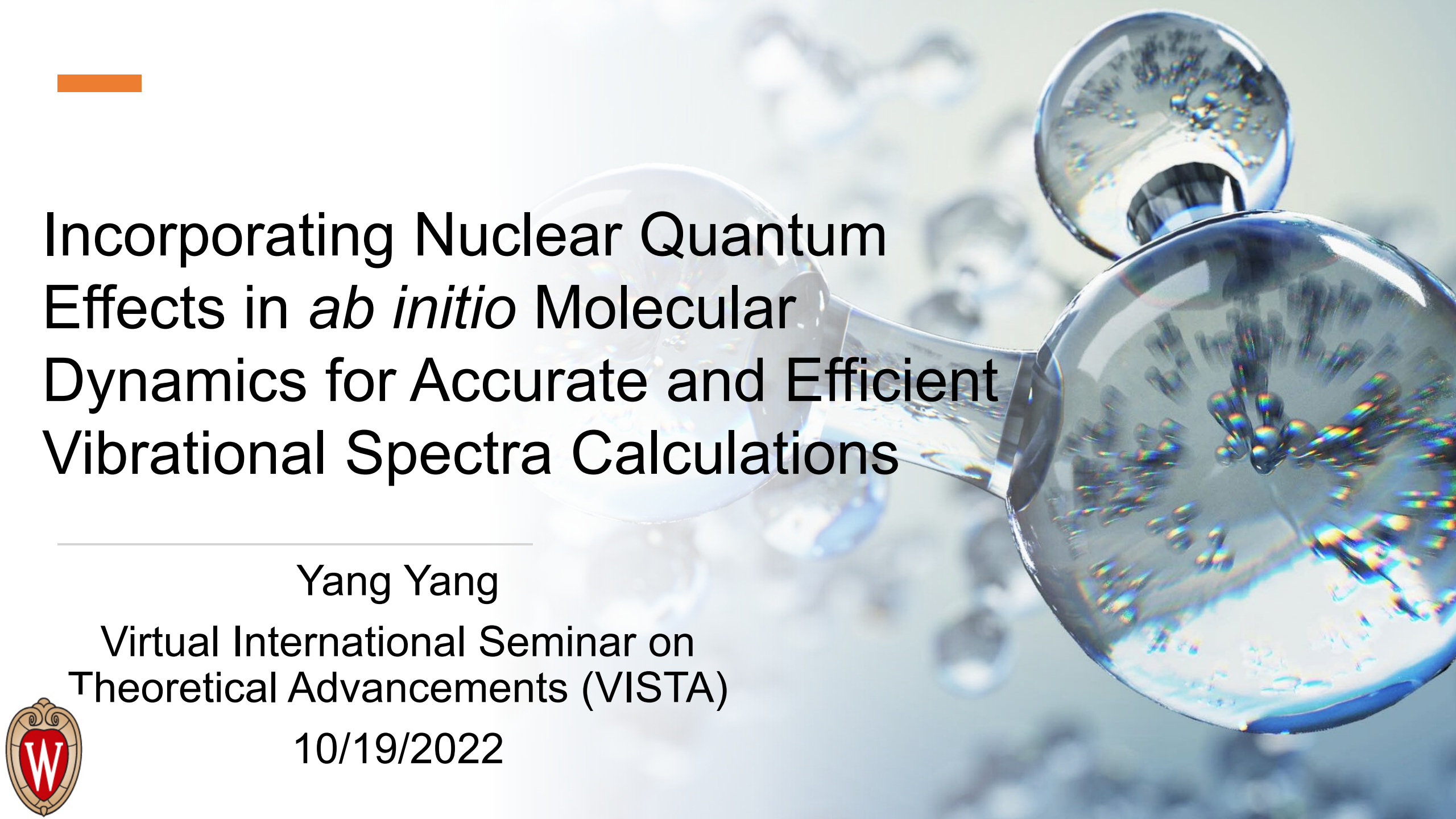
Incorporating Nuclear Quantum Effects in *ab initio* Molecular Dynamics for Accurate and Efficient Vibrational Spectra Calculations

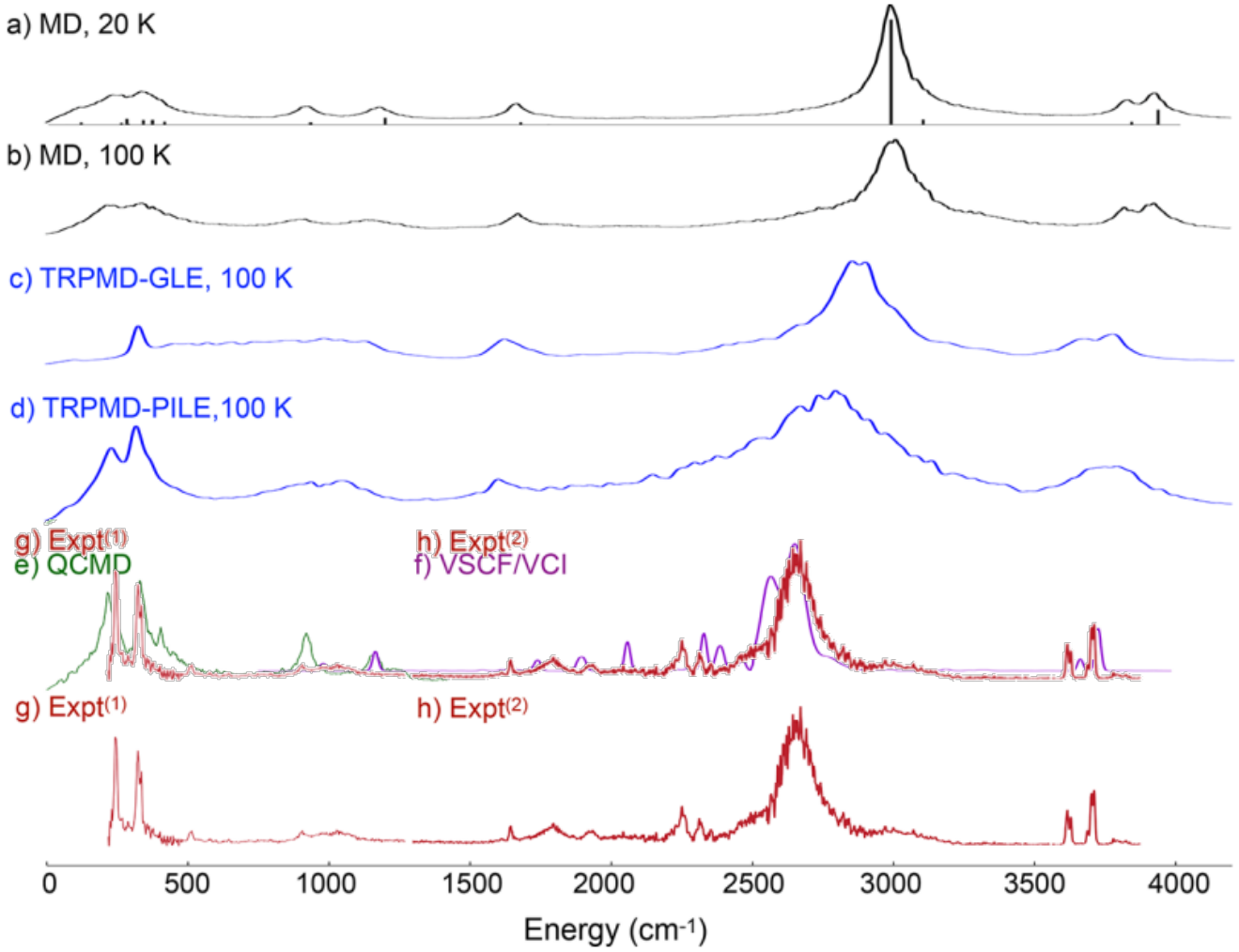


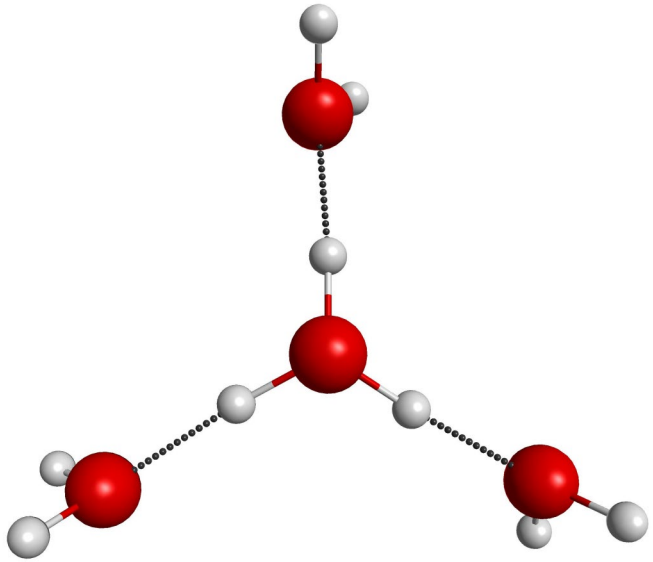
Yang Yang

Virtual International Seminar on Theoretical Advancements (VISTA)

10/19/2022

Challenging IR spectrum of $H_9O_4^+$





- Problematic conventional MD
- TRPMD broad peaks
- Expensive VSCF/VCI

Y. Qi, and J. Bowman, *J. Am. Chem. Soc.* **139**, 10984 (2017)
Y. Qi, and J. Bowman, *J. Phys. Chem. A.* **123**, 1399 (2019)

Nuclear Quantum Effects (NQEs)

Outline

- Background: Nuclear quantum effects (NQEs)
- Method development 1: Constrained multicomponent DFT
- Method development 2: Molecular dynamics with NQEs
- Combination: CNEO-MD and results in molecules
- Summary

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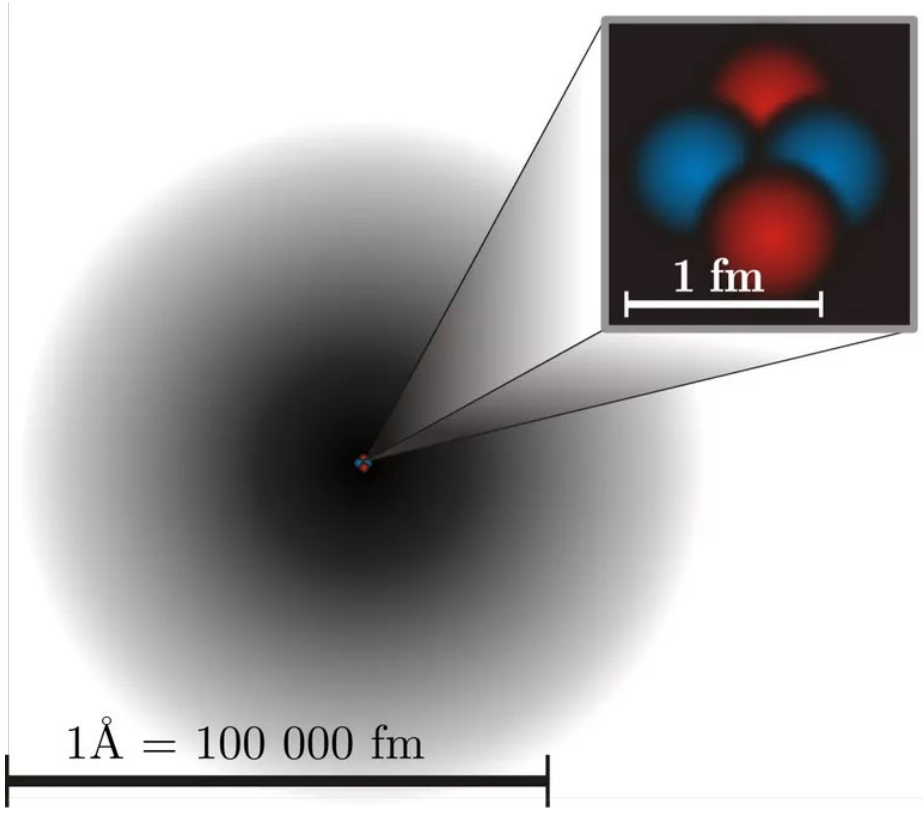
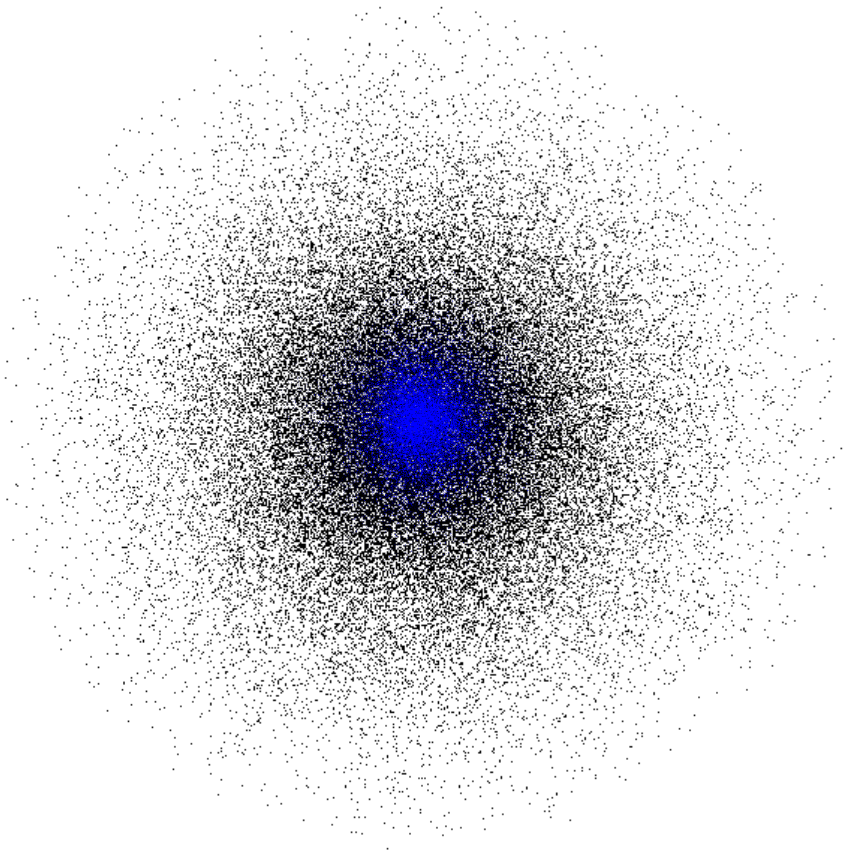
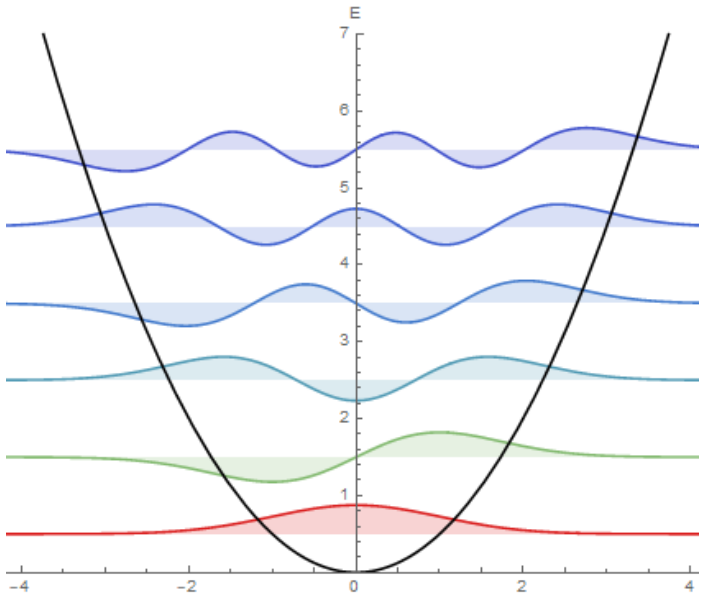
Electron cloud and nuclear cloud





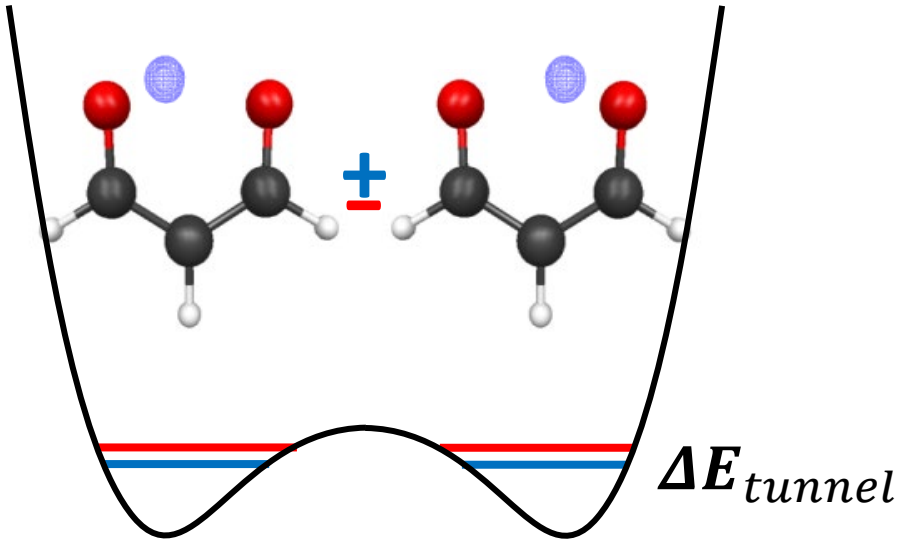
What are nuclear quantum effects?



Vibrational excited states

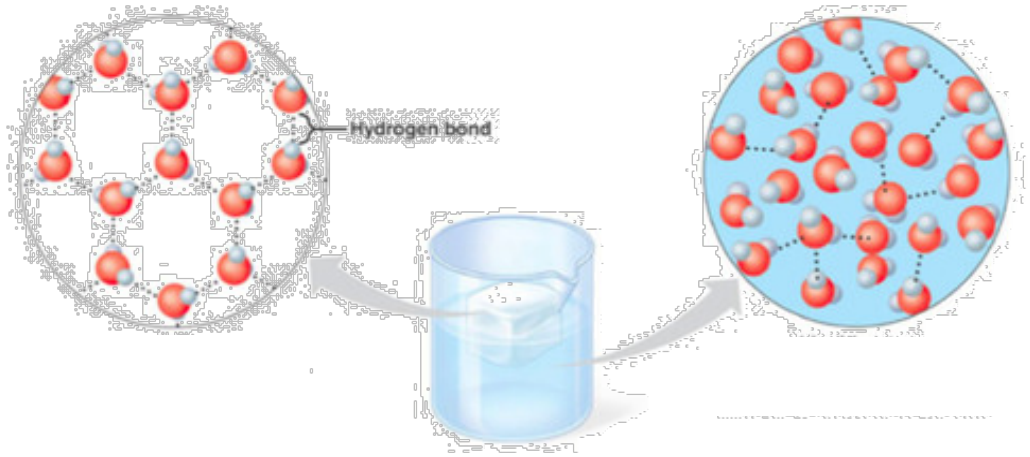
Zero-point energy

Quantum Delocalization

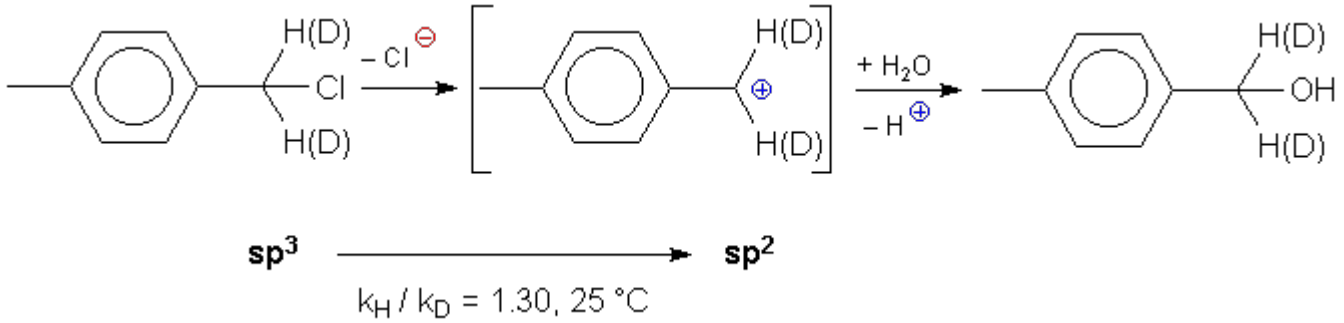


Tunneling

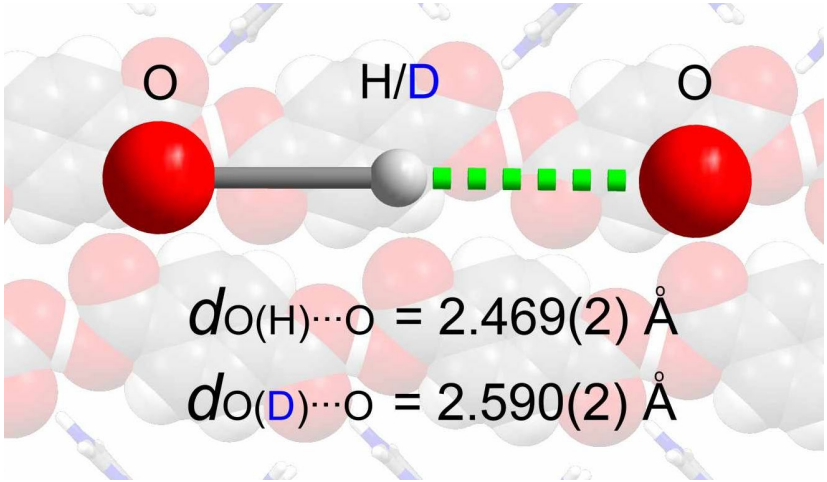
Nuclear quantum effects in physics, chemistry, and biology



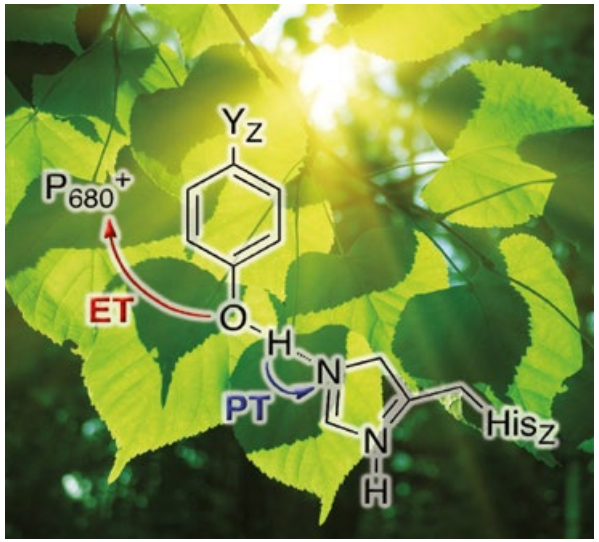
Hydrogen bonds and Water properties



Kinetic isotope effect



Geometric isotope effect

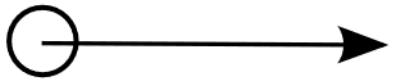


Proton coupled electron transfer

Image from RSC Publishing

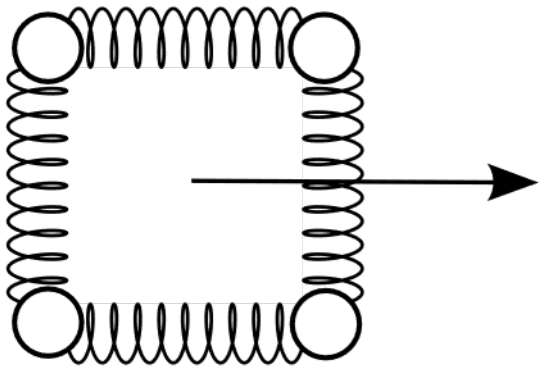
Commonly used methods for molecular simulations

$$F = m\ddot{x}$$



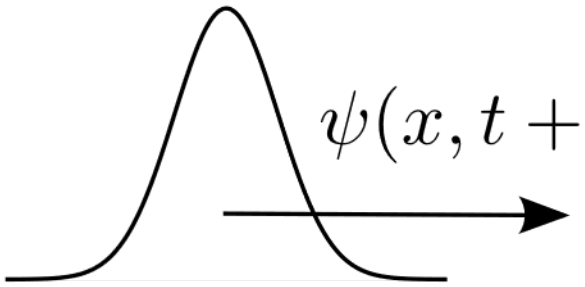
Classical Mechanics

Very good and cheap



Path-integral formulation

Pretty good and less expensive



$$\psi(x, t + \Delta t) = U(\Delta t)\psi(x, t)$$

Quantum dynamics

Accurate but expensive

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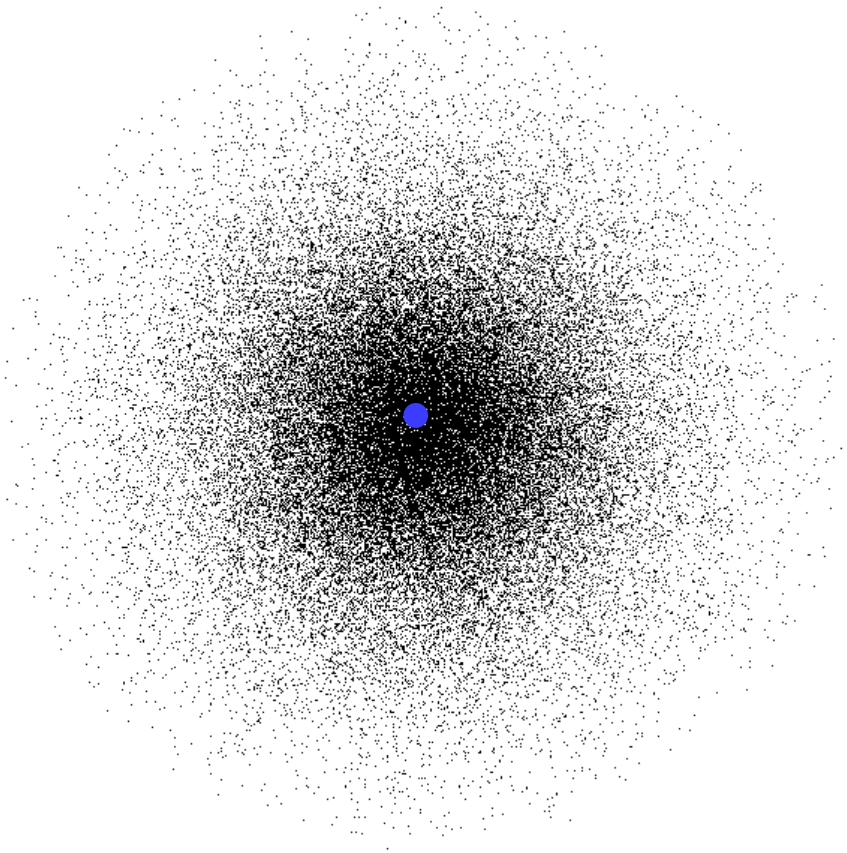
Classical MD picture: point charge nuclei



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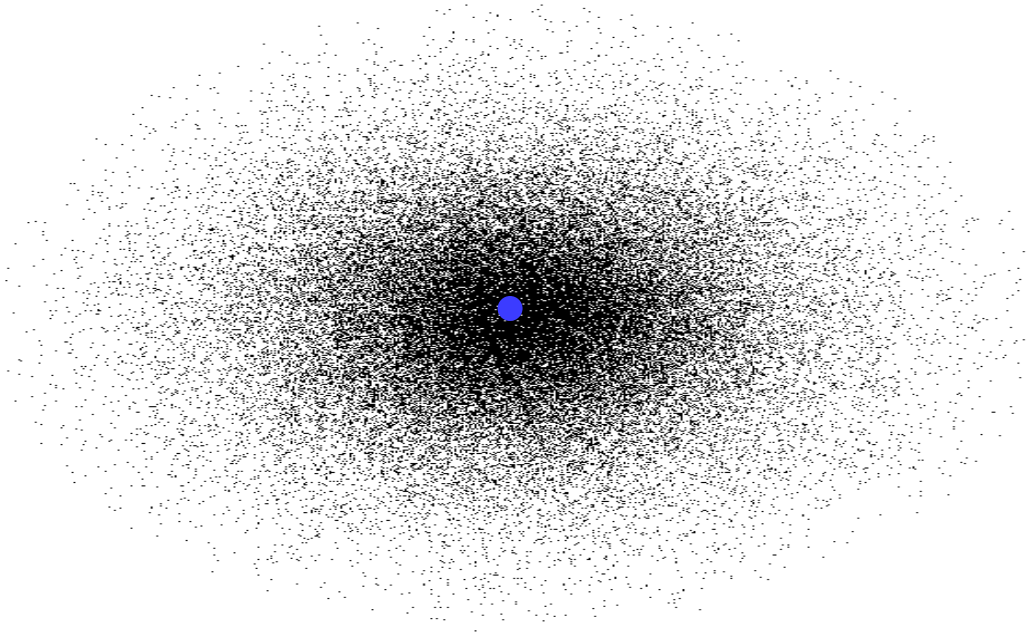
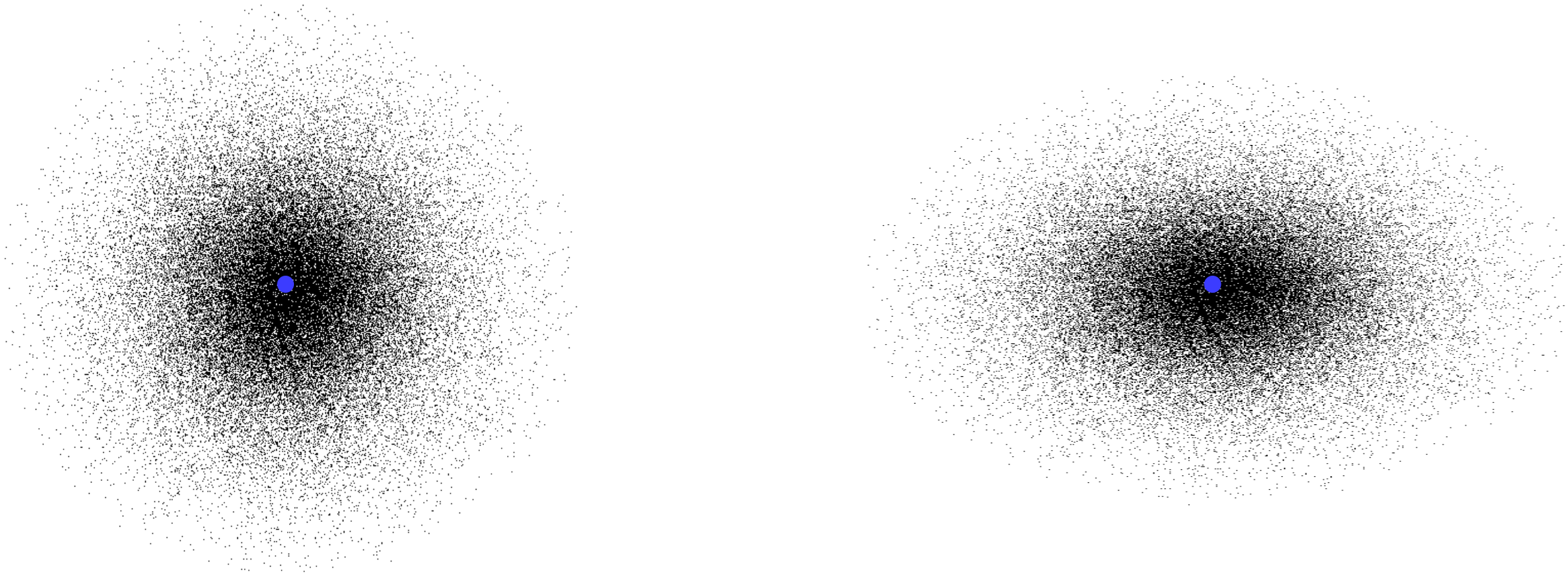
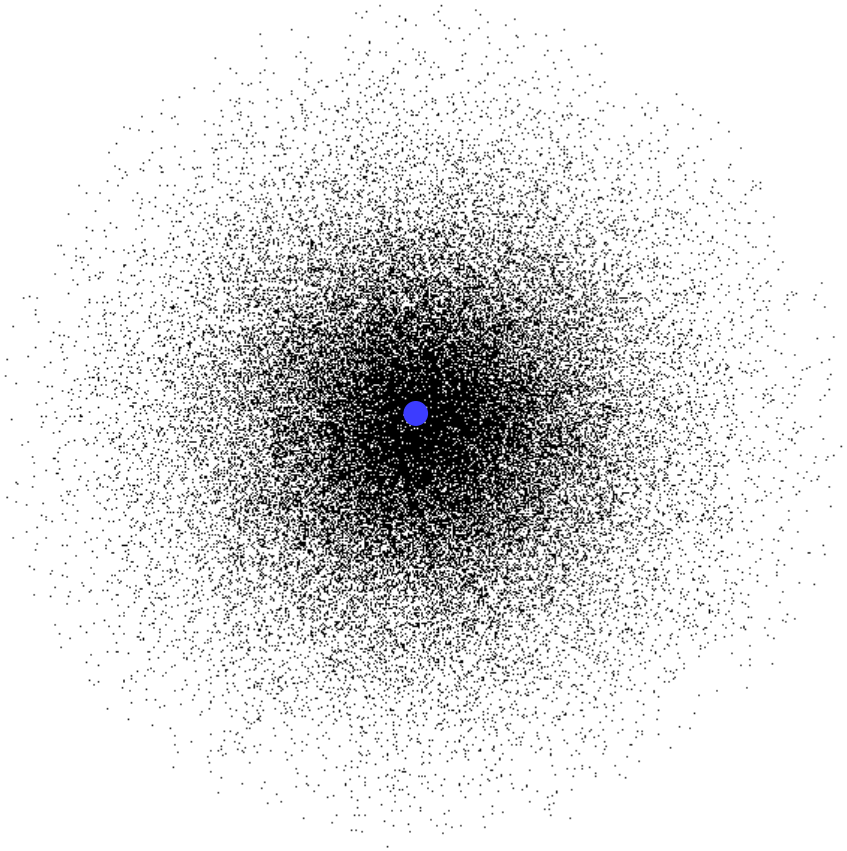


Classical MD picture: Adiabatic approximation

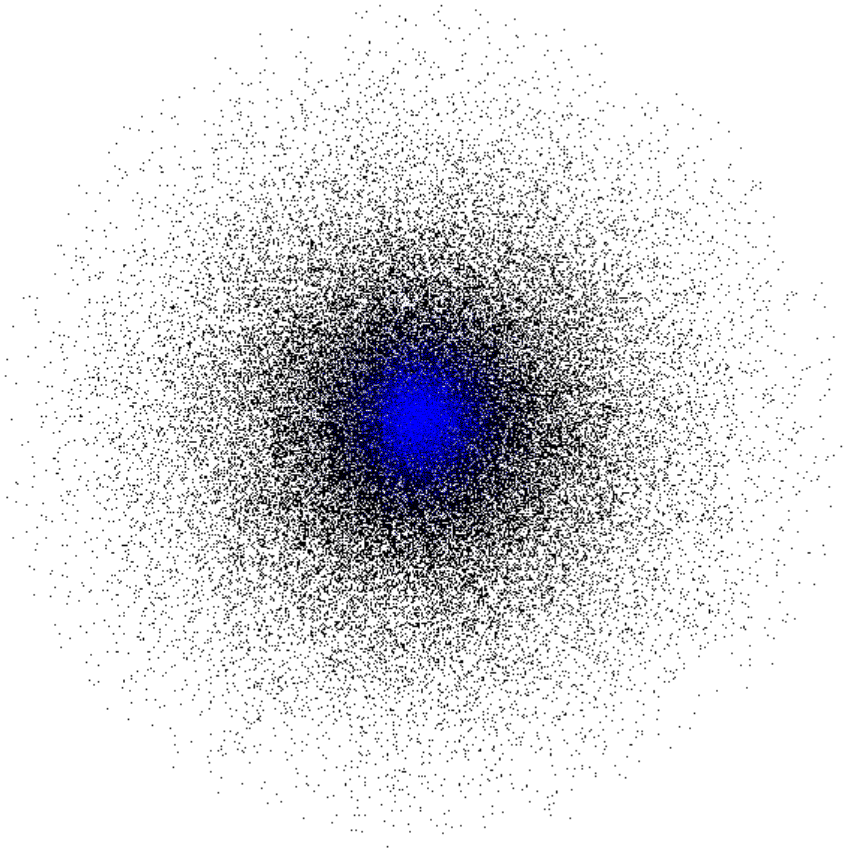


- Classical nuclei
- Quantum electrons
  - Common assumption: relax adiabatically (Usually ground state $\Psi(\mathbf{r}_e;\mathbf{R}_n)$)

Real picture: nuclei NOT point charges

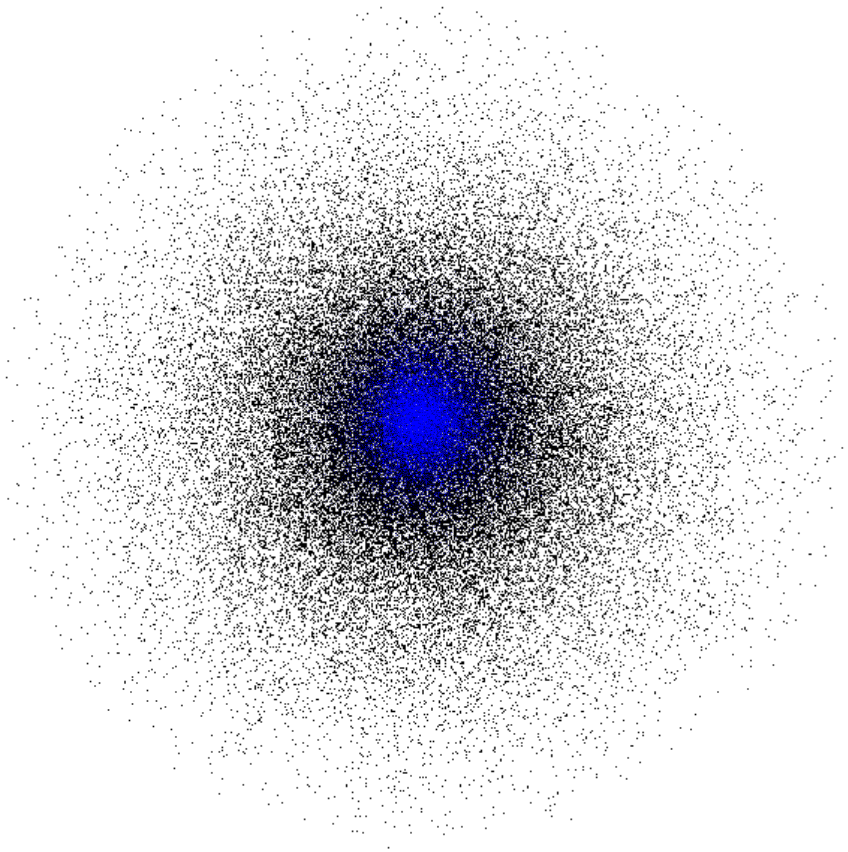


Incorrect picture: Point charge

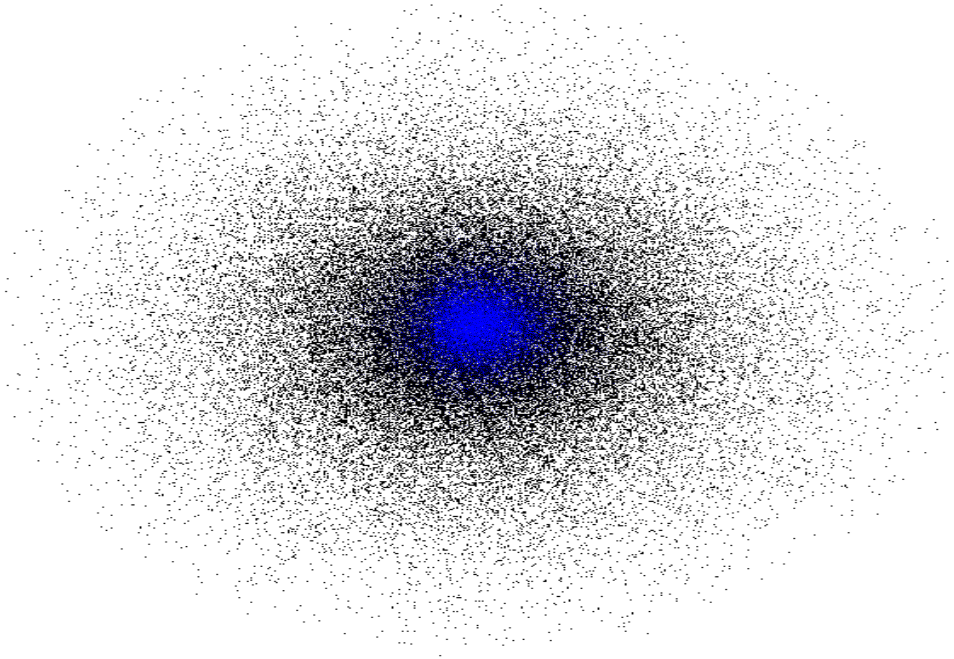


Correct picture: Nuclear cloud

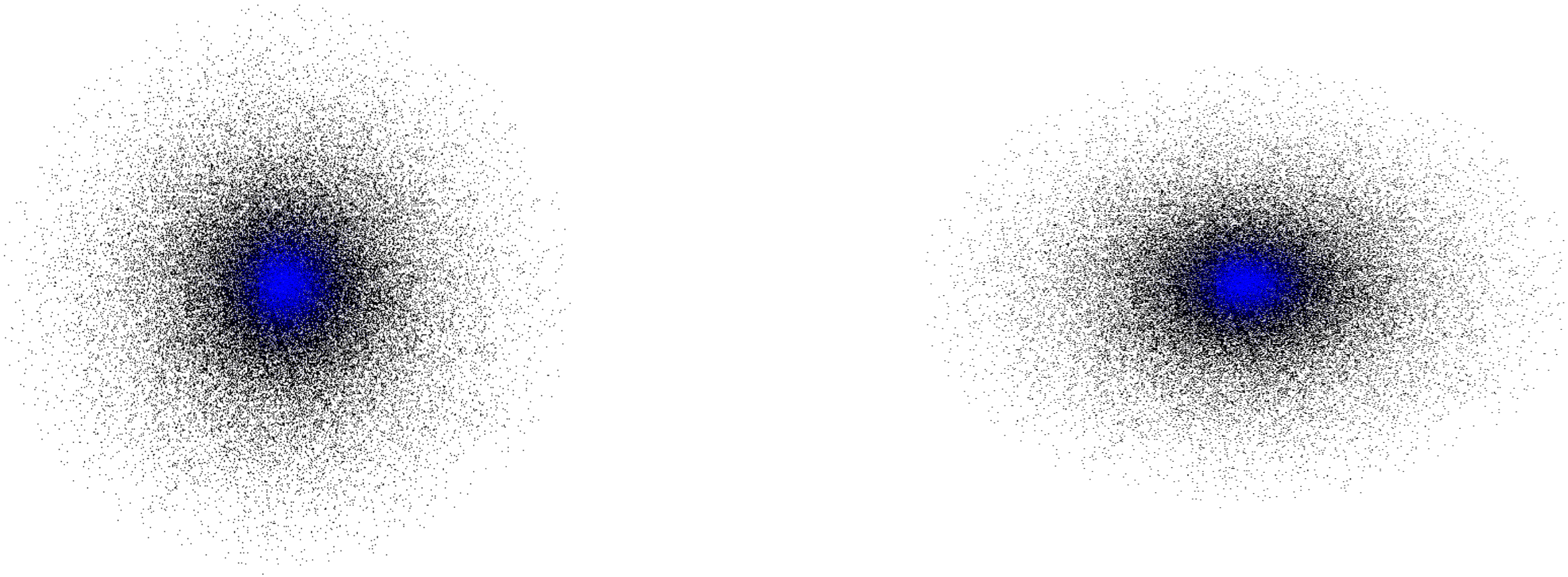
Real dynamics picture



Real dynamics picture



A new way of performing MD



- Quantum nuclei and quantum electrons
- **Key assumption 1:** Quantum nuclear expectation positions denote geometries
- **Key assumption 2:** Both nuclei and electrons relax adiabatically $\Psi(\mathbf{r}_e, \mathbf{R}_n; \langle \mathbf{R}_n \rangle)$

Need a quantum chemistry method that…

- Treats both electrons and nuclei quantum mechanically

  Multicomponent density functional theory: $E = E[\rho^e, \{\rho^n\}]$

- Gives energy surface as a function of nuclear expectation positions

  Satisfies: $\langle \phi^n \left| \mathbf{r} \right| \phi^n \rangle = \mathbf{R}^n$

- Minimizes energy (Adiabatic approximation) at a particular geometry

  Find solution: $\min E$

J. Capitani, R. F. Nalewajski, and R. G. Parr, *J. Chem. Phys*. **76**, 568 (1972)

Existence of multicomponent density functional theory

- Hohenberg-Kohn theorem for multicomponent system

$$E = E[\rho^e, \{\rho^n\}]$$

- Kohn-Sham Formalism

$$(-\frac{1}{2}\nabla^2 + v^e)\phi^e = \epsilon^e \phi^e$$

$$(-\frac{1}{2m^n}\nabla^2 + v^n)\phi^n = \epsilon^n \phi^n$$

- Many names: NOMO, MCMO, NEO, APMO…

J. Capitani, R. F. Nalewajski, and R. G. Parr, *J. Chem. Phys*. **76**, 568 (1972)

Constrained multicomponent density functional theory (CNEO-DFT)

- Modified Lagrange multiplier in Lagrangian

$$L = E[\rho^e, \rho^n] - \sum_i \epsilon_i \left(\langle \phi_i \mid \phi_i \rangle - 1 \right) + \sum_n \mathbf{f}^n \cdot \left(\langle \phi^n \left| \mathbf{r} \right| \phi^n \rangle - \mathbf{R}^n \right)$$

- Electronic equation

$$(-\frac{1}{2}\nabla^2 + v^e)\phi^e = \epsilon^e \phi^e$$

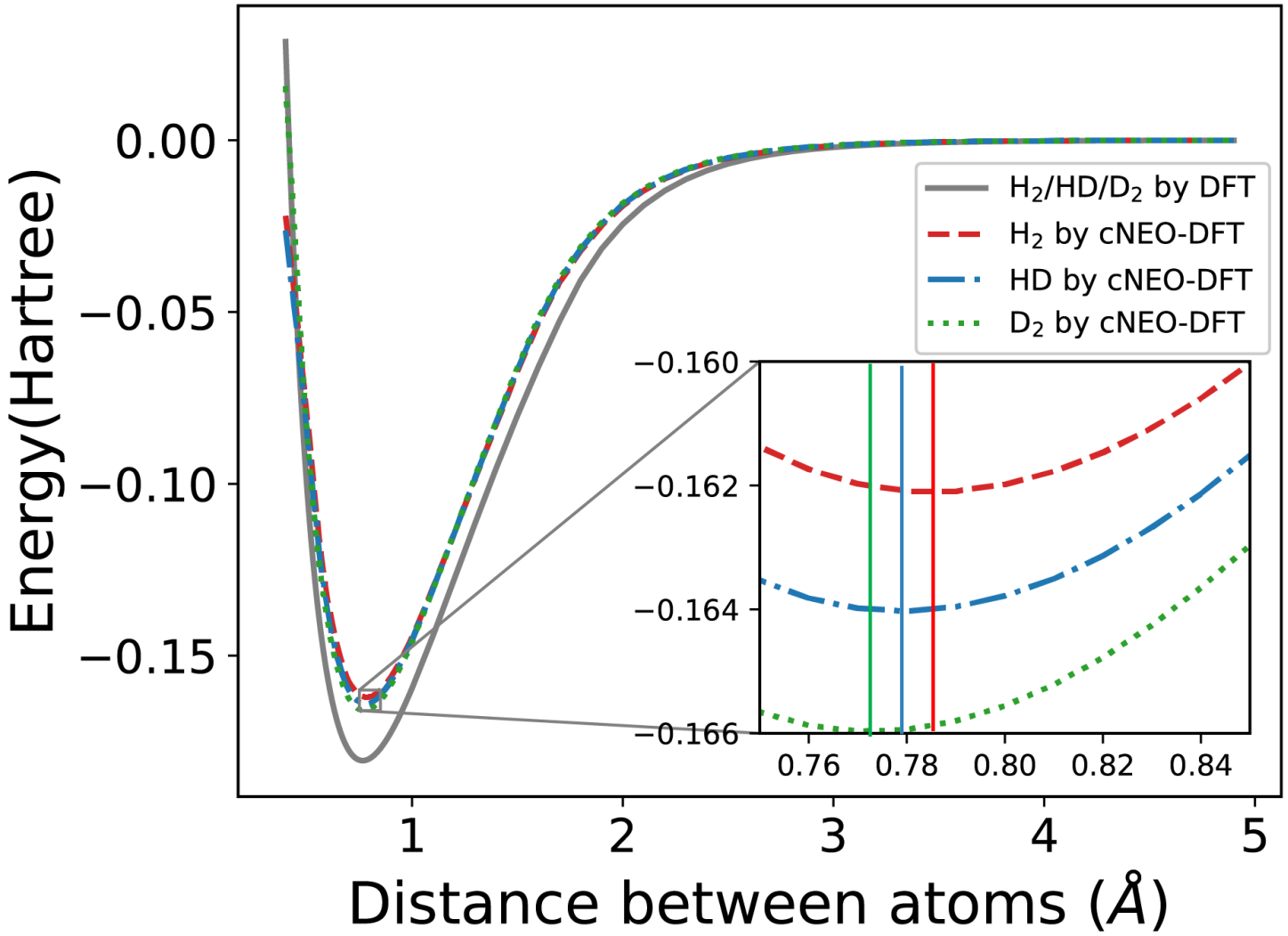
- An extra term for nuclear equation

$$(-\frac{1}{2m^n}\nabla^2 + v^n + \mathbf{f}^n \cdot \mathbf{r})\phi^n = \epsilon^n \phi^n$$

SCF solve for ϕ^e and ϕ^n at each geometry, evaluate energy $E(\mathbf{R}^n)$

X. Xu and Y. Yang, *J. Chem. Phys.* **152**, 084107 (2020)
X. Xu, and Y. Yang, *J. Chem. Phys.* **153**, 074106 (2020)

Energy surface: ZPE and geometric isotope effects



- ZPE included in calculations
- Smaller ZPE for heavier isotopes
- Shorter bond length for heavier isotopes

X. Xu and Y. Yang, *J. Chem. Phys.* **152**, 084107 (2020)
X. Xu, and Y. Yang, *J. Chem. Phys.* **153**, 074106 (2020)

Perform MD using
Newton's Equations?

Theoretical Justification?

Outline

- Background: Nuclear quantum effects (NQEs)
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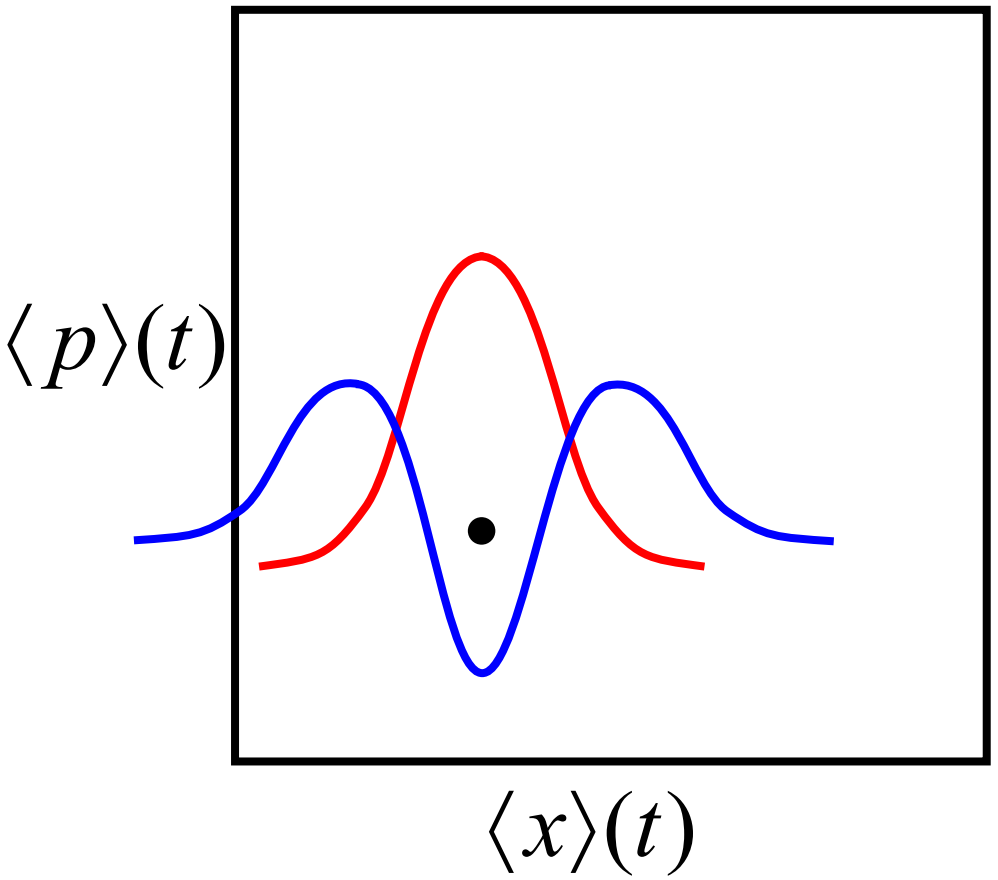
Ehrenfest Theorem: Connect quantum and classical

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x\rangle = \frac{\langle p\rangle}{m}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle p\rangle = -\langle\frac{\mathrm{d}}{\mathrm{d}x}V(x)\rangle$$

- Highly similar to classical equations
- Under special conditions
- Classical equations for expectation position and momentum
- Justify classical MD, but no nuclear quantum effects

Alternative formulation: Constrained minimization



- 1 phase point ↔ ∞ wave functions
- Adiabatic assumption: At a phase point, always relax to lowest-energy wave function
- Like constrained search

Zehua Chen, and Yang Yang, arXiv:2111.12832

Brief derivation

$$\psi(x,t) = A(x,t)\exp(\mathrm{i}S(x,t)/\hbar)$$

$$\langle \hat{T} \rangle(t) = \langle A(t) \mid \hat{T} \mid A(t) \rangle + \frac{\langle \hat{p} \rangle^2(t)}{2m} + \frac{\sigma_p^2(t)}{2m}$$

Quantum delocalization kinetic energy (ZPE)

Variance term

Observable kinetic energy

Conventional MD: Only observable kinetic energy (no ZPE)

Zehua Chen, and Yang Yang, arXiv:2111.12832

Brief derivation

$$\psi(x,t) = A(x,t)\exp(\mathrm{i}S(x,t)/\hbar)$$

$$\langle \hat{T} \rangle(t) = \langle A(t) | \hat{T} | A(t) \rangle + \frac{\langle \hat{p} \rangle^2(t)}{2m} + \frac{\sigma_p^2(t)}{2m}$$

$$\frac{\langle \hat{p} \rangle}{m} \cdot \frac{d\langle \hat{p} \rangle}{dt} = \left\langle \frac{\partial V}{\partial t} \right\rangle - \frac{d}{dt}\langle A(t) | \hat{H}(t) | A(t) \rangle - \frac{d}{dt}\frac{\sigma_p^2}{2m}$$

$$\approx \cdots$$

$$= -\frac{\langle \hat{p} \rangle}{m} \cdot \frac{d}{d\langle x \rangle}\langle A | \hat{H}(t) | A \rangle$$

Constrained Minimized Energy Surface (CMES)

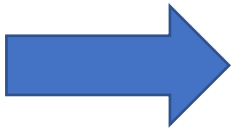
$$\frac{d\langle \hat{p} \rangle}{dt} \approx -\frac{d}{d\langle x \rangle}\langle A | \hat{H}(t) | A \rangle \equiv -\frac{d}{d\langle x \rangle} V^{\mathrm{CMES}}(\langle \hat{x} \rangle)$$

Zehua Chen, and Yang Yang, arXiv:2111.12832

Alternative classical equations for quantum system

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p\rangle}{m}$$

$$\frac{d}{dt}\langle p\rangle \approx -\frac{d}{d\langle x\rangle}V(\langle x\rangle)$$



$$\frac{d}{dt}\langle x\rangle = \frac{\langle p\rangle}{m}$$

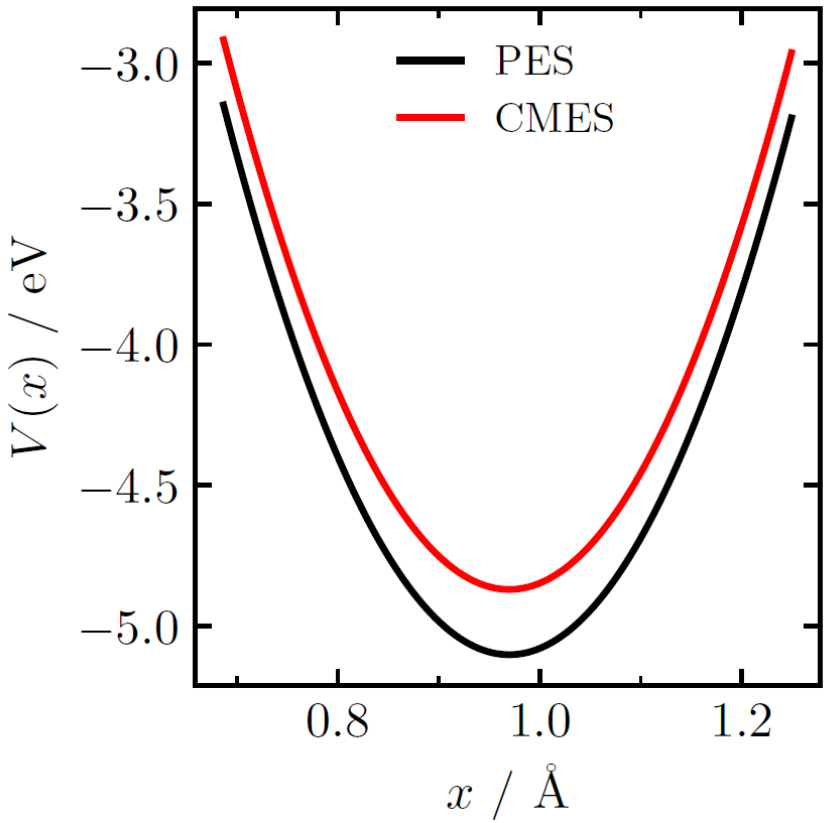
$$\frac{d}{dt}\langle p\rangle \approx -\frac{d}{d\langle x\rangle}V^{\mathrm{CMES}}(\langle \hat{x}\rangle)$$

$\langle A(t)|\hat{T}|A(t)\rangle$ included

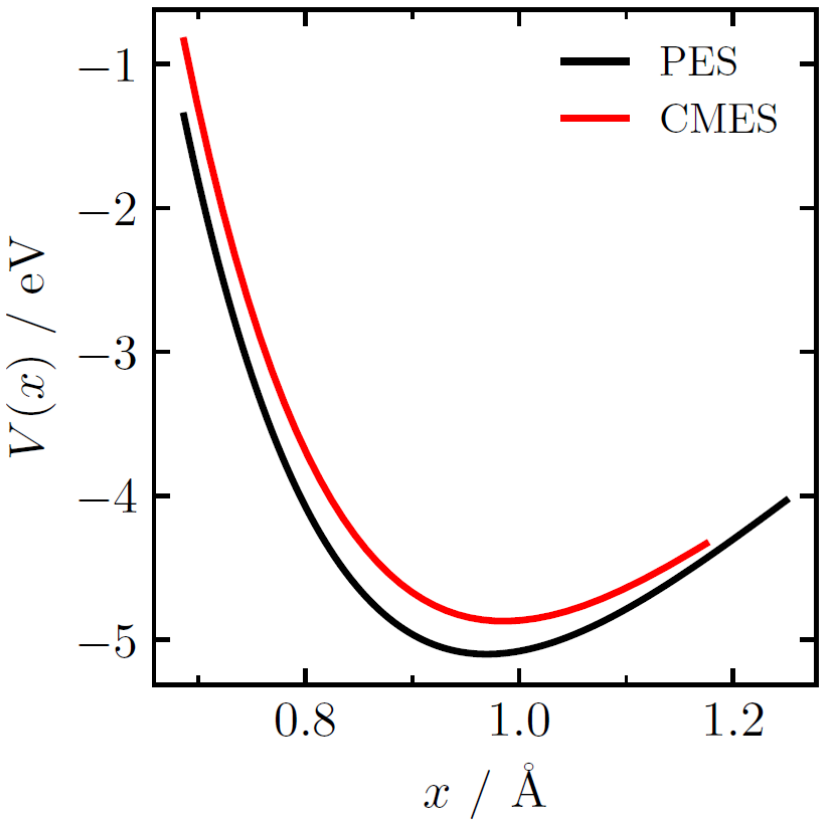
Quantum delocalization kinetic energy
Zero-point energy (ZPE)

Zehua Chen, and Yang Yang, arXiv:2111.12832

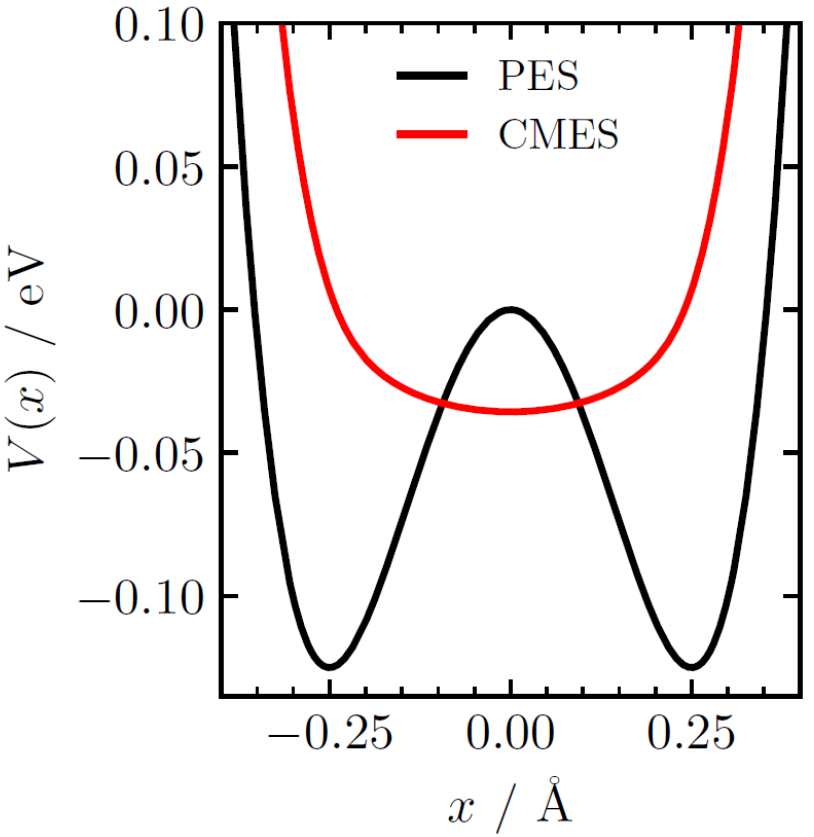
Model tests: PES vs CMES



Harmonic oscillator



Morse oscillator



Double-well potential

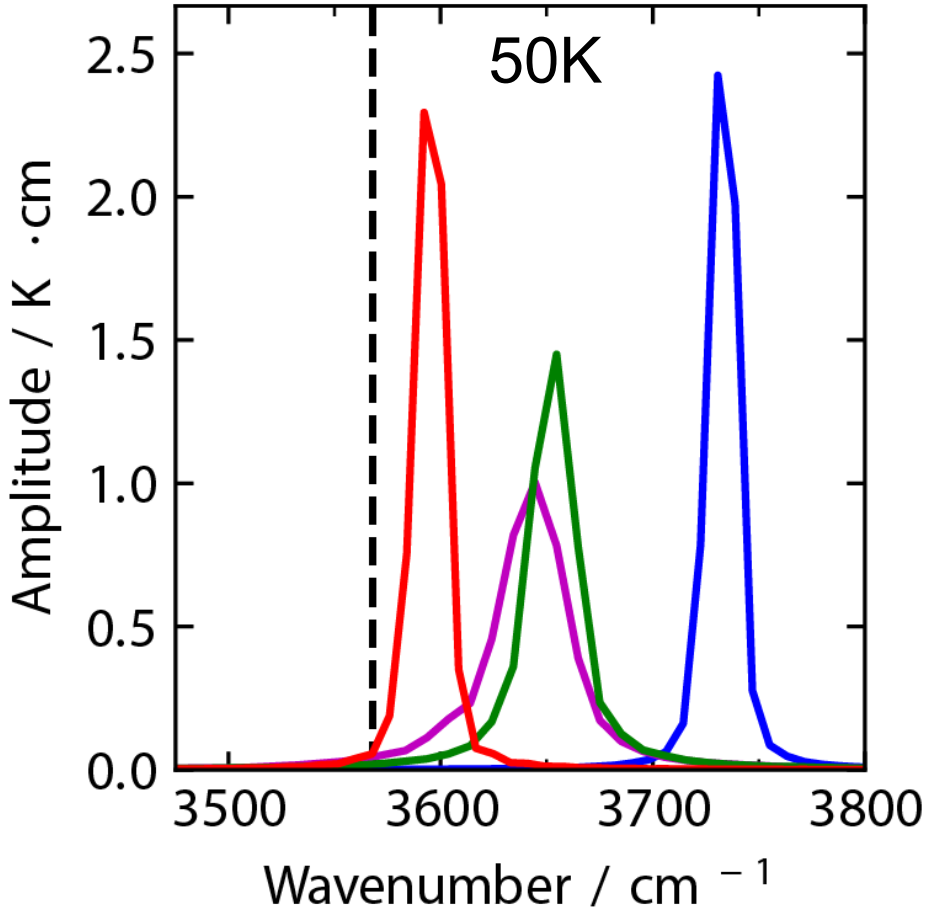
Zehua Chen, and Yang Yang, arXiv:2111.12832

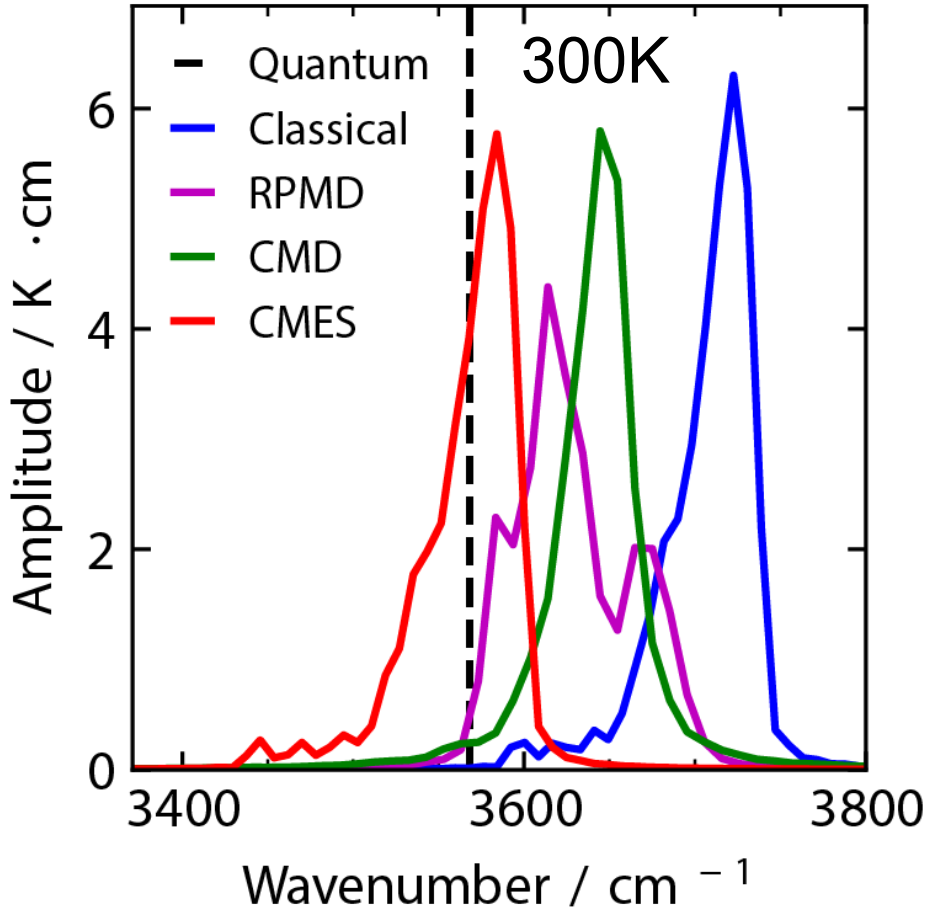
Harmonic Oscillator:

Same as classical MD, exact

Zehua Chen, and Yang Yang, arXiv:2111.12832

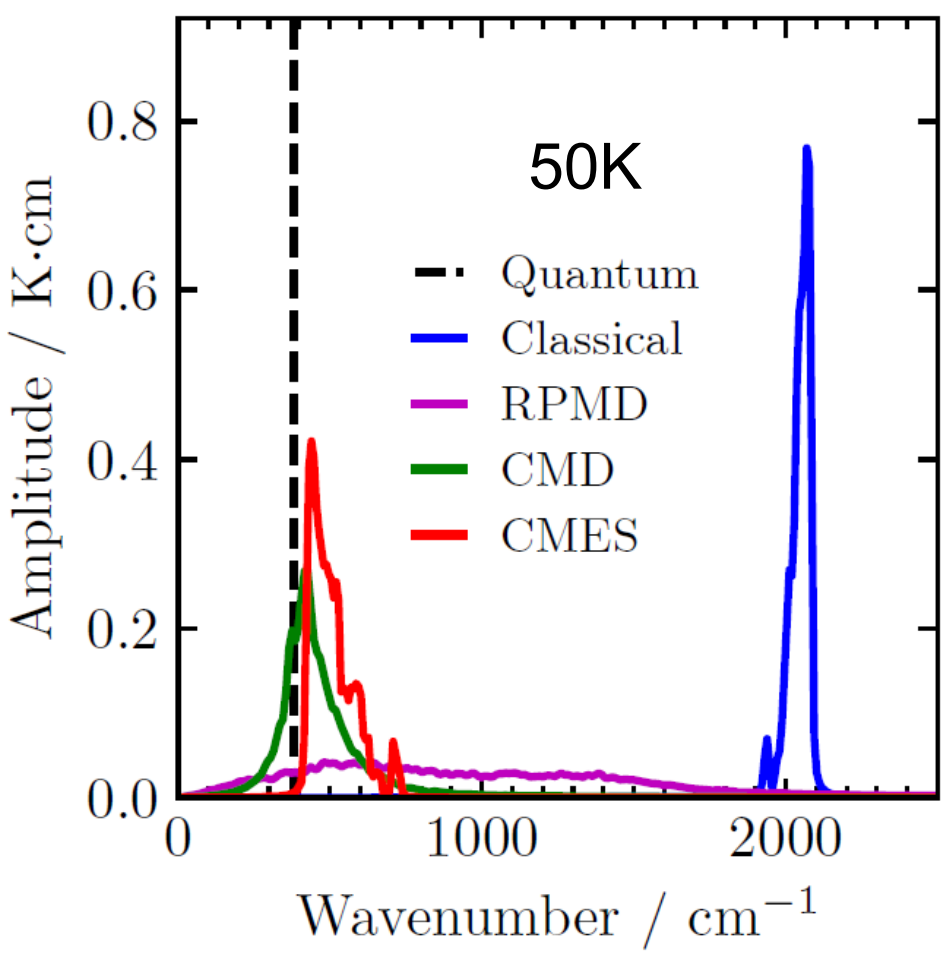
Morse Oscillator: More accurate than existing MD methods

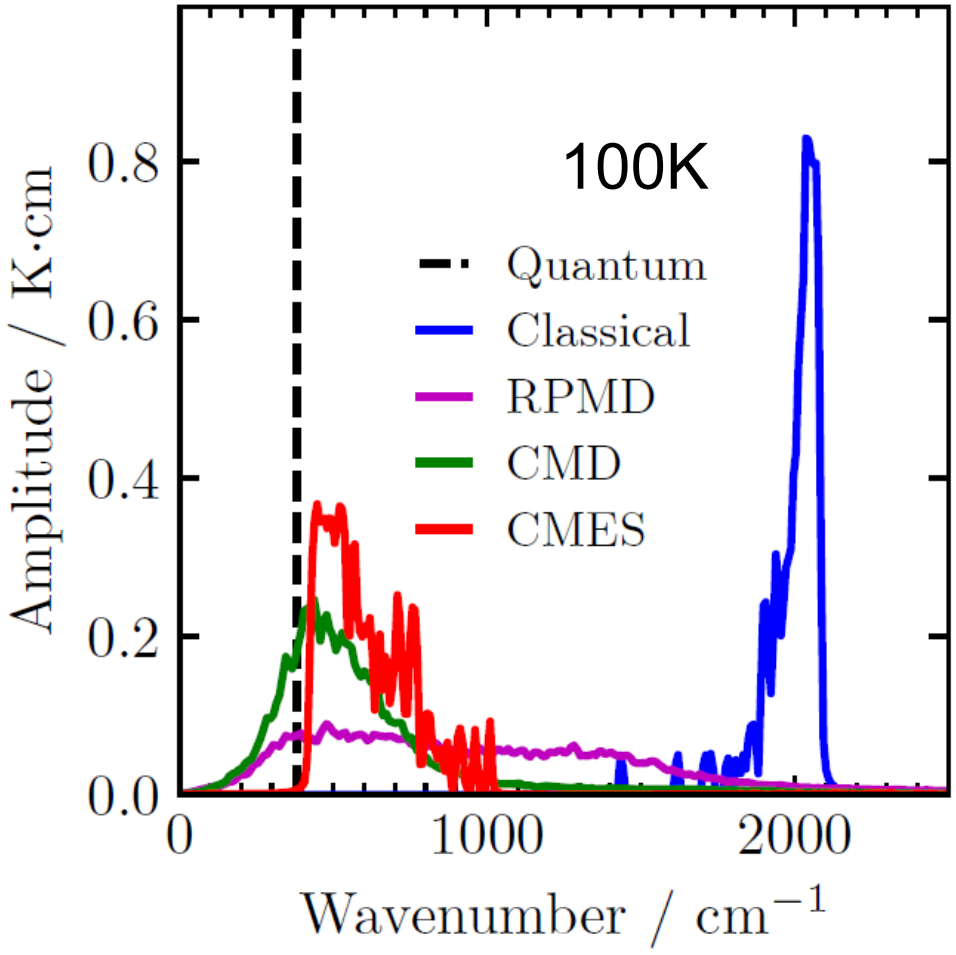




Zehua Chen, and Yang Yang, arXiv:2111.12832

Double-well potential: Get tunneling





Zehua Chen, and Yang Yang, arXiv:2111.12832

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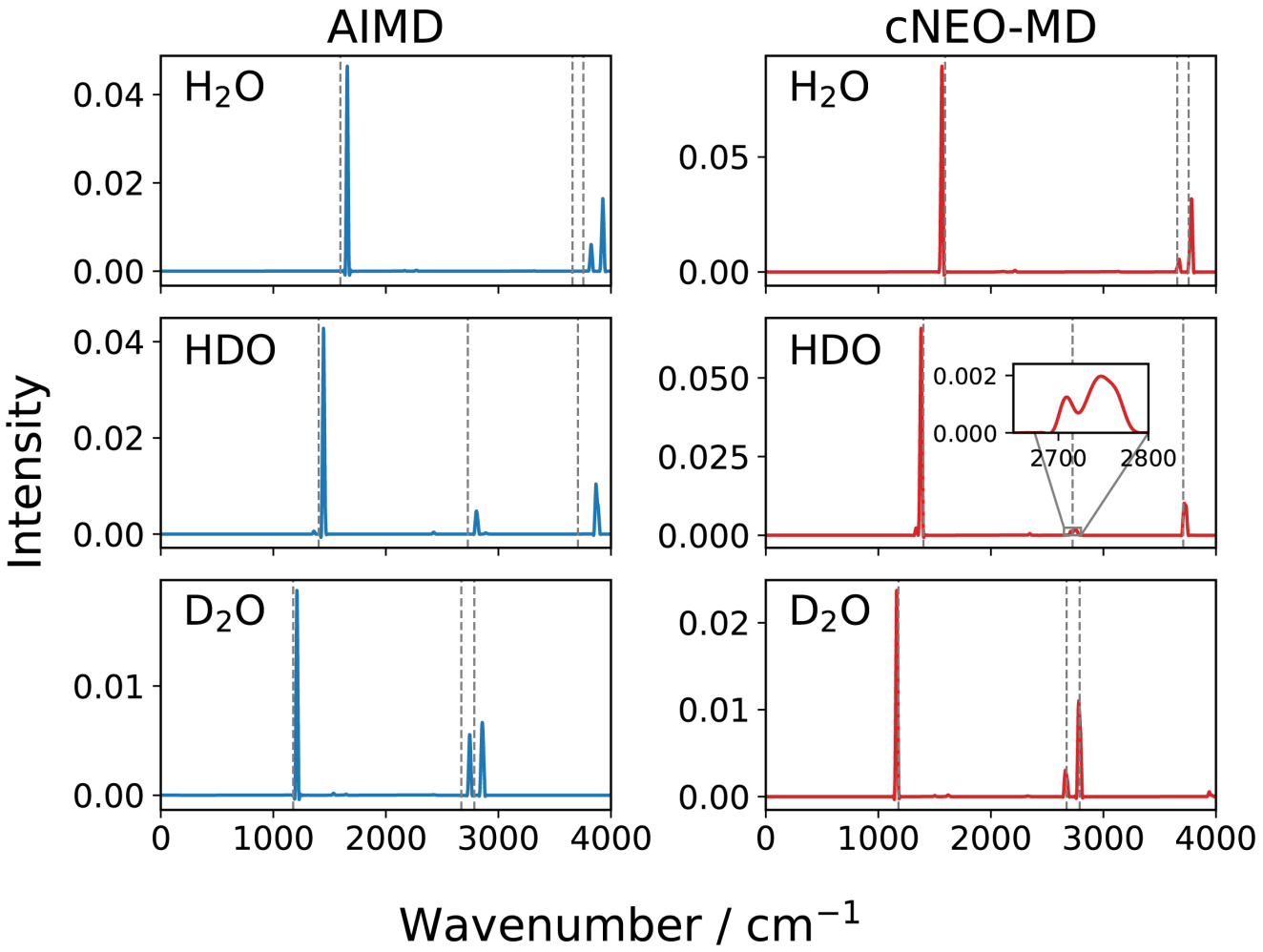
cNEO-MD working equation

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p\rangle}{m}$$

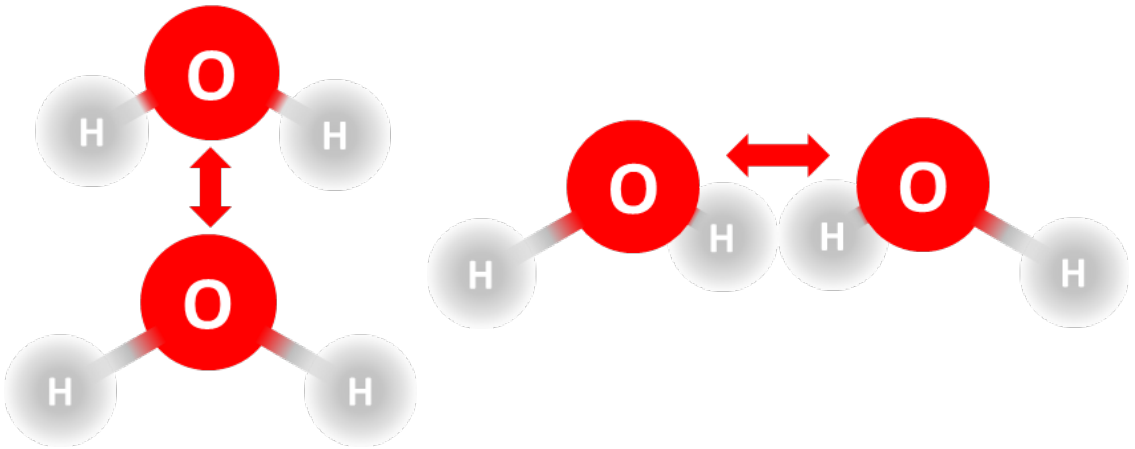
$$\frac{d}{dt}\langle p\rangle \approx -\frac{d}{d\langle x\rangle} V^{\text{cNEO-DFT}}(\langle x\rangle)$$

- Highly similar to AIMD: DFT→CNEO-DFT
- Same computational scaling
- Practical tests: 1.5-3 times more expensive

Results: H_2O, HDO, and D_2O IR spectra



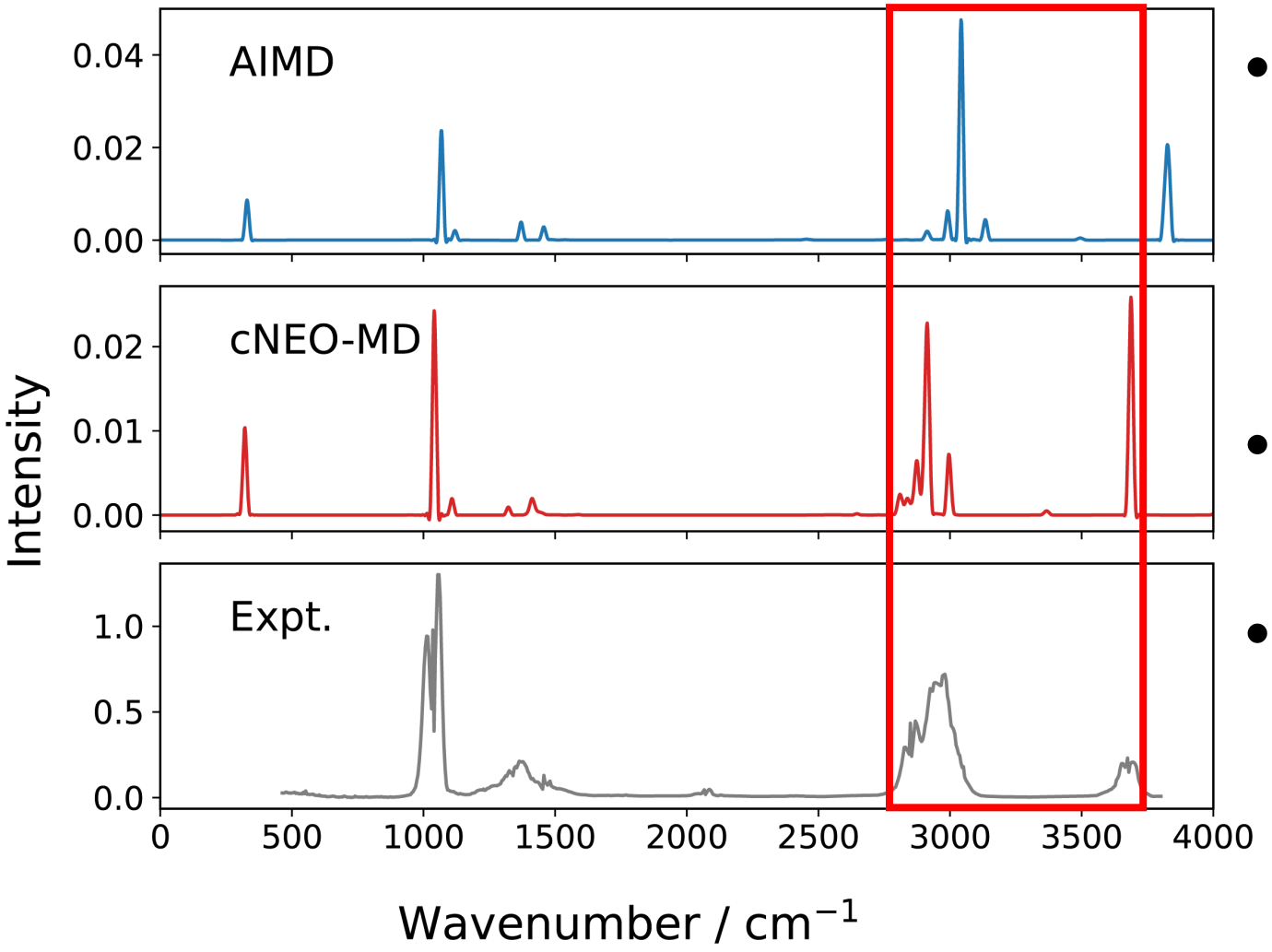
- Significantly outperforms conventional AIMD



- Also excellent for isotopes
- Fermi resonance in HDO

X. Xu, Z. Chen, and Y. Yang, *J. Am. Chem. Soc.* **14**, 4039 (2022)

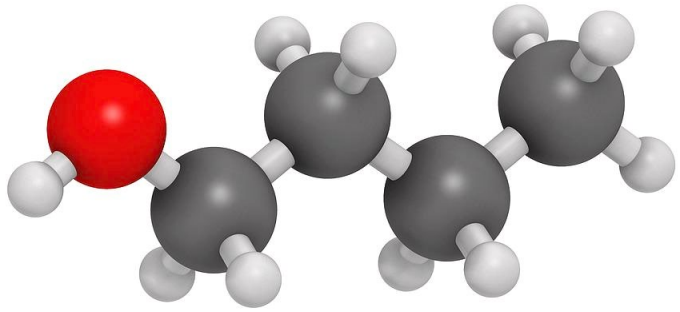
CH_3OH IR spectra by cNEO-MD



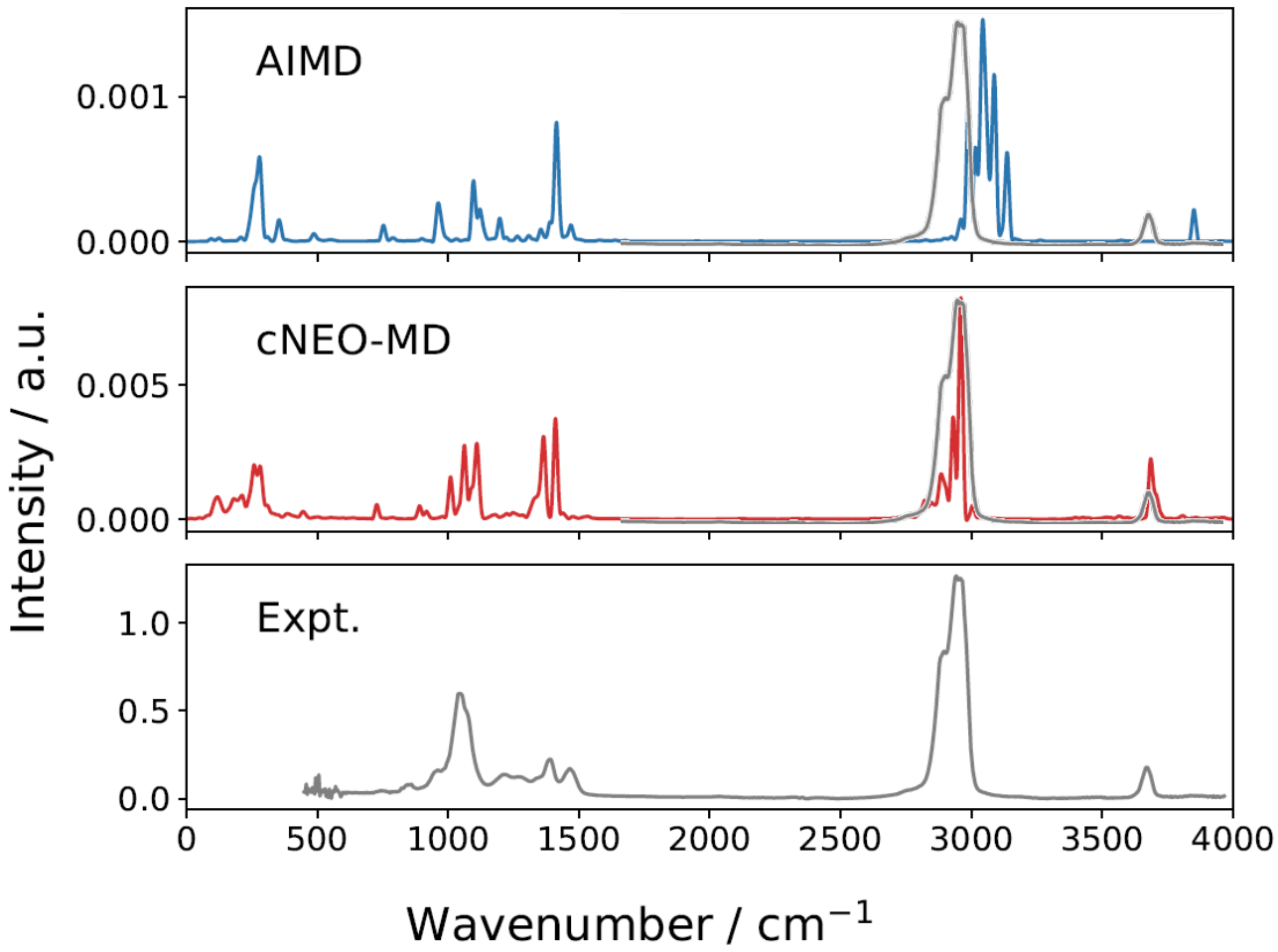
- Significantly outperforms AIMD for OH and CH stretches
- Error: reduced to 1/10
- Reason: Nuclear quantum effects

X. Xu, Z. Chen, and Y. Yang, *J. Am. Chem. Soc.* **14**, 4039 (2022)

Results: 1-butanol IR spectra

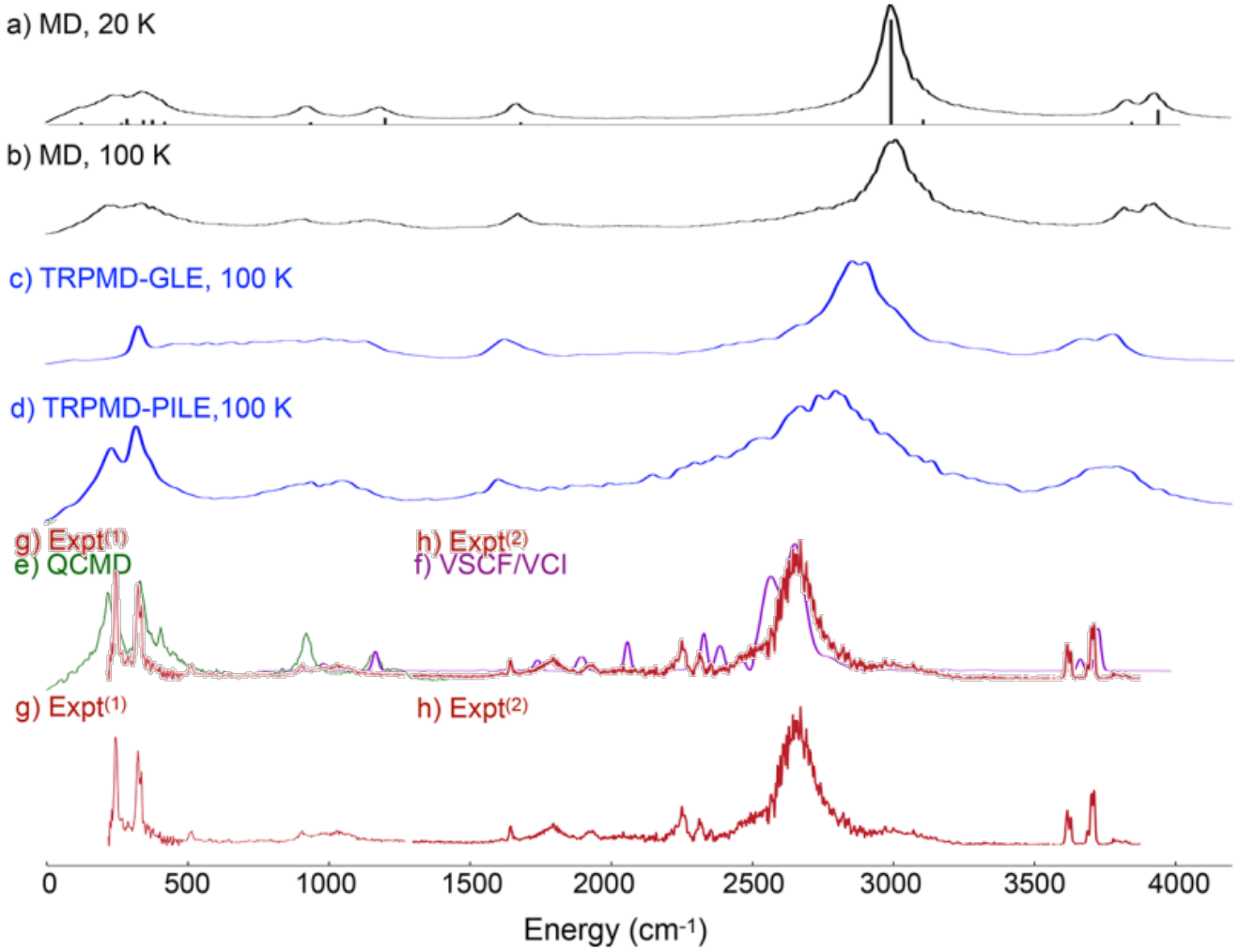


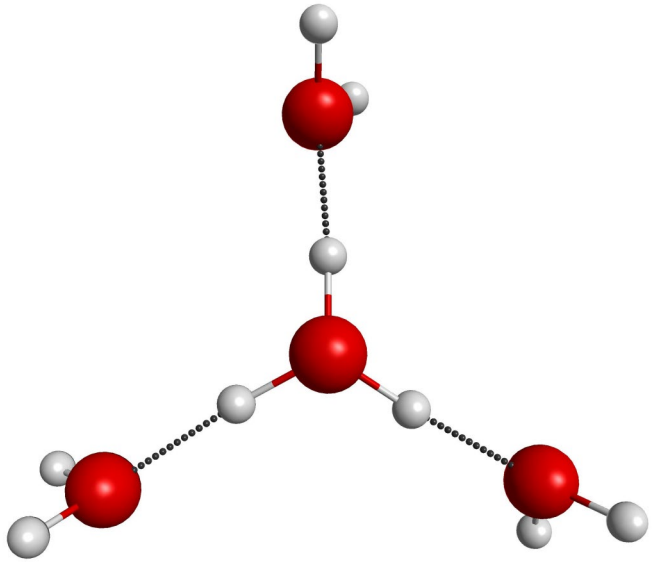
- Excellent agreement with experiments for C-H and O-H stretches



X. Xu, Z. Chen, and Y. Yang, *J. Am. Chem. Soc.* **14**, 4039 (2022)

Challenging IR spectrum of $H_9O_4^+$





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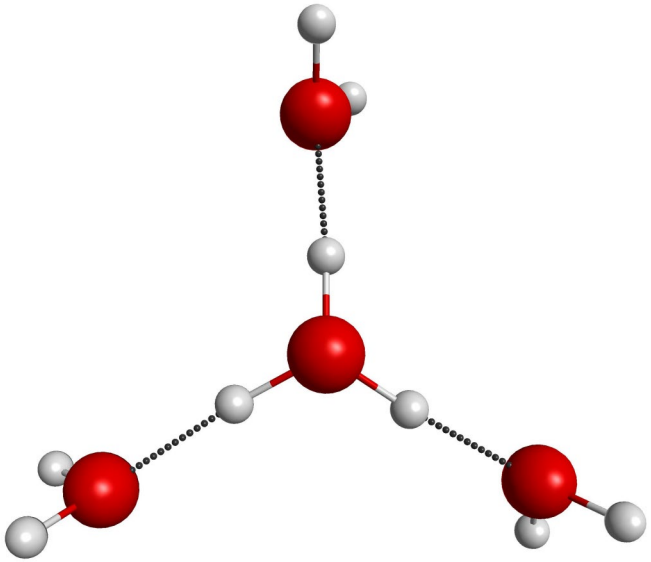
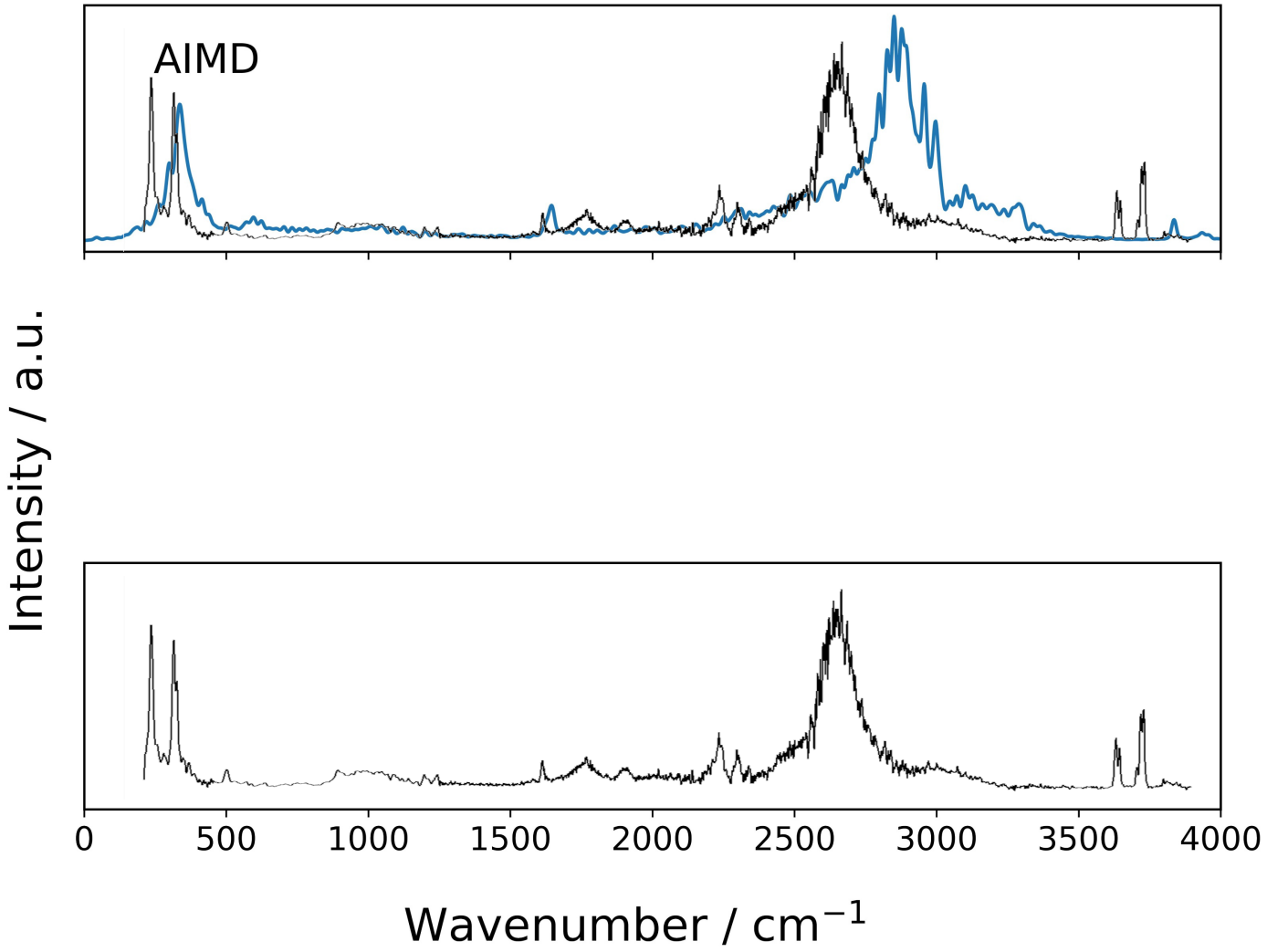
- Expensive VSCF/VCI

Y. Qi, and J. Bowman, *J. Am. Chem. Soc.* **139**, 10984 (2017)
Y. Qi, and J. Bowman, *J. Phys. Chem. A.* **123**, 1399 (2019)

IR spectrum of $H_9O_4^+$





More exciting results to come!

X. Xu, and Y. Yang, preliminary data

Outline

- Background: Nuclear quantum effects (NQEs)
- Method development 1: Constrained multicomponent DFT
- Method development 2: Molecular dynamics with NQEs
- Combination: CNEO-MD and results in molecules
- Summary

Difference between NEO dynamics and CNEO-MD

	NEO Dynamics (Hammes-Schiffer & Li)	CNEO-MD (Yang)
		

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Cost	Higher	Lower
Future	Nonadiabatic PCET	Replace past AIMD

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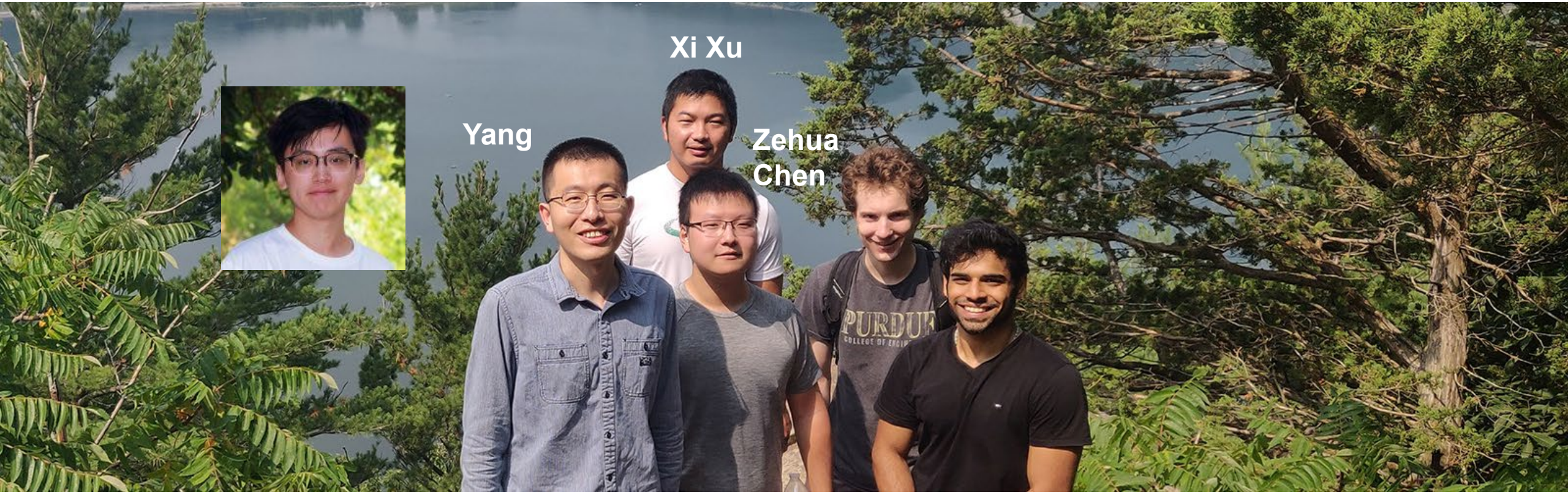
Summary

- CNEO-DFT
  - Constraints on nuclear expectation positions
  - Energy as a function of nuclear expectation positions
  - Energy surface with NQEs
- CMES-MD
  - Alternative approximation to Ehrenfest theorem
  - Incorporating nuclear quantum effects in classical MD
  - Good performance on model systems
- CNEO-MD
  - Highly similar to AIMD, but DFT→CNEO-DFT
  - Same formal scaling as conventional AIMD
  - Excellent results, greatly outperforms conventional AIMD
  - Future applications: Water, bulk, reaction rates, excited states, non-adiabaticity…

Acknowledgement



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