QXMD: Quantum Material Dynamics at the Nexus of Exascale Computing, Artificial Intelligence and Quantum Computing

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Collaborators:
F. Shimojo, K. Shimamura, S. Fukushima, (*Kumamoto, Japan*)

Excited States and Nonadiabatic Dynamics CyberTraining Workshop

Organizer: Prof. Alexey Akimov

June 21, 2021, University at Buffalo, SUNY

Outline

1. Introduction: Extreme-scale quantum simulations
2. Quantum molecular dynamics (QMD)
3. Nonadiabatic quantum molecular dynamics (NAQMD)
4. Moving forward: Quantum material dynamics at the nexus of exascale computing, artificial intelligence & quantum computing

Current & Future Computing Platforms

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

U.S. DEPARTMENT OF ENERGY
INCITE
LEADERSHIP COMPUTING

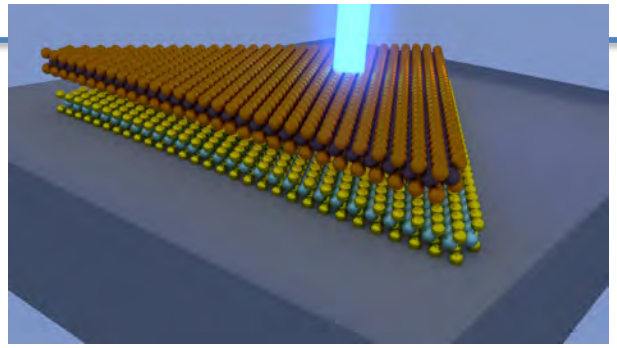
- **NAQMD & RMD simulations on full 800K cores**

Innovative & Novel Computational Impact on Theory & Experiment

Title: "Petascale Simulations for Layered Materials Genome"

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

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



AURORA | EARLY SCIENCE PROGRAM

Early Science Projects for Aurora Supercomputer Announced

Metascalable layered materials genome

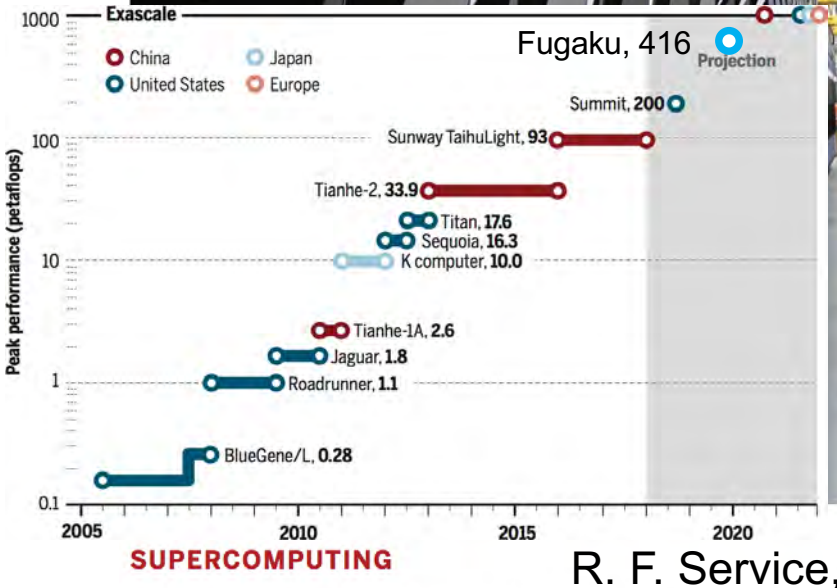
Investigator: Aiichiro Nakano, University of Southern California

Exaflop/s
Intel Aurora (forthcoming)

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

- **One of the 10 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.

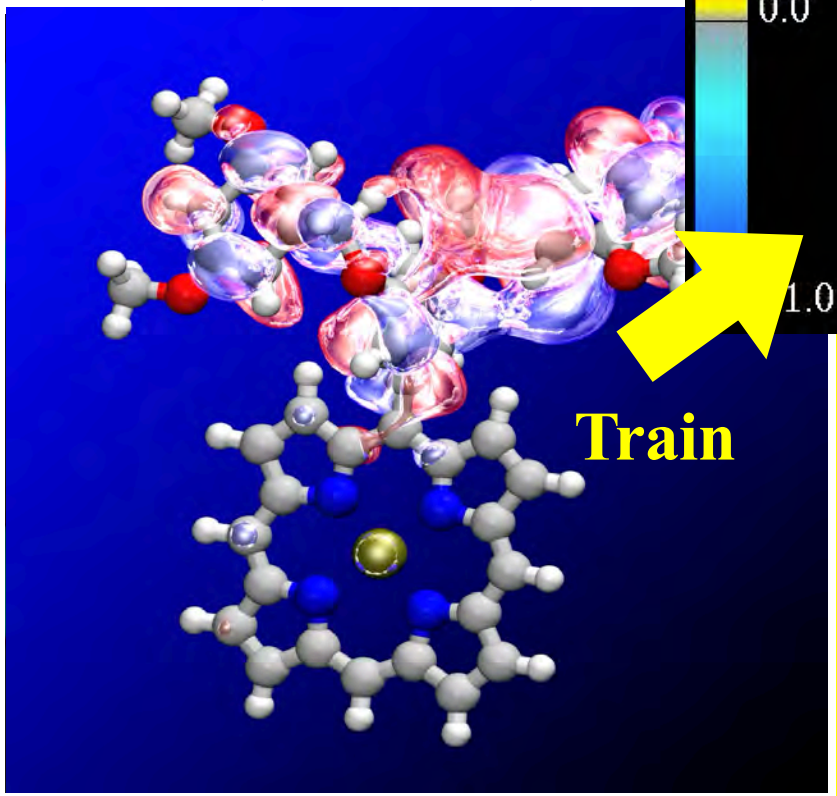
Exa(peta)flop/s = 10^{18} (10^{15}) floating-point operations per second

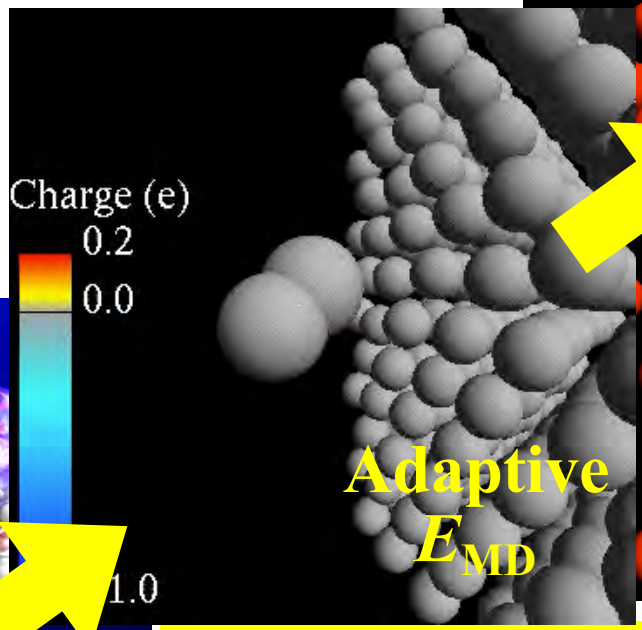
Simulation Engines: NAQMD & RMD

Molecular Dynamics (MD)

Reactive MD (RMD)

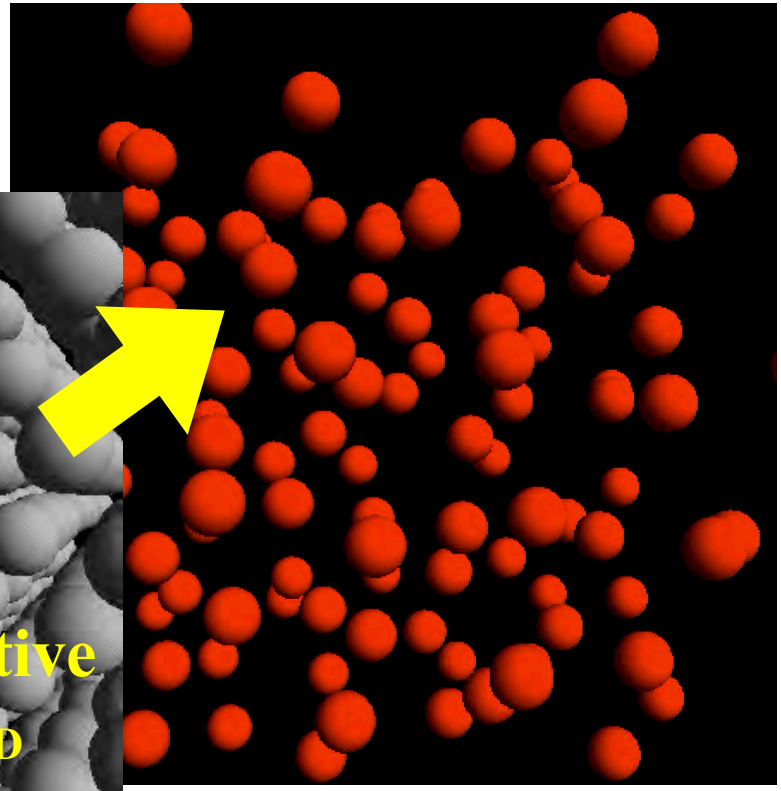
Nonadiabatic quantum MD (NAQMD)





Train

Adaptive E_{MD}

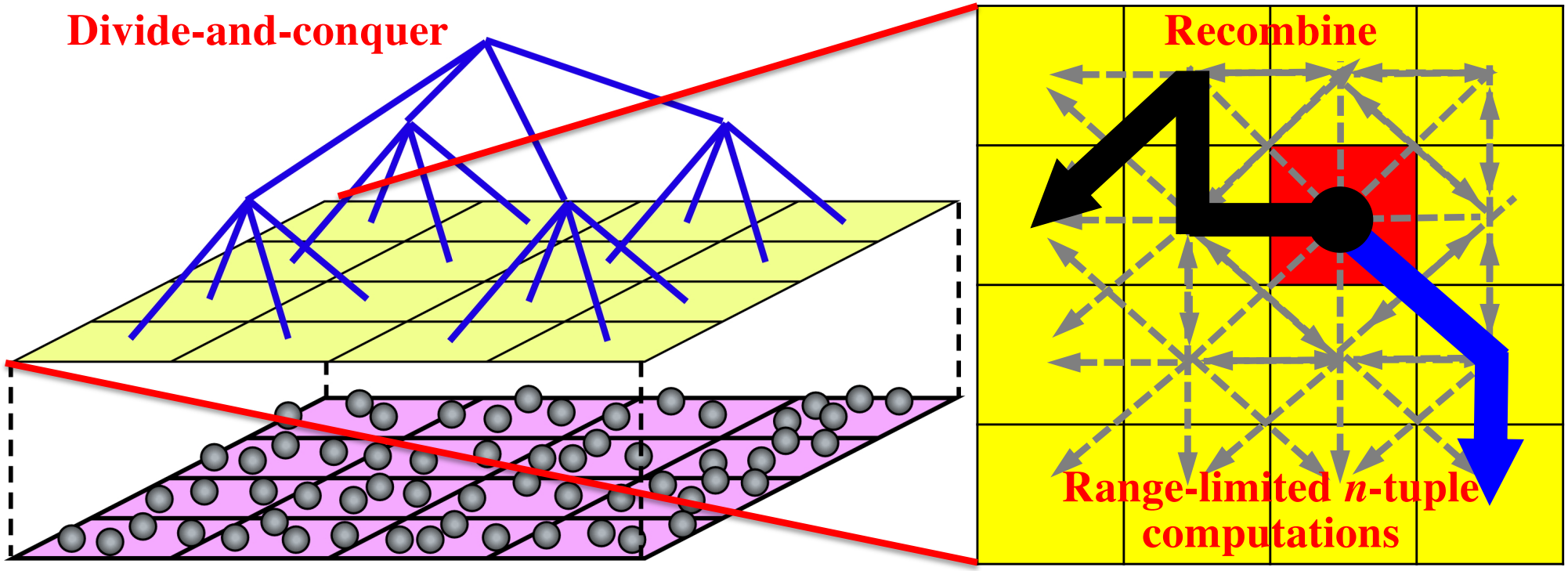


First principles-based reactive force-fields

- **Reactive bond order $\{BO_{ij}\}$**
  → Bond breakage & formation
- **Charge equilibration (QEq) $\{q_i\}$**
  → Charge transfer

Tersoff, Brenner, Sinnott *et al.*; Streitz & Mintmire *et al.*; van Duin & Goddard (ReaxFF)

Divide-Conquer-Recombine (DCR) Engines



M. Kunaseth *et al.*, *ACM/IEEE SC13*

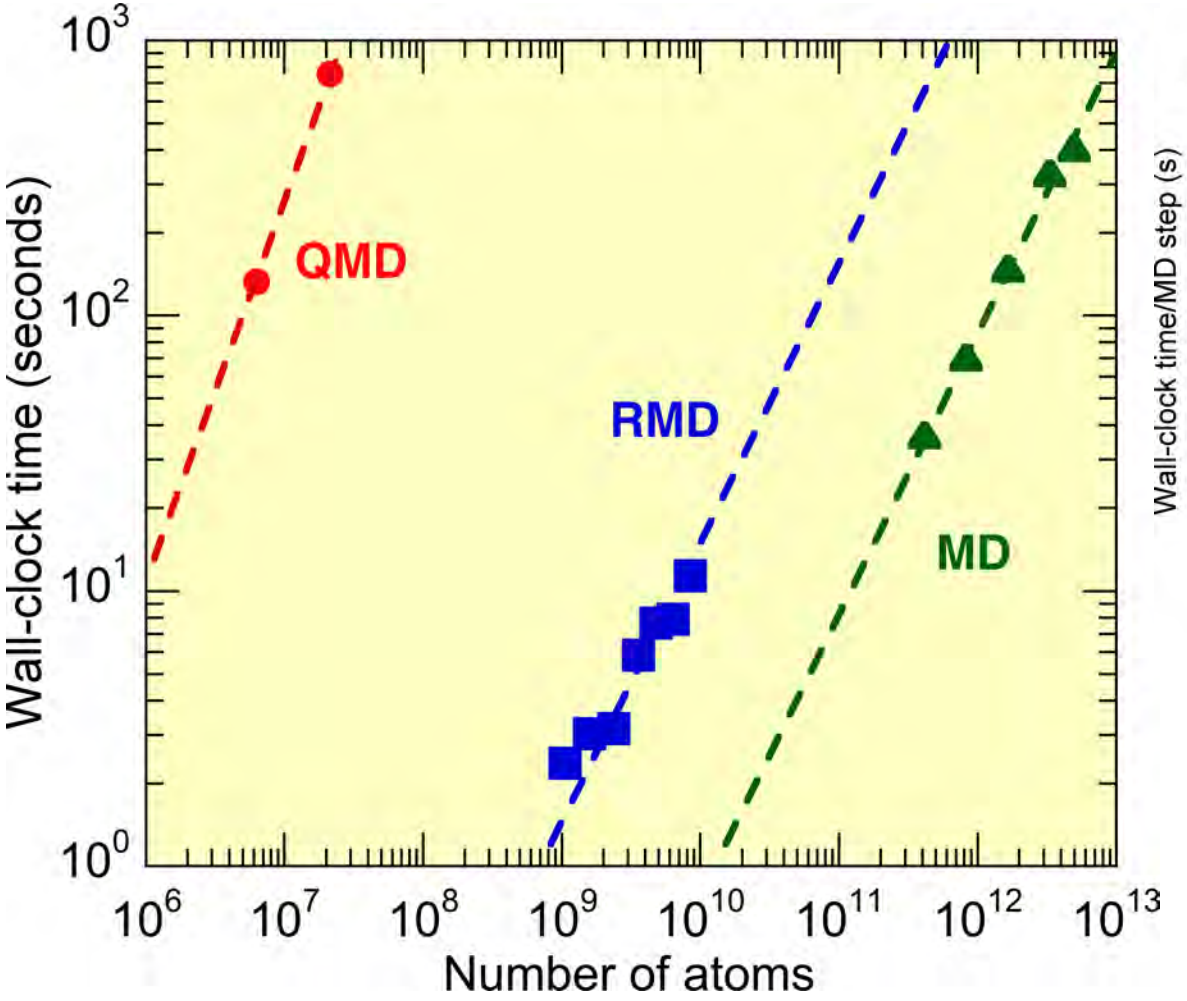
- **Lean divide-&-conquer density functional theory (LDC-DFT) algorithm minimizes the prefactor of $O(N)$ computational cost**

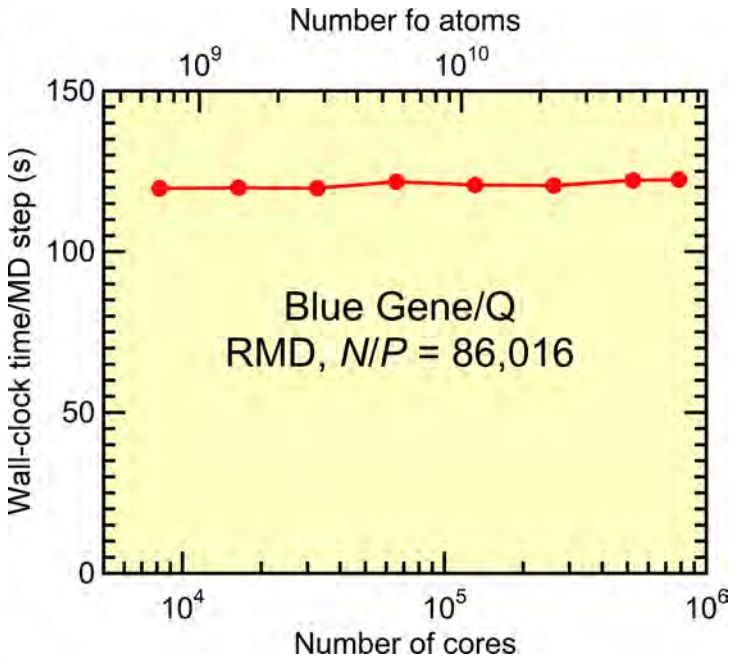
  F. Shimojo *et al.*, *J. Chem. Phys.* **140**, 18A529 ('14); K. Nomura *et al.*, *IEEE/ACM SC14*

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

  K. Nomura *et al.*, *Comput. Phys. Commun.* **192**, 91 ('15); K. Liu *et al.*, *IEEE/ACM ScalA18*

Scalable Simulation Algorithm Suite





QMD (quantum molecular dynamics): DC-DFT

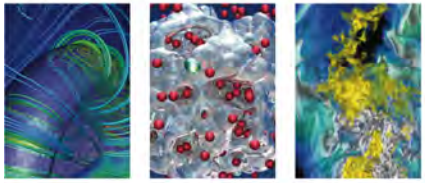
RMD (reactive molecular dynamics): F-ReaxFF

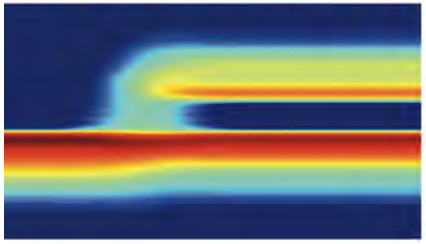
MD (molecular dynamics): MRMD

- **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

BES





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An Office of Science review sponsored jointly by
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NOVEMBER 3–5, 2015

ROCKVILLE, MARYLAND

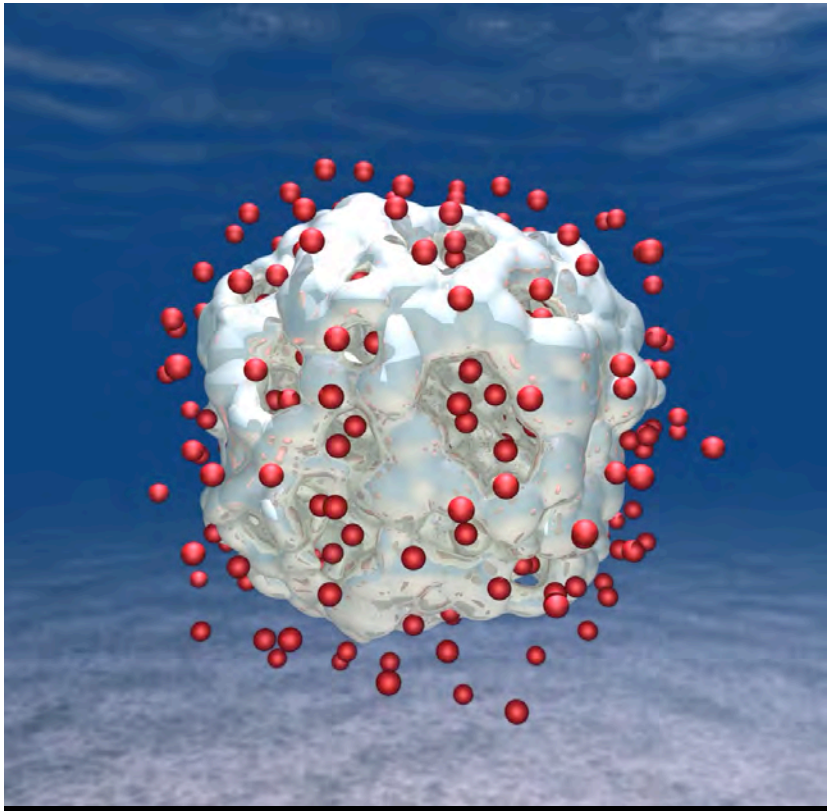
U.S. DEPARTMENT OF ENERGY

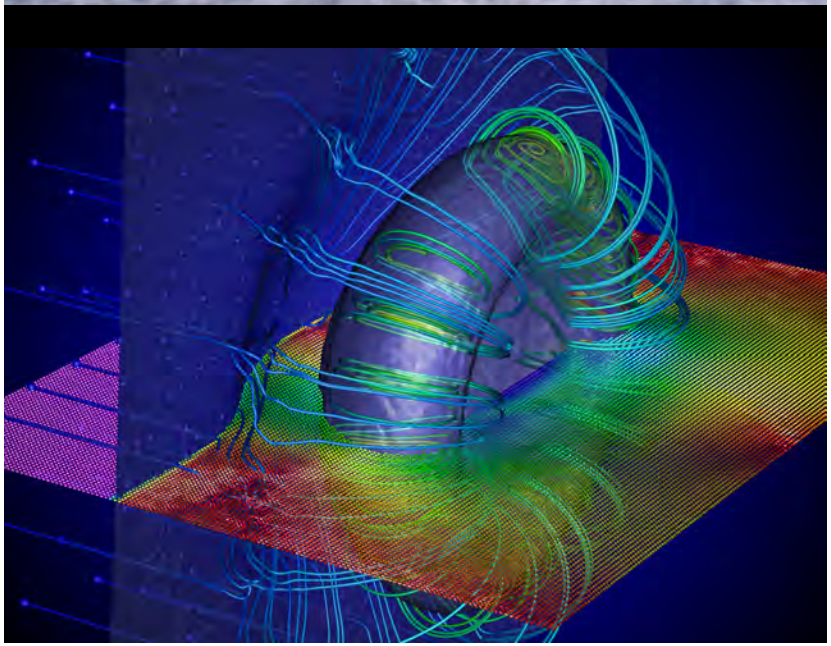
16,661-atom QMD

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

10^9-atom RMD

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





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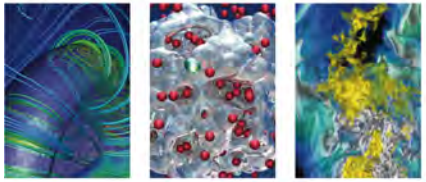

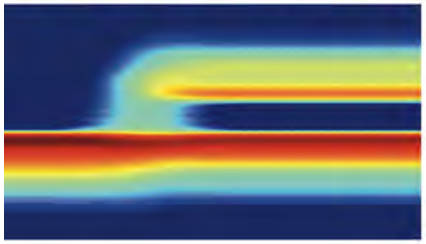

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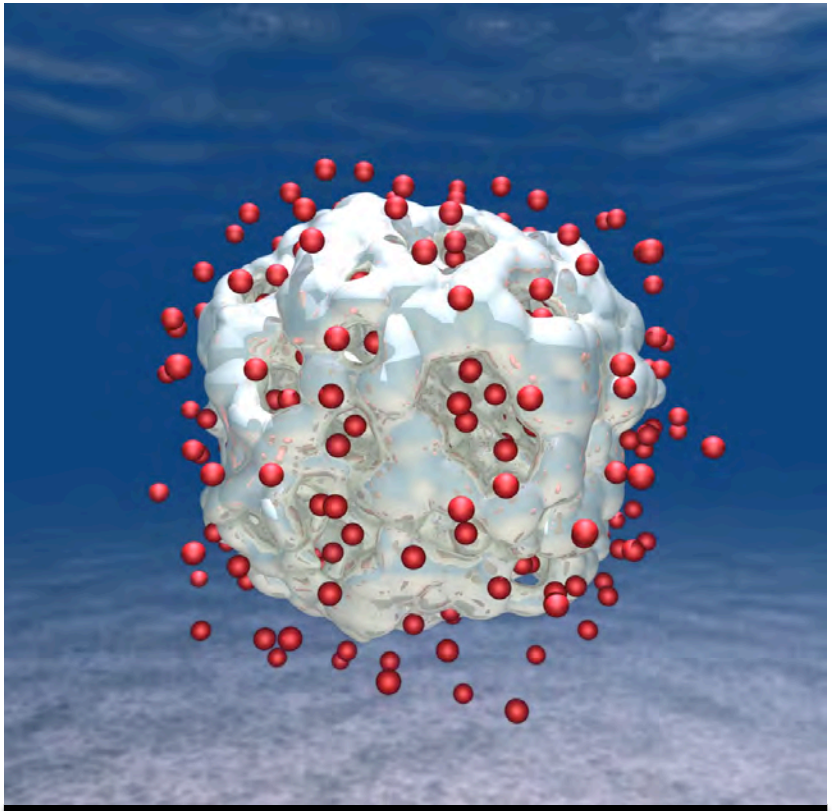
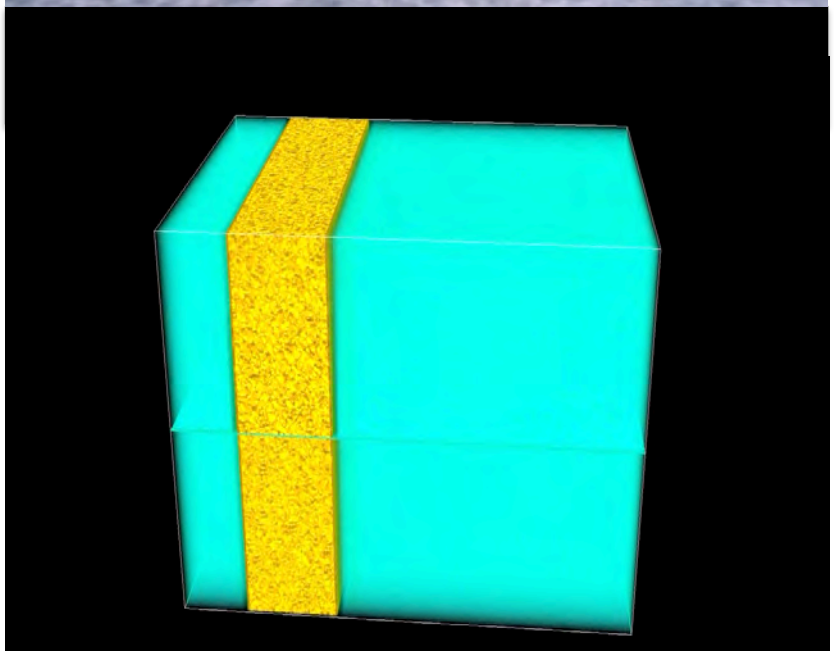
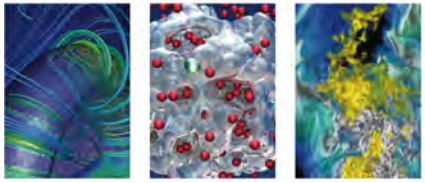
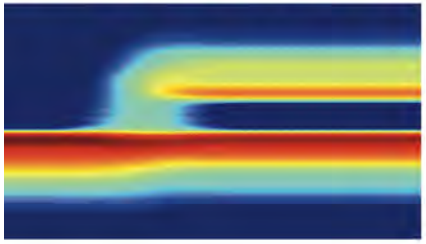




BES

EXASCALE COMPUTING FOR SCIENCE





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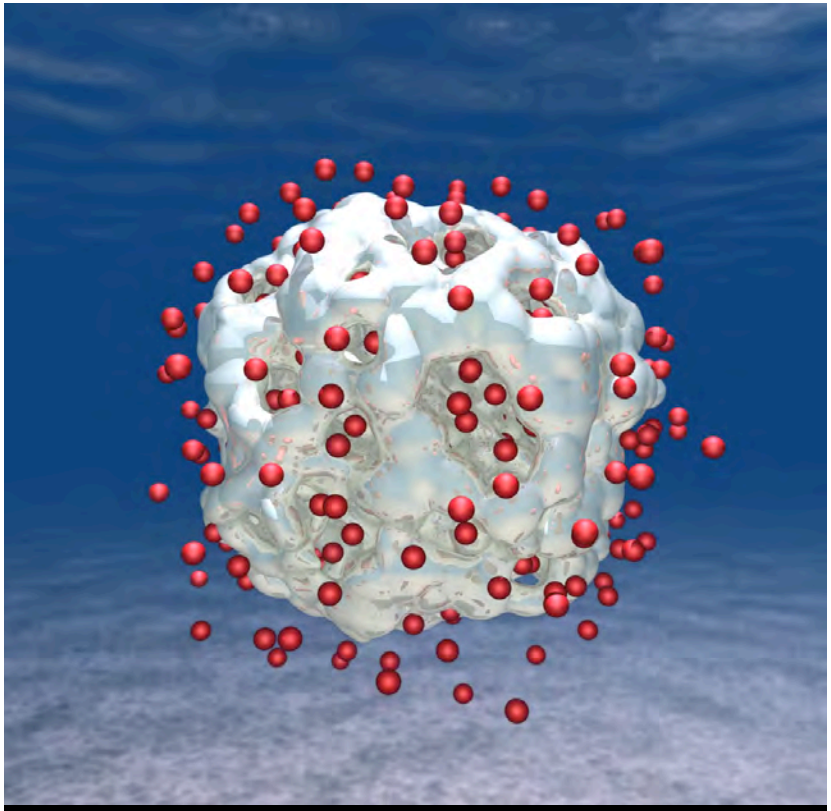

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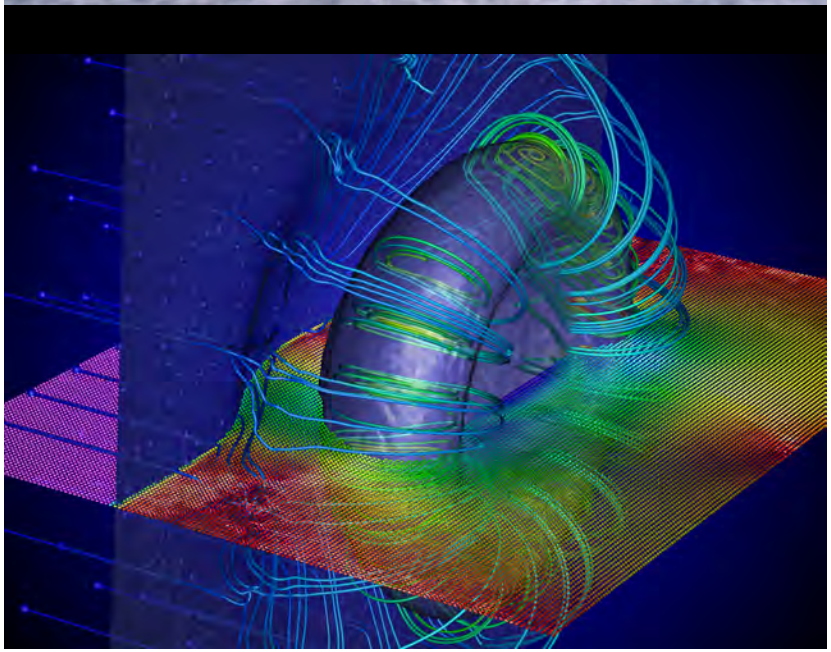

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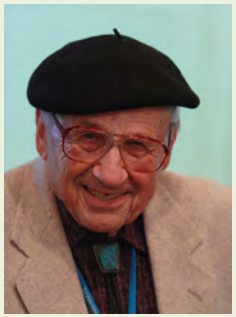
Quantum Molecular Dynamics (QMD)

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

First molecular dynamics using an empirical interatomic interaction

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



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

Density functional theory (DFT)

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

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

$O(C^N)$ → $O(N^3)$

1 *N*-electron problem intractable → ***N* 1-electron problems tractable**

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

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 nice review** [Bowler & Miyazaki, *Rep. Prog. Phys*. **75**, 036503 ('12)]

Complexity Reduction: Density Functional Theory

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

  Proved 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

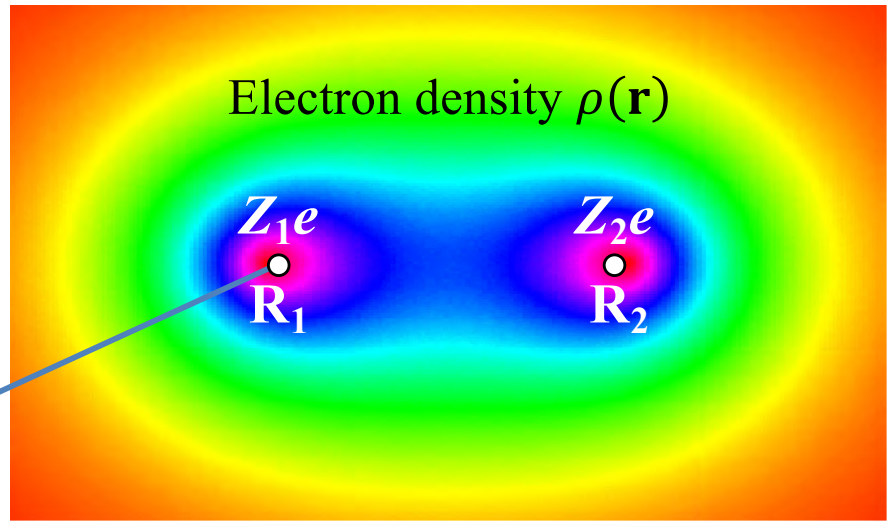
$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})]$$

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**

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

KS wave function — KS energy

- **KS potential**

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

exchange-correlation (xc) potential

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

step function — chemical potential

$$v_{\mathrm{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\mathrm{xc}}}{\delta\rho(\mathbf{r})}$$

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

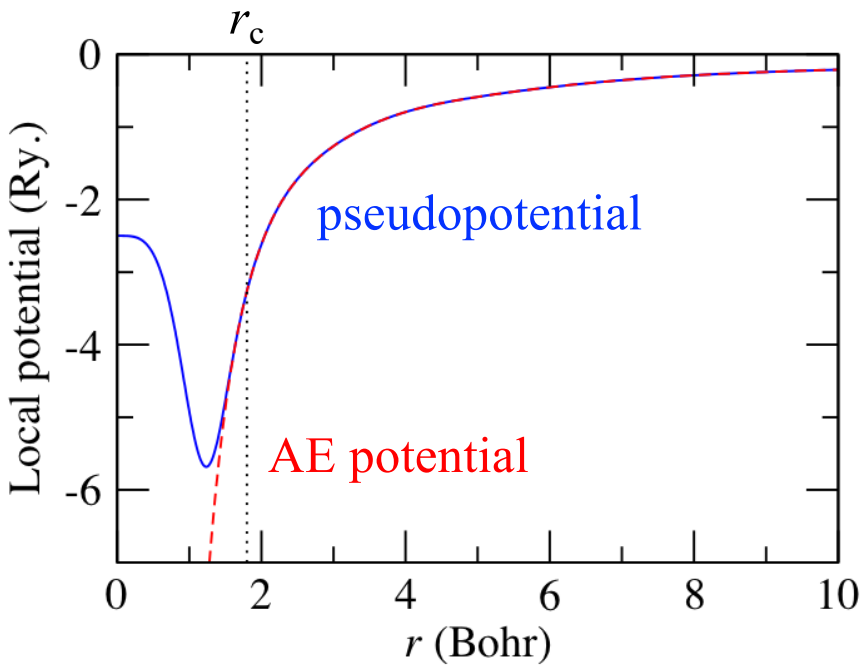
W. Kohn & L. J. Sham,
"Self-consistent equations including exchange and correlation effects,"
Phys. Rev. **140**, A1133 ('65)

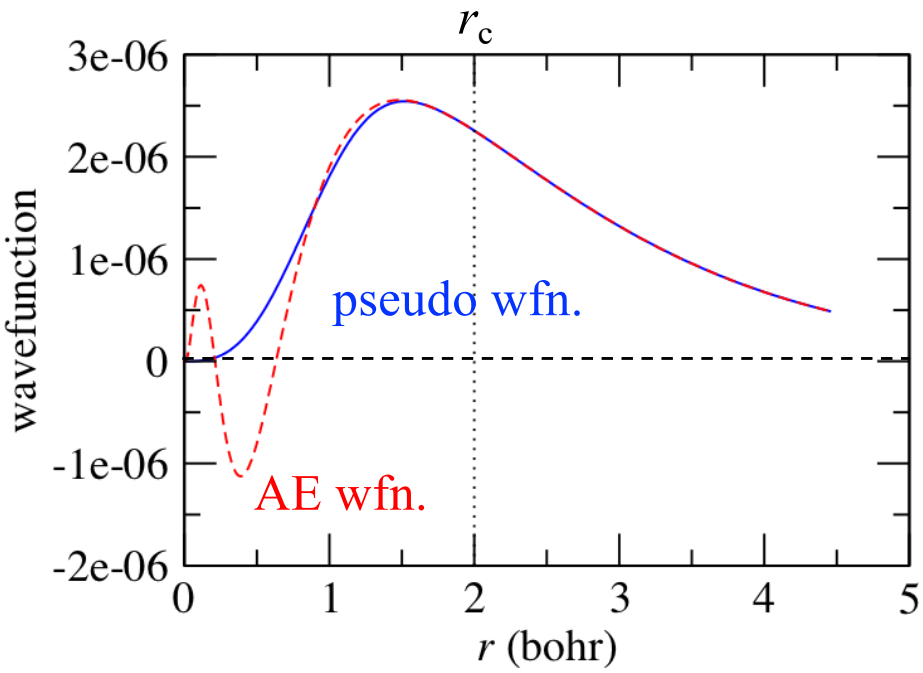
Abstraction: Exchange-Correlation Functional

- **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**
    $\delta E_{\mathrm{LDA+U}}/\delta n_i = \epsilon_{\mathrm{LDA}} + U(\frac{1}{2} - n_i)$
    Anisimov *et al*., *Phys. Rev. B* **44**, 943 ('91)
  - > **DFT-D: van der Waals (vDW) functional for molecular crystals & layered materials**
    $E_{\mathrm{disp}} = -s_6 \sum_{i<j} \frac{C_{ij}}{R_{ij}^6} f_{\mathrm{damp}}(R_{ij})$
    Grimme, *J. Comput. Chem*. **25**, 1463 ('04); *J. Chem. Phys*. **132**, 154104 ('10)
  - > **vdW: Nonlocal correlation functional**
    $E_{\mathrm{c}}^{\mathrm{nl}} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \, \rho(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$
    Dion *et al*., *Phys. Rev. Lett*. **92**, 246401 ('04)

Abstraction: Pseudopotential

- **Consider only (chemically active) valence electrons**
  ***e.g.* silicon — $1s^2 2s^2 2p^6 3s^2 3p^2$**
- **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 (SCF) 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 $\rho(\mathbf{r})$

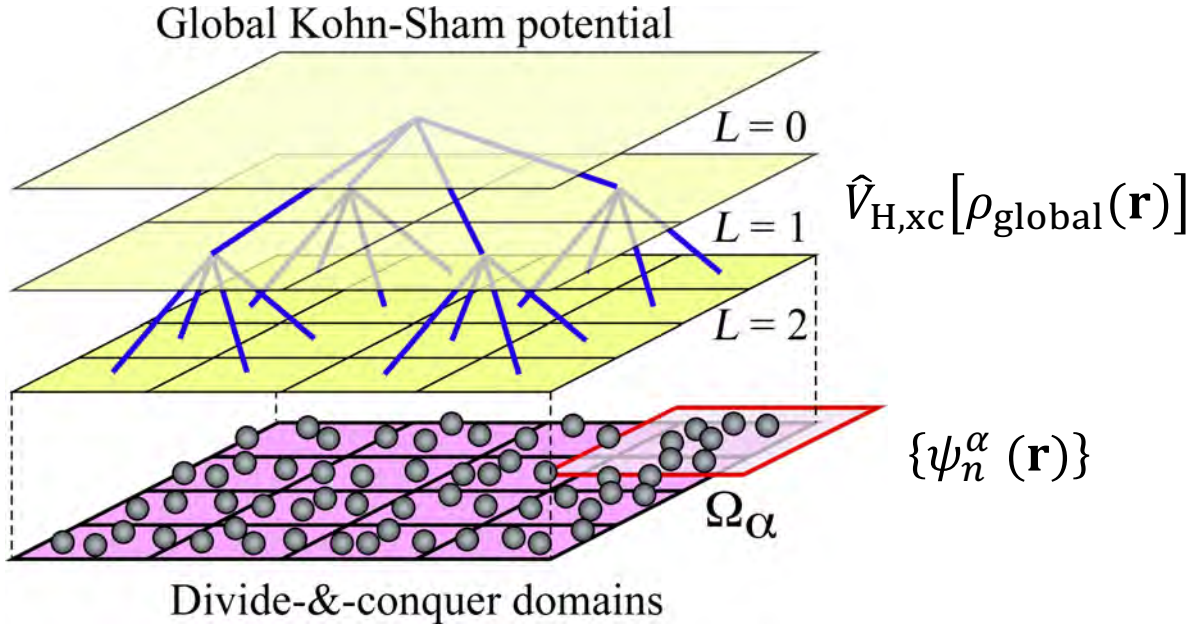
$$\rho(\mathbf{r})=\sum_n |\psi_n(\mathbf{r})|^2\,\Theta(\mu-\epsilon_n)$$

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

Divide-&-Conquer Density Functional Theory



- **Overlapping spatial domains:** $\Omega = \cup_\alpha \Omega_\alpha$
- **Domain Kohn-Sham equations**

Global-local self-consistent field (SCF) iteration

$$\left(-\frac{1}{2}\nabla^2 + \hat{V}_{\mathrm{ion}} + \hat{V}_{\mathrm{H,xc}}[\rho_{\mathrm{global}}(\mathbf{r})]\right)\psi_n^\alpha(\mathbf{r}) = \epsilon_n^\alpha \psi_n^\alpha(\mathbf{r})$$

- **Global & domain electron densities**

$$\rho_{\mathrm{global}}(\mathbf{r}) = \Sigma_\alpha\, p_\alpha(\mathbf{r})\rho_\alpha(\mathbf{r}) \leftarrow \rho_\alpha(\mathbf{r}) = \Sigma_n |\psi_n^\alpha|^2\, \Theta(\mu - \epsilon_n^\alpha)$$

Domain support function

$$\Sigma_\alpha\, p_\alpha(\mathbf{r}) = 1$$

Global chemical potential

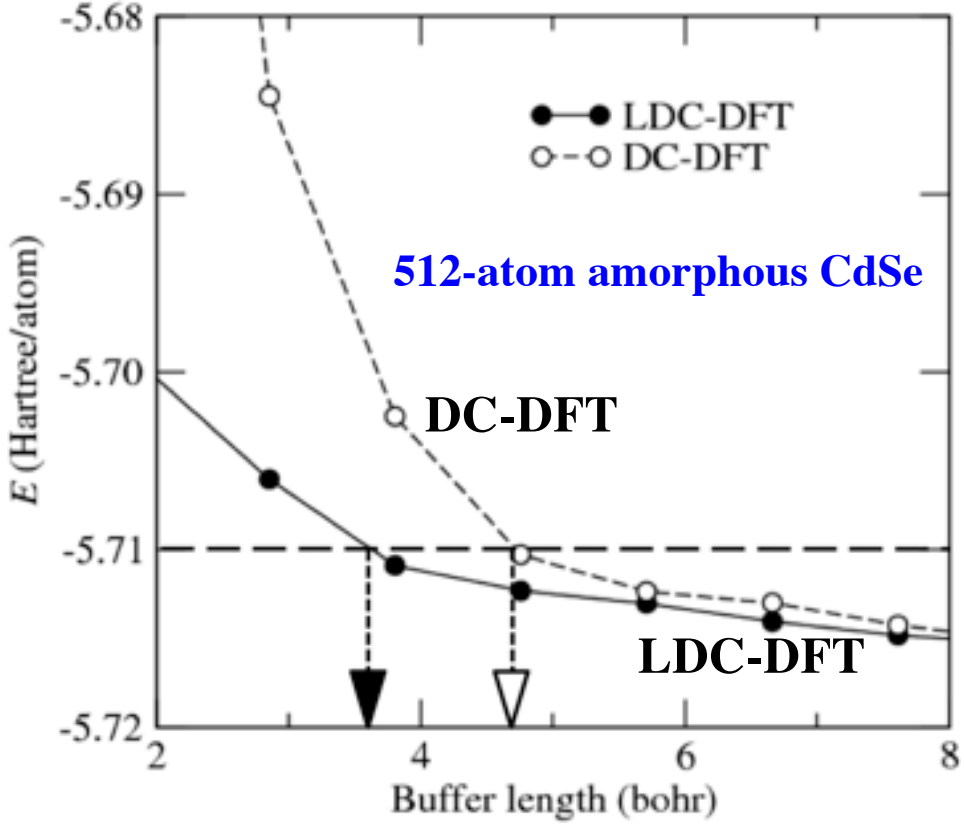
$$N = \int d\mathbf{r}\, \rho_{\mathrm{global}}(\mathbf{r})$$

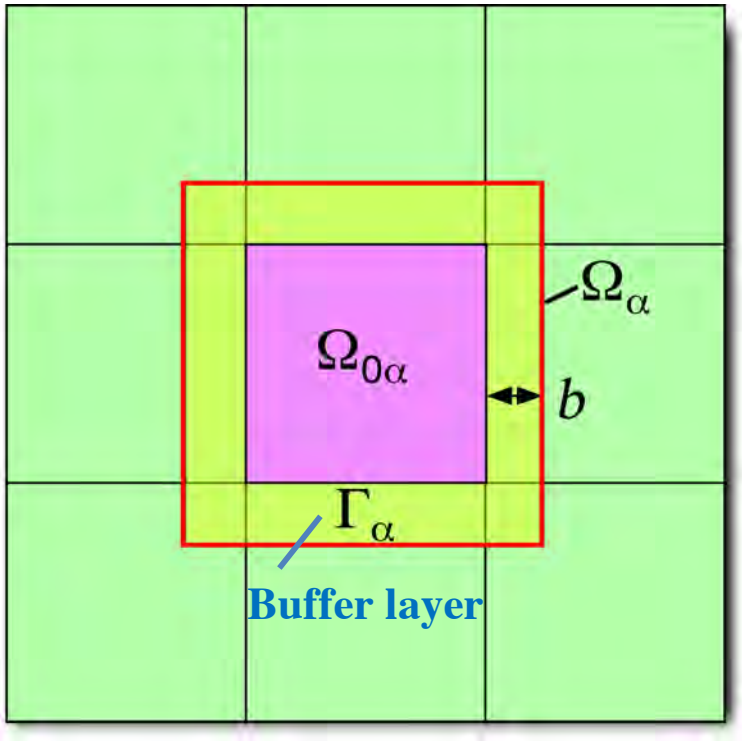
Lean Divide-&-Conquer (LDC) DFT

- **Density-adaptive boundary potential to reduce the $O(N)$ prefactor**

$$v_\alpha^{\mathrm{bc}}(\mathbf{r}) = \int d\mathbf{r}' \frac{\partial v(\mathbf{r})}{\partial \rho(\mathbf{r}')}\Big(\rho_\alpha(\mathbf{r}) - \rho_{\mathrm{global}}(\mathbf{r})\Big) \cong \frac{\rho_\alpha(\mathbf{r}) - \rho_{\mathrm{global}}(\mathbf{r})}{\xi}$$

- **More rapid energy convergence of LDC-DFT compared with nonadaptive DC-DFT**



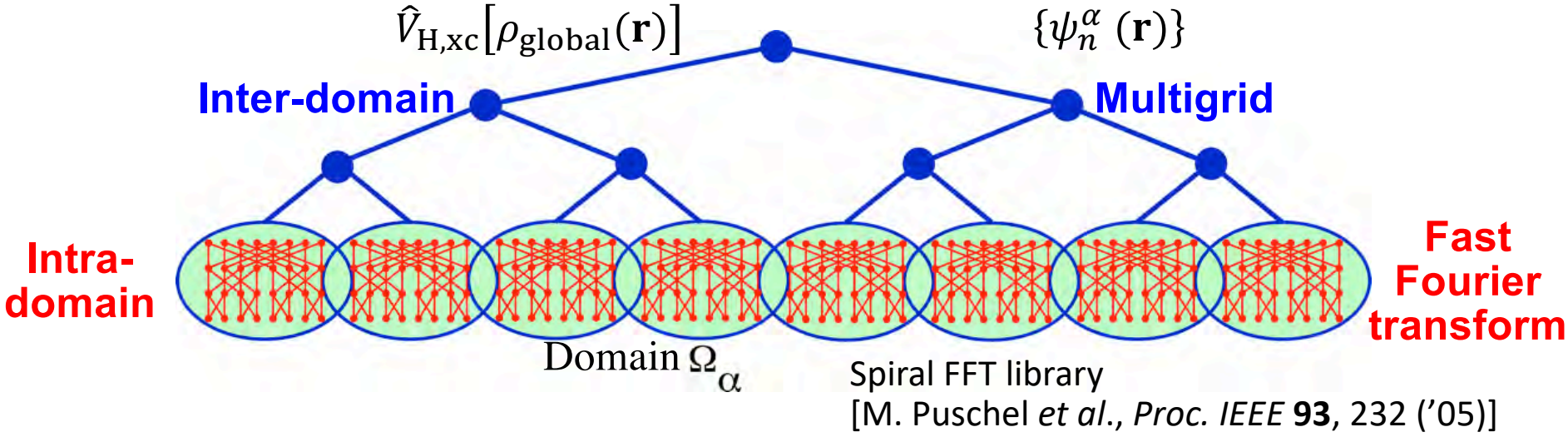


- **Factor 2.03 (for ν = 2) ~ 2.89 (for ν = 3) reduction of the computational cost with an error tolerance of 5×10^{-3} a.u. (per-domain complexity: n^ν)**

F. Shimojo *et al.*, *J. Chem. Phys.* **140**, 18A529 ('14)

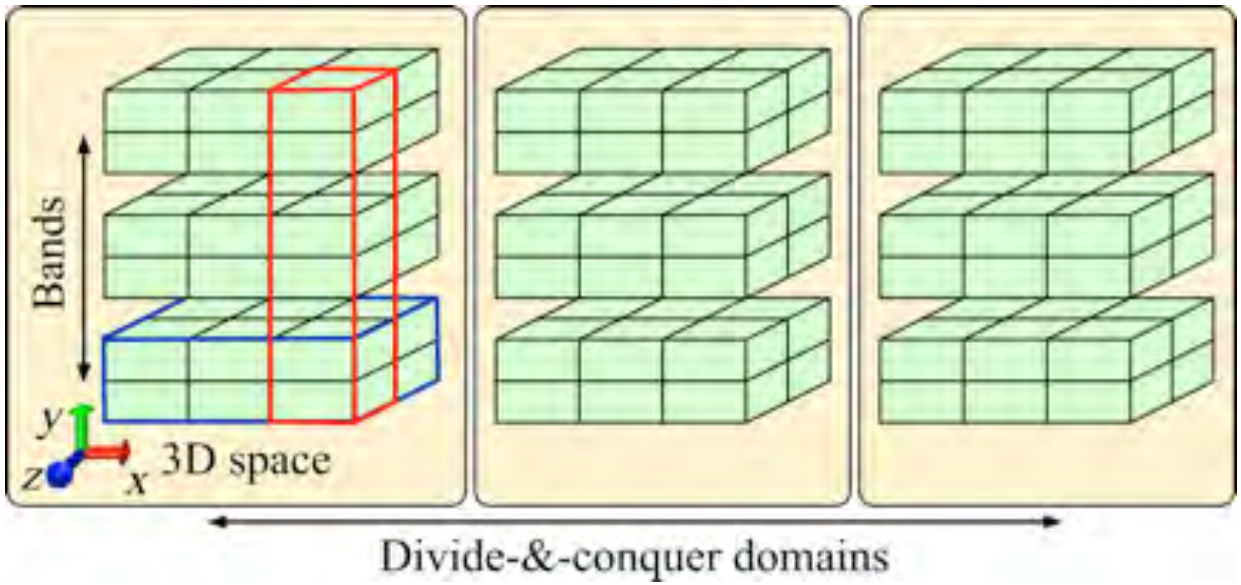
Hierarchical Computing

- **Globally scalable (real-space multigrid) + locally fast (plane wave) electronic solver**



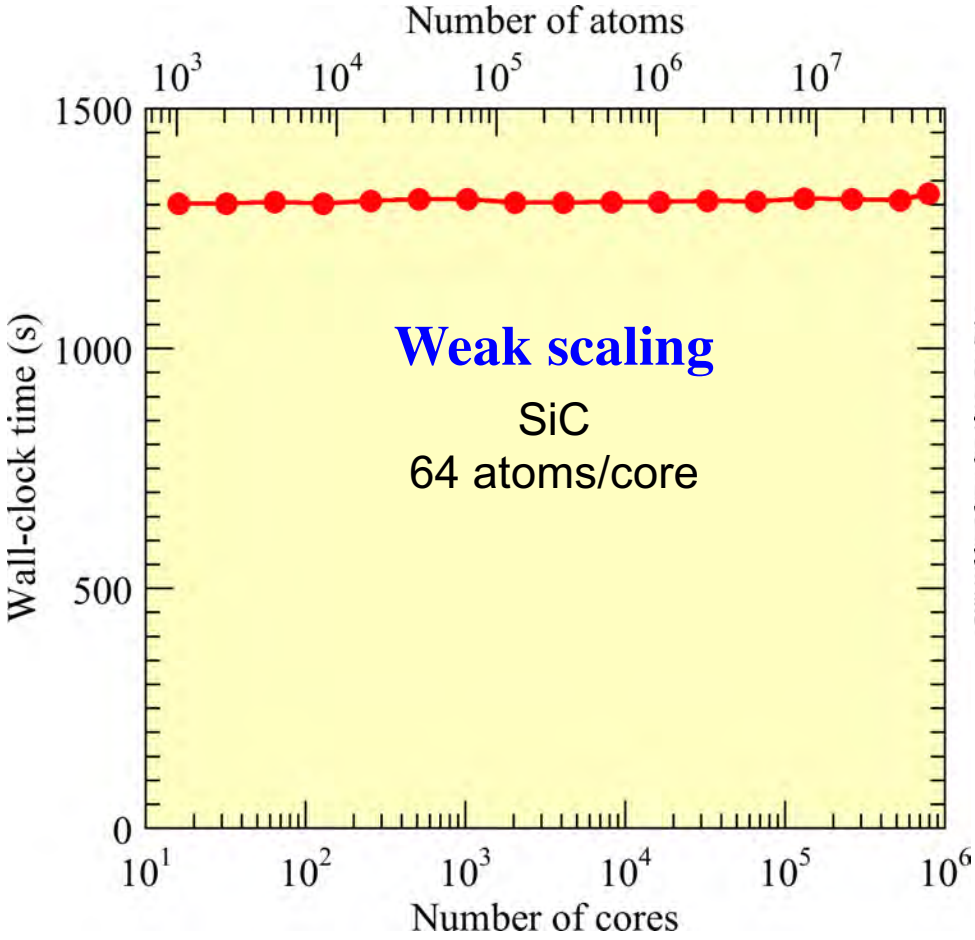
Spiral FFT library
[M. Puschel *et al.*, *Proc. IEEE* **93**, 232 ('05)]

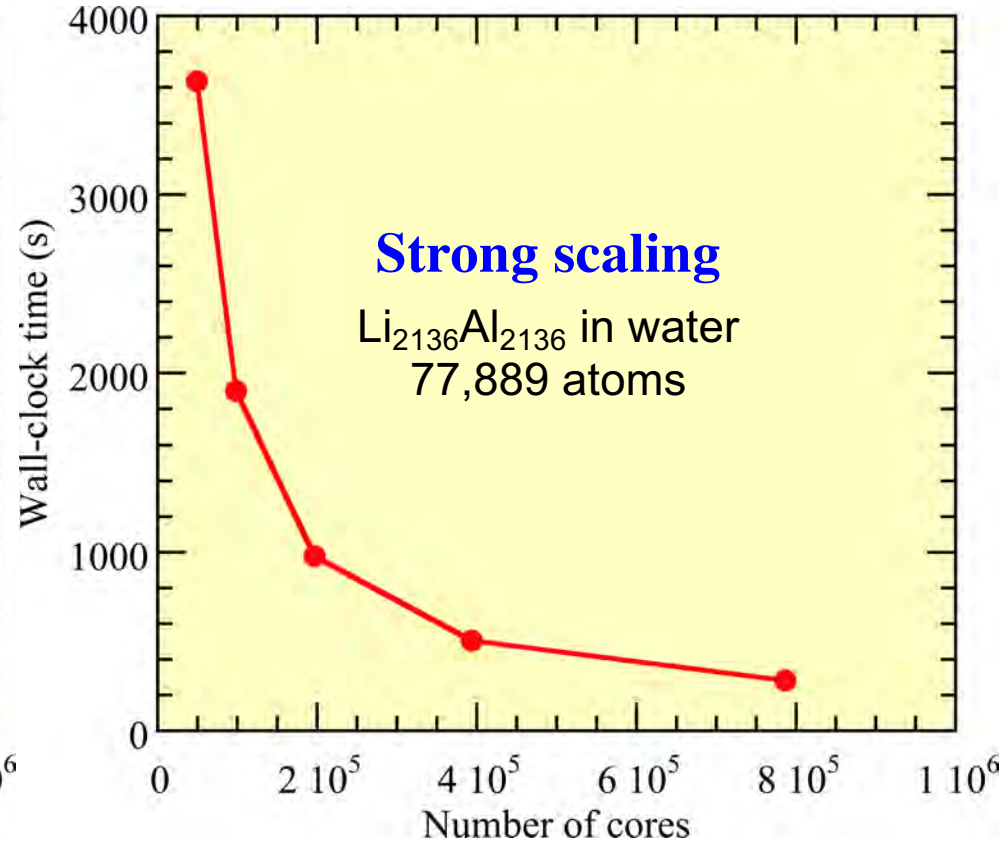
- **Hierarchical band (*i.e.* Kohn-Sham orbital) + space + domain (BSD) decomposition**



Parallel Performance

- **Weak-scaling parallel efficiency is 0.984 on 786,432 Blue Gene/Q cores for a 50,331,648-atom SiC system**
- **Strong-scale parallel efficiency is 0.803 on 786,432 Blue Gene/Q cores**





- **62-fold reduction of time-to-solution** [441 s/SCF-step for 50.3M atoms] **from the previous state-of-the-art** [55 s/SCF-step for 102K atoms, Osei-Kuffuor *et al.*, *PRL* '14]

K. Nomura *et al.*, *IEEE/ACM Supercomputing, SC14* ('14)

Floating Point Performance

- **Transform from band-by-band to all-band computations to utilize a matrix-matrix subroutine (DGEMM) in the level 3 basic linear algebra subprograms (BLAS3) library**
- **Algebraic transformation of computations**

Example: Nonlocal pseudopotential operation

D. Vanderbilt, *Phys. Rev. B* **41**, 7892 ('90)

$$\hat{v}_{\mathrm{nl}}|\psi_n^\alpha\rangle = \sum_I^{N_{\mathrm{atom}}} \sum_{ij}^{L_{\mathrm{max}}} |\beta_{i,I}\rangle D_{ij,I} \langle\beta_{j,I}|\psi_n^\alpha\rangle \quad (n = 1, \ldots, N_{\mathrm{band}})$$

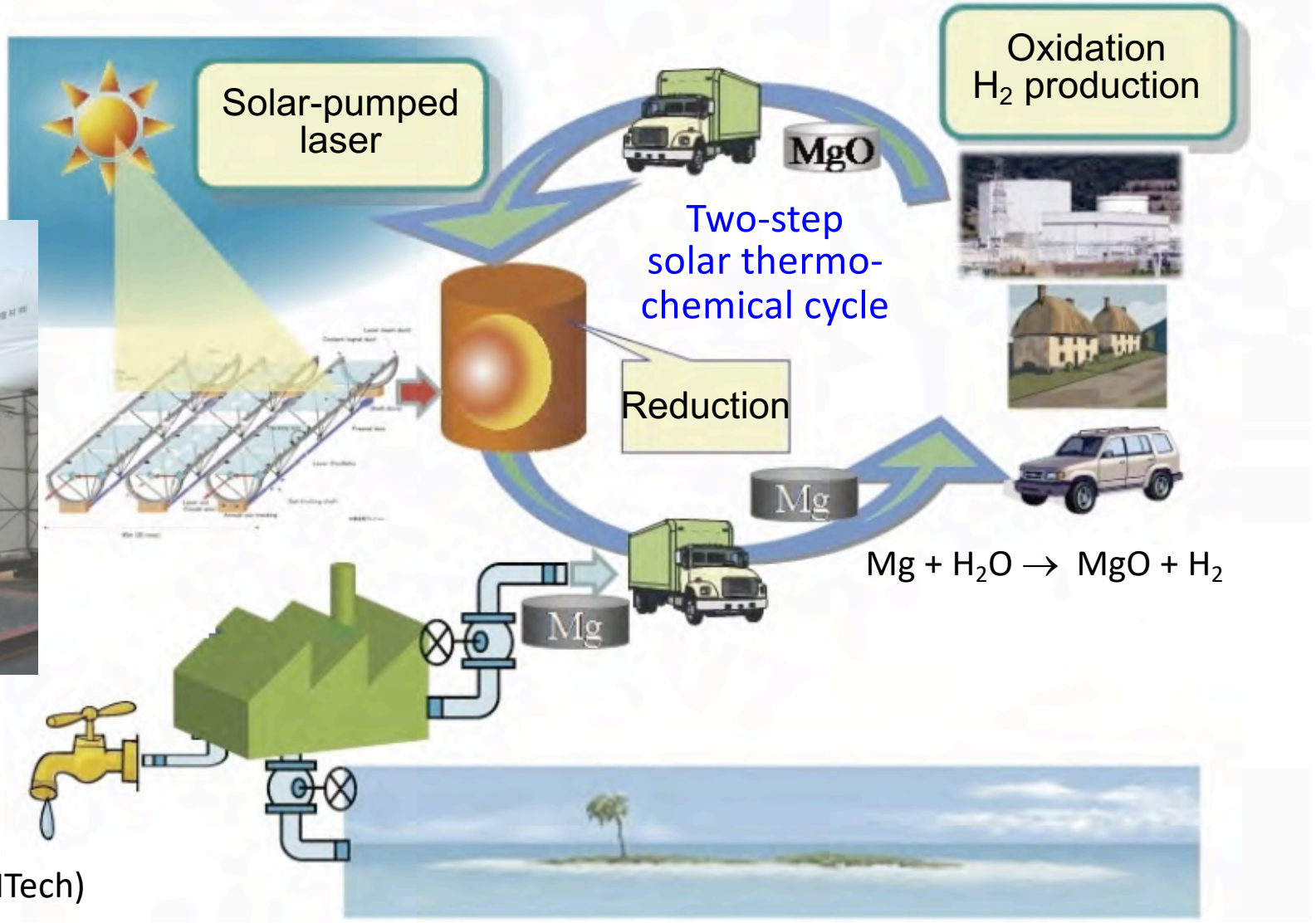
$$\boldsymbol{\Psi} = \left[|\psi_1^\alpha\rangle, \ldots, |\psi_{N_{\mathrm{band}}}^\alpha\rangle\right] \widetilde{\mathbf{B}}(i) = \left[|\beta_{i,1}\rangle, \ldots, |\beta_{i,N_{\mathrm{atom}}}\rangle\right] \left[\widetilde{\mathbf{D}}(i,j)\right]_{I,J} = D_{ij,I}\delta_{IJ}$$

$$\hat{v}_{\mathrm{nl}}\boldsymbol{\Psi} = \sum_{i,j}^{L} \widetilde{\mathbf{B}}(i)\widetilde{\mathbf{D}}(i,j)\widetilde{\mathbf{B}}(j)^T$$

- **50.5% of the theoretical peak FLOP/s performance on 786,432 Blue Gene/Q cores (entire Mira at the Argonne Leadership Computing Facility)**
- **55% of the theoretical peak FLOP/s on Intel Xeon E5-2665**

K. Nomura *et al.*, *IEEE/ACM Supercomputing, SC14* ('14)

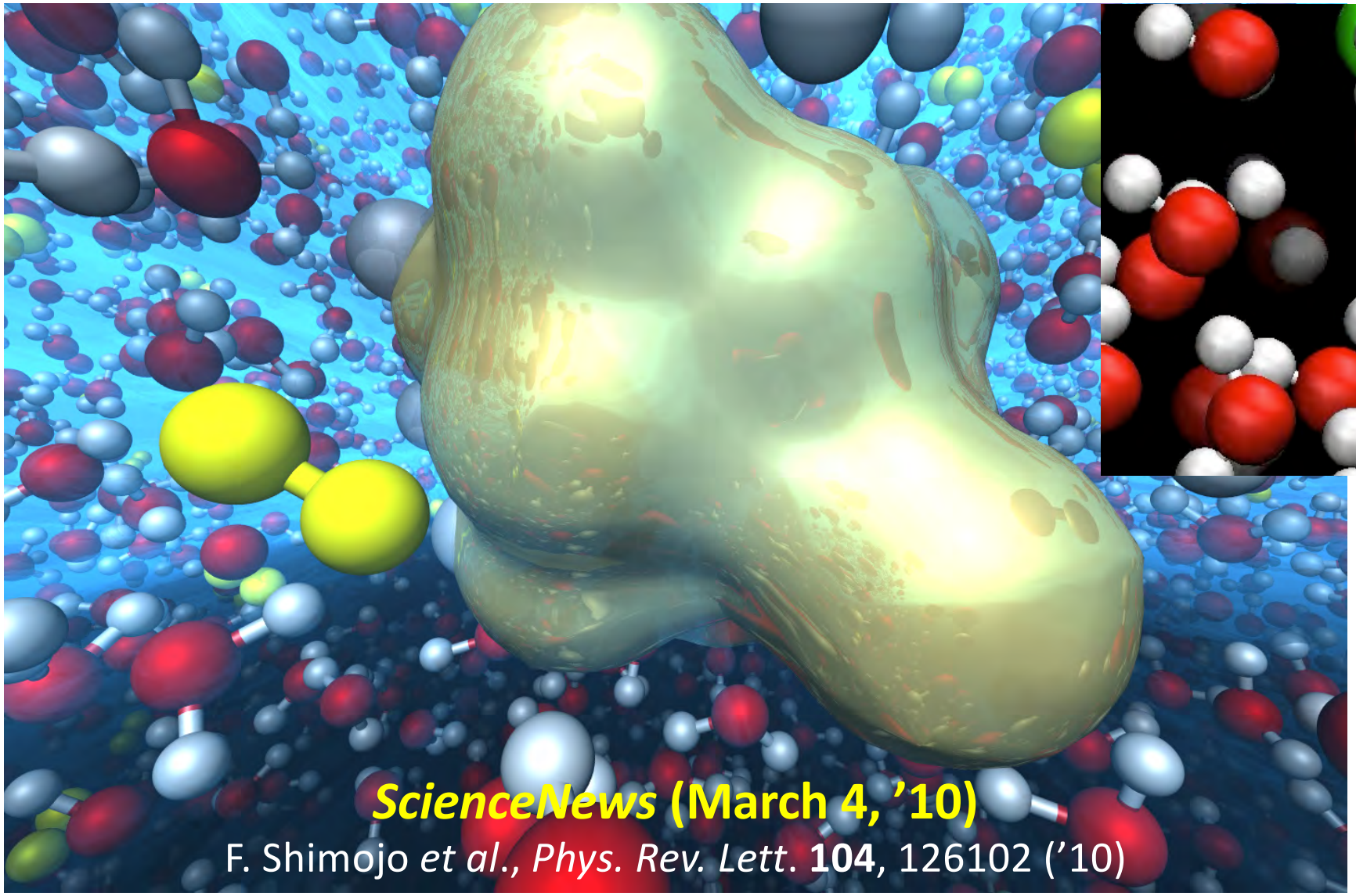
Renewal Energy Cycle by Metal Carriers



T. Yabe (TITech)

- **Problem: Accelerated hydrogen-production reaction kinetics for metal (Mg, Al, Zn, Fe) + water?**

Nanotechnology Solution



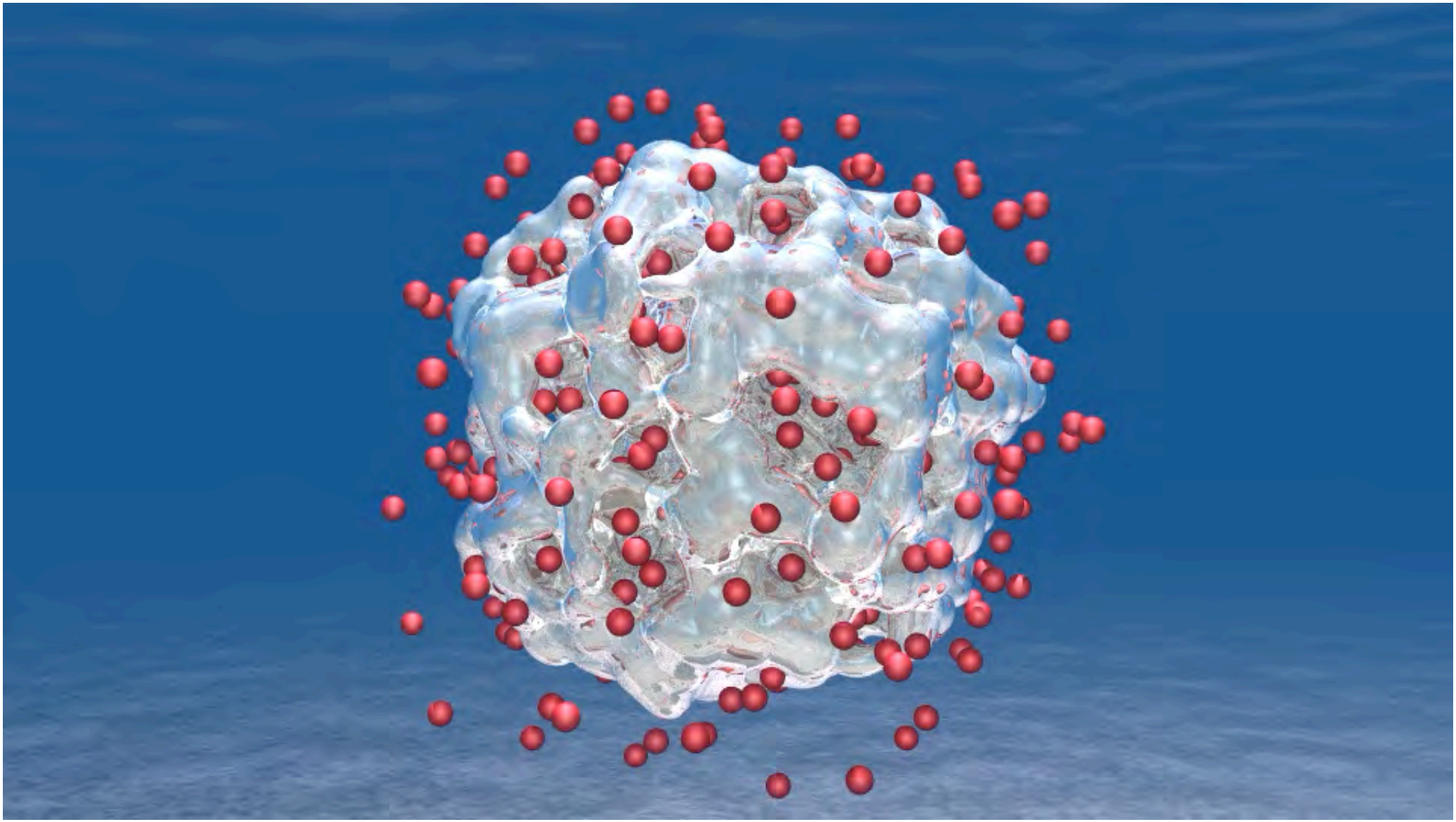
- **QMD simulation shows rapid H_2 production from water by a superatom* (Al_{17}), but the technology is not scalable to larger particle sizes**

*Roach, Castleman, Khanna *et al.*, *Science* **323**, 492 ('09)

H_2 Production from Water Using LiAl Particles

16,661-atom QMD simulation of $Li_{441}Al_{441}$ in water on 786,432 IBM Blue Gene/Q cores

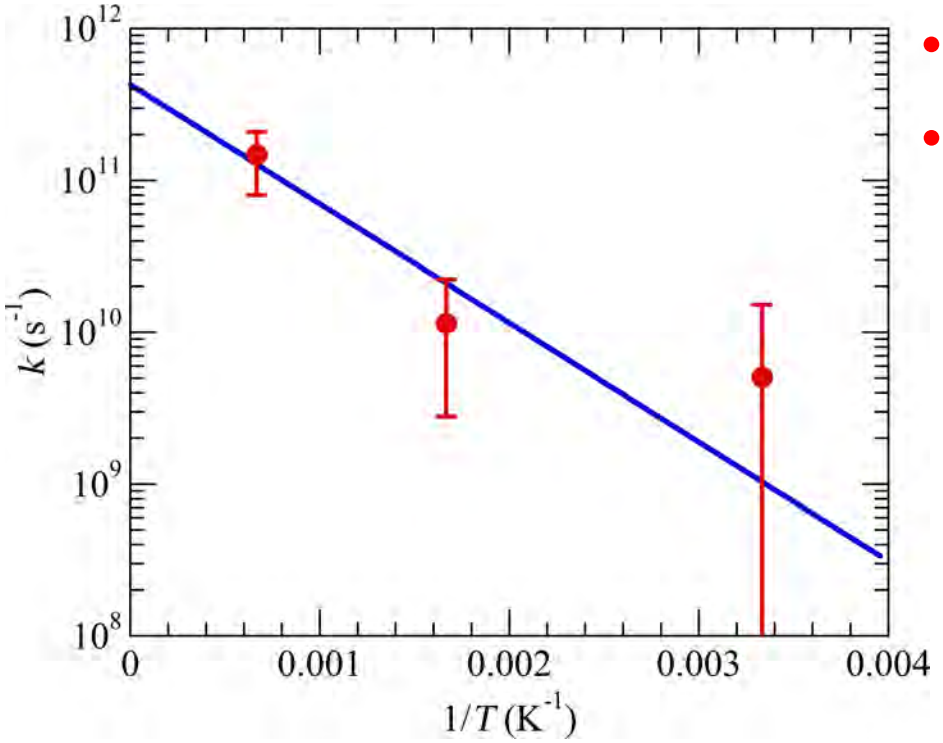
K. Shimamura *et al.*, *Nano Lett*. **14**, 4090 ('14)



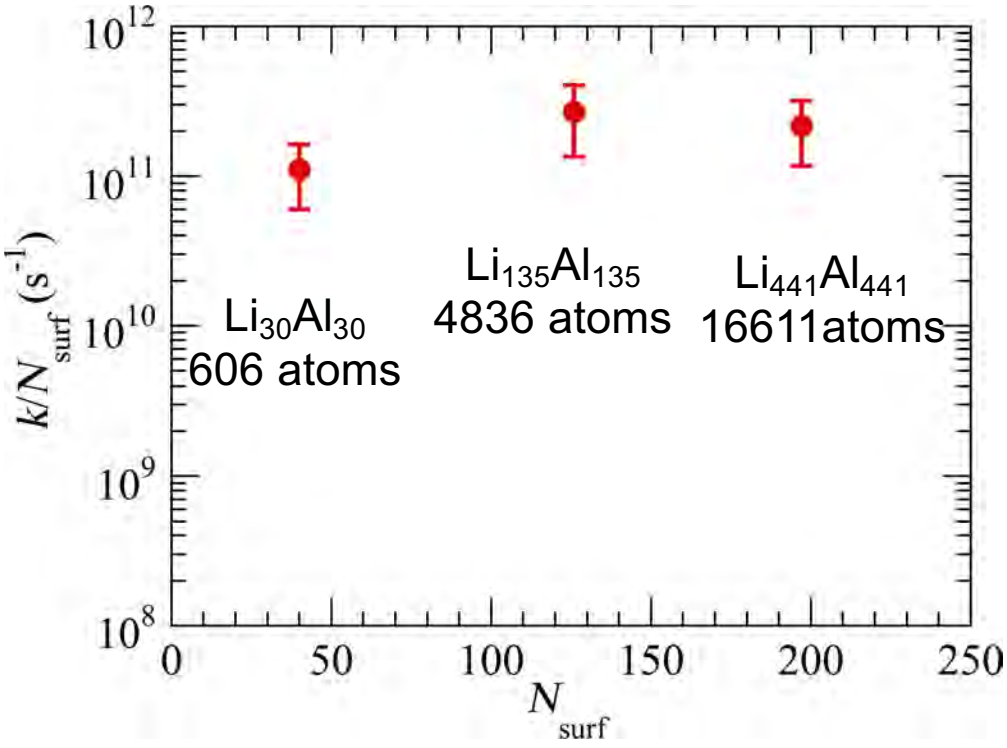
21,140 time steps (129,208 self-consistent-field iterations)

Rapid & Scalable H_2 Production

- **Orders-of-magnitude faster H_2 production from water than with pure Al**



- **Activation barrier = 0.068 eV**
- **Reaction rate = 1.04×10^{9} (s^{-1}) per LiAl pair at 300 K**



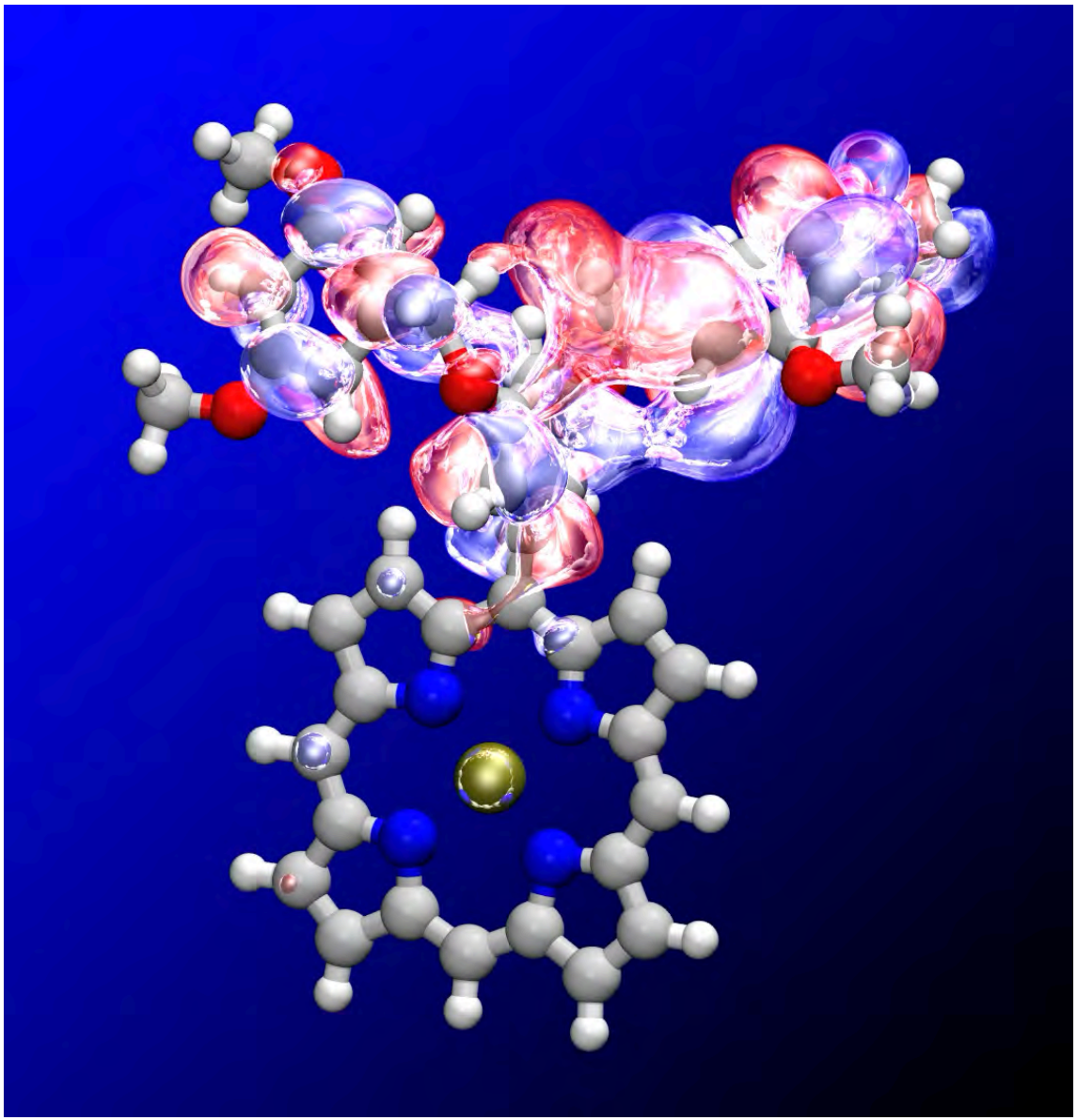
- **Reaction rate does not decrease for larger particles → industrial scalability**

K. Shimamura *et al.*, *Nano Lett.* **14**, 4090 ('14); K. Nomura *et al.*, *IEEE/ACM SC14* ('14)

Outline

1. Introduction: Extreme-scale quantum simulations
2. Quantum molecular dynamics (QMD)
3. Nonadiabatic quantum molecular dynamics (NAQMD)
4. Moving forward: Quantum material dynamics at the nexus of exascale computing, artificial intelligence & quantum computing

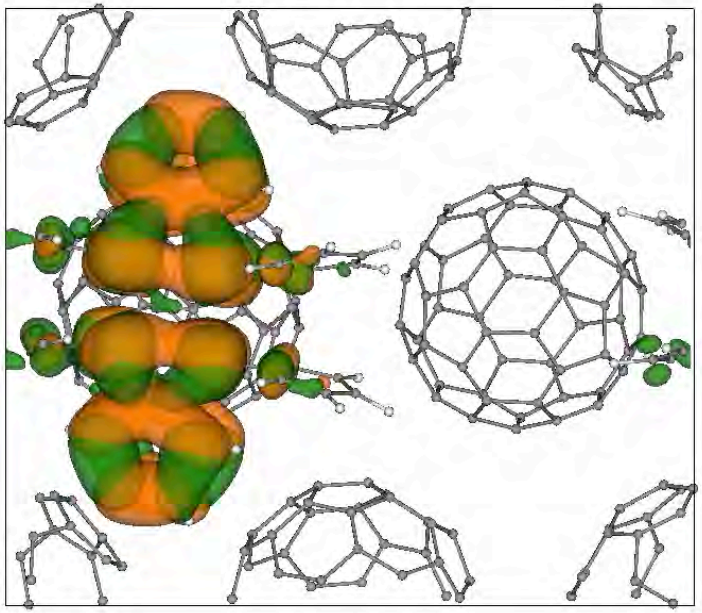
Nonadiabatic Quantum Molecular Dynamics



Appl. Phys. Lett. **98**, 113301 ('11); *ibid*. **100**, 203306 ('12); *J. Chem. Phys*. **136**, 184705 ('12); *Comput. Phys. Commun*. **184**, 1 ('13); *Appl. Phys. Lett*. **102**, 093302 ('13); *ibid*. **102**, 173301 ('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)

Zn porphyrin

Rubrene/C_{60}



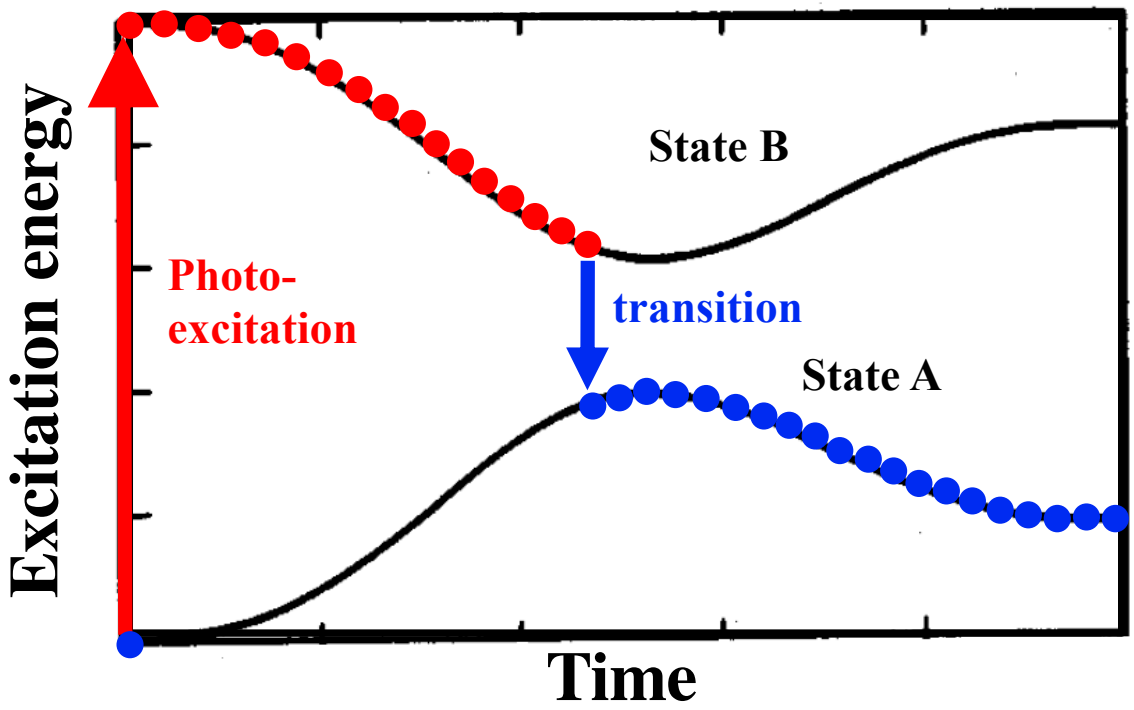
quasi-electron; quasi-hole

- **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

$$\Psi(\mathbf{r},t) = \sum_J C_J^{(I)}(t)\Phi_J(\mathbf{r};\mathbf{R}(t)) \qquad C_I^{(I)}(0) = \delta_{I,J}$$

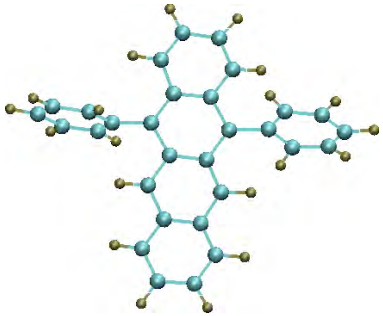
$$\frac{d}{dt}C_J^{(I)}(t) = -\sum_k C_k^{(I)}(t)\left(i\omega_K\delta_{JK} + \left\langle \Phi_J \left| \frac{\partial}{\partial t} \right| \Phi_K \right\rangle\right)$$

J-th adiabatic excited state

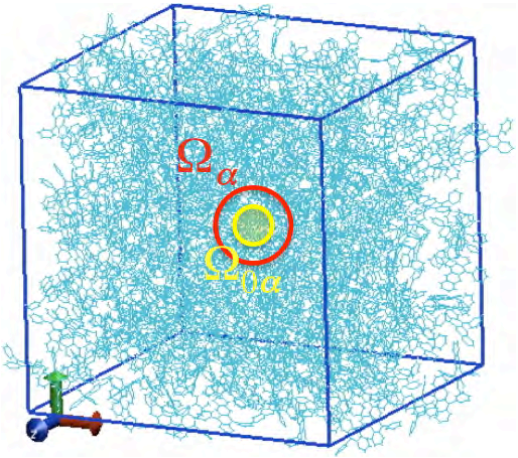
Electronic transition assisted by nuclei motion

Singlet Fission in Amorphous DPT

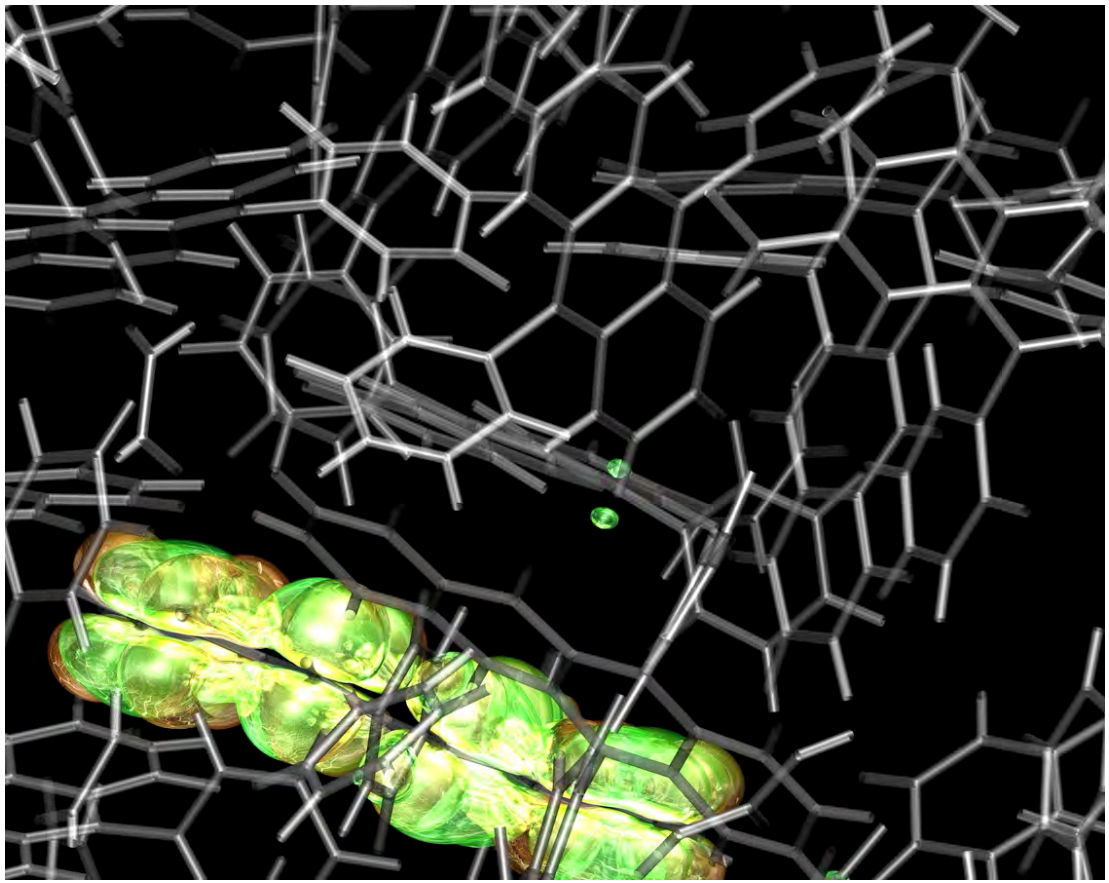
- **Photo-current doubling by splitting a singlet exciton into 2 triplet excitons**
- **Singlet fission in mass-produced disordered organic solid → efficient low-cost solar cells**
- **Experimental breakthrough: SF found in amorphous diphenyl tetracene (DPT)**



DPT molecule



Amorphous DPT



Quasi-electron

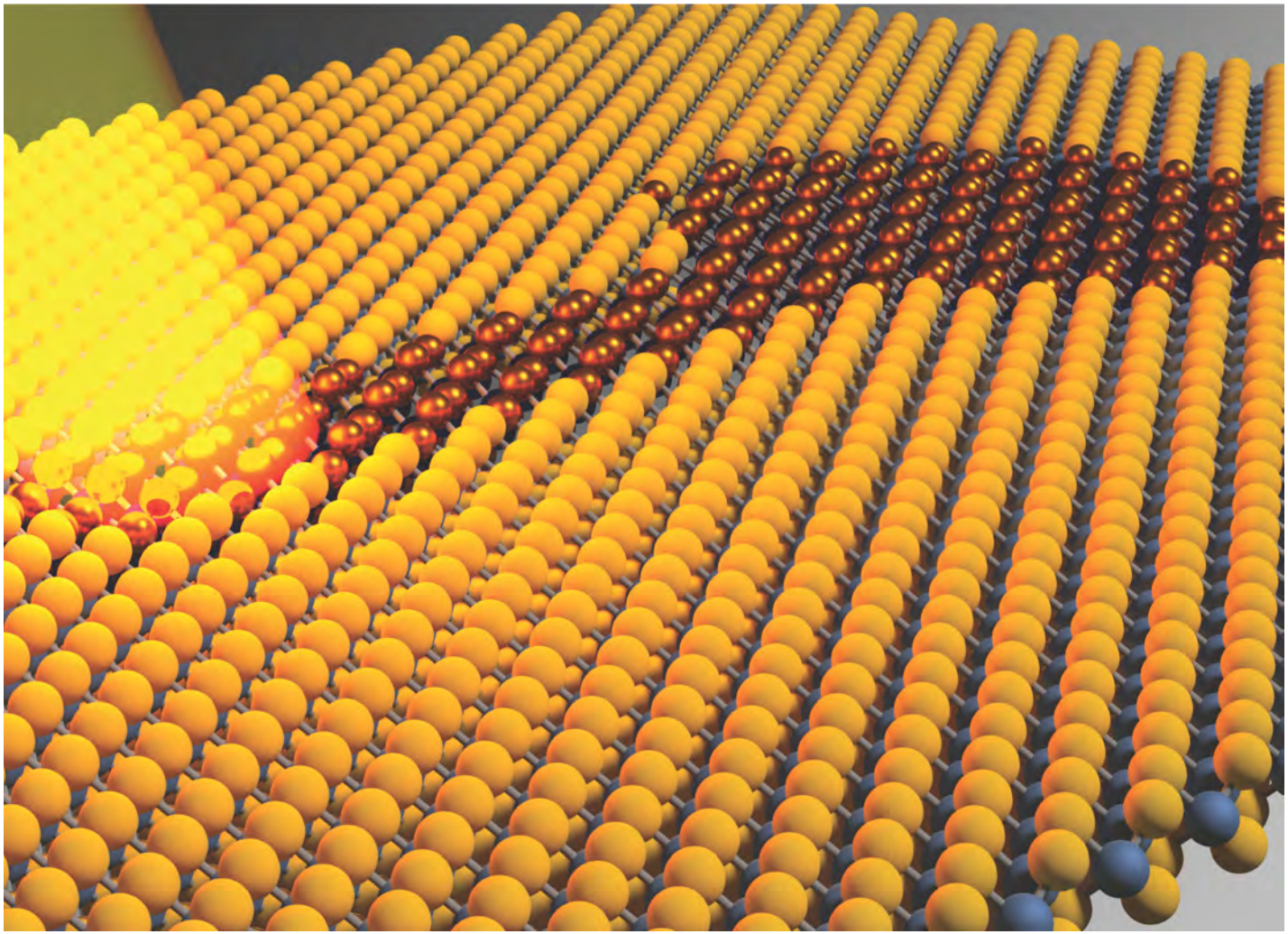
Quasi-hole

W. Mou *et al.*, *Appl. Phys. Lett.* **102**, 173301 ('13)

- **Divide-conquer-recombine nonadiabatic QMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT**

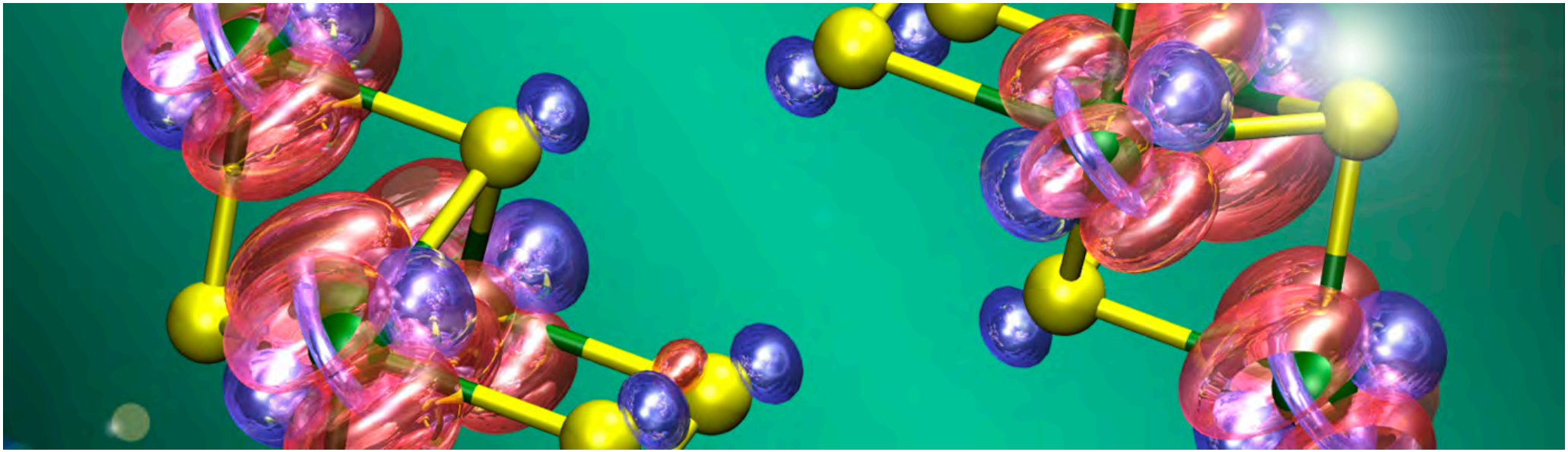
Ultrafast Control of Materials

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

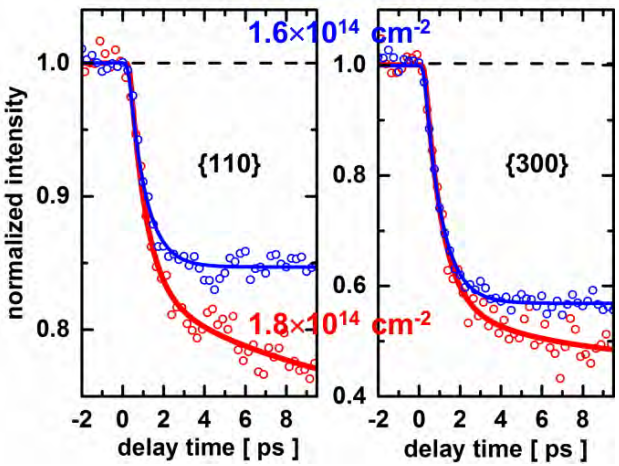
Simulation-Experiment Synergy

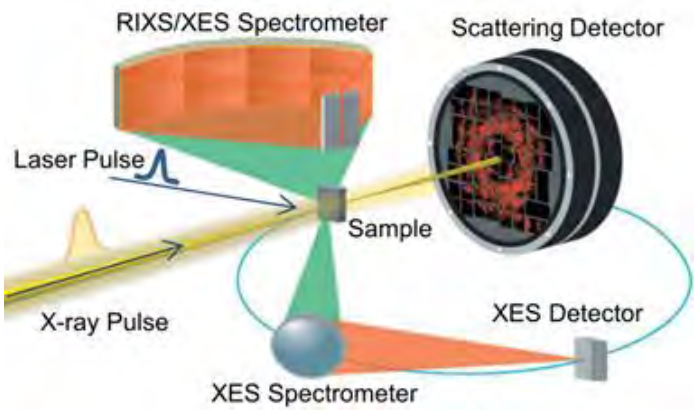


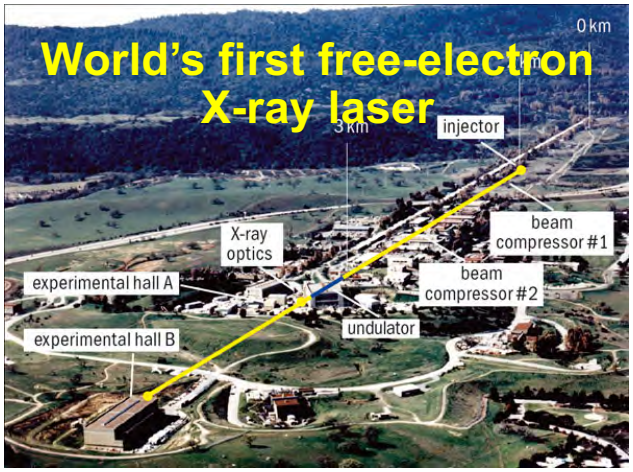
- **In ultrafast 'electron & X-ray cameras,' laser light hitting a material is almost completely converted into nuclear motions — key to switching material properties on & off at will for future electronics applications.**
- **High-end nonadiabatic quantum molecular dynamics simulations reproduce the 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)

INCITE|AURORA–MAGICS–LCLS Synergy





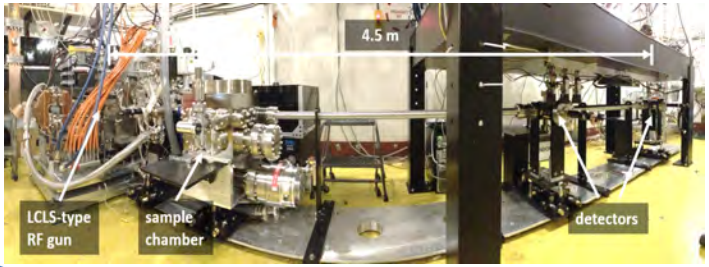


Linac Coherent Light Source

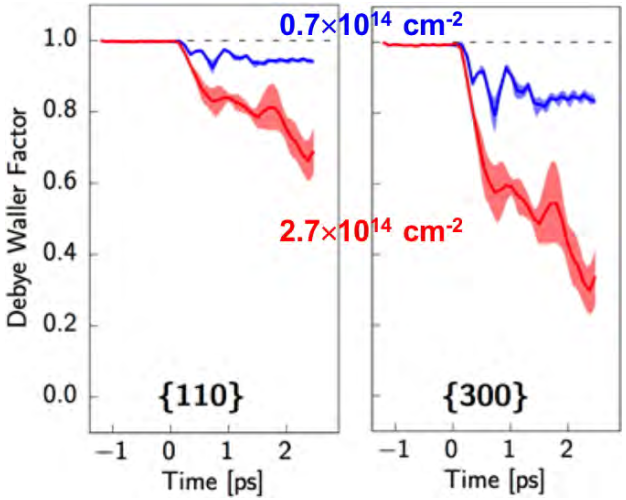
LCLS

DOE INCITE & Aurora ESP Awards

MAGICS
Materials Genome Innovation for Computational Software

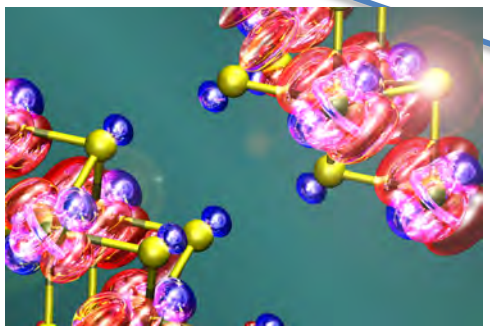


Ultrafast electron diffraction (UED) at SLAC



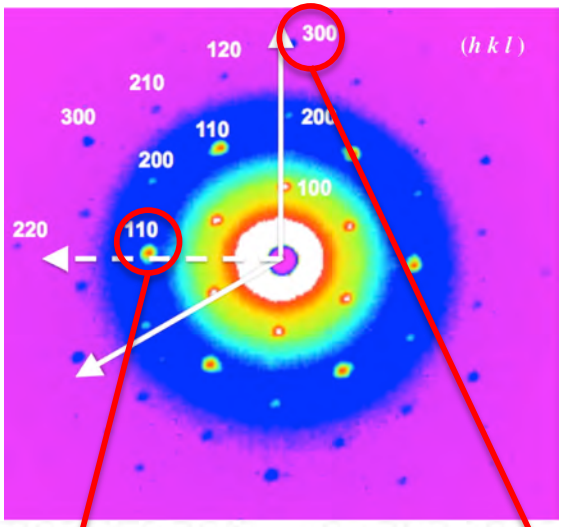
U.S. DEPARTMENT OF ENERGY
INCITE
LEADERSHIP COMPUTING

AURORA | EARLY SCIENCE PROGRAM

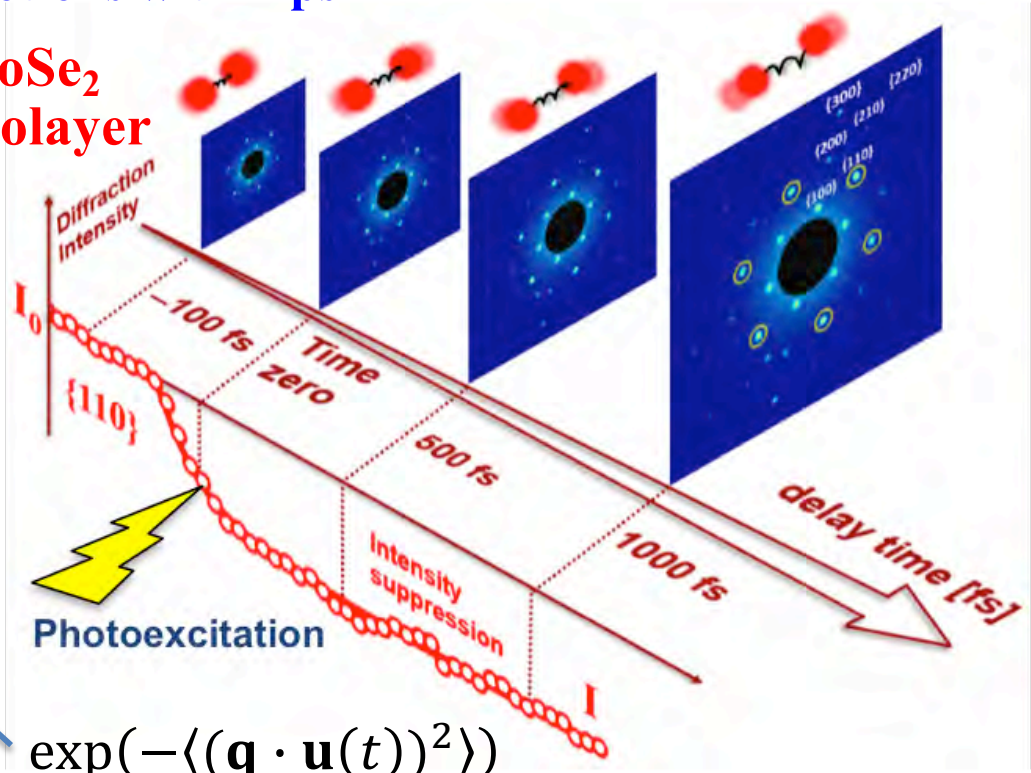


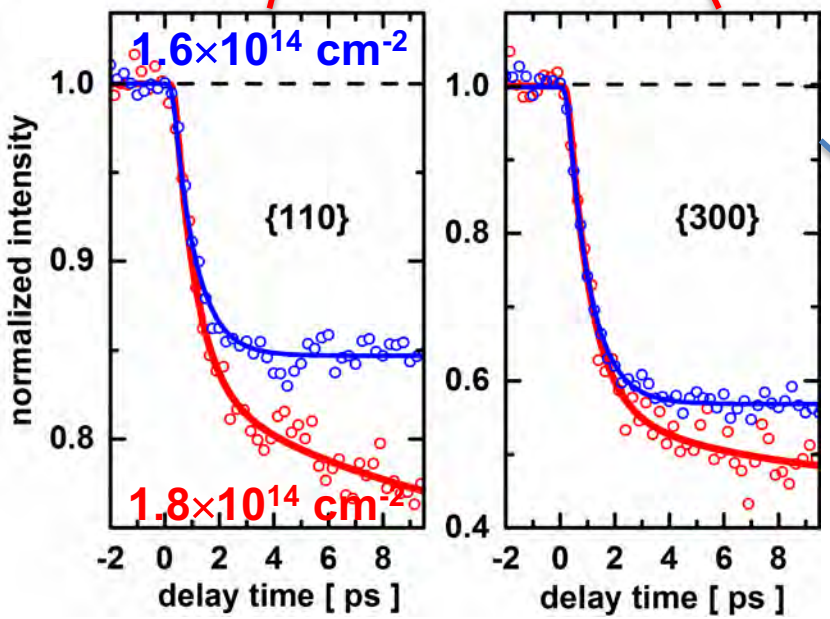
Ultrafast Coupled Electron-Lattice Dynamics

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



$MoSe_2$ monolayer





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

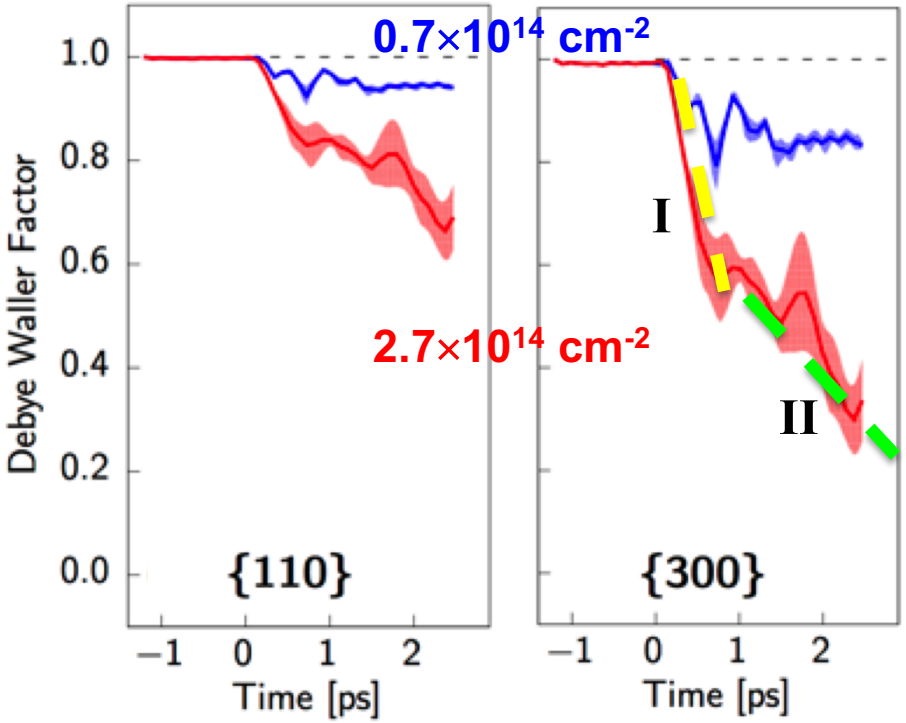
atomic displacement

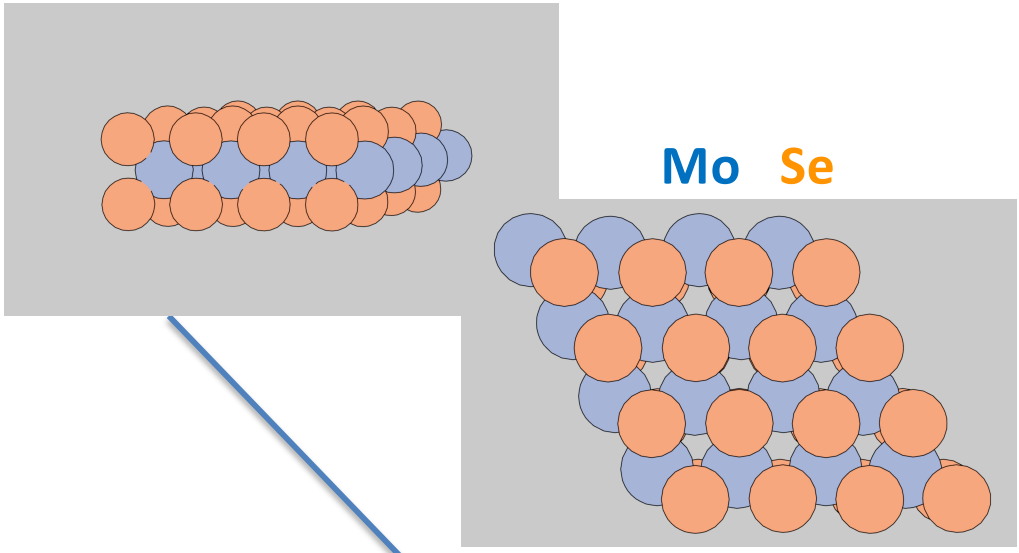
- **Dynamics of Debye-Waller factor reveals rapid disordering for both {300} & {110} peaks**
- **Transition from mono- to bi-exponential decay at higher electron-hole density**

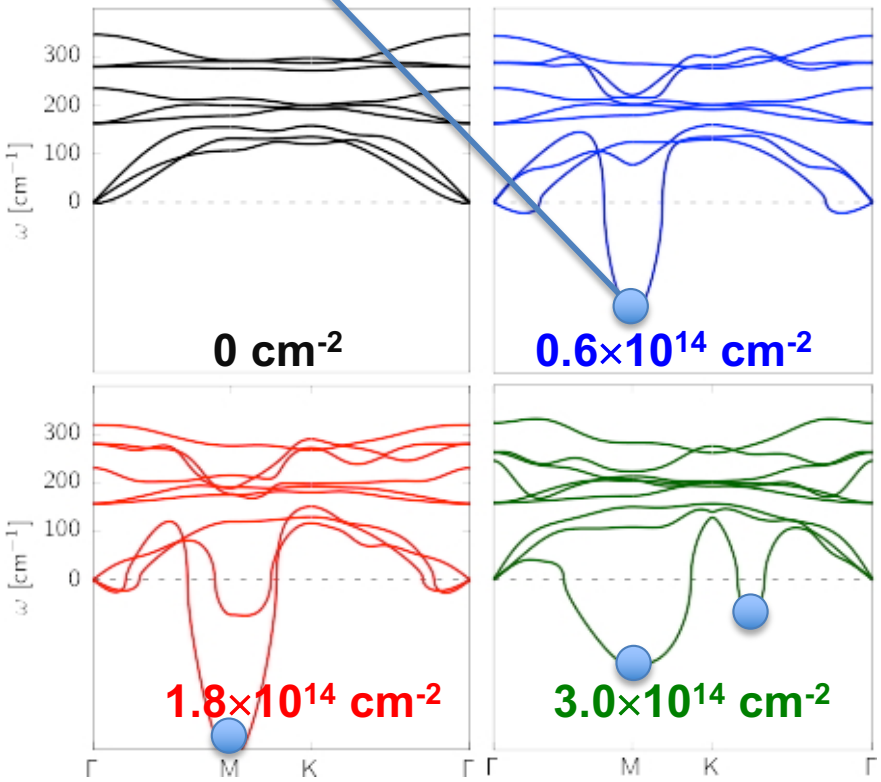
M.F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)

Strong Electron-Lattice Coupling

- **NAQMD simulations reproduce (1) rapid photo-induced lattice dynamics & (2) mono- to bi-exponential transition at higher electron-hole density**





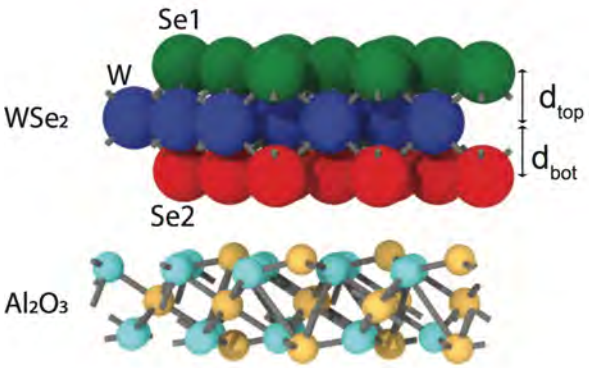


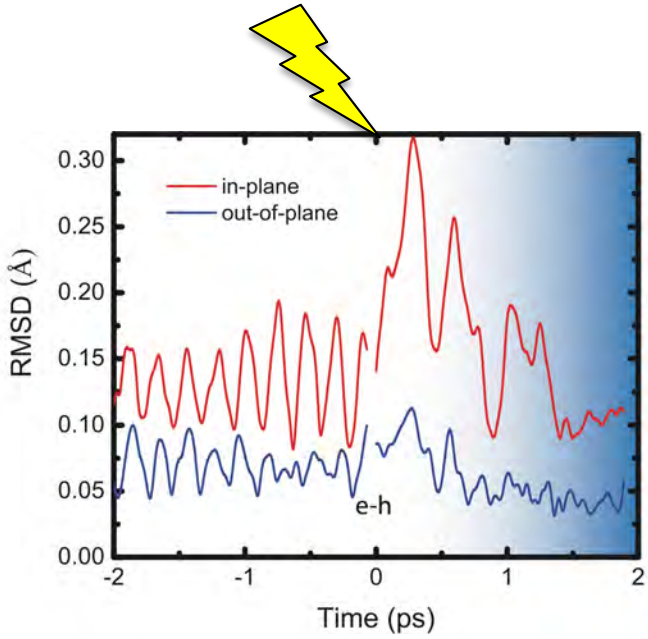
- **Rapid lattice dynamics is explained by the softening of M-point (1/2 0 0) phonon**
- **Bi-exponential transition is explained by the softening of additional phonon modes at higher electron-hole densities**

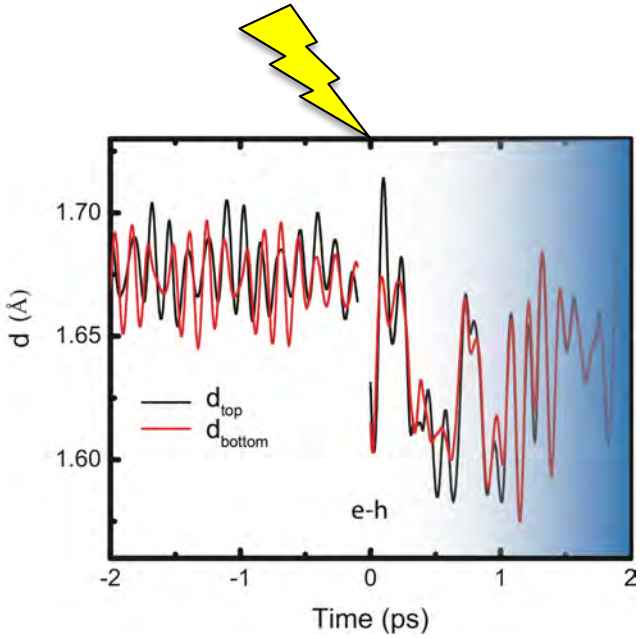
M.F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)
L. Bassman *et al.*, *Nano Lett.* **18**, 4653 ('18)

WSe_2 Monolayer on Al_2O_3 Substrate

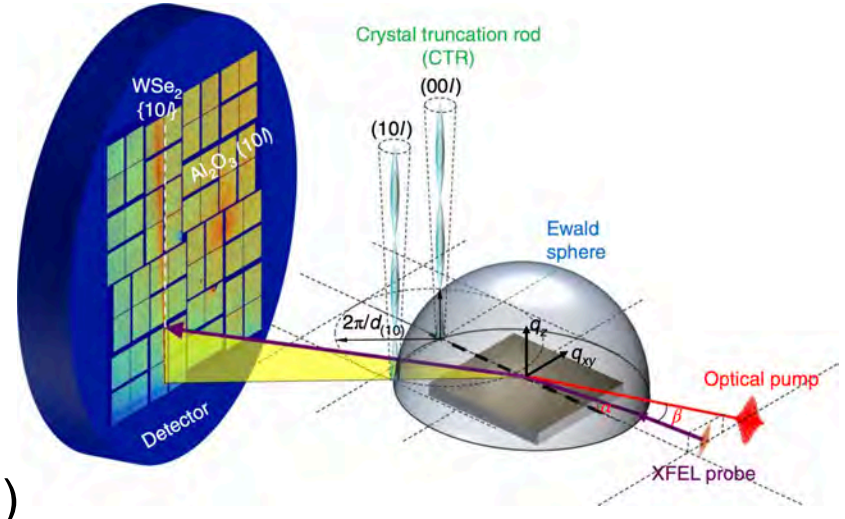
- **NAQMD simulation to study photoexcitation dynamics of WSe_2 monolayer on Al_2O_3 substrate**







- **Enhanced in-plane atomic displacements upon photoexcitation**
- **Photo-induced intralayer contraction of W-Se distances**
- **Good agreement with femtosecond surface X-ray scattering experiments at LCLS**



I.-C. Tung, *et al.*, *Nature Photonics* **13**, 425 ('19)

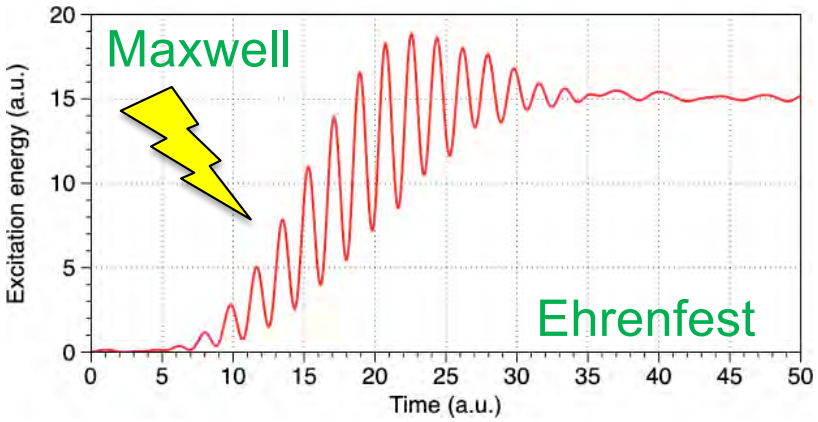
New: Maxwell-Ehrenfest-Surface Hopping

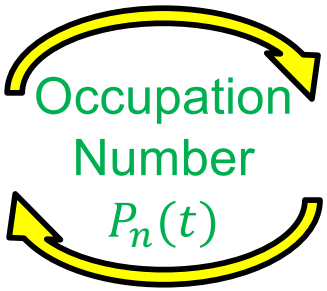
- **Excited electron-lattice dynamics incorporating both many-electron & field dynamics (Maxwell-Ehrenfest dynamics) & electron-lattice interaction (surface hopping)**

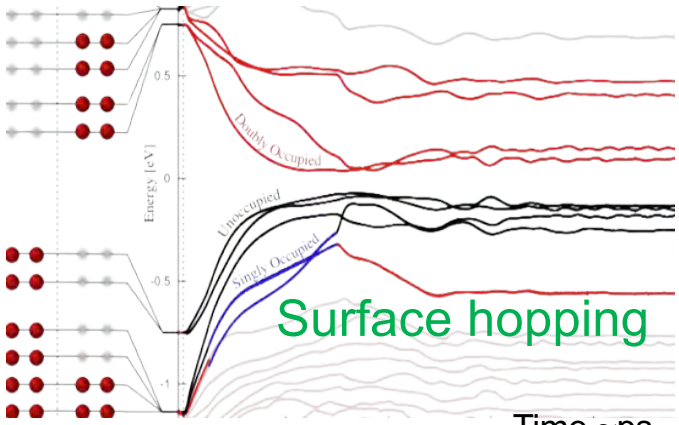
Many-electron & EM dynamics Electron-lattice dynamics

$$\psi(\mathbf{r}, t+\Delta) = e^{-i\delta\hat{h}(\dot{\mathbf{R}})\Delta/2\hbar} T\exp\left(-\frac{i}{\hbar}\int_t^{t+\Delta} dt'\,\hat{h}(t')\right) e^{-i\delta\hat{h}(\dot{\mathbf{R}})\Delta/2\hbar}\psi(\mathbf{r}, t)$$

- **Ehrenfest-surface hopping handshaking *via* electronic occupation numbers**
  [*cf*. Lee & Schleife, *Nano Lett*. **19**, 3939 ('19)]
- **Real-time time-dependent density function theory (RT-TDDFT) equations for electrons & Maxwell equations for electromagnetic field in Lorenz gauge**
  [Yabana *et al*., *Phys. Rev. B* **85**, 045134 ('12); Gabay *et al*., *Phys. Rev. B* **101**, 235101 ('20)]
- **Stencil computations: space-splitting method (SSM) for electron dynamics** [Richardson, *Comput. Phys. Commun.* **63**, 84 ('91); Nakano *et al*., *ibid.* **83**, 181 ('94)] **& finite-difference vector-scalar field solvers** [Car & Parrinello, *Solid St. Commun.* **62**, 403 ('87)]







QXMD Software & Quantum@Scale

SoftwareX 10 (2019) 100307

Contents lists available at ScienceDirect

SoftwareX

journal homepage: www.elsevier.com/locate/softx

Original software publication

QXMD: An open-source program for nonadiabatic quantum molecular dynamics

Fuyuki Shimojo [a], Shogo Fukushima [a], Hiroyuki Kumazoe [a], Masaaki Misawa [b], Satoshi Ohmura [c], Pankaj Rajak [d], Kohei Shimamura [e], Lindsay Bassman [f], Subodh Tiwari [f], Rajiv K. Kalia [f], Aiichiro Nakano [f,*], Priya Vashishta [f]

https://github.com/USCCACS/QXMD

Quantum dynamics at scale: ultrafast control of emergent functional materials

S. C. Tiwari, P. Sakdhnagool, R. K. Kalia, A. Krishnamoorthy, M. Kunaseth, A. Nakano, K. Nomura, P. Rajak, F. Shimojo, Y. Luo & P. Vashishta

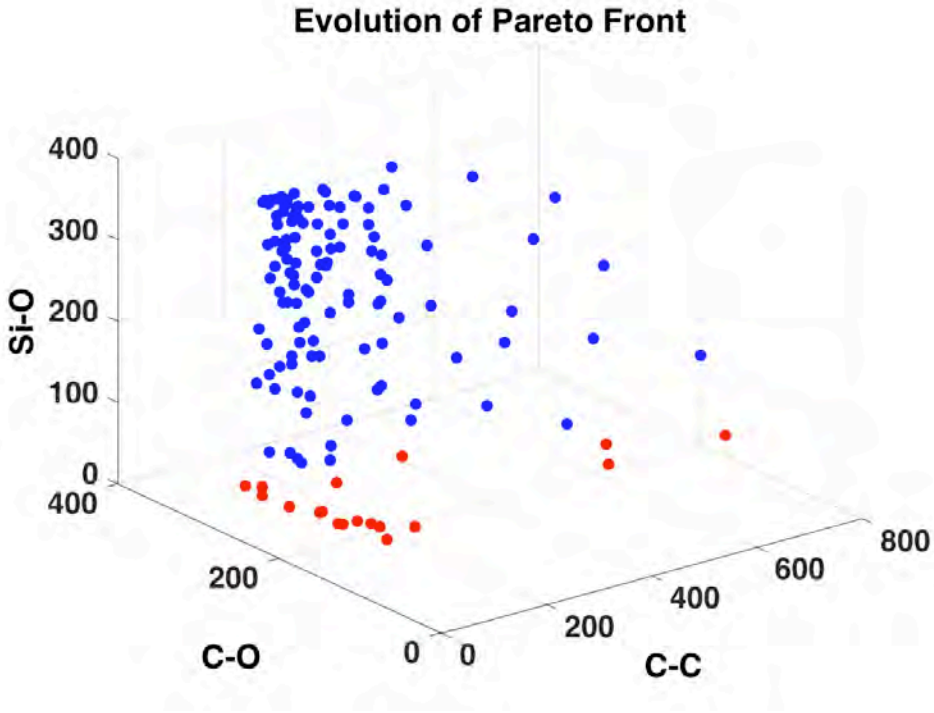
Best Paper in *ACM HPCAsia 2020*

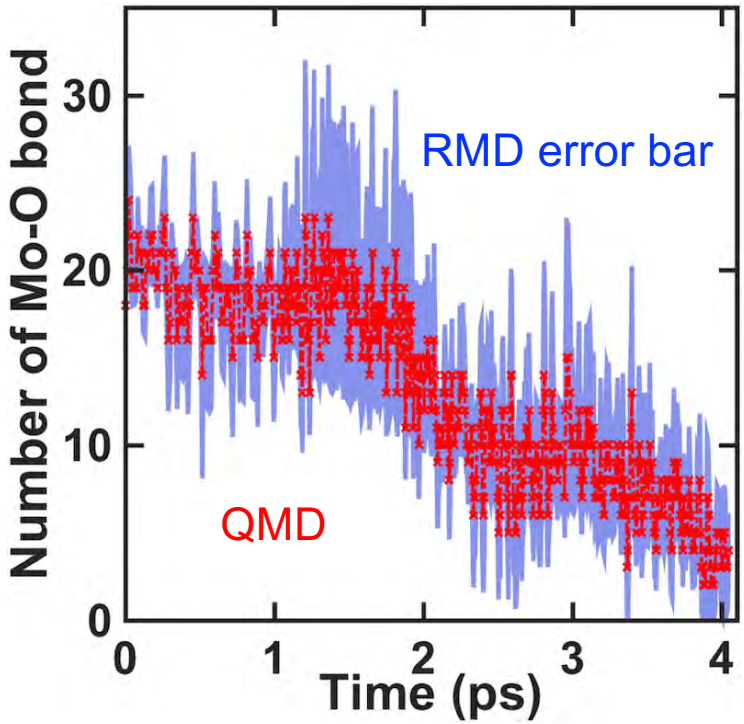
QXMD Code

- **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**

Pareto-Frontal Uncertainty Quantification

- **Train reactive force-field parameters by dynamically fitting reactive molecular dynamics (RMD) trajectories to quantum molecular dynamics (QMD) trajectories on-the-fly**
- **Pareto optimal front in multiobjective genetic algorithm (MOGA) provides an ensemble of force fields to enable uncertainty quantification (UQ)**



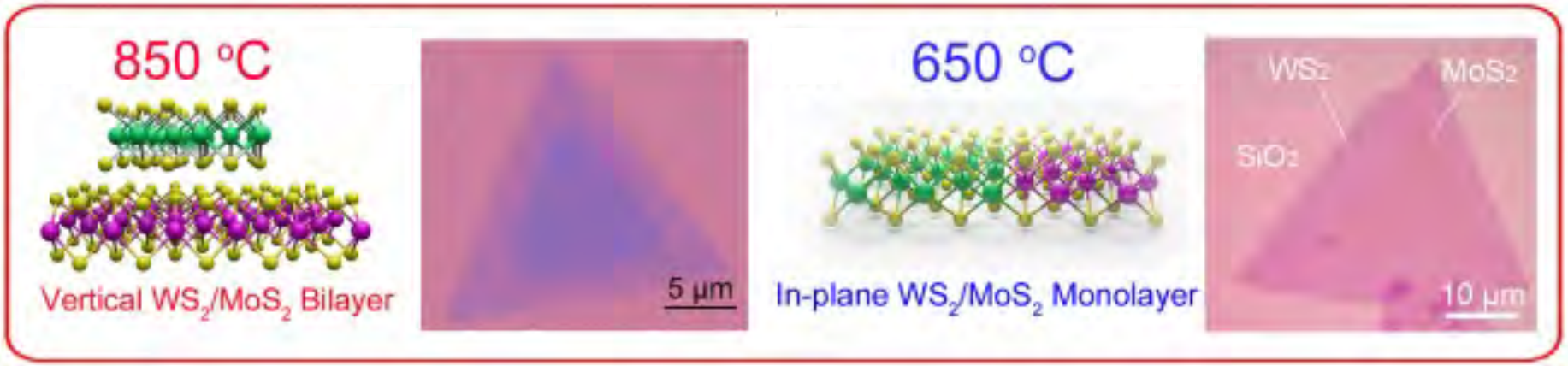


- Pareto-optimal solutions during genetic training (RMD errors for three quantities-of-interest)
- Converged Pareto-optimal front

A. Mishra *et al.*, *npj Comput. Mater.* **4**, 42 ('18)

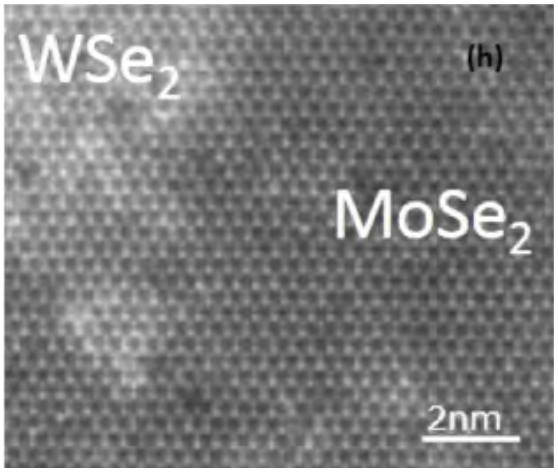
In-Plane 2D Heterostructure

- **Stacked & in-plane transition metal dichalcogenide (TMDC) hetero-structures can be synthesized in different CVD (chemical vapor deposition) conditions by the Ajayan group (Rice Univ.)**

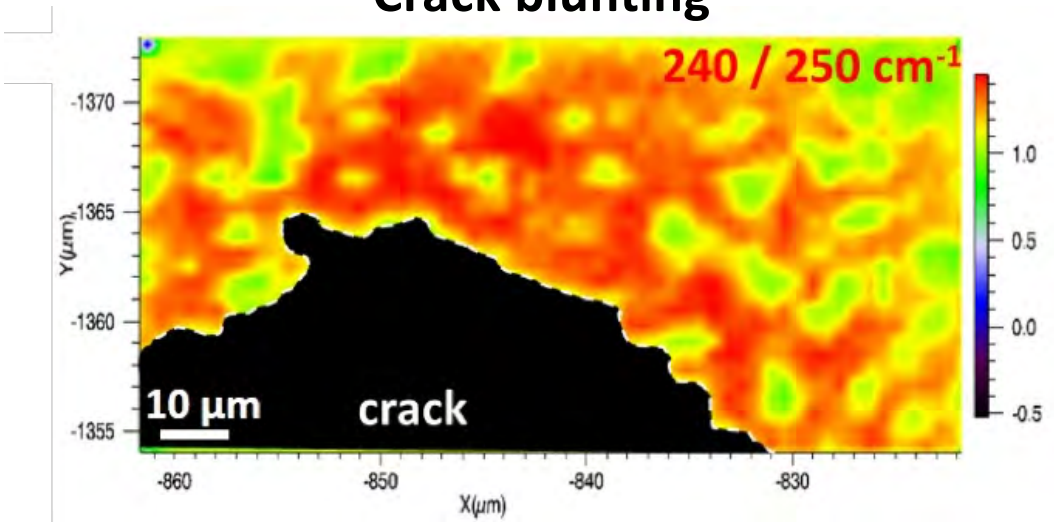


- **Crack blunting observed during fracture of $MoSe_2/WSe_2$ monolayer**

Z-contrast STEM image



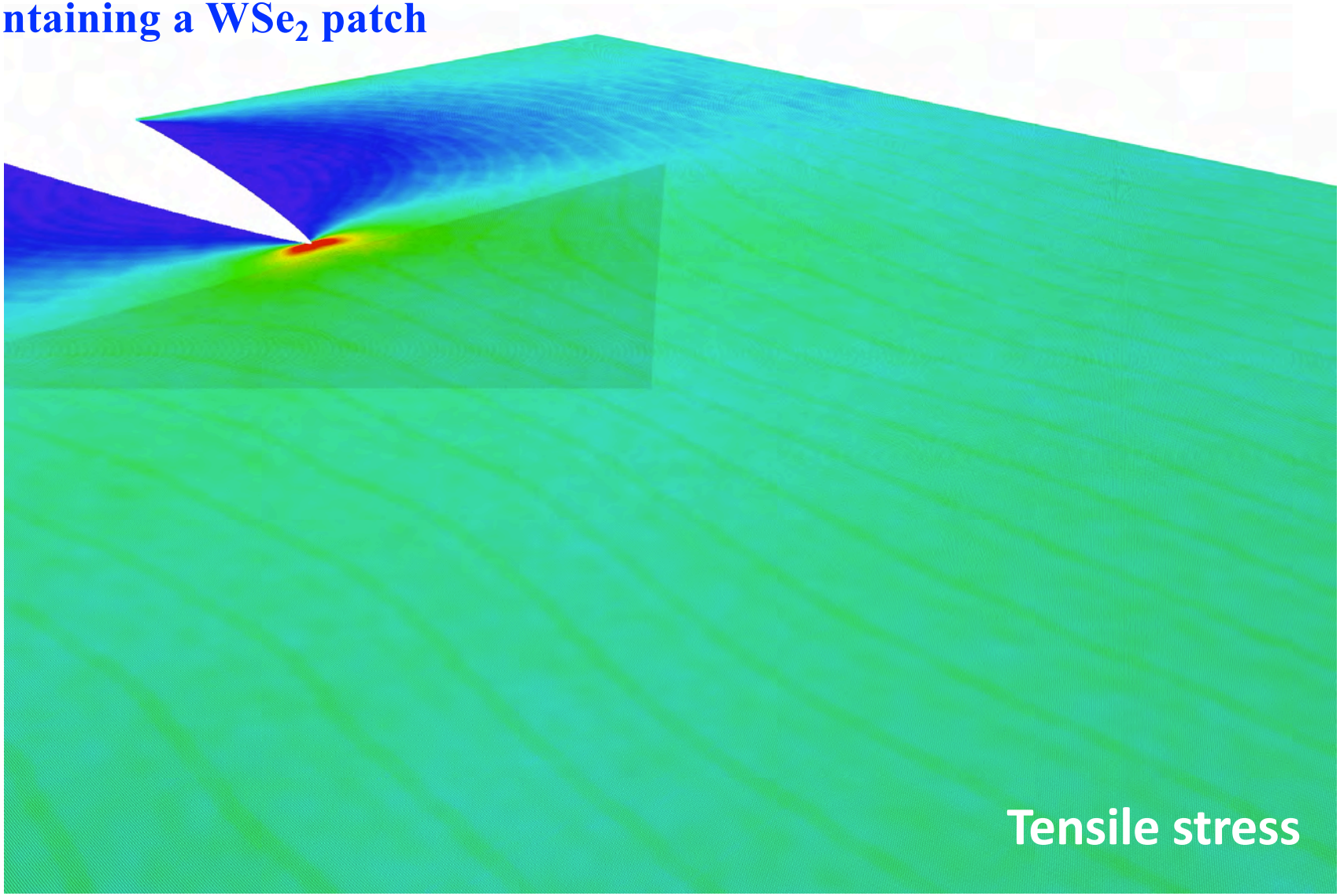
Crack blunting



A. Apte *et al.*, *ACS Nano* **12**, 3468 ('18)

Molecular Dynamics Simulation of Fracture

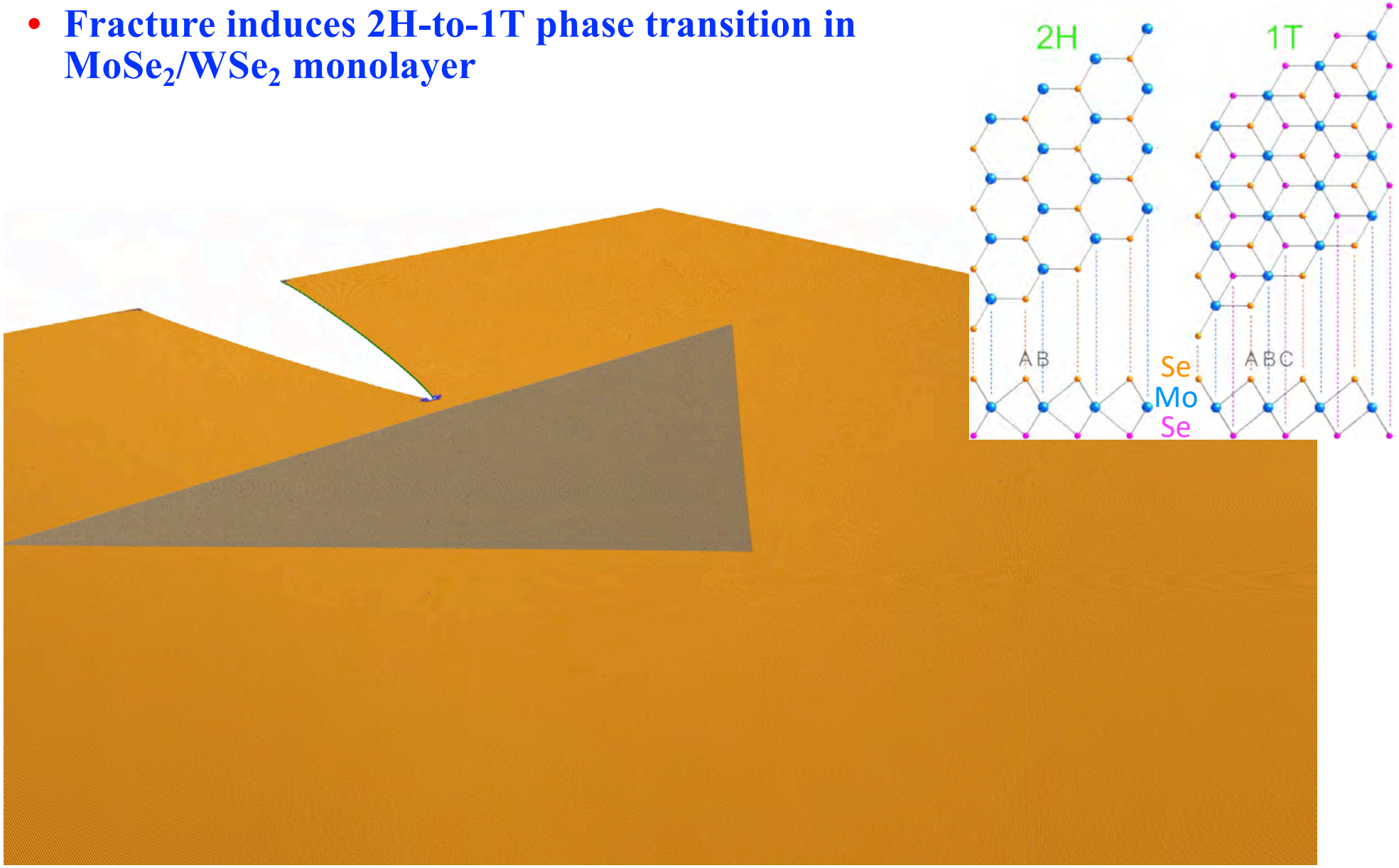
- **MD simulation of crack propagation in 0.5 μm × 0.5 μm $MoSe_2$ monolayer containing a WSe_2 patch**



A. Apte *et al.*, *ACS Nano* **12**, 3468 ('18)

Fracture-induced 2H-to-1T Transition

- **Fracture induces 2H-to-1T phase transition in $MoSe_2/WSe_2$ monolayer**



A. Apte *et al.*, *ACS Nano* **12**, 3468 ('18)

Open-Source RXMD Software

SoftwareX 11 (2020) 100389

Contents lists available at ScienceDirect

SoftwareX

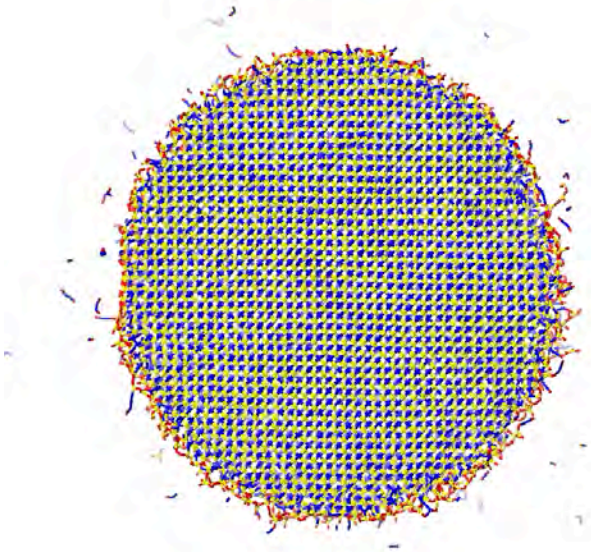
journal homepage: www.elsevier.com/locate/softx

Original software publication

RXMD: A scalable reactive molecular dynamics simulator for optimized time-to-solution

Ken-ichi Nomura [a,d,*], Rajiv K. Kalia [a,b,c,d], Aiichiro Nakano [a,b,c,d,e], Pankaj Rajak [f], Priya Vashishta [a,b,c,d]

https://github.com/USCCACS/RXMD



Outline

1. Introduction: Extreme-scale quantum simulations
2. Quantum molecular dynamics (QMD)
3. Nonadiabatic quantum molecular dynamics (NAQMD)
4. Moving forward: Quantum material dynamics at the nexus of exascale computing, artificial intelligence & quantum computing

Changing Computing Landscape for Science

Postexascale Computing for Science

Compute Cambrian explosion

AI for Science

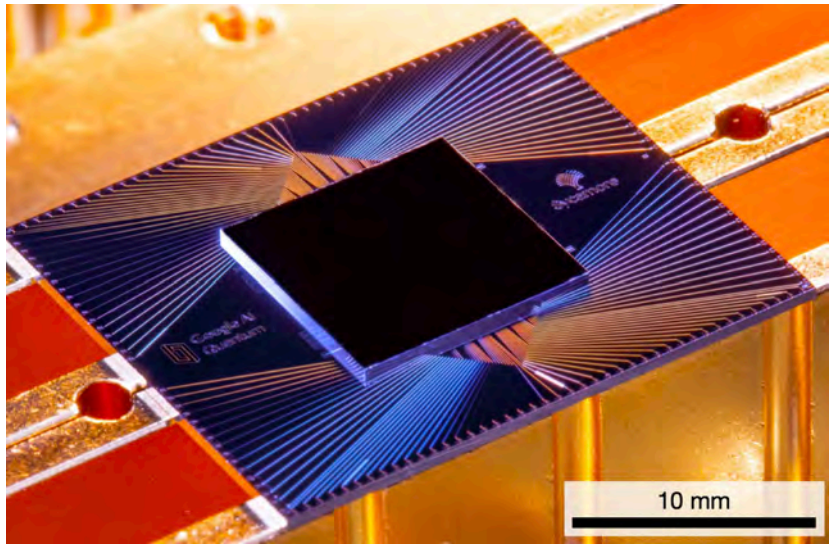
DOE readies multibillion-dollar AI push

U.S. supercomputing leader is the latest big backer in a globally crowded field

By **Robert F. Service**, *in Washington, D.C.*

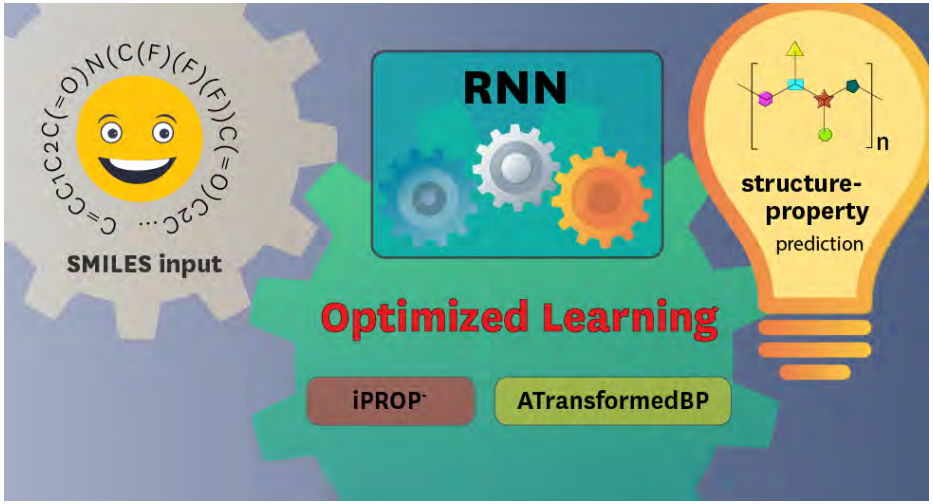
Science **366**, 559 (Nov. 1, '19)

Quantum Computing for Science



Use all to advance science!

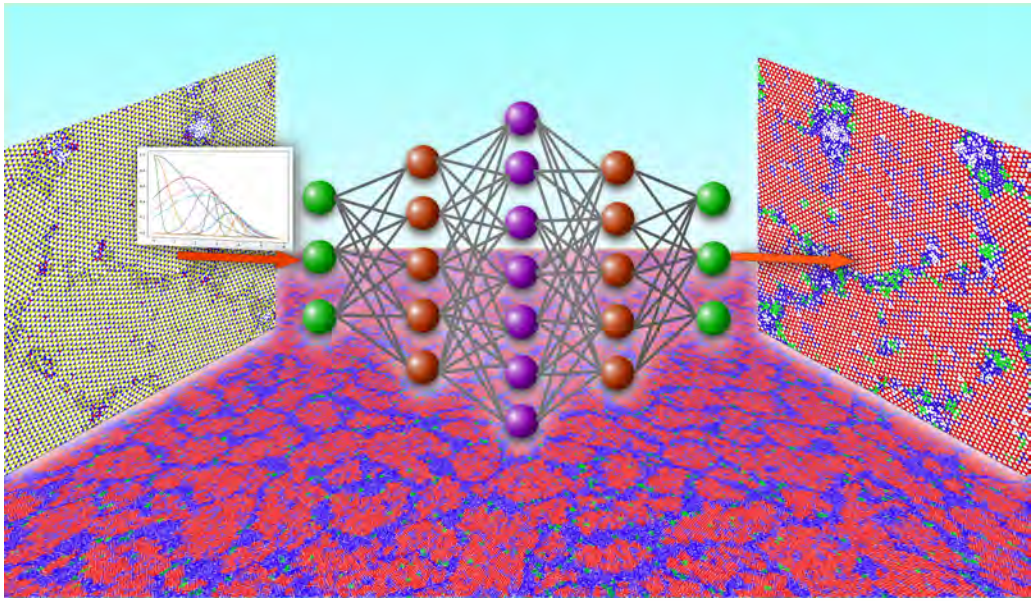
Learning Structure-Property Relationship



Dielectric Polymer Property Prediction Using Recurrent Neural Networks with Optimizations

A. Nazarova *et al.*,
J. Chem. Info. Model. **61**, 2175 ('21)

Learning Material Phases & Defects

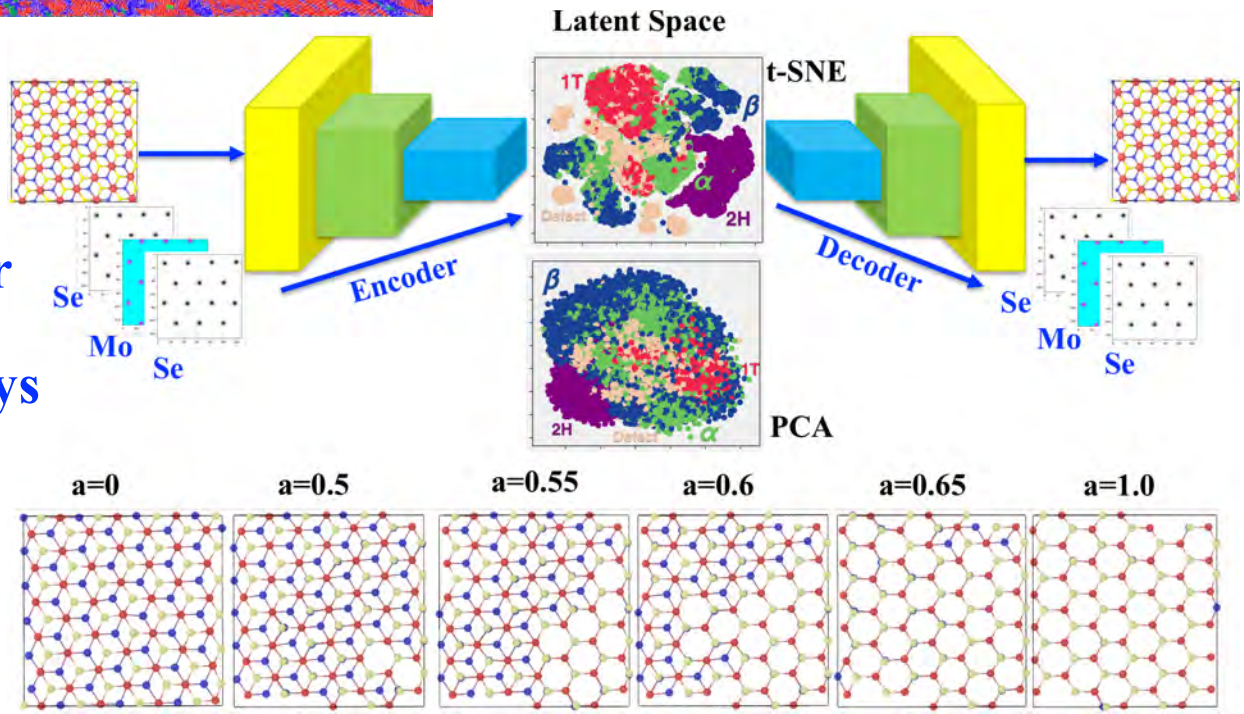


- **Feedforward neural network to learn phases from local symmetry functions**

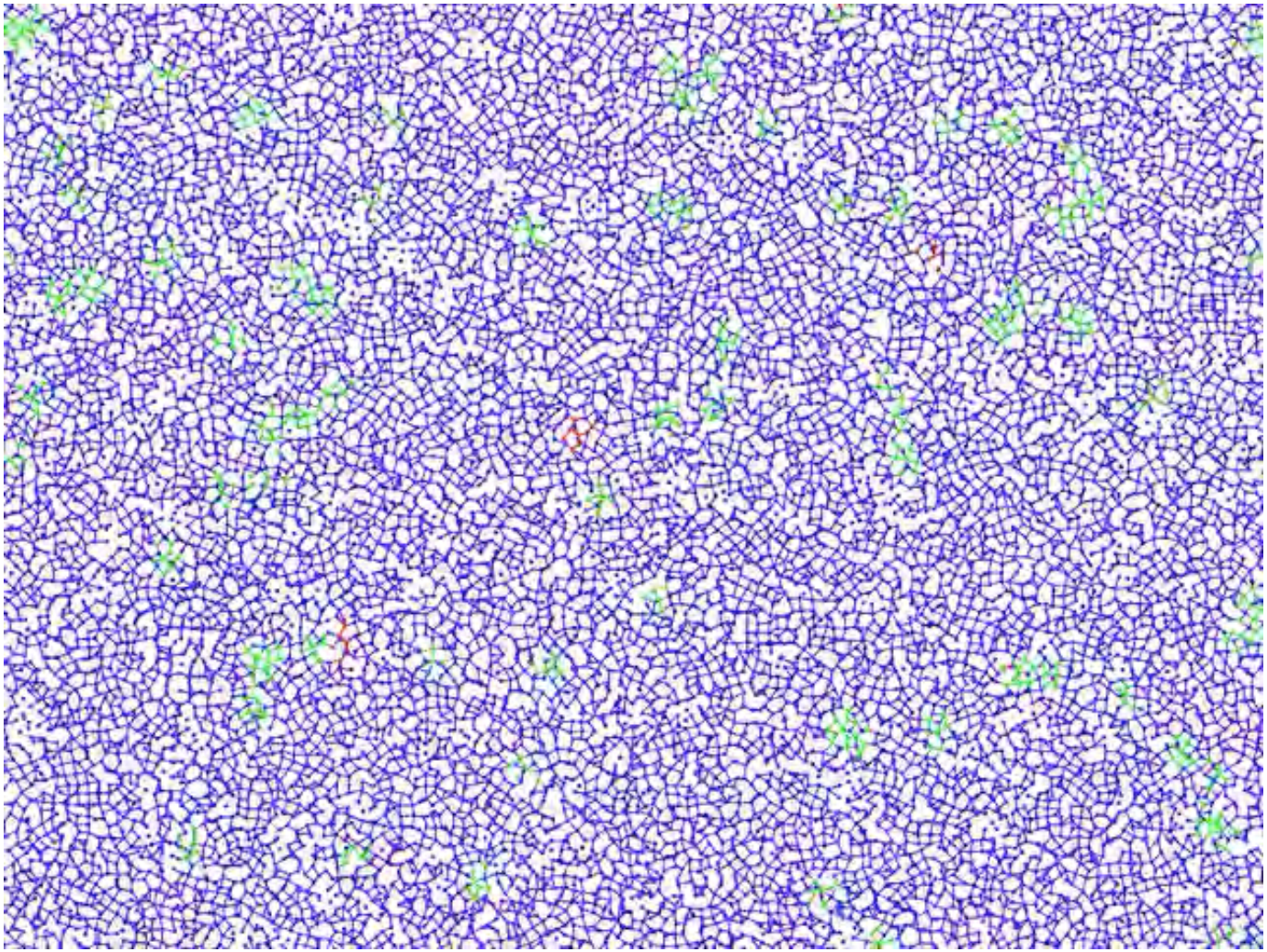
K. Liu *et al.*, *Proc. ScalA18* ('18)
S. Hong *et al.*, *JPCL* **10**, 2739 ('19)

- **Variational autoencoder to generate transformation pathways from images & latent-space algebra**

P. Rajak *et al.*, *Phys. Rev. B* **100**, 014108 ('19)



Learning Transformation Pathways

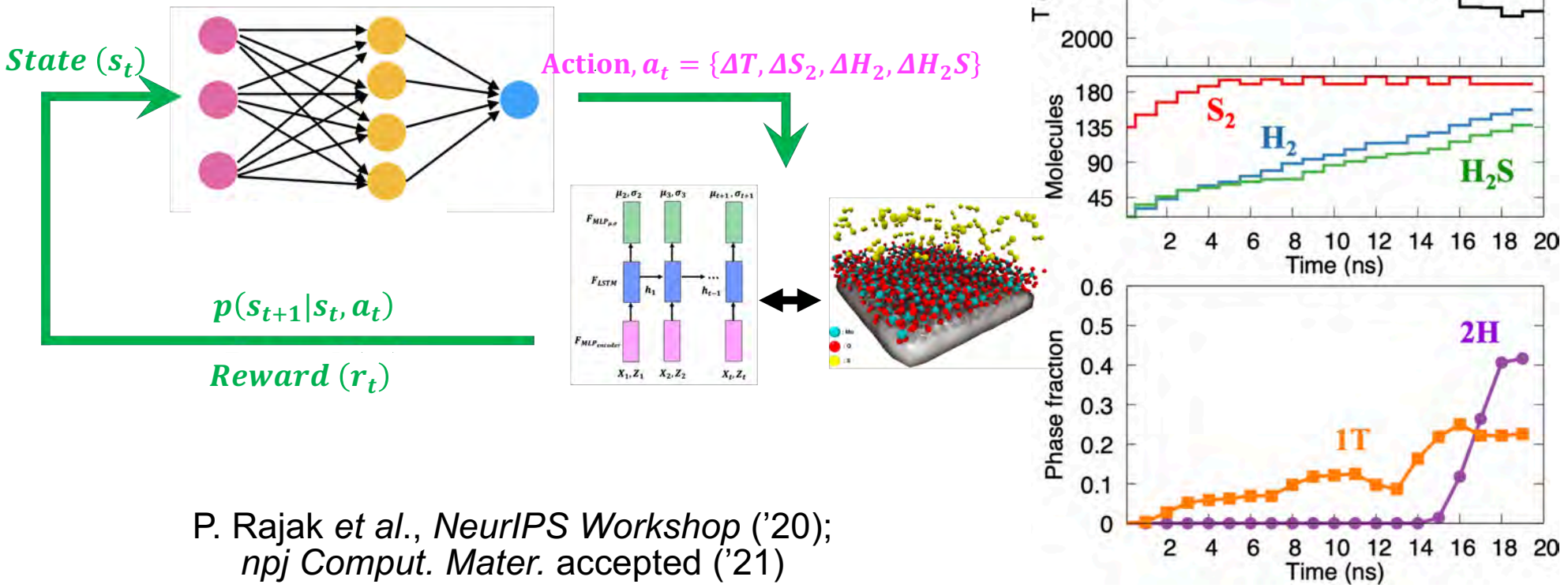


- **Found novel transformation pathways to the stable 2H phase *via* the metastable 1T phase during chemical vapor deposition (CVD) growth of MoS_2**

S. Hong *et al.*, *J. Phys. Chem. Lett.* **10**, 2739 ('19)

Reinforcement Learning for Growth

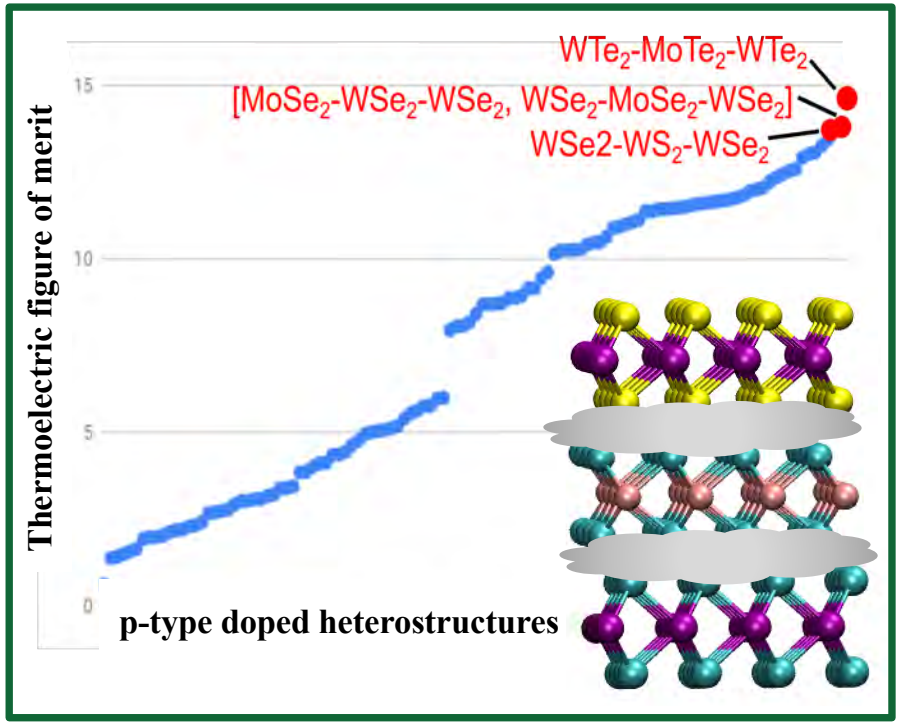
- **In a manner AI plays a board game of Go, use reinforcement learning (RL) to design optimal growth conditions (*e.g.*, temperature & gas-pressure control) to achieve desired properties such as minimal defect density**
- **AI model combines:**
  1. **RL agent to design actions**
  2. **Neural network-based dynamic model trained by molecular-dynamics (MD) simulation to predict new states**

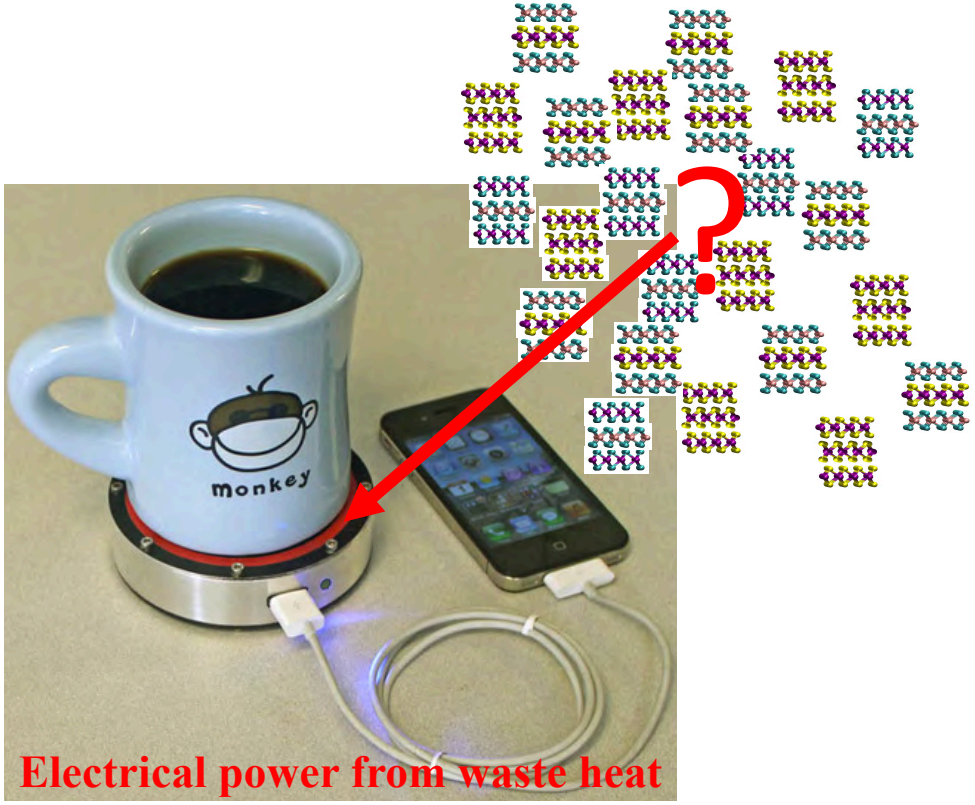


P. Rajak *et al.*, *NeurIPS Workshop* ('20);
npj Comput. Mater. accepted ('21)

Active Learning of Optimal Materials

- **Bayesian optimization balances exploitation & exploration to find a structure with the desired property with a minimal number of quantum-mechanical calculations**
- **Predicted three-layered transition-metal chalcogenide (TMDC) heterostacks with the largest thermoelectric figure-of-merit**

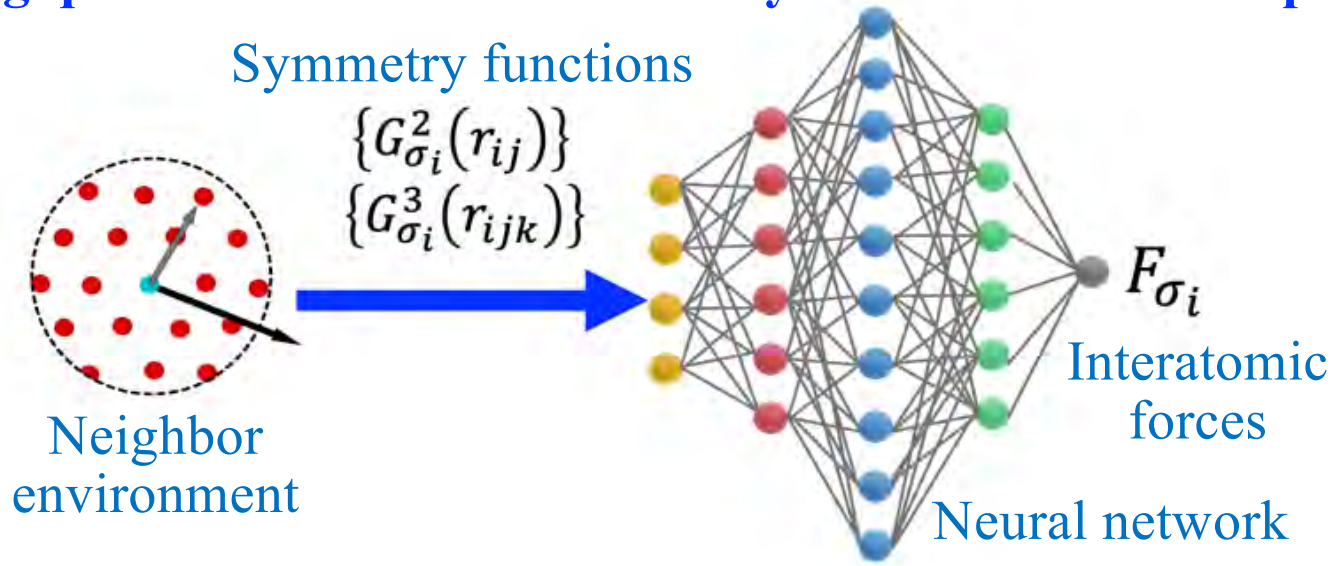




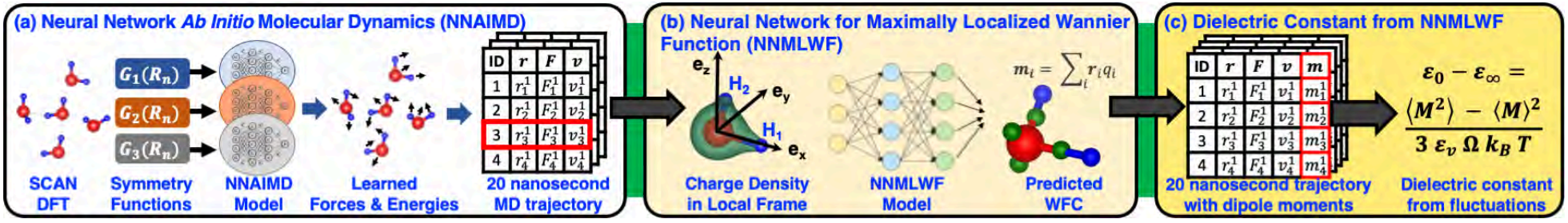
L. Bassman *et al.*, *npj Comput. Mater.* **4**, 74 ('18)

Neural-Network Quantum Molecular Dynamics

- **NNQMD@scale could revolutionize atomistic modeling of materials, providing quantum-mechanical accuracy at a fraction of computational cost**

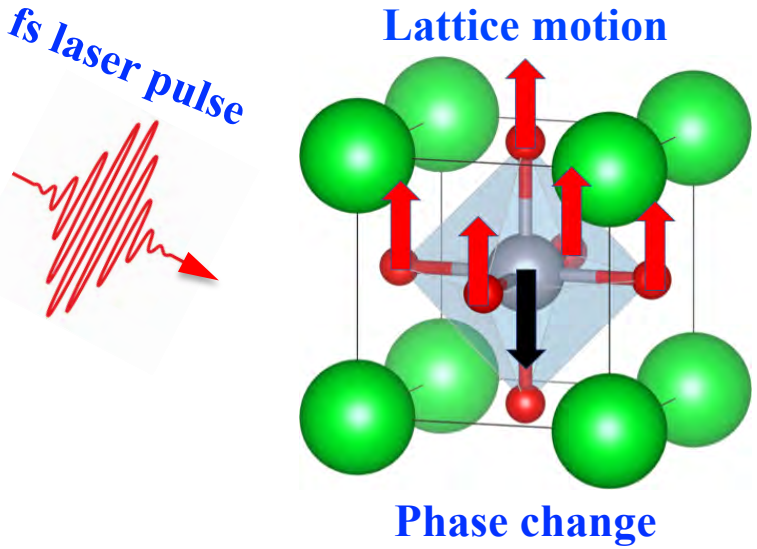


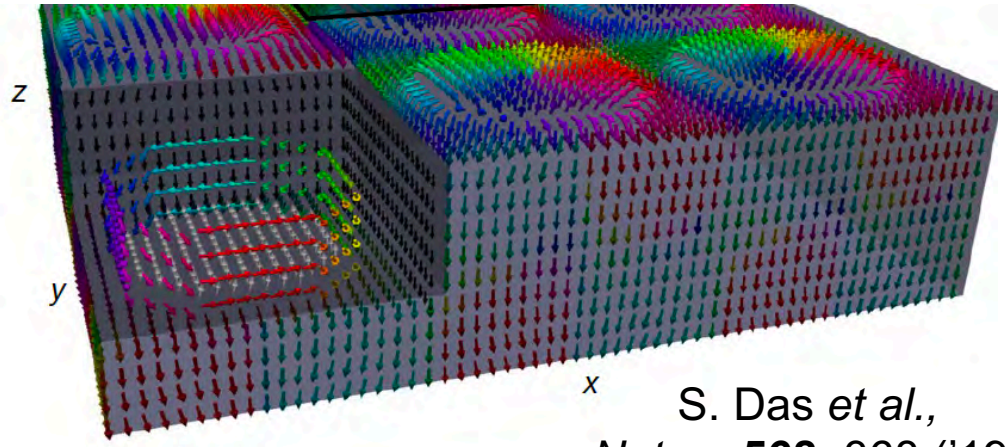
- **Combine neural networks to predict: (1) atomic forces for performing MD simulations; and (2) maximally-localized Wannier-function (MLWF) centers for computing dielectric constant**



P. Rajak *et al.*, "Neural network molecular dynamics at scale," *IPDPS-ScaDL* ('20)
A. Krishnamoorthy *et al.*, *Phys. Rev. Lett.* **126**, 216403 ('21)

Light Control of Polarization Vortices





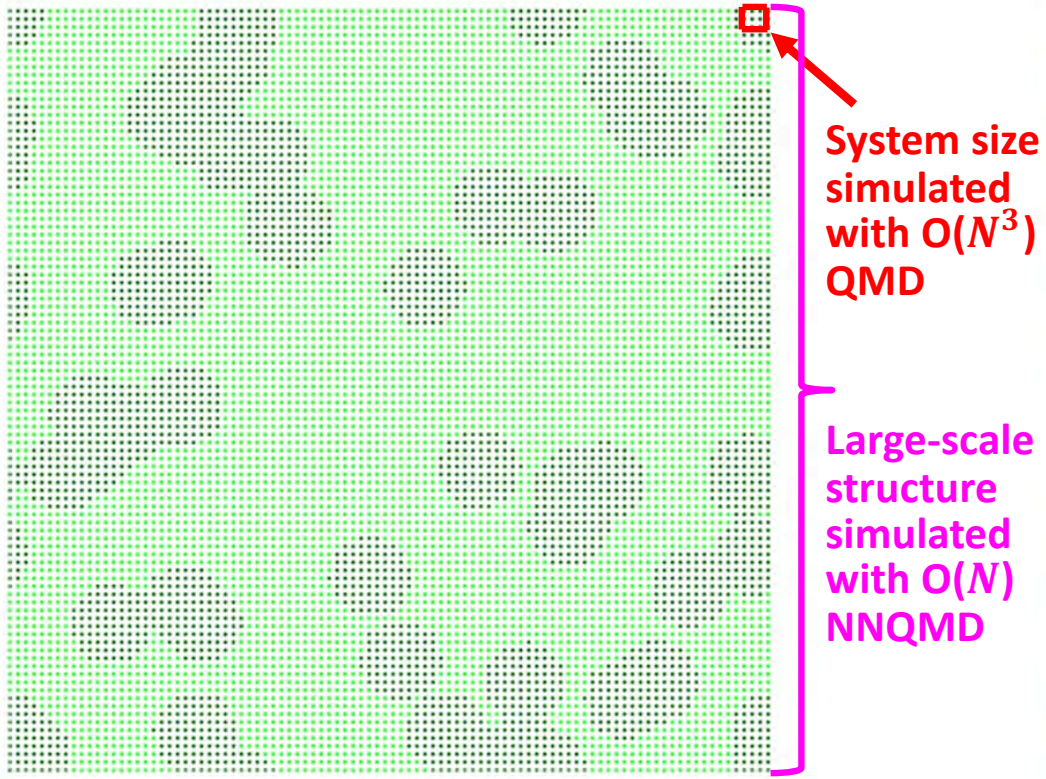
S. Das *et al.*, *Nature* **568,** 368 ('19)

- **Ultrafast laser pulse can induce lattice motions that result in phase changes to produce on-demand quantum materials**
- **Novel polarization vortices were produced in $PbTiO_3$, which has ultrafast & ultralow-power memory applications**
- **Developed excited-state neural-network quantum molecular dynamics (XS-NNQMD) trained by nonadiabatic quantum molecular dynamics (NAQMD)**

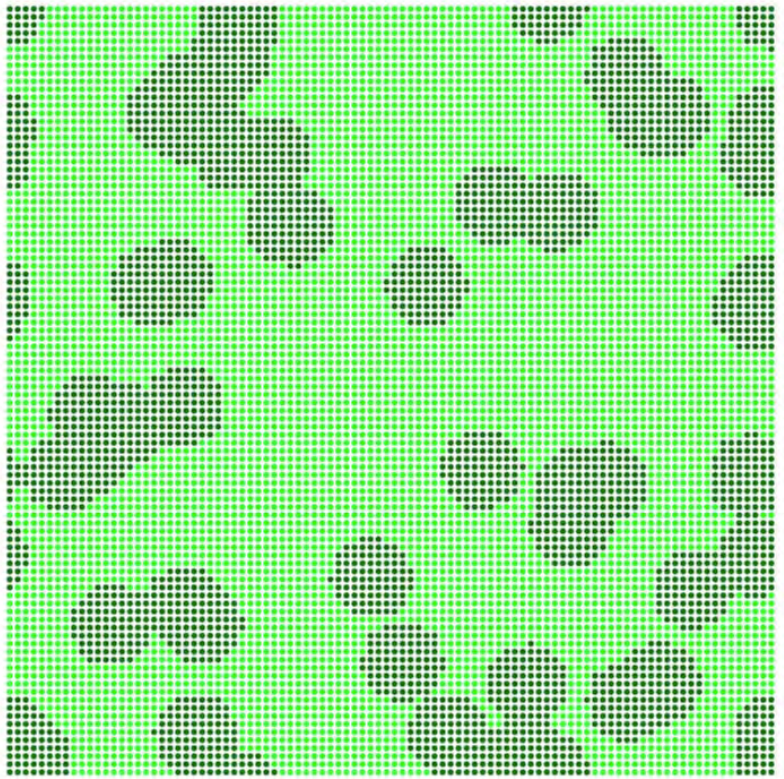
P. Rajak, T. Linker *et al.*, *Proc. ScaDL* ('21)
T. Linker *et al.*, to be published ('21)

Excited-State NNQMD@Scale

Polar vortex formation in ground-state NNQMD



Light-induced phase transition in excited-state NNQMD



- NNQMD can not only simulate the formation of vortices, but also their far-from equilibrium control by laser excitation
- NNQMD reveals light-induced topological phase transition dynamics akin to Kibble-Zurek mechanism in cosmology
- Ultrafast, ultralow-power "topotronics" applications

Synergy with AI-Quantum Computing

FMRG: Artificial Intelligence Driven Cybermanufacturing of Quantum Material Architectures

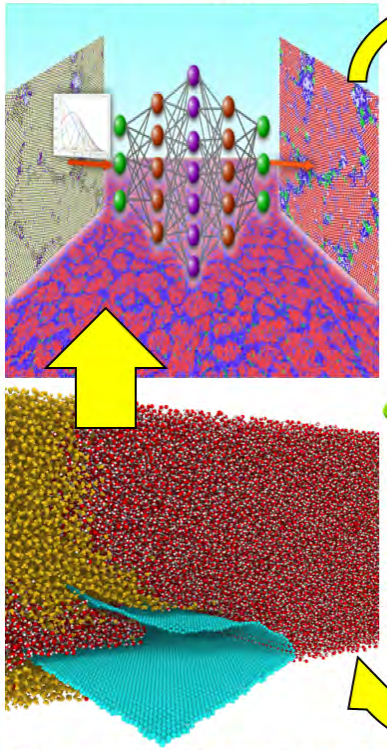
$3.75M NSF project (9/1/2020-8/31/2025)

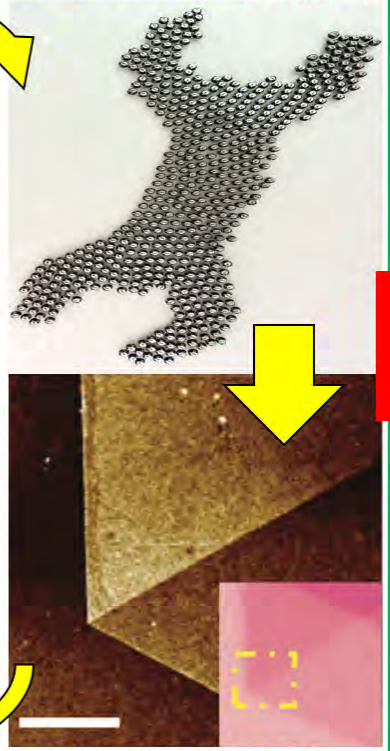
Multidisciplinary Closed-Loop Approach

Machine learning & multiscaling (*Kalia*)

AI-guided self-assembly & collective robotics (*Nagpal*)

Cyber-physical system (*Rawat*)



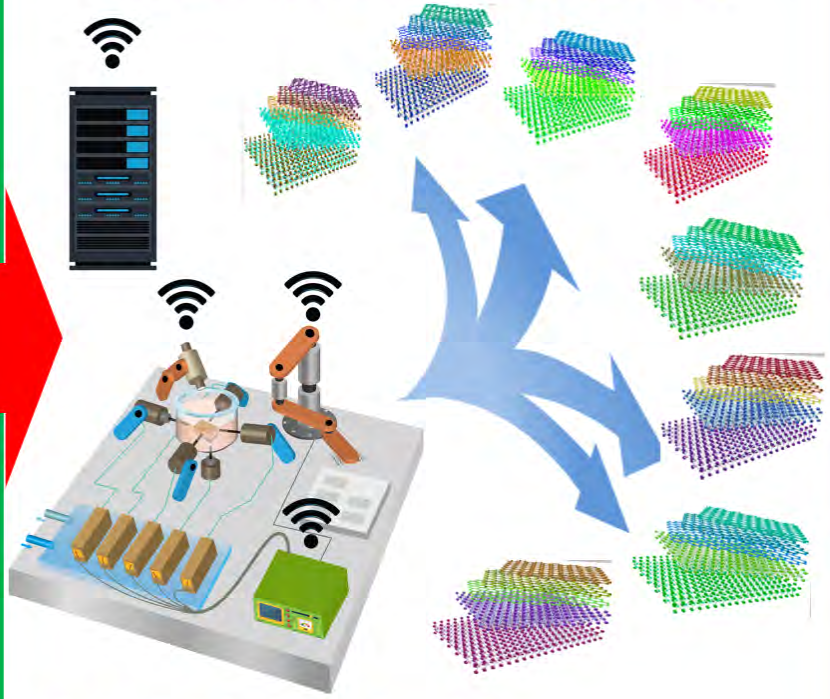


First-principles-based simulations (*Nakano*)

Novel fluidic-folding synthesis (*Wang*)

Future Manufacturing Goal

Precisely aligned van der Waals hetero-structures to enable future twistronics



AI- & robotics-guided, scalable manufacturing platform

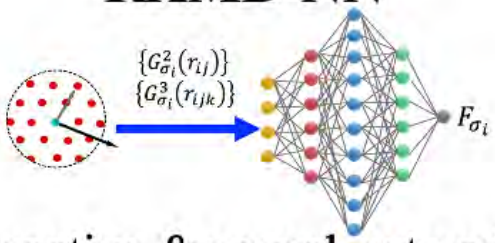
AIQMS Software Suite

AI & Quantum-Computing Enabled Quantum Materials Simulator

QXMD

Nonadiabatic quantum molecular dynamics

RXMD-NN



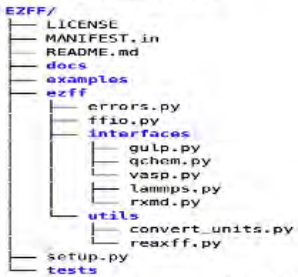
Reactive & neural-network molecular dynamics

Aurora ESP engine

GEARS

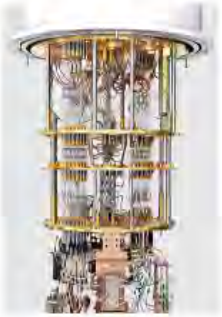
Augmented-reality user interface

EZFF



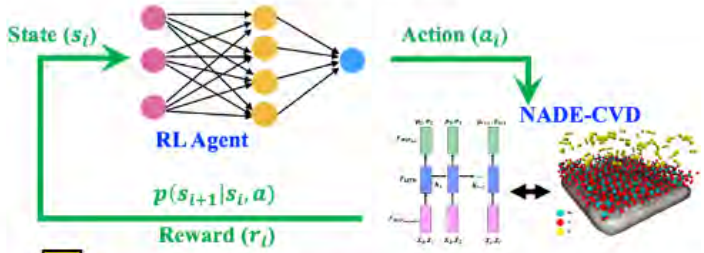
Easy force-field parameterization & uncertain quantification

MISTIQS



Quantum many-body dynamics on quantum computers

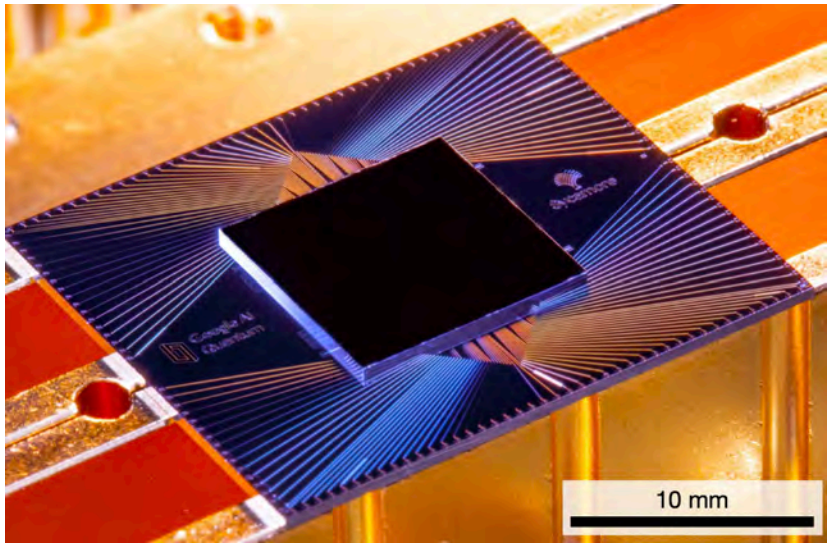
MAITAI



AI tools for materials design

Quantum Computing (QC) for Science

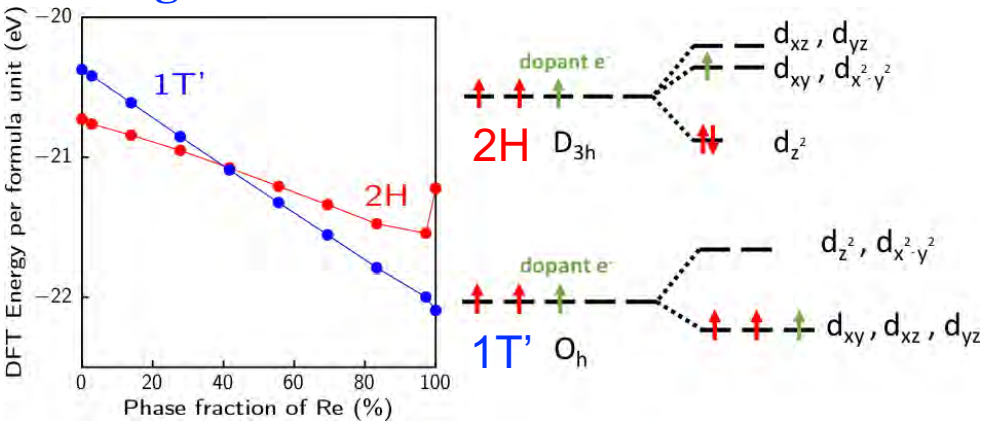
- **U.S. Congress (Dec. 21, '18) signed National Quantum Initiative Act (NQIA) to ensure leadership in quantum computing & its applications**
- **Quantum supremacy demonstrated by Google** [F. Arute, *Nature* **574**, 505 ('19)]
- **Quantum computing for science: *Universal simulator of quantum many-body systems*** [R. P. Feynman, *Int. J. Theo. Phys.* **21**, 467 ('82); S. Lloyd, *Science* **273**, 1073 ('96)]
- **Success in simulating *static* properties of quantum systems (*i.e.*, ground-state energy of small molecules)** [A. Aspuru-Guzik *et al.*, *Science* **309**, 1704 ('05)]
- **Challenge: Simulate quantum many-body *dynamics* on current-to-near-future noisy intermediate-scale quantum (NISQ) computers** [J. Preskill, *Quantum* **2**, 79 ('18)]
- **Successfully simulated nontrivial quantum dynamics on publicly-available IBM's Q16 Melbourne & Rigetti's Aspen NISQ computers, *i.e.*, ultrafast control of emergent magnetism by THz radiation in 2D material**

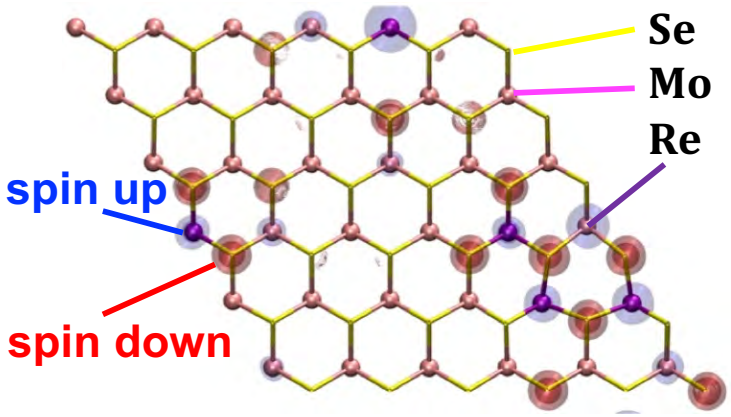


54-qubit Google Sycamore chip

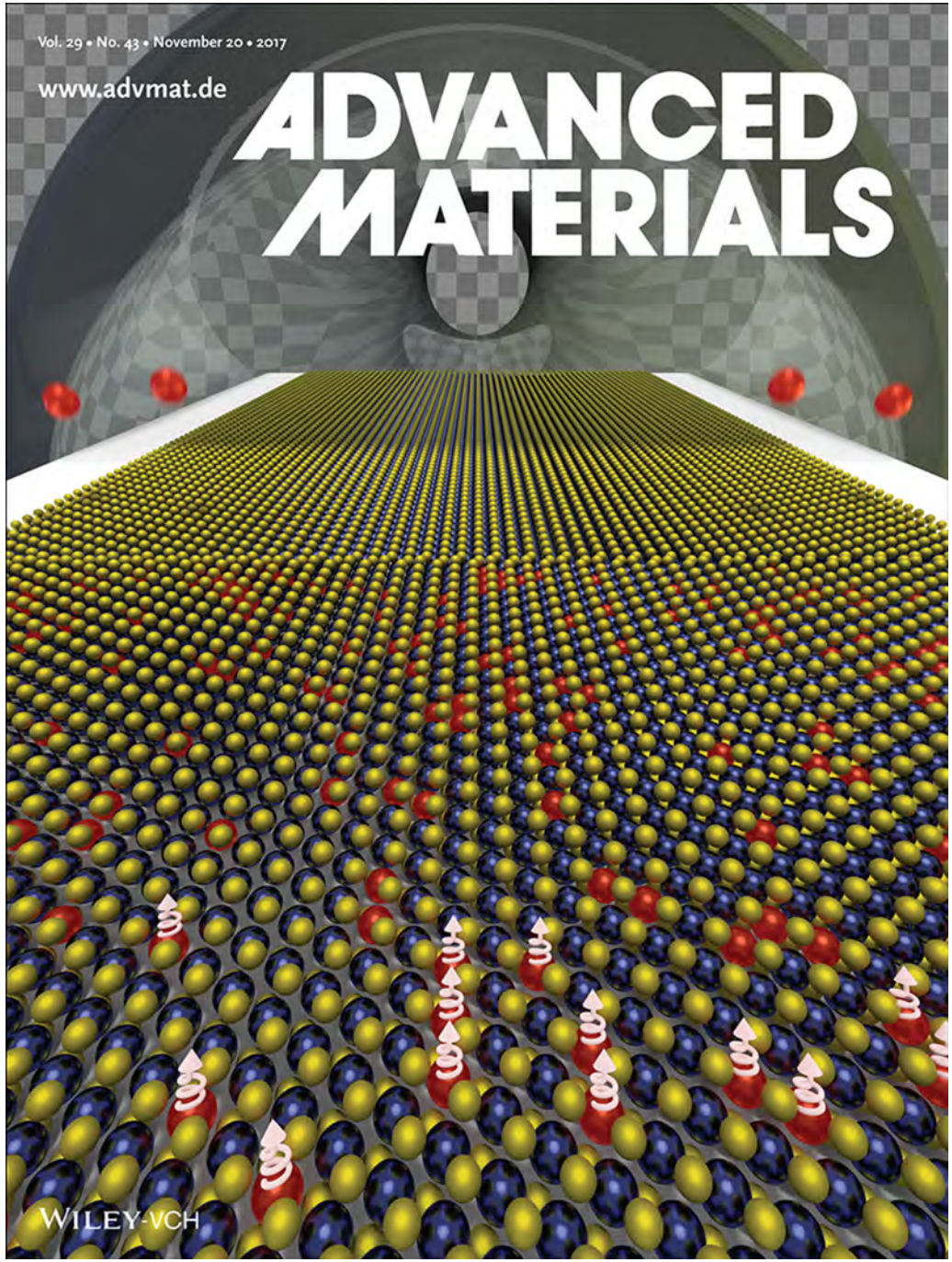
Emergent Magnetism: Structural Transition *via* Doping

- **Experiment at Rice shows 2H-to-1T' phase transformation by alloying $MoSe_2$ with Re**
- **QMD simulations at USC elucidate its electronic origin**
- **Simulation & experiment show novel magnetism centered at Re atoms**



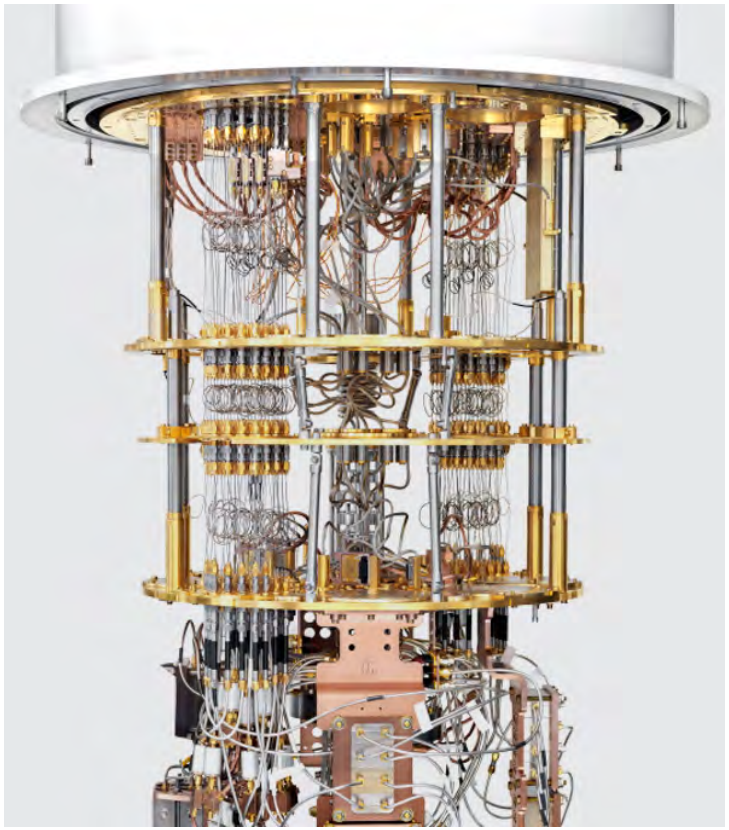


V. Kochat *et al.*, *Adv. Mater*. **29**, 1703754 ('17)

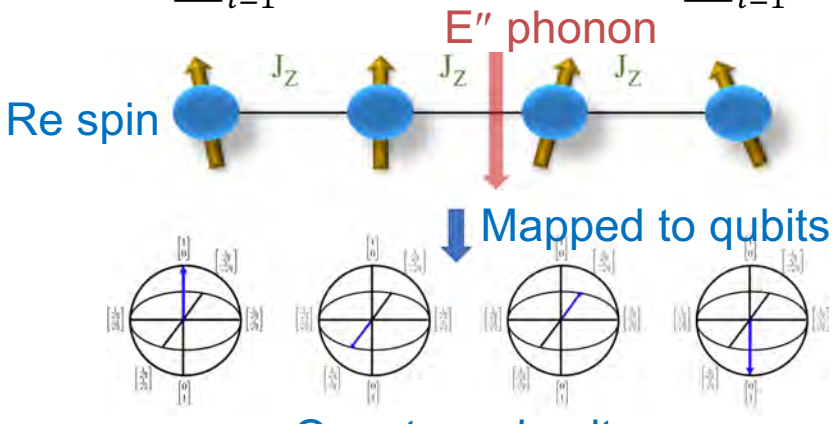


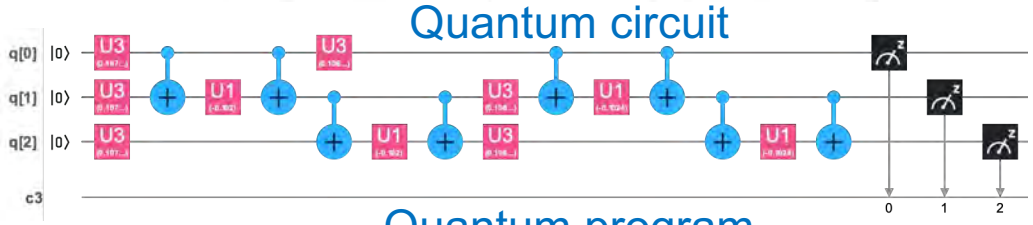
Quantum Computing of Magnetism

- **Simulated quantum many-body dynamics on IBM's Q16 Melbourne & Rigetti's Aspen quantum processors**
- **Electromagnetic-field control of quantum states in a chain of rhenium-magnets in $MoSe_2$ monolayer to realize desired material properties on demand, thereby pushing the envelope of "quantum materials science"**



$$H(t) = -J_z \sum_{i=1}^{N-1} \boldsymbol{\sigma}_z^i \boldsymbol{\sigma}_z^{i+1} - \varepsilon_{ph} \sin(\omega_{ph} t) \sum_{i=1}^{N} \boldsymbol{\sigma}_x^i$$





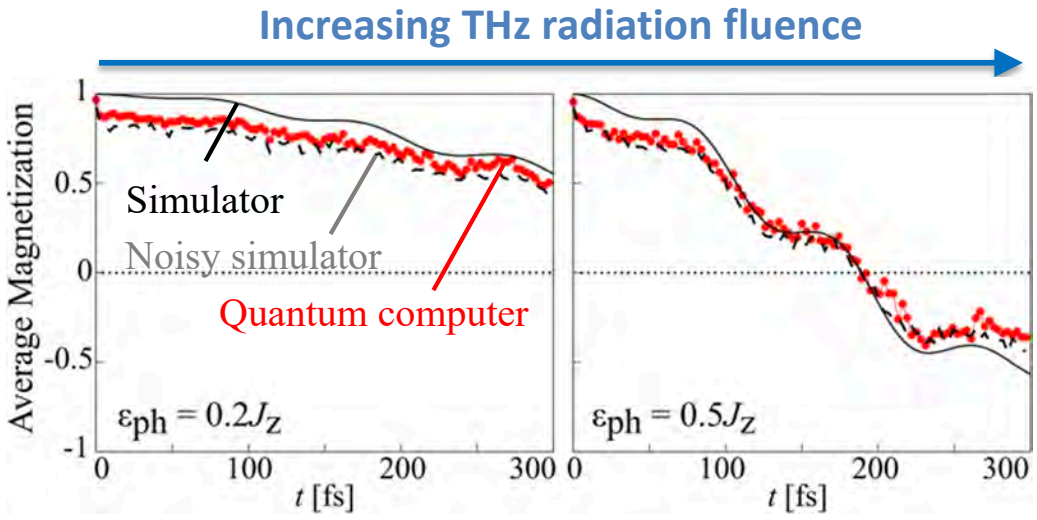
Quantum program

```
····#define·the·two·non-commuting·terms·that·comprise·the·Hamiltonian¬
····Hz·=·PauliTerm("Z",·0,·epsilon_0)¬
····Hy·=·PauliTerm("Y",·0,·epsilon_ph*np.sin(w_ph*t))¬
····#exponentiate·the·terms·of·the·Hamiltonian·for·use·in·Trotter·approx¬
····exp_Hz·=·exponential_map(Hz)(delta_t/(2.0*hbar))¬
····exp_Hy·=·exponential_map(Hy)(delta_t/hbar)¬
```

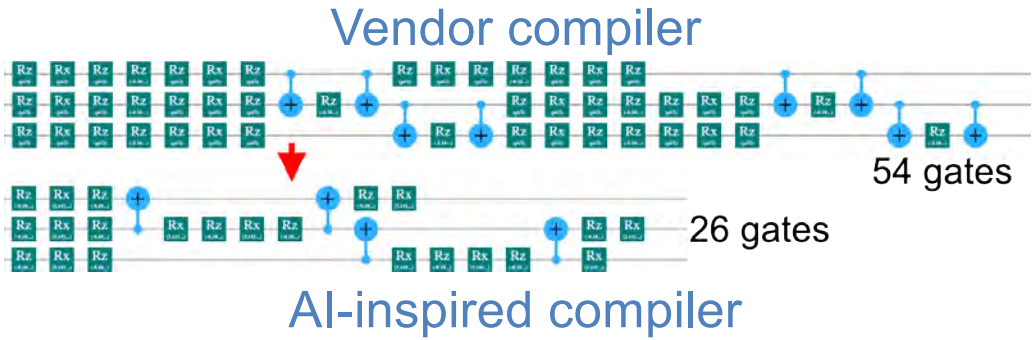
Quantum Dynamics on NISQ Computers

- **Quantum-dynamics simulations on NISQ computers show dynamic suppression of magnetization by THz radiation**

L. Bassman *et al.*,
Phys. Rev. **101**, 184305 ('20)



- **AI-inspired quantum compiler reduced the circuit size by 30% to mitigate environmental noise**

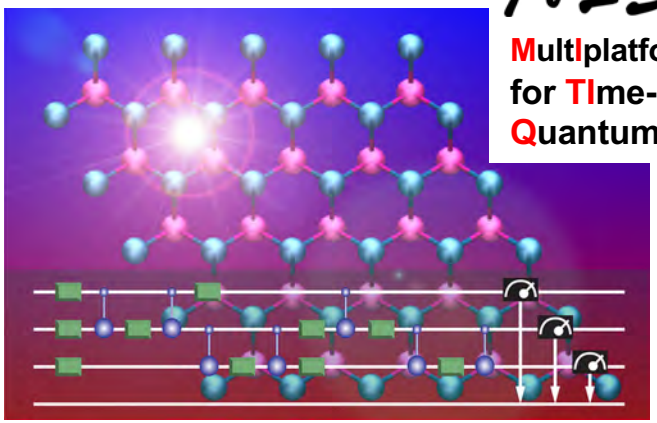


L. Bassman *et al.*,
Quantum Sci. Tech. **6**, 014007 ('21)

- **Full-stack, cross-platform software for quantum dynamics simulations on NISQ computers**

MISTIQS

Mult**I**platform **S**oftware for **TI**me-dependent **Q**uantum **S**imulation

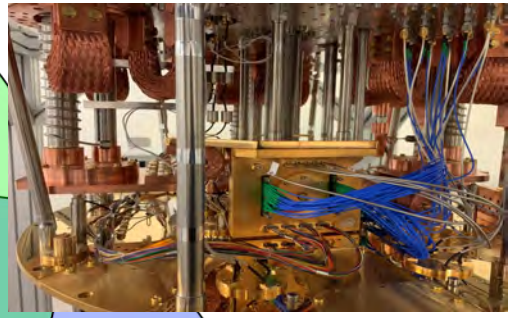


C. Powers *et al.*, *SoftwareX* **14**, 100696 ('21)
https://github.com/USCCACS/MISTIQS

Training Cyber Science Workforce

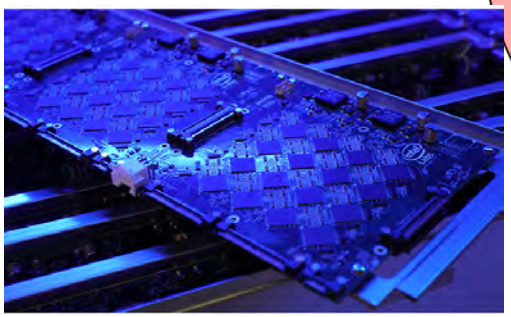
- New generation of computational scientists at the nexus of exascale computing, quantum computing & AI
- Unique dual-degree program: Ph.D. in materials science or physics, along with MS in computer science specialized in high-performance computing & simulations, MS in quantum information science or MS in materials engineering with AI

Horse Ridge II
Quantum computer



Cybertraining on exa + quantum + AI platforms

Neuromorphic
Pohoiki Springs



Exascale
Aurora

Additional Resources

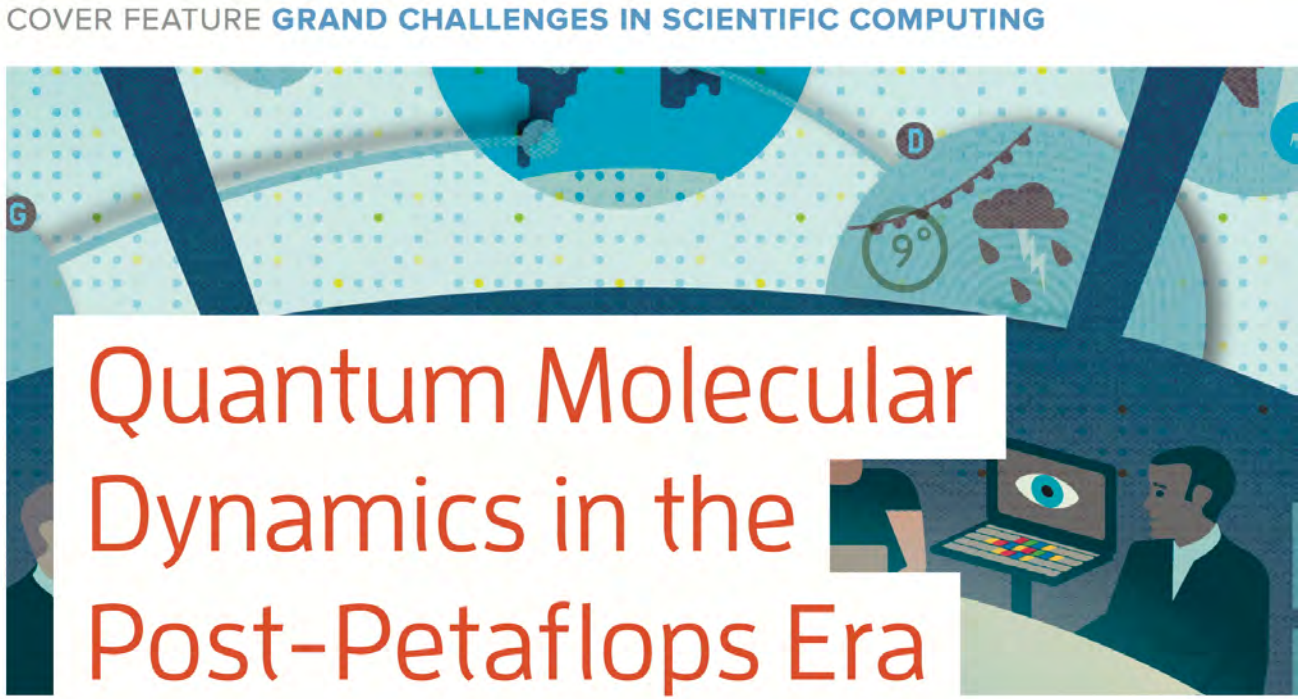
Detailed lecture notes are available at a USC course home page

EXTREME-SCALE QUANTUM SIMULATIONS

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

https://aiichironakano.github.io/cs699.html

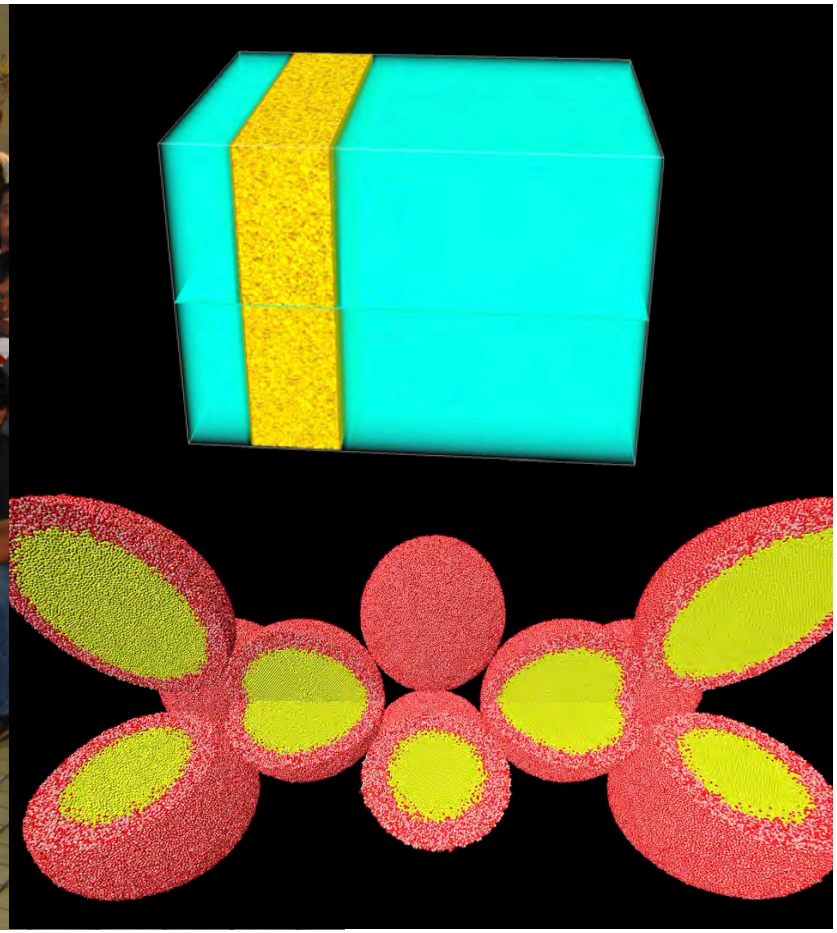
See also N. Romero *et al.*, *IEEE Computer* **48(11)**, 33 ('15)
https://aiichironakano.github.io/cs653/Romero-QMD-IEEEComputer15.pdf



Conclusion

1. Large spatiotemporal-scale quantum & reactive molecular dynamics simulations enabled by divide-conquer-recombine
2. Broad applications of (HPC+AI+QC)4Science

Thank You



Research supported by
DOE-CMS/BES/INCITE/Aurora-ESP,
ONR-MURI, NSF-FM, Intel

Extra Slides

Divide-&-conquer accelerated dynamics

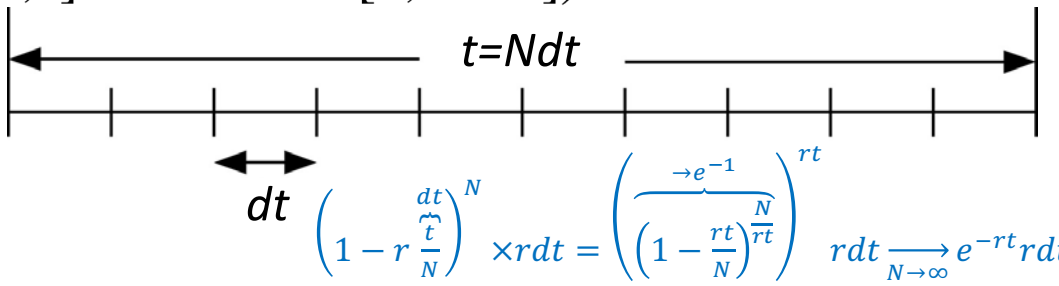
Kinetic Monte Carlo (KMC) Simulation

- **Probability density $P(t)$ of time t between successive events**

$$P(t)dt = \text{probability}(\text{no event in } [0,t] \wedge 1 \text{ event in } [t, t+dt])$$

$$= P(0,t) \times rdt = e^{-rt} \times rdt$$

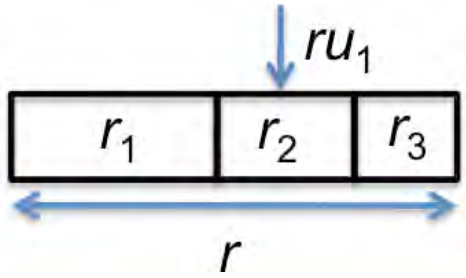
$$\therefore P(t) = re^{-rt}$$



- **Random time-interval generation: Let u be a uniform random number in [0,1] & generate $t = -\ln(u)/r \in [0,\infty]$**

$$\because P(t) = P(u)\left|\frac{du}{dt}\right| = 1 \times re^{-rt} = re^{-rt} \qquad u = e^{-rt}$$

- **KMC algorithm: Let $\{r_1, r_2, \ldots\}$ be a set of possible events, $r = \Sigma_i r_i$, and u_1 & u_2 are uniform random numbers in [0,1]:**



1. **Pick the next event i as** $i = \min_j \left\{ \sum_{k=1}^{j} \frac{r_k}{r} > u_1 \right\}$
   Pick i-th event with probability $p_i = r_i/r$
2. **Advance the time by** $t = -\ln(u_2)/r$

$$P(t)dt = \overbrace{e^{-rt}}^{\text{no evt in } [0,t]} \overbrace{(r_1 + r_2 + \cdots)dt}^{\text{evt 1 or 2 or ... in } [t.t+dt]}$$

K. A. Fichthorn & W. H. Weinberg, *J. Chem. Phys.* **95**, 1090 ('91)

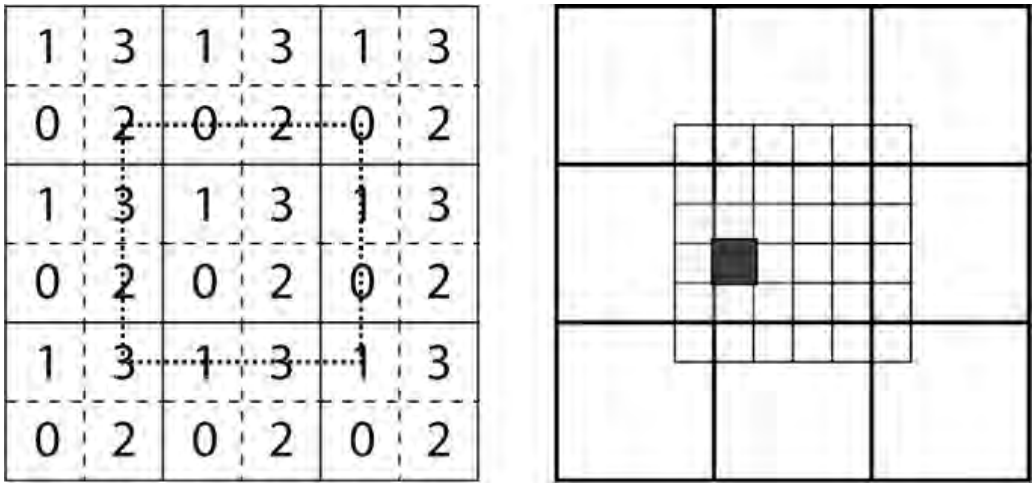
See lecture notes at https://aiichironakano.github.io/phys516-lecture.html

Divide-&-Conquer KMC Algorithm

- **Domain decomposition: Concurrent events among multiple domains, *d***

$$\Delta t = -\ln(rnd) / \sum_d r_d = O(N^{-1}) \quad \Rightarrow \quad -\ln(rnd) / \max_d (r_d) = O(1)$$

- **Colored domain blocks: Avoids conflicting events by allowing concurrent events only with domains of the same color, which are well-separated**



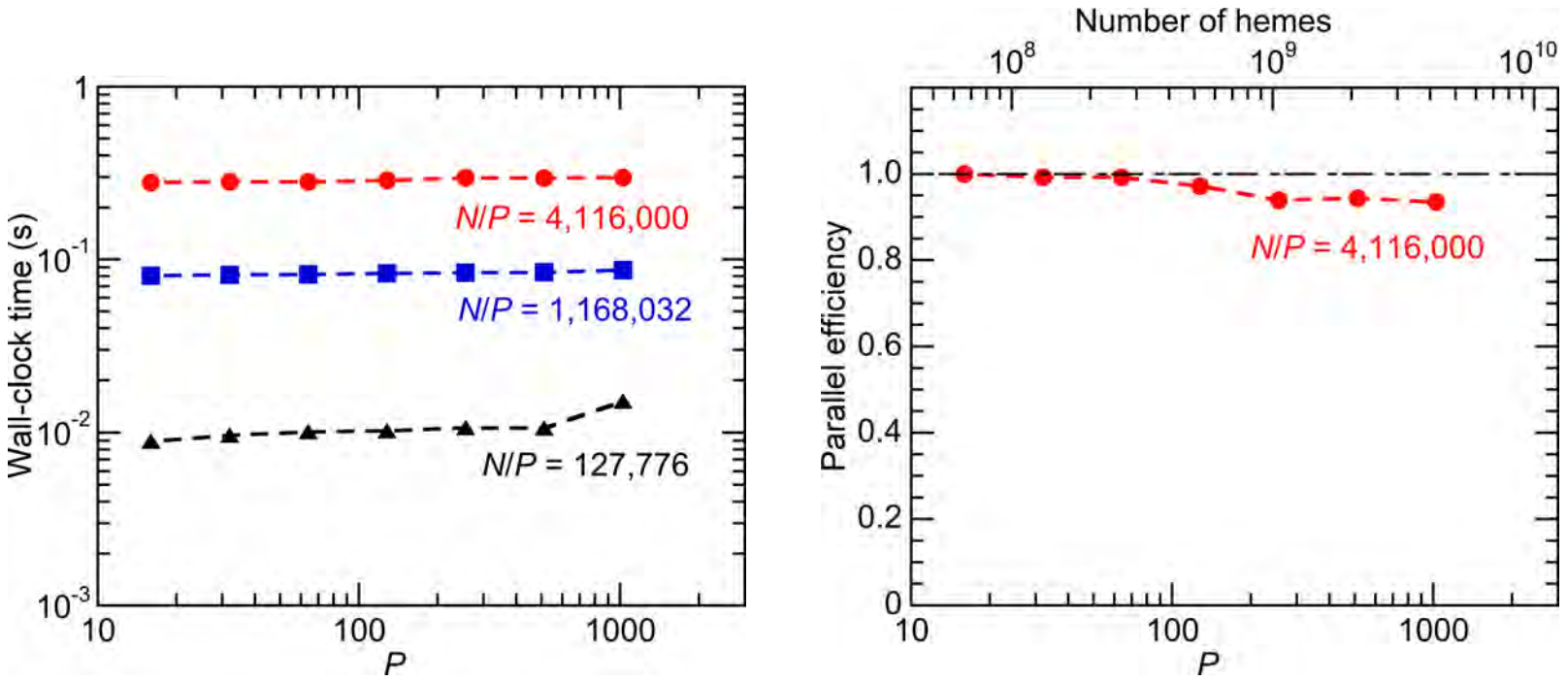
E. Martinez *et al.*, *J. Comp. Phys.* **230**, 1359 ('11)

- **Neighbor-domain caching for spatial decomposition via message-passing**
- **Dual linked-list cell method: (1) small cells for constructing neighbor lists for nearest-neighbor hopping events; (2) large cells for domain-block coloring**

H. Byun *et al.*, *Comput. Phys. Commun.* **219**, 246 ('17)

Scalable Parallel KMC

- **Benchmark tests on electron transfer in heme aggregates**
- **Better weak-scaling for coarser granularity (*N* hemes on *P* procesors)**



- **Weak-scaling parallel efficiency 0.935 for a 4.2 billion-heme system on 1,024 Intel Xeon processors**

H. Byun *et al.*, *Comput. Phys. Commun*. **219**, 246 ('17)

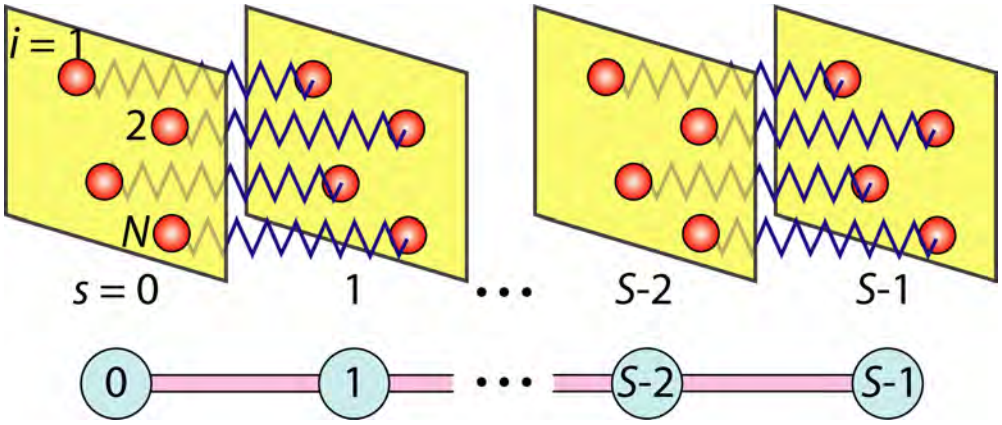
Temporal Locality in Long-Time Dynamics

- **Temporal locality:** Rare transitions between local minimum-energy states
- **Transition state theory:** Reformulate *sequential* long-time dynamics as *parallel* search for low activation-barrier transition events
- **Discrete graph abstraction:** Linear combinations of atomistic events (LCAE)

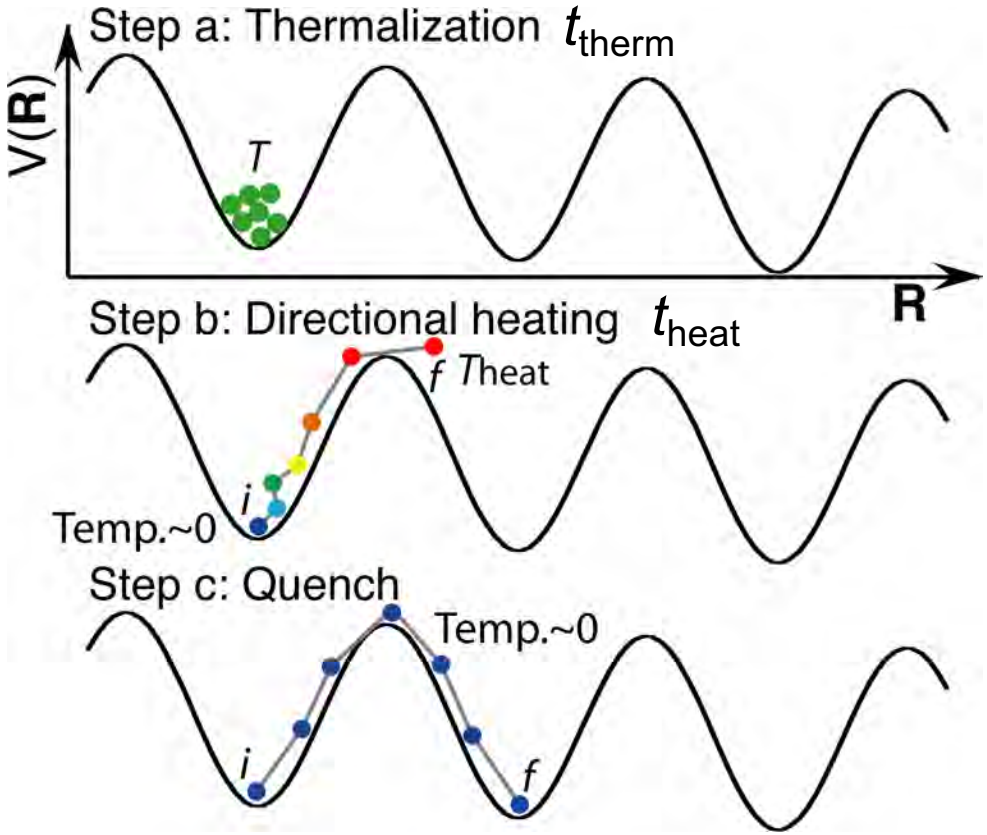
A. Nakano, *Comput. Phys. Commun.* **176**, 292 ('07)

- **Directionally heated nudged elastic band (NEB) method:** Search for thermally activated events without the knowledge of final states

$$\mathbf{M}\ddot{\mathbf{R}}_s = \mathbf{F}_s - M\gamma_s\dot{\mathbf{R}}_s \quad (s = 0, \ldots, S-1)$$



$$\mathbf{F}_s = \begin{cases} -\left.\dfrac{\partial V}{\partial \mathbf{R}_s}\right|_{\perp} + \left.\mathbf{F}_s^{\mathrm{spr}}\right|_{\parallel} & (1 \le s \le S-2) \\ -\dfrac{\partial V}{\partial \mathbf{R}_s} & (s = 0, S-1) \end{cases}$$



Space-Time-Ensemble Parallel (STEP) NEB

- **Path ensemble method (PEM): Long-time simulation in the framework of kinetic Monte Carlo—*molecular kinetics simulation***

$$r_b = \left\{ t_{\text{therm}} + t_{\text{heat}} \exp\left[\frac{\Delta_b}{k_B} \left(\frac{1}{T} - \frac{1}{T_{\text{heat}}} \right) \right] \right\}^{-1}$$

$$P_b = \frac{r_b}{r} = \frac{r_b}{\sum_{b=0}^{B-1} r_b}$$

- **Space-time-ensemble parallelism (STEP)**

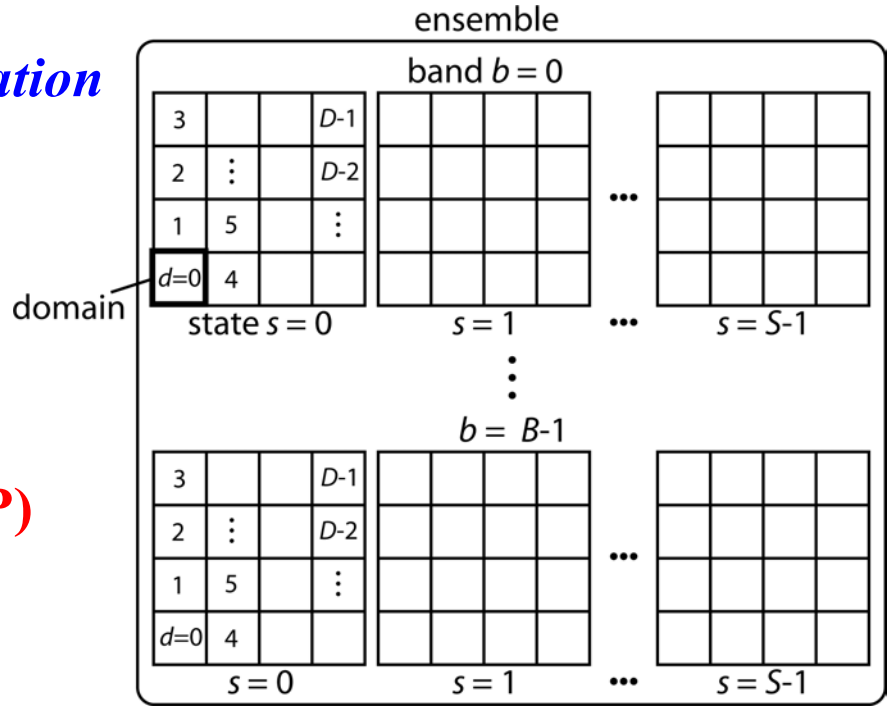
= **spatial decomposition within each state (*D* domains)**

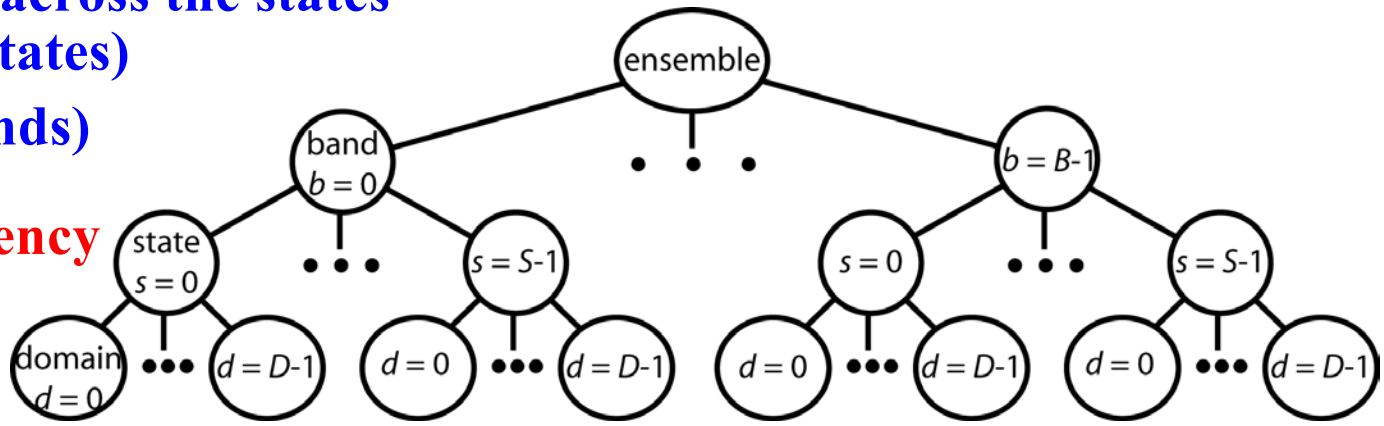
+ **temporal parallelism across the states within each band (*S* states)**

+ **band ensemble (*B* bands)**

- **Hierarchical concurrency**

$P = BSD$





A. Nakano, *Comput. Phys. Commun.* **178**, 280 ('08)