Exact Kohn-Sham eigenstates vs many-body quasi-particles in simple models of strongly correlated electrons

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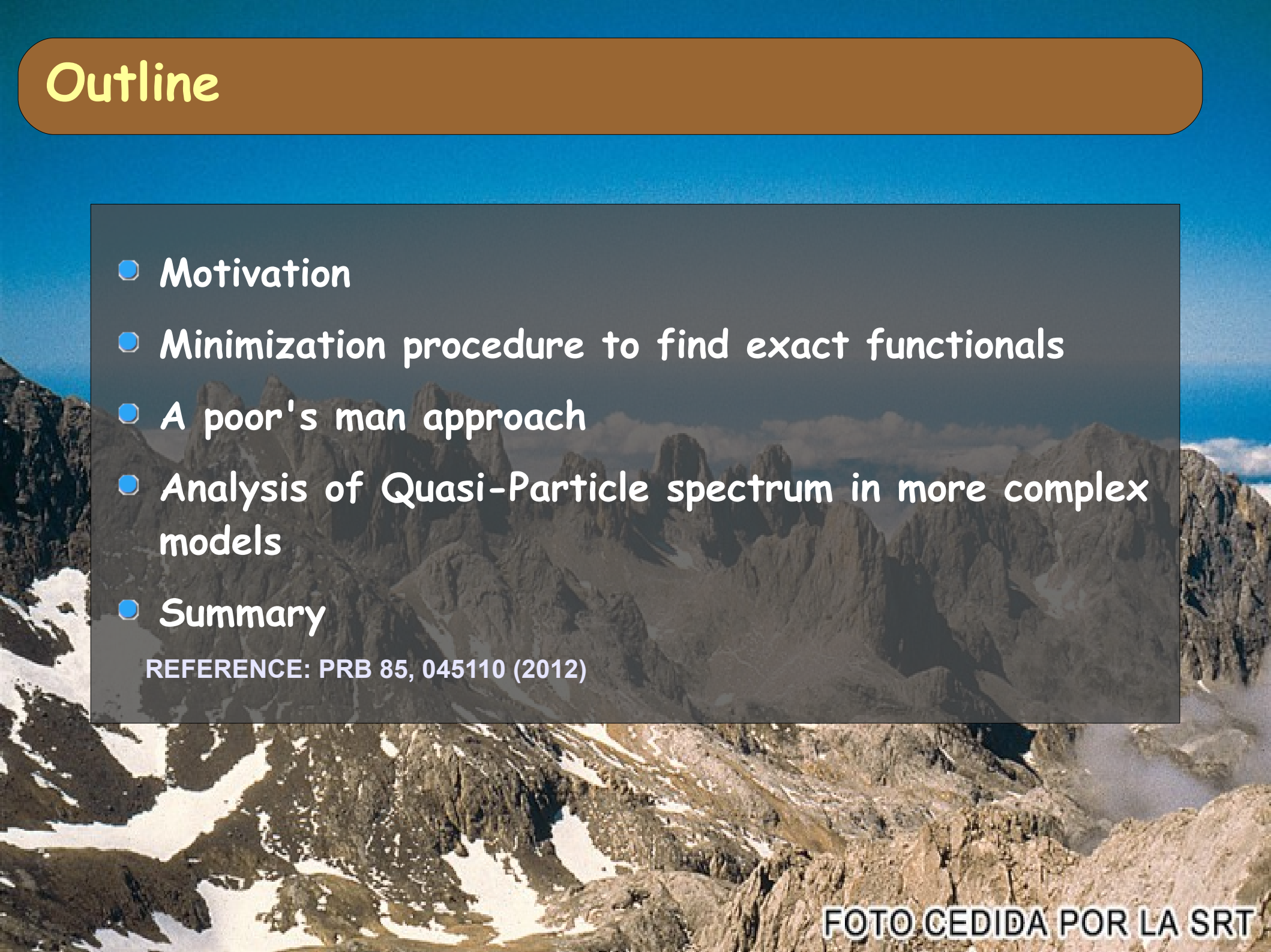
Outline

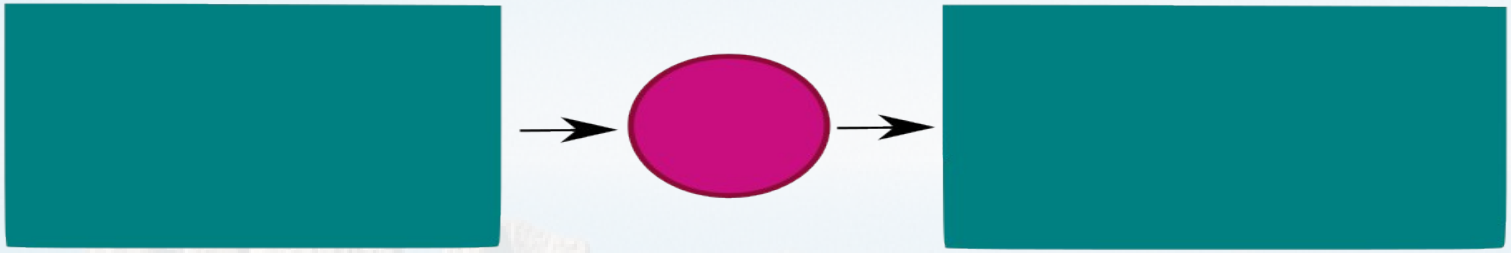
- Motivation
- Minimization procedure to find exact functionals
- A poor's man approach
- Analysis of Quasi-Particle spectrum in more complex models
- Summary

REFERENCE: PRB 85, 045110 (2012)



Motivation

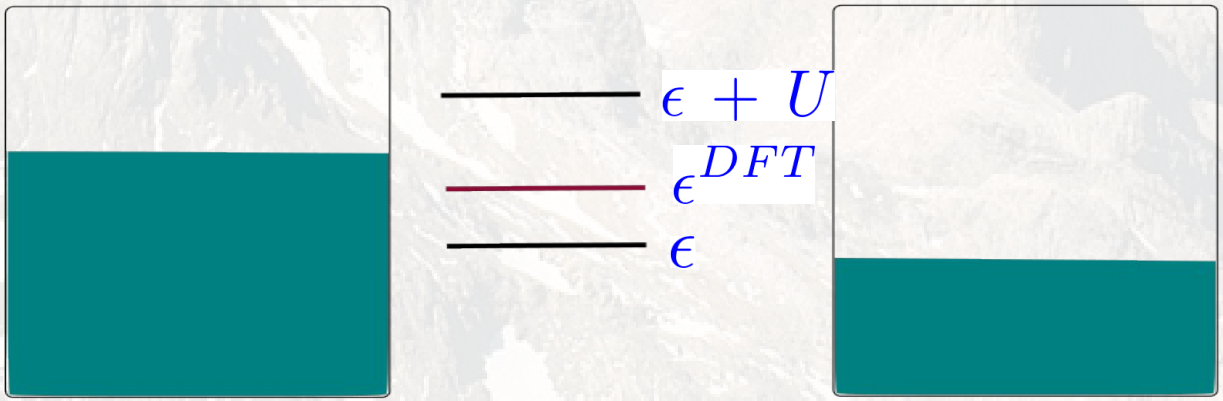
Transport theory of a (possibly) strongly correlated scattering region



Anderson / Hubbard -derived models → Many-body theory → correct QPs

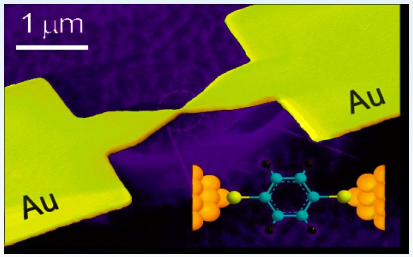
Density Functional theory + Keldish →

Take account of materials & chemistry details (+)
Screws up strong correlations (-)



Motivation

Attempts to extend DFT or to merge both worlds:
LDA + U, Dynamical Mean Field Theory, ...



Is this a problem of approximations to DFT or is it inherent to DFT ?

DFT provides information about the ground state, but not about excitations

To what extent excitations would be wrong ?

No one really knows, because no one has ever found an exact DF !!

What would we learn from such a one ?

Motivation

- What would be the correspondence between exact KS eigenstates and many-body quasi-particles ?
- Would it be possible to describe Kondo peaks, Lower/Upper Hubbard bands, etc. ?
- Would it be possible to include it in a NEGF code (e.g.: SMEAGOL) ?

Motivation

Turn around the question:

Find out very simple models
- Whose exact Density Functional can be found analytically
- That can be also solved exactly

- Extract knowledge from them
- Use them to find solutions of more complex models

Or

- find accurate approximate functionals beyond LDA

Minimization Procedure

Formulate Density Functional Theory for a lattice model

- **Schönhammer, Gunnarsson & Noack (PRB 1995) defined LDA**
- **A number of other people has explored LDA**

Real-space DFT

Basic variable → electron density $n_\sigma(\vec{r})$

Basic tool → Energy functional $Q[n_\sigma(\vec{r})]$

Lattice DFT

Basic variable → site electron occupation $n_{i,\sigma}$

Basic tool → Energy function $Q(n_{i,\sigma})$

Minimization Procedure

Single-site Anderson-Hubbard model

$$\hat{H} = \epsilon_0 \, \hat{n}_\uparrow + \epsilon_0 \, \hat{n}_\downarrow + U \, \hat{n}_\uparrow \, \hat{n}_\downarrow$$

Double-site Hubbard model

$$\hat{H} = \sum_\sigma \epsilon_d \, \hat{n}_{1,\sigma} + \sum_\sigma \epsilon_d \, \hat{n}_{2,\sigma} - t \sum_\sigma (\hat{d}^\dagger_{1,\sigma} \, \hat{d}_{2,\sigma} + h.c.) + U \sum_{i=1,2} \hat{n}_{i,\uparrow} \, \hat{n}_{i,\downarrow}$$

Double-site Anderson model

$$\hat{H} = \sum_\sigma \epsilon_c \, \hat{n}_{c,\sigma} + \sum_\sigma \epsilon_d \, \hat{n}_{d,\sigma} - t \sum_\sigma (\hat{c}^\dagger_\sigma \, \hat{d}_\sigma + h.c.) + U \, \hat{n}_{d,\uparrow} \, \hat{n}_{d,\downarrow}$$

Four-site spinless fermion model

$$\hat{H} = \epsilon_0 \, (\hat{n}_1 + \hat{n}_2 + \hat{n}_3 + \hat{n}_4) - t \, (\hat{c}^\dagger_1 \, \hat{c}_2 + \hat{c}^\dagger_2 \, \hat{c}_3 + \hat{c}^\dagger_3 \, \hat{c}_4 + h.c.) + U \, (\hat{n}_1 \, \hat{n}_2 + \hat{n}_2 \, \hat{n}_3 + \hat{n}_3 \, \hat{n}_4)$$

Minimization Procedure

Consider a system of N electrons with the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i v(\vec{\mathbf{r}}_i) - 2\mu \sum_i B(\vec{r}_i)\hat{s}_z^i, \tag{9}$$

where $v(\vec{\mathbf{r}})$ and $B(\vec{\mathbf{r}})$ are external scalar and magnetic fields (the latter coupling to electron spin $\hat{s}_z^i$), and $\hat{T}$ is the kinetic energy operator. Let $n_\uparrow(\vec{\mathbf{r}})$ and $n_\downarrow(\vec{\mathbf{r}})$ be up- and down-spin number densities, and define the universal functional[35]

$$Q[n_\uparrow, n_\downarrow] = \min\langle \hat{T} + \hat{V}_{ee}\rangle, \tag{10}$$

which searches the set of all N-particle antisymmetric wave functions producing the given spin densities $n_\sigma(\vec{\mathbf{r}}) = \langle \hat{n}_\sigma(\vec{\mathbf{r}})\rangle$, and delivers the minimum expectation value. Then the usual variational principle ($\langle \hat{H}\rangle \geq$ the ground-state energy E) implies that for any choice of trial spin densities $n_\uparrow$ and $n_\downarrow$ representing N electrons,

$$Q[n_\uparrow, n_\downarrow] + \int d^3r\, v(\vec{\mathbf{r}})n(\vec{\mathbf{r}}) - 2\mu \int d^3r\, B(\vec{\mathbf{r}}) \sum_\sigma \sigma n_\sigma(\vec{\mathbf{r}}) \geq E, \tag{11}$$

where $n = \sum_\sigma n_\sigma$. Furthermore, the true ground-state spin densities are those which make Eq. (11) an equality. (This is the generalized Hohenberg-Kohn[6] theorem. Note that the argument does not

The variational principle (11) may be used to calculate $n_\uparrow$, $n_\downarrow$, and E, if the functional dependence of Q on $n_\uparrow$ and $n_\downarrow$ is known. It is convenient to break Q up into three parts as follows:

$$Q[n_\uparrow, n_\downarrow] = T[n_\uparrow, n_\downarrow] + U[n] + E_{xc}[n_\uparrow, n_\downarrow], \tag{12}$$

where $T[n_\uparrow, n_\downarrow]$ is the "noninteracting" kinetic energy defined below, $U[n]$ is the direct Coulomb energy of Eq. (2), and $E_{xc}[n_\uparrow, n_\downarrow]$ is the exchange-correlation energy.

The spin densities can always be written (nonuniquely) in terms of orthonormal orbitals $\psi_{\alpha\sigma}(\vec{\mathbf{r}})$ and occupation numbers in the interval $0 \leq f_{\alpha\sigma} \leq 1$:

$$n_\sigma(\vec{\mathbf{r}}) = \sum_\alpha f_{\alpha\sigma} |\psi_{\alpha\sigma}(\vec{\mathbf{r}})|^2. \tag{13}$$

We define[36]

$$T[n_\uparrow, n_\downarrow] = \min\left(\sum_{\alpha\sigma} f_{\alpha\sigma} \langle \psi_{\alpha\sigma} | -\tfrac{1}{2}\nabla^2 | \psi_{\alpha\sigma}\rangle \right), \tag{14}$$

where the minimum is over all possible $f_{\alpha\sigma}$ and $\psi_{\alpha\sigma}$ yielding the given spin densities. (For further

$$[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}^\sigma(\vec{\mathbf{r}})]\psi_{\alpha\sigma}(\vec{\mathbf{r}}) = \epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\vec{\mathbf{r}}),$$

with an effective one-body potential

$$v_{\text{eff}}^\sigma(\vec{\mathbf{r}}) = v(\vec{\mathbf{r}}) - 2\mu\sigma B(\vec{\mathbf{r}}) + u([n]; \vec{\mathbf{r}}) + v_{xc}^\sigma([n_\uparrow, n_\downarrow]; \vec{\mathbf{r}}),$$

and the exchange-correlation potential is

$$v_{xc}^\sigma([n_\uparrow, n_\downarrow]; \vec{\mathbf{r}}) = \frac{\delta}{\delta n_\sigma(\vec{\mathbf{r}})} E_{xc}[n_\uparrow, n_\downarrow]. \tag{20}$$

Minimization Procedure (double-site model)

Fock space: $\{|\, n_{c,\uparrow},\, n_{c,\downarrow},\, n_{d,\uparrow},\, n_{d,\downarrow} >\}$ ⟹ $|\psi> = \sum_{i,j,k,l=(0,1)} a_{i,j,k,l}\, |i,j,k,l>$

Compute expectation values

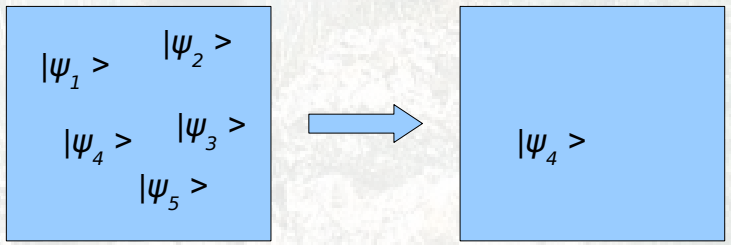
$$n_{\alpha=(c,d),\sigma}(\psi) = \frac{<\psi|\,\hat{n}_{\alpha,\sigma}\,|\psi>}{<\psi|\psi>} \Longrightarrow N_\sigma = n_{c,\sigma} + n_{d,\sigma}$$

$$E(\psi) = \frac{<\psi|\,\hat{H}\,|\psi>}{<\psi|\psi>}$$

All states $|\psi>$ have tagged an energy E and a set of occupations $\{\, n_{c,\uparrow},\, n_{c,\downarrow},\, n_{d,\uparrow},\, n_{d,\downarrow}\,\} = \{n_{\alpha,\sigma}\}$

Classify all $|\psi>$ in boxes defined by $\{\, n_{\alpha,\,\sigma}\,\}$

In each box, there are many $|\psi>$.
Pick the one with lowest energy.
Throw the rest to the trash can.
Now each box contains a single $|\psi>$



In each box, there is a one-to-one correspondence between $|\psi>$, $E(|\psi>)$ and $\{\, n_{\alpha,\sigma}\,\}$
This procedure defines the functional – Notice that N is not fixed!!

A poor's man approach

Example with a toy model

Single-site Anderson-Hubbard model

$$\hat{H} = \epsilon_0 \, \hat{n}_\uparrow + \epsilon_0 \, \hat{n}_\downarrow + U \, \hat{n}_\uparrow \, \hat{n}_\downarrow$$

Has no exchange (Fock term) by construction

It is self-interaction free

Can be solved exactly

Can be solved in Hartree approximation

The exact DF can be written down

A poor's man approach

$$|\psi> = a_0\,|0> + a_\uparrow\,|\uparrow> + a_\downarrow\,|\downarrow> + a_2\,|\uparrow,\downarrow>$$

$$n_\sigma(|\psi>) = n_\sigma(a_0, a_\uparrow, a_\downarrow, a2) = \frac{<\psi\,|\,\hat{n}_\sigma\,|\,\psi>}{<\psi\,|\,\psi>} = \frac{|a_\sigma|^2 + |a_2|^2}{|a_0|^2 + |a_\uparrow|^2 + |a_\downarrow|^2 + |a_2|^2}$$

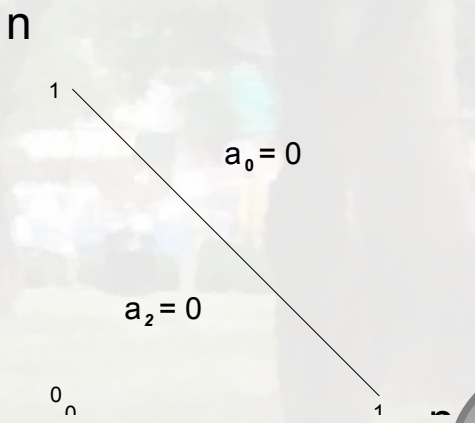
$$E(a_0, a_\uparrow, a_\downarrow, a_2) = \frac{<\psi\,|\,\hat{H}_\sigma\,|\,\psi>}{<\psi\,|\,\psi>} = \epsilon_0\,(n_\uparrow + n_\downarrow) + U\,\frac{|a_2|^2}{|a_0|^2 + |a_\uparrow|^2 + |a_\downarrow|^2 + |a_2|^2}$$

Goal: eliminate a's in terms of n_σ ⟹ $|a_\sigma|^2\,(1 - n_\uparrow - n_\downarrow) = |a_0|^2\,n_\sigma - |a_2|^2\,(1 - n_{-\sigma})$

$$E(a_0, a_2, n_\uparrow, n_\downarrow) = \epsilon_0\,(n_\uparrow + n_\downarrow) + U\,(n_\uparrow + n_\downarrow - 1)\,\frac{|a_2|^2}{|a_2|^2 - |a_0|^2}$$

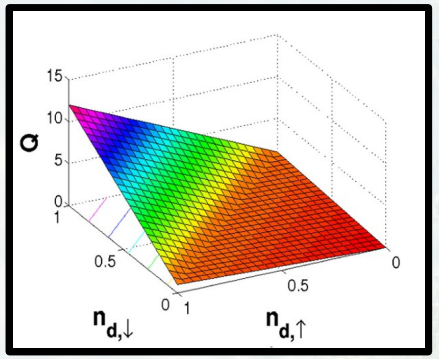
$$\begin{aligned} \mathrm{E}(\mathrm{n}_\uparrow, n_\downarrow) &= \epsilon_0\,(n_\uparrow + n_\downarrow), && 0 \le n_\uparrow + n_\downarrow \le 1 \\ &= \epsilon_0\,(n_\uparrow + n_\downarrow) + U\,(n_\uparrow + n_\downarrow - 1), && 1 \le n_\uparrow + n_\downarrow \le 2 \end{aligned}$$

$$Q[n_\uparrow, n_\downarrow] = \epsilon_0\,(n_\uparrow + n_\downarrow) + U\,(n_\uparrow + n_\downarrow - 1)\,\theta(n_\uparrow + n_\downarrow - 1)$$



A poor's man approach

Energy functional $Q[n_\uparrow, n_\downarrow] = \epsilon_0 (n_\uparrow + n_\downarrow) + U (n_\uparrow + n_\downarrow - 1)\, \theta(n_\uparrow + n_\downarrow - 1)$



Ground state-energy for target $N = n_\uparrow + n_\downarrow = N^0$

$$E^0 = \epsilon_d\, N^0 + U\, (N^0 - 1)\, \theta(N^0 - 1)$$

Exchange-Correlation functional $E^{XC} = Q - Q(U=0) = Q - T = U\,(N-1)\,\theta(N-1)$

Exchange-Correlation potential $V^{XC}_{d,\sigma} = \dfrac{\partial E^{XC}}{n_{d,\sigma}} = U\,\theta(N-1)$

KS hamiltonian $H^{KS} = \sum_\sigma (\epsilon_0 + U\,\theta(N-1))\,\hat{n}_\sigma - U\,\theta(N-1)$

$$\hat{H} = \epsilon_0\, \hat{n}_\uparrow + \epsilon_0\, \hat{n}_\downarrow + U\, \hat{n}_\uparrow\, \hat{n}_\downarrow$$

A poor's man approach - Energies

$$\hat{H} = \epsilon_0 \, \hat{n}_\uparrow + \epsilon_0 \, \hat{n}_\downarrow + U \, \hat{n}_\uparrow \, \hat{n}_\downarrow$$

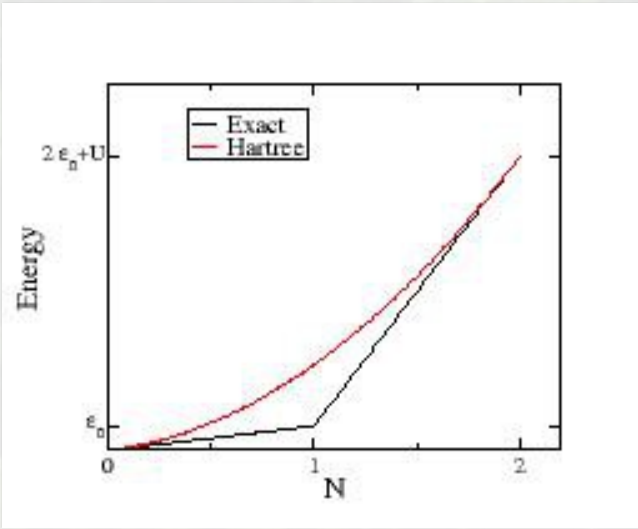
$$E_{\text{exact}} = \epsilon_0 \, N + U \, \theta(N-1) \, (N-1)$$

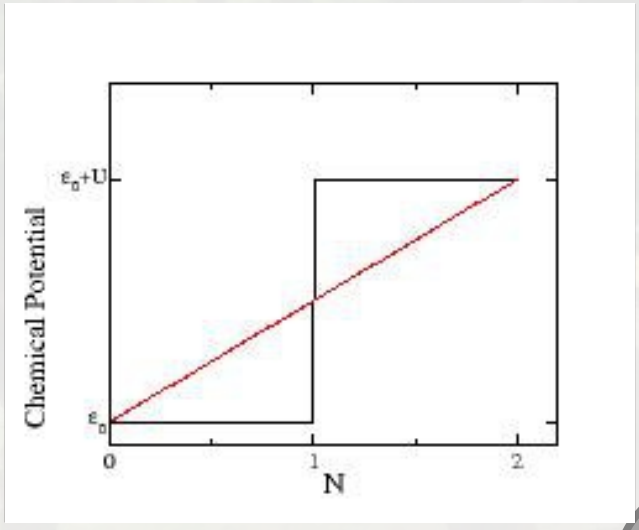
Hartree ~ LDA ~ approximate DFT

$$E_{\text{H}} = \epsilon_0 \, N + U \, N_\uparrow \, N_\downarrow$$

$$E_{\text{H-para}} = \epsilon_0 \, N + U \, \frac{N^2}{4}$$

$$E_{\text{H,Spin-Pol}} = \epsilon_0 \, N + U \, \theta(N-1) \, (N-1)$$





A poor's man approach: quasiparticle spectrum

$$\hat{H} = \sum_{\sigma} \epsilon_0 \, \hat{n}_\sigma \; + \; U \, \hat{n}_\uparrow \, \hat{n}_\downarrow$$

$$G_{d,\sigma}(\omega) = \frac{1 - n_{d,-\sigma}}{\omega - \epsilon_d + i\delta} + \frac{n_{d,-\sigma}}{\omega - (\epsilon_d + U) + i\delta}$$

$$\hat{H}^H = \sum_{\sigma} \left(\epsilon_0 + U \, n_{-\sigma}\right) \, \hat{n}_\sigma \; - \; U \, n_\uparrow \, n_\downarrow$$

$$G^H_{d,\sigma}(\omega) = \frac{1}{\omega - (\epsilon_d + U \, n_{d,-\sigma}) + i\delta}$$

$$\hat{H}^{KS} = \sum_{\sigma} \left(\epsilon_0 + U\theta(N-1)\right) \, \hat{n}_\sigma \; - \; U\theta(N-1)$$

$$G^{KS}_{d,\sigma}(\omega) = \frac{\theta(1-N)}{\omega - \epsilon_d + i\delta} + \frac{\theta(N-1)}{\omega - (\epsilon_d + U) + i\delta}$$

A poor's man approach: quasiparticle spectrum

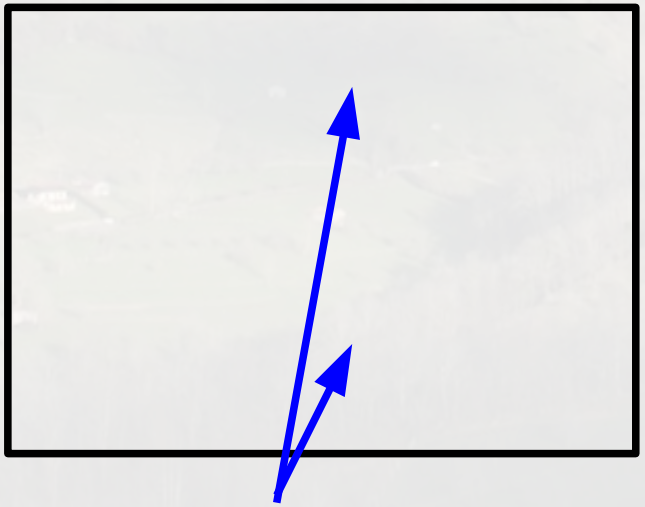
$$G_{d,\sigma}(\omega) = \frac{1 - n_{d,-\sigma}}{\omega - \epsilon_d + i\delta} + \frac{n_{d,-\sigma}}{\omega - (\epsilon_d + U) + i\delta}$$

$$G^{MF}_{d,\sigma}(\omega) = \frac{1}{\omega - (\epsilon_d + U\, n_{d,-\sigma}) + i\delta}$$

Gray: many-body

Black: KS **Red: Mean field**

Paramagnetic Ground state



Discontinuous KS eigenstates

Spin polarized / quantum point particle

Avoided
discontinuous KS eigenstates

A poor's man approach: quasiparticle spectrum

Gray: many-body **Black: KS** **Red: Mean field**

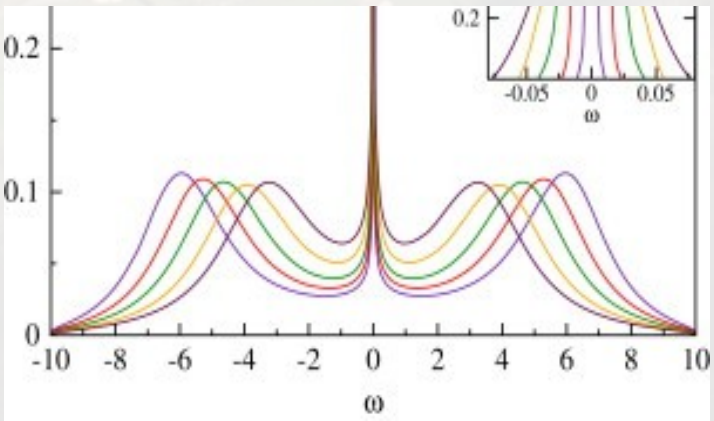
$$G_{d,\sigma}(\omega) = \frac{1 - n_{d,-\sigma}}{\omega - \epsilon_d + i\delta} + \frac{n_{d,-\sigma}}{\omega - (\epsilon_d + U) + i\delta}$$

$$G^{MF}_{d,\sigma}(\omega) = \frac{1}{\omega - (\epsilon_d + U\, n_{d,-\sigma}) + i\delta}$$

Hartree: single peak, moves up with N

Many-body: Several peaks
Do not shift with N
Weight continuous with N

Exact DF: Single peak
Does not shift with N
Discontinuities in weight



This three-peak structure can not be obtained by DFT (even if exact)

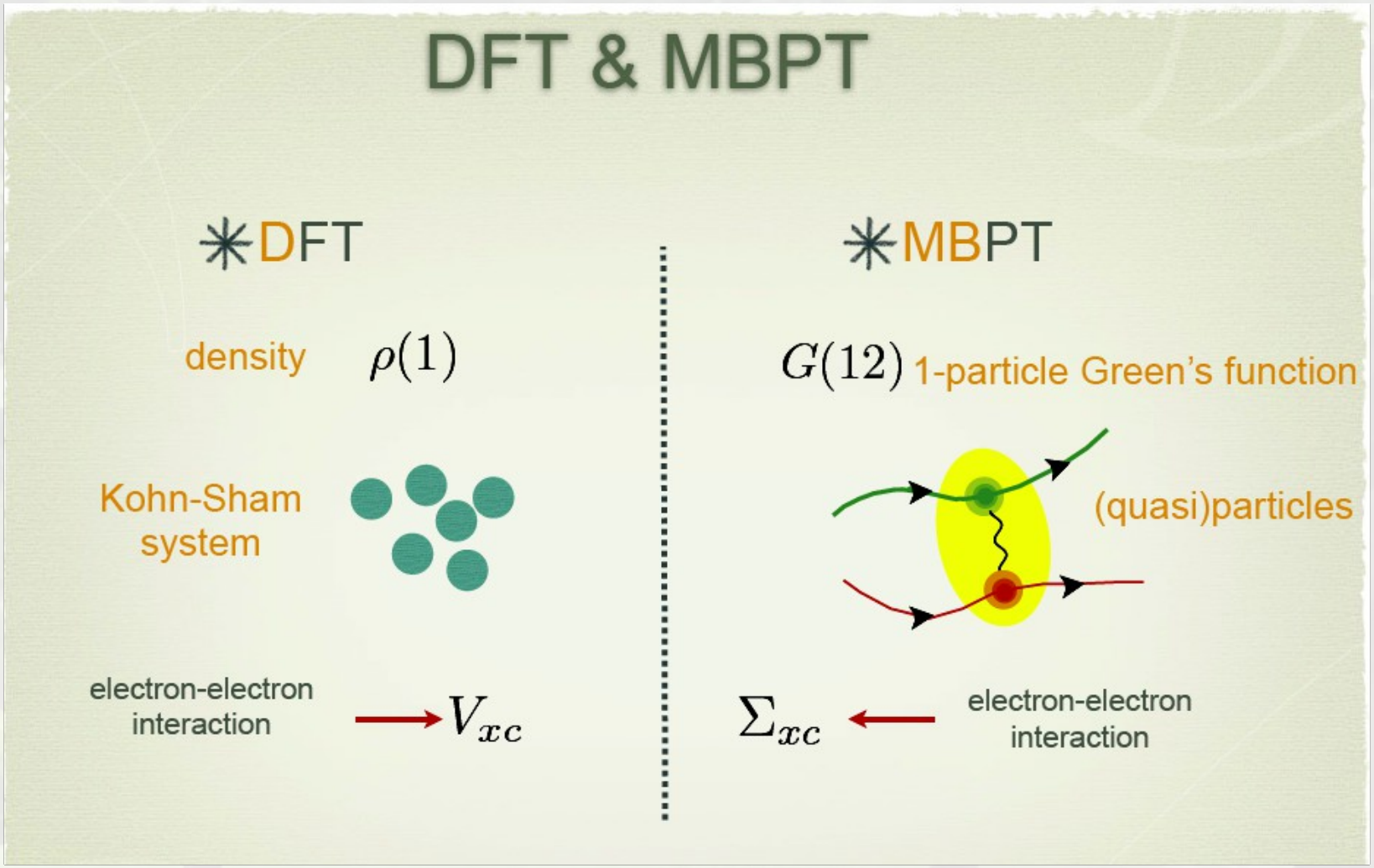
A poor's man approach: quasiparticle spectrum

The heart of the matter

Electronic energy gap and other electronic transitions not given by exact DFT

Gray: many-body **Black: KS** **Red: Mean field**

Summary of KS versus QP pictures



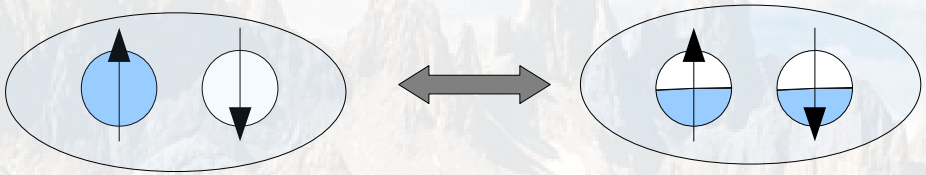
(From a talk by Pina Romaniello & Lucia Reining)

A poor's man approach

$$\hat{H} = \sum_{\sigma} \epsilon_d \, \hat{n}_{d,\sigma} + U \, \hat{n}_{d,\uparrow} \, \hat{n}_{d,\downarrow}$$

These models avoid the **SI Error** by construction

Static Correlation Error exemplified for single-site Hubbard model & N=1



Quantum point particle

$$E = \epsilon_d$$

Charge cloud

$$E = \epsilon_d + U \, N/2$$

A poor's man approach

* Many-Body spectrum and exact KS eigenstates are flat as a function of N

* This contrast to Hartree – LDA: approximate KS eigenstates depend on N because of the static correlation error (Yang & Mori)

Could this term be extrapolated to non-homogeneous Coulomb systems ?

Analyze the double-site Anderson model

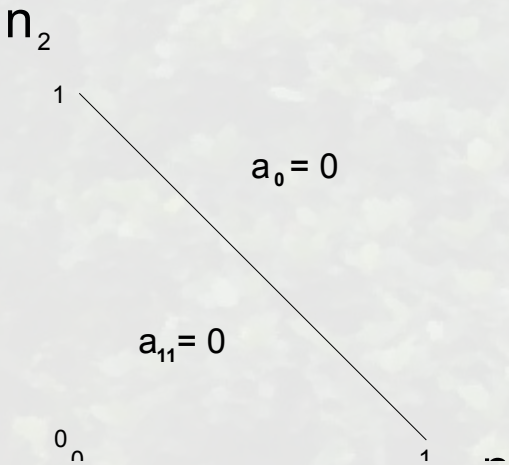
$$\hat{H} = \sum_{\sigma} \epsilon_c \, \hat{n}_{c,\sigma} + \sum_{\sigma} \epsilon_d \, \hat{n}_{d,\sigma} - t \sum_{\sigma} (\hat{c}^{\dagger}_{\sigma} \, \hat{d}_{\sigma} + h.c.) + U \, \hat{n}_{d,\uparrow} \, \hat{n}_{d,\downarrow}$$

A diversion: vanilla double site

$$\hat{H} = \epsilon_1 \hat{n}_1 + \epsilon_2 \hat{n}_2 - t\,(\hat{c}_1^\dagger \hat{c}_2 + \hat{c}_2^\dagger \hat{c}_1)$$

$$|\psi> = a_0\,|0> + a_{10}\,|1,0> + a_{01}\,|0,1> + a_{11}\,|1,1>$$

$$\begin{aligned} Q[n_1, n_2] &= \epsilon_1 n_1 + \epsilon_2 n_2 - 2\,|t|\,\sqrt{n_1 n_2} && 0 \le n_1 + n_2 \le 1 \\ &= \epsilon_1 n_1 + \epsilon_2 n_2 - 2\,|t|\,\sqrt{(1-n_1)(1-n_2)} && 1 \le n_1 + n_2 \le 2 \end{aligned}$$



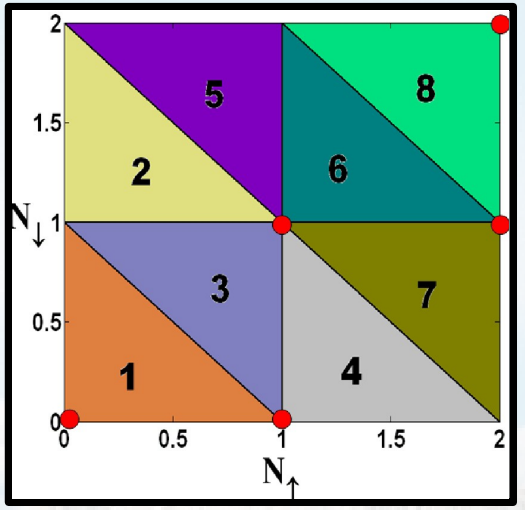
Add spin:

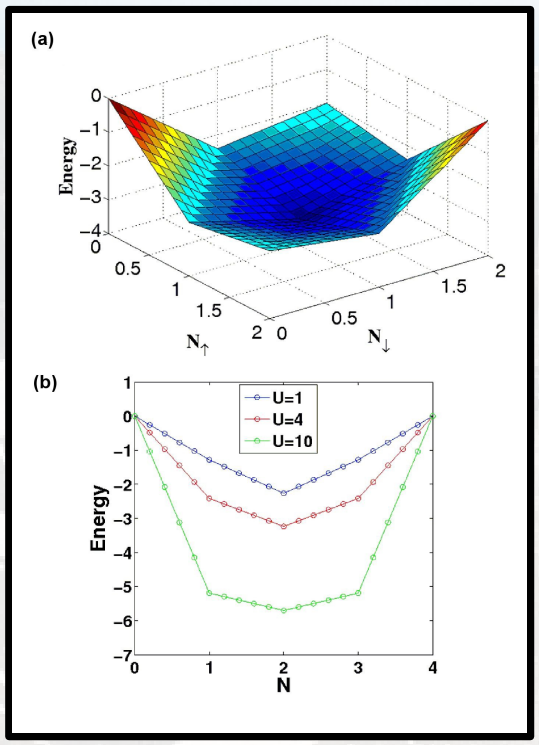
$$\begin{aligned} Q[n_{1,\sigma}, n_{2,\sigma}] &= \textstyle\sum_\sigma (\epsilon_{1\sigma} n_{1\sigma} + \epsilon_{2\sigma} n_{2\sigma}) - 2|t|\,(\sqrt{n_{1\uparrow} n_{2\uparrow}} + \sqrt{n_{1\downarrow} n_{2\downarrow}}) \\ &= \textstyle\sum_\sigma (\epsilon_{1\sigma} n_{1\sigma} + \epsilon_{2\sigma} n_{2\sigma}) - 2\,|t|\,(\sqrt{(1-n_{1\uparrow})(1-n_{2\uparrow})} + (\sqrt{(1-n_{1\downarrow})(1-n_{2\downarrow})} \end{aligned}$$

Double-site Anderson model

$$\hat{H} = \sum_{\sigma} \epsilon_c \, \hat{n}_{c,\sigma} + \sum_{\sigma} \epsilon_d \, \hat{n}_{d,\sigma} - t \sum_{\sigma} (\hat{c}^{\dagger}_{\sigma} \, \hat{d}_{\sigma} + h.c.) + U \, \hat{n}_{d,\uparrow} \, \hat{n}_{d,\downarrow}$$

Evaluation of wave function coefficients different for each triangle
This leads to a polygonal-shaped Energy Functional Q





Analytic formulae are lengthy,
can be found in the reference paper

The ground-state energy is also polygonal-shaped

KS Hamiltonian

$$H_{KS} = \sum_{i=(c,d),\sigma} (\epsilon_i + V^{XC}_{i,\sigma}) \, \hat{n}_{i,\sigma} - t \sum_{\sigma} (\hat{c}^{\dagger}_{\sigma} \, \hat{d}_{\sigma} + \hat{d}^{\dagger}_{\sigma} \, \hat{c}_{\sigma}) - H_{dc}$$

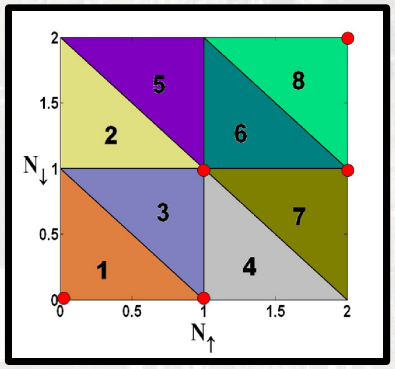
Double-site Anderson model

Many-body Green's functions can be computed for integer *N*

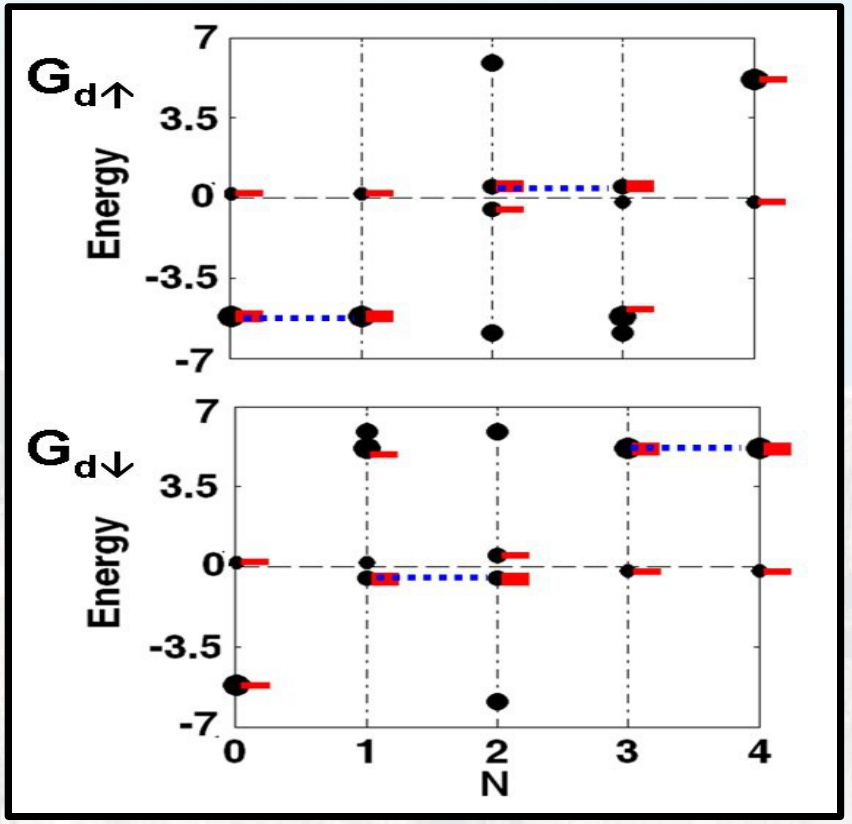
$$G^{KS}_{d,\sigma} = \frac{\omega - \epsilon_c - V^{XC}_{c,\sigma}}{(\omega - \epsilon_c - V^{XC}_{c,\sigma})(\omega - \epsilon_d - V^{XC}_{d,\sigma}) - |t|^2}$$

V^{XC} is discontinuous at integer *N*
(as well as KS eigenstates)

We follow the path sketched below



Green's function poles for U/t=10



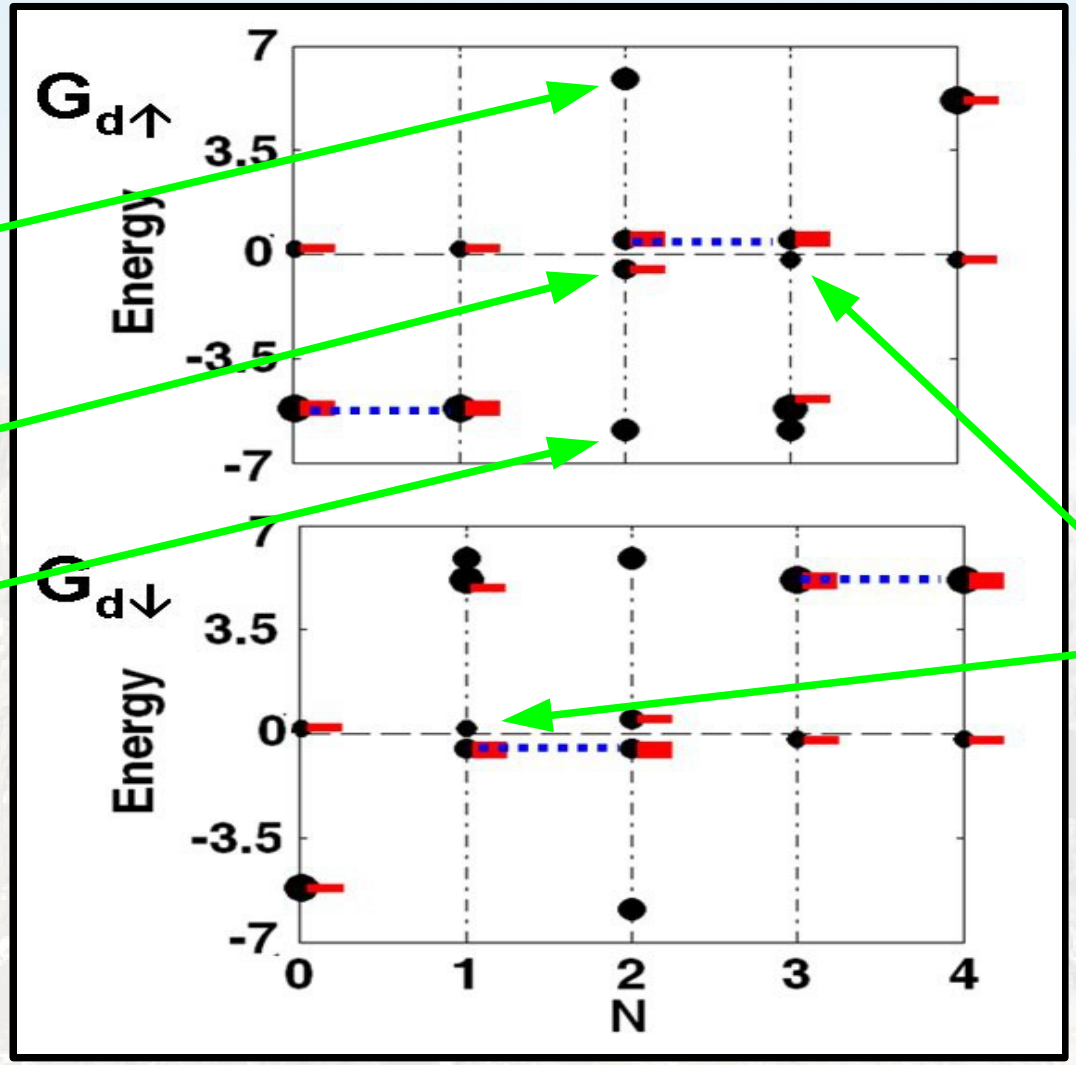
Black: many-body Red: Kohn-Sham
Blue: chemical potential

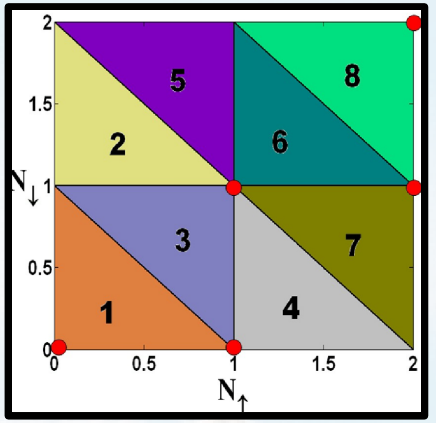
Double-site Anderson model

Upper HB

Kondo features

Lower HB





Low-energy many-body Qps with no KS analog

Black: many-body

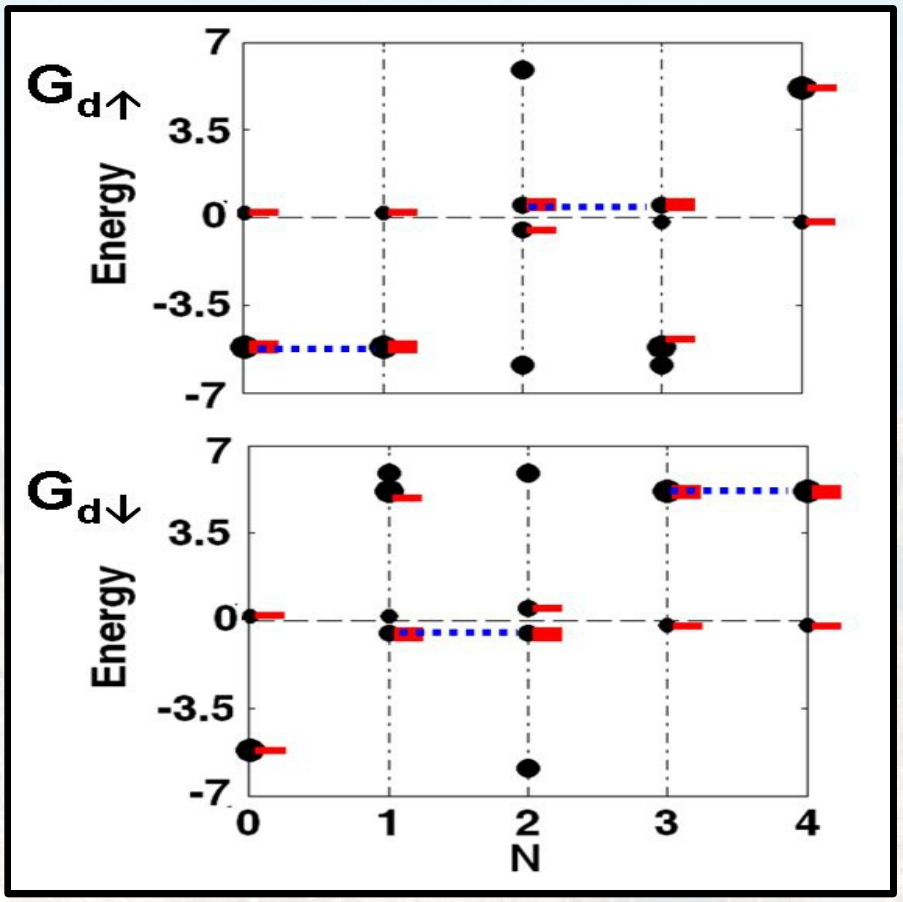
Red: Kohn-Sham

U/t = 10

Double-site Anderson model

The energy gap problem

$$E_g(N) = \mu(N+1) - \mu(N)$$



Black: many-body

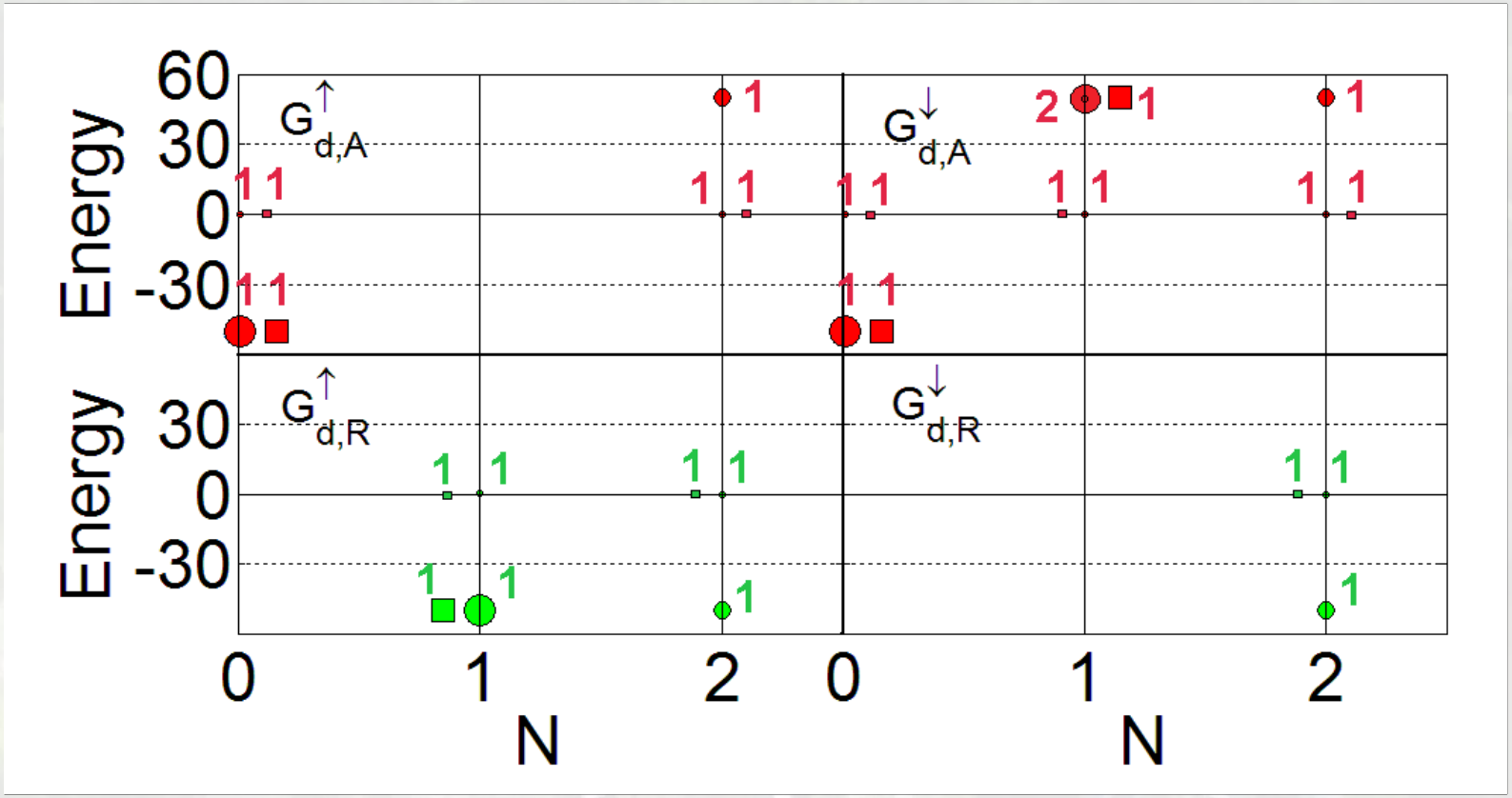
U/t = 10

Red: Kohn-Sham

Blue: chemical potential

Double-site Anderson model: KS vs QP

Local Green's function at the d-site



QP (circles) and KS eigenstates (squares) for U/t=100 as a function of the electron number N. The panels show the poles of G_A and G_R to display the energies for electron addition and removal.

Double-site Anderson model - Summary

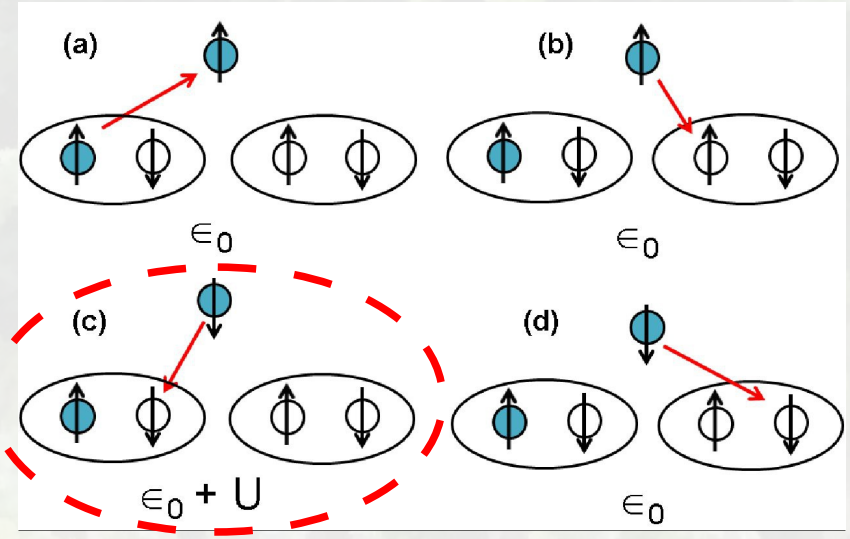
- Gap problem remains
- Exact DFT describes correctly the Kondo peak
- However, it does not deliver all excited states.
  - It fails to deliver the Lower & Upper Hubbard bands.
  - It fails to provide relevant low-energy QPs for spin-polarized GS.

Double-site Hubbard model: KS vs QP

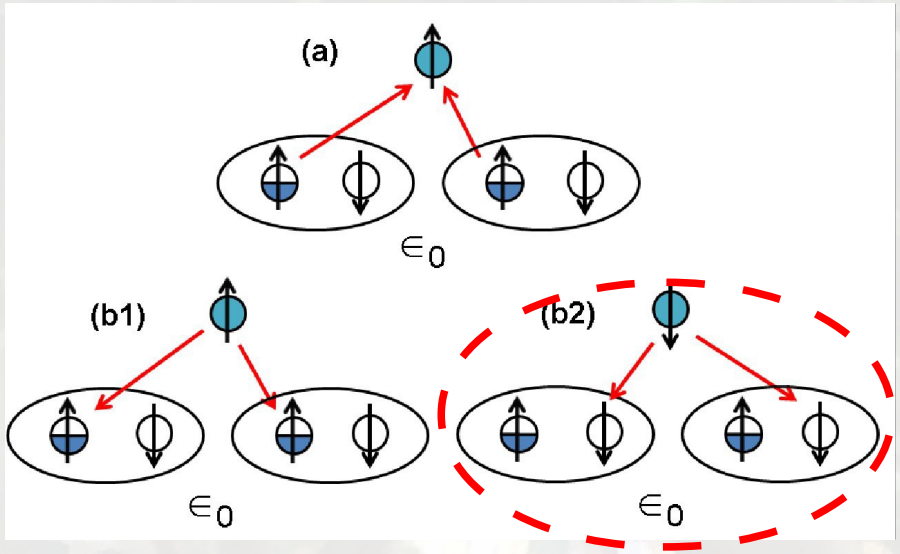
My picture: Quasiparticles interact as point particles
Approximate or even exact KS electrons interact as delocalized charge clouds

N=1

Quasiparticles



Kohn-Sham eigenstates



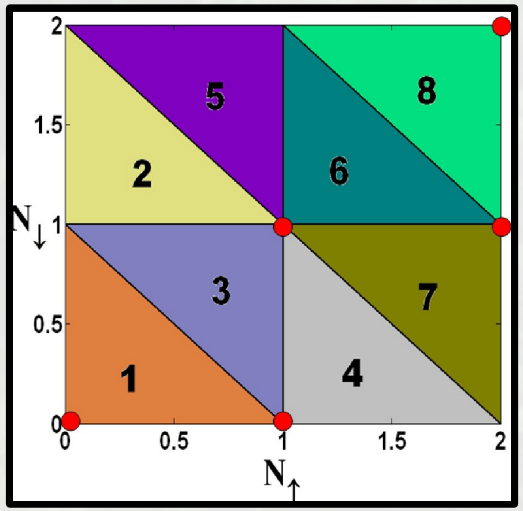
Exact DFT dissociation energies have no delocalization error
Exact DFT addition/removal have delocalization error arising from the inherent mean-field description of electrons in KS hamiltonian

Double-site Hubbard model: KS vs QP

$$\hat{H} = \sum_{i=(1,2),\sigma} \epsilon_d \, \hat{n}_{d,i,\sigma} \; - \; t_0 \sum_{\sigma} \left(\hat{d}^{\dagger}_{1,\sigma} \, \hat{d}_{2,\sigma} + h.c. \right) \; + U \sum_{i=1,2} \hat{n}_{d,i,\uparrow} \, \hat{n}_{d,i,\downarrow}$$

$$G^{\sigma}_{A}(\omega) = \sum_{\alpha} \frac{\left| \left\langle \psi^{N+1}_{\alpha} \right| \hat{c}^{\dagger}_{i\sigma} \left| \psi^{N}_{0,\sigma'} \right\rangle \right|^2}{\omega + E^{N}_{\sigma'} - E^{N+1}_{\alpha}}$$

$$G^{\sigma}_{R}(\omega) = \sum_{\alpha} \frac{\left| \left\langle \psi^{N-1}_{\alpha} \right| \hat{c}_{i\sigma} \left| \psi^{N}_{0,\sigma'} \right\rangle \right|^2}{\omega - E^{N}_{\sigma'} + E^{N-1}_{\alpha}}$$



QP addition and removal energy spectrum.

U⁺ , U⁻ stand for $\dfrac{U \pm \sqrt{U^2 + 16t^2}}{2}$

N	$G^{\uparrow}_{A}$	$G^{\downarrow}_{A}$	$G^{\uparrow}_{R}$	$G^{\downarrow}_{R}$
0	$\epsilon_0 + t$ $\epsilon_0 - t$	$\epsilon_0 + t$ $\epsilon_0 - t$	-	-
1	$\epsilon_0 + t$	$\epsilon_0 + t$ $\epsilon_0 + t + U$ $\epsilon_0 + t + U^+$ $\epsilon_0 + t + U^-$	$\epsilon_0 - t$	-
2	$\epsilon_0 + t + U^+$ $\epsilon_0 - t + U^+$	$\epsilon_0 + t + U^+$ $\epsilon_0 - t + U^+$	$\epsilon_0 - t + U^-$ $\epsilon_0 + t + U^-$	$\epsilon_0 - t + U^-$ $\epsilon_0 + t + U^-$

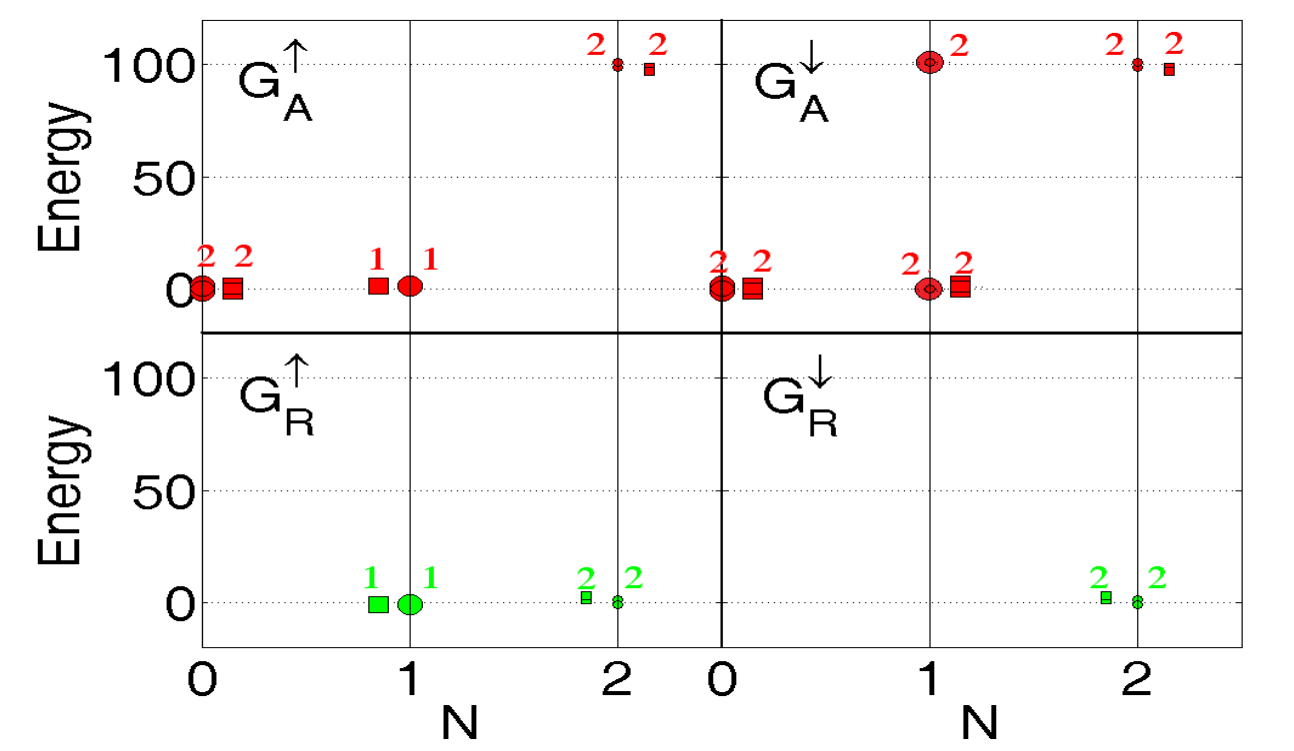
Addition and removal energy spectrum of KS eigenstates

N	$G^{\uparrow}_{A}$	$G^{\downarrow}_{A}$	$G^{\uparrow}_{R}$	$G^{\downarrow}_{R}$
0	$\epsilon_0 + t$ $\epsilon_0 - t$	$\epsilon_0 + t$ $\epsilon_0 - t$	-	-
1	$\epsilon_0 + t$	$\epsilon_0 + t + U^-$ $\epsilon_0 + 3t + U^-$	$\epsilon_0 - t$	-
2	$\epsilon_0 - t + U^+$ $\epsilon_0 - 3t + U^+$	$\epsilon_0 - t + U^+$ $\epsilon_0 - 3t + U^+$	$\epsilon_0 + t + U^-$ $\epsilon_0 + 3t + U^-$	$\epsilon_0 + t + U^-$ $\epsilon_0 + 3t + U^-$

Double-site Hubbard model: KS vs QP

$$G_A^\sigma(\omega) = \sum_\alpha \frac{\left|\left\langle \psi_\alpha^{N+1} \right| \hat{c}_{i\sigma}^\dagger \left| \psi_{0,\sigma'}^N \right\rangle\right|^2}{\omega + E_{\sigma'}^N - E_\alpha^{N+1}}$$

$$G_R^\sigma(\omega) = \sum_\alpha \frac{\left|\left\langle \psi_\alpha^{N-1} \right| \hat{c}_{i\sigma} \left| \psi_{0,\sigma'}^N \right\rangle\right|^2}{\omega - E_{\sigma'}^N + E_\alpha^{N-1}}$$



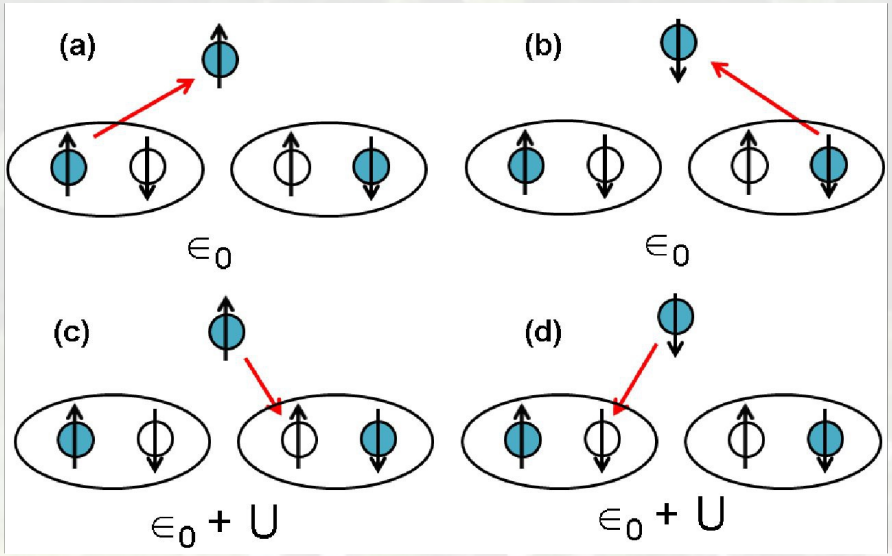
QP (circles) and KS eigenstates (squares) for U/t=100 as a function of the electron number N. The panels show the poles of G_A and G_R to display the energies for electron addition and removal.

Double-site Hubbard model: KS vs QP

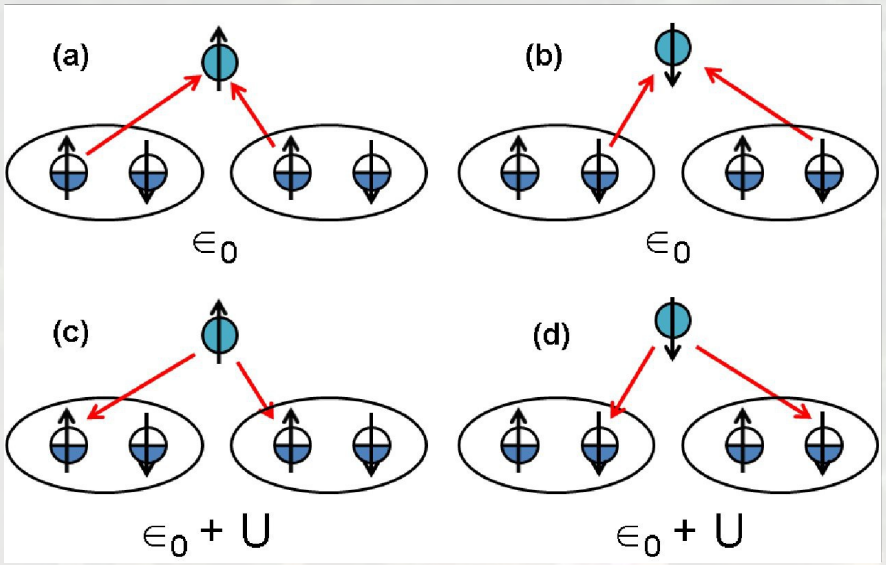
My picture: Quasiparticles interact as point particles
Approximate or even exact KS electrons interact as delocalized charge clouds

N=2

Quasiparticles



Kohn-Sham eigenstates



Exact DFT dissociation energies have no delocalization error
Exact DFT addition/removal have delocalization error arising from the inherent mean-field description of electrons in KS hamiltonian

Double-site Hubbard model: KS vs QP

Ground states in the dissociation limit

Particle number basis: $|n_{1,\uparrow}, n_{1,\downarrow}, n_{2,\uparrow}, n_{2,\downarrow}\rangle$

$$\left|\psi^{1}_{0,\uparrow}\right\rangle = \frac{1}{\sqrt{2}}\left(|1,0,0,0\rangle + |0,0,1,0\rangle\right)$$

$$\left|\psi^{2,MB}_{0}\right\rangle = \frac{1}{\sqrt{2}}\left(|1,0,0,1\rangle + |0,1,1,0\rangle\right) = \left(|1,2> + |2,1>\right)\left(|\uparrow,\downarrow> - |\downarrow,\uparrow>\right)$$

Notice the difference between MB and KS GSs

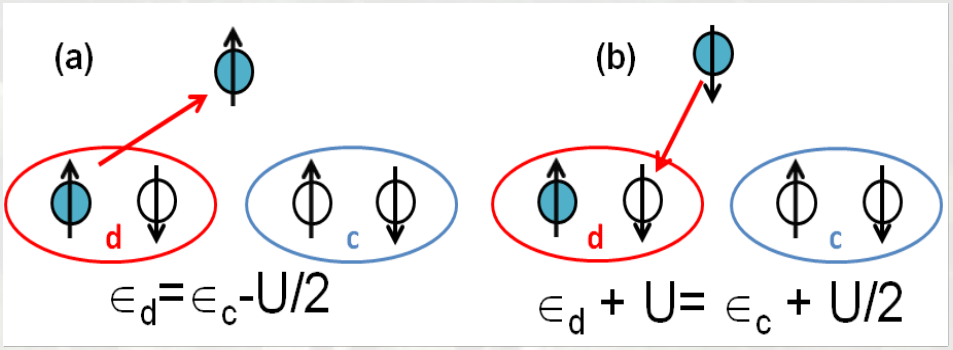
$$\left|\psi^{2,KS}_{0}\right\rangle = \frac{1}{2}\left(|1,0,0,0\rangle + |0,0,1,0\rangle\right) \otimes \left(|0,1,0,0\rangle + |0,0,0,1\rangle\right)$$

Double-site Anderson model: KS vs QP

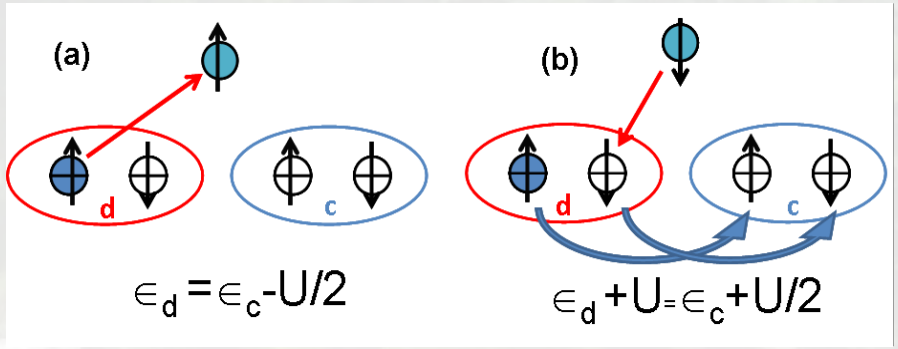
Local Green's function at the d-site

N=1

Quasiparticles



Kohn-Sham eigenstates



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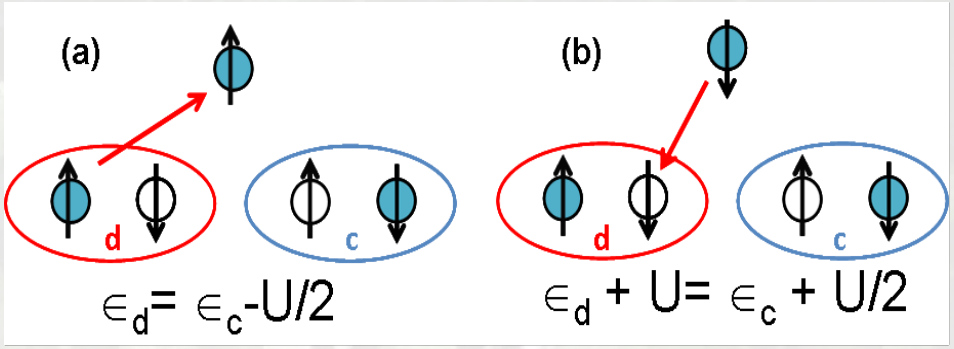
Double-site Anderson model: KS vs QP

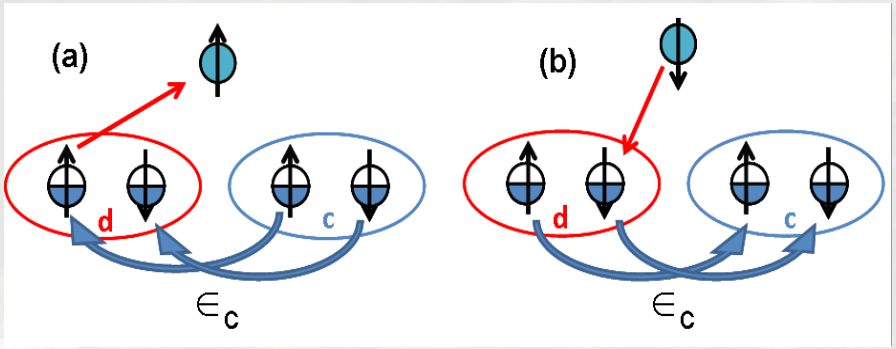
Local Green's function at the d-site

N=2

Quasiparticles



Kohn-Sham eigenstates



Process hindered by t small--> small weight

Exact DFT dissociation energies have no delocalization error
Exact DFT addition/removal have delocalization error arising from the inherent mean-field description of electrons in KS hamiltonian

SUMMARY

Exact Density Functional of simple Anderson, Hubbard and spinless fermion models

Quasiparticle spectrum is partly given by the eigenstates of the exact KS hamiltonians
But relevant pieces of the spectrum are missing

- Excited states of the Anderson model in the dissociation limit:
  - Correct KS eigenstates for N=1.
  - N=2: correct "Kondo" peak, absence of Lower & Upper Hubbard bands

- Excited states of the Hubbard model in the dissociation limit:
  - Wrong KS eigenstates for N = 1
  - Correct KS eigenstates for N=2

REFERENCE: PRB 85, 045110 (2012)

SUMMARY