# Exact Hohenberg-Kohn Functional for a Lattice System

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# Density Functional Theory

Kohn-Sham System: Exact density of an interacting system can be calculated as density of a non-interacting system

$$n(\vec{r}) = \sum_{j=1}^{N} |\phi_j(\vec{r})|^2,$$

where the Kohn-Sham orbitals are given by

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + v_{\text{ext}}(\vec{r}) + v_{\text{h}}(\vec{r}) + v_{\text{xc}}\left[n\right](\vec{r}) \right) \phi_j(\vec{r}) = \epsilon_j \phi_j(\vec{r})$$

$\rightarrow$ Density Functional Theory is formally exact, but approximations of $v_{\text{xc}}$ are needed.

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# Limitations of Functionals in Density Functional Theory

- Simple approximations for $v_{xc}$ work well for many chemical and physical problems.
- Delocalization Error: transition state energies and barriers of chemical reactions, band gaps of materials, energies of dissociating molecular ions, excitation and binding energies of charge transfer
- To gain insight and to understand current limitations of functionals, we study the exact functional for model systems.

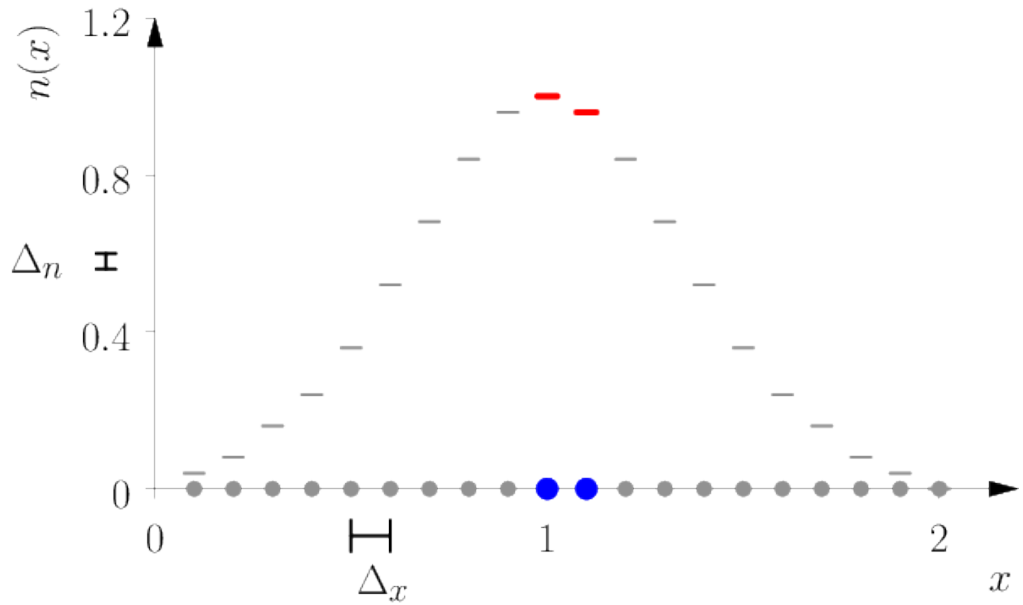
# Our Model-System: Hamiltonian on a 1D Real-Space Lattice

$$\hat{T} = -t_0 \sum_{l,\sigma} (\hat{c}^\dagger_{l,\sigma} \hat{c}_{l+1,\sigma} + \hat{c}^\dagger_{l+1,\sigma} \hat{c}_{l,\sigma}) + 2t_0 \sum_{l,\sigma} \hat{n}_{l,\sigma}, \qquad t_0 = \frac{1}{2 m_e \Delta x^2}$$

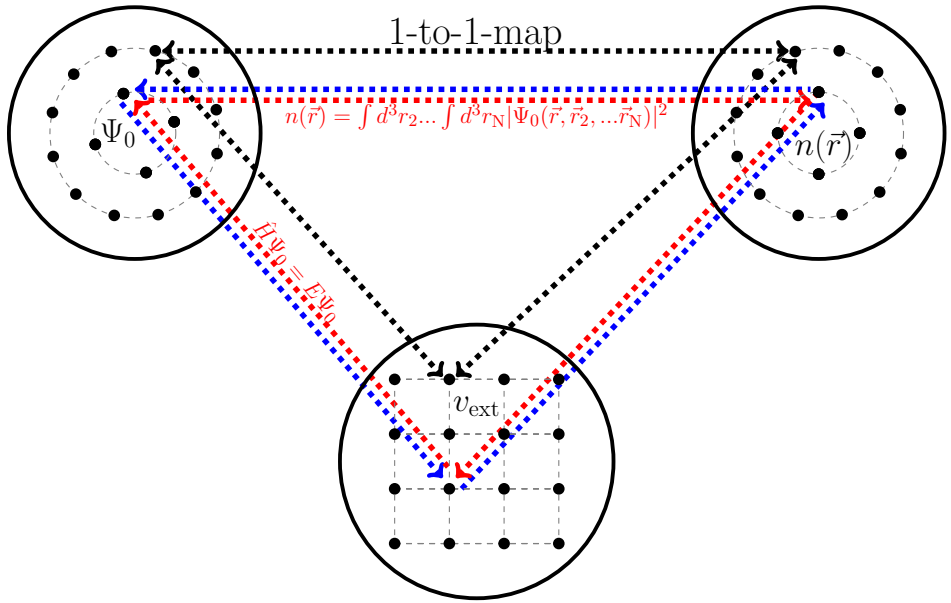
$$\hat{V}_{ee} = \sum_{l,m,\sigma,\sigma'} \frac{\hat{c}^\dagger_{l,\sigma} \hat{c}^\dagger_{m,\sigma'} \hat{c}_{m,\sigma'} \hat{c}_{l,\sigma}}{2\sqrt{(l\Delta x - m\Delta x)^2 + 1}}, \qquad \hat{V}_{ee} = U \sum_l \hat{n}_{l,\uparrow} \hat{n}_{l,\downarrow}$$

$$\hat{V}_{\text{ext}} = \sum_{l,\sigma} V_{ext}(l) \hat{n}_{l,\sigma}$$

$$\hat{V}_{\text{N}} = \mu \hat{N}$$



# Levy-Lieb Constrained Search

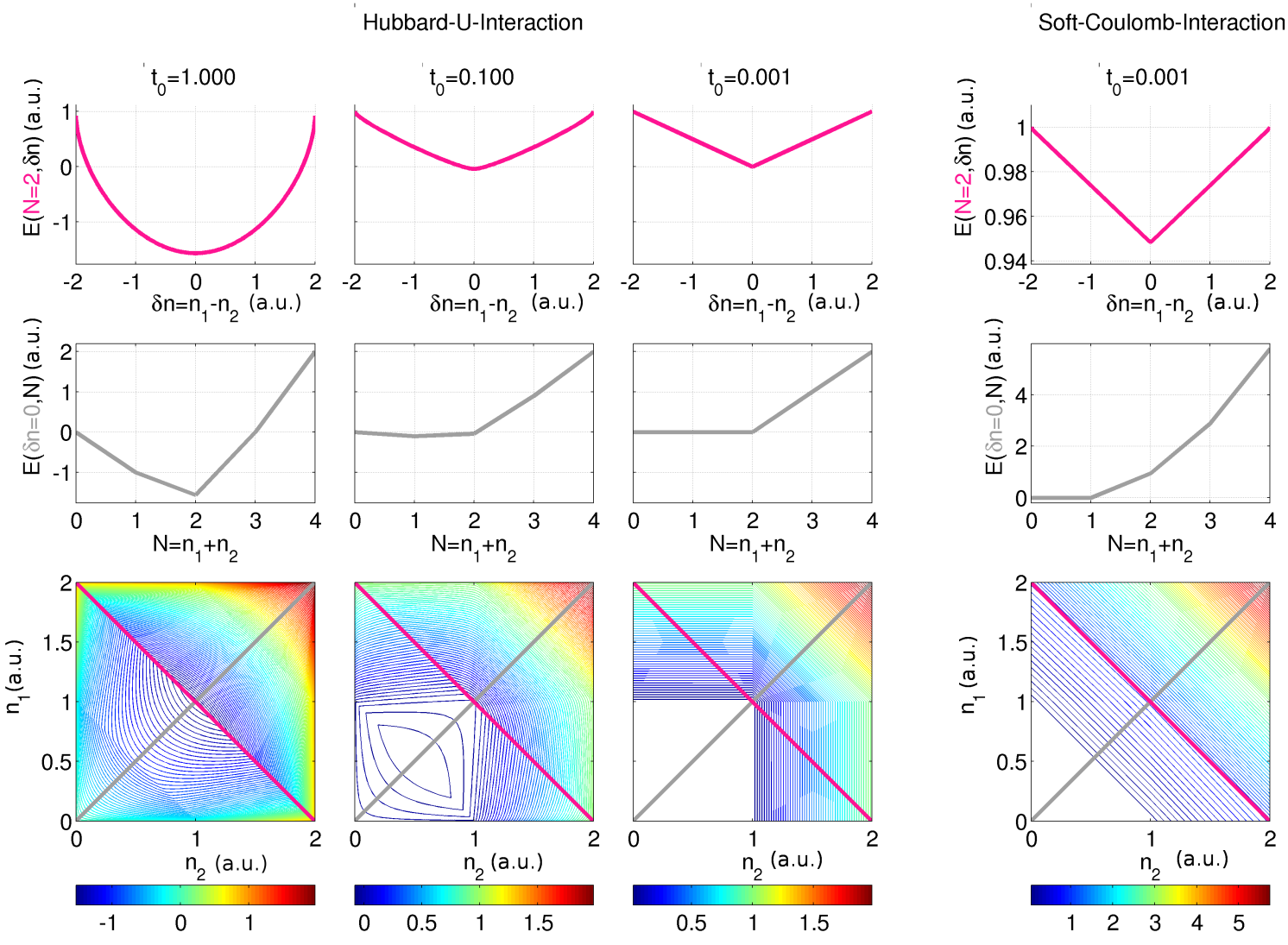



Hohenberg-Kohn functional

$$F_{HK}[n(\vec{r})] = \min_{\Psi \to n(\vec{r})} \langle \Psi[n(\vec{r})] | \hat{T} + \hat{V}_{ee} | \Psi[n(\vec{r})] \rangle$$

Hohenberg-Kohn functional for two sites $F_{HK}[n_1, n_2]$

# The Exact Hohenberg-Kohn Functional for Two Sites

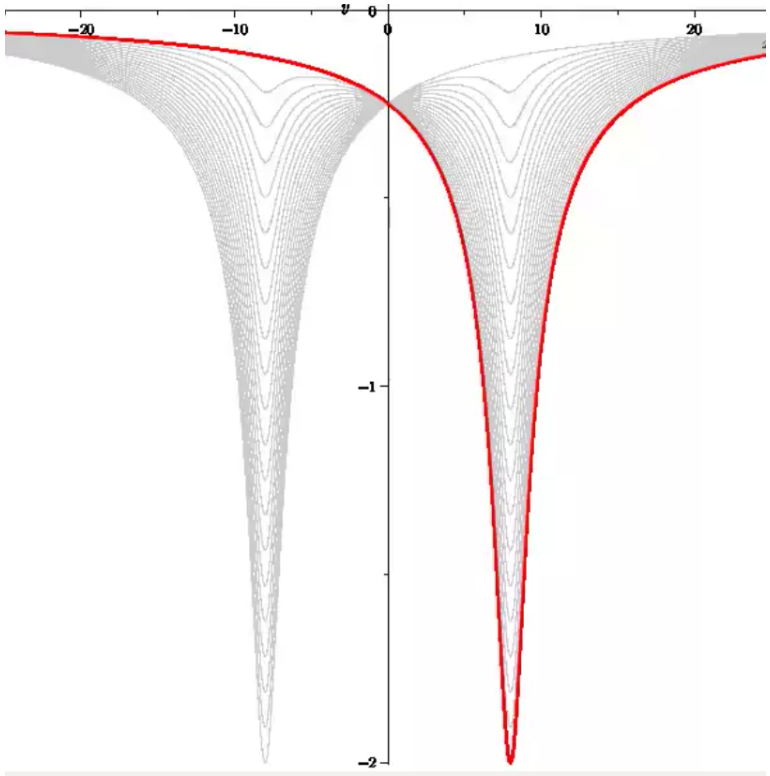


# Soft-Coulomb Molecules in 1D

$$\hat{H}(\alpha) = \hat{T} + \hat{W} + \hat{V}(\alpha)$$

$$\hat{T} = \sum_{j=1}^{2} -\frac{d^2}{dx_j^2}$$

$$\hat{W} = \frac{1}{2} \sum_{i \neq j}^{2} \frac{1}{\sqrt{(x_i - x_j)^2 + 1}}$$




$$\hat{V}(\alpha) = \sum_{j=1}^{2} \frac{Z_1(\alpha)}{\sqrt{(x_j - d)^2 + 1}} + \frac{Z_2(\alpha)}{\sqrt{(x_j + d)^2 + 1}}$$

$$Z_1(\alpha) = -\alpha,\ Z_2(\alpha) = -(2 - \alpha),\ \alpha \in [0, 2], \quad d = 3,8 \text{ Bohr}$$

# Exact Density and Kohn-Sham Potential

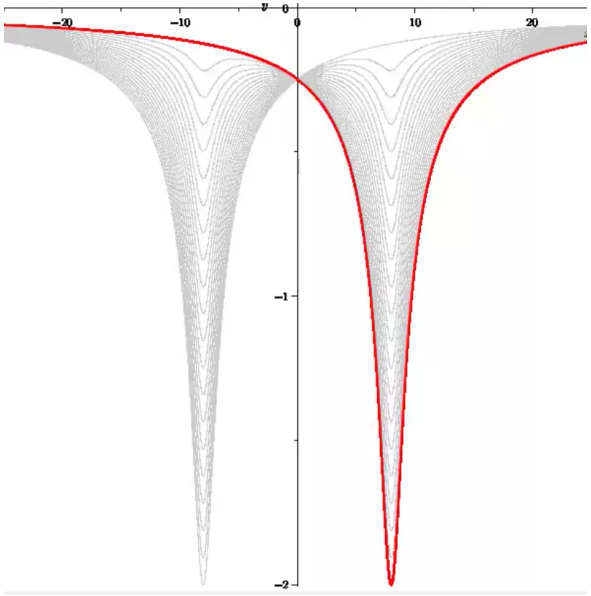
Exact Kohn-Sham potential for two electrons in spin singlet configuration (Helbig et al. 2009 )

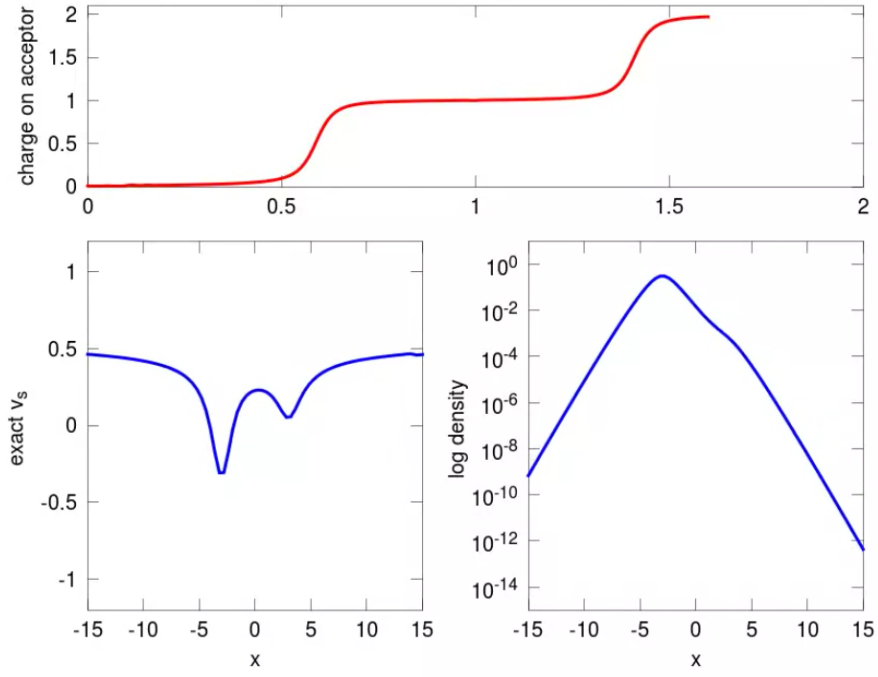
$$v_{\mathrm{KS}}(x) = \frac{1}{2}\frac{\nabla^2\sqrt{n(x)}}{\sqrt{n(x)}} + \epsilon_1$$

Exact solution of static two-electron Schrödinger equation with octopus (A. Castro et al.)

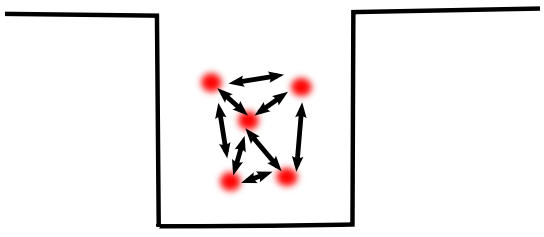
$$\begin{aligned}\hat{H}(\alpha)\Psi_j(\alpha) &= E_j(\alpha)\Psi_j(\alpha)\\ n(x) &= \langle\Psi|\,\hat{n}(x)\,|\Psi\rangle\\ \hat{n}(x) &= \sum_j \delta(x - x_j)\end{aligned}$$

# Intra-System Derivative Discontinuity for 1D Molecules



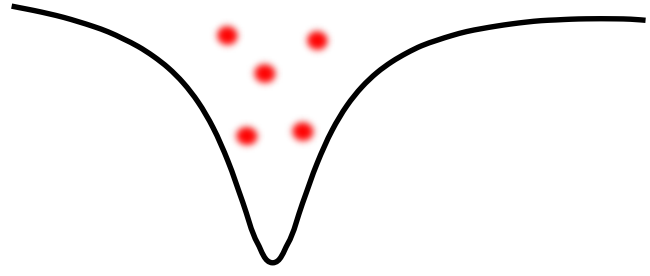




Interacting System



External Potential

Kohn-Sham-System



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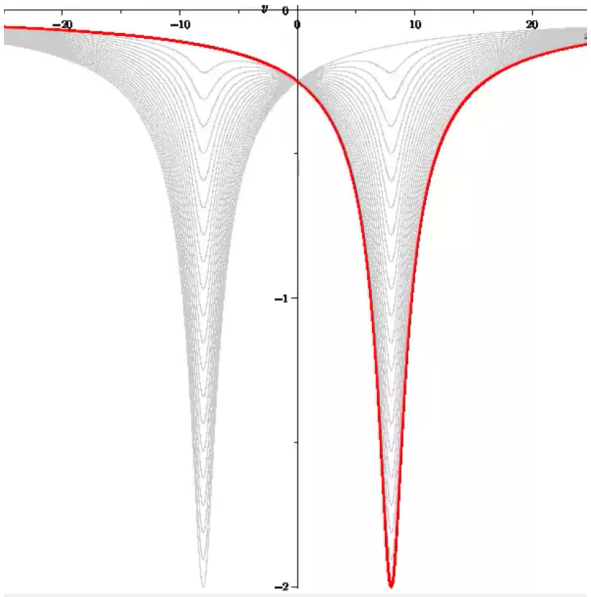


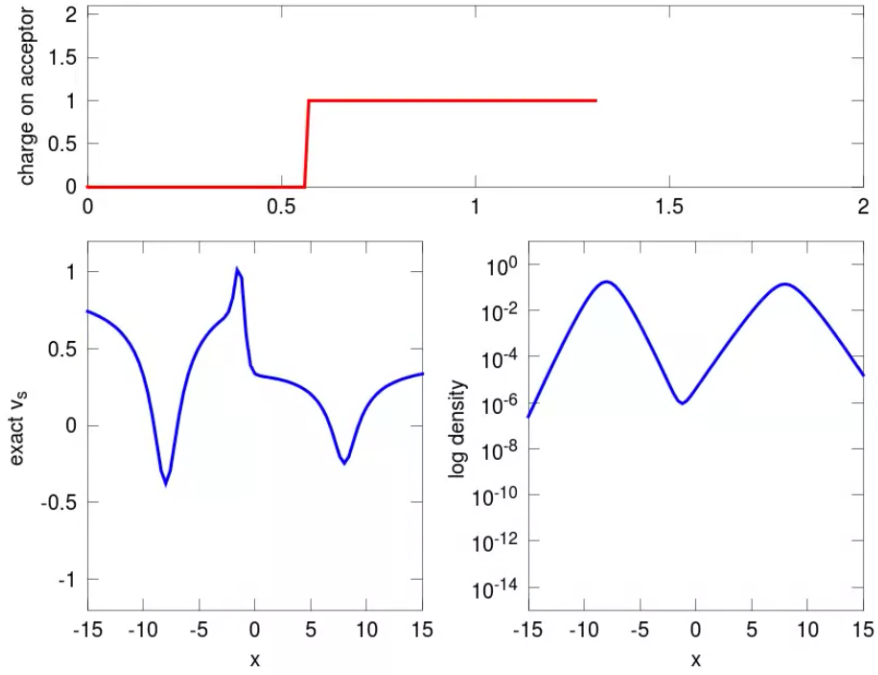


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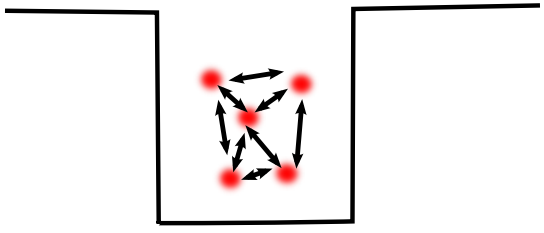

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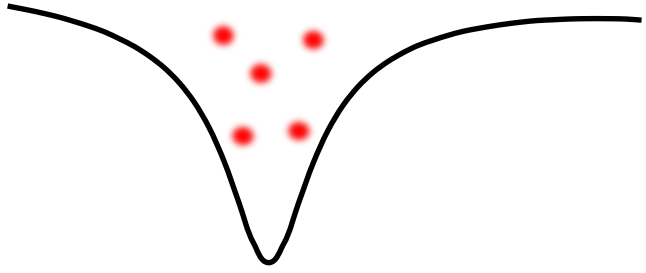

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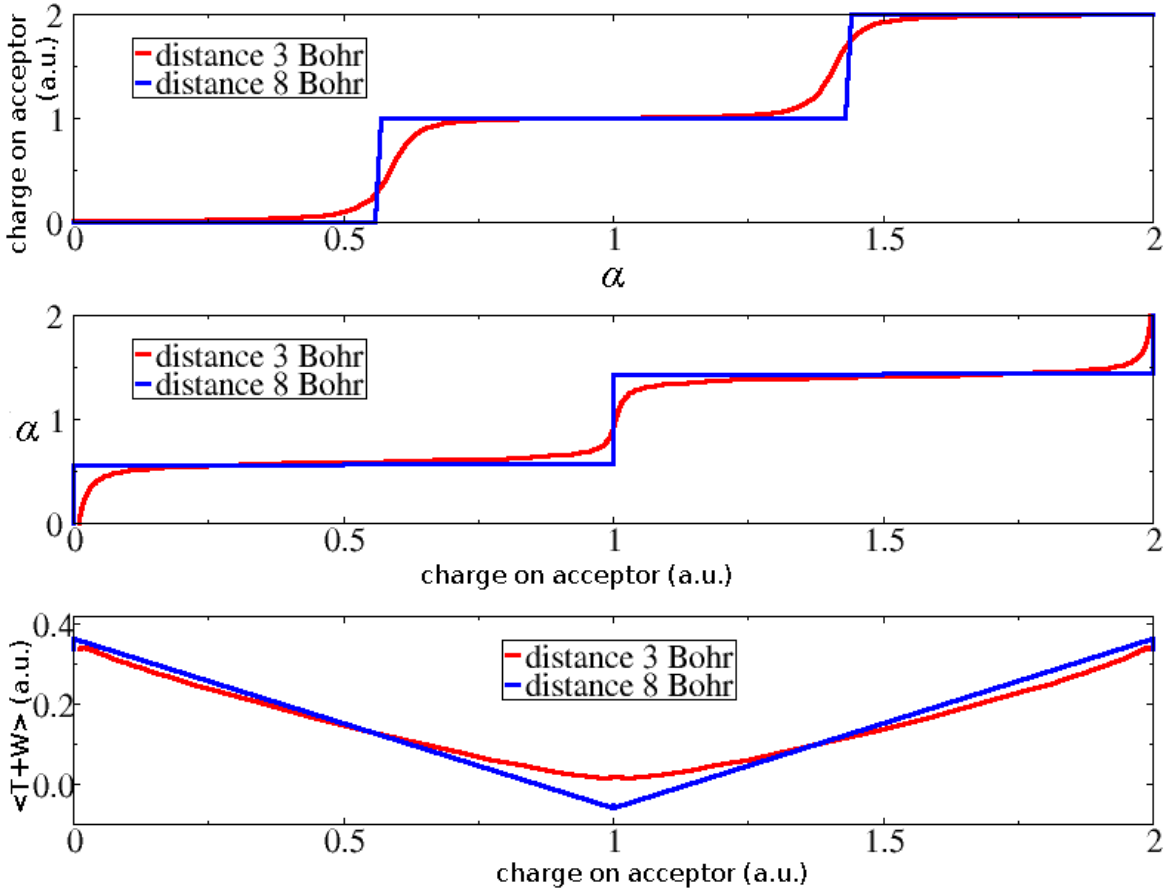

# Summary & Outlook

- Density Functional Theory is efficient, and formally exact.
- Approximations for $v_{\mathrm{xc}}$ needed.
- Exact $v_{\mathrm{xc}}(x)$ has steps and peaks (Helbig et al. 2009).
- Intra- (and Inter-) system derivative discontinuity of exact functional $v_{\mathrm{xc}}[n(x)]$ for n-site model
- We link the intra-system derivative discontinuity of the n-site model to the intra-system derivative discontinuity of two particles in 1D-molecules.
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Thank you!