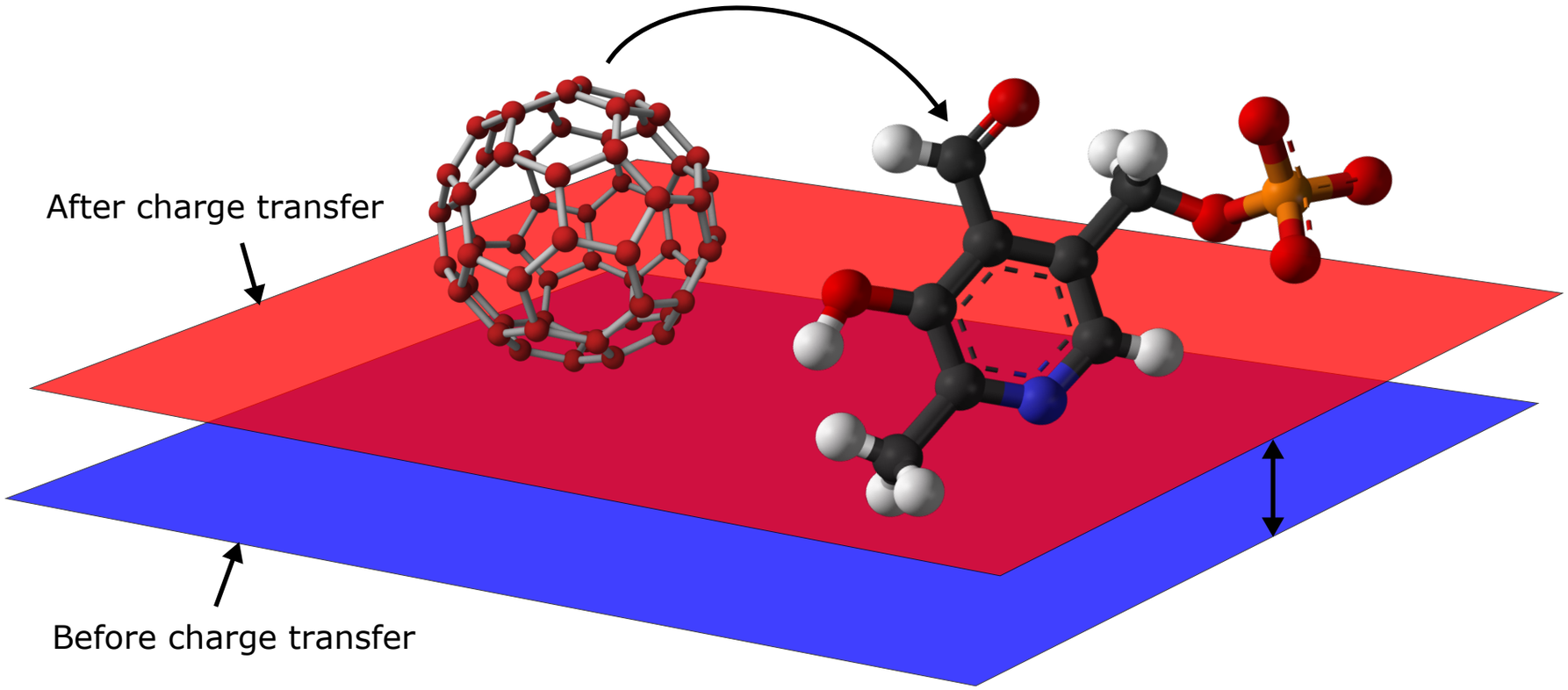
Should discontinuities in the Kohn-Sham potential be avoided or exploited?

Nankai University Zoom symposium on modern methods in theory and computation, 10/06/2022



Matt Hodgson, University of York, UK (matt.hodgson@york.ac.uk)

Density functional theory

$$O = \langle \Psi | \hat{O} | \Psi \rangle$$

Density functional theory

$$O = \langle \Psi | \hat{O} | \Psi \rangle$$ ~~Ψ~~

Density functional theory

$$O = \langle \Psi | \hat{O} | \Psi \rangle$$ ~~Ψ~~

$$O = O[n]$$

Density functional theory

$$O = \langle \Psi | \hat{O} | \Psi \rangle$$ ~~Ψ~~

$$O = O[n] \qquad n = ?$$

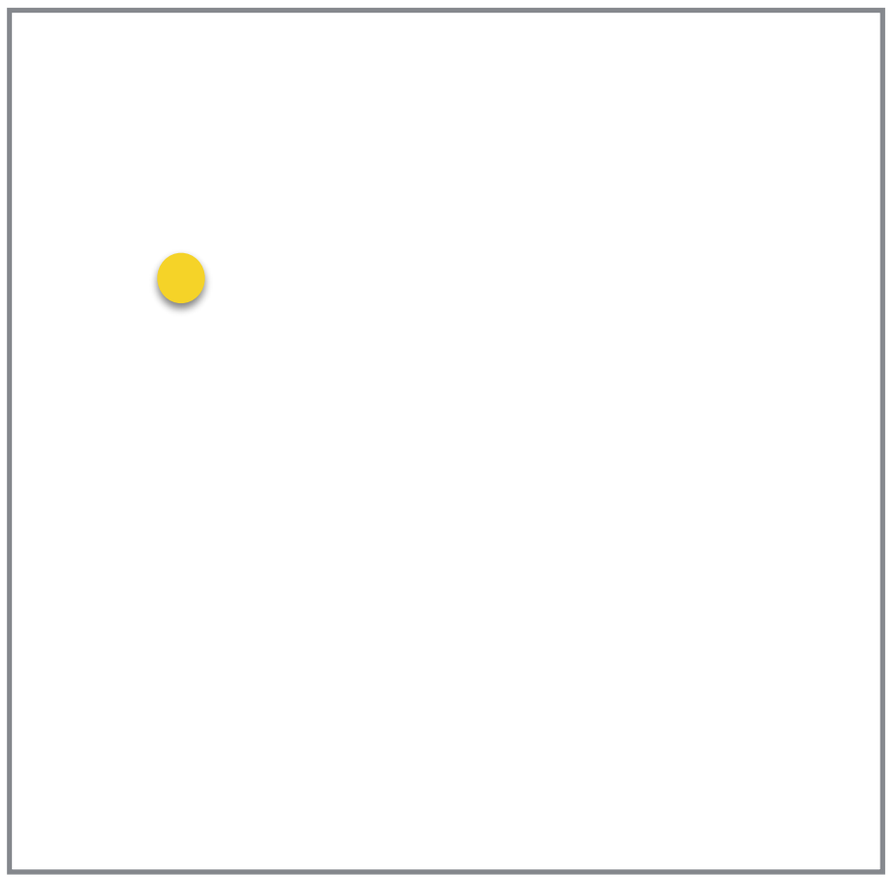
Kohn-Sham

density functional theory

Many-body system

No. interactions = 0

v_{ext}

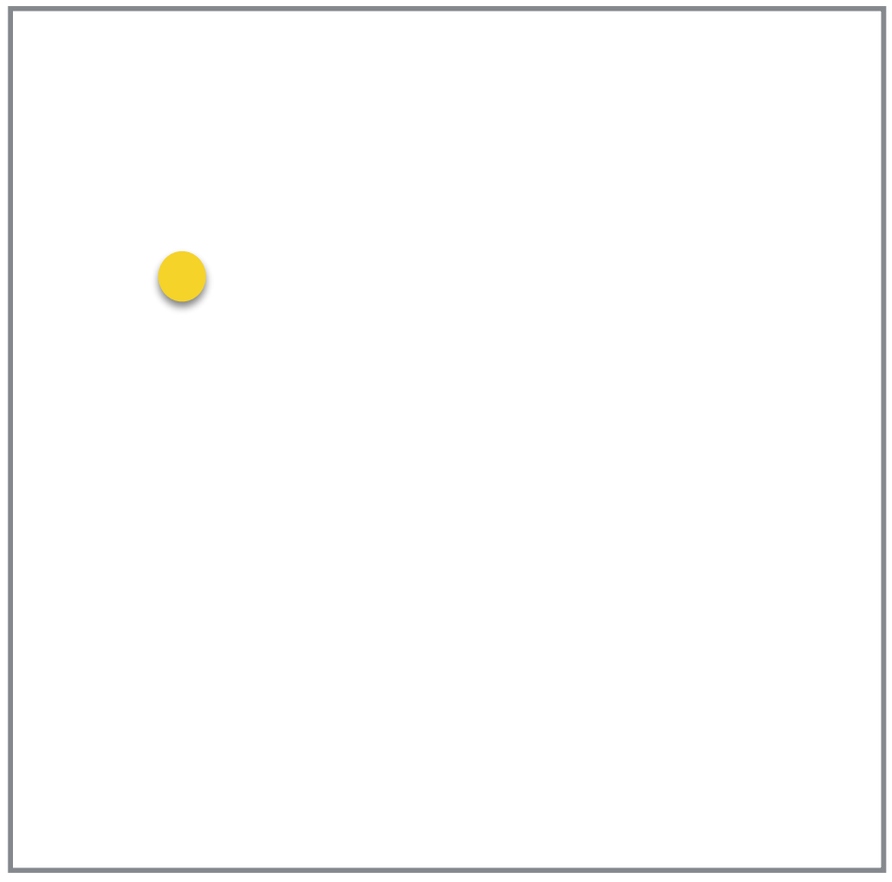


Computational Scaling = k^3

Kohn-Sham system

No. interactions = 0

v_{KS}



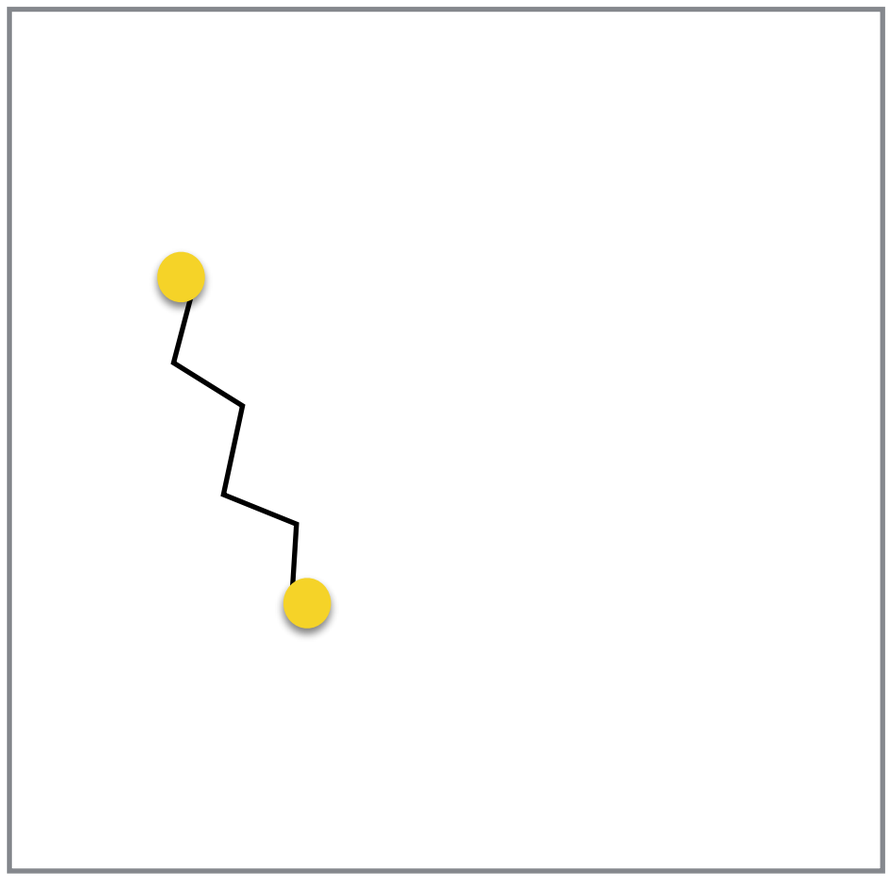
Computational Scaling = $(1\ k)^3$

Kohn-Sham

density functional theory

Many-body system

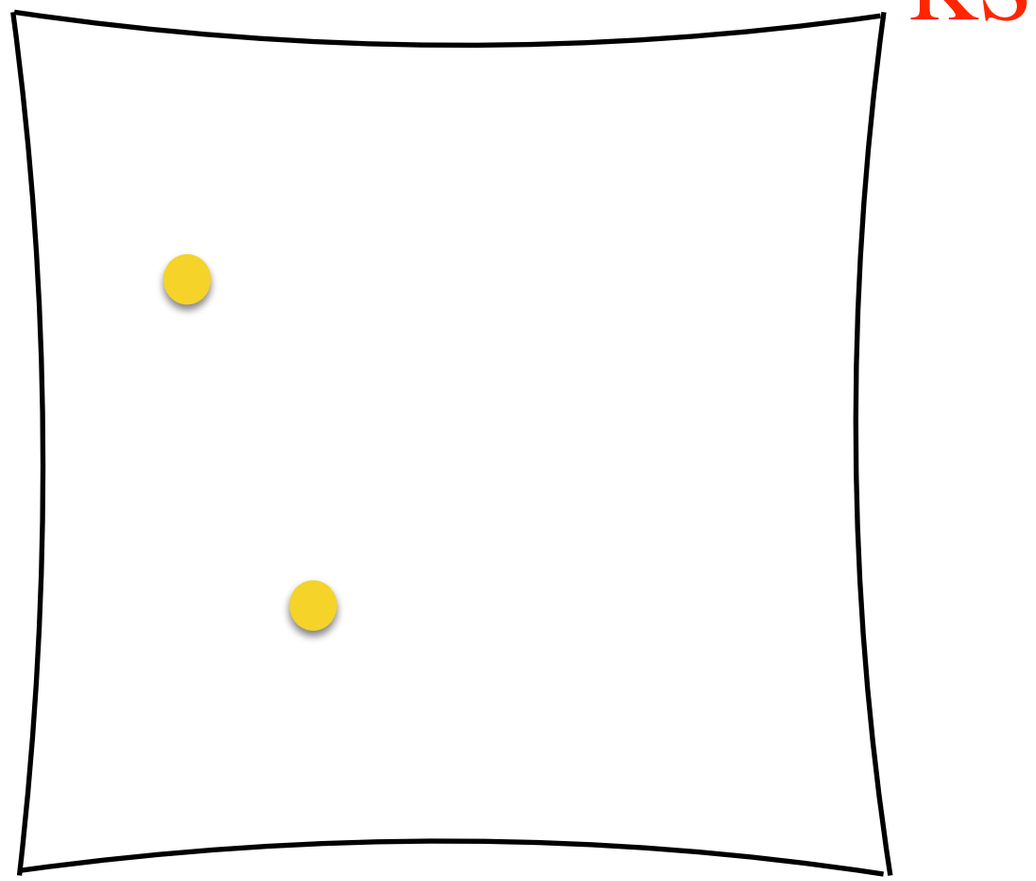
No. interactions = 1



Computational Scaling = k^6

Kohn-Sham system

No. interactions = 0



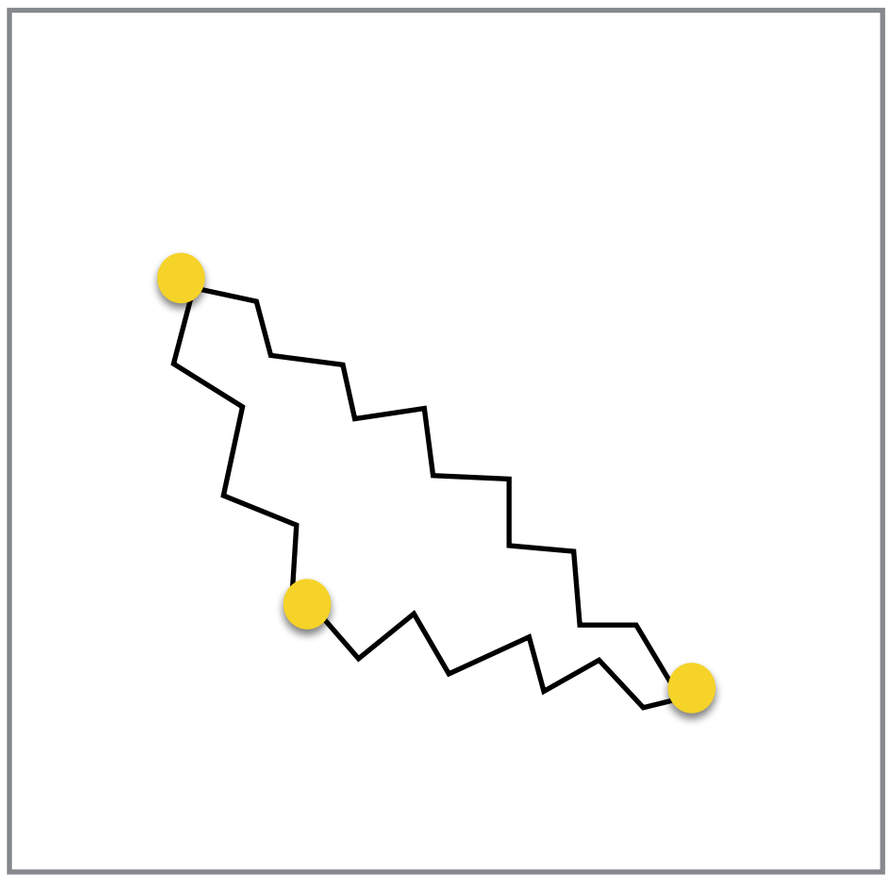
Computational Scaling = $(2\,k)^3$

Kohn-Sham

density functional theory

Many-body system

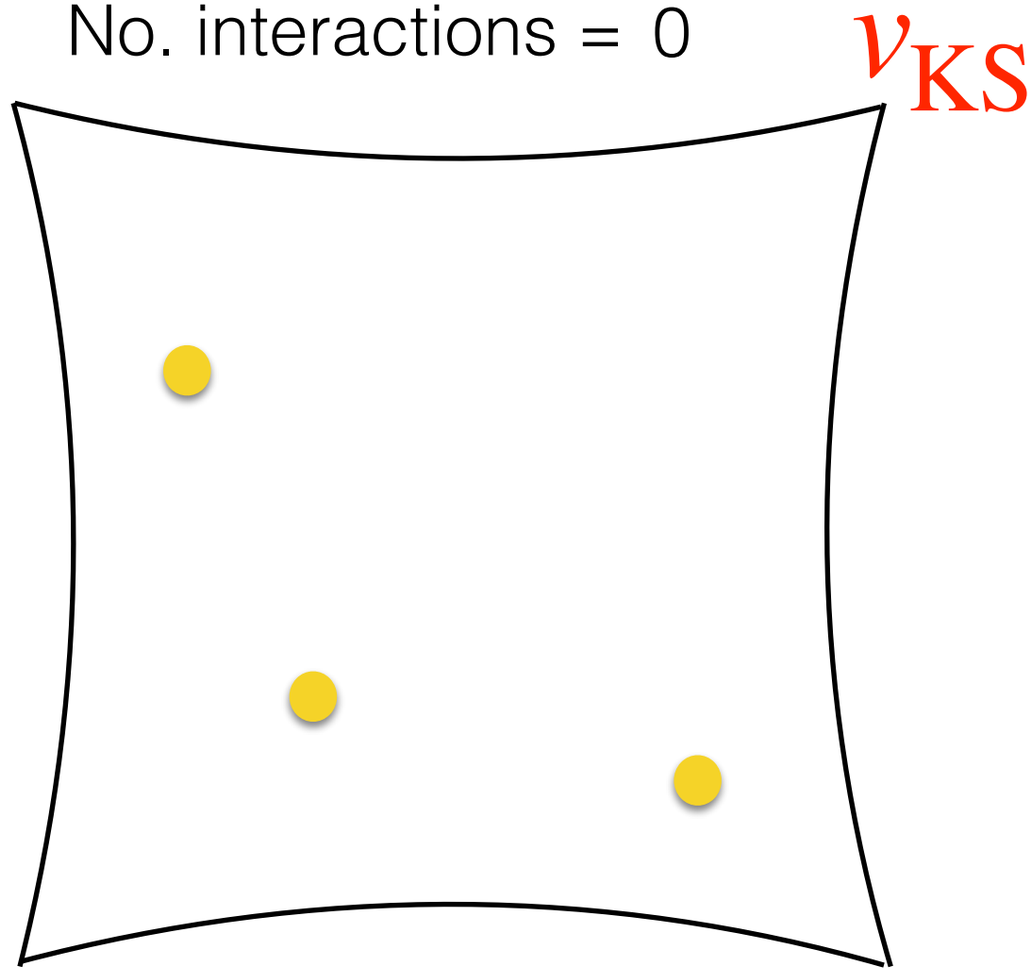
No. interactions = 3



Computational Scaling = k^9

Kohn-Sham system

No. interactions = 0



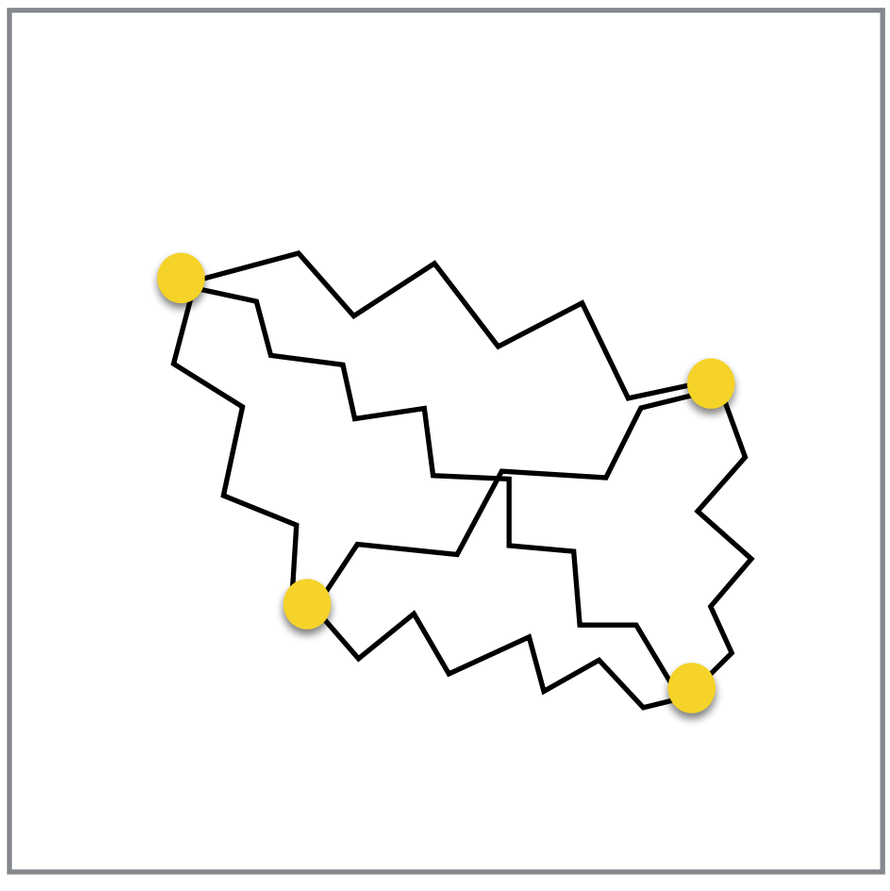
Computational Scaling = $(3\,k)^3$

Kohn-Sham

density functional theory

Many-body system

No. interactions = 6

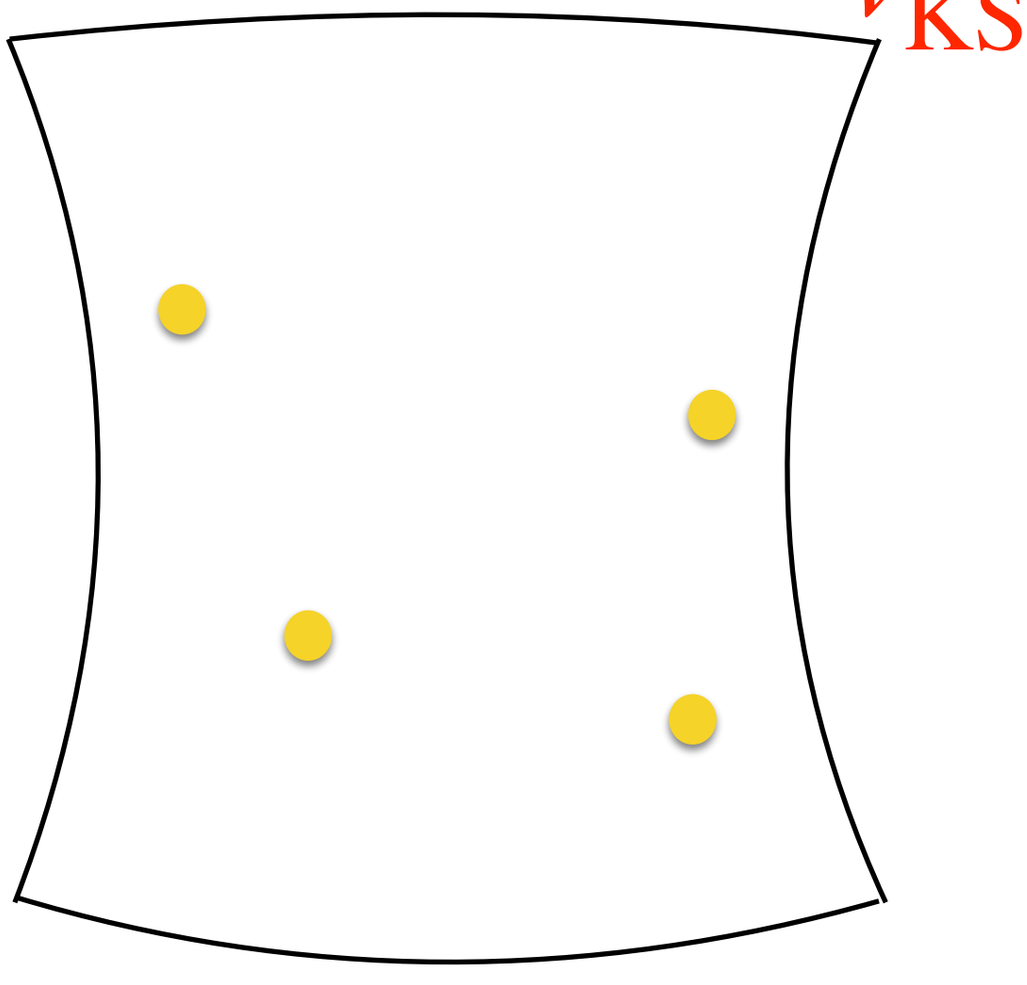


v_{ext}

Computational Scaling = k^{12}

Kohn-Sham system

No. interactions = 0



v_{KS}

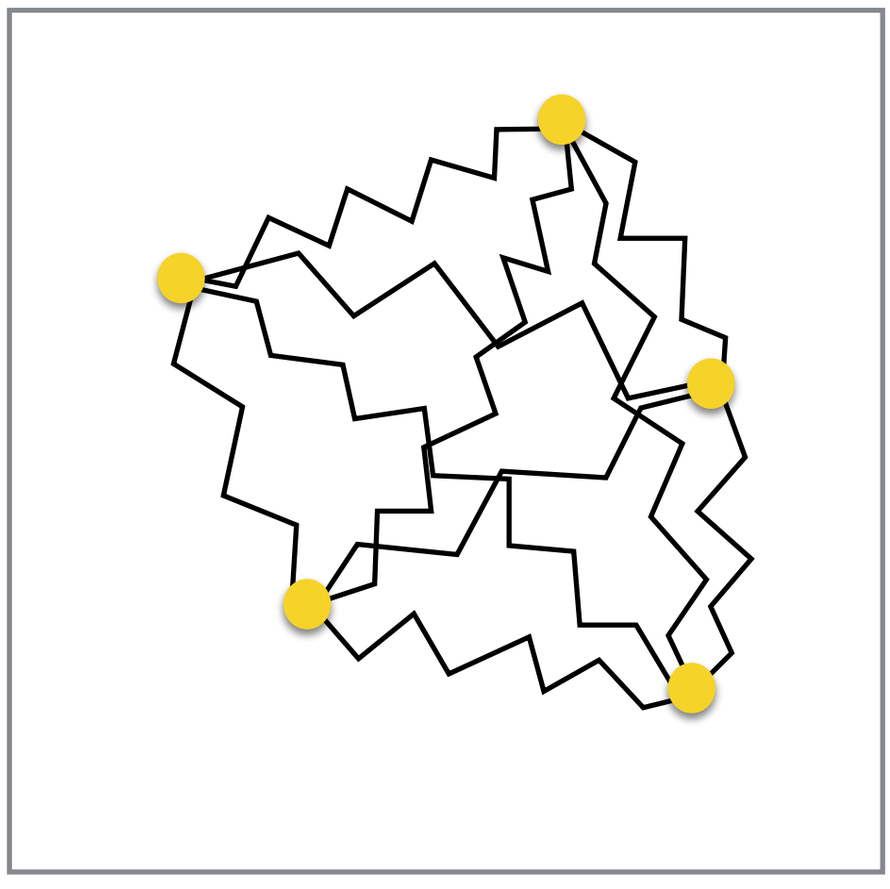
Computational Scaling = $(4\,k)^3$

Kohn-Sham

density functional theory

Many-body system

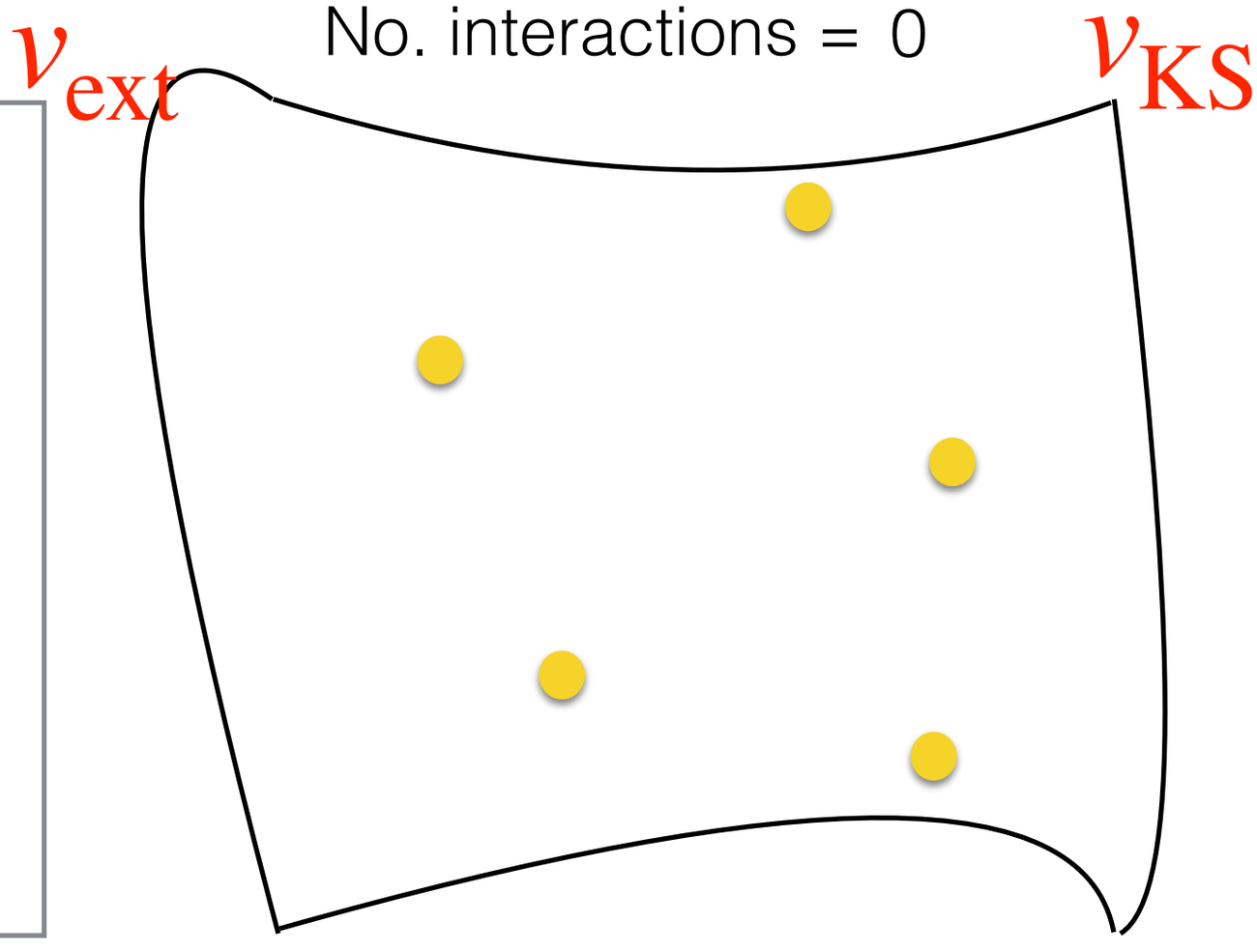
No. interactions = 10



Computational Scaling = k^{15}

Kohn-Sham system

No. interactions = 0



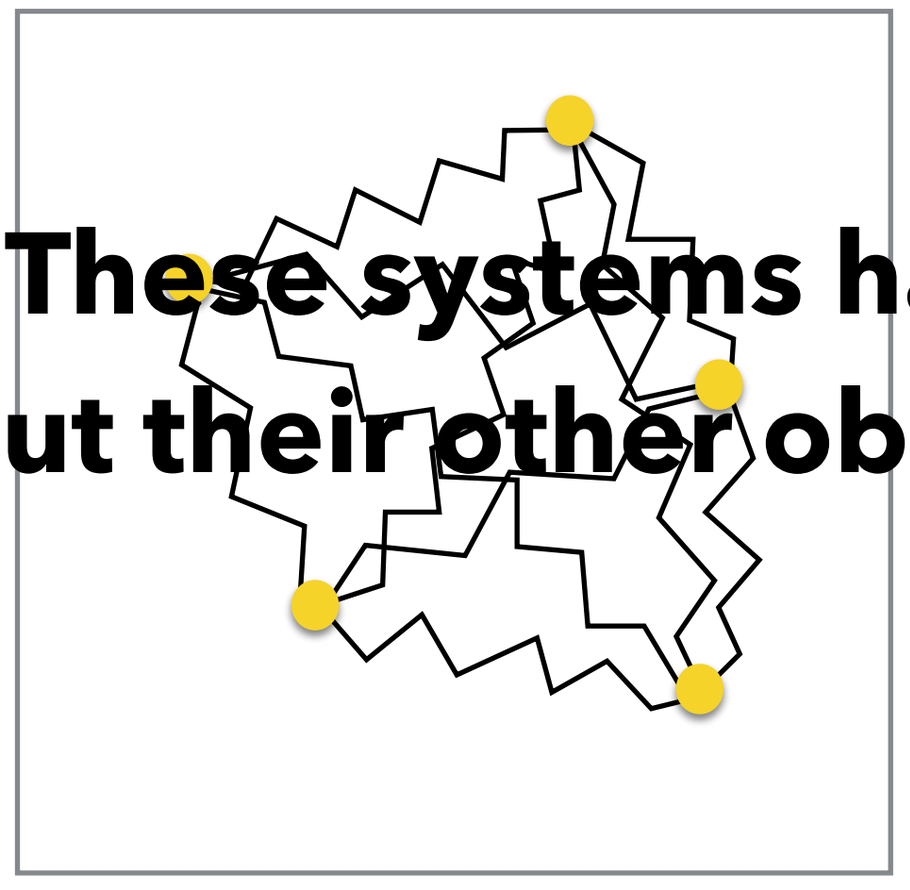
Computational Scaling = $(5\,k)^3$

Kohn-Sham

density functional theory

Many-body system

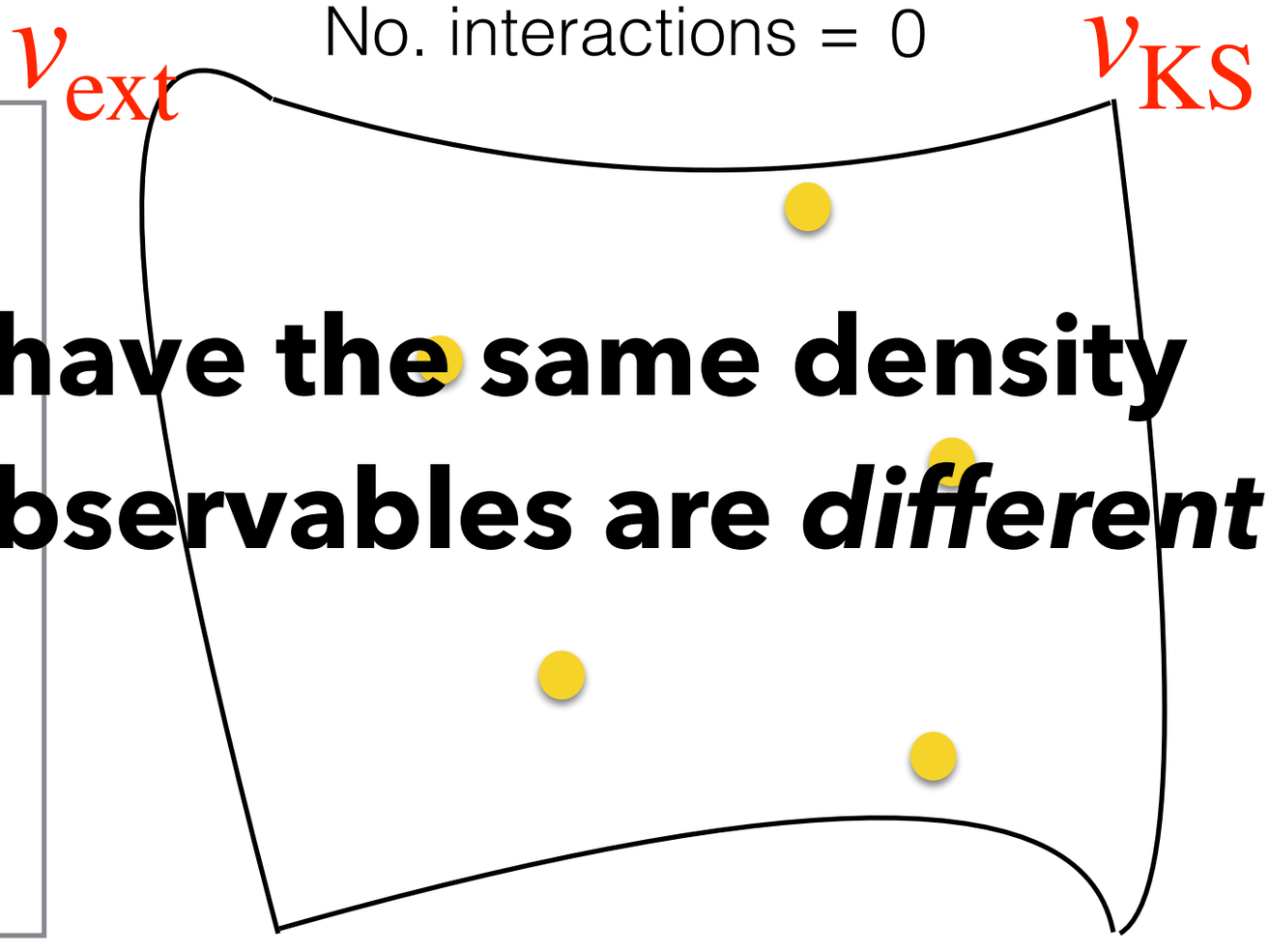
No. interactions = 10



Computational Scaling = k^{15}

Kohn-Sham system

No. interactions = 0



Computational Scaling = $(5\,k)^3$

These systems have the same density but their other observables are *different*

Kohn-Sham

density functional theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}\right)\phi_j = \varepsilon_j \phi_j$$

$$v_{\mathrm{KS}} = v_{\mathrm{ext}} + v_{\mathrm{Hxc}} = v_{\mathrm{ext}} + v_{\mathrm{H}} + v_{\mathrm{xc}}$$

Kohn-Sham

density functional theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}\right)\phi_j = \varepsilon_j \phi_j$$

$$v_{\mathrm{KS}} = v_{\mathrm{ext}} + v_{\mathrm{Hxc}} = v_{\mathrm{ext}} + v_{\mathrm{H}} + v_{\mathrm{xc}}$$

$$n = \sum_j \left|\phi_j\right|^2$$

Density functional theory

$$O = O[n] \qquad n = \sum_j \left| \phi_j \right|^2$$

Density functional theory

$$O = O[n] \qquad n = \sum_j \left| \phi_j \right|^2$$

Density functional theory

$$O = O[n] \qquad n = \sum_j \left| \phi_j \right|^2$$

$$O[n] = ?$$

Density functional theory

$$O = O[n] \qquad n = \sum_j \left| \phi_j \right|^2$$

$$O[n] = ?$$

$$E_{\mathrm{FG}} = I - A = E_{\mathrm{FG}}[n] = ?$$

Kohn-Sham

density functional theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}\right)\phi_j = \varepsilon_j \phi_j$$

$$\downarrow$$

$$\{\varepsilon_j\}$$

Kohn-Sham

density functional theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}\right)\phi_j = \varepsilon_j \phi_j$$

$$\downarrow$$

$$\{\varepsilon_j\}$$

$$\downarrow$$

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

Kohn-Sham

density functional theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}\right)\phi_j = \varepsilon_j \phi_j$$

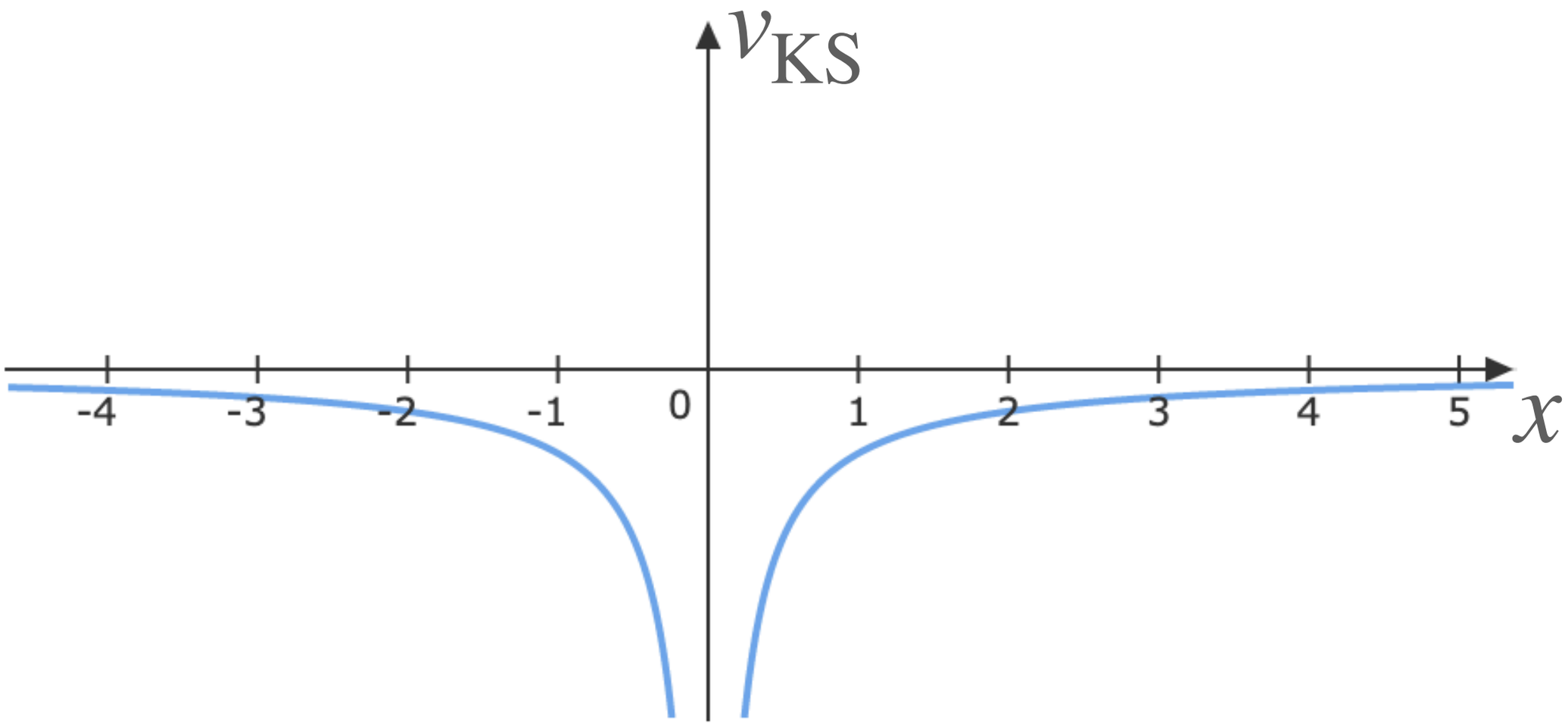
$$\downarrow$$

$$\{\varepsilon_j\}$$

$$\downarrow$$

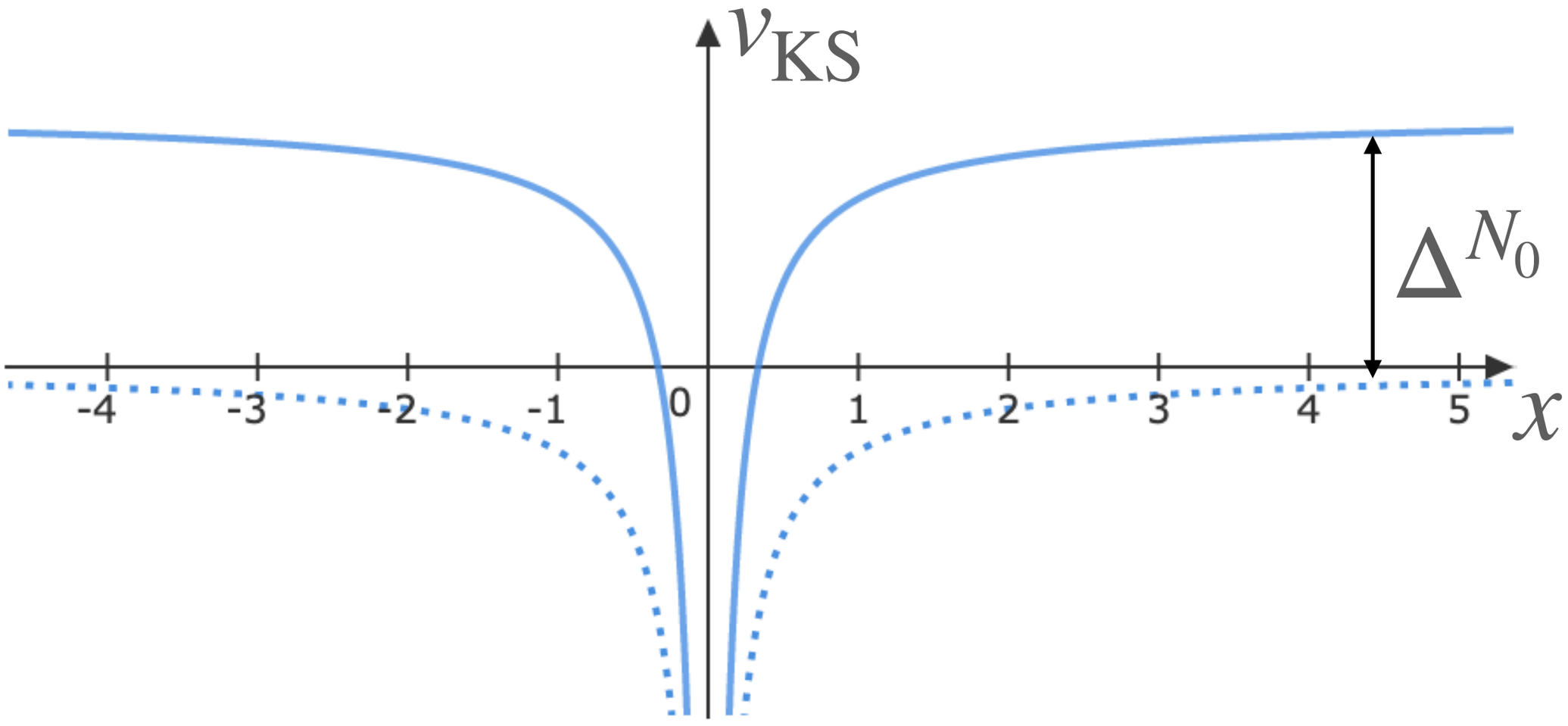
$$E_{\mathrm{FG}} \approx \varepsilon_{\mathrm{FG}}$$ ✗

Discontinuity in the Kohn-Sham potential



$$N = N_0$$

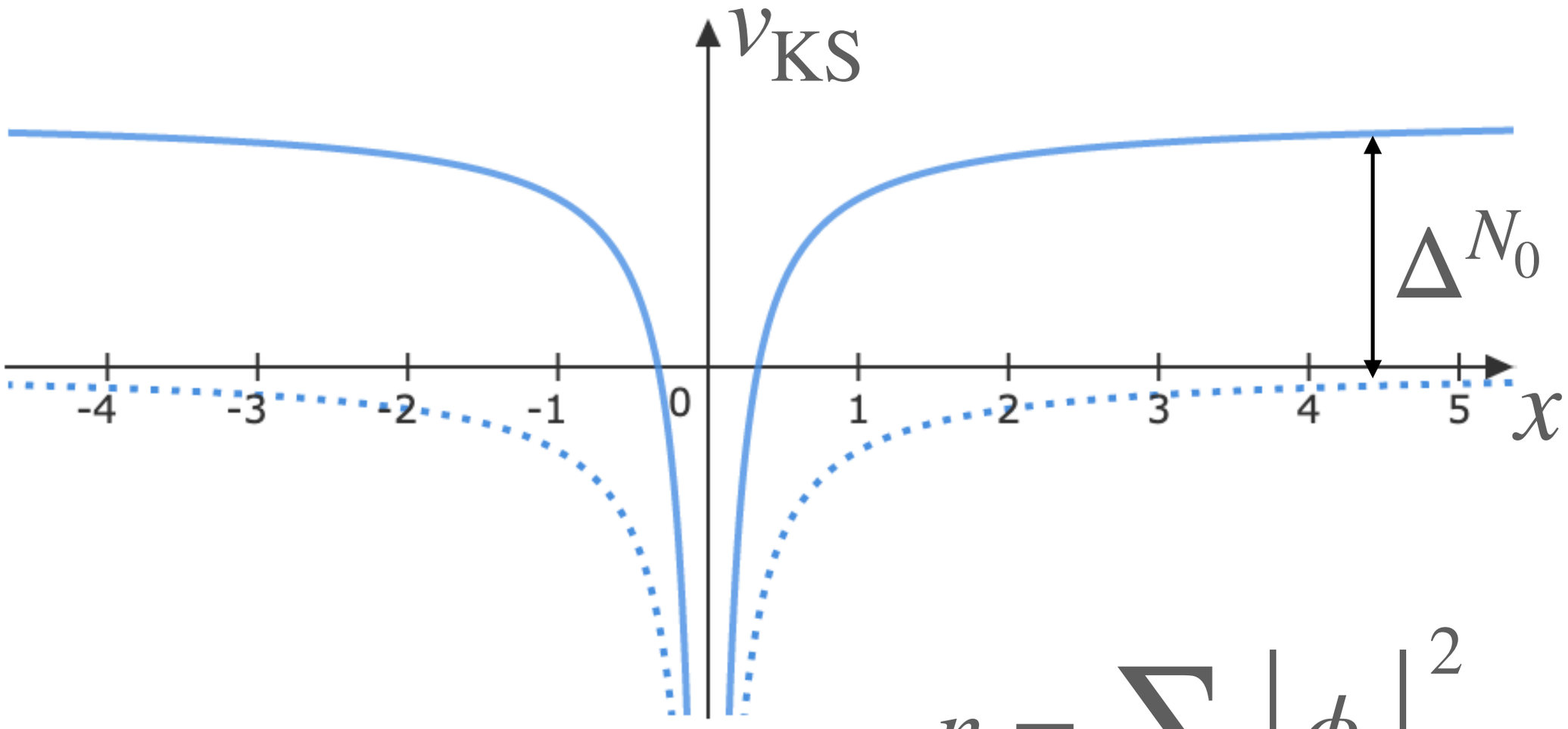
‘Derivative discontinuity’



$$N = \lim_{\delta \to 0^+} N_0 + \delta$$

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)

‘Derivative discontinuity’



$$N = \lim_{\delta \to 0^+} N_0 + \delta$$

$$n = \sum_j \left| \phi_j \right|^2$$

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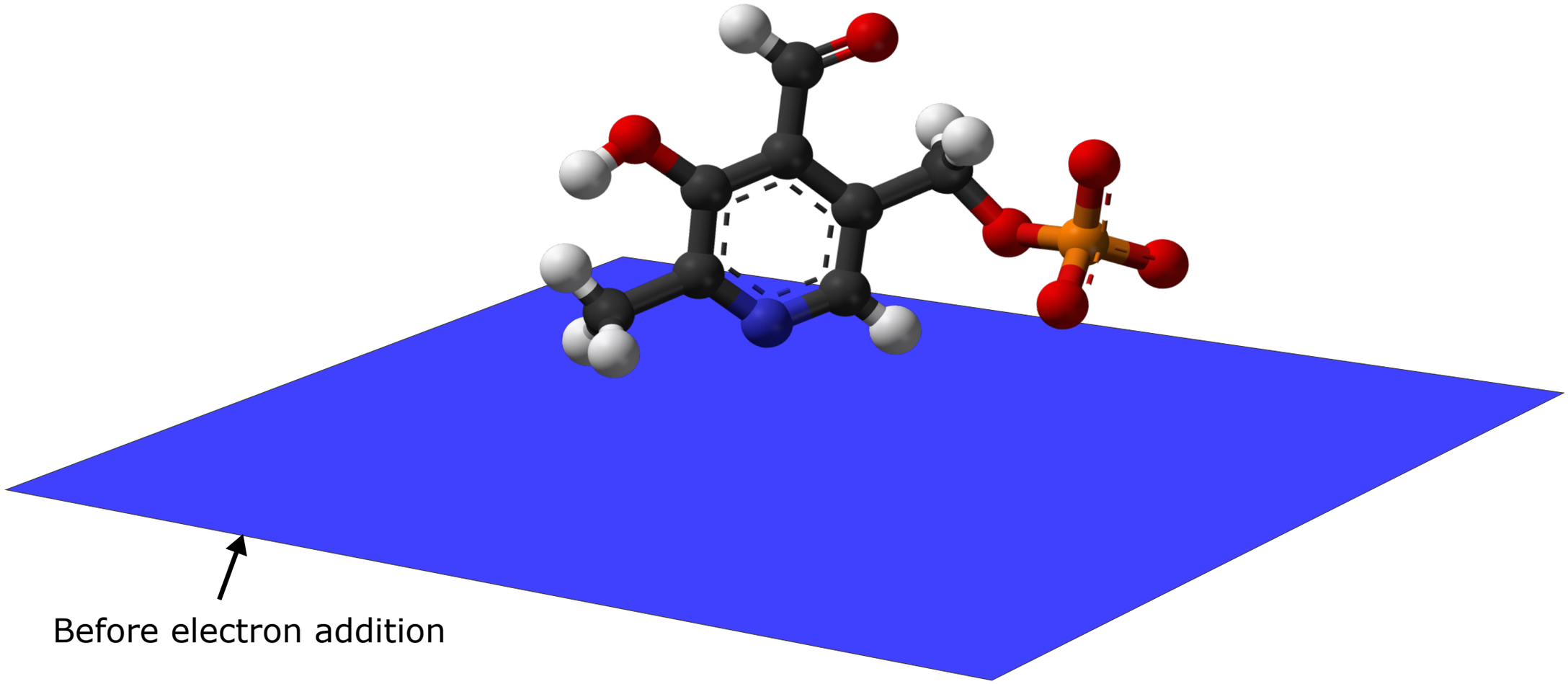
Fundamental gap

from the exact Kohn-Sham system



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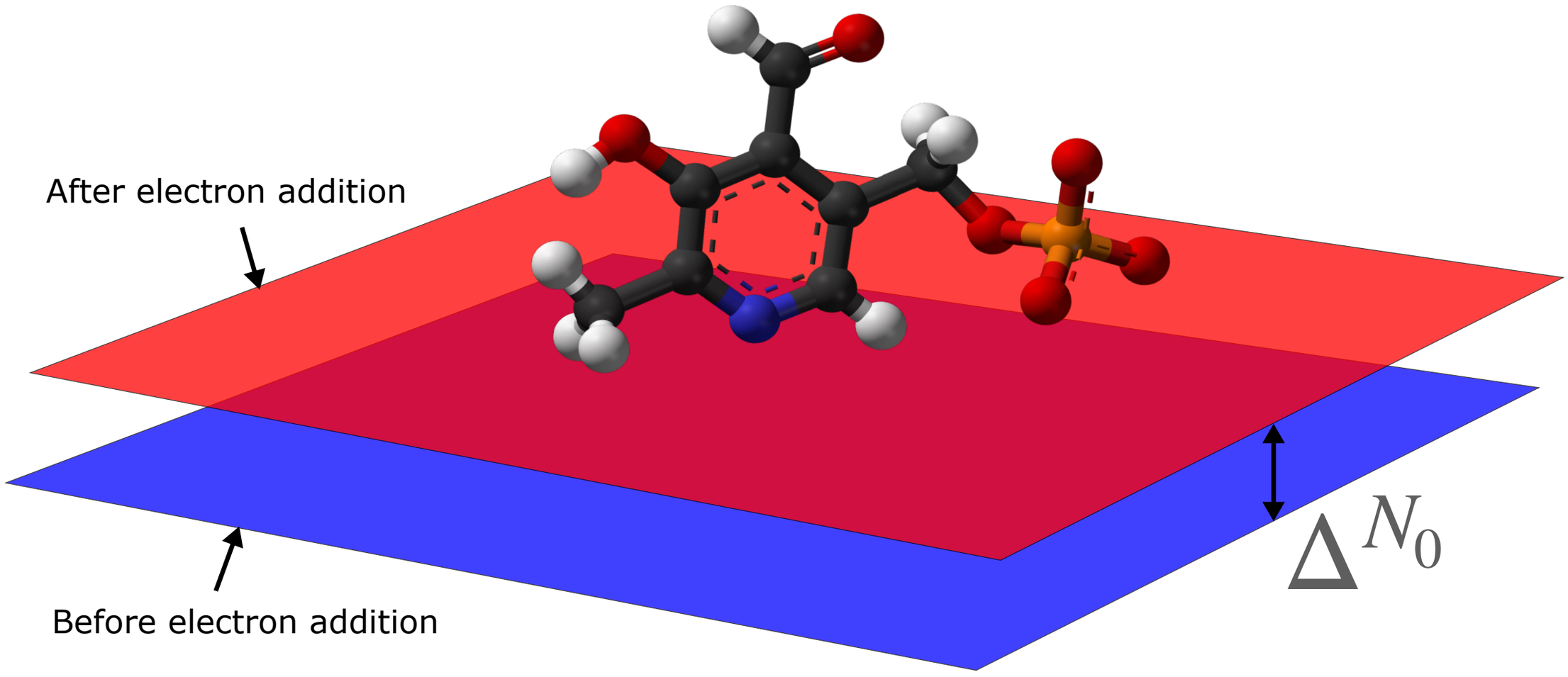

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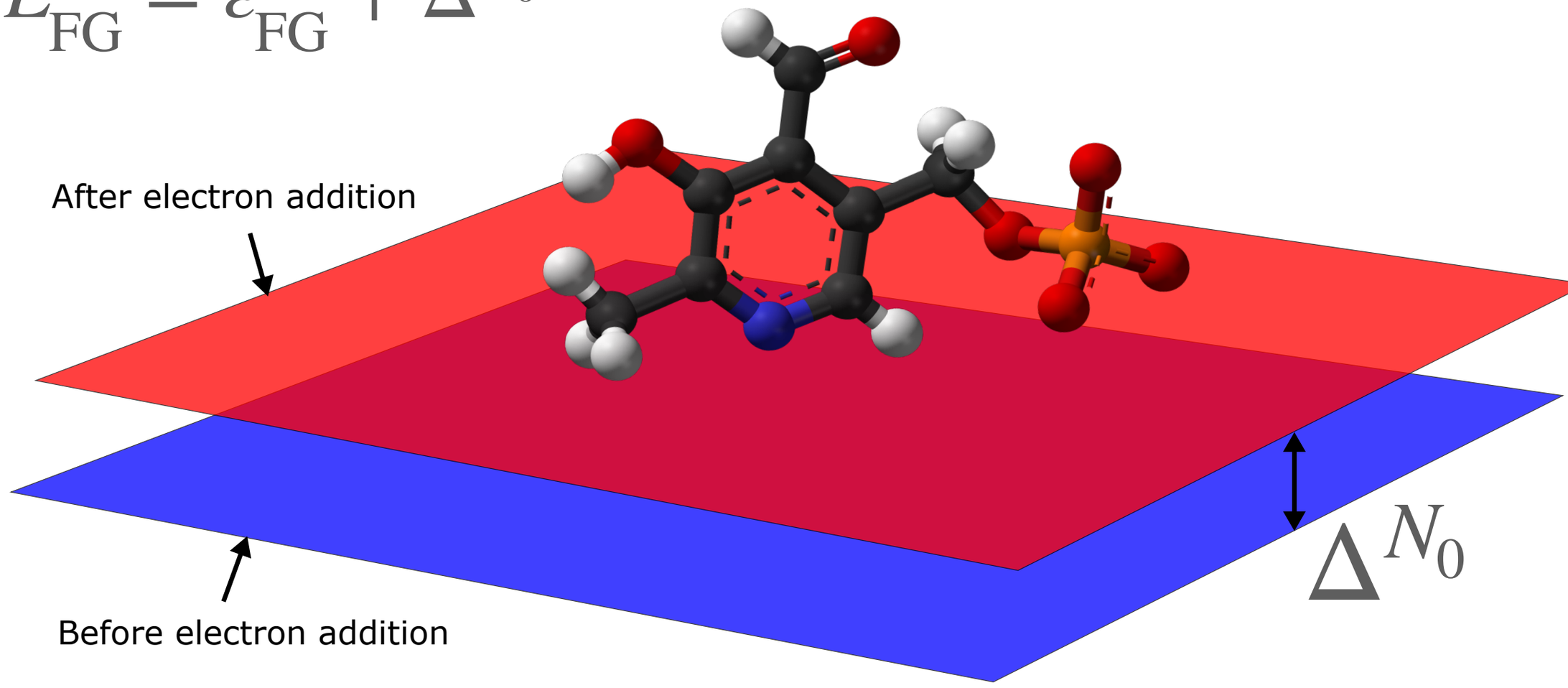
Fundamental gap

from the exact Kohn-Sham system

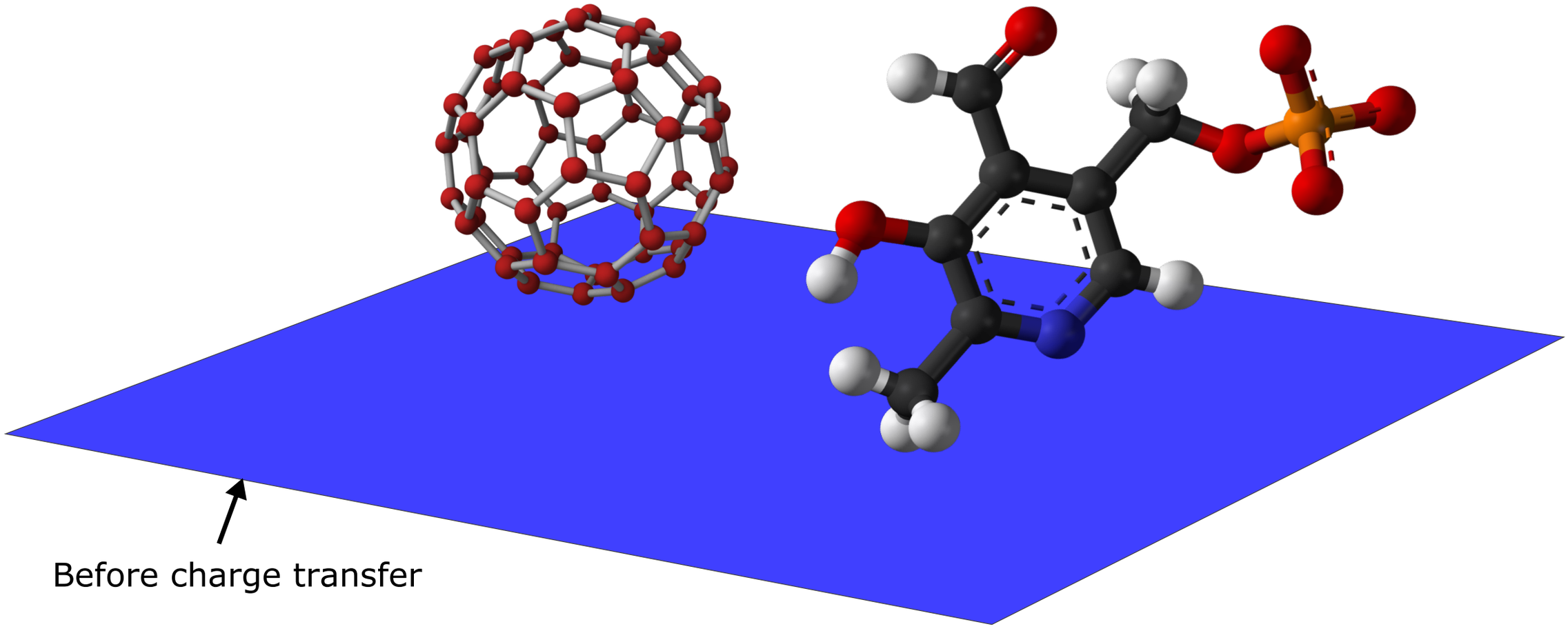
$$E_{\mathrm{FG}}^{N_0} = \varepsilon_{\mathrm{FG}}^{N_0} + \Delta^{N_0}$$



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)

Charge transfer

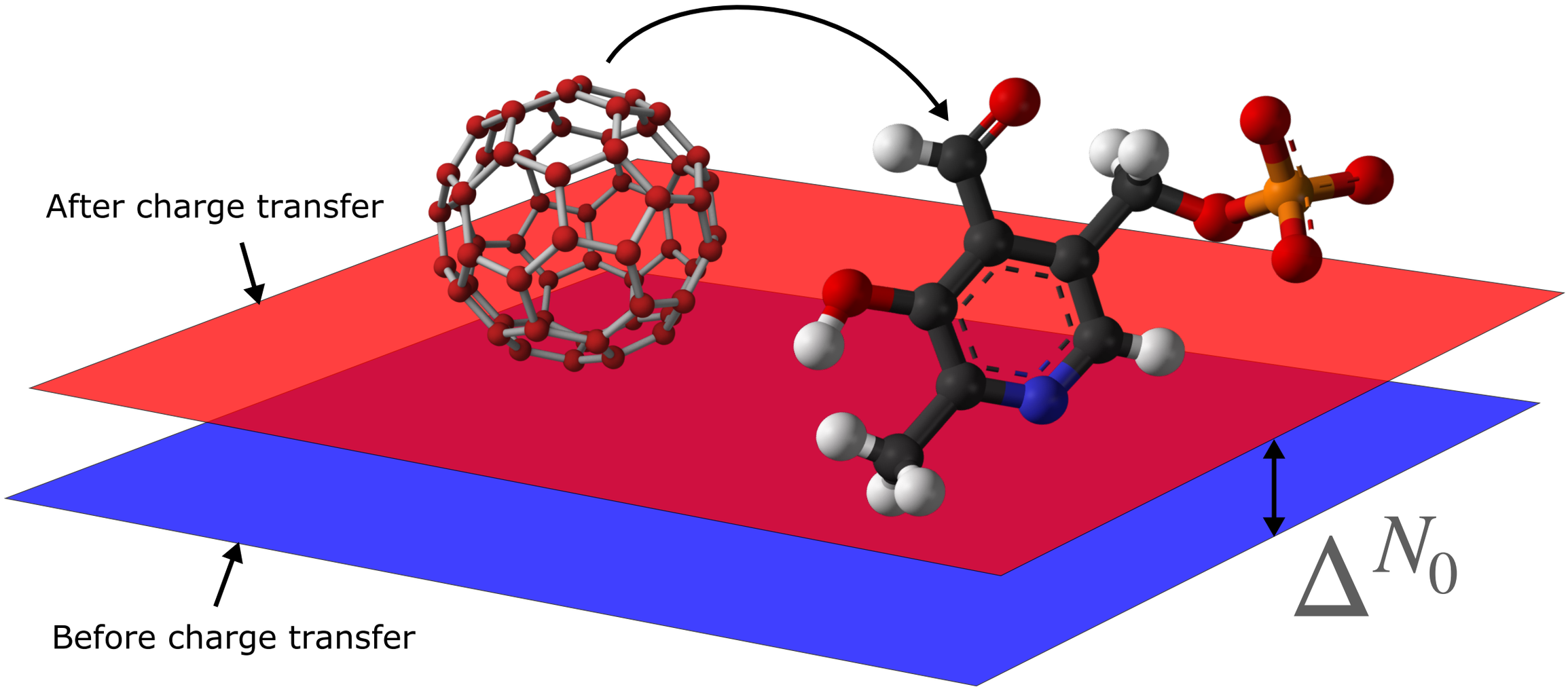
in the exact Kohn-Sham system



“From Kohn-Sham to many-electron energies via step structures in the exchange-correlation potential” Eli Kraisler, M. J. P. Hodgson and E. K. U. Gross, Journal of Chemical Theory and Computation **17** (3), 1390–1407 (2021)

Charge transfer

in the exact Kohn-Sham system



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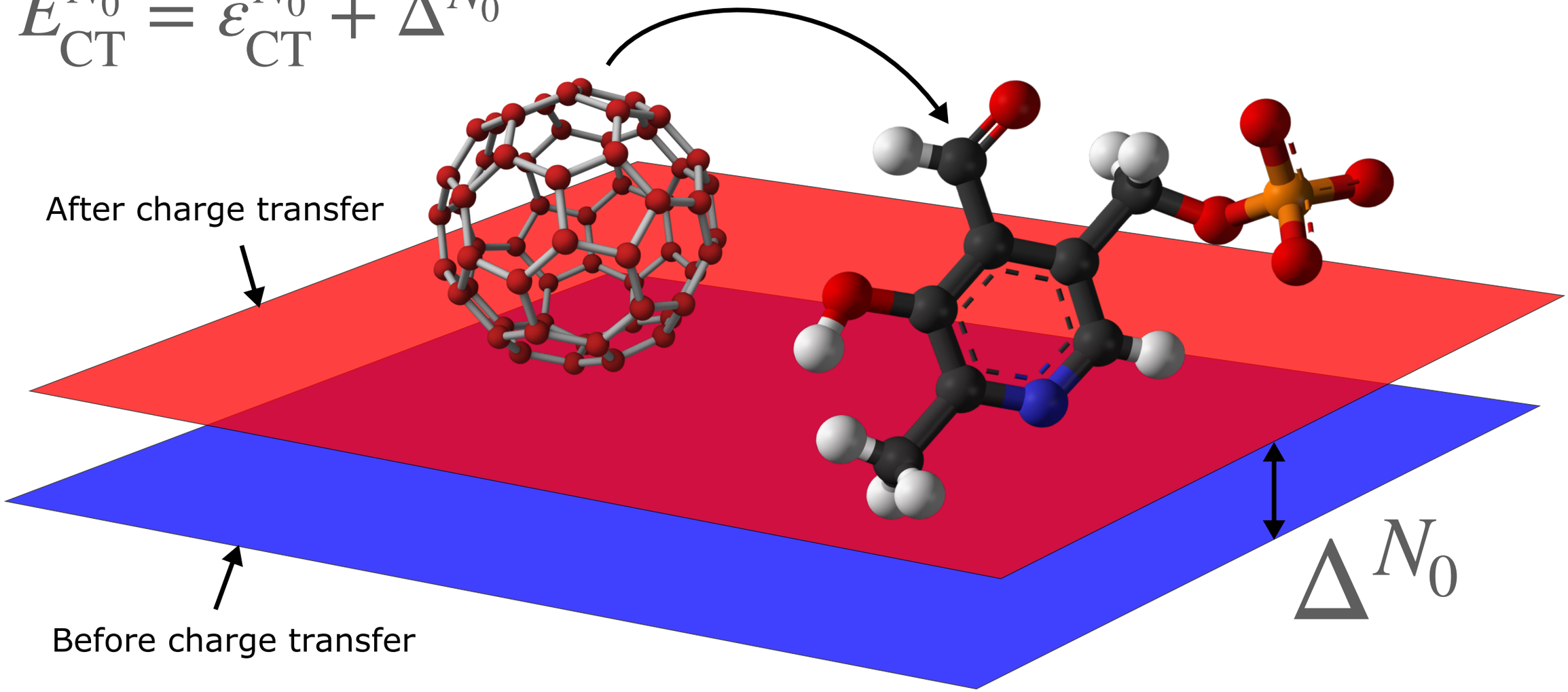
Charge transfer

in the exact Kohn-Sham system

$$E_{\mathrm{CT}}^{N_0} = \varepsilon_{\mathrm{CT}}^{N_0} + \Delta^{N_0}$$



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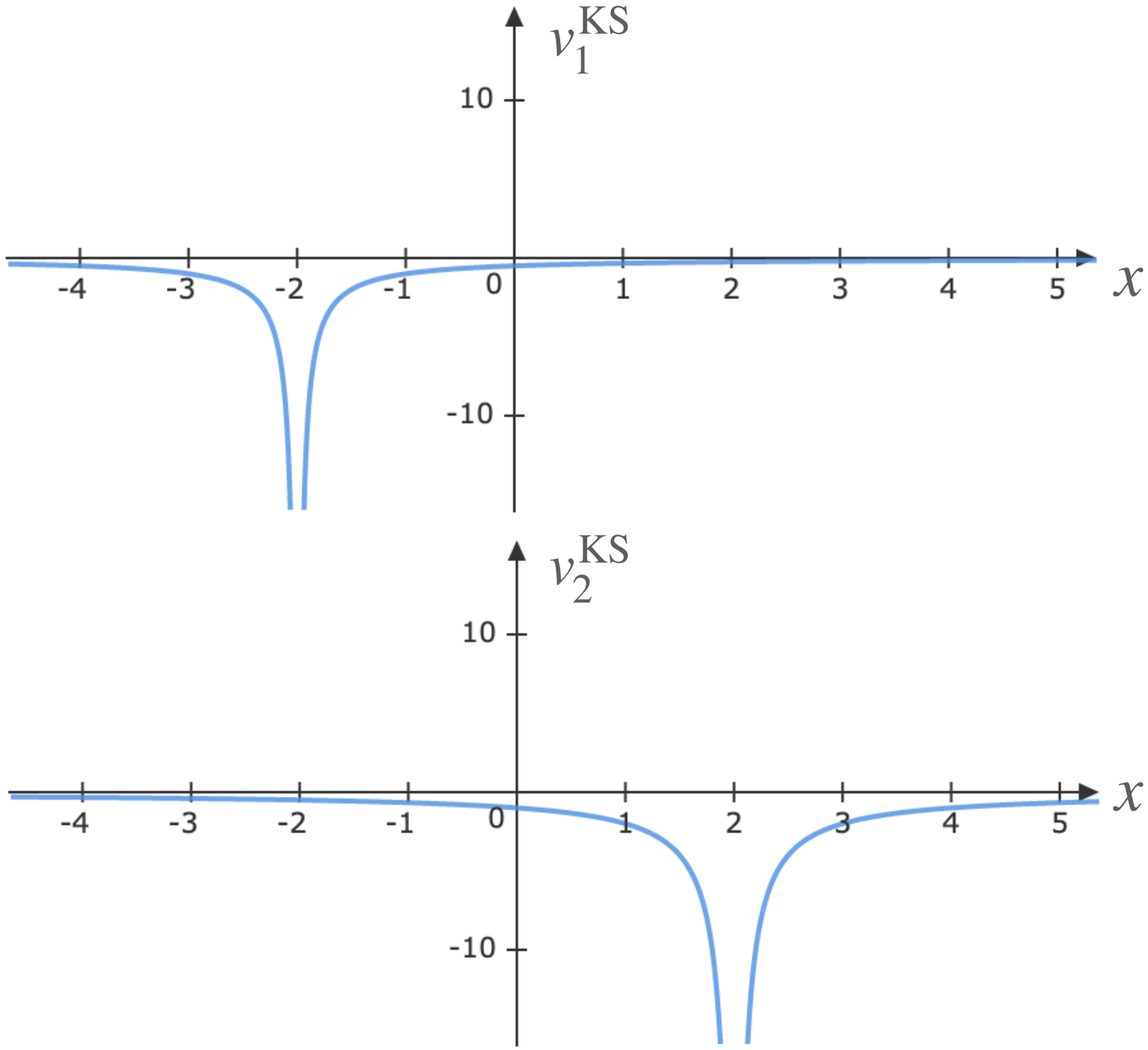
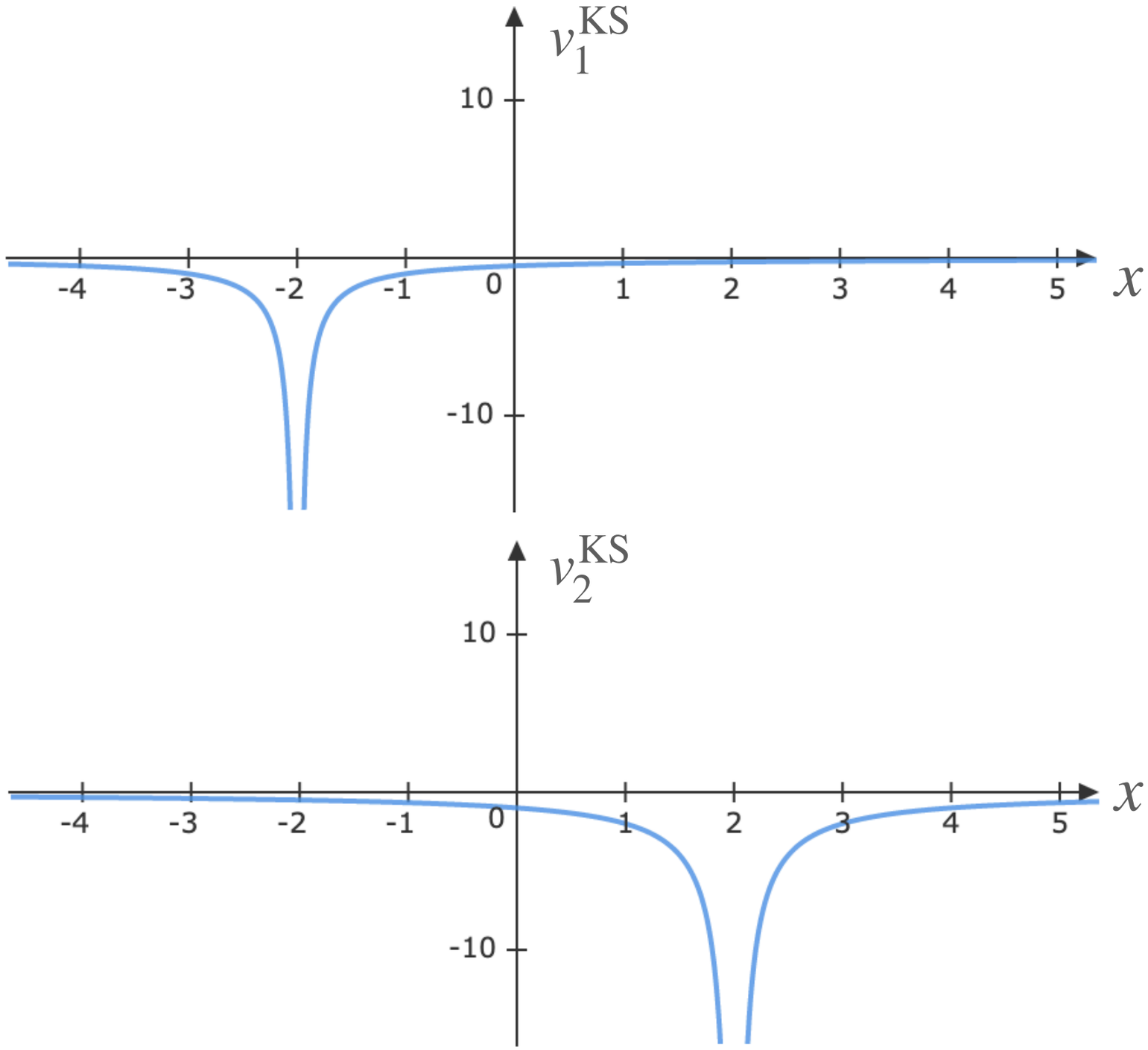
Discontinuity in the Kohn-Sham potential

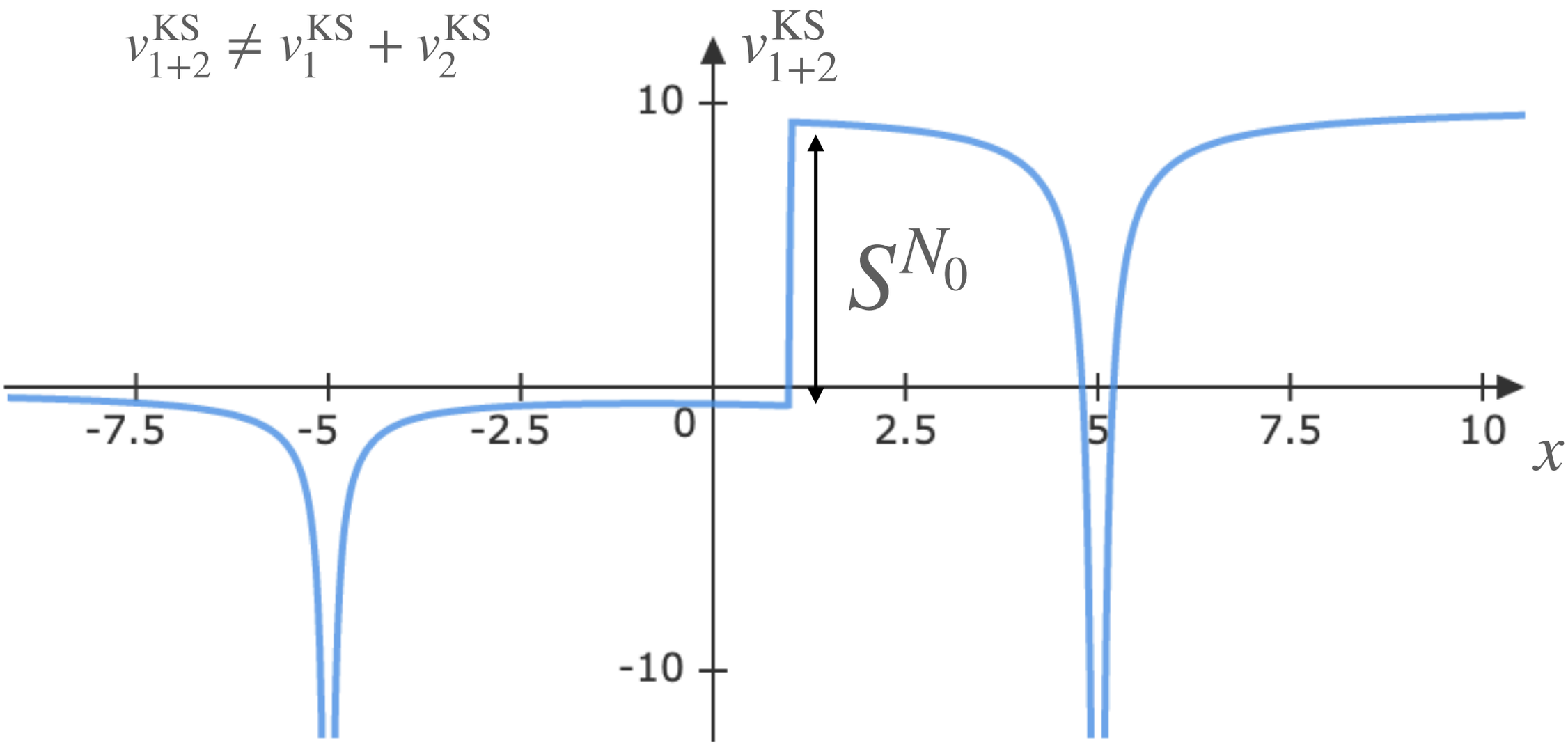


Discontinuity in the Kohn-Sham potential

$$v_{1+2}^{\mathrm{KS}} = v_1^{\mathrm{KS}} + v_2^{\mathrm{KS}} \; ?$$

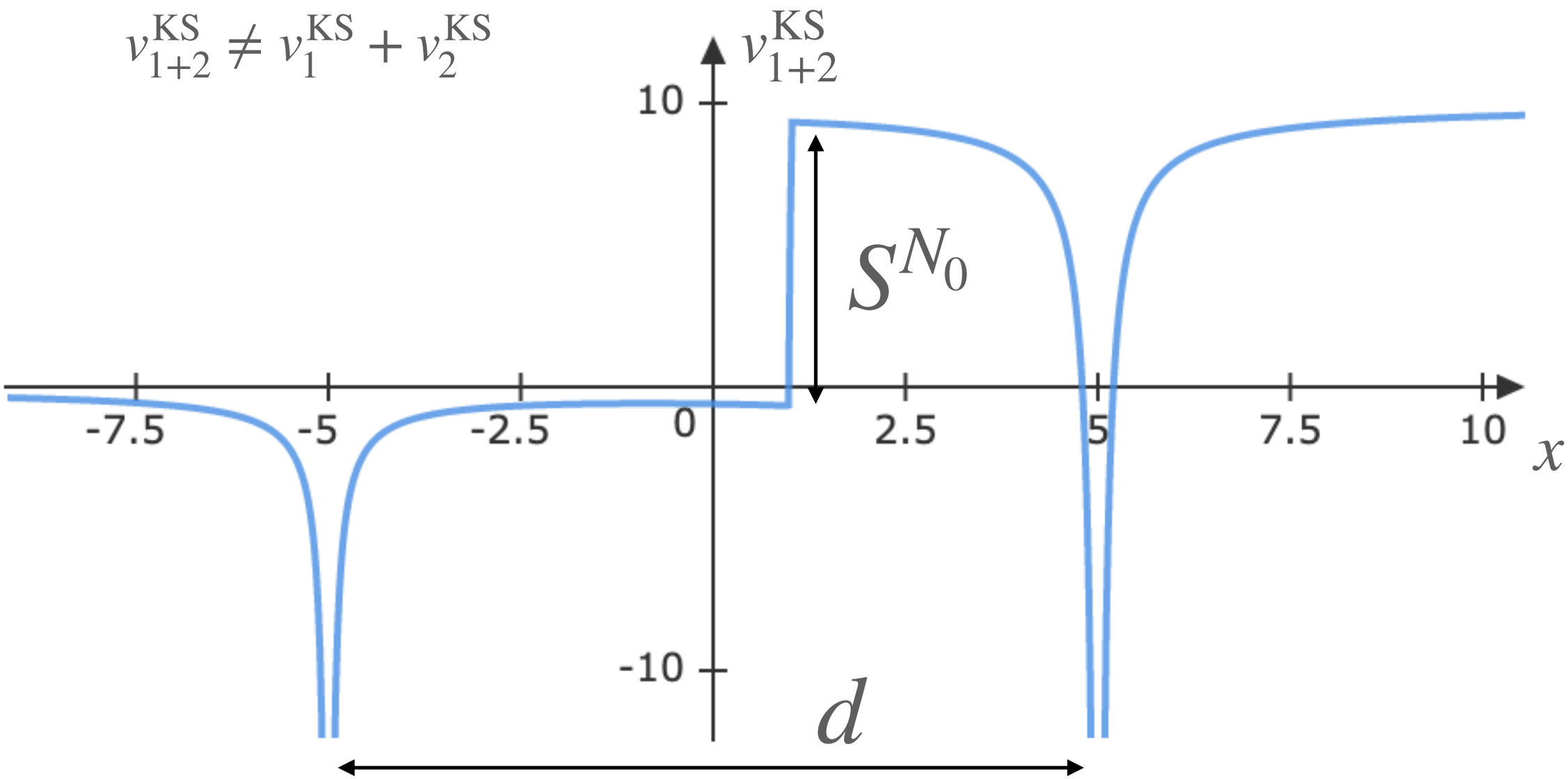


‘Step in the potential’



“Origin of static and dynamic steps in exact Kohn-Sham potentials” M. J. P. Hodgson, J. D. Ramsden and R. W. Godby, Physical Review B **93**, 155146 (2016)

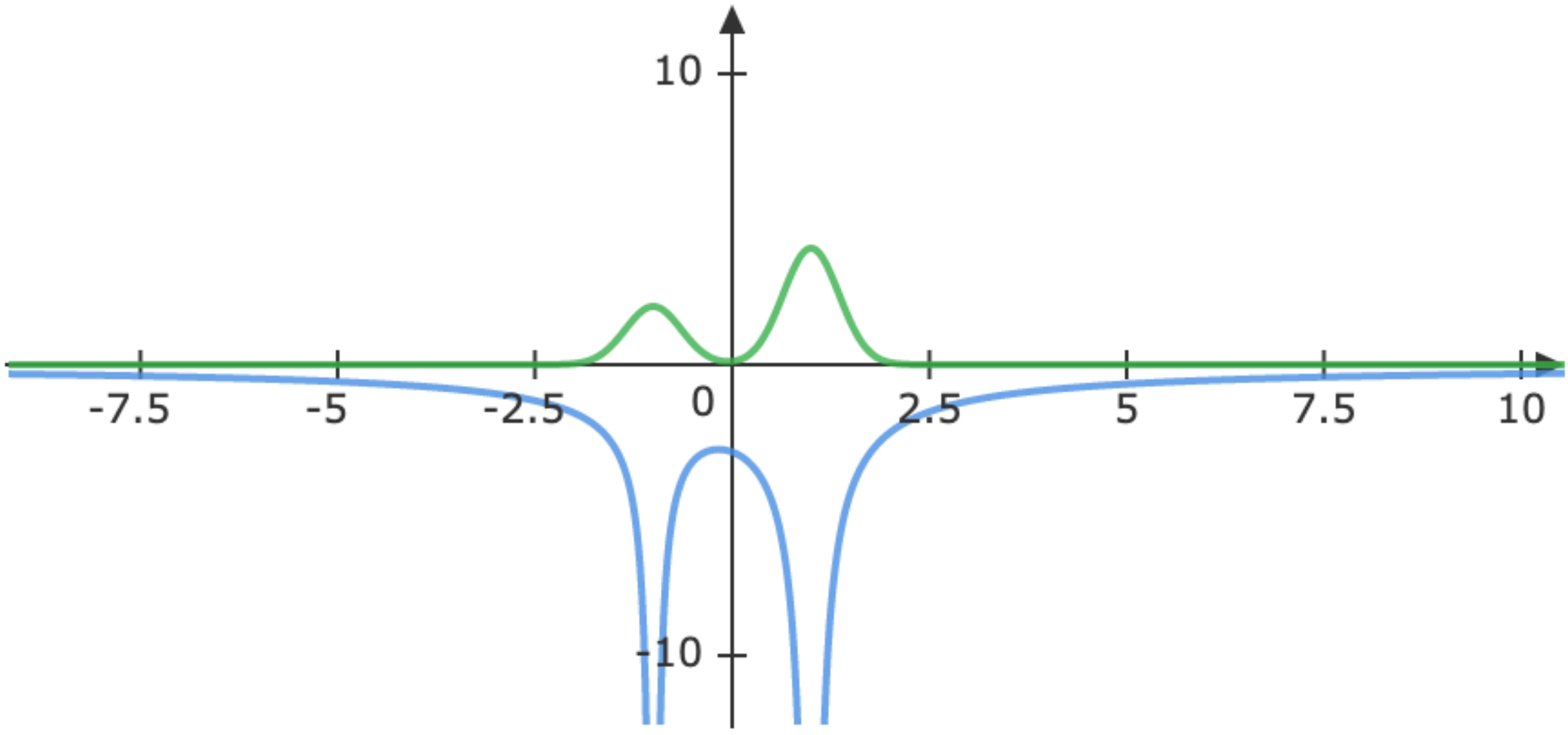
‘Step in the potential’



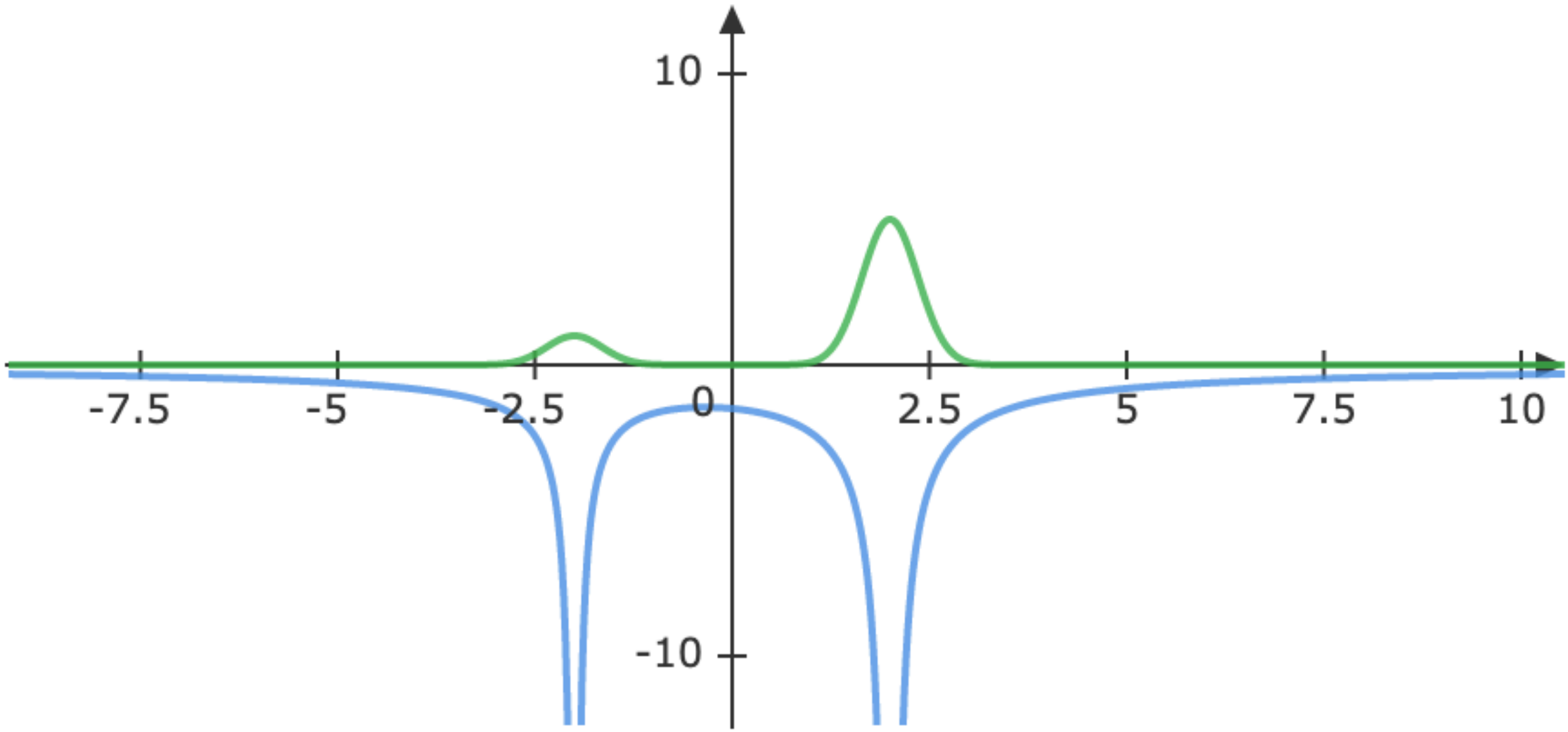
$$\lim_{d\to\infty} S^{N_0} = \Delta^{N_0-1}$$

“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)

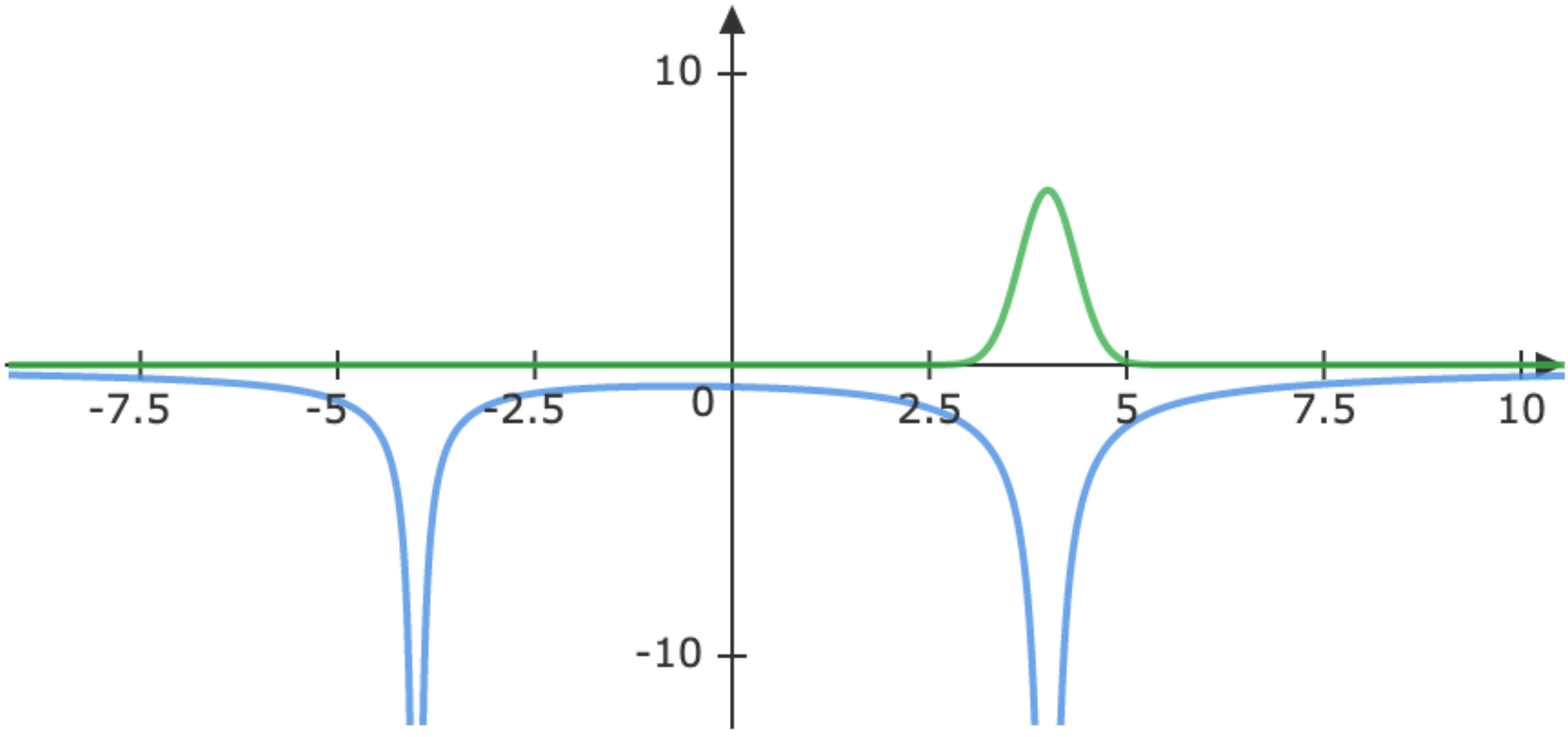
No step in the Kohn-Sham potential



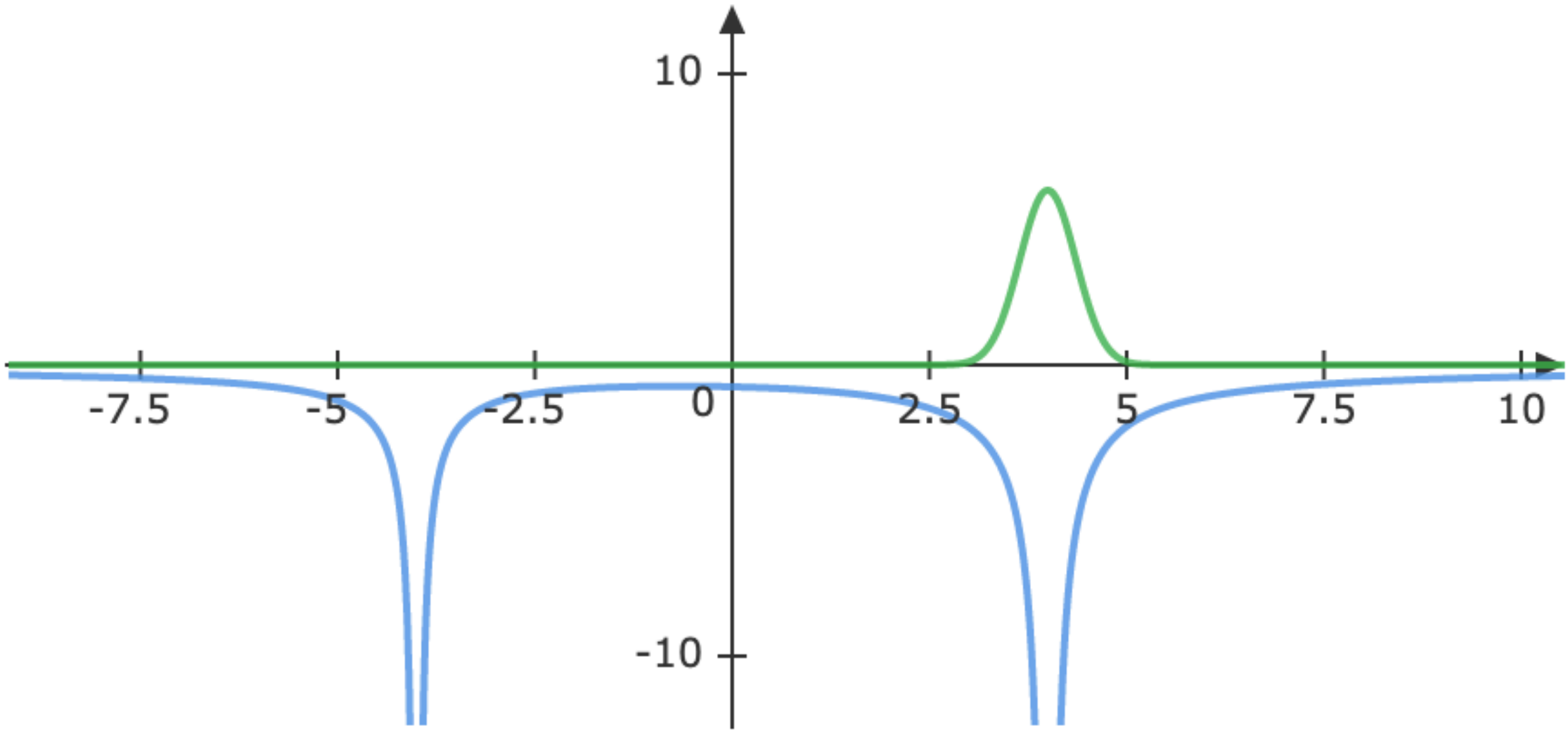
No step in the Kohn-Sham potential



No step in the Kohn-Sham potential



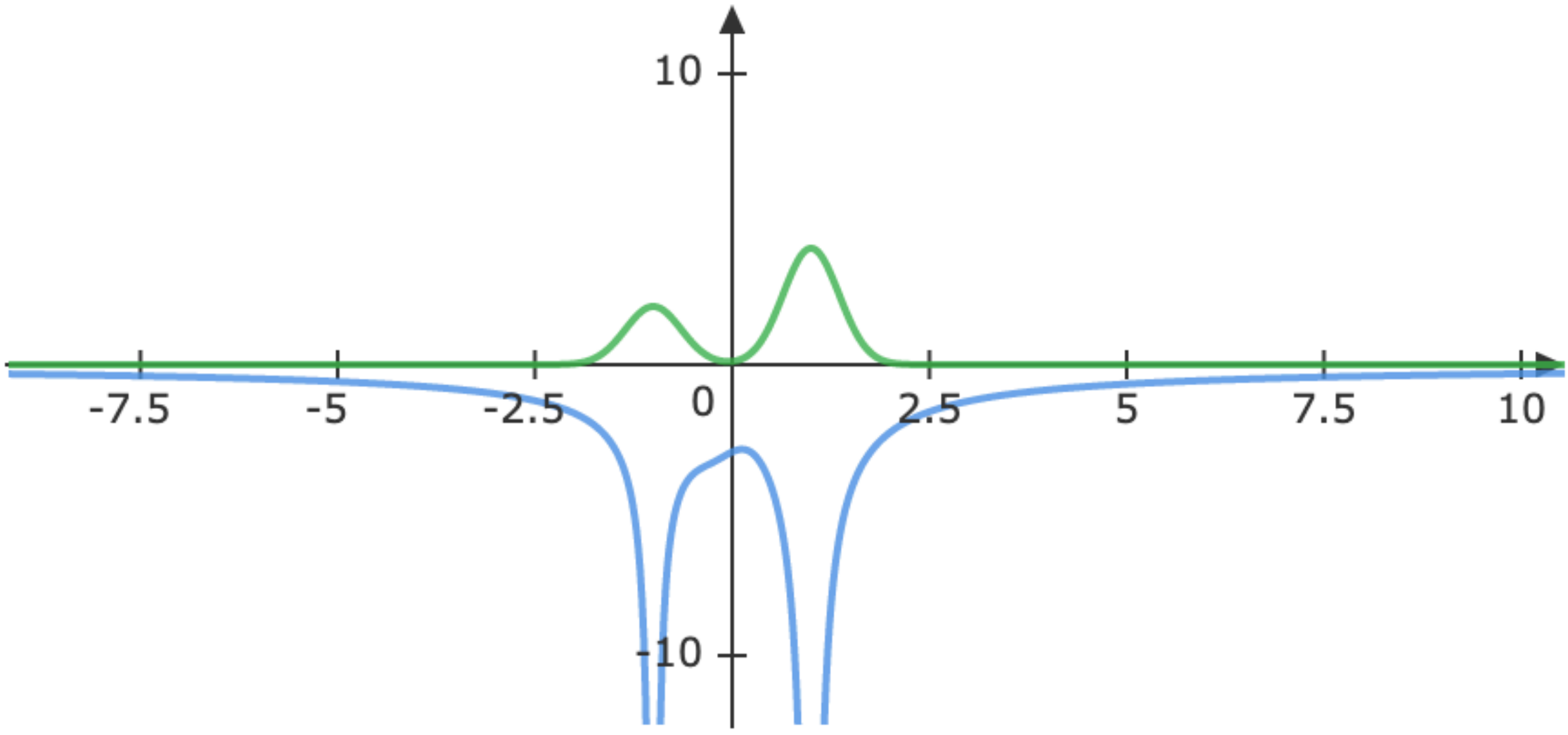
No step in the Kohn-Sham potential



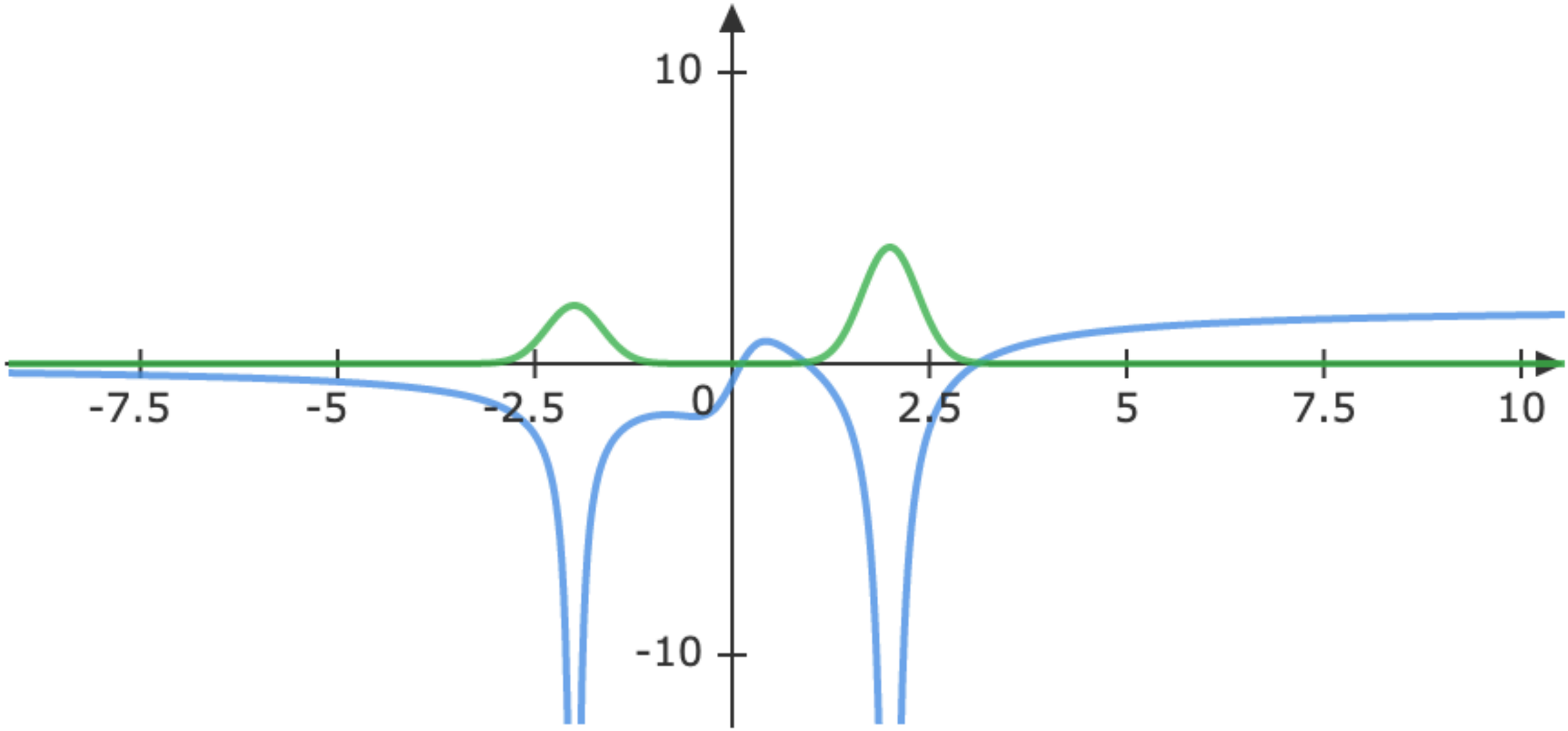
‘Delocalisation error’

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

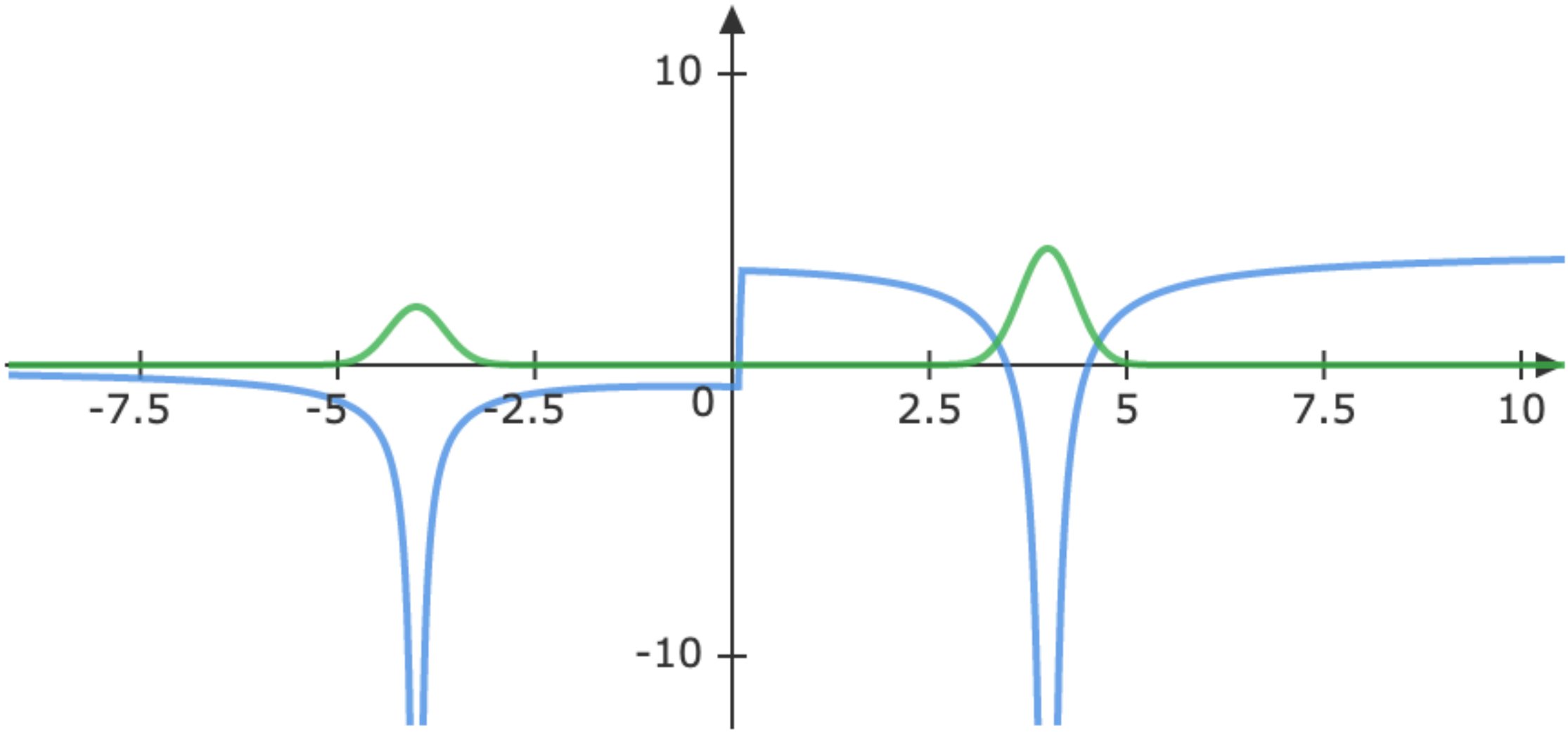
Step in the Kohn-Sham potential



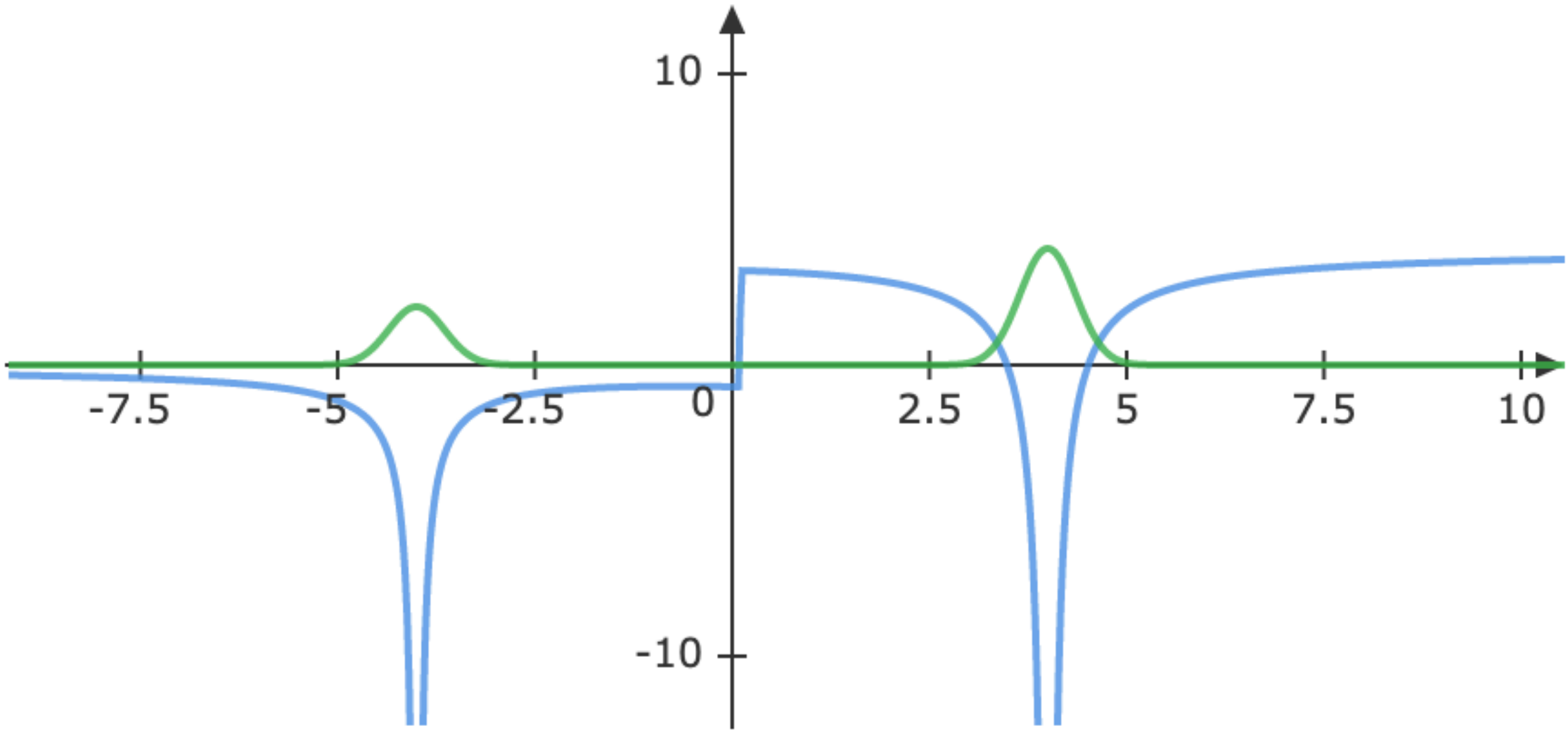
Step in the Kohn-Sham potential



Step in the Kohn-Sham potential

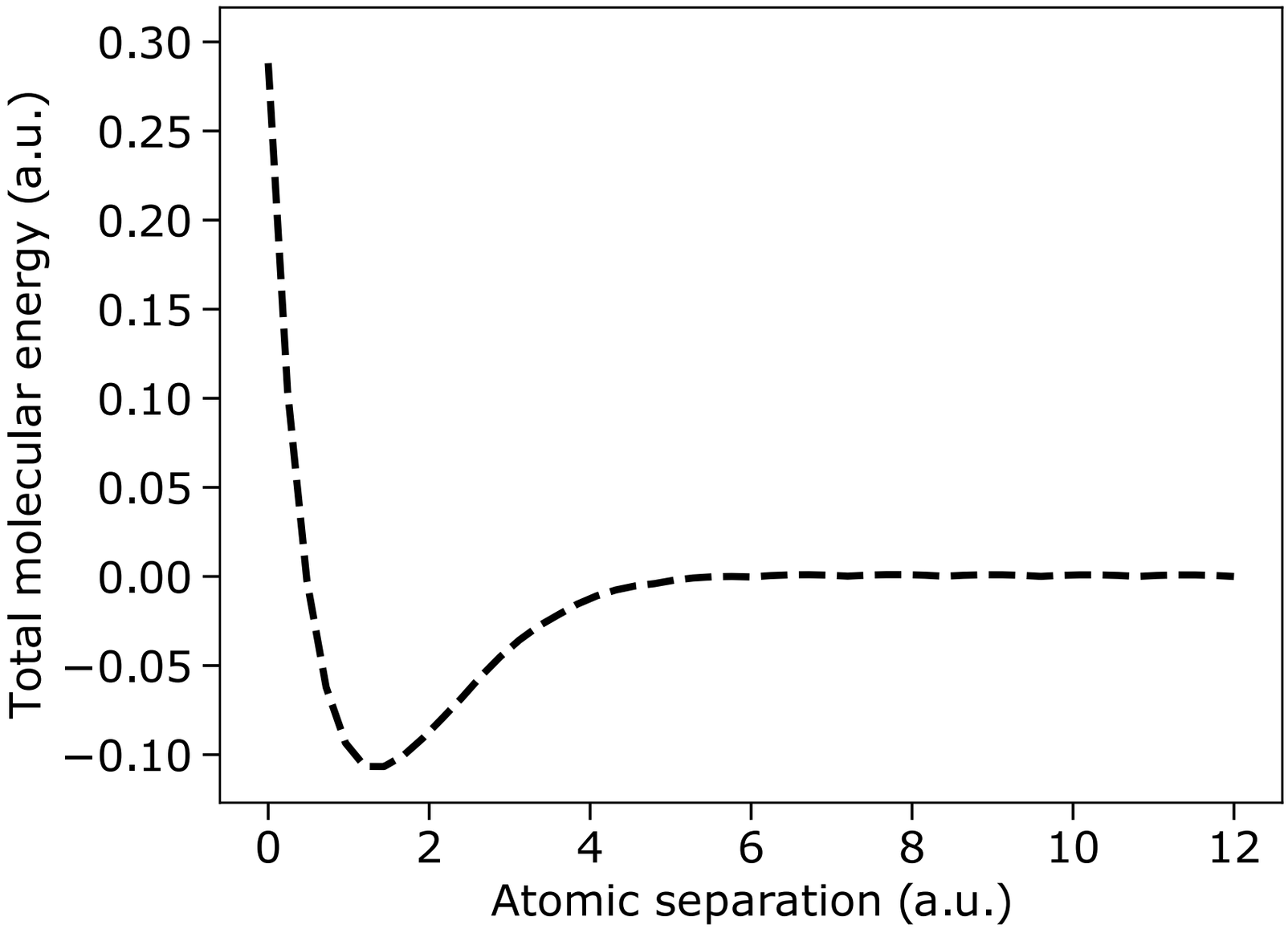


Step in the Kohn-Sham potential



$$n = \sum_j \left| \phi_j \right|^2$$

Step in the Kohn-Sham potential



The iDEA code

interacting Dynamic Electrons Approach

1) Calculate the fully correlated many-body wavefunction for two or three electrons for any system we choose in one-dimensional real space

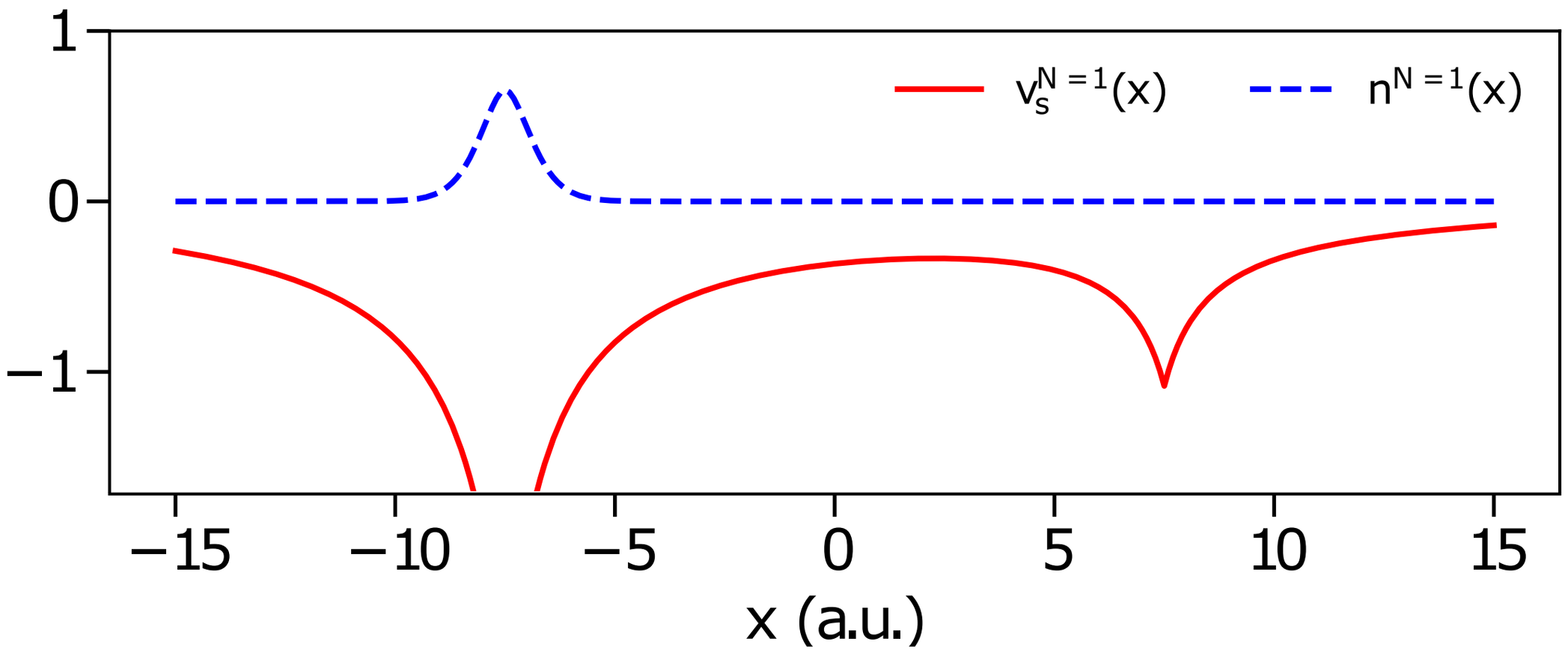
2) Then compute the exact electron density and 'reverse engineer' it to get the exact Kohn-Sham potential

3) The electrons' spin state can be chosen, e.g. spin singlet or triplet

"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)

The system:

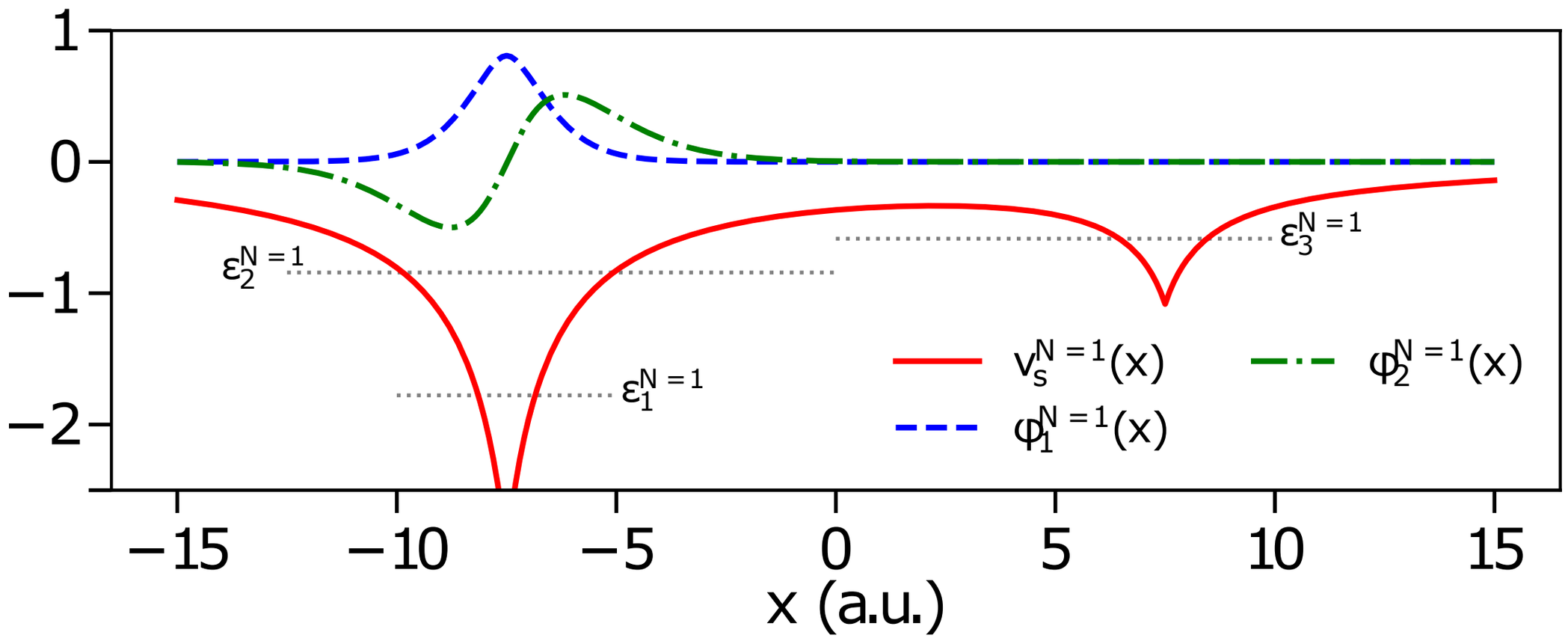
• One electron in a double-well external potential



“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)

The system:

• One electron in a double-well external potential



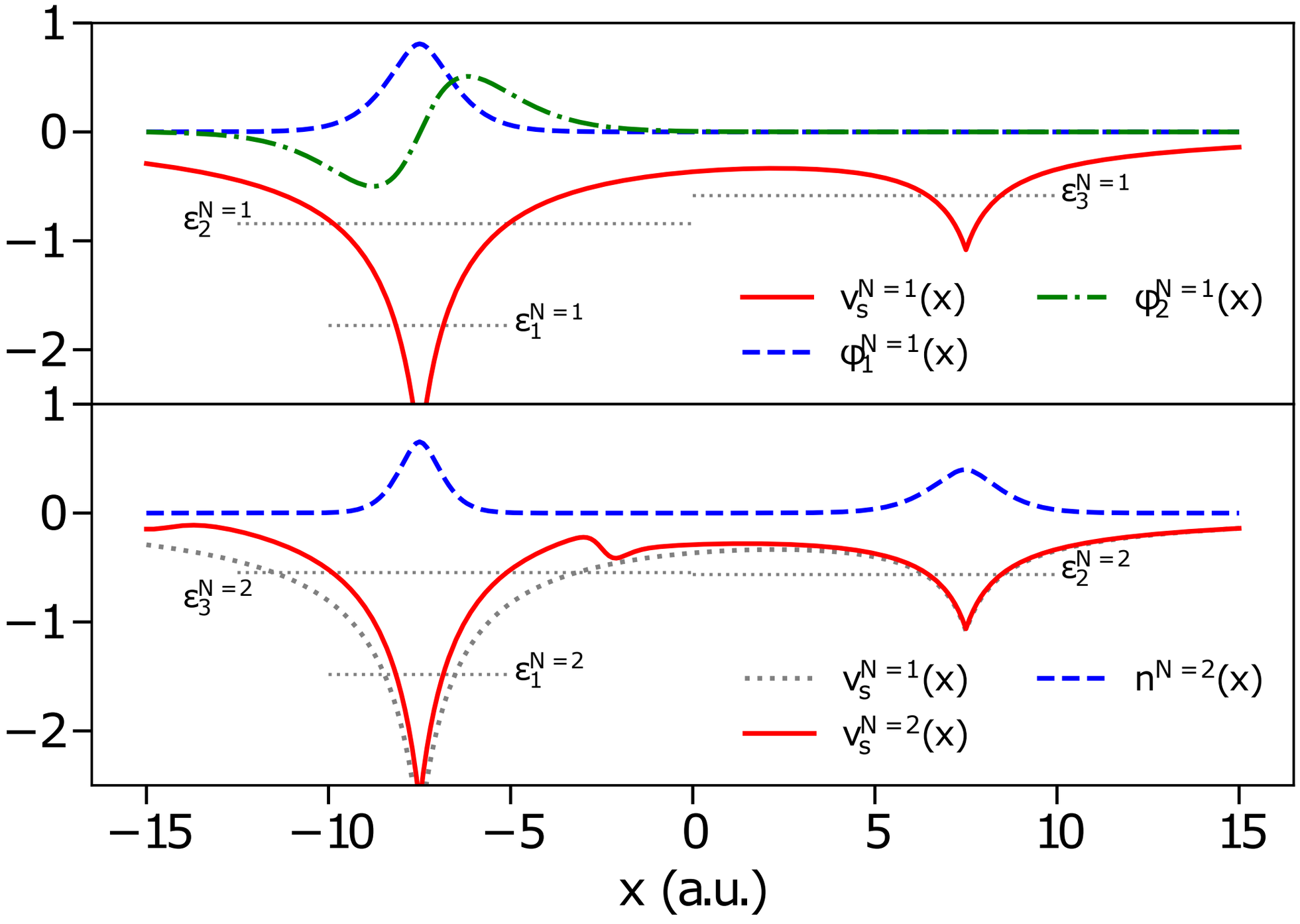
“Exact expressions for the height of the interatomic step in the exchange-correlation potential from the derivative discontinuity of the energy” M. J. P. Hodgson, Physical Review A **104**, 032803 (2021)

The top system:

• One electron in a double-well external potential

The bottom system:

• Two electrons in a spin triplet in the same double-well external potential



Option 1:
Design an auxiliary system without discontinuities

"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)

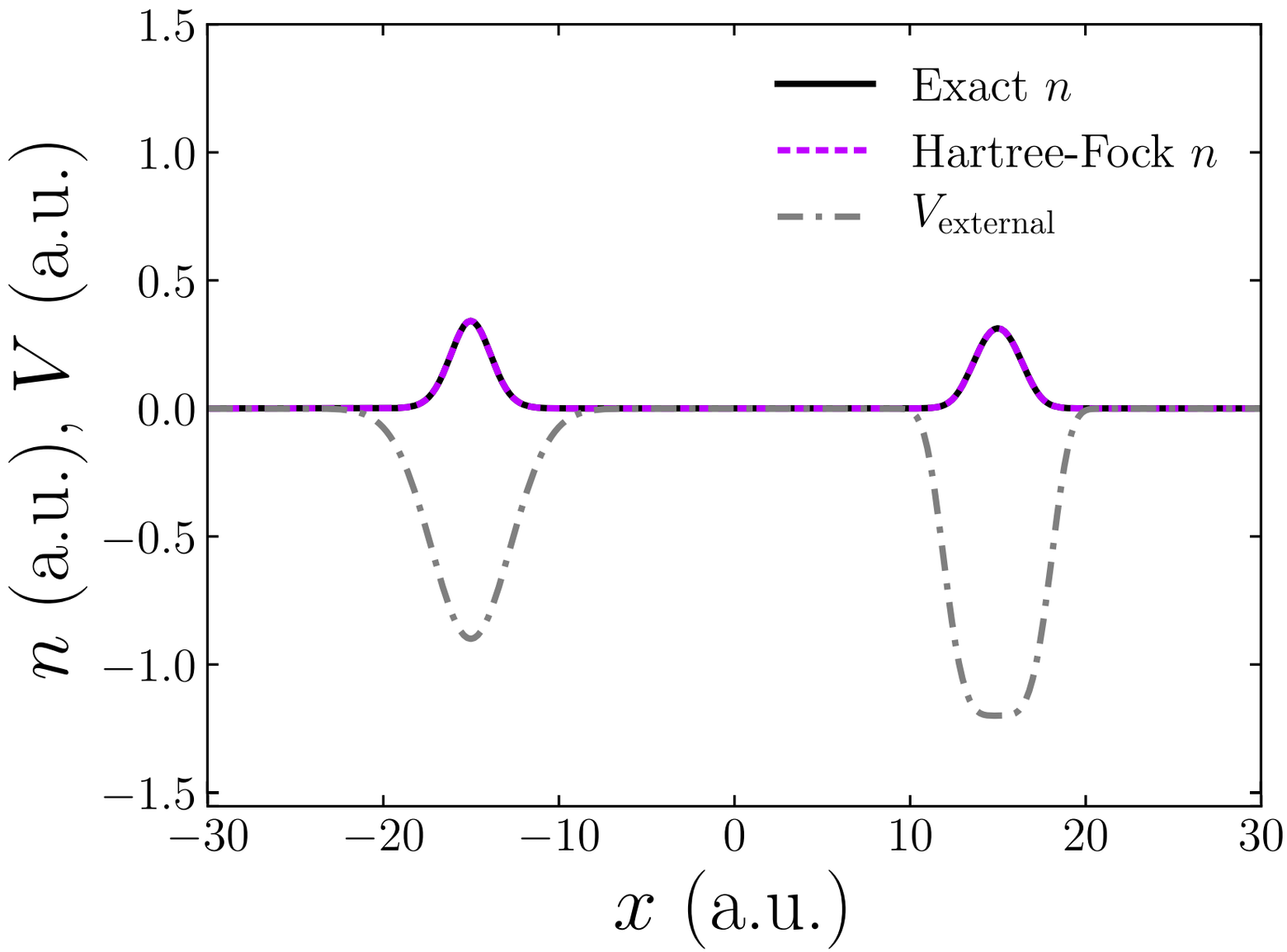
Option 2:
Add additional constraints to existing approximations

"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)

Option 3:
Use a power numerical technique to capture the non-analytic nature of the potential

"Machine learning the derivative discontinuity of density-functional theory" J. Gedeon, J. Schmidt, M. J. P. Hodgson, J. Wetherell, C. L. Benavides-Riveros and M. A. L. Marques, 2022 *Mach. Learn.: Sci. Technol*. **3** 015011 (2021)

Option 1:
Design an auxiliary system without discontinuities

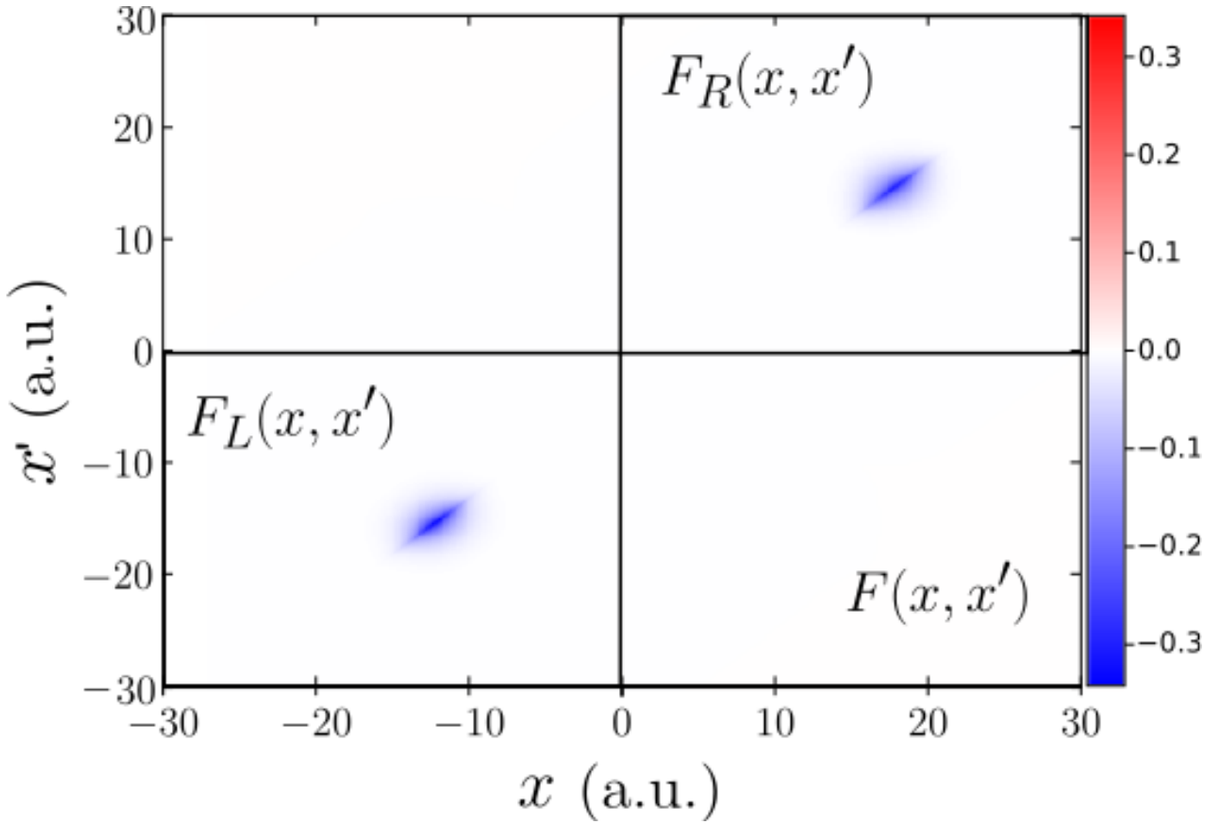


Option 1:
Design an auxiliary system without discontinuities

- The Fock operator in the vicinity of each electron is only concerned with the local density

$$F_{\mathrm{L+R}}(x,x') = F_{\mathrm{L}}(x,x') + F_{\mathrm{R}}(x,x')$$

- Kohn called this property "**nearsightedness**"

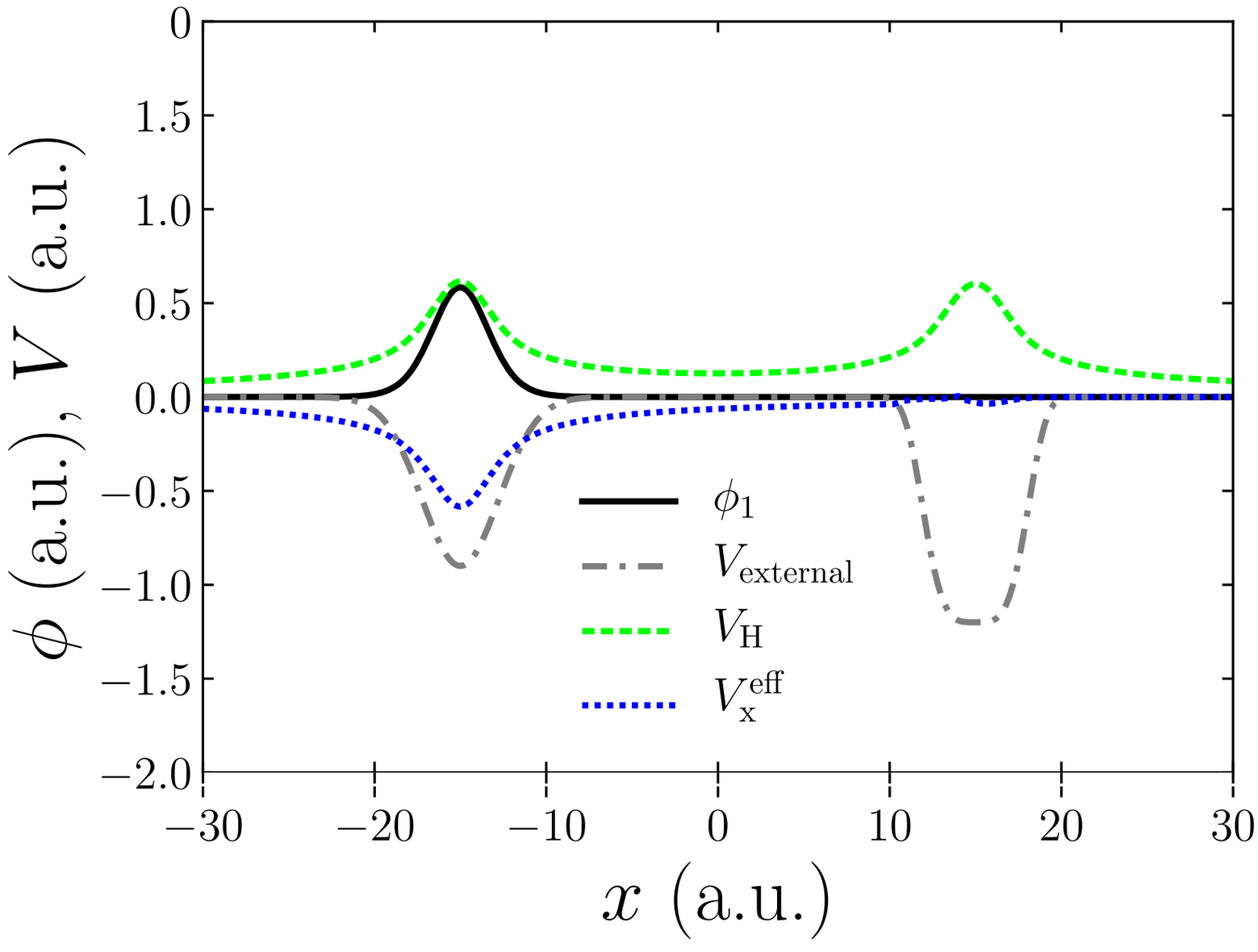


"Advantageous nearsightedness of many-body perturbation theory contrasted with Kohn-Sham density functional theory" J. Wetherell, M. J. P. Hodgson, L. Talirz, and R. W. Godby, Physical Review B **99**, 045129 (2019)

Option 1: Design an auxiliary system without discontinuities

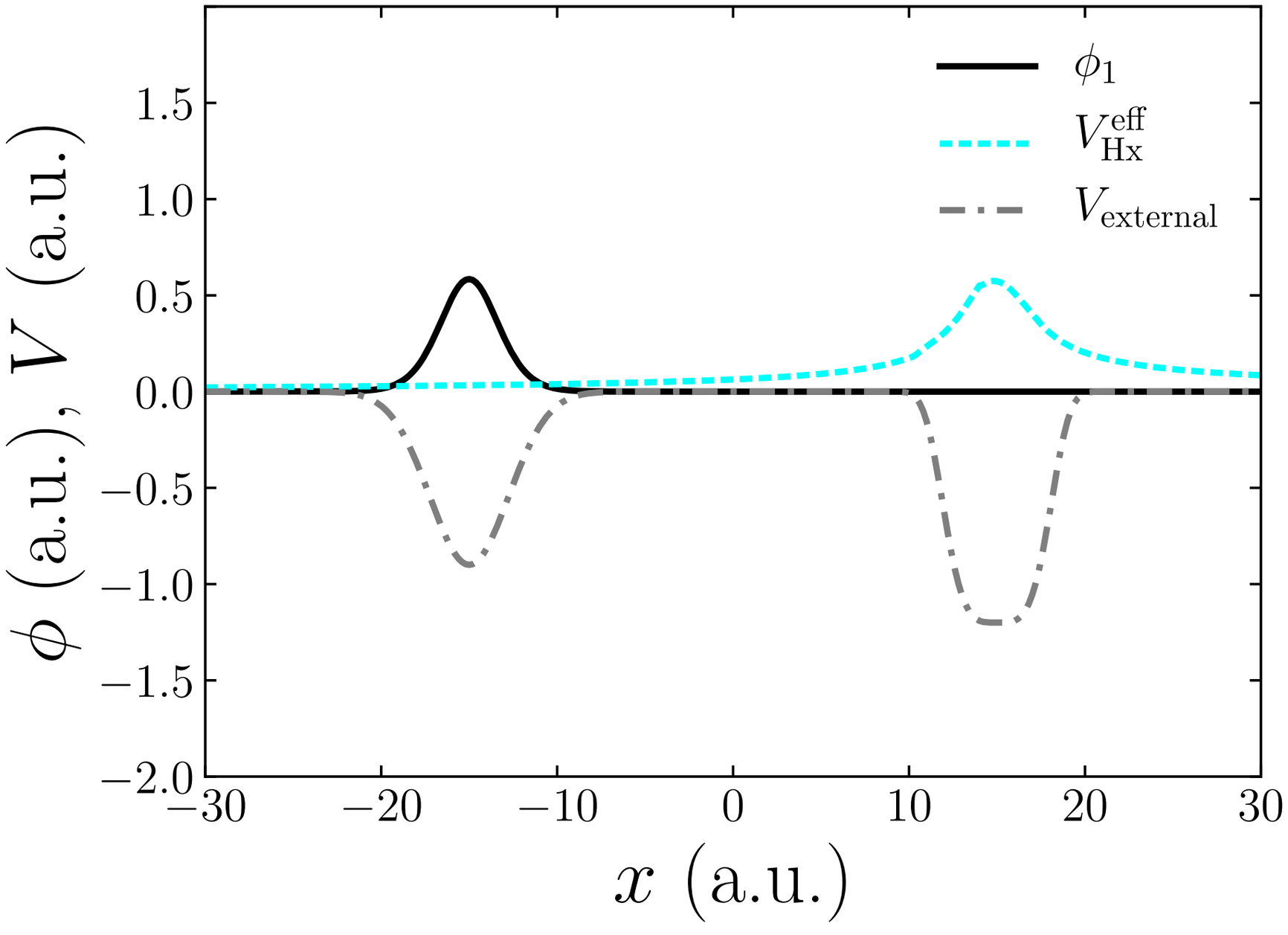
$$v_{\mathrm{x}}^{\mathrm{eff}}(x) = \frac{1}{\phi_1(x)} \int F(x, x')\phi_1(x')\mathrm{d}x'$$

- The effective potential for each orbital is different
- For this localised orbital it the effective potential is only a self interaction correction



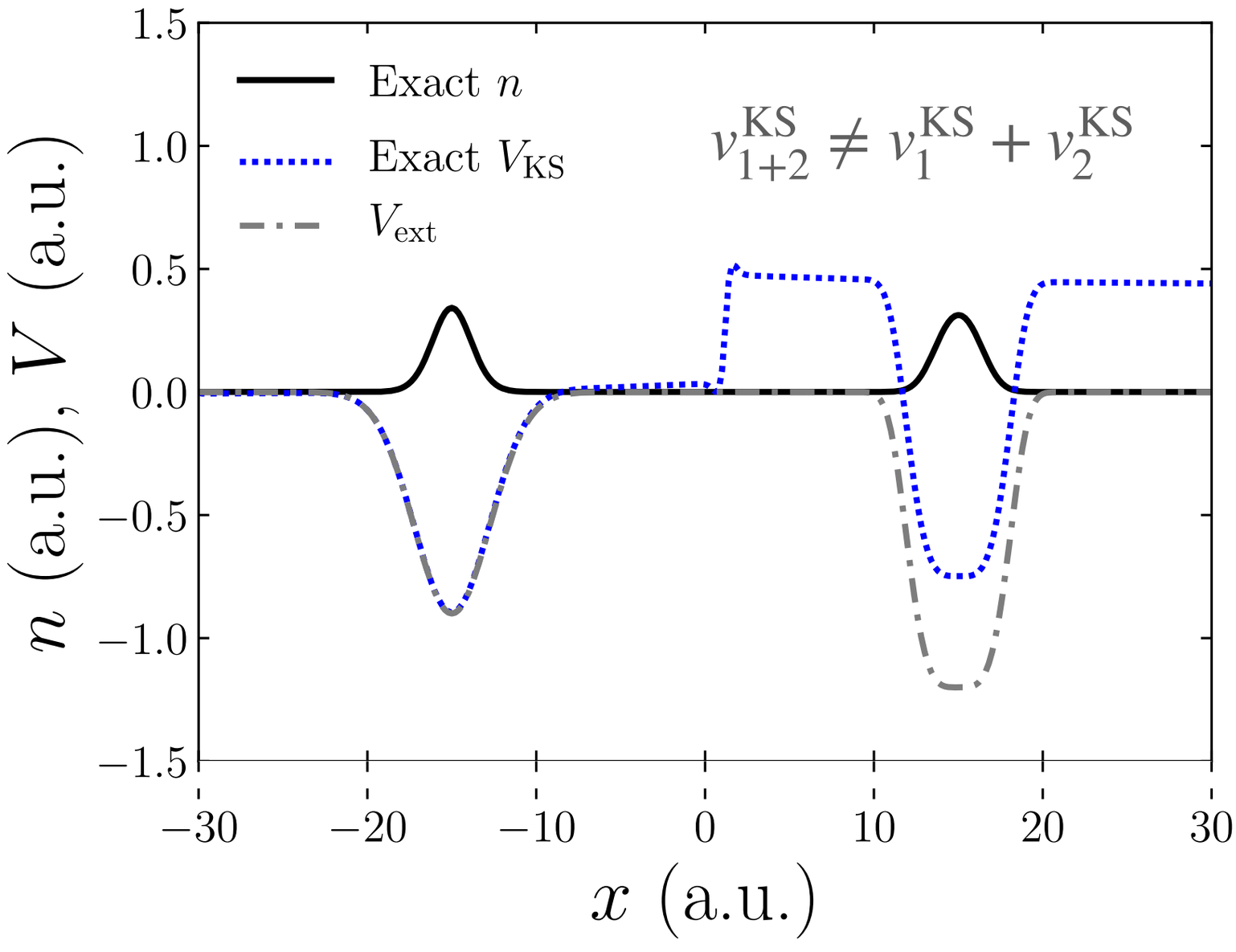
Option 1: Design an auxiliary system without discontinuities

- Each electron experiences a Hartree repulsion from the opposite well and no step is needed



Option 1:
Design an auxiliary system without discontinuities

- The Kohn-Sham potential is not nearsighted as in the vicinity of each electron, the potential is concerned with the electron density of the opposite well



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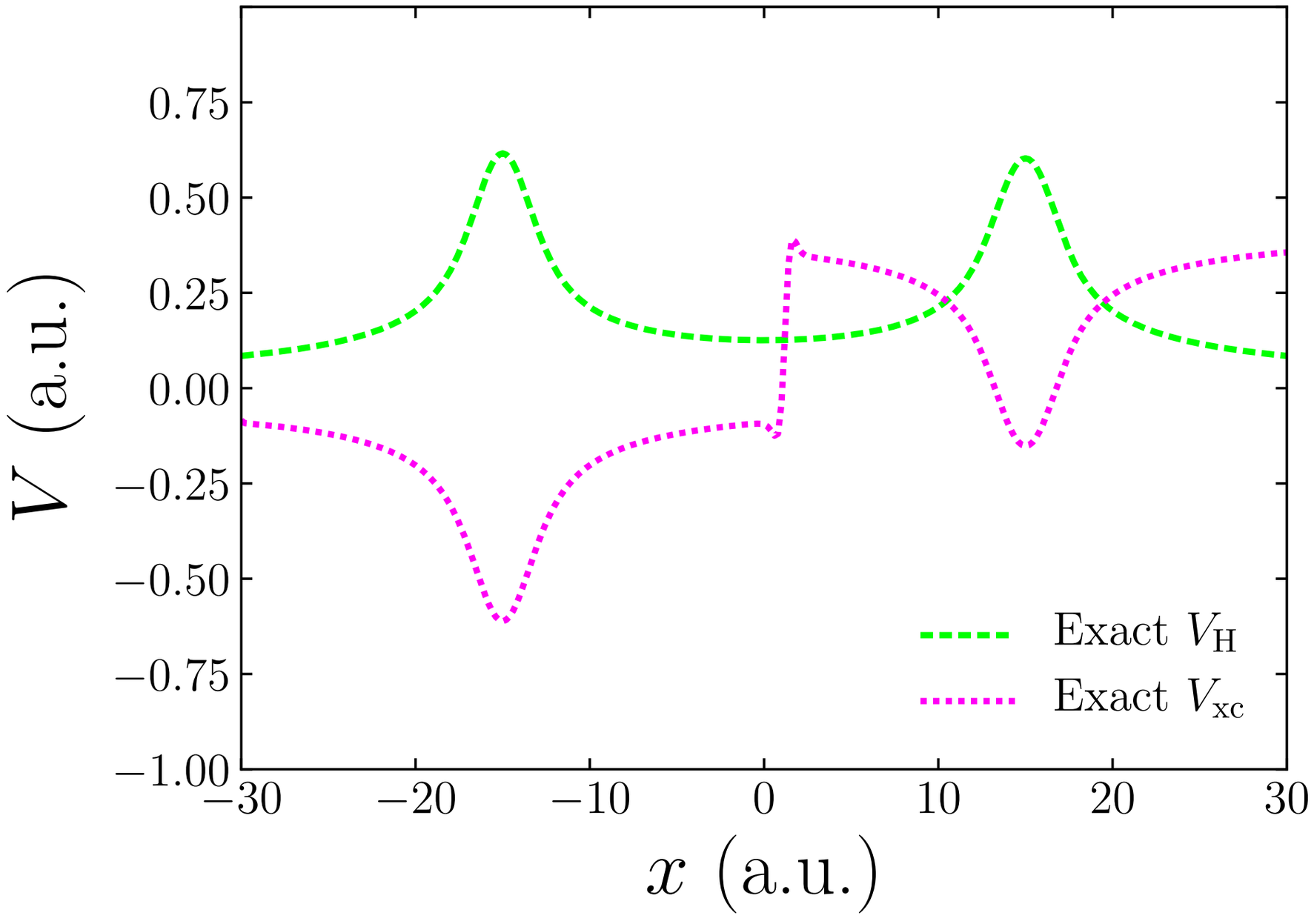

Option 1:
Design an auxiliary system without discontinuities

Kohn-Sham theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{L}}(x)\right)\phi_j = \varepsilon_j \phi_j$$

Generalised Kohn-Sham theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{L}}(x)\right)\phi_j + \int v_{\mathrm{NL}}(x,x')\phi_j(x')\mathrm{d}x' = \varepsilon_j \phi_j$$

Option 1:
Design an auxiliary system without discontinuities

Standard Kohn-Sham theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}} + v_{\text{H}} + v_{\text{xc}}\right)\phi_j = \varepsilon_j \phi_j$$

Unrestricted Hartree-Fock Kohn-Sham theory

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}} + v_{\text{H}} + v_{\text{c}}\right)\phi_j^\gamma + \int F^\gamma(x,x')\phi_j^\gamma(x')\mathrm{d}x' = \varepsilon_j^\gamma \phi_j^\gamma$$

"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)

Option 1:
Design an auxiliary system without discontinuities

Standard Kohn-Sham theory Not nearsighted

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}} + v_{\text{H}} + v_{\text{xc}}\right)\phi_j = \varepsilon_j \phi_j$$

Unrestricted Hartree-Fock Kohn-Sham theory Nearsighted

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}} + v_{\text{H}} + v_{\text{c}}\right)\phi_j^\gamma + \int F^\gamma(x,x')\phi_j^\gamma(x')\mathrm{d}x' = \varepsilon_j^\gamma \phi_j^\gamma$$

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Option 1:
Design an auxiliary system without discontinuities

The system:

- Two electrons in a spin singlet state in an asymmetric double-well external potential

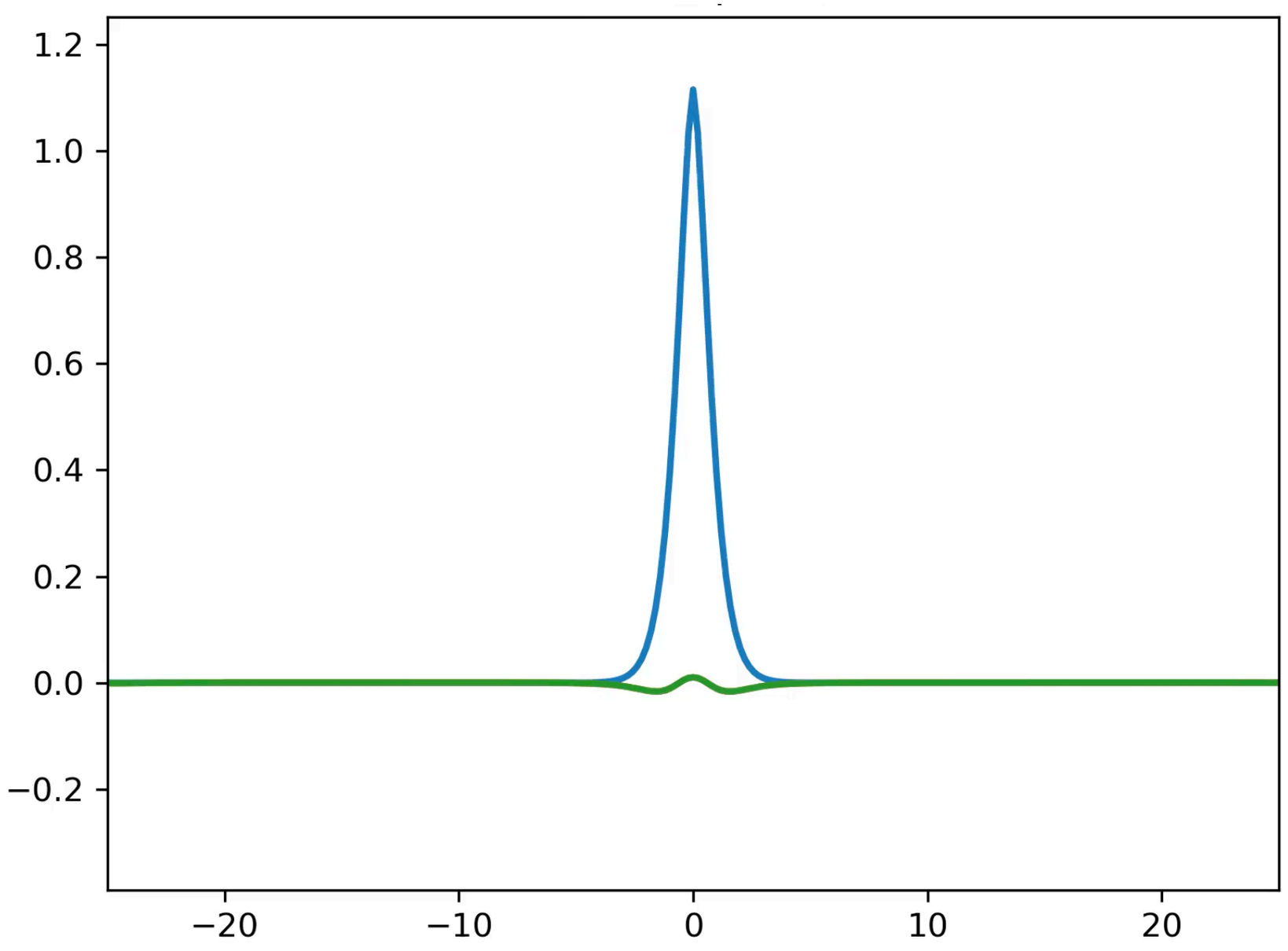
The calculations

- Calculate the exact exchange-correlation potential for standard Kohn-Sham theory

- Calculate the exact correlation potential for unrestricted Hartree-Fock Kohn-Sham theory

Option 1:
Design an auxiliary system without discontinuities

- Blue – electron density
- Green – unrestricted Hartree-Fock Kohn-Sham correlation potential
- Orange – standard Kohn-Sham xc potential



Option 1:
Design an auxiliary system without discontinuities

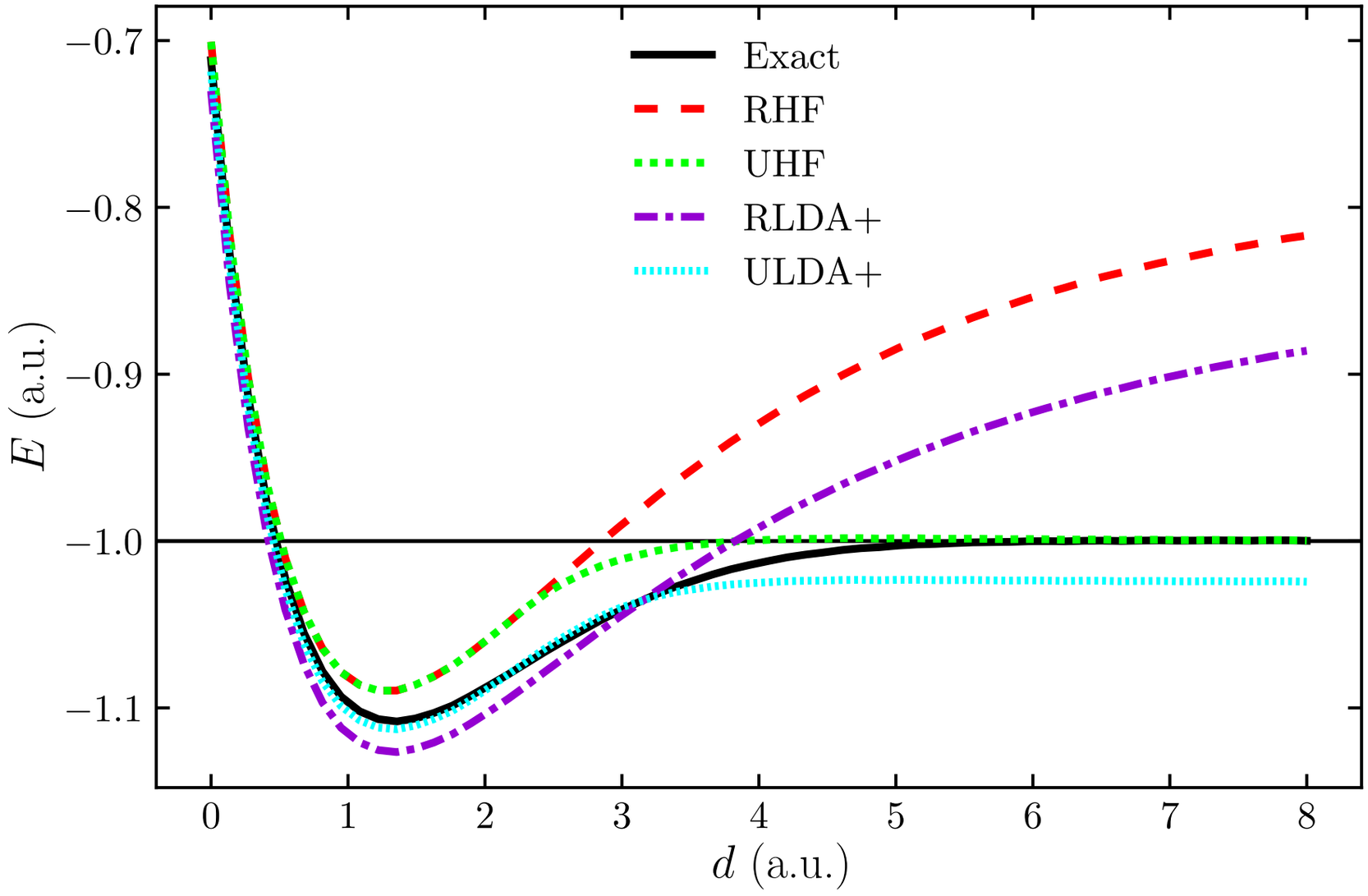
The system:

- Two electrons in a spin singlet state in a symmetric double-well external potential

The calculations

- Bonding energy curves

Option 1:
Design an auxiliary system without discontinuities



“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)

Option 2:
Add additional constraints to existing approximations

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

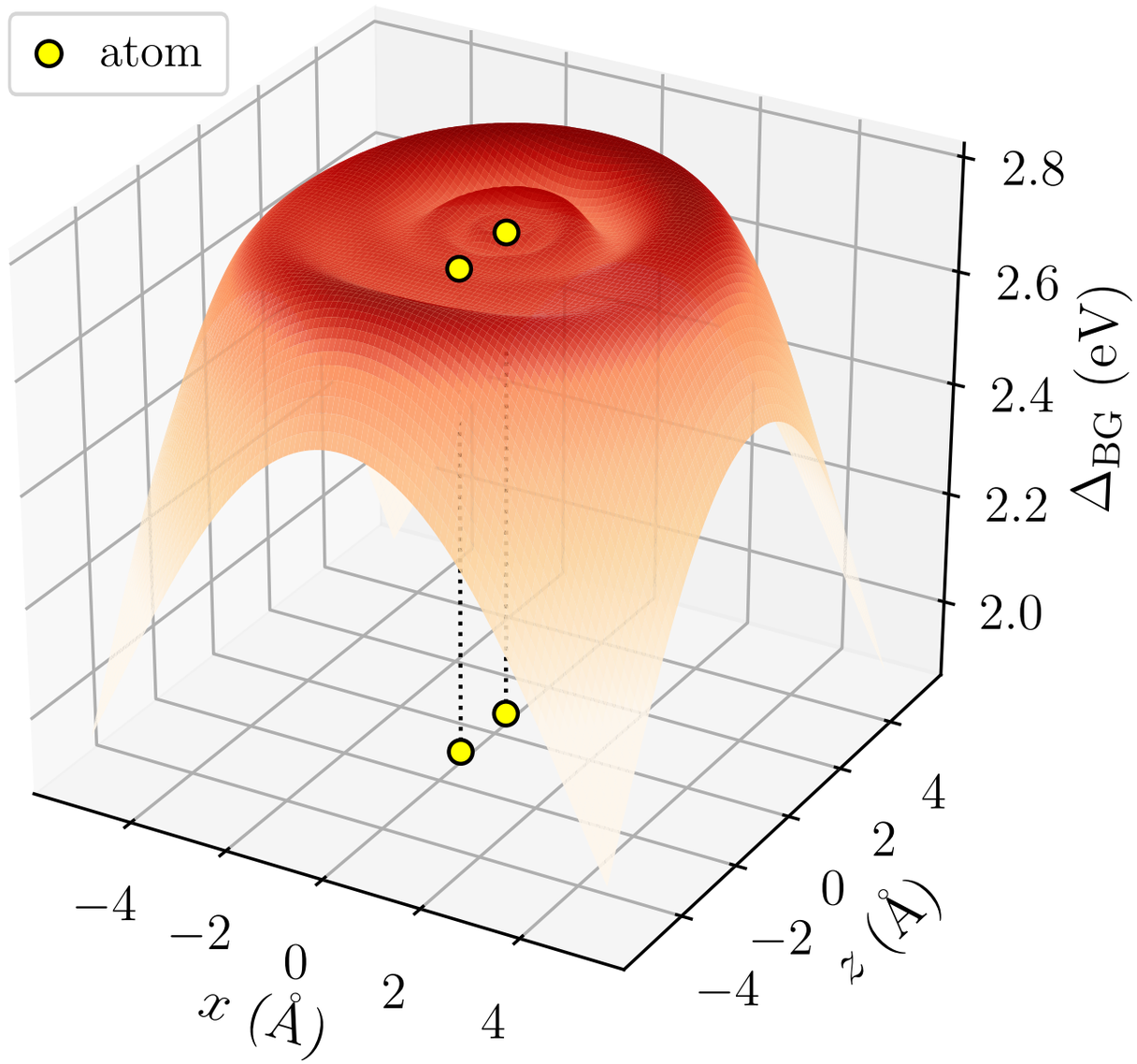
$$Q_{\mathrm{Hxc}} = \int \rho_{\mathrm{Hxc}} \mathrm{d}^3 r = N_0 - 1$$

“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)

Option 2:
Add additional constraints to existing approximations

$$Q_{\mathrm{Hxc}}^{N_0} = N_0 - 1$$

$$\lim_{\delta \to 0^+} Q_{\mathrm{Hxc}}^{N_0+\delta} = N_0$$



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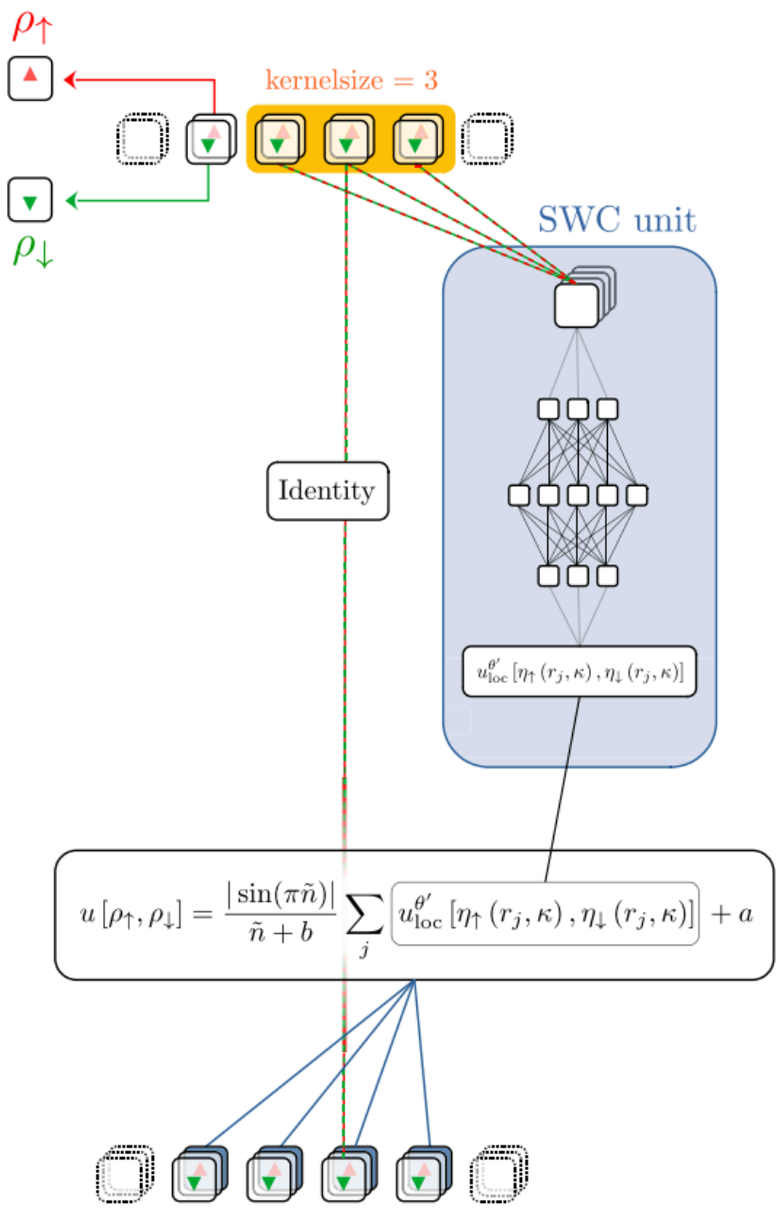
Option 3:
Use a power numerical technique to capture the non-analytic nature of the potential



- Train a neural network on model systems
- Model A was trained solely using integer density systems
- Model B was shown fractional densities

"Machine learning the derivative discontinuity of density-functional theory" J. Gedeon, J. Schmidt, M. J. P. Hodgson, J. Wetherell, C. L. Benavides-Riveros and M. A. L. Marques, 2022 *Mach. Learn.: Sci. Technol*. **3** 015011 (2021)

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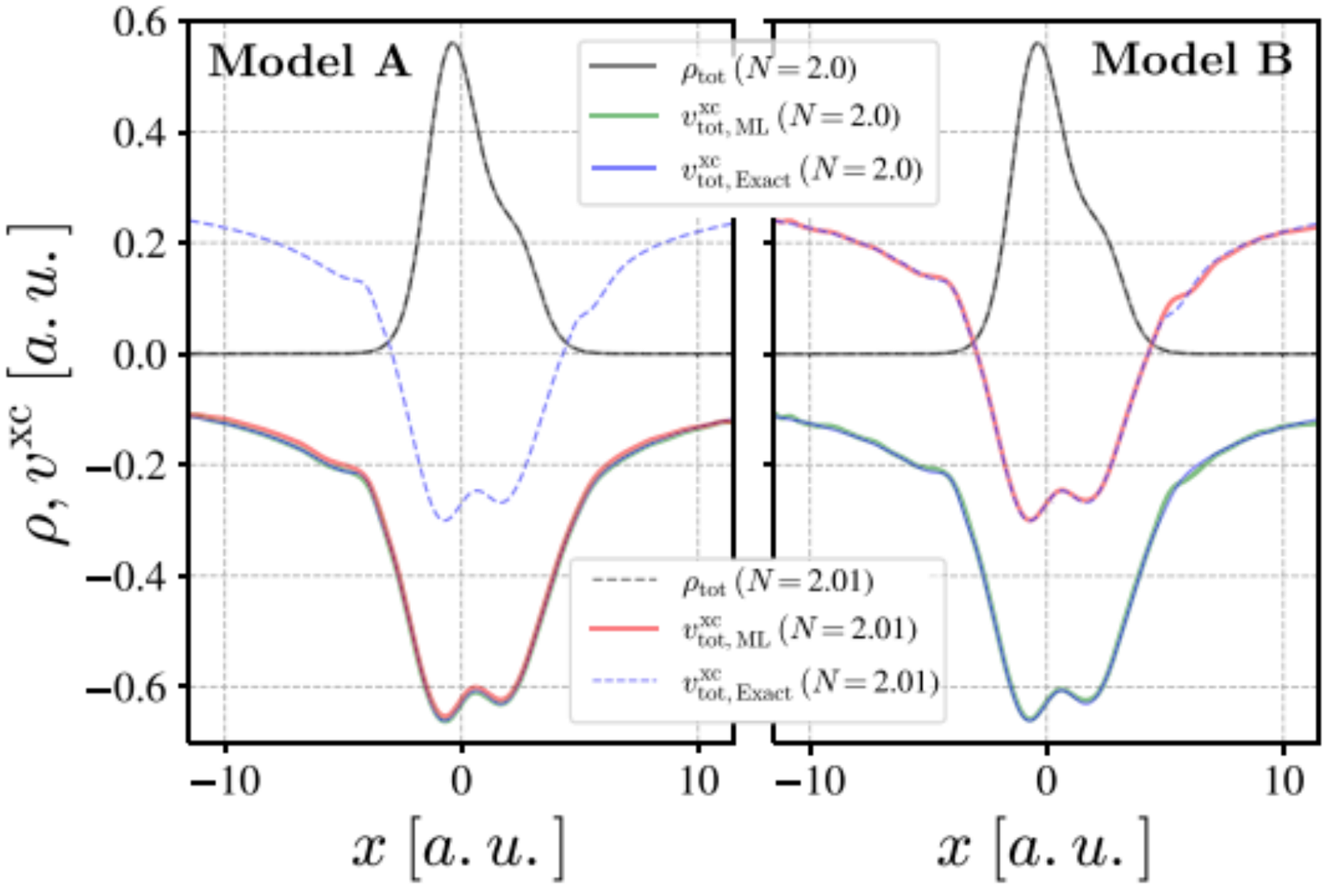

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Summary

- Discontinuities are present in the exact Kohn-Sham potential
- In principle, this non-analytic behaviour can be used to calculate useful quantities
- In practice, the existing approximations are unable to capture these discontinuities and hence more advanced approaches are required:

1. **Redesigning the Kohn-Sham system without discontinuities, e.g. using ‘nearsighted’ potentials**
2. **Employing advanced numerical techniques such as machine learning.**

Option 1 (alternative): Design an auxiliary system without discontinuities

- Design the non-interacting system so that the fundamental gap can be obtained but the number of electrons is always fixed

“Unified formulation of fundamental and optical gap problems in density-functional theory for ensembles” Bruno Senjean and Emmanuel Fromager Phys. Rev. A **98**, 022513

Option 1 (alternative): Design an auxiliary system without discontinuities

- Design the non-interacting system so that the fundamental gap can be obtained but the number of electrons is always fixed

- The system is an ensemble, where the density is given by

$$n = \xi^{-} n^{N_0-1} + \xi^{+} n^{N_0+1} + \left(1 - \xi^{-} \frac{N_0 - 1}{N_0} - \xi_{+} \frac{N_0 + 1}{N_0} \right) n^{N_0}$$

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$$\Rightarrow \int n \, \mathrm{d}^3 r = \xi^-(N_0 - 1) + \xi^+(N_0 + 1) + \left(1 - \xi^- \frac{N_0 - 1}{N_0} - \xi^+ \frac{N_0 + 1}{N_0}\right) N_0$$

$$= N_0$$

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- No discontinuity in the potential needed!

$$\Delta^{N_0} = \left.\frac{\partial E_{\mathrm{xc}}^{\xi}[n^{N_0}]}{\partial \xi}\right|_{\xi=0}$$

“Exact exchange-correlation potentials for calculating the fundamental gap with a fixed number of electrons” M. J. P. Hodgson, J. Wetherell and Emmanuel Fromager, Physical Review A **103**, 012806 (2021)