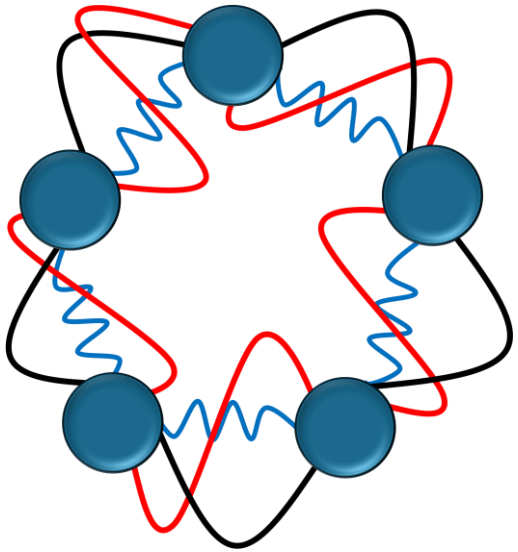
REAL-TIME DYNAMICS IN BEAD-FOURIER PATH INTEGRAL REPRESENTATION

$$Tr\left[e^{-\beta\hat{H}}\right] \equiv$$



MOHAMMAD R. MOMENI
Assistant Professor
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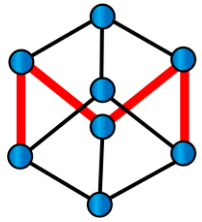
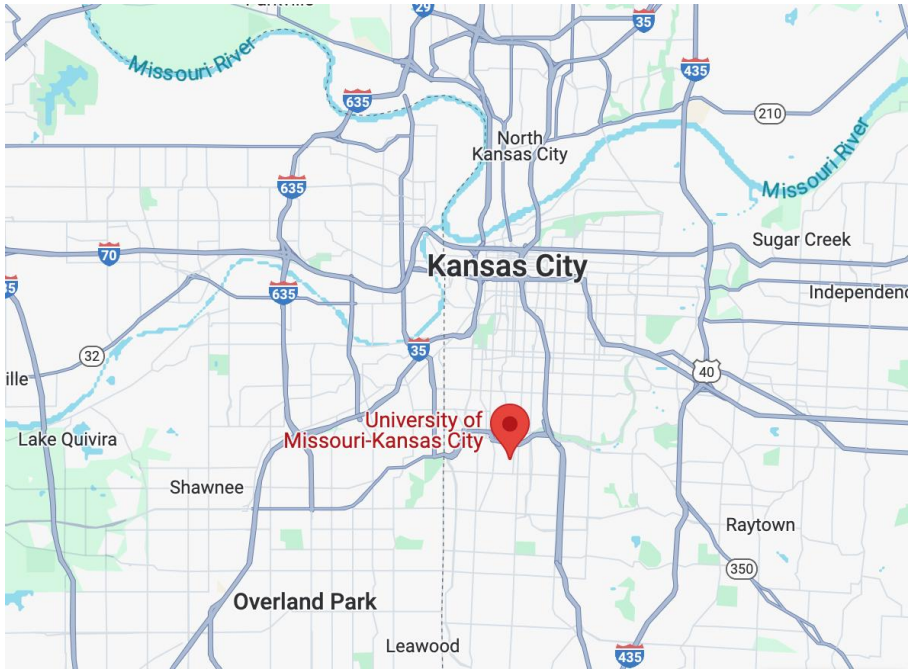
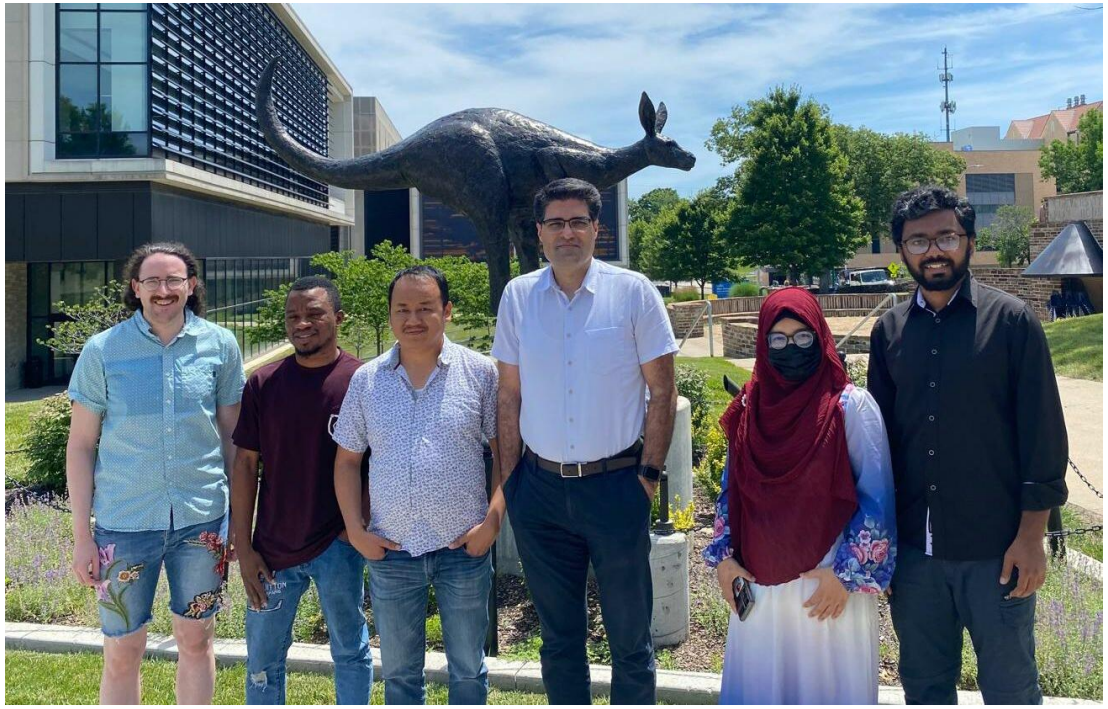
VISTA Seminar 91
June 4, 2025



Momeni Research Group

Momeni Research Group at UMKC



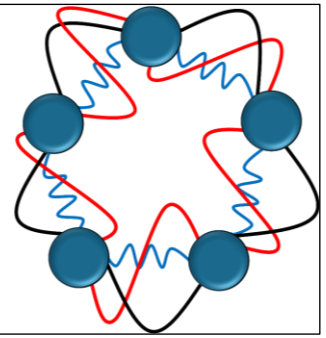


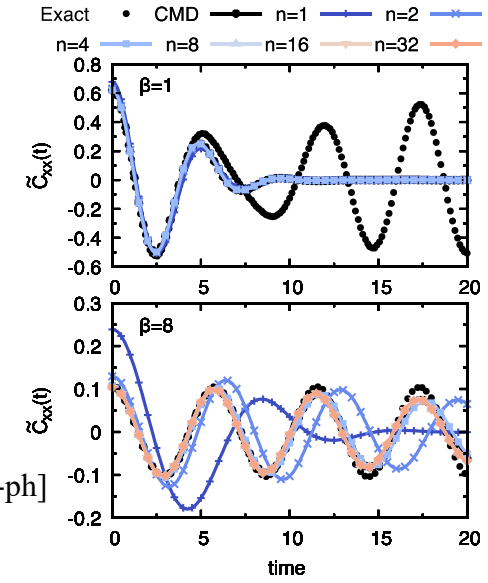
https://info.umkc.edu/momenigroup/

Real-Time Quantum Dynamic Methods

Bead-Fourier Path Integrals

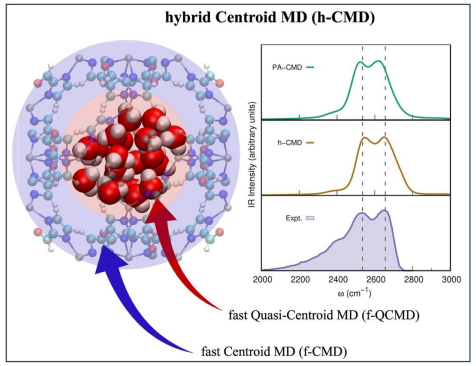
$$Tr\left[e^{-\beta\hat{H}}\right] \equiv$$

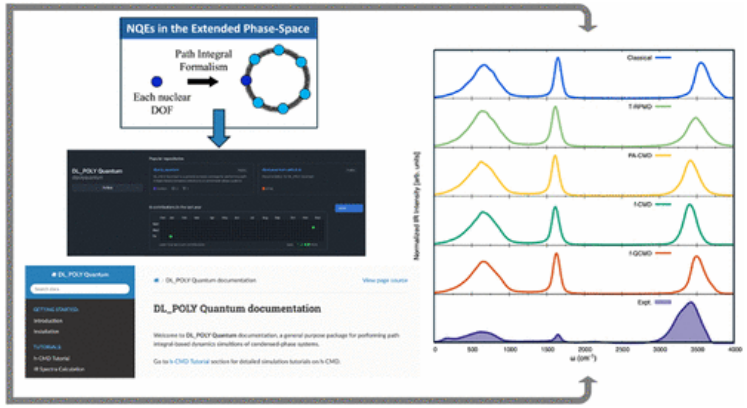




London & Momeni arXiv:2505.13707 [physics.chem-ph]
London & Momeni, In Preparation (2025).

Quantum Vibrational Spectroscopy





Limbu et al. J. Chem. Phys. **162**, 014111 (2025).
Faruque, London, & Momeni, In Preparation (2025).

Data-Driven Design of Energetic Materials

Akter & Momeni J. Phys. Chem. C **129**, 9518 (2025).
Akter et al. Langmuir **40**, 24934 (2024).
Faruque et al. Cryst. Growth. Des. **24**, 8950 (2024).

Biased ML-MD/PIMD Simulations

Biased ML-MD

Adewuyi, et al. arXiv:2505.04644 [physics.chem-ph]
London et al. J. Phys. Chem. A **129**, 4015 (2025).
London et al. J. Chem. Phys. **160**, 132501 (2024).

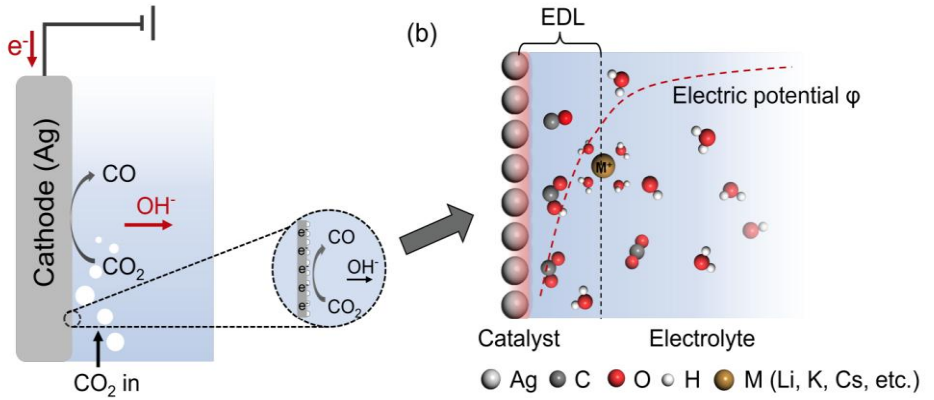
4G-HDcNNP-Enabled "Biased" Path Integrals Simulations

DLPOLY QUANTUM

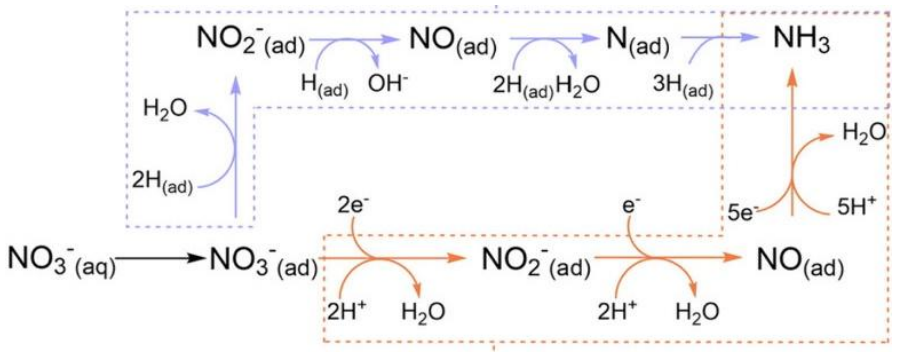
Parallel software for large-scale quantum dynamics simulations enabled by 4G-HDcNNPs

Probing Vibrational Spectra of Aqueous Electrochemical RXNs

- Electrochemical CO_2 to CO and nitrate reduction reaction to ammonia (NO_3RR).

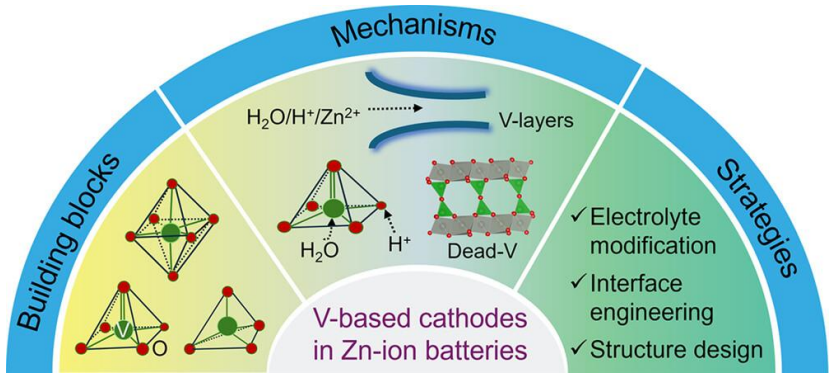


ACS Nano **18**, 27833 (2024).
J. Mater. Chem. A **10**, 9707 (2022).



Tian et al. ChemRxiv. 2025; doi:10.26434/chemrxiv-2025-n41q2

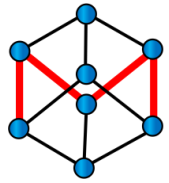
- Aqueous Zn^{2+}, Na^{+}, and Mg^{2+} ion batteries for large-scale energy storage.



Acc. Chem. Res. **57**, 2887 (2024).

- Probing interfaces with vibrational spectra:
- Rigorous modeling without fittings or *ad hoc* parameterizations.

✓ An MD method for calculating TCFs (IR, vSFG, etc.) → **Real-Time Bead-Fourier**
✓ Accurate PESs → **4G-HDcNNPs in DL_POLY Quantum**



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Feynman's Path Integrals

- Quantum mechanics is hard (exponential scaling) $i\hbar \frac{\partial \Psi(r,t)}{\partial t} = \hat{H}\Psi(r,t)$

- Need better, more suitable methods for many particle systems in condensed phases where all other quantum mechanical effects are washed out.

1918-1988

✓ Feynman looked for ideas to connect QM to such classical ideas as the Lagrangian (L), or Hamilton's principle function, action (S), the indefinite integral of L.

1902-1984

The transformation functions in (8) and (9) are very fundamental things in the quantum theory and it is satisfactory to find that they have their classical analogues, expressible simply in terms of the Lagrangian. We have here the natural extension of the well-known result that the phase of the wave function corresponds to Hamilton's principle function in classical theory. The analogy (9) suggests that we ought to consider the classical Lagrangian, not as a function of the coordinates and velocities, but rather as a function of the coordinates at time t and the coordinates at time $t+dt$.

For simplicity in the further discussion in this section we shall take the case of a single degree of freedom, although the argument applies also to the general case. We shall use the notation

$$\exp\left[i\int_t^{t'} L\,dt/h\right] = A(tT),$$

REVIEWS OF

MODERN PHYSICS

VOLUME 20, NUMBER 2 APRIL, 1948

Space-Time Approach to Non-Relativistic Quantum Mechanics

R. P. FEYNMAN

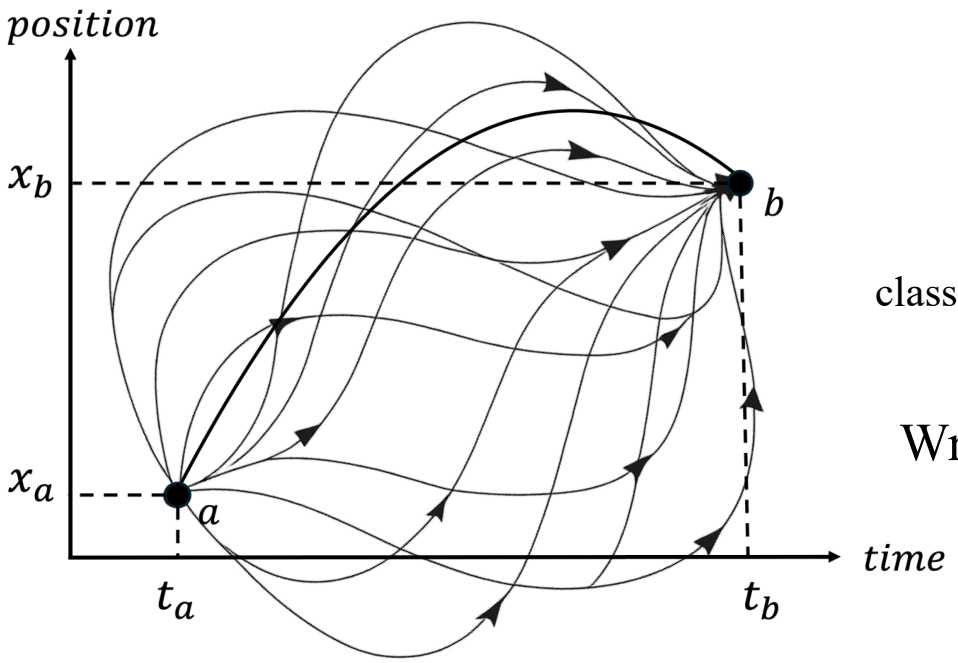
Cornell University, Ithaca, New York

Non-relativistic quantum mechanics is formulated here in a different way. It is, however, mathematically equivalent to the familiar formulation. In quantum mechanics the probability of an event which can happen in several different ways is the absolute square of a sum of complex contributions, one from each alternative way. The probability that a particle will be

Feynman changed the analogy to identity!

Feynman's Path Integrals: Sum Over All Possible Paths

Feynman's path integral states that to calculate the overall probability amplitude of a non-relativistic spin-less QM particle, we must consider, in addition to the classical path, all possible paths.



$$\langle x_b | e^{-i\hat{H}t/\hbar} | x_a \rangle = \sum_{all\ paths} e^{iS[x(t)]/\hbar}$$

where $S[x_a, x_b, t_b - t_a] = \int_{t_a}^{t_b} L(x, \dot{x}, t)dt$ with $L = T - V$

classical action functional along the path

Write the infinite sum over all paths in a less restrictive way as integrals:

$$K(x_a, x_b, t_b - t_a) = \int_{t_a}^{t_b} Dx(t)\, e^{iS[x_a, x_b]/\hbar}$$

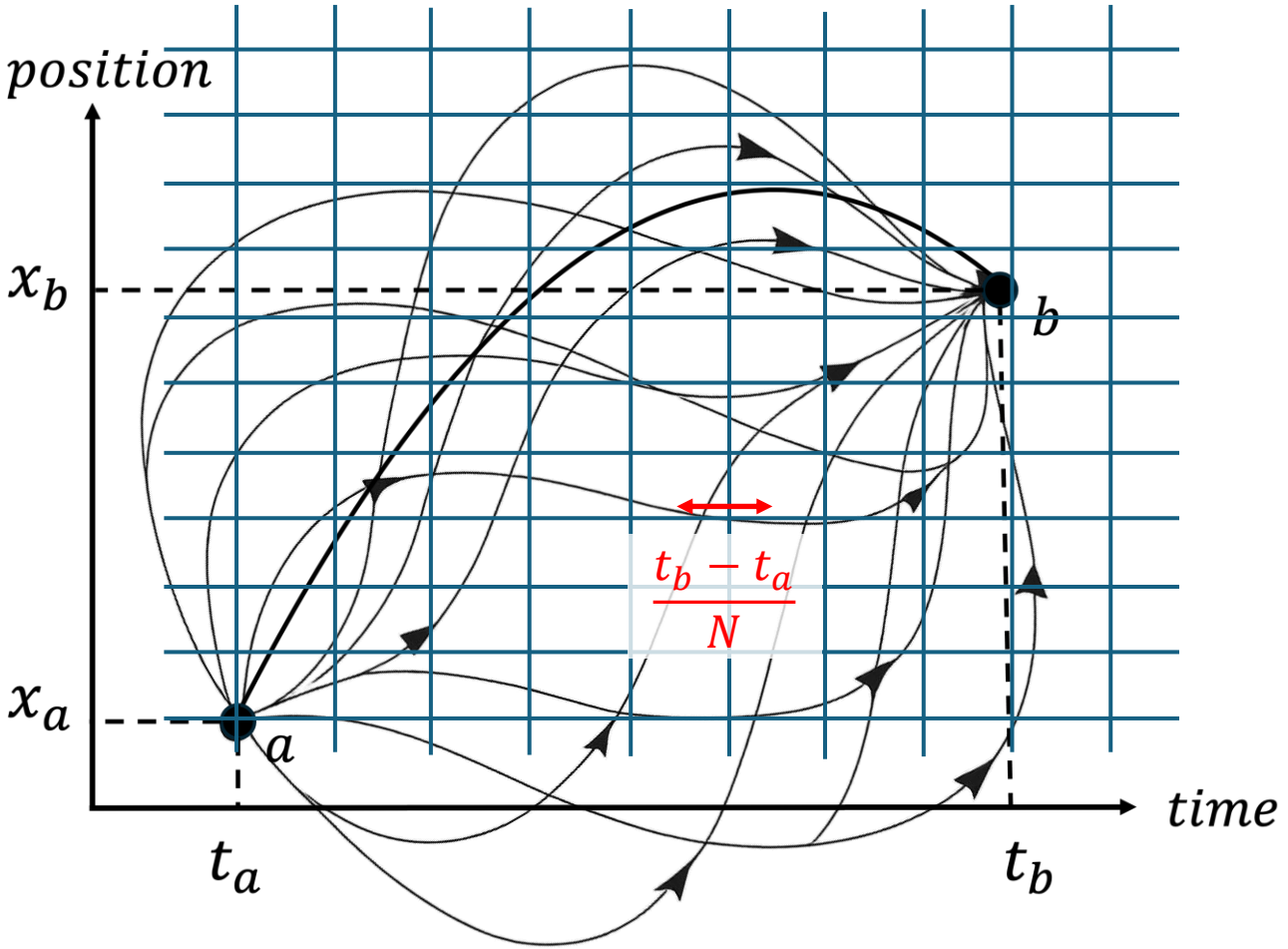
$$P = |K|^2\, dx$$ probability

Feynman & Hibbs (1965). Quantum Mechanics and Path Integrals.

Feynman's "Discretized" Path Integrals

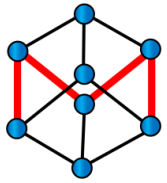
- In practice, we solve this numerically on a space-time grid by dividing each finite path into N equally spaced discrete linear time slices, solved numerically using the trapezoid rule.

$$K = \lim_{N\to\infty} \int \dots \int Dx_1 Dx_2 \dots Dx_{N-1}\, e^{iS[x(x_a,x_b)]/\hbar}$$



- The oscillatory phase (sign) problem: action changes quadratically with path variables (position) and leads to highly oscillatory amplitudes.

Morita J. Phys. Soc. Jap. **35**, 980 (1973).



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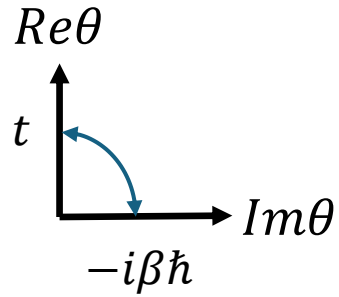
Feynman's "Discretized" Imaginary-Time Path Integrals

- Using Wick rotation, represent PIs in Euclidean (imaginary) time ($t \to -iu$ with $0 \le u \le \beta\hbar$), resulting in real decaying exponentials that we know how to handle numerically.
- This is why we refer to Feynman PIs as Feynman imaginary-time PIs.
- Using phase space variables, the partition function is
- For a given Euclidean path, the imaginary-time action functional for a particle of mass m and potential V is

$$K(x_a, x_b, u) = \int_0^{\beta\hbar} Dx(u)\, e^{-S[x(u)]/\hbar}$$



$$Z = \oint Dq(\tau)\, Dp(\tau)\, e^{-S[q(\tau)p(\tau)]/\hbar}$$

$q(\tau)$ and $p(\tau)$ are closed phase space paths in imaginary time, i.e., $q(0) = q(\beta\hbar)$

$$S\,[(q(u), p(u)] = \int_0^{\beta\hbar} du \left[ip(u)\dot{q}(u) + \frac{m}{2}\dot{q}^2(u) + V[q(u)] \right]$$

Feynman & Hibbs (1965). Quantum Mechanics and Path Integrals.

Fourier Path Integrals

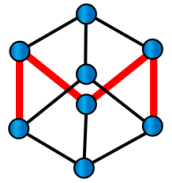
- In the Fourier path integral method, the imaginary time path is expanded in a Fourier sine series:

$$q(\xi) = q + (q' - q)\,\xi + \sum_{k=1}^{\infty} a_k \sin(k\pi\xi) \qquad \text{where } \xi = \frac{u}{\beta\hbar} \qquad 0 \le \xi \le 1$$

path starting and end points — Fourier amplitudes

- Hundreds of Fourier terms needed even for simulations with heavy atoms.

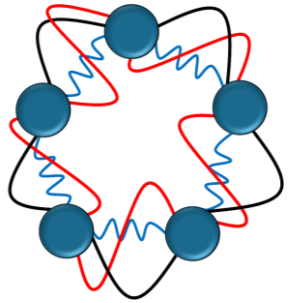
Doll and Freeman JCP **80**, 2239 (1984). Freeman and Doll JCP **80**, 5709 (1984). Doll et al. Phys. Rev. Lett. **55**, 1 (1985). Vorontsov-Velyaminov et al. Phys. Rev. E **55**, 1979 (1997).



Bead-Fourier (BF-) PIMD and BF-RPMD

- The bead-Fourier (BF) method combines bead and Fourier approaches to imaginary time PIs into one method. Here, each time slice is expanded in a Fourier sine series:

$$x_i(\xi) = x_i + (x_{i+1} - x_i)\,\xi + \sum_{k=1}^{k_{max}} a_{ik} \sin(k\pi\xi)$$



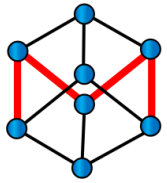
- BF partition function: $Z \cong \int \prod_{i=1}^{n} \left(dx_i \prod_{k=1}^{k_{max}} da_{ik} \right) e^{-\beta H_{BF}(x_i, a_{ik})}$

x and a are the set of bead positions & Fourier amplitudes

$$H_{BF}(x_i, a_{ik}) = \sum_{i=1}^{n} \left[\frac{{p_i}^2}{2m} + \sum_{k=1}^{k_{max}} \frac{{p_{ik}}^2}{2m_k} + \frac{1}{2}{\omega_n}^2 \left((x_{i+1} - x_i)^2 + \sum_{k=1}^{k_{max}} \frac{(k\pi)^2}{2} a_{ik}^2 \right) + \frac{1}{n} \int_0^1 d\xi\, V[x_i(\xi)] \right]$$

- The two limiting cases easily recovered for pure bead ($k_{max} = 0$) and pure Fourier ($n = 1$) methods.
- Similar to B-RPMD, in BF-RPMD, we use physical mass and no thermostatting.

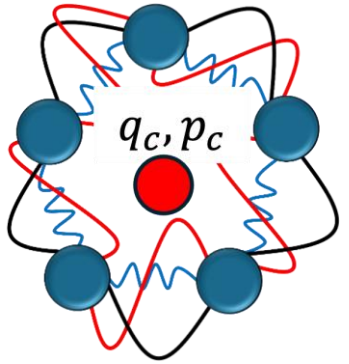
Phys. Rev. E **55**, 1979 (1997). Phys. Rev. E **67**, 066710 (2003)



Introducing Bead-Fourier CMD (BF-CMD)

Nathan London

- We extended BF-PIs to real-time methods through CMD.



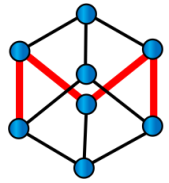
$$\tilde{C}_{AB}(t) = \frac{1}{(2\pi\hbar)^2 Z}\int_0^\beta dq_c dp_c\, e^{-\beta \hat{H}_{BF-CMD}[q_c,p_c]}\hat{A}[q_c(0)\,\hat{B}[q_c(t)]$$

$$\hat{H}_{BF-CMD} = \frac{p_c^2}{2m} + F(q_c) \qquad -\frac{\partial F(q_c)}{\partial q_c} = -\left\langle \frac{\partial V(q)}{\partial q_c} \right\rangle_{q_c}$$

- We use both continuous (left) and bead (right) estimators for calculating the centroid PMF:

$$-\frac{\partial F(q_c)}{\partial q_c} = -\left\langle \frac{\partial \left(\sum_{i=1}^n \int_0^1 d\xi\, V[x_i(\xi)]\right)}{\partial q_c} \right\rangle_{q_c} \qquad -\frac{\partial F(q_c)}{\partial q_c} = -\left\langle \frac{\partial \left(\frac{1}{n}\sum_{i=1}^n V(x_i)\right)}{\partial q_c} \right\rangle_{q_c}$$

Cao and Voth JCP 100, 5093 (1994).
London and Momeni arXiv:2505.13707 [physics.chem-ph].



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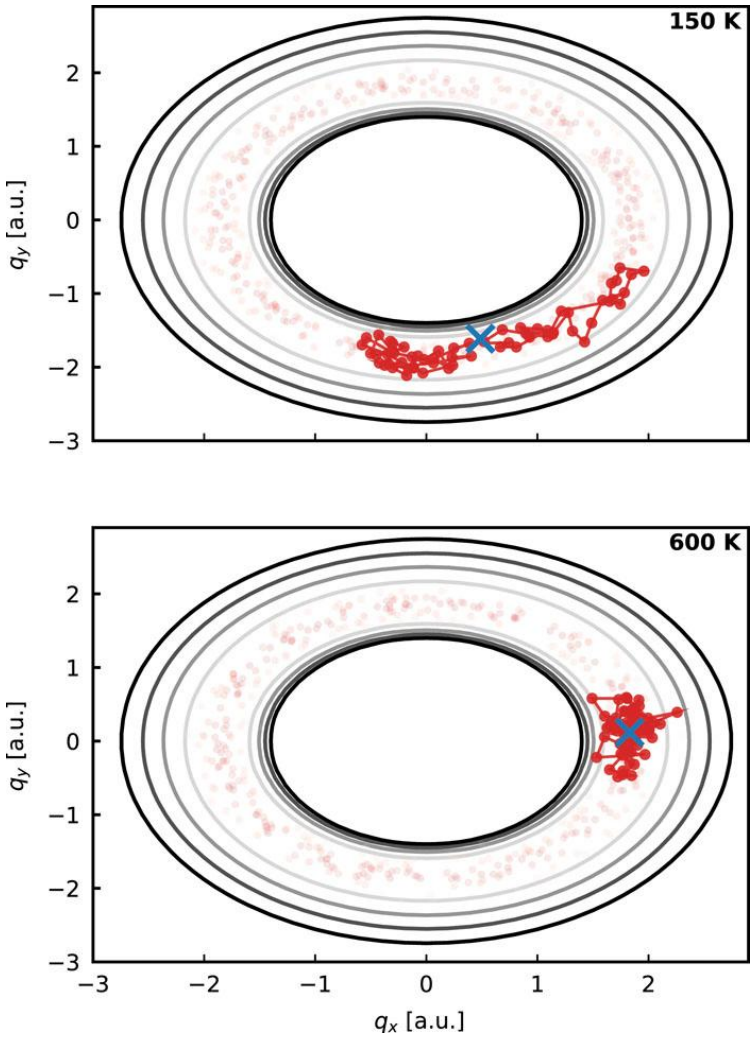
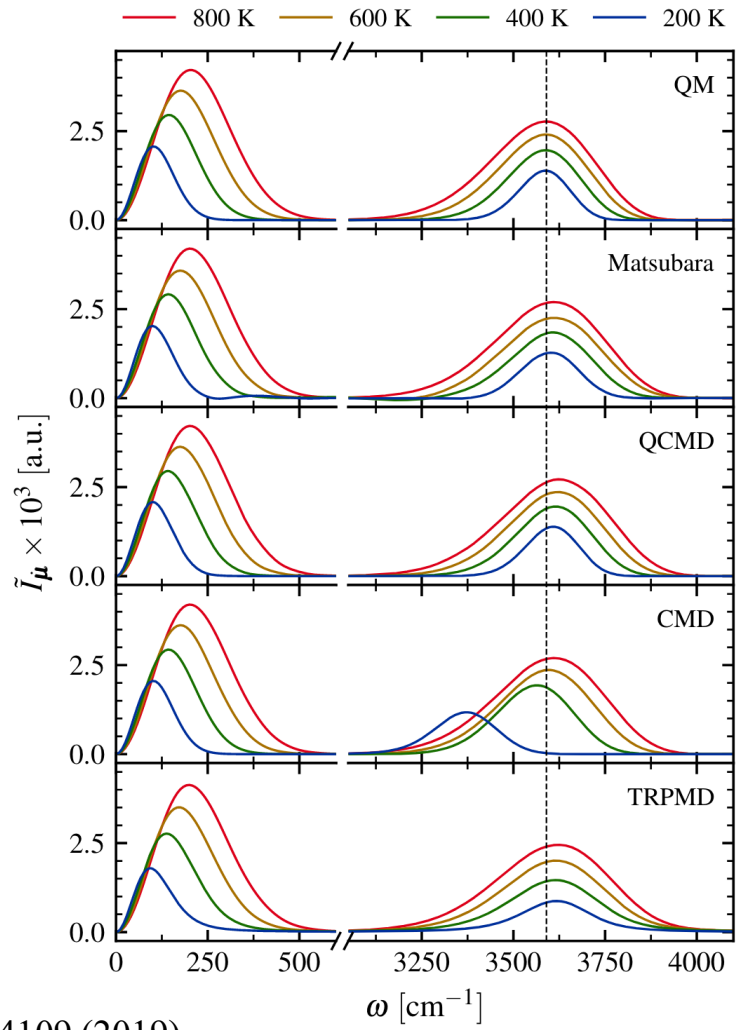
Curvature Problem of CMD for Quantum Vibrational Spectra

- Treating the CMD curvature problem (artificial red-shift and broadening of the OH stretch) with QCMD, f-QCMD, Te-PIGS, ...

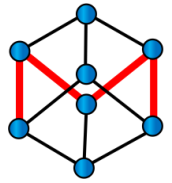
- All these methods have their own limitations and computational complexities.





JCP **151**, 054109 (2019).

JCP **155**, 231101 (2021); JCP **157**, 181102 (2022).



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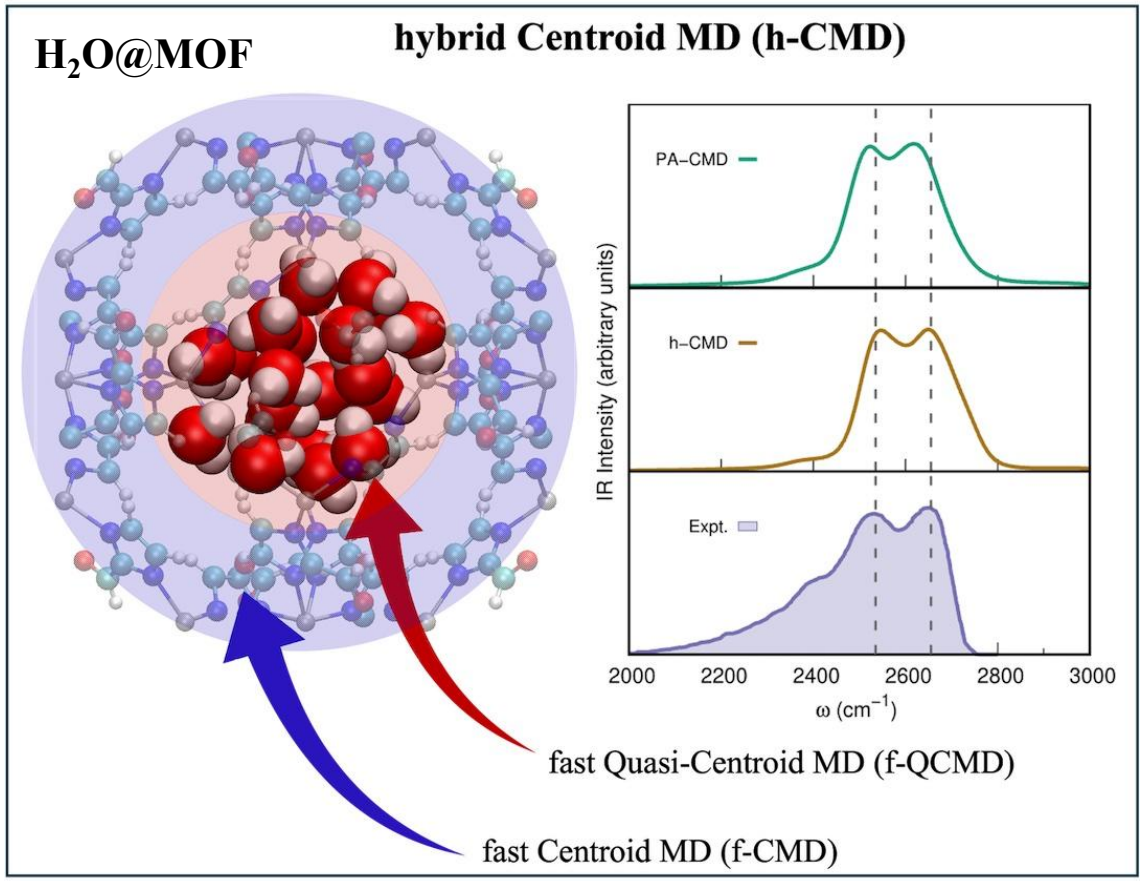
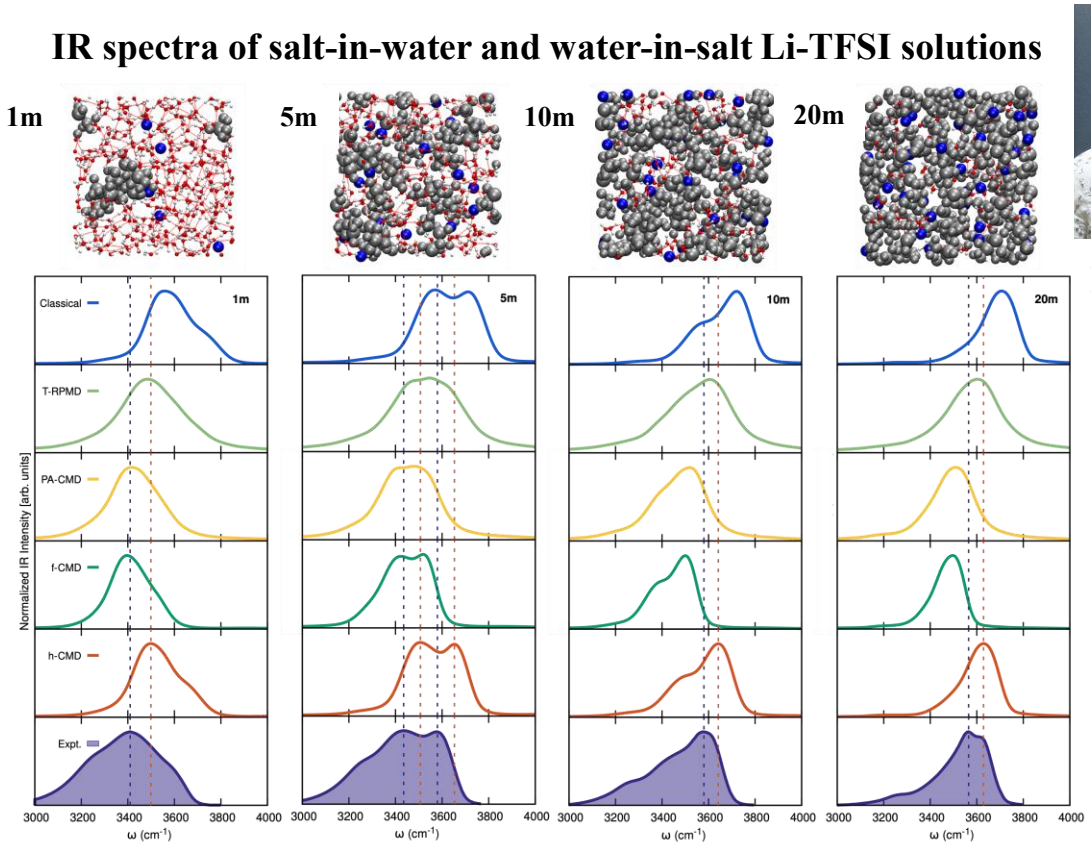
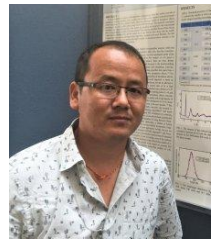
Curvature Problem of CMD for Quantum Vibrational Spectra

- We developed the hybrid CMD (h-CMD) method for treating the "curvature problem" of CMD.







Dil Limbu

- h-CMD suffers where spectral features of interest become part of the large molecule/framework treated with f-CMD.

Limbu et al. JCP **162**, 014111 (2025).
London et al. J. Phys. Chem. A **129**, 4015 (2025).

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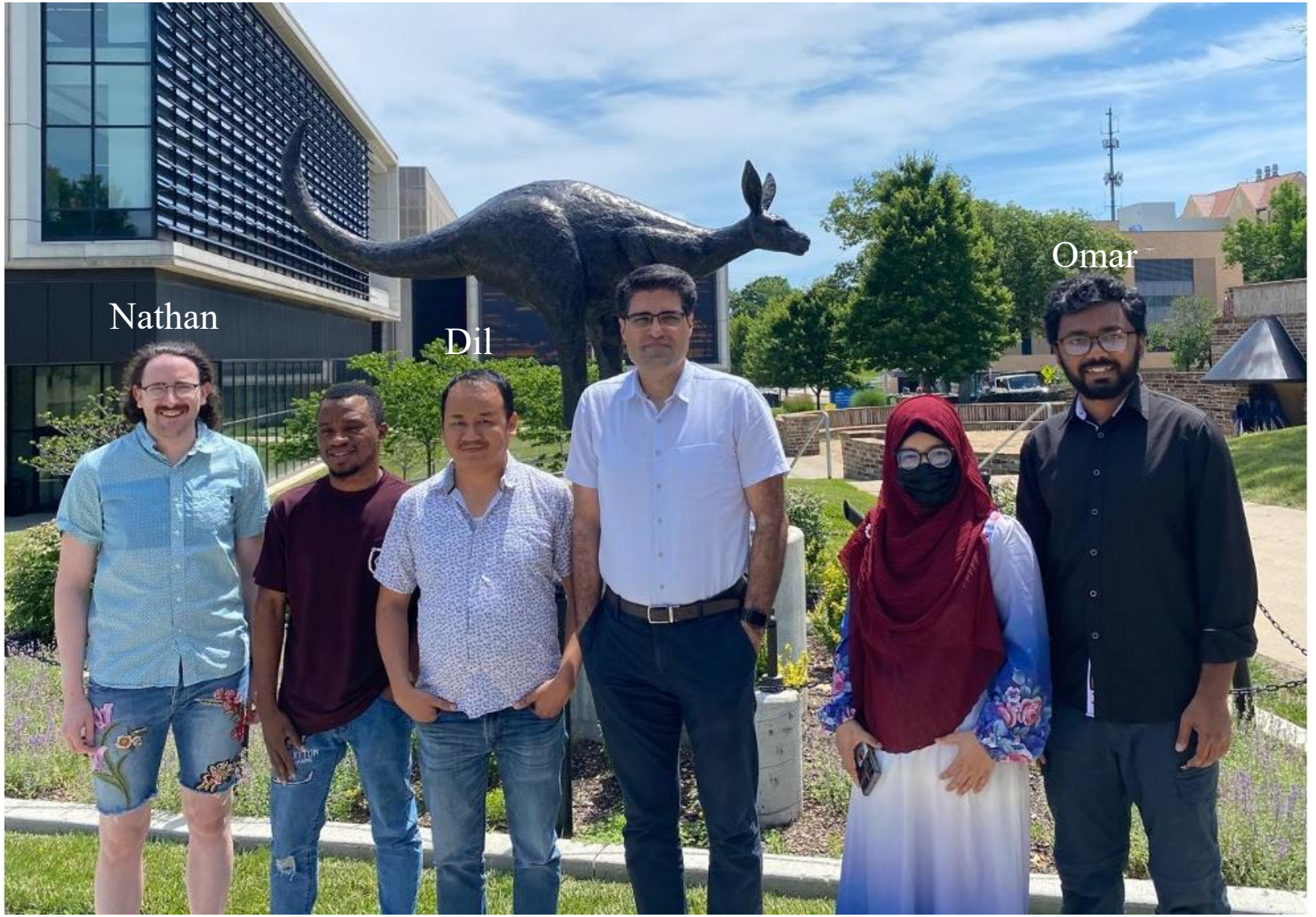
Acknowledgement



From L: Nathan London, Quadri Adewuyi, Dil Limbu, Mohammad Momeni, Suchona Akter, Md Omar Faruque

UMKC School of Science and Engineering

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