Quantum Molecular Dynamics Simulations

Aiichiro Nakano

Collaboratory for Advanced Computing & Simulations
Depts. of Computer Science, Physics & Astronomy, Chemical Engineering & Materials Science, and Biological Sciences
University of Southern California

Email: anakano@usc.edu

QXMD tutorial:

Subodh Tiwari, Lindsay Bassman, Hiroyuki Kumazoe, Aravind Krishnamoorthy

Ken-ichi Nomura

MAGICS Workshop

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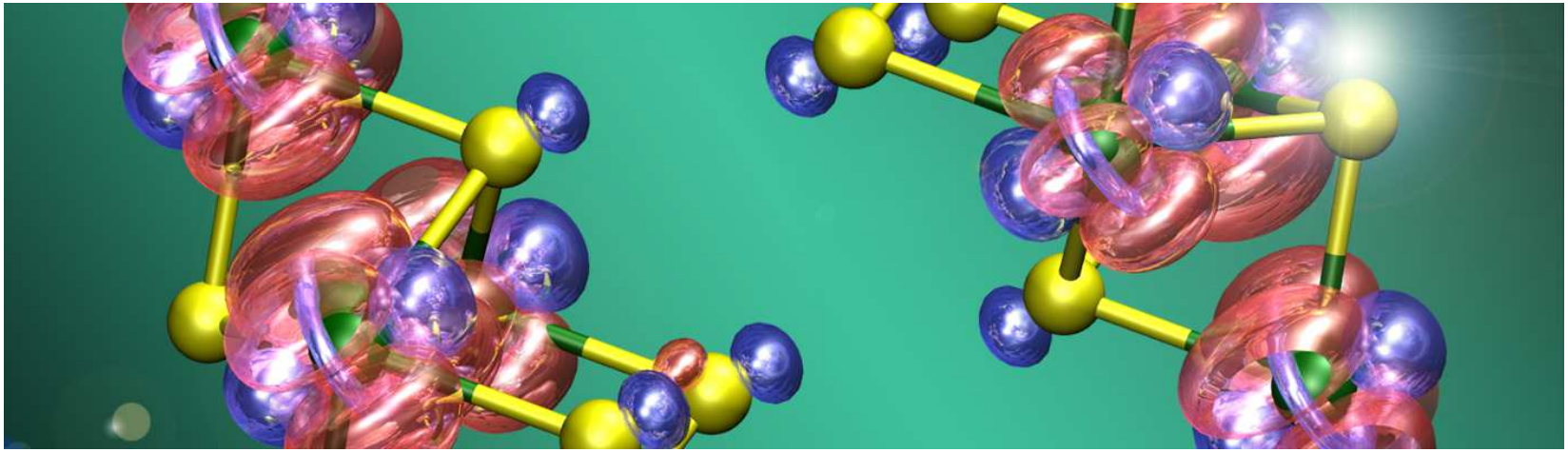
Additional Resources

Detailed lecture notes are available at a USC course home page

EXTREME-SCALE QUANTUM SIMULATIONS

Course Description

Computer simulation of quantum-mechanical dynamics has become an essential enabling technology for physical, chemical & biological sciences & engineering. Quantum-dynamics simulations on extreme-scale parallel supercomputers would provide unprecedented predictive power, but pose enormous challenges as well. 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".



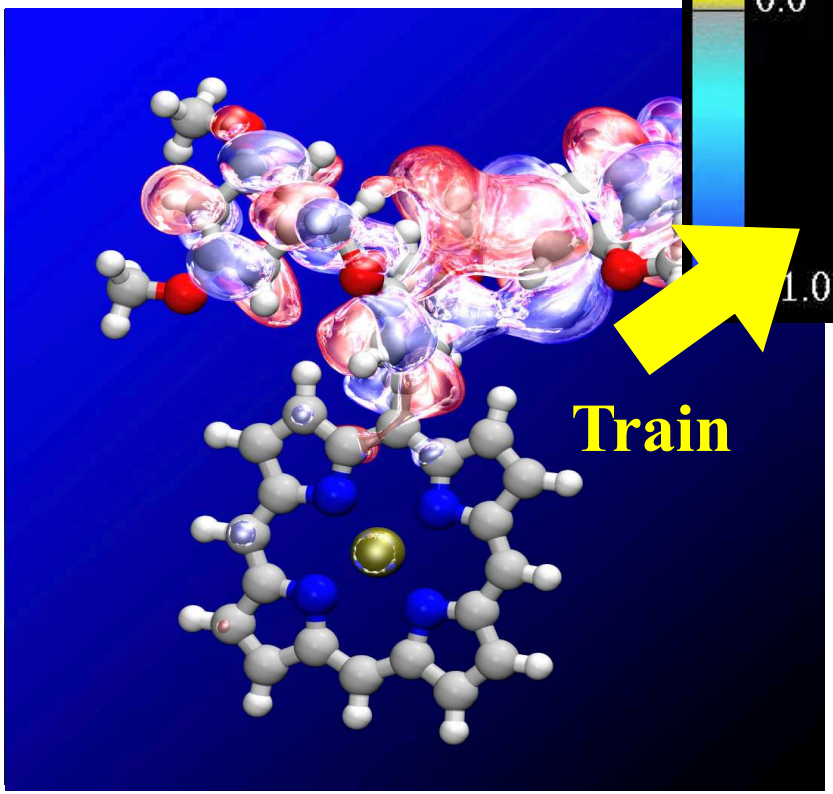
http://cacs.usc.edu/education/cs699-lecture.html

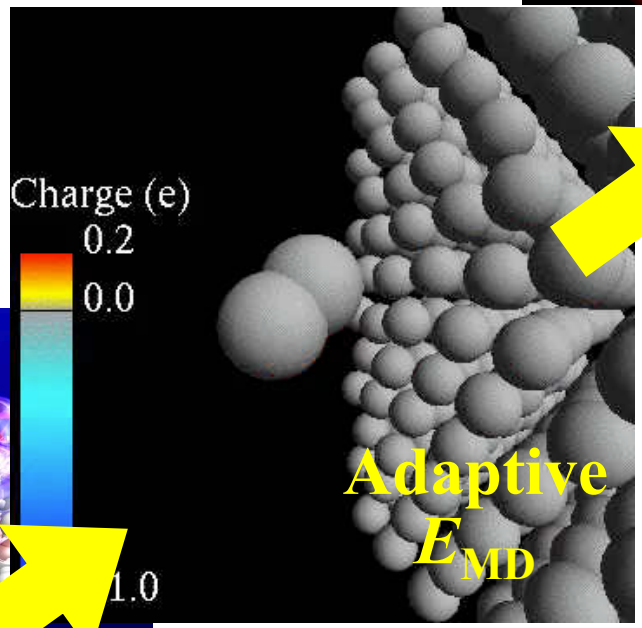
Molecular Dynamics Hierarchy

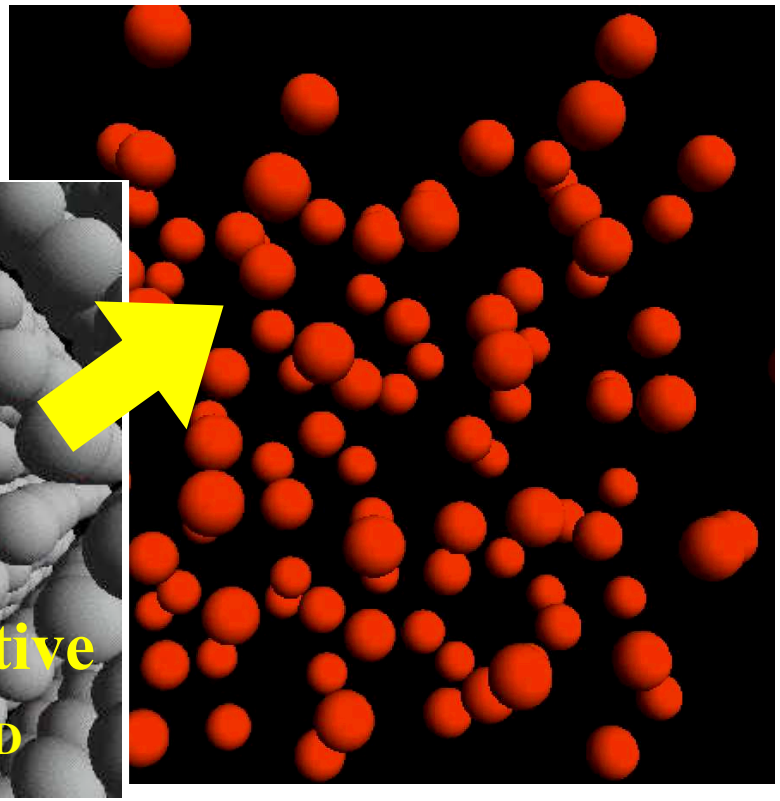
Molecular Dynamics (MD)

Reactive MD (RMD)

Nonadiabatic quantum MD (NAQMD)







Train

First principles-based reactive force-fields

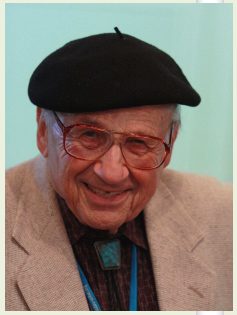
- **Reactive bond order $\{BO_{ij}\}$**
  → Bond breakage & formation
- **Charge equilibration (QEq) $\{q_i\}$**
  → Charge transfer

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

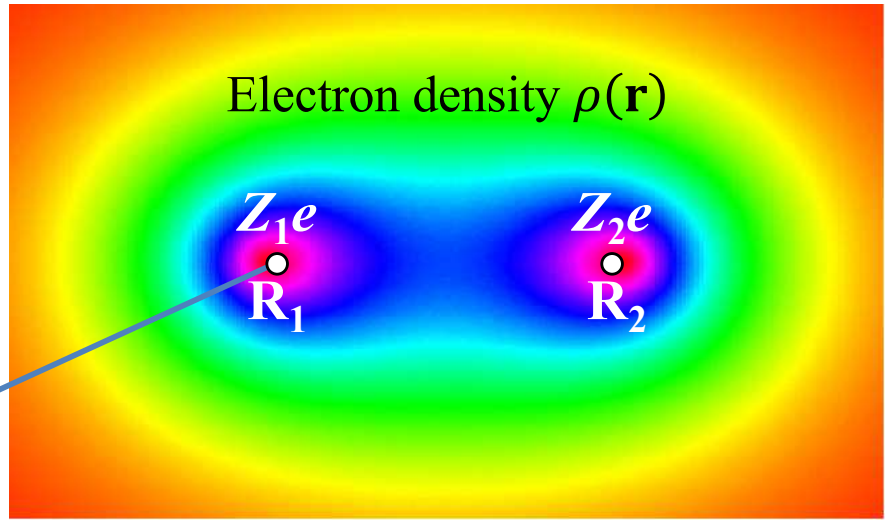
$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})]$$

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)

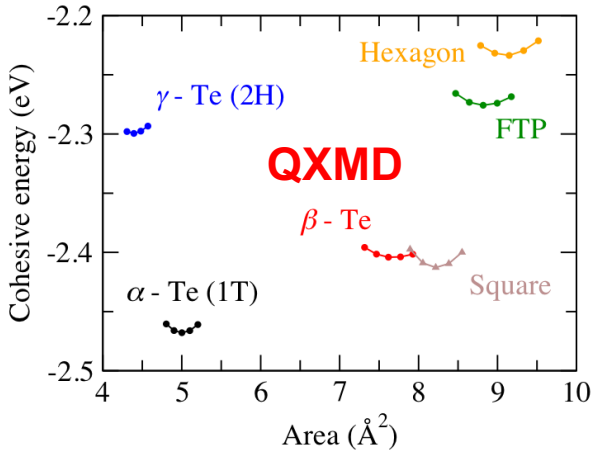
Abstraction: Exchange-Correlation Functional

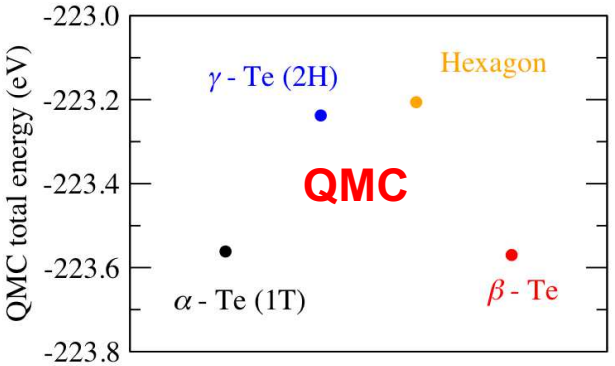
- **Universal functional (of density) that describes many-body effects beyond the mean-field approximation**
- **Some commonly used exchange-correlation functionals**
  - > **GGA (generalized gradient approximation)**
    PBE: Perdew, Burke & Ernzerhof, *Phys. Rev. Lett*. **77**, 3865 ('96)
  - > **MetaGGA**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

Validation of XC Functional

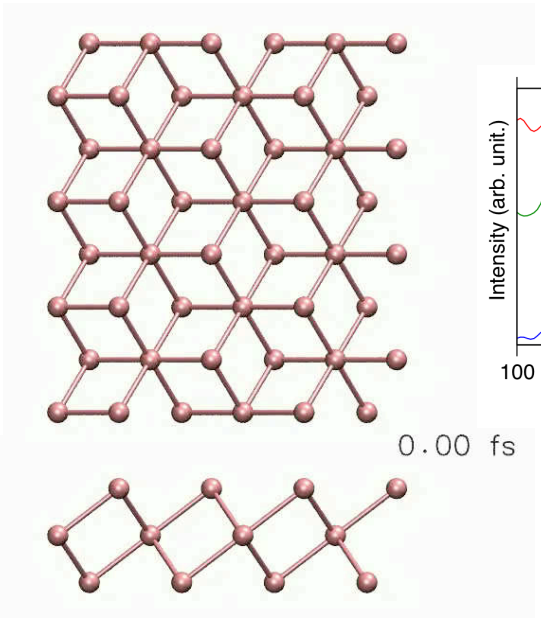
- Comparison with high accuracy methods, such as quantum Monte Carlo (QMC), & experimental data
- Sensitivity analysis among different exchange-correlation (xc) functionals
- Consistency of the derived conclusion with the level of approximation

Example: Atomically thin tellurium (tellurene)

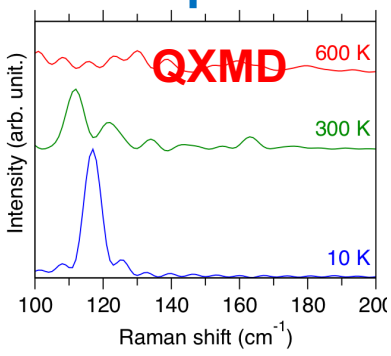


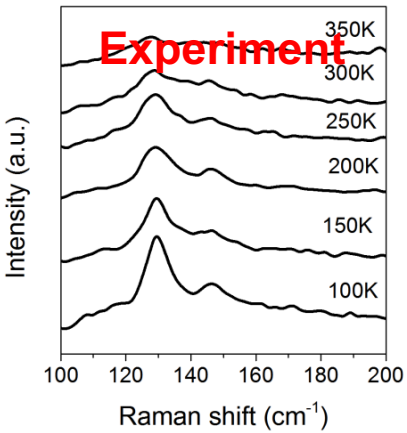


Casino QMC (https://vallico.net/casinoqmc)



Raman spectrum



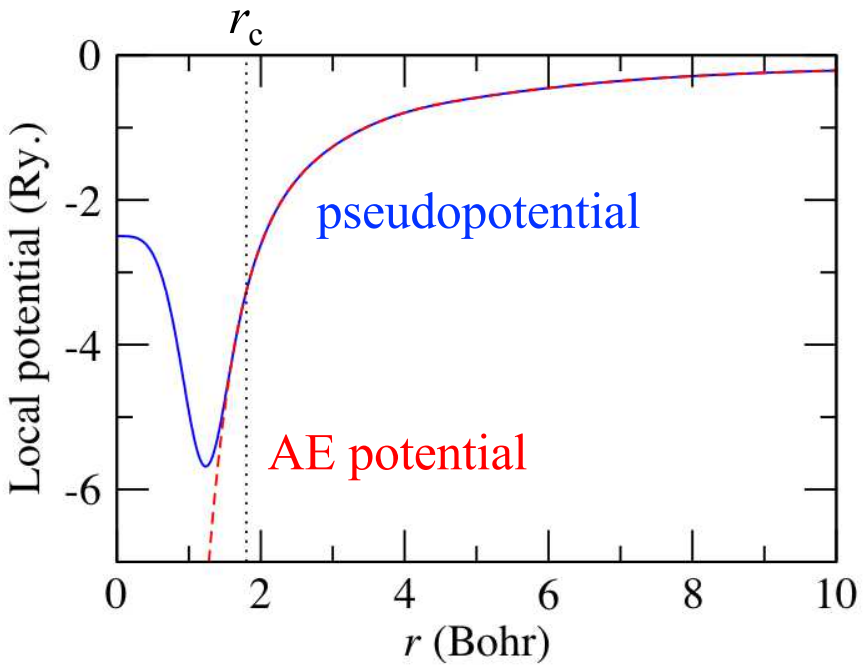


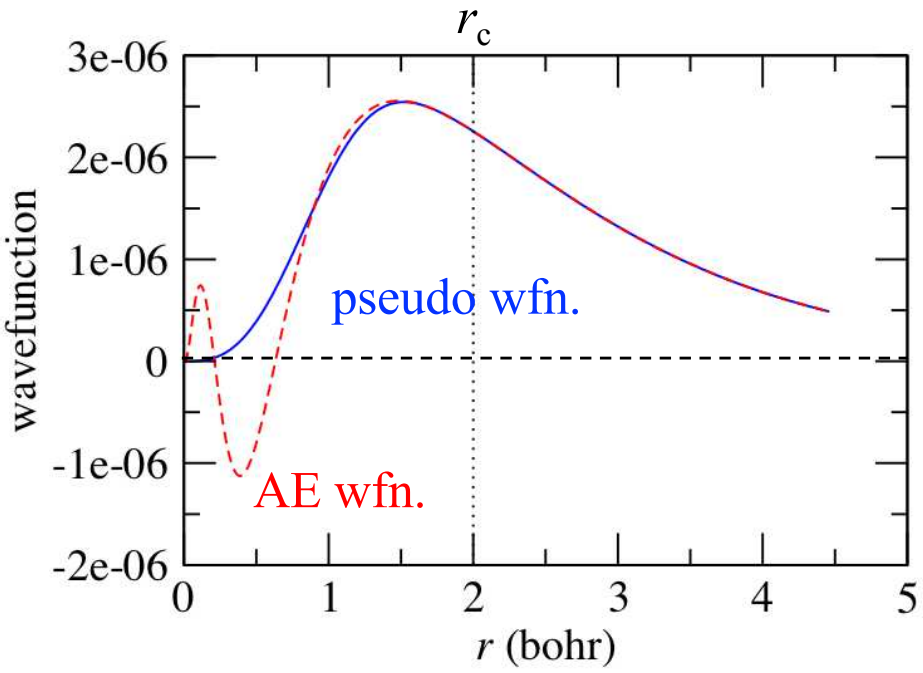
	a (Å)	*B* (N/m)
GGA	4.26	23.2138
GGA-D	4.17	28.6845
Spin GGA	4.26	22.1372
Hybrid HSE	-	23.8448
Hybrid HSE with GGA-D	-	29.7649

a: Lattice constant
B: Bulk modulus

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)

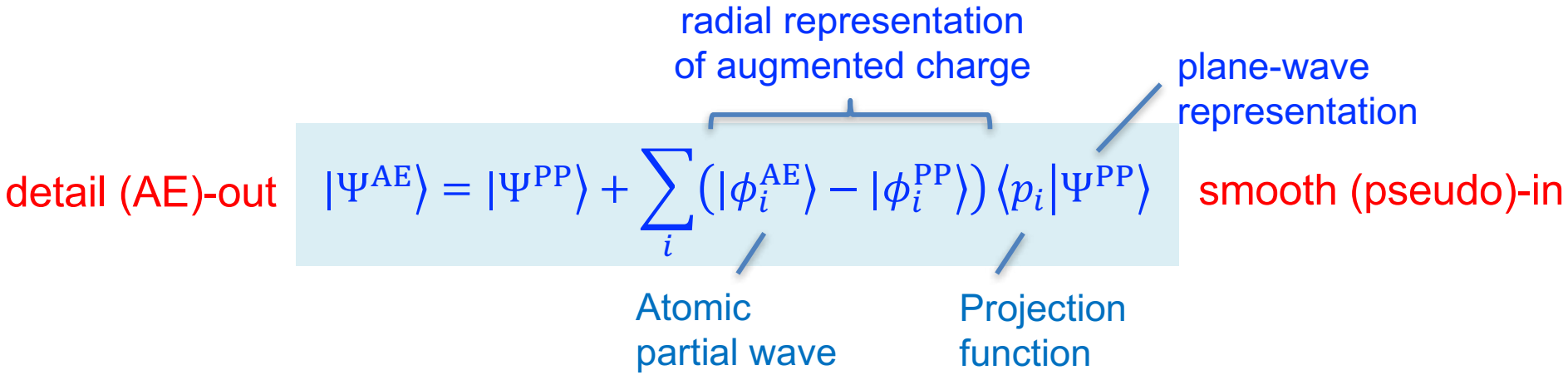
Projector-Augmented Wave (PAW)

- **Retaining core charges significantly increases the transferability**

$$\tilde{v}_{\mathrm{xc}}(\mathbf{r}) = v_{\mathrm{xc}}([\rho_{\mathrm{PP}}], \mathbf{r}) + [v_{\mathrm{xc}}([\rho_{\mathrm{PP}} + \rho_{\mathrm{core}}], \mathbf{r}) - v_{\mathrm{xc}}([\rho_{\mathrm{PP}}], \mathbf{r})]$$

Louie, Froyen & Cohen, *Phys. Rev. B* **50**, 1738 ('82)

- **PAW: An "all-electron" (AE) electronic structure calculation that separates smooth pseudo-wave functions (PP) & rapidly varying AE wave functions by using projection function**



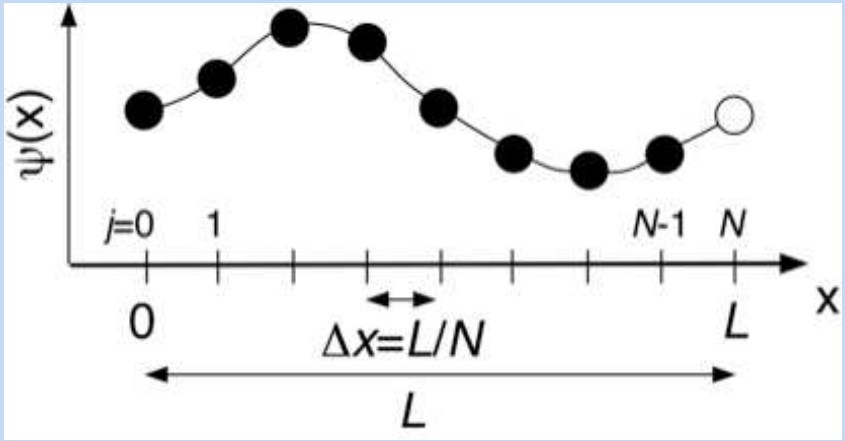
Blochl, *Phys. Rev. B* **50**, 17953 ('94)

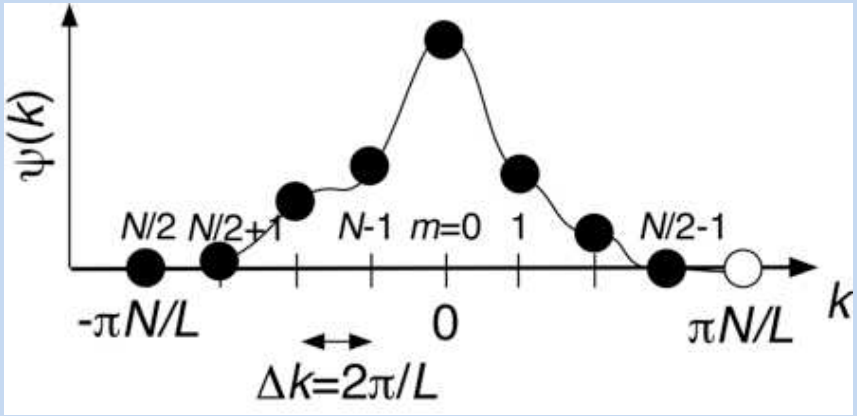
Representation: Plane-Wave Basis

- **Pseudopotentials result in slowly varying wave functions that can be represented on a regular grid, which in turn can be represented as a linear combination of plane waves, *i.e.*, Fourier transform**

$$\psi(\mathbf{r}_j) = \sum_{\mathbf{k}_n} \psi_{\mathbf{k}_n} \exp(i\mathbf{k}_n \bullet \mathbf{r}_j)$$

1D example



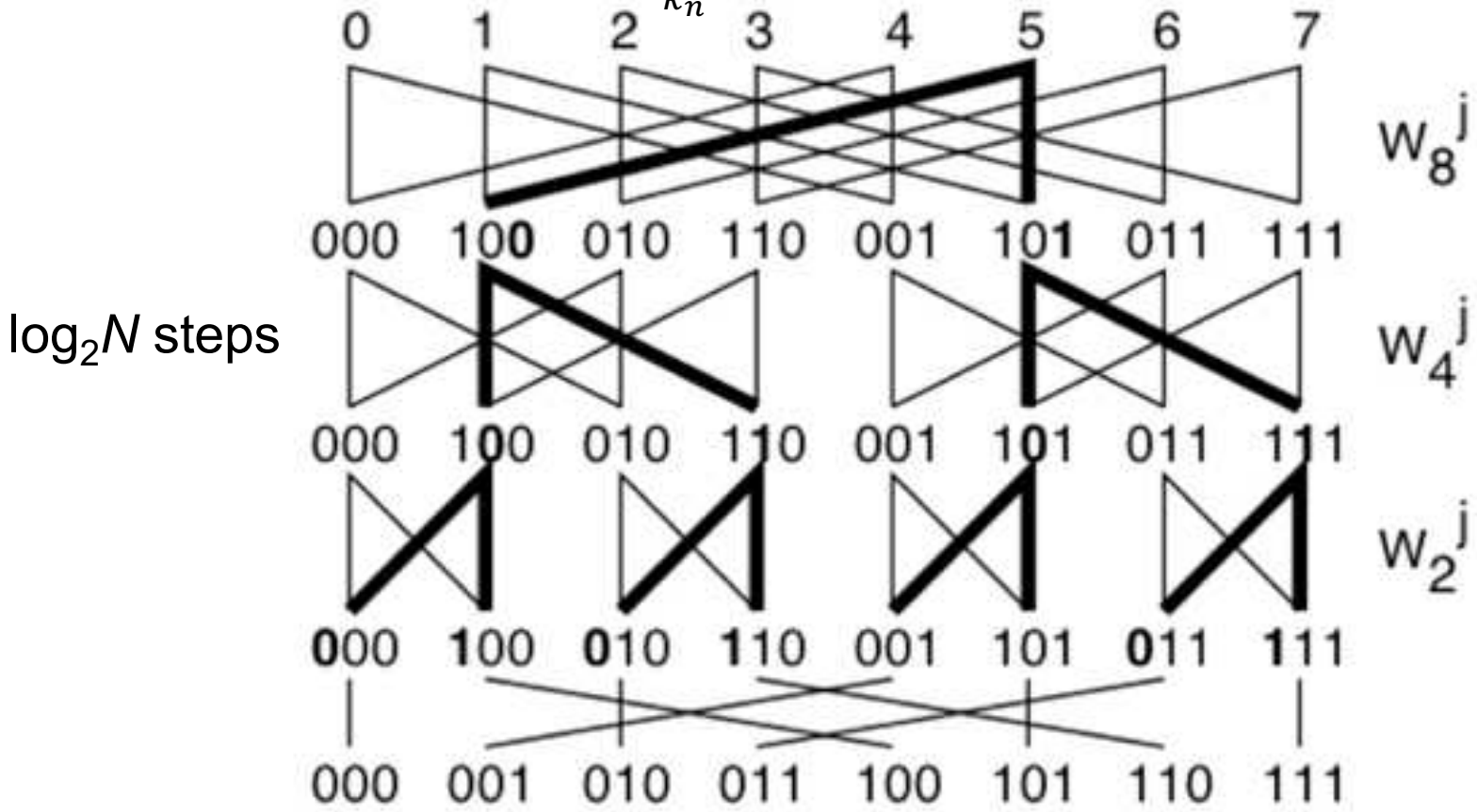


$$x_j = \frac{jL}{N};\ k_n = \frac{2\pi n}{L}$$

Numerics: Fast Fourier Transform

- ***O*(*N*log*N*) fast Fourier-transform (FFT) algorithm is typically used to perform Fourier transform**

$$\psi(x_j) = \sum_{k_n} \psi_{k_n} \exp(ik_n x_j)$$



Butterfly (hypercube) data-exchange network

See PHYS 516 lecture on quantum dynamics

http://cacs.usc.edu/education/phys516/03QD-slide.pdf

Top 10 Algorithms in History

In putting together this issue of *Computing in Science & Engineering*, we knew three things: it would be difficult to list just 10 algorithms; it would be fun to assemble the authors and read their papers; and, whatever we came up with in the end, it would be controversial. We tried to assemble the 10 algorithms with the greatest influence on the development and practice of science and engineering in the 20th century. Following is our list (here, the list is in chronological order; however, the articles appear in no particular order):

IEEE CiSE, Jan/Feb ('00)

- Metropolis Algorithm for Monte Carlo
- Simplex Method for Linear Programming
- Krylov Subspace Iteration Methods
- The Decompositional Approach to Matrix Computations
- The Fortran Optimizing Compiler
- QR Algorithm for Computing Eigenvalues
- Quicksort Algorithm for Sorting
- Fast Fourier Transform
- Integer Relation Detection
- Fast Multipole Method

PHYS 516
CSCI 596
CSCI 653

http://cacs.usc.edu/education/phys516.html
http://cacs.usc.edu/education/cs596.html
http://cacs.usc.edu/education/cs653.html

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 $\rho(\mathbf{r})$

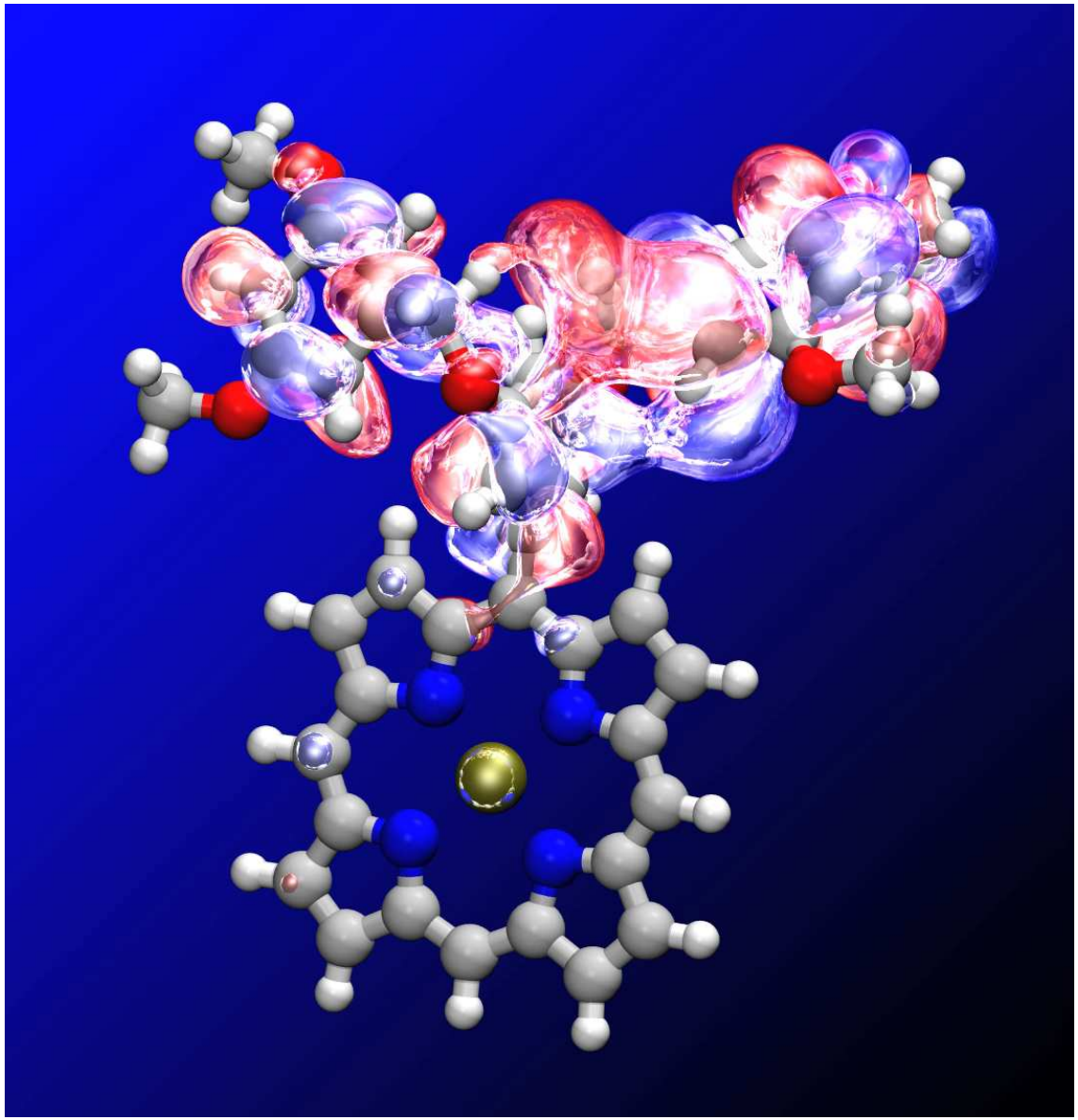
$$\rho(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2 \, \Theta(\mu - \epsilon_n)$$

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

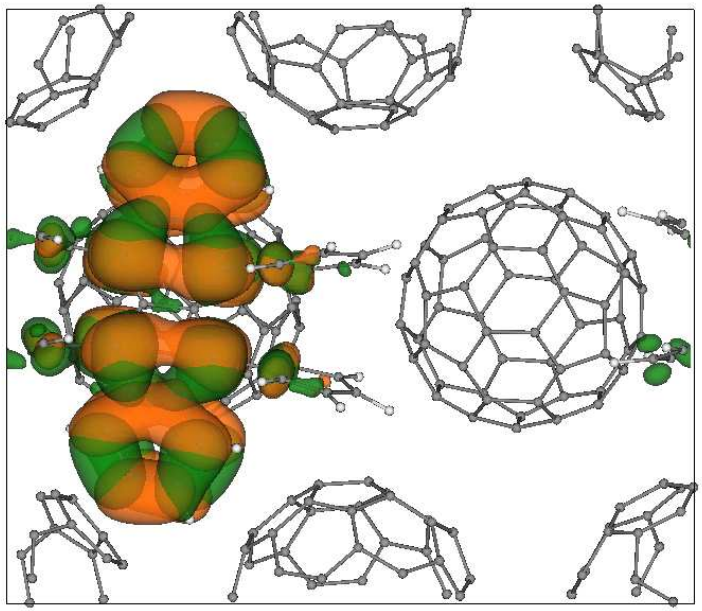
Nonadiabatic Quantum Molecular Dynamics



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}



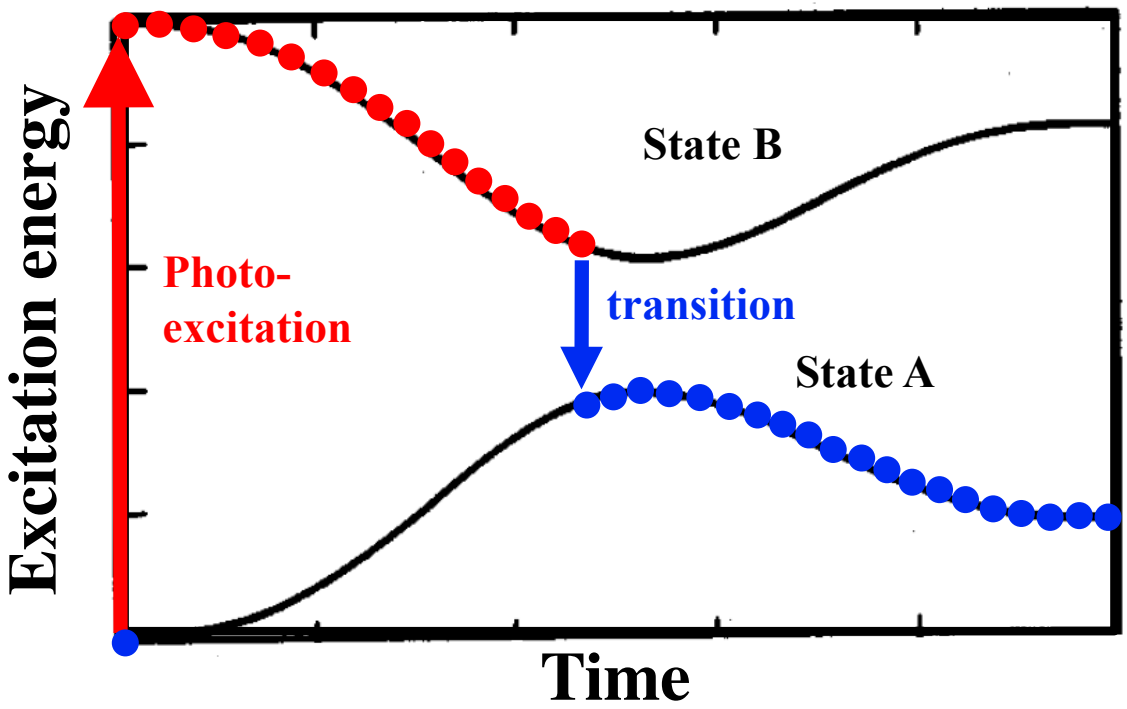
quasi-electron; quasi-hole

- **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

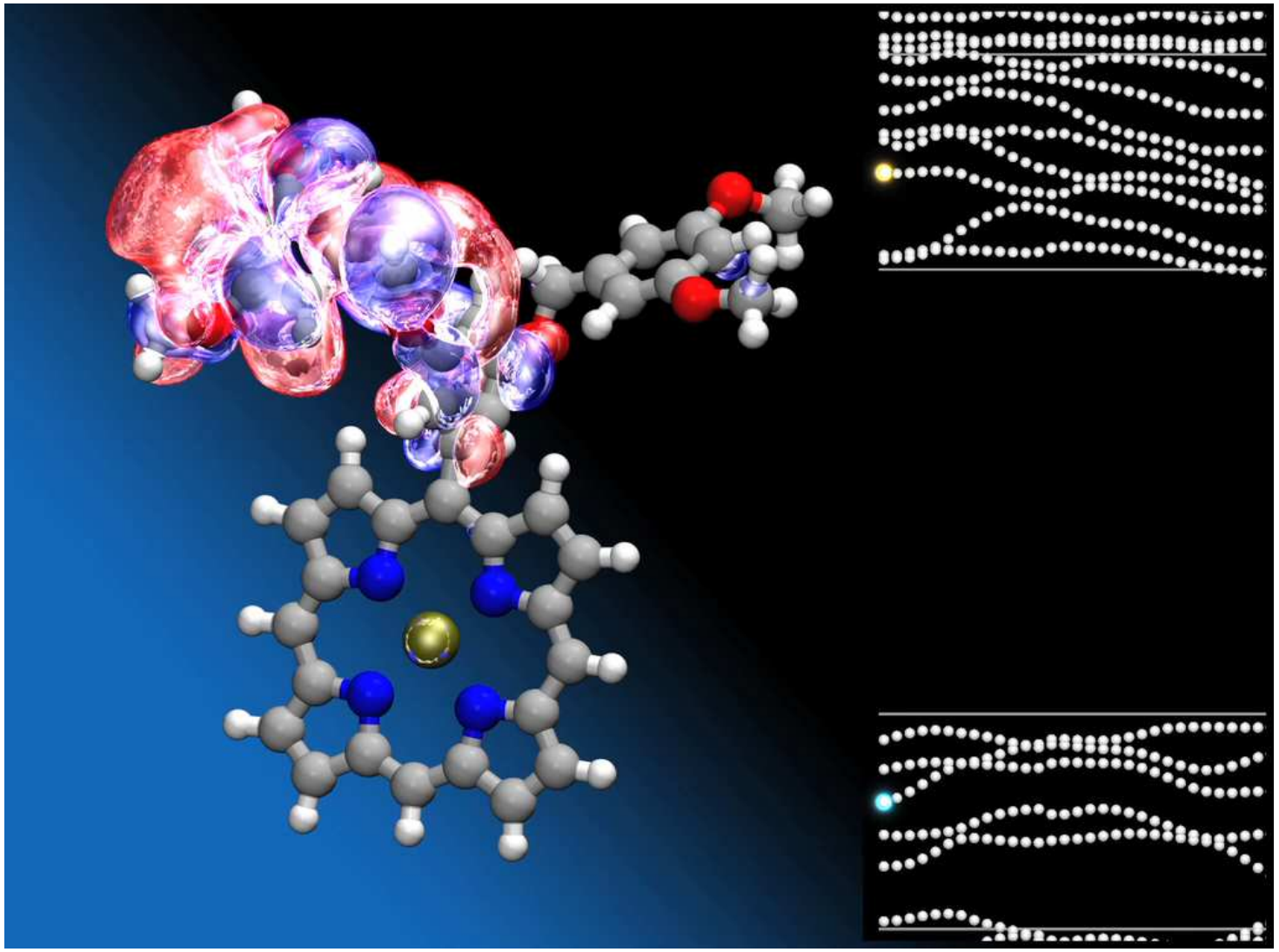
$$\Psi(\mathbf{r},t) = \sum_J C_J^{(I)}(t)\Phi_J(\mathbf{r};\mathbf{R}(t)) \qquad C_I^{(I)}(0) = \delta_{I,J}$$

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

J-th adiabatic excited state

Electronic transition assisted by nuclei motion

Electron Transfer in a Light-Harvesting Dendrimer



- **The photoexcited electron at the peripheral antenna is transferred to the core due to the energy-crossing & overlapping of orbitals assisted by thermal molecular motions**

Excitonic Effects: LR-TDDFT

- **Excited electron-hole pairs within the linear-response time-dependent density functional theory (LR-TDDFT)**

$$\delta V(t) = \delta v_{kl\tau}(t)\hat{a}^{+}_{k\tau}\hat{a}_{l\tau} \longrightarrow \delta P_{ij\sigma}(t) = \delta\langle\Phi(t)|\hat{a}^{+}_{i\sigma}\hat{a}_{j\sigma}|\Phi(t)\rangle$$

electron hole

$$\chi_{ij\sigma,kl\tau}(t-t') = \delta P_{ij\sigma}(t)/\delta v_{kl\tau}(t')$$

- **Excitation energies from the poles of the response function $\chi_{ij\tau,kl\sigma}(\omega)$**

$2N_{\text{unoccupied}}N_{\text{occupied}} \times 2N_{\text{unoccupied}}N_{\text{occupied}}$ matrix eigenequation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^{*} & \mathbf{A}^{*} \end{pmatrix}\begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix} = \hbar\omega_I \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}\begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix}$$

I-th excitation energy

Kohn-Sham energy

$$A_{ia\sigma,jb\tau} = \delta_{\sigma,\tau}\delta_{i,j}\delta_{a,b}(\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) + K_{ia\sigma,jb\tau} \qquad B_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau}$$

$$K_{ia\sigma,i'a'\sigma'} = \iint \psi^{*}_{i\sigma}(\mathbf{r})\psi_{a\sigma}(\mathbf{r})\left(\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta\rho_{\sigma}(\mathbf{r})\delta\rho_{\sigma'}(\mathbf{r}')}\right)\psi_{i'\sigma'}(\mathbf{r}')\psi^{*}_{a'\sigma'}(\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$$

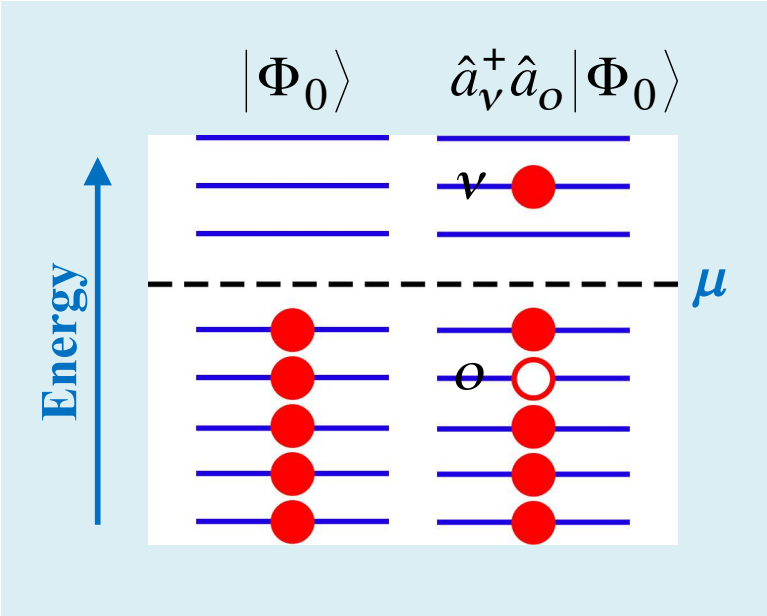
Coulomb & exchange-correlation interaction matrix elements

Electronic Excited States

- ***I*-th excited state**

$$\left|\Phi_I(\mathbf{r};\mathbf{R})\right\rangle = \sum_{i\in\{\text{occupied}\}} \sum_{a\in\{\text{unoccupied}\}} \sum_{\sigma} \sqrt{\frac{\varepsilon_{a\sigma}-\varepsilon_{i\sigma}}{\hbar\omega_I}} \left(X_{I,ia\sigma}+Y_{I,ia\sigma}\right) \hat{a}^{+}_{a\sigma}\hat{a}_{i\sigma} \left|\Phi_0(\mathbf{r};\mathbf{R})\right\rangle$$

electron-hole pair ground state



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

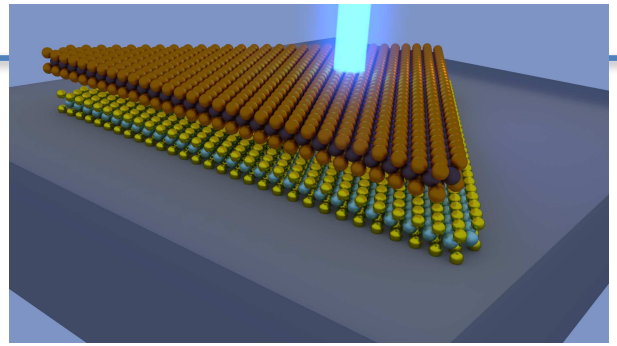
- **NAQMD & RMD simulations on full 800K cores**

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

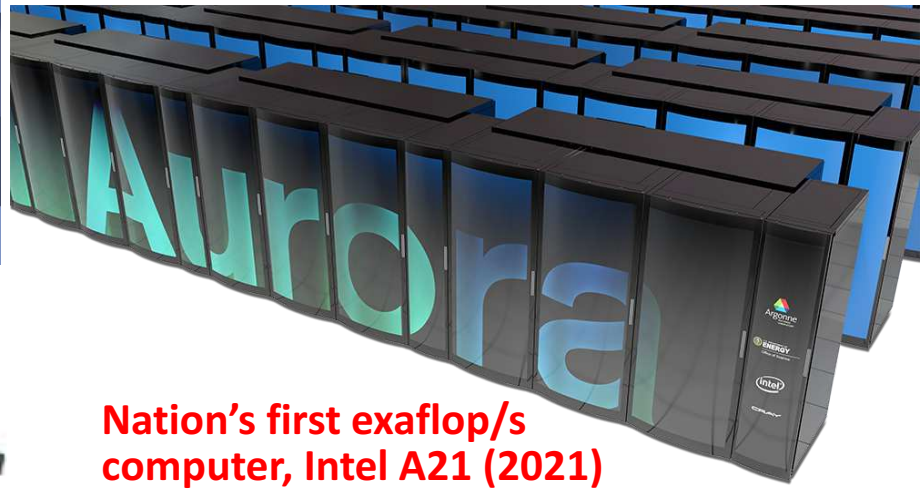


AURORA | EARLY SCIENCE PROGRAM

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)

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

MAGICS@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

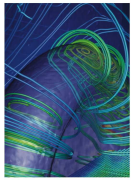
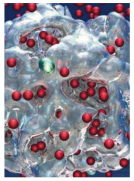
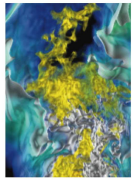
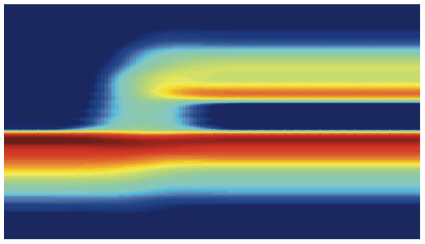
By **Robert F. Service**

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.

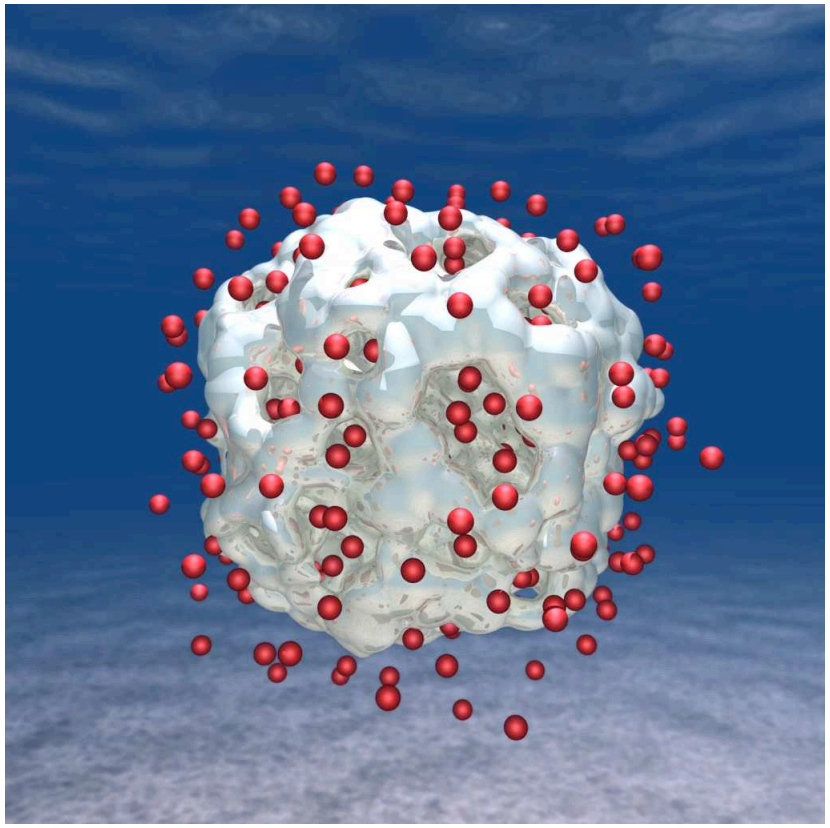
BES

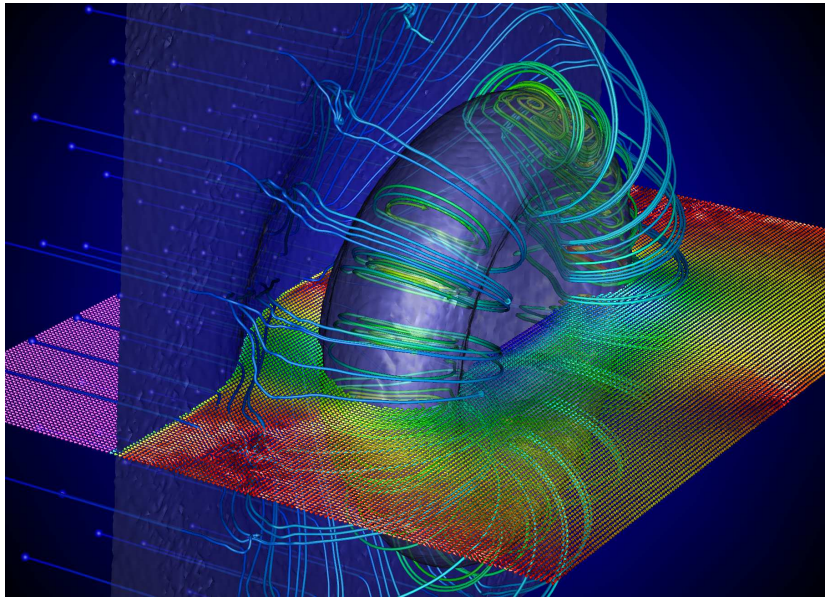
BASIC ENERGY SCIENCES

EXASCALE REQUIREMENTS REVIEW

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



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



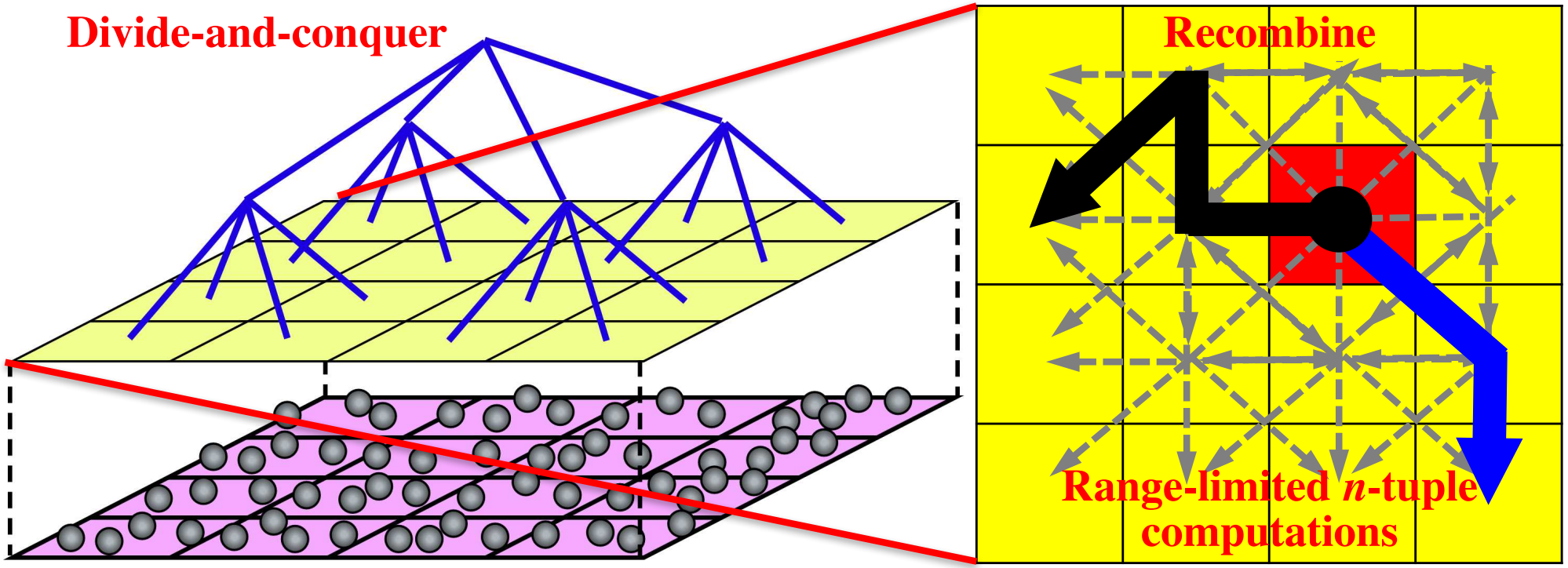
Shekhar *et al.*,
Phys. Rev. Lett.
111, 184503 ('13)

NOVEMBER 3–5, 2015

ROCKVILLE, MARYLAND

U.S. DEPARTMENT OF ENERGY

Divide-Conquer-Recombine (DCR) Engines



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

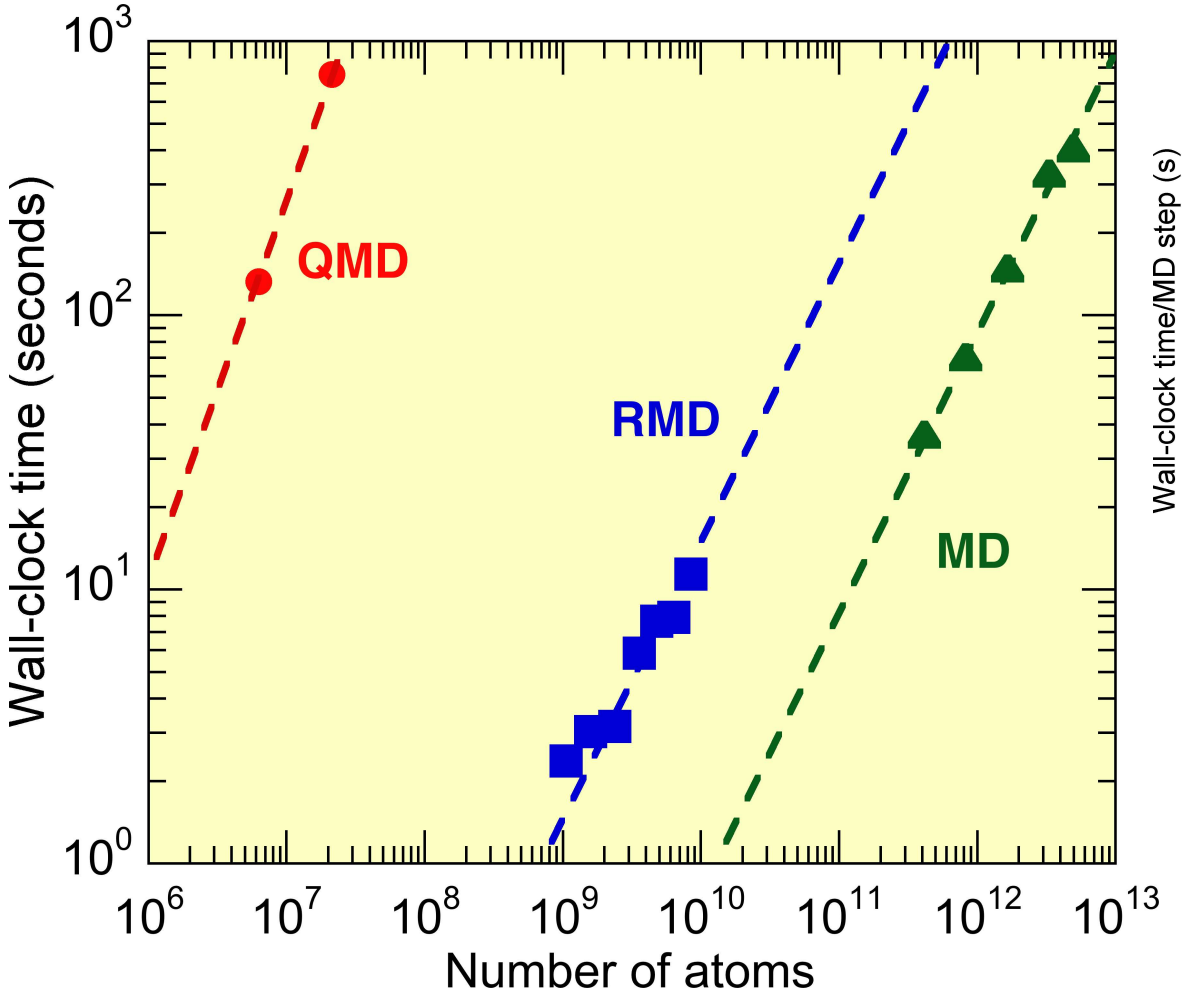
- **Lean divide-&-conquer density functional theory (LDC-DFT) algorithm minimizes the prefactor of $O(N)$ computational cost**

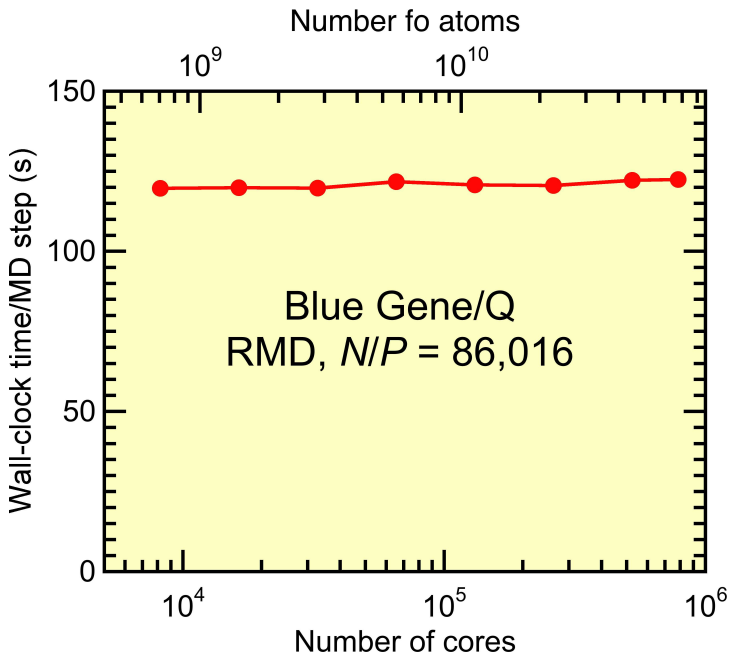
  F. Shimojo *et al.*, *J. Chem. Phys.* **140**, 18A529 ('14); K. Nomura *et al.*, *IEEE/ACM SC14*

- **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

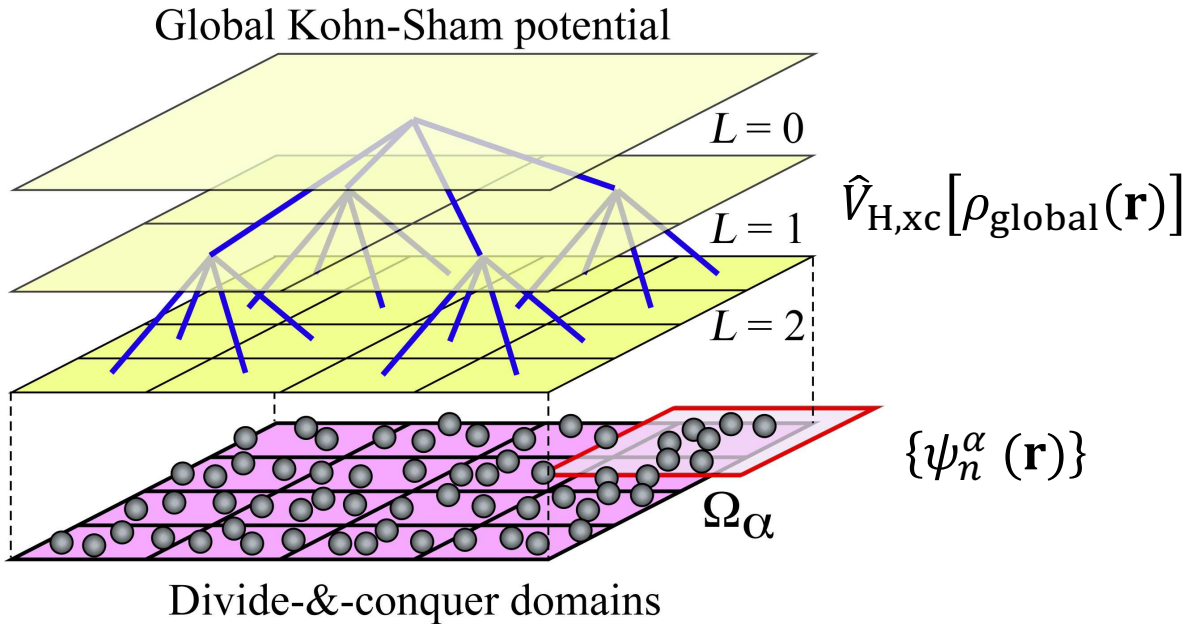
RMD (reactive molecular dynamics): F-ReaxFF

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

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

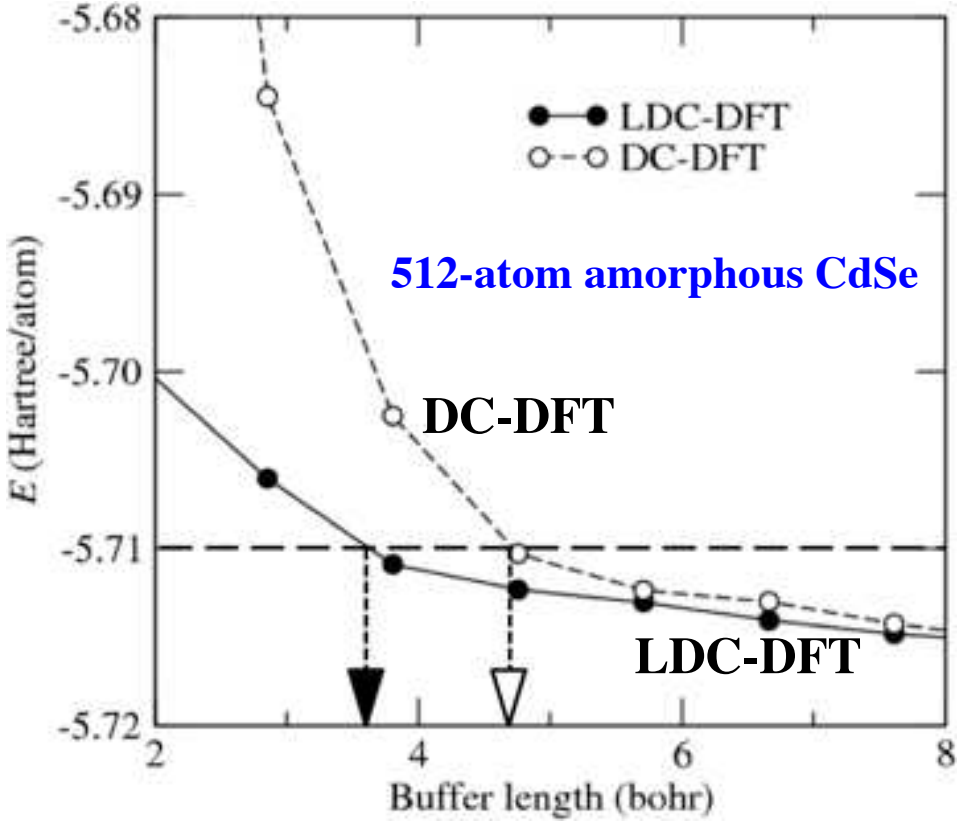
$$N = \int d\mathbf{r}\, \rho_{\mathrm{global}}(\mathbf{r})$$

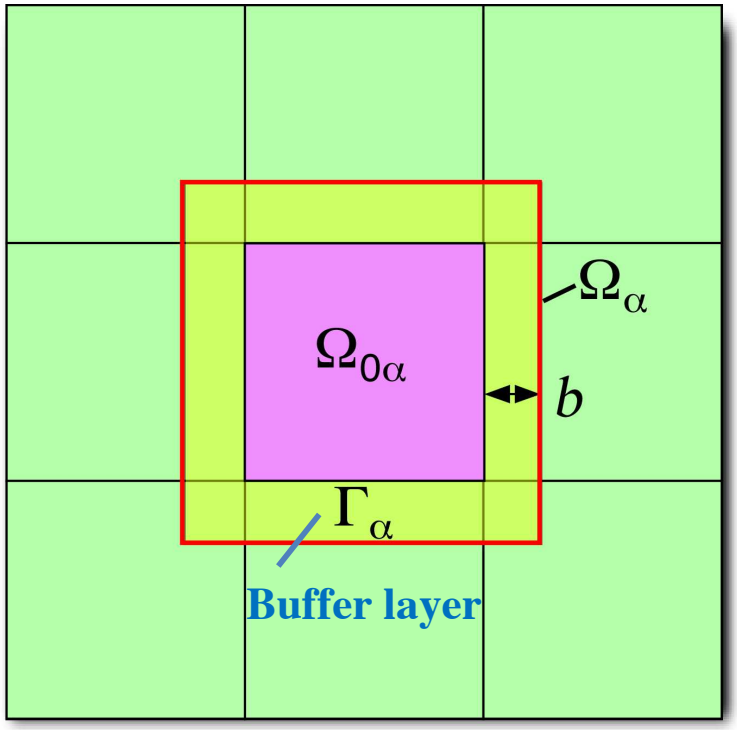
Lean Divide-&-Conquer (LDC) DFT

- **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**



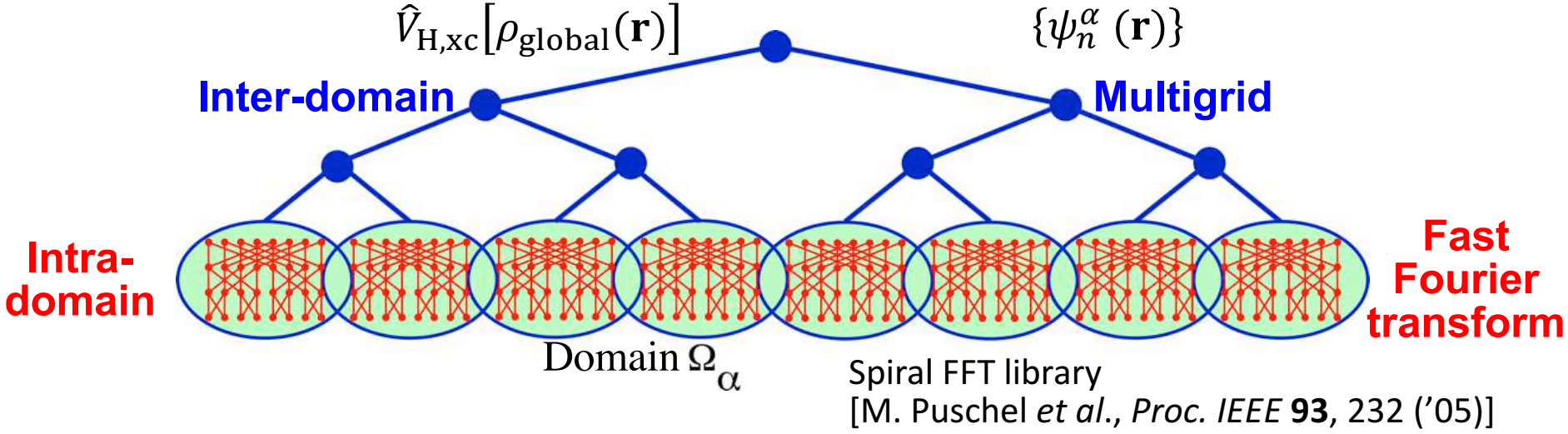


- **Factor 2.03 (for ν = 2) ~ 2.89 (for ν = 3) reduction of the computational cost with an error tolerance of 5×10^{-3} a.u. (per-domain complexity: n^ν)**

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

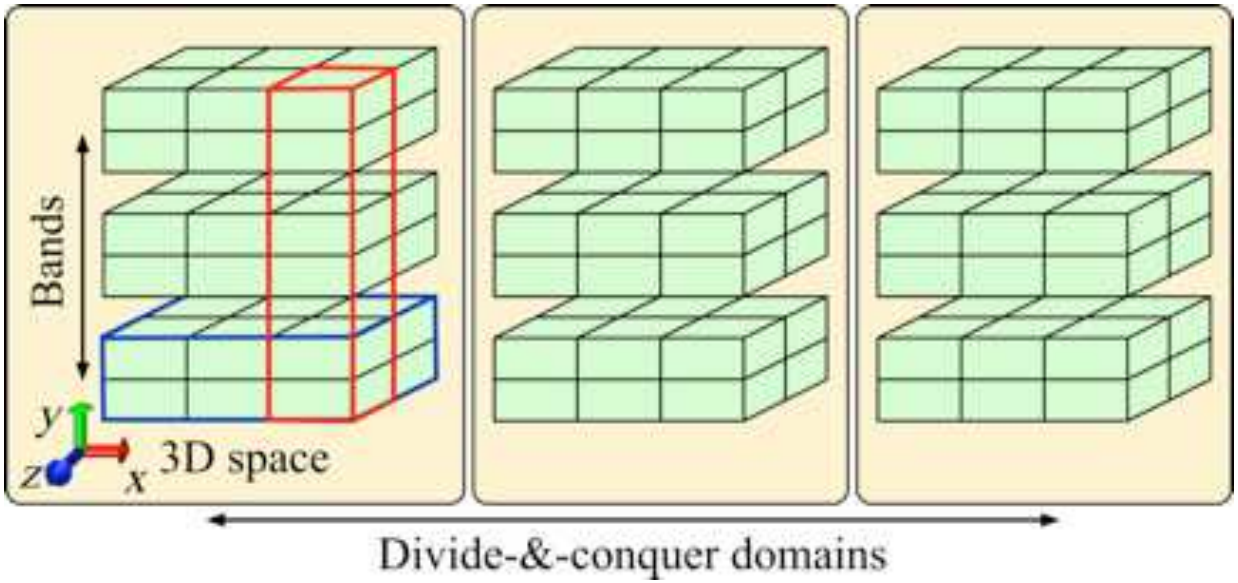
Hierarchical Computing

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



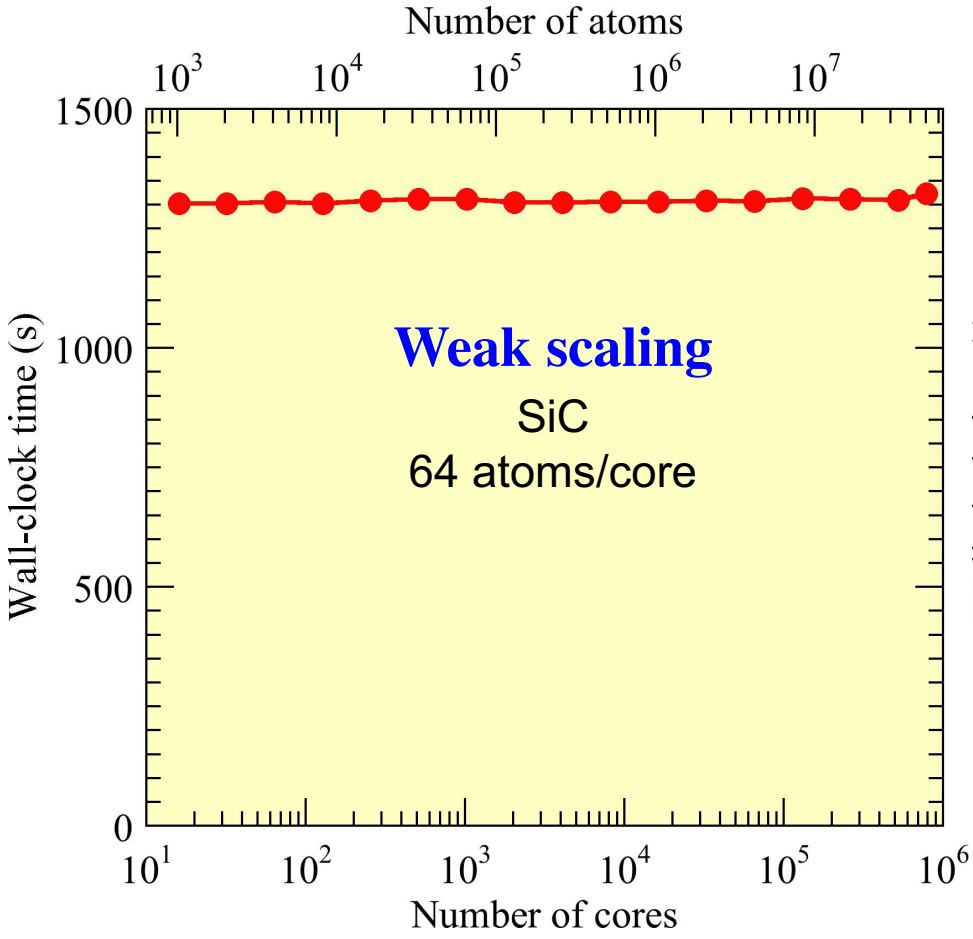
Spiral FFT library
[M. Puschel *et al.*, *Proc. IEEE* **93**, 232 ('05)]

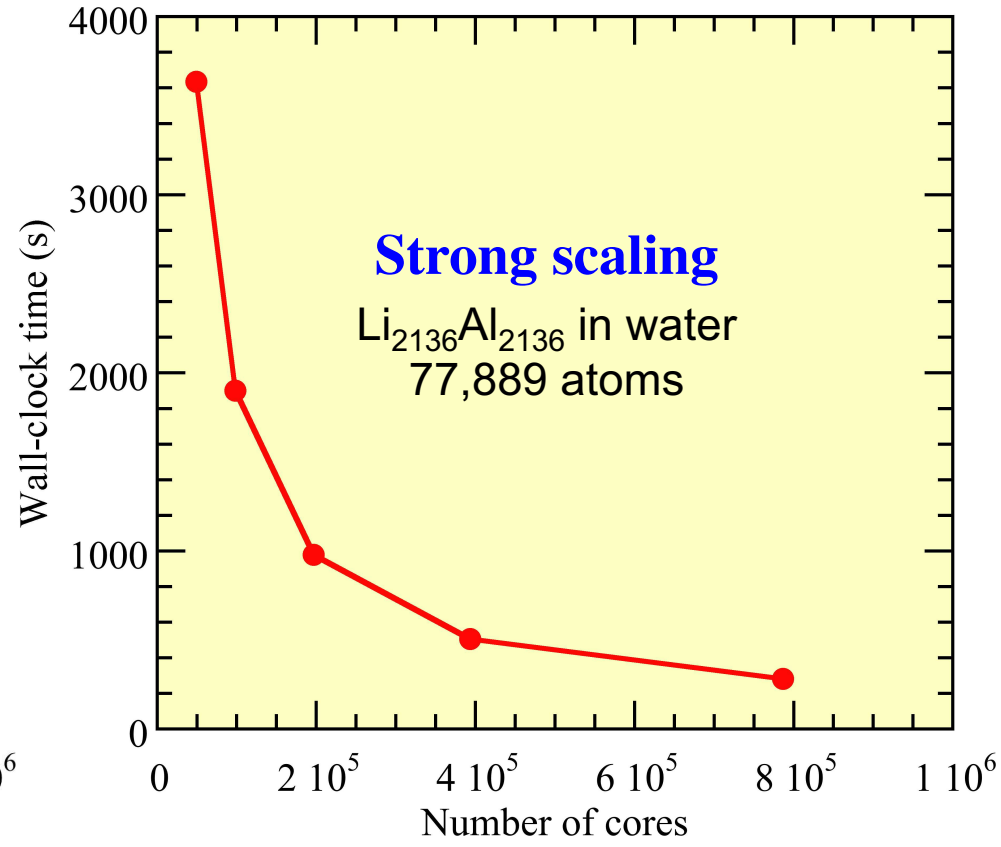
- **Hierarchical band (*i.e.* Kohn-Sham orbital) + space + domain (BSD) decomposition**



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**

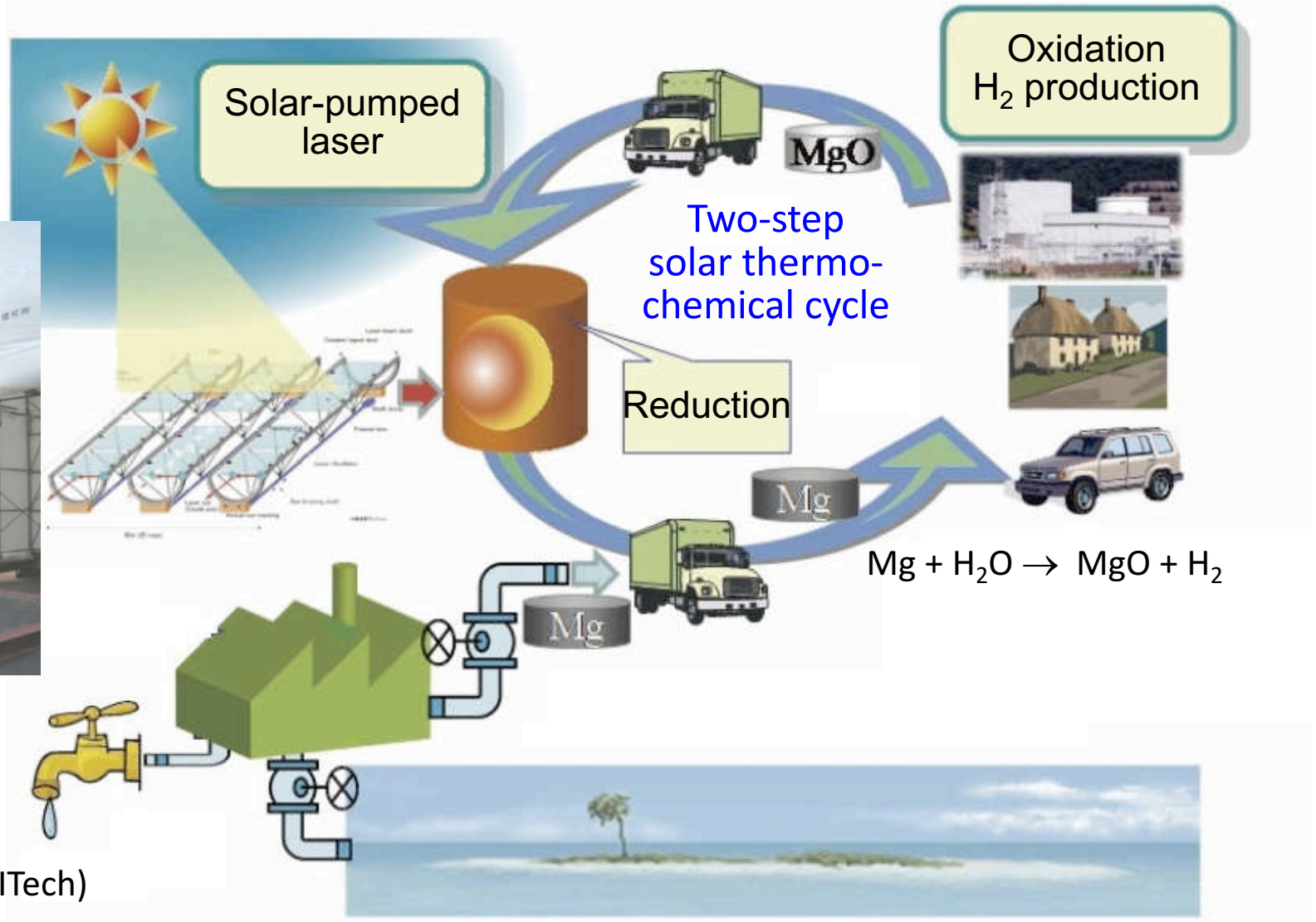




- **62-fold reduction of time-to-solution** [441 s/SCF-step for 50.3M atoms] **from the previous state-of-the-art** [55 s/SCF-step for 102K atoms, Osei-Kuffuor *et al.*, *PRL* '14]

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

Renewal Energy Cycle by Metal Carriers



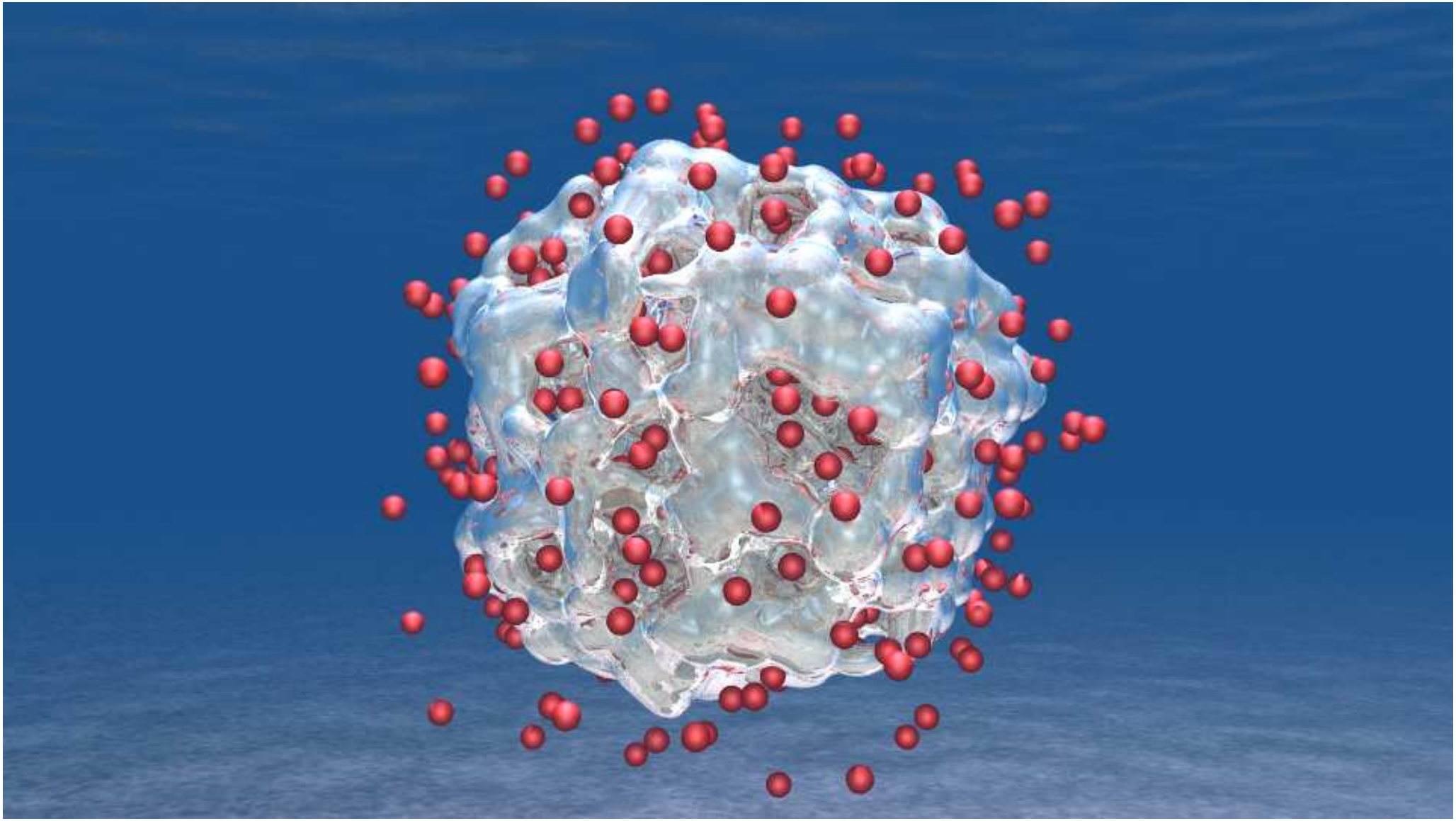
T. Yabe (TITech)

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

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

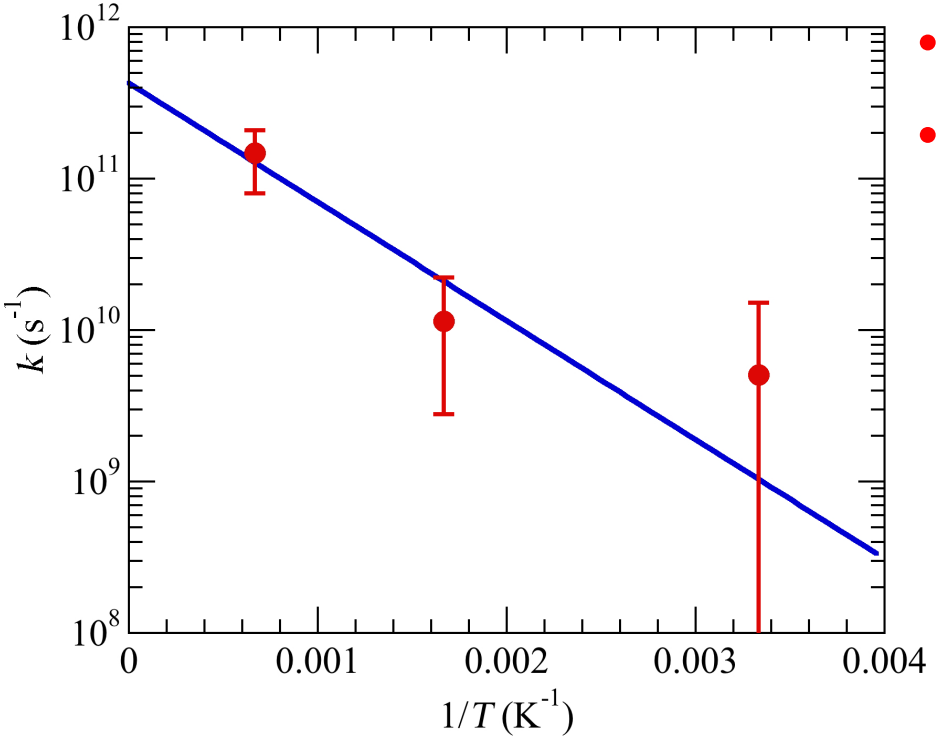
K. Shimamura *et al.*, *Nano Lett*. **14**, 4090 ('14)



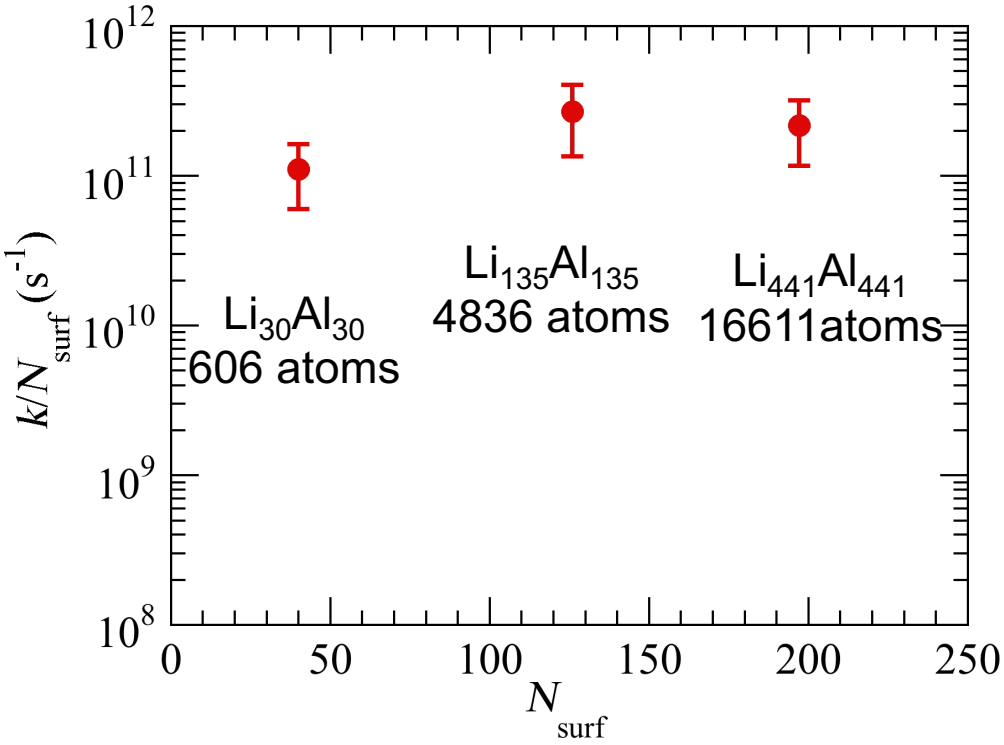
21,140 time steps (129,208 self-consistent-field iterations)

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**

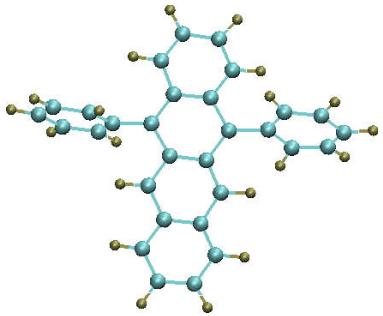


- **Reaction rate does not decrease for larger particles → industrial scalability**

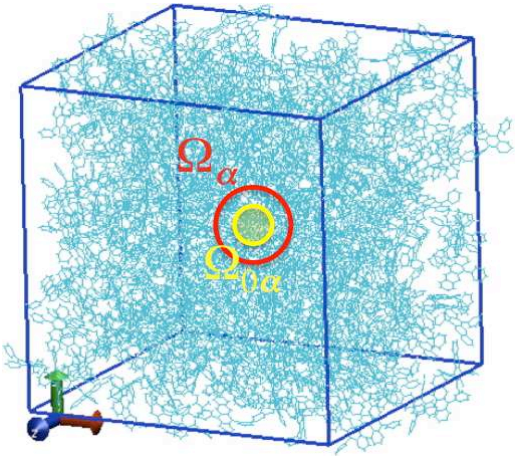
K. Shimamura *et al*., *Nano Lett*. **14**, 4090 ('14); K. Nomura *et al*., *IEEE/ACM SC14* ('14)

Singlet Fission in Amorphous DPT

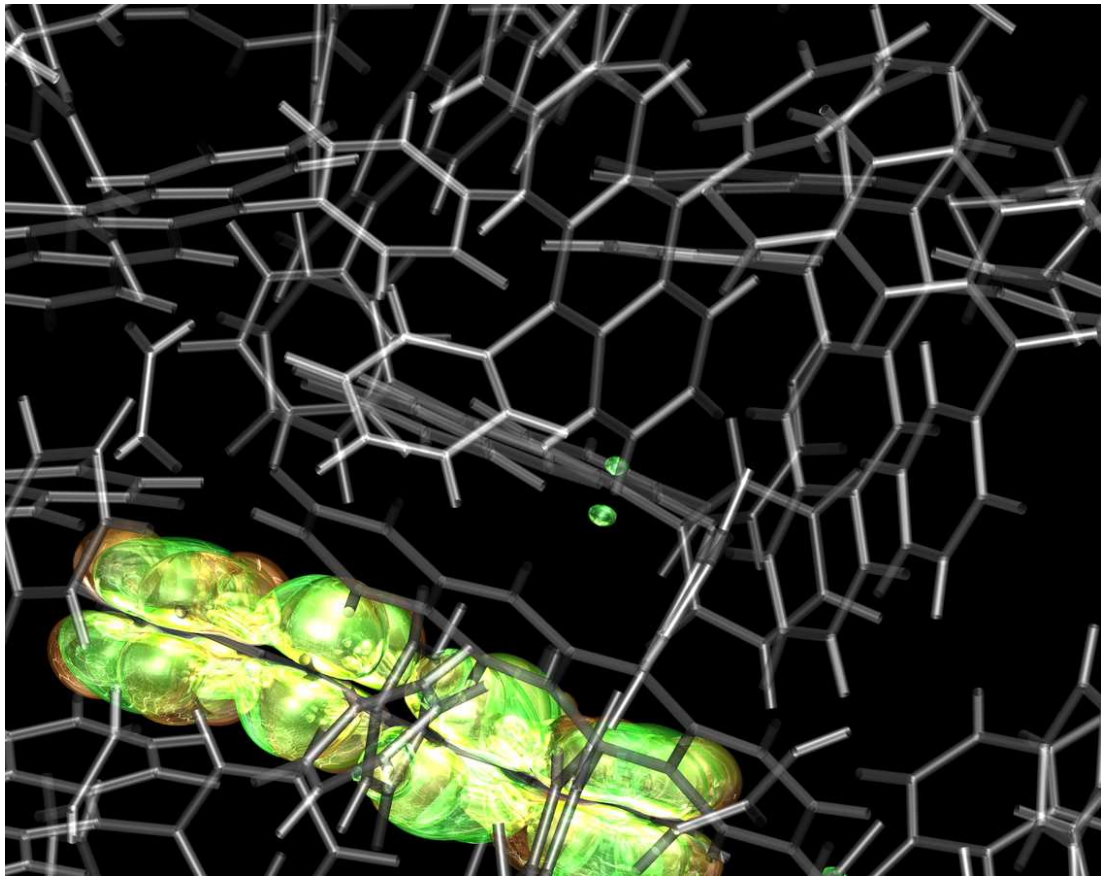
- Photo-current doubling by splitting a singlet exciton into 2 triplet excitons
- Singlet fission in mass-produced disordered organic solid → efficient low-cost solar cells
- Experimental breakthrough: SF found in amorphous diphenyl tetracene (DPT)



DPT molecule



Amorphous DPT



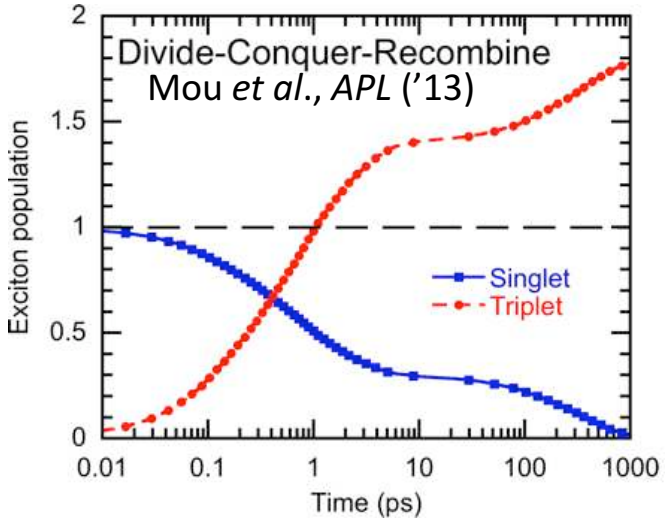
Quasi-electron

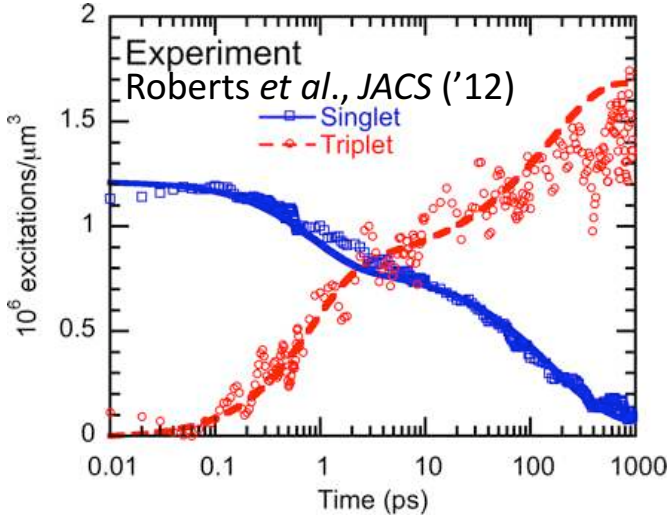
Quasi-hole

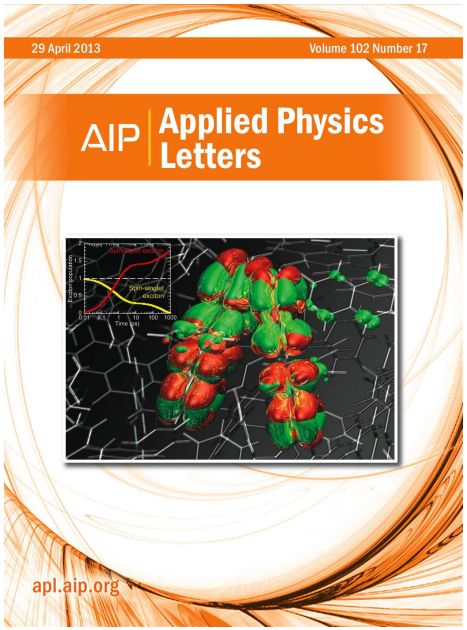
- Divide-conquer-recombine nonadiabatic QMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT

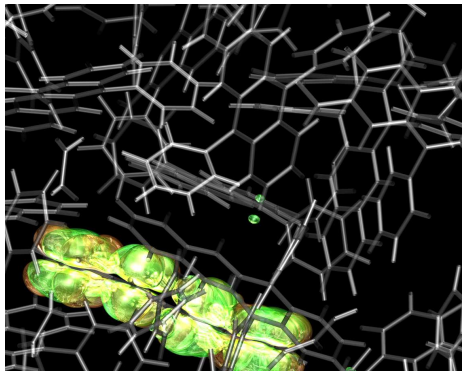
Singlet-Fission Hot Spot

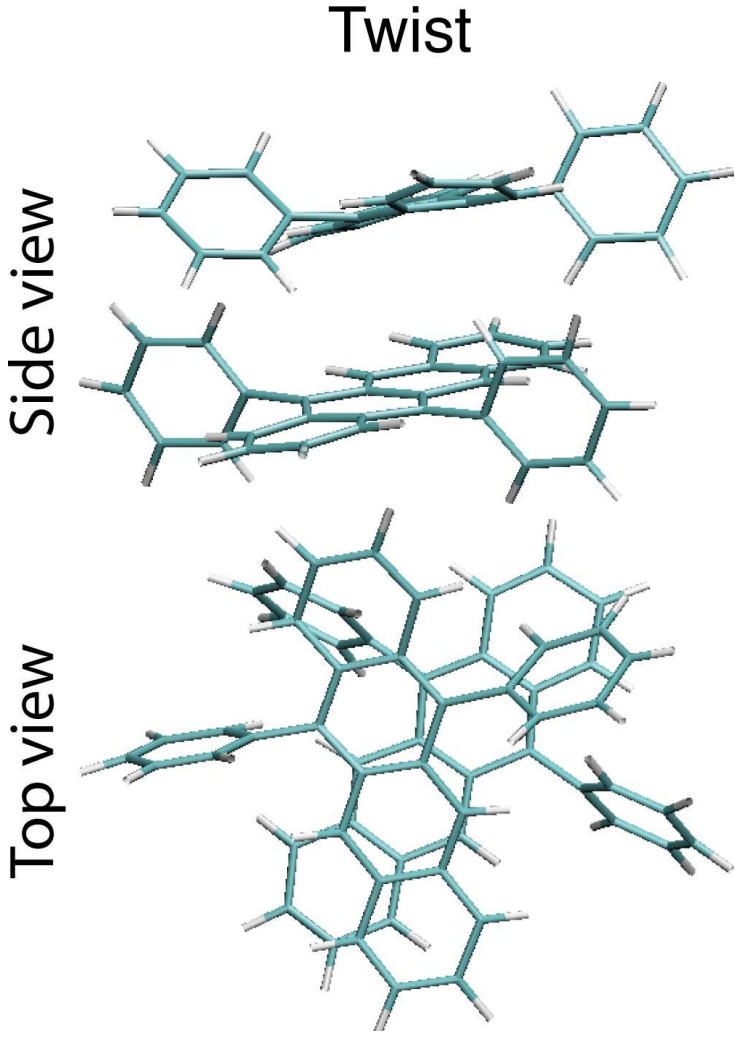
- **Nonadiabatic quantum molecular dynamics simulations not only reproduced experimentally measured exciton population dynamics but also revealed unknown molecular geometry of singlet fission hot spots**



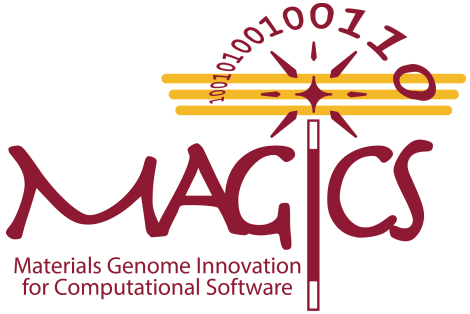








MAterials Genome Innovation for Computational Software



U.S. DEPARTMENT OF ENERGY | Office of Science

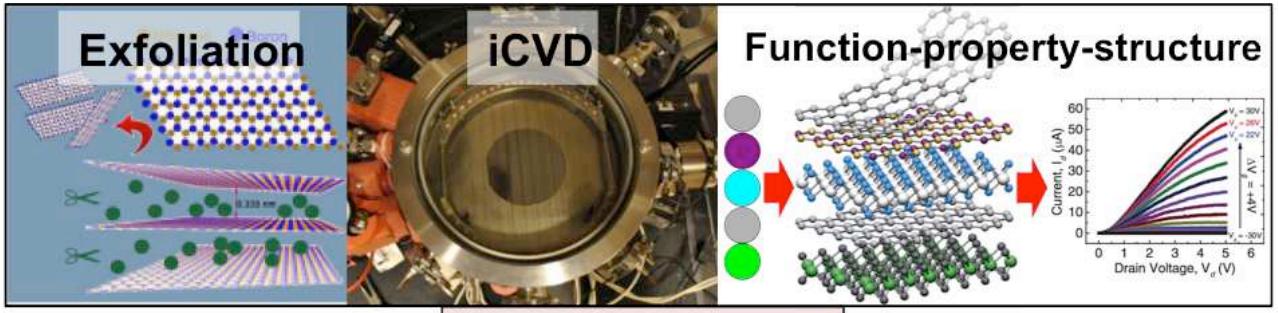
Basic Energy Sciences

Priya Vashishta-PI, Malancha Gupta, Rajiv K. Kalia, Aiichiro Nakano,
Oleg Prezhdo *University of Southern California*
Uwe Bergmann and David Fritz *Linac Coherent Light Source, SLAC*
William A. Goddard, III *California Institute of Technology*
Kristin A. Persson *Lawrence Berkeley National Laboratory*
David J. Singh *University of Missouri*
Pulickel M. Ajayan *Rice University*

USC

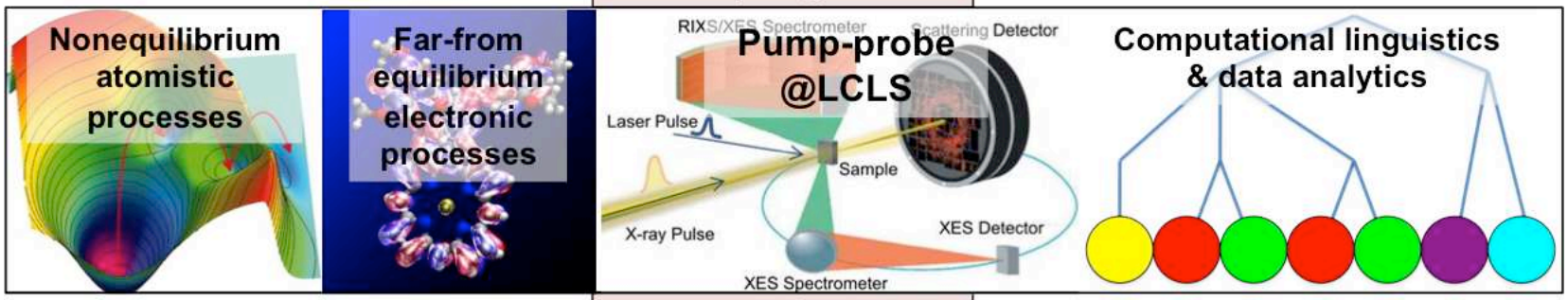
SLAC

Computational Synthesis of Functional Layered Materials: MAGICS Software Stack



3 Extensible plug-ins – Computational synthesis

Scripting API



2 Core libraries – Elementary processes

Core API

NAQMD	RMD	AMD
MPI	OpenMP	CUDA/Phi

Current/future platforms

1 Scalable simulation engines

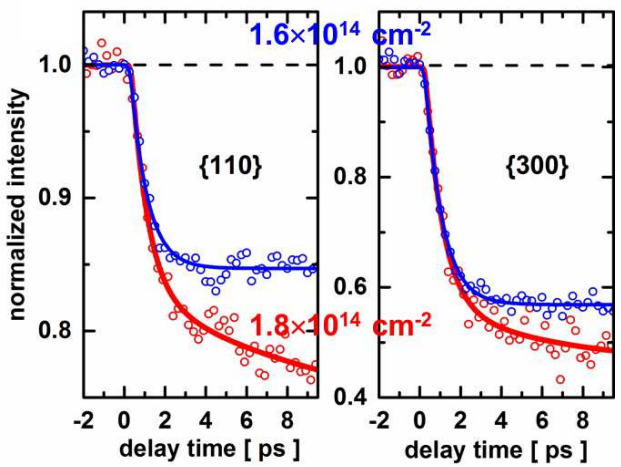
U.S. DEPARTMENT OF ENERGY INCITE LEADERSHIP COMPUTING

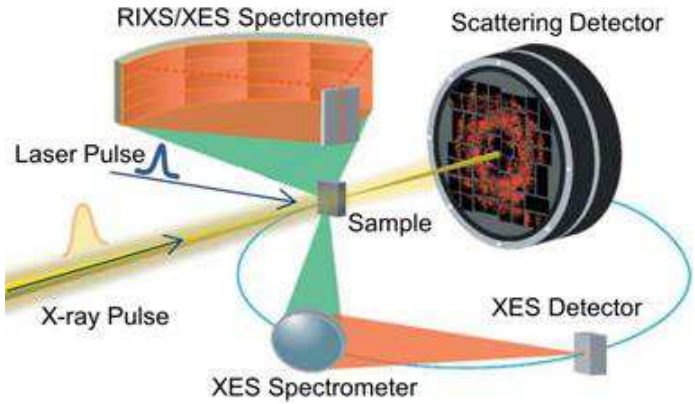
AURORA EARLY SCIENCE PROGRAM

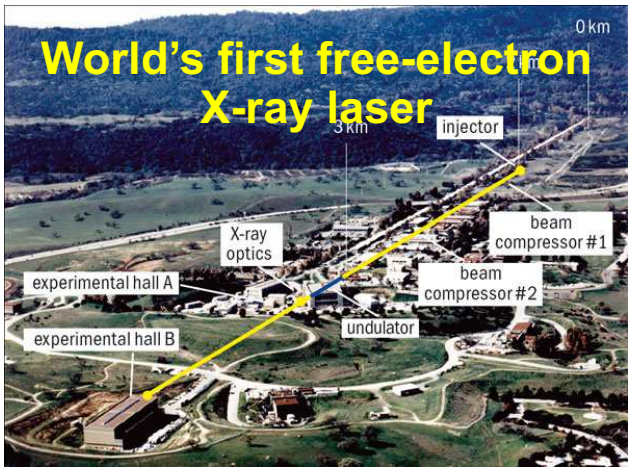
MAGICS Materials Genome Innovation for Computational Software

LCLS X-ray free-electron laser

INCITE|A21–MAGICS–LCLS Synergy



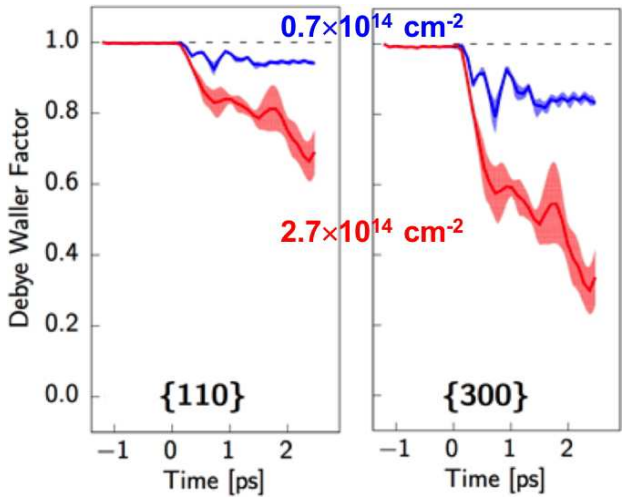




Linac Coherent Light Source

LCLS

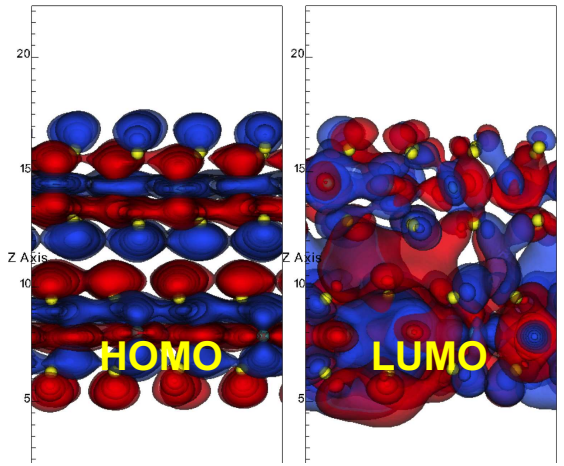
DOE INCITE & Aurora ESP Awards



MAGICS
Materials Genome Innovation for Computational Software

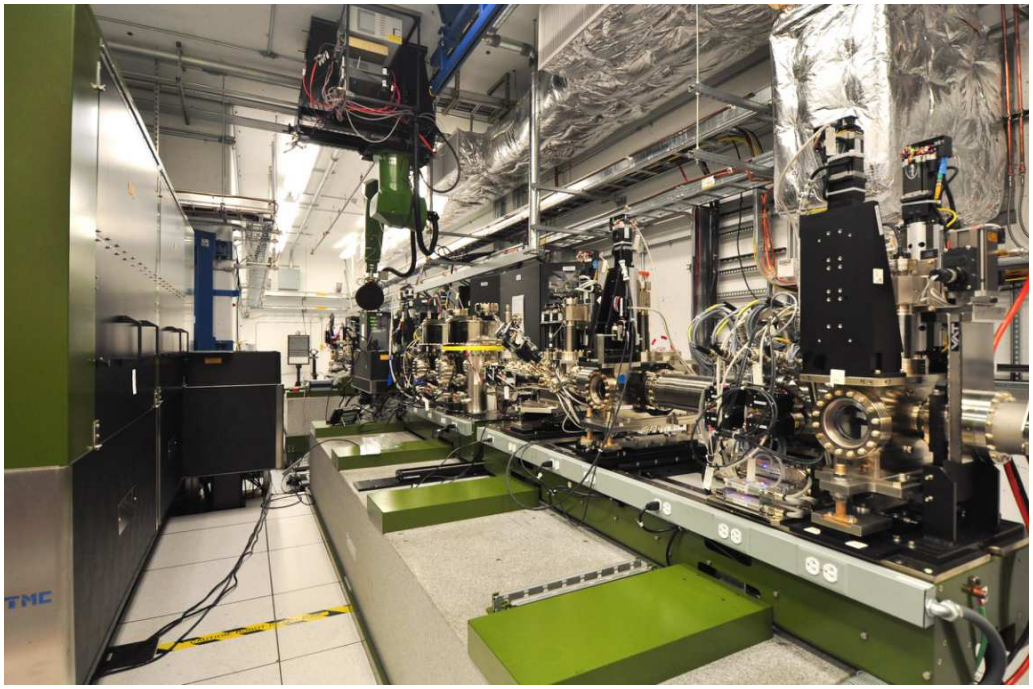
U.S. DEPARTMENT OF ENERGY
INCITE
LEADERSHIP COMPUTING

AURORA | EARLY SCIENCE PROGRAM

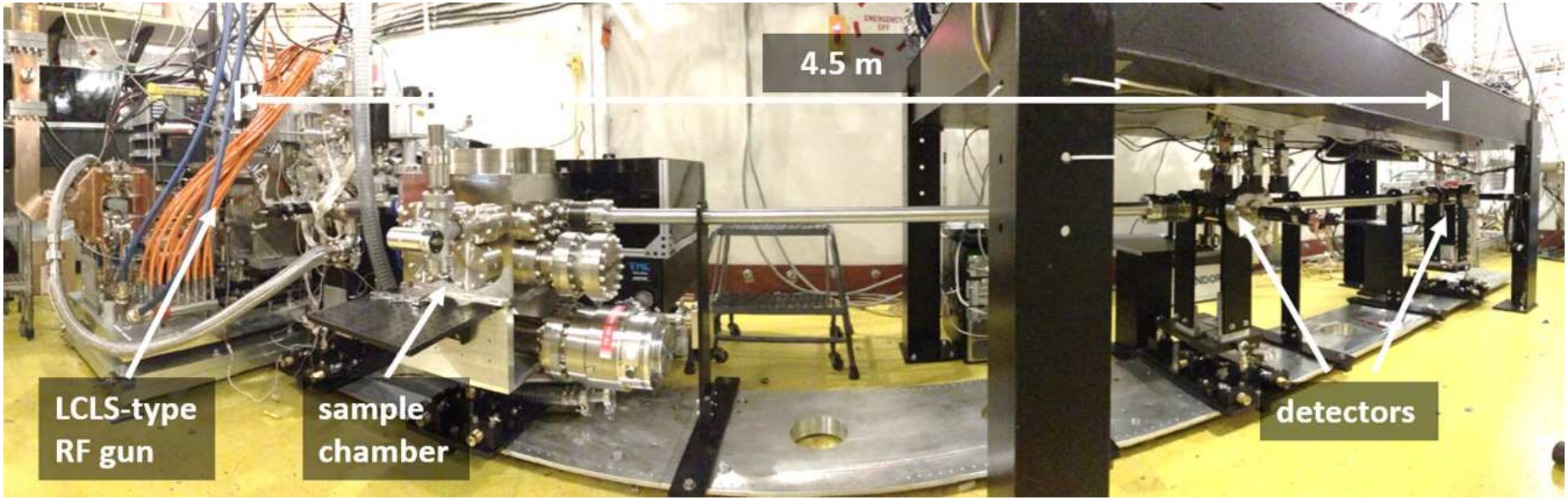


ULTRAFAST PUMP-PROBE EXPERIMENTS

X-ray pump-probe (XPP) instrument: 4-25 KeV

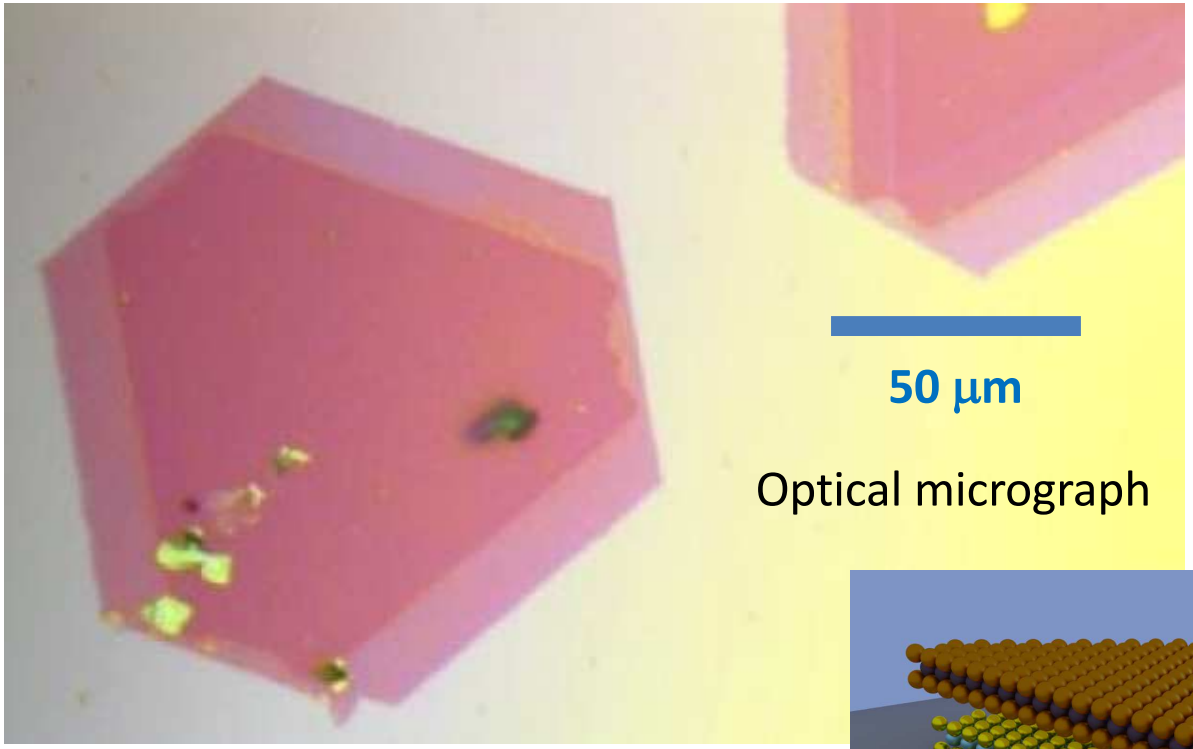


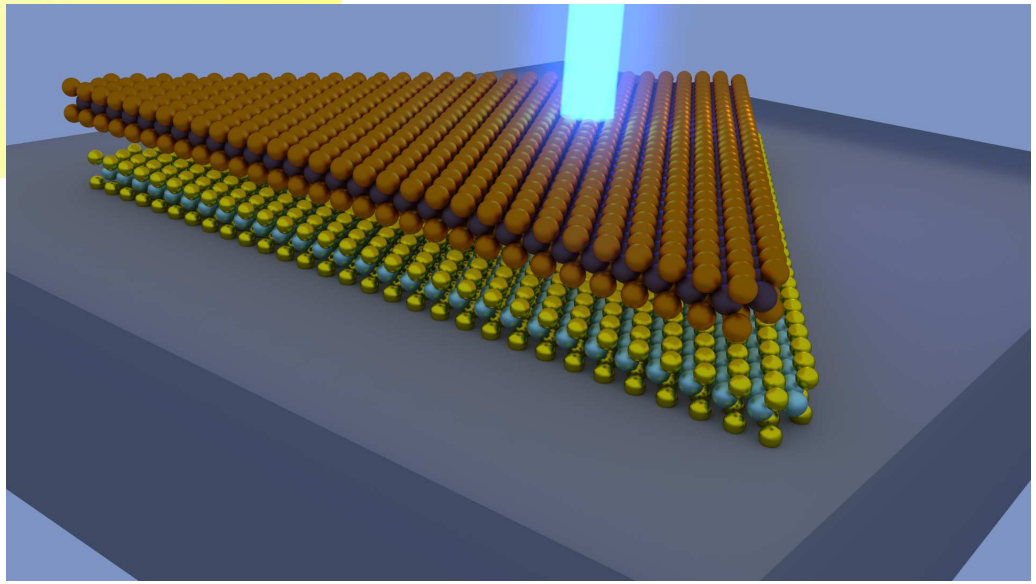
Ultrafast electron diffraction (UED) instrument: 3-5 MeV



2D Transition Metal Dichalcogenide (TMDC)

- **Mono- and bi-layer $MoSe_2$ synthesized by the Rice group (P. Ajayan)**

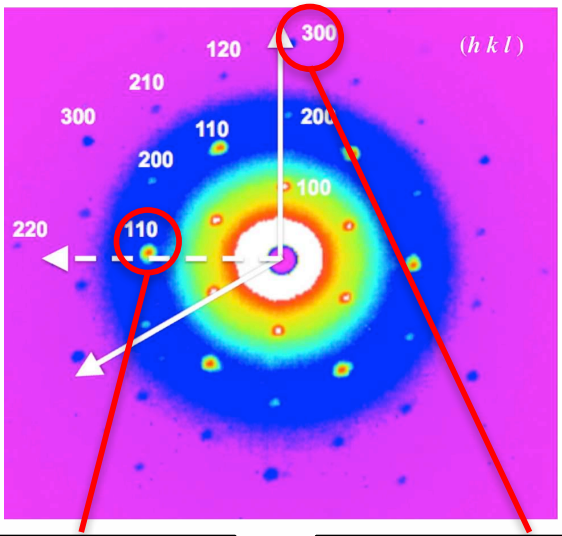


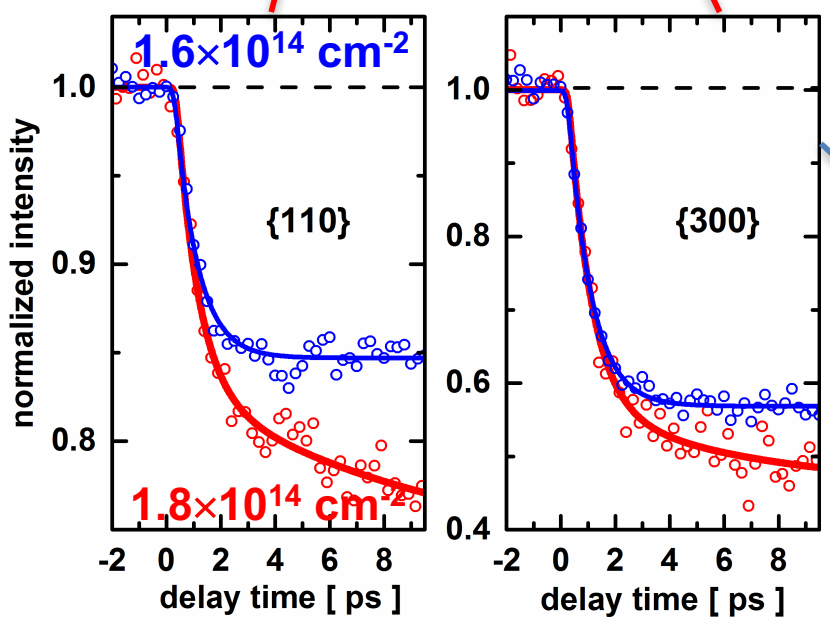


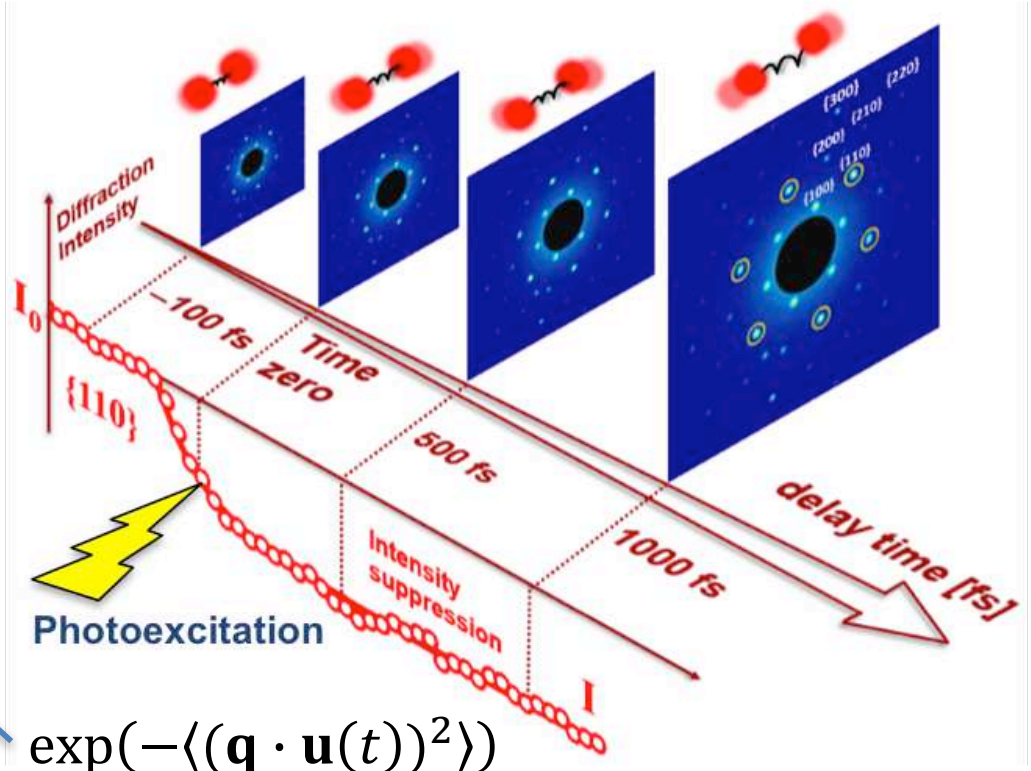
- **Question: What is the nature of optically induced lattice dynamics for photo-patterning (*e.g.*, semiconducting 2H to metallic 1T' phases) of TMDC?**

Ultrafast Coupled Electron-Lattice Dynamics

- **Ultrafast electron diffraction experiment shows nearly perfect energy conversion from electronic excitation to lattice motions within ps** [M.F. Lin *et al.*, unpublished]







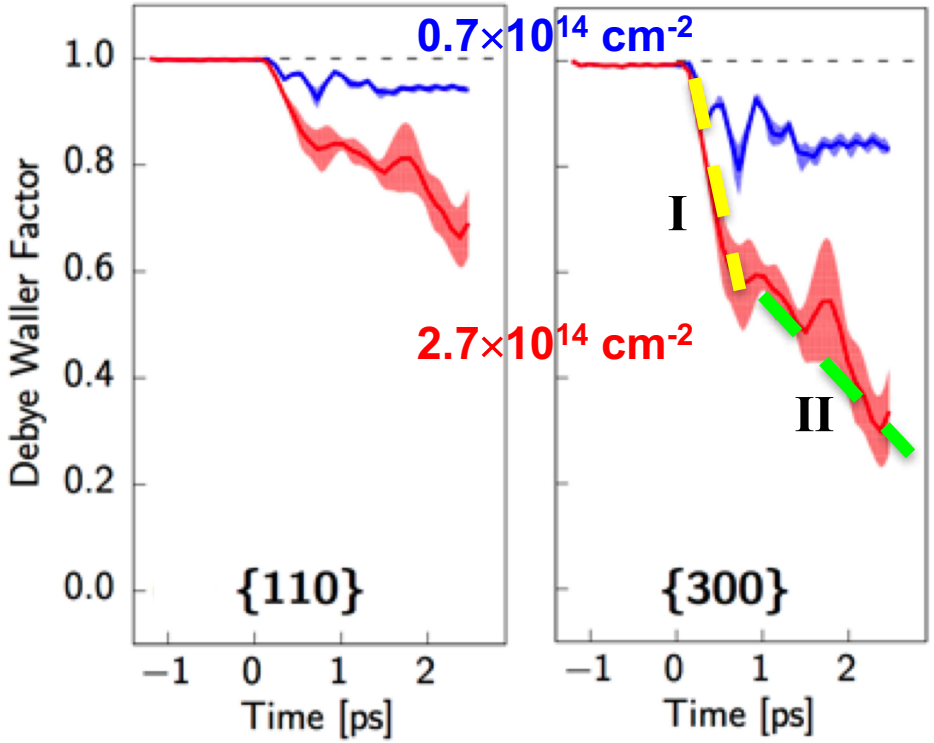
$$\exp(-\langle(\mathbf{q}\cdot\mathbf{u}(t))^2\rangle)$$

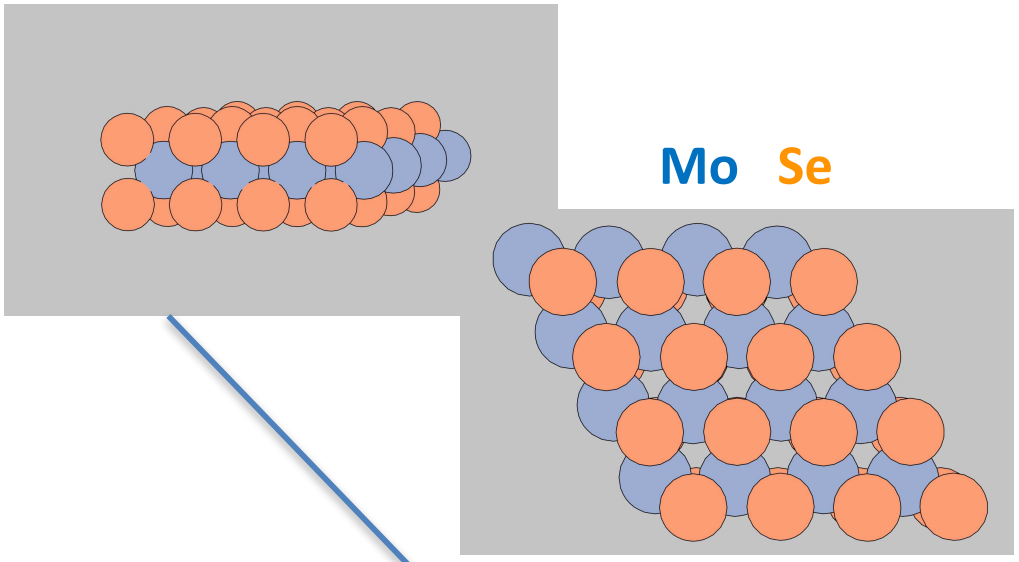
atomic displacement

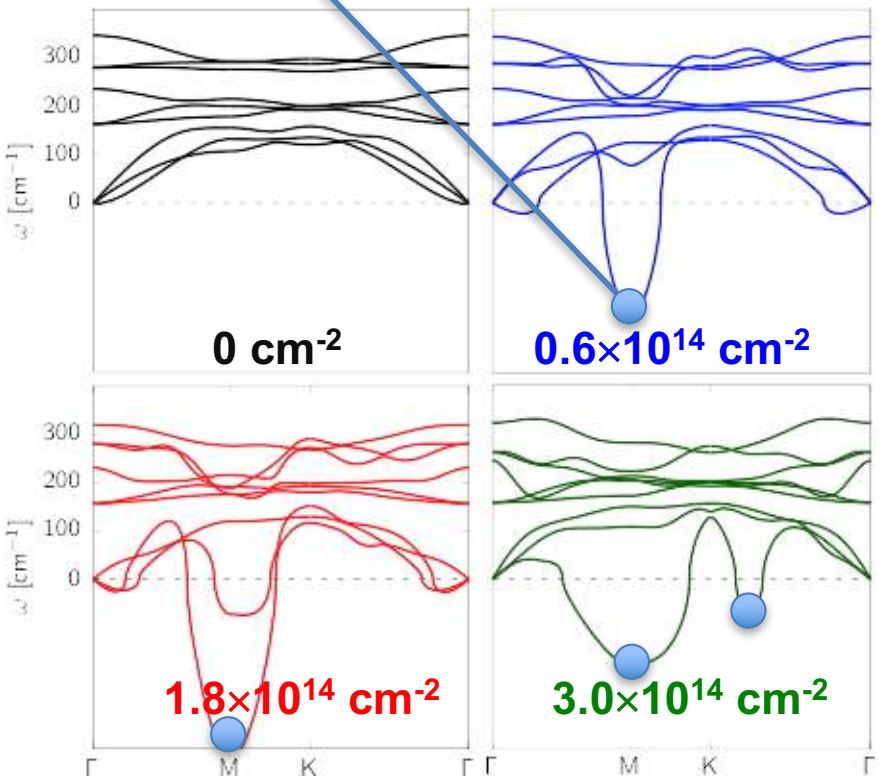
- **Dynamics of Debye-Waller factor reveals rapid disordering for both {300} & {110} peaks**
- **Transition from mono- to bi-exponential decay at higher electron-hole density**

Strong Electron-Lattice Coupling

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



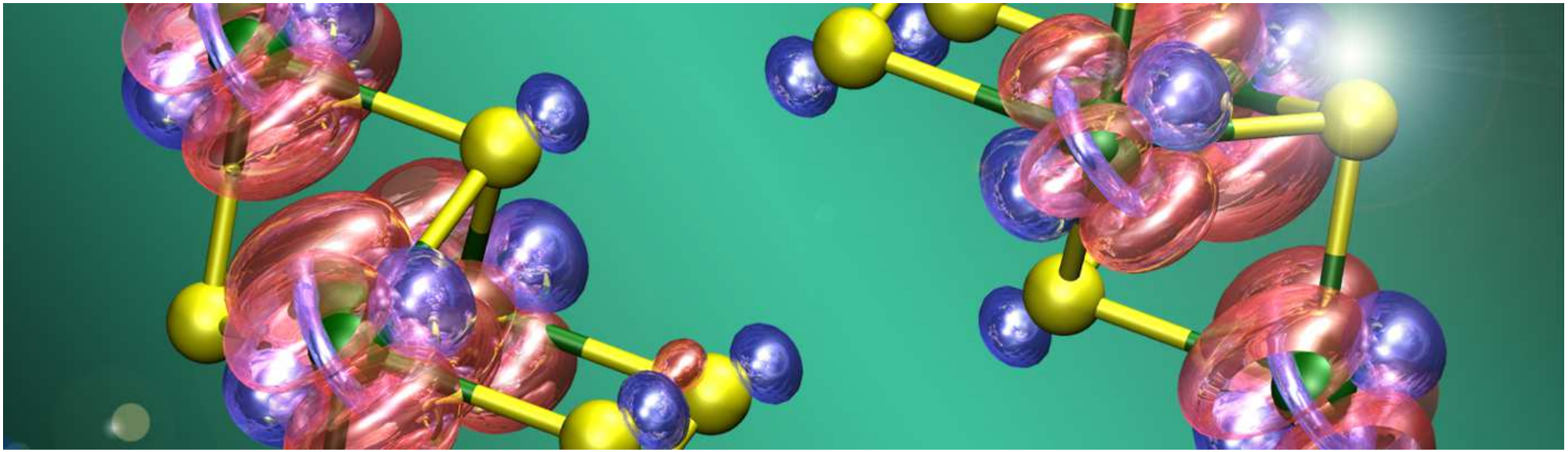




- **Rapid lattice dynamics is explained by the softening of M-point (1/2 0 0) phonon**
- **Bi-exponential transition is explained by the softening of additional phonon modes at higher electron-hole densities**

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

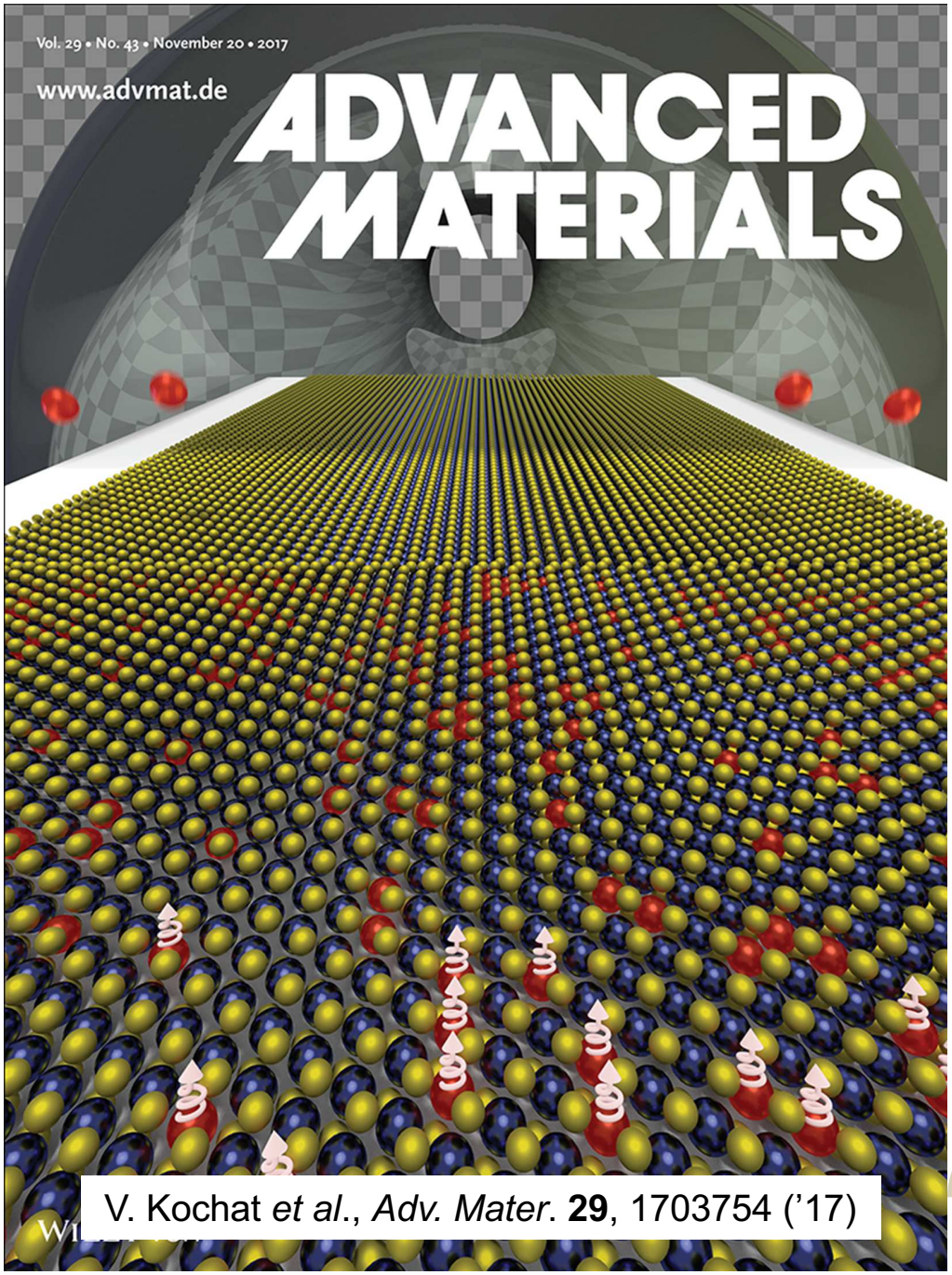
Simulation-Experiment Synergy



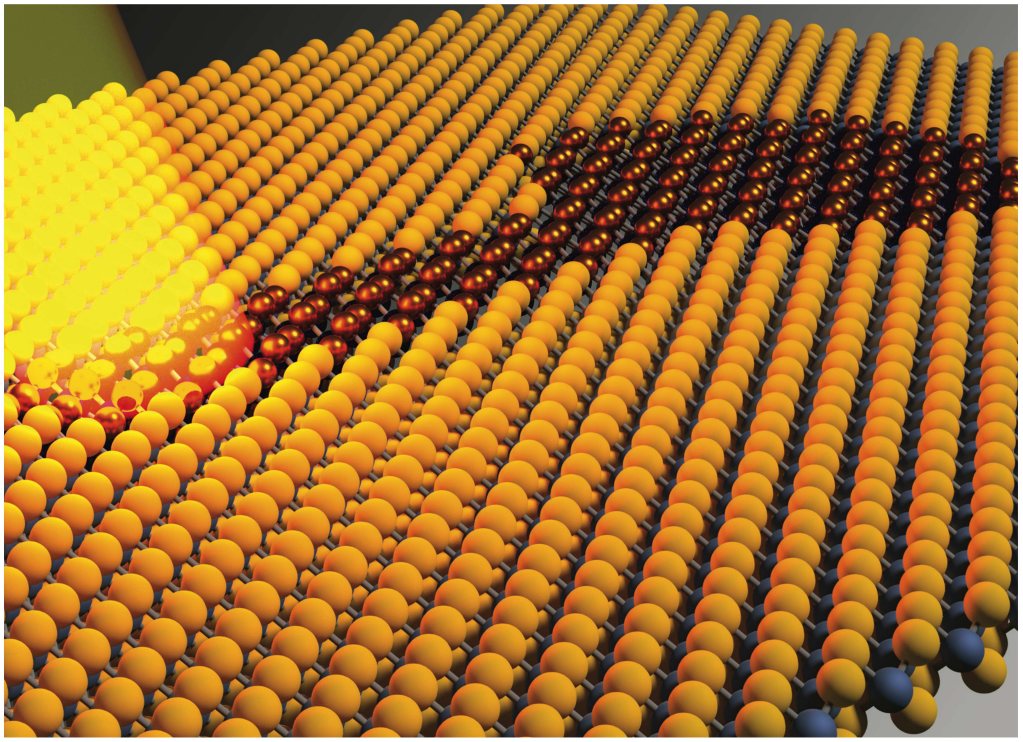
- **In the ultrafast 'electron camera,' laser light hitting a material is almost completely converted into nuclear vibrations — key to switching material properties on & off at will for future electronics applications**
- **High-end quantum simulations reproduce the ultrafast energy conversion at exactly 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)

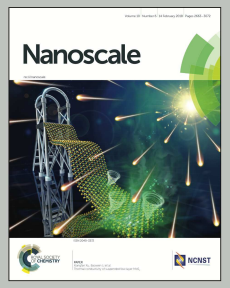


Showcasing research from Collaboratory for Advanced Computing and Simulations (CACS), University of Southern California, Los Angeles, USA.

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.

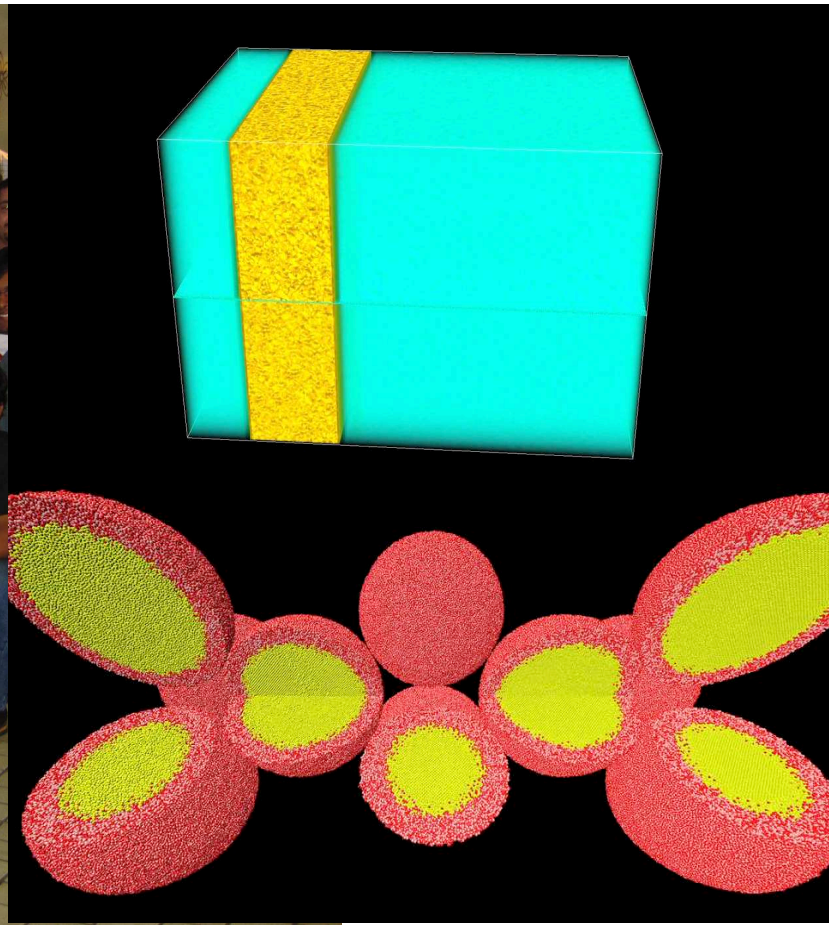
A. Krishnamoorthy *et al.*, *Nanoscale* **10**, 2742 ('18)

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



Supported as part of the Computational Materials Sciences Program funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award Number DE-SC00014607