Functionalized Carbon Nanotubes

Organic chemistry meets electronics

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

Covalent Functionalization

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

Generalized Wannier Functions for Composite Bands

- \{ |R_n\rangle \} span the same space as \{ |\Psi_{nk}\rangle \}

- \langle R_n | R' m \rangle = \delta_{n,m} \delta_{R,R'}

- “maximally” localized

Silicon

Valence bands

Wannier function
From Bloch Orbitals to Wannier Functions

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

$$|Rn\rangle = \int_{BZ} \Psi_{nk}(r) e^{-i k \cdot R} \, dk$$

Gauge freedoms

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

$$|Rn\rangle = \int_{BZ} \sum_{m} U^{(k)}_{mn} \Psi_{mk}(r) e^{-i k \cdot R} \, dk$$
Silicon, GaAs, Amorphous Silicon, Benzene
Pristine Carbon Nanotubes

\[ C_h = n \, a_1 + m \, a_2 \]

- **Armchair** \((n, n)\)
- **Zig-Zag** \((n, 0)\)
- **Chiral** \((n, m)\) \(n \neq m\)
2-Dimensional Band Structure of Graphene


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
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

\[ \Omega = \sum_n \left[ \left\langle r^2 \right\rangle_n - \left\langle r \right\rangle_n^2 \right] \]

exploiting the arbitrariness of the unitary transformations between the Bloch orbitals

\[ |R_n \rangle = \int_{BZ} \sum_m U_{mn}^{(k)} \Psi_{mk}(r) e^{-ik \cdot R} \, dk \]
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

\[ H = \begin{pmatrix}
    0 & H_{01}^* & H_{10} & H_{01} \\
    H_{01} & 0 & H_{10} & H_{01} \\
    H_{10} & H_{10} & 0 & H_{01} \\
    H_{01} & H_{01} & H_{01} & 0
\end{pmatrix} \]

No interaction
Max-loc WFs ↔ “Exact” Tight-Binding

Compact mapping of Bloch states into local orbitals

\[ |R_n\rangle \omega_n(r - R) \frac{V}{8\pi^3} \int_{BZ} e^{-ik\cdot R} \psi_{nk}(r) dk \]

\[ \psi_{nk}(r) \frac{1}{\sqrt{N_R}} \sum_R e^{ik\cdot R} \omega_n(r - R) \]

\[ \left< \psi_{ik} | \hat{H} | \psi_{jk} \right> = H_{ij}^{00} + e^{ik\cdot R} H_{ij}^{01} + e^{-ik\cdot R} H_{ij}^{0\bar{1}} \]

⇒ 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 $\Rightarrow$ localized p orbitals

_charge density injected when $\text{-NO}_2$ replaced by $\text{-NH}_2$

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

![Graphs showing conductance as a function of energy for different numbers of pairs and combinations of 1000 and 3000 atoms.](image)

- 10 pairs / 1000 atoms
- 10 pairs / 3000 atoms
- 30 pairs / 3000 atoms
Large Scale Calculations

- Parameterization

- 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