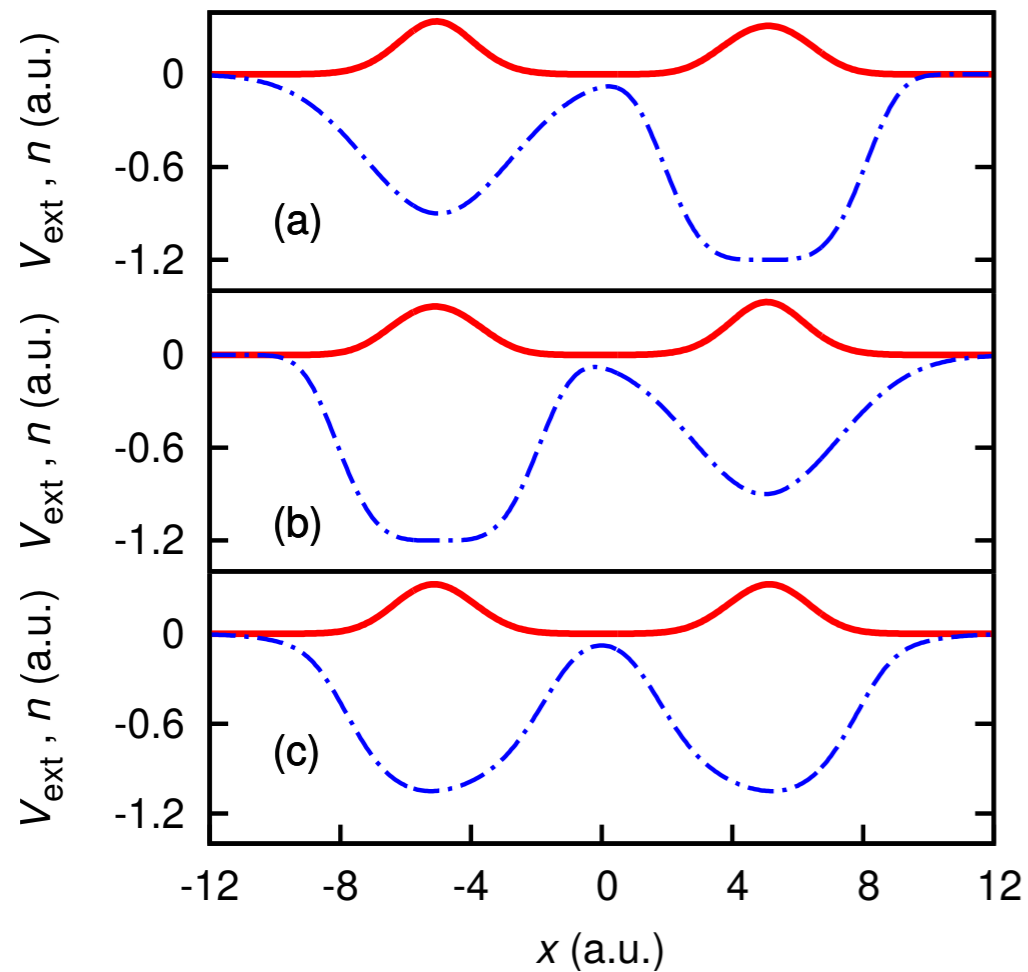
The analog of this effect in the Kohn-Sham picture is the crossover of localised KS single-particle densities. This gives rise to a step with magnitude

$$S_{\text{xc}}^\epsilon = \epsilon_R - \epsilon_L$$

For a general system these steps superimpose to give one step with magnitude

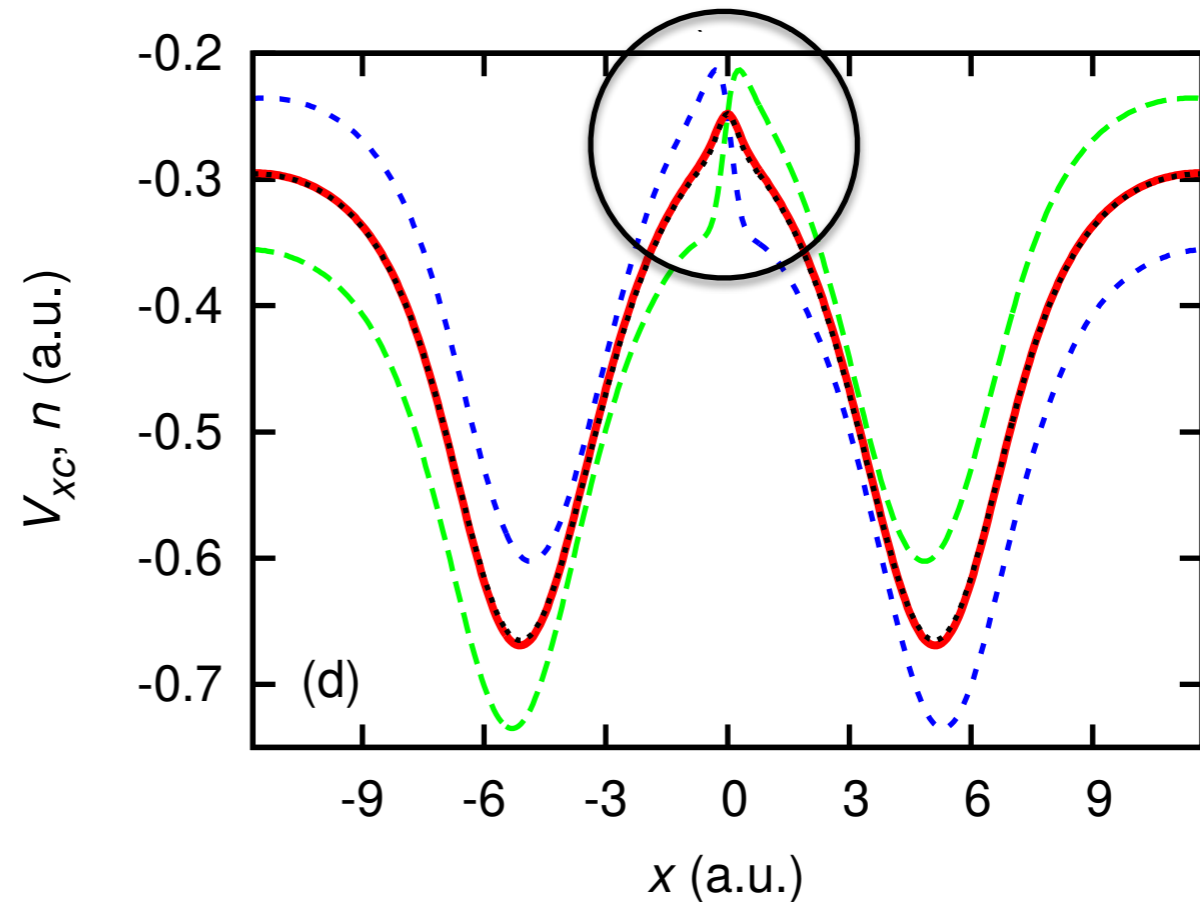
$$S_{\text{xc}} = S_{\text{xc}}^I + S_{\text{xc}}^\epsilon = (I_R - I_L) + (\epsilon_R - \epsilon_L)$$

# Symmetric example (ground state)



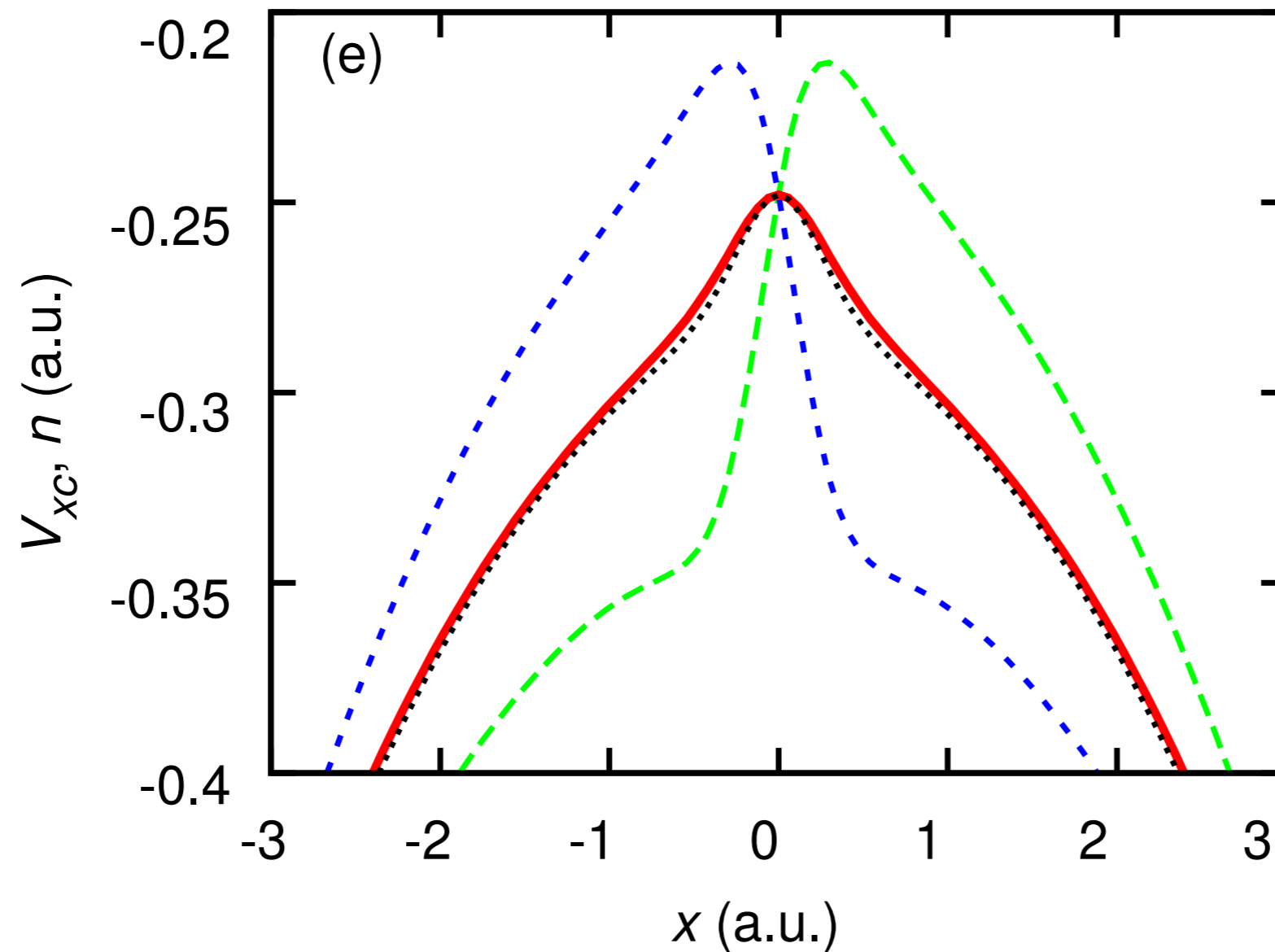
Three systems chosen:

- Two electron double well
- Mirror image
- Superimpose the first two



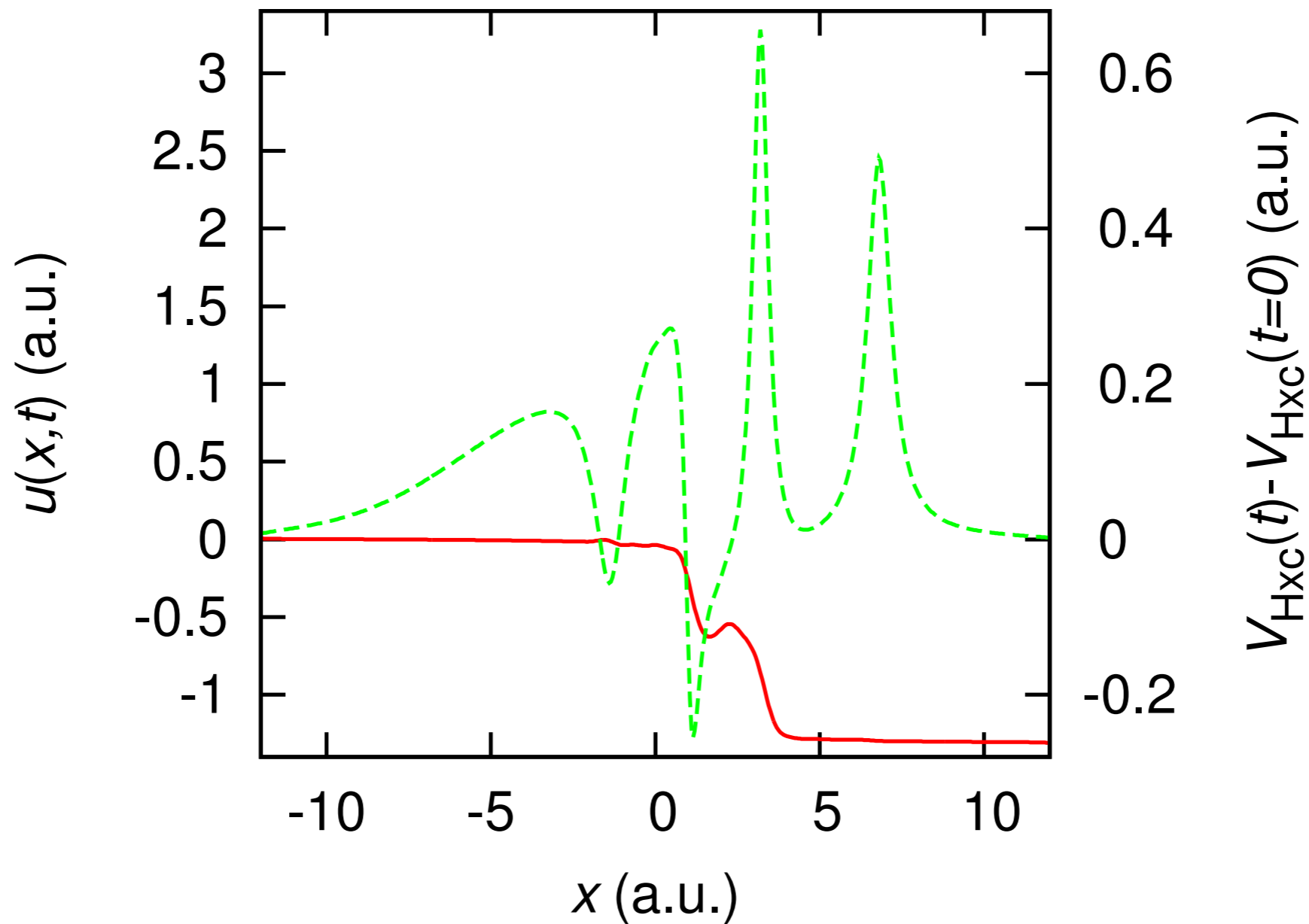
Using arguments based on linear response, we can superimpose the exchange-correlation potentials of the first two system in the same way

# Symmetric example (ground state)

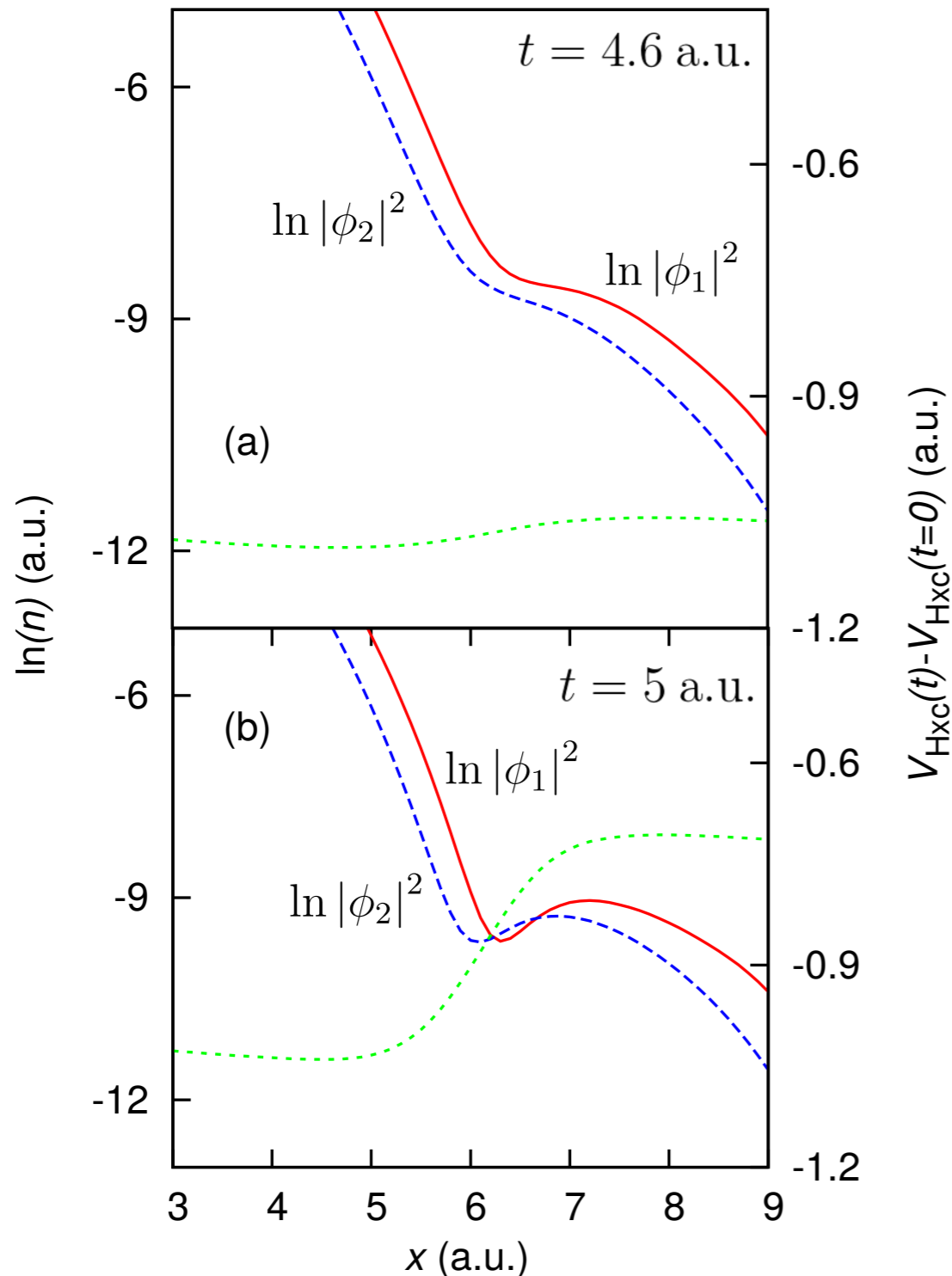


The steps which form superimpose to give a very good representation of the symmetric bump which forms for our third system

# Time-dependent steps



# Origin of time-dependent steps



A system of two spinless electrons in a ground-state double-well

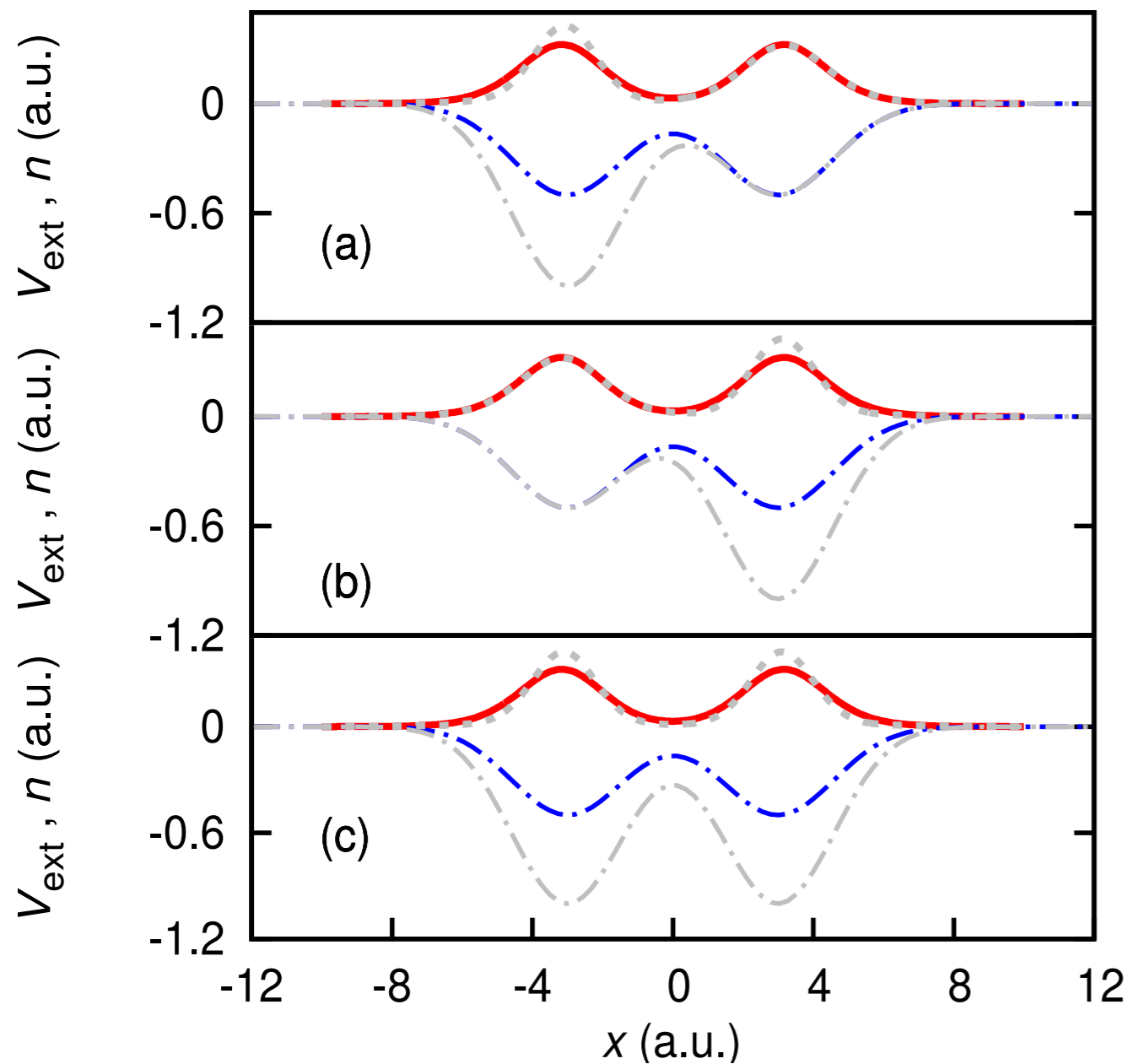
The system is perturbed and evolved through time

(a) the single-particle KS densities have not crossed

(b) once they cross a dynamic step forms

**What is the magnitude?**

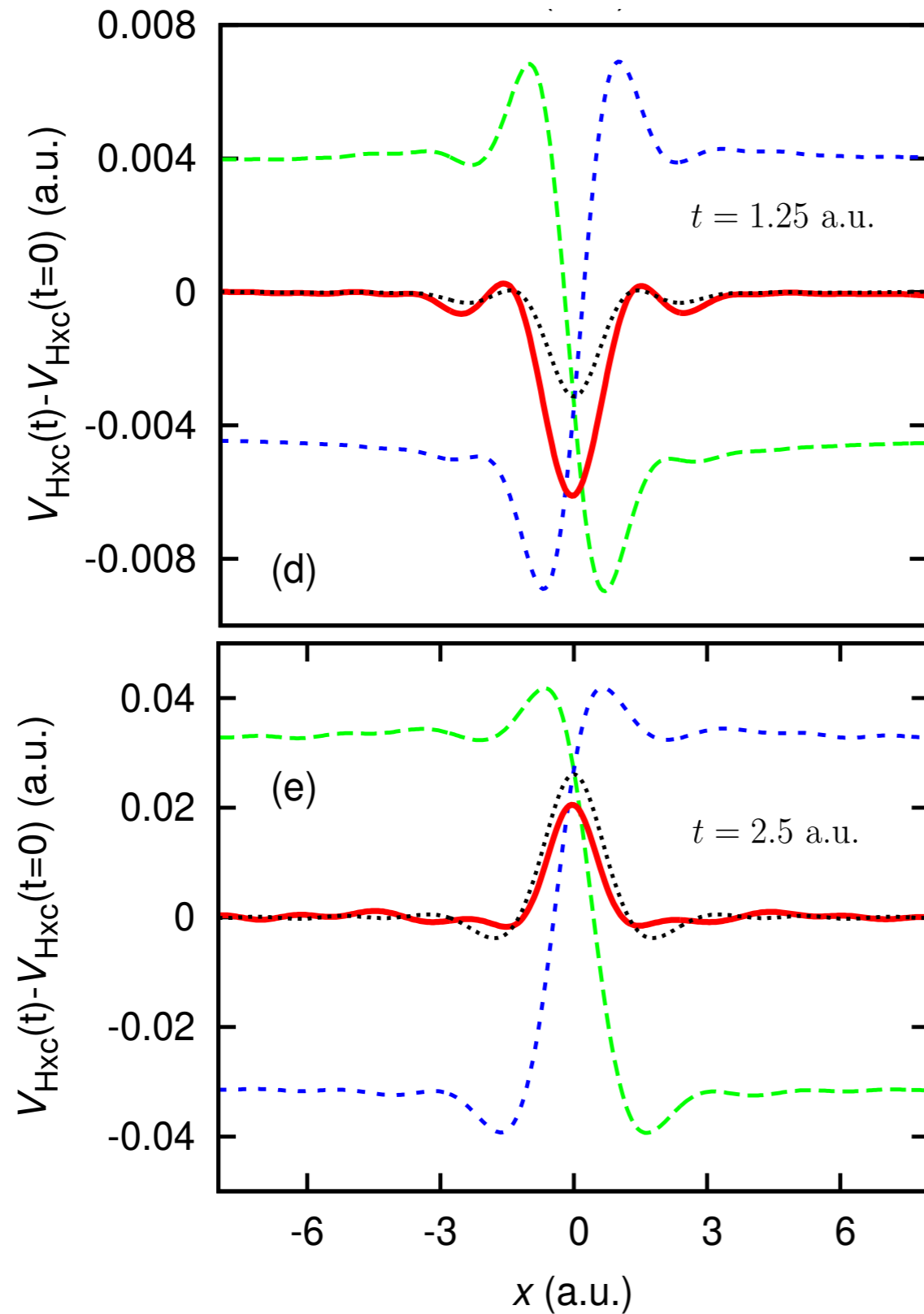
# Superimposing steps (time dependent)



Using arguments based on linear response, we can superimpose the time-dependent Hartree exchange-correlation potentials of the first two system in the same way

The steps which form, superimpose to give a very good representation of the symmetric bump, then dip, feature at each point in time

# Superimposing steps (time dependent)



- Three *time-dependent* systems chosen:
- Two electron double well
  - Mirror image
  - Superimpose the first two

# Conclusions

- Change in local effective ionisation energy gives rise to a step
- Single-particle Kohn-Sham densities crossing gives rise to steps, even in the time-dependent regime
- Steps superimpose to form other features in the exact Kohn-Sham potential

*Poster: The role of electron localisation in density functionals*

*References: “Origin of static and dynamic steps in exact Kohn-Sham potentials”, M. J. P. Hodgson et al., ArXiv (2016)*



Extra slides

# Adiabatic steps

The concept of a well defined ionisation energy is lost in the time-dependent regime

If the system evolves slowly enough then the arguments we made for the ground-state can be used for time-dependent systems

Further investigation is required in order to determine what happens to the local effective ionisation energy for a time-dependent system

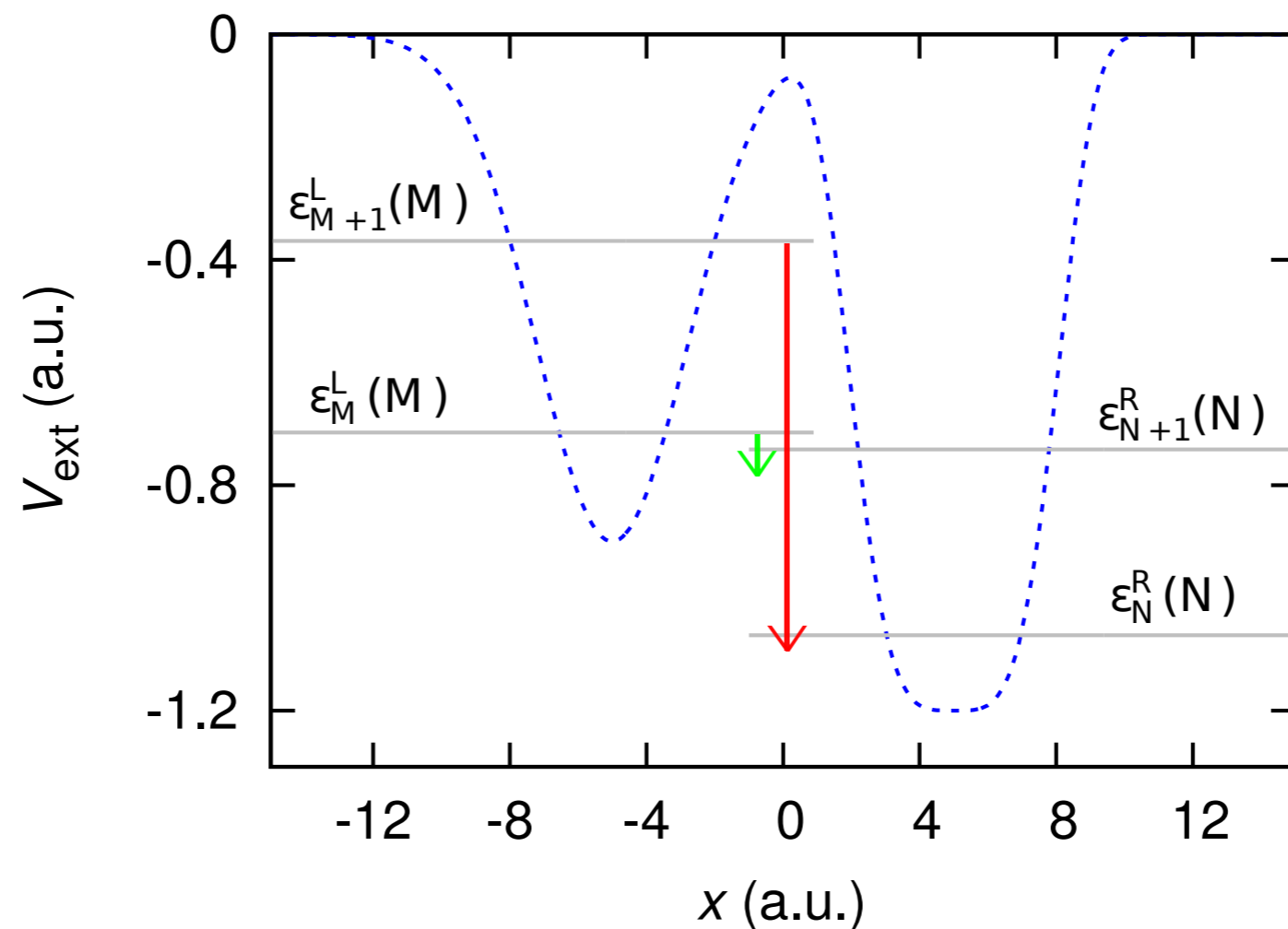
How can this fundamental description of steps be used practically?

# What height works for the ground state?

While it is not possible to calculate the step height without knowing the KS system beforehand

An allowed range can be derived from simple arguments

$$\varepsilon_N^R(N) - \varepsilon_{M+1}^L(M) < S_{xc} < \varepsilon_{N+1}^R(N) - \varepsilon_M^L(M)$$



# How to predict where the step will form for the ground state

A density minimum is one indicator of where a step will form

However, our example before showed that some minima do not form steps

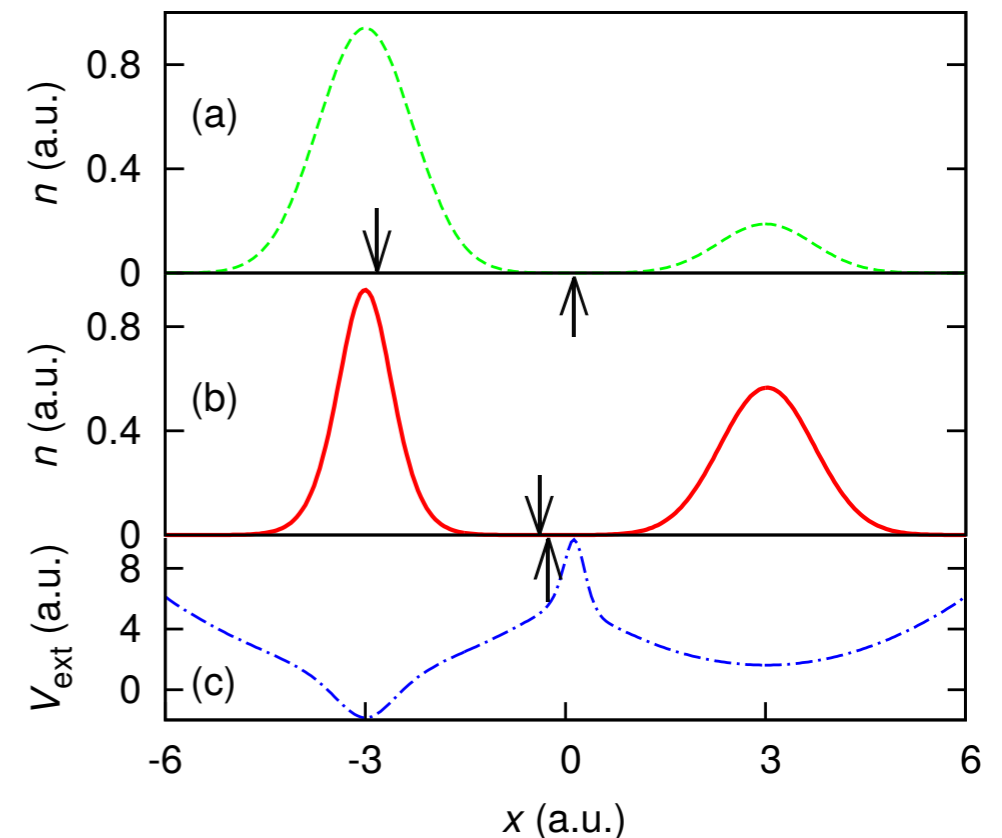
For a region predominantly occupied by a single electron, there can be no change in the effective ionisation energy of the density

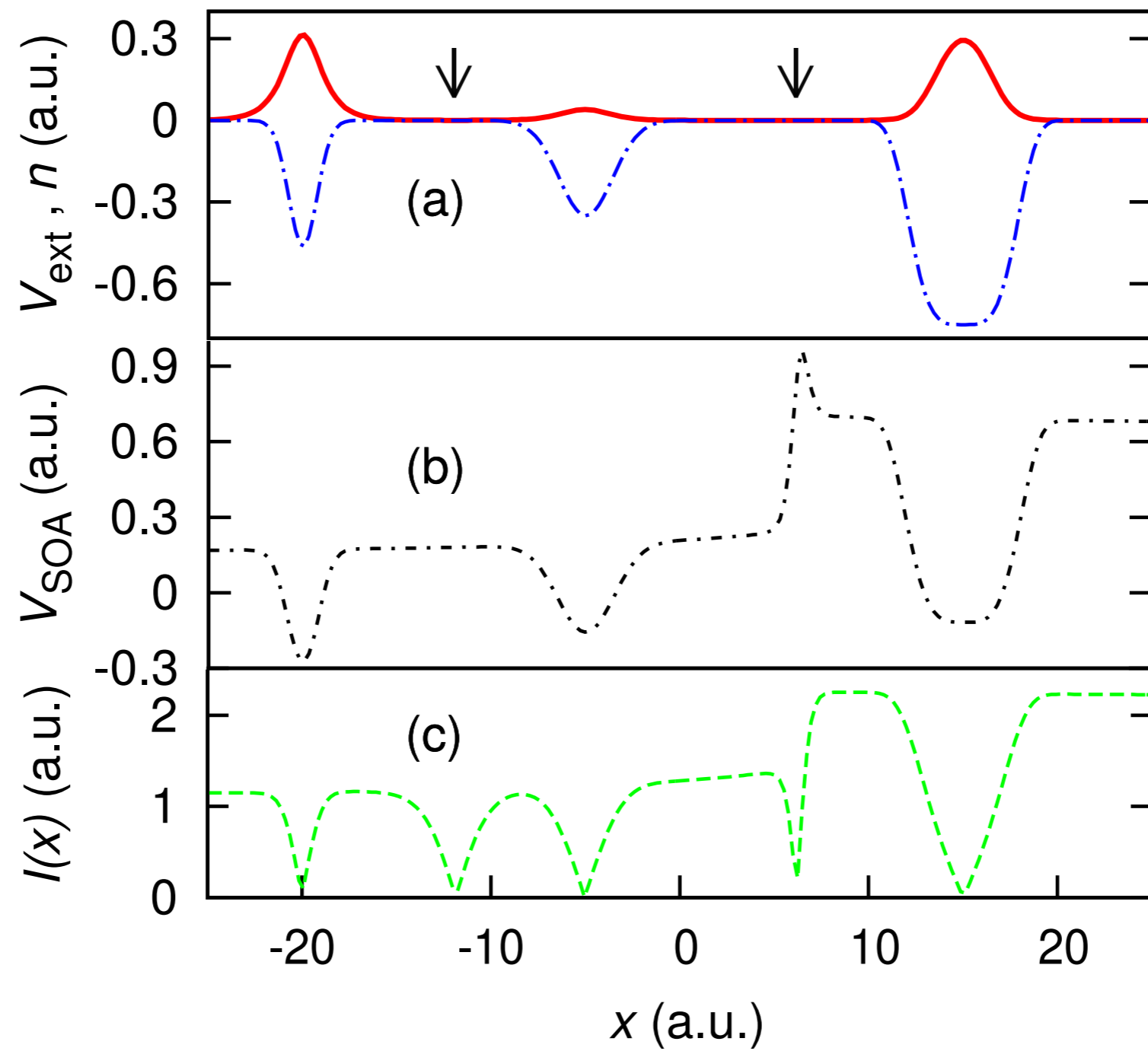
For there to be a change in the effective ionisation energy there must be at least two electrons in the vicinity

Hence, we define the 'integer electron point' (IEP)

$$\int_a^b n(x) dx = 1$$

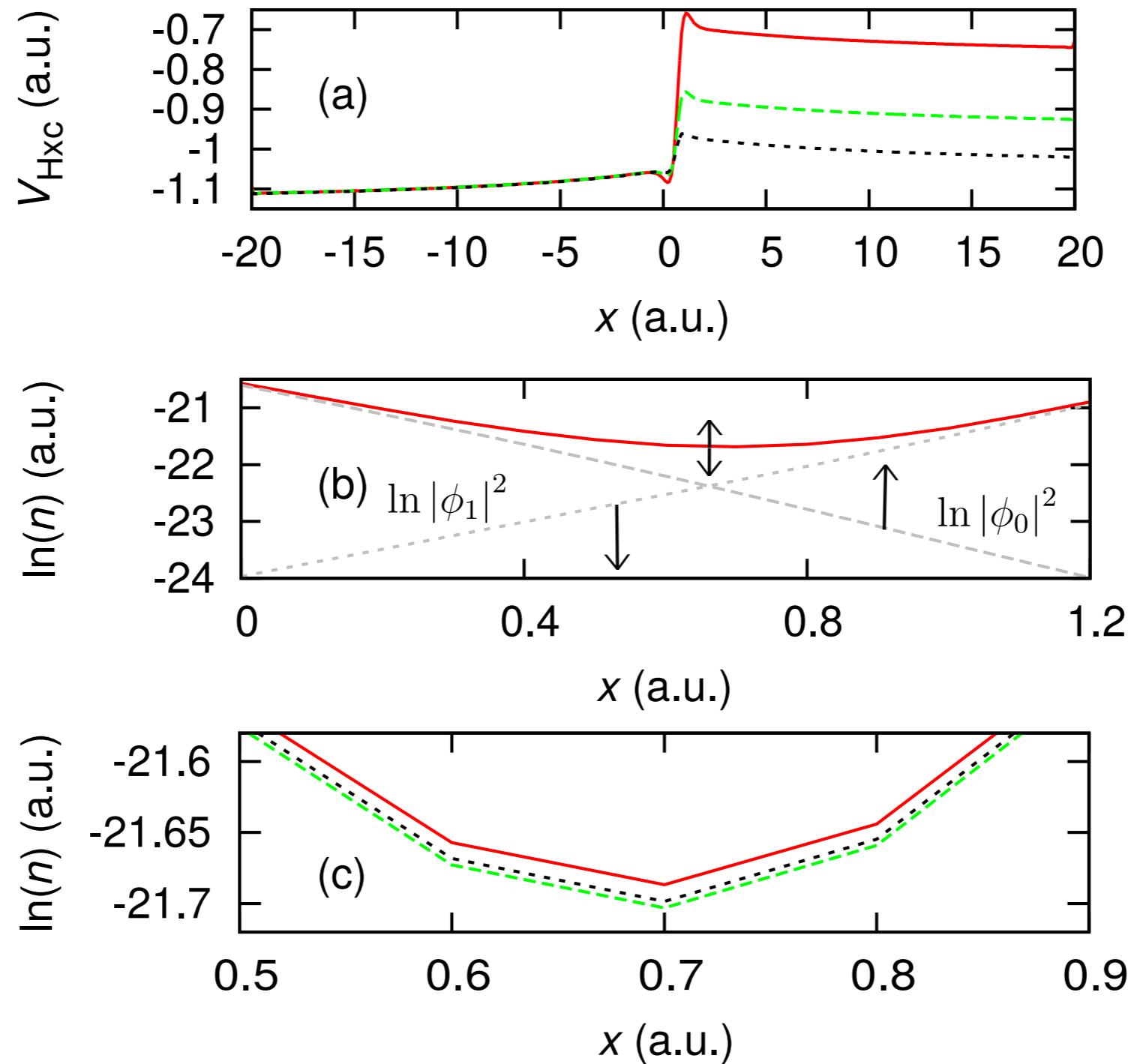
The IEP coincides with the density minimum owing to localisation and the Coulomb repulsion





What about time-  
dependence?

# The effect of changing the step height





# The effect of delocalisation

