

Reduced Density Matrix Functional Theory

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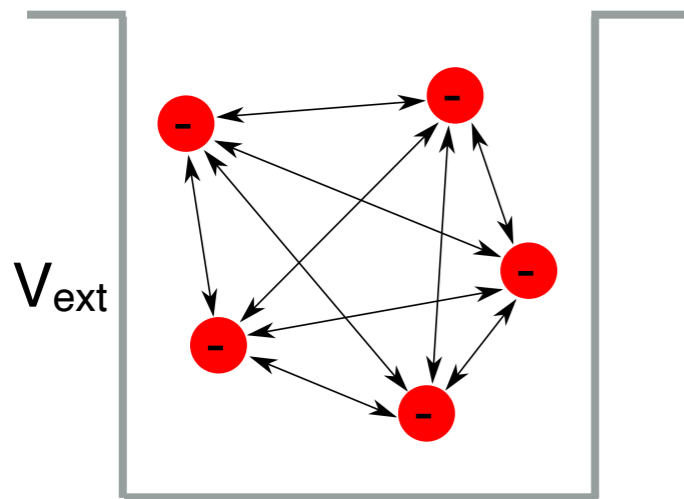
Laboratoire de Physique Théorique, Université de Toulouse

ISTPC 2024
AUSOIS

Theoretical background

* Wavefunction-based approaches

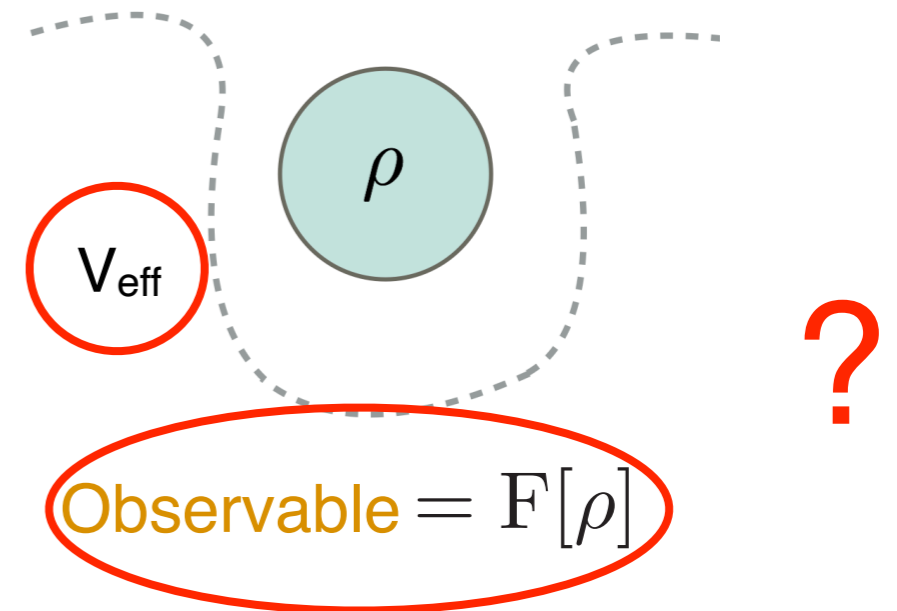
Key quantity: many-body wavefunction



$$\text{Observable} = \langle \Psi | \hat{O} | \Psi \rangle$$

* Reduced-quantity based approaches

Key quantity: Simpler physical quantity, e.g. the density



Theoretical background

* Reduced quantities

density $\rho(\mathbf{r})$

Density Functional Theory

current-density $\mathbf{j}(\mathbf{r})$

Current-Density Functional Theory

1-body density matrix $\gamma(\mathbf{r}, \mathbf{r}')$

Reduced Density Matrix Functional Theory

1-body Green's function $G(\mathbf{r}, \mathbf{r}'; t - t')$

Many-Body Perturbation theory

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Theoretical background

* Reduced quantities

density $\rho(\mathbf{r})$

Density Functional Theory

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Current-Density Functional Theory

1-body density matrix $\gamma(\mathbf{r}, \mathbf{r}')$

Reduced Density Matrix Functional Theory

1-body Green's function $G(\mathbf{r}, \mathbf{r}'; t - t')$ Many-Body Perturbation theory

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Functional theories

MBPT

$$G(\mathbf{r}, \mathbf{r}'; t - t')$$

RDMFT

$$\gamma(\mathbf{r}, \mathbf{r}') = -iG(\mathbf{r}, \mathbf{r}'; t - t^+)$$

DFT

$$\rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$$

► Functional to approximate:

$$\Phi_{xc}[G]$$

or

$$\Sigma_{xc}[G]$$

$$E_{xc}[\gamma]$$

$$E_{xc}[\rho]$$

or

$$v_{xc}[\rho]$$

“easy” (e.g., GW) to approximate

difficult

very difficult

Computationally heavy

moderate

light

► Observables:

“easy” (e.g., PES) to get

difficult

very difficult

RDMFT in a nutshell

- * There is a one-to-one map $\Psi_0 \leftrightarrow \gamma$ (Gilbert 1975)

$$\gamma(\mathbf{x}_1, \mathbf{x}'_1) = N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

- * Expectation values of any GS operator are functionals of γ

$$O[\gamma] = \langle \Psi_0[\gamma] | \hat{O} | \Psi_0[\gamma] \rangle$$

$$E[\gamma] = E_{kin}[\gamma] + E_{ext}[\gamma] + E_H[\gamma] + E_{xc}[\gamma]$$

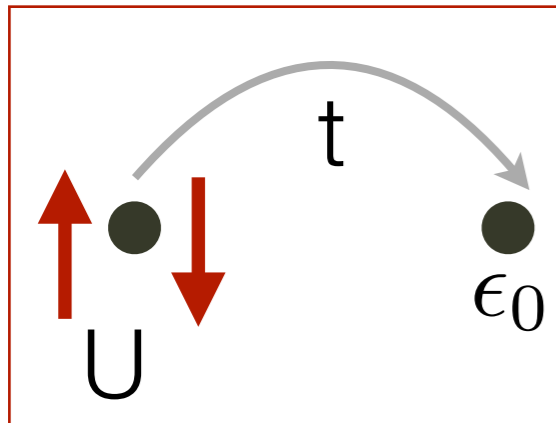
- * Ground-state energy calculated by minimising $E[\gamma]$

Program of the lecture

- * Preliminaries
- * Hohenberg-Kohn theorem for nonlocal potentials (Gilbert 1975)
- * Energy functional approximations
- * Energy minimisation
- * Observables
- * Some results

Hubbard model

* Hubbard dimer

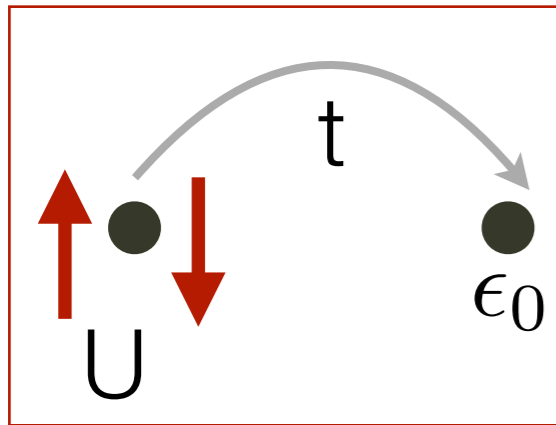


$$H = -t \sum_{\substack{i,j=1,2 \\ i \neq j}} \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U}{2} \sum_{i=1,2} \sum_{\sigma\sigma'} c_{i\sigma}^{\dagger} c_{i\sigma'}^{\dagger} c_{i\sigma'} c_{i\sigma} + \epsilon_0 \sum_{\sigma,i=1,2} n_{i\sigma} + V_0$$

N=1 (1/4 filling) and **N=2** (1/2 filling) in the ground state

Hubbard model

* Hubbard dimer



$$H = -t \sum_{\substack{i,j=1,2 \\ i \neq j}} \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U}{2} \sum_{i=1,2} \sum_{\sigma\sigma'} c_{i\sigma}^{\dagger} c_{i\sigma'}^{\dagger} c_{i\sigma'} c_{i\sigma} + \epsilon_0 \sum_{\sigma,i=1,2} n_{i\sigma} + V_0$$

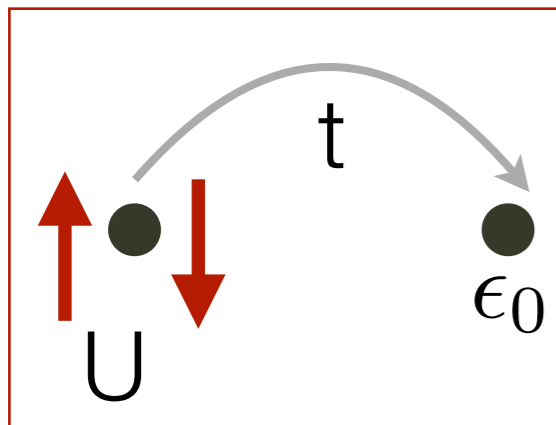
N=1 (1/4 filling) and **N=2** (1/2 filling) in the ground state

weakly and strongly correlated regimes:

- ▶ $U \rightarrow 0$ noninteracting limit
- ▶ $U \rightarrow \infty$ ($t \rightarrow 0$) strongly correlated limit

Hubbard model

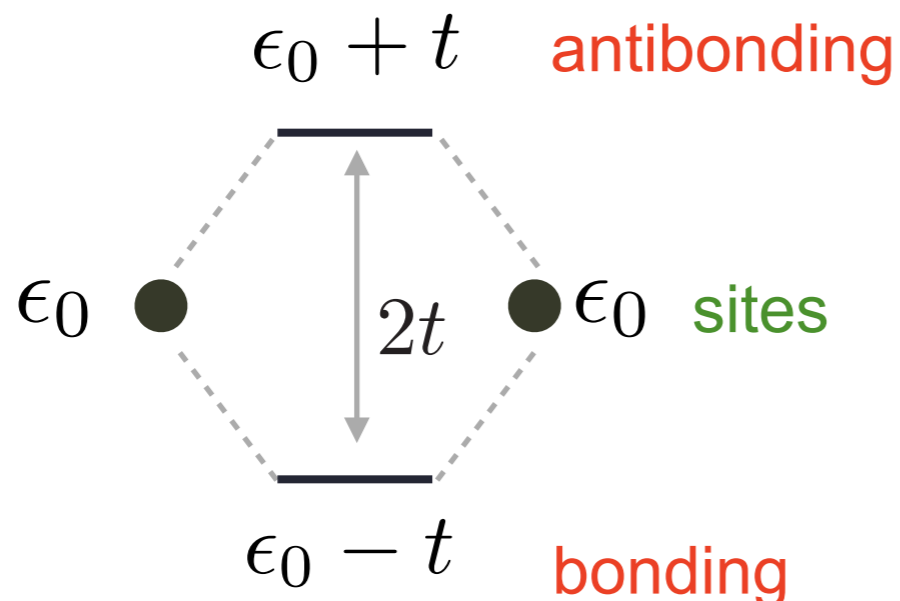
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$$H = -t \sum_{\substack{i,j=1,2 \\ i \neq j}} \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U}{2} \sum_{i=1,2} \sum_{\sigma\sigma'} c_{i\sigma}^{\dagger} c_{i\sigma'}^{\dagger} c_{i\sigma'} c_{i\sigma} + \epsilon_0 \sum_{\sigma,i=1,2} n_{i\sigma} + V_0$$

N=1 (1/4 filling) and **N=2** (1/2 filling) in the ground state

* Site vs bonding/antibonding basis

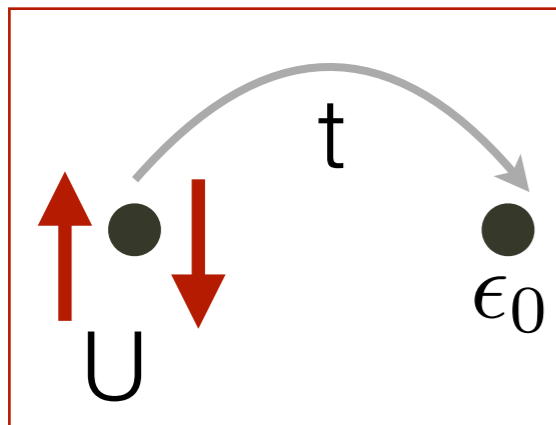


$$\psi_b(\mathbf{x}) = \frac{1}{\sqrt{2}} [\varphi_1(\mathbf{x}) + \varphi_2(\mathbf{x})]$$

$$\psi_a(\mathbf{x}) = \frac{1}{\sqrt{2}} [\varphi_1(\mathbf{x}) - \varphi_2(\mathbf{x})]$$

Hubbard model

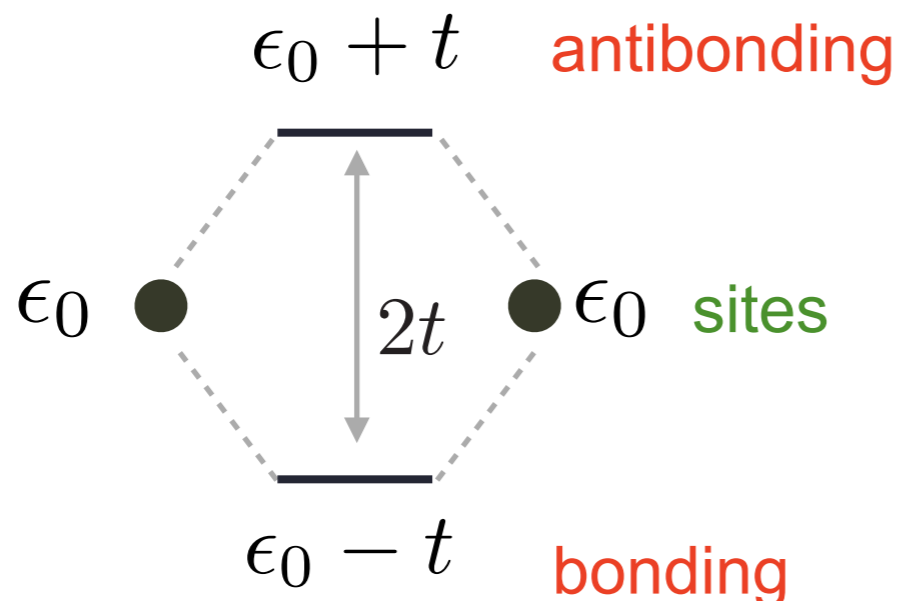
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$$H = -t \sum_{\substack{i,j=1,2 \\ i \neq j}} \sum_{\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{U}{2} \sum_{i=1,2} \sum_{\sigma\sigma'} c_{i\sigma}^{\dagger} c_{i\sigma'}^{\dagger} c_{i\sigma'} c_{i\sigma} + \epsilon_0 \sum_{\sigma,i=1,2} n_{i\sigma} + V_0$$

N=1 (1/4 filling) and **N=2** (1/2 filling) in the ground state

* Site vs bonding/antibonding basis



$$\psi_b(\mathbf{x}) = \frac{1}{\sqrt{2}} [\varphi_1(\mathbf{x}) + \varphi_2(\mathbf{x})]$$

$$\psi_a(\mathbf{x}) = \frac{1}{\sqrt{2}} [\varphi_1(\mathbf{x}) - \varphi_2(\mathbf{x})]$$

Definitions

* Many-body hamiltonian

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}$$

Kinetic energy

$$\hat{T} = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \hat{\psi}(\mathbf{x}),$$

Non-local potential

$$\hat{V} = \int d\mathbf{x} d\mathbf{x}' \hat{\psi}^\dagger(\mathbf{x}') v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \hat{\psi}(\mathbf{x}),$$

e-e interaction

$$\hat{W} = \frac{1}{2} \int d\mathbf{x}' d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x}),$$

$$\mathbf{x} = (\mathbf{r}, s)$$

Definitions

* n-body density matrix

$$\begin{aligned}\Gamma^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n; \mathbf{x}'_1, \dots, \mathbf{x}'_n) &\equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_n) \dots \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) \dots \hat{\psi}(\mathbf{x}_n) | \Psi \rangle \\ &= \frac{N!}{(N-n)!} \int d\mathbf{x}_{n+1} \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_n, \mathbf{x}_{n+1}, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)\end{aligned}$$

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* 2-body density matrix

$$\begin{aligned}\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) &\equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_2) \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) \hat{\psi}(\mathbf{x}_2) | \Psi \rangle \\ &= N(N-1) \int d\mathbf{x}_3 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)\end{aligned}$$

Definitions

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$$\begin{aligned}\gamma(\mathbf{x}, \mathbf{x}') &\equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) | \Psi \rangle \\ &= N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}', \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)\end{aligned}$$

Definitions

* n-body density matrix

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NOTE:

$$\rho(\mathbf{x}) = \gamma(\mathbf{x}, \mathbf{x}) = N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi^*(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \longrightarrow \text{Tr } \gamma(\mathbf{x}, \mathbf{x}') \equiv \int d\mathbf{x} \gamma(\mathbf{x}, \mathbf{x}) = N$$

Definitions

* n-body density matrix

$$\begin{aligned}\Gamma^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_n; \mathbf{x}'_1, \dots, \mathbf{x}'_n) &\equiv \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}'_n) \dots \hat{\psi}^\dagger(\mathbf{x}'_1) \hat{\psi}(\mathbf{x}_1) \dots \hat{\psi}(\mathbf{x}_n) | \Psi \rangle \\ &= \frac{N!}{(N-n)!} \int d\mathbf{x}_{n+1} \dots d\mathbf{x}_N \Psi^*(\mathbf{x}'_1, \dots, \mathbf{x}'_n, \mathbf{x}_{n+1}, \dots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)\end{aligned}$$

* Relations between density matrices

$$\Gamma^{(n-1)}(\mathbf{x}_1, \dots, \mathbf{x}_{n-1}; \mathbf{x}'_1, \dots, \mathbf{x}'_{n-1}) = \frac{1}{N-n+1} \int d\mathbf{x}_n \Gamma^{(n)}(\mathbf{x}_1, \dots, \mathbf{x}_{n-1}, \mathbf{x}_n; \mathbf{x}'_1, \dots, \mathbf{x}'_{n-1}, \mathbf{x}_n)$$

In particular for $n=2$:

$$\begin{aligned}\gamma(\mathbf{x}_1, \mathbf{x}'_1) &= \frac{1}{N-1} \int d\mathbf{x}_2 \Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}_2) \\ &= \frac{1}{(N-1)!} \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Gamma^{(N)}(\mathbf{x}_1, \mathbf{x}_2 \dots \mathbf{x}_N; \mathbf{x}'_1, \mathbf{x}_2 \dots \mathbf{x}_N)\end{aligned}$$

Link to Green's functions

* n-body Green's function (zero T, equilibrium, time-ordered)

$$G^{(n)}(1, 2, \dots, n; 1', 2', \dots, n') \equiv (-i)^n \frac{\langle \Psi_0 | T[\hat{\psi}_H(1) \dots \hat{\psi}_H(n) \hat{\psi}_H^\dagger(n') \dots \hat{\psi}_H^\dagger(1')] | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

$$\hat{\psi}_H^\dagger(1) = e^{i\hat{H}t_1} \hat{\psi}^\dagger(\mathbf{x}_1) e^{-i\hat{H}t_1}$$

$$\hat{\psi}_H(1) = e^{i\hat{H}t_1} \hat{\psi}(\mathbf{x}_1) e^{-i\hat{H}t_1}$$

In particular for $n=1$:

$$G(1, 1') = -i \langle \Psi_0 | T[\hat{\psi}_H(1) \hat{\psi}_H^\dagger(1')] | \Psi_0 \rangle$$

$$T[\hat{\psi}_H(1) \hat{\psi}_H^\dagger(1')] = \begin{cases} \hat{\psi}_H(1) \hat{\psi}_H^\dagger(1') & \text{for } t_1 > t_1' \\ -\hat{\psi}_H^\dagger(1') \hat{\psi}_H(1) & \text{for } t_1' > t_1 \end{cases}$$

$$G(1, 1') = -i\theta(t_1 - t_1') \langle \Psi_0 | \hat{\psi}_H(1) \hat{\psi}_H^\dagger(1') | \Psi_0 \rangle + i\theta(t_1' - t_1) \langle \Psi_0 | \hat{\psi}_H^\dagger(1') \hat{\psi}_H(1) | \Psi_0 \rangle$$

$$\gamma(\mathbf{x}_1, \mathbf{x}_1') = -iG(\mathbf{x}_1 t_1, \mathbf{x}_1' t_1')$$

Definitions

* Total energy

$$E = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \gamma(\mathbf{x}, \mathbf{x}') + \int d\mathbf{x} d\mathbf{x}' v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') \\ + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \Gamma^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$$

Definitions

* Total energy

$$E = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \gamma(\mathbf{x}, \mathbf{x}') + \int d\mathbf{x} d\mathbf{x}' v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') \quad \text{1-RDM in terms of 2-RDM}$$
$$+ \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \Gamma^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}') \quad \text{diagonal part of the 2-RDM or pair density}$$

The total energy can be expressed as a functional of the 2-RDM. One can minimise the total energy with respect to the 2-RDM. So, **why don't we formulate a 2-RDM functional theory?**

Definitions

* Total energy

$$E = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \gamma(\mathbf{x}, \mathbf{x}') + \int d\mathbf{x} d\mathbf{x}' v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') \quad \text{1-RDM in terms of 2-RDM}$$

$$+ \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \Gamma^{(2)}(\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}') \quad \text{diagonal part of the 2-RDM or pair density}$$

The total energy can be expressed as a functional of the 2-RDM. One can minimise the total energy with respect to the 2-RDM. So, **why don't we formulate a 2-RDM functional theory?**

Practical necessary and sufficient N-representable conditions are not known

Some simple properties of the 2-RDM

$$\int d\mathbf{x}_2 \Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}_2) = (N - 1) \gamma(\mathbf{x}_1, \mathbf{x}'_1)$$

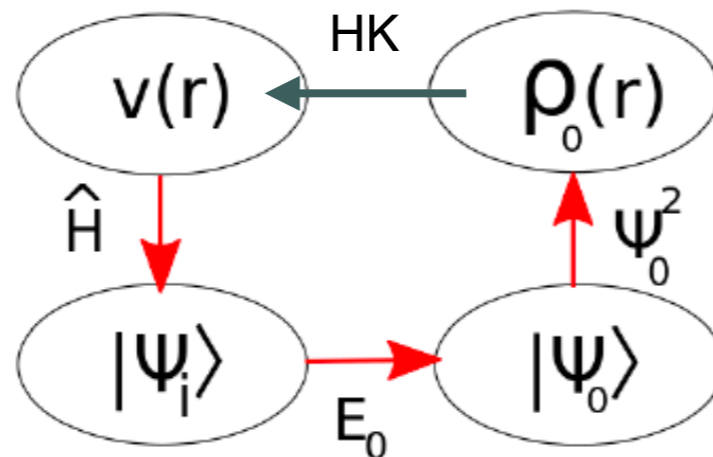
$$\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_2) \geq 0 \quad \Gamma^{(2)}(\mathbf{x}, \mathbf{x}, \mathbf{x}, \mathbf{x}) = 0$$

$$\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_2) = \Gamma^{(2)}(\mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1)$$

are not sufficient

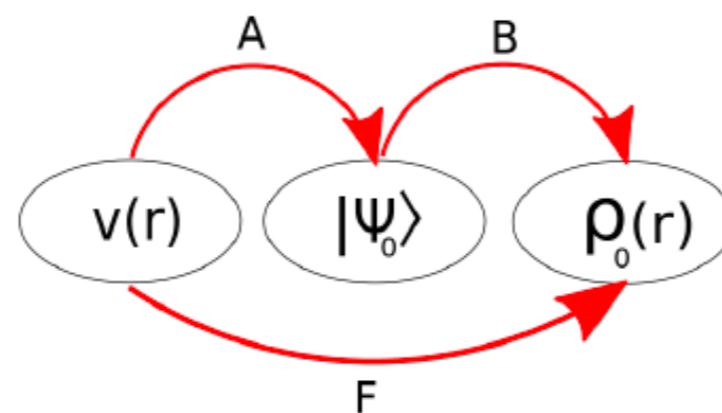
HK theorem for local potentials (HK 1964)

* DFT



$$v(\mathbf{r}) \leftrightarrow \rho_0(\mathbf{r})$$

one-to-one mapping

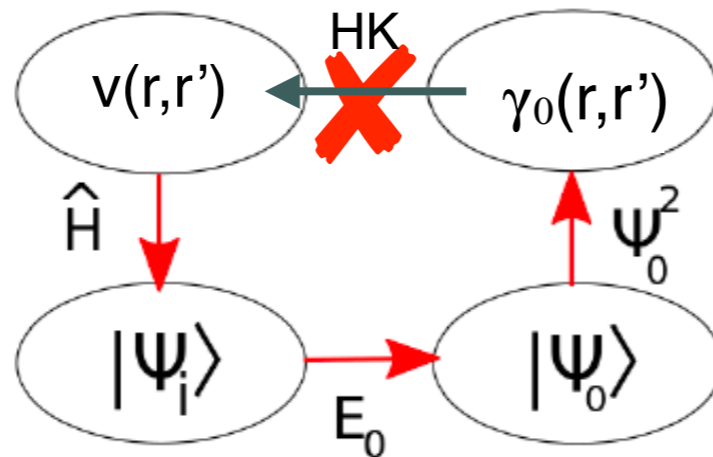


Hohenberg-Kohn theorem:

▶ A is invertible
▶ B is invertible } $\Rightarrow F$ is invertible

HK theorem for nonlocal potentials (Gilbert 1975)

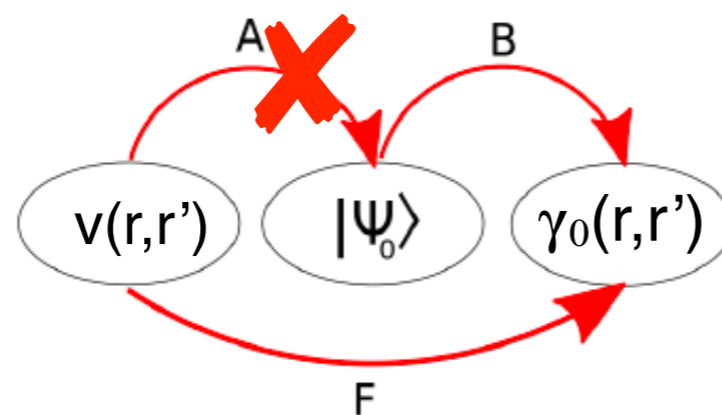
* RDMFT



$$v(\mathbf{r}, \mathbf{r}') \not\leftrightarrow \gamma_0(\mathbf{r}, \mathbf{r}')$$

$$\Psi_0 \leftrightarrow \gamma_0$$

one-to-one mapping



Hohenberg-Kohn theorem:

▶ A is invertible???

▶ B is invertible

HK theorem for nonlocal potentials (Gilbert 1975)

* $\Psi_0 \rightarrow \gamma_0$ Obvious (as in DFT)

* HK: proof $\gamma_0 \rightarrow \Psi_0$ (reductio ad absurdum)

Suppose γ and γ' are the GS 1-RDM corresponding to v_{ext} and v'_{ext} , respectively.
Using the variational principle

$$\begin{aligned} E &= \langle \Psi_0 | \hat{H} | \Psi_0 \rangle < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle \\ &= \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle + \int d\mathbf{x}d\mathbf{x}' [v_{\text{ext}}(\mathbf{x}, \mathbf{x}') - v'_{\text{ext}}(\mathbf{x}, \mathbf{x}')] \gamma'(\mathbf{x}, \mathbf{x}') \\ &= E' + \int d\mathbf{x}d\mathbf{x}' [v_{\text{ext}}(\mathbf{x}, \mathbf{x}') - v'_{\text{ext}}(\mathbf{x}, \mathbf{x}')] \gamma'(\mathbf{x}, \mathbf{x}') \end{aligned}$$

Interchanging the roles of v_{ext} and v'_{ext}

$$E' < E + \int d\mathbf{x}d\mathbf{x}' [v'_{\text{ext}}(\mathbf{x}, \mathbf{x}') - v_{\text{ext}}(\mathbf{x}, \mathbf{x}')] \gamma(\mathbf{x}, \mathbf{x}')$$

Adding the two inequalities

$$\int d\mathbf{x}d\mathbf{x}' [v'_{\text{ext}}(\mathbf{x}, \mathbf{x}') - v_{\text{ext}}(\mathbf{x}, \mathbf{x}')] [\gamma'(\mathbf{x}, \mathbf{x}') - \gamma(\mathbf{x}, \mathbf{x}')] < 0$$

HK theorem for nonlocal potentials (Gilbert 1975)

* $\Psi_0 \rightarrow \gamma_0$ Obvious (as in DFT)

* HK: proof $\gamma_0 \rightarrow \Psi_0$ (reductio ad absurdum)

Suppose γ and γ' are the GS 1-RDM corresponding to v_{ext} and v'_{ext} , respectively.
Using the variational principle

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$$\text{if } \gamma = \gamma' \Rightarrow 0 < 0$$

contradiction!

1-RDM functional

* Ground-state observables as functional of 1-RDM

FROM HK ==> expectation value of any GS operator as functional of 1-RDM

$$O[\gamma] \equiv \langle \Psi_0[\gamma] | \hat{O} | \Psi_0[\gamma] \rangle.$$

* Energy functional

$$\begin{aligned} E_v[\gamma] &= \langle \Psi_0[\gamma] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\gamma] \rangle \\ &= \int d\mathbf{x}d\mathbf{x}' h(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') + \underbrace{\langle \Psi_0[\gamma] | \hat{W} | \Psi_0[\gamma] \rangle}_{W_{\text{HK}}[\gamma]} \end{aligned}$$

with

$$h(\mathbf{x}, \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}') \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) + v_{\text{ext}}(\mathbf{x}, \mathbf{x}')$$

THE ADVANTAGE to use 1-RDM instead of the density is that the kinetic energy is a well-known functional of the 1-RDM

$$\text{DFT} \quad E[\rho] = F_{\text{HK}}[\rho] + \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r}) = T_{\text{KS}}[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho] + \int d\mathbf{r} v(\mathbf{r}) \rho(\mathbf{r})$$

Variational principle

* The GS 1-RDM minimises the total energy

Suppose γ and γ' are the GS 1-RDM corresponding to v_{ext} and v'_{ext} , respectively.
Using the variational principle

$$\begin{aligned} E_v[\gamma'] &= \langle \Psi_0[\gamma'] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\gamma'] \rangle \\ &\geq \langle \Psi_0[\gamma] | \hat{T} + \hat{V} + \hat{W} | \Psi_0[\gamma] \rangle = E_v[\gamma] \end{aligned}$$

The exact GS 1-RDM hence minimises the total energy functional
The GS energy can be found as

$$E_0 = \inf_{\gamma \in \text{v-rep}} \left\{ \langle \Psi_0[\gamma] | \hat{W} | \Psi_0[\gamma] \rangle + \int d\mathbf{x} d\mathbf{x}' h(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') \right\}$$

defined for **pure-state v-representable** 1-RDMs

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► Levy extended the domain of a density matrix functional to all **pure-state N-representable 1-RDMs** by defining the electron repulsion functional as

$$E_{ee}^L[\gamma] = \min_{\Psi \rightarrow \gamma} \langle \Psi | \hat{W} | \Psi \rangle$$

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► Levy's constrained search definition has been further extended to **ensemble N-representable** 1-RDMs by Valone. A 1-RDM is ensemble N representable is a set of pure state $|\Psi_i\rangle$ and weights w_i ($\sum_i w_i = 1$) exist such that

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_i w_i \langle \Psi_i | \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}') | \Psi_i \rangle$$

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The infimum is search over ensemble N-representability density

N-representable conditions

* Ensemble N -representable conditions (Coleman 1963)

The 1-RDM is a hermitian matrix, thus its eigenvalues are real. Its spectral representation reads

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_i n_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}')$$

The 1-RDM is ensemble N -representable if

$$0 \leq n_i \leq 1 \quad \sum_i n_i = N$$

EC are sufficient to guarantee that the minimising 1-RDM corresponds to a pure state for non-degenerate GS. There are also necessary for closed shell and spin compensated systems.

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* Are there pure-state N -representable conditions?

- ▶ Yes, that are the generalised Pauli Constraints for (N, M) ; N =number of electrons; M =size of the Hilbert space
- ▶ Recently a method to generate them for all pairs (N, M)
- ▶ Unfortunately their number explodes as N and M increase
- ▶ It has been shown that their application in RDMFT calculations for 3-electron systems improves the results for approximate 1-RDM functionals

What about a KS system?

Occupation numbers and correlation

Many-body wavefunction as linear combination of Slater determinants built from the natural orbitals

$$\Psi_0(\mathbf{x}_1 \dots \mathbf{x}_N) = \sum_i C_i \Phi_i(\mathbf{x}_1 \dots \mathbf{x}_N)$$

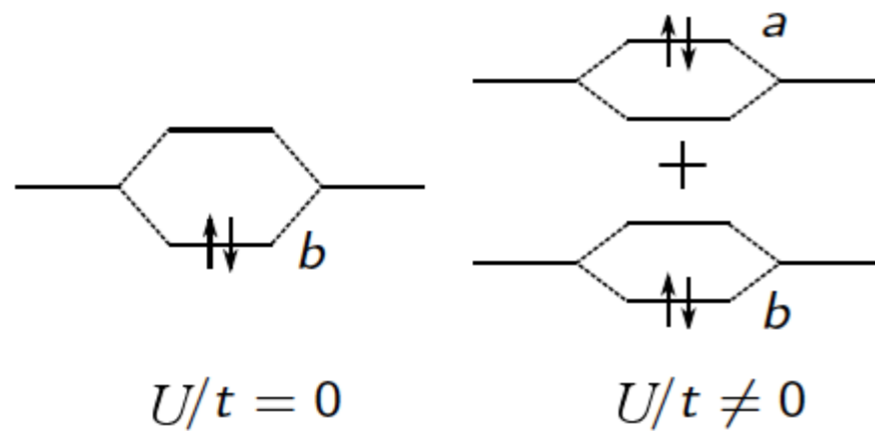
$$\gamma(\mathbf{x}, \mathbf{x}') = N \sum_{ij} \int d\mathbf{x}_2 \dots d\mathbf{x}_N C_i^* C_j \Phi_i^*(\mathbf{x}', \mathbf{x}_2 \dots \mathbf{x}_N) \Phi_j(\mathbf{x}, \mathbf{x}_2 \dots \mathbf{x}_N) = \sum_i |C_i|^2 \gamma_i(\mathbf{x}, \mathbf{x}')$$

with $\gamma_i(\mathbf{x}, \mathbf{x}') = \sum_k \phi_k^i(\mathbf{x}) \phi_k^{i*}(\mathbf{x}')$ 1-RDM corresponding to the i -th Slater determinant

Occupation numbers and correlation

* Hubbard dimer at 1/2 filling

singlet wavefunction $\Psi_0(\mathbf{x}_1, \mathbf{x}_2) = \sum_{i=1,2} C_i \Phi_i(\mathbf{x}_1, \mathbf{x}_2)$



$$|\Psi_0\rangle = \sqrt{n_b} |b \uparrow, b \downarrow\rangle - \sqrt{n_a} |a \uparrow, a \downarrow\rangle$$

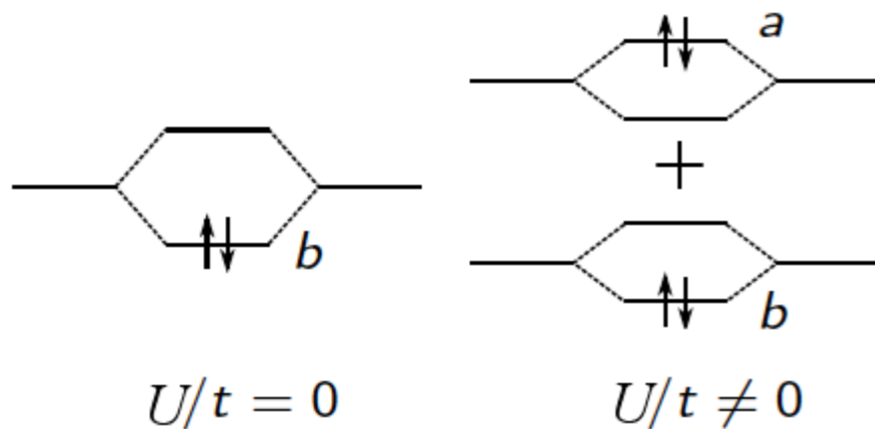
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$$= \sum_{i=b\uparrow, b\downarrow, a\uparrow, a\downarrow} n_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}')$$



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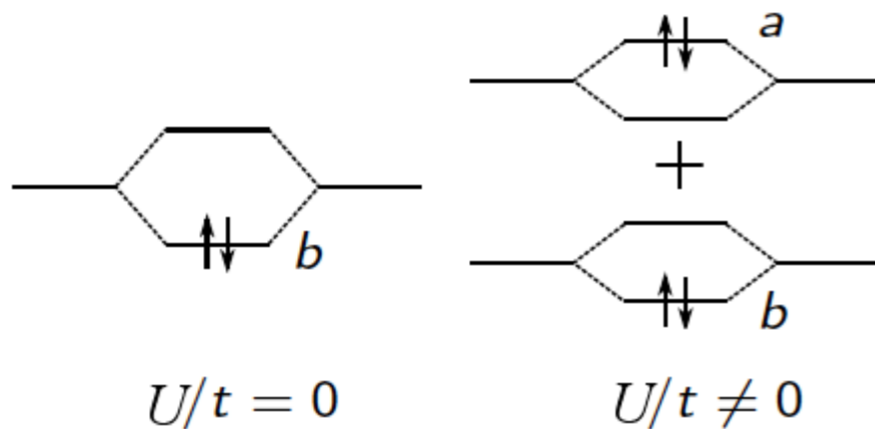
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$$= \sum_{i=b\uparrow, b\downarrow, a\uparrow, a\downarrow} n_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}') \quad \left\{ \begin{array}{l} n_{b\uparrow} = n_{b\downarrow} = |C_1|^2 \\ n_{a\uparrow} = n_{a\downarrow} = |C_2|^2 \\ |C_1|^2 + |C_2|^2 = 1 \end{array} \right.$$



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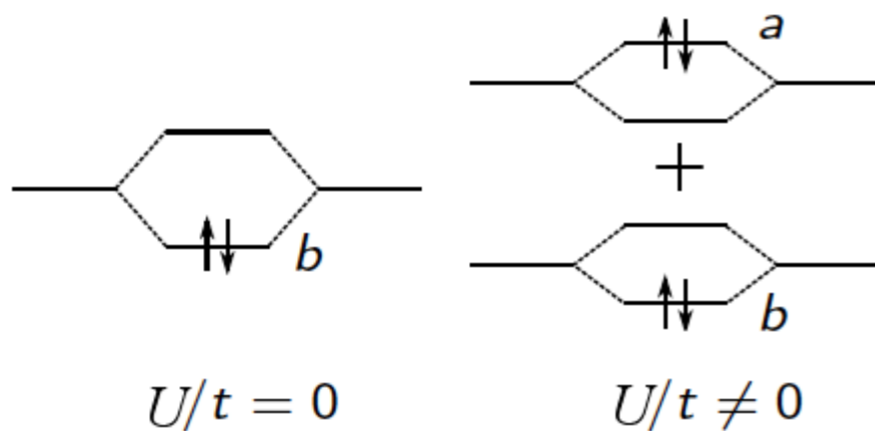
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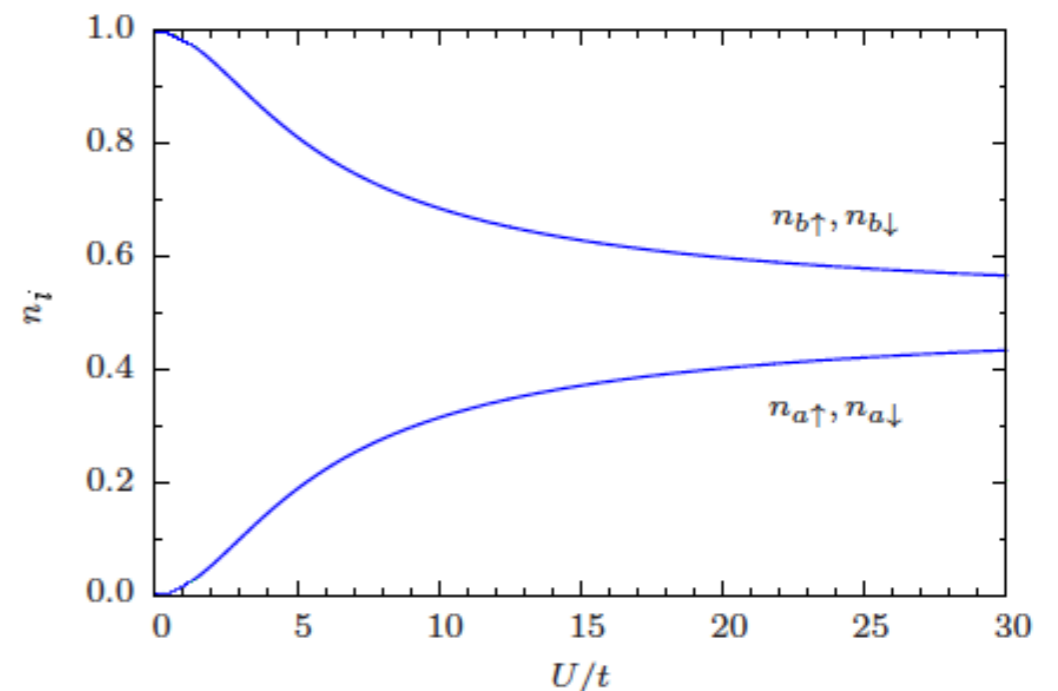
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$$= \sum_{i=b\uparrow, b\downarrow, a\uparrow, a\downarrow} n_i \phi_i(\mathbf{x}) \phi_i^*(\mathbf{x}') \quad \begin{cases} n_{b\uparrow} = n_{b\downarrow} = |C_1|^2 \\ n_{a\uparrow} = n_{a\downarrow} = |C_2|^2 \\ |C_1|^2 + |C_2|^2 = 1 \end{cases}$$



$$|\Psi_0\rangle = \sqrt{n_b} |b \uparrow, b \downarrow\rangle - \sqrt{n_a} |a \uparrow, a \downarrow\rangle$$



What about a KS system?

The 1RDM for a Slater determinant is idempotent

$$\int dy \gamma(x, y) \gamma(y, x') = \gamma(x, x') \quad \Leftrightarrow \quad \forall i \quad n_i = 0 \vee n_i = 1$$

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$$\int dy \gamma(x, y) \gamma(y, x') = \gamma(x, x') \quad \Leftrightarrow \quad \forall i \quad n_i = 0 \vee n_i = 1$$

and therefore a system of noninteracting electrons cannot reproduce the 1RDM of the interacting system (at least at zero temperature)

Energy functional approximations

$$E[\gamma] = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \gamma(\mathbf{x}, \mathbf{x}') + \int d\mathbf{x} d\mathbf{x}' v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \Gamma^{(2)}[\gamma](\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$$

$$\Gamma^{(2)}[\gamma](\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}') = \gamma(\mathbf{x}, \mathbf{x}) \gamma(\mathbf{x}', \mathbf{x}') - \gamma(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}', \mathbf{x}) + \Gamma_c^{(2)}[\gamma](\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$$

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$$\Gamma^{(2)}[\gamma](\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}') = \gamma(\mathbf{x}, \mathbf{x})\gamma(\mathbf{x}', \mathbf{x}') - \gamma(\mathbf{x}, \mathbf{x}')\gamma(\mathbf{x}', \mathbf{x}) + \Gamma_c^{(2)}[\gamma](\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$$

* HF

$$E_H[\gamma] = \frac{1}{2} \int d\mathbf{x}d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{x}, \mathbf{x})\gamma(\mathbf{x}', \mathbf{x}')$$

$$E_x[\gamma] = \frac{1}{2} \int d\mathbf{x}d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \gamma(\mathbf{x}, \mathbf{x}')\gamma(\mathbf{x}', \mathbf{x})$$

Using the fact that

$$\gamma(x, x') = \sum_i \phi_i(x) \phi_i^*(x')$$

for a single Slater determinant we get back the usual HF equations for the total energy

$$E_{\text{HF}}[\{n_i\}, \{\phi_i\}] = \frac{1}{2} \sum_{jk} n_j n_k \int d\mathbf{x}d\mathbf{x}' \phi_j^*(\mathbf{x}) \phi_k^*(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \phi_j(\mathbf{x}) \phi_k(\mathbf{x}') - \frac{1}{2} \sum_{jk} n_j n_k \int d\mathbf{x}d\mathbf{x}' \phi_j^*(\mathbf{x}) \phi_k^*(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \phi_k(\mathbf{x}) \phi_j(\mathbf{x}')$$

Energy functional approximations

$$E[\gamma] = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \gamma(\mathbf{x}, \mathbf{x}') + \int d\mathbf{x} d\mathbf{x}' v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \Gamma^{(2)}[\gamma](\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$$

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* two-electron system (Löwdin-Shull functional)

$$|\Psi_0\rangle = \sum_p c_p |\phi_p, \phi_{\bar{p}}\rangle \longrightarrow E_{ee}^{\text{LS}}[\gamma] = \frac{1}{2} \sum_{pq} f_p f_q \sqrt{n_p n_q} \langle pq | qp \rangle \quad f_p = \pm 1$$

Energy functional approximations

$$E[\gamma] = \int d\mathbf{x} \lim_{\mathbf{x}' \rightarrow \mathbf{x}} \left(-\frac{\nabla_{\mathbf{r}}^2}{2} \right) \gamma(\mathbf{x}, \mathbf{x}') + \int d\mathbf{x} d\mathbf{x}' v_{\text{ext}}(\mathbf{x}, \mathbf{x}') \gamma(\mathbf{x}, \mathbf{x}') + \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' v_c(\mathbf{r}, \mathbf{r}') \Gamma^{(2)}[\gamma](\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$$

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* JK functional

$$E_{\text{xc}}[\{n_i\}, \{\phi_i\}] = -\frac{1}{2} \sum_{jk} f(n_j, n_k) \int d\mathbf{x} d\mathbf{x}' \phi_j^*(\mathbf{x}) \phi_k^*(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \phi_k(\mathbf{x}) \phi_j(\mathbf{x}')$$

Energy functional approximations

* Müller functional

$$\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \gamma(\mathbf{x}_1, \mathbf{x}'_1)\gamma(\mathbf{x}_2, \mathbf{x}'_2) - \sum_{ij} n_i^{\frac{1}{2}+p} n_j^{\frac{1}{2}-p} \phi_i(\mathbf{x}_1)\phi_i^*(\mathbf{x}'_2)\phi_j(\mathbf{x}_2)\phi_j^*(\mathbf{x}'_1)$$

$$-1/2 \leq p \leq 1/2$$

$p=0$ minimizes the fact that $\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2)$ is negative

$$\Gamma^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \gamma(\mathbf{x}_1, \mathbf{x}'_1)\gamma(\mathbf{x}_2, \mathbf{x}'_2) - \gamma^{\frac{1}{2}}(\mathbf{x}_2, \mathbf{x}'_1)\gamma^{\frac{1}{2}}(\mathbf{x}_1, \mathbf{x}'_2)$$

$$\gamma^{\frac{1}{2}}(\mathbf{x}_1, \mathbf{x}_2) = \sum_i n_i^{\frac{1}{2}} \phi_i(\mathbf{x}_1)\phi_i^*(\mathbf{x}_2)$$

$$f^{\text{Müller}}(n_j, n_k) = \sqrt{n_j n_k}$$

Energy functional approximations

* Self-interaction correction Goedecker-Umrigar functional (1998)

$$f^{\text{GU}}(n_j, n_k) = \sqrt{n_j n_k} - \delta_{jk}(n_j - n_j^2)$$

Correction to Müller by explicitly removing all terms $j = k$
This functional is orbital self-interaction free

Energy functional approximations

* The BBC functionals

► **BBC1**: sign change of f if both orbitals are weakly occupied

$$f^{\text{BBC1}}(n_i, n_j) = \begin{cases} -\sqrt{n_i n_j} & i \neq j \text{ weakly occupied} \\ \sqrt{n_i n_j} & \text{otherwise} \end{cases}$$

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$$f^{\text{BBC1}}(n_i, n_j) = \begin{cases} -\sqrt{n_i n_j} & i \neq j \text{ weakly occupied} \\ \sqrt{n_i n_j} & \text{otherwise} \end{cases}$$

- ▶ **BBC2**: Additionally, omission of square root for strongly occupied orbitals

$$f^{\text{BBC2}}(n_i, n_j) = \begin{cases} -\sqrt{n_i n_j} & \text{for } i \neq j \text{ weakly occupied} \\ n_i n_j & \text{for } i \neq j \text{ strongly occupied} \\ \sqrt{n_i n_j} & \text{otherwise} \end{cases}$$

- ▶ **BBC3**: Inclusion of antibonding in the strongly occupied orbital list, unless it interacts with bonding. Removal of SI

$$f^{\text{BBC3}}(n_i, n_j) = \begin{cases} -\sqrt{n_i n_j} & \text{for } i \neq j \text{ weakly occupied} \\ n_i n_j & \begin{cases} \text{for } i \neq j \text{ strongly occupied} \\ \text{for } i \text{ (} j \text{) antibonding, } j \text{ (} i \text{) not bonding} \end{cases} \\ n_i^2 & i=j \text{ not (anti)bonding} \\ \sqrt{n_i n_j} & \text{otherwise} \end{cases}$$

Energy functional approximations

* The Power functional (molecules and solids)

$$f^{\text{Power}}(n_j, n_k) = n_j^\alpha n_k^\alpha \quad \frac{1}{2} \leq \alpha \leq 1$$

Optimal value for α

- ▶ $\alpha = 0.525$ for stretched H_2
- ▶ $\alpha = 0.578$ for molecules at equilibrium
- ▶ $\alpha = 0.55$ for HEG
- ▶ $0.65 \leq \alpha \leq 0.7$ for solids

Energy functional approximations

* Piris Natural Orbital Functionals (PNOF)

Functionals based on the reconstruction of the 2-RDM in terms of the 1-RDM

$$\Gamma_{ijkl}^{(2)} = n_i n_j (\delta_{il} \delta_{jk} - \delta_{ik} \delta_{jl}) + \lambda_{ijkl}[\gamma]$$

PNOFn, n=1,7 (λ as functional of occupation numbers)

- ▶ γ not idempotent and $\lambda \neq 0$
- ▶ hermiticity $\Gamma_{ijkl} = \Gamma_{klij}^*$
- ▶ antisymmetry $\Gamma_{ijkl} = -\Gamma_{jikl} = -\Gamma_{ijlk}$
- ▶ sum rule $\sum \Gamma_{ijkj} = (N - 1)n_i \delta_{ik}$
- ▶ only $\langle ij|ij \rangle$, $\langle ij|ji \rangle$, $\langle ii|jj \rangle$ integrals allowed

$$E_{\text{HXC}}^{\text{PNOF}}[\gamma] = \sum_{ij} n_i n_j (2\langle ij|ij \rangle - \langle ij|ji \rangle) - \sum_{ij} \left[\left(\Delta_{ij}^{\alpha\alpha} + \Delta_{ij}^{\alpha\beta} \right) \langle ij|ij \rangle - \Delta_{ij}^{\alpha\alpha} \langle ij|ji \rangle \right] + \sum_{ij} \Pi_{ij} \langle ii|jj \rangle$$

Energy minimisation

* Constraints

▶ ensemble N-representable constraints: $0 \leq n_i \leq 1$, $\sum_i n_i = N$

▶ orthonormality constraint: $\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$

$$n_i = \cos^2 \theta_i$$

} Enforced through
Lagrange multipliers

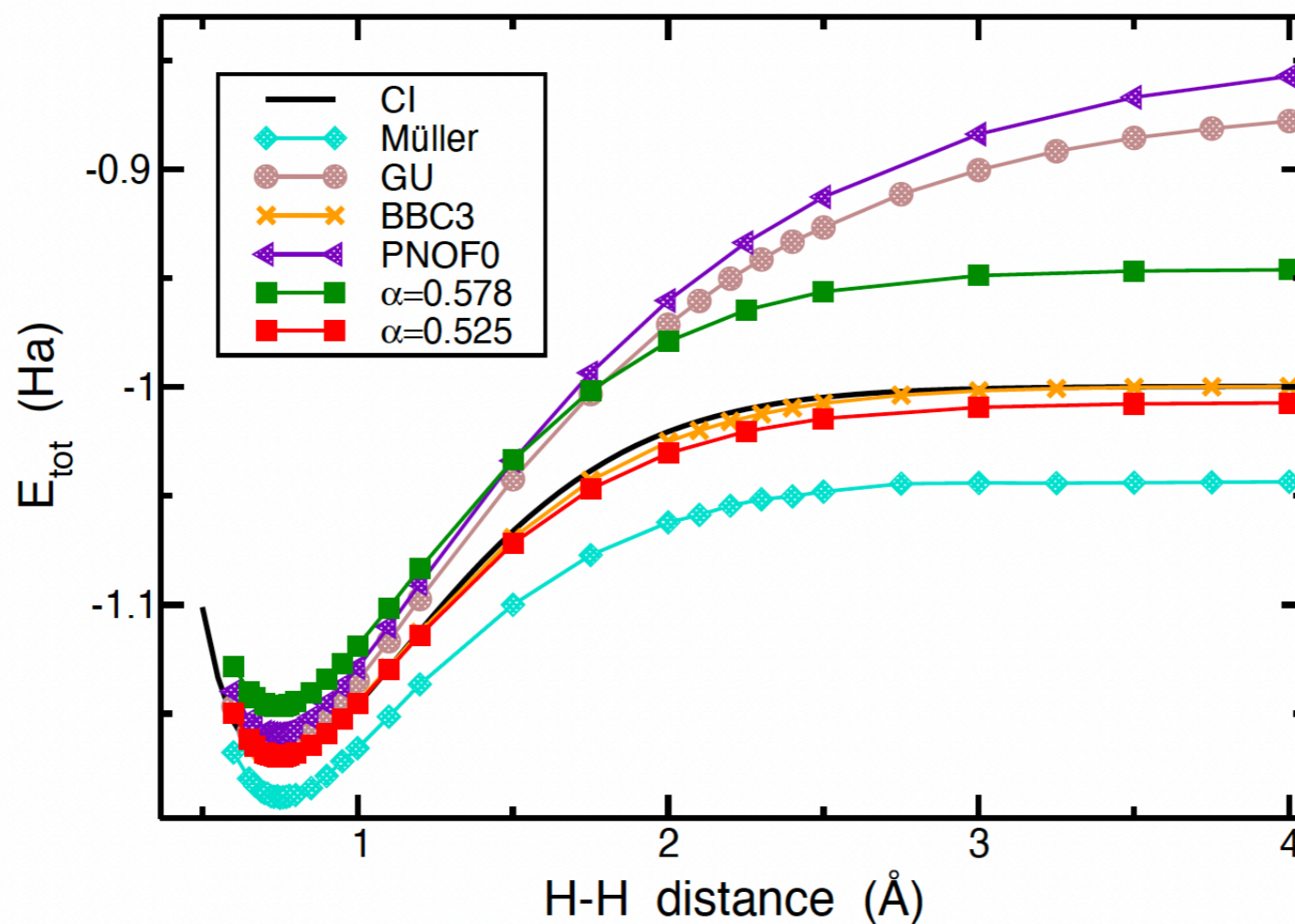
* Functional to minimise

$$\Omega[\{\theta_i\}, \{\phi_i\}] = E[\{n_i(\theta_i)\}, \{\phi_i\}] - \mu \left(\sum_j \cos^2 \theta_j - N \right) - \sum_{jk} \lambda_{jk} (\langle \phi_j | \phi_k \rangle - \delta_{jk})$$

Orbital minimisation bottleneck: scaling M^5 (M =Hilbert space size)

Performance of various functionals

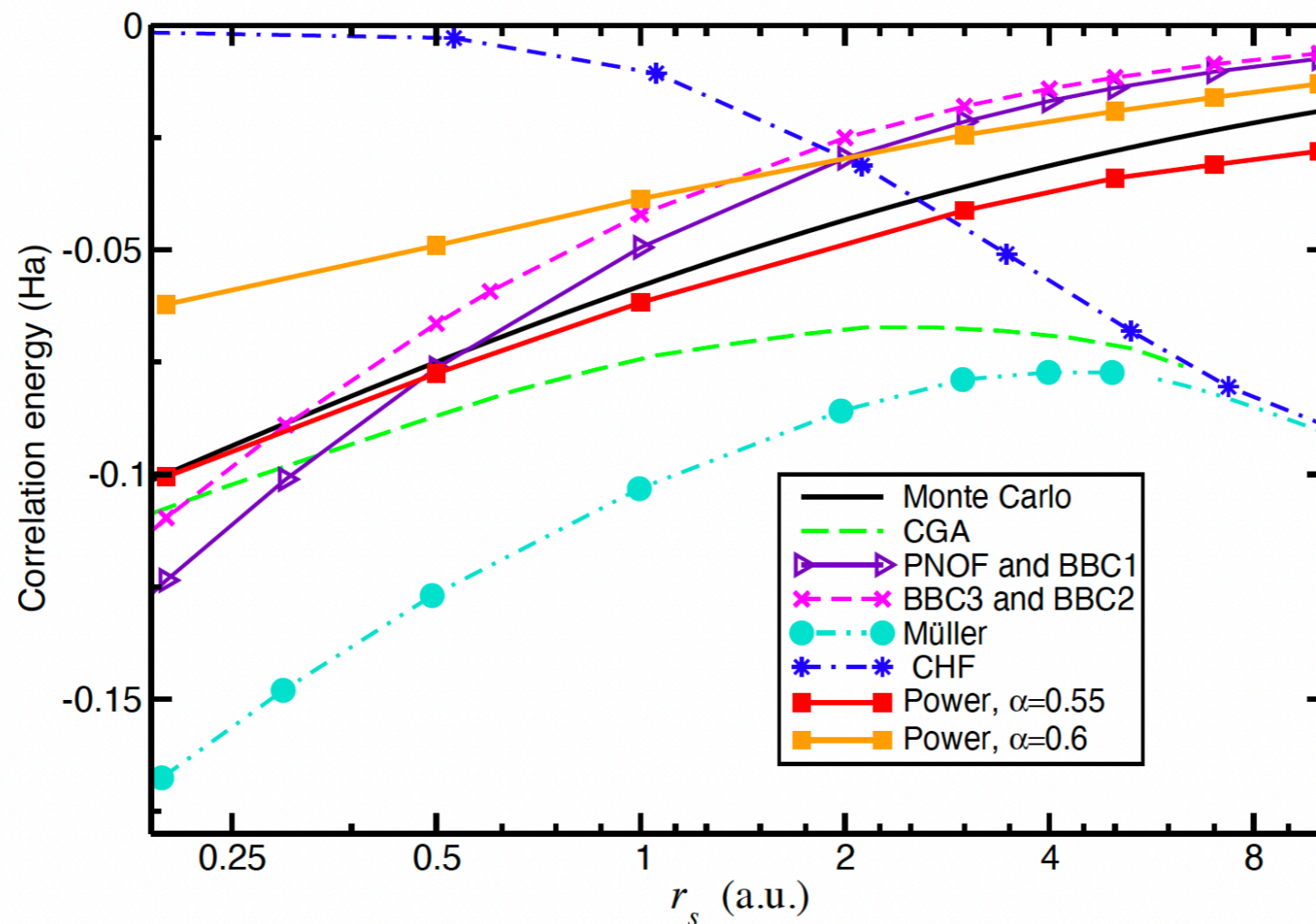
* Total energy of H₂ molecule



thanks to fractional
occupation numbers RDMFT
can capture static correlation

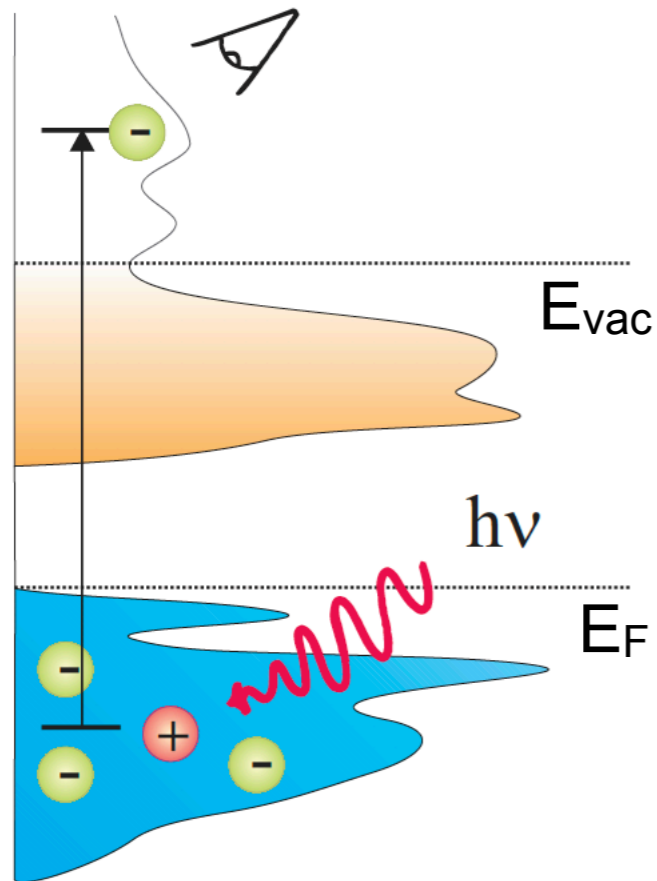
Performance of various functionals

* Correlation energy of HEG



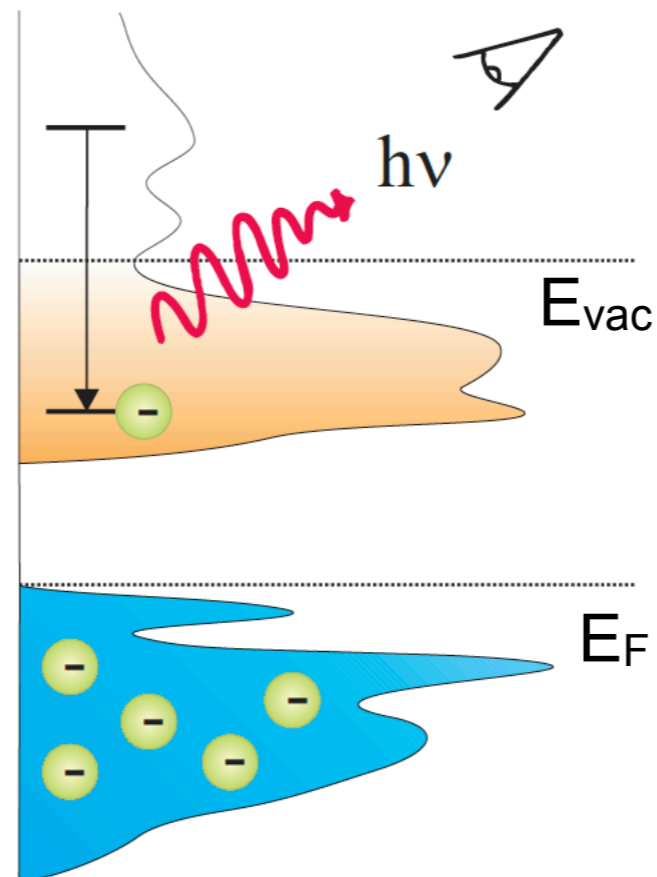
Properties: spectroscopy

Direct Photoemission



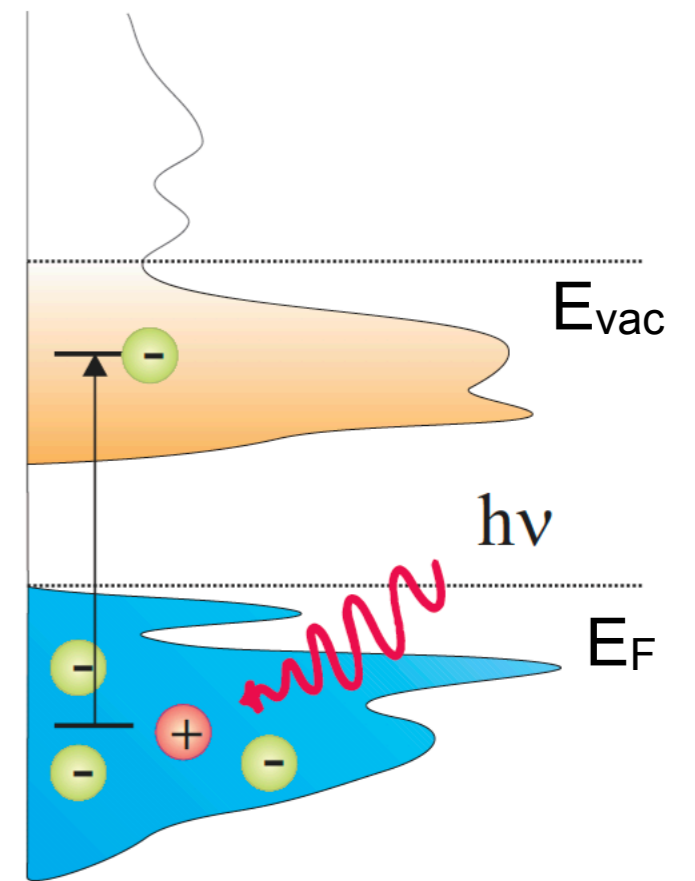
$$N \rightarrow N-1$$

Inverse Photoemission



$$N \rightarrow N+1$$

Absorption



$$N \rightarrow N^*$$

Properties: IPs and EAs

* Extended Koopmans' Theorem: IPs

ansatz $|\Psi_\nu^{N-1}\rangle = \hat{O}_\nu |\Psi_0^N\rangle \quad \hat{O}_\nu = \sum_i C_{\nu i}^R \hat{a}_i$

$$\epsilon_\nu^R = E_0^N - E_\nu^{N-1} = \langle \Psi_0^N | \hat{H} | \Psi_0^N \rangle - \langle \Psi_\nu^{N-1} | \hat{H} | \Psi_\nu^{N-1} \rangle = \langle \Psi_0^N | \hat{H} | \Psi_0^N \rangle - \frac{\langle \hat{O}_\nu \Psi_0^N | \hat{H} | \hat{O}_\nu \Psi_0^N \rangle}{\langle \Psi_0^N | \hat{O}_\nu^\dagger \hat{O}_\nu | \Psi_0^N \rangle}$$

$$= - \frac{\langle \Psi_0^N | \hat{O}_\nu^\dagger [\hat{H}, \hat{O}_\nu] | \Psi_0^N \rangle}{\langle \Psi_0^N | \hat{O}_\nu^\dagger \hat{O}_\nu | \Psi_0^N \rangle}$$

Stationarity with respect to the coefficient

Generalized eigenvalue problem $(\mathbf{V}^\nu - \epsilon_\nu \mathbf{S}^\nu) \mathbf{C}_\nu = 0$

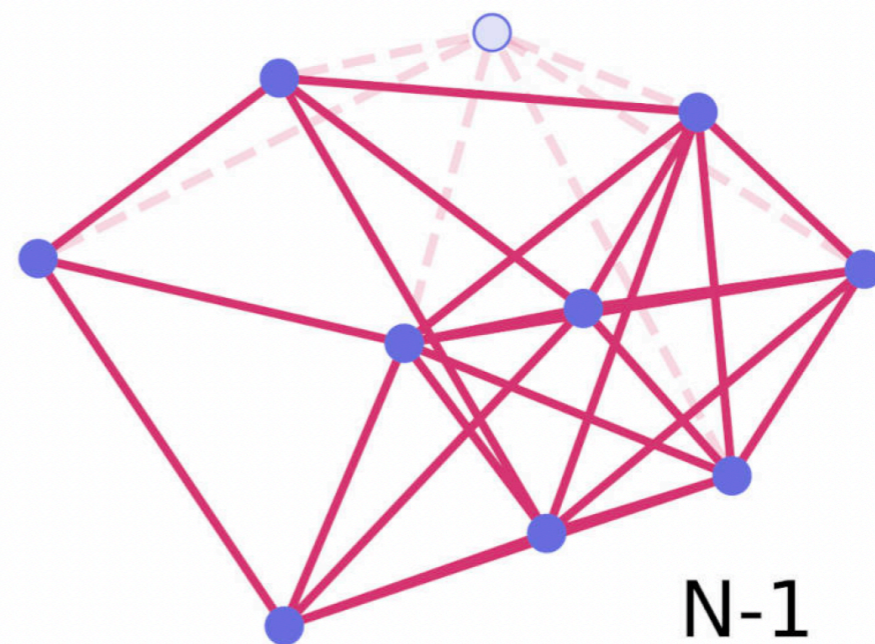
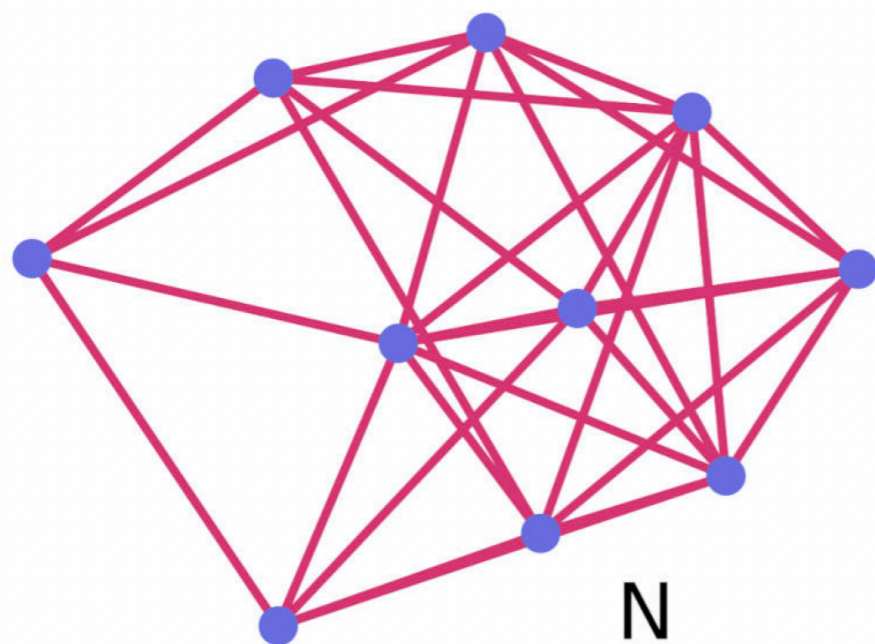
$$V_{ij}^\nu = -\langle \Psi_0^N | \hat{a}_j^\dagger [\hat{H}, \hat{a}_i] | \Psi_0^N \rangle \quad S_{ij}^\nu = \gamma_{ij} = \langle \Psi_0^N | \hat{a}_j^\dagger \hat{a}_i | \Psi_0^N \rangle \quad \leftarrow V^\nu, S^\nu$$

from various framework (e.g, QMC, CI, RDMFT)

Properties: IPs and EAs

* Physical meaning of EKT

Quasiparticle-like ansatz for $(N - 1)$ - and $(N + 1)$ -particle wavefunctions:
correlation is included, but no relaxation of the other orbitals



Properties: IPs and EAs

* Extended Koopmans' Theorem: IPs

ansatz $|\Psi_\nu^{N-1}\rangle = \hat{O}_\nu |\Psi_0^N\rangle \quad \hat{O}_\nu = \sum_i C_{\nu i}^R \hat{a}_i$

$$\epsilon_\nu^R = E_0^N - E_\nu^{N-1} = \langle \Psi_0^N | \hat{H} | \Psi_0^N \rangle - \langle \Psi_\nu^{N-1} | \hat{H} | \Psi_\nu^{N-1} \rangle = \langle \Psi_0^N | \hat{H} | \Psi_0^N \rangle - \frac{\langle \hat{O}_\nu \Psi_0^N | \hat{H} | \hat{O}_\nu \Psi_0^N \rangle}{\langle \Psi_0^N | \hat{O}_\nu^\dagger \hat{O}_\nu | \Psi_0^N \rangle}$$

$$= - \frac{\langle \Psi_0^N | \hat{O}_\nu^\dagger [\hat{H}, \hat{O}_\nu] | \Psi_0^N \rangle}{\langle \Psi_0^N | \hat{O}_\nu^\dagger \hat{O}_\nu | \Psi_0^N \rangle}$$

Stationarity with respect to the coefficient

Generalized eigenvalue problem $(\mathbf{V}^\nu - \epsilon_\nu \mathbf{S}^\nu) \mathbf{C}_\nu = 0$

$$V_{ij}^\nu = -\langle \Psi_0^N | \hat{a}_j^\dagger [\hat{H}, \hat{a}_i] | \Psi_0^N \rangle \quad S_{ij}^\nu = \gamma_{ij} = \langle \Psi_0^N | \hat{a}_j^\dagger \hat{a}_i | \Psi_0^N \rangle \quad \leftarrow V^\nu, S^\nu$$

from various framework (e.g, QMC, CI, RDMFT)

Properties: IPs and EAs

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ansatz $|\Psi_\nu^{N-1}\rangle = \hat{O}_\nu |\Psi_0^N\rangle \quad \hat{O}_\nu = \sum_i C_{\nu i}^R \hat{a}_i$

$$\epsilon_\nu^R = E_0^N - E_\nu^{N-1} = \langle \Psi_0^N | \hat{H} | \Psi_0^N \rangle - \langle \Psi_\nu^{N-1} | \hat{H} | \Psi_\nu^{N-1} \rangle = \langle \Psi_0^N | \hat{H} | \Psi_0^N \rangle - \frac{\langle \hat{O}_\nu \Psi_0^N | \hat{H} | \hat{O}_\nu \Psi_0^N \rangle}{\langle \Psi_0^N | \hat{O}_\nu^\dagger \hat{O}_\nu | \Psi_0^N \rangle}$$

$$= - \frac{\langle \Psi_0^N | \hat{O}_\nu^\dagger [\hat{H}, \hat{O}_\nu] | \Psi_0^N \rangle}{\langle \Psi_0^N | \hat{O}_\nu^\dagger \hat{O}_\nu | \Psi_0^N \rangle}$$

Stationarity with respect to the coefficient

Generalized eigenvalue problem $(\mathbf{V}^\nu - \epsilon_\nu \mathbf{S}^\nu) \mathbf{C}_\nu = 0$

$$V_{ij}^\nu = -\langle \Psi_0^N | \hat{a}_j^\dagger [\hat{H}, \hat{a}_i] | \Psi_0^N \rangle \quad S_{ij}^\nu = \gamma_{ij} = \langle \Psi_0^N | \hat{a}_j^\dagger \hat{a}_i | \Psi_0^N \rangle \quad \leftarrow V^\nu, S^\nu$$

working out the commutator, use natural orbitals basis

from various framework (e.g, QMC, CI, RDMFT)

$$\Lambda_{ij}^R = \frac{1}{\sqrt{n_i n_j}} \left[n_i h_{ji} + \sum_{klm} V_{jmk} \Gamma_{klmi}^{(2)} \right] \longrightarrow \epsilon_k^R$$

$$\Gamma_{klmi}^{(2)} = \langle \Psi_0 | \hat{c}_i^\dagger \hat{c}_m^\dagger \hat{c}_l \hat{c}_k | \Psi_0 \rangle \quad V_{jmk} = \int d\mathbf{x} d\mathbf{x}' \phi_j^*(\mathbf{x}) \phi_m^*(\mathbf{x}') v_c(\mathbf{r}, \mathbf{r}') \phi_k(\mathbf{x}) \phi_l(\mathbf{x}') \quad h_{ij} = \int d\mathbf{x} \phi_i^*(\mathbf{x}) h(\mathbf{r}) \phi_j(\mathbf{x})$$

Properties: IPs and EAs

* Extended Koopmans' Theorem: EAs

$$\Lambda_{ij}^A = \frac{1}{(1 - n_i)} \left[(1 - n_i)h_{ji} + \sum_k (V_{jkik} - V_{jkki}) n_k - \sum_{klm} V_{jmk} \Gamma_{klmi}^{(2)} \right] \longrightarrow \epsilon_k^A$$

* Extended Koopmans' Theorem: Spectral function

$$A(\omega) \approx \sum_i \left[\gamma_{ii} \delta(\omega - \epsilon_i^R) + (1 - \gamma_{ii}) \delta(\omega - \epsilon_i^A) \right]$$

Properties: IPs and EAs

* DIF/DER method

DIF $\epsilon_k^- = -\epsilon_k^+ = \epsilon_k = E[\{n_i\}, \{\phi_i\}]|_{n_k=1} - E[\{n_i\}, \{\phi_i\}]|_{n_k=0}$

DER $E[\{n_i\}, \{\phi_i\}]|_{n_k=1} - E[\{n_i\}, \{\phi_i\}]|_{n_k=0} \approx \left. \frac{\partial E}{\partial n_k} \right|_{n_k=1/2}$

justified if the total energy is linear in the occupation number n_k

Idea: Taylor expansion around $n = 1/2$

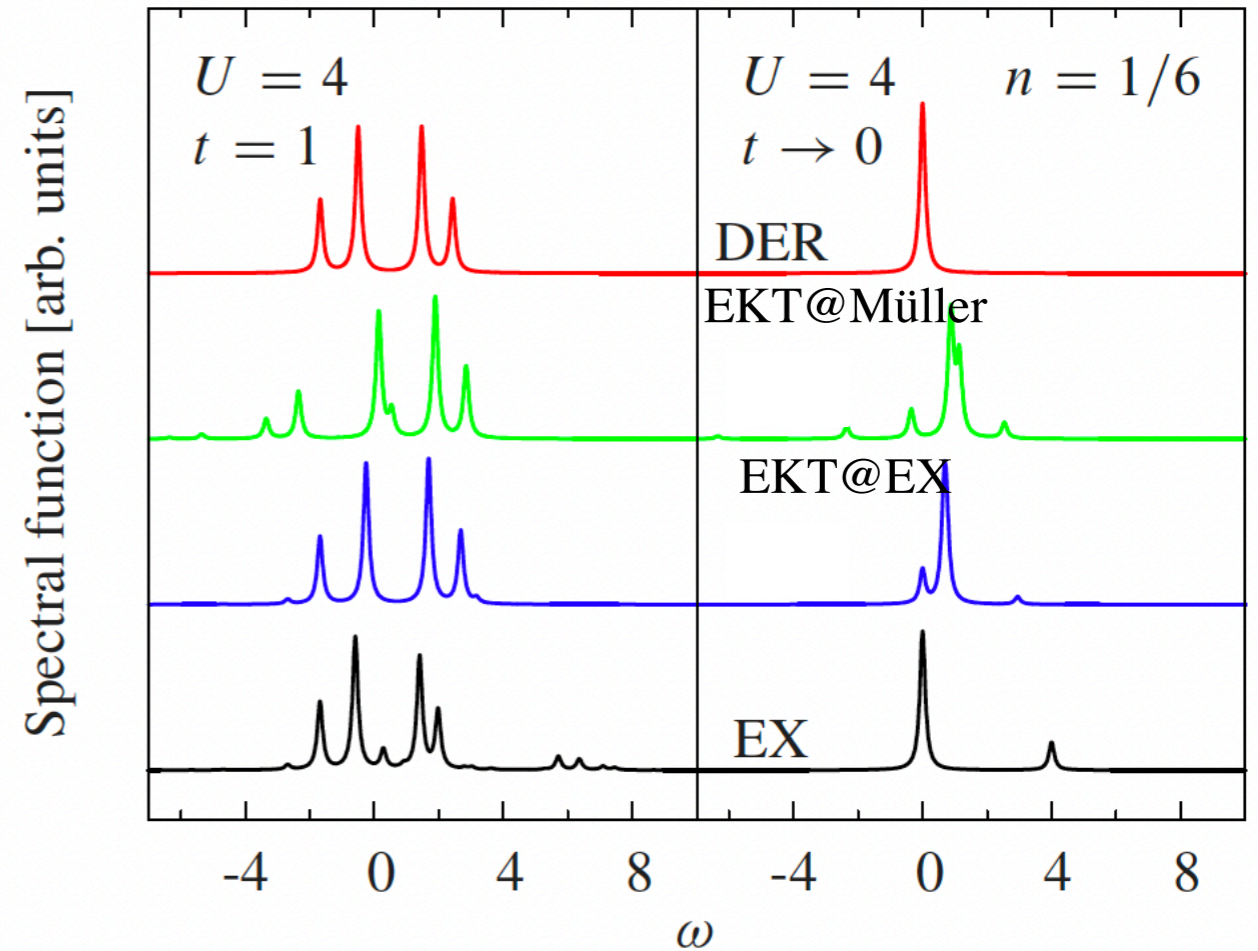
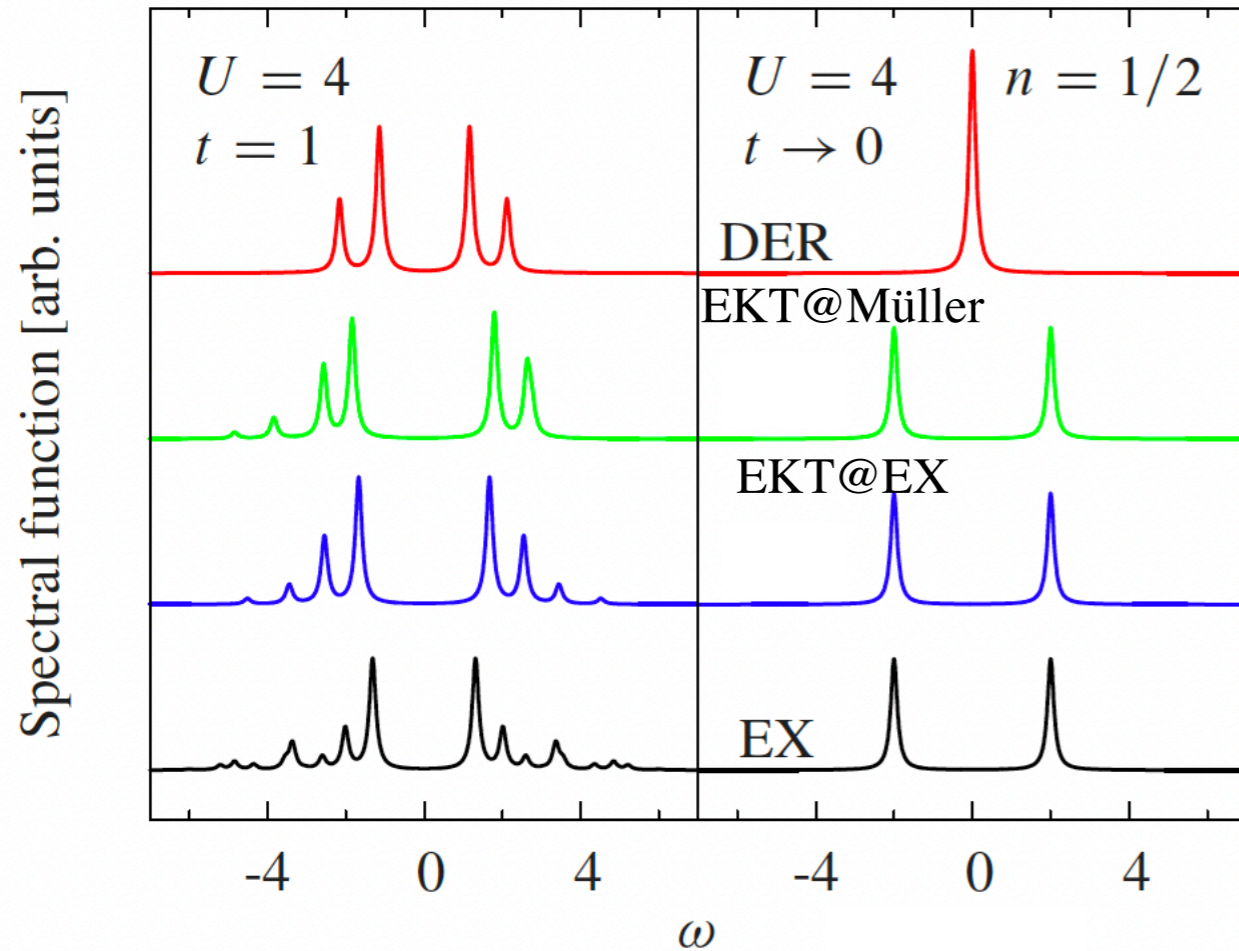
$$E(1) = E(1/2) + E'(1/2)\delta n + \frac{1}{2}E''(1/2)\delta n^2 + \dots (\delta n = 1/2)$$

$$E(0) = E(1/2) + E'(1/2)\delta n + \frac{1}{2}E''(1/2)\delta n^2 + \dots (\delta n = -1/2)$$

$$E(1) - E(0) = E'(1/2)\delta n + O(\delta n^3) \longrightarrow \epsilon_k = \left. \frac{\partial E(n_k)}{\partial n_k} \right|_{n_k=1/2}$$

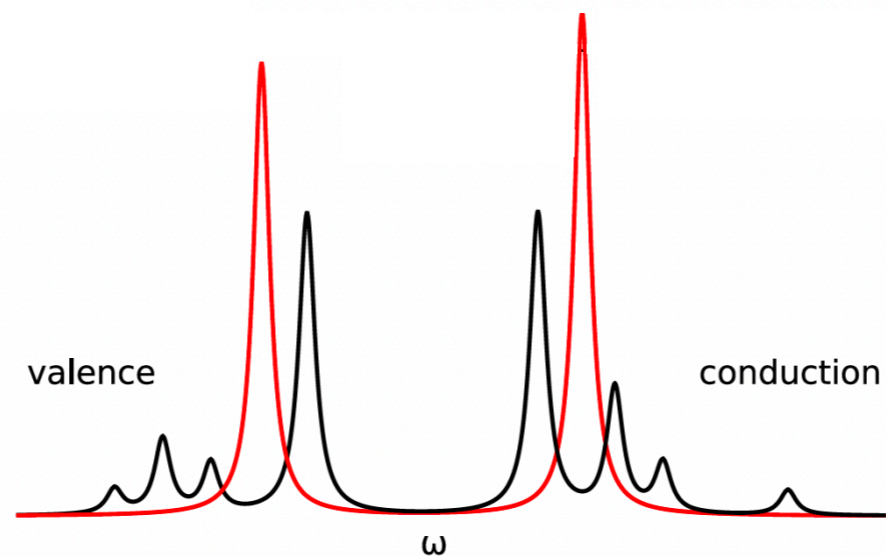
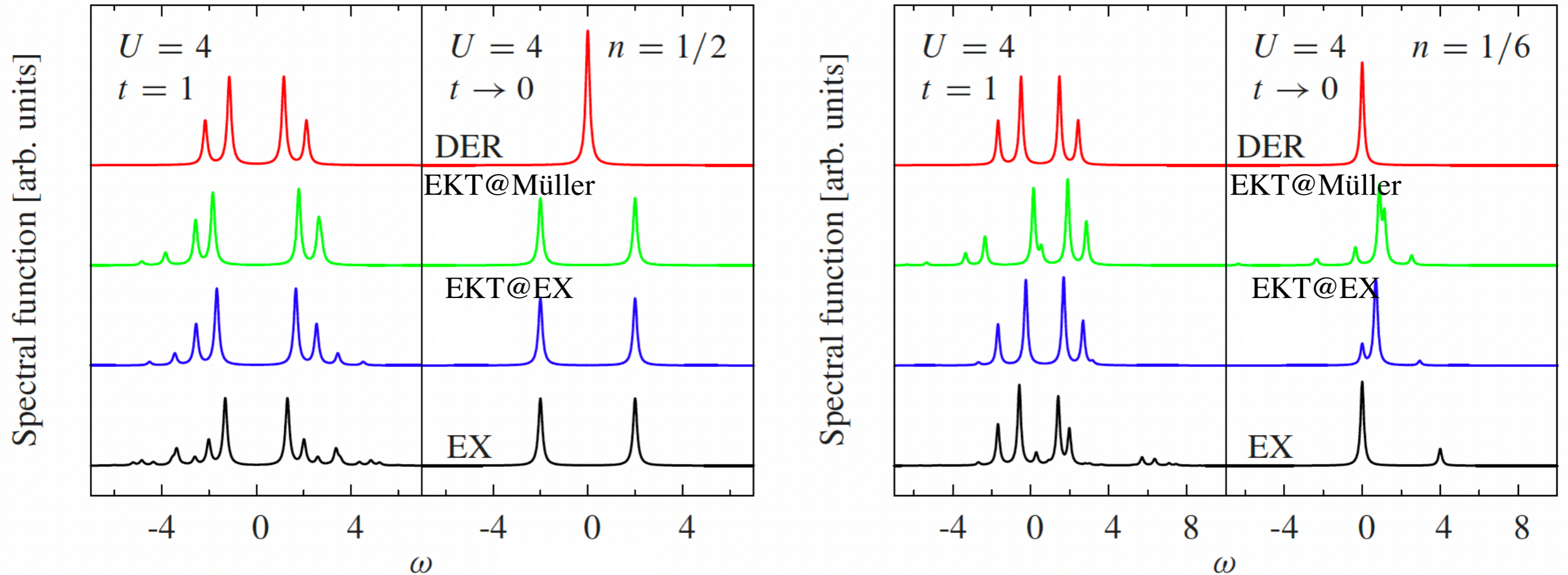
Performance of EKT/DER

* Spectral function 6-site Hubbard ring



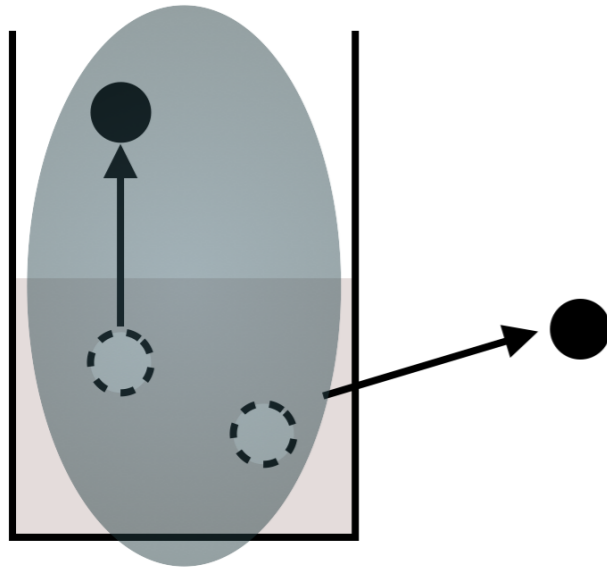
Performance of EKT/DER

* Spectral function 6-site Hubbard ring



Beyond EKT

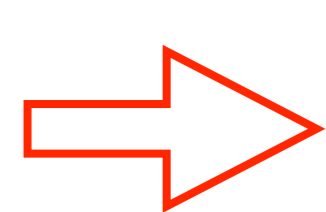
* EKT-3

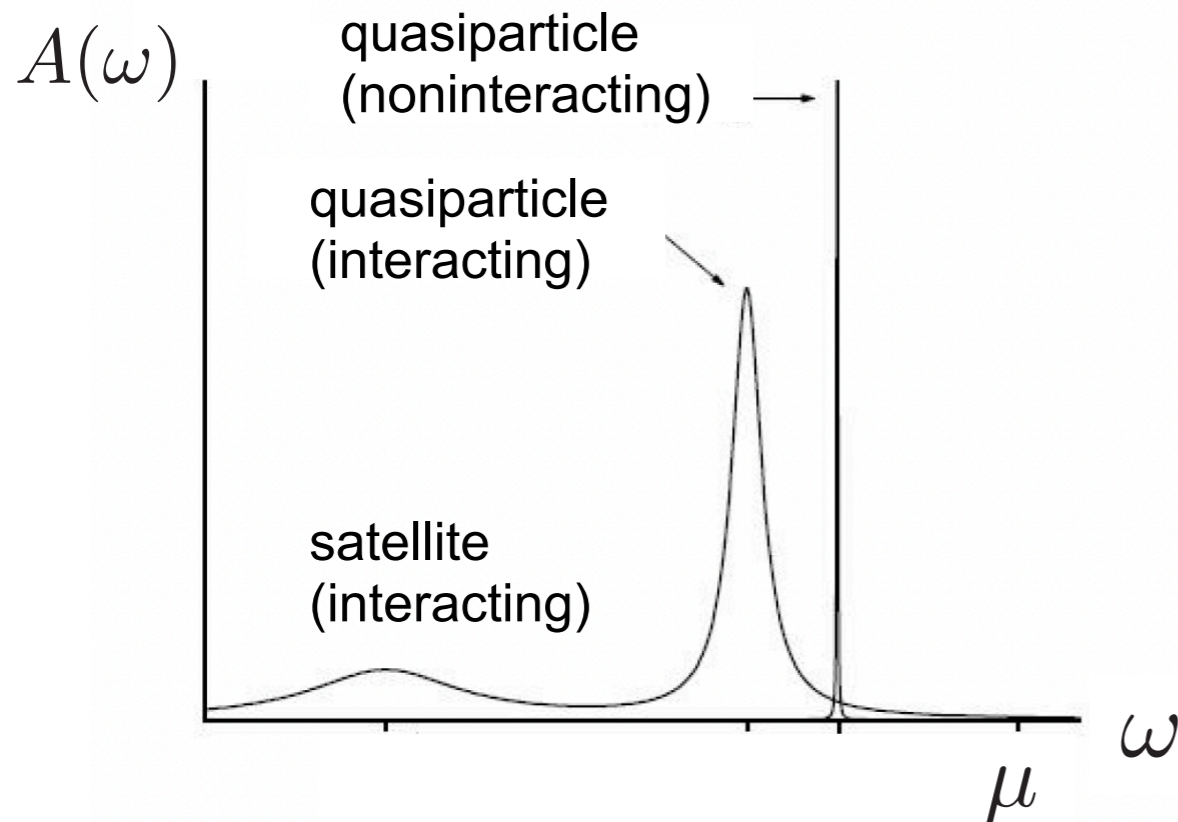


Photoemission is a three-particle process: consider 2e1h and 2h1e excitations!

$$\hat{O}_\nu = \sum_{ijk} C_{\nu ijk}^R \hat{c}_k^\dagger \hat{c}_j \hat{c}_i$$

$$\hat{O}_\nu^\dagger = \sum_{ijk} C_{\nu ijk}^A \hat{c}_k \hat{c}_j^\dagger \hat{c}_i^\dagger$$


 $\Gamma^{(3)}$ and $\Gamma^{(4)}$ enter into the equations!

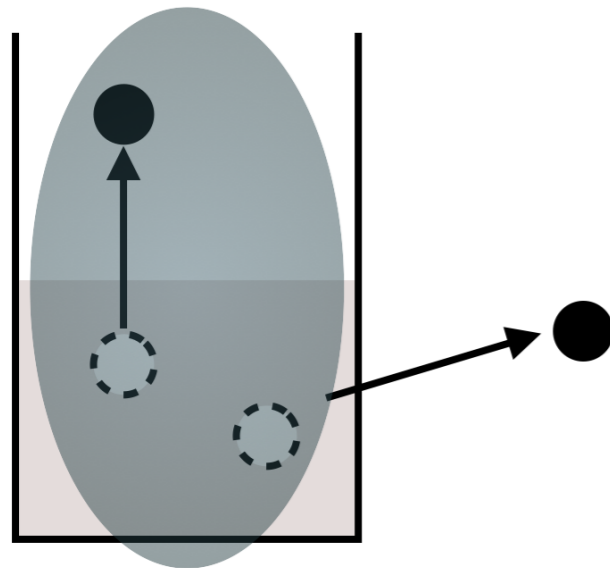


$$G_1 \xrightleftharpoons[\text{downfolding}]{\text{upfolding}} G_3$$

$$\Sigma_1(\omega) \xrightleftharpoons[\text{downfolding}]{\text{upfolding}} \Sigma_3$$

Beyond EKT

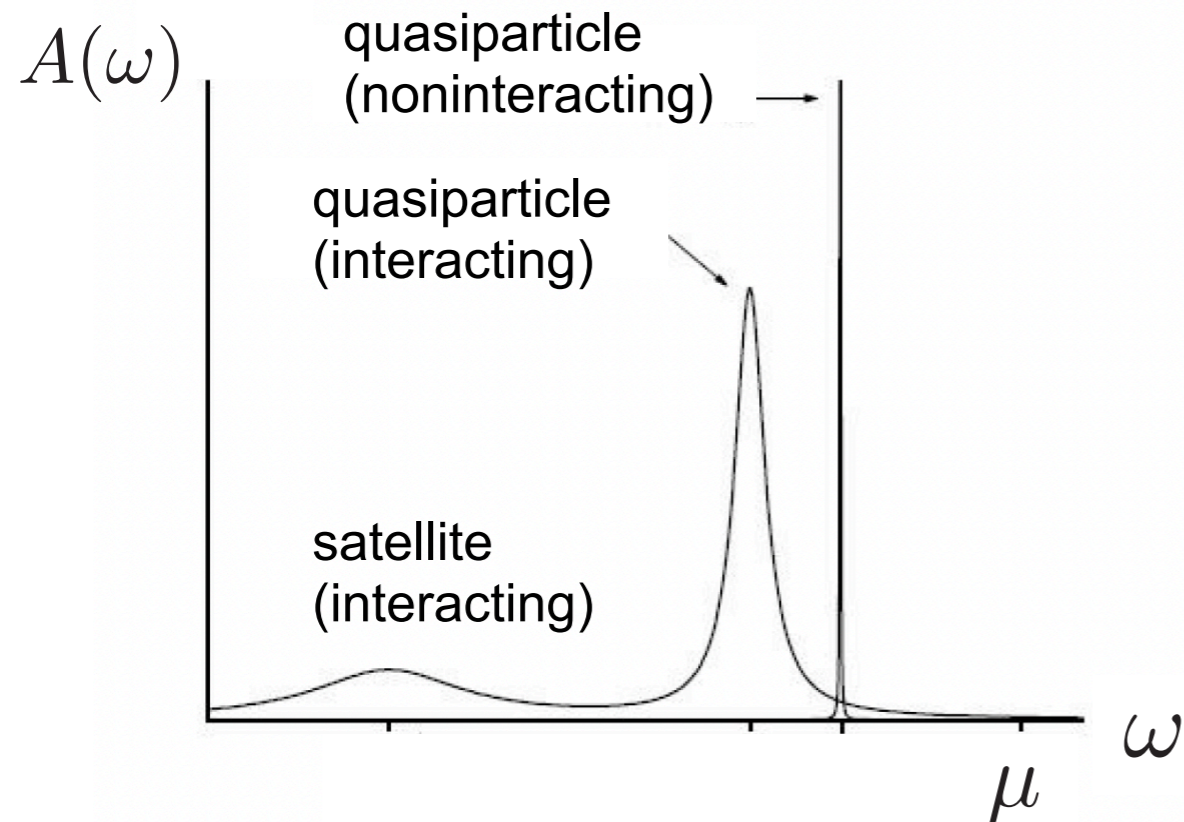
* SEKT (screened EKT)



Photoemission is a three-particle process: consider 2e1h and 2h1e excitations!

$$\epsilon_i^R = h_{ii} + \sum_j V_{ijij} n_j + \frac{1}{n_i} \sum_{jkl} W_{ijkl} \Gamma_{xc,klji}^{(2)}$$

$$\epsilon_i^A = h_{ii} + \sum_j V_{ijij} n_j - \frac{1}{1 - n_i} \left[\sum_j W_{ijji} n_j - \sum_{jkl} W_{ijkl} \Gamma_{xc,klji}^{(2)} \right]$$



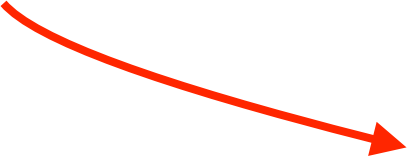
Why don't we use GF theory?

* Spectral function from the 1-GF

$$G(\mathbf{x}, \mathbf{x}'; \omega) = \lim_{\eta \rightarrow 0^+} \left[\sum_m \frac{f_m(\mathbf{x}) f_m^*(\mathbf{x}')}{\omega - (E_m^{N+1} - E_0^N) + i\eta} + \sum_n \frac{g_n(\mathbf{x}) g_n^*(\mathbf{x}')}{\omega - (E_0^N - E_n^{N-1}) - i\eta} \right]$$

$$f_m(\mathbf{x}) = \langle \Psi_0 | \hat{\psi}(\mathbf{x}) | \Psi_m^{N+1} \rangle$$

$$g_n(\mathbf{x}) = \langle \Psi_n^{N-1} | \hat{\psi}(\mathbf{x}) | \Psi_0 \rangle$$


$$A(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{\pi} \text{sign}(\mu - \omega) \text{Im} G(\mathbf{x}, \mathbf{x}'; \omega)$$

Why don't we use GF theory?

* Spectral function from the 1-GF

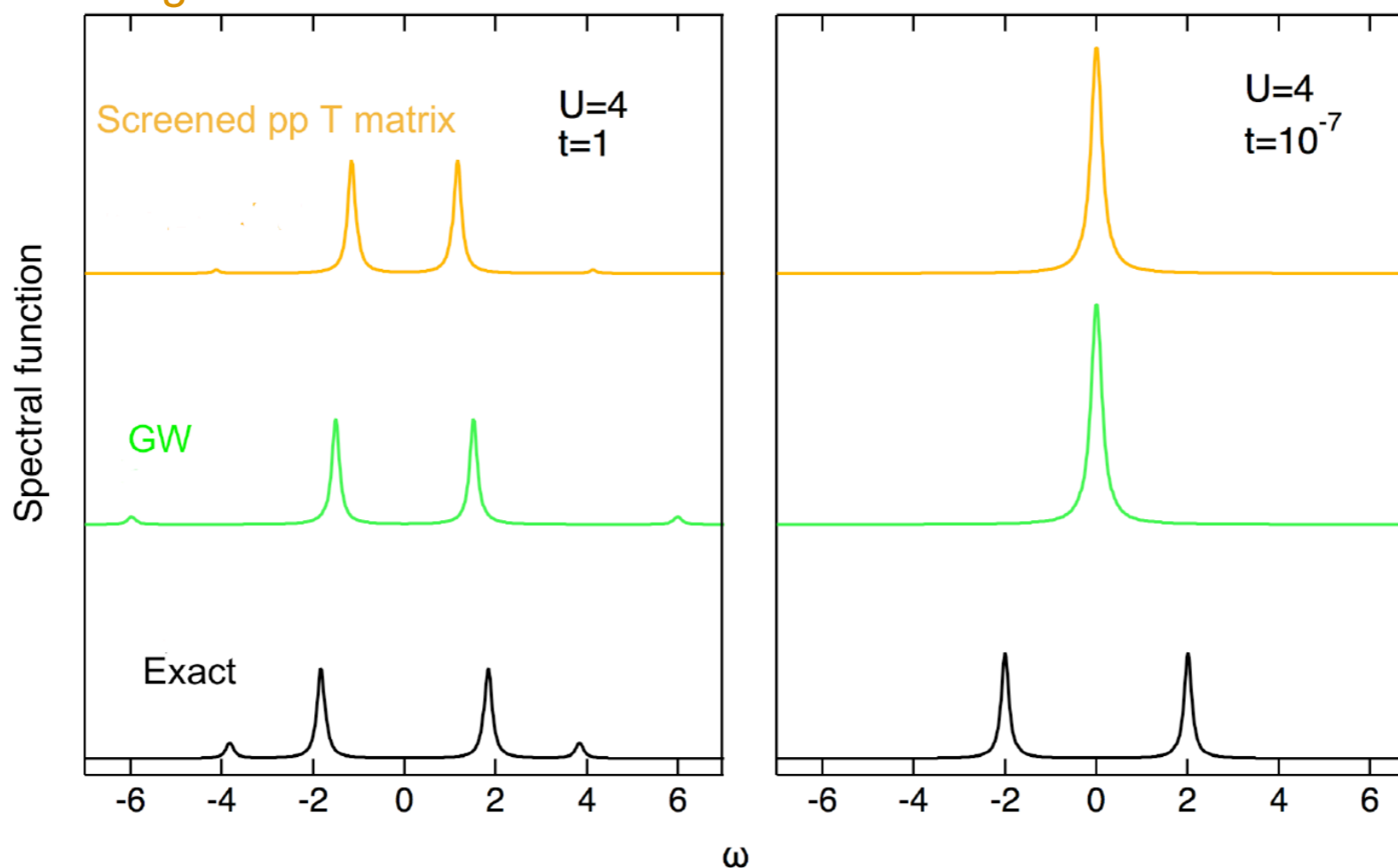
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Hubbard dimer at 1/2 filling



Atomic limit remains a challenge!

Why don't we use GF theory?

* Spectral function from the 1-GF

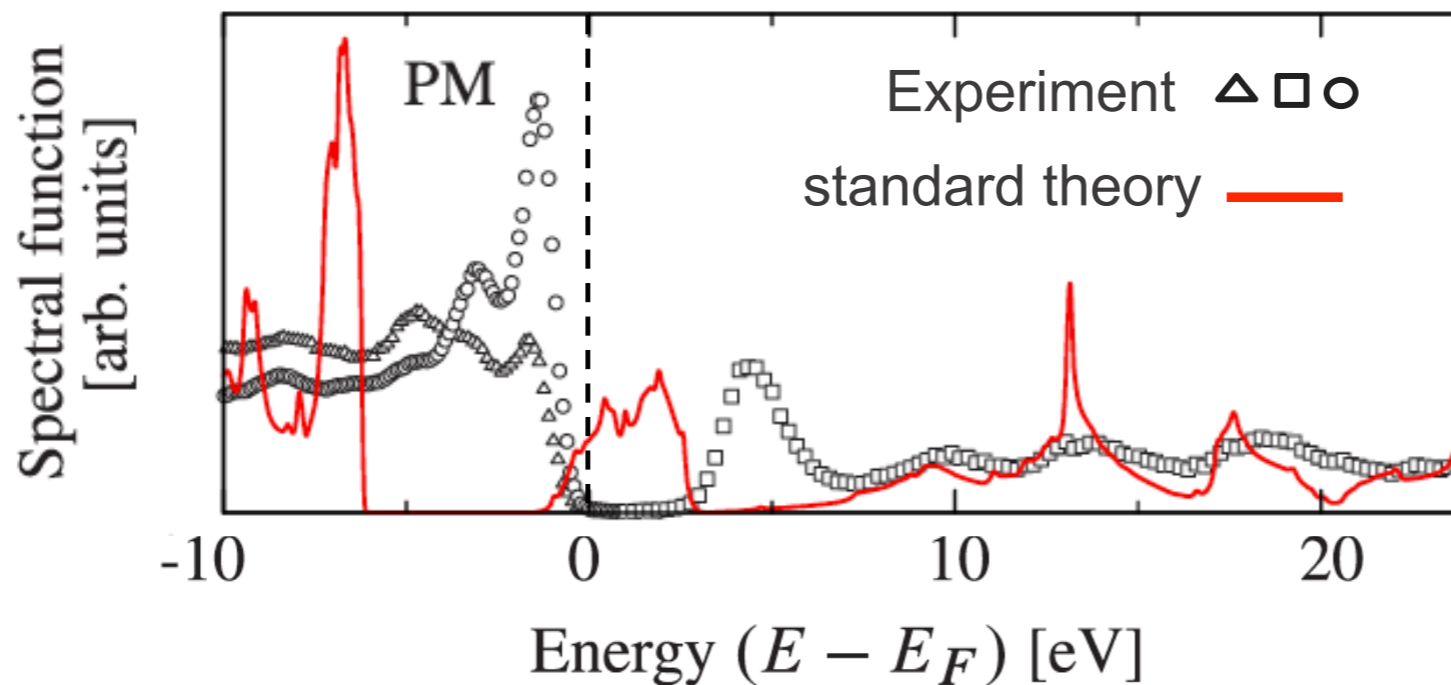
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$$A(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{\pi} \text{sign}(\mu - \omega) \text{Im} G(\mathbf{x}, \mathbf{x}'; \omega)$$

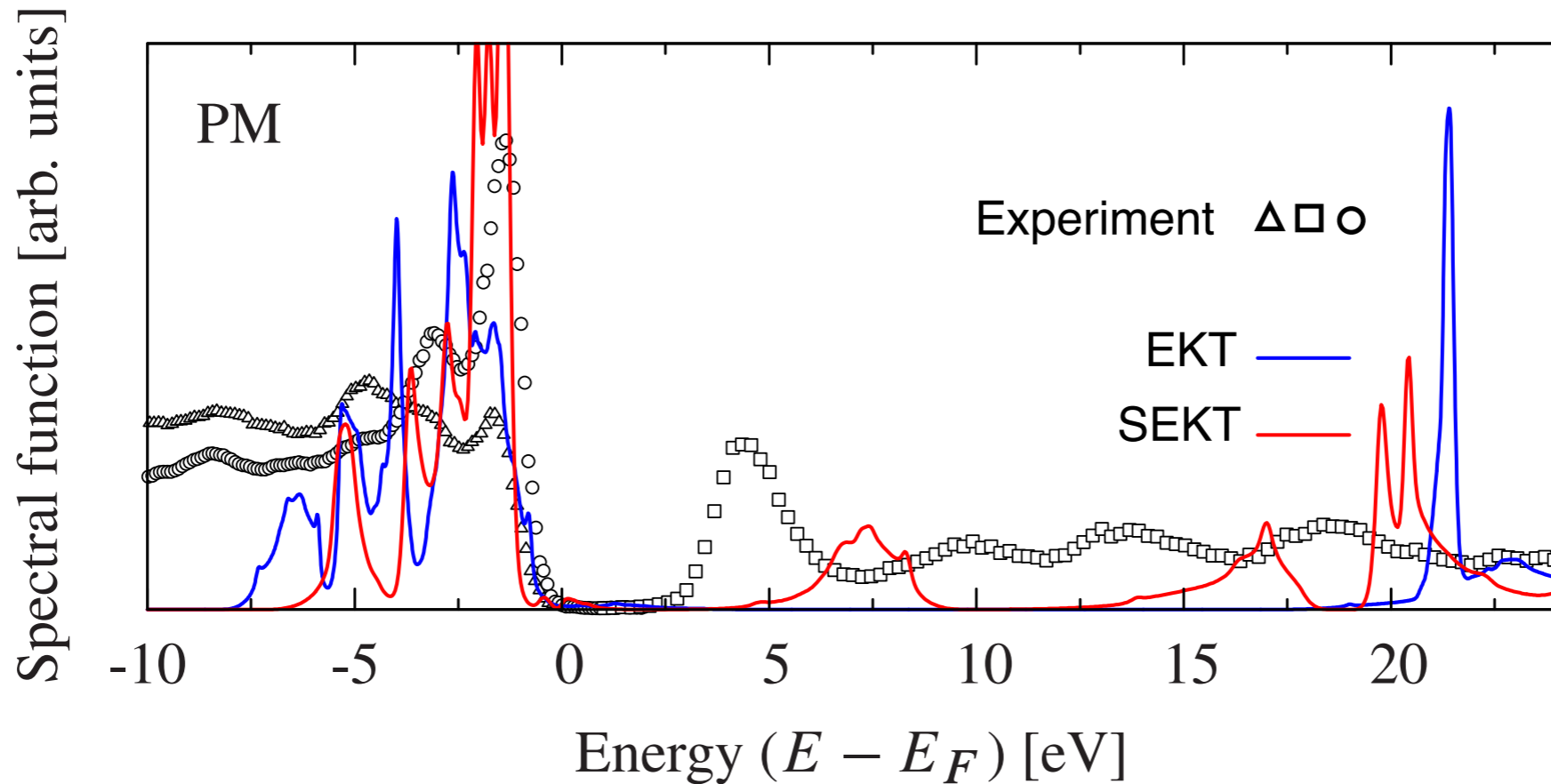
Realistic systems: bulk PM NiO



Strongly correlated systems remain a challenge!

EKT for realistic systems

Realistic systems:bulk PM NiO



Does EKT@RDMFT offer a path to PES of strongly correlated systems?

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