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Hands-on Tutorial on Electronic Structure Computations

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From Bloch to Wannier

Nicola Marzari
Department of Materials, University of Oxford
Oxford
UK

Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

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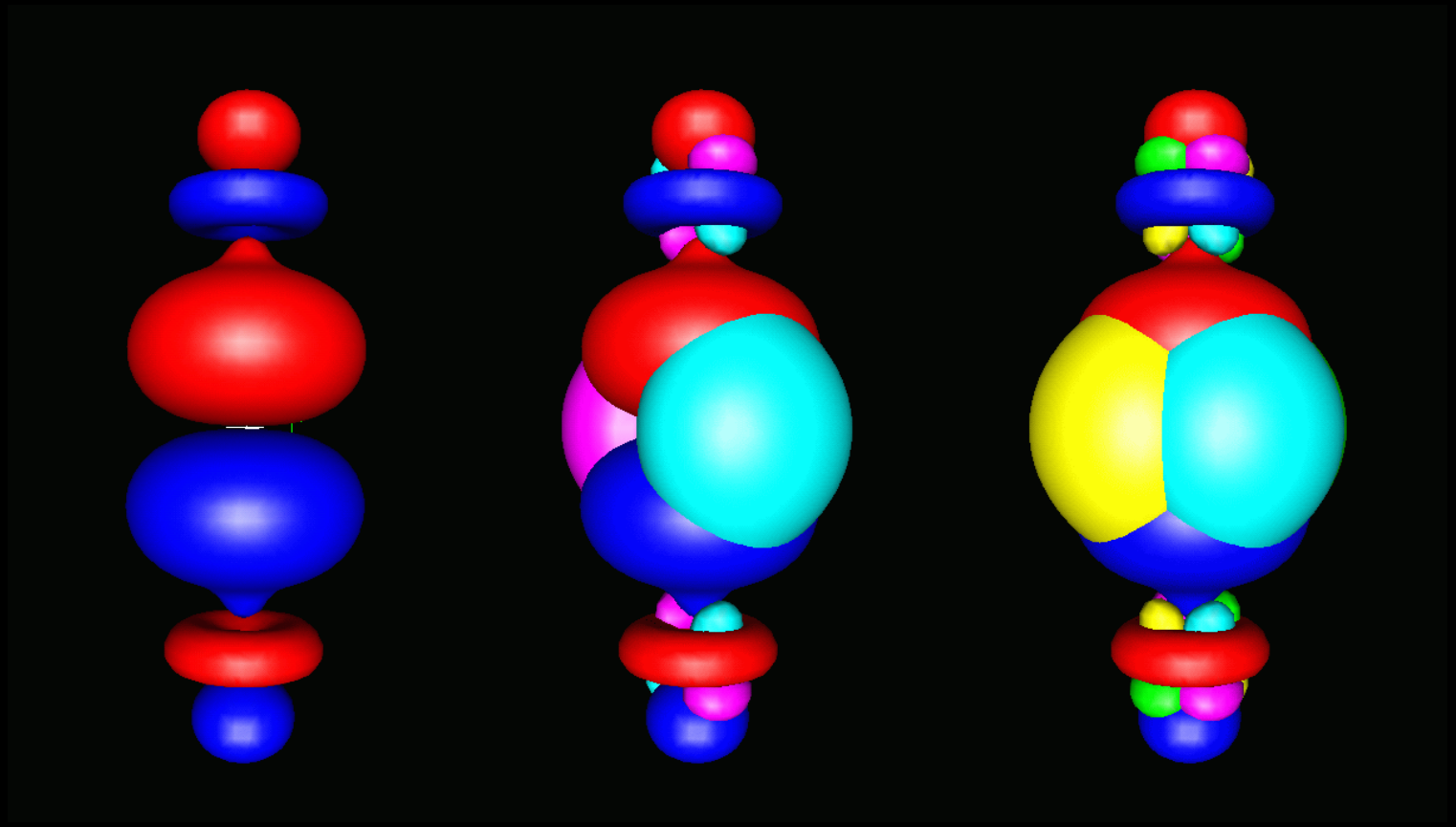


Bravais Lattices

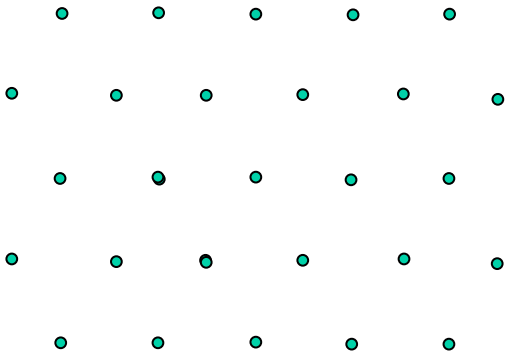
- Infinite array of points with an arrangement and orientation that appears exactly the same regardless of the point from which the array is viewed.

$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3 \quad \text{l,m and n integers}$$

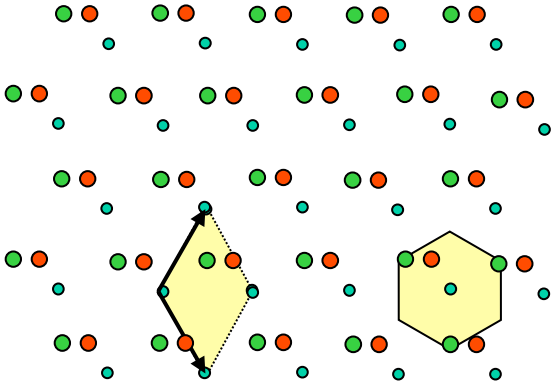
$$\vec{a}_1, \vec{a}_2 \text{ and } \vec{a}_3 \text{ primitive lattice vectors}$$

- 14 Bravais lattices exist in 3 dimensions (1848)
- M. L. Frankenheimer in 1842 thought they were 15. So, so naïve…

Crystal Structure = Lattice + Basis



Lattice



Crystal Structure = Lattice + basis

Basis

Bloch Theorem

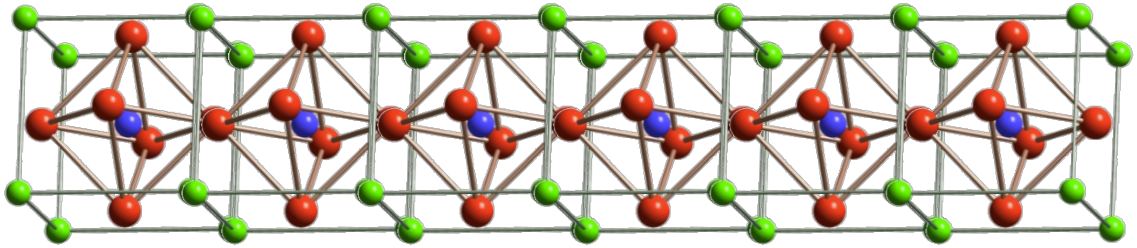
The one-particle effective Hamiltonian $\hat{H}$ in a periodic lattice commutes with the lattice-translation operator $\hat{T}_{\mathbf{R}}$, allowing us to choose the common eigenstates according to the prescriptions of Bloch theorem:

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

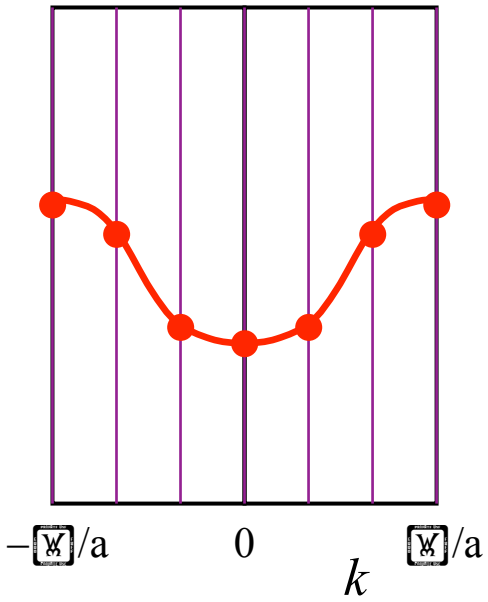
- *n, k* are the quantum numbers (band index and crystal momentum), *u* is periodic
- From two requirements: a translation can't change the charge density, and two translations must be equivalent to one that is the sum of the two

Bloch Theorem

Crystal in real space:

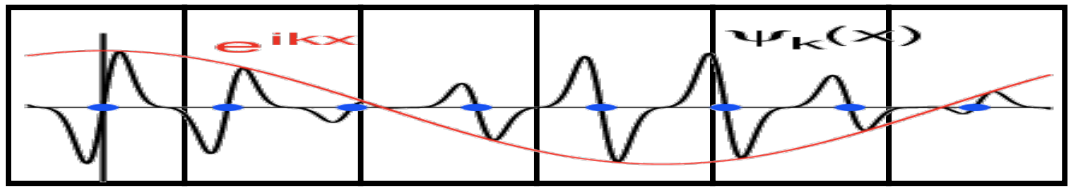


Brillouin zone in reciprocal space:

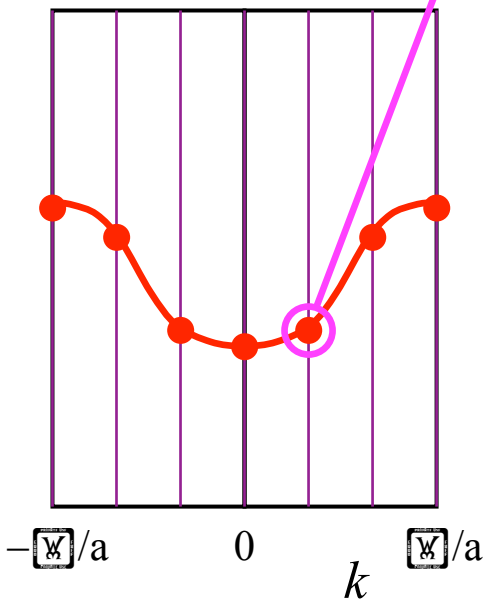


Bloch Theorem

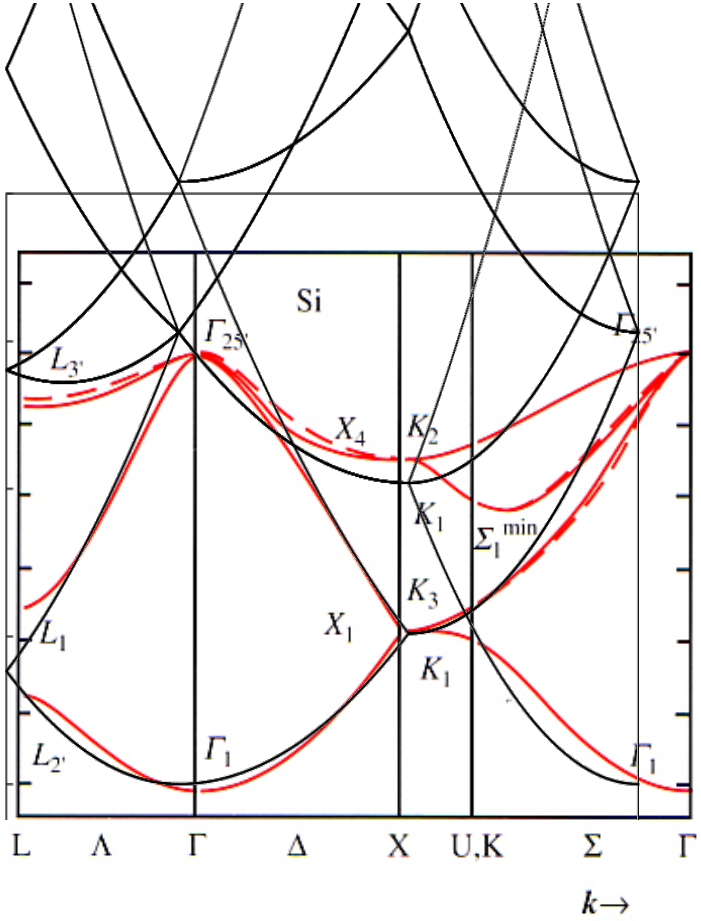
Crystal in real space:



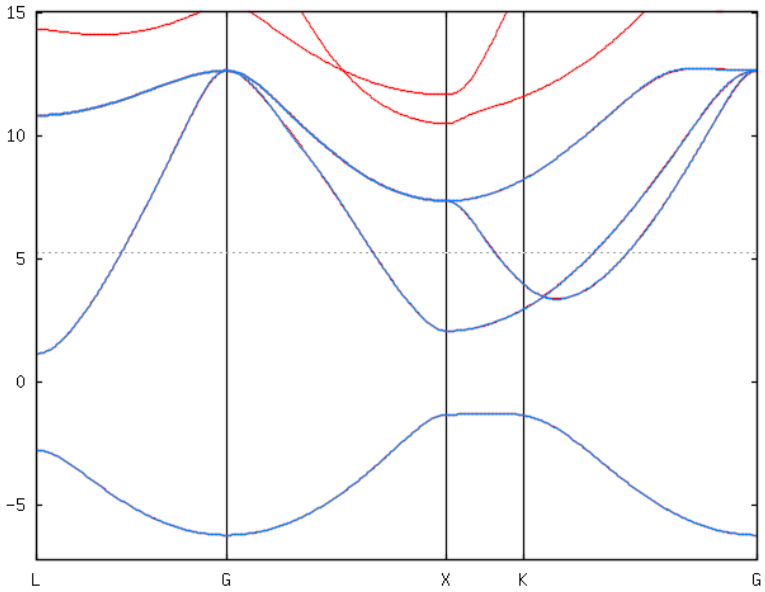
Brillouin zone in reciprocal space:



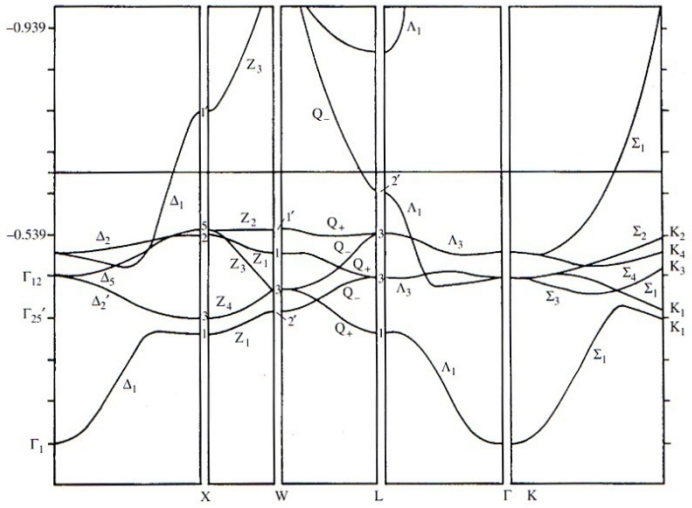
Silicon



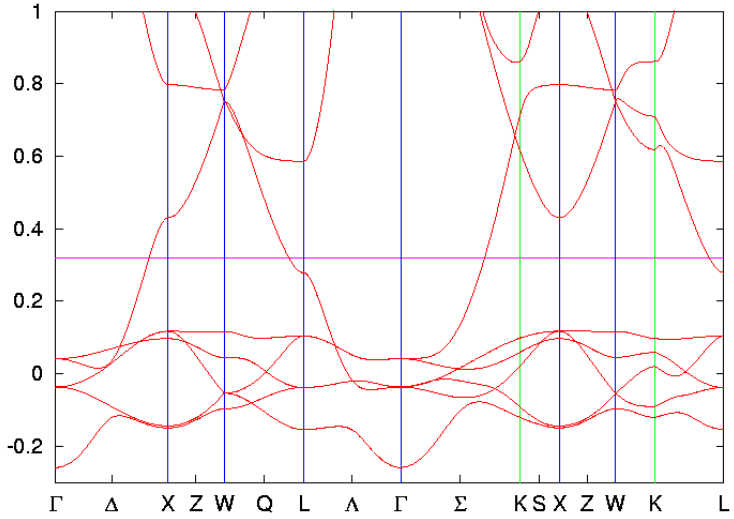
Lead



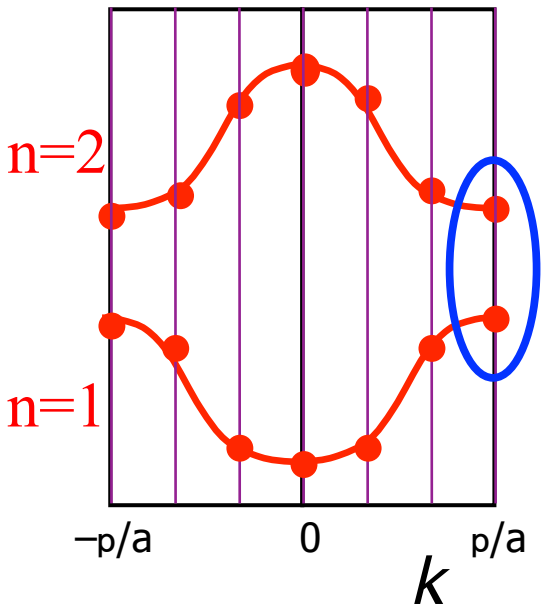
Copper



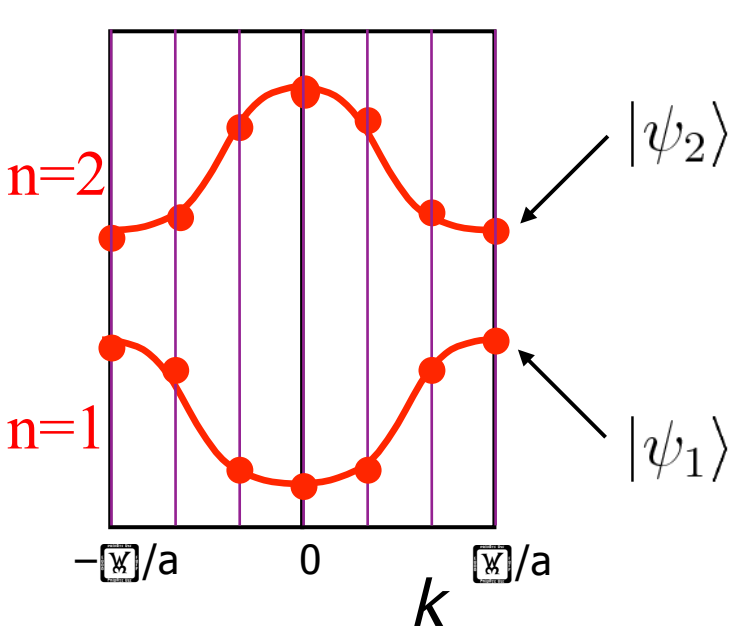
Silver

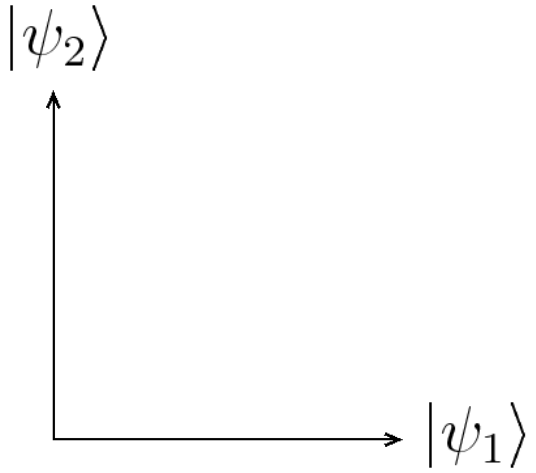


Orthogonal and unitary transformations



Orthogonal and unitary transformations



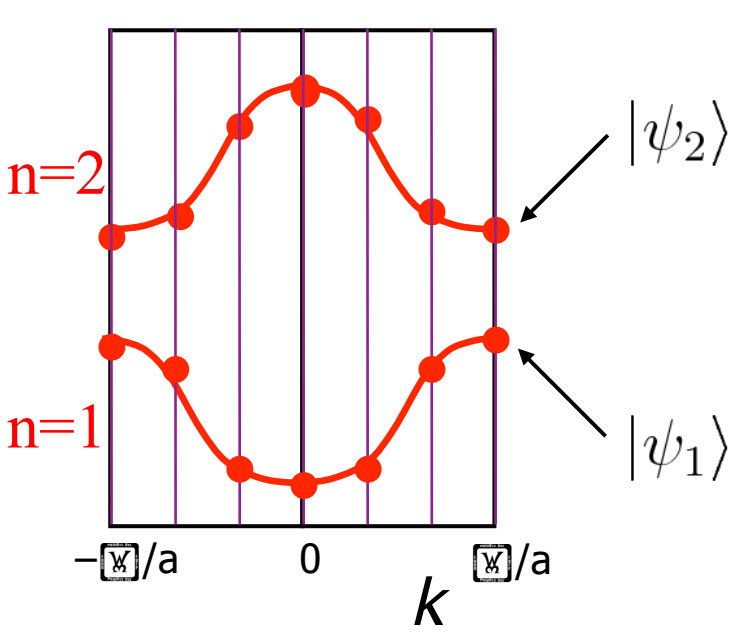


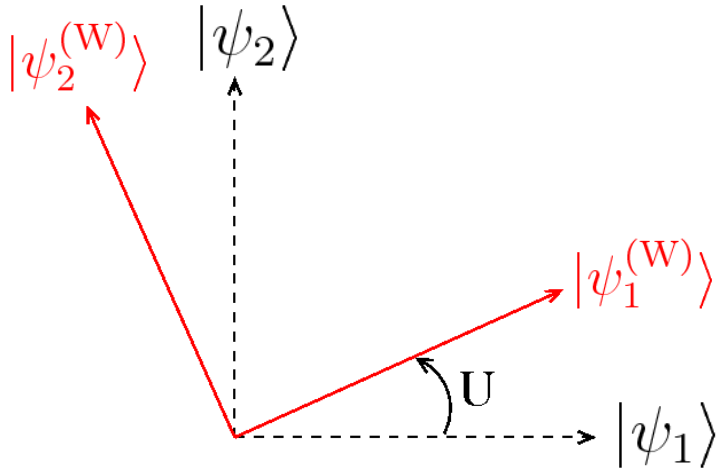
Orthogonal and unitary transformations

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

Rotated Bloch function

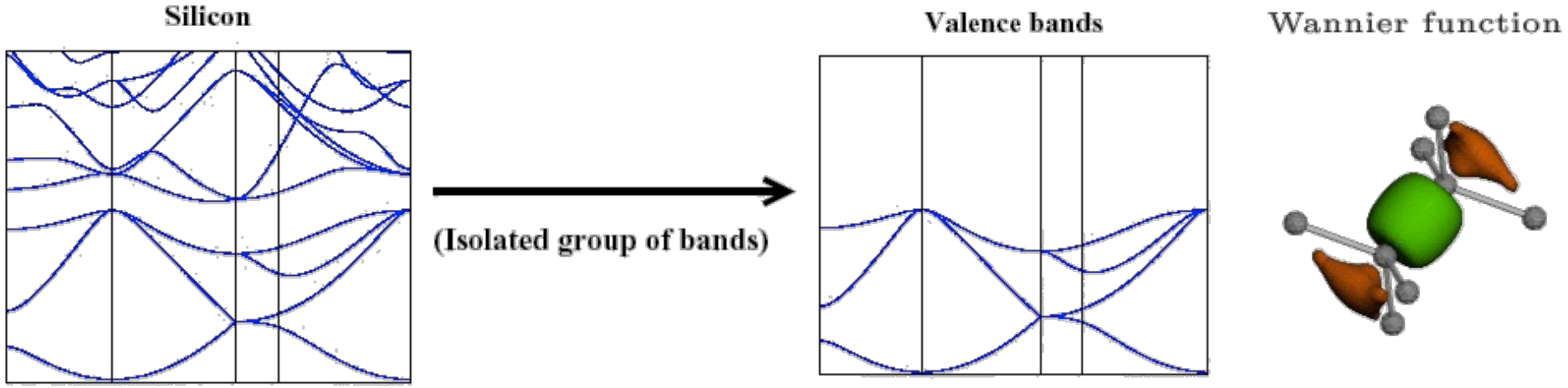
Unitary matrix





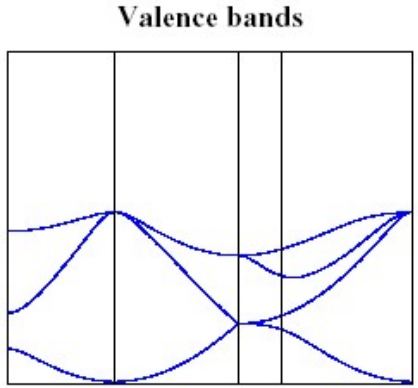
Generalized Wannier Functions for Composite Bands

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



From Bloch Orbitals to Wannier Functions

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



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

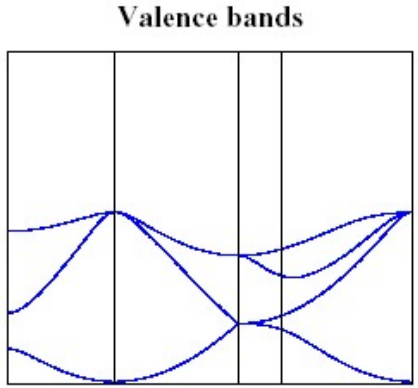
Gauge freedoms

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

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

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

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

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

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

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

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

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

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

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

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

Ω_I is gauge invariant, positive definite

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

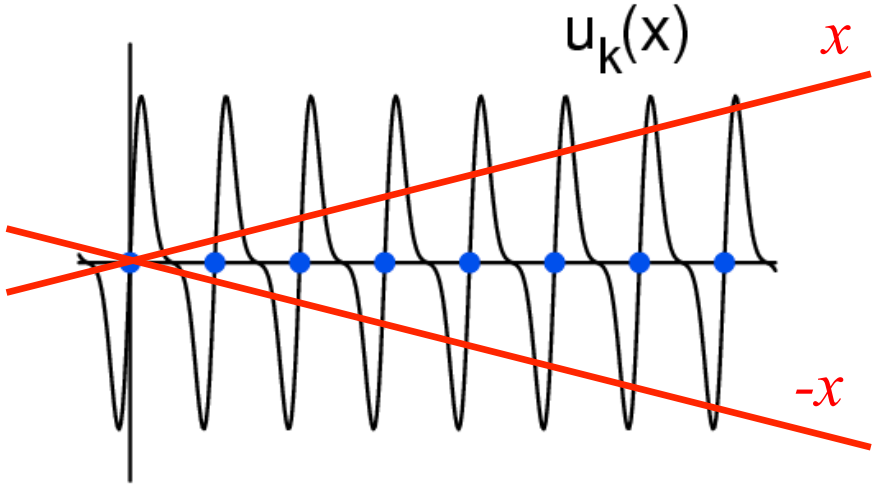
$$= \sum_{n,\alpha} \langle 0n | r_\alpha r_\alpha | 0n \rangle_n - \sum_{n,\alpha} \left[\sum_{\mathbf{R}m} \langle 0n | r_\alpha | \mathbf{R}m \rangle \langle \mathbf{R}m | r_\alpha | 0n \rangle \right] =$$

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

(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:

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

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.

$$\mathbf{r}_n = \langle\, w_{n\mathbf{0}} \,|\, \mathbf{r} \,|\, w_{n\mathbf{0}} \,\rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \langle\, u_{n\mathbf{k}} \,|\, i\frac{\partial}{\partial \mathbf{k}} \,|\, u_{n\mathbf{k}} \,\rangle =$$

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

The Localization Procedure

At the minimum, the Wannier functions are real

Unique global minimum when Γ sampling is used
(at least with 6 b-vectors)

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 $A_{in}^{(\mathbf{k})} = \langle \Psi_{n\mathbf{k}} | \Phi_i \rangle$,

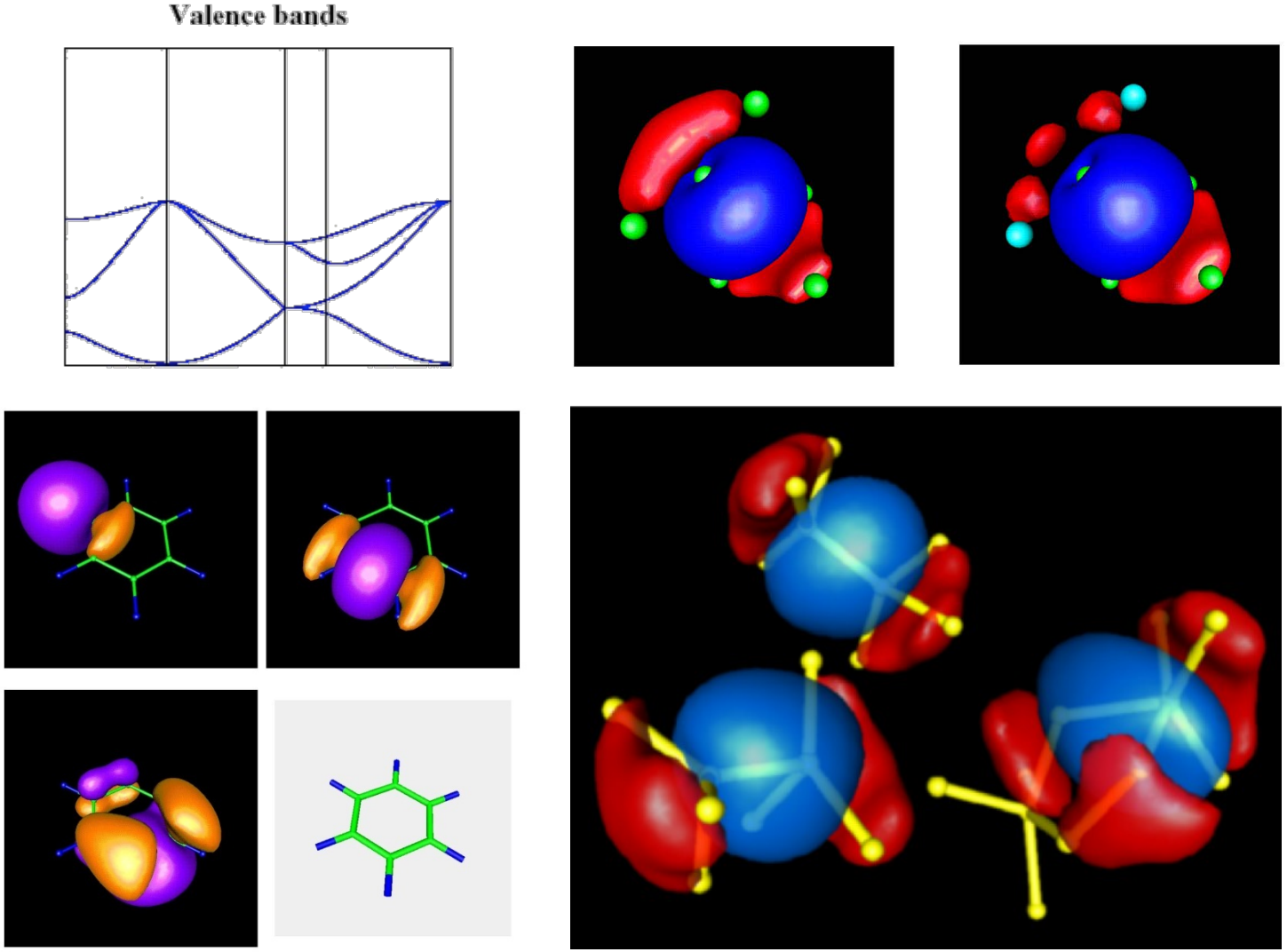
$$| w_i \rangle = \sum_{\mathbf{k}} | \Psi_{n\mathbf{k}} \rangle \langle \Psi_{n\mathbf{k}} | \Phi_i \rangle = \sum_{\mathbf{k}} A_{in}^{(\mathbf{k})} | \Psi_{n\mathbf{k}} \rangle \quad .$$

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

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

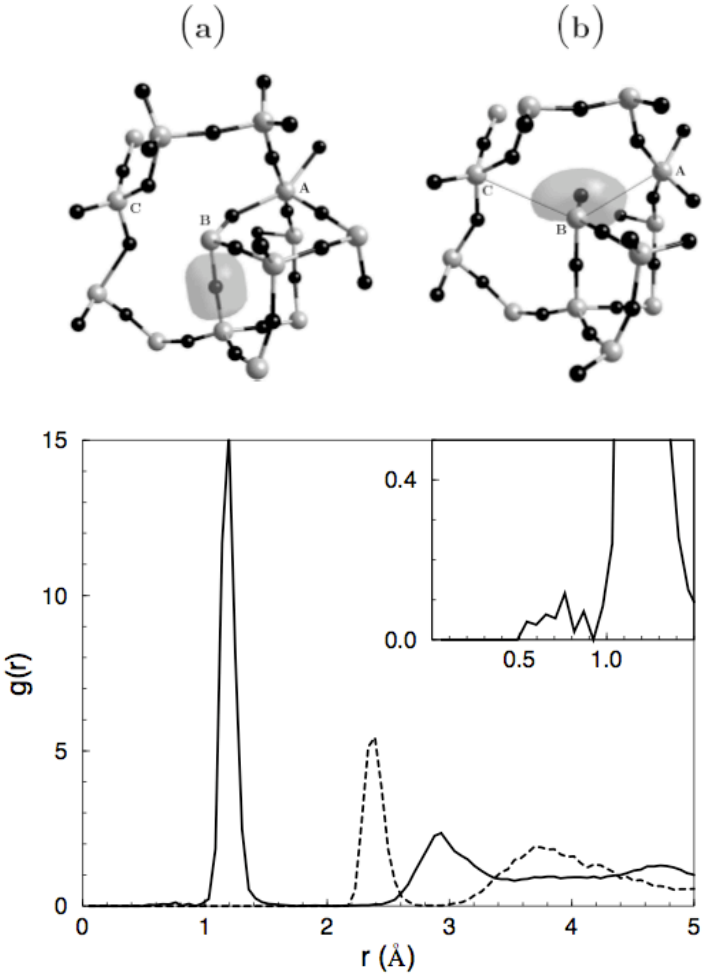
(the last equality can be proved using the Singular Value Decomposition for $A = U_1\,(diag)\,U_2$; it is $U = U_1\,\frac{(diag)}{|(diag)|}\,U_2$).

Silicon, GaAs, Amorphous Silicon, Benzene

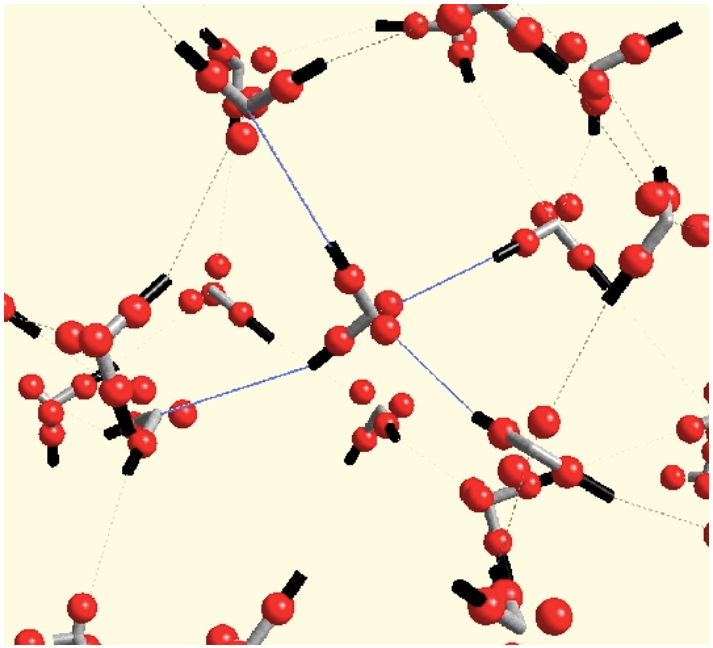


M. Fornari, N. Marzari, M. Peressi, and A. Baldereschi, Comp. Mater. Science 20, 337 (2001)

Wannier functions in *a-Si*



Wannier functions in *l-H_2O*



Silvestrelli et al.

Some conclusions

- Modern theory of polarization: the polarization is given by the sum of the centers of charge for the Wannier functions

$$\mathbf{P} = -\frac{e}{\Omega} \sum_n \langle\, \mathbf{0}n \,|\, \mathbf{r} \,|\, \mathbf{0}n \,\rangle$$

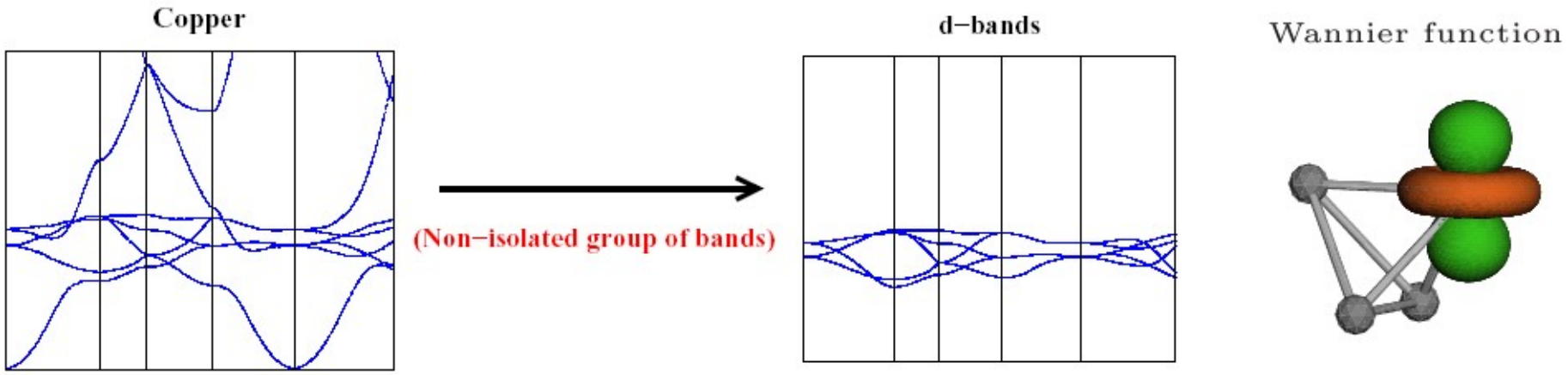
- Quantum dielectric properties are mapped onto a classical picture (e.g. the Born effective charges)

- Chemical intuition: the nature of hybridization and bonding in going from the atoms to the solid

- Linear-scaling algorithms: orthogonality needs to be imposed only with the overlapping neighbors

Disentanglement of Attached Bands

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



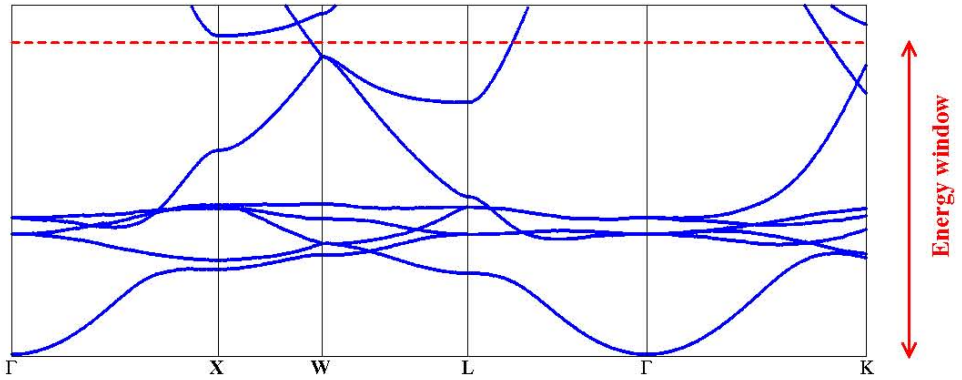
I. Souza, N. Marzari and D. Vanderbilt, Phys. Rev. B 65, 035109 (2002)

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 $\Omega_{\rm I}$



- **Step 2:** Obtain maximally-localized WFs

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

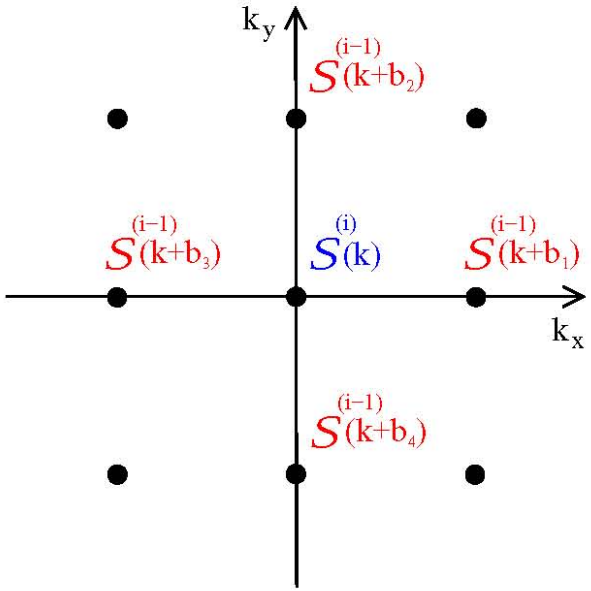
$$\Omega_{\rm I} = \frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \left(J - \sum_{mn} |M_{mn}^{(\mathbf{k},\mathbf{b})}|^2 \right)$$

• $\Omega_{\rm I}$ 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 $\mathcal{S}(\mathbf{k})$.

$\Rightarrow$ 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.

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

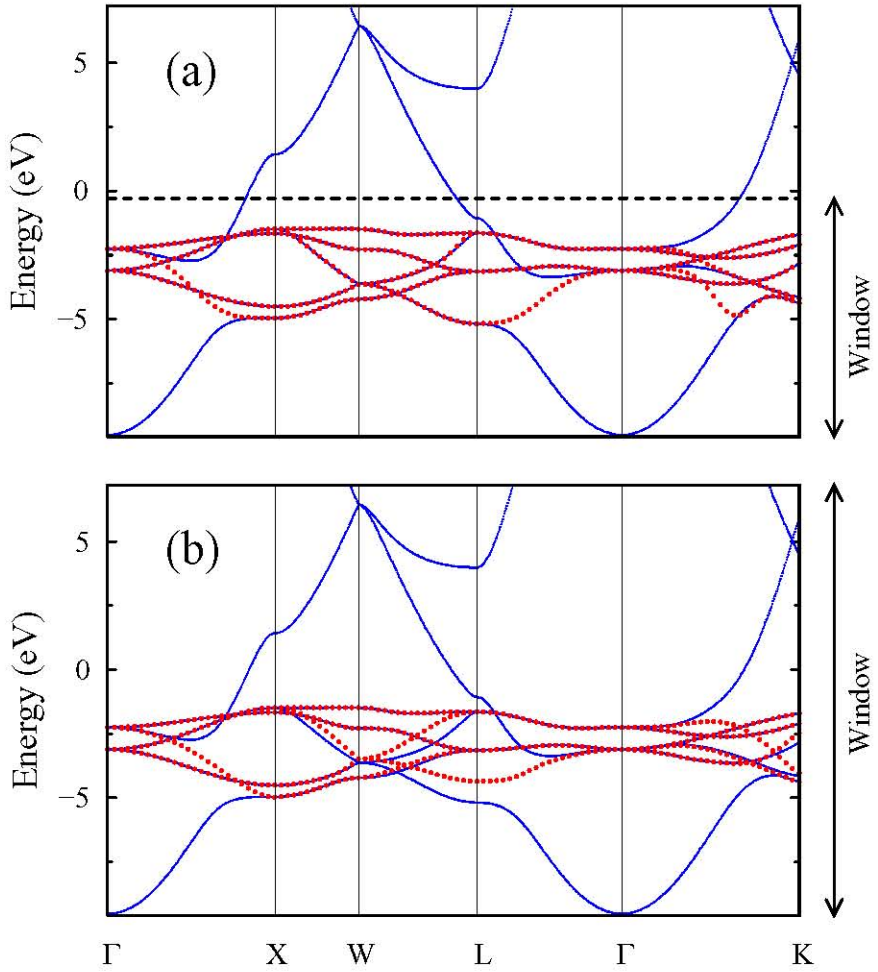
$$\left[\sum_{\mathbf{b}} \hat{P}_{\mathbf{k}+\mathbf{b}}^{(i-1)} \right] \left| u_{n\mathbf{k}}^{(i)} \right\rangle = \lambda_{n\mathbf{k}}^{(i)} \left| u_{n\mathbf{k}}^{(i)} \right\rangle$$

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

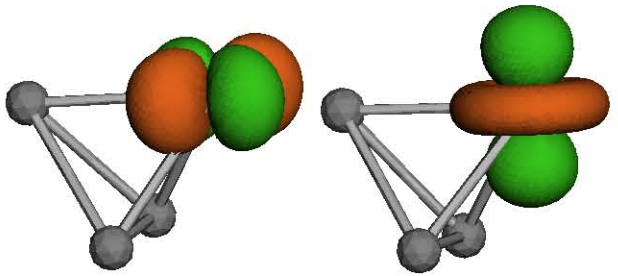
- Repeat until self-consistency (when spaces $\mathcal{S}(\mathbf{k})$ stabilize)

d Bands of Copper

Two possible choices of energy window



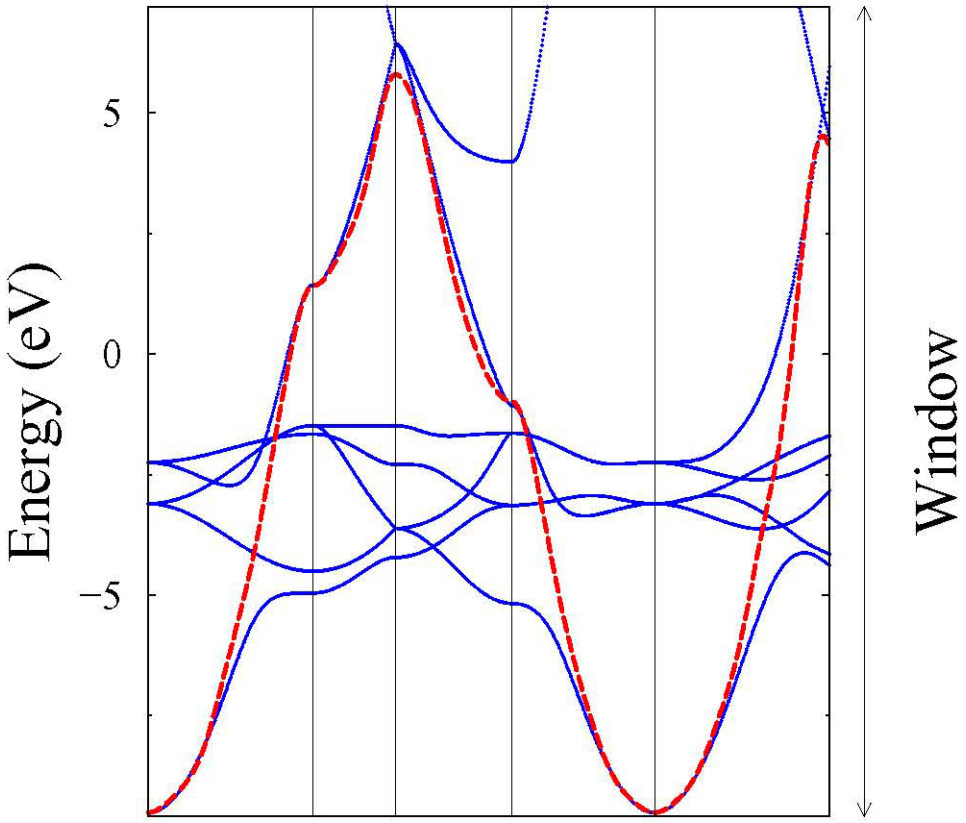
The e_g d WFs of panel (b)

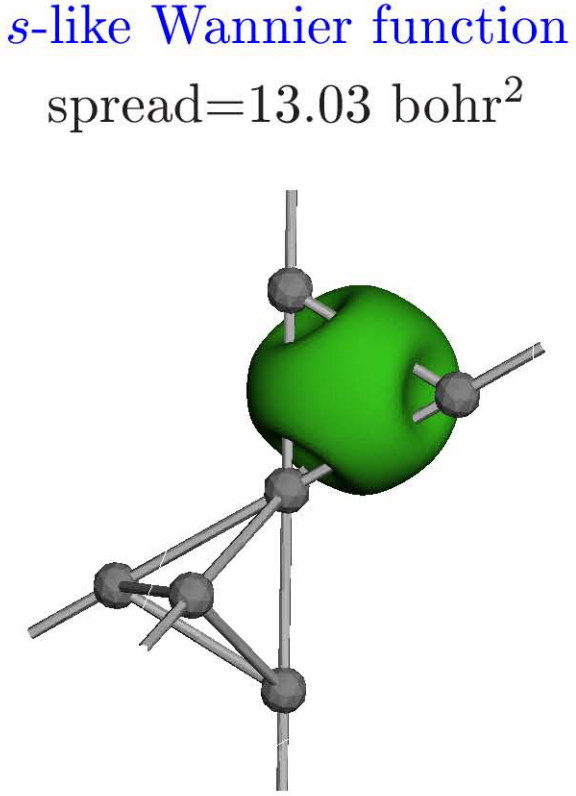


$\text{spread}(e_g)=1.700\ \text{bohr}^2$

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

s Band of Copper

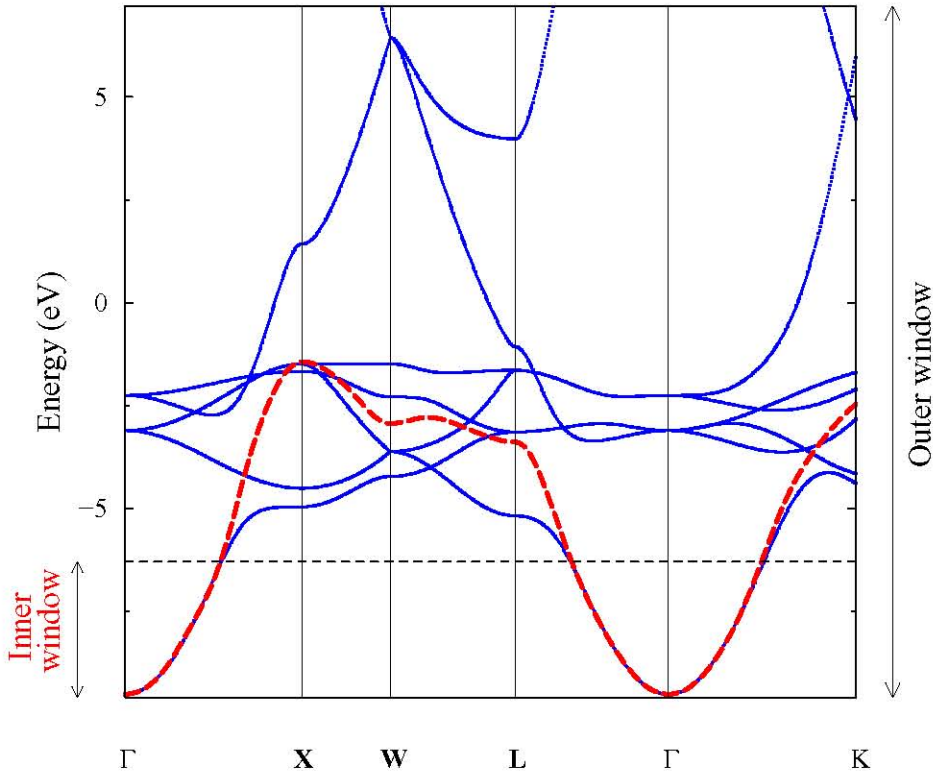




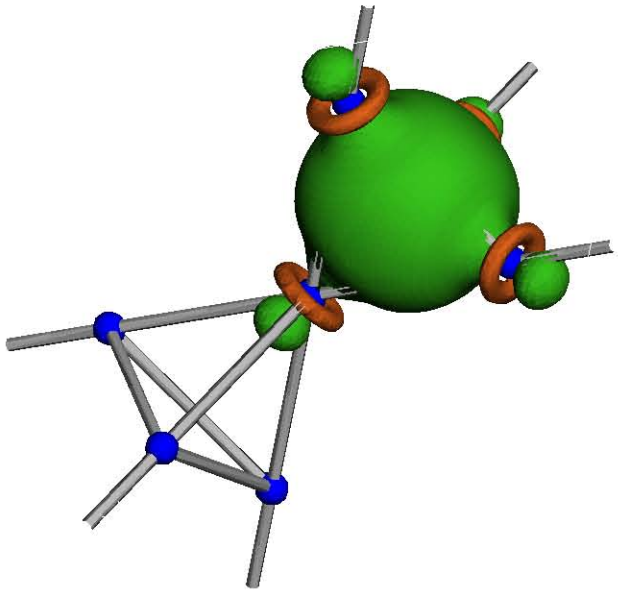
Exact Constraints on the Inner Energy

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

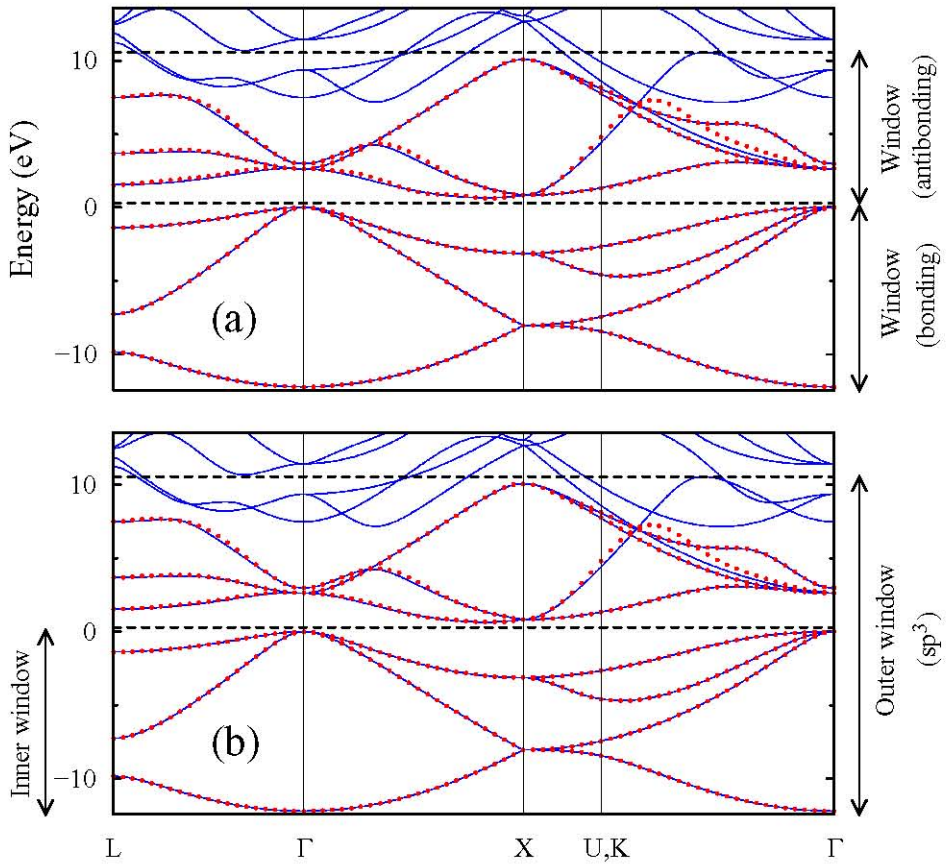
$\Rightarrow$ Minimize $\Omega_{\rm I}$ w/ constraint that states inside inner window are included in the optimal subspaces $\mathcal{S}(\mathbf{k})$

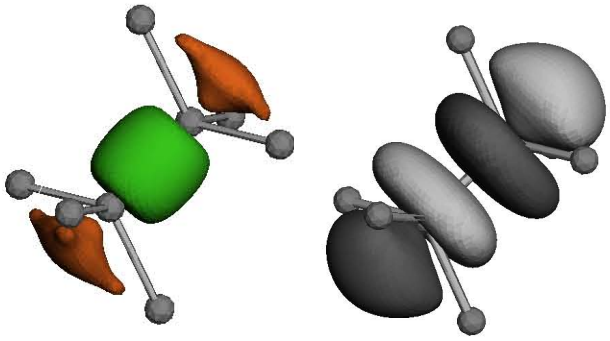


Hybrid *s*-*d* character:

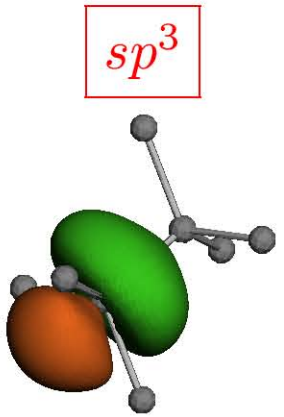


Silicon: Bonding and Antibonding Orbitals





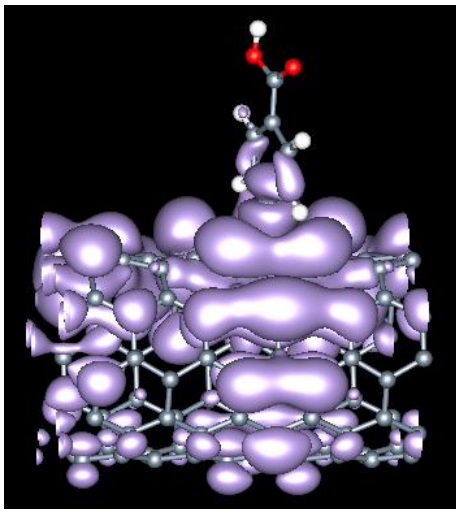
7.53 bohr^2 24.37 bohr^2



spread=10.68 bohr^2

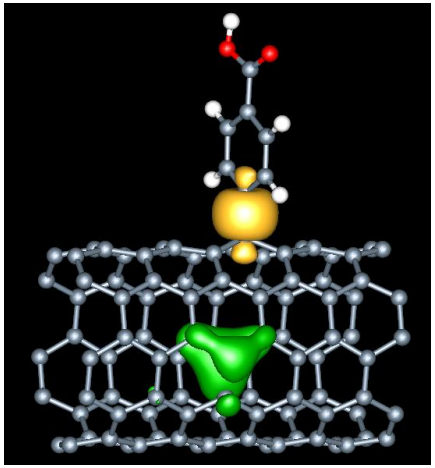
Electronic Structure of Large Nanostructures

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

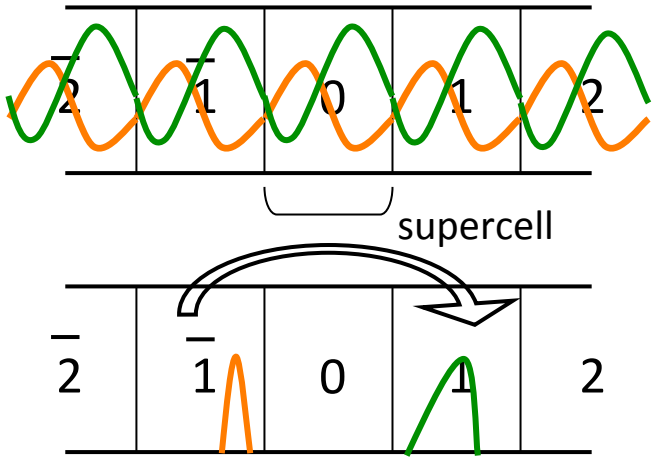
$$\Omega = \sum_n [\langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2]$$



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**



No interaction

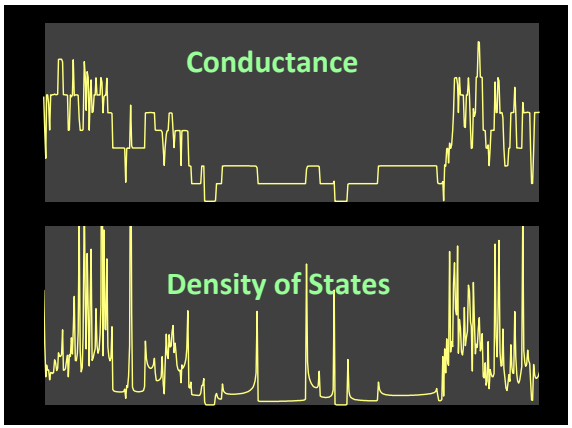
$$H_{00}\ ,\ H_{01} \Rightarrow G_C^r(E)$$

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

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

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

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

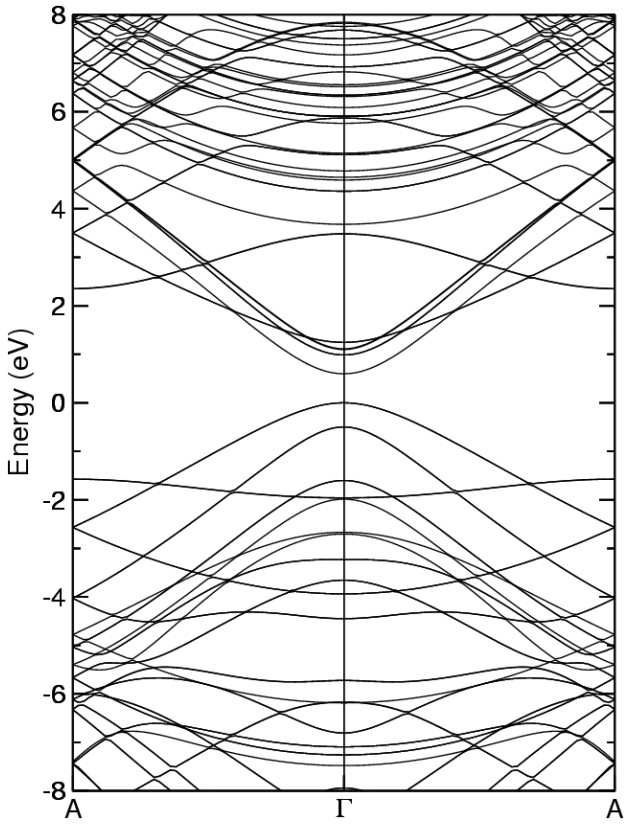


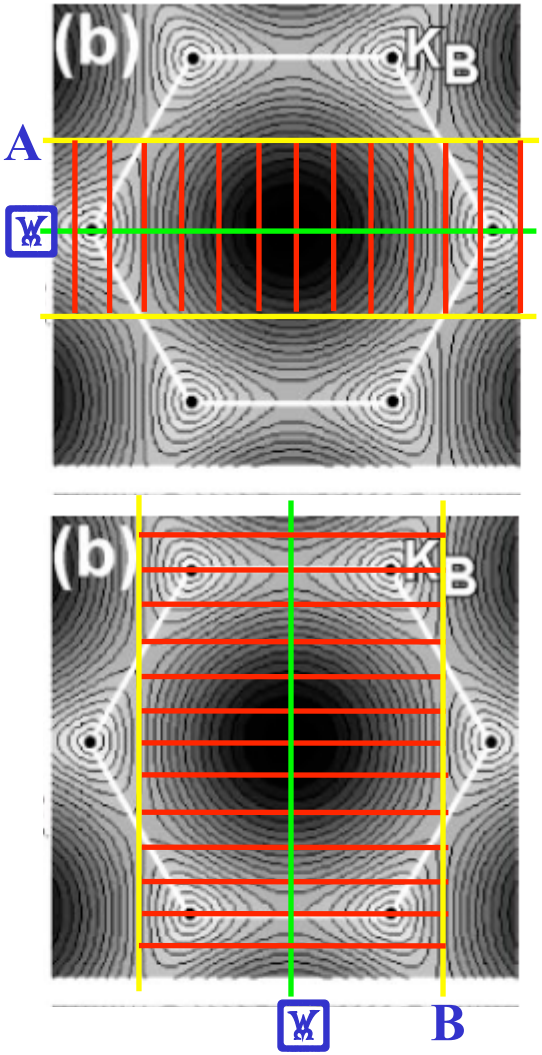
M. B. Nardelli, Phys. Rev. B 60, 7828 (1999)

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

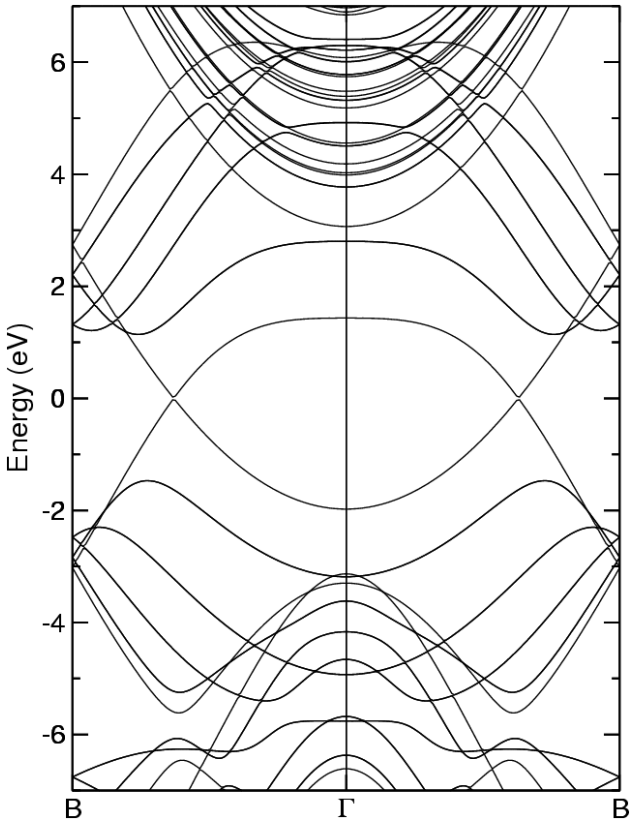
Band Structure of (8,0) and (5,5) SWNT

(8,0) semiconducting

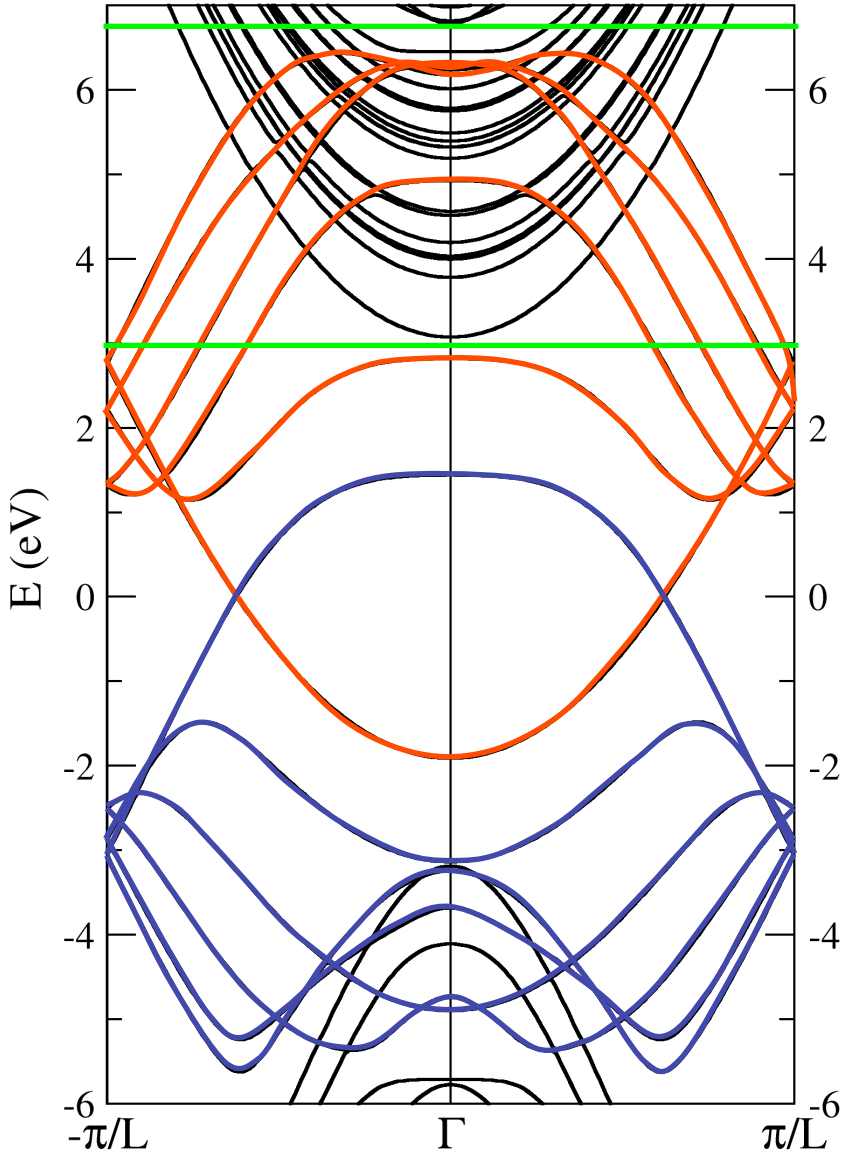




(5,5) metallic



Disentanglement: Conduction Bands in (5,5) SWNT



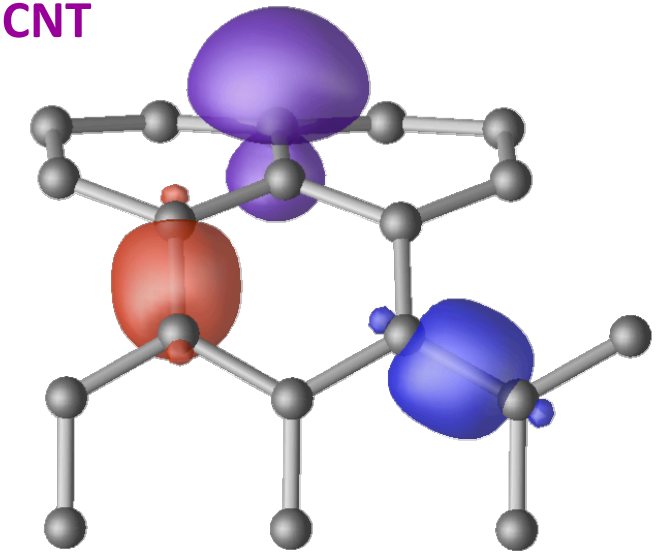
MLWFs from the Disentangled Subspace

- Localization after disentanglement

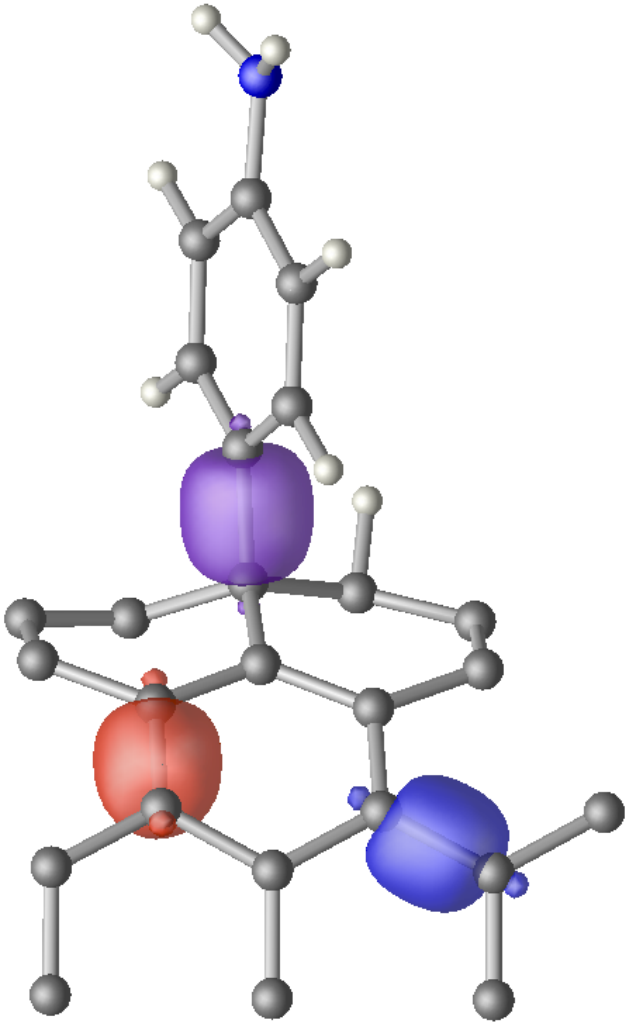
$$w_n = \sum_{m=1}^{N} U_{mn} \psi_m$$

- MLWFs from the disentangled subspace
  - s bond orbitals + p orbitals

(5,5) CNT



(5,5) CNT + Nitrophenyl

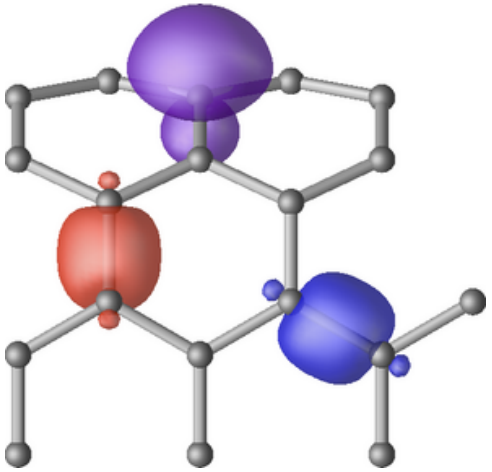


Max-loc WFs ↔ "Exact" Tight-Binding

Compact mapping of Bloch states into local orbitals

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

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



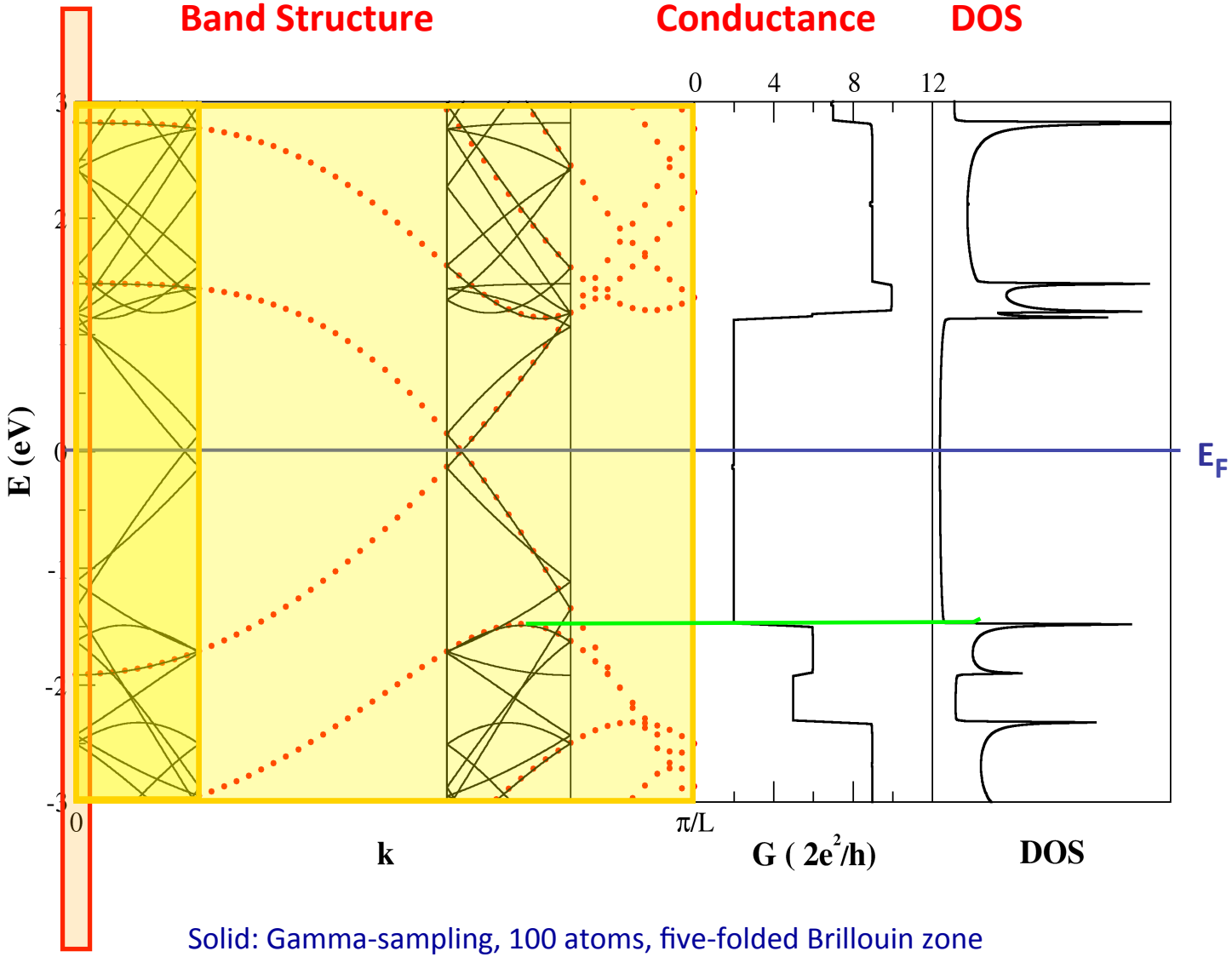
$$\left\langle \psi_{i\mathbf{k}} \middle| \hat{\mathrm{H}} \middle| \psi_{j\mathbf{k}} \right\rangle = H_{ij}^{00} + e^{i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{01} + e^{-i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{0\bar{1}}$$ ⇨ Diagonalize H Matrix

Band Structure and Conductance of a (5,5) SWCNT

Gamma-point :

~2eV pseudo gap

Two eigenchannels at E_F ⇨ perfect recovery of metallic character !

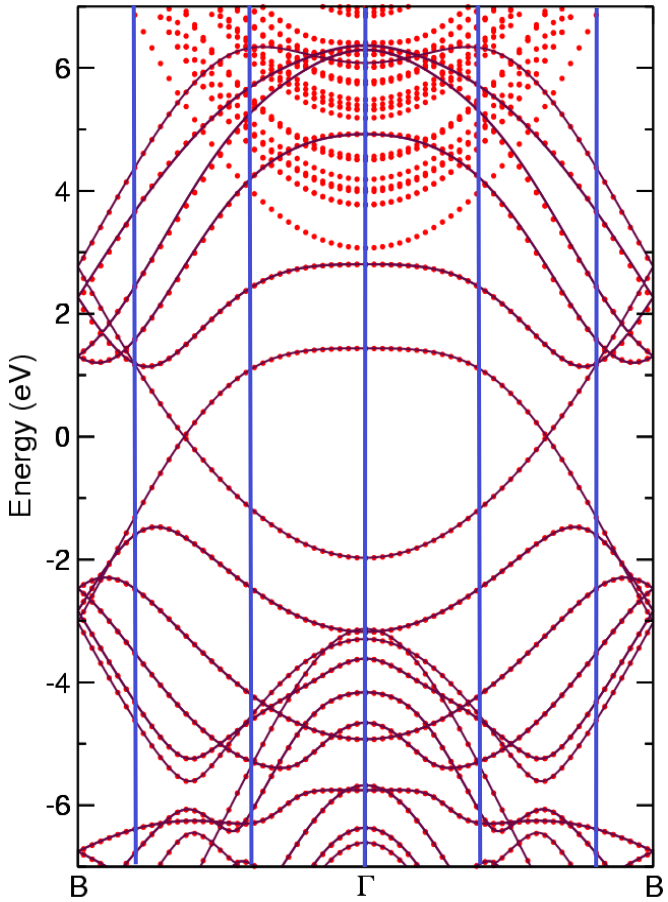


Solid: Gamma-sampling, 100 atoms, five-folded Brillouin zone

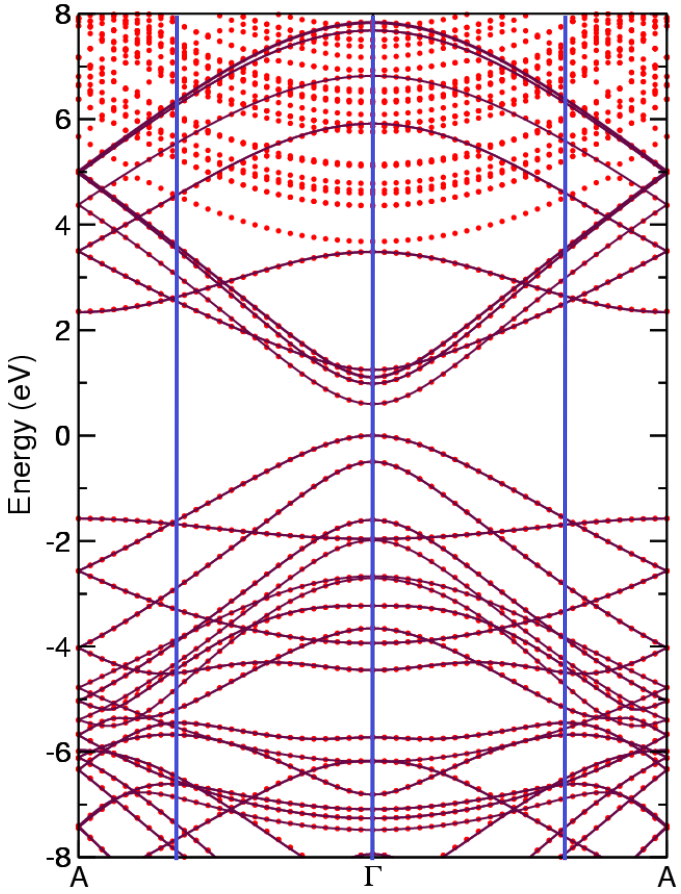
Dotted: Full SCF calculation (5 k-points, 20 atoms supercell)

Exact Mapping onto a Tight-Binding Hamiltonian

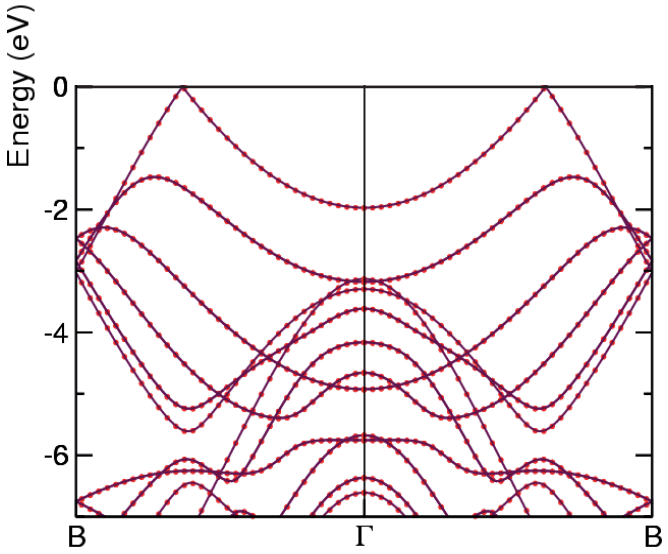
(5,5) SWCNT

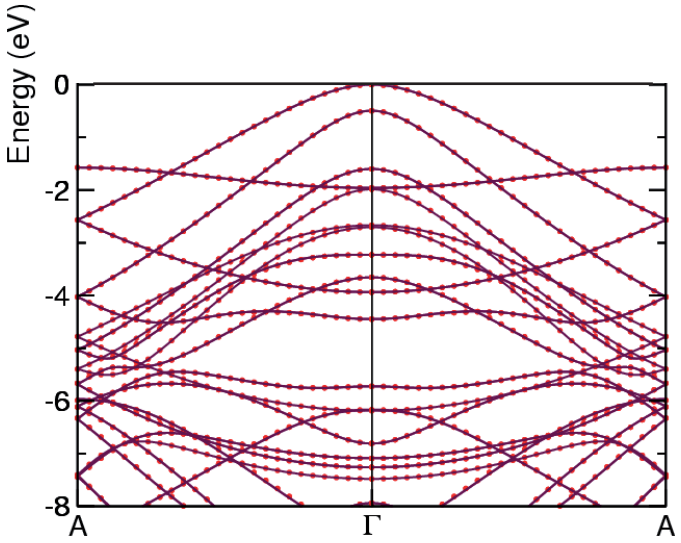


(8,0) SWCNT



Band Structure of (5,5) and (8,0) SWCNTs



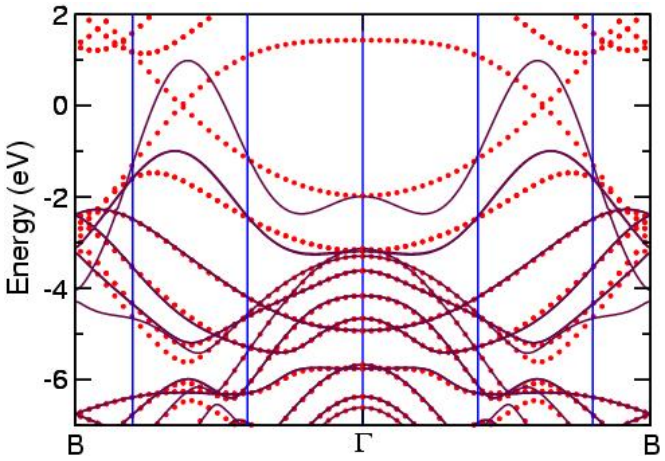


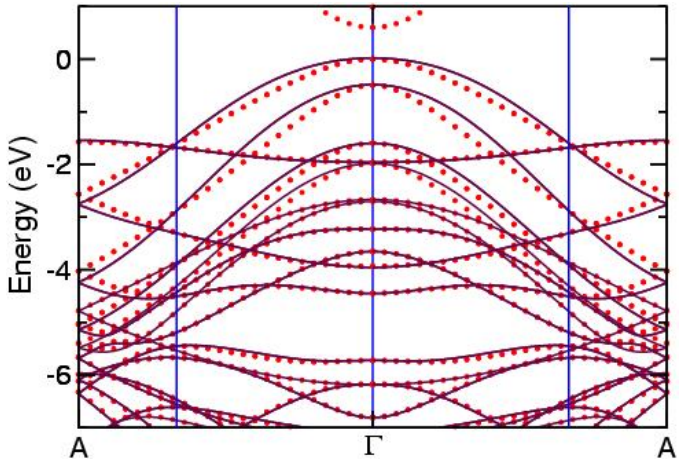
Band Structure of (5,5) and (8,0) SWCNTs

(5,5) SWCNT

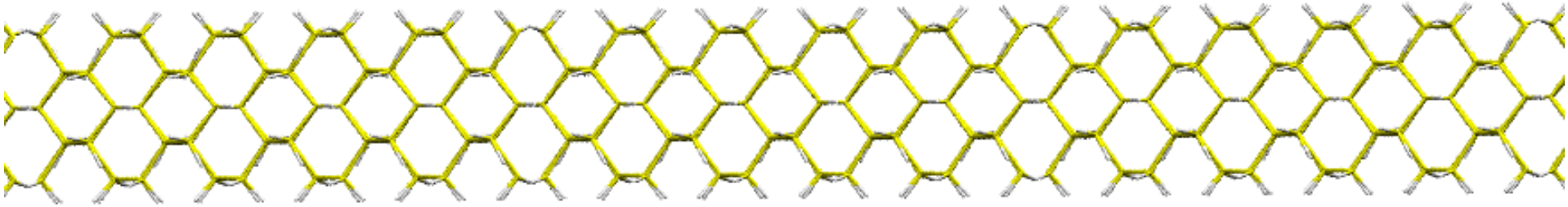
(8,0) SWCNT

Occupied states only, no disentanglement !

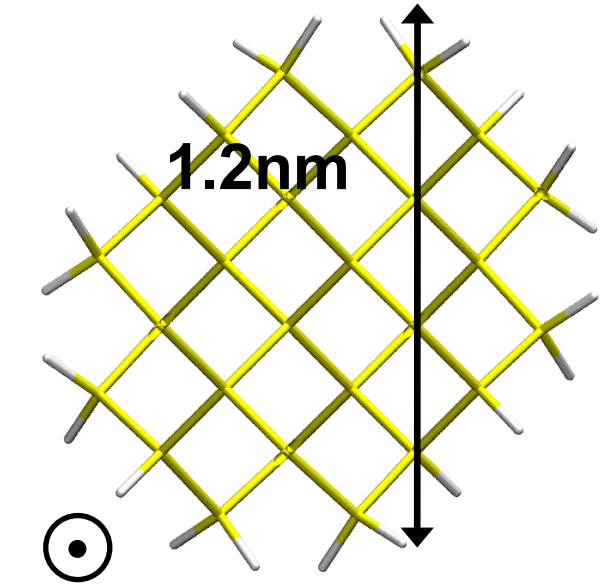




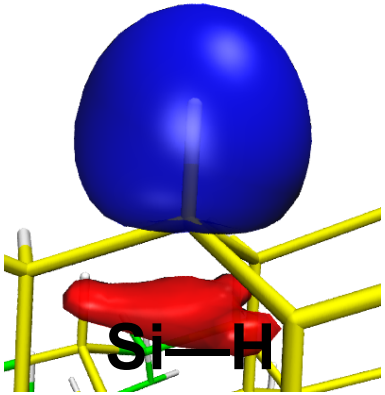
Silicon Nanowires

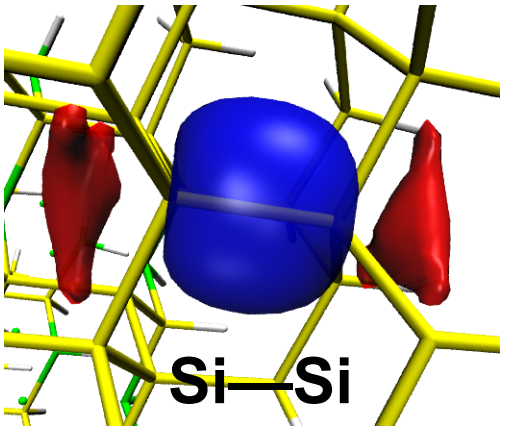


(001)

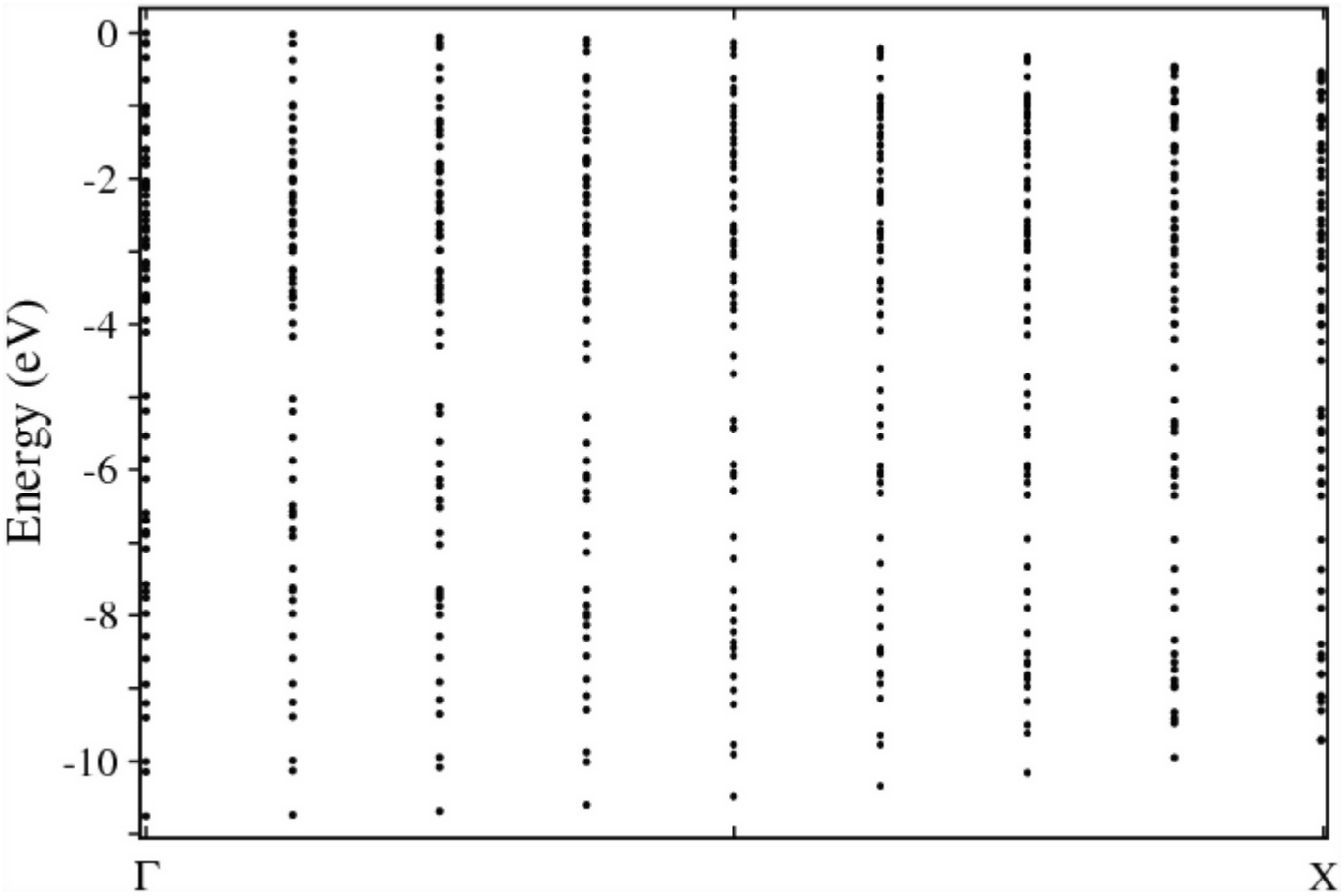


MLWFs for the Occupied Manifold

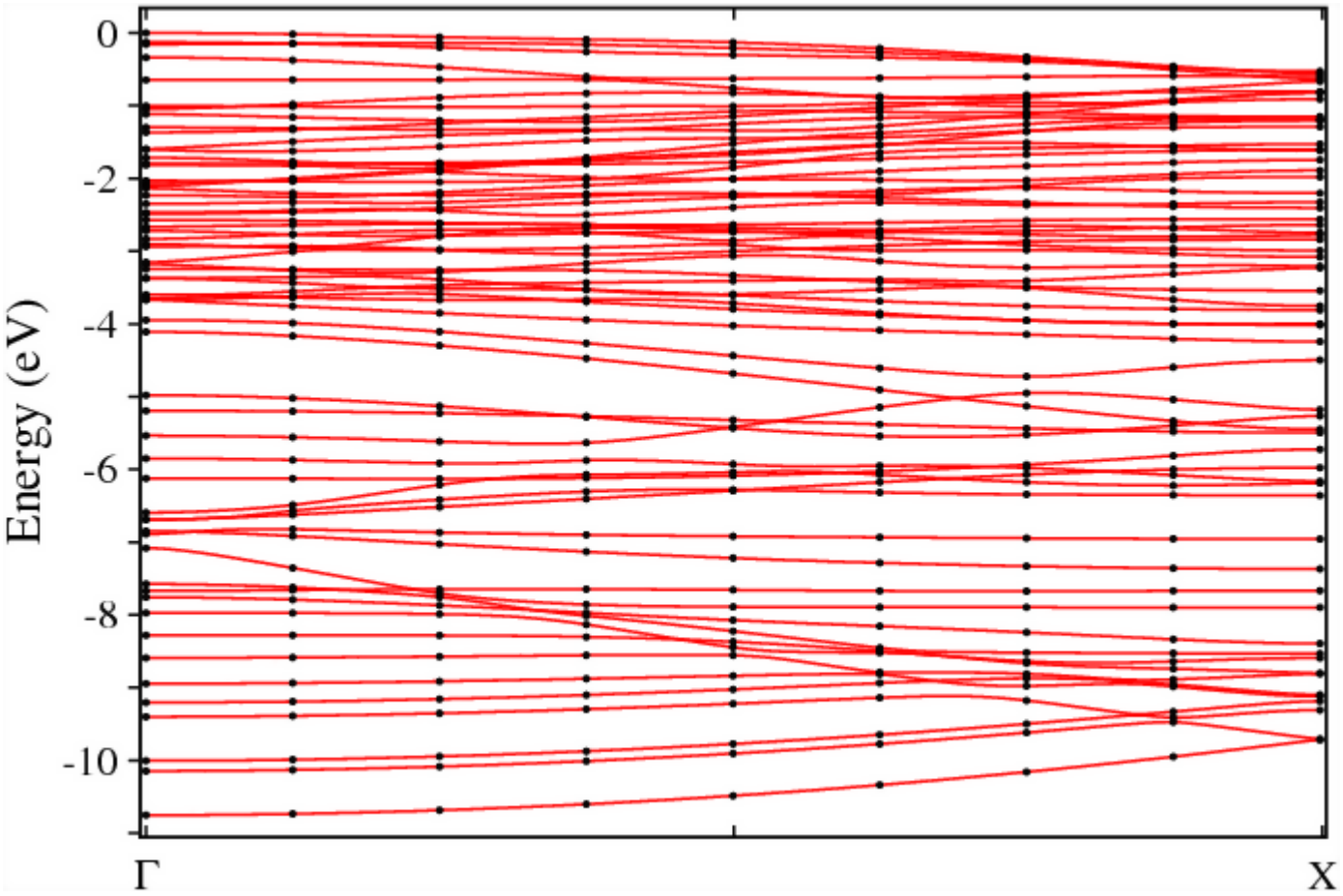




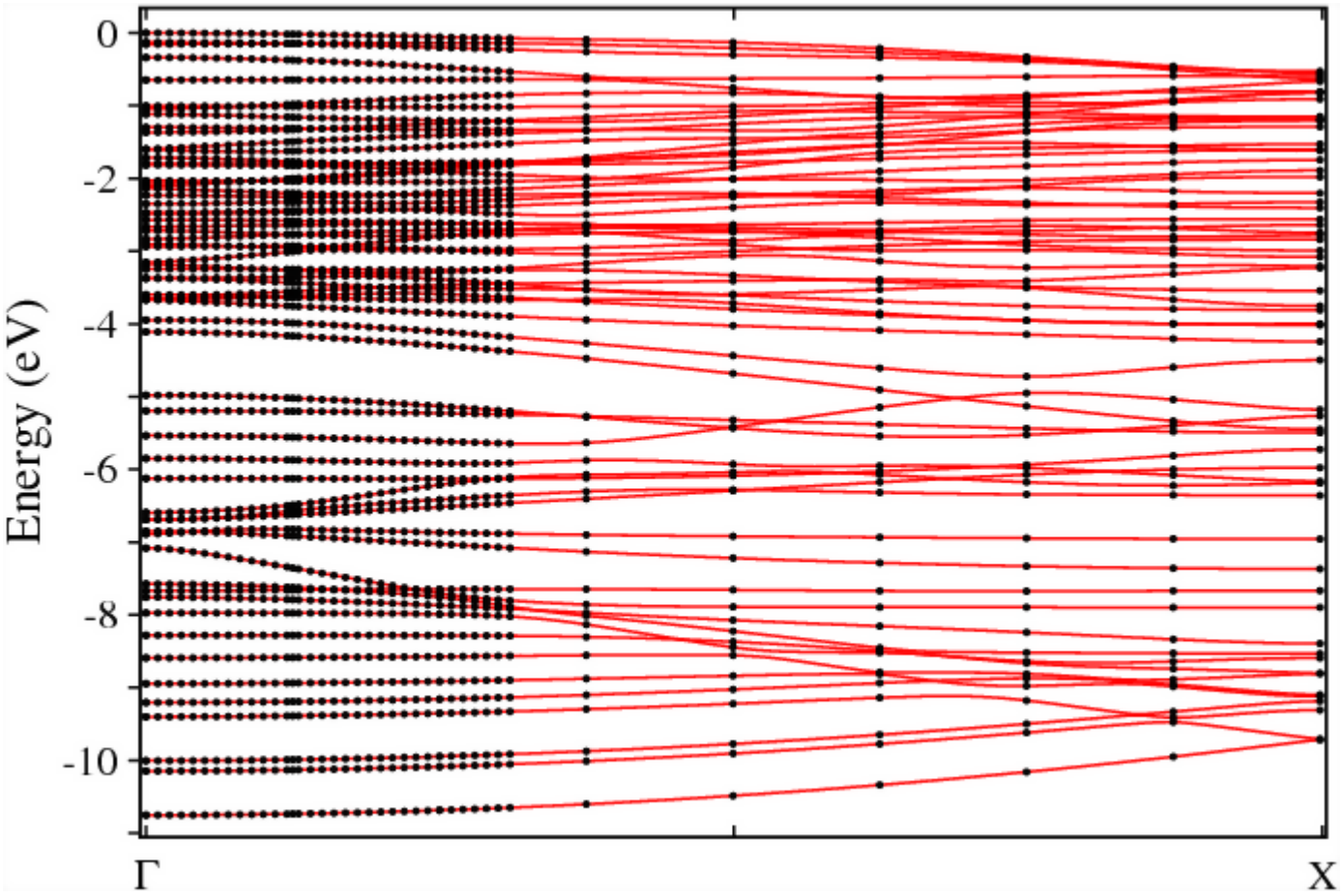
Accurate interpolation



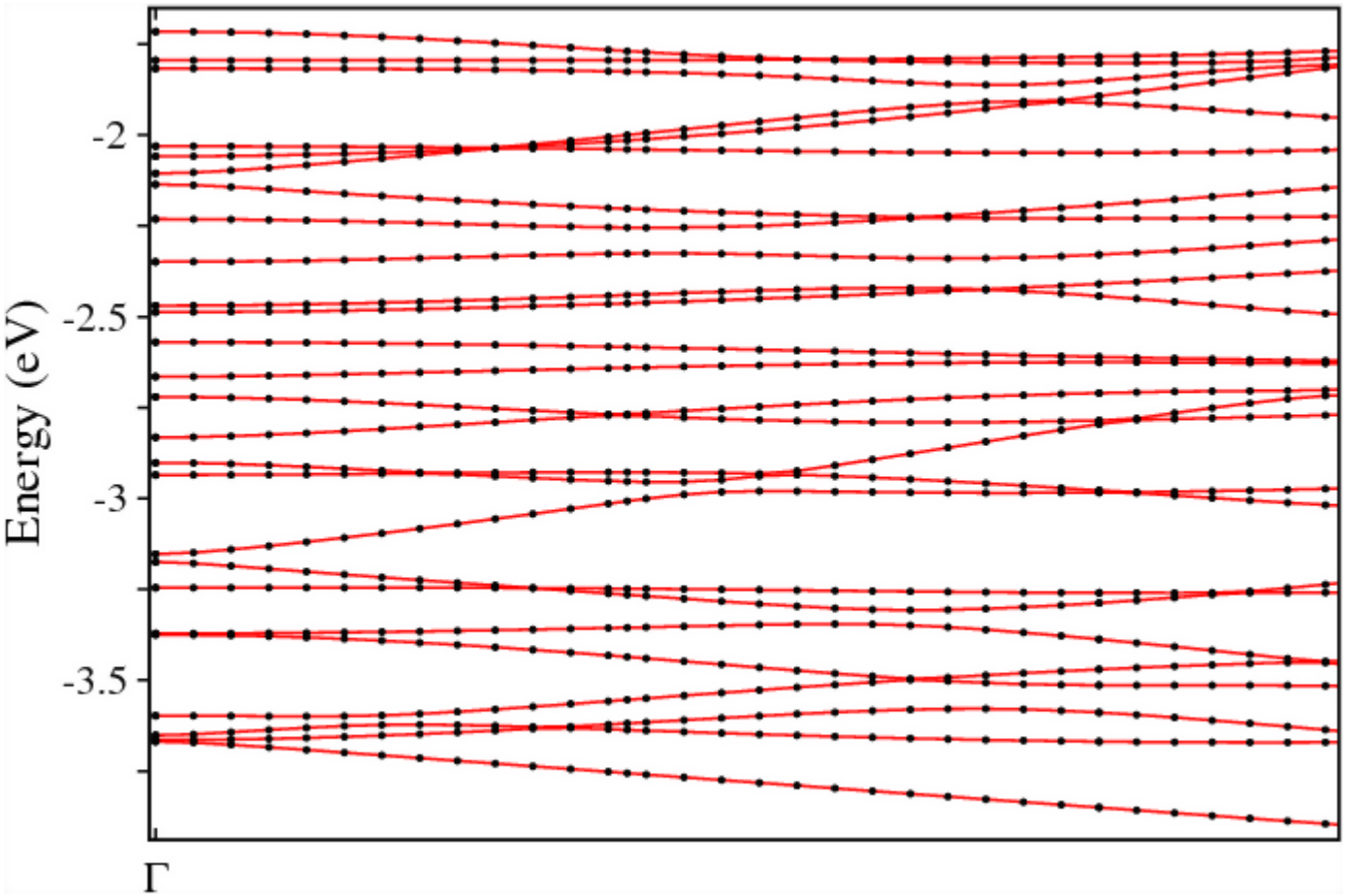
Accurate interpolation



Accurate interpolation



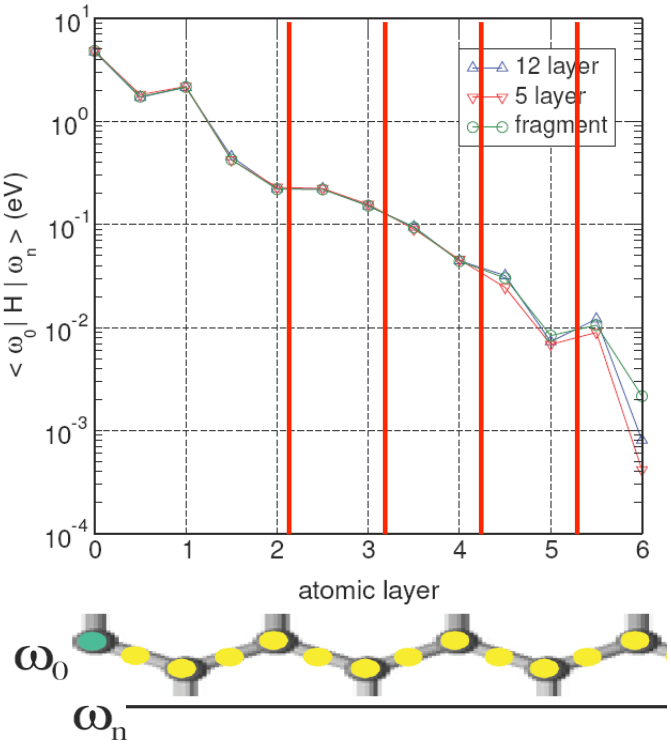
Accurate interpolation

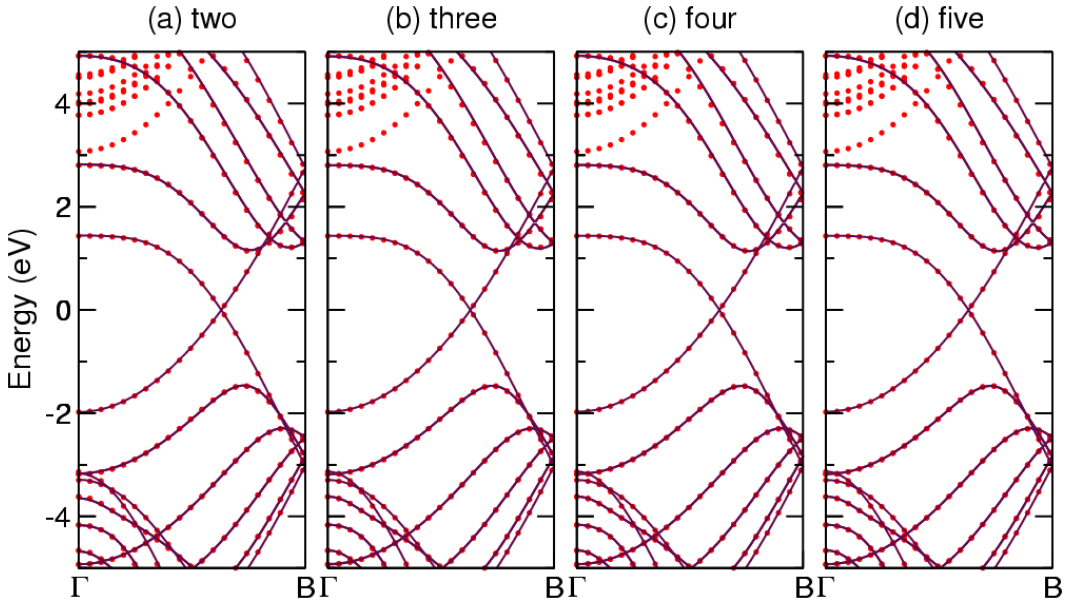


Exponential Decay

Even in a metal, we have smoothly connected manifolds – no relation with the physical decay of the density matrix

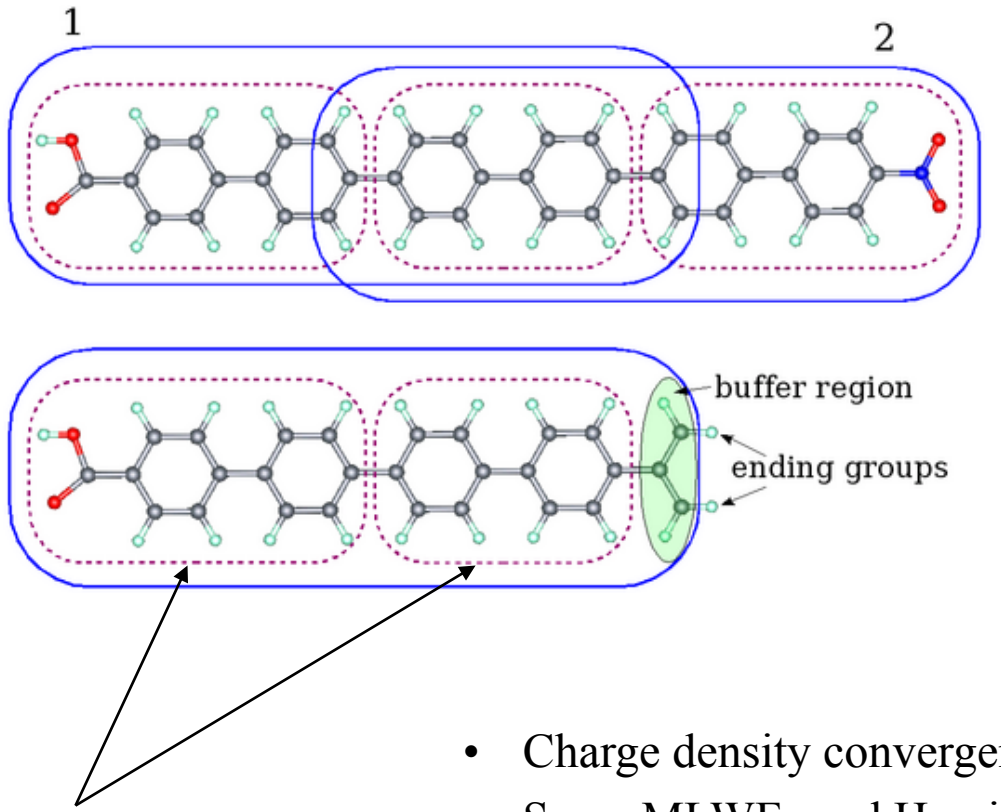
$$\langle \omega_0 | \hat{H} | \omega_n \rangle$$





Large Scale Calculations

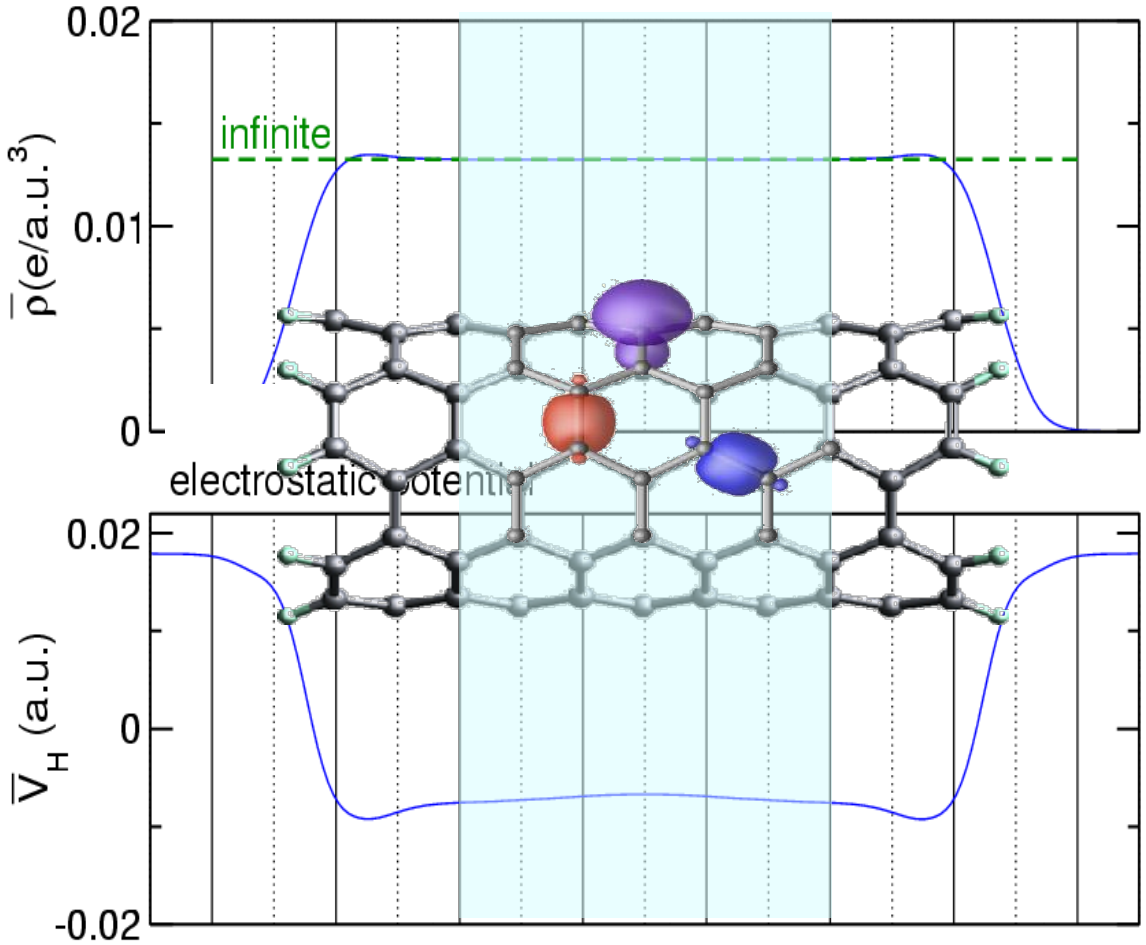
- Parameterization

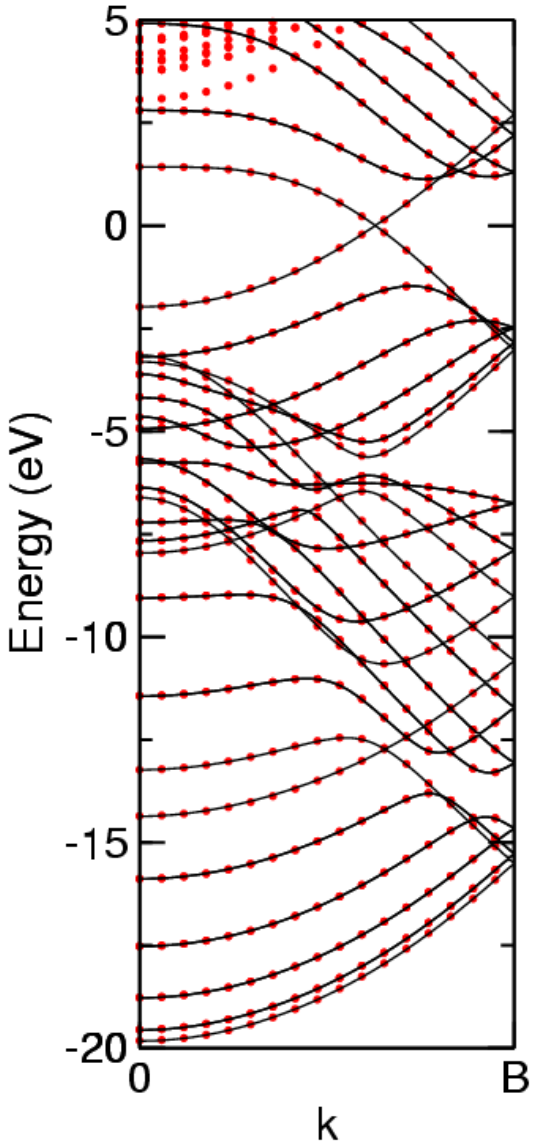


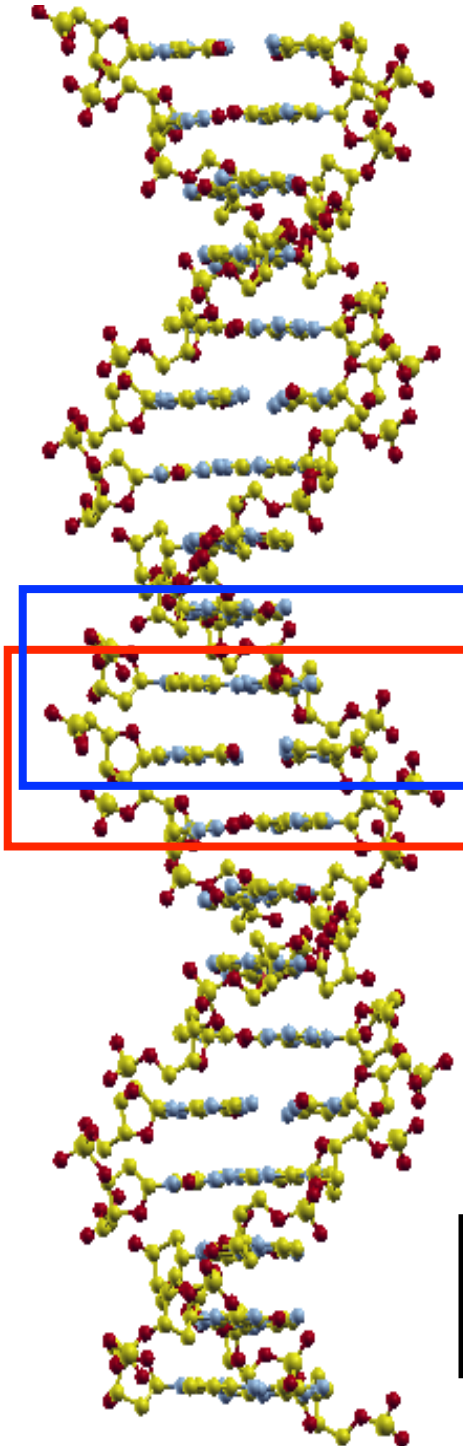
- principal layer

- Charge density convergence
- Same MLWFs and Hamiltonian matrix elements in overlapping region
- Electronic structure of long 1-D structure with a little cost

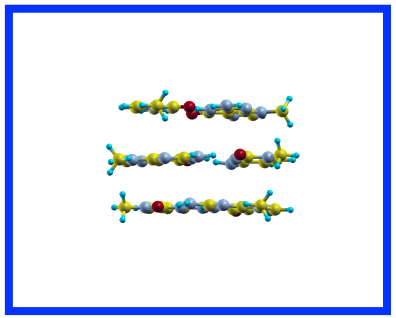
MLWFs Extraction From a Saturated Cluster







polyd(*CpGp*) *B*-DNA



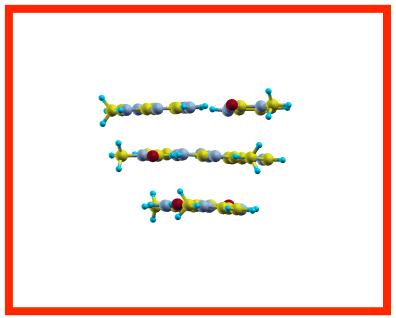
B
A
B

WANNIER FUNCTIONS

$$H = \begin{pmatrix} \ddots & \vdots & 0 & 0 & 0 \\ \cdots & AA & AB & 0 & 0 \\ 0 & (AB)^\dagger & BB & BA & 0 \\ 0 & 0 & (BA)^\dagger & AA & \cdots \\ 0 & 0 & 0 & \vdots & \ddots \end{pmatrix}$$

A = G — C

B = C — G



A
B
A

WANNIER FUNCTIONS

First-principles DFT, Γ-Point only
Ultrasoft pseudopotentials
GGA exchange-correlation functional

Optimal model Hamiltonian for infinite system

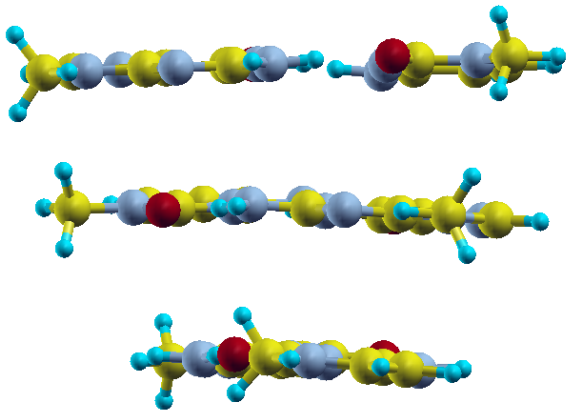
B A B A B A B A B A B A B A B A B A B A B A B A B A B

B-DNA Configuration

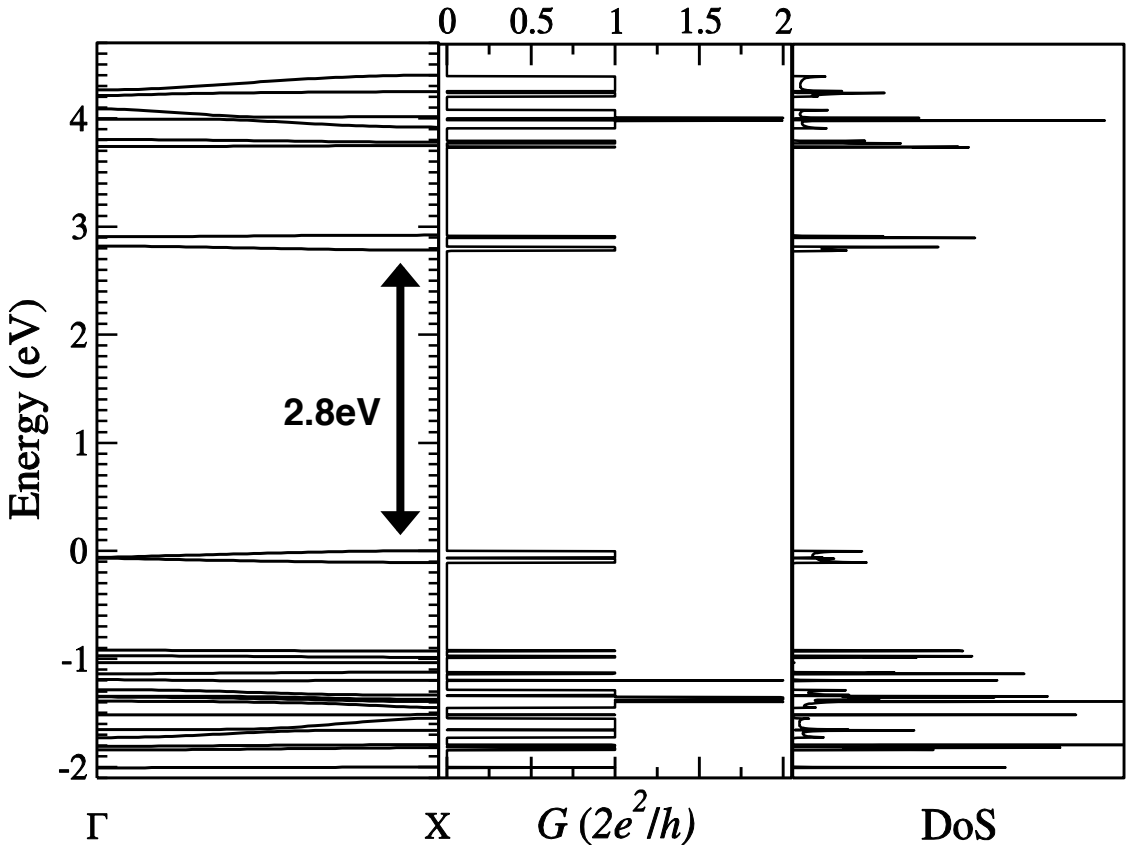
Dry, no backbone, 36° twist

Isolated fragments

- 105 atoms
- 330 electrons
- 18 Å cubic cell
- 186 WFs



Equivalent to 350 atom calculation



LUMO bandwidth = 37 meV
HOMO bandwidth = 60 meV

Green's Function

- Green's function of the whole system, leads + conductor:

$$(E - H)G = I$$

- For real-space Hamiltonians the above Green's function can be partitioned into matrices that correspond to the individual subsystems:

$$\begin{pmatrix} G_L & G_{LC} & G_{LCR} \\ G_{CL} & G_C & G_{CR} \\ G_{LRC} & G_{RC} & G_R \end{pmatrix} = \begin{pmatrix} (E - H_L) & h_{LC} & 0 \\ h_{LC}^{\dagger} & (E - H_C) & h_{CR} \\ 0 & h_{CR}^{\dagger} & (E - H_R) \end{pmatrix}^{-1}$$

$(E - H_C)$ = finite isolated conductor

$(E - H_{\{R,L\}})$ = infinite leads

h_{CR} and h_{LC} = coupling matrices between the conductor and the leads

Green's Function (II)

- Solving for G_C we obtain:

$$G_C = (E - H_C - \Sigma_L - \Sigma_R)^{-1}$$

where

$$\Sigma_L = h_{LC}^{\dagger} G_L h_{LC} \quad \text{and} \quad \Sigma_R = h_{RC} G_R h_{RC}^{\dagger}$$

- $\Sigma =$ self-energy $=$ non-local effective Hamiltonians from the coupling of the conductor and the leads.

- replace an infinite open system with a finite one.

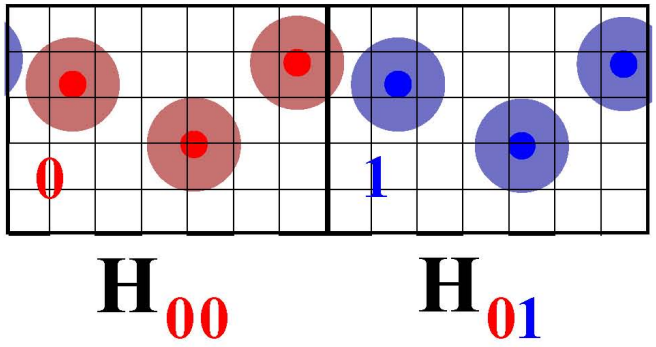
- provide a compact form for the transmission function:

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

where $\Gamma_{\{L,R\}} = \mathrm{i}[\Sigma^r_{\{L,R\}} - \Sigma^a_{\{L,R\}}]$

Transfer Matrices

- Solid as an infinite stack of principal layers with 1^{st} nn interaction:



- If leads and conductor are of the same material and introducing the transfer matrices for the electronic system, we can write

$$G_C = (E - H_{00} - H_{01}T - H_{01}^{\dagger}\overline{T})^{-1}$$

and we identify the self-energies

$$\Sigma_L = H_{01}^{\dagger}\overline{T}, \qquad \Sigma_R = H_{01}T.$$

Iterative Transfer Matrices

$$(\epsilon - H_{00}) G_{00} = I + H_{01} G_{10} ,$$

$$(\epsilon - H_{00}) G_{10} = H_{01}^{\dagger} G_{00} + H_{01} G_{20} ,$$

$$\ldots ,$$

$$(\epsilon - H_{00}) G_{n0} = H_{01}^{\dagger} G_{n-1,0} + H_{01} G_{n+1,0} ,$$

$$T = t_0 + \tilde{t}_0 t_1 + \tilde{t}_0 \tilde{t}_1 t_2 + \ldots + \tilde{t}_0 \tilde{t}_1 \tilde{t}_2 \cdots t_n ,$$

$$\bar{T} = \tilde{t}_0 + t_0 \tilde{t}_1 + t_0 t_1 \tilde{t}_2 + \ldots + t_0 t_1 t_2 \cdots \tilde{t}_n ,$$

where t_i and $\tilde{t}_i$ are defined via the recursion formulas:

$$t_i = (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} t_{i-1}^2 ,$$

$$\tilde{t}_i = (I - t_{i-1} \tilde{t}_{i-1} - \tilde{t}_{i-1} t_{i-1})^{-1} \tilde{t}_{i-1}^2$$

and

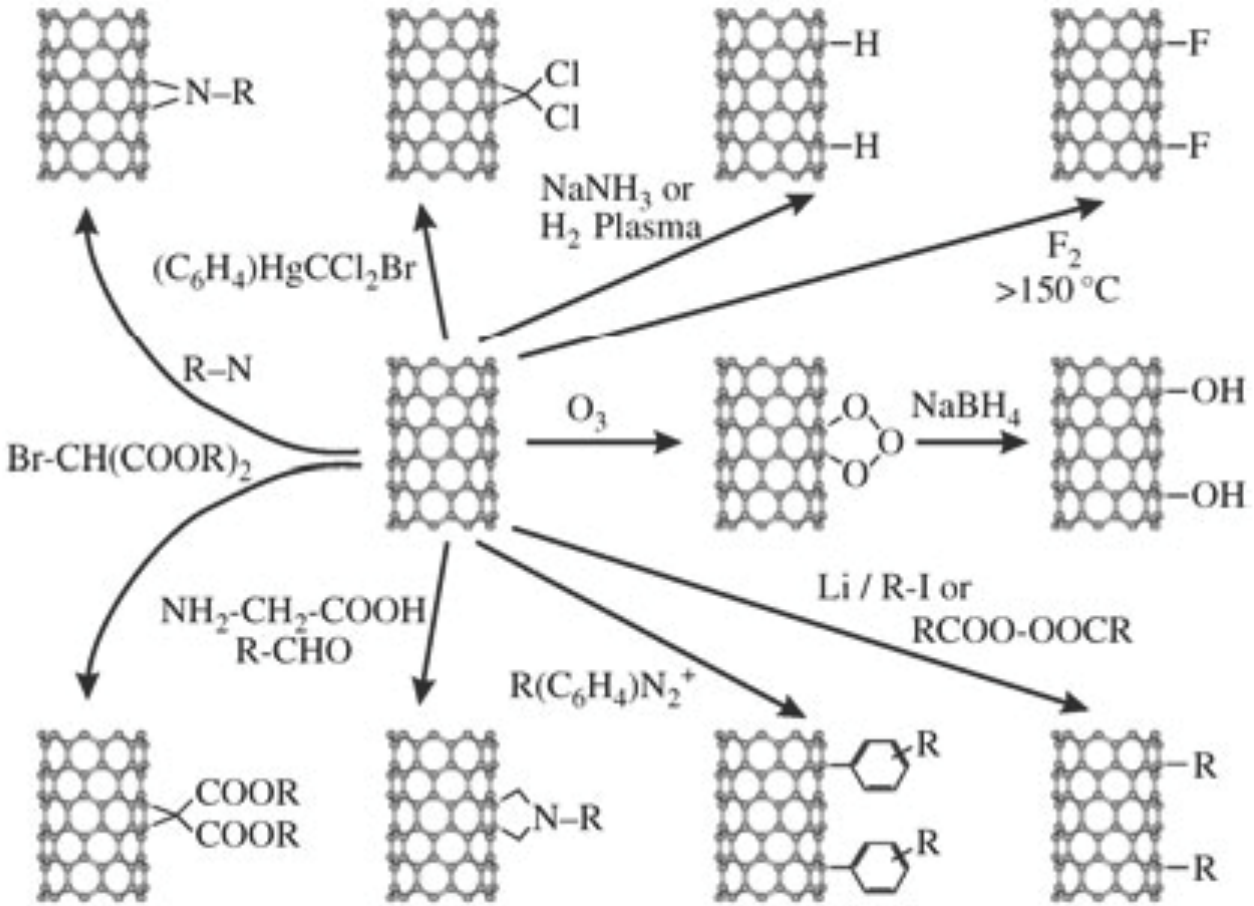
$$t_0 = (\epsilon - H_{00})^{-1} H_{01}^{\dagger} ,$$

$$\tilde{t}_0 = (\epsilon - H_{00})^{-1} H_{01} .$$

See M. B. Nardelli PRB (1999) for a comprensive formulation

First-Principles Study of Functionalizations

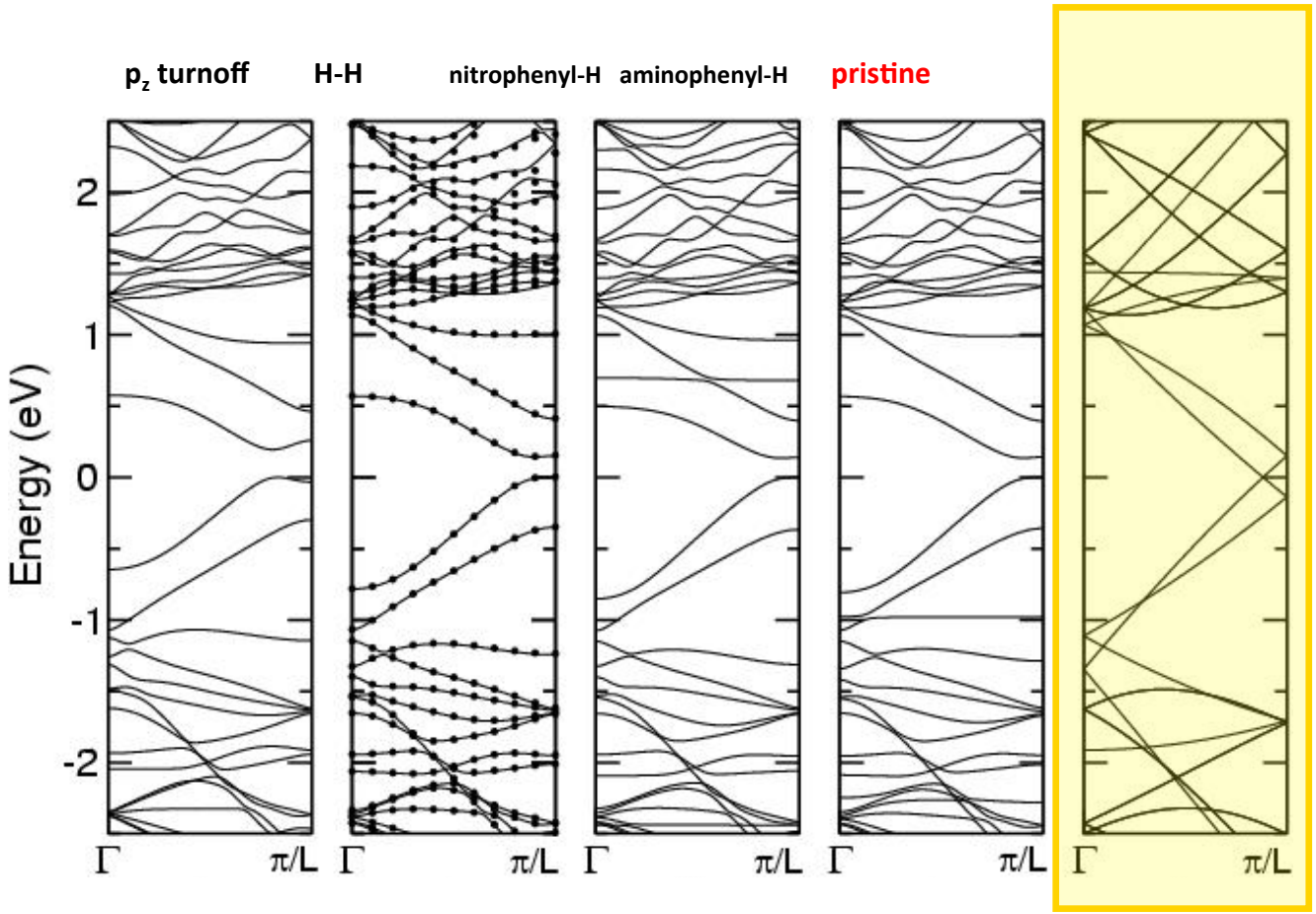
- Currently available covalent functionalizations

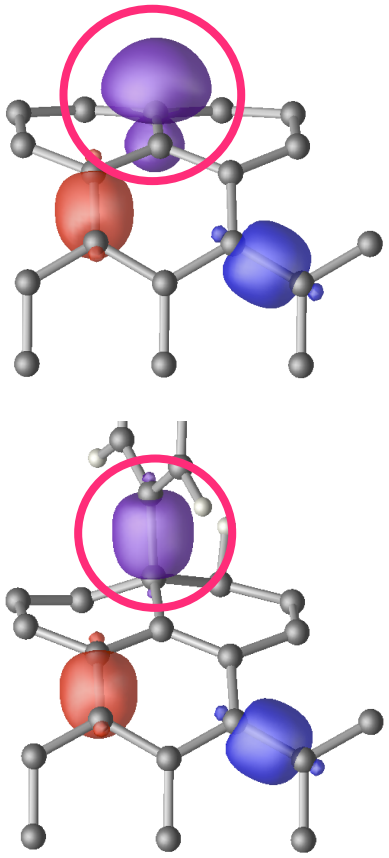


K. Balasubramanian and M. Burghard, Small, **1**, 180 (2005)

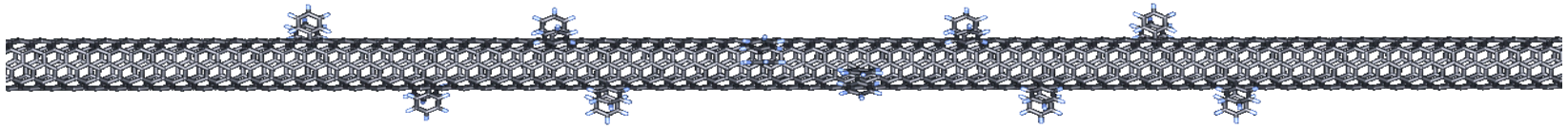
Aryl / Hydrogen

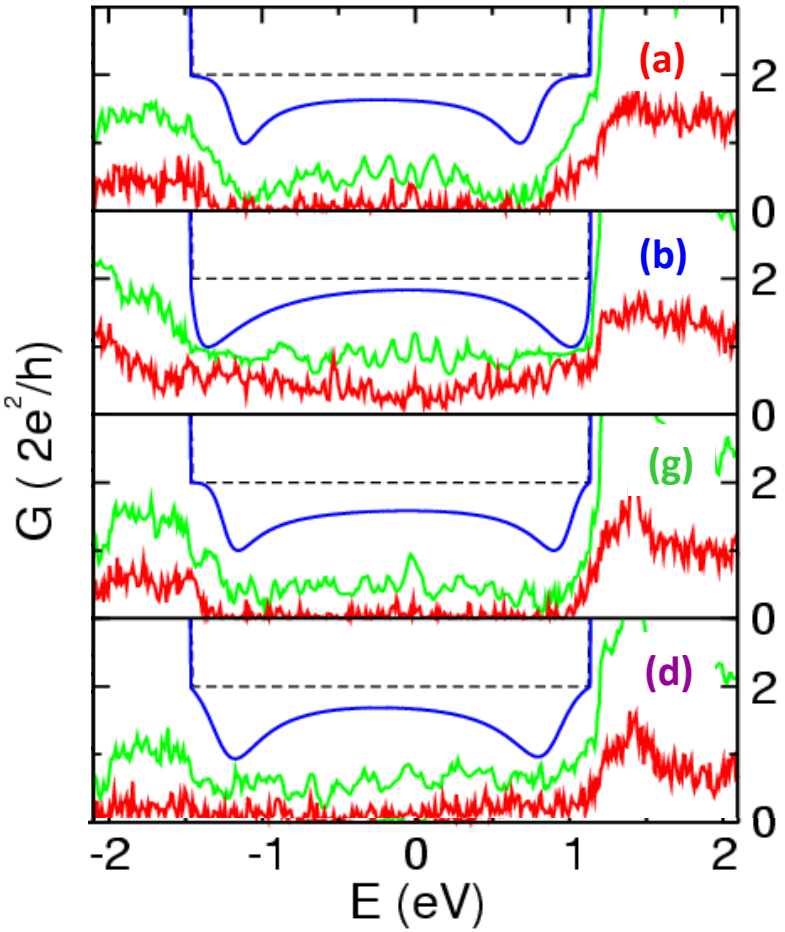
Band structure does not depend on the chemical nature of the functional groups





Aryl / Hydrogen - Quantum Conductance





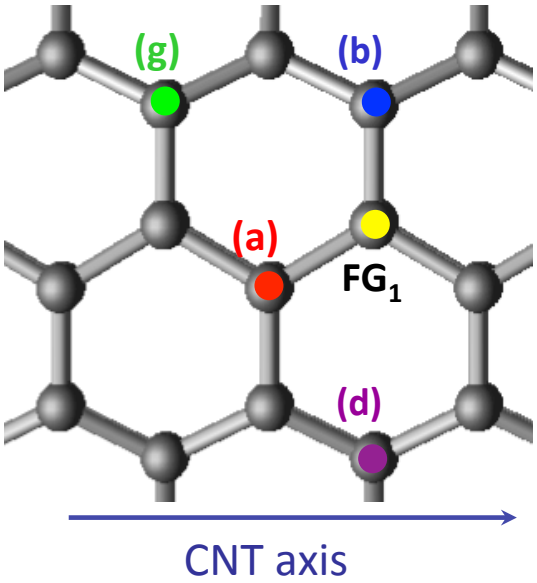
Functionalized region in an infinite (5,5) tube

1 pair of functional groups

10 pairs / 1000 atoms / 37 nm

30 pairs / 3000 atoms / 37 nm

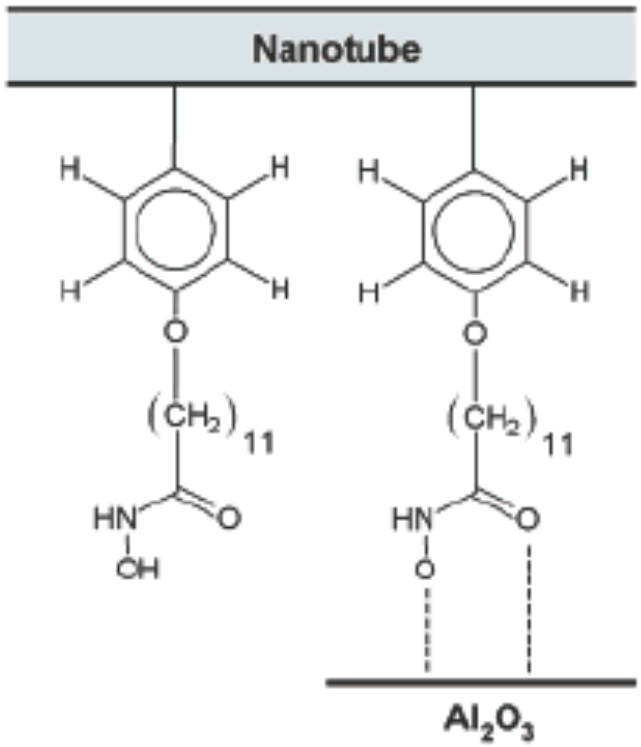
Rapid decay of the quantum conductance

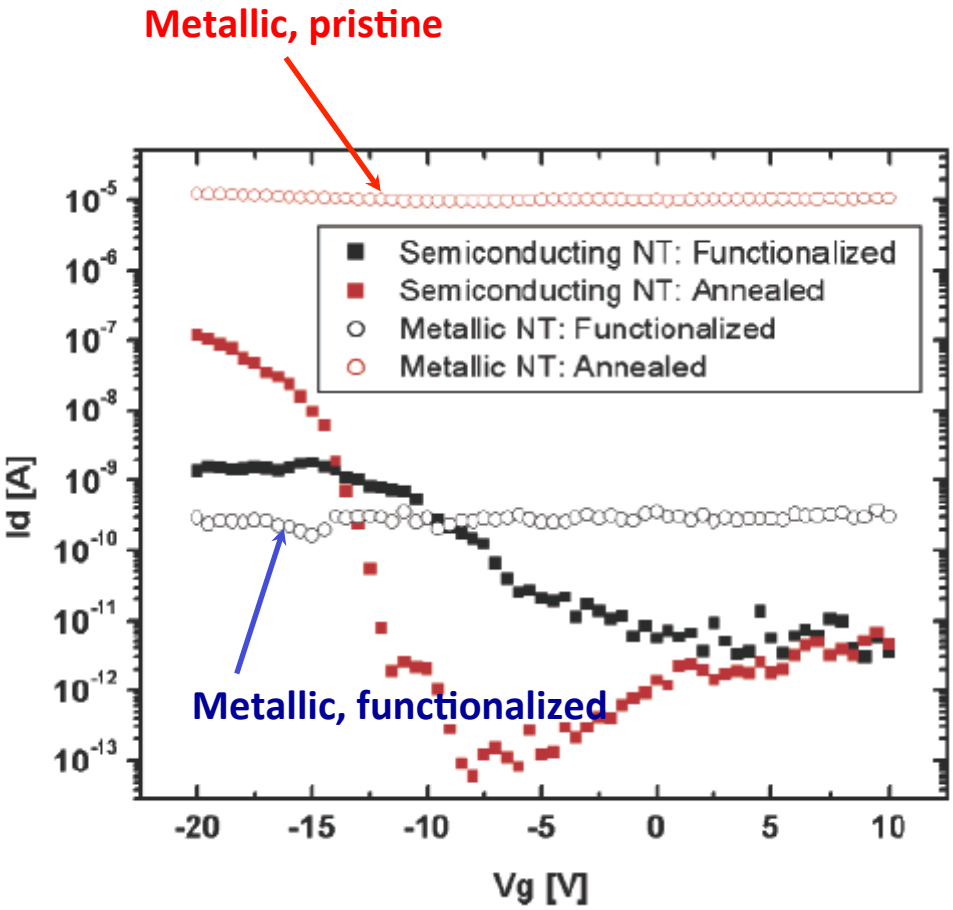


Y.-S. Lee, M. Buongiorno Nardelli, and N. Marzari, Phys. Rev. Lett. 95, 076804 (2005)

Electrical Transport Measurements

IBM/Avouris: conductance decreases 5 orders of magnitude after aryl functionalization





C. Klinke et al., Nano Lett. 6, 906 (2006)

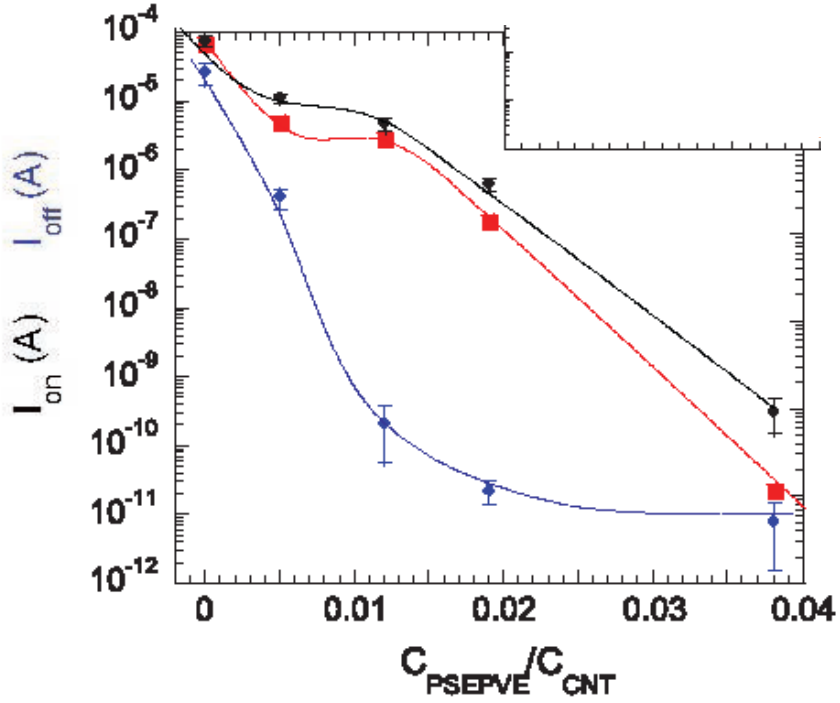
Electrical Transport Measurements

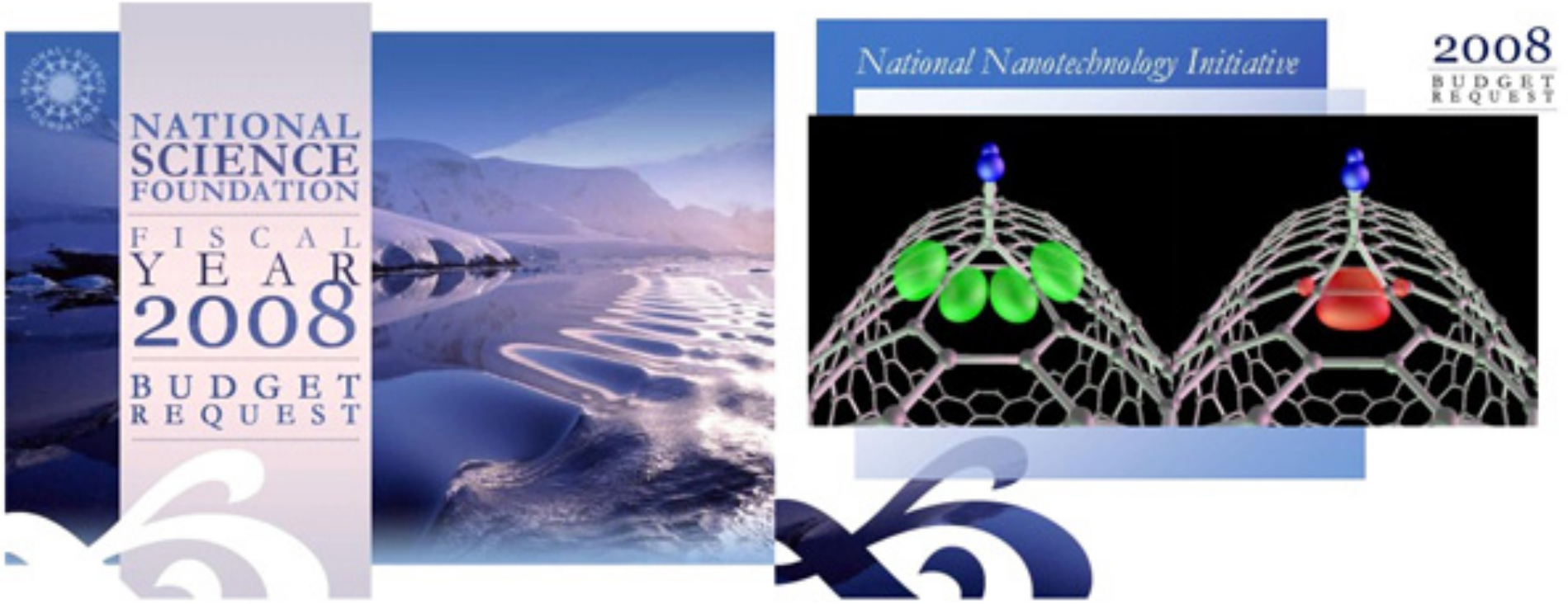
9 JANUARY 2009 VOL 323 **SCIENCE** www.sciencema

Suppression of Metallic Conductivity of Single-Walled Carbon Nanotubes by Cycloaddition Reactions

Mandakini Kanungo,[1] Helen Lu,[2] George G. Malliaras,[1] Graciela B. Blanchet[2]*

The high carrier mobility of films of semiconducting single-walled carbon nanotubes (SWNTs) is attractive for electronics applications, but the presence of metallic SWNTs leads to high off-currer in transistor applications. The method presented here, cycloaddition of fluorinated olefins, represents an effective approach toward converting the "as grown" commercial SWNT mats into high-mobility semiconducting tubes with high yield and without further need for carbon nanotu separation. Thin-film transistors, fabricated from percolating arrays of functionalized carbon nanotubes, exhibit mobilities >100 square centimeters per volt-second and on-off ratios of 100,000. This method should allow for the use of semiconducting carbon nanotubes in commerc electronic devices and provide a low-cost route to the fabrication of electronic inks.





Dr. Arden L. Bement Jr., Director, National Science Foundation

FY 2008 Budget Presentation http://www.nsf.gov/news/speeches/bement/07/alb070205_budget.jsp

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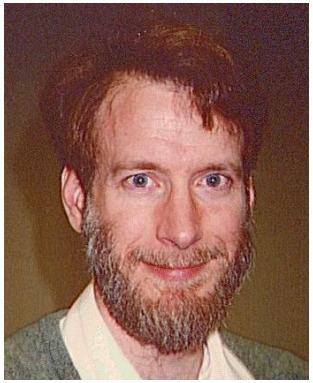
- **Theory:** David Vanderbilt (Department of Physics, Rutgers University), Ivo Souza (Department of Physics, UC Berkeley)




- **Wannier 90:** Arash Mostofi (Imperial College, London), Jonathan Yates (University of Oxford), Nicolas Poilvert (MIT), Matt Shelley (Imperial College),
- **Transport:** Young-Su Lee (MIT), Elise Li (MIT), Giovanni Cantele (University of Naples)




Ω_I is Positive Definite and Gauge Invariant

We introduce the projection operators on the occupied and unoccupied subspaces

$$\mathbb{P} = \sum_{\mathbf{R}m} |\mathbf{R}m\rangle\langle\mathbf{R}m| \quad ; \quad \mathbb{Q} = \mathbb{I} - \mathbb{P}$$

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

$$= \sum_{n,\alpha} \langle \mathbf{0}n|r_\alpha(\mathbb{I}-\mathbb{P})r_\alpha|\mathbf{0}n\rangle =$$

$$= \sum_\alpha {\rm tr_c}[r_\alpha \mathbb{Q}\, r_\alpha] = \sum_\alpha \|\mathbb{P} r_\alpha \mathbb{Q}\|_{\rm c}^2$$

Ω_I is Gauge Invariant

$$
\begin{aligned}
\Omega_{\mathrm{I}} &= \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_b \left(N_{bands} - \sum_{mn} |M_{mn}^{(\mathbf{k},\mathbf{b})}|^2 \right) \\
&= \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_b \sum_{m} \left(1 - \sum_{n} \langle u_{m\mathbf{k}} | u_{n\mathbf{k}+\mathbf{b}} \rangle \langle u_{n\mathbf{k}+\mathbf{b}} | u_{m\mathbf{k}} \rangle \right) \\
&= \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_b \, \mathrm{tr} \left[\mathbb{P}^{(\mathbf{k})} \mathbb{Q}^{(\mathbf{k}+\mathbf{b})} \right]
\end{aligned}
$$

where $\mathbb{P}^{(\mathbf{k})} = \sum_n |u_{n\mathbf{k}}\rangle\langle u_{n\mathbf{k}}|$, $\mathbb{Q}^{(\mathbf{k})} = \mathbb{I} - \mathbb{P}^{(\mathbf{k})}$

Ω_{I} is a *measure* of the band dispersion in the BZ (and $dl^2 = \mathrm{tr}\left[\mathbb{P}^{(\mathbf{k})}\mathbb{Q}^{(\mathbf{k}')}\right]$ defines its *metric*)

We consider an infinitesimal rotation of the Bloch orbitals

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

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

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

since dQ is anti-hermitian, $M^{(\mathbf{k},\mathbf{b})} = (M^{(\mathbf{k}+\mathbf{b},-\mathbf{b})})^\dagger$, and having defined $R^{(\mathbf{k},\mathbf{b})}_{mn} = M^{(\mathbf{k},\mathbf{b})}_{mn} * M^{(\mathbf{k},\mathbf{b})*}_{nn}$ and $\widetilde{R}^{(\mathbf{k},\mathbf{b})}_{mn} = M^{(\mathbf{k},\mathbf{b})}_{mn} / M^{(\mathbf{k},\mathbf{b})}_{nn}$. Introducing the super-operators:

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

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

In a general 3-dimensional case, the matrix elements for the position operator $\mathbf{r}$ and its powers are, in the Wannier representation,

$$\langle\, w_{n0} \,|\, \mathbf{r}^{l} \,|\, w_{m0} \,\rangle \;=\; \frac{\Omega}{(2\pi)^3} \int \langle\, u_{n\mathbf{k}} \,|\, \left(i\frac{\partial}{\partial \mathbf{k}} \right)^{l} \,|\, u_{m\mathbf{k}} \,\rangle \, d\mathbf{k} \quad .$$

If we define $\mathfrak{r}_{nm} \;=\; \langle\, u_{n\mathbf{k}} \,|\, i\frac{\partial}{\partial \mathbf{k}} \,|\, u_{m\mathbf{k}} \,\rangle$ we obtain

$$\langle\, w_{n0} \,|\, \mathbf{r} \,|\, w_{n0} \,\rangle \;=\; \frac{\Omega}{(2\pi)^3} \int \mathfrak{r}_{nn} \, d\mathbf{k} \quad ,$$

$$\langle\, w_{n0} \,|\, r^2 \,|\, w_{n0} \,\rangle \;=\; \frac{\Omega}{(2\pi)^3} \int (\mathfrak{r}^2)_{nn} \, d\mathbf{k} \quad .$$

In non-pathological cases the following equivalence holds (Blount 1962):

$$\min \left(\langle\, w_{n0} \,|\, r^2 \,|\, w_{n0} \,\rangle \;-\; \langle\, w_{n0} \,|\, \mathbf{r} \,|\, w_{n0} \,\rangle^2 \right) \;\Leftrightarrow\; \nabla \cdot \mathfrak{r}_{nn} \;=\; 0 \; .$$

For an isolated band in 1 dimension, the most localized set of Wannier functions is thus obtained from u_k's that satisfy the condition:

$$i\frac{\partial}{\partial k} \langle\, u_k \,|\, i\frac{\partial}{\partial k} \,|\, u_k \,\rangle = 0 \;\Rightarrow\; \langle\, u_k \,|\, u_{k+dk} \,\rangle = const = \frac{(\phi_{\mathrm{Berry}})}{N} \; .$$

The Reciprocal Space Representation...

Position operator $\Rightarrow$ Gradient

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

Example: 1 band in 1 dimension

The minimum Ω is found (Blount 1962) when the phases are such that

$$i\frac{\partial}{\partial k} \langle\, u_k \,|\, i\frac{\partial}{\partial k} \,|\, u_k \,\rangle = 0 \;\Rightarrow\; \langle\, u_k \,|\, u_{k+dk} \,\rangle = const = \frac{(\phi_{\mathrm{Berry}})}{N} \,.$$

The Definition of Wannier Functions

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:

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

where the arbitrary phase $\phi_n(\mathbf{k})$ that is not assigned by the Schrödinger equation is written explicitly. We obtain a (non-unique) Wannier representation with any unitary transformation of the form $\langle\, n\mathbf{R}\,|\,n\mathbf{k}\,\rangle = e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}}$:

$$w_{n\mathbf{R}} \;=\; \int_{BZ} \Psi_{n\mathbf{k}}(\mathbf{r})\,e^{i\varphi_n(\mathbf{k})-i\mathbf{k}\cdot\mathbf{R}}\,d\mathbf{k} \quad .$$

Since that the Schrödinger equation is also invariant for a unitary transformation of the occupied Bloch orbitals (in the presence of a gap), the most general transformation is

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

$w_{n\mathbf{R}}$ is a "localized" function: for a $\mathbf{R}_i$ distant from $\mathbf{R}$, $w_n(\mathbf{R}_i-\mathbf{R})$ is a combination of terms like $\int_{BZ} u_{m\mathbf{k}}(0)e^{i\mathbf{k}\cdot(\mathbf{R_i}-\mathbf{R})}\,d\mathbf{k}$, which are small due to the rapidly varying character of the exponential factor.

- Modern theory of polarization: the spontaneous polarization of an insulating crystalline solid is an invariant Berry phase of the occupied Bloch manifold, and can be written as the sum of the centers of charge of the Wannier functions of the occupied bands:

$$\mathbf{P} = -\frac{e}{\Omega} \sum_n \int \langle\, w_{n0} \,|\, \mathbf{r} \,|\, w_{n0} \,\rangle$$

- Linear-scaling methods: orbital-based electronic-strucure methods whose computational cost scales linearly with size rely on the assumption that the system studied allows for "localization" regions that are (much) smaller than the system itself

- Non-periodic perturbations: the study of non-lattice periodic perturbations (namely the response to a non-zero electric field) requires a careful handling of the singular terms in rather complex perturbative expansions; real-space methods based on localized orbitals provide a much simpler and more straightforward approach to the problem

$$\Omega \;=\; \sum_n \Big(\langle\, r_n^2 \,\rangle \;-\; \mathbf{r}_n \cdot \mathbf{r}_n \Big)$$

From the previous identities, and with $w_b = 3/(Zb^2)$, we have:

$$\langle\, r_n^2 \,\rangle = \langle\, w_{n0} \,|\, r^2 \,|\, w_{n0} \,\rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \langle\, u_{n\mathbf{k}} \,|\, -\frac{\partial^2}{\partial k^2} \,|\, u_{n\mathbf{k}} \,\rangle =$$

$$\frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \langle \frac{\partial u_{n\mathbf{k}}}{\partial \mathbf{k}} | \frac{\partial u_{n\mathbf{k}}}{\partial \mathbf{k}} \rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_b \Big[-2\mathrm{Re}\, \phi_n^{(\mathbf{k},\mathbf{b})} \;+\; (\,\mathrm{Im}\, \phi_n^{(\mathbf{k},\mathbf{b})}\,)^2 \Big] \;,$$

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

$$-\frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_b\, \mathbf{b}\, \mathrm{Im}\, [\, \langle\, u_{n\mathbf{k}} \,|\, u_{n,\mathbf{k}+\mathbf{b}} \,\rangle - 1] = -\frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathbf{b}} w_b\, \mathbf{b}\, \mathrm{Im}\, \phi_n^{(\mathbf{k},\mathbf{b})} \;,$$

The logarithmic form for $\langle\, r_n^2 \,\rangle$ and $\mathbf{r}_n$ guarantees that the functional is invariant under a lattice translation for w_{n0}, where $u_{n\mathbf{k}}(\mathbf{r}) \rightarrow e^{-i\mathbf{k}\cdot\mathbf{R}} u_{n\mathbf{k}}(\mathbf{r})$ (i.e. $\mathbf{r}_n \rightarrow \mathbf{r}_n + \mathbf{R}$, $\langle\, r_n^2 \,\rangle \rightarrow \langle\, r_n^2 \,\rangle + 2\mathbf{r}_n \cdot \mathbf{R} + R^2$).

Ω_D and Ω_{OD} in the k-space Representation

The diagonal and off-diagonal terms in the localization functional are those that can be minimized with an appropriate choice of unitary transformations $U_{mn}^{(\mathrm{k})}$ for the Bloch orbitals. Their **k**-representation provides also a more intuitive picture:

$$\Omega_{\mathrm{OD}} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathrm{b}} w_b \sum_{m \neq n} |M_{mn}^{(\mathrm{k},\mathrm{b})}|^2$$

$$\Omega_{\mathrm{D}} = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k},\mathrm{b}} w_b \sum_{n} \left(\mathrm{Im} \ln M_{nn}^{(\mathrm{k},\mathrm{b})} - \overline{\mathrm{Im} \ln M_{nn}^{(\mathrm{k},\mathrm{b})}} \right)^2$$

Ω_{OD} derives from the *"misalignment"* of the Bloch orbitals across the BZ, and Ω_{D} from the *"non-uniformity of phase twists"*

The functional Ω is minimized with steepest descents: we calculate $d\Omega$ corresponding to a set of infinitesimal unitary rotations $dQ^{(\mathbf{k})}_{mn}$ among the Bloch orbitals (i.e. $|\, u_{n\mathbf{k}}\,\rangle \rightarrow |\, u_{n\mathbf{k}}\,\rangle + \sum_m dQ^{(\mathbf{k})}_{mn} |\, u_{m\mathbf{k}}\,\rangle$). Now:

$$dM^{(\mathbf{k},\mathbf{b})}_{nn} \;=\; -[\, dQ^{(\mathbf{k})}\, M^{(\mathbf{k},\mathbf{b})}\,]_{nn} \;-\; [\, dQ^{(\mathbf{k}+\mathbf{b})}\, M^{(\mathbf{k}+\mathbf{b},-\mathbf{b})}\,]^*_{nn} \quad ,$$

$$d\phi^{(\mathbf{k},\mathbf{b})}_{n} \;=\; -[\, dQ^{(\mathbf{k})}\, R^{(\mathbf{k},\mathbf{b})}\,]_{nn} \;-\; [\, dQ^{(\mathbf{k}+\mathbf{b})}\, R^{(\mathbf{k}+\mathbf{b},-\mathbf{b})}\,]^*_{nn} \quad ,$$

since dQ is anti-hermitian, $M^{(\mathbf{k},\mathbf{b})} = (M^{(\mathbf{k}+\mathbf{b},-\mathbf{b})})^\dagger$, and having defined $R^{(\mathbf{k},\mathbf{b})}_{mn} = M^{(\mathbf{k},\mathbf{b})}_{mn} * M^{(\mathbf{k},\mathbf{b})*}_{nn}$ and $\widetilde{R}^{(\mathbf{k},\mathbf{b})}_{mn} = M^{(\mathbf{k},\mathbf{b})}_{mn} / M^{(\mathbf{k},\mathbf{b})}_{nn}$. Introducing the super-operators:

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

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

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

$\boldsymbol{\Omega}$

It is convenient to decompose $\widetilde{\Omega}$ in two different contributions, coming from band-diagonal and band-off-diagonal terms:

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

$$\Omega_{\rm I} = \sum_n \left[\langle r^2 \rangle_n - \sum_{\mathbf{R}m} \left| \langle \mathbf{R}m|\mathbf{r}|0n\rangle \right|^2 \right] = \sum_\alpha \|\mathbb{P} r_\alpha \mathbb{Q}\|_{\rm c}^2$$

$$\Omega_{\rm D} = \sum_n \sum_{\mathbf{R}\neq\mathbf{0}} \left| \langle \mathbf{R}n|\mathbf{r}|0n\rangle \right|^2$$

$$\Omega_{\rm OD} = \sum_{m\neq n} \sum_{\mathbf{R}} \left| \langle \mathbf{R}m|\mathbf{r}|0n\rangle \right|^2$$

The Localization Functional Ω

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

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

The functional Ω can be decomposed in two terms:

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

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

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

Decomposing Ω (tilde)

$\widetilde{\Omega}$ is decomposed in two different contributions, coming from band-diagonal and band-off-diagonal terms:

$$\Omega_{\mathrm{D}} = \sum_{n} \sum_{\mathbf{R}\neq\mathbf{0}} \left| \langle \mathbf{R}n|\mathbf{r}|\mathbf{0}n\rangle \right|^2$$

$$\Omega_{\mathrm{OD}} = \sum_{m\neq n} \sum_{\mathbf{R}} \left| \langle \mathbf{R}m|\mathbf{r}|\mathbf{0}n\rangle \right|^2$$

Minimization Strategy

$$\Omega_{\rm I}=\frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_b\left(J-\sum_{mn} |M_{mn}^{(\mathbf{k},\mathbf{b})}|^2\right) \qquad \Omega_{\rm OD}=\frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_b \sum_{m\neq n} |M_{mn}^{(\mathbf{k},\mathbf{b})}|^2$$

$$\Omega_{\rm D}=\frac{1}{N}\sum_{\mathbf{k},\mathbf{b}} w_b \sum_{n} (-\mathrm{Im}\,\ln M_{nn}^{(\mathbf{k},\mathbf{b})}-\mathbf{b}\cdot\bar{\mathbf{r}}_n)^2.$$

We consider an infinitesimal rotation of the Bloch orbitals

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

$$G^{(\mathbf{k})} = \frac{d\Omega}{dW^{(\mathbf{k})}} = \text{function of } M_{mn}^{(\mathbf{k})}$$

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

The functional Ω is minimized with steepest descents: we calculate $d\Omega$ corresponding to a set of infinitesimal unitary rotations $dQ^{(\mathbf{k})}_{mn}$ among the Bloch orbitals (i.e. $|\, u_{n\mathbf{k}}\,\rangle \longrightarrow |\, u_{n\mathbf{k}}\,\rangle + \sum_m dQ^{(\mathbf{k})}_{mn} |\, u_{m\mathbf{k}}\,\rangle$). Now:

$$
\begin{aligned}
dM^{(\mathbf{k},\mathbf{b})}_{nn} &= -[\, dQ^{(\mathbf{k})}\, M^{(\mathbf{k},\mathbf{b})}\,]_{nn} - [\, dQ^{(\mathbf{k}+\mathbf{b})}\, M^{(\mathbf{k}+\mathbf{b},-\mathbf{b})}\,]^*_{nn} \quad , \\
d\phi^{(\mathbf{k},\mathbf{b})}_{n} &= -[\, dQ^{(\mathbf{k})}\, R^{(\mathbf{k},\mathbf{b})}\,]_{nn} - [\, dQ^{(\mathbf{k}+\mathbf{b})}\, R^{(\mathbf{k}+\mathbf{b},-\mathbf{b})}\,]^*_{nn} \quad ,
\end{aligned}
$$

since dQ is anti-hermitian, $M^{(\mathbf{k},\mathbf{b})} = (M^{(\mathbf{k}+\mathbf{b},-\mathbf{b})})^\dagger$, and having defined $R^{(\mathbf{k},\mathbf{b})}_{mn} = M^{(\mathbf{k},\mathbf{b})}_{mn} * M^{(\mathbf{k},\mathbf{b})*}_{nn}$ and $\widetilde{R}^{(\mathbf{k},\mathbf{b})}_{mn} = M^{(\mathbf{k},\mathbf{b})}_{mn} / M^{(\mathbf{k},\mathbf{b})}_{nn}$. Introducing the super-operators:

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

and defining $q^{(\mathbf{k},\mathbf{b})}_n = \mathrm{Im}\,\phi^{(\mathbf{k},\mathbf{b})}_n + \mathbf{b}\cdot\mathbf{r}_n$, $T^{(\mathbf{k},\mathbf{b})}_{mn} = \widetilde{R}^{(\mathbf{k},\mathbf{b})}_{mn}\, q^{(\mathbf{k},\mathbf{b})}_n$, we finally obtain the functional derivative as

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

The Reciprocal Space Representation

Position operator $\Rightarrow$ Gradient

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

Example: 1 band in 1 dimension

The minimum Ω is found (Blount 1962) when the phases are such that

$$i\frac{\partial}{\partial k} \langle\, u_k \,|\, i\frac{\partial}{\partial k} \,|\, u_k \,\rangle = 0 \;\Rightarrow\; \langle\, u_k \,|\, u_{k+dk} \,\rangle = const = \frac{(\phi_{\mathrm{Berry}})}{N} \,.$$

Blount identities

Position operator $\Rightarrow$ Gradient

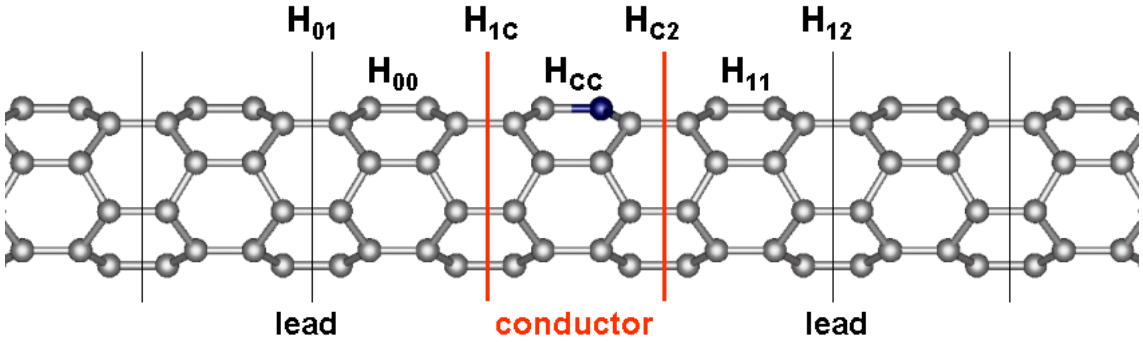
$$\langle\, \mathbf{0}n \,|\, \mathbf{r}^l \,|\, \mathbf{0}m \,\rangle \;=\; \frac{V}{(2\pi)^3} \int \langle\, u_{n\mathbf{k}} \,|\, \left(i\frac{\partial}{\partial \mathbf{k}} \right)^l \,|\, u_{m\mathbf{k}} \,\rangle \, d\mathbf{k}$$

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

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

Green's Function in a localized basis

M. B. Nardelli Phys. Rev. B 60, 7828 (1999)
Datta, "Electronic Transport in Mesoscopic Systems"



$$G = \frac{2e^2}{h} T = \frac{2e^2}{h} Tr(\Gamma_L G_C^r \Gamma_R G_C^a)$$

$$G_C = (\varepsilon - H_C - \Sigma_L - \Sigma_R)^{-1}$$

$$\Gamma_{\{L,R\}} = i[\Sigma^r_{\{L,R\}} - \Sigma^a_{\{L,R\}}]$$

- **G_C -- Green's function of the conductor**
- **$\Gamma_{L,R}$ -- coupling functions between the conductor and the leads.**
- **H = Hamiltonian**

- **Self-energies are computed using surface Green's function matching theory and the concept of layer orbitals:** *(Garcia-Moliner and Velasco, 1991, 1992)*

$$\Sigma_L = (\varepsilon - H_{LC})^+ (\varepsilon - H^L_{00} + (\varepsilon - H^L_{01})^+ \overline{T_L})^{-1} (\varepsilon - H_{LC})$$
$$\Sigma_R = (\varepsilon - H_{RC}) (\varepsilon - H^R_{00} + (\varepsilon - H^R_{01})^+ T_R)^{-1} (\varepsilon - H_{CR})^+$$