Multi-Orbital Cluster Perturbation Theory for Transition-Metal Oxides

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CNRNANO MODENA S3

- CPT basics
- Benchmarking CPT
- CPT for transition-metal oxides

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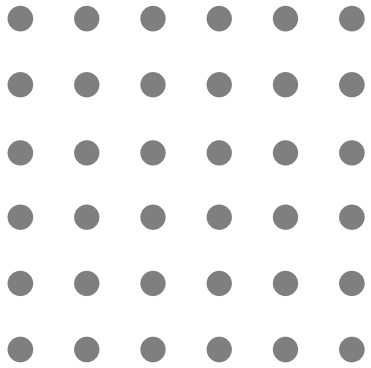
Cluster **P**erturbation **T**heory *Senechal et al PRL 84 (2000)*

Senechal,Lecture Notes vol 5 (2015)

CPT, together with Dynamical Cluster Approach and Cellular Dynamical Mean Field Theory, belongs to the class of Quantum Cluster theories *Maier et al, Rev. Mod Phys. 77 (2005)*

A ***divide et impera*** strategy: solve the many body problem in a subsystem of finite size and then embed it within the infinite medium

Cluster **P**erturbation **T**heory



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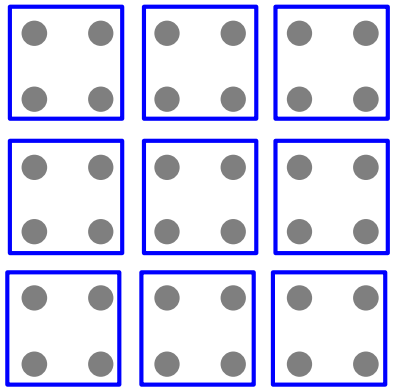
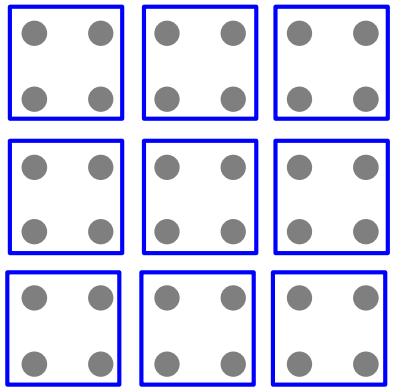


The lattice is seen as the periodic repetition of identical clusters (“tiling”).

Cluster Perturbation Theory



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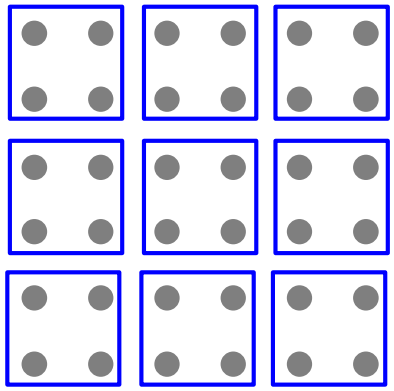
Intra- cluster *Inter- cluster*

$$\hat{H} = \sum_{l} \hat{H}_l + \sum_{l \neq l'} \hat{H}_{ll'}$$

Cluster Perturbation Theory



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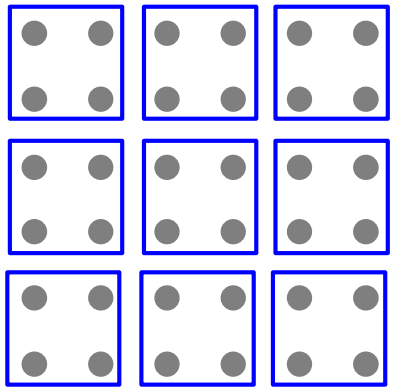
$\hat{H}_c$ $\hat{V}$

$$\hat{H}_c = \sum_{il\alpha} \varepsilon_{il\alpha}\, \hat{n}_{il\alpha} + \sum_{\alpha\beta} \sum_{ijl} t_{il\alpha,jl\beta}\, \hat{c}^{\dagger}_{il\alpha} \hat{c}_{jl\beta} + \sum_{il\alpha\beta} U^{i}_{\alpha\beta}\, \hat{n}_{il\alpha\uparrow} \hat{n}_{il\beta\downarrow}$$

$$\hat{V} = \sum_{\alpha\beta} \sum_{ij,l\neq l'} t_{il\alpha,jl'\beta}\, \hat{c}^{\dagger}_{il\alpha} \hat{c}_{jl'\beta} \; .$$

Cluster Perturbation Theory



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$$\hat{V} = \sum_{\alpha\beta} \sum_{ij,l \neq l'} t_{il\alpha,jl'\beta}\, \hat{c}^{\dagger}_{il\alpha} \hat{c}_{jl'\beta} \,.$$

inter-cluster is single-particle and the many-body term is in the intra-cluster only

Two (trivial) limiting cases:

- U<<t non-interacting electrons
- U>>t atomic limit

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- U<<t non-interacting electrons
- U>>t atomic limit

… but the interesting physics comes from the co-existence of the two terms

In the limit U>>t $\hat{H} \simeq \hat{H}_c$ no mixing between atoms belonging to different clusters

the eigenstates of the extended lattice are a product of the few-body eigenstates of the isolated cluster

$$|\Psi_n^N\rangle = |\Phi_n^N\rangle = \prod_{l=1}^{L\to\infty} |\phi_n^K(l)\rangle$$

The partition of the Hamiltonian into intra-cluster and inter-cluster terms gives rise to some **exact** expressions and suggests some relevant **approximations**.

EXACT

$$\hat{G}^{-1}(z) \equiv z - \hat{H}_c - \hat{V} \qquad \hat{G^c}^{-1} \equiv z - \hat{H}_c$$

$$\hat{G}^{-1}(z) = \hat{G^c}^{-1} - \hat{V} \longrightarrow \boxed{\hat{G} = \hat{G^c} + \hat{G^c}\,\hat{V}\,\hat{G}}$$

Dyson-like equation

EXACT

Hole and particle propagators as expectation values of the resolvent over the interacting state with one removed/added particle

$$\mathcal{G}^{-}(\mathbf{k}n\omega) = \langle \Psi_0^N | \, \hat{c}^{\dagger}_{\mathbf{k}n} \, \hat{G}(-\omega + E_0^N + i\eta) \, \hat{c}_{\mathbf{k}n} \, | \Psi_0^N \rangle$$

$$\mathcal{G}^{+}(\mathbf{k}n\omega) = \langle \Psi_0^N | \, \hat{c}_{\mathbf{k}n} \, \hat{G}(\quad \omega + E_0^N + i\eta) \, \hat{c}^{\dagger}_{\mathbf{k}n} \, | \Psi_0^N \rangle$$

$$\mathcal{G}(\mathbf{k}n\omega) = \mathcal{G}^{+}(\mathbf{k}n\omega) + \mathcal{G}^{-}(\mathbf{k}n\omega)$$

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$$\mathcal{G}(\mathbf{k}n\omega) = \mathcal{G}^{+}(\mathbf{k}n\omega) + \mathcal{G}^{-}(\mathbf{k}n\omega)$$

Since we are looking for a relationship between lattice and cluster Green's function it is useful to introduce a transformation from Bloch to localized basis

EXACT

$$\hat{c}_{\mathbf{k}n} = \frac{1}{\sqrt{K \times L}} \sum_{il\alpha} \mathcal{C}^n_{i\alpha}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{R}_l + \mathbf{r}_i)} \, \hat{c}_{il\alpha}$$

$$\mathcal{G}(\mathbf{k}n\omega) = \frac{1}{K} \sum_{ii'\alpha\beta} e^{-i\mathbf{k}\cdot(\mathbf{r}_i - \mathbf{r}_{i'})} \, \mathcal{C}^n_{i\alpha}(\mathbf{k})^* \mathcal{C}^n_{i'\beta}(\mathbf{k}) \, \mathcal{G}_{i\alpha i'\beta}(\mathbf{k}\omega)$$

$$\mathcal{G}_{i\alpha i'\beta}(\mathbf{k}\omega) = \frac{1}{L} \sum_{ll'} e^{-i\mathbf{k}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})} \, \mathcal{G}_{\substack{i\alpha i'\beta \\ ll'}}(\omega)$$

$$\begin{aligned} \mathcal{G}_{\substack{i\alpha i'\beta \\ ll'}}(\omega) \quad = \quad & \left\langle \Psi_0^N \left| \hat{c}^\dagger_{il\alpha} \left(\hat{G}^c(\omega) + \hat{G}^c(\omega) \hat{V} \hat{G}(\omega) \right) \hat{c}_{i'l'\beta} \right| \Psi_0^N \right\rangle \\ & + \left\langle \Psi_0^N \left| \hat{c}_{il\alpha} \left(\hat{G}^c(\omega) + \hat{G}^c(\omega) \hat{V} \hat{G}(\omega) \right) \hat{c}^\dagger_{i'l'\beta} \right| \Psi_0^N \right\rangle \end{aligned}$$

APPROXIMATIONS

$$|\Psi_0^N\rangle \sim |\Phi_0^N\rangle = \prod_{l=1}^{L\to\infty} |\phi_0^K(l)\rangle$$

$$\sum_m |\Phi_m^{N-1}\rangle\langle\Phi_m^{N-1}| \sim \sum_{il\alpha} \hat{c}_{il\alpha} |\Phi_0^N\rangle\langle\Phi_0^N| \hat{c}_{il\alpha}^\dagger = 1$$

$$\sum_m |\Phi_m^{N+1}\rangle\langle\Phi_m^{N+1}| \sim \sum_{il\alpha} \hat{c}_{il\alpha}^\dagger |\Phi_0^N\rangle\langle\Phi_0^N| \hat{c}_{il\alpha} = 1$$

$$\mathcal{G}_{i\alpha i'\beta}(\mathbf{k}\omega) = \mathcal{G}^c_{i\alpha i'\beta}(\omega) + \sum_{i'''\gamma'} B_{i\alpha i'''\gamma'}(\mathbf{k}\omega)\, \mathcal{G}_{i'''\gamma' i'\beta}(\mathbf{k}\omega)$$

CPT

$$\mathcal{G}_{i\alpha i'\beta}(\mathbf{k}\omega) = \mathcal{G}^{c}_{i\alpha i'\beta}(\omega) + \sum_{i'''\gamma'} B_{i\alpha i'''\gamma'}(\mathbf{k}\omega)\, \mathcal{G}_{i'''\gamma' i'\beta}(\mathbf{k}\omega)$$

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$\hat{G}^{c}\hat{V}$

Green's function for an isolated cluster

$$\mathcal{G}^{c}_{i\alpha i'\beta}(\omega) = \sum_{n} \frac{\langle \phi_0^K | \hat{c}^{\dagger}_{i\alpha} | \phi_n^{K-1} \rangle \langle \phi_n^{K-1} | \hat{c}_{i'\beta} | \Phi_0^K \rangle}{\omega - (E_0^K - E_n^{K-1})} +$$

$$\sum_{n} \frac{\langle \phi_0^K | \hat{c}_{i\alpha} | \phi_n^{K+1} \rangle \langle \phi_n^{K+1} | \hat{c}^{\dagger}_{i'\beta} | \phi_0^K \rangle}{\omega - (E_n^{K+1} - E_0^K)}$$

Cluster Exact Diagonalization

$$|\Phi_n^N >= \sum_l^{nconf} C_l^n |S_l > \qquad nconf = (\frac{K!}{N!(K-N)!})^2$$

$$|S_l >= \hat{c}^\dagger_{l_1\uparrow}\hat{c}^\dagger_{l_2\uparrow}...\hat{c}^\dagger_{l_N\uparrow}\hat{c}^\dagger_{l_{N+1}\downarrow}\hat{c}^\dagger_{l_{N+2}\downarrow}...\hat{c}^\dagger_{l_{N+N}\downarrow}|0>$$

Lanczos algorithm to obtain *some* cluster eigenstates and from them the cluster Green fnct. in the Lehman representation

At the end the spectral function is obtained

$$A(\mathbf{k}\omega) = \frac{1}{\pi}\sum_{n} Im\mathcal{G}(\mathbf{k}n\omega)$$

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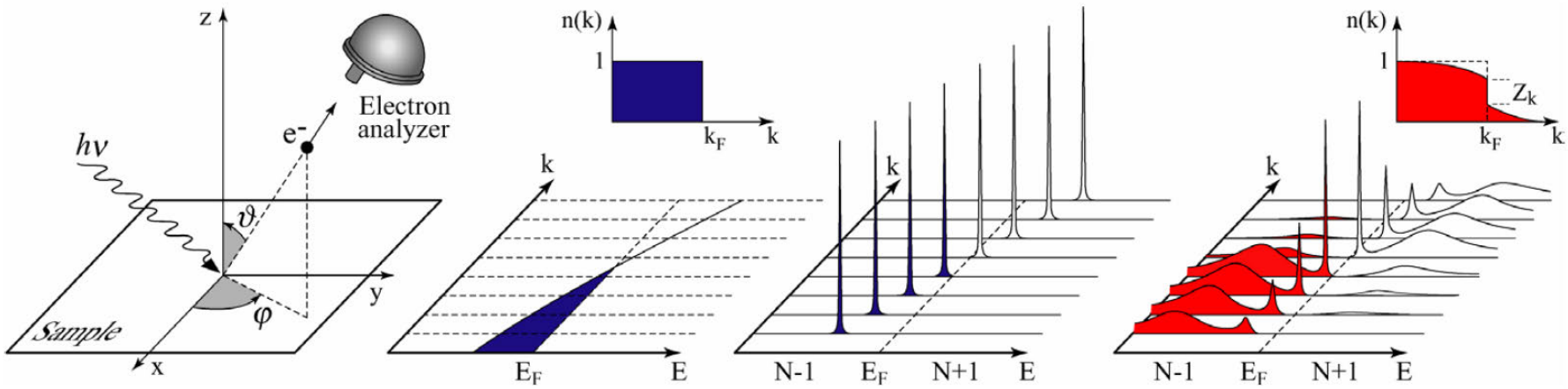
and compared with experiments – quasi-particle band structure

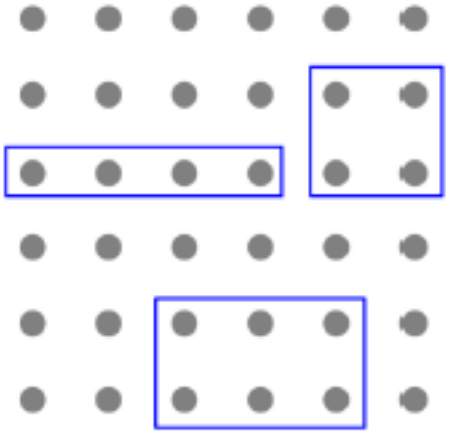


CPT IN PRACTICE

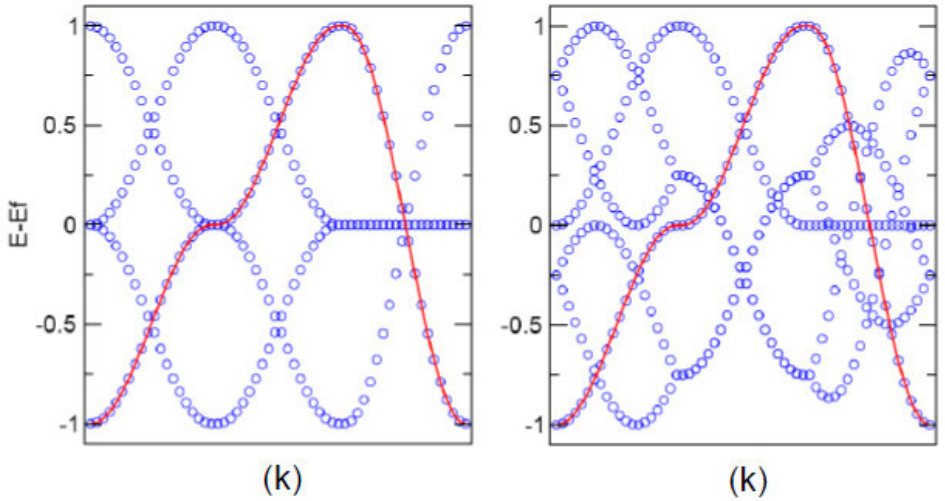
- Choose a “tiling” of the lattice
- Perform Exact diagonalization for a single cluster and calculate $G_{cluster}$
- “periodicize” it by solving the Dyson-like equation by matrix inversion
- Switch appropriately from localized to Bloch basis
- Obtain $G(k,n,\omega)$, spectral functions and quasiparticle band structure

CPT implementation - The role of symmetry

Large arbitrariness exists in the choice of the elementary unit that describes a crystalline solid:
either the primitive cell that contains the minimum number of atoms, or any larger unit that, via translation invariance, reproduces the crystalline lattice.



the band structure of ***non-interacting electrons*** *can be calculated using unit cells containing a variable number of atoms, providing exactly the same result, except for a trivial "band folding" that can be easily eliminated*

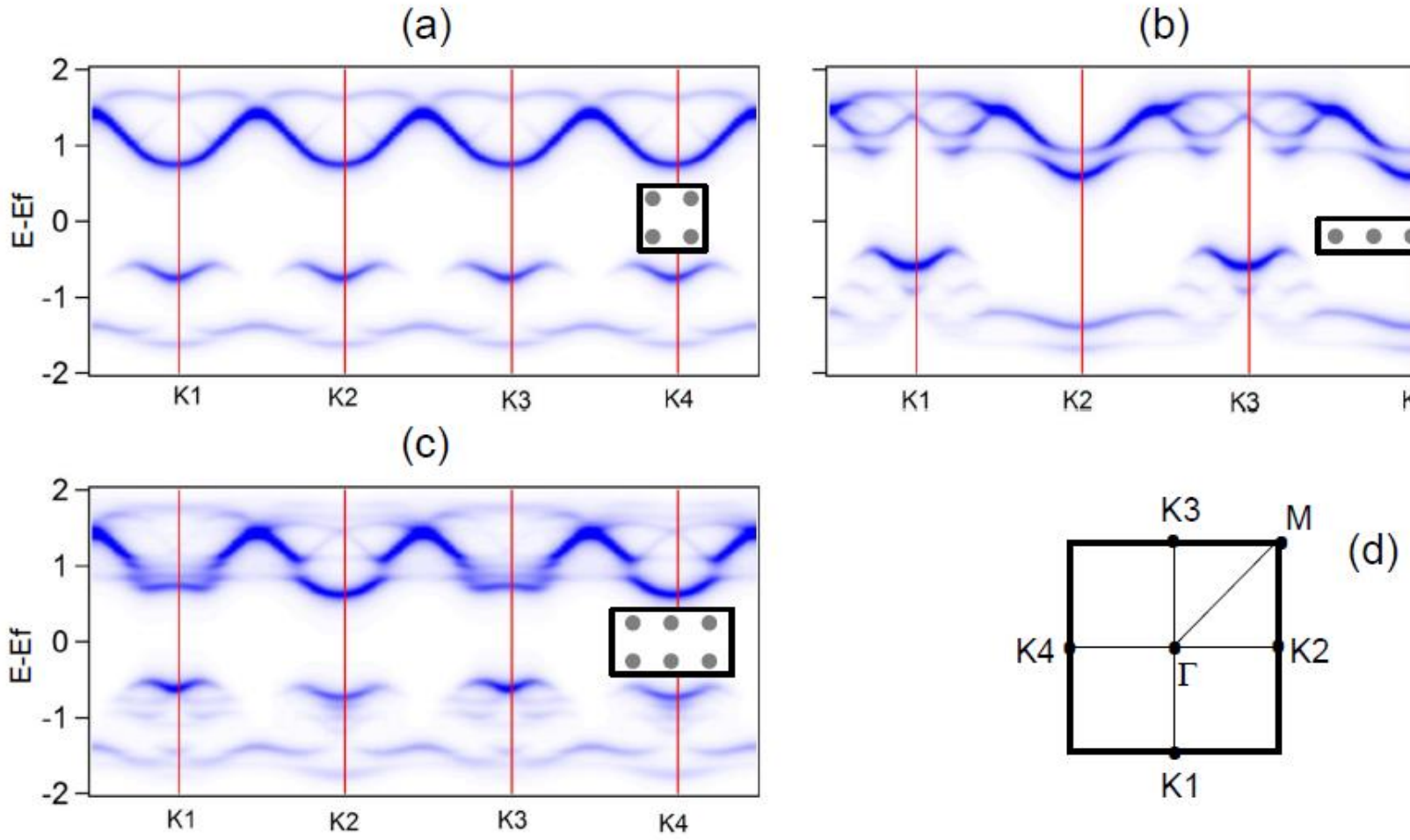


The situation is quite different for **interacting electrons** as described by QC theories.

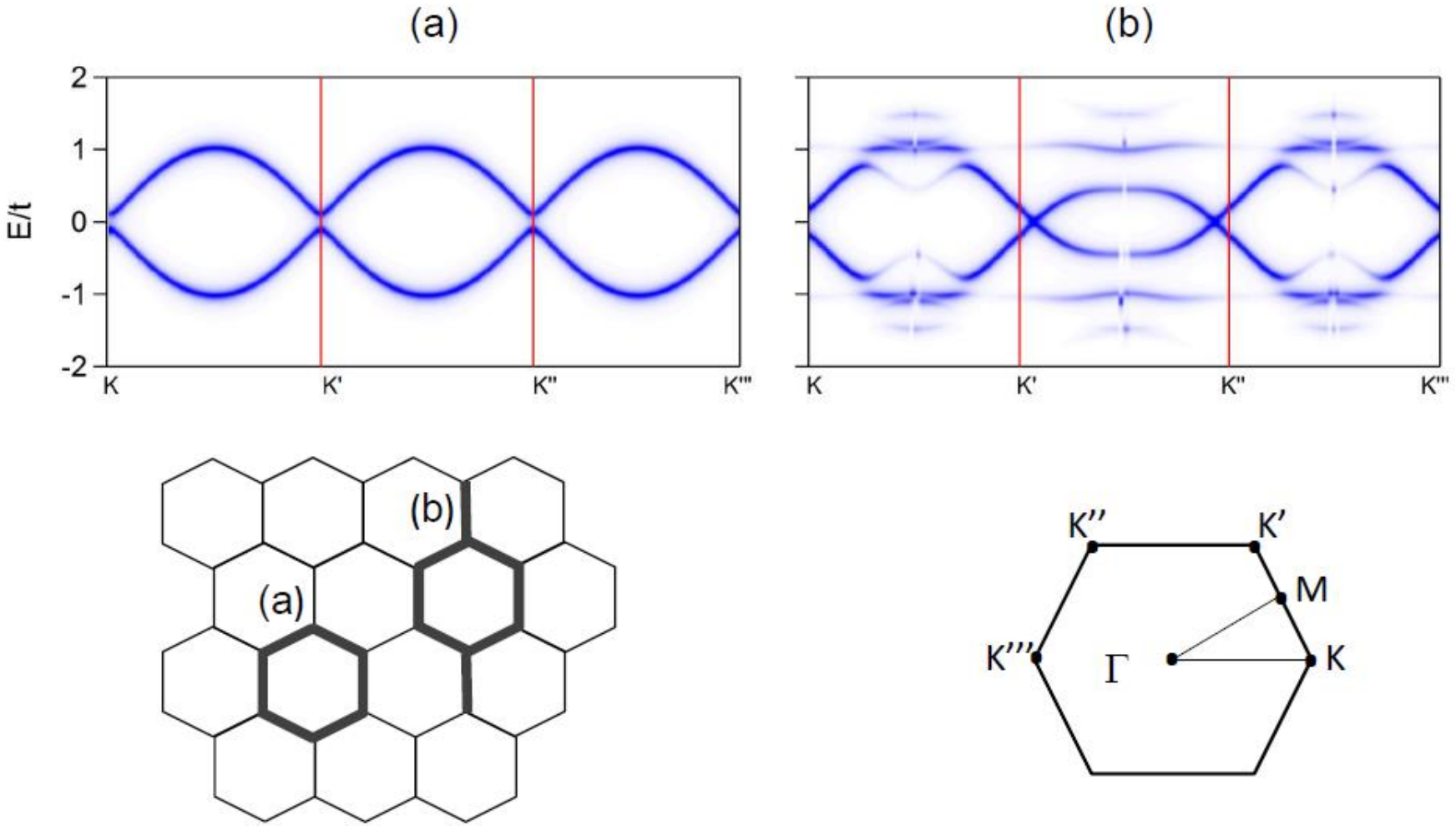
- The e-e interaction gives rise to hopping renormalization inside the cluster, while the inter-cluster hopping is unaffected.

- Translation symmetry is preserved only at the superlattice level

- Cluster must have the same rotational symmetry of the lattice



Quasiparticle energies should be identical at k-points K_1 and K_2 connected by a point-group rotation but for the 4-site chain and the 6-site rectangle they are not



Quasiparticle energies at k and Rk are different, violating a very basic rule of solid state theory.

- In any QC approach cluster symmetry should be as close as possible to the lattice one.

- Any significant deviation from this requirement would induce a wrong behaviour of the quasi-particle band dispersion.

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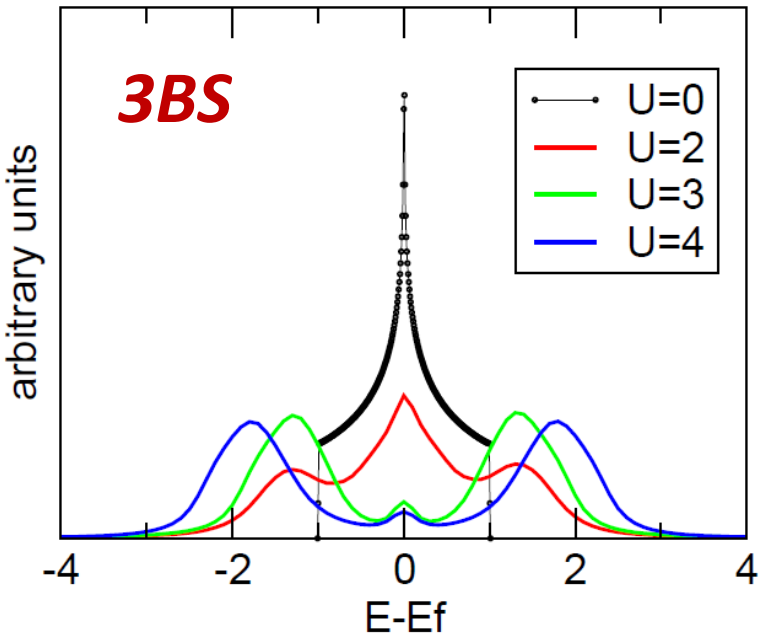
Many-body quasi-particle band structure calculations rely on approximations that may work as ad-hoc ingredients that affect the final result

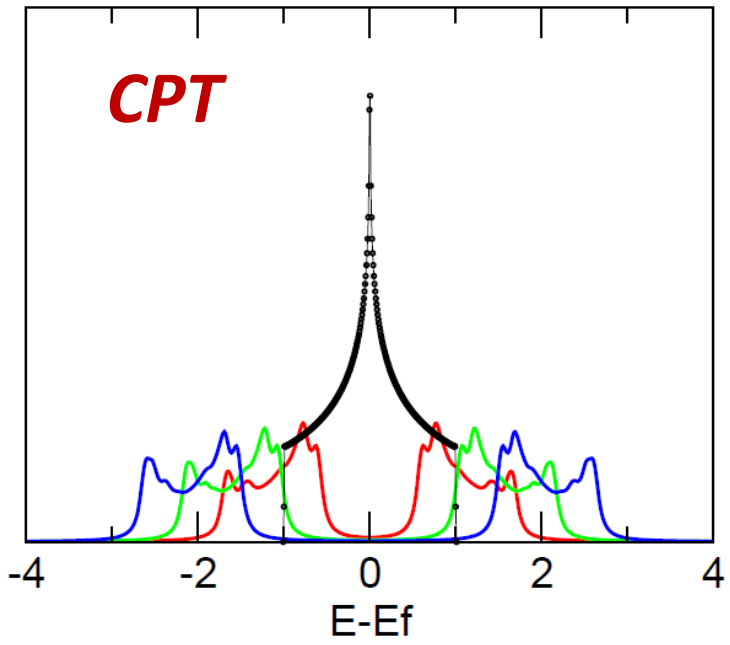
- different single-particle band structure as a starting point
- different strategies to correct the double-counting of e-e interaction, etc.

$$\mathcal{G}(\mathbf{k}n\omega) = \frac{1}{\omega - e_{\mathbf{k}n} - \Sigma(\mathbf{k}n\omega)}$$

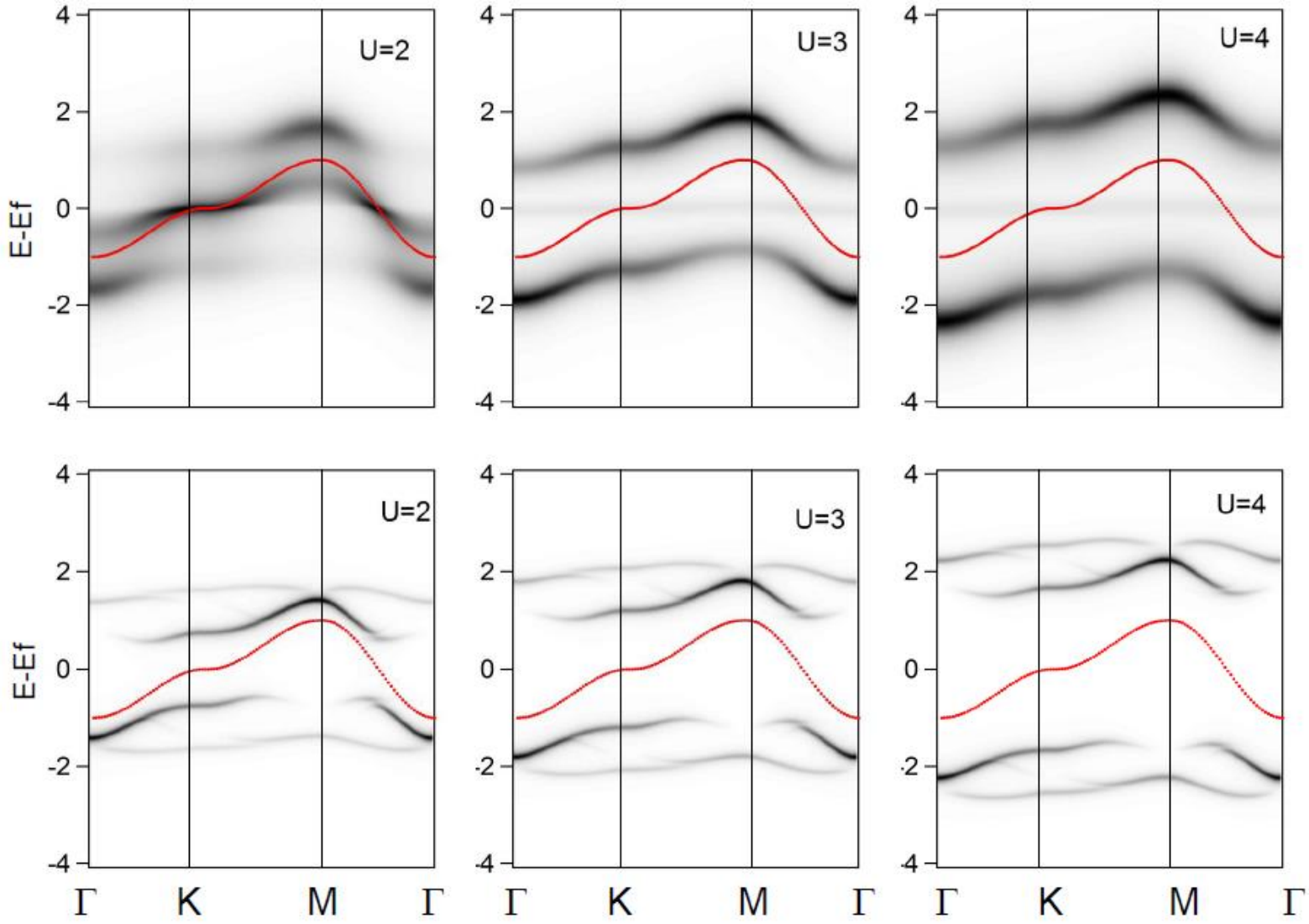
→ Self-energy scheme (3BS) vs CPT

Square lattice at half occupation





In both cases Mott-insulator at sufficiently large values of U but different values of Uc



Different quasi-particle k-dispersion

CPT Self-energy is strongly k-dependent

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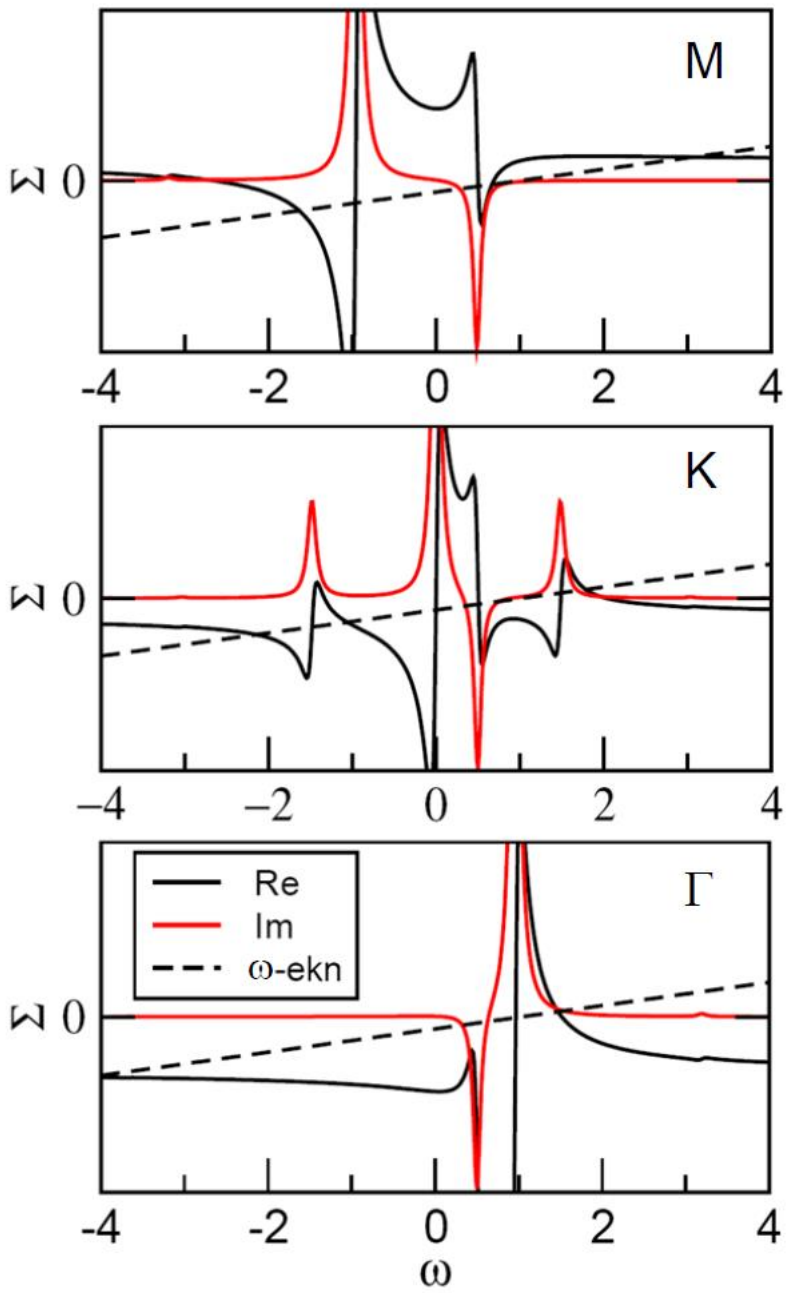
$$\Sigma(\mathbf{k}n\omega) = \omega - e_{\mathbf{k}n} - \mathcal{G}(\mathbf{k}n\omega)^{-1}$$



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- Model systems – good to validate approximate methods

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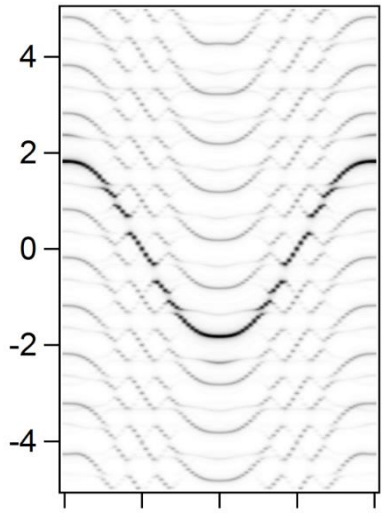
- and a playground to search novel phenomena

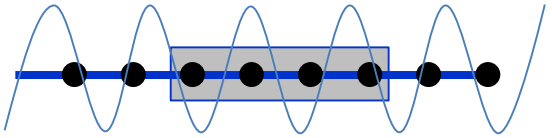
Strongly correlated electrons under external periodic driving

Time-dependent periodic fields are an external tunable control to engineer new phases.

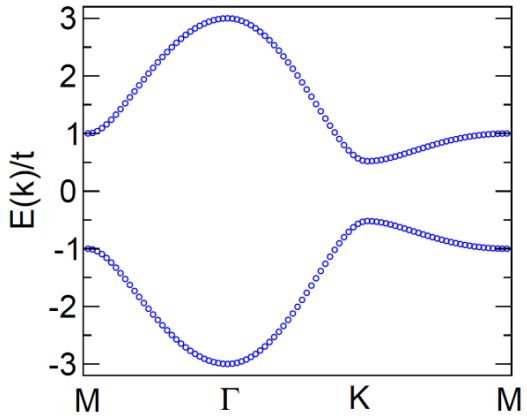
Photo-induced insulator-to-metal transitions in 1D?

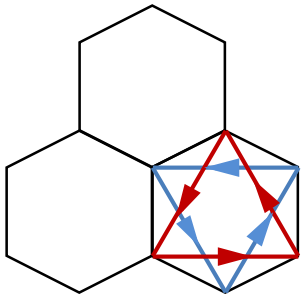


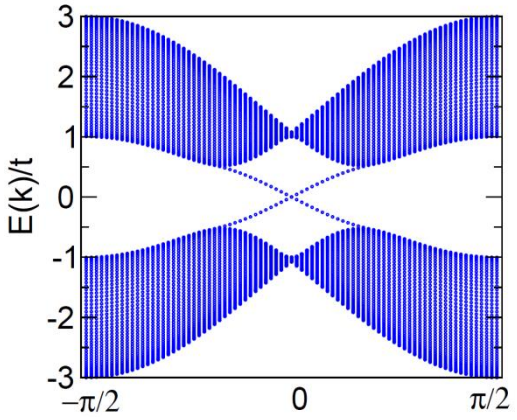
Periodically driven interacting electrons in 1D: a many-body Floquet approach
Puviani and FM to appear on PRB



Haldane/Kane/Mele model of graphene



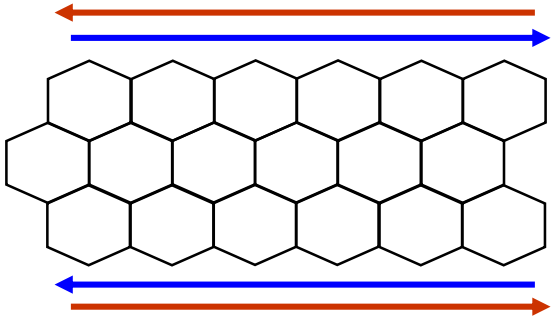




gapped bulk bands

gapless edge states

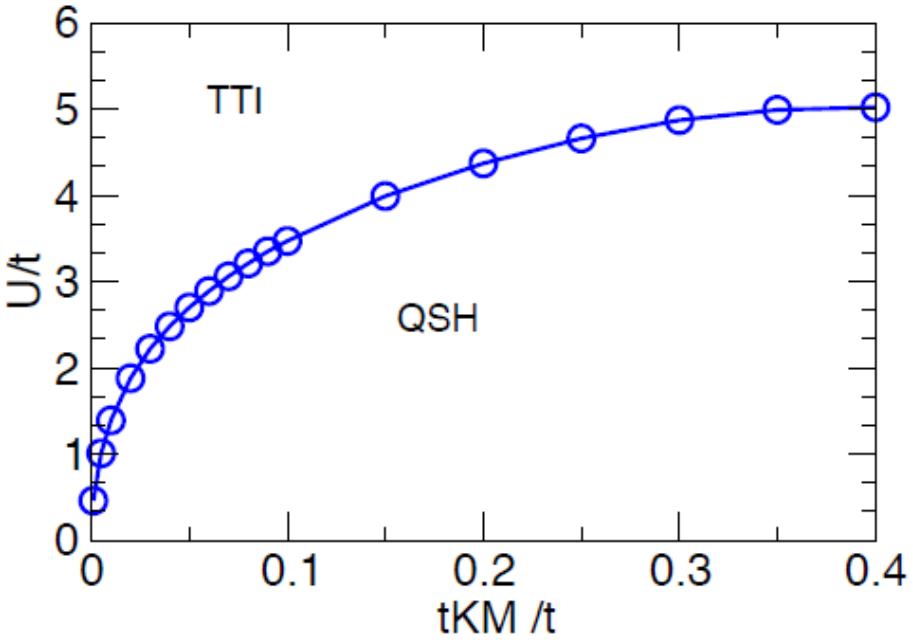
the emergence of non-vanishing topological invariants ensures the robustness of the edge states.



Haldane/Kane/Mele model of graphene **+ e-e**

The inverse of the Green's function at zero frequency defines a fictitious non-interacting topological hamiltonian

$$h_{topo}(k) \equiv -G^{-1}(k,0)$$



Topological invariants in interacting Quantum Spin Hall: a CPT approach

New J. Phys. 17 (2015) 023004

Topological properties of the bond-modulated honeycomb lattice

Phys.Rev.B91:115112 (2015)

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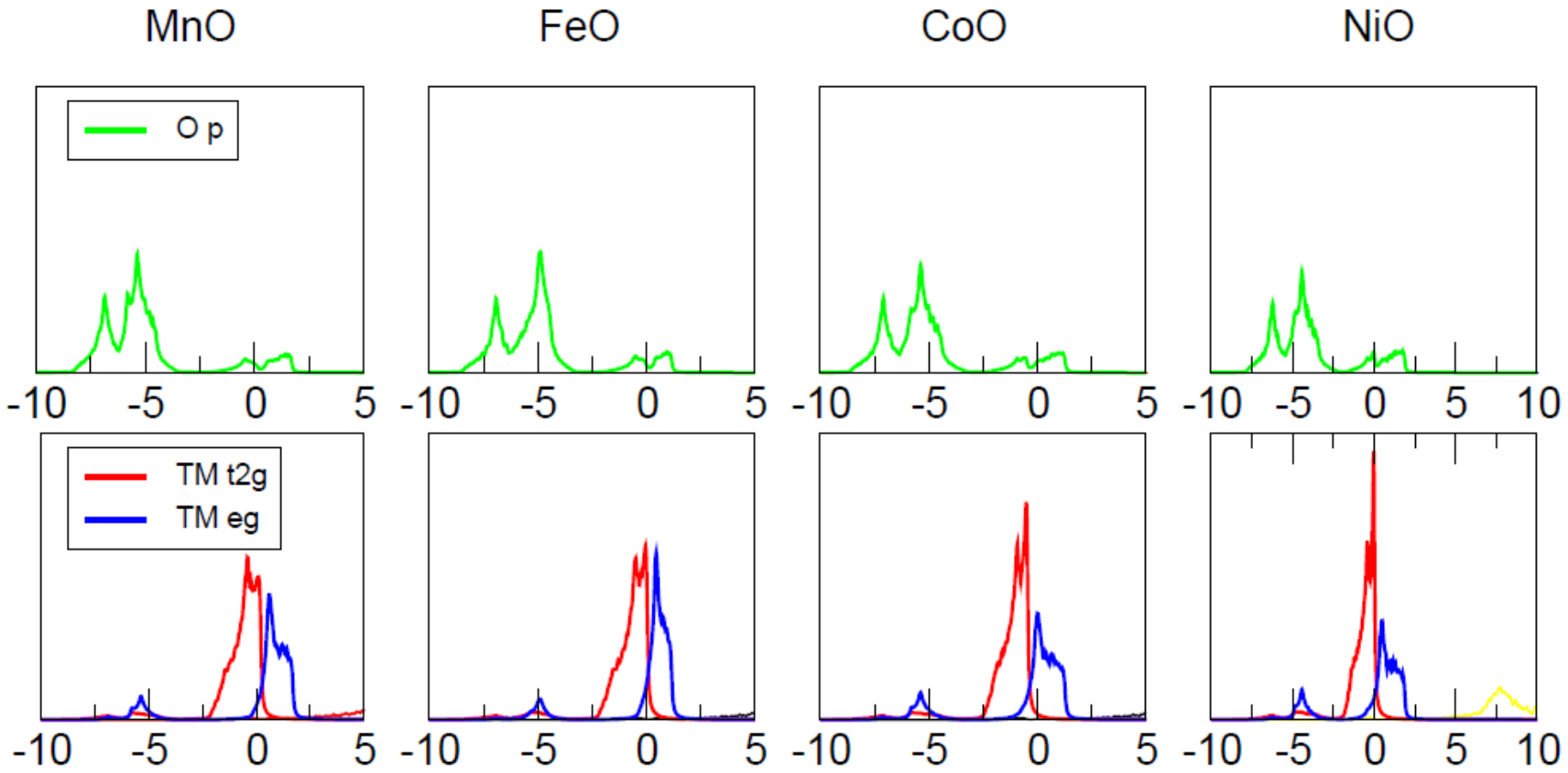
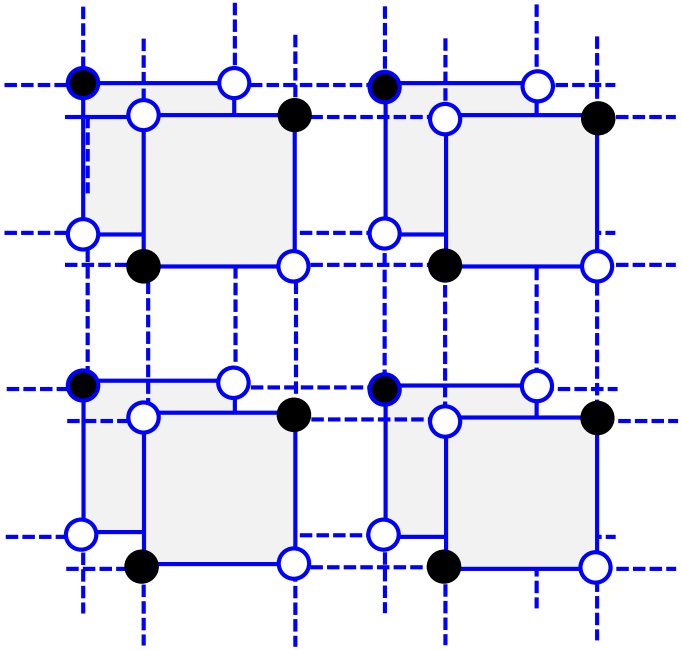
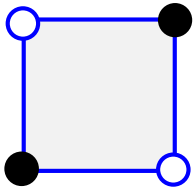


	MnO	FeO	CoO	NiO
n_{t2g}	4.941	5.770	5.961	5.966
n_{eg}	0.599	0.672	1.614	2.556
n_d	5.540	6.441	7.575	8.522

Tiling the rocksalt structure



The smallest cluster containing more than one TM atom and reproducing without overlaps the 3D rocksalt lattice is the plaquette with 2 TM atoms and 2 oxygens.



The bands of TM oxides around the Fermi Energy are described by 9 spd orbitals for each TM atom and 4 sp orbitals for each oxygen.

Then the dimension of the Hilbert space spanned by the Slater determinants obtained by populating in all possible ways K=26 orbitals with P electrons of a given spin (P = 13 ÷ 16 from MnO to NiO) is far too big for exact diagonalization.

Tiling – a multi partition strategy

A reduction of the number of sites/orbitals per cluster is mandatory.

To this end we identify, within a single cluster, two classes of orbitals A and B centered on different sites and with different symmetry

We write the cluster Hamiltonian as the sum of on-site and inter-site terms connecting all orbitals: A-A, B-B (diagonal) and A-B (off diagonal)

$$\hat{H}_c = \hat{H}^{\mathrm{diag}} + \hat{V}_{AB}$$

$$\hat{H}^{\mathrm{diag}} = \hat{H}_c^{AA} + \hat{H}_c^{BB}$$

$$\hat{G^c}^{-1} = z - \hat{H}_c = (\hat{G}^{\mathrm{diag}})^{-1} - \hat{V}_{AB}$$

As before this turns out into a Dyson-like eqn. for resolvents

$$\hat{G}^c = \hat{G}^{\mathrm{diag}} + \hat{G}^{\mathrm{diag}}\,\hat{V}_{AB}\,\hat{G}^c$$

Multiple partition - within the lattice and within the cluster

CPT prescriptions may be rephrased as follows:

- chose a partition of the lattice Hamiltonian into a set of non overlapping clusters connected by inter-cluster hopping;
- make a further partition inside each cluster defining a suitable collection of sites/orbitals;
- perform separate exact diagonalizations plus matrix inversion to calculate the cluster Green function in local basis
- finally obtain the full lattice Green function in Bloch basis

- This technique can be extended to more than two subsets of sites/orbitals, and we have applied it to a triple partition (subsets A, B and C)

- It has the advantage to replace an unmanageable exact diagonalization with two or more separate ones followed by a matrix inversion.

- It shares with CPT the assumption about the states of the interacting electrons – a drastic approximation whose validity must be verified performing calculations with different partitions and/or finding explicit rules for the adopted choice.

- These rules must be based on sound conjectures and will be inevitably system-dependent.

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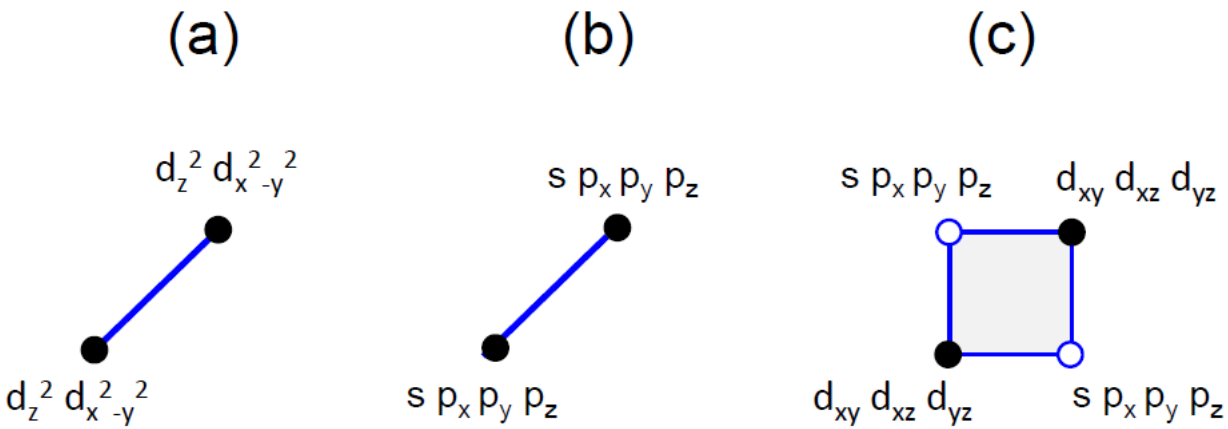
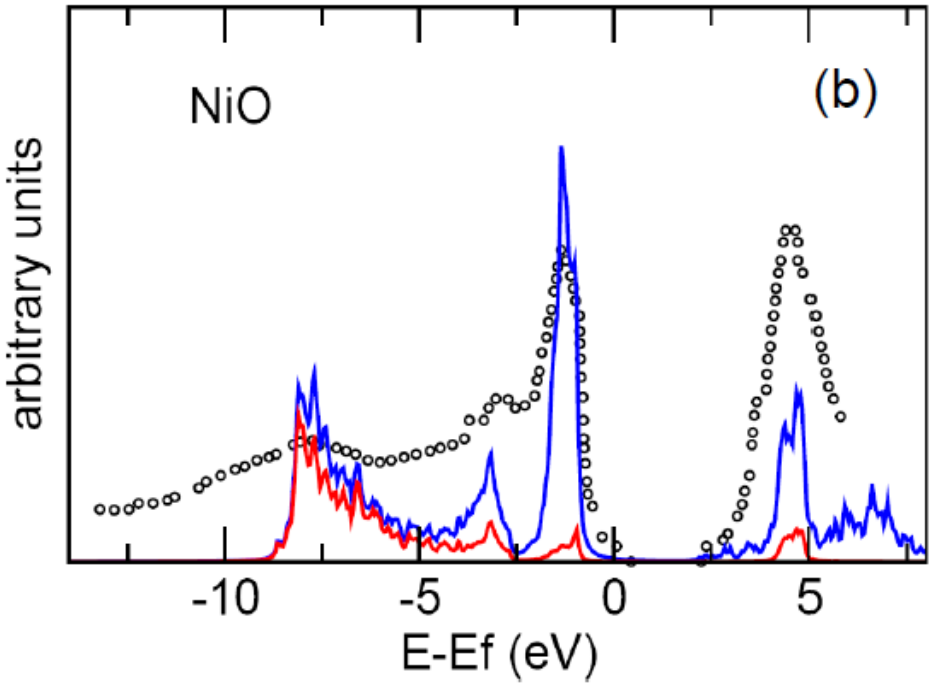
n_{eg}	0.599	0.672	1.614	2.556
n_d	5.540	6.441	7.575	8.522

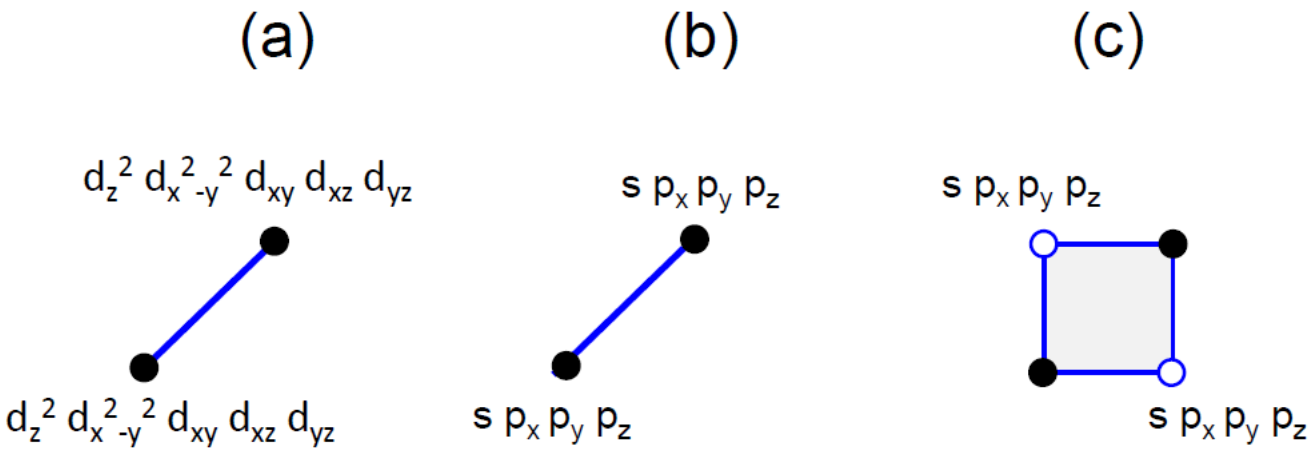
Only partially occupied shells are affected by e-e interaction this suggests different partitions for TM oxides

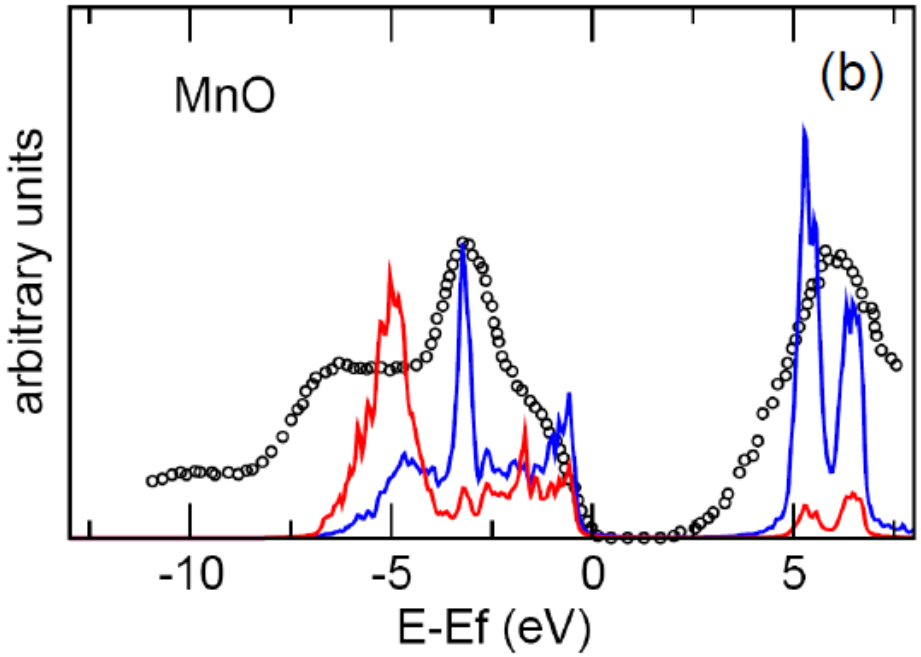
NiO, CoO with only eg orbitals centered on the two TM atoms in the plaquette

FeO, MnO with both t2g - eg orbitals

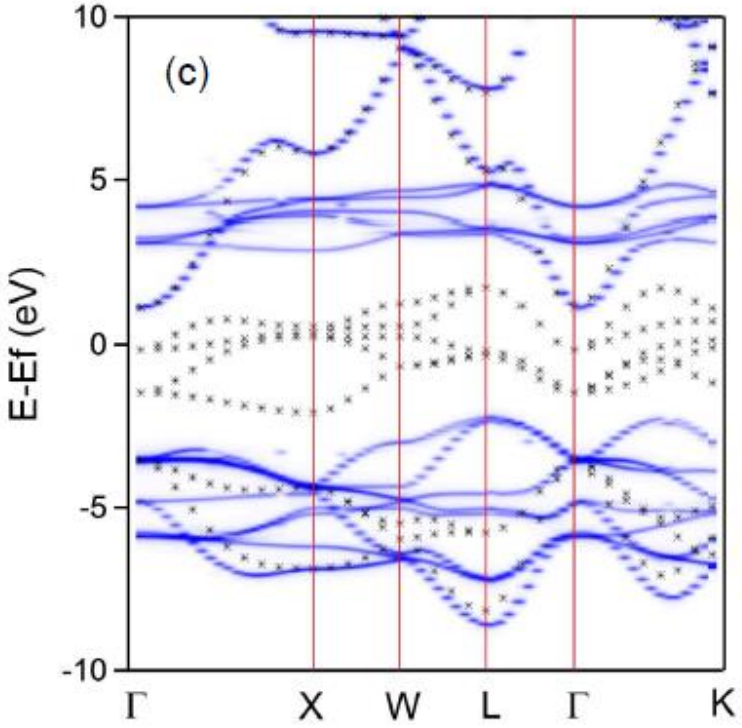

(a)
(b)
(c)
d_{z^2} $d_{x^2-y^2}$
d_{z^2} $d_{x^2-y^2}$
s p_x p_y p_z
s p_x p_y p_z
s p_x p_y p_z
d_{xy} d_{xz} d_{yz}
d_{xy} d_{xz} d_{yz}
s p_x p_y p_z


NiO
(b)
arbitrary units
-10
-5
0
5
E-Ef (eV)

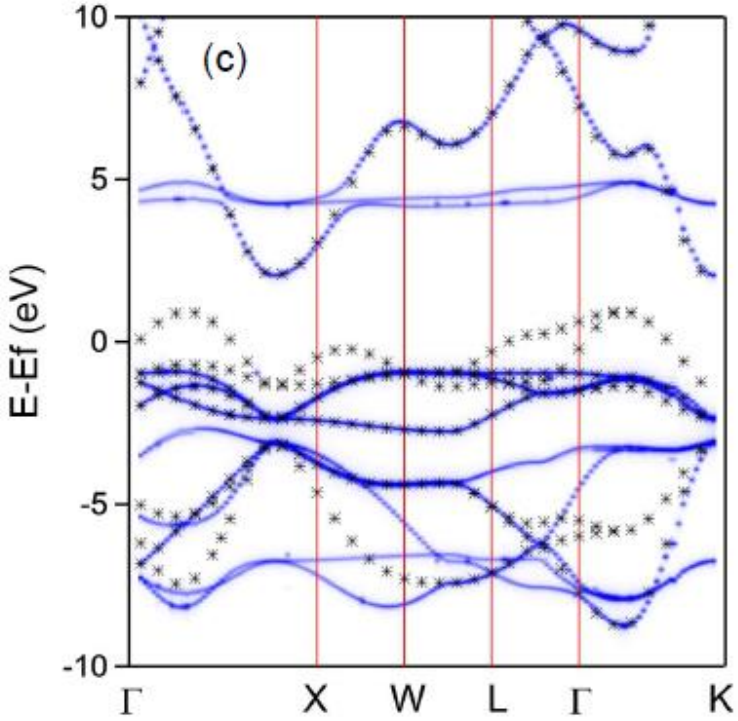

(a)
(b)
(c)
d_z^2 $d_{x^2-y^2}$ d_{xy} d_{xz} d_{yz}
s p_x p_y p_z
s p_x p_y p_z
d_z^2 $d_{x^2-y^2}$ d_{xy} d_{xz} d_{yz}
s p_x p_y p_z
s p_x p_y p_z


MnO
(b)
arbitrary units
-10
-5
0
5
E-Ef (eV)

MnO



NiO

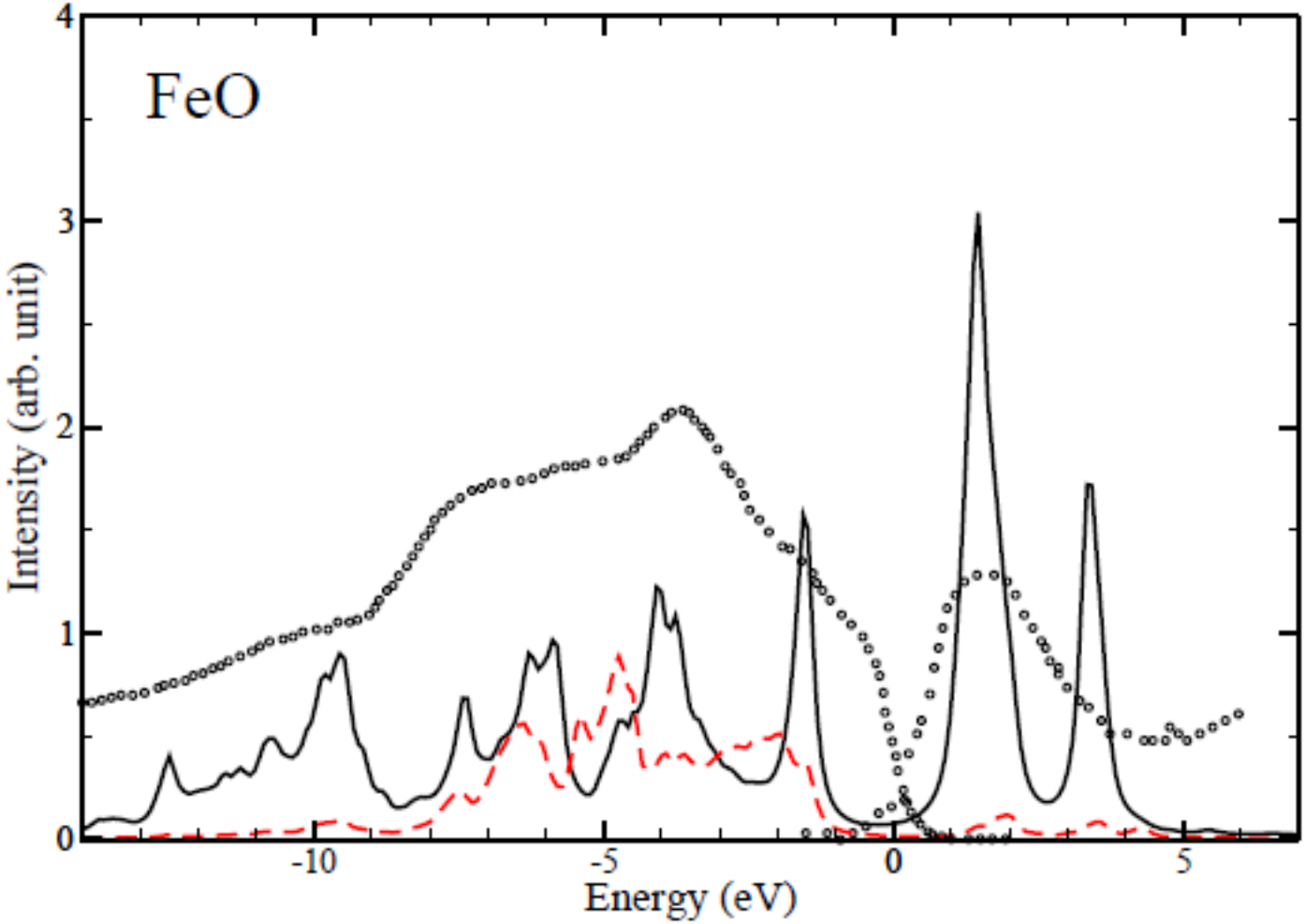


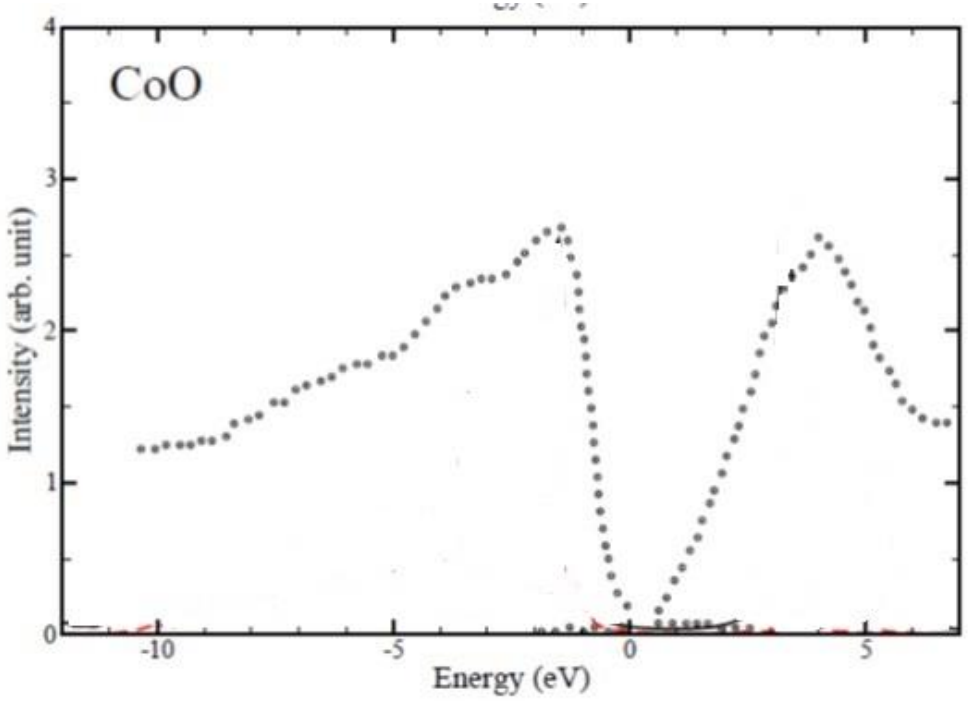
Concluding remarks

- CPT is a prototype of QC method. Its application to model systems shows the importance of cluster symmetry in all QC calculations

- CPT describes novel phases (topological, out of equilibrium) of correlated systems

- For real materials a multi-partition strategy has been devised to deal with exceedingly large dimensions of Hilbert space.


FeO
Intensity (arb. unit)
Energy (eV)
0
1
2
3
4
-10
-5
0
5


CoO
Intensity (arb. unit)
Energy (eV)
0
1
2
3
4
-10
-5
0
5