Iterative Energy Minimization for Quantum Molecular Dynamics

Aiichiro Nakano

Collaboratory for Advanced Computing & Simulations
Department of Computer Science
Department of Physics & Astronomy
Department of Chemical Engineering & Materials Science
Department of Quantitative & Computational Biology
University of Southern California

Email: anakano@usc.edu

From quantum dynamics to eigenvalue problems

Imaginary-Time Quantum Dynamics

- **Quantum dynamics**

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

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

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

Repeat
$|\psi\rangle \leftarrow \exp(-\hat{H}\Delta\tau)|\psi\rangle$
$|\psi\rangle \leftarrow |\psi\rangle/\sqrt{\langle\psi|\psi\rangle}$

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

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

- **Filtering in the ground state**

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

$$\exp(-\hat{H}\tau)|\psi_{\text{init}}\rangle = \exp(-\hat{H}\tau)\overbrace{\sum_{n\geq 0}|n\rangle\langle n|}^{1}\psi_{\text{init}}\rangle$$

$$= \sum_{n\geq 0}|n\rangle\langle n|\psi_{\text{init}}\rangle\exp(-\epsilon_n\tau) \underset{\tau\to\infty}{\longrightarrow} |0\rangle\langle 0|\psi_{\text{init}}\rangle\exp(-\epsilon_0\tau)$$

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

Obtaining Excited States

- **Filter-project imaginary-time quantum dynamics**

Repeat

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

$|\psi\rangle \leftarrow |\psi\rangle - |0\rangle\langle 0|\psi\rangle$

$|\psi\rangle \leftarrow |\psi\rangle / \sqrt{\langle\psi|\psi\rangle}$

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

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

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

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

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

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

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

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

$$\mathbf{r} \leftrightarrow \mathbf{r}'$$

$$= \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r})\delta\rho(\mathbf{r}') + \rho(\mathbf{r}')\delta\rho(\mathbf{r}) + \cancel{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|}$$

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

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

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**

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

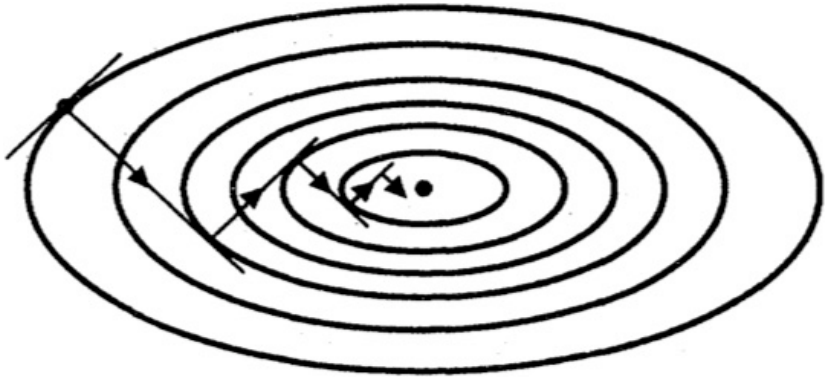
- **Gradient (for a normalized wave function)**

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

- **Steepest descent**

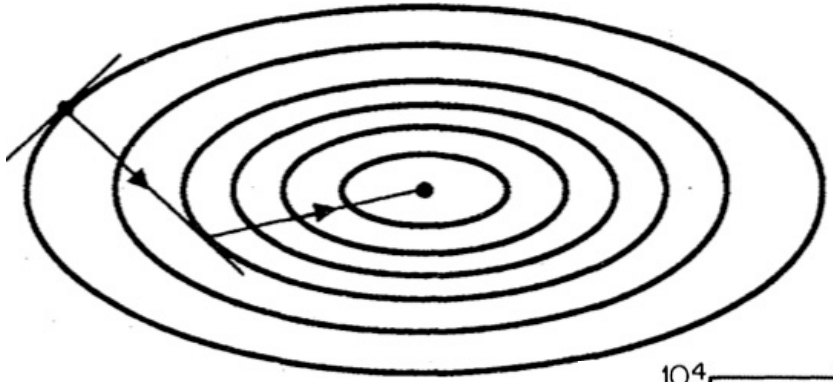
Repeat

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



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

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

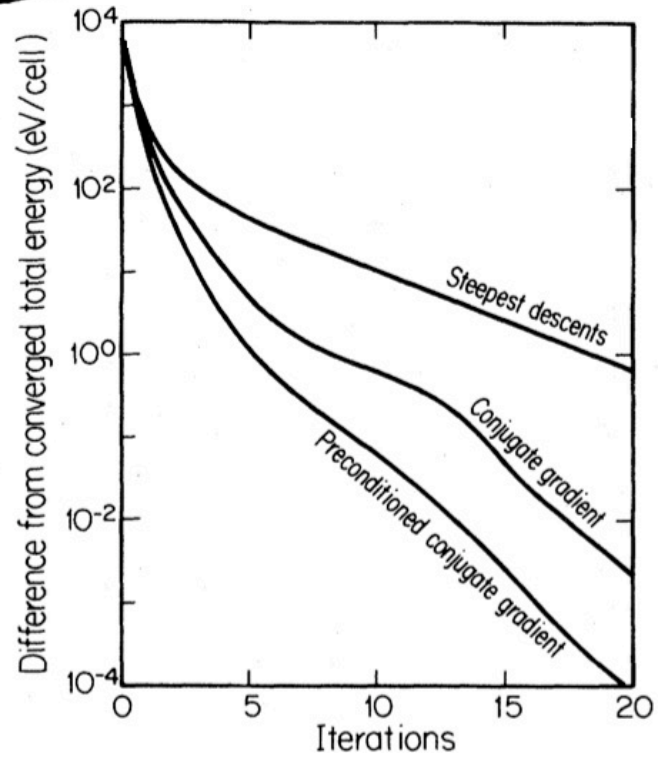
  endif

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

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

  if convergent, **exit**

endfor



See *Numerical Recipes*, Sec. 10.6

M.C. Payne *et al.*, *Rev. Mod. Phys.* **64**, 1045 ('92)

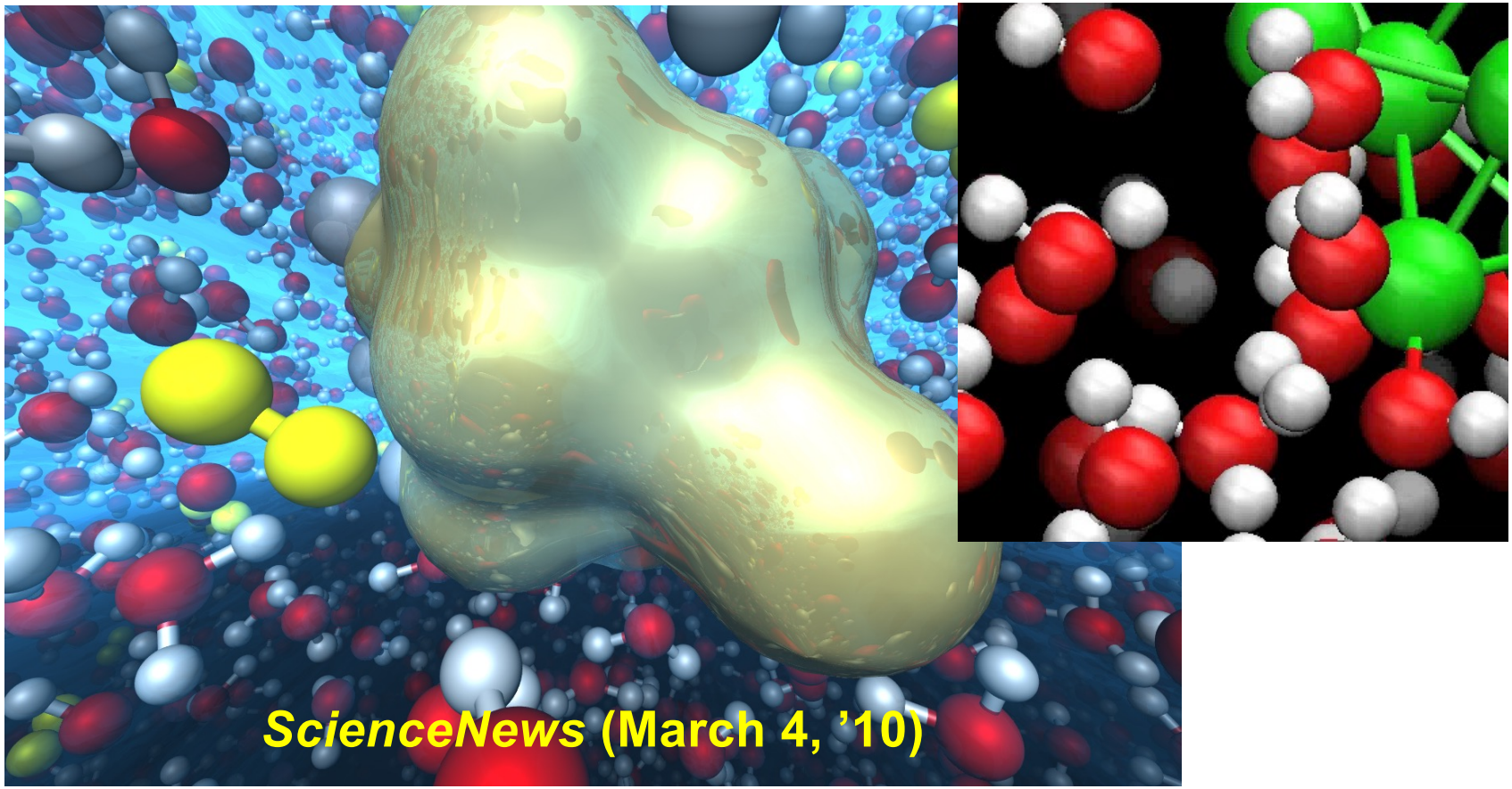
Quantum Molecular Dynamics

- **Born-Oppenheimer (adiabatic) approximation: Electron wave function $\psi(\mathbf{r}_1,\ldots,\mathbf{r}_{N\text{electron}})$ is determined with fixed nuclei positions $\mathbf{R}_n$ ($n = 1,\ldots,N_{\text{nucleus}}$)**

$$\psi_*(\mathbf{r}_1,\ldots,\mathbf{r}_{N\text{electron}}) \leftarrow \operatorname{argmin} E[\psi(\mathbf{r}_1,\ldots,\mathbf{r}_{N\text{electron}}),\{\mathbf{R}_n\}]$$ **CG**

- **Newton's equations for the classical motion of nuclei**

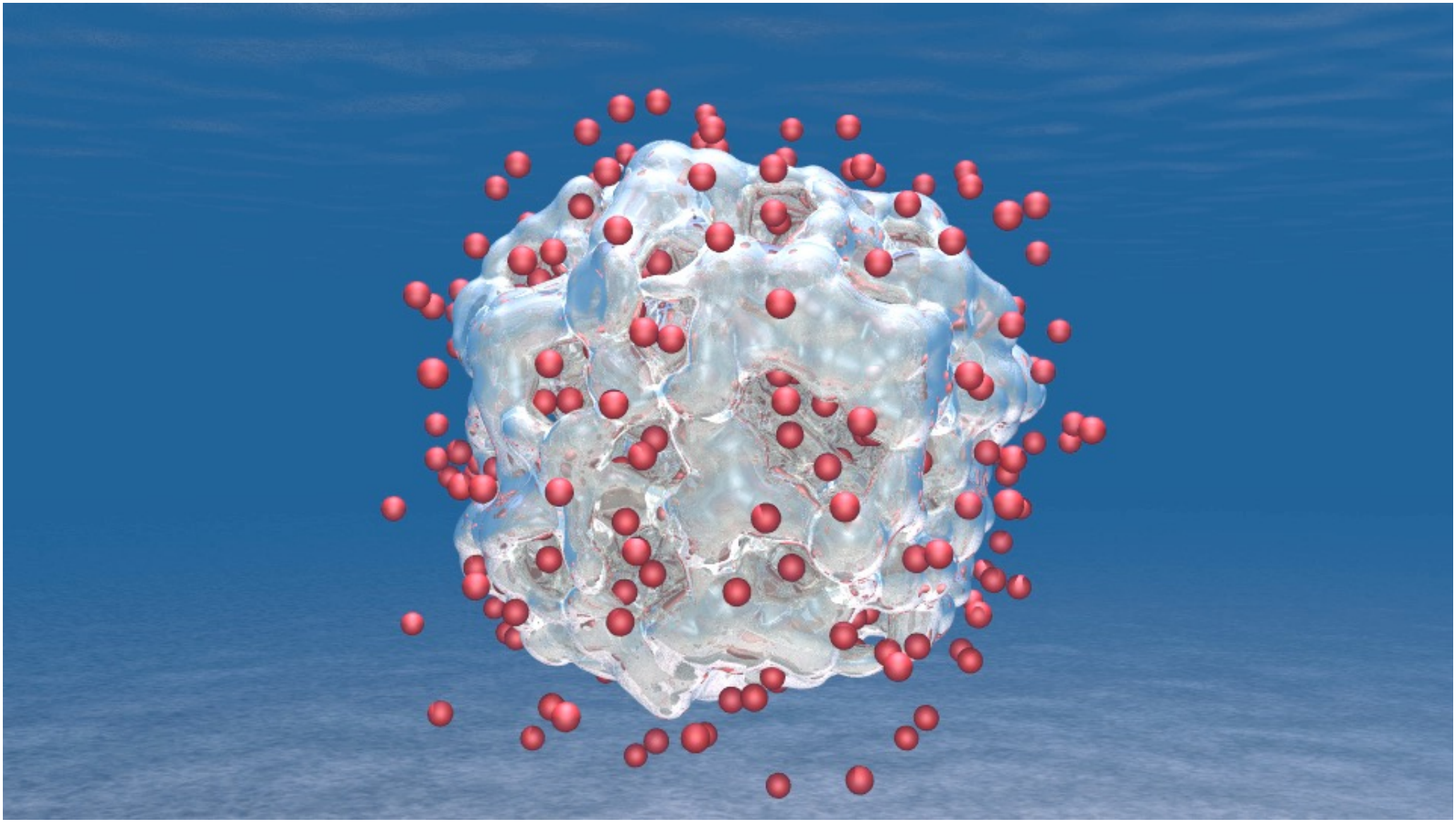
$$M_n \frac{d^2}{dt^2}\mathbf{R}_n = -\frac{\partial}{\partial \mathbf{R}_n} E[\psi_*(\mathbf{r}_1,\ldots,\mathbf{r}_{N\text{electron}}),\{\mathbf{R}_n\}]$$ **MD**



F. Shimojo *et al.*, *Phys. Rev. Lett.* **104**, 126102 ('10); *ibid*. **111**, 066103 ('13)

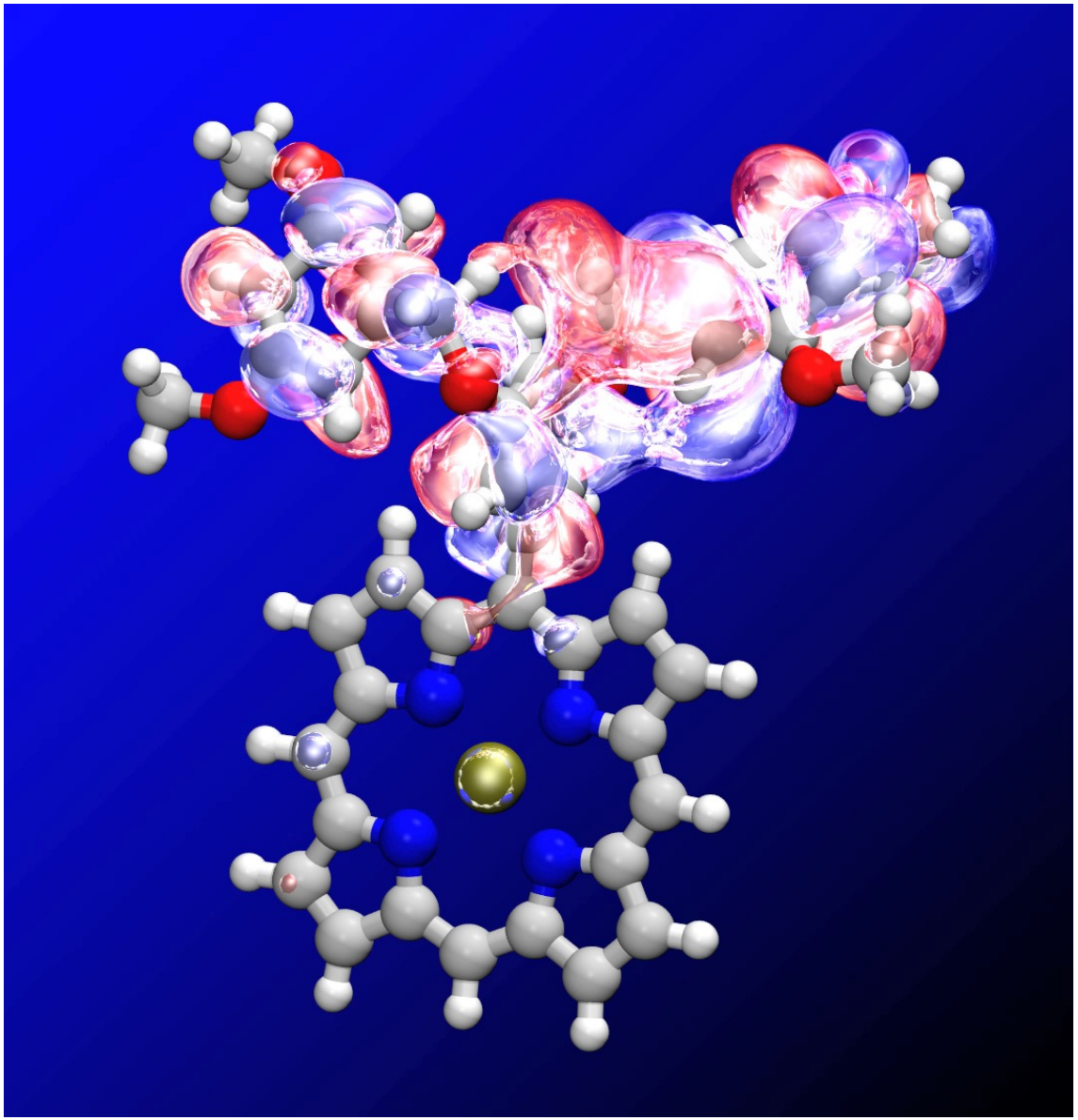
H_2 Production from Water Using LiAl Particles

16,661-atom QMD simulation of $Li_{441}Al_{441}$ in water on 786,432 IBM BlueGene/Q cores



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

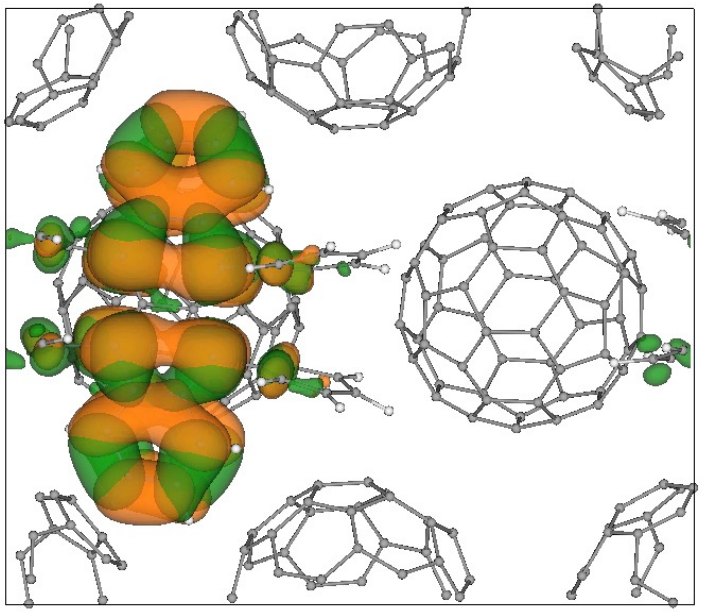
Nonadiabatic Quantum Molecular Dynamics



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/C_{60}

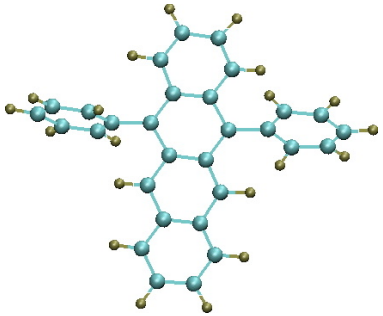


quasi-electron; **quasi-hole**

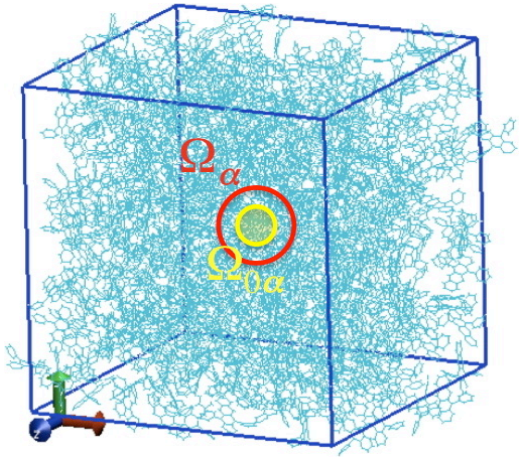
- **Excited states: Linear-response time-dependent density functional theory** [Casida, '95]
- **Interstate transitions: Surface hopping** [Tully, '90; Jaeger, Fisher & Prezhdo, '12]

Simulating SF in Amorphous DPT

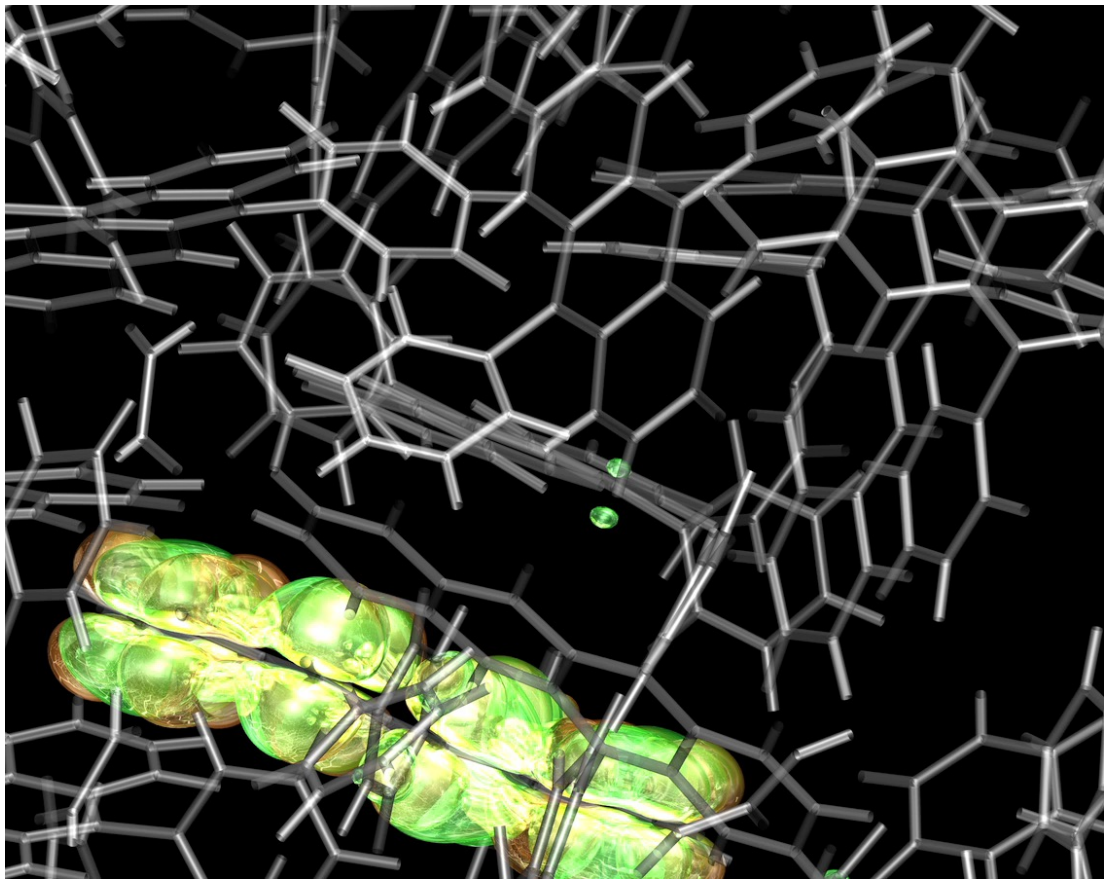
- Move up from molecules to microstructures
- Challenge: Unprecedented 10^4-atom NAQMD simulation
- Computational approach: Divide-conquer-recombine (DCR) NAQMD



DPT molecule



Amorphous DPT



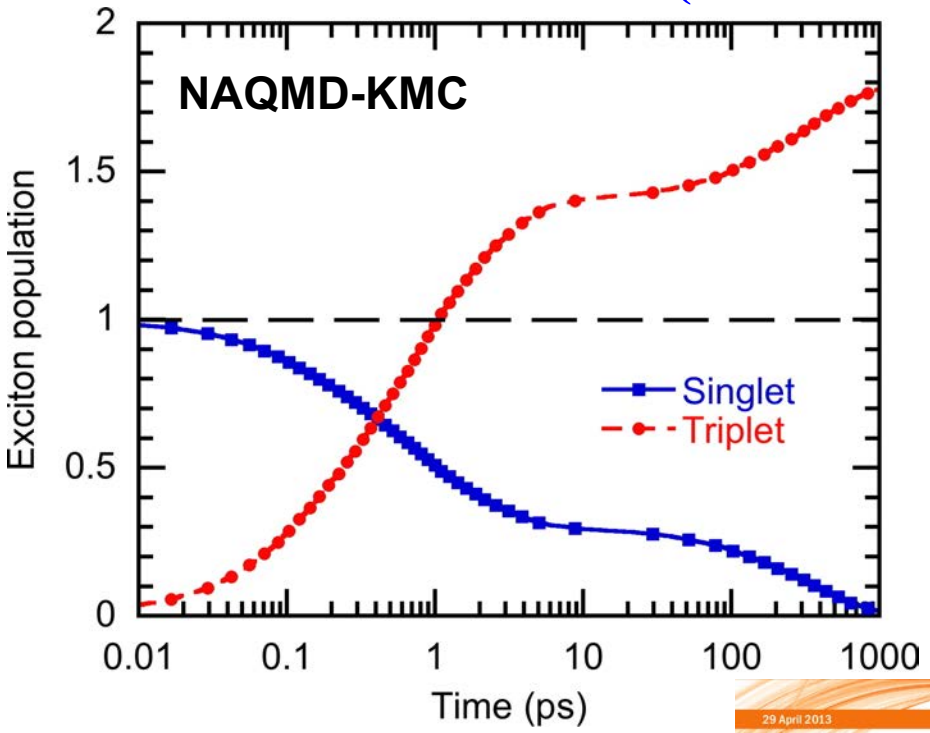
Quasi-electron

Quasi-hole

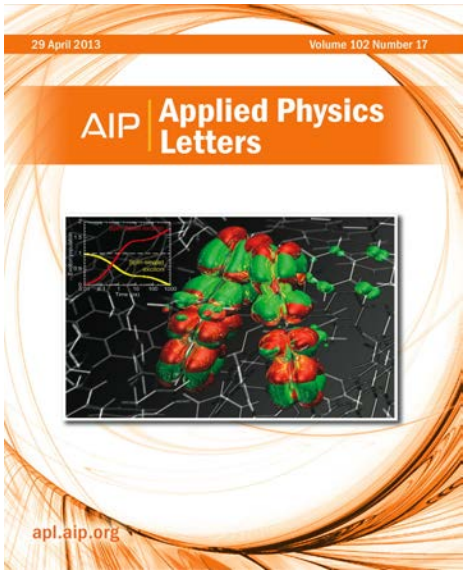
- Divide-conquer-recombine NAQMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT

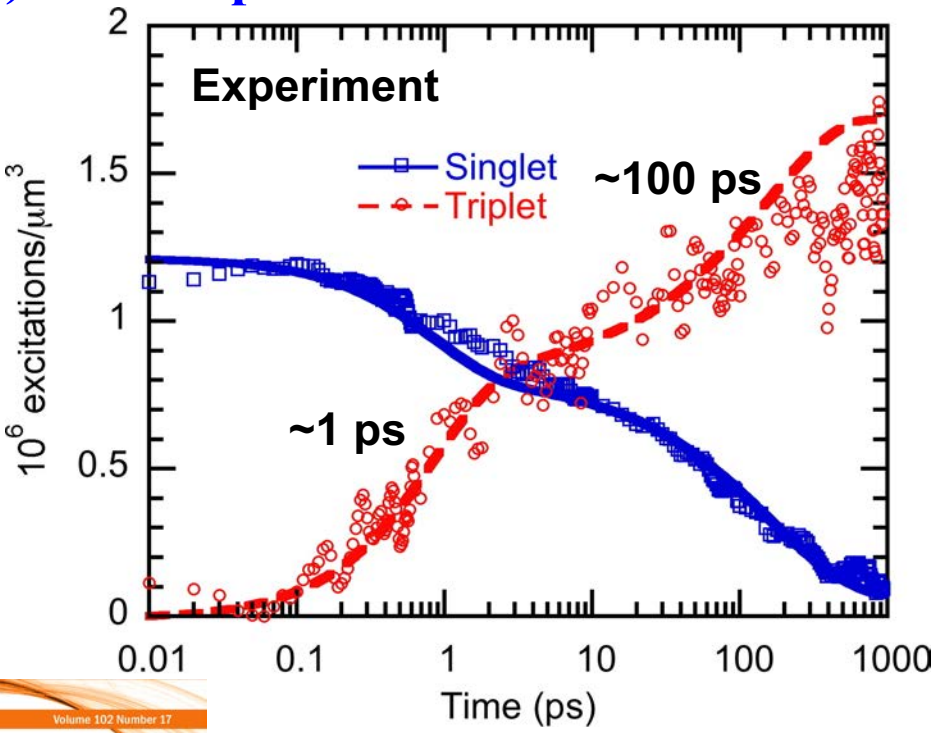
NAQMD-informed Kinetic Monte Carlo

- **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)

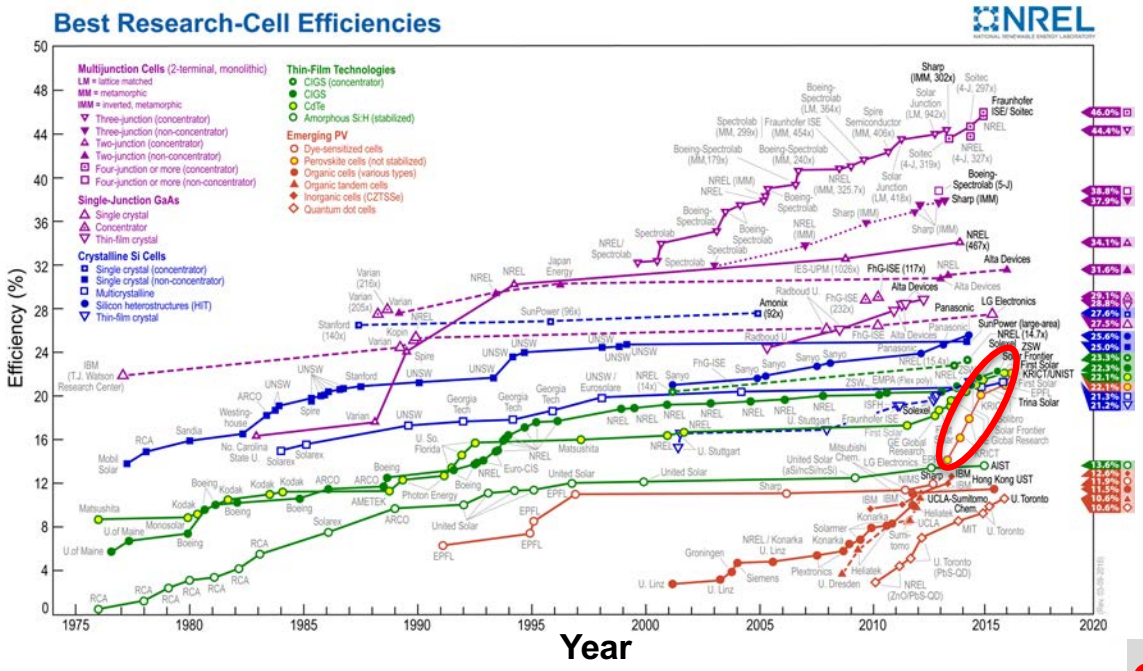


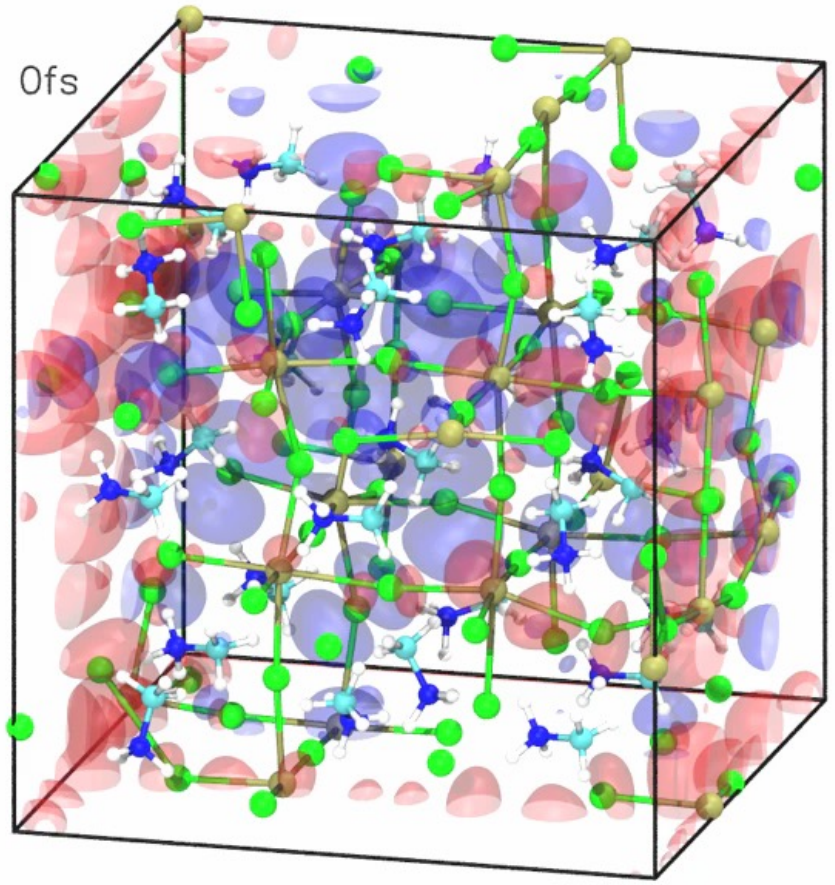


S. T. Roberts *et al.*,
J. Am. Chem. Soc.
134, 6388 ('12)

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)



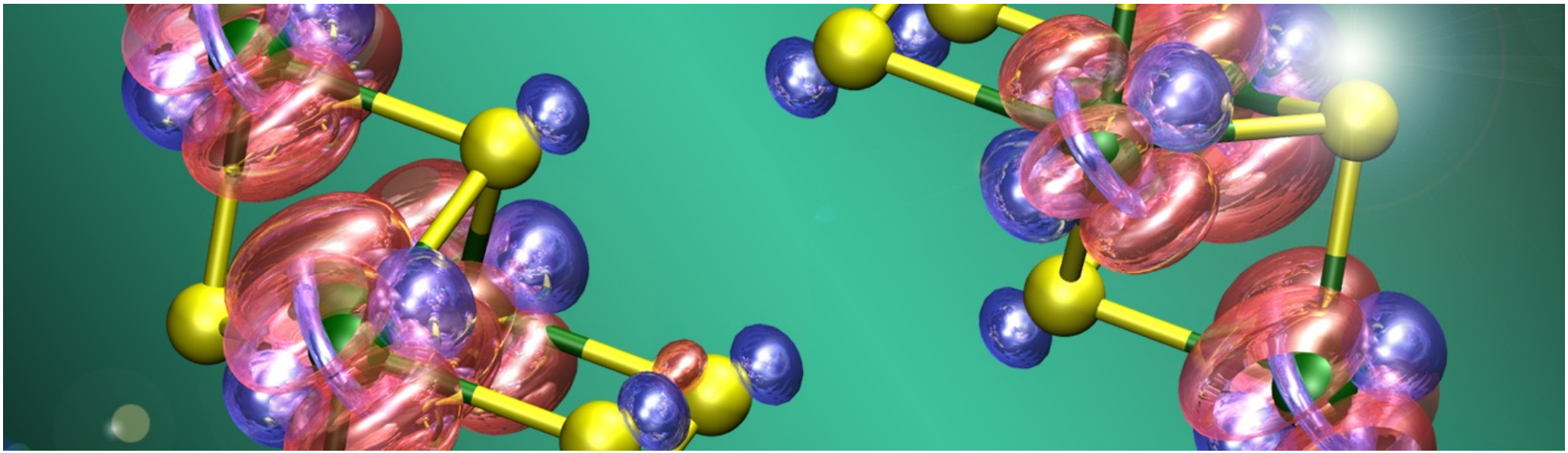


Quasi-electron Quasi-hole H, C, N, I, Pb

- **Nonabiabatic 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)]

T. Hakamata *et al.*, *Sci. Rep.* **5**, 19599 ('16)

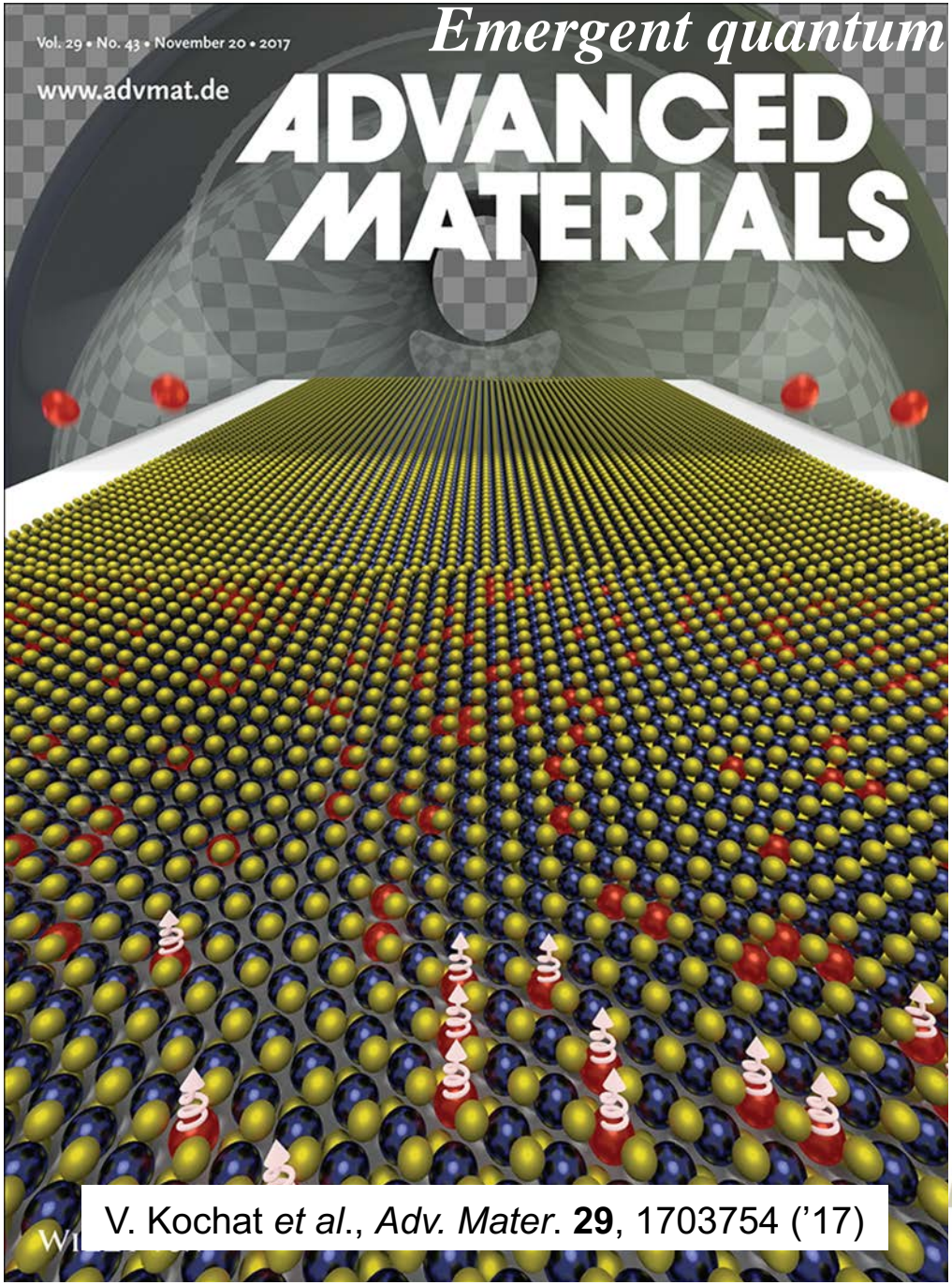
Simulation-Experiment Synergy



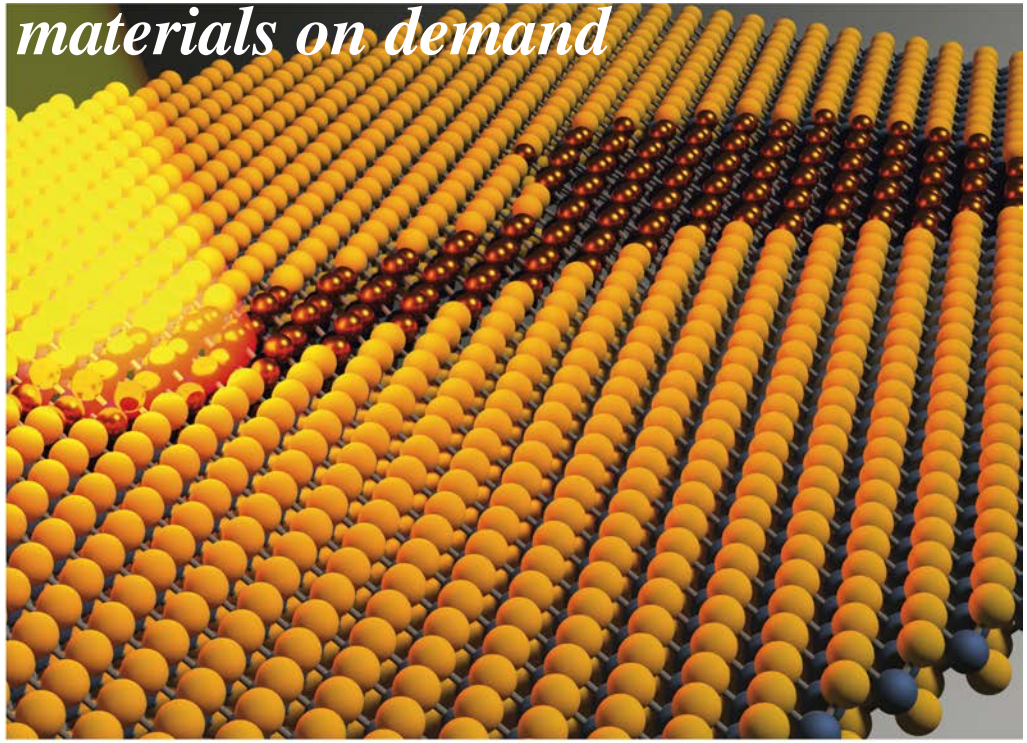
- **In ultrafast 'electron & X-ray cameras', laser light hitting a material is almost completely converted into nuclear vibrations — key to switching material properties on & off at will for future electronics applications**
- **High-end quantum simulations reproduce the ultrafast energy conversion at 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)
I. Tung *et al*., *Nature Photon*. **13**, 425 ('19)

Quantum Molecular Dynamics Simulations



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

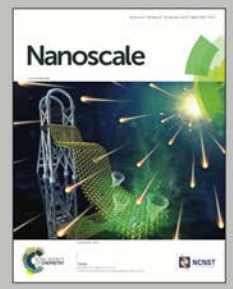


Showcasing research from Collaboratory for Advanced Computing and Simulations (CACS), University of Southern California, Los Angeles, USA.

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

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

As featured in:



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

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

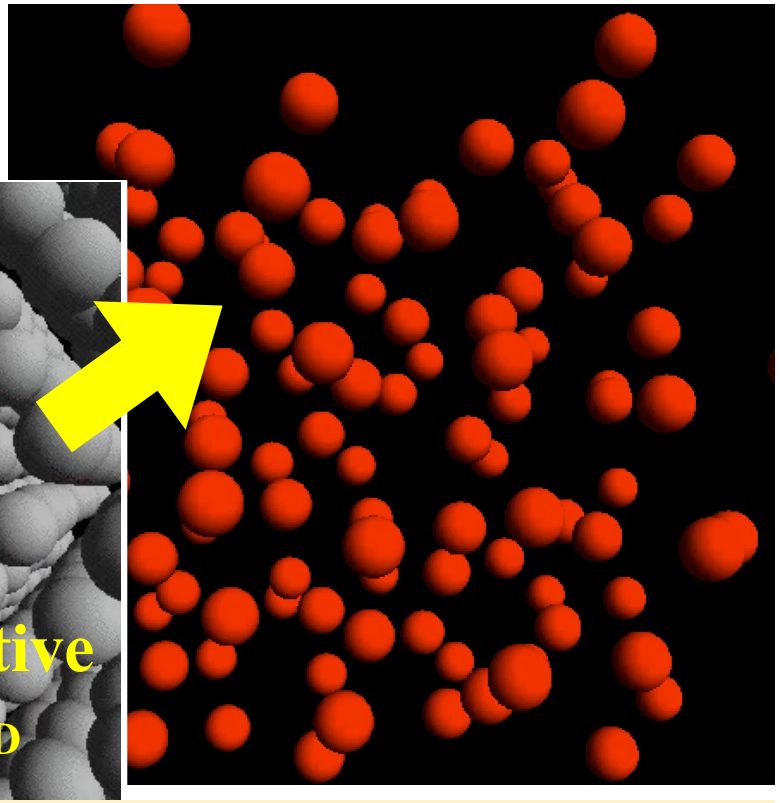
ROYAL SOCIETY OF CHEMISTRY

rsc.li/nanoscale

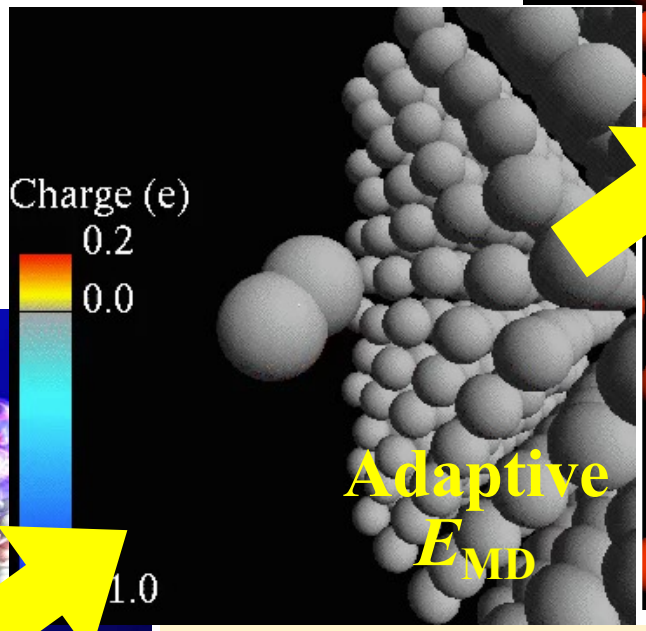
Registered charity number: 207890

Molecular Dynamics & Machine Learning

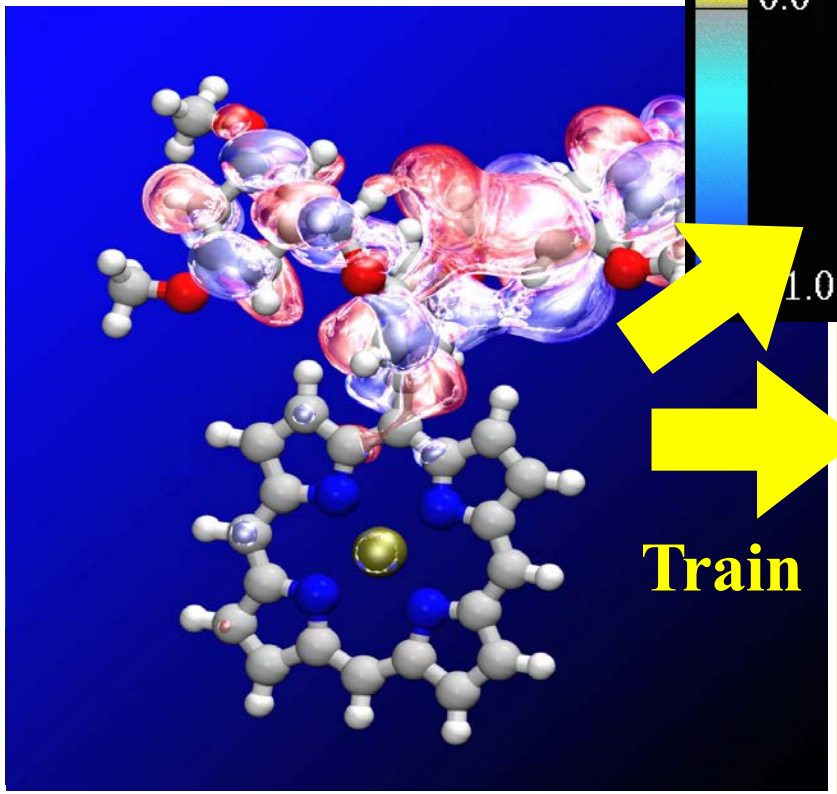
Molecular Dynamics (*MD*)



Reactive MD (*RMD*)

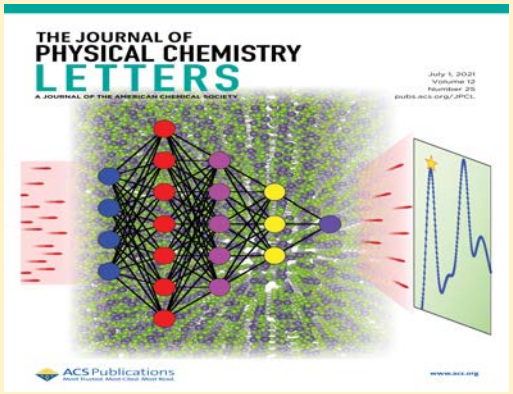


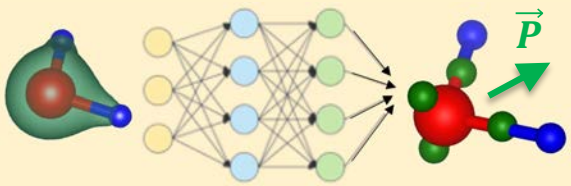
Nonadiabatic quantum MD (*NAQMD*)



Train

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

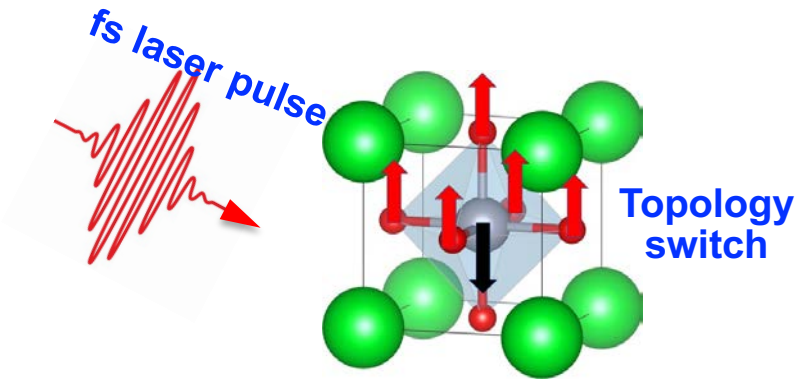




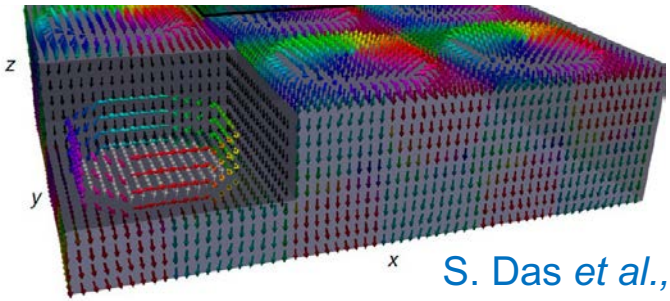
Physical Review Letters
Editor's choice
[**126**, 216403 ('21)]

JPCL **12**, 6020 ('21)

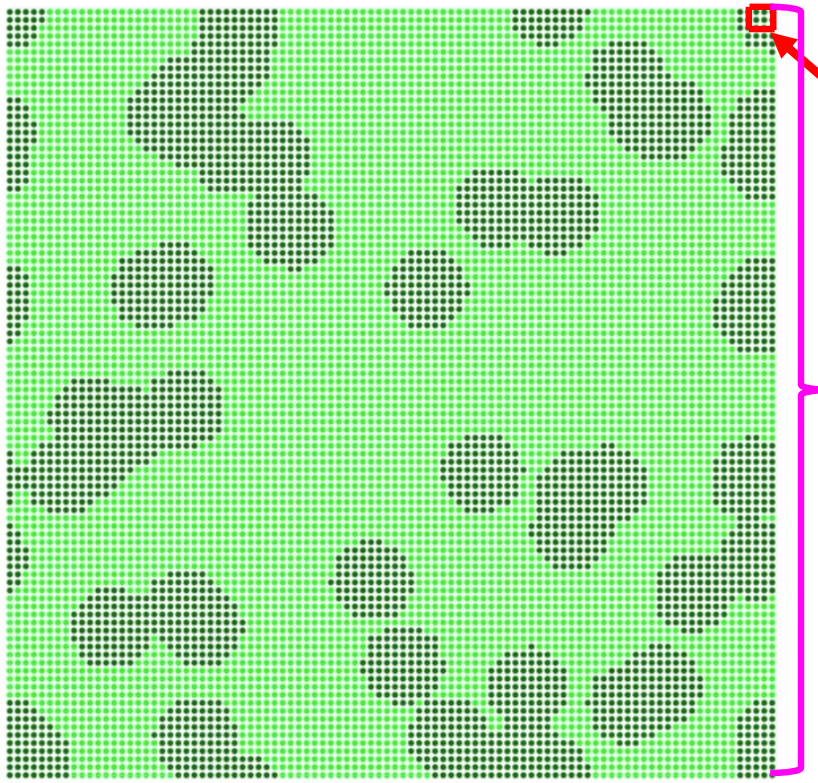
NNQMD Application: Polar Topotronics



Ferroelectrics (*e.g.*, $PbTiO_3$)



S. Das *et al.*, *Nature* **568**, 368 ('19)



System size simulated with $O(N^3)$ NAQMD

Large-scale structure simulated with $O(N)$ NNQMD

- **Photo-switch of ferroelectric topology (*e.g.*, polar skyrmion) for ultrafast, ultralow-power opto-electronics**
- **Excited-state NNQMD reveals topological phase-transition dynamics similar to Kibble-Zurek mechanism in cosmology**

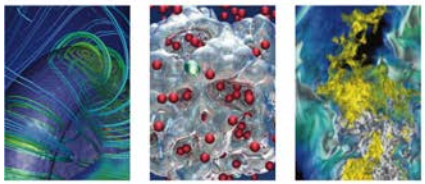
T. Linker *et al.*, *Sci. Adv.* ('22)

Exa-leadership

BES

BASIC ENERGY SCIENCES

EXASCALE REQUIREMENTS REVIEW



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

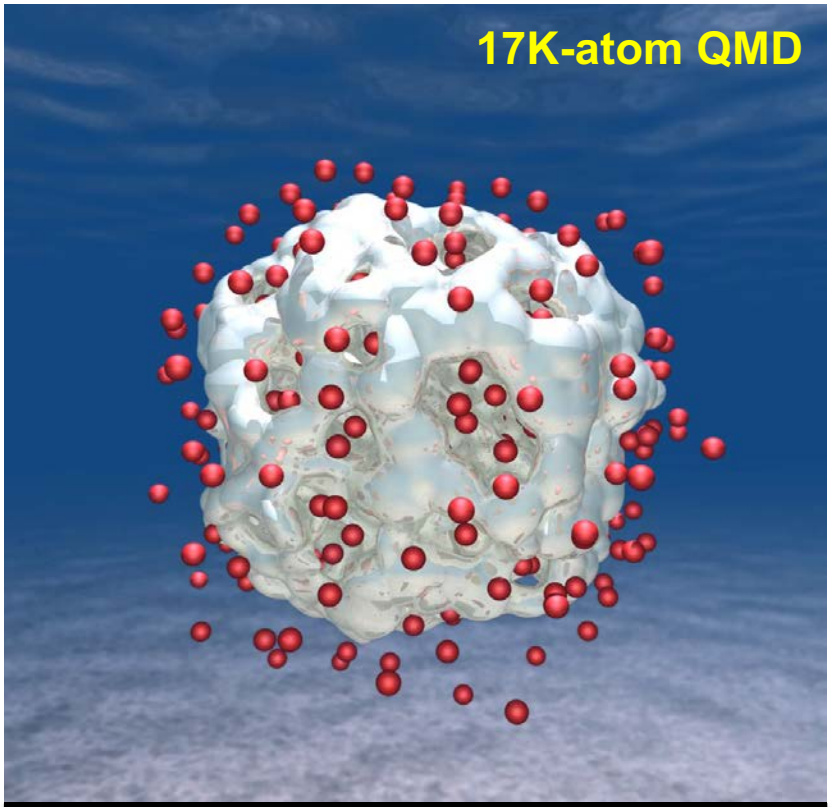
NOVEMBER 3–5, 2015

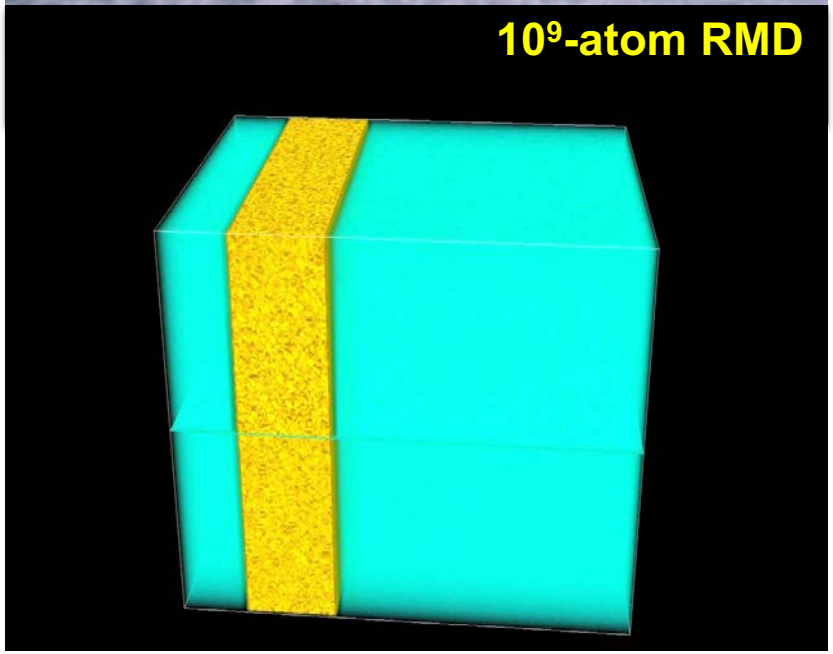
ROCKVILLE, MARYLAND

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

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

U.S. DEPARTMENT OF ENERGY





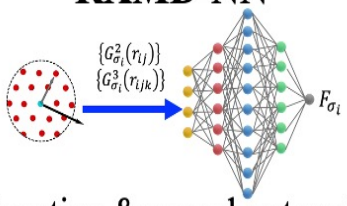
AIQ-XMaS Software for Manufacturing

AI and Quantum-Computing Enabled Exascale Materials Simulator

QXMD

Nonadiabatic quantum molecular dynamics

RXMD-NN



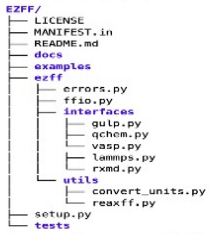
Reactive & neural-network molecular dynamics

Aurora exa-engine

GEARS

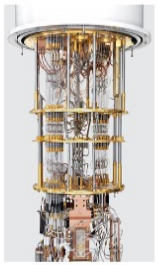
Augmented-reality user interface

EZFF



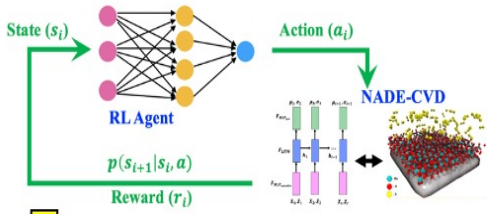
Easy force-field parameterization & uncertain quantification

MISTIQS



Quantum many-body dynamics on quantum computers

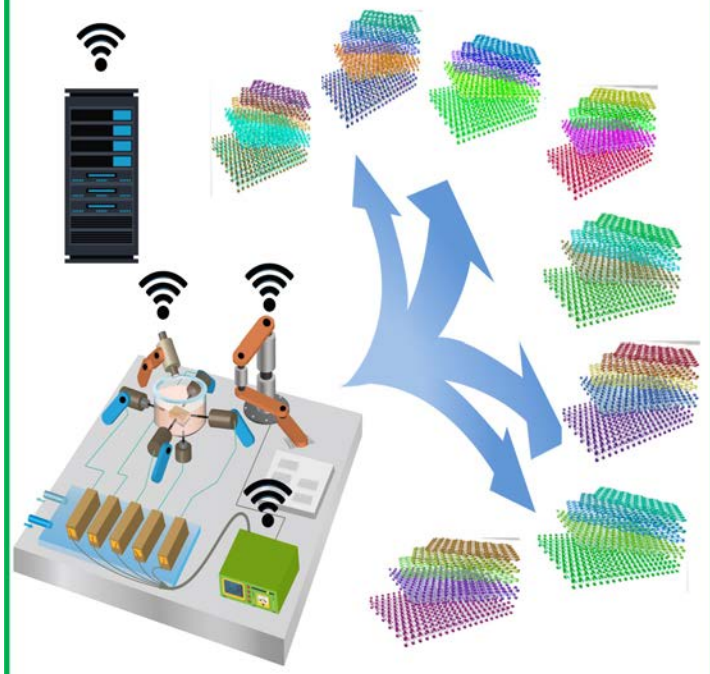
MAITAI



AI tools for materials design

Future Manufacturing Impact

Precisely aligned van der Waals hetero-structures to enable future twistronics



AI- & robotics-guided, scalable manufacturing platform

Synergy with $3.75M NSF Future Manufacturing (2020-25) and $1M NSF CyberTraining (2021-25) projects

Additional Resources

Detailed lecture notes on quantum molecular dynamics (QMD) simulations are available at a USC course home page

EXTREME-SCALE QUANTUM SIMULATIONS

Course Description

Computer simulation of quantum-mechanical dynamics has become an essential enabling technology for physical, chemical & biological sciences & engineering. Quantum-dynamics simulations on extreme-scale parallel supercomputers would provide unprecedented predictive power, but pose enormous challenges as well. This course surveys & projects algorithmic & computing technologies that will make quantum-dynamics simulations metascalable, *i.e.*, "design once, continue to scale on future computer architectures".

https://aiichironakano.github.io/cs699.html