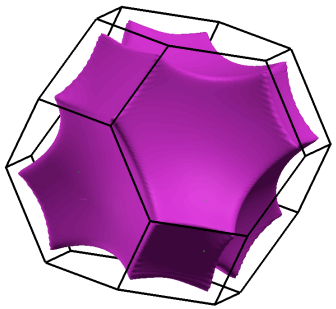
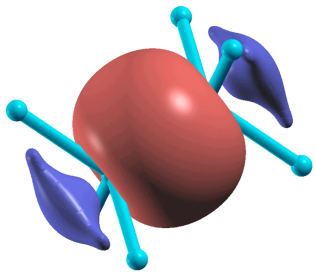
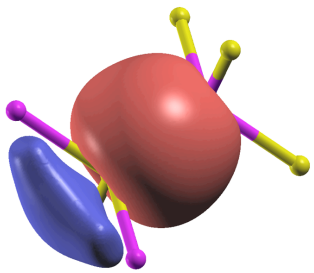
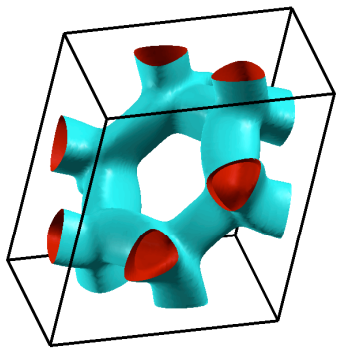
Wannier Functions: *ab-initio* tight-binding

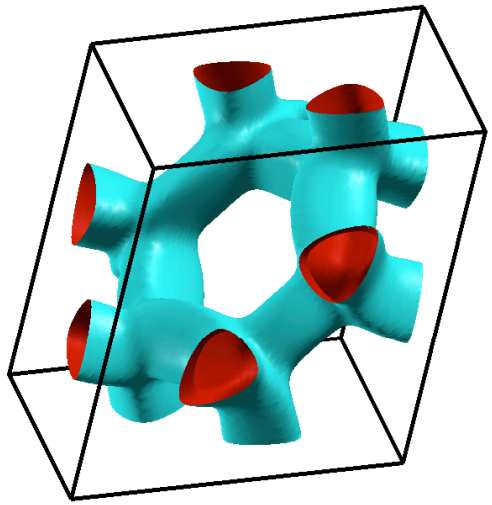
Jonathan Yates

Cavendish Laboratory, Cambridge University

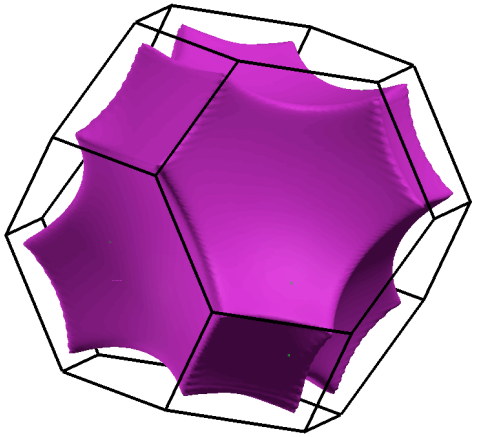





Representing a Fermi Surface

Accurate description of Fermi surface properties requires a detailed sampling of the Brillouin Zone



Lead Fermi surface

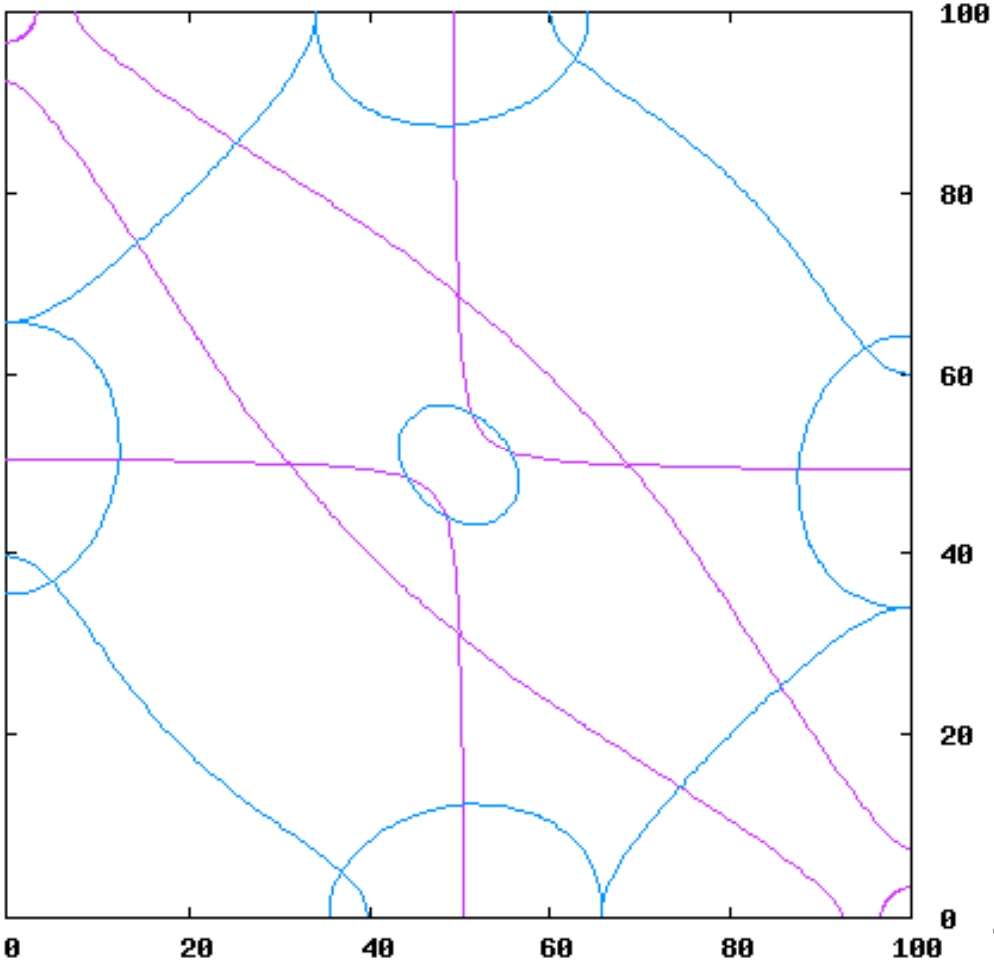


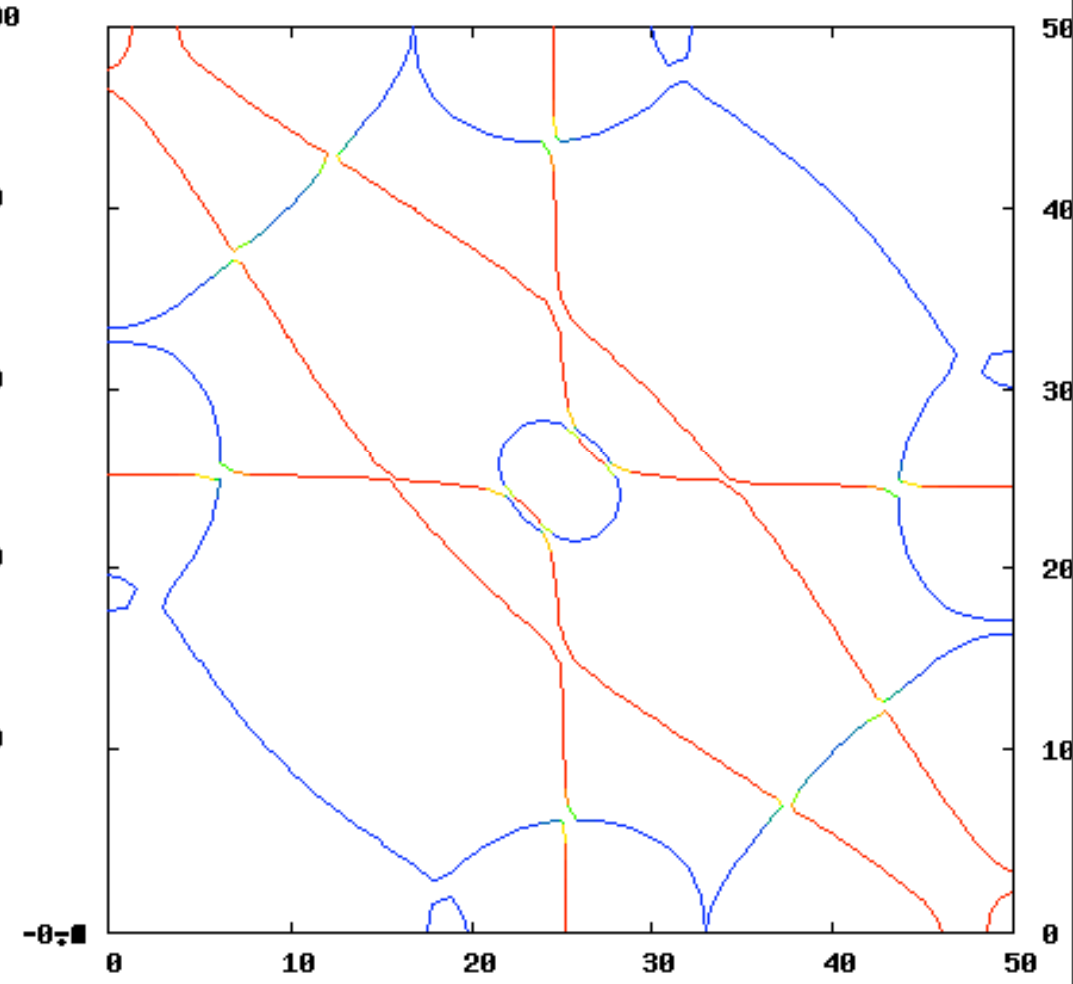
Al Fermi surface

Representing a Fermi Surface

Fe fermi surface

Scalar Relativistic In the (010) plane with spin-orbit coupling





Outline

- Wannier Functions
  - *One band*
  - *Isolated Set of Bands*
  - *Entangled Bands*
- Wannier Interpolation
  - *Accurate and Efficient approach to Fermi surface and spectral properties*
- Examples
  - *Anomalous Hall Effect*
  - *Electron-Phonon Coupling*

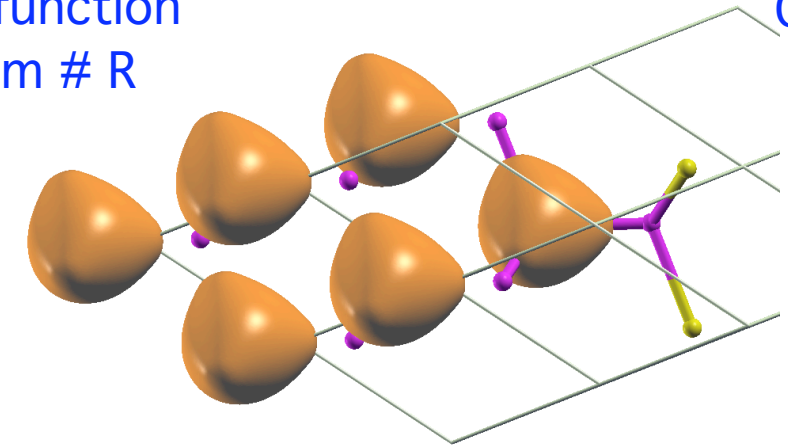
Wannier Functions

$$w_{n\mathbf{R}}(\mathbf{r}) = \frac{V}{(2\pi)^3}\int_{BZ}\psi_{n\mathbf{k}}(\mathbf{r})e^{-i\mathbf{k}.\mathbf{R}}d\mathbf{k}$$

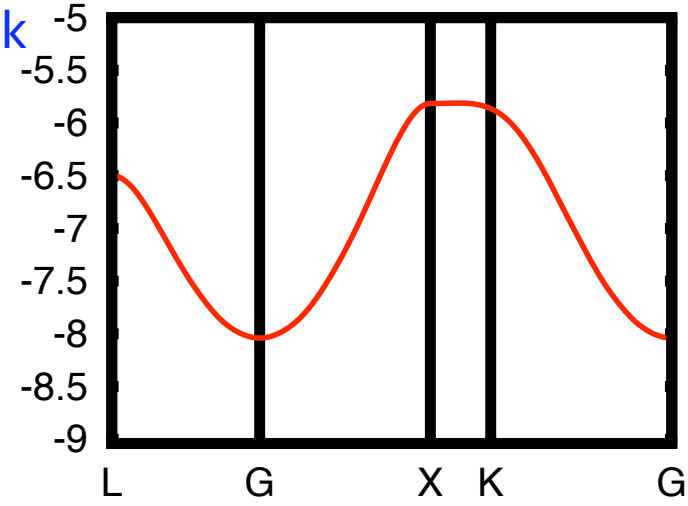
Wannier function
Quantum # R

Bloch state
Quantum # k

$$\psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow e^{-i\phi(\mathbf{k})}\psi_{n\mathbf{k}}(\mathbf{r})$$



GaAs



Wannier Functions

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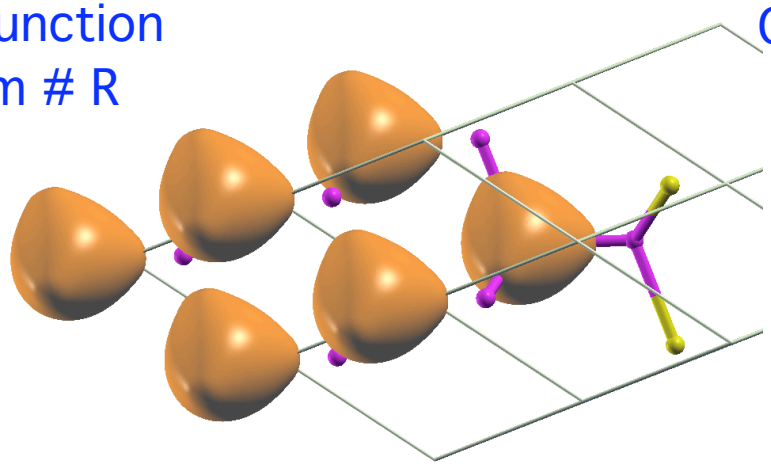
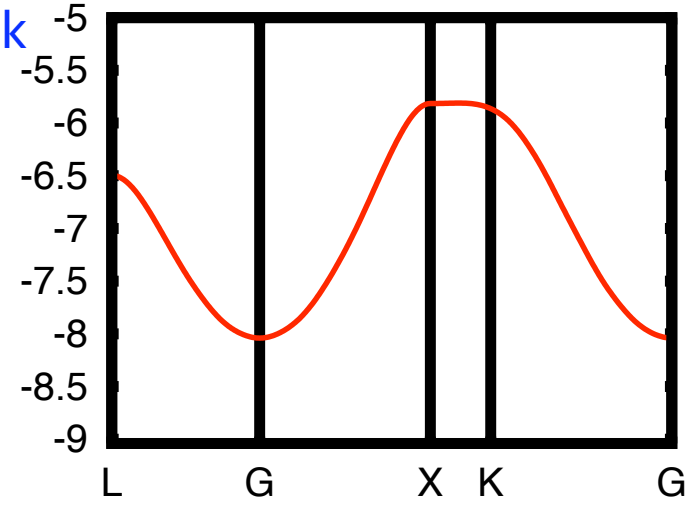


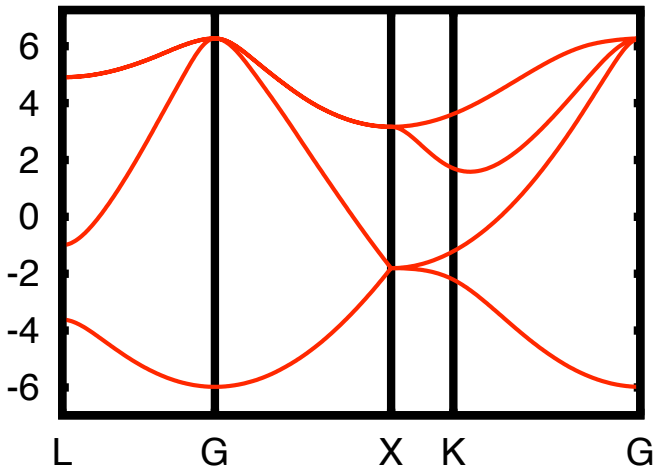
GaAs



Multiband - Generalized WF

$$\psi_{n\mathbf{k}}(\mathbf{r}) \rightarrow \sum_n U_{mn}^{(\mathbf{k})}\psi_{m\mathbf{k}}(\mathbf{r})$$

Si

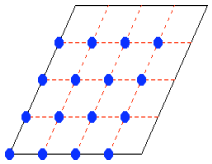


Maximally Localised Wannier Functions

$$w_{n\mathbf{R}}(\mathbf{r}) = \frac{V}{(2\pi)^3}\int_{BZ}\left[\sum_m U^{(\mathbf{k})}_{mn}\psi_{m\mathbf{k}}(\mathbf{r})\right]e^{-\mathbf{k}.\mathbf{R}}d\mathbf{k}$$

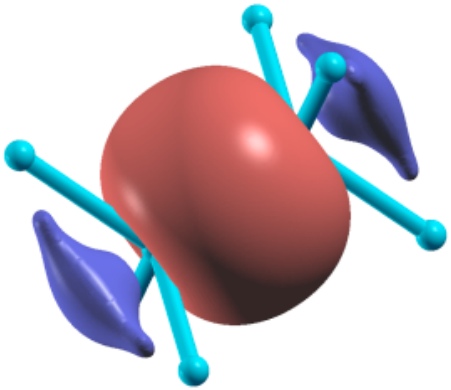
Choose U^k to minimise quadratic spread
(Marzari, Vanderbilt)

Ab-initio code $\xrightarrow{\langle u_{\mathbf{k}}|u_{\mathbf{k+b}}\rangle}$ Wannier code $\longrightarrow U^{(\mathbf{k})}$

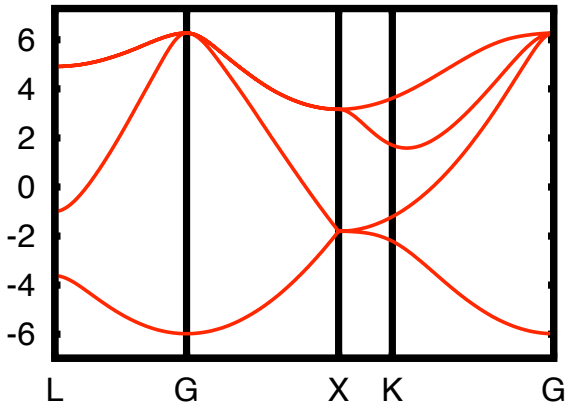


$|u_{\mathbf{k}}\rangle$

WF defined in basis of bloch states



Si valence bands

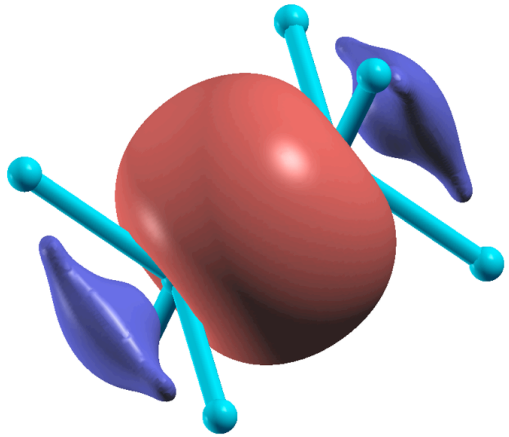


Wannier localisation in R gives
Bloch smoothness in k

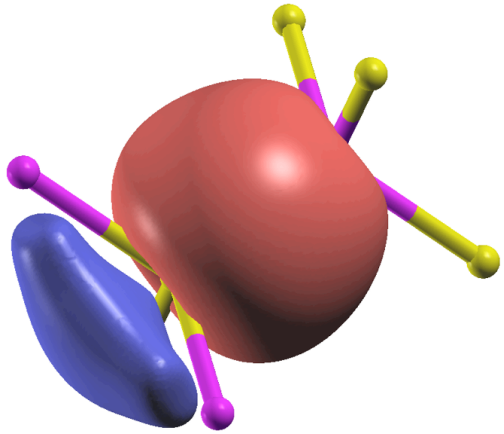
$$\psi^{rot}_{n\mathbf{k}}(\mathbf{r}) = \sum_m U^{(\mathbf{k})}_{mn}\psi_{m\mathbf{k}}(\mathbf{r})$$

Wannier Functions: A local picture

1- Intuitive picture of local bonding

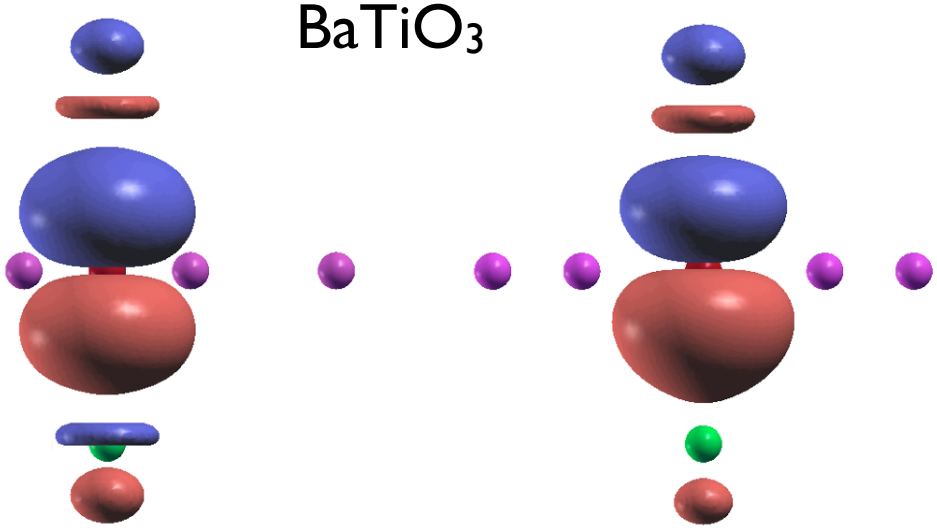


Si



GaAs

$BaTiO_3$



Paraelectric

Ferroelectric

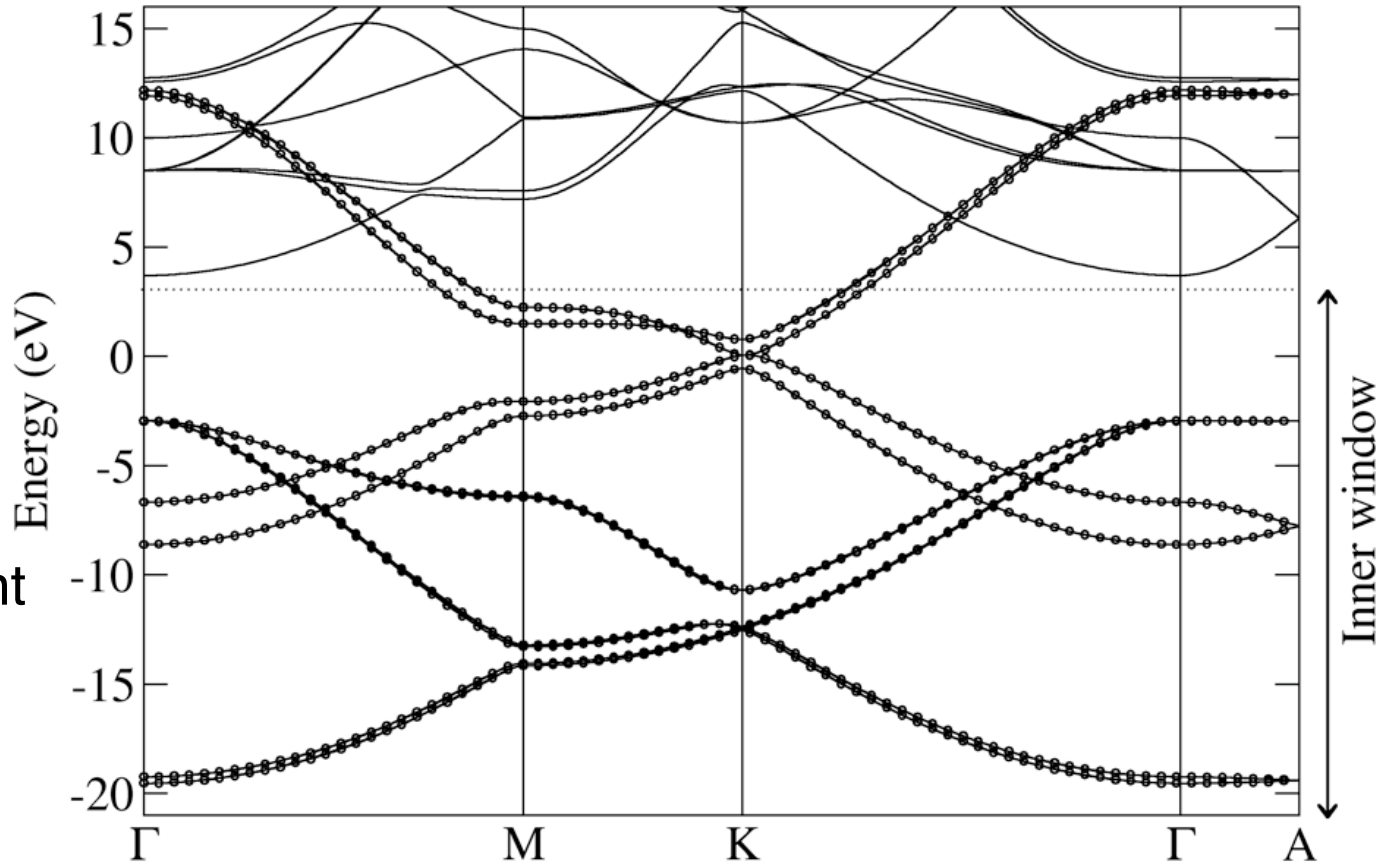
2- Wannier centres give bulk polarisation in a ferroelectric

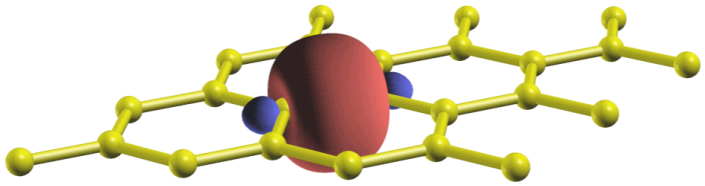
MLWF - Entangled Bands

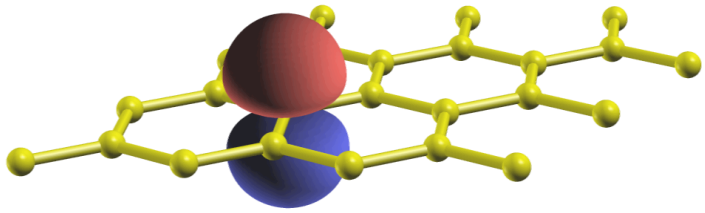
Disentanglement procedure
(Souza, Marzari and Vanderbilt)

Obtain “partially occupied” Wannier functions

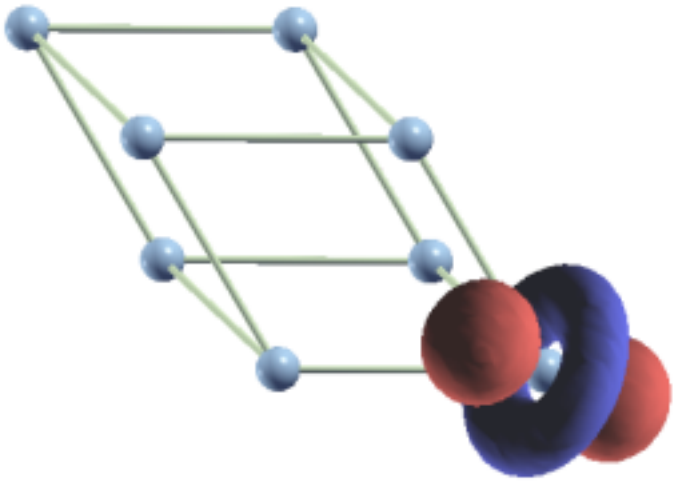
Essentially perfect agreement within given energy window

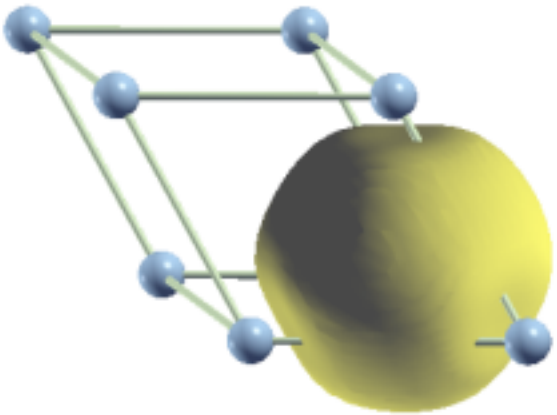


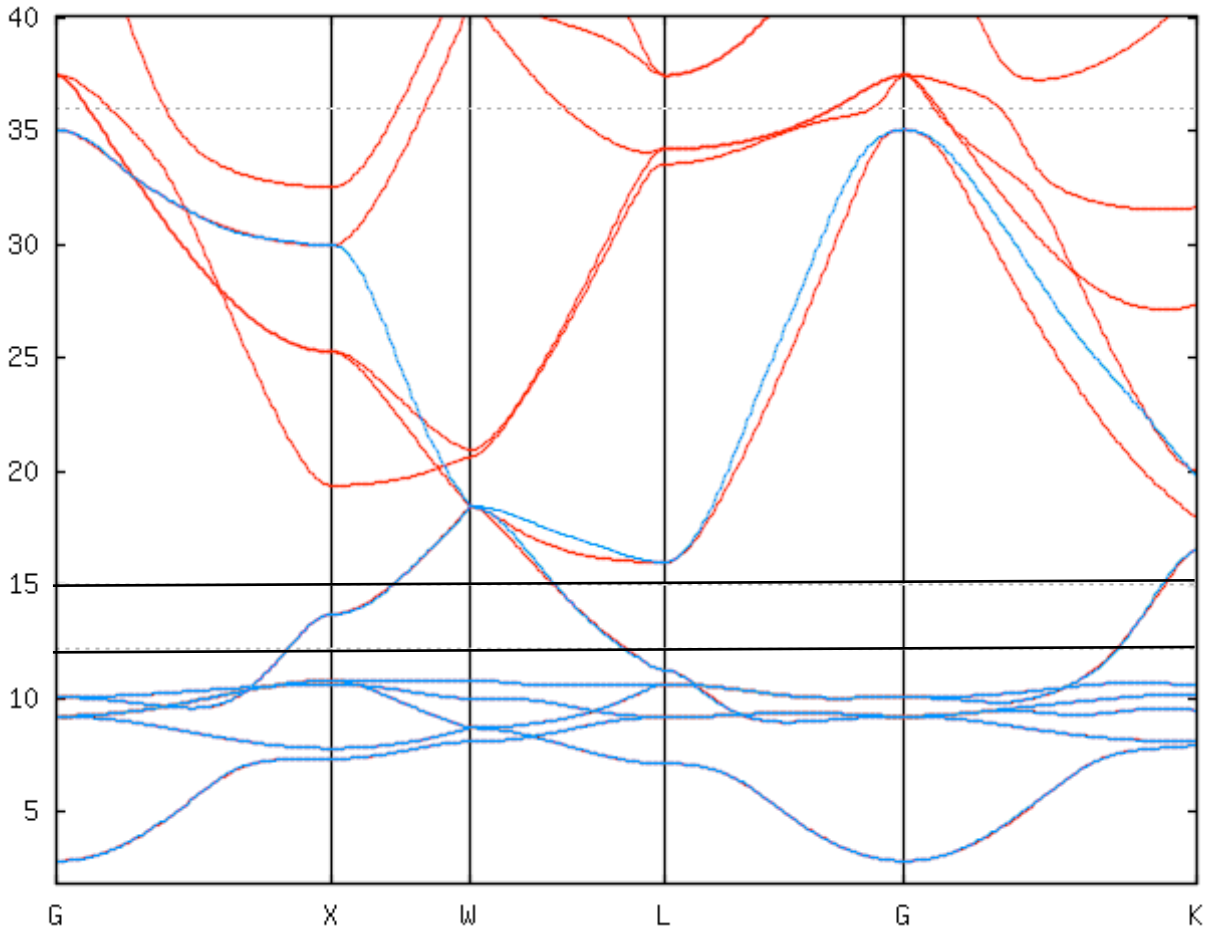




Copper



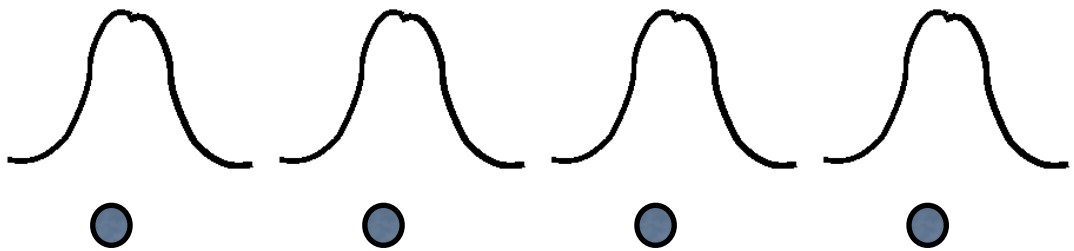


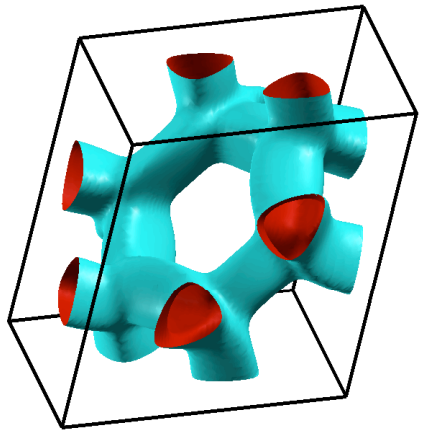


Wannier Interpolation

Accurate and Efficient approach to Fermi surface and spectral properties

- Exploit localisation of Wannier functions.
- Require only matrix elements between close neighbours.





Lead Fermi surface

1st principles accuracy at tight-binding cost

Interpolation of any one-electron operator

Wannier Interpolation

1- Obtain operator in Wannier basis

$$O_{mn}(\mathbf{R}) = \langle Om|\hat{O}|Rn\rangle$$

Wannier Interpolation

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$$O_{mn}(\mathbf{R}) = \langle Om|\hat{O}|Rn\rangle$$

2- Fourier transform to an arbitrary k-point, k'

$$O_{mn}(\mathbf{k}') = \sum_{\mathbf{R}} e^{i\mathbf{k}.\cdot\mathbf{R}}\, O_{mn}(\mathbf{R})$$

Wannier Interpolation

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$$O_{mn}(\mathbf{k}') = \sum_{\mathbf{R}} e^{i\mathbf{k}.\cdot\mathbf{R}}\, O_{mn}(\mathbf{R})$$

3- Un-rotate matrix at k'

$$\langle \psi_{m,\mathbf{k}'}|O|\psi_{n,\mathbf{k}'}\rangle = [U^{\dagger}_{\mathbf{k}'} O(\mathbf{k}') U_{\mathbf{k}'}]$$

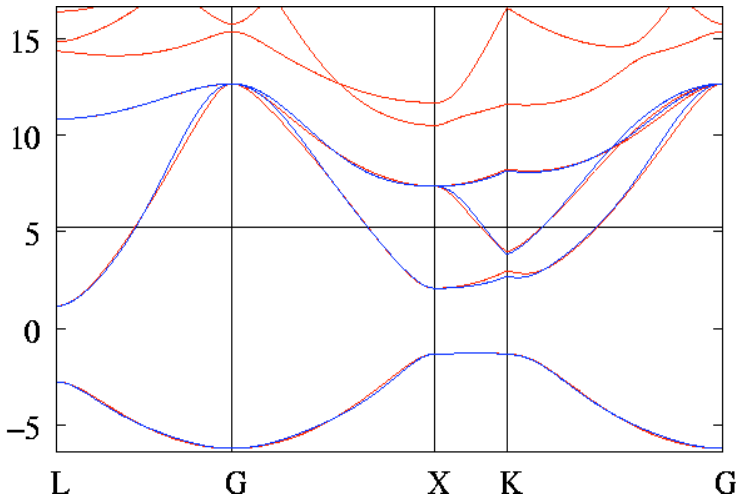
What we need

diagonalises H

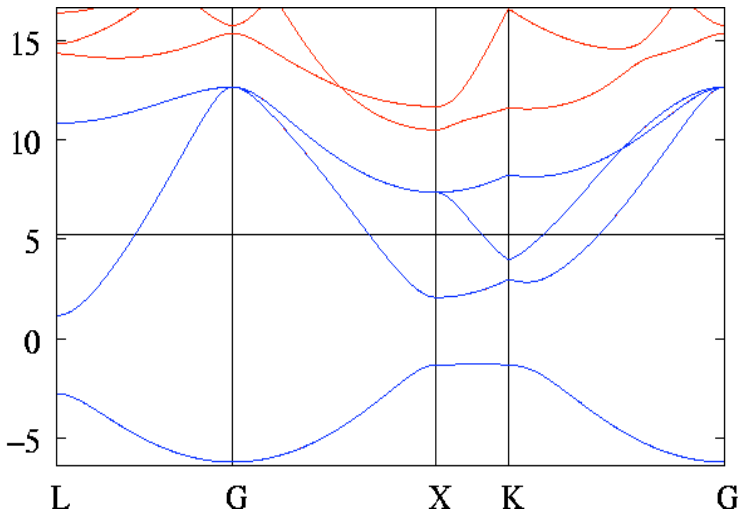
All operations involve small matrices (N_{wan}xN_{wan})
=> FAST!

Convergence

Lead



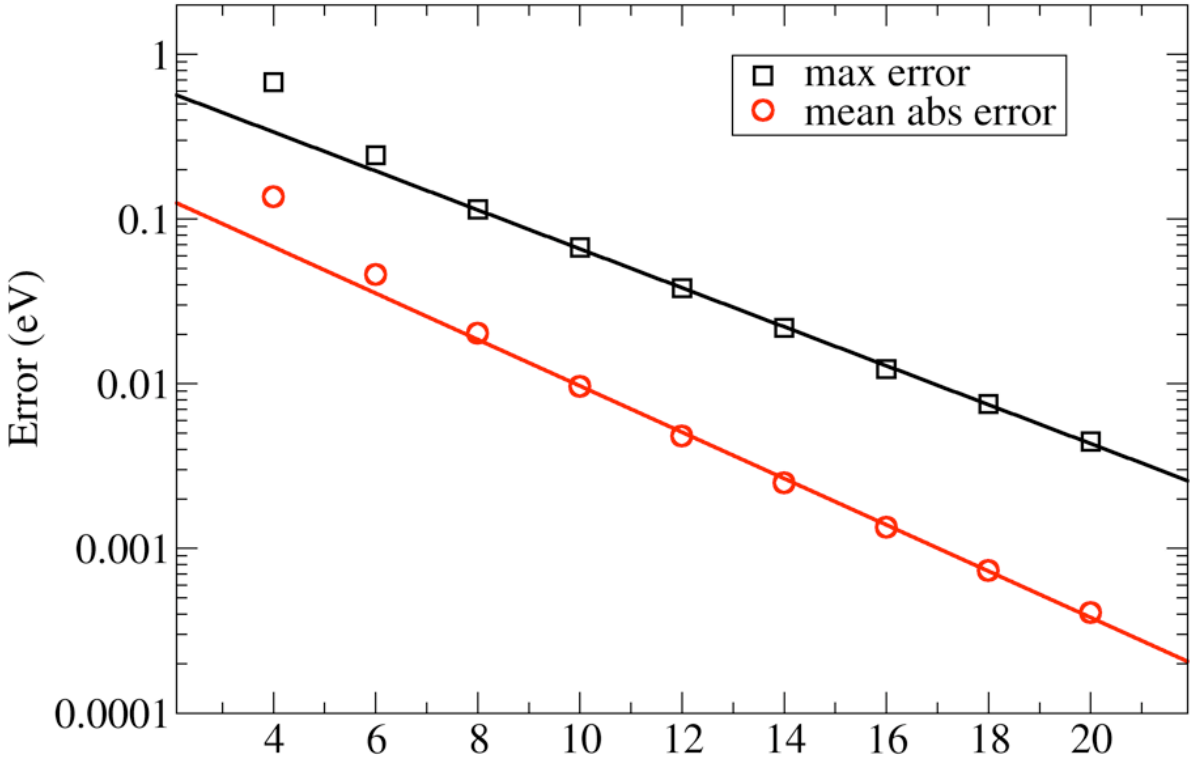
4x4x4



10x10x10

Wannier interpolated object converges to ab-initio value, exponentially with k-grid sampling.

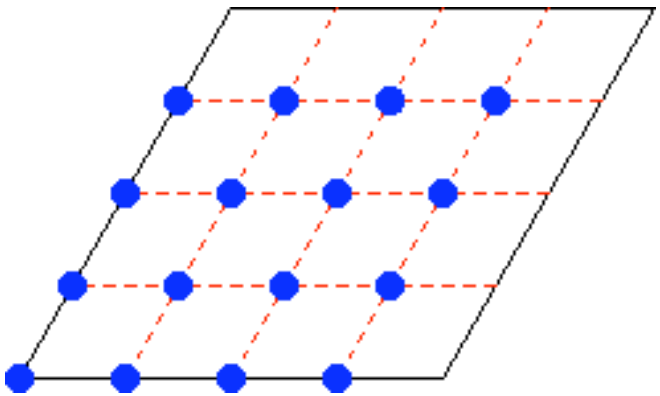
Band interpolation error



Wannier Interpolation - Summary

Bloch States
eg planewave basis

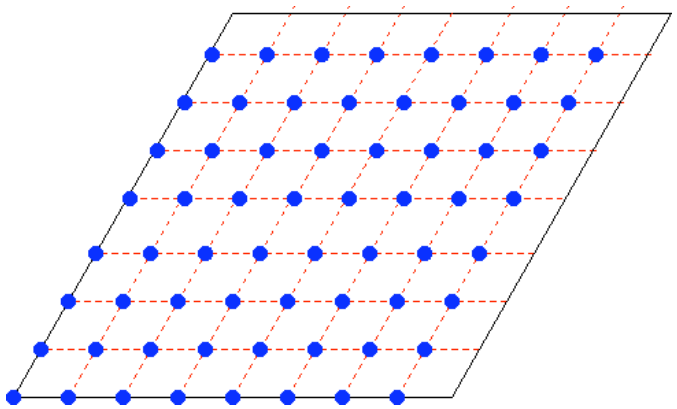
- Each k-point expensive
- Calculation of MLWF converges exponentially



Sample on coarse grid

Wannier basis

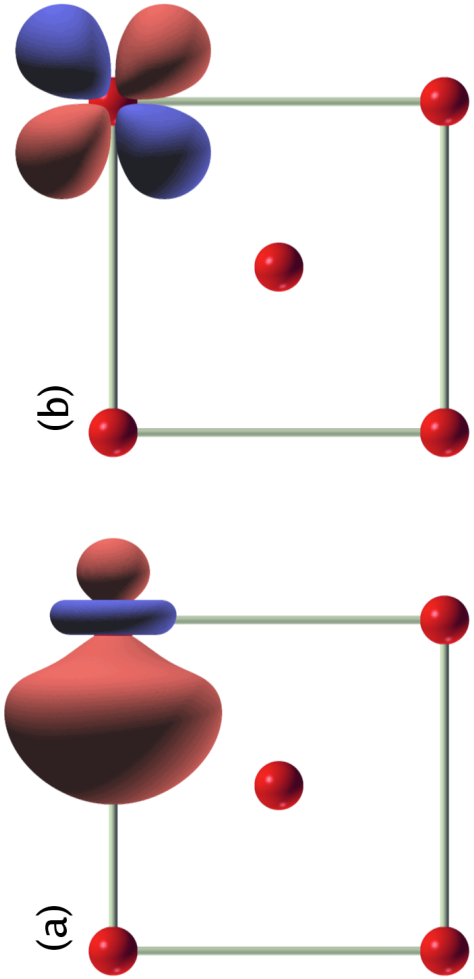
- Each k-point cheap
- Introduce occupancies and compute properties (only polynomial convergence)

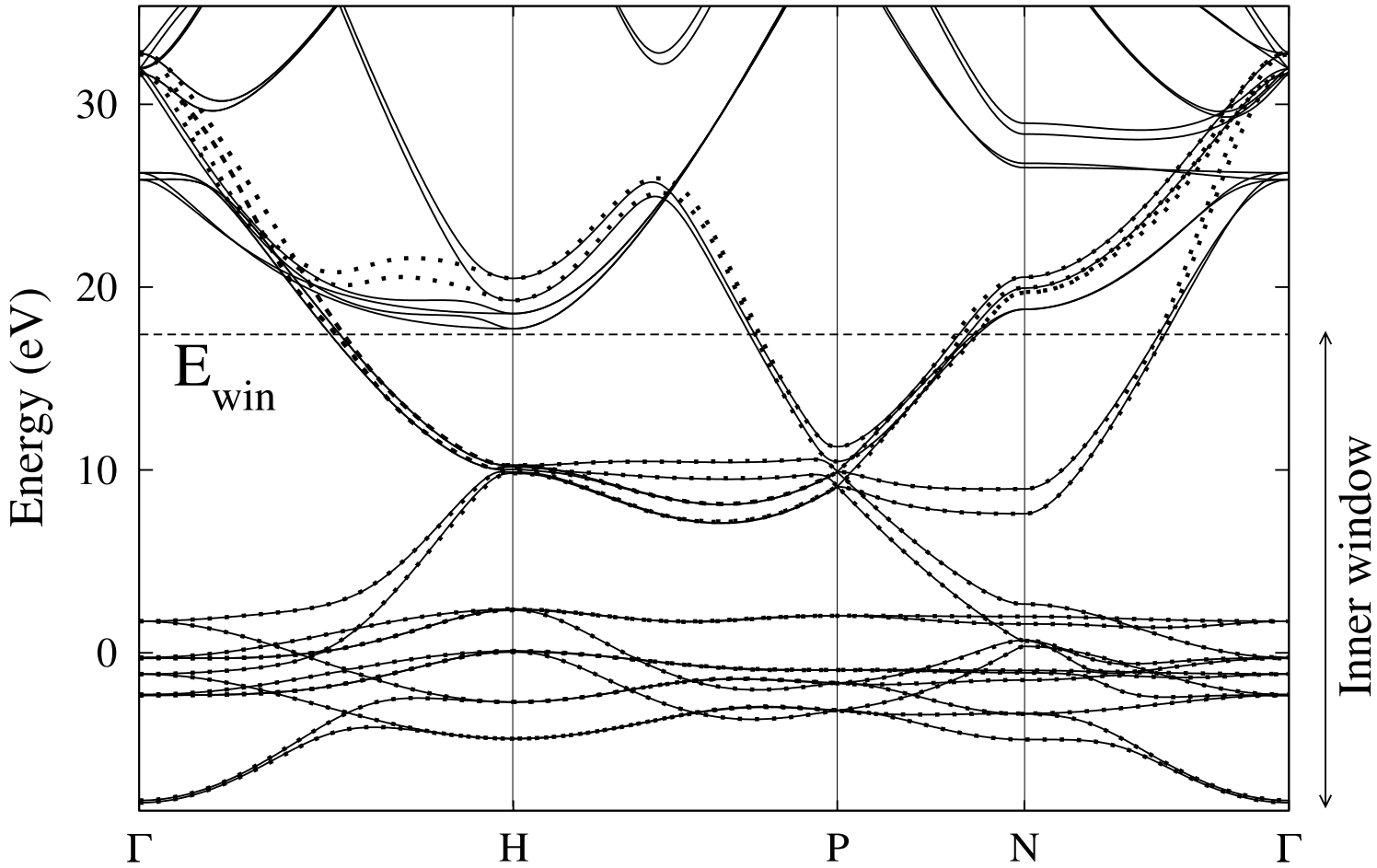


Sample on fine grid

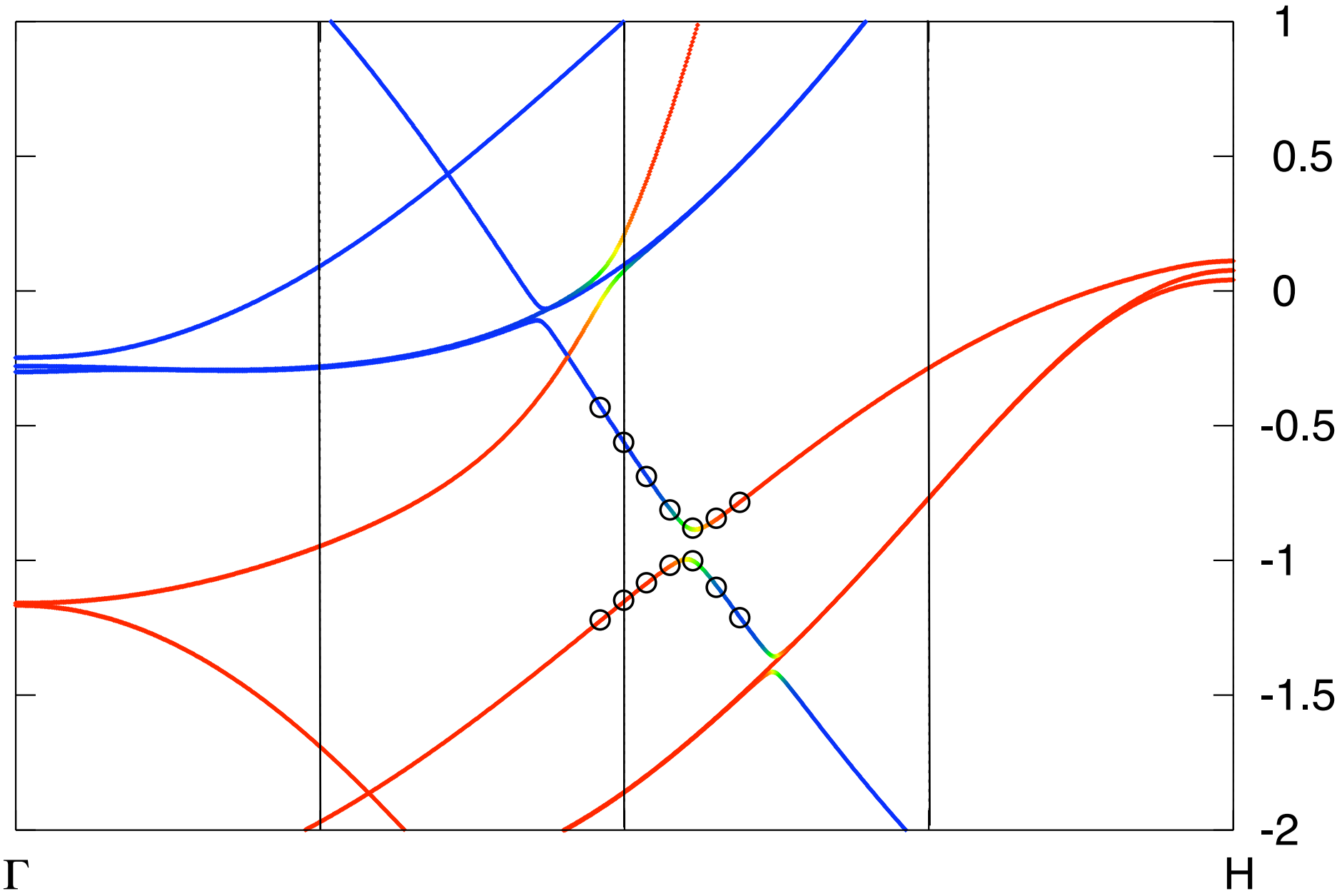
Wannier Interpolation - Fe

- 18 spinor Wannier functions
- Keep up to 4th neighbour overlaps
- Cost 1/2000 of full calculation





Wannier Interpolation



Wannier Interpolation pt2

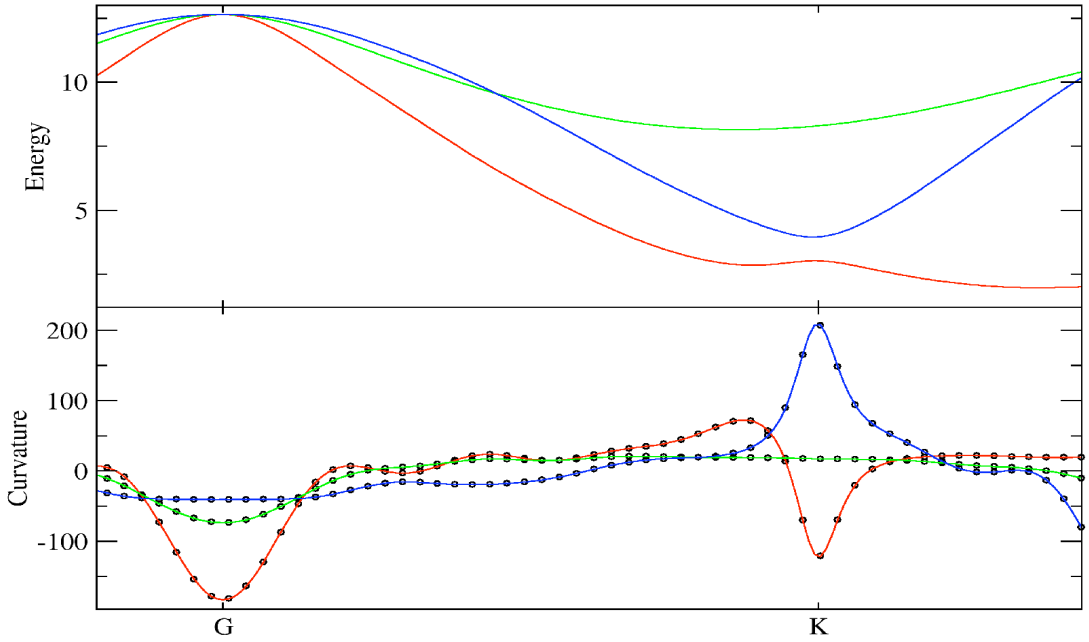
1- k-derivatives can be taken analytically

eg band gradient

$$H_{\mathbf{k}} = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} H(\mathbf{R})$$

$$\frac{\partial H_{\mathbf{k}}}{\partial \mathbf{k}_\alpha} = i \sum_{\mathbf{R}} R_\alpha e^{i\mathbf{k}\cdot\mathbf{R}} H(\mathbf{R})$$

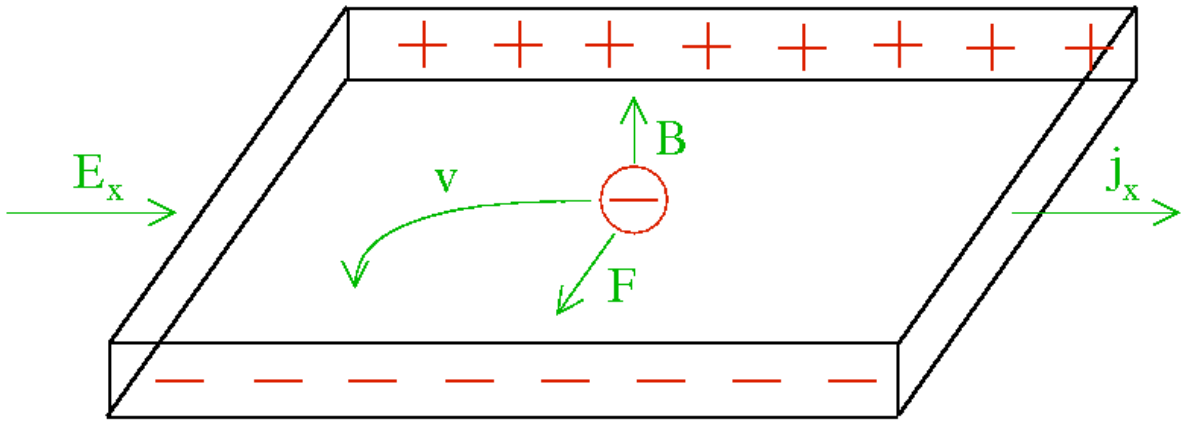
repeat for higher derivatives



2- Position operator matrix elements well defined

Hall Effect

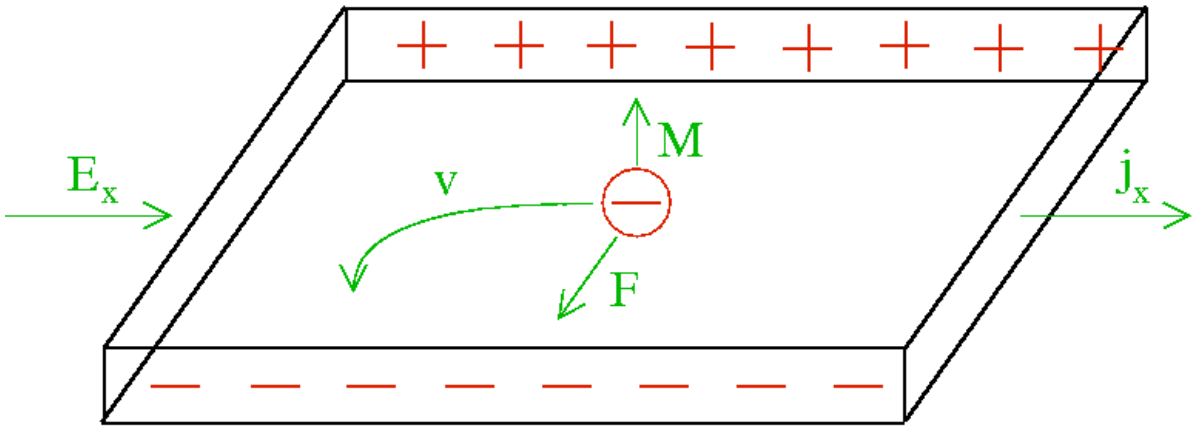
Ordinary Hall Effect (Hall 1879)



Crossed E and B fields

B breaks time-reversal

Anomalous Hall Effect (Hall 1880)



No B field needed!

Ferromagnetism breaks time-reversal

Mechanisms for the AHE

Intrinsic

1954 Karplus and Luttinger

property of electron motion in perfect lattice

"dissipationless" current (spin-orbit effect)

Extrinsic

1955 Smit "skew scattering"

1970 Berger "side-jump"

Intrinsic (again)

1996- Rexamination of KL in terms of Berry's phases

Niu (Texas), Nagaosa (Tokyo)

Electron Dynamics

Textbook wavepacket dynamics

$$\dot{\mathbf{r}} = \frac{1}{\hbar}\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial \mathbf{k}}$$

$$\hbar\dot{\mathbf{k}} = -e\mathbf{E} - e\dot{\mathbf{r}} \times \mathbf{B}$$

Electron Dynamics

Textbook wavepacket dynamics missing a term: "anomalous velocity"

$$\dot{\mathbf{r}} = \frac{1}{\hbar}\frac{\partial \varepsilon_{n\mathbf{k}}}{\partial \mathbf{k}} - \dot{\mathbf{k}} \times \boldsymbol{\Omega}_n(\mathbf{k})$$

"k-space magnetic field" caused by lattice potential

"k-space Lorentz force" even when B=0

$$\hbar\dot{\mathbf{k}} = -e\mathbf{E} - e\dot{\mathbf{r}} \times \mathbf{B}$$

Anomalous Hall Conductivity

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

Fermi function

Berry Curvature

Berry Curvature

Berry Curvature

$$\Omega_n(\mathbf{k}) = -Im\langle \nabla_{\mathbf{k}} u_{n,\mathbf{k}}| \times |\nabla_{\mathbf{k}} u_{n,\mathbf{k}}\rangle$$

cell periodic Bloch state

Berry Potential

$$\mathbf{A}_n(\mathbf{k}) = i\langle u_{n\mathbf{k}}|\boldsymbol{\nabla}_{\mathbf{k}}|u_{n\mathbf{k}}\rangle \qquad \boldsymbol{\Omega}_n(\mathbf{k}) = \boldsymbol{\nabla} \times \mathbf{A}_n(\mathbf{k})$$

Ab-initio Calculation

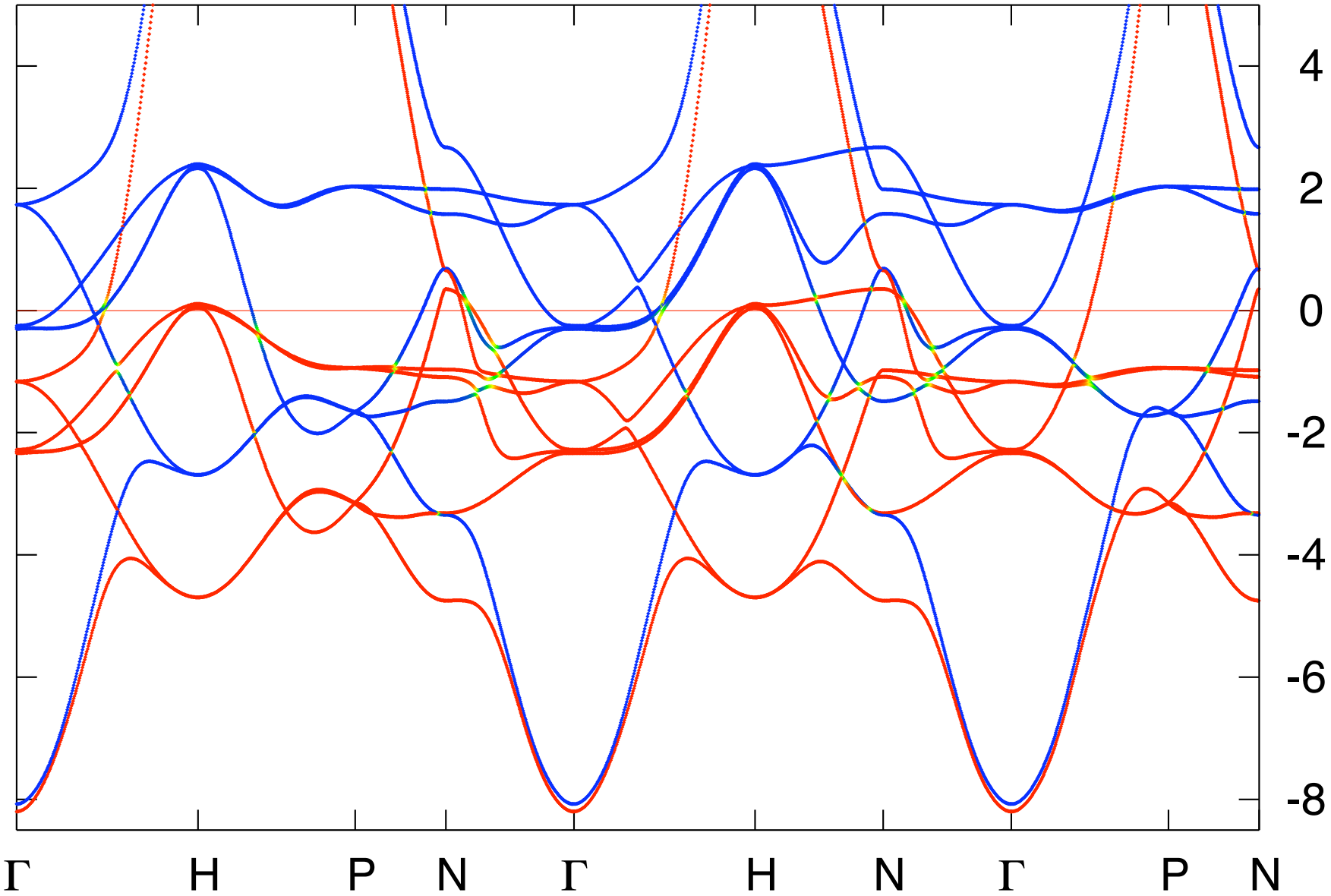
Finite-differences difficult: phases, band-crossings

bcc iron (LAPW) Yao et al (PRL 2004)

Kubo formula $$\Omega_{n,z}(\mathbf{k}) = -2\mathrm{Im}\sum_{m\neq n} \frac{v_{nm,x}(\mathbf{k})\, v_{mn,y}(\mathbf{k})}{(\omega_m(\mathbf{k}) - \omega_n(\mathbf{k}))^2}$$

Extremely computationally expensive!
final number within 20% of experiment

Band-structure bcc Fe

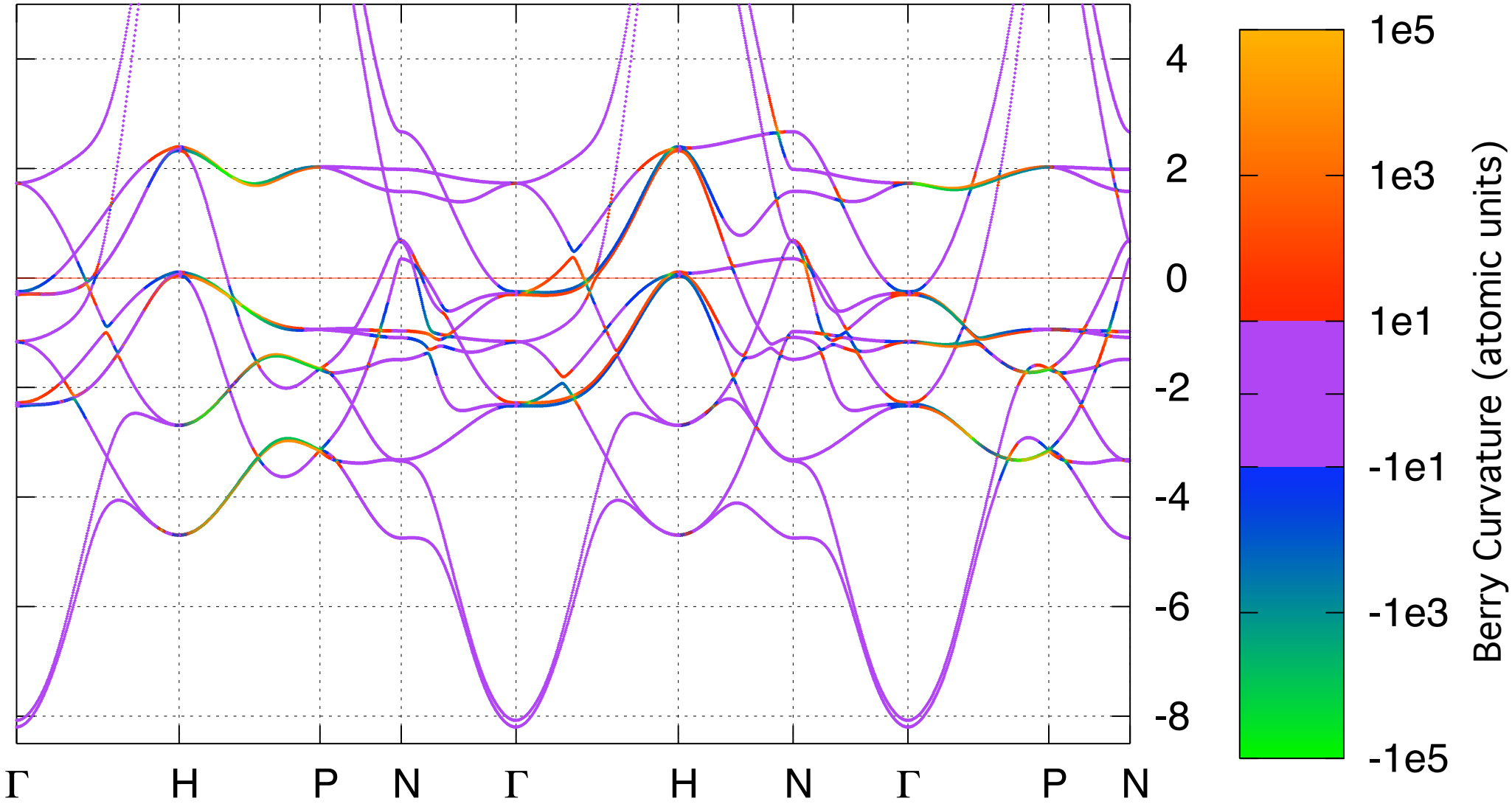


DFT (PBE) + spin-orbit

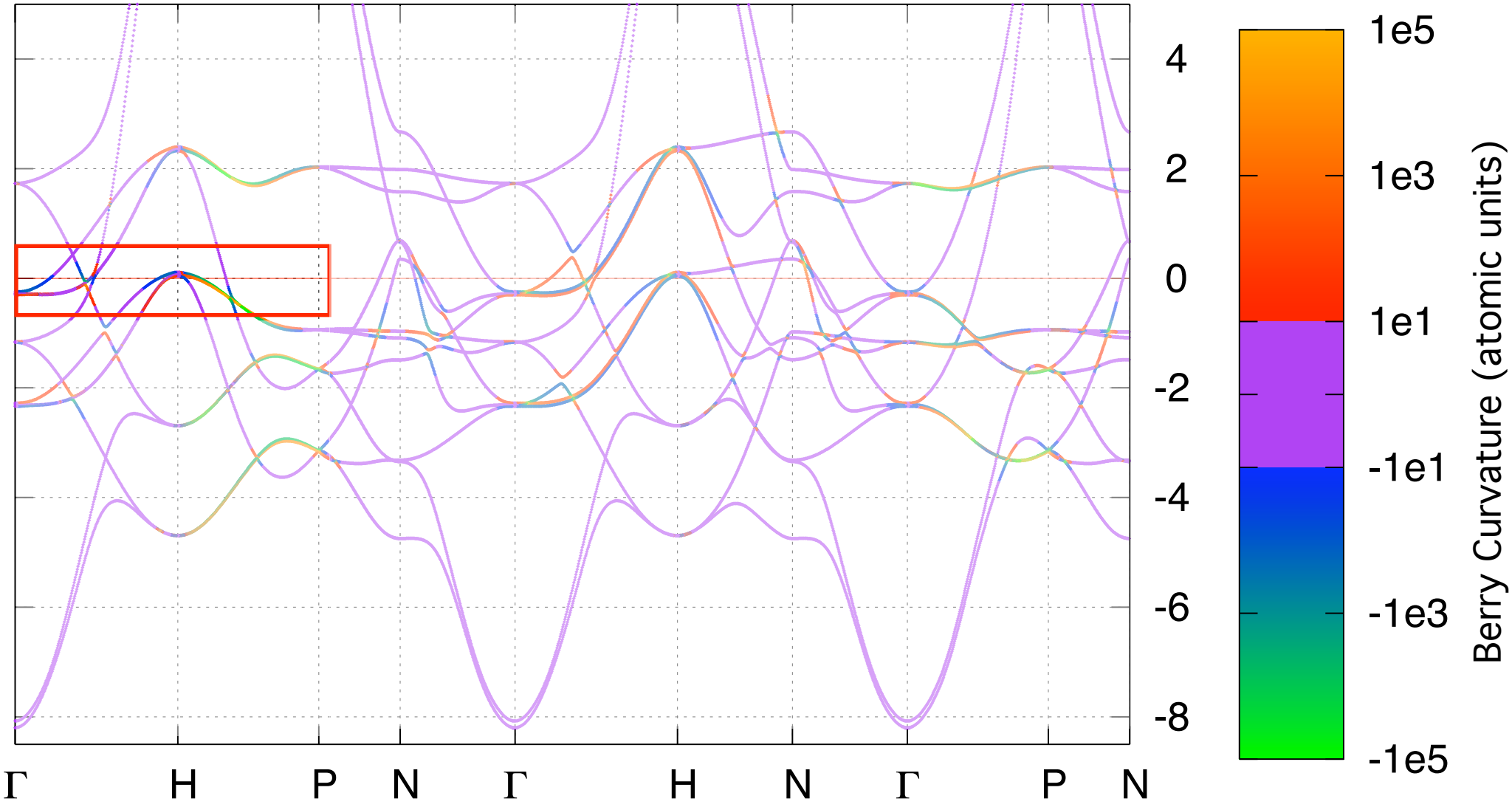
Spin up

Spin down

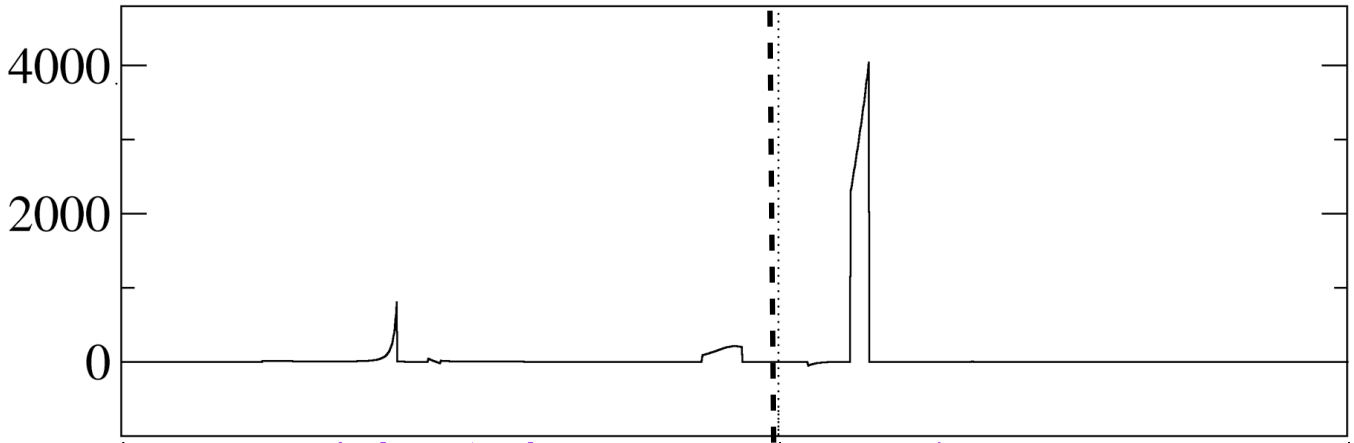
Berry curvature bcc Fe



Berry curvature bcc Fe

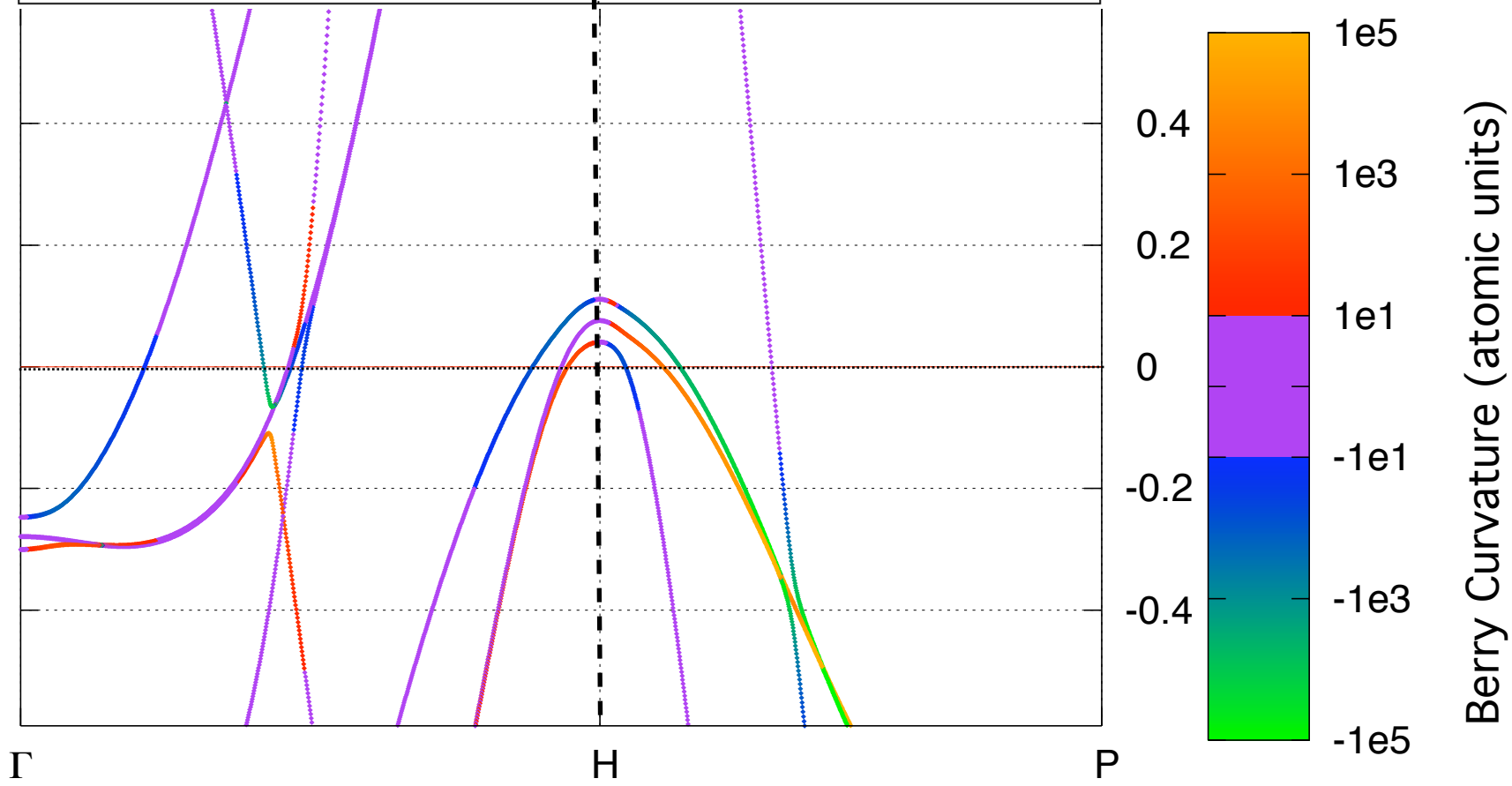


Berry Curvature



Total Berry Curvature

$$\Omega_{tot,z} = \sum_n f_n(\mathbf{k})\,\Omega_{n,z}(\mathbf{k})$$



Our Calculation

Ab-initio k-grid: 8x8x8

Interpolation k-grid: 320x320x320 + 7x7x7 “adaptive refinement”

(when Ω> 100 a.u.)

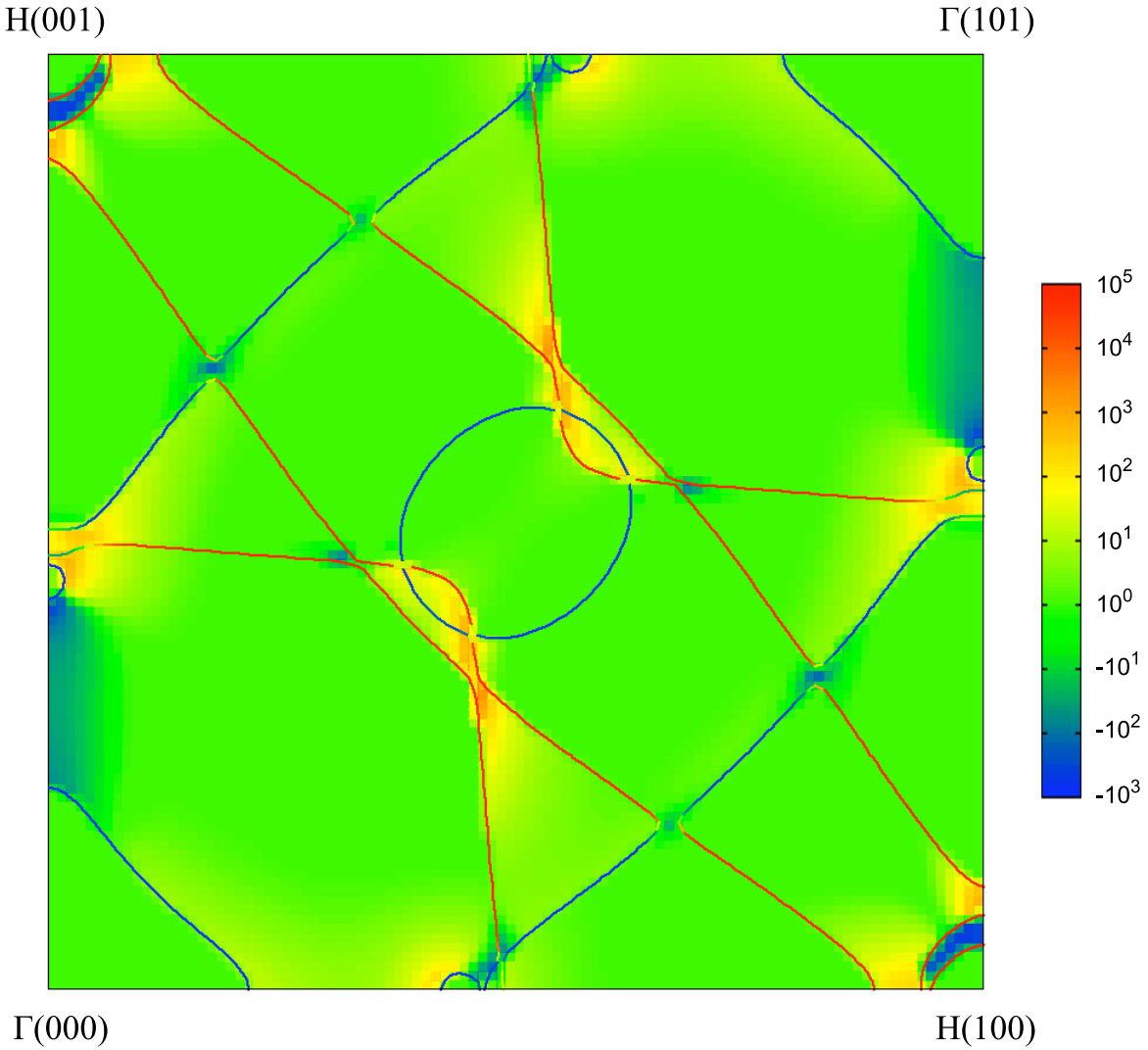
Wannier Interpolation	Existing Calculation*
planewaves + pseudopotentials	Kubo formula + LAPW
758 $(\Omega\ cm)^{-1}$	751 $(\Omega\ cm)^{-1}$

Experiment ~1000 $(\Omega\ cm)^{-1}$

Differences: Scattering, Approximate DFT, Experimental uncertainty

*Yao et al PRL (2004)

Berry curvature in k_y=0 plane

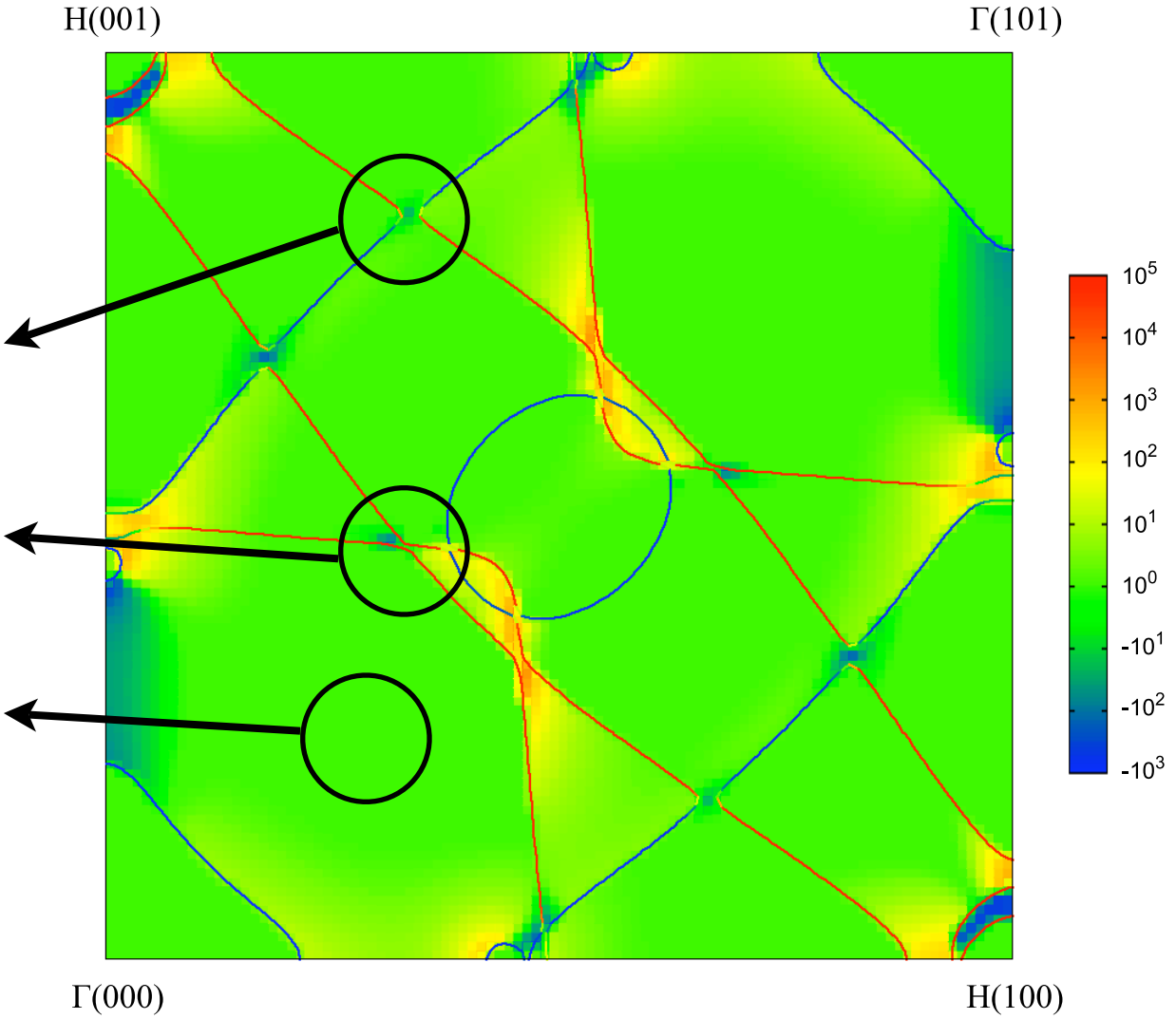


Total Berry curvature (atomic units)

Berry curvature in k_y=0 plane

Contributions

26%	opposite spin
21%	like spin
53%	smooth background



Total Berry curvature (atomic units)

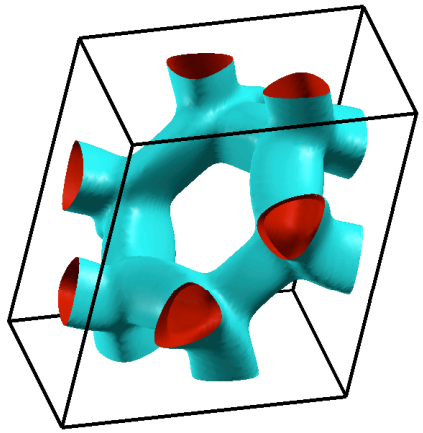
Wannier Interpolation

- Map low energy electronic structure onto “exact tight binding model”

- Compute quantities with ab-initio accuracy and tight-binding cost

> Basis set independent (planewaves, LAPW, guassians etc)
> Any single particle level of theory (LDA, LDA+U, GW)

- Many applications:
  - Accurate DOS, joint-DOS, Fermi Surfaces
  - Spin-relaxation
  - Magneto-crystalline anisotropy
  - NMR in metals (Knight shift)
  - Electron-phonon interaction



Acknowledgments

Ivo Souza : UC Berkeley
Wannier Interpolation: Phys Rev B 75 195121 (2007)

Anomalous Hall Effect
Xinjie Wang, David Vanderbilt : Rutgers University
Phys Rev B 74 195118 (2006)

Wannier90 code
Arash Mostofi, Nicola Marzari MIT
Released under the GPL at www.wannier.org

Electron-Phonon
Feliciano Guistino, Marvin Cohen, Steven Louie : UCB
Phys Rev Lett 94 047005 (2007)

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