Picking flowers: Hands-on FLEUR
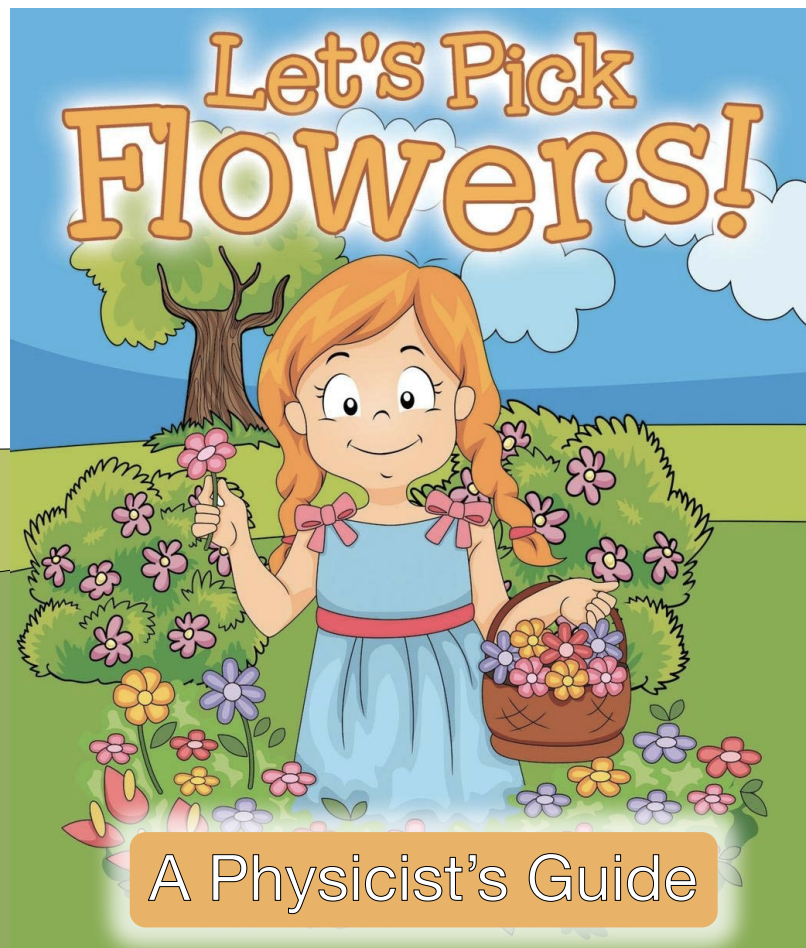
Wannier functions
Theory and Applications

Jan-Philipp Hanke

10.09.2019

DRIVING THE EXASCALE TRANSITION

Peter Grünberg Institut and
Institute for Advanced Simulation
Forschungszentrum Jülich and JARA

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Bouquet of Flowers

Let's Pick Flowers!

A Physicist's Guide

Bloch Orbitals

Gauge Freedom
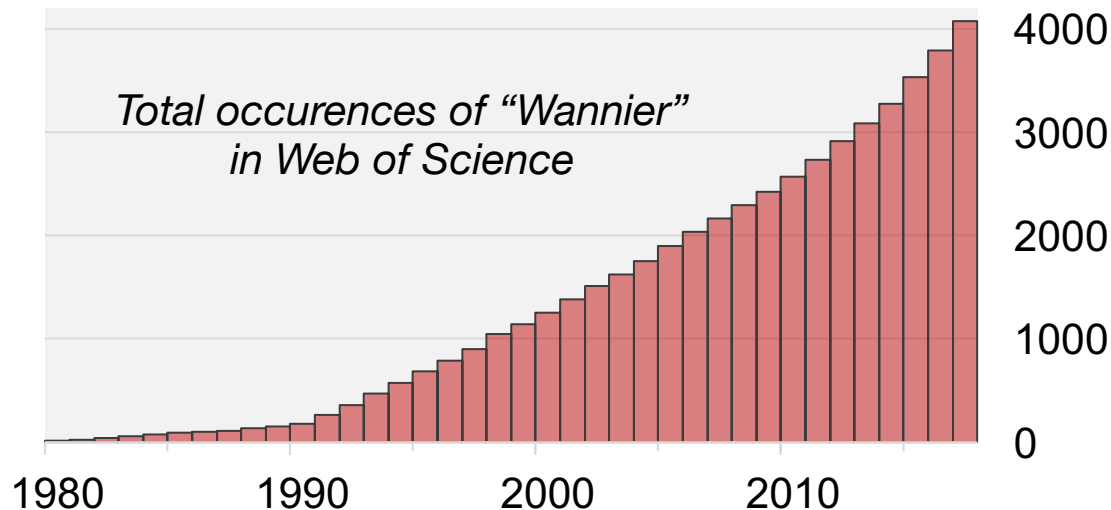
Localization

Wannier Functions

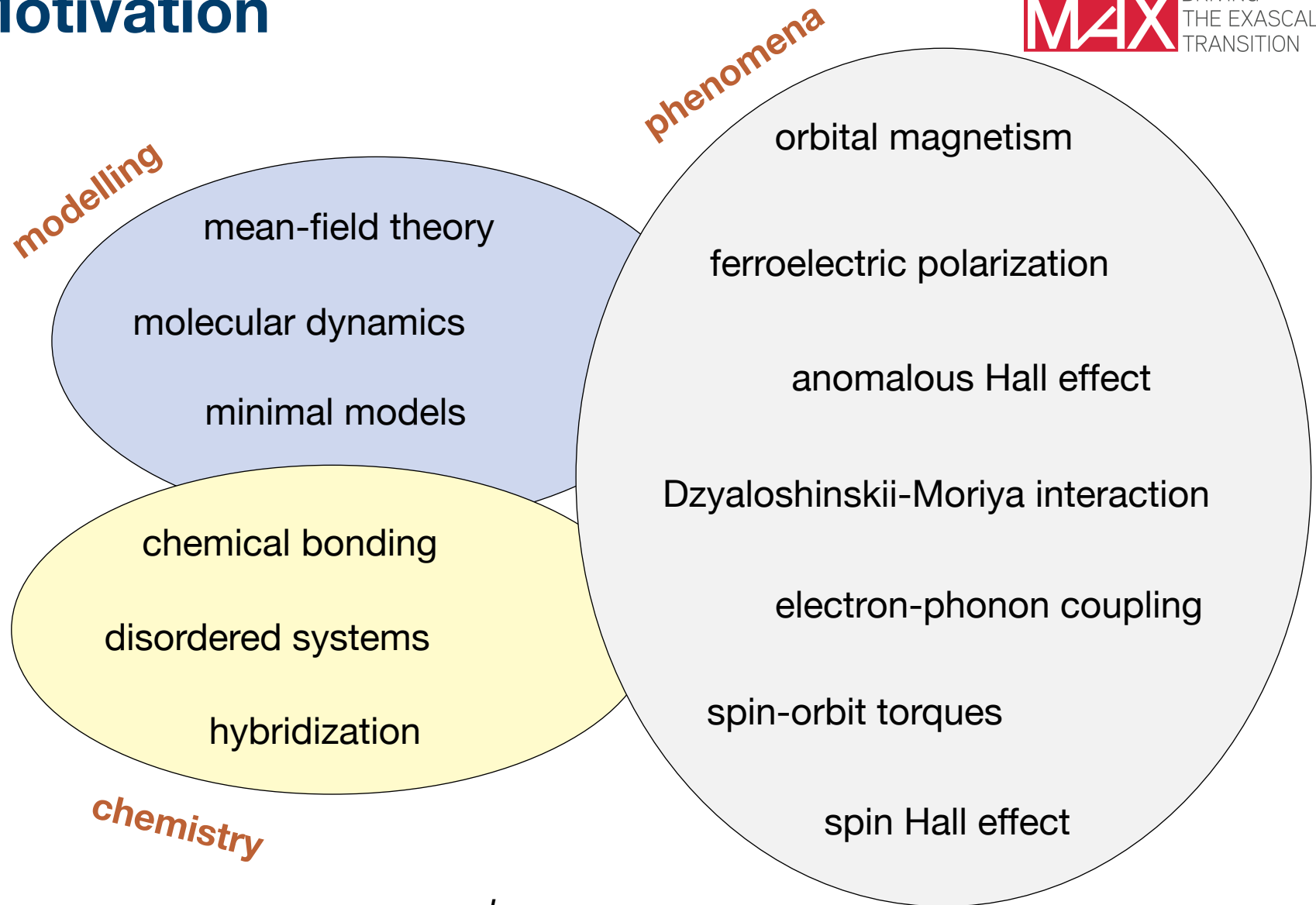Wannier90 Code

Interpolation

FLEUR Interface

Workflows

Motivation

➢ The formalism of Wannier functions constitutes a *very efficient* and *widely applied* electronic-structure method in order to study the bulk properties of crystalline materials.

➢ Combining the automatic construction of these objects with public density functional theory (DFT) programs made systematic studies of *otherwise hardly accessible* solid-state effects in complex materials possible for a large community of researchers.

Total occurences of "Wannier" in Web of Science

Motivation

phenomena

modelling

mean-field theory

molecular dynamics

minimal models

orbital magnetism

ferroelectric polarization

anomalous Hall effect

Dzyaloshinskii-Moriya interaction

electron-phonon coupling

spin-orbit torques

spin Hall effect

chemical bonding

disordered systems

hybridization

chemistry

… and many more

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Bloch Functions 101

➤ We are interested in the bulk properties of crystalline materials within the approximation of **non-interacting electrons**. Thus, the electronic Hamiltonian assumes the form

$$\mathcal{H} = \sum_{i=1}^{N_e} \left[\frac{\boldsymbol{p}_i^2}{2m_e} + U(\boldsymbol{r}_i) \right] \quad \text{with} \quad U(\boldsymbol{r}_i + \boldsymbol{R}_n) = U(\boldsymbol{r}_i)$$

➤ This is a sum of single-particle Hamiltonians. The solutions for each can be obtained by solving the single-particle Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + U(\boldsymbol{r}) \right] \psi_i(\boldsymbol{r}) = \epsilon_i \psi_i(\boldsymbol{r})$$

➤ If we can solve this equation (e.g., via DFT), we know everything about the system; but it is often a highly non-trivial problem that is hard to solve even on modern supercomputers.

Bloch Functions 101

➢ Exploiting the translational invariance of the considered solid, we use periodic boundary conditions to solve the differential equation. This leads to the fundamental **Bloch theorem**:

$$\psi_{\boldsymbol{k}n}(\boldsymbol{r} + \boldsymbol{R}_m) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}_m}\psi_{\boldsymbol{k}n}(\boldsymbol{r})$$

➢ Here, the crystal momentum **k** can take only discrete values in the first Brillouin zone. An equivalent formulation of the Bloch theorem is:

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

➢ Each of the so-called lattice period states $u_{\boldsymbol{k}n}$ obeys the following modified Schrödinger equation:

$$\left[\frac{(\boldsymbol{p} + \hbar\boldsymbol{k})^2}{2m_e} + U(\boldsymbol{r})\right]u_{\boldsymbol{k}n}(\boldsymbol{r}) = \epsilon_{\boldsymbol{k}n}u_{\boldsymbol{k}n}(\boldsymbol{r})$$

Bloch Functions 101

➤ The lattice-periodic parts $u_{\mathbf{k}n}$ are periodic in real space with respect to the unit cell of the crystal. Therefore, we can set up the Fourier series

$$u_{\boldsymbol{k}n}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}} c_{\boldsymbol{k}+\boldsymbol{G}n}$$

where **G** is a reciprocal lattice vector (i.e., **k** and **k+G** are equivalent):

$$\Rightarrow u_{\boldsymbol{k}+\boldsymbol{G}'n}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}} c_{\boldsymbol{k}+\boldsymbol{G}'+\boldsymbol{G}n}$$

$$= e^{-i\boldsymbol{G}'\cdot\boldsymbol{r}} \sum_{\boldsymbol{g}} e^{i\boldsymbol{g}\cdot\boldsymbol{r}} c_{\boldsymbol{k}+\boldsymbol{g}n}$$

$$= e^{-i\boldsymbol{G}'\cdot\boldsymbol{r}} u_{\boldsymbol{k}n}(\boldsymbol{r})$$

➤ We can exploit this relation to prove the periodicity of the Bloch states in momentum space:

$$\Psi_{\boldsymbol{k}+\boldsymbol{G}'n}(\boldsymbol{r}) = e^{i\boldsymbol{G}'\cdot\boldsymbol{r}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}+\boldsymbol{G}'n}(\boldsymbol{r})$$

$$= e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}n}(\boldsymbol{r})$$

$$= \Psi_{\boldsymbol{k}n}(\boldsymbol{r})$$

Bloch Functions 101

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$$\psi_{\boldsymbol{k}n}(\boldsymbol{r})$$

$$\boldsymbol{k} = 0$$

$$\boldsymbol{k} = \boldsymbol{k}_1$$

$$\boldsymbol{k} = \boldsymbol{k}_2$$

unit cell
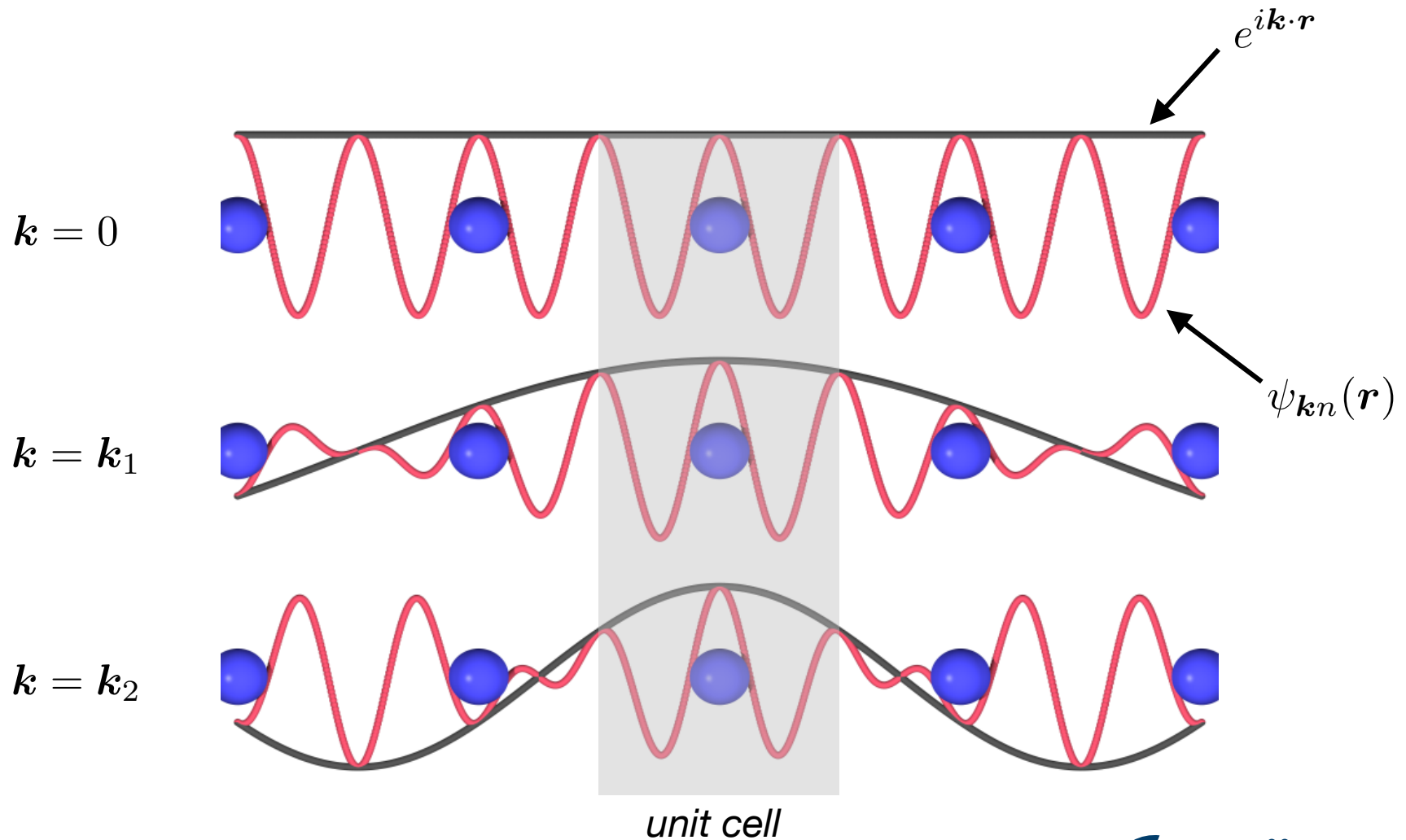
Introduction to Wannier Functions

➢ While Bloch functions are the eigenstates of the Hamiltonian for a given band and a given crystal momentum, they are **oscillating** and **delocalized** in real space.

➢ Often, orbitals that are **localized** in real space offer more microscopic insights into the underlying chemical and physical processes.

$$e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$$\delta(\boldsymbol{r} - \boldsymbol{R}_0)$$

(9)

Introduction to WFs
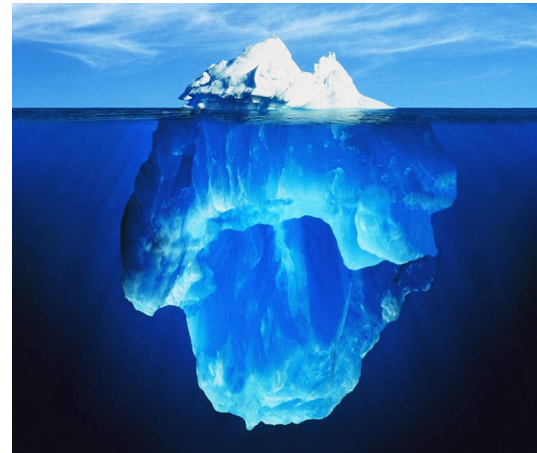
- As the Bloch states are periodic in momentum space, we may express them in terms of a **Fourier series**:

$$\psi_{\boldsymbol{k}n}(\boldsymbol{r}) = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} W_{\boldsymbol{R}n}(\boldsymbol{r})$$

- The inverse of this series leads to so-called **Wannier functions** (WFs) that are Fourier transformations of the original Bloch states:

$$W_{\boldsymbol{R}n}(\boldsymbol{r}) = \frac{1}{N} \sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \psi_{\boldsymbol{k}n}(\boldsymbol{r})$$

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

- We will show later that these objects can become strongly localized in real space – in contrast to the Bloch functions. Thus, they provide a complementary perspective for many effects in solids.

- The WFs are not eigenstates of the single-particle Hamiltonian, but they are still very useful…

Introduction to WFs

➢ Similarly to the well-known Bloch functions, the set of the WFs forms an orthogonal and complete basis.

Bloch states:

$$\int_{\text{supercell}} \psi^*_{\boldsymbol{k}n}(\boldsymbol{r})\psi_{\boldsymbol{k}'n'}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{nn'} \qquad \sum_{\boldsymbol{k}n}\psi^*_{\boldsymbol{k}n}(\boldsymbol{r})\psi_{\boldsymbol{k}n}(\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}')$$

Wannier functions:

$$\int_{\text{supercell}} W^*_{\boldsymbol{R}n}(\boldsymbol{r})W_{\boldsymbol{R}'n'}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = \delta_{\boldsymbol{R}\boldsymbol{R}'}\delta_{nn'} \qquad \sum_{\boldsymbol{R}n}W^*_{\boldsymbol{R}n}(\boldsymbol{r})W_{\boldsymbol{R}n}(\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}')$$

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Introduction to WFs

➢ We may associate to a given Wannier orbital a **center** in real space:

$$\langle W_{\mathbf{0}n} | \boldsymbol{r} | W_{\mathbf{0}n} \rangle = \int_{\text{supercell}} W_{\mathbf{0}n}^*(\boldsymbol{r}) \, \boldsymbol{r} \, W_{\mathbf{0}n}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}$$

⟶ *cf. electric polarization*

➢ What is the role of the **real-space vector R** for the WFs?

$$W_{\boldsymbol{R}n}(\boldsymbol{r}) = \frac{1}{N} \sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \psi_{\boldsymbol{k}n}(\boldsymbol{r})$$

$$= \frac{1}{N} \sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{\boldsymbol{k}n}(\boldsymbol{r})$$

$$= \frac{1}{N} \sum_{\boldsymbol{k}} \psi_{\boldsymbol{k}n}(\boldsymbol{r} - \boldsymbol{R})$$

$$= W_{\mathbf{0}n}(\boldsymbol{r} - \boldsymbol{R})$$

Introduction to WFs

Property of Fourier transform
smooth f(k) → localized f(r)

$R = 0$

$R = R_1$

$W_{Rn}(r)$

$R = R_2$

0 R_1 R_2
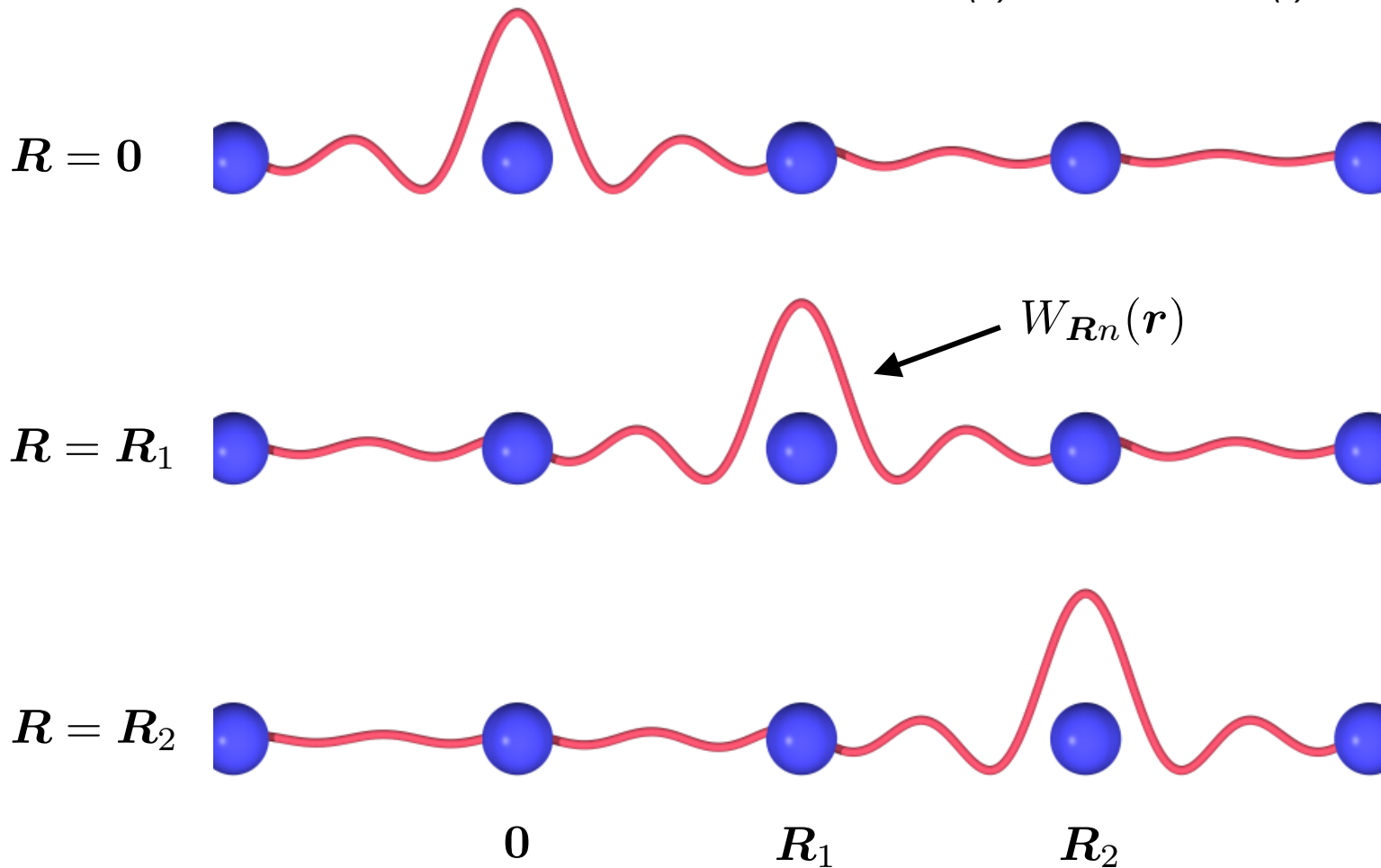
Example in 1D

➢ Consider as an example a Wannier orbital that can be obtained from the Bloch states in a periodic one-dimensional potential. What happens if we introduce a different **phase** in front of the Bloch states (leads to the same observable electron density)?

gauge A

from: Freimuth, PhD thesis, FZJ
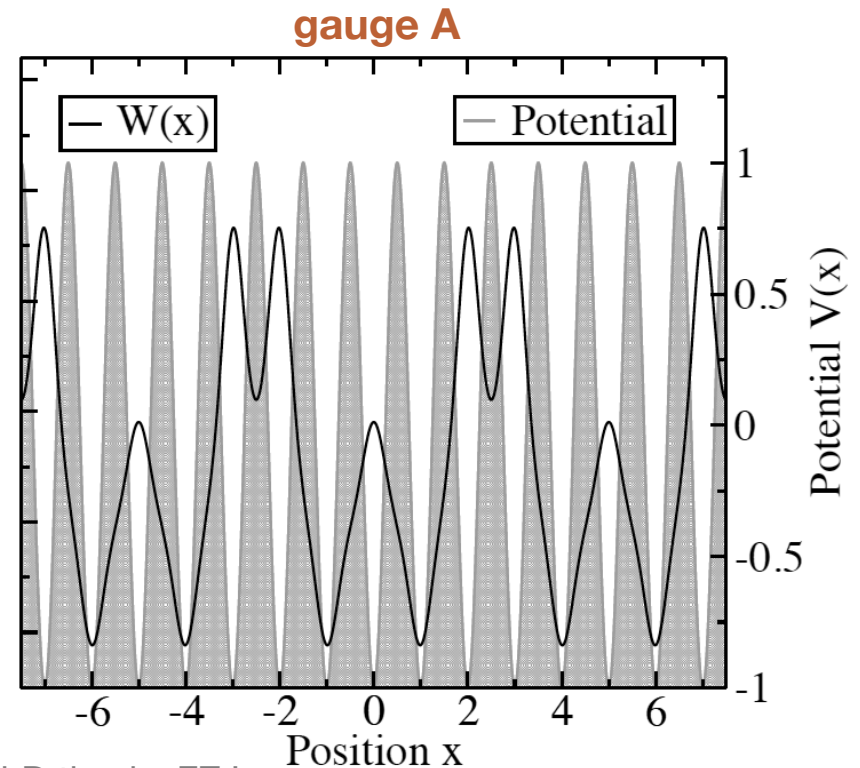
Localization of WFs

➢ As we saw in the previous simple example, choosing a different phase for the Bloch states (i.e., exploiting their **gauge freedom**) will lead to new Wannier orbitals that may exhibit very different shapes in real space. Engineering the degree of localization of WFs is a highly non-trivial question, and a lot of research has been devoted to its answer.

➢ Is it possible to choose a **unique gauge** such that the set of WFs becomes as **localized** as possible in real space?

isolated band

$$\psi_{\boldsymbol{k}n} \longrightarrow e^{i\varphi(\boldsymbol{k})}\psi_{\boldsymbol{k}n}$$

$\epsilon_{\boldsymbol{k}n}$

composite bands

$$\psi_{\boldsymbol{k}n} \longrightarrow \sum_m U^{(\boldsymbol{k})}_{mn}\psi_{\boldsymbol{k}m}$$

$\epsilon_{\boldsymbol{k}n}$
$\epsilon_{\boldsymbol{k}m}$

Maximal Localization of WFs
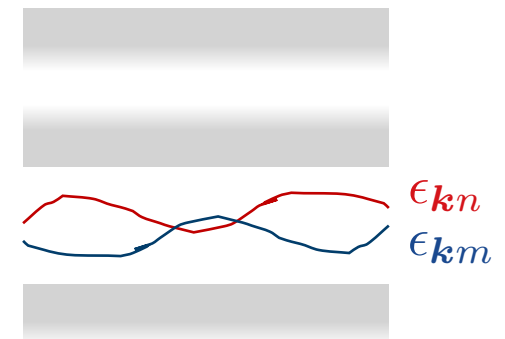
Maximally localized generalized Wannier functions for composite energy bands

Nicola Marzari and David Vanderbilt

Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849

(Received 10 July 1997)

We discuss a method for determining the optimally localized set of generalized Wannier functions associated with a set of Bloch bands in a crystalline solid. By ''generalized Wannier functions'' we mean a set of localized orthonormal orbitals spanning the same space as the specified set of Bloch bands. Although we minimize a functional that represents the total spread $\Sigma_n \langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2$ of the Wannier functions in real space, our method proceeds directly from the Bloch functions as represented on a mesh of k points, and carries out the minimization in a space of unitary matrices $U_{mn}^{(\mathbf{k})}$ describing the rotation among the Bloch bands at each k point. The method is thus suitable for use in connection with conventional electronic-structure codes. The procedure also returns the total electric polarization as well as the location of each Wannier center. Sample results for Si, GaAs, molecular C_2H_4, and LiCl will be presented. [S0163-1829(97)02944-5]

Maximal Localization of WFs

➢ A starting point for the **procedure of maximal localization** are the definitions of the center and the second moment of the WF at the origin with **R**=**0**:
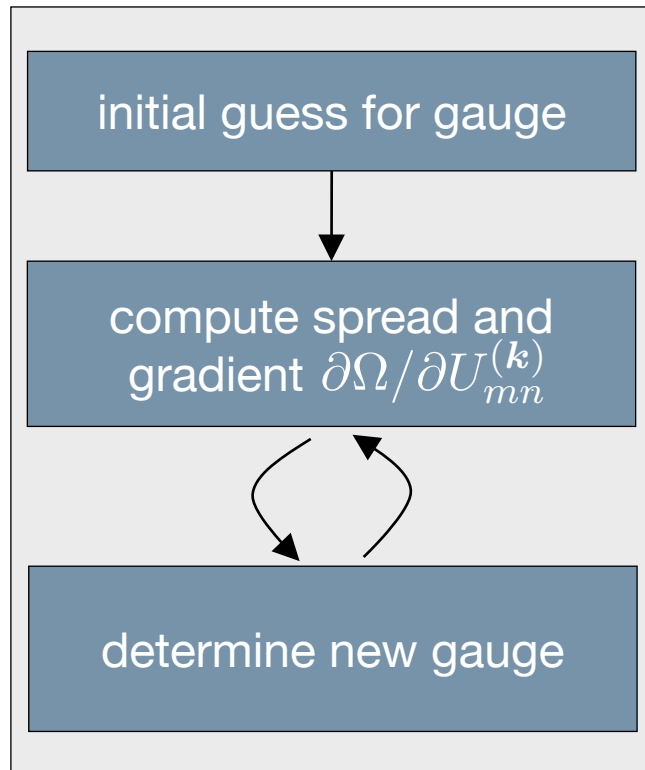
$$\bar{\boldsymbol{r}}_n = \langle W_{\mathbf{0}n}|\boldsymbol{r}|W_{\mathbf{0}n}\rangle \qquad \langle r^2\rangle_n = \langle W_{\mathbf{0}n}|r^2|W_{\mathbf{0}n}\rangle$$

where both quantities can be evaluated from the Bloch orbitals and a fixed choice of the gauge. The real-space spread of all the Wannier orbitals is given by

$$\Omega[U^{(\boldsymbol{k})}] = \sum_n \left(\langle r^2\rangle_n - \bar{\boldsymbol{r}}_n^2\right)$$

This quantity is a functional of the gauge matrices U$^{(\mathbf{k})}$, which allows us to **minimize the spread** by variation of these unitary matrices. To systematically perform this minimization, for example, a steepest-descent algorithm can be used if dΩ/dU$^{(\mathbf{k})}$ is known.

Maximal Localization of WFs

➤ Based on a DFT calculation of the Kohn-Sham orbitals, this automatic procedure can be carried out in a post-processing step in order to obtain **maximally localized WFs (MLWFs)**.

```
┌─────────────────────────────────┐
│   ┌─────────────────────────┐   │
│   │  initial guess for gauge │   │
│   └─────────────────────────┘   │
│               │                 │
│               ▼                 │
│   ┌─────────────────────────┐   │
│   │   compute spread and     │   │
│   │  gradient ∂Ω/∂U^(k)_mn   │   │
│   └─────────────────────────┘   │
│             ↻↺                  │
│   ┌─────────────────────────┐   │
│   │   determine new gauge    │   │
│   └─────────────────────────┘   │
└─────────────────────────────────┘
```

Compute spread and gradient $\partial\Omega / \partial U_{mn}^{(\boldsymbol{k})}$

➤ Many modern DFT codes feature interfaces to the publicly available program package "wannier90".

An updated version of `wannier90`: A tool for obtaining maximally-localised Wannier functions

Arash A. Mostofi [a,*], Jonathan R. Yates [b], Giovanni Pizzi [f], Young-Su Lee [c], Ivo Souza [d], David Vanderbilt [e], Nicola Marzari [f]

➤ Although the procedure itself is automatized, it requires a lot of user experience to generate a physical set of MLWFs.

… and in Practice?
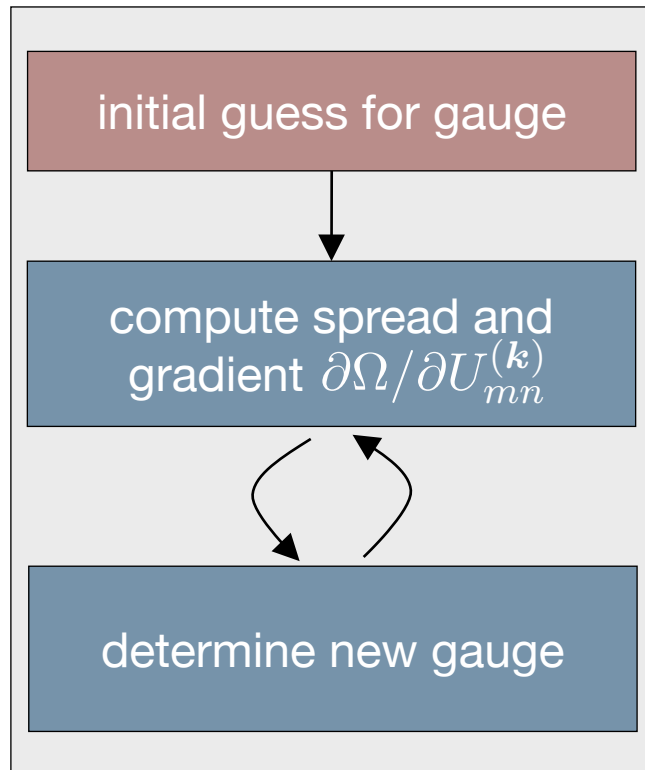
Trial orbitals such as s, p,… or hybrids

$$|\tilde{W}_{\mathbf{0}n}\rangle = \frac{1}{N} \sum_{\boldsymbol{k}m} |\Psi_{\boldsymbol{k}m}\rangle\langle\Psi_{\boldsymbol{k}m}|g_n\rangle$$

initial guess for gauge

compute spread and gradient $\partial\Omega/\partial U^{(\boldsymbol{k})}_{mn}$

determine new gauge

Requires **projections**

$$A_{mn}(\boldsymbol{k}) = \langle\Psi_{\boldsymbol{k}m}|g_n\rangle$$

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(19)

… and in Practice?

Gauge enters!

$$\langle W_{\boldsymbol{R}n}|\boldsymbol{r}|W_{\boldsymbol{0}m}\rangle = i\frac{V}{(2\pi)^3}\int d^3k\, \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{R}}\langle u_{\boldsymbol{k}n}|\nabla_{\boldsymbol{k}}|u_{\boldsymbol{k}m}\rangle$$

Evaluate via finite differences:

initial guess for gauge

compute spread and gradient $\partial\Omega/\partial U_{mn}^{(\boldsymbol{k})}$

determine new gauge

$$\boldsymbol{k}-\boldsymbol{b} \qquad \boldsymbol{k} \qquad \boldsymbol{k}+\boldsymbol{b}$$

$$w_b \qquad w_b$$
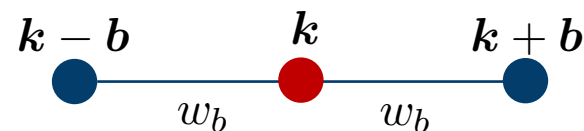
$$\langle W_{\boldsymbol{0}n}|\boldsymbol{r}|W_{\boldsymbol{0}n}\rangle = -\frac{1}{N}\sum_{\boldsymbol{k}\boldsymbol{b}} w_b\boldsymbol{b}\,\mathrm{Im}\ln M_{nn}^{(\boldsymbol{k},\boldsymbol{b})}$$

Requires **overlaps**

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

(20)

The Wannier Workflow

Self-consistent calculation of **charge density** in FLEUR

Prepare Wannier step

→ WF1.win

Generate necessary **matrices** for MLWFs

→ WF1.amn, .mmn, .eig

http://www.wannier.org

Wannierization using wannier90 code

→ WF1.wout, .chk

Post-processing (FLEUR/wannier90)

```
[hanke2@jrl12 workflow]$ cat wann_inp
byindex 1 4
!projgen
prepwan90
matrixmmn
matrixamn
endjobs
```
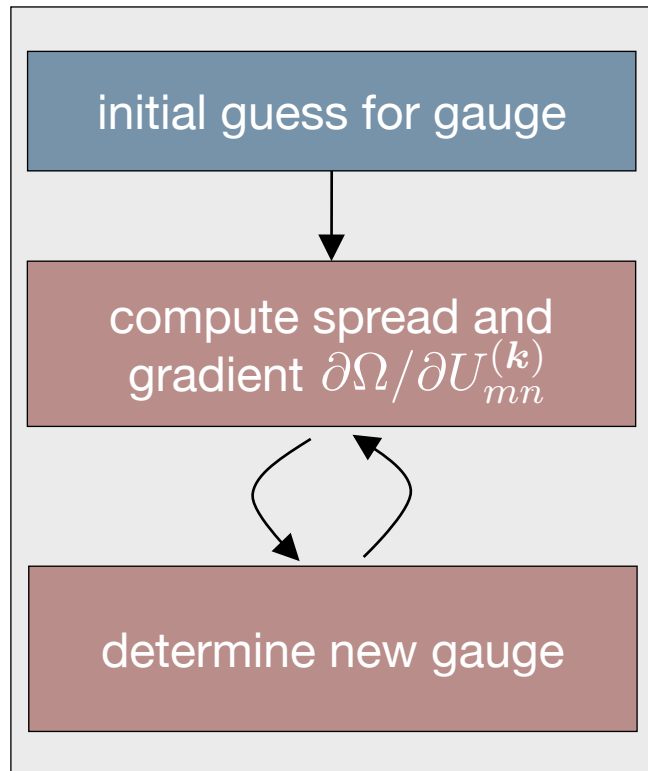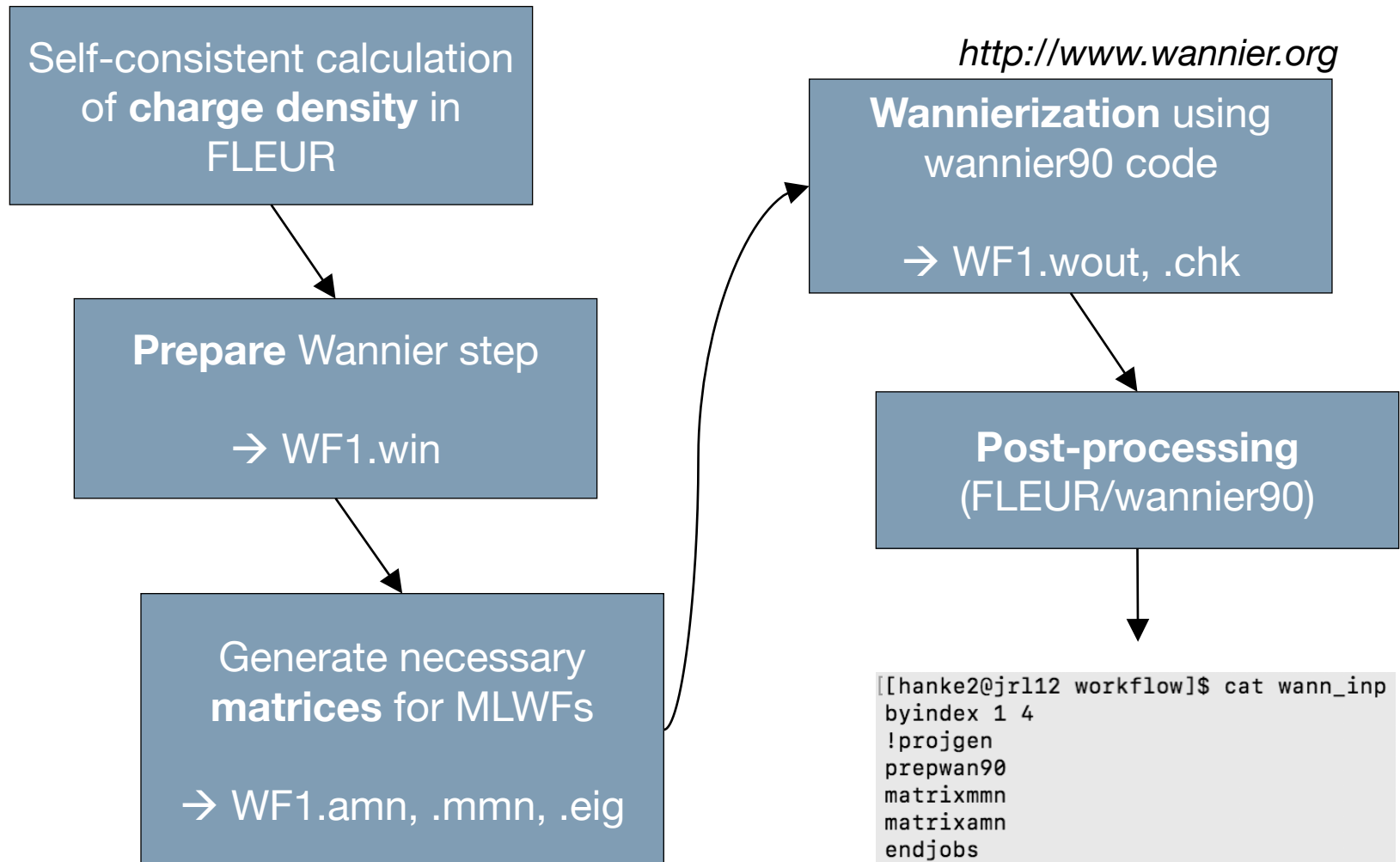
Freimuth *et al*. PRB **78**, 035120 (2008)

Shape of WFs

Reflect the covalent nature of chemical bonds!

**Semiconductors
(direct band gap)**

GaAs

Si

$\mathrm{sp^3 d^2}$

d_{xy}
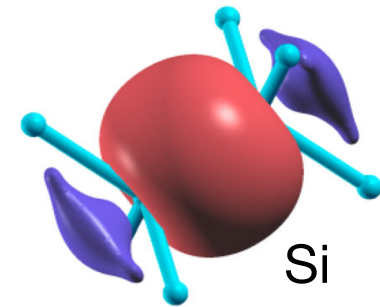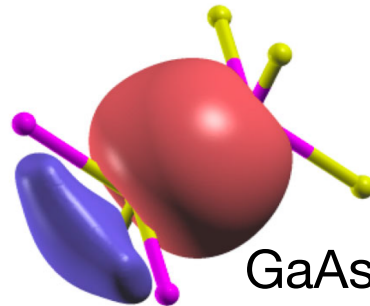
**Metals
(here: bcc Fe)**
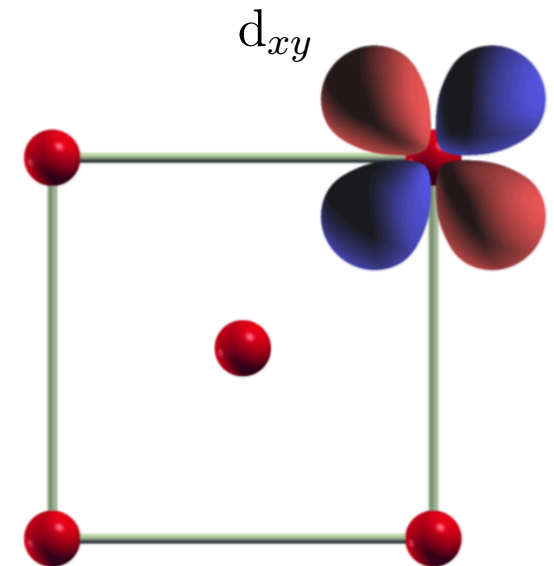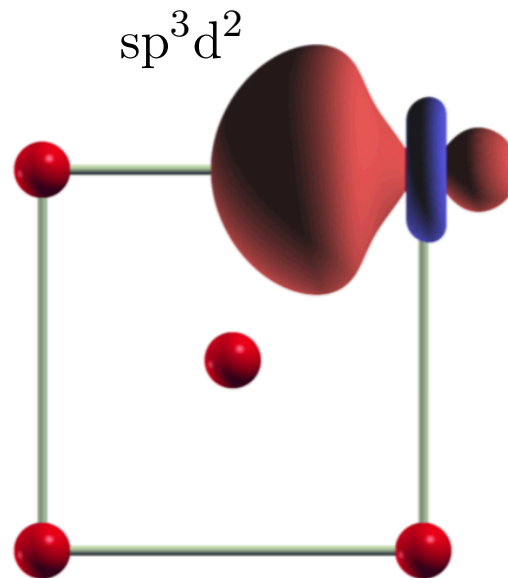
Bonding / Anti-Bonding Orbitals

Rev. Mod. Phys 84, 1419 (2012)

Model Hamiltonians
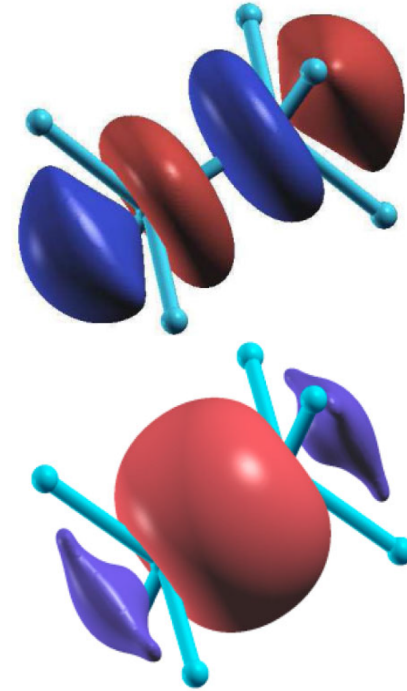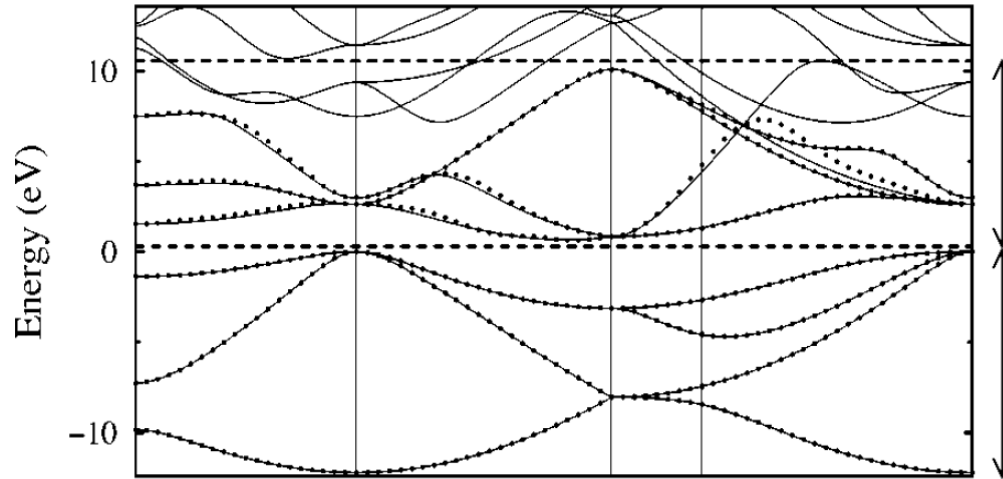
> **Tight-binding model:** The electrons are considered to be tightly bound to nuclei such that the hopping processes to different lattice sites can be viewed as small perturbations that give rise to hybridization and dispersive energy bands. This typically provides a better and more natural description of the electronic structure of solids than the picture of free electrons.

$$H = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{ij} t_{ij} c_i^\dagger c_j + \dots$$

on-site energies

hopping parameters

Model Hamiltonians
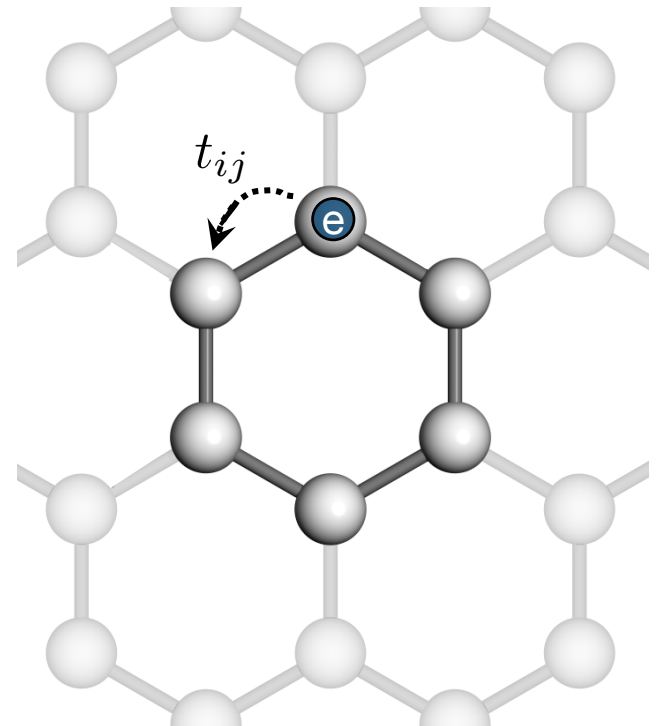
➢ The (unique) set of localized WFs constitutes an orthogonal, complete basis, which enables us to use these orbitals as a starting point for setting up **effective model Hamiltonians** in real space.

$$H = \sum_{\boldsymbol{R}\boldsymbol{R}'} \sum_{nn'} t_{nn'}(\boldsymbol{R}, \boldsymbol{R}') |W_{\boldsymbol{R}n}\rangle \langle W_{\boldsymbol{R}'n'}|$$

Here, the hopping parameters can be easily shown to depend only on the distance vector connecting the WFs

$$
\begin{aligned}
t_{nn'}(\boldsymbol{R}, \boldsymbol{R}') &= \langle W_{\boldsymbol{R}n} | H | W_{\boldsymbol{R}'n'} \rangle \\
&= \langle W_{\boldsymbol{0}n} | H | W_{\boldsymbol{R}'-\boldsymbol{R}n'} \rangle \\
&= t_{nn'}(\boldsymbol{R}' - \boldsymbol{R})
\end{aligned}
$$

Model Hamiltonians
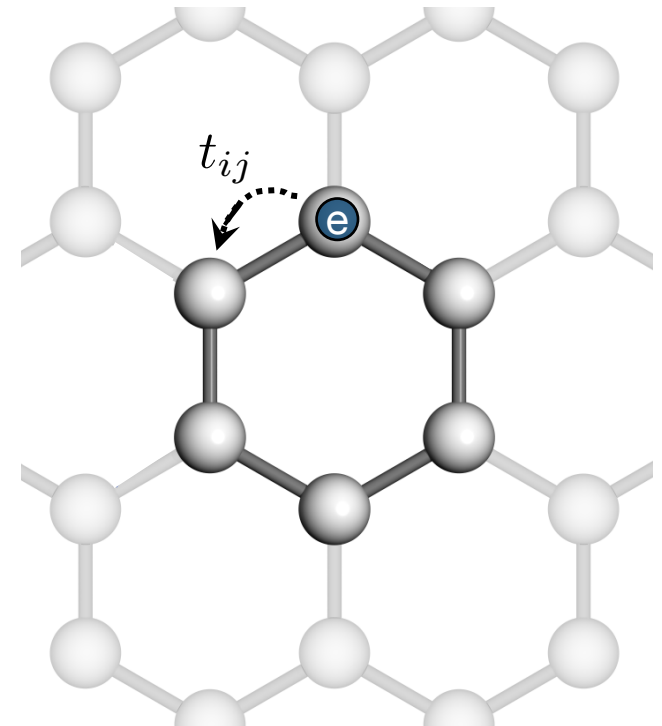
> Using a Fourier transformation of the real-space Hamiltonian in the basis of MLWFs, we can get back to **momentum space** and extract properties such as the band structure. For this purpose, we need to diagonalize

$$H_{nn'}(\boldsymbol{q}) = \sum_{\boldsymbol{R}} e^{i\boldsymbol{q}\cdot\boldsymbol{R}} \, t_{nn'}(\boldsymbol{R})$$

energies

gauge

$$= \sum_{\boldsymbol{R}} e^{i\boldsymbol{q}\cdot\boldsymbol{R}} \left\{ \frac{1}{N} \sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \left[U^{(\boldsymbol{k})\dagger} \epsilon(\boldsymbol{k}) U^{(\boldsymbol{k})} \right]_{nn'} \right\}$$

> A **fundamental question** arises: Did we gain anything in this construction or did we simply run in circles (from Bloch orbitals over Wannier functions back to Bloch orbitals)?

Wannier Interpolation

> The previous procedure is particularly useful: we established an extremely important and widely applied computational technique that is known as **Wannier interpolation**.

$$H(\boldsymbol{k}) \qquad H(\boldsymbol{R}) \qquad H(\boldsymbol{q})$$
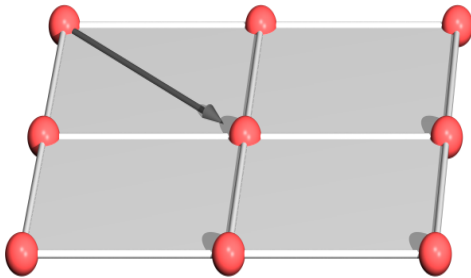
*DFT on coarse mesh (e.g., 8^3 **k**-points)*
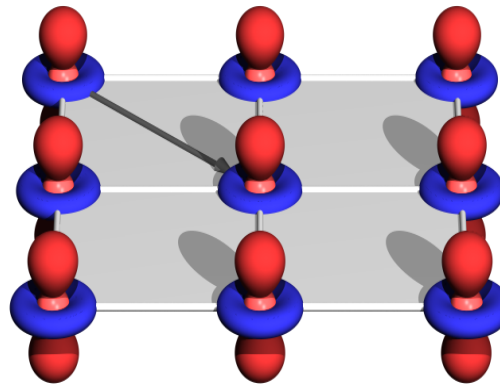
maximally localized Wannier functions
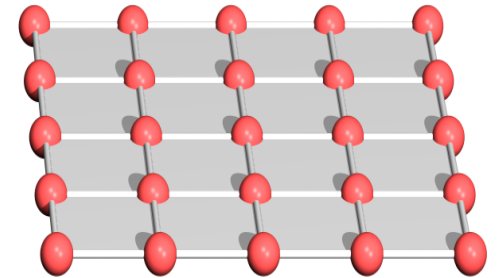
*much finer sampling (e.g., 200^3 **q**-points)*

How does it work?

➢ Before we discuss first examples of the Wannier interpolation, let us briefly elucidate how the **Fourier transformation** of the hopping integrals between localized WFs can provide an efficient but accurate interpolation method for properties in momentum space.

➢ To address this question, we need to consider the WFs for continuous and discrete values of **k**. Consider a 1D example of plane waves:

$$W(x) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{ikx} \, \mathrm{d}k$$
$$= \frac{\sin(\pi x)}{\pi x}$$
$$= j_0(\pi x)$$

$$W(x) = \frac{1}{N} \sum_{k \in \mathrm{BZ}} e^{ikx}$$
$$= \frac{1}{N} \frac{1 - e^{2\pi i x}}{1 - e^{2\pi i x/N}}$$

How does it work?

➢ We can extract information for any desired **k** via the interpolation since the "true" Wannier orbitals are very well approximated by the MLWFs obtained on a relatively coarse momentum mesh.

➢ In the discrete case, **periodic images** appear, which should not interact appreciably to achieve high accuracy of the interpolation. This is known as **sampling theorem** in digital signal processing.
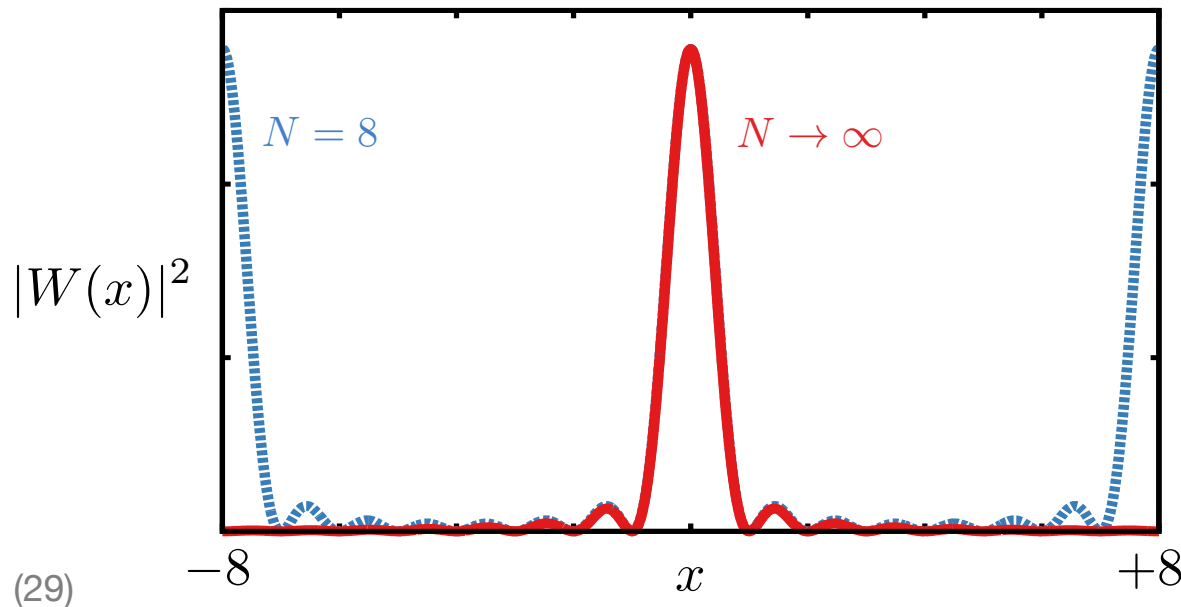
$$W(x) = \frac{1}{N} \sum_{k \in \text{BZ}} e^{ikx}$$

$$= \frac{1}{N} \frac{1 - e^{2\pi i x}}{1 - e^{2\pi i x / N}}$$

$N = 8$ $N \to \infty$

$|W(x)|^2$

-8 x $+8$

Interpolation in Real Materials

bcc iron
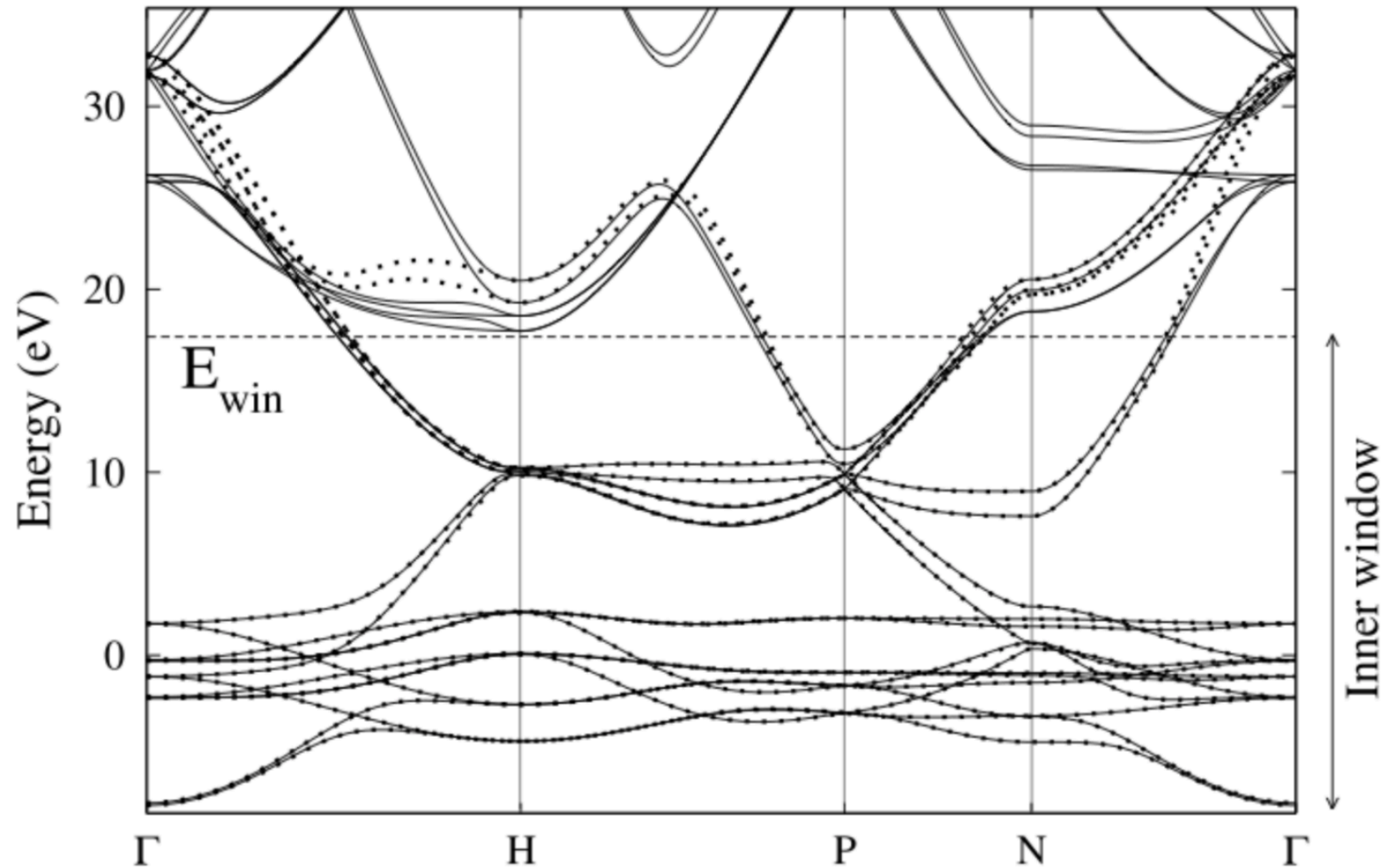
from: Wang et al, Phys. Rev. B **74**, 195118 (2006)

Interpolation in Real Materials

bcc iron
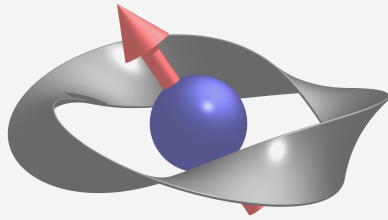
Can you see the bands?

DFT

Γ   H

Interpolation in Real Materials

bcc iron

Now you can!

from: Yates et al, Phys. Rev. B **75**, 195121 (2007)
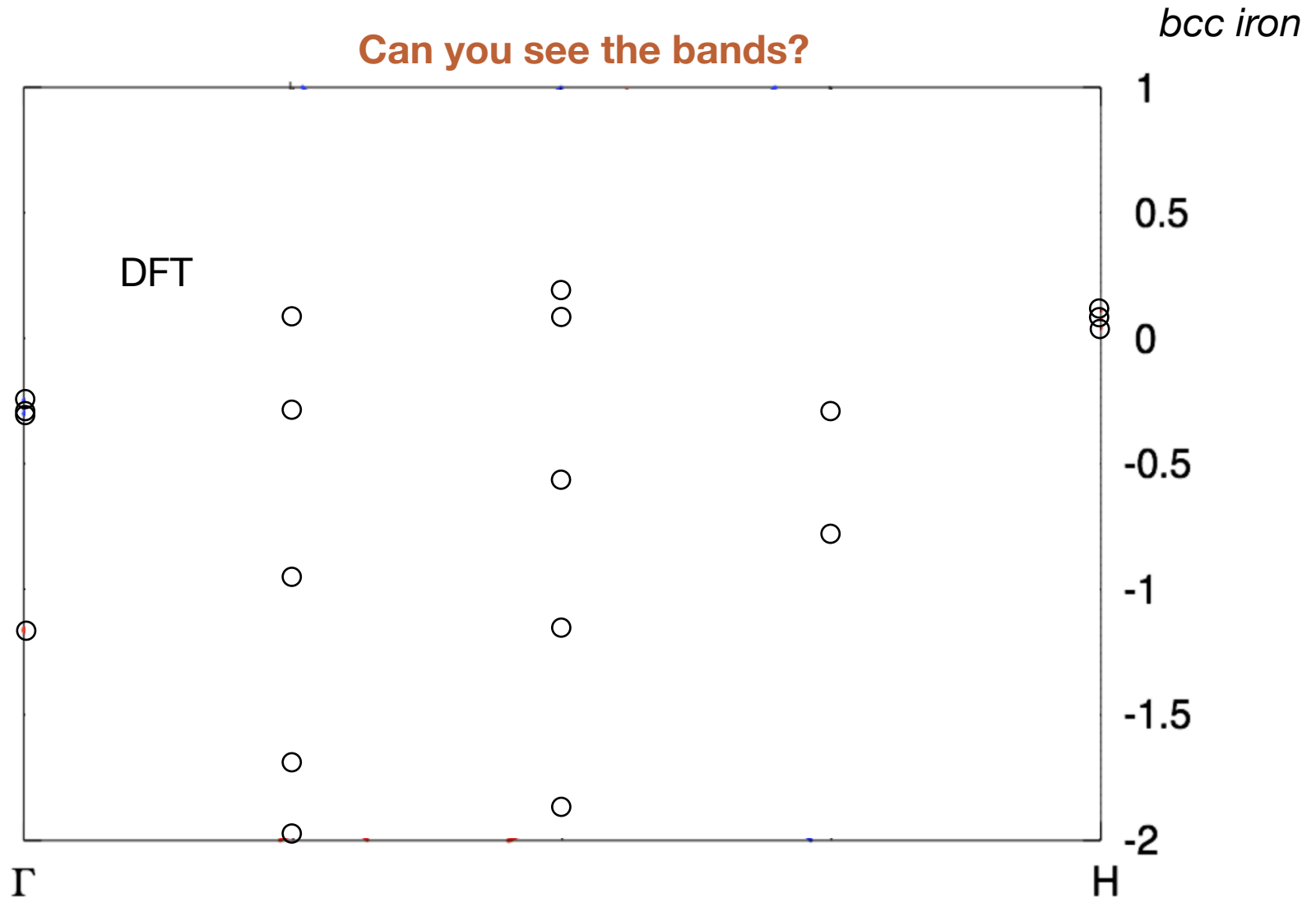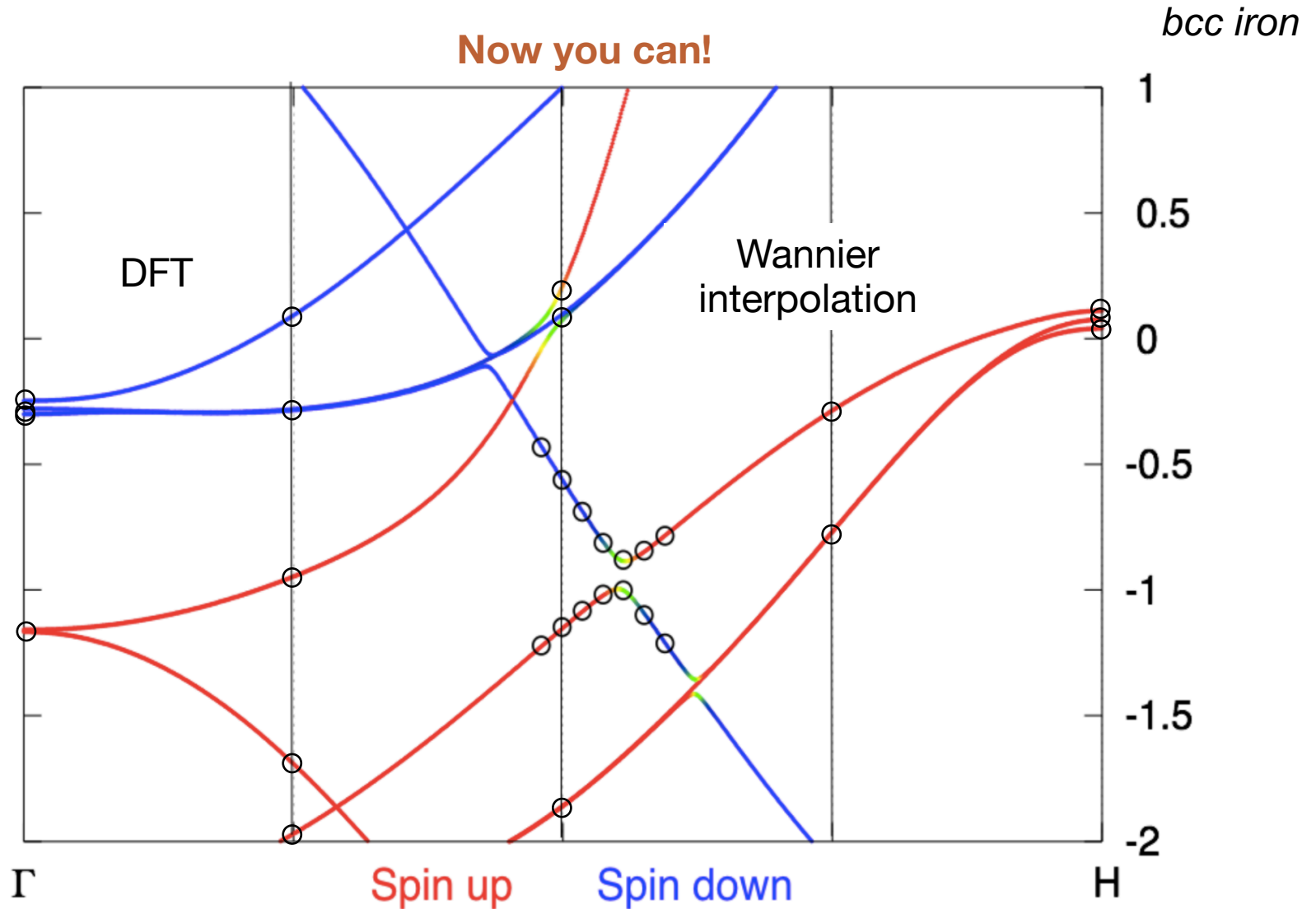
Applications

Berry Phases

Topological Properties

Exchange Interactions

$$\Omega_{ij}^n(\boldsymbol{\lambda}) = -2\,\mathrm{Im}\left\langle \frac{\partial u_{\boldsymbol{\lambda}n}}{\partial \lambda_i} \middle| \frac{\partial u_{\boldsymbol{\lambda}n}}{\partial \lambda_j} \right\rangle$$

Anomalous Hall Effect

(b)

(a)

$\hat{m}$

z

$E, \boldsymbol{j}$

e

I

Spin-Orbit Torques

$\boldsymbol{T}^{\mathrm{odd}}$

z

$\boldsymbol{T}^{\mathrm{even}}$

$\hat{m}$

$E, \boldsymbol{j}$
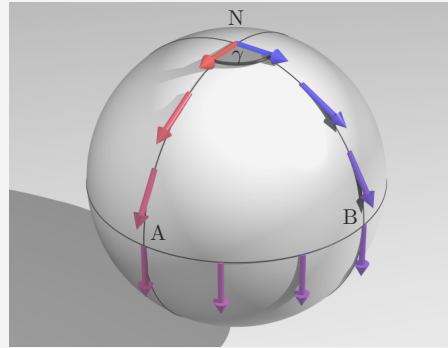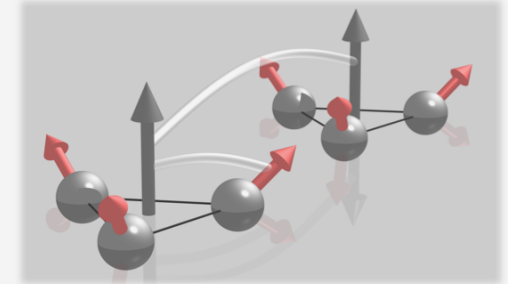
all effect
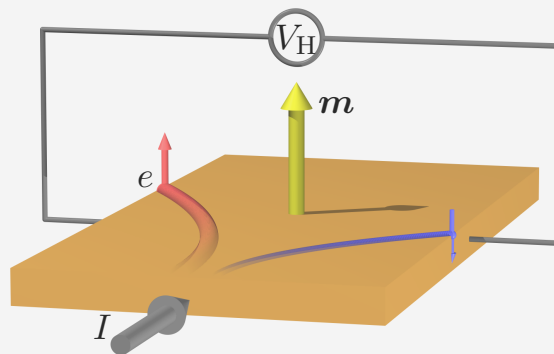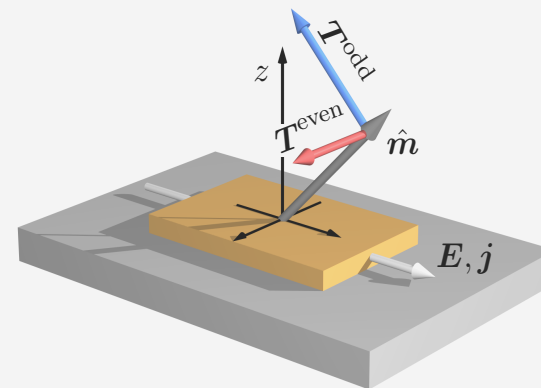
Sampling Momentum Space

➤ The Berry curvature in metallic magnets is **sharply peaked** if two energy bands cross (degeneracy or monopole) or if two levels repel each other (avoided crossing). Consequently, calculating accurately the integral of the curvature over the Brillouin zone – to determine the conductivity – requires an ultra-dense sampling of momentum space.
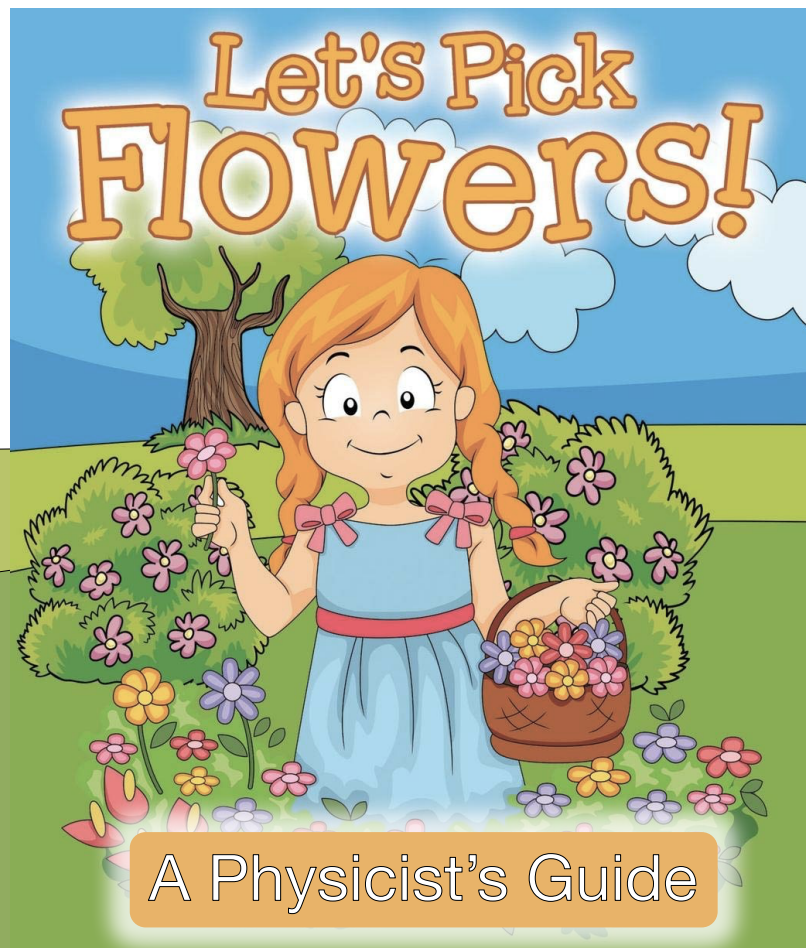
from: Wang et al, Phys. Rev. B **74**, 195118 (2006)

(34)

Literature
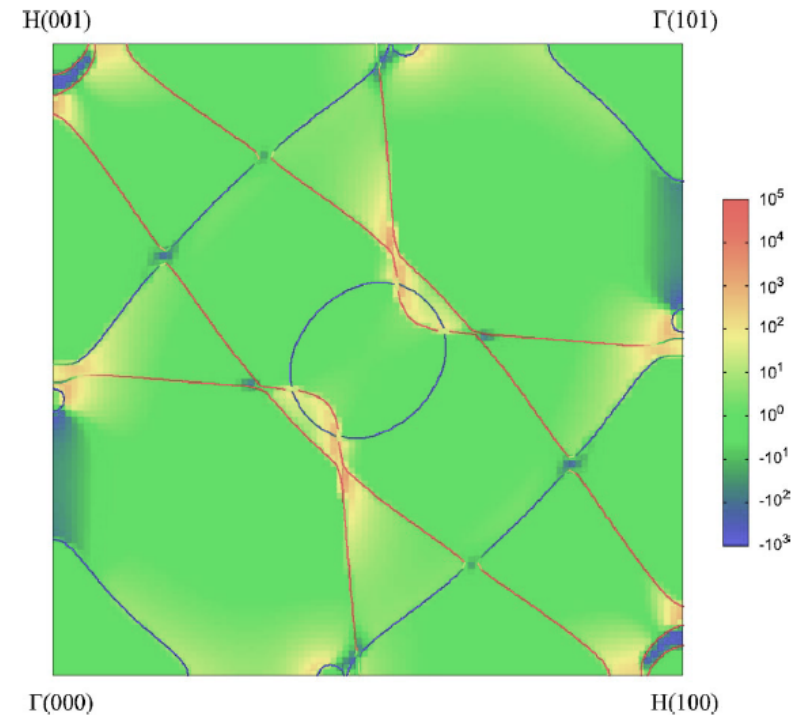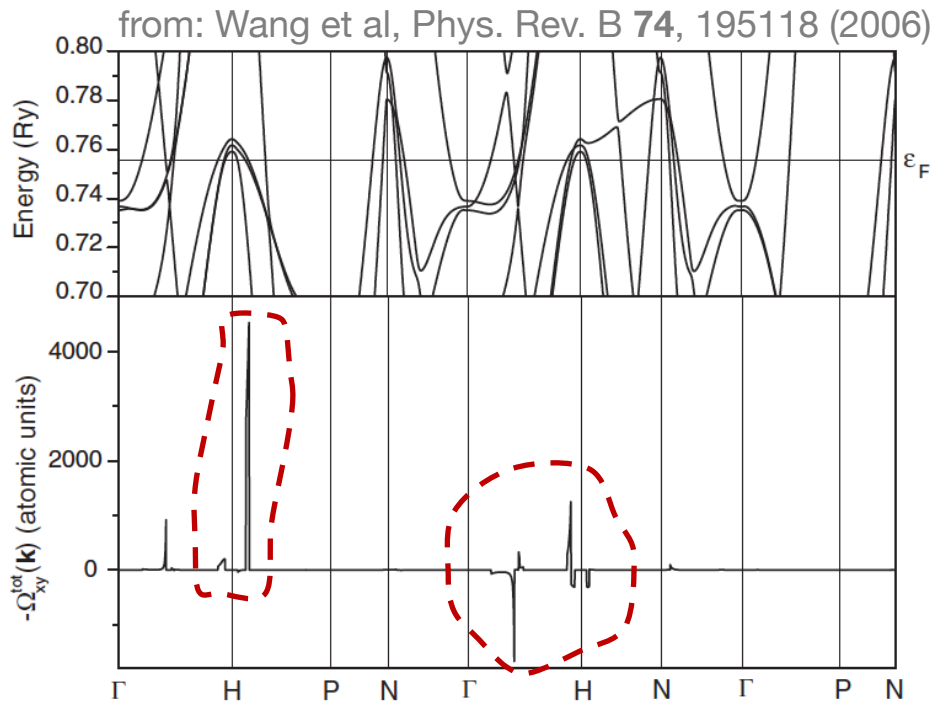
➢ Ashcroft & Mermin, *Solid State Physics*

➢ Grosso, *Solid State Physics*

➢ Sólyom, *Fundamentals of the Physics of Solids, Volume II*

➢ Bernevig, *Topological Insulators and Topological Superconductors*

➢ Rabe, *Physics of Ferroelectrics: A Modern Perspective*

Some further reading

➢ Marzari et al, Rev. Mod. Phys. **84**, 1419 (2012)

➢ Resta, Rev. Mod. Phys. **66**, 899 (1994)

➢ King-Smith & Vanderbilt, Phys. Rev. B **47**, 1651 (1993)

Questions?

Bloch Orbitals

Gauge Freedom

Localization

Wannier Functions

Wannier90 Code

Interpolation

FLEUR Interface

Workflows