ICTP/Psi-k/CECAM School on Electron-Phonon Physics from First Principles

Trieste, 19-23 March 2018

cecam
Centre Européen de Calcul Atomique et Moléculaire

Maximally-localized Wannier functions

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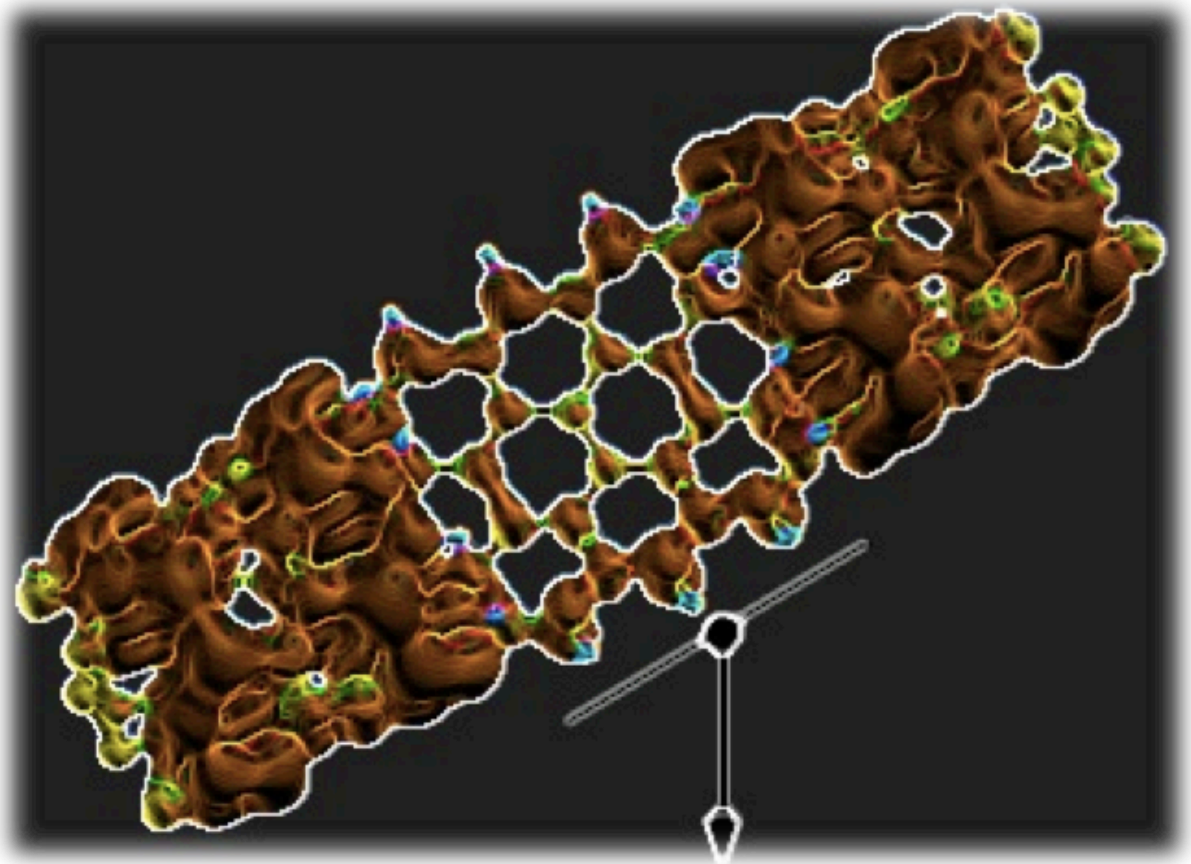
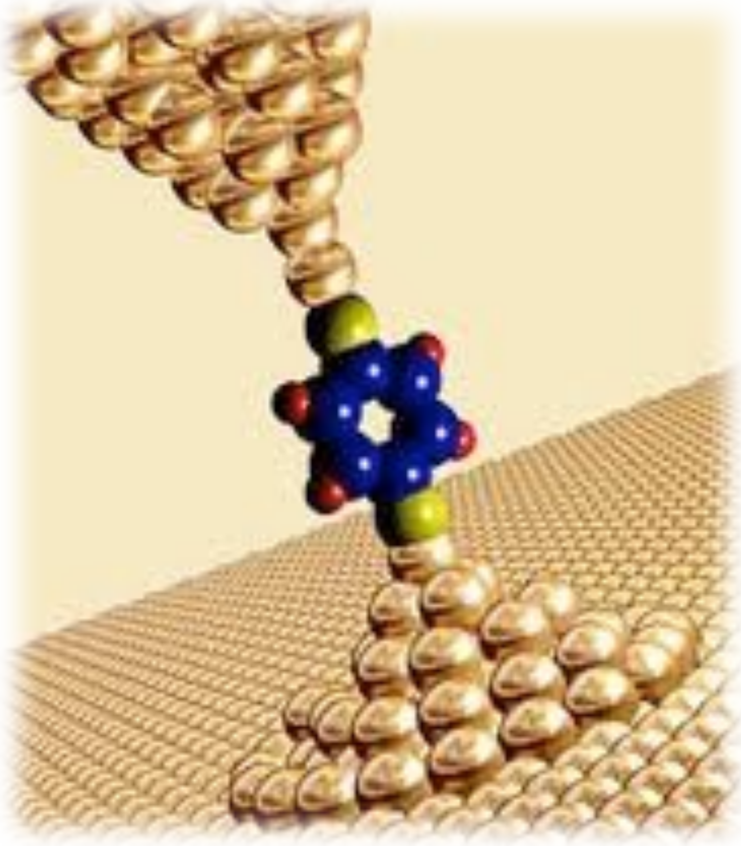
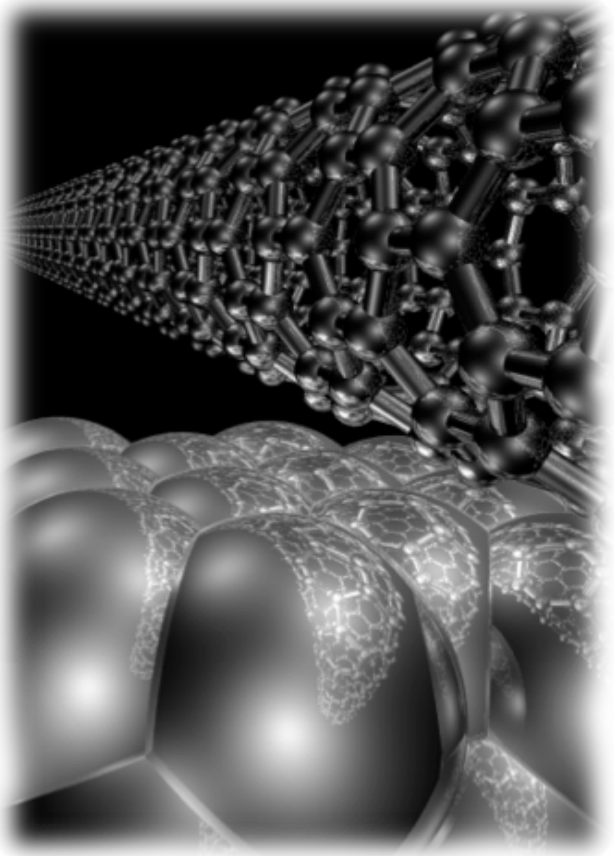
School on Electron-Phonon Physics from First Principles
Trieste, March 20th, 2018







References

- Marzari, N., and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997)
- Souza, I., N. Marzari, and D. Vanderbilt, Phys. Rev. B 65, 035109 (2001)
- N. Marzari et al., Rev. Mod. Phys. 84, 1419–1475 (2012)
- R. M. Martin, Electronic Structure: Basic Theory and Practical Methods, Cambridge, 2004
- www.wannier.org

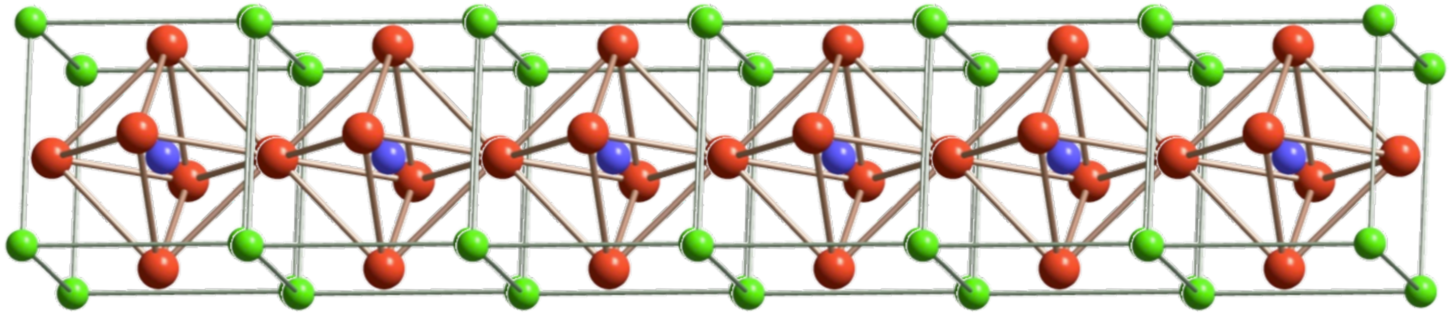
- **First part of the slides: courtesy of Prof. Nicola Marzari.**
  Can be found on the Wannier90 website: www.wannier.org under
  User Guide > NSF Summer School 2009 > N. Marzari Lecture Slides

PART I

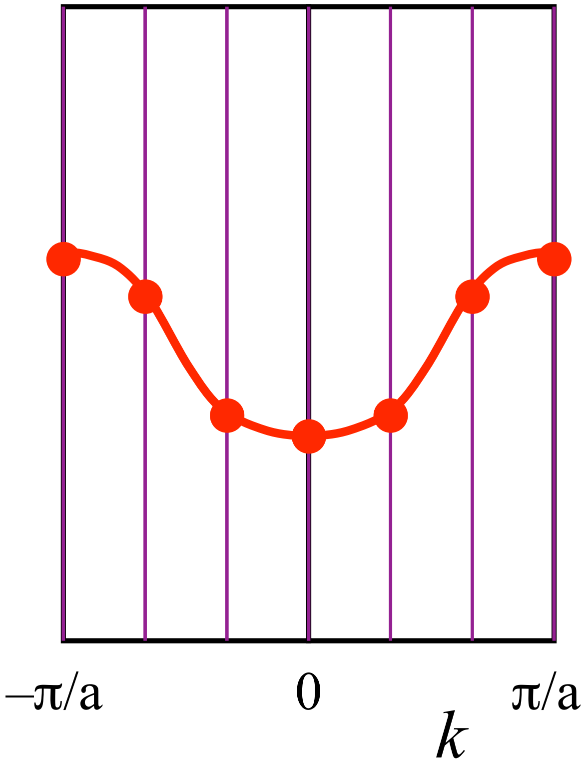
Wannier functions

Bloch Theorem

Crystal in real space:



Brillouin zone in reciprocal space:

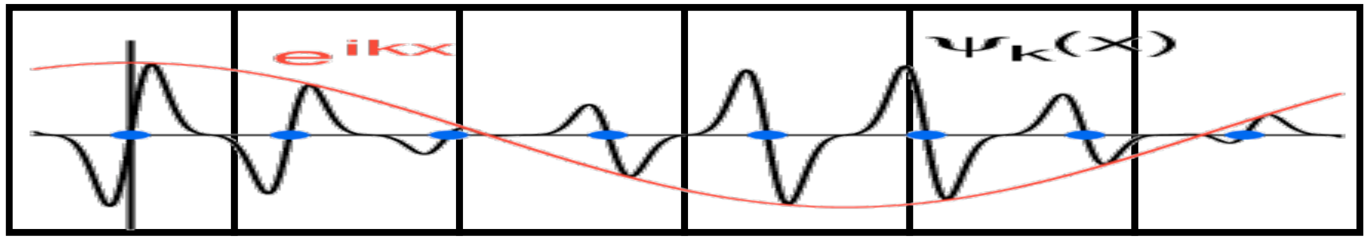


Courtesy of I. Souza / D. Vanderbilt

Bloch Theorem

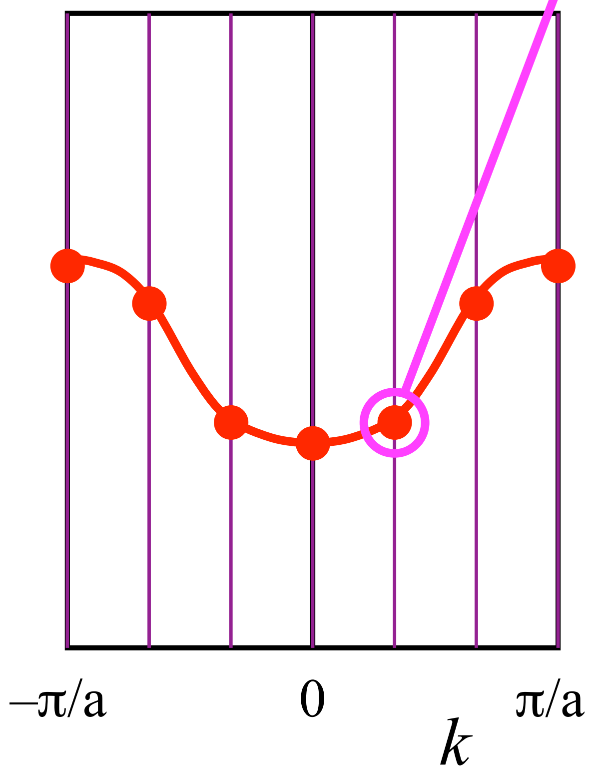
Crystal in real space:

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



defined on the whole
unit cell and periodic
over the cells

Brillouin zone in reciprocal space:



If there is only one band (*n*=1):

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

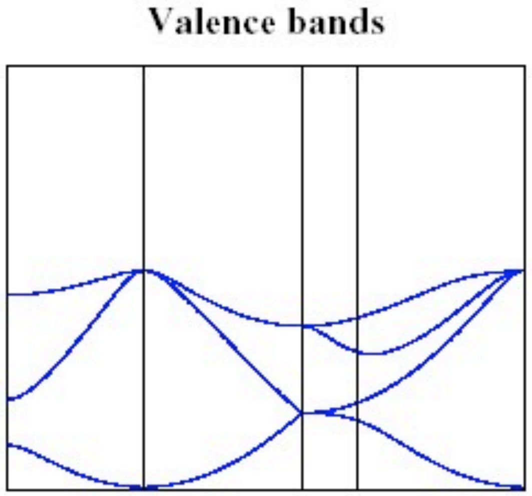
And we can define the Wannier functions:

$$|\boldsymbol{R}\rangle = \int_{BZ} \Psi_{\boldsymbol{k}}(\boldsymbol{r})e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}d\boldsymbol{k}$$

- One WF per lattice vector ***R*:** *N* in total with Born-von Karman PBC with *N* total unit cells
- They are all identical, only shifted: if we have $|\boldsymbol{R}_1\rangle$, $|\boldsymbol{R}_2\rangle$ they are shifted by $\boldsymbol{R}_2$ - $\boldsymbol{R}_1$

From Bloch Orbitals to Wannier Functions

Periodic $V_{\text{ext}} \quad \Rightarrow \quad \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}$



Multiband case, simplest thing to do:

$$|\mathbf{R}n\rangle = \int_{BZ} \Psi_{n\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

Gauge freedoms

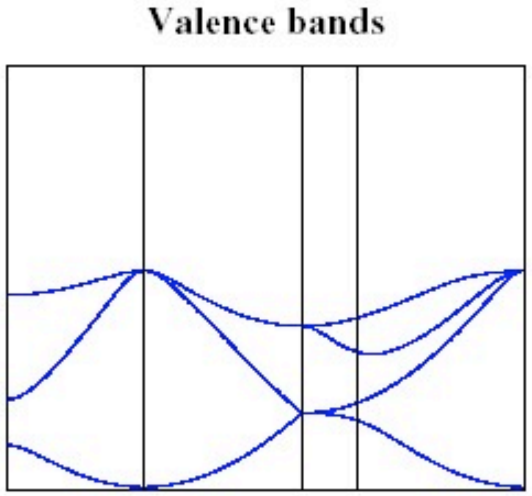
- Arbitrary phase factor for every $n\mathbf{k}$ (Schrödinger)

$$|\mathbf{R}n\rangle = \int_{BZ} \left[e^{i\phi_n(\mathbf{k})} \psi_{n\mathbf{k}}(\mathbf{r}) \right] e^{-i\mathbf{k}.\mathbf{R}} d\mathbf{k}$$

Note:
The shape of the
WFs (in real space)
will be different
for every phase!

From Bloch Orbitals to Wannier Functions

$$\text{Periodic } V_{\text{ext}} \;\Rightarrow\; \Psi_{n\mathbf{k}}(\mathbf{r}) \;=\; u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}$$



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$$|\mathbf{R}n\rangle \;=\; \int_{BZ} \Psi_{n\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

Gauge freedoms

- Arbitrary phase factor for every $n\mathbf{k}$ (Schrödinger)

More generally:
- Arbitrary unitary rotations $U_{mn}^{(\mathbf{k})}$ for every $\mathbf{k}$ (DFT)

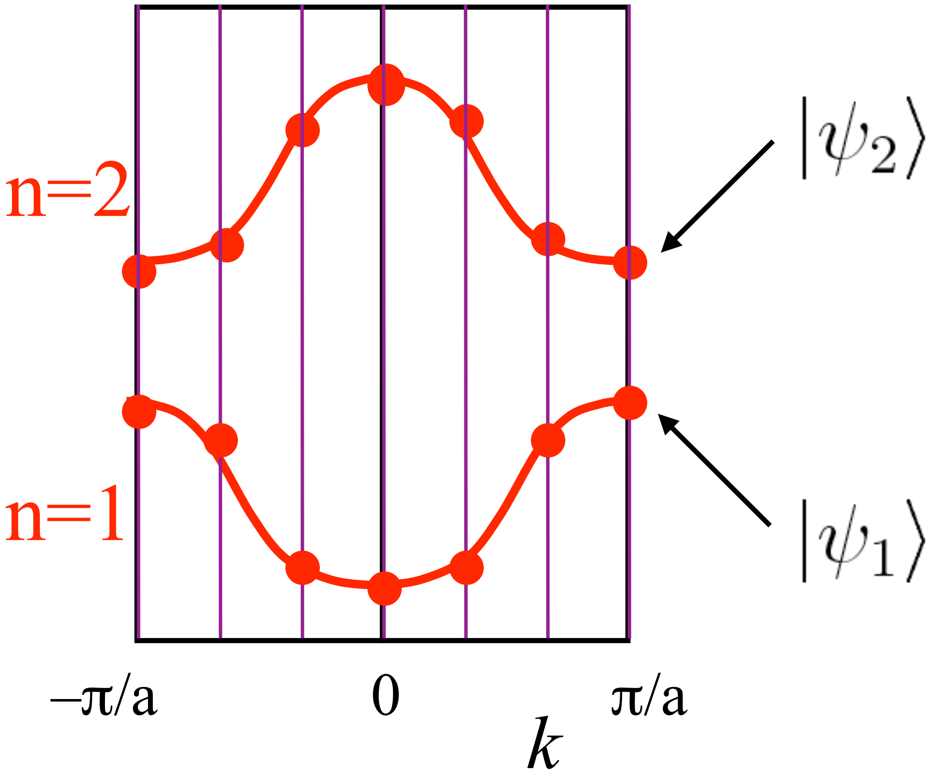
$$|\mathbf{R}n\rangle \;=\; \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})}\, \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

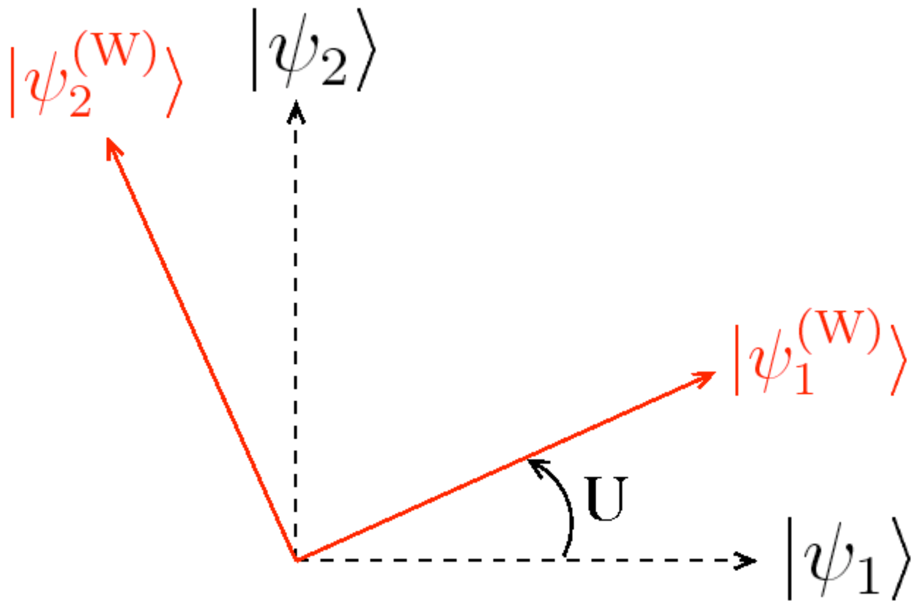
Orthogonal and unitary transformations

$$|\psi^{(\mathrm{W})}_{n\mathbf{k}}\rangle = \sum_m |\psi_{m\mathbf{k}}\rangle U^{(\mathbf{k})}_{mn}$$

Rotated Bloch function

Unitary matrix



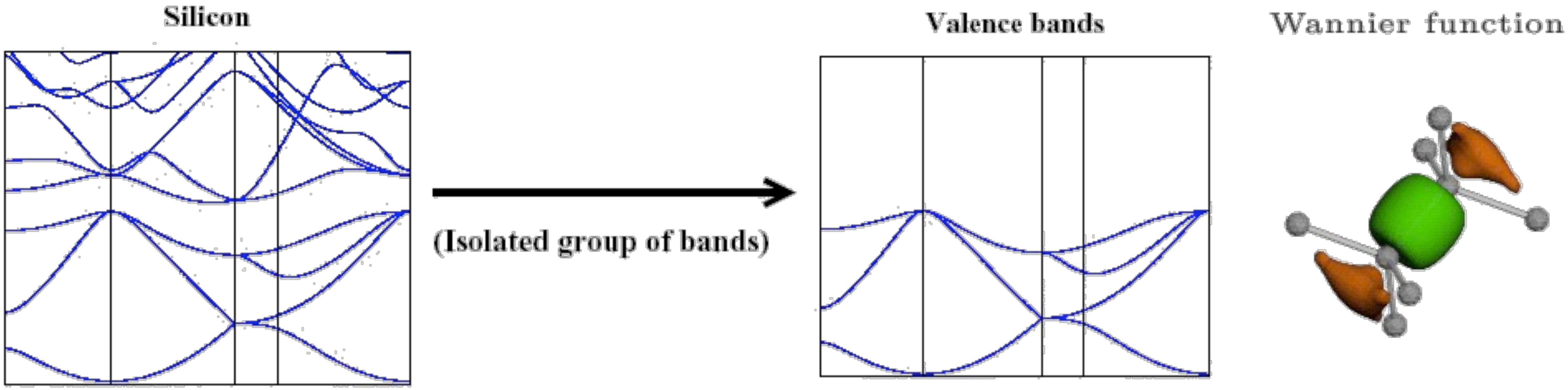


Courtesy of I. Souza / D. Vanderbilt

Generalized Wannier Functions for Composite Bands

- $\{|\mathbf{R}n\rangle\}$ span the same space as $\{|\Psi_{n\mathbf{k}}\rangle\}$
- $|\mathbf{R}n\rangle = w_n(\mathbf{r}-\mathbf{R})$ (translational images)
- $\langle\mathbf{R}n|\mathbf{R}'m\rangle = \delta_{n,m}\,\delta_{\mathbf{R},\mathbf{R}'}$

Each unitary matrix chooses a different set of WFs. We would like to choose the "best", i.e. the "maximally-localized"



The Localization Functional (Foster-Boys)

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

For a given set of Bloch orbitals, our goal is to minimize Ω with respect all the sets of unitary transformations $U_{mn}^{(\mathbf{k})}$

$$|\mathbf{R}n\rangle \;=\; \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \, \Psi_{m\mathbf{k}}(\mathbf{r}) \, e^{-i\mathbf{k}\cdot\mathbf{R}} \, d\mathbf{k}$$

N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997)

Decomposition of the Localization Functional

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

$$\Omega_{\mathrm{I}} = \sum_n \left[\langle r^2 \rangle_n - \sum_{\mathbf{R}m} \left| \langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle \right|^2 \right] \quad ,$$

$$\widetilde{\Omega} = \sum_n \sum_{\mathbf{R}m \neq \mathbf{0}n} \left| \langle \mathbf{R}m | \mathbf{r} | \mathbf{0}n \rangle \right|^2 \quad .$$

Ω_{I} and $\widetilde{\Omega}$ are *positive-definite* and Ω_{I} is *gauge-invariant*!

How to compute?
Blount identities

Centers of Wannier functions:

$$|\,w_0\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\;|\psi_{\mathbf{k}}\rangle \qquad \textit{definition}$$

$$= \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\; e^{i\mathbf{k}\cdot\mathbf{r}}\,|u_{\mathbf{k}}\rangle \qquad \textit{Bloch theorem}$$

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

$$\mathbf{r}\,|\,w_0\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\;\left(-i\nabla_{\mathbf{k}}\,e^{i\mathbf{k}\cdot\mathbf{r}}\right)|u_{\mathbf{k}}\rangle$$

$$= i\,\frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\; e^{i\mathbf{k}\cdot\mathbf{r}}\left(\nabla_{\mathbf{k}}\,|u_{\mathbf{k}}\rangle\right)$$

$$\boxed{\langle w_0\,|\,\mathbf{r}\,|\,w_0\rangle = i\,\frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\;\langle u_{\mathbf{k}}|\,\nabla_{\mathbf{k}}\,|u_{\mathbf{k}}\rangle}$$

WF center

Blount identities

Therefore:

Position operator ⇒ Gradient

$$\langle\, \mathbf{0}n \,|\, \mathbf{r}^l \,|\, \mathbf{0}m \,\rangle \;=\; \frac{V}{(2\pi)^3}\int \langle\, u_{n\mathbf{k}} \,|\left(i\frac{\partial}{\partial \mathbf{k}} \right)^l |\, u_{m\mathbf{k}} \,\rangle \, d\mathbf{k}$$

Numerical approach: numerical derivatives on a uniform k grid in the BZ

$$\nabla f(\mathbf{k}) \;=\; \frac{3}{Zb^2}\sum_{\mathbf{b}} \mathbf{b}\,[f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k})] \;\; .$$

We can then express positions and spreads as a function of the phase relations between neighboring Bloch orbitals

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

We can express the relevant quantities as a function of the *M*

$$\bar{\mathbf{r}}_n = -\frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_b\, \mathbf{b}\, \mathrm{Im}\ln M_{nn}^{(\mathbf{k},\mathbf{b})}$$

$$\langle r^2 \rangle_n = \frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_b \left\{ \left[1 - |M_{nn}^{(\mathbf{k},\mathbf{b})}|^2 \right] + \left[\mathrm{Im}\ln M_{nn}^{(\mathbf{k},\mathbf{b})} \right]^2 \right\}$$

To compute the maximal localization,
we *do not need to know the wavefunctions*, but only the overlaps M_{mn} matrices at neighbouring k-points

(after minimization, if we want to plot the Wannier functions in real space, we need instead to know the u_{nk} - in the code: files UNK)

Numerical approach: numerical derivatives on a uniform k grid in the BZ

$$\nabla f(\mathbf{k}) = \frac{3}{Zb^2} \sum_{\mathbf{b}} \mathbf{b} \left[f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k}) \right] \ .$$

We can then express positions and spreads as a function of the phase relations between neighboring Bloch orbitals

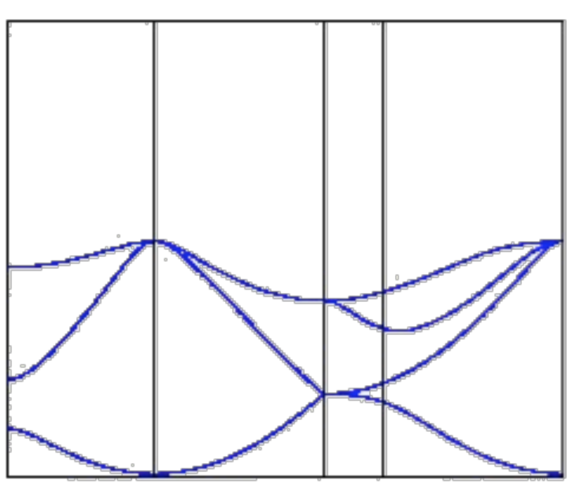
$$M_{mn}^{(\mathbf{k},\mathbf{b})} = \langle u_{m\mathbf{k}} \,|\, u_{n,\mathbf{k}+\mathbf{b}} \rangle$$

We can express the relevant quantities as a function of the M_{mn} matrices (these will be one of the main inputs to Wannier90)

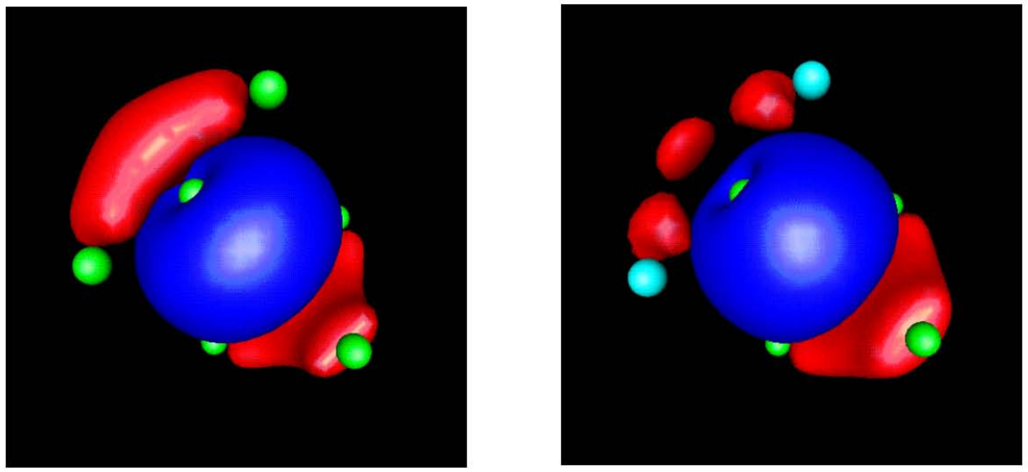
$$\bar{\mathbf{r}}_n = -\frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \, \mathbf{b} \, \mathrm{Im} \ln M_{nn}^{(\mathbf{k},\mathbf{b})}$$

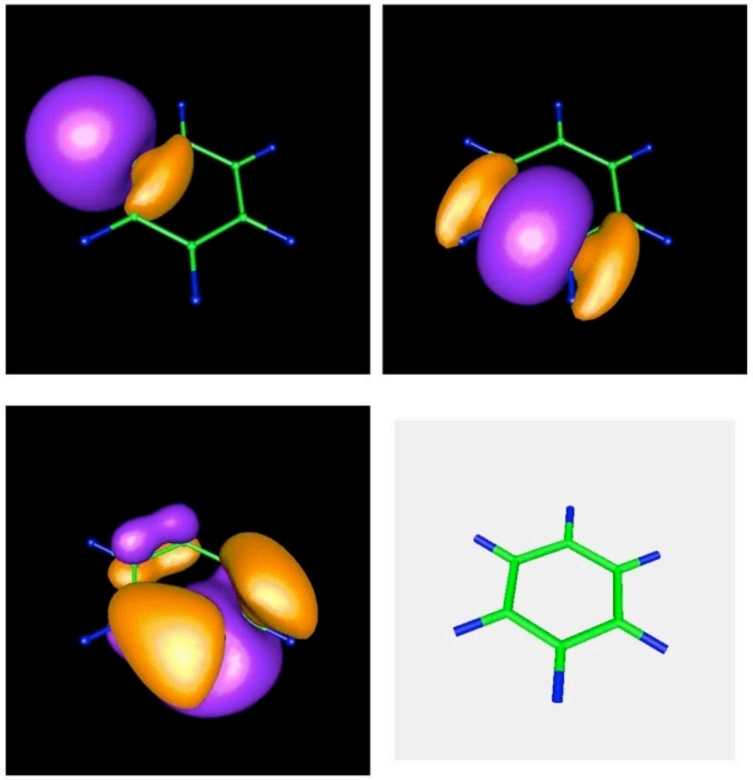
$$\langle r^2 \rangle_n = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \left\{ \left[1 - |M_{nn}^{(\mathbf{k},\mathbf{b})}|^2 \right] + \left[\mathrm{Im} \ln M_{nn}^{(\mathbf{k},\mathbf{b})} \right]^2 \right\}$$

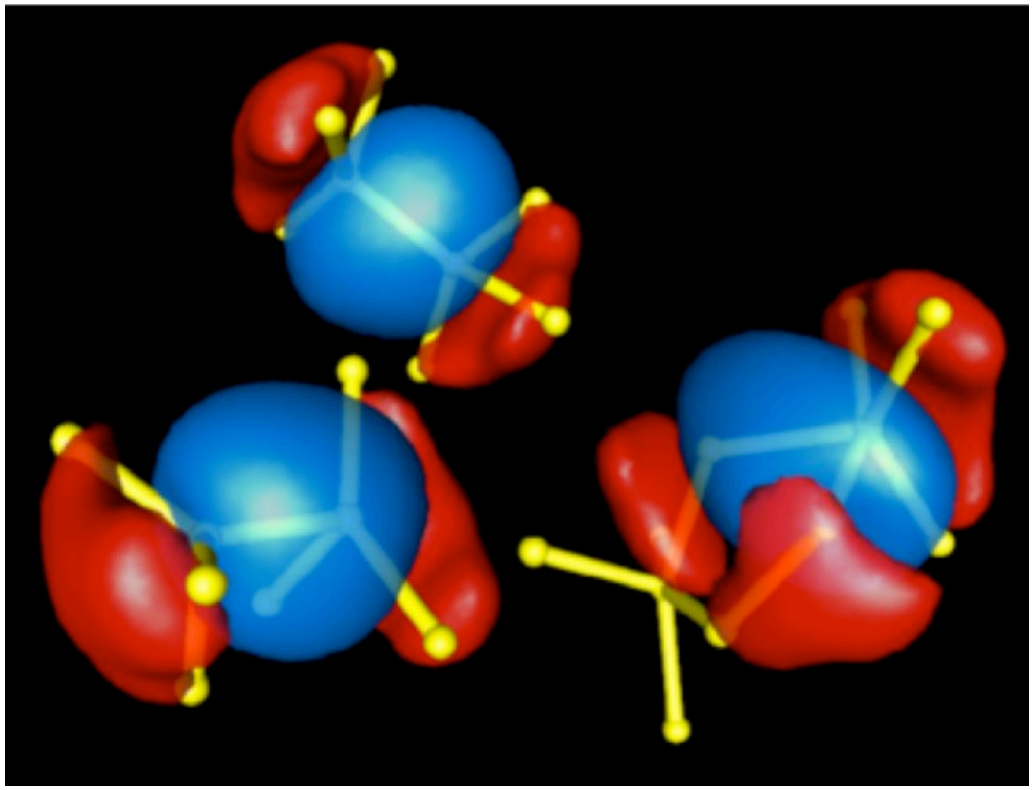
Silicon, GaAs, Amorphous Silicon, Benzene



Valence bands







M. Fornari, N. Marzari, M. Peressi, and A. Baldereschi, Comp. Mater. Science 20, 337 (2001)

The localisation procedure

- **Long-range decay**: Wannier functions corresponding to isolated valence bands decay to zero exponentially with the distance from their center

- At the *global* minimum (maximally-localized WFs) the Wannier functions are real
  (the code prints the max. absolute ratio of imaginary and real part to check this)

- We might find a *local* minimum! Care is needed

- If we expect (from physical/chemical considerations) the shape and position of Wannier functions, we can give an **initial guess** in the form of *projections on localised orbitals*

Real-Space Projectors

We can choose a real-space target function Φ_i (e.g. a Gaussian centered on bond i) to pick up a consistent phase that does not depend on the arbitrary $\phi_n(\mathbf{k})$ in $\Psi_{n\mathbf{k}}(\mathbf{r})$. Let $A_{in}^{(\mathbf{k})} = \langle \Psi_{n\mathbf{k}} | \Phi_i \rangle$,

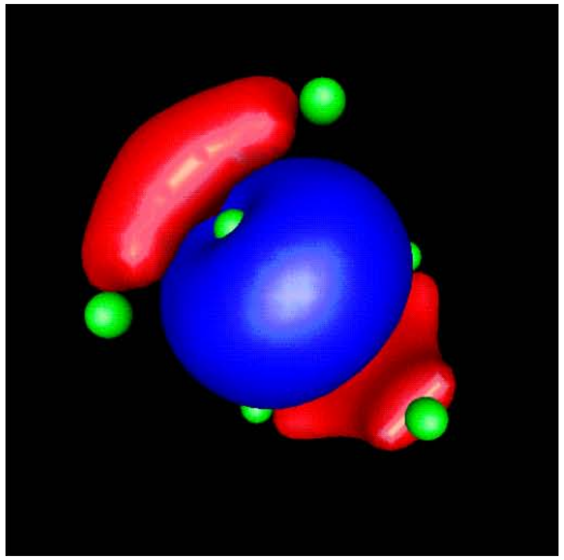
$$| w_i \rangle = \sum_{\mathbf{k}} | \Psi_{n\mathbf{k}} \rangle \langle \Psi_{n\mathbf{k}} | \Phi_i \rangle = \sum_{\mathbf{k}} A_{in}^{(\mathbf{k})} | \Psi_{n\mathbf{k}} \rangle \quad .$$

$A_{in}^{(\mathbf{k})}$ is not unitary, and so we use its unitary projection $U_{in}^{(\mathbf{k})}$:

$$A \rightarrow A\, A^{\dagger} \rightarrow U = (A\, A^{\dagger})^{-1/2} A = A\, (A^{\dagger} A)^{-1/2}$$

(the last equality can be proved using the Singular Value Decomposition for $A = U_1\, (diag)\, U_2$; it is $U = U_1 \frac{(diag)}{|(diag)|} U_2$).

Band structure interpolation



Wannier functions are defined by:

$$|\boldsymbol{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\boldsymbol{k})} \Psi_{m\boldsymbol{k}}(\boldsymbol{r}) e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} d\boldsymbol{k}$$

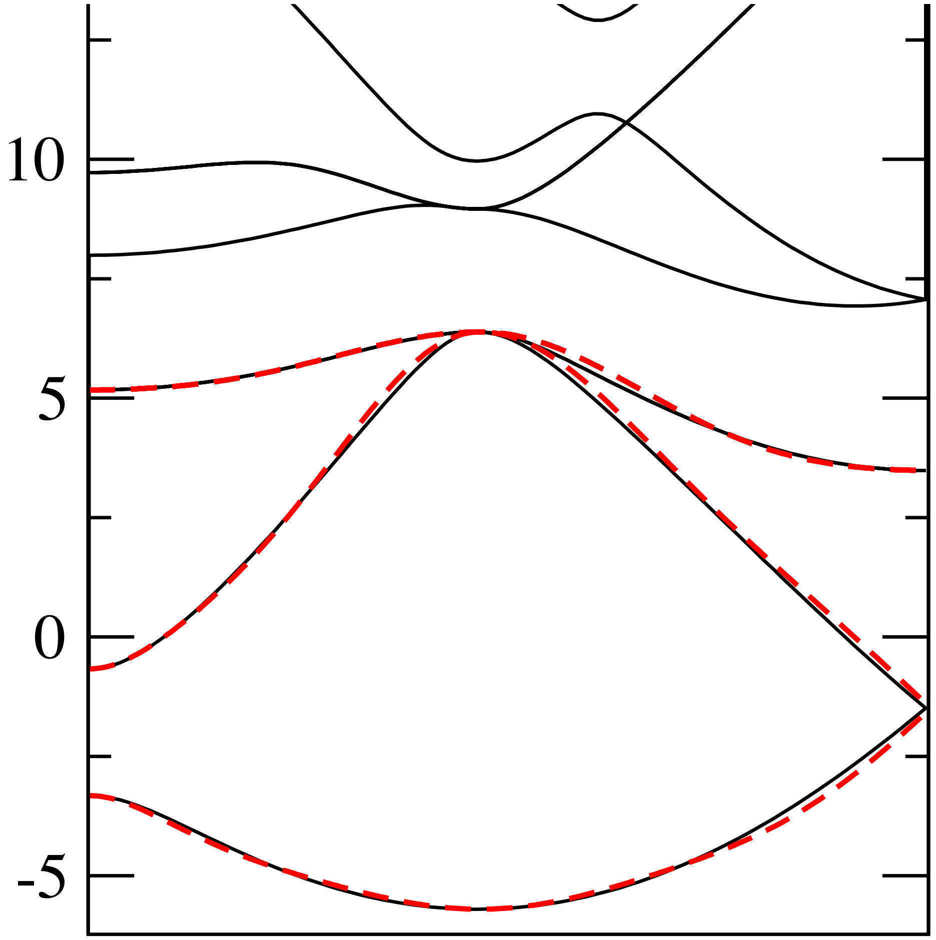
Where the U_{mn} are chosen by the minimisation procedure (one per every *k*-point in the ab-initio grid, typically relatively coarse, e.g. 6x6x6)

Conversely, we can Fourier-interpolate the Hamiltonian at any ***k***' vector even outside the original coarse grid:

$$H_{nm}^{W}(\boldsymbol{k}') = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}'\cdot\boldsymbol{R}} \langle \boldsymbol{0}n|H|\boldsymbol{R}m\rangle$$

where the Hamiltonian matrix elements are obtained from Fourier interpolation of the initial ab-initio Hamiltonian matrix, after rotating the basis set with the unitary *U* matrices.

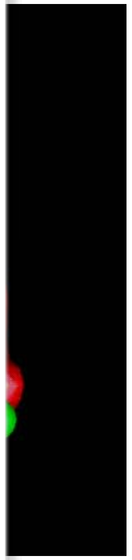
$$\langle \boldsymbol{0}n|H|\boldsymbol{R}m\rangle = \sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} [U^{\dagger}(\boldsymbol{k})H(\boldsymbol{k})U(\boldsymbol{k})]$$



The maximal localisation tries to make sure that the matrix elements of Wannier functions that are far away go quickly to zero.

In this way, the Fourier interpolation is very accurate

(choosing a 6x6x6 k-grid in the ab-initio calculation corresponds to cutting to zero matrix elements beyond a 6x6x6 supercell in real space)



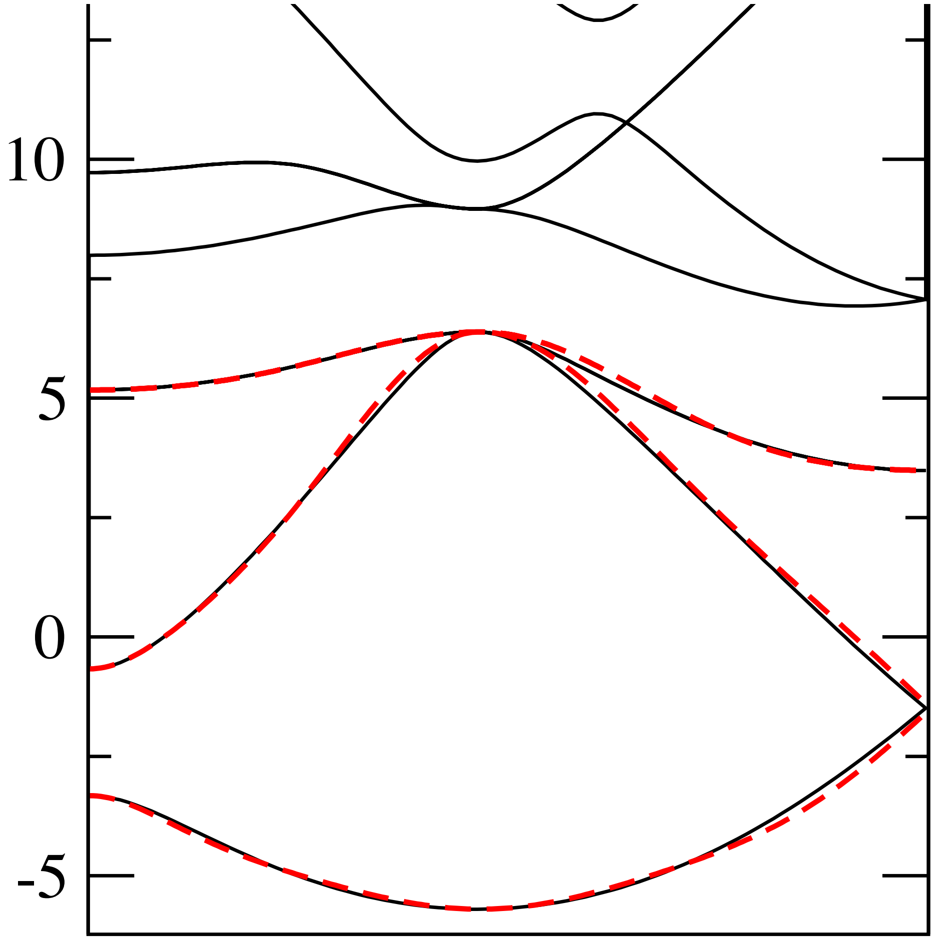
6)

Conversely, we can Fourier-interpolate the Hamiltonian at any ***k***' vector even outside the original coarse grid:

$$H^W_{nm}(\boldsymbol{k}') = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}'\cdot\boldsymbol{R}} \langle \boldsymbol{0}n|H|\boldsymbol{R}m\rangle$$

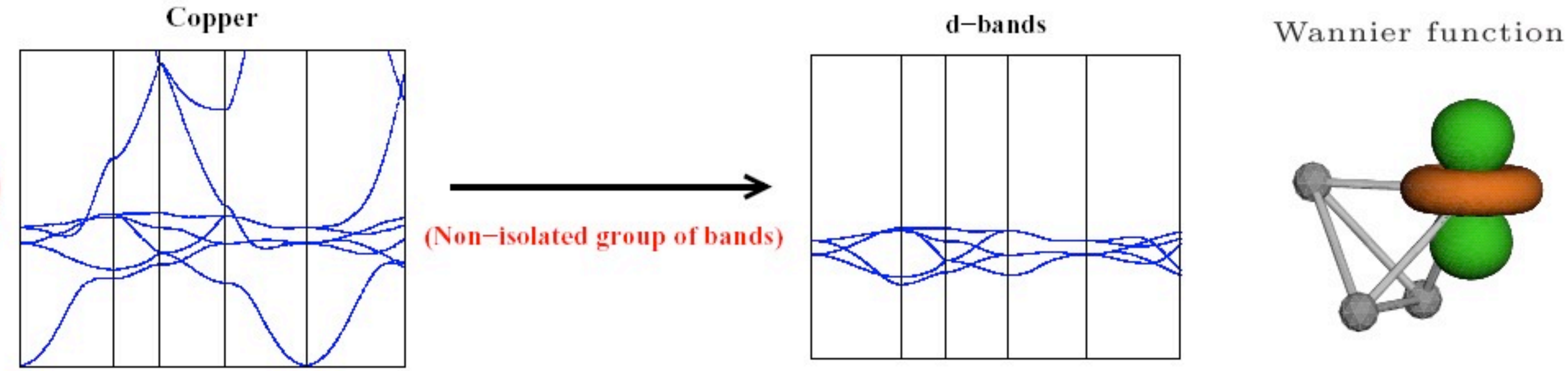
where the Hamiltonian matrix elements are obtained from Fourier interpolation of the initial ab-initio Hamiltonian matrix, after rotating the basis set with the unitary *U* matrices.

$$\langle \boldsymbol{0}n|H|\boldsymbol{R}m\rangle = \sum_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}[U^\dagger(\boldsymbol{k})H(\boldsymbol{k})U(\boldsymbol{k})]$$

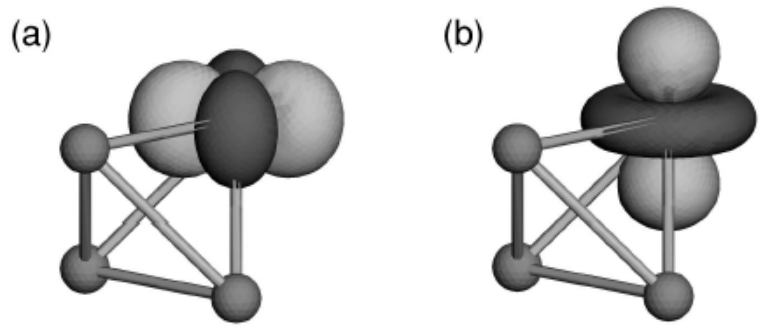


Disentanglement of Attached Bands

- Maximally-localized Wannier-like functions for conduction subspace
- Extract differentiable manifold with **optimal smoothness**



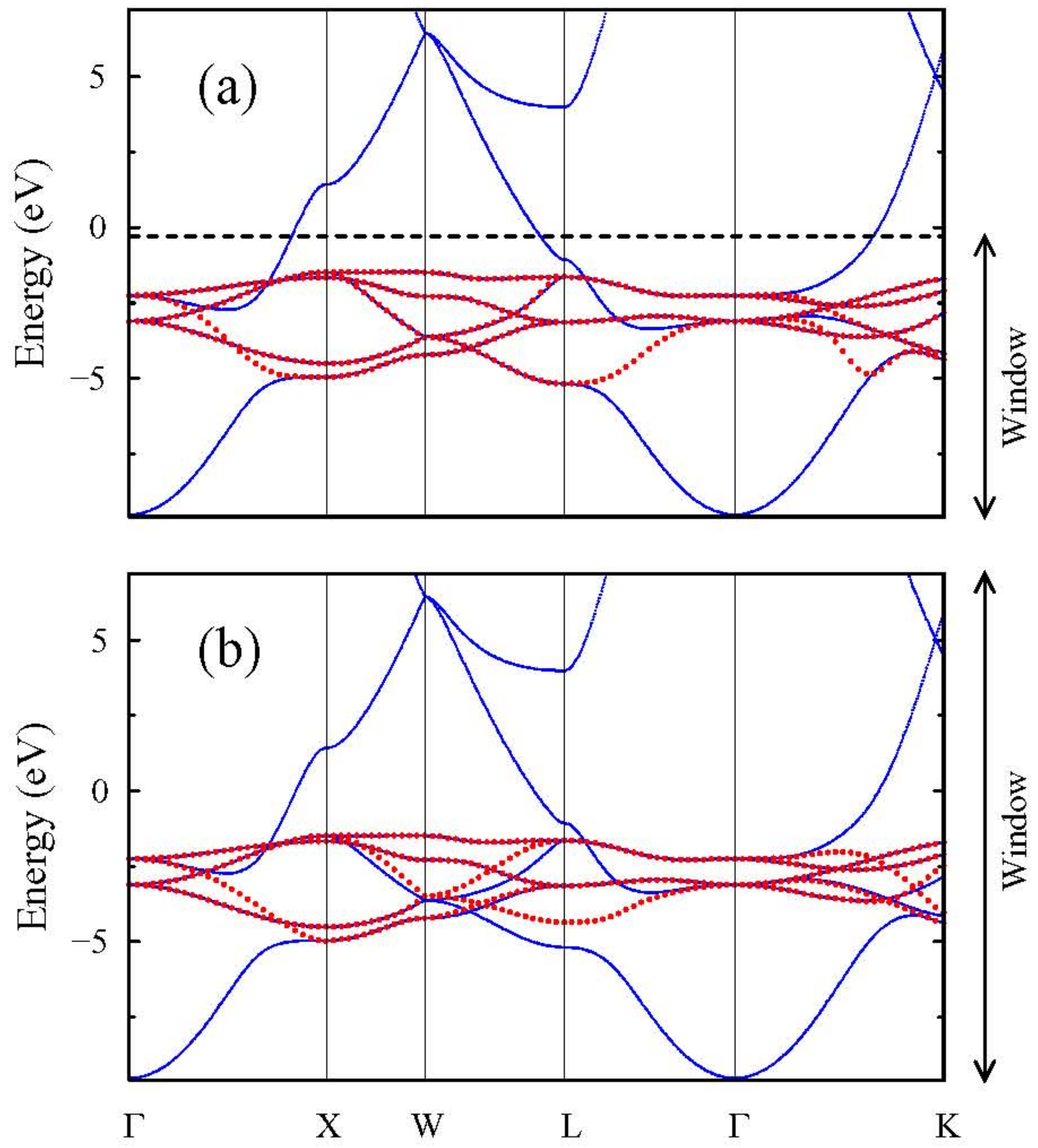
I. Souza, N. Marzari and D. Vanderbilt, Phys. Rev. B 65, 035109 (2002)



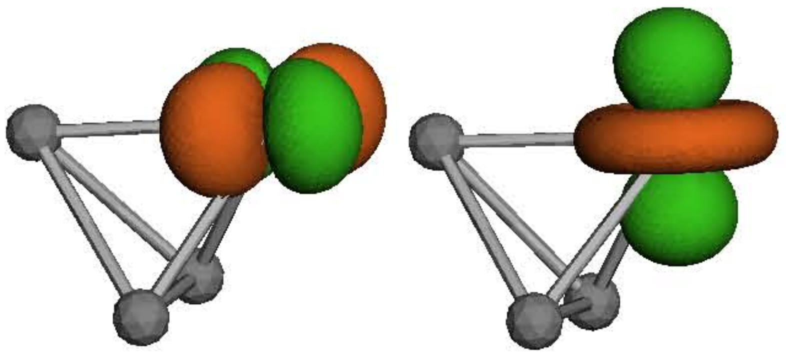
5 d orbitals

d Bands of Copper

Two possible choices of energy window



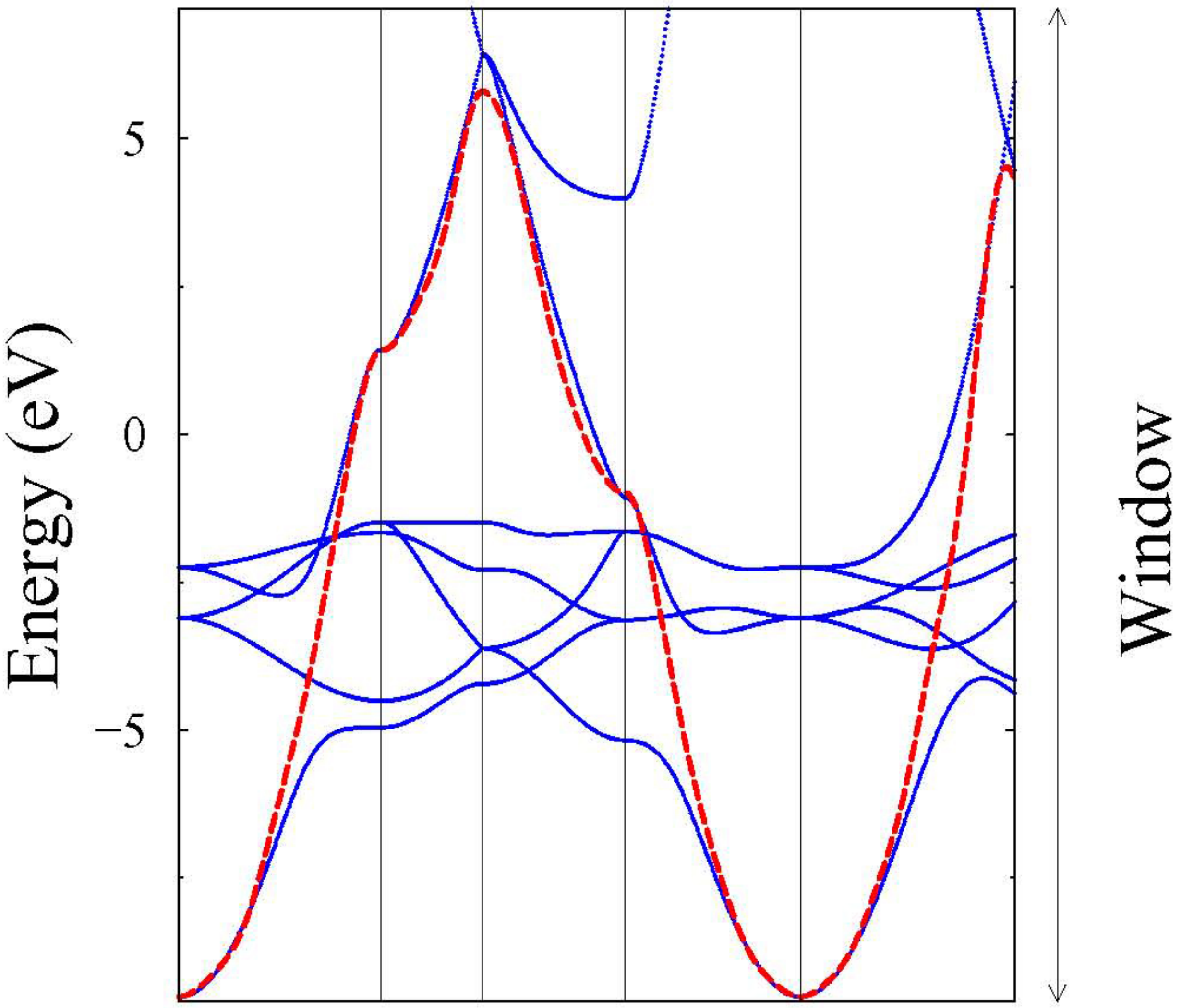
The e_g d WFs of panel (b)



spread(e_g)=1.700 bohr^2

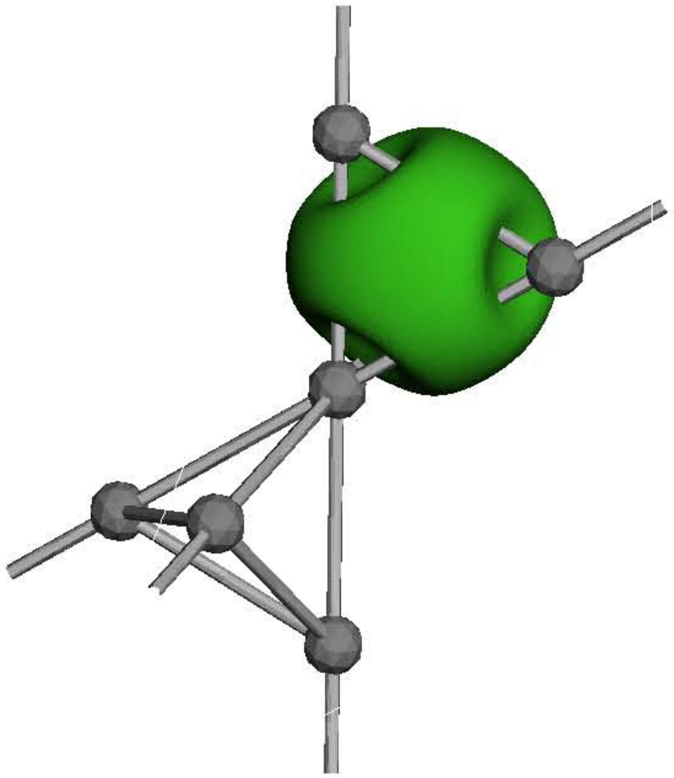
spread(e_g)=1.718 bohr^2

s Band of Copper



s-like Wannier function

spread=13.03 bohr^2

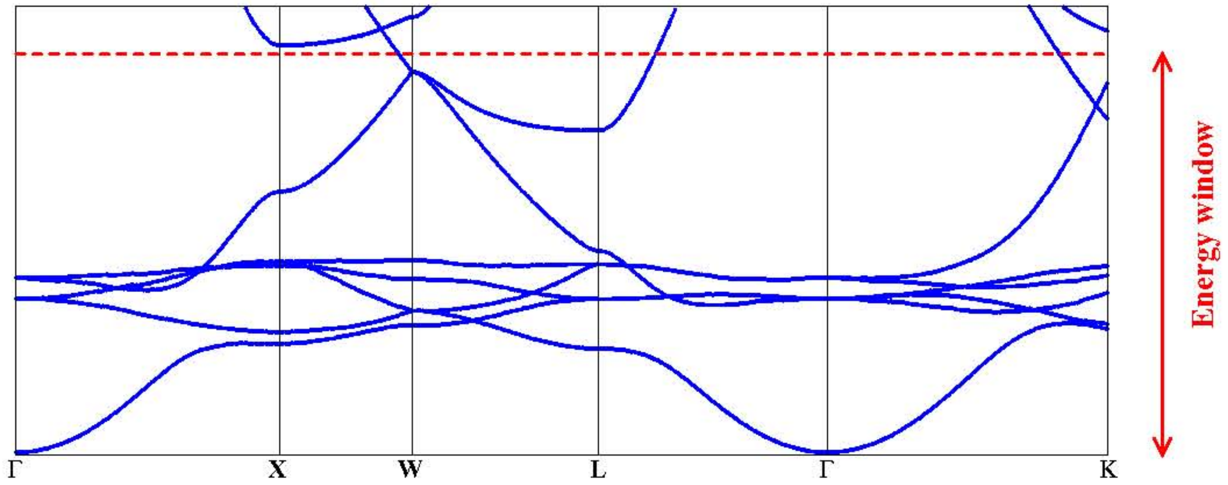


Disentanglement

- Step 1: "Disentangle the N bands of interest" from the rest

Cut out an energy window, so that at each $\mathbf{k}$ $N_{\mathbf{k}} \geq N$, where $N_{\mathbf{k}}$ is the number of bands that fall inside the window; this defines an $N_{\mathbf{k}}$-dimensional space.

If $N_{\mathbf{k}} > N$, find the N-dimensional subspace $\mathcal{S}(\mathbf{k})$ that minimizes Ω_{I}



- Step 2: Obtain maximally-localized WFs

Within the subspaces $\mathcal{S}(\mathbf{k})$ determined in Step 1 (which have a fixed Ω_{I}) minimize $\widetilde{\Omega}$, using the algorithm of Marzari & Vanderbilt

$$\boxed{\Omega_{\rm I} = \sum_n \left[\langle r^2\rangle_n - \sum_{\mathbf{R}m} \left|\langle \mathbf{R}m|\mathbf{r}|\mathbf{0}n\rangle\right|^2 \right]}, \qquad \widetilde{\Omega} = \sum_n \sum_{\mathbf{R}m\neq\mathbf{0}n} \left|\langle \mathbf{R}m|\mathbf{r}|\mathbf{0}n\rangle\right|^2 .$$

- $\Omega_{\rm I}$ measures the change of character across the Brillouin zone of the states in the spaces $\mathcal{S}(\mathbf{k})$: Large $|\langle u_{n\mathbf{k}}|u_{m,\mathbf{k}+\delta\mathbf{k}}\rangle| \Rightarrow$ small $\Omega_{\rm I}$

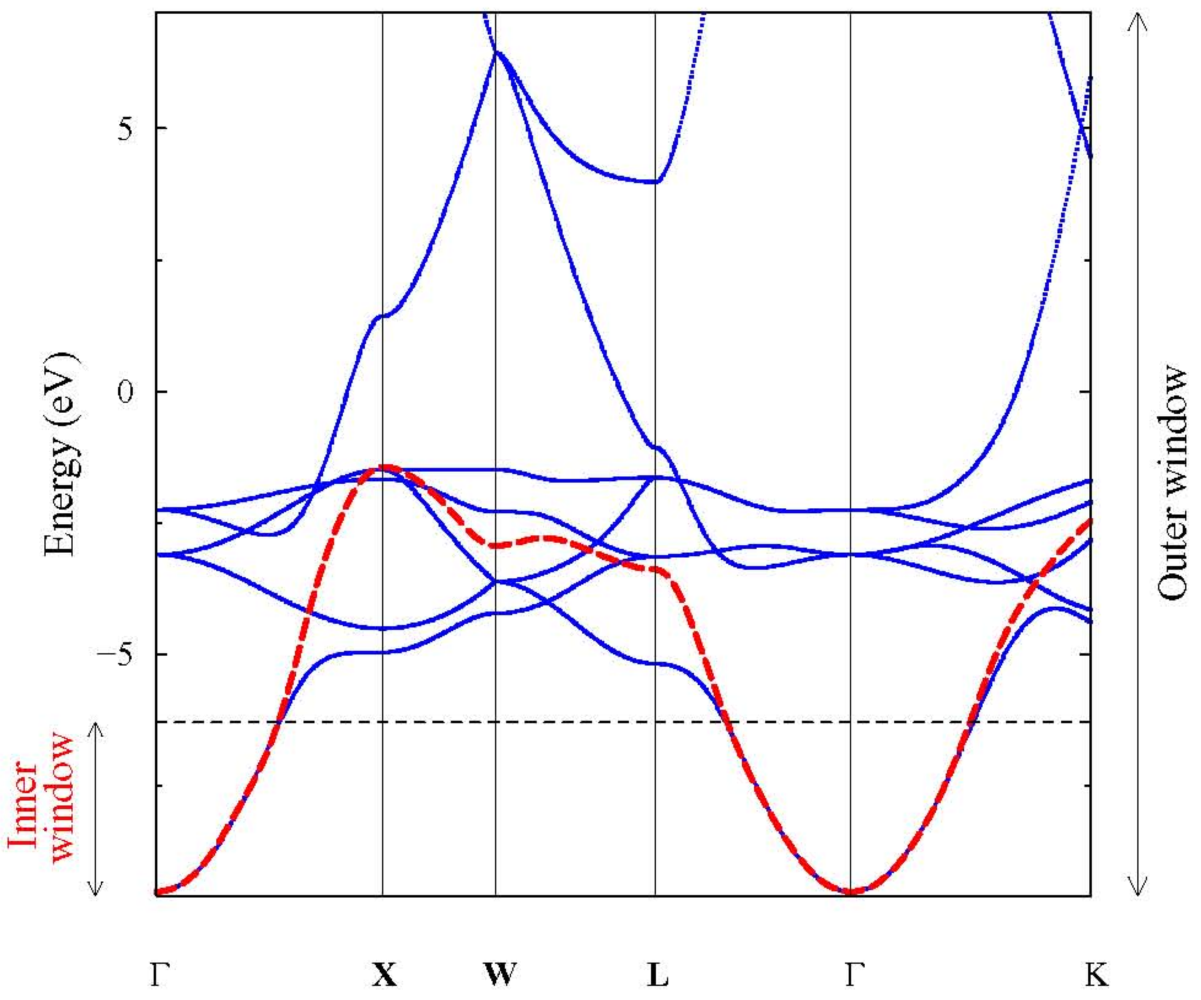
- $\Omega_{\rm I}$ measures the degree of mismatch, or "spillage", between the nearby spaces $\mathcal{S}(\mathbf{k})$.

$\Longrightarrow$ In the case of copper, when choosing $N = 5$ the minimization of $\Omega_{\rm I}$ will extract a 5-dimensional subspace containing the d-like states at each $\mathbf{k}$ – which have a similar character – while excluding the s band, which has a very different character.

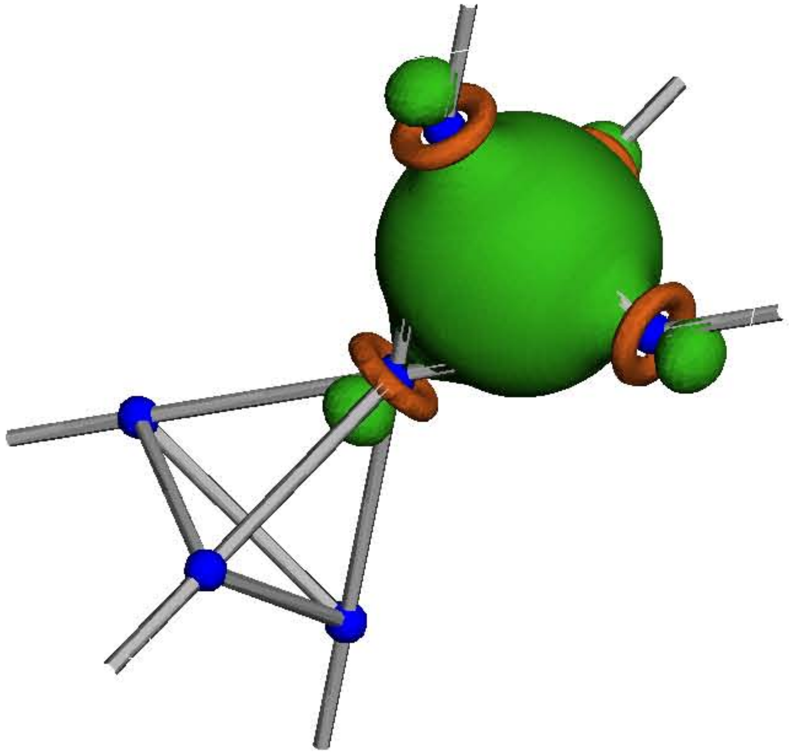
Exact Constraints on the Inner Energy

Suppose we want WFs to describe the original bands exactly in a prescribed energy range ("inner window").

$\Rightarrow$ Minimize Ω_{I} w/ constraint that states inside inner window are included in the optimal subspaces $\mathcal{S}(\mathbf{k})$



Hybrid *s*-*d* character:

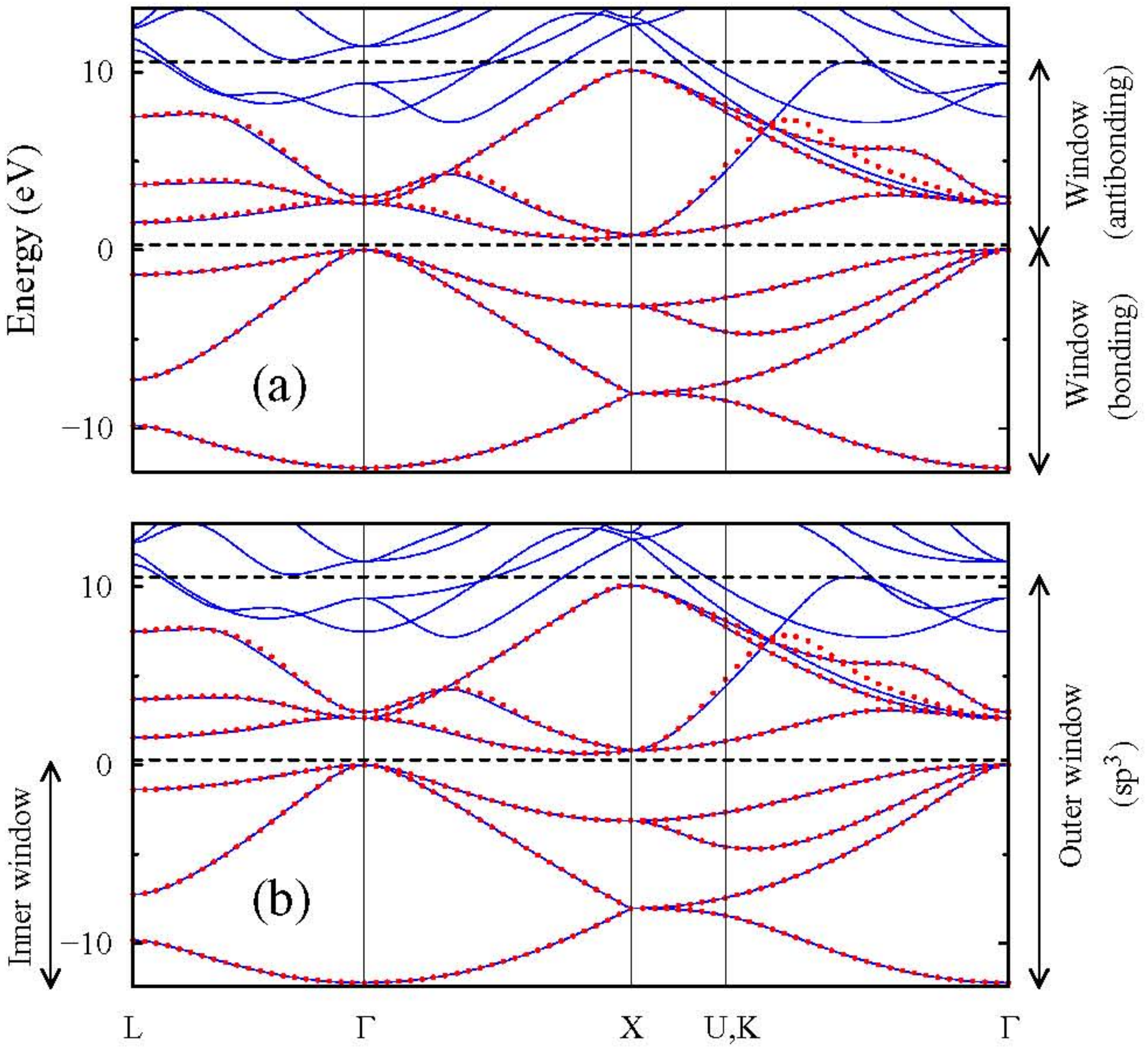


Disentanglement with a frozen window is also useful in an insulator/semiconductor

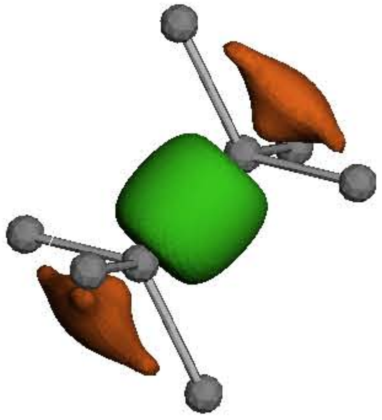
The case of conduction bands of silicon

With two independent Wannierizations (valence & conduction)

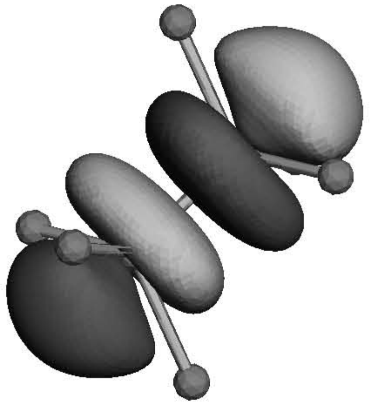
With a single Wannierization for valence+conduction



Bonding

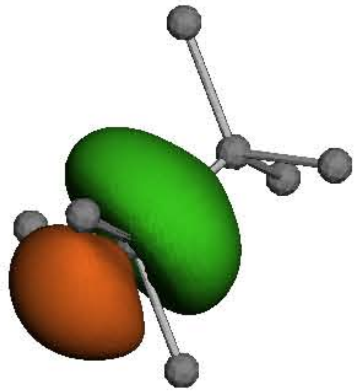


Antibonding



$7.53\ \text{bohr}^2$ $24.37\ \text{bohr}^2$

sp^3



spread$=10.68\ \text{bohr}^2$

Disentanglement: Conduction Bands in (5,5) SWNT