Maximally localized Wannier functions

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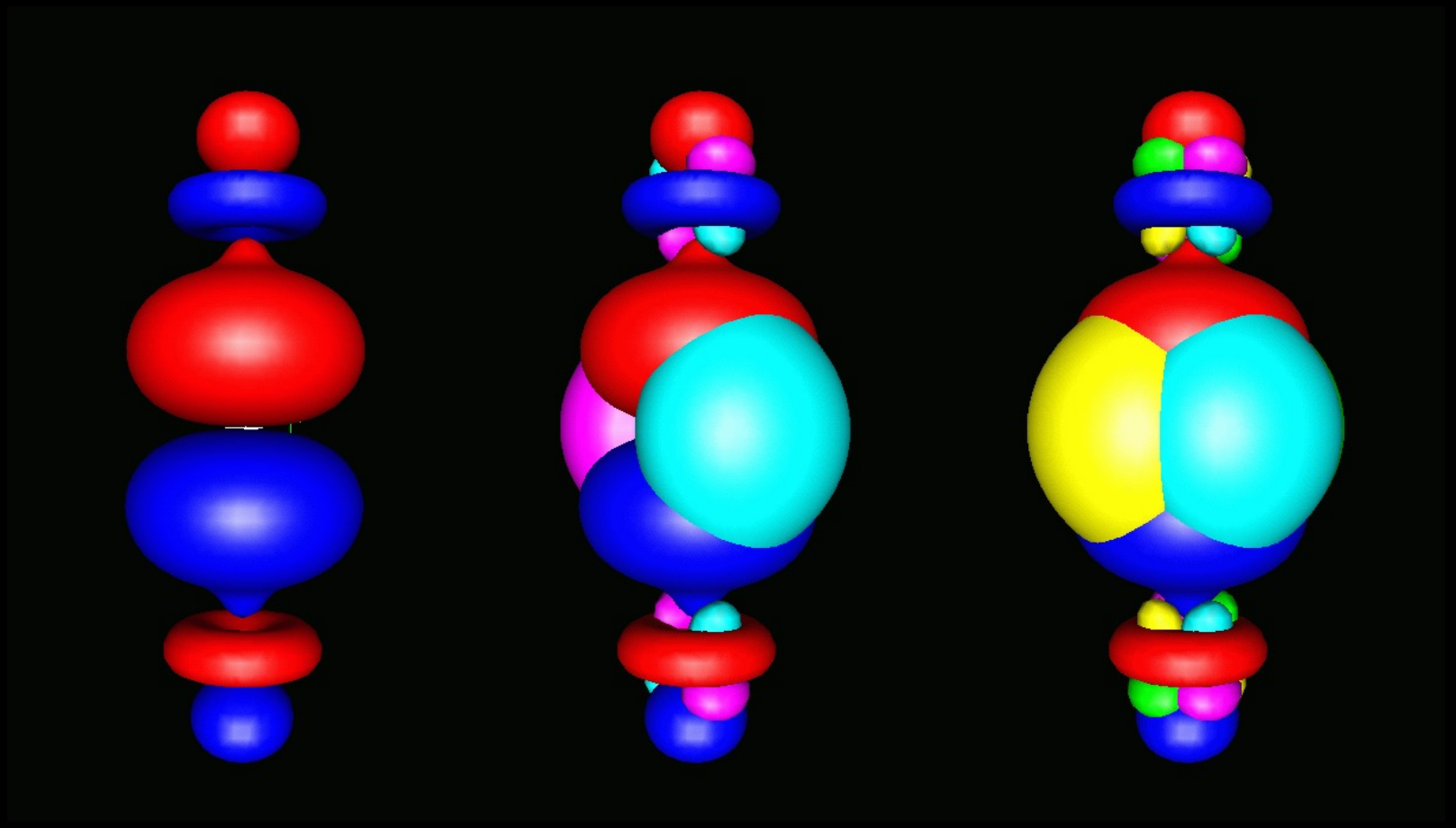
Theory and Simulation of Materials (THEOS), EPFL



Acknowledgments

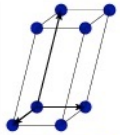
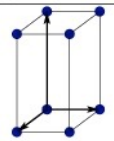
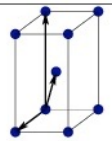
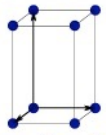
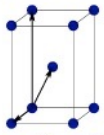
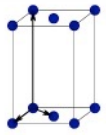
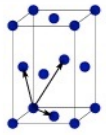
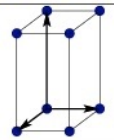
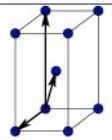
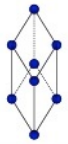
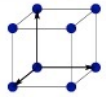
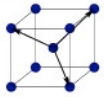
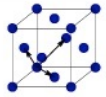
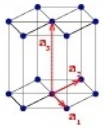
Giovanni Pizzi – EPFL
Arash Mostofi - Imperial College
Jonathan Yates – University of Oxford
Ivo Souza - San Sebastian
David Vanderbilt - Rutgers

Maximally localized Wannier functions: Theory and applications
Nicola Marzari, Arash A. Mostofi, Jonathan R. Yates, Ivo Souza, David Vanderbilt
Rev. Mod. Phys. 84, 1419-1475 (2012)

Wannier90 as a community code: new features and applications
G. Pizzi et al., J. Phys. Cond. Matt. 32, 165902 (2020)

www.wannier.org

Direct and reciprocal lattice

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

$\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ define the primitive unit cell

$$\vec{G}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$$

$\vec{G}_1$, $\vec{G}_2$ and $\vec{G}_3$ span the reciprocal lattice

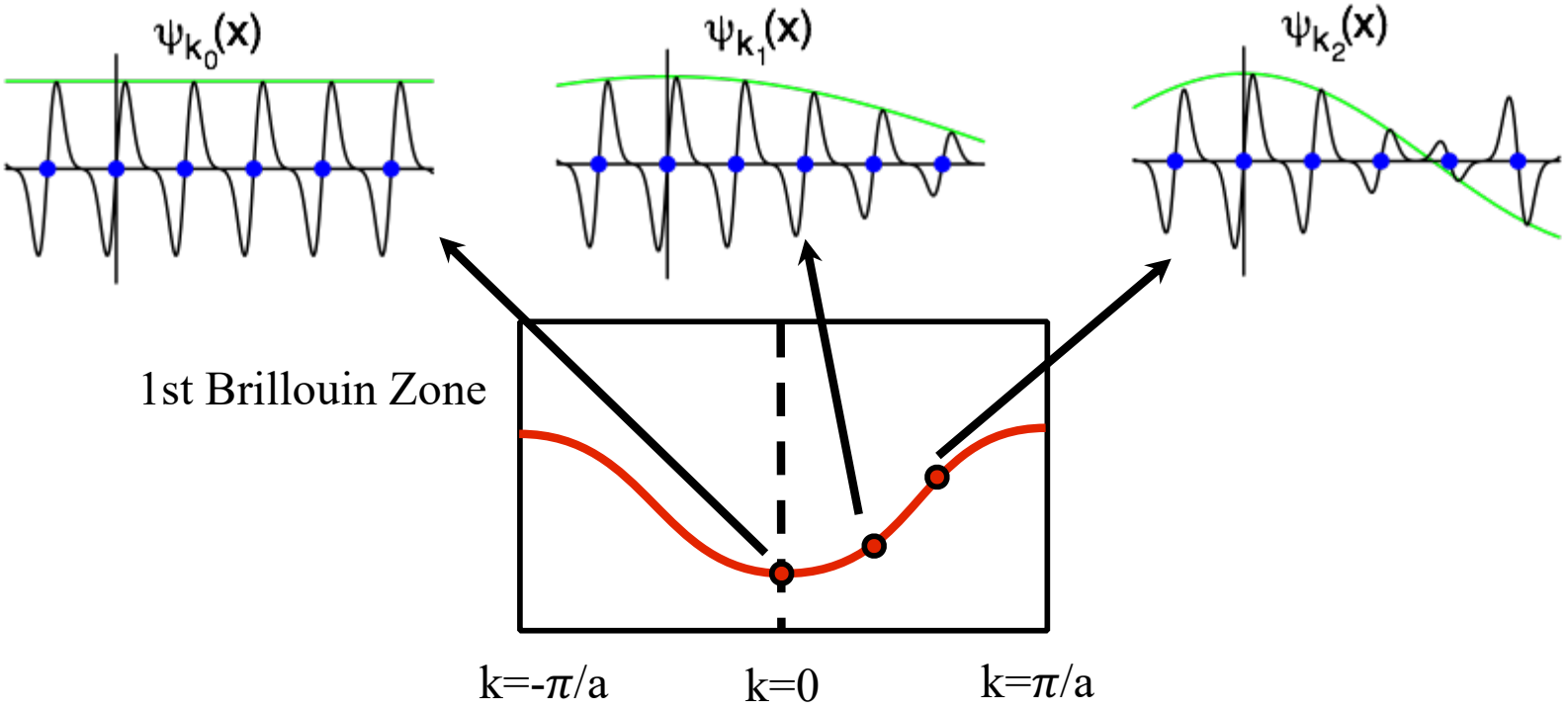
Bloch Theorem

The one-particle effective Hamiltonian $\hat{H}$ in a periodic lattice commutes with the lattice-translation operator $\hat{T}_{\mathrm{R}}$, allowing us to choose the common eigenstates according to the prescriptions of Bloch theorem:

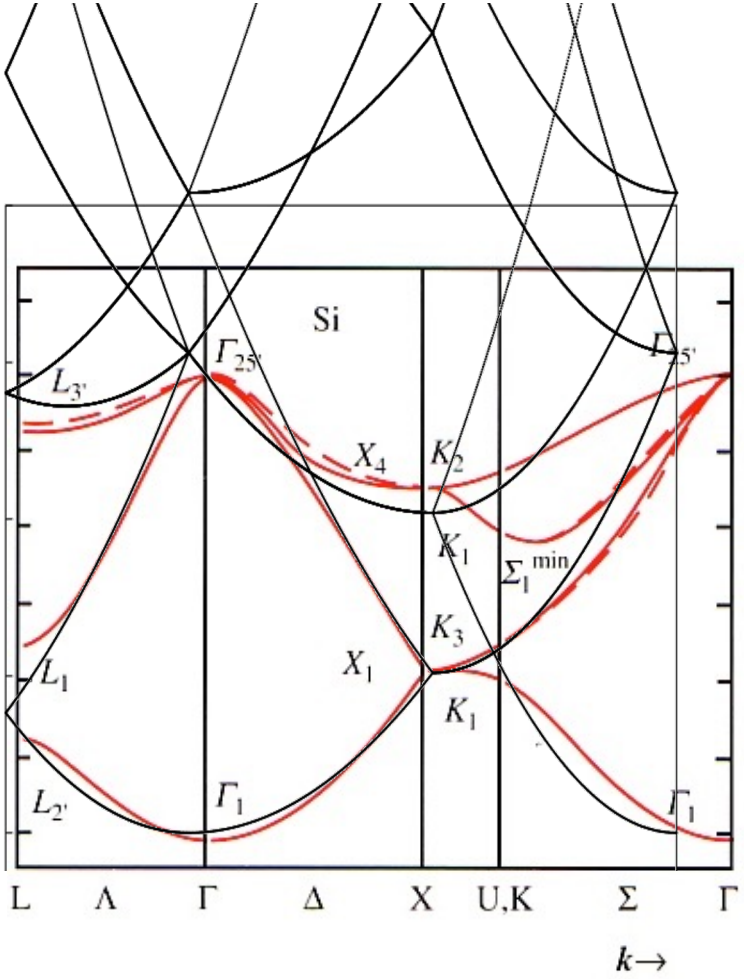
$$[\hat{H}, \hat{T}_{\mathrm{R}}] = 0 \quad \Rightarrow \quad \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}$$

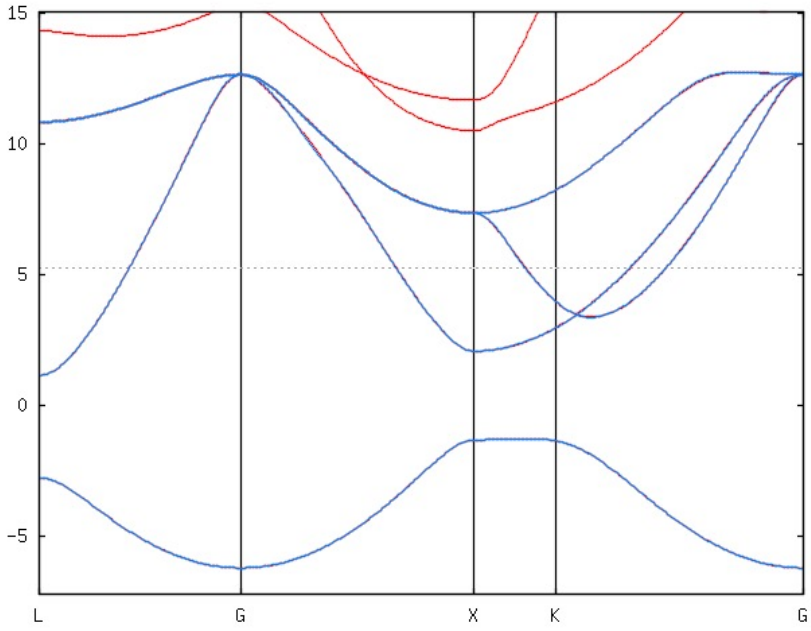
- *n, k* are the quantum numbers (band index and crystal momentum), *u* is periodic
- From two requirements: a translation can't change the charge density, and two translations must be equivalent to one that is the sum of the two

Bloch wavefunctions in 1d



Band Structures: Si and Pb

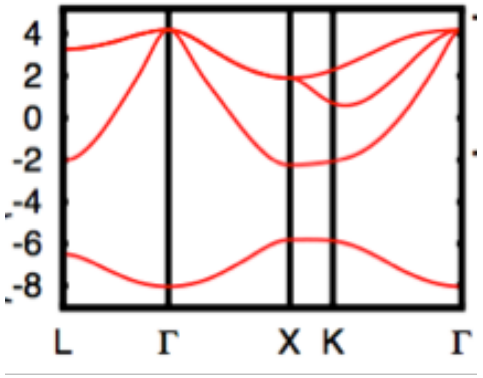




From Bloch Orbitals to Wannier Functions

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

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



Gauge freedoms

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

From Bloch Orbitals to Wannier Functions

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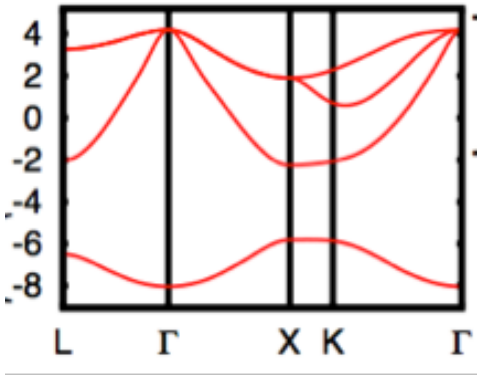


Gauge freedoms

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

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

Long-Range Decay (Heuristic...)

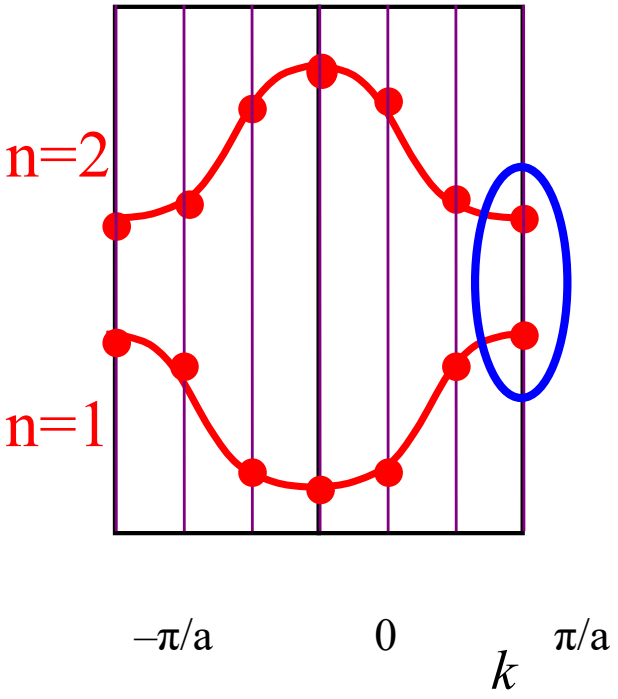
Isolated band, Wannier function around the origin

$$w_0(\mathbf{r}) = \int_{BZ} \Psi_{\mathbf{k}}(\mathbf{r})\, d\mathbf{k} = \int_{BZ} u_{\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{k}$$

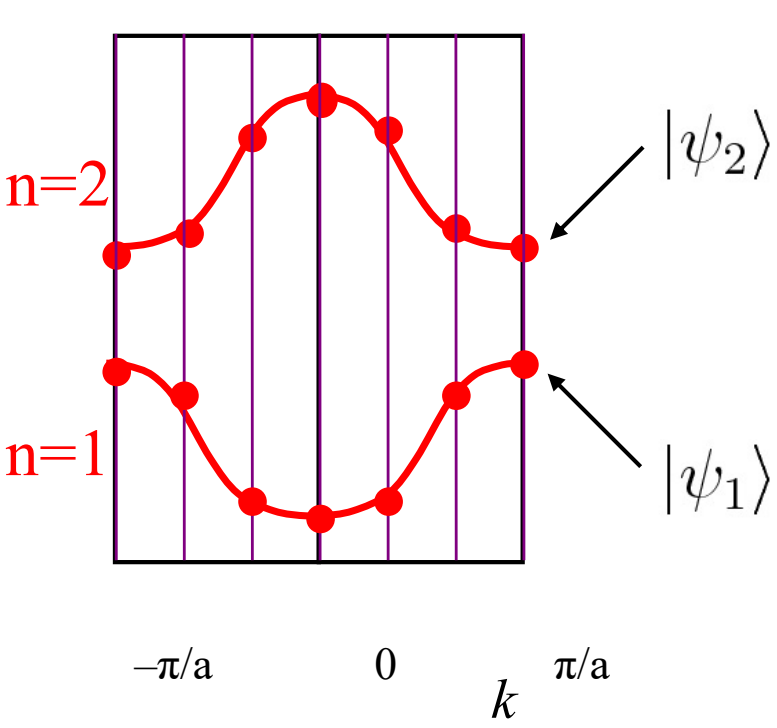
For $\mathbf{r} \to \infty, \mathbf{r} = \mathbf{R}_i$

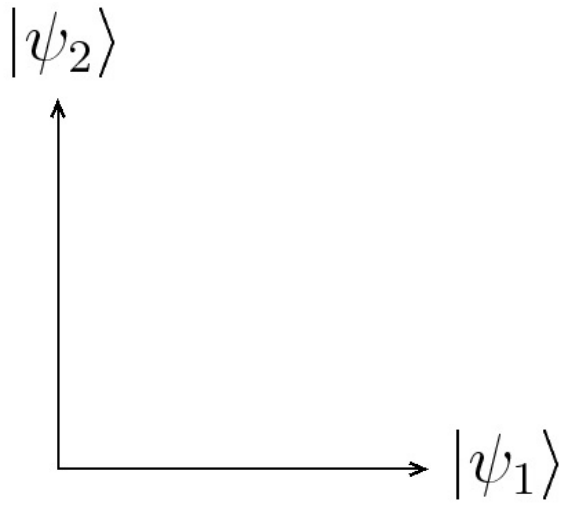
$$w_0(\mathbf{R}_i) = \int_{BZ} u_{\mathbf{k}}(0)\, e^{i\mathbf{k}\cdot\mathbf{R}_i}\, d\mathbf{k}$$

Orthogonal and unitary transformations



Orthogonal and unitary transformations



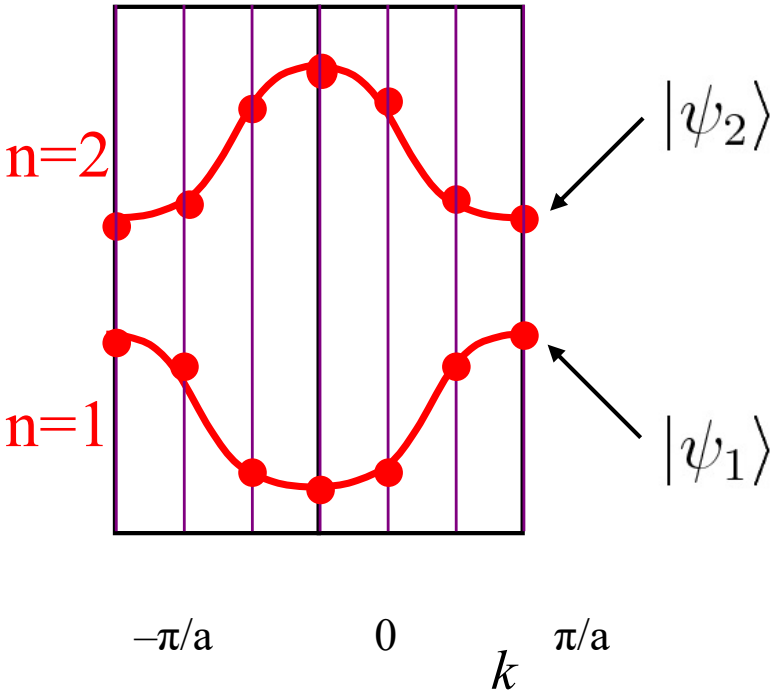


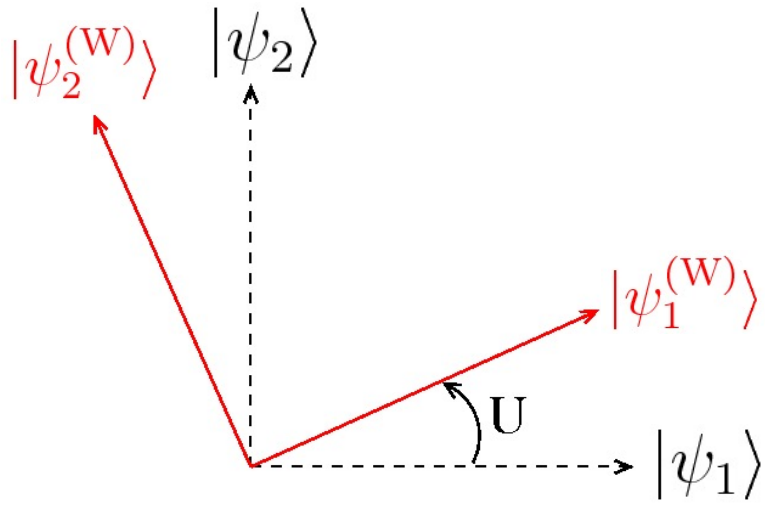
Orthogonal and unitary transformations

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

Rotated Bloch function

Unitary matrix





From Bloch Orbitals to Wannier Functions

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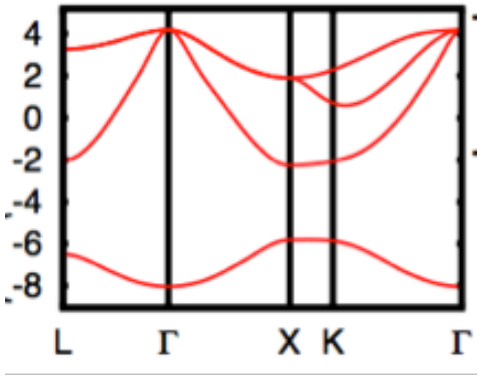
$$|\mathbf{R}n\rangle \;=\; \int_{BZ} \Psi_{n\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$



Gauge freedoms

- Arbitrary phase factor for every $n\mathbf{k}$ (Schrödinger)
- Arbitrary unitary rotations $U^{(\mathbf{k})}_{mn}$ for every $\mathbf{k}$ (DFT)

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

Generalized Wannier Functions for Composite Bands

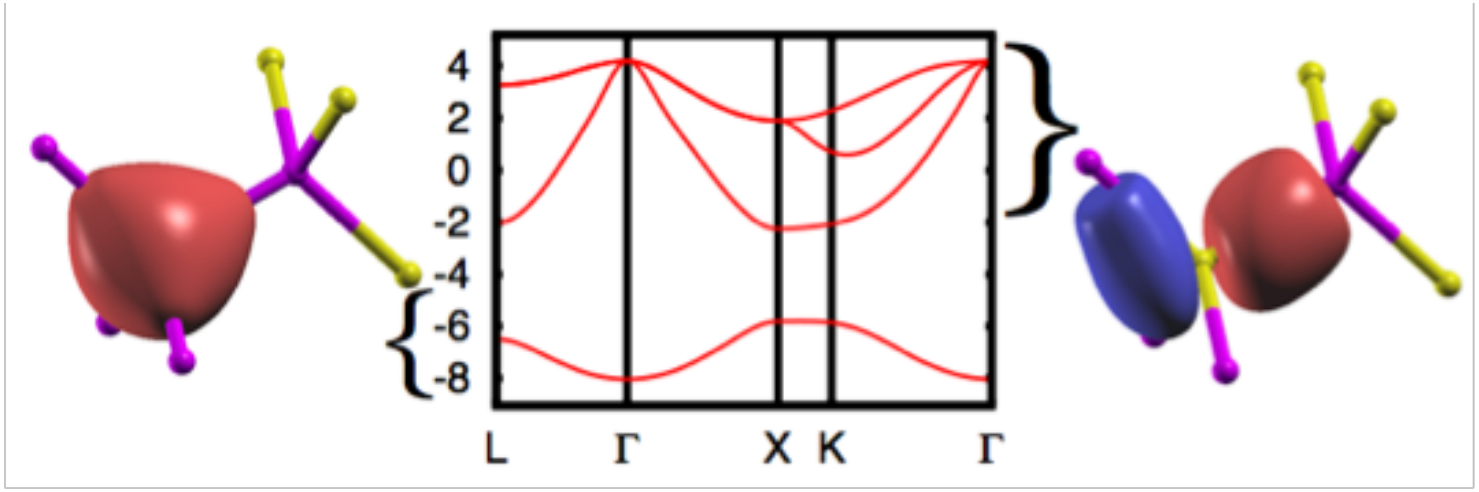
$$|\mathbf{R}n\rangle = \int_{BZ} \sum_{m} U^{(\mathbf{k})}_{mn} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

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

Generalized Wannier Functions for Composite Bands

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

But how to choose U?



U and WFs by projection

A simple route is to obtain U through a projection onto a pre-defined set of local orbitals g_n

$$|\phi_{n\mathbf{k}}\rangle = \sum_{m=1}^{J} |\psi_{m\mathbf{k}}\rangle\langle\psi_{m\mathbf{k}}|g_n\rangle$$

Can we choose U without reference to predetermined states?

Use Lowdin scheme to generate orthonormal states

$$(A_{\mathbf{k}})_{mn} = \langle\psi_{m\mathbf{k}}|g_n\rangle$$

$$(S_{\mathbf{k}})_{mn} = \langle\phi_{m\mathbf{k}}|\phi_{n\mathbf{k}}\rangle = (A_{\mathbf{k}}^{\dagger}A_{\mathbf{k}})_{mn}$$

$$|\tilde{\psi}_{n\mathbf{k}}\rangle = \sum_{m=1}^{J} |\phi_{m\mathbf{k}}\rangle(S_{\mathbf{k}}^{-1/2})_{mn}$$

U and WFs by localization

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

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)

Outline

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

Outline

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

Bloch states from favourite electronic-structure code

Outline

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

2 unitary transformations

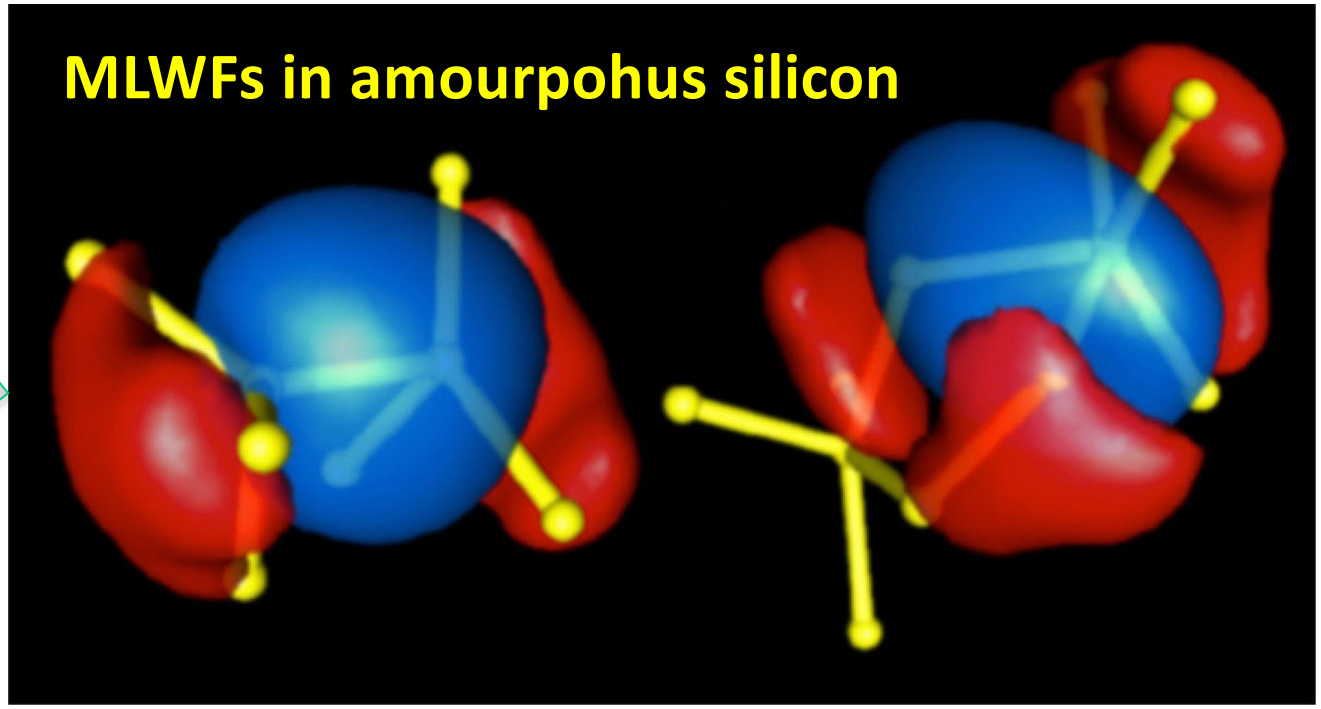
Outline

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

Iteratively refine $U_{mn}^{(k)}$ to localize|Rn>

Outline

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



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

Outline

- general algorithm to characterize the Wannier functions (or localized orbitals) of any given system
- applicable to periodic crystals, disordered systems, isolated molecules, in the spirit of supercell calculations
- post-processing of a conventional electronic-structure calculation
- maximal localization in the orbitals obtained in the Bloch-to-Wannier transformation

Decomposition of the Localization Functional

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

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

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

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

Ω_I is gauge invariant, positive definite

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

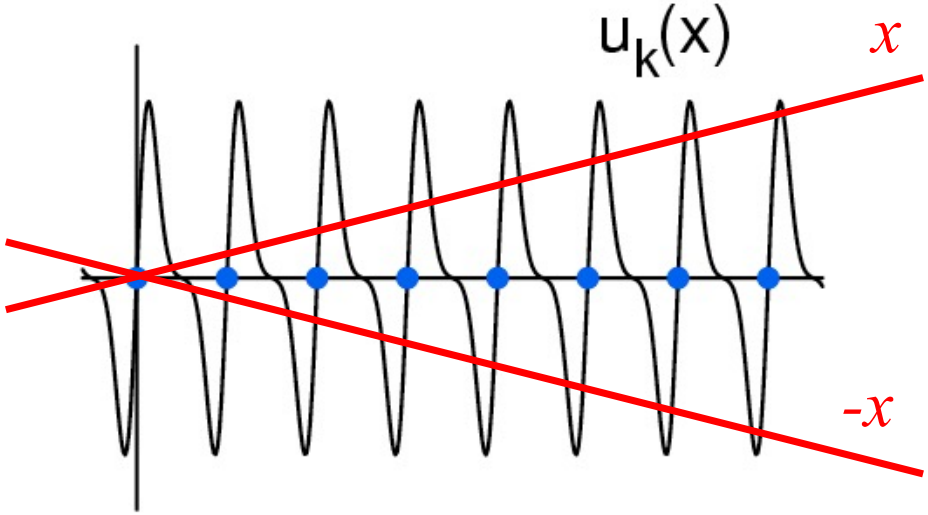
$$= \sum_{n,\alpha} \langle 0n | r_\alpha r_\alpha | 0n \rangle_n - \sum_{n,\alpha} \left[\sum_{\mathbf{R}m} \langle 0n | r_\alpha | \mathbf{R}m \rangle \langle \mathbf{R}m | r_\alpha | 0n \rangle \right] =$$

$$= \sum_{n,\alpha} \langle 0n | r_\alpha (\mathbb{I} - \mathbb{P}) r_\alpha | 0n \rangle = \sum_\alpha \mathrm{tr}_{\rm c} [r_\alpha \mathbb{Q}\, r_\alpha] = \sum_\alpha \| \mathbb{P} r_\alpha \mathbb{Q} \|_{\rm c}^2$$

(with the projection operators $\mathbb{P} = \sum_{\mathbf{R}m} |\mathbf{R}m\rangle\langle\mathbf{R}m|$ and $\mathbb{Q} = \mathbb{I} - \mathbb{P}$)

Position operator is ill defined !

$$\langle \psi_k | x | \psi_k \rangle = \int_{-\infty}^{\infty} x \, |u_k(x)|^2 \, dx$$



Blount identities

Centers of Wannier functions:

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

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

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

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

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

The Reciprocal Space Representation

a) we need to be able to calculate derivatives on regular meshes in k-space; i f cubic symmetry is assumed, with each of the N k-points having $Z = 6, 8$ or 12 first-neighbors $\mathbf{k} + \mathbf{b}$, then:

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

b) we need to express the positions of the Wannier functions and their spread as a function of the phase relations between the Bloch orbitals.

$$\mathbf{r}_n = \langle\, w_{n0} \,|\, \mathbf{r} \,|\, w_{n0} \,\rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \langle\, u_{n\mathbf{k}} \,|\, i\frac{\partial}{\partial \mathbf{k}} \,|\, u_{n\mathbf{k}} \,\rangle =$$

The Reciprocal Space Representation

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

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

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

The Localization Procedure

We consider an infinitesimal rotation of the Bloch orbitals

$$|u_{n\mathbf{k}}\rangle \;\rightarrow\; |u_{n\mathbf{k}}\rangle + \sum_m dW^{(\mathbf{k})}_{mn}\,|u_{m\mathbf{k}}\rangle$$

The Localization Procedure

We consider an infinitesimal rotation of the Bloch orbitals

$$|u_{n\mathbf{k}}\rangle \;\rightarrow\; |u_{n\mathbf{k}}\rangle + \sum_m dW^{(\mathbf{k})}_{mn}\,|u_{m\mathbf{k}}\rangle$$

The Gradient

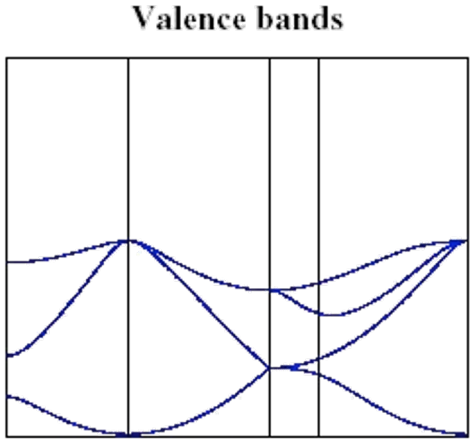
$$G^{(\mathbf{k})} = \frac{d\Omega}{dW^{(\mathbf{k})}} = 4\sum_{\mathbf{b}} w_b \left(\mathcal{A}[R^{(\mathbf{k},\mathbf{b})}] - \mathcal{S}[T^{(\mathbf{k},\mathbf{b})}]\right)$$

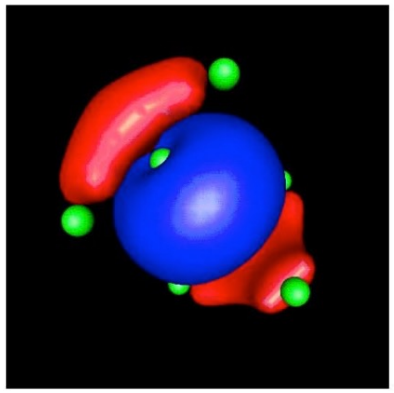
provides an equation of motion (e.g. conjugate-gradient) for the evolution of the $U^{(\mathbf{k})}_{mn}$ towards the minimum of Ω.

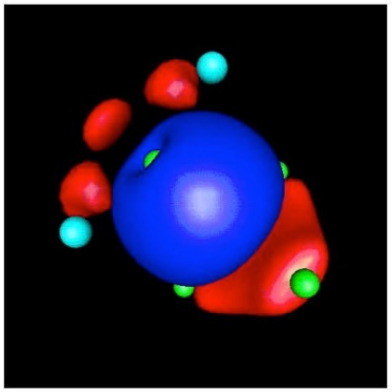
$$\mathcal{A}\,[B] = \frac{B - B^\dagger}{2} \quad , \qquad \mathcal{S}[B] = \frac{B + B^\dagger}{2i} \quad ,$$

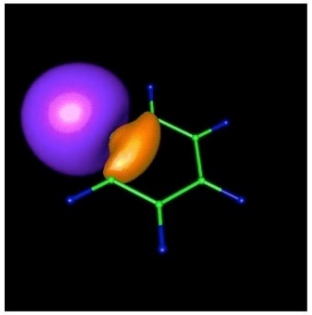
and defining $q^{(\mathbf{k},\mathbf{b})}_n \;=\; \mathrm{Im}\,\phi^{(\mathbf{k},\mathbf{b})}_n + \mathbf{b}\cdot\mathbf{r}_n \;\;,\;\; T^{(\mathbf{k},\mathbf{b})}_{mn} \;=\; \widetilde{R}^{(\mathbf{k},\mathbf{b})}_{mn}\, q^{(\mathbf{k},\mathbf{b})}_n,$

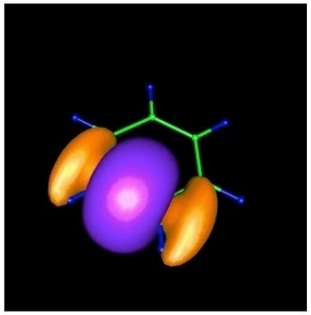
Silicon, GaAs, amorphous silicon, benzene

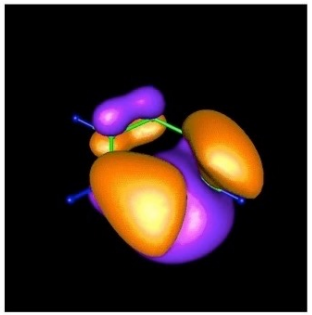


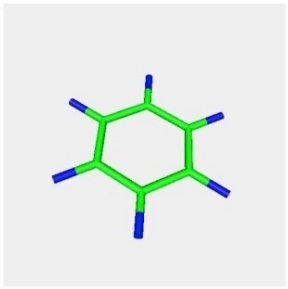


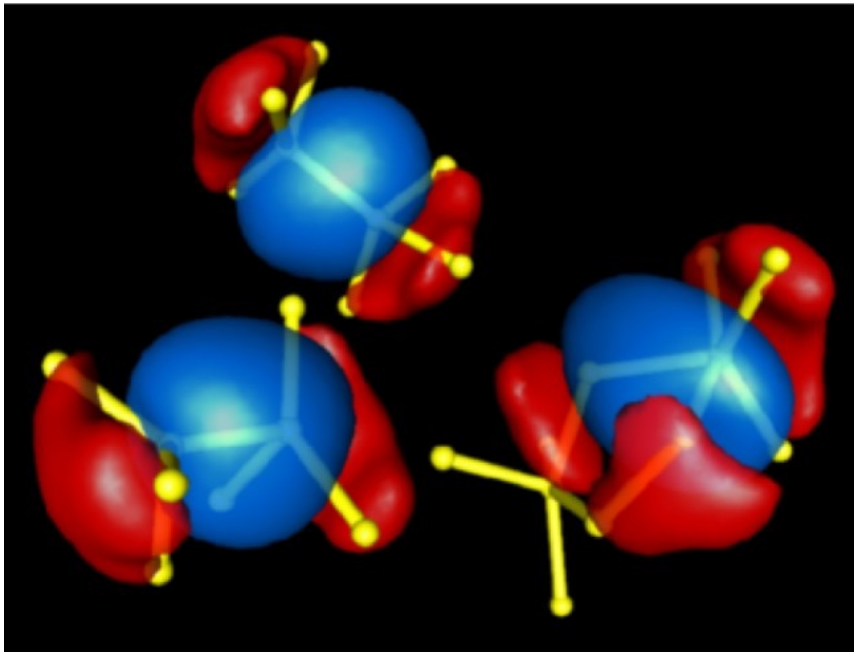






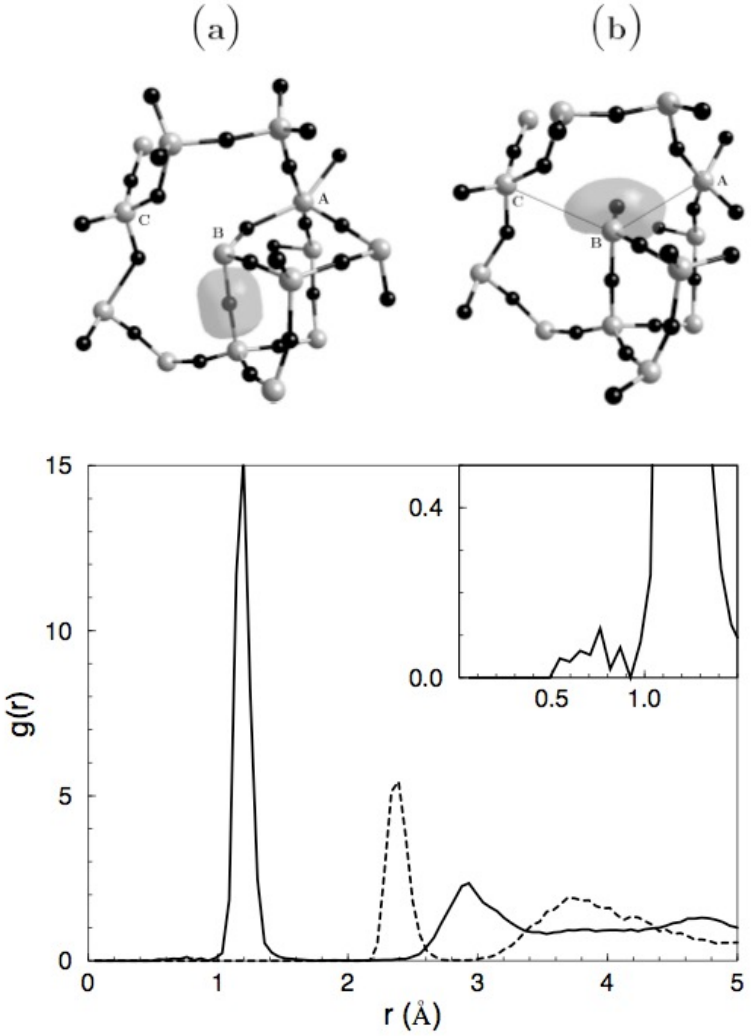




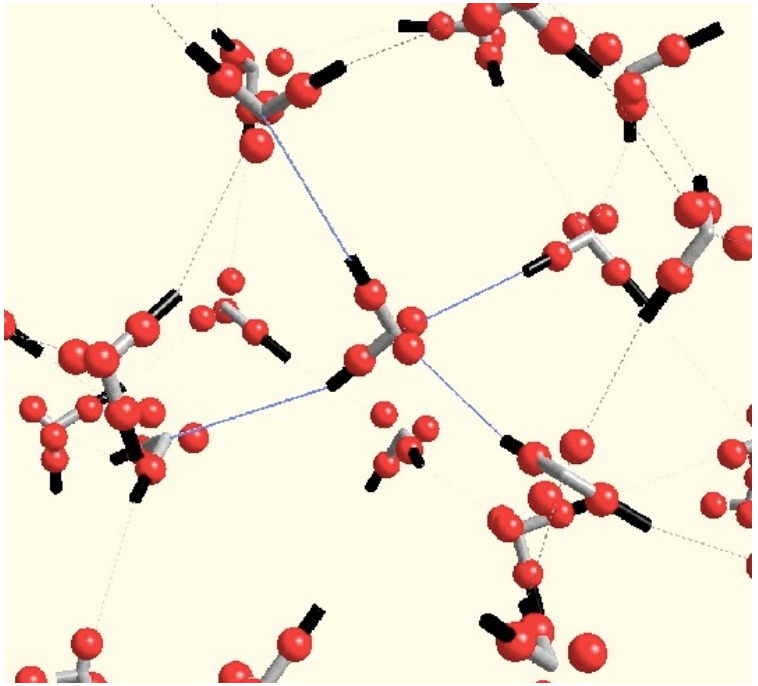


M. Fornari, N. Marzari, M. Peressi, and A. Baldereschi, Comp. Mater. Science 20, 337 (2001)

Wannier functions in *a-Si*



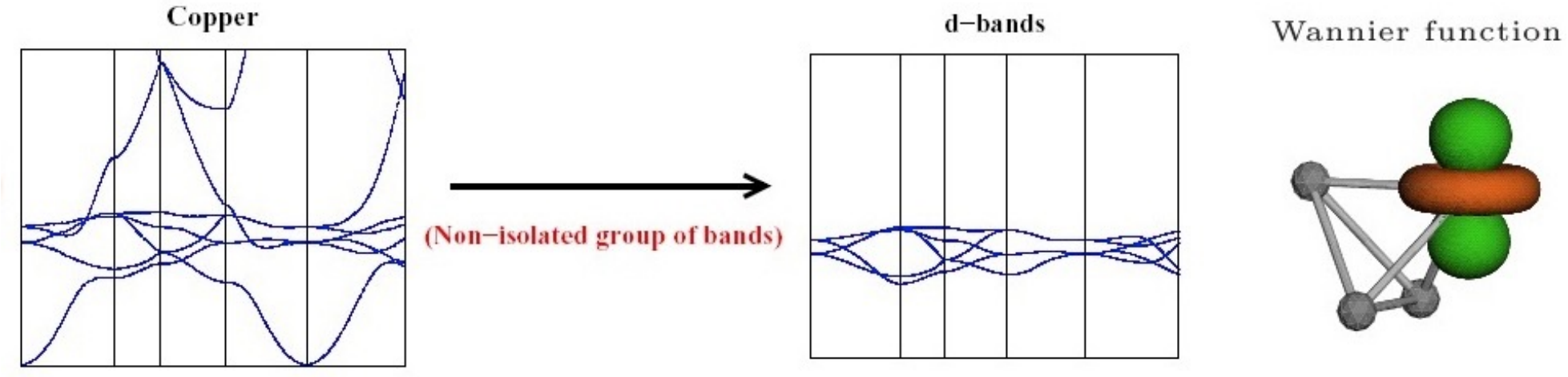
Wannier functions in *l-H_2O*



Silvestrelli et al.

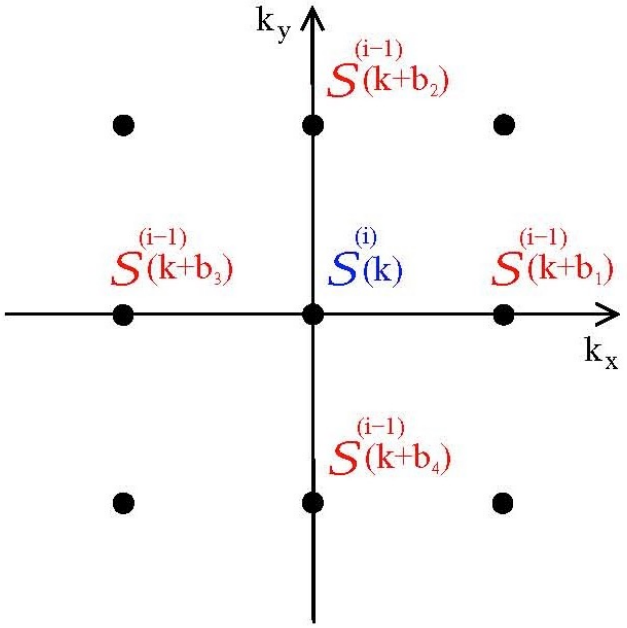
Disentanglement of Attached Bands

- 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)

Iterative Minimization of Ω_I



Minimize degree of mismatch between $\mathcal{S}^{(i)}(\mathbf{k})$ and $\mathcal{S}^{(i-1)}(\mathbf{k}+\mathbf{b})$, i.e., maximize overlap $\sum_{\mathbf{b}} \sum_{m=1}^{N} \left| \left\langle u_{n\mathbf{k}}^{(i)} \middle| u_{m,\mathbf{k}+\mathbf{b}}^{(i-1)} \right\rangle \right|^2$

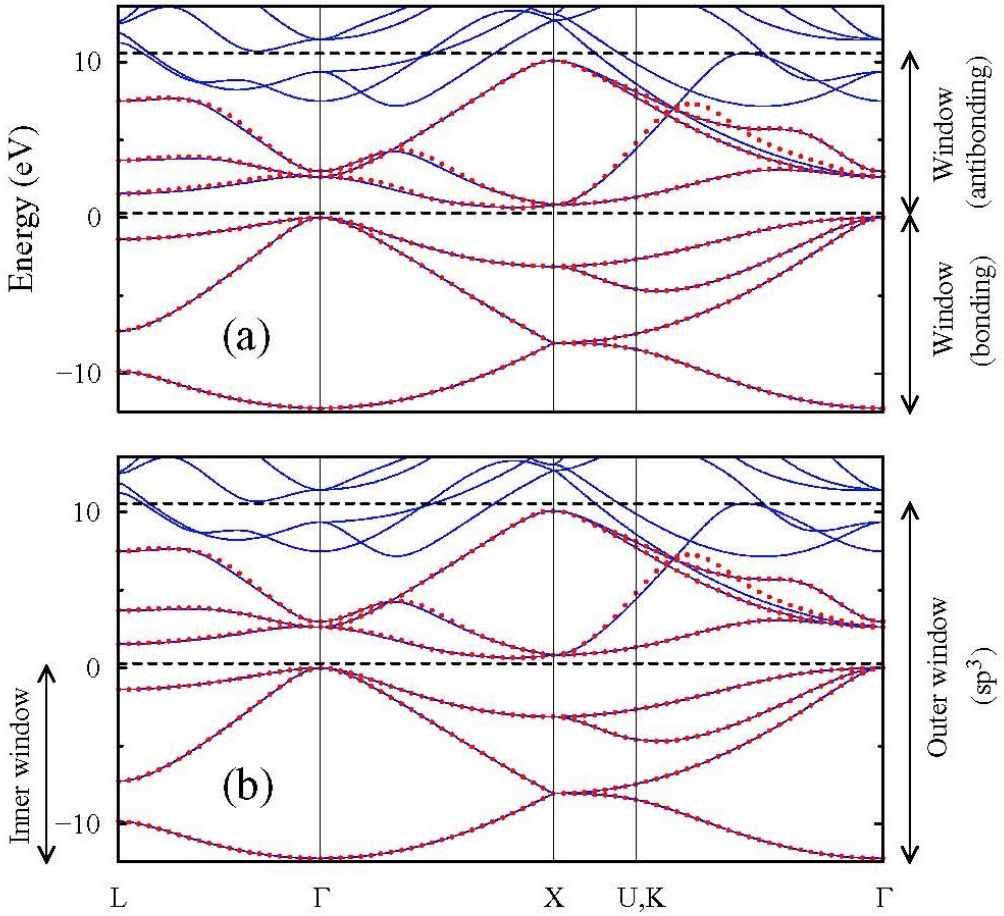
- 1^{st} iteration: Choose trial subspace at each $\mathbf{k}$ (e.g. projected orbitals)
- i^{th} iteration: At each $\mathbf{k}$ pick the N highest eigenvectors of

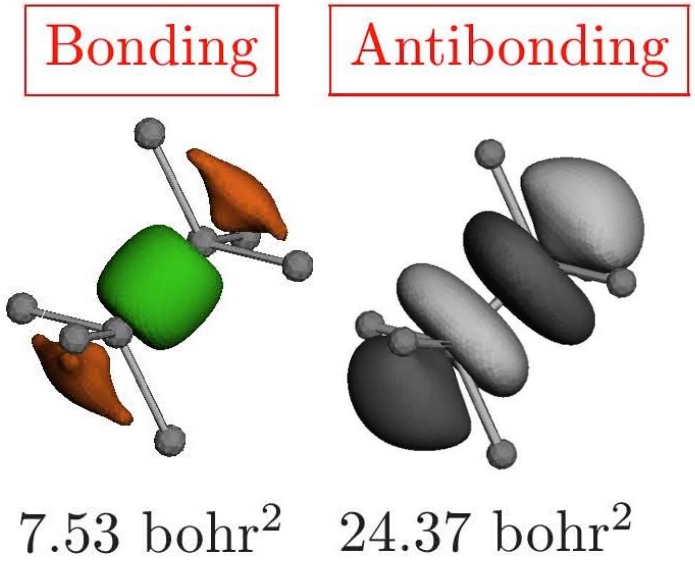
$$\left[\sum_{\mathbf{b}} \hat{P}_{\mathbf{k}+\mathbf{b}}^{(i-1)} \right] \left| u_{n\mathbf{k}}^{(i)} \right\rangle = \lambda_{n\mathbf{k}}^{(i)} \left| u_{n\mathbf{k}}^{(i)} \right\rangle$$

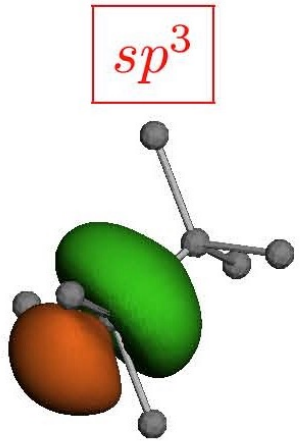
$\hat{P}_{\mathbf{k}+\mathbf{b}}^{(i-1)}$: Projector onto $\mathcal{S}^{(i-1)}(\mathbf{k}+\mathbf{b})$

- Repeat until self-consistency (when spaces $\mathcal{S}(\mathbf{k})$ stabilize)

Silicon: Bonding and Antibonding Orbitals

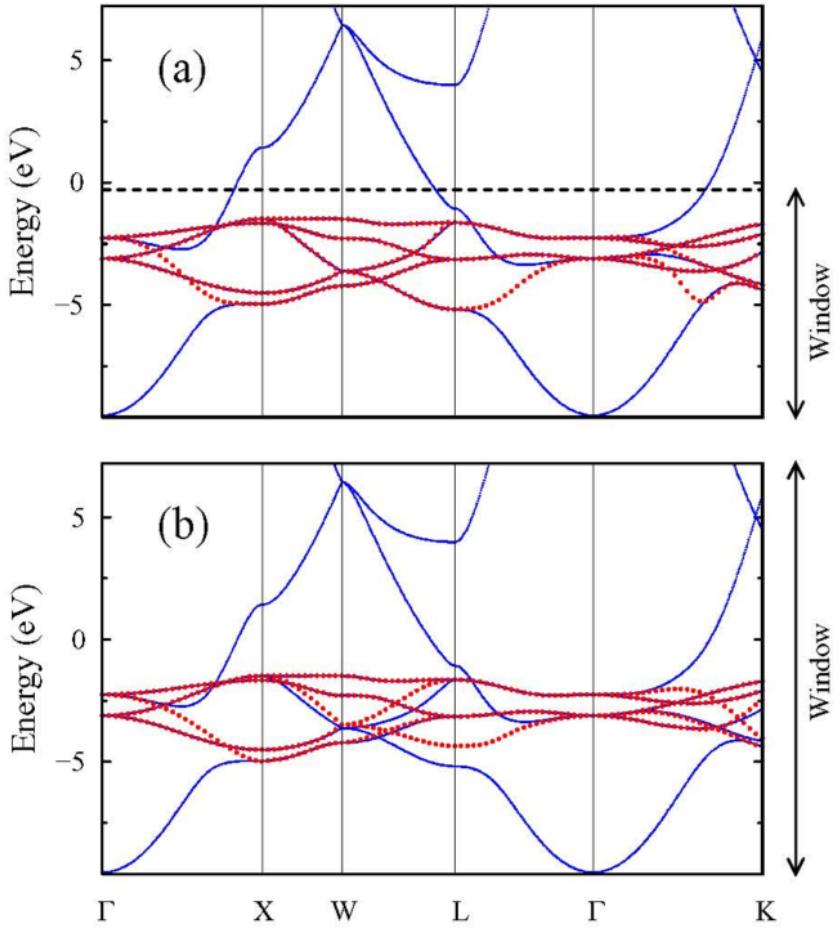




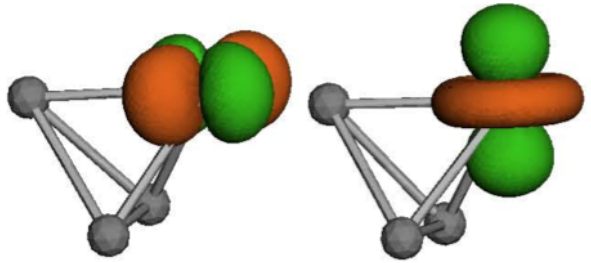


d Bands of Copper

Two possible choices of energy window



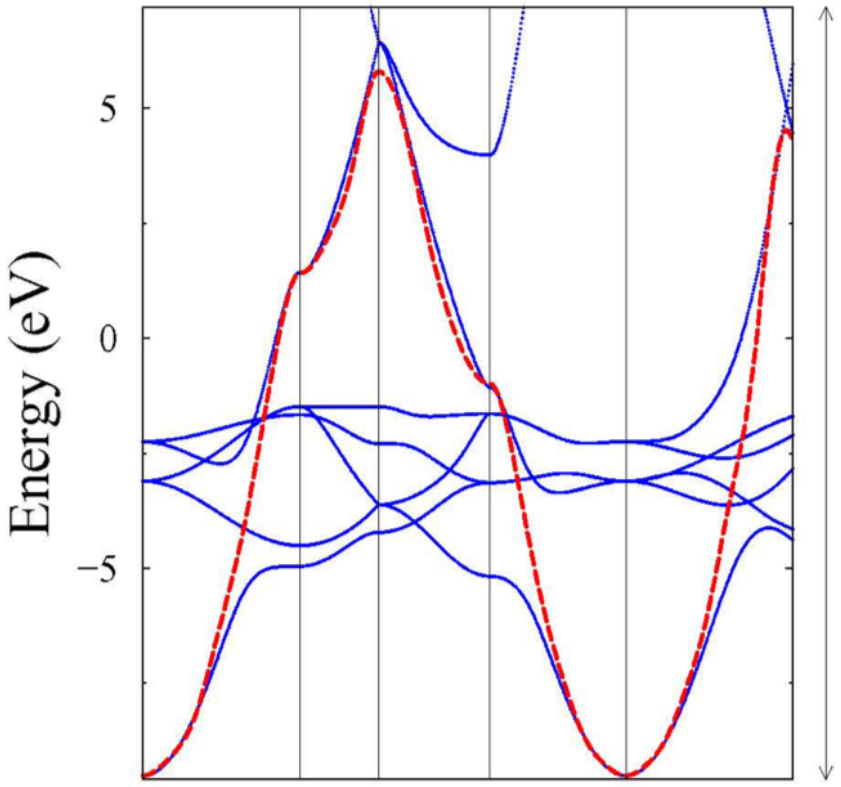
The e_g d WFs of panel (b)

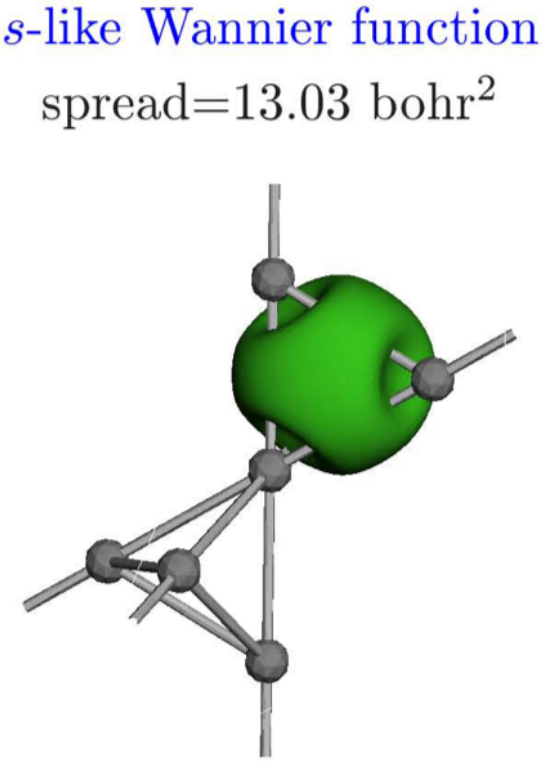


$\text{spread}(e_g)=1.700\ \text{bohr}^2$

$\text{spread}(e_g)=1.718\ \text{bohr}^2$

s Band of Copper

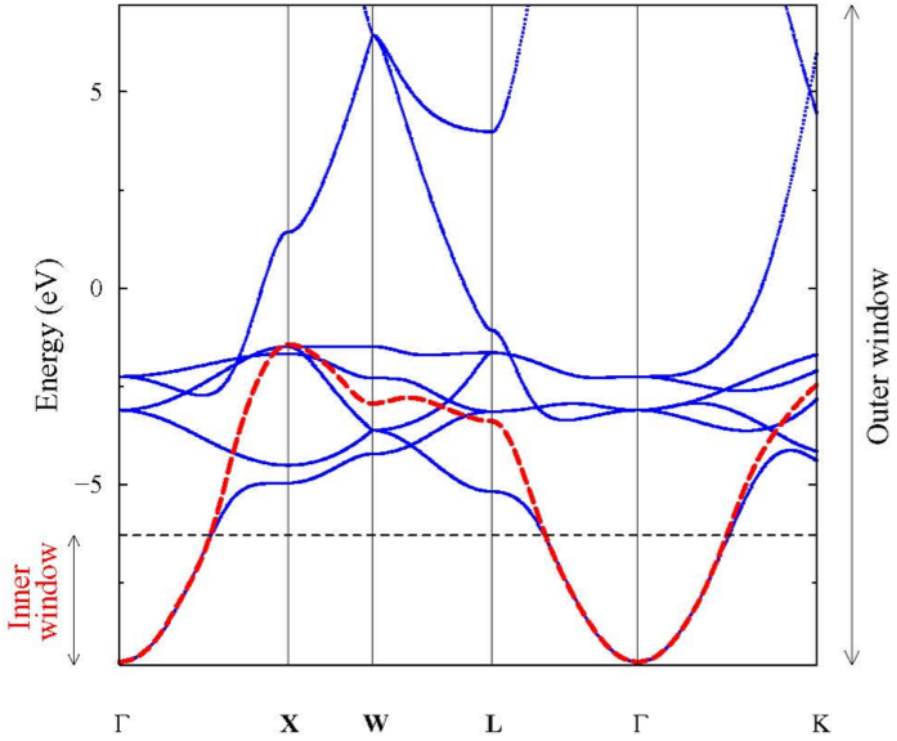




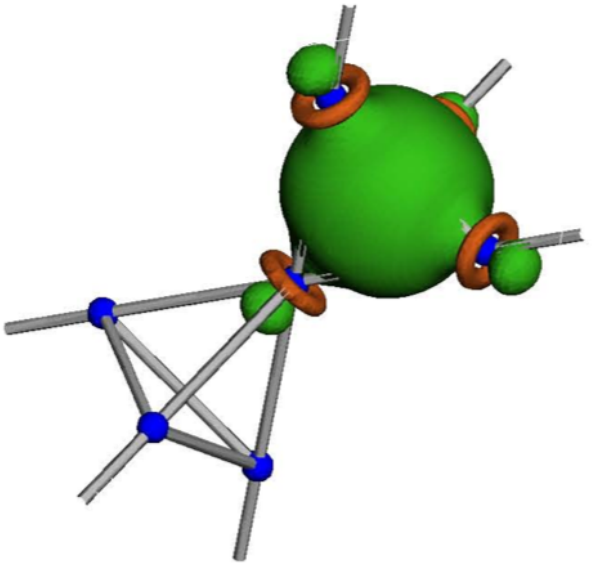
Exact Constraints on the Inner Energy

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

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

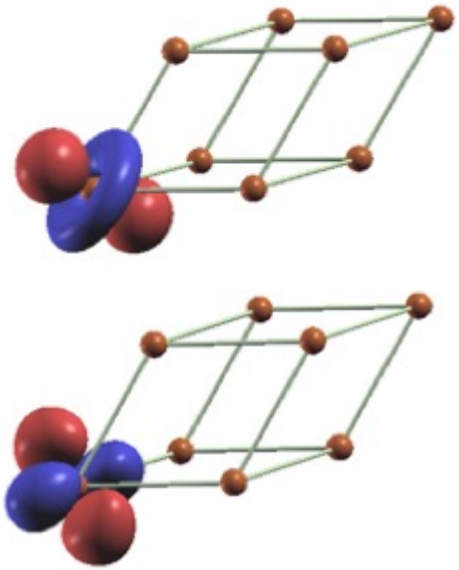


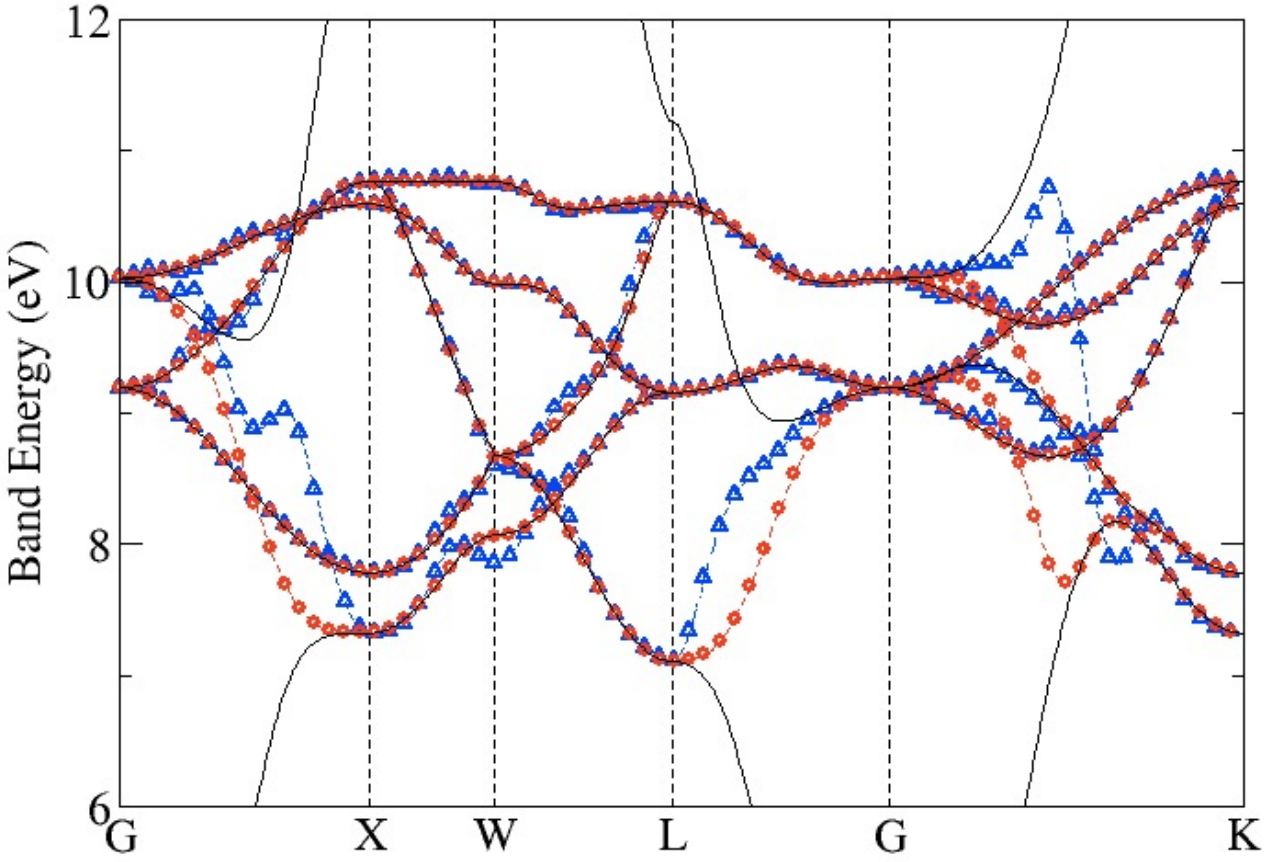
Hybrid *s*-*d* character:



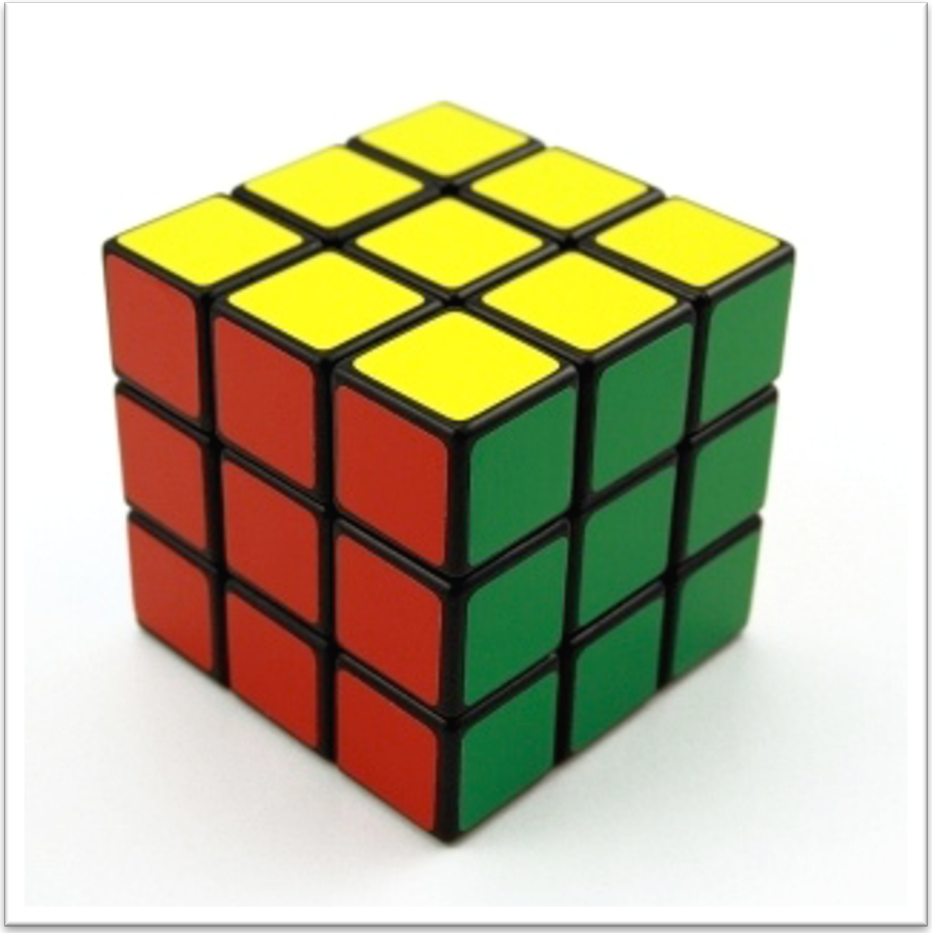
Projection vs Disentanglement

projection onto atom centred d orbitals followed by minimisation



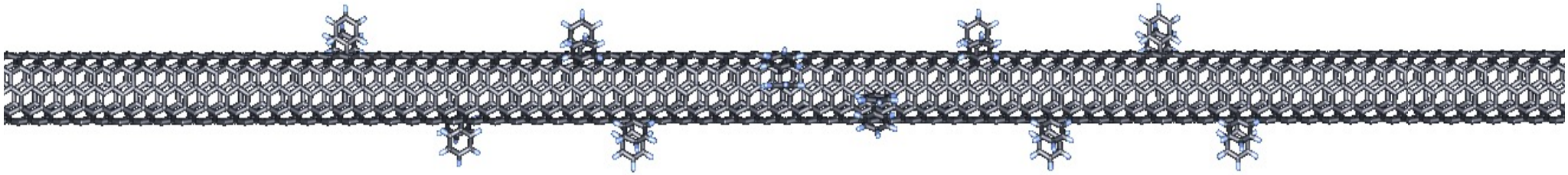


Building nanostructures Bloch by Bloch: model Hamiltonian and transport



Electronic Structure of Large Nanostructures

10 – 50 nm

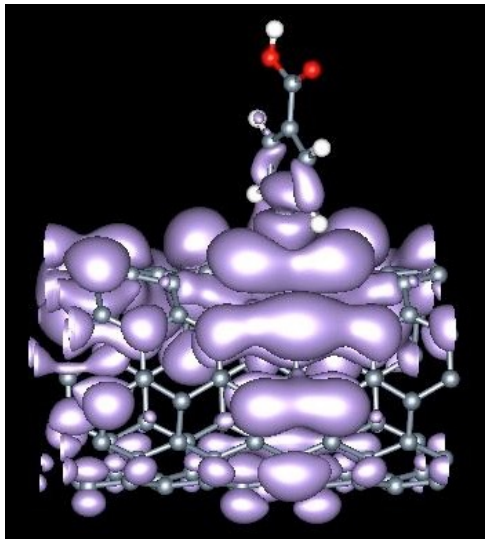


- **Electronic-structure of nanostructures with tens of thousands of atoms from maximally-localized Wannier functions**

- **Characterization and screening of the most promising functionalization avenues**

Electronic Structure of Large Nanostructures

Electronic Ground State From Static or Dynamical Large-Scale Simulations → **Optimal Unitary Transformation of the Bloch Orbitals** → **Real Space Maximally-Localized Wannier Functions**

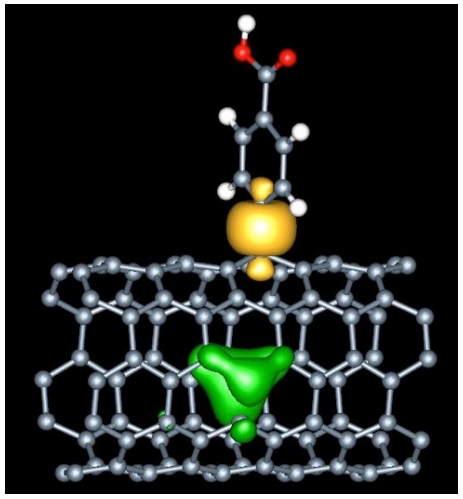


Minimization of the spread functional

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

exploiting the arbitrariness of the unitary transformations between the Bloch orbitals

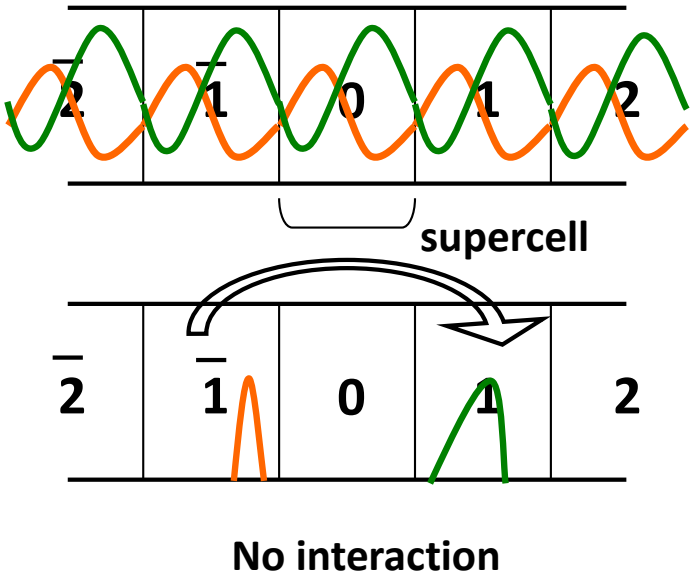
$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$



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

Electronic Structure of Large Nanostructures

Sparse Hamiltonian Matrix → **Green's Function Transmission Function** → **Ballistic Conductance Density of States**



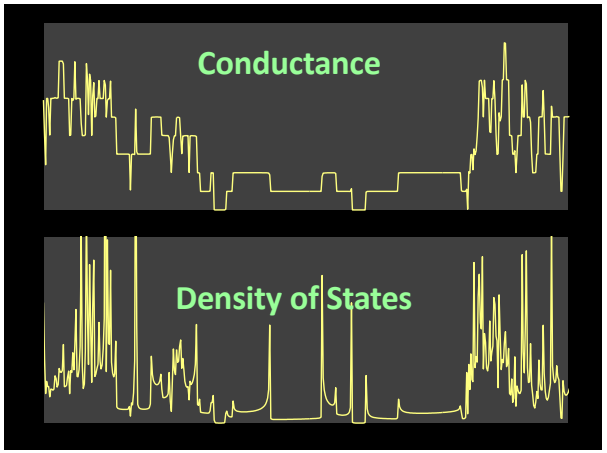
$$H_{00}\ ,\ H_{01} \Rightarrow G_C^r(E)$$

$$T(E) = \mathrm{Tr}(\Gamma_L G_C^r \Gamma_R G_C^a)$$

$$\mathbf{H} = \begin{pmatrix} H_{00} & H_{01} & 0 \\ H_{01}^{+} & H_{00} & H_{01} \\ 0 & H_{01}^{+} & H_{00} \end{pmatrix}$$

$$G(E) = \frac{2e^2}{h} T(E)$$

$$N(E) = -(1/\pi)\,\mathrm{Im}[\mathrm{Tr} G_C^r(E)]$$



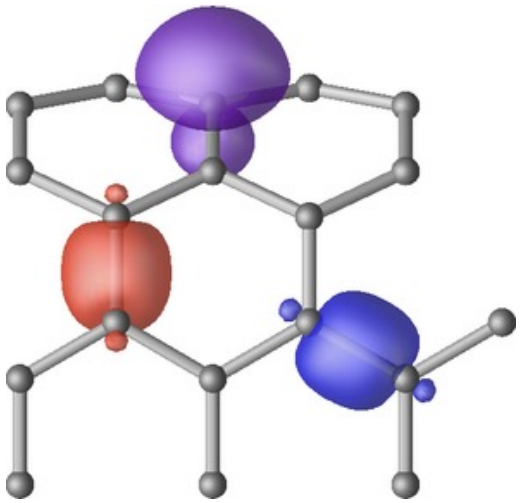
A. Calzolari, N. Marzari, I. Souza, M. B. Nardelli, Phys. Reb. B 69, 035108 (2004)

Max-loc WFs ↔ "Exact" Tight-Binding

Compact mapping of Bloch states into local orbitals

$$\omega_n(\mathbf{r}-\mathbf{R}) = \frac{V}{8\pi^3}\int_{BZ} e^{-i\mathbf{k}\cdot\mathbf{R}}\psi_{n\mathbf{k}}(\mathbf{r})d\mathbf{k}$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_R}}\sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\ \omega_n(\mathbf{r}-\mathbf{R})$$



$$\left\langle \psi_{i\mathbf{k}} \middle| \hat{\mathrm{H}} \middle| \psi_{j\mathbf{k}} \right\rangle = H_{ij}^{00} + e^{i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{01} + e^{-i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{0\bar{1}}$$

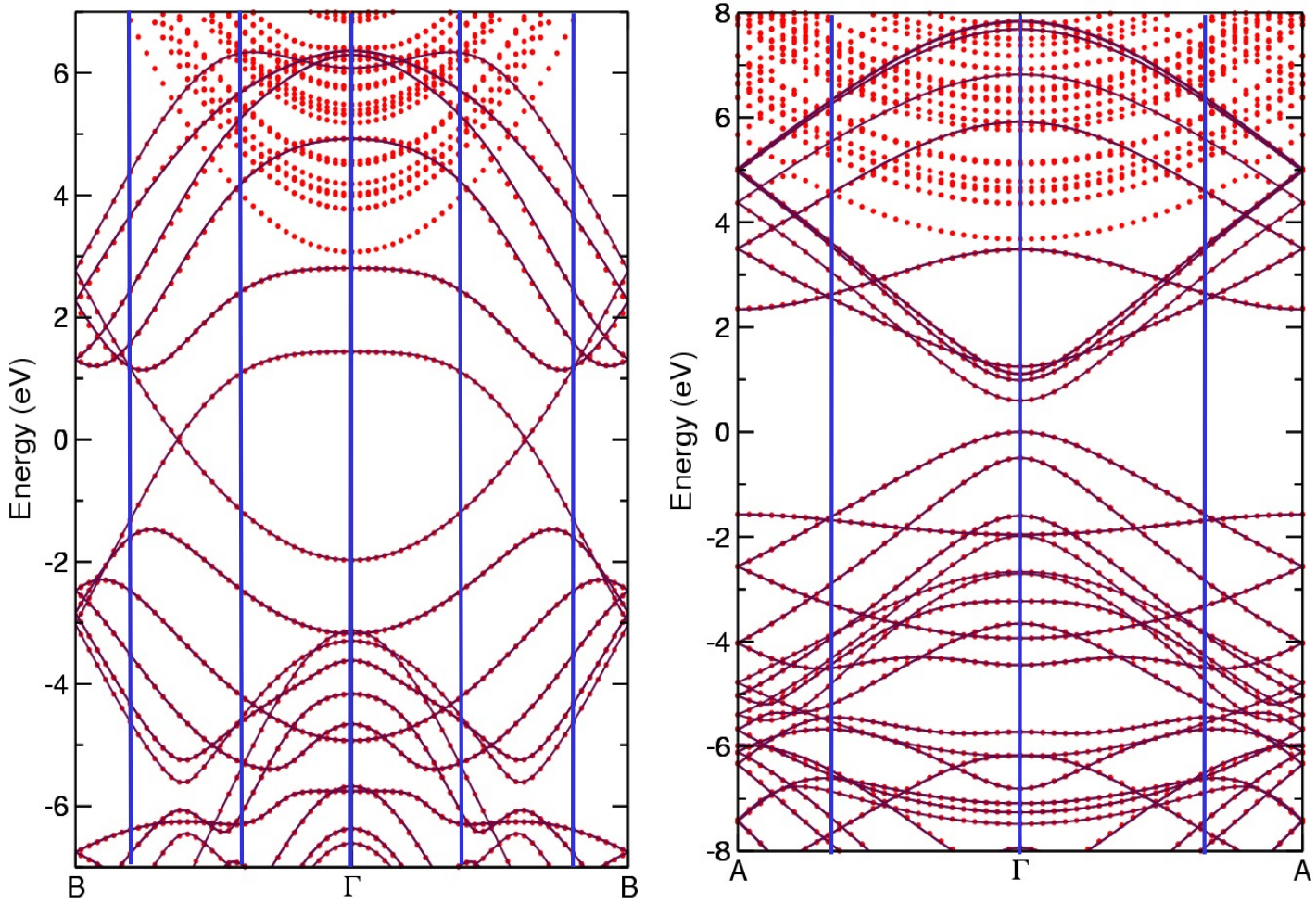
⇨ **Diagonalize H Matrix**

Y.-S. Lee, M. B. Nardelli, and N. Marzari, Phys. Rev. Lett. 95, 076804 (2005)

The LEGO bricks of electronic structure

(5,5) SWCNT

(8,0) SWCNT



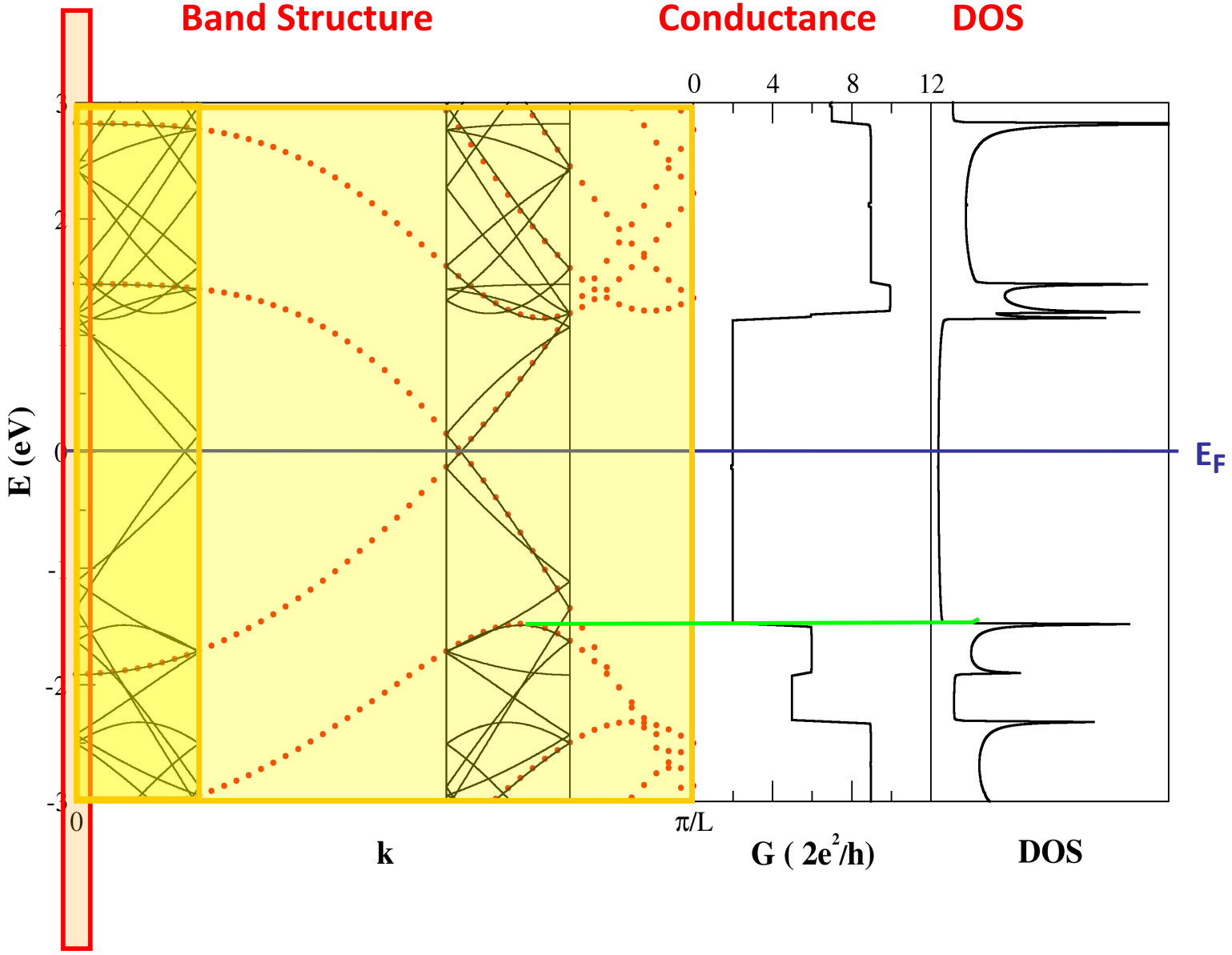
Y.-S. Lee, M. B. Nardelli, and N. Marzari, Phys. Rev. Lett. 95, 076804 (2005)

Band Structure and Conductance of a SWCNT

Γ-point:

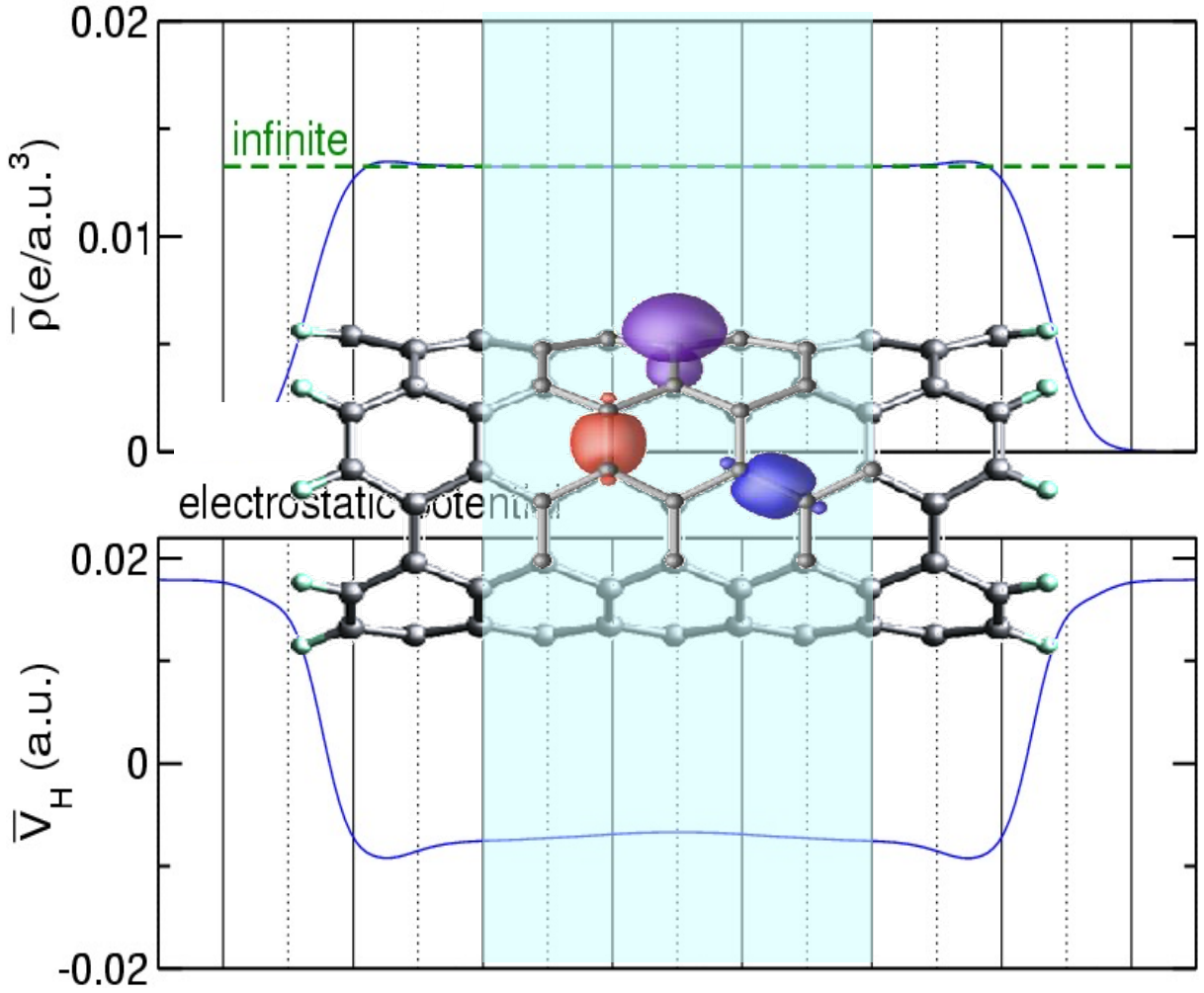
2eV pseudo gap

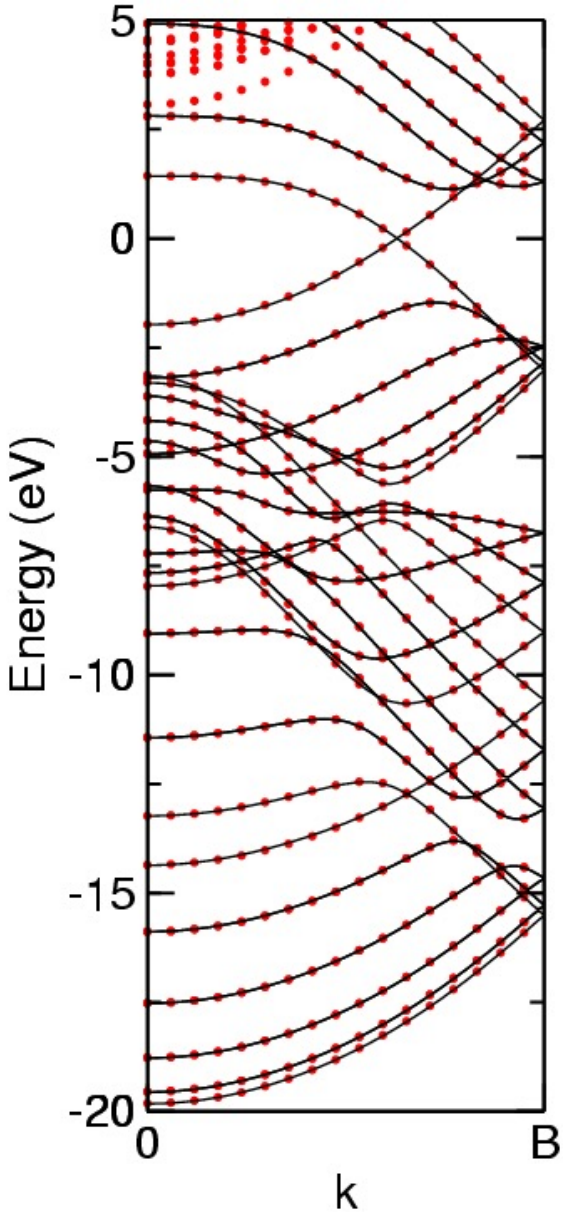
Two eigenchannels at E_F ⇨ perfect recovery of metallic character !



Y.-S. Lee, M. B. Nardelli, and N. Marzari, Phys. Rev. Lett. 95, 076804 (2005)

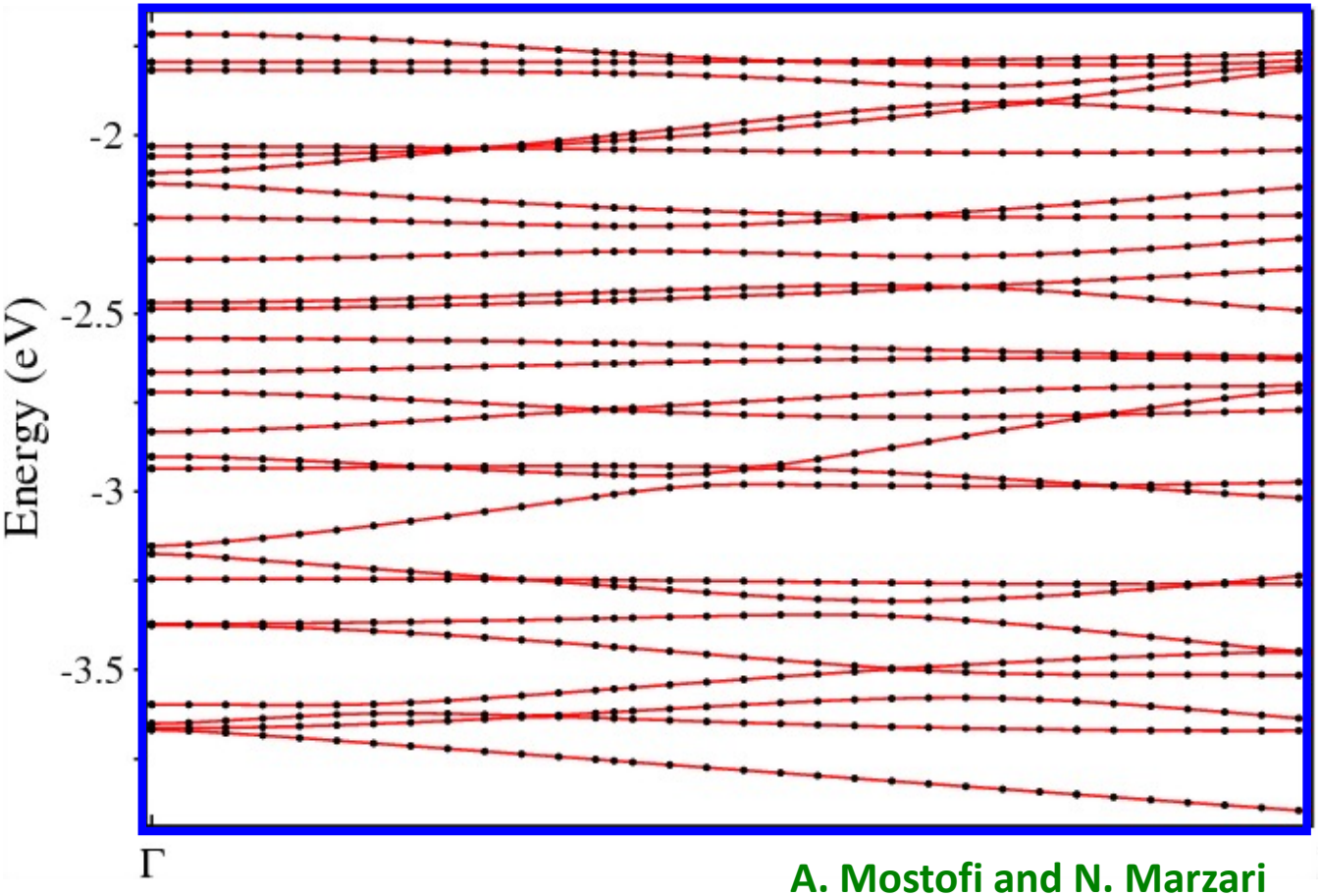
MLWFs Extraction From a Saturated Cluster





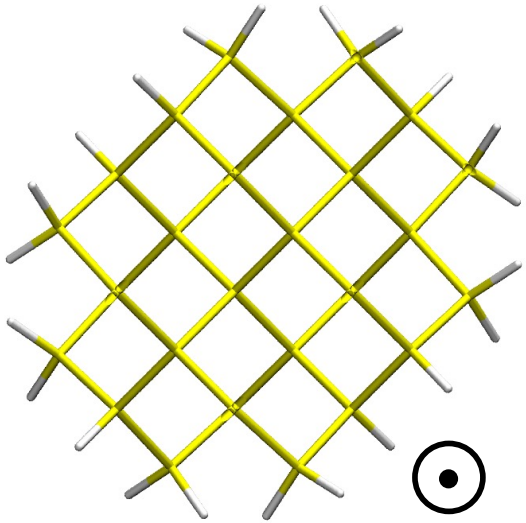
A very accurate interpolator

J. Yates et al., Phys. Rev. B. (2007)



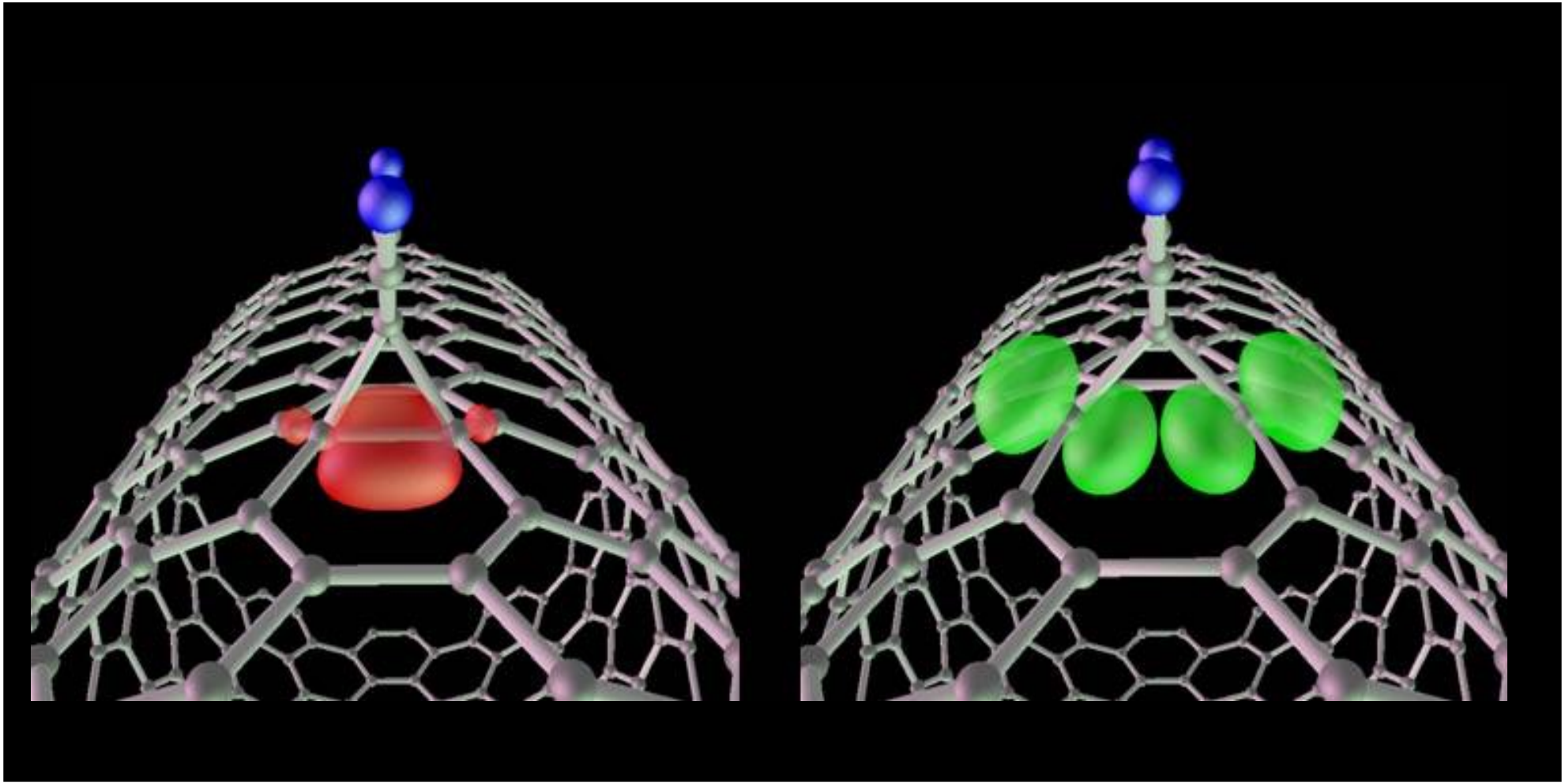
A. Mostofi and N. Marzari

Silicon nanowire



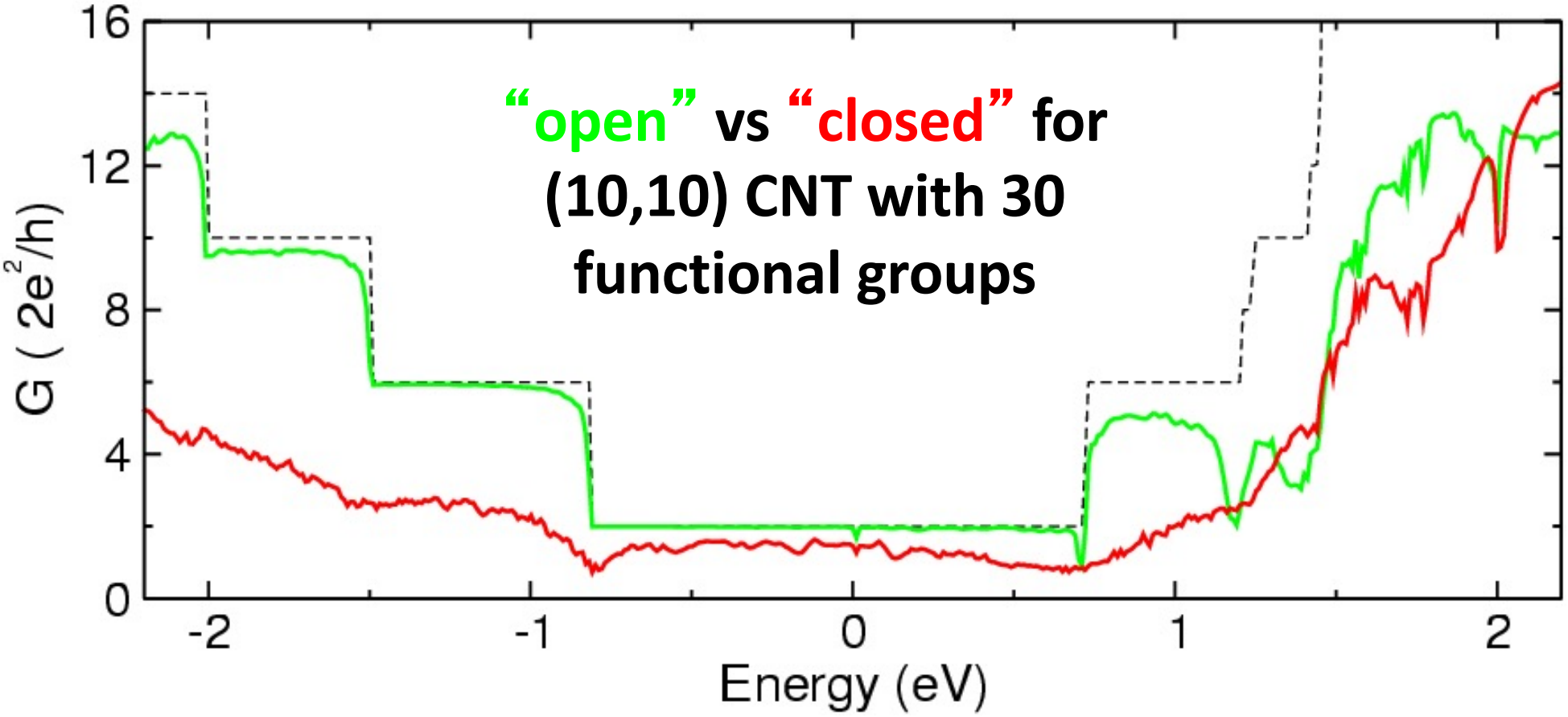
(001)

[2+1] cycloadditions protect sp^2 manifold



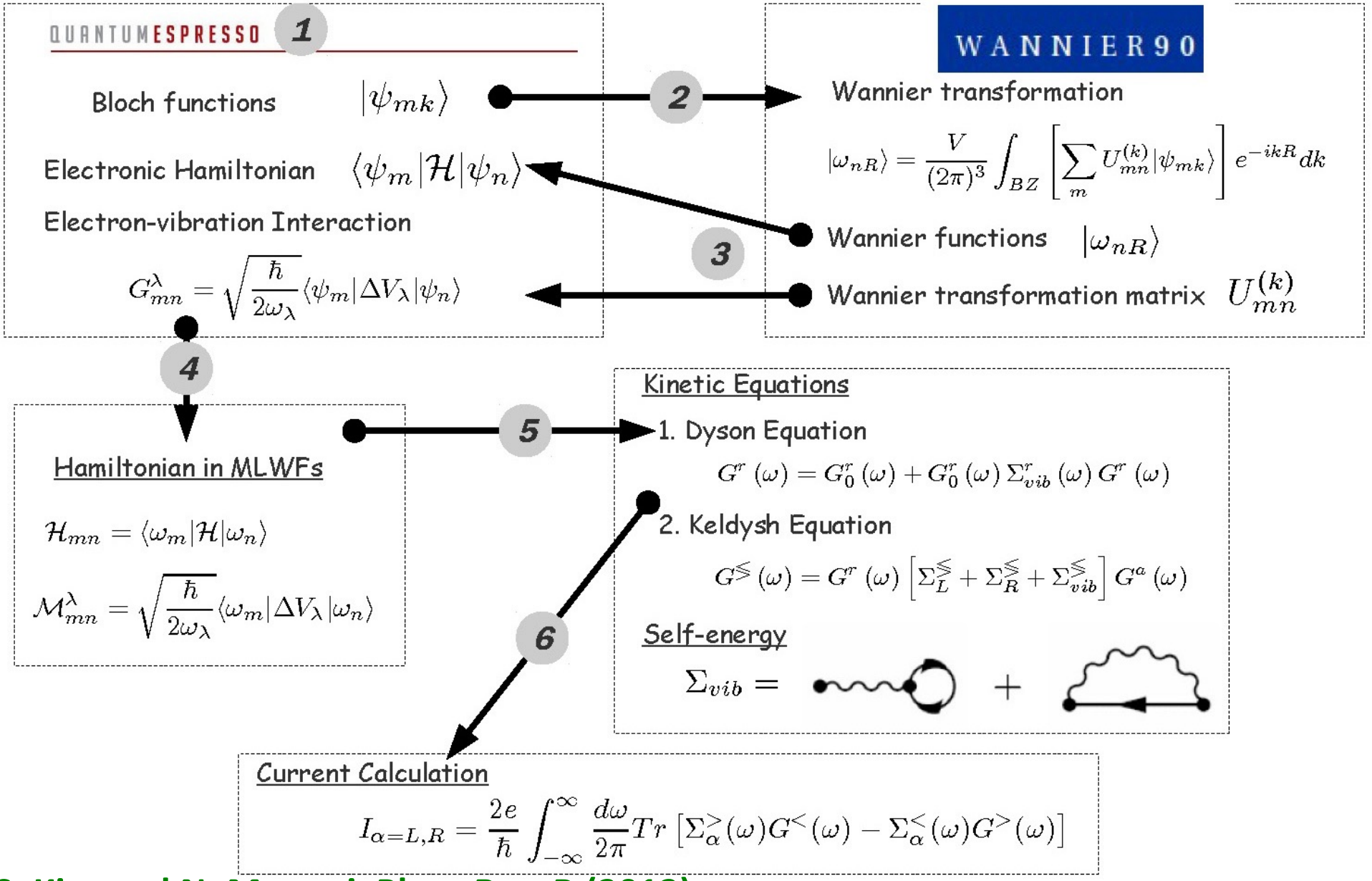
Y.-S. Lee and N. Marzari, Phys. Rev. Lett. 97, 116801 (2006)

Cycloadditions as functionalizations that preserve conductance



Y.-S. Lee and N. Marzari, Phys. Rev. Lett. 97, 116801 (2006)

Inelastic Quantum Transport

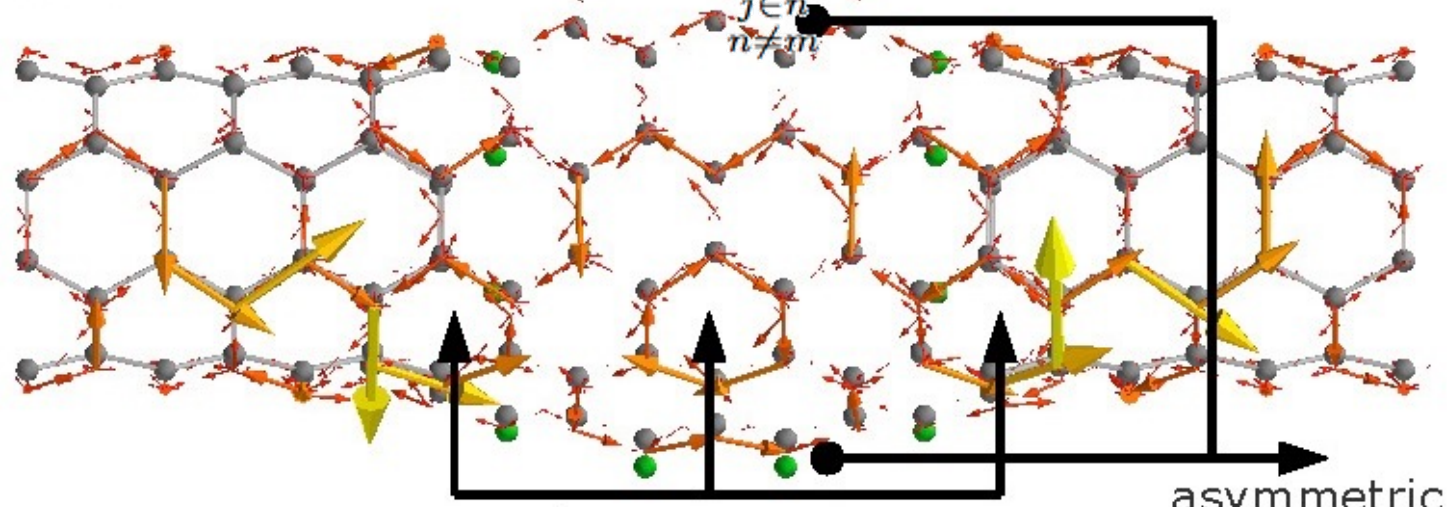


S. Kim and N. Marzari, Phys. Rev. B (2013)

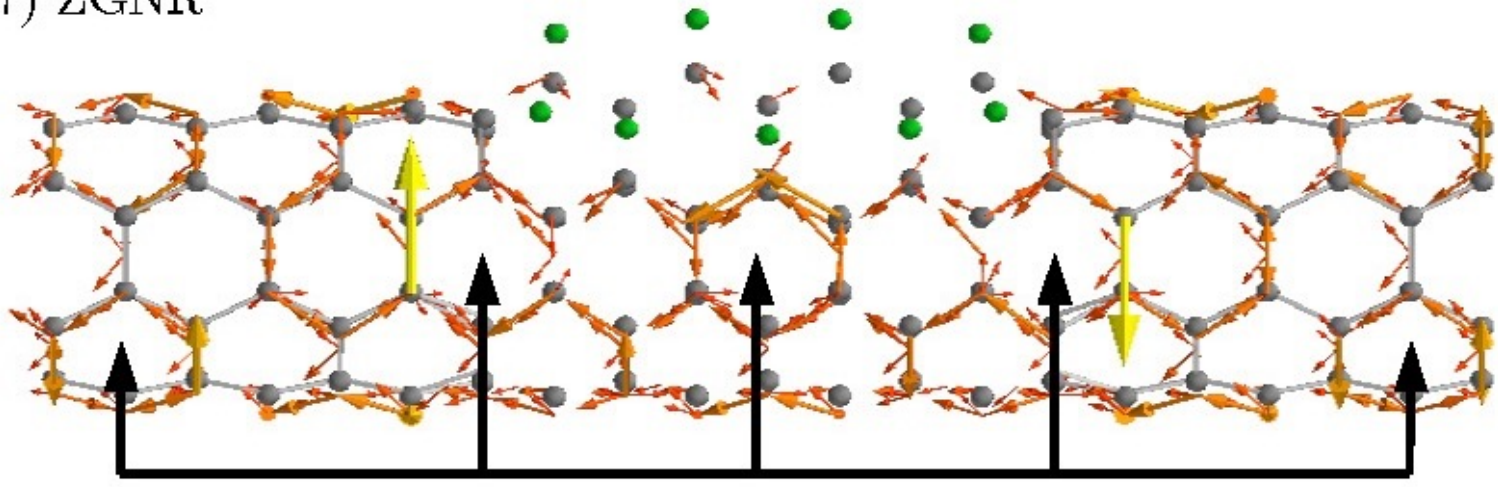
Inelastic currents: loops and backflows

$$I^{vib}_{mn} = \frac{2e}{\hbar} \sum_{\substack{i\in m \\ j\in n \\ n\neq m}} \sum_{\lambda} \int \frac{d\varepsilon}{2\pi} \left[\mathcal{M}^{\lambda}_{ij} G^{<}_{j,\lambda i}(\varepsilon) - \mathcal{M}^{\lambda}_{ji} G^{<}_{i,\lambda j}(\varepsilon) \right].$$

(N=5) ZGNR



(N=7) ZGNR



KOOPMANS' COMPLIANT SPECTRAL FUNCTIONALS

For every orbital the expectation value

$$\epsilon_i = \langle \varphi_i | \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle$$

does not depend on the occupation of the orbital

I. Dabo, M. Cococcioni, and N. Marzari, arXiv:0910.2637 (2009)
I. Dabo et al., Phys. Rev. B 82, 115121 (2010)

LINEARIZATION (FIRST, AT FROZEN ORBITALS)

add linear Koopmans

$$E^{\mathrm{KI}} = E^{\mathrm{DFT}} + \sum_i \left[-\int_0^{f_i} \langle\varphi_i|\hat{H}^{\mathrm{DFT}}|\varphi_i\rangle + f_i \int_0^1 \langle\varphi_i|\hat{H}^{\mathrm{DFT}}|\varphi_i\rangle \right]$$

remove ~quadratic Slater

I. Dabo et al., Phys. Rev. B 82, 115121 (2010)
G. Borghi et al., Phys. Rev. B 90, 075135 (2014)

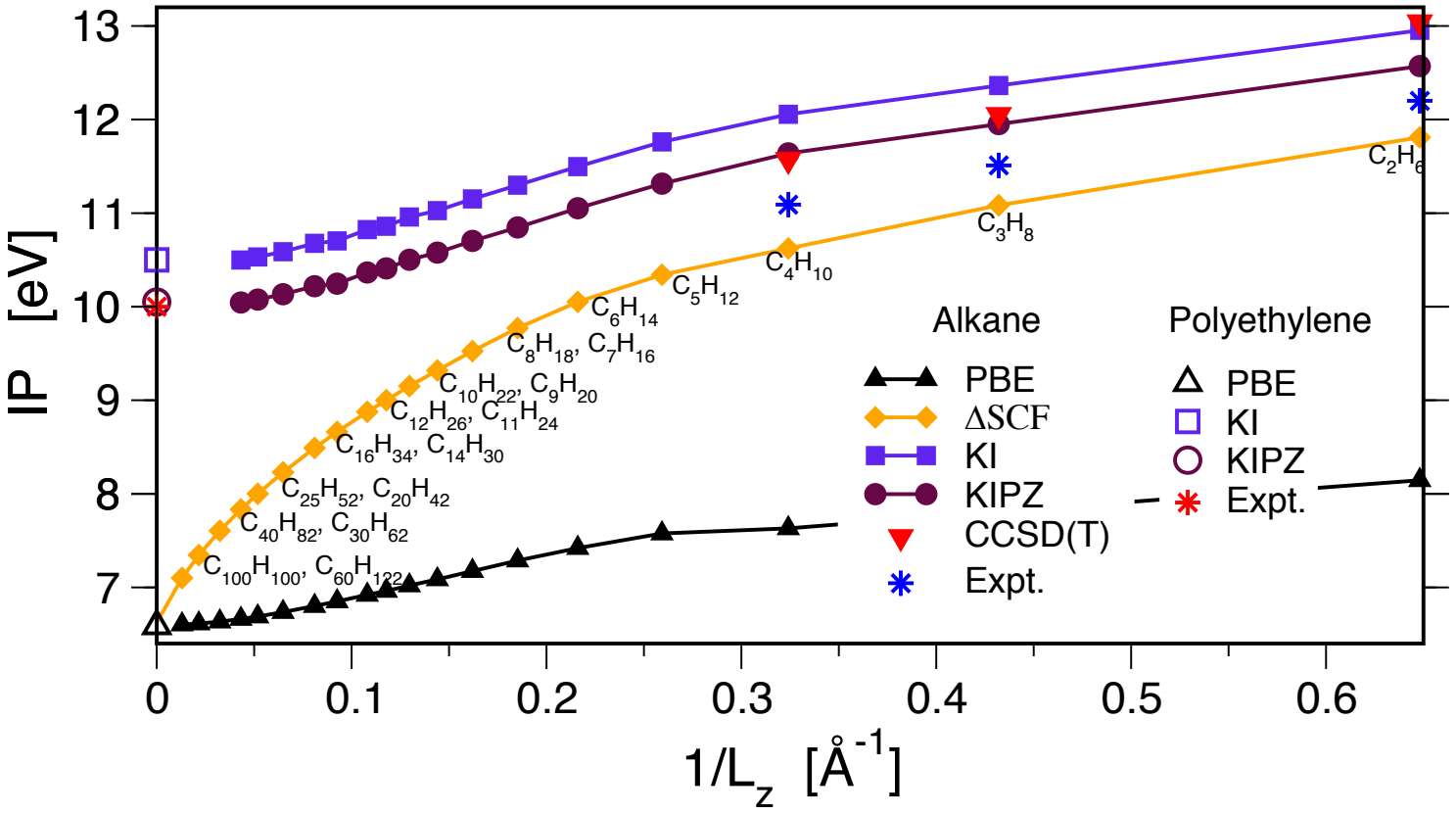
SCREENING TO ACCOUNT FOR ORBITAL RELAXATIONS

$$E^{\mathrm{KI}} = E^{\mathrm{DFT}} + \sum_i \alpha_i \left[-\int_0^{f_i} \langle \varphi_i | \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle + f_i \int_0^1 \langle \varphi_i | \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle \right]$$

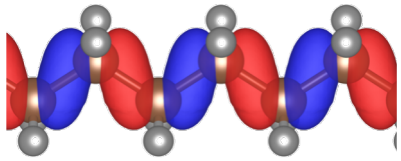
orbital-dependent screening coefficient

I. Dabo et al., Phys. Rev. B 82, 115121 (2010)
N. Colonna et al., JCTC in press (2018), and arXiv

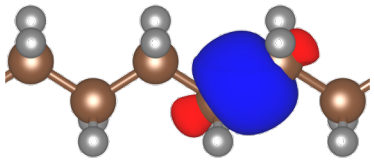
SOLID-STATE LIMIT



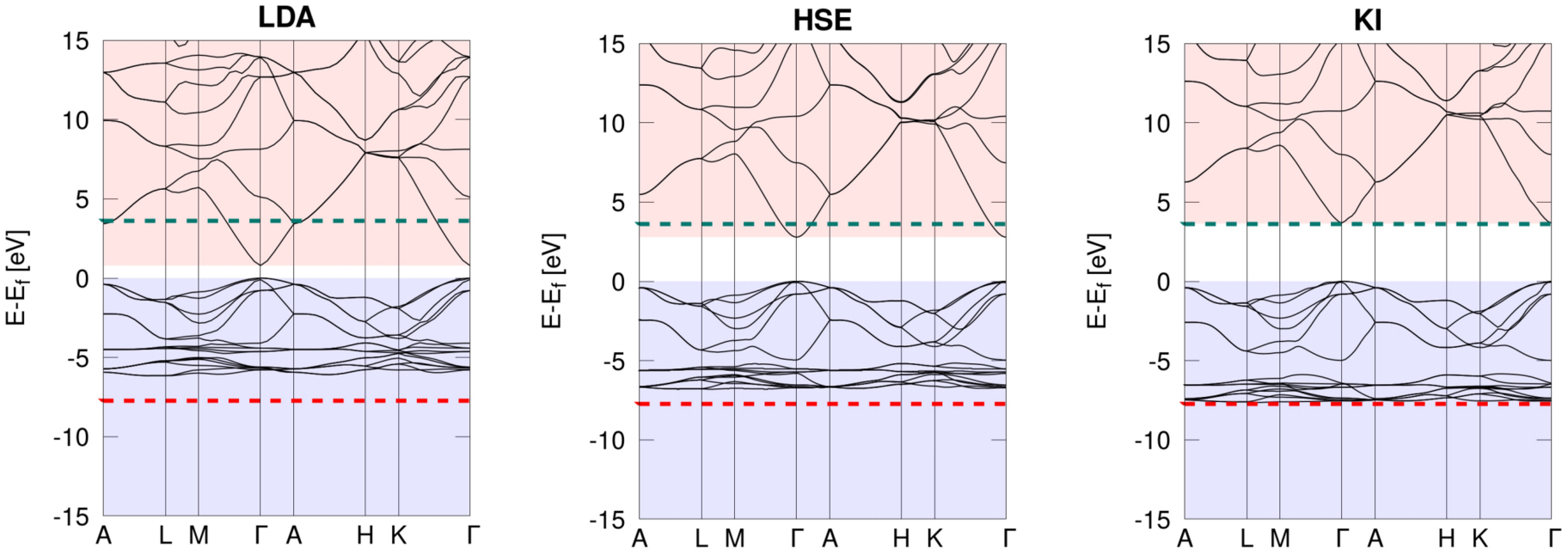
Canonical orbital



Variational (minimizing) orbital



BAND STRUCTURES



	LDA	HSE	GW_0	scG$\hat{W}$	KI	Exp
E_g (eV)	0.79	2.79	3.0	3.2	**3.62**	**3.60**
$\langle\varepsilon_d\rangle$ (eV)	-5.1	-6.1	-6.4	-6.7	**-6.9**	**[-7.5;-8.0]**

L. Nguyen, N. Colonna, A. Ferretti, and N. Marzari, PRX (2018)
N. Colonna et al., (2021)

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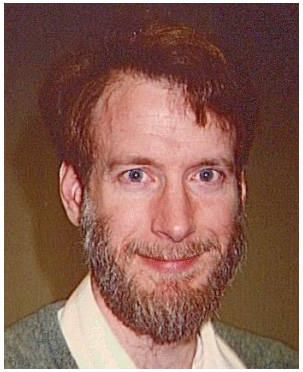



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- **Transport:** Young-Su Lee (MIT->KIST), Elise Li (MIT->NTNU), Matt Shelley (Imperial), Nicolas Poilvert (MIT->Penn S.), Giovanni Cantele (University of Naples), S. Kim (MIT->KIAS)
- **Koopmans:** Nicola Colonna (PSI), Andrea Ferretti (CNR), and EPFL Edward Linscott, Riccardo de Gennaro, Linh Nguyen, et al…