Electron localisation in exact time-dependent density-functional potentials

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February 27, 2015

What's coming up?

- 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

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

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.

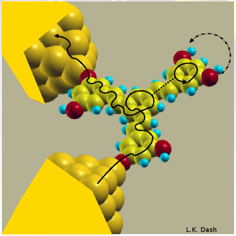
The accuracy of the method hinges on approximating the time-dependent exchange-correlation potential. Where

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

E.g. quantum transport

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.


L.K. Dash

Often the currents predicted are orders of magnitude out!

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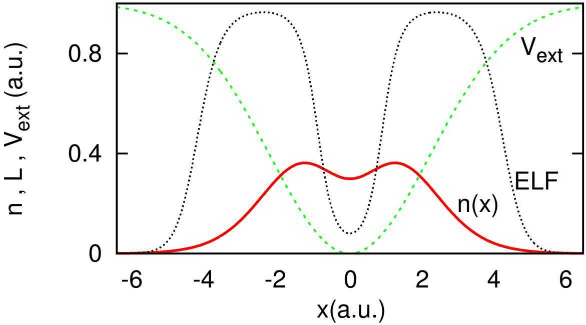
- Then we apply a bias and propagate $\Psi(x_1, x_2, x_3, t)$ through time
- *Reverse engineer*: $n(x,t) \rightarrow V_{\mathrm{KS}}(x,t)$

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 $\phi_{\mathrm{KS}} \propto \sqrt{n}$

For a single occupied orbital (1):

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

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

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(1) D. W. Smith, S. Jagannathan, and G. S. Handler, Int. J. Quantum Chem. **16**, 103 (1979).
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$$V_{\mathrm{KS}}^{\mathrm{SOA}}(\mathbf{r}, t) = \frac{\nabla^2 n}{4n} - \frac{[\nabla n]^2}{8n^2} - \int_{-\infty}^{\mathbf{r}} \frac{\partial \mathbf{u}}{\partial t} \cdot \mathrm{d}\mathbf{r}' - \frac{1}{2} u^2$$

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(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:

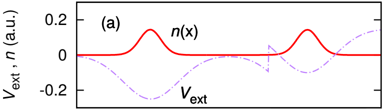
$$V_{\mathrm{KS}}^{\mathrm{MLP}} = f V_{\mathrm{KS}}^{\mathrm{SOA}} + (1 - f) V_{\mathrm{KS}}^{\mathrm{ref}}.$$

We term this the mixed localisation potential (MLP).

Key points:
Takes into account delocalisation
Can be used self-consistently

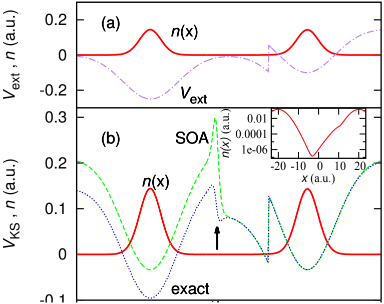
Approximate density functionals – ground-state (strong localisation)

- Coulomb repulsion ensures each electron is in its own well



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



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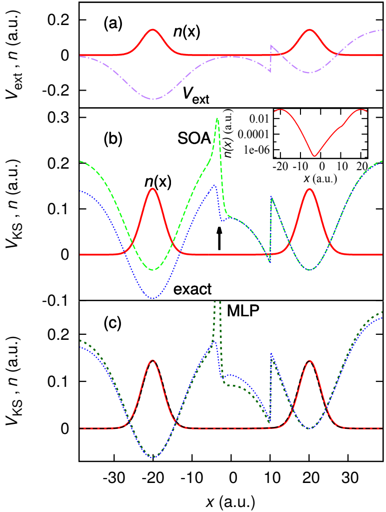
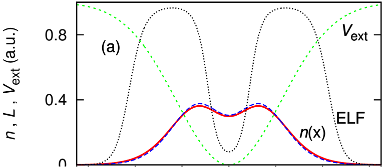
- Coulomb repulsion ensures each electron is in its own well
- Exact V_{KS} acquires additional step (similar to Almbladh-von Barth)
- SOA also has a step
- MLP, even when used self-consistently, has a good step!
- $f = 0.6$ shown

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



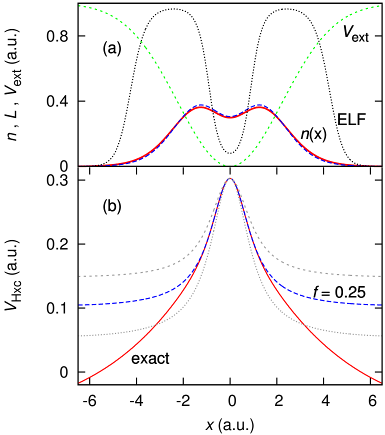
Approximate density functionals – ground-state (partial delocalisation)

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



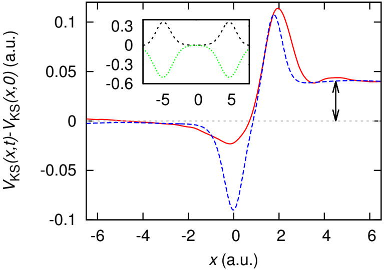
Approximate density functionals – ground-state (partial delocalisation)

- 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



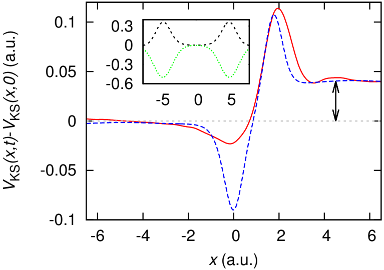
Approximate density functionals – time-dependent

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



Approximate density functionals – time-dependent

- 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



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  → gives accurate steps and densities when used self-consistently, even for time-dependent steps
  → works well even for regions of delocalisation

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}
- 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)

Acknowledgements: Funding from EPSRC

Extra slides – finding $f(x)$

$f(x)$ 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.

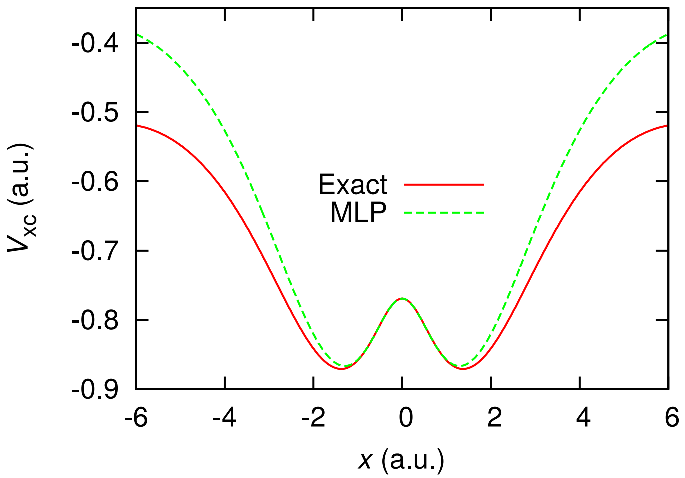
For our three model systems f is approximated as a constant for the whole system.

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.

Extra slides – exchange-correlation potentials



Extra slides – self-consistent ground-state

See videos...