Petaflops Simulation and Design of Nanoscale Materials and Devices

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I. RMG – petascale, open-source electronic structure code
Blue Waters community Portal
Part of Sustained Petascale Performance benchmark
Version 3: Cuda-managed memory, Volta support, multiple GPUs per node.
Quantum transport (NEGF) module

II. Atomically precise bottom-up graphene nanoribbons (GNRs) and devices
Molecular mechanism of bottom-up growth
Electronic properties of GNR junctions
GNR-based devices with negative differential resistance (NDR)
**Real-space Multi-Grid method (RMG)**

- Density functional equations solved directly on the grid
- Multigrid techniques remove instabilities by working on one length scale at a time
- Non-periodic boundary conditions are as easy as periodic
- Compact “Mehrstellen” discretization
  \[ A[\phi_i] + B[(V_{eff} + V_{NL})\phi_i] = \varepsilon_i B[S\phi_i] \]
- Allows for efficient massively parallel implementation

www.rmgdft.org

Largest run used 139,392 CPU cores and 8,712 GPU's, > 6.5 PF

RMG open source [sourceforge.net/projects/rmgdft/](http://sourceforge.net/projects/rmgdft/)

Performance on 3,872 Cray XK7 (K20x GPU) Blue Water nodes: 1.14 PFLOPS

Amyloid β 1-42, 634 atoms

Cray XK7 ORNL

1 node = 16 Opteron cores + 1 Nvidia K20x GPU

> 2,300 downloads
Workstation calculation
- Dual Xeon E5-2630v2 workstation. Total of 12 CPU cores and 32 GBytes RAM. Nvidia GP100 Pascal, 16GBytes HBM memory and \(5.3\) TFLOPS double precision.

Test problem 256 atom copper cell

Execution time dominated by eigensolver and large matrix operations
- CPU only run required \(94.4\) seconds/SCF step.
- CPU/GPU run required \(19.7\) seconds/SCF step.

A single GPU produces a speedup by a factor of \(4.8\)!
RMG Version 3.0 (to be released next week)

- **Design considerations and goals**
  - Restructure build process and improve code maintainability. Focus on next generation hardware features.
  - Open source release of additional components of RMG.

- **Bulk of computational power will come from GPUs**
  - Much easier to write clean high performance code for more recent hardware. Parallelizes to ~10k of multi-core CPU/multi-GPU nodes.
  - Version 3.0 switches from explicit buffer management to Cuda-managed memory.
  - May not run well (or at all) on older hardware. Use 2.x versions on them. Nvidia Pascal and later recommended for Version 3.0.

- **Additional components to be released in a couple of months**
  - Nearly linearly scaling localized orbital code
  - Electron transport module (Non-equilibrium Green's function formalism).

Release and tutorial at joint Electronic Structure Workshop (ES18) and Penn Conference in Theoretical Chemistry (PCTC18), June 11-14, 2018.
Bottom-up Synthesis of Graphene Nanoribbons

- **Molecular precursor:**
  - 10,10’-dibromo-9,9’-bianthryl (DBBA)
  - Adsorbs on metal surfaces Au(111)

- **Polymerization at 200°C**
  - Debromination: molecular precursors lose Br
  - Self-assembly: poly-anthrylene is formed.

- **Cyclodehydrogenation at 400°C**
  - Cyclization: poly-anthrylene forms additional C-C bonds.
  - Dehydrogenation: removal of hydrogen atoms to form graphene nanoribbons.

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3D atomic structure of polymer on Au(111)

3D atomic structure of GNR on Au(111)
Polymer to GNR transition

- Studying separately:
  - Cyclization
  - Dehydrogenation

- Methods:
  - Density functional theory
  - Van der Walls correction for interaction between metal substrate and molecule:
    - Vdw-df non-local functional with PBE exchange correlation
  - Nudged Elastic Band method:
    - Minimum energy pathway
    - Energy barriers

Proposed intermediate state in periodic model
Cyclodehydrogenation
Cyclization Dehydrogenation
Substrate effect on conversion to GNR

**Cyclization:**
- DBDA adsorption on substrate lowers the polymer formation energy and cyclization barrier
- Energy barrier in vacuum: 2.5 eV
- Energy barrier on Au: 1.8 eV

**Dehydrogenation:**
- Hydrogen atoms adsorb on Au surface
- The product is GNR and adsorbed H atoms
- Energy barrier for direct desorption in vacuum: 2.2 eV
- Energy barrier for adsorption on Au: 1.3 eV

**Substrate effect:**
- Adsorption of polymer on metal catalyzes the cyclization reaction
- H desorption onto metal substrate promotes dehydrogenation reaction by significantly decreasing the energy barrier
Dehydrogenation step

**Dimer model:**
- Finite oligomer structure: represents orbital symmetry in the reaction
- Vacuum environment: Allows for a charged system

**Reaction pathway:**
- H atoms remain on different sides after C-C bond formation
- One H atom migrates to an edge site by 1-3 sigmatropic rearrangement.
- Two H atoms desorb as H₂

**Charge effect:**
- Unstable C-C bond formation in the neutral case.
- Arenium ion stabilizes the transition state in the 2+ charge.
- Avoids the high energy barrier of H-atom rotation.

Transition state energy results:

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<th>-2e</th>
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<td>4.2</td>
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<tr>
<td>Step 3</td>
<td>1.3</td>
<td>3.2</td>
<td>4.2</td>
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Nanoscale Device with Negative Differential Resistance

Double barrier resonant tunneling device

A: threshold
B: resonant tunneling
C: current valley

Barriers:
- Large gap → narrow ribbon

Quantum dot structure
- Small gap → wide ribbon
- → hybrid ribbon
Electronic structure of the GNR-Hybrid junction

- Hybrid has a smaller band gap than GNP
- Type-I band alignment

Band alignment from theory agrees with experiment, except for band gap underestimation due to DFT.

LDOS mapping from experiment and calculations.
GNR-based devices

- 7-aGNR, has a large gap, can serve as a barrier.
- Hybrid polymer/ribbon has a small gap; can act as a quantum dot.
- Sizes of the barrier and of the quantum dot affect the negative differential resistance (NDR).
- Quantum transport calculations for a variety of structures to identify promising device structures.
GNR-Hybrid-GNR Device

Barriers: two segments of 7-aGNR, length of 8.5 Å
Quantum dot: hybrid structure, length of 8.5Å

- Interface levels $E_1$ and $E_2$ are broadened and decay slowly into both GNR and graphene region.
- The interface states overlap strongly with HOMO and LUMO of the hybrid structure.
- The device is too short, 7-aGNR fails to act as a barrier.
- Direct tunneling between leads occurs.
- No clear NDR feature for this short device.
GNR-Hybrid-GNR Device

Barriers: two segments of 7-aGNR, length of 26 Å
Quantum dot: hybrid structure, length of 30 Å

- 7-aGNR is a true potential barrier for both electron and hole transport.
- NDR appears at 0.65 eV with peak/valley of 1.8.
- The current at NDR point is too small (<0.01nA) for a real application.
Designed new multi-segment structure

- Decrease segment length for larger current
- Add two more hybrid segments for easier band alignment
- 5 parts: Hybrid-GNR-Hybrid-GNR-Hybrid
  - GNRs still serve as barriers
- Increase peak/valley ratio (PVR) of current
Levels at different segments and interfaces align at 0.38 V bias leading to maximum current and NDR.

At further increase of bias, the levels become misaligned and current decreases.

Peak/valley ratio of practical use ~3.1 at ~ 1 nA current.

Differential conductance 5.0 nA/V
Summary

- **RMG** -- a petaflops-capable open source electronic structure code
  - Effective use of multiple multi-core CPUs and multiple GPUs per node
  - Pseudopotential libraries: ultrasoft & norm-conserving
  - Graphical user interface (GUI)
  - Released under GPL: [www.rmgdft.org](http://www.rmgdft.org)
  - Blue Waters community Portal: [https://bluewaters.ncsa.illinois.edu/rmg](https://bluewaters.ncsa.illinois.edu/rmg)
  - Part of NSF’s *Sustained Petascale Performance* benchmarks
  - Cuda-managed memory, ports easily to the latest architectures
  - Upcoming release of quantum transport (NEGF) module, can handle ~20k atoms
- **Understanding of the molecular growth mechanism of bottom-up graphene nanoribbon synthesis.**
  - Ability to locally control polymer-GNR conversion with an STM tip.
- **STM tip-controllable fabrication of GNR/GNR-hybrid junctions can be used to make NDR devices**
  - Several experimentally realizable structures with NDR have been designed.