

Iterative Energy Minimization for Quantum Molecular Dynamics

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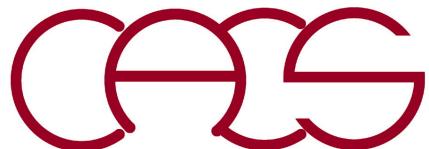
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From quantum dynamics to eigenvalue problems



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

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

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

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

- Filtering in the ground state

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

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

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

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

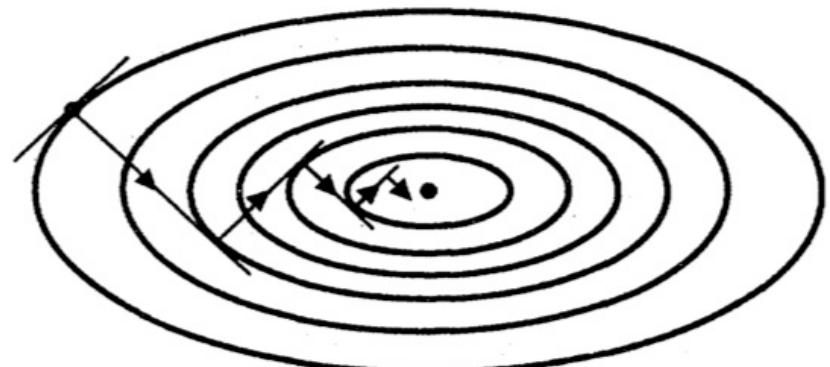
- Gradient (for a normalized wave function)

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

- 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

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

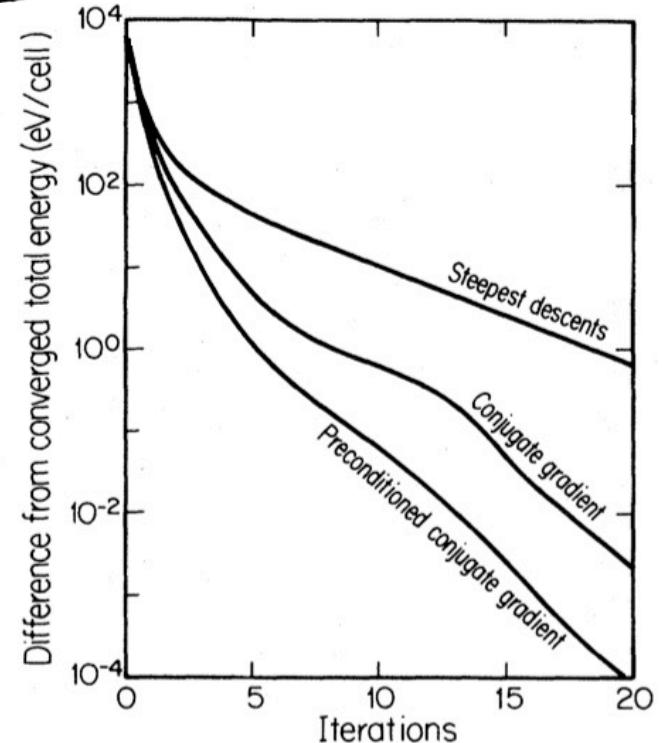
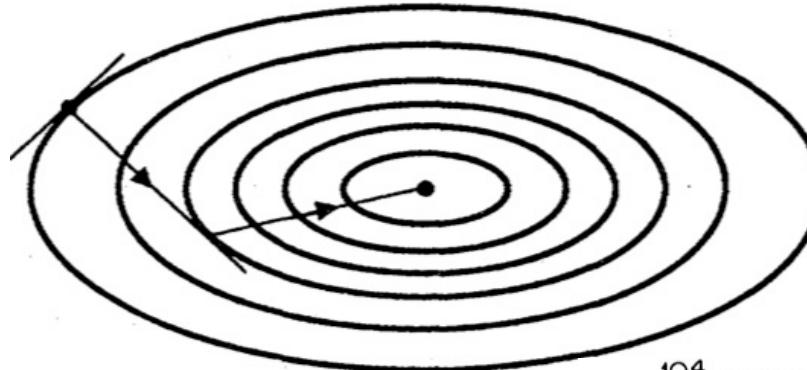
$$g_i \leftarrow g_{i-1} - \frac{g_{i-1} \cdot g_{i-1}}{\tilde{g}_i \cdot h \cdot \tilde{g}_i} h \cdot \tilde{g}_i$$

if convergent, **exit**

endfor

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

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



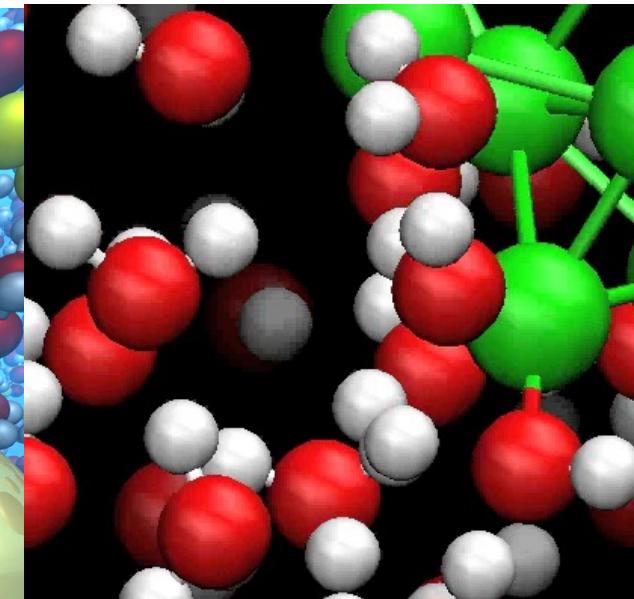
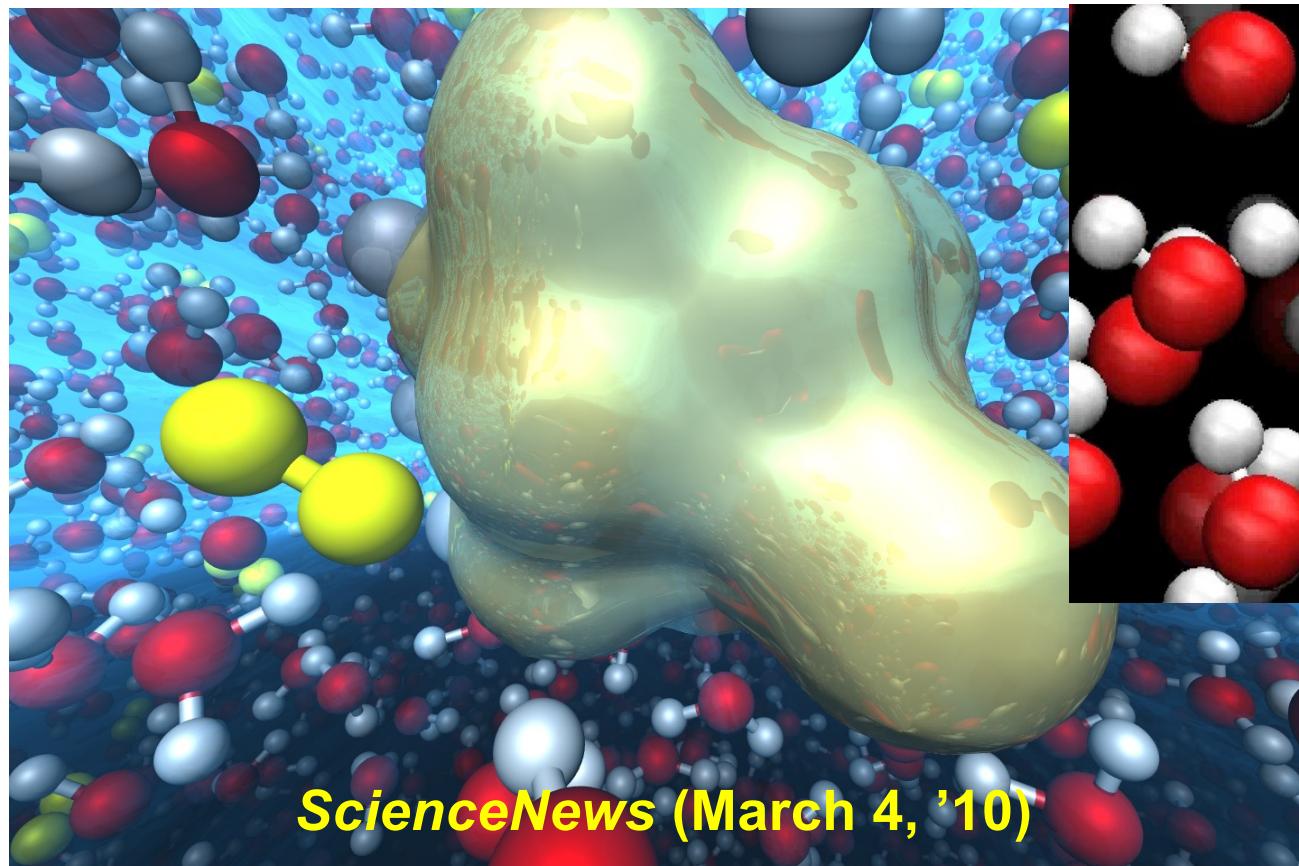
Quantum Molecular Dynamics

- 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 ($n = 1, \dots, N_{\text{nucleus}}$)
 $\psi_*(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}}) \leftarrow \text{argmin}_E[\psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}}), \{\mathbf{R}_n\}]$ CG

- 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



Born-Oppenheimer Approximation



1927

Nº 20

ANNALEN DER PHYSIK VIERTE FOLGE. BAND 84

1. *Zur Quantentheorie der Moleküle;*
von M. Born und R. Oppenheimer

Academic Genealogy

LINDSAY BASSMAN PEDIGREE

CARL GAUSS

1777 - 1855
University of Gottingen
Math/Physics 1799

CHRISTOPHER GUDERMANN

1798 - 1852
University of Gottingen
Math 1832

KARL WEIERSTRASS

1815 - 1897
University of Bonn
Math

CARL RUNGE

1856 - 1927
Berlin University
Math/Physics 1880

MAX BORN

1882 - 1970
University of Göttingen
Physics/Math 1906

J. ROBERT OPPENHEIMER

1904 - 1967
University of Göttingen
Physics 1927

DAVID BOHM

1917 - 1992
University of California, Berkeley
Physics 1943

PHYSICAL REVIEW

VOLUME 92, NUMBER 3

NOVEMBER 1, 1953

A Collective Description of Electron Interactions : III. Coulomb Interactions in a Degenerate Electron Gas

DAVID BOHM, Faculdade de Filosofia, Ciencias e Letras, Universidade de São Paulo, São Paulo, Brazil

AND

DAVID PINES, Department of Physics, University of Illinois, Urbana, Illinois

SETSUO ICHIMARU

1935 -
University of Illinois
Physics 1962

AIICHIRO NAKANO

1963 -
University of Tokyo
Physics 1989

LINDSAY ELIZABETH BASSMAN

1989 -
University of Southern California
Physics 2020

In the Beginning ...



Journey of Electrons and Atoms: Personal Story of Quantum Mechanics and Supercomputing (Nov. 16 & 17, '24, Culver City, CA)



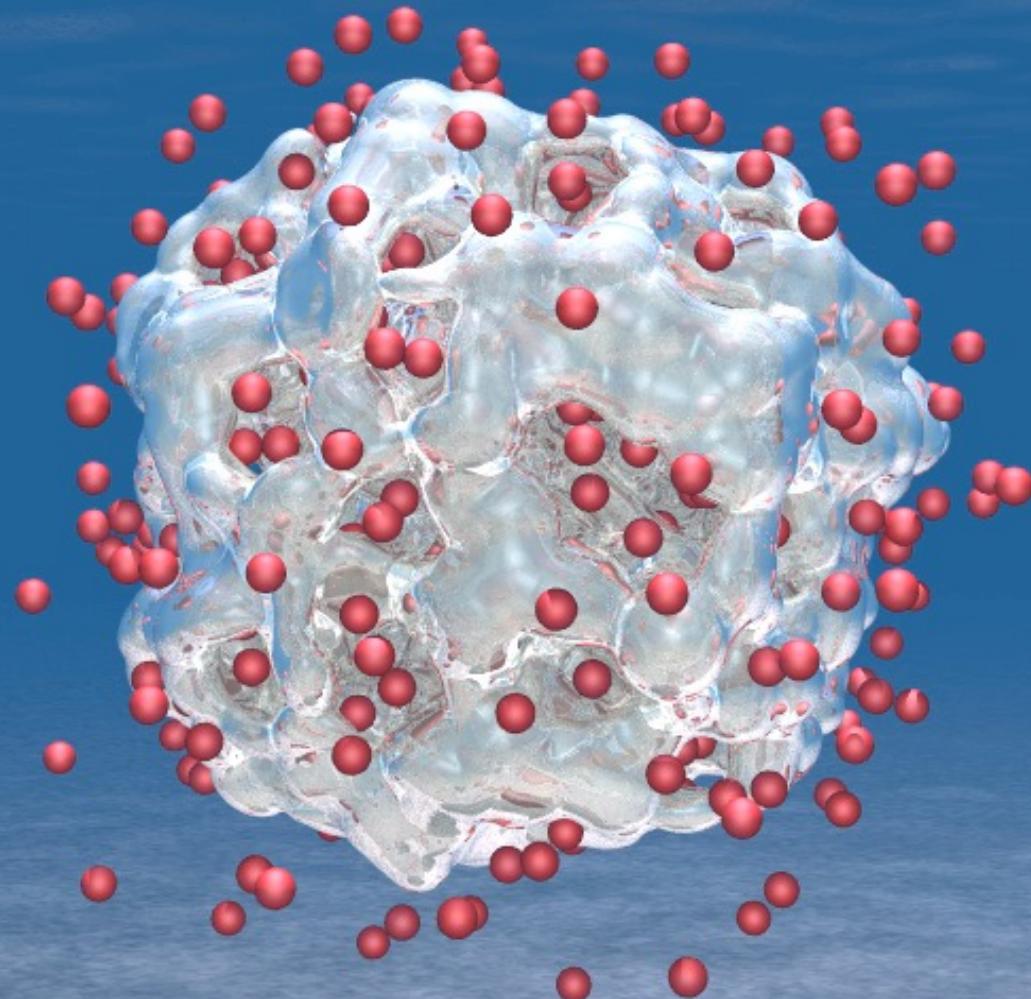
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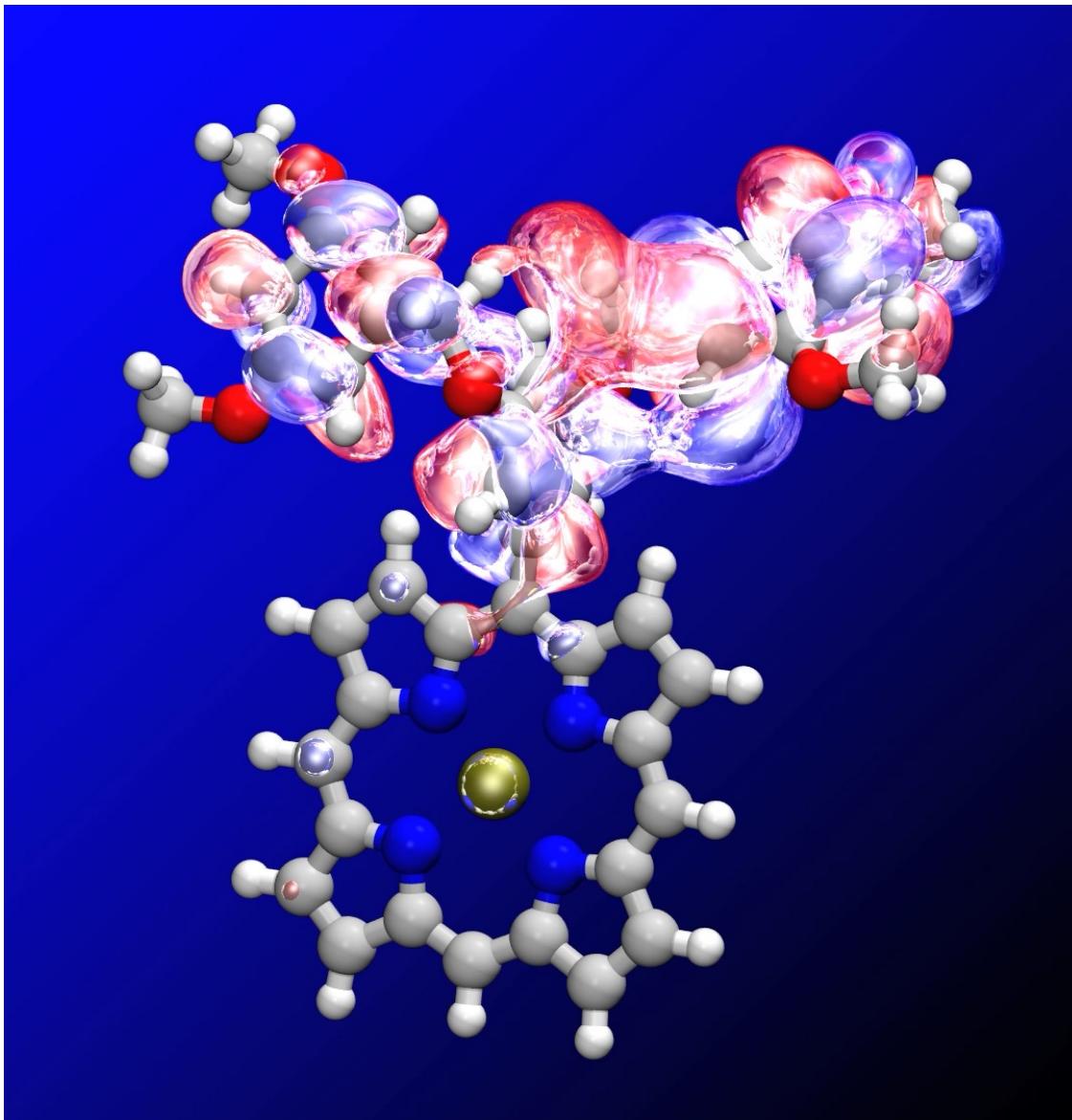
H₂ Production from Water Using LiAl Particles

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



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

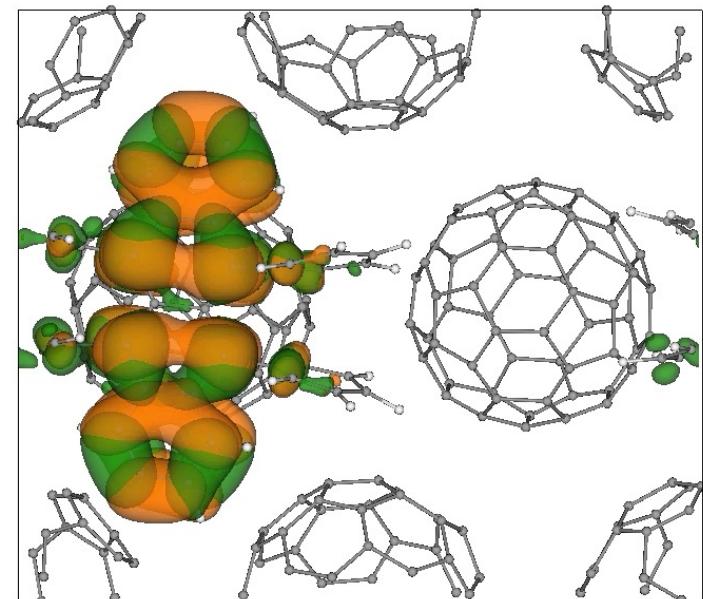
Nonadiabatic Quantum Molecular Dynamics



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

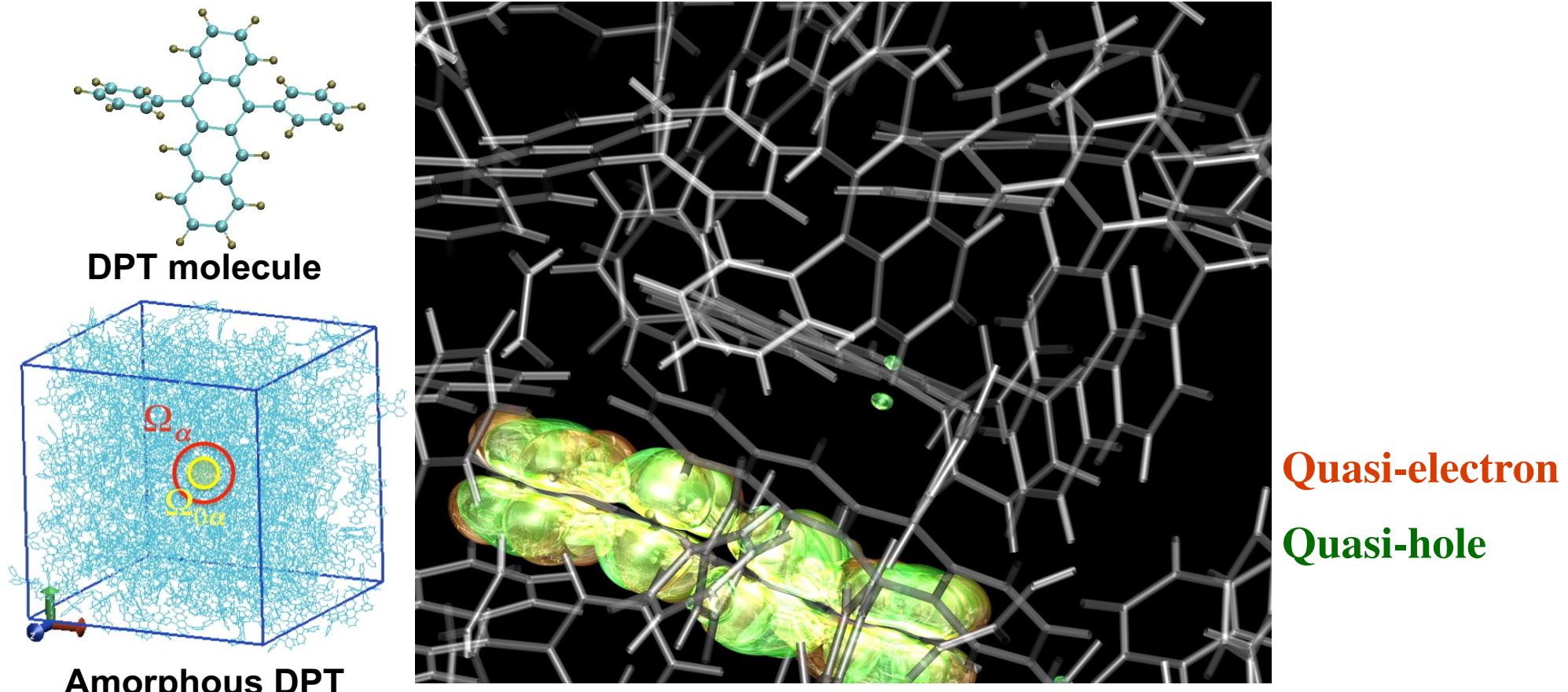


quasi-electron; quasi-hole

- **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

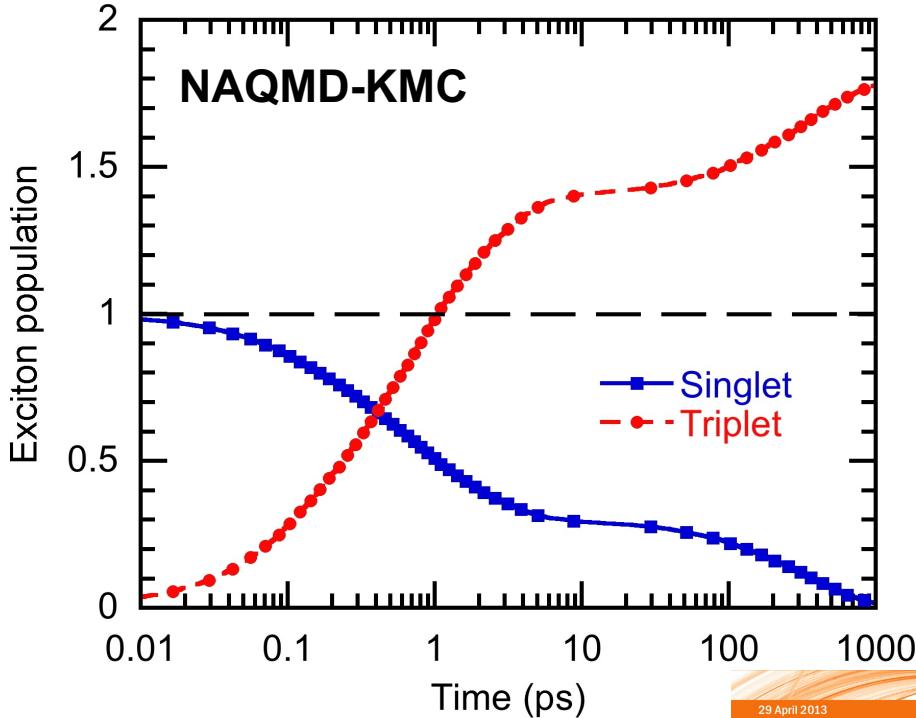
- Move up from molecules to microstructures
- Challenge: Unprecedented 10^4 -atom NAQMD simulation
- Computational approach: Divide-conquer-recombine (DCR) NAQMD



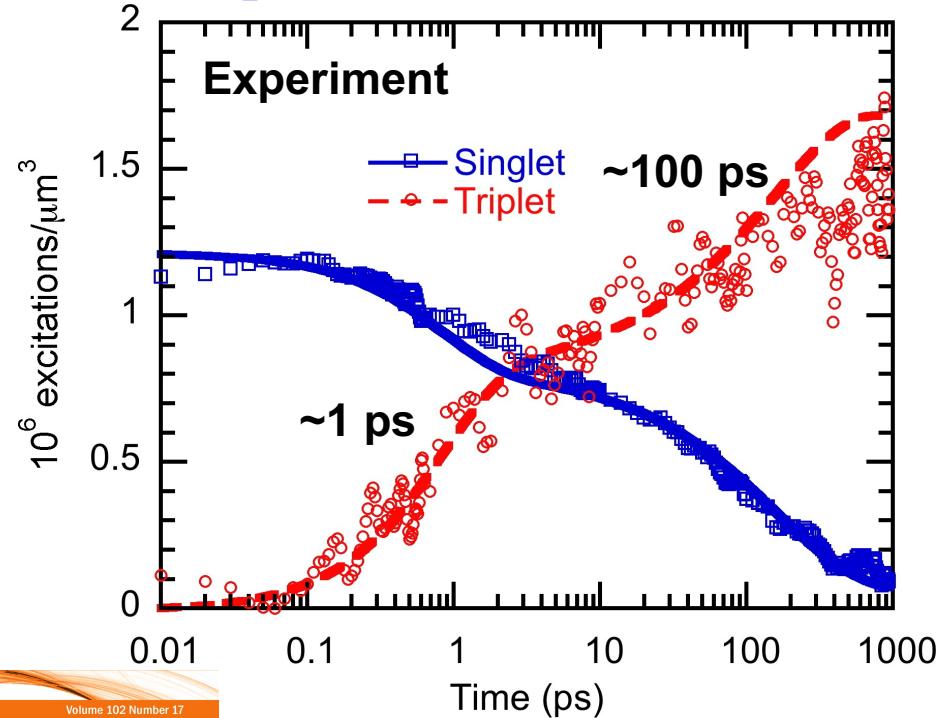
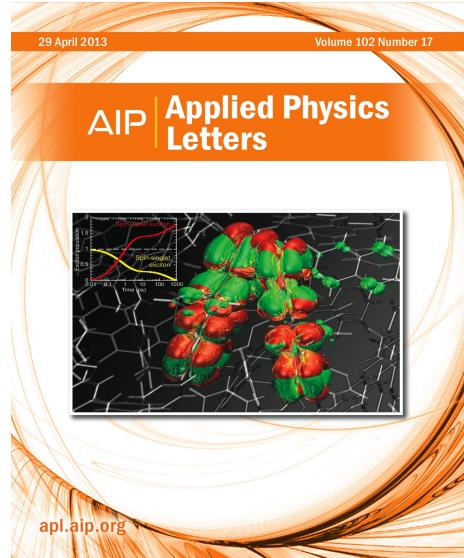
- Divide-conquer-recombine NAQMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT

NAQMD-informed Kinetic Monte Carlo

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

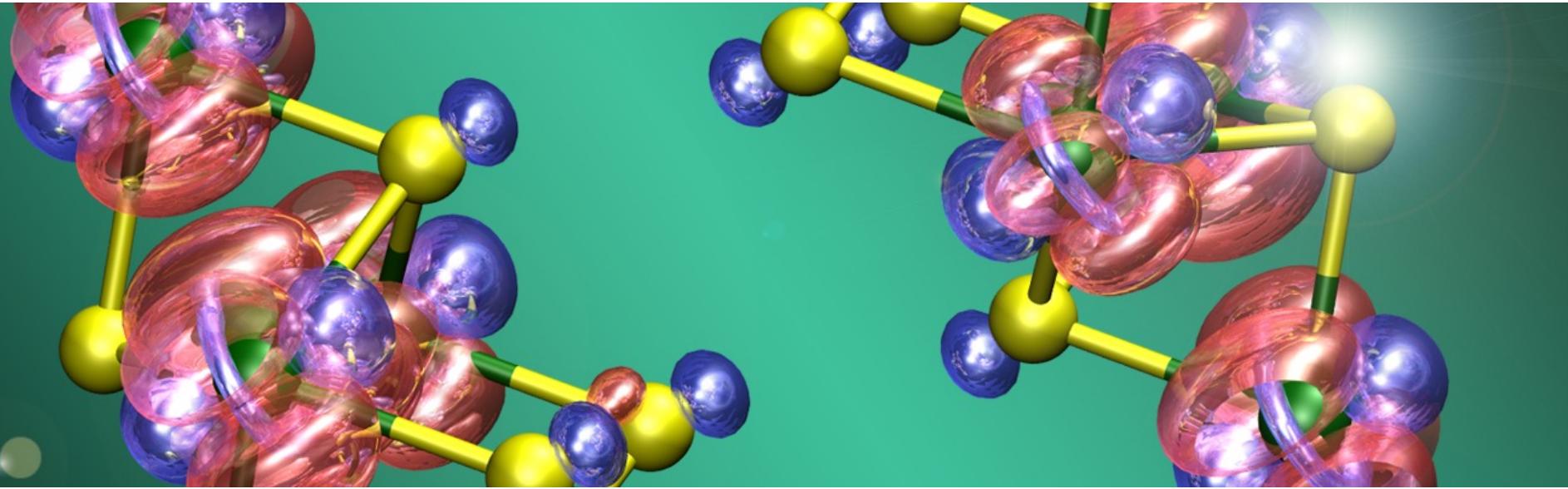


W. Mou *et al.*,
Appl. Phys. Lett.
100, 173301 ('13)

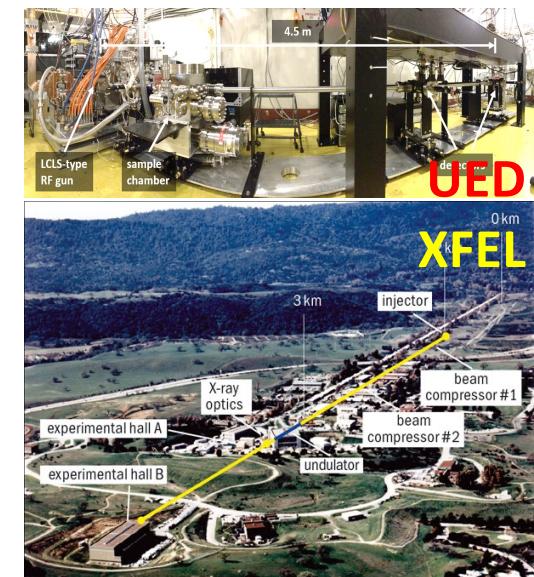


S. T. Roberts *et al.*,
J. Am. Chem. Soc.
134, 6388 ('12)

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)

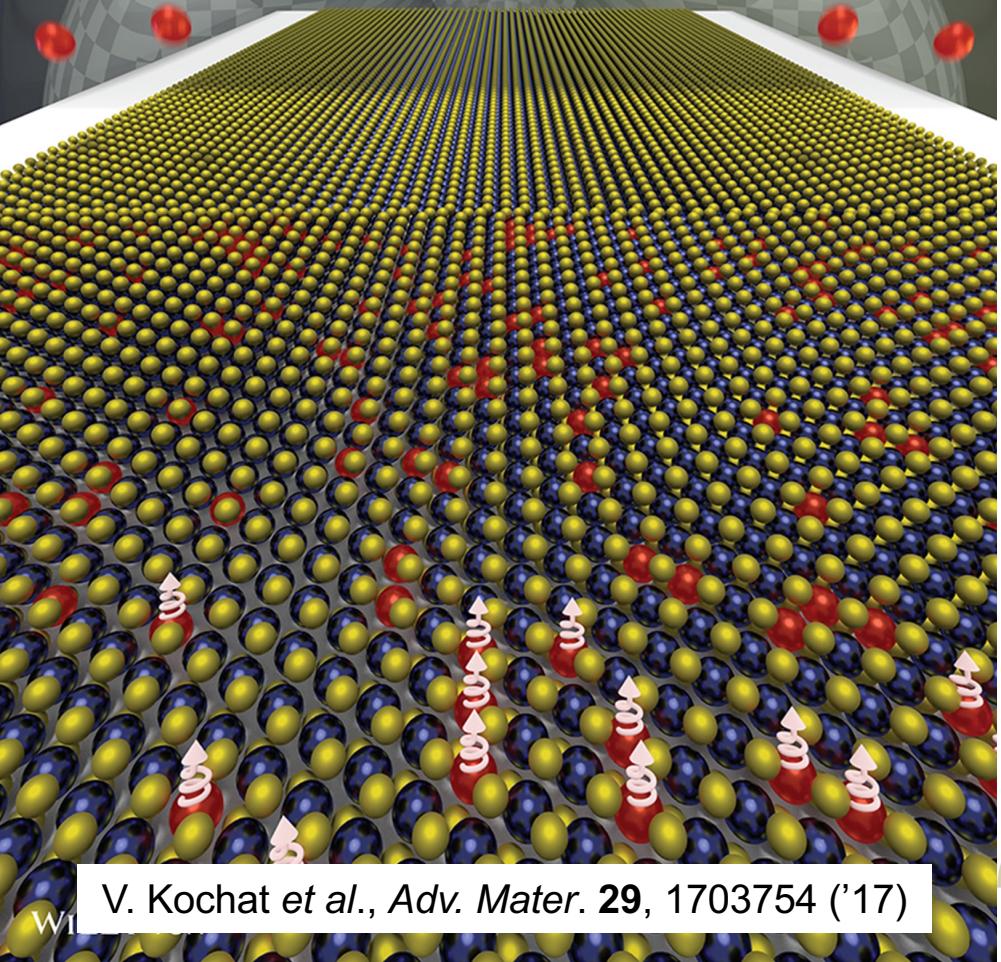
Quantum Molecular Dynamics Simulations

Vol. 29 • No. 43 • November 20 • 2017

www.advmat.de

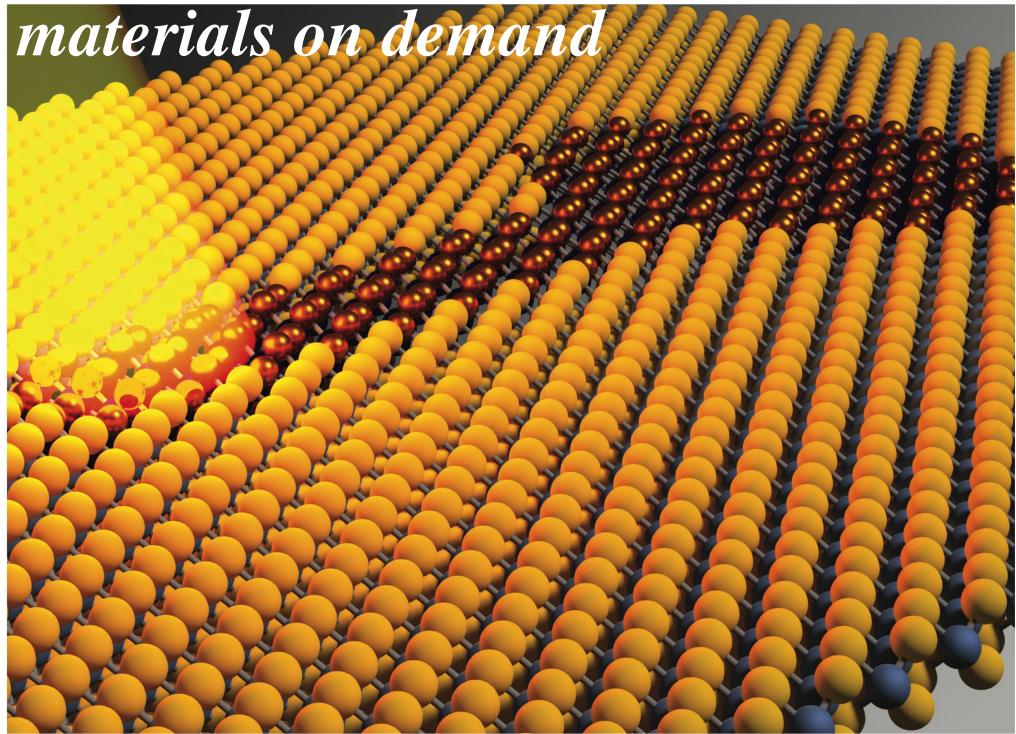
Emergent quantum

ADVANCED MATERIALS



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

materials on demand

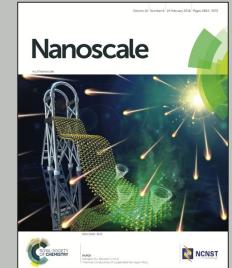


Showcasing research from Collaboratory for Advanced Computing and Simulations (CACS), University of Southern California, Los Angeles, USA.

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)



rsc.li/nanoscale

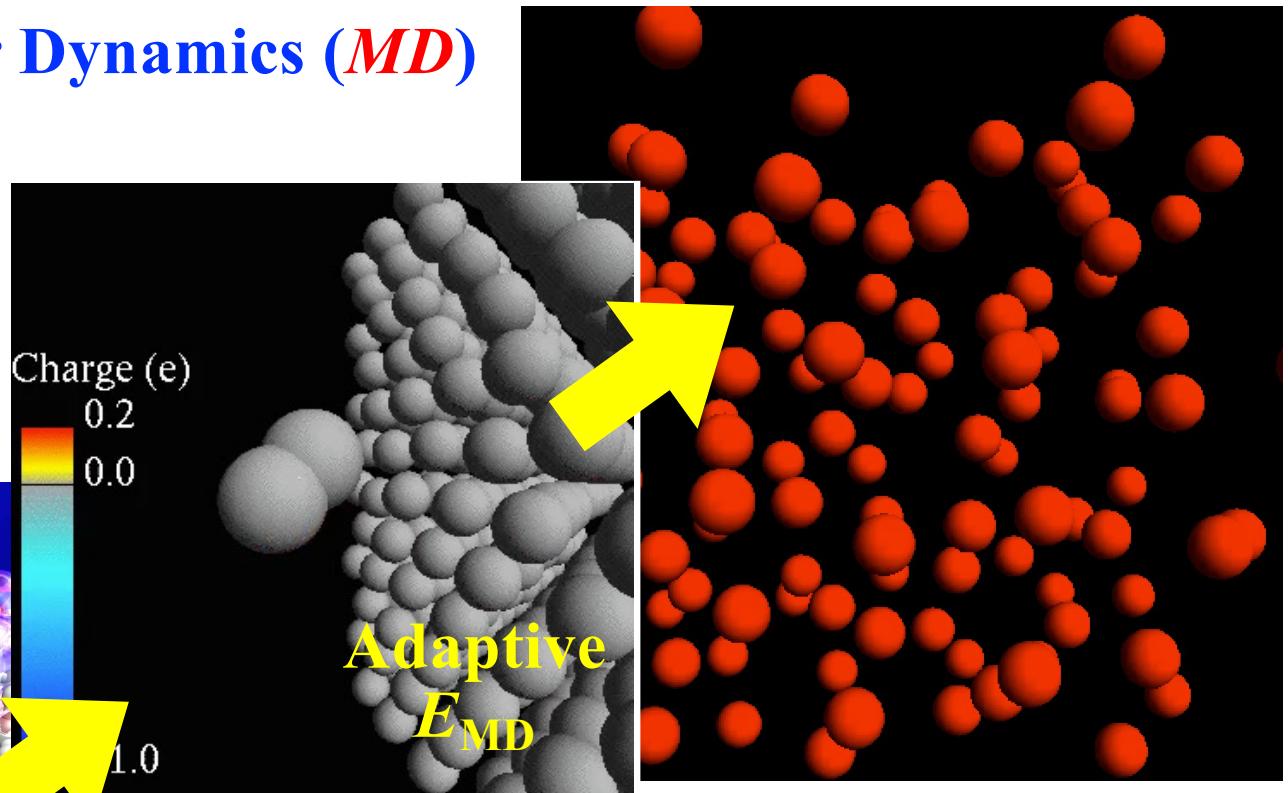
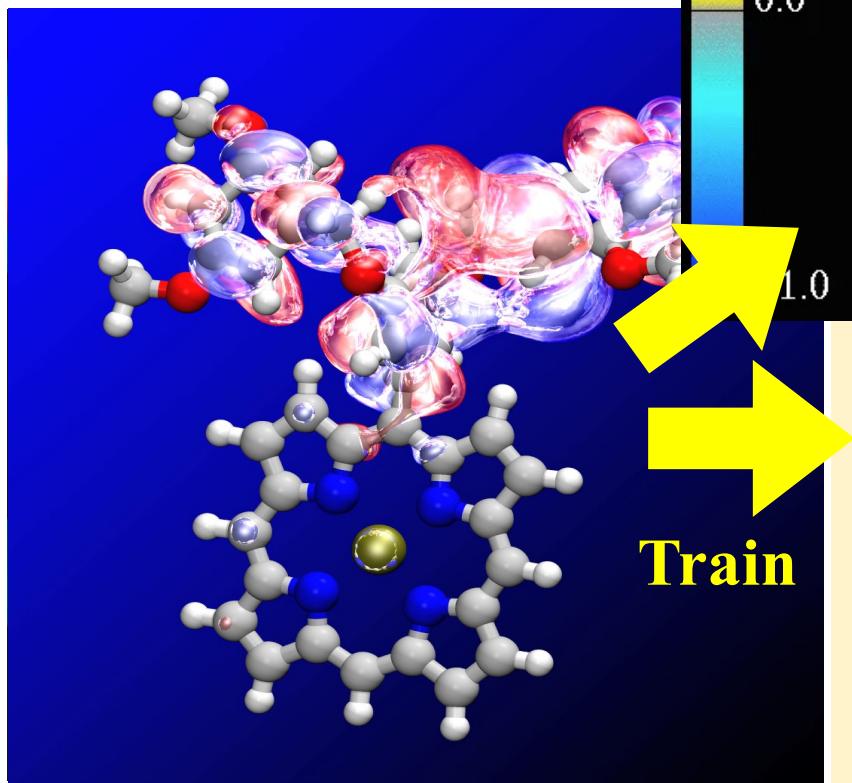
Registered charity number: 207890

Molecular Dynamics & Machine Learning

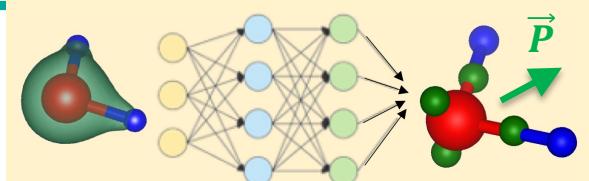
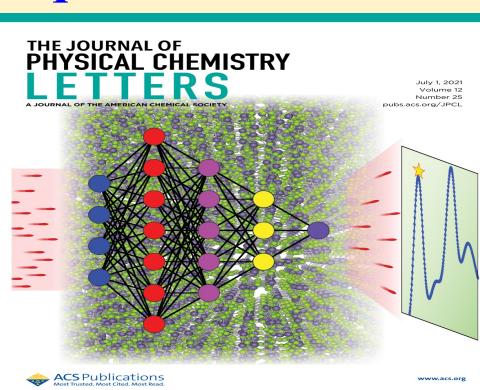
Molecular Dynamics (*MD*)

Reactive MD (*RMD*)

Nonadiabatic quantum MD (*NAQMD*)



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

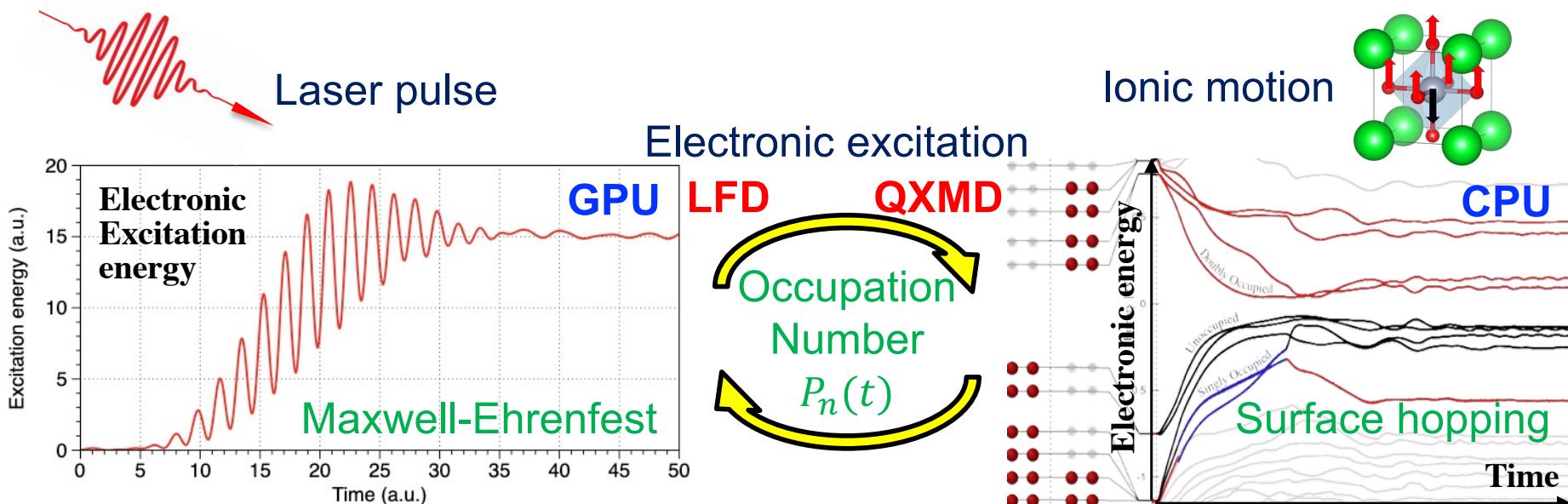


Physical Review Letters
Editor's choice
[126, 216403 ('21)]

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

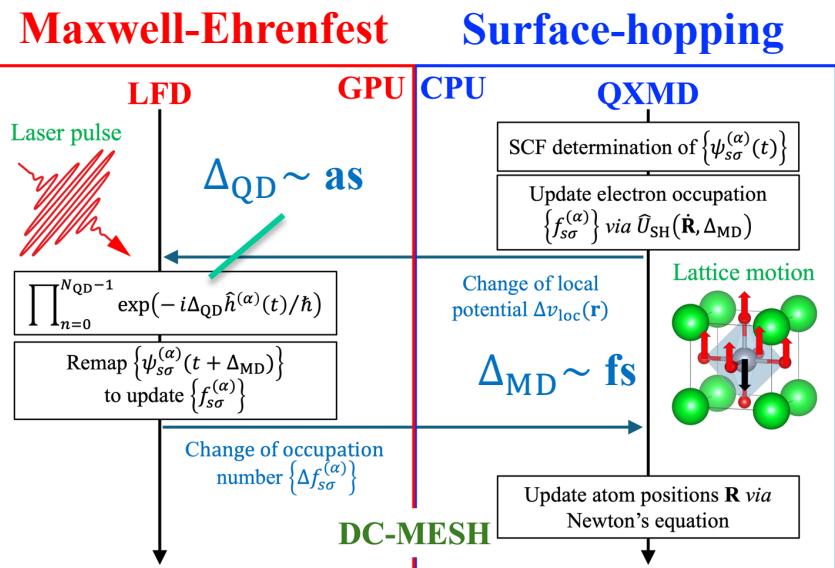
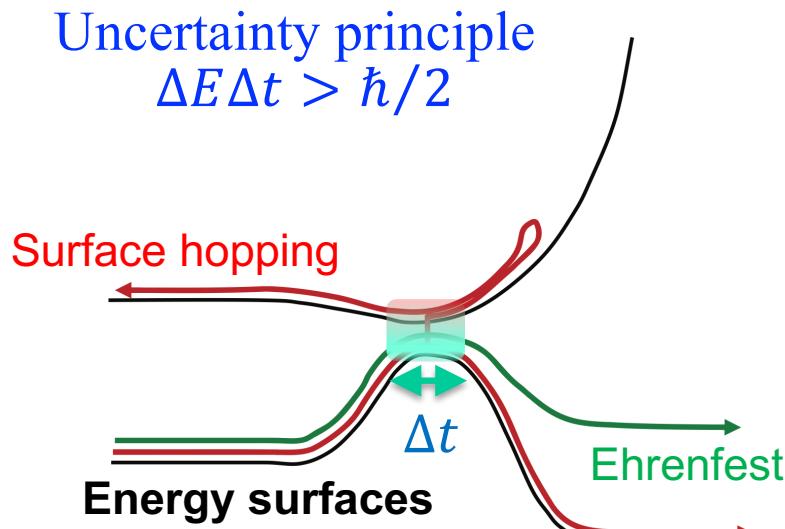
- **MESH (Maxwell + Ehrenfest + surface-hopping):** Maxwell equations for light + real-time time-dependent density functional theory equations for electrons + *short-time Ehrenfest dynamics & long-time surface-hopping dynamics* for atoms

James Clark Maxwell
(1831-1879)

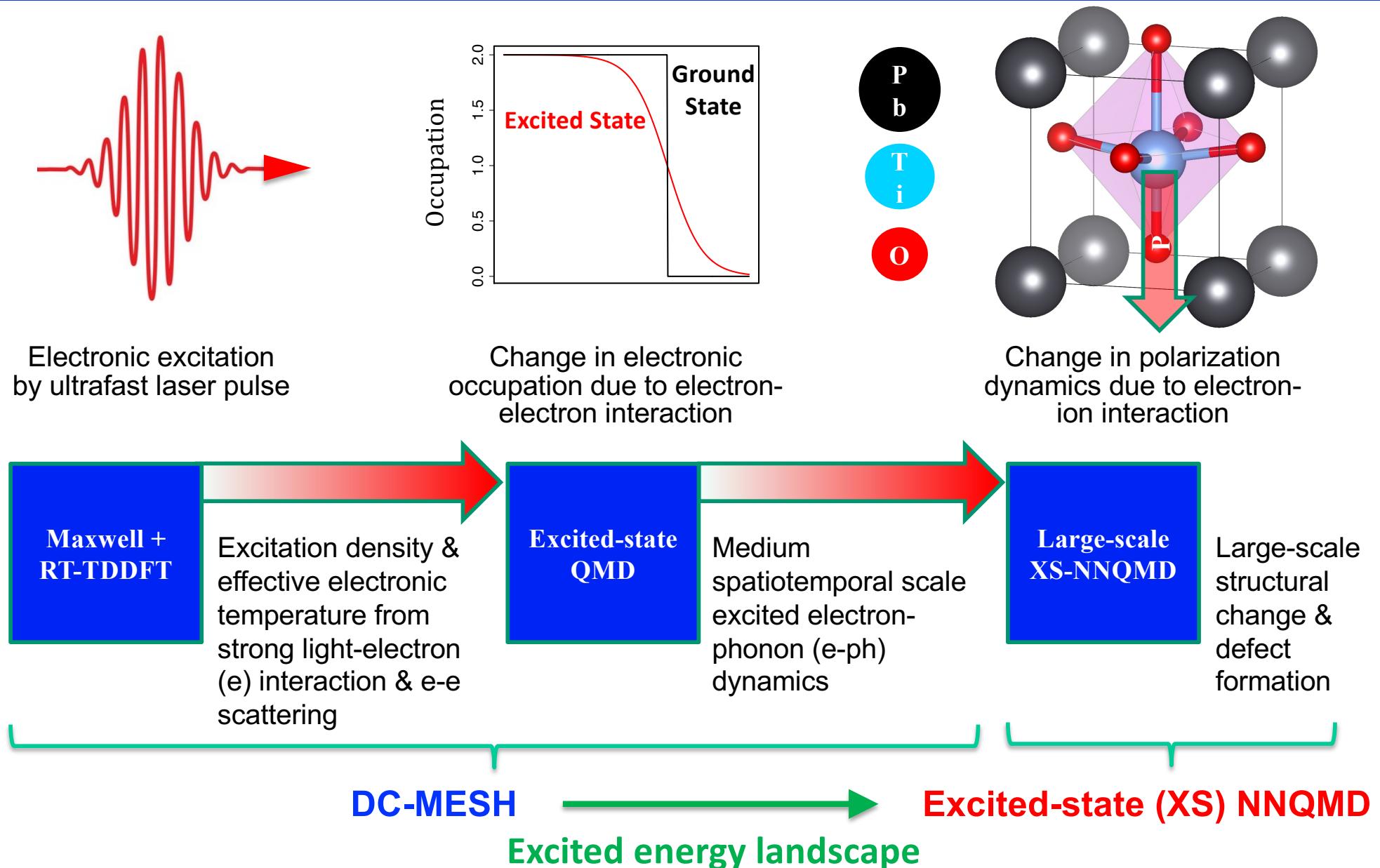


Surface-hopping
John Tully
(1942-)

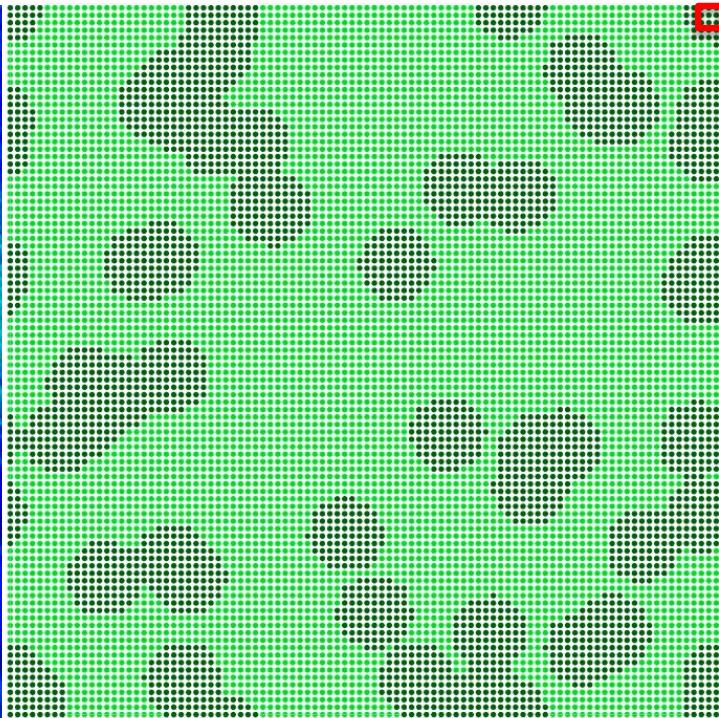
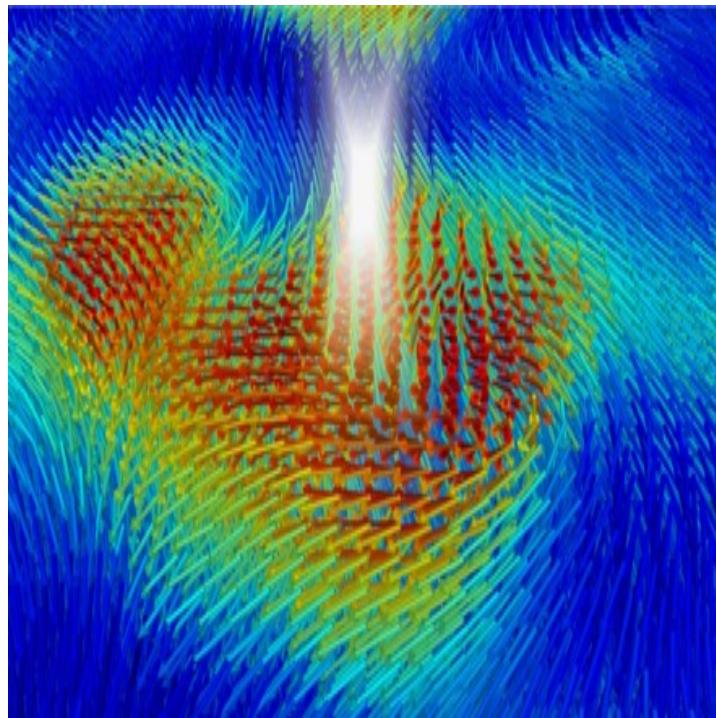
Paul Ehrenfest (1880-1933)



Multiscaling from DC-MESH to XS-NNQMD



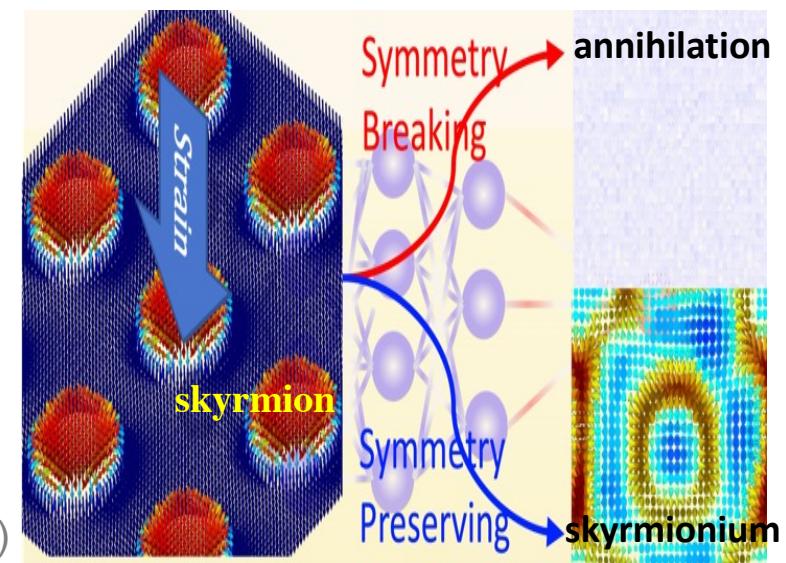
Application: Ferroelectric Opto-Toptronics



System size
simulated
with
NAQMD

Large-scale
structure
simulated
with
NNQMD

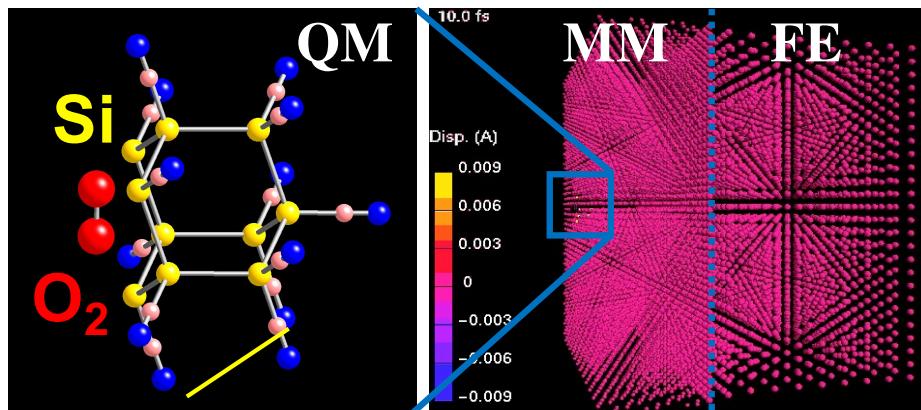
- Quantized ferroelectric topology is protected against thermal noise → future ultralow-power opto-electronics applications
- Billion-atom NNQMD revealed photo-induced topological phase-transition dynamics (*cf.* Kibble-Zurek mechanism in cosmology)
- Symmetry-controlled skyrmion-to-skyrmionium* switching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



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)

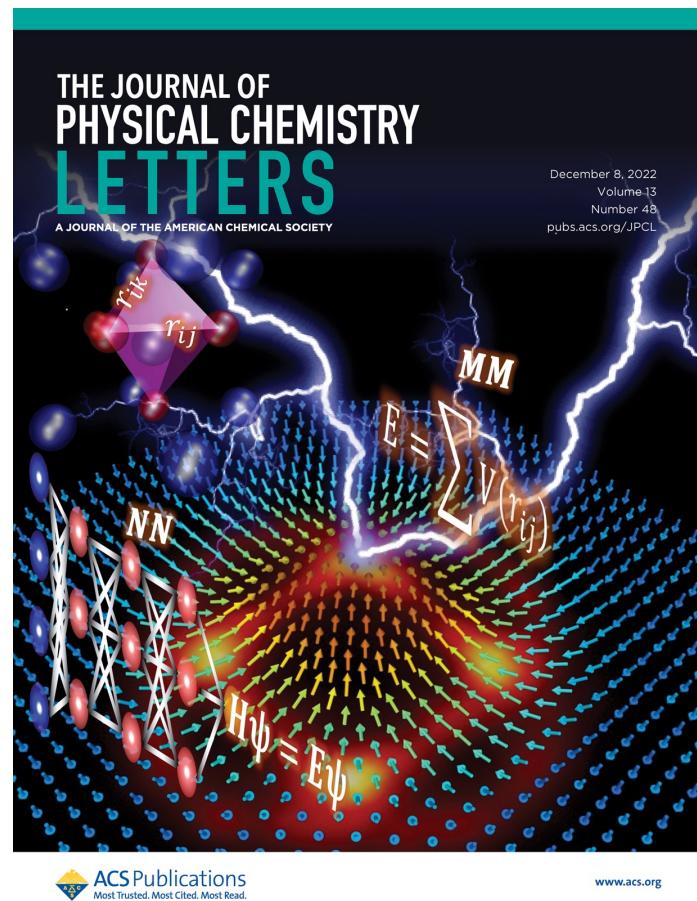
Warshel, *Angew. Chem.* **53**, 10020 ('14)



QM/MM/FE (finite-element method)

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

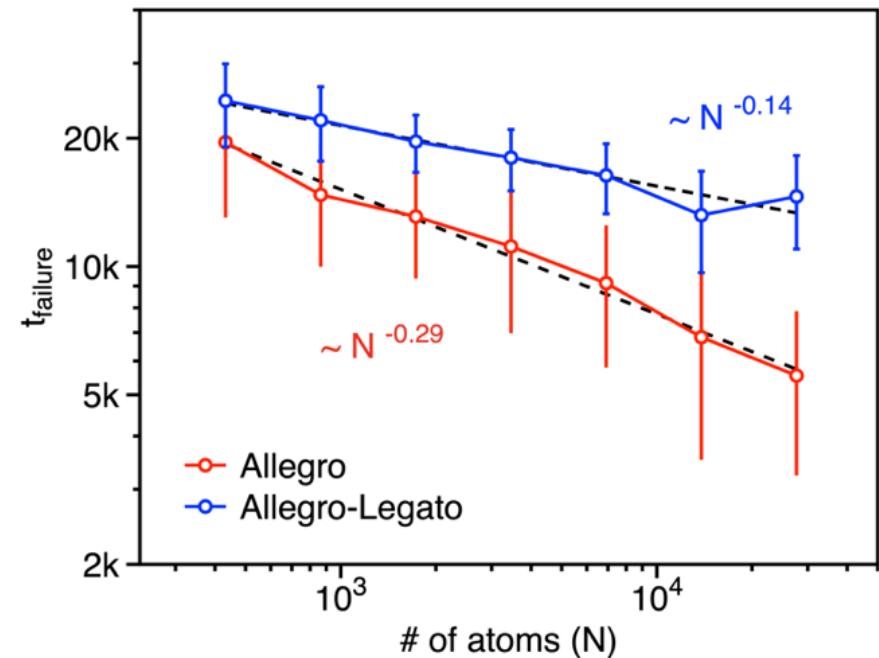
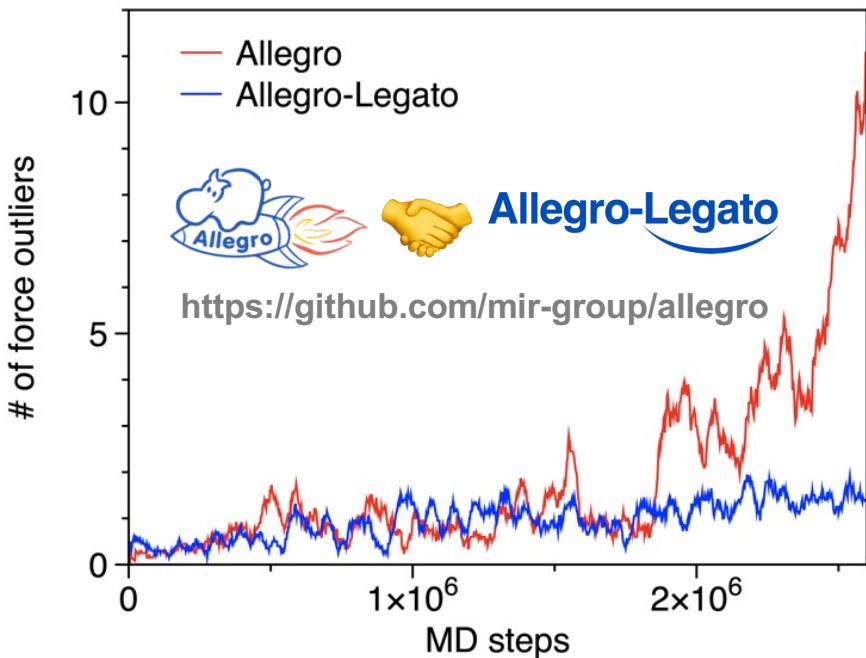
- **NN/MM:** NNQMD for ferroelectric (PbTiO₃: PTO) embedded in MM for paraelectric (SrTiO₃: STO) to apply appropriate strain boundary condition



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

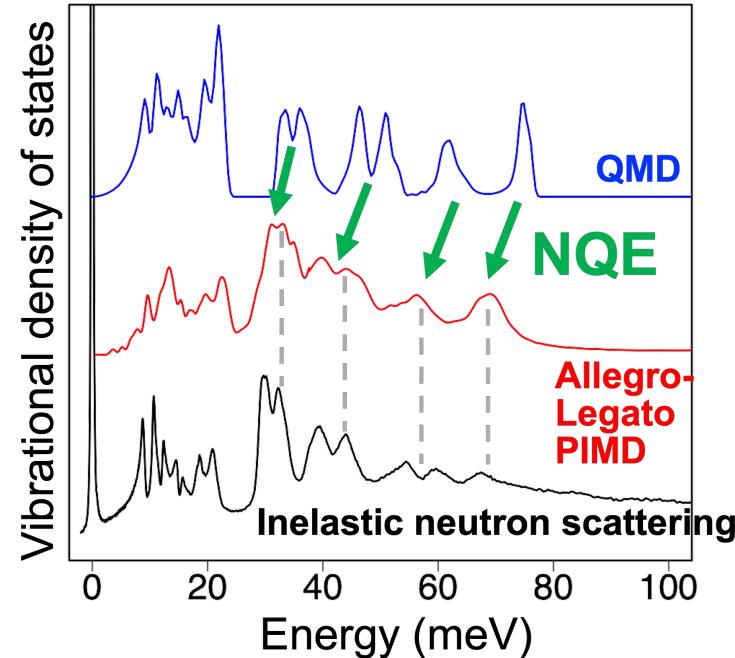
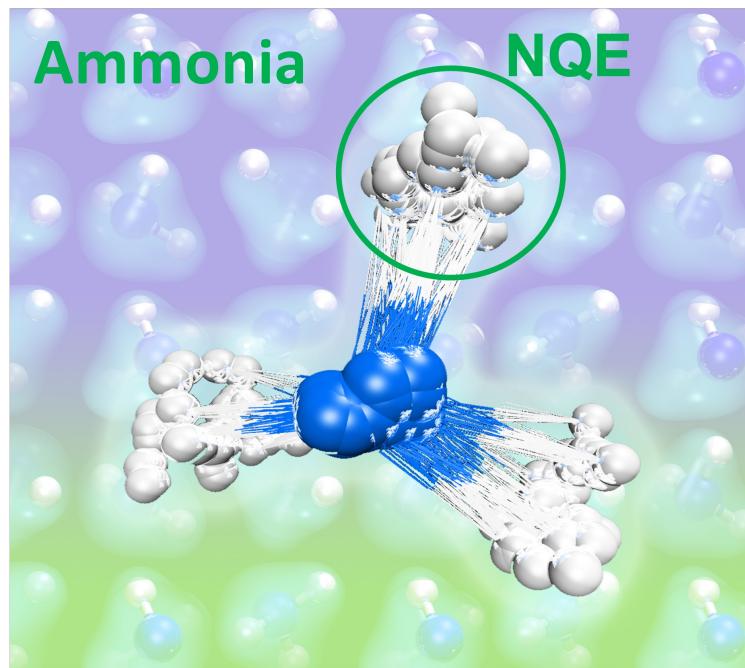
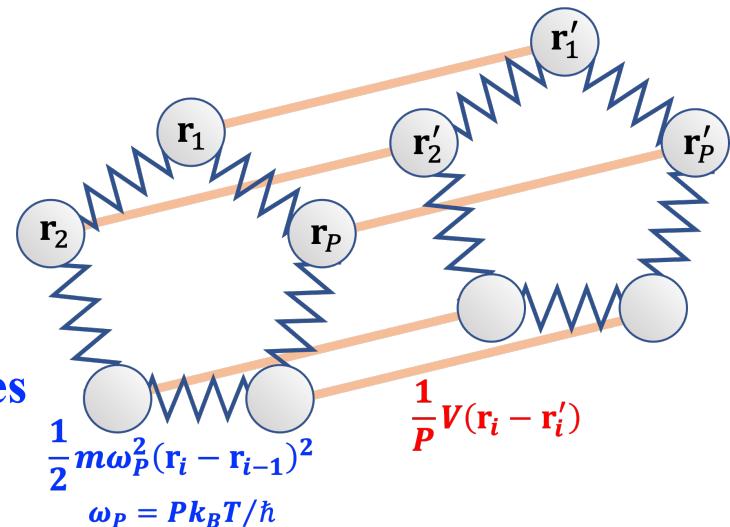
Fast & Robust NNQMD: Allegro-Legato

- **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

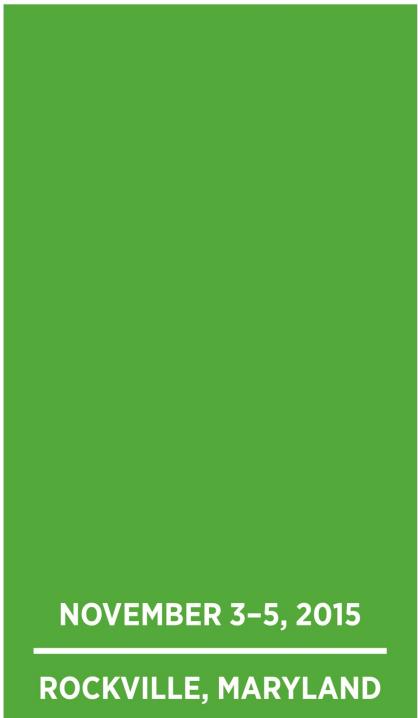
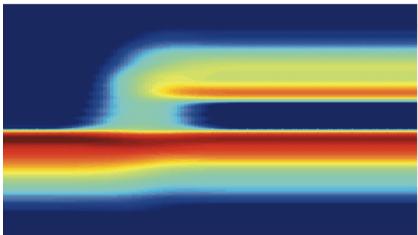
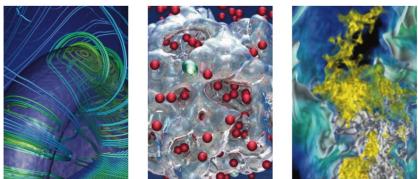


Nuclear-Quantum NNQMD

- **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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BASIC ENERGY SCIENCES

EXASCALE REQUIREMENTS REVIEW

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

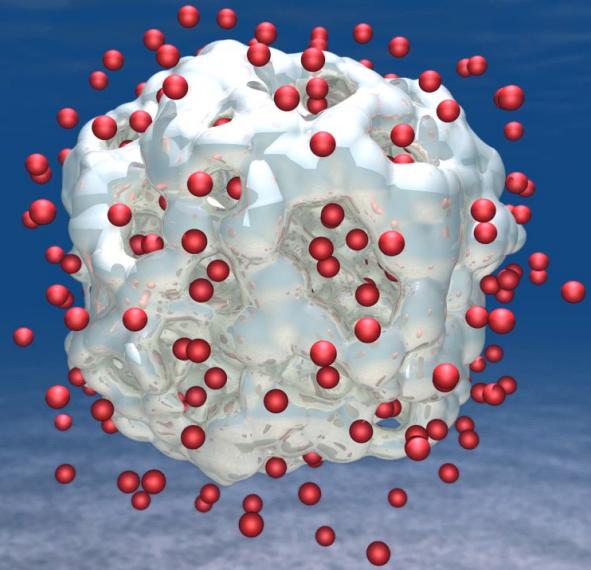
One of the 10 initial
simulation users of the
2 exaflop/s* Aurora



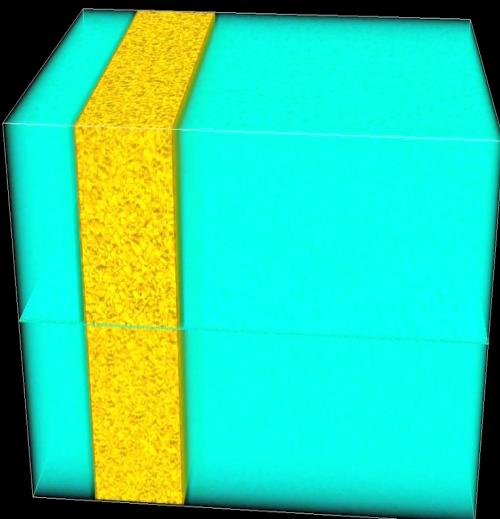
*exaflop/s = 10^{18} mathematical operations per second



17K-atom QMD

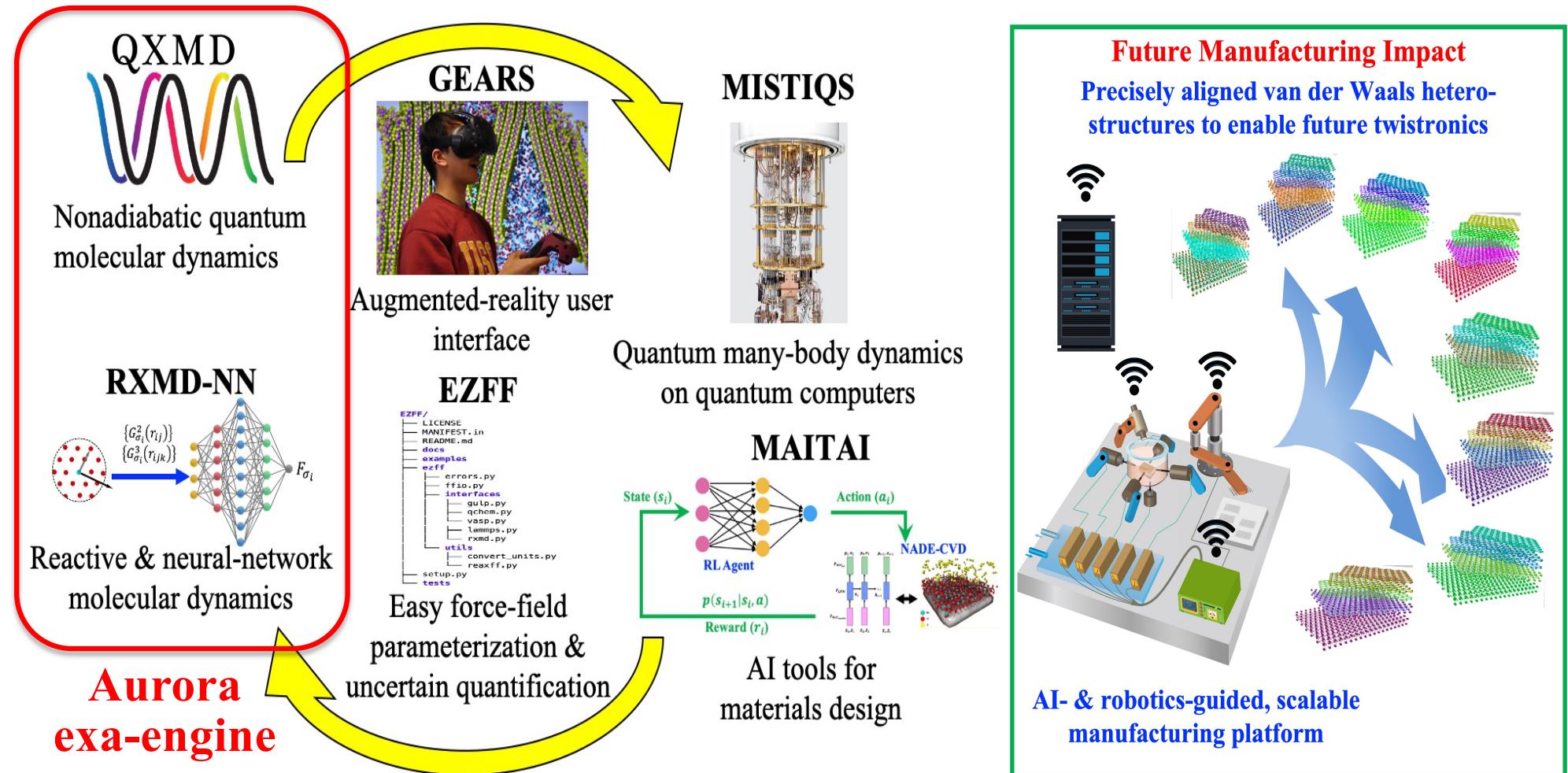


10⁹-atom RMD



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/>