Quantum Molecular Dynamics Simulations

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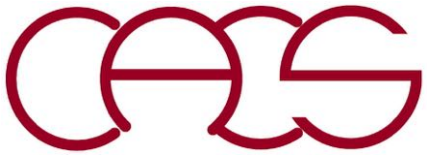
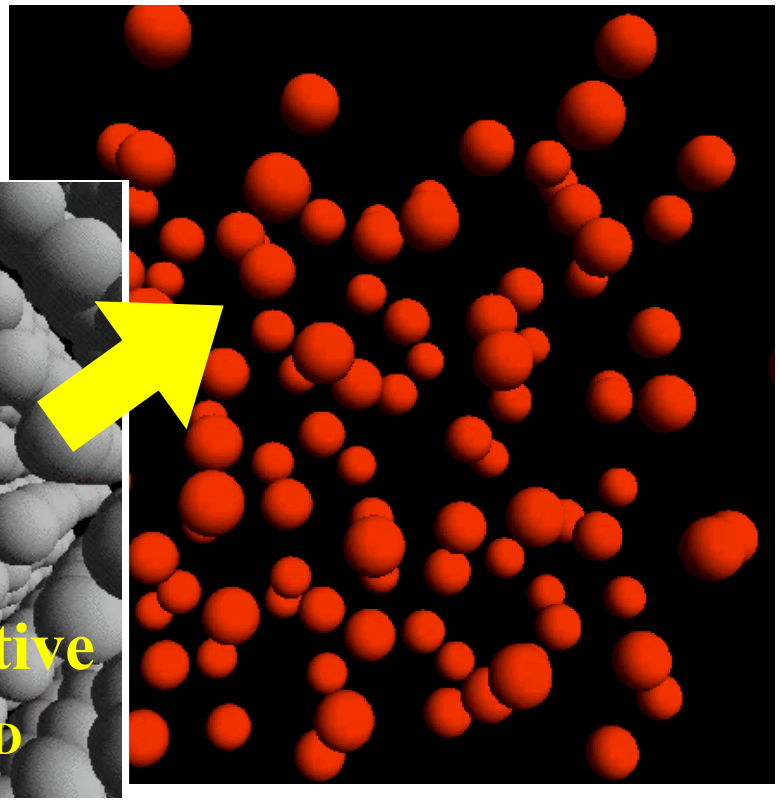
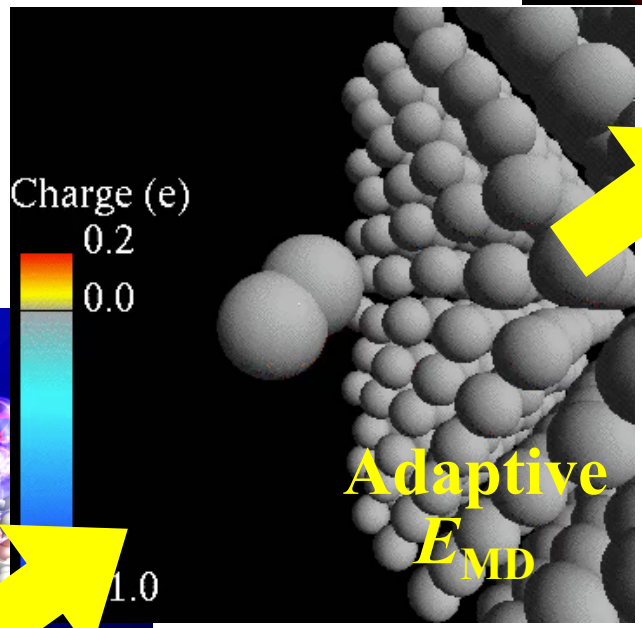


Molecular Dynamics Hierarchy

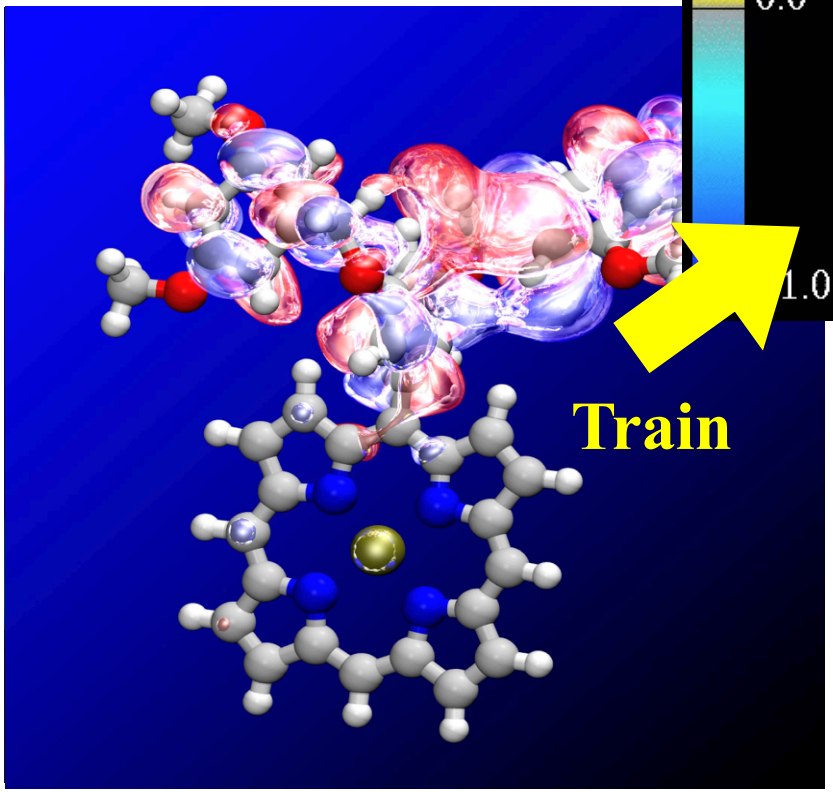
Molecular Dynamics (MD)



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

$O(C^N)$ → $O(N^3)$

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

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

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

Born-Oppenheimer Approximation

- **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

- **Due to the much larger nuclei masses (M_I) compared to the electron mass (m), the quantum-mechanical wave function of the system is separable to those of the electrons & nuclei**
- **At ambient conditions, 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

Kohn-Sham Energy Eigenstates

- **Time-independent Schrödinger equation**

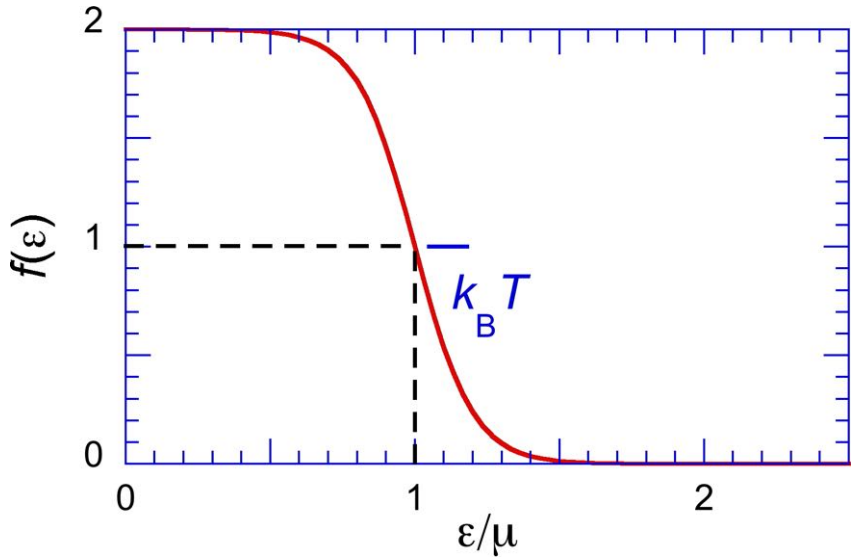
Hamiltonian operator → $H\psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r})$ ← Eigenstate

Eigenvalue

- **Stationary state**

$$i\hbar \frac{\partial}{\partial t}\psi(t) = H\psi(t)$$

$$\psi(t) = \exp(-i\epsilon_n t/\hbar)\psi_n$$



- **Hamiltonian operator**

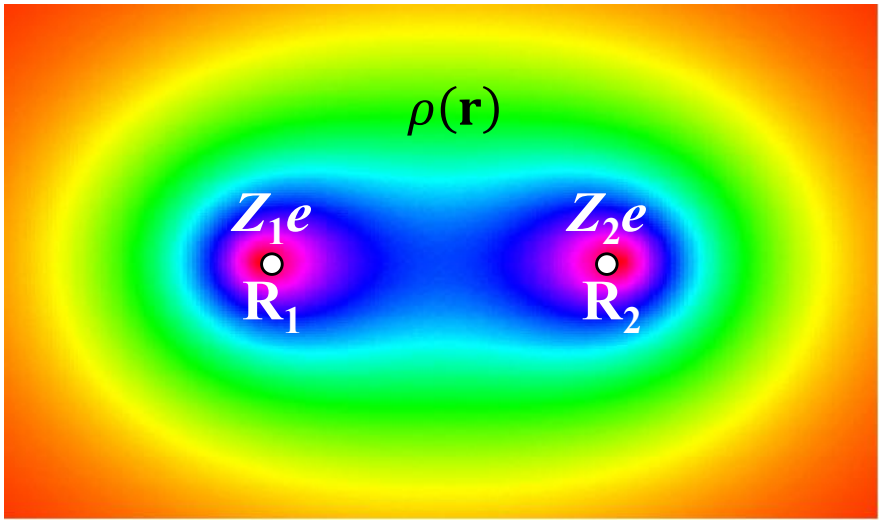
$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}_i^2} + v(\mathbf{r})$$

- **Density functional theory***

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

$$\rho(\mathbf{r}) = \sum_n \frac{2}{\exp\left(\frac{\varepsilon_n - \mu}{k_B T}\right) + 1}|\psi_n(\mathbf{r})|^2$$

exchange-correlation potential



*$T = 0$ in Kohn-Sham'65; *cf.* Mermin

[*Phy. Rev.* **137**, A1441 ('65)]

Abstraction: Exchange-Correlation Functional

- **Universal functional (of density) that describes many-body effects beyond the mean-field approximation**

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

potential energy due to electron-electron interaction

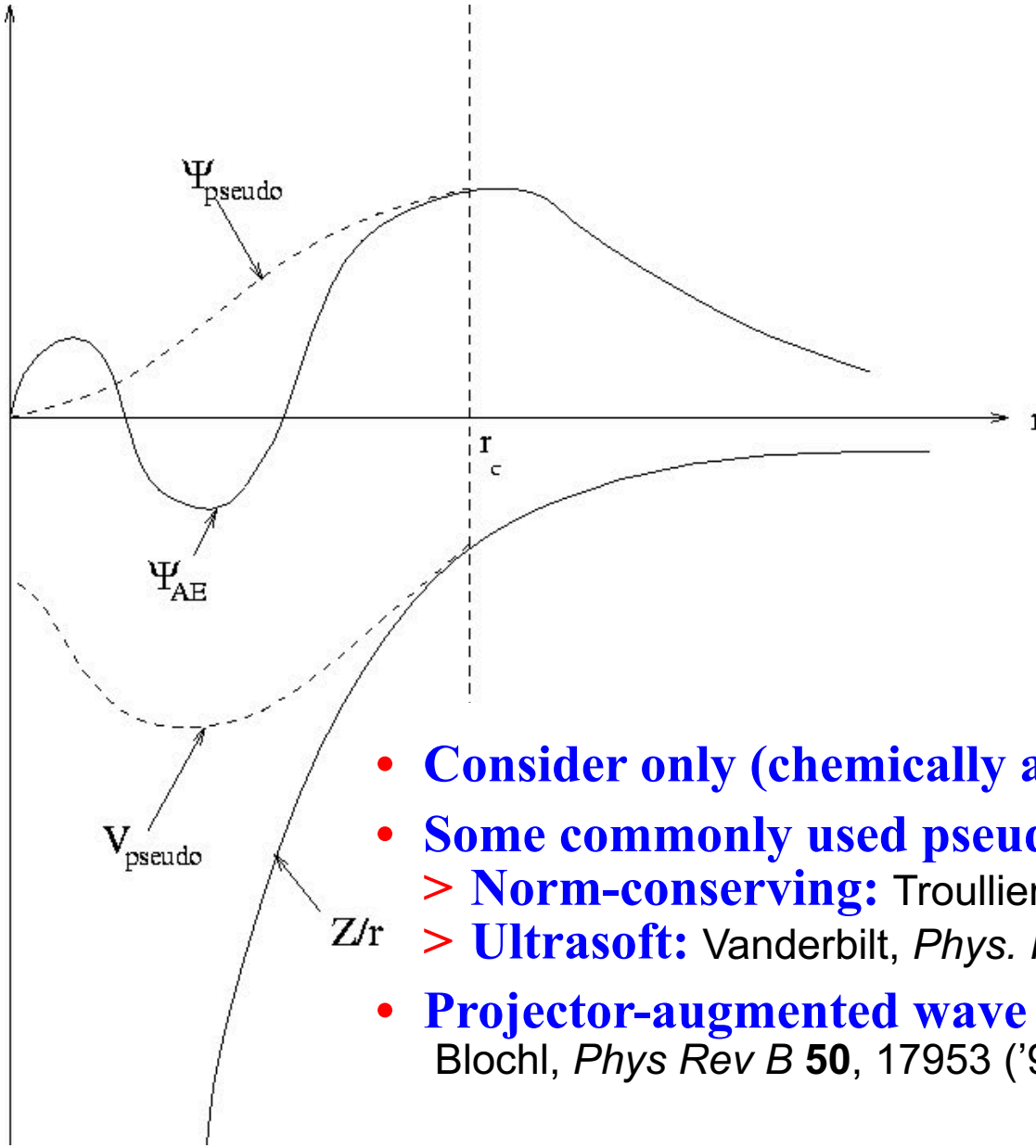
Hartree (mean-field) potential

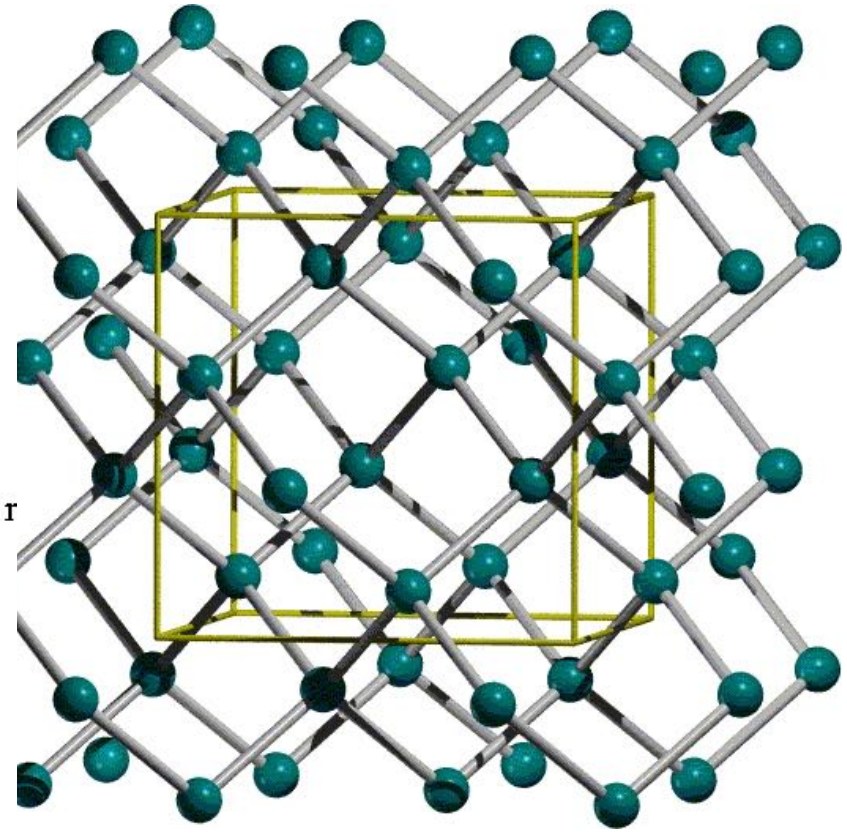
exchange-correlation potential

- **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)

Abstraction: Pseudopotential

- **Silicon — $1s^2 2s^2 2p^6 3s^2 3p^2$**





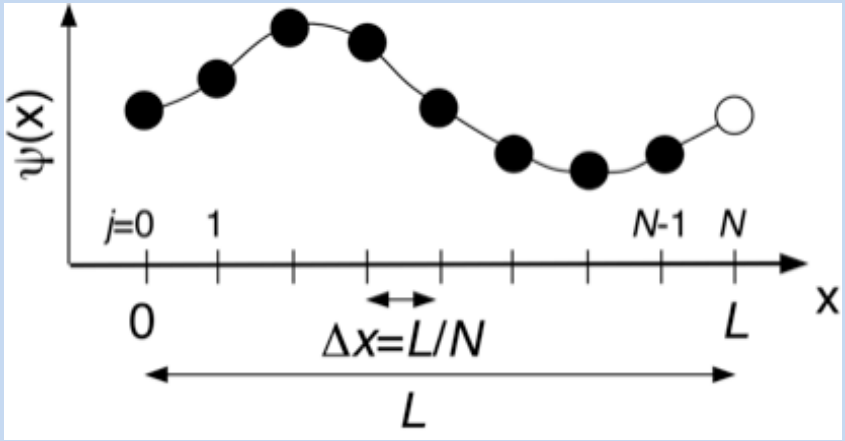
- **Consider only (chemically active) valence electrons**
- **Some commonly used pseudopotentials**
  - > **Norm-conserving:** Troullier & Martins, *Phys. Rev. B* **41**, 1993 ('91)
  - > **Ultrasoft:** Vanderbilt, *Phys. Rev. B* **41**, 7892 ('90)
- **Projector-augmented wave (PAW) method**
  Blochl, *Phys Rev B* **50**, 17953 ('94)

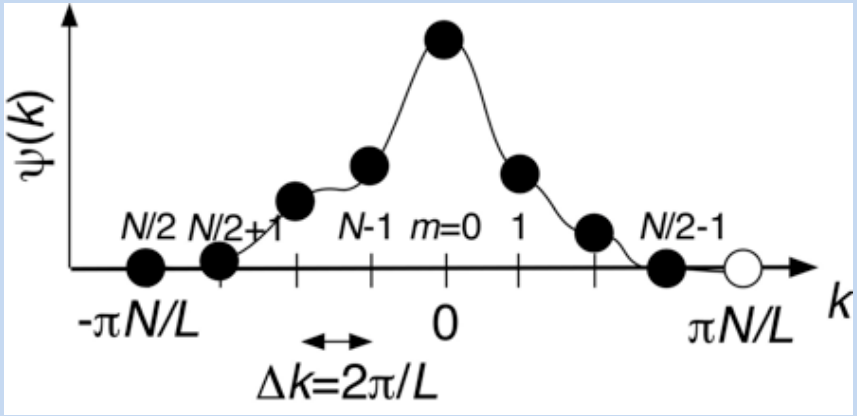
Representation: Plane-Wave Basis

- **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



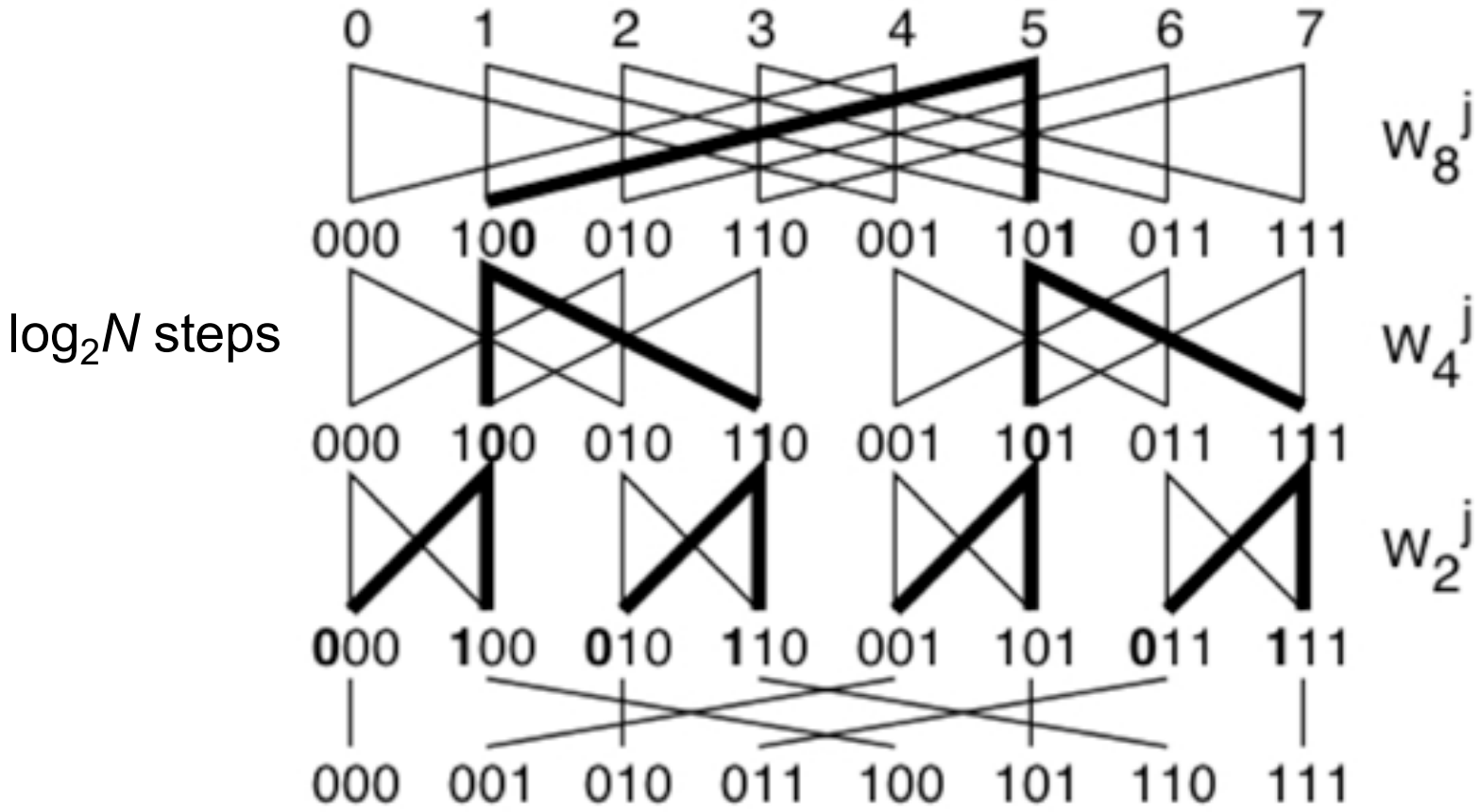


$$x_j = \frac{jL}{N};\ k_n = \frac{2\pi n}{L}$$

Numerics: Fast Fourier Transform

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

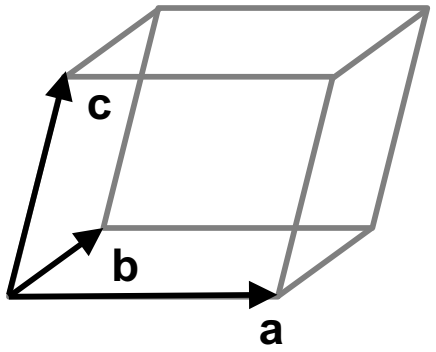
$$\psi(x_j) = \sum_{k_n} \psi_{k_n} \exp(i k_n x_j)$$



Butterfly (hypercube) data-exchange network

Periodic Solid

- **Consider a periodic solid with the unit cell spanned by vectors a, b & c**



- **Fourier transform of a periodic function**

$$u(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{G}} \exp(i\mathbf{G} \bullet \mathbf{r})$$

$$\mathbf{G} = \frac{2\pi}{\mathbf{a} \bullet (\mathbf{b} \times \mathbf{c})} [l(\mathbf{b} \times \mathbf{c}), m(\mathbf{c} \times \mathbf{a}), n(\mathbf{a} \times \mathbf{b})] \quad (l, m, n \in \mathbb{Z})$$

- **Bloch's theorem**

band index

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \bullet \mathbf{r})\, u_{n,\mathbf{k}}(\mathbf{r})$$

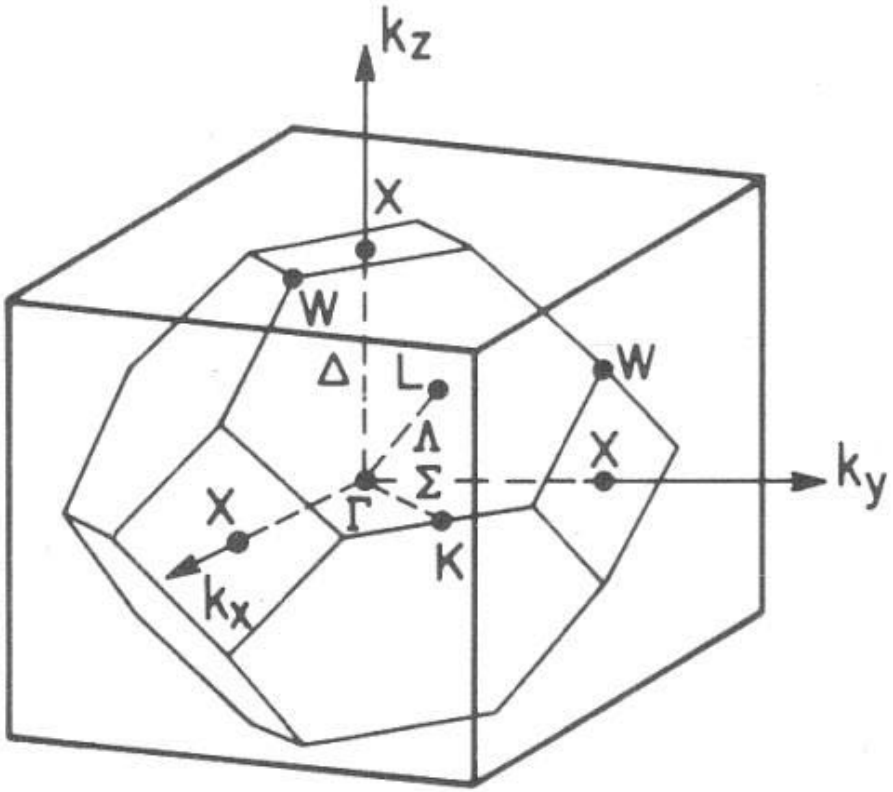
$$= \sum_{\mathbf{G}} u_{n,\mathbf{k}}(\mathbf{G}) \exp(i(\mathbf{k} + \mathbf{G}) \bullet \mathbf{r})$$

$\mathbf{k} \in$ first Brillouin zone in the reciprocal space

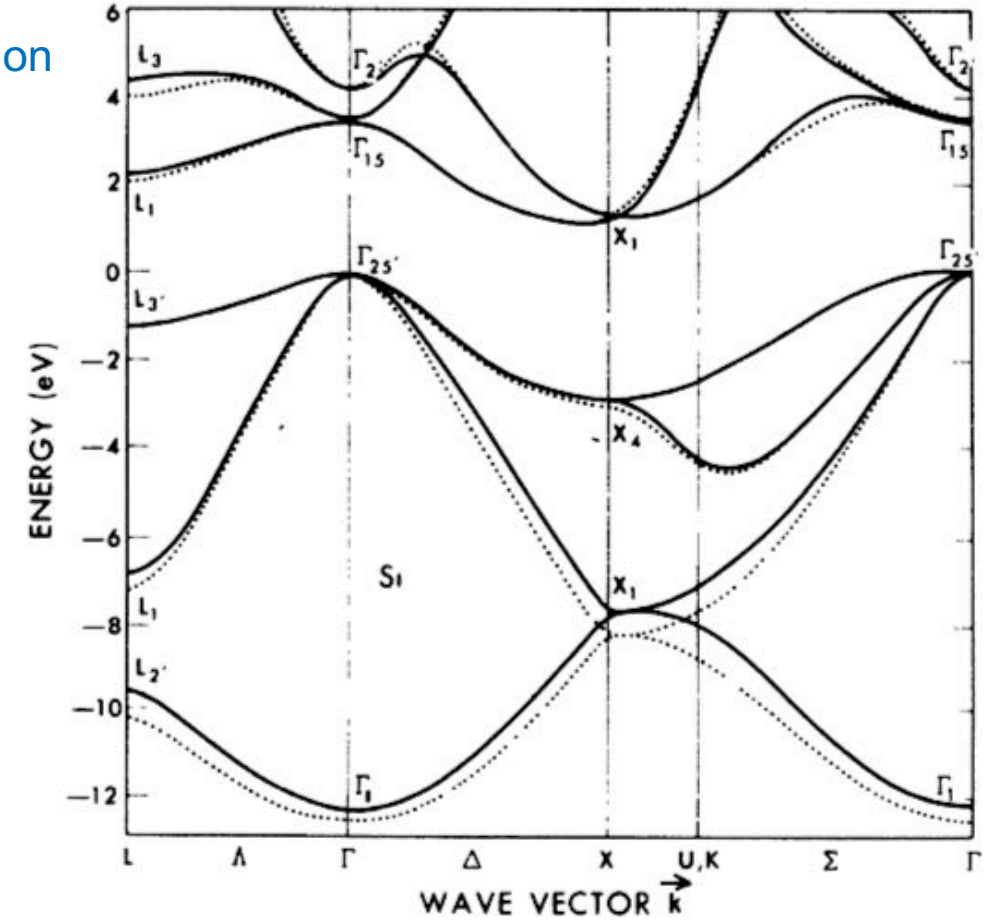
Electronic Bands: Infinite Lattice

- **Bloch theorem:** $\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \bullet \mathbf{r}) u_{n,\mathbf{k}}(\mathbf{r})$

band index periodic function



Brillouin zone of Si crystal



Kohn-Sham energy

J. R. Chelikowsky & M. L. Cohen, *Phys. Rev. B* 10, 5095 ('74)

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

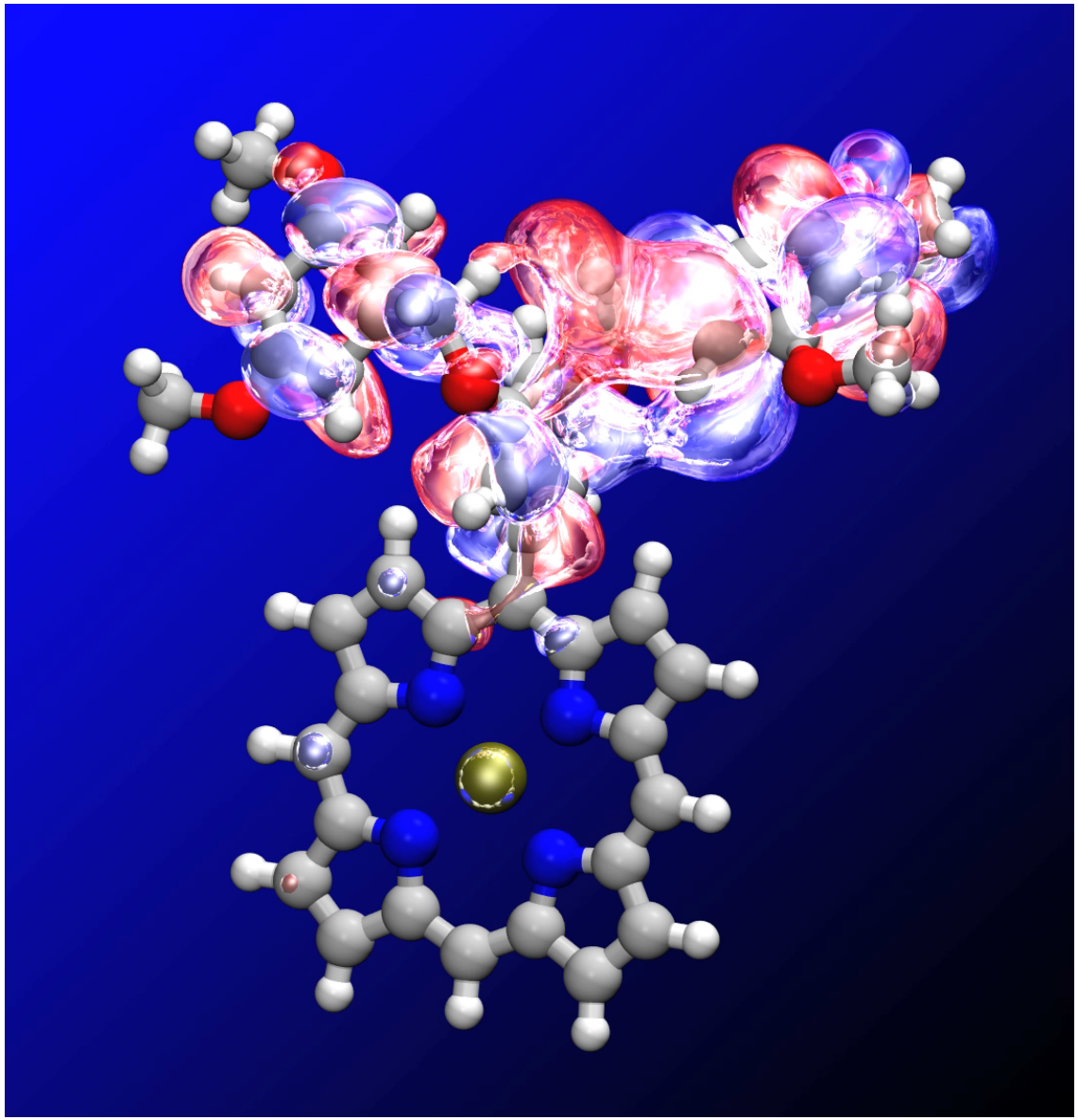
Given $\{\psi_n, \epsilon_n\}$, determine μ and compute $\rho(\mathbf{r})$

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

Chemical potential

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

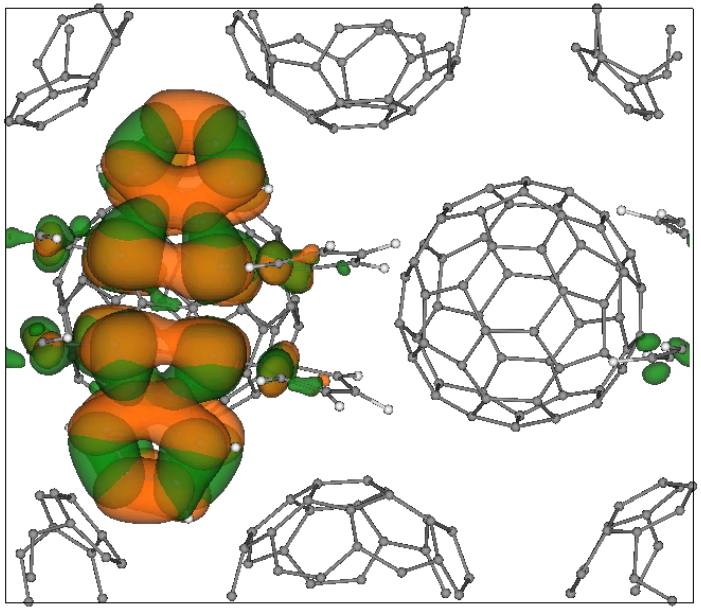
Nonadiabatic Quantum Molecular Dynamics



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}



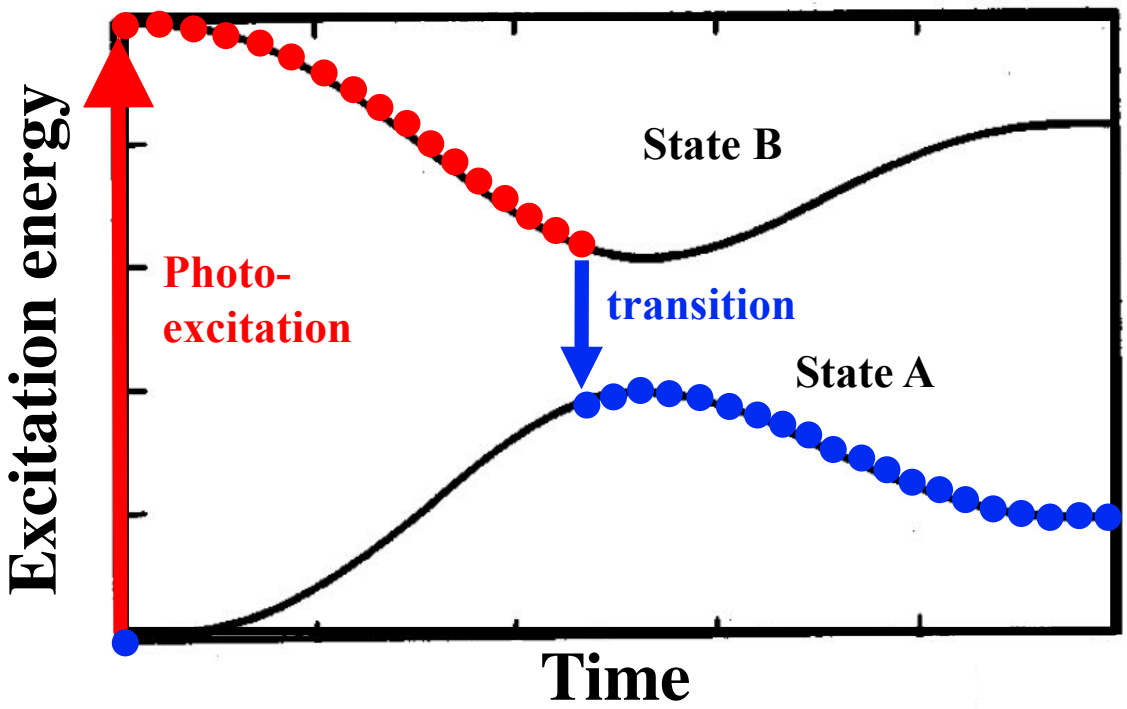
quasi-electron; quasi-hole

- **Excited states: Linear-response time-dependent density functional theory** [Casida, '95]
- **Interstate transitions: Surface hopping** [Tully, '90; Jaeger, Fisher & Prezhdo, '12]

TDDFT & Surface Hopping

- **Incorporate electron transitions with the time-dependent density-functional theory (TDDFT) & surface-hopping method**

  Tully, *J. Chem. Phys*. **93**, 1061 ('90); Craig *et al*., *Phys. Rev. Lett*. **95**, 163001 ('05)



- **Electronic transitions from the current state to another occur stochastically based on the switching probability obtained by solving TDDFT equations**

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

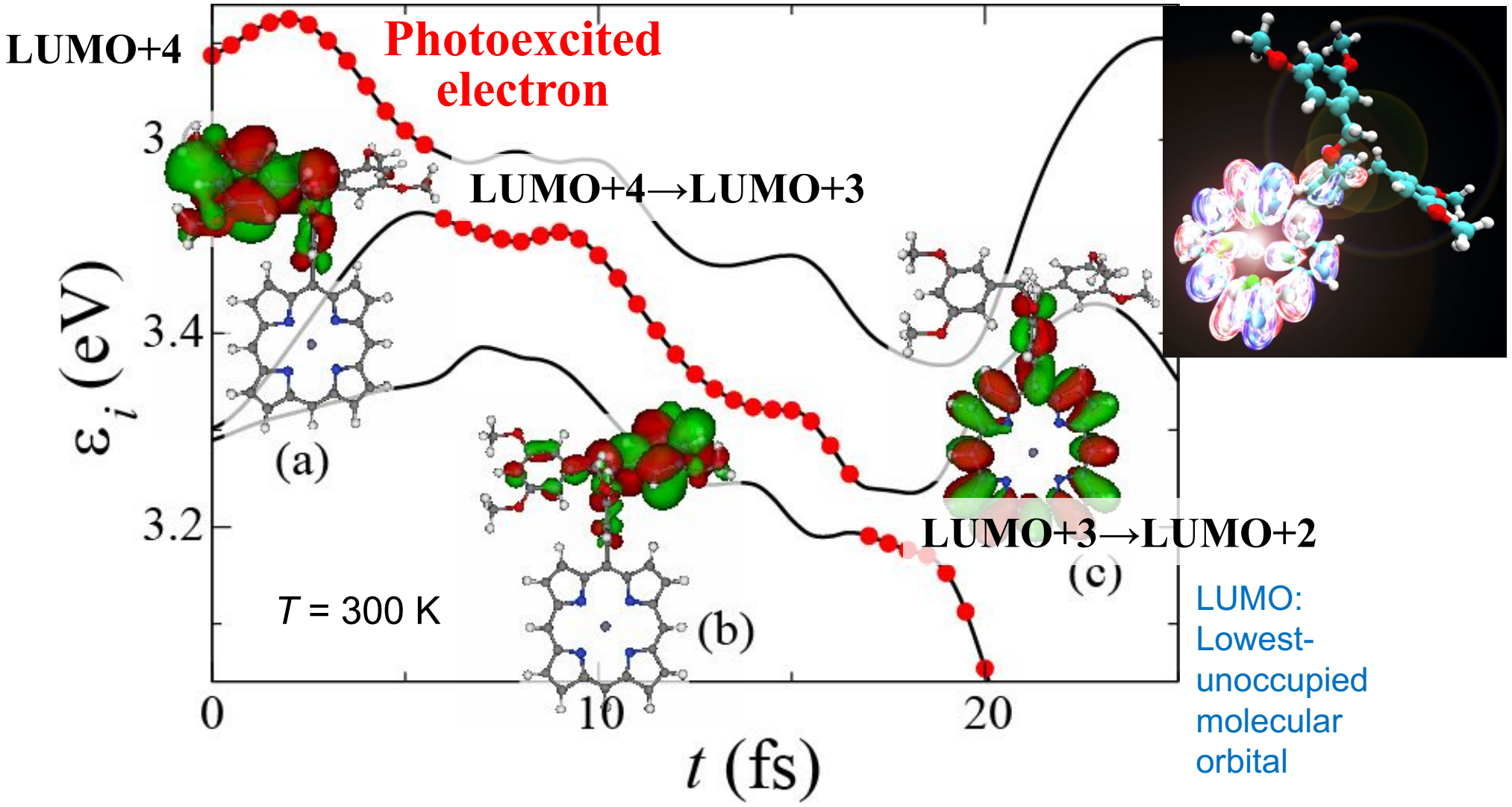
$$\frac{d}{dt}C_J^{(I)}(t) = -\sum_k C_k^{(I)}(t)\left(i\omega_K\delta_{JK} + \left\langle \Phi_J \middle| \frac{\partial}{\partial t} \middle| \Phi_K \right\rangle\right)$$

J-th adiabatic excited state

K-th excitation frequency

Nonadiabatic coupling

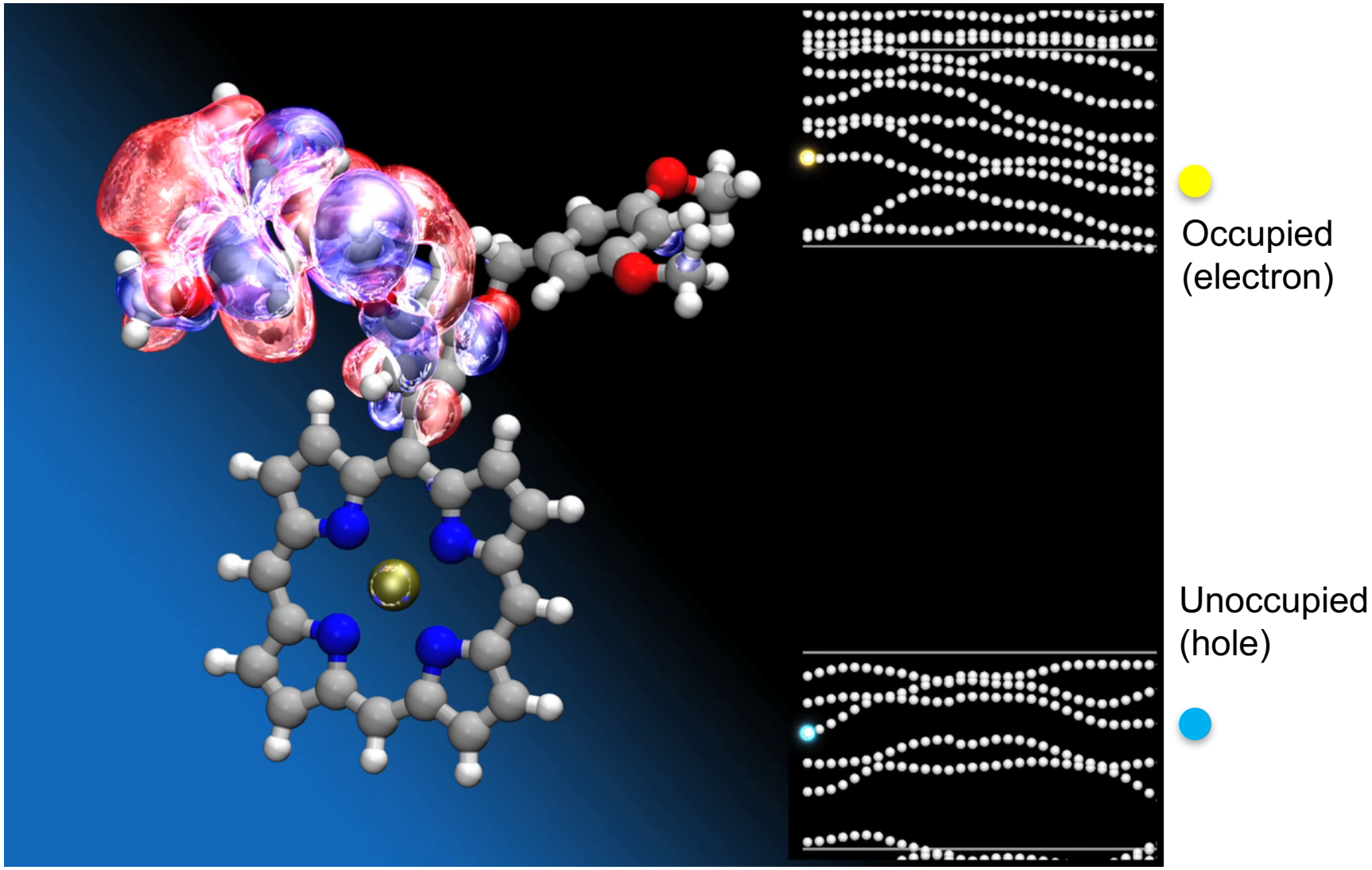
Example: Electron Transfer in a Dendrimer



LUMO: Lowest-unoccupied molecular orbital

- **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**

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)** [Casida, '95]

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

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

electron, hole

- **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

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

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

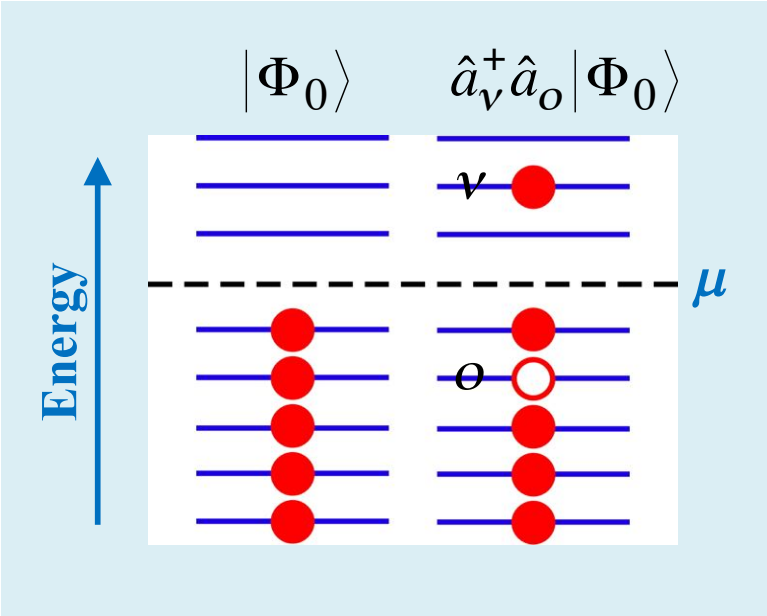
Coulomb & exchange-correlation interaction matrix elements

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)
  - > **Berry-phase computation of bulk polarization**
- **Other features:**
  - > **Various functionals: spin-polarized, GGA+U, DFT+D, nonlocal correlation**
  - > **Nudged elastic band (NEB) method for energy-barrier calculation**

GitHub repository:
https://github.com/USCCACS/QXMD_Course

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

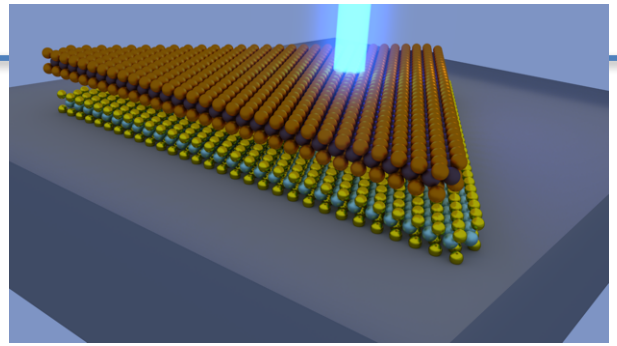
- **NAQMD & RMD simulations on full 800K cores**

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

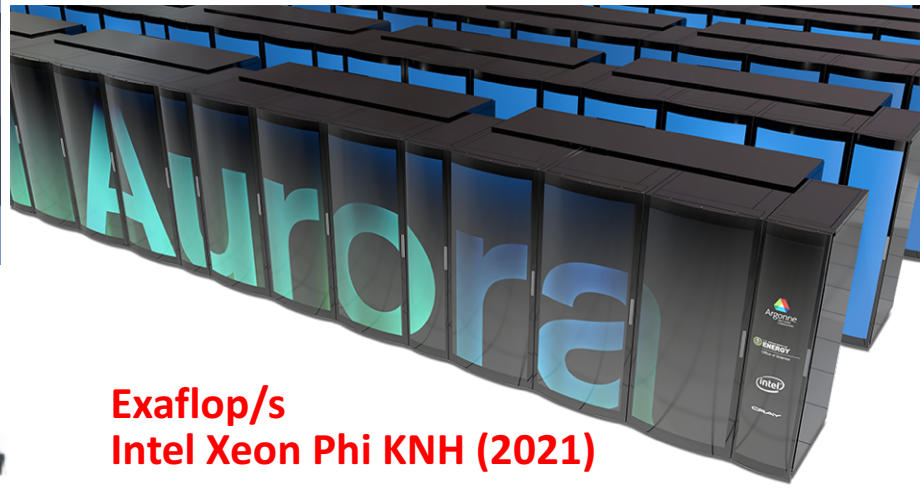


AURORA | EARLY SCIENCE PROGRAM

Early Science Projects for Aurora Supercomputer Announced

Metascalable layered materials genome

Investigator: Aiichiro Nakano, University of Southern California



Exaflop/s
Intel Xeon Phi KNH (2021)

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

But...

TOP 500 The List.

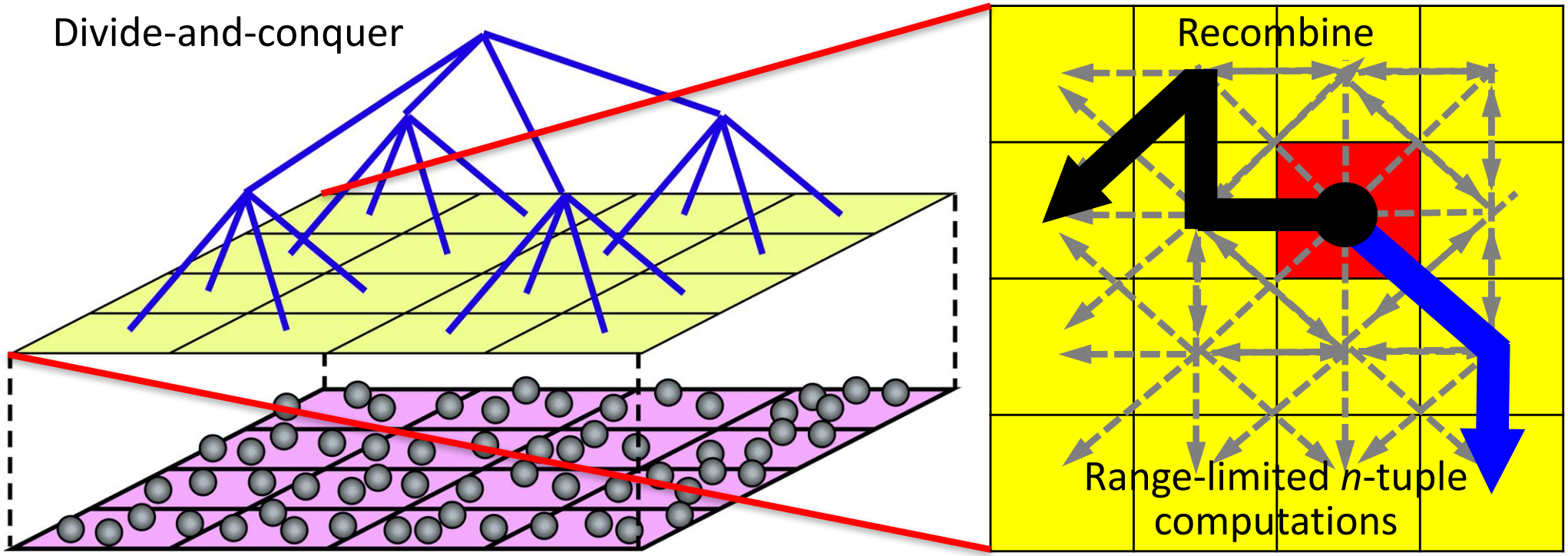
Intel Dumps Knights Hill, Future of Xeon Phi Product Line Uncertain

Michael Feldman | November 15, 2017 04:34 CET

https://www.top500.org/news/

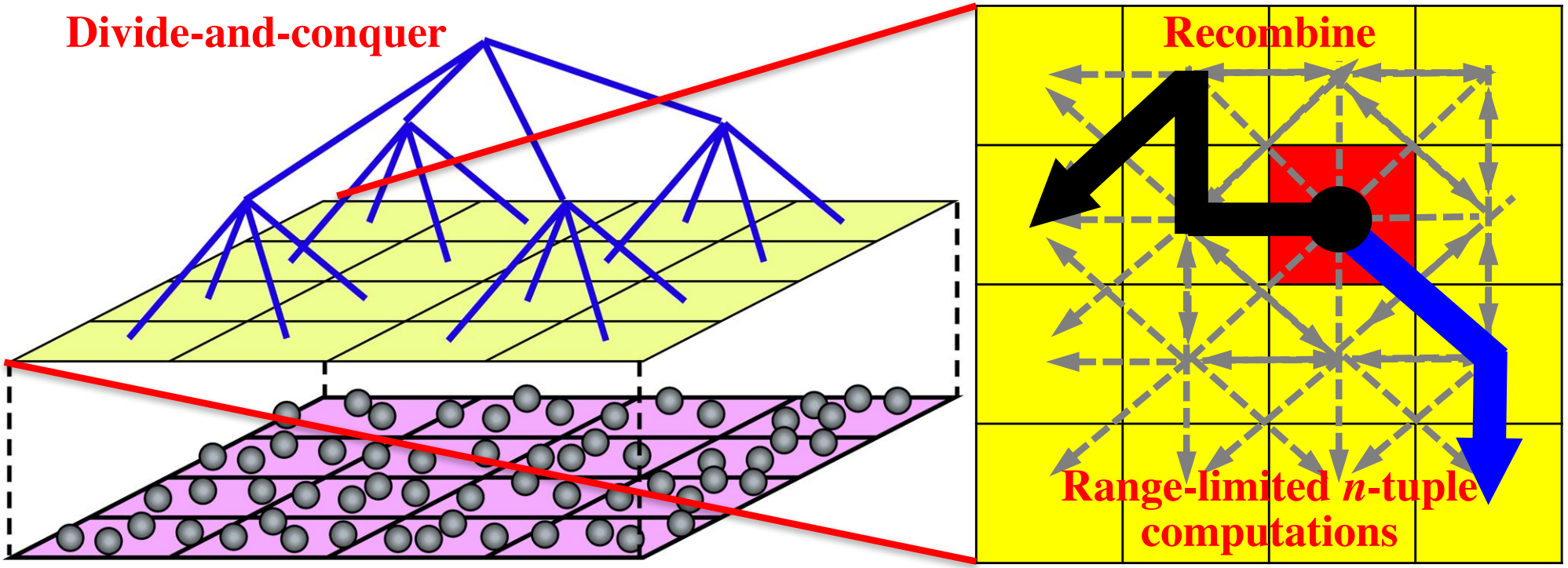
- **Need *metascalable* (or "design once, scale on new architectures") parallel applications**
- **Proposed *divide-conquer-recombine***

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



M. Kunaseth *et al.*, *ACM/IEEE SC13* ('13)

Divide-Conquer-Recombine (DCR) Engines



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

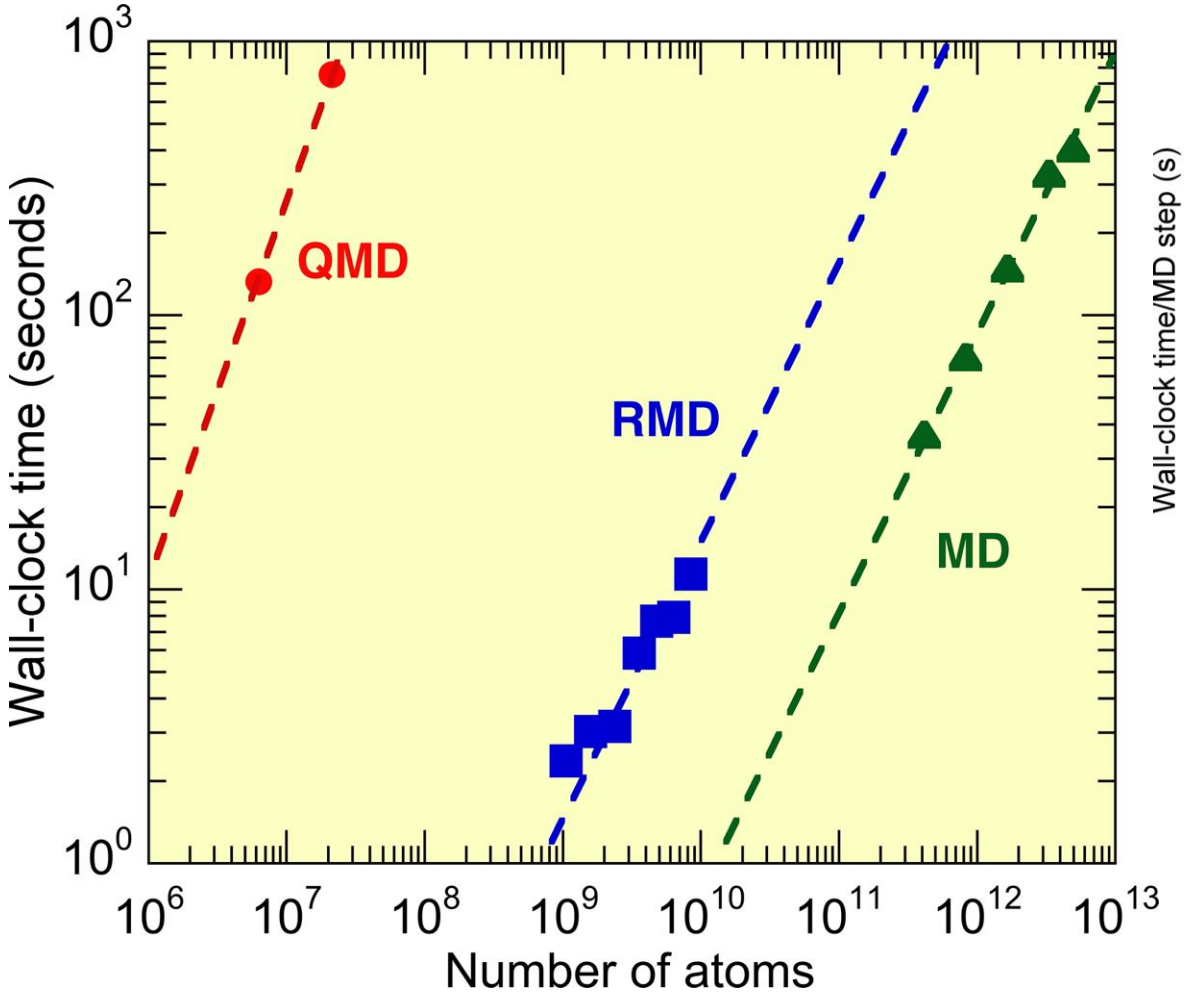
- **Quantum MD: Lean divide-&-conquer density functional theory (LDC-DFT) algorithm minimizes the prefactor of $O(N)$ computational cost**

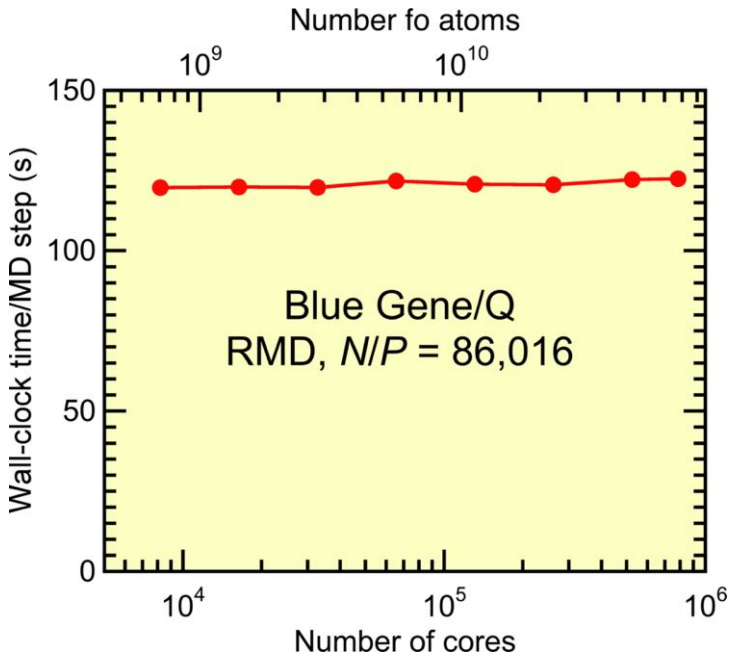
  F. Shimojo *et al.*, *J. Chem. Phys.* **140**, 18A529 ('14); K. Nomura *et al.*, *IEEE/ACM SC14*

- **Reactive MD: 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

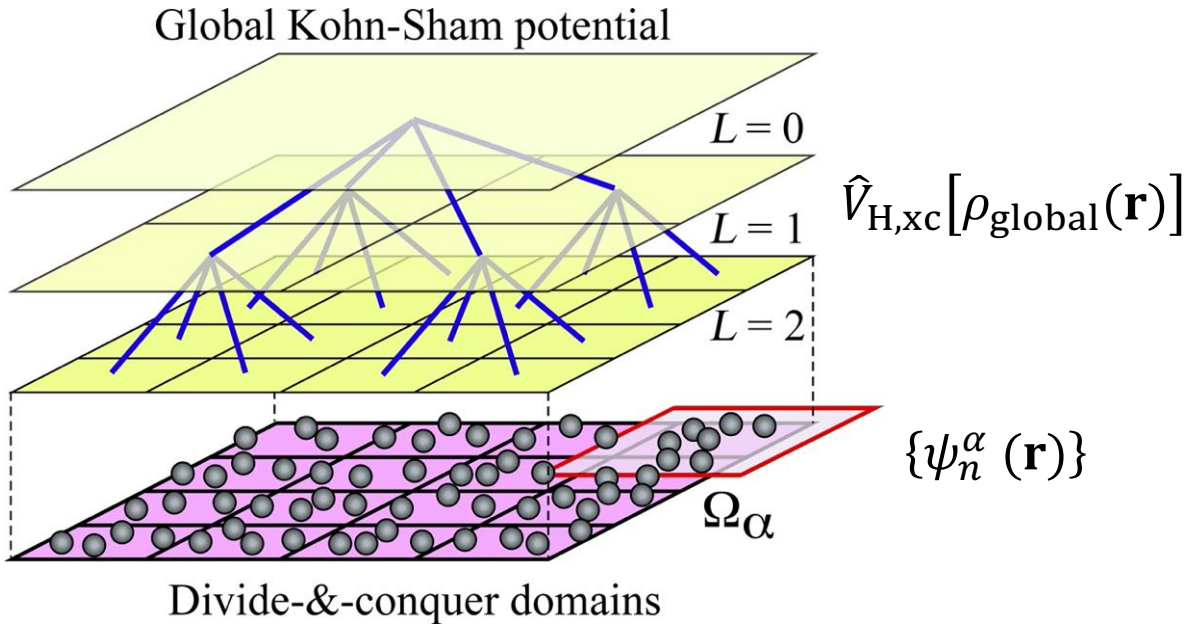
RMD (reactive molecular dynamics): F-ReaxFF

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

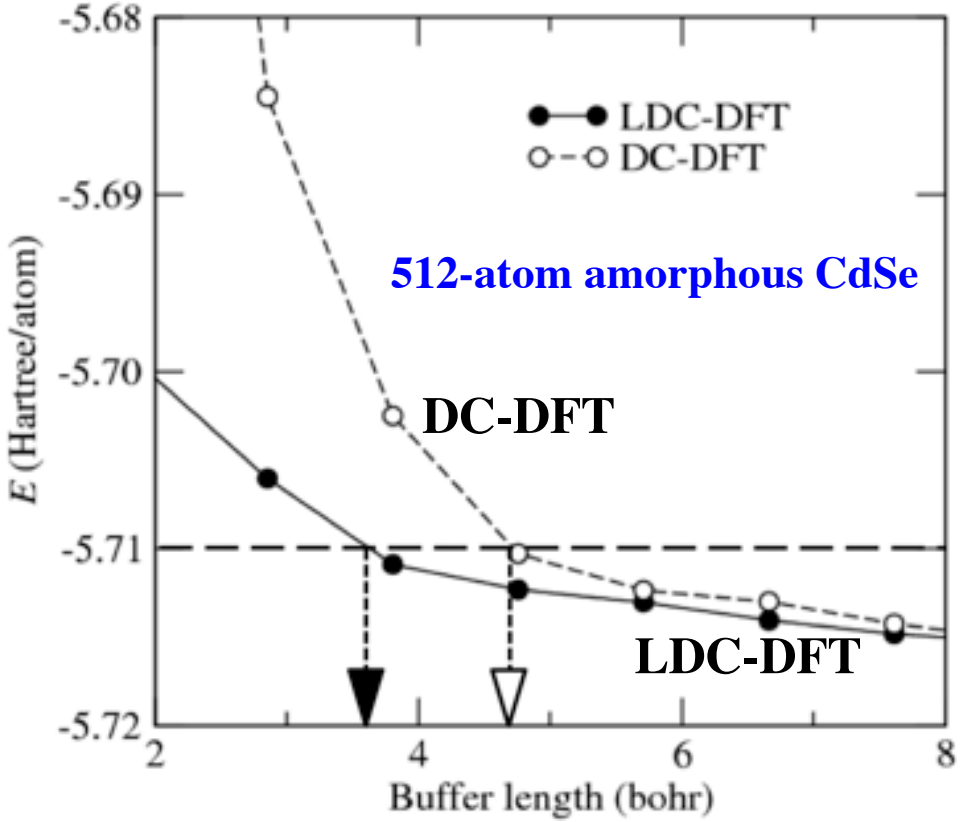
$$N = \int d\mathbf{r}\, \rho_{\mathrm{global}}(\mathbf{r})$$

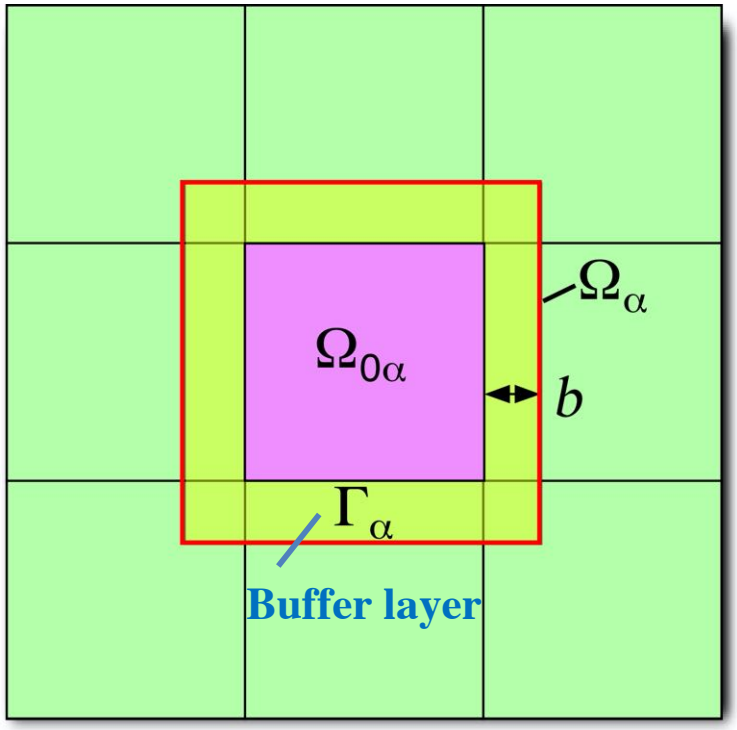
Lean Divide-&-Conquer (LDC) DFT

- **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**



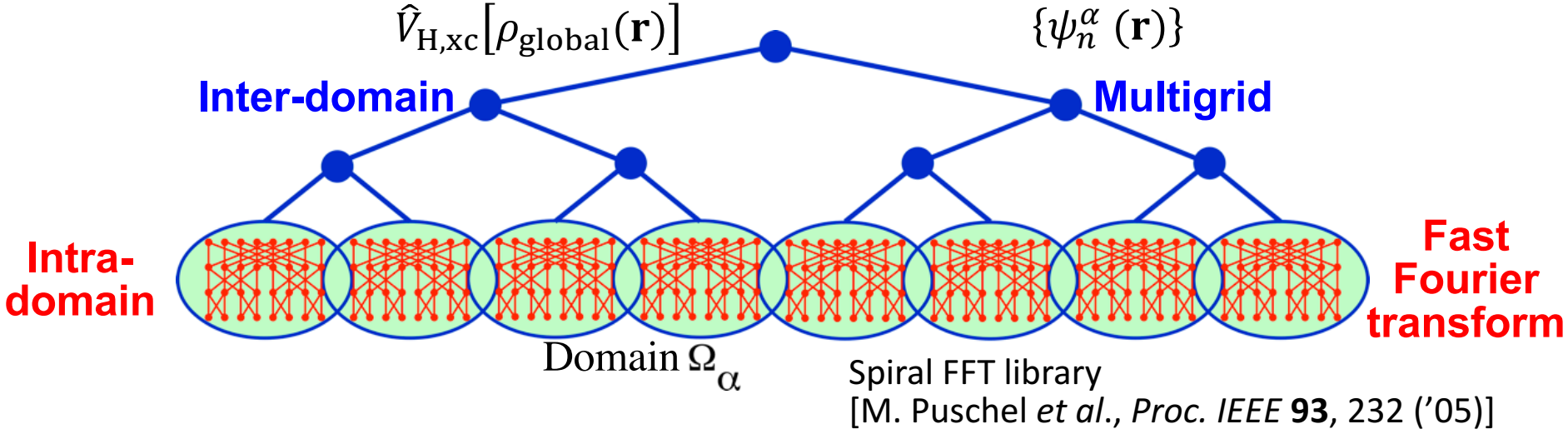


- **Factor 2.03 (for ν = 2) ~ 2.89 (for ν = 3) reduction of the computational cost with an error tolerance of 5×10^{-3} a.u. (per-domain complexity: n^ν)**

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

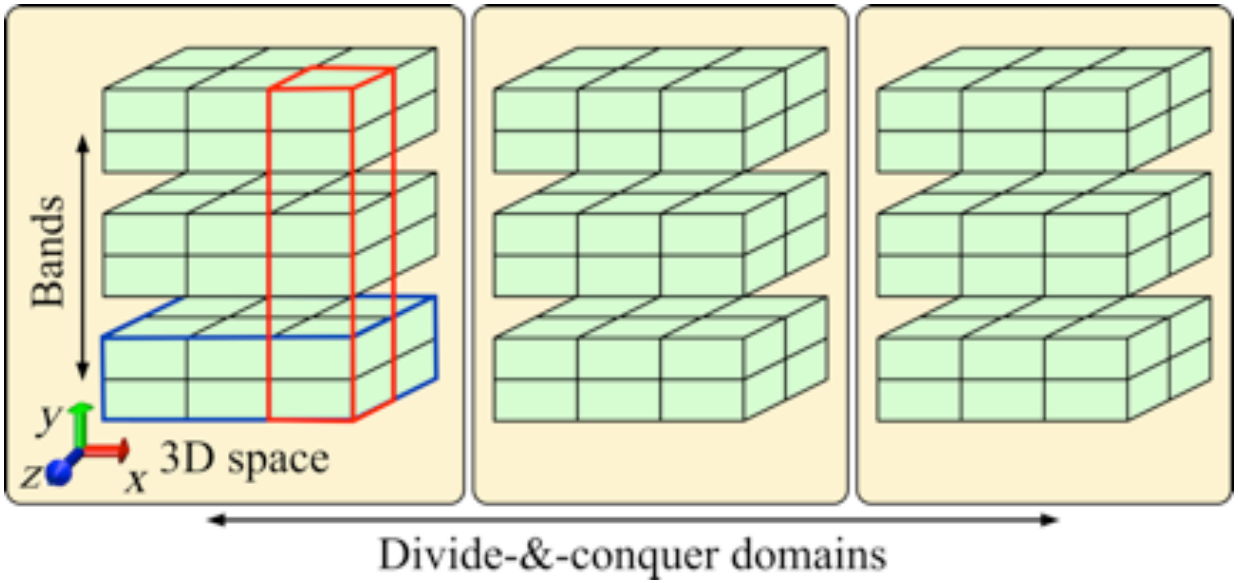
Hierarchical Computing

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



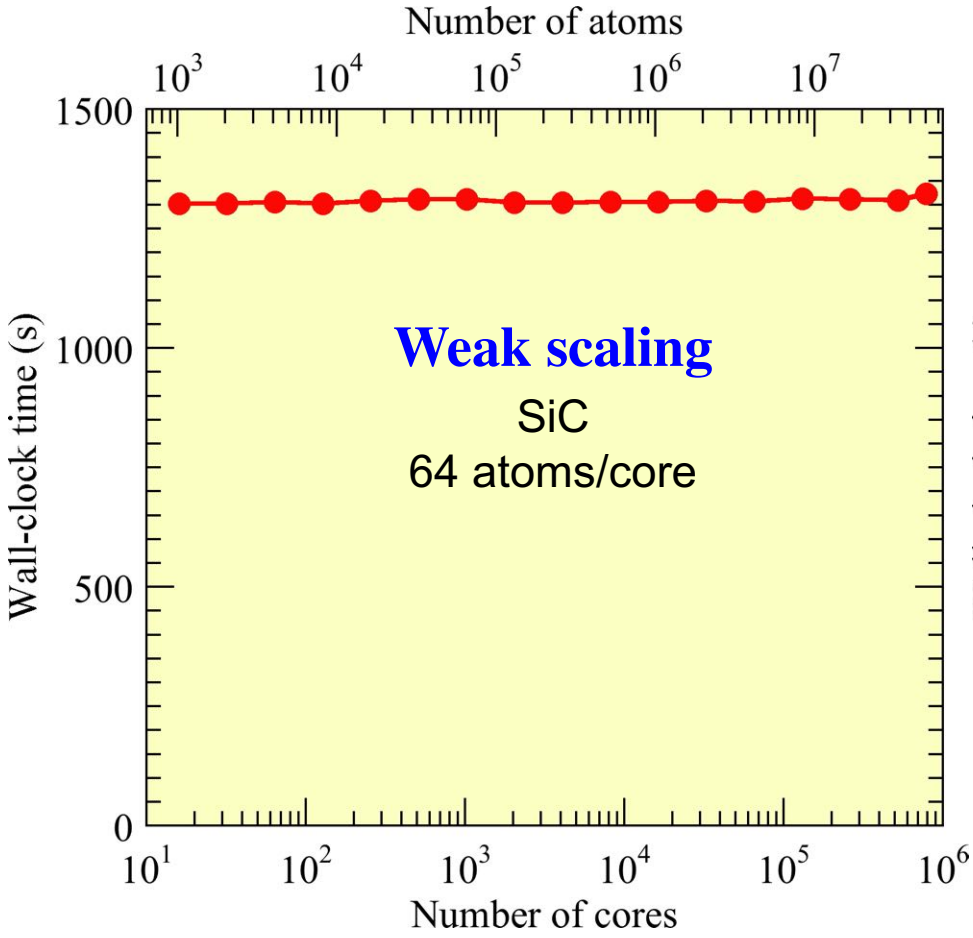
Spiral FFT library
[M. Puschel *et al.*, *Proc. IEEE* **93**, 232 ('05)]

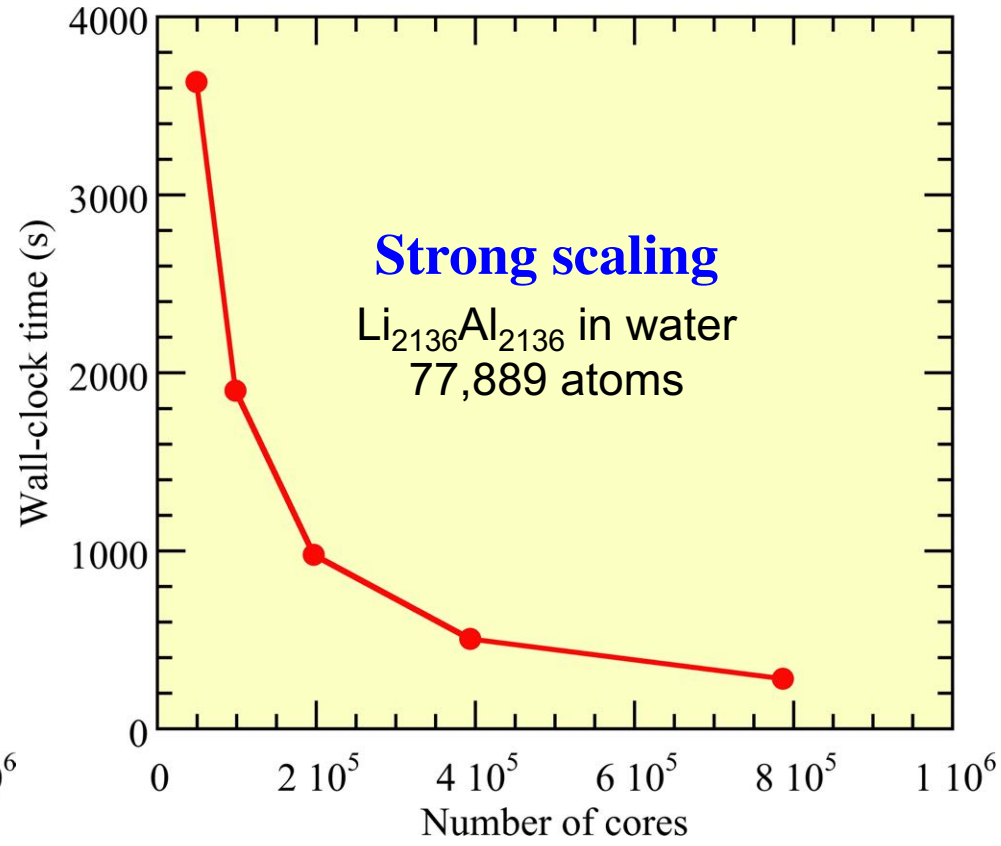
- **Hierarchical band (*i.e.* Kohn-Sham orbital) + space + domain (BSD) decomposition**



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)

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)

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

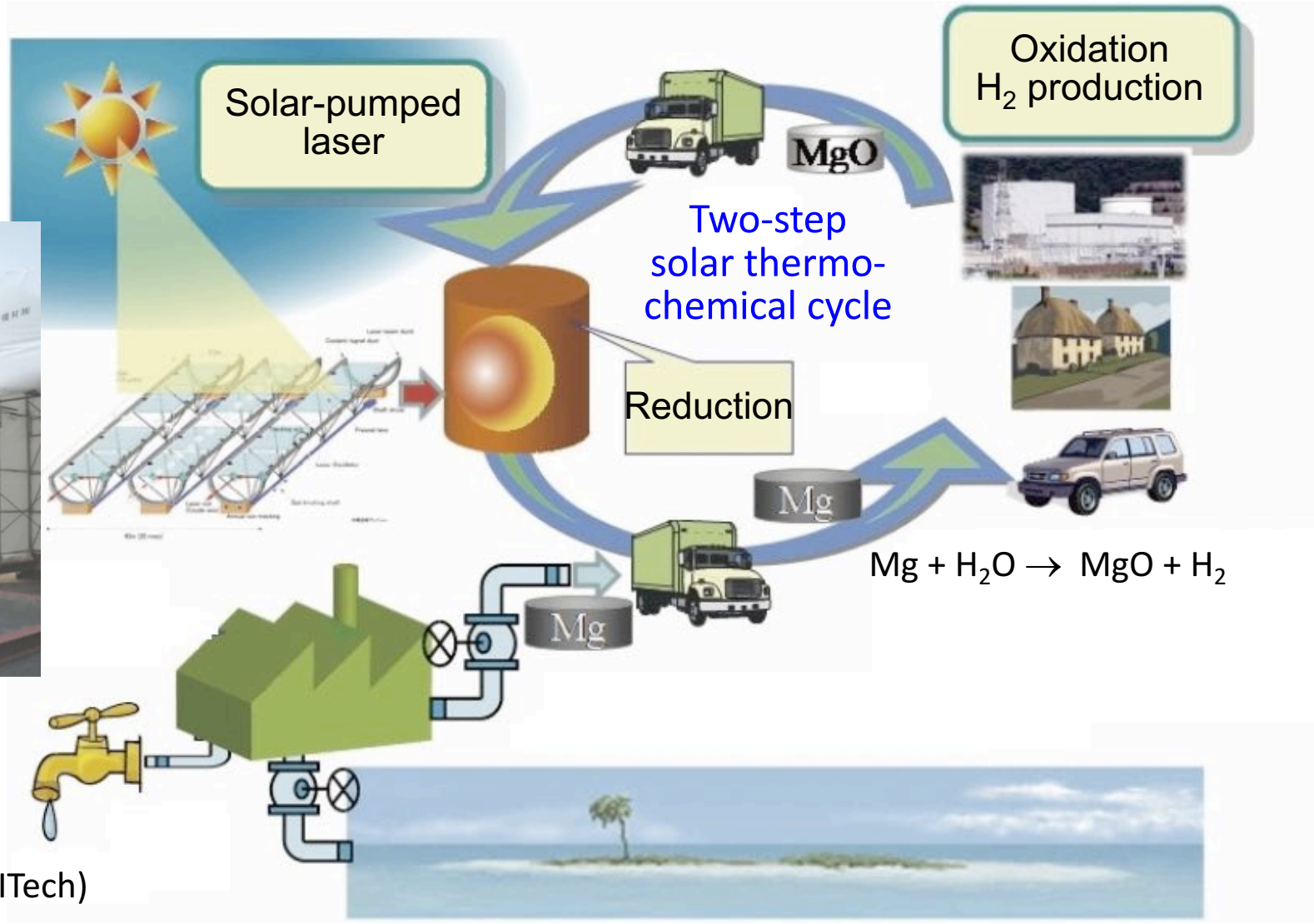
$$\boldsymbol{\Psi} = \left[|\psi_1^\alpha\rangle, \ldots, |\psi_{N_{\mathrm{band}}}^\alpha\rangle\right] \widetilde{\mathbf{B}}(i) = \left[|\beta_{i,1}\rangle, \ldots, |\beta_{i,N_{\mathrm{atom}}}\rangle\right] \left[\widetilde{\mathbf{D}}(i,j)\right]_{I,J} = D_{ij,I}\delta_{IJ}$$

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

- **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)

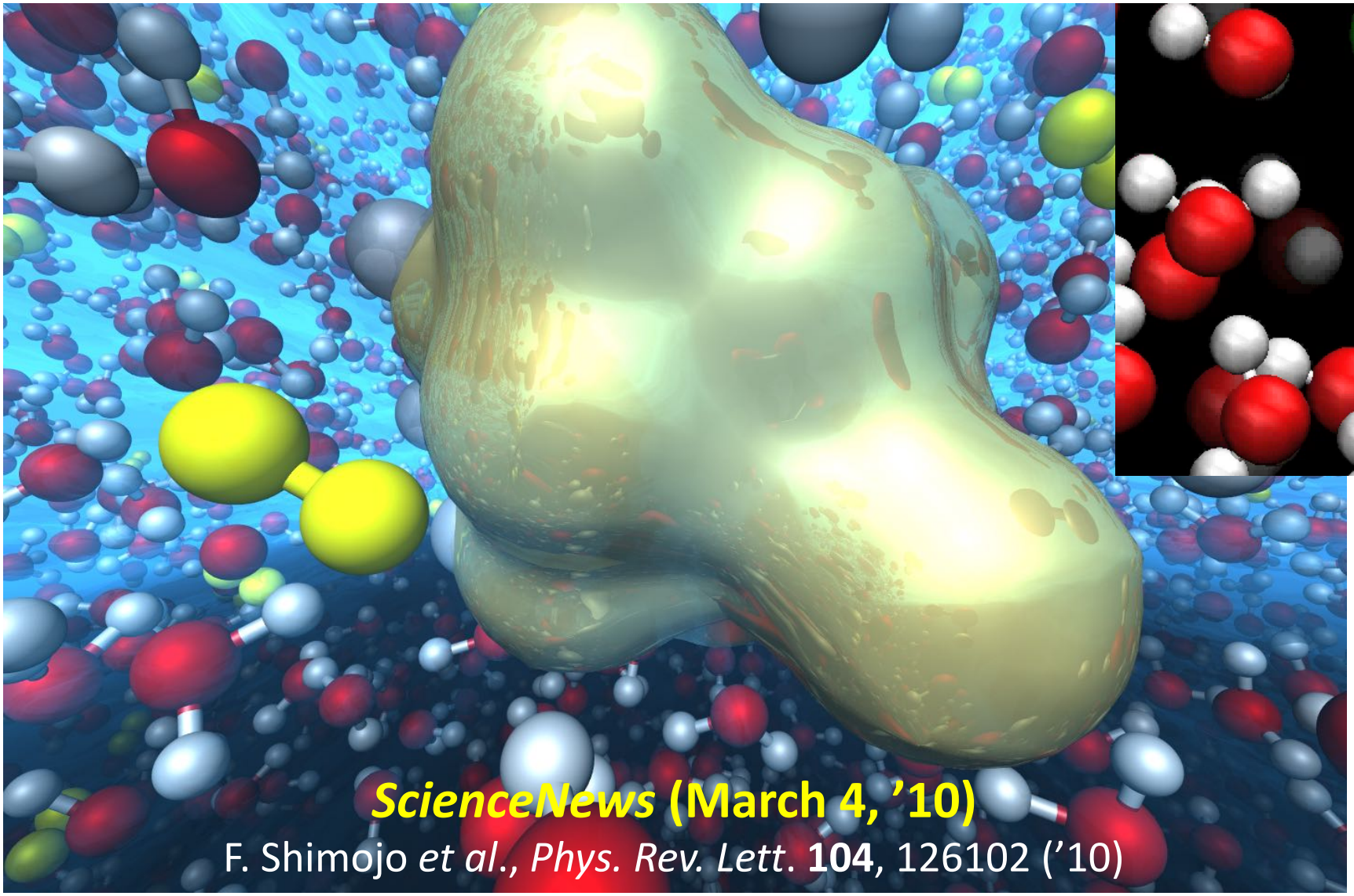
Renewal Energy Cycle by Metal Carriers



T. Yabe (TITech)

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

Nanotechnology Solution



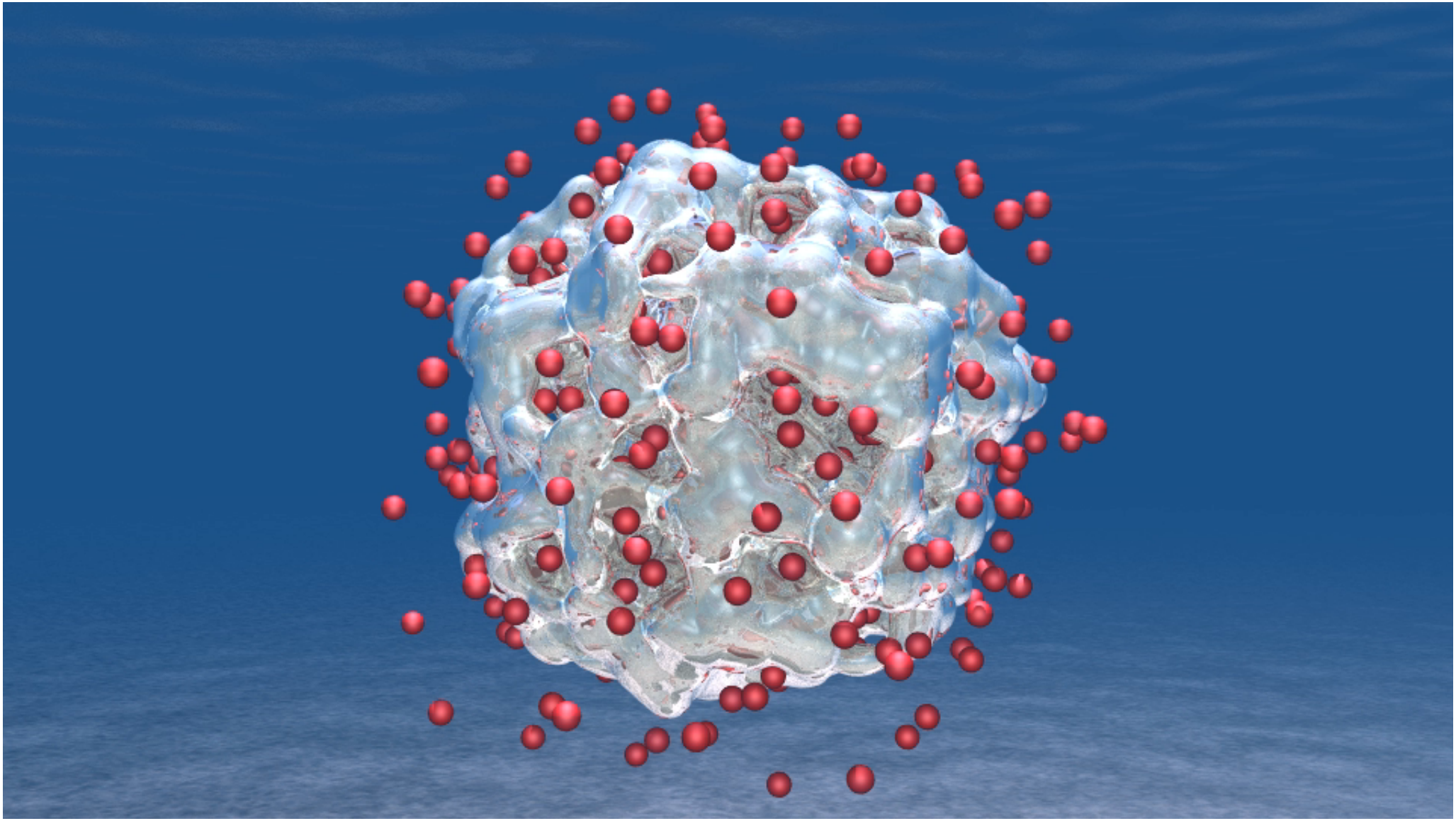
- **QMD simulation shows rapid H_2 production from water by a superatom* (Al_{17}), but the technology is not scalable to larger particle sizes**

*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

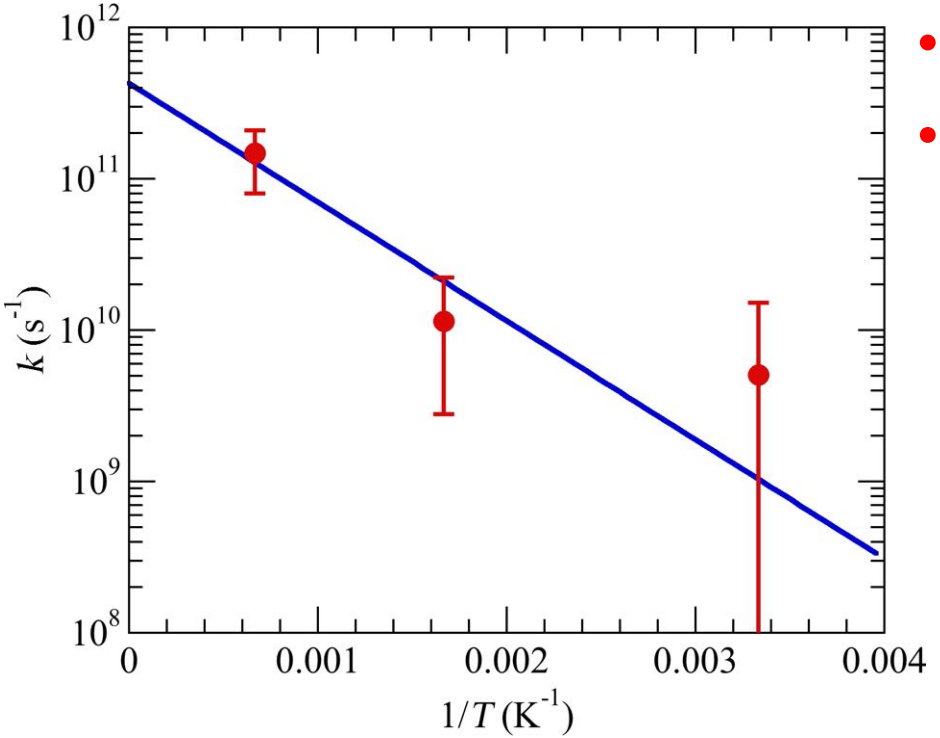
K. Shimamura *et al.*, *Nano Lett*. **14**, 4090 ('14)



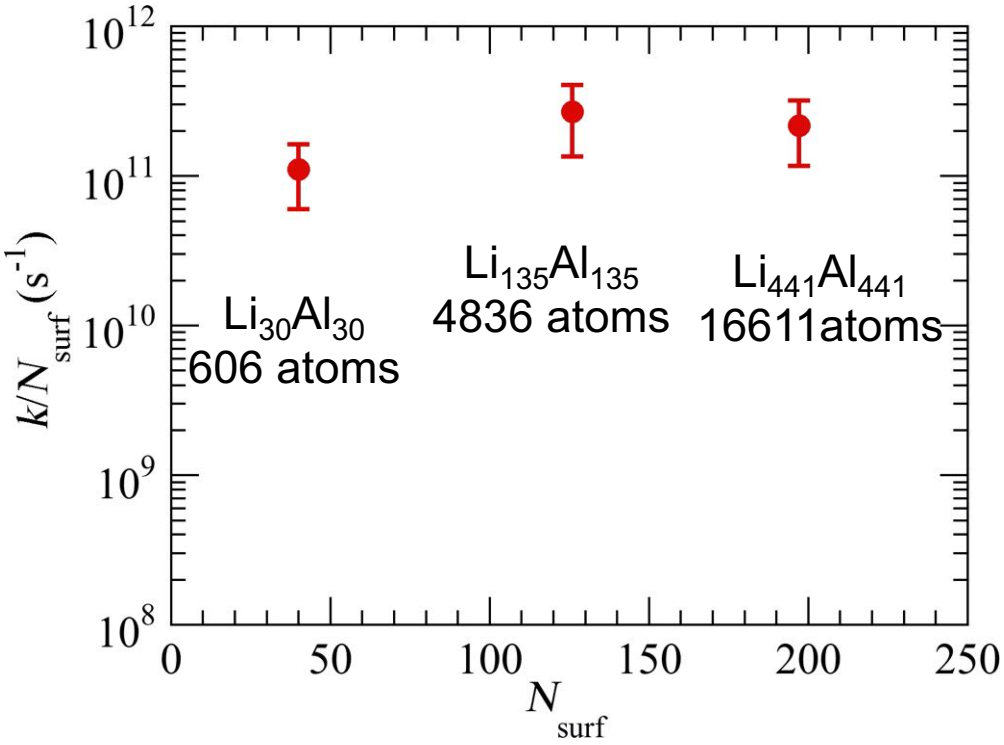
21,140 time steps (129,208 self-consistent-field iterations)

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**

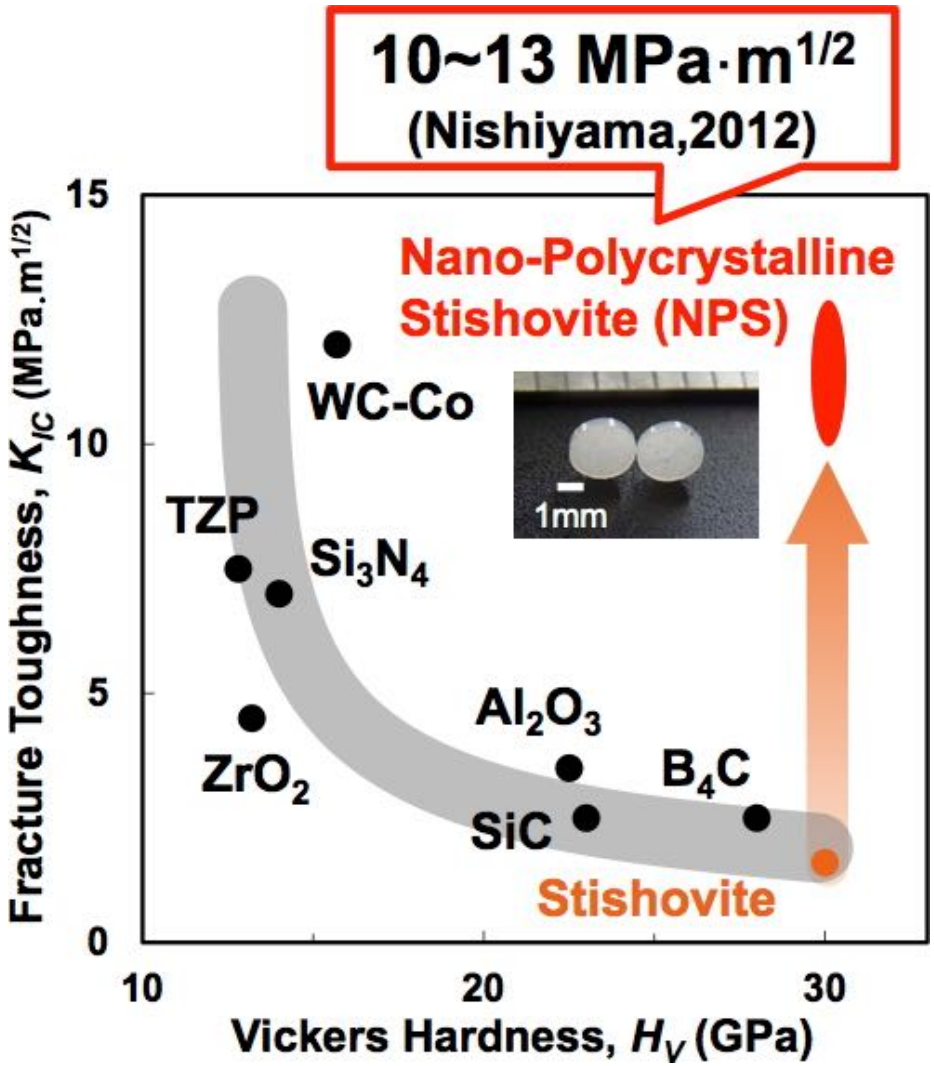


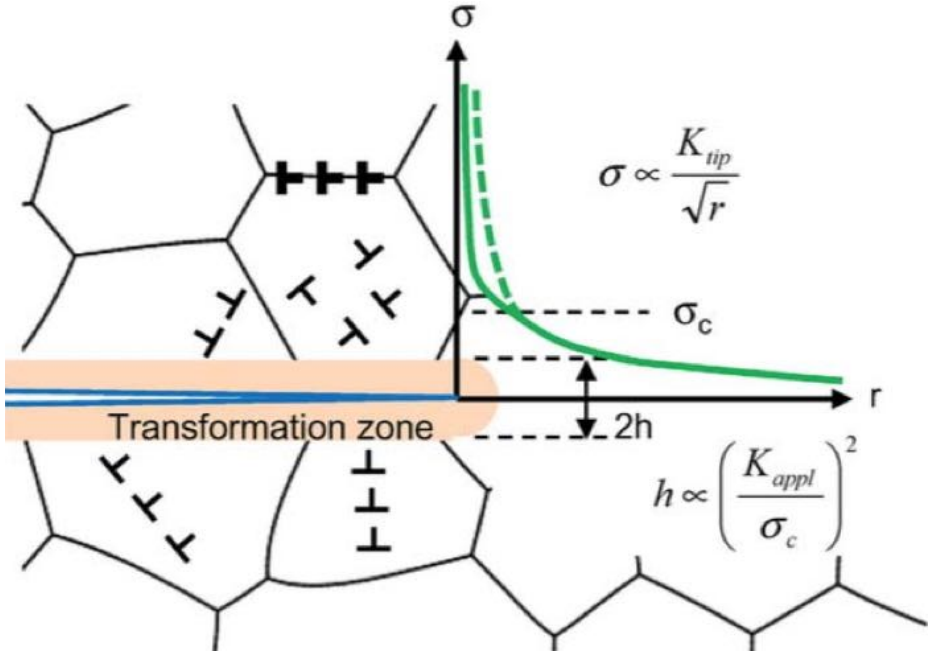
- **Reaction rate does not decrease for larger particles → industrial scalability**

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

Crack Self-Healing Stishovite

- **Superhard, ultratough nano-polycrystalline stishovite (NPS) synthesized**
  N. Nishiyama *et al.*, *Scripta Mater.* **67**, 955 ('12); *Sci. Rep*. **4**, 6588 ('14)
- **Made of Earth-abundant silica glass, NPS provides sustainable supply of high-performance ceramics**



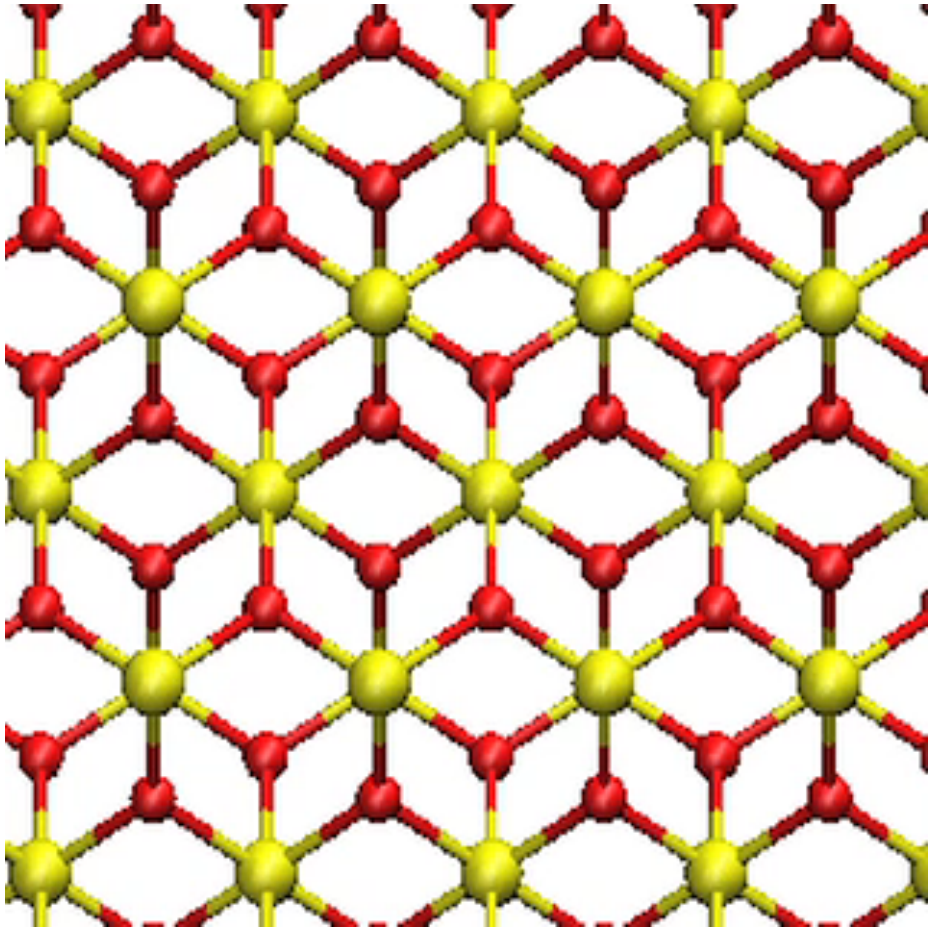


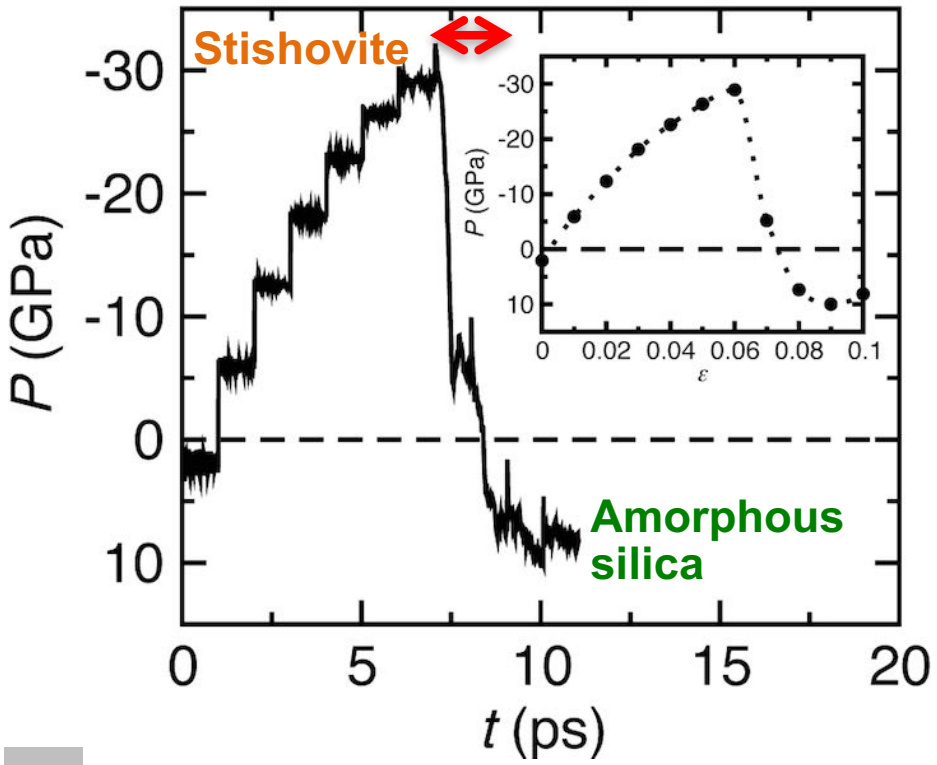
K. Yoshida *et al.*, *Sci. Rep*. **5**, 10993 ('15); *Acta Mater*. **124**, 316 ('17)

- **Toughening mechanism hypothesized to be amorphization under tension**
- **To catch up with a fast moving crack, amorphization needs rapid, but no theoretical nor experimental evidence**

Rapid Tensile Amorphization

- **QMD simulation reveals rapid amorphization of stishovite within picoseconds under tension ~ 30 GPa**





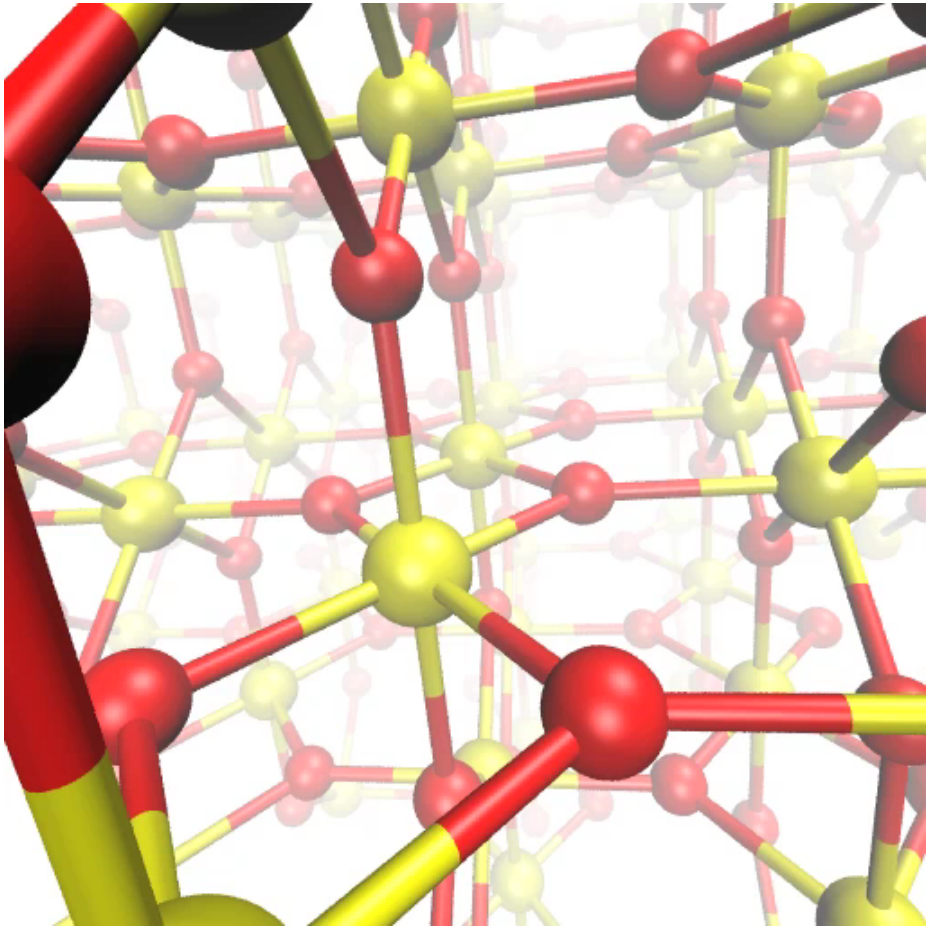
$Volume_{amorphous\ silica} \sim 2 \times Volume_{stishovite}$

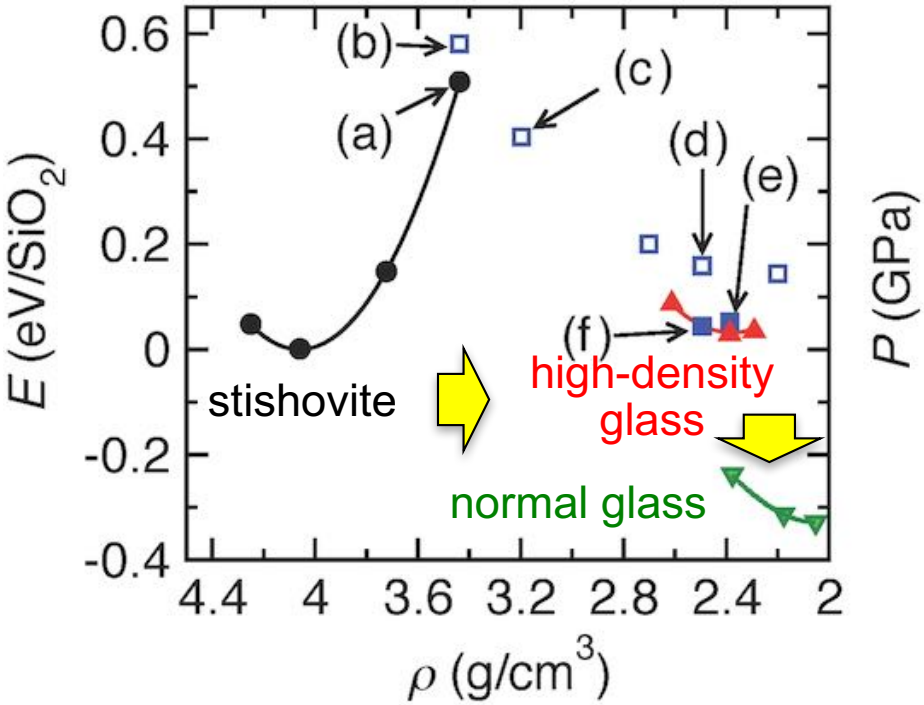
- **The rapid & expansive amorphization can catch up with, screen & self-heal a fast moving crack**

M. Misawa *et al.*, *Science Advances* **3**, e1602339 ('17)

Rapid Amorphization Mechanism

- **Found a displacive amorphization mechanism that only involves short-distance collective motions of atoms, thereby facilitating the rapid transformation**

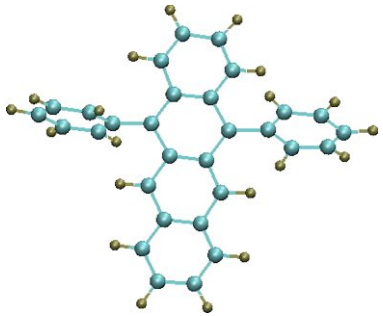




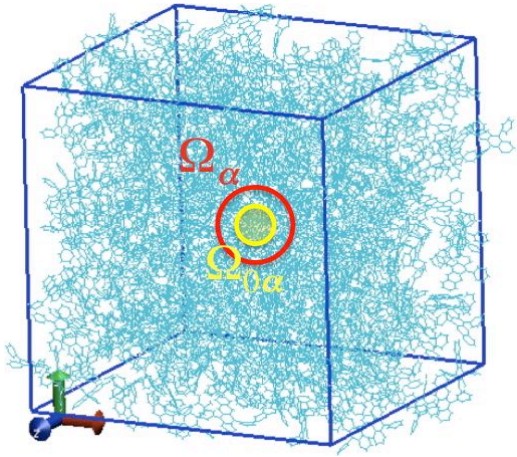
- **Two-step amorphization pathway from stishovite to glass involves an intermediate state akin to an experimentally suggested "high-density glass polymorph"**

Singlet Fission in Amorphous DPT

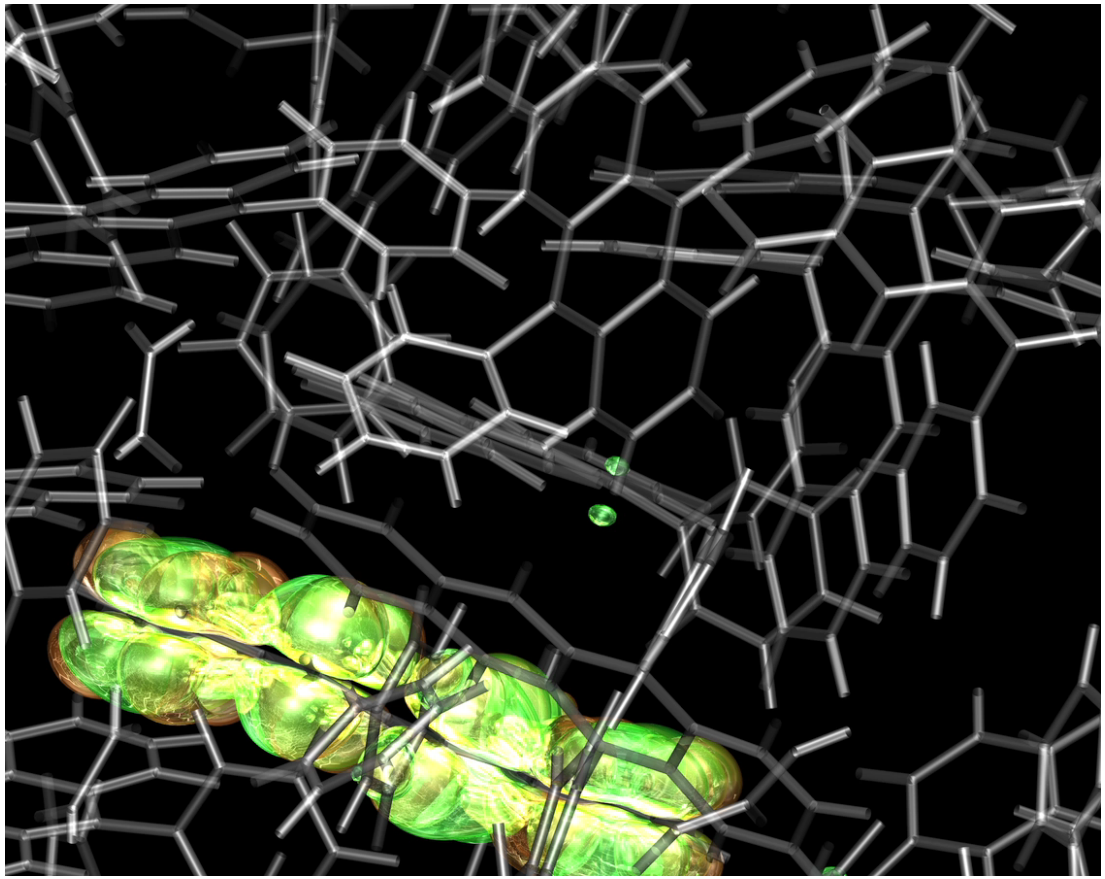
- Photo-current doubling by splitting a singlet exciton into 2 triplet excitons
- Singlet fission in mass-produced disordered organic solid → efficient low-cost solar cells
- Experimental breakthrough: SF found in amorphous diphenyl tetracene (DPT)



DPT molecule



Amorphous DPT



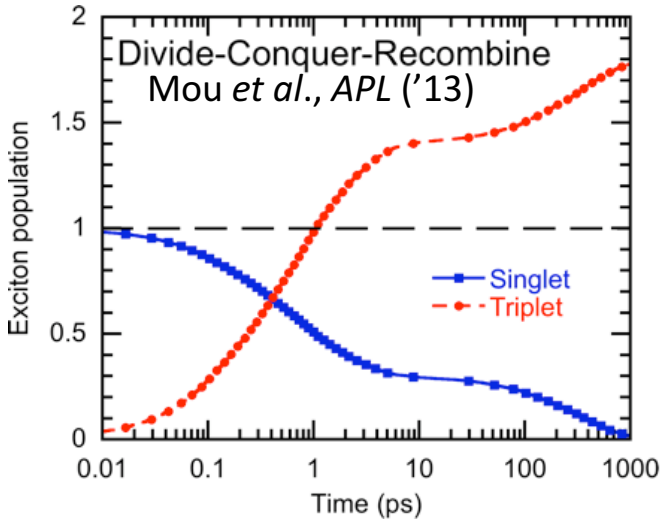
Quasi-electron

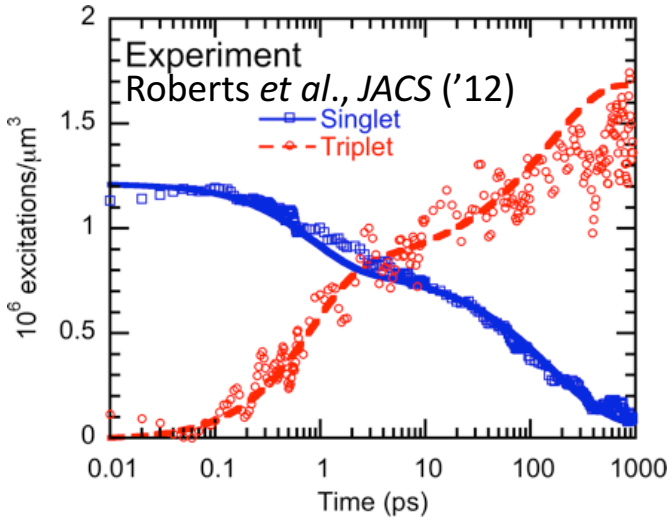
Quasi-hole

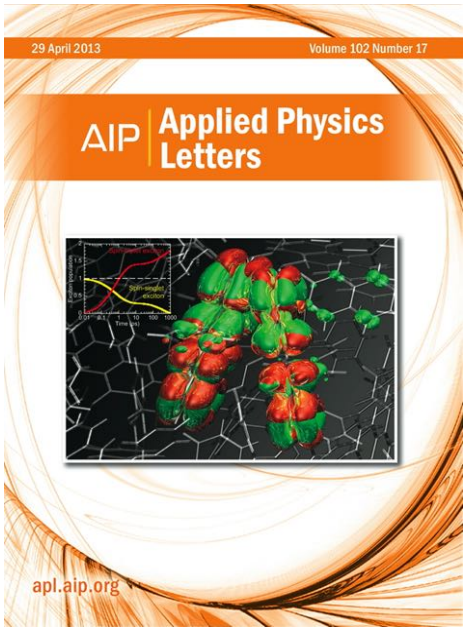
- Divide-conquer-recombine nonadiabatic QMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT

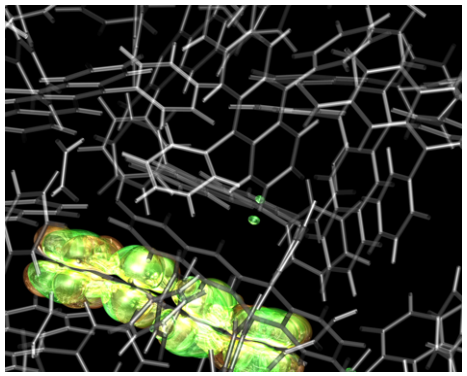
Singlet-Fission Hot Spot

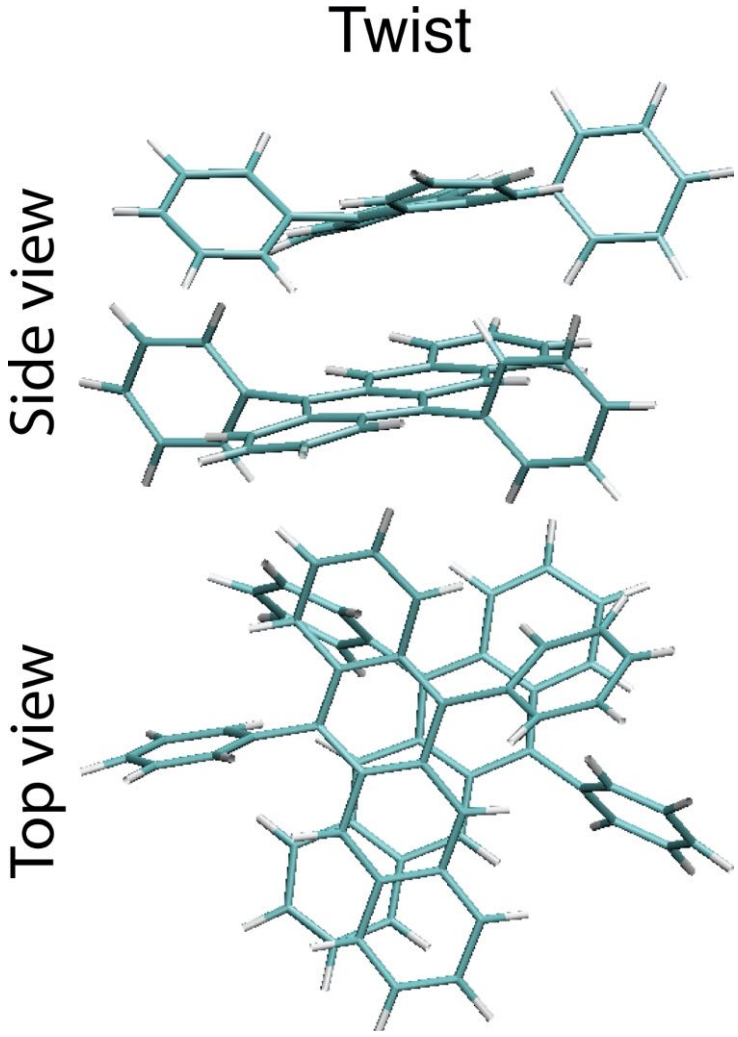
- **Nonadiabatic quantum molecular dynamics simulations not only reproduced experimentally measured exciton population dynamics but also revealed unknown molecular geometry of singlet fission hot spots**





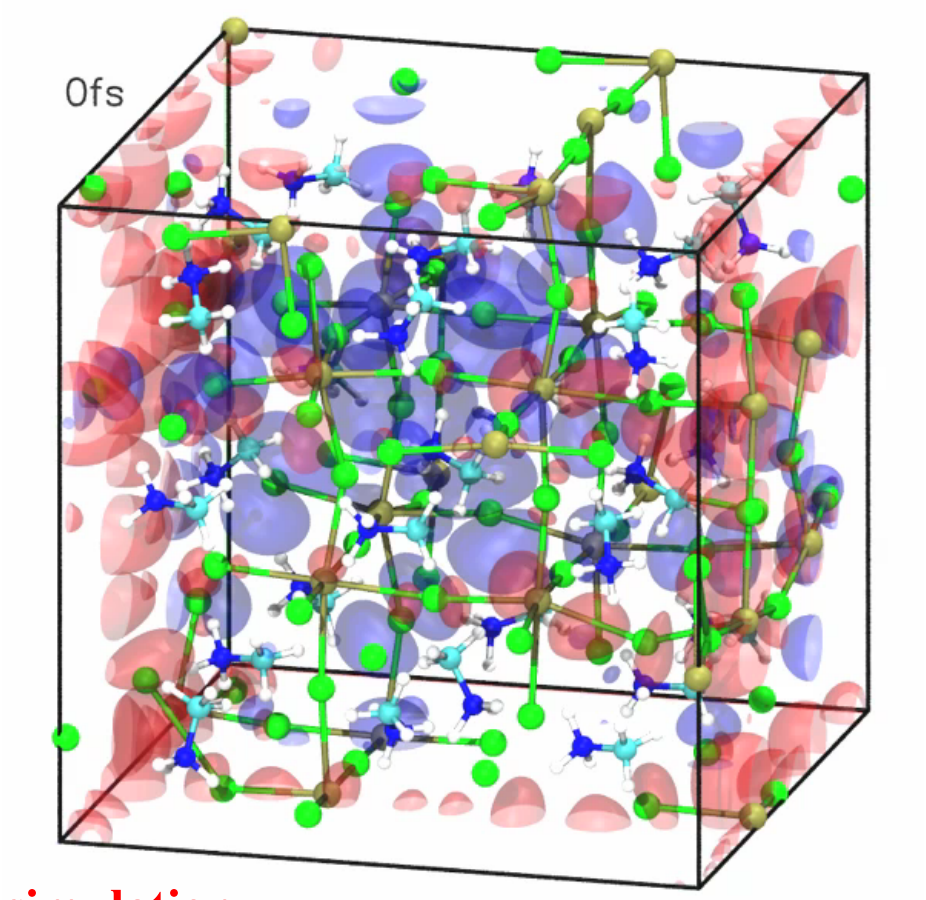






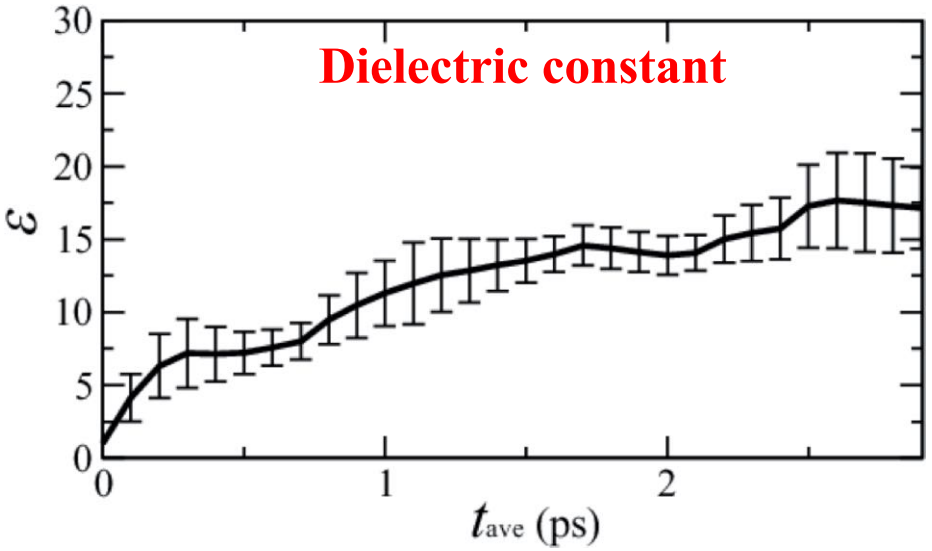
Photoexcited Carriers in $MAPbI_3$

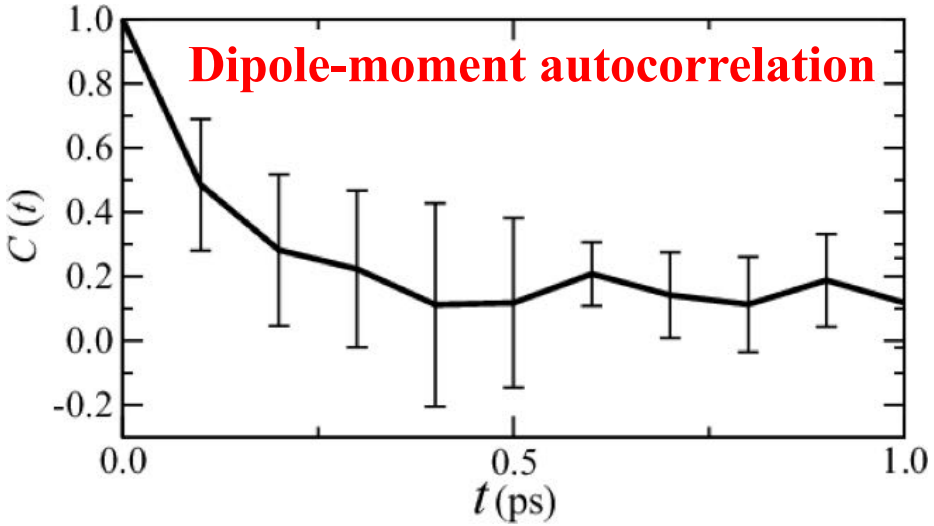
- **Organometal halide perovskites (*e.g.* methylammonium lead iodide, $CH_3NH_3PbI_3$ or $MAPbI_3$) for solar cells with high power conversion efficiency > 20%**
  [Stranks & Snaith, *Nat. Nanotechnol.* **10**, 391 ('15)]



- **Nonabiadiabatic QMD simulation**
  Pb & I sublattices act as disjunct pathways for rapid & balanced transport of free electrons & holes — electron (63% Pb-6p) & hole (90% I-5p);
  diffusion coefficients $D_e = (1.16\pm0.31)\times10^{-2}$ cm^2/s & $D_h = (1.01\pm0.42)\times10^{-2}$ cm^2/s
  Expt: $D_e = (1.7\pm1.1)\times10^{-2}$ cm^2/s & $D_h = (1.1\pm0.7)\times10^{-2}$ cm^2/s [Stranks *et al.*, *Science* **342**, 341 ('13)]

Screening Role of Methylammonium Sublattice





$$\varepsilon = 1 + \frac{4\pi}{3k_B TV}(\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2)$$

time average; dipole moment

$cf.\ \varepsilon_{expt}\,(10^{12}\ \text{Hz}) = 7\text{-}10$

Lin *et al.*, *Nat. Photonics* **9**, 106 ('15)

$$C(t) = \frac{\langle \mathbf{M}(t + t_0) \cdot \mathbf{M}(t_0) \rangle}{\langle \mathbf{M}(t_0) \cdot \mathbf{M}(t_0) \rangle}$$

Rapid response time ~ 1 ps

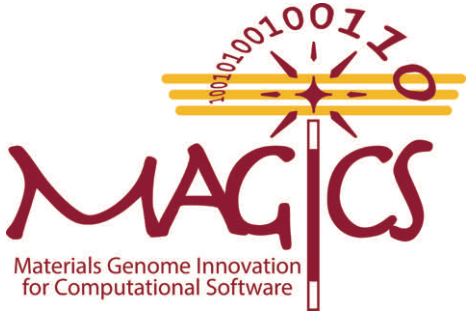
$cf.\ \tau_{expt} = 2$ ps

Deschler *et al.*, *JPCL* **5**, 1421 ('15)

- **Large dielectric constant of MA sublattice causes small exciton binding energy, 0.012 ± 0.009 eV (experimental upper bound = 0.05 eV** [D'Innocenzo *et al.*, *Nat. Commun*. **5**, 3586 ('14)]**)**
- **MA sublattice quickly screens out electrostatic electron-hole attraction to unbind an exciton & generate free carriers within 1 ps** [*cf.* Zhu *et al.*, *Science* **353**, 1409 ('16)]

Hakamata *et al.*, *Sci. Rep.* **5**, 19599 ('16)

MAterials Genome Innovation for Computational Software



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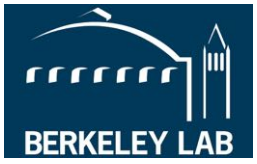
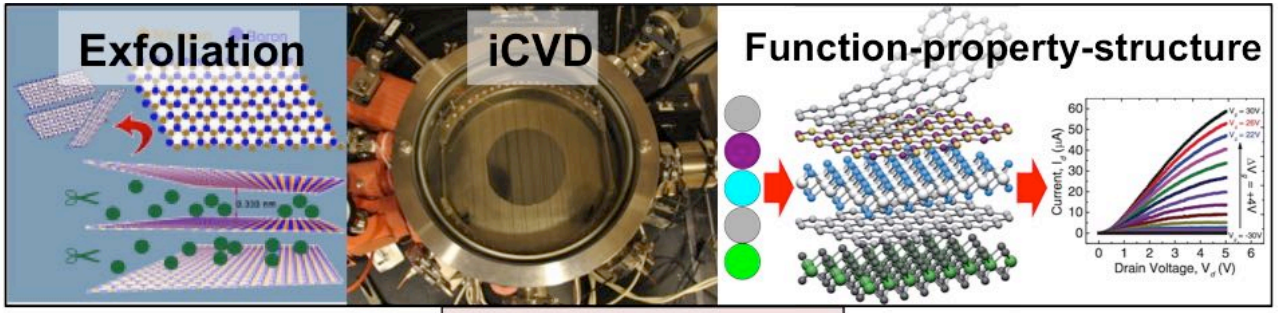
David J. Singh *University of Missouri*
Pulickel M. Ajayan *Rice University*

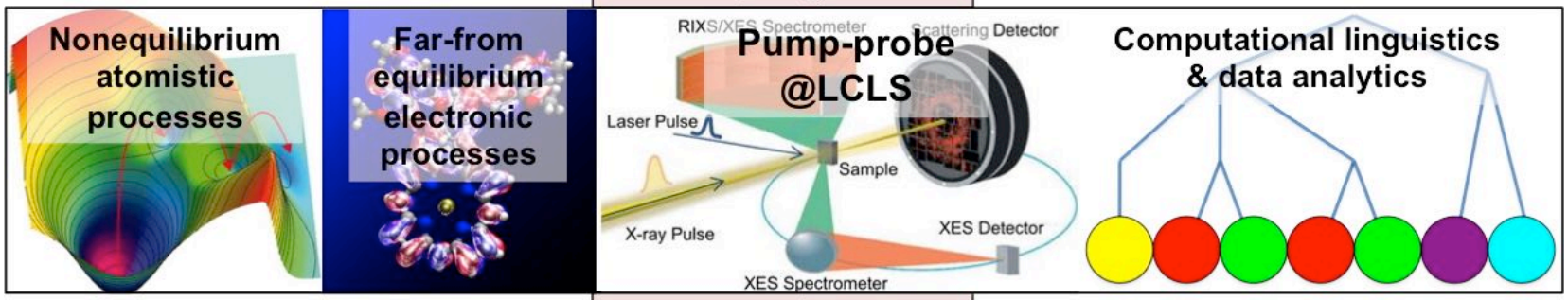
USC SLAC    

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

1 Scalable simulation engines

Current/future platforms

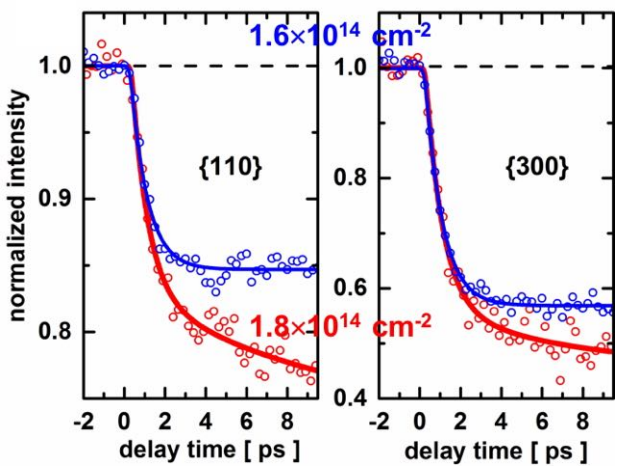
U.S. DEPARTMENT OF ENERGY INCITE LEADERSHIP COMPUTING

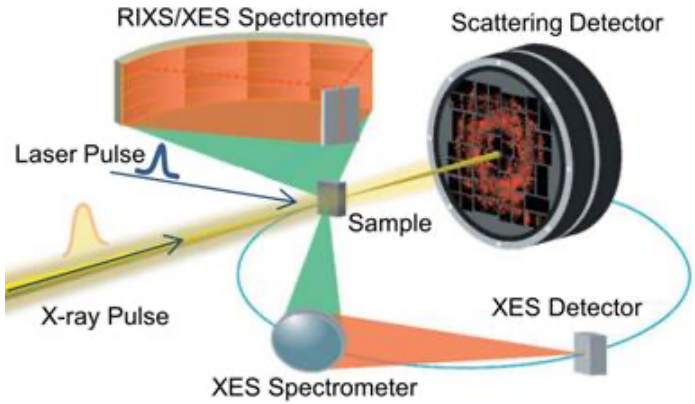
AURORA EARLY SCIENCE PROGRAM

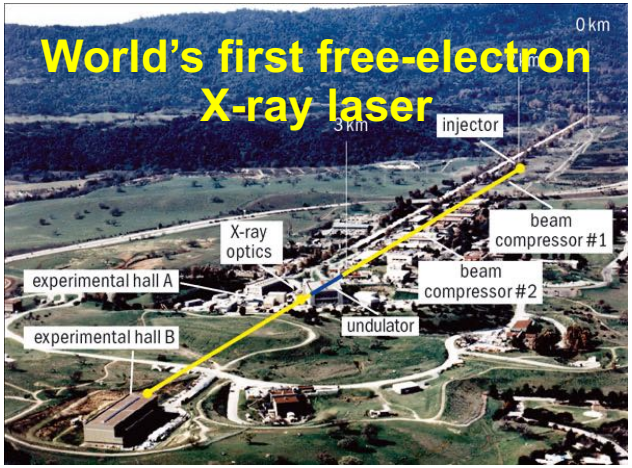
MAGICS Materials Genome Innovation for Computational Software

LCLS X-ray free-electron laser

INCITE|AURORA–MAGICS–LCLS Synergy



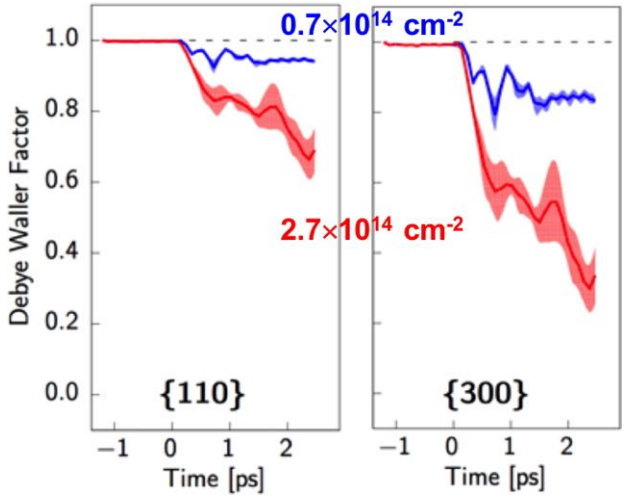




Linac Coherent Light Source

LCLS

DOE INCITE & Aurora ESP Awards



MAGICS
Materials Genome Innovation for Computational Software

U.S. DEPARTMENT OF ENERGY
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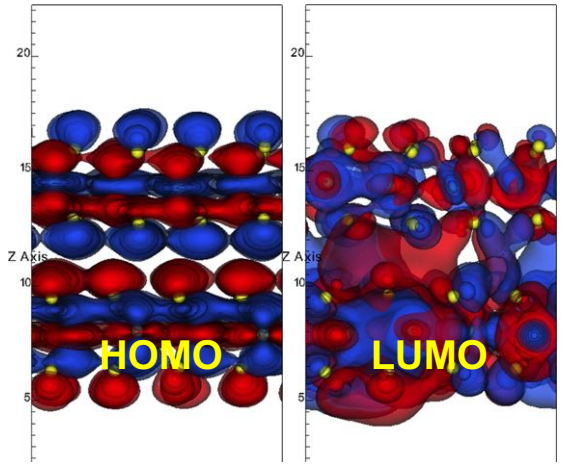
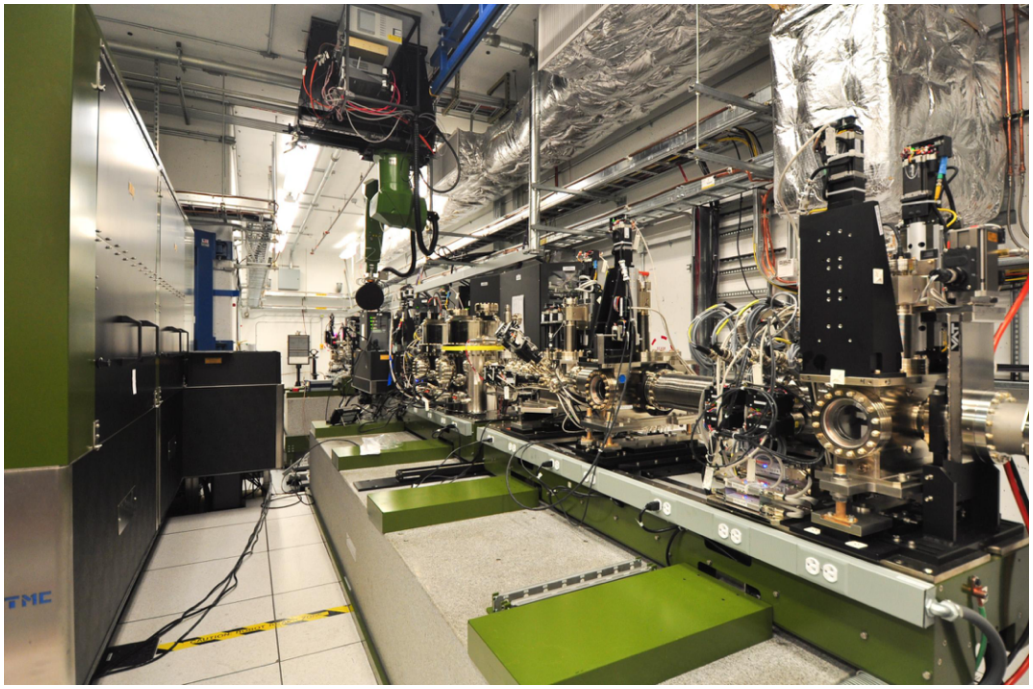
LEADERSHIP COMPUTING

AURORA | EARLY SCIENCE PROGRAM

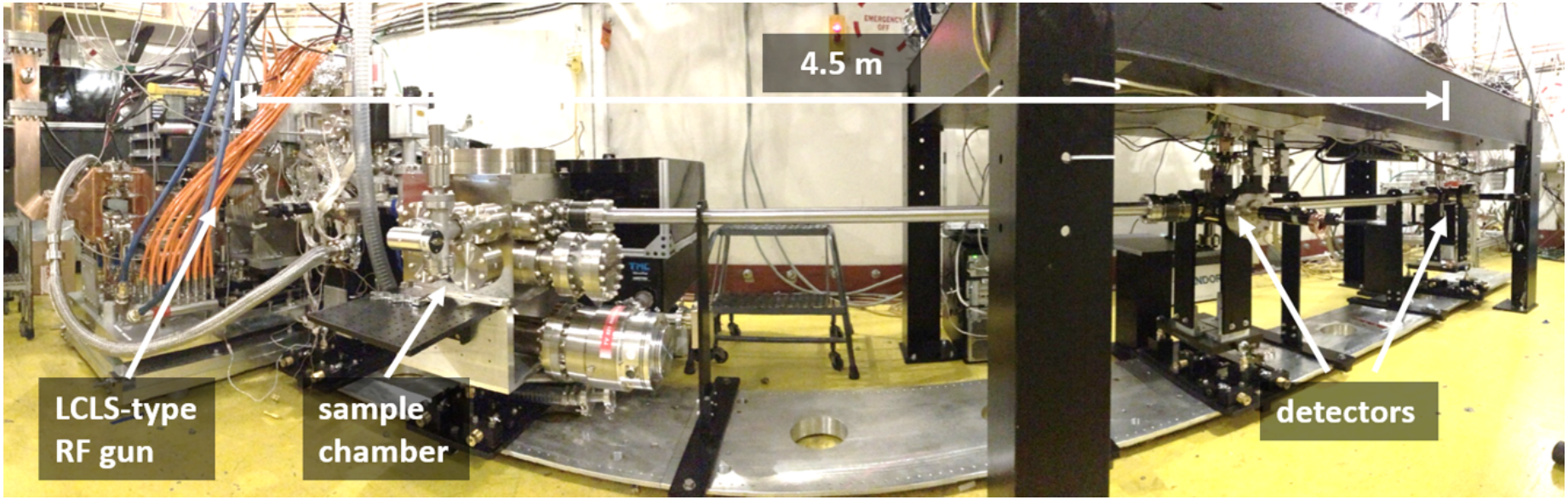


ULTRAFAST PUMP-PROBE EXPERIMENTS

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

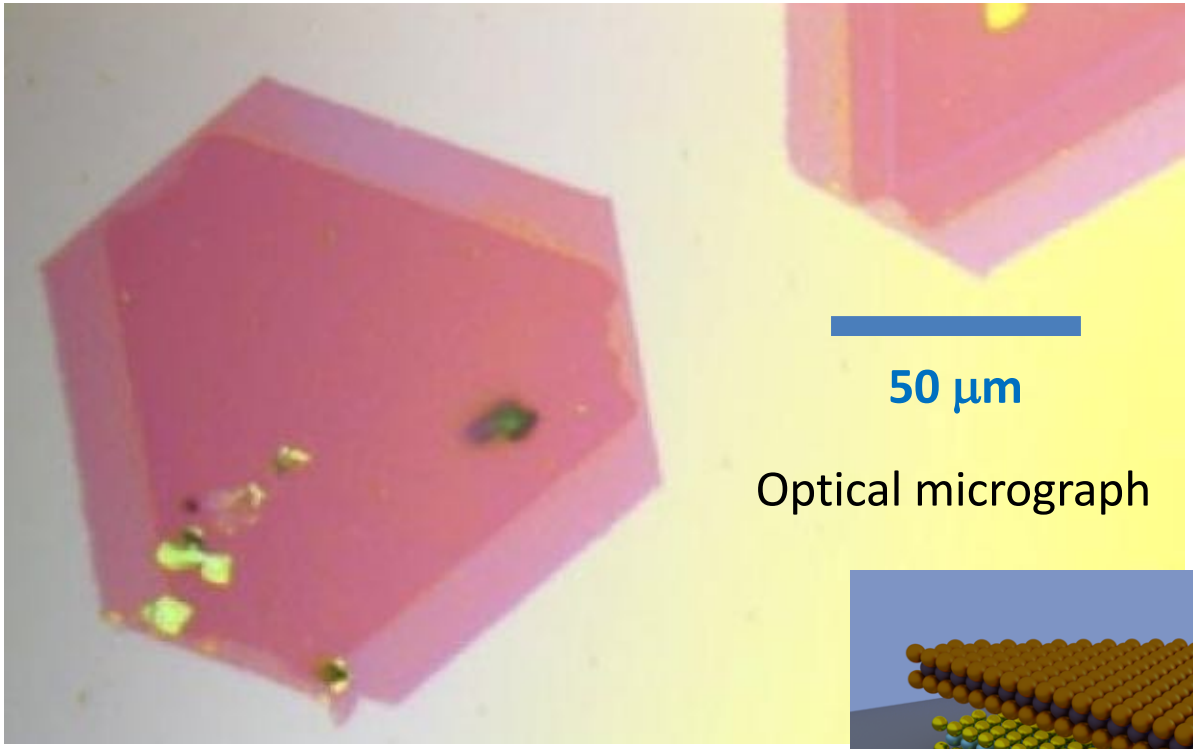


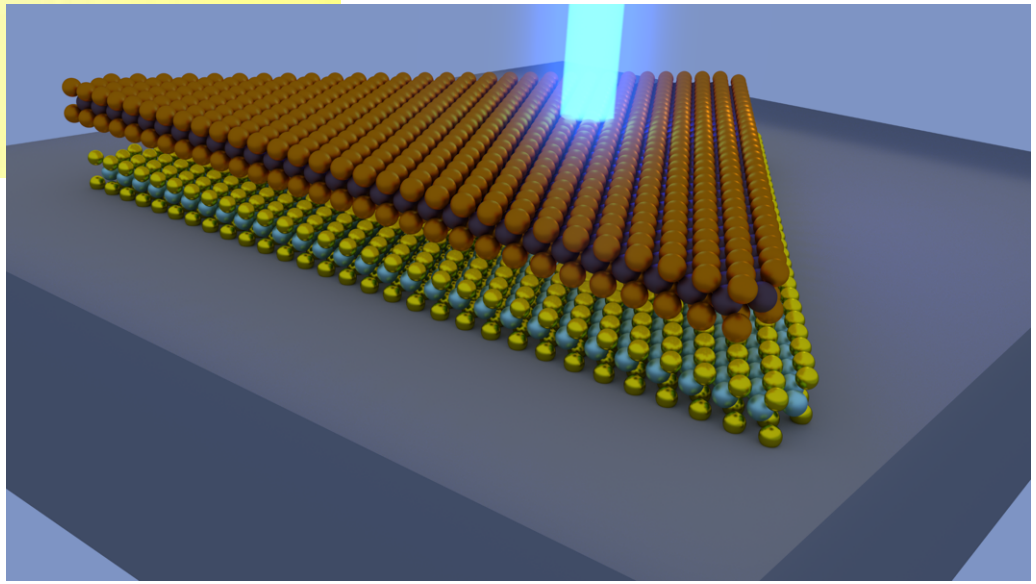
Ultrafast electron diffraction (UED) instrument: 3-5 MeV



2D Transition Metal Dichalcogenide (TMDC)

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

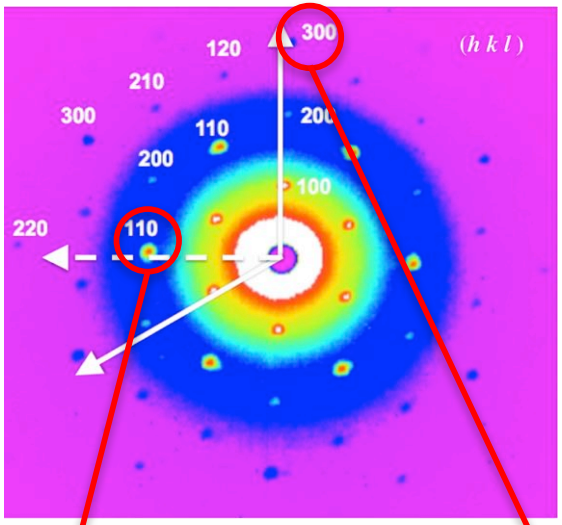


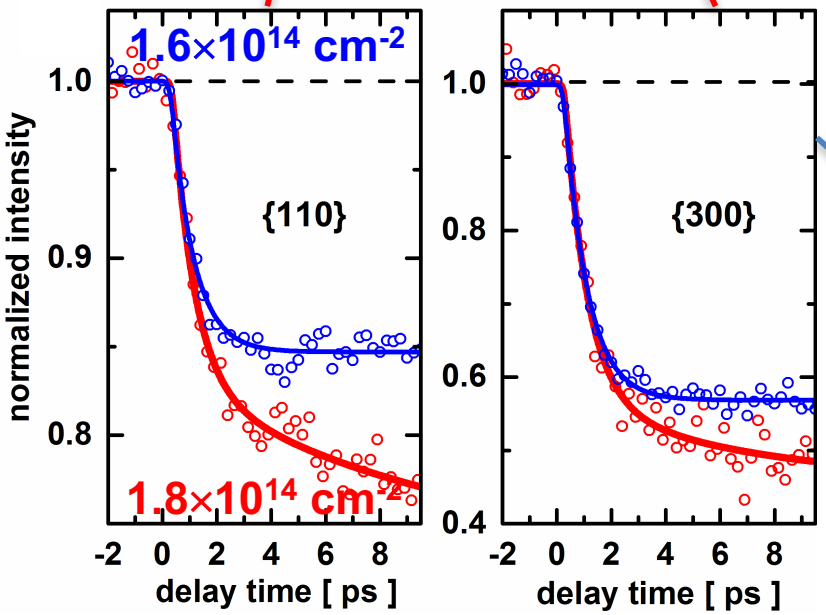


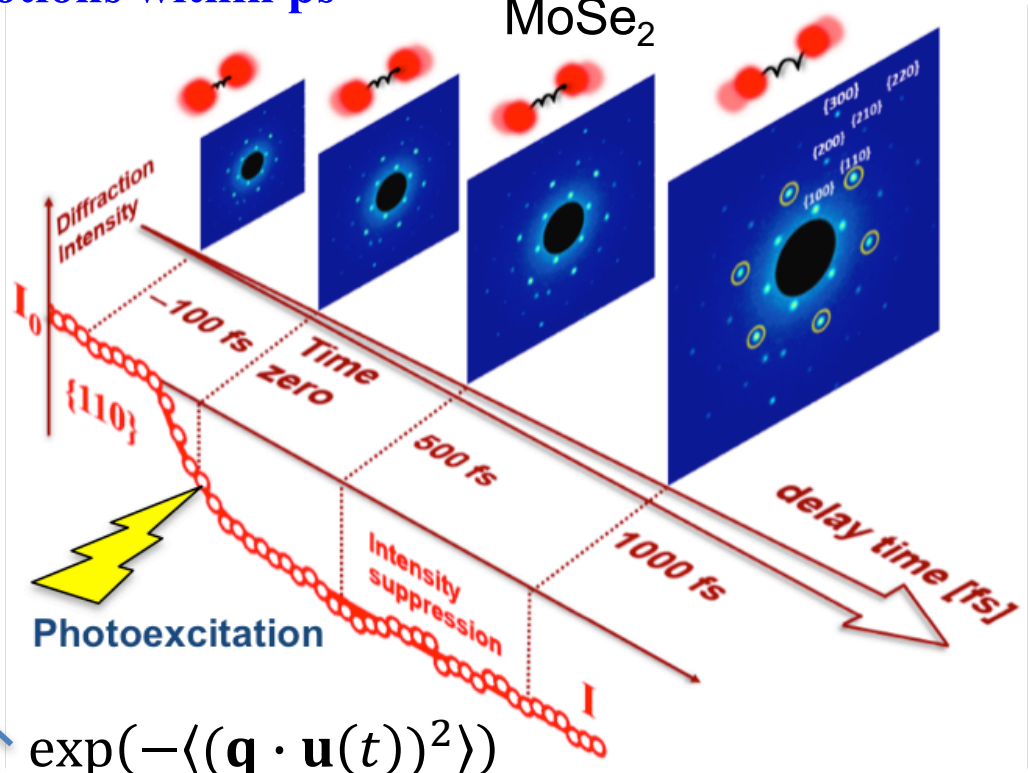
- **Question: What is the nature of optically induced lattice dynamics for photo-patterning (*e.g.*, semiconducting 2H to metallic 1T' phases) of TMDC?**

Ultrafast Coupled Electron-Lattice Dynamics

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







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

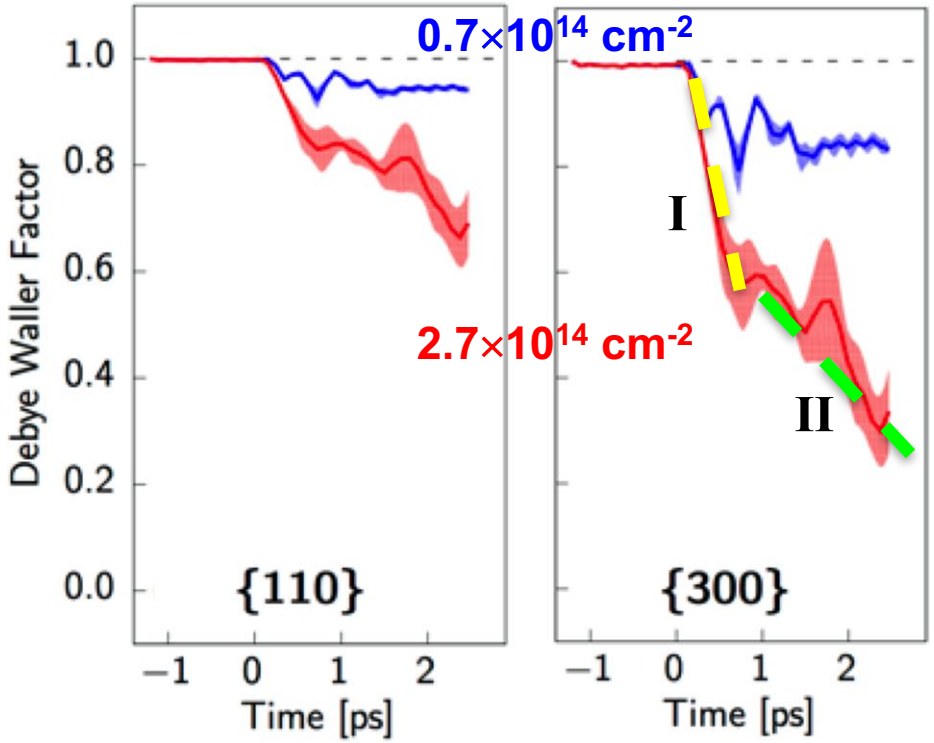
atomic displacement

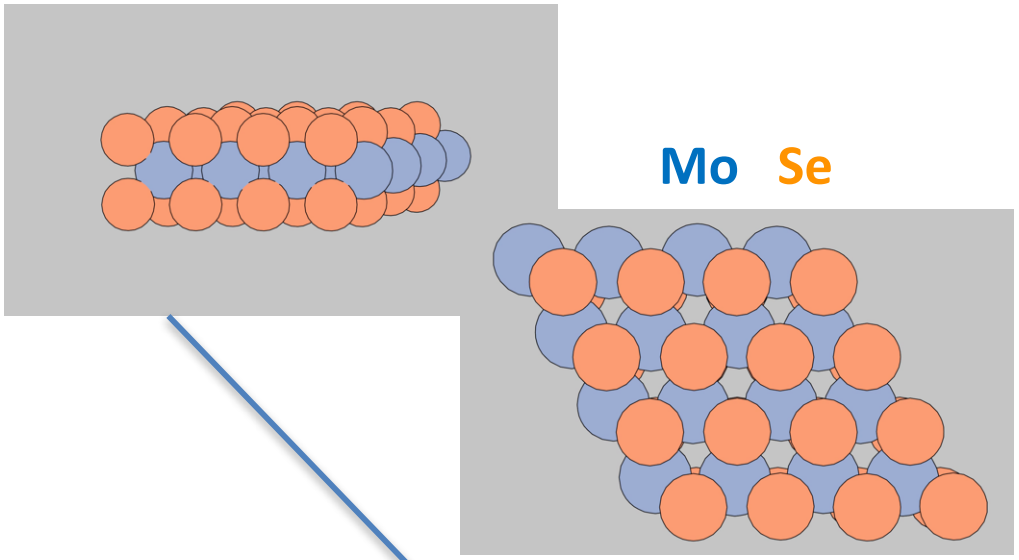
- **Dynamics of Debye-Waller factor reveals rapid disordering for both {300} & {110} peaks**
- **Transition from mono- to bi-exponential decay at higher electron-hole density**

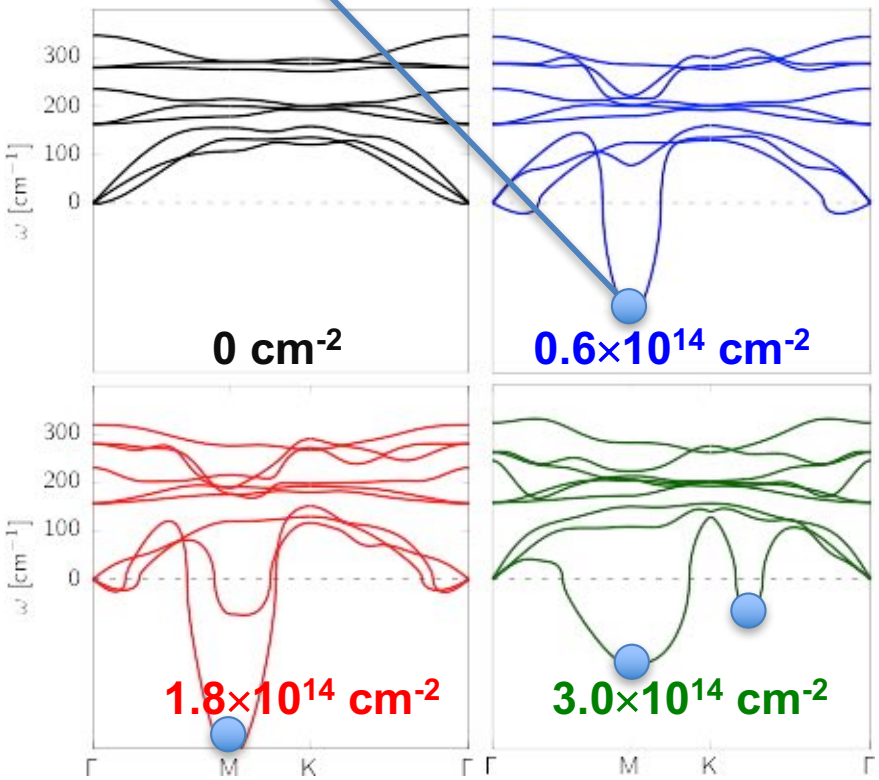
M.F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)

Strong Electron-Lattice Coupling

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





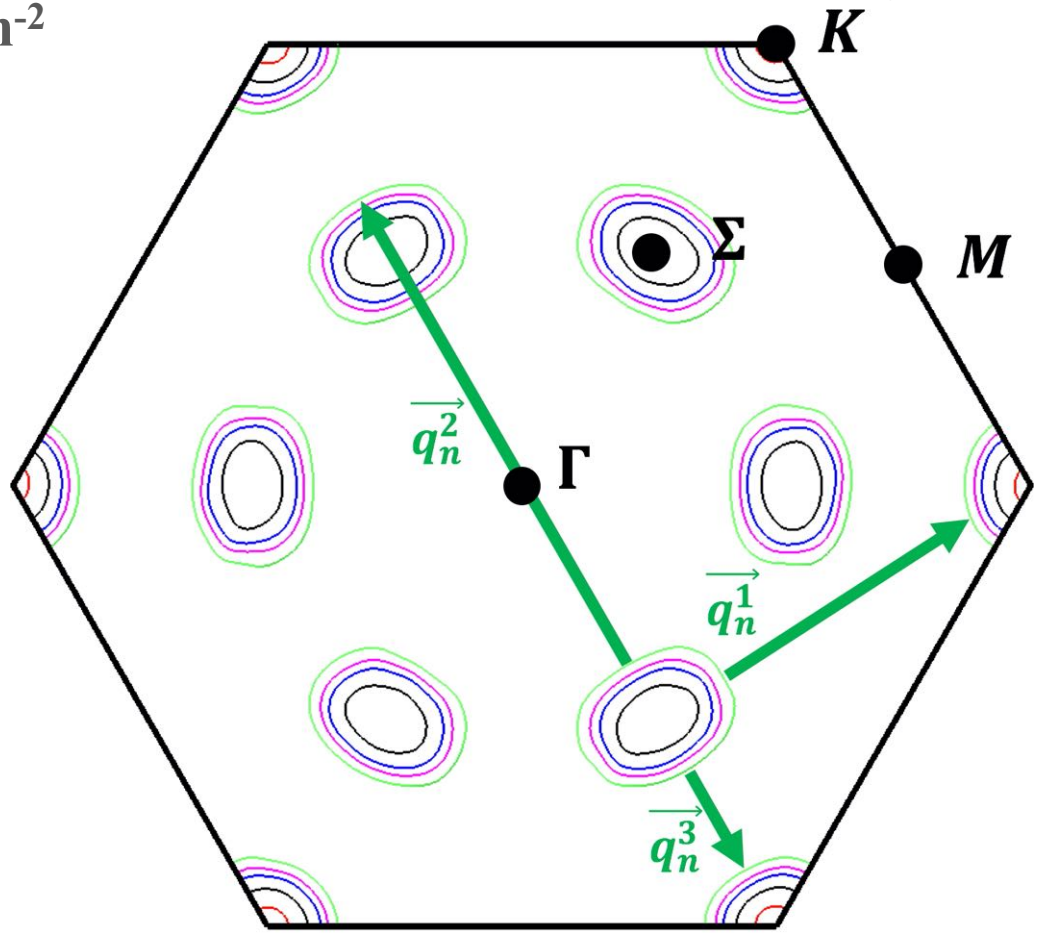


- **Rapid lattice dynamics is explained by the softening of M-point (1/2 0 0) phonon**
- **Bi-exponential transition is explained by the softening of additional phonon modes at higher electron-hole densities**

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

Electronic Origin of Phonon Softening

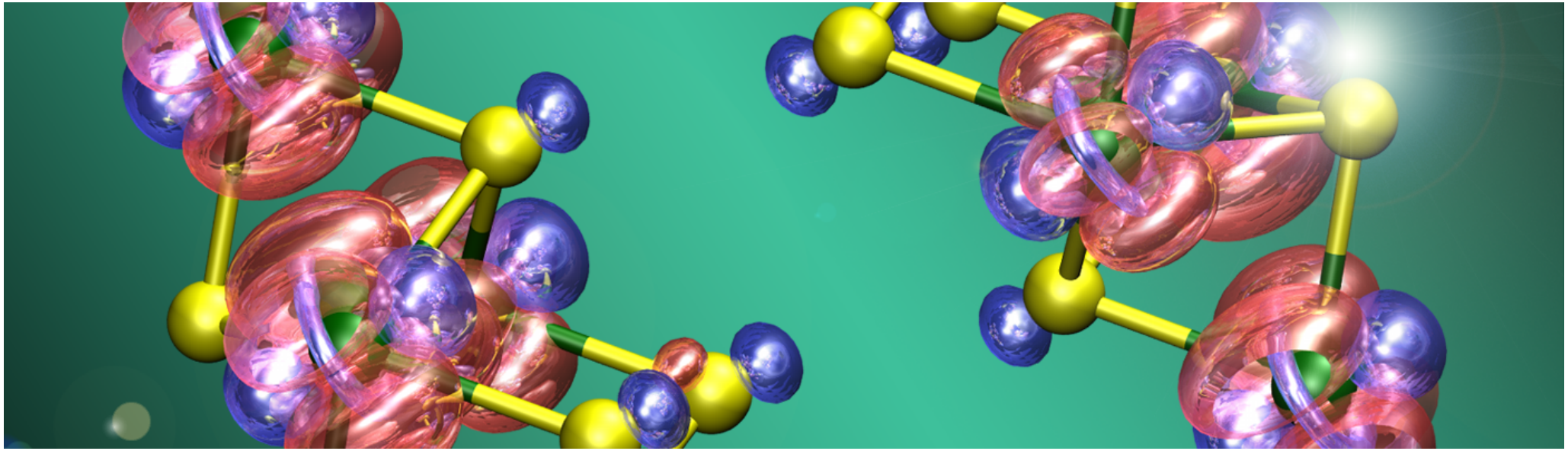
- Electronic Fermi surface for the electron-hole density *n*(e-h) ranging from 0.2 to 2×10^{14} cm^{-2}



n(e-h) = 0.22, 1, 2, 3, 4 $\times10^{14}$ cm^{-2}

- While the Fermi surface is localized at K-points at minimal excitation (**red**), it 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) and $\vec{q}_n^3$ (K) phonons

Simulation-Experiment Synergy

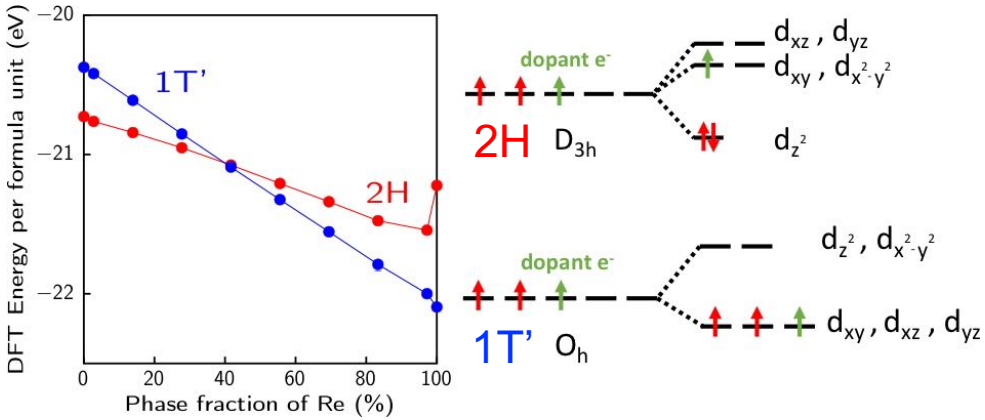


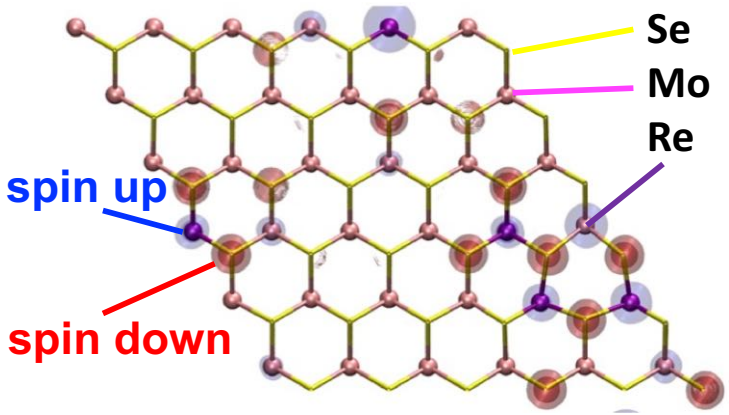
- **In the ultrafast 'electron camera,' laser light hitting a material is almost completely converted into nuclear vibrations — key to switching material properties on & off at will for future electronics applications**
- **High-end quantum simulations reproduce the ultrafast energy conversion at exactly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

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

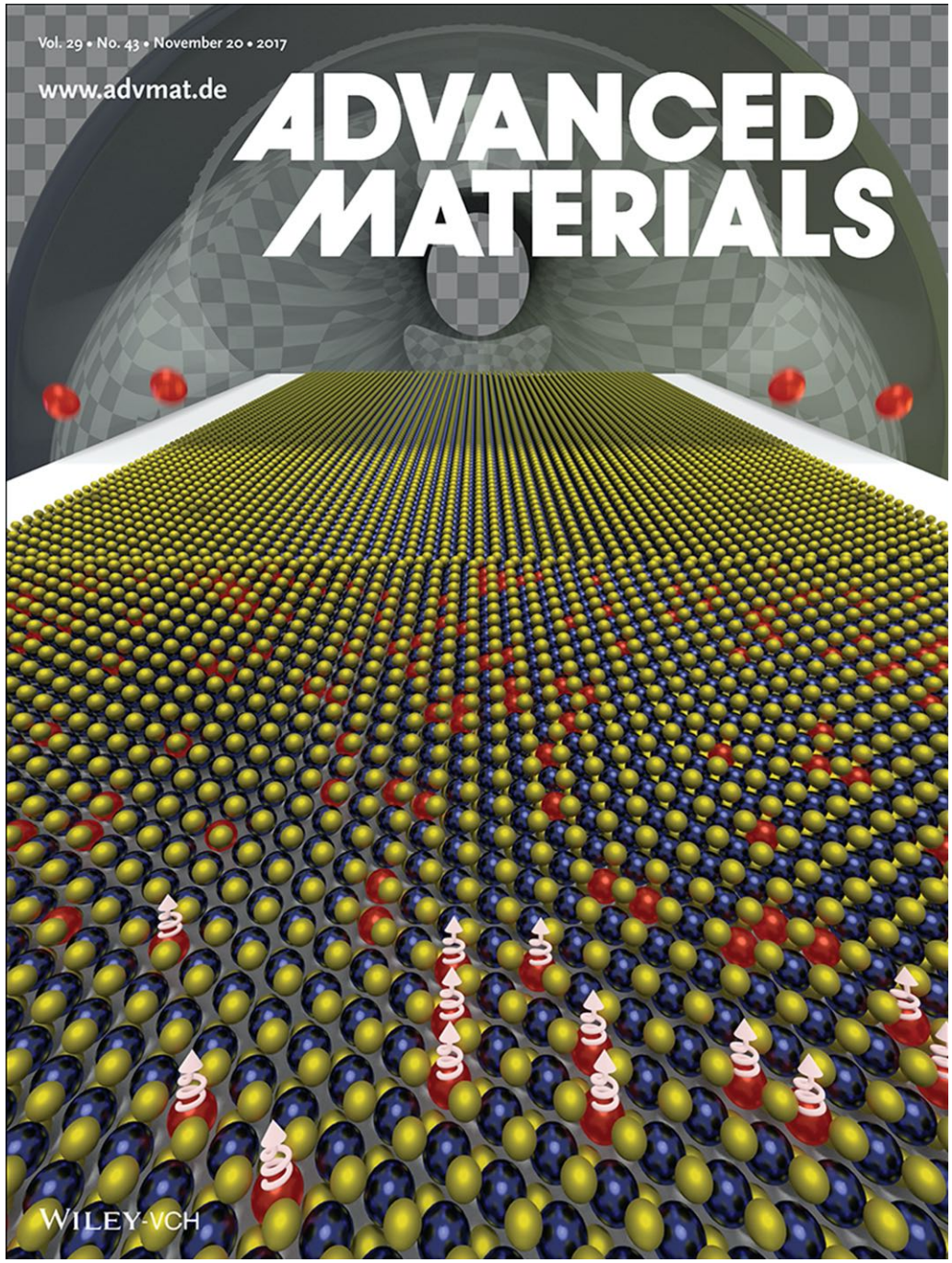
Semiconductor-to-Metal Transition *via* Doping

- **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)



Conclusion

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