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 \}

- |R_n\rangle = w_n(r - R) (translational images)

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

- “maximally” localized

Silicon  \hspace{2cm} \text{(Isolated group of bands)} \hspace{2cm} \text{Valence bands} \hspace{2cm} \text{Wannier function}
From Bloch Orbitals to Wannier Functions

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

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

Gauge freedoms

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

$$|R_n\rangle = \int_{BZ} \sum_m U_{mn}^{(k)} \Psi_{mk}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k}$$
Silicon, GaAs, Amorphous Silicon, Benzene
Armchair (n,n)
Zig-Zag (n,0)
Chiral (n,m) $n \neq m$

Pristine Carbon Nanotubes

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

(n, n) armchair
(n, 0) zigzag
mod(3) rule: if (n-m) is a multiple of 3 the tube is metallic

Image removed for copyright reasons.
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
Minimization of the spread functional

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

exploiting the arbitrariness of the unitary transformations between the Bloch orbitals

\[ |R_n \rangle = \int_{BZ} \sum_m U_{mn}^{(k)} \Psi_{mk}(r) e^{-i\mathbf{k} \cdot \mathbf{R}} \, d\mathbf{k} \]
Zero interaction between Wannier orbitals whose centers are further apart than decay length.

\[ H = \begin{pmatrix} H_{00} & H_{01} & 0 \\ H_{01}^* & H_{00} & H_{01} \\ 0 & H_{01}^* & H_{00} & H_{01} \end{pmatrix} \]
Max-loc WFs ↔ “Exact” Tight-Binding

Compact mapping of Bloch states into local orbitals

\[ |R_n\rangle = \phi_n(r - R) = \frac{V}{8\pi^3} \int_{BZ} e^{-i\mathbf{k} \cdot \mathbf{R}} \psi_{nk}(r) d\mathbf{k} \]

\[ \psi_{nk}(r) = \frac{1}{\sqrt{N_R}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi_n(r - \mathbf{R}) \]

\[ \langle \psi_{ik} | \hat{H} | \psi_{jk} \rangle = H_{ij}^{00} + e^{i\mathbf{k} \cdot \mathbf{R}} H_{ij}^{01} + e^{-i\mathbf{k} \cdot \mathbf{R}} H_{ij}^{0\bar{1}} \Rightarrow \text{Diagonalize H Matrix} \]
Band Structure of (5,5) and (8,0) SWCNTs
Exponential Decay

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

\[ \left\langle \omega_0 \left| \hat{H} \right| \omega_n \right\rangle \]
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 -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

![Graph showing conductivity vs energy for different configurations and numbers of pairs](image-url)

- (a) 10 pairs / 1000 atoms
- (b) 10 pairs / 3000 atoms
- (c) 30 pairs / 3000 atoms

(d) single group
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