Quantum Molecular Dynamics Simulations

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QXMD tutorial:
Subodh Tiwari, Lindsay Bassman,
Aravind Krishnamoorthy,
Ken-ichi Nomura

MAGICS Workshop
November 12, 2018, Washington, DC

Additional Resources

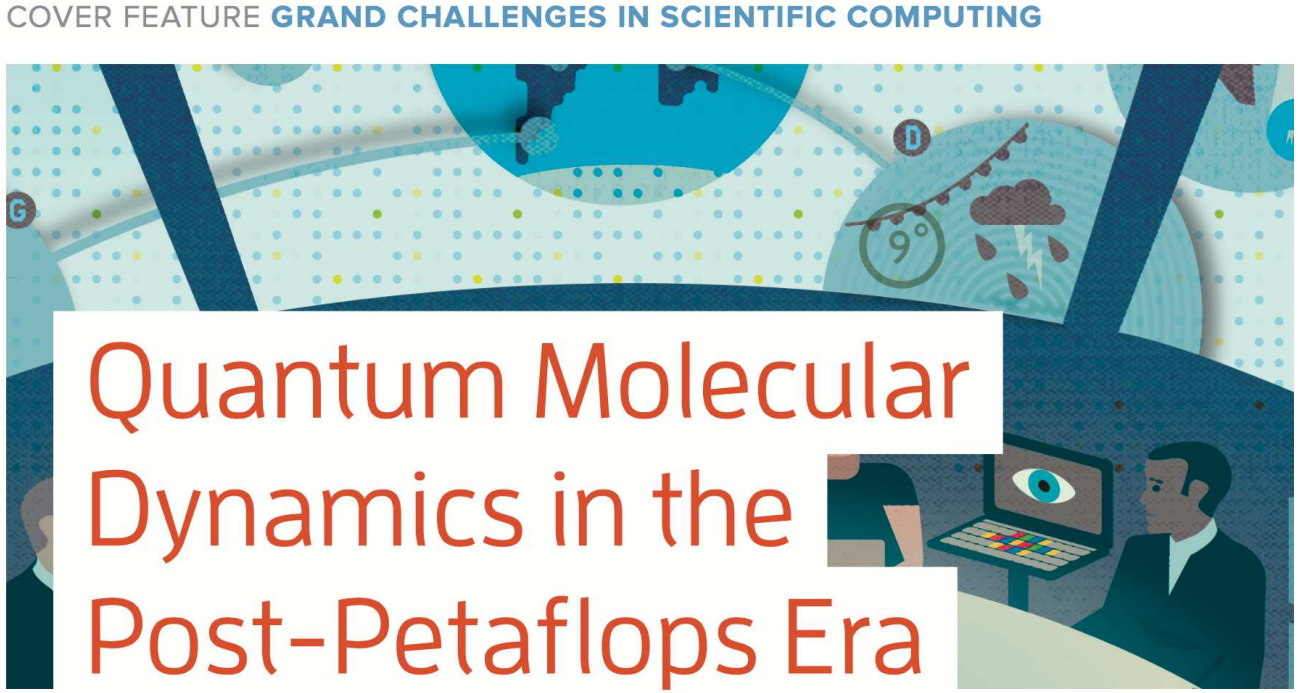
Detailed lecture notes are available at a USC course home page

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".

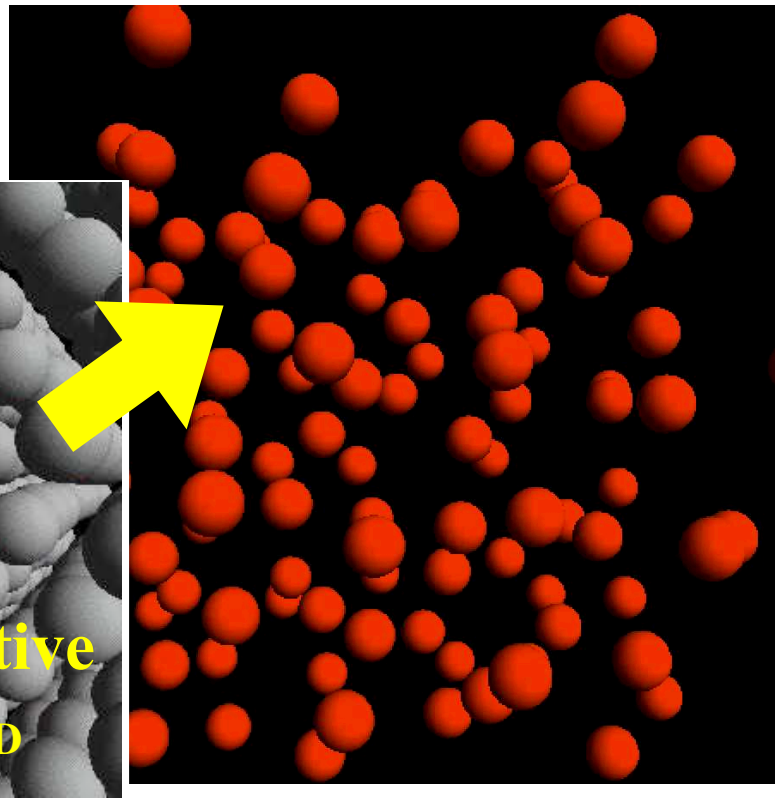
http://cacs.usc.edu/education/cs699-lecture.html

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

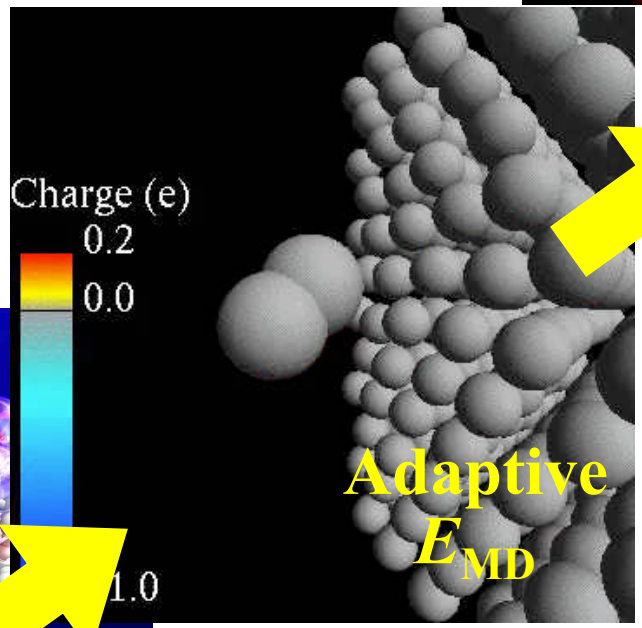


Molecular Dynamics Hierarchy

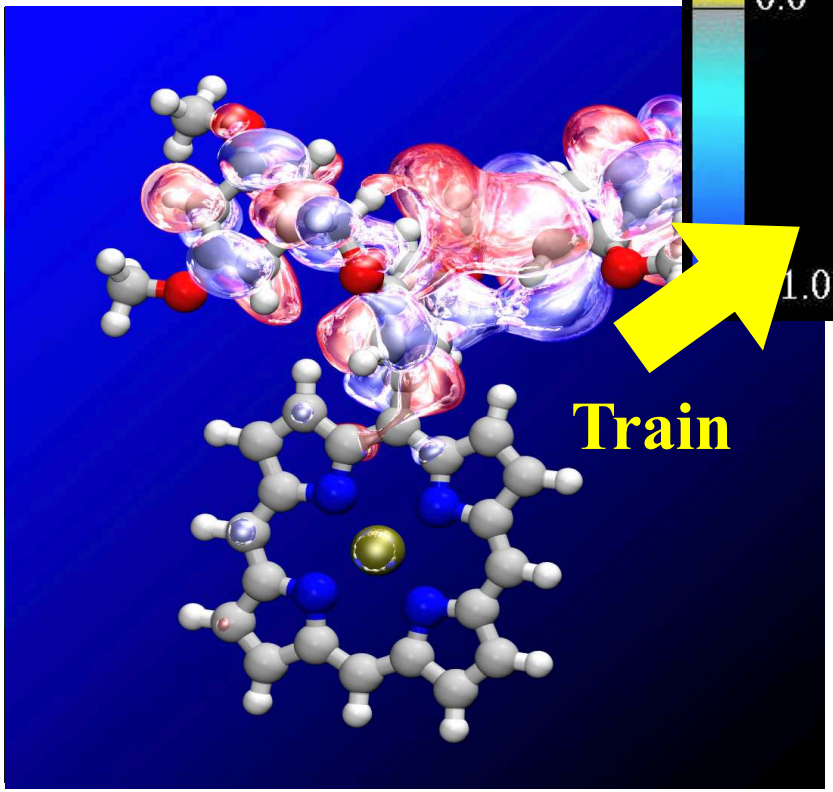
Molecular Dynamics (MD)



Reactive MD (RMD)



Nonadiabatic quantum MD (NAQMD)



First principles-based reactive force-fields

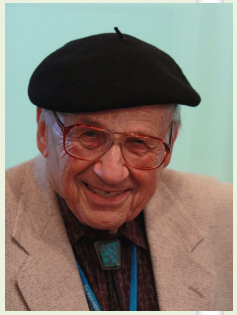
- **Reactive bond order $\{BO_{ij}\}$**
  → Bond breakage & formation
- **Charge equilibration (QEq) $\{q_i\}$**
  → Charge transfer

Quantum Molecular Dynamics (QMD)

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

First molecular dynamics using an empirical interatomic interaction

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



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

Density functional theory (DFT)

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

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

$O(C^N)$	$\rightarrow$	$O(N^3)$
1 N-electron problem		N 1-electron problems
intractable		tractable
$\psi(\mathbf{r}_1 \ldots, \mathbf{r}_N)$		$\{\psi_i(\mathbf{r}) \mid i = 1, \ldots, N\}$

$O(N)$ 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_{atom} nuclei, with the Hamiltonian**

$$\widetilde{H} = \sum_{I=1}^{N_{\text{atom}}} \frac{\mathbf{P}_I^2}{2M_I} + H(\{\mathbf{r}_i\},\{\mathbf{R}_I\})$$

nucleus momentum; electron position; nucleus position

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

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 $\rho(\mathbf{r})$

- **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

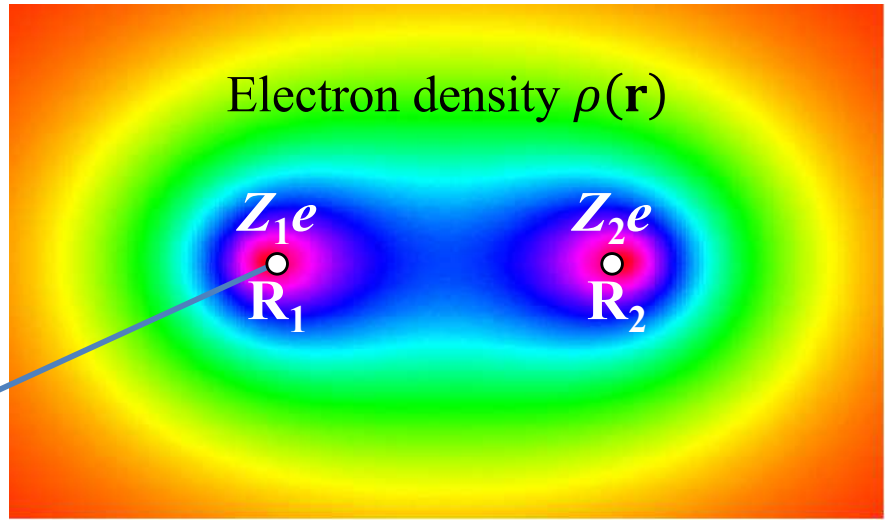
$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})]$$

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

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

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

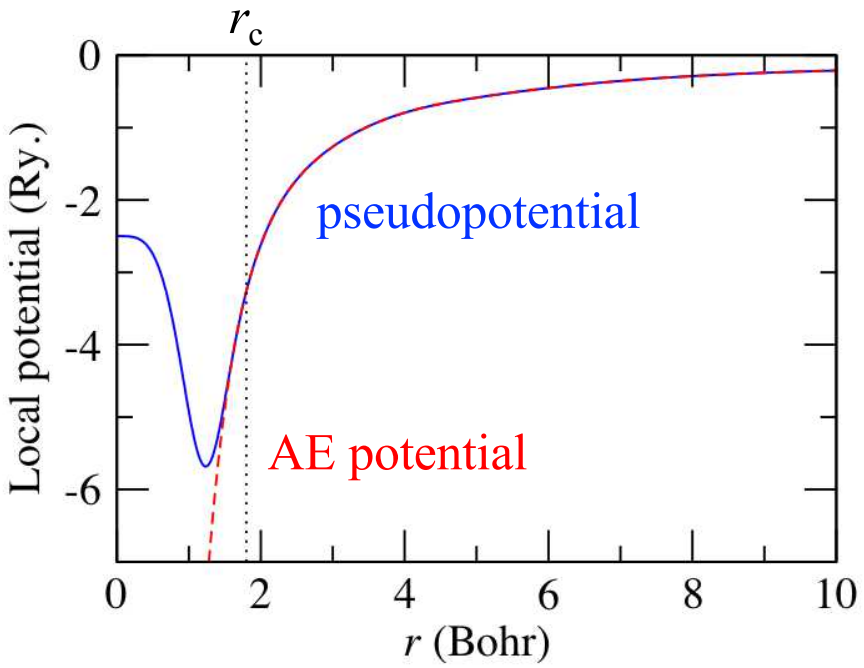
W. Kohn & L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev*. **140**, A1133 ('65)

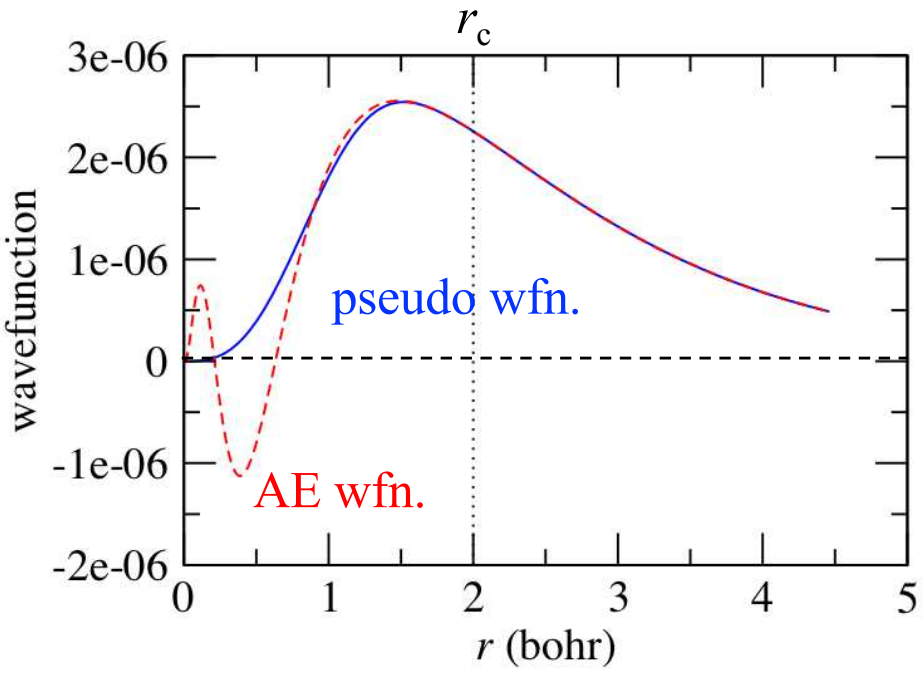
Abstraction: Exchange-Correlation Functional

- **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 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 $\rho(\mathbf{r})$

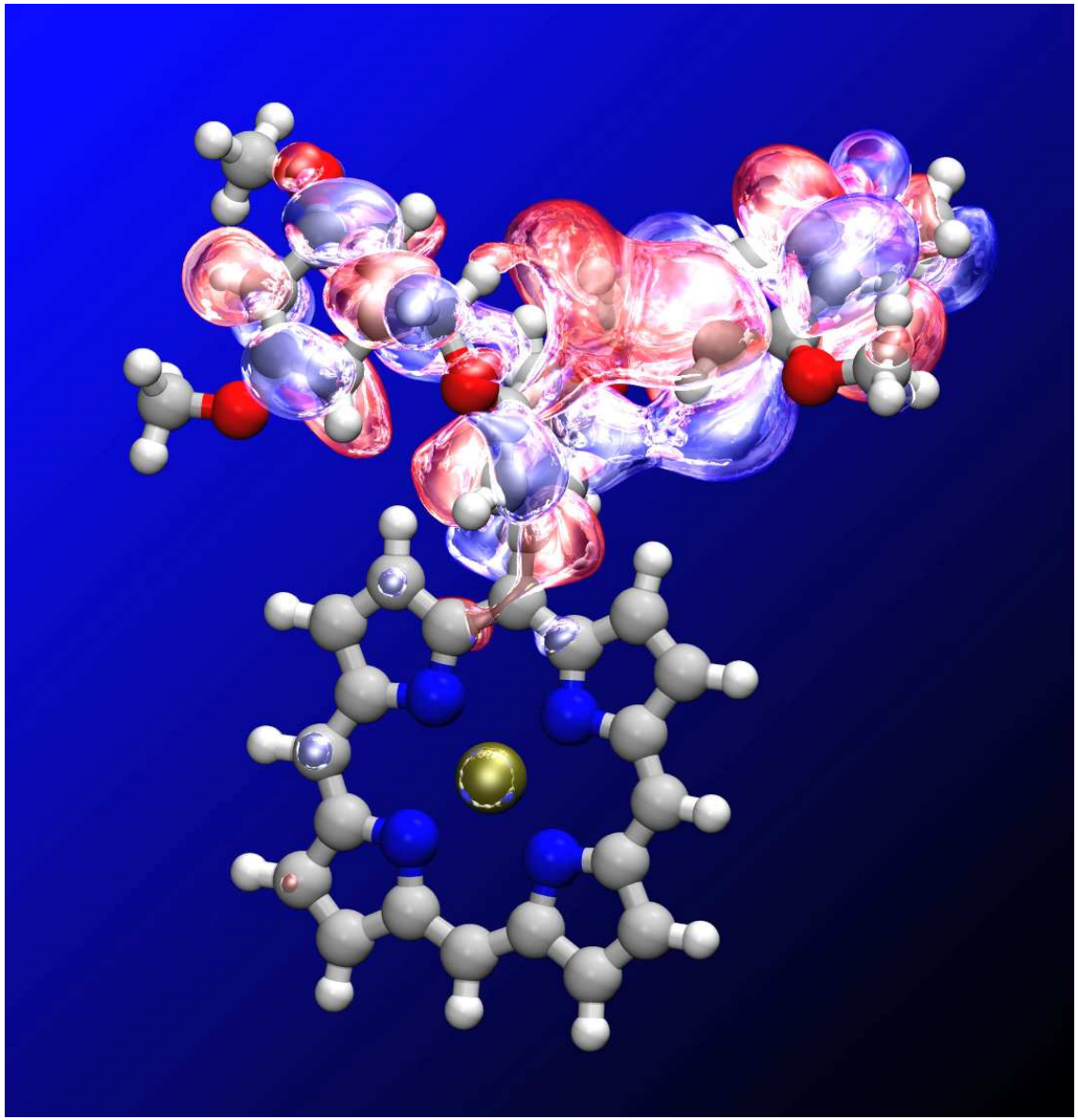
$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \, \Theta(\mu - \epsilon_n)$$

Chemical potential

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

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

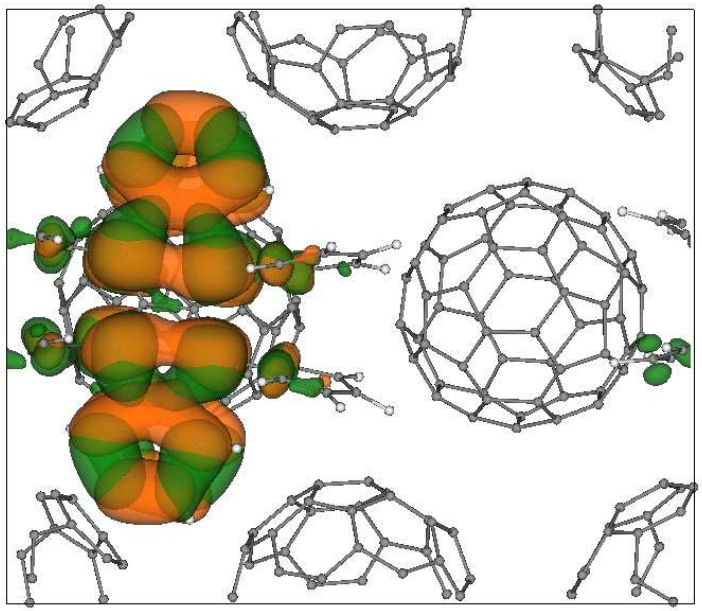
Nonadiabatic Quantum Molecular Dynamics



W. Mou *et al*., *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)

Zn porphyrin

Rubrene/C_{60}



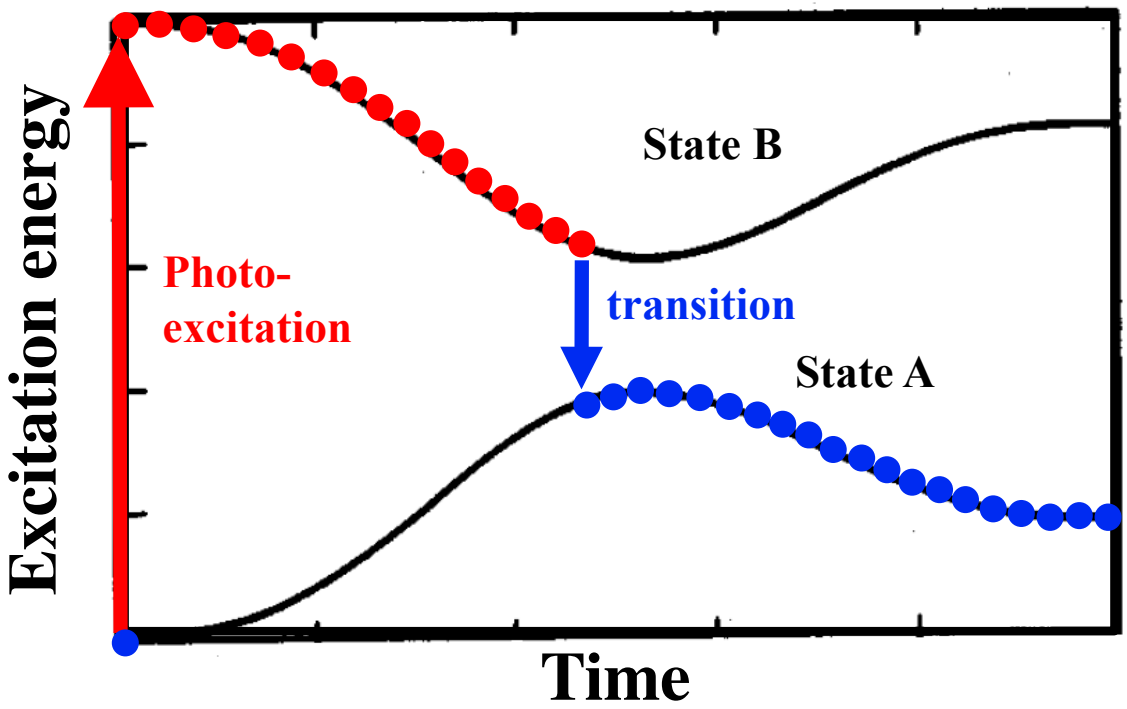
quasi-electron; quasi-hole

- **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

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

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

J-th adiabatic excited state

Electronic transition assisted by nuclei motion

QXMD Code

- **Quantum molecular dynamics (QMD) code developed by Prof. Fuyuki Shimojo at Kumamoto University in Japan**
- **Various eXtensions co-developed with USC-CACS: Nonadiabatic QMD, linear-scaling divide-&-conquer, parallelization, *etc*.**
- **Unique features:**
  - **> Interatomic forces with electronic excitation to study photo-excited lattice dynamics**
    Shimojo *et al*., *Comput. Phys. Commun*. **184**, 1 ('13)
  - **> Range-separated hybrid exact-exchange functional for exciton binding**
    Tawada *et al*., *J. Chem. Phys*. **120**, 8425 ('04)
  - **> Lean divide-&-conquer density functional theory (LDF-DFT) with small $O(N)$ prefactor**
    Shimojo *et al*., *J. Chem. Phys*. **140**, 18A529 ('14)
  - **> Omni-directional multiscale shock technique (OD-MSST)**
    Shimamura *et al*., *Appl. Phys. Lett*. **107**, 231903 ('15); **108**, 071901 ('16)
- **Other features:**
  - **> Various functionals: spin-polarized, GGA+U, DFT+D, nonlocal correlation**
  - **> Nudged elastic band (NEB) method for energy-barrier calculation**
  - **> Berry-phase computation of polarization**

Software download site:
https://magics.usc.edu/qxmd

Current & Future Computing Platforms

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

U.S. DEPARTMENT OF ENERGY
INCITE
LEADERSHIP COMPUTING

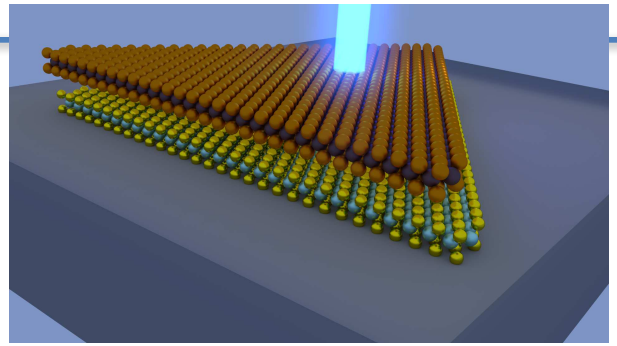
- **NAQMD & RMD simulations on full 800K cores**

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

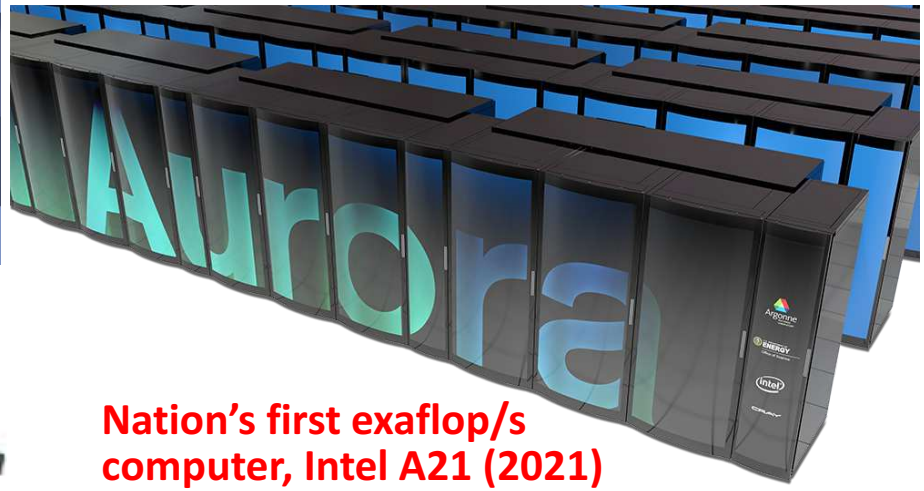


AURORA | EARLY SCIENCE PROGRAM

Early Science Projects for Aurora Supercomputer Announced

Metascalable layered materials genome

Investigator: Aiichiro Nakano, University of Southern California



Nation's first exaflop/s computer, Intel A21 (2021)

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

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

CACS@A21 in the Global Exascale Race

SUPERCOMPUTING

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

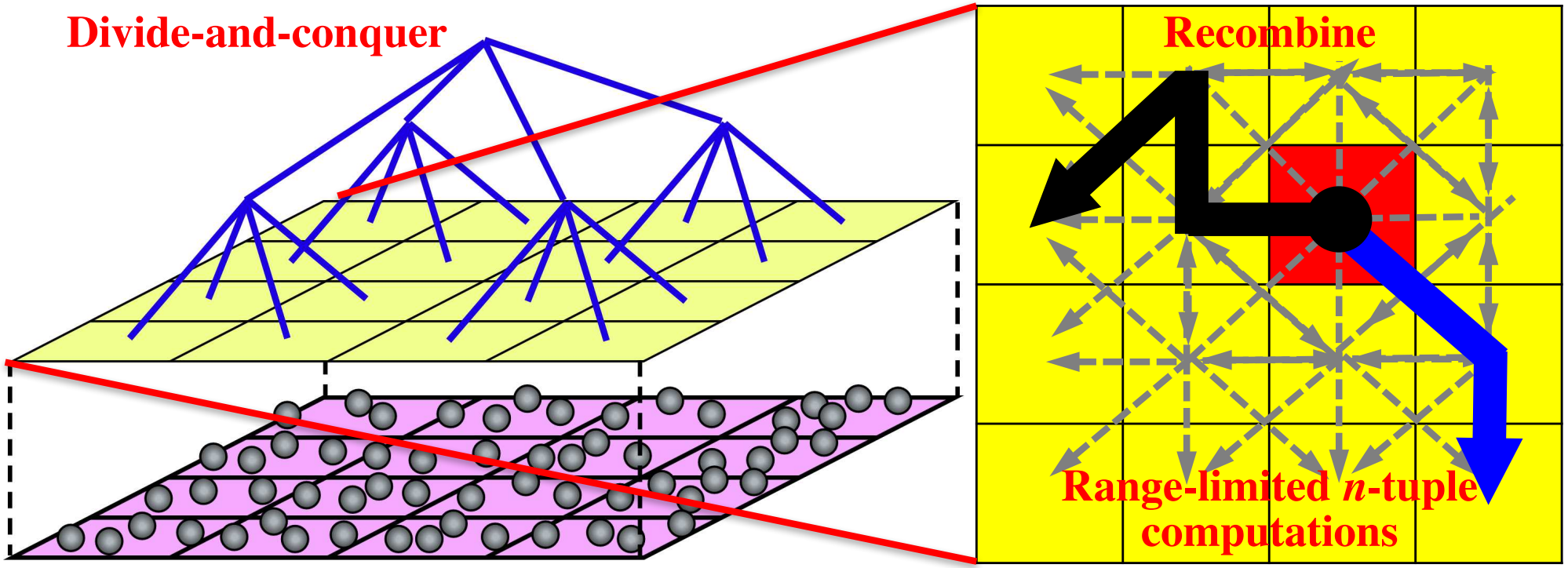
By **Robert F. Service**

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.

Divide-Conquer-Recombine (DCR) Engines



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

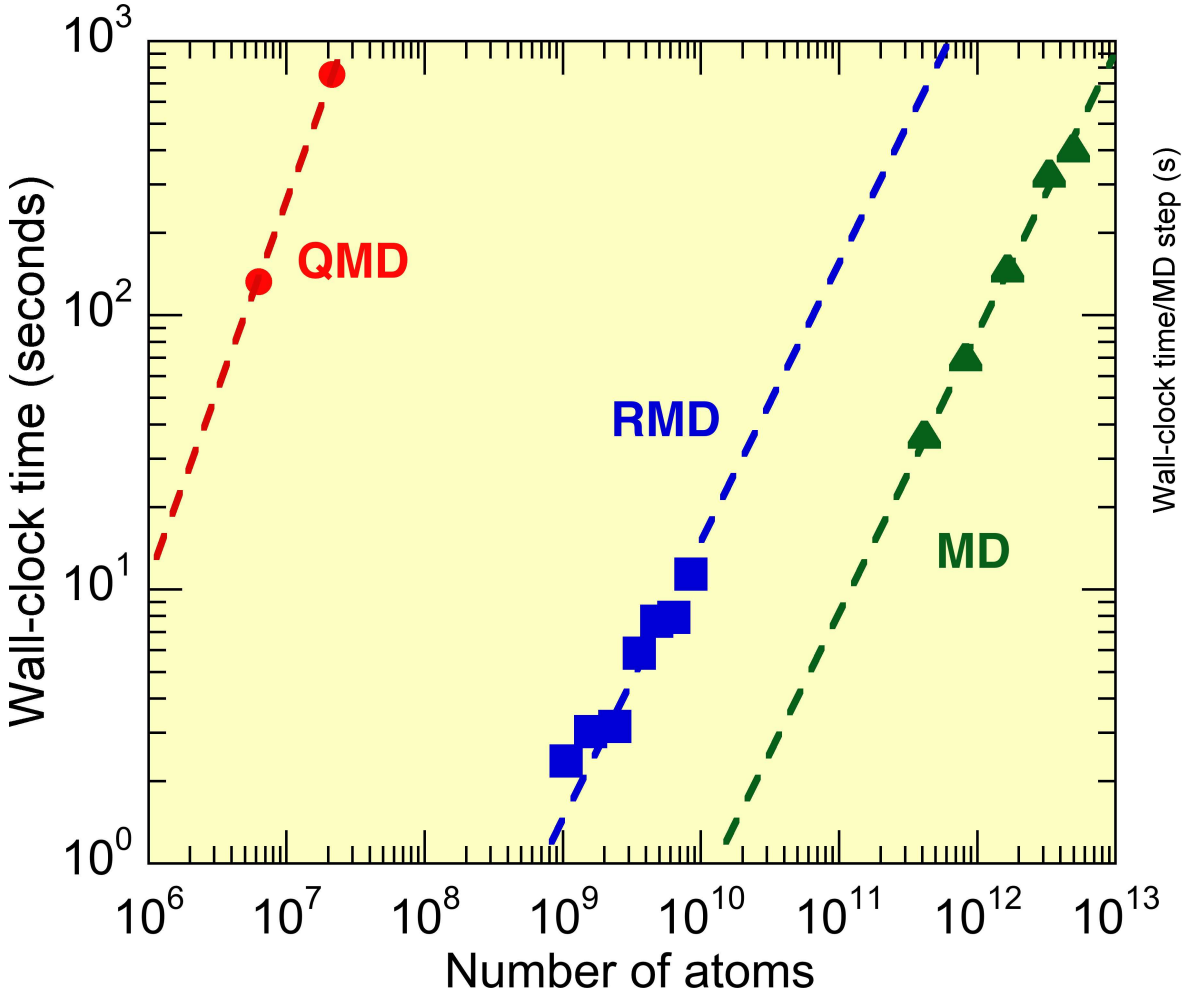
- **Lean divide-&-conquer density functional theory (LDC-DFT) algorithm minimizes the prefactor of $O(N)$ computational cost**

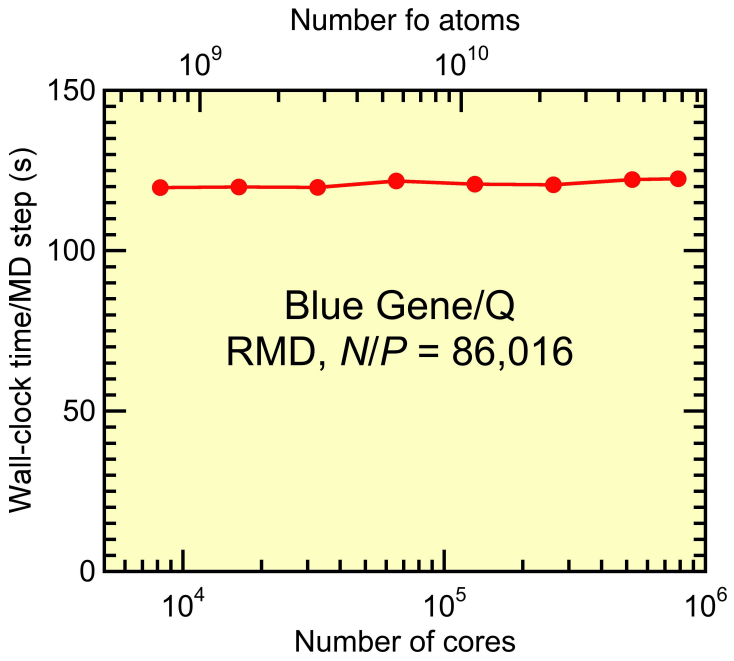
  F. Shimojo *et al.*, *J. Chem. Phys.* **140**, 18A529 ('14); K. Nomura *et al.*, *IEEE/ACM SC14*

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

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

Scalable Simulation Algorithm Suite





QMD (quantum molecular dynamics): DC-DFT

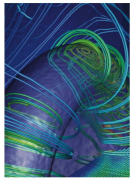
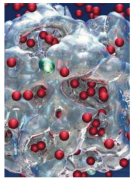
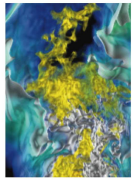
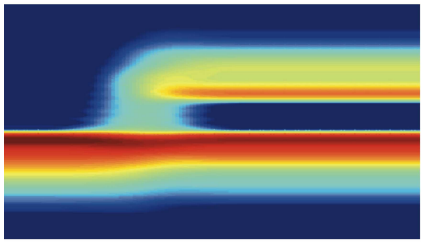
RMD (reactive molecular dynamics): F-ReaxFF

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

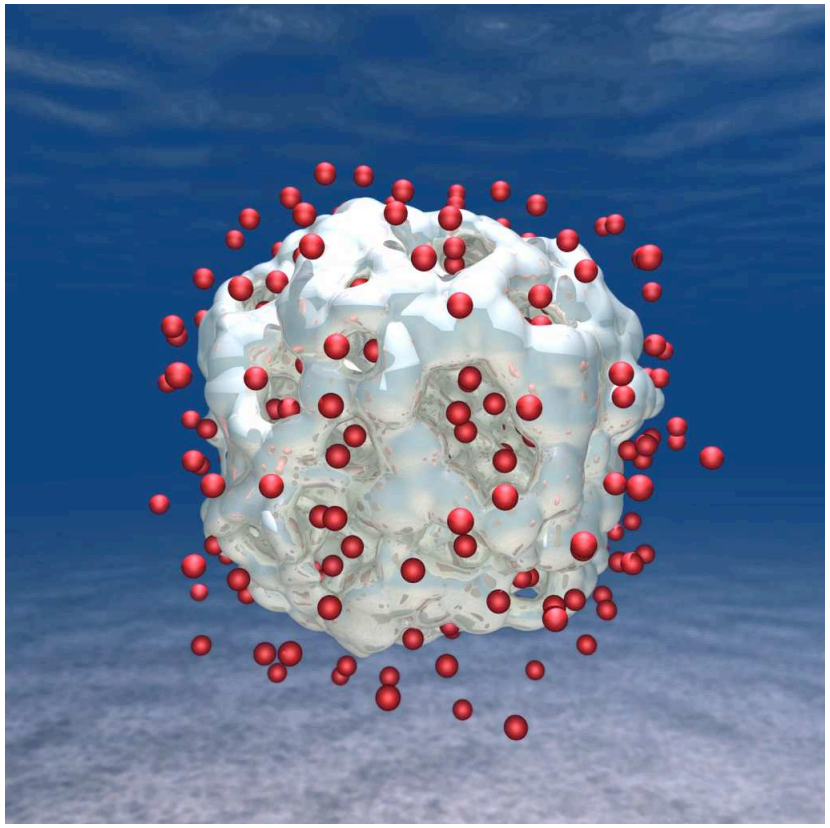
BASIC ENERGY SCIENCES

EXASCALE REQUIREMENTS REVIEW

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

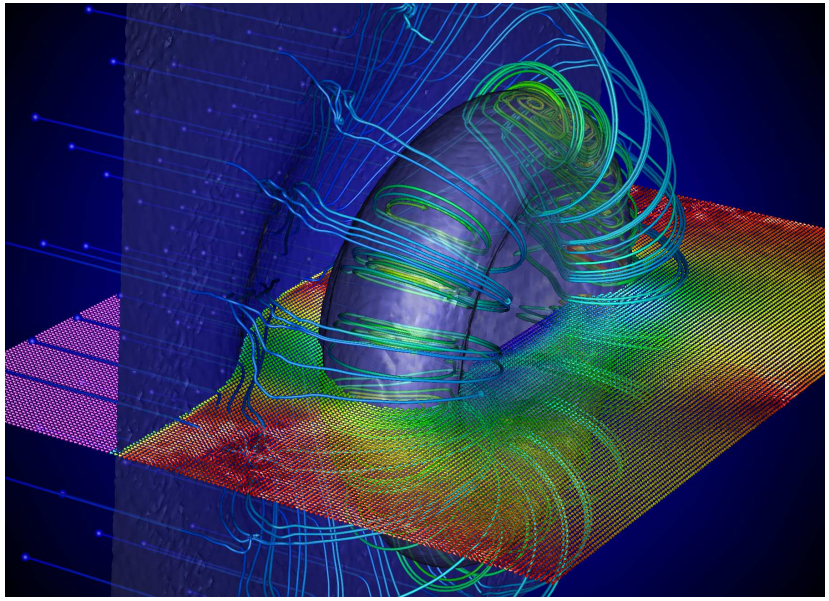
NOVEMBER 3–5, 2015

ROCKVILLE, MARYLAND



16,661-atom QMD

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

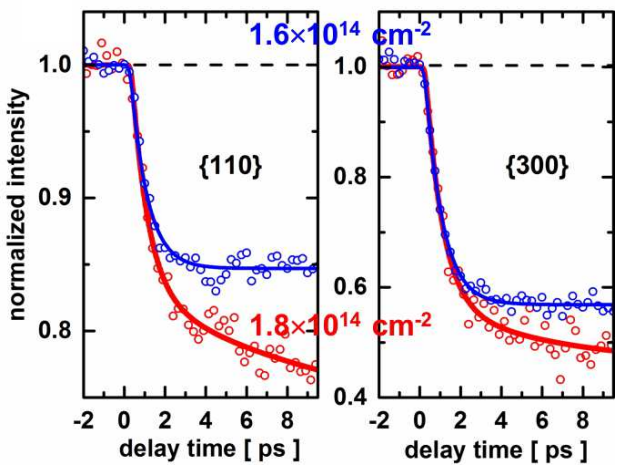


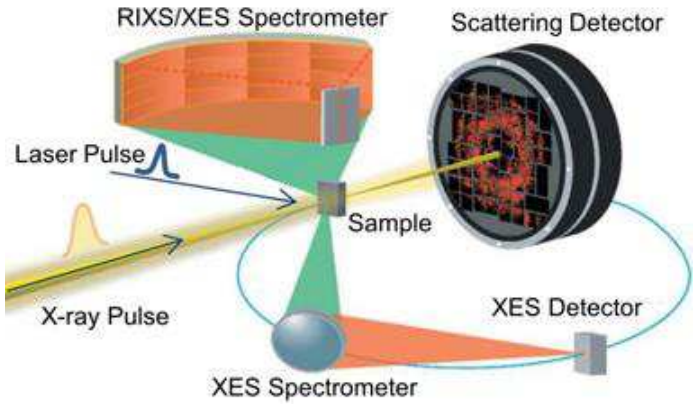
10^9-atom RMD

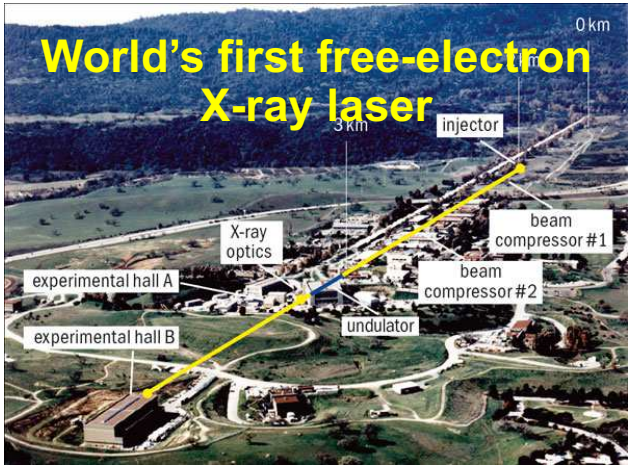
Shekhar *et al.*,
Phys. Rev. Lett.
111, 184503 (’13)

U.S. DEPARTMENT OF ENERGY

INCITE|AURORA–MAGICS–LCLS Synergy





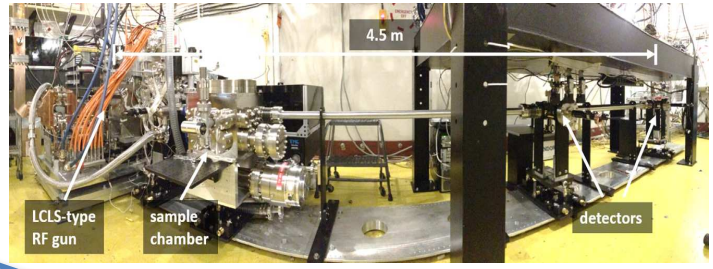


Linac Coherent Light Source

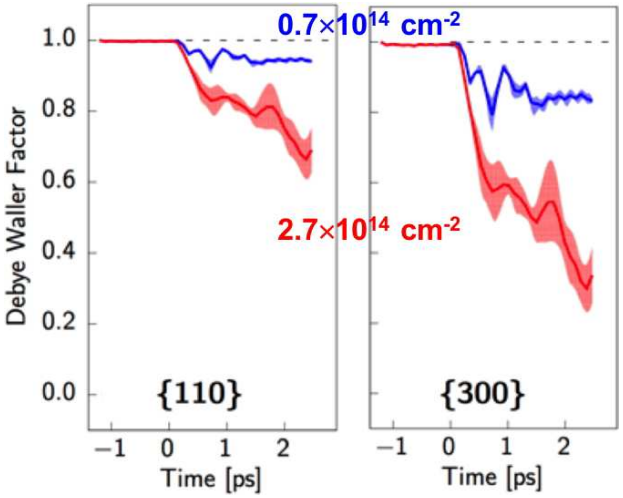
LCLS

DOE INCITE & Aurora ESP Awards

MAGICS
Materials Genome Innovation for Computational Software



Ultrafast electron diffraction (UED) at SLAC



U.S. DEPARTMENT OF ENERGY
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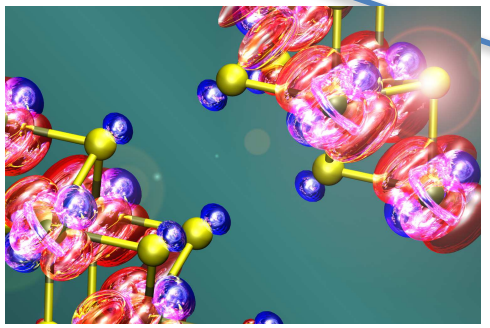
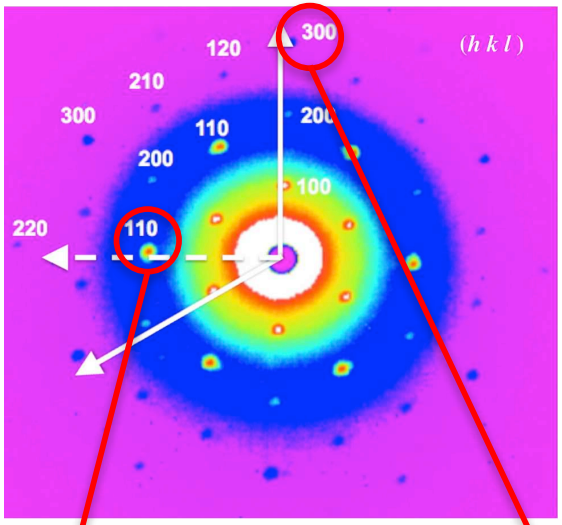
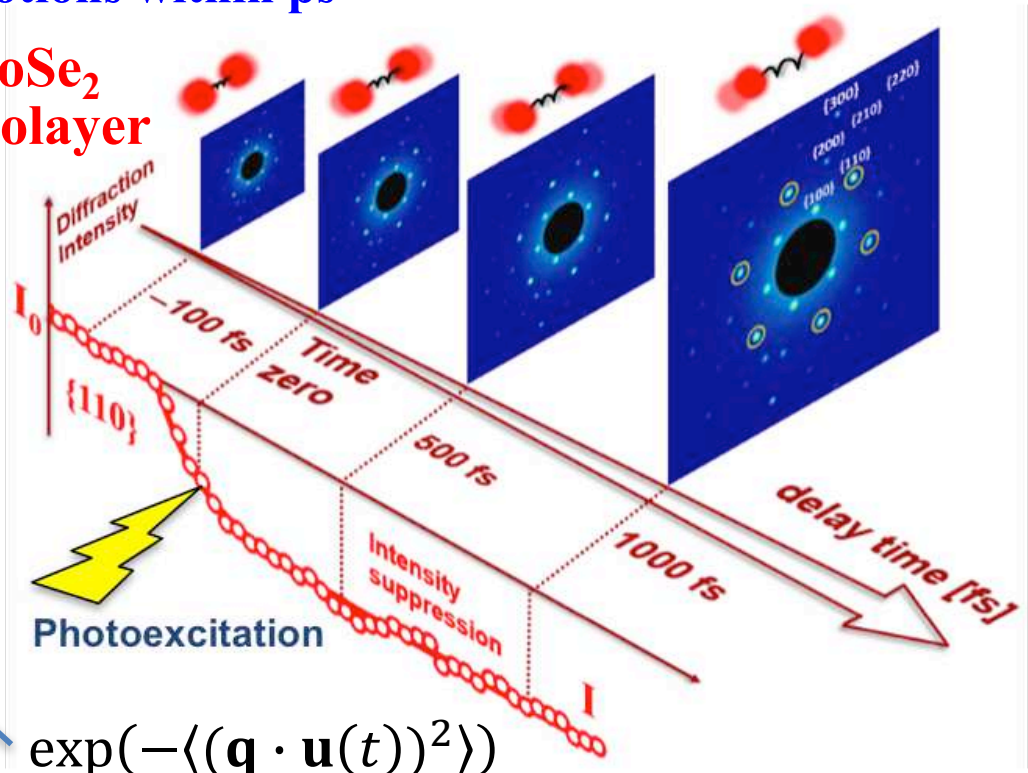


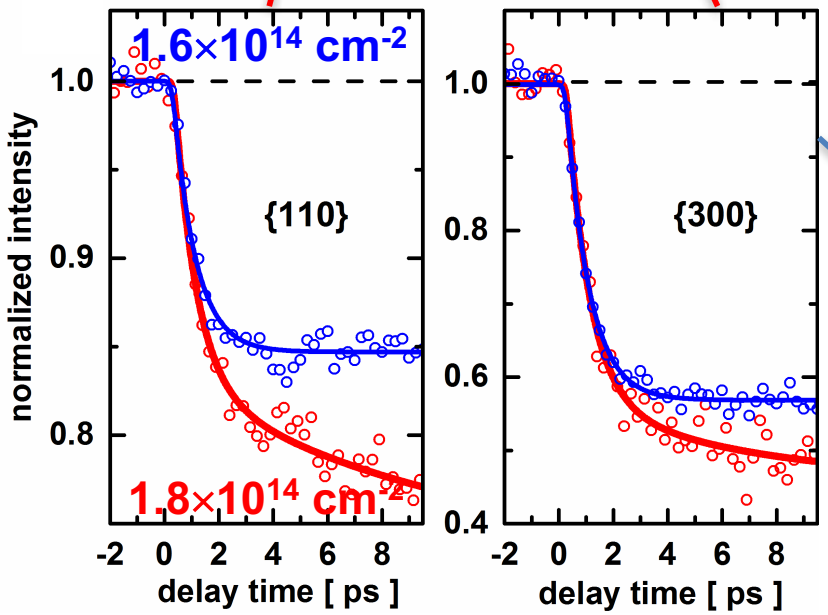
Ultrafast Coupled Electron-Lattice Dynamics

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



$MoSe_2$ monolayer





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

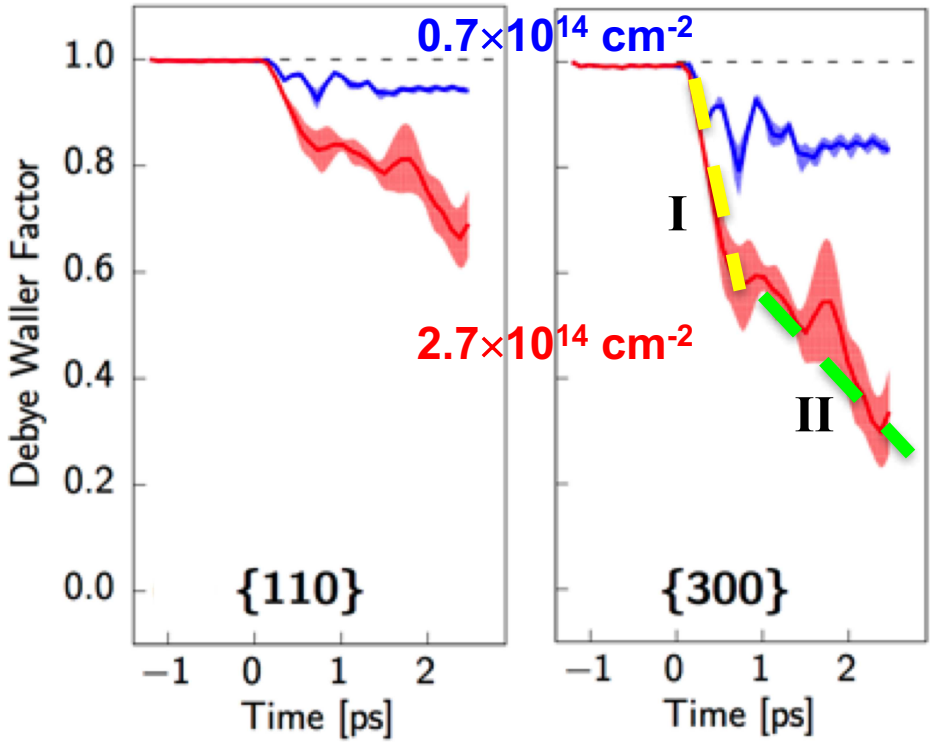
atomic displacement

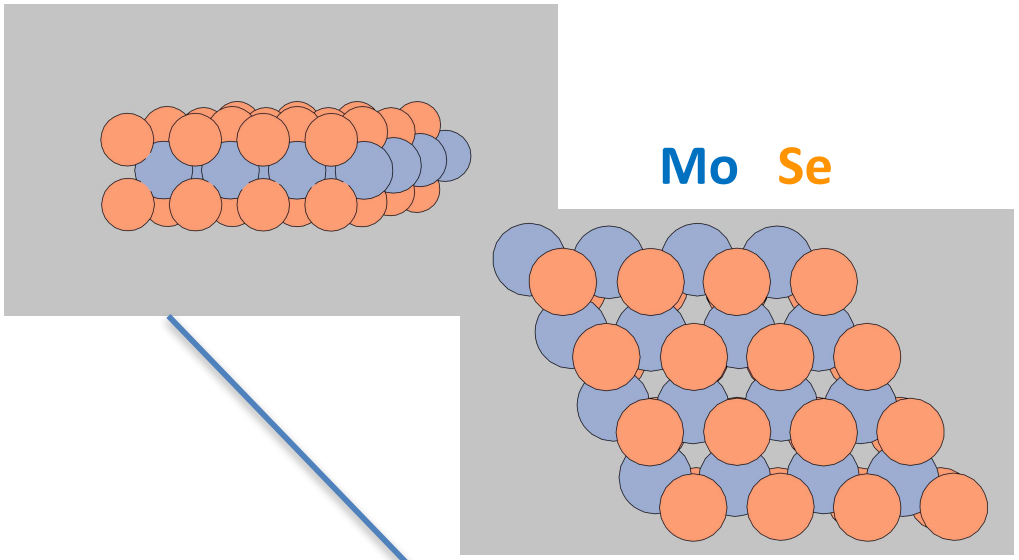
- **Dynamics of Debye-Waller factor reveals rapid disordering for both {300} & {110} peaks**
- **Transition from mono- to bi-exponential decay at higher electron-hole density**

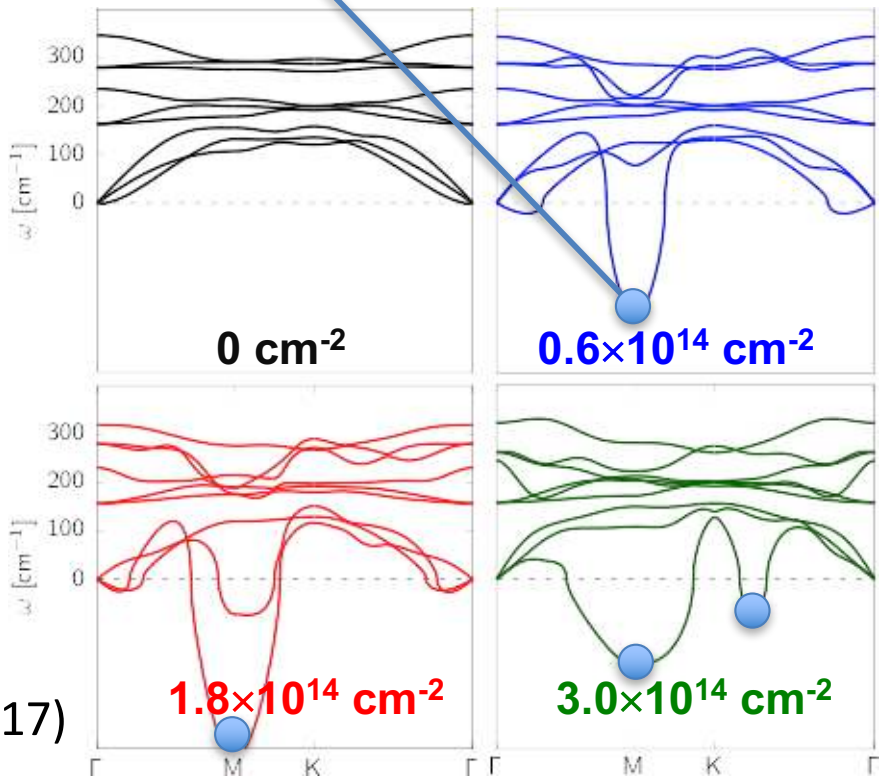
M.F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)

Strong Electron-Lattice Coupling

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





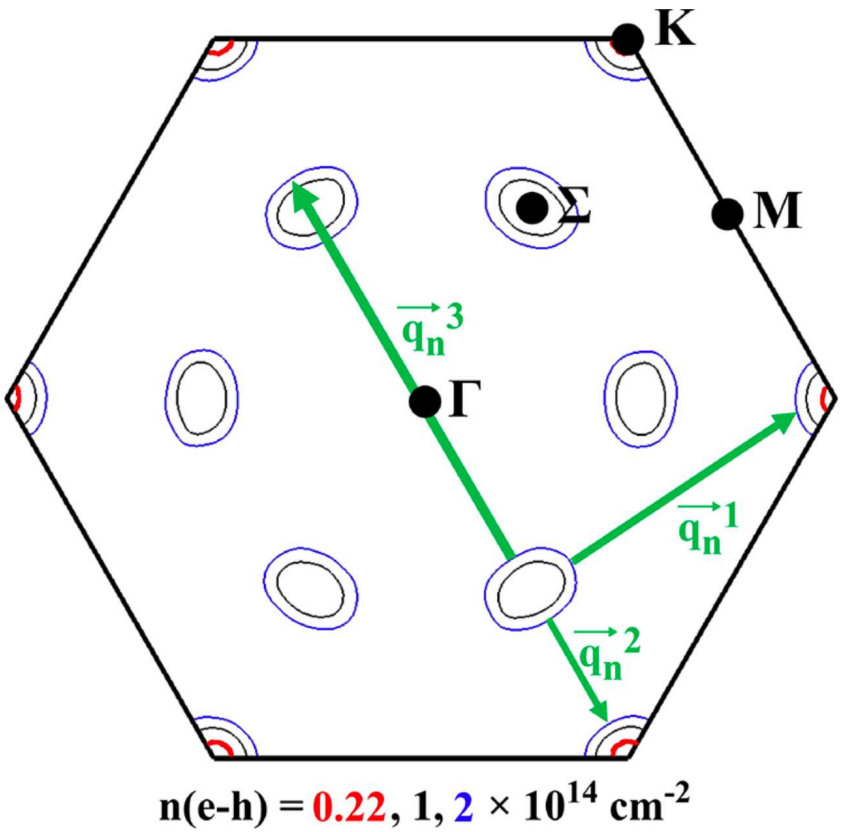


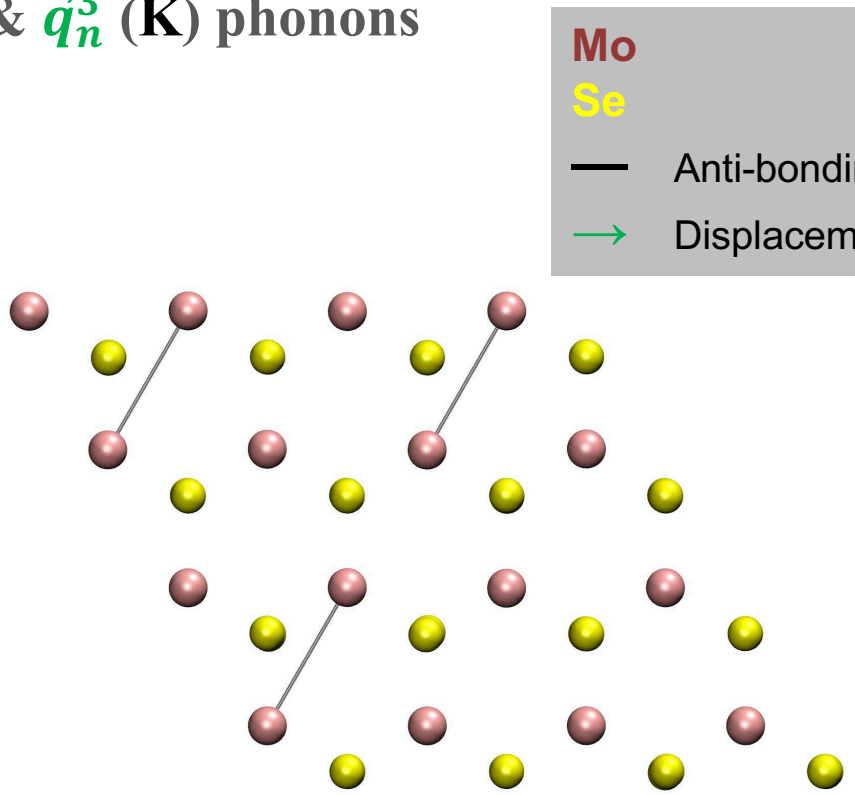
- **Rapid lattice dynamics is explained by the softening of M-point (1/2 0 0) phonon**
- **Bi-exponential transition is explained by the softening of additional phonon modes at higher electron-hole densities**

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

Electronic Origin of Phonon Softening

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

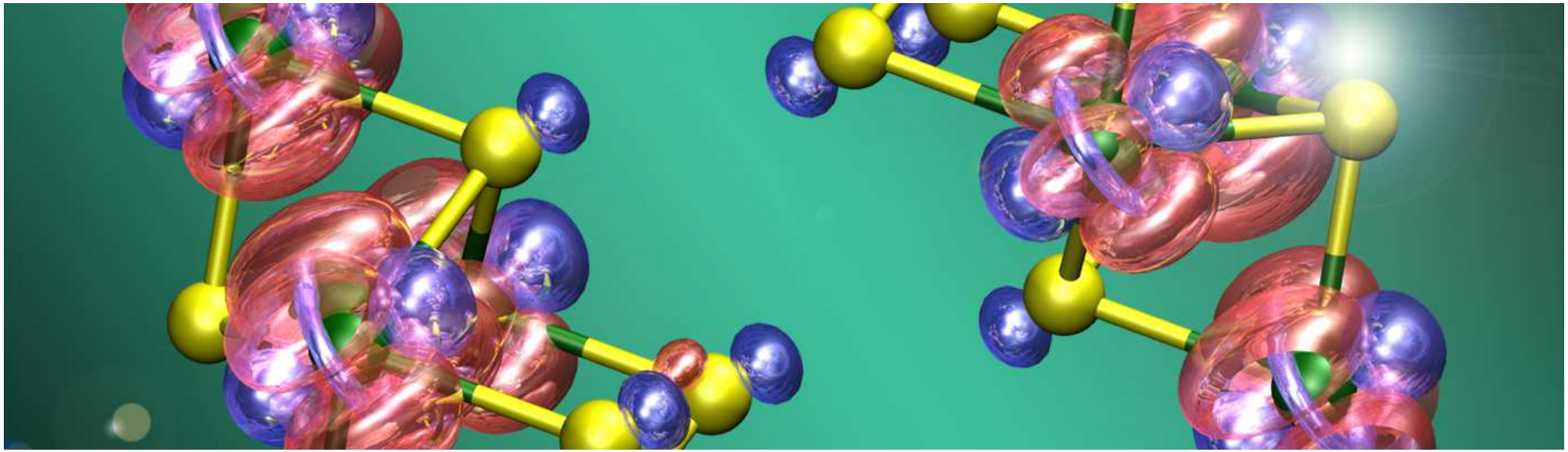




- Increased anti-bonding upon photo-excitation drives the displacements of atoms

L. Bassman *et al.*, *Nano Lett.* **18**, 4653 ('18)

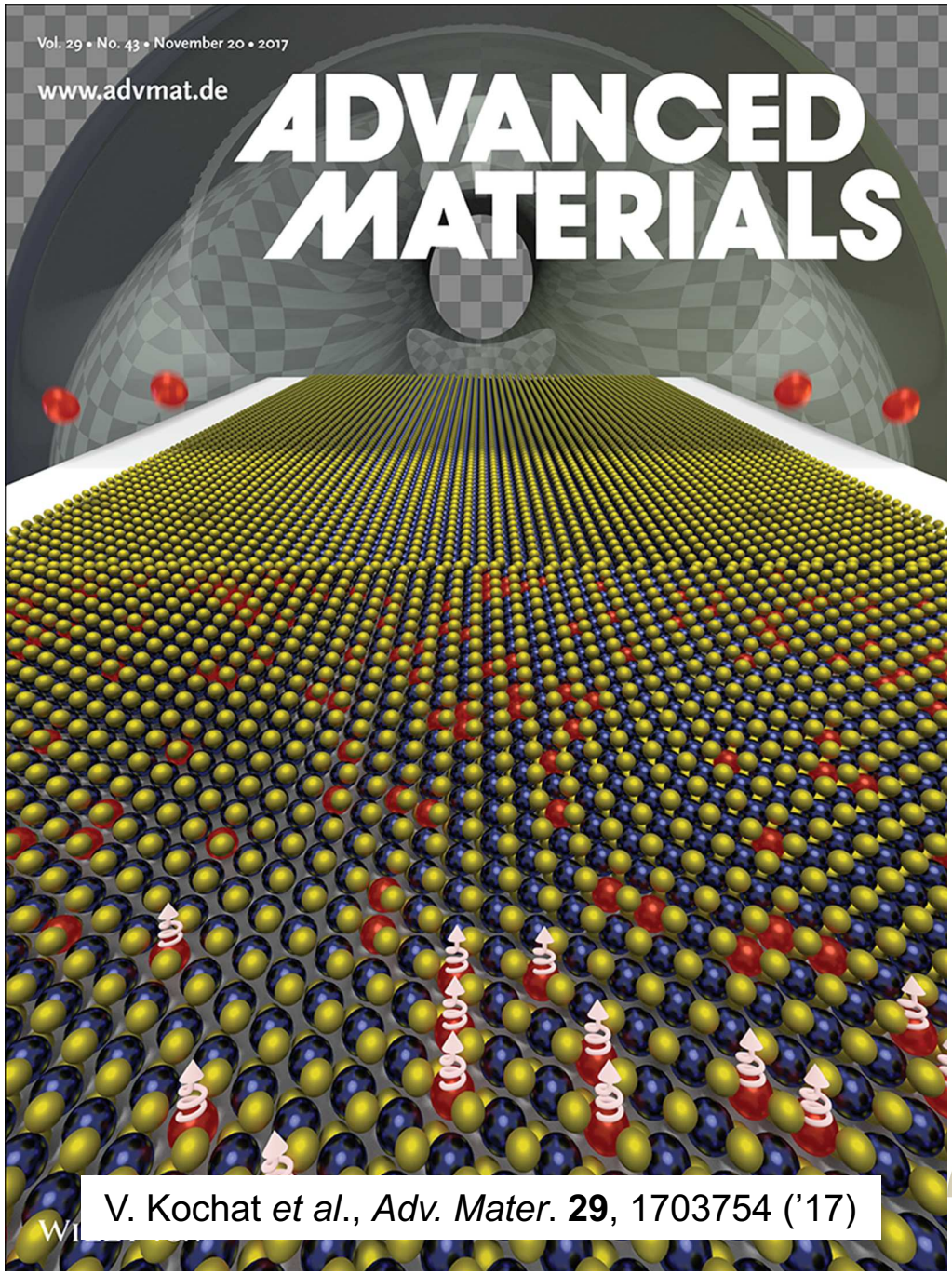
Simulation-Experiment Synergy



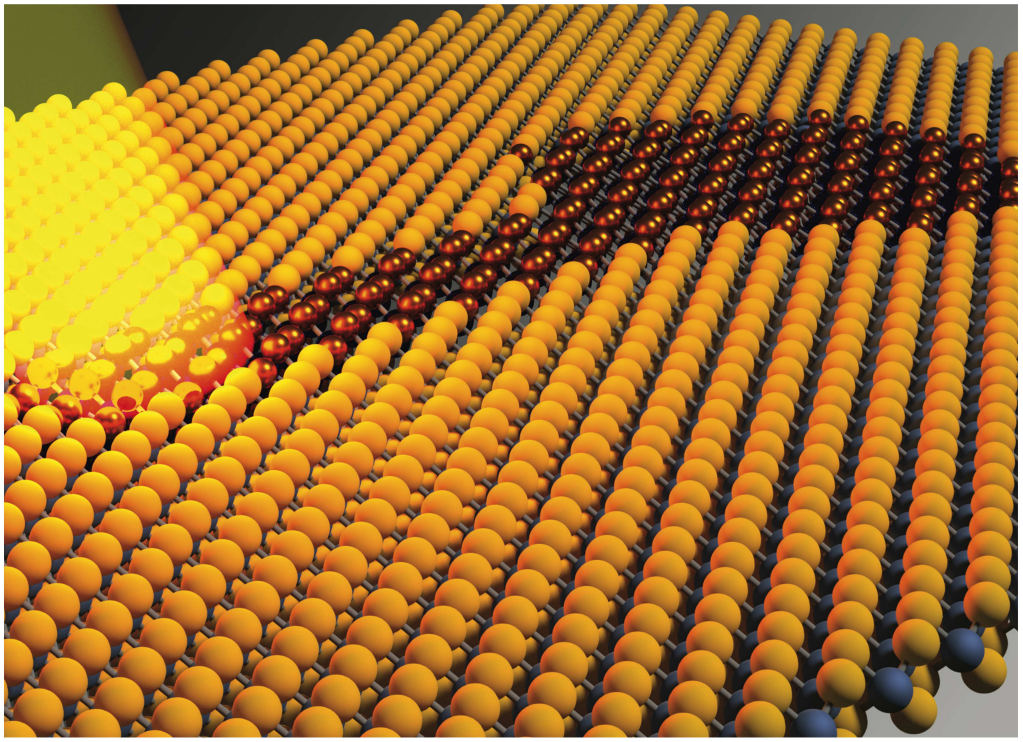
- **In the ultrafast 'electron camera,' laser light hitting a material is almost completely converted into nuclear vibrations — key to switching material properties on & off at will for future electronics applications**
- **High-end quantum simulations reproduce the ultrafast energy conversion at exactly the same space & time scales, & explain it as a consequence of photo-induced phonon softening**

Ming-Fu Lin, Vidya Kochat, **Aravind Krishnamoorthy**, **Lindsay Bassman**, Clemens Weninger, Qiang Zheng, Xiang Zhang, Amey Apte, Chandra Sekhar Tiwary, Xiaozhe Shen, Renkai Li, Rajiv Kalia, Pulickel Ajayan, Aiichiro Nakano, Priya Vashishta, Fuyuki Shimojo, Xijie Wang, David Fritz, Uwe Bergmann, *Nature Commun*. **8**, 1745 ('17)

MAGICS QMD Simulations



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

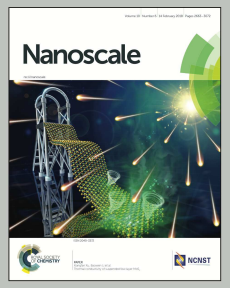


Showcasing research from Collaboratory for Advanced Computing and Simulations (CACS), University of Southern California, Los Angeles, USA.

Semiconductor–metal structural phase transformation in $MoTe_2$ monolayers by electronic excitation

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

As featured in:



See Aravind Krishnamoorthy *et al.*, *Nanoscale*, 2018, **10**, 2742.

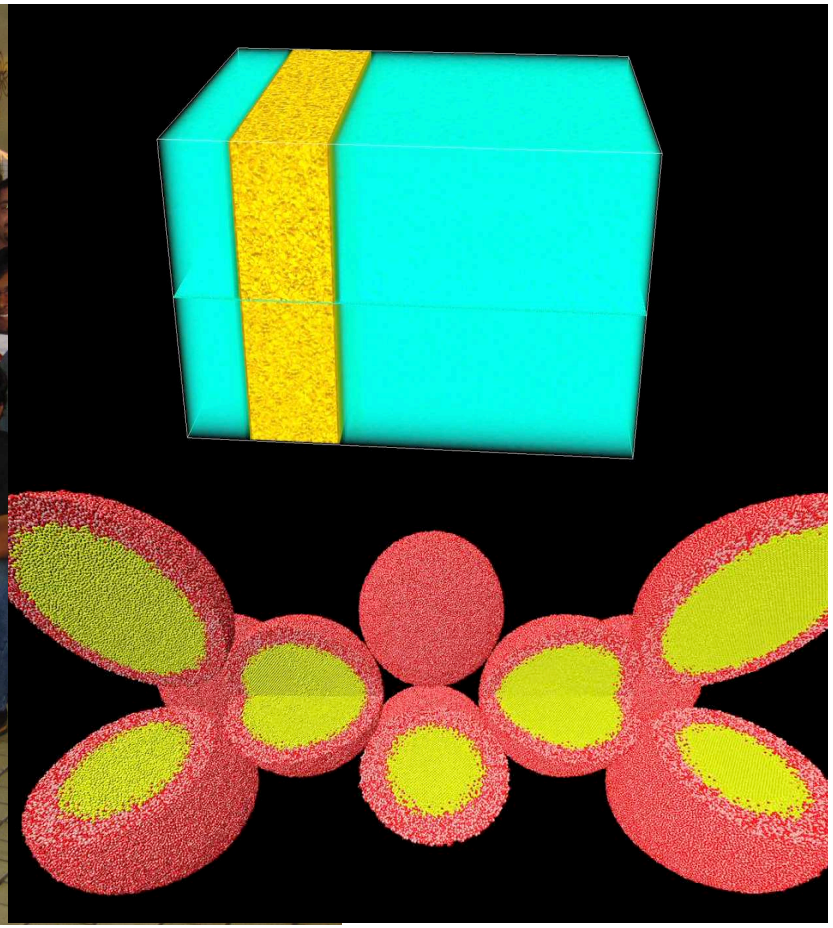
A. Krishnamoorthy *et al.*, *Nanoscale* **10**, 2742 ('18)

ROYAL SOCIETY OF CHEMISTRY

rsc.li/nanoscale

Conclusion

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



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