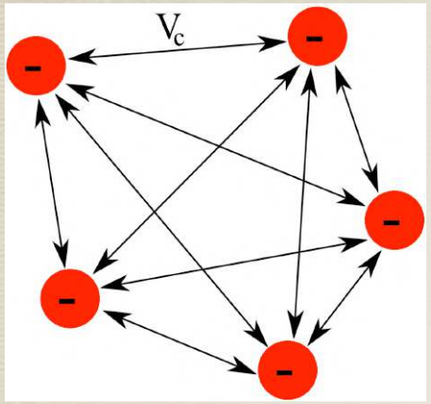
The N-Body problem in condensed matter

Pina Romaniello

Laboratoire de Physique Théorique, Université de Toulouse, France

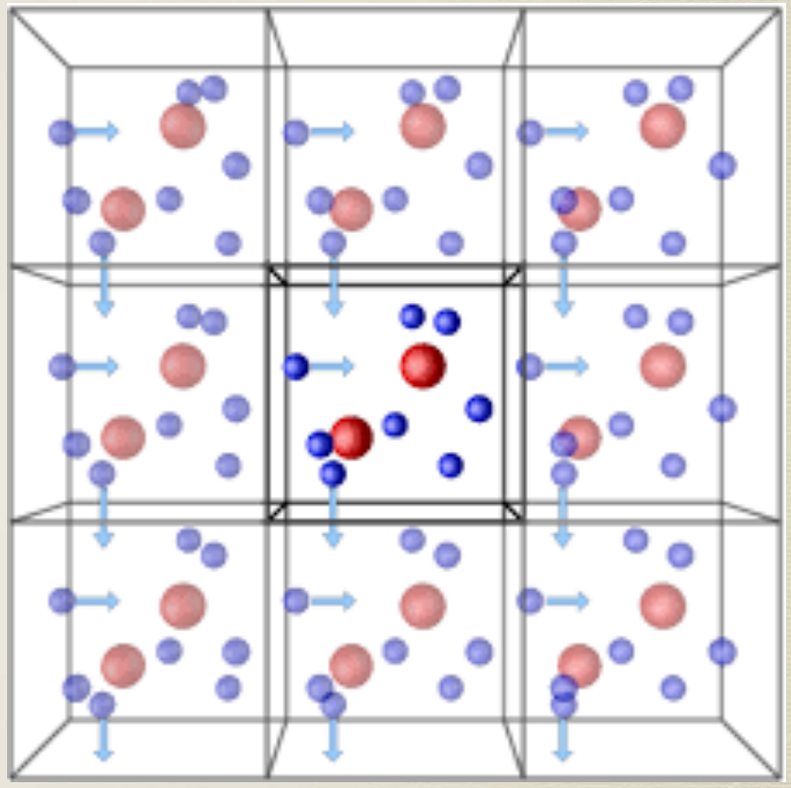
Many-Body problem: same old problem but with an infinite number of electrons



Many-Body problem

↓

Infinitely many-body problem

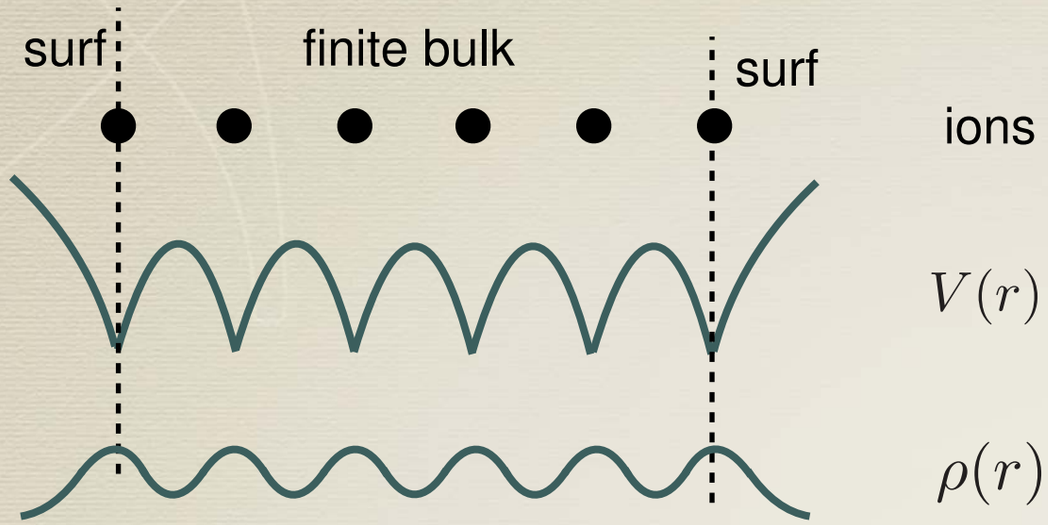


A perfect crystal

Outline

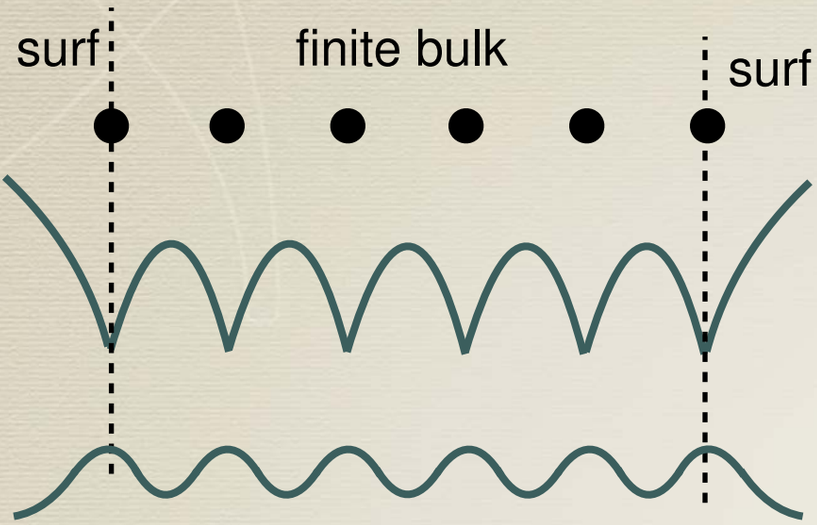
- Some notions on periodicity and band structure
- Properties of interest: Photoemission and Absorption
- Two state-of-the-art methods for solid state: DFT & MBPT
- Conclusions

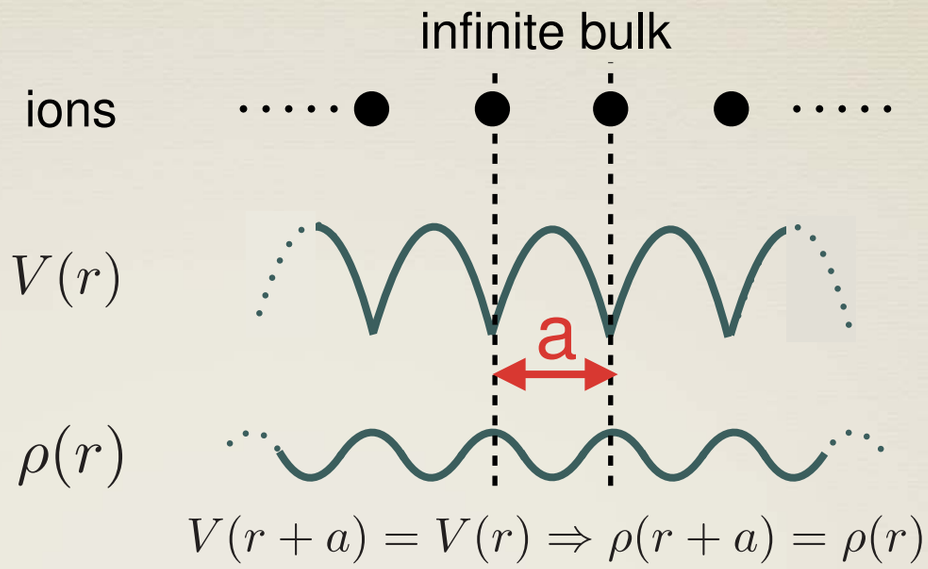
How to model a solid?



How to model a solid?

- Periodic approach (solid=system with translational symmetry)



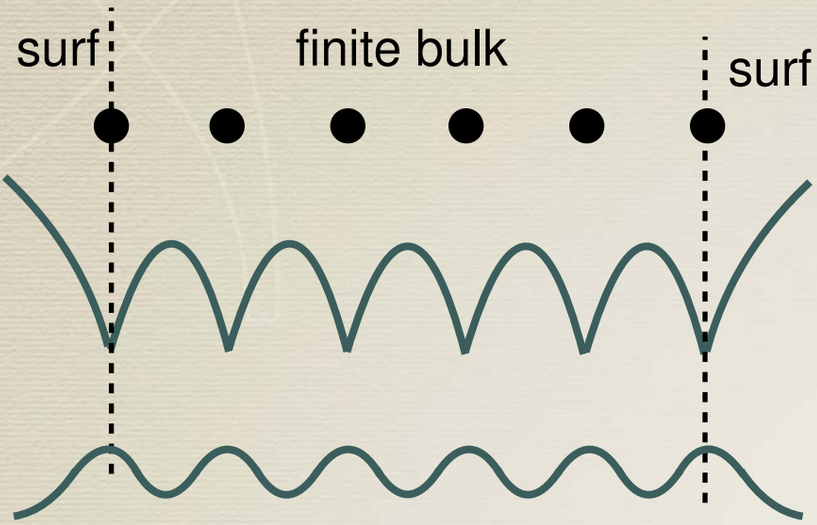


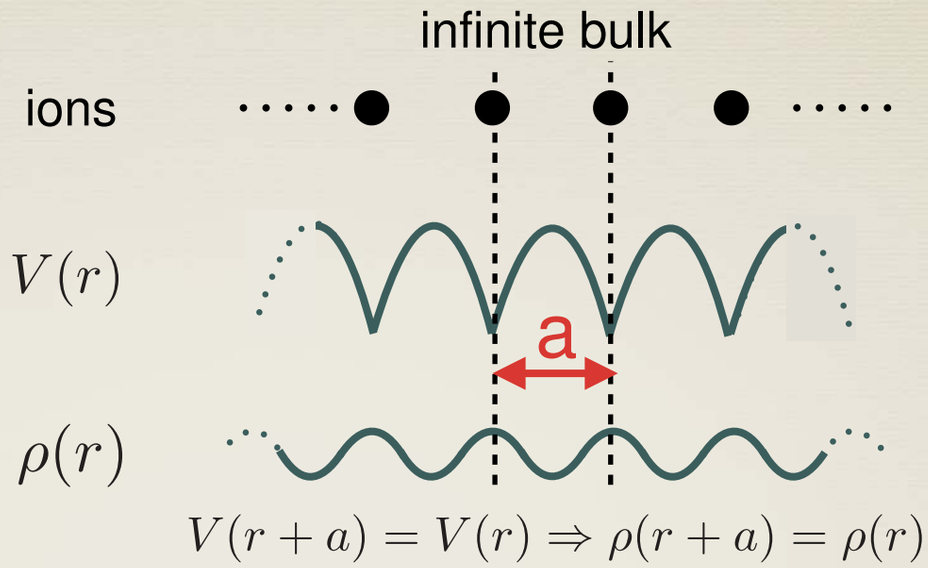
$$V(r+a) = V(r) \Rightarrow \rho(r+a) = \rho(r)$$

An elementary unit (one or more atoms) is repeated throughout space

How to model a solid?

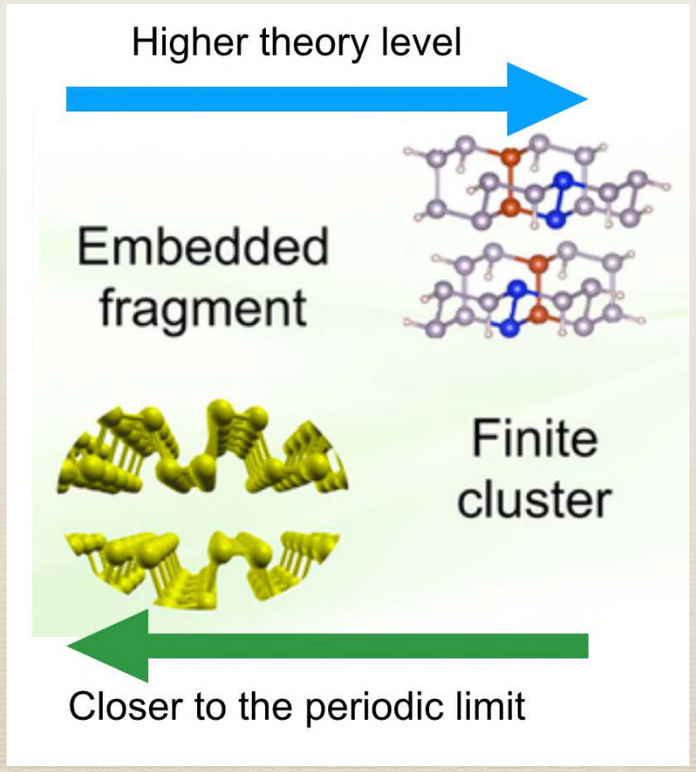
✳ Periodic approach (solid=system with translational symmetry)





An elementary unit (one or more atoms) is repeated throughout space

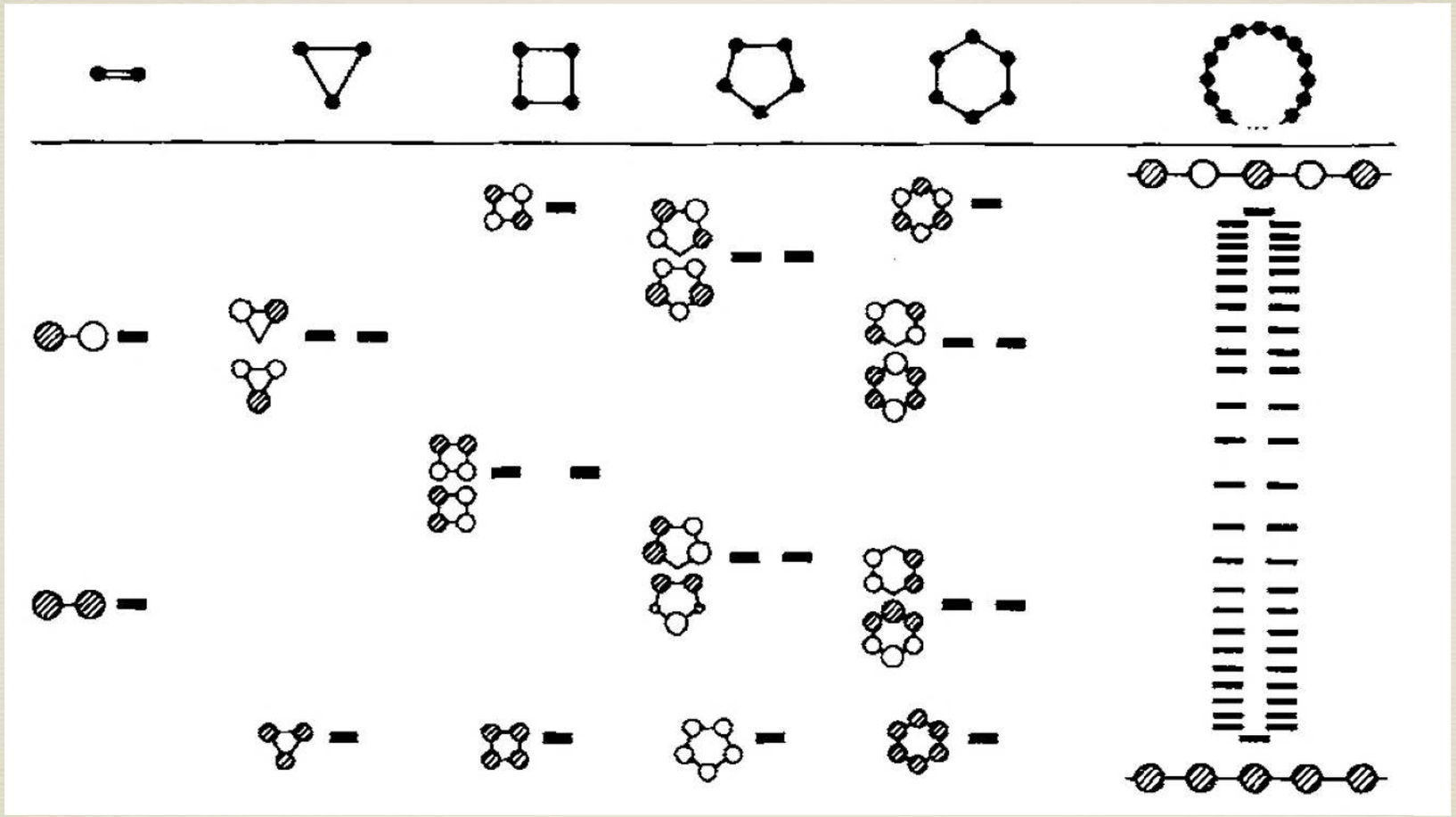
✳ Finite-cluster approach (solid=cluster, fragment or both (optionally embedded))

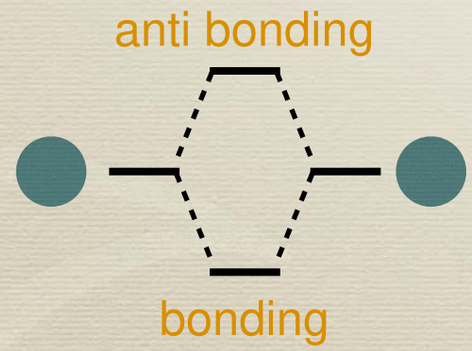


Adapted from: Usvyat *et al.,* WIREs Comput Mol Sci. 8, e1357 (2018)

From molecular orbitals to band structure: the chemist's view

Electronic bands as limit of bonding and antibonding combinations of atomic orbitals





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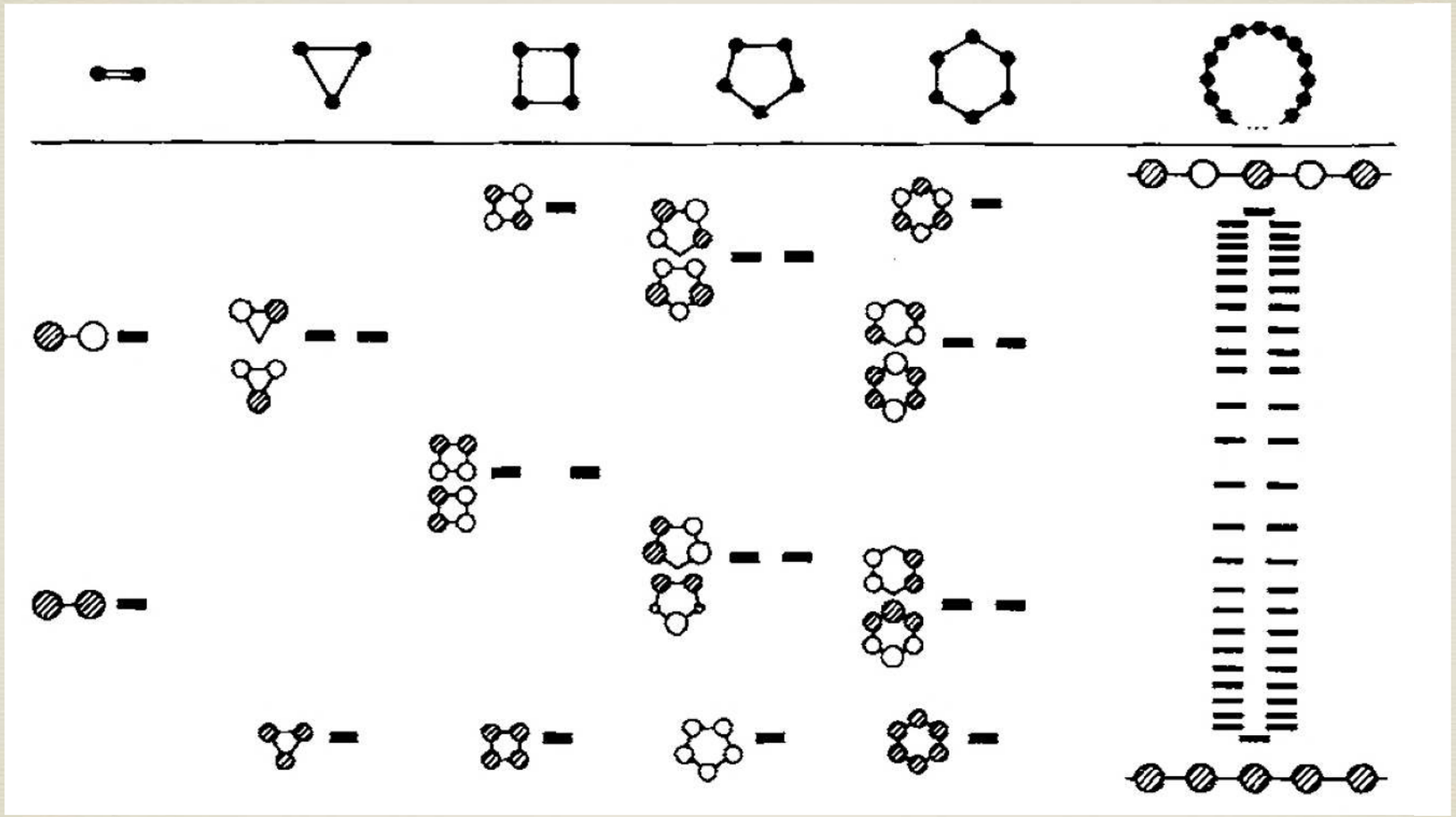

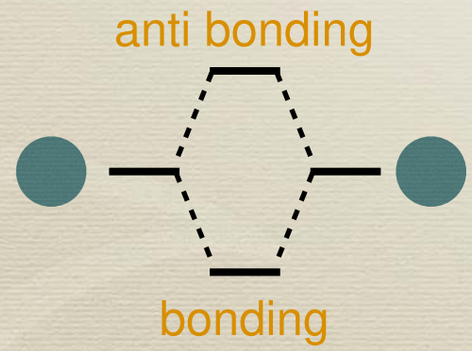

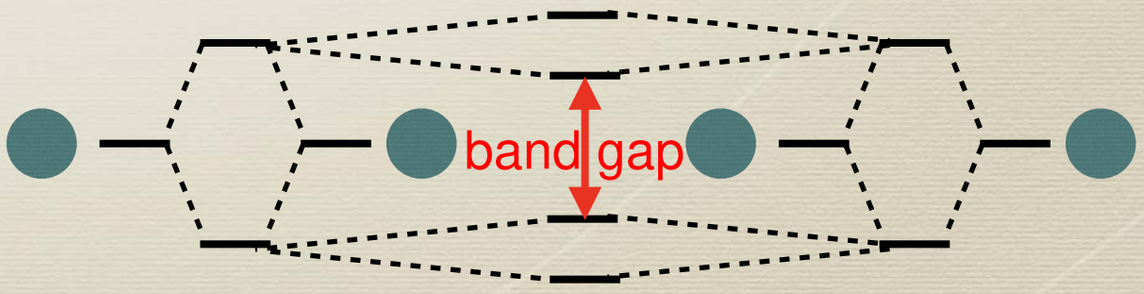

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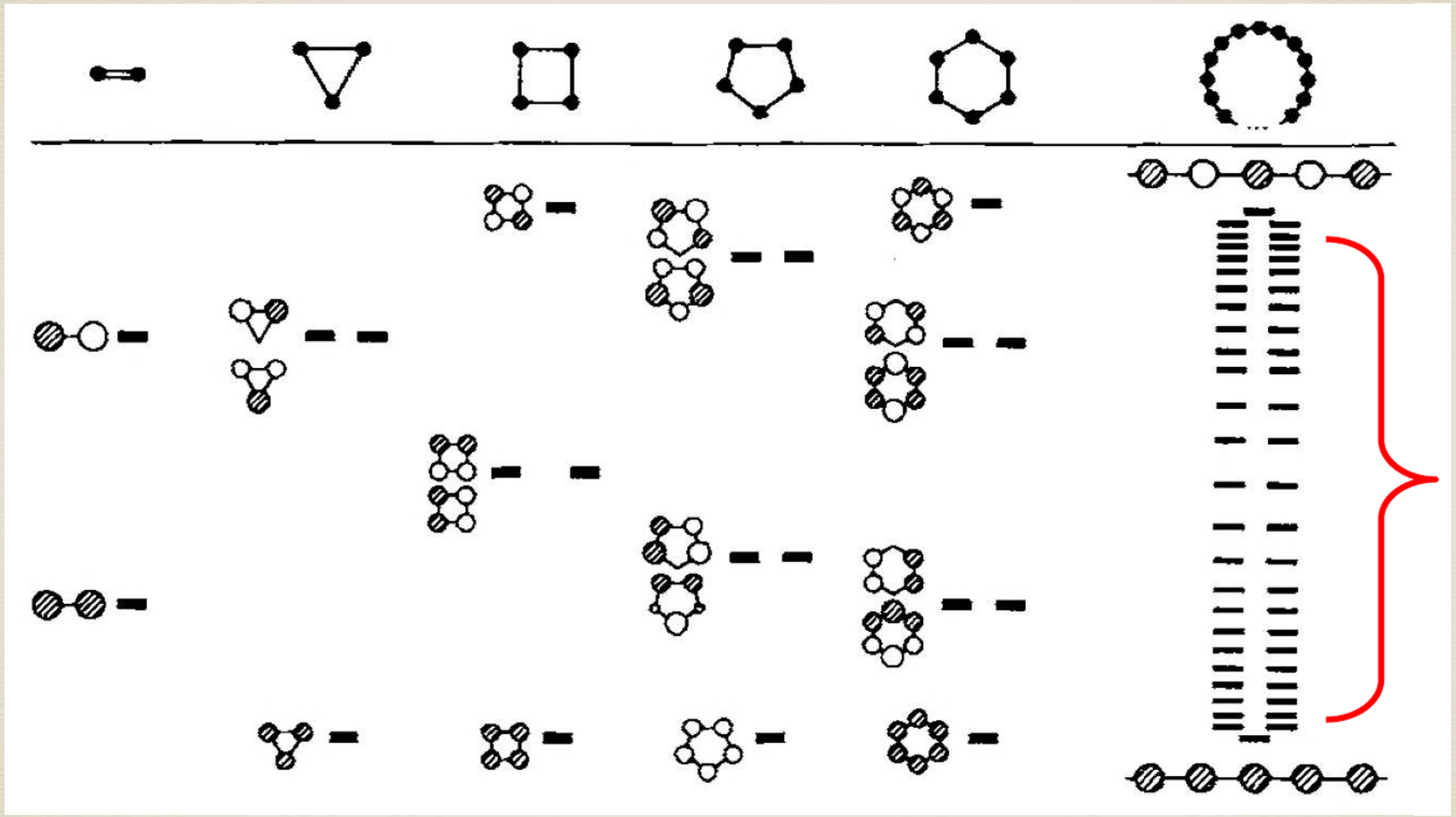

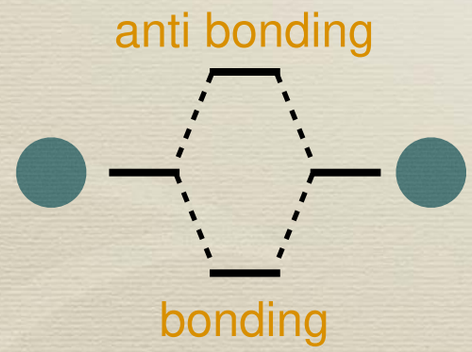

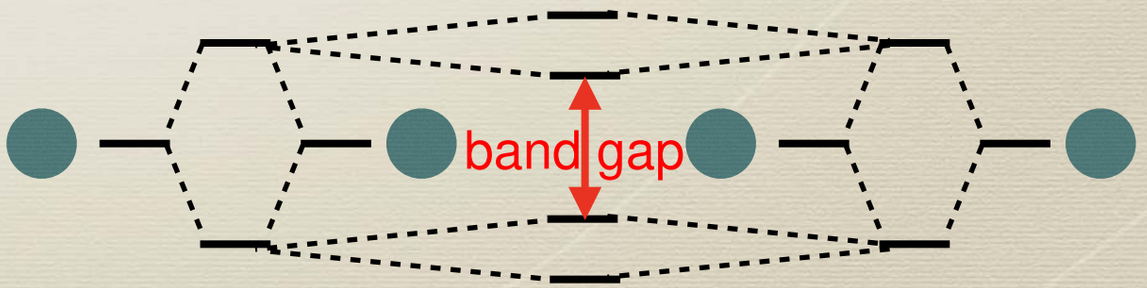

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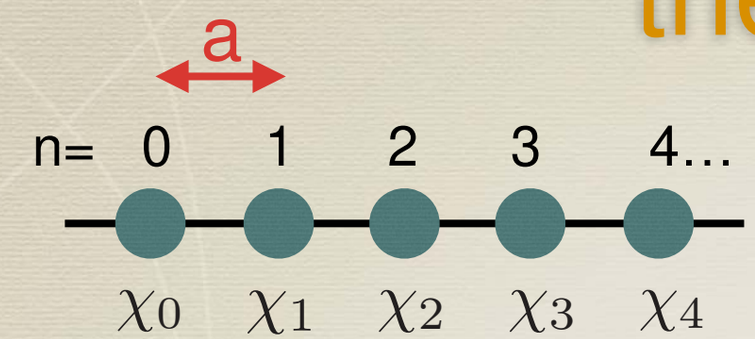

$$\psi_k = \sum_n e^{iknna} \chi_n$$

Bloch's functions

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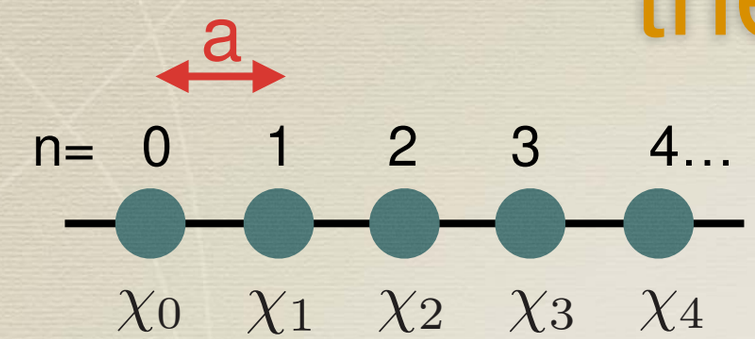

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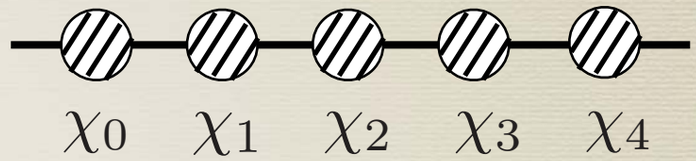
Bloch's functions

$$k = 0 \rightarrow \psi_0 = \sum_n e^0 \chi_n = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \chi_4 \cdots$$



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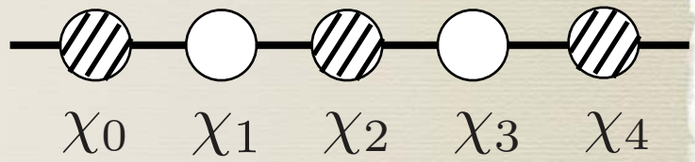

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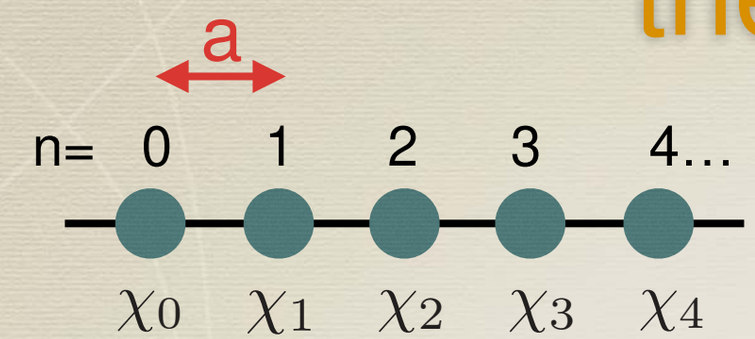

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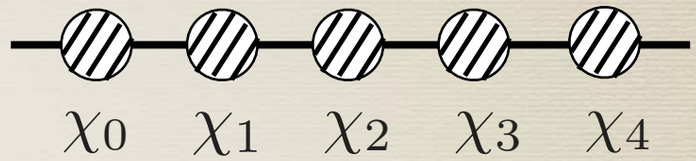

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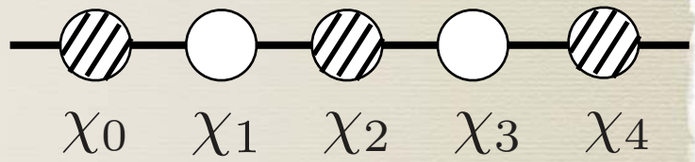

k is a symmetry label and a node counter, and represents electron momentum $\left(k = \frac{1}{\lambda} = \frac{p}{h}\right)$

The space of k is called reciprocal or momentum space

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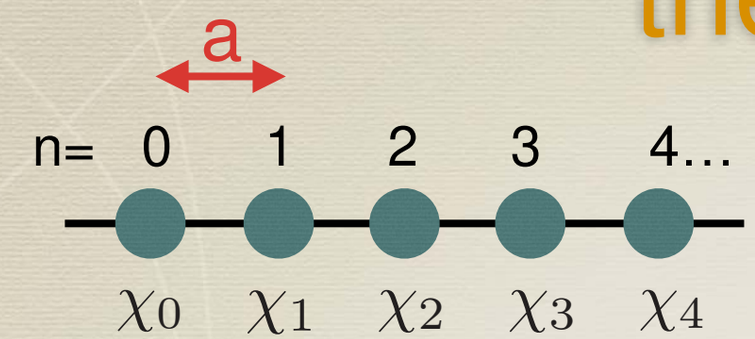

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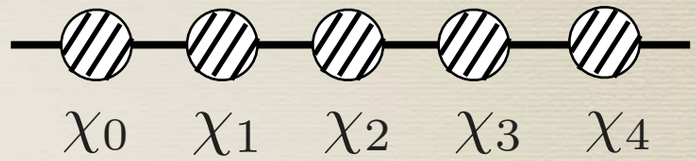

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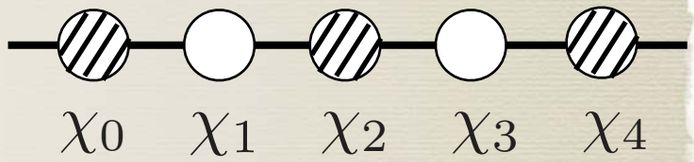

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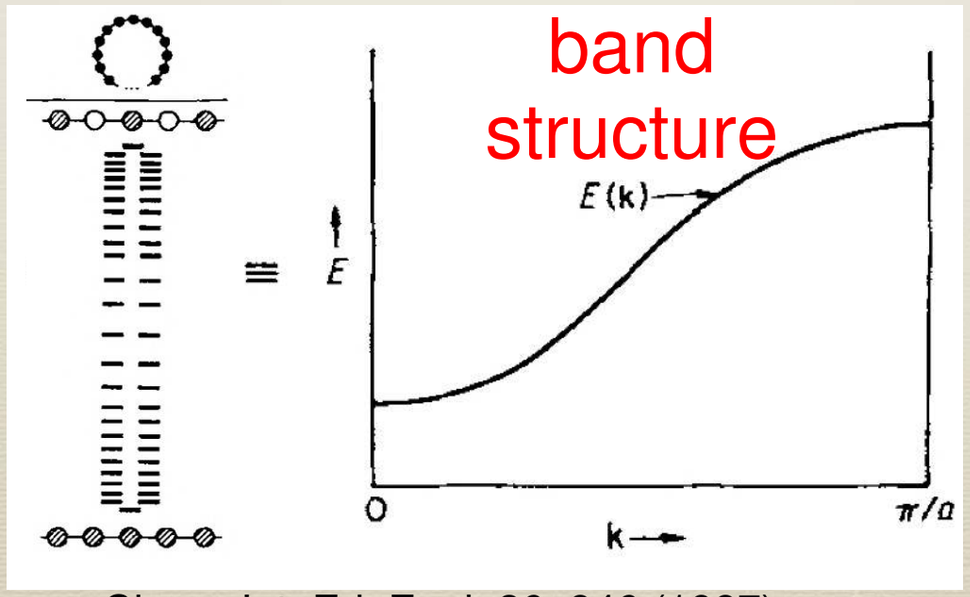

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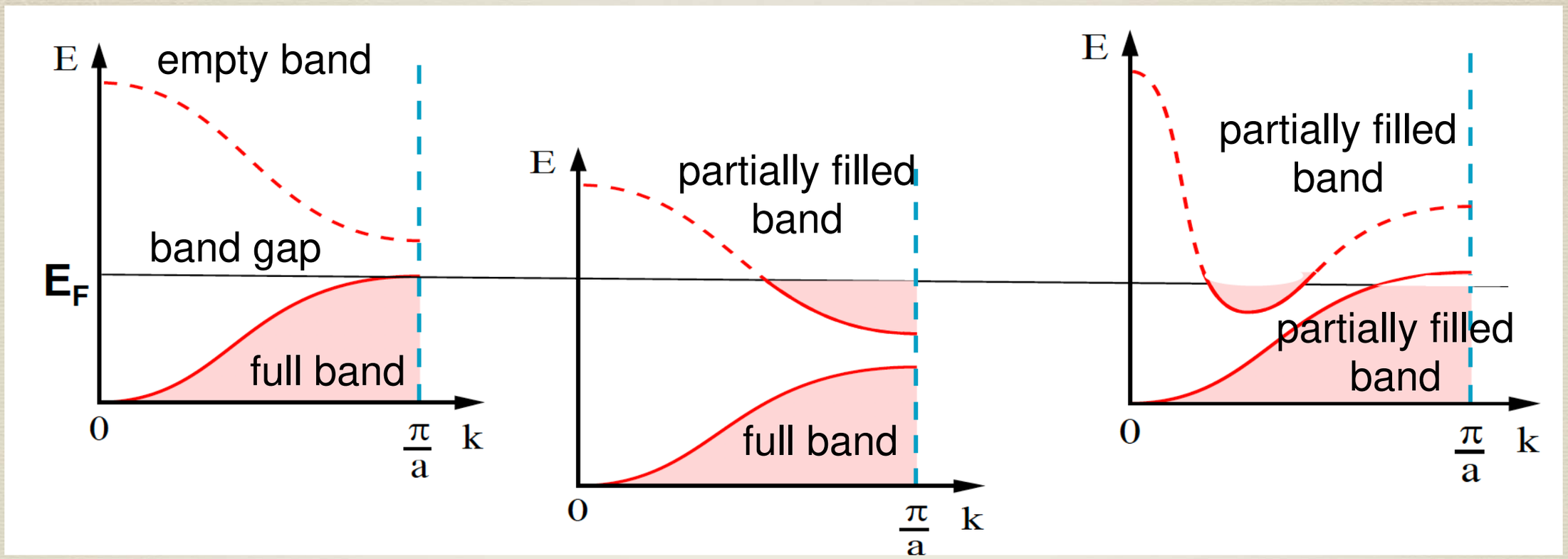
Insulators, semiconductors, (semi)metals



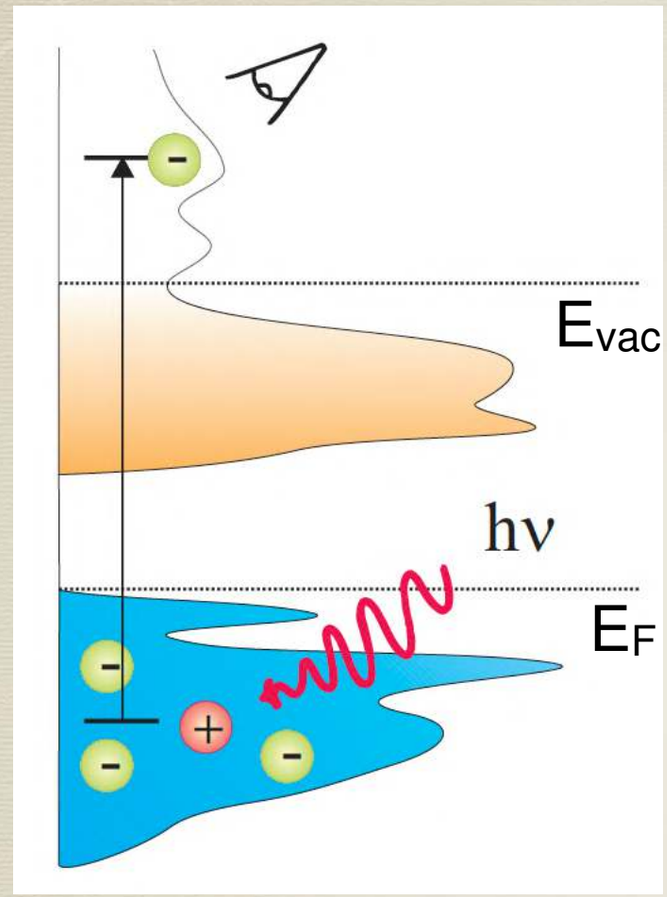
INSULATOR
(band gap $>> K_B T$)
or
SEMICONDUCTOR
(band gap $\approx K_B T$)

METAL
(band gap=0)

METAL or
SEMIMETAL

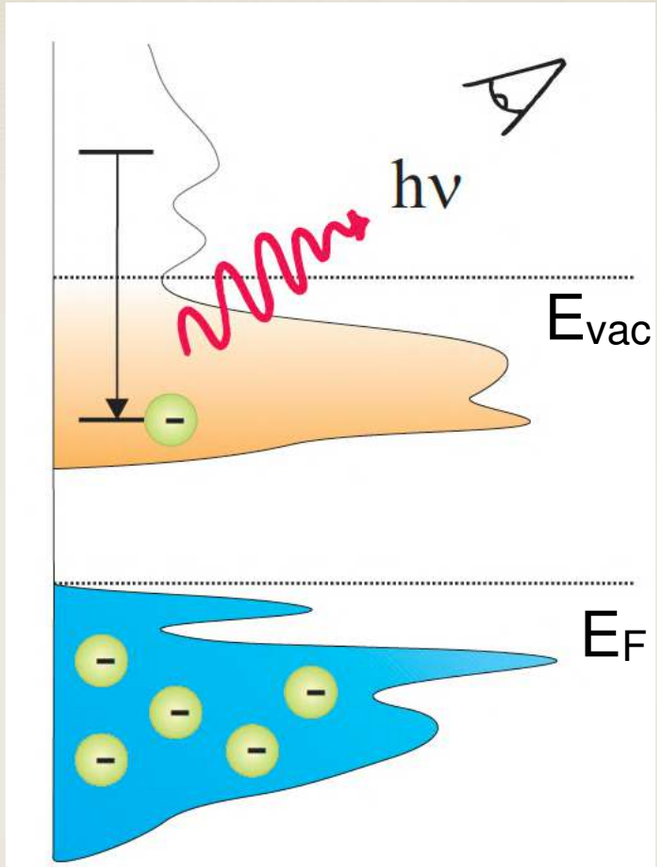
Properties: spectroscopy

Direct Photoemission



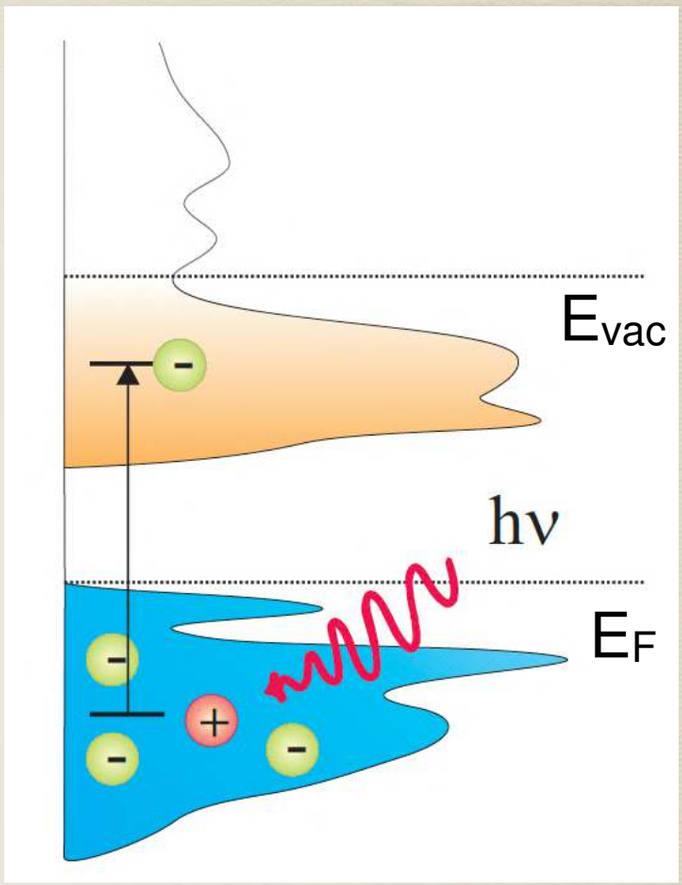
N ⟶ N-1

Inverse Photoemission



N ⟶ N+1

Absorption

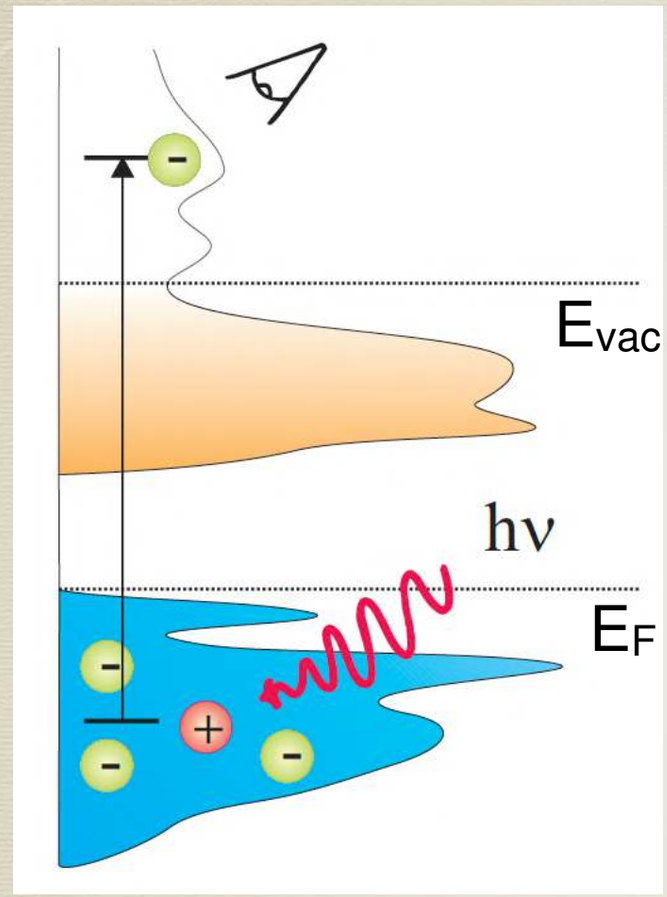


N ⟶ N*

Adapted from: Patrick Rinke, Hands-on Tutorial on *Ab Initio* Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions

Properties: spectroscopy

Direct Photoemission



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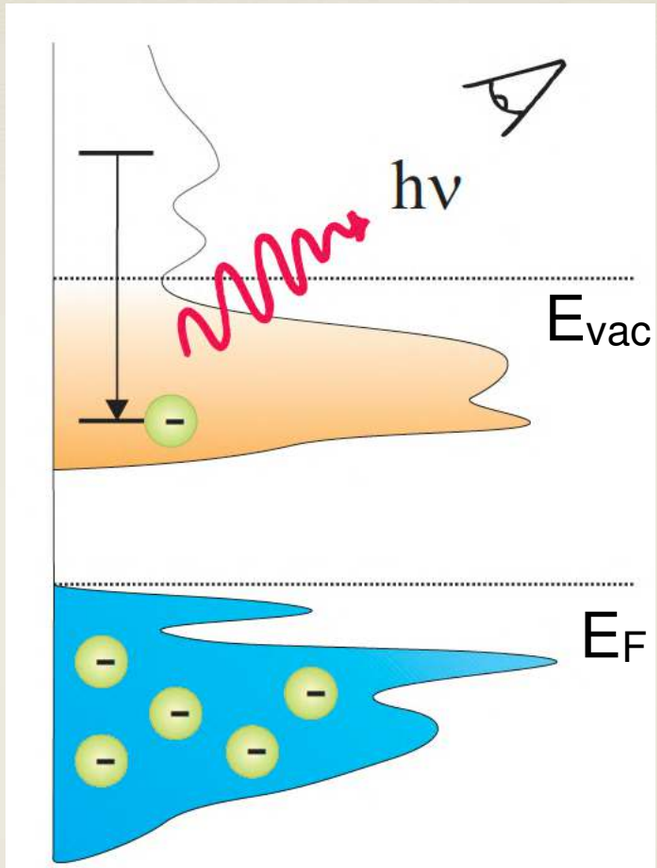

N ⟶ N+1

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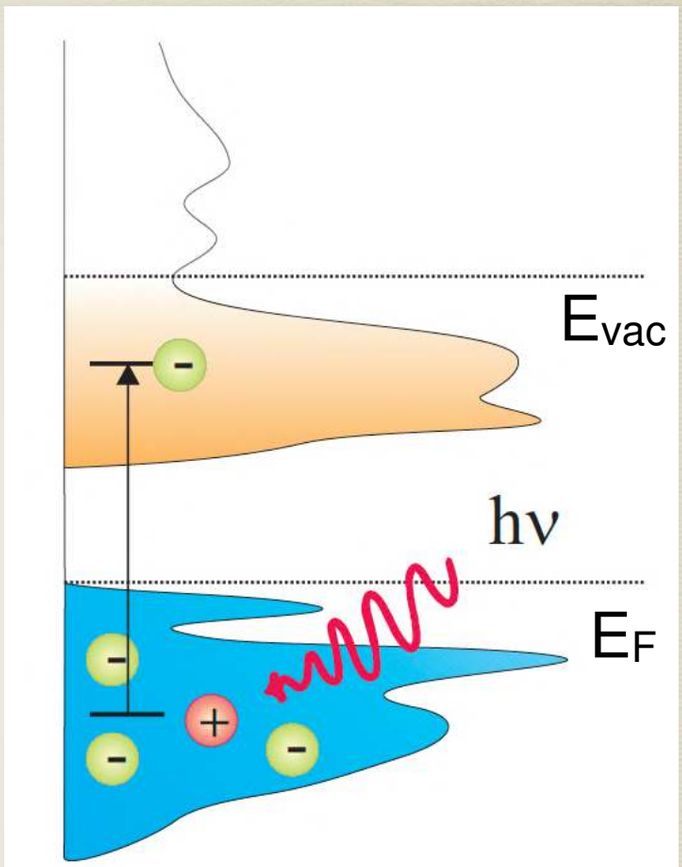
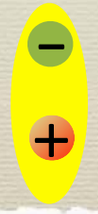


N ⟶ N*

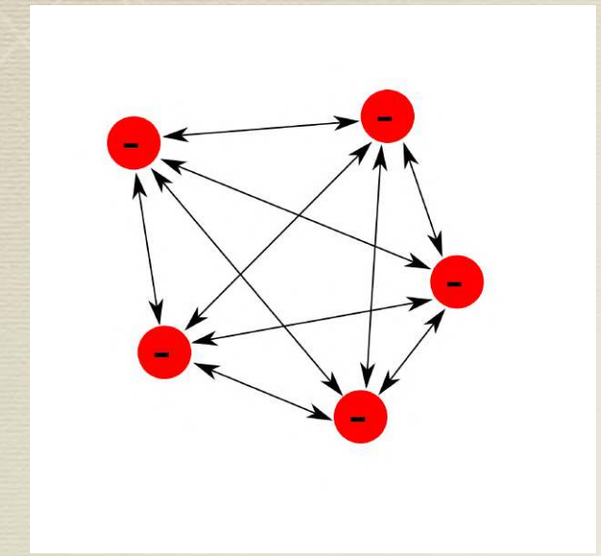
New concepts: quasiparticles

satellites (e.g., plasmons)

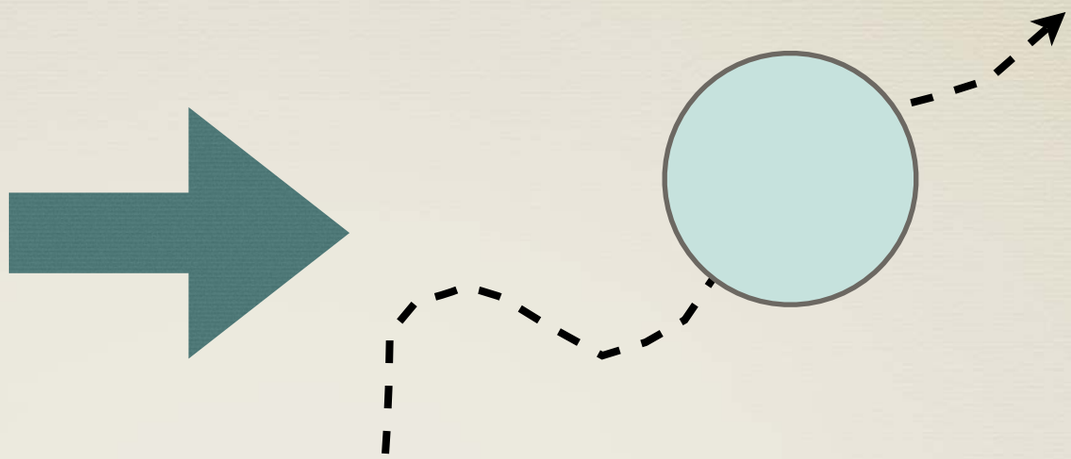
excitons



Ab-initio theories: functional theories



Interacting system



Simpler physical quantity, e.g. the density or quasiparticles

Theoretical framework

✳ Electron correlation

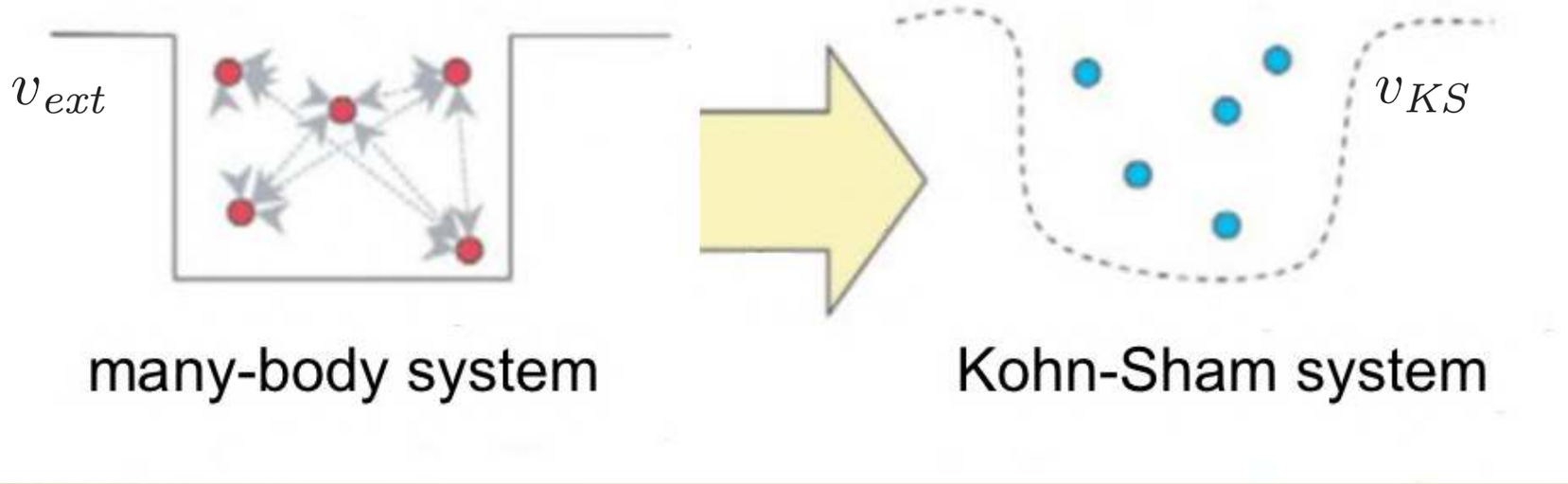
how do we approximate many-body effects ?

✳ Observables

how do we express the observable of interest in terms of the reduced quantity of choice ?

Density Functional Theory

$$\rho(\mathbf{r}) = \rho_{KS}(\mathbf{r})$$



KS equations

$$\left[-\frac{1}{2}\nabla^2 + v_{KS}(\mathbf{r})\right]\phi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\phi_i^{KS}(\mathbf{r})$$

KS potential

$$v_{KS}[\rho](\mathbf{r}) = v_{ext}[\rho](\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r})$$

Self-consistent solution

density

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i^{KS}(\mathbf{r})|^2$$

Hohenberg & Kohn, PR 136 , B864 (1964); Kohn & Sham, PRA 140 , 1133 (1965)

Density Functional Theory

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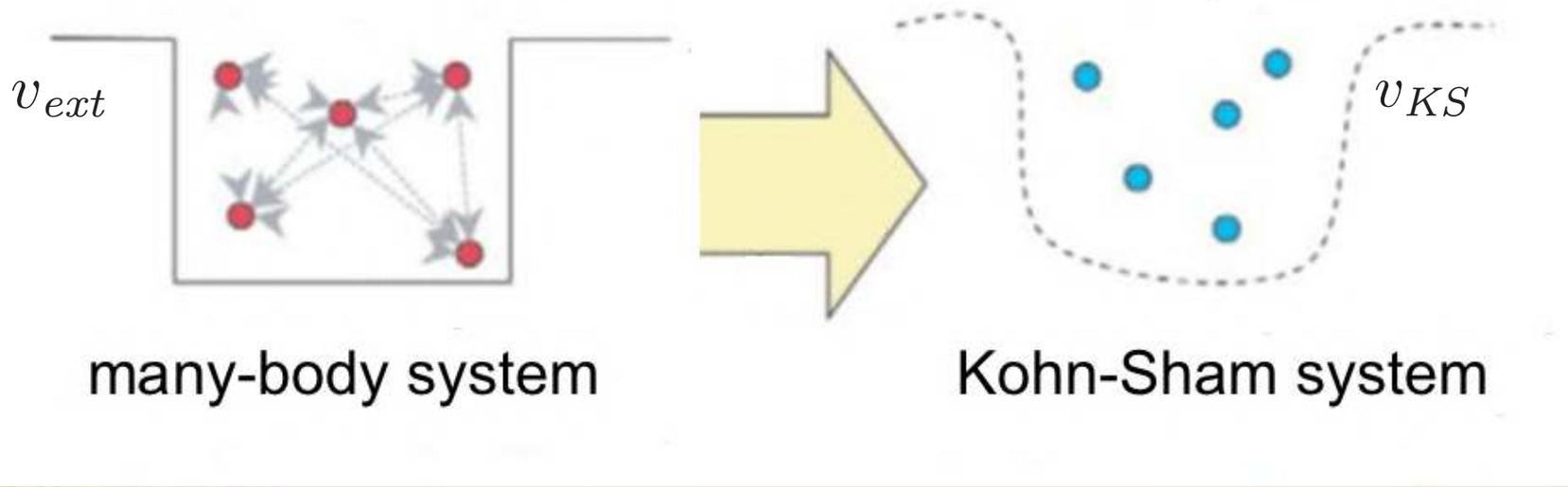

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LDA

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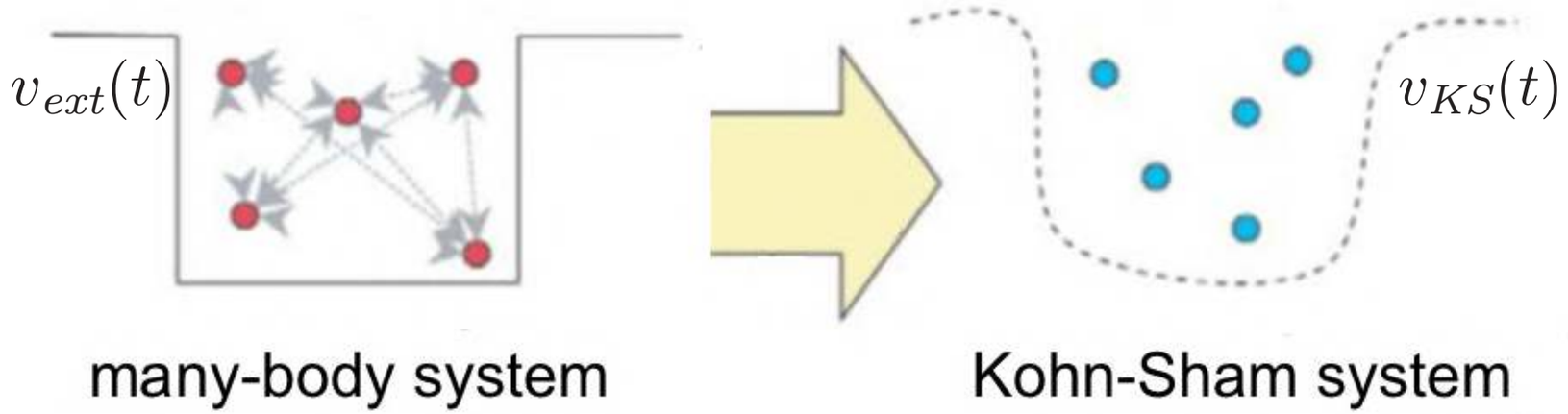
Time-dependent Density Functional Theory

$$\rho(\mathbf{r},t) = \rho_{KS}(\mathbf{r},t)$$



KS equations

$$\left[-\frac{1}{2}\nabla^2 + v_{KS}(\mathbf{r},t)\right]\phi_i^{KS}(\mathbf{r},t) = i\frac{\partial}{\partial t}\phi_i^{KS}(\mathbf{r},t)$$

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Runge & Gross, Phys. Rev. Lett. 52, 997 (1984)

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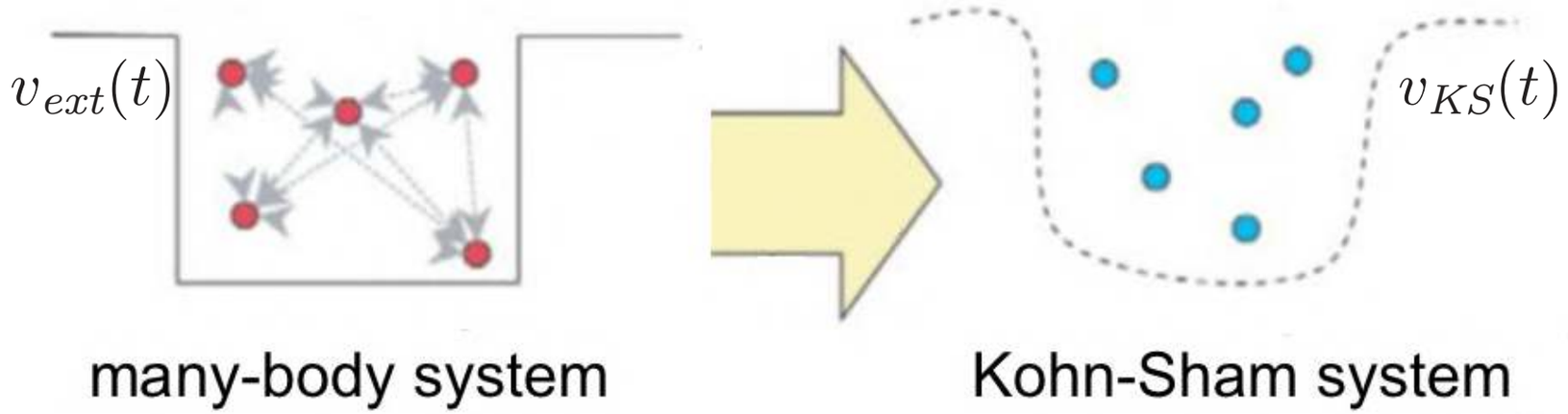

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$$\left[-\frac{1}{2}\nabla^2 + v_{KS}(\mathbf{r},t)\right]\phi_i^{KS}(\mathbf{r},t) = i\frac{\partial}{\partial t}\phi_i^{KS}(\mathbf{r},t)$$

KS potential

$$v_{KS}[\rho](\mathbf{r},t) = v_{ext}[\rho](\mathbf{r},t) + v_H[\rho](\mathbf{r},t) + v_{xc}[\rho](\mathbf{r},t)$$

Self-consistent solution

RPA/ALDA

density

$$\rho(\mathbf{r},t) = \sum_{i=1}^{N} |\phi_i^{KS}(\mathbf{r},t)|^2$$

Runge & Gross, Phys. Rev. Lett. 52, 997 (1984)

(TD)-Density Functional Theory

✳ Observables

- total energy

$$E_0[\rho] = \sum_{i=1}^{N} -\frac{1}{2}\int d\mathbf{r}\phi_i^{KS*}(\mathbf{r})\nabla^2\phi_i^{KS}(\mathbf{r}) + \int d\mathbf{r}v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho]$$

- Ionisation potential (minimal energy to remove an electron)

$$I = E_0(N-1) - E_0(N) = -\epsilon_H^{KS}$$

- Fundamental band gap

$$G_{\text{fund}} = I - A = G_{\text{KS}} + \Delta$$

- Neutral excitations

$$\chi(\omega) = \chi_{KS}(\omega) + \chi_{KS}(\omega)f_{Hxc}(\omega)\chi(\omega)$$

- ...

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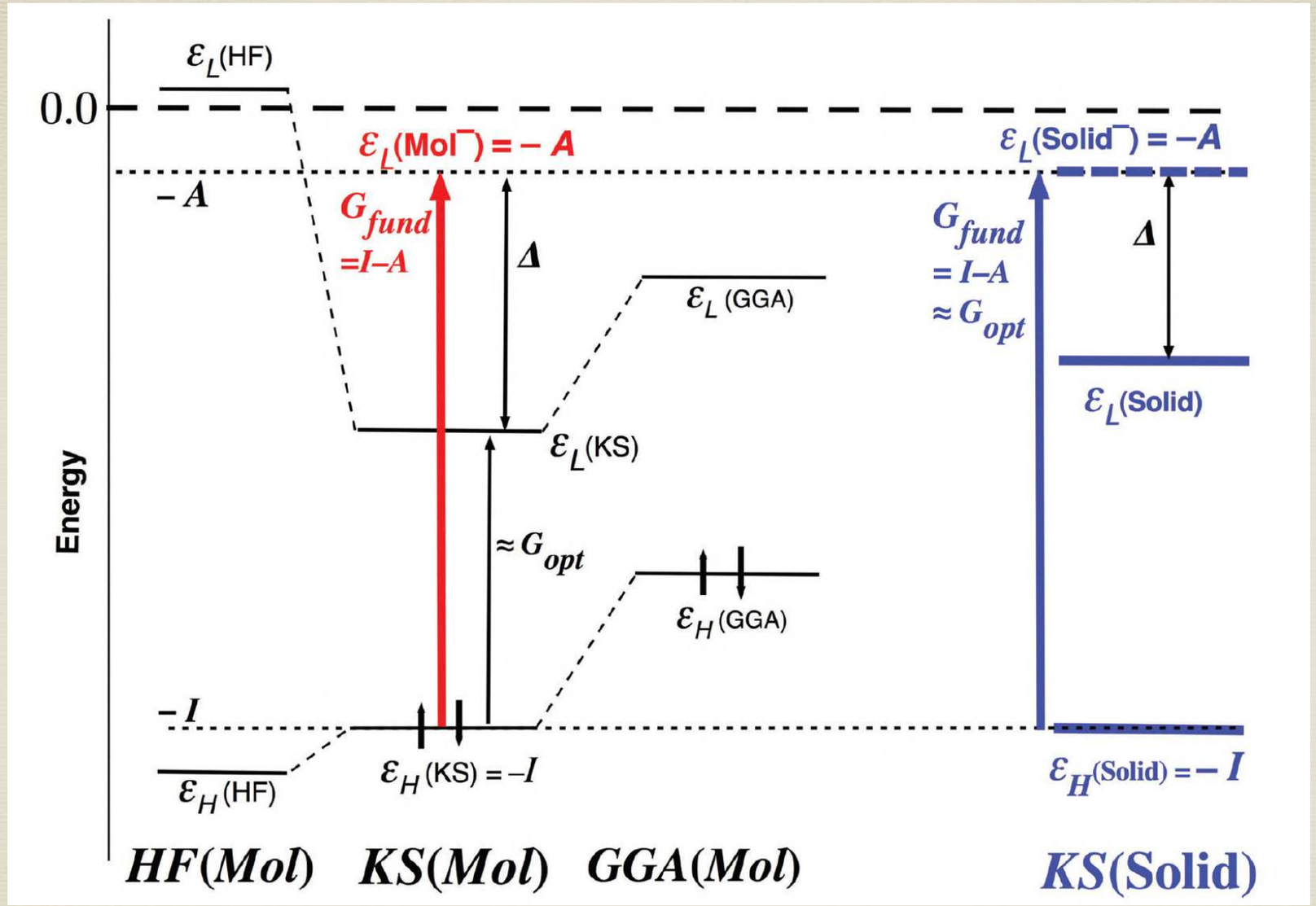
RPA/ALDA

- ...

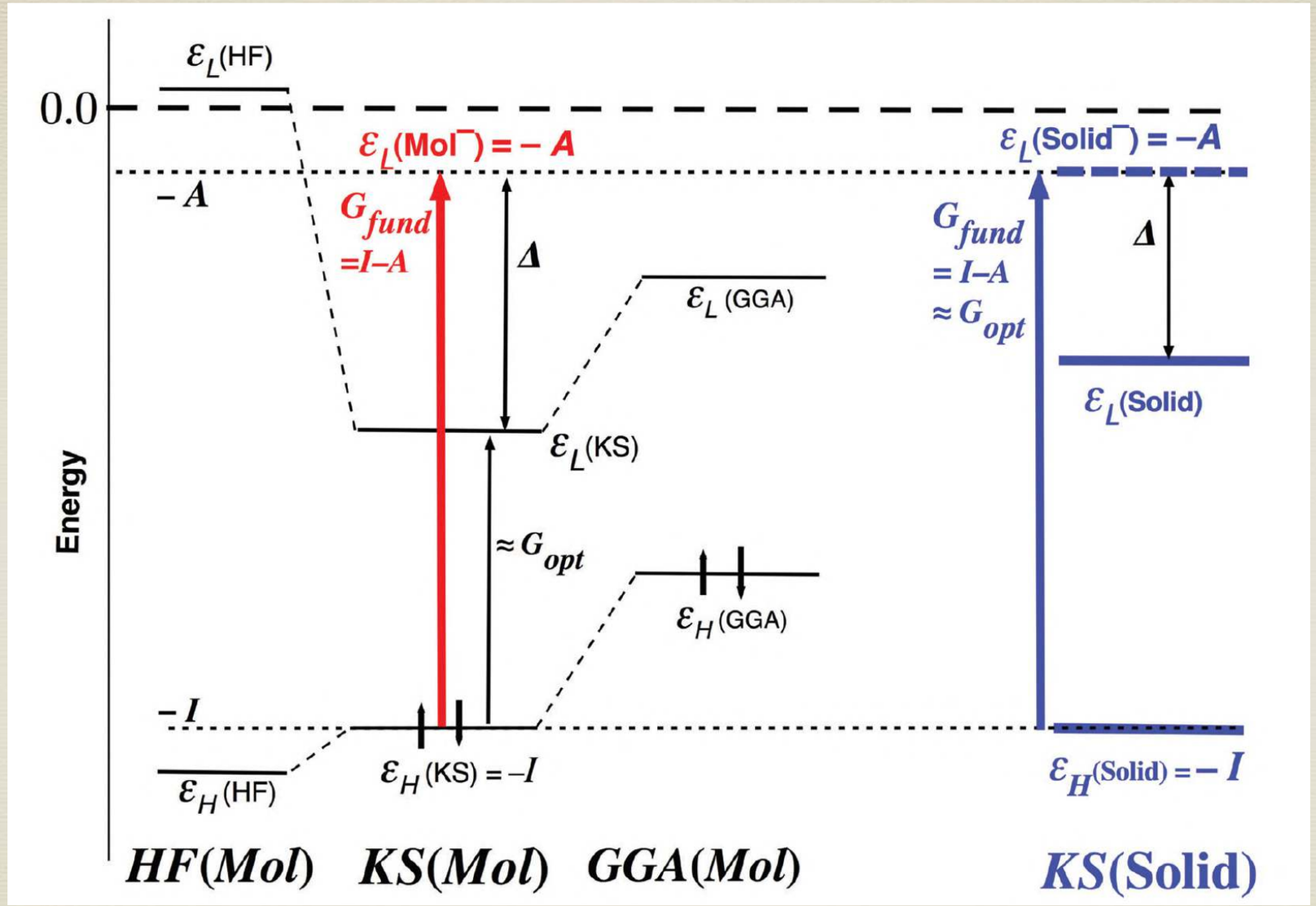
DFT: fundamental gap



$$G_{\mathrm{fund}} = G_{\mathrm{KS}} + \Delta$$

Baerends, Phys.Chem.Chem.Phys. 19, 15639 (2017)

DFT: fundamental gap



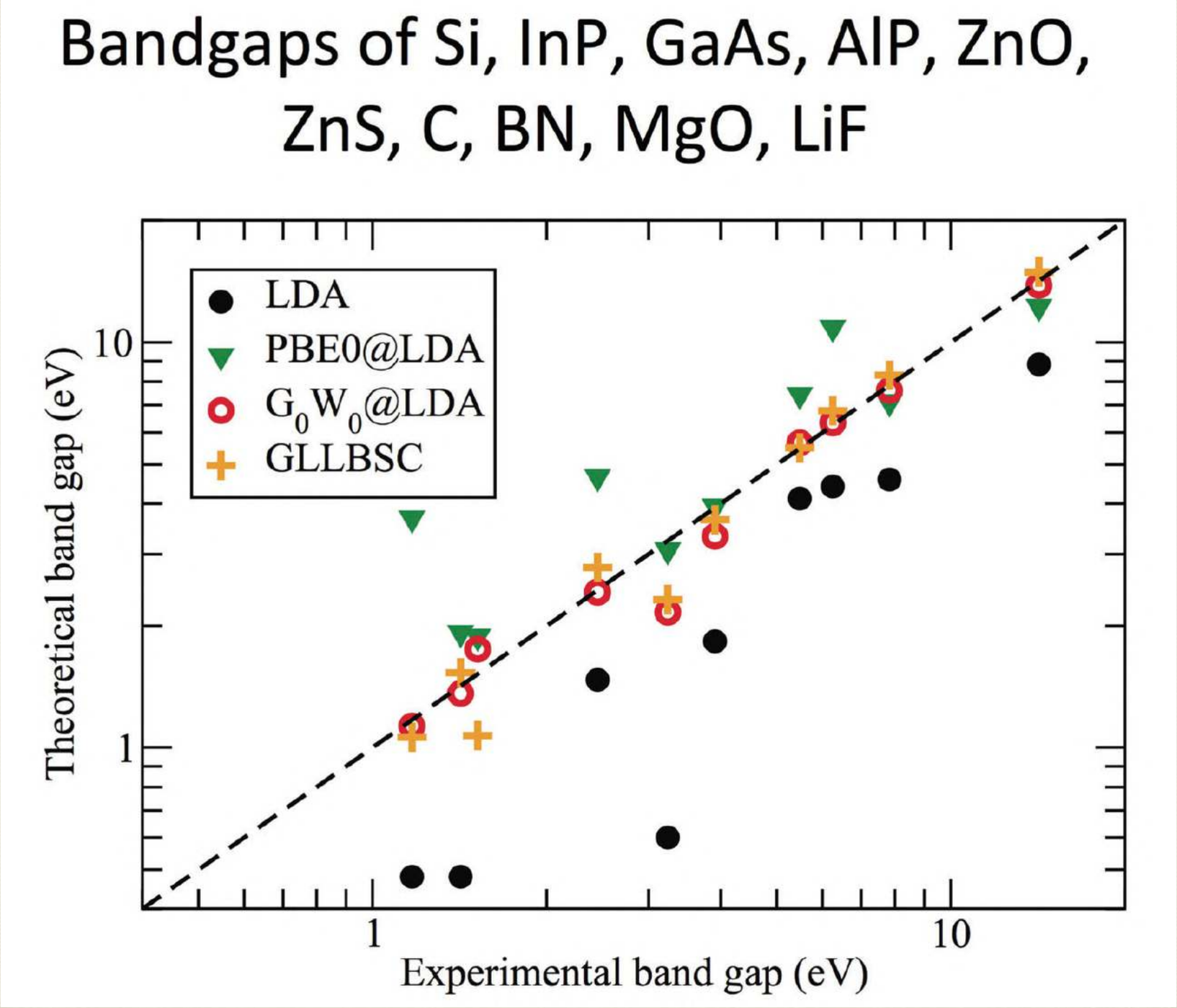
$$G_{\mathrm{fund}} = G_{\mathrm{KS}} + \Delta$$

GLLB model →

$$\Delta = K_x \sum_{i=1}^{N} \left[\sqrt{\epsilon_{\mathrm{L}} - \epsilon_i} - \sqrt{\epsilon_{\mathrm{H}} - \epsilon_i}\right] \langle \phi_{\mathrm{L}} | \frac{|\phi_i|^2}{\rho_0} | \phi_{\mathrm{L}} \rangle$$

Baerends, Phys.Chem.Chem.Phys. 19, 15639 (2017); Gritsenko *et al.,* PRA 51, 1944 (1995)

DFT: fundamental gap



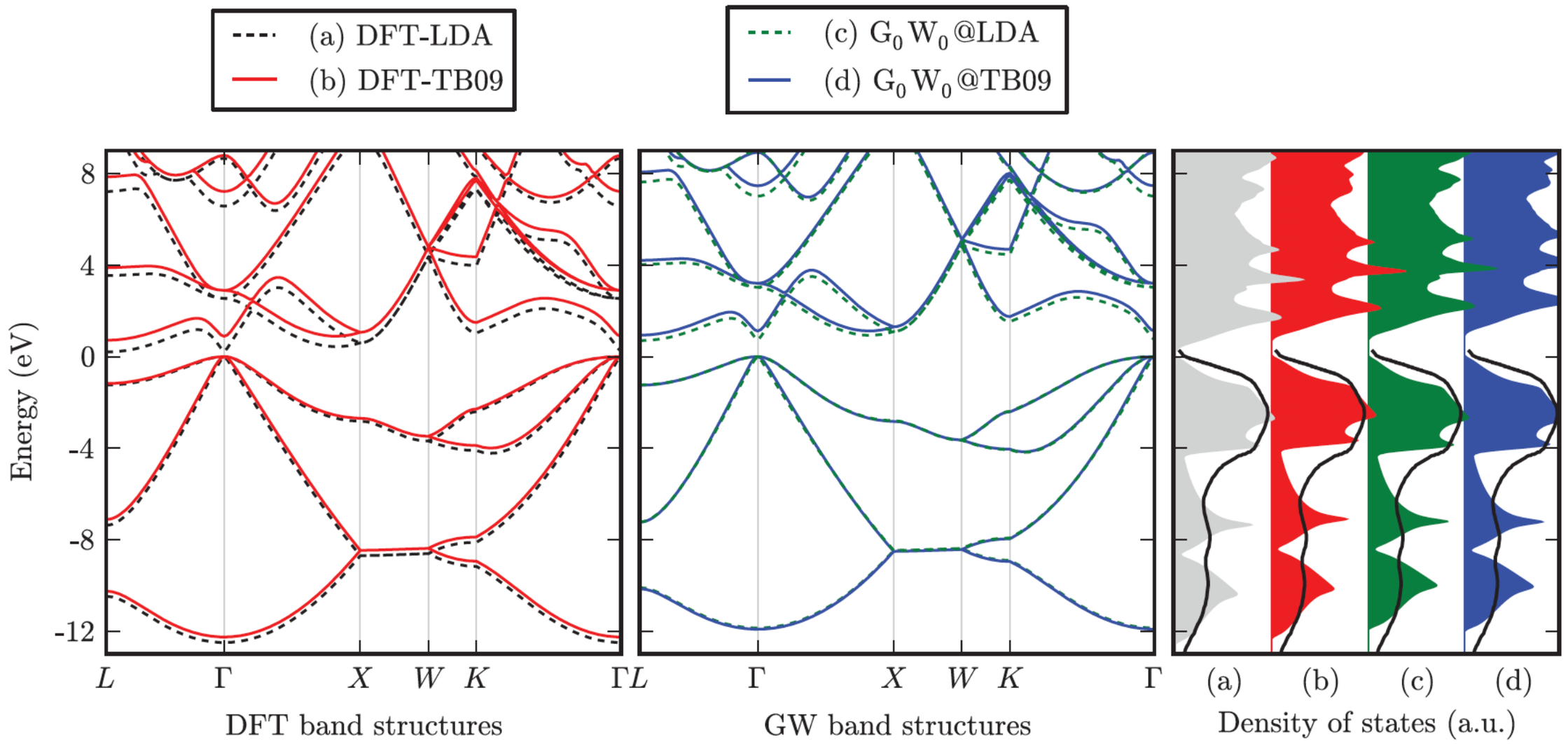
Baerends, Phys.Chem.Chem.Phys. 19, 15639 (2017; Hüser *et al.* Phys. Rev. B: Condens. Matter Mater. Phys. 87, 235132 (2013)

DFT: Photoemission spectra

DOS=Density of state

$$D(E) = \frac{1}{V} \sum_{i=1}^{N} \delta(E - E(\mathbf{k}_i))$$

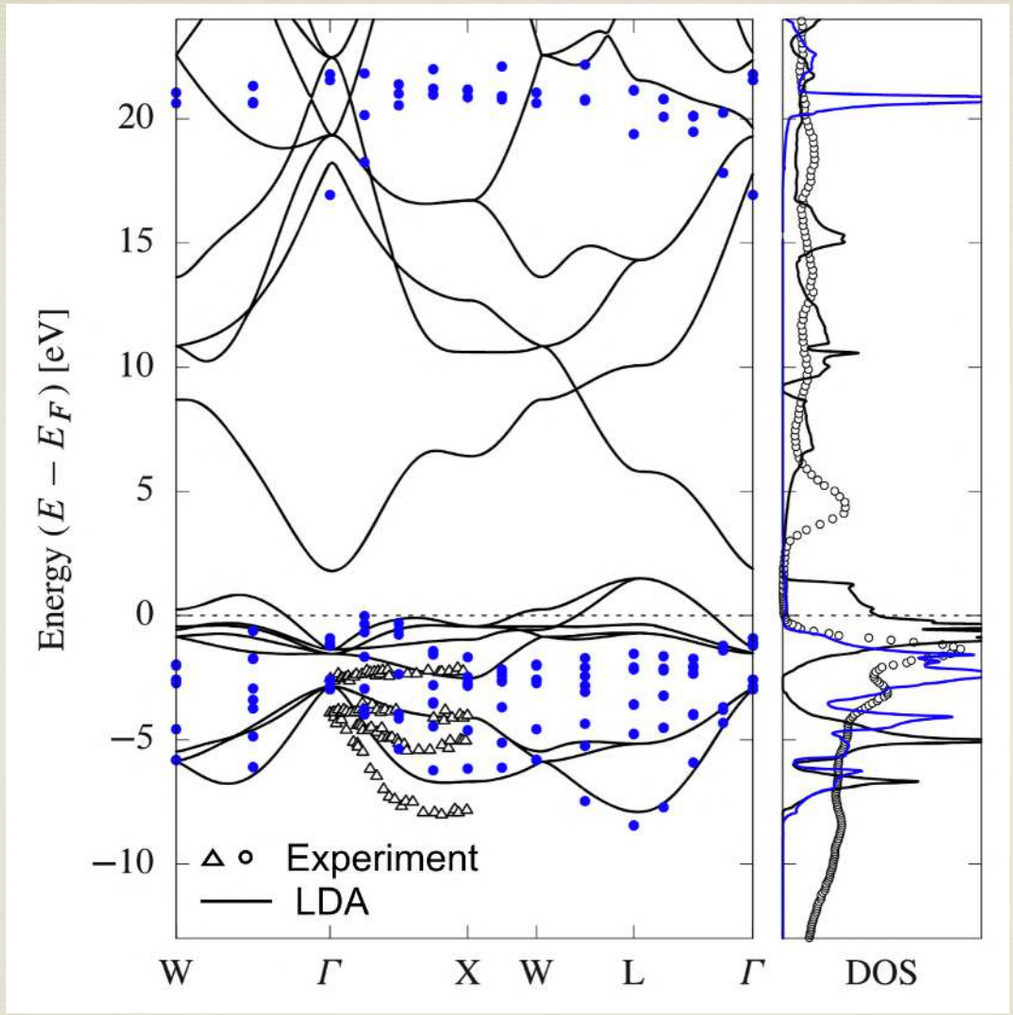
✳ Bulk Si



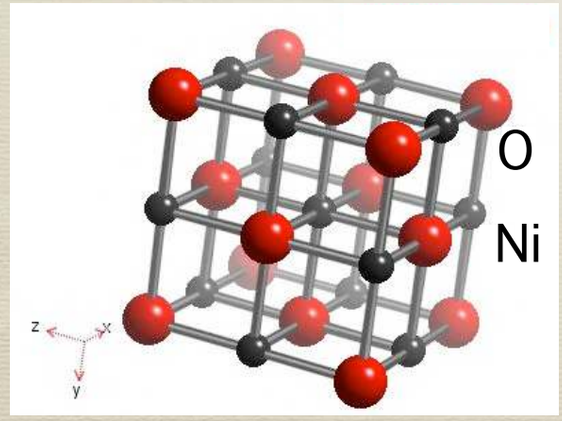
Waroquiers *et al.* PRB 87, 075121 (2013)

DFT: Photoemission spectra

- Bulk NiO (ParaMagnetic phase)



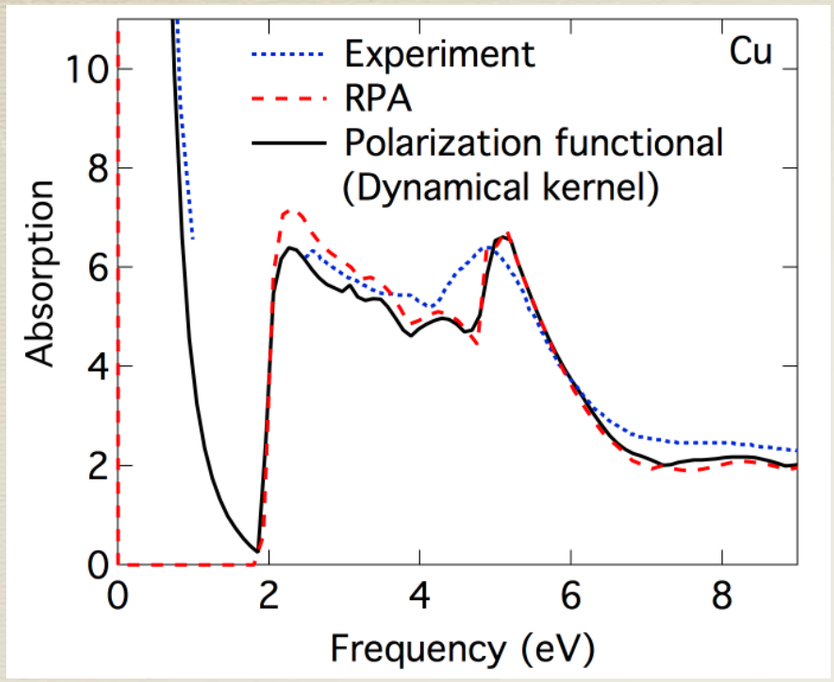
Rosksalt structure



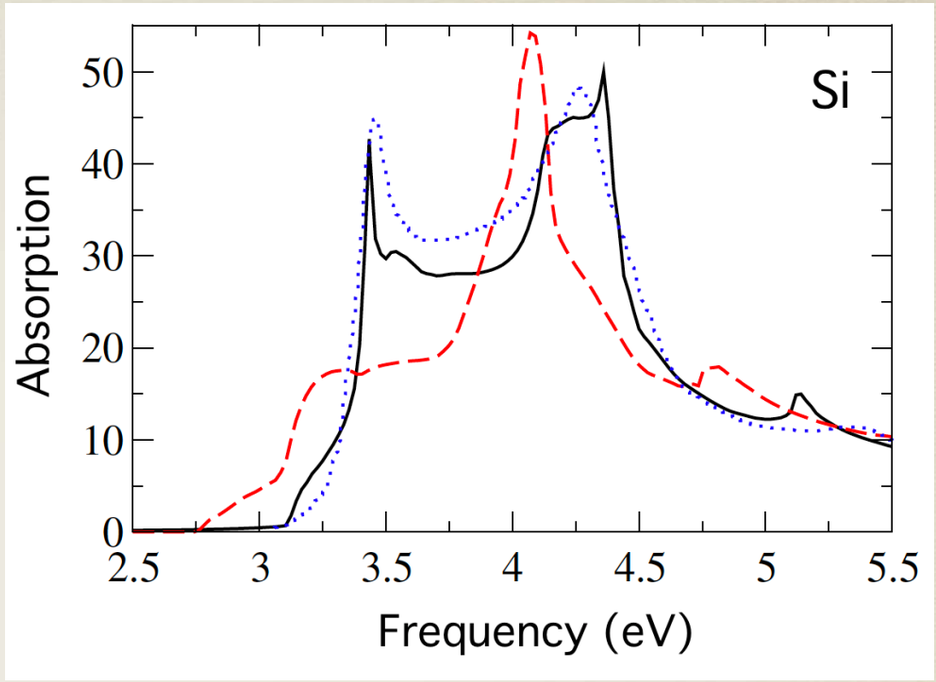
Di Sabatino, Berger & Romaniello JCTC 15, 5080 (2019)

DFT: Optical spectra

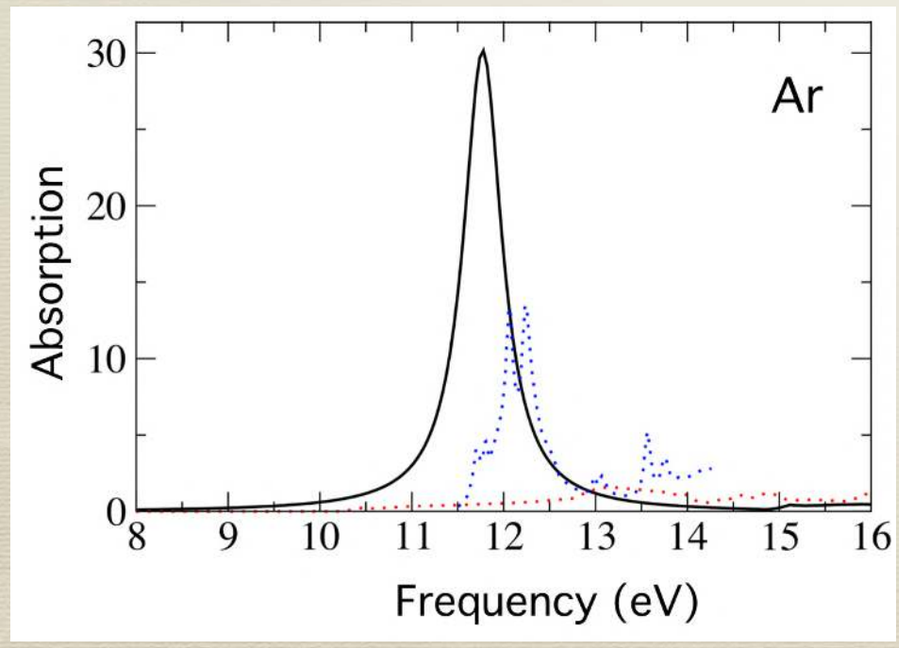
✳ Simple metals



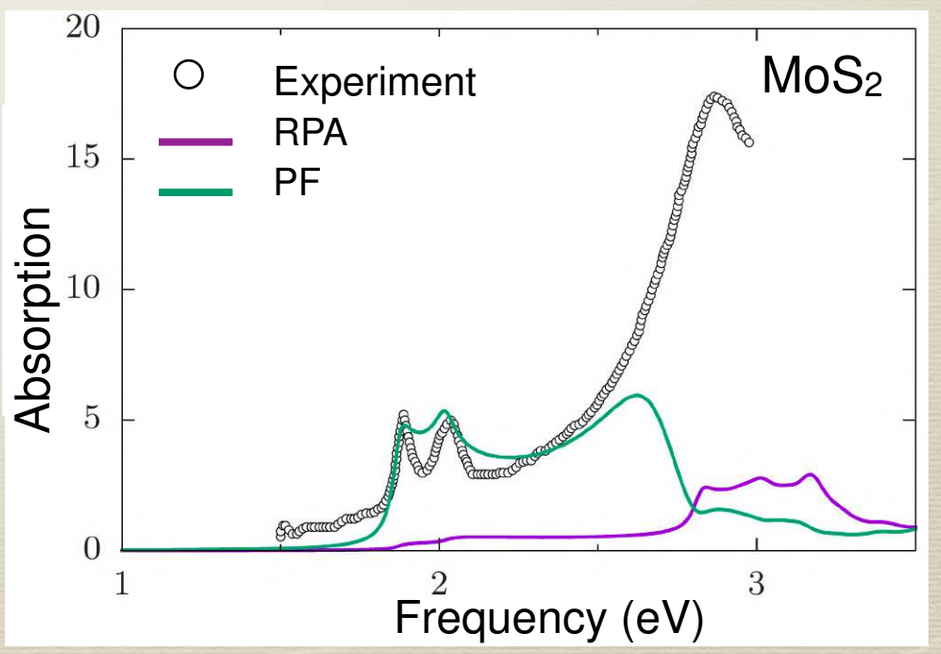
✳ Standard semiconductors



✳ Wide-gap insulators



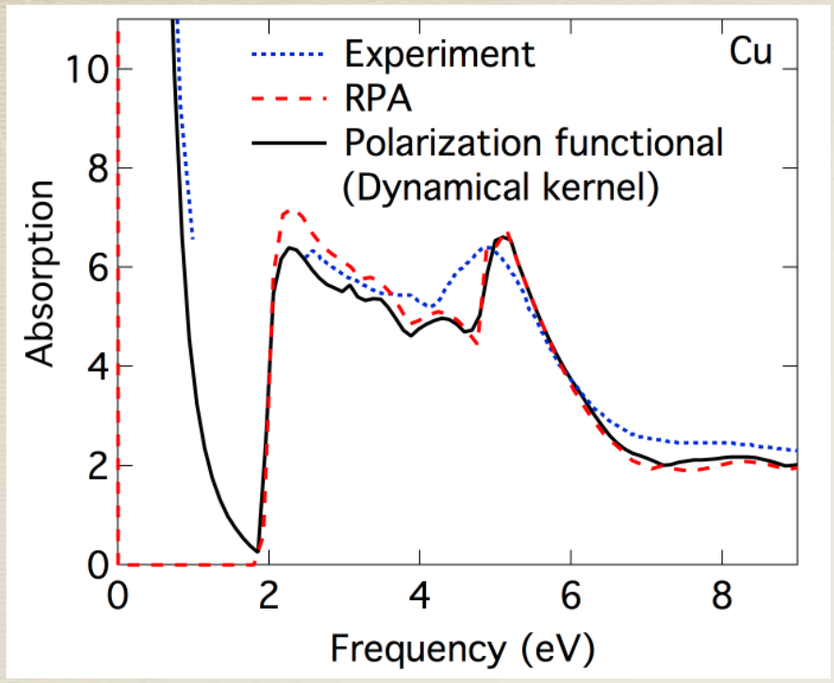
✳ 2D materials



Berger, PRL 115, 137402 (2015); Cavo, Berger & Romaniello, arXiv:1908.00808; Di Sabatino, Berger & Romaniello in preparation

DFT: Optical spectra

✳ Simple metals



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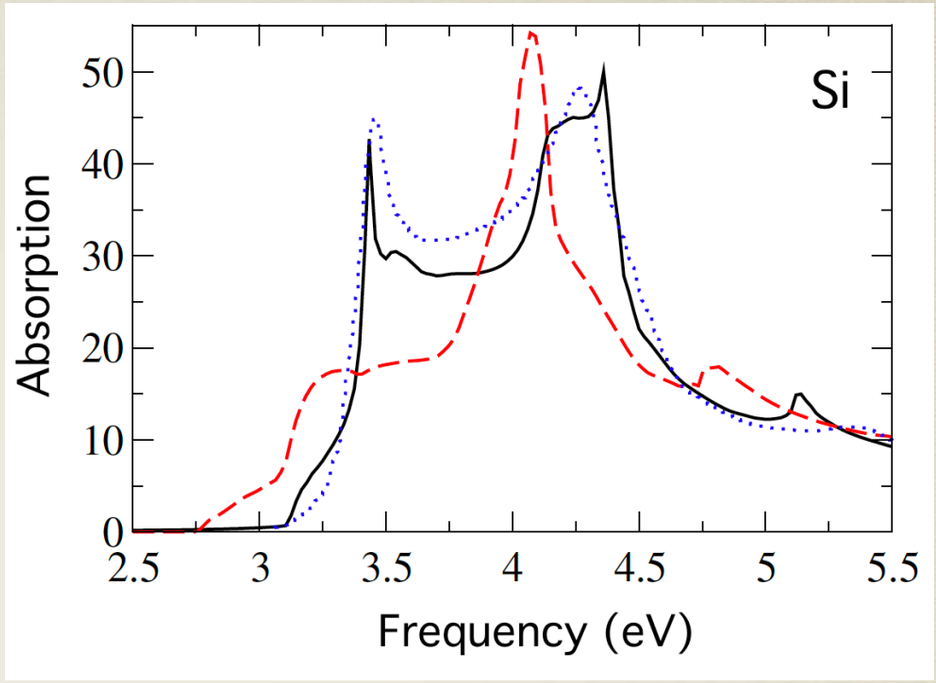

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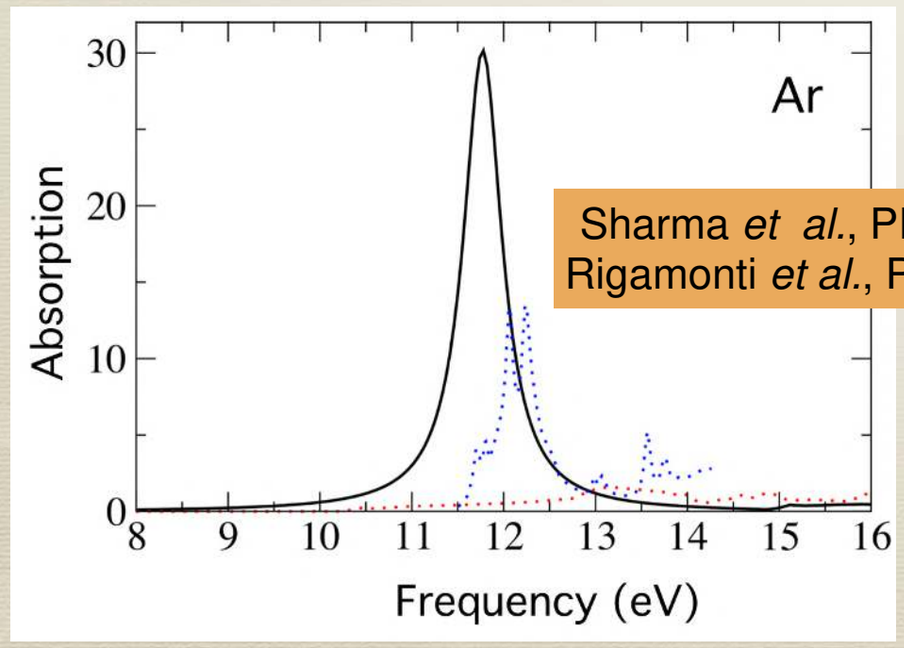
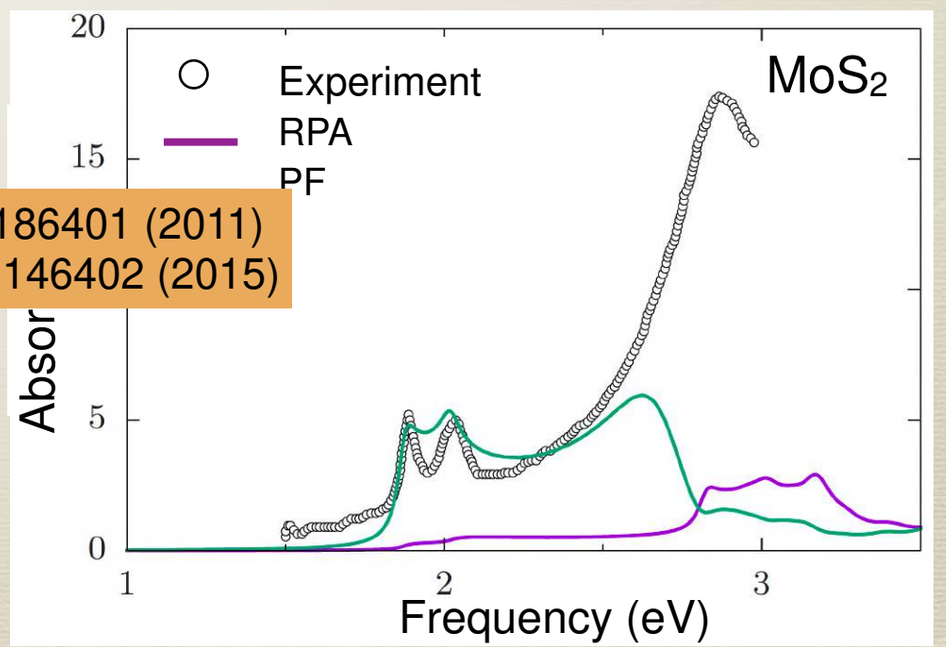


Sharma *et al.*, PRL 107, 186401 (2011)
Rigamonti *et al.*, PRL 114, 146402 (2015)

✳ 2D materials



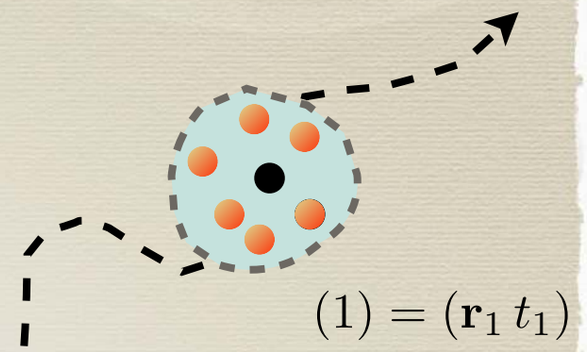
Berger, PRL 115, 137402 (2015); Cavo, Berger & Romaniello, arXiv:1908.00808; Di Sabatino, Berger & Romaniello in preparation

DFT: conclusions

- Band gap, direct (quasiparticle) photoemission spectra, optical spectra well described in simple metals and standard gapped materials
- Strongly correlated materials, photoemission spectra, optical spectra of 2D/van der Waals materials still a major challenge

Many-Body Perturbation Theory

1-body Green's function $$G(1,2) = -i\langle \Psi_0 | \mathcal{T}\left[\hat{\psi}(1)\hat{\psi}^\dagger(2)\right] | \Psi_0 \rangle$$



Hedin, PR 139, A796 (1965)

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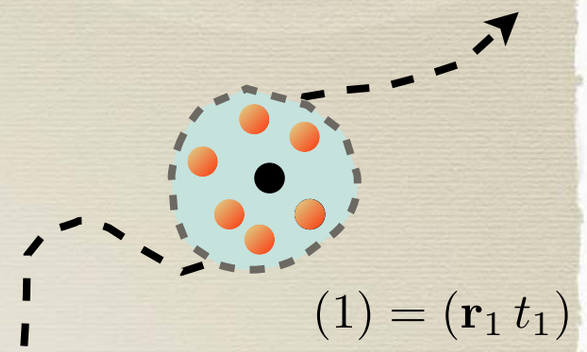
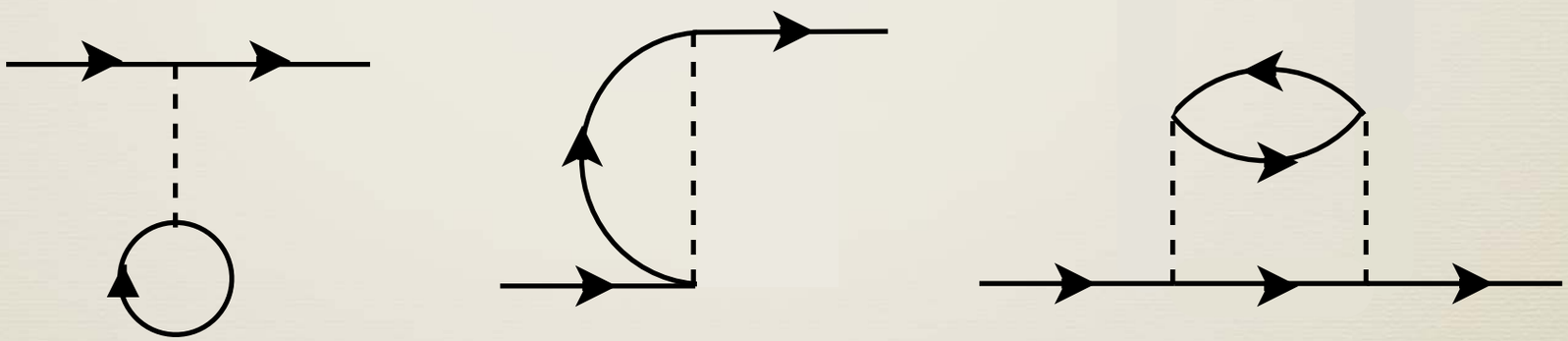


Dyson's equation $$G = G_0 + G_0 \Sigma[G] G$$

self-energy $\Sigma =$



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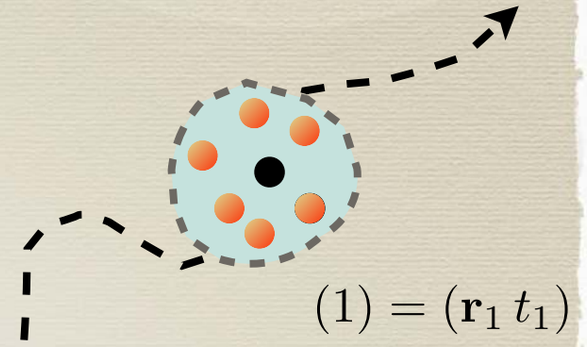

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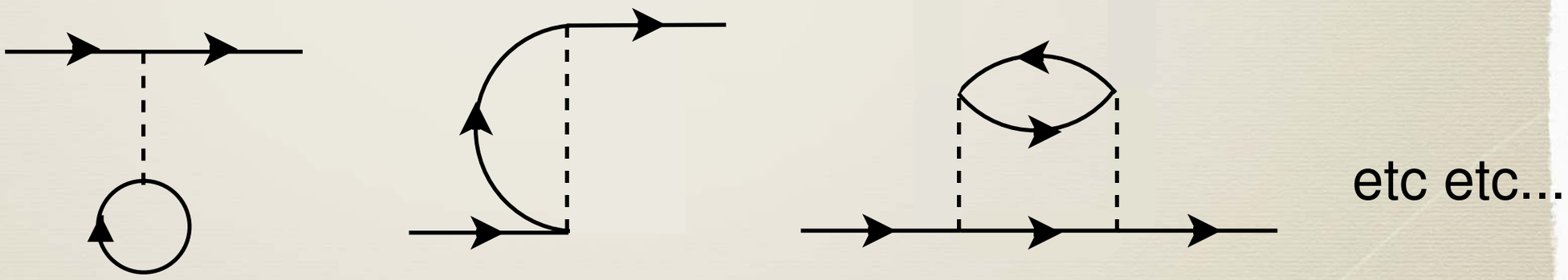

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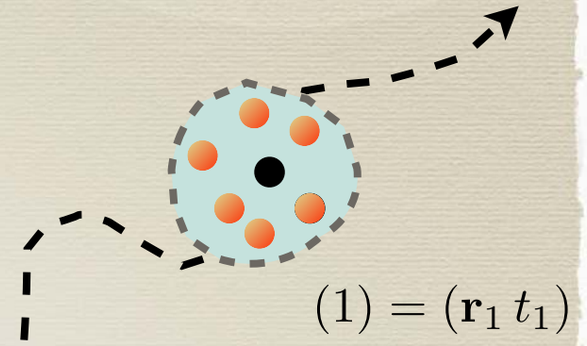

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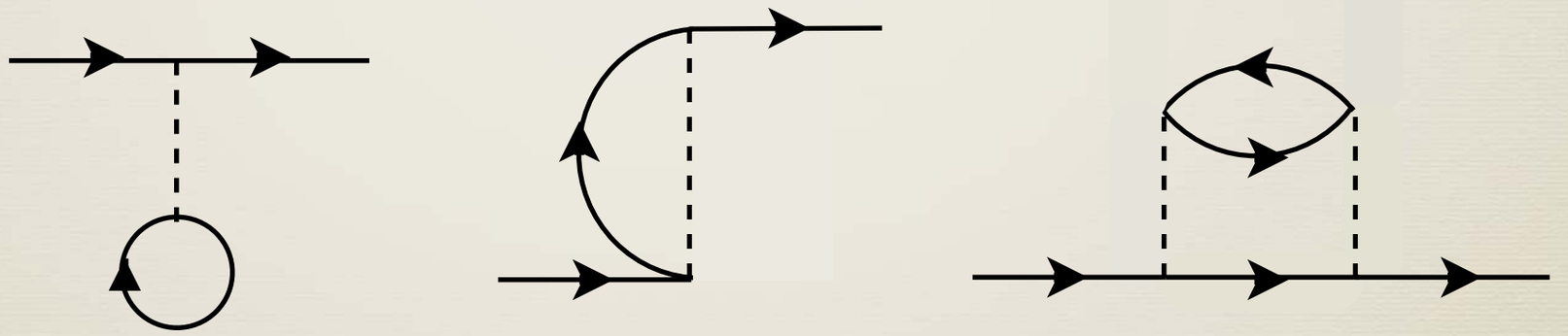
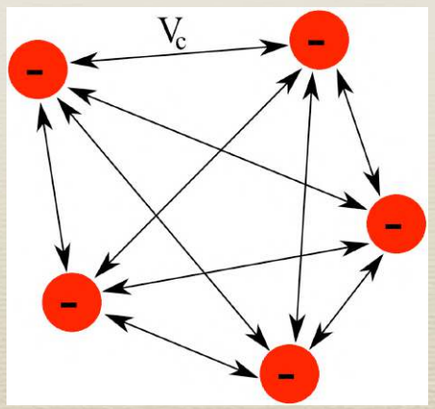
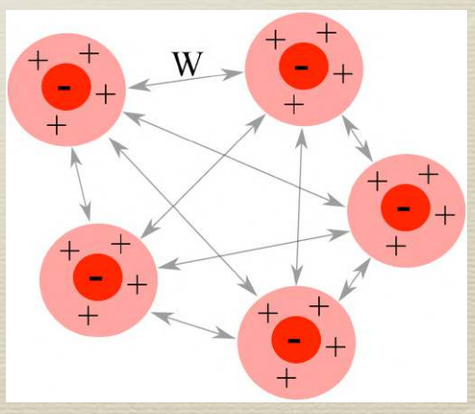


etc etc...

$$\Sigma \approx v_H + iGW$$

GW approximation





Hedin, PR 139, A796 (1965)

MBPT: Levels of self-consistency

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- One shot GW: best G best W philosophy (usually from KS G)

$$G^0(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_n \frac{\phi_n(\mathbf{r}_1)\phi_n^*(\mathbf{r}_2)}{\omega - \epsilon_n + i\eta sign(\epsilon_n - \mu)}$$

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- scQP equation

$$h_0(\mathbf{r})\psi_n^{\mathrm{QP}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_n^{\mathrm{QP}})\psi_n^{\mathrm{QP}}(\mathbf{r}') = \epsilon_n^{\mathrm{QP}}\psi_n^{\mathrm{QP}}(\mathbf{r})$$

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$$\psi_n^{\mathrm{QP}}\approx\phi_n$$

$$\epsilon_n^{QP}=\epsilon_n+\langle\phi_n|\Sigma(\epsilon_n^{QP})|\phi_n\rangle$$ eigenvalue QP equation

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$$\psi_n^{\mathrm{QP}}\approx\phi_n$$

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$$\langle\Sigma(\epsilon_n^{\mathrm{QP}})\rangle=\langle\Sigma(\epsilon_n)\rangle+\langle\left.\frac{\partial\Sigma(\epsilon_n^{\mathrm{QP}})}{\partial\omega}\right|_{\omega=\epsilon_n}\rangle(\epsilon_n^{\mathrm{QP}}-\epsilon_n)+O((\epsilon_n^{\mathrm{QP}}-\epsilon_n)^2)$$

$$\epsilon_n^{\mathrm{QP}}=\epsilon_n+Z_n(\epsilon_n)\langle\phi_n|\Sigma(\epsilon)|\phi_n\rangle$$ linearised QP equation

$$Z_n=\left(1-\langle\left.\frac{\partial\Sigma(\omega)}{\partial\omega}\right|_{\omega=\epsilon_n}\rangle\right)^{-1}$$

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$\psi_n^{\mathrm{QP}}\approx\phi_n$

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- towards full self consistency

Many-Body Perturbation Theory

Observables

- total energy

$$E_0 = -\frac{i}{2}\int d\mathbf{x}_1 \lim_{2\to 1^+}\left(i\frac{\partial}{\partial t_1} + h_0(\mathbf{r}_1)\right) G(1,2)$$

- density matrix

$$\gamma(\mathbf{x}_1,\mathbf{x}_2) = -iG(1,\mathbf{x}_2 t_1^+) = -i\int \frac{d\omega}{2\pi}\, G(\omega) e^{i\omega 0^+}$$

- removal/addition energies

$$G(\omega) = \sum_k \frac{A^{k,R}}{\omega - \epsilon_k^R - i\eta} + \sum_k \frac{B^{k,A}}{\omega - \epsilon_k^A + i\eta}$$

- spectral function (PES)

$$A(\omega) = \frac{1}{\pi}|\Im G(\omega)|$$

- Neutral excitations

$$L(\omega) \approx L_0(\omega) + L_0(\omega)\Xi_{Hxc}L(\omega)$$

- ...

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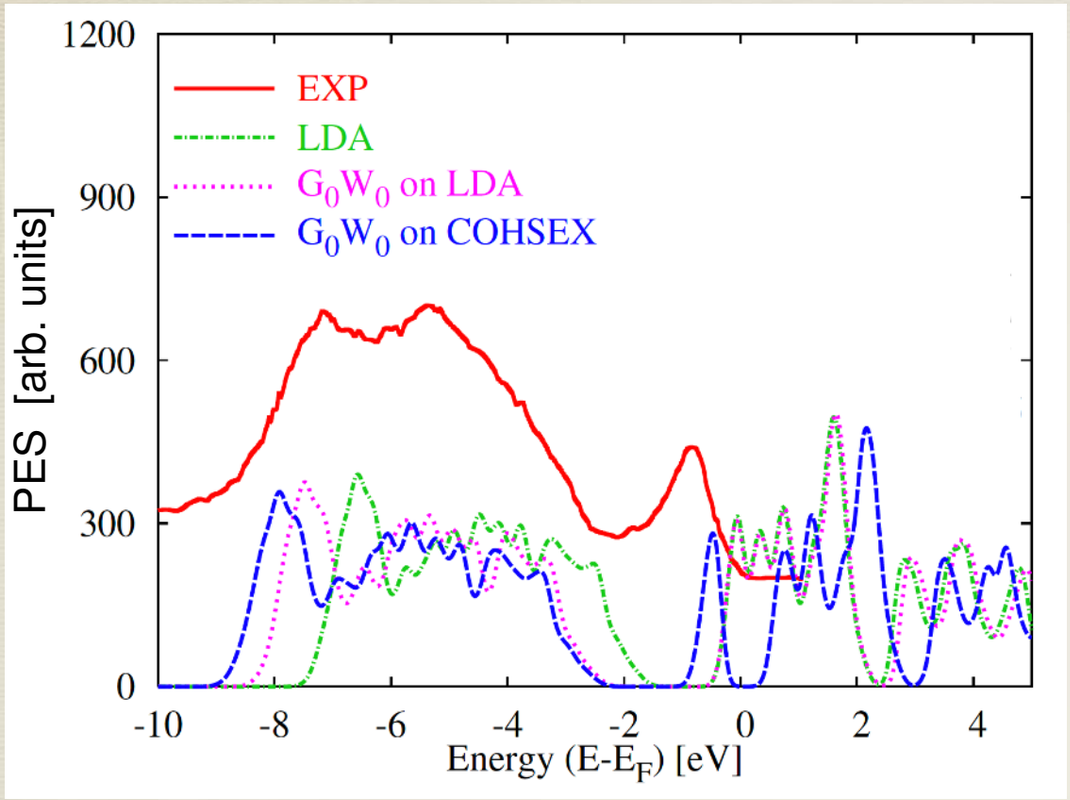
static kernel

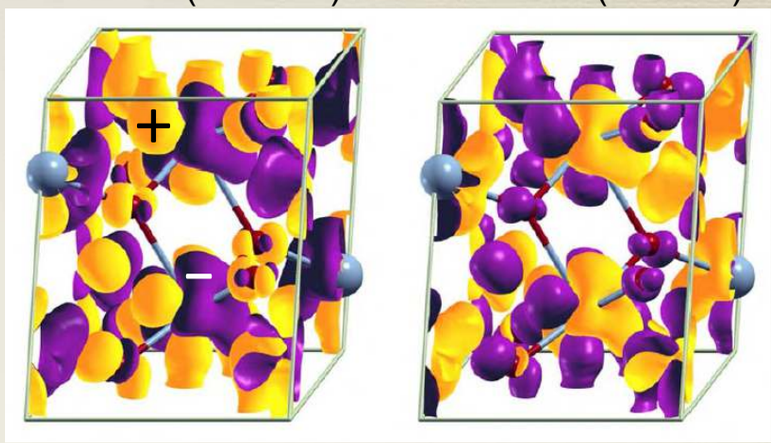
- ...

MBPT: Photoemission spectra

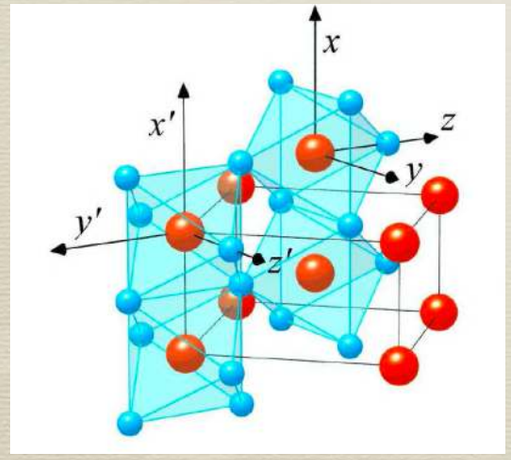
Bulk VO_2 (insulating phase)



VBM (HOMO) CBM (LUMO)

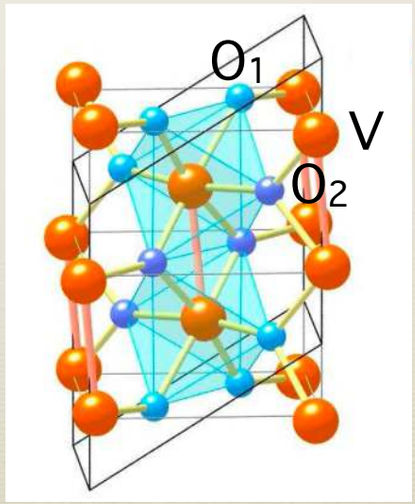


Difference between COHSEX and LDA wave functions



rutile metallic phase

Temperature



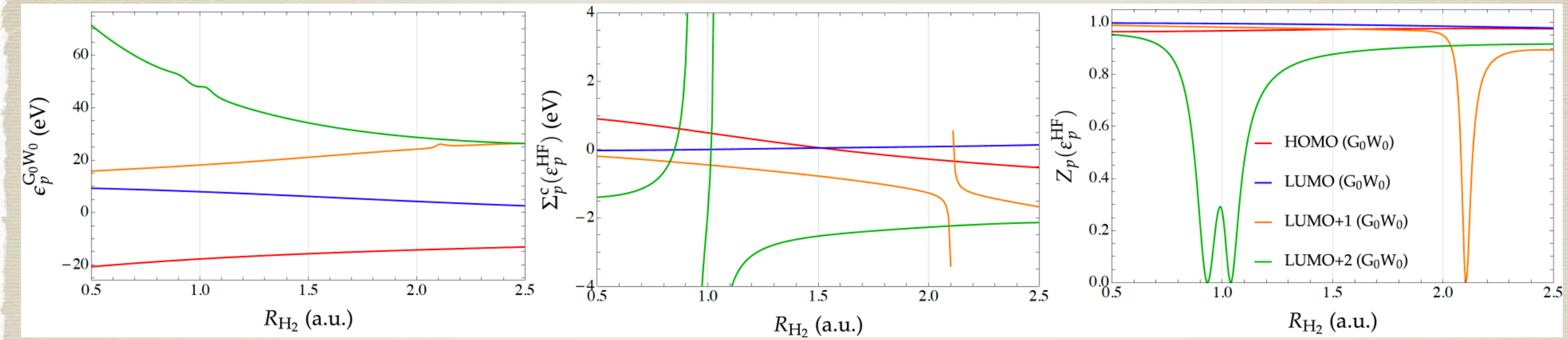
monoclinic insulating phase

Gatti *et al.* PRL 99, 266402 (2007); Gatti, PhD thesis, École polytechnique (2007)

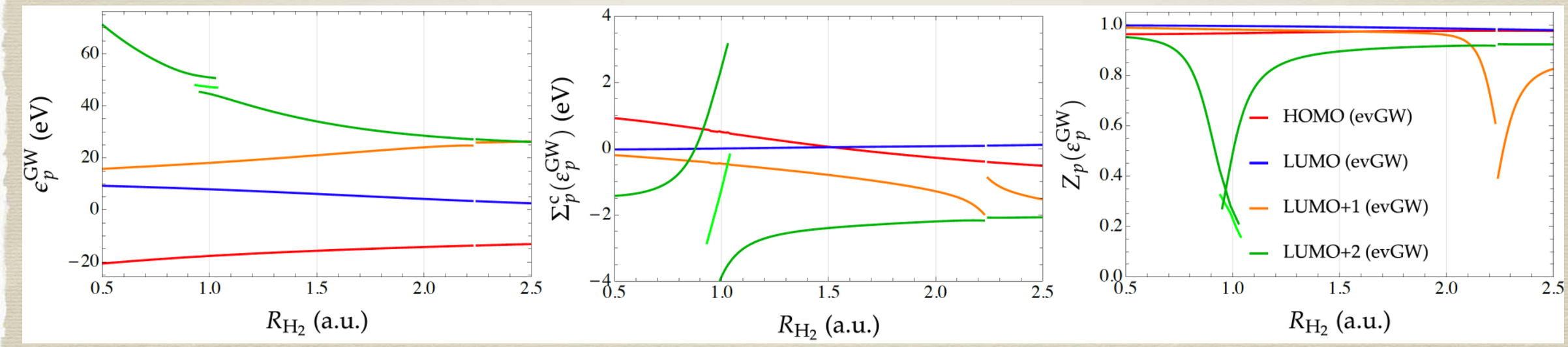
Multiple quasiparticle solutions

H_2 molecule

- Linearised QP equation $\epsilon_p^{G_0W_0} = \epsilon_p^{HF} + Z_p(\epsilon_p^{HF})\Re[\Sigma_p^c(\epsilon_p^{HF})]$ $Z_p(\omega) = \left[1 - \frac{\partial \Re[\Sigma_p^c(\omega)]}{\partial \omega}\right]^{-1}$



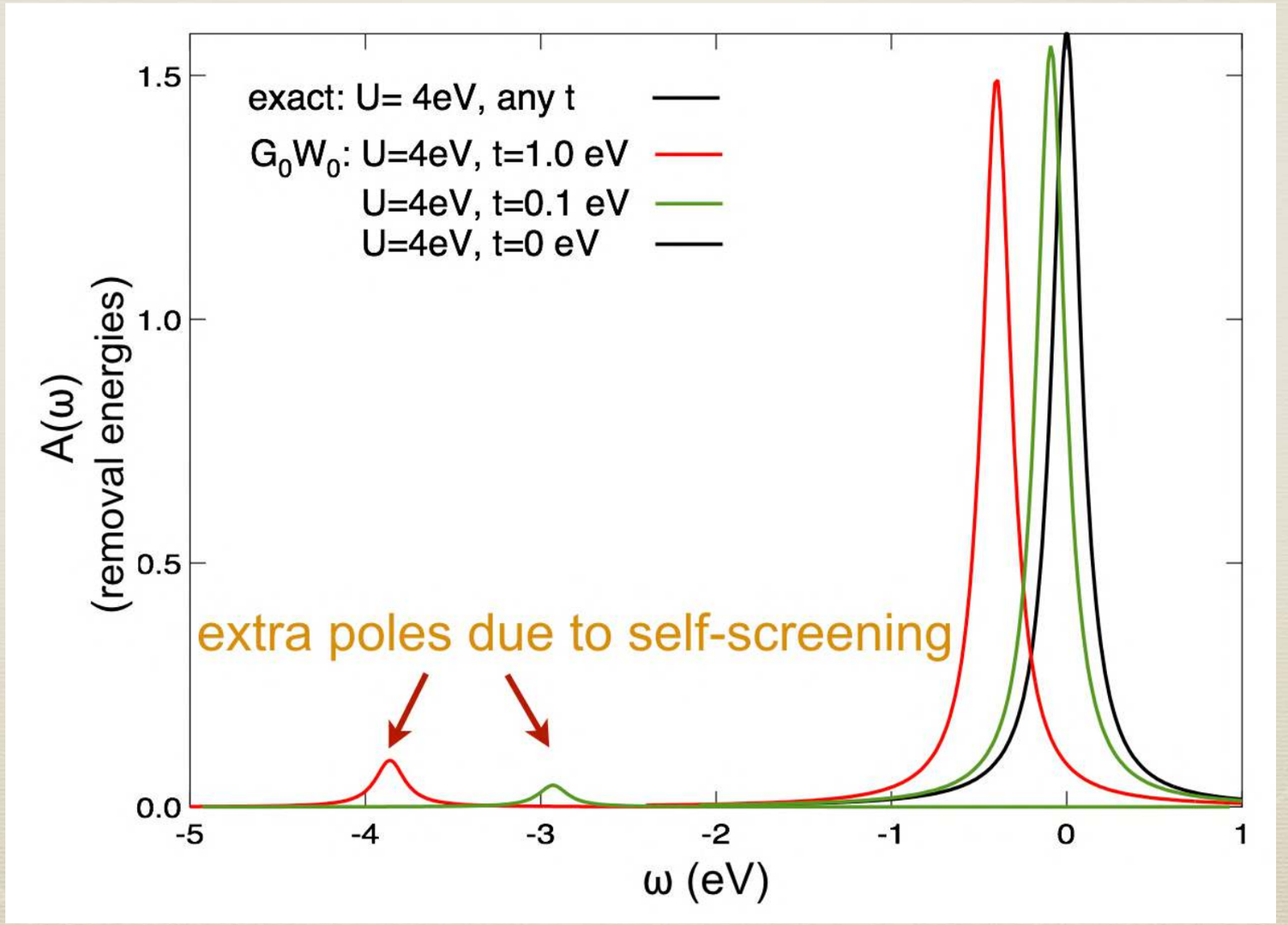
- Eigenvalue QP equation $\omega = \epsilon_p^{HF} + \Re[\Sigma_p^c(\omega)]$



Véril, Romaniello, Berger & Loos, JCTC 14, 5220 (2018); Loos, Romaniello & Berger, JCTC 14, 3071 (2018)

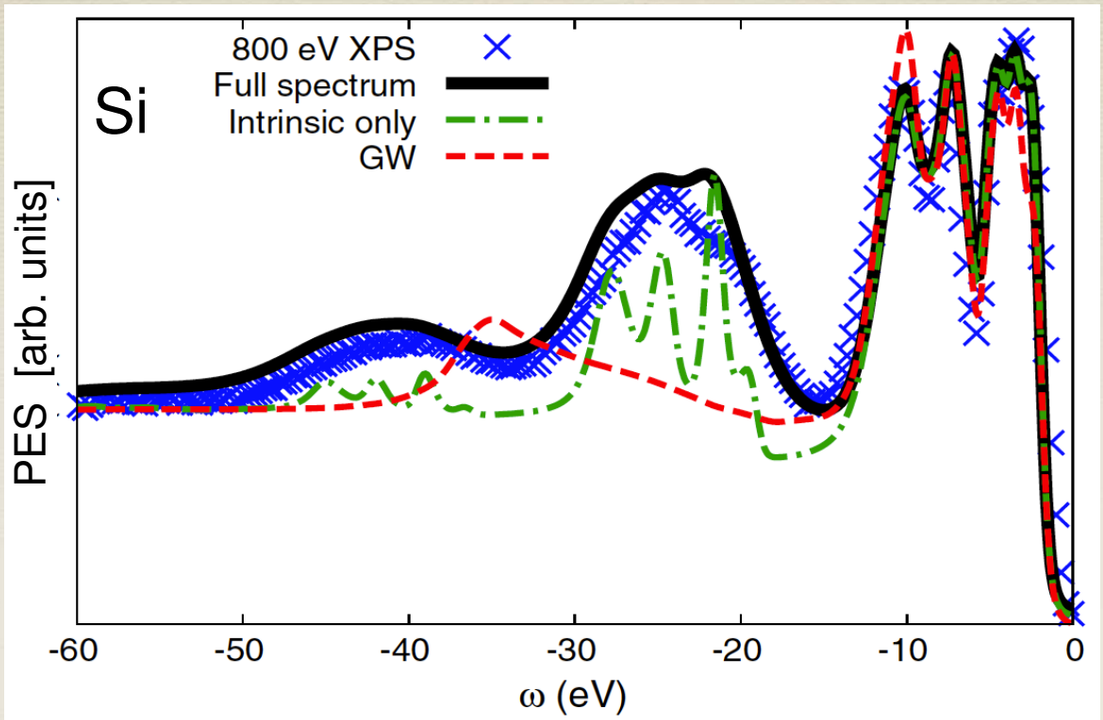
Self-screening problem

- Hubbard dimer 1/4 filling

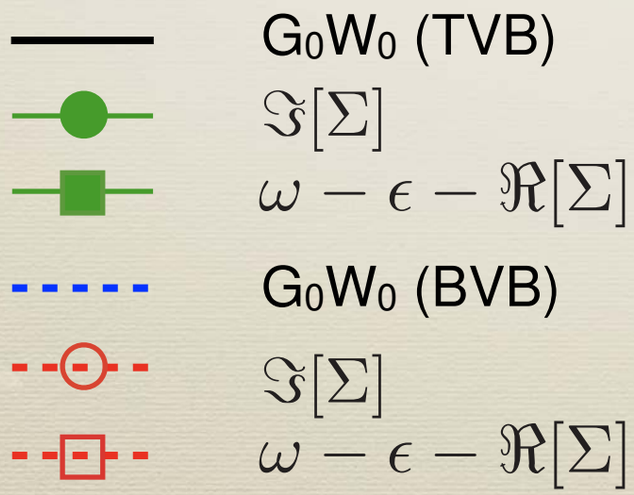


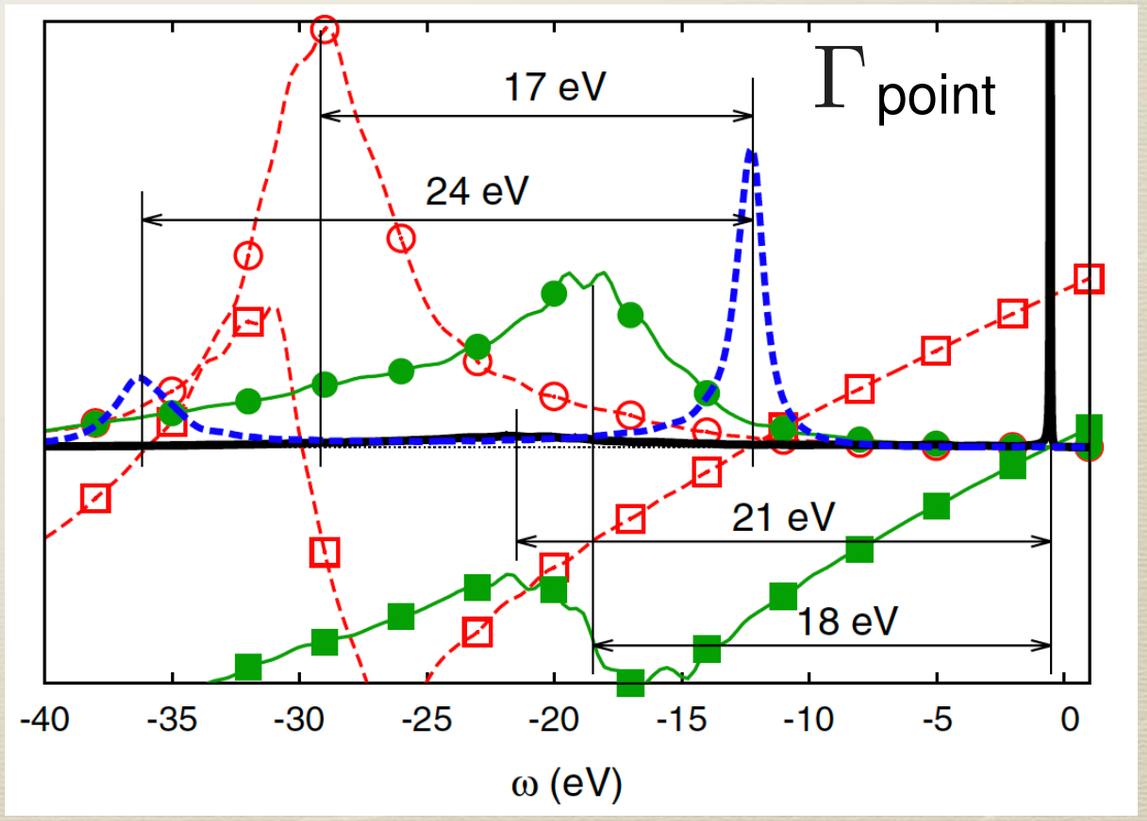
Romaniello, Guyot & Reining, JCP 131, 154111 (2009); Nelson *et al.* PRA,75, 032505 (2007); Caruso *et al.* PRL 86, 081102 (2012)

Plasmaron (hole-plasmon) artifact



$$A_{nn}(\omega) = \frac{1}{\pi} \frac{|\Im[\Sigma_n(\omega)]|}{(\omega - \epsilon_n - \Re[\Sigma_n(\omega)])^2 + (\Im[\Sigma_n(\omega)])^2}$$

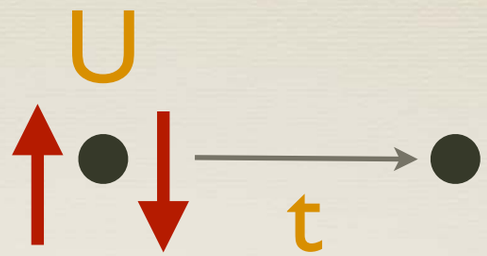


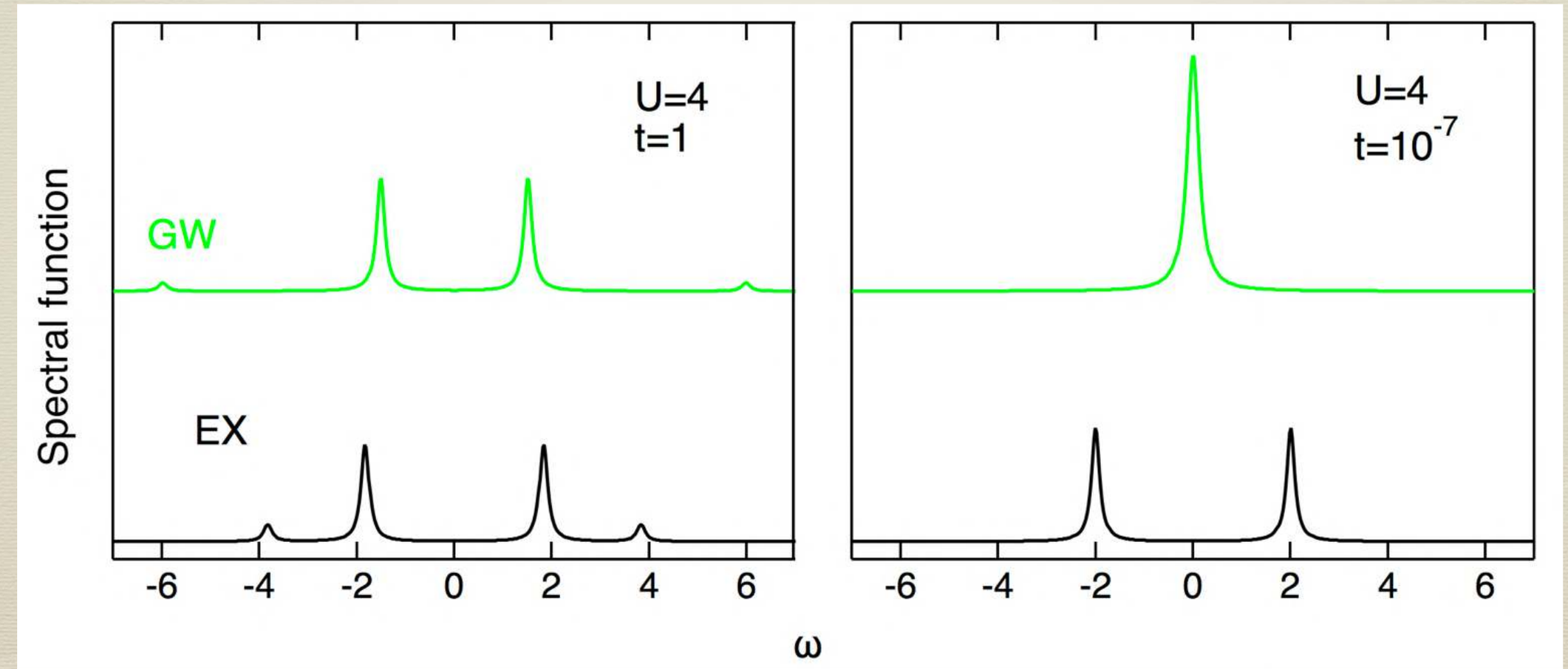


Guzzo *et al.*, PRL 107, 166401 (2011)

Missing strong correlation

✳ Hubbard dimer 1/2 filling

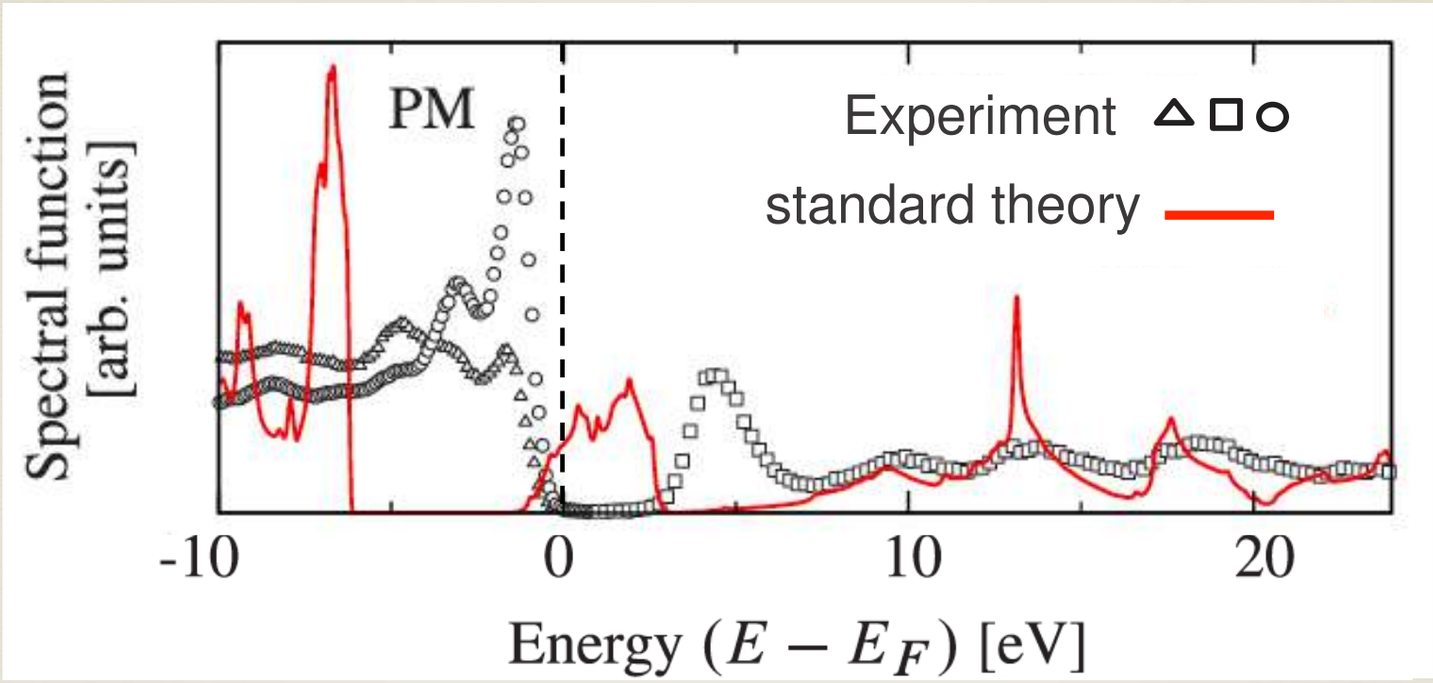




Romaniello, Bechstedt & Reining, PRB 85, 155131 (2012)

Missing strong correlation

- Bulk NiO (ParaMagnetic phase)

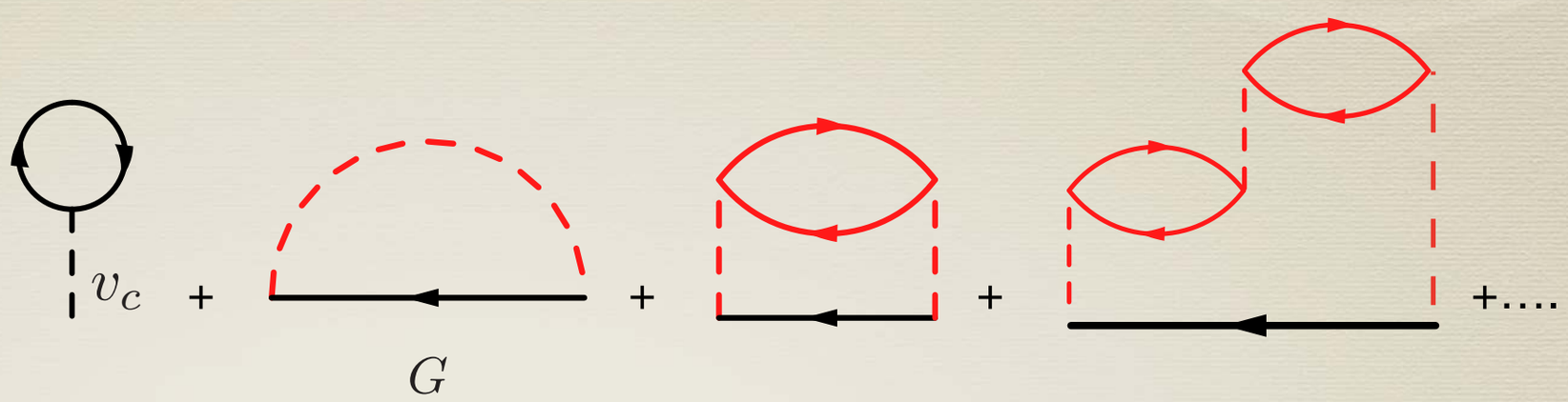


Stefano Di Sabatino's private communication

Beyond GW: screened T matrix

✳ GW

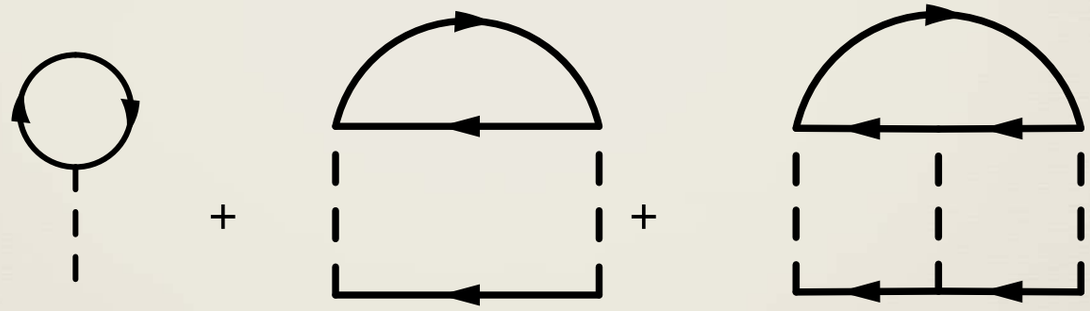
$\Sigma = v_H + iGW$ =



(high-density limit)

✳ T-matrix

$\Sigma = iGT$ =



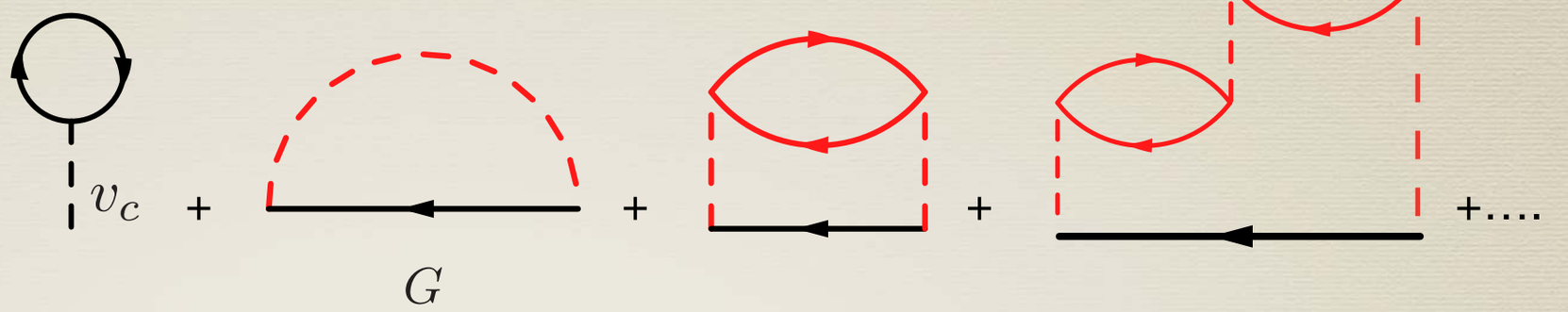
+ ….. + exchange terms

(low-density limit)

Beyond GW: screened T matrix

- GW

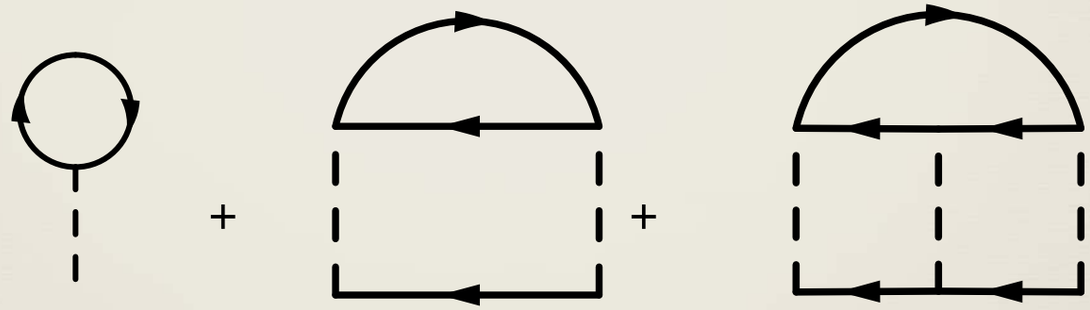
$\Sigma = v_H + iGW$ =



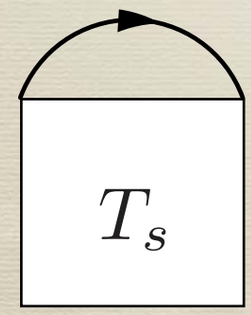
(high-density limit)

- T-matrix

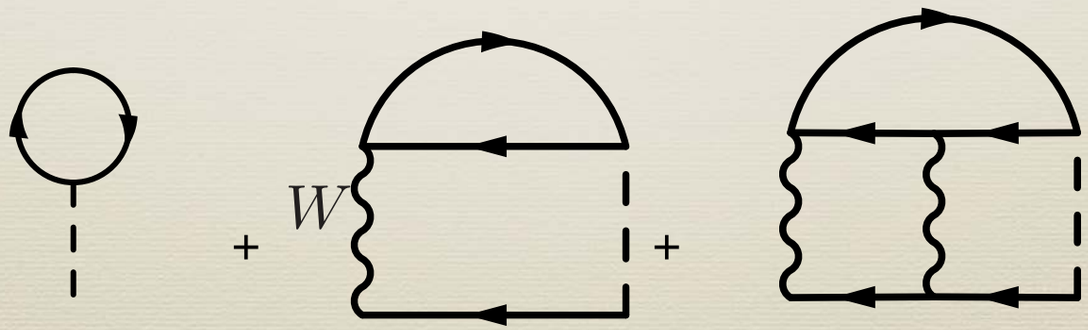
$\Sigma = iGT$ =



(low-density limit)



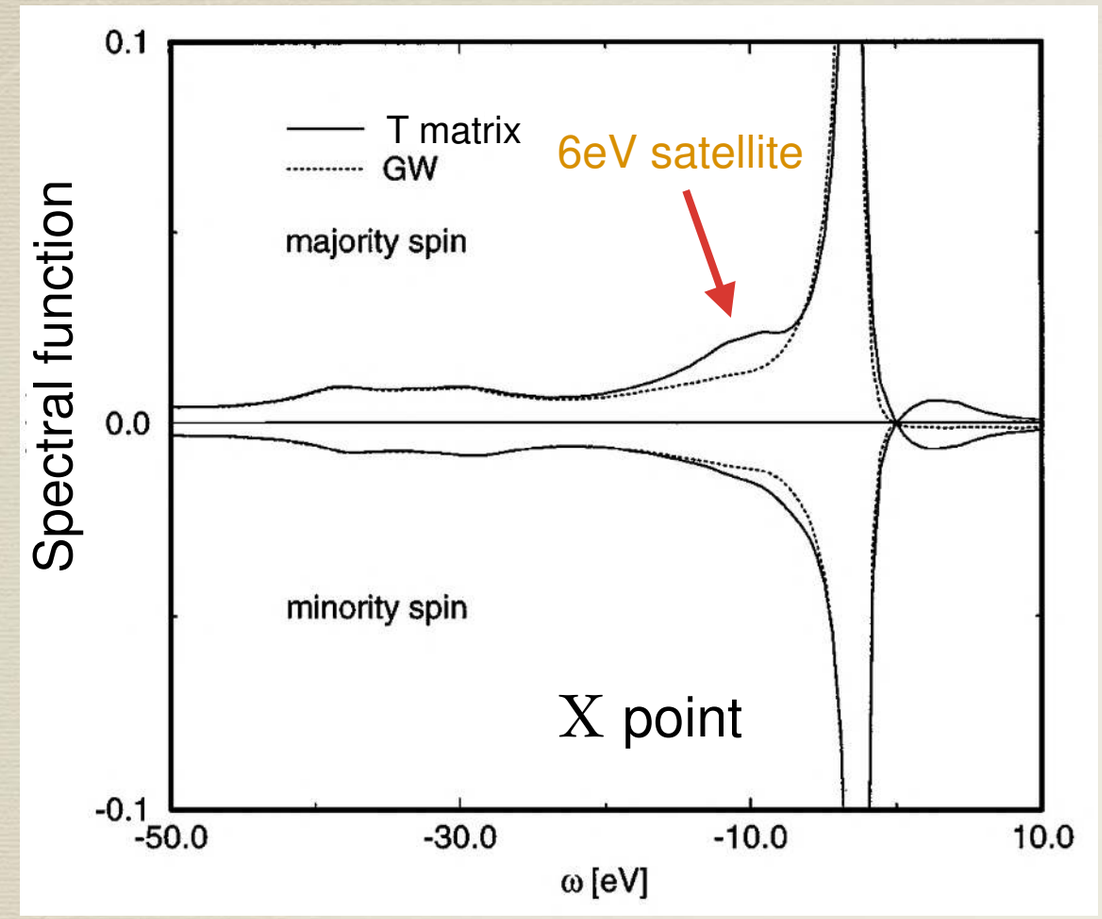
$\Sigma = iGT_s$ =

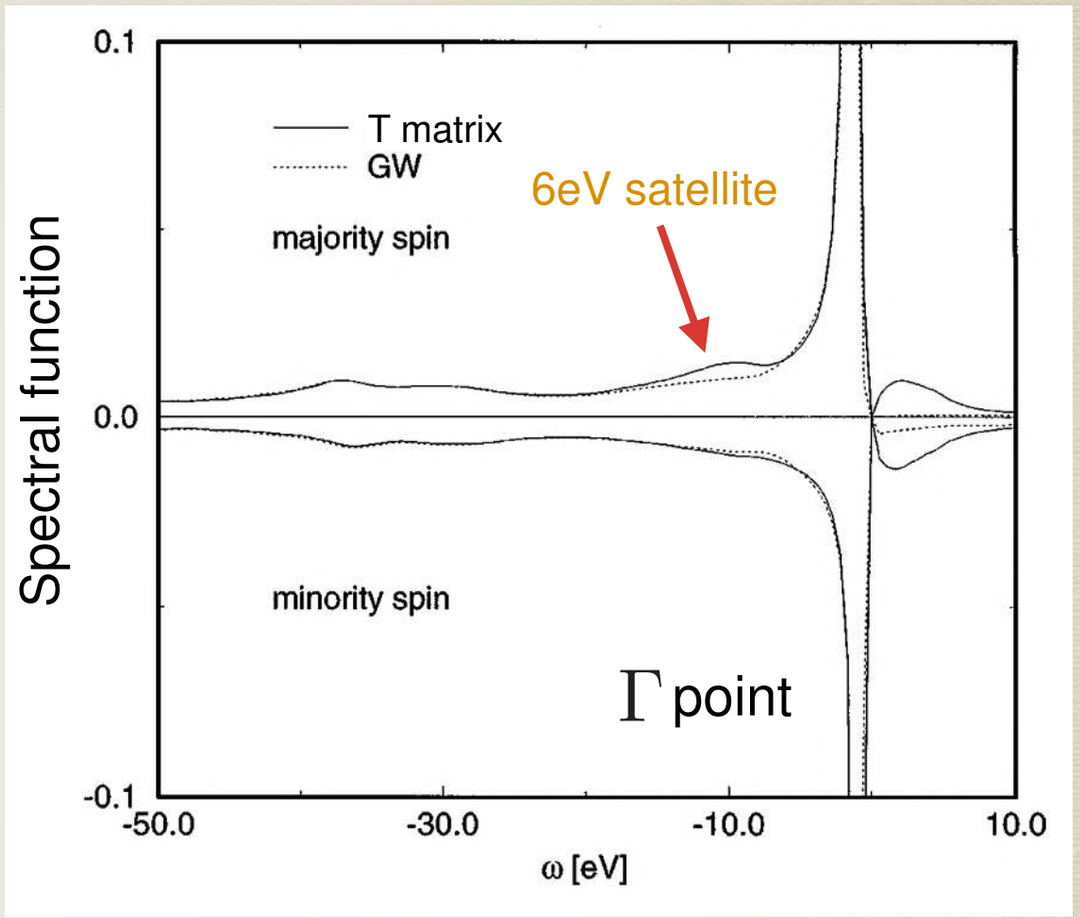


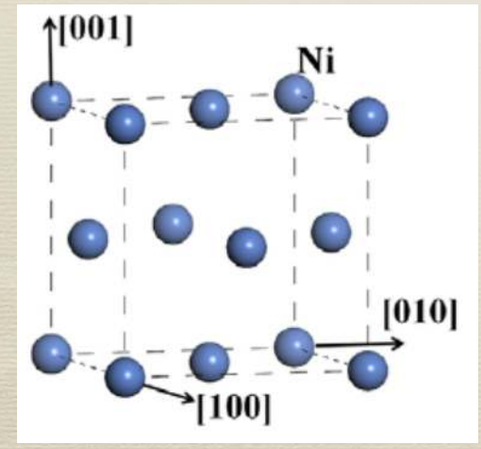
Romaniello, Bechstedt & Reining, PRB 85, 155131 (2012); Springer *et al.*, PRL 80, 2389 (1998)

Beyond GW: screened T matrix

- The 6eV satellite in Ni PES







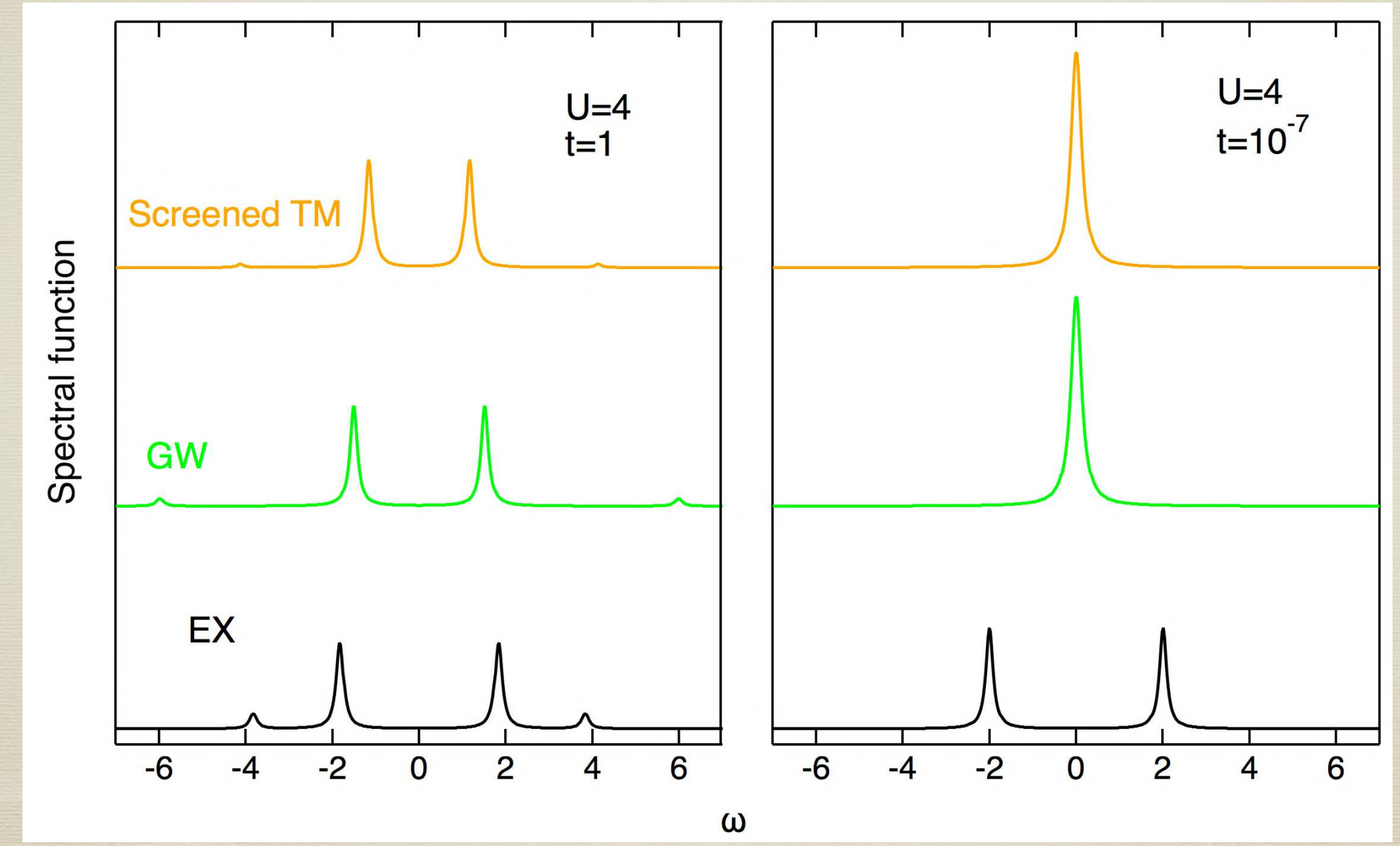
majority spin minority spin

Ni d^9

Springer *et al.*, PRL 80, 2389 (1998)

Beyond GW: screened T matrix

- Hubbard dimer at 1/2 filling



Romaniello, Bechstedt & Reining, PRB 85, 155131 (2012)

Multiple solutions

Dyson equation $G = G_0 + G_0 \Sigma[G] G \xrightarrow[G_0 \to G]{}$ multiple solutions

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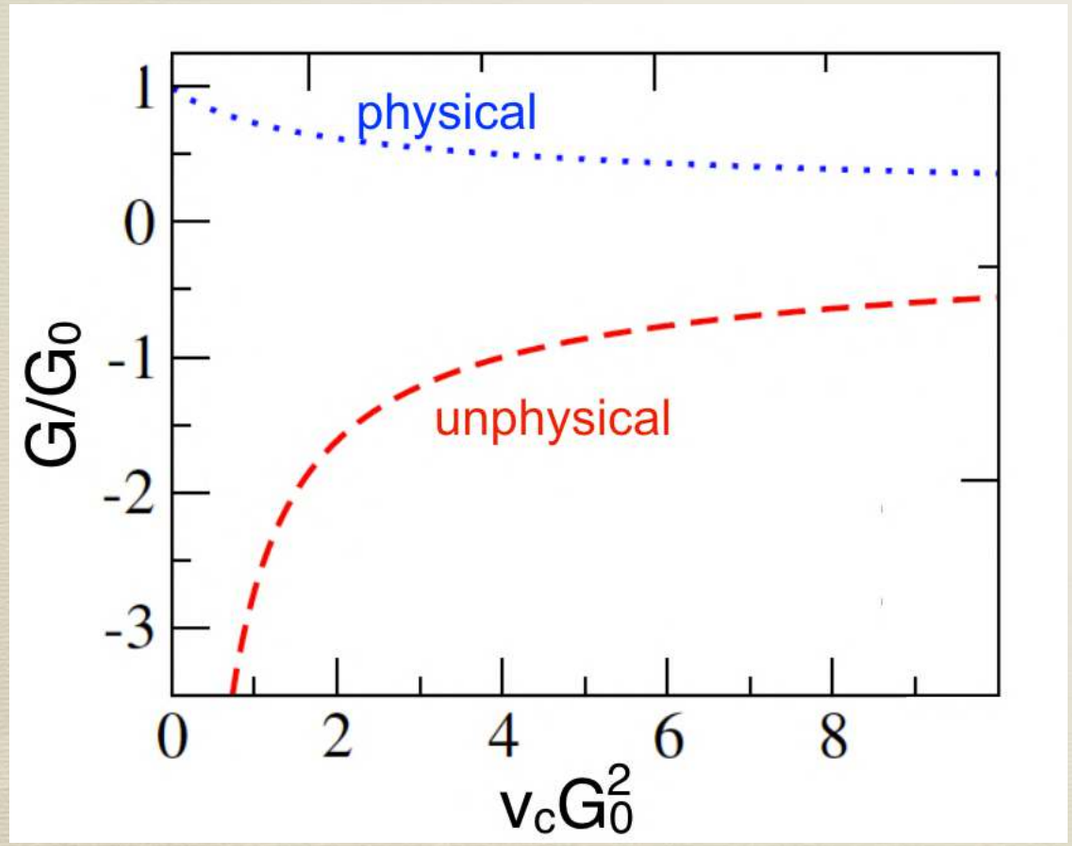
one-point model

$$\Sigma^{HF}[G, v_c] = -\frac{1}{2} v_c G$$



Stan, Romaniello, Rigamonti, Reining & Berger
NJP 17, 093045 (2015)

Tandetzky *et al.* 92, 115125 (2015)

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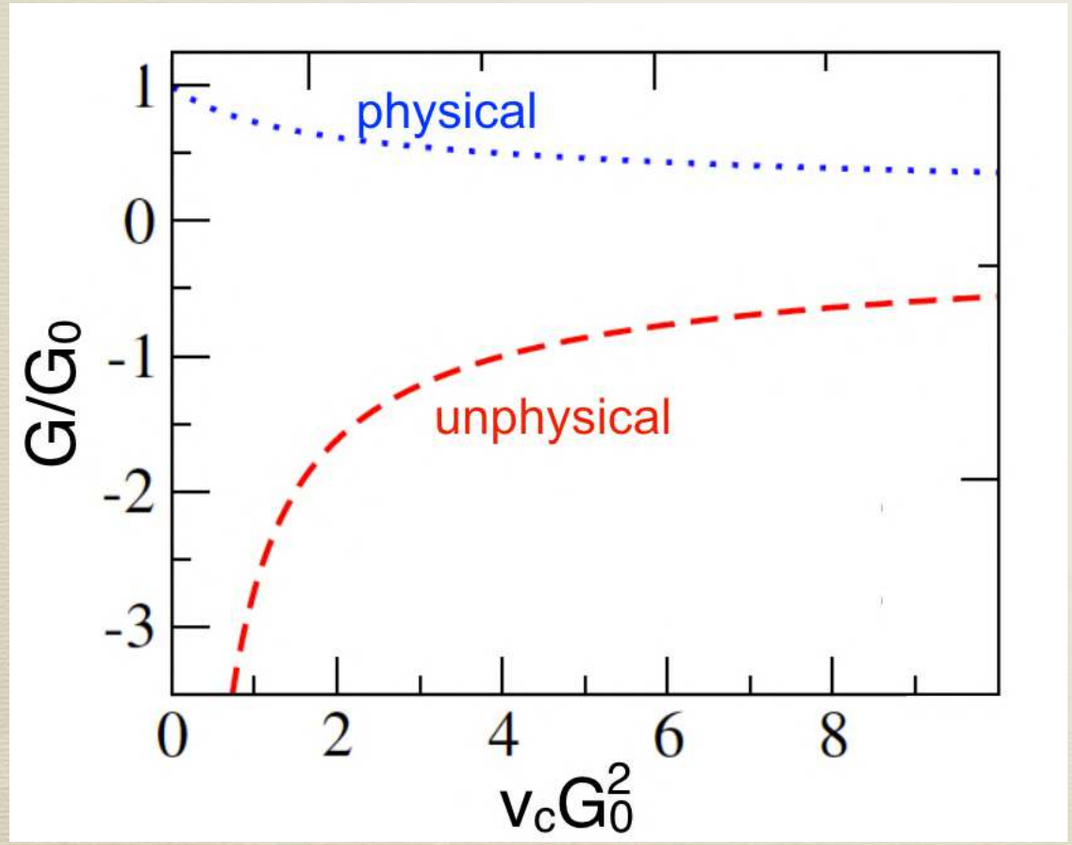
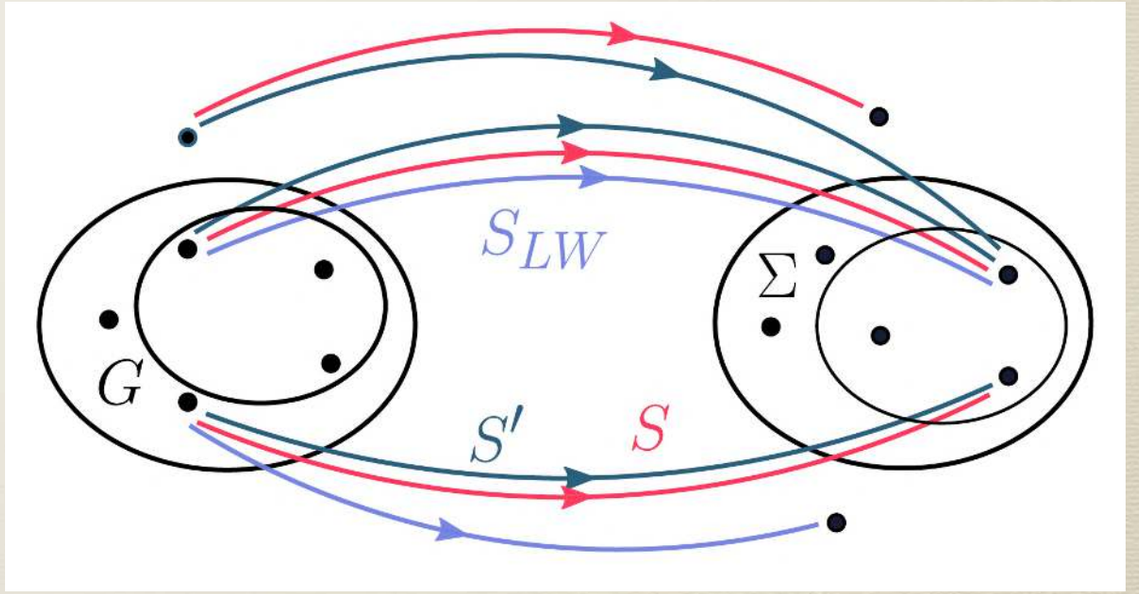


Stan, Romaniello, Rigamonti, Reining & Berger
NJP 17, 093045 (2015)

Tandetzky *et al.* 92, 115125 (2015)

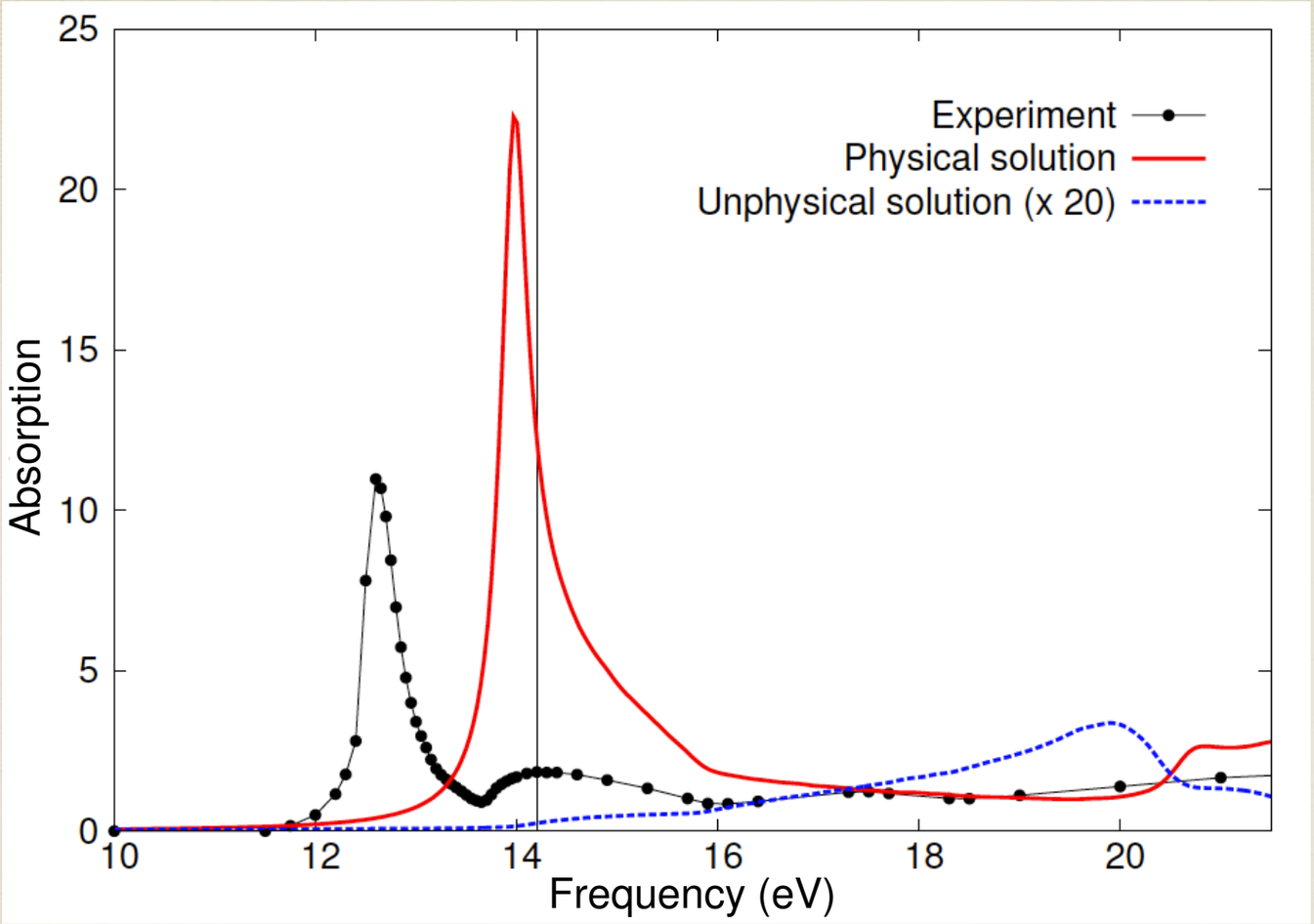
Unconstrained domain of the self-energy



Tarantino, Romaniello, Berger & Reining
PRB 96, 045124 (2017)

Multiple solutions: a realistic example

- Absorption spectrum of LiF



$$\epsilon(\omega) = 1/[1 + v_c\chi(\omega)]$$

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega) f_{Hxc}[\chi]\chi(\omega) \qquad f_{xc} = \frac{1 + v_c\chi(\omega = 0)}{\chi_0(\omega = 0)}$$

Sharma et. al. PRL (2011)

Multiple solutions: a realistic example

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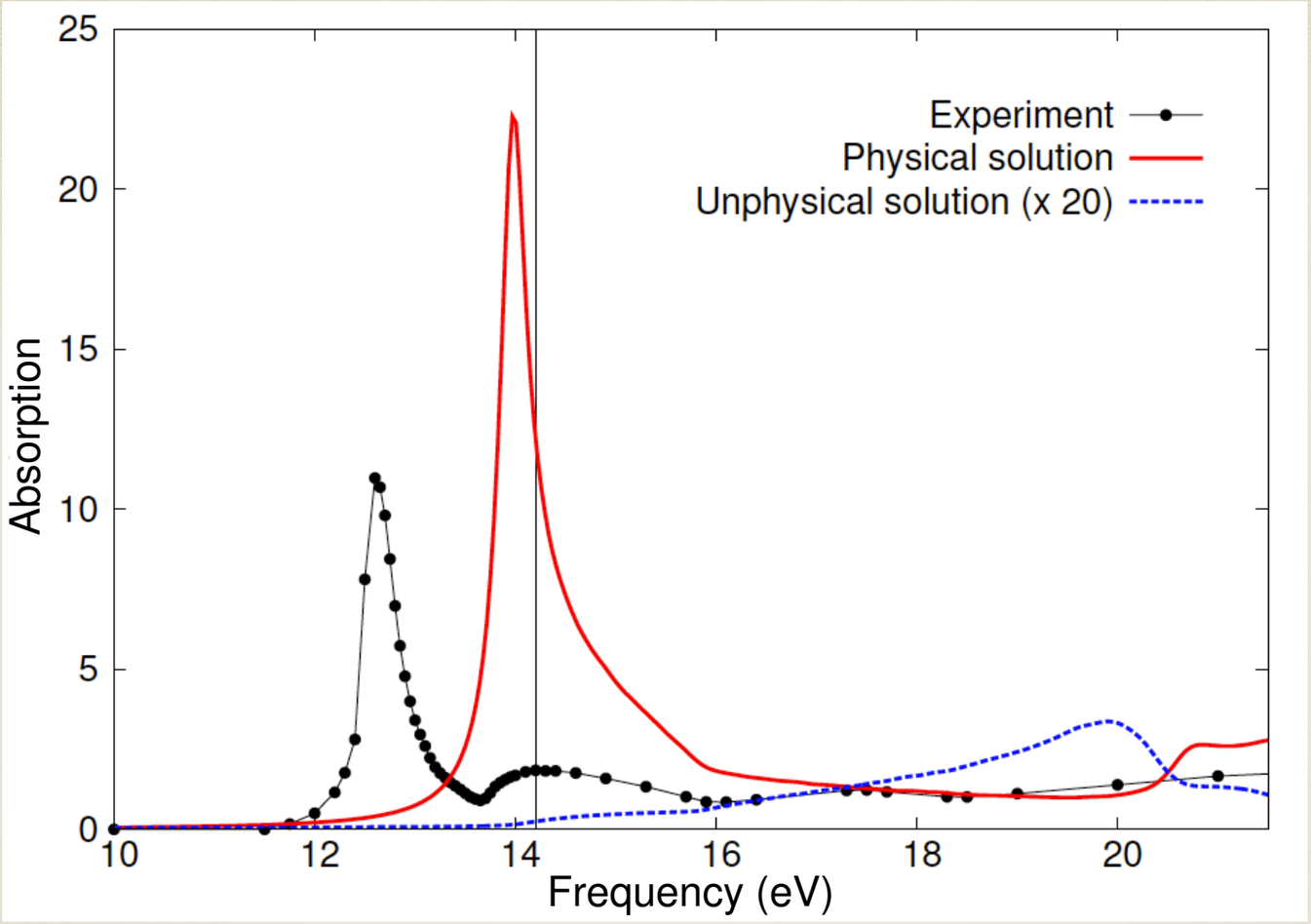

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Sharma et. al. PRL (2011)

Stan, Romaniello, Rigamonti, Reining & Berger, NJP 17, 093045 (2015)

G from a functional differential equation

- Dyson eq.

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

G from a functional differential equation

✳ Dyson eq.

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

$$\Sigma = v_H + i v_c \frac{\delta G}{\delta V_{ext}} G^{-1}$$

✳ 1st order nonlinear coupled functional differential eqs

$$G = G_0 + G_0 v_H G + G_0 V_{ext} G + i G_0 v_c \frac{\delta G}{\delta V_{ext}}$$

Kadanoff & Baym -Quantum Statistical Mechanics NY (1962) p. 44

G from a functional differential equation

✳ Dyson eq.

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✳ 1st order nonlinear coupled functional differential eqs

$$G = G_0 + G_0 v_H G + G_0 V_{ext} G + i G_0 v_c \frac{\delta G}{\delta V_{ext}}$$

What strategy can be used to find the general solution?

Is there more than one solution?

If yes, how can the physical solution be determined?

G from a functional differential equation

✳ Dyson eq.

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

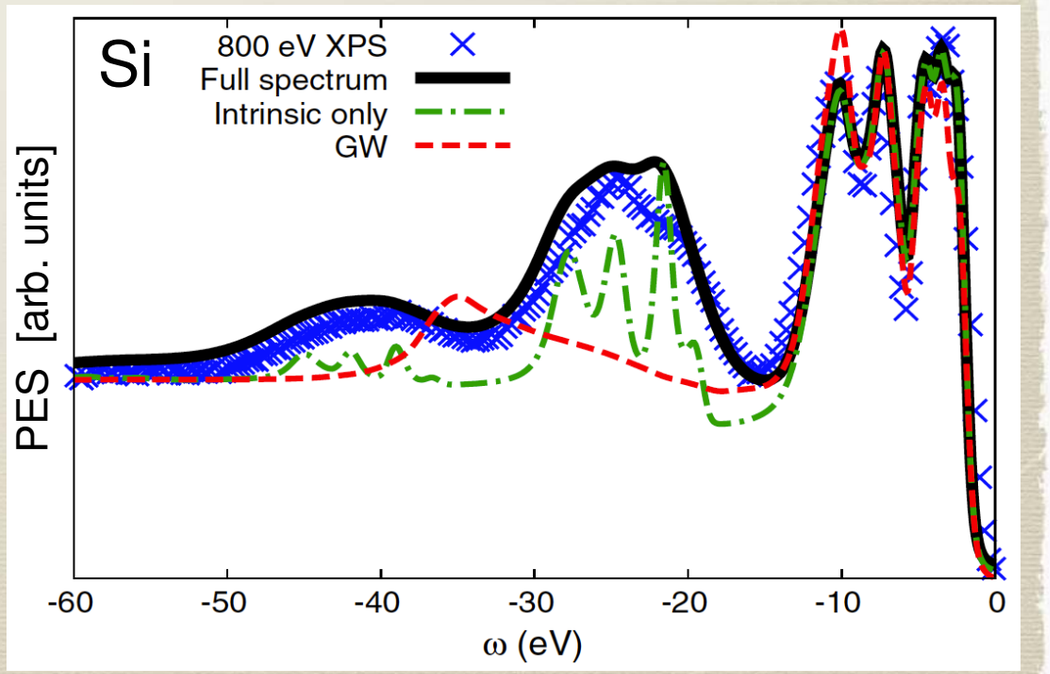
$$\Sigma = v_H + i v_c \frac{\delta G}{\delta V_{ext}} G^{-1}$$

✳ 1st order nonlinear coupled functional differential eqs

$$G = G_0 + G_0 v_H G + G_0 V_{ext} G + i G_0 v_c \frac{\delta G}{\delta V_{ext}}$$

linearization + spin/space decoupling

cumulant $G = G^0 e^C$



Guzzo *et al.*, PRL 107, 166401 (2011)

The Many-Body Effective Energy Theory

The Many-Body Effective Energy Theory

1.Treat separately $G^R_{ii}(\omega)$ and $G^A_{ii}(\omega)$ as it is done in experiments.

$$G_{ii}(\omega) = \underbrace{\sum_k \frac{B^{k,R}_{ii}}{\omega - \epsilon^R_k}}_{direct\ photoemission\ (G^R_{ii})} + \underbrace{\sum_k \frac{B^{k,A}_{ii}}{\omega - \epsilon^A_k}}_{inverse\ photoemission\ (G^A_{ii})}$$

The Many-Body Effective Energy Theory

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

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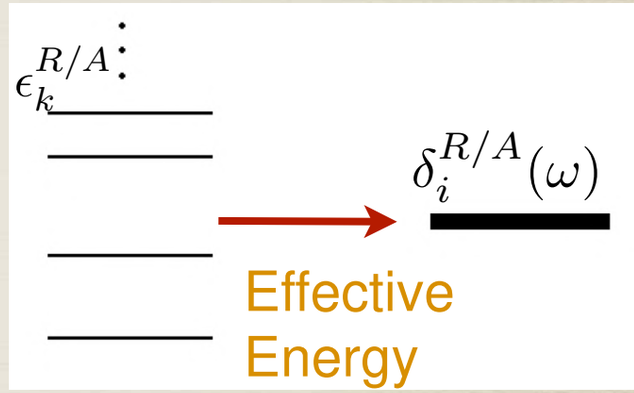
2. Introduce a dynamical effective energy, $\delta_i^{R/A}(\omega)$, which describes all the poles of $G_{ii}^{R/A}(\omega)$.
This effective energy can be expressed as a continued fraction of moments of $G^{R/A}$



Berger *et al.* PRB 82, 041103(R) (2010)
Di Sabatino, Berger, Reining & Romaniello, PRB 94, 155141 (2016)
Di Sabatino, Berger & Romaniello JCTC 15, 5080 (2019)

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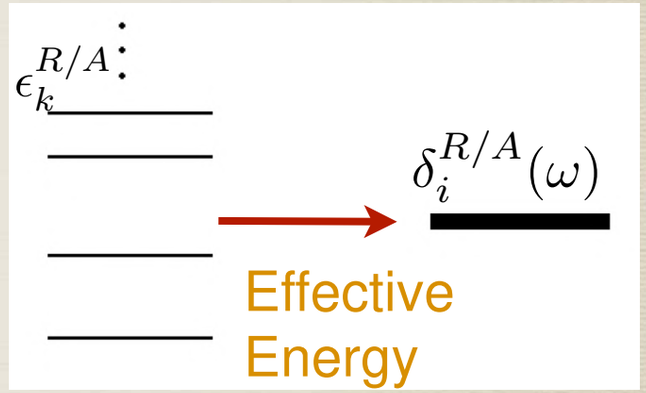
$$\mu_{n,i} = \frac{\sum_k B_{ii}^k (\epsilon_k)^n}{\sum_k B_{ii}^k}$$



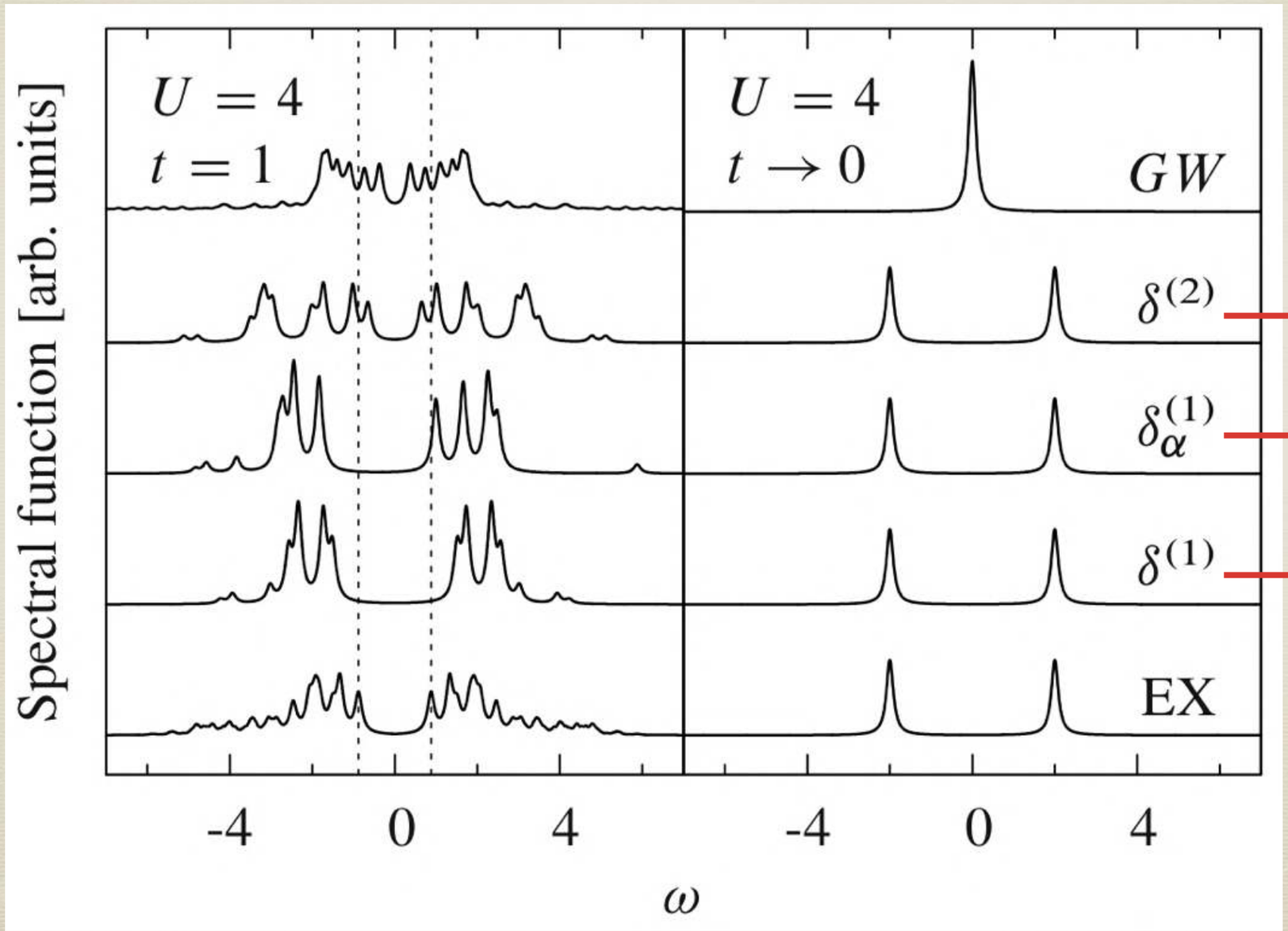
3. Truncate the continued fraction to obtain practical approximations

$$G_{ii}^R(\omega) = \cfrac{n_i}{\omega - \mu_{1,i}^R \cfrac{\omega - \mu_{1,i}^R \cdots}{\omega - \cfrac{\mu_{2,i}^R}{\mu_{1,i}^R} \cdots}}$$

Berger *et al.* PRB 82, 041103(R) (2010)
Di Sabatino, Berger, Reining & Romaniello, PRB 94, 155141 (2016)
Di Sabatino, Berger & Romaniello JCTC 15, 5080 (2019)

The Many-Body Effective Energy Theory

- 12-site Hubbard model at 1/2 filling



μ_1, μ_2

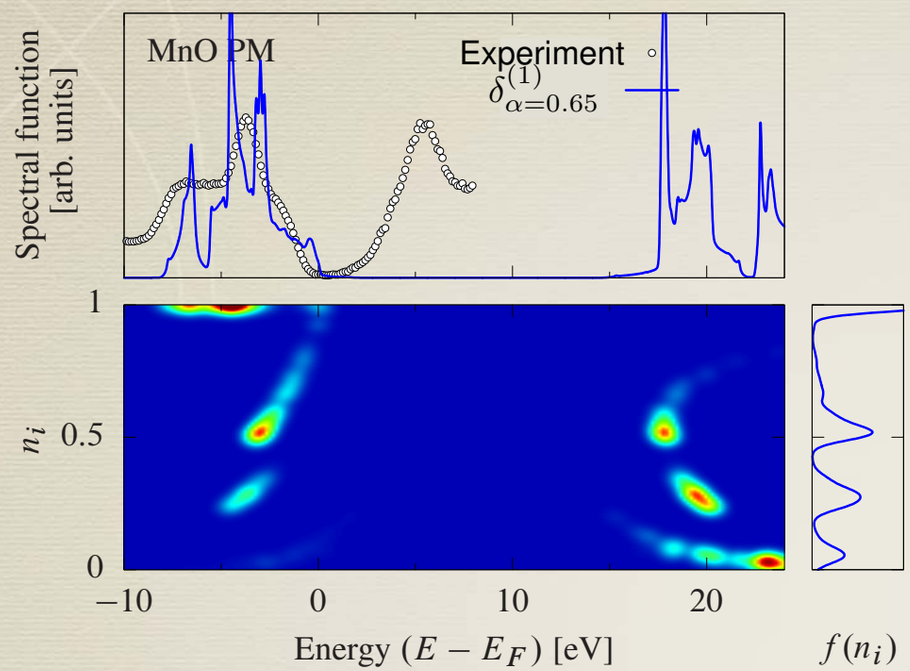
μ_1 from RDMFT

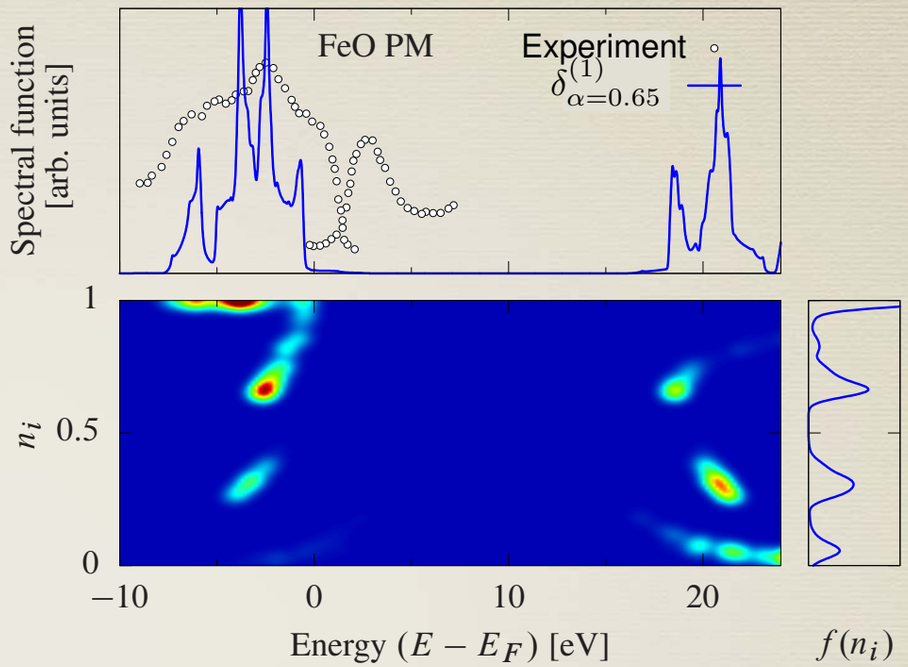
μ_1

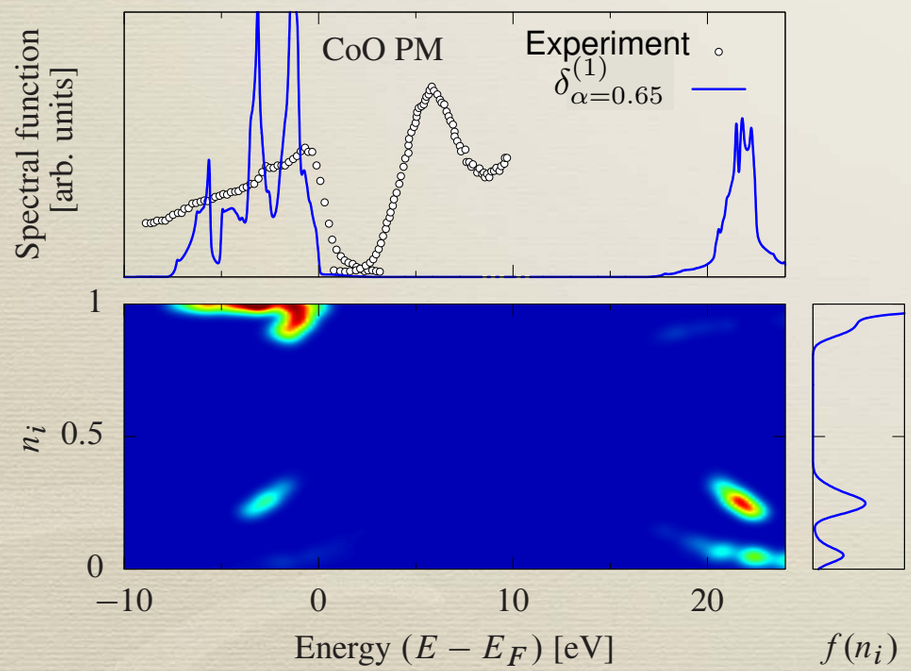
Di Sabatino, Berger, Reining & Romaniello, PRB 94, 155141 (2016)

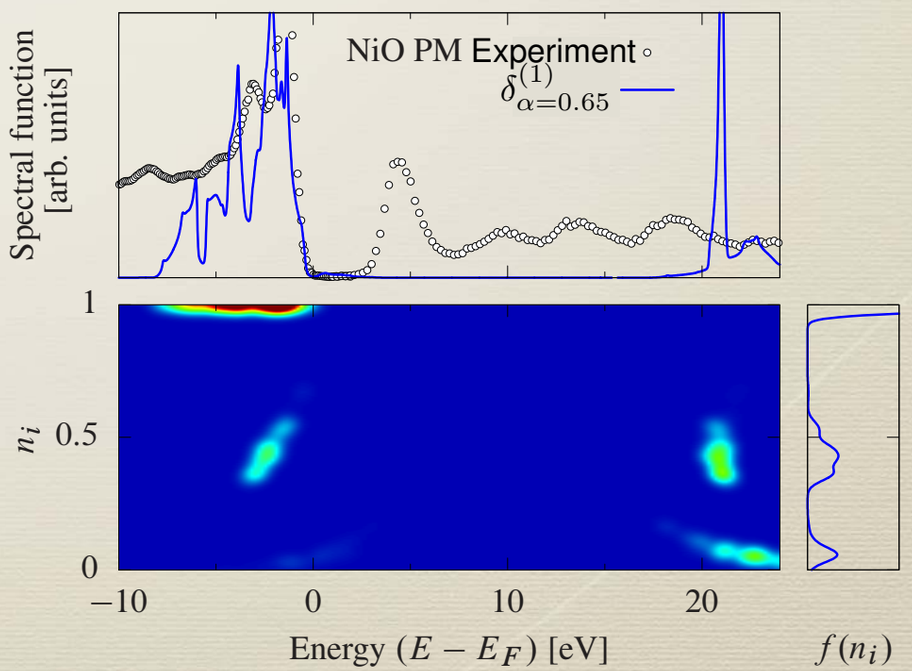
The Many-Body Effective Energy Theory

✳ Paramagnetic MnO, FeO, CoO, NiO





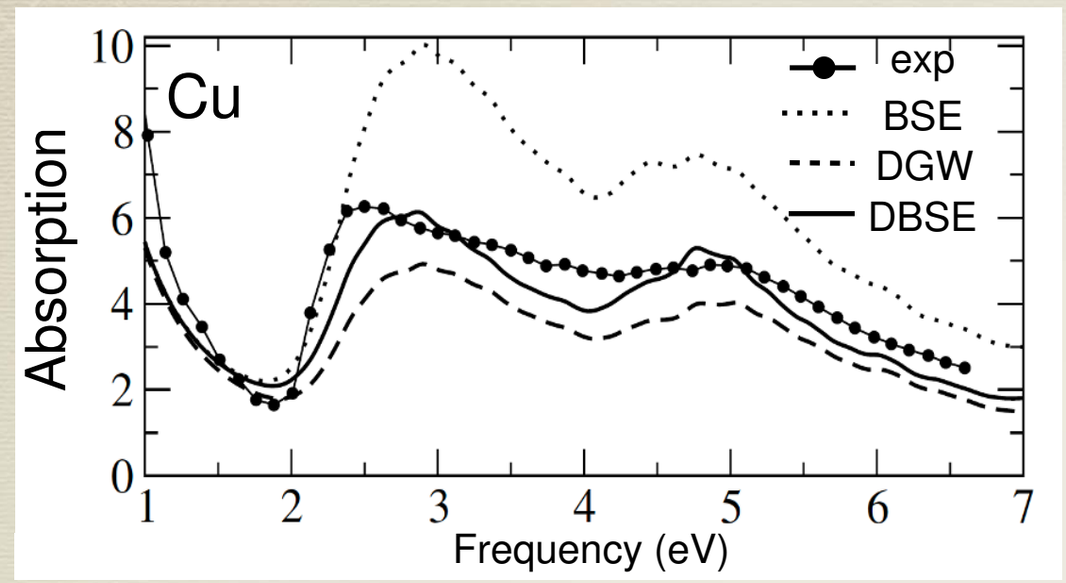




Di Sabatino, Berger & Romaniello JCTC 15, 5080 (2019)

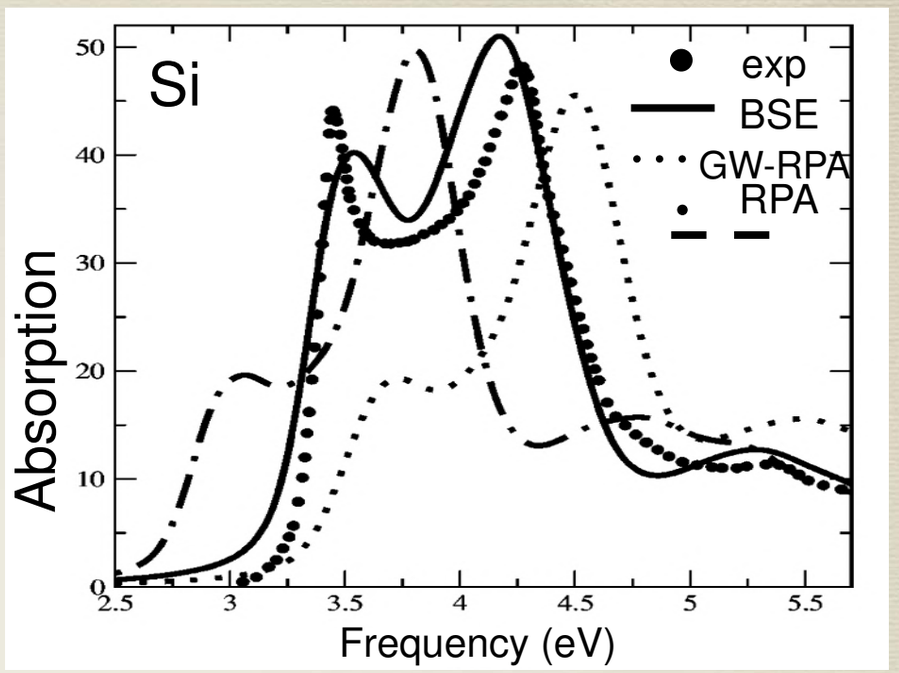
MBPT: Optical spectra

✳ Simple metals



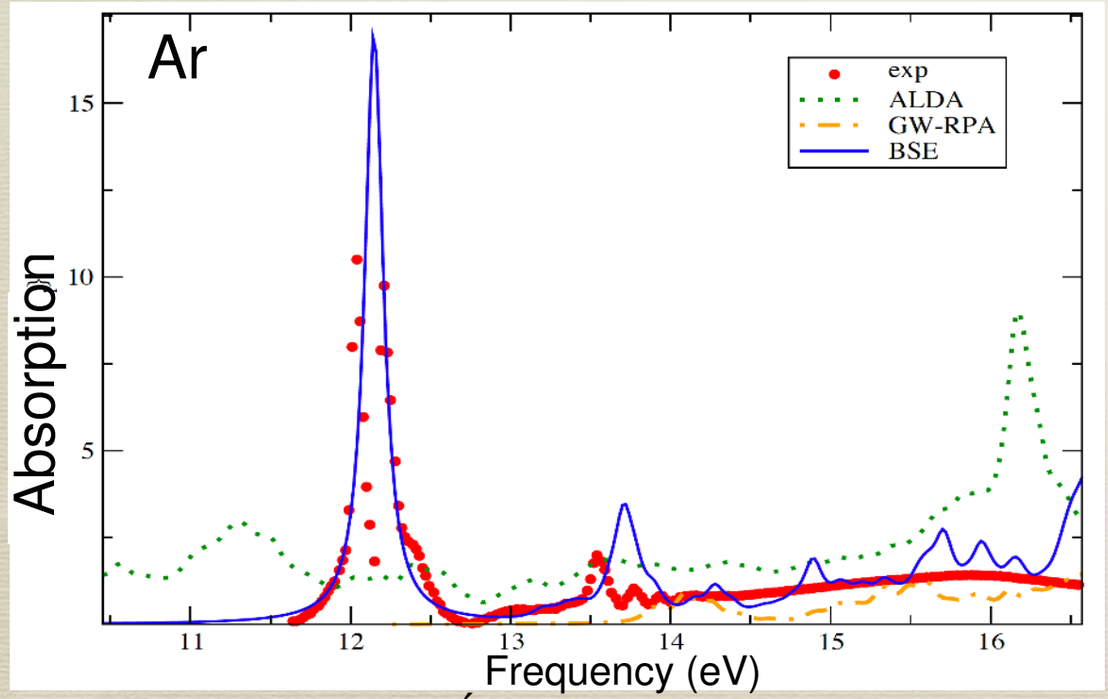
Marini *et al.,* PRL. 91, 601 (2002)

✳ Standard semiconductors



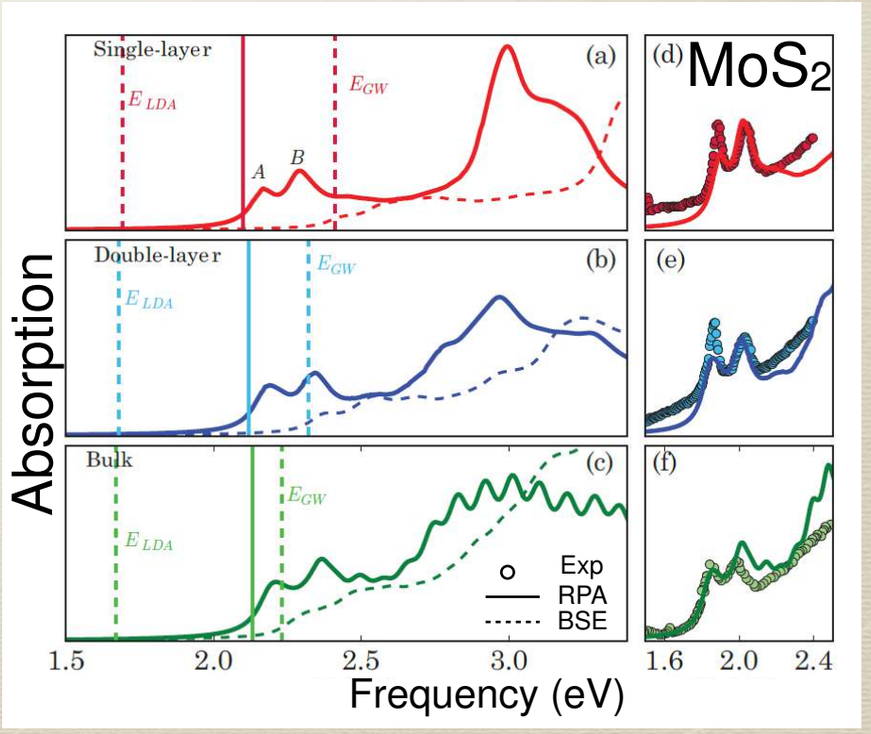
Onida *et al.,* RMP 74, 601 (2002)

✳ Wide-gap insulators



Sottile, PhD thesis, École polytechnique (2003)

✳ 2D materials

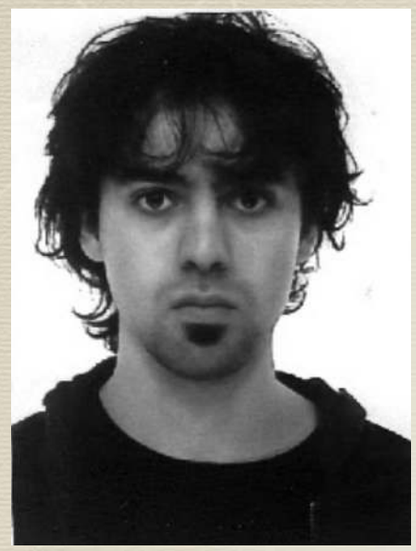


Molina-Sánchez *et al.* PRB 88, 045412 (2013)

MBPT: conclusions

- Band gap, photoemission spectra, optical spectra well described in standard, wide-gap & 2D/van der Waals gapped materials
- Strongly correlated materials & beyond adiabatic approximation still a major challenge

Acknowledgements



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