A Guide to Wannier Functions

FLEUR hands-on workshop (April 2021)

Dongwook Go

Topological Nanoelectronics Group

Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich
Institute of Physics, Johannes Gutenberg University Mainz

d.go@fz-juelich.de

spintronicsphysics.blog

@DongwookGo

TOPOLOGICAL NANOELECTRONICS

JÜLICH Forschungszentrum

JOHANNES GUTENBERG UNIVERSITÄT MAINZ

JG|U

www.flapw.de

fleur

Why Wannier functions?

Analysis of chemical bonding

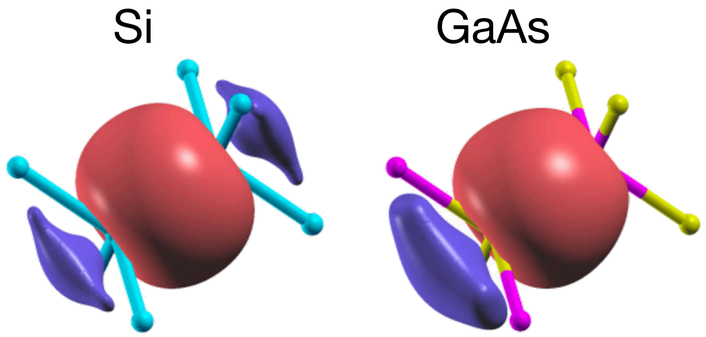


Figure taken from Marzari *et al.* Rev. Mod. Phys. **84**, 1419 (2012)

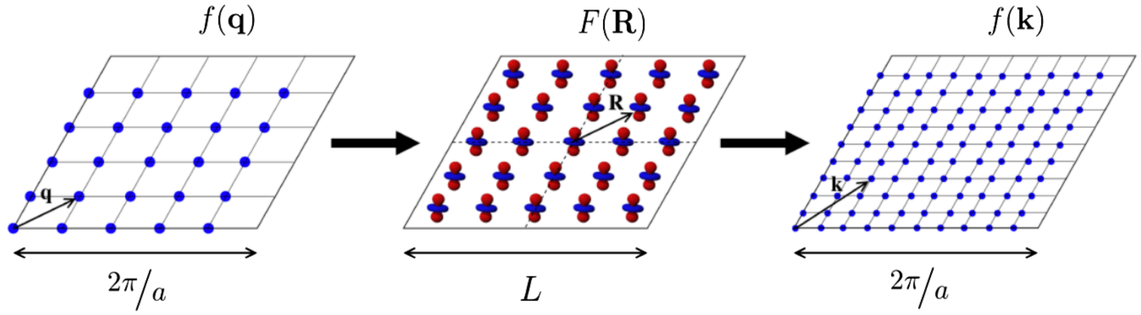
Construction of model Hamiltonian

Ex. (Multi-orbital) Hubbard model

$$\mathcal{H} = \sum_{\langle ij \rangle} t_{ij} c_i^\dagger c_j + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Wannier interpolation & Berry phase theory

Figure taken from Marzari *et al.*
Rev. Mod. Phys. **84**, 1419 (2012)



WFs as building blocks for large-scale simulation

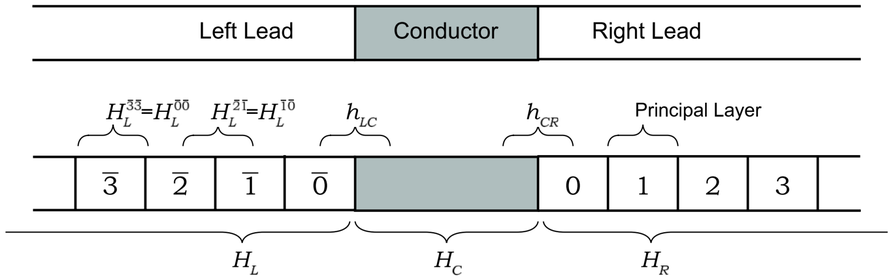


Figure taken from Shelley *et al*. Comp. Phys. Comm. **182**, 2174 (2011)

What I will cover

- Theoretical backgrounds & physical insight
- Concepts of major keywords
  - Gauge indeterminacy
  - Projection
  - Disentanglement
  - Energy window (outer, inner/frozen)
  - Wannier interpolation
- Examples:
  - $PbTiO_3$ (insulator)
  - Fe (metal)
- Practical usages will be covered in the hands-on session on Friday.

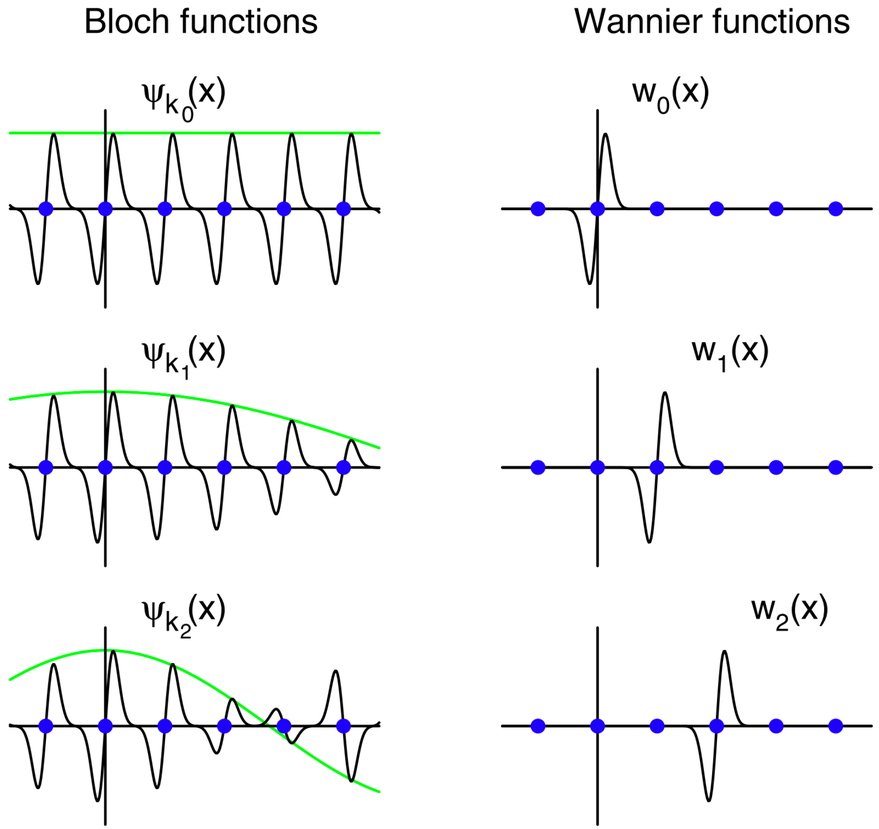
What is the Wannier function?

Bloch function: $|\psi_{n\mathbf{k}}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}\,|u_{n\mathbf{k}}\rangle$

Wannier function:

$$|\mathbf{R}n\rangle = \frac{V_\mathrm{c}}{(2\pi)^3}\int d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}}\,|\psi_{n\mathbf{k}}\rangle$$

$$|\psi_{n\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\,|\mathbf{R}n\rangle$$



G. H. Wannier, Phys. Rev. **52**, 191 (1937)

Marzari *et al.* Rev. Mod. Phys. **84**, 1479 (2012)

Basic Properties of the WFs

$$|\psi_{n\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\mathbf{R}n\rangle$$

$$|\mathbf{R}n\rangle = \frac{V_\mathrm{c}}{(2\pi)^3} \int d\mathbf{k}\; e^{-i\mathbf{k}\cdot\mathbf{R}} |\psi_{n\mathbf{k}}\rangle$$
$$= \frac{V_\mathrm{c}}{(2\pi)^3} \int d\mathbf{k}\; e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{r})} |u_{n\mathbf{k}}\rangle$$

Bloch theorem: $T_{\mathbf{R}} |\psi_{n\mathbf{k}}\rangle = e^{i\mathbf{k}\cdot\mathbf{R}} |\psi_{n\mathbf{k}}\rangle$

$$|\psi_{n\mathbf{k}+\mathbf{G}}\rangle = |\psi_{n\mathbf{k}}\rangle$$

Orthonormality: $\langle\psi_{n\mathbf{k}}|\psi_{n'\mathbf{k}'}\rangle = \frac{(2\pi)^3}{V_\mathrm{c}} \delta_{nn'} \delta^3(\mathbf{k}-\mathbf{k}')$

implies $\langle\mathbf{R}n|\mathbf{R}'n'\rangle = \delta_{nn'}\delta_{\mathbf{R}\mathbf{R}'}$

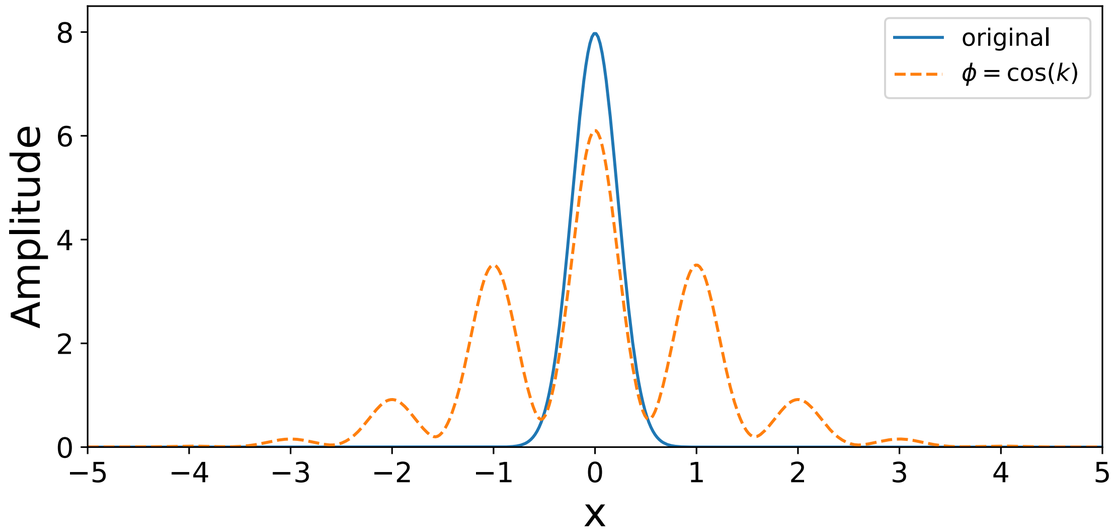
Completeness?

Localized around $\mathbf{r} = \mathbf{R}$ if $u_{n\mathbf{k}}$ is a smooth function of $\mathbf{k}$ ($\Delta r \Delta k \sim 1$)

The gauge indeterminacy

Gauge = Choice of a phase factor in the wave function

$$|u_{n\mathbf{k}}\rangle \rightarrow e^{i\phi_n(\mathbf{k})} |u_{n\mathbf{k}}\rangle$$



$$\psi_k(x) = \sum_R e^{ikR} w(x - R)$$

$$w'(x - R) = \frac{1}{2\pi} \int dk \; e^{-ikR} e^{i\phi(k)} \psi_k(x)$$

Computer algorithms calculate Bloch states independently for each **k**-point.

→ Arbitrariness of the phase factor!

Maximally-localized WFs

SU(N) gauge degree of freedom: $|u_{n\mathbf{k}}\rangle \rightarrow \sum_m |u_{m\mathbf{k}}\rangle U_{mn}(\mathbf{k})$

$$|\mathbf{R}n\rangle = \frac{V_\mathrm{c}}{(2\pi)^3} \sum_m \int d\mathbf{k}\; e^{-i\mathbf{k}\cdot(\mathbf{R}-\mathbf{r})}\, |u_{m\mathbf{k}}\rangle U_{mn}(\mathbf{k})$$

A goal: To find U that minimizes the spread of the WFs

$$\Omega = \sum_n \left[\langle \mathbf{0}n|\, r^2\, |\mathbf{0}n\rangle - \langle \mathbf{0}n|\, \mathbf{r}\, |\mathbf{0}n\rangle^2\right] = \sum_n \left[\langle r^2\rangle_n - \bar{\mathbf{r}}_n^2\right]$$

This can be done in **k**-space!

📚 Marzari and Vanderbilt, Phys. Rev. B **56**, 12847 (1997)

The spread functional in k-space

📚 Marzari and Vanderbilt, Phys. Rev. B **56**, 12847 (1997)

$$\Omega = \sum_n \left[\langle \mathbf{0}n | \, r^2 \, | \mathbf{0}n \rangle - \langle \mathbf{0}n | \, \mathbf{r} \, | \mathbf{0}n \rangle^2 \right] = \sum_n \left[\langle r^2 \rangle_n - \bar{\mathbf{r}}_n^2 \right]$$

The spread functional can be expressed in **k**-space.

$$\bar{\mathbf{r}}_n = \frac{iV_\mathrm{c}}{(2\pi)^3} \int d\mathbf{k} \;\; \langle u_{n\mathbf{k}} | \partial_{\mathbf{k}} u_{n\mathbf{k}} \rangle$$

$$\langle r^2 \rangle_n = \frac{V_\mathrm{c}}{(2\pi)^3} \int d\mathbf{k} \;\; \langle \partial_{\mathbf{k}} u_{n\mathbf{k}} | \cdot | \partial_{\mathbf{k}} u_{n\mathbf{k}} \rangle$$

“Berry phase theory of electric polarization”

📚 Resta, Ferroelectrics **136**, 51 (1992)
📚 King-Smith and Vanderbilt, Phys. Rev. B **47**, 1651 (1993)

Minimizing the spread in **r**-space ⟷ Smoothening the gauge in **k**-space

Minimizing the spread functional

$$\Omega = \sum_n \left[\langle r^2 \rangle_n - \bar{\mathbf{r}}_n^2 \right]$$

$$\langle r^2 \rangle_n = \frac{V_\mathrm{c}}{(2\pi)^3} \int d\mathbf{k} \ \langle \partial_\mathbf{k} u_{n\mathbf{k}} | \cdot | \partial_\mathbf{k} u_{n\mathbf{k}} \rangle \qquad \bar{\mathbf{r}}_n = \frac{i V_\mathrm{c}}{(2\pi)^3} \int d\mathbf{k} \ \langle u_{n\mathbf{k}} | \partial_\mathbf{k} u_{n\mathbf{k}} \rangle$$

Our goal: To find U that minimizes the spread of the WFs for $|u_{n\mathbf{k}}\rangle \rightarrow \sum_m |u_{m\mathbf{k}}\rangle \, U_{mn}(\mathbf{k})$

Calculate $\dfrac{\delta\Omega}{\delta U(\mathbf{k})}$ and find the steepest “direction”

Update $U(\mathbf{k}) \rightarrow U(\mathbf{k}) + \delta U(\mathbf{k})$

Iterate until $\dfrac{\delta\Omega}{\delta U(\mathbf{k})}$ becomes sufficiently small

Workflow

1. Converge the charge density.
   From the converged potential, obtain the Bloch states.

2. Project initial Wannier states onto Bloch states.

$$|\phi_{n\mathbf{k}}\rangle = \sum_{m=1}^{N} |\psi_{m\mathbf{k}}\rangle\, A_{mn}(\mathbf{k}), \quad A_{mn}(\mathbf{k}) = \langle\psi_{m\mathbf{k}}|g_n\rangle$$

3. Minimize the spread functional in **k**-space.

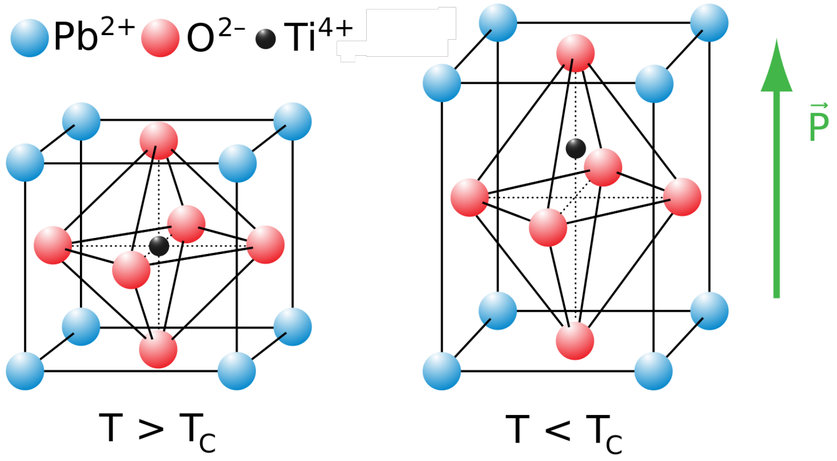
$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}}|u_{n\mathbf{k}+\mathbf{b}}\rangle$$

Prepared from FLEUR
(WF1.amn, WF1.mmn)

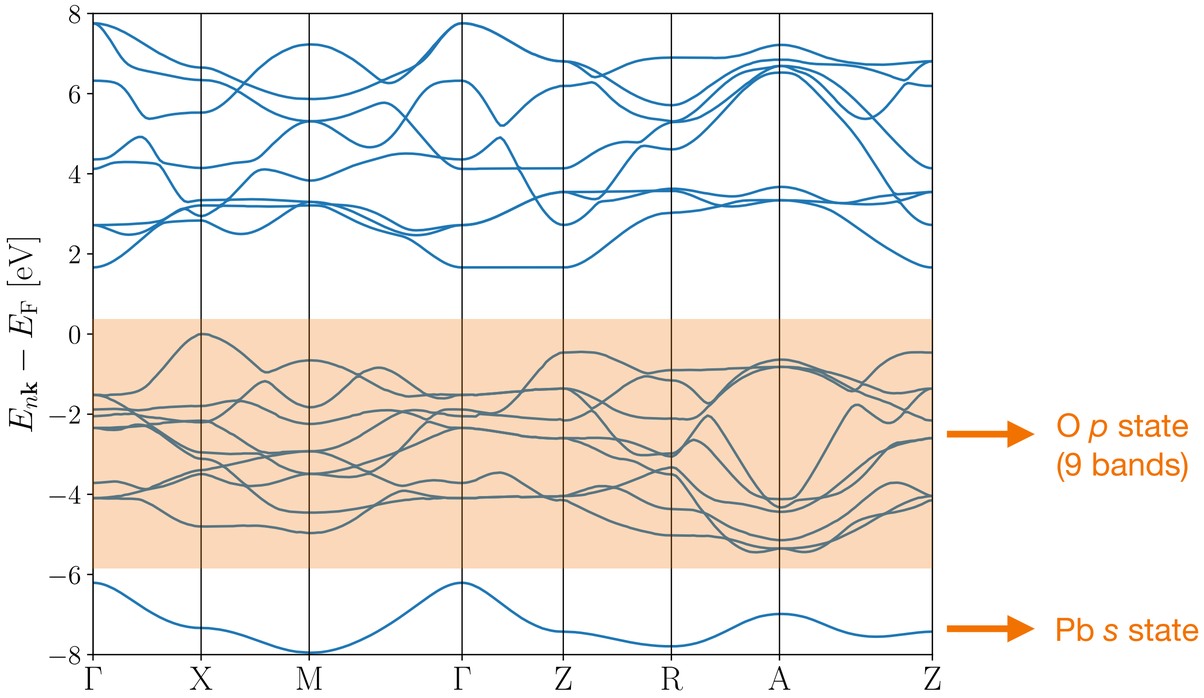
$$\Omega_{\mathrm{D}} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_{\mathbf{b}} \sum_{n} \left[-\mathrm{Im}\, \ln M_{nn}^{(\mathbf{k},\mathbf{b})} - \mathbf{b}\cdot\bar{\mathbf{r}}_n \right]^2, \qquad \Omega_{\mathrm{OD}} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_{\mathbf{b}} \sum_{m\neq n} \left| M_{mn}^{(\mathbf{k},\mathbf{b})} \right|^2$$

Example: Ferroelectric $PbTiO_3$

https://en.wikipedia.org/wiki/Lead_titanate



- Second order phase transition at Tc = 760 K.
- Tetragonal phase has spontaneous ferroelectric polarization.
- Technologically one of the most important ferroelectric/piezoelectric materials.

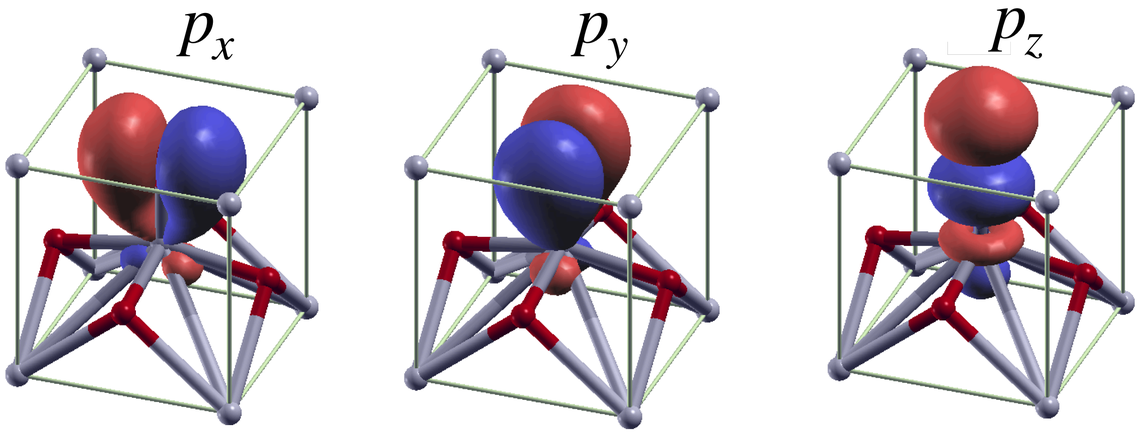


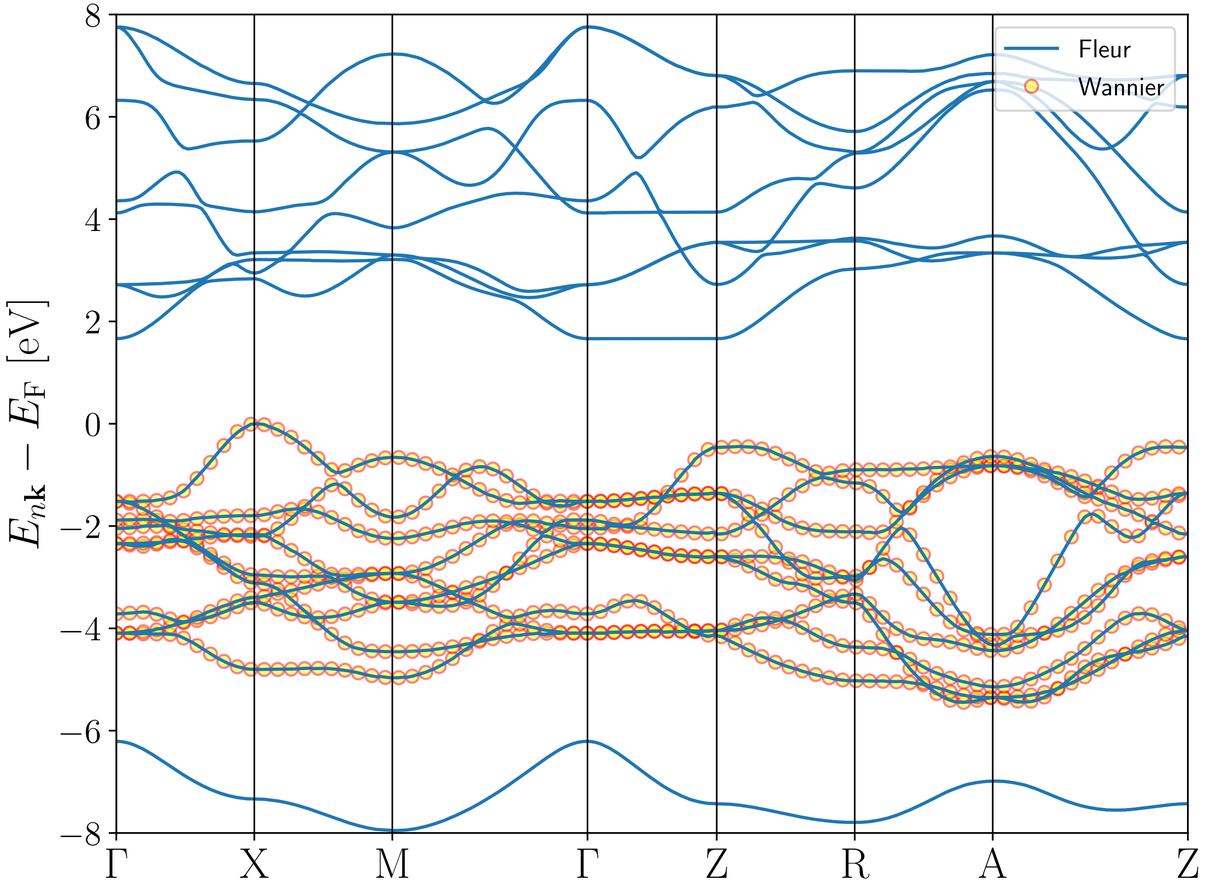
Projection to p_x, p_y, p_z orbitals localized around the O atom
(Total 3 x 3 = 9 WFs)

Example: Ferroelectric $PbTiO_3$

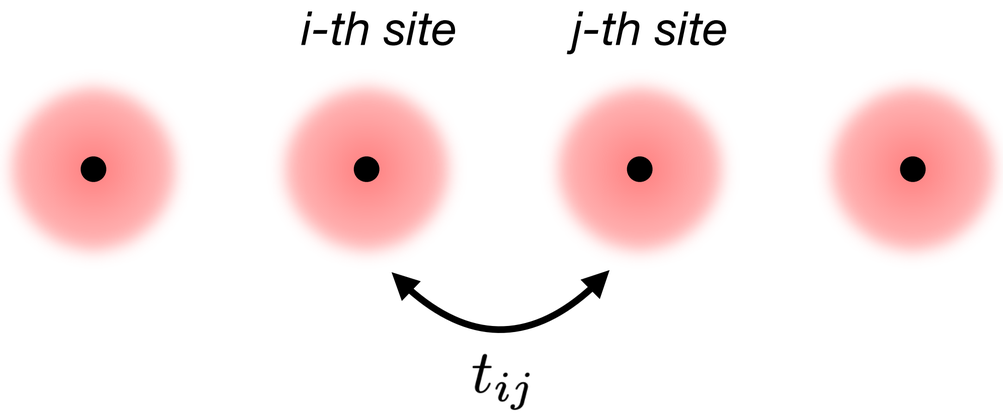
WF1.wout

```
       O_D=      0.1640608 O_OD=      4.0545921 O_TOT=     62.8240153 <-- SPRD
Delta: O_D=  0.6305573E-12 O_OD= -0.7852442E-11 O_TOT= -0.7218886E-11 <-- DLTA
------------------------------------------------------------------------------

Writing checkpoint file WF1.chk... done

Final State
 WF centre and spread    1  (  3.667190,  3.667190,  1.004375 )     4.76208290
 WF centre and spread    2  (  3.667190,  3.667190,  1.012015 )     7.50569513
 WF centre and spread    3  (  3.667190,  3.667190,  1.012163 )     7.50727039
 WF centre and spread    4  (  3.667190, -0.000000, -2.875182 )     7.88913140
 WF centre and spread    5  (  3.667190, -0.000000, -2.651426 )     8.97500908
 WF centre and spread    6  (  3.667190, -0.000000, -3.085762 )     4.66055573
 WF centre and spread    7  (  0.000000,  3.667190, -2.875086 )     7.89365336
 WF centre and spread    8  (  0.000000,  3.667190, -2.651951 )     8.95964148
 WF centre and spread    9  ( -0.000000,  3.667190, -3.085915 )     4.67097587
 Sum of centres and spreads ( 22.003140, 22.003140,-14.196768 )    62.82401535
```





Tight-binding model



$$\mathcal{H}_{\mathrm{TB}} = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{\langle ij \rangle} t_{ij} c_i^\dagger c_j + \cdots$$

on-site energies — hopping parameters

$$\begin{aligned}\mathcal{H} &= \sum_{\mathbf{R}n} \sum_{\mathbf{R}'n'} |\mathbf{R}n\rangle \langle \mathbf{R}n| \mathcal{H} |\mathbf{R}'n'\rangle \langle \mathbf{R}'n'| \\ &= \sum_{\mathbf{R}n} \sum_{\mathbf{R}'n'} |\mathbf{R}n\rangle \mathcal{H}_{nn'}(\mathbf{R}' - \mathbf{R}) \langle \mathbf{R}'n'|\end{aligned}$$

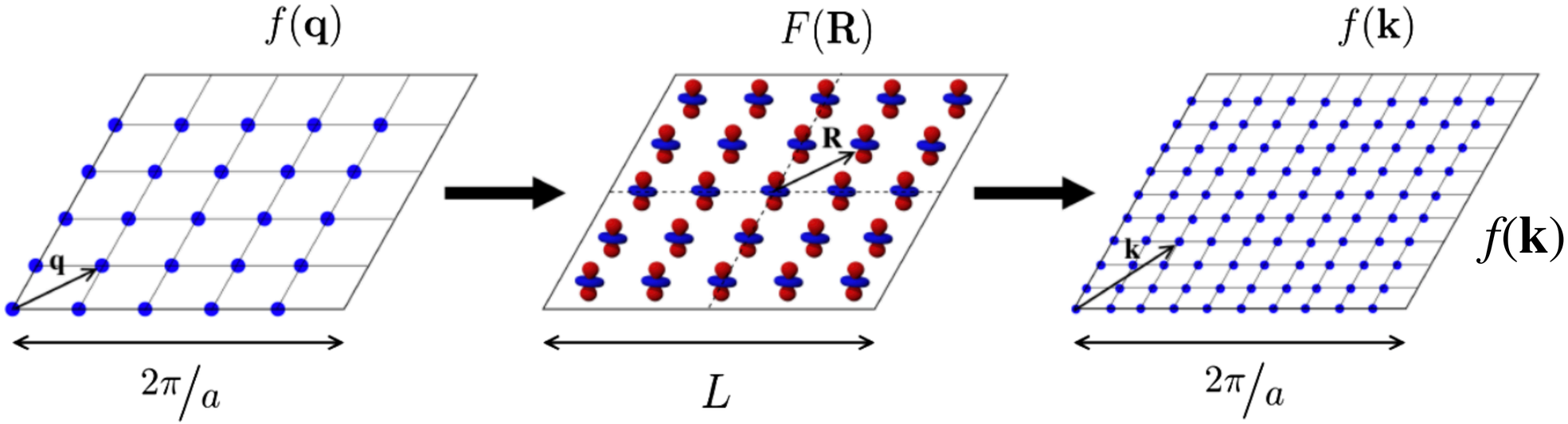
$$\mathcal{H} = \frac{V_\mathrm{c}}{(2\pi)^3} \int d\mathbf{k} \, |\phi_{n\mathbf{k}}\rangle \mathcal{H}_{nn'}(\mathbf{k}) \langle \phi_{n'\mathbf{k}}|$$

FT: $|\mathbf{R}n\rangle = \frac{V_\mathrm{c}}{(2\pi)^3} \int d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} |\phi_{n\mathbf{k}}\rangle$

where $\mathcal{H}_{nn'}(\mathbf{k}) = \sum_{\mathbf{R}} \mathcal{H}_{nn'}(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}}$

Wannier interpolation

📚 Figure taken from Marzari *et al.* Rev. Mod. Phys. **84**, 1419 (2012)



FLEUR

- Coarse **q**-mesh (e.g. 8x8x8).
- Converge the charge density
- Obtain the Bloch states
- Find a representation of an observable $f(\mathbf{q})$ within the Bloch basis
- Ex: Hamiltonian, Pauli matrices, spin torque, orbital angular momentum, orbital character, etc.

WANNIER90

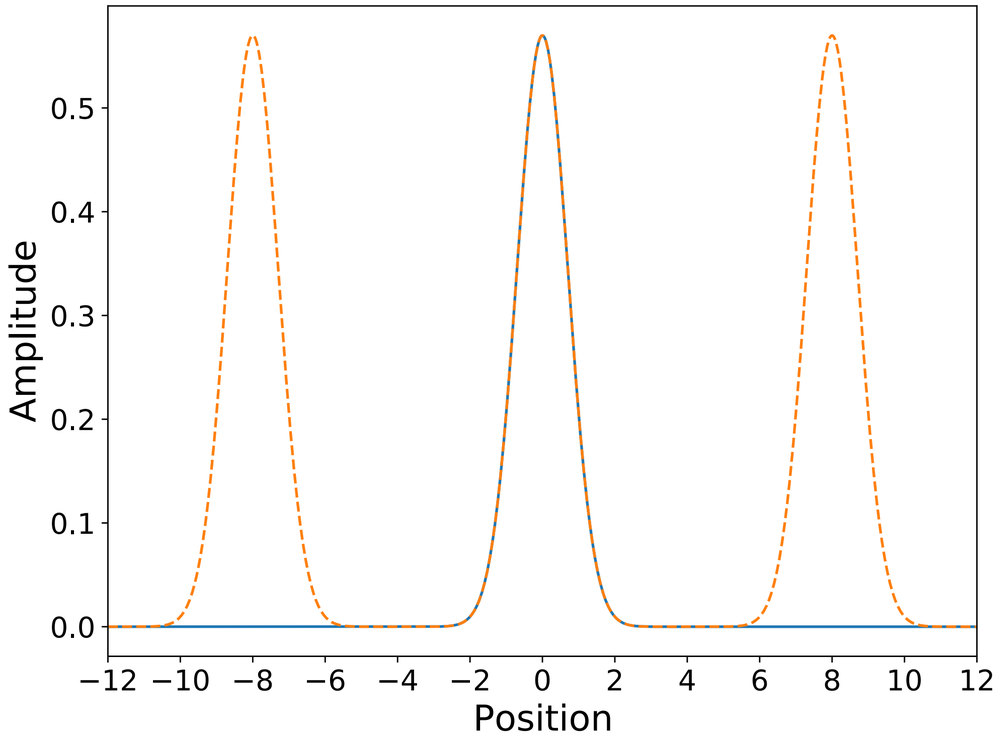
- Obtain maximally-localized WFs.
- Transform $f(\mathbf{q})$ to R-space using $U(\mathbf{q})$ to obtain $F(\mathbf{R})$
- $F(\mathbf{R}) = \frac{V_c}{(2\pi)^3} \int d\mathbf{q} e^{-i\mathbf{q}\cdot\mathbf{R}} \times U^\dagger(\mathbf{q}) f(\mathbf{q}) U(\mathbf{q})$

POSTW90/others

- Calculate the observable efficiently in dense interpolated **k**-mesh. (e.g. 512x512x512)
- $f(\mathbf{k}) = \sum_{\mathbf{R}} F(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}}$

How does it work?

From **q**-space to **R**-space, and back to **k**-space …



- Discrete Fourier transform in 8x8x8 **q**-point mesh implies the periodicity in every 8 unit cells.
- The spread of the WF has to be smaller than 8 unit cell.
- Otherwise, the k-space interpolation is problematic.
- **Remark**:
  fine details in **k**-space = long-range behavior in **R**-space.

Conclusion: The Wannier interpolation works because the WFs are localized.

An example: Berry curvature

PHYSICAL REVIEW B **74**, 195118 (2006)

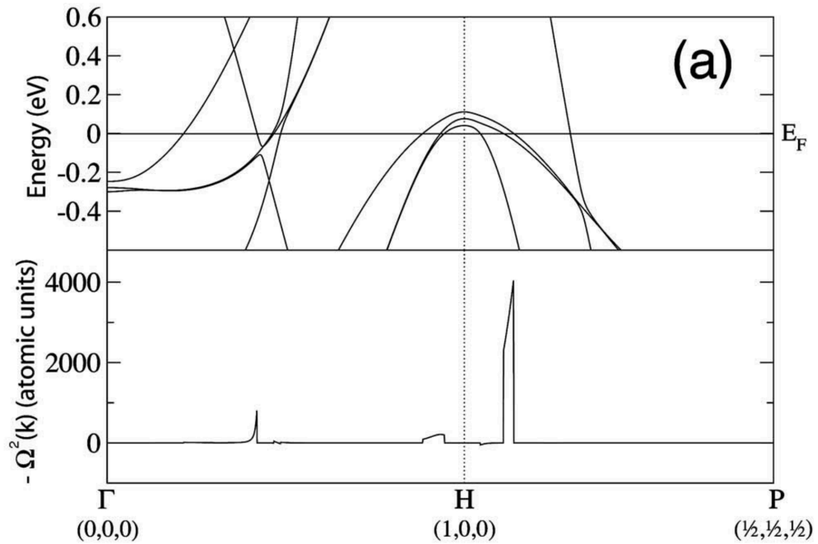
***Ab initio* calculation of the anomalous Hall conductivity by Wannier interpolation**

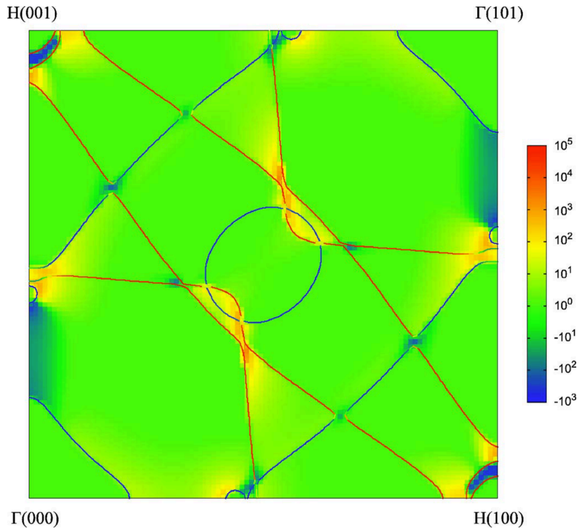
Xinjie Wang,[1] Jonathan R. Yates,[2,3] Ivo Souza,[2,3] and David Vanderbilt[1]

$$\sigma_{xy} = -\frac{e^2}{\hbar}\sum_n \int_{\mathrm{BZ}} \frac{d\mathbf{k}}{(2\pi)^3} f_n(\mathbf{k})\Omega_{n,z}(\mathbf{k}),$$

$$\Omega_{n,\gamma}(\mathbf{k}) = \epsilon_{\alpha\beta\gamma}\Omega_{n,\alpha\beta}(\mathbf{k}),$$

$$\Omega_{n,\alpha\beta}(\mathbf{k}) = -2\,\mathrm{Im}\left\langle \frac{\partial u_{n\mathbf{k}}}{\partial k_\alpha} \middle| \frac{\partial u_{n\mathbf{k}}}{\partial k_\beta} \right\rangle$$

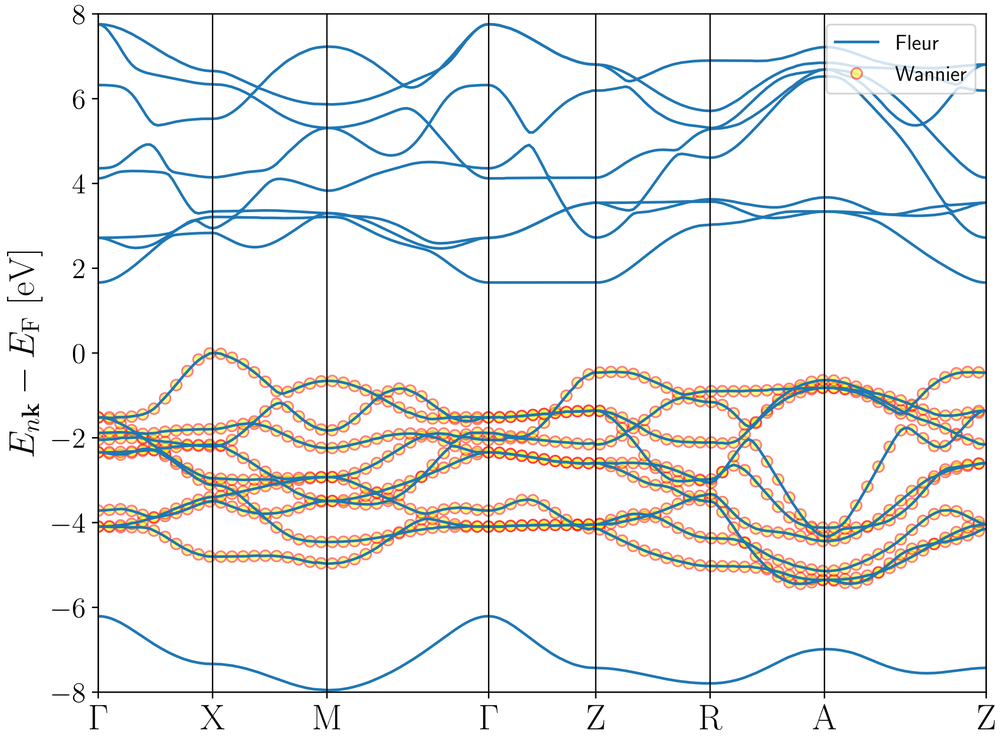




The Berry curvature exhibits spiky behavior in k-space → Requires sampling in a dense k-mesh

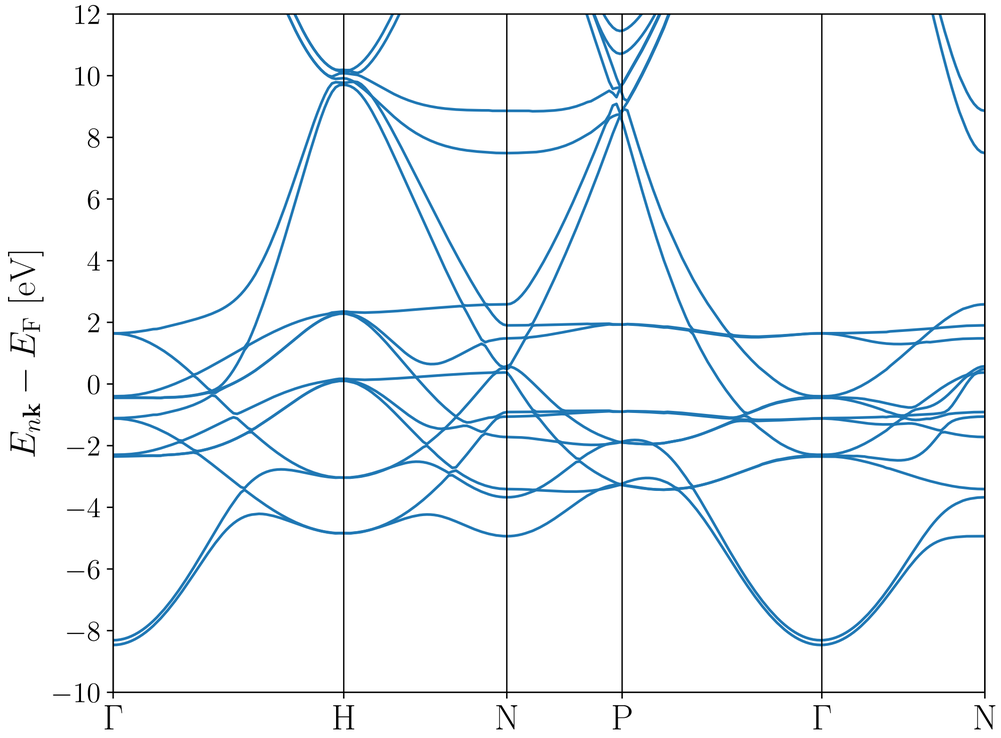
Entangled bands in metals

Insulator (PbTiO3)



A set of composite bands is isolated from the rest of the bands.

Metal (bcc Fe)



It is not possible to separate a set of bands.
→ Entangled bands

Obtaining WFs from entangled bands

📚 Souza, Marzari, and Vanderbilt, Phys. Rev. B **65**, 035109 (2001)

1. Disentanglement (subspace optimization)

- Find a set of Bloch states that are “disentangled” from the rest of the Bloch states.
- We select the smoothest possible subspace starting from $N_{\text{band}} \geq N_{\text{wann}}$ Bloch states.

2. Gauge optimization

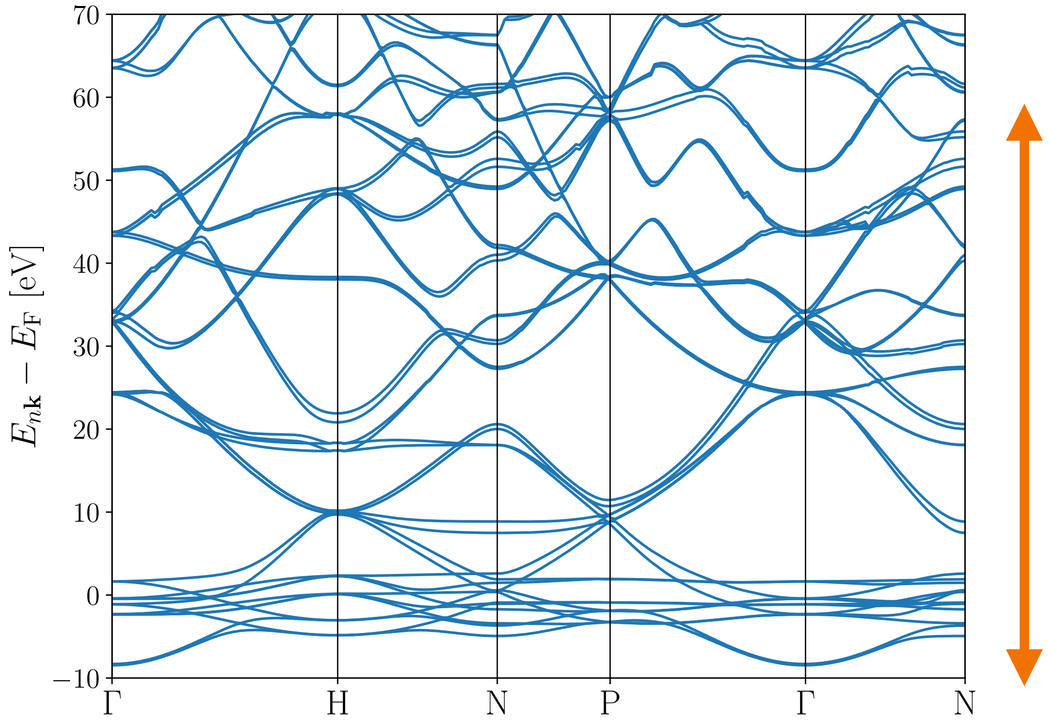
- After the disentanglement step, find a gauge that minimizes the spread.
- This step is the same as for isolated bands.

Disentangling bands

1. Projection

# of Bloch states $N_{\mathrm{band}} \geq N_{\mathrm{wann}}$

$$|\widetilde{\psi}_{n\mathbf{k}}\rangle = \sum_{m}^{N_{\mathrm{band}}} |\psi_{m\mathbf{k}}\rangle\, A_{mn}(\mathbf{k}), \quad A_{mn}(\mathbf{k}) = \langle \psi_{m\mathbf{k}} | g_n \rangle$$



This defines the **outer window**, which should be

- sufficiently wide so that it includes major weights of the Wannier projection.
- not too wide to avoid unwanted character of the Bloch states (and to reduce the computation cost)
- N_{band} may depend on $\mathbf{k}$.

Disentangling bands

2. Find an “optimal” subspace that minimizes the spread

$$\Omega = \Omega_{\mathrm{I}} + \Omega_{\mathrm{D}} + \Omega_{\mathrm{OD}}$$

$$\Omega_{\mathrm{D}} = \sum_{n} \sum_{\mathbf{R}\neq\mathbf{0}} \left|\langle \mathbf{R}n| \, \mathbf{r} \, |\mathbf{0}n\rangle\right|^2, \quad \Omega_{\mathrm{OD}} = \sum_{n\neq m} \sum_{\mathbf{R}} \left|\langle \mathbf{R}m| \, \mathbf{r} \, |\mathbf{0}n\rangle\right|^2 \longrightarrow \text{Gauge-dependent}$$

$$\Omega_{\mathrm{I}} = \sum_{n} \left[\langle \mathbf{0}n| \, r^2 \, |\mathbf{0}n\rangle - \sum_{\mathbf{R}m} \left|\langle \mathbf{R}m| \, \mathbf{r} \, |\mathbf{0}n\rangle\right|^2 \right] \longrightarrow \text{Gauge-independent}$$

$$\Omega_{\mathrm{I}} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_{\mathbf{b}} \mathrm{Tr}\left[P_{\mathbf{k}} Q_{\mathbf{k}+\mathbf{b}}\right] \quad \text{where} \quad P_{\mathbf{k}} = \sum_{n}^{N_{\mathrm{wann}}} \left|\widetilde{u}_{n\mathbf{k}}\right\rangle \left\langle \widetilde{u}_{n\mathbf{k}}\right|, \quad Q_{\mathbf{k}} = 1 - P_{\mathbf{k}}$$

Physical meaning of Ω_{I}

📚 Souza, Marzari, and Vanderbilt, Phys. Rev. B **65**, 035109 (2001)

$$\Omega_{\mathrm{I}} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_{\mathbf{b}} \mathrm{Tr}\left[P_{\mathbf{k}} Q_{\mathbf{k}+\mathbf{b}}\right]$$

$$\text{where} \quad P_{\mathbf{k}} = \sum_{n}^{N_{\mathrm{wann}}} \left|\widetilde{u}_{n\mathbf{k}}\right\rangle \left\langle\widetilde{u}_{n\mathbf{k}}\right|, \quad Q_{\mathbf{k}} = 1 - P_{\mathbf{k}}$$

- Ω_{I} measures the average of the mismatch of the subspaces at $\mathbf{k}$ and $\mathbf{k}+\mathbf{b}$.
- Minimizing Ω_{I} corresponds to finding an “optimally-connected” subspace in $\mathbf{k}$-space.
- This is done by iteratively solving an eigenvalue problem

$$\left[\sum_{\mathbf{b}} w_{\mathbf{b}} P^{(i-1)}_{\mathbf{k}+\mathbf{b}}\right] \left|\widetilde{u}^{(i)}_{n\mathbf{k}}\right\rangle = \lambda^{(i)}_{n\mathbf{k}} \left|\widetilde{u}^{(i)}_{n\mathbf{k}}\right\rangle$$ and picking N_{wann} leading eigenvectors.

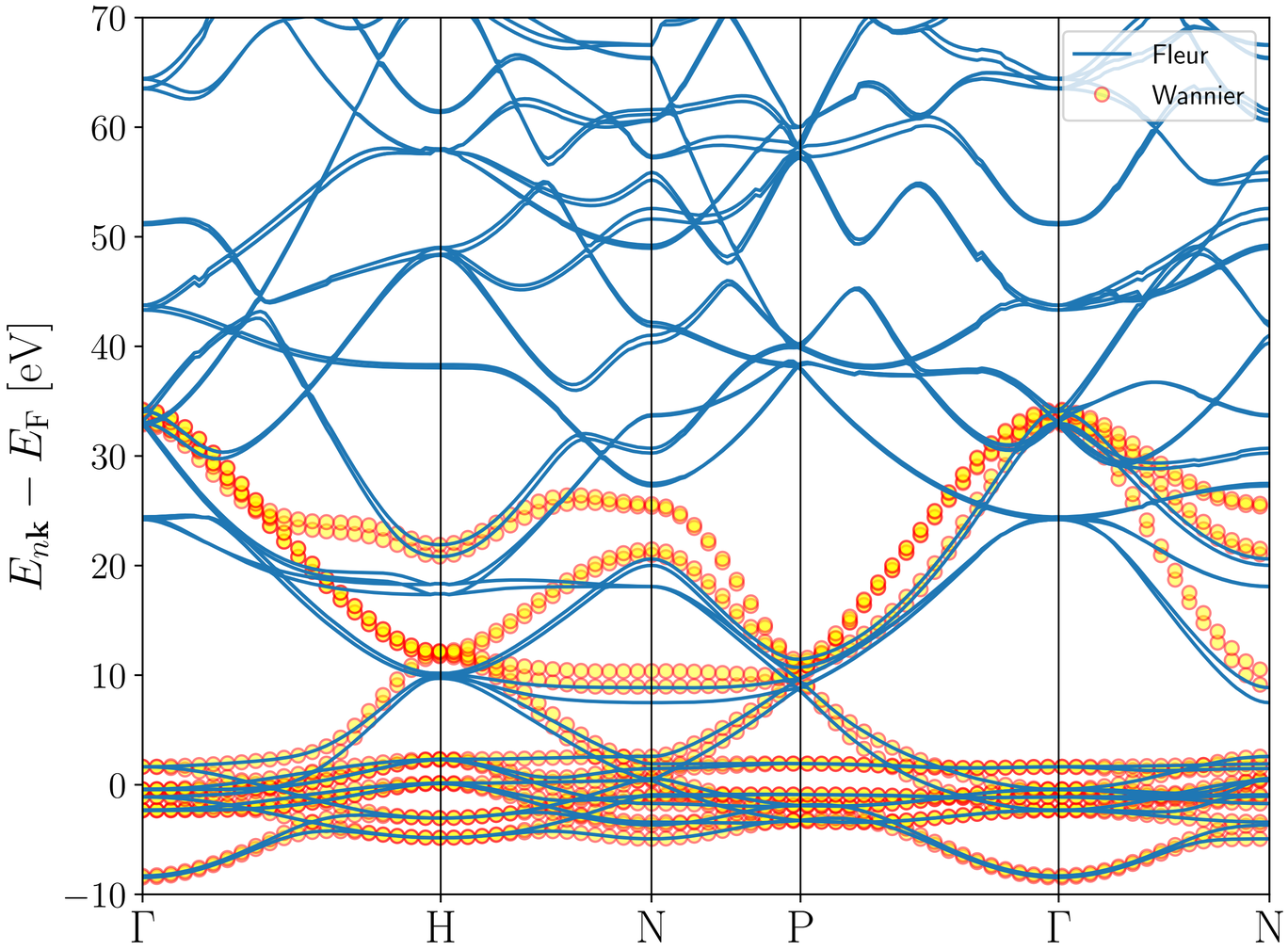
Frozen window (inner window)

- **How to construct WFs that describe the original bands “exactly” in a limited energy window?**
- **How to achieve this goal while keep WFs as localized as possible?**

📚 Sec. IIIG, Souza, Marzari, and Vanderbilt, Phys. Rev. B **65**, 035109 (2001)

- We can enforce certain Bloch states to be included in the subspace
  → **frozen window (inner window)**
- Since N_{froz} states are already included in the subspace, we choose the rest $N_{\mathrm{wann}} - N_{\mathrm{froz}}$ states out of $N_{\mathrm{band}} - N_{\mathrm{froz}}$ states.

Example: bcc Fe

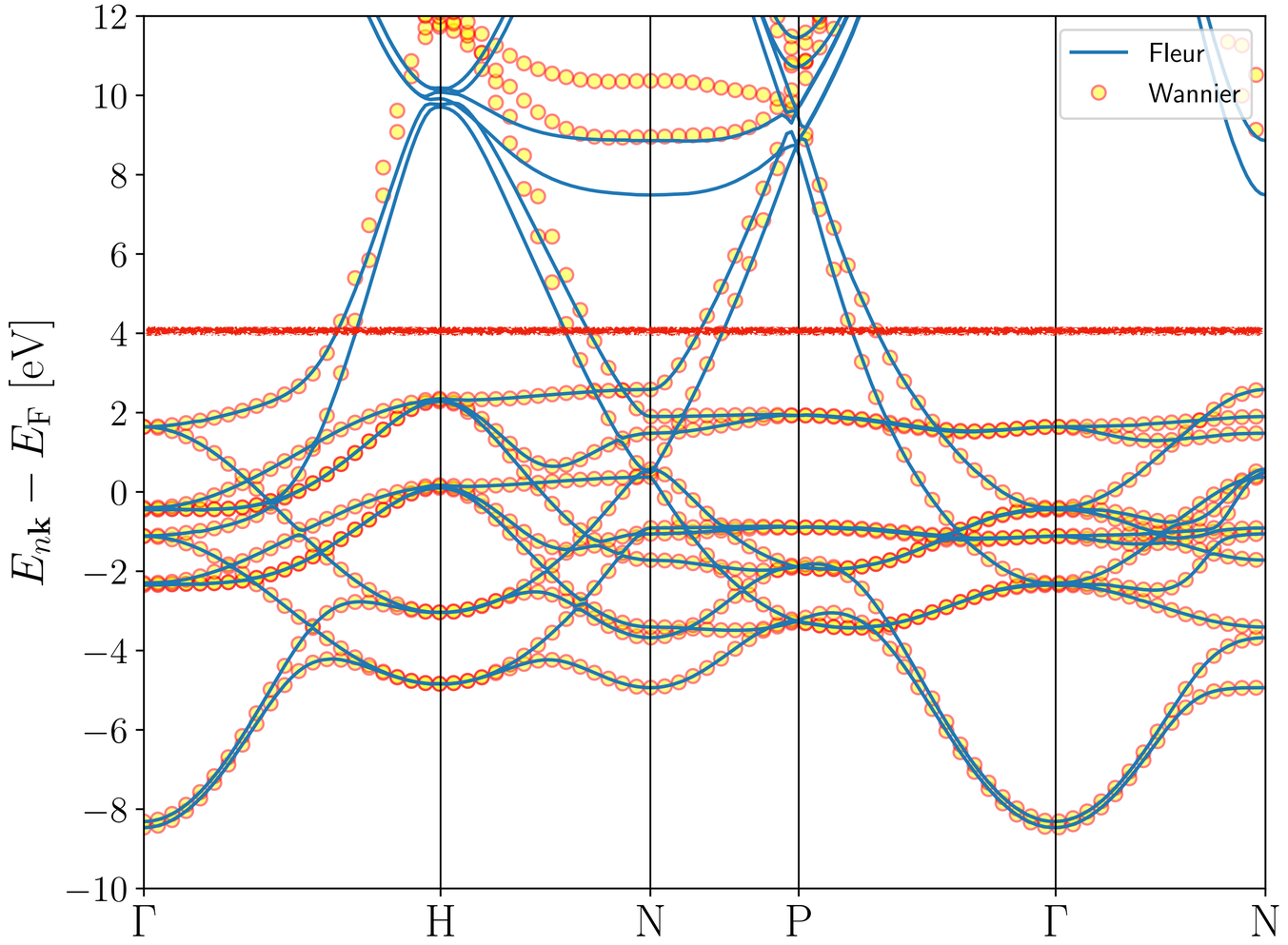


- $N_{\mathrm{band}} = 36$
- $N_{\mathrm{wann}} = 18$ (proj. to *s*, *p*, *d* trial orbitals)
- Max. froz. Win = + 4 eV

Outer window

Inner (frozen) window

Example: bcc Fe

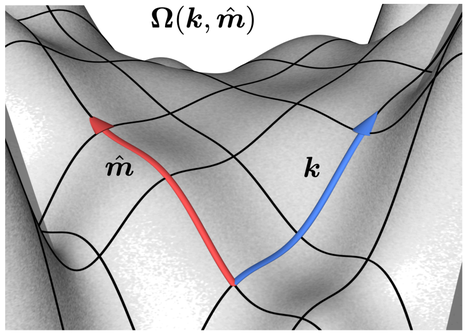


- $N_{\mathrm{band}} = 36$
- $N_{\mathrm{wann}} = 18$ (proj. to *s*, *p*, *d* trial orbitals)
- Max. froz. Win = + 4 eV

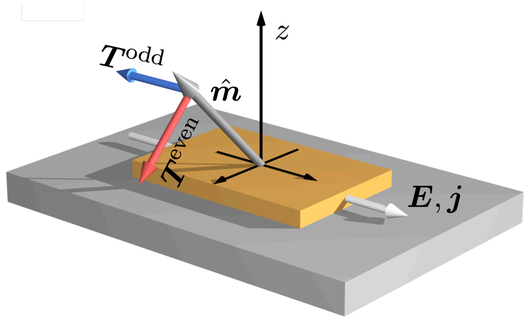
Inner (frozen) window

What you can do from FLEUR-WANNIER90

Berry phase effect

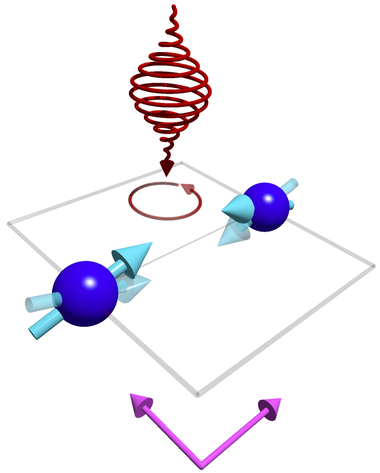


Spintronics & Orbitronics



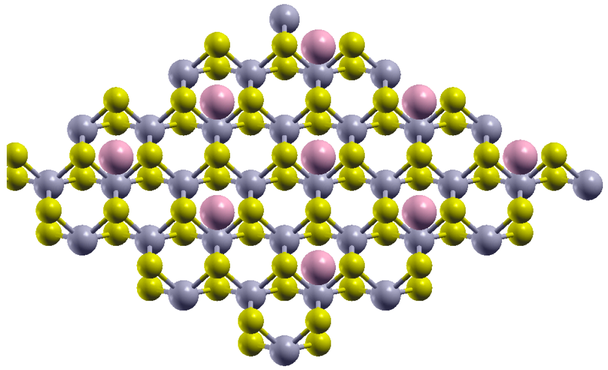
Dongwook Go, Tom Saunderson,
Frank Freimuth

Photo-induced spin/orbital response



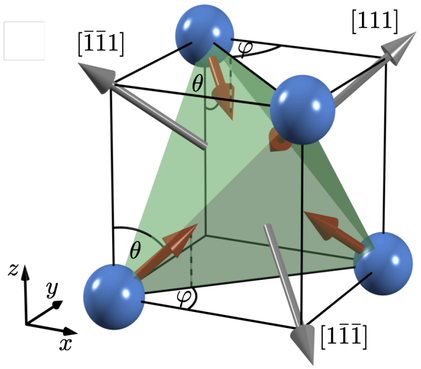
Maximilian Merte, Frank Freimuth,
Theodoros Adamantopoulos

2D materials



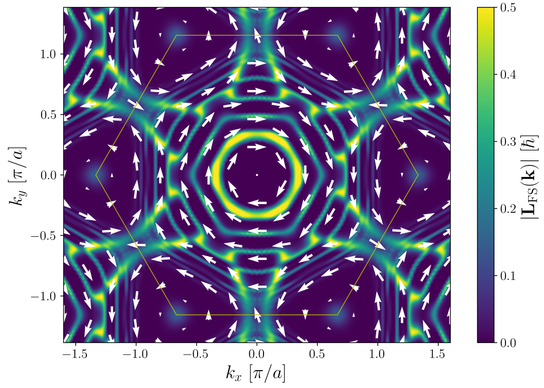
Tom Saunderson
Mahmoud Alzeer
Johanna Carbone

Topological orbital magnetism



Jan-Philipp Hanke

Orbital Rashba effect



Dongwook Go

Now it's your turn!

Thank You!

References

- Marzari and Vanderbilt, Phys. Rev. B **56**, 12847 (1997)
- Souza, Marzari, and Vanderbilt, Phys. Rev. B **65**, 035109 (2001)
- Marzari *et al.* Rev. Mod. Phys. **84**, 1419 (2012)
- Pizzi *et al*. J. Phys.: Condens. Matter **32** 165902 (2020)