Anomalous scaling and breakdown of conventional DFT methods in Mott systems

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References:

- Z.-J. Ying, V. Brosco *et al.* Phys. Rev. B **94**, 075154 (2016)
- V. Brosco *et al.* arxiv: 1609.02904 (2016)

Two problems

- Basic features of the Kohn-Sham potential of a correlated system across the transition from weak to the strong correlation,

- Relation between lattice and continuum approaches to the electronic properties of matter, *i.e.*
    - what is the best single-particle basis to write a lattice model?

Many-body problem

Non-relativistic quantum Hamiltonian:

$$H_C = \boxed{\sum_\sigma \int \Psi^\dagger_\sigma(\mathbf{r})\hat{h}_{\mathbf{r}}\Psi_\sigma(\mathbf{r})d\mathbf{r}} + \boxed{\frac{1}{2}\sum_{\sigma,\sigma'}\int\int \Psi^\dagger_\sigma(\mathbf{r})\Psi^\dagger_{\sigma'}(\mathbf{r}')w(\mathbf{r}-\mathbf{r}')\Psi_{\sigma'}(\mathbf{r}')\Psi_\sigma(\mathbf{r})d\mathbf{r}d\mathbf{r}'}$$

• 1-body part	$\hat{h}_{\mathbf{r}} = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r})$	V_{ext}= nuclear potential (Born-Oppenheimer Approximation)
• Interaction	$w(\mathbf{r}-\mathbf{r}')$	Coulomb interaction
• Electronic fields	$\Psi_\sigma(\mathbf{r})$ $\Psi^\dagger_\sigma(\mathbf{r})$	Electron annihilation and creation at **r** with spin σ

Two classes of approaches

◎ **Ab-initio approaches**

- Standard functional theories, e.g. LDA, …
- Wave-function approaches: Quantum Chemistry methods

Generally inadequate for **strongly correlated solids**

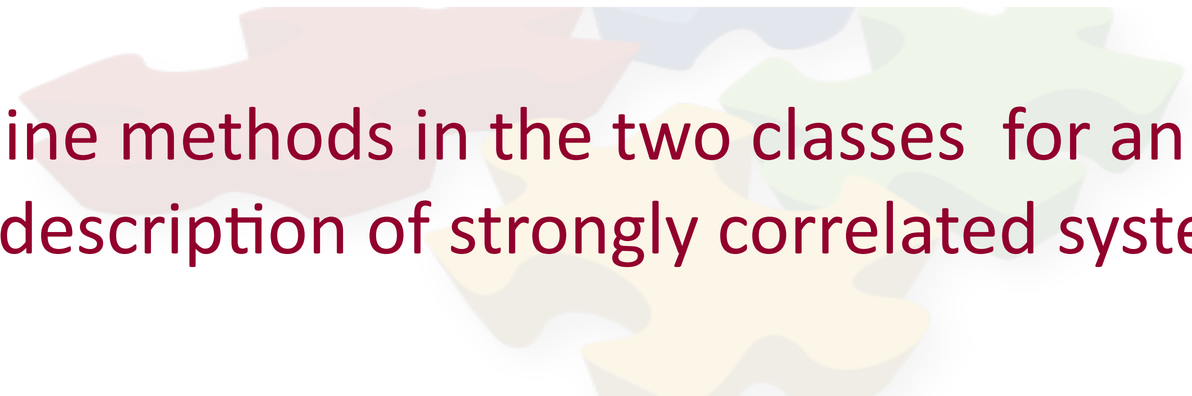
◎ **Lattice approaches (minimal basis models)**

Based on effective models with only few relevant degrees of freedom, *e.g.* Hubbard

- Analytical methods, DMFT, Gutzwiller , RG…

Not *ab-initio*, **require input**

Good description of strong correlation effects



Combine methods in the two classes for an *ab-initio* description of strongly correlated systems

Many successful works in this directions, such as

- LDA+U
- Gutzwiller +DFT
- DMFT+DFT

yet many open questions remain, namely,

what is a systematic and practical way to:

- relate lattice and continuum models?
- extend lattice methods to the continuum?

- when are lattice methods quantitative and not only qualitative?

Lattice-continuum mapping

In principle can be done exactly…

Complete single particle-basis $\Psi_\sigma(\mathbf{r}) = \sum_i c_{i\sigma}\phi_{i\sigma}(\mathbf{r})$

$$\boxed{H = \sum_{ij\sigma} h_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \frac{1}{2}\sum_{ijkl\sigma\sigma'} w_{ik,jl}\, c^\dagger_{i\sigma} c^\dagger_{j\sigma'} c_{l\sigma'} c_{k\sigma}}$$

Generalized single-band Hubbard model

$$h_{ij} = \int d\mathbf{r}\,\phi_i^*(\mathbf{r})\hat{h}_{\mathbf{r}}\phi_j(\mathbf{r})$$

$$w_{ij,kl} = \int d^3\mathbf{r}\, d^3\mathbf{r}'\,\phi_k^*(\mathbf{r})\phi_i^*(\mathbf{r}')w(\mathbf{r},\mathbf{r}')\phi_j(\mathbf{r}')\phi_l(\mathbf{r})$$

But actually…

- Truncate the basis, e.g. keep just one band: $\phi_{i\sigma}(\mathbf{r})$ =Wannier orbital at site *i*
- Neglect some matrix elements; then *e.g.* H➔H_H

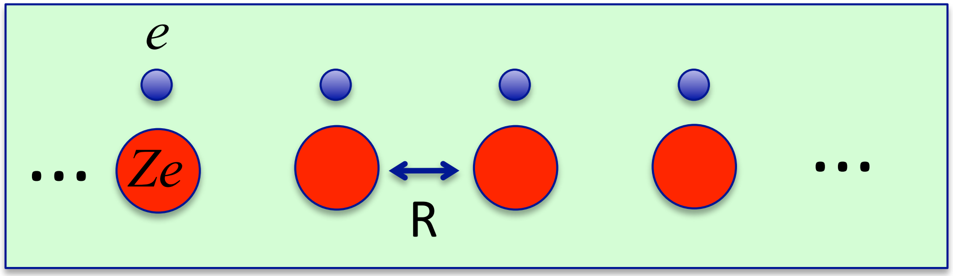
$$H_H = -t\sum_{\langle ij\rangle}\left(c^\dagger_{i\sigma}c_{j\sigma} + H.c\right) + U\sum_i n_{i\uparrow}n_{i\downarrow} + \sum_{i\sigma} v_i n_{i\sigma}$$

U and t

$$t = -h_{ij}$$
$$U = w_{ii,\,ii}$$

- Lattice-continuum mapping is basis dependent

Our playground: a one-electron ions lattice



Scaled Hartee units $\left\{ \begin{array}{l} \text{Distance: } a_0/Z \\ \text{Energy: } Z^2 E_H \end{array} \right.$

L= number of sites= number of electrons

Z-independent single-particle Hamiltonian

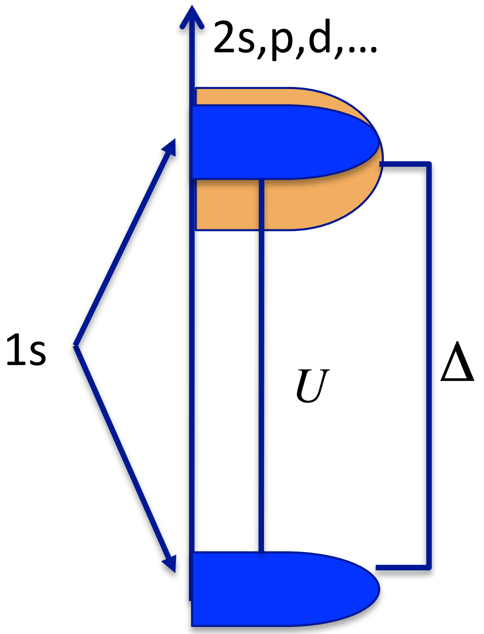
$$\hat{h}_{\mathbf{r}} = -\frac{1}{2}\nabla^2_{\mathbf{r}} - \sum\nolimits_i \frac{1}{|\mathbf{r} - \mathbf{R}_i|}$$

Electron-electron interaction scaling as 1/Z

$$w(\mathbf{r} - \mathbf{r}') = \frac{1}{Z|\mathbf{r} - \mathbf{r}'|}$$

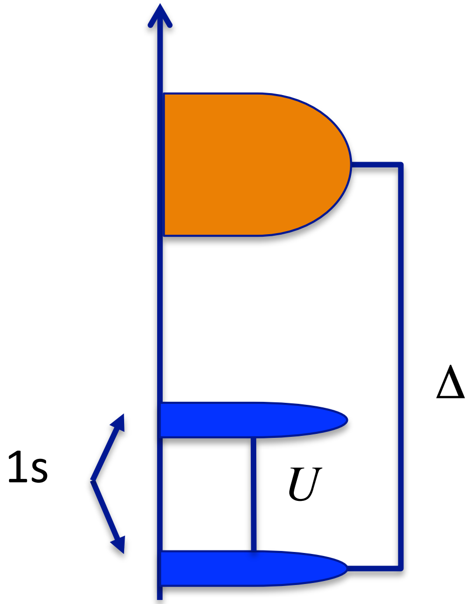
Two knobs to drive the system into different regimes: Z and R

The one-band Hubbard limit: large Z



Increasing Z…

$$U \propto \frac{1}{Z} \qquad \Delta \propto Z^0$$



H lattice (Z=1)

Large Z limit at fixed U/ t , e.g. Ne^{9+} (Z=10)

Lattice description only qualitative

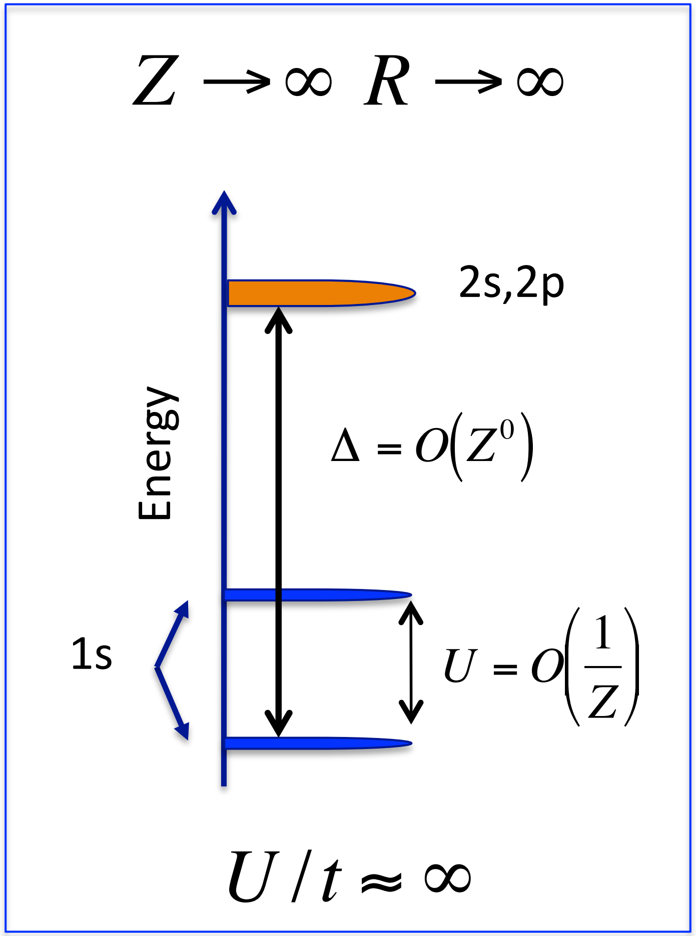
Quantitative agreement

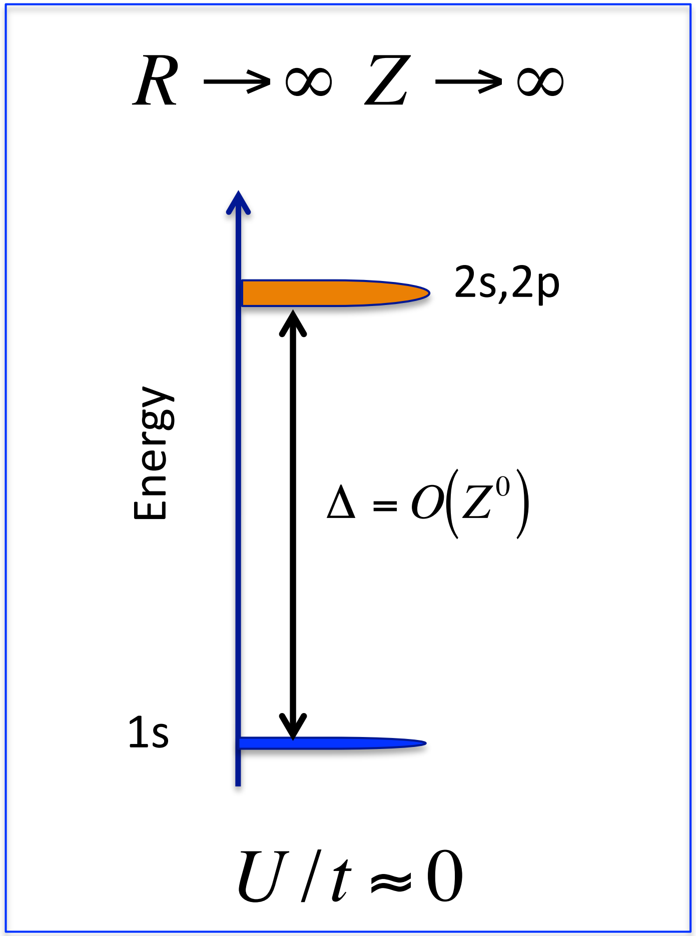
$$t \propto e^{-R}$$

Z and R can be used to tune independently: correlation and mixing with higher energy bands

Large/small U/t implies strong/weak correlation

Warning: order of limits is important!





- At large Z lattice models become quantitatively correct, tune R to change U/t and “see” the emergence of strong-correlation effects, WITH QUANTITATIVE ACCURACY!
- At small Z mixing with higher states become important

Single-particle basis choices

- Atomic orbitals
- Molecular orbitals
- Hartree-Fock states
- …

Different lattice models, different accuracy of approximations, different correlation functions when going back to continuum

How to make a choice valid across different regimes?

Two nested problems to be solved self-consistently

- Choice of the basis;
- Solution of the lattice model.

Optimum basis for a one-electron ion lattice

- **Single-band Ansatz:** the ground state lives in the "low-energy subspace" spanned by $\left\{\phi_1 \cdots \phi_L\right\}$
- **Lattice Hamiltonian:** single-band generalized Hubbard model, H
- **Lattice solver:** any

$|\Phi_L\rangle$=Lattice ground-state   Variational energy: $E[\phi_i, \phi_i^*, \Phi_L] = \langle \Phi_L | H | \Phi_L \rangle$

$$E[\phi_i, \phi_i^*, \Phi_L] = E_{1\mathrm{b}}[\phi_i, \phi_i^*, \Phi_L] + W[\phi_i, \phi_i^*, \Phi_L] + \sum_{ij} \Omega_{ij}(\langle \phi_i | \phi_j \rangle - \delta_{ij})$$

$$\left\{ \begin{aligned} W[\varphi_i, \varphi_i^*, \Phi_L] &= \frac{1}{2} \sum_{ijkl\sigma\sigma'} w_{ik,jl} \langle c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{l\sigma'} c_{k\sigma} \rangle \\ E_{1\mathrm{b}}[\varphi_i, \varphi_i^*, \Phi_L] &= \sum_{ij\sigma} h_{ij} \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle \end{aligned} \right.$$

Interacting electrons problem decomposed into two:

- determination of lattice ground-state
- basis optimization

Orbital optimization equations

$$\boxed{\frac{\delta E[\varphi_i, \varphi_i^*, \Phi_L]}{\delta \varphi_i^*(\mathbf{r})} = 0}$$

$$\boxed{\sum_j \left(\hat{h}_{\mathbf{r}}\, \rho_{ij} + \sum_{kl} w_{kl}(\mathbf{r}) D_{ij,kl} - \Omega_{ij} \right) \phi_j(\mathbf{r}) = 0}$$

Effective potentials : $w_{kl}(\mathbf{r}) = \int d^3\mathbf{r}' \phi_k(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') \phi_l(\mathbf{r})$

Spin-averaged density matrices

$$D_{ij,kl} = \sum_{\sigma\sigma'} \langle c_{i\sigma}^\dagger c_{k\sigma'}^\dagger c_{l\sigma'} c_{j\sigma} \rangle$$

$$\rho_{ij} = \sum_\sigma \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle$$

Determined by the lattice ground-state

Lattice ground-state has to be self-consistently determined by solving $H|\Phi_L\rangle = E_0|\Phi_L\rangle$

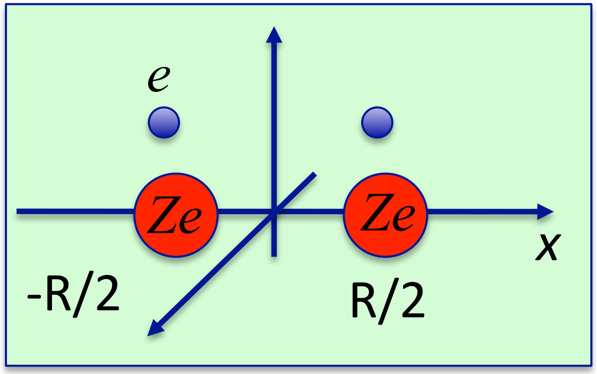
J. Spalek and co-workers, Phys. Rev. B (2013).

◎ DFT exchange-correlation potential across the weak-strong correlation crossover

- ○ Anomalous scaling of the xc-potential
- ○ Lattice + Reverse engineering potential (L+REP)

◎ Consequences of basis optimization and properties of the best single-particle basis

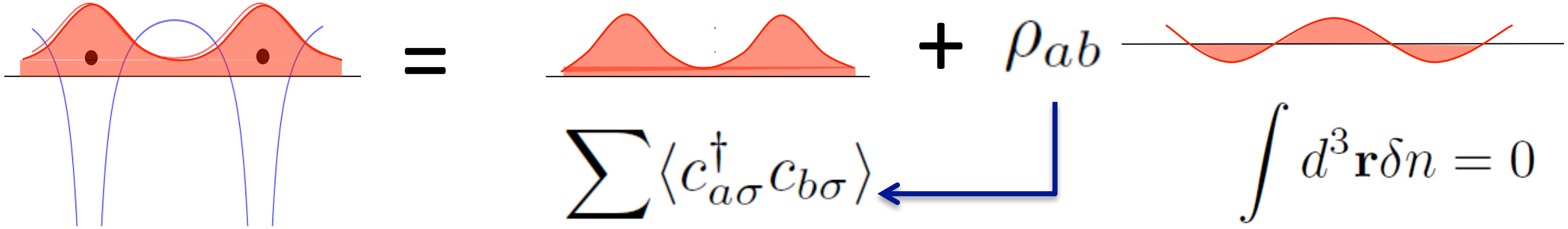
2-site molecule



Two orbitals in the single-band limit

$\phi_a \,, \phi_b$

Density $n(\mathbf{r}) = \phi_a(\mathbf{r})^2 + \phi_b(\mathbf{r})^2 + \boxed{2\rho_{ab}\phi_a(\mathbf{r})\phi_b(\mathbf{r})}$



$=$ $+ \ \rho_{ab}$

$\sum_\sigma \langle c^\dagger_{a\sigma} c_{b\sigma} \rangle$

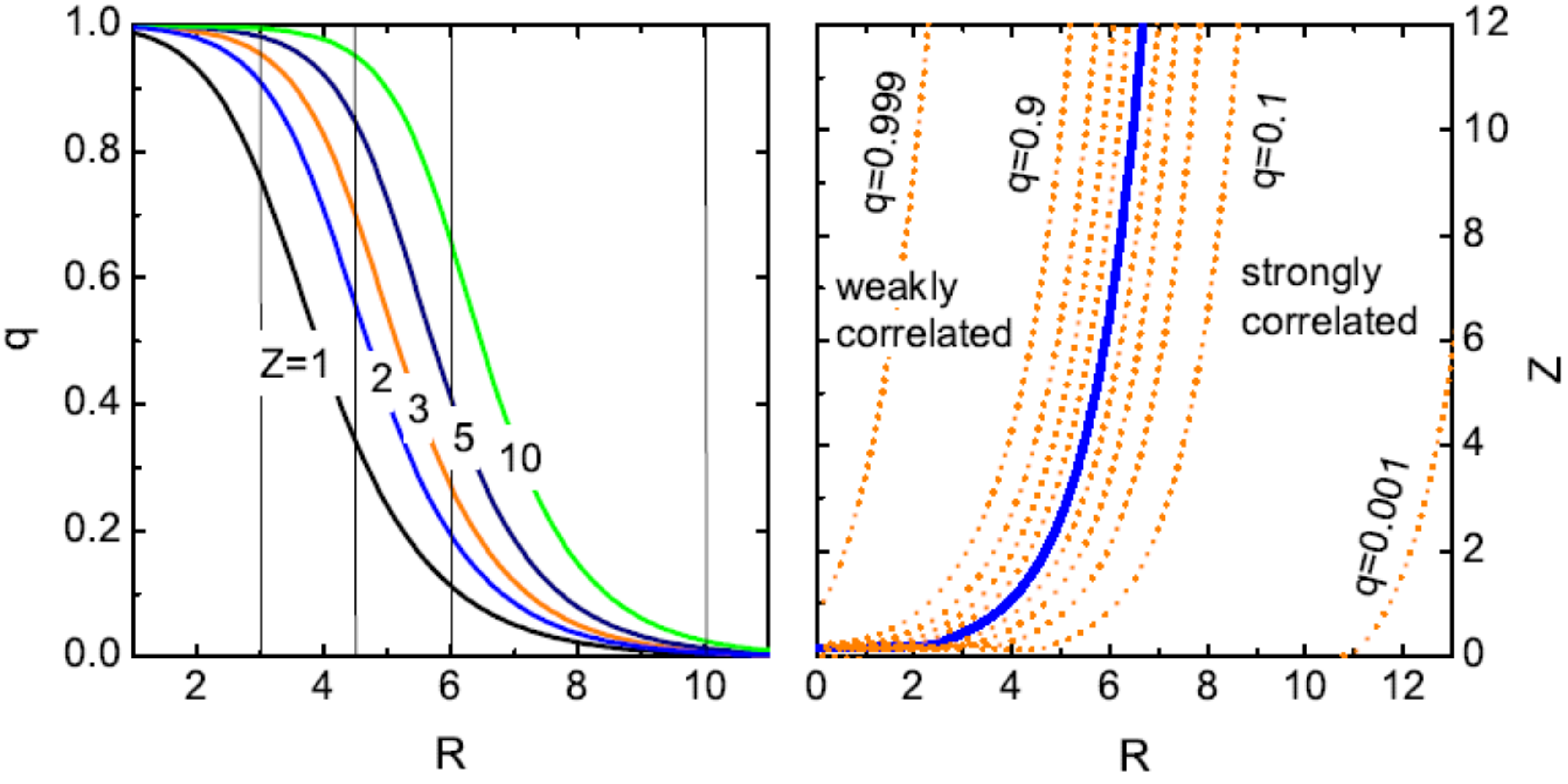
$\int d^3\mathbf{r}\,\delta n = 0$

Bond charge encodes correlation effects

$n_0(\mathbf{r}) = \phi_a^2 + \phi_b^2 + 2\phi_a\phi_b$

$q = \dfrac{\rho_{ab}}{\rho^0_{ab}} \longrightarrow$ Hopping reduction factor $\longrightarrow$ Can be expressed in terms of lattice parameters, U, V, t…

Weak-strong correlation cross-over



$q \to 0$ ⇔ $U/t \to \infty$

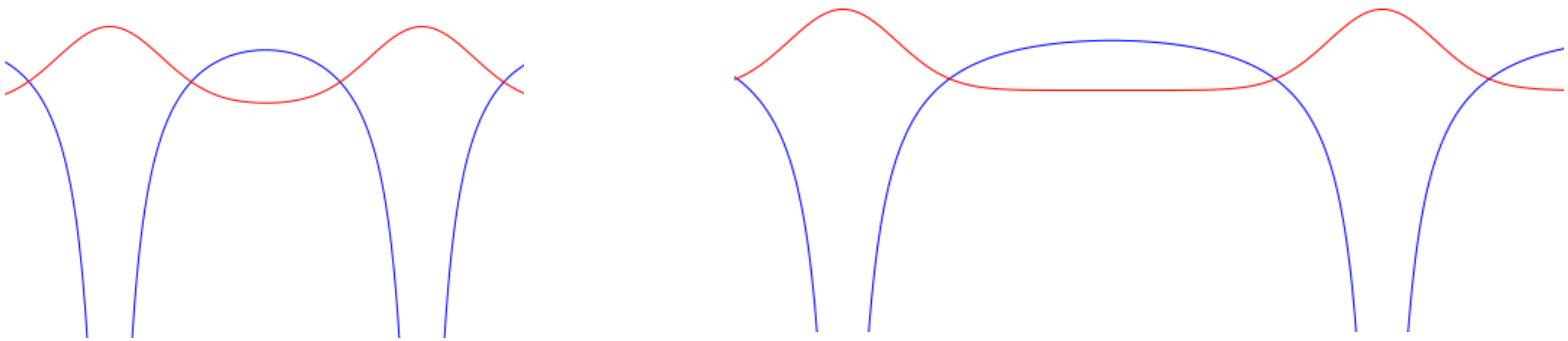
$q = 1$ ⇔ $U/t \to 0$

Mott barriers

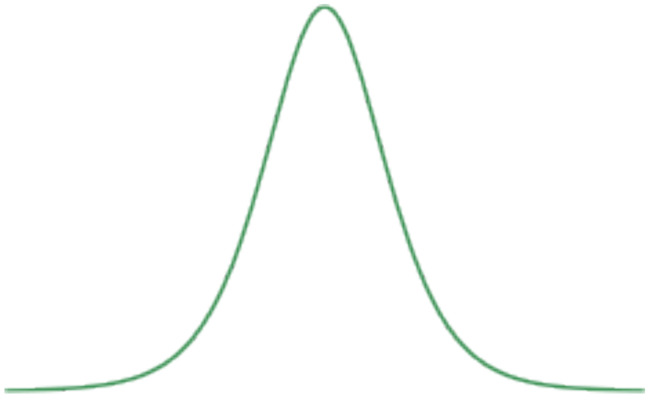
Mimic the effect of band renormalization
on the density by an external potential

Mott transition

R



Emergence of Mott barriers



- **Mott barriers are of order Δ**

In the single-band limit the only non-interacting ground state possible is

$$n^H(\mathbf{r}) = \phi_a(\mathbf{r})^2 + \phi_b(\mathbf{r})^2 + 2\phi_a(\mathbf{r})\phi_b(\mathbf{r})$$

Mixing with higher states required to have a barrier in KS of order Δ

- **LDA does not have a barrier**

Hartree initial guess is solution

$$\varphi_H(\mathbf{r}) = \frac{1}{\sqrt{2}}[\phi_a(\mathbf{r}) + \phi_b(\mathbf{r})]$$

$$v_{xc}^{LDA}[n(\mathbf{r})]/\Delta \sim 1/Z$$

KS state
in “single-band” limit

No-go theorem

To describe Mott phenomena $v_{xc}(\mathbf{r})$ must be $O(Z^0)$

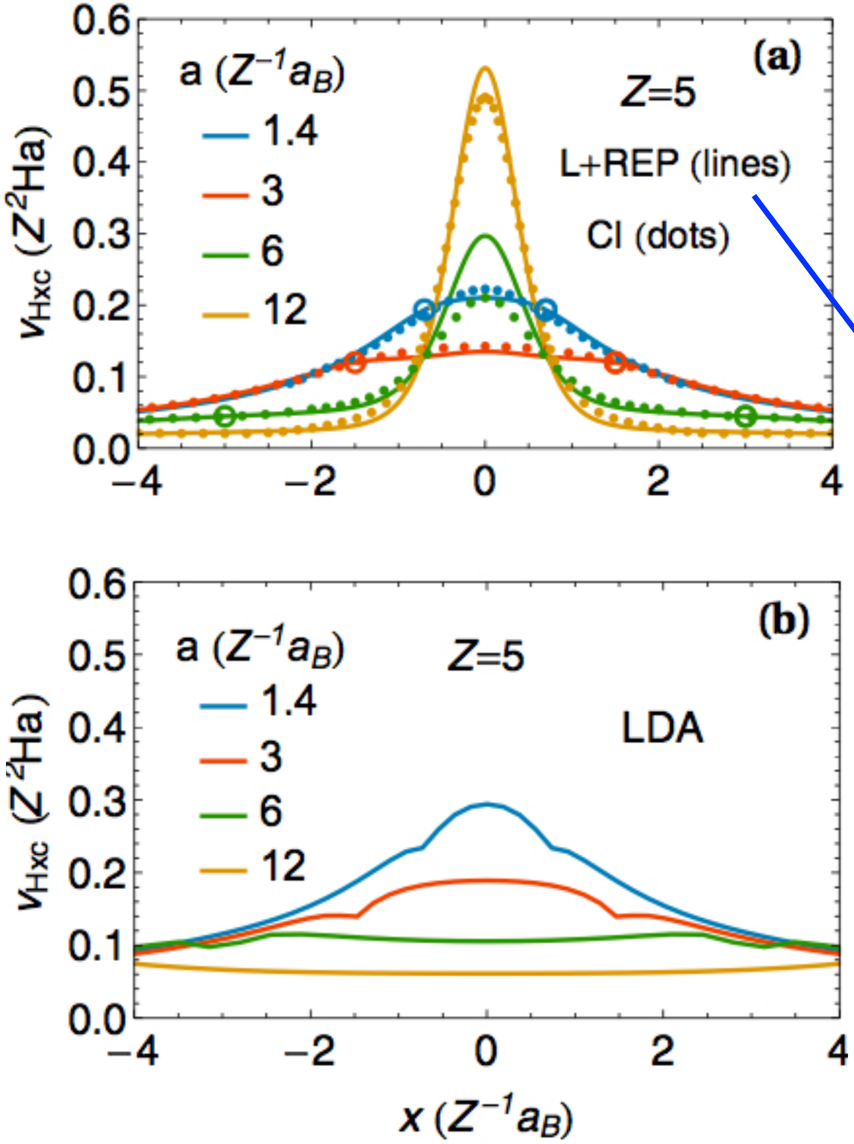
Corollary I

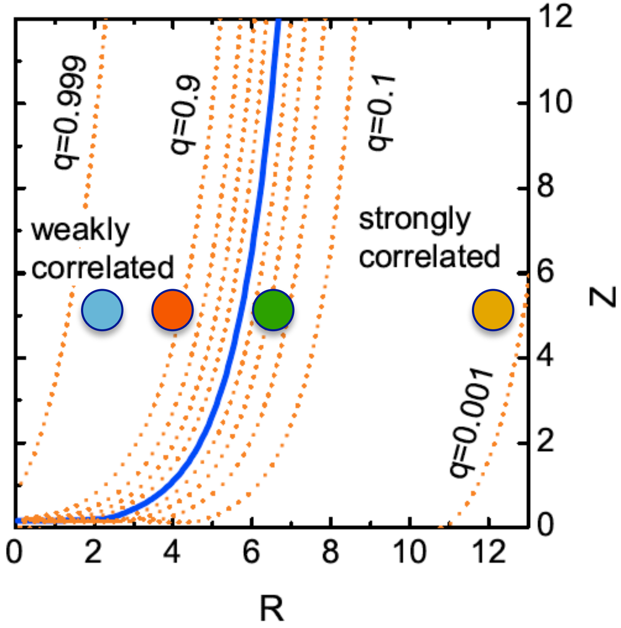
DFT an a single band description are incompatible.

Corollary II

It is not possible to describe Mott phenomena with a local or semilocal functionals since they are all $O(1/Z)$

Hxc potentials





Lattice + reverse engineering potential (L+REP)

Exact lattice ground-state and basis optimization

L+REP potential

$$V^{\rho}_{Hxc} = \frac{\nabla^2\sqrt{\rho}}{2\sqrt{\rho}} - V_N - I$$

+ Optimization equations

$$v_{\mathrm{Hxc}}(\mathbf{r}) = v_{\mathrm{c}}^{\mathrm{kin}}(\mathbf{r}) + v_{\mathrm{xc}}^{\mathrm{resp}}(\mathbf{r}) + v_{\mathrm{Hxc}}^{\mathrm{cond}}(\mathbf{r})$$

$$v_{\mathrm{c}}^{\mathrm{kin}}(\mathbf{r}) = \frac{(1-q^2)}{2}\frac{|\phi_a(\mathbf{r})\vec{\nabla}\phi_b(\mathbf{r}) - \phi_b(\mathbf{r})\vec{\nabla}\phi_a(\mathbf{r})|^2}{n^2(\mathbf{r})}$$

- Order Z^0
- Independent of R for large R

$$v_{\mathrm{xc}}^{\mathrm{resp}}(\mathbf{r}) = \frac{t(1-q)[\phi_a(\mathbf{r}) - \phi_b(\mathbf{r})]^2}{n(\mathbf{r})} + \delta\epsilon_g$$

- Order Z^0
- Scales as e^{-R}

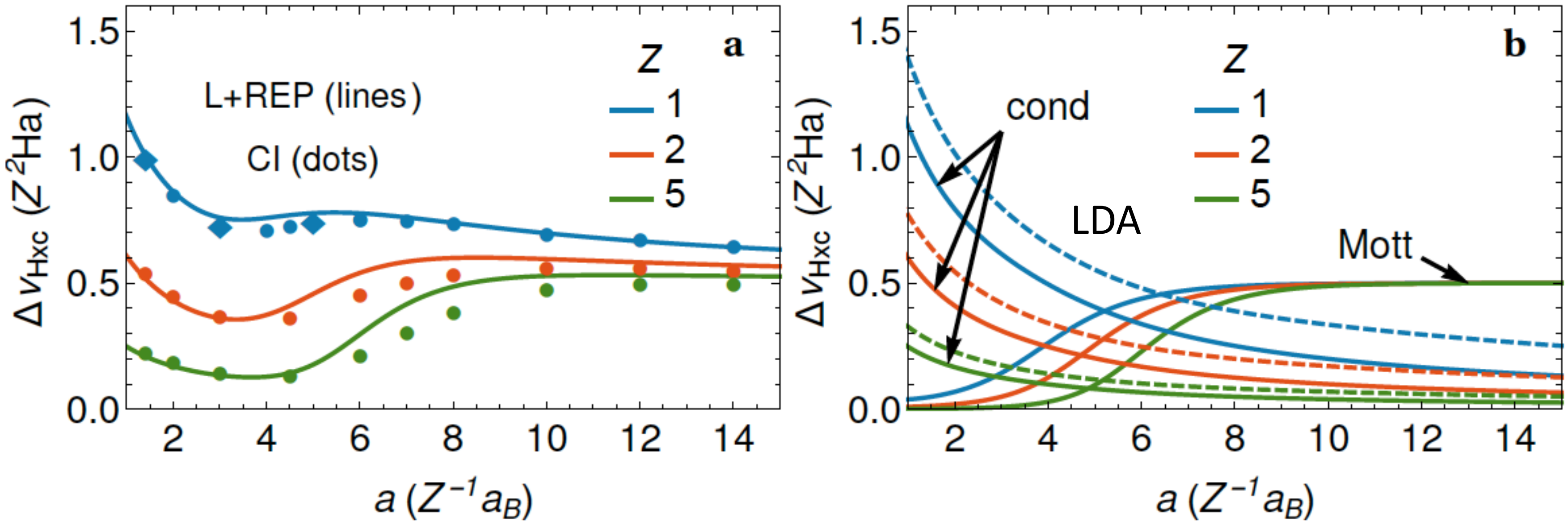
$$v_{\mathrm{Hxc}}^{\mathrm{cond}} = \frac{1}{Z}\int\frac{\Gamma_2(\mathbf{r},\mathbf{r}')}{n(\mathbf{r})|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

- Order Z^{-1}
- Scales as 1/R

Diagonal two-particle density matrix: $\Gamma_2(\mathbf{r},\mathbf{r}') = \sum_{\sigma\sigma'}\langle\Psi_\sigma^\dagger(\mathbf{r})\Psi_{\sigma'}^\dagger(\mathbf{r}')\Psi_{\sigma'}(\mathbf{r}')\Psi_\sigma(\mathbf{r})\rangle$

In this form the potential becomes insensitive to the choice of the orbitals!

Two contributions to barrier height in the bond region



$$v_{\rm Hxc}^{\rm kin}(0) \simeq \frac{(1-q)}{2(1+q)} \qquad v_{\rm Hxc}^{\rm cond}(0) \simeq \frac{1}{ZR}$$

Many-site extension

$$v_{\mathrm{Hxc}} \simeq v_{\mathrm{Hxc}}^{\mathrm{c}} + v_{\mathrm{Hxc}}^{\mathrm{cond}} + v_{\mathrm{xc}}^{\mathrm{resp}}$$

$$v_{\mathrm{Hxc}}^{\mathrm{cond}} = \frac{1}{Z} \int \frac{\Gamma_2(\mathbf{r},\mathbf{r}')}{n(\mathbf{r})|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

Simple generalization of
2-site expression

Most relevant in the strong-correlation limit:

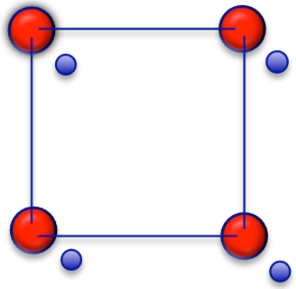
$$\begin{aligned} v_{\mathrm{Hxc}}^{\mathrm{kin}}(\mathbf{r}) &= \frac{(1-q^2)}{2} \sum_{\langle ij \rangle} \frac{|\phi_i(\mathbf{r})\vec{\nabla}\phi_j(\mathbf{r}) - \phi_j(\mathbf{r})\vec{\nabla}\phi_i(\mathbf{r})|^2}{n^2(\mathbf{r})} \\ v_{\mathrm{Hxc}}^{\mathrm{resp}}(\mathbf{r}) &= t(1-q) \sum_{\langle ij \rangle} \frac{[\phi_i(\mathbf{r}) - \phi_j(\mathbf{r})]^2}{n(\mathbf{r})} + \langle \psi_0 | \hat{h} | \psi_0 \rangle - \epsilon_g \end{aligned}$$

Only nearest-
neighbor correlation

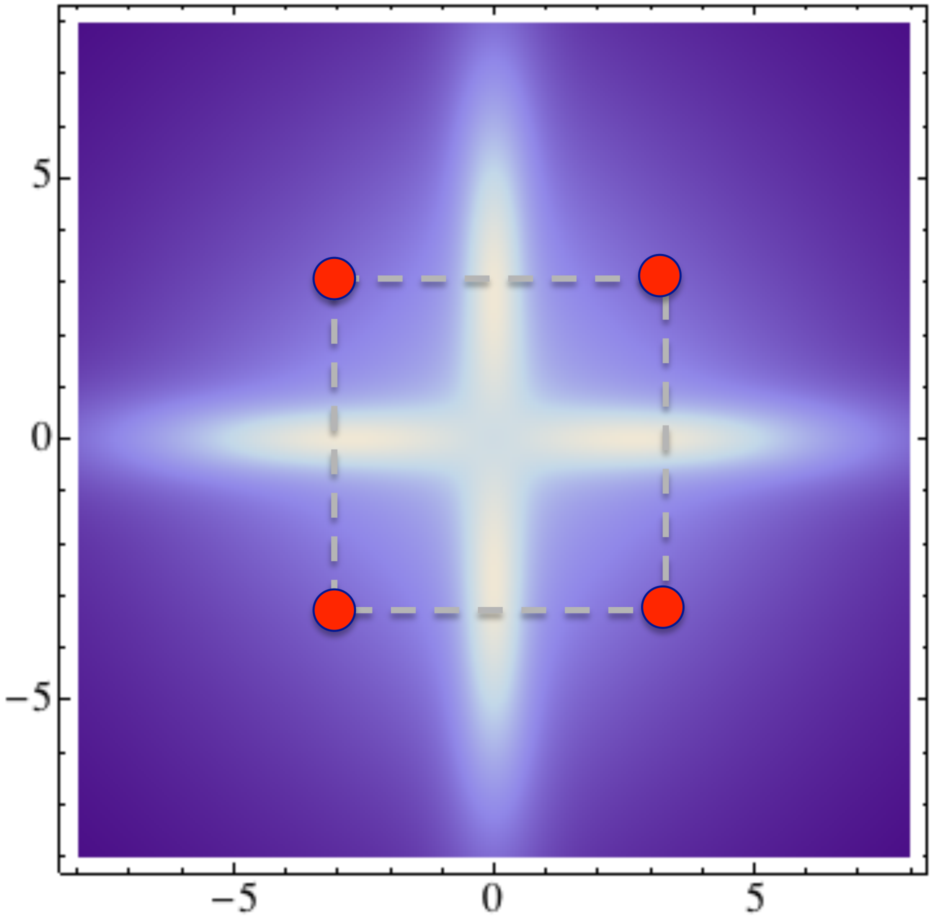
1- and 2- body lattice correlations, e.g. *q* and *d,* estimated by lattice methods

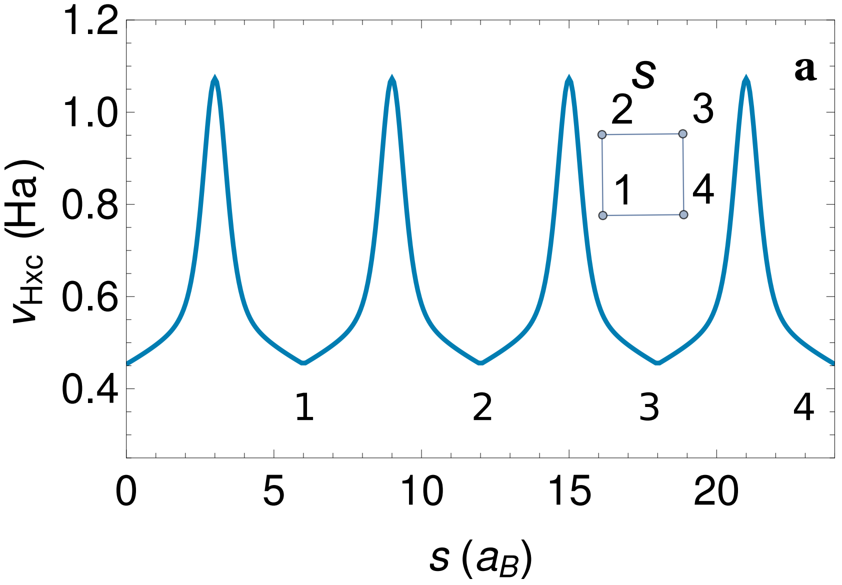
L+REP potential

Example: Hubbard plaquette



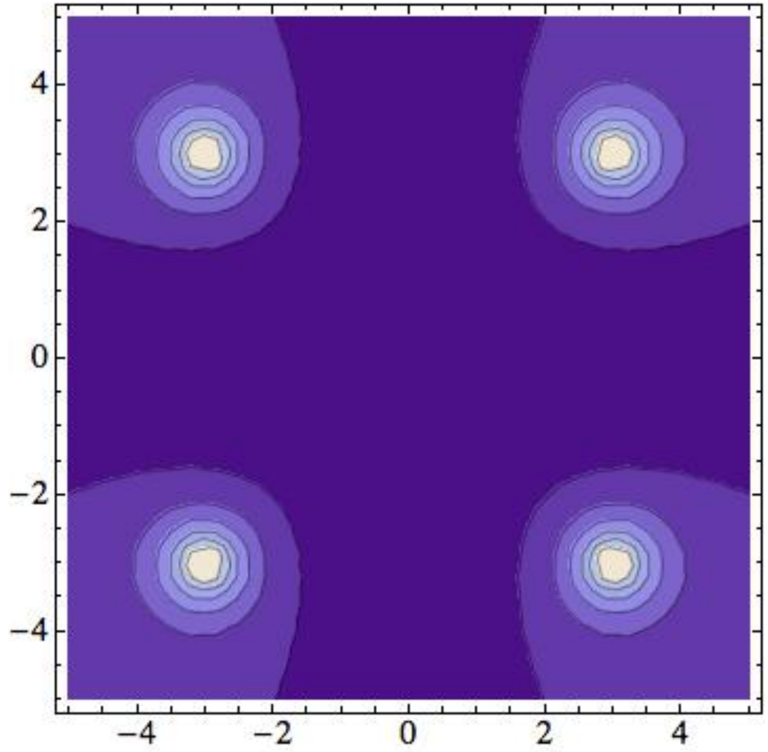
L+REP potential



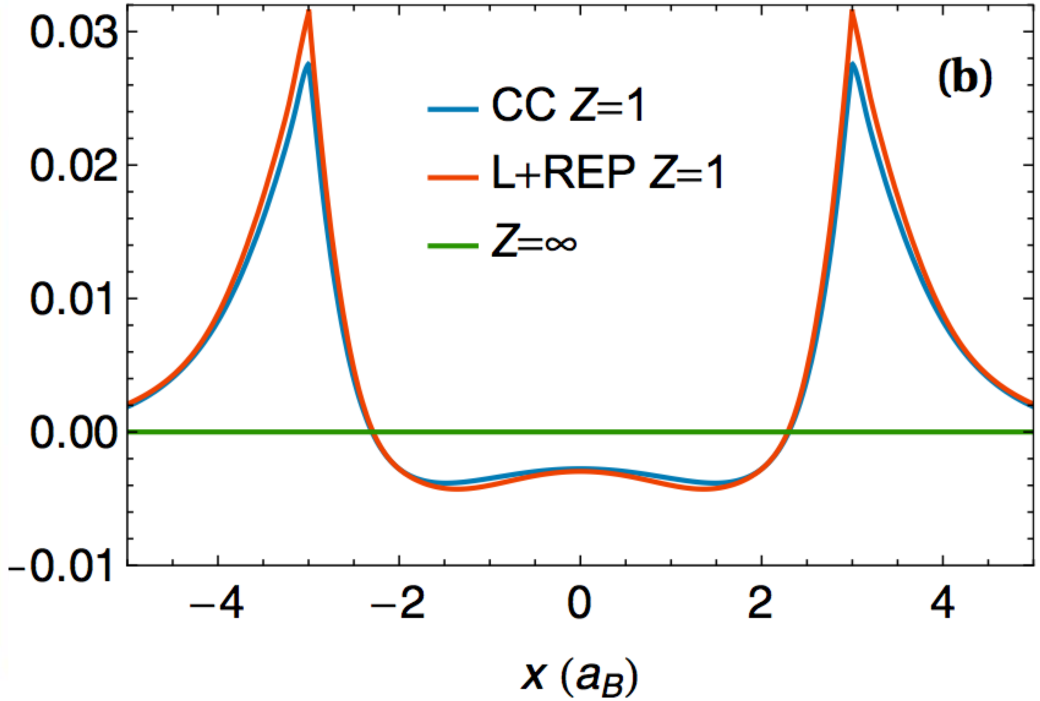


Charge difference, $n - n_0$

Plane view



Along a bond



◎ DFT exchange-correlation potential across the weak-strong correlation crossover

- Anomalous scaling of the xc-potential
- Lattice + Reverse engineering potential (L+REP)

◎ Consequences of basis optimization and properties of the best single-particle basis

Gutzwiller Ansatz: an interacting system should have less doubly occupied sites than a non-interacting one

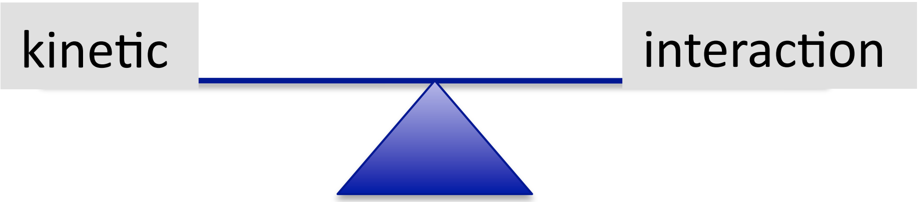
$$|\Phi_\gamma\rangle = \frac{\gamma^D}{C_\gamma^{1/2}}|\Phi_0\rangle$$

Slater determinant

$$\gamma \in [0,1] \qquad D = \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$\gamma = \gamma(d) \qquad d = \frac{\langle D \rangle}{L}$$

d is the fundamental variational object → in the continuum: pair density functional



Alternative view: *q* is the fundamental variational object $\gamma = \gamma(q)$ In the continuum: one-particle density matrix functional

→ Reduced Density Matrix Functional Theory (RDMFT)
S. Sharma et al. Phys. Rev. Lett. (2013).

Natural orbital basis

$$\psi_0 = \frac{\varphi_a + \varphi_b}{\sqrt{2}} \qquad \psi_1 = \frac{\varphi_a - \varphi_b}{\sqrt{2}}$$

Gutzwiller wavefunction:

$$|\Phi_\gamma\rangle = \frac{1}{C_\gamma^{1/2}} \left[(\gamma + 1) a_{0\uparrow}^\dagger a_{0\downarrow}^\dagger + (\gamma - 1) a_{1\uparrow}^\dagger a_{1\downarrow}^\dagger \right] |\emptyset\rangle$$

To write the energy we just need the one-body and the diagonal two-body density matrices

$$\Gamma_1^{\mathrm{G}}(\mathbf{r}, \mathbf{r}') = (1 + q)\psi_0(\mathbf{r})\psi_0(\mathbf{r}') + (1 - q)\psi_1(\mathbf{r})\psi_1(\mathbf{r}')$$

$$\Gamma_2^{\mathrm{G}}(\mathbf{r}, \mathbf{r}') \ = \ \left(\sqrt{1+q}\,\psi_0(\mathbf{r})\psi_0(\mathbf{r}') - \sqrt{1-q}\,\psi_1(\mathbf{r})\psi_1(\mathbf{r}') \right)^2$$

Optimized Gutzwiller theory ⟺ Löwdin and Shull RDMF in a truncated basis

Löwdin and Shull wavefunction in terms of NOs (1956)

$$\Psi_{LS}(\mathbf{r}, \mathbf{r}') = \sum_i \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')c_i \longrightarrow \text{Exact}$$

$$c_i = f_i \sqrt{\rho_i/2}$$

$$f_i = \pm 1$$

Optimization equations

$$\sum_\nu \hat{\mathcal{H}}_{\mu\nu}\psi_\nu = \Omega_\mu \psi_\mu \quad \mu,\nu \in [0,1]$$

$$\hat{\mathcal{H}}(\mathbf{r}) = \begin{pmatrix} [\hat{h}(\mathbf{r}) + \lambda\,\bar{w}_{00}(\mathbf{r})]\bar{\rho}_0 & -\lambda\,\bar{w}_{01}(\mathbf{r})\sqrt{\bar{\rho}_0\bar{\rho}_1} \\ -\lambda\,\bar{w}_{10}(\mathbf{r})\sqrt{\bar{\rho}_0\bar{\rho}_1} & (\hat{h}(\mathbf{r}) + \lambda\,\bar{w}_{11}(\mathbf{r}))\bar{\rho}_1 \end{pmatrix}$$

Occupation of the natural orbitals

$$\begin{cases} \rho_0 = 1 + q \\ \rho_1 = 1 - q \end{cases}$$

Self-consistent potentials

$$\bar{w}_{\mu\nu}(\mathbf{r}) = \int \frac{\psi_\mu(\mathbf{r}')\psi^*_\nu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

In the non-interacting limit the antibonding orbital is undetermined since $\rho_1 = 0$

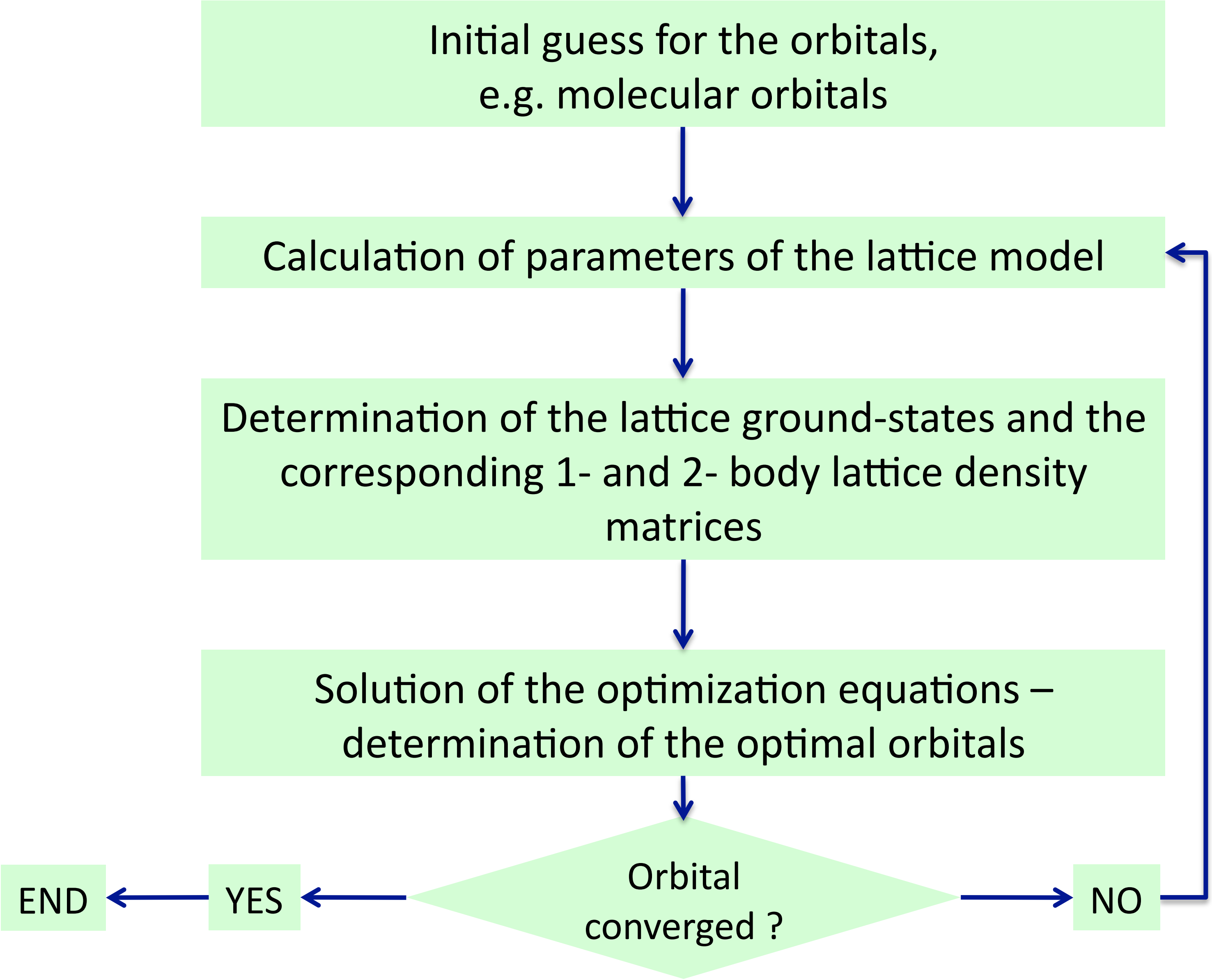
On the contrary for a vanishingly small interaction

$$\hat{h}(\mathbf{r})\,\psi_0(\mathbf{r}) = \epsilon_0\psi_0(\mathbf{r}) \qquad \Omega_\mu = \rho_\mu\varepsilon_\mu$$

$$\hat{h}(\mathbf{r})\,\psi_1(\mathbf{r}) - \frac{8t}{U-V}\,\bar{w}_{01}(\mathbf{r})\psi_0(\mathbf{r}) = \epsilon_1\psi_1(\mathbf{r})$$

Optimization equations are singular at in the weak-interaction limit!

Orbital optimization algorithm



Initial guess for the orbitals,
e.g. molecular orbitals

Calculation of parameters of the lattice model

Determination of the lattice ground-states and the corresponding 1- and 2- body lattice density matrices

Solution of the optimization equations – determination of the optimal orbitals

Orbital converged ?

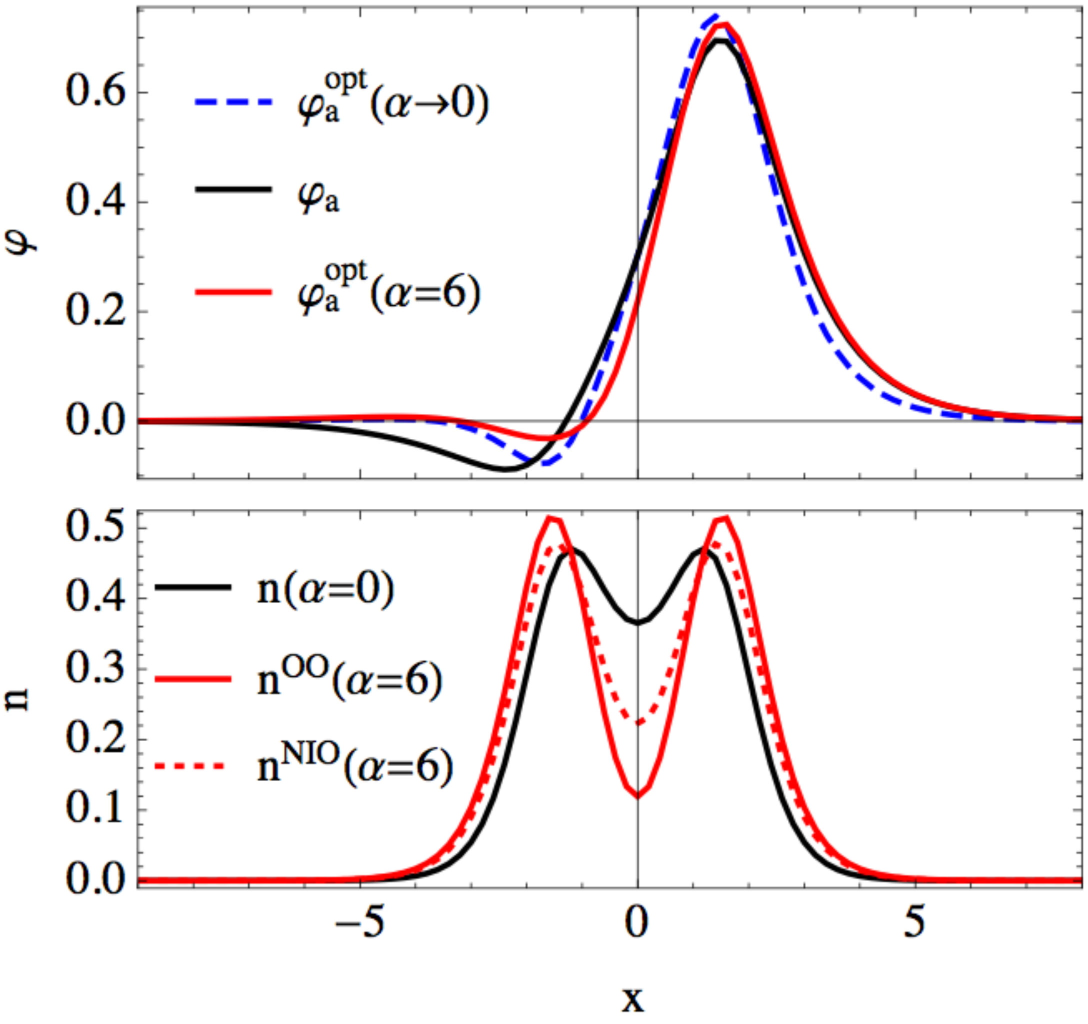
YES

END

NO

Optimized orbitals

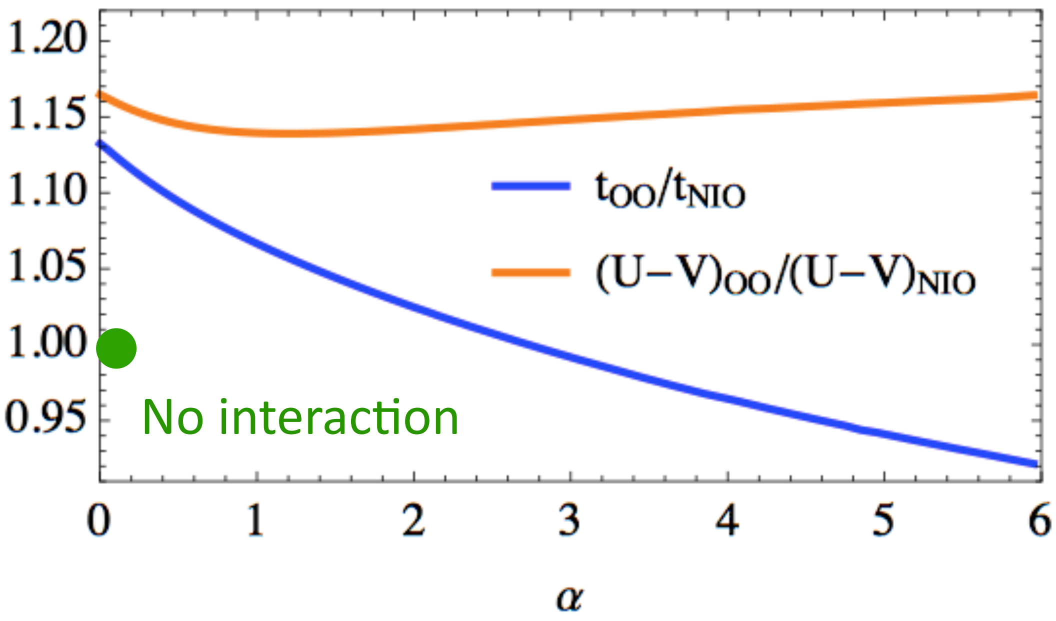
1D Toy model: two-well potential + δ-interaction



α= coupling constant plays the role of 1/Z

Significant effects of orbital optimization on the density

Renormalization of U-V and t



NIO = non-interacting orbitals
OO = optimized orbitals

$$(U-V)_{NIO}/(\alpha\ t_{NIO}) \approx 3$$

Within our model, orbital optimization always increases
local Hubbard correlation, i.e. (U-V)/(αt) increases

Renormalization of exchange interactions

Super-exchange interaction:

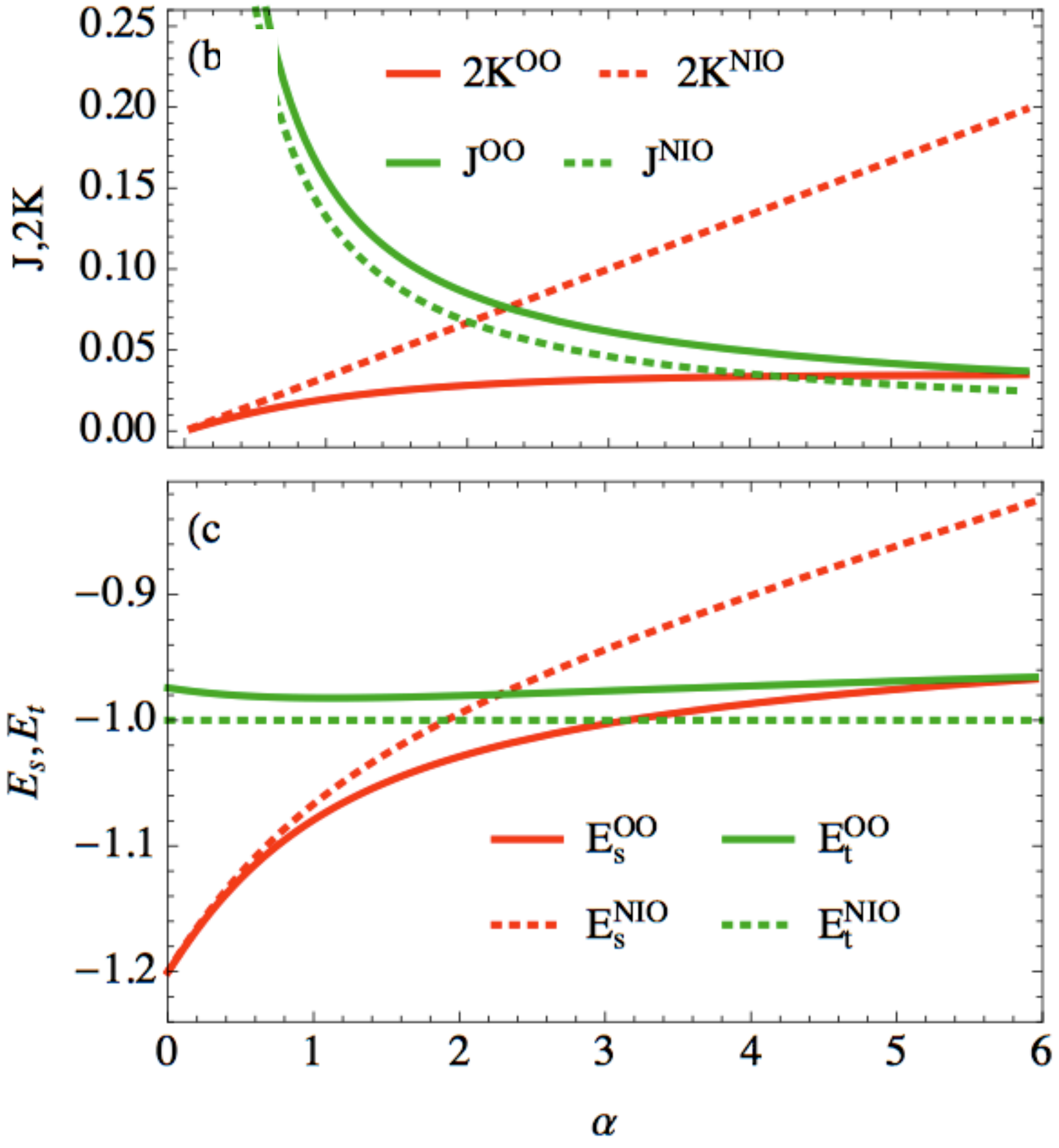
$$J = \frac{4(t - t_c)^2}{U - V}$$

Direct exchange:

$$K = \alpha \int \varphi_a^2(r)\, \varphi_b^2(r)\, dr$$

Strong renormalization of K by orbital optimization prevents magnetic ordering

$$E_t - E_s \approx J - 2K$$



Take-home messages

- ◎ "No-go" theorem for local DFT approaches applied to strongly correlated systems
- ◎ Orbital optimization can give significant qualitative and quantitative effects

In progress

- ◎ Designing RDMFT functionals
- ◎ Implementation of L+REP potential

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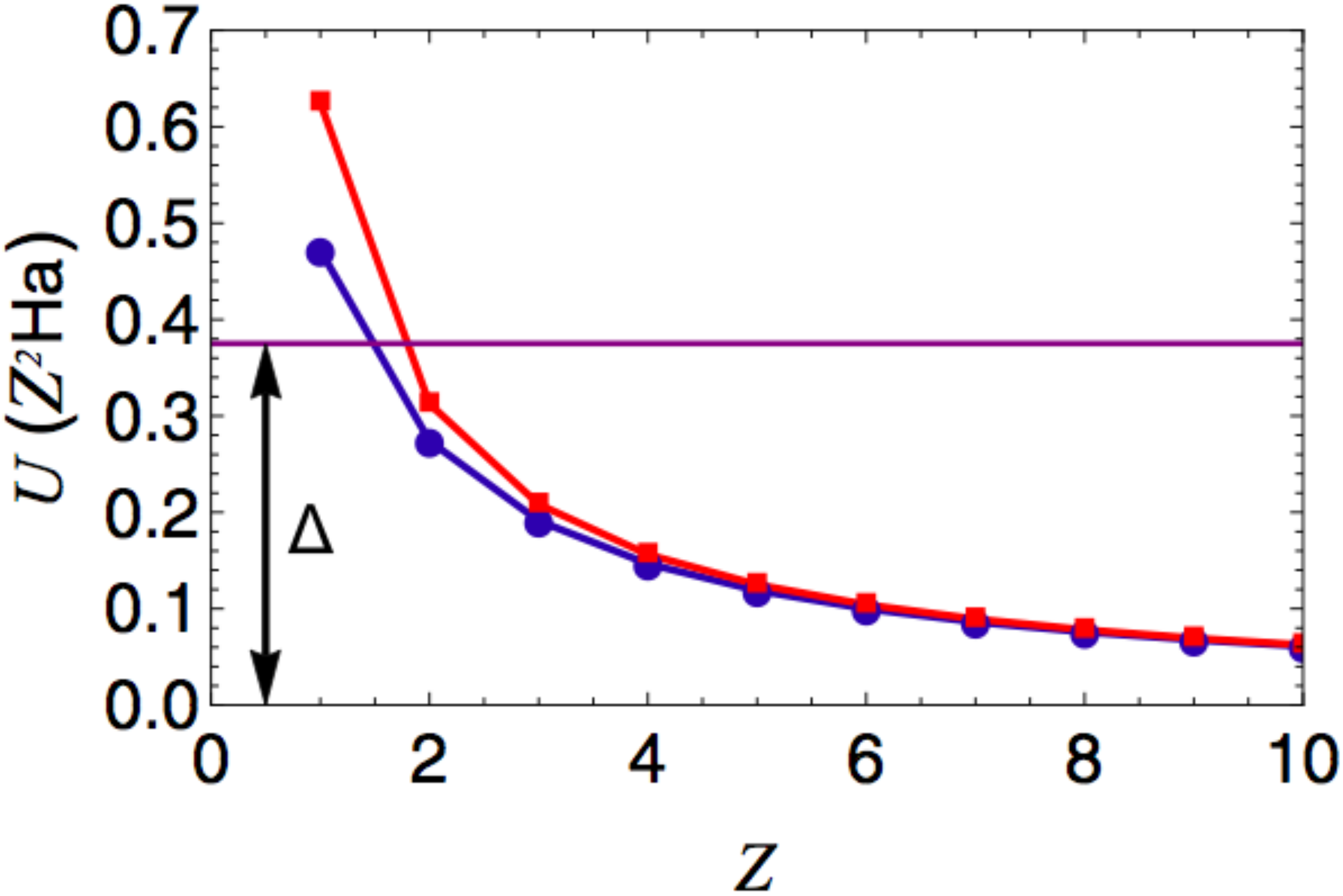
starting
from Gutzwiller
approximation

Screening effects on U



Recent applications of RDMFT

Molecules and clusters:	N. Lathiotakis et al. Phys. Rev. A (2005) N. Helbig et al. Phys. Rev. A (2009) O. Gritsenko et al. J. Chem Phys. (2005) M. Piris, Int. J. of Quant. Chem. (2014) …
Solids:	S. Sharma et al. Phys. Rev B (2008). S. Sharma et al. Phys. Rev. Lett. (2013). …
Time-Dependent:	K. Giesbertz et al. Phys. Rev. Lett. (2013) K. Pernal Phys. Rev. Lett. (2008) …

What is RDMFT?

Fundamental theorem by Gilbert: There exist a one-to-one correspondence between the one-body density matrix and the ground state wave-function

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The energy can be written as a functional of the one-body density matrix

$$\Gamma_1(\mathbf{r},\mathbf{r}') = \langle \Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}')\rangle$$

$$E\left[\Gamma_1\right] = \boxed{\begin{array}{c} T[\Gamma_1] \\ \text{Exact!} \end{array}} + E_{\mathrm{H}}[\Gamma_1] + \boxed{\begin{array}{c} E_{\mathrm{xc}}[\Gamma_1] \\ \text{Unknown} \end{array}} + \int v(\mathbf{r})\Gamma_1(\mathbf{r},\mathbf{r})d\mathbf{r}$$

- The one-body density matrix is determined by the natural orbitals and their occupancies

$$\Gamma(\mathbf{r},\mathbf{r}') = \sum_n \psi_n(\mathbf{r})\psi_n(\mathbf{r}')\rho_n$$

- E_{xc} depends on the diagonal two body density matrix:

$$\Gamma_2(\mathbf{r},\mathbf{r}') = \sum_{\sigma\sigma'} \langle \Psi^\dagger_\sigma(\mathbf{r})\Psi^\dagger_{\sigma'}(\mathbf{r}')\Psi_{\sigma'}(\mathbf{r}')\Psi_\sigma(\mathbf{r})\rangle$$

Functional of the natural orbitals and their occupancies ⇔ Implicit functional of Γ_1