Nano-Materials Simulations

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Nonorthogonal Tight-Binding Molecular Dynamics


Main Features:

- Minimal number of adjustable parameters (4) are employed
- Much improved transferability between bulk-solid and cluster for bond lengths and vibrational frequencies
- Ground state for Si is found to be the diamond structure
Nonorthogonal Tight-Binding Scheme

\[ \psi_n = \sum_a c_a^n \phi_a. \]

\[ \sum_j (H_{ij} - E_n S_{ij}) c_j^n = 0, \]

\[ H_{ij} = \int \phi^*_i H \phi_j \ d^3 r, \]

\[ S_{ij} = \int \phi^*_i \phi_j \ d^3 r. \]

\[ V_{\lambda \lambda' \mu}(r) = V_{\lambda \lambda' \mu}(d_0) e^{-\alpha(r-d_0)}, \]

\[ \phi(r) = \phi_0 e^{-\beta(r-d_0)}, \]

\[ \beta = 4\alpha. \]

\[ H_{ij} = V_{ij} [1 + \frac{1}{K} - S_2^2], \]

\[ S_2 = \frac{(S_{ss\sigma} - 2\sqrt{3}S_{sp\sigma} - 3S_{pp\sigma})}{4} \]

\[ S_{\lambda \lambda' \mu} = \frac{2V_{\lambda \lambda' \mu}}{K(\varepsilon_{\lambda} + \varepsilon_{\lambda'})} \]
Hellmann-Feynman theorem for non-orthogonal basis

\[
\frac{\partial E_n}{\partial x} = \frac{C^{n\dagger}(\frac{\partial H}{\partial x} - E_n \frac{\partial S}{\partial x})C^n}{C^{n\dagger}SC^n}
\]

Vibrational Frequencies

\[
\sum_{n}^{\text{occ}} \frac{\partial^2 E_n}{\partial x_i \partial x_j} = \\
\sum_{n}^{\text{occ}} C^{n\dagger}(\frac{\partial^2 H}{\partial x_i \partial x_j} - E_n \frac{\partial^2 S}{\partial x_i \partial x_j})C^n \\
- \sum_{n}^{\text{occ}} \sum_{m}^{\text{occ}} [C^{n\dagger}(\frac{\partial H}{\partial x_i} - E_n \frac{\partial S}{\partial x_i})C^m C^{m\dagger} \frac{\partial S}{\partial x_j} C^n \\
+ (i \leftrightarrow j)] \\
+ \sum_{n}^{\text{occ \, unocc}} \sum_{m} \frac{1}{(E_n - E_m)} [C^{n\dagger}(\frac{\partial H}{\partial x_i} - E_n \frac{\partial S}{\partial x_i})C^m C^{m\dagger} C^n \\
(\frac{\partial H}{\partial x_j} - E_n \frac{\partial S}{\partial x_j})C^n \\
+ (i \leftrightarrow j)].
\]
Useful Features

- Supercell formulation
- Constant pressure ("movable wall") ensemble
- Multiple k-points
- Vibrational frequency analysis
- Parallel implementation
Parallelization and large scale simulations

\[ Hx = E_n Sx \]

• Parallel dense eigensolvers
• Scalapack
• MPI
Si Nanowires


- Quasi-one dimensional
- Three classes with $D_{nh}$ symmetry
- four-fold coordinated core surrounded by three-fold coordinated outer surface atoms
- Growth in the (111) direction
- Direct band gap material
Si Nanowires

Figure 1: (a) The “superatom” cluster containing 84 atoms ($D_{6h}$ symmetry). Surface reconstruction results in the formation of symmetric tilted dimers. (b) A section of QOD Si (class structure obtained by stacking the superatom units on top of each other and performing GTBMD relaxation. The ends of the segment show (111) features.
Si Nanowires

Figure 2: Superatom cluster units for QOD structures belonging to (a) (class 2) and (b) (class 3). All three-fold coordinated atoms are shaded light.
Si Nanowires

Figure 3: Electronic density of states for the QOD Si structure in Fig. 1. The density of states show a gap of 0.84 eV.
Nanotubes Under Compression


- Graphite ($sp^2$) to Diamond ($sp^3$) transition
- Critical Stress $\approx 153$ G Pa in agreement with experiment

Nanotubes Under Compression

Figure 4: Four stages of spontaneous plastic collapse of the 12% compressed (8,0) carbon nanotube showing; (a) nucleation of the deformations, (b) and (c) inward collapse at the locations of deformations, and (d) graphitic to diamond like structural transition at the location of the collapse.
Figure 5: (a) Strain energy as a function of strain in an axially compressed (8,0) nanotube. Filled circles are for compression computed with the quantum GTBMD method whereas stars are for the values computed with classical MD method. Inset (b) shows the strain energy minimization at 12% strain as a function of number of GTBMD relaxation steps.
Boron Nitride Nanotube


• “Rippled” surface due to relaxation
• Tube closing a function of chirality
• “Zig-Zag” Nanotubes most stable
• Anisotropic Nanomechanics
Figure 6: A rotated BN bond at 9.7 degrees away from the tube axis in an (8,0) BN nanotube in comparison with (b) a non-rotated C-C bond in a similar C nanotube.
Figure 7: Five stages of spontaneous plastic collapse of the 14.25% compressed (8,0) BN nanotube.
Boron Nitride Nanotube

Figure 8: (a) Strain energy as a function of axial compression in (8,0) BN (solid) and C (dotted) nanotubes. Both the curves are computed with the quantum GTBMD method. Inset (b) shows the strain energy minimization for BN (solid) and C (dotted) nanotubes at 14.25% and 12% strain respectively.
\((\text{C}_{60})_n\text{Ni}_m\) Clusters


- \text{C}_{60} acts as an \(\eta^3\) or \(\eta^2\) ligand towards \text{Ni}

- \text{Ni} retains small magnetic moment

- Direction of charge transfer depends on geometry

- Organo-metallic polymer
Figure 9: The three binding sites of Ni on $\text{C}_6\text{O}_2$; (a) bridge site between two hexagons (b) bridge site between a hexagon and a pentagon and (c) atop site on a C atom of a pentagonal ring.
Figure 10: Relaxed geometries for the Ni(C$_{60}$)$_2$ system.

Figure 11: The most stable geometry and the bonding of the Ni$_2$(C$_{60}$)$_2$ cluster.
Ni on Carbon Nanotube


• Curvature dependent bonding sites

• “Atop” and “bridge” sites favored

• Direction of the charge transfer depends on the bonding sites

• Ni assisted nanotube growth
Figure 12: The two stable binding sites for a single Ni on carbon nanotube wall; (a) atop site and (b) bridge site.
Figure 13: The two stable binding sites for a Ni$_2$ dimer on carbon nanotube wall; (a) atop-atop site and (b) bridge-bridge site.
Quantum Conductance of Carbon Nanotubes

1. Embedding Approach to Conductivity

2. Single Wall Carbon Nanotubes
   - Defects
   - Adsorbates
   - Y-Junctions
The Green’s Function Embedding Scheme


\( G(\mathbf{r}_1, \mathbf{r}_2; E) \): Green’s function

Dirichlet’s boundary condition on boundary surface \( S \)

Self Energy (host tube interaction):

\[
\Sigma_S(\mathbf{r}_1, \mathbf{r}_2; E) = -\frac{1}{4} \frac{\partial^2}{\partial n_1 \partial n_2} G(\mathbf{r}_1, \mathbf{r}_2; E)
\]

\( G_C \): Green’s function for tube+leads

\( T(E) \): Transmission function

\[
T(E, V_b) = tr[\Gamma_L G_C \Gamma_R G_C^\dagger] ,
\]

where

\[
\Gamma_j(E; V_b) = i(\Sigma_j - \Sigma_j^\dagger) , j = L, R
\]

\[
I(V_b) = \frac{2e}{h} \int_{-\infty}^{+\infty} T(E, V_b) [f_E(\mu_L) - f_E(\mu_R)] dE
\]
Y-Junctions


-template-based chemical vapor deposition


-pyrolysis method produced multiple Y-junctions along a continuous nanotube
Results


• End-contact geometry favored for SWCN

• Rectification for Y-junctions

• Gate voltage
Figure 14: (a) Schematic plot of the nanotube connected to semi-infinite metal leads at both ends. (b) Metal leads connected to nanotube in a lateral-contact geometry and (c) end-contact geometry with a relaxed substitutional Ni. The carbon atoms of the SWCN in contact with the metal leads are shown in dark circles.
Figure 15: I-V characteristics (at various levels of approximations) for a (5,5) tube corresponding to the end-contact geometry shown in Fig.14a, (middle set of curves), lateral-contact geometry shown in Fig.14b, (lower set of curves), and end-contact geometry with the tube containing one relaxed substitutional Ni-impurity atom.
Figure 16: The calculated I-V curves for the Y-junction shown in inset. The I-V curves show asymmetric behavior and rectification. The voltage configuration for this plot has been set to $V_2 = V_3 = 0.0$ V, making it a two terminal device for enabling direct comparison with experiment.
Figure 17: The current in the primary channel, $I_1$, as a function of the bias voltage $V_1$ for 5 different values of the gate voltage $V_g$ for the symmetric Y-junction. The figure shows asymmetry in the I-V behavior with current saturation for positive values of $V_1$ for all values of $V_g$. 
Figure 18: (a) (5,5)-(10,0)-(5,5) T-junction with six heptagonal defects. (b) (9,0)-(10,0)-(9,0) T-junction with eight heptagons and two pentagons.

Formation Pathways


  1. X-shaped molecular connections by welding achieved by electron beam irradiation of crossing SWCNs.
  2. Selectively remove one of the arms of the X-junction to create Y- and T-junctions.


  1. All $sp^2$ step process.
  2. Conductivity.
(9,0)-(10,0)-(9,0) T-junction Formation

Figure 19:

(5,5)-(10,0)-(5,5) T-junction Formation

Figure 20:

Energetics of T-junction Formation

Figure 21: Relative energies at each step of the formation of (9,0)-(10,0)-(9,0) and (5,5)-(10,0)-(5,5) T-junctions (large circles and large squares, respectively), as calculated using the GTBMD scheme. Intermediate energy points are represented by small circles and squares.
Figure 22: The I-V characteristics of the (9,0)-(10,0)-(9,0) T-junction. The figure shows asymmetry in the I-V behavior with current saturation for positive values of $V_s$ for all values of $V_g$. The main effect of the variation in $V_g$ is the modulation of the current.
Y-junction formation

Figure 23: (6,6)-(6,6)-(6,6) Y-junction formation. Only 8 of the 21 steps are shown.
X-junction formation

Figure 24: \((6,6)-(6,6)-(6,6)-(6,6)\) X-junction formation.