Wannier functions theory and selected applications

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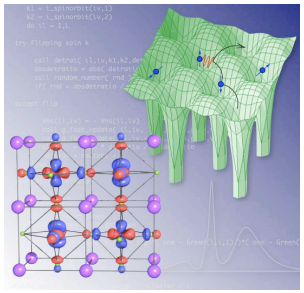
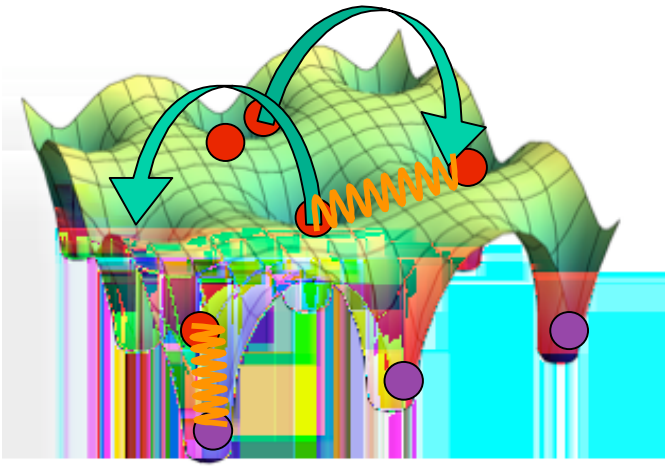


DFG FOR 1346
Dynamical Mean-Field Approach with Predictive Power for Strongly Correlated Materials

Outline

- Motivation
- Fourier transform
- Exponential localization and band topology
- Examples
- Crystal field parameters for rare earths in oxides

Electrons in periodic potential



Bloch theorem

$$-\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r})$$

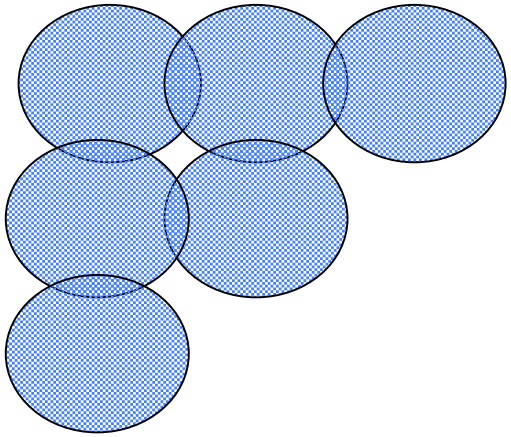
$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}u_{n,\mathbf{k}}(\mathbf{r})$$

Bloch waves are not necessarily the best basis for further developments, e.g. perturbative treatment of the interaction.

Localized and orthonormal orbitals

- Useful basis for treatment of local perturbations (impurities, defects, on-site interaction)
- Obey canonical commutation relations
- Explicit translational symmetry
- Compromise between localization in space and 'localization' in the energy domain (minimal basis)
- Analytic tool - chemist's view

Orthogonal atomic orbitals



Bloch sum (Fourier series)

$$\phi(\mathbf{k},\mathbf{x}) = \frac{A(\mathbf{k})}{N^{1/2}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} v(\mathbf{x}-\mathbf{R})$$

normalization

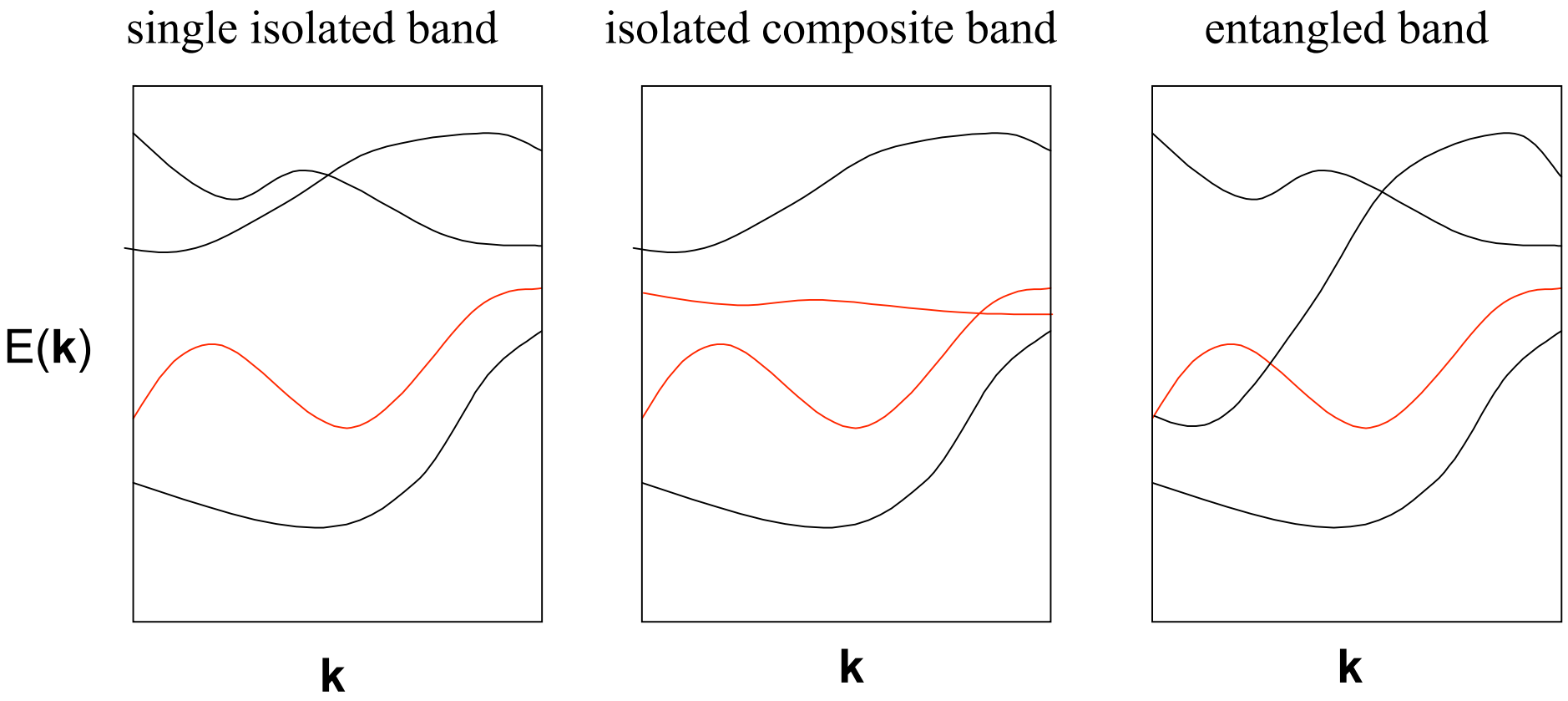
$$\frac{1}{A(\mathbf{k})^2} = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \int d\mathbf{x} v^*(\mathbf{x}) v(\mathbf{x}-\mathbf{R})$$

Fourier coefficient

$$w(\mathbf{R},\mathbf{x}) = \frac{1}{N^{1/2}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{k},\mathbf{x})$$

$$= \sum_{\mathbf{R}'} c(\mathbf{R}-\mathbf{R}') v(\mathbf{x}-\mathbf{R}')$$

Wannier functions



WF of single isolated band

Fourier coefficient

$$w_n(\mathbf{r}-\mathbf{R}) = \frac{V}{(2\pi)^d}\int_{\mathrm{BZ}} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}}\psi_{n,\mathbf{k}}(\mathbf{r})$$

Fourier series

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} w_n(\mathbf{r}-\mathbf{R})$$

$$\psi_{n,\mathbf{k}}(\mathbf{r}) \longrightarrow e^{i\phi(\mathbf{k})}\psi_{n,\mathbf{k}}(\mathbf{r})$$

Gauge freedom

WF of isolated composite band

Fourier coefficient

$$\mathbf{w}(\mathbf{r}-\mathbf{R}) = \frac{V}{(2\pi)^d}\int_{\mathrm{BZ}} d\mathbf{k}\mathbf{U}(\mathbf{k})\boldsymbol{\psi}_{\mathbf{k}}(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{R}}$$

Fourier series

$$\tilde{\boldsymbol{\psi}}_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\mathbf{w}(\mathbf{r}-\mathbf{R})$$

$$\psi'_{n,\mathbf{k}}(\mathbf{r}) = U_{n\bar{m}}(\mathbf{k})\psi_{\bar{m},\mathbf{k}}(\mathbf{r})$$

Gauge freedom

WF properties

Explicit periodicity

$$w_{\mathbf{R}}(\mathbf{r}) = w(\mathbf{r} - \mathbf{R})$$

Orthogonality

$$\langle w(\mathbf{r} - \mathbf{R}) | w(\mathbf{r} - \mathbf{R}') \rangle = \delta_{\mathbf{R},\mathbf{R}'}$$

Uniqueness of Wannier center

$$\tilde{\psi} = e^{i\phi}\psi$$

$$\begin{aligned} \langle \tilde{w} | \mathbf{r} | \tilde{w} \rangle &= \langle w | \mathbf{r} | w \rangle + \frac{V}{(2\pi)^d} \int_{\mathrm{BZ}} d\mathbf{k} \nabla_{\mathbf{k}} \phi(\mathbf{k}) \\ &= \langle w | \mathbf{r} | w \rangle + \mathbf{R} \end{aligned}$$

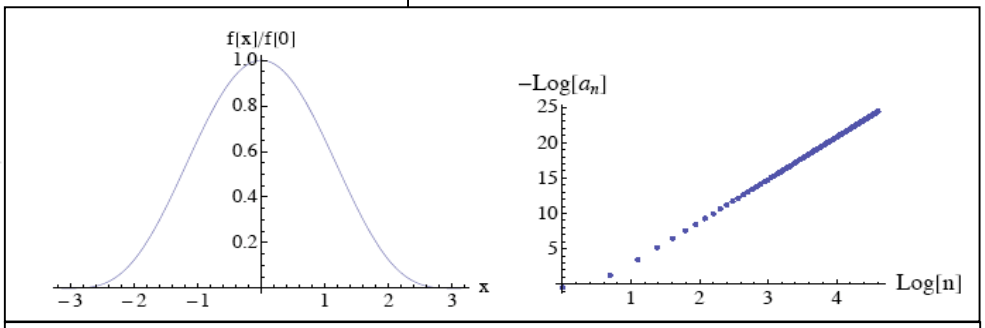
Convergence of Fourier coefficients

$f(x)$	$a_n = \frac{1}{2\pi}\int_0^{2\pi} dx e^{-inx} f(x)$
$(1-\frac{x}{\pi})^4(1+\frac{x}{\pi})^4$	$\sim n^{-5}$
$(1+\cos(x))\sqrt{1.1+\cos(x)}$	$\sim e^{-\alpha n}$
$\exp(-\frac{1}{1-(x/\pi)^2})$	$\sim \lvert\pi n\rvert^{-3/4} exp(-\sqrt{\lvert\pi n\rvert})$

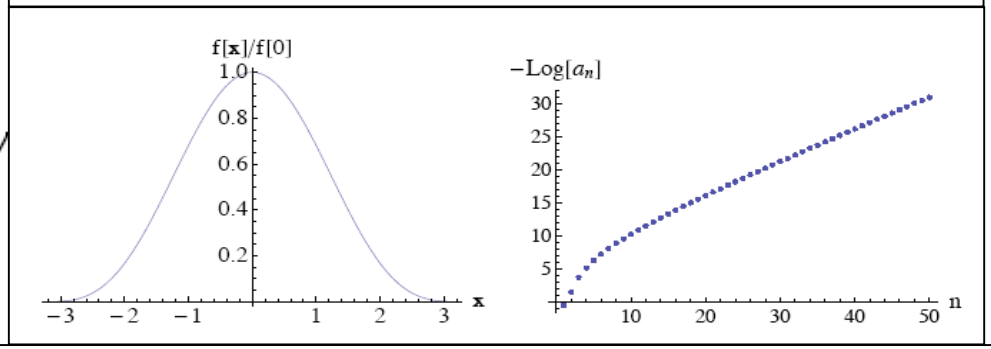
Convergence of Fourier coefficients

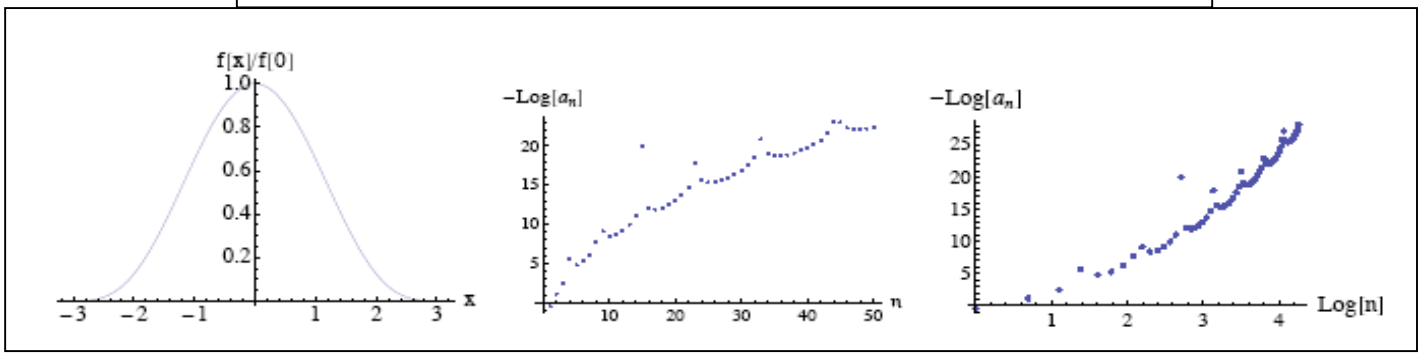
$f(x)$ | $a_n = \frac{1}{2\pi}\int_0^{2\pi} dx e^{-inx} f(x)$

$(1 -$



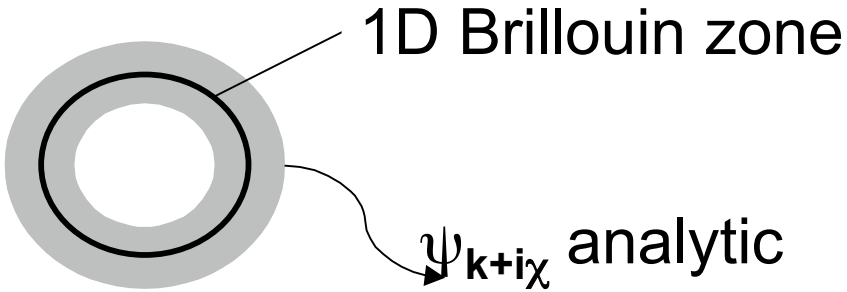
$(1 + \cos(x))\sqrt{}$

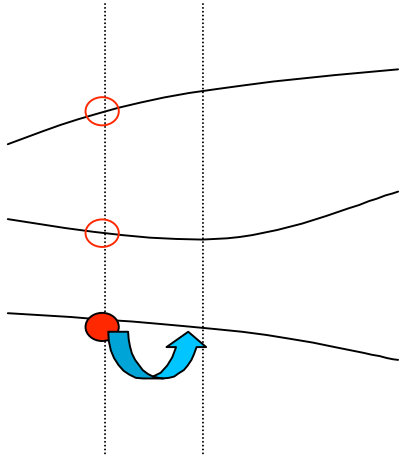




Exponential localization of WFs

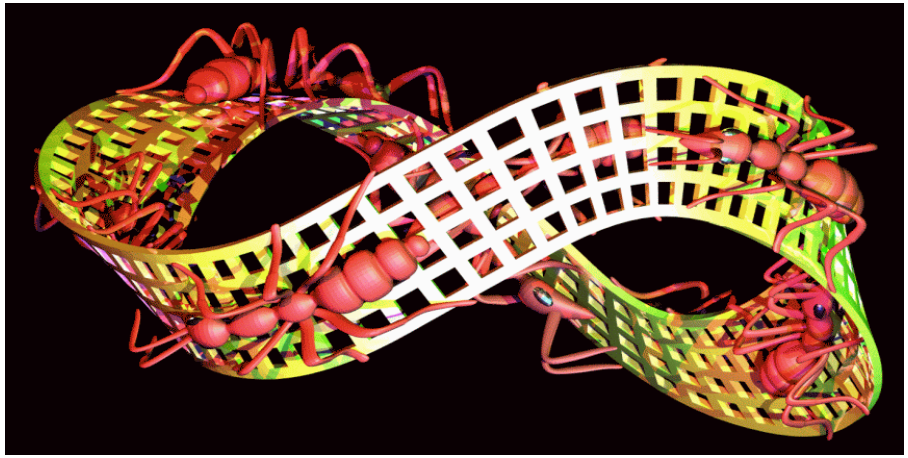
Can we make ψ_k analytic?





ψ_k can be made locally analytic - **k .p** expansion:

Can it be done globally?



This is a non-trivial topological question.

Brief excursion to topology

(Berry) connection gauge dependent

$$A^{\alpha}_{mn}(\mathbf{k}) = \langle u_{n,\mathbf{k}} | \frac{\partial}{\partial k_\alpha} u_{m,\mathbf{k}} \rangle$$

(Berry) curvature gauge invariant

$$B^{\alpha\beta}(\mathbf{k}) = \mathrm{tr}\left(\frac{\partial \mathbf{A}^{\beta}}{\partial k_\alpha} - \frac{\partial \mathbf{A}^{\alpha}}{\partial k_\beta} - [\mathbf{A}^{\alpha}, \mathbf{A}^{\beta}]\right)$$

$$= 2\,\mathrm{Im} \sum_{n=n_{\min}}^{n_{\max}} \langle \frac{\partial}{\partial k_\alpha} u_{n,\mathbf{k}} | \frac{\partial}{\partial k_\beta} u_{n,\mathbf{k}} \rangle$$

Exponentially localized WF exist if all Chern numbers associated with $B^{\alpha\beta}(\boldsymbol{k})$ are zero.

Construction of WFs

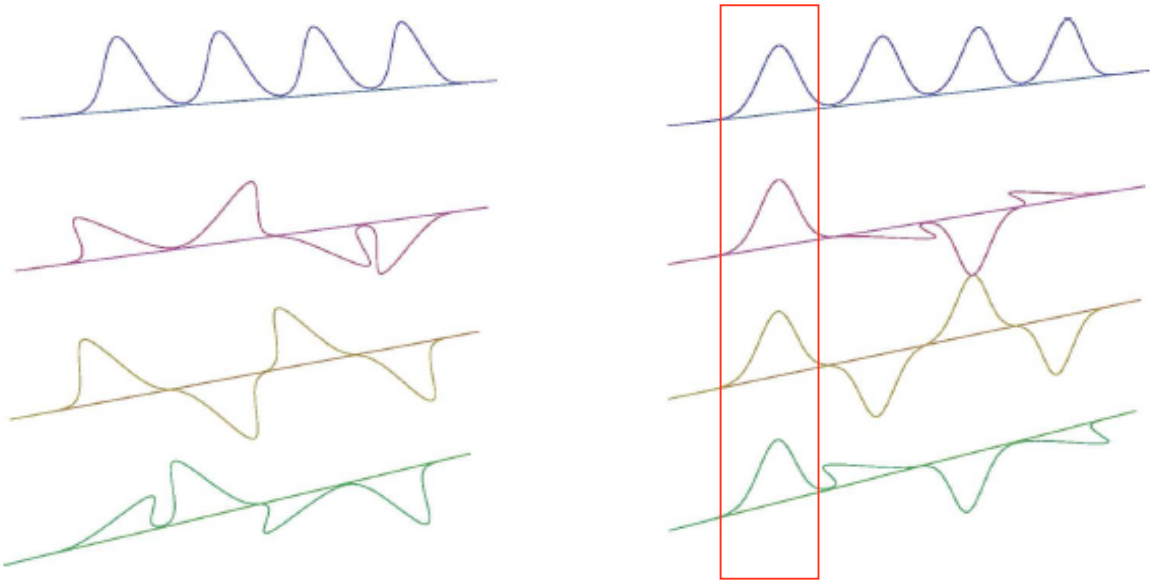
Localization of WF reflects the variation of $u_k(r)$ through BZ.

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r})$$

Projection technique - aligns the phase of Bloch waves on a given site

random phase

aligned phase

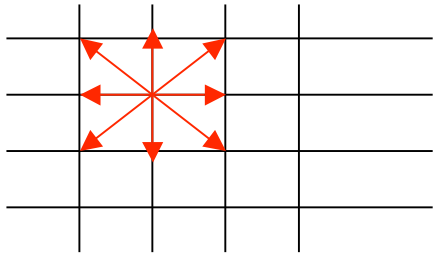


- always works in 1D
- in 2D and 3D there are system where finite projection everywhere in BZ is not possible (QHE)

Construction of WFs

Maximum localization method - minimizes 2nd moment of WF

- Formulated in basis independent way
- Input: $M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}} | u_{n\mathbf{k}+\mathbf{b}} \rangle = \langle \psi_{m\mathbf{k}} | e^{-i\mathbf{b}\cdot\mathbf{r}} | \psi_{n\mathbf{k}+\mathbf{b}} \rangle$

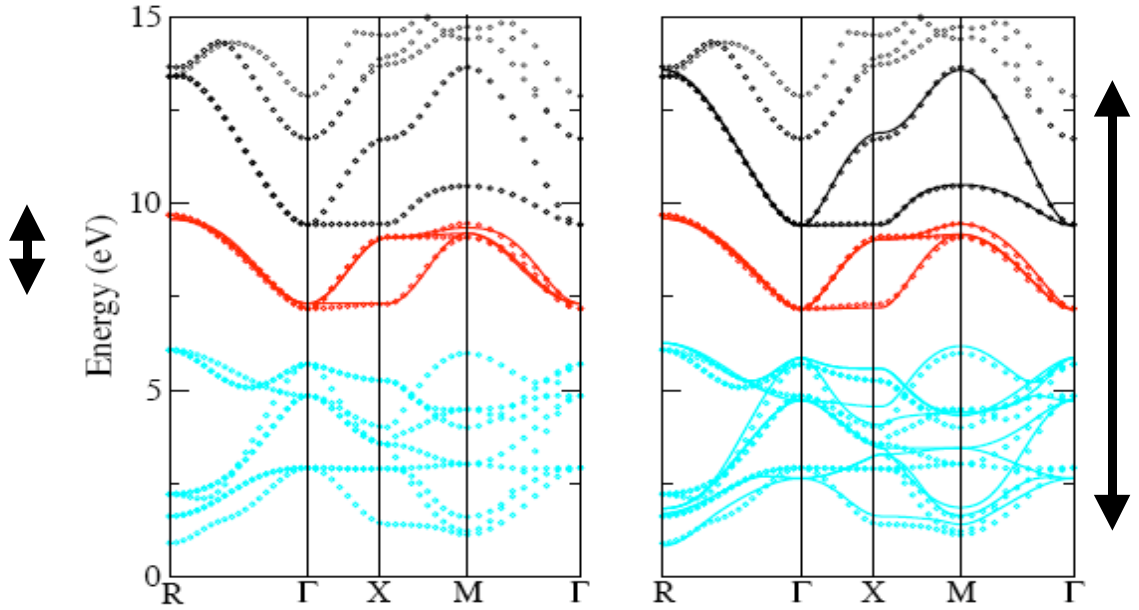


- Additional input: $A_{mn}^{(\mathbf{k})} = \langle \psi_{m\mathbf{k}} | g_n \rangle$
- Output: $\boldsymbol{U}(\boldsymbol{k})$ unitary transformation between the Bloch and WF basis

Technical difficulty - to find a discrete approximation of $\langle u_{n,\mathbf{k}} | \frac{\partial}{\partial k_\alpha} u_{m,\mathbf{k}} \rangle$ in terms of $M_{mn}^{(\mathbf{k},\mathbf{b})}$

Examples - large vs small energy window

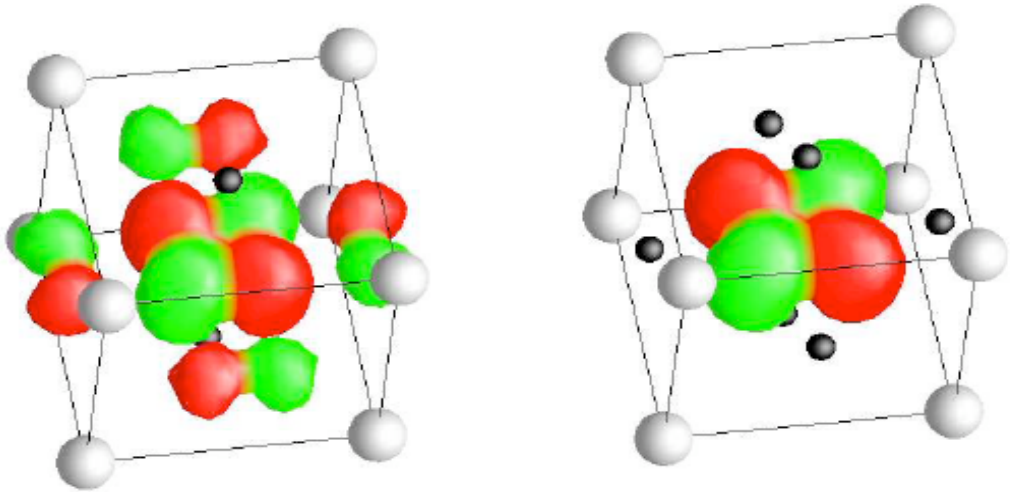
$SrVO_3$



V-d e_g

V-d t_{2g}

O-p



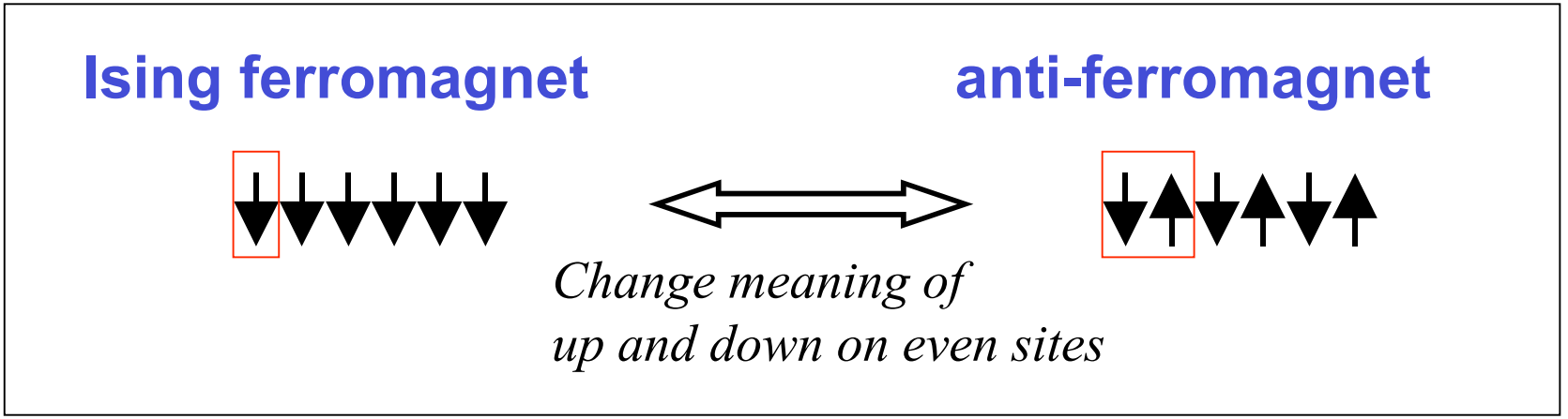
V-centered
xy orbital

Examples - symmetries and tight-binding representation

How to make use of weakly broken symmetries ?

- We want to treat symmetry breaking term as perturbation and need to identify it and quantify

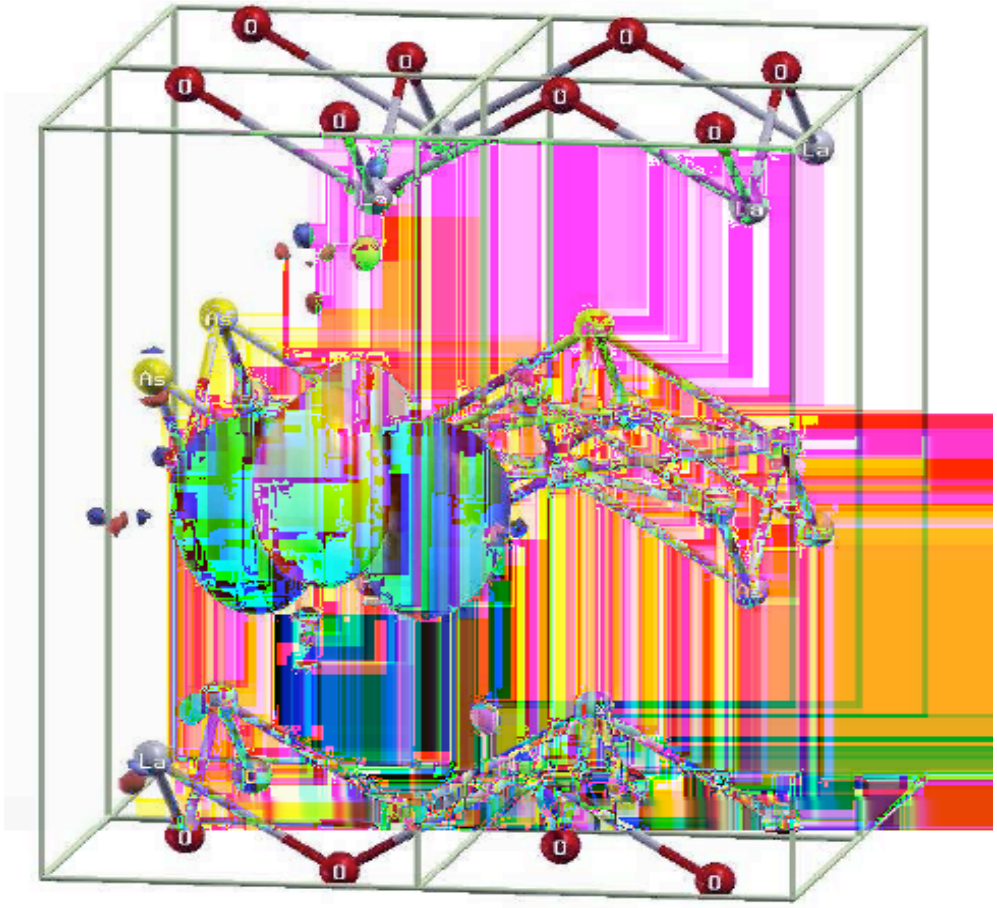
- TB Hamiltonian has higher symmetry than underlying the crystal structure



Examples - symmetries and tight-binding representation

LaOFeAs - construction of model with 1 f.u. per u.c

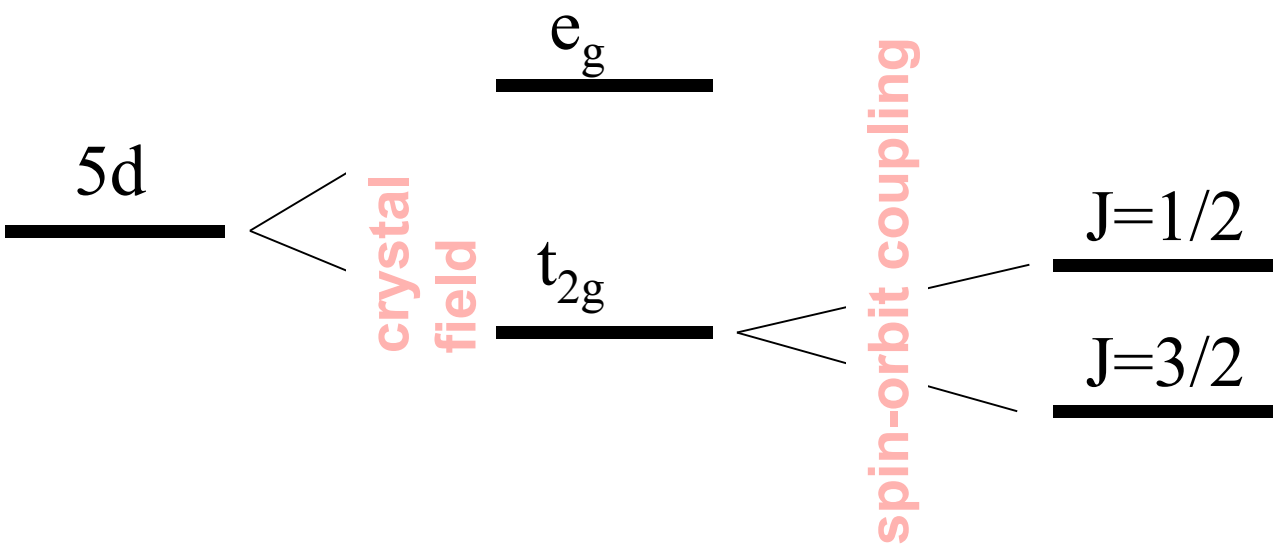
Hoppings have higher translational symmetry than the crystal structure in proper basis!



Information about the crystal symmetry is ‘hidden’ in the shape of WFs

Examples - spin-orbital coupling

Sr_2IrO_4 (hypothetical symmetrized structure)



We want to construct J=1/2-like WFs out of t_{2g} band.

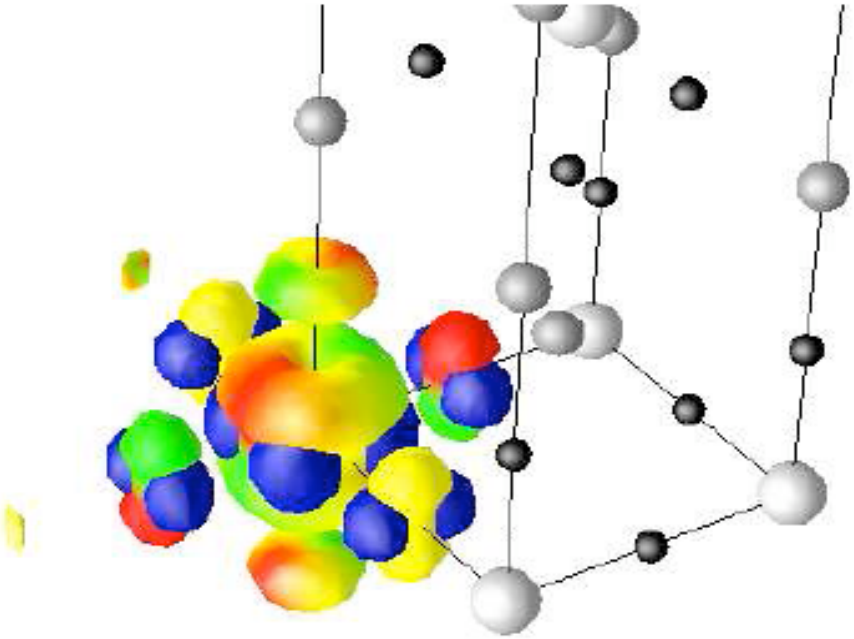
$$w(\mathbf{r}) \sim \begin{pmatrix} \alpha z(x+iy) \\ xy \end{pmatrix}$$

Examples - spin-orbital coupling

Sr_2IrO_4 (hypothetical symmetrized structure)

$$\langle \psi | \psi' \rangle = \int d\mathbf{r} \psi^*(\mathbf{r}) \psi'(\mathbf{r}) \quad \Longrightarrow \quad \langle \psi | \psi' \rangle = \sum_\sigma \int d\mathbf{r} \psi^*_\sigma(\mathbf{r}) \psi'_\sigma(\mathbf{r})$$

$$w(\mathbf{r}) \sim \begin{pmatrix} \alpha z(x+iy) \\ xy \end{pmatrix}$$



JK *et al.,* Comput. Phys. Commun. 2010

Disentanglement

WFs are not unitary images of Bloch waves but an optimized projections.

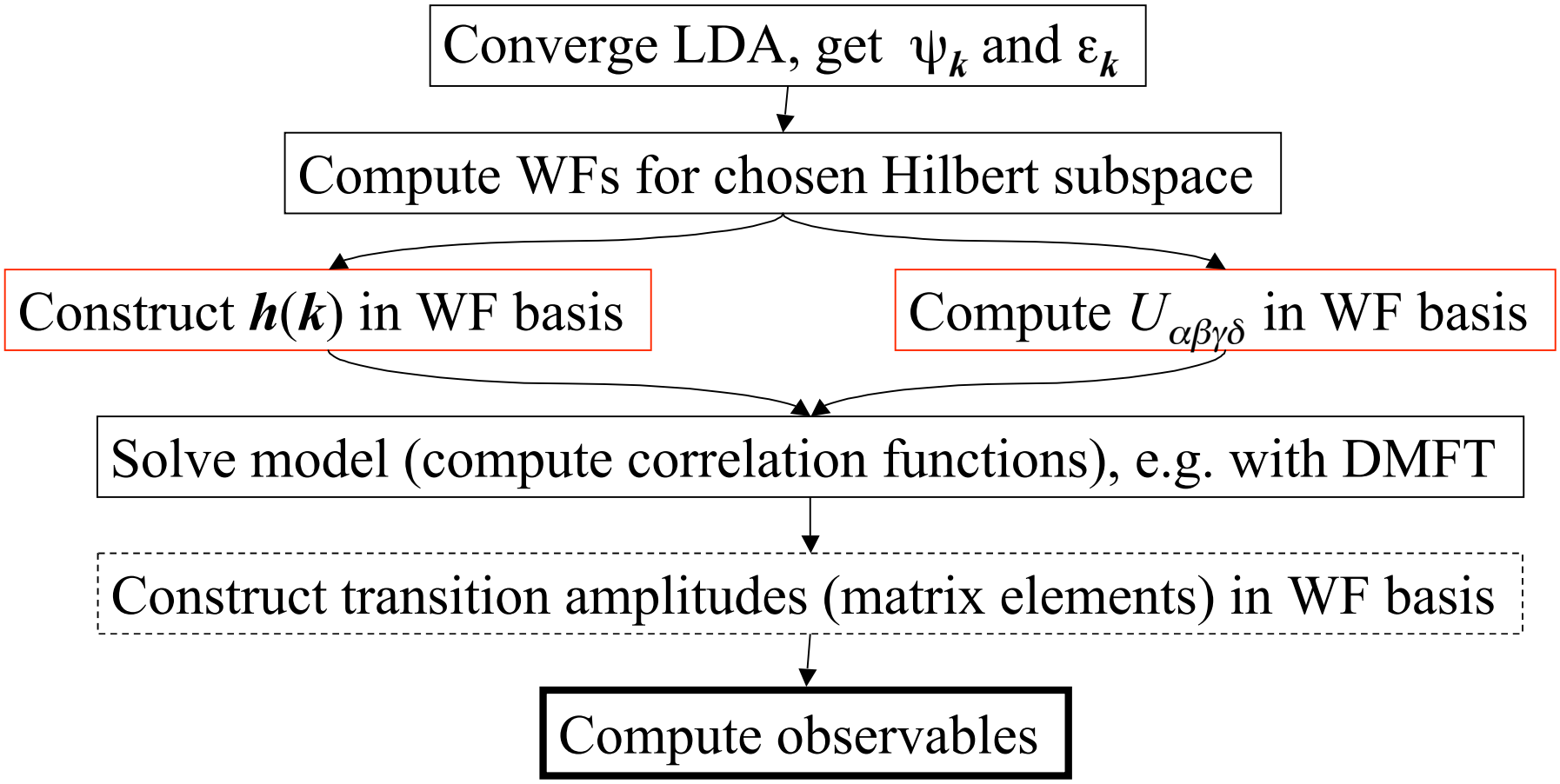
$$N_{WF} < N_{bands}$$

Projection method: Maximize overlap with a given subspace at each ***k***-point

MALOC method: Find the smoothest N_{WF}-dimensional connection in a given N_{bands}-dimensional subspace

WFs and effective models

$$H = \sum_{\mathbf{k}} \left([h^{dd}(\mathbf{k})]_{\alpha\beta} d^{\dagger}_{\boldsymbol{k}\alpha} d_{\boldsymbol{k}\beta} + [h^{pp}(\mathbf{k})]_{\gamma\delta} p^{\dagger}_{\boldsymbol{k}\gamma} p_{\boldsymbol{k}\delta} + [h^{dp}(\mathbf{k})]_{\alpha\gamma} d^{\dagger}_{\boldsymbol{k}\alpha} p_{\boldsymbol{k}\gamma} + [h^{pd}(\mathbf{k})]_{\gamma\alpha} p^{\dagger}_{\boldsymbol{k}\gamma} d_{\boldsymbol{k}\alpha} \right)$$
$$+ \sum_{i} U_{\alpha\beta\gamma\delta} d^{\dagger}_{i\alpha} d^{\dagger}_{i\beta} d_{i\gamma} d_{i\delta} - H_{\mathrm{dc}},$$



WFs and effective models

$$H = \sum_{\mathbf{k}} \Big([h^{dd}(\mathbf{k})]_{\alpha\beta} d^{\dagger}_{\boldsymbol{k}\alpha} d_{\boldsymbol{k}\beta} + [h^{pp}(\mathbf{k})]_{\gamma\delta} p^{\dagger}_{\boldsymbol{k}\gamma} p_{\boldsymbol{k}\delta} + [h^{dp}(\mathbf{k})]_{\alpha\gamma} d^{\dagger}_{\boldsymbol{k}\alpha} p_{\boldsymbol{k}\gamma} + [h^{pd}(\mathbf{k})]_{\gamma\alpha} p^{\dagger}_{\boldsymbol{k}\gamma} d_{\boldsymbol{k}\alpha} \Big)$$
$$+ \sum_{i} U_{\alpha\beta\gamma\delta} d^{\dagger}_{i\alpha} d^{\dagger}_{i\beta} d_{i\gamma} d_{i\delta} - H_{\mathrm{dc}},$$

Converge LDA, get $\psi_{\boldsymbol{k}}$ and $\varepsilon_{\boldsymbol{k}}$

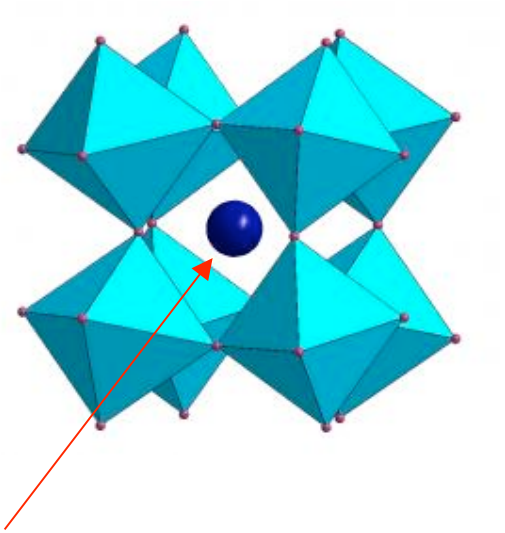
Compute WFs for chosen Hilbert subspace

Construct $\boldsymbol{h}(\boldsymbol{k})$ in WF basis

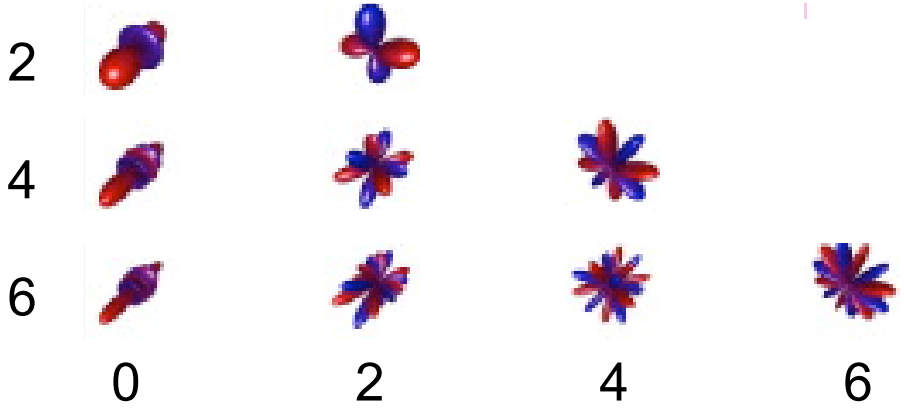
Compute $U_{\alpha\beta\gamma\delta}$ in WF basis

By choosing WFs we specify which interactions are treated explicitly and for which (static) mean-field decoupling is used.

Crystal field parameters: R in $YAlO_3$



15 crystal field parameters:



Nd, Tb, Er

Experiment: optical transitions between mutliplet states
Theory: exact diagonalization for 4f shell in crystal field (CF)

How to get the CF parameters?

Crystal field parameters: R in $YAlO_3$

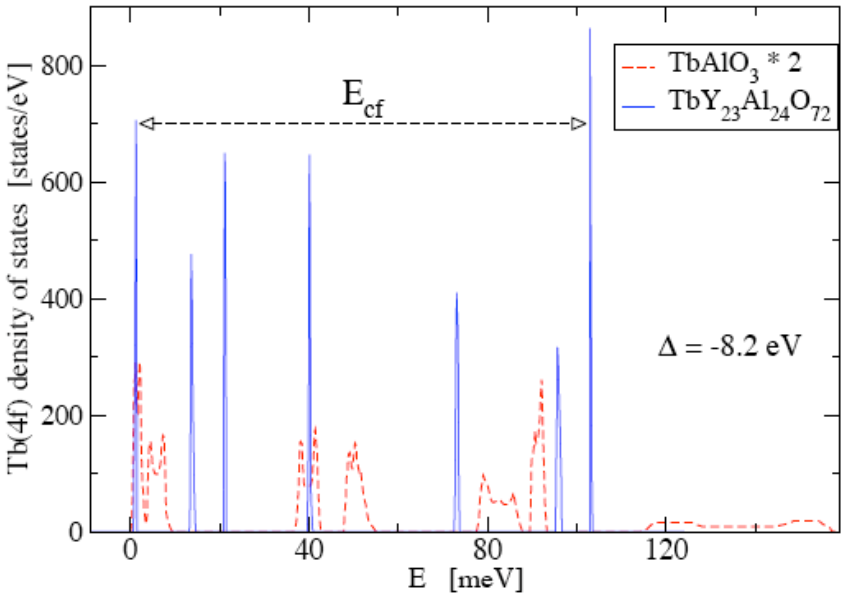
4f weakly coupled to the crystal environment - hybridization treated perturbatively

$$\hat{H} = \sum_{i,j} \left(h_{ij}^{\mathrm{at}} + \sum_{k} \frac{V_{ik} V_{kj}}{\Delta_{\mathrm{fp}}} \right) \hat{f}_i^{\dagger} \hat{f}_j + \hat{W}_f$$

adjustable by orbital dependent shift

Extracting CF parameters

old way



using WFs

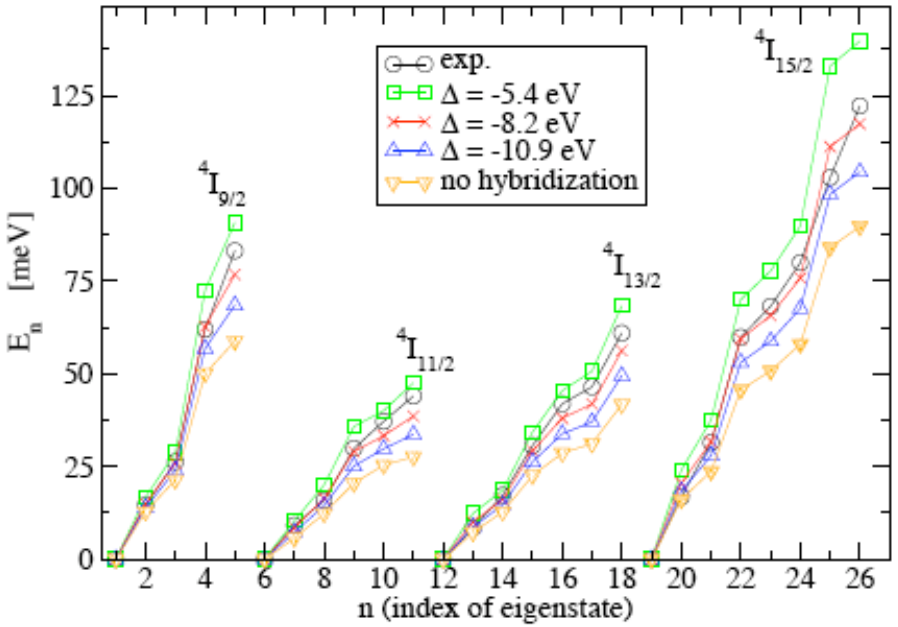
- converge Wien2k with 4f in core
- get band structure with 4f in valence and shifted Op orbitals
- construct WFs from 4f window
- expand

$$\hat{H}_{CF} = \sum_{k=0}^{k_{max}} \sum_{q=-k}^{k} B_q^{(k)} \hat{C}_q^{(k)}$$

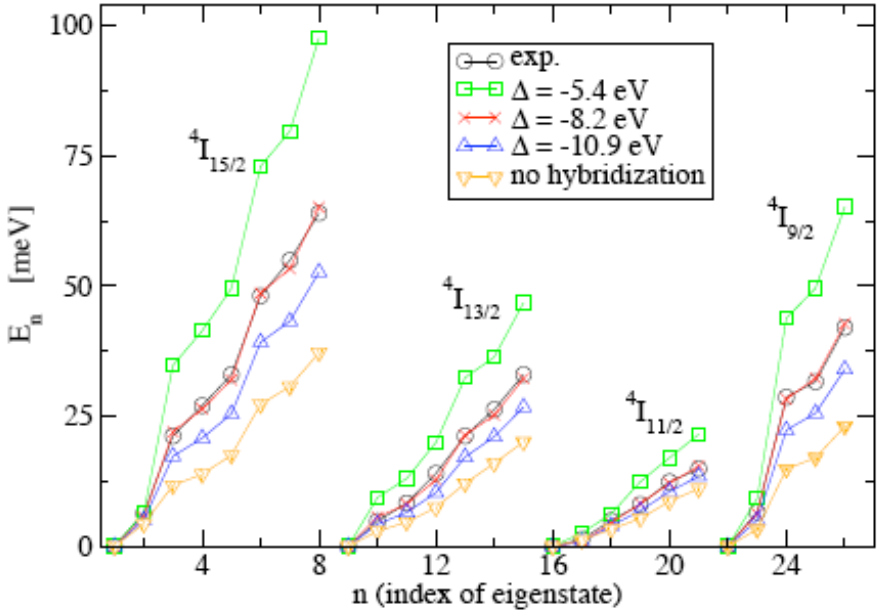
Crystal field parameters: R in $YAlO_3$

Theory vs experiment: CF splittings of various multiplets

Nd:$YAlO_3$



Er:$YAlO_3$



experiment: Duan *et al.,* PRB 2007
Donlan&Santiago, J. Chem. Phys. 1972

theory: Novák *et al.,* PRB 2013
Novák *et al.,* arXiv:1306.5948

Summary

- There is an close relationship between ***k***-smoothness of Bloch waves and localization of Wannier functions.
- Existence of exponentially localized WFs is a topological property of a given (composite) band.
- Larger energy window => more localized WFs.
- For typical applications in LDA+DMFT (i.e. large energy windows) the projection and MALOC methods give similar WFs.

Construction of WFs using w2w and wannier90

1) complete wien2k scf calculation

2) prepare a uniform k-mesh — init_w2w

prepare *case.ksym* with 1 sym. operation

x kgen -so -> *case.klist*

3) prepare *case.w2win* and *w2w.def*

choose bands

choose initial projections

write_w2win *case*

write_w2wdef *case*

4) prepare *case.win*

chose band and orbitals

add the list of k-points

write_win *case*

5) prepare the list of k-connections *case.nnkp*

wannier90.x -pp *case*

6) prepare ψ_{nk} on a uniform k-mesh

x lapw1 -> *case.vector*

7) run w2w *w2w.def* -> *case.mmn, case.amn, case.eig*

8) run wannier90.x *case* -> *case.wout, case_band.dat, case_hr.dat*

9) wplot *case*

10) convert_Hamiltonian *case*

Construction of WFs using w2w and wannier90

case.w2win:

```
BOTH
  21  23     # min band Nmin, max band Nmax
  3  3       # LJMAX max in exp(ibr) expansion, #Wannier functions
2         #d-xy orbital
 2 2 -2   0.00000000   0.70710677   # index of atom, L, M, coefficient (complex)
 2 2  2   0.00000000  -0.70710677   # index of atom, L, M, coefficient (complex)
2         #d-yz orbital
 2 2 -1   0.00000000   0.70710677   # index of atom, L, M, coefficient (complex)
 2 2  1   0.00000000   0.70710677   # index of atom, L, M, coefficient (complex)
2         #d-xz orbital
 2 2 -1   0.70710677   0.00000000   # index of atom, L, M, coefficient (complex)
 2 2  1  -0.70710677   0.00000000   # index of atom, L, M, coefficient (complex)
```

$Y_{22}-Y_{2-2}$

$Y_{21}+Y_{2-1}$

$Y_{21}-Y_{2-1}$

Construction of WFs using w2w and wannier90

case.nnkp:

```
…
begin kpoints
   125
    0.00000000    0.00000000    0.00000000
    0.00000000    0.00000000    0.20000000
    0.00000000    0.00000000    0.40000000

….
end kpoints

begin projections
end projections

begin nnkpts
  6
    1     2      0   0   0
    1     6      0   0   0
    1    26      0   0   0
    1     5      0   0  -1
    1    21      0  -1   0
    1   101     -1   0   0
    2     1      0   0   0
   ….
```

Construction of WFs using w2w and wannier90

case.win:

```
 iprint = 3
 num_bands       =   3
 num_wann        =   3
 num_iter        = 1000
 num_print_cycles =100
…

 begin kpoint_path
  R  0.50  0.5   0.5  GAM  0.    0.    0.
 GAM  0.00  0.00  0.00   X  0.50  0.00  0.00
  X  0.50  0.00  0.00   M  0.50  0.50  0.00
  M  0.50  0.50  0.00 GAM  0.00  0.00  0.00
 end kpoint_path
…

 bands_plot = .true.
!restart = plot
 hr_plot = .true.
 …
 mp_grid :           5          5          5
 begin kpoints
  0.000000000  0.000000000  0.000000000
  0.000000000  0.000000000  0.200000003
  …
```

Disentanglement

Cu