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# Electronic-structure and Transport in Nanostructures based on Wannier Function

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# Building nanostructures Bloch by Bloch

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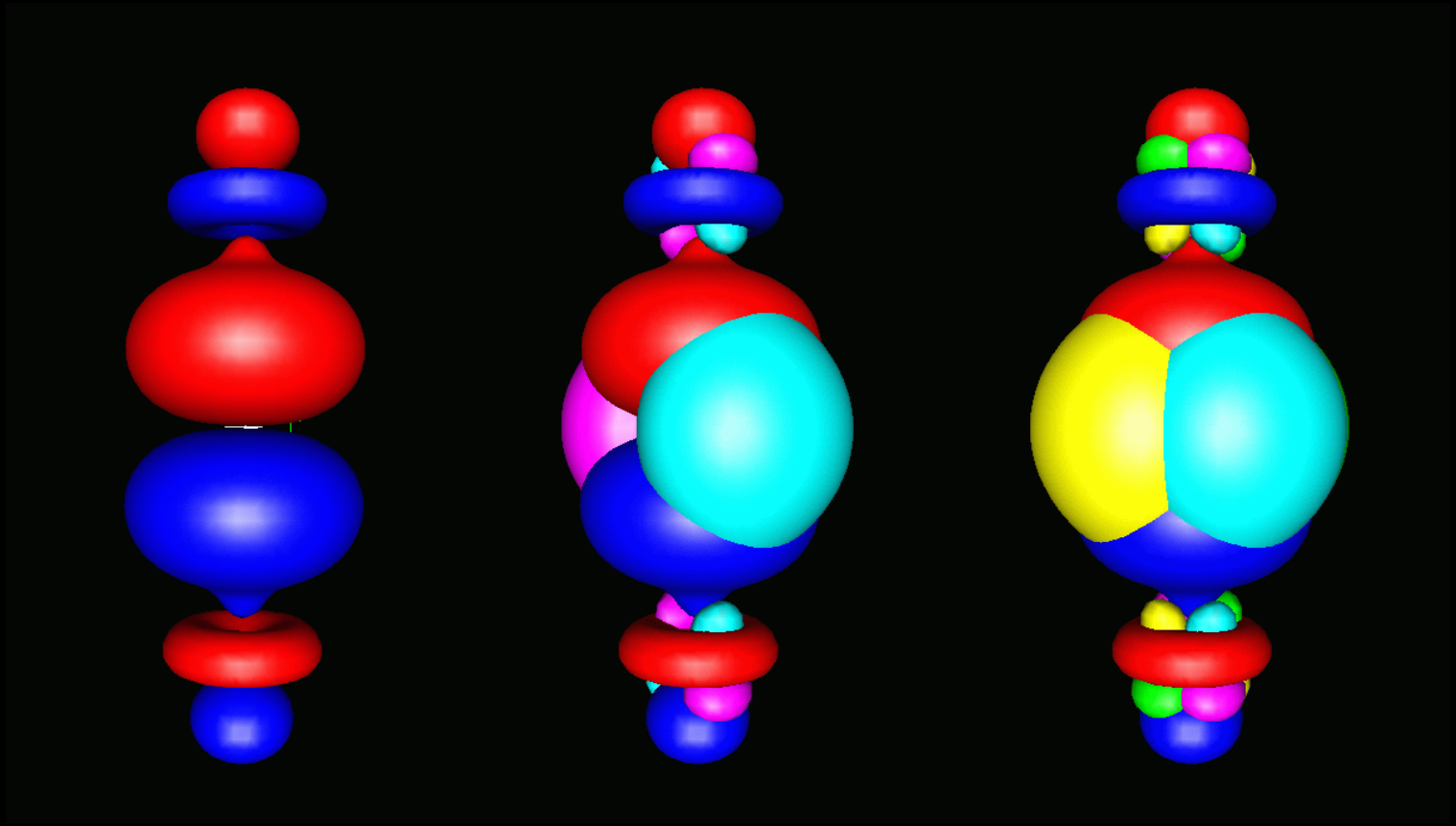
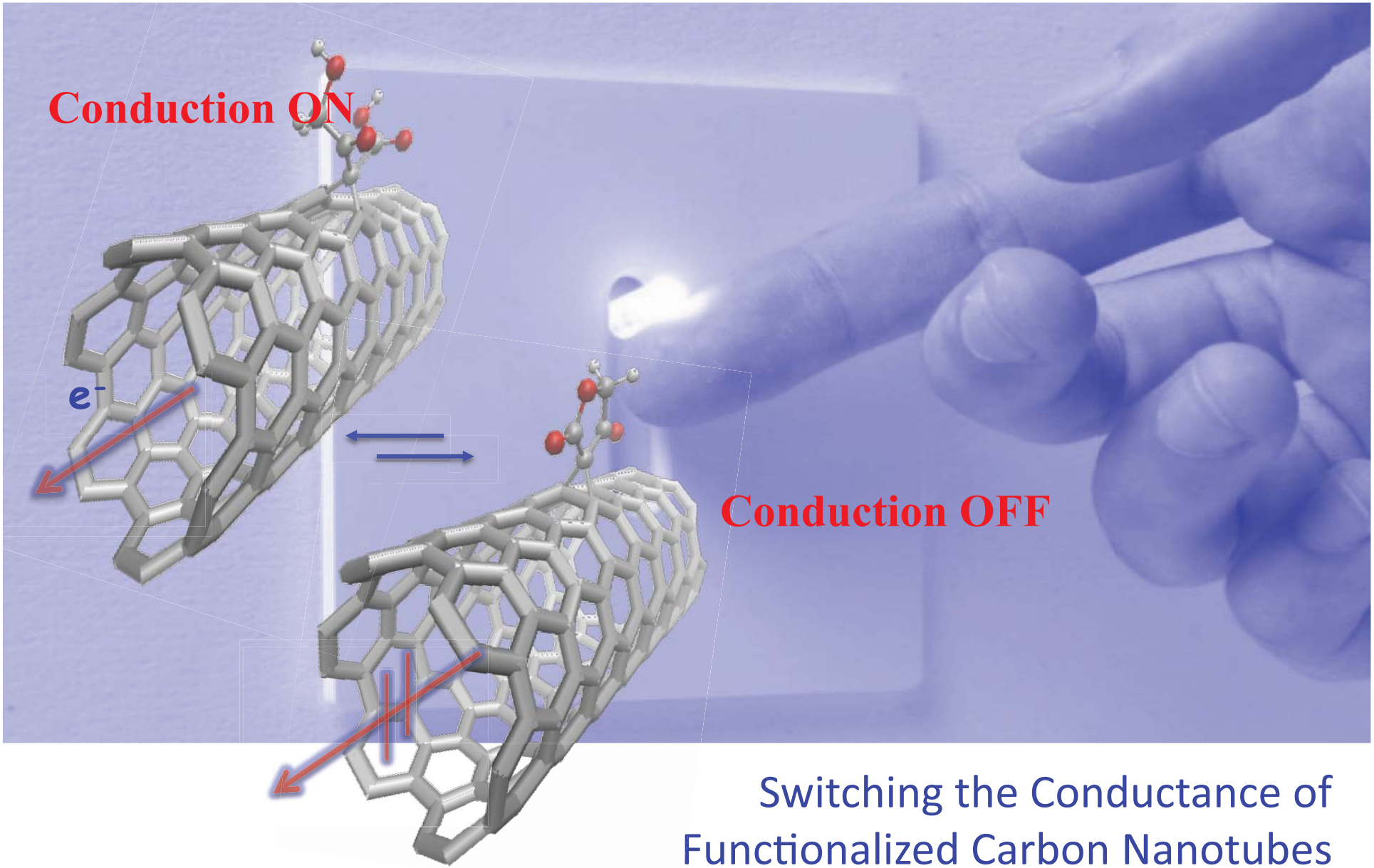
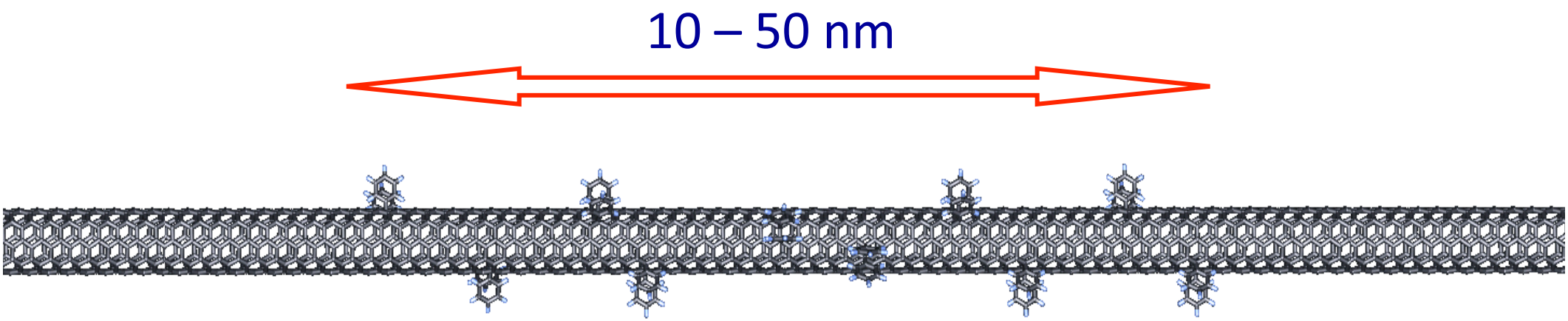





Switching the Conductance of Functionalized Carbon Nanotubes

# Electronic-structure and quantum conductance




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

# Bloch Theorem

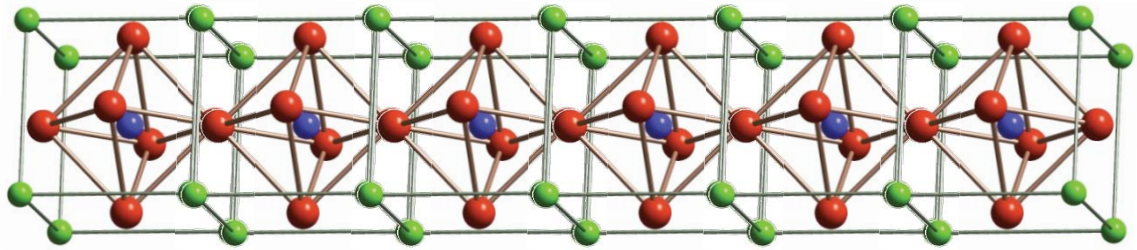
The one-particle effective Hamiltonian $\hat{H}$ in a periodic lattice commutes with the lattice-translation operator $\hat{T}_{\mathrm{R}}$, allowing us to choose the common eigenstates according to the prescriptions of Bloch theorem:

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

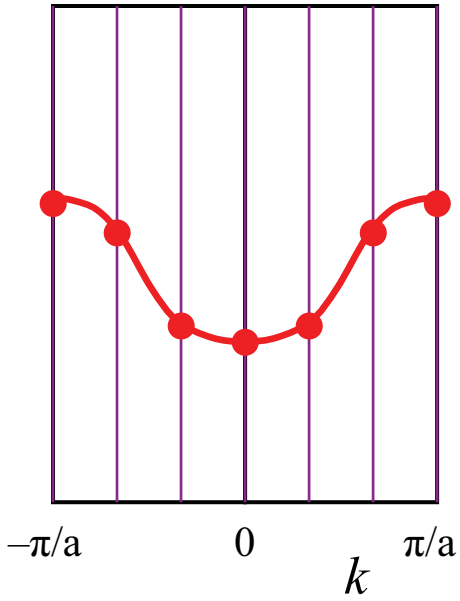
- *n, k* are the quantum numbers (band index and crystal momentum), *u* is periodi

# Bloch Theorem

Crystal in real space:

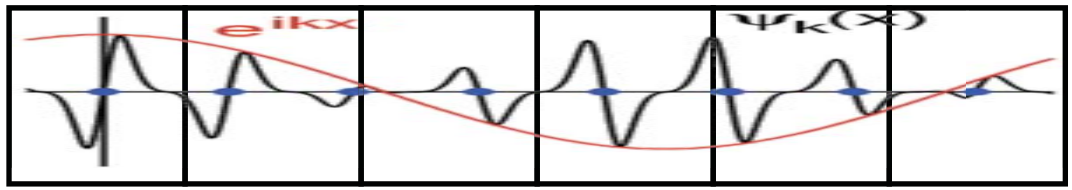


Brillouin zone in reciprocal space:

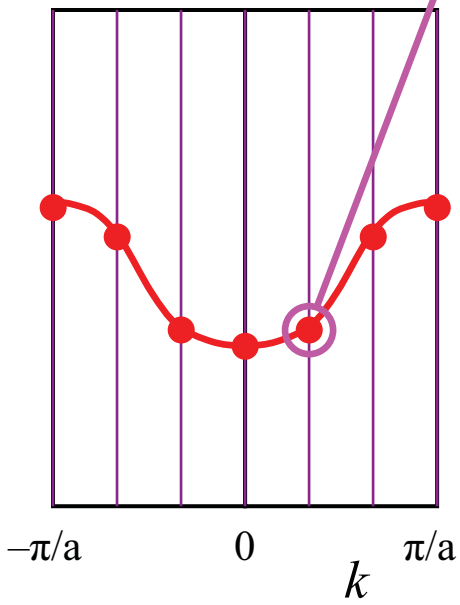


# Bloch Theorem

Crystal in real space:

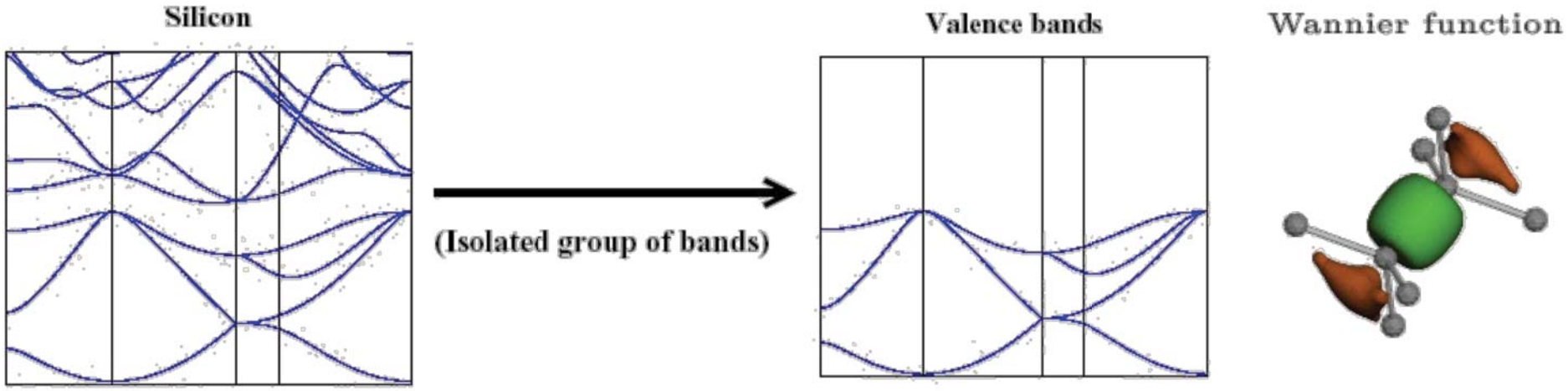



Brillouin zone in reciprocal space:



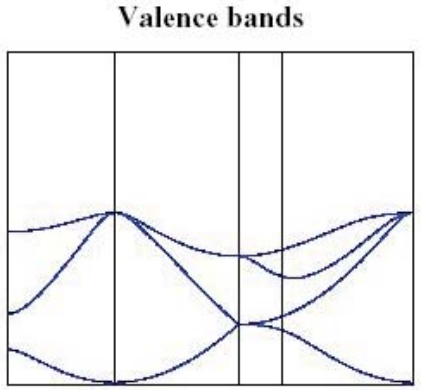
# Generalized Wannier Functions for Composite Bands

- $\{|\mathbf{R}n\rangle\}$ 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

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



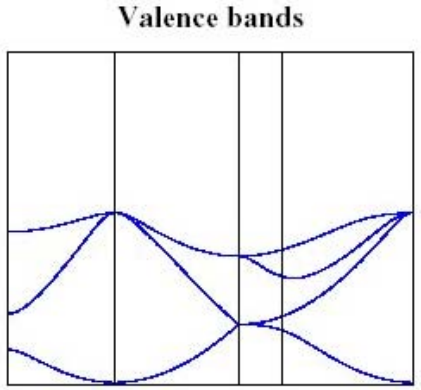

## Gauge freedoms

- 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

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




## Gauge freedoms

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

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

# The Localization Functional (Foster-Boys)

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

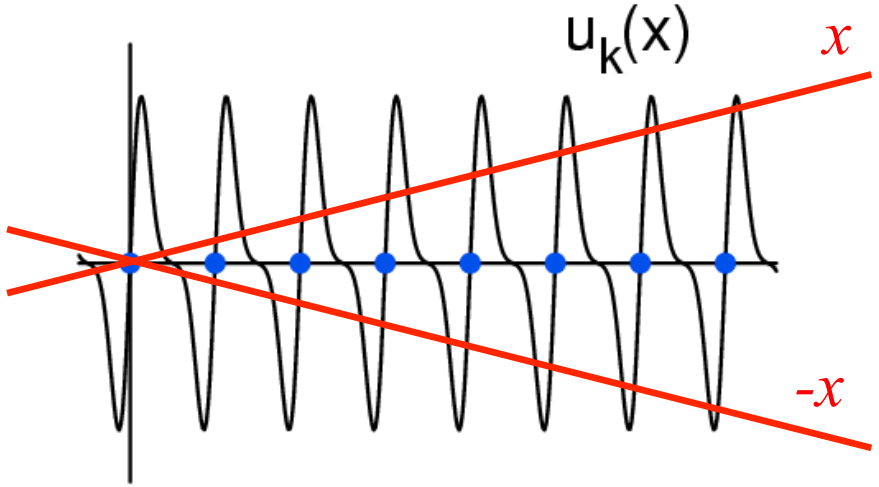
For a given set of Bloch orbitals, our goal is to minimize $\Omega$ with respect all the sets of unitary transformations $U_{mn}^{(\mathbf{k})}$

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

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

# Position operator is ill defined !

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



# Blount identities

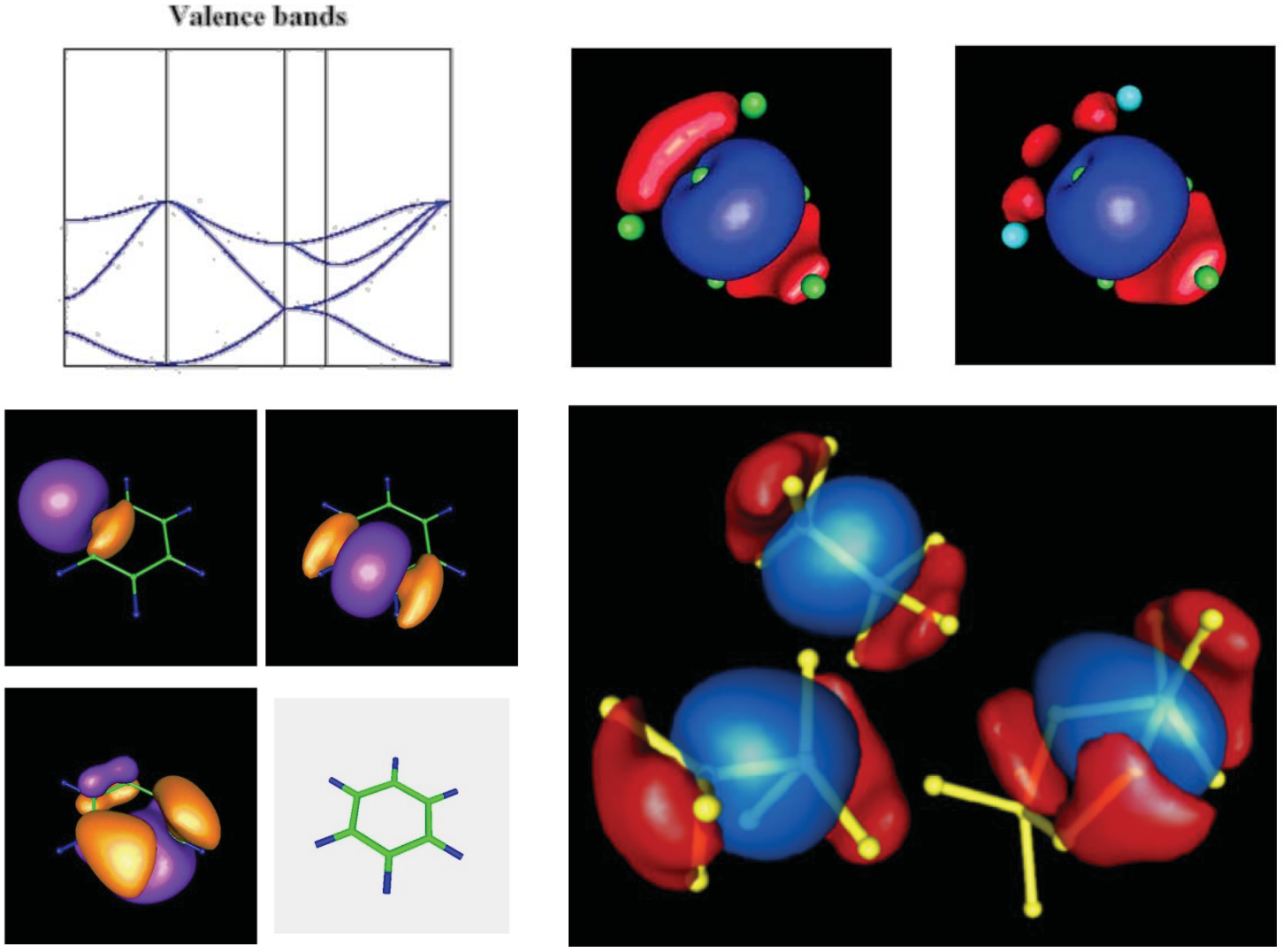
Position operator $\Rightarrow$ Gradient

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

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

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

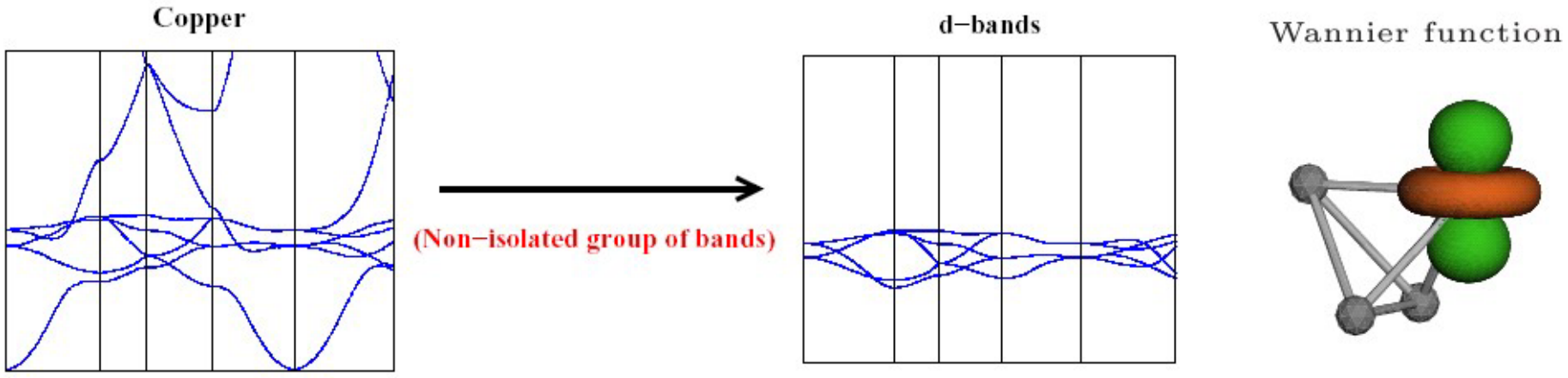
# Silicon, GaAs, Amorphous Silicon, Benzene




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

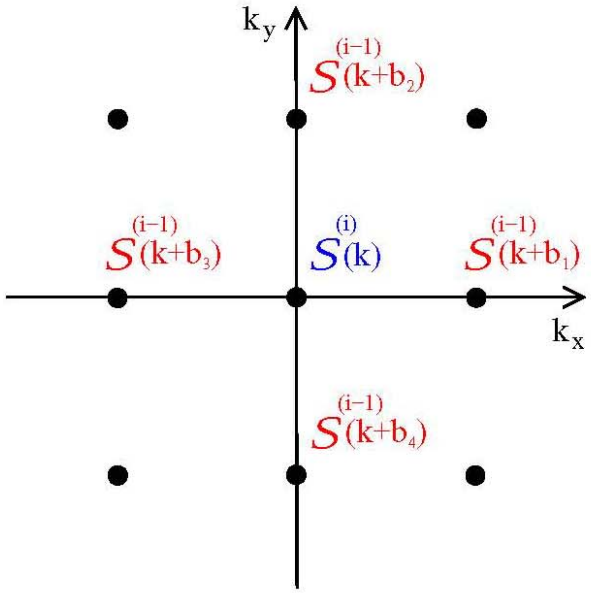
# Disentanglement of Attached Bands

- 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 $\Omega_I$




Minimize degree of mismatch between $\mathcal{S}^{(i)}(\mathbf{k})$ and $\mathcal{S}^{(i-1)}(\mathbf{k}+\mathbf{b})$, i.e.,

maximize overlap $\sum_{\mathbf{b}} \sum_{m=1}^{N} \left| \left\langle u_{n\mathbf{k}}^{(i)} \middle| u_{m,\mathbf{k}+\mathbf{b}}^{(i-1)} \right\rangle \right|^2$

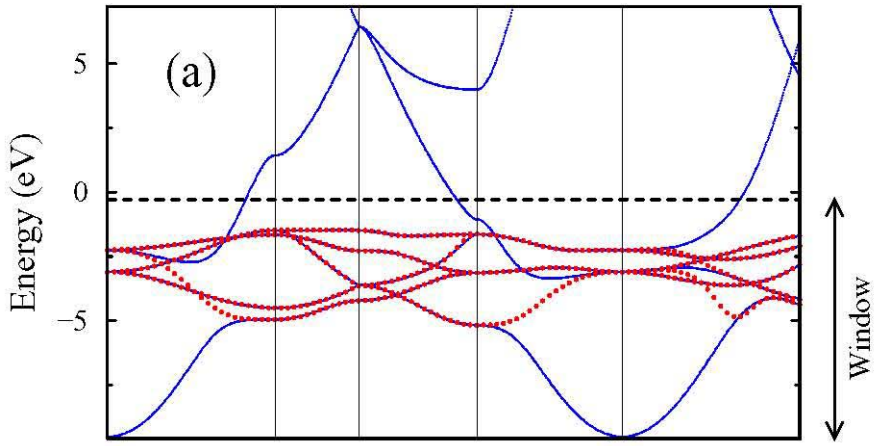
- $1^{\text{st}}$ iteration: Choose trial subspace at each $\mathbf{k}$ (e.g. projected orbitals)
- $i^{\text{th}}$ iteration: At each $\mathbf{k}$ pick the $N$ highest eigenvectors of

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

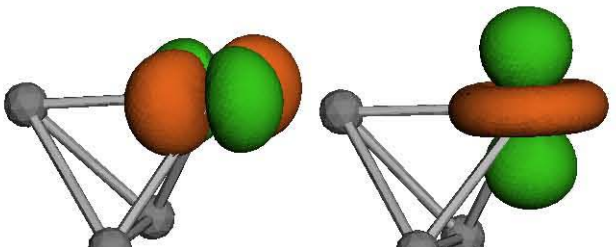
$\hat{P}_{\mathbf{k}+\mathbf{b}}^{(i-1)}$ : Projector onto $\mathcal{S}^{(i-1)}(\mathbf{k}+\mathbf{b})$

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

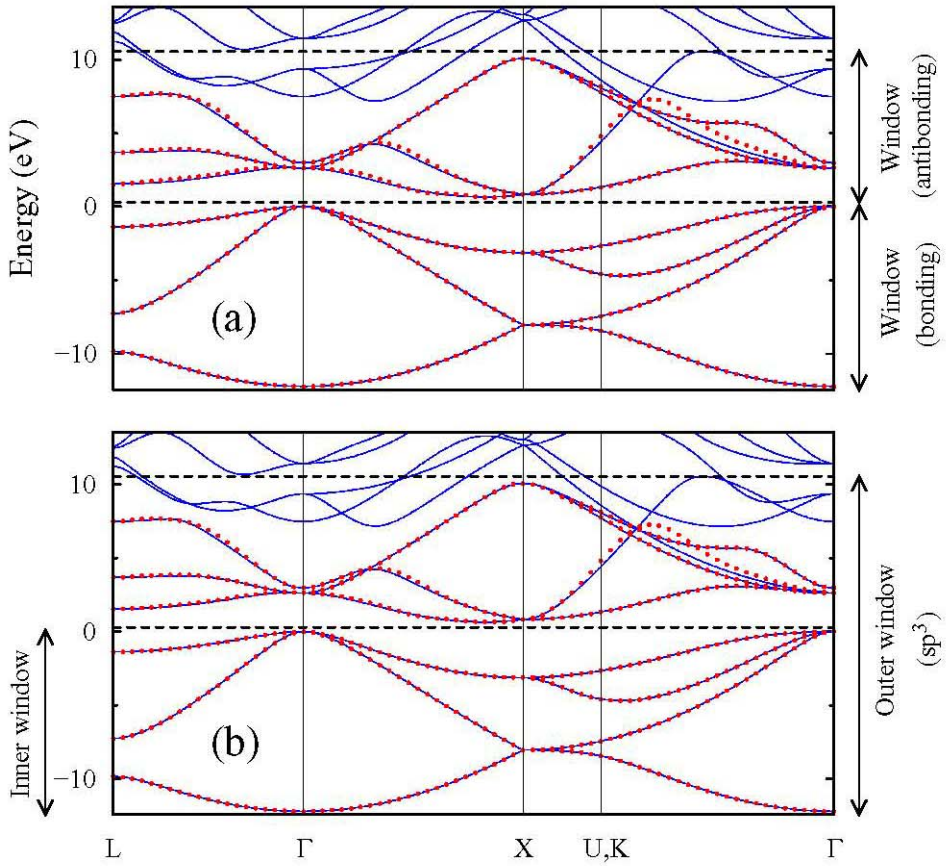
# *d* Bands of Copper

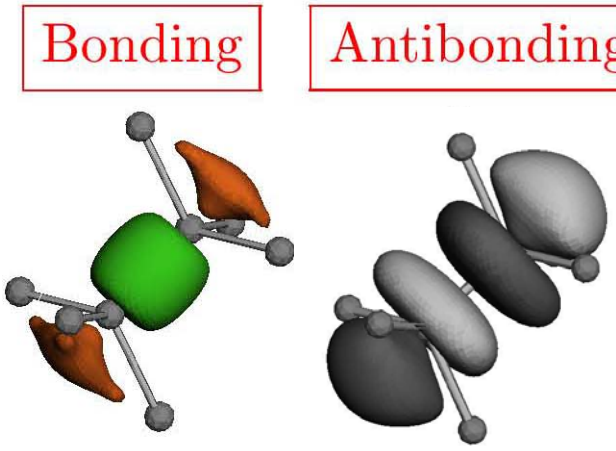



The $e_g$ $d$ WFs of panel (b)

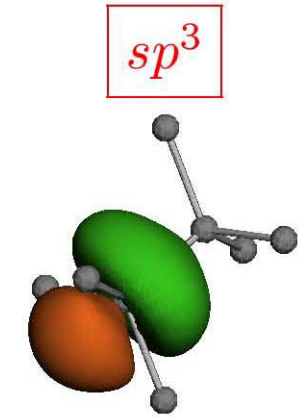


# Silicon: Bonding and Antibonding Orbitals




7.53 bohr$^2$ 24.37 bohr$^2$




spread=10.68 bohr$^2$

WANNIER 90

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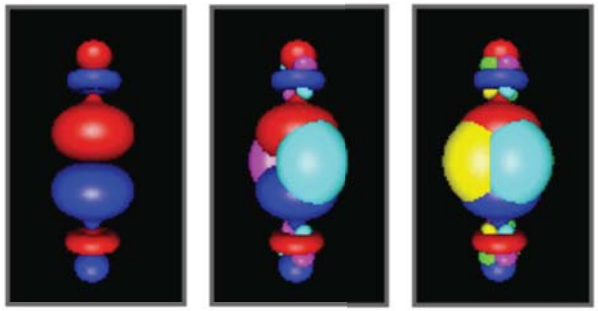
## Welcome!

This is the home of maximally-localised Wannier functions (MLWFs) and Wannier90, the computer program that calculates them. Wannier90 is released under the GNU General Public License.



## Latest News

**15 JAN 2010**

Wannier90 (v1.2) is now available for download here.

See here for our news archive.

**Wannier90 seamlessly interfaced to Quantum-ESPRESSO, Abinit, Siesta, FLEUR …**

Please cite

*Wannier90: A Tool for Obtaining Maximally-Localised Wannier Functions*
A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt and N. Marzari
*Comput. Phys. Commun.* **178**, 685 (2008) [ONLINE JOURNAL]

in all publications resulting from your use of Wannier90.

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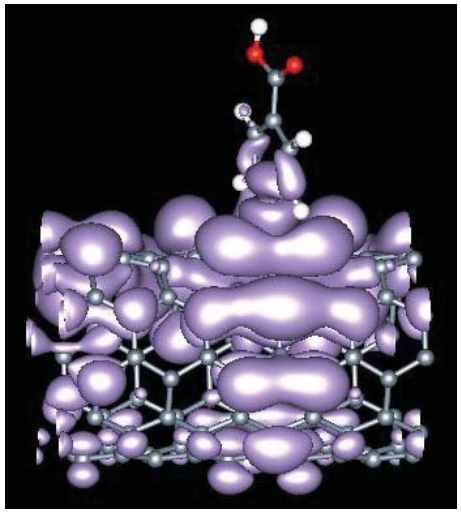
Imperial College London

THE STATE UNIVERSITY OF NEW JERSEY RUTGERS

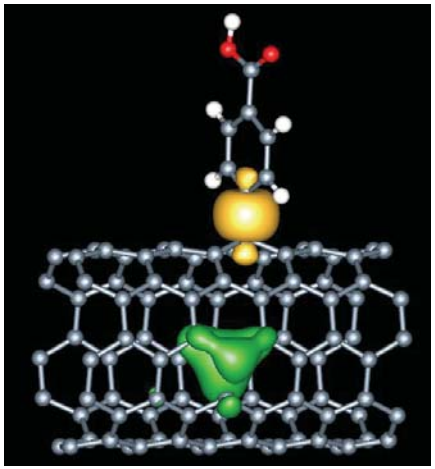
# Electronic Structure of Large Nanostructures

**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

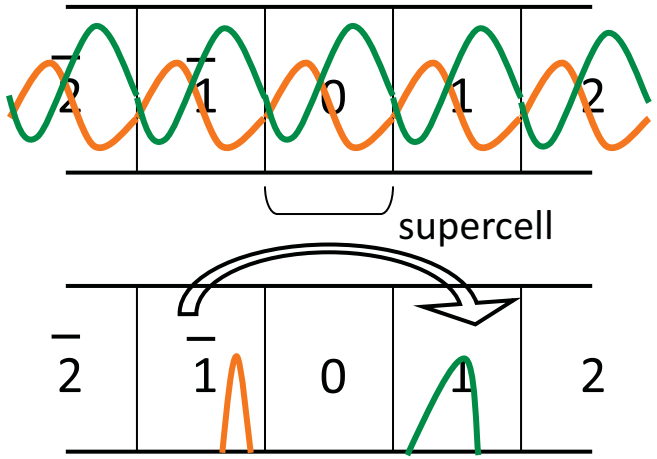
$$\Omega = \sum_n [\langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2]$$



*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

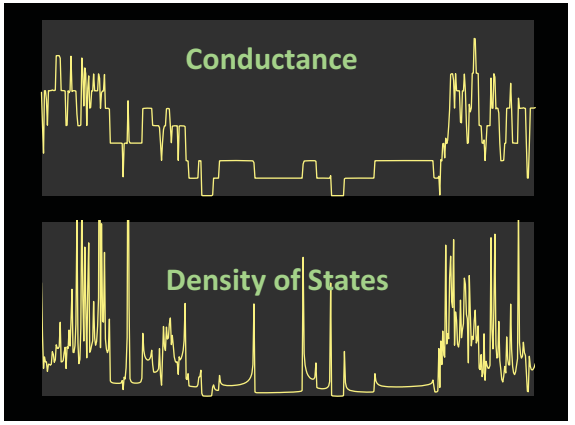
$$H_{00}\,,\,H_{01} \Rightarrow G_C^r(E)$$

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

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

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

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



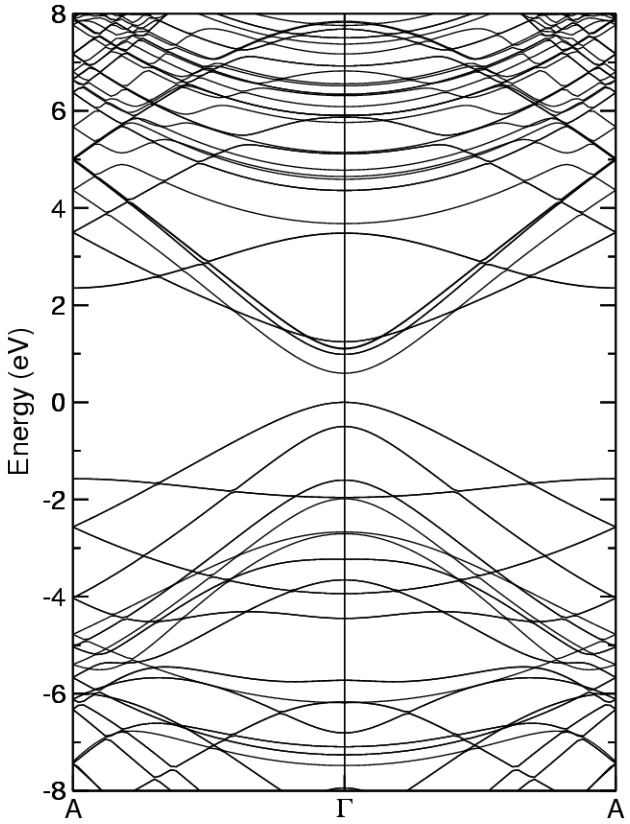


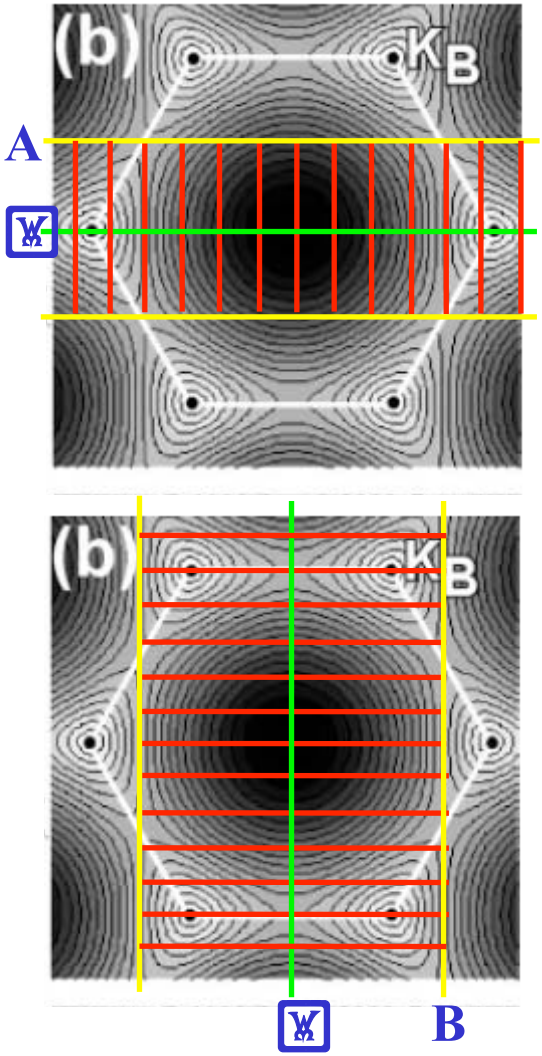
*M. B. Nardelli, Phys. Rev. B 60, 7828 (1999)*

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

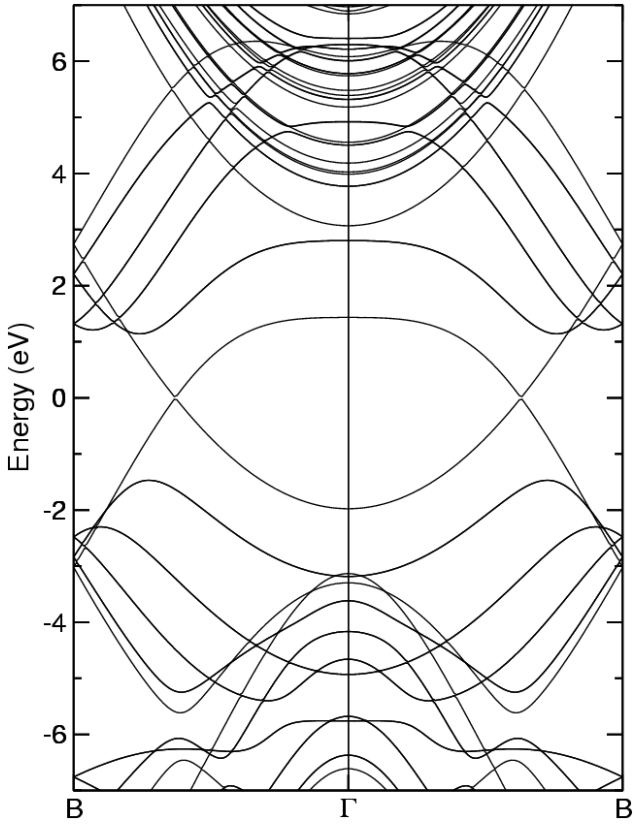
# Band Structure of (8,0) and (5,5) SWNT

(8,0) semiconducting

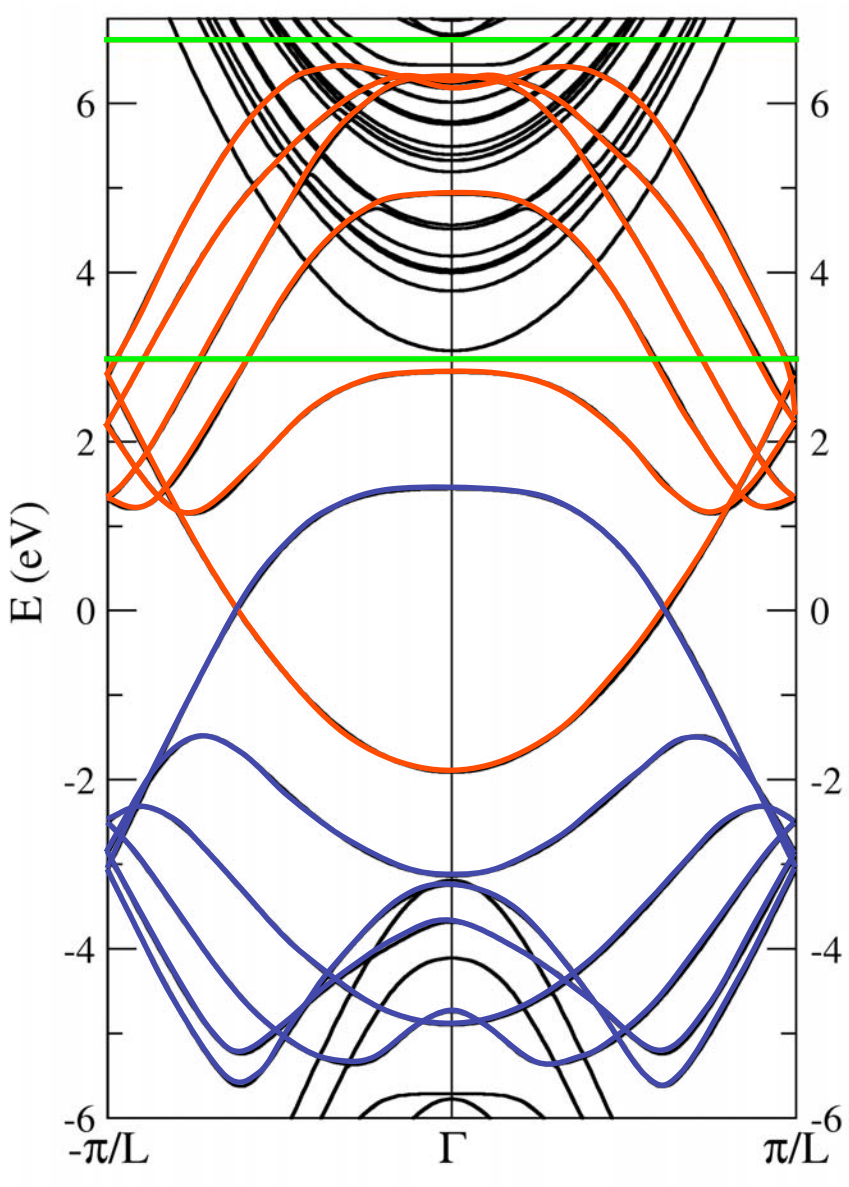



(5,5) metallic



# Disentanglement: Conduction Bands in (5,5) SWNT



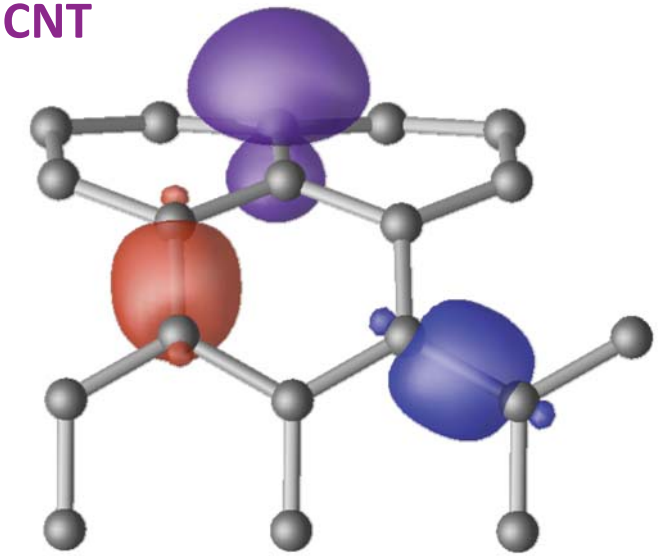
# MLWFs from the Disentangled Subspace

- Localization after disentanglement

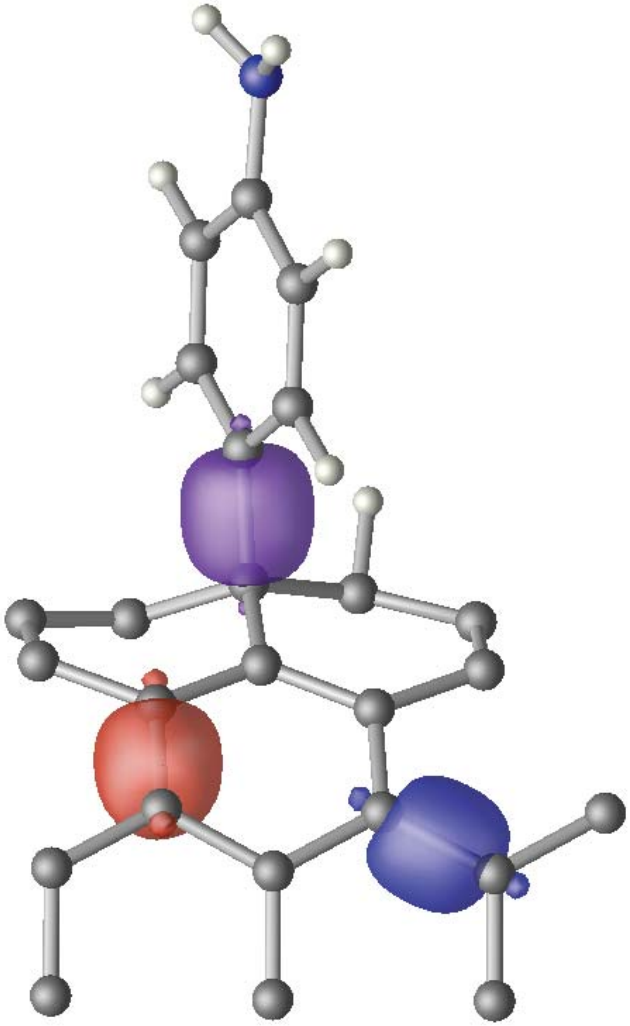
$$w_n = \sum_{m=1}^{N} U_{mn} \psi_m$$

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

**(5,5) CNT**



**(5,5) CNT + Nitrophenyl**

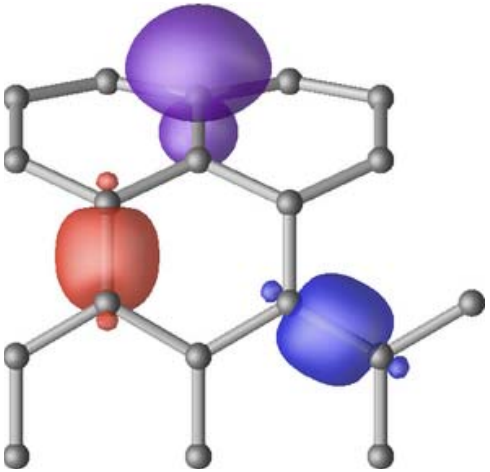


# Max-loc WFs ↔ "Exact" Tight-Binding

Compact mapping of Bloch states into local orbitals

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

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



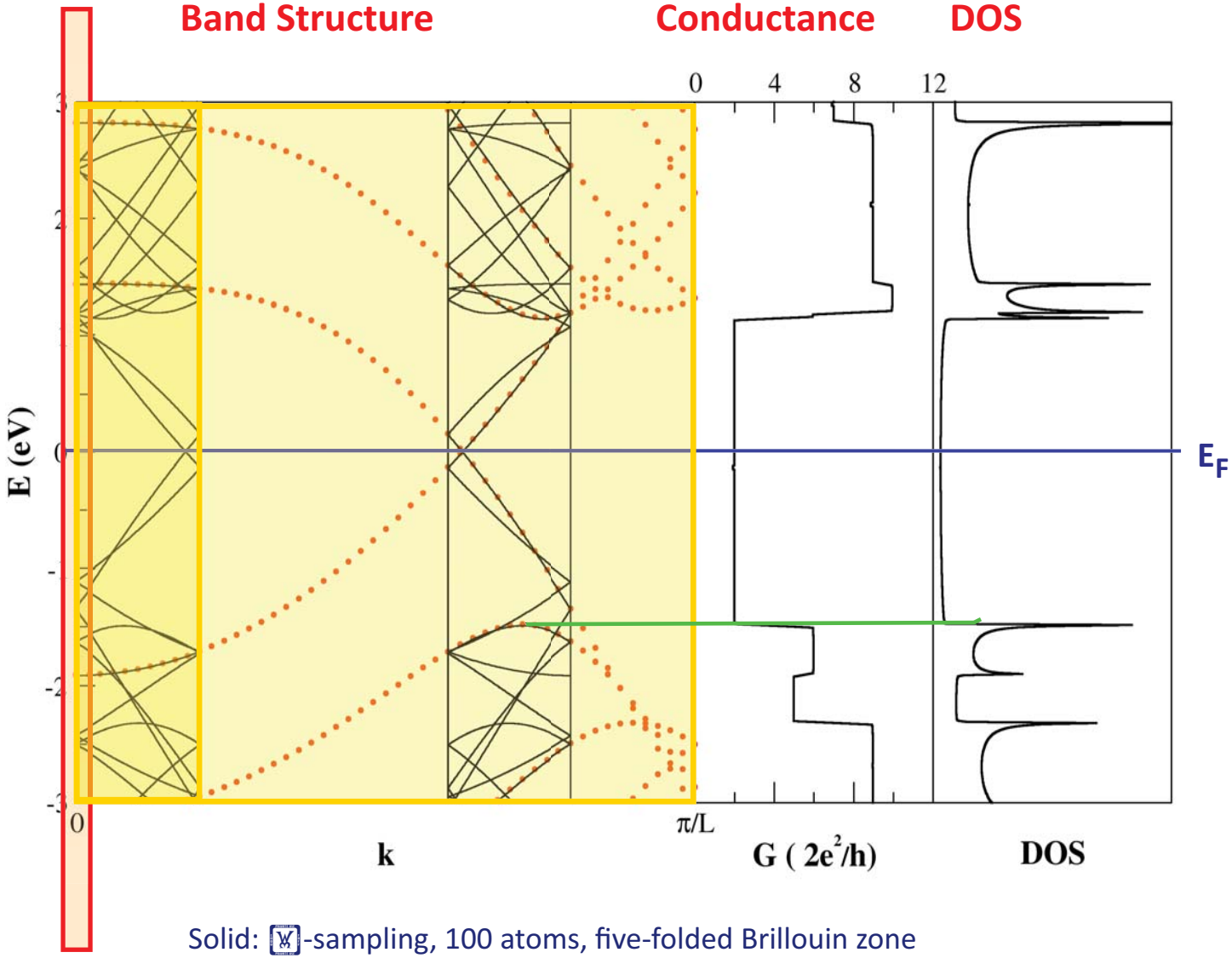
$$\left\langle \psi_{i\mathbf{k}} \middle| \hat{\mathrm{H}} \middle| \psi_{j\mathbf{k}} \right\rangle = H_{ij}^{00} + e^{i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{01} + e^{-i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{0\bar{1}}$$

⇨ Diagonalize H Matrix

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

Γ-point : ~ 2eV pseudo gap

Two eigenchannels at $E_F$ ⇨ perfect recovery of metallic character !

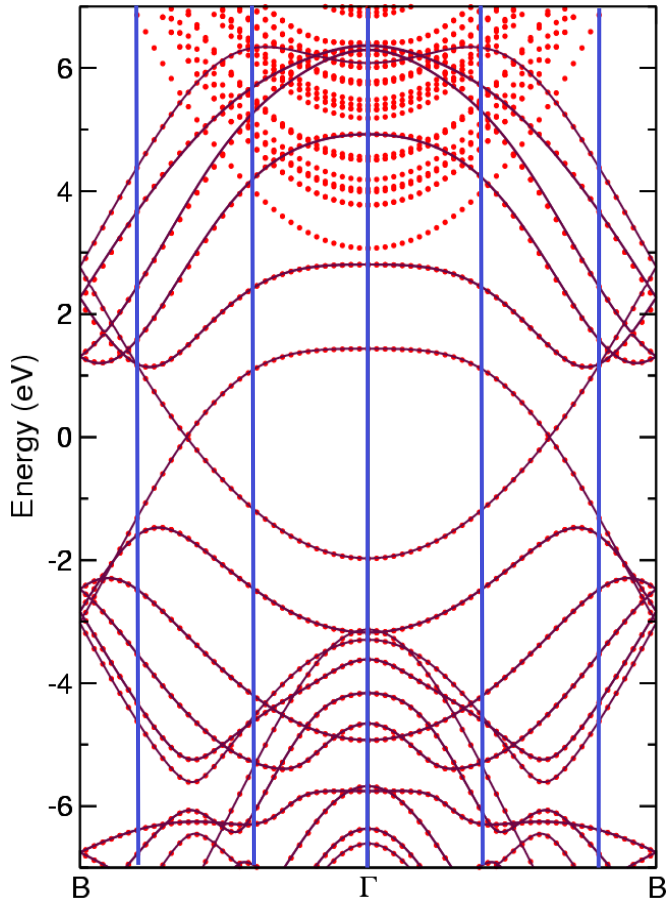



Solid: Γ-sampling, 100 atoms, five-folded Brillouin zone

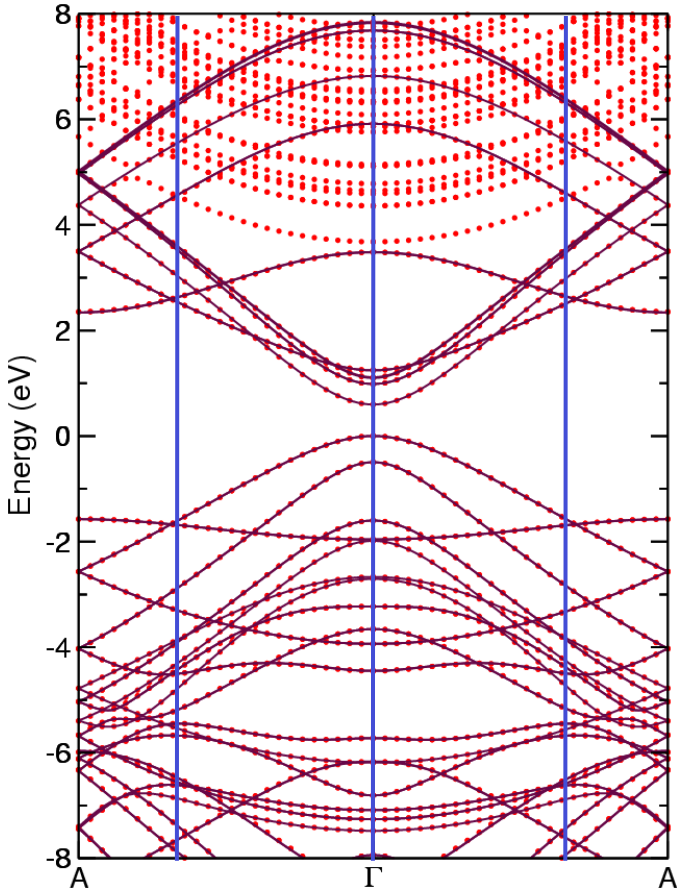
Dotted: Full SCF calculation (5 k-points, 20 atoms supercell)

# Exact Mapping onto a Tight-Binding Hamiltonian

**(5,5) SWCNT**



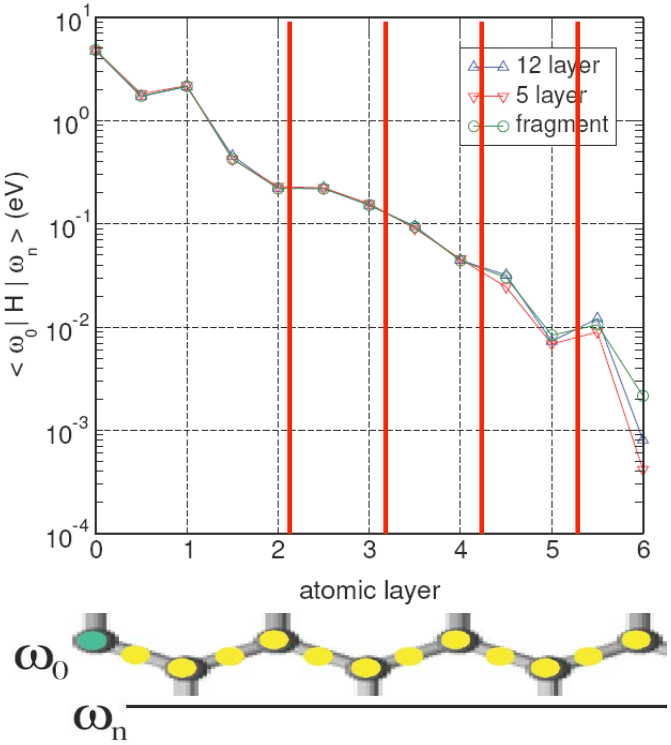

**(8,0) SWCNT**

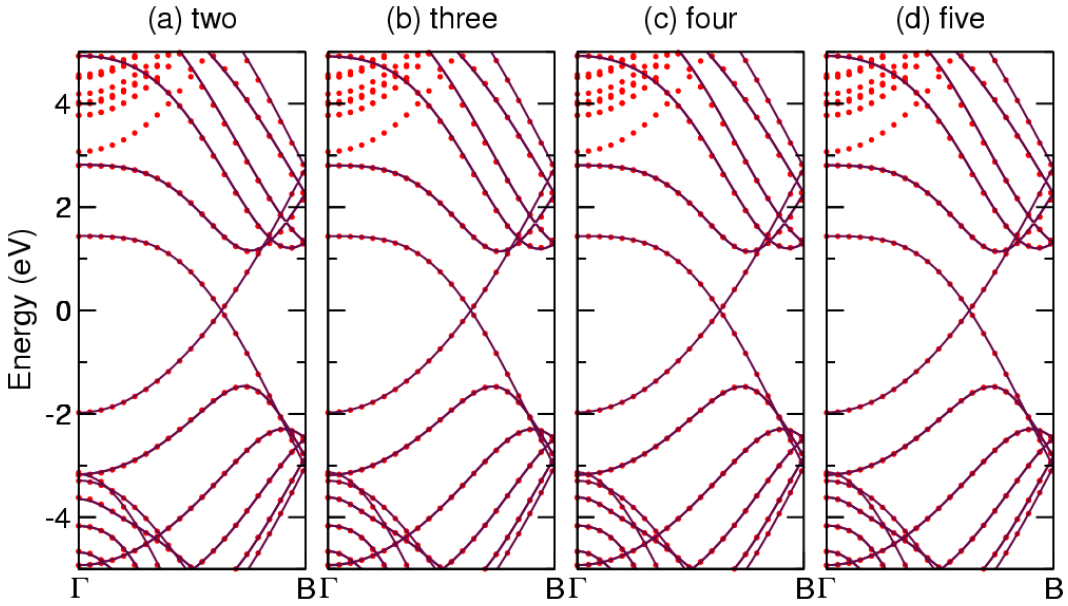


# Exponential Decay

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

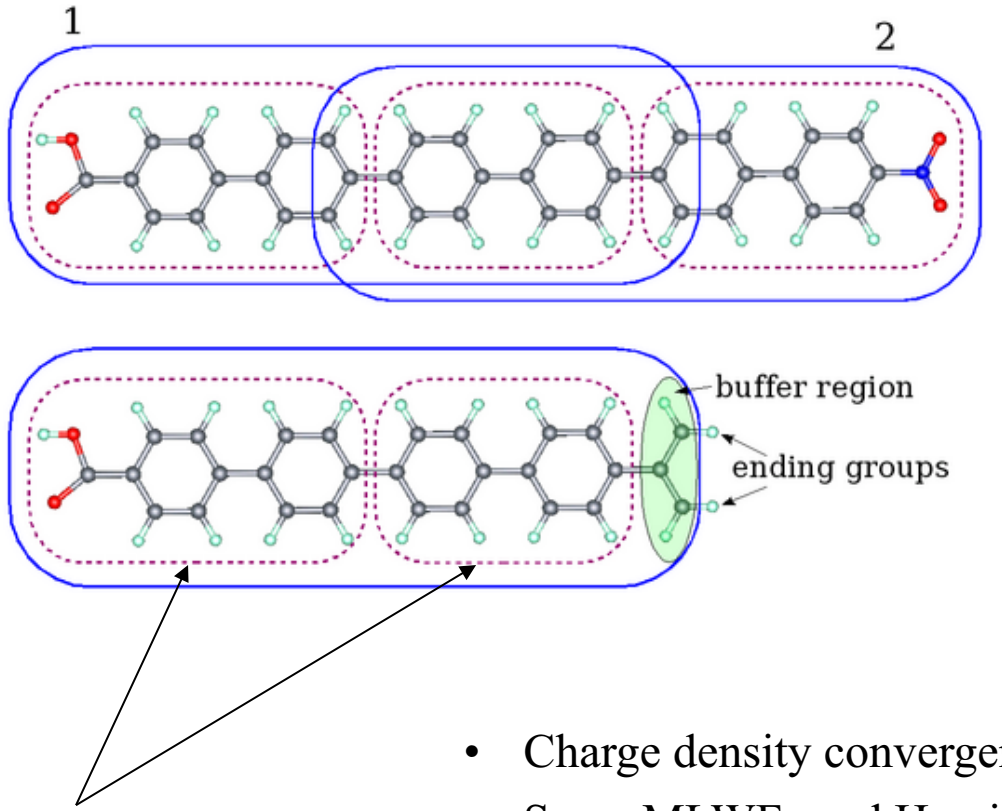
$$\langle \omega_0 | \hat{H} | \omega_n \rangle$$



# Large Scale Calculations

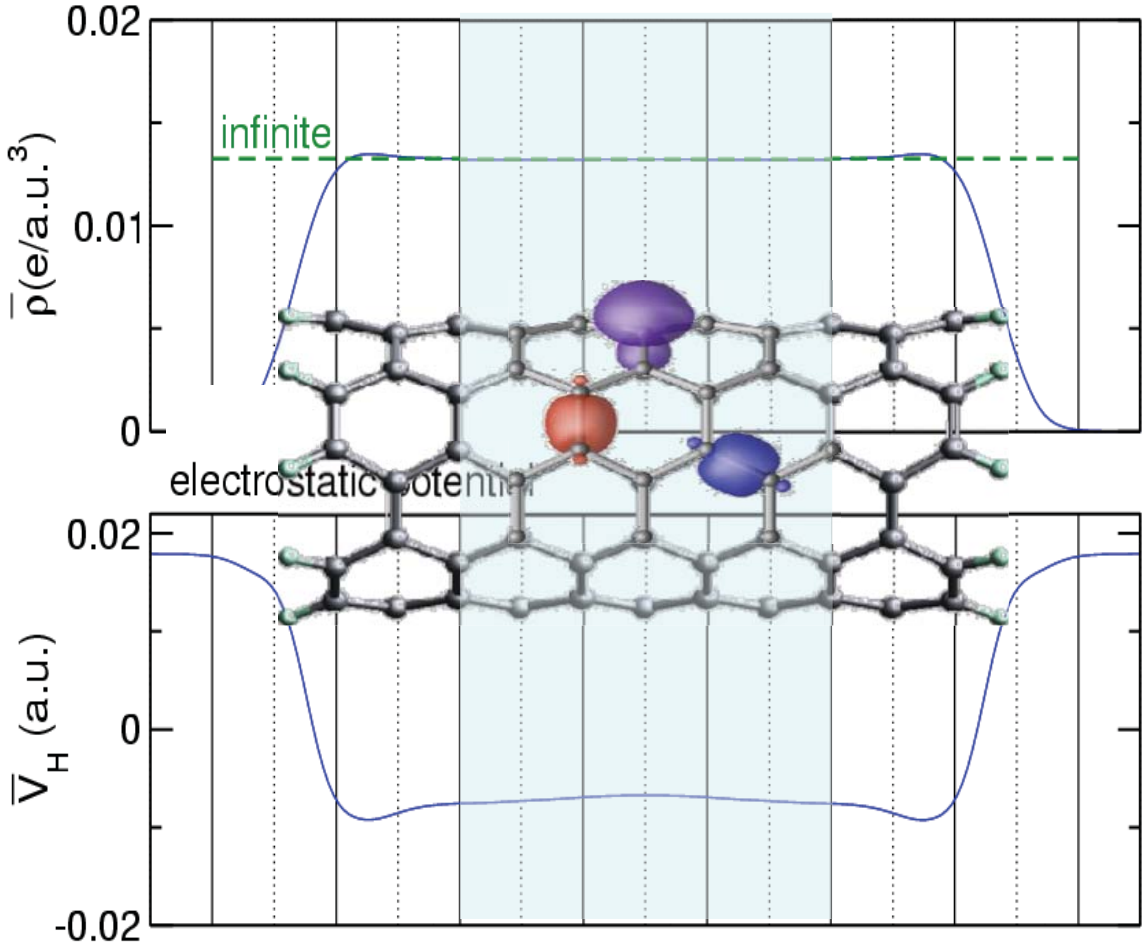
- Parameterization

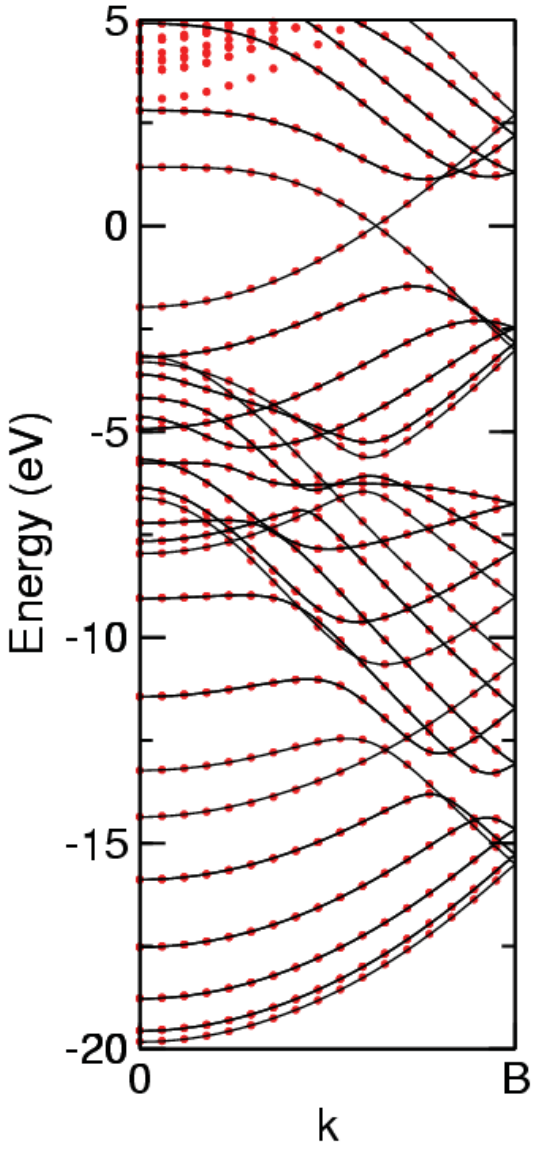


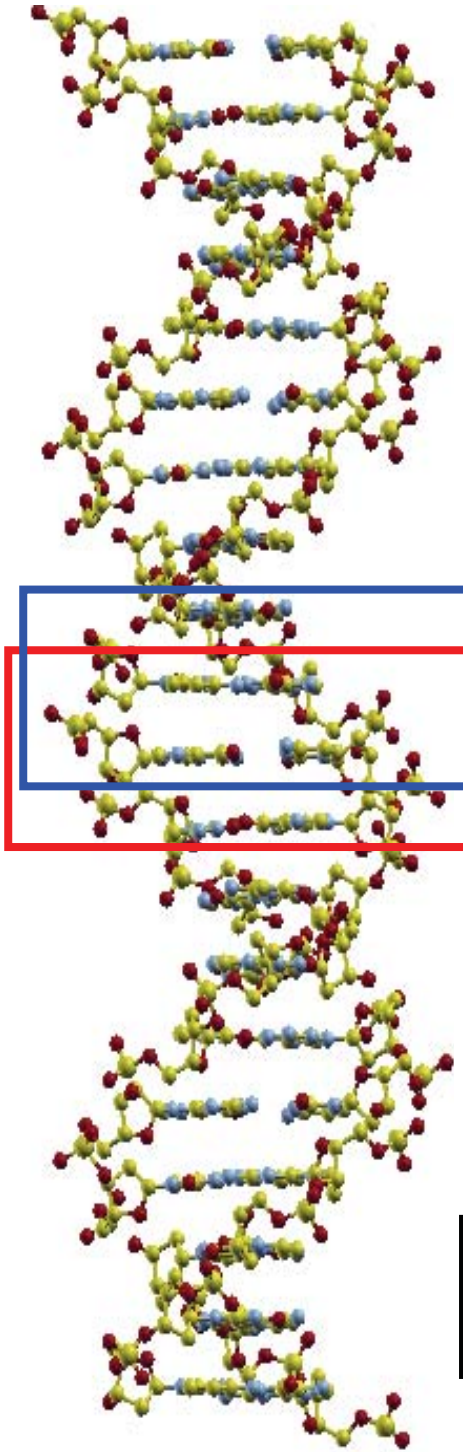

- principal layer

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

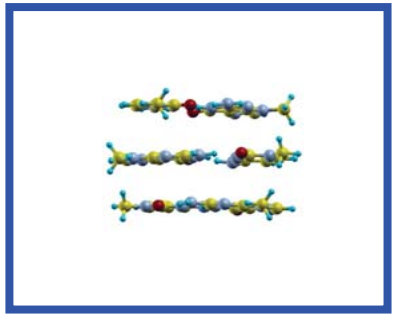
# MLWFs Extraction From a Saturated Cluster



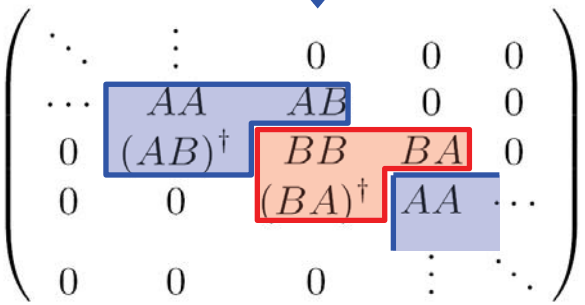


# polyd(*CpGp*) *B*-DNA



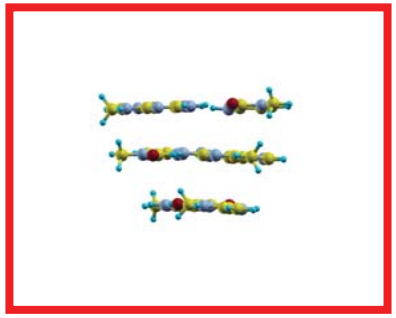
B
A
B

WANNIER FUNCTIONS




*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

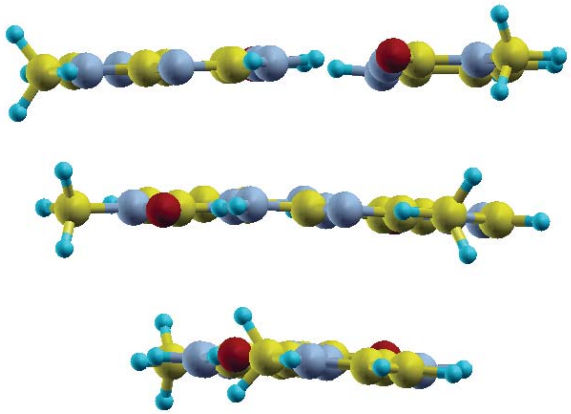
B A B A B A B A B A B A B A B A B A B A B A B A B A B A

# *B*-DNA Configuration

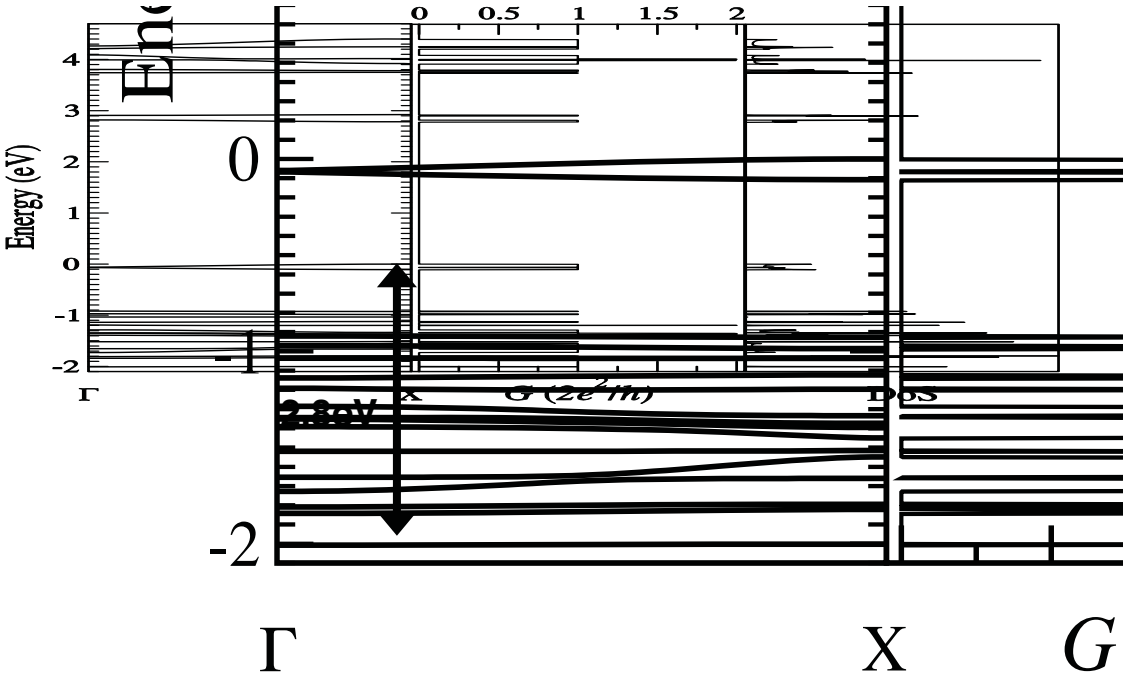
Dry, no backbone, 36° twist

**Isolated fragments**

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



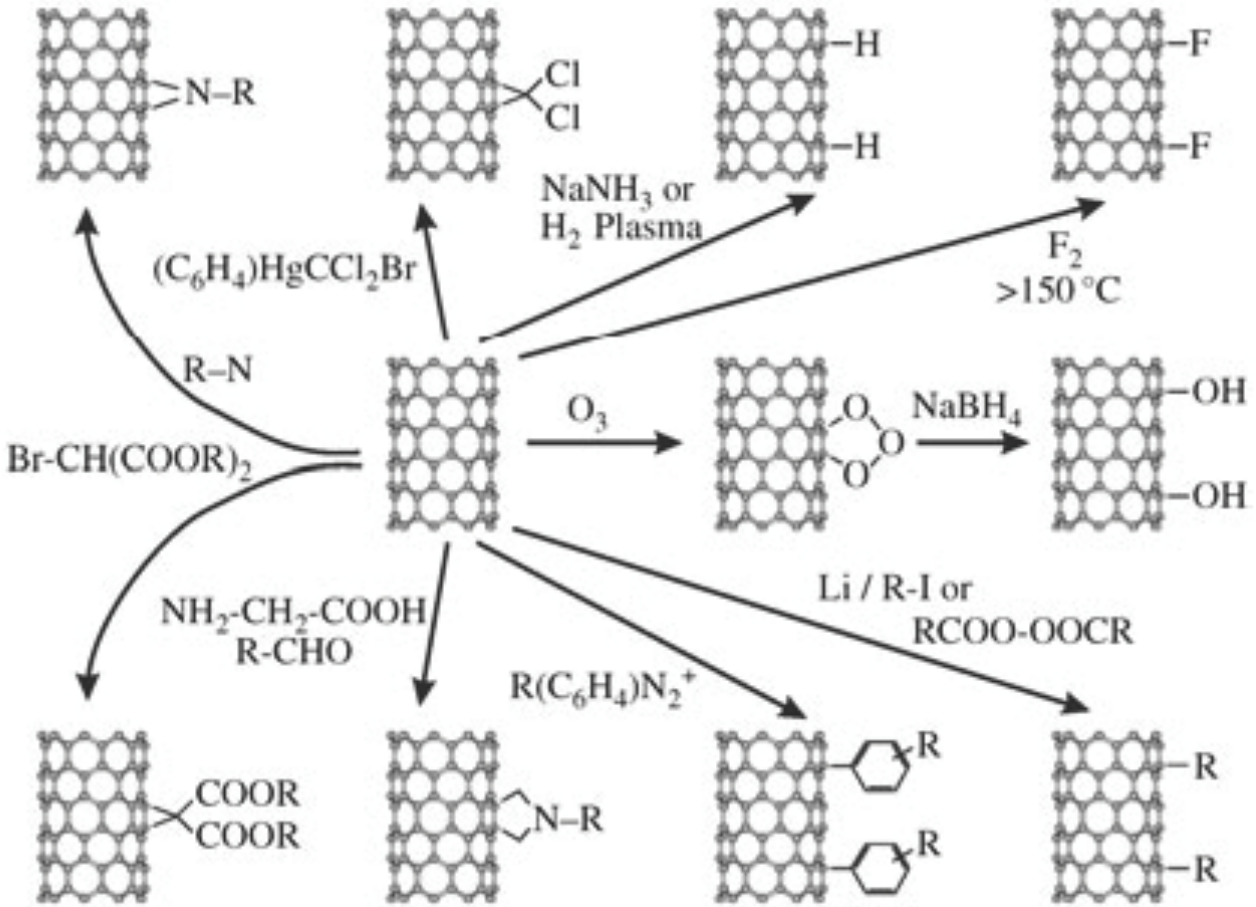
**Equivalent to 350 atom calculation**




**LUMO bandwidth = 37 meV**
**HOMO bandwidth = 60 meV**

# First-Principles Study of Functionalizations

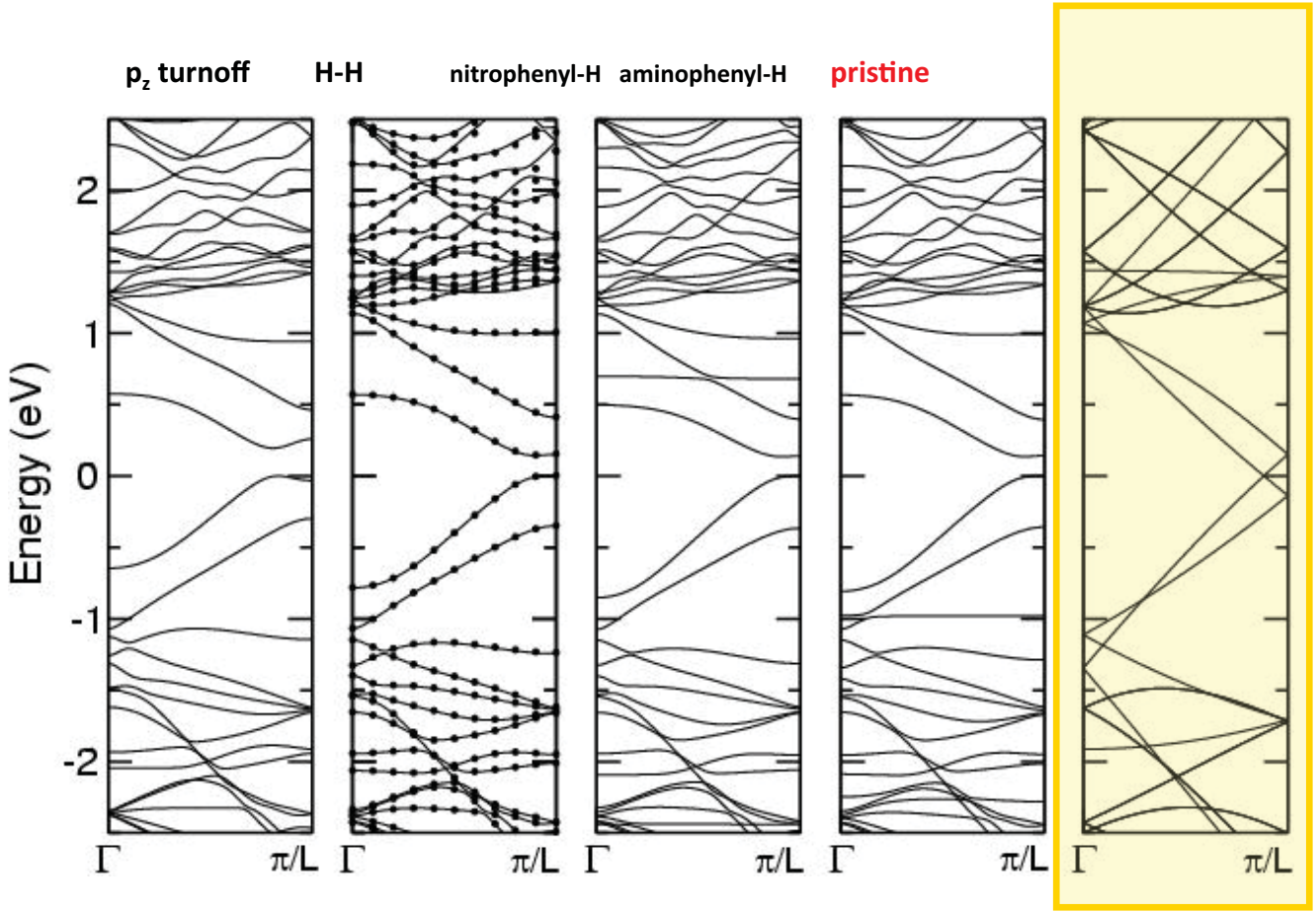
- Currently available covalent functionalizations

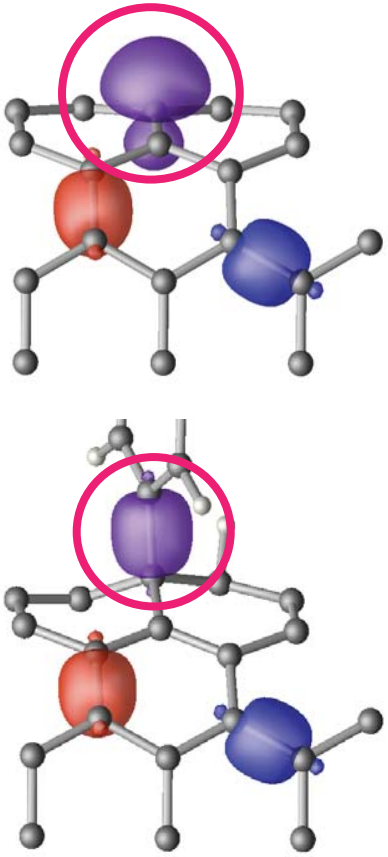



K. Balasubramanian and M. Burghard, Small, **1**, 180 (2005)

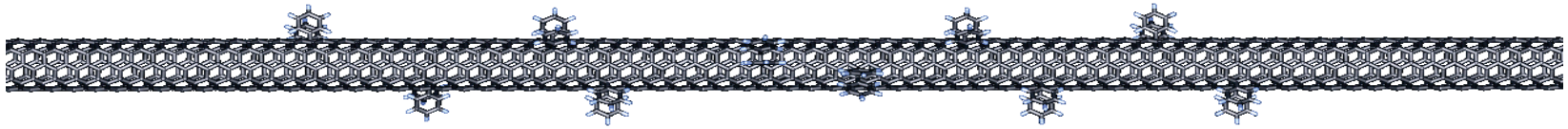
# Aryl / Hydrogen

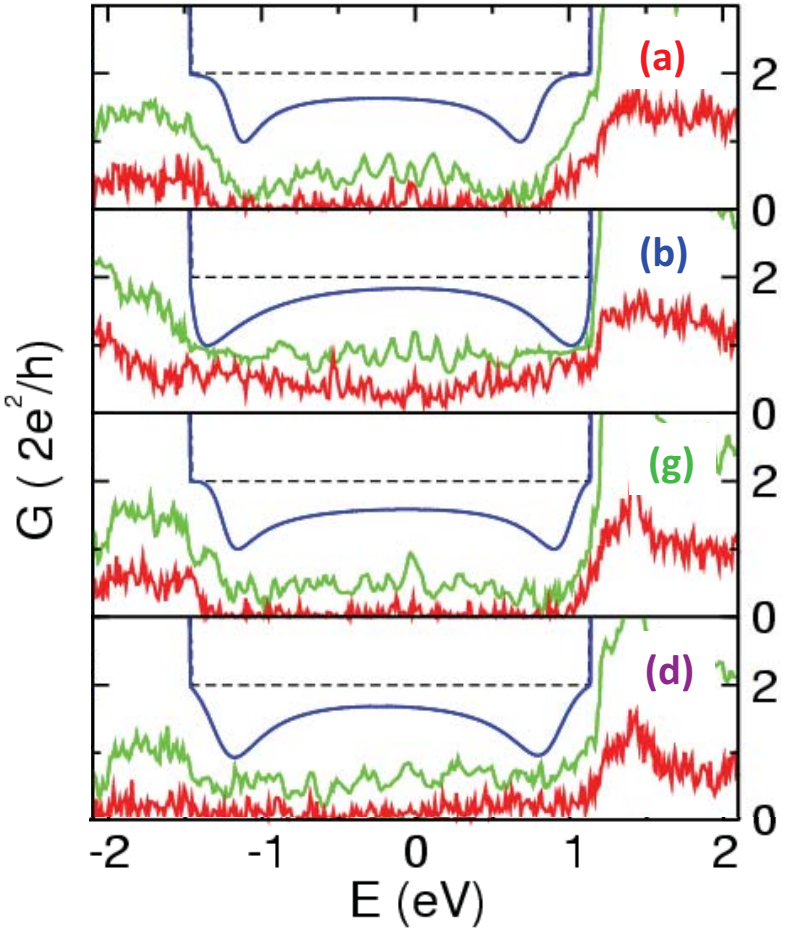
Band structure does not depend on the chemical nature of the functional groups



# Aryl / Hydrogen - Quantum Conductance





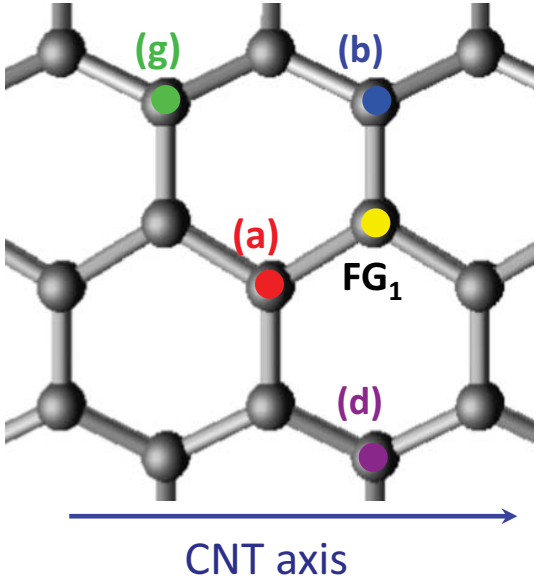

Functionalized region in an infinite (5,5) tube

1 pair of functional groups

10 pairs / 1000 atoms / 37 nm

30 pairs / 3000 atoms / 37 nm

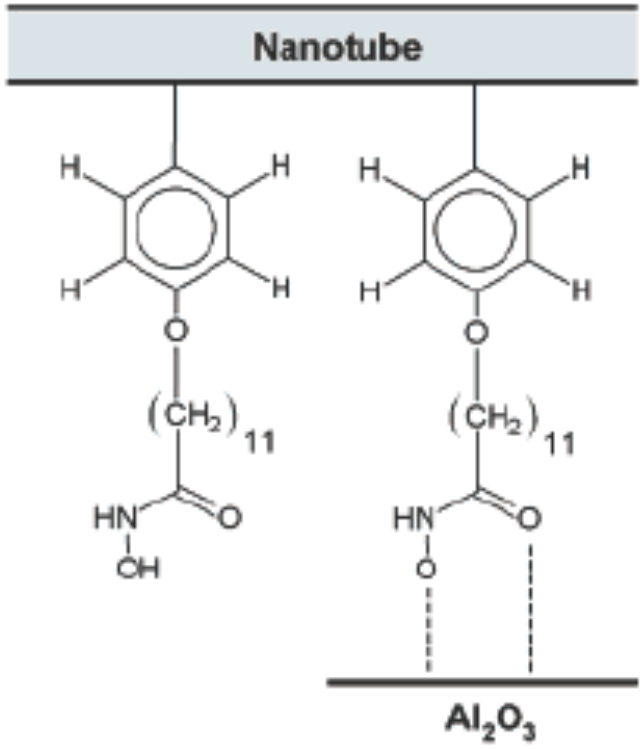
Rapid decay of the quantum conductance

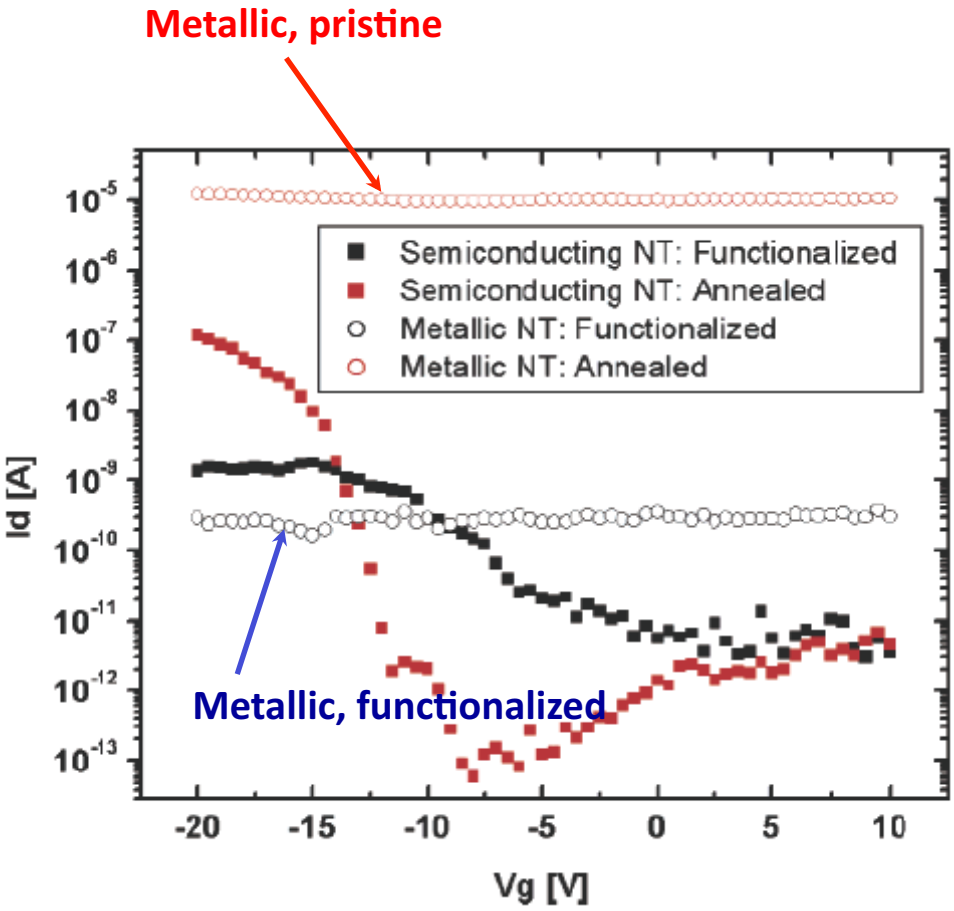



Y.-S. Lee, M. Buongiorno Nardelli, and N. Marzari, Phys. Rev. Lett. 95, 076804 (2005)

# Electrical Transport Measurements

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




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

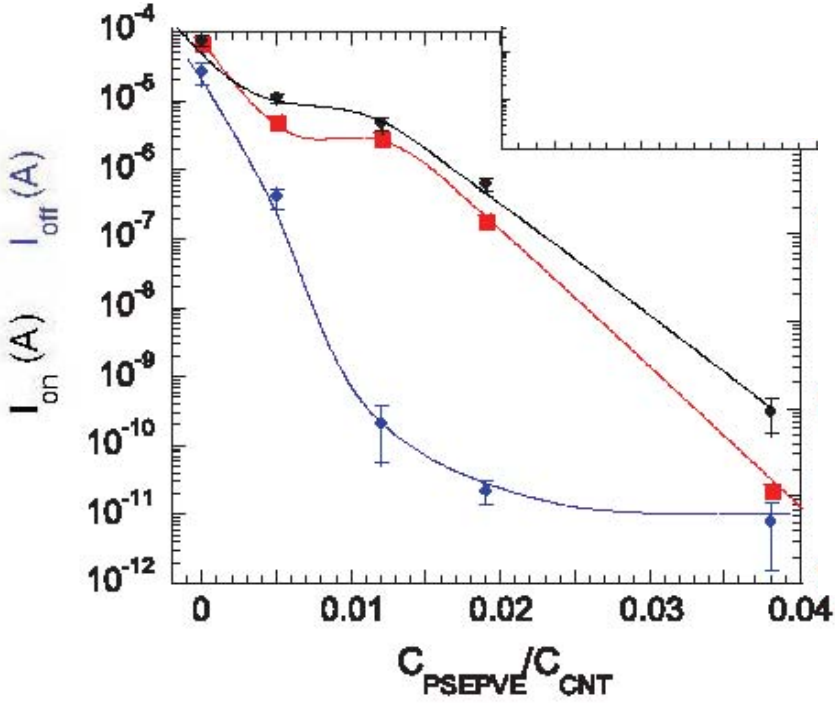
# Electrical Transport Measurements

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 commerci electronic devices and provide a low-cost route to the fabrication of electronic inks.



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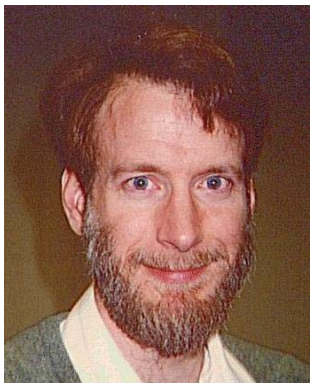
- **Theory:** David Vanderbilt (Department of Physics, Rutgers University), Ivo Souza (Department of Physics, UC Berkeley)




- **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)




# Conclusions

- Sparse Hamiltonians with chemical accuracy: Exact mapping of first-principles calculations onto tight binding Hamiltonians, using maximally-localized Wannier functions.

- Cycloadditions preserve the metallic conductance of carbon nanotubes even at high degrees of coverage

- Selected addends display fluxional tautomerism that
  - Can be directed with optical, chemical, or electrochemical means
  - Directly controls the conductance of the nanotubes