Quantum Molecular Dynamics Simulations

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QXMD tutorial:
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Additional Resources

Detailed lecture notes are available at a USC course home page

EXTREME-SCALE QUANTUM SIMULATIONS
This course surveys & projects algorithmic & computing technologies that will make quantum-dynamics simulations metascaleable, i.e., "design once, continue to scale on future computer architectures".

http://cacs.usc.edu/education/cs699-lecture.html

See also N. Romero et al., *IEEE Computer* 48(11), 33 ('15)
http://cacs.usc.edu/education/cs653/Romero-QMD-IEEEComputer15.pdf
Molecular Dynamics Hierarchy

Molecular Dynamics (MD)

Reactive MD (RMD)

Nonadiabatic quantum MD (NAQMD)

First principles-based reactive force-fields
- Reactive bond order \( \{BO_{ij}\} \)
  \( \rightarrow \) Bond breakage & formation
- Charge equilibration (QEq) \( \{q_{ii}\} \)
  \( \rightarrow \) Charge transfer
Quantum Molecular Dynamics (QMD)

\[ M_I \frac{d^2}{dt^2} \mathbf{R}_I = -\frac{\partial}{\partial \mathbf{R}_I} E[\{\mathbf{R}_I\}, \psi(\mathbf{r}_1, ..., \mathbf{r}_N)] \quad (I = 1, ..., N_{\text{atom}}) \]

First molecular dynamics using an empirical interatomic interaction

\[ \psi(\mathbf{r}_1, ..., \mathbf{r}_N) \leftarrow \arg\min_{\psi} E[\{\mathbf{R}_I\}, \psi(\mathbf{r}_1, ..., \mathbf{r}_N)] \]

Density functional theory (DFT)
W. Kohn, \textit{Nobel chemistry prize}, '98

\[ O(C^N) \quad \rightarrow \quad O(N^3) \]

1 \(N\)-electron problem intractable
\(N\) 1-electron problems tractable

\[ \psi(\mathbf{r}_1, ..., \mathbf{r}_N) \quad \{\psi_i(\mathbf{r}) | i = 1, ..., N\} \]

\(O(N)\) DFT algorithms


- **A recent review** [Bowler & Miyazaki, \textit{Rep. Prog. Phys.} \textbf{75}, 036503 ('12)]
Adiabatic Quantum Molecular Dynamics

- Consider a system of $N$ electrons & $N_{\text{atom}}$ nuclei, with the Hamiltonian

$$\tilde{H} = \sum_{l=1}^{N_{\text{atom}}} \frac{P_l^2}{2M_l} + H(\{r_i\}, \{R_l\})$$

- In adiabatic quantum molecular dynamics based on Born-Oppenheimer approximation, the electronic wave function remains in its ground state ($|\Psi_0\rangle$) corresponding to the instantaneous nuclei positions ($\{R_l\}$), with the latter following classical mechanics

$$M_l \frac{d^2}{dt^2} R_l = - \frac{\partial}{\partial R_l} \langle \Psi_0 | H(\{r_i\}, \{R_l\}) | \Psi_0 \rangle$$
Complexity Reduction: Density Functional Theory

- P. Hohenberg & W. Kohn, “Inhomogeneous electron gas”
  *Phys. Rev.* **136**, B864 ('64)

  The electronic ground state is a functional of the electron density $\rho(r)$

- W. Kohn & L. Sham, “Self-consistent equations including exchange & correlation effects”
  *Phys. Rev.* **140**, A1133 ('65)

  Derived a formally exact self-consistent single-electron equations for a many-electron system
Energy Functional

Exchange-correlation (xc) functional via Kohn-Sham decomposition

\[ E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})] \]

- Kinetic energy of non-interacting electrons
- Hartree energy (mean-field approximation to the electron-electron interaction energy)
- Exchange-correlation energy

Electron density \( \rho(\mathbf{r}) \)

External potential

Nucleus charge


Kohn-Sham Equation

• Many-electron problem is equivalent to solving a set of one-electron Schrödinger equations called Kohn-Sham (KS) equations

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \nu_{KS}(\mathbf{r}) \right] \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})
\]

KS wave function  
KS energy

• KS potential

\[
\nu_{KS} = \nu(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \nu_{xc}(\mathbf{r})
\]

\[
\rho(\mathbf{r}) = \sum_n \Theta(\mu - \epsilon_n) |\psi_n(\mathbf{r})|^2
\]

exchange-correlation (xc) potential
step function  
chemical potential

\[
N = \sum_n \Theta(\mu - \epsilon_n)
\]

Abstraction: Exchange-Correlation Functional

- Universal functional (of density) that describes many-body effects beyond the mean-field approximation
- Some commonly used exchange-correlation functionals
  - GGA (generalized gradient approximation)
    PBE: Perdew, Burke & Ernzerhof, Phys. Rev. Lett. 77, 3865 ('96)
  - MetaGGA
    SCAN: Sun, Ruzsinszky & Perdew, Phys. Rev. Lett. 115, 036402 ('15)
  - Hybrid exact-exchange (Hartree-Fock) functionals
- Others supported by QXMD code: Select an appropriate functional for the material system & purpose
  - LDA+U method for transition metals
    \[ \frac{\delta E_{\text{LDA+U}}}{\delta n_i} = \epsilon_{\text{LDA}} + U\left(\frac{1}{2} - n_i\right) \]
    Anisimov et al., Phys. Rev. B 44, 943 ('91)
  - DFT-D: van der Waals (vDW) functional for molecular crystals & layered materials
    \[ E_{\text{disp}} = -s_6 \sum_{i<j} \frac{c_{ij}}{R_{ij}} f_{\text{damp}}(R_{ij}) \]
  - vDW: Nonlocal correlation functional
    \[ E_{\text{C}}^{\text{nl}} = \frac{1}{2} \int dr \int dr' \rho(r) \phi(r, r') \rho(r') \]
    Dion et al., Phys. Rev. Lett. 92, 246401 ('04)
Abstraction: Pseudopotential

- Consider only (chemically active) valence electrons
  *e.g.* silicon — $1s^22s^22p^63s^23p^2$
- Pseudopotentials & smooth, nodeless pseudo-wave functions are constructed to agree with the all-electron (AE) counterparts beyond a cutoff radius $r_c$

- Commonly used pseudopotentials
Self-Consistent Field Iteration

\[
\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + \hat{V}_{\text{ion}} + \hat{V}_{\text{H,xc}}[\rho(\mathbf{r})] \right) \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})
\]

Given \( \rho(\mathbf{r}) \), iteratively obtain \( \{\psi_n, \epsilon_n\} \), e.g., by preconditioned conjugate gradient

\[
\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \Theta(\mu - \epsilon_n)
\]

Given \( \{\psi_n, \epsilon_n\} \), determine \( \mu \) and compute \( \rho(\mathbf{r}) \)

Chemical potential

\[
N = \int d\mathbf{r} \rho(\mathbf{r})
\]

See PHYS 516 lecture on iterative energy minimization
http://cacs.usc.edu/education/phys516/QD2CG.pdf
Nonadiabatic Quantum Molecular Dynamics

- **Excited states:** Linear-response time-dependent density functional theory [Casida, ’95]
- **Interstate transitions:** Surface hopping [Tully, ’90; Jaeger, Fisher & Prezhdo, ’12]

Surface-Hopping NAQMD

- Incorporate electron transitions with the time-dependent density-functional theory (TDDFT) & surface-hopping method

Tully, J. Chem. Phys. 93, 1061 ('90), *ibid.* 129, 044104 ('08); Duncan et al., J. Am. Chem. Soc. 129, 8528 ('07)

- Electronic transitions from the current state to another occur stochastically based on the switching probability obtained by solving TDDFT equations

\[
\psi(r,t) = \sum J C_J^{(I)}(t)\Phi_J(r; R(t)) \quad C_J^{(I)}(0) = \delta_{IJ}
\]

\[
\frac{d}{dt} C_J^{(I)}(t) = -\sum_k C_k^{(I)}(t) \left( i\omega_K\delta_{JK} + \langle \Phi_J | \frac{\partial}{\partial t} | \Phi_K \rangle \right)
\]

$K$-th excitation frequency

$J$-th adiabatic excited state

Electronic transition assisted by nuclei motion
QXMD Code

• Quantum molecular dynamics (QMD) code developed by Prof. Fuyuki Shimojo at Kumamoto University in Japan

• Various eXtensions co-developed with USC-CACS: Nonadiabatic QMD, linear-scaling divide-&-conquer, parallelization, etc.

• Unique features:
  > Interatomic forces with electronic excitation to study photo-excited lattice dynamics
    Shimojo et al., Comput. Phys. Commun. 184, 1 (’13)
  > Range-separated hybrid exact-exchange functional for exciton binding
    Tawada et al., J. Chem. Phys. 120, 8425 (’04)
  > Lean divide-&-conquer density functional theory (LDF-DFT) with small \( O(N) \) prefactor
    Shimojo et al., J. Chem. Phys. 140, 18A529 (’14)
  > Omni-directional multiscale shock technique (OD-MSST)
    Shimamura et al., Appl. Phys. Lett. 107, 231903 (’15); 108, 071901 (’16)

• Other features:
  > Various functionals: spin-polarized, GGA+U, DFT+D, nonlocal correlation
  > Nudged elastic band (NEB) method for energy-barrier calculation
  > Berry-phase computation of polarization

Software download site:
https://magics.usc.edu/qxmd
Current & Future Computing Platforms

• Won two DOE supercomputing awards to develop & deploy metascalable (“design once, scale on future platforms”) simulation algorithms (2017-2020)

• NAQMD & RMD simulations on full 800K cores

Principle Investigator: Aiichiro Nakano, University of Southern California
Co-Investigator: Priya Vashishta, University of Southern California

Early Science Projects for Aurora
Supercomputer Announced
Metascalable layered materials genome
Investigator: Aiichiro Nakano, University of Southern California

786,432-core IBM Blue Gene/Q

Nation’s first exaflop/s computer, Intel A21 (2021)
exaflop/s = $10^{18}$ mathematical operations per second

• One of the 10 initial users of the next-generation DOE supercomputer
CACS@A21 in the Global Exascale Race

R. F. Service, Science 359, 617 (’18)

Design for U.S. exascale computer takes shape

Competition with China accelerates plans for next great leap in supercomputing power

By Robert F. Service

In 1957, the launch of the Sputnik satellite vaulted the Soviet Union to the lead in the space race and galvanized the United States. U.S. supercomputer researchers are today facing their own

Leumont, Illinois. That’s 2 years earlier than planned. “It’s a pretty exciting time,” says Aichiro Nakano, a physicist at the University of Southern California in Los Angeles who uses supercomputers to model materials made by layering stacks of atomic sheets like graphene.

pace reflects a change of strategy by DOE officials last fall. Initially, the agency set up a “two lanes” approach to overcoming the challenges of an exascale machine, in particular a potentially ravenous appetite for electricity that could require the output of a small nuclear plant.
Divide-Conquer-Recombine (DCR) Engines

- **Lean divide-&-conquer density functional theory (LDC-DFT) algorithm** minimizes the prefactor of $O(N)$ computational cost
  

- **Extended-Lagrangian reactive molecular dynamics (XRMD) algorithm** eliminates the speed-limiting charge iteration
  
Scalable Simulation Algorithm Suite

- 4.9 trillion-atom space-time multiresolution MD (MRMD) of SiO$_2$
- 67.6 billion-atom fast reactive force-field (F-ReaxFF) RMD of RDX
- 39.8 trillion grid points (50.3 million-atom) DC-DFT QMD of SiC
  parallel efficiency 0.984 on 786,432 Blue Gene/Q cores

QMD (quantum molecular dynamics): DC-DFT
RMD (reactive molecular dynamics): F-ReaxFF
MD (molecular dynamics): MRMD
16,661-atom QMD
Shimamura et al., *Nano Lett.*
14, 4090 ('14)

$10^9$-atom RMD
Shekhar et al., *Phys. Rev. Lett.*
111, 184503 ('13)
INCITE|AURORA–MAGICS–LCLS Synergy

Linac Coherent Light Source

World’s first free-electron X-ray laser

DOE INCITE & Aurora ESP Awards

Ultrafast electron diffraction (UED) at SLAC
Ultrafast Coupled Electron-Lattice Dynamics

- Ultrafast electron diffraction experiment shows nearly perfect energy conversion from electronic excitation to lattice motions within ps

\[ \exp(-\langle (\mathbf{q} \cdot \mathbf{u}(t))^2 \rangle) \]

- Dynamics of Debye-Waller factor reveals rapid disordering for both \{300\} & \{110\} peaks

- Transition from mono- to bi-exponential decay at higher electron-hole density

Mo\textsubscript{Se\textsubscript{2}} monolayer

M.F. Lin et al., Nature Commun. 8, 1745 ('17)
**Strong Electron-Lattice Coupling**

- NAQMD simulations reproduce (1) rapid photo-induced lattice dynamics & (2) mono- to bi-exponential transition at higher electron-hole density
  - Rapid lattice dynamics is explained by the softening of M-point \( \frac{1}{2} 0 0 \) phonon
  - Bi-exponential transition is explained by the softening of additional phonon modes at higher electron-hole densities

M.F. Lin et al., *Nature Commun.* 8, 1745 ('17)
Electronic Origin of Phonon Softening

- Electronic Fermi surfaces at increased electron-hole densities $n(e-h)$
- While the Fermi surface is localized at K-points at minimal excitation (red), it also occupies $\Sigma$-pockets at larger $n(e-h)$ (black & blue), enabling electron scattering by emitting $\overrightarrow{q}^1_n$ (M), $\overrightarrow{q}^2_n$ (Sigma) & $\overrightarrow{q}^3_n$ (K) phonons

$L. Bassman et al., Nano Lett. 18, 4653 (’18)$
• In the ultrafast ‘electron camera,’ laser light hitting a material is almost completely converted into nuclear vibrations — key to switching material properties on & off at will for future electronics applications

• High-end quantum simulations reproduce the ultrafast energy conversion at exactly the same space & time scales, & explain it as a consequence of photo-induced phonon softening

Showcasing research from Collaboratory for Advanced Computing and Simulations (CACS), University of Southern California, Los Angeles, USA.

Semiconductor–metal structural phase transformation in MoTe₂ monolayers by electronic excitation

Optical control of transformations between semiconducting and metallic phases of two-dimensional materials can open the door for phase patterning of heterostructures for 2D electronics and catalysis applications. This work shows how optically-induced changes to the electronic structure and Fermi surface of monolayer semiconductors couple to lattice distortions, resulting in a more facile phase transformation pathway. This work highlights photoexcitation as a viable technique for functionalizing these material systems.

A. Krishnamoorthy et al., Nanoscale 10, 2742 ('18)
Conclusion

1. Large spatiotemporal-scale quantum molecular dynamics simulations enabled by divide-conquer-recombine
2. Broad materials & energy applications

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