Excited State Specific Functionals of the Asymmetric Hubbard Dimer

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Collaboratrice

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Giarrusso & Loos, JPCL 14 (2023) 8780 (arXiv:2303.15084)
Loos & Giarrusso (in preparation)

Why State-Specific DFT?

- Orbital-optimized DFT (ΔSCF) more accurate than TDDFT in some cases (*not always!*)
  Hait & Head-Gordon, JPCL 12 (2021) 4517
  Levi et al. JCTC 16 (2020) 6968
- Excited-state-specific functionals are being developed (*but it's hard!*)
  Gould et al. PRX 14 (2024) 041045; arXiv:2406.18105
- Formal foundation is getting traction recently (*although I don't really understand these papers!*)
  Yang & Ayers, arXiv:2403.04604
  Gould, arXiv:2404.12593
  Fromager, arXiv:2409.17000
- *Let's see what we can do in a simple case!*

Levy's Variational Principle

Levy's constrained search for ground state

Kinetic, Repulsion

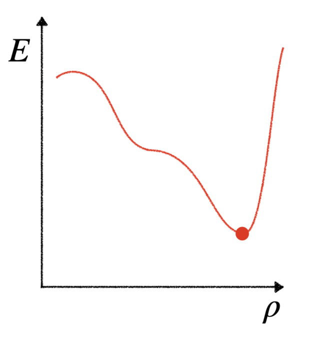
$$F^{(0)}[\rho] = \min_{\substack{\Psi \\ \rho_\Psi = \rho}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle = \langle \Psi^{(0)}[\rho] | \hat{T} + \hat{W} | \Psi^{(0)}[\rho] \rangle$$

Ground-state energy, External potential, Ground-state functional

$$E^{(0)}[v] = \min_{\rho} \left\{ F^{(0)}[\rho] + \int v(\boldsymbol{r}) \rho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \right\}$$

Ground-state density

$$\rho^{(0)}(\boldsymbol{r}) = \arg\min_{\rho} \left\{ F^{(0)}[\rho] + \int v(\boldsymbol{r}) \rho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \right\}$$



Levy PNAS 76 (1979) 6062

Görling's Stationary Principle

Generalized constrained search for excited states

*m*th excited-state energy

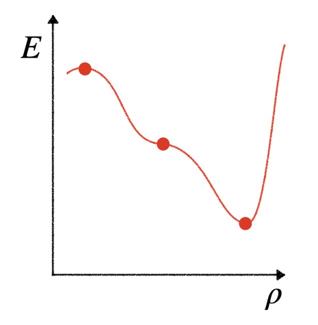
$$E^{(m)}[v] = \underset{\rho}{\mathrm{stat}} \left\{ F^{(m)}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} \right\}$$

Excited-state functional

$$F^{(m)}[\rho] = \underset{\substack{\Psi \\ \rho_\Psi = \rho}}{\mathrm{stat}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$$

Excited-state density

$$\rho^{(m)}(\mathbf{r}) = \underset{\rho}{\arg\mathrm{stat}} \left\{ F^{(m)}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} \right\}$$



Görling PRA 59 (1999) 3359

Generic singlet wave function & density

$$|\Psi\rangle = x\,|0_\uparrow 0_\downarrow\rangle + y\,\frac{|0_\uparrow 1_\downarrow\rangle - |0_\downarrow 1_\uparrow\rangle}{\sqrt{2}} + z\,|1_\uparrow 1_\downarrow\rangle$$

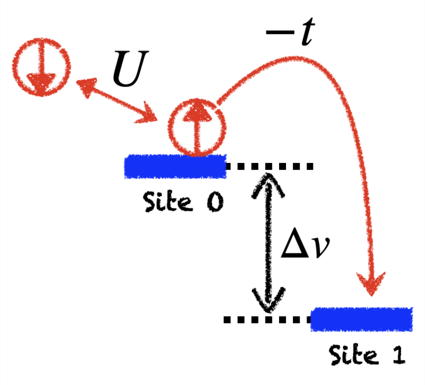
$$\rho = \frac{\Delta n}{2} = \frac{n_1 - n_0}{2} = z^2 - x^2 \qquad (-1 \le \rho \le 1)$$

Exact Energy

Total → E · Kinetic → T · Repulsion → W · External → V

$$E = T + W + V$$

$$T = -2\sqrt{2}\,t\,y\,(x+z) \qquad W = U\left(x^2 + z^2\right) \qquad V = \rho\,\Delta v$$



Carrascal et al. JPCM 27 (2015) 393001

Stationary Principle

Normalization

$$x^2 + y^2 + z^2 = 1 \quad \Rightarrow \text{This is a sphere!}$$

Density

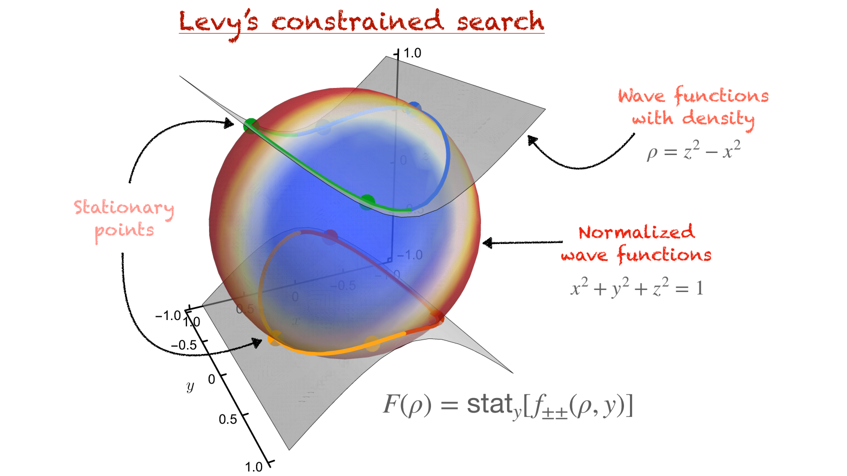
$$\rho = z^2 - x^2 \quad \Rightarrow \text{This is a parabola!}$$

Stationary condition

$$\boxed{F(\rho) = \underset{\substack{\Psi \\ \rho_\Psi = \rho}}{\text{stat}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle = \underset{\substack{\Psi \\ \rho_\Psi = \rho}}{\text{stat}} \left[-2\sqrt{2}\, t\, y\, (x + z) + U\left(x^2 + z^2\right) \right] = \underset{y}{\text{stat}} \left[f_{\pm\pm}(\rho, y) \right]}$$

$$f_{\pm\pm}(\rho, y) = -2ty\left(\pm\sqrt{1 - y^2 - \rho} \pm \sqrt{1 - y^2 + \rho} \right) + U\left(1 - y^2\right)$$

Geometrical Perspective of the Levy-Lieb Constrained Search



Lieb's Convex Formulation

Lieb's Variational Principle

Ground-state functional

Ground-state potential

$$F^{(0)}[\rho] = \max_{v} \left\{ E^{(0)}[v] - \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} \right\} \qquad v^{(0)}[\rho] = \arg\max_{v} \left\{ E^{(0)}[v] - \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} \right\}$$

$$E^{(0)}[v] = \min_{\Psi} \langle \Psi | \hat{H}[v] | \Psi \rangle \qquad \hat{H}[v] = \hat{T} + \hat{W} + \hat{V}[v]$$

Ground-state energy

Hamiltonian

Lieb IJQC 24 (1983) 243

Lieb's Stationary Principle

Generalized stationary principle for excited states

*m*th excited-state functional

Excited-state potential

$$F^{(m)}[\rho] = \underset{v}{\mathrm{stat}} \left\{ E^{(m)}[v] - \int v(\boldsymbol{r})\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \right\} \qquad v^{(m)}[\rho] = \underset{v}{\mathrm{stat}} \left\{ E^{(m)}[v] - \int v(\boldsymbol{r})\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \right\}$$

$$E^{(m)}[v] = \underset{\Psi}{\mathrm{stat}} \langle \Psi | \hat{H}[v] | \Psi \rangle$$

Excited-state energy

Lieb's Formulation Applied to the Hubbard Dimer

Stationary principle

$$F^{(m)}(\rho) = \operatorname*{stat}_{\Delta v} \left[f^{(m)}(\rho, \Delta v) \right]$$

$$f^{(m)}(\rho, \Delta v) = E^{(m)} - \rho \Delta v$$

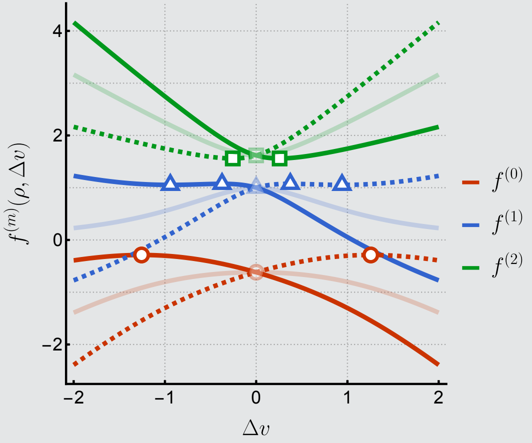
$$= \langle \Psi^{(m)} | \hat{\mathcal{H}} | \Psi^{(m)} \rangle - \rho \Delta v$$

Hubbard Hamiltonian

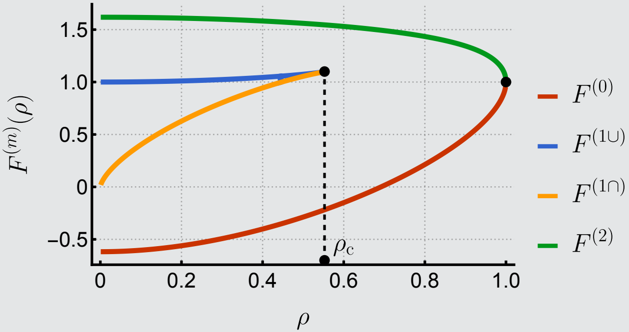
Hamiltonian matrix

$$\mathcal{H} = \begin{pmatrix} -\Delta v + U & -\sqrt{2}t & 0 \\ -\sqrt{2}t & 0 & -\sqrt{2}t \\ 0 & -\sqrt{2}t & +\Delta v + U \end{pmatrix}$$

$f^{(m)}$ as a function of Δv ($t = 1/2$, $U = 1$, and $\rho = \pm 1/2$)



Exact Functionals of asymmetric Hubbard dimer ($U = 1$ and $t = 1/2$)



Dual Relationships for Ground State

The functional and the energy are conjugate functions or Fenchel conjugates

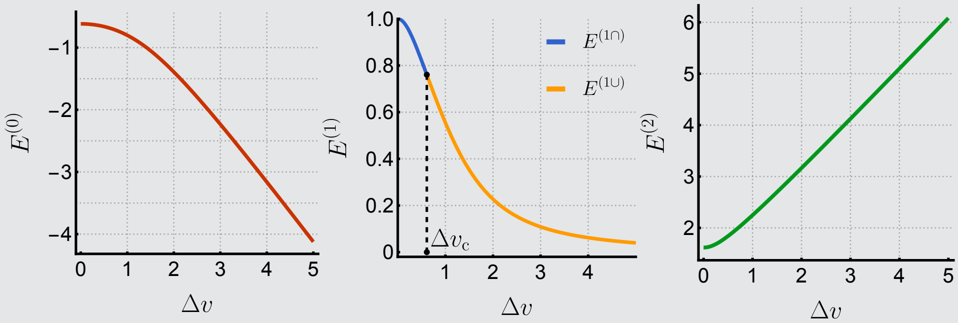
$$F^{(0)}[\rho] = \max_{v} \left\{ E^{(0)}[v] - \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} \right\} \quad \Leftrightarrow \quad E^{(0)}[v] = \min_{\rho} \left\{ F^{(0)}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\mathrm{d}\mathbf{r} \right\}$$

$$v(\mathbf{r}) = -\frac{\delta F^{(0)}[\rho]}{\delta \rho(\mathbf{r})} \quad \Leftrightarrow \quad \rho(\mathbf{r}) = +\frac{\delta E^{(0)}[v]}{\delta v(\mathbf{r})}$$

Helgaker & Teale, The Physics and Mathematics of Elliott Lieb (2022) 527

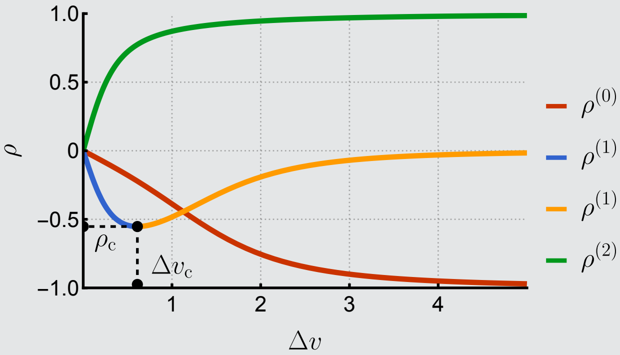
Energies

Exact energies of asymmetric Hubbard dimer ($U = 1$ and $t = 1/2$)



Densities

Exact densities of asymmetric Hubbard dimer ($U = 1$ and $t = 1/2$)



What About Kohn-Sham?

Generalized adiabatic connection for excited states

λ-dependent Hamiltonian

external potential that fixes ρ

$$\hat{H}_\lambda[v_\lambda^{(m)}] = \hat{T} + \lambda \hat{W} + \hat{V}[v_\lambda^{(m)}]$$

interaction strength

λ-dependent functional

$$F_\lambda^{(m)}[\rho] = \underset{\substack{\Psi \\ \rho_\Psi = \rho}}{\text{stat}} \langle \Psi | \hat{T} + \lambda \hat{W} | \Psi \rangle = \langle \Psi_\lambda^{(m)}[\rho] | \hat{T} + \lambda \hat{W} | \Psi_\lambda^{(m)}[\rho] \rangle$$

$$F_\lambda^{(m)}[\rho] = \underset{v}{\text{stat}} \left\{ E_\lambda^{(m)}[v] - \int v(\boldsymbol{r})\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \right\}$$

$$F_{\lambda=0}^{(m)}[\rho] = T_s^{(m)}[\rho]$$

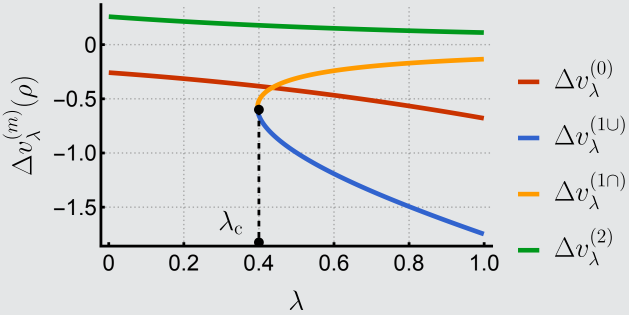
Non-interacting limit

$$F_{\lambda=1}^{(m)}[\rho] = F^{(m)}[\rho]$$

Fully-interacting limit

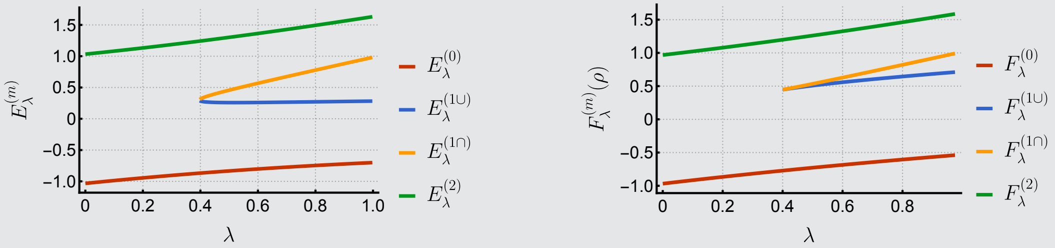
Optimizer as a function of the interaction strength ($U = 1$ and $t = 1/2$)

$$\Delta v_\lambda^{(m)}(\rho) = \arg\operatorname*{stat}_{\Delta v}\left[f_\lambda^{(m)}(\rho, \Delta v)\right] \quad \text{with} \quad f_\lambda^{(m)}(\rho, \Delta v) = E_\lambda^{(m)} - \rho\Delta v = \frac{\langle \Psi_\lambda^{(m)} | \hat{\mathcal{H}} | \Psi_\lambda^{(m)} \rangle}{\langle \Psi_\lambda^{(m)} | \Psi_\lambda^{(m)} \rangle} - \rho\Delta v$$



Adiabatic Connection: Energies and Functionals

Energy and functional as functions of the interaction strength ($U = 1$ and $t = 1/2$)



Analytic Continuation

Definition

"In complex analysis, a branch of mathematics, analytic continuation is a technique to extend the domain of definition of a given analytic function. Analytic continuation often succeeds in defining further values of a function, for example in a new region where the infinite series representation which initially defined the function becomes divergent."

From https://en.wikipedia.org/wiki/Analytic_continuation

Inner product for symmetric non-Hermitian operators

$$\langle f|g\rangle = \int f^*(\boldsymbol{r})g(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \quad \rightsquigarrow \quad \langle f|g\rangle_{\mathrm{c}} = \langle f^*|g\rangle = \int f(\boldsymbol{r})g(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$$

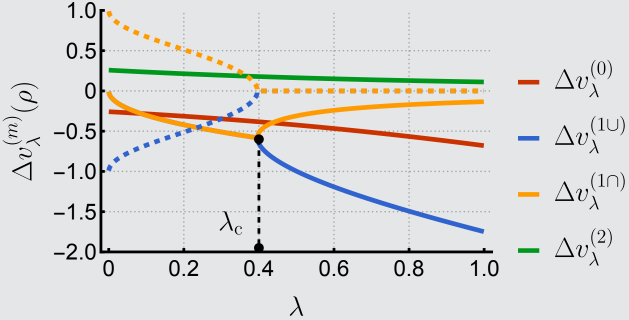
variational principle $\rightsquigarrow$ complex-stationary principle

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad \rightsquigarrow \quad E = \frac{\langle\Psi|\hat{H}|\Psi\rangle_{\mathrm{c}}}{\langle\Psi|\Psi\rangle_{\mathrm{c}}}$$

Analytically-Continued Adiabatic Connection: Optimizers

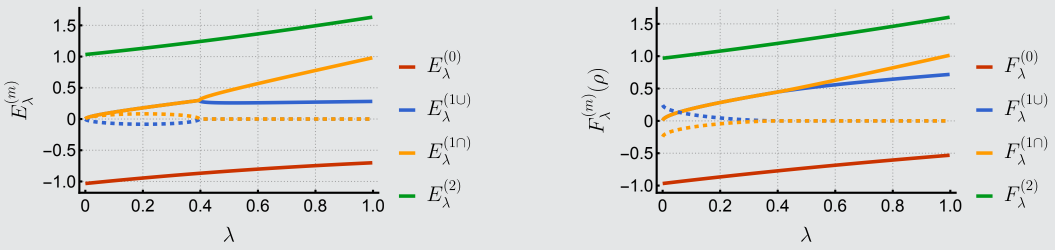
Optimizer as a function of the interaction strength ($U = 1$ and $t = 1/2$)

$$\Delta v_\lambda^{(m)}(\rho) = \underset{\Delta v}{\text{arg stat}} \left[f_\lambda^{(m)}(\rho, \Delta v) \right] \quad \text{with} \quad f_\lambda^{(m)}(\rho, \Delta v) = \frac{\langle \Psi_\lambda^{(m)} | \hat{\mathcal{H}} | \Psi_\lambda^{(m)} \rangle_c}{\langle \Psi_\lambda^{(m)} | \Psi_\lambda^{(m)} \rangle_c} - \rho \Delta v$$



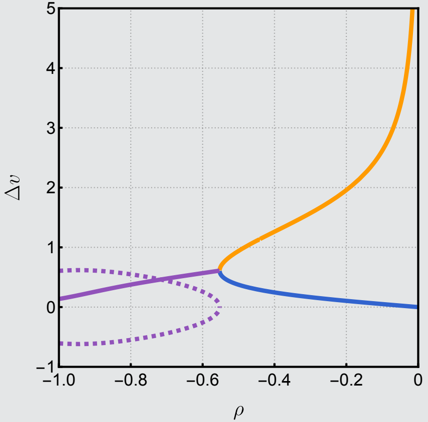
Analytically-Continued Adiabatic Connection: Energies and Functionals

Energy and functional as functions of the interaction strength ($U = 1$ and $t = 1/2$)



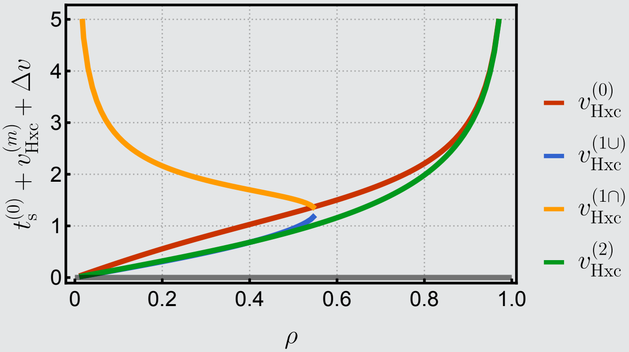
⇝ The densities of the first excited state are non-interacting complex-v-representable

Density-potential map for the first excited state ($U = 1$ and $t = 1/2$)



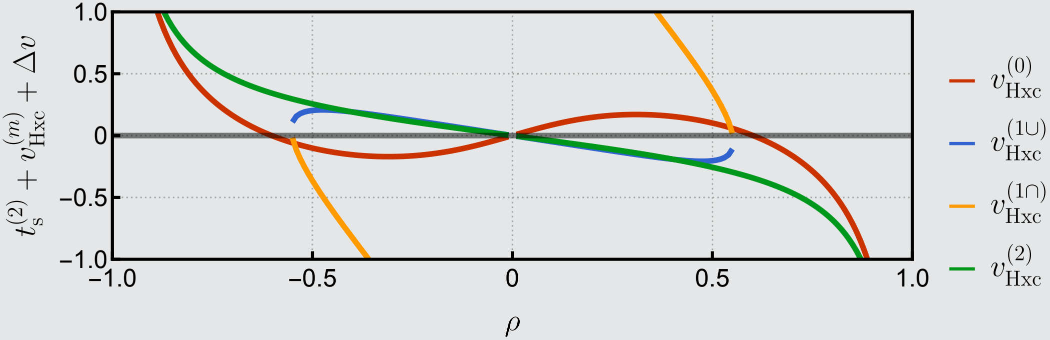
State-Specific KS Calculation: Ground State

Ground-state KS calculation ($U = 1$ and $t = 1/2$)



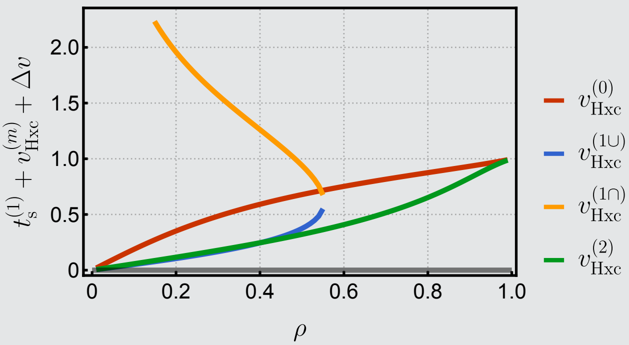
State-Specific KS Calculation: Doubly Excited State

Doubly-excited-state KS calculation ($U = 1$ and $t = 1/2$)



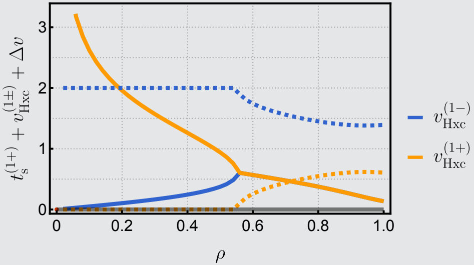
State-Specific KS Calculation: Singly Excited State

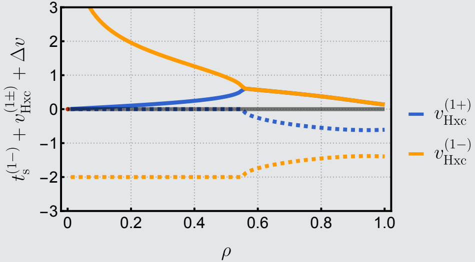
Singly-excited-state KS calculation ($U = 1$ and $t = 1/2$)



Complex State-Specific KS Calculation

Singly-excited-state complex KS calculation ($U = 1$ and $t = 1/2$)





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