

Quantum Molecular Dynamics Simulations

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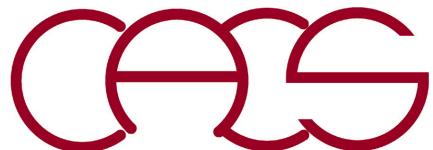
Email: anakano@usc.edu

QXMD software tutorial:

Anikeya Aditya, Suryakanti Debata, Hinata Hokyo,
Taufeq Razakh, Logan Yamamoto



Supported by National Science Foundation,
Award OAC-2118061



CyberMAGICS Workshop
June 25, 2024

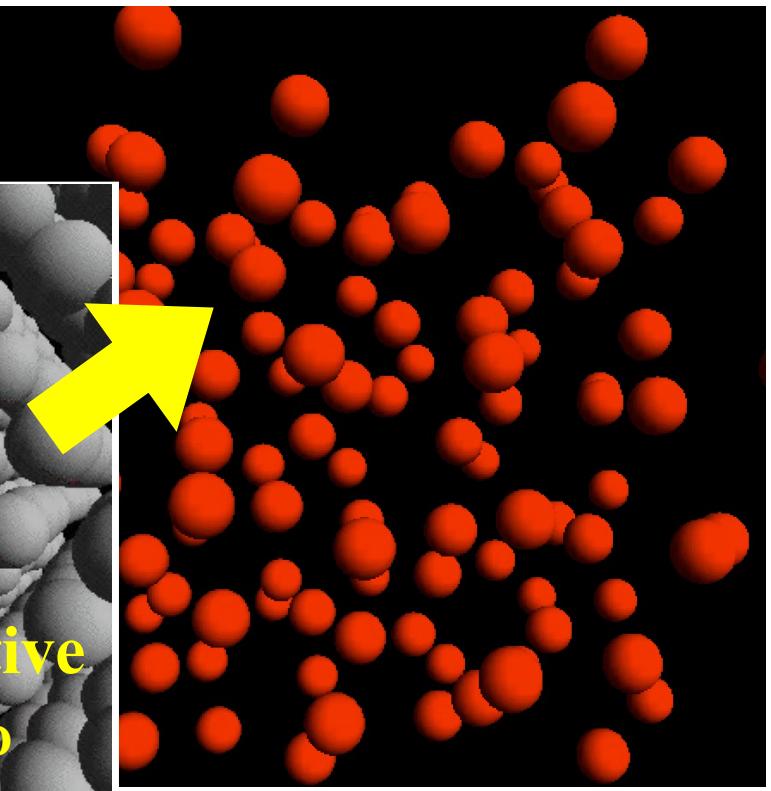
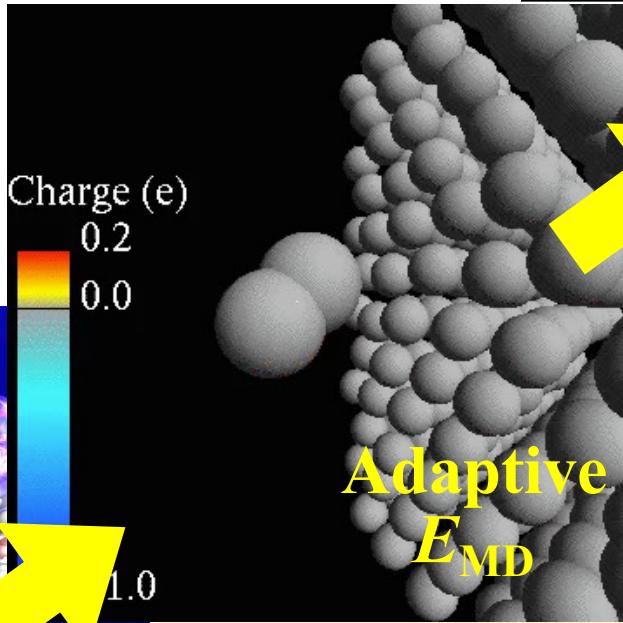
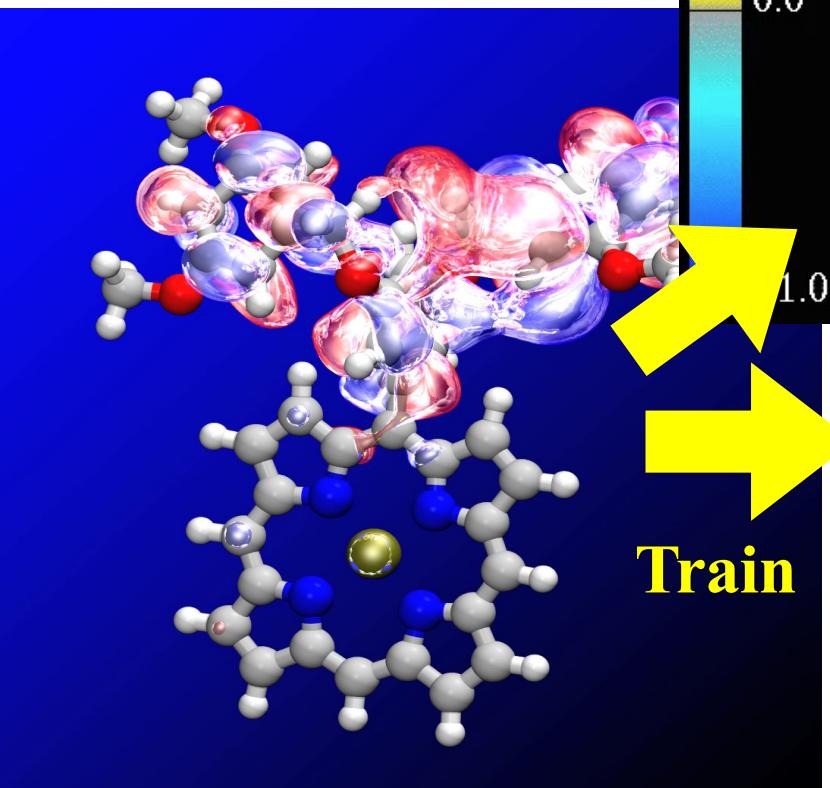


Molecular Dynamics

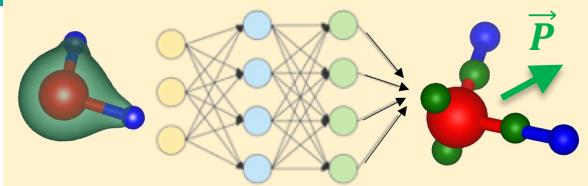
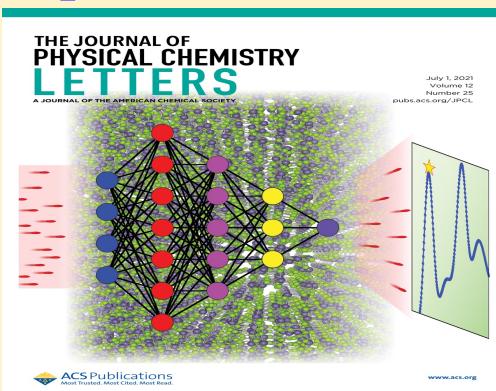
Molecular Dynamics (*MD*)

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)



G. Battimelli *et al.*, Computer Meets Theoretical Physics ('20)

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

Density functional theory (DFT)

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

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

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

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

$O(N)$ 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 comprehensive review** [Bowler & Miyazaki, *Rep. Prog. Phys.* **75**, 036503 ('12)]

Adiabatic Quantum Molecular Dynamics

- Consider a system of N electrons & N_{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

Kohn & Vashishta, *General Density Functional Theory* ('83)



Sholl & Steckel, *Density Functional Theory: A Practical Introduction* ('23)

Energy Functional

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

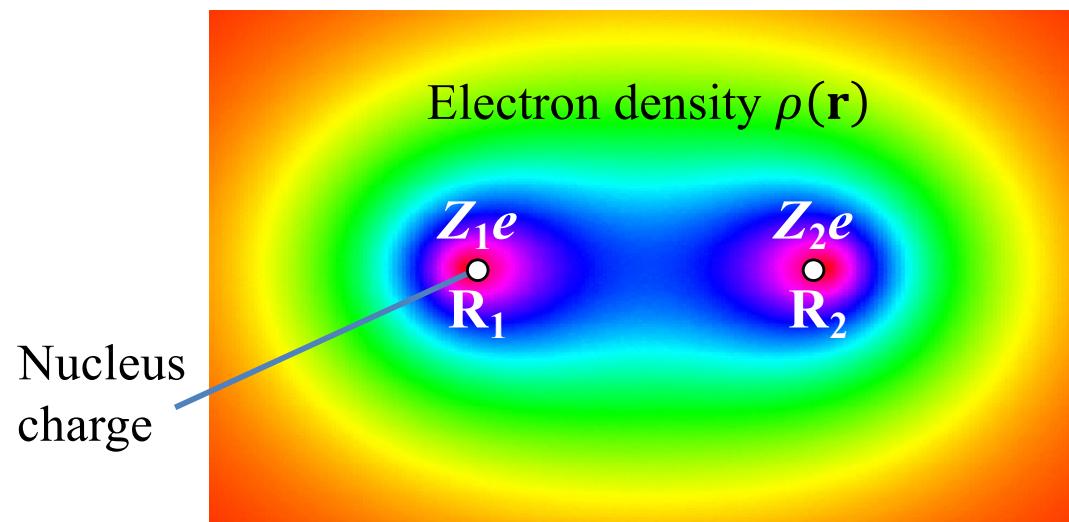
$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})]$$

Kinetic energy of non-interacting electrons

Hartree energy (mean-field approximation to the electron-electron interaction energy)

Exchange-correlation energy

External potential



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

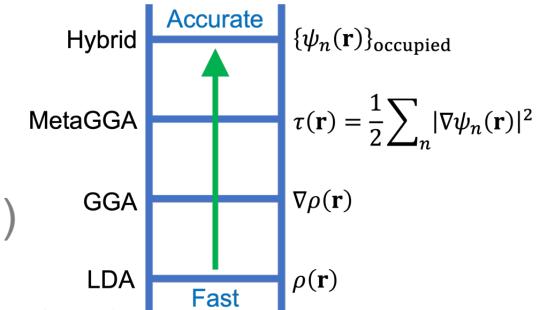
exchange-correlation (xc) potential
 $v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}$

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

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

Abstraction: Exchange-Correlation Functional

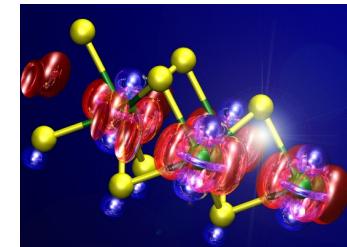
- Universal functional (of density) that describes many-body effects beyond the mean-field approximation
- Some commonly used exchange-correlation functionals
 - > GGA (generalized gradient approximation)
PBE: Perdew, Burke & Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 ('96)
 - > MetaGGA
SCAN: Sun, Ruzsinszky & 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



DFT+U method for transition metals

$$\delta E_{\text{DFT+U}} / \delta n_i = \epsilon_{\text{DFT}} + U \left(\frac{1}{2} - n_i \right)$$

Anisimov *et al.*, *Phys. Rev. B* **44**, 943 ('91)



Localized
d-electrons

DFT-D: van der Waals (vdW) functional for molecular crystals & layered materials

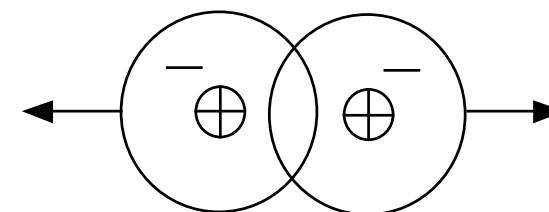
$$E_{\text{disp}} = -s_6 \sum_{i < j} \frac{c_{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij})$$

Grimme, *J. Chem. Phys.* **132**, 154104 ('10)

vdW: Nonlocal correlation functional

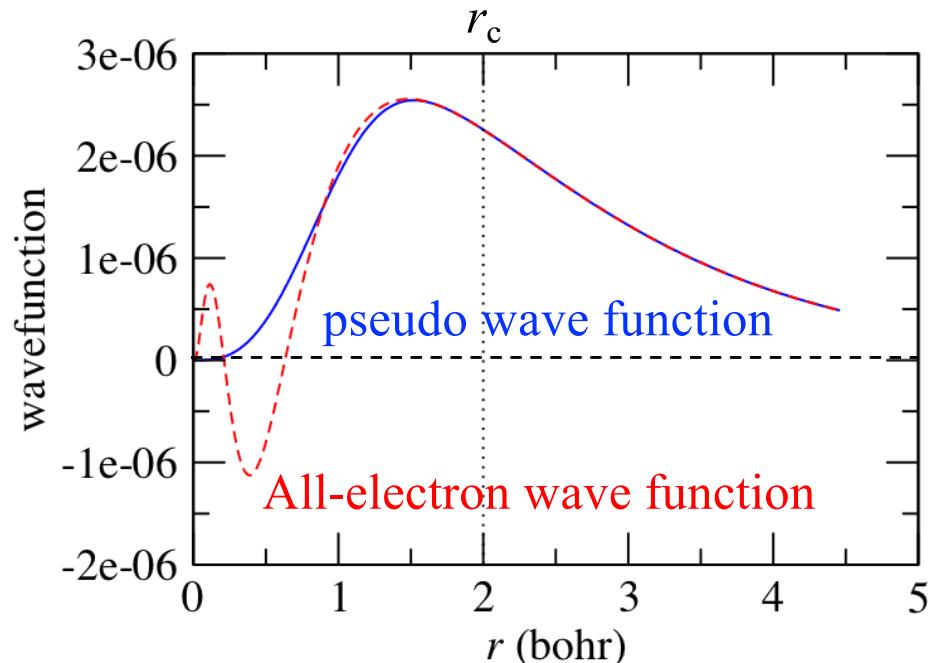
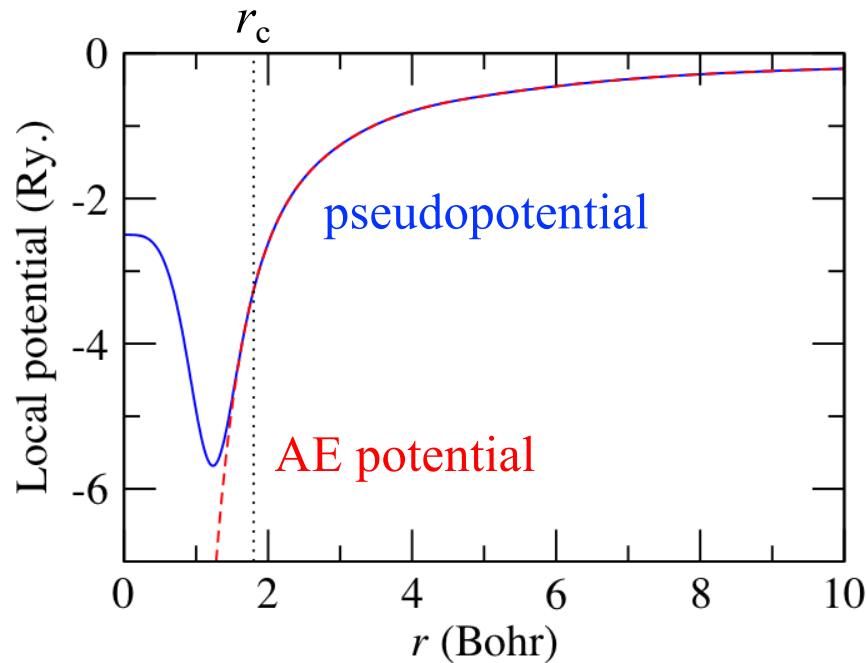
$$E_c^{\text{nl}} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$$

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 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 μ and
compute $\rho(\mathbf{r})$

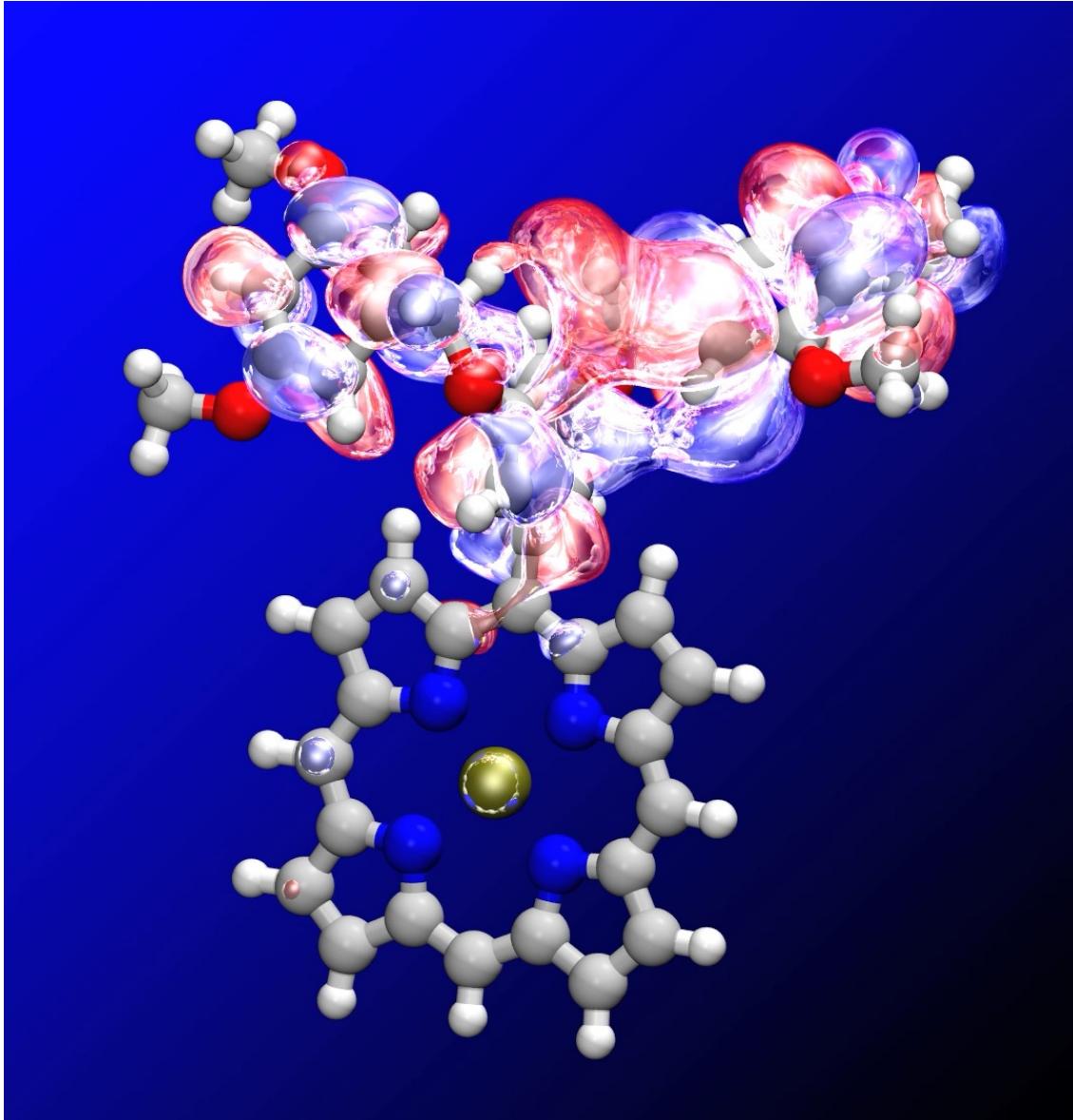
$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \Theta(\mu - \epsilon_n)$$

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>

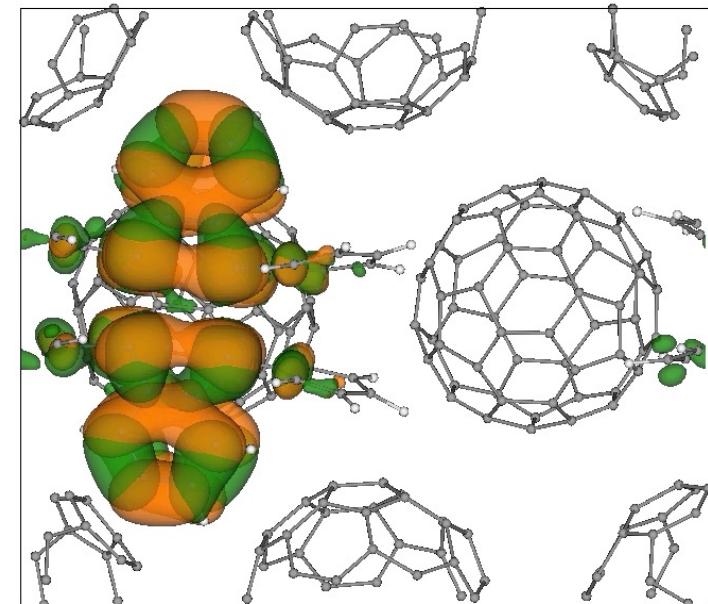
Nonadiabatic Quantum Molecular Dynamics



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/C₆₀



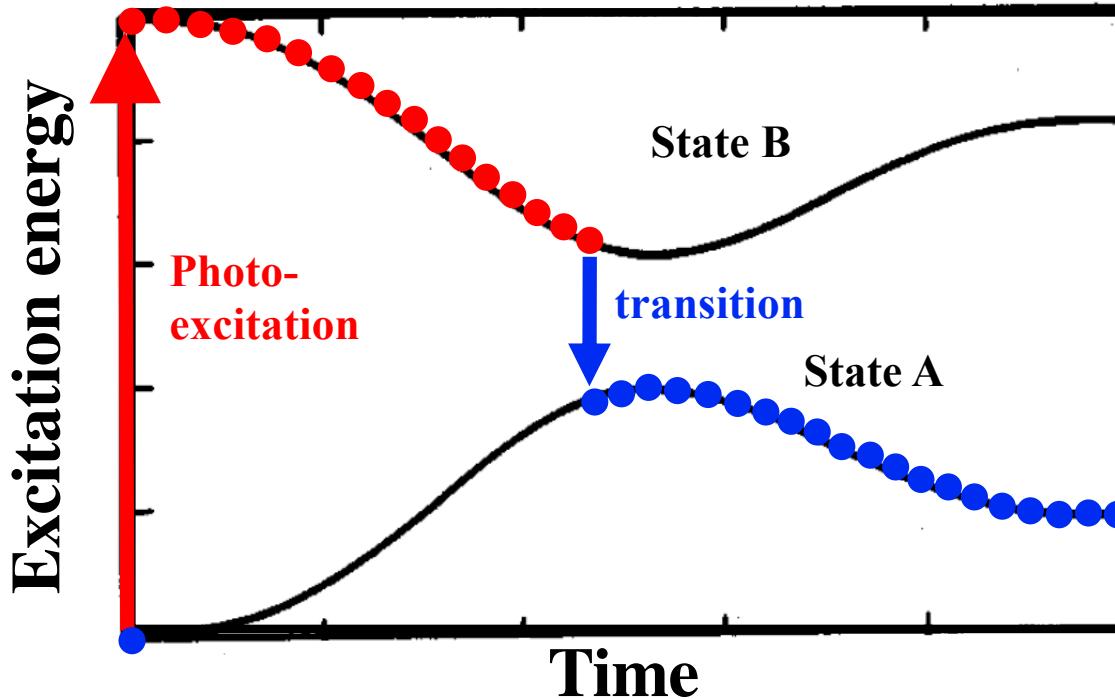
quasi-electron; quasi-hole

- **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

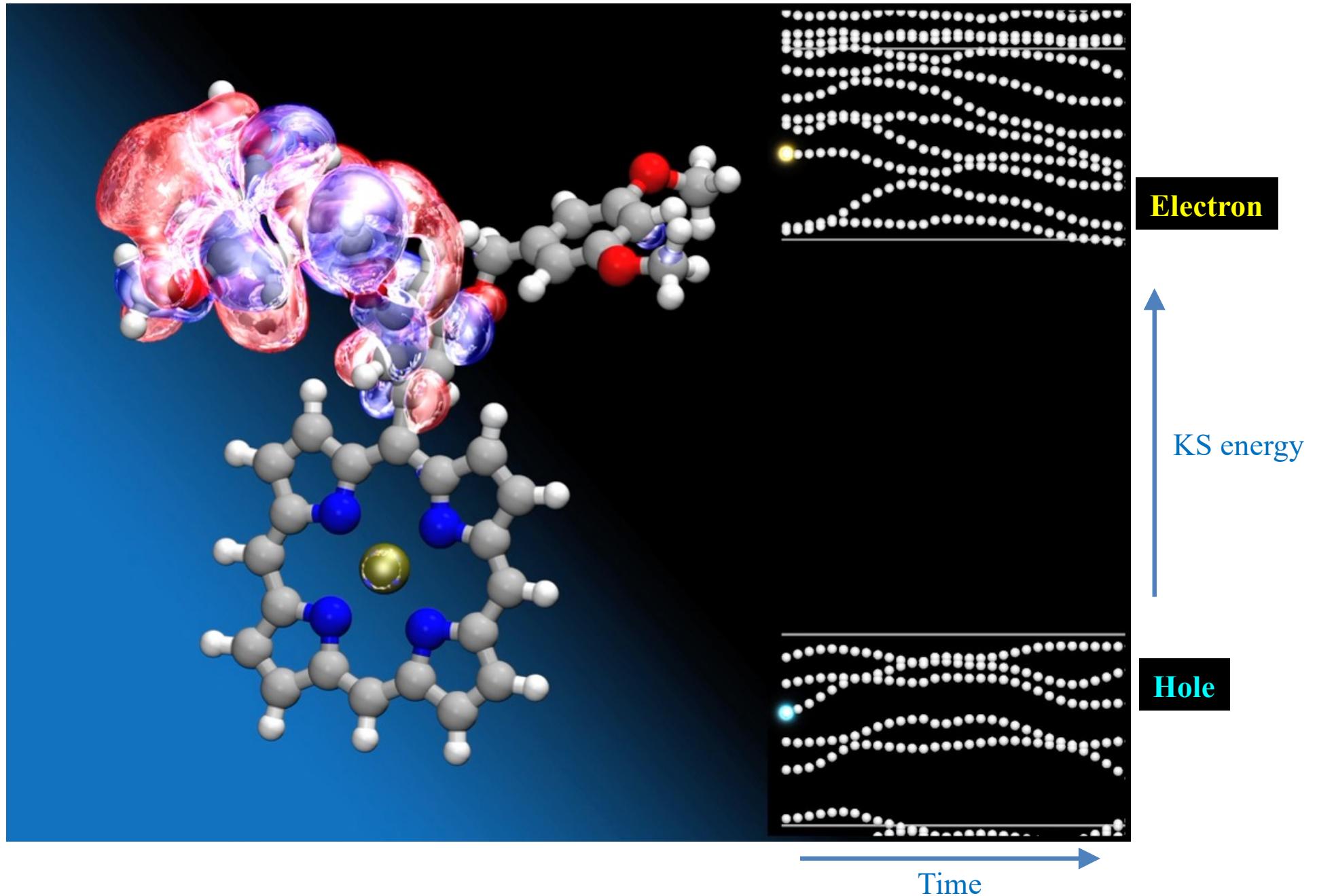
K -th excitation frequency

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

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 \('19\)](#)

Also use [VASP](#) & [Quantum Espresso](#)

Current & Future Supercomputing

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



Innovative & Novel Computational Impact on Theory & Experiment

Title: AI-Guided Exascale Simulations of Quantum Materials Manufacturing and Control

PI and Co-PIs: Aiichiro Nakano—PI, Rajiv K. Kalia, Ken-ichi Nomura, Priya Vasishta

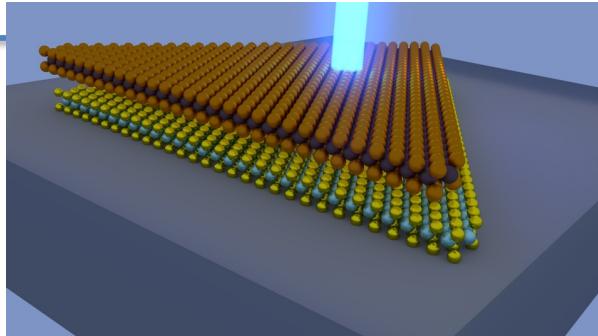
- Atomistic simulations on million cores (pre-exascale)



786,432-core IBM Blue Gene/Q

281,088-core Intel Xeon Phi

560-node (2,240-GPU) AMD/NVIDIA Polaris



Early Science Projects for Aurora

Supercomputer Announced

Metascalable layered materials genome

Investigator: Aiichiro Nakano, University of Southern California

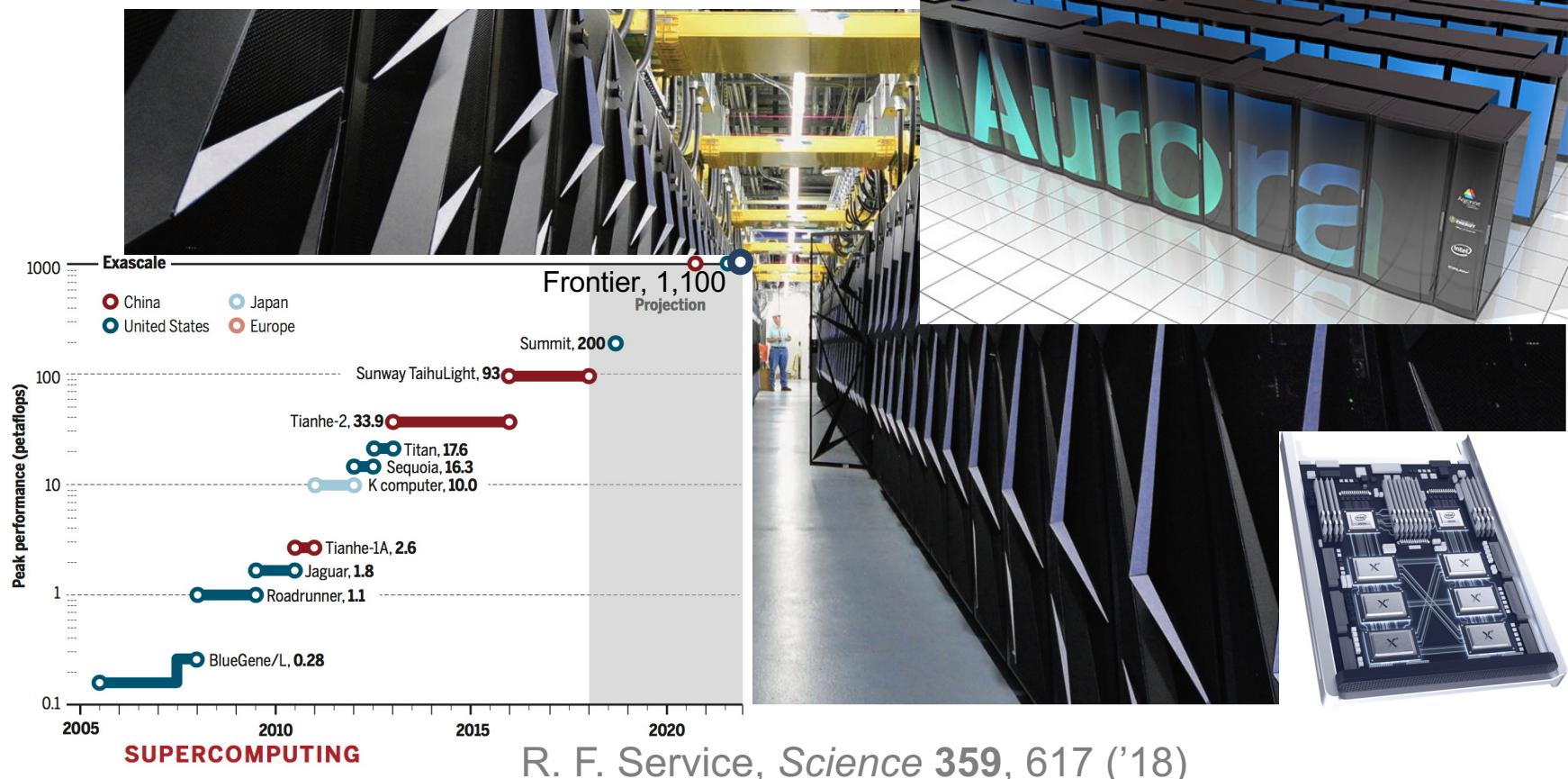


1.01 exaflop/s
Intel Aurora

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

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

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

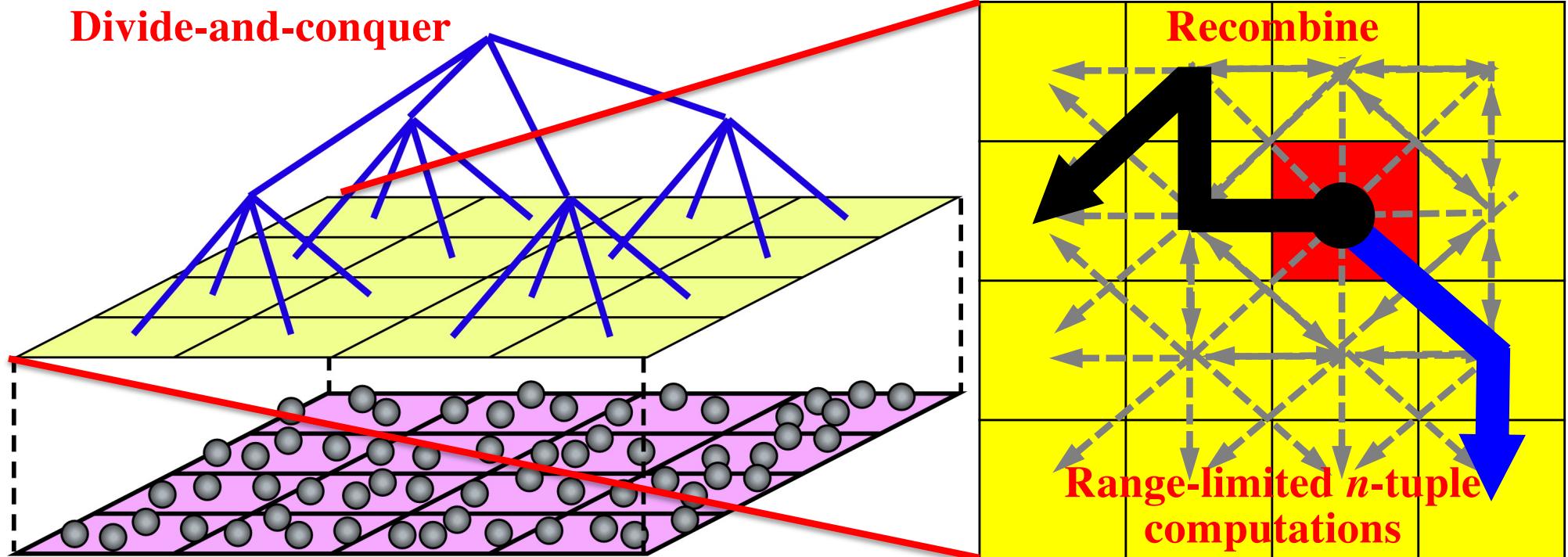
In 1957, the launch of the Sputnik satellite vaulted the Soviet Union to the lead in the space race and galvanized the United States. U.S. supercomputer researchers are today facing their own

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

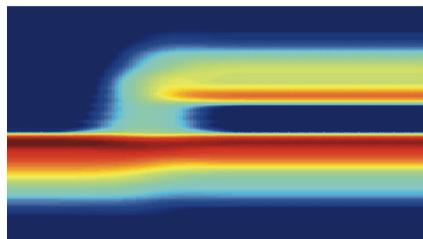
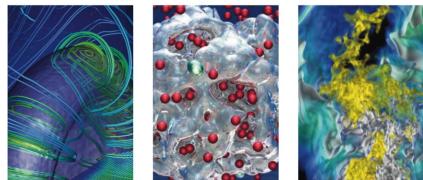
- Lean divide-&-conquer density functional theory (LDC-DFT) algorithm minimizes the prefactor of $O(N)$ computational cost

F. Shimojo et al., *J. Chem. Phys.* **140**, 18A529 ('14); S. Tiwari et al., *HPCAsia20 Best Paper*

- Extended-Lagrangian reactive molecular dynamics (XRMD) algorithm eliminates the speed-limiting charge iteration

K. Nomura et al., *Comput. Phys. Commun.* **192**, 91 ('15)

BES



Early Science Projects for Aurora
Supercomputer Announced

Metascalable layered materials genome

Investigator: Aiichiro Nakano, University of Southern California

One of the initial simulation users of the exaflop/s Aurora supercomputer

Exa-leadership

BASIC ENERGY SCIENCES

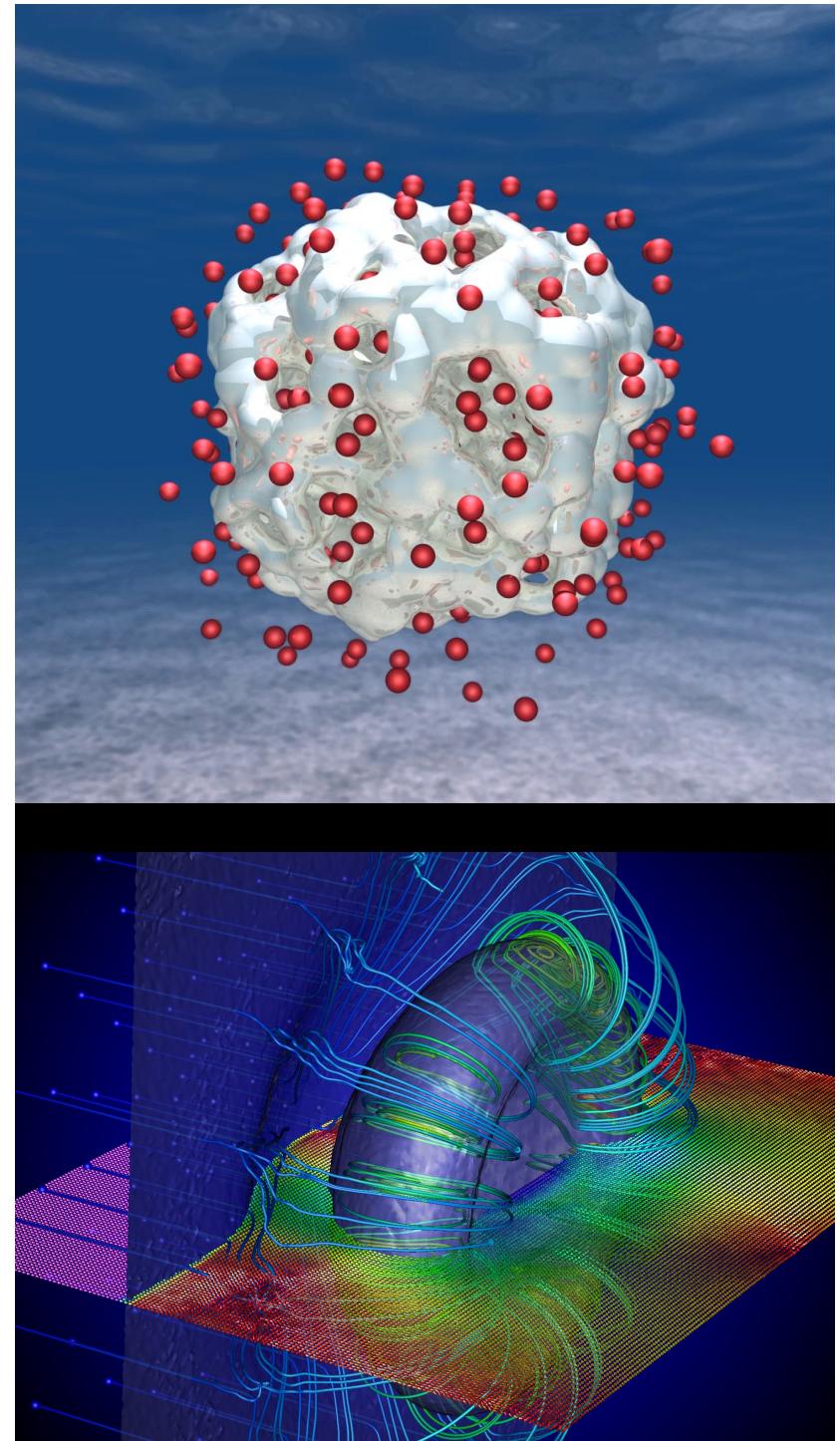
EXASCALE REQUIREMENTS REVIEW

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

16,661-atom QMD

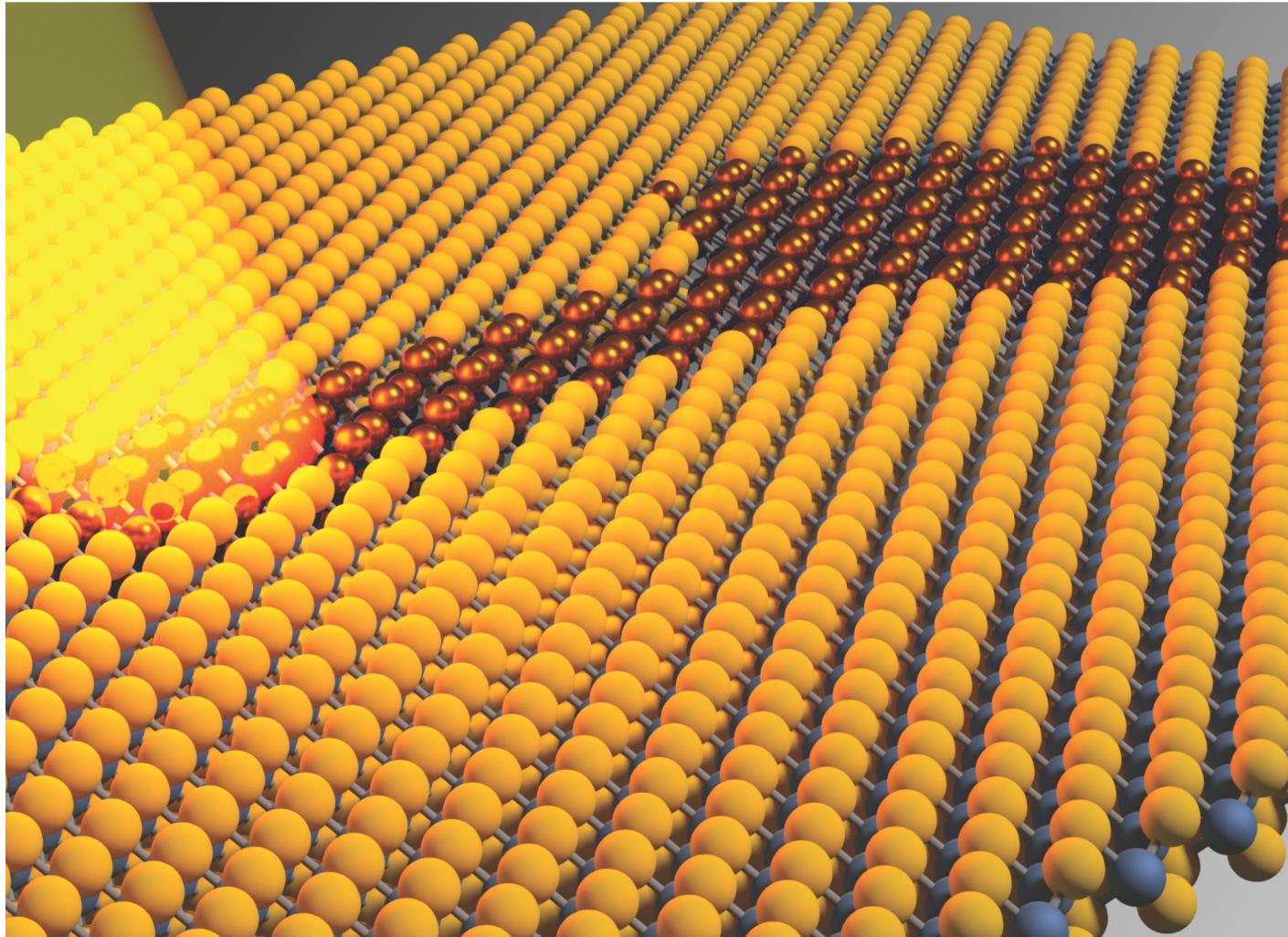
10⁹-atom RMD

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



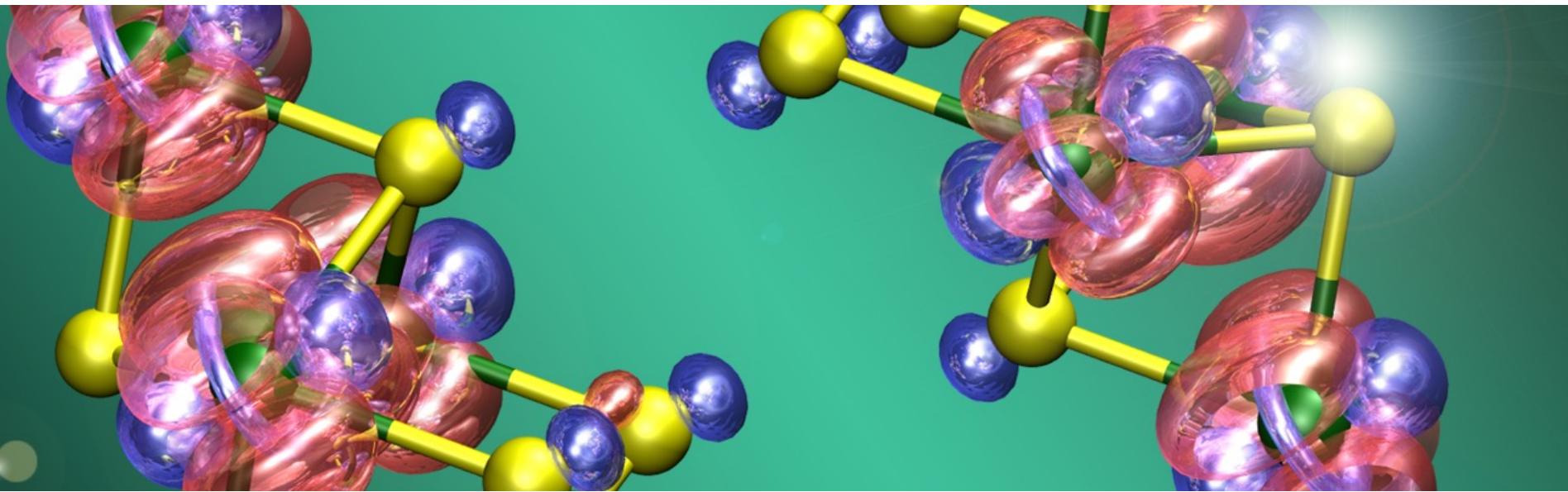
Ultrafast Control of Materials

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

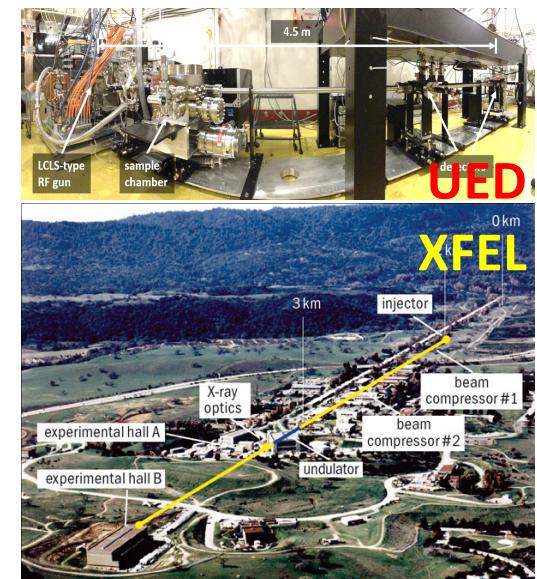


A. Krishnamoorthy *et al.*, *Nanoscale* **10**, 2742 ('18); journal cover

Simulation-Experiment Synergy

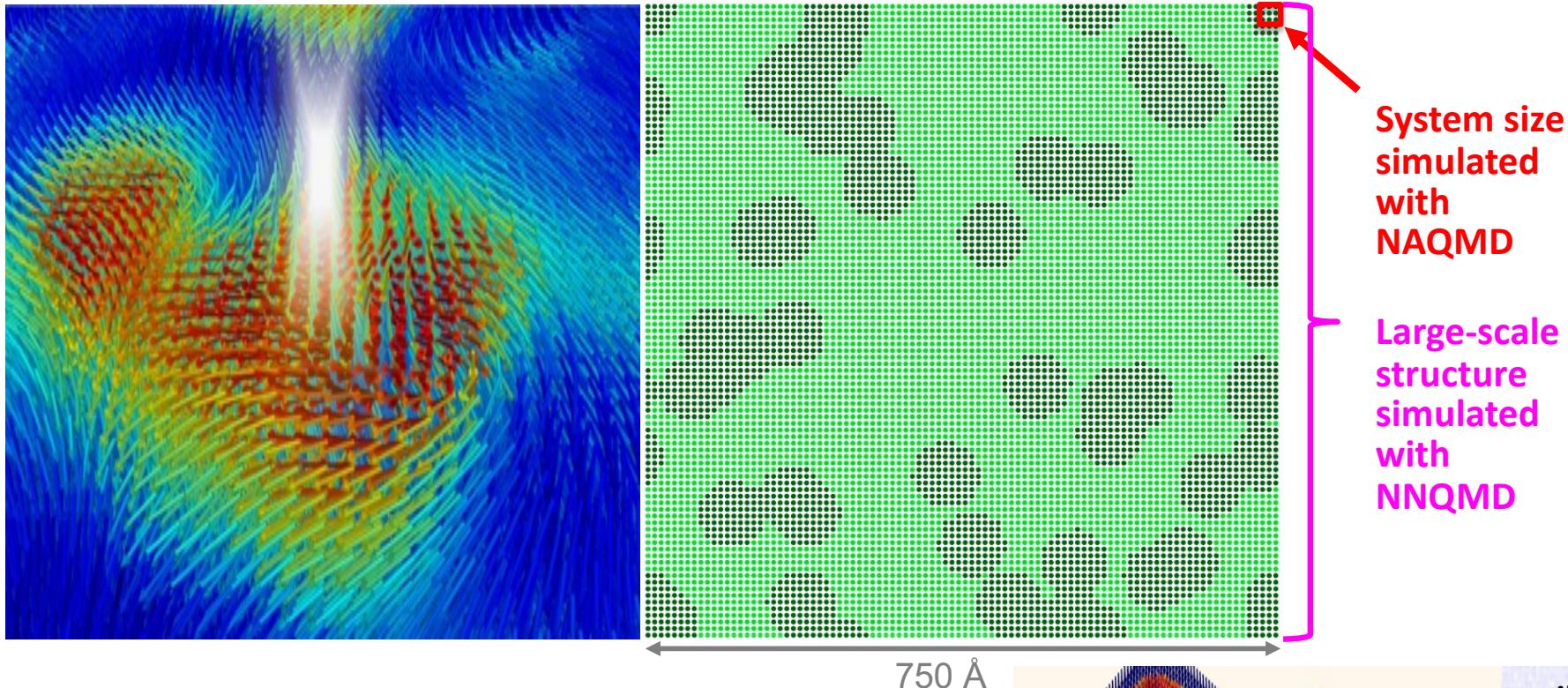


- In ultrafast ‘electron & X-ray cameras,’ laser light hitting a material is almost completely converted into nuclear motions — key to switching material properties on & off at will for future electronics applications.
- High-end nonadiabatic quantum molecular dynamics simulations reproduce the ultrafast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



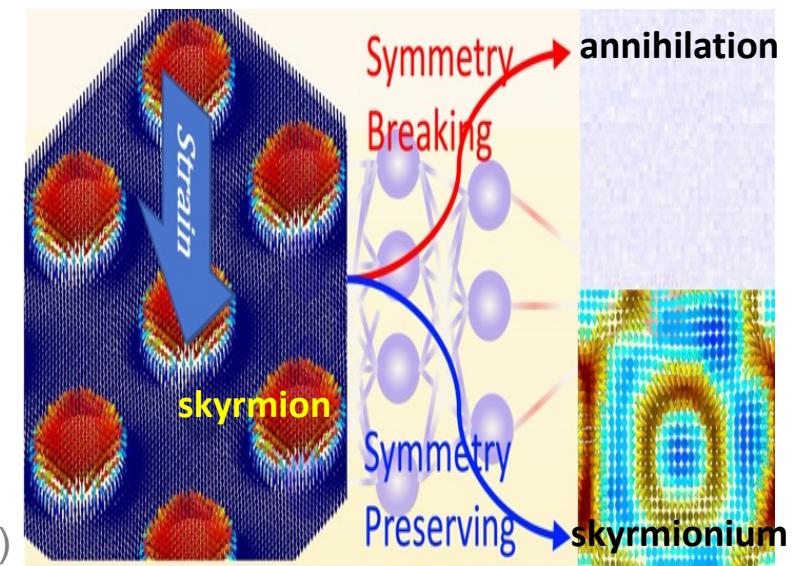
Ultrafast electron diffraction: M.F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)
X-ray free-electron laser: I. Tung *et al.*, *Nature Photon.* **13**, 425 ('19)

Application: Ferroelectric Opto-Toptronics



- Quantized ferroelectric topology is protected against thermal noise → future ultralow-power opto-electronics applications
- Billion-atom NNQMD revealed photo-induced topological phase-transition dynamics (*cf.* Kibble-Zurek mechanism in cosmology)
- Symmetry-controlled skyrmion-to-skyrmionium* switching *Composite of skyrmions with opposite topological charges

Linker et al., *Science Adv.* 8, eabk2625 ('22); *JPCL* 13, 11335 ('22)



Where to Go from Here

Detailed lecture notes are available at a USC course home page

EXTREME-SCALE QUANTUM SIMULATIONS

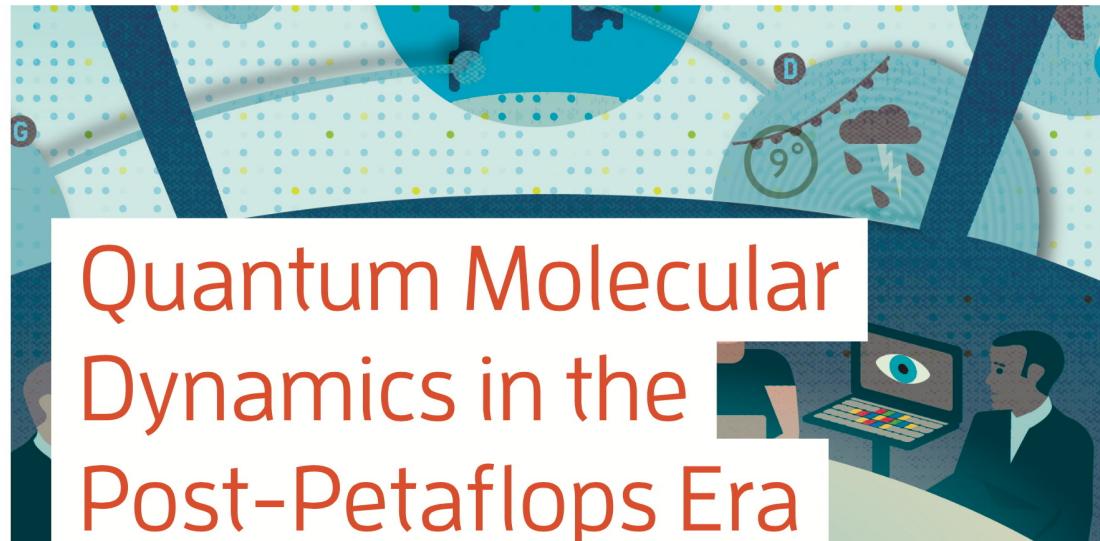
This course surveys & projects algorithmic & computing technologies that will make quantum-dynamics simulations metascalable, *i.e.*, "design once, continue to scale on future computer architectures".

<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.pdf>

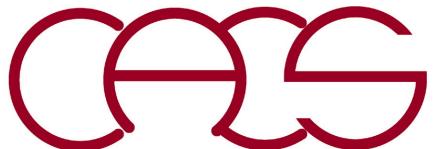
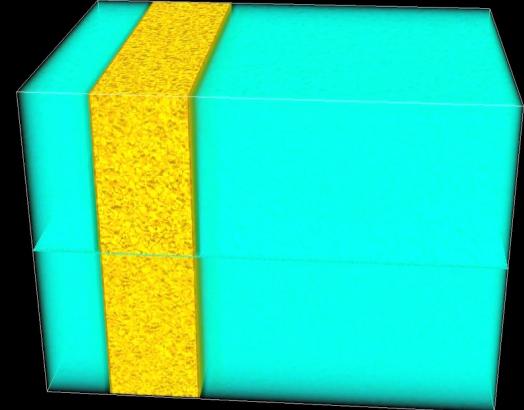
COVER FEATURE GRAND CHALLENGES IN SCIENTIFIC COMPUTING



Standard textbook: R. Martin, [*Electronic Structure*](#) (Cambridge Univ. Press, '20)

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,
CyberTraining Award OAC-2118061

