

The role of localisation in density functionals

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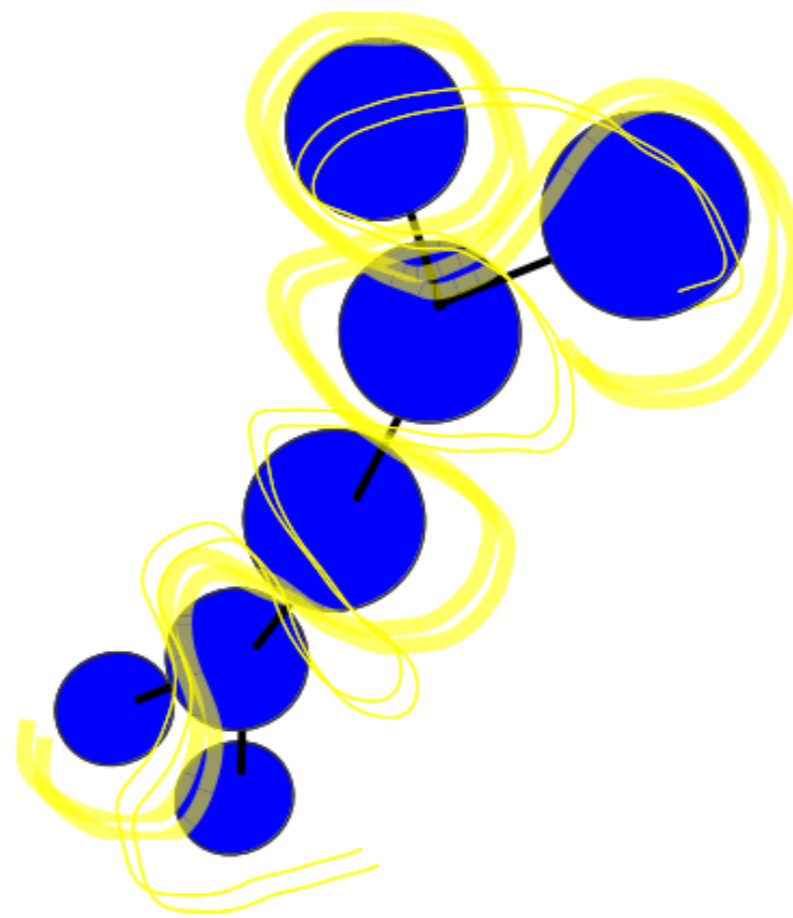
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Introduction

The practical advances made in synthesising nanostructures has broadened the range of nanotechnology in scientific research; from medical treatments to electronic devices built from single molecules. For such tiny systems understanding the quantum mechanics of interacting electrons is crucial in making theoretical predictions.

The accuracy of time-dependent density functional theory (TDDFT) hinges on approximating the exchange-correlation (xc) term in the Kohn-Sham (KS) potential – crucial for describing the interaction between the electrons. Usual approximations based on the local density become much less secure for the types of systems we have already mentioned. The approximations for the xc potential must be improved.



Objectives

1. Identify that which is missing from the usual approximations of the xc potential.
2. Develop new, accurate approximations for the xc potential for quantum transport systems.

What's the big iDEA?

We find the exact electron density, via the many-body fully correlated wave-function, for systems of 2 and 3 electrons (i.e. systems for which the many-body Schrödinger equation can be solved exactly).

We reverse engineer the Kohn-Sham (KS) potential using our **iDEA** (interacting dynamic electrons approach) code; by optimising the potential experienced by non-interacting electrons, in the same system as the many-body case, so that the non-interacting charge and current densities match those of the many-body system [1].

Single orbital approximation (SOA)

The KS potential for a single occupied KS orbital is

$$V_{\text{KS}}^{\text{SOA}}(\mathbf{r}, t) = \frac{\nabla^2 n}{4n} - \frac{[\nabla n]^2}{8n^2} - \int_{-\infty}^{\mathbf{r}} \frac{\partial \mathbf{u}}{\partial t} \cdot d\mathbf{r}' - \frac{1}{2}u^2. \quad (1)$$

For systems with regions of highly localised electrons, i.e. the electron density can be well described by a single KS orbital, we use Eq. 1 as an approximation to the universal KS potential, we term this the *single orbital approximation* (SOA).

Mixed localisation potential (MLP)

- We mix the SOA potential with a reference potential.
- For regions of strong localisation more of the SOA is used.

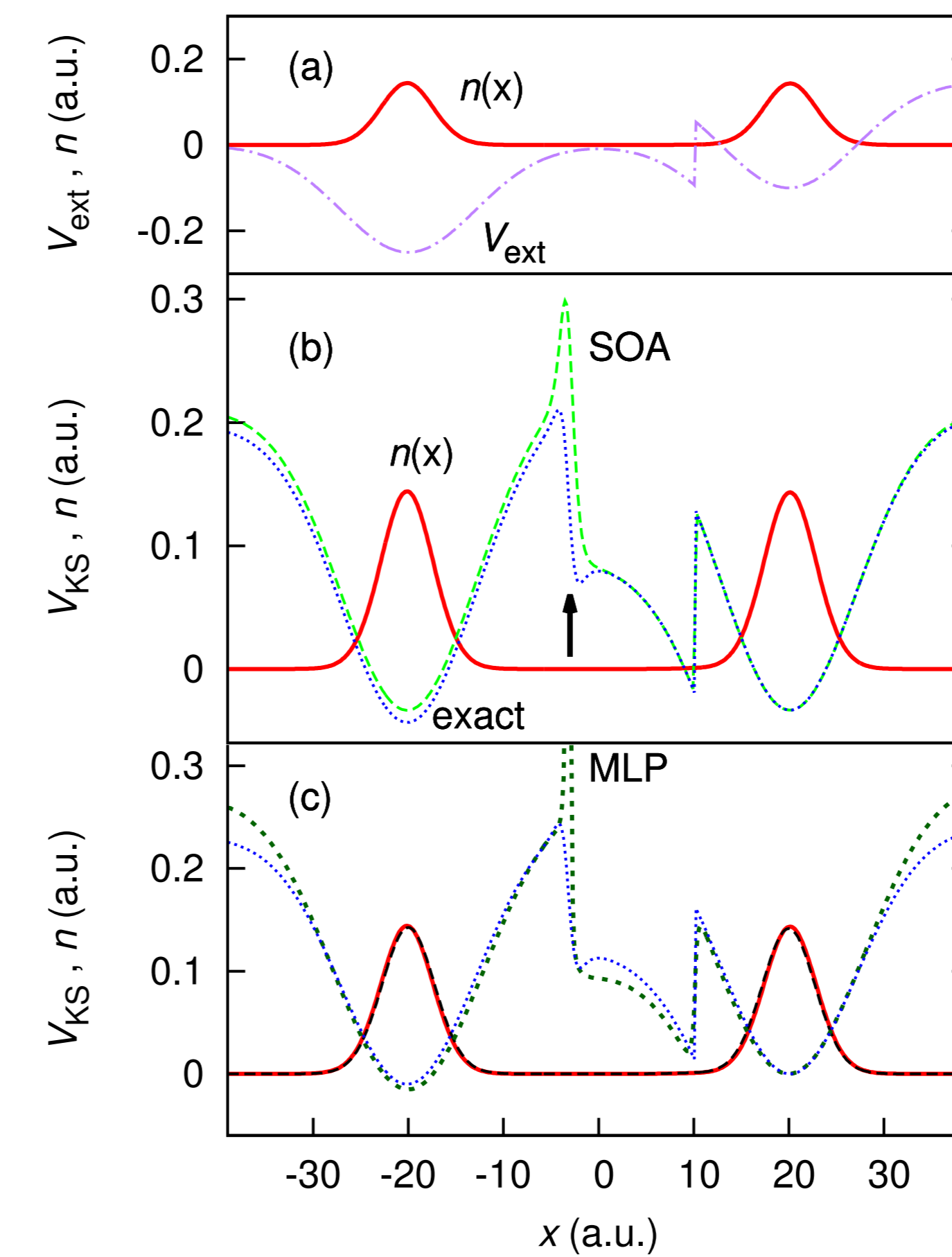
We term this the *mixed localisation potential* (MLP) [2].

Conclusions

- Local approximate functionals of the density are missing key features present in the exact KS potential.
- The MLP can produce accurate electron densities for systems where the local approximations are known to fail.

Double well

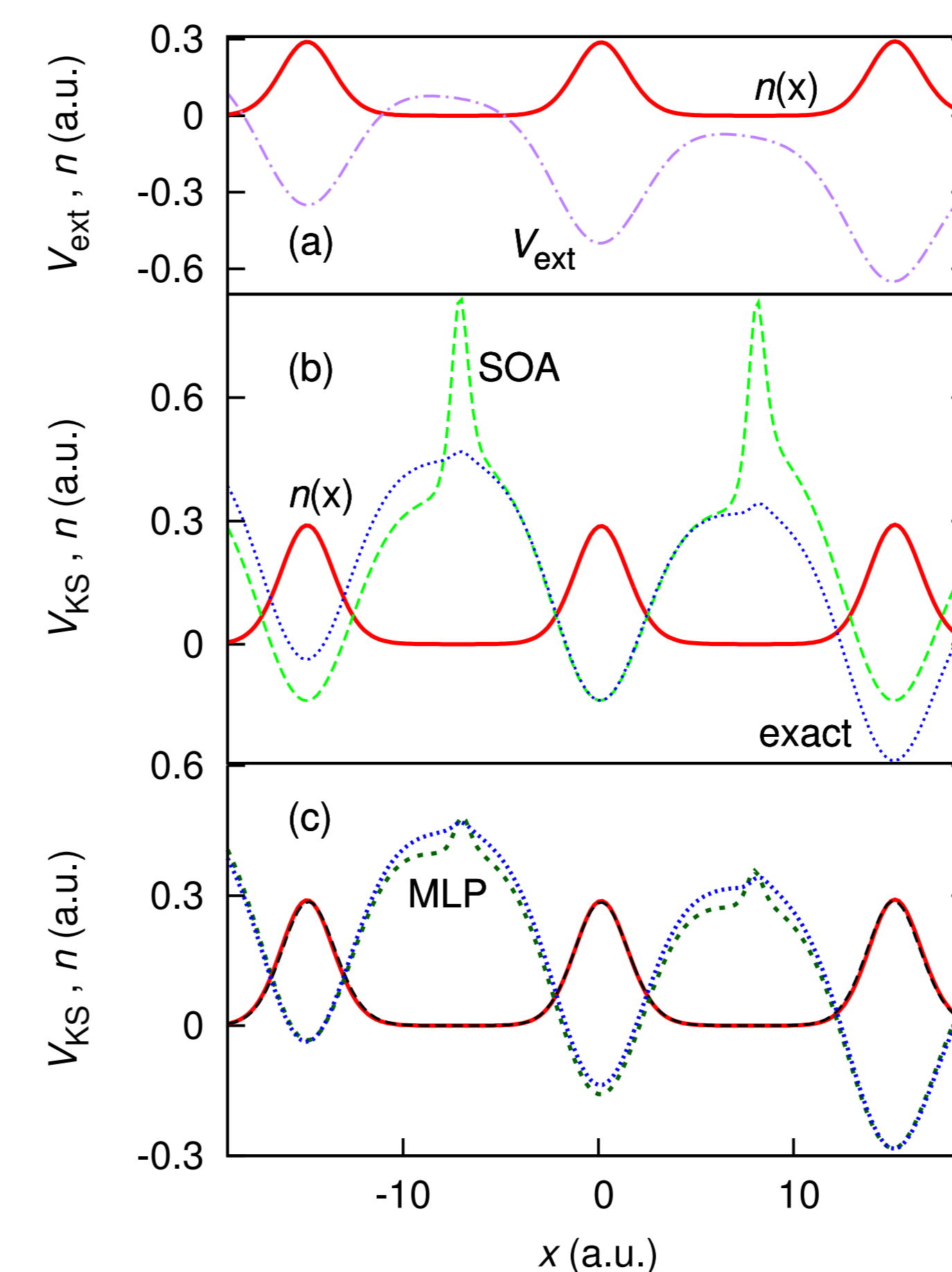
We have tested the MLP for a series of ground-state and time-dependent test systems:



(a) The exact many-body electron density, with the external potential. A potential step gives the right-hand well a lower ionization energy, while the Coulomb repulsion ensures one electron per well. (b) The exact KS potential; an xc potential step (arrow) forms at the minimum in the electron density. The SOA potential replicates the position and magnitude of the step remarkably well. (c) The

self-consistent MLP potential with the corresponding electron density, which matches the exact density very well.

Three atom chain

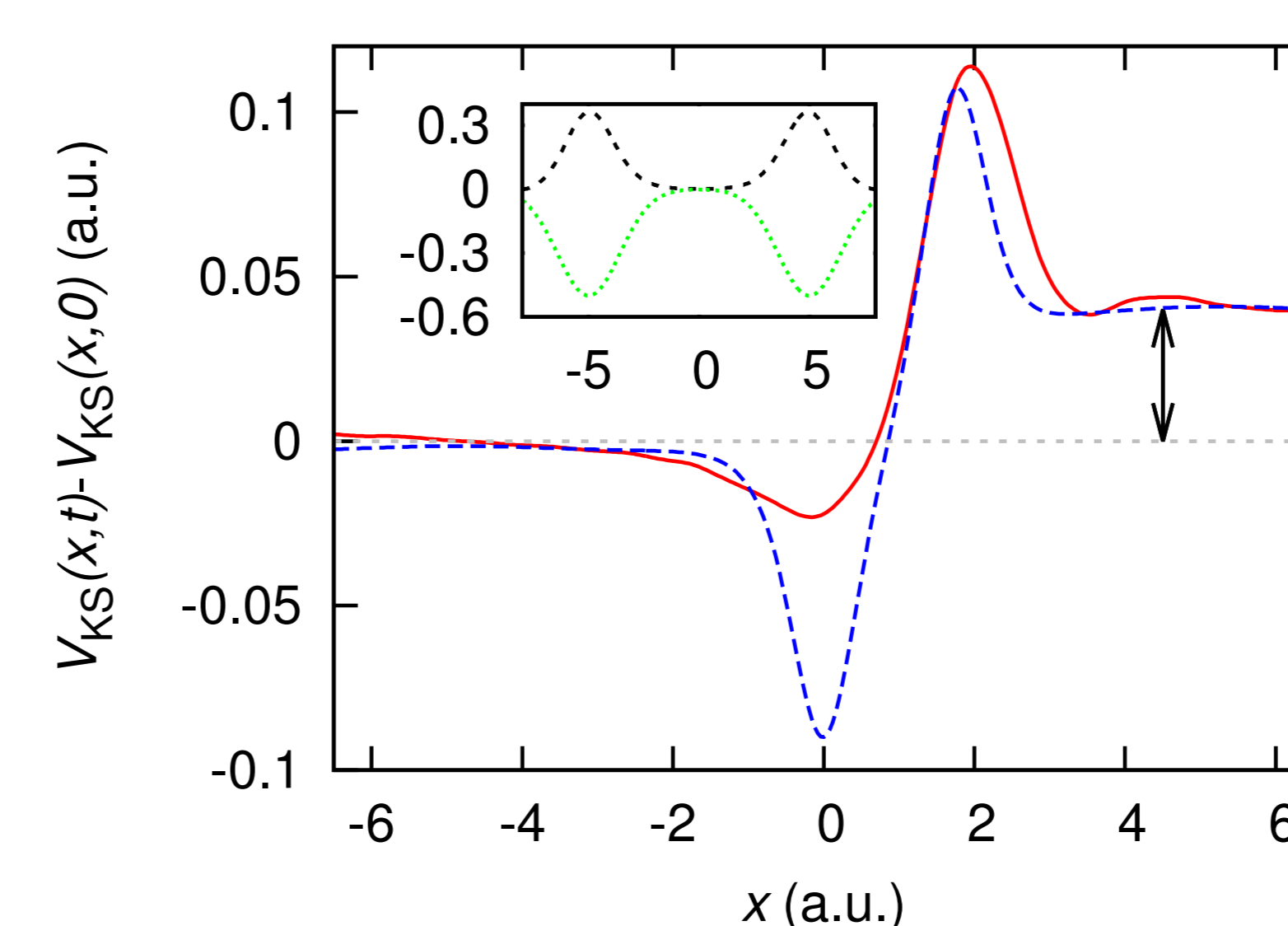


(a) The electron density for a chain of three atoms, with the external potential. (b) The exact KS potential; xc steps act to screen the external electric field. (c) The self-consistent MLP KS potential; mixing in the external potential gives an accurate representation of the screening.

Time-dependent double well

Inset: ground-state external potential and ground-state density. Main panel:

exact $V_{\text{KS}}(x, t) - V_{\text{KS}}(x, 0)$, at $t = 5$ a.u., together with the corresponding quantity for the MLP: both replicate the potential step introduced by the time-evolution (arrow).



References

- [1] M. J. P. Hodgson, J. D. Ramsden, J. B. J. Chapman, P. Lillystone, and R. W. Godby. Exact time-dependent density-functional potentials for strongly correlated tunneling electrons. *Phys. Rev. B*, 88:241102, Dec 2013.
- [2] M. J. P. Hodgson, J. D. Ramsden, T. R. Durrant, and R. W. Godby. The role of electron localization in density functionals. *Submitted*.