

# Quantum Molecular Dynamics Simulations

---

Aiichiro Nakano

*Collaboratory for Advanced Computing & Simulations  
Departments of Computer Science, Physics & Astronomy,  
and Quantitative & Computational Biology  
University of Southern California*

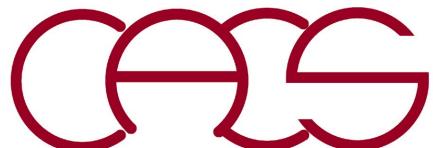
Email: [anakano@usc.edu](mailto:anakano@usc.edu)

QXMD software tutorial:

Anikeya Aditya, Thomas Linker, Liqiu Yang



Supported by National Science Foundation,  
Award OAC-2118061



*CyberMAGICS Workshop*  
July 1, 2022

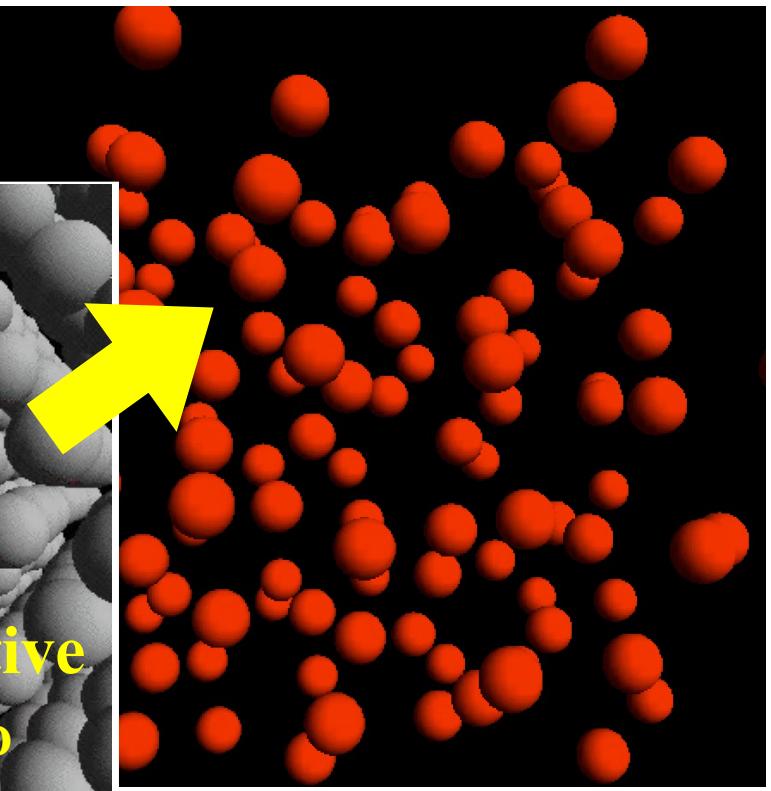
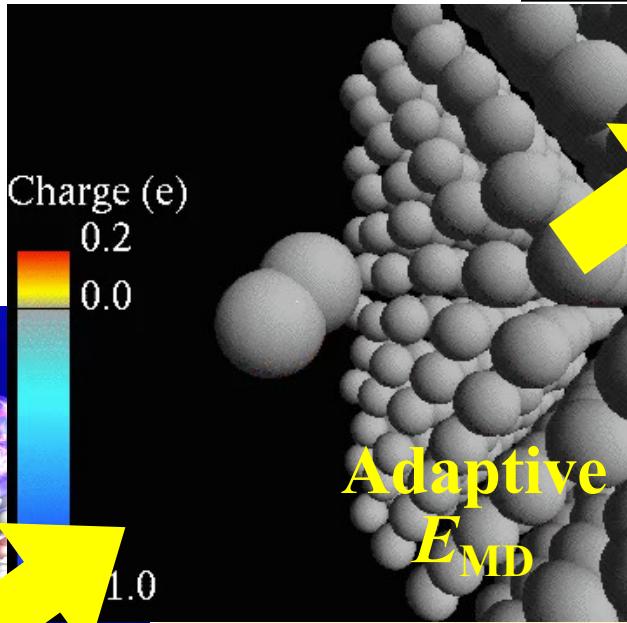
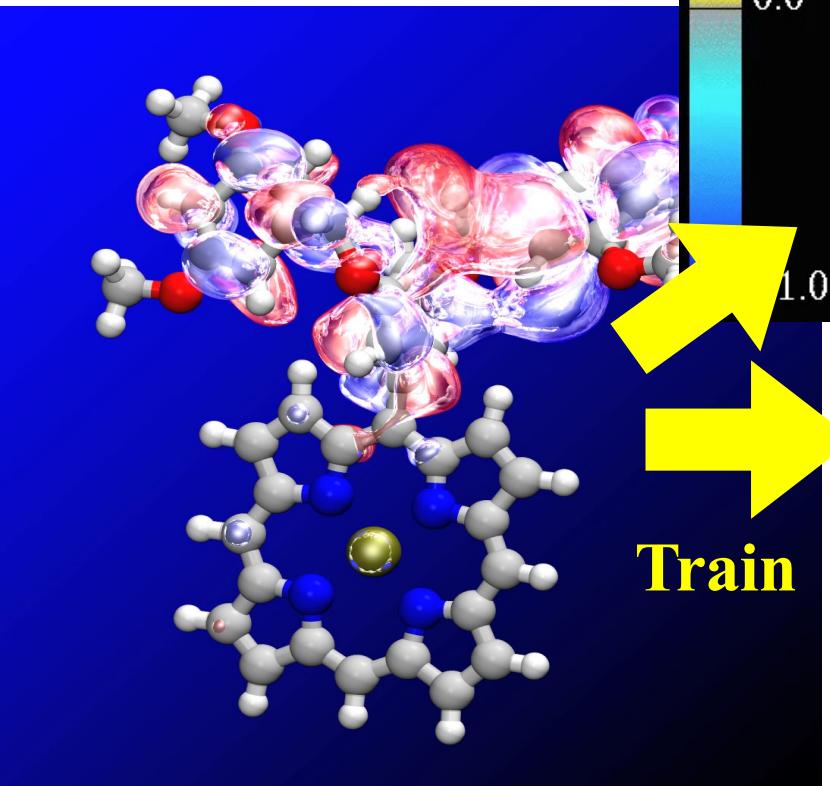


# Molecular Dynamics

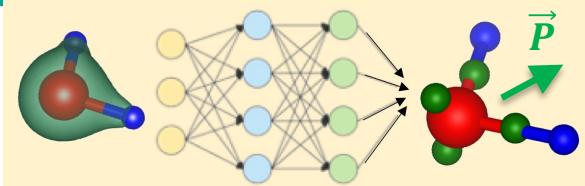
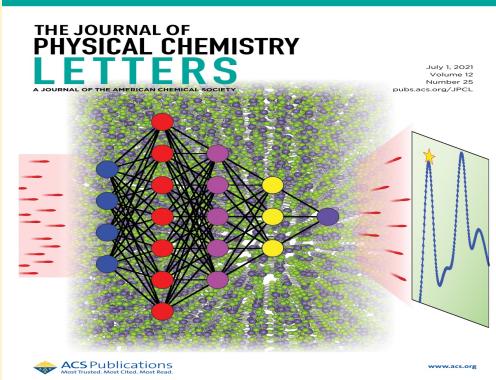
## Molecular Dynamics (*MD*)

### Reactive MD (*RMD*)

### Nonadiabatic quantum MD (*NAQMD*)



First principles-based neural-network quantum molecular dynamics (*NNQMD*)



Physical Review Letters  
Editor's choice  
(May 25, 2021)

# Quantum Molecular Dynamics (QMD)

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

**First molecular dynamics using an empirical interatomic interaction**

A. Rahman, *Phys. Rev.* **136**, A405 ('64)



$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \leftarrow \operatorname{argmin} E[\{\mathbf{R}_I\}, \psi(\mathbf{r}_1, \dots, \mathbf{r}_N)]$$

**Density functional theory (DFT)**

Hohenberg & Kohn, *Phys. Rev.* **136**, B864 ('64)

W. Kohn, *Nobel chemistry prize*, '98

$$\begin{array}{ccc} O(C^N) & \rightarrow & O(N^3) \\ \text{1 } N\text{-electron problem} & & N \text{ 1-electron problems} \\ \text{intractable} & & \text{tractable} \end{array}$$

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad \{\psi_i(\mathbf{r}) | i = 1, \dots, N\}$$

## **$O(N)$ DFT algorithms**

- **Divide-&-conquer DFT** [W. Yang, *Phys. Rev. Lett.* **66**, 1438 ('91); F. Shimojo *et al.*, *Comput. Phys. Commun.* **167**, 151 ('05); *Phys Rev. B* **77**, 085103 ('08); *Appl. Phys. Lett.* **95**, 043114 ('09); *J. Chem. Phys.* **140**, 18A529 ('14)]
- **Quantum nearsightedness principle** [W. Kohn, *Phys. Rev. Lett.* **76**, 3168 ('96); E. Prodan & W. Kohn, *P. Nat. Acad. Sci.* **102**, 11635 ('05)]
- **A recent review** [Bowler & Miyazaki, *Rep. Prog. Phys.* **75**, 036503 ('12)]

# Adiabatic Quantum Molecular Dynamics

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

$$\begin{aligned}\tilde{H} &= \sum_{I=1}^{N_{\text{atom}}} \frac{\mathbf{P}_I^2}{2M_I} + H(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \\ &= \sum_{I=1}^{N_{\text{atom}}} \left[ \frac{\mathbf{P}_I^2}{2M_I} + V_{\text{ext}}(\mathbf{R}_I) \right] + \sum_{i=1}^N \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v_{\text{ext}}(\mathbf{r}_i) \right] \\ &\quad + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,J} \frac{Z_J e^2}{|\mathbf{r}_i - \mathbf{R}_J|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}\end{aligned}$$

nucleus momentum  
electron position  
nucleus position  
nucleus charge

- 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 ( $\{\mathbf{R}_I\}$ ), with the latter following classical mechanics

$$M_I \frac{d^2}{dt^2} \mathbf{R}_I = -\frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | H(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) | \Psi_0 \rangle$$

# 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

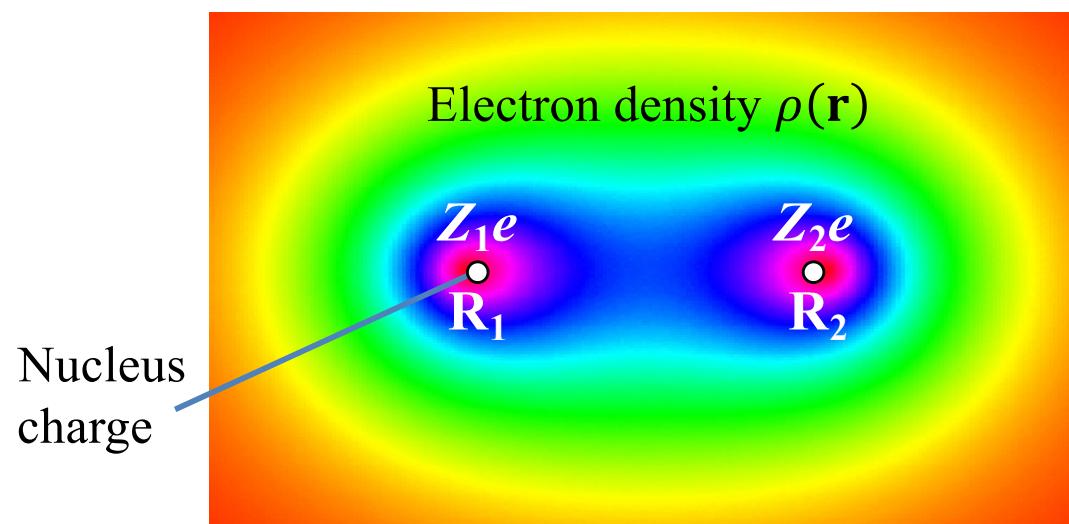


# Energy Functional

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  
External potential  
Hartree energy (mean-field approximation to the electron-electron interaction energy)  
Exchange-correlation energy



# Kohn-Sham Equation

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

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

KS wave function      KS energy

- **KS potential**

$$v_{\text{KS}} = v(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_n \Theta(\mu - \varepsilon_n) |\psi_n(\mathbf{r})|^2$$

step function    chemical potential

exchange-correlation (xc) potential  
 $v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}$

$$N = \sum_n \Theta(\mu - \varepsilon_n)$$

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

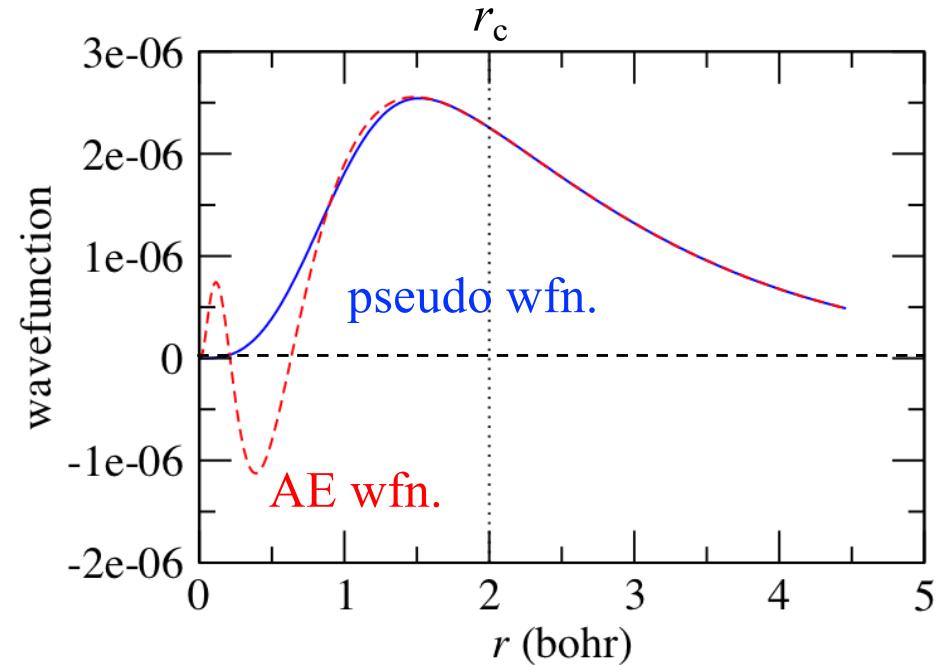
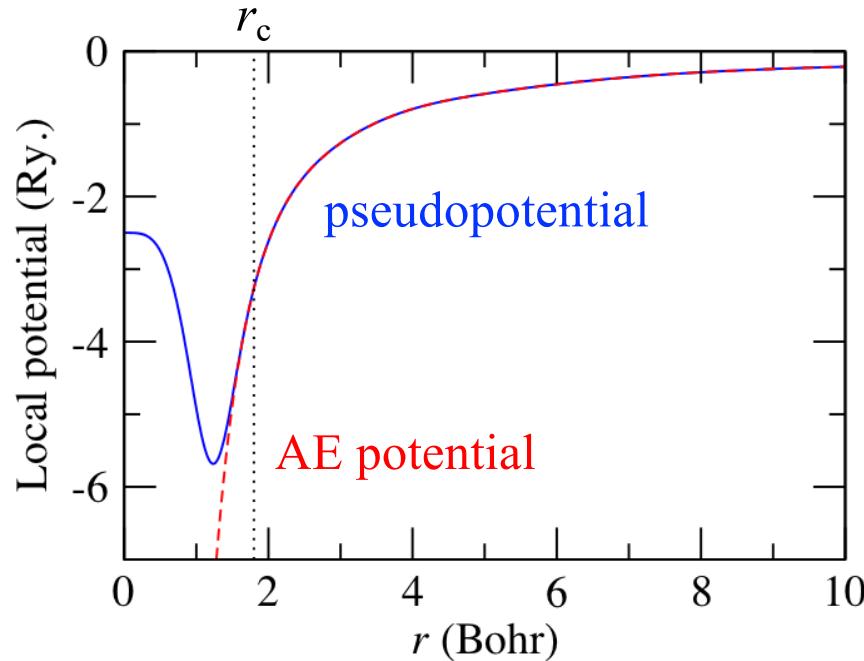
# Abstraction: Exchange-Correlation Functional

---

- 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  
**HSE**: Heyd, Scuseria & Ernzerhof, *J. Chem. Phys.* **118**, 8207 ('03)
- Others supported by QXMD code: Select an appropriate functional for the material system & purpose
  - > LDA+U method for transition metals
$$\delta E_{\text{LDA+U}} / \delta n_i = \epsilon_{\text{LDA}} + U\left(\frac{1}{2} - n_i\right)$$
Anisimov *et al.*, *Phys. Rev. B* **44**, 943 ('91)
  - > DFT-D: van der Waals (vdW) functional for molecular crystals & layered materials
$$E_{\text{disp}} = -s_6 \sum_{i < j} \frac{c_{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij})$$
Grimme, *J. Comput. Chem.* **25**, 1463 ('04); *J. Chem. Phys.* **132**, 154104 ('10)
  - > vdW: Nonlocal correlation functional
$$E_c^{\text{nl}} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r})\phi(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}')$$
Dion *et al.*, *Phys. Rev. Lett.* **92**, 246401 ('04)

# Abstraction: Pseudopotential

- Consider only (chemically active) valence electrons  
*e.g.* silicon —  $1s^2 2s^2 2p^6 \textcolor{red}{3s^2 3p^2}$
- 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
  - > Norm-conserving: Troullier & Martins, *Phys. Rev. B* **41**, 1993 ('91)
  - > Ultrasoft: Vanderbilt, *Phys. Rev. B* **41**, 7892 ('90)
  - > Projector augmented wave (PAW): Blochl, *Phys. Rev. B* **50**, 17953 ('94)

# 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

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

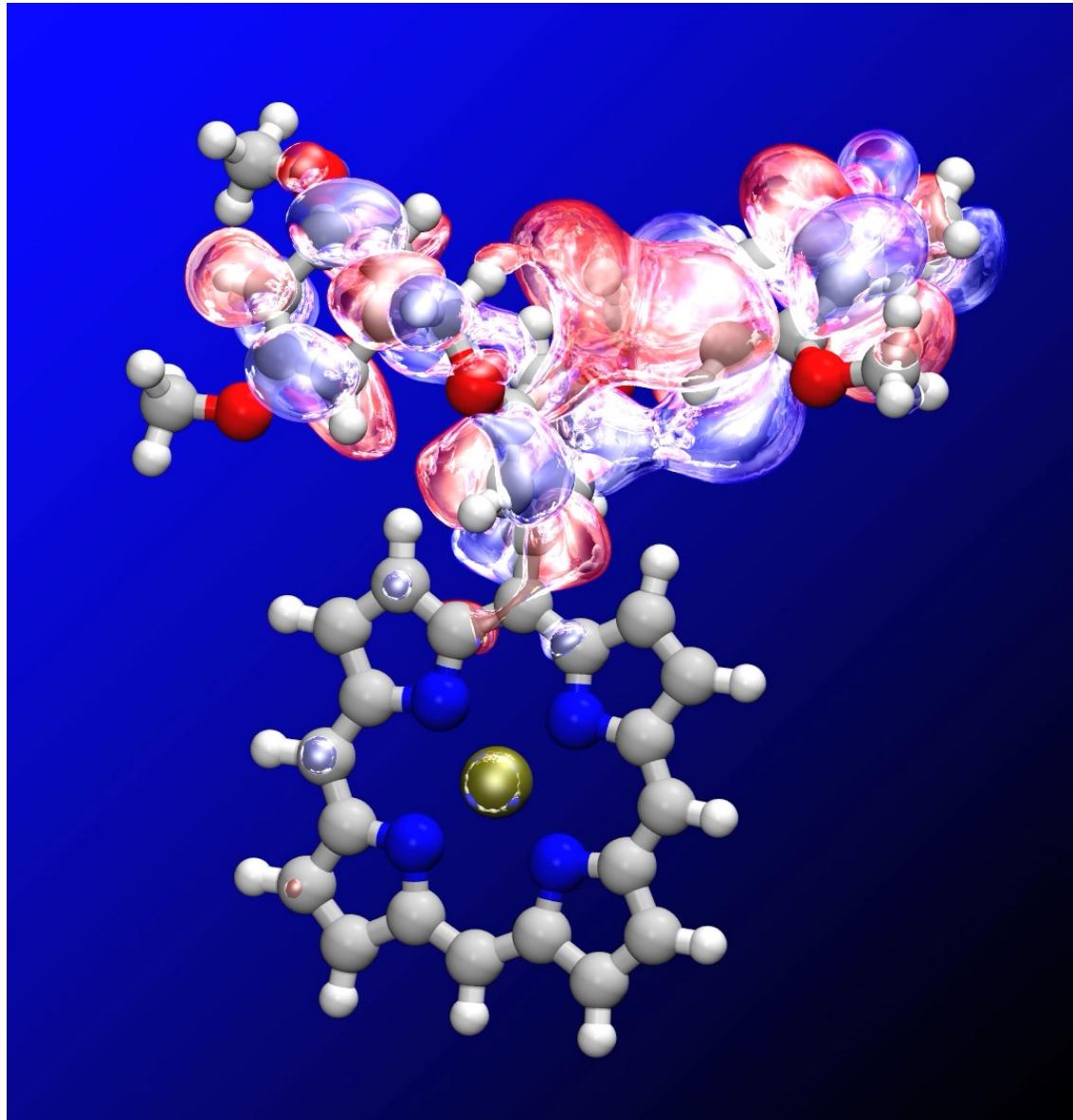
$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \Theta(\mu - \epsilon_n)$$

Chemical potential

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

See PHYS 516 lecture on iterative energy minimization  
<https://aiichironakano.github.io/phys516/QD2CG.pdf>

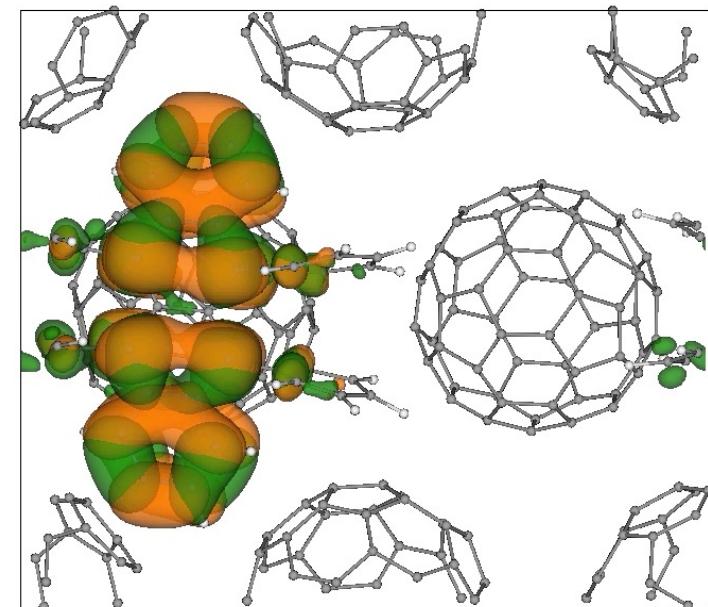
# Nonadiabatic Quantum Molecular Dynamics



*Appl. Phys. Lett.* **98**, 113302 ('11); *ibid.* **100**, 203306 ('12); *ibid.* **102**, 173301 ('13); *Comput. Phys. Commun.* **184**, 1 ('13); *J. Chem. Phys.* **140**, 18A529 ('14); *IEEE Computer* **48**(11), 33 ('15); *Sci. Rep.* **5**, 19599 ('16); *Nature Commun.* **8**, 1745 ('17); *Nano Lett.* **18**, 4653 ('18); *Nature Photon.* **13**, 425 ('19); *Sci Adv.* **8**, eabk2625 ('22)

Zn porphyrin

Rubrene/C<sub>60</sub>



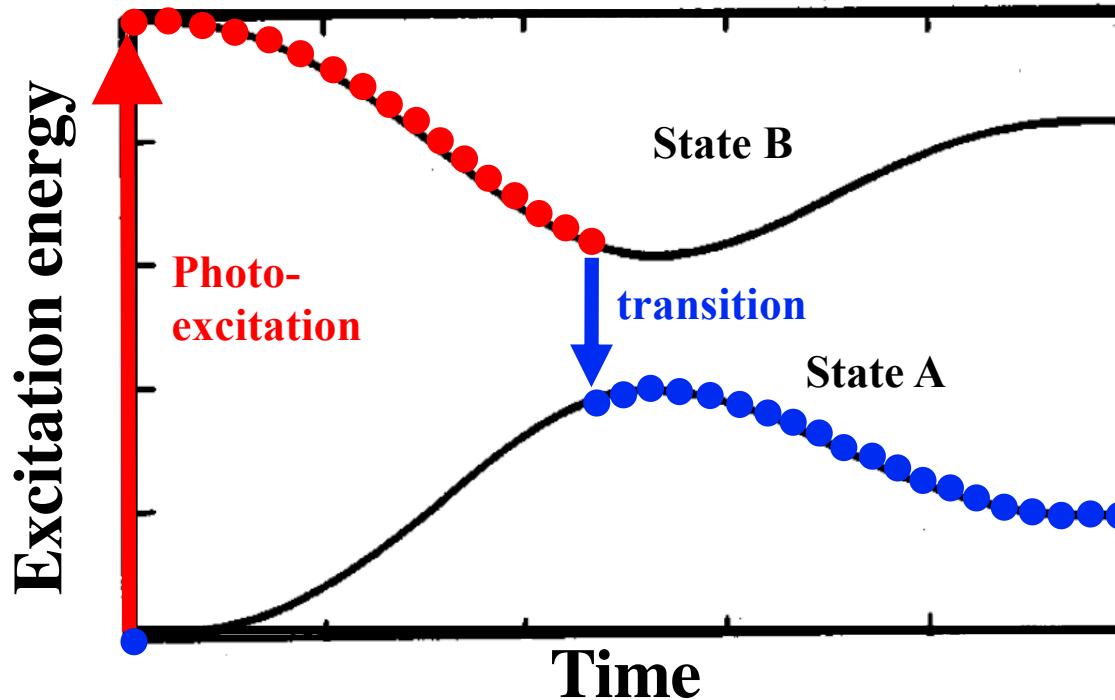
quasi-electron; quasi-hole

- **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

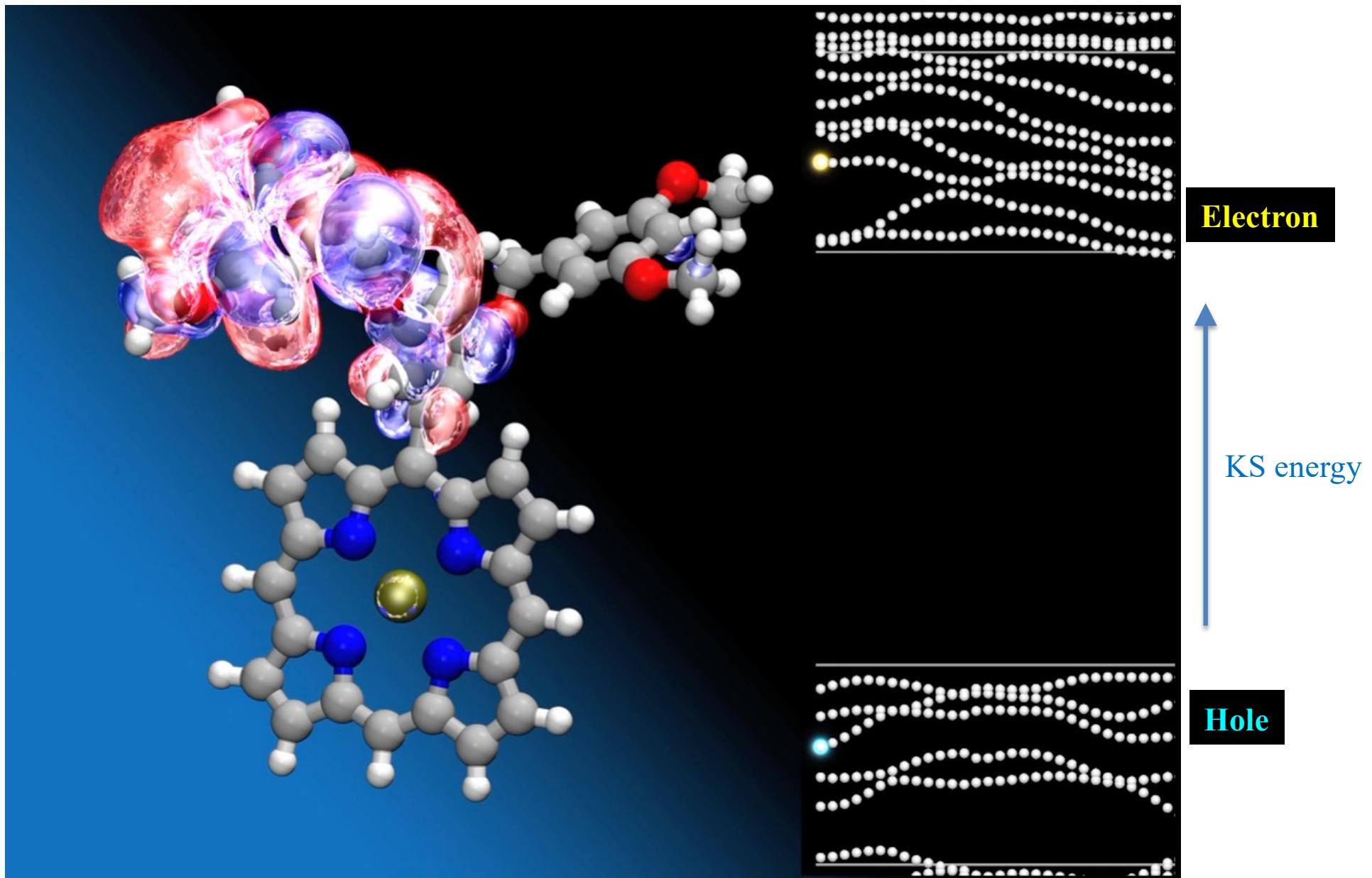
K-th excitation frequency

$$\Psi(\mathbf{r}, t) = \sum_J C_J^{(I)}(t) \Phi_J(\mathbf{r}; \mathbf{R}(t)) \quad C_I^{(I)}(0) = \delta_{I,J}$$
$$\frac{d}{dt} C_J^{(I)}(t) = - \sum_k C_k^{(I)}(t) \left( i\omega_K \delta_{JK} + \langle \Phi_J | \frac{\partial}{\partial t} | \Phi_K \rangle \right)$$

J-th adiabatic excited state

Electronic transition assisted by nuclei motion

# Surface-Hopping in Action



# 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

Open-source software publication: [Shimojo \*et al.\*, SoftwareX 10, 100307 \('19\)](#)

# Current & Future Supercomputing

- Won two DOE supercomputing awards to develop & deploy metascalable (“design once, scale on future platforms”) simulation algorithms (2017-2023)



## Innovative & Novel Computational Impact on Theory & Experiment

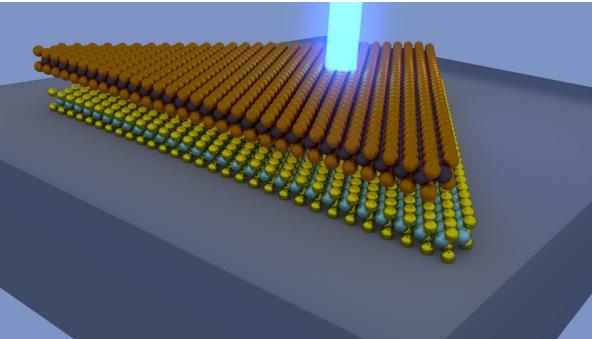
**Title:** “Petascale Simulations for Layered Materials Genome”

**Principal Investigator:**

**Co-Investigator:**

Aiichiro Nakano, University of Southern California

Priya Vashishta, University of Southern California



Early Science Projects for Aurora

Supercomputer Announced

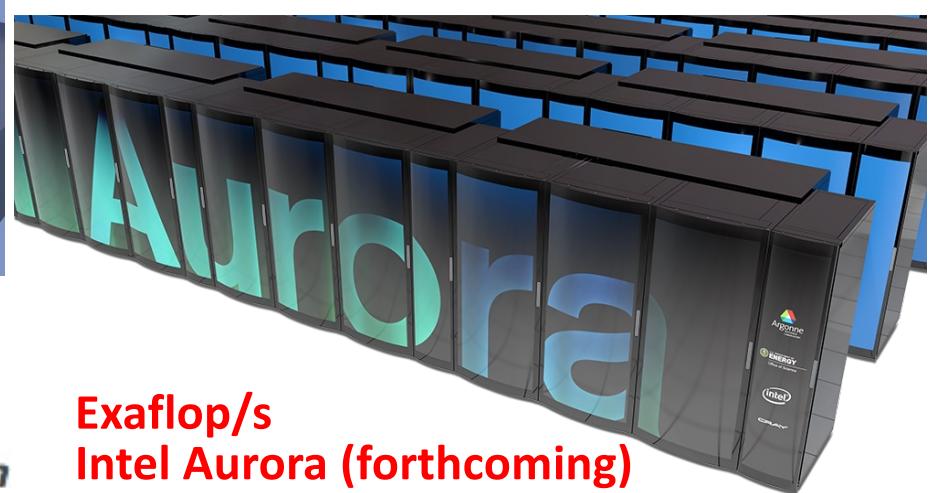
**Metascalable layered materials genome**

**Investigator: Aiichiro Nakano, University of Southern California**

- One of the 10 initial simulation users of the next-generation DOE supercomputer



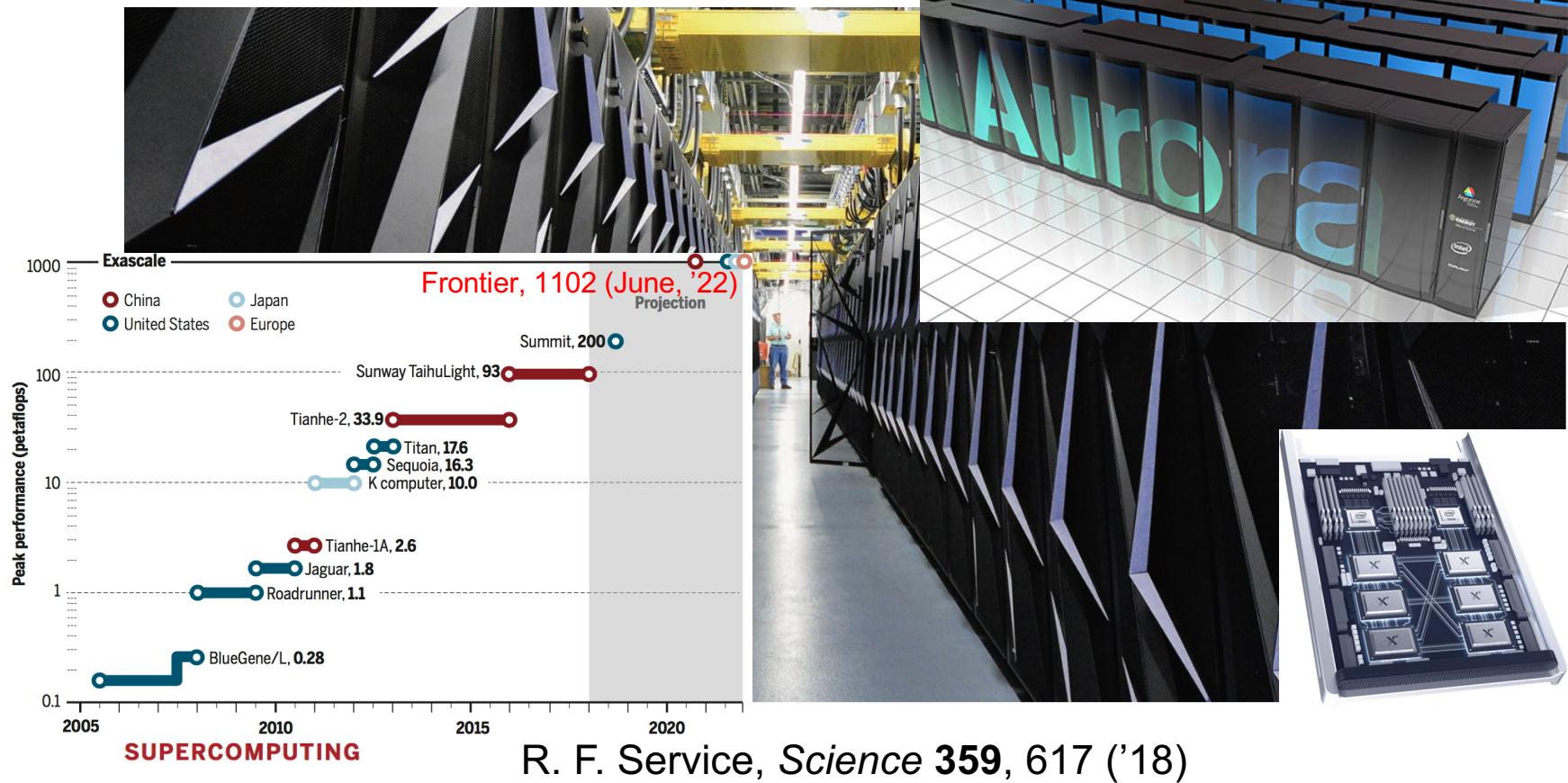
**786,432-core IBM Blue Gene/Q  
281,088-core Intel Xeon Phi**



**Exaflop/s  
Intel Aurora (forthcoming)**

exaflop/s =  $10^{18}$  mathematical operations per second

# CACS@Aurora 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

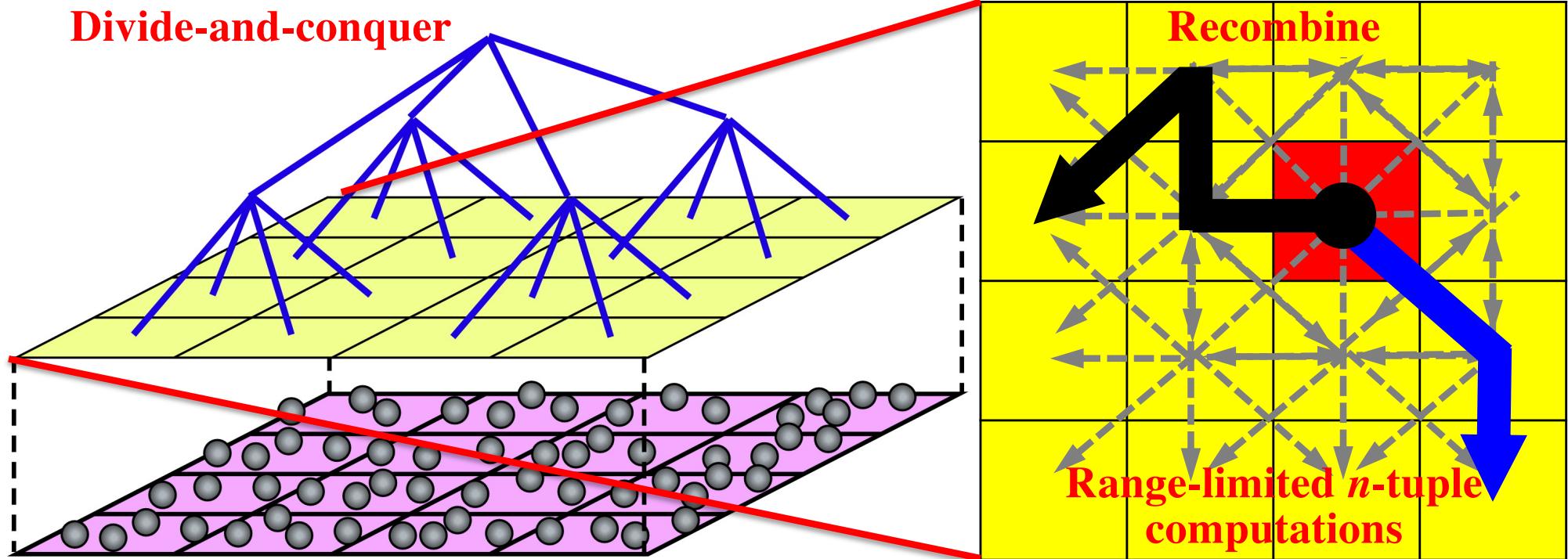
In 1957, the launch of the Sputnik satellite vaulted the Soviet Union to the lead in the space race and galvanized the United States. U.S. supercomputer researchers are today facing their own

Lemont, Illinois. That's 2 years earlier than planned. "It's a pretty exciting time," says Aiichiro 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.

Exa(peta)flop/s =  $10^{18}$  ( $10^{15}$ ) floating-point operations per second

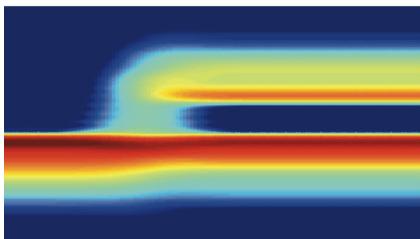
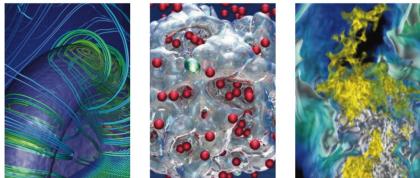
# Divide-Conquer-Recombine (DCR) Engines



M. Kunaseth et al., ACM/IEEE SC13

- Lean divide-&-conquer density functional theory (LDC-DFT) algorithm minimizes the prefactor of  $O(N)$  computational cost  
F. Shimojo et al., *J. Chem. Phys.* **140**, 18A529 ('14); K. Nomura et al., *IEEE/ACM SC14*
- Extended-Lagrangian reactive molecular dynamics (XRMD) algorithm eliminates the speed-limiting charge iteration  
K. Nomura et al., *Comput. Phys. Commun.* **192**, 91 ('15)

# BES



NOVEMBER 3-5, 2015

ROCKVILLE, MARYLAND

BASIC ENERGY SCIENCES

## EXASCALE REQUIREMENTS REVIEW

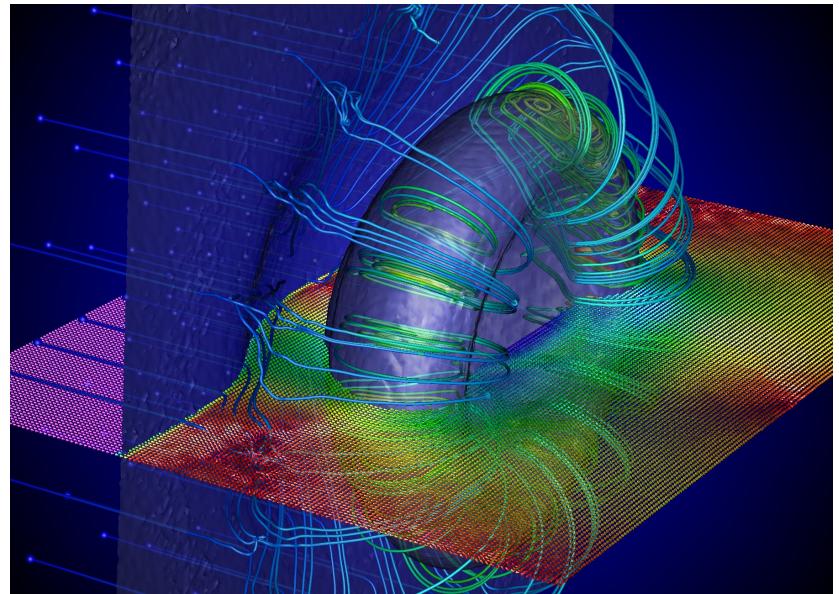
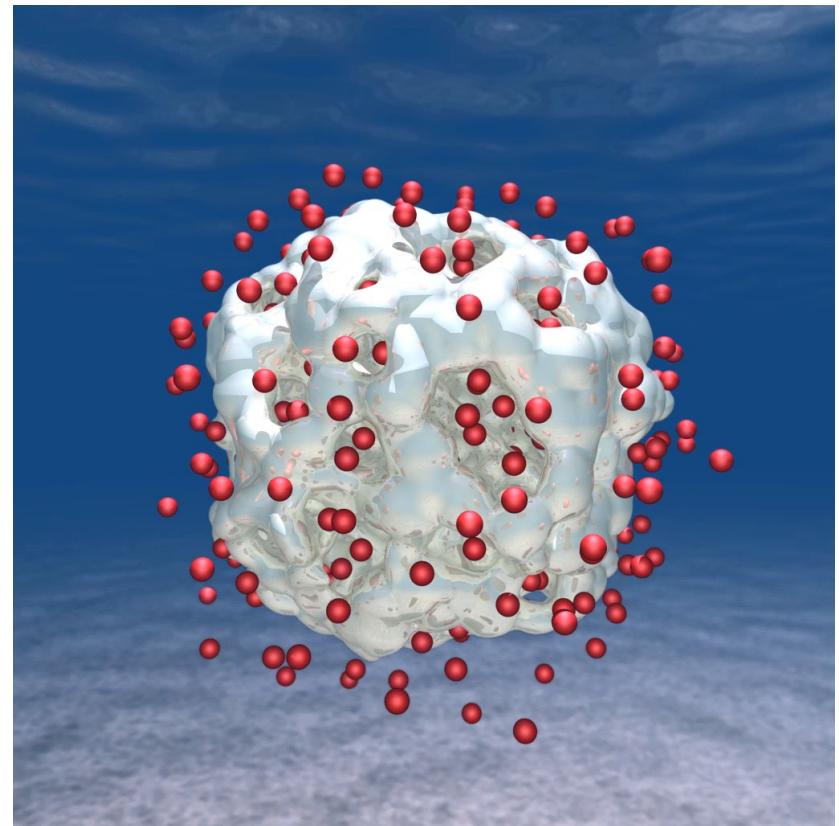
An Office of Science review sponsored jointly by  
Advanced Scientific Computing Research and Basic Energy Sciences

16,661-atom QMD

Shimamura *et al.*,  
*Nano Lett.*  
**14**, 4090 ('14)

$10^9$ -atom RMD

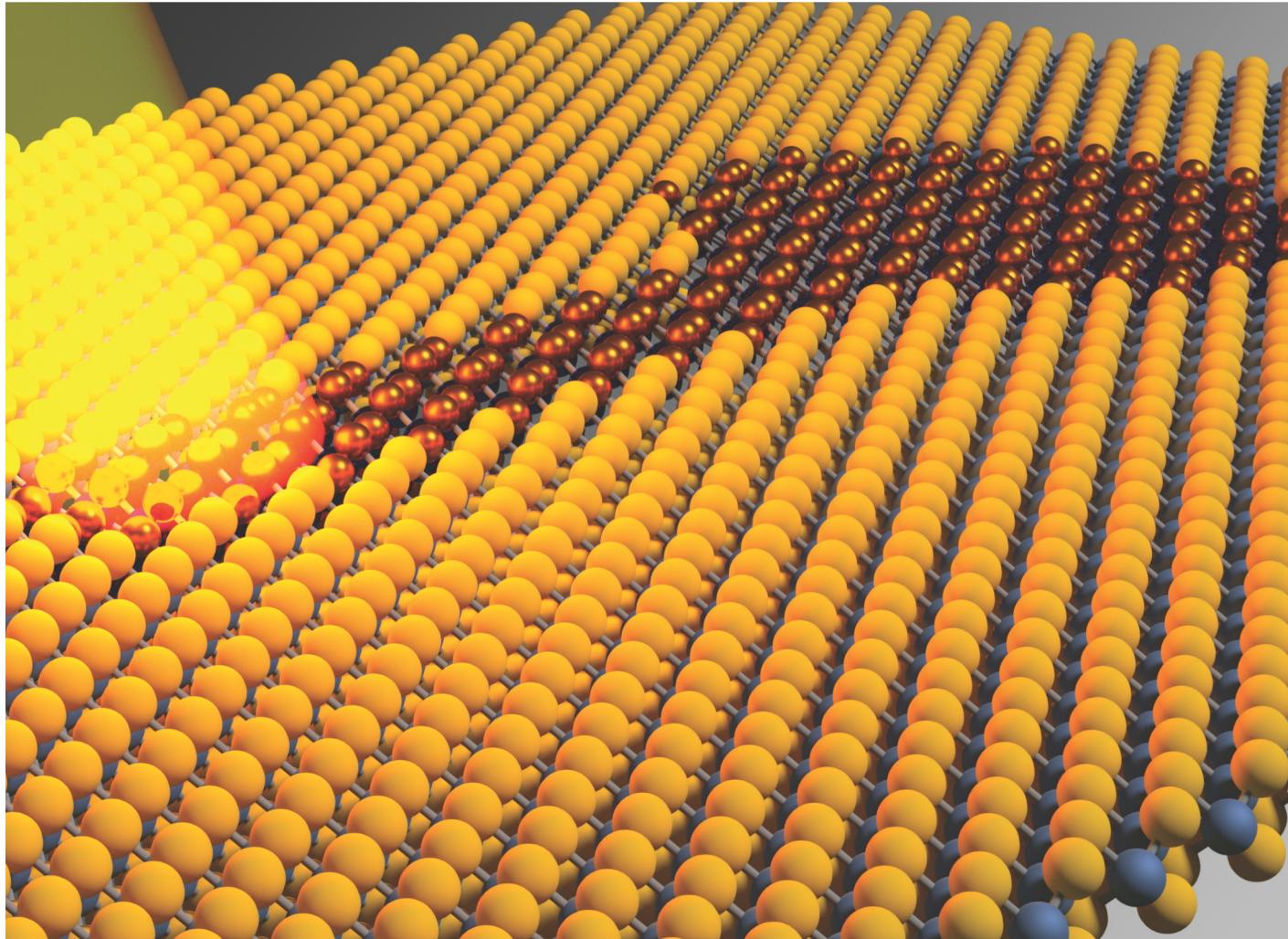
Shekhar *et al.*,  
*Phys. Rev. Lett.*  
**111**, 184503 ('13)



# Ultrafast Control of Materials

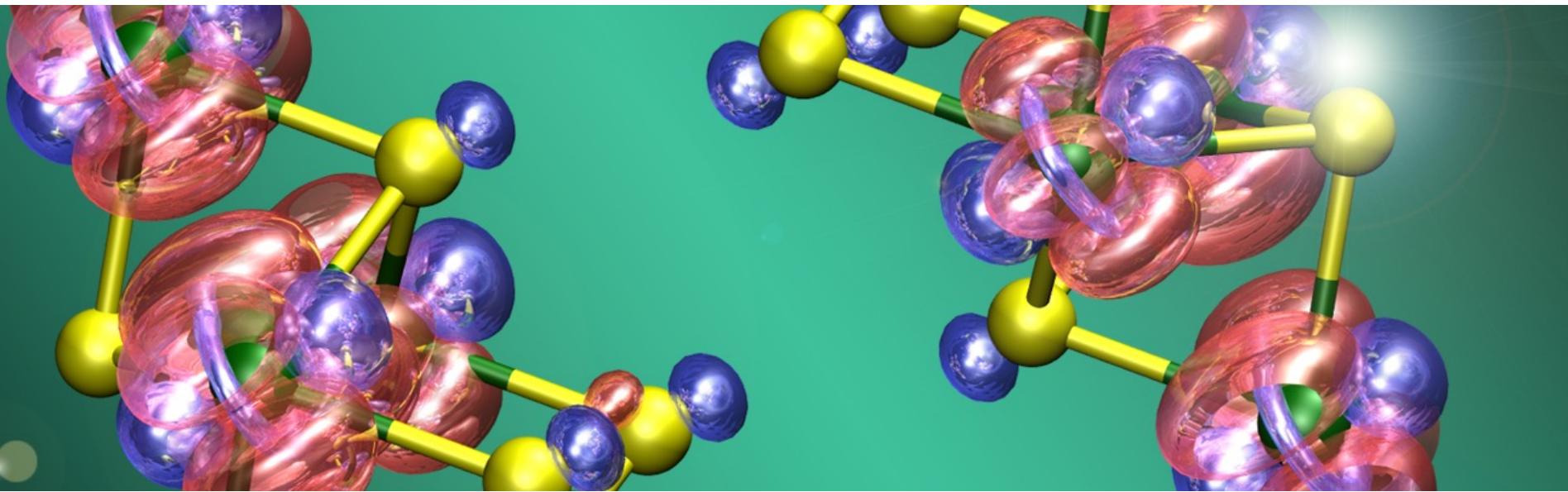
---

**Goal:** Use ultrafast laser pulses to transform material structures & properties  
(e.g. semiconductor-to-metal) on demand

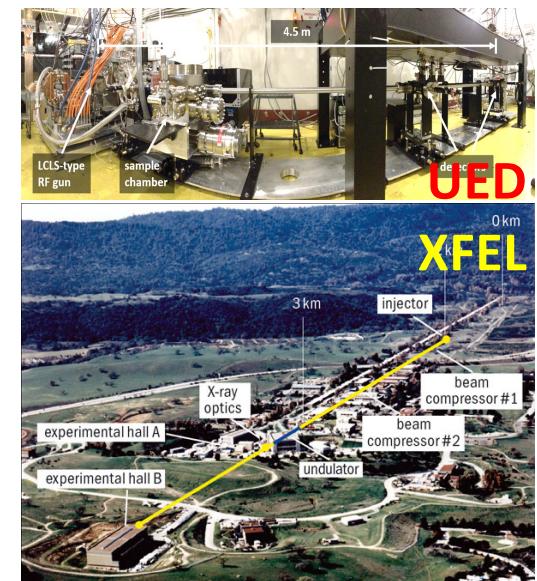


A. Krishnamoorthy *et al.*, *Nanoscale* **10**, 2742 ('18); journal cover

# Simulation-Experiment Synergy

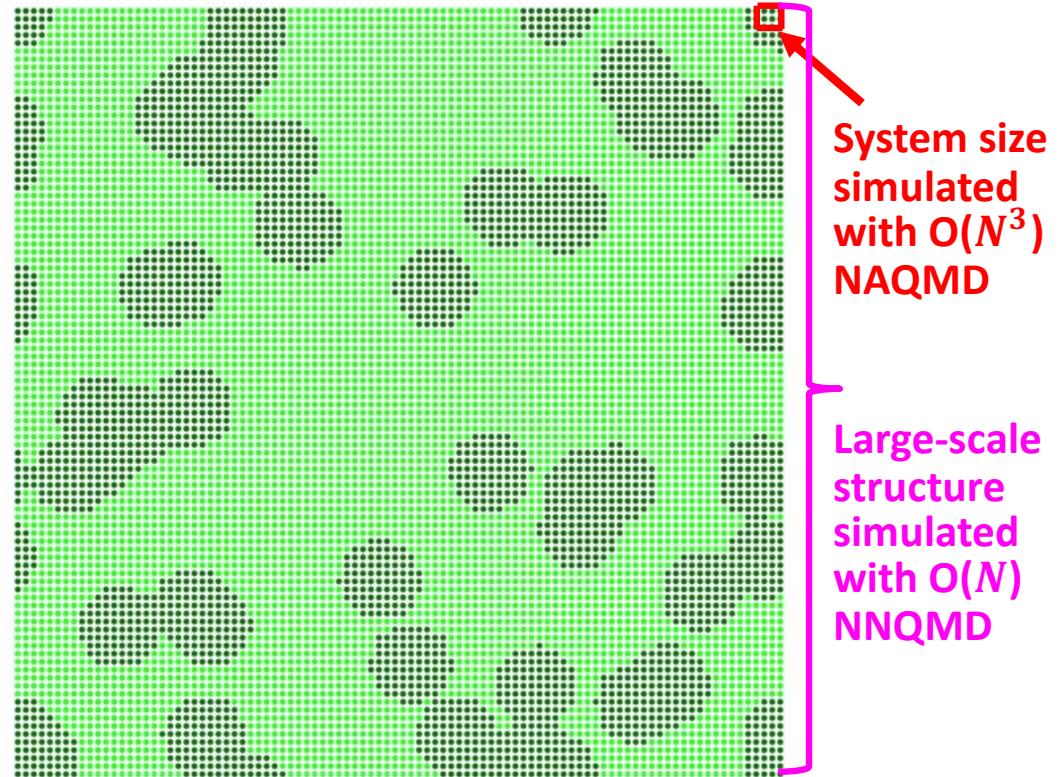
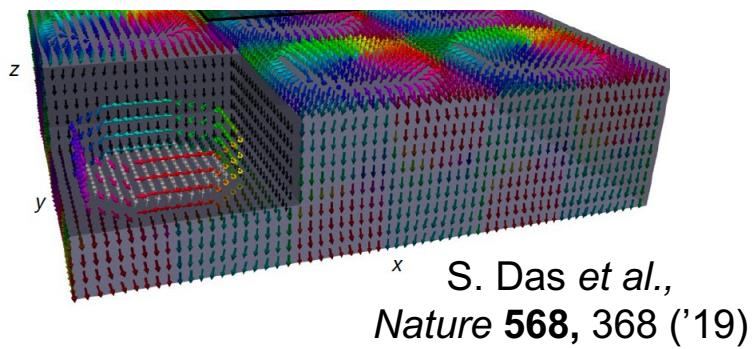
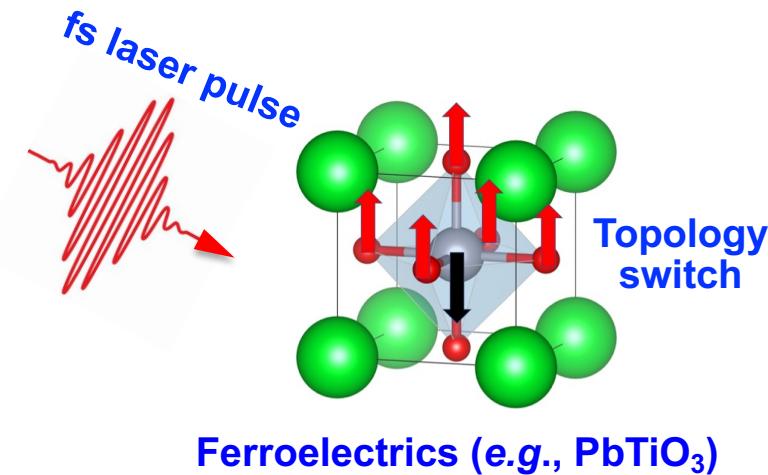


- In ultrafast ‘electron & X-ray cameras,’ laser light hitting a material is almost completely converted into nuclear motions — key to switching material properties on & off at will for future electronics applications.
- High-end nonadiabatic quantum molecular dynamics simulations reproduce the ultrafast energy conversion at exactly the same space & time scales, and explain it as a consequence of photo-induced phonon softening.



**Ultrafast electron diffraction:** M.F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)  
**X-ray free-electron laser:** I. Tung *et al.*, *Nature Photon.* **13**, 425 ('19)

# New Application: Polar Opto-Toptronics



- **Goal:** Photo-switch of ferroelectric topology (e.g., polar skyrmion) for ultrafast, ultralow-power opto-electronics
- Excited-state NNQMD reveals topological phase-transition dynamics similar to Kibble-Zurek mechanism in cosmology

# Where to Go from Here

---

Detailed lecture notes are available at a USC course home page

## EXTREME-SCALE QUANTUM SIMULATIONS

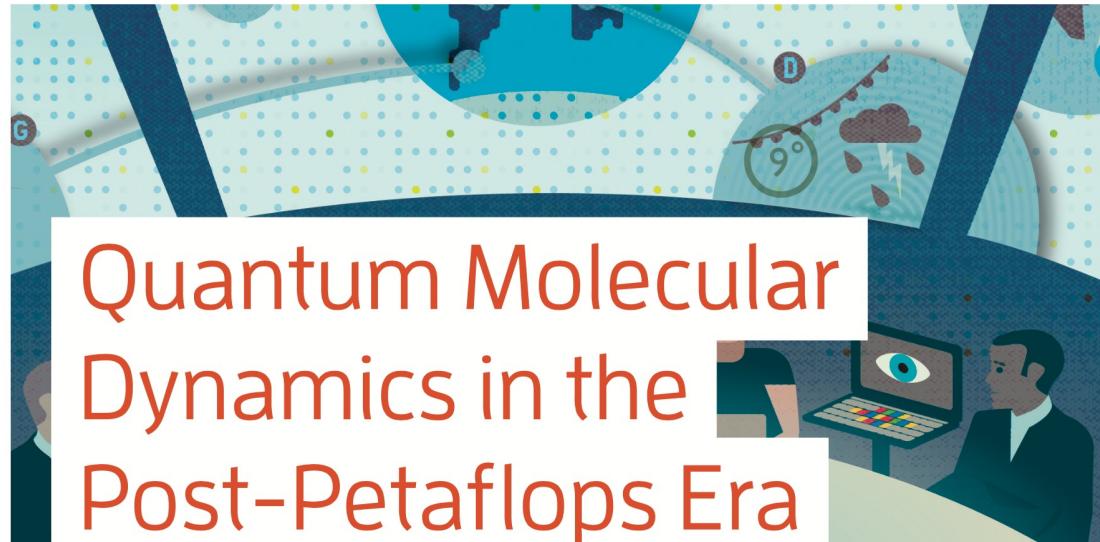
This course surveys & projects algorithmic & computing technologies that will make quantum-dynamics simulations metascalable, *i.e.*, "design once, continue to scale on future computer architectures".

<https://aiichironakano.github.io/cs699-lecture.html>

See also N. Romero *et al.*, *IEEE Computer* **48(11)**, 33 ('15)

<https://aiichironakano.github.io/phys516/Romero-QMD-IEEEComputer15.pdf0>

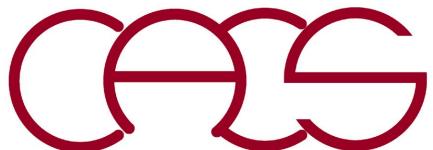
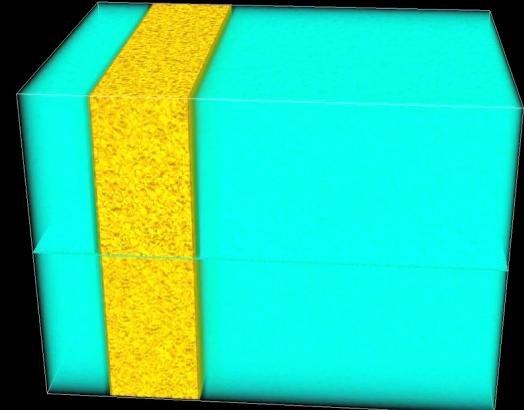
COVER FEATURE GRAND CHALLENGES IN SCIENTIFIC COMPUTING



Standard text book: R. Martin, [\*Electronic Structure\*](#) (Cambridge Univ. Press, '04)

# Conclusion

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



Supported by the National Science Foundation,  
Award OAC-2118061

