NSF/ITR: LARGE-SCALE QUANTUM-MECHANICAL MOLECULAR DYNAMICS SIMULATIONS

C. S. Jayanthi and S.Y. Wu (Principal Investigators)

Lei Liu (Post-doc)
Ming Yu (Post-doc)
Chris Leahy (Graduate Student)
Alex Tchernatinsky (Graduate Student)
Kevin Driver (Undergraduate Student)

University of Louisville

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Motivation and Objective

• The objective of our research is to develop transferable and reliable semi-empirical LCAO Hamiltonians and the O(N) molecular dynamics corresponding to this Hamiltonian so that properties of complex systems with reduced symmetry may be studied.

• Why develop another LCAO Hamiltonian?

• Will it have the predictive power of a first-principles calculation?
OBJECTIVES

A GENERAL FRAMEWORK FOR SEMI-EMPIRICAL HAMILTONIAN

Multi-Center Interactions

Charge Redistributions

SCED-LCAO

LARGE-SCALE SIMULATIONS O(N)/SCED-LCAO

APPLICATIONS TO CARBON-BASED NANOSTRUCTURES

Environment-Dependent Effects

Self-consistency
**CURRENT STATUS OF LCAO HAMILTONIANS**

<table>
<thead>
<tr>
<th></th>
<th>Environment Effects</th>
<th>Self-consistency</th>
<th>Other Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames</td>
<td>Yes</td>
<td>No</td>
<td>OTB **</td>
</tr>
<tr>
<td>NRL</td>
<td>Yes</td>
<td>No</td>
<td>NOTB **</td>
</tr>
<tr>
<td>Menon</td>
<td>No</td>
<td>No</td>
<td>NOTB**</td>
</tr>
<tr>
<td>Kaxiras</td>
<td>No</td>
<td>No</td>
<td>NOTB**</td>
</tr>
</tbody>
</table>
| Frauenheim     | Yes**               | Yes              | Two-center + $H_{env}$ **  
|                |                     |                  | 2-center terms explicitly calculated using “pseudo-atomic” orbitals |

**Environment-dependent effects disappear for systems with no charge redistributions => Poor bulk phase diagram for high coordinated bulk phases (FCC, etc)**
\[ H_{i\alpha,j\beta} = H_{i\alpha,j\beta}^0 + \frac{1}{2} \cdot [(N_i - Z_i) + (N_j - Z_j)] \cdot U \]
\[ + \frac{1}{2} \cdot \left[ \sum_{k \neq i} N_k \cdot V_N(R_{ik}) - Z_k \cdot V_Z(R_{ik}) \right] \cdot S_{i\alpha,j\beta} \]
\[ + \frac{1}{2} \cdot \left[ \sum_{k \neq j} N_k \cdot V_N(R_{jk}) - Z_k \cdot V_Z(R_{jk}) \right] \cdot S_{i\alpha,j\beta} \]

- Multi-Center Interactions and Environment-Dependence included
- On-Site Electron-Electron Correlations modeled via Hubbard-like Term
- Inter-site Electron-Electron Correlations modeled via a parameterized function \( V_N \)
- Electron-Ion interactions modeled via a parameterized function \( V_Z \)
- Charge distribution \( N_k \) at a given site \((k)\) depends on its environment and is determined Self-Consistently
TOTAL ENERGY WITHIN SCED-LCAO

\[ E_{\text{tot}} = E_{\text{band}} + \frac{1}{2} \cdot \sum_i (Z_i^2 - N_i^2) \cdot U - \frac{1}{2} \cdot \sum_{i,k : k \neq i} N_i N_k \cdot V_N(R_{ik}) \]

\[ + \frac{1}{2} \cdot \sum_{i,k : k \neq i} Z_i Z_k \cdot V_C(R_{ik}) \]

\[ V_C(R) = \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{R} = \frac{E_0}{R} \quad \text{Coulomb Term} \]

I: Band Structure Energy (Sum over eigenenergies of occupied states)

II and III: Double-counting corrections

IV: Repulsive ion-ion interaction energy
BULK PHASE DIAGRAMS FOR SILICON

Phase diagrams of bulk Si

Wu

Menon

Kaxiras

Frauenheim

Wang and Ho

NRL

LCAO

DFT

cdia

sc

bcc

fcc

cdia

sc

bcc

fcc

binding energy per atom

relative atomic volume

0.4 0.6 0.8 1 1.2

0.4 0.6 0.8 1 1.2

0.4 0.6 0.8 1 1.2

0.4 0.6 0.8 1 1.2
BULK PHASE DIAGRAMS FOR CARBON

SCED–LCAO
Frauenheim
Menon

Energy per Atom (Ry)

Relative Atomic Volume

LCAO
DFT

fcc
bcc
sc
cdia

graphite
cdia
cdia
BULK PHASE DIAGRAM OF GERMANIUM
TEST OF SCED-LCAO-MD

Si (001) C4x2 surface reconstruction

\[ E_{\text{tot}}/\text{atom (eV)} \]

- 0 100 200 300 400 500 600

- time step (one time step = 2.5 fs)
A MOLECULAR DYNAMICS STUDY OF THE LOCAL BENDING OF A SWCNT BY AN AFM TIP

The buckle region behaves as a nanoscale potential barrier.
## Magnetic Moments for Carbon Structures

<table>
<thead>
<tr>
<th></th>
<th>Magnetic Moment (emu/g)</th>
<th>B=0.1 Tesla</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.0017</td>
<td></td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>-0.00036</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>-0.03 ( T &lt; 100 K)</td>
<td></td>
</tr>
<tr>
<td>Carbon Nanotube</td>
<td>-0.025</td>
<td></td>
</tr>
<tr>
<td>Carbon Nanotori</td>
<td>$\sim$ 27</td>
<td></td>
</tr>
</tbody>
</table>

Magnetic Responses of Carbon Tori

Ring Current - Metal

(5,5)/1200
A Simple Picture for Colossal Paramagnetism
Magnetic Responses of all types of Carbon Nanotori

\[ L = pT = q\lambda_F \]

Metal Tori
- \((5,5)/1500 \quad L=75T\)
- \((5,5)/1200 \quad L=60T\)
- \((7,4)/1860 \quad L=15T\)
- \((9,0)/1332 \quad L=37T\)
- \((9,0)/1296 \quad L=36T\)

Semiconducting
- \((5,5)/1480 \quad L=74T\)
- \((7,4)/1364 \quad L=11T\)
- \((7,3)/1580; (10,0)/1600\)

Formed from Semiconducting NT
\{ p = 3 q \}
\{ p = q \}
\{ p \neq 3 q \}

\( q \neq \) Metal Tori
\( q = \) Semiconducting
\( q \neq \) Semiconducting
• Nanotori formed from **Metal-I** Carbon Nanotubes exhibit **Giant Paramagnetic** moments at any **Radius**

• Nanotori formed from **Metal-II** Carbon Nanotubes exhibit **Giant Paramagnetic** moments at **Selected Radii** or "Magic Radii", as dictated by the relation \( L = (3q)T \)

• The enhanced magnetic moment has been explained in terms of the interplay between the geometric structure and the ballistic motion of de-localized \( \pi \)-electrons in the metallic nanotube.
Multi-walled nanotube differential resistance measured in either parallel or perpendicular magnetic field.

Bias for maximum resistance (Vmax) shifts with increasing magnetic field.

Splitting reflects Fermi energy shift between two field orientations.
Questions

• How does the band structure evolve as additional shells are added to the MWNT?

• How does the Fermi Energy Change as a function of the applied magnetic field?
ELECTRONIC STRUCTURE
OF MULTI-WALL CARBON NANOTUBES

(1) Single Wall: (7,7) and (12,12)

(2) Double Walls: (7,7)@(12,12)

(3) Three Walls: (7,7)@.(17,17)

(4) Four Walls: (7,7)@..(22,22)

(5) Five Walls: (7,7)@...(27,27)

(6) Six Walls: (7,7)@....(32,32)

(7) Seven Walls: (7,7)@....(37,37)

(8) Eight Walls: (7,7)@....(42,42)

(7,7)@(12,12)@(17,17)@(22,22)
@(27,27)@(32,32)@(37,37)@(42, 42)
Magnetic Field-Dependence of Fermi Energy

Double Walls: (7,7)@(12,12)

Four Walls: (7,7)@..@(22,22)

Three Walls: (7,7)@.@(17,17)

Five Walls: (7,7)@...@(27,27)

Six Walls: (7,7)@...@32,32

Seven Walls: (7,7)@...@37,37
The framework of our SCED-LCAO Hamiltonian is complete and the parameterized semi-empirical Hamiltonian for Si, Ge, and C are available for applications.

Codes for total energy calculations and molecular dynamics, including the O(N) scheme for large-scale simulations are complete.

Bulk phases of Silicon, Carbon, and Germanium have been tested against first-principles calculations and compared with other LCAO Hamiltonians.

SCED-LCAO-MD has been applied to study the surface reconstruction of Si(100) and the stable configurations of ad-dimers of silicon on Si(100).

In tandem with the methodology development of SCED-LCAO, studies on the electronic, magnetic, and the mechanical properties of carbon nanostructures have been initiated. Specifically, the projects studied include:

* The electronic structure of multi-wall carbon nanotubes
* Colossal paramagnetism in metallic carbon nanotori
* A molecular dynamics study of the various stages of bending including the cutting of a nanotube by an AFM tip
Significance of our Findings and their Scientific Impact

• The framework of our SCED-LCAO Hamiltonian has a transparent physical foundation. Our case studies have demonstrated that the inclusion of environment-dependent and charge redistribution effects in a flexible manner allows the Hamiltonian to predict the properties of complex systems with low-symmetries.

• Our finding on the “giant paramagnetic moment of metallic carbon nanotori” may lead to the development of nano-scale ultra-sensitive magnetic sensors.

• Our simulation study on the deformation of SWCNTs has clarified the nature of nanoscale potential barriers created by the buckle.

• Our study on the electronic structure of MWCNTs is expected to provide an understanding of the quantum transport in these systems.
Collaborations with the Experimental Group of Dr. J. Liu (Duke University) on the “magnetic properties of carbon nanotori”

Collaborations with Dr. Alphenaar (EE Department, University of Louisville) on the “Electronic and Transport properties of Multi-wall carbon nanotubes”

Collaborations with Dr. Dai at Stanford University on the “Manipulation of SWCNTs by an AFM tip”