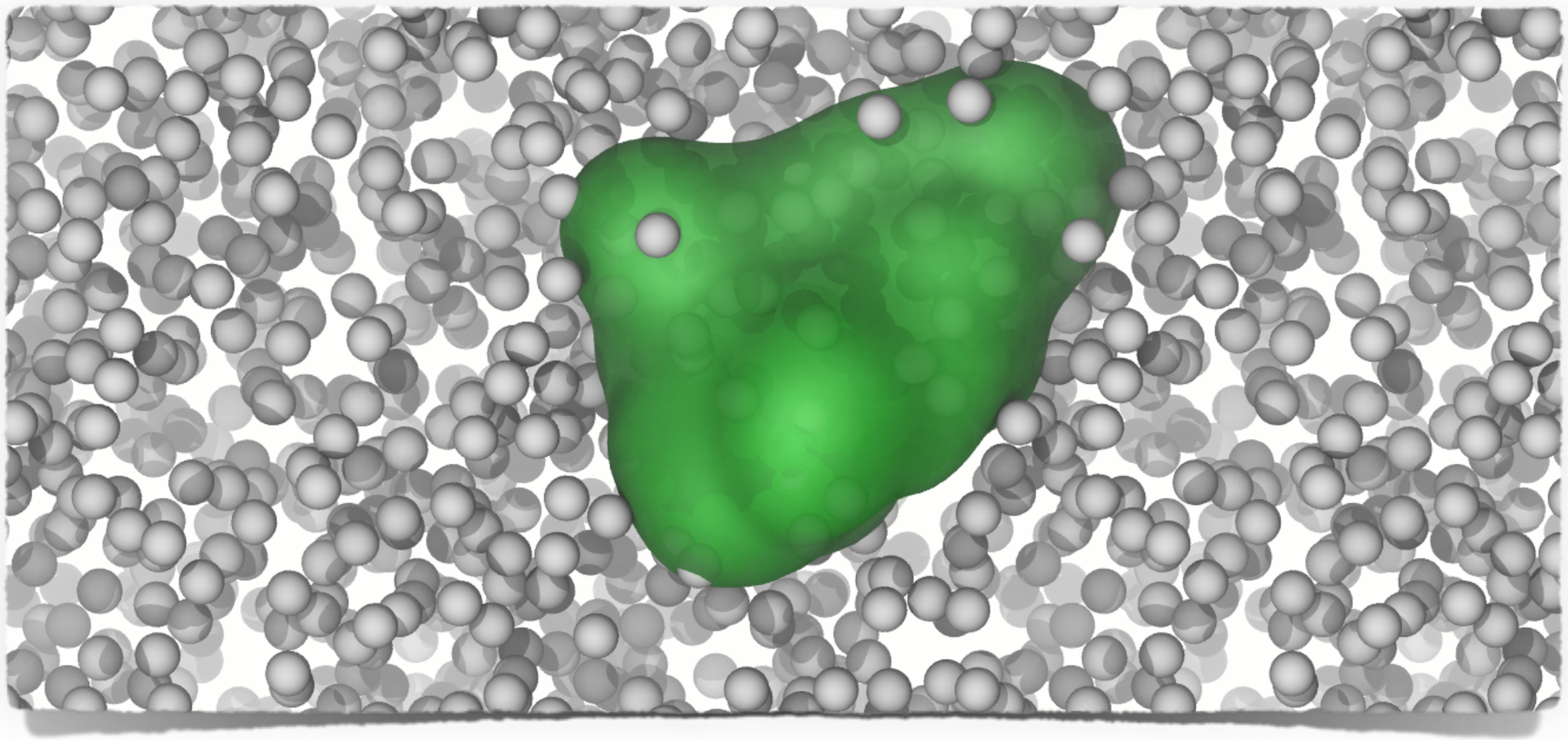
Simulating Quantum Processes with Classical Mechanics



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Institute for Computational Molecular Science

TEMPLE UNIVERSITY

Goals of this Lecture

- Very brief introducing to molecular dynamics simulations
- Simulate quantum particles with classical mechanics through **path integral** formulation of quantum mechanics
- Convince you that this is a useful technique (*examples*)
- Enable you to use these approaches if/when you need to account for quantum effects

What do we want to do?

- ***Statistics*** of quantum processes (*fluctuations*)
  - **Free energies**
  - **Rate constants**
  - Structure and dynamics of quantal systems

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- *How???*
  - **Statistical Mechanics**
  - **Computer simulations**

Computer Simulations

- *Goal*: Generate samples consistent with statistical mechanics

$$P_n = \frac{e^{-\beta \varepsilon_n}}{Q(\beta)} \qquad \beta = 1/(k_{\mathrm{B}} T)$$

- ***Partition Function:*** $Q = \sum_n e^{-\beta \varepsilon_n}$

Molecular Dynamics Simulations

- Evolve the system according to dynamical rules (**F=ma**)
  - Deterministic (Newtonian, etc.) or Stochastic (Langevin)

Molecular Dynamics Simulations

- Evolve the system according to dynamical rules
  - Deterministic (Newtonian, etc.) or Stochastic (Langevin)
  - Work under *assumption of* ***ergodicity***

$$\langle O(\mathbf{\Gamma})\rangle = \frac{\int d\mathbf{\Gamma} O(\mathbf{\Gamma}) e^{-\beta \mathcal{H}(\mathbf{\Gamma})}}{Q}$$

- **Ergodic hypothesis** allows us to write ensemble average as time average (at long times)

$$\langle O(\mathbf{\Gamma})\rangle \approx \lim_{\tau \to \infty} \int_0^\tau O(\mathbf{\Gamma}(t)) dt$$

- This is how we compute averages in simulation

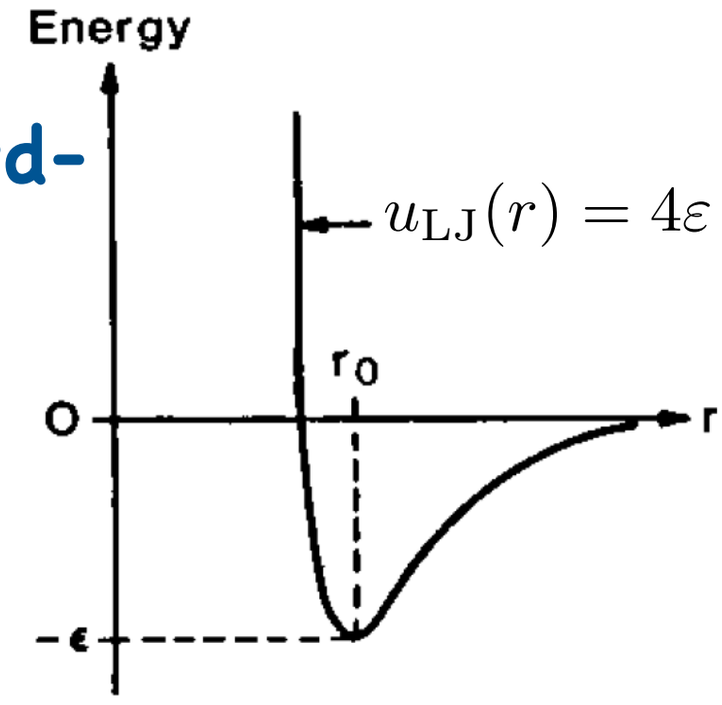
Molecular Dynamics Simulations

- Evolve the system according to dynamical rules
- F=ma

$$F(\mathbf{r}_i) = -\nabla V(\mathbf{r}_i)$$

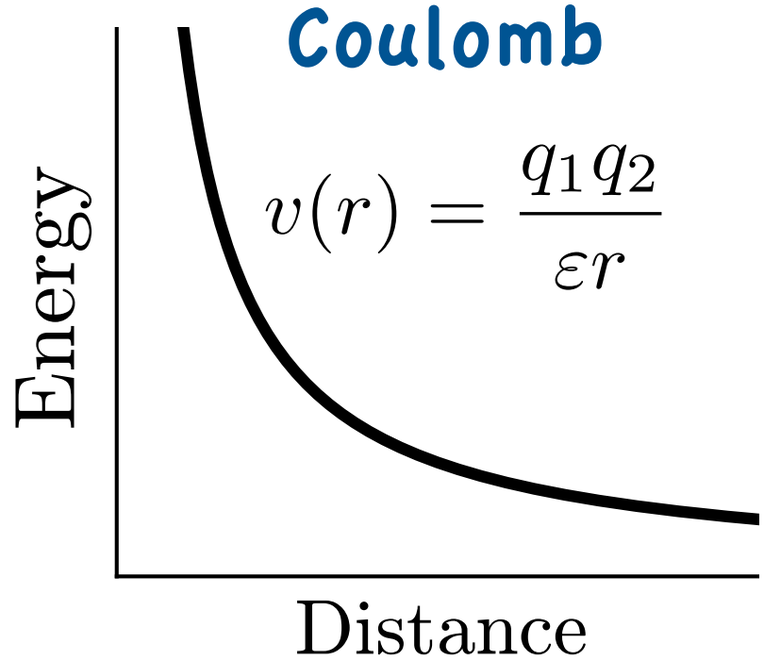
- *Where to get the potential?*
  - Quantum mechanics (DFT, …)
  - Empirical functions

Lennard-Jones



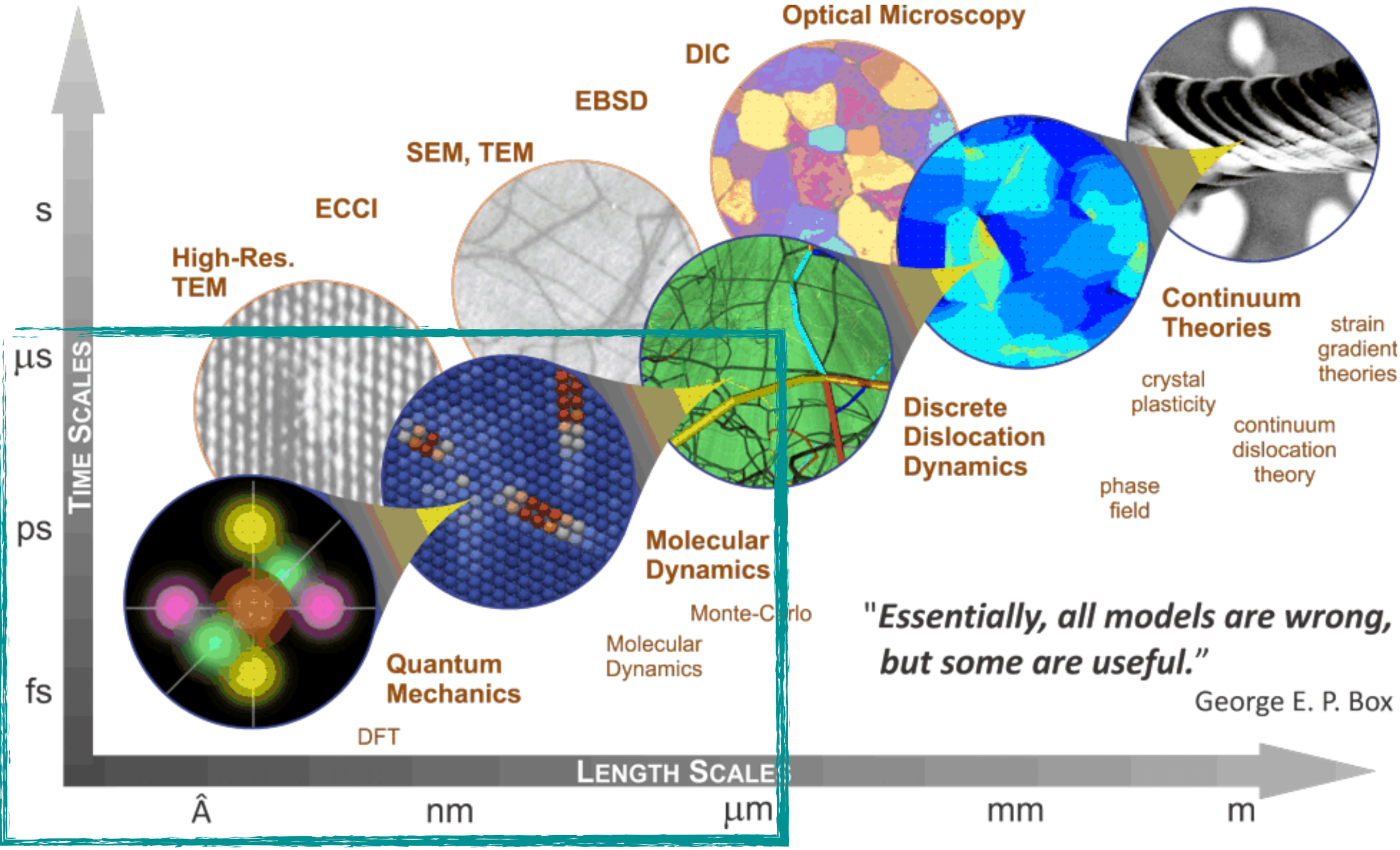
$$u_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Coulomb



$$v(r) = \frac{q_1 q_2}{\varepsilon r}$$

Why Empirical Potentials?



http://www.kochmann.caltech.edu/research_QC.html

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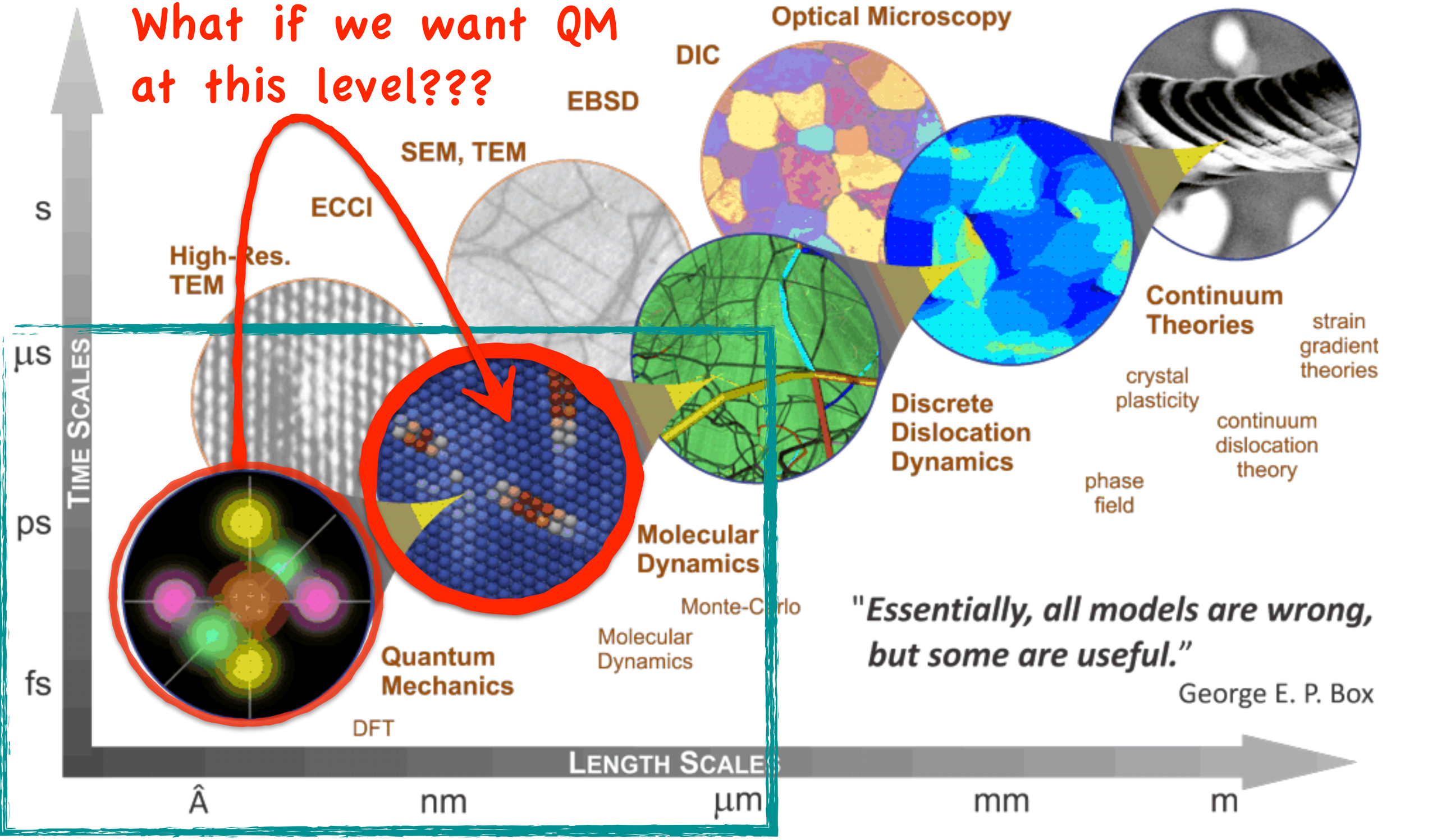

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How to study quantum particles?

- **Consider a single electron:**

$$\mathcal{H} = \frac{p^2}{2m} + V(\mathbf{r})$$

- **Partition Function:**

$$Q = \sum_n e^{-\beta \varepsilon_n}$$

$$\mathcal{H}\psi_n = \varepsilon_n \psi_n$$

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- *How can we make progress?*

Spatial Representation

- $\psi_n(\mathbf{r}) = \langle n|\mathbf{r}\rangle$

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- ***Thermal*** *density matrix* $\quad Q = \int d\mathbf{r}\, \rho(\mathbf{r}, \mathbf{r}; \beta)$

Dynamical Interpretation

- **How to interpret?**

$$Q = \int d\mathbf{r} \left\langle \mathbf{r} | e^{-\beta \mathcal{H}} | \mathbf{r} \right\rangle$$

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- Partition function is overlap of initial $|\mathbf{r}\rangle$ with propagation of that state to ***imaginary time*** $-i\beta\hbar$

- *How can we use this?*

Dividing Q into time slices

- **Slice "time" into *P* increments** (cyclic boundary: P+1=1)

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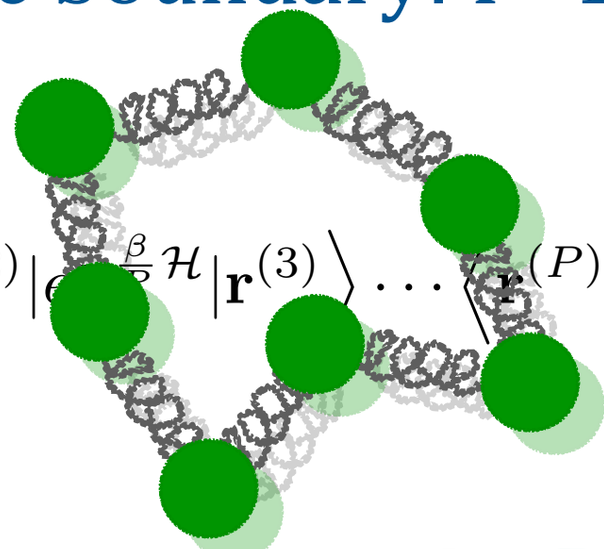

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- Partition function for a cyclic, **classical** ***ring polymer***
- **Harmonic bonds** with spring constant: $k = \dfrac{Pm}{\hbar^2\beta^2}$
- **Potential distributed equally among beads**

Partition function is a **Path Integral**

- Partition function has form: $$Q = \int \mathcal{D}\mathbf{r}(t) e^{S[\mathbf{r}(t)]}$$

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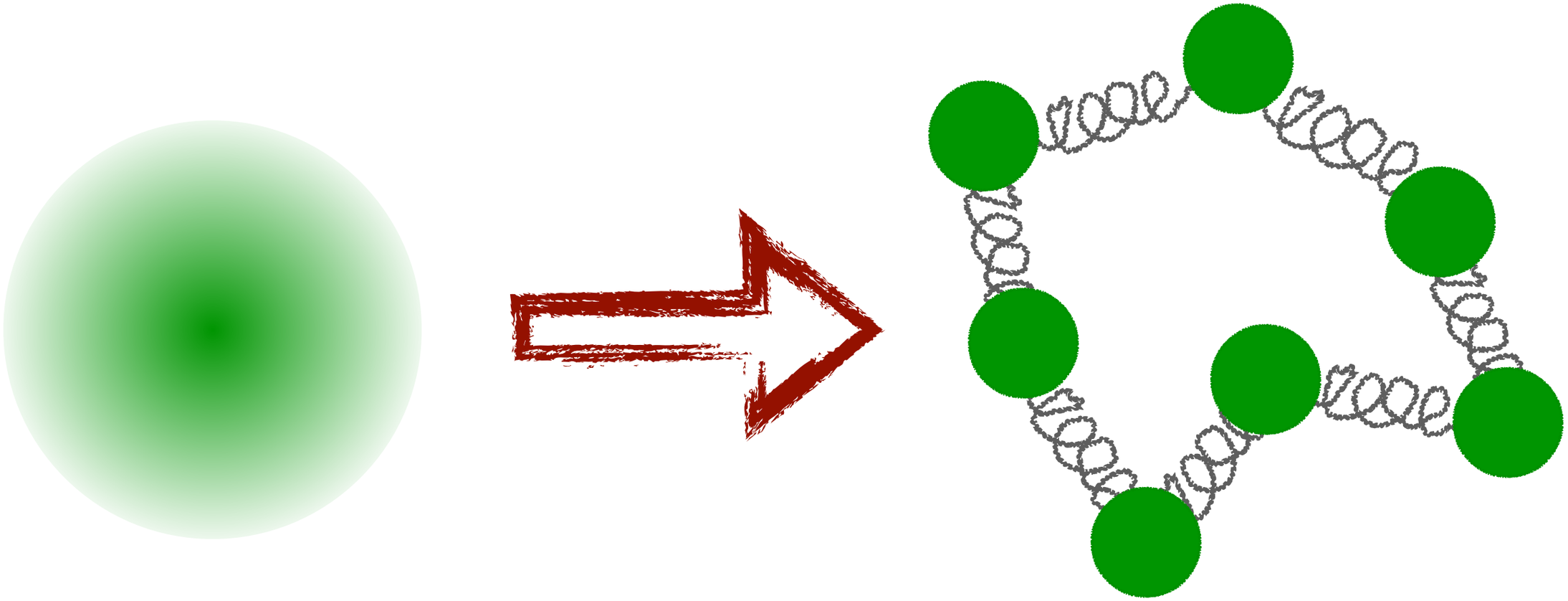
- "Action": $$S\left[\mathbf{r}(t)\right] = -\int_0^{\beta\hbar} \frac{dt}{\hbar} \left\{ \frac{1}{2} m |\dot{\mathbf{r}}(t)|^2 + V[\mathbf{r}(t)] \right\}$$

$$t \leftrightarrow \frac{\beta\hbar\alpha}{P} \qquad\qquad \dot{\mathbf{r}}(t) = \lim_{P\to\infty} \left[\mathbf{r}^{(\alpha+1)} - \mathbf{r}^{(\alpha)} \right] / (\beta\hbar/P)$$

- *A **single configuration** of the ring polymer = **specific quantum path** of the electron*

So what have we accomplished?

- **Quantized electron** is ***isomorphic*** to **classical ring polymer**



- Quantum stat mech from **classical simulations!**

Chandler & Wolynes, J. Chem. Phys. **74**, 4078 (1981)

What do we still need?

- Interactions: electron-bath **pseudopotentials**

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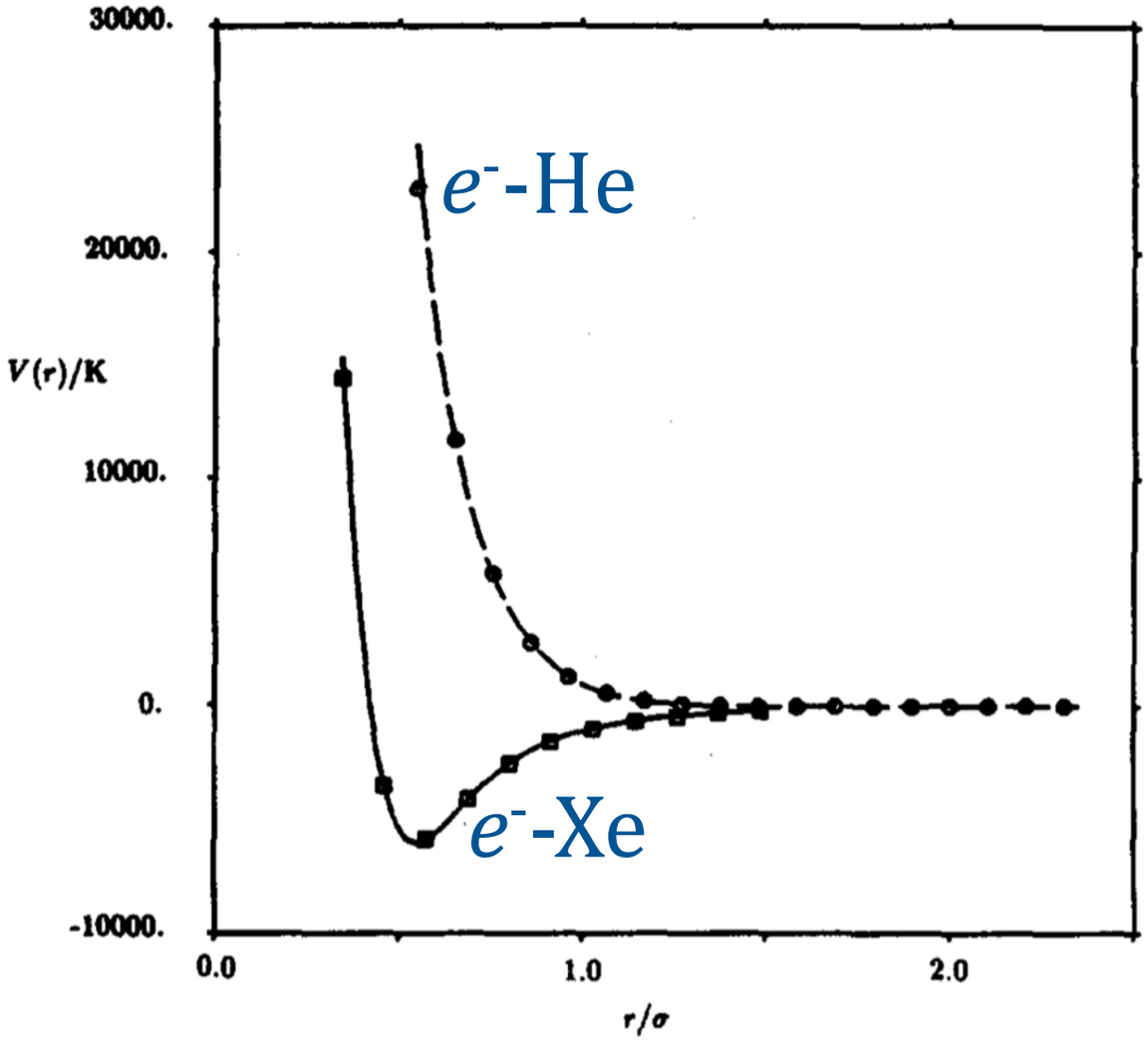
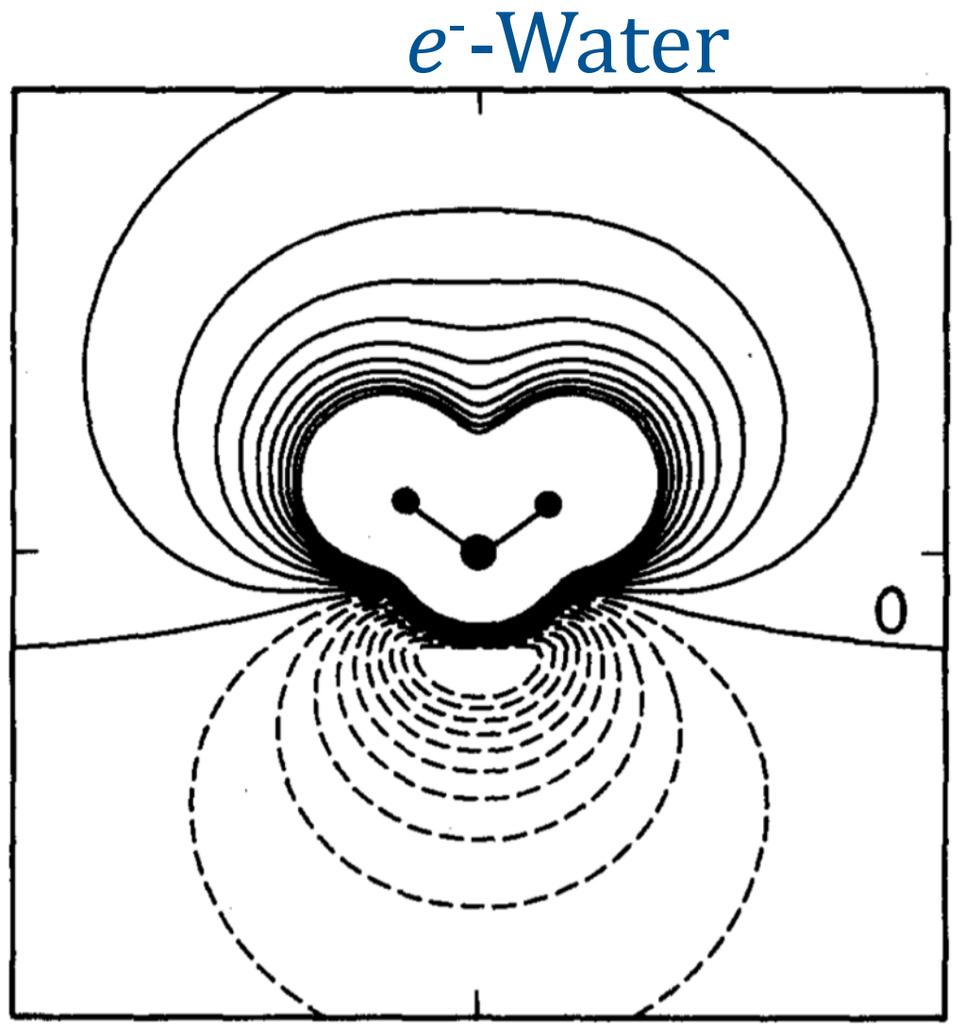


Coker, Berne, & Thirumalai, J. Chem. Phys. **86**, 5689 (1987)



Schnitker & Rossky, J. Chem. Phys. **86**, 3462 (1987)

Example: Excess Electron in Liquid He

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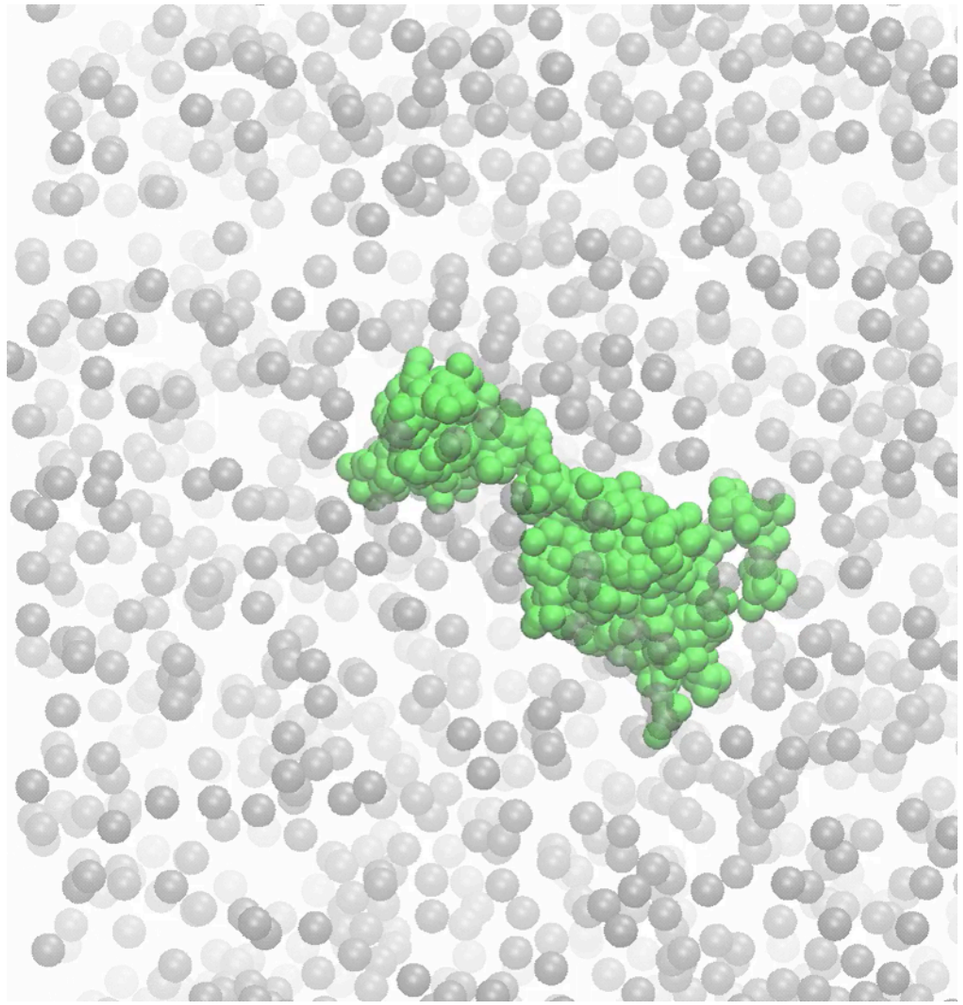

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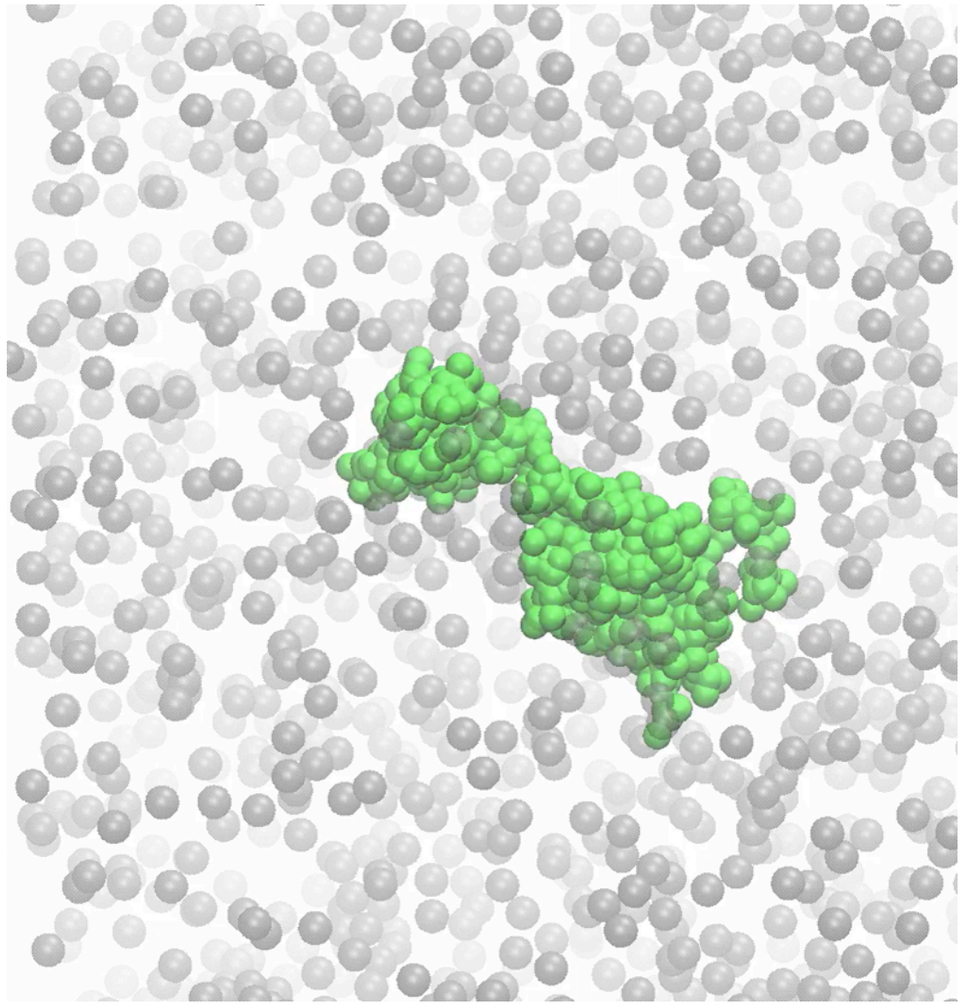

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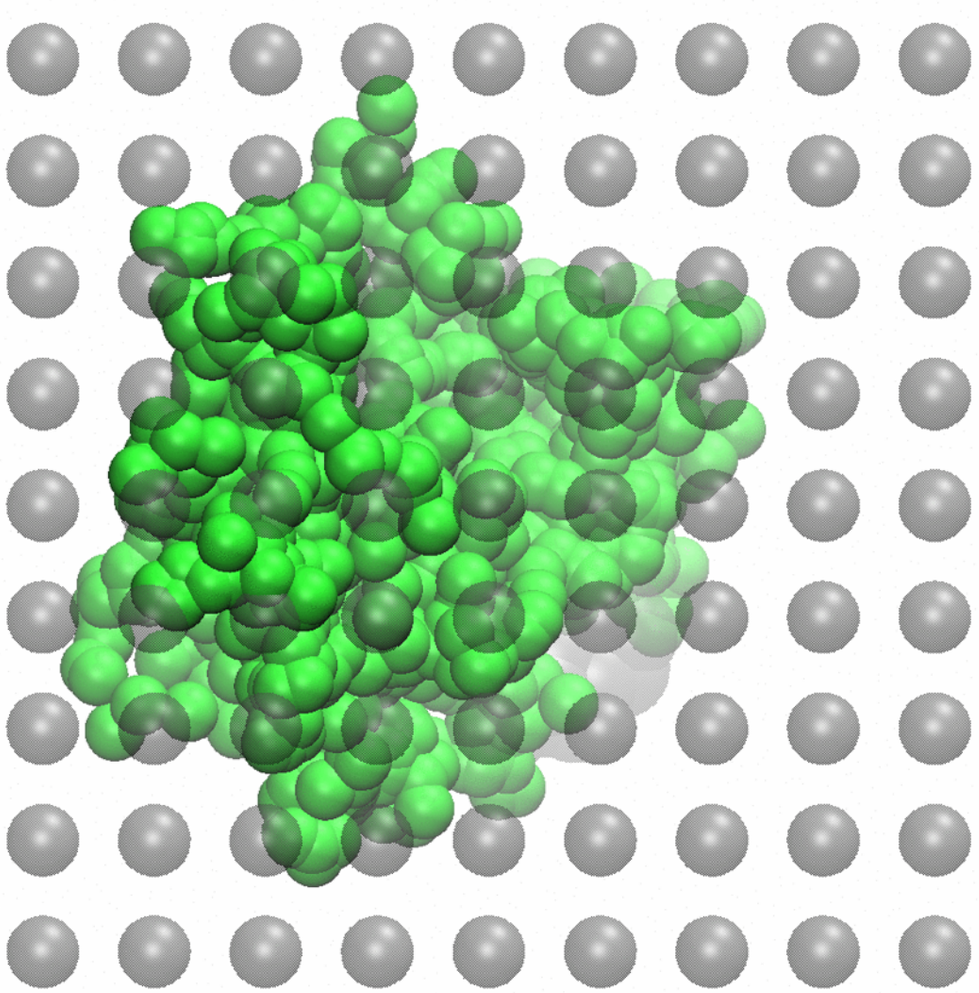

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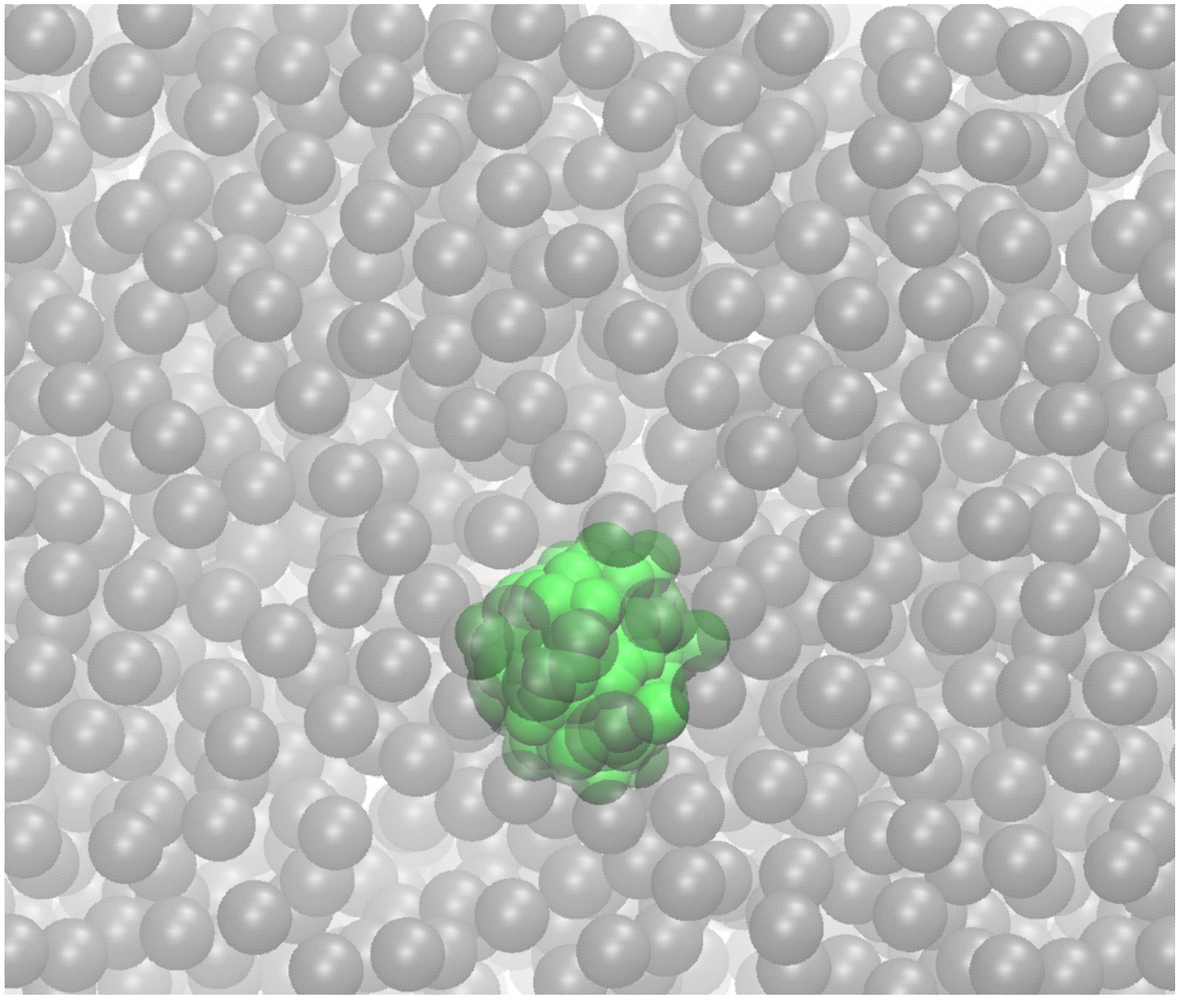

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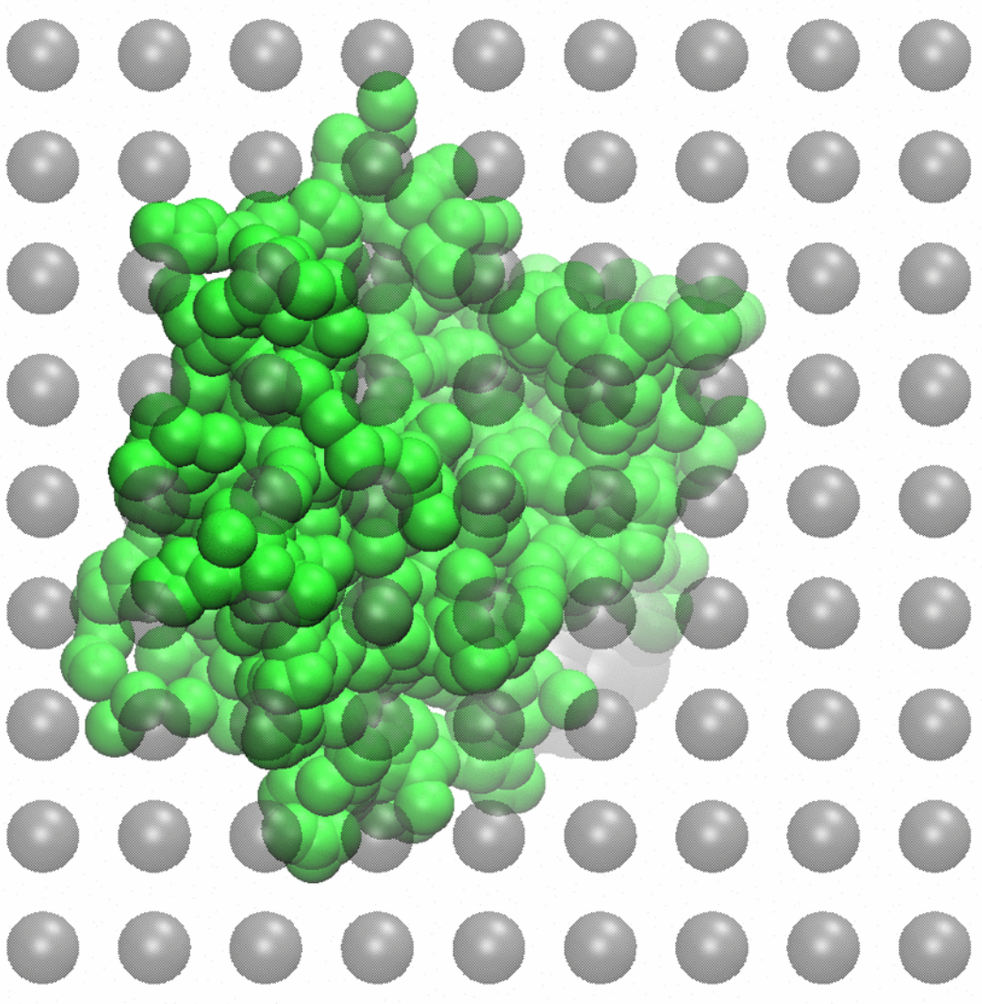

Quantifying Localization of Electron

- Quantifying the "size" of the electron

$$\mathcal{R}^2(\tau-\tau') = \left\langle |\mathbf{r}(\tau)-\mathbf{r}(\tau')|^2 \right\rangle \qquad \mathcal{R}^2_{\text{free}}(\tau-\tau') = 3\lambda^2 \left(\frac{\tau}{\beta\hbar}\right)\left(1-\frac{\tau}{\beta\hbar}\right)$$

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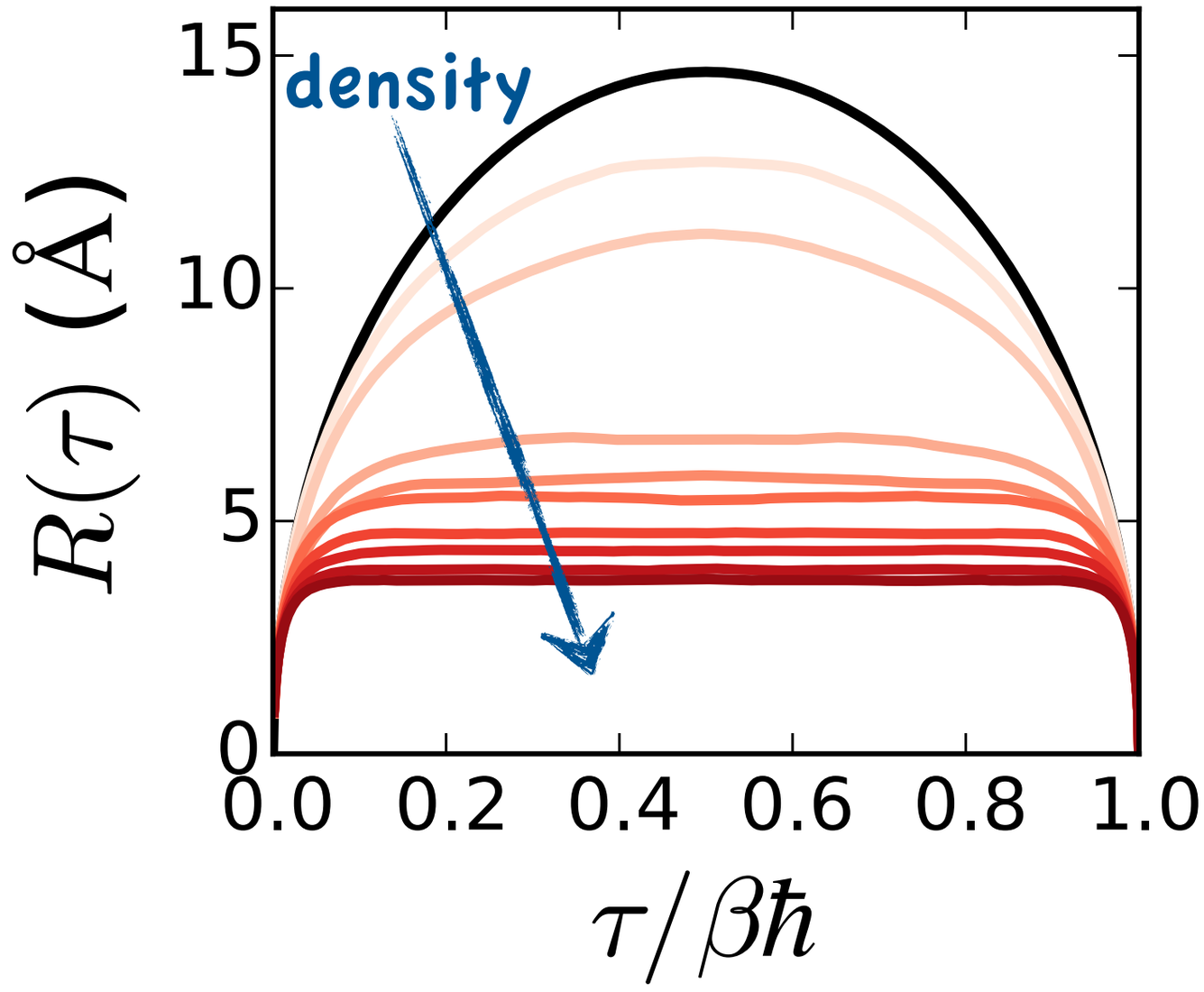
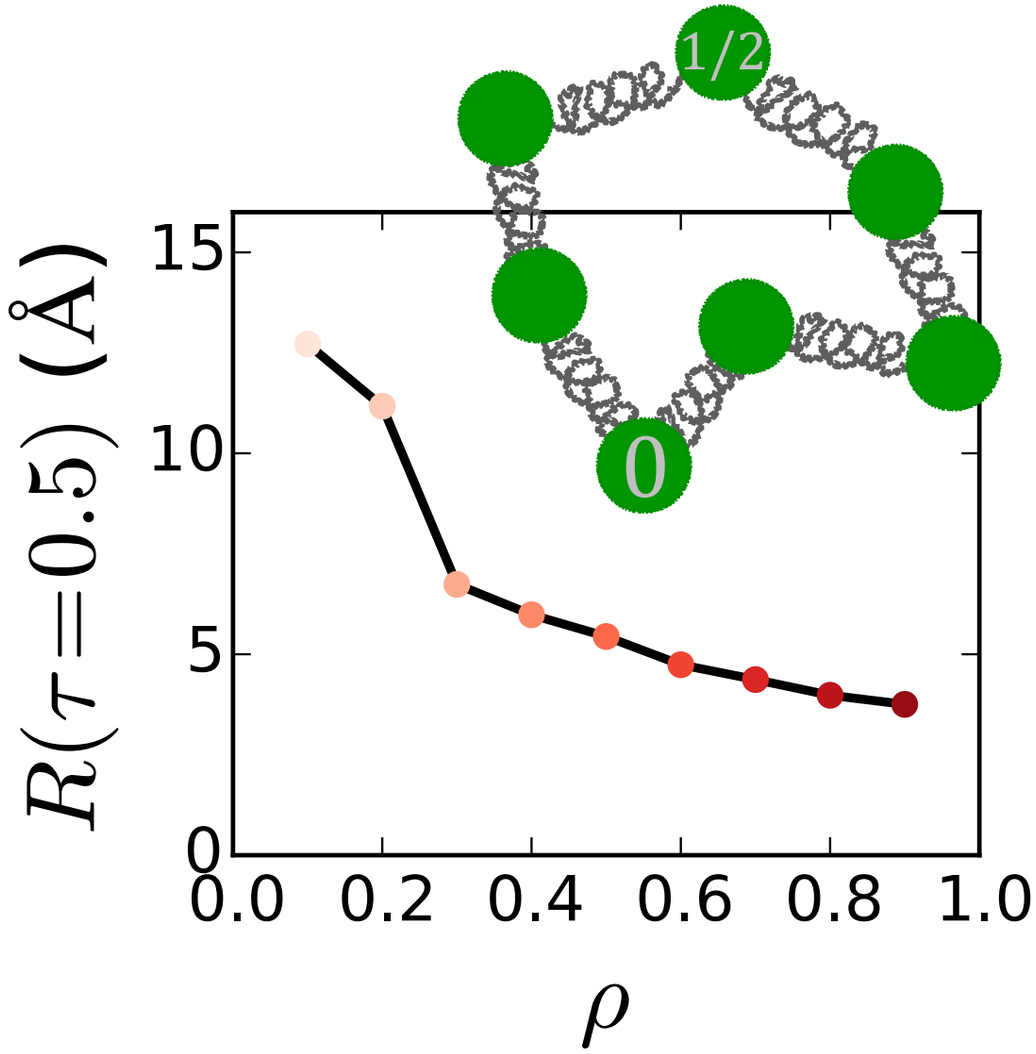
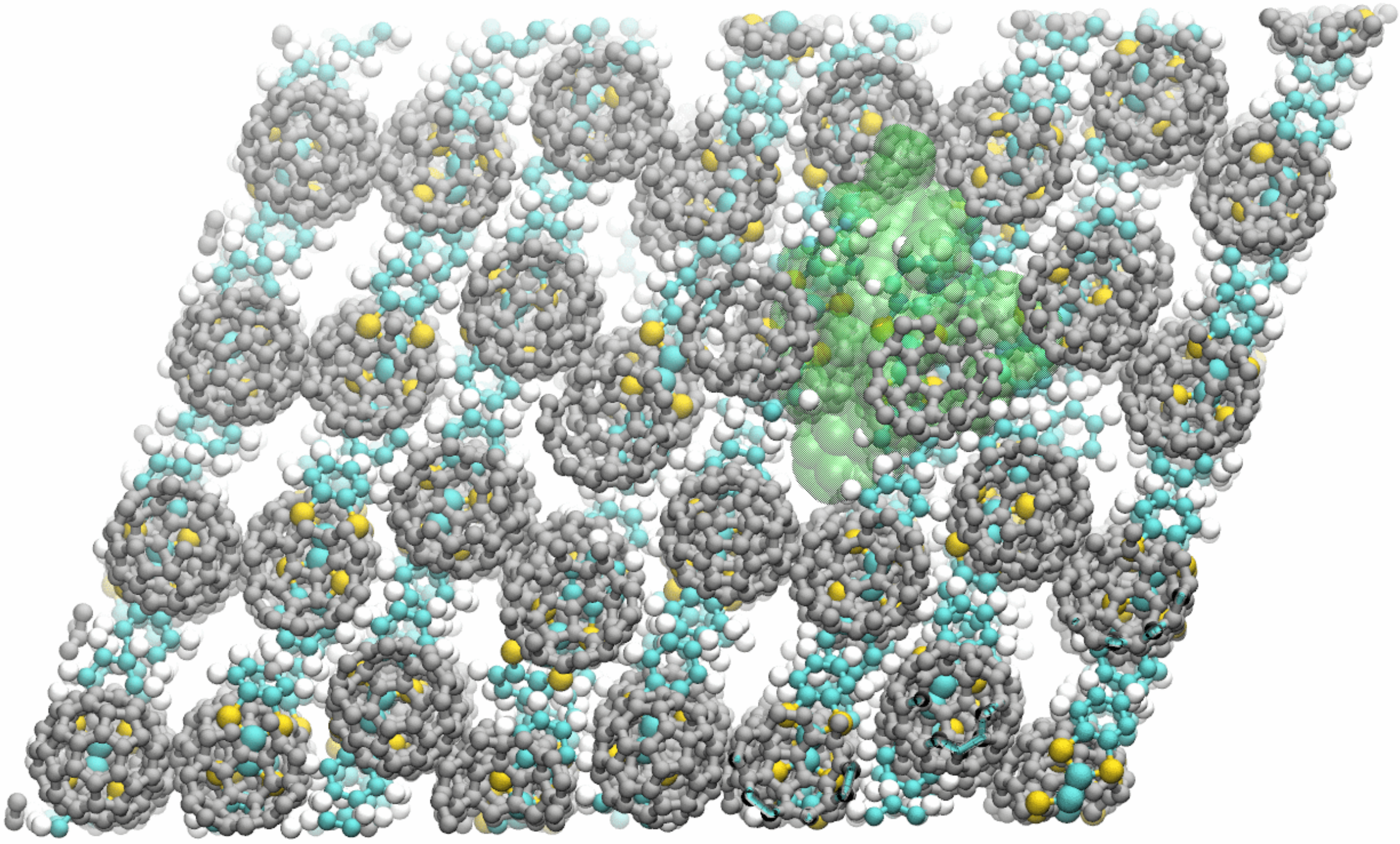




Can Simulate Electrons in Large Systems



- Polaron structure/dynamics in organic semiconductor

Modeling Electron Transfer: **Iron self-exchange**

- Fe^{2+} - Fe^{3+} electron transfer reaction
  - Most heavily studied system by simulation

$$\mathrm{Fe}^{2+} + \mathrm{Fe}^{3+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{Fe}^{2+}$$

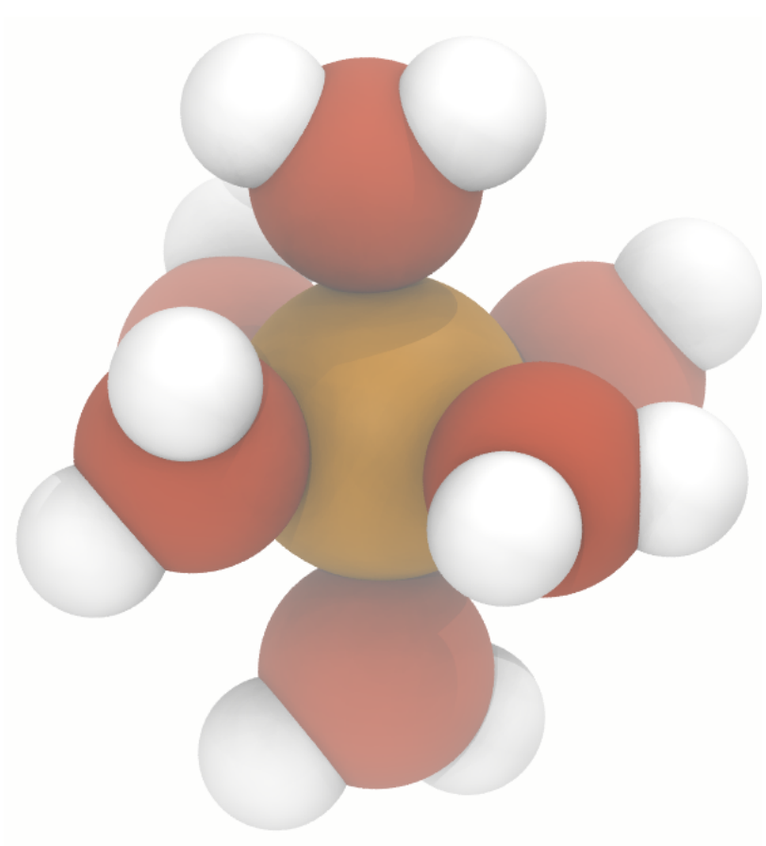
- First, how to model a single ion? Then pair…

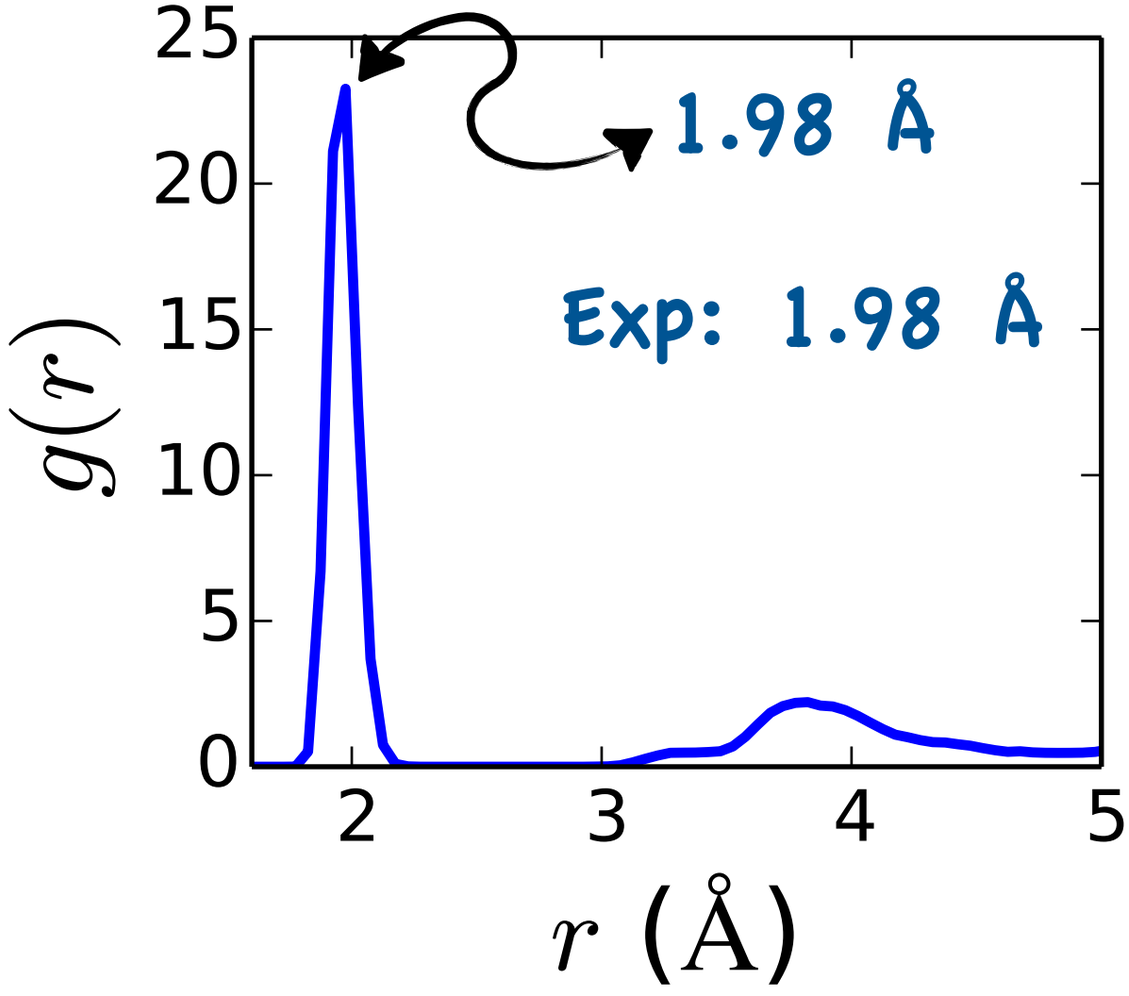
Kuharski, Bader, Chandler, Sprik, Klein, & Impey, J. Chem. Phys. **89**, 3248 (1988)

Modeling Fe^{3+}

$$V_{\mathrm{Fe^{3+}-H_2O}} = \frac{A}{|\mathbf{r} - \mathbf{r}_1^{(\mathrm{O})}|^9} + 3e \sum_{\gamma} \frac{q_\gamma}{|\mathbf{r} - \mathbf{r}_1^{(\gamma)}|}$$

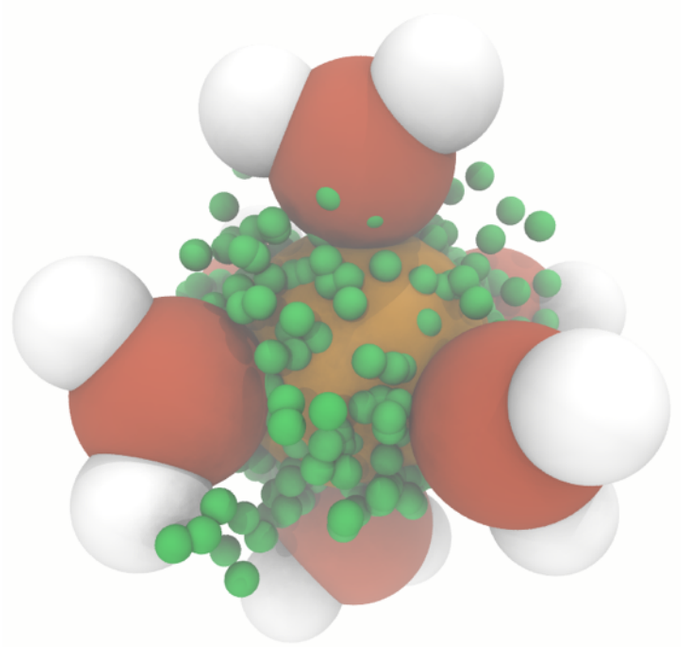
- Fe^{3+} completely classical (empirical)

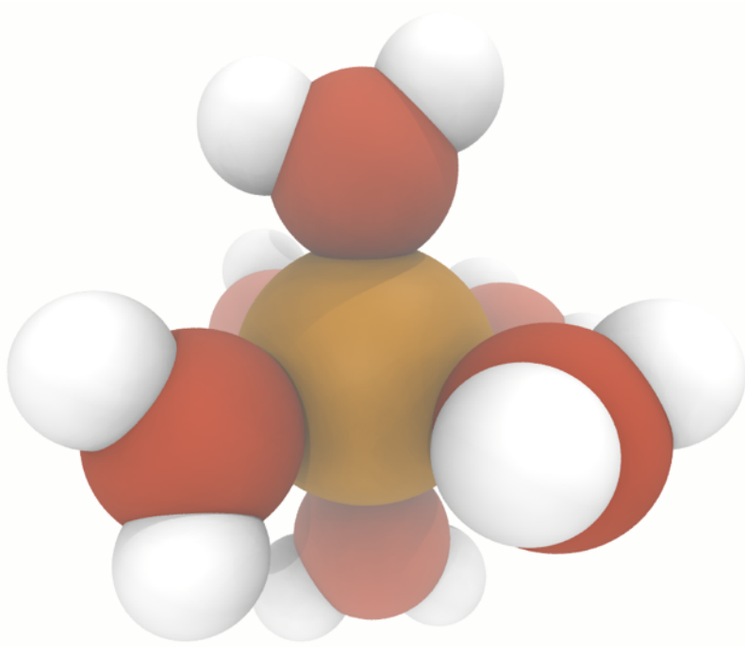




Modeling Fe^{2+}

- Fe^{3+} + path integral electron or completely classical?





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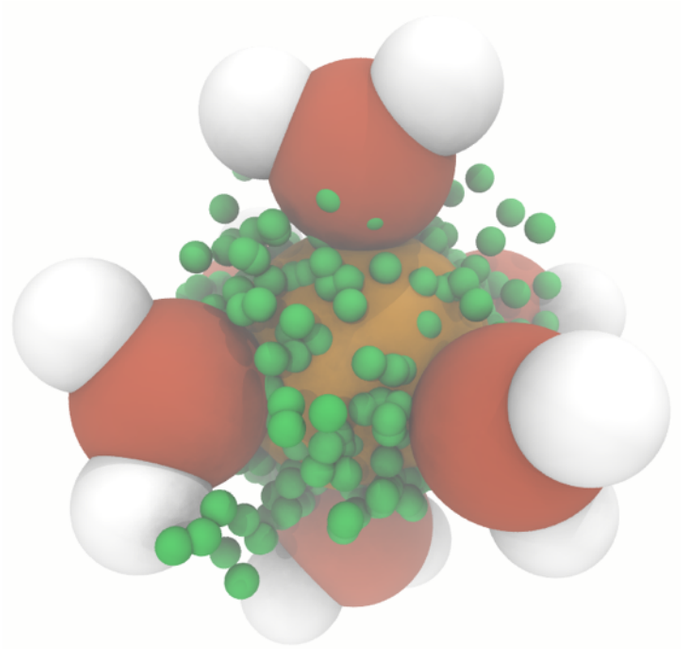
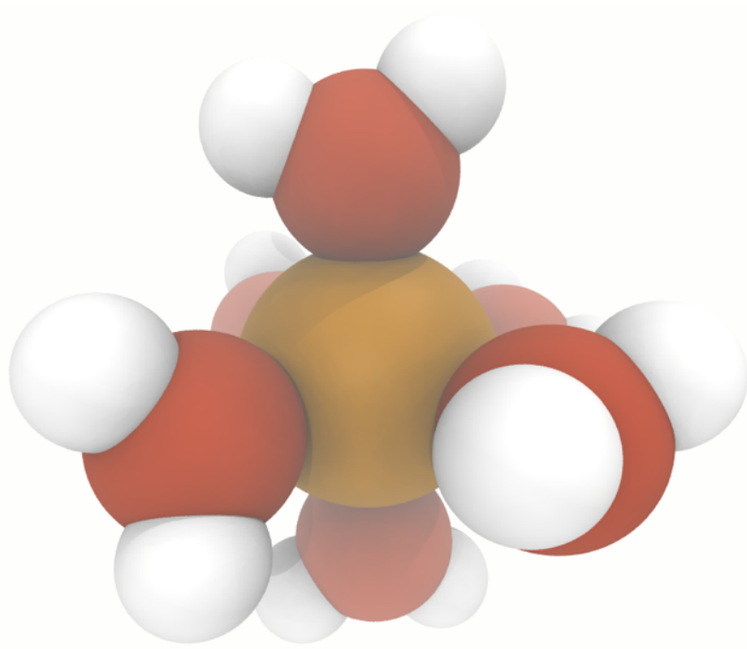
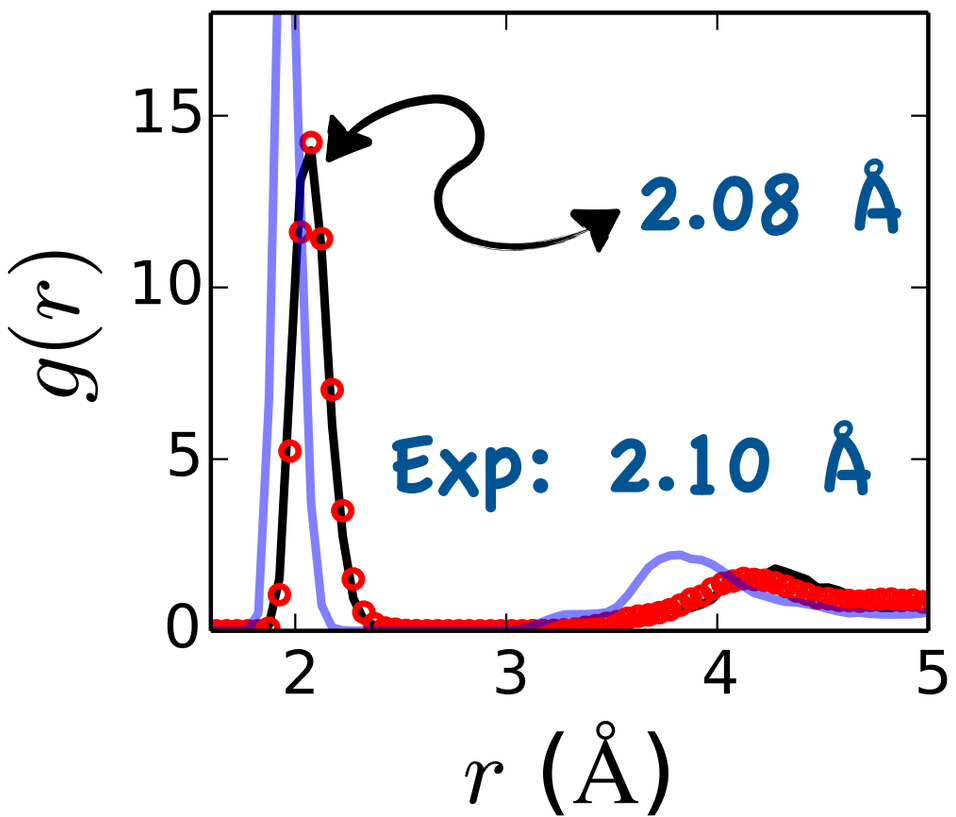


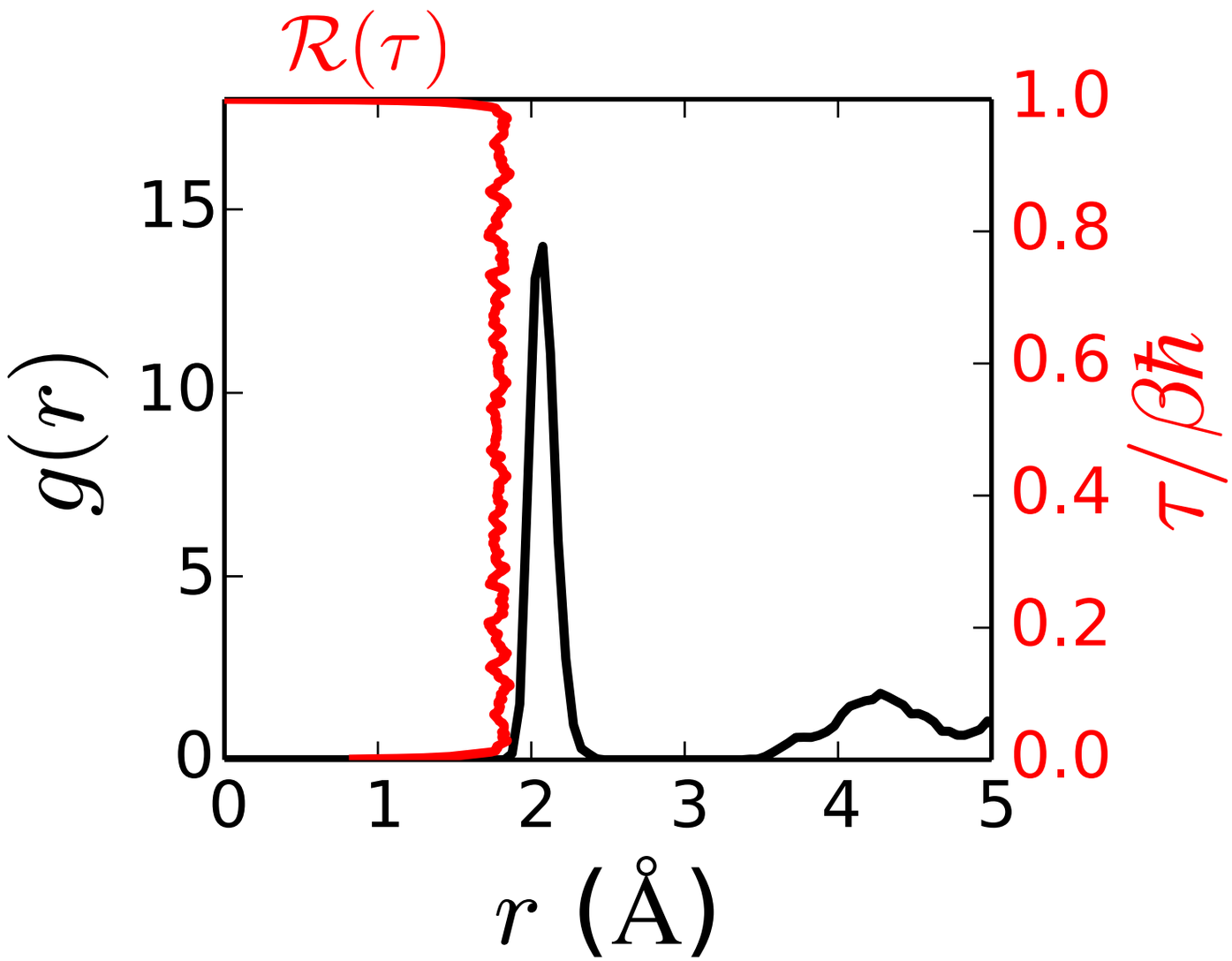




- **Same Structure!**
- ***Why?***

Electron is completely inside the ion core!

...on average

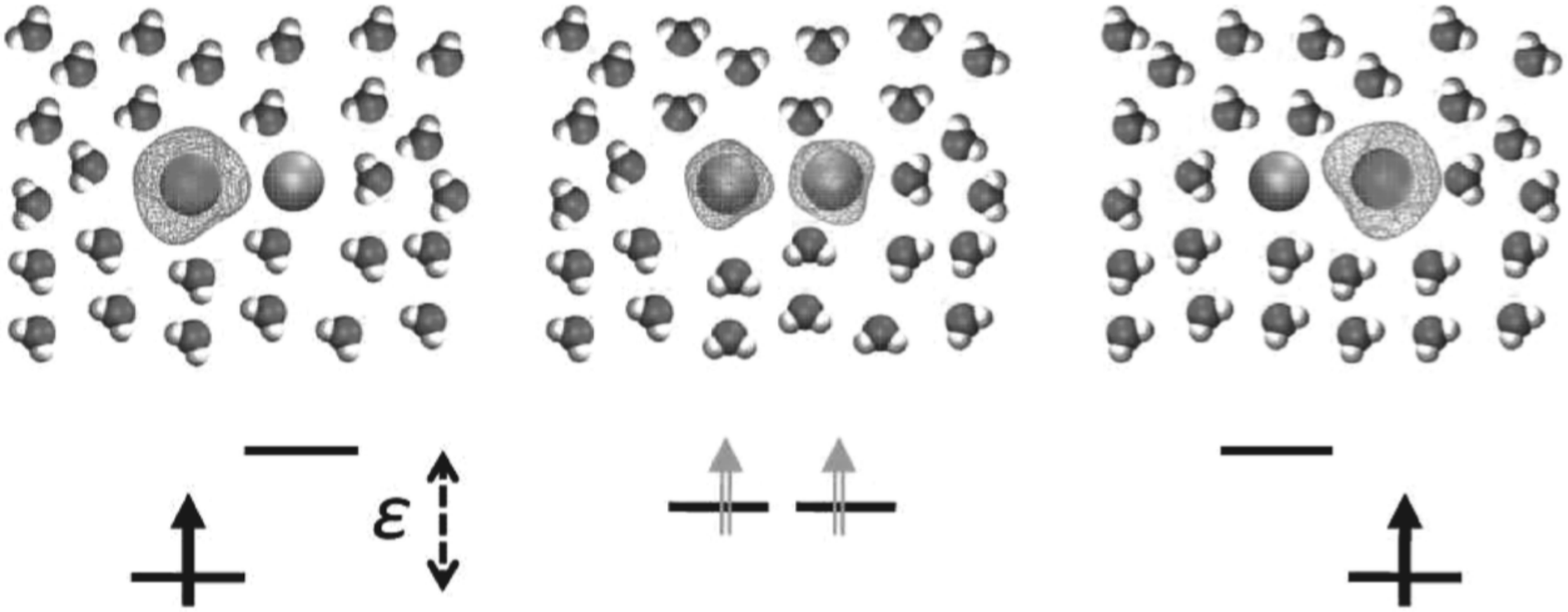


- ***Treat both ions as point charges inside repulsive cores!***
- **"Tight-binding" approximation**
- Electron transfer is analogous to changing magnitude of point charges!!!

Electron Transfer Free Energies

- What is the order parameter for this reaction?
  … what is ΔG a function of? What governs this reaction?

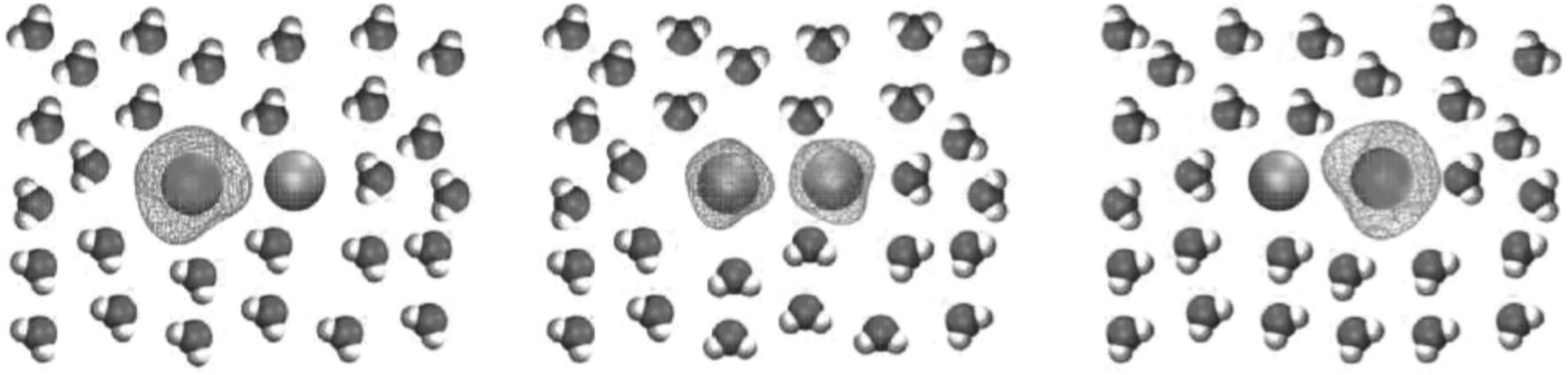
- ***Solvent Fluctuations***



Solvent-Based Reaction Coordinate

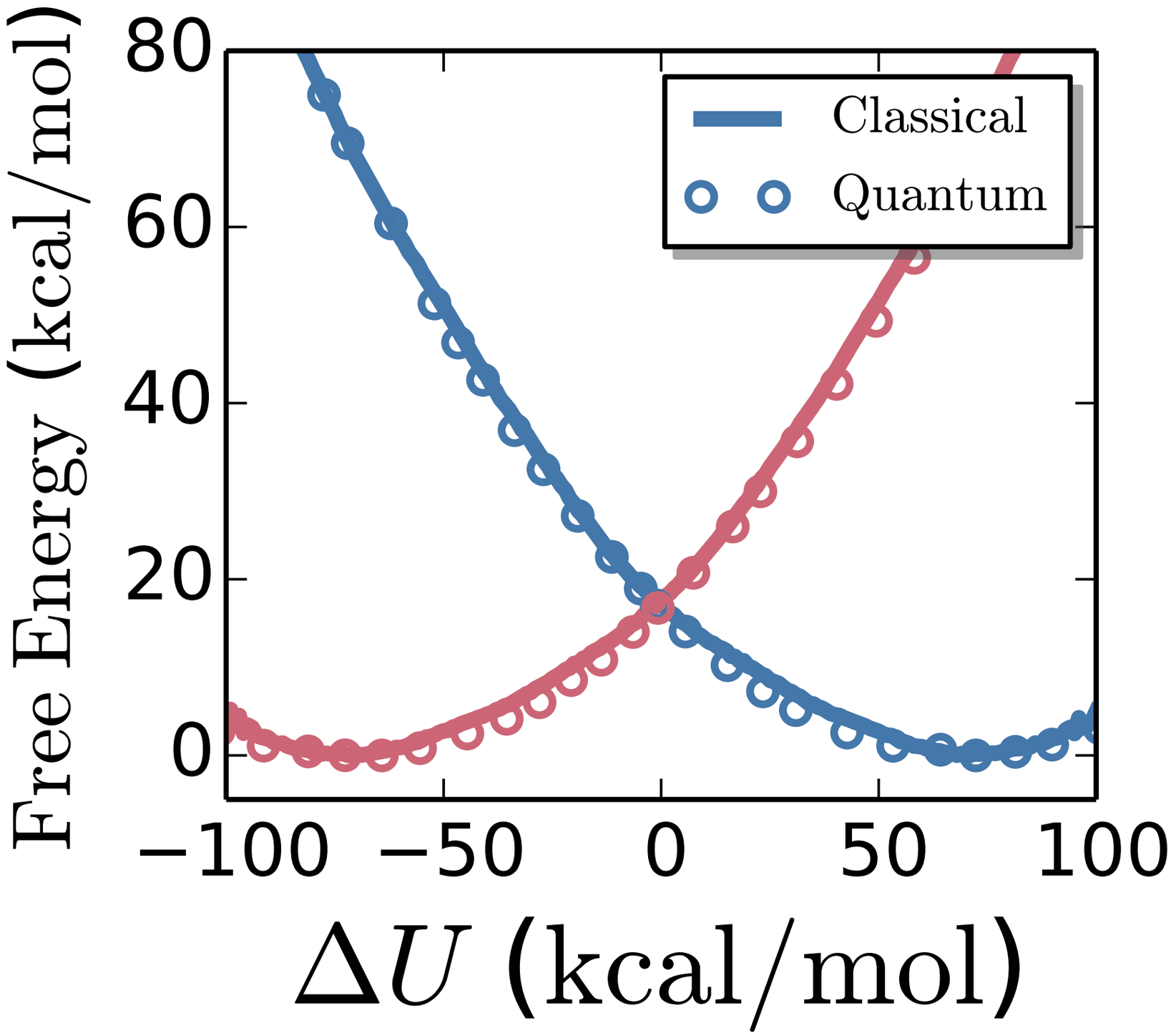
- Difference in electrostatic potentials at the center of each ion

$$\Delta U(\mathbf{\Gamma}) = \sum_{i=1}^{N} \left[\frac{q_i}{|\mathbf{r}_2 - \mathbf{r}_i|} - \frac{q_i}{|\mathbf{r}_1 - \mathbf{r}_i|} \right]$$



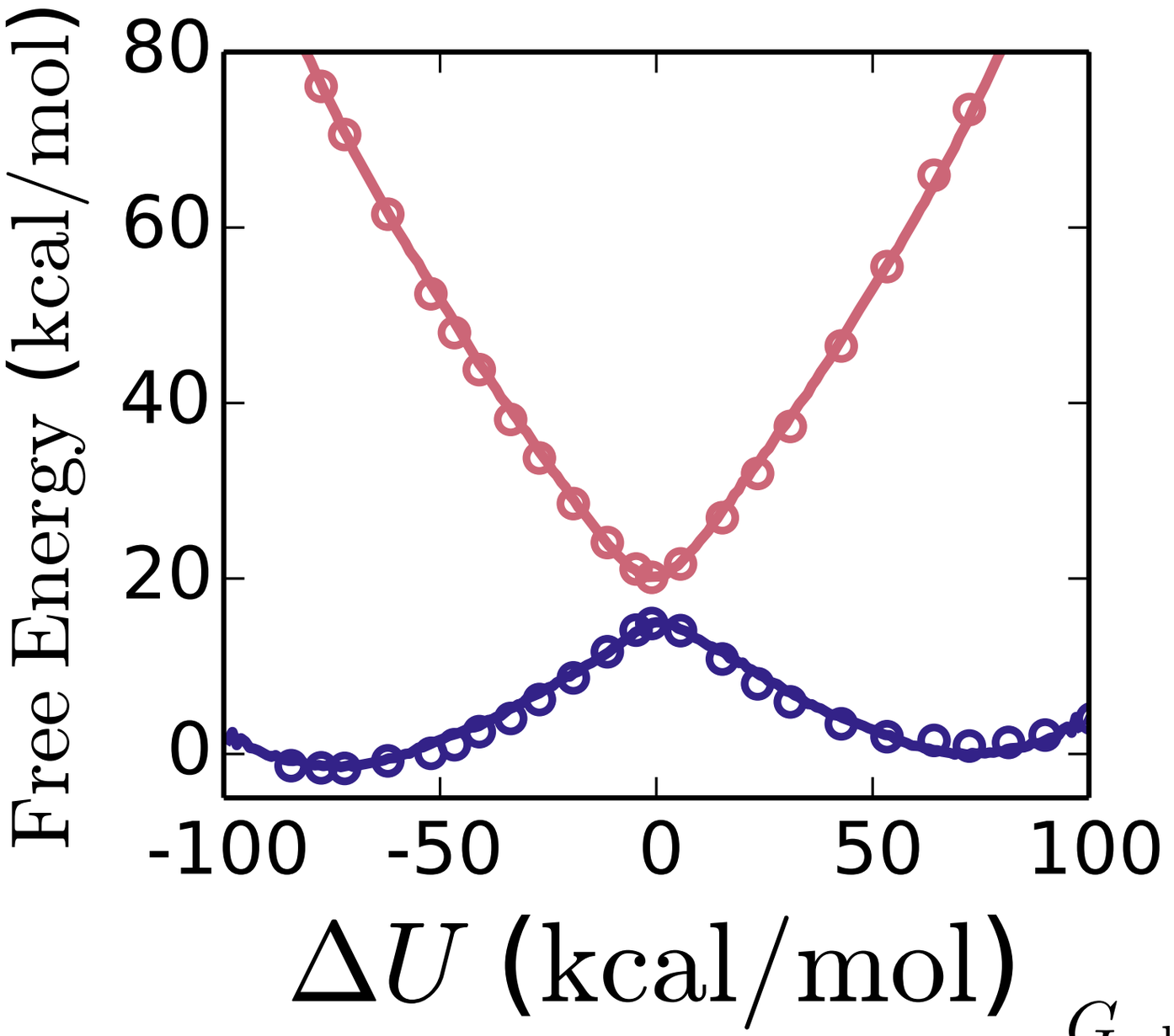
- Compute free energy as a function of ΔU
- Need non-Boltzmann sampling (*e.g.* umbrella sampling…)

Free Energies are Independent of Electron Quantization



- Diabatic representation, what about adiabatic?

Adiabatic Representation from Diabatic States



- Diagonalize the 2x2 Hamiltonian

$$\mathbf{H} = \begin{pmatrix} \mathcal{H}_0 & \Gamma_{01} \\ \Gamma_{01} & \mathcal{H}_1 \end{pmatrix}$$

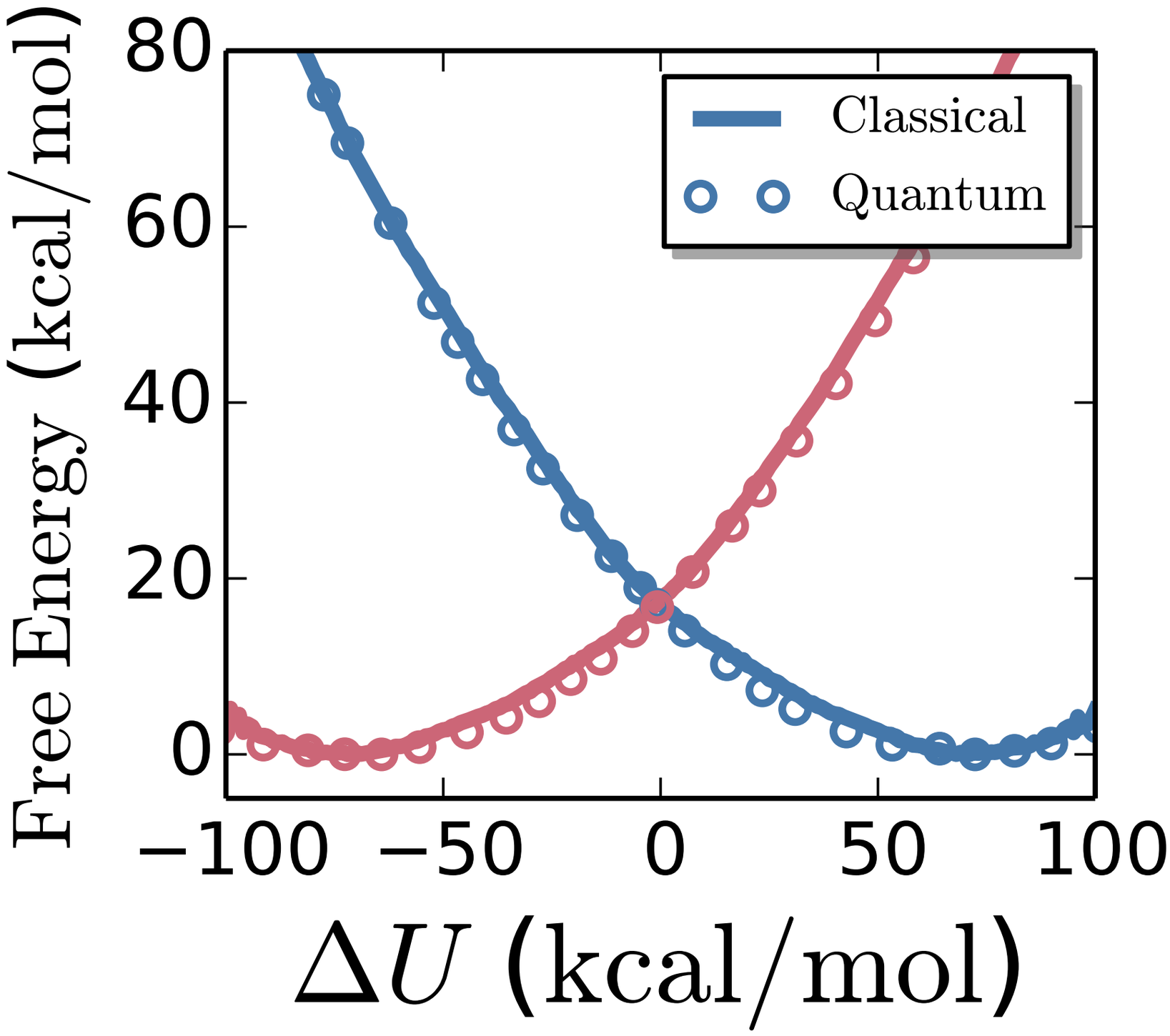
- Solutions recast into form of free energies:

$$G_{\mathrm{ad}}(\Delta E) = G_0(\Delta E) + \frac{1}{2}\left[\Delta e \pm \left(\Delta e^2 + 4\Gamma_{01}^2\right)^{1/2}\right]$$

$$\Delta e \equiv \Delta E - \Delta E^{\ddagger}$$

- Same qualitative picture as diabats

Free Energies are Independent of Electron Quantization



- ***What about reaction rates???***

Transition State Theory

- Rates are related to barriers and well curvature

$$k_{\mathrm{TST}} = \frac{\omega_{\mathrm{R}}}{2\pi} e^{-\beta \Delta G^{\ddagger}}$$

$$\omega_{\mathrm{R}}^2 = \frac{\left\langle \Delta \dot{U}^2 \right\rangle}{\langle (\Delta U - \langle \Delta U \rangle)^2 \rangle}$$

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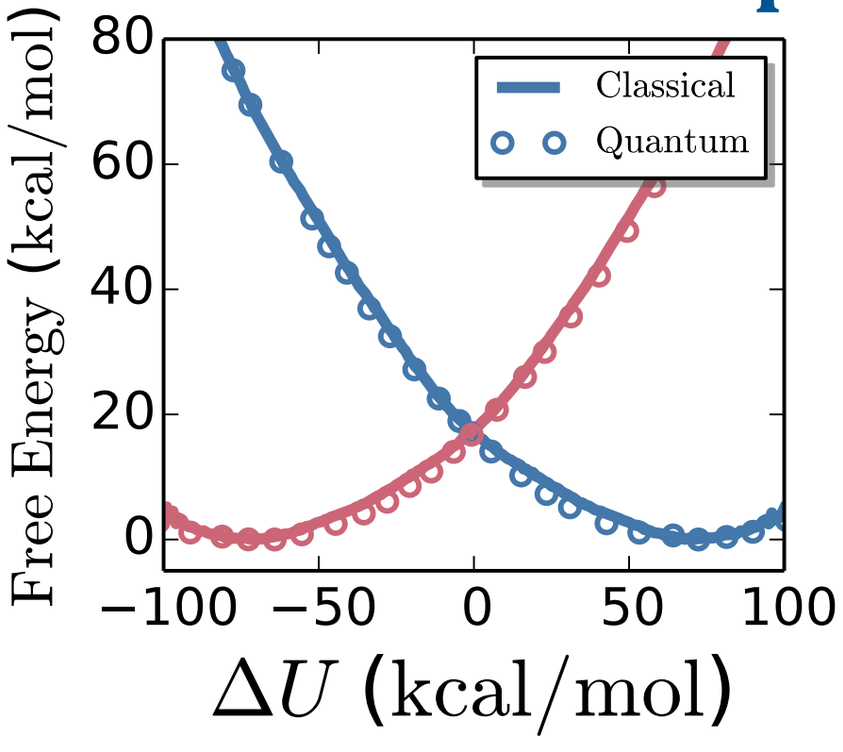
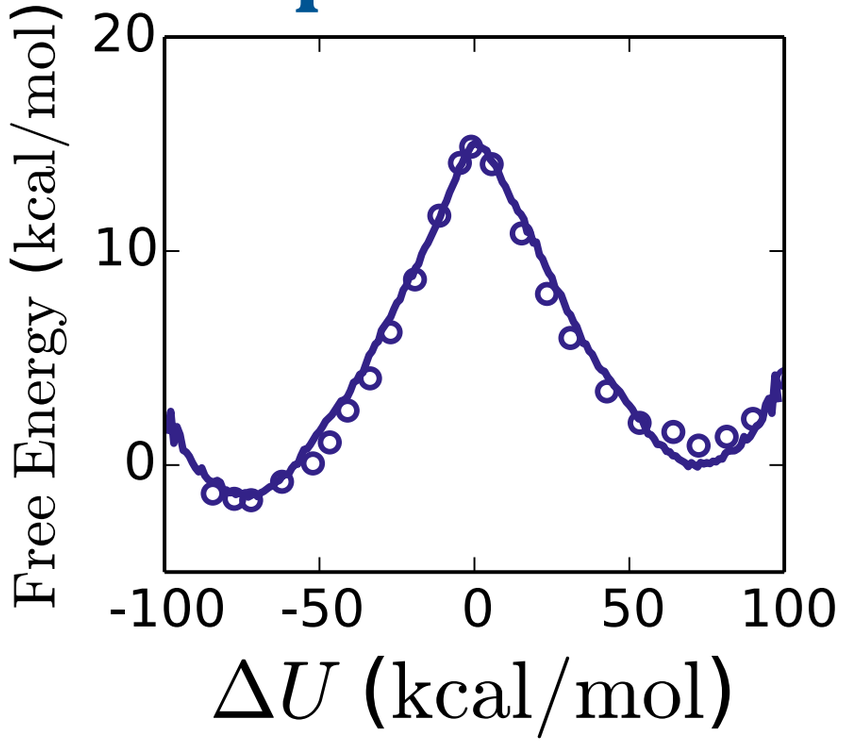
Rates are independent of e^- quantization!





Transition State Theory

- Rates are related to barriers and well curvature

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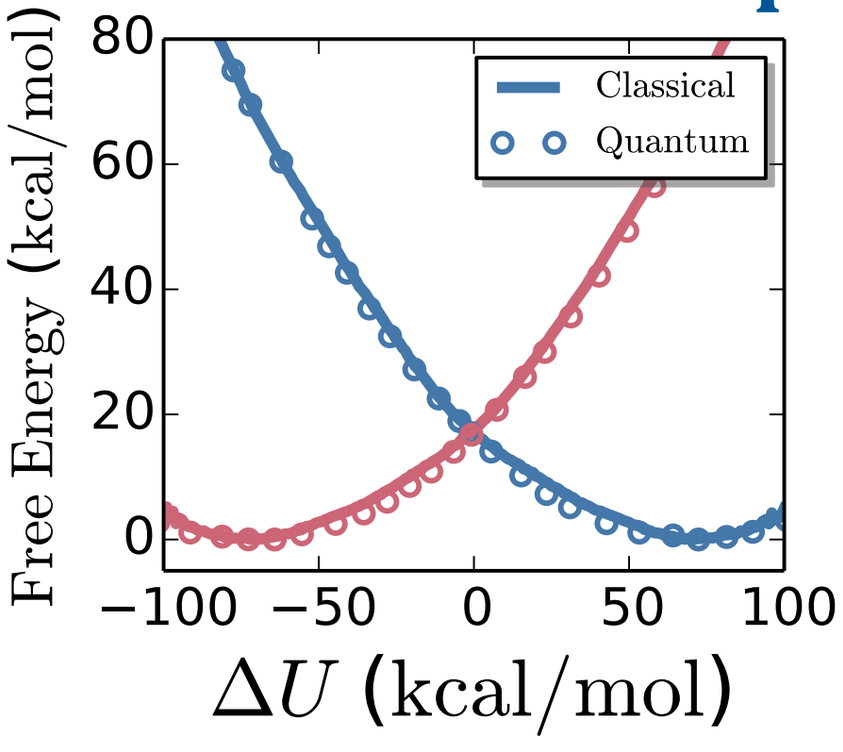
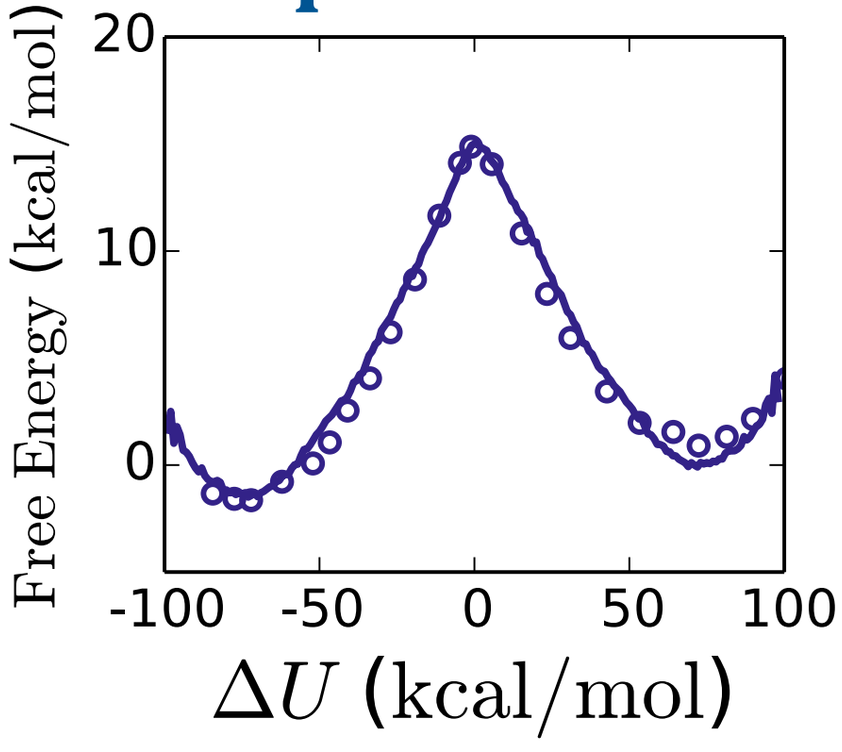
Rates are independent of *e*⁻ quantization!



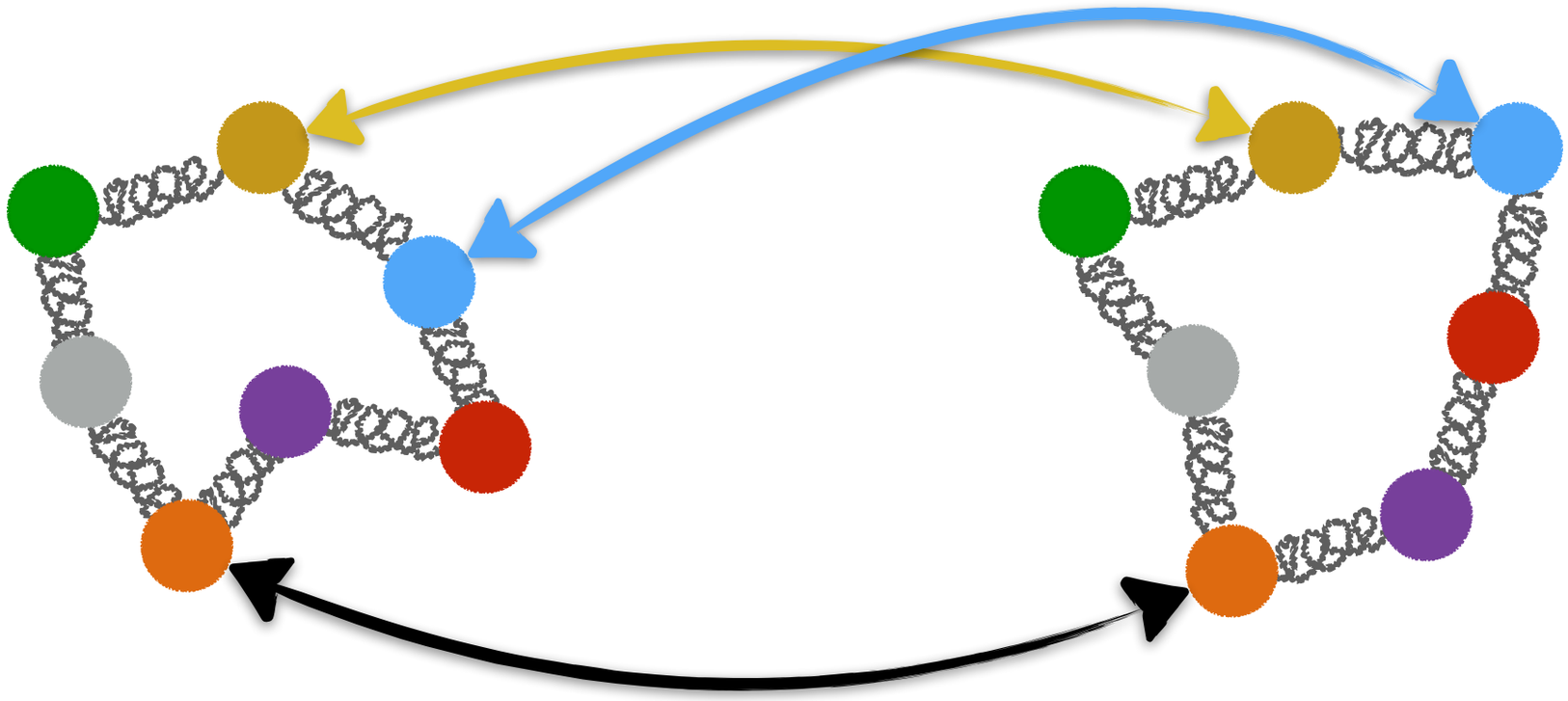


- Omits dynamics of barrier recrossing, but can correct with reactive flux formalism…

When else can we use this?

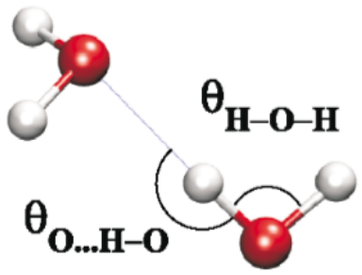
- **Nuclear Quantum Effects**
  - Quantum effects are important for light nuclei even at room temperature

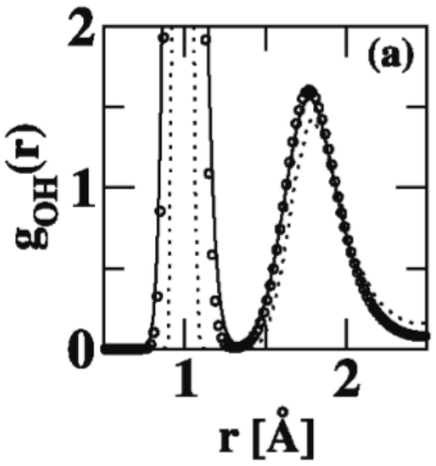
- **Hydrogen** (or D) atoms in **water**

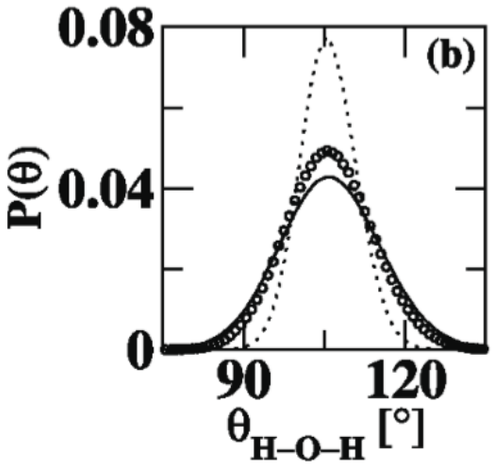


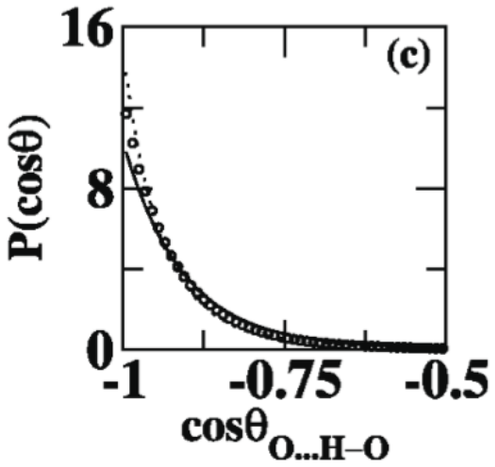
- **Do NQEs impact anything relevant?**

Nuclear Quantum Effects on Water Structure

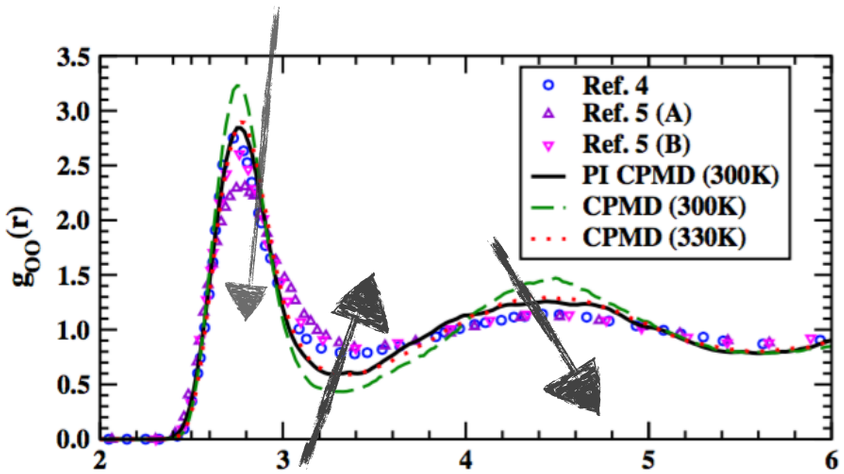


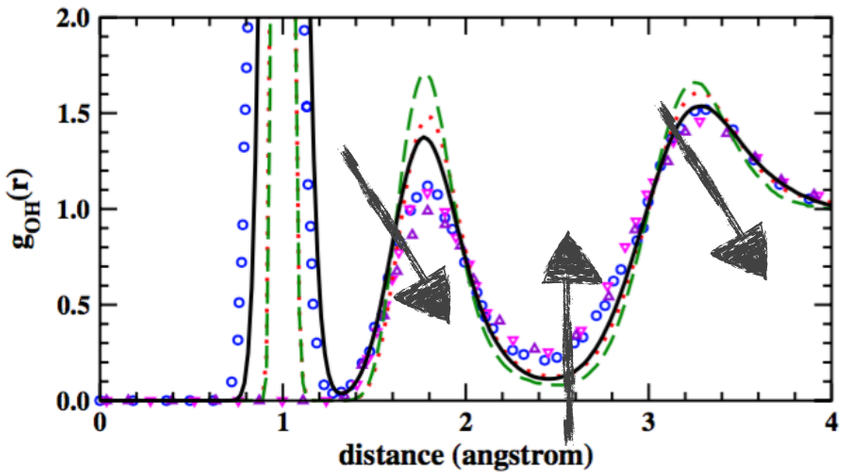






Chen, Yvanov, Klein, & Parrinello, Phys. Rev. Lett. **91**, 215503 (2003)





Morrone & Car, Phys. Rev. Lett. **101**, 017801 (2008)

- NQEs impact water structure

- Also influence dynamics (faster diffusion, etc.)
  - *NQEs in ET impact ΔG more than electron quantization*

Nuclear Quantum Effects on Water Structure

CHEMICAL REVIEWS

Review

pubs.acs.org/CR

Nuclear Quantum Effects in Water and Aqueous Systems: Experiment, Theory, and Current Challenges

Michele Ceriotti,[†] Wei Fang,[‡] Peter G. Kusalik,[§] Ross H. McKenzie,[∥] Angelos Michaelides,[‡] Miguel A. Morales,[⊥] and Thomas E. Markland[*,#]

[†]Laboratory of Computational Science and Modeling, Institute of Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

[‡]Thomas Young Centre, London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

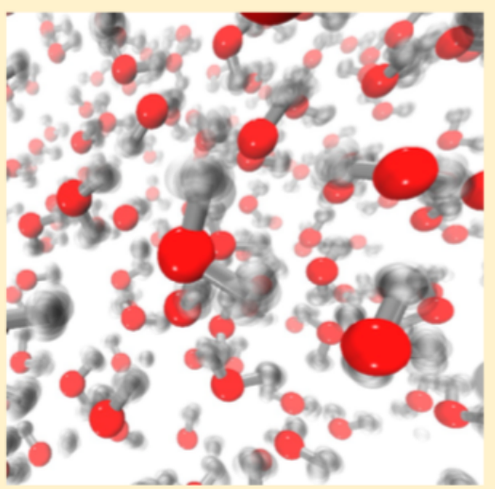
[§]Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada

[∥]School of Mathematics and Physics, University of Queensland, Brisbane, 4072 Queensland Australia

[⊥]Lawrence Livermore National Laboratory, Livermore, California 94550, United States

[#]Department of Chemistry, Stanford University, 333 Campus Drive, Stanford, California 94305, United States

ABSTRACT: Nuclear quantum effects influence the structure and dynamics of hydrogen-bonded systems, such as water, which impacts their observed properties with widely varying magnitudes. This review highlights the recent significant developments in the experiment, theory, and simulation of nuclear quantum effects in water. Novel experimental techniques, such as deep inelastic neutron scattering, now provide a detailed view of the role of nuclear quantum effects in water's properties. These have been combined with theoretical developments such as the introduction of the principle of competing quantum effects that allows the subtle interplay of water's quantum effects and their manifestation in experimental observables to be explained. We discuss how this principle has recently been used to explain the apparent dichotomy in water's isotope effects, which can range from very large to almost nonexistent depending on the property and conditions. We then review the latest major developments in simulation algorithms and theory that have enabled the efficient inclusion of nuclear quantum effects in molecular simulations, permitting their combination with on-the-fly evaluation of the potential energy surface using electronic structure theory. Finally, we identify current challenges and future opportunities in this area of research.



Path Integral Simulations with **i-PI**

Computer Physics Communications 185 (2014) 1019–1026

Contents lists available at ScienceDirect

Computer Physics Communications

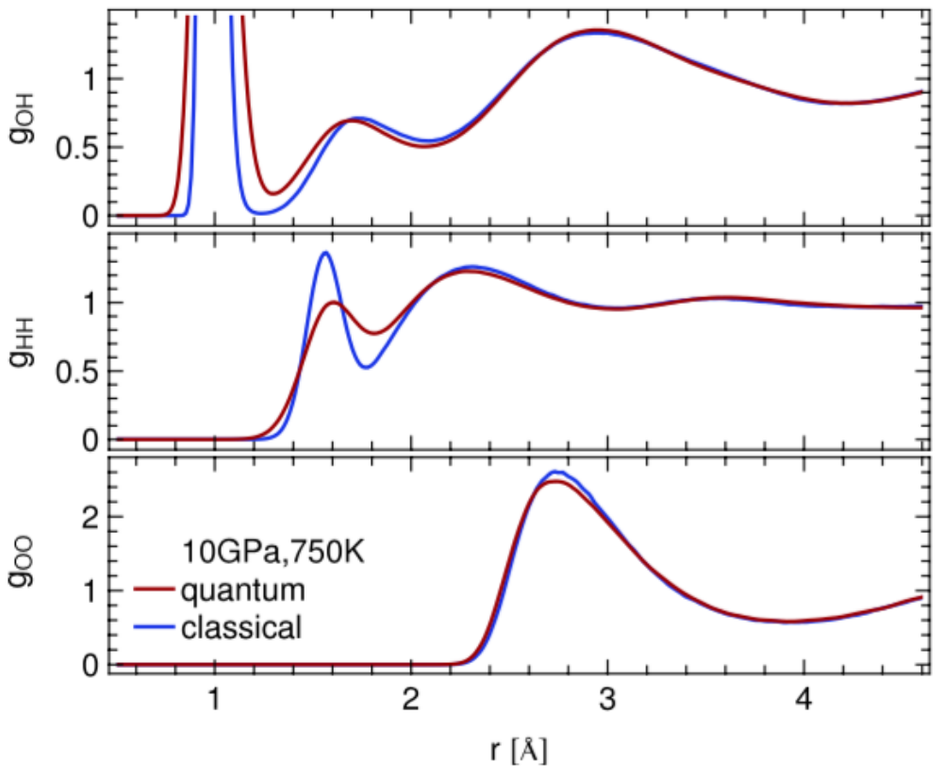
journal homepage: www.elsevier.com/locate/cpc

i-PI: A Python interface for ab initio path integral molecular dynamics simulations☆

Michele Ceriotti *, Joshua More, David E. Manolopoulos

Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK

- Patch for: **LAMMPS, Quantum-Espresso, & CP2K**



https://github.com/i-pi/i-pi

Frontiers in PIMD

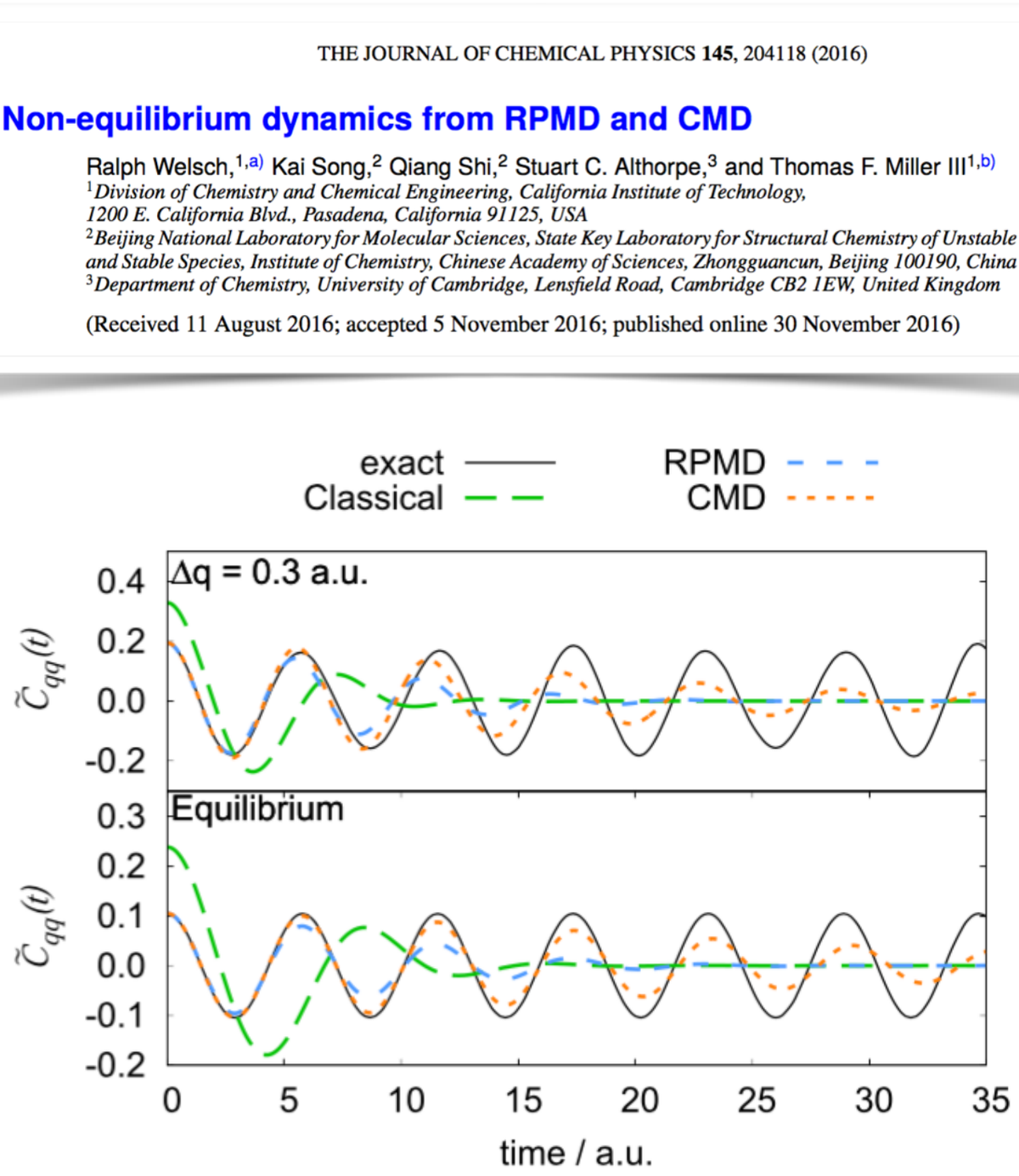
- **Quantum dynamics methods:** PIMD/RPMD is not exact

THE JOURNAL OF CHEMICAL PHYSICS **145**, 204118 (2016)

Non-equilibrium dynamics from RPMD and CMD

Ralph Welsch,[1,a)] Kai Song,[2] Qiang Shi,[2] Stuart C. Althorpe,[3] and Thomas F. Miller III[1,b)]
[1]*Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 E. California Blvd., Pasadena, California 91125, USA*
[2]*Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Beijing 100190, China*
[3]*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

(Received 11 August 2016; accepted 5 November 2016; published online 30 November 2016)



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Non-equilibrium dynamics from RPMD and CMD

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[1]*Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 E. California Blvd., Pasadena, California 91125, USA*
[2]*Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Beijing 100190, China*
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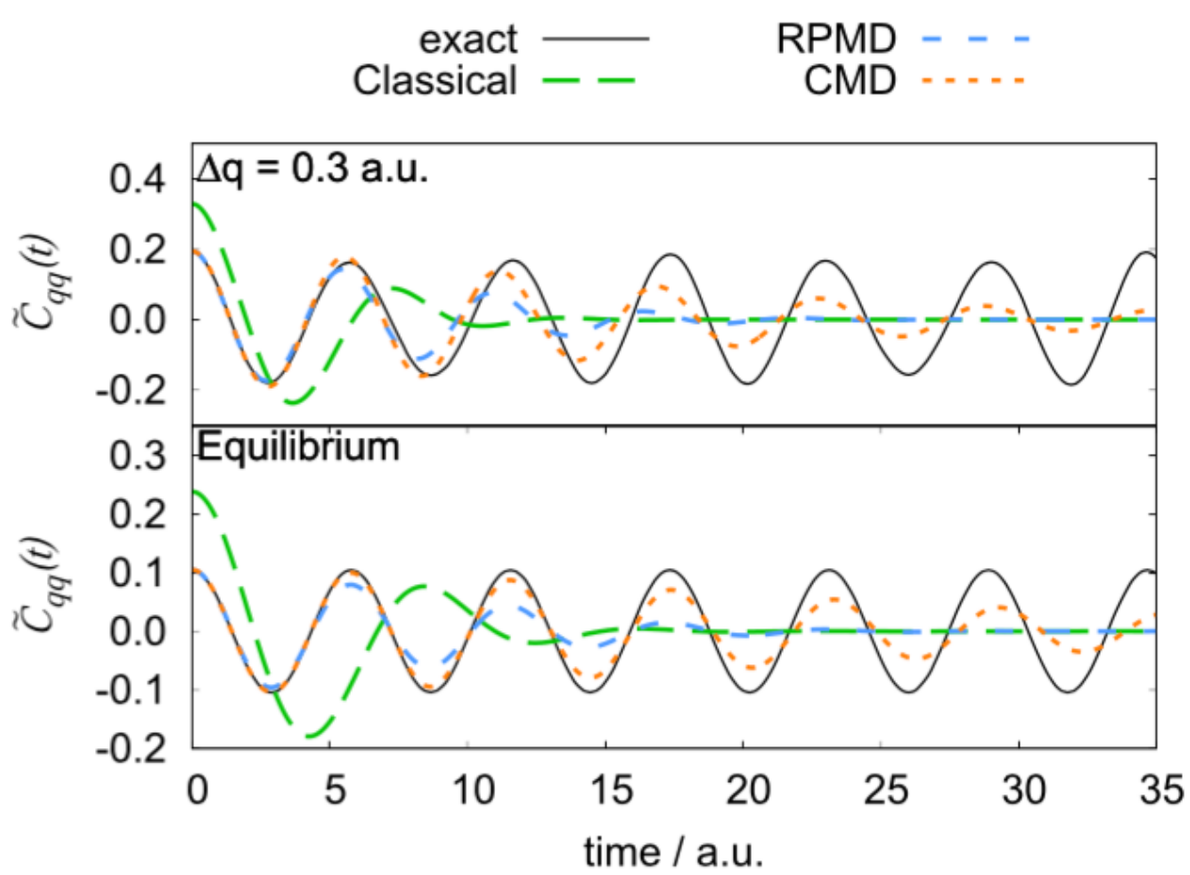
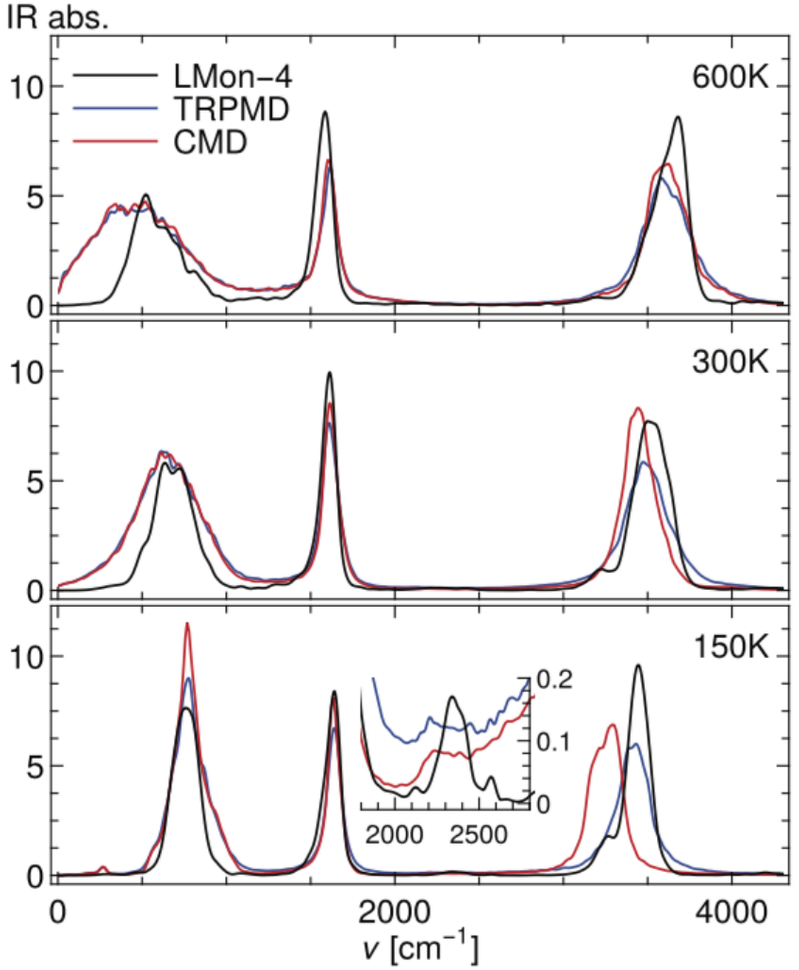


THE JOURNAL OF CHEMICAL PHYSICS **141**, 181101 (2014)

Communication: On the consistency of approximate quantum dynamics simulation methods for vibrational spectra in the condensed phase

Mariana Rossi,[1] Hanchao Liu,[2] Francesco Paesani,[3] Joel Bowman,[2] and Michele Ceriotti[4]
[1]*Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom*
[2]*Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322, USA*
[3]*Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0314, USA*
[4]*Laboratory of Computational Science and Modeling, IMX, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*

(Received 26 September 2014; accepted 27 October 2014; published online 10 November 2014)



Frontiers in PIMD

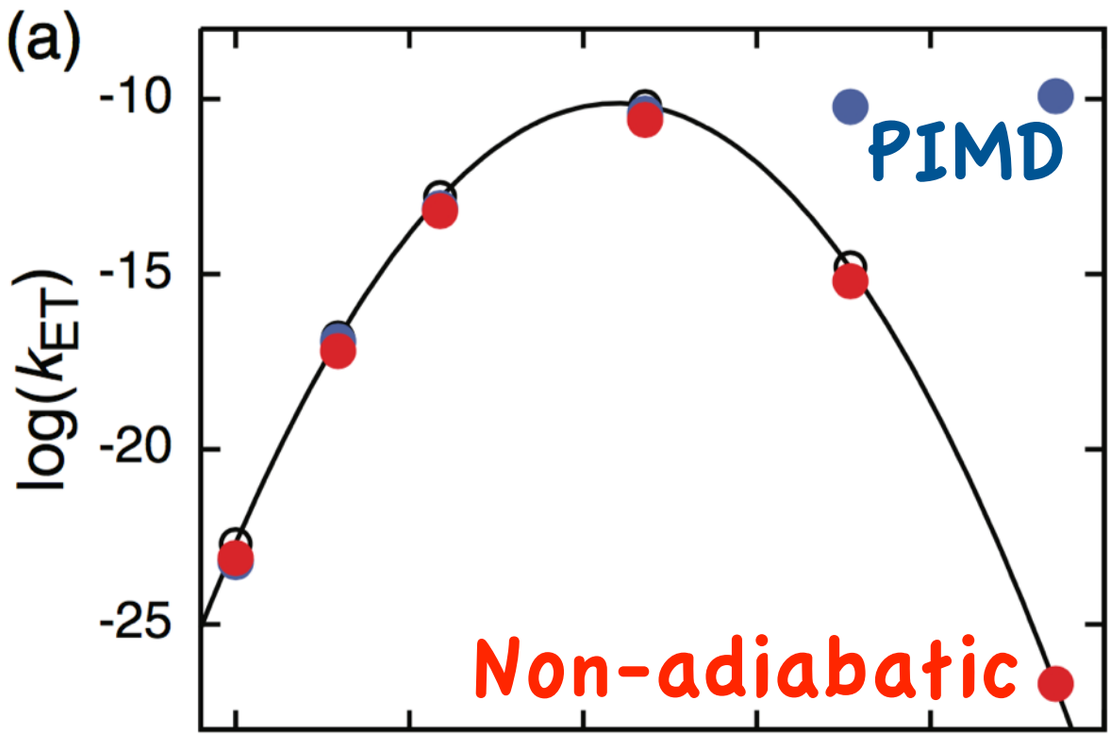
- **Non-adiabatic dynamics and excited states**

THE JOURNAL OF CHEMICAL PHYSICS **140**, 064103 (2014)

Kinetically constrained ring-polymer molecular dynamics for non-adiabatic chemical reactions

Artur R. Menzeleev, Franziska Bell, and Thomas F. Miller III[a)]
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

(Received 20 November 2013; accepted 21 January 2014; published online 11 February 2014)



Frontiers in PIMD

✤ Non-adiabatic dynamics and excited states

THE JOURNAL OF CHEMICAL PHYSICS **140**, 064103 (2014)

Kinetically constrained ring-polymer molecular dynamics for non-adiabatic chemical reactions

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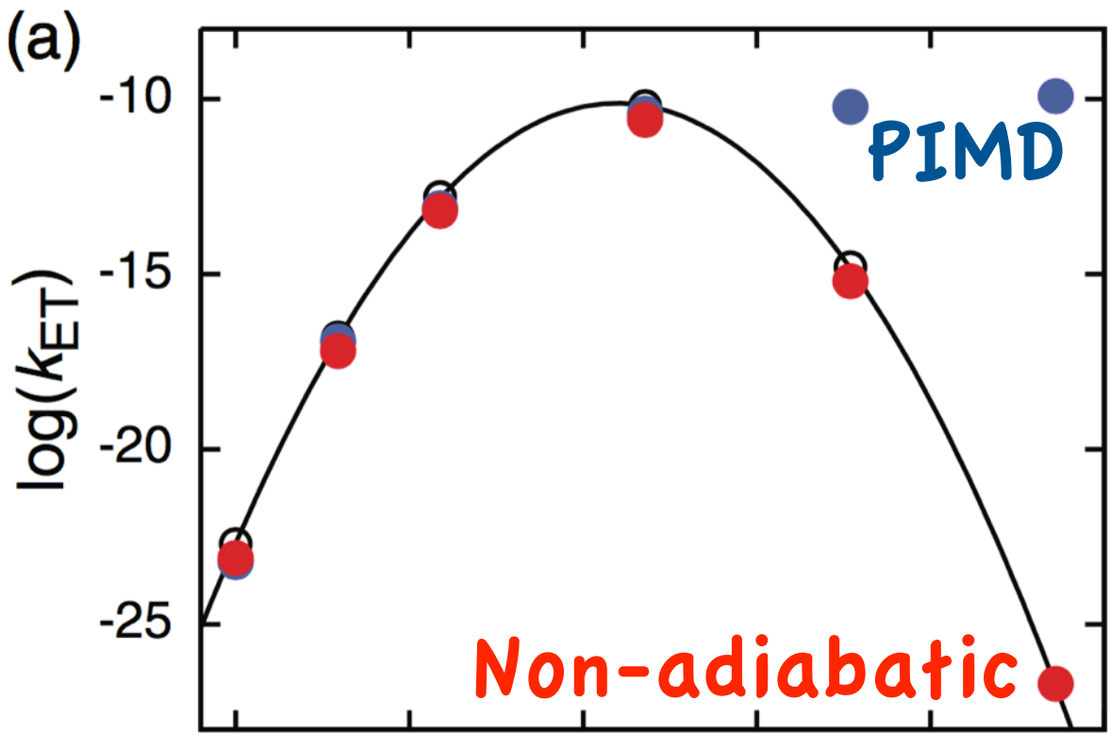


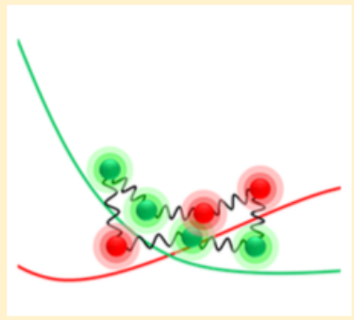
Simulating Excited State Dynamics in Systems with Multiple Avoided Crossings Using Mapping Variable Ring Polymer Molecular Dynamics

Jessica R. Duke and Nandini Ananth*

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

Supporting Information

ABSTRACT: Mapping variable ring polymer molecular dynamics (MV-RPMD) is an approximate quantum dynamics method based on imaginary-time path integrals for simulating electronically nonadiabatic photochemical processes. By employing a mapping protocol to transform from a discrete electronic state basis to continuous Cartesian phase-space variables, the method captures electronic state transitions coupled to nuclear motion using only classical MD trajectories. In this work, we extend the applicability of MV-RPMD to simulations of photoinduced excited electronic state dynamics in nonadiabatic systems with multiple avoided crossings. We achieve this by deriving a new electronic state population estimator in the phase space of electronic variables that is exact at equilibrium and numerically accurate in real time. Further, we introduce an efficient constraint protocol to initialize an MV-RPMD simulation to a particular electronic state. We numerically demonstrate the accuracy of this estimator and constraint technique in describing electronic state dynamics from an initial nonequilibrium state in six model systems, three of which describe photodissociation.

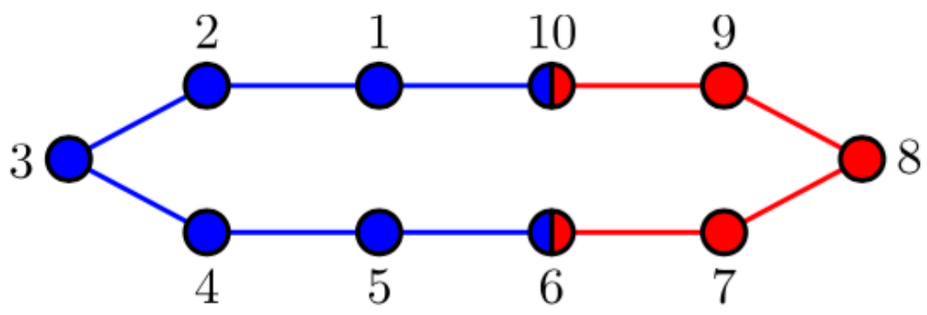


THE JOURNAL OF CHEMICAL PHYSICS **143**, 134116 (2015)

Ring-polymer instanton theory of electron transfer in the nonadiabatic limit

Jeremy O. Richardson[a)]
Institut für Theoretische Physik und Interdisziplinäres Zentrum für Molekulare Materialien, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Staudtstraße 7/B2, 91058 Erlangen, Germany

(Received 19 August 2015; accepted 23 September 2015; published online 7 October 2015)



Frontiers in PIMD

- **Thermostatting (colored noise)**
- **Ring-Polymer Contraction**
- **Quantum-based enhanced sampling techniques**
- **And more…**

JCTC Journal of Chemical Theory and Computation

Colored-Noise Thermostats à la Carte

Michele Ceriotti,*,† Giovanni Bussi,‡ and Michele Parrinello†

Computational Science, Department of Chemistry and Applied Biosciences, ETH Zürich, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland and Università di Modena e Reggio Emilia and INFM-CNR-S3, via Campi 213/A, 41100 Modena, Italy

JCTC Journal of Chemical Theory and Computation Article pubs.acs.org/JCTC

Path Integral Metadynamics

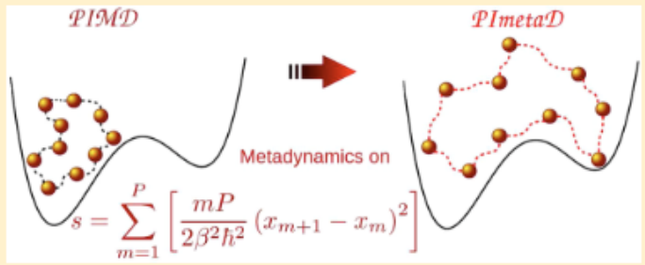
Ruge Quhe,†,‡ Marco Nava,*,† Pratyush Tiwary,† and Michele Parrinello*,†

†Department of Chemistry and Applied Biosciences, ETH Zurich, and Facoltà di Informatica, Istituto di Scienze Computazionali, Università della Svizzera Italiana, Via G. Buffi 13, 6900 Lugano, Switzerland

‡State Key Laboratory of Mesoscopic Physics, Department of Physics and Academy for Advanced Interdisciplinary Studies, Peking University, Beijing 100871, P. R. China

Supporting Information

ABSTRACT: We develop a new efficient approach for the simulation of static properties of quantum systems using path integral molecular dynamics in combination with metadynamics. We use the isomorphism between a quantum system and a classical one in which a quantum particle is mapped into a ring polymer. A history dependent biasing potential is built as a function of the elastic energy of the isomorphic polymer. This enhances fluctuations in the shape and size of the necklace in a controllable manner and allows escaping deep energy minima in a limited computer time. In this way, we are able to sample high free energy regions and cross barriers, which would otherwise be insurmountable with unbiased methods. This substantially improves the ability of finding the global free energy minimum as well as exploring other metastable states. The performance of the new technique is demonstrated by illustrative applications on model potentials of varying complexity.



Relation to CCDM

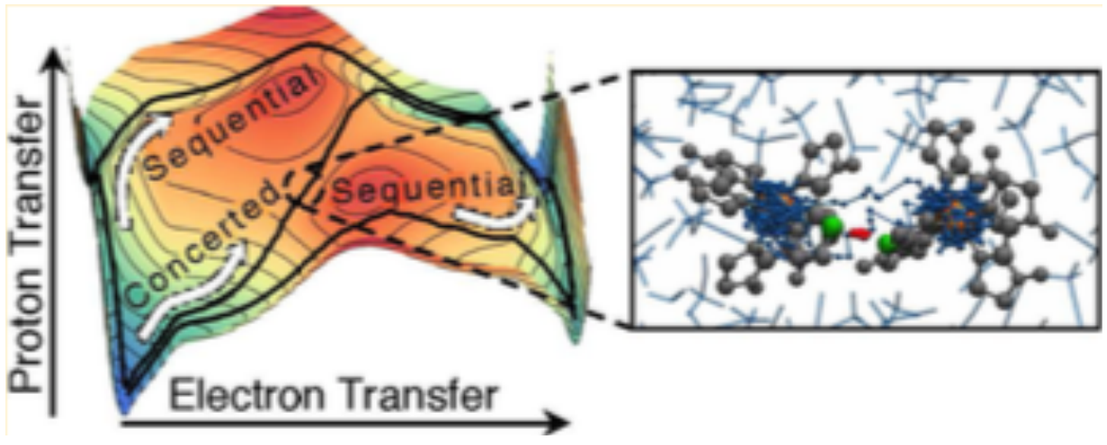
- **Proton-Coupled Electron Transfer in Water Splitting**


Inorganic Chemistry
Article
pubs.acs.org/IC

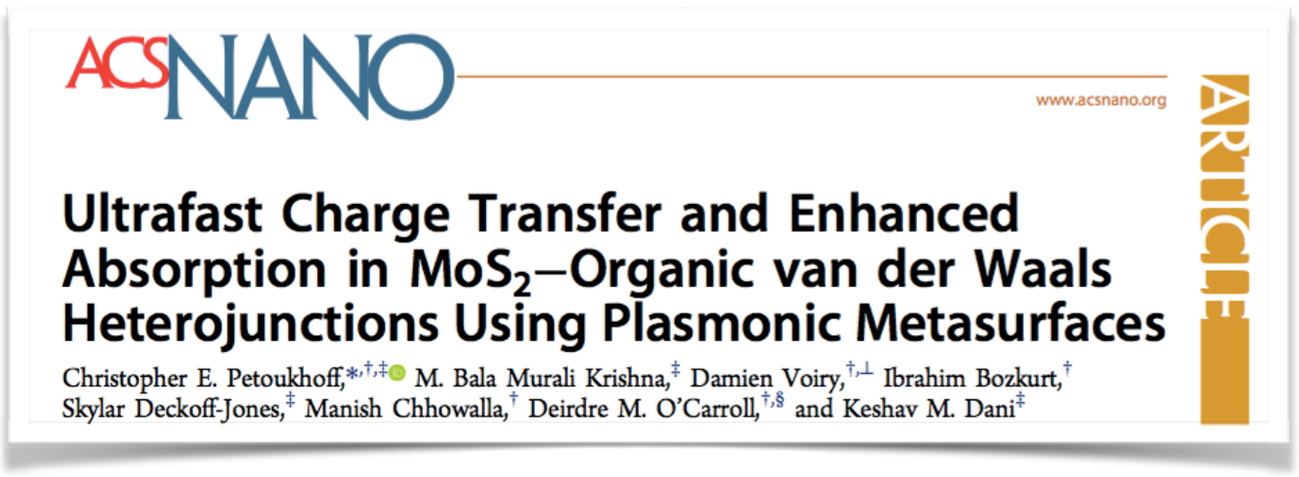
Tipping the Balance between Concerted versus Sequential Proton-Coupled Electron Transfer

Joshua S. Kretchmer and Thomas F. Miller III*

Department of Chemistry and ChemicalEngineering, California Institute of Technology, Pasadena, California 91125, United States



- **Layered organic-inorganic hybrids**


ACSNANO
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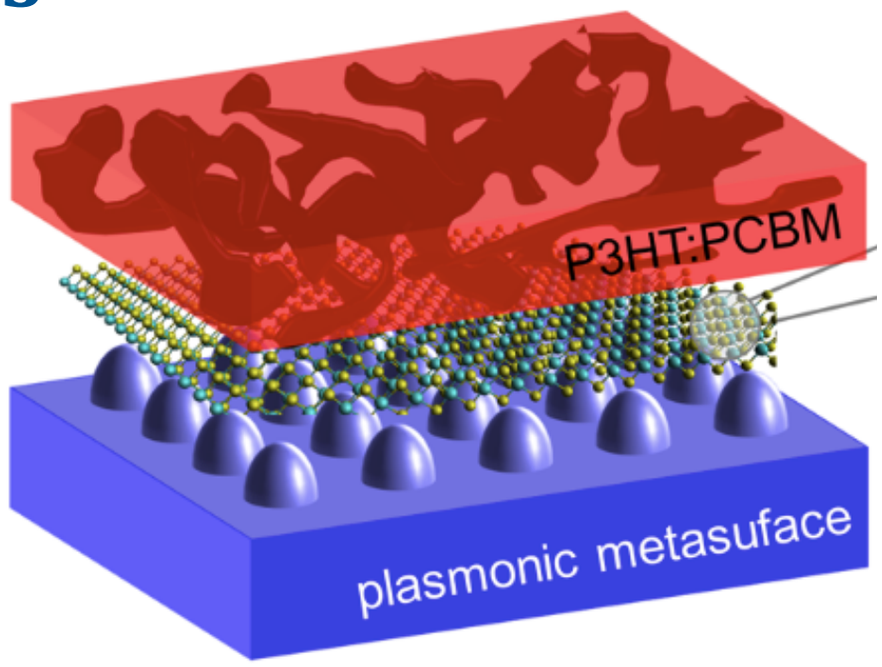
ARTICLE

Ultrafast Charge Transfer and Enhanced Absorption in MoS_2–Organic van der Waals Heterojunctions Using Plasmonic Metasurfaces

Christopher E. Petoukhoff,*,†,‡ M. Bala Murali Krishna,‡ Damien Voiry,†,⊥ Ibrahim Bozkurt,† Skylar Deckoff-Jones,‡ Manish Chhowalla,† Deirdre M. O'Carroll,†,§ and Keshav M. Dani‡

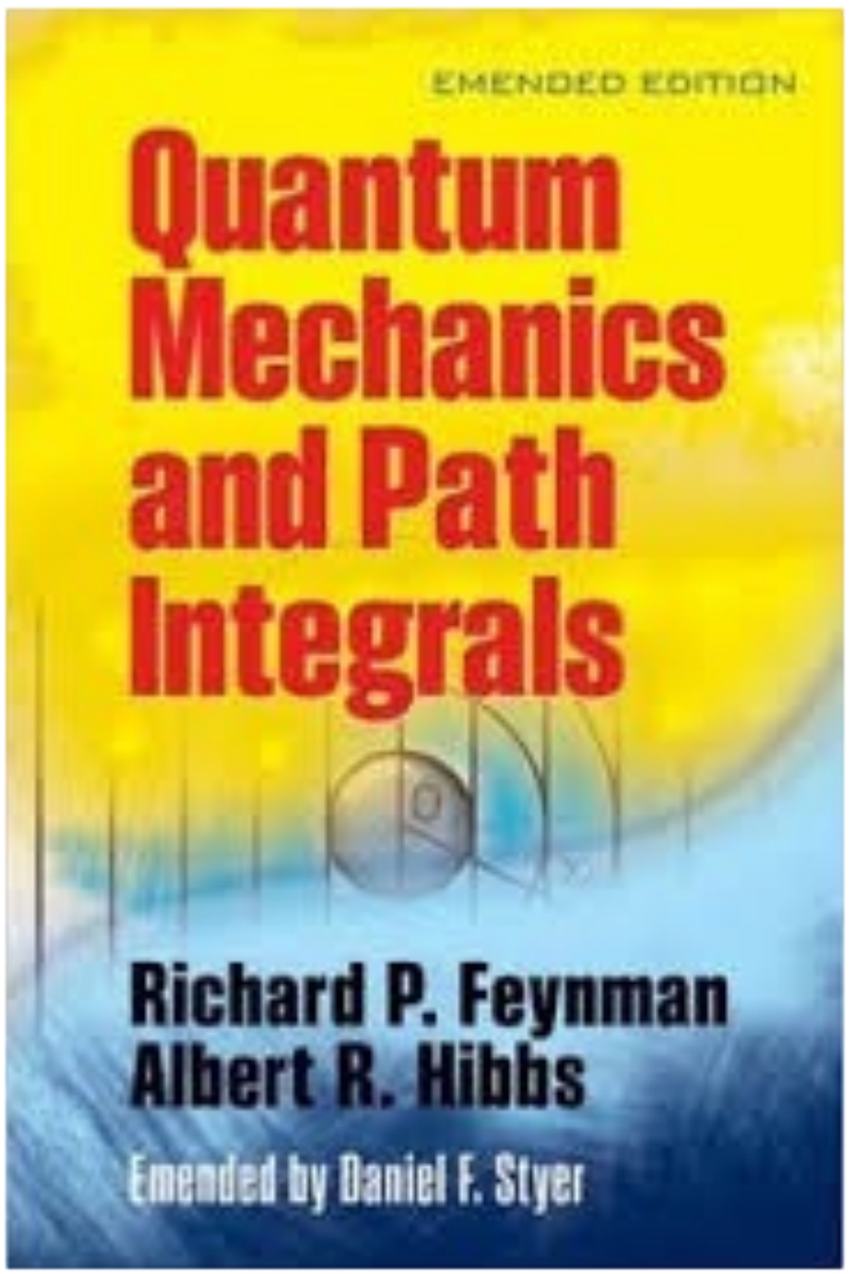


- ***Quantum effects at large length and time scales***

Goals of this Lecture

- Introduction to molecular dynamics simulations
- Quantum particles can be simulated using classical mechanics through **path integral** formulation
- **Useful in a wide variety of processes**
- Can use these approaches easily with i-PI package

Good Resources



Ring-Polymer Molecular Dynamics: Quantum Effects in Chemical Dynamics from Classical Trajectories in an Extended Phase Space

Scott Habershon,[1] David E. Manolopoulos,[2] Thomas E. Markland,[3] and Thomas F. Miller III[4]

[1]Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom; email: S.Habershon@warwick.ac.uk

[2]Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford OX1 3QZ, United Kingdom; email: david.manolopoulos@chem.ox.ac.uk

[3]Department of Chemistry, Stanford University, Stanford, California 94305; email: tmarkland@stanford.edu

[4]Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125; email: tfm@caltech.edu

Modeling the Quantum Nature of Atomic Nuclei by Imaginary Time Path Integrals and Colored Noise

Michele Ceriotti

Laboratory of Computational Science and Modeling, IMX,
École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

E-mail: michele.ceriotti@epfl.ch

Good Resources

Computer Physics Reports 7 (1988) 147–166
North-Holland, Amsterdam

APPLICATION OF PATH INTEGRAL SIMULATIONS TO THE STUDY OF ELECTRON SOLVATION IN POLAR FLUIDS

Michiel SPRIK and Michael L. KLEIN

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA

Ann. Rev. Phys. Chem. 1986. 37 : 401–24

ON THE SIMULATION OF QUANTUM SYSTEMS: PATH INTEGRAL METHODS

Bruce J. Berne

Department of Chemistry, Columbia University, New York, New York 10027

D. Thirumalai

Institute of Physical Science & Technology, and Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

EXCESS ELECTRONS IN LIQUIDS: Geometrical Perspectives

David Chandler and Kevin Leung

Department of Chemistry, University of California, Berkeley, California 94720

COURSE 4

THEORY OF QUANTUM PROCESSES IN LIQUIDS

DAVID CHANDLER

Department of Chemistry, University of California Berkeley, CA 94720 USA

J. P. Hansen, D. Levesque and J. Zinn-Justin, eds.
Les Houches, Session LI, 1989
Liquides, Cristallisation et Transition Vitreuse/
Liquids, Freezing and Glass Transition

Goals of this Lecture

- Introduction to molecular dynamics simulations
- Quantum particles can be simulated using classical mechanics through **path integral** formulation
- **Useful in a wide variety of processes**
- Can use these approaches easily with i-PI package