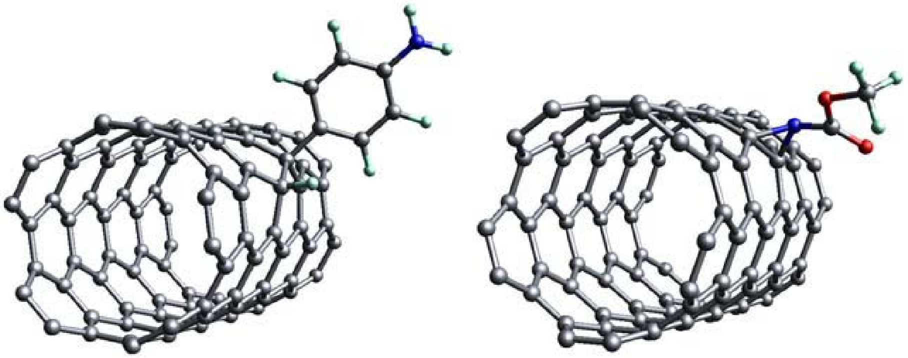
Functionalized Carbon Nanotubes

Organic chemistry meets electronics

engineer multiple functionalities in carbon nanotubes with ligands attached to the sidewalls

Covalent Functionalization



J.L.Bahr et al., J. Am. Chem. Soc., **123** 6536 (2001)
M.Holzinger et al., J. Am. Chem. Soc., **125** 8566 (2003)

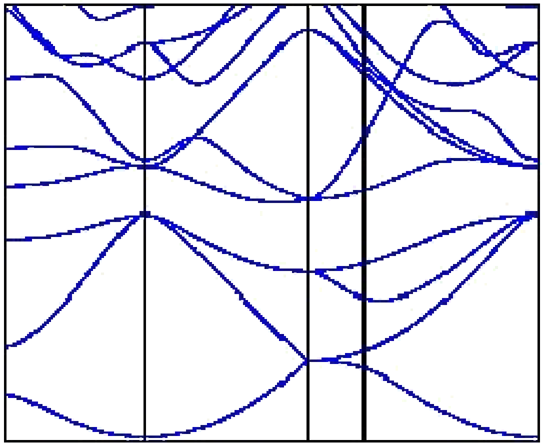
- Robust attachment of sidewalls ligands
- Several groups have succeeded in covalent linking of hydrogen, fluorine, methyl, dichlorocarbene, nitrene, carboxyl
- Disrupted π-bonding detected by Raman spectroscopy

A. Hirsch, Angew. Chem. Int. Ed., 41, 1853 (2002)
S. Niyogi *et al*, Acc. Chem. Res., 35, 1105 (2002)
J. L. Bahr *et al*, J. Mater. Chem., 12, 1952 (2002)

Generalized Wannier Functions for Composite Bands

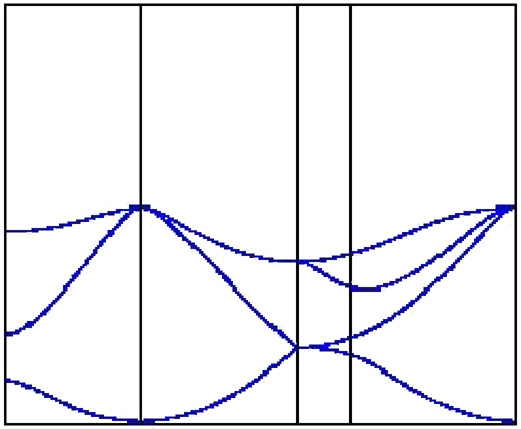
- $\{|\mathbf{R}n\rangle\}$ span the same space as $\{|\Psi_{n\mathrm{k}}\rangle\}$
- $|\mathbf{R}n\rangle \; = \; w_n(\mathbf{r}-\mathbf{R})$ (translational images)
- $\langle \mathbf{R}n|\mathbf{R}'m\rangle \; = \; \delta_{n,m}\,\delta_{\mathbf{R},\mathbf{R}'}$
- "maximally" localized

Silicon

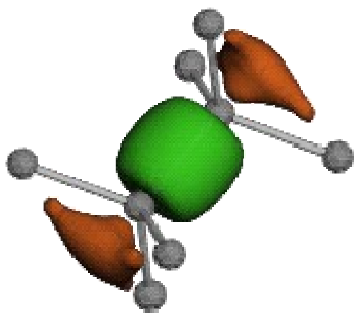


(Isolated group of bands)

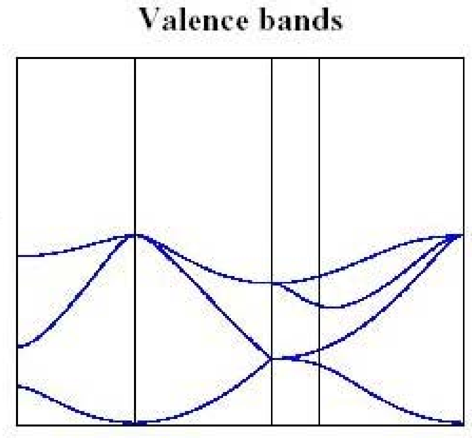
Valence bands



Wannier function



From Bloch Orbitals to Wannier Functions



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

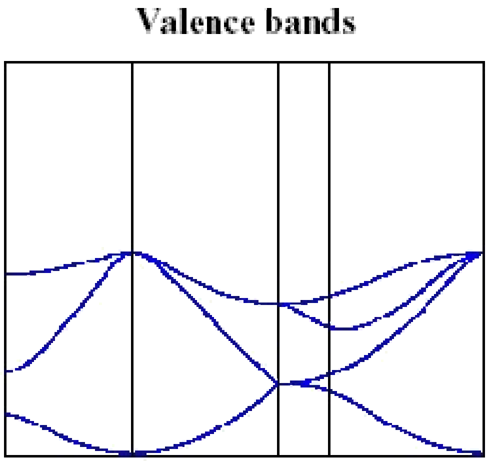
$$|\mathbf{R}n\rangle = \int_{BZ} \Psi_{n\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

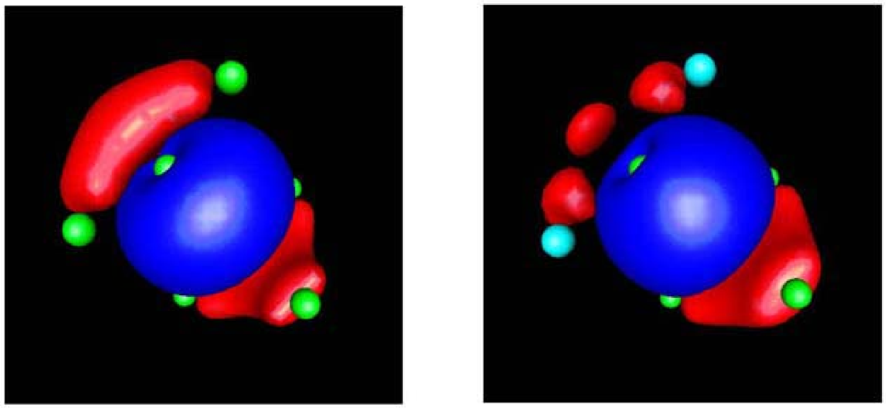
Gauge freedoms

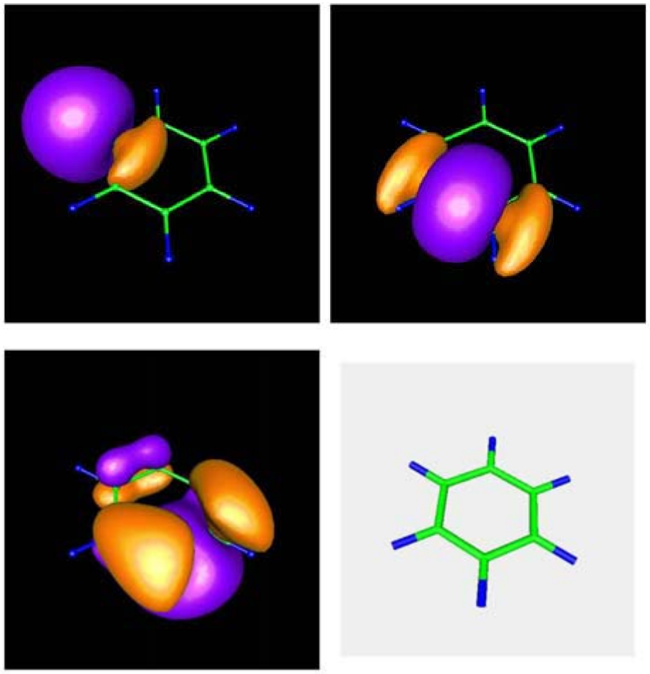
- Arbitrary phase factor for every $n\mathbf{k}$ (Schrödinger)
- Arbitrary unitary rotations $U^{(\mathbf{k})}_{mn}$ for every $\mathbf{k}$ (DFT)

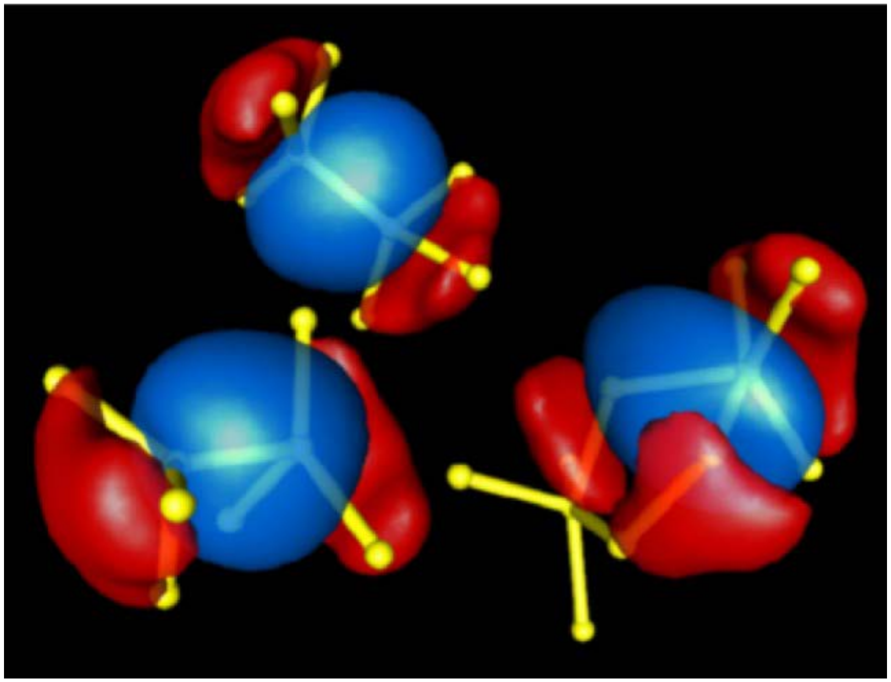
$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U^{(\mathbf{k})}_{mn}\, \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

Silicon, GaAs, Amorphous Silicon, Benzene

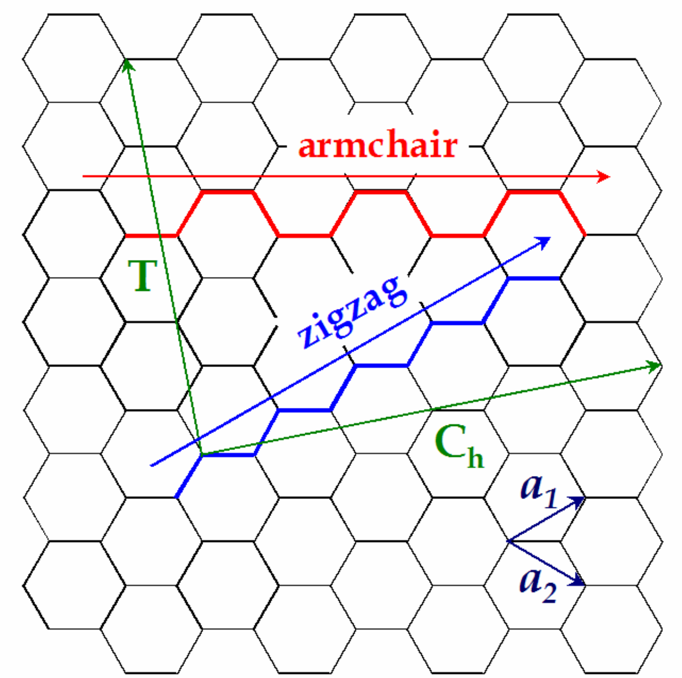

Valence bands





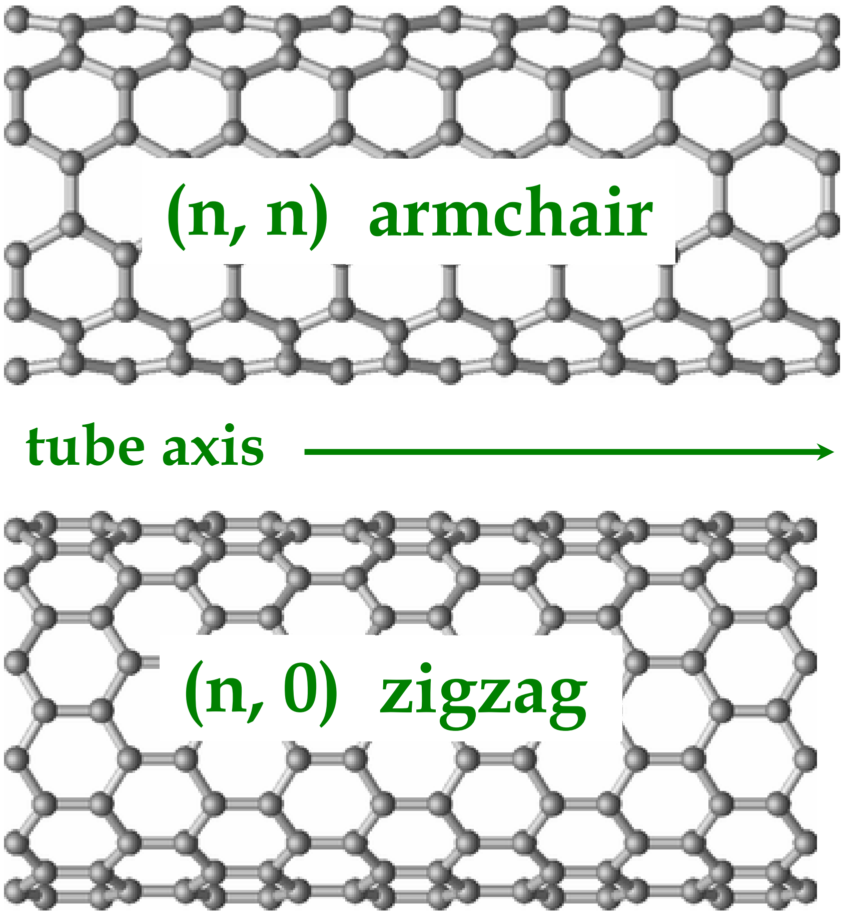


Pristine Carbon Nanotubes



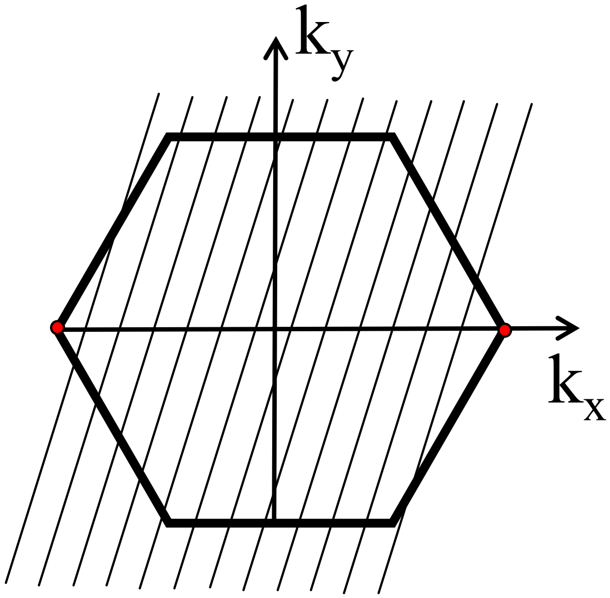
$$C_h = n\, a_1 + m\, a_2$$

- **Armchair (n,n)**
- **Zig-Zag (n,0)**
- **Chiral (n,m) n≠m**



2-Dimensional Band Structure of Graphene

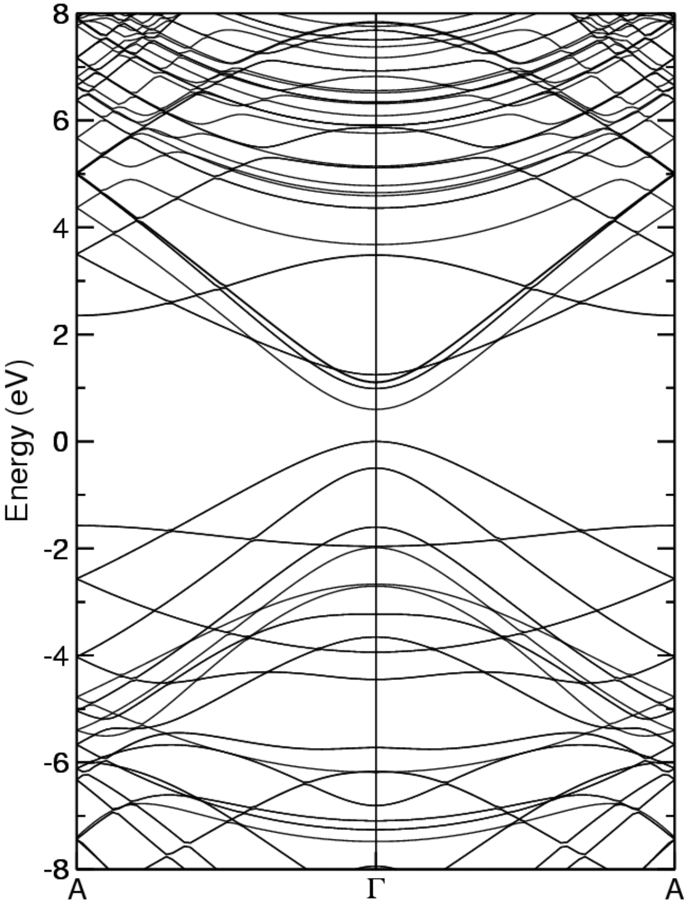
Image removed for copyright reasons.
See Souza, I., N. Marzari and D. Vanderbilt.
“Maximally localized Wannier functions for entangled energy bands.” *Physical Review B* 65 (2001).

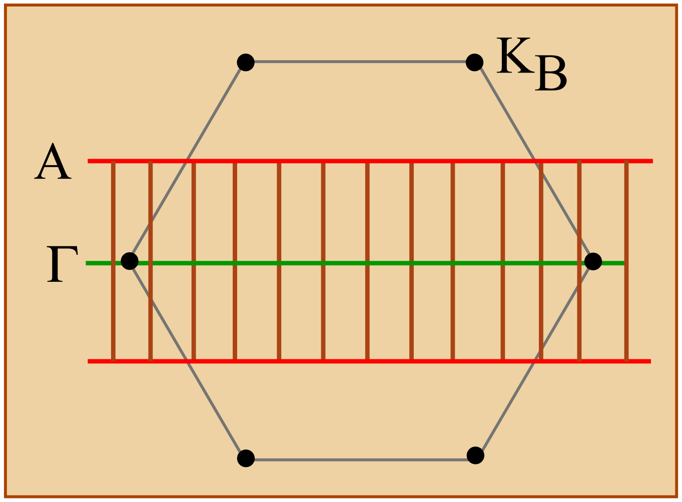


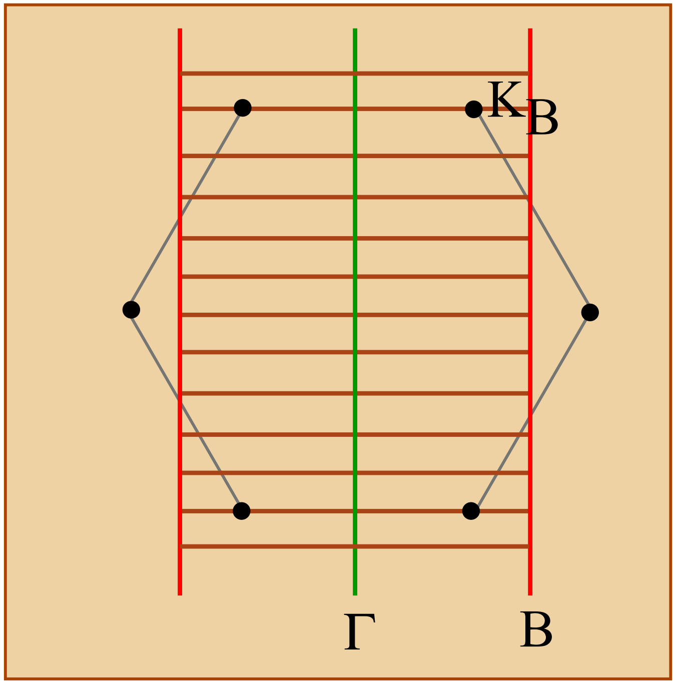
- **mod(3) rule**: **if (n-m) is a multiple of 3 the tube is metallic**

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

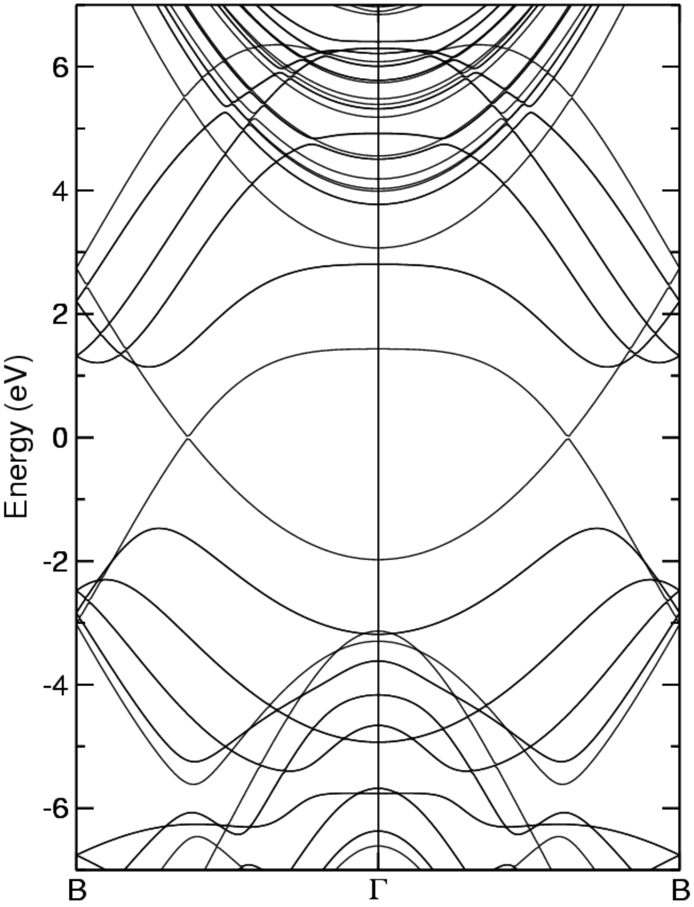
(8,0) semiconducting





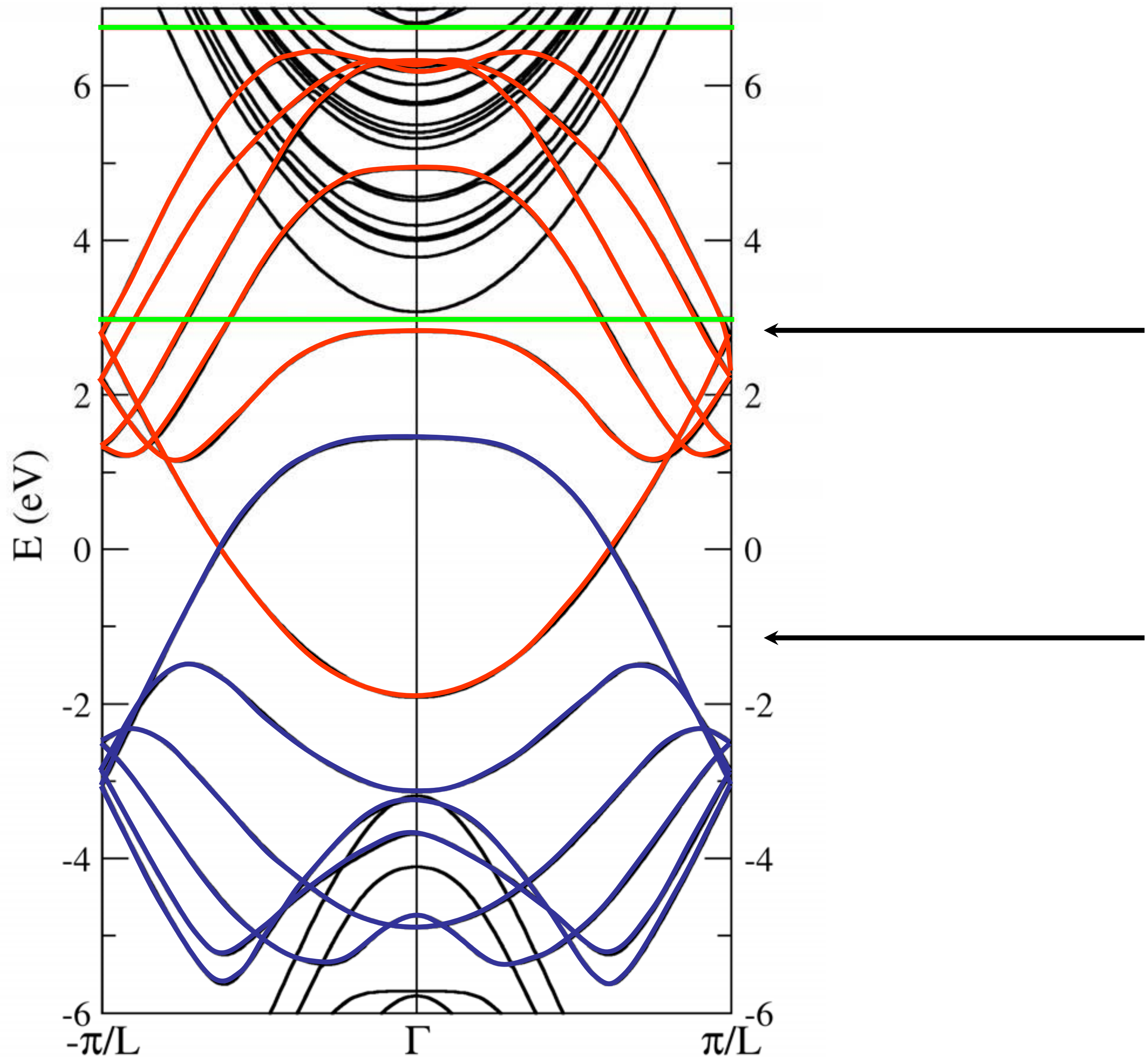


(5,5) metallic



Figures by MIT OCW.

Disentanglement: Conduction Bands in (5,5) SWNT

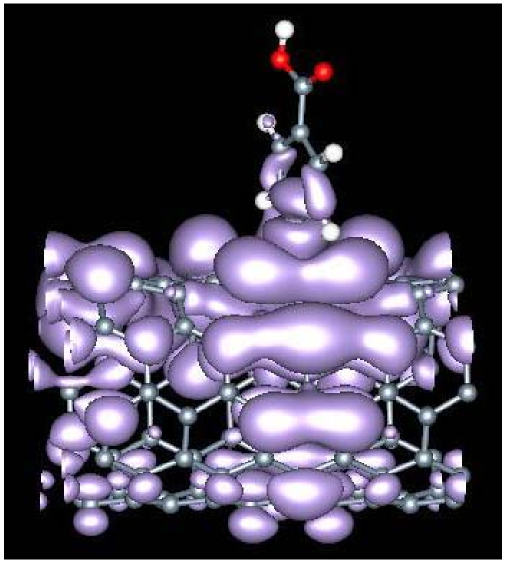


π*

π

The LEGO Bricks of Electronic Structure

First-Principles Molecular Dynamics: Time Evolution of the Electronic Ground State → **Optimal Unitary Transformation of the Bloch Orbitals** → **Real Space Maximally-Localized Wannier Functions**

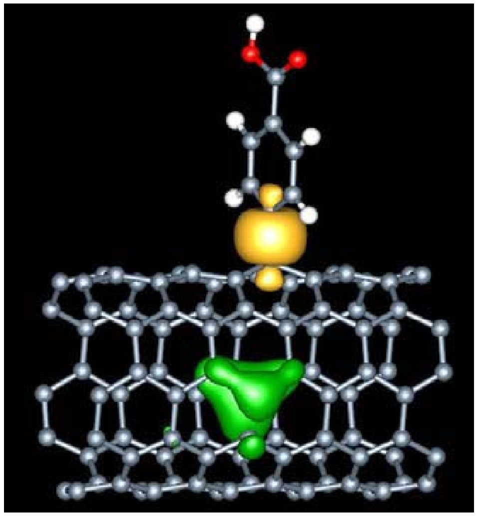


Minimization of the spread functional

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

exploiting the arbitrariness of the unitary transformations between the Bloch orbitals

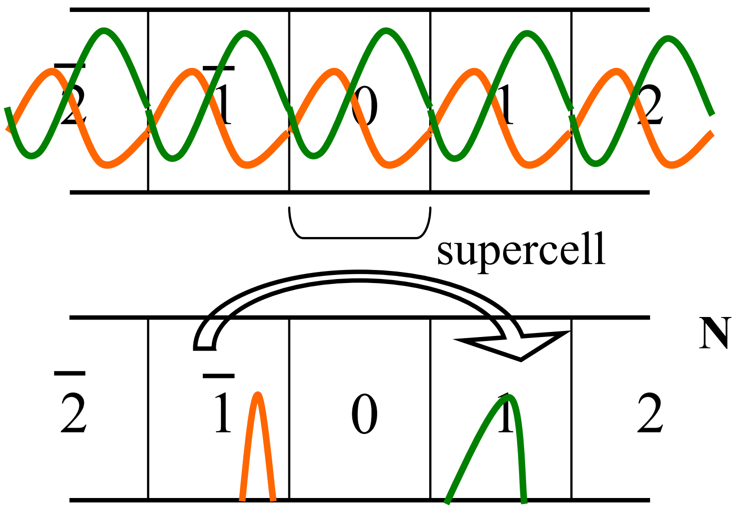
$$|\mathbf{R}n\rangle \;=\; \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})}\, \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$



The LEGO Bricks of Electronic Structure

Sparse Hamiltonian Matrix → **Large Scale Calculations**

Zero interaction between Wannier orbitals whose centers are further apart than decay length



No interaction

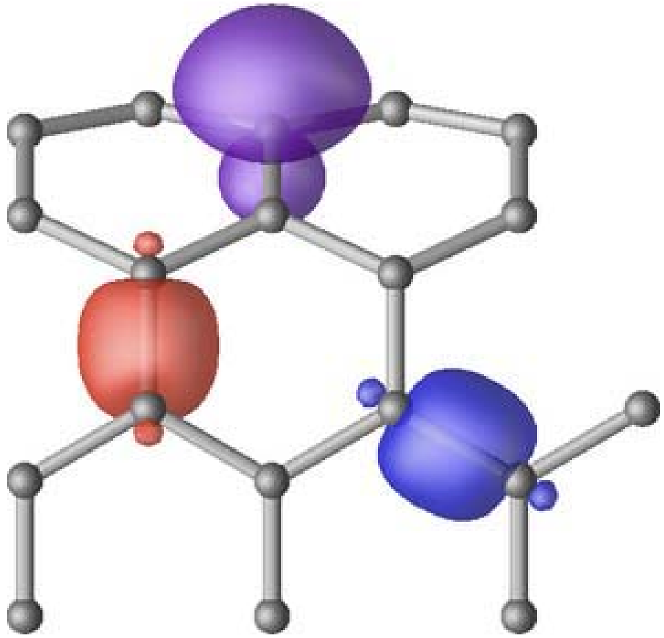
$$H = \begin{pmatrix} H_{01}^{+} & H_{00} & H_{01} & & 0 \\ & H_{01}^{+} & H_{00} & H_{01} & \\ 0 & & H_{01}^{+} & H_{00} & H_{01} \end{pmatrix}$$

Max-loc WFs ↔ “Exact” Tight-Binding

Compact mapping of Bloch states into local orbitals

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

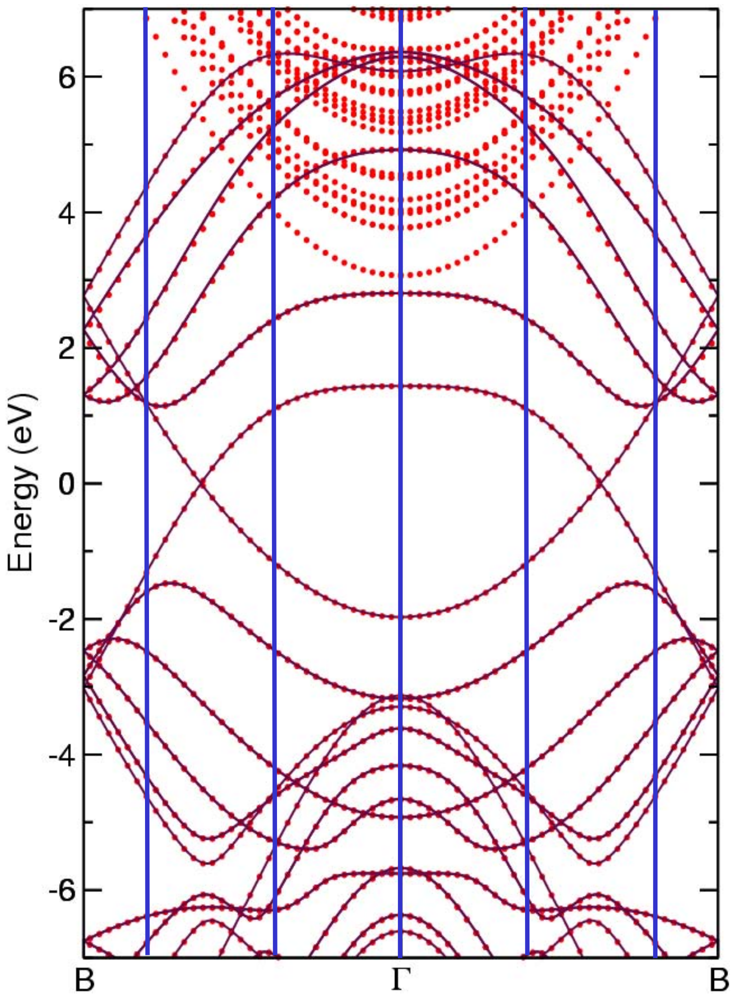
$$\psi_{n\mathbf{k}}(\mathbf{r}) \quad \frac{1}{\sqrt{N_R}}\sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\,\omega_n(\mathbf{r}-\mathbf{R})$$

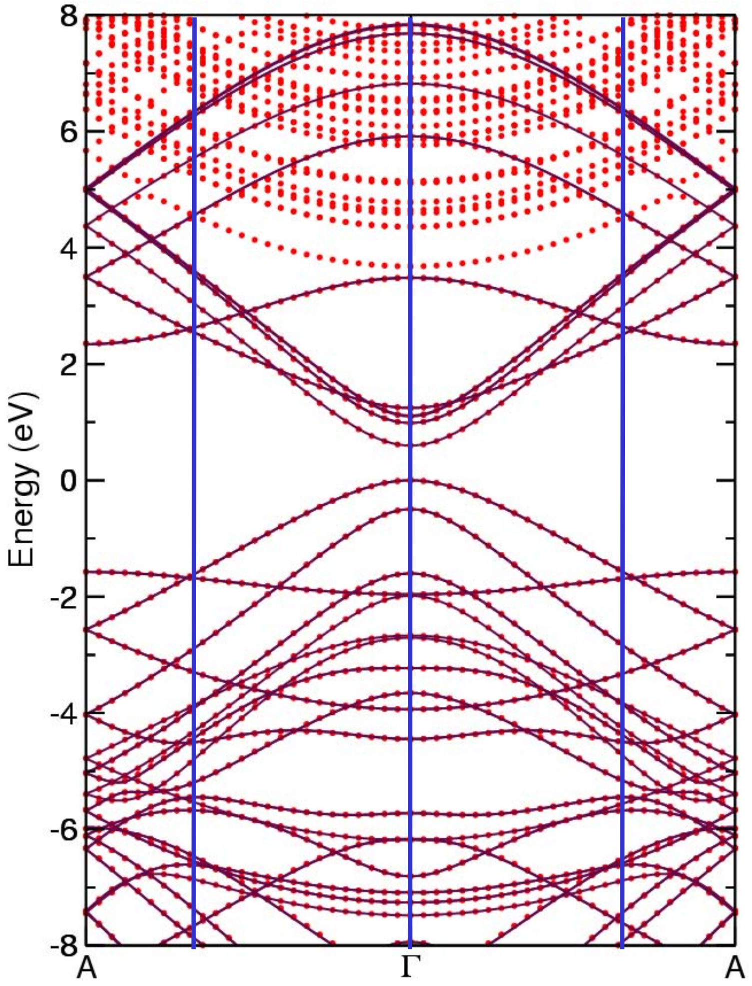


$$\langle\psi_{i\mathbf{k}}|\hat{\mathrm{H}}|\psi_{j\mathbf{k}}\rangle \quad H_{ij}^{00}+e^{i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{01}+e^{-i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{0\bar{1}}$$

⇨ Diagonalize H Matrix

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

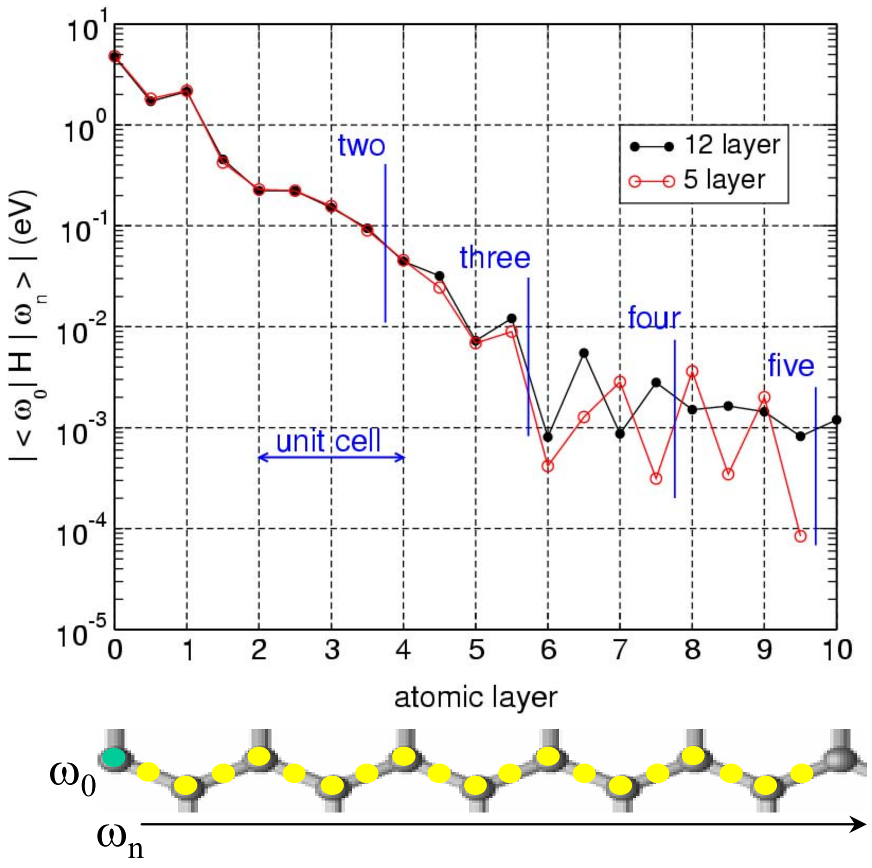

(5,5) SWCNT

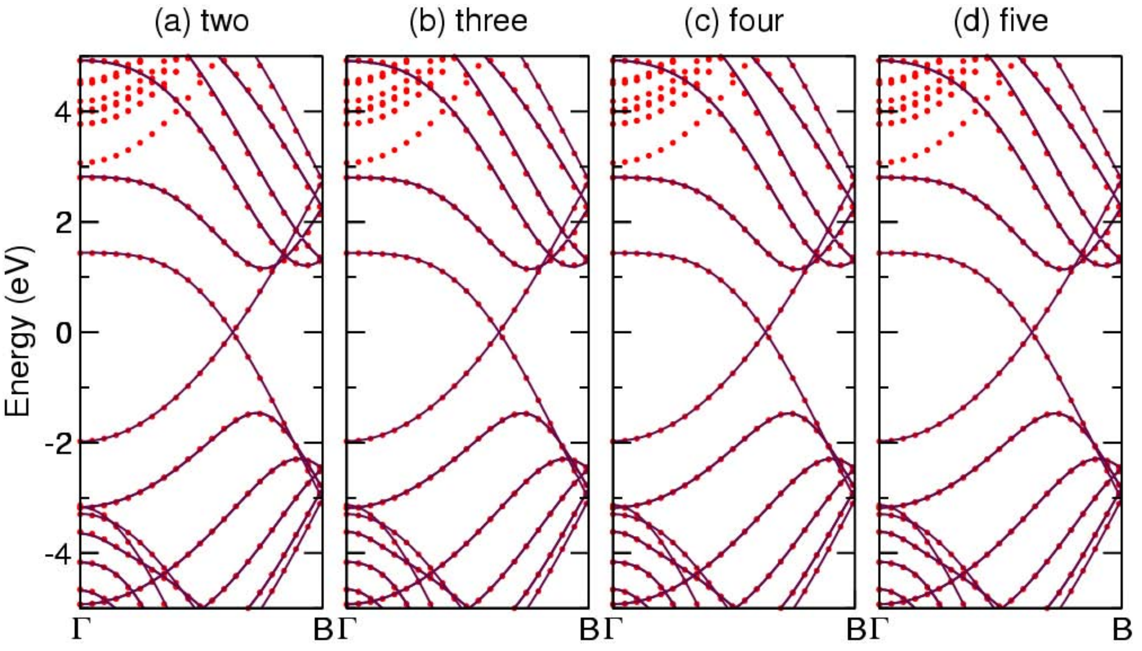

(8,0) SWCNT

Exponential Decay

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

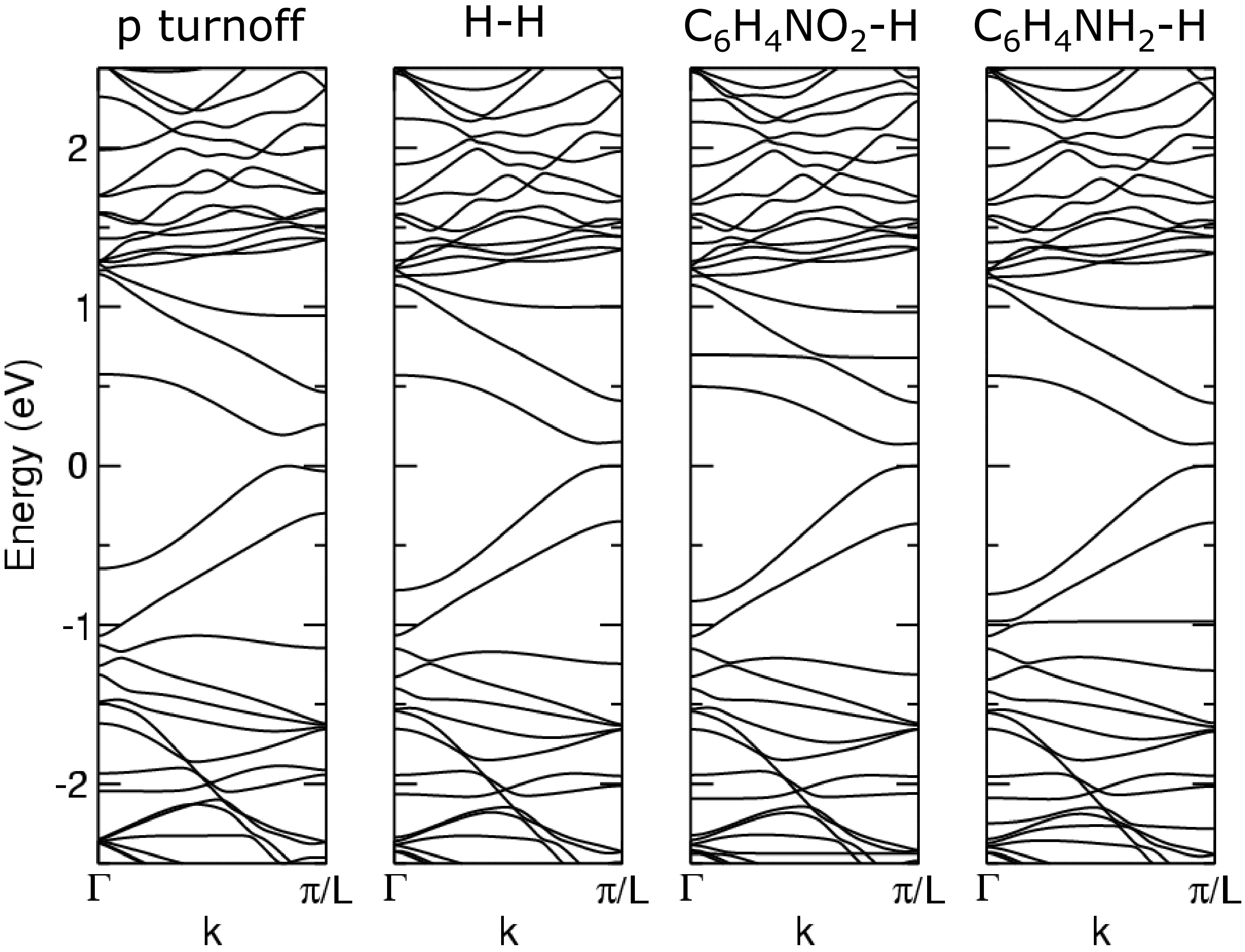
$$\langle \omega_0 | \hat{H} | \omega_n \rangle$$

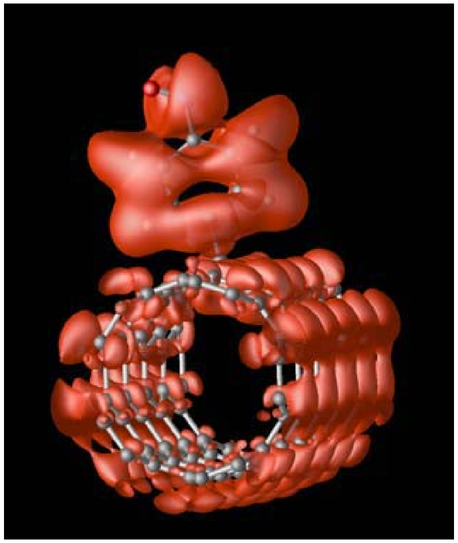




Aryl / Hydrogen

- Band structure / Different functional groups
  - Band structure is not so much dependent on functional groups
  - Net effect of covalent functionalization can be mimicked by removing p-MLWFs ⇨ localized p orbitals



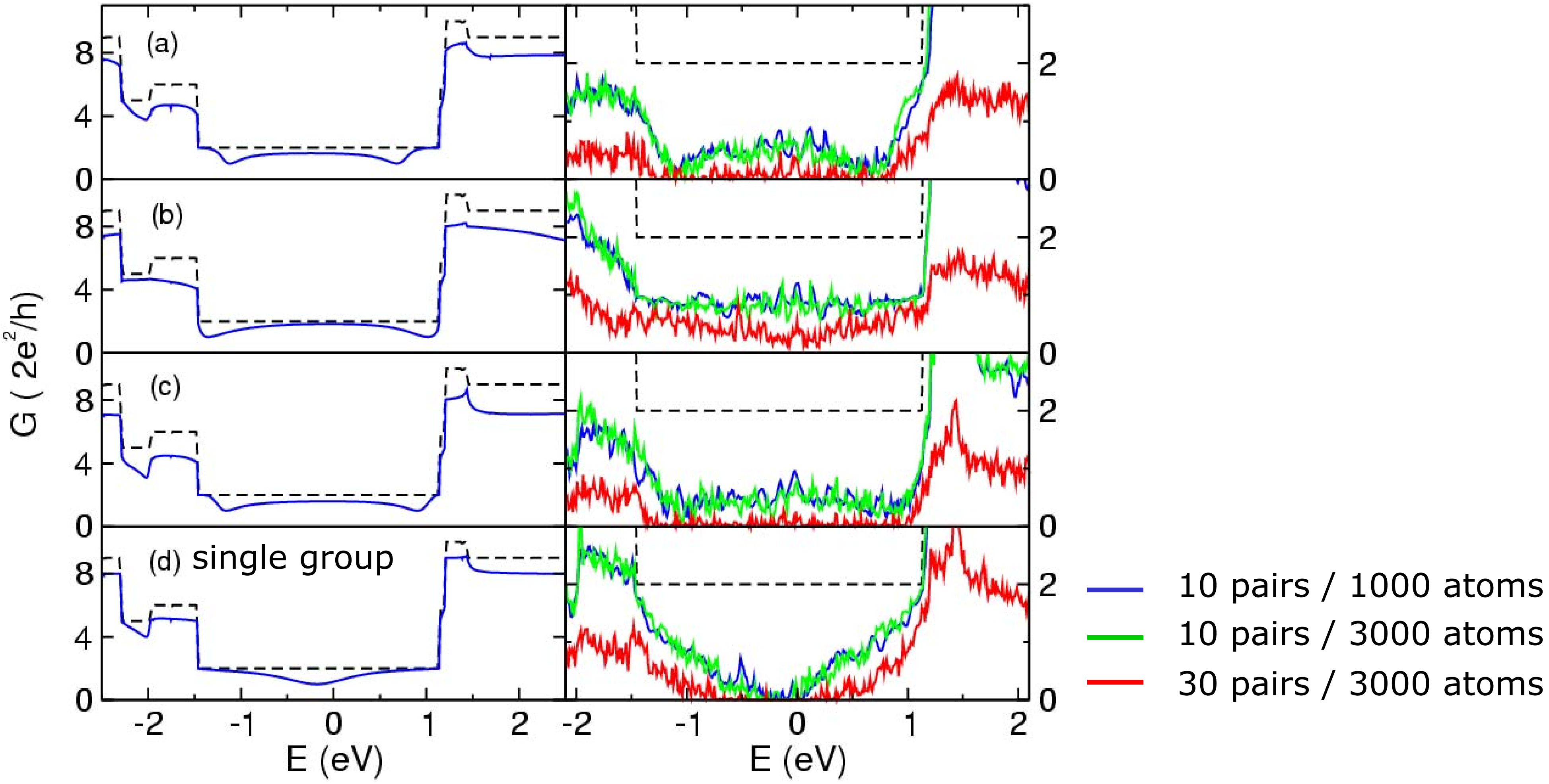


charge density injected when $-NO_2$ replaced by $-NH_2$

aminophenyl group is more electropositive than nitrophenyl group

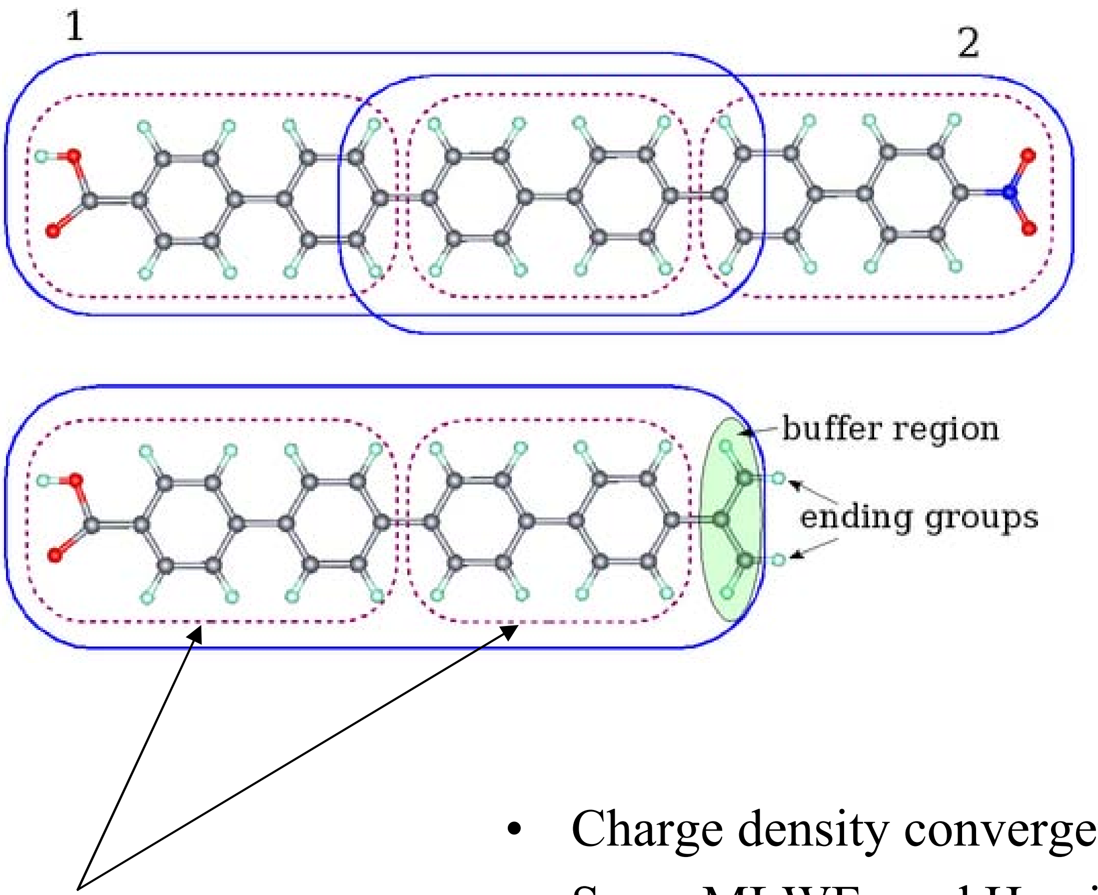
Aryl / Hydrogen

- Large scale simulations
  - Conductor part : 1000-3000 atoms / 12-37 nm
  - Average of five random configurations



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