CORRELATION AND SPECTROSCOPY IN REDUCED DENSITY MATRIX FUNCTIONAL THEORY

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Acknowledgements

- Stefano Di Sabatino

  Laboratoire des Solides Irradiés, Ecole Polytechnique, Palaiseau, France
- Arjan Berger

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- Lucia Reining

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Many-Body problem

✳ Many-Body wavefunction

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) \longrightarrow \langle \Psi | \hat{O} | \Psi \rangle \qquad \mathbf{x} = \mathbf{r}s$$

✳ Reduced quantities

- density $\rho(\mathbf{x})$
- current-density $\mathbf{j}(\mathbf{x})$
- 1-body density matrix $\gamma(\mathbf{x}, \mathbf{x}')$
- 1-body Green's function $G(\mathbf{x}, \mathbf{x}'; \omega)$

$$A(\omega) = \sum_i |\Im G_{ii}(\omega)| / \pi$$

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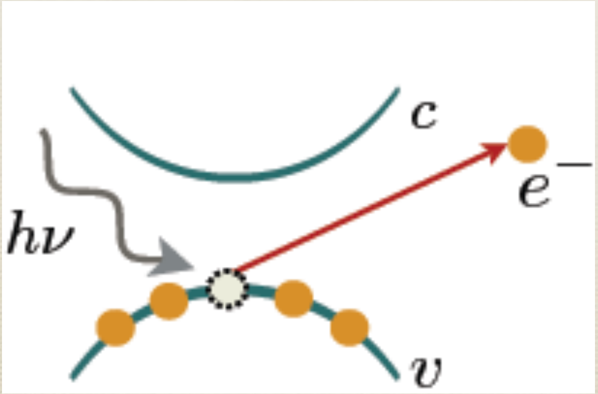
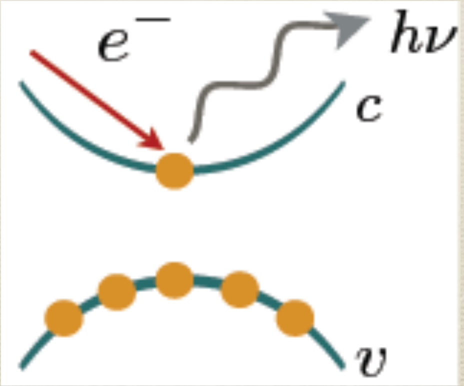


direct photoemission : $N \longrightarrow N\text{-}1$



inverse photoemission : $N \longrightarrow N\text{+}1$

Many-Body Perturbation Theory

- 1-body Green's function

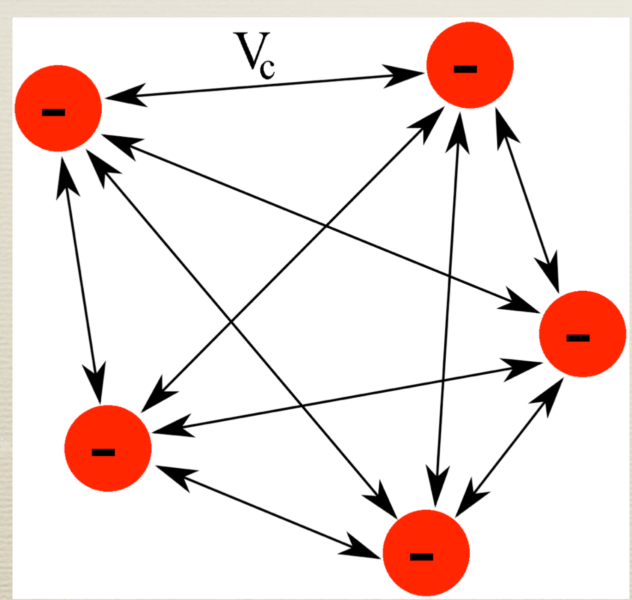
$$G(1,2) = -i\langle\Psi_0|\mathcal{T}[\hat{\psi}(1)\hat{\psi}^\dagger(2)]|\Psi_0\rangle$$

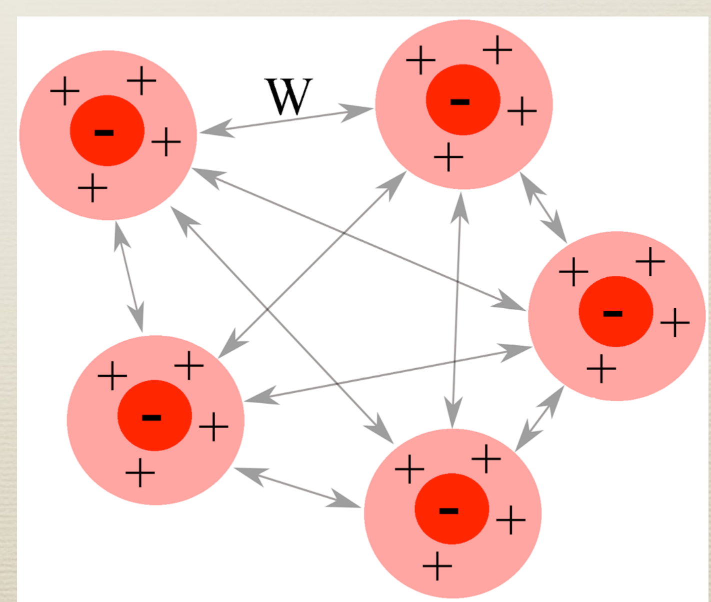
- Dyson equation

$$G = G_0 + G_0\Sigma G$$

- Self-energy

$$\Sigma = -iv_c G_2 G^{-1} \approx v_H + iGW$$

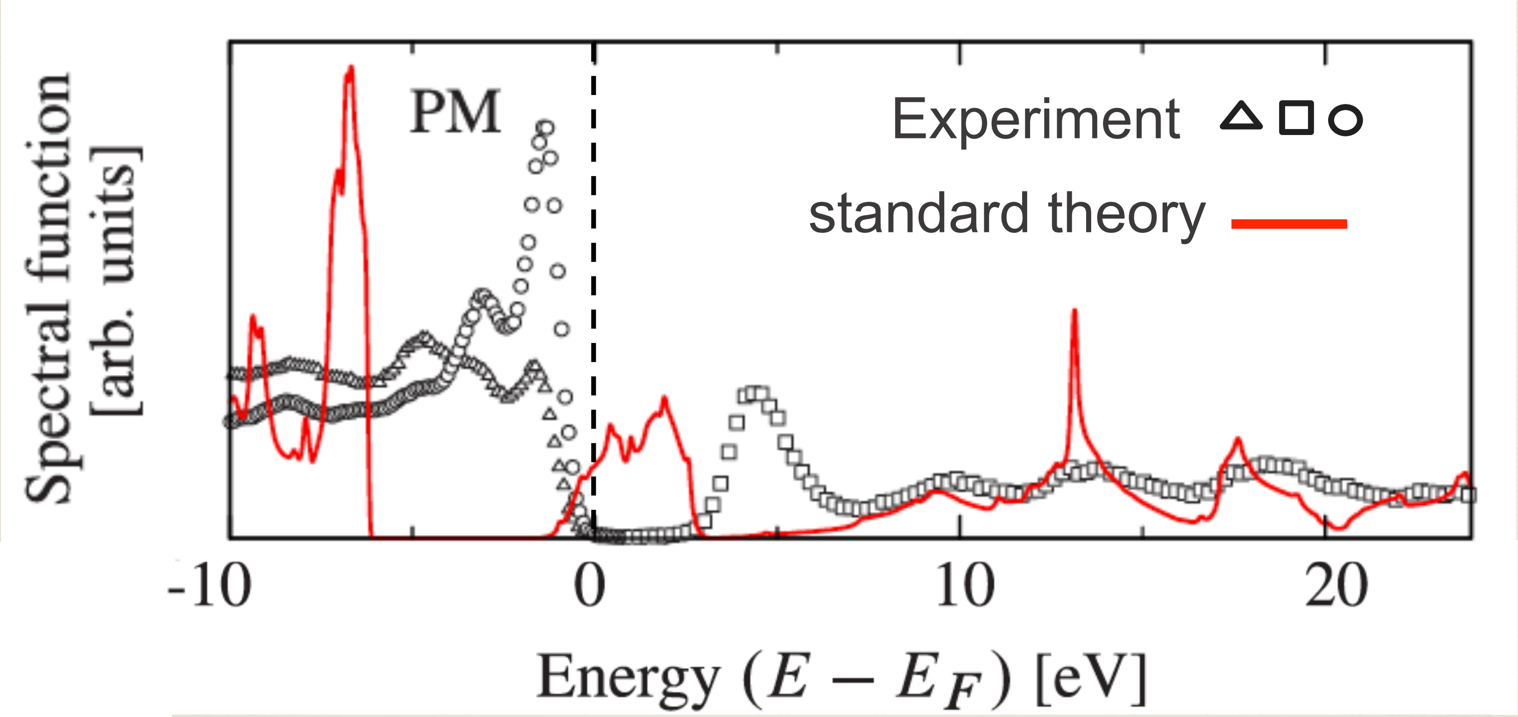




L. Hedin, Phys. Rev. 139, A796 (1965)

Strong correlation: how to capture it?

- Bulk NiO (ParaMagnetic phase)



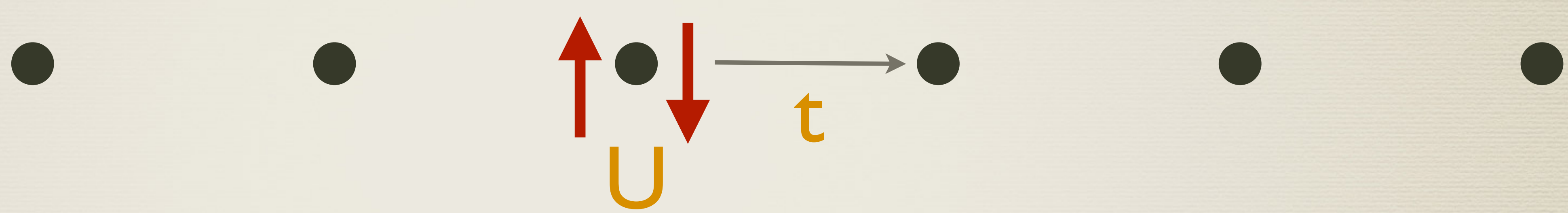
Stefano Di Sabatino's private communication

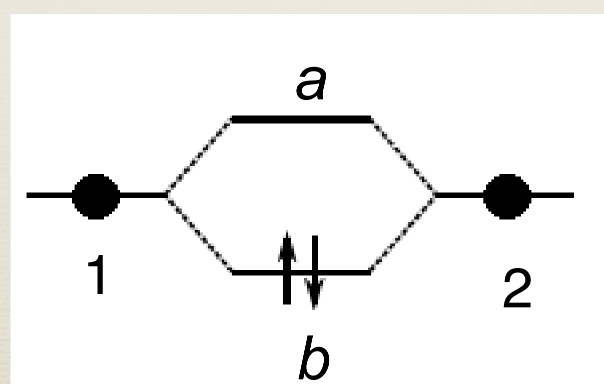
ferromagnetic planes are stacked antiferromagnetically along the [111] axes with their magnetic moments aligned in the [111] planes along one of the [11-2] directions

Test model

- Simple system
- Exact solution for benchmarking
- Direct link between molecular orbitals and natural orbitals
- Study quasi-degeneracies and (spin/charge) symmetry breaking

Hubbard model





natural orbitals
=
bonding/antibonding orbitals

Test model

- Simple system
- Exact solution for benchmarking
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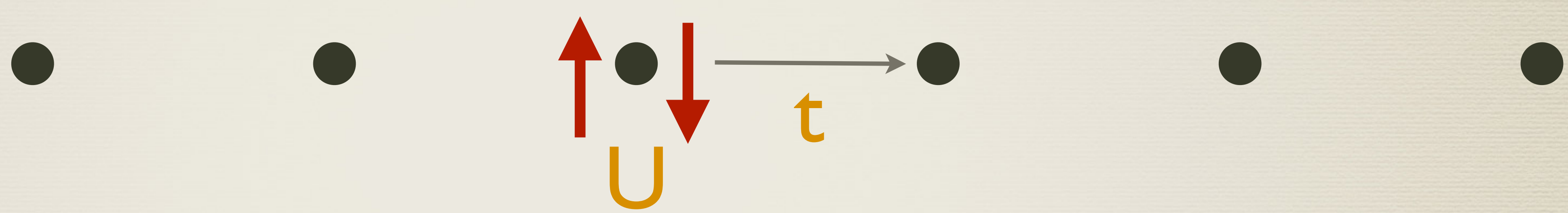
Hubbard model



Atomic limit $t \to 0$

at 1/2 filling

$$|{}^{S}\Psi_0\rangle = \frac{1}{\sqrt{2}}\left[|1\uparrow,2\downarrow\rangle - |1\downarrow,2\uparrow\rangle\right]$$

$$|{}^{T}\Psi\rangle = \begin{cases} \frac{1}{\sqrt{2}}\left[|1\uparrow,2\downarrow\rangle + |1\downarrow,2\uparrow\rangle\right] \\ |1\uparrow,2\uparrow\rangle \\ |1\downarrow,2\downarrow\rangle \end{cases}$$

$$|{}^{SB}\Psi\rangle = \begin{cases} |1\uparrow,2\downarrow\rangle \\ |1\downarrow,2\uparrow\rangle \end{cases}$$

degenerate

Outline

- Correlated or not correlated
- Observables in RDMFT: momentum distribution and spectral function
- Conclusions & Outlooks

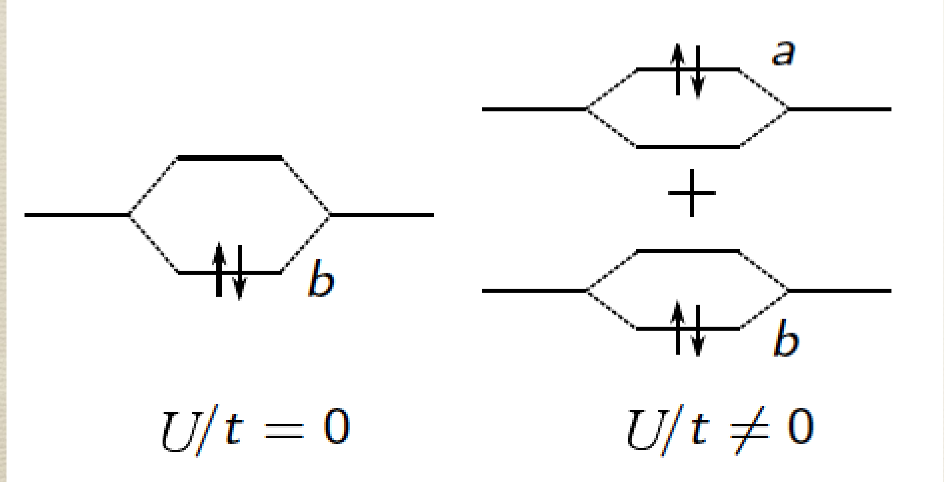
Occupation numbers and correlation

- Dimer at 1/2 filling

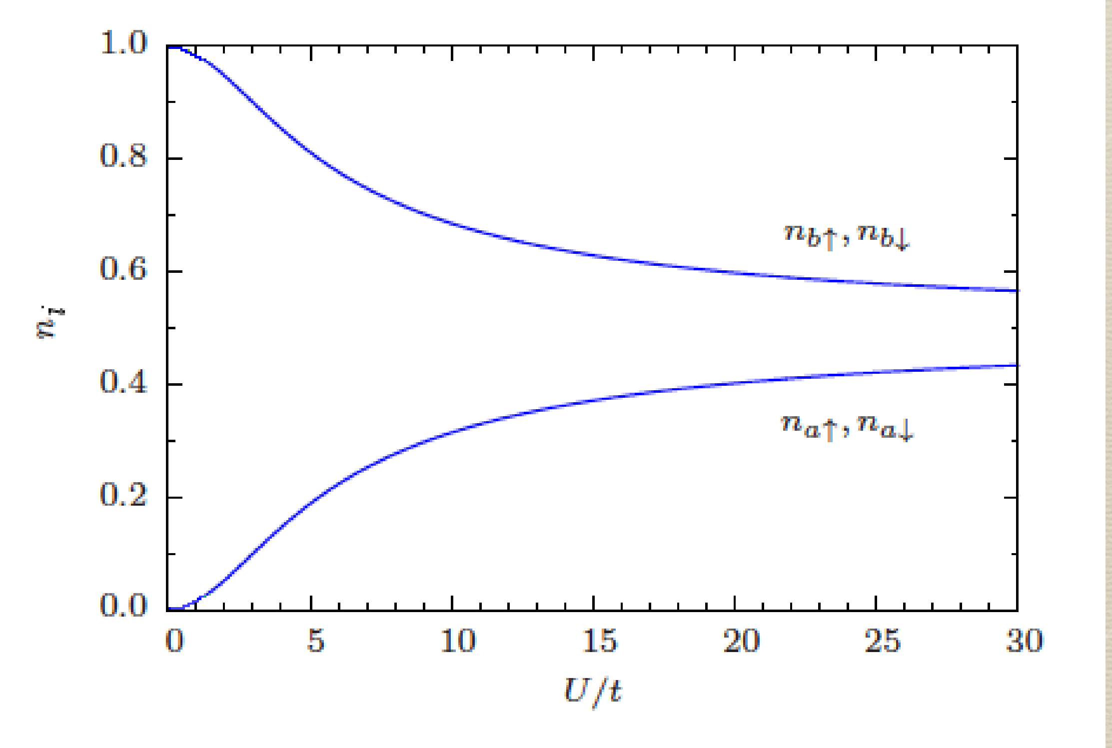
singlet wavefunction $\Psi_0(\mathbf{x}_1,\mathbf{x}_2)=\sum_{i=1,2} C_i\Phi_i(\mathbf{x}_1,\mathbf{x}_2)$

density matrix $\gamma(\mathbf{x},\mathbf{x}')=|C_1|^2\sum_{i=b\uparrow,b\downarrow}\phi_i(\mathbf{x})\phi_i^*(\mathbf{x}')+|C_2|^2\sum_{i=a\uparrow,a\downarrow}\phi_i(\mathbf{x})\phi_i^*(\mathbf{x}')$

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



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

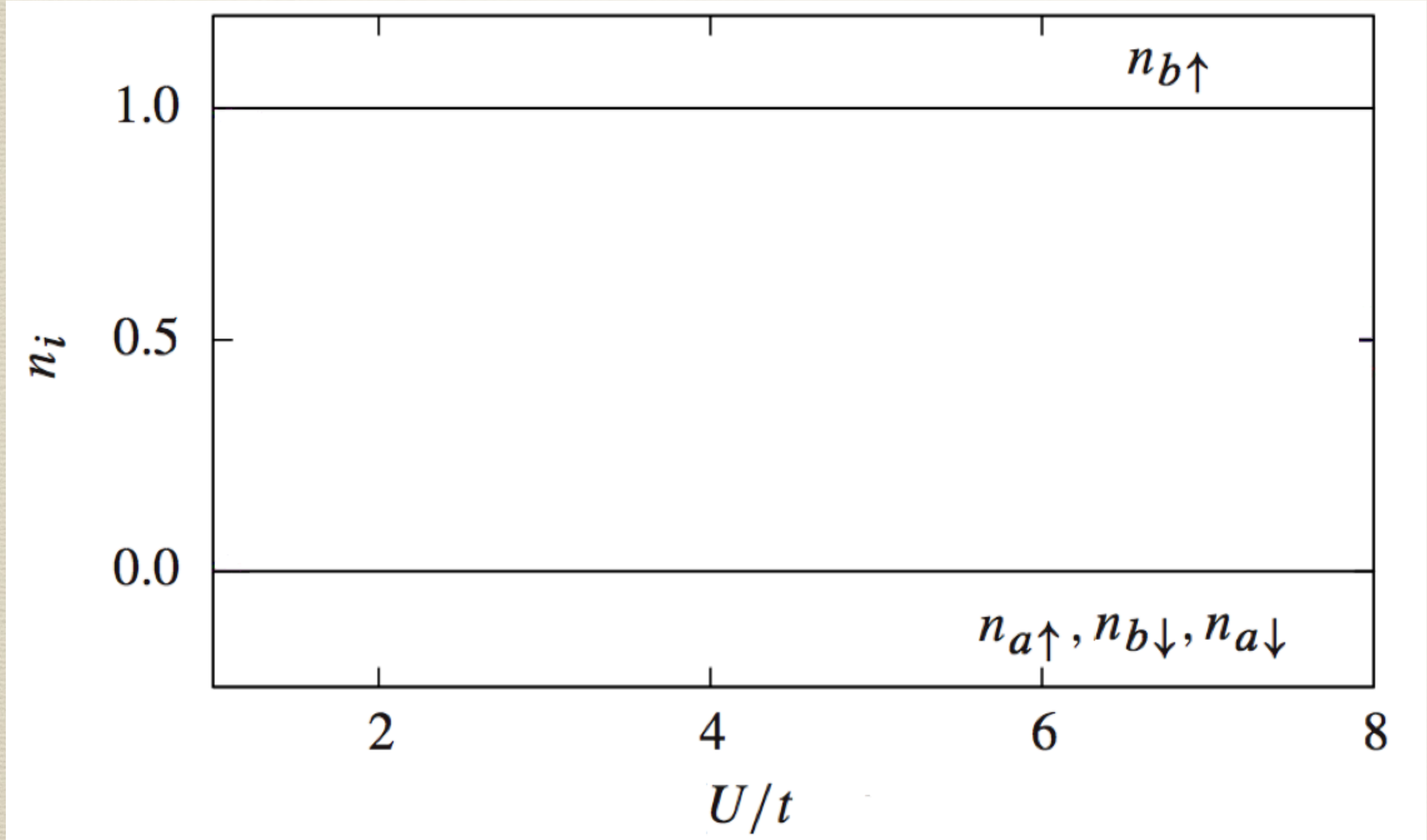


S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Occupation numbers and correlation

- Dimer at 1/4 filling

$$|\Psi_0\rangle = |b\uparrow\rangle$$

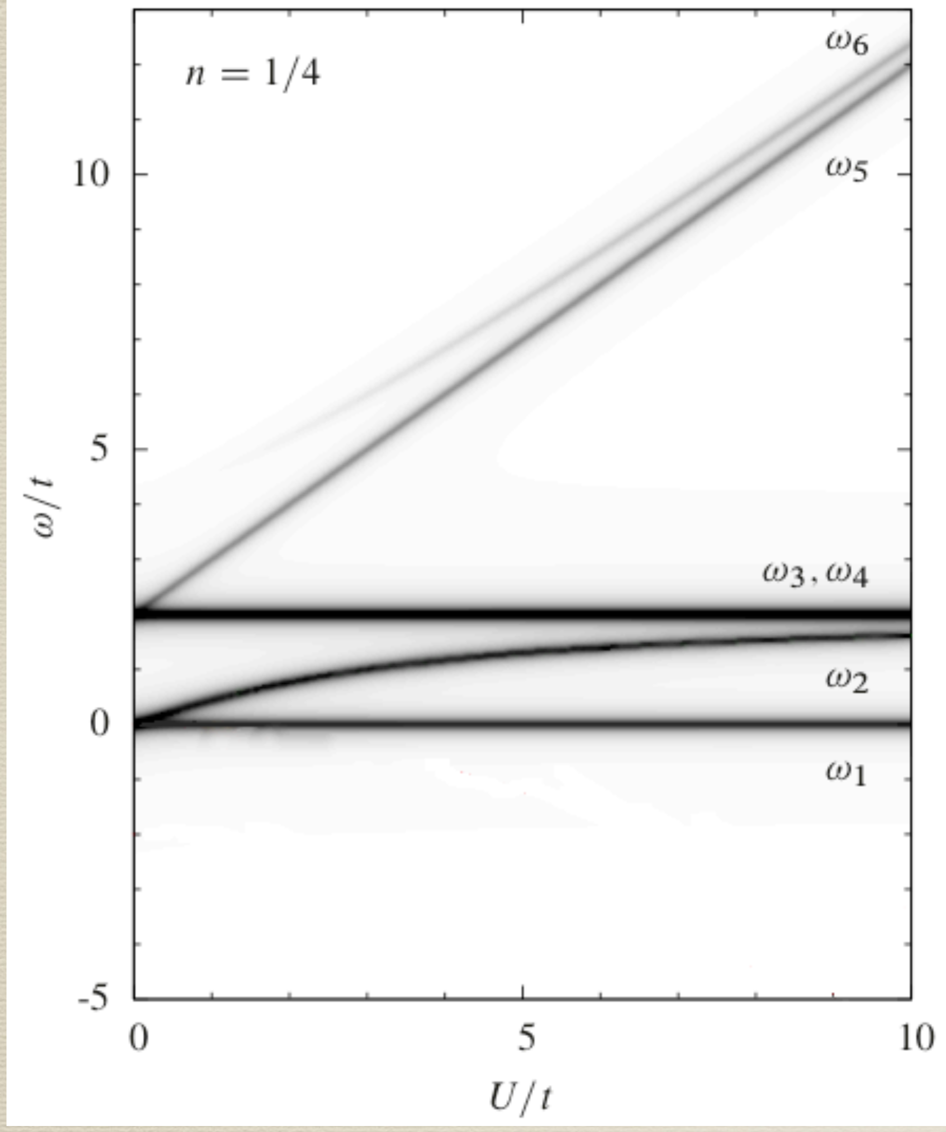


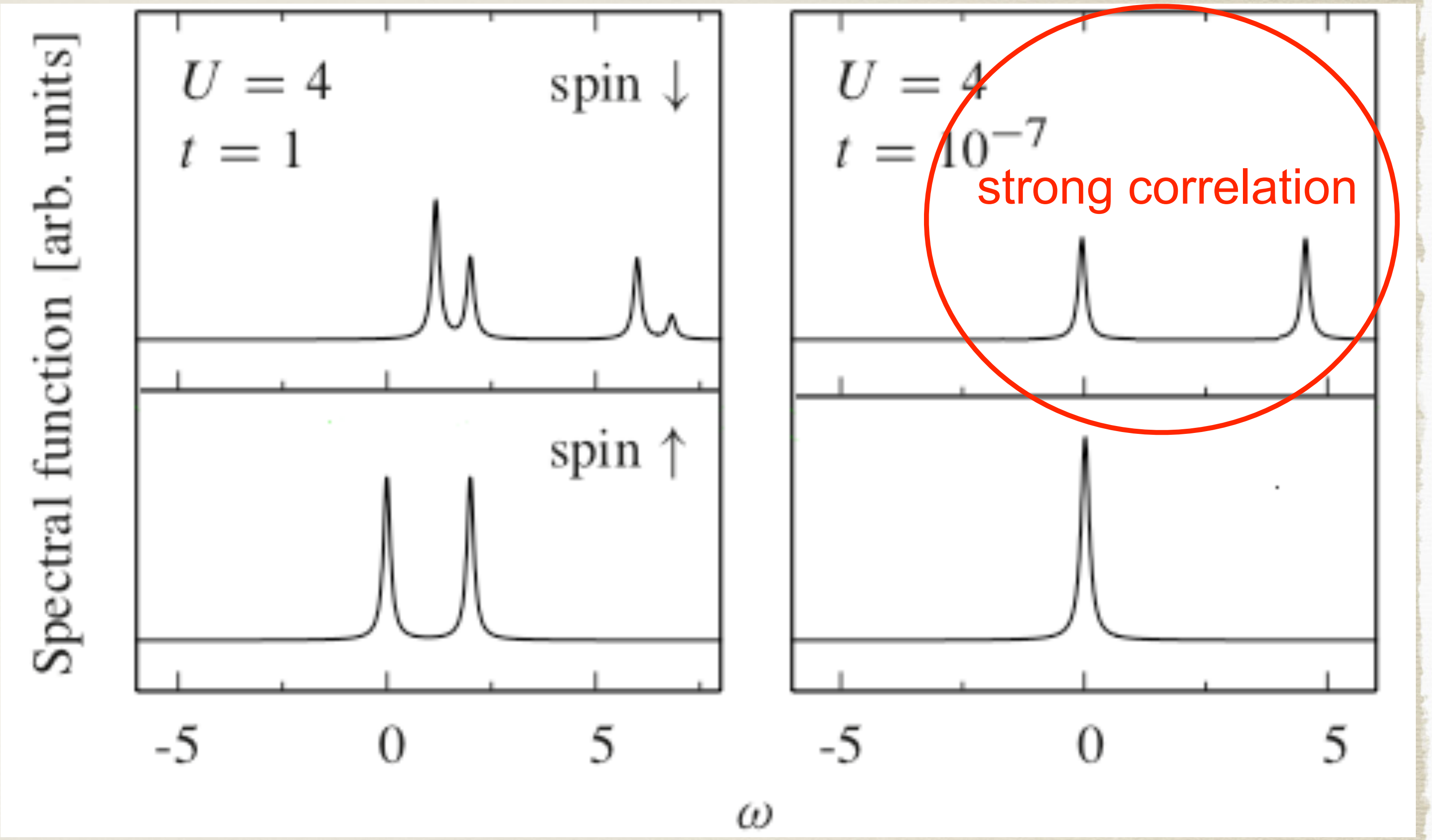
No correlation in the ground state

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Spectral function and correlation

- Dimer at 1/4 filling





There is correlation in the electron addition!

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Atomic limit at 1/2 filling

strong correlation $\left|{}^{S}\Psi_0\right\rangle = \frac{1}{\sqrt{2}}\left[\left|1\uparrow,2\downarrow\right\rangle - \left|1\downarrow,2\uparrow\right\rangle\right]$

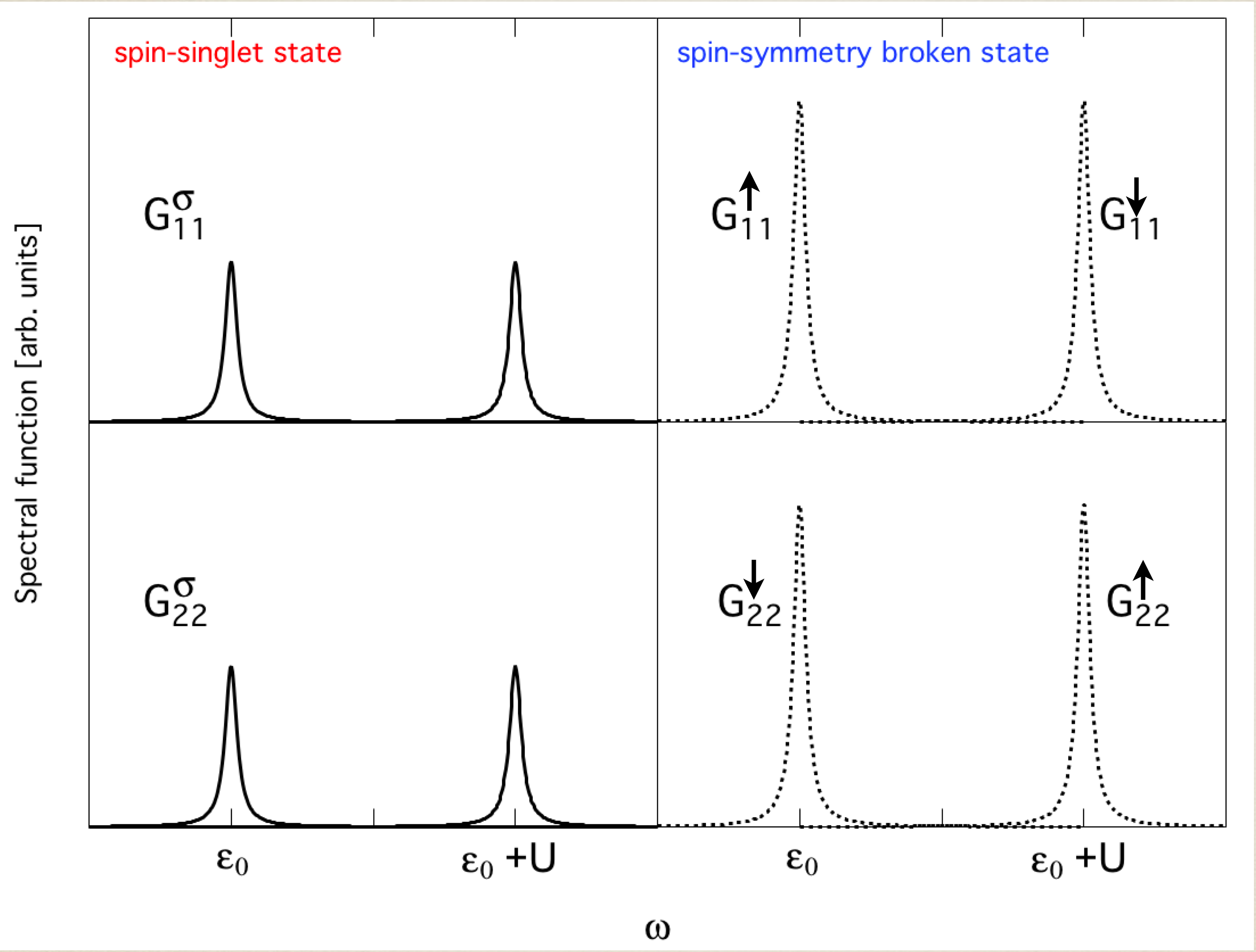
weak correlation $\left|{}^{SB}\Psi\right\rangle = \begin{cases}\left|1\uparrow,2\downarrow\right\rangle \\ \left|1\downarrow,2\uparrow\right\rangle\end{cases}$

} degenerate

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Spectral function and correlation

- Dimer at 1/2 filling

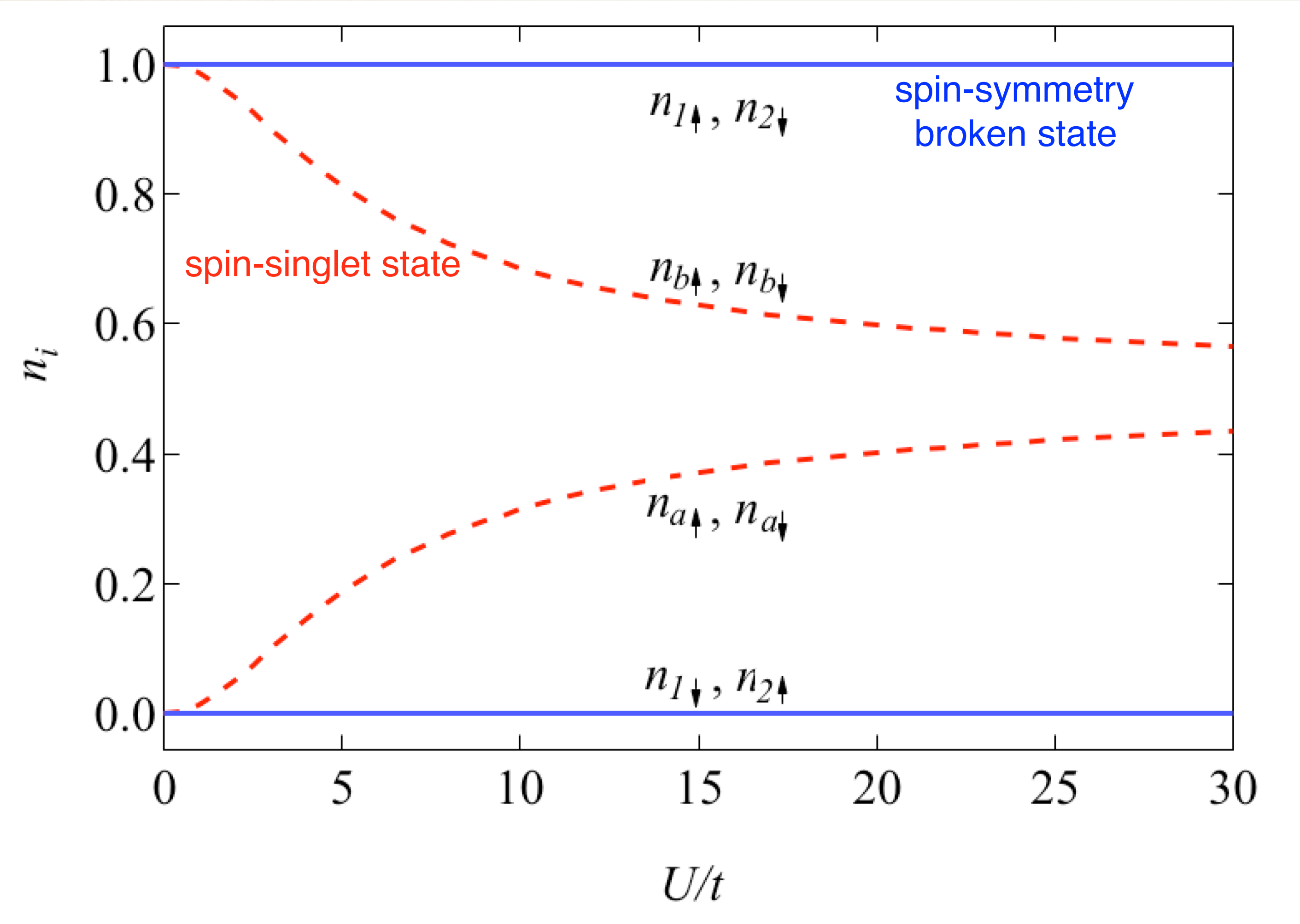


$$A^{\sigma}(\omega) = \sum_i \left|\Im G^{\sigma}_{ii}(\omega)\right| / \pi$$ **is the same for the two spin structures!**

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Occupation numbers and correlation

- Dimer at 1/2 filling

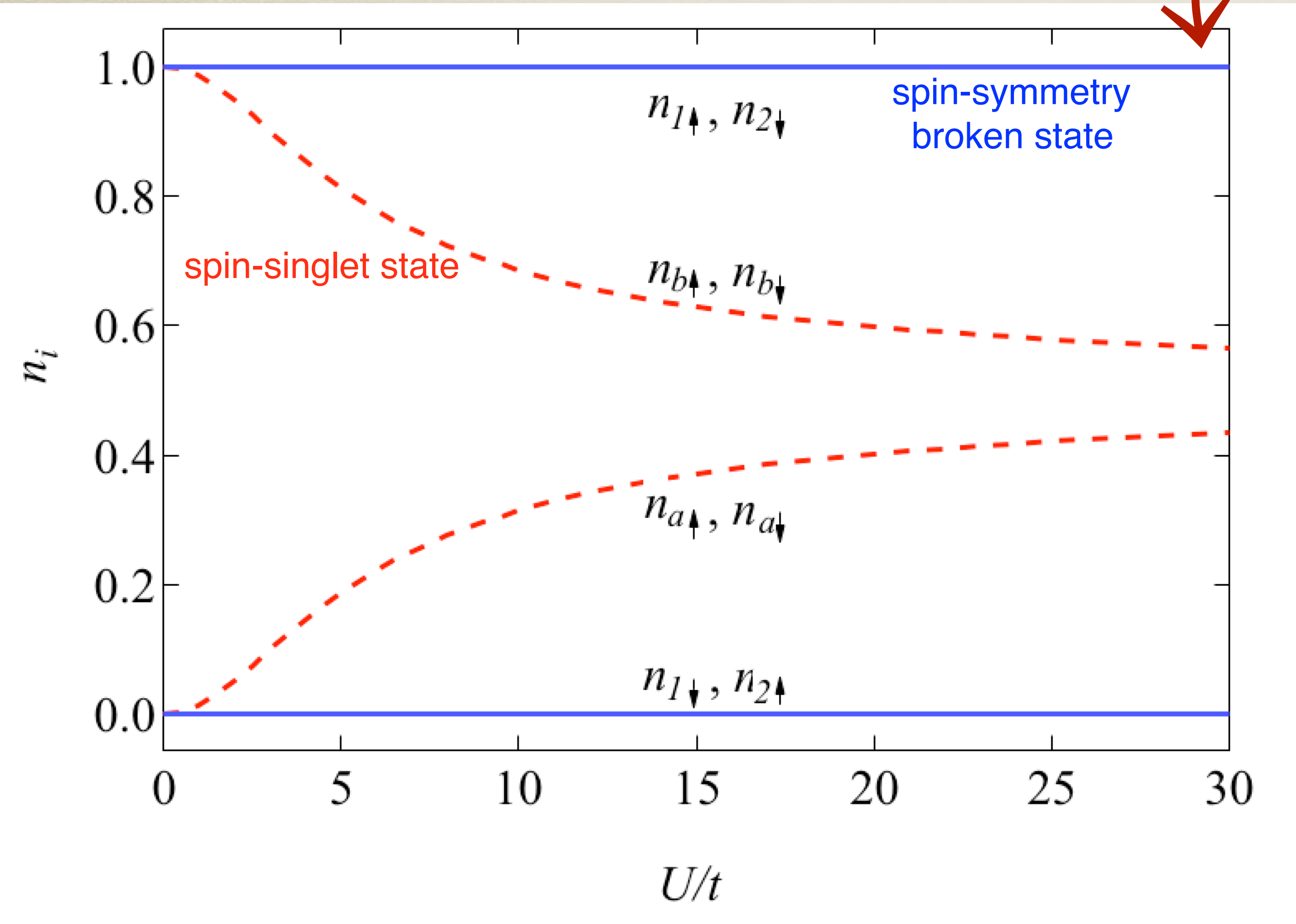


S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Occupation numbers and correlation

* Dimer at 1/2 filling

$$n(\mathbf{p}) \propto \int d\mathbf{r}d\mathbf{r}' e^{-i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')}\gamma(\mathbf{r},\mathbf{r}')$$



projection on the bonding/ antibonding basis

$$n^{S}_{b\sigma/a\sigma} = n^{SB}_{b\sigma/a\sigma} = \frac{1}{2}$$

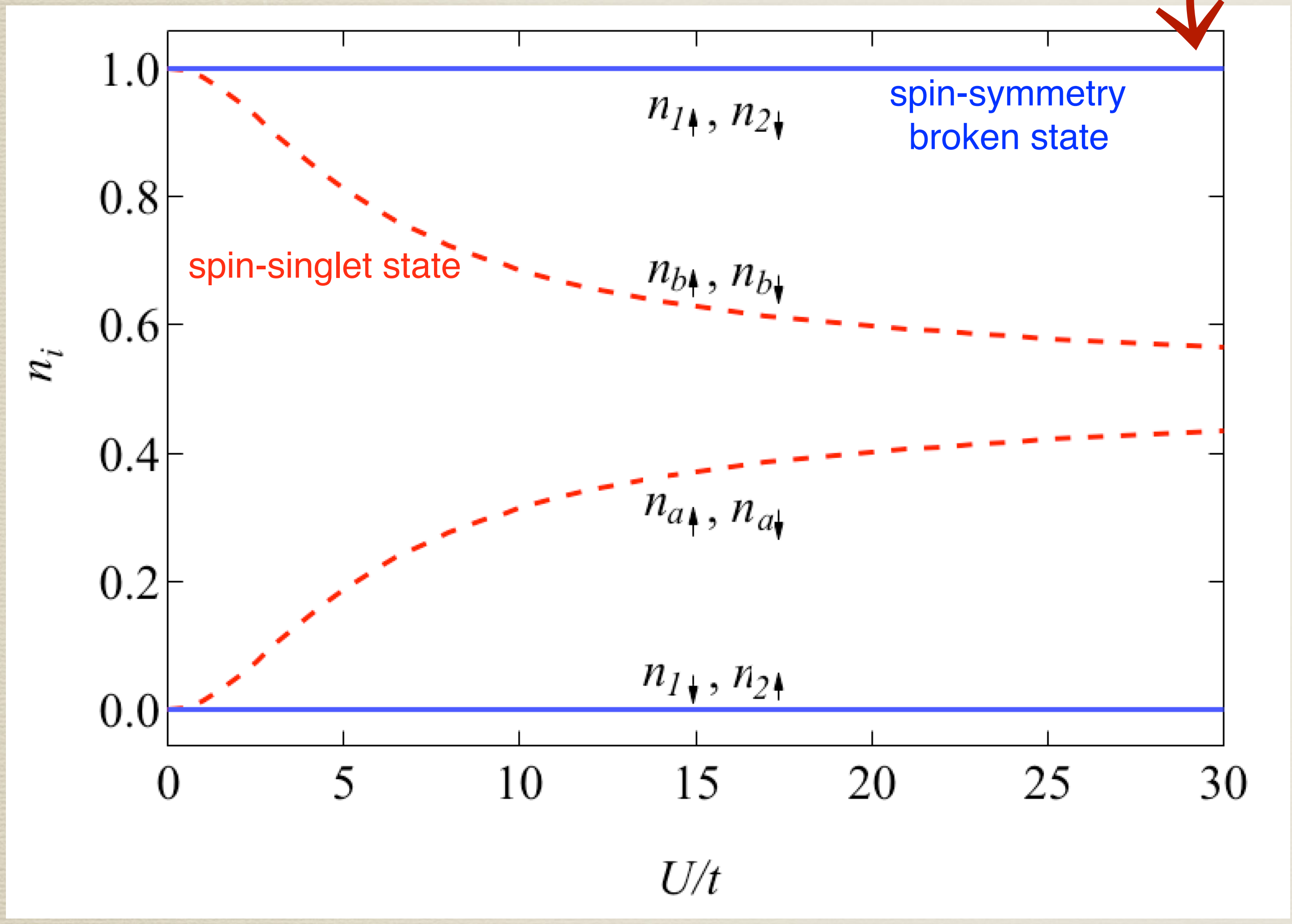
Spin-resolved momentum distribution is the same for the two spin strictures!

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Occupation numbers and correlation

- Dimer at 1/2 filling

$$n(\mathbf{p}) \propto \int d\mathbf{r}d\mathbf{r}' e^{-i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')}\gamma(\mathbf{r},\mathbf{r}')$$



projection on the bonding/ antibonding basis

$$n^{S}_{b\sigma/a\sigma} = n^{SB}_{b\sigma/a\sigma} = \frac{1}{2}$$

projection on the site basis

$$n^{S}_{i\sigma} = \frac{1}{2}$$

$$n^{SB}_{1\uparrow} = n^{SB}_{2\downarrow} = 1$$

$$n^{SB}_{1\downarrow} = n^{SB}_{2\uparrow} = 0$$

Spin- and space-resolved momentum distribution distinguishes the two spin strictures!

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Reduced Density-Matrix Functional Theory

✳ 1-body density matrix

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

$$\gamma \leftrightarrow \Psi$$

$$E_0[\gamma] = E_{kin}[\gamma] + E_{ext}[\gamma] + E_H[\gamma] + E_{xc}[\gamma]$$

✳ Exchange-correlation energy functional

$$E_{xc}[\gamma] = \int d\mathbf{x}\, d\mathbf{x}'\, v_c(\mathbf{x}, \mathbf{x}')\Gamma^{(2)}_{xc}[\gamma](\mathbf{x}, \mathbf{x}'; \mathbf{x}, \mathbf{x}')$$

$$\approx -\int d\mathbf{x}\, d\mathbf{x}'\, v_c(\mathbf{x}, \mathbf{x}')\gamma^\alpha(\mathbf{x}', \mathbf{x})\gamma^\alpha(\mathbf{x}, \mathbf{x}')$$

$$0.5 \leq \alpha \leq 1$$

Müller HF

natural orbitals and occupation numbers

$$\gamma^\alpha(\mathbf{x}, \mathbf{x}') = \sum_j n_j^\alpha \phi_j(\mathbf{x})\phi_j^*(\mathbf{x}')$$

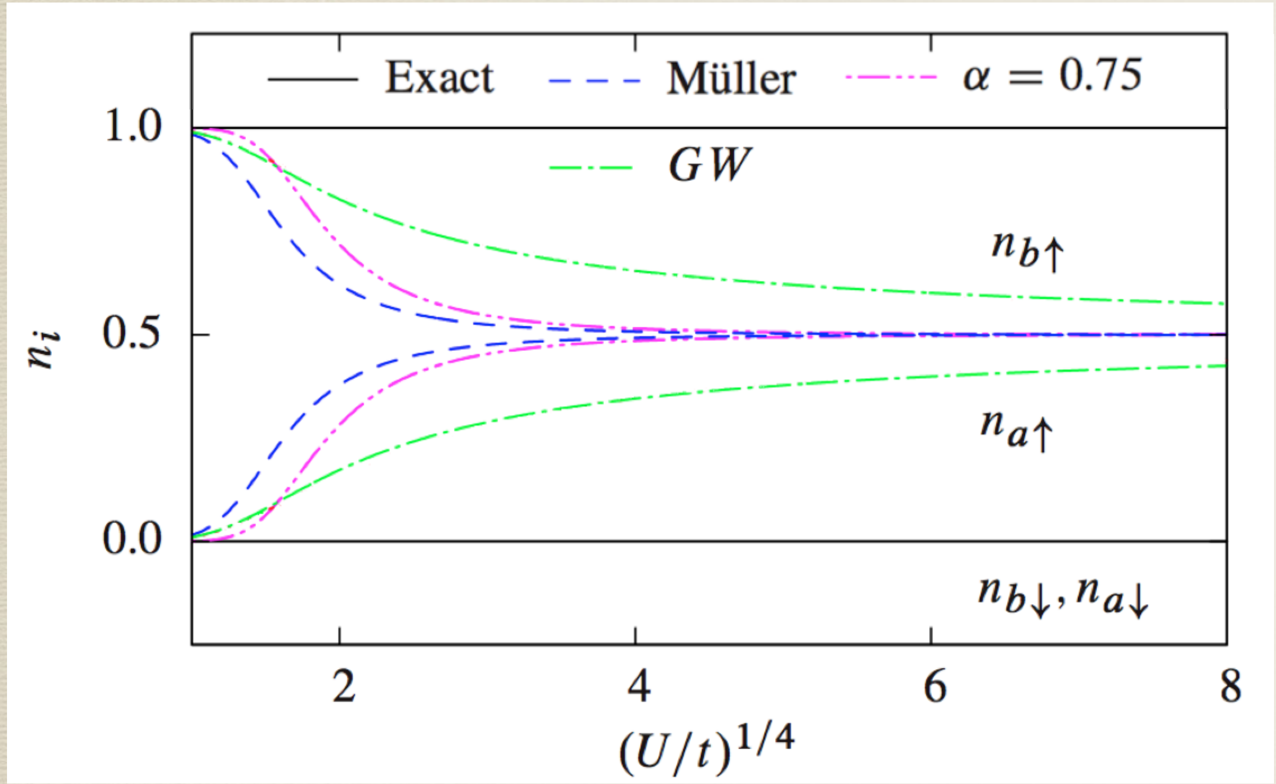
$$0 \leq n_i \leq 1$$

A. Müller, Phys. Lett. A 105, 446 (1984)

Occupation numbers in RDMFT

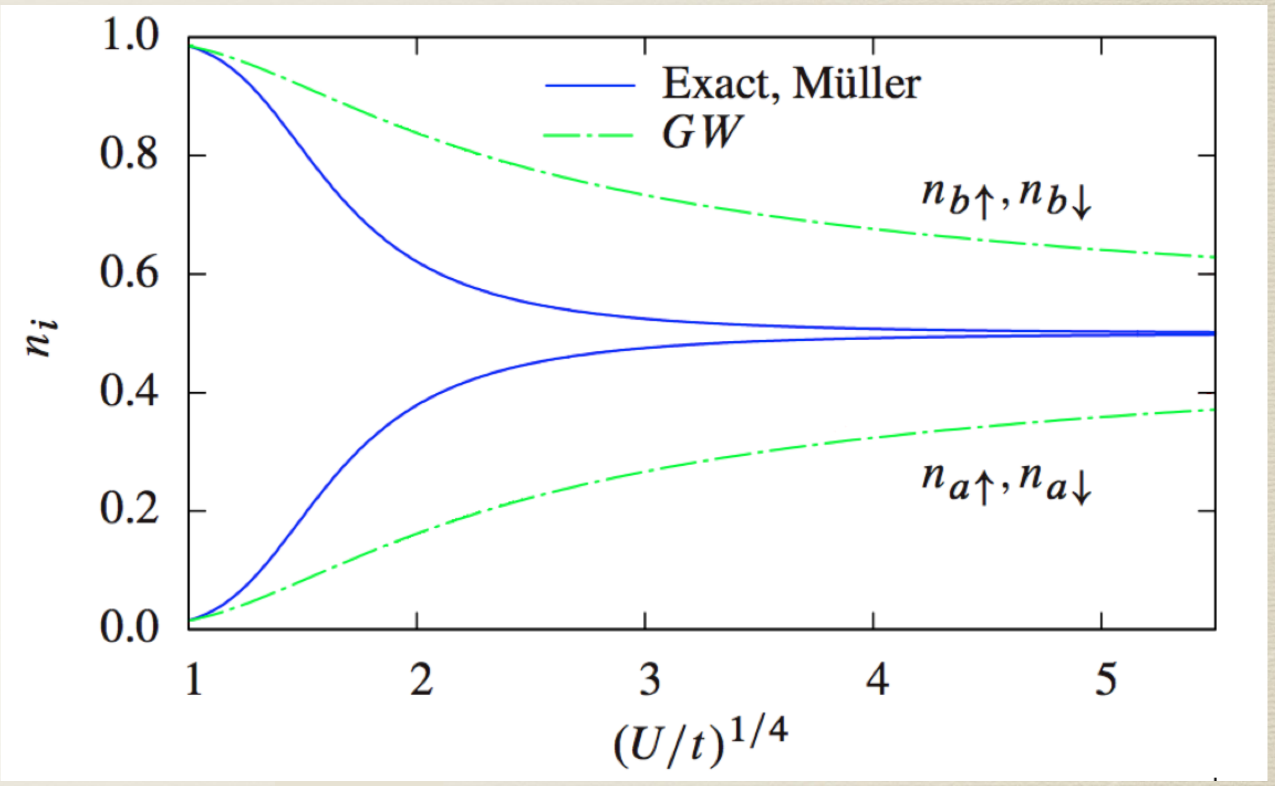
- Dimer at 1/4 filling

$$|\Psi_0\rangle = |b\uparrow\rangle$$



- Dimer at 1/2 filling

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



$$\Gamma^{(2)}_\alpha = \gamma\gamma - \gamma^\alpha\gamma^\alpha, \;\; (0.5 \leq \alpha \leq 1)$$

HF exact at 1/4 filling, Müller exact at 1/2 filling

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., J. Chem. Phys. 143, 024108 (2015)

Spectral function in RDMFT???

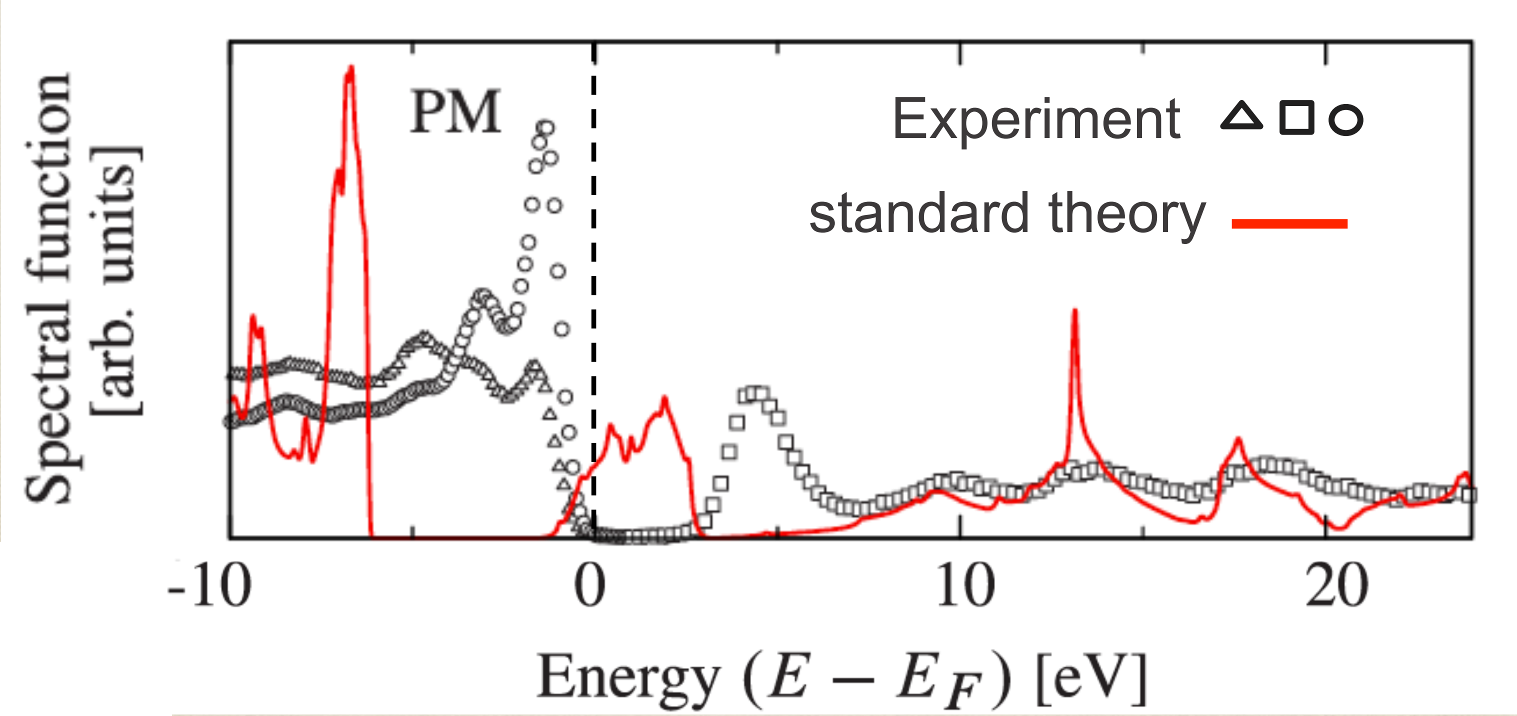
Spectral function in MBPT

spectral function

$$A(\omega) = \sum_i |\Im G_{ii}(\omega)| / \pi$$

one-body Green's function

$$G_{ii}(\omega) = \underbrace{\sum_k \frac{B_{ii}^{k,R}}{\omega - \epsilon_k^R}}_{direct\ photoemission\ (G_{ii}^R)} + \underbrace{\sum_k \frac{B_{ii}^{k,A}}{\omega - \epsilon_k^A}}_{inverse\ photoemission\ (G_{ii}^A)}$$



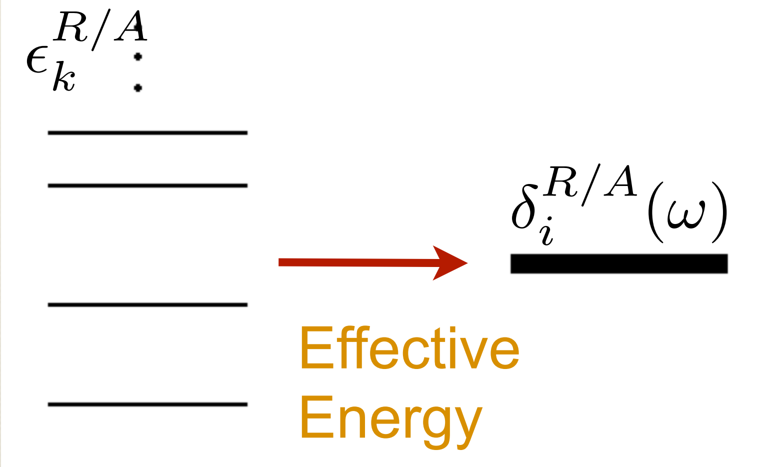
Stefano Di Sabatino's private communication

The Many-Body Effective Energy Theory

1. Treat separately $G_{ii}^R(\omega)$ and $G_{ii}^A(\omega)$ as it is done in experiments.

$$G_{ii}(\omega) = \underbrace{\sum_k \frac{B_{ii}^{k,R}}{\omega - \epsilon_k^R}}_{direct\ photoemission\,(G_{ii}^R)} + \underbrace{\sum_k \frac{B_{ii}^{k,A}}{\omega - \epsilon_k^A}}_{inverse\ photoemission\,(G_{ii}^A)}$$

2. Introduce a dynamical effective energy, $\delta_i^{R/A}(\omega)$, which describes all the poles of $G_{ii}^{R/A}(\omega)$.
   This effective energy can be expressed in terms of n-body density matrices.



3. Truncate the series in terms of density matrices to low order to obtain practical approximations.

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., Phys. Rev. B 94, 155141 (2016)

The Many-Body Effective Energy Theory

- Spectral representation of G

$$G_{ii}(\omega) = \sum_k \frac{B_{ii}^{k,R}}{\omega - \epsilon_k^R} + \sum_k \frac{B_{ii}^{k,A}}{\omega - \epsilon_k^A}$$

$$B_{ii}^{k,R} = \langle \Psi_0 | \hat{c}_i^\dagger | \Psi_k^{N-1} \rangle \langle \Psi_k^{N-1} | \hat{c}_i | \Psi_0 \rangle$$

$$B_{ii}^{k,A} = \langle \Psi_0 | \hat{c}_i | \Psi_k^{N+1} \rangle \langle \Psi_k^{N+1} | \hat{c}_i^\dagger | \Psi_0 \rangle$$

basis of natural orbitals

$$\sum_k B_{ii}^{k,R} = n_i$$

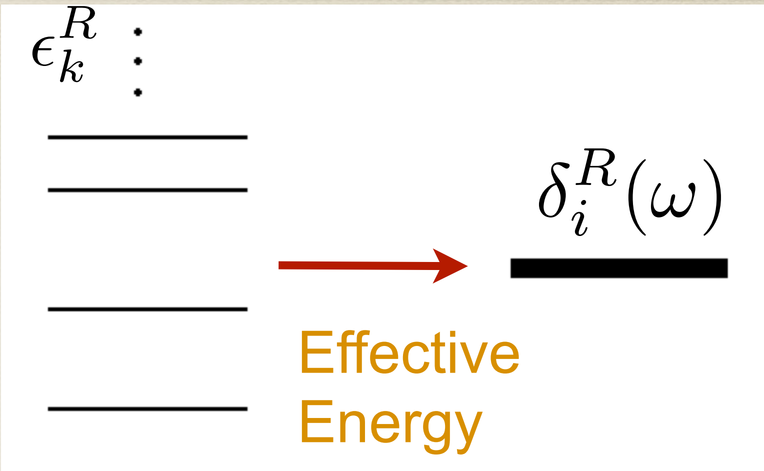
$$\sum_k B_{ii}^{k,A} = 1 - n_i$$

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., Phys. Rev. B 94, 155141 (2016)

The Many-Body Effective Energy Theory

* Removal part of G

$$G_{ii}^{R}(\omega) = \sum_k \frac{B_{ii}^{k,R}}{\omega - \epsilon_k^R} = \frac{\sum_k B_{ii}^{k,R}}{\omega - \delta_i^R(\omega)} = \frac{n_i}{\omega - \delta_i^R(\omega)}$$



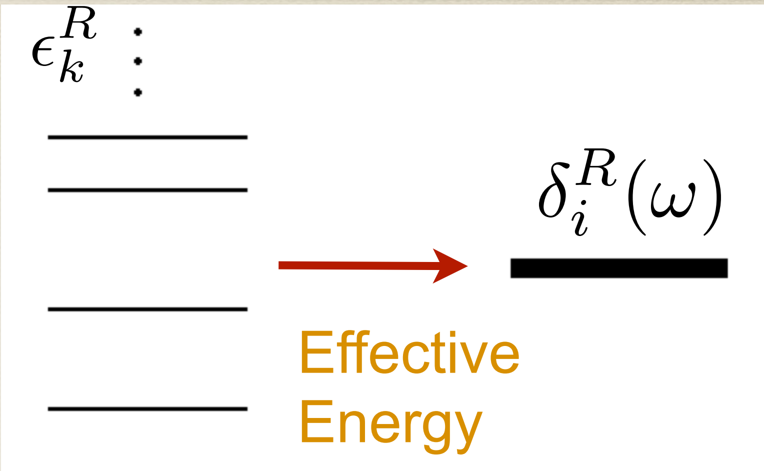
$$\delta_i^R(\omega) = \frac{1}{G_{ii}^R(\omega)} \sum_k \frac{\langle \Psi_0 | \hat{c}_i^\dagger | \Psi_k^{N-1} \rangle \langle \Psi_k^{N-1} | \hat{c}_i | \Psi_0 \rangle}{\omega - \epsilon_k^R} \epsilon_k^R$$

S. Di Sabatino, J.A. Berger, L. Reining, and P. R., Phys. Rev. B 94, 155141 (2016)

The Many-Body Effective Energy Theory

- Removal part of G

$$G^R_{ii}(\omega) = \sum_k \frac{B^{k,R}_{ii}}{\omega - \epsilon^R_k} = \frac{\sum_k B^{k,R}_{ii}}{\omega - \delta^R_i(\omega)} = \frac{n_i}{\omega - \delta^R_i(\omega)}$$



$$\delta^R_i(\omega) = \frac{1}{G^R_{ii}(\omega)} \sum_k \frac{\langle \Psi_0 | \hat{c}^\dagger_i | \Psi^{N-1}_k \rangle \langle \Psi^{N-1}_k | [\hat{c}_i, \hat{H}] | \Psi_0 \rangle}{\omega - \epsilon^R_k} = \frac{\tilde{G}^R_{ii}(\omega)}{G^R_{ii}(\omega)}$$

$$= \frac{\tilde{n}^R_i}{n_i} \frac{\omega - \frac{\tilde{G}^R_{ii}(\omega)}{G^R_{ii}(\omega)}}{\omega - \frac{\tilde{\tilde{G}}^R_{ii}(\omega)}{\tilde{G}^R_{ii}(\omega)}}$$

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The Many-Body Effective Energy Theory

- Approximations to the removal effective energy $\delta_i^R(\omega)$

$$\delta_i^{R,(1)} = \frac{\tilde{n}_i^R}{n_i}$$

$$\delta_i^{R,(2)}(\omega) = \frac{\tilde{n}_i^R}{n_i} \frac{\omega - \frac{\tilde{n}_i^R}{n_i}}{\omega - \frac{\tilde{\tilde{n}}_i^R}{\tilde{n}_i^R}}$$

$\delta_i^{R,(n)}$ in terms of reduced density matrices

$$\tilde{n}_i^R = \langle \Psi_0 \hat{c}_i^\dagger [\hat{c}_i, \hat{H}] \rangle \Psi_0 = h_{ii} n_i + \sum_{jkl} V_{ijkl} \Gamma^{(2)}_{klji}$$

$$\tilde{\tilde{n}}_i^R = \langle \Psi_0 [\hat{H}, \hat{c}_i^\dagger][\hat{c}_i, \hat{H}] \rangle \Psi_0 = h_{ii}^2 n_i + h_{ii} \sum_{jkl} \left(V_{ijkl} \Gamma^{(2)}_{klji} + V_{klij} \Gamma^{(2)}_{ijlk} \right)$$

$$+ \sum_{jklqs} V_{klij} V_{ijqs} \Gamma^{(2)}_{qslk} + \sum_{jklpqs} V_{klij} V_{ipqs} \Gamma^{(3)}_{qjsplk}$$

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The Many-Body Effective Energy Theory

- Approximations to $\delta_i^R(\omega)$ and $\delta_i^A(\omega)$

$$\delta_i^{R,(1)} = \frac{\tilde{n}_i^R}{n_i}$$

$$\delta_i^{A,(1)} = \frac{\tilde{n}_i^A}{1-n_i}$$

$$\delta_i^{R,(2)}(\omega) = \frac{\tilde{n}_i^R}{n_i} \frac{\omega - \frac{\tilde{n}_i^R}{n_i}}{\omega - \frac{\tilde{\tilde{n}}_i^R}{\tilde{n}_i^R}}$$

$$\delta_i^{A,(2)}(\omega) = \frac{\tilde{n}_i^A}{1-n_i} \frac{\omega - \frac{\tilde{n}_i^A}{1-n_i}}{\omega - \frac{\tilde{\tilde{n}}_i^A}{\tilde{n}_i^A}}$$

- Spectral function

$$A_{ii}(\omega) = n_i \delta(\omega - \delta_i^R(\omega)) + (1-n_i)\delta(\omega - \delta_i^A(\omega))$$

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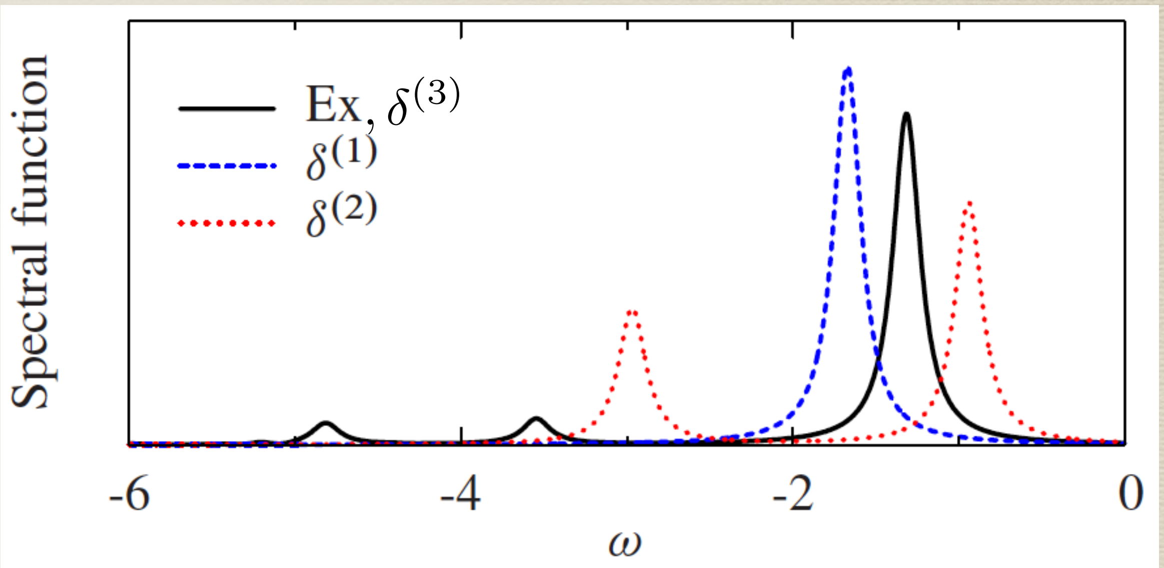
Physical meaning of $\delta_i^{(R/A)}(\omega)$

- Approximations to $\delta_i^{R/A}(\omega)$ and moments of $G_{ii}^{R/A}$

$$\delta_i^{R,(1)} = \frac{\sum_k B_{ii}^{k,R}\epsilon_k^R}{\sum_k B_{ii}^{k,R}} = \mu_{1,i}^R$$

$$\delta_i^{R,(2)} \rightarrow \mu_{1,i}^R,\ \mu_{2,i}^R$$

$$\delta_i^{R,(n)} \rightarrow \mu_{1,i}^R,\ \mu_{2,i}^R, \ldots, \mu_{n,i}^R$$



- Total energy

$$E_0 = \frac{1}{2}\sum_i \left(\sum_k B_{ii}^{k,R}\epsilon_k + n_i h_{ii}\right) = \frac{1}{2}\sum_i n_i\left(\mu_{1,i}^R + h_{ii}\right)$$

- Relation to HF self-energy

$$\Gamma^{(2)} \approx \Gamma_{HF}^{(2)} \rightarrow \delta_i^{R/A,(1)} = \epsilon_i^{HF}$$

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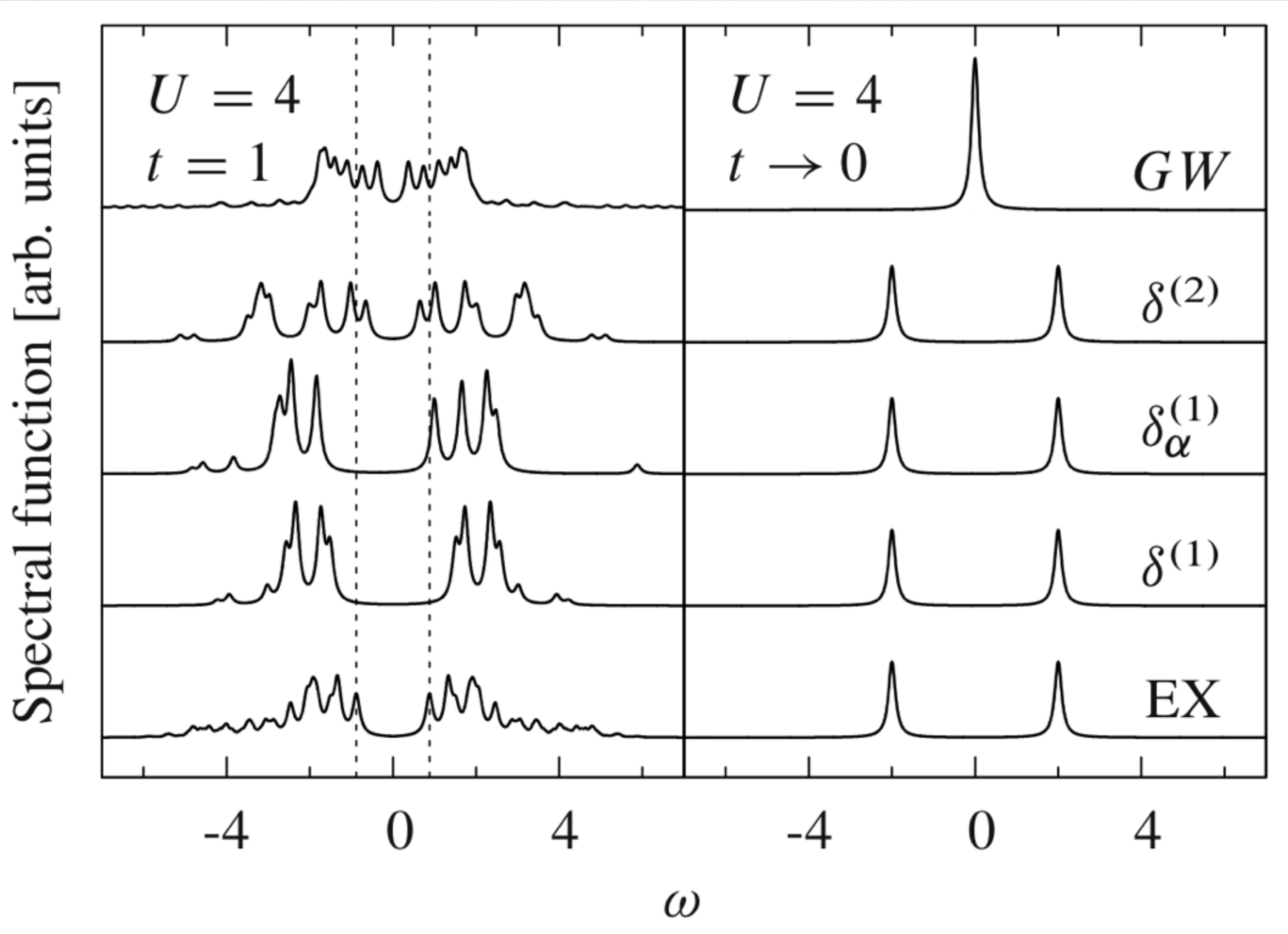
The Many-Body Effective Energy Theory

* 12 sites at 1/2 filling



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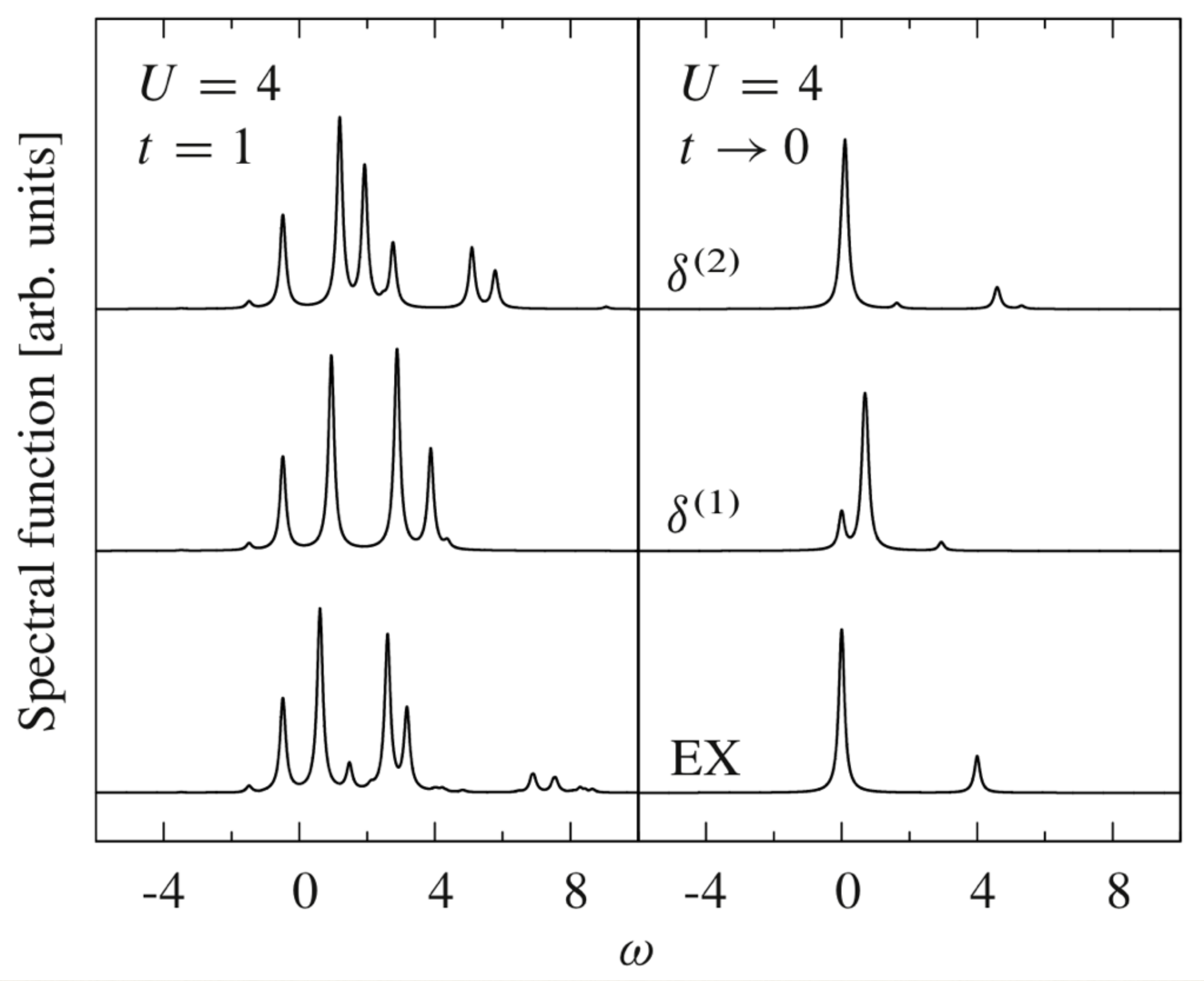
The Many-Body Effective Energy Theory

- 6 sites at 1/6 filling



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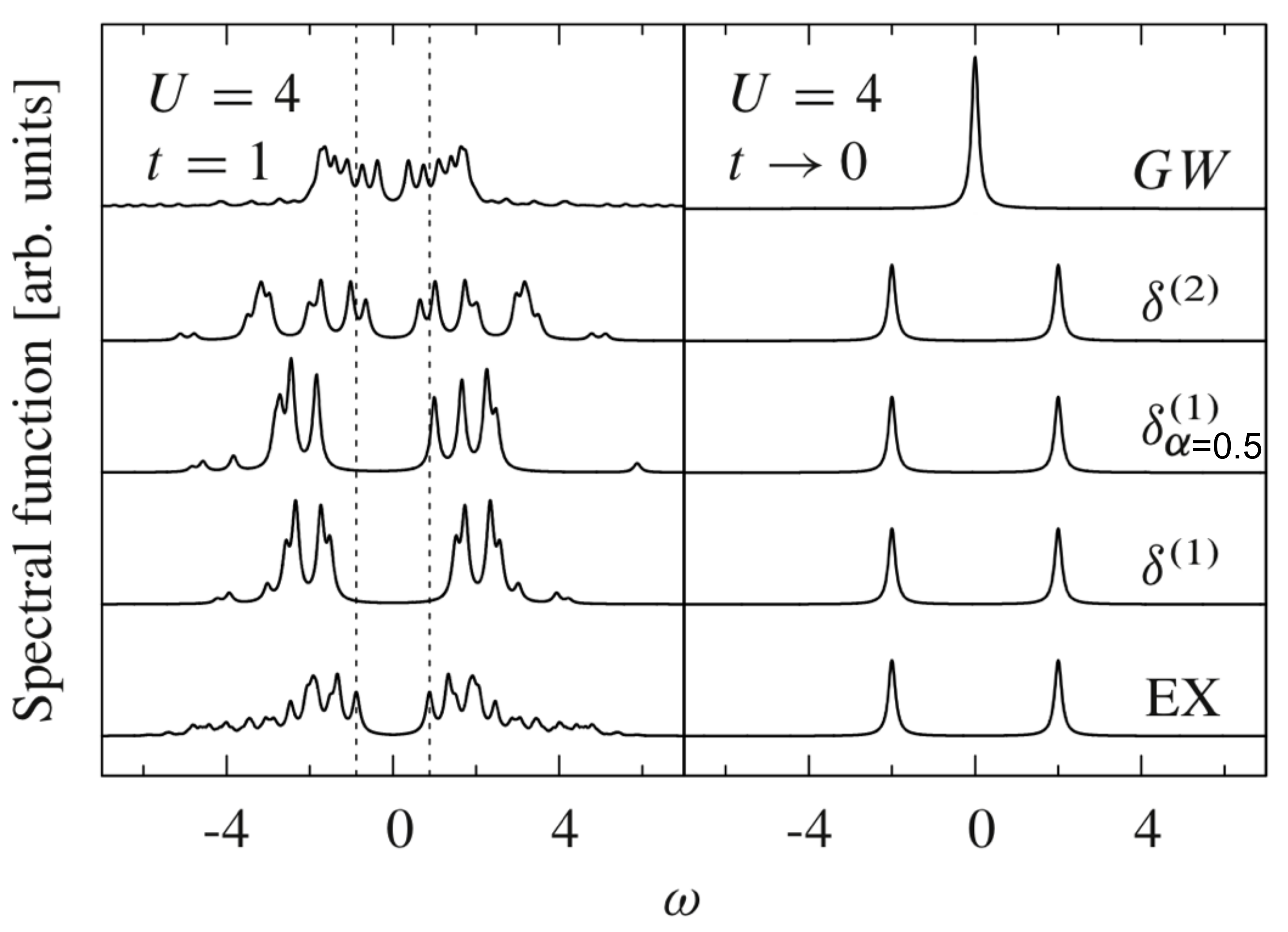
The Many-Body Effective Energy Theory

- 12 sites at 1/2 filling



$$\Gamma_{\alpha}^{(2)} = \gamma\gamma - \gamma^{\alpha}\gamma^{\alpha}, \quad (0.5 \leq \alpha \leq 1)$$

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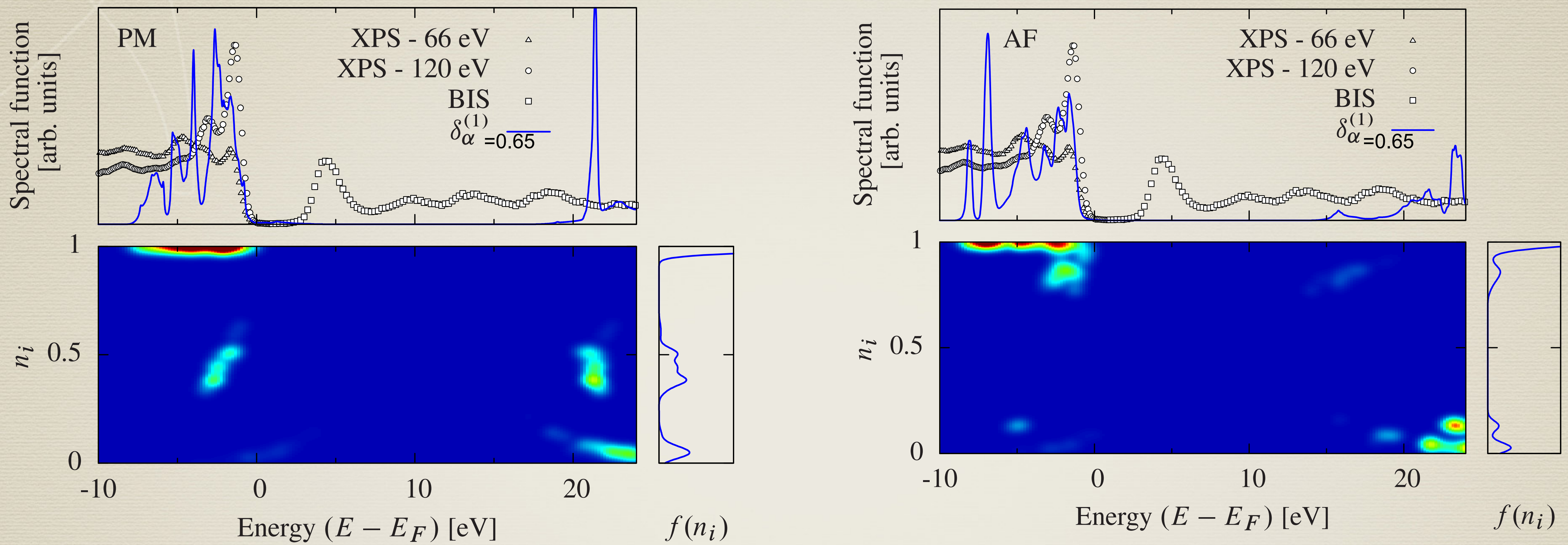
MEET + RDMFT

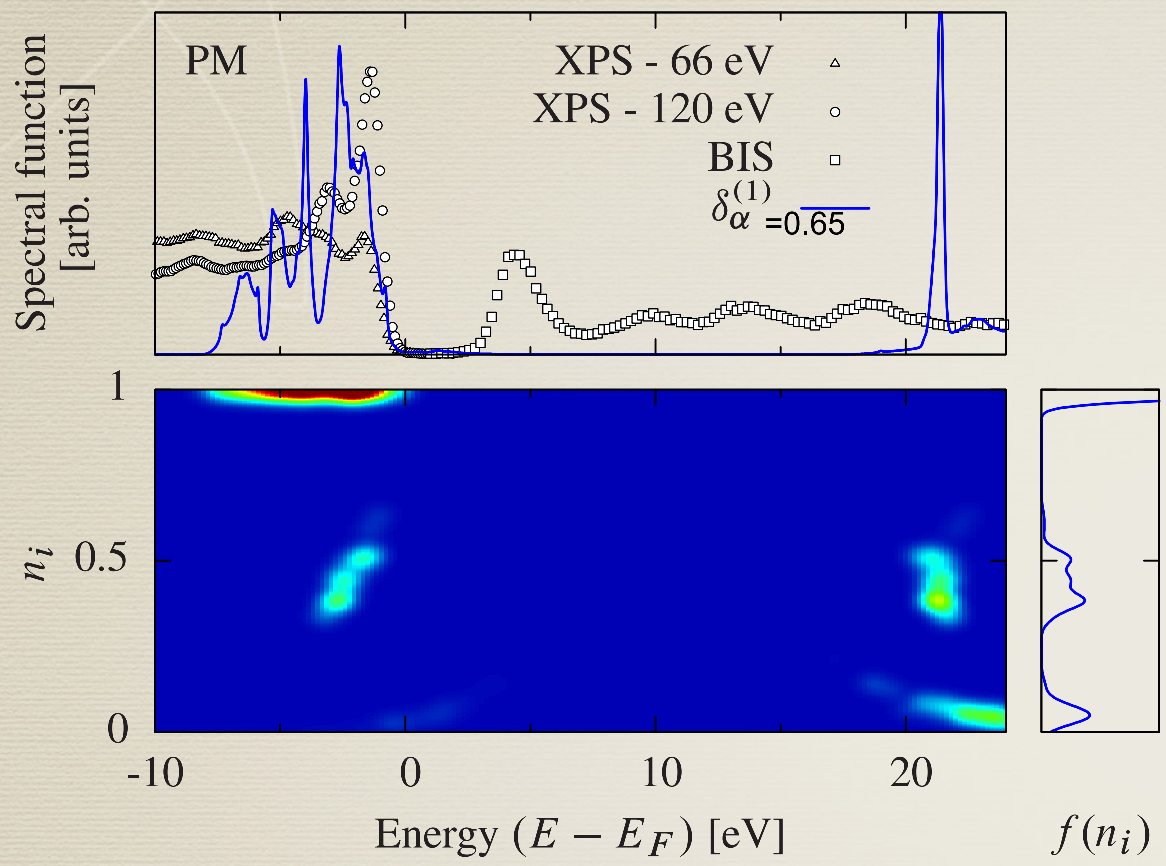
- NiO

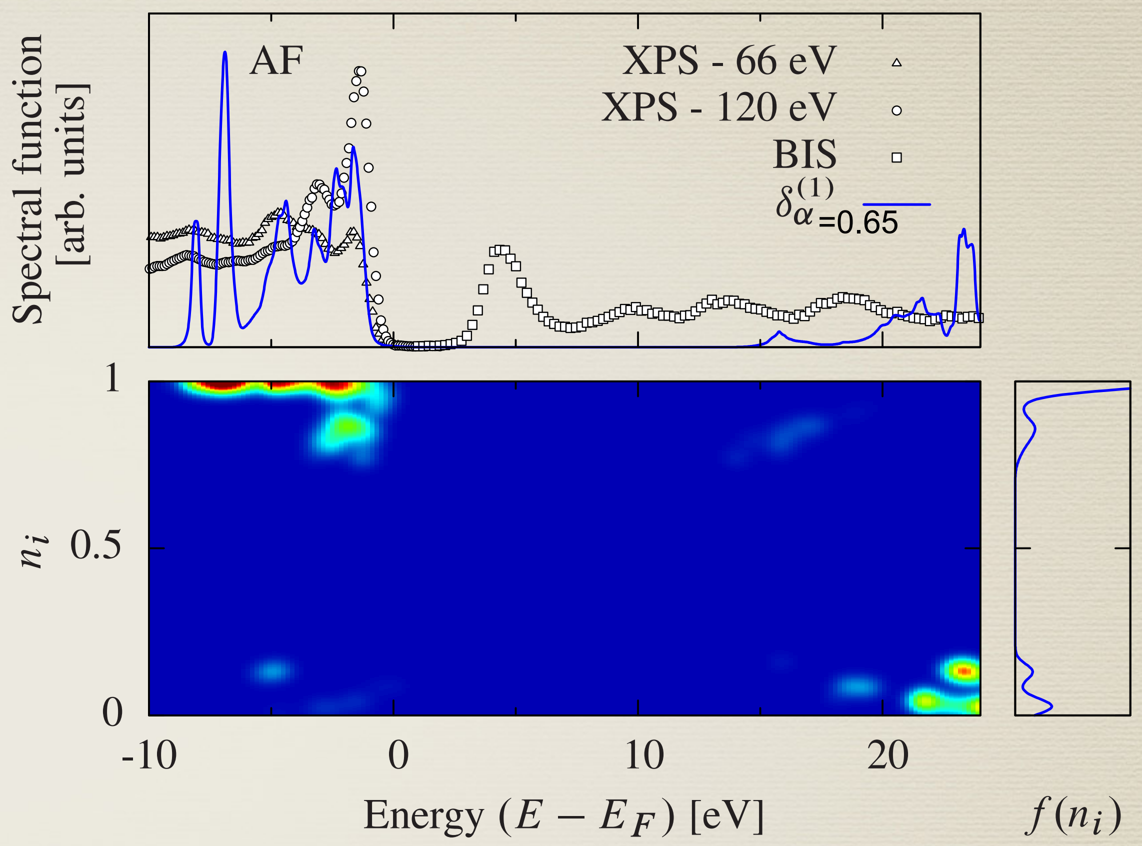


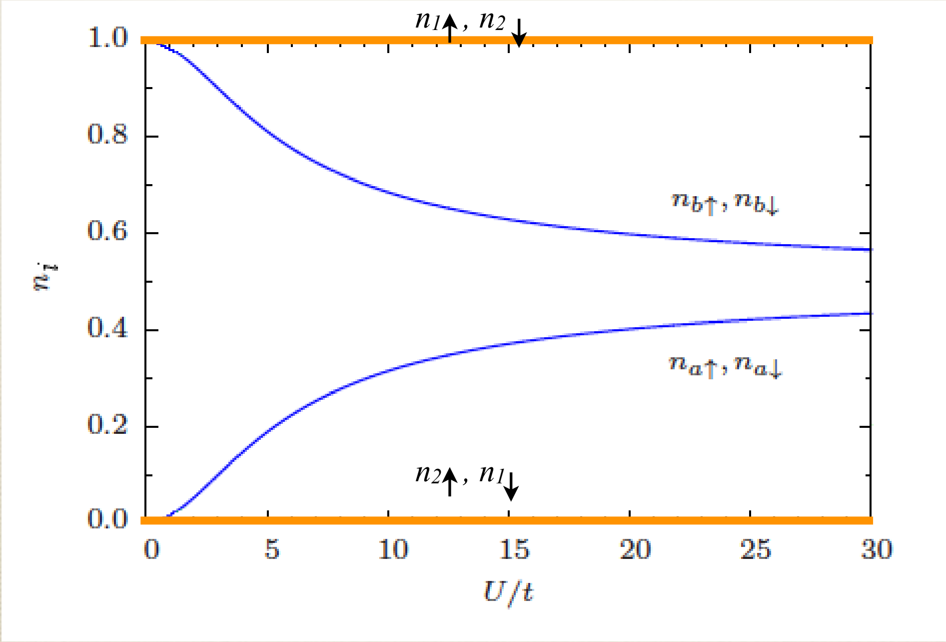
S. Di Sabatino, J.A. Berger, L. Reining, and P. R., Phys. Rev. B 94, 155141 (2016)

MEET + RDMFT

- NiO







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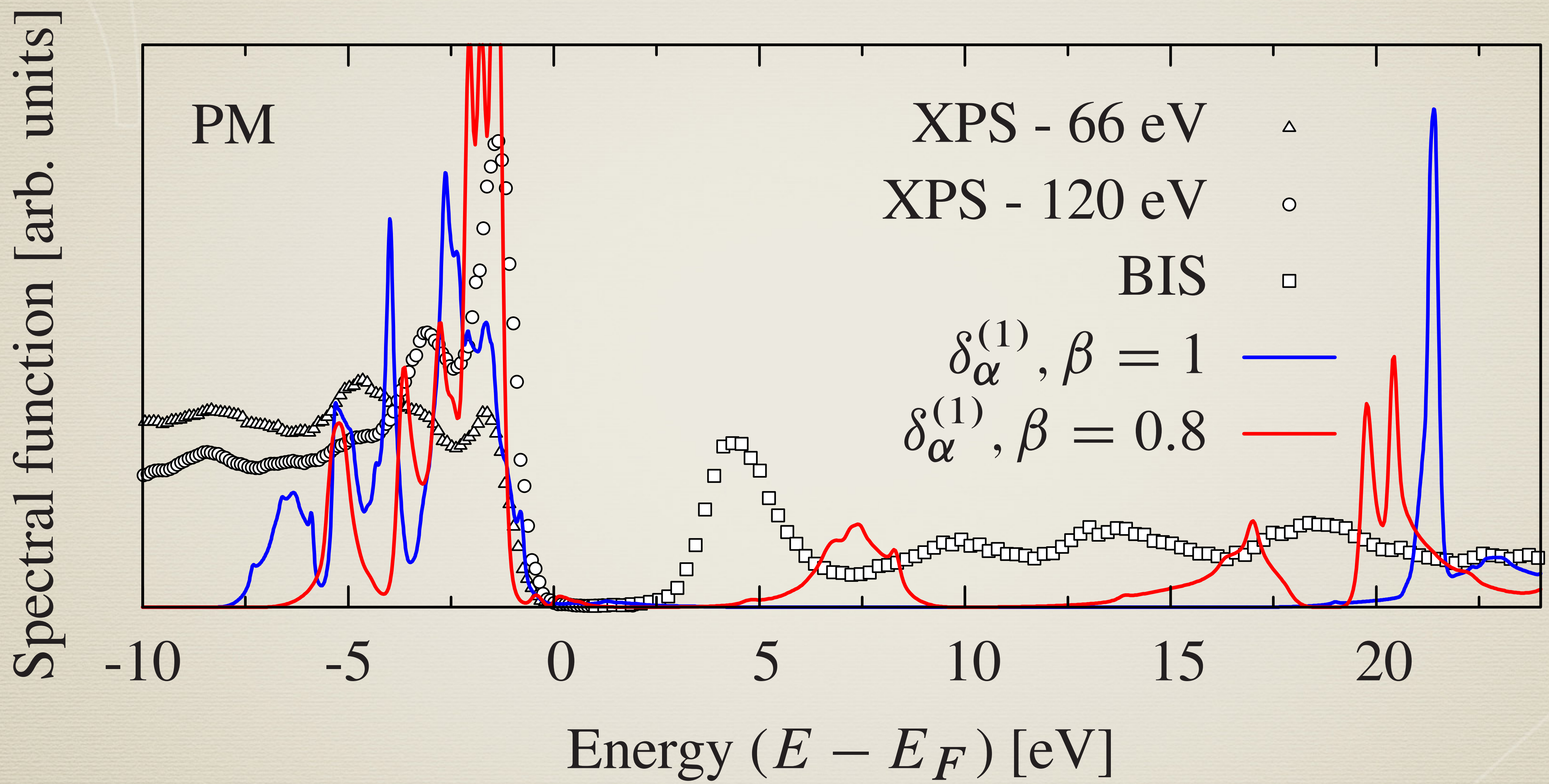
MEET + RDMFT

- PM NiO



$$\delta_i^{R,(1)} = h_{ii} + \sum_j V_{ijij} n_j + \frac{\beta_i}{n_i} \sum_{jkl} V_{ijkl} \Gamma^{(2)}_{\mathrm{xc},klji} \qquad (0 \leq \beta_i \leq 1)$$

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Conclusions & Outlooks

* Whether a system "is" correlated or not depends on how one looks at it

* Spin-resolved total spectral function and momentum distribution cannot distinguish between AF and PM phases.

* Spectral function from a many-body effective energy theory promising
  - Simple approximations give accurate spectra in model systems at weak and strong correlation (without symmetry breaking)
  - $\delta^{(1)}(\omega)$(1- and 2-body reduced density matrices) produces a qualitative correct spectra for the AF and PM phases
  - How to go beyond $\delta^{(1)}(\omega)$?
    - Reduced density matrices from QMC
    - Effective $\delta^{(1)}(\omega)$