

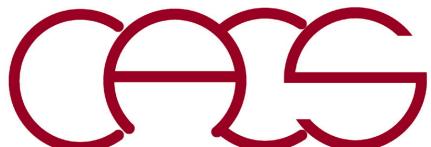
Iterative Energy Minimization for Quantum Molecular Dynamics

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From quantum dynamics to eigenvalue problems



Imaginary-Time Quantum Dynamics

- Quantum dynamics

Repeat

$$|\psi\rangle \leftarrow \exp(-i\hat{H}\Delta t)|\psi\rangle$$

$$\begin{cases} uv[2j] = \cos(-\nu[j]\Delta t/2) \\ uv[2j + 1] = \sin(-\nu[j]\Delta t/2) \end{cases} \Rightarrow \begin{cases} \exp(-\nu[j]\Delta t/2) \\ 0 \end{cases}$$

- Imaginary-time quantum dynamics: $i\Delta t \rightarrow \Delta\tau$

Repeat

$$\begin{aligned} |\psi\rangle &\leftarrow \exp(-\hat{H}\Delta\tau)|\psi\rangle \\ |\psi\rangle &\leftarrow |\psi\rangle/\sqrt{\langle\psi|\psi\rangle} \end{aligned}$$

$$\frac{\partial}{\partial\tau}\psi(x,\tau) = \overbrace{\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}\psi(x,\tau)}^{\text{diffusion}} - \overbrace{\frac{V(x)}{\hbar}\psi(x,\tau)}^{\text{reaction (birth/death)}}$$

$$\exp(-\hat{H}\Delta\tau) = \exp(-V(x)\Delta\tau/2)\exp\left(\frac{\nabla^2}{2}\Delta\tau\right)\exp(-V(x)\Delta\tau/2)$$

- Filtering in the ground state

Eigensystem: $\hat{H}|n\rangle = \epsilon_n|n\rangle$ $\epsilon_0 < \epsilon_1 < \dots$ $\langle m|n\rangle = \delta_{mn}$

$$\begin{aligned} \exp(-\hat{H}\tau)|\psi_{\text{init}}\rangle &= \exp(-\hat{H}\tau)\underbrace{\sum_{n \geq 0} |n\rangle\langle n|}_{\substack{1 \text{ another resolution of identity}}} \psi_{\text{init}}\rangle \\ &= \sum_{n \geq 0} |n\rangle\langle n| \psi_{\text{init}}\rangle \exp(-\epsilon_n\tau) \xrightarrow{\tau \rightarrow \infty} |0\rangle\langle 0| \psi_{\text{init}}\rangle \exp(-\epsilon_0\tau) \end{aligned}$$

cf. Quantum imaginary time evolution (QITE): Motta et al., Nat. Phys. 16, 205 ('19)

Obtaining Excited States

- Filter-project imaginary-time quantum dynamics

Repeat

$$\begin{aligned} |\psi\rangle &\leftarrow \exp(-\hat{H}\Delta\tau)|\psi\rangle \\ |\psi\rangle &\leftarrow |\psi\rangle - |0\rangle\langle 0|\psi\rangle \\ |\psi\rangle &\leftarrow |\psi\rangle/\sqrt{\langle\psi|\psi\rangle} \end{aligned}$$

Projecting out — $\hat{P}_{\text{out}} = 1 - |0\rangle\langle 0|$:

$$\langle 0|\{|\psi\rangle - |0\rangle\langle 0|\psi\rangle\} = \langle 0|\psi\rangle - \overbrace{\langle 0|0\rangle}^1 \langle 0|\psi\rangle = 0$$

$$(1 - |0\rangle\langle 0|)\exp(-\hat{H}\tau)|\psi_{\text{init}}\rangle \xrightarrow[\tau \rightarrow \infty]{} |1\rangle$$

- Problem: Convergence is too slow



Solution: Use the conjugate-gradient method (see next viewgraphs)

- If all the eigenstates (not only a few lowest-lying states) are needed



Use matrix diagonalization (see the next section)

Functional Derivative Basics

- **Functional derivative:** $\delta E = \int d\mathbf{r} \frac{\delta E}{\delta f(\mathbf{r})} \delta f(\mathbf{r})$ **functional = function of function:** $E[f(\mathbf{r})]$

- **Example 1:** $E[f(\mathbf{r})] = \int d\mathbf{r} (f(\mathbf{r}))^2$

$$E[f(\mathbf{r}) + \delta f(\mathbf{r})] - E[f(\mathbf{r})] = \int d\mathbf{r} \{ [f(\mathbf{r}) + \delta f(\mathbf{r})]^2 - f^2(\mathbf{r}) \} = \int d\mathbf{r} [2f(\mathbf{r})\delta f(\mathbf{r}) + \cancel{\delta f^2(\mathbf{r})}]$$

$$\therefore \frac{\delta E}{\delta f(\mathbf{r})} = 2f(\mathbf{r})$$

- **Example 2:** $E[\rho(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

$$\begin{aligned} E[\rho(\mathbf{r}) + \delta\rho(\mathbf{r})] - E[\rho(\mathbf{r})] &= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{[\rho(\mathbf{r}) + \delta\rho(\mathbf{r})][\rho(\mathbf{r}') + \delta\rho(\mathbf{r}')] - \rho(\mathbf{r})\rho(\mathbf{r}')} {|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\delta\rho(\mathbf{r}') + \rho(\mathbf{r}')\delta\rho(\mathbf{r}) + \cancel{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}} {|\mathbf{r} - \mathbf{r}'|} \end{aligned}$$

Inhomogeneous electron gas

P Hohenberg, W Kohn

Physical review, 1964 • APS

☆ Save ⚙ Cite Cited by 69405

$$= \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \delta\rho(\mathbf{r})$$

$$\therefore \frac{\delta E}{\delta\rho(\mathbf{r})} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

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

Rayleigh-Ritz Variational Principle

- Complex functional derivative

$$\psi(\mathbf{r}) = \psi_1(\mathbf{r}) + i\psi_2(\mathbf{r}); \psi^*(\mathbf{r}) = \psi_1(\mathbf{r}) - i\psi_2(\mathbf{r})$$

- Energy functional

$$E[\psi(\mathbf{r})] = \frac{\langle \psi | \hat{h} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int d\mathbf{r} \psi^*(\mathbf{r}) \hat{h}(\mathbf{r}) \psi(\mathbf{r})}{\int d\mathbf{r} \psi^*(\mathbf{r}) \psi(\mathbf{r})} = \frac{\int d\mathbf{r} \psi^*(\mathbf{r}) \left[-\frac{\nabla^2}{2} + v(\mathbf{r}) \right] \psi(\mathbf{r})}{\int d\mathbf{r} \psi^*(\mathbf{r}) \psi(\mathbf{r})}$$

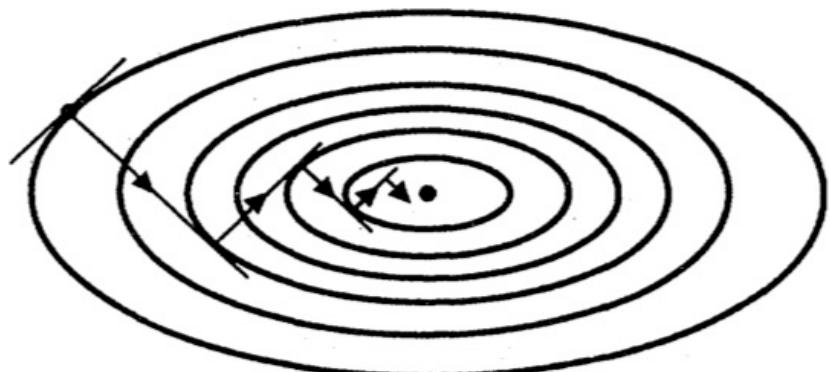
- Gradient (for a normalized wave function)

$$\frac{\delta E}{\delta \psi^*(\mathbf{r})} = (\hat{h}(\mathbf{r}) - \langle \psi | \hat{h} | \psi \rangle) \psi(\mathbf{r})$$

- Steepest descent

Repeat

$$\psi(\mathbf{r}) \leftarrow \psi(\mathbf{r}) - \Delta\tau (\hat{h}(\mathbf{r}) - \langle \psi | \hat{h} | \psi \rangle) \psi(\mathbf{r})$$



Conjugate Gradient Method

1. Conjugate gradient: Does not spoil the minimizations in the previous iteration steps
2. Line minimization: Directly moves to the minimum along the conjugate-gradient direction

for $i \leftarrow 1$ to $Max_iteration$

 if $i = 1$

$$\tilde{g}_i \leftarrow g_i$$

 else

$$\tilde{g}_i \leftarrow g_i + \frac{g_i \cdot g_i}{g_{i-1} \cdot g_{i-1}} \tilde{g}_{i-1}$$

 endif

$$\psi_i \leftarrow \psi_{i-1} + \frac{g_{i-1} \cdot g_{i-1}}{\tilde{g}_i \cdot h \cdot \tilde{g}_i} \tilde{g}_i$$

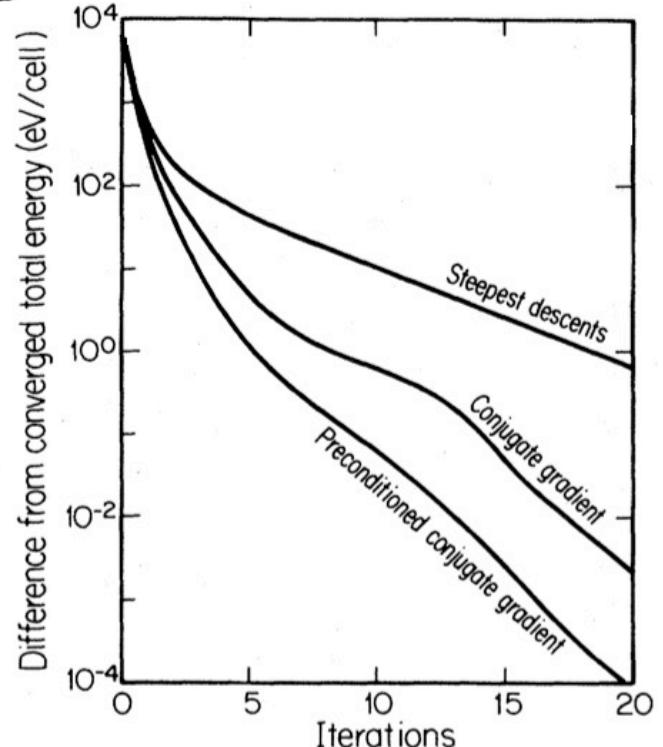
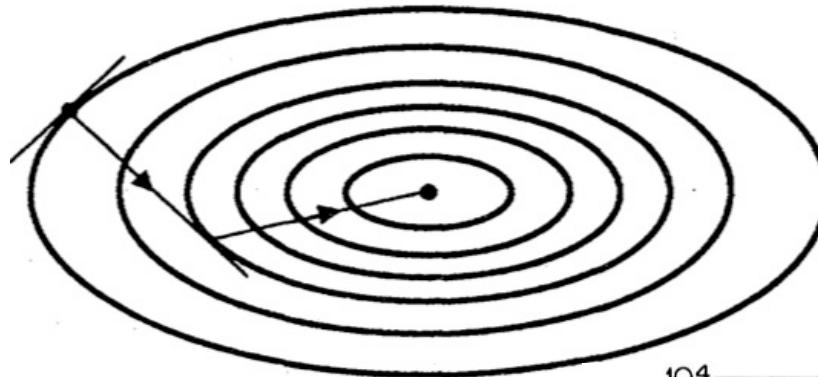
$$g_i \leftarrow g_{i-1} - \frac{g_{i-1} \cdot g_{i-1}}{\tilde{g}_i \cdot h \cdot \tilde{g}_i} h \cdot \tilde{g}_i$$

 if convergent, exit

endfor

See [Numerical Recipes](#), Sec. 10.6

M.C. Payne et al., [Rev. Mod. Phys. 64, 1045 \('92\)](#)



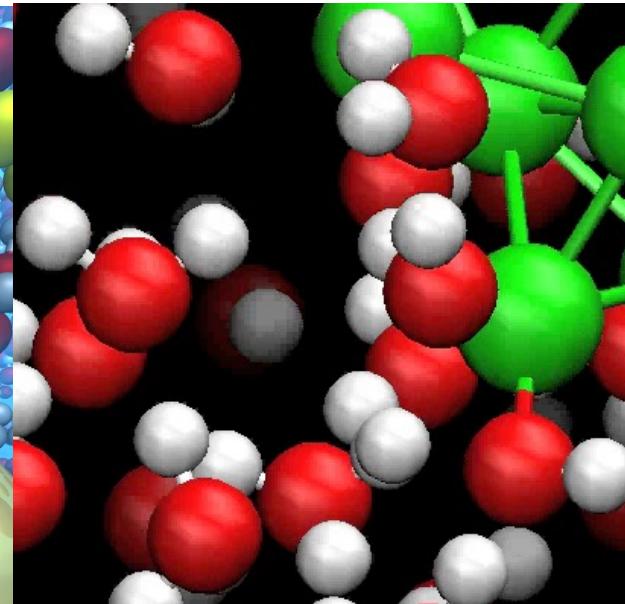
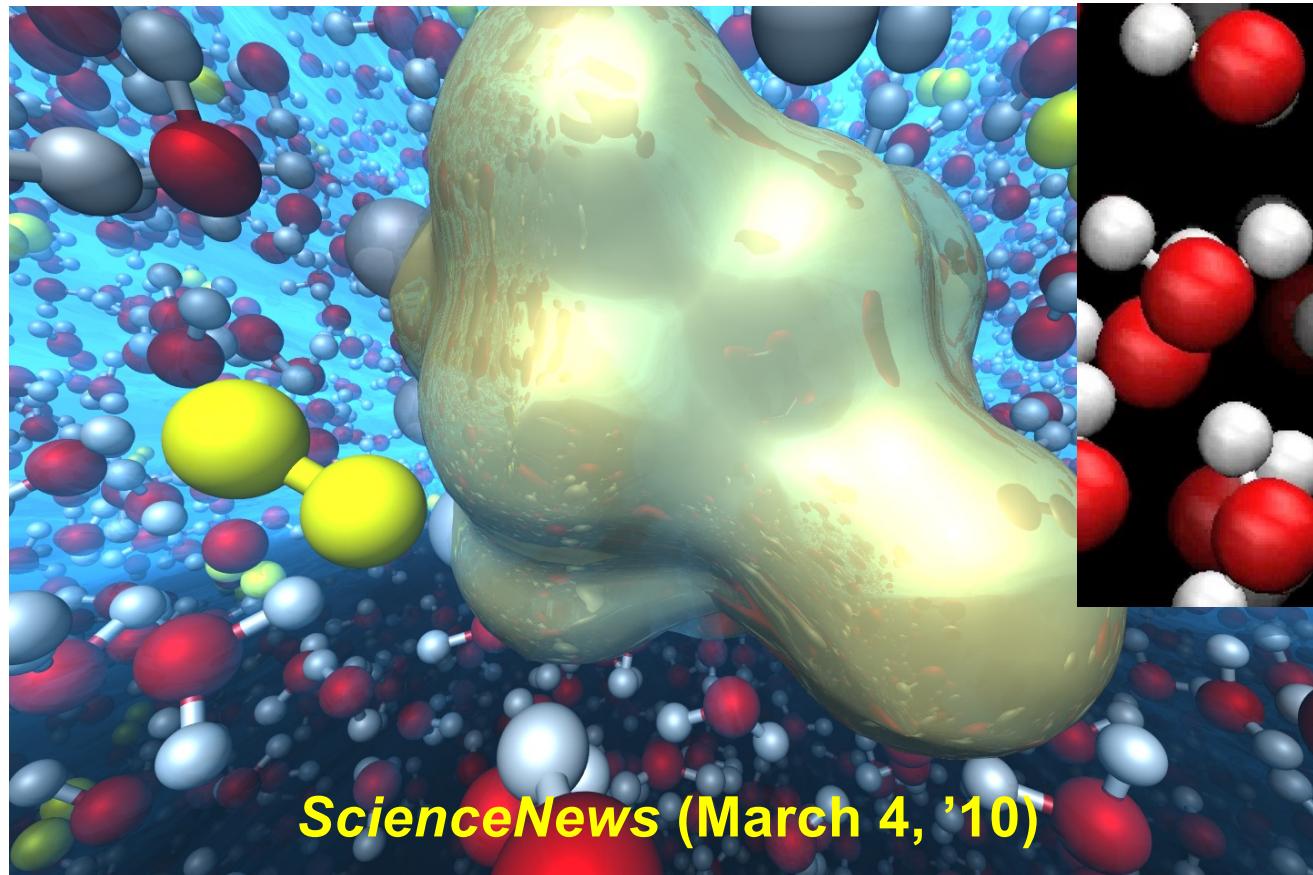
Quantum Molecular Dynamics

- Born-Oppenheimer (adiabatic) approximation: Electron wave function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}})$ is determined with fixed nuclei positions \mathbf{R}_n ($n = 1, \dots, N_{\text{nucleus}}$)
 $\psi_*(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}}) \leftarrow \underset{\text{CG}}{\operatorname{argmin}} E[\psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}}), \{\mathbf{R}_n\}]$

- Newton's equations for the classical motion of nuclei

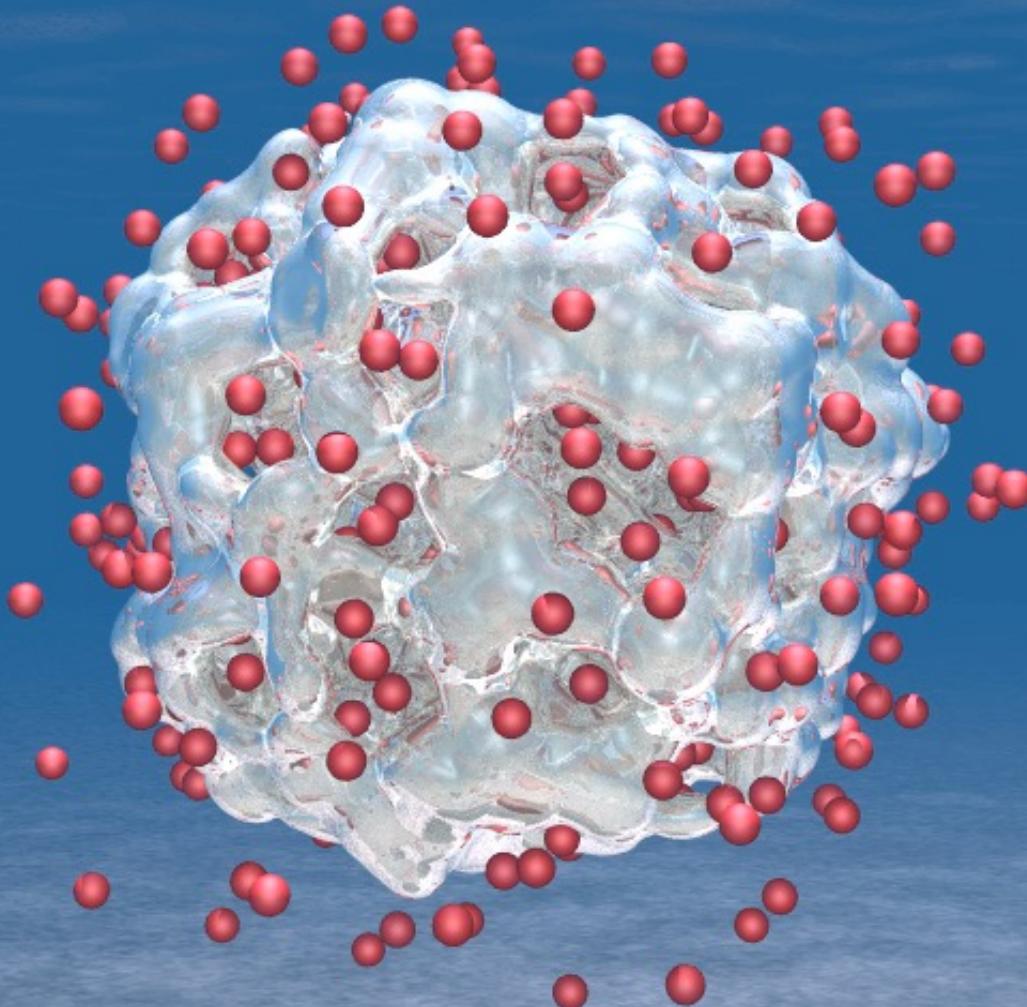
$$M_n \frac{d^2}{dt^2} \mathbf{R}_n = - \frac{\partial}{\partial \mathbf{R}_n} E[\psi_*(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}}), \{\mathbf{R}_n\}]$$

MD

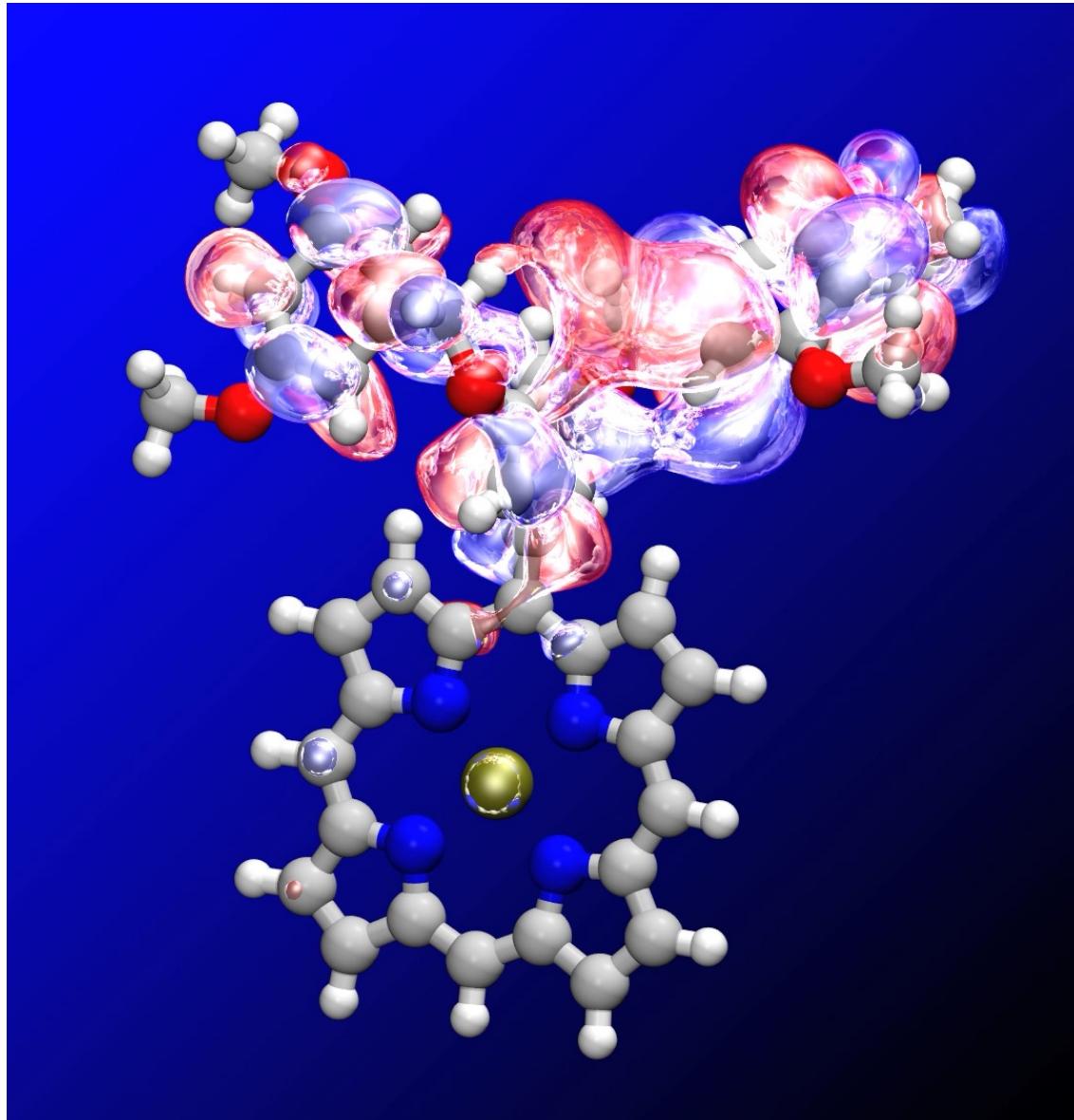


H₂ Production from Water Using LiAl Particles

16,661-atom QMD simulation of Li₄₄₁Al₄₄₁ in water
on 786,432 IBM BlueGene/Q cores



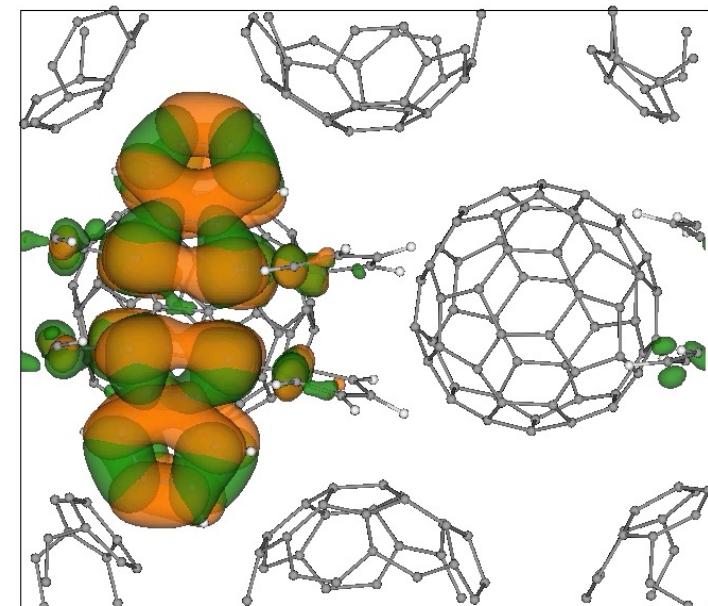
Nonadiabatic Quantum Molecular Dynamics



Appl. Phys. Lett. **98**, 113301 ('11); *ibid.* **100**, 203306 ('12); *J. Chem. Phys.* **136**, 184705 ('12); *Comput. Phys. Commun.* **184**, 1 ('13); *Appl. Phys. Lett.* **102**, 093302 ('13); *ibid.* **102**, 173301 ('13); *J. Chem. Phys.* **140**, 18A529 ('14); *IEEE Computer* **48**(11), 33 ('15); *Sci. Rep.* **5**, 19599 ('16); *Nature Commun.* **8**, 1745 ('17); *Nano Lett.* **18**, 4653 ('18); *Nature Photon.* **13**, 425 ('19)

Zn porphyrin

Rubrene/C₆₀

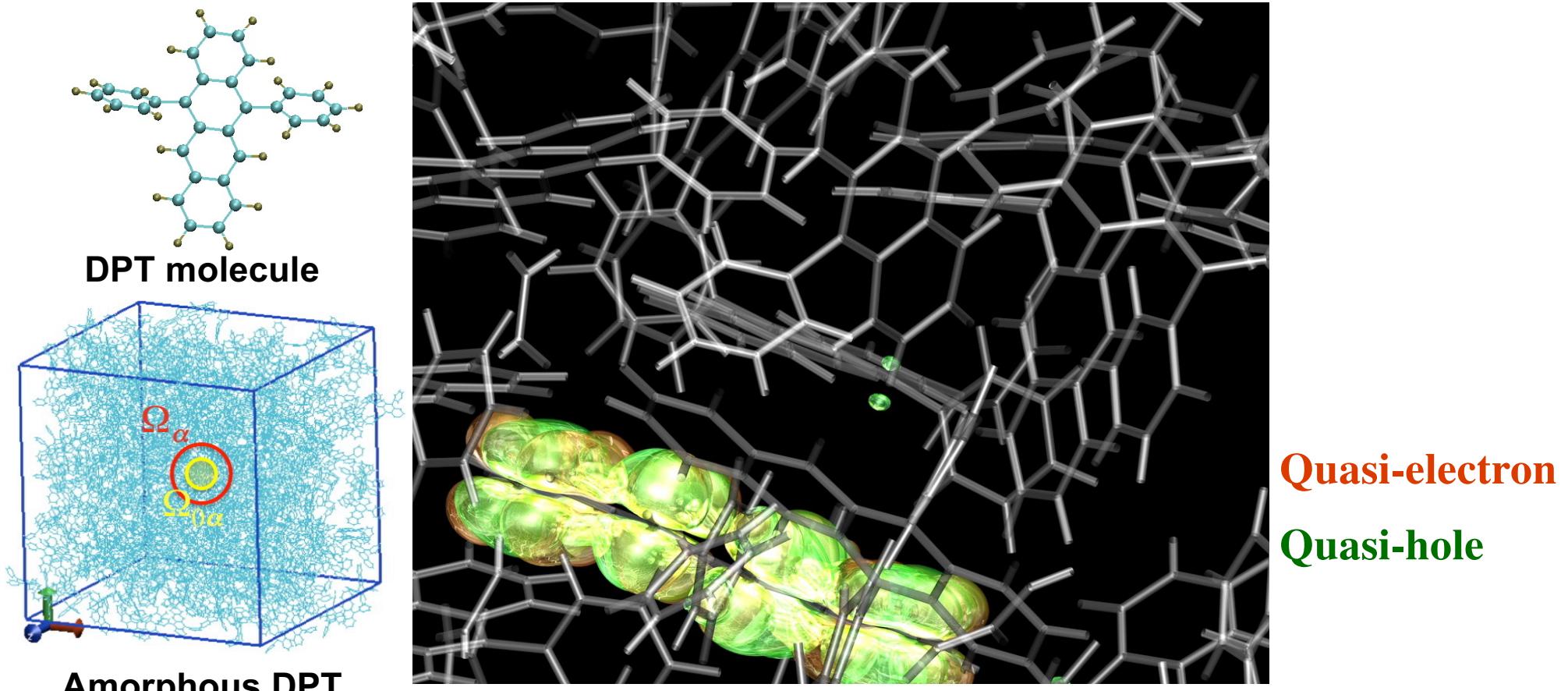


quasi-electron; quasi-hole

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

Simulating SF in Amorphous DPT

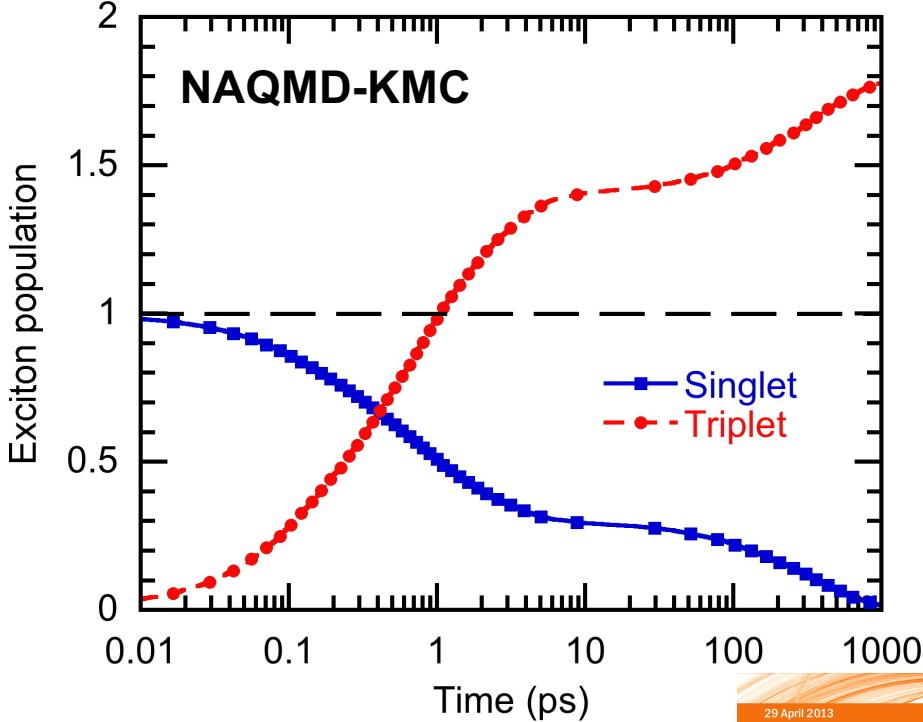
- Move up from molecules to microstructures
- Challenge: Unprecedented 10^4 -atom NAQMD simulation
- Computational approach: Divide-conquer-recombine (DCR) NAQMD



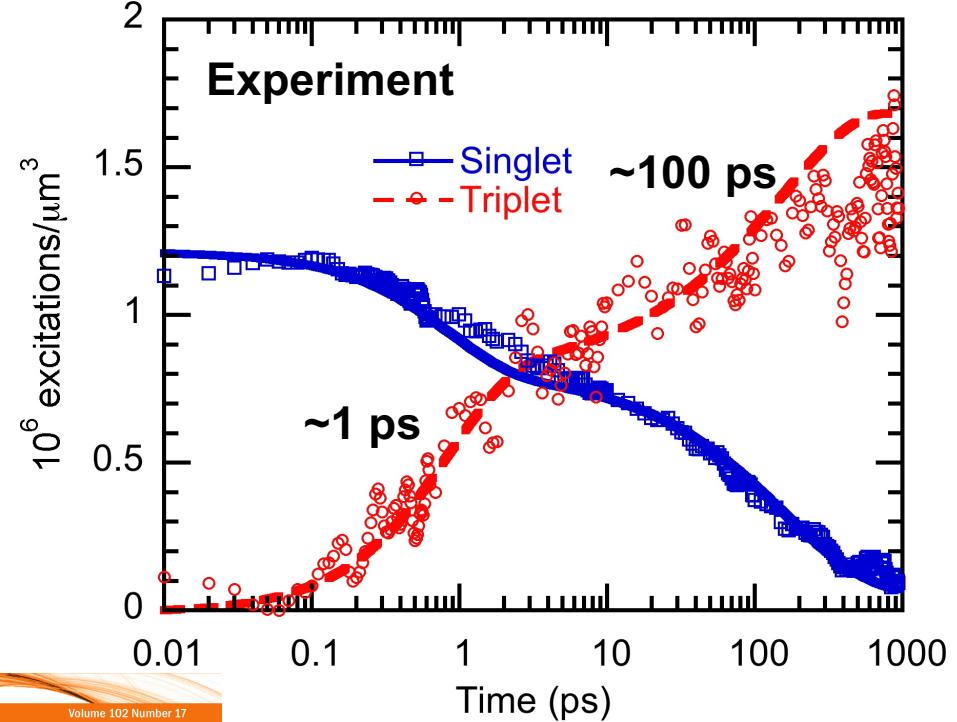
- Divide-conquer-recombine NAQMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT

NAQMD-informed Kinetic Monte Carlo

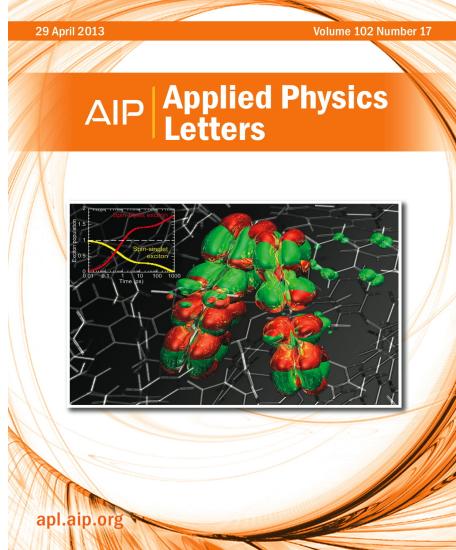
- NAQMD-KMC exciton population dynamics reproduces the experimentally observed two time scales (~ 1 & 100 ps) in amorphous DPT



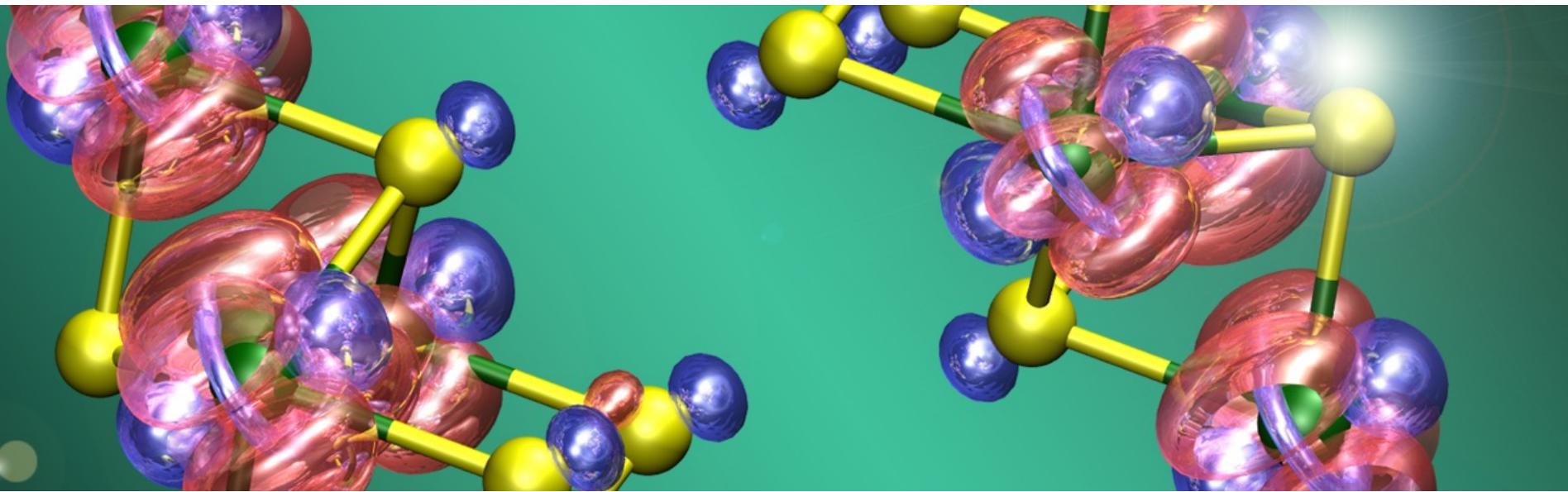
W. Mou *et al.*,
Appl. Phys. Lett.
100, 173301 ('13)



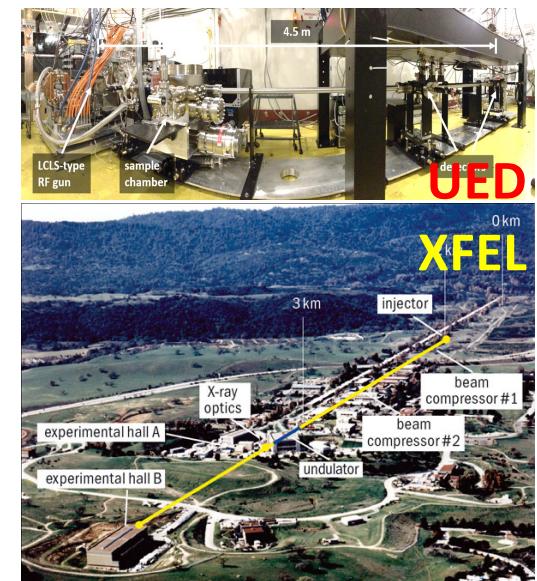
S. T. Roberts *et al.*,
J. Am. Chem. Soc.
134, 6388 ('12)



Simulation-Experiment Synergy



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



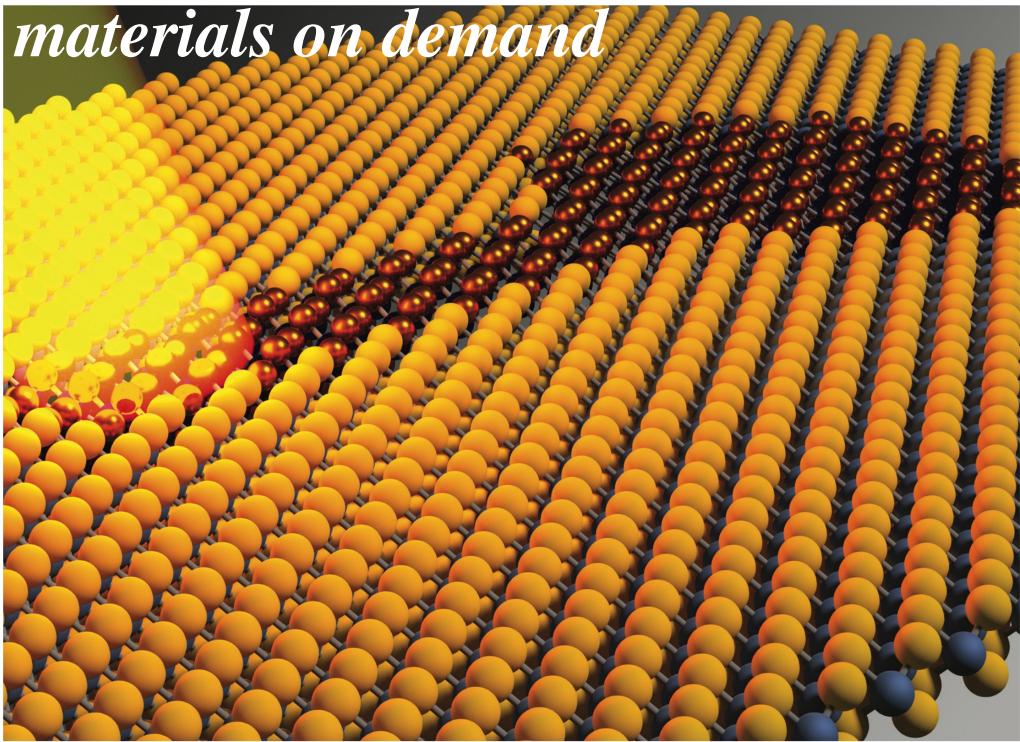
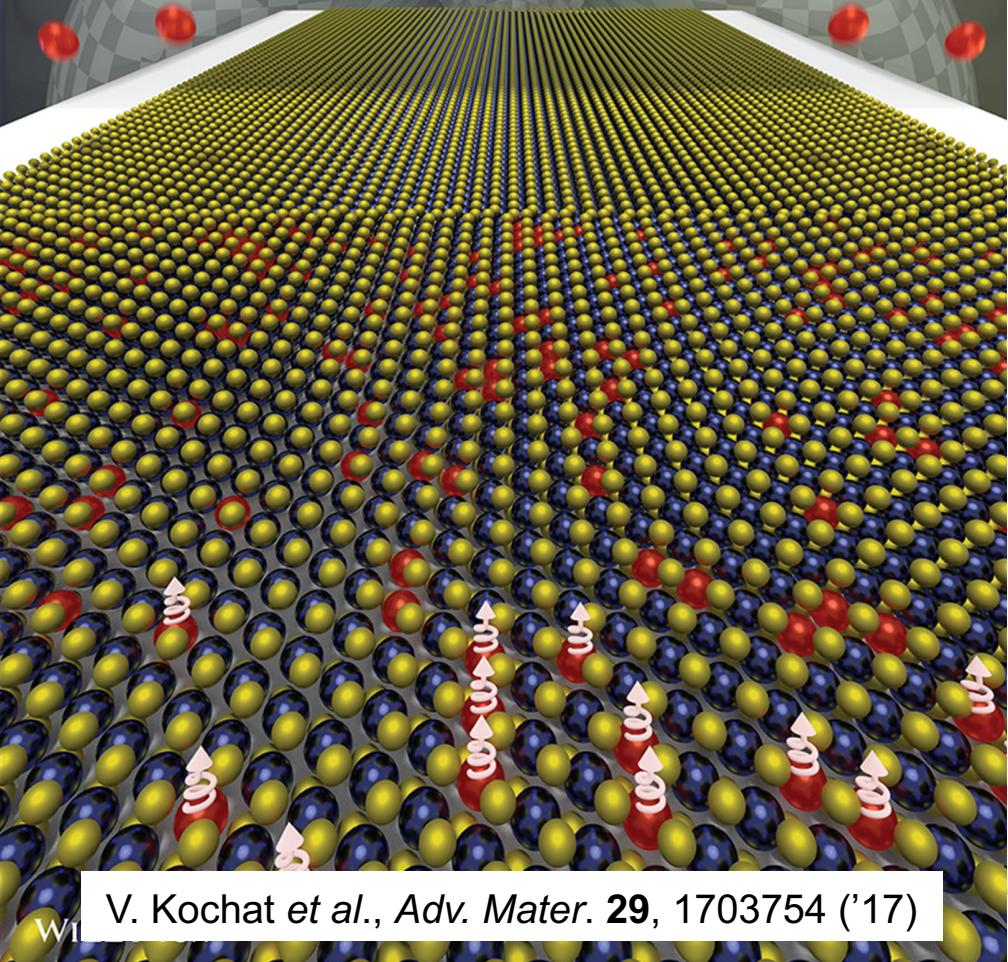
Ultrafast electron diffraction: M.F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)
X-ray free-electron laser: I. Tung *et al.*, *Nature Photon.* **13**, 425 ('19)

Quantum Molecular Dynamics Simulations

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Emergent quantum ADVANCED MATERIALS

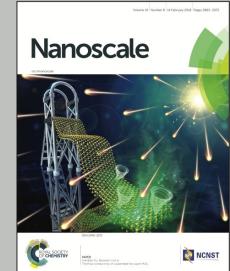


Showcasing research from Collaboratory for Advanced Computing and Simulations (CACS), University of Southern California, Los Angeles, USA.

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* **10**, 2742 ('18).

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



rsc.li/nanoscale

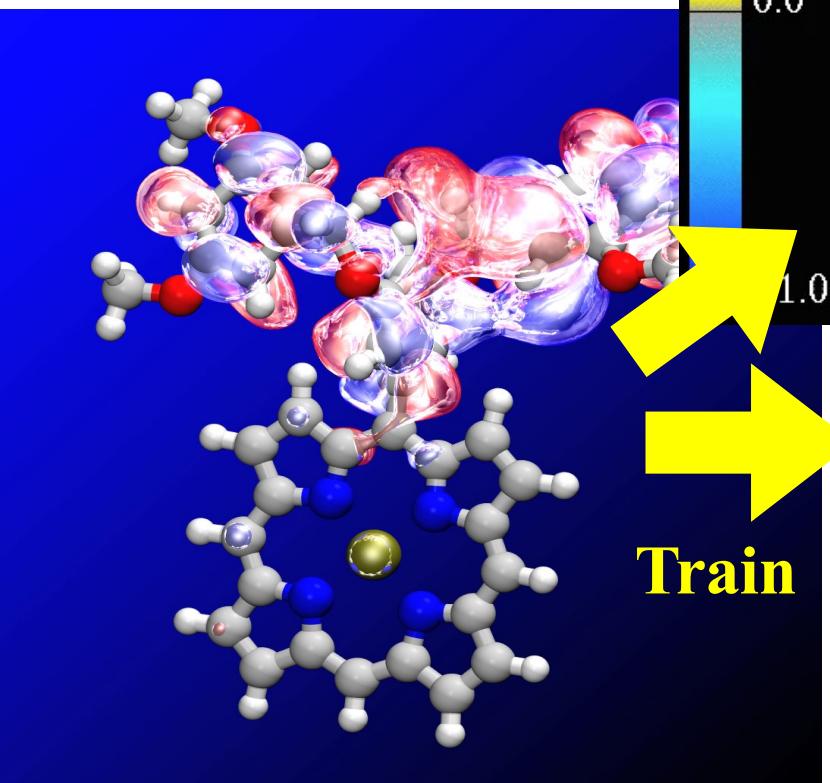
Registered charity number: 207890

Molecular Dynamics & Machine Learning

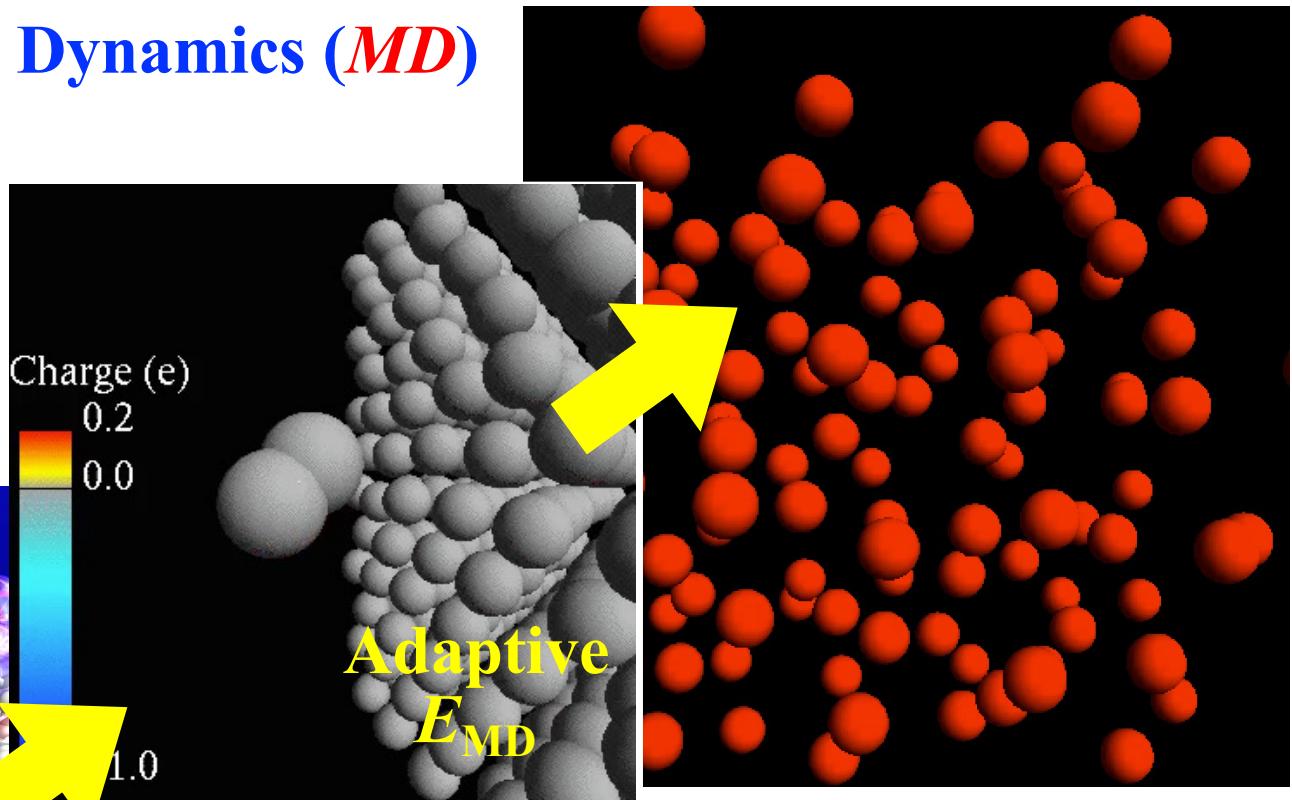
Molecular Dynamics (*MD*)

Reactive MD (*RMD*)

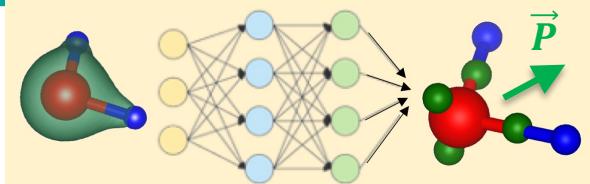
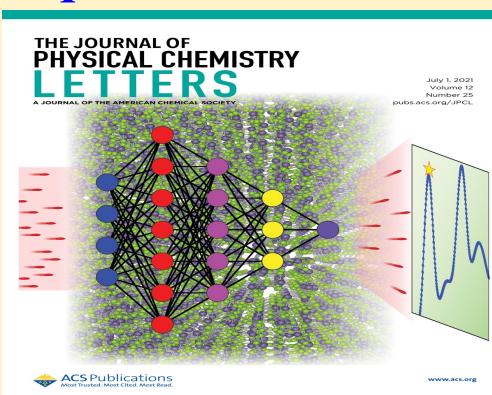
Nonadiabatic quantum MD (*NAQMD*)



[JPCL 12, 6020 \('21\)](#)



First principles-based neural-network quantum molecular dynamics (*NNQMD*)

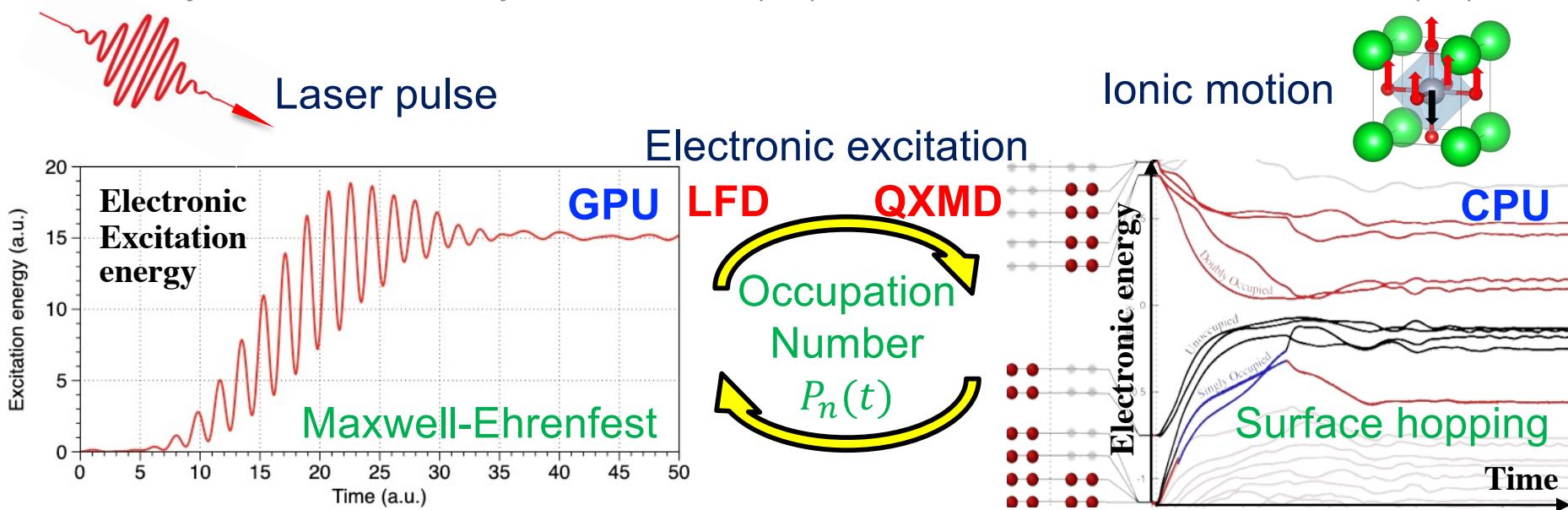


[Physical Review Letters Editor's choice \[126, 216403 \('21\)\]](#)

Light-Matter Interaction: DC-MESH

- DC-MESH (divide-&-conquer Maxwell + Ehrenfest + surface-hopping): $O(N)$ algorithm to simulate photo-induced quantum materials dynamics
- LFD (local field dynamics): Maxwell equations for light & real-time time-dependent density functional theory equations for electrons to describe light-matter interaction
- QXMD (quantum molecular dynamics with excitation): Nonadiabatic coupling of excited electrons & ionic motions based on surface-hopping approach
- “Shadow” LFD (GPU)-QXMD (CPU) handshaking *via* electronic occupation numbers with minimal CPU-GPU data transfer [Niklasson, *J. Chem. Phys.* 158, 154105 ('23)]
- GSLD: Globally sparse (interdomain Hartree coupling *via* multigrid) & locally dense (intradomain nonlocal exchange-correlation computation *via* BLAS) solver

Shimojo *et al.*, *J. Chem. Phys.* 140, 18A529 ('14); Lam *et al.*, *Nature Commun.* 15, 3479 ('24)



Linker *et al.*, *Science Adv.* 8, eabk2625 ('22); Razakh *et al.*, PDSEC (IEEE, '24)

DC-MESH Physics

- **MESH (Maxwell + Ehrenfest + surface-hopping):** Maxwell equations for light + real-time time-dependent density functional theory equations for electrons + *short-time Ehrenfest dynamics & long-time surface-hopping dynamics* for atoms

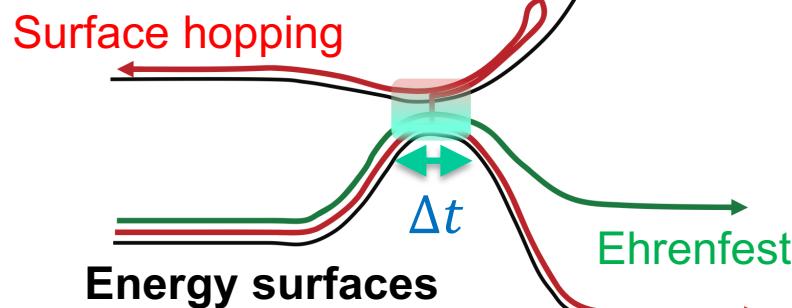
James Clark Maxwell
(1831-1879)



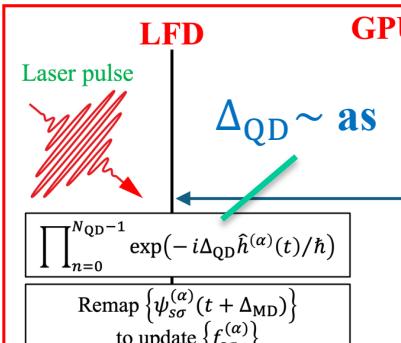
Surface-hopping
John Tully
(1942-)

Paul Ehrenfest (1880-1933)

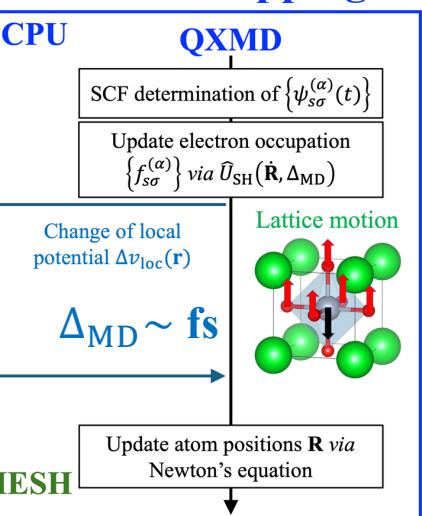
Uncertainty principle
 $\Delta E \Delta t > \hbar/2$



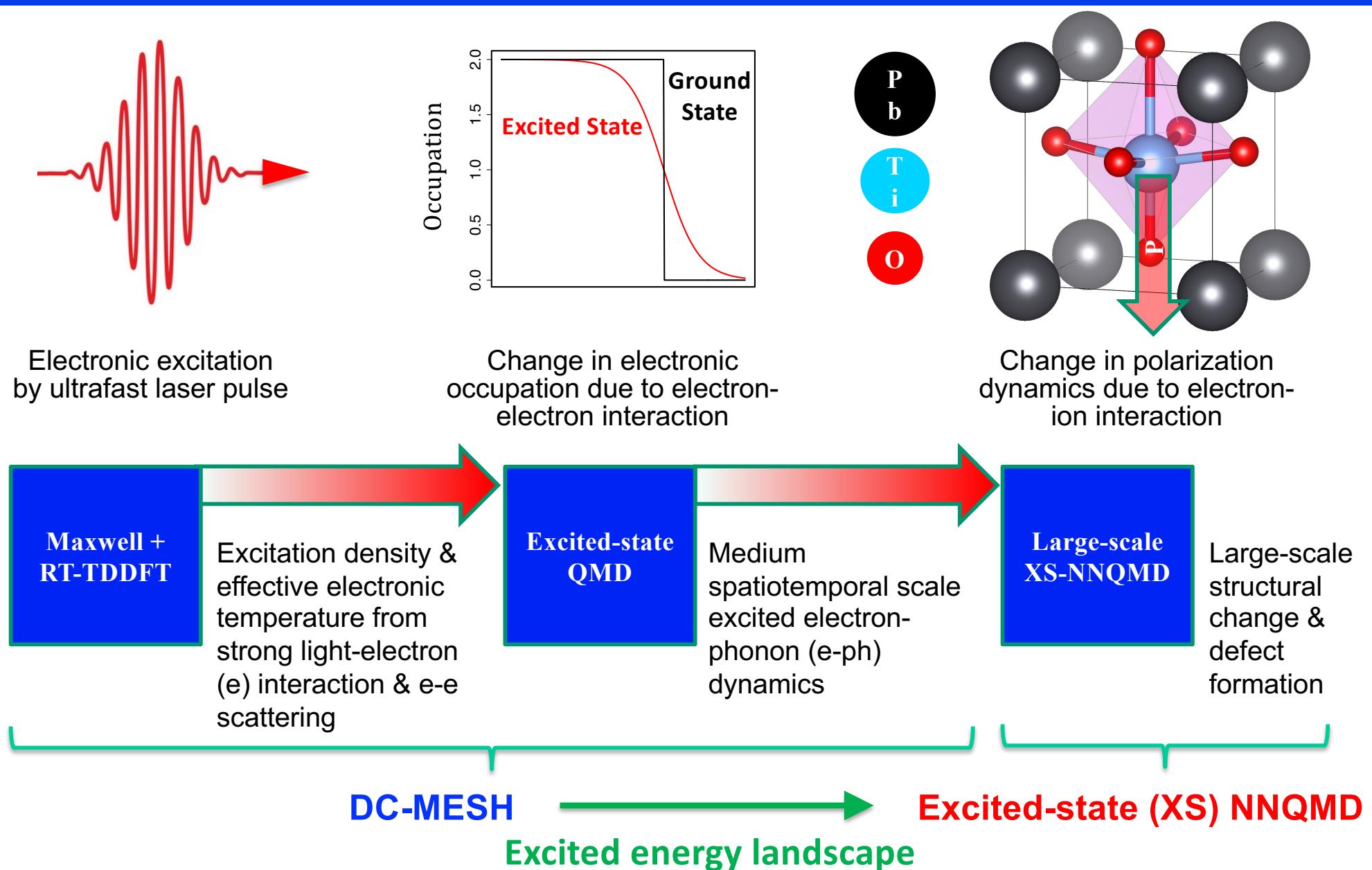
Maxwell-Ehrenfest



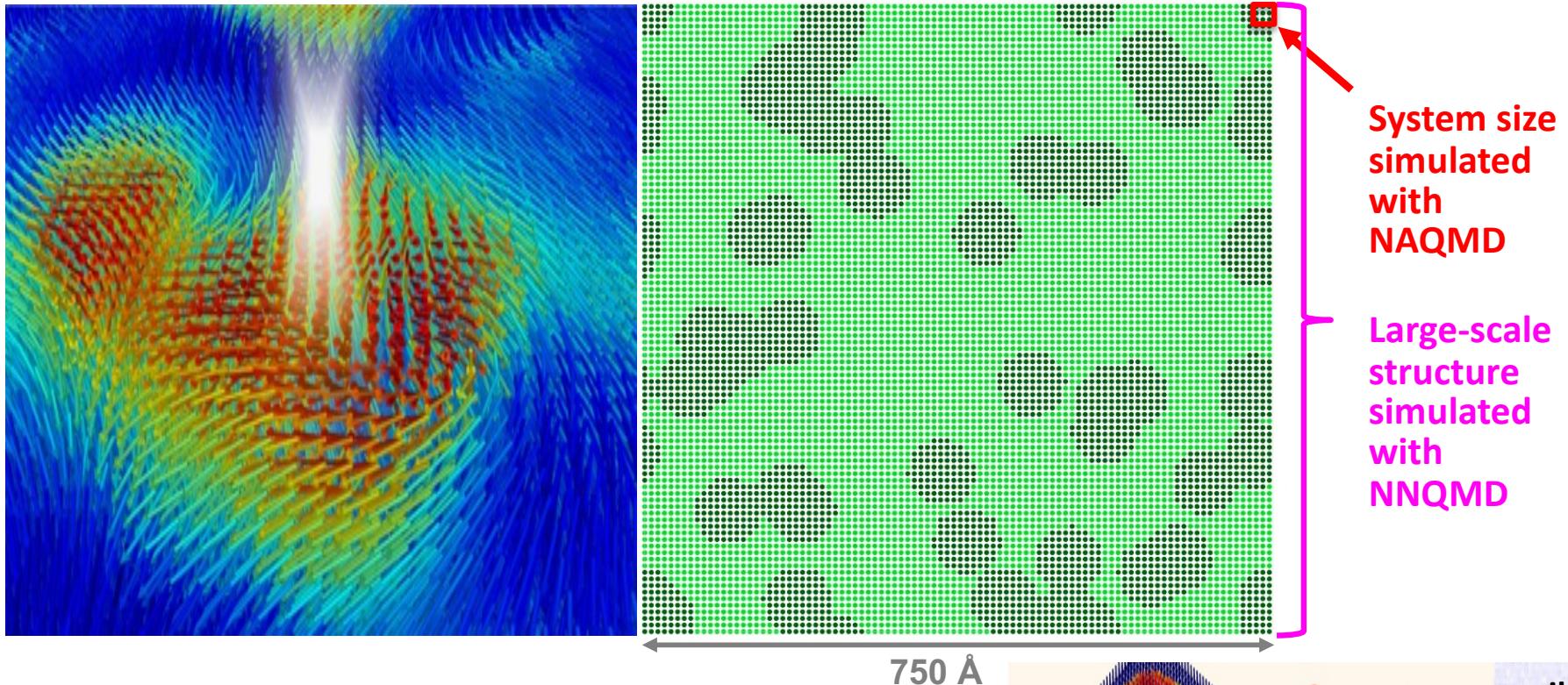
Surface-hopping



Multiscaling from DC-MESH to XS-NNQMD

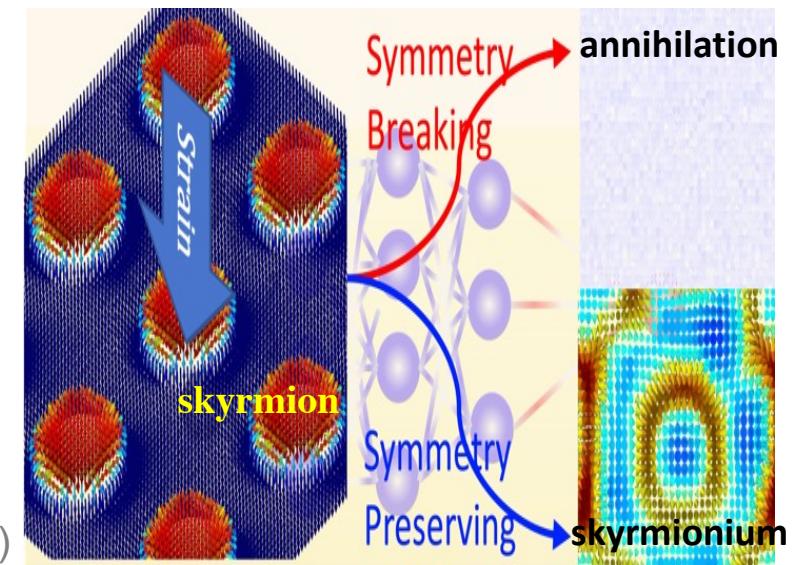


Application: Ferroelectric Opto-Toptronics



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

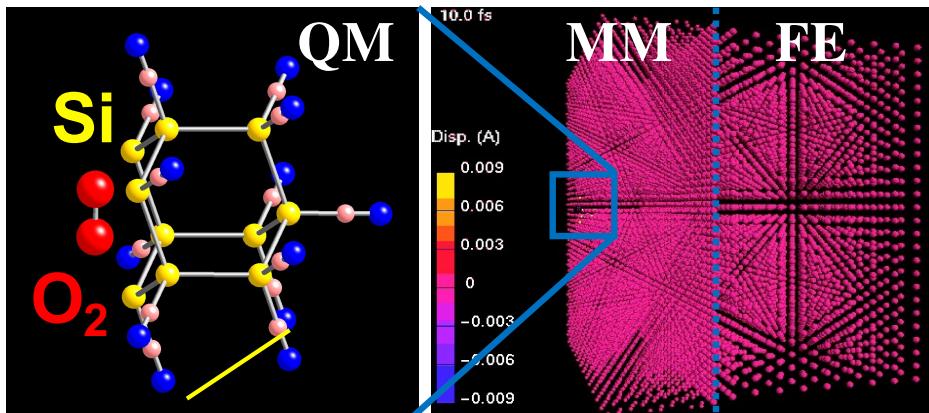
Linker et al., *Science Adv.* 8, eabk2625 ('22); *JPCL* 13, 11335 ('22)



Multiscale QM/MM → NN/MM

- **Multiscale quantum challenge:** Complex response of ferroelectric topological defects to external stimuli encompasses picosecond-to-nanosecond time & nanometer-to-micrometer length scales
- **QM/MM:** Overcame the challenge taking cue from multiscale quantum-mechanics (QM)/molecular mechanics (MM) approach (2013 Nobel chemistry prize)

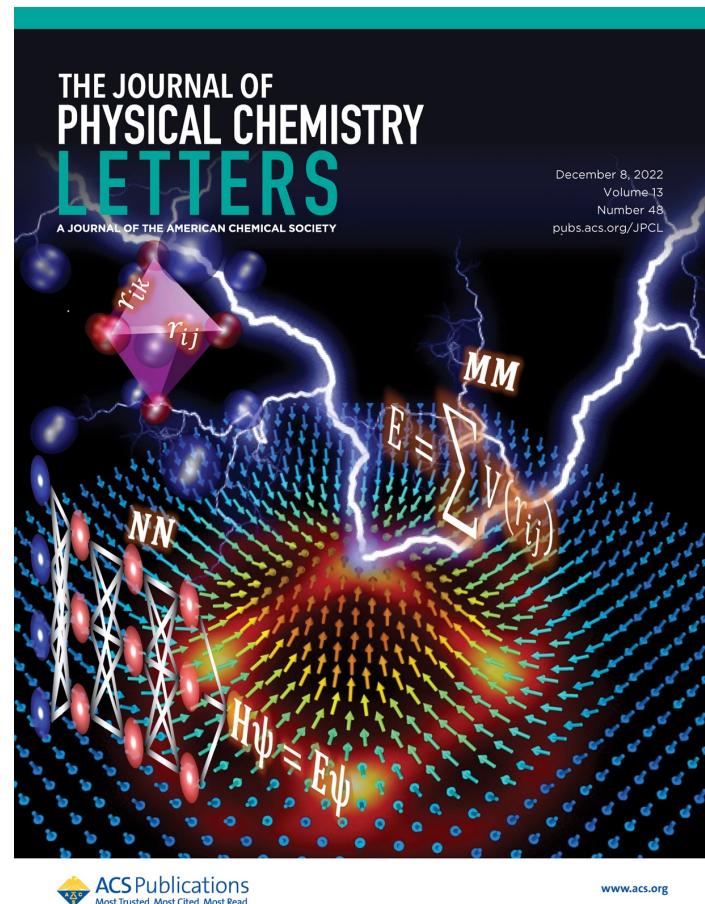
Warshel, *Angew. Chem.* **53**, 10020 ('14)



QM/MM/FE (finite-element method)

Ogata et al, *Comput. Phys. Commun.* **138**, 143 ('01)

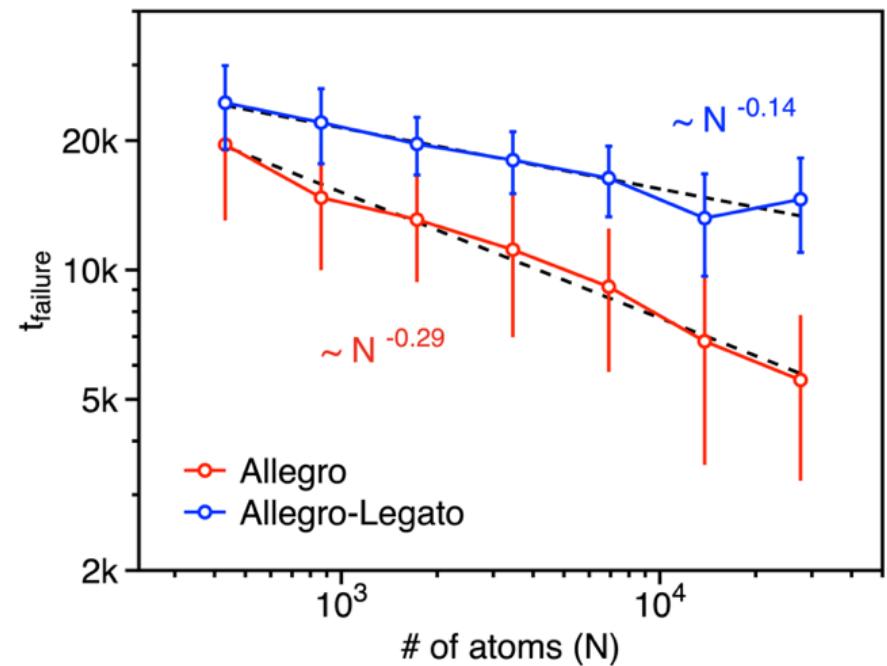
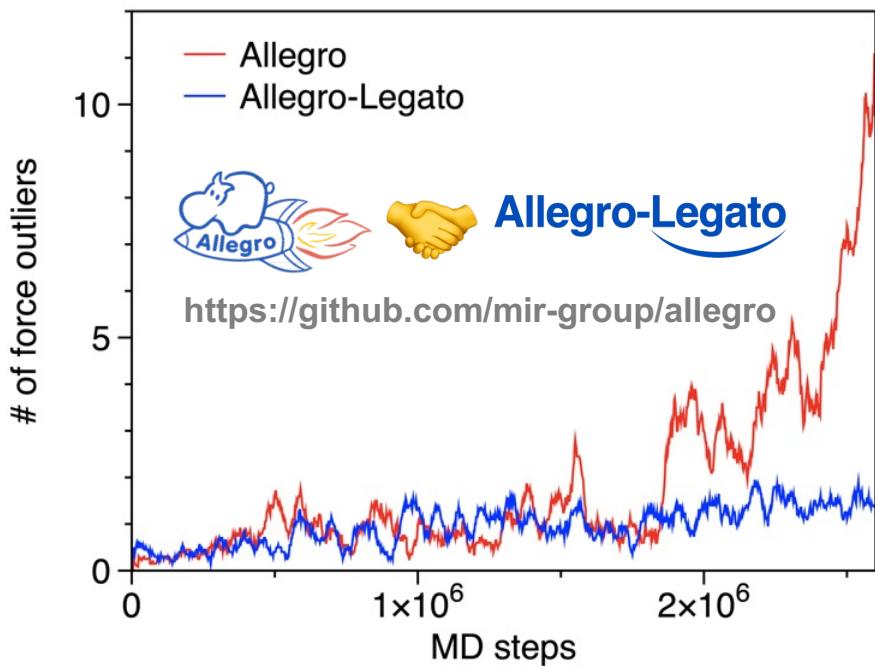
- **NN/MM:** NNQMD for ferroelectric (PbTiO_3 : PTO) embedded in MM for paraelectric (SrTiO_3 : STO) to apply appropriate strain boundary condition



Linker et al., *J. Phys. Chem. Lett.*
13, 11335 ('22)

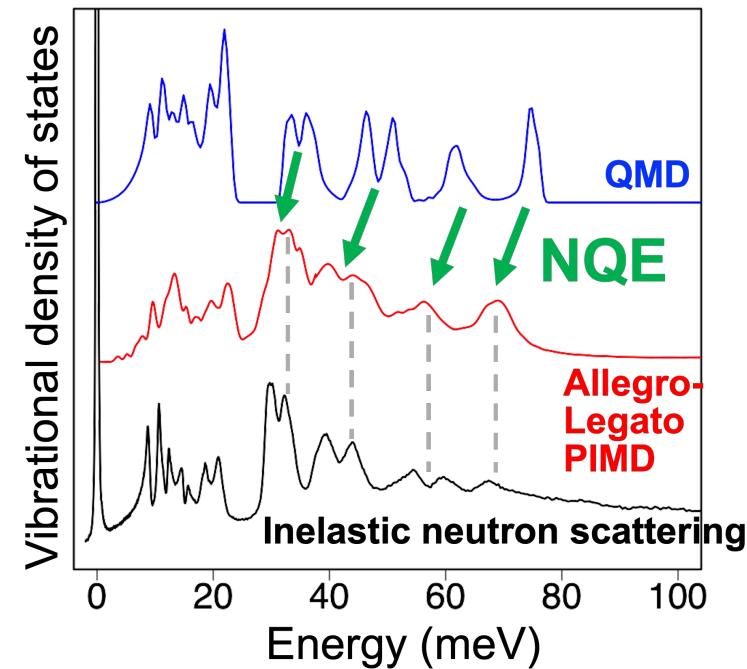
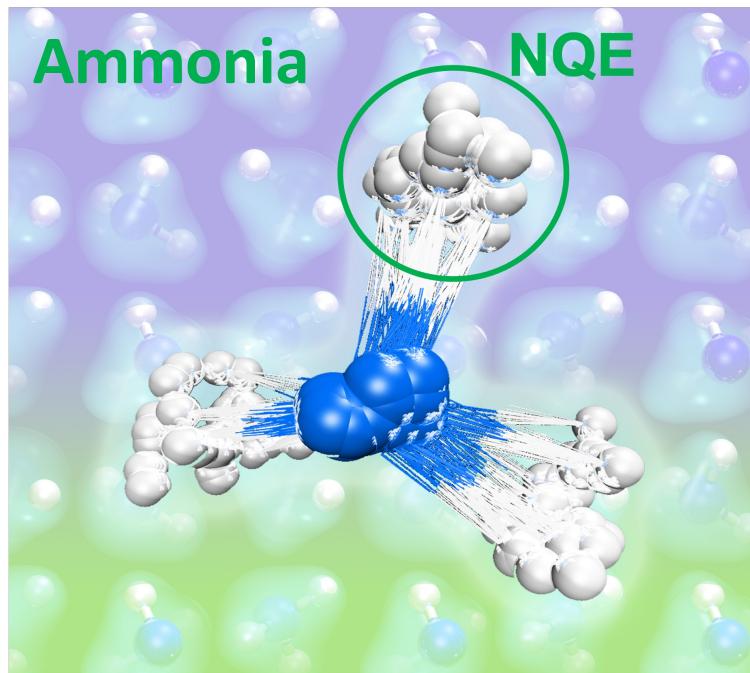
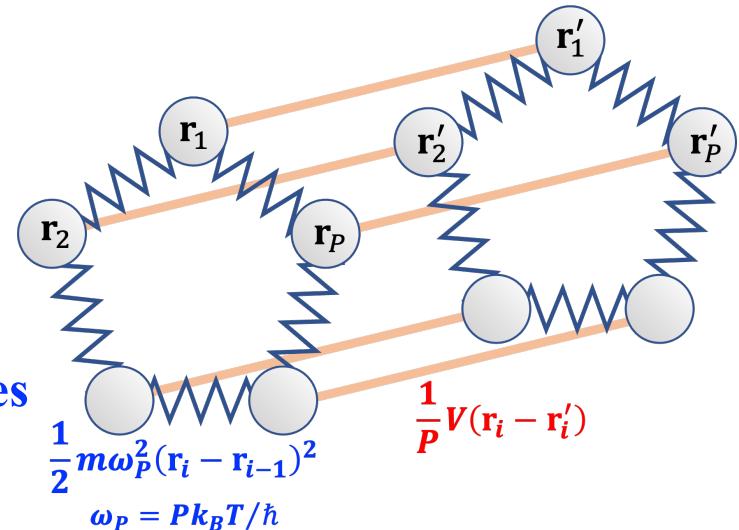
Fast & Robust NNQMD: Allegro-Legato

- **Allegro (fast) NNQMD:** State-of-the-art *accuracy & speed* founded on group-theoretical equivariance & local descriptors [Musaelian et al., *Nat. Commun.* **14**, 579 ('23)]
 - **Fidelity-scaling problem:** On massively parallel computers, growing number of unphysical (adversarial) force predictions prohibits simulations involving larger numbers of atoms for longer times
 - **Allegro-Legato (fast and “smooth”):** *Sharpness aware minimization (SAM)* enhances the *robustness* of Allegro through improved smoothness of loss landscape
- $\mathbf{w}_* = \operatorname{argmin}_{\mathbf{w}} [L(\mathbf{w}) + \max_{\|\boldsymbol{\epsilon}\|_2 \leq \rho} \{L(\mathbf{w} + \boldsymbol{\epsilon}) - L(\mathbf{w})\}]$ (L : loss; \mathbf{w} : model parameters)
- **Elongated time-to-failure scaling, $t_{\text{failure}} = O(N^{-\beta})$,** without sacrificing accuracy or speed, thereby achieving spectroscopically stable long-time Hamiltonian trajectory

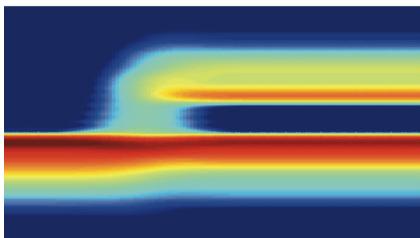
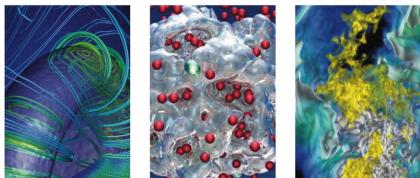


Nuclear-Quantum NNQMD

- **Allegro-Legato-PIMD:** Incorporate nuclear quantum effect (NQE) through path-integral molecular dynamics (PIMD)
- NNQMD trained by QMD achieves the required large number (P) of replicas at low temperature & long-time Hamiltonian dynamics
- NQE down-shifts inter-molecular vibrational modes in ammonia to explain high-resolution inelastic neutron scattering experiments



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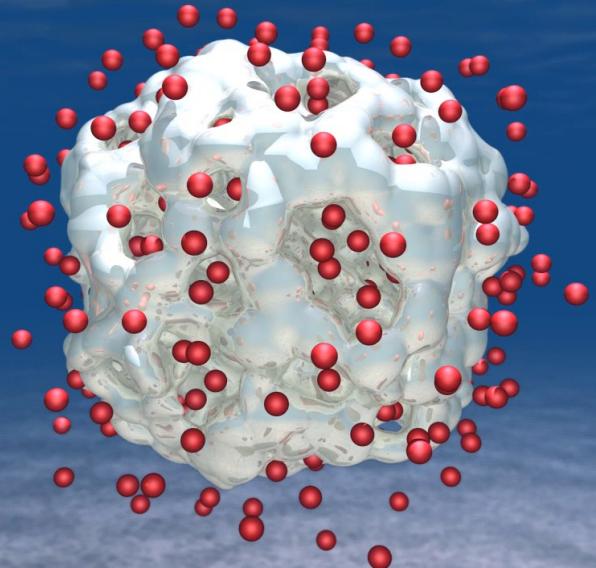
One of the 10 initial
simulation users of the
2 exaflop/s* Aurora



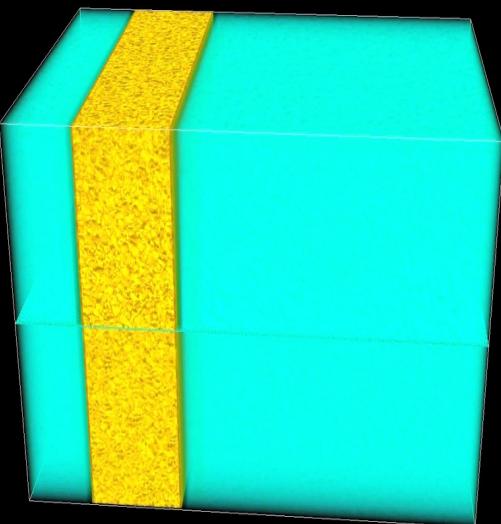
*exaflop/s = 10^{18} mathematical
operations per second



17K-atom QMD

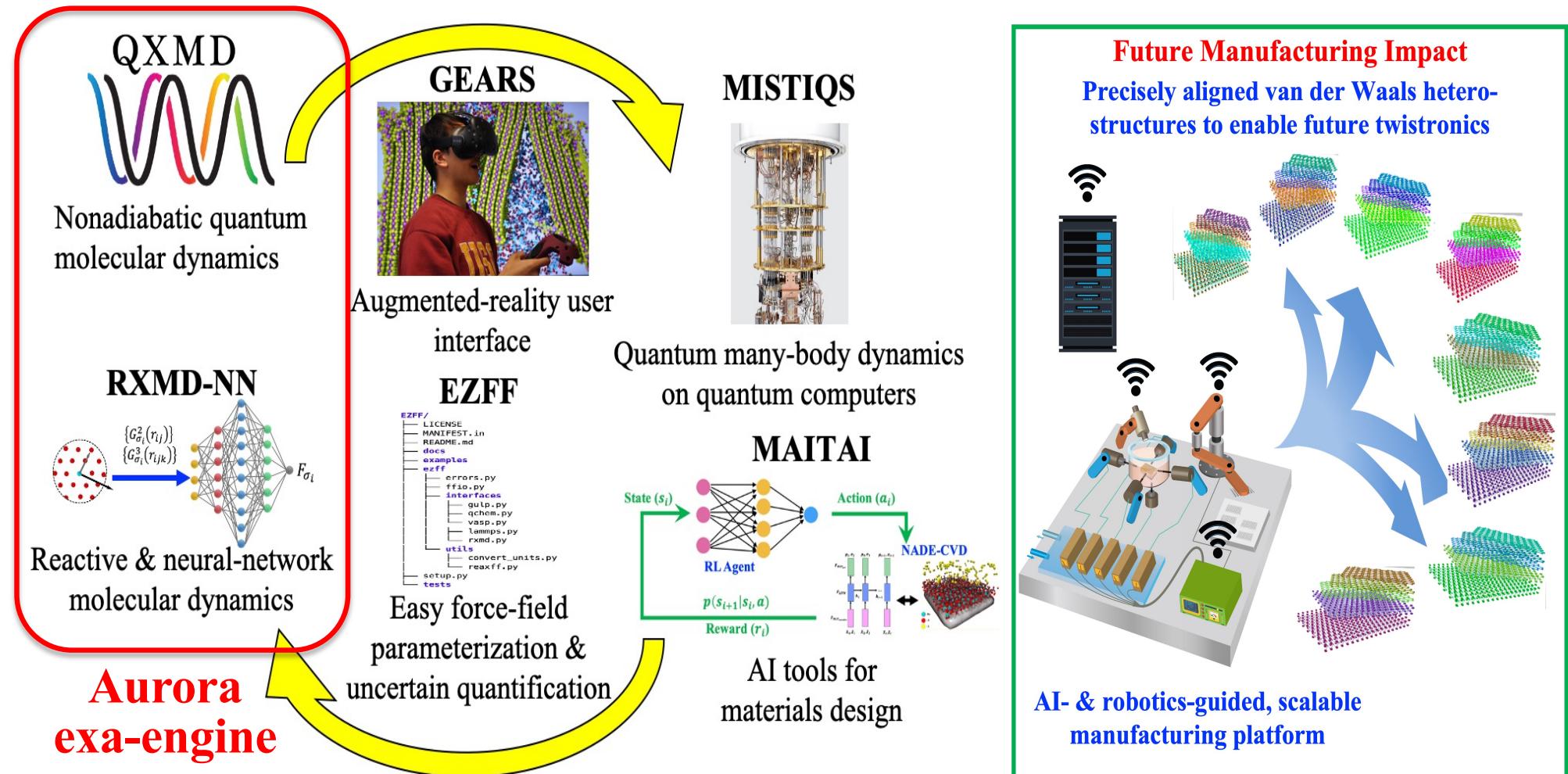


10⁹-atom RMD



AIQ-XMaS Software for Manufacturing

AI and Quantum-Computing Enabled Exascale Materials Simulator



Synergy with \$3.75M NSF Future Manufacturing and
\$1M NSF CyberTraining projects

Where to Go from Here

- Quantum molecular dynamics (QMD) simulation, *i.e.*, combination of QD and MD simulations

PHYS 760: *Extreme-scale quantum simulations*

Detailed lecture notes on QMD simulations are available at

<https://aiichironakano.github.io/phys760.html>

- Textbooks on QMD simulation

***Ab Initio Molecular Dynamics*, D. Marx & J. Hutter** (Cambridge University Press, '09)

***Electronic Structure*, R. M. Martin** (Cambridge University Press, '04)

- QMD simulation software

VASP: <https://vasp.at>

Quantum Espresso: <https://www.quantum-espresso.org>

QXMD: <https://usccacs.github.io/QXMD/>