

Origin of steps in exact Kohn-Sham potentials



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Density Functional Theory (DFT)

DFT [1], in the Kohn-Sham (KS) approach [2], is widely used in quantum chemistry and solid state physics. Nonlocal 'steps' in the KS potential are crucial in certain circumstances for accurate electron densities. However, the commonly used approximations cannot give step features in the KS potential, and little about steps is understood. Here we give a fundamental understanding of the origin of steps.

Local effective ionisation energy

Away from any subsystem, the exact many-electron density decays asymptotically – proportional to the square root of the ionisation energy of the subsystem [3] –

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

Key new concept

At the interface between adjacent subsystems, the *local effective ionisation energy* can change –

local effective ionisation energy:
$$\tilde{I}(x) = \frac{1}{8n^2} \left(\frac{\partial n}{\partial x} \right)^2$$

– [see Fig.1 (b) and Fig.2 (c)].

This change leads to a rapid increase in the level of the exact Kohn-Sham potential, *i.e.*, a potential step [see Fig.1 (c)].

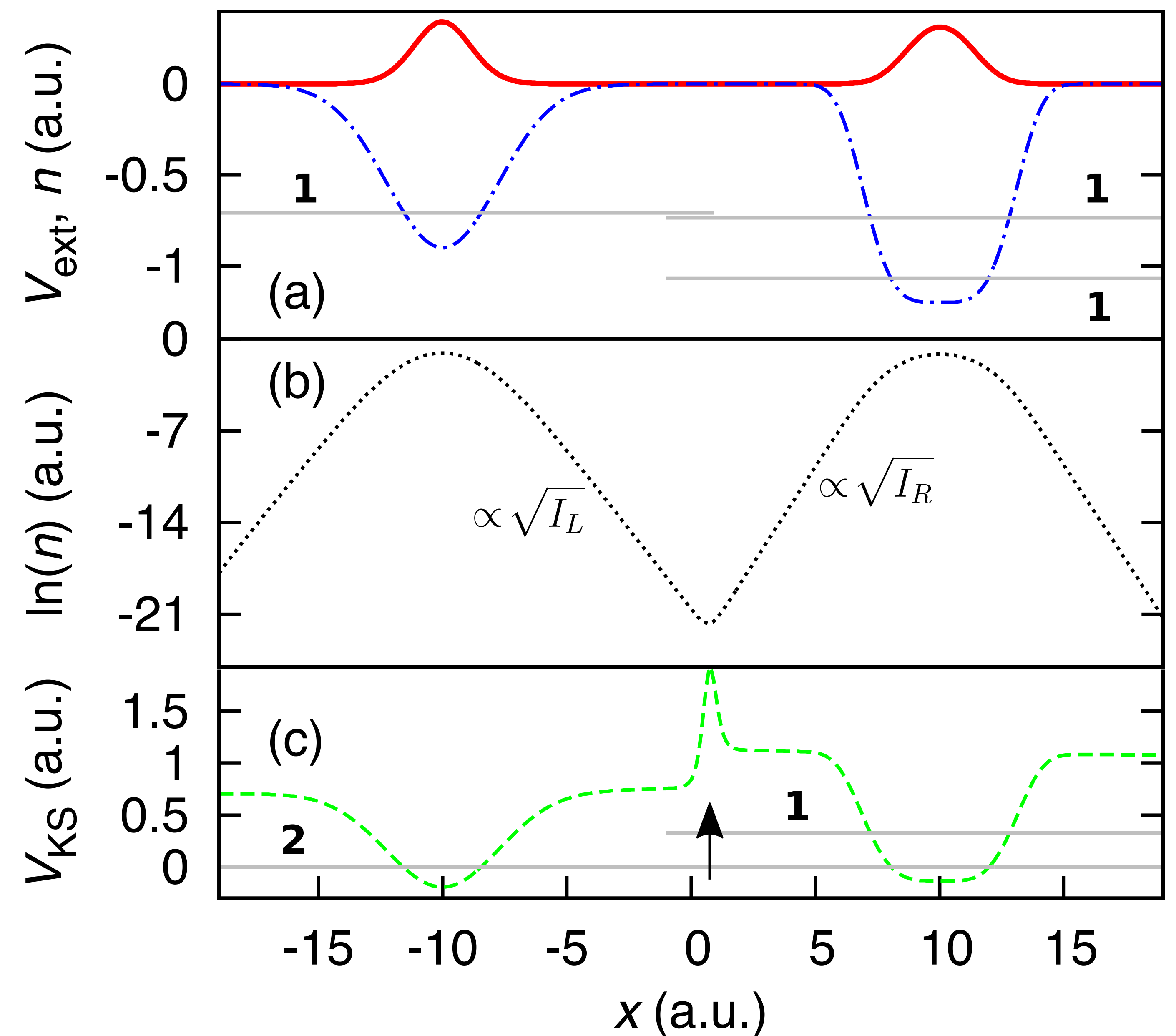
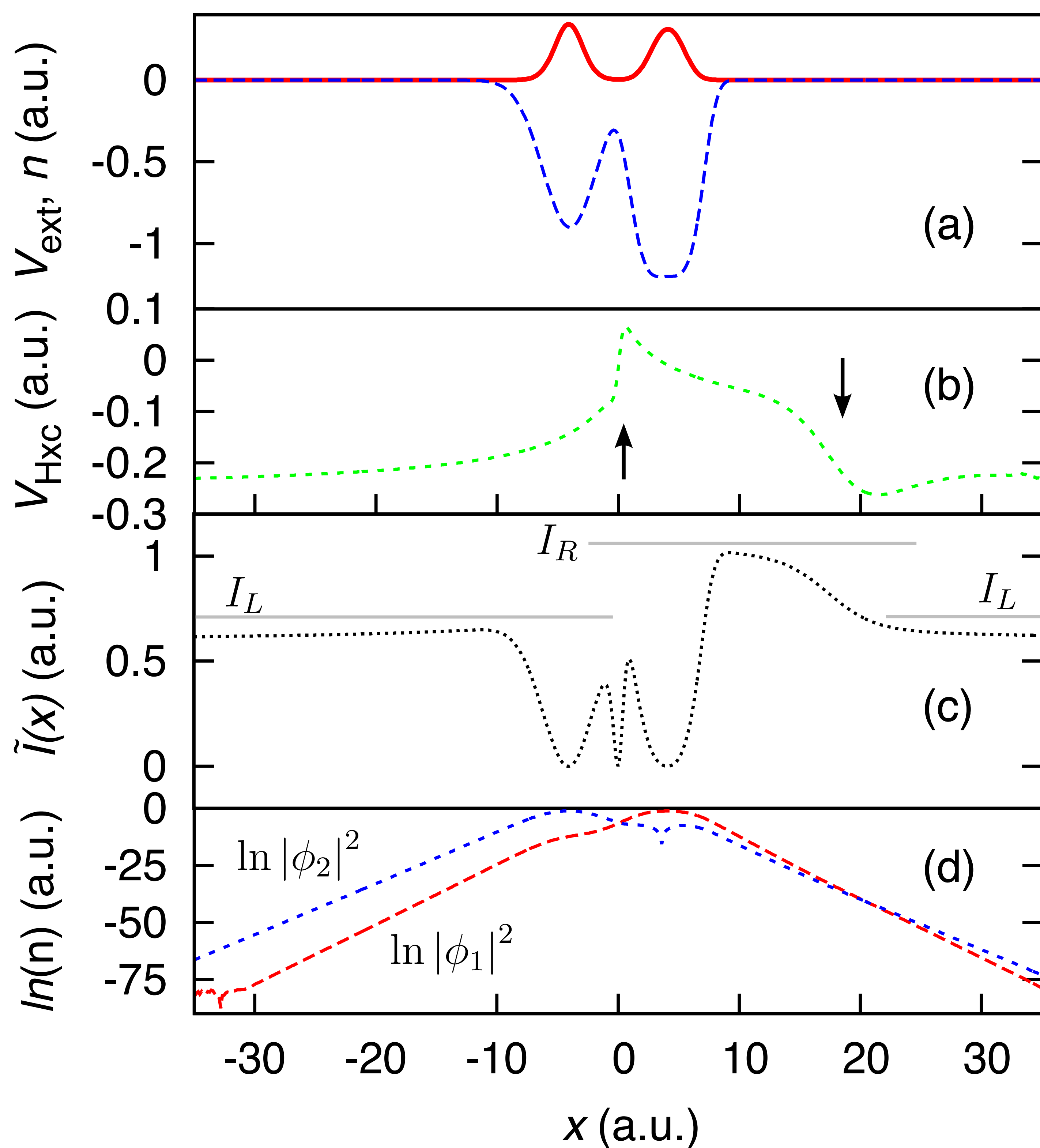


Figure 1 (above): spin-singlet in two separated atoms (wells) (a). A step forms in the Kohn-Sham potential in order to align the ionisation energies of the atoms (c). This occurs at the density minimum, *i.e.*, where the local ionisation energy changes (b).



Multiple occupied orbitals

When multiple Kohn-Sham orbitals are occupied the analogue of the change in the local effective ionisation energy happens in the Kohn-Sham picture – the crossing from one dominate single-particle density to another – this *also* gives rise to step. **This is even true for a time-dependent system.**

When these effects happen at the same point in space, the *two* steps superimpose and form *one* step of magnitude

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

I_R – ionisation energy of the right subsystem

ϵ_R – Kohn-Sham HOMO for right subsystem

(left defined correspondingly).

Superimposing steps give rise to other features in the KS potential, (*e.g.*, bumps and peaks) as well as the step structure; see Fig.1 (c).

Figure 2 (left): two *spinless* electrons in a molecule (a), so two Kohn-Sham orbitals are occupied. Far from the molecule there is a second change in the local effective ionisation energy (c) and a crossing of the Kohn-Sham single-particle densities (d). These two effects cause a step to form in the exact Kohn-Sham potential (arrows) (b).

Conclusions:

- 1) Steps in the Kohn-Sham (KS) potential are crucial in certain systems for accurate electron densities.
- 2) Steps arise in the KS potential when there is a change in the local effective ionisation energy or a crossing of the single-particle KS densities, *even for a time-dependent system*. (These are common occurrences for finite systems.)
- 3) Steps superimpose to form step, peak and bump features in the exact KS potential.

The exact many-electron Schrödinger equation is solved to find the exact electron density, using our **iDEA** code [4]

Reference: poster based on M. J. P. Hodgson *et al.*, Physical Review B **93**, 155146 (2016). [1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964). [2] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965). [3] J. P. Perdew *et al.*, Phys. Rev. Lett. **49**, 1691 (1982). [4] M. J. P. Hodgson *et al.*, Phys. Rev. B **88**, 241102(R) (2013).