Repulsively diverging gradient of the density functional in the Reduced Density Matrix Functional Theory

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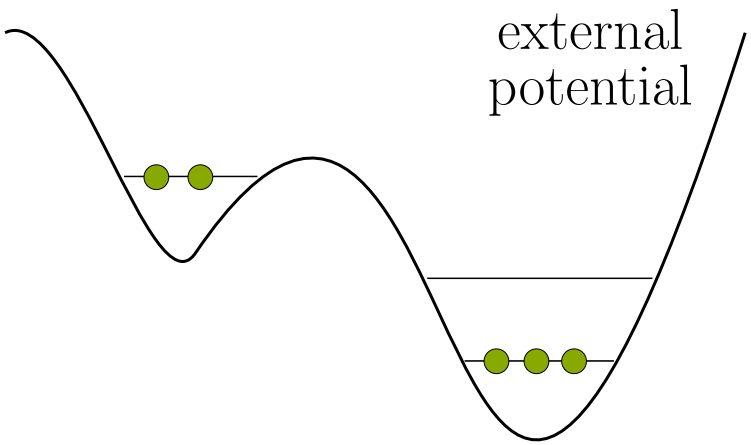
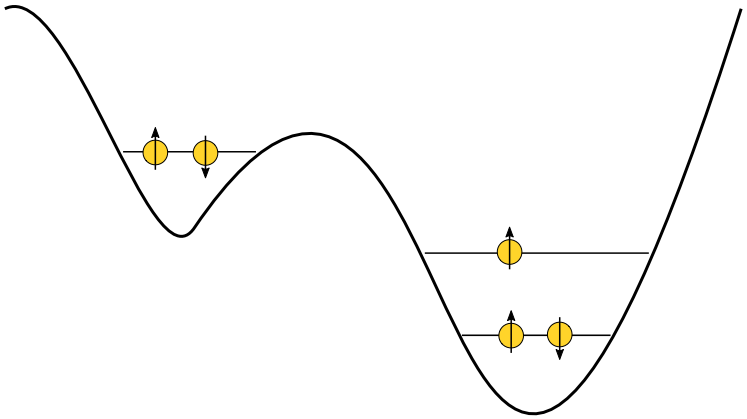
T. Maciazek, New Journal of Physics 23 (11), 113006 (2021)

Ground state problem



pair − interacting
spinless bosons



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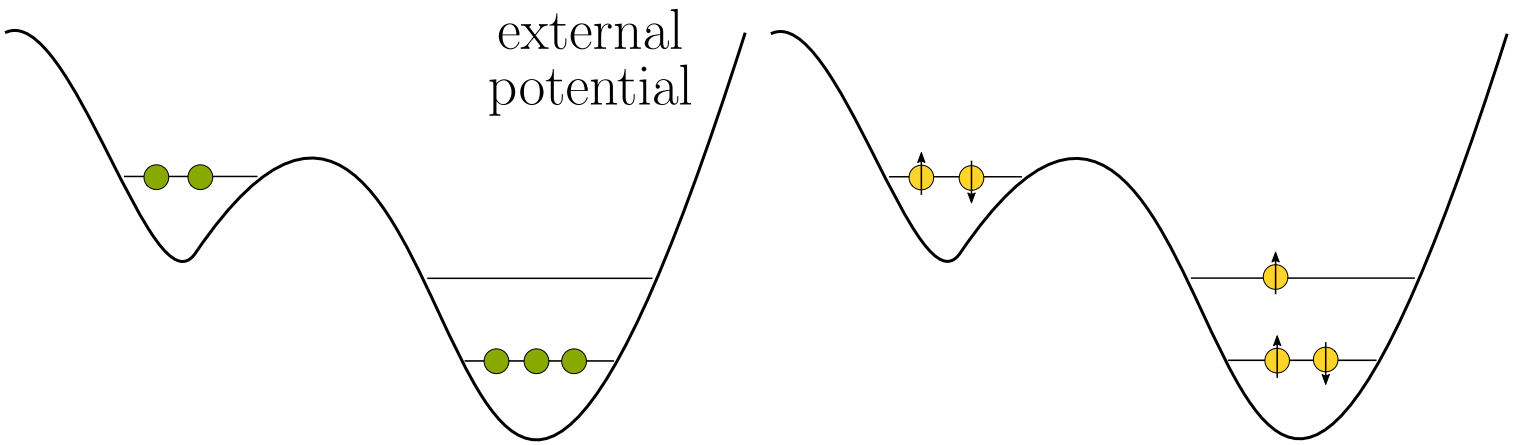

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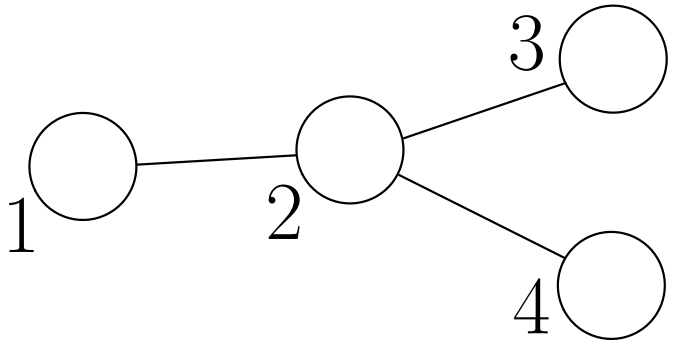
Finite-dimensional, discrete setting.



Ground-state energy via the minimisation

$$E = \min_{|\Psi_N\rangle \in \mathcal{H}_N} \langle \Psi_N | \hat{H} | \Psi_N \rangle .$$

Works for any $\hat{H}$, but the dimension of $\mathcal{H}_N$ grows exponentially with N.

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Functional theories build minimisation problems for specific families of $\hat{H}$ and thus reduce the dimensionality.

$$\hat{H} = \hat{h} + \hat{W}.$$

- $\hat{h}$ – single-particle terms
- $\hat{W}$ – **fixed** interaction (e.g. Coulomb, Hubbard).

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$$E_{\hat{W}}(\hat{h}) = \min_{|\Psi_N\rangle \in \mathcal{H}_N} \langle \Psi_N | \, \underline{\hat{h}} + \hat{W} \, | \Psi_N \rangle$$

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$$\equiv \min_{\hat{\rho}} \left[\mathrm{Tr}\left(\hat{h}\hat{\rho}\right) + \mathcal{F}_{\hat{W}}(\hat{\rho}) \right].$$

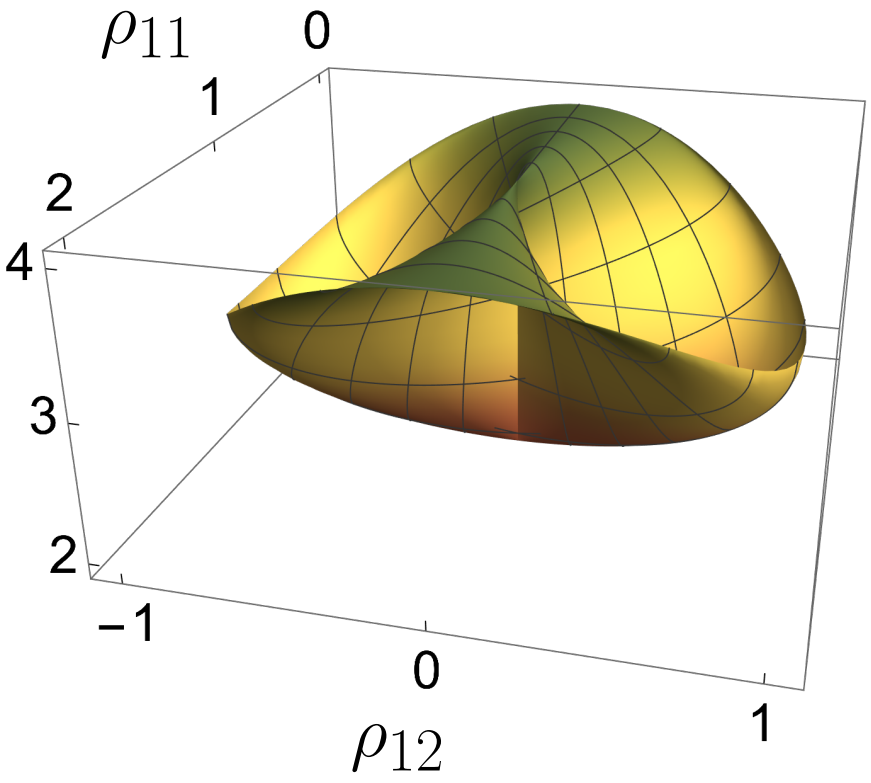
The universal Reduced Density Matrix Functional

$$\mathcal{F}_{\hat{W}}(\hat{\rho}) := \min_{\mathcal{H}_N \ni |\Psi_N\rangle \mapsto \hat{\rho}} \langle \Psi_N | \hat{W} | \Psi_N \rangle.$$

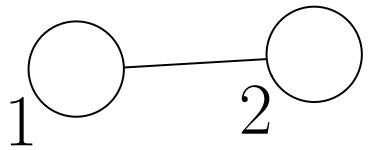
The functional for the Hubbard dimer

$$\hat{W}_{BH} = \hat{n}_1^2 + \hat{n}_2^2, \quad \hat{W}_{FH} = \hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{2\uparrow}\hat{n}_{2\downarrow}$$

$$N = 2$$

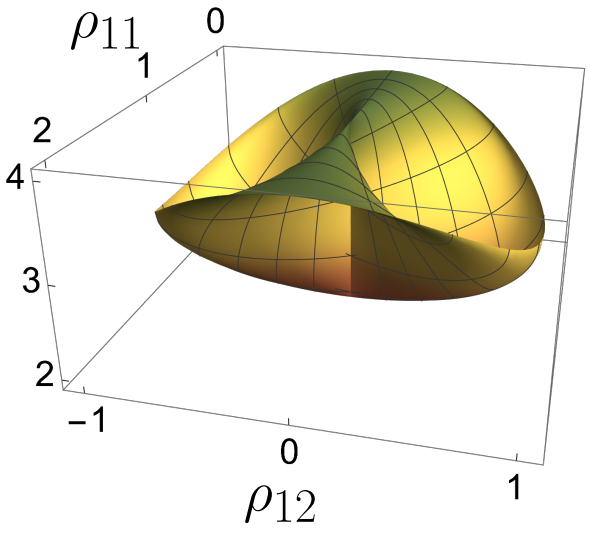


$$\begin{pmatrix} \boxed{\rho_{11}} & \boxed{\rho_{12}} \\ \rho_{12} & \rho_{22} \end{pmatrix}$$

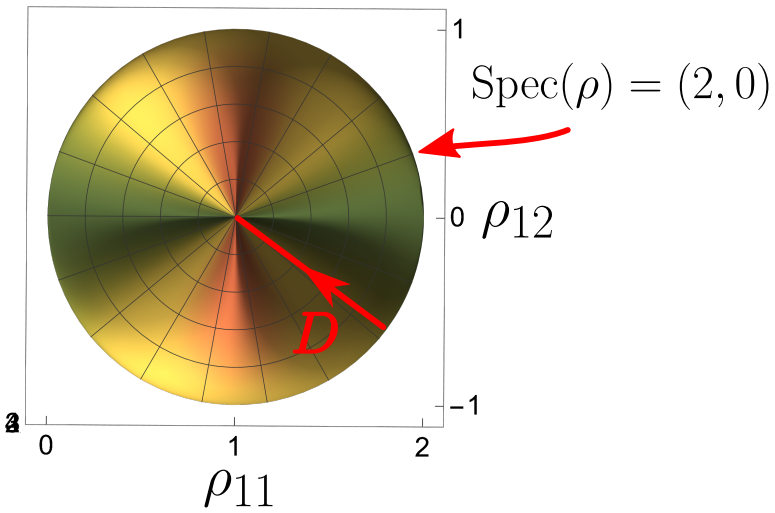


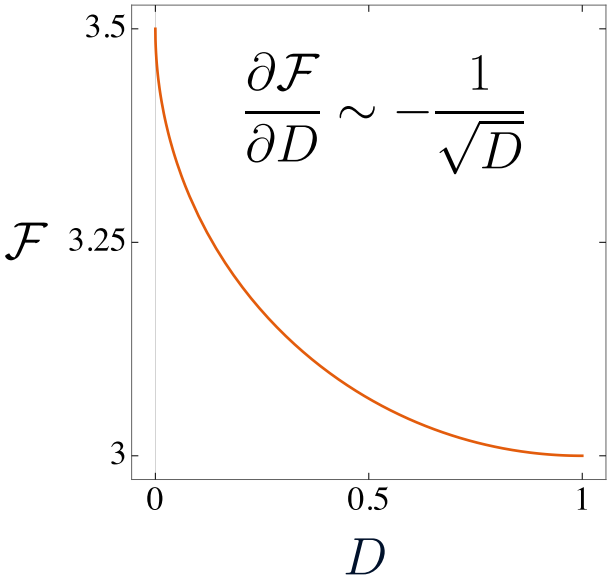
[A. J. Cohen and P. Mori-Sanchez, Phys. Rev. A 93, 042511 (2016), L. Benavides-Riveros, J. Wolff, M. A. L. Marques, and C. Schilling, Phys. Rev. Lett. 124, 180603 (2020)]

Diverging gradient at the boundary of the domain



$$\rho_{12}^2 + (\rho_{11} - 1)^2 \leq 1$$





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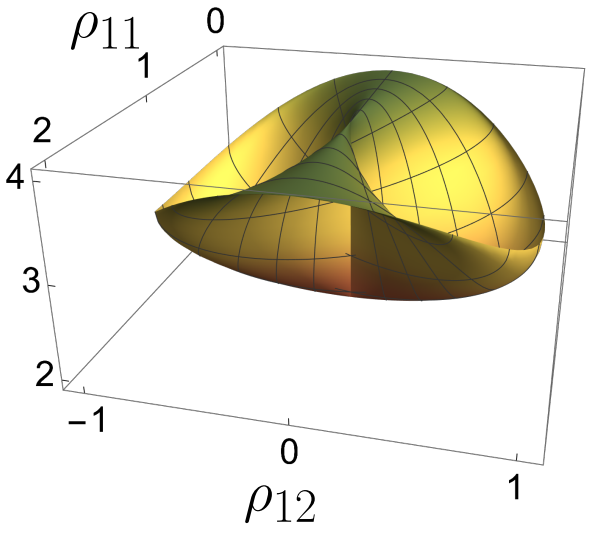

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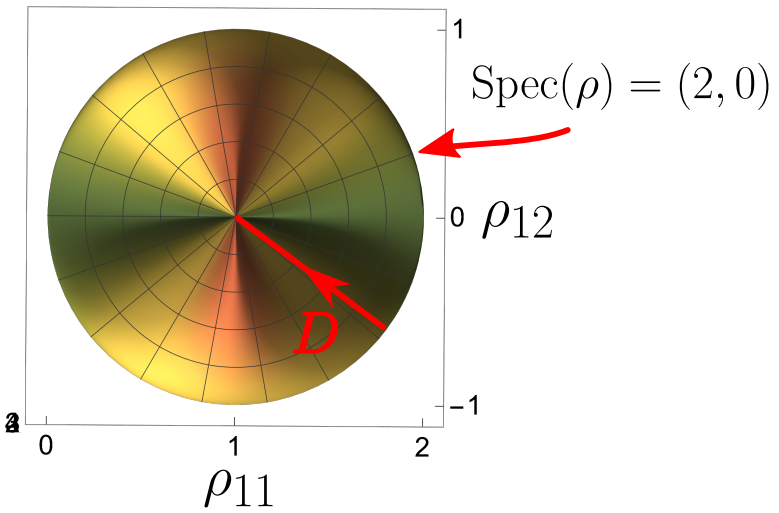
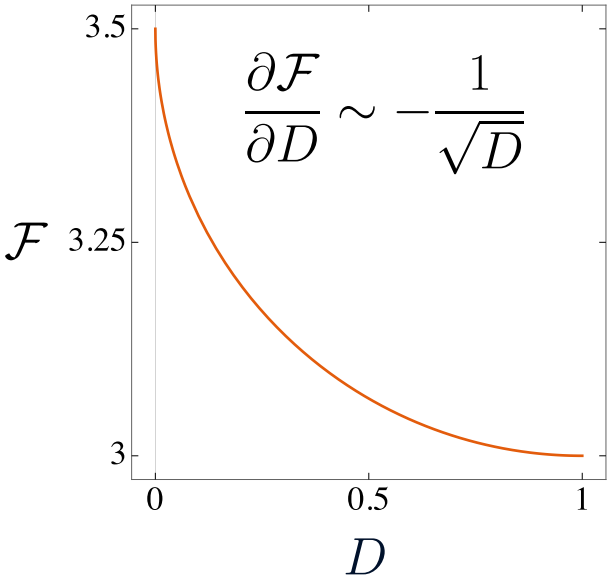
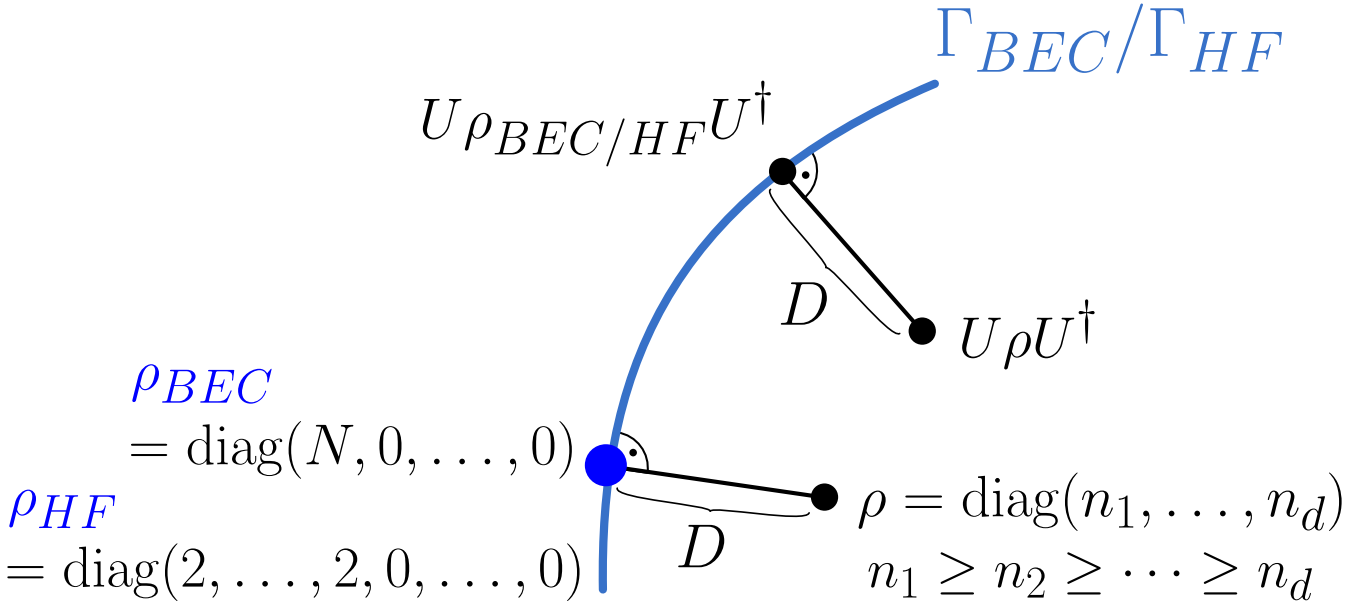




- "exchange force" (fermions)
- "Bose-Einstein condensation force"

[C. Schilling and R. Schilling, Phys. Rev. Lett. 122, 013001 (2019), C. L. Benavides-Riveros, et al., Phys. Rev. Lett. 124, 180603 (2020), Julia Liebert and Christian Schilling, Phys. Rev. Research 3, 013282 (2021)]

Diverging gradient – the main result



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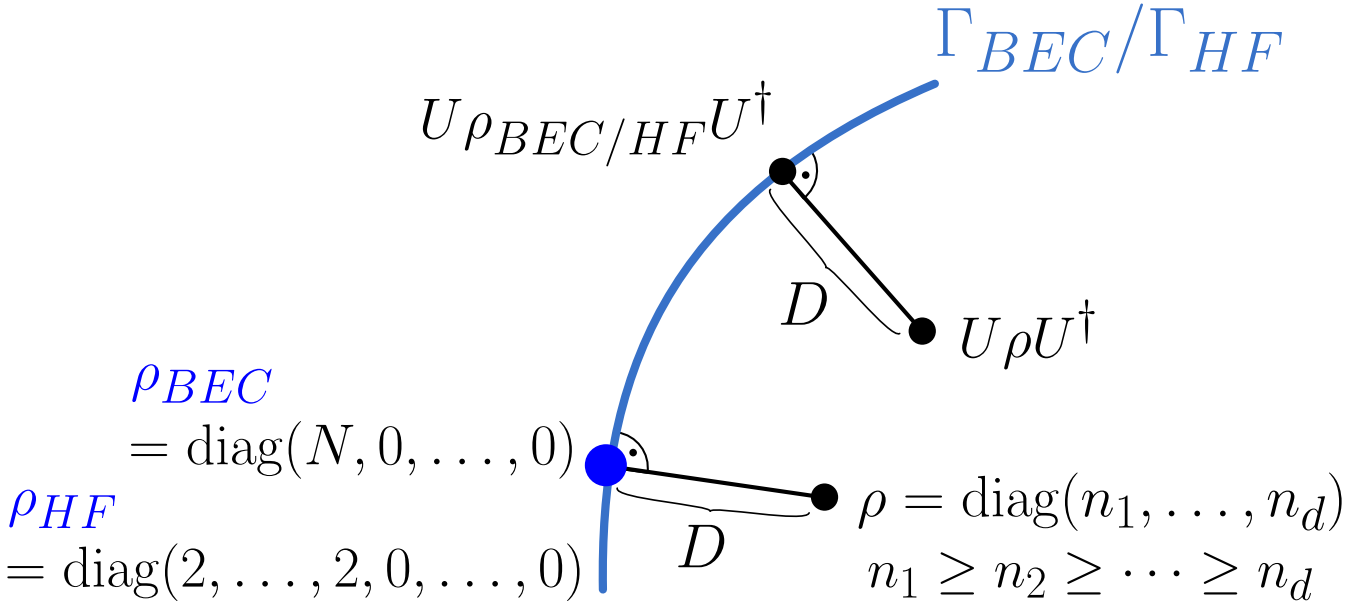

$$\mathcal{F}\left(U\rho U^\dagger\right) \leq \left(1 - \frac{D}{\beta_d}\right)\mathcal{F}\left(U\rho_{BEC/HF}U^\dagger\right) +$$

$$+c_1(U)\sqrt{\frac{D}{\beta_d}\left(1 - \frac{D}{\beta_d}\right)} + c_2(U)\frac{D}{\beta_d}, \quad c_1(U) < 0$$

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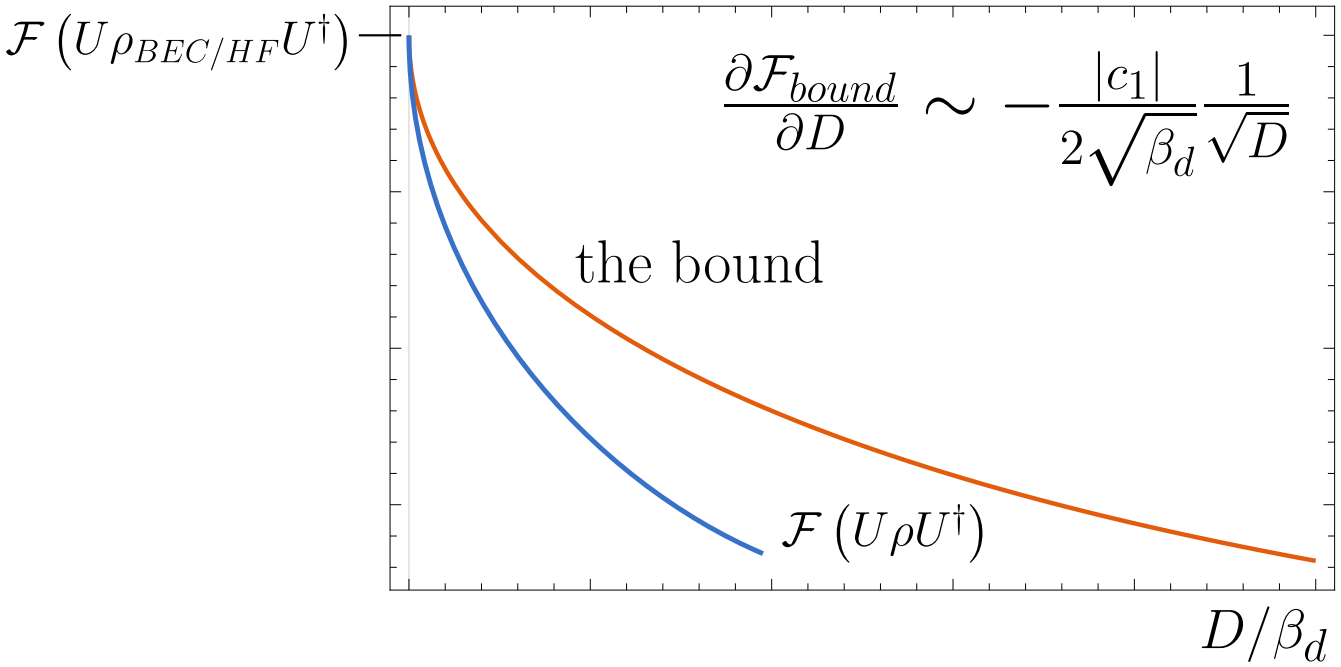
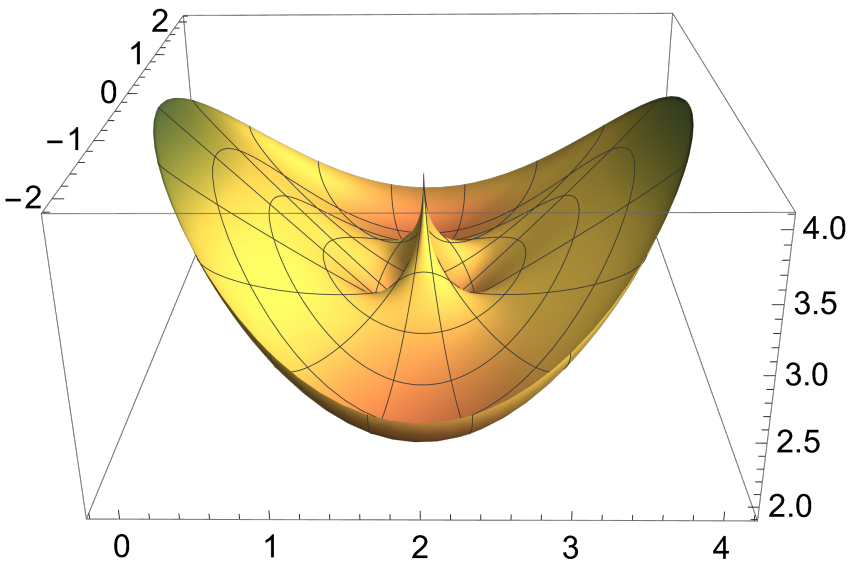


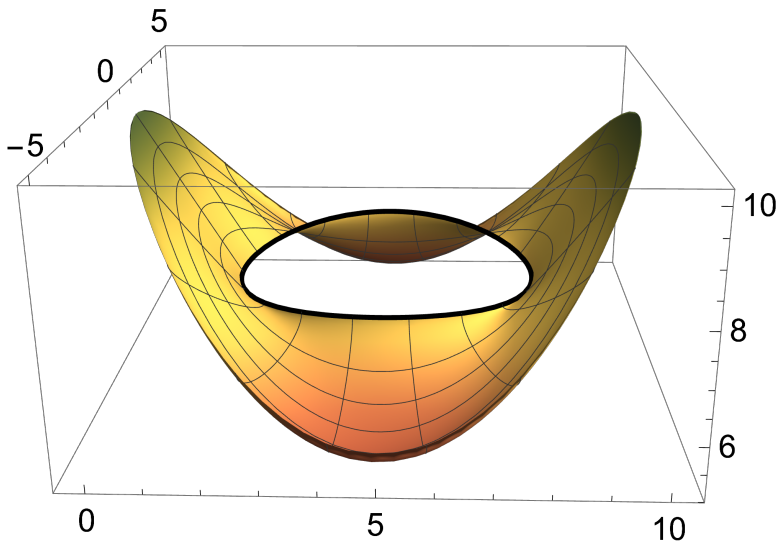
The upper bound for the Bose-Hubbard dimer

$$\mathcal{F}_{BH}^{bound}(D,\phi) = \frac{1}{4}N\left(1+3N+(N-1)\cos(2\phi)\right)+$$
$$-\sin^2\phi\sqrt{\frac{N(N-1)}{2}}\sqrt{D(2-D)}-\frac{D}{2}(N-2)(1+3\cos(2\phi)).$$

$N=4$



$N=10$



The wavefunction ansatz

$$\mathcal{F}_{\hat{W}}(\rho) := \min_{\mathcal{H}_N \ni |\Psi_N\rangle \mapsto \rho} \langle \Psi_N | \hat{W} | \Psi_N \rangle \leq \langle \Phi_N | \hat{W} | \Phi_N \rangle , \quad |\Phi_N\rangle \mapsto \rho$$

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$$\mathcal{F}_{bound}(\rho) = \langle \Phi_N(\rho) | \hat{W} | \Phi_N(\rho) \rangle$$

$|\Phi_N(\rho)\rangle$ determined by ρ.

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- invert the map $|\Psi_N\rangle \mapsto \rho$ for any ρ,
- control the geometry of the problem,
- extract the dependence on the D-variable.

The wavefunction ansatz for the singlet sector

$|\Phi_N(\rho)\rangle$ determined by the eigendecomposition of ρ.

$$\rho = \sum_{i=1}^{d} \nu_i \, |\phi_i\rangle\langle\phi_i| \,, \quad 2 \geq \nu_1 \geq \nu_2 \geq \cdots \geq \nu_d \geq 0$$

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Define the Slater-determinantal (Hartree-Fock) state
$|HF(\rho)\rangle := \left|\phi_1 \downarrow, \phi_1 \uparrow, \ldots, \phi_{N/2} \downarrow, \phi_{N/2} \uparrow\right\rangle$.

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$\sum_{i=1}^{N/2} \sum_{j=N/2+1}^{d} \alpha_{i,j}^2 = 1$, $\epsilon > 0$. Parameters $\alpha_{i,j}$ and ϵ found from the condition $|\Phi_N(\rho)\rangle \mapsto \rho$. In particular,

$$D = \beta_d \frac{\epsilon^2}{1+\epsilon^2} = \frac{1}{2}\beta_d (N - N_{HF}), \quad N_{HF} := \sum_{i=1}^{N/2} \nu_i.$$

Extra: An approximate functional/MCSCF ansatz?

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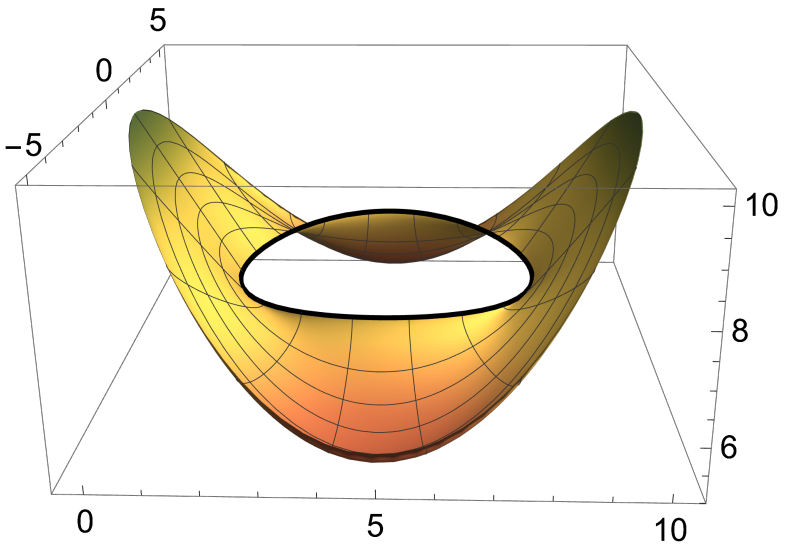
$$N = 10$$



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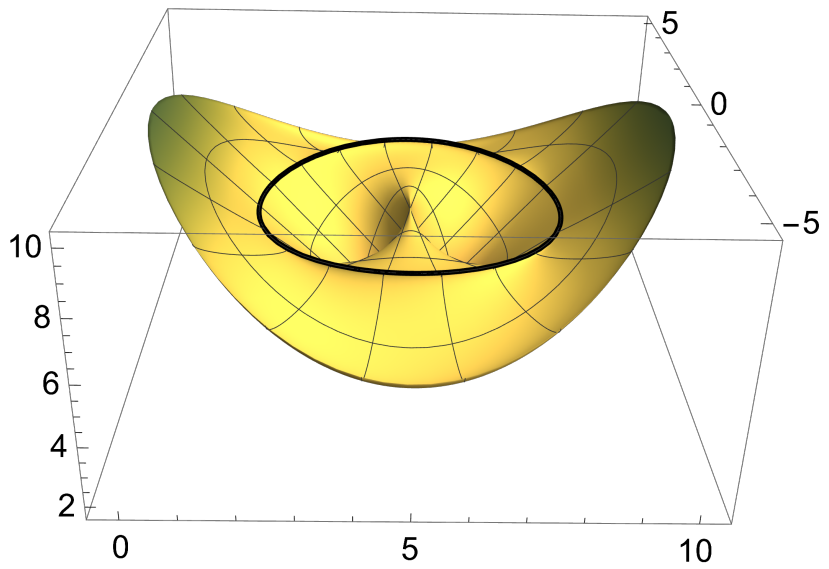

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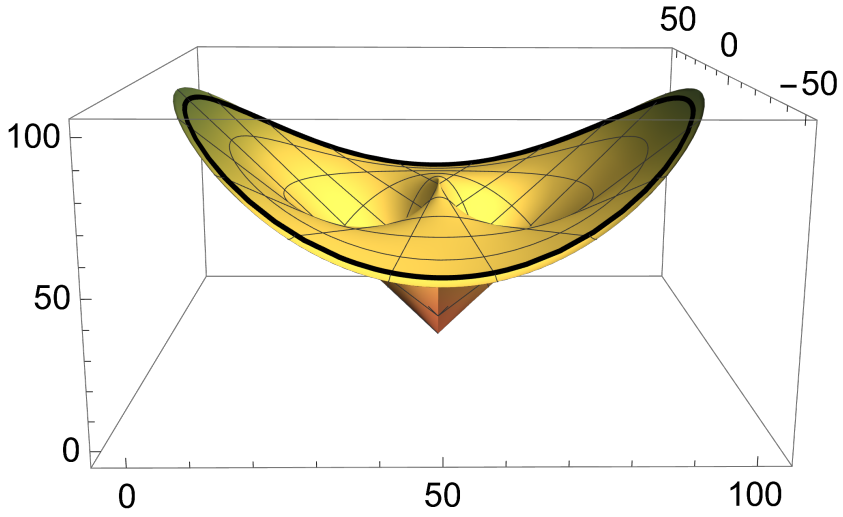
$N = 100$



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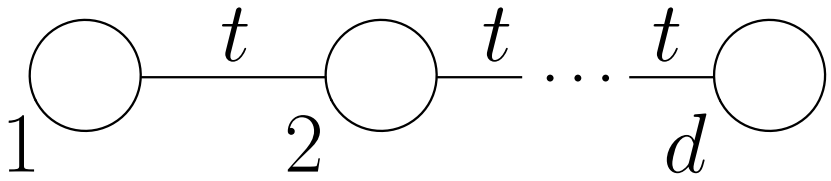
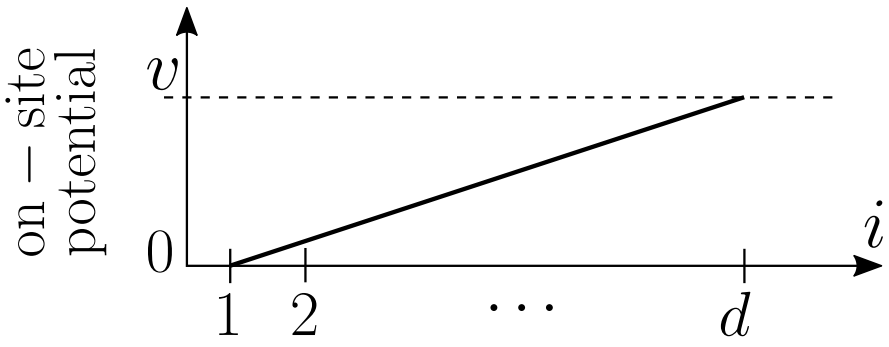
Application to the electron transfer problem.





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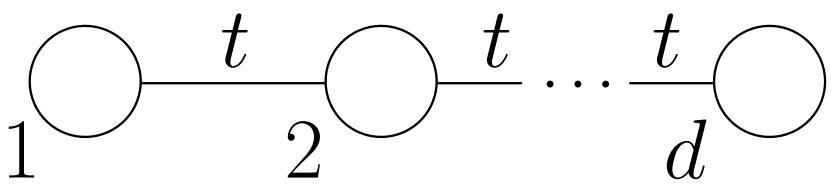

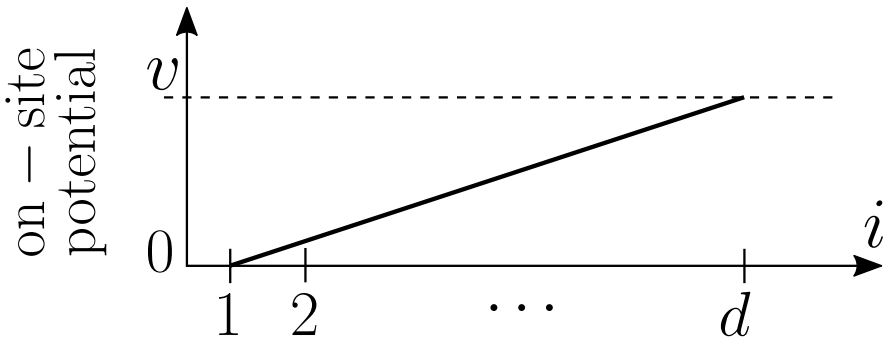

$$\langle \hat{n}_i \rangle = \rho_{ii} = ?$$

$$\hat{H}_{FH} = t \sum_{i=1}^{d-1} \sum_{\sigma \in \{\uparrow,\downarrow\}} \left(\hat{a}^\dagger_{i\sigma} \hat{a}_{(i+1)\sigma} + \hat{a}^\dagger_{(i+1)\sigma} \hat{a}_{i\sigma} \right) + \sum_{i=1}^{d} \sum_{\sigma \in \{\uparrow,\downarrow\}} v_i \hat{n}_{i\sigma} + V \sum_{i=1}^{d} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

Electron transfer in the Fermi-Hubbard chain

Electron transfer calculations

- pointed out as one of the current challenges of the Reduced Density Matrix Functional Theory,
- some RDMFT functionals (HF, Power, Müller) give qualitatively incorrect results even for the Fermi-Hubbard dimer ($d = 2$) in the strong interaction limit.

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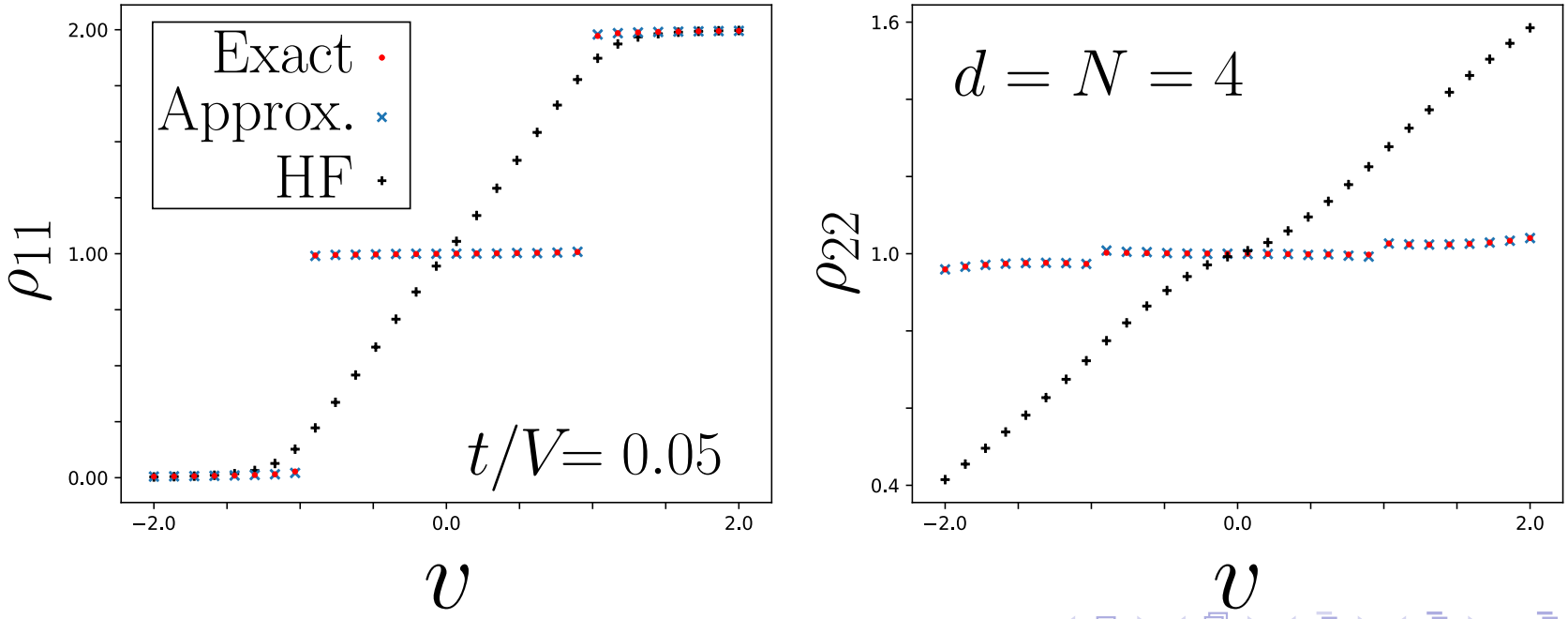
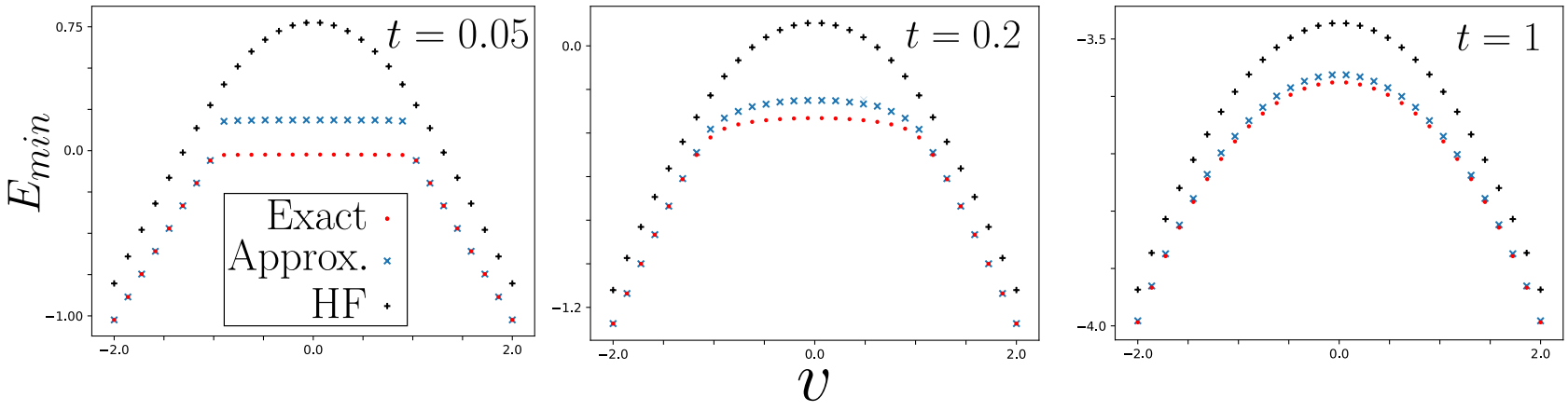


Electron transfer in the Fermi-Hubbard chain

However, there are significant errors for the correlation energy in the strong interaction limit.



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- Approximate RDMFT functional for electron transfer? Generalise by taking higher excitation spaces, etc...