

# Electron localisation in exact time-dependent density-functional potentials

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# What's coming up?

## Introduction

Exact KS potentials

Electron localisation

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- TDDFT
- Exact Kohn-Sham potentials
- Electron localisation
- Approximate density functionals – based on localisation:
  - Ground-state
  - Time-dependent
- Summary

# Time-dependent Density Functional Theory (TDDFT)

An auxiliary system of *non-interacting* electrons follow the time-dependent KS equations

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{KS}}\right) \phi(\mathbf{r}, t) = i\frac{\partial}{\partial t}\phi(\mathbf{r}, t),$$

electron density given by

$$n(\mathbf{r}, t) = \sum_{i=1}^N |\phi(\mathbf{r}, t)|^2.$$

The density exactly matches the density of the 'real' system of *interacting* electrons.

The accuracy of the method hinges on approximating the **time-dependent exchange-correlation potential**. Where

$$V_{\text{KS}} = V_{\text{ext}} + V_{\text{H}} + V_{\text{xc}}.$$

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# E.g. quantum transport

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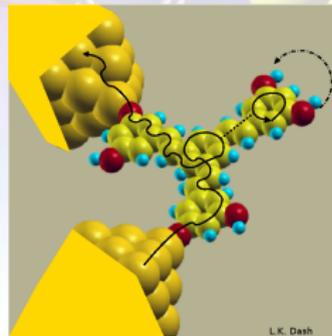
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TDDFT – exact in principle – when applied suffers from the approximation of  $V_{xc}$ .

Or non-interacting theory (Landauer-Büttiker) together with the ground-state Kohn-Sham (KS) potential is used.

Often the currents predicted are orders of magnitude out!





# What's the big iDEA?

The approximations made within DFT do not perform well for time-dependent systems. Why?

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We have developed the **iDEA code** (interacting dynamic electrons approach).

Steps:



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Steps:

- We find the **fully correlated many-body ground-state**



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We have developed the **iDEA code** (interacting dynamic electrons approach).

Steps:

- We find the **fully correlated many-body ground-state**
- Then we apply a bias and propagate  $\Psi(x_1, x_2, x_3, t)$  through time



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The approximations made within DFT do not perform well for time-dependent systems. Why?

We have developed the **iDEA code** (interacting dynamic electrons approach).

Steps:

- We find the **fully correlated many-body ground-state**
- Then we apply a bias and propagate  $\Psi(x_1, x_2, x_3, t)$  through time
- *Reverse engineer*:  $n(x, t) \rightarrow V_{\text{KS}}(x, t)$



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Some details:

- Our systems are one-dimensional – we are modelling nanowires



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Some details:

- Our systems are one-dimensional – we are modelling nanowires
- Our electrons are spinless – more correlation for a given computational effort



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## Some details:

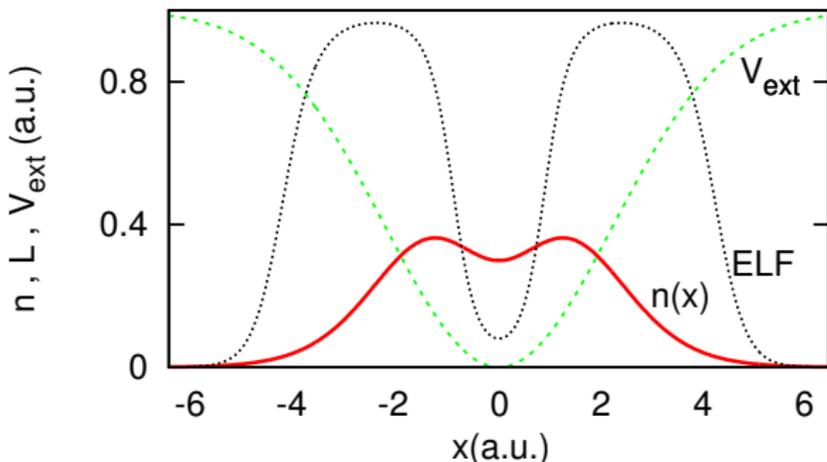
- Our systems are one-dimensional – we are modelling nanowires
- Our electrons are spinless – more correlation for a given computational effort
- We are limited to modelling 3 electrons owing to the computational difficulties of solving the many-electron Schrödinger equation



# Electron localisation

Localisation (in a many-body sense) – the degree to which one electron excludes another from its vicinity.

For our finite systems (modelled using iDEA) we find that there is a strong degree of localisation – owing to Pauli exchange and Coulomb repulsion.



# Approximate density functionals – based on electron localisation

Provided the electrons are sufficiently localised  $\phi_{\text{KS}} \propto \sqrt{n}$

For a single occupied orbital <sup>(1)</sup>:

$$V_{\text{KS}}^{\text{SOA}}(\mathbf{r}) = \frac{\nabla^2 n}{4n} - \frac{[\nabla n]^2}{8n^2}$$

We apply this to systems with multiple occupied orbitals – we term this the single orbital approximation (SOA).

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<sup>(1)</sup>D. W. Smith, S. Jagannathan, and G. S. Handler, Int. J. Quantum Chem. **16**, 103 (1979).

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# Approximate density functionals – based on electron localisation

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For a single occupied orbital <sup>(1)</sup>:

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

We apply this to systems with multiple occupied orbitals - we term this the single orbital approximation (SOA).

(Red: purely time-dependent terms.)

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# Approximate density functionals – based on electron localisation

What if we have an intermediate degree of localisation?

We then mix the SOA with a ‘reference’ potential (e.g. LDA) in proportions based on the degree of localisation:

$$V_{\text{KS}}^{\text{MLP}} = fV_{\text{KS}}^{\text{SOA}} + (1 - f)V_{\text{KS}}^{\text{ref}}.$$

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

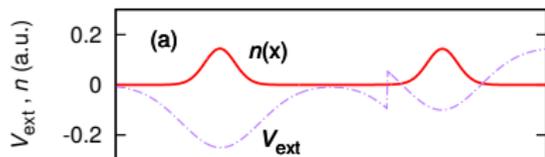
**Key points:**

**Takes into account delocalisation**

**Can be used self-consistently**

# Approximate density functionals – ground-state (strong localisation)

- Coulomb repulsion ensures each electron is in its own well



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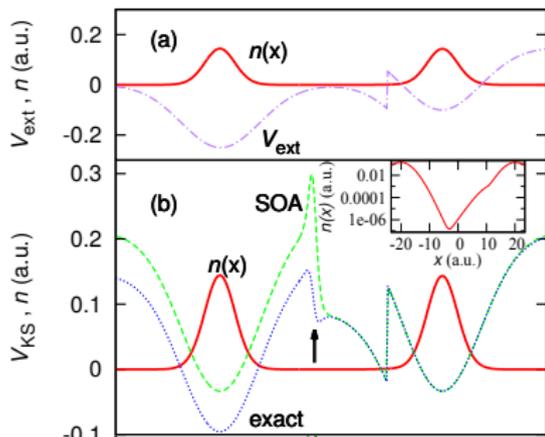
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# Approximate density functionals – ground-state (strong localisation)

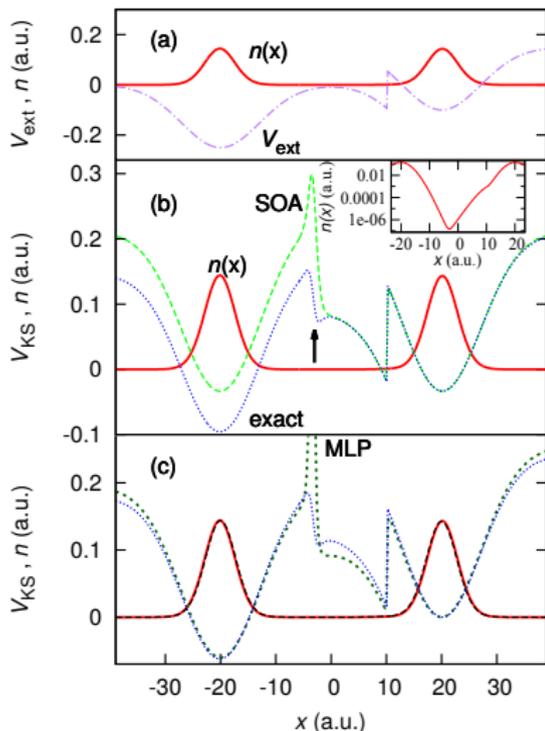
- Coulomb repulsion ensures each electron is in its own well
- Exact  $V_{KS}$  acquires additional step (similar to Almbladh-von Barth)
- SOA also has a step



# Approximate density functionals – ground-state (strong localisation)

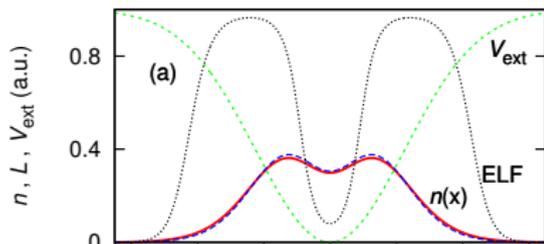
- Coulomb repulsion ensures each electron is in its own well
- Exact  $V_{KS}$  acquires additional step (similar to Almbladh-von Barth)
- SOA also has a step
- MLP, even when used self-consistently, has a good step!
- $f = 0.6$  shown

M. J. P. Hodgson *et al.*,  
 Phys. Rev. B **90**,  
 241107(R) (2014).



# Approximate density functionals – ground-state (partial delocalisation)

- Delocalisation in the centre  
(confirmed by “exact ELF”)



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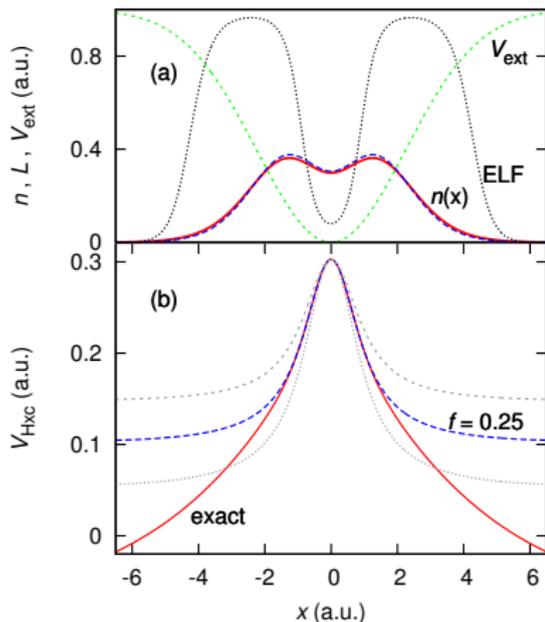
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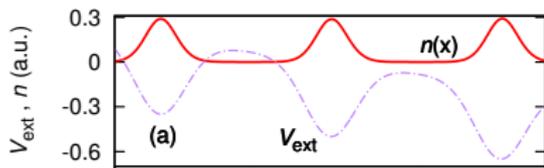
# Approximate density functionals – ground-state (partial delocalisation)

- Delocalisation in the centre (confirmed by “exact ELF”)
- Exact  $V_{KS}$  shows marked (non-LDA) “bump” in the centre
- MLP, even when used self-consistently, has a good bump!
- $f = 0.2, 0.25, 0.3$  shown



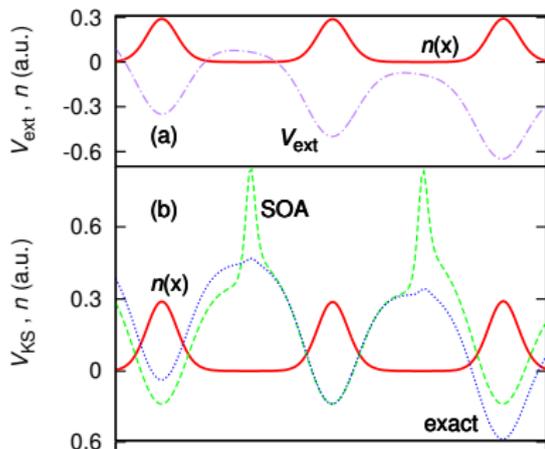
# Approximate density functionals – ground-state (polarised 3-atom chain)

- Exact  $V_{KS}$  shows xc  
'electric field' plus steps  
which keeps electrons on  
their atoms



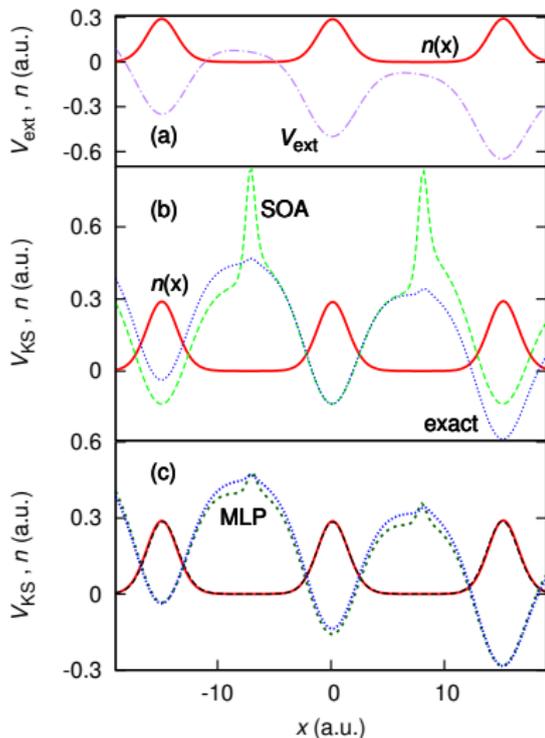
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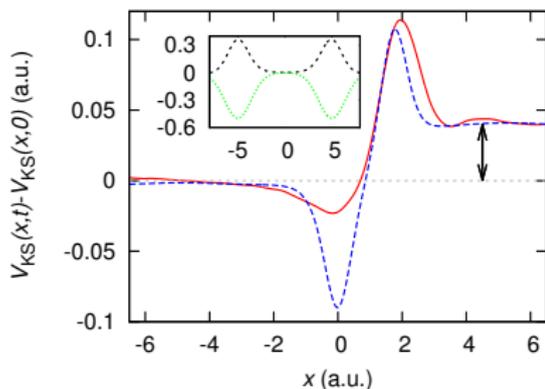
# Approximate density functionals – ground-state (polarised 3-atom chain)

- Exact  $V_{KS}$  shows xc ‘electric field’ plus steps which keeps electrons on their atoms
- SOA has steps and xc field
- MLP has good steps and good field, even when applied self-consistently!
- $f = 0.17$  shown



# Approximate density functionals – time-dependent

- Figure shows  $t = 5$  a.u.
- Exact  $V_{KS}$  shows dynamic step which regulates tunnelling rate between wells



# Approximate density functionals – time-dependent

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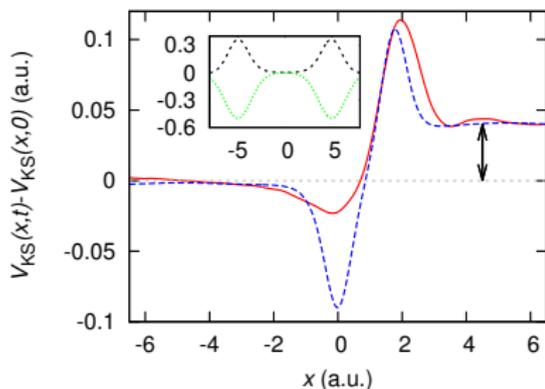
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- Figure shows  $t = 5$  a.u.
- Exact  $V_{KS}$  shows dynamic step which regulates tunnelling rate between wells
- MLP, even when the density is propagated self-consistently, has a good step!
- $f = 0.2$  shown





# Focus on $f(x)$

$f(x)$  determines the degree at which the SOA is used over the reference potential at each point in space.

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# Focus on $f(x)$

$f(x)$  determines the degree at which the SOA is used over the reference potential at each point in space.

$f(x)$ , therefore, must be a measure of the degree of localisation in the system.

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For our four model systems  $f$  is approximated as a constant for the whole system.

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We base the local  $f$  on the ELF for that region.

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We use a **range** of values of  $f$ , and find accurate results across that range.



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For our four model systems  $f$  is approximated as a constant for the whole system.

We base the local  $f$  on the ELF for that region.

We use a **range** of values of  $f$ , and find accurate results across that range.

The next step is to find accurate enough measures of localisation so that  $f$  can be a function of space.



# Summary

- Steps in  $V_{xc}$  are crucial in many cases for producing accurate electron densities

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# Summary

- Steps in  $V_{xc}$  are crucial in many cases for producing accurate electron densities
- Commonly used approximate functionals do not produce steps in  $V_{xc}$

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- Steps in  $V_{xc}$  are crucial in many cases for producing accurate electron densities
- Commonly used approximate functionals do not produce steps in  $V_{xc}$
- The MLP:

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- Steps in  $V_{xc}$  are crucial in many cases for producing accurate electron densities
- Commonly used approximate functionals do not produce steps in  $V_{xc}$
- The MLP:
  - gives accurate steps and densities when used self-consistently, even for time-dependent steps



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- Steps in  $V_{xc}$  are crucial in many cases for producing accurate electron densities
- Commonly used approximate functionals do not produce steps in  $V_{xc}$
- The MLP:
  - gives accurate steps and densities when used self-consistently, even for time-dependent steps
  - works well even for regions of delocalisation

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- Steps in  $V_{xc}$  are crucial in many cases for producing accurate electron densities
- Commonly used approximate functionals do not produce steps in  $V_{xc}$
- The MLP:
  - gives accurate steps and densities when used self-consistently, even for time-dependent steps
  - works well even for regions of delocalisation
  - offers a new approach to approximate density functionals

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**Paper:** M.J.P. Hodgson *et al.*, Phys. Rev. B **90**, 241107(R) (2014)

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# Extra slides – exchange-correlation potentials

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