

The exact Hohenberg-Kohn functional for a lattice model

Tanja Dimitrov¹(dimitrov@fhi-berlin.mpg.de), Heiko Appel¹, Angel Rubio^{1,2}

[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
[2] NanoBio Spectroscopy group and ETSF, Universidad del País Vasco, San Sebastián, Spain



MAX-PLANCK-GESELLSCHAFT

Introduction

For a discretized soft-Coulomb lattice model we investigate the exact solution of the many-body Schrödinger equation in Fock space. Using quadratic optimization with quadratic constraints, or alternatively exact diagonalization, we explicitly construct the exact Hohenberg-Kohn functional and the mapping from densities to wavefunctions. We analyze the resulting exact Hohenberg-Kohn functional and draw conclusions for the construction of approximate functionals.

Two-site soft-Coulomb model

Hamiltonian

$$\begin{aligned} \hat{H} &= \hat{T} + \hat{W} + \hat{V} \\ \hat{T} &= -t_0 \sum_{l,\sigma} (\hat{c}_{l,\sigma}^\dagger \hat{c}_{l+1,\sigma} + \hat{c}_{l+1,\sigma}^\dagger \hat{c}_{l,\sigma}) + 2t_0 \sum_{l,\sigma} \hat{n}_{l,\sigma} \\ t_0 &= \frac{\hbar^2}{2m_e \Delta^2} \\ \hat{W} &= \sum_{l,m,\sigma,\sigma'} \frac{e^2 \hat{c}_{l,\sigma}^\dagger \hat{c}_{m,\sigma'}^\dagger \hat{c}_{m,\sigma} \hat{c}_{l,\sigma}}{2\sqrt{(l\Delta - m\Delta)^2 + c}} \\ \hat{V} &= \sum_{l,\sigma} \hat{n}_{l,\sigma} \cdot v_{l,\sigma} \end{aligned}$$

Density and spin operators

$$\begin{aligned} \hat{n} &= \sum_{j,\sigma} \hat{c}_{j,\sigma}^\dagger \hat{c}_{j,\sigma} \\ \hat{S}_x &= \frac{1}{2} \sum_j (\hat{c}_{j,\uparrow}^\dagger \hat{c}_{j,\downarrow} + \hat{c}_{j,\downarrow}^\dagger \hat{c}_{j,\uparrow}) \\ \hat{S}_y &= \frac{1}{2i} \sum_j (-\hat{c}_{j,\uparrow}^\dagger \hat{c}_{j,\downarrow} + \hat{c}_{j,\downarrow}^\dagger \hat{c}_{j,\uparrow}) \\ \hat{S}_z &= \frac{1}{2} \sum_j (\hat{n}_{j,\uparrow} - \hat{n}_{j,\downarrow}) \\ \hat{S}^2 &= \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \end{aligned}$$

We consider different particle numbers by including a chemical potential μ .

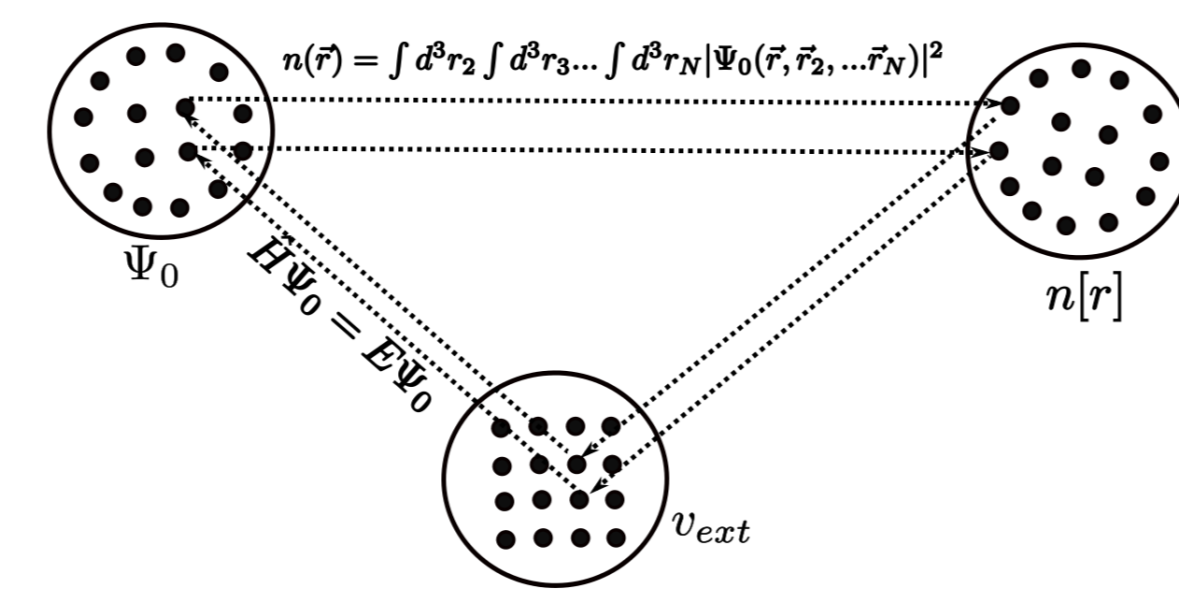
Levy-Lieb constraint search (M. Levy 1979 [1], E. Lieb 1983 [2])

Expand eigenfunctions in a complete basis set (energy eigenfunctions, Slater-Determinants, etc.)

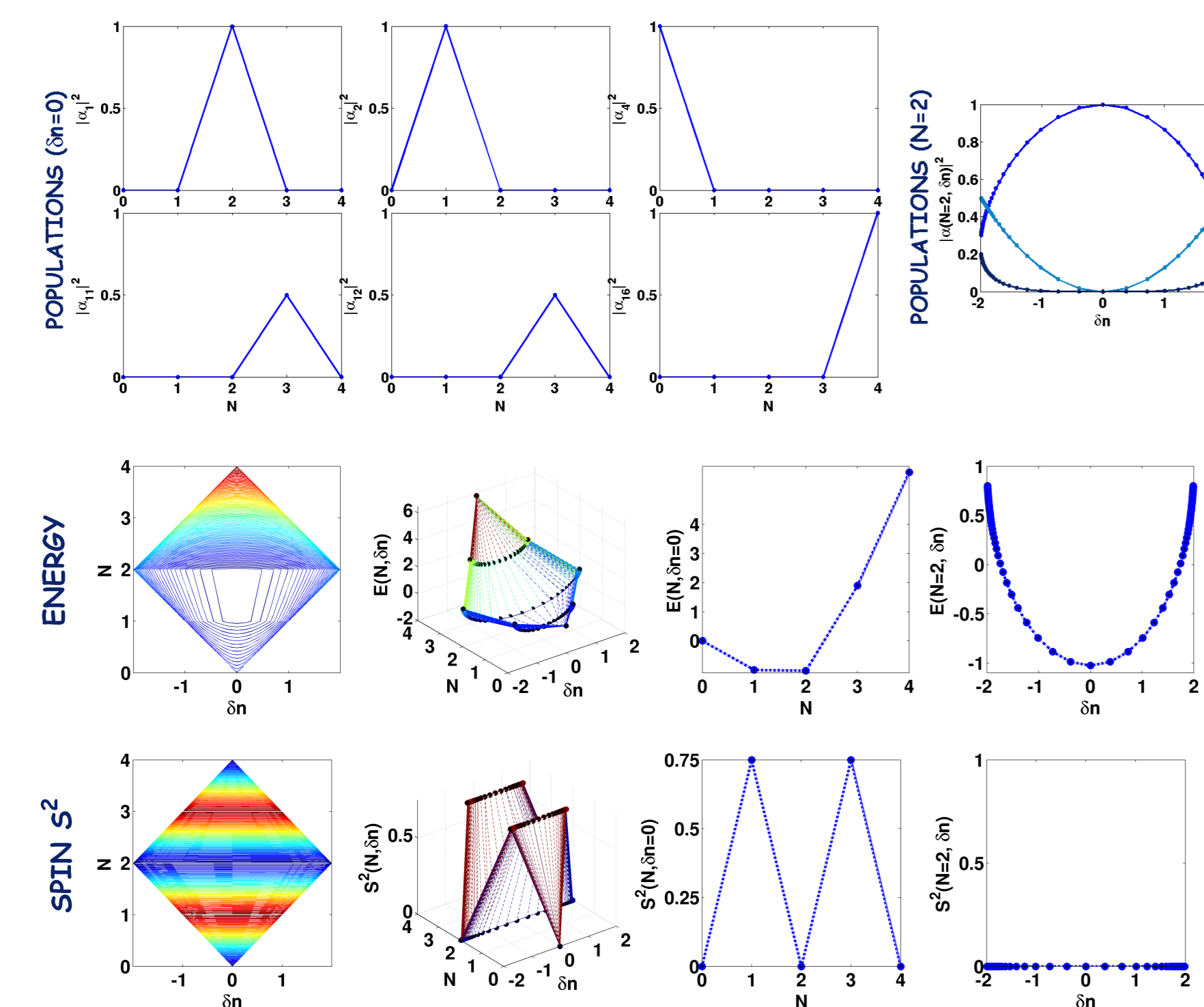
$$|\Psi[n]\rangle = \sum_{j=1}^{4^M} \alpha_j[n] |\phi_j\rangle, \quad M \text{ number of sites}$$

Hohenberg-Kohn functional

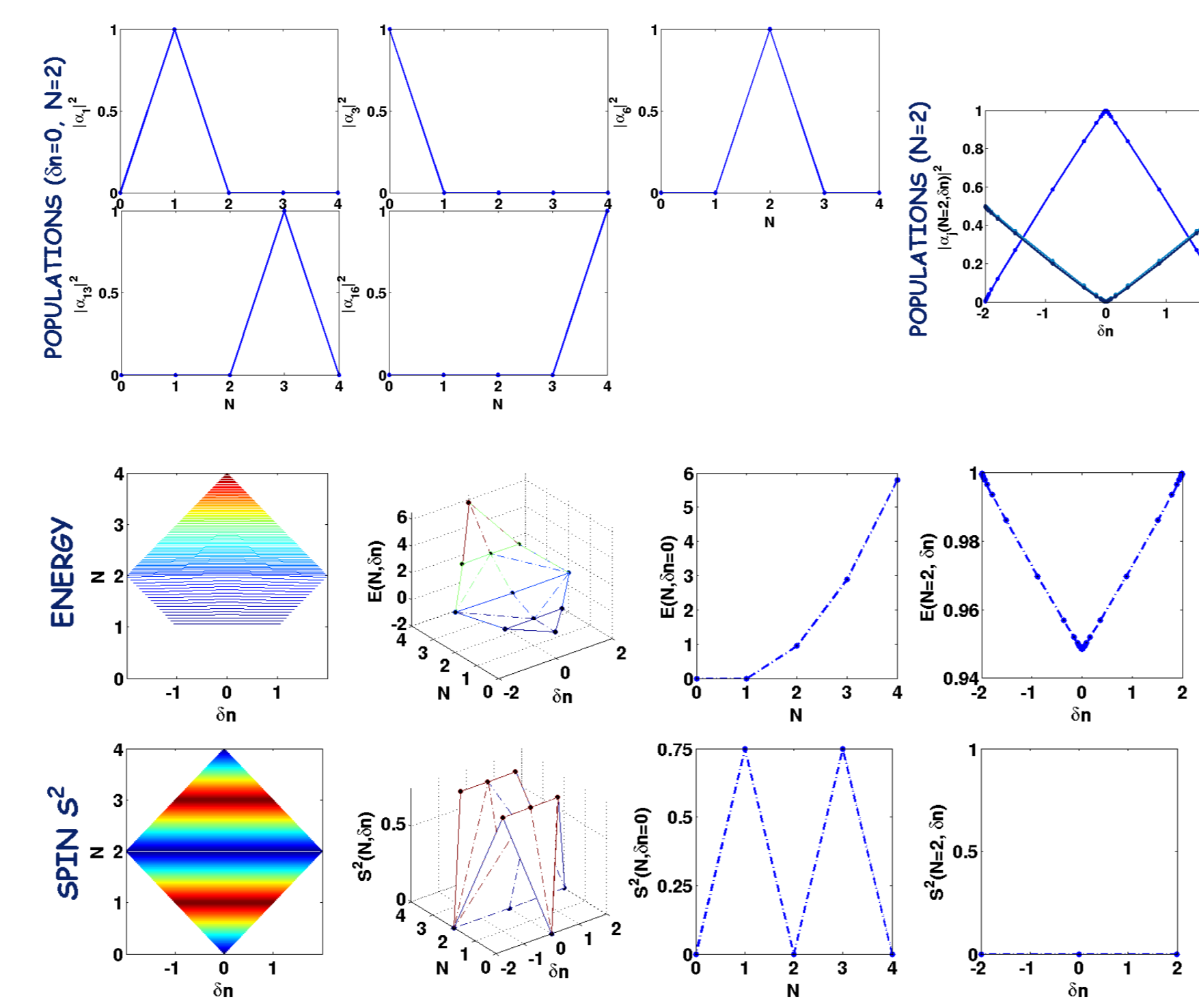
$$\begin{aligned} F_{\text{HK}}(\alpha_1, \dots, \alpha_{4^M})[n] &= \min_{\Psi \rightarrow n} \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle \\ &= \min_{\Psi \rightarrow n} \sum_{j,k=1}^{4^M} \alpha_j^* \alpha_k [n] \langle \phi_j | \hat{T} + \hat{W} | \phi_k \rangle \end{aligned}$$



High-density limit (large hopping $t_0 = 1$)



Low-density limit (small hopping $t_0 = 0.001$)



Conclusion & Outlook

- The exact Hohenberg-Kohn functional shows a softened intra-system derivative discontinuity in the low-density limit.
- Similarly to the energy functional, also the populations as functional of the density show a softened intra-system derivative discontinuity.
- Expectation values of operators are affected by the softened intra-system derivative discontinuity of populations.

Soft-Coulomb molecules in 1D

Hamiltonian

$$\begin{aligned} \hat{H}(\alpha) &= \hat{T} + \hat{W} + \hat{V}(\alpha) \\ \hat{T} &= \sum_{j=1}^2 -\frac{d^2}{dx_j^2} \\ \hat{W} &= \frac{1}{2} \sum_{j \neq j'} \frac{1}{\sqrt{(x_j - x_{j'})^2 + 1}} \\ \hat{V}(\alpha) &= \sum_{j=1}^2 \frac{Z_1(\alpha)}{\sqrt{(x_j - d)^2 + 1}} + \frac{Z_2(\alpha)}{\sqrt{(x_j + d)^2 + 1}} \\ Z_1(\alpha) &= -\alpha, \quad Z_2(\alpha) = -(2 - \alpha), \quad \alpha \in [0, 2], \quad d = 3, 8 \text{ Bohr} \end{aligned}$$

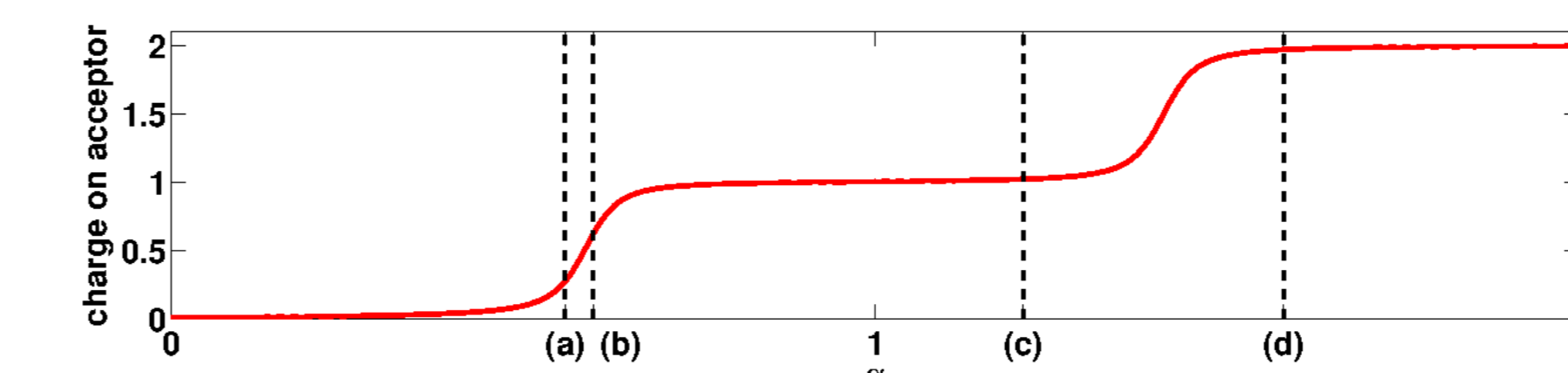
Exact Kohn-Sham potential for two electrons in spin singlet configuration (Helbig et al. 2009 [3])

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

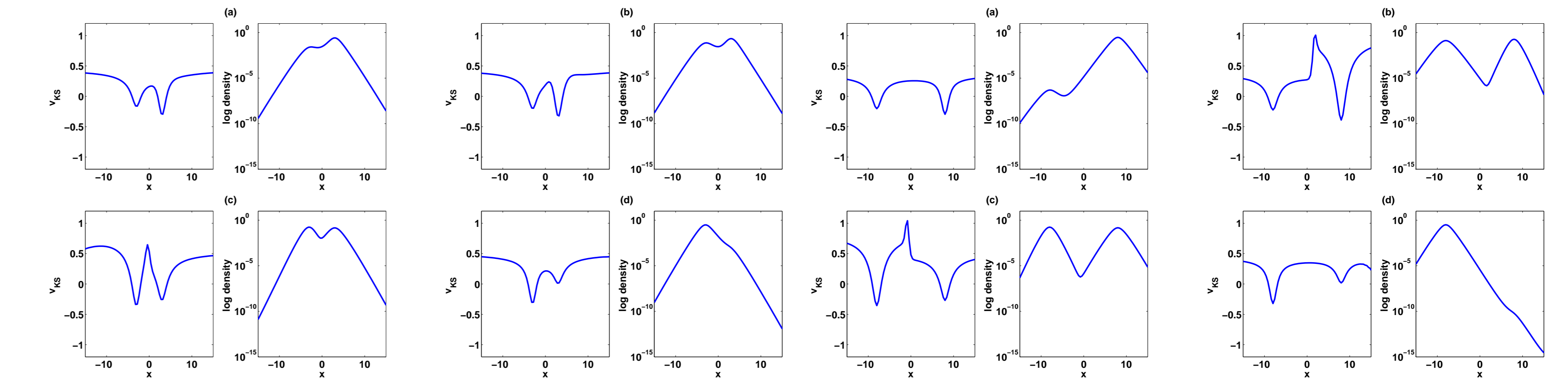
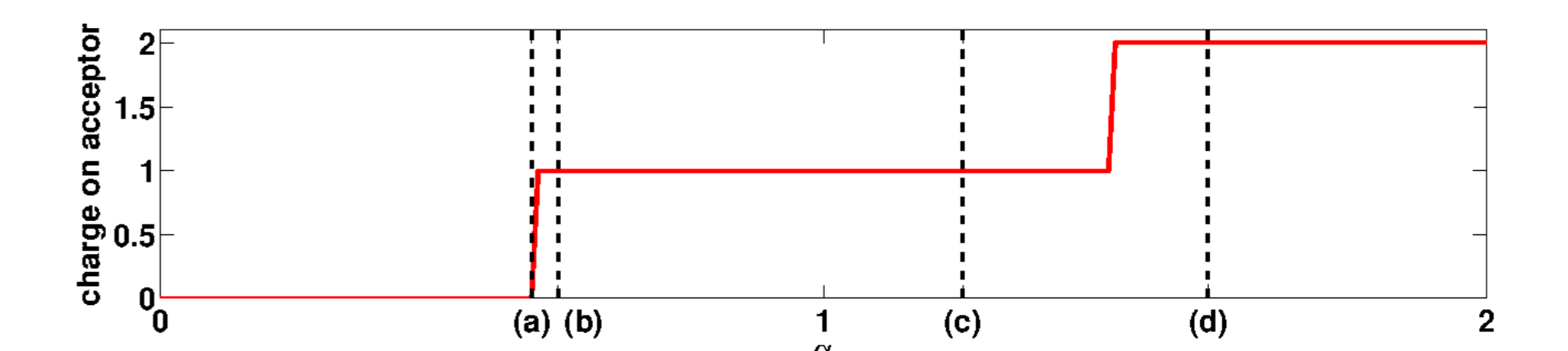
Exact solution of static two-electron Schrödinger equation with octopus (A. Castro et al. [4])

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

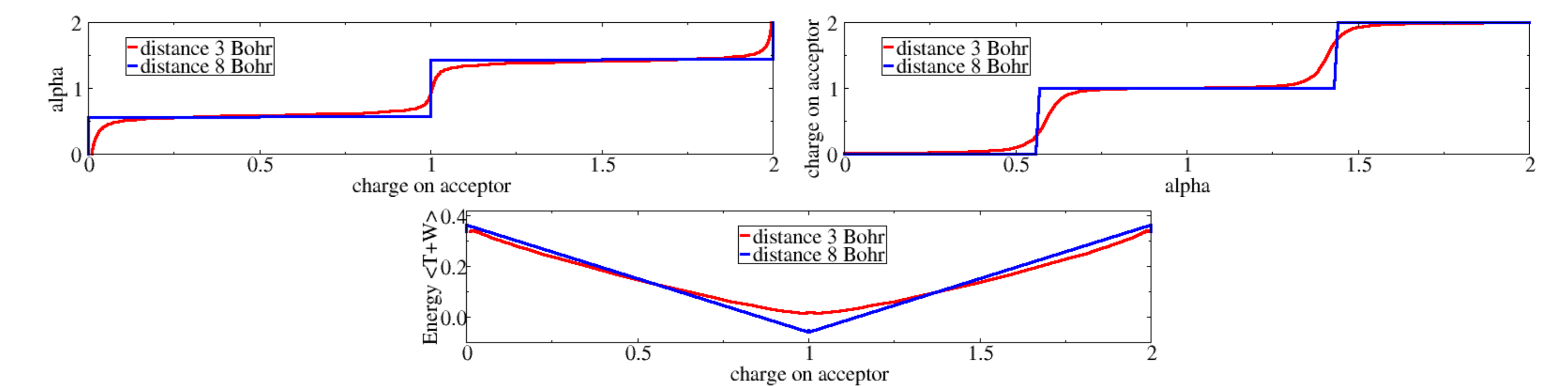
High-density limit (small distance $d = 3$ Bohr)



Low-density limit (large distance $d = 8$ Bohr)



Softened intra-system derivative discontinuity



Conclusion & Outlook

- We observe softened intra-system derivative discontinuity also for soft-Coulomb molecules in 1D.
- We currently develop an approximate functional which incorporates the intra-system derivative discontinuity.

References

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