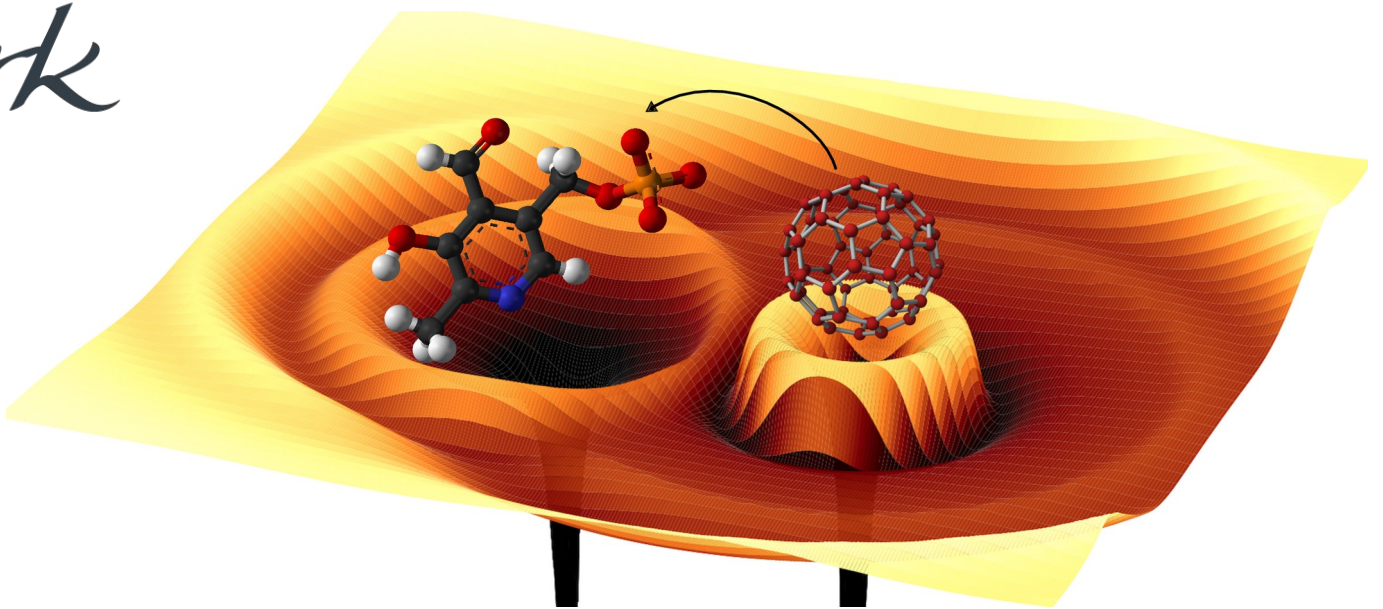
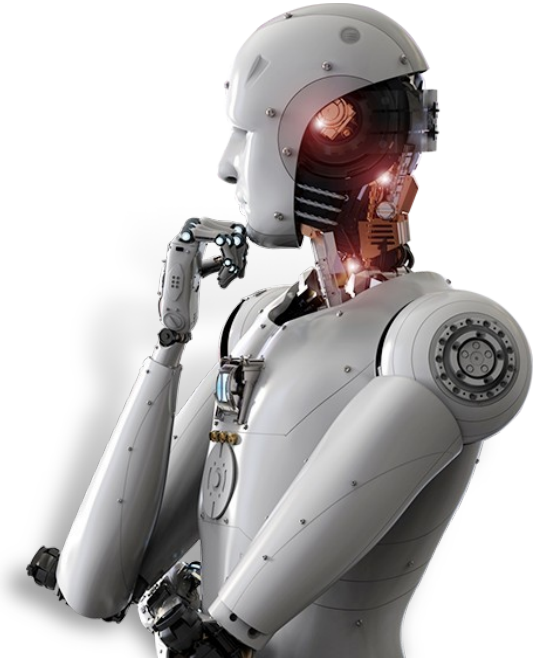
Should discontinuities in the Kohn-Sham potential be avoided or exploited?



Matt Hodgson
CCP9 conference 2022, Manchester

Why do we care about Kohn-Sham density functional theory?

The next generation of technologies require reliable models of electron excitation



Why does density functional theory need the Kohn-Sham system?

Rather than calculating the energy from the wavefunction:

$$E = \langle \Psi | \hat{H} | \Psi \rangle$$

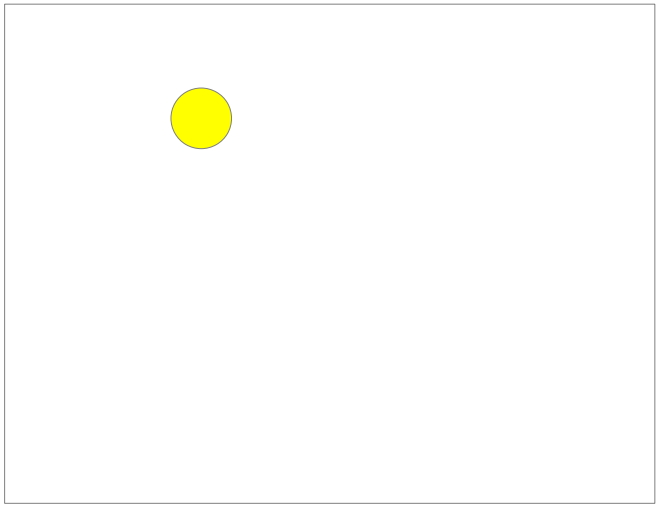
We calculate the energy from the density

$$E = E[n]$$

Why does density functional theory need the Kohn-Sham system?

Real system of
interacting electrons

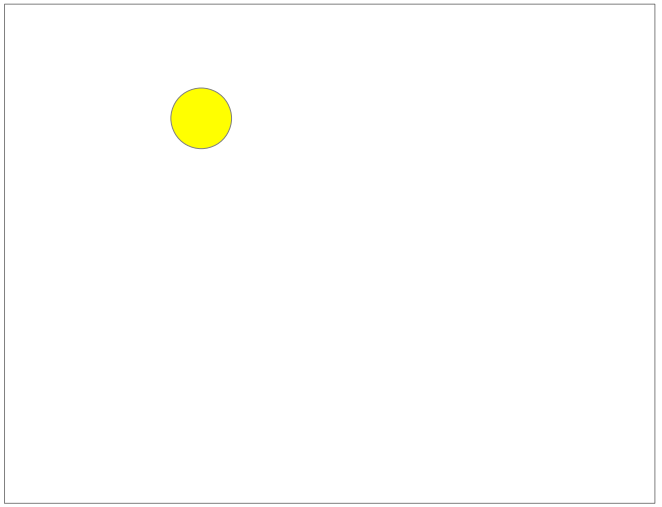
$V(\vec{r})$



$\Psi(\vec{r}_1)$

Fictitious system of
non-interacting electrons

$V_s(\vec{r})$



$\phi(\vec{r}_1)$

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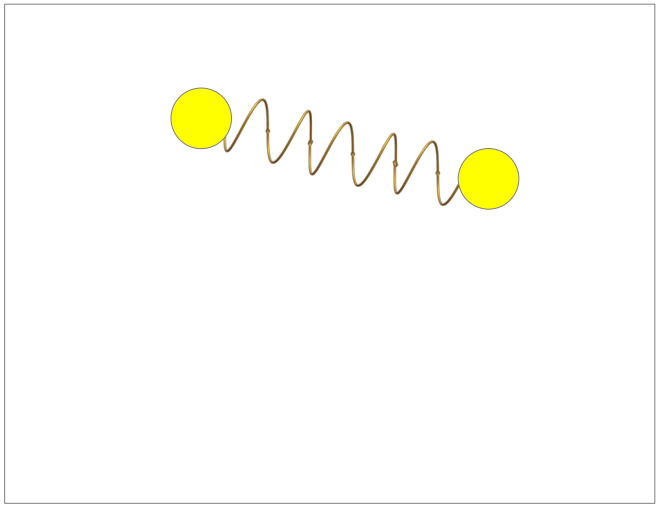
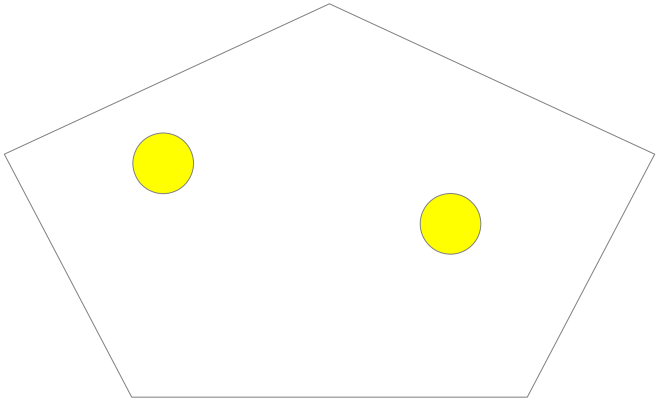


$\Psi(\vec{r}_1, \vec{r}_2)$

Fictitious system of
non-interacting electrons

$V_s(\vec{r})$



$\phi(\vec{r}_1), \phi(\vec{r}_2)$

Why does density functional theory need the Kohn-Sham system?

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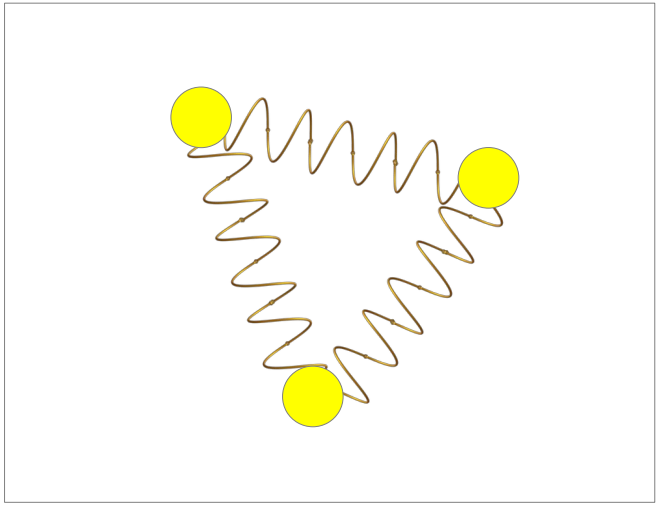
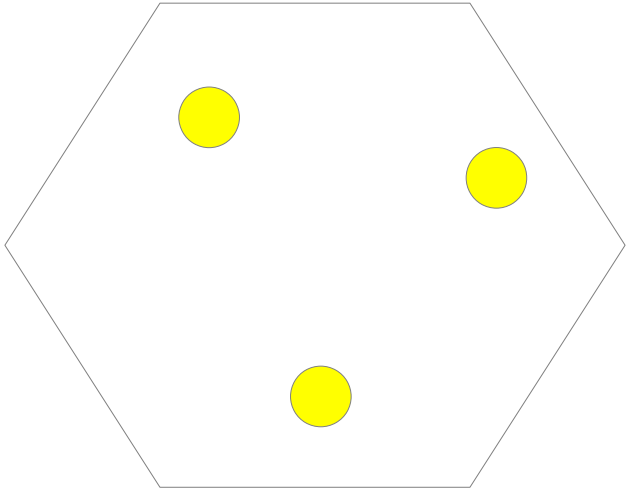


$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3)$

Fictitious system of
non-interacting electrons

$V_s(\vec{r})$



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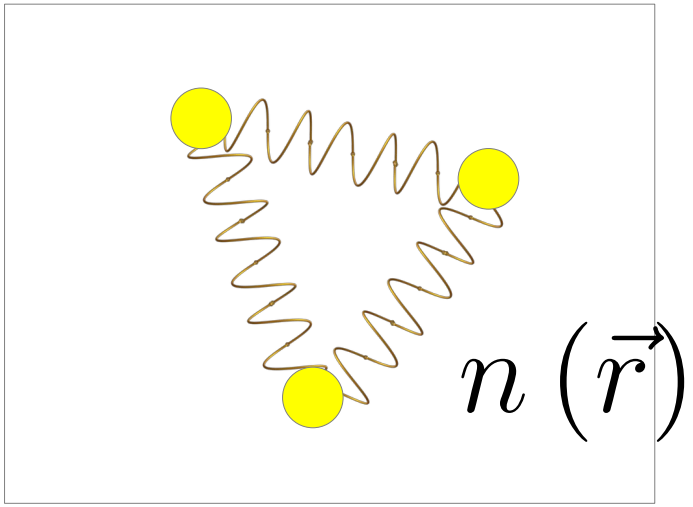

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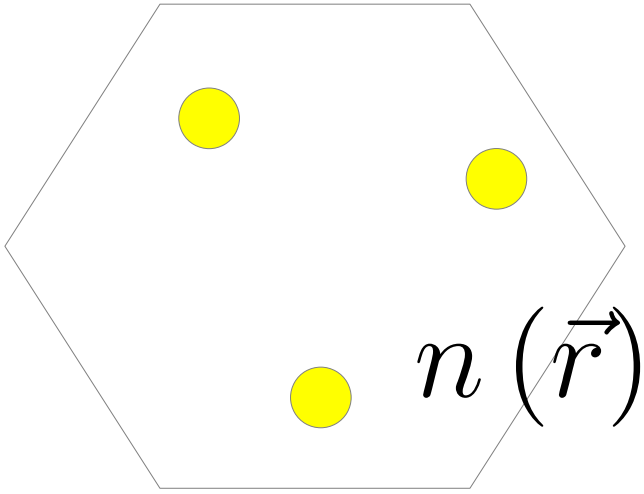


$\phi(\vec{r}_1), \phi(\vec{r}_2), \phi(\vec{r}_3)$

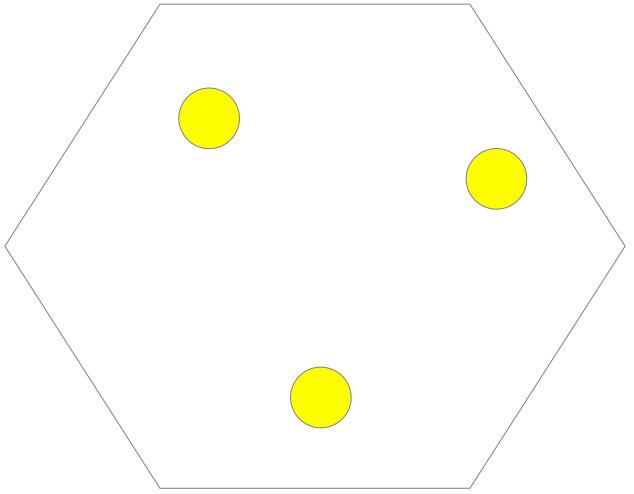
Why does density functional theory need the Kohn-Sham system?

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{s}}(\vec{r})\right)\phi(\vec{r}) = \varepsilon\phi(\vec{r})$$

$$n(\vec{r}) = \sum |\phi(\vec{r})|^2$$

Fictitious system of
non-interacting electrons

$V_{\mathrm{s}}(\vec{r})$



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Fictitious system of
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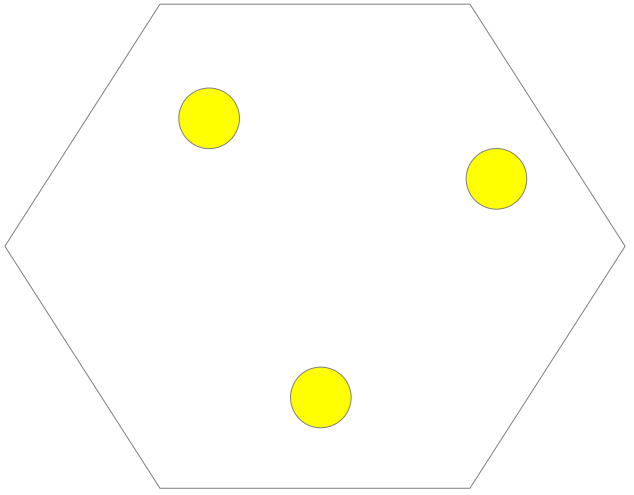

$$\phi(\vec{r}_1), \phi(\vec{r}_2), \phi(\vec{r}_3)$$

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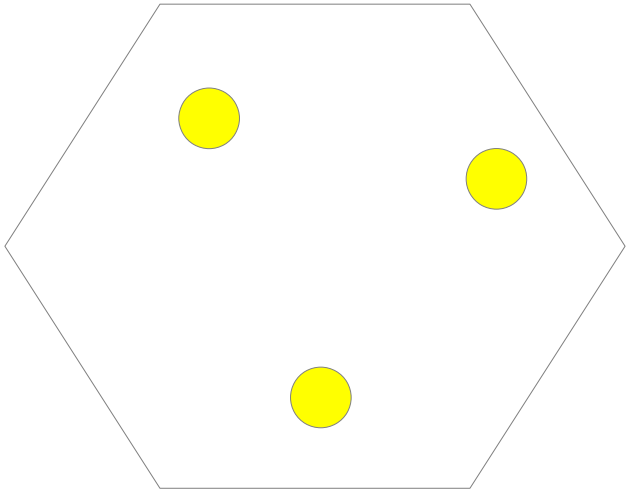
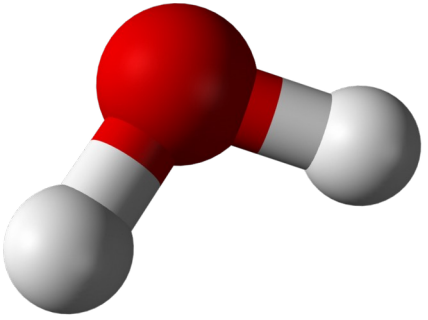


$\phi(\vec{r}_1), \phi(\vec{r}_2), \phi(\vec{r}_3)$

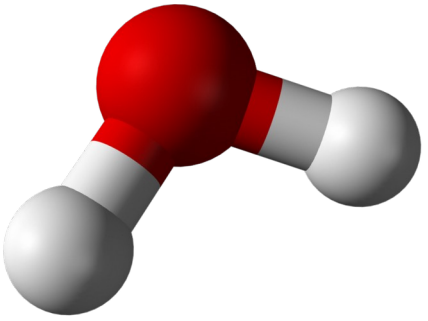
Studying the *exact* Kohn-Sham system

V_{ext}



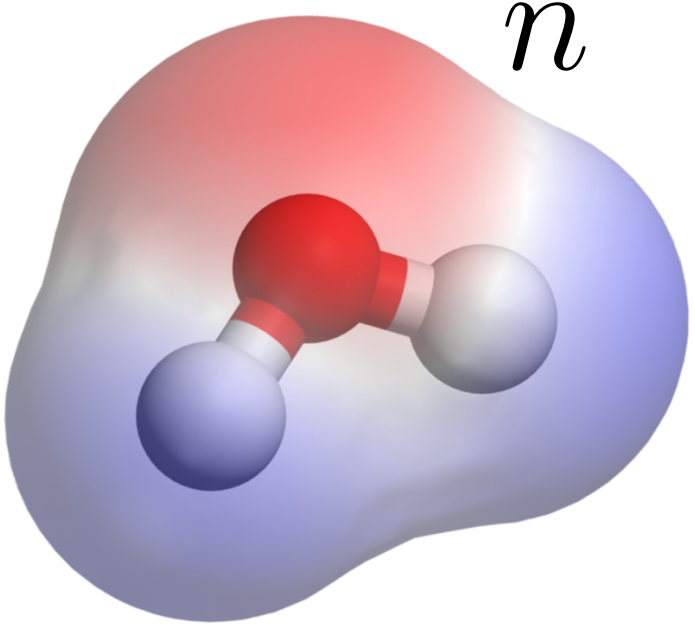
Studying the *exact* Kohn-Sham system

V_{ext}



$\hat{H}\Psi = E\Psi$

n



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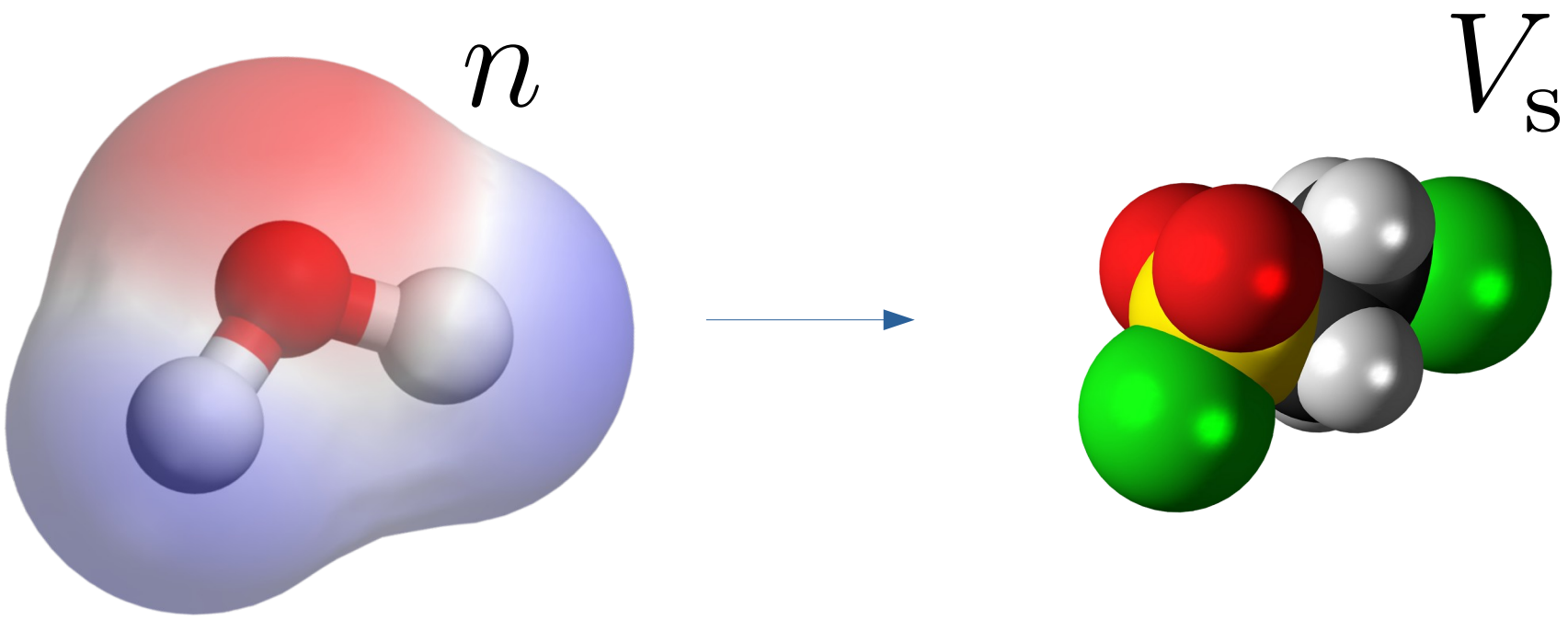
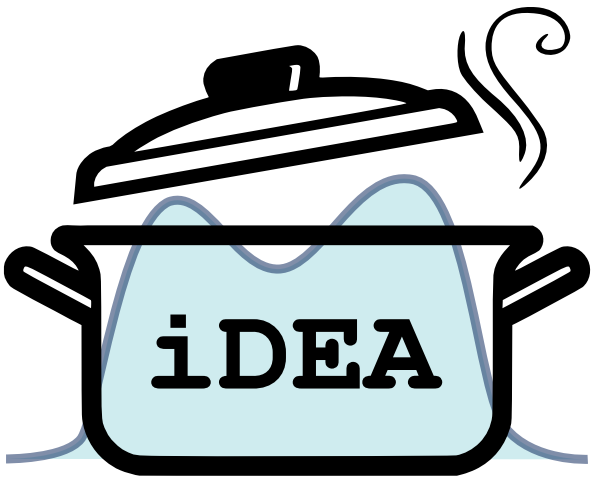


‘DFT in reverse’

The iDEA code

- Exact solutions to the many-electron problem in 1D
- Free choice of external potential (that may be time-dependent) for any number of electrons with any spin configuration
- Implementation of various approximate methods for comparison
- Implementation of all common observables
- Reverse-engineering to solve potential inversion, from exact Kohn-Sham DFT and beyond



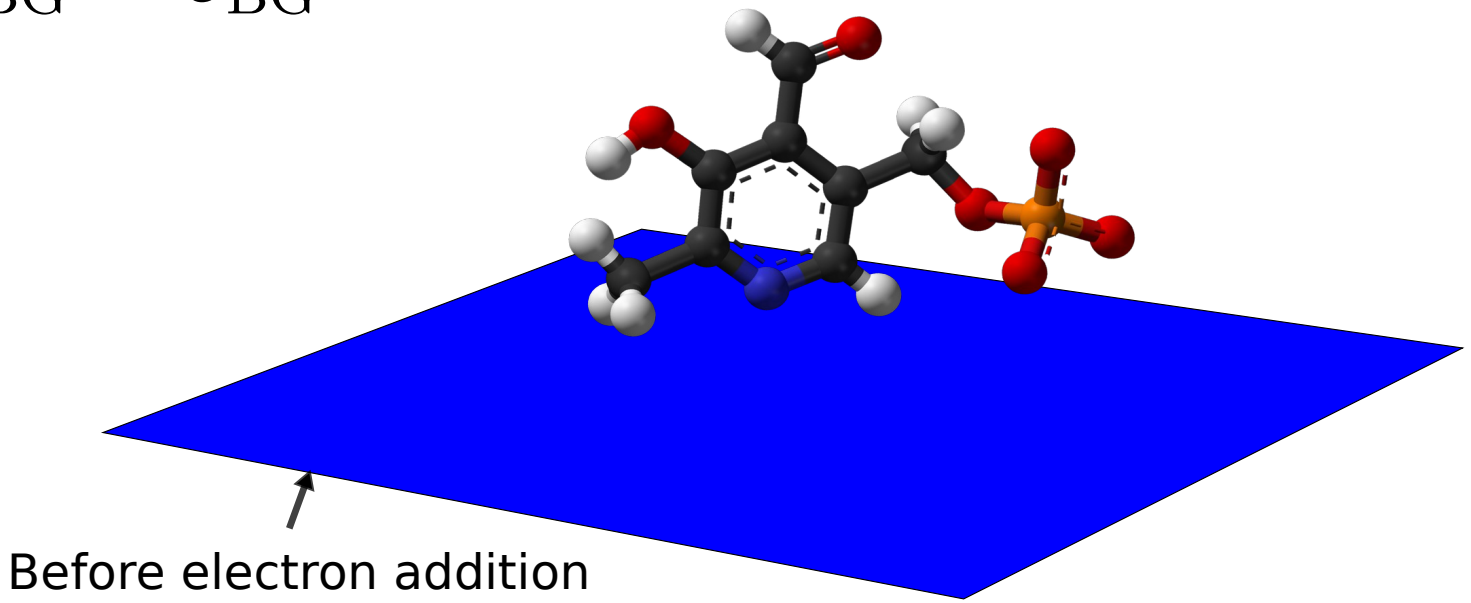
“Exploring exact solutions and practical approximations in many-electron quantum mechanics”

- Fully parallelised using OpenBLAS
- Fully parallelised for all cuda supporting GPUS

“Exact time-dependent density-functional potentials for strongly correlated tunneling electrons”
M. J. P. Hodgson, J. D. Ramsden, J. B. J. Chapman, P. Lillystone, and R. W. Godby, Physical Review B **88**, 241102(R) (2013)

Band gap from the Kohn-Sham system

$$E_{\mathrm{BG}} \approx \varepsilon_{\mathrm{BG}}$$



"Density-Functional Theory for Fractional Particle Number: Derivative Discontinuities of the Energy"
J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz Jr, Phys. Rev. Lett. **49**, 1691 (1982)

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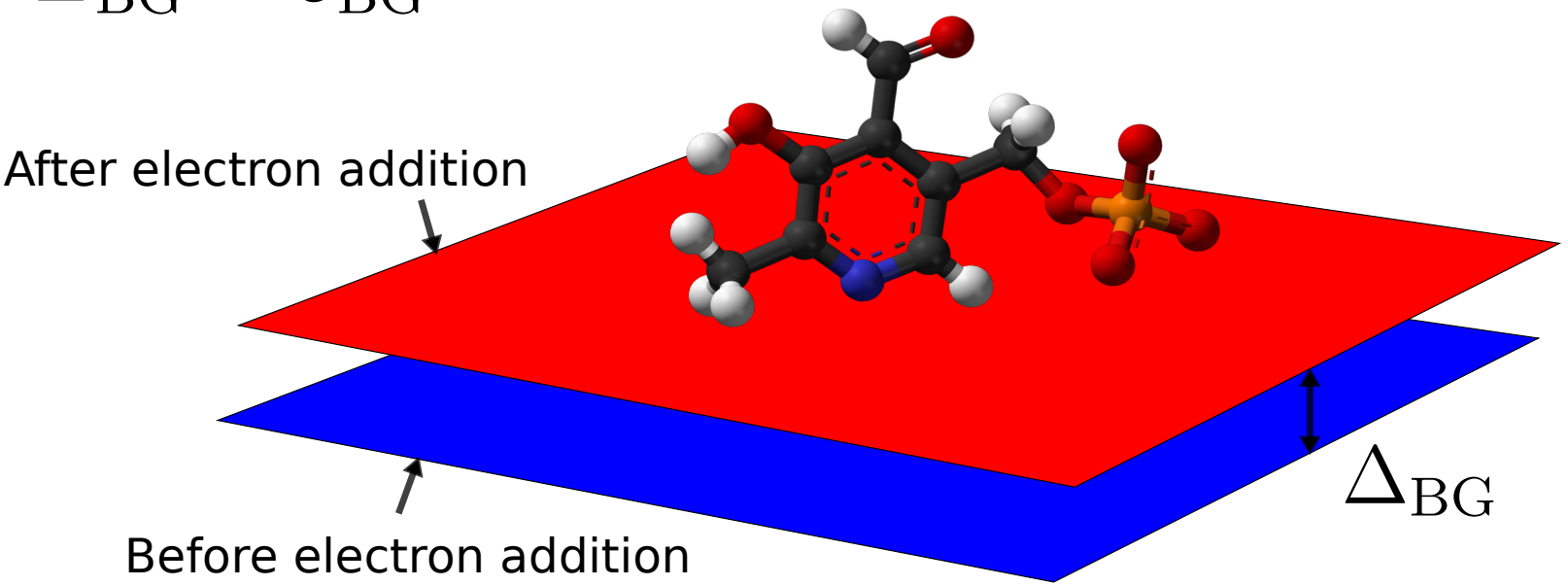

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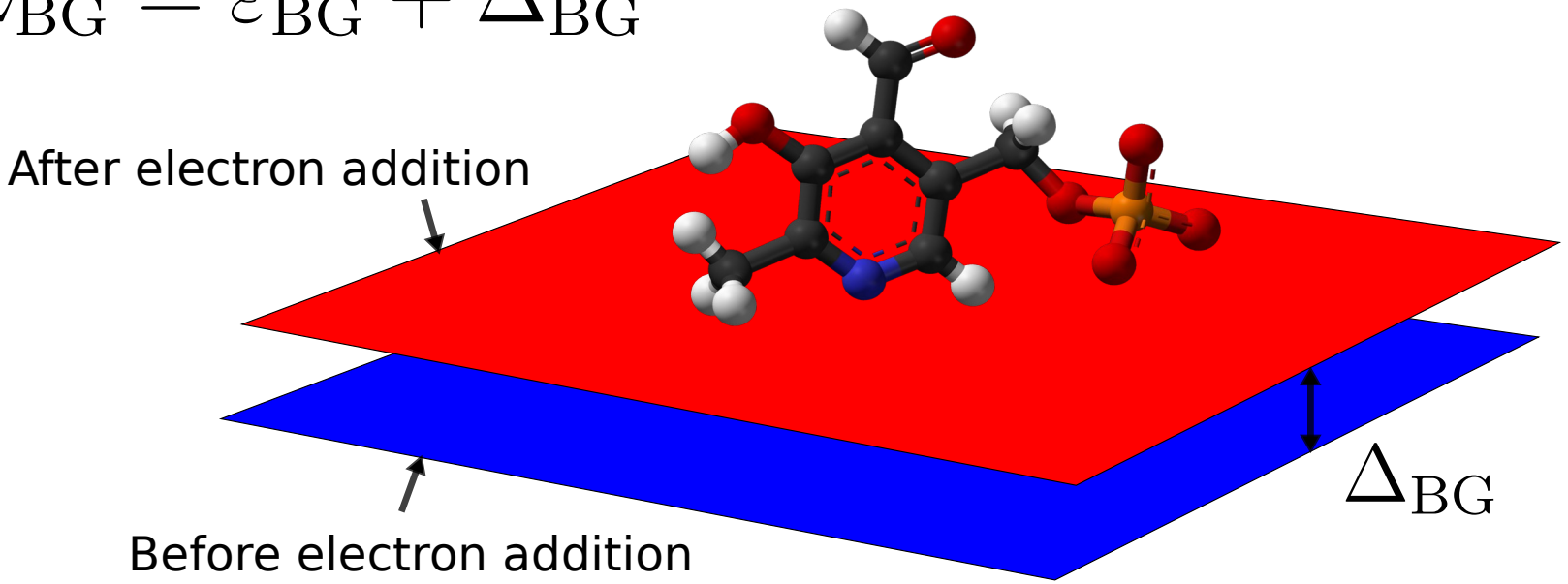

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How can get excitation energies from the Kohn-Sham system?

"From Kohn-Sham to many-electron energies via step structures in the exchange-correlation potential",

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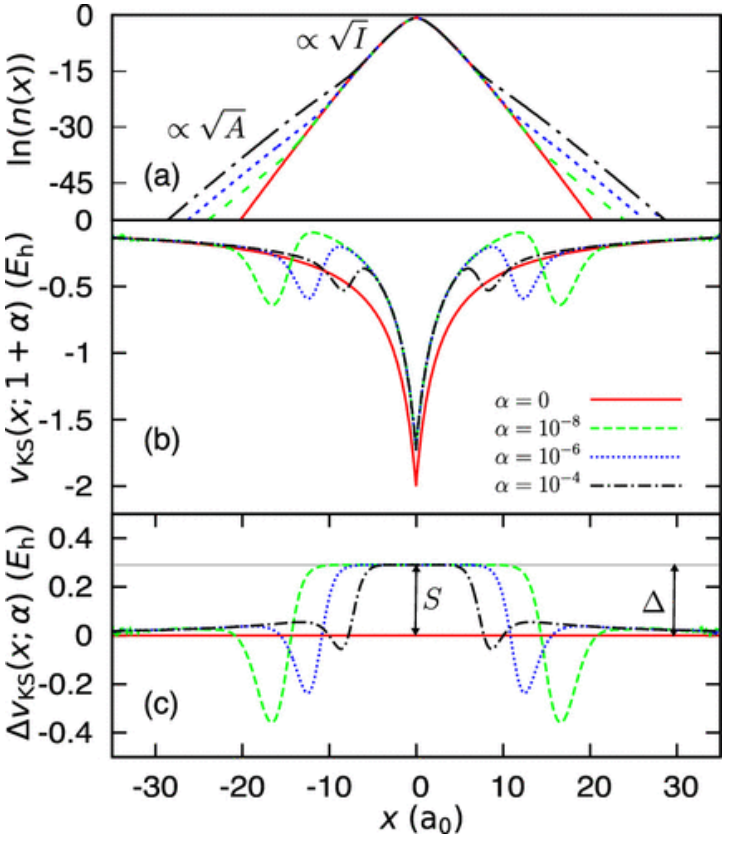
Journal of Chemical Theory and Computation
17 (3), 1390–1407 (2021)



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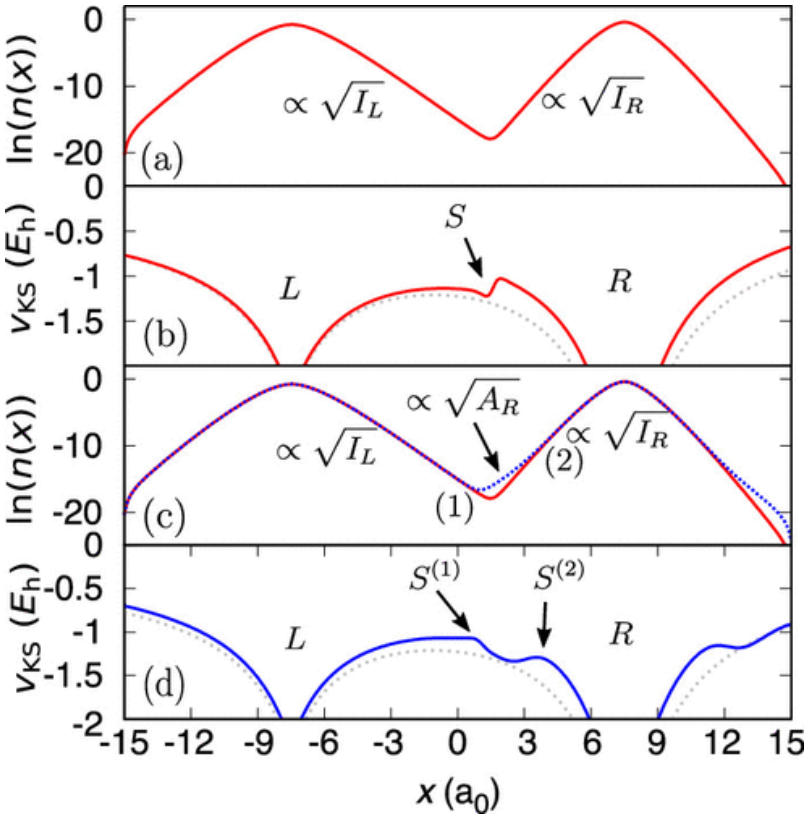
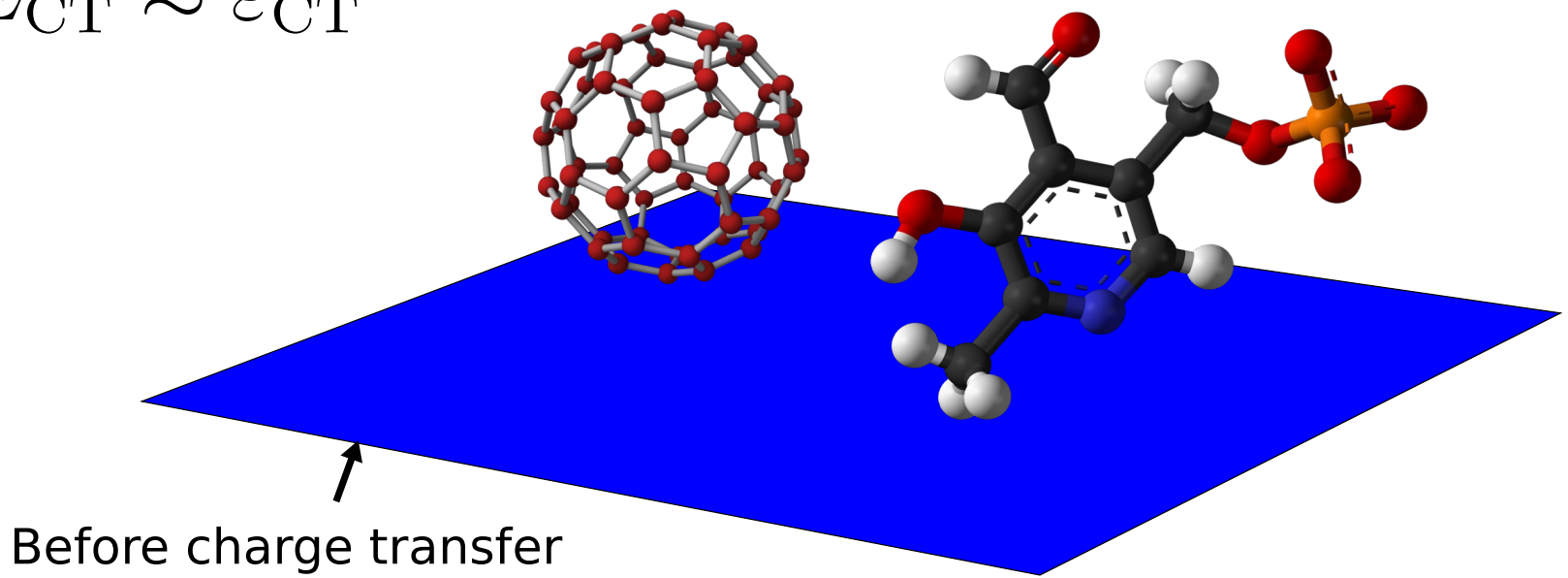


Charge-transfer energy from the Kohn-Sham system

$$E_{\mathrm{CT}} \approx \varepsilon_{\mathrm{CT}}$$



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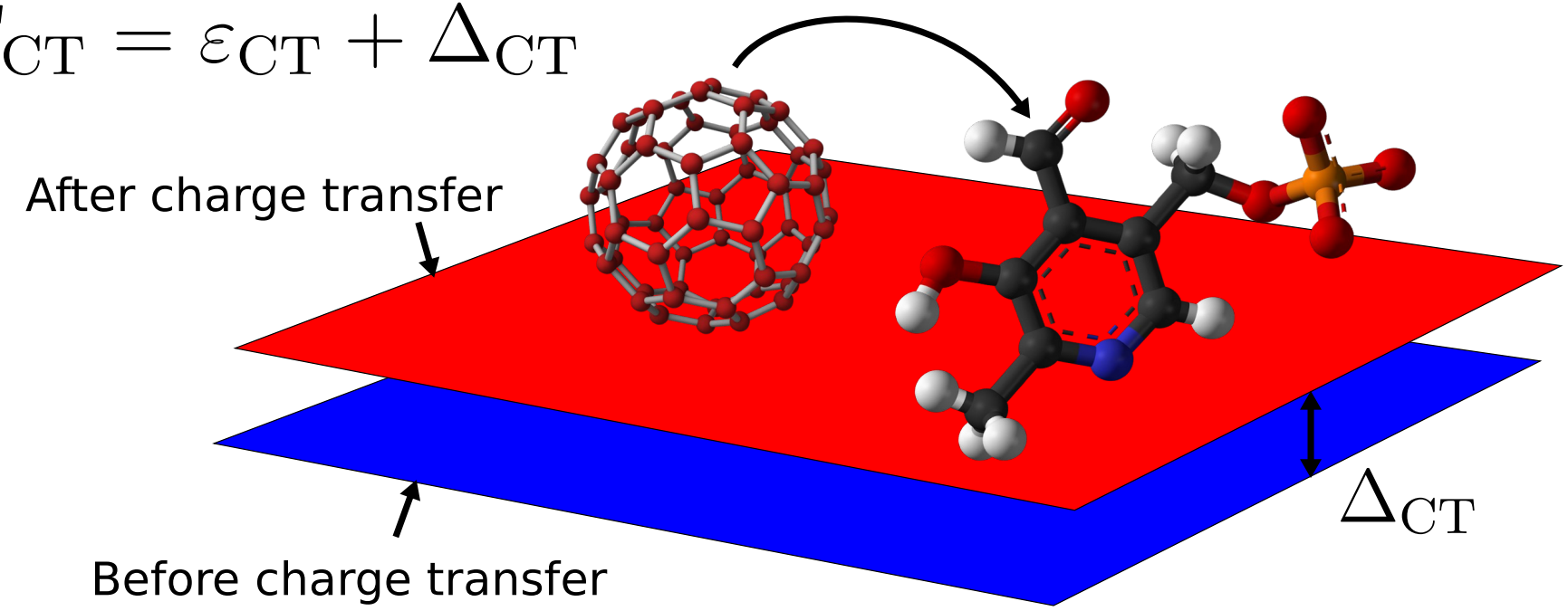
$$E_{\mathrm{CT}} = \varepsilon_{\mathrm{CT}} + \Delta_{\mathrm{CT}}$$



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How do we capture these shifts in approximations?

$$\nabla^2 V = -4\pi\rho$$

“Improving the exchange and correlation potential in density functional approximations through constraints”,
T. J. Callow, B. J. Pearce, T. Pitts, N. N. Lathiotakis, M. J. P. Hodgson and N. I. Gidopoulos, Faraday Discussions 224, 126-144 (2020)

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$$\nabla^2 V = -4\pi\rho$$

$$\nabla^2 V_{\mathrm{Hxc}} = -4\pi\rho_{\mathrm{Hxc}}$$

$$V_{\mathrm{Hxc}} = V_{\mathrm{s}} - V_{\mathrm{ext}}$$

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$$\nabla^2 V_{\mathrm{Hxc}} = -4\pi\rho_{\mathrm{Hxc}}$$

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$$Q^N_{\mathrm{Hxc}} = \int \rho^N_{\mathrm{Hxc}}(\vec{r})\ \mathrm{d}^3 r = N - 1$$

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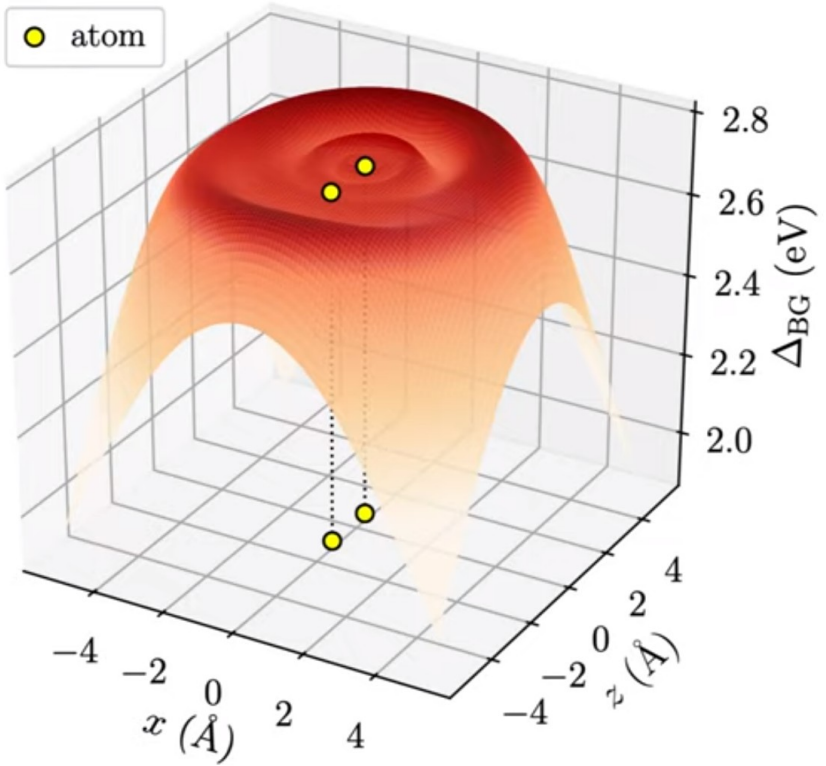
How do we capture these shifts in approximations?

$$Q^N_{\mathrm{Hxc}} = N - 1$$

$$\lim_{\delta \to 0} Q^{N+\delta}_{\mathrm{Hxc}} = N$$



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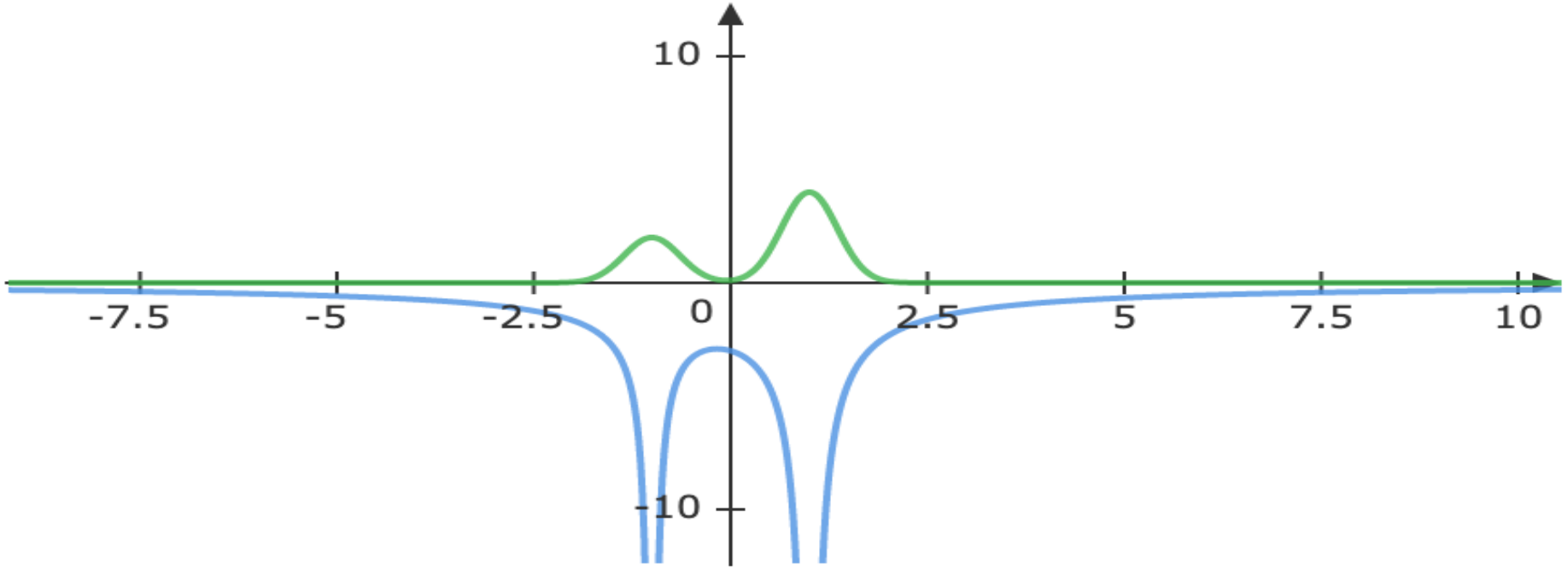
Molecular disassociation in the Kohn-Sham system



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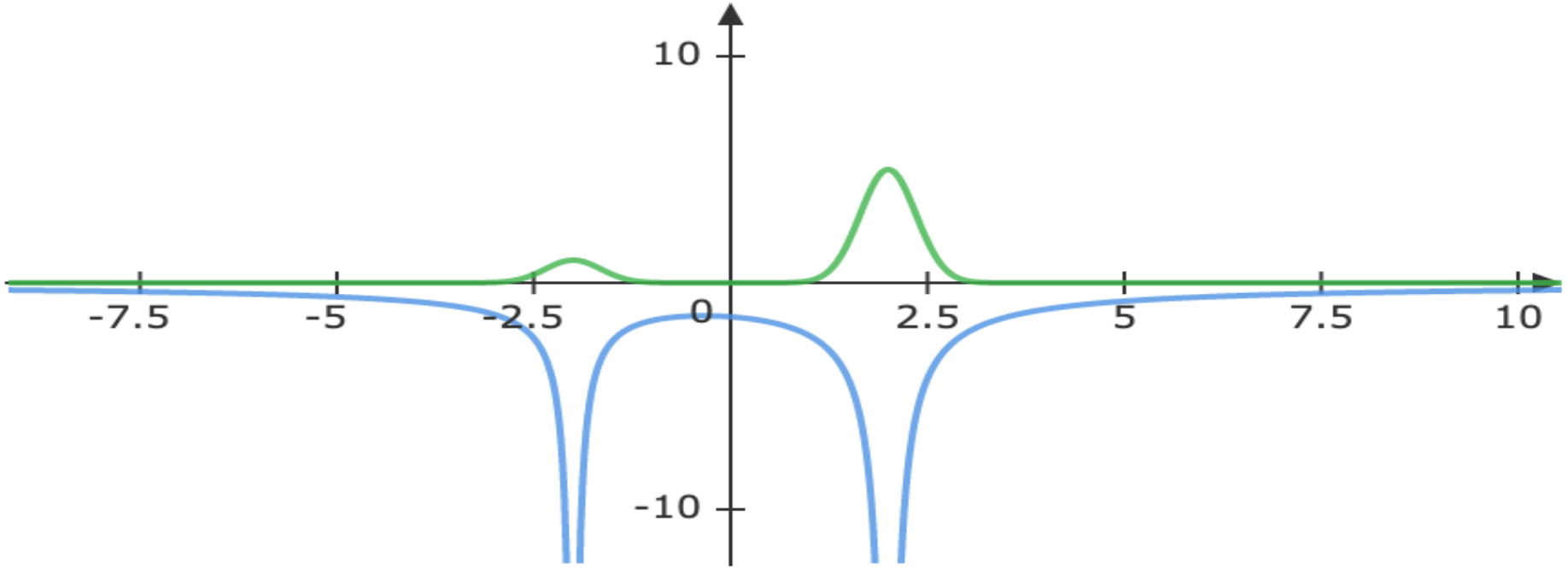

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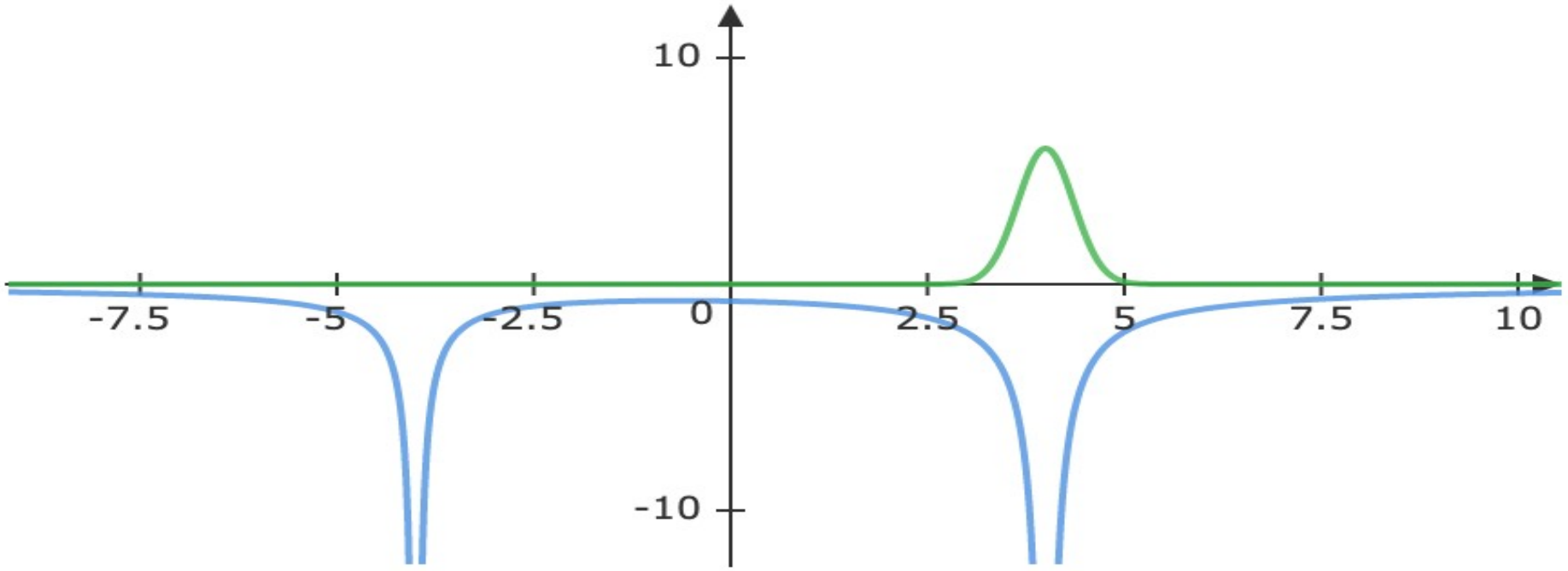

“Challenges for Density Functional Theory”
Aron J. Cohen, Paula Mori-Sánchez, and Weitao Yang, Chem. Rev. 2012, **112**, 1, 289–320

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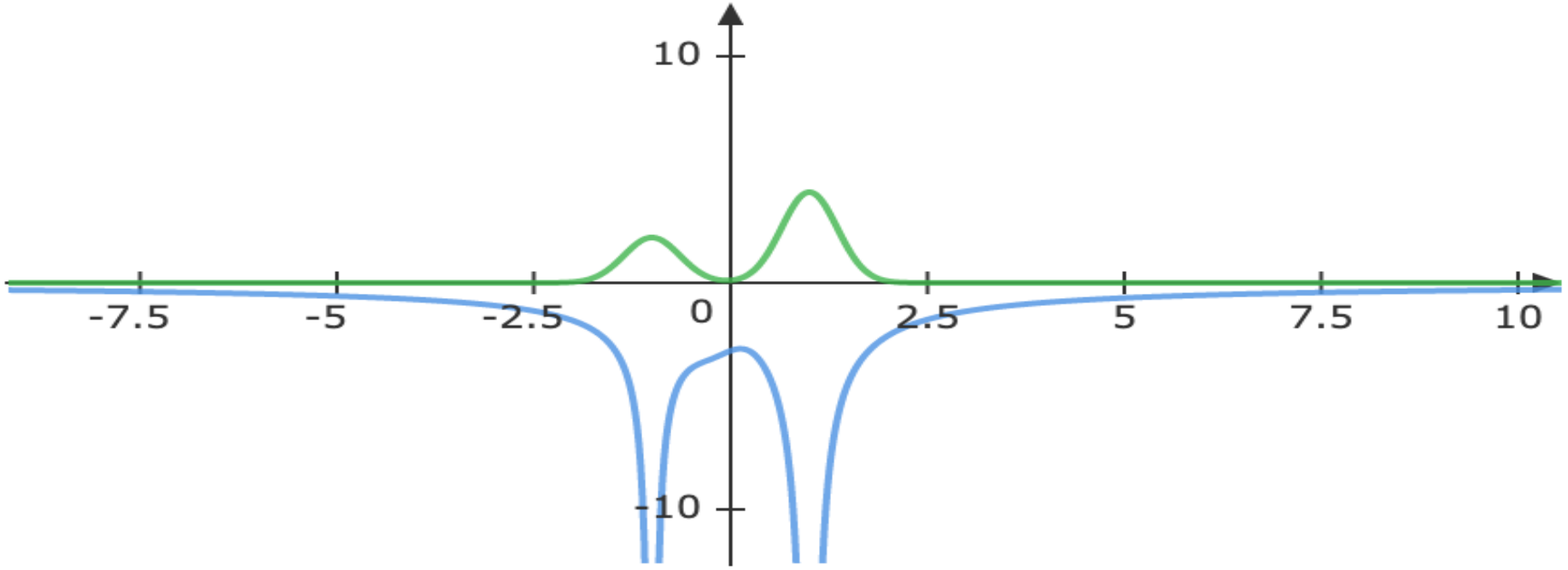

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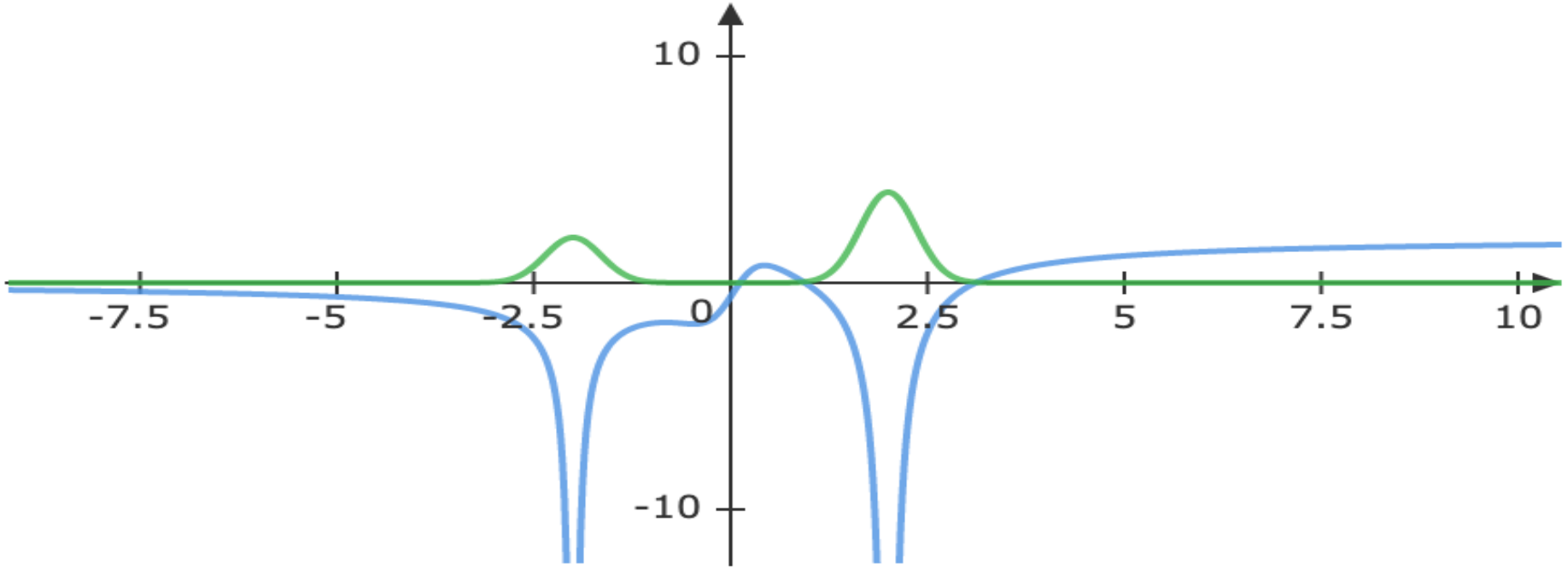

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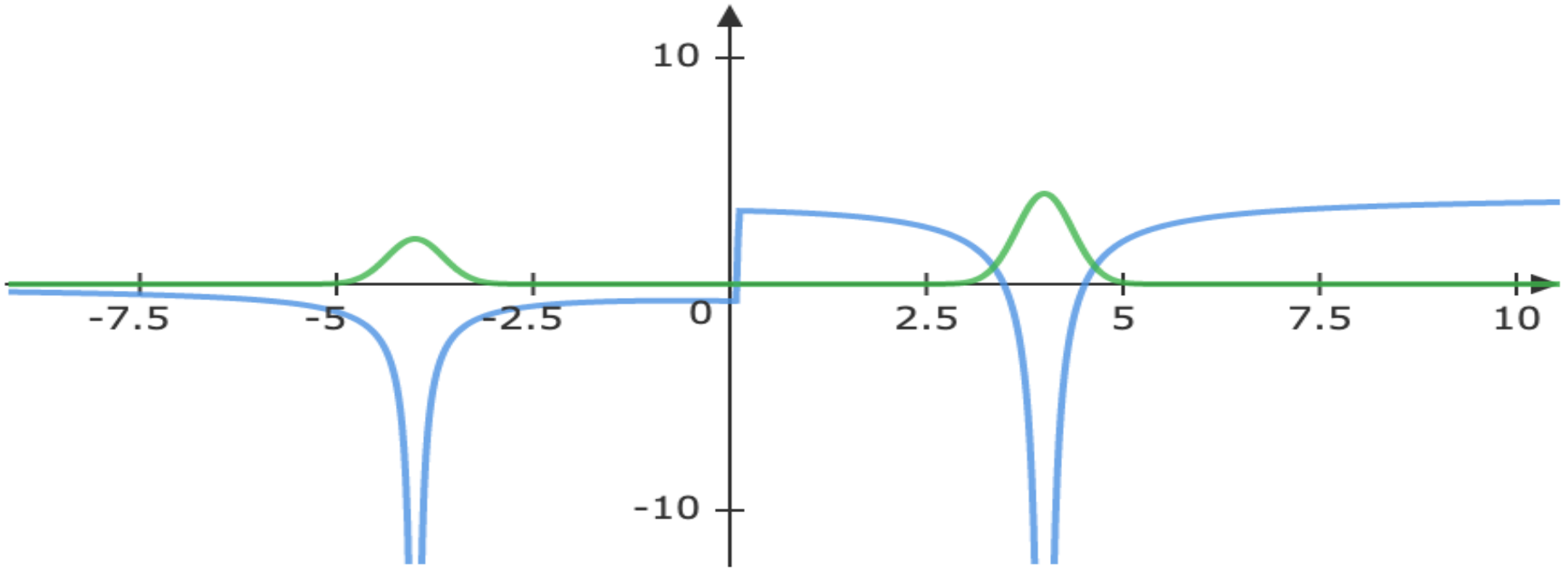
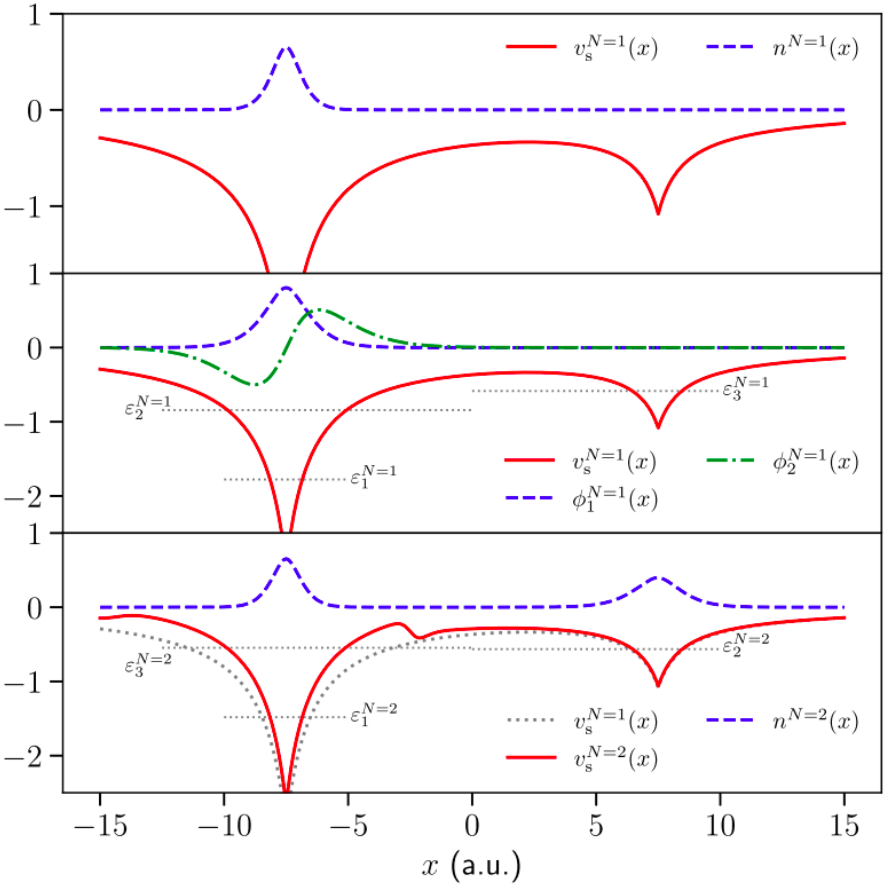


“How Interatomic Steps in the Exact Kohn-Sham Potential Relate to Derivative Discontinuities of the Energy”,
M. J. P. Hodgson, E. Kraisler, A. Schild, and E. K. U. Gross, The Journal of Physical Chemistry Letters 8 (24), 5974–5980 (2017)

Molecular disassociation in the Kohn-Sham system

“Exact expressions for the height of the interatomic step in the exchange-correlation potential from the derivative discontinuity of the energy”

M. J. P. Hodgson, Physical Review A **104**, 032803 (2021)



How do we capture these shifts in approximations?

Kohn-Sham

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{s}}(\vec{r})\right)\phi(\vec{r}) = \varepsilon\phi(\vec{r})$$

Generalised Kohn-Sham

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{L}}(\vec{r})\right)\phi(\vec{r}) + \int V_{\mathrm{NL}}(\vec{r},\vec{r}\,')\phi(\vec{r}\,')\mathrm{d}^3r' = \varepsilon\phi(\vec{r})$$

How do we capture these shifts in approximations?

Kohn-Sham

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{s}}(\vec{r})\right)\phi(\vec{r}) = \varepsilon\phi(\vec{r})$$

Unrestricted Hartree-Fock Kohn-Sham

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\vec{r}) + V_{\mathrm{H}}(\vec{r}) + V_{\mathrm{c}}(\vec{r})\right)\phi^{\gamma}(\vec{r}) + \int F_{\mathrm{x}}^{\gamma}(\vec{r},\vec{r}\,')\phi^{\gamma}(\vec{r}\,')\mathrm{d}^3r' = \varepsilon\phi^{\gamma}(\vec{r})$$

"Accurate real-time evolution of electron densities and ground-state properties from generalized Kohn-Sham theory", M. J. P. Hodgson and J. Wetherell, Physical Review A **101**, 032502 (2020)

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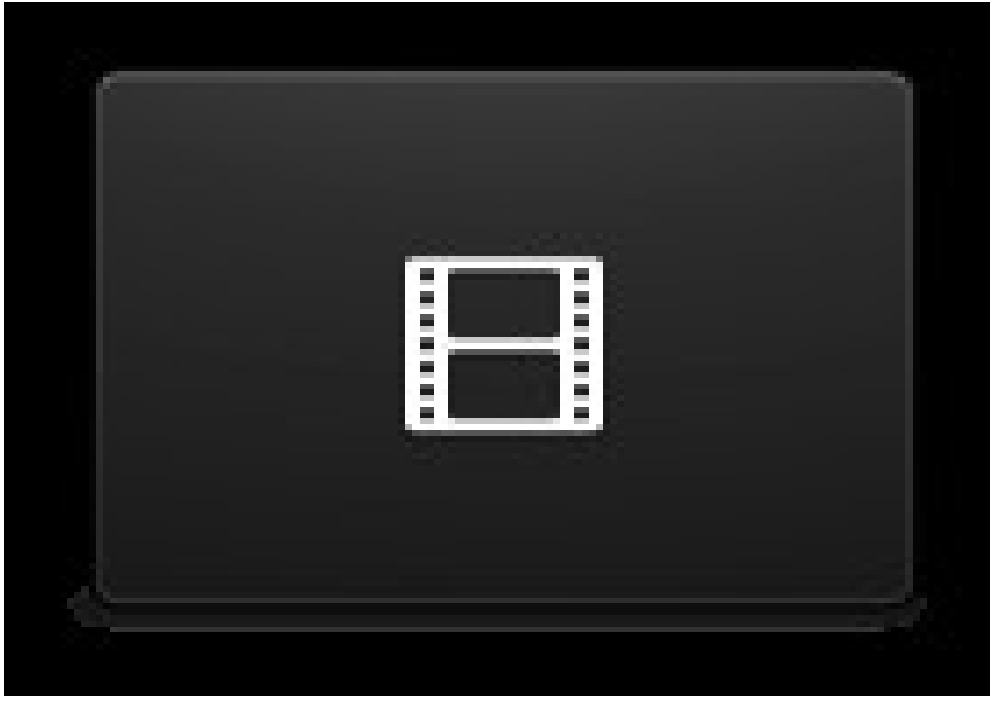


Summary

- Some features of the exact Kohn-Sham potential are discontinuous
- These features are needed to describe excitation properties
- We can either try to capture them with advanced approximations or redesign the Kohn-Sham system

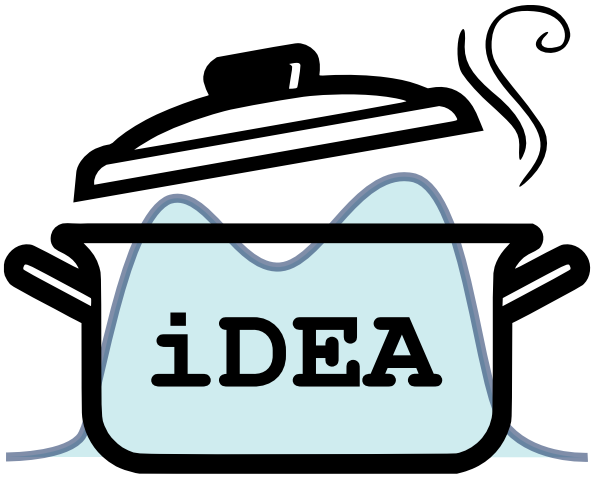
The iDEA code

To install the latest version of the iDEA code:

- pip install iDEA-latest

To add iDEA to your poetry environment:

- poetry add iDEA-latest



“Exploring exact solutions and practical approximations in many-electron quantum mechanics”

iDEA webpage: https://idea-org.github.io/

Fork from Github: https://github.com/iDEA-org/iDEA.git