

Iterative Energy Minimization for Quantum Molecular Dynamics

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From quantum dynamics to eigenvalue problems



Imaginary-Time Quantum Dynamics

- Quantum dynamics

Repeat

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

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

Repeat

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

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

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

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

- Filtering in the ground state

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

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

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 — $\hat{P}_{out} = 1 - |0\rangle\langle 0|$:
 $\langle 0|\{|\psi\rangle - |0\rangle\langle 0|\psi\rangle\} = \langle 0|\psi\rangle - \underbrace{\langle 0|0\rangle\langle 0|\psi\rangle}_0 = 0$

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

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

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

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

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

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

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

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

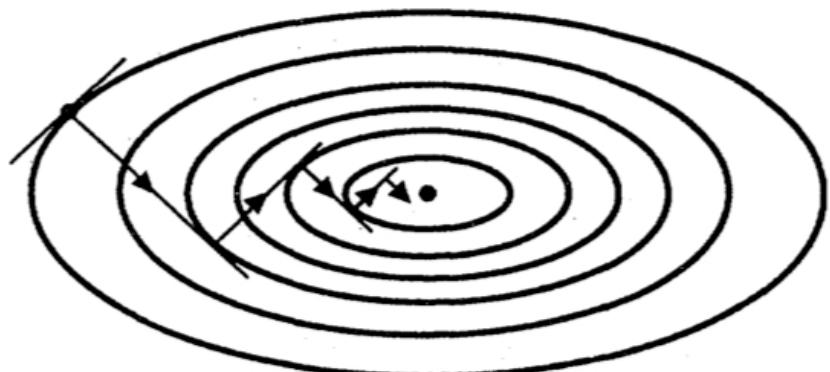
- Gradient (for a normalized wave function)

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

- 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

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

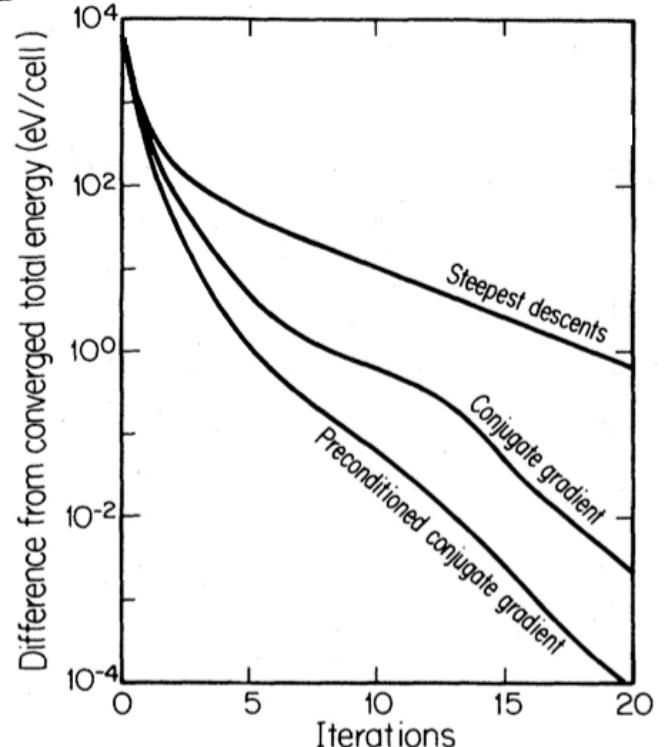
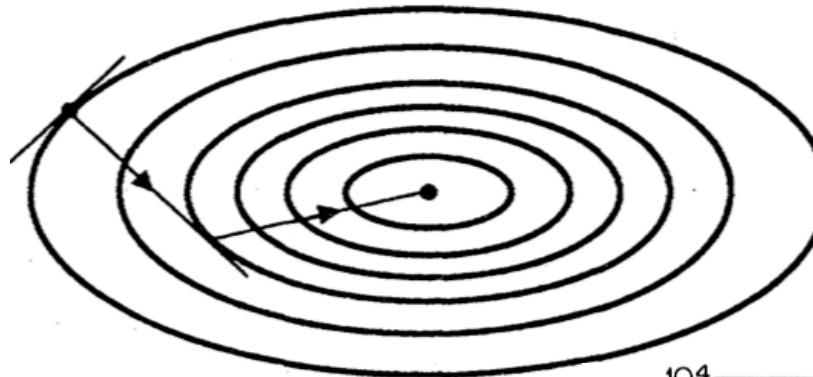
 endif

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

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

 if convergent, exit

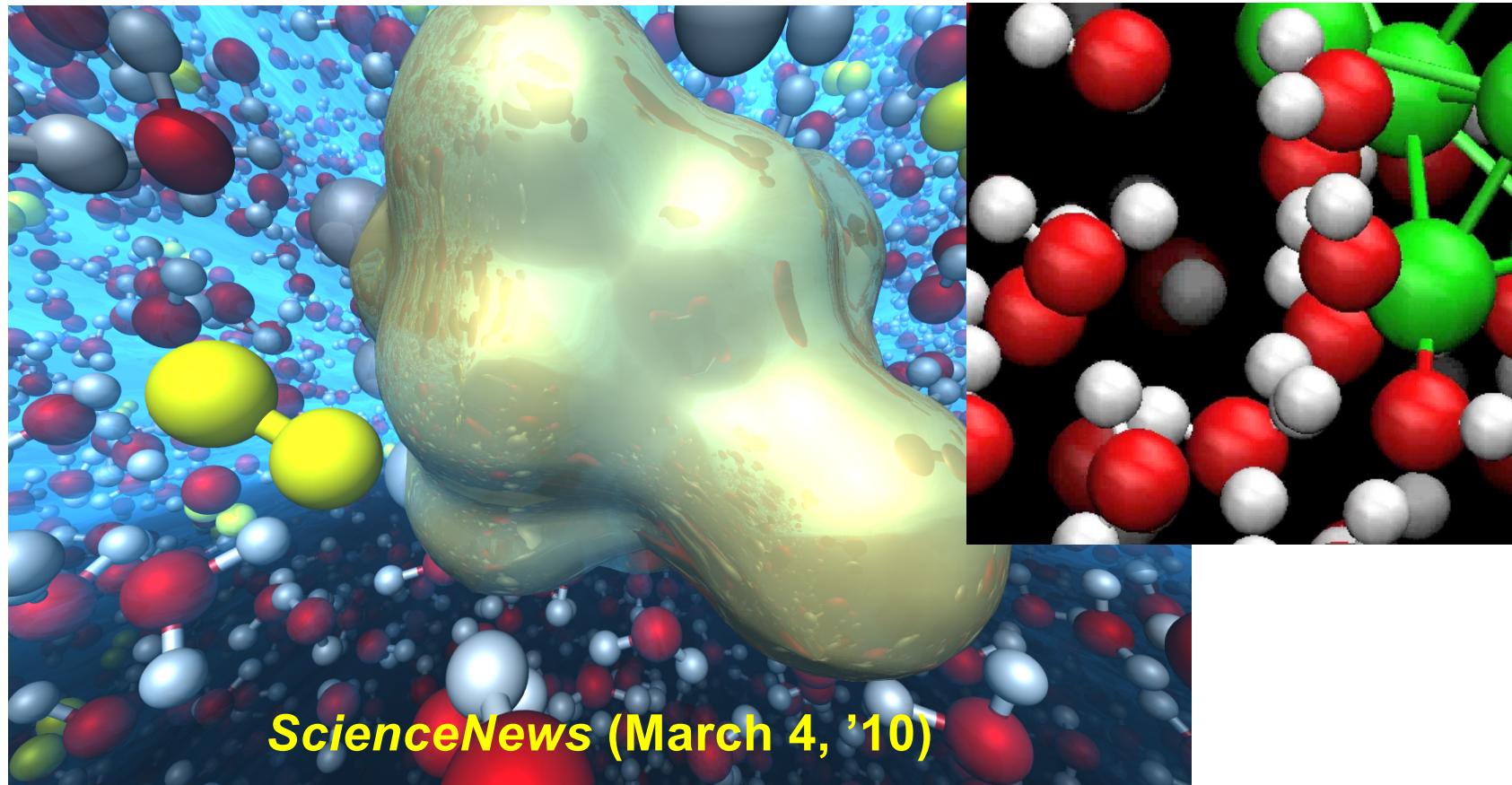
endfor



Quantum Molecular Dynamics

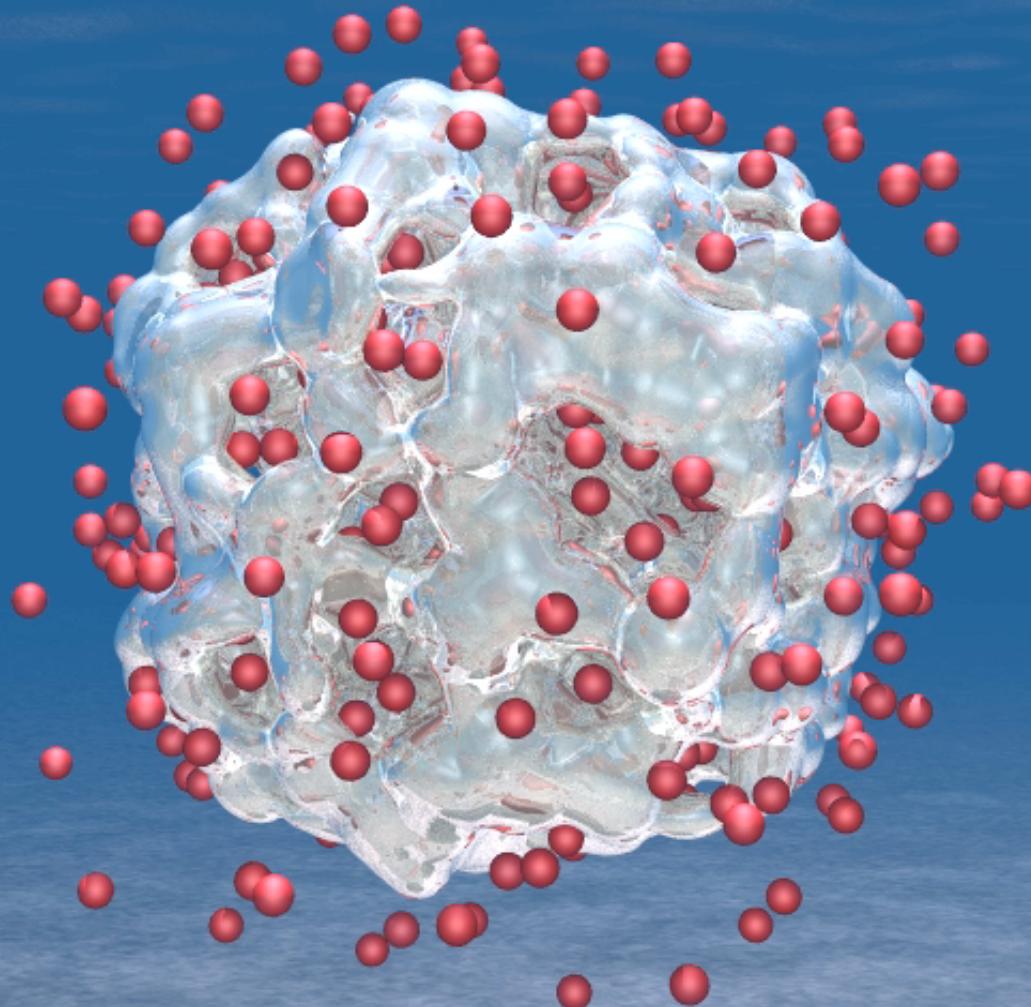
- Born-Oppenheimer (adiabatic) approximation: Electron wave function $\psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}})$ is determined with fixed nuclei positions \mathbf{R}_n ($n = 1, \dots, N_{\text{nucleus}}$)
 $\psi_*(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}}) \leftarrow \text{argmin}_E [\psi(\mathbf{r}_1, \dots, \mathbf{r}_{N_{\text{electron}}}), \{\mathbf{R}_n\}]$ CG
- Newton's equations for the classical motion of nuclei

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

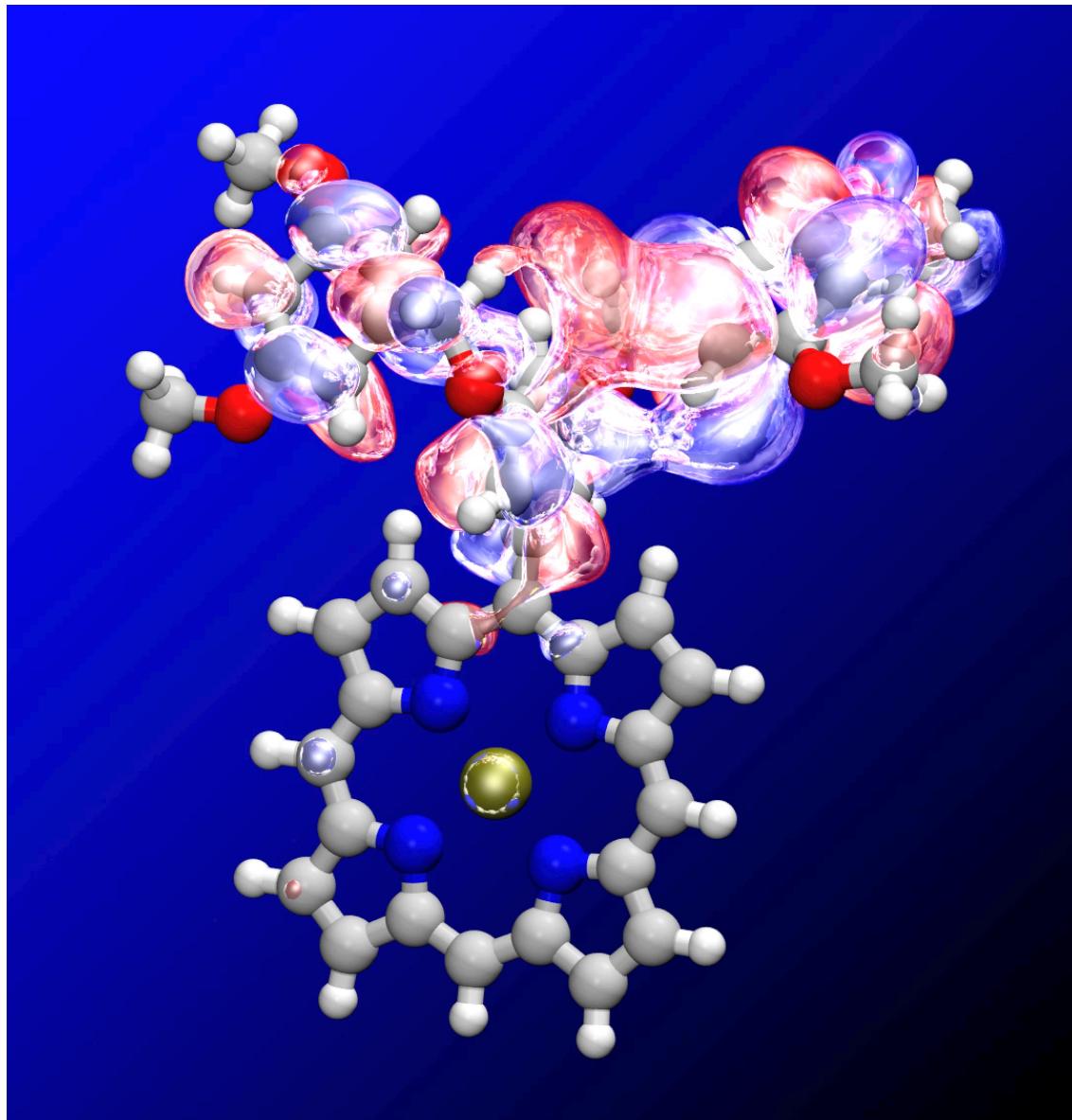


H₂ Production from Water Using LiAl Particles

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



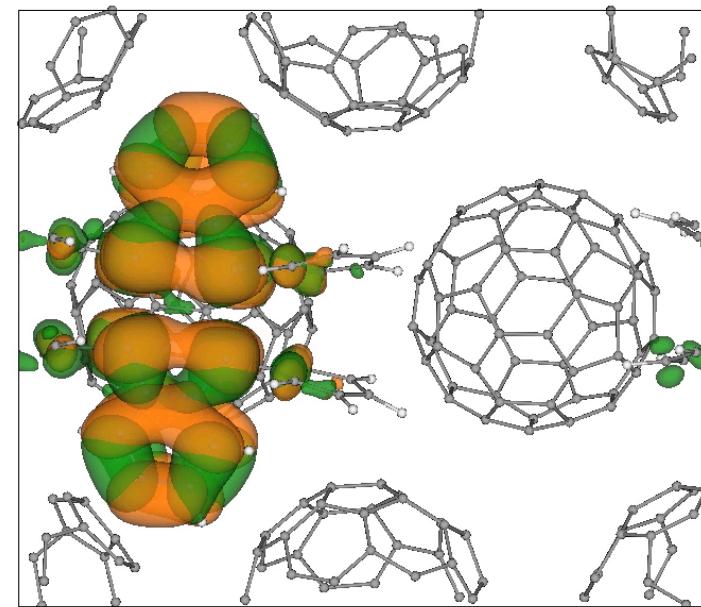
Nonadiabatic Quantum Molecular Dynamics



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

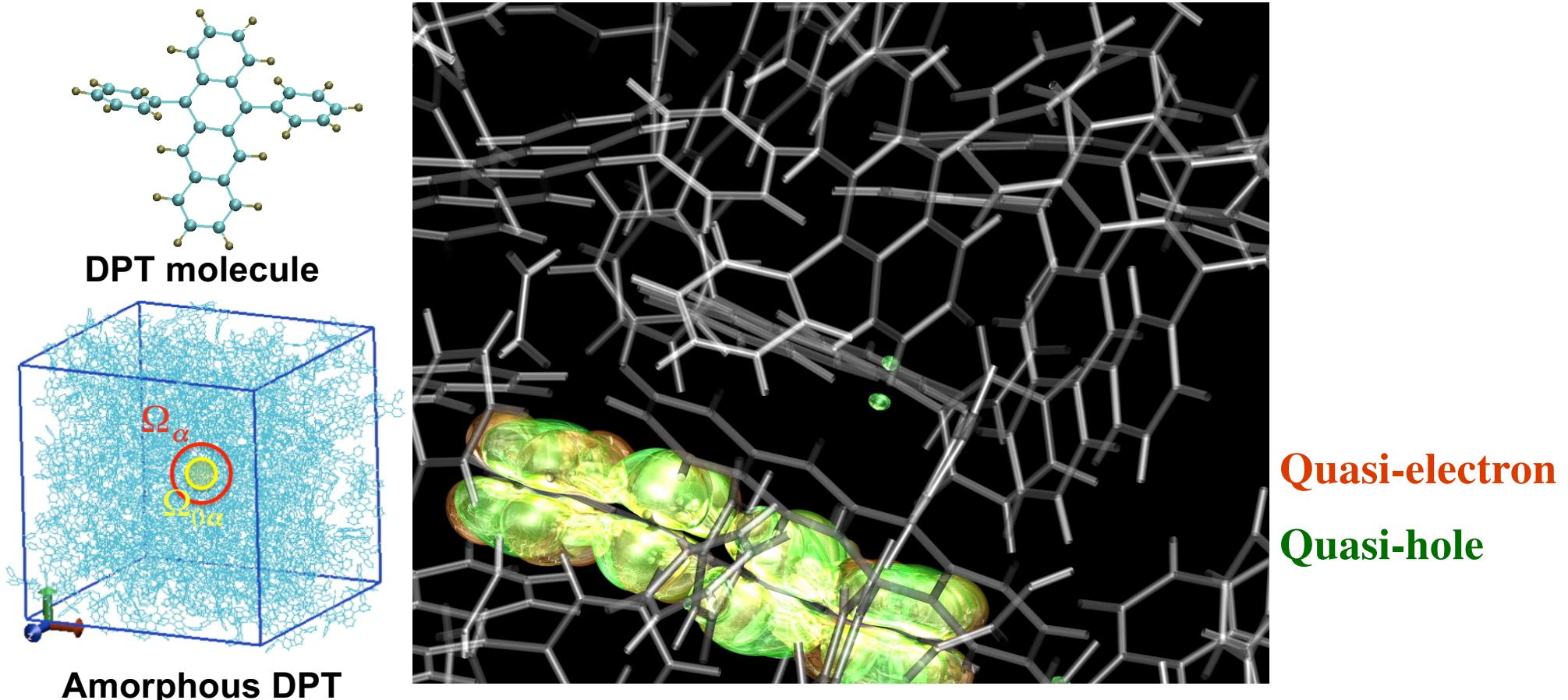


quasi-electron; quasi-hole

- **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

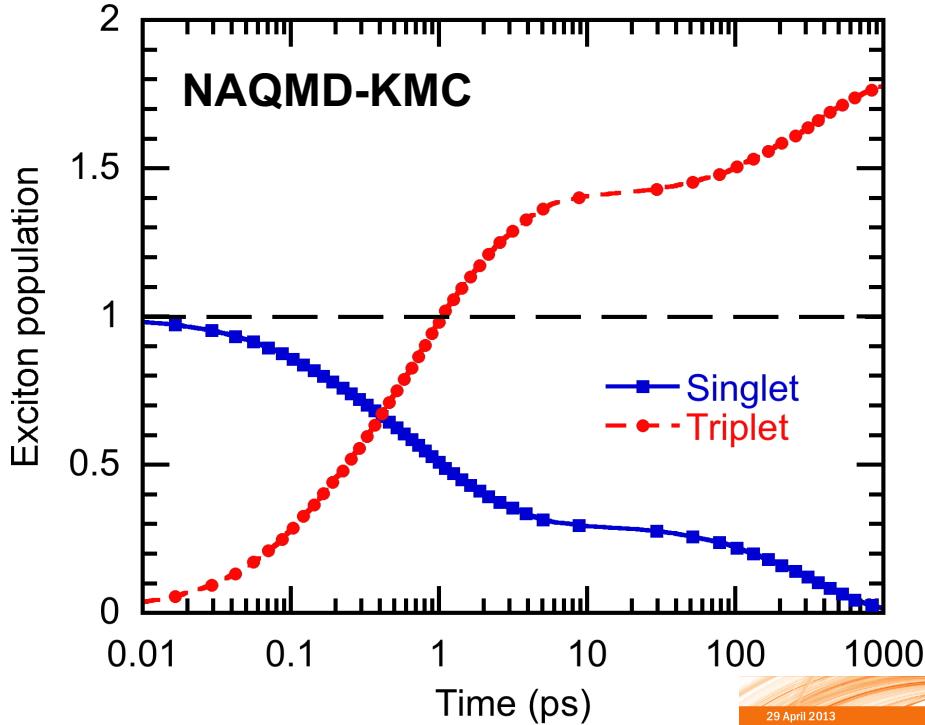
- Move up from molecules to microstructures
- Challenge: Unprecedented 10^4 -atom NAQMD simulation
- Computational approach: Divide-conquer-recombine (DCR) NAQMD



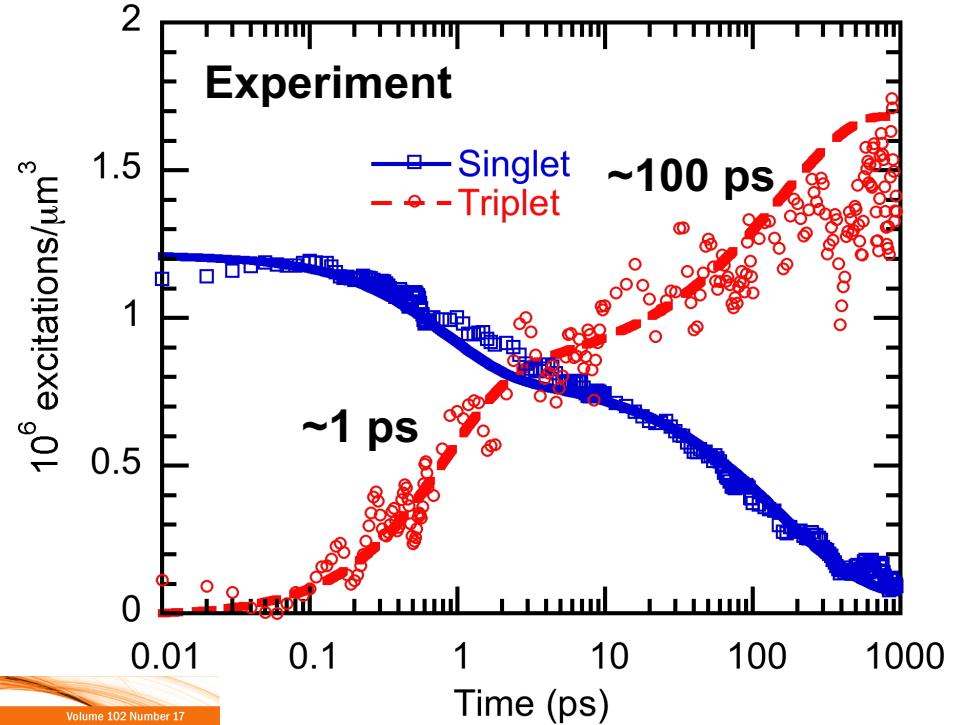
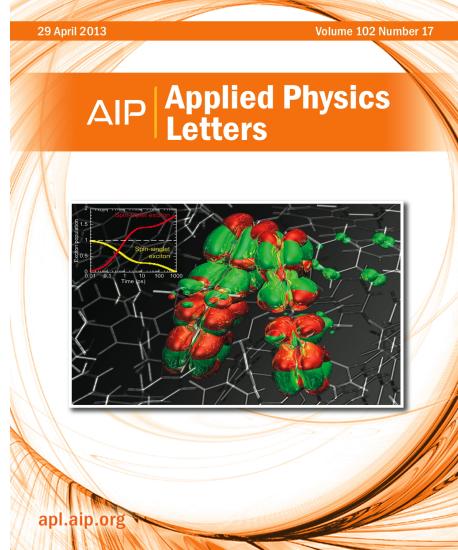
- Divide-conquer-recombine NAQMD (phonon-assisted exciton dynamics) + time-dependent perturbation theory (singlet-fission rate) + kinetic Monte Carlo calculations of exciton population dynamics in 6,400-atom amorphous DPT

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)

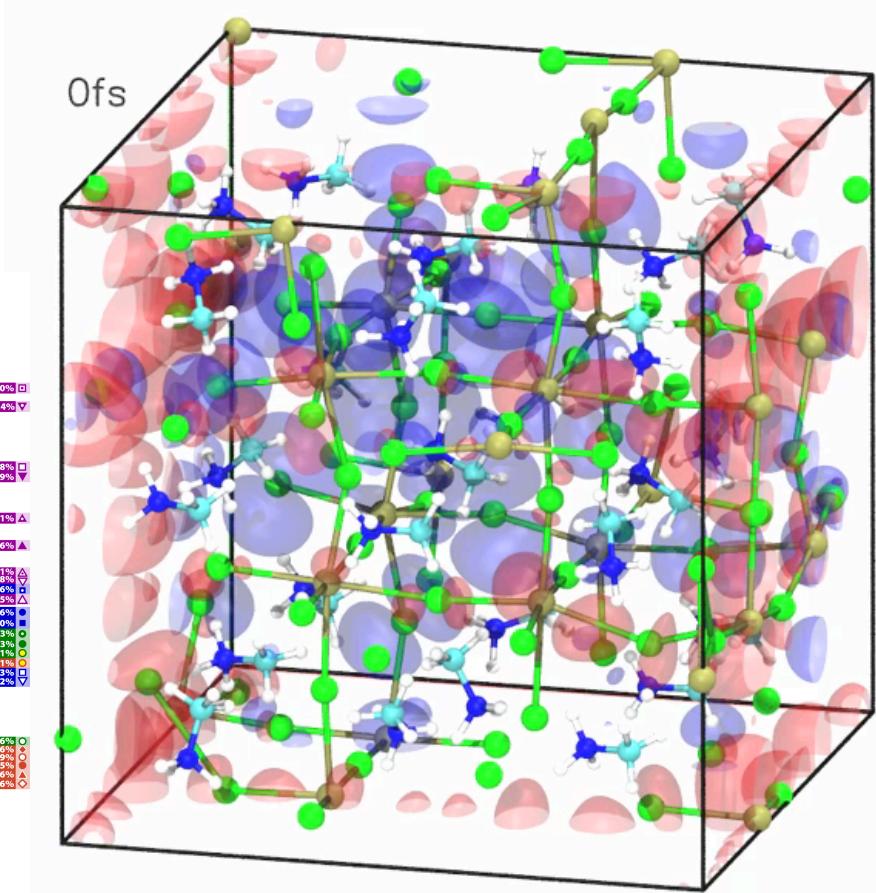
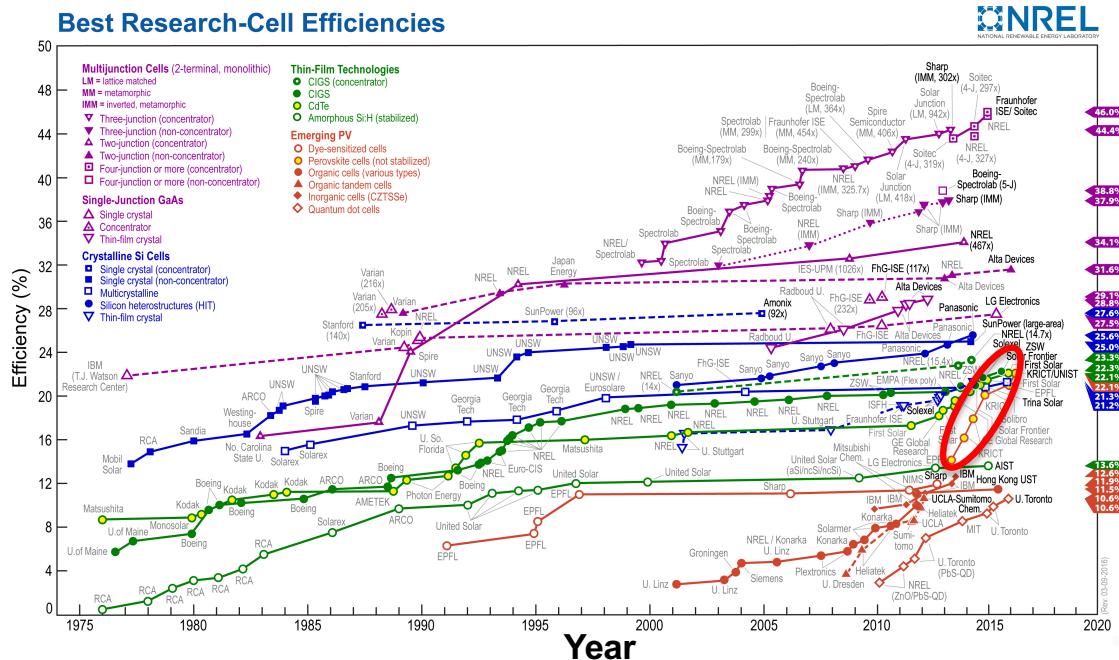


S. T. Roberts *et al.*,
J. Am. Chem. Soc.
134, 6388 ('12)

Photoexcited Carriers in MAPbI_3

- Organometal halide perovskites (*e.g.* methylammonium lead iodide, $\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) for solar cells with high power conversion efficiency > 20%

Stranks & Snaith, *Nat. Nanotechnol.* 10, 391 ('15)



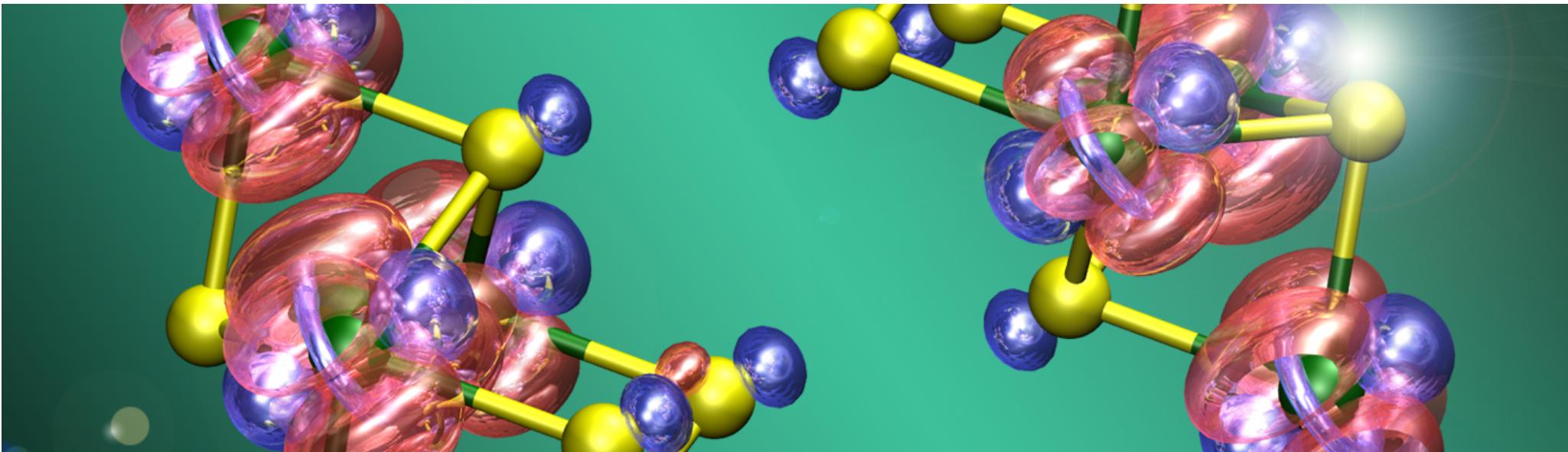
- Nonadiabatic QMD simulation

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 $D_e = (1.16 \pm 0.31) \times 10^{-2} \text{ cm}^2/\text{s}$ & $D_h = (1.01 \pm 0.42) \times 10^{-2} \text{ cm}^2/\text{s}$

Expt: $D_e = (1.7 \pm 1.1) \times 10^{-2} \text{ cm}^2/\text{s}$ & $D_h = (1.1 \pm 0.7) \times 10^{-2} \text{ cm}^2/\text{s}$ [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

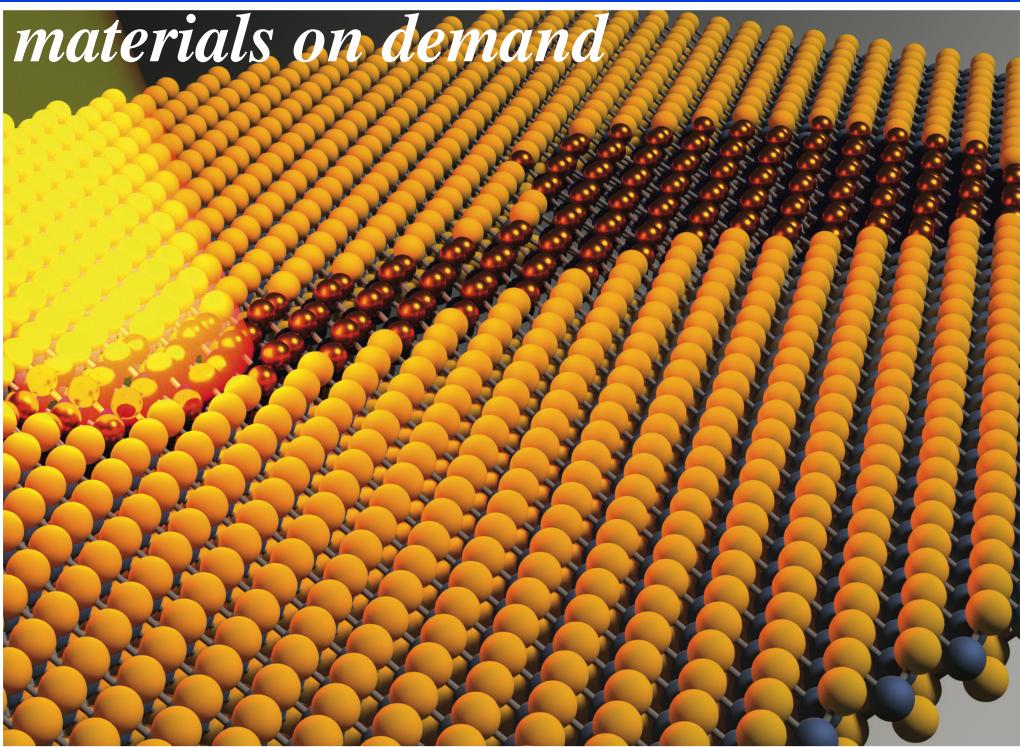
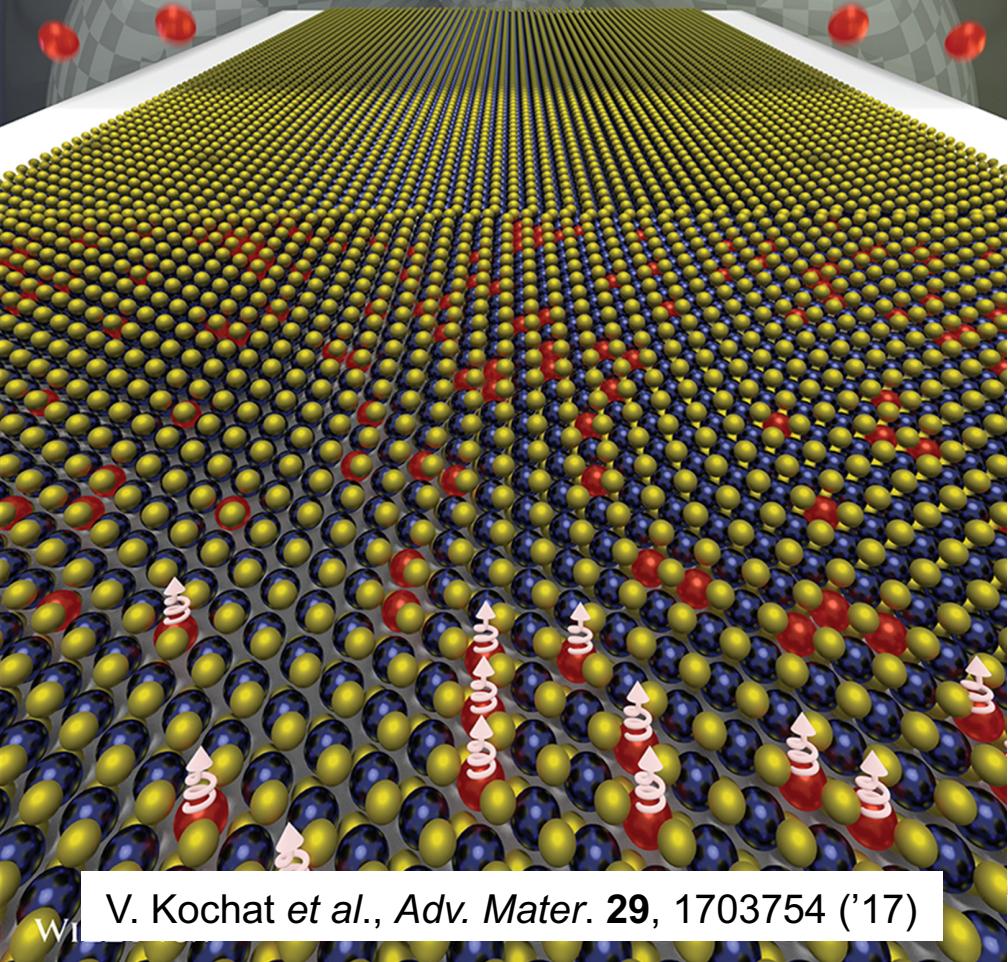
M.F. Lin *et al.*, *Nature Commun.* **8**, 1745 ('17)
I. Tung *et al.*, *Nature Photon.* **13**, 425 ('19)

Quantum Molecular Dynamics Simulations

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Emergent quantum ADVANCED MATERIALS

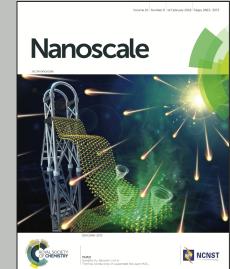


Showcasing research from Collaboratory for Advanced Computing and Simulations (CACS), University of Southern California, Los Angeles, USA.

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

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>