Ab-Initio Path-Integral Molecular Dynamics

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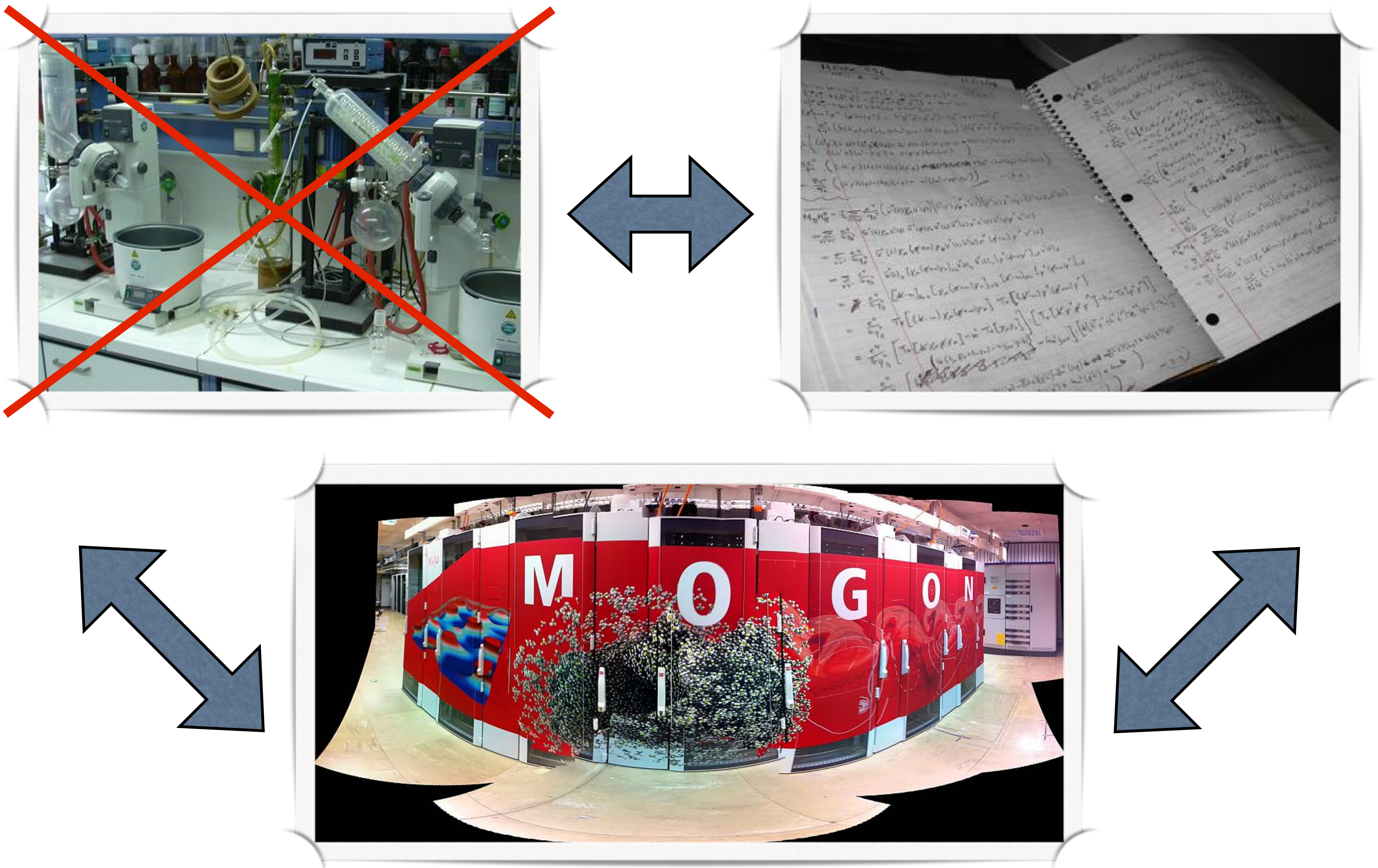
The Virtual Chemistry Lab

The Virtual Chemistry Lab



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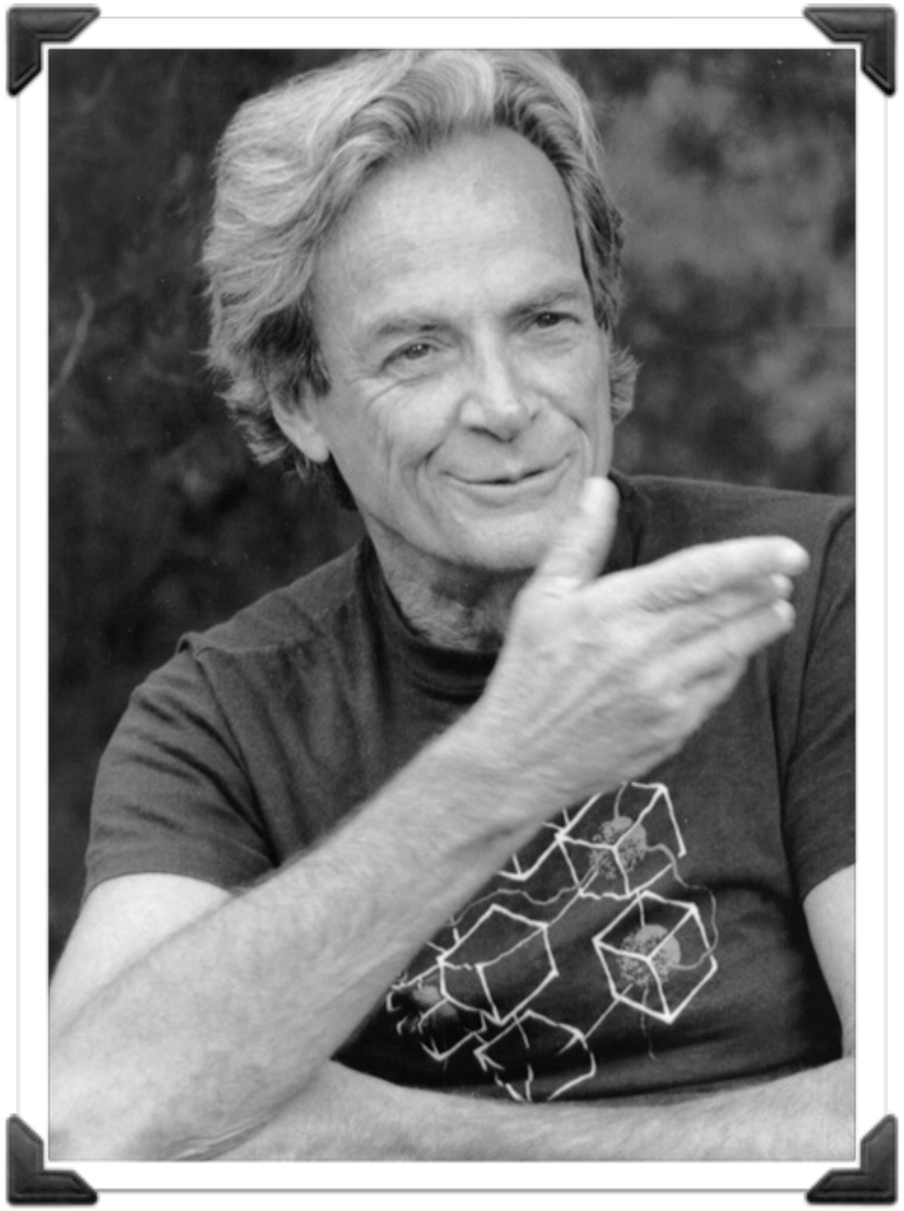
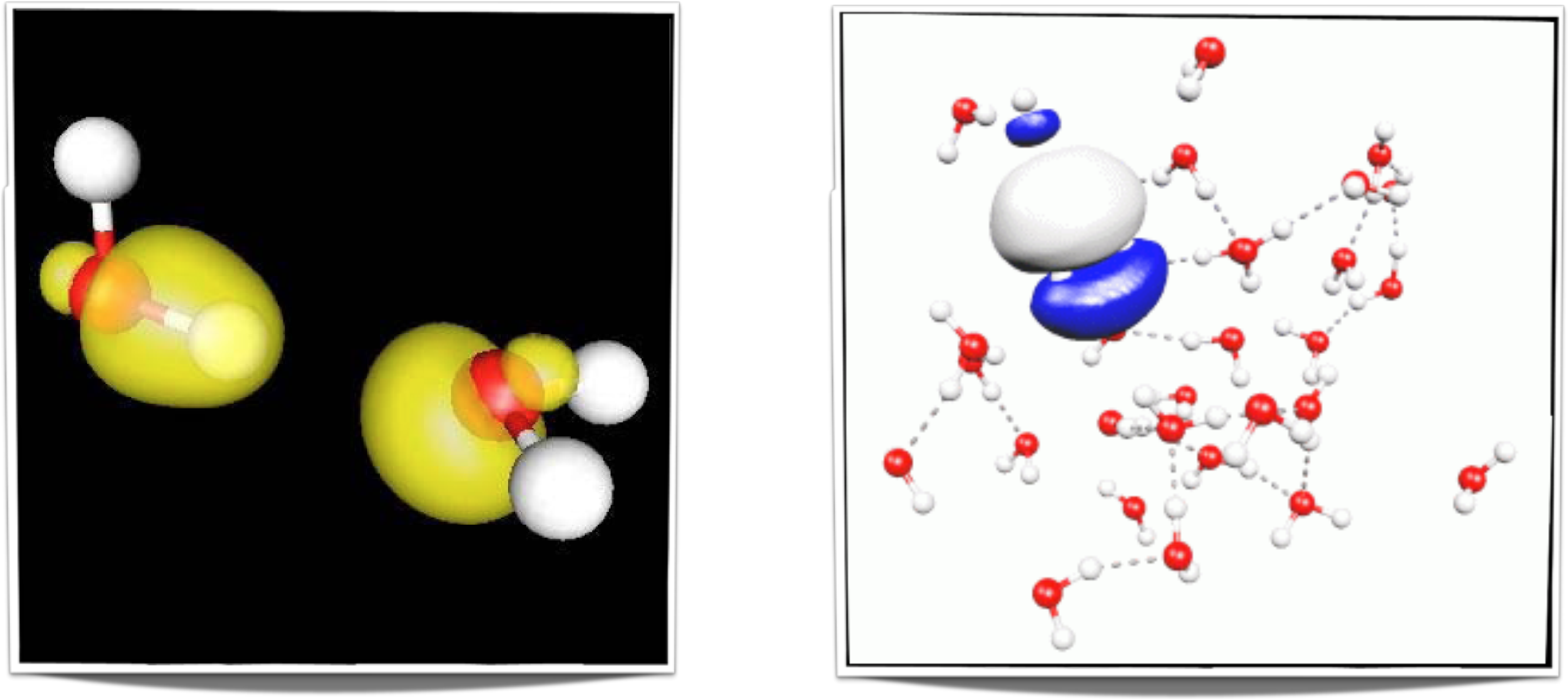


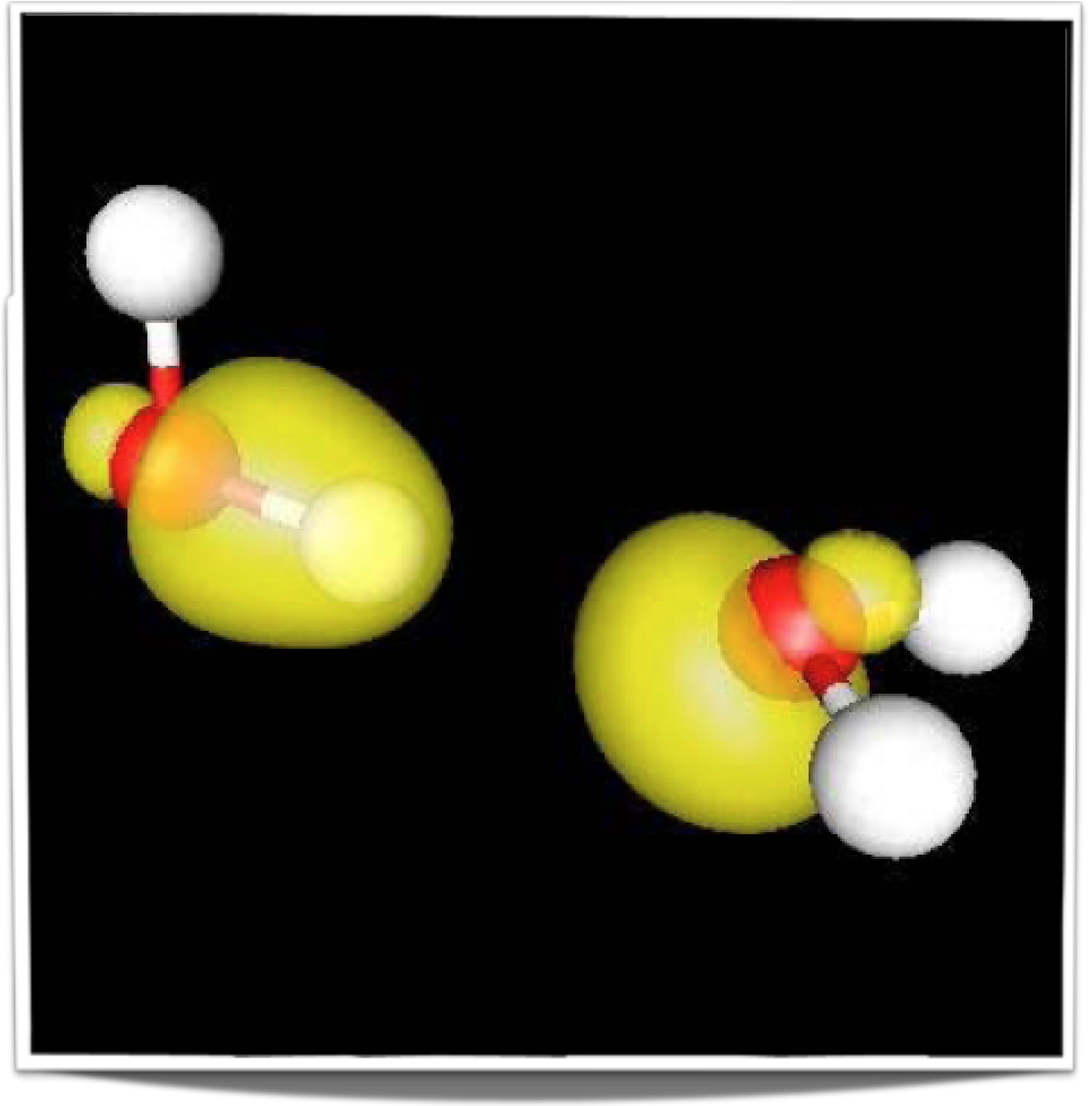
„The most important hypothesis in all of biology, chemistry and physics is that everything is made of atoms, and that everything living things do can be understood in terms of the jigglings and wigglings of atoms“

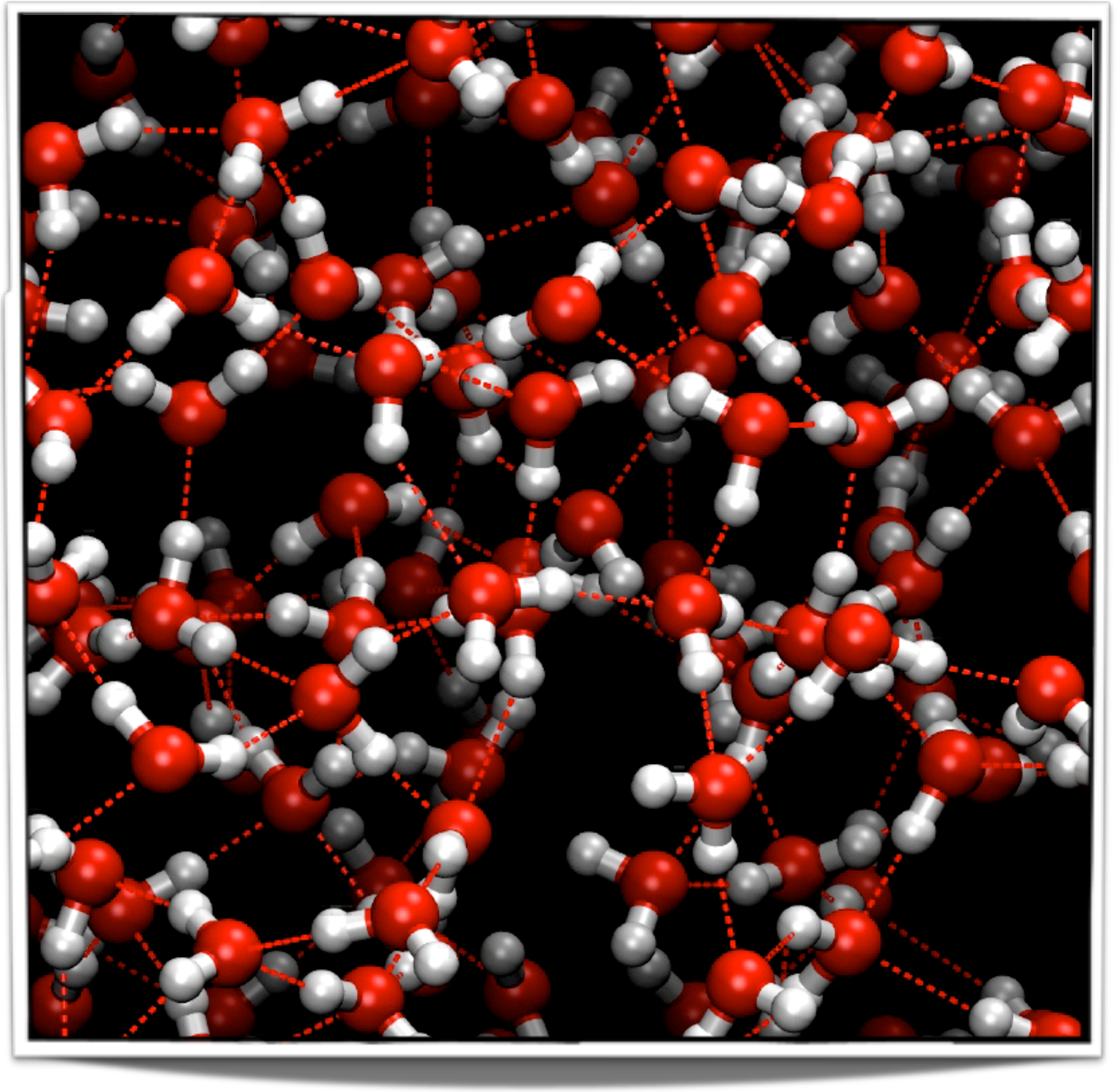
Liquid Water



Quantum mechanical description is essential

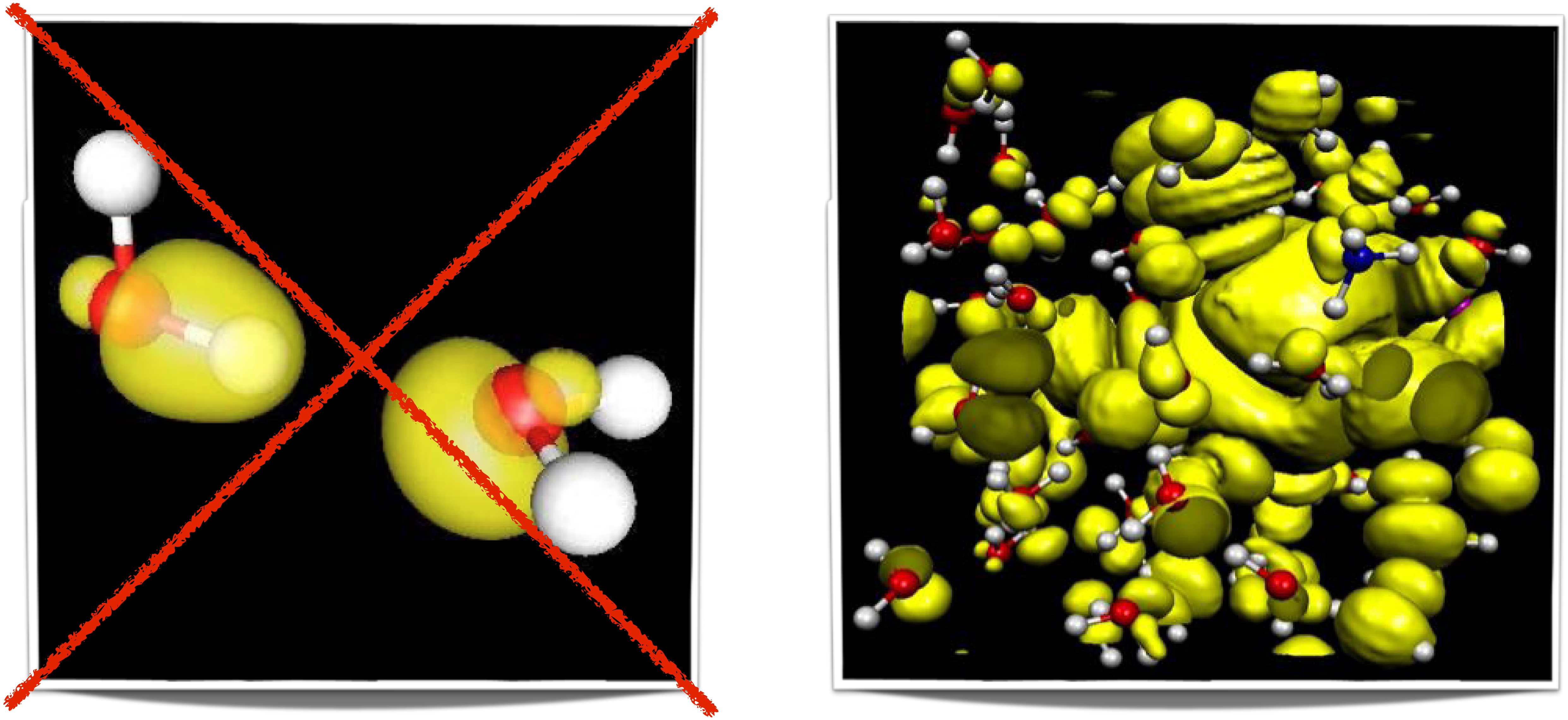
Liquid Water





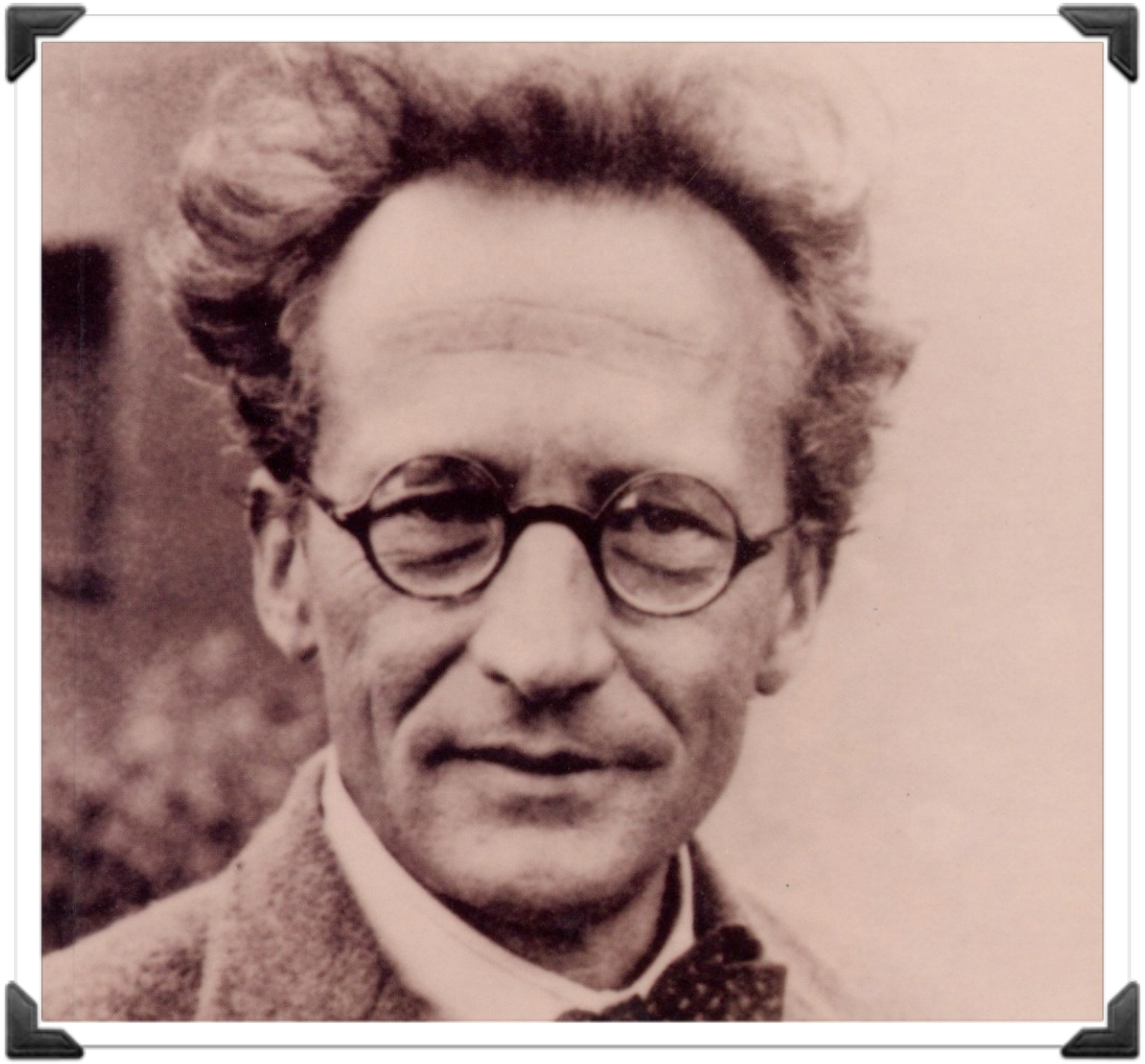
Dynamics is indispensable

Liquid Water

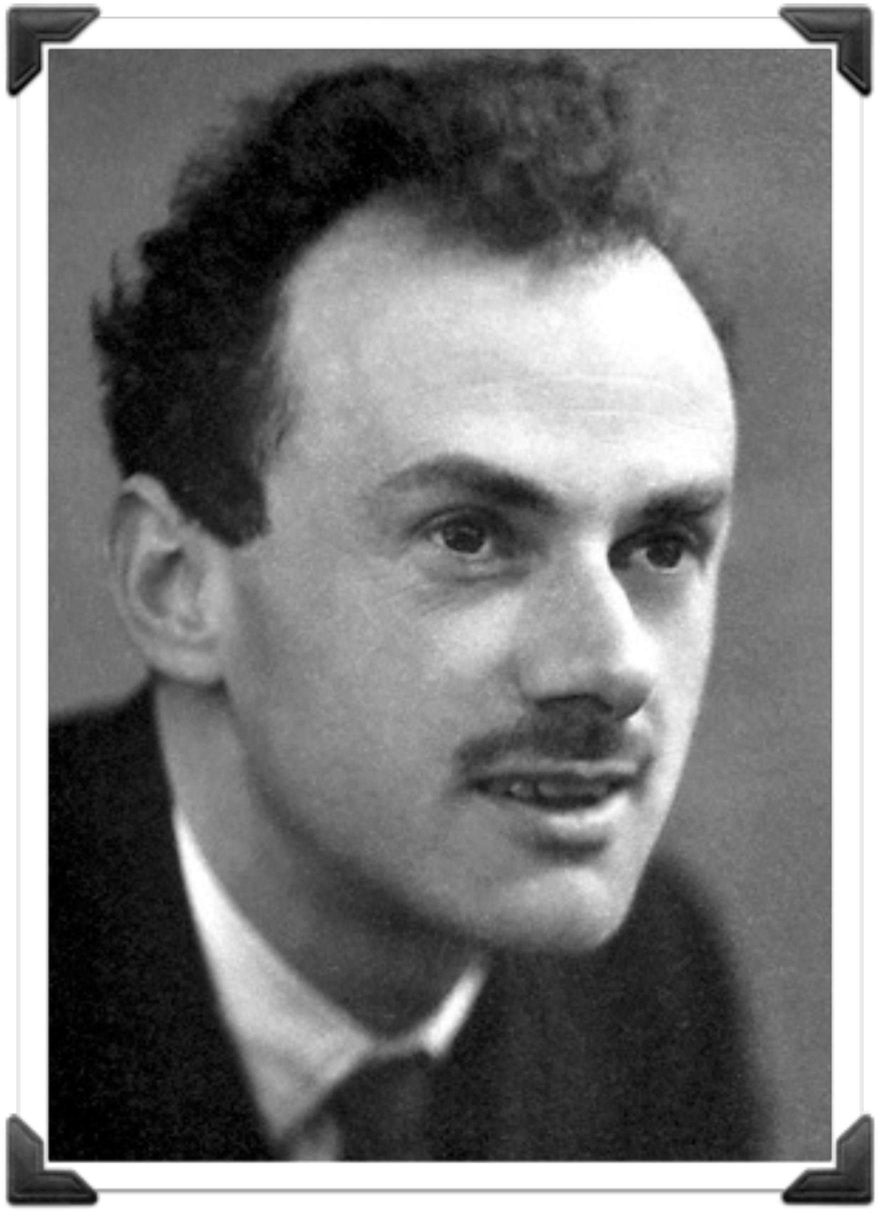


Dynamics & QM on large length and time scales

Schrödinger Equation



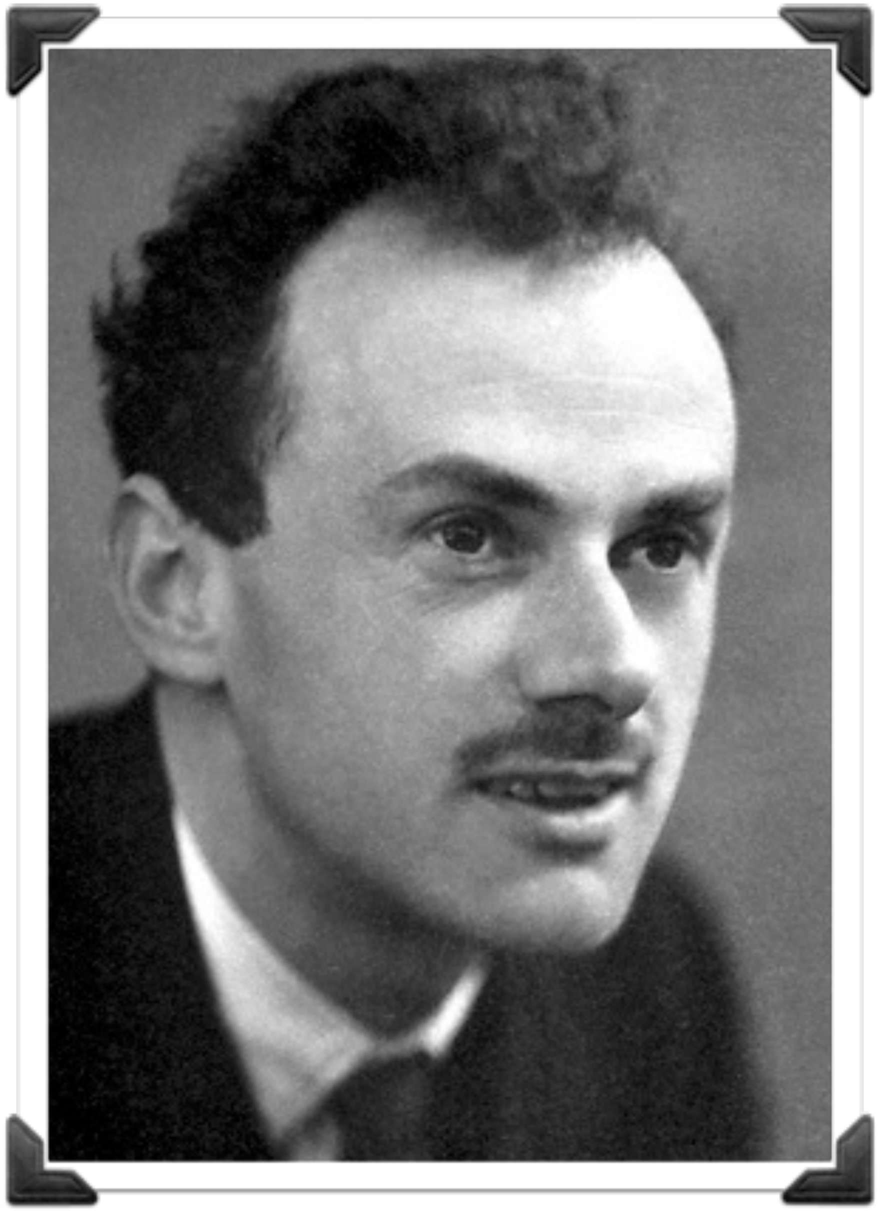
Schrödinger Equation



„The fundamental laws necessary for the mathematical treatment of large parts of physics and **the whole of chemistry are thus fully known** …“

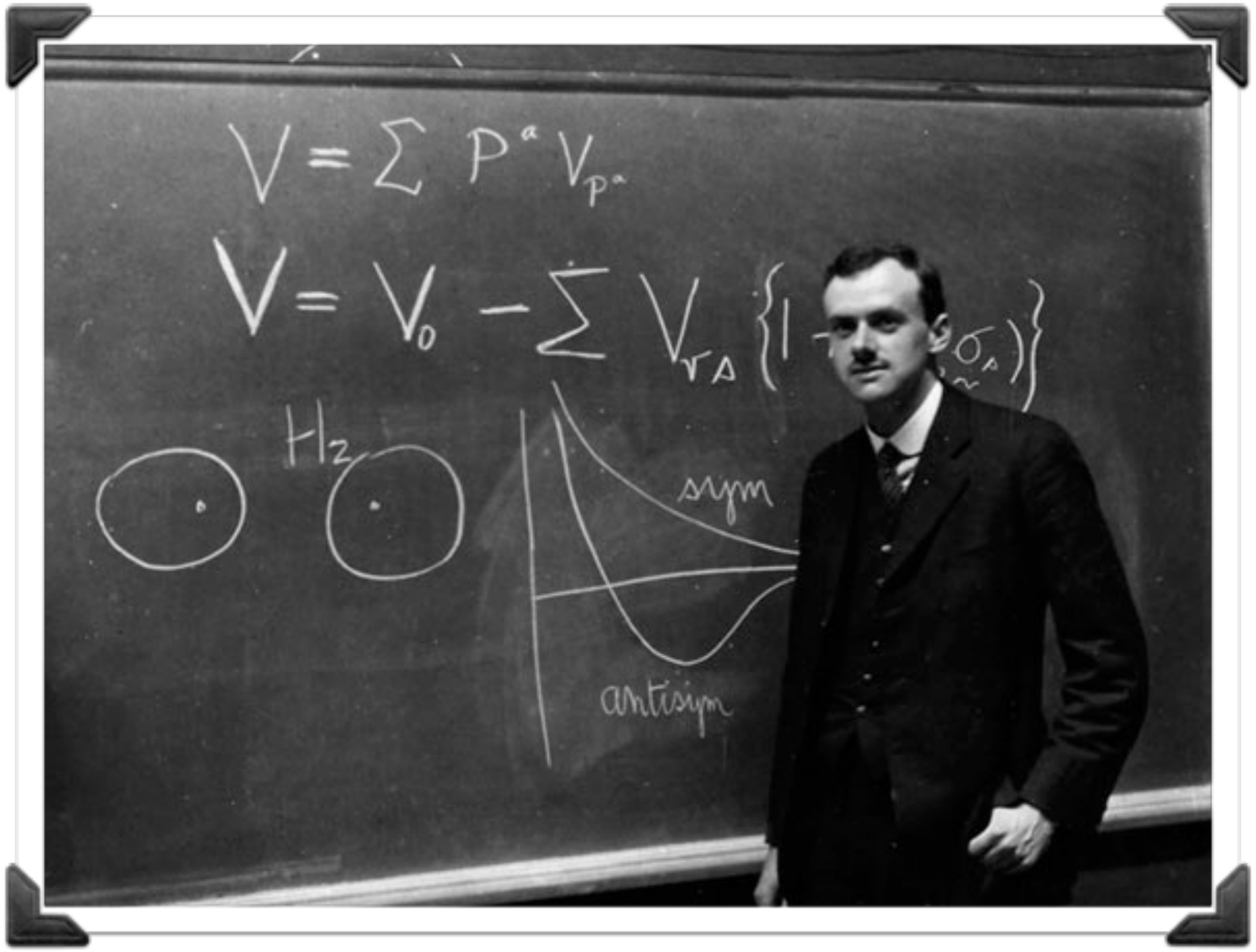
$$\mathcal{H}(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R})$$

Schrödinger Equation



„... the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved“

Schrödinger Equation



„... hence it would be desirable to develop practical approximation schemes for the application of quantum mechanics“

Schrödinger Equation

„Any attempt to use mathematical methods for the investigation of chemical questions must be considered as completely irrational and is strongly opposing the spirit of chemistry. If mathematics will ever occupy a prominent place in chemistry - an absurd idea that fortunately is completely unrealistic - this would lead to a rapid and irreversible decay of this scientific discipline“

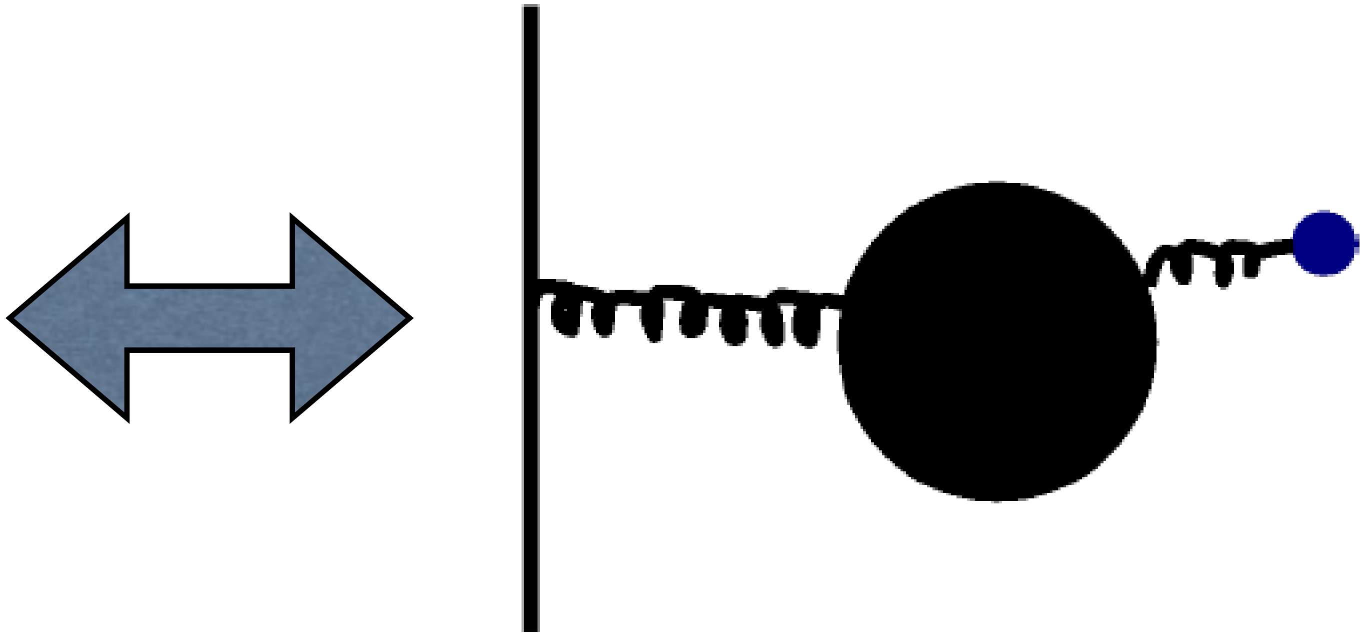
Isidore Marie Auguste
François Xavier Comte
(1798-1857)

Born-Oppenheimer

$$\mathcal{H}(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R}), \text{mit}$$

$$\mathcal{H}(\mathbf{r},\mathbf{R}) = T_e + T_K + V_{ee}(\mathbf{r}) + V_{eK}(\mathbf{r},\mathbf{R}) + V_{KK}(\mathbf{R})$$

$$M_I \approx 1836 m_e$$



$$\Psi(\mathbf{r},\mathbf{R}) \approx \psi(\mathbf{r};\mathbf{R})\chi(\mathbf{R})$$

Born-Oppenheimer

$$\mathcal{H}(\boldsymbol{r},\boldsymbol{R}) = \mathcal{H}_e(\boldsymbol{r};\boldsymbol{R}) + \mathcal{H}_K(\boldsymbol{R}) \ \ \& \ \ \nabla^2_{\boldsymbol{R}_I}\chi(\boldsymbol{R}) >> \nabla^2_{\boldsymbol{R}_I}\psi(\boldsymbol{r};\boldsymbol{R})$$

$$\frac{\mathcal{H}_e(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})}{\psi(\boldsymbol{r};\boldsymbol{R})} = E - \frac{\mathcal{H}_K(\boldsymbol{R})\chi(\boldsymbol{R})}{\chi(\boldsymbol{R})} = \varepsilon(\boldsymbol{R})$$

$$\mathcal{H}_e(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R}) = \varepsilon(\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})$$

$$\left[\mathcal{H}_K(\boldsymbol{R}) + \varepsilon(\boldsymbol{R})\right]\chi(\boldsymbol{R}) = E\chi(\boldsymbol{R})$$

Born-Oppenheimer

$$\mathcal{H}(\boldsymbol{r},\boldsymbol{R}) = \mathcal{H}_e(\boldsymbol{r};\boldsymbol{R}) + \mathcal{H}_K(\boldsymbol{R}) \;\;\&\;\; \nabla^2_{\boldsymbol{R}_I}\chi(\boldsymbol{R}) >> \nabla^2_{\boldsymbol{R}_I}\psi(\boldsymbol{r};\boldsymbol{R})$$

$$\frac{\mathcal{H}_e(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})}{\psi(\boldsymbol{r};\boldsymbol{R})} = E - \frac{\mathcal{H}_K(\boldsymbol{R})\chi(\boldsymbol{R})}{\chi(\boldsymbol{R})} = \varepsilon(\boldsymbol{R})$$

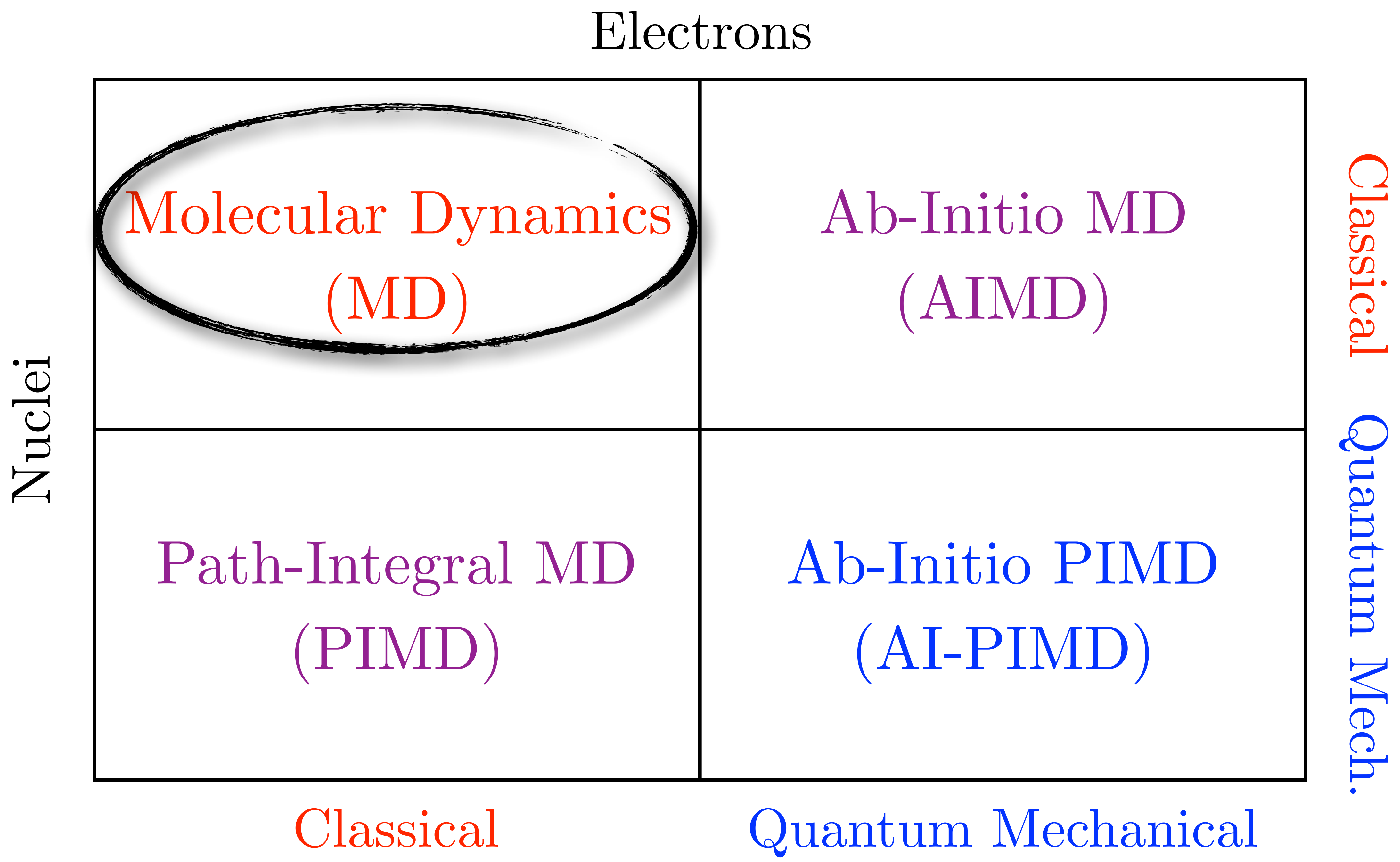
$$\varepsilon(\boldsymbol{R}) + V_{KK}(\boldsymbol{R}) \approx \sum_I v_1(\boldsymbol{R}_I) + \sum_{I<J} v_2(\boldsymbol{R}_I,\boldsymbol{R}_J) + \ldots$$

$$M_I\ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I}\left[\varepsilon(\boldsymbol{R}) + V_{KK}(\boldsymbol{R})\right]$$

Born-Oppenheimer

Electrons

Nuclei	Classical	Quantum Mechanical
Classical	Molecular Dynamics (MD)	Ab-Initio MD (AIMD)
Quantum Mech.	Path-Integral MD (PIMD)	Ab-Initio PIMD (PI-AIMD)



Nuclei \ Electrons	Classical	Quantum Mechanical
Classical	Molecular Dynamics (MD)	Ab-Initio MD (AIMD)
Quantum Mech.	Path-Integral MD (PIMD)	Ab-Initio PIMD (AI-PIMD)

$$\varepsilon(\boldsymbol{R}) + V_{KK}(\boldsymbol{R}) \approx \sum_I v_1(\boldsymbol{R}_I) + \sum_{I<J} v_2(\boldsymbol{R}_I, \boldsymbol{R}_J) + \ldots$$

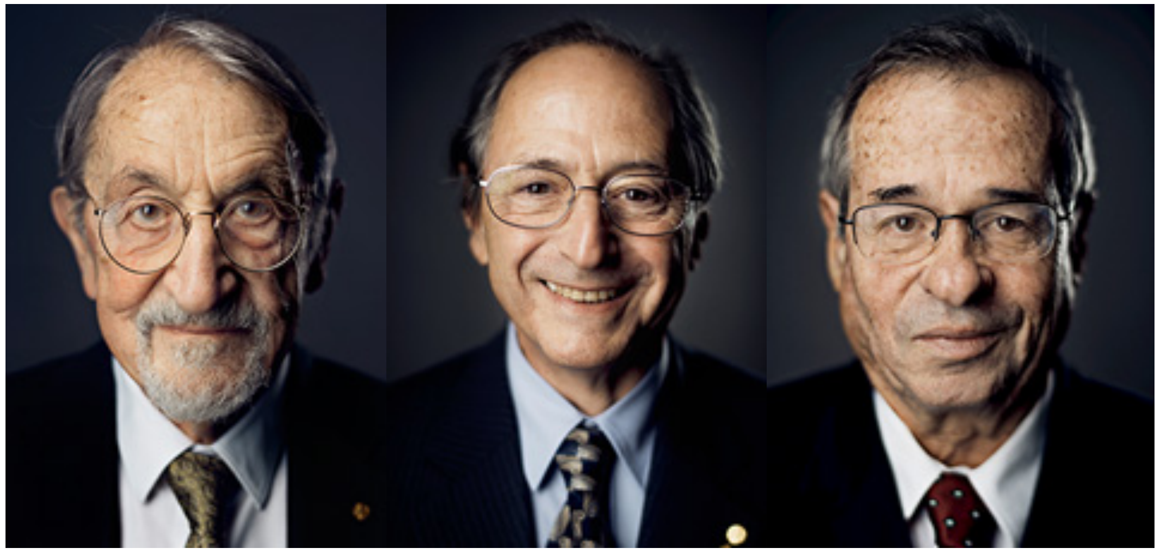
$$M_I \ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I} \left[\varepsilon(\boldsymbol{R}) + V_{KK}(\boldsymbol{R})\right]$$

Molecular Dynamics

"for the development of multiscale models for complex chemical systems".

- protein folding,
- catalysis,
- electron transfer,
- drug design
- ...

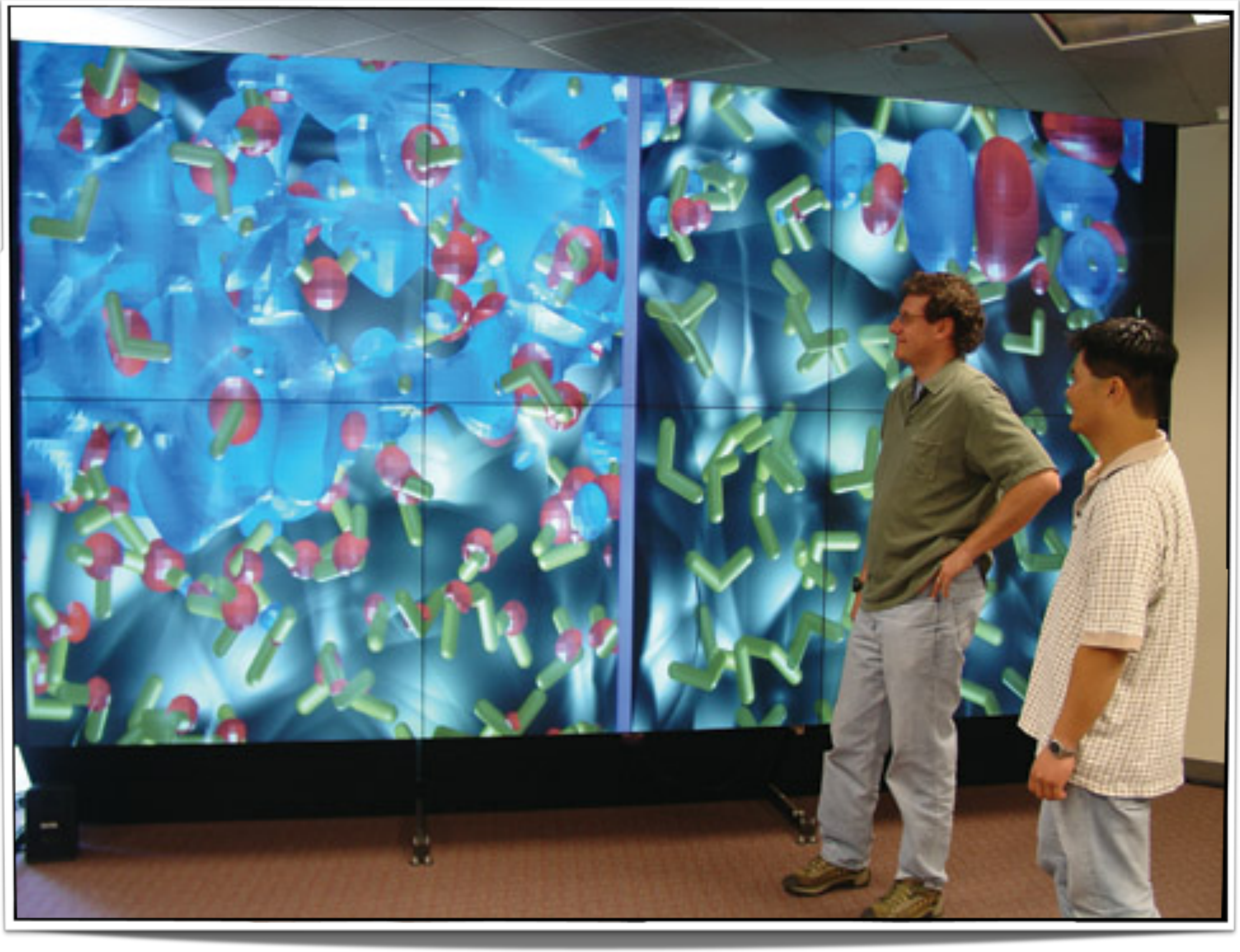
Winners of Nobel Prize in Chemistry 2013



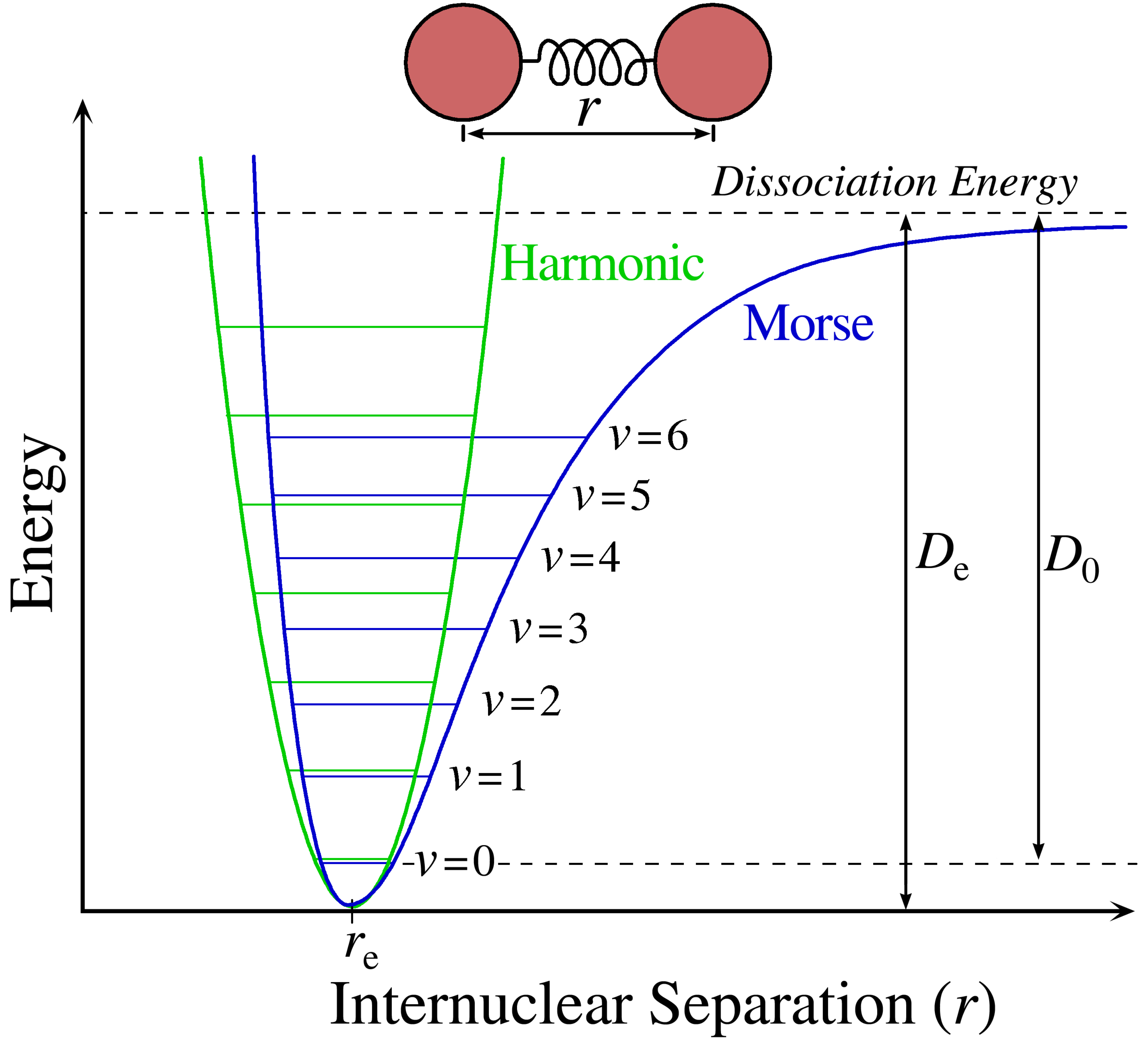
Martin Karplus Michael Levitt Arieh Warshel

1. Alder, B. J. and Wainwright, T. E. *J. Chem. Phys.* **27**, 1208 (1957)
2. Alder, B. J. and Wainwright, T. E. *J. Chem. Phys.* **31**, 459 (1959)
3. Rahman, A. *Phys. Rev.* **A136**, 405 (1964)
4. Stillinger, F. H. and Rahman, A. *J. Chem. Phys.* **60**, 1545 (1974)
5. McCammon, J. A., Gelin, B. R., and Karplus, M. *Nature (Lond.)* **267**, 585 (1977)

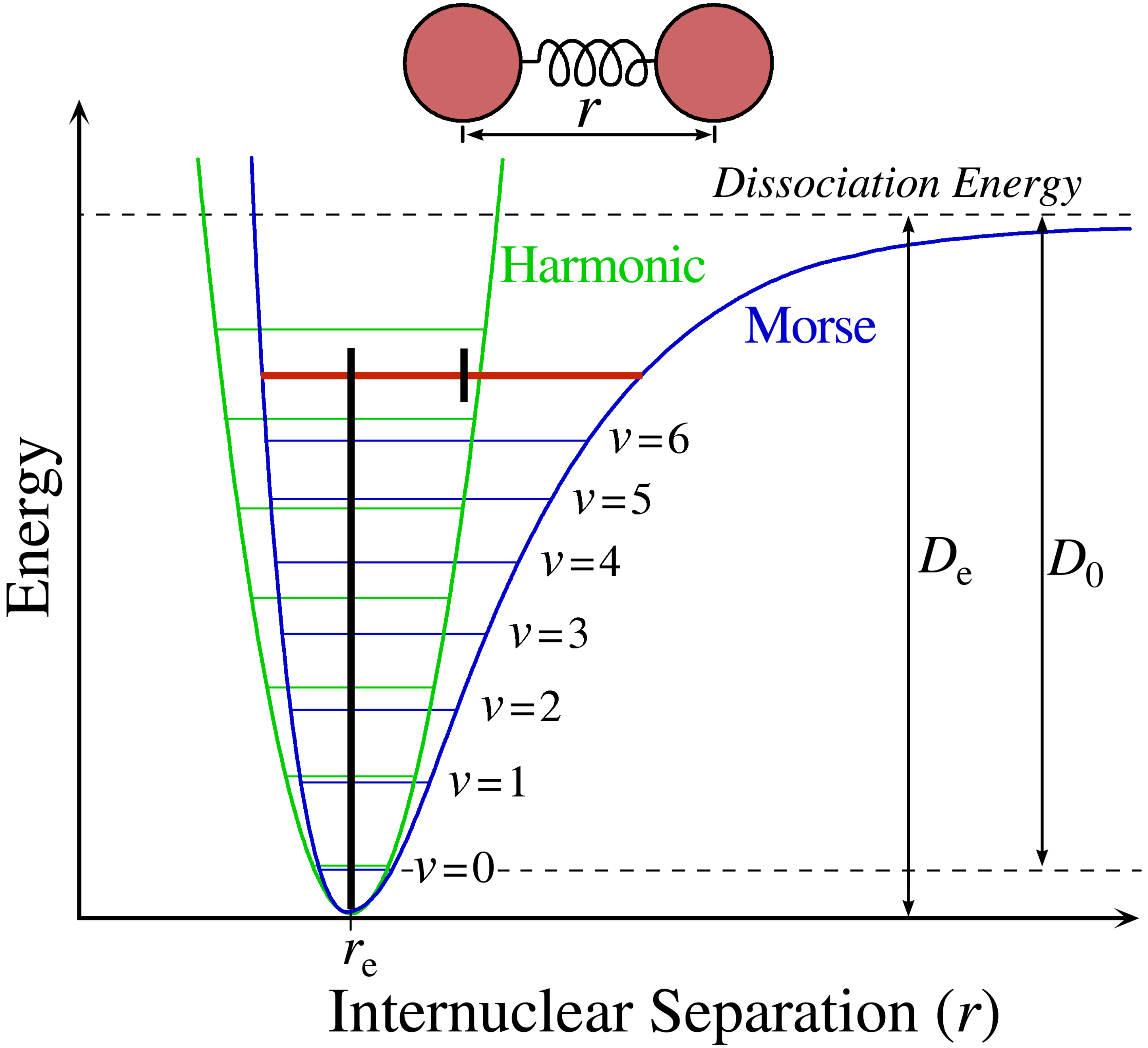
What MD is NOT!



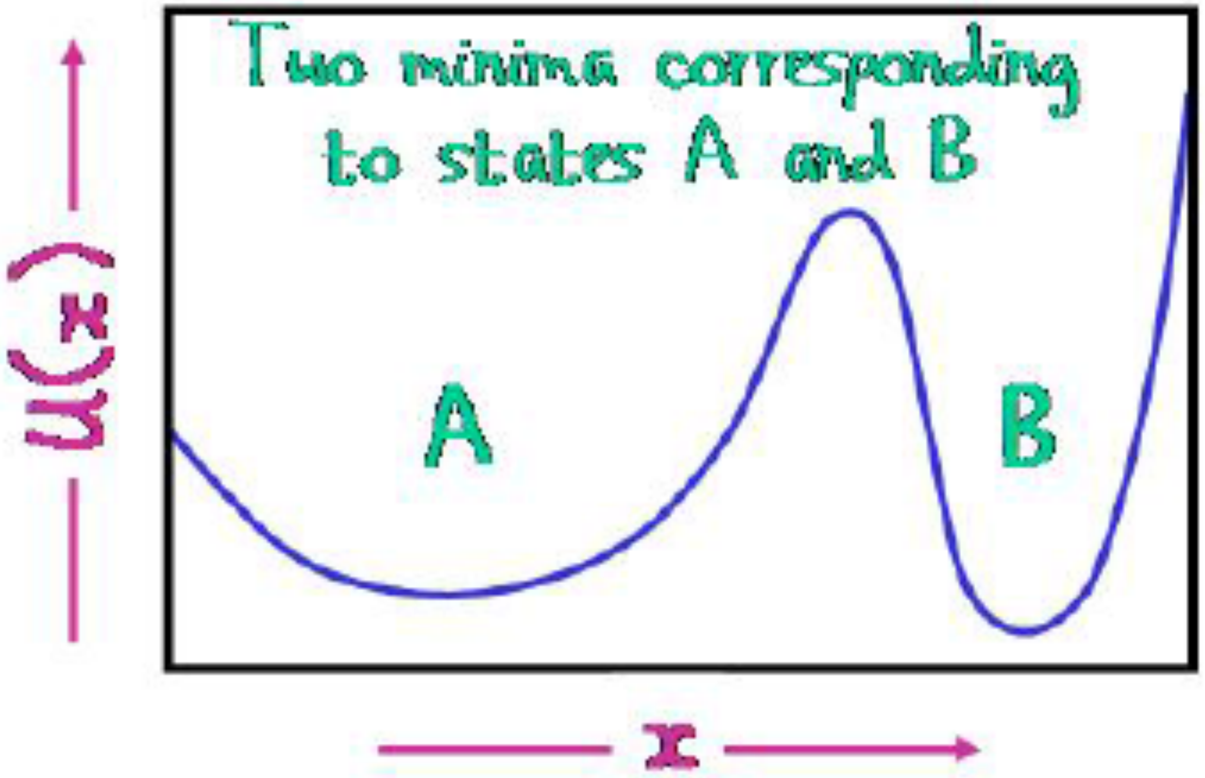
The Essence of MD

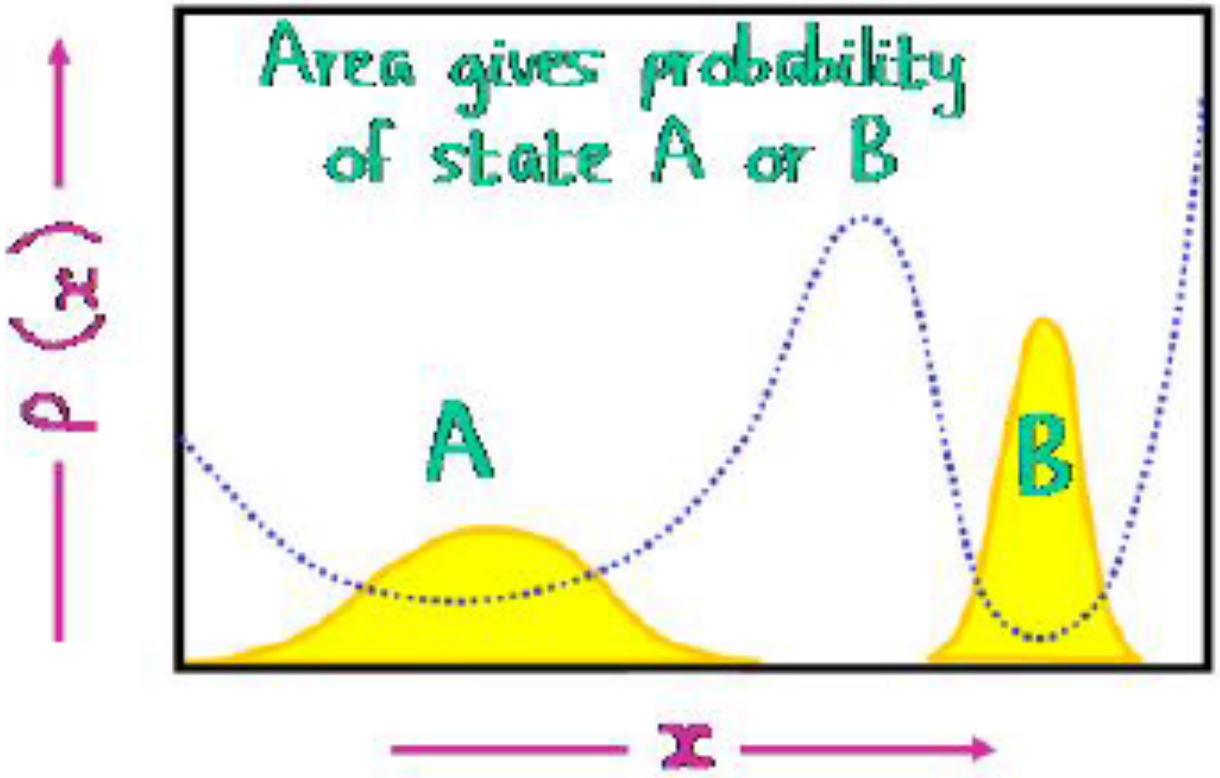


The Essence of MD



Boltzmann Distribution





- Absolute probability P of a system to be in position x:

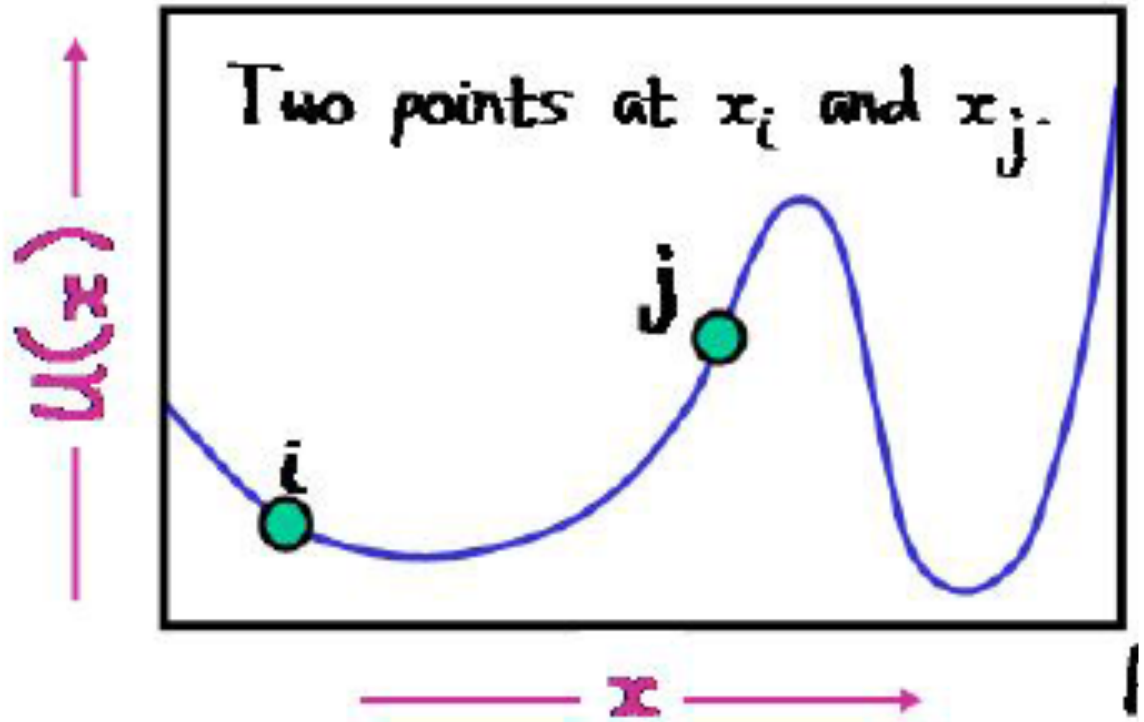
$$P(x) = e^{-\frac{U(x)}{k_B T}} / \mathcal{Z}$$

- U(x): Potential energy of a system at position x
- $\mathcal{Z} = \sum_x e^{-\frac{U(x)}{k_B T}}$: Partition function, so that $\sum_x P(x) = 1$

Relative Probability

- The calculation of $\mathcal{Z} = \sum_x e^{-\frac{U(x)}{k_B T}}$ however, is very demanding!
- Analytic determination of Z is generally impossible!
- Evaluating Z at random points is not accurate enough!
- Approximating Z at nuclear ground-state only valid for T=0 K!
- Calculation of P(x) by MD/MC requires unlimited computer time!
- Computing rel. probability is easy:

$$\begin{aligned} P(x_i) &= e^{-\frac{U(x_i)}{k_b T}} / \mathcal{Z} \\ P(x_j) &= e^{-\frac{U(x_j)}{k_b T}} / \mathcal{Z} \\ \frac{P(x_i)}{P(x_j)} &= e^{-\frac{U(x_i)-U(x_j)}{k_b T}} \end{aligned}$$



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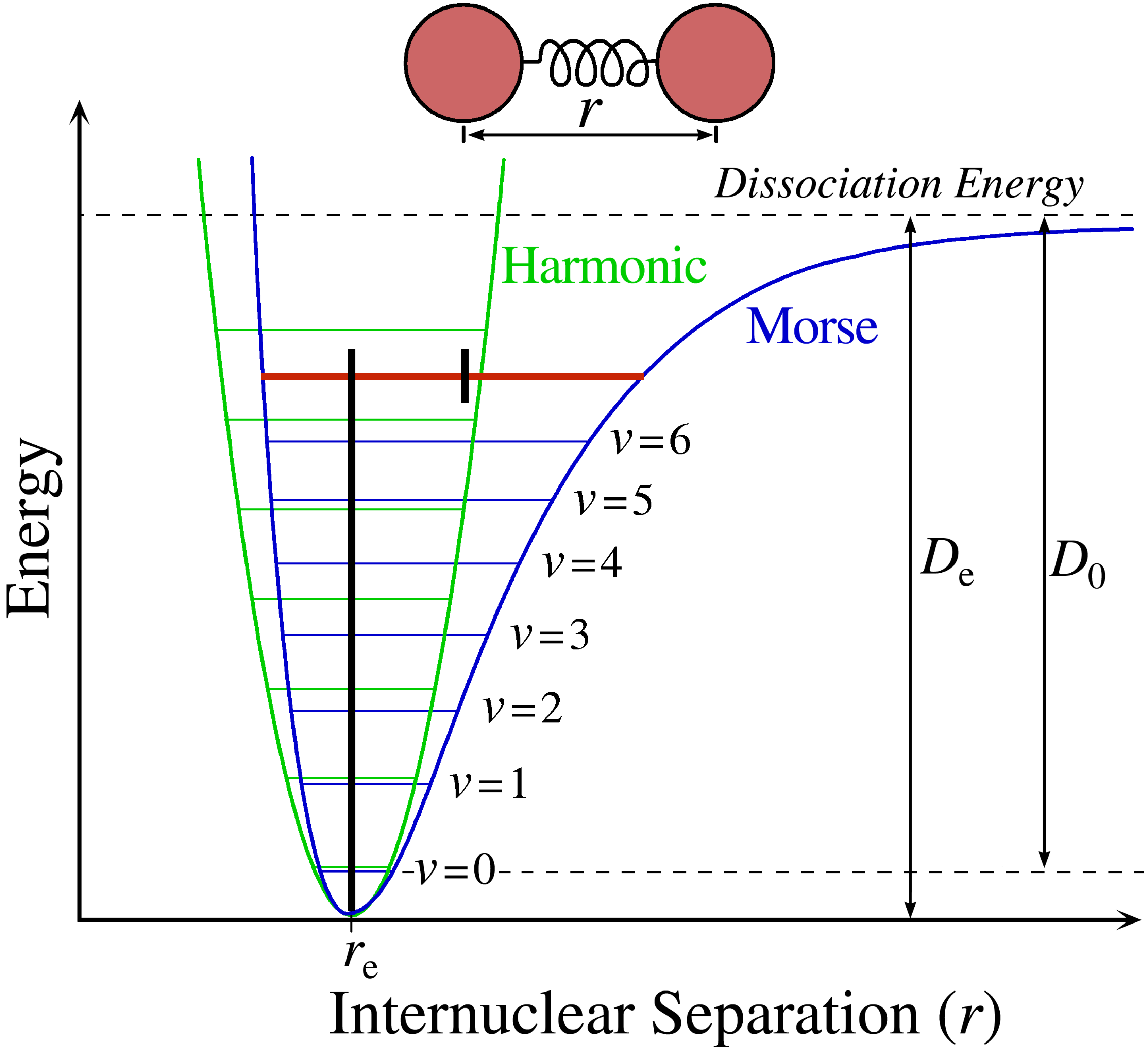
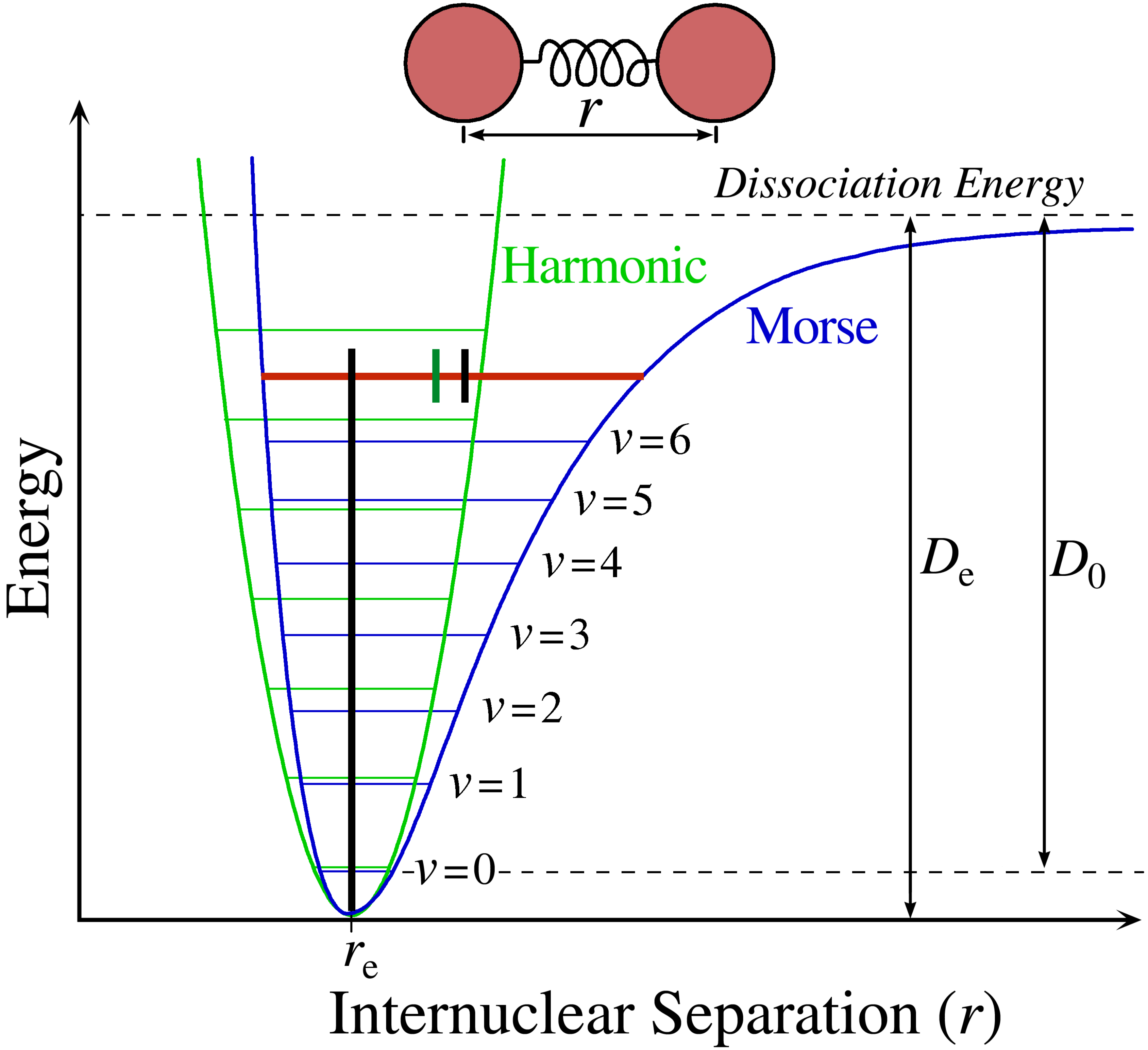


The Essence of MD



Importance Sampling

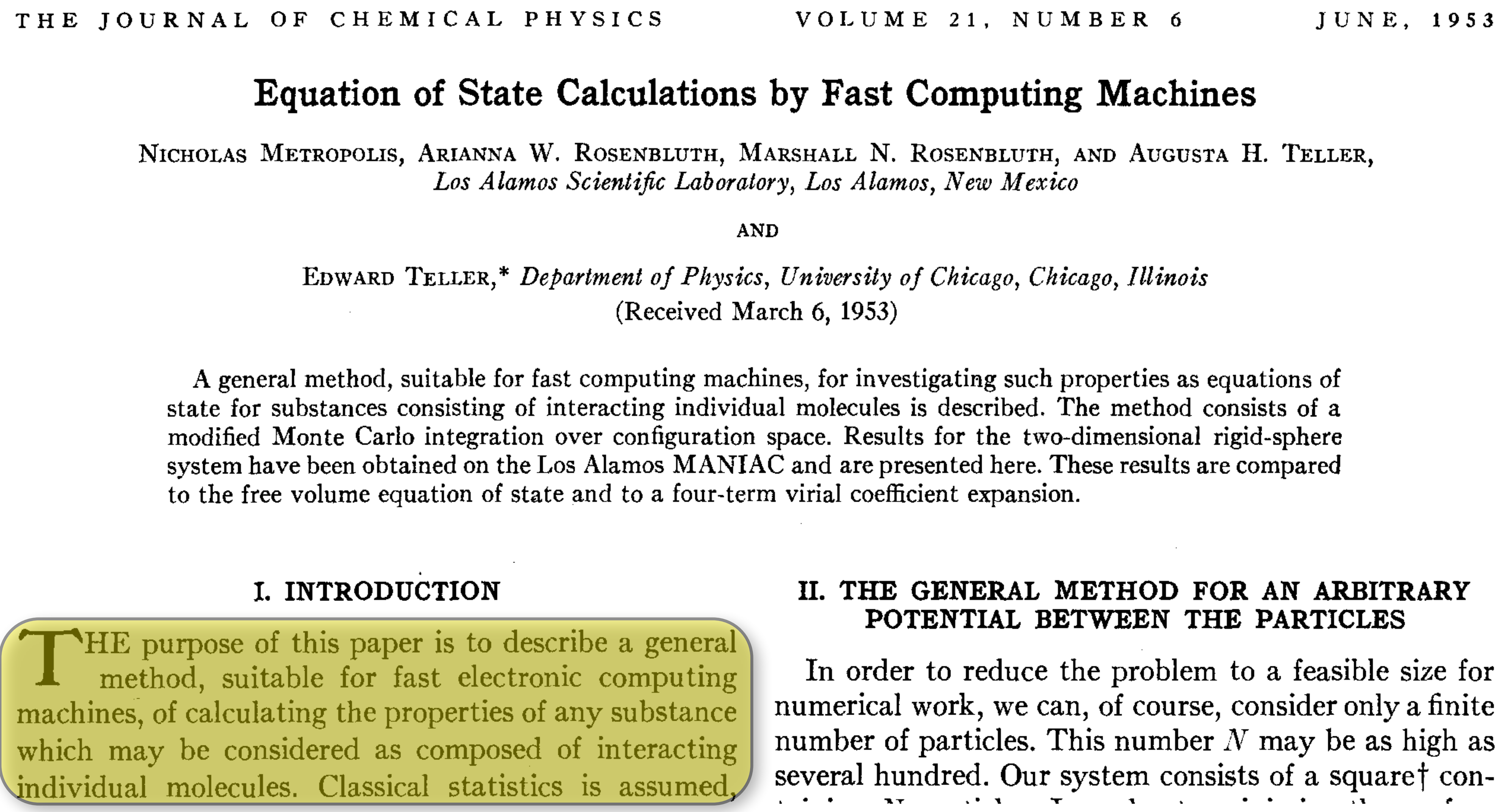
- Till now we were selecting our configurations from a uniform distribution and weight the configurations *a posteriori* by means of the relative Boltzmann probability $\frac{P(x_i)}{P(x_j)} \quad = \quad e^{-\frac{U(x_i)-U(x_j)}{k_b T}}$
- Instead, we would like to sample *a priori* from the Boltzmann distribution and weight the configurations equally, i.e.

$$\rho(x) \quad \propto \quad e^{-\frac{U(x)}{k_B T}}$$

$$\langle A \rangle \quad = \quad \lim_{L\to\infty} \frac{1}{L} \sum_{i=1}^{L} \rho_i(x) A(x_i)$$

- But how? Since knowing the whole $\rho(x)$ corresponds to know Z!

Metropolis Monte Carlo



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 6 JUNE, 1953

Equation of State Calculations by Fast Computing Machines

NICHOLAS METROPOLIS, ARIANNA W. ROSENBLUTH, MARSHALL N. ROSENBLUTH, AND AUGUSTA H. TELLER,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

AND

EDWARD TELLER,* *Department of Physics, University of Chicago, Chicago, Illinois*

(Received March 6, 1953)

A general method, suitable for fast computing machines, for investigating such properties as equations of state for substances consisting of interacting individual molecules is described. The method consists of a modified Monte Carlo integration over configuration space. Results for the two-dimensional rigid-sphere system have been obtained on the Los Alamos MANIAC and are presented here. These results are compared to the free volume equation of state and to a four-term virial coefficient expansion.

I. INTRODUCTION

THE purpose of this paper is to describe a general method, suitable for fast electronic computing machines, of calculating the properties of any substance which may be considered as composed of interacting individual molecules. Classical statistics is assumed,

II. THE GENERAL METHOD FOR AN ARBITRARY POTENTIAL BETWEEN THE PARTICLES

In order to reduce the problem to a feasible size for numerical work, we can, of course, consider only a finite number of particles. This number N may be as high as several hundred. Our system consists of a square† con-

Molecular Dynamics

Time evolution of a classical many-body system in a potential

$$\mathcal{L}(\boldsymbol{R},\dot{\boldsymbol{R}}) = T(\dot{\boldsymbol{R}}) - V(\boldsymbol{R}) \quad = \quad \frac{1}{2}\sum_I M_I \dot{\boldsymbol{R}}_I^2 - \Phi(\{\boldsymbol{R}_I\})$$

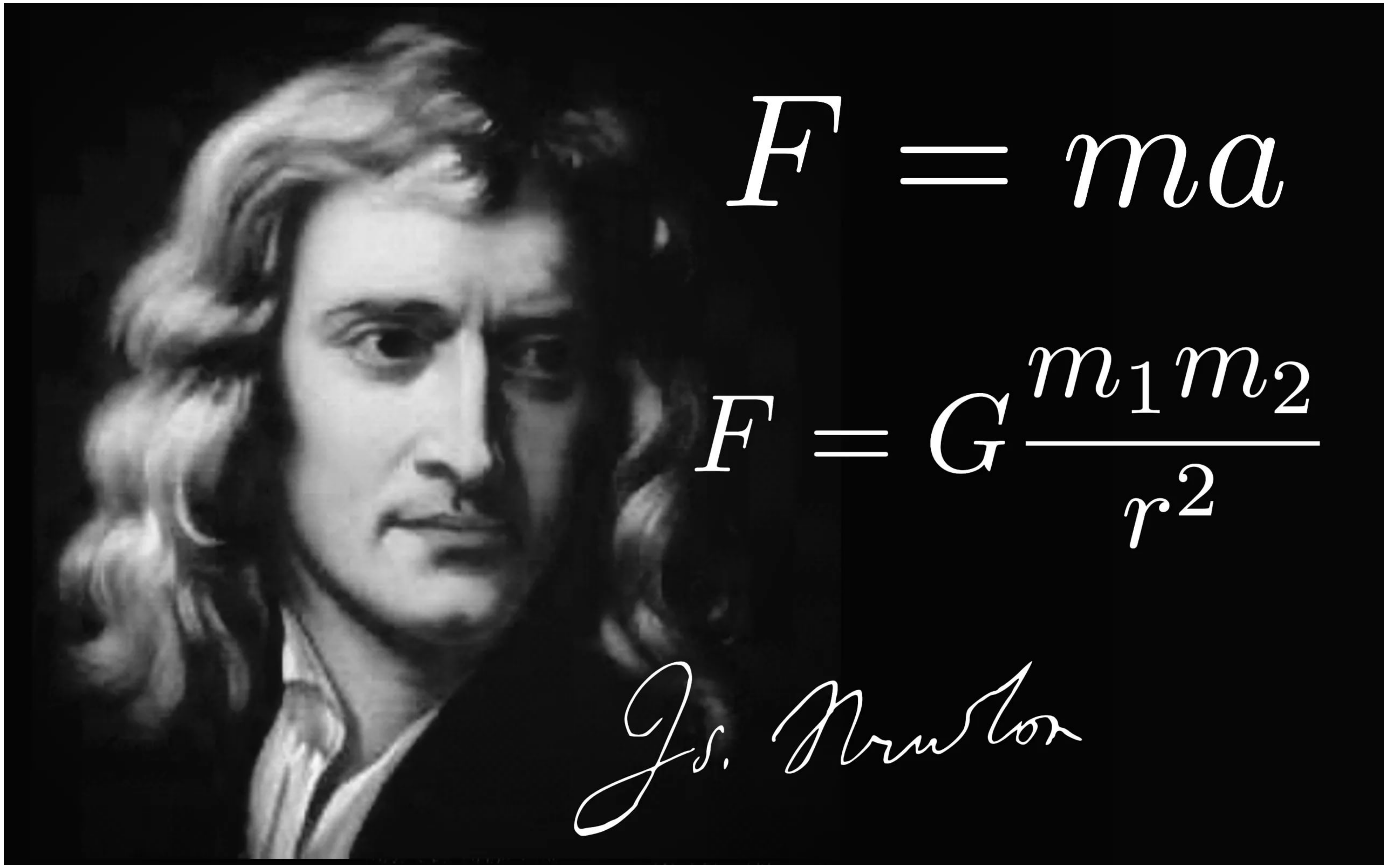
Euler-Lagrange equation

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{R}}_I} \quad = \quad \frac{\partial \mathcal{L}}{\partial \boldsymbol{R}_I}$$

Equation of motion

$$M_I \ddot{\boldsymbol{R}}_I \quad = \quad -\frac{\partial \Phi(\{\boldsymbol{R}_I\})}{\partial \boldsymbol{R}_I} = \boldsymbol{F}_I$$

Molecular Dynamics



$$\mathbf{F}_I = -M_I\ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I}E(\mathbf{R})$$

What we are interested in?

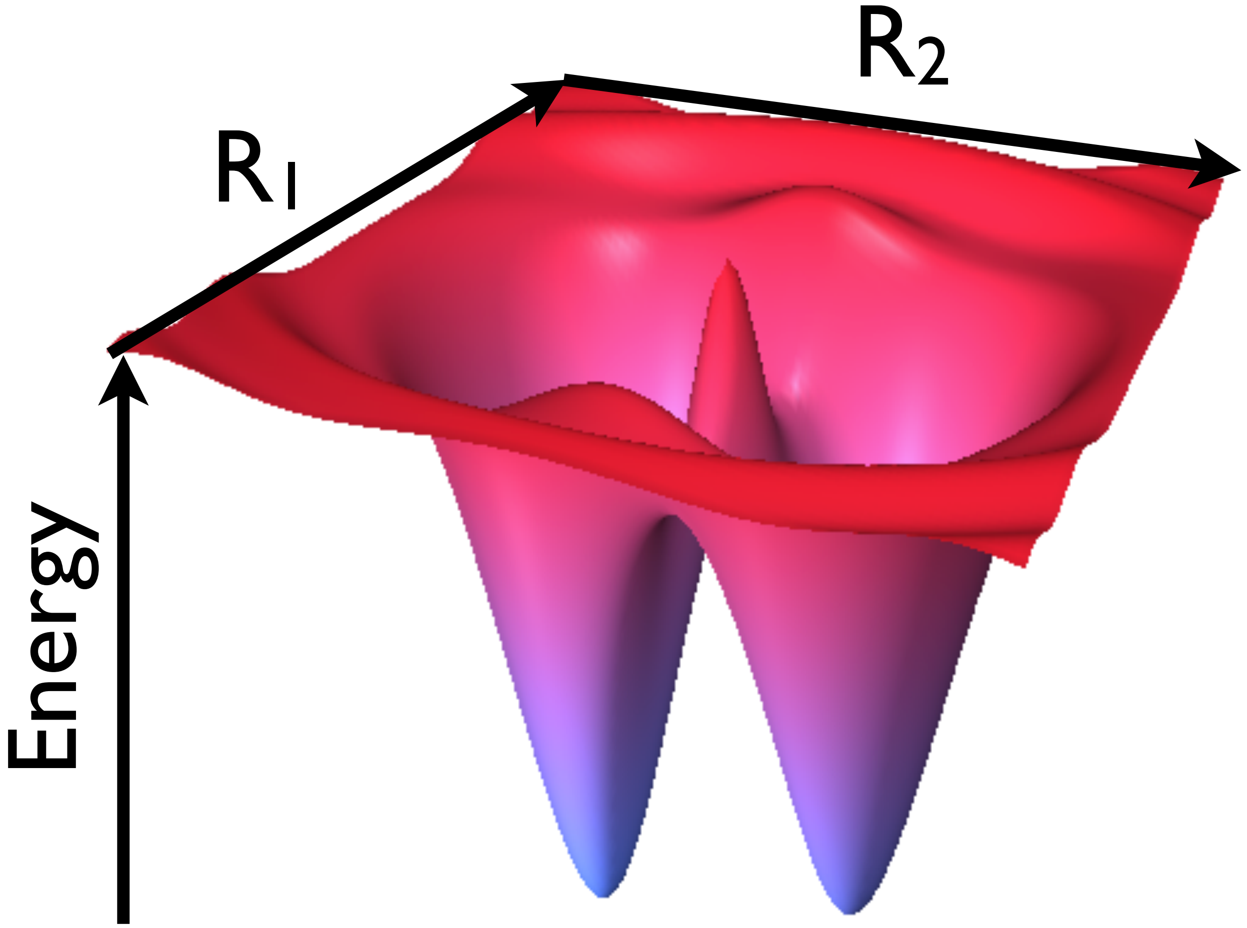
- Thermodynamic ensemble properties:

Partition Function

Hamiltonian

Static equilibrium properties: $\langle A \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p \; \mathrm{e}^{-\mathcal{H}/k_BT} A(p,R)$

Dynamic properties: $\langle A(0)B(t) \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p \; \mathrm{e}^{-\mathcal{H}/k_BT} A(p(0),R(0))B(p(t),R(t))$

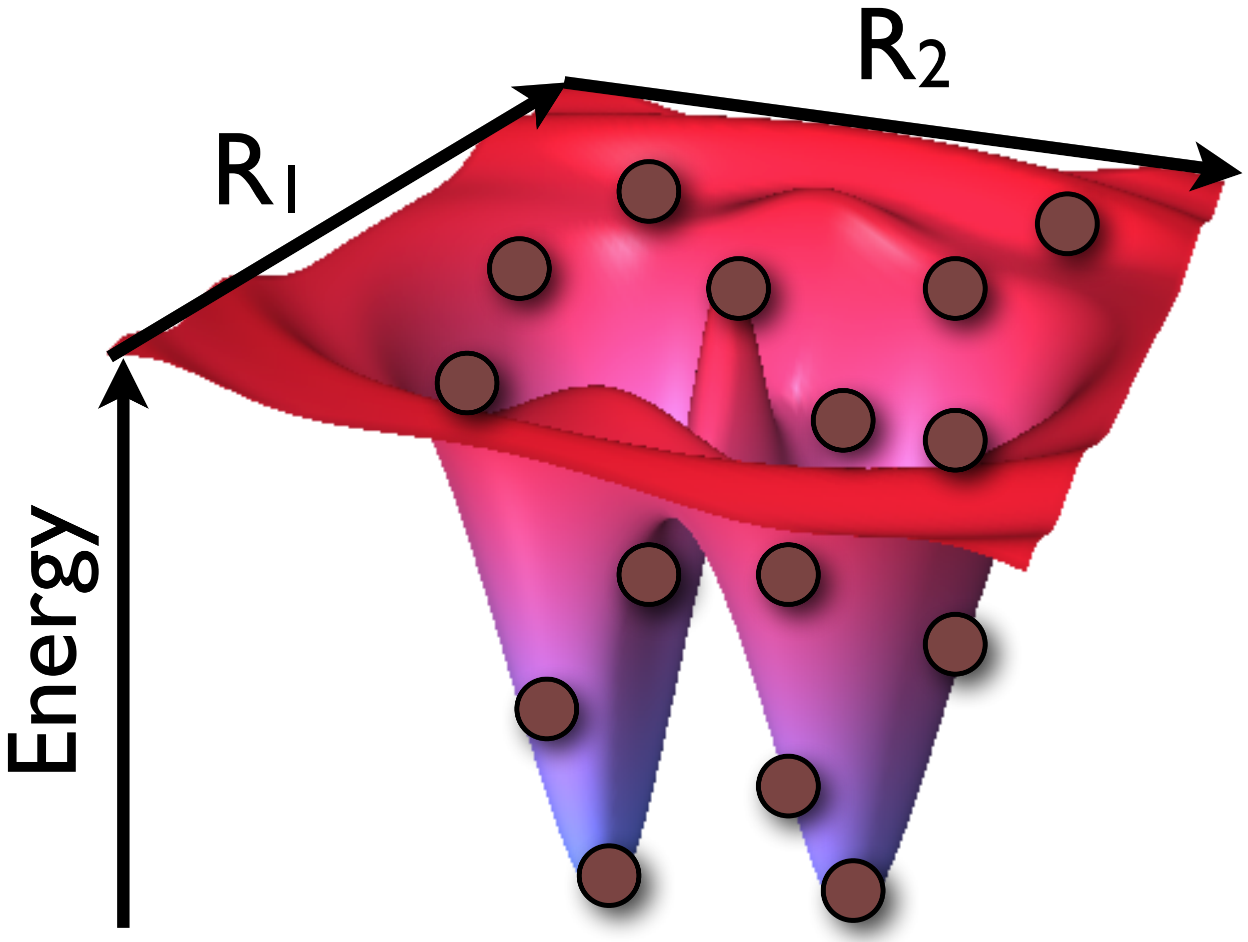


What we are interested in?

- Ergodic hypothesis: ensemble average equal to time average

$$\langle A \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p \; \mathrm{e}^{-\mathcal{H}/k_BT} A(p,R)$$

$$\langle A(0)B(t) \rangle = \frac{1}{Z} \int d^{3N}R \int d^{3N}p \; \mathrm{e}^{-\mathcal{H}/k_BT} A(p(0),R(0))B(p(t),R(t))$$

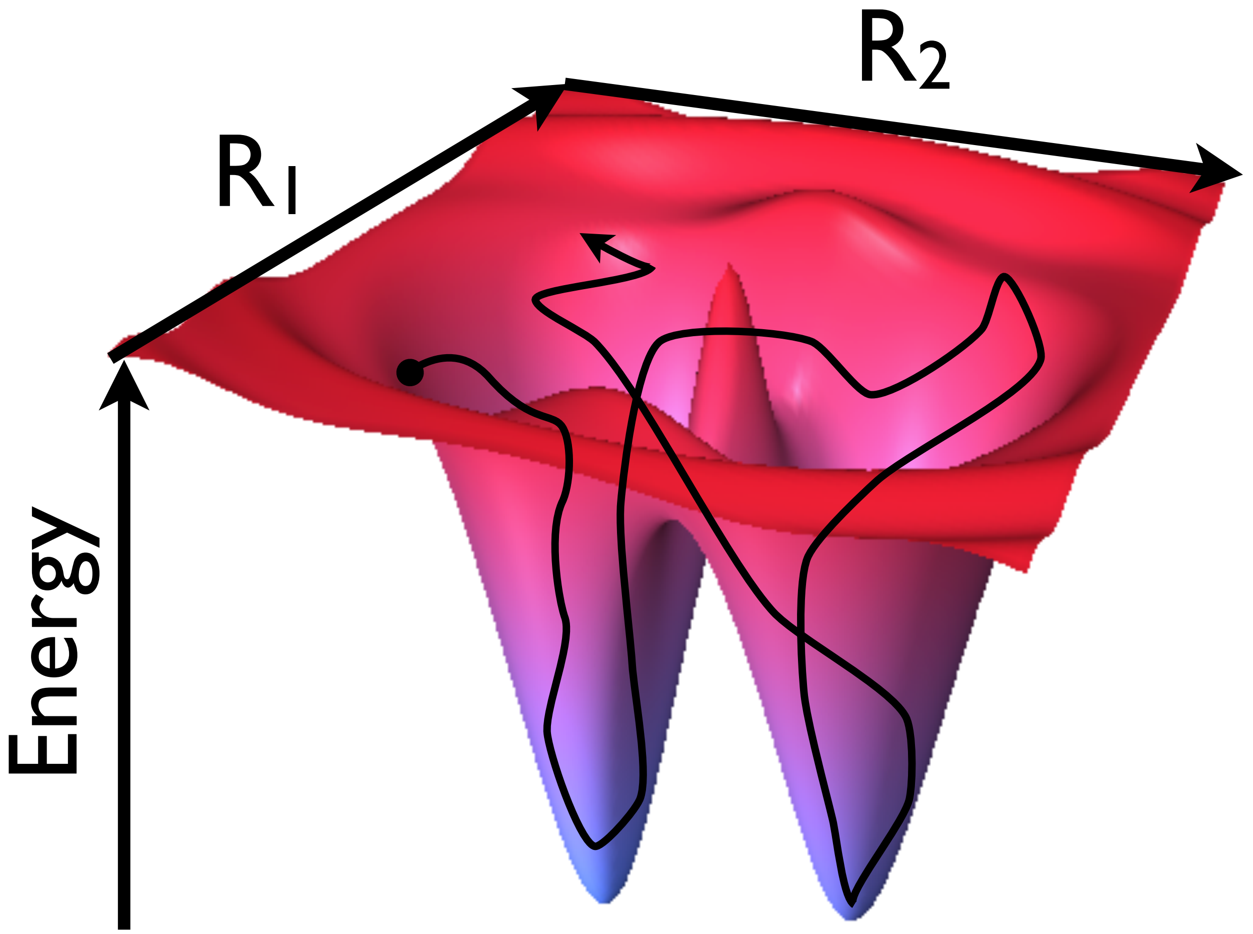


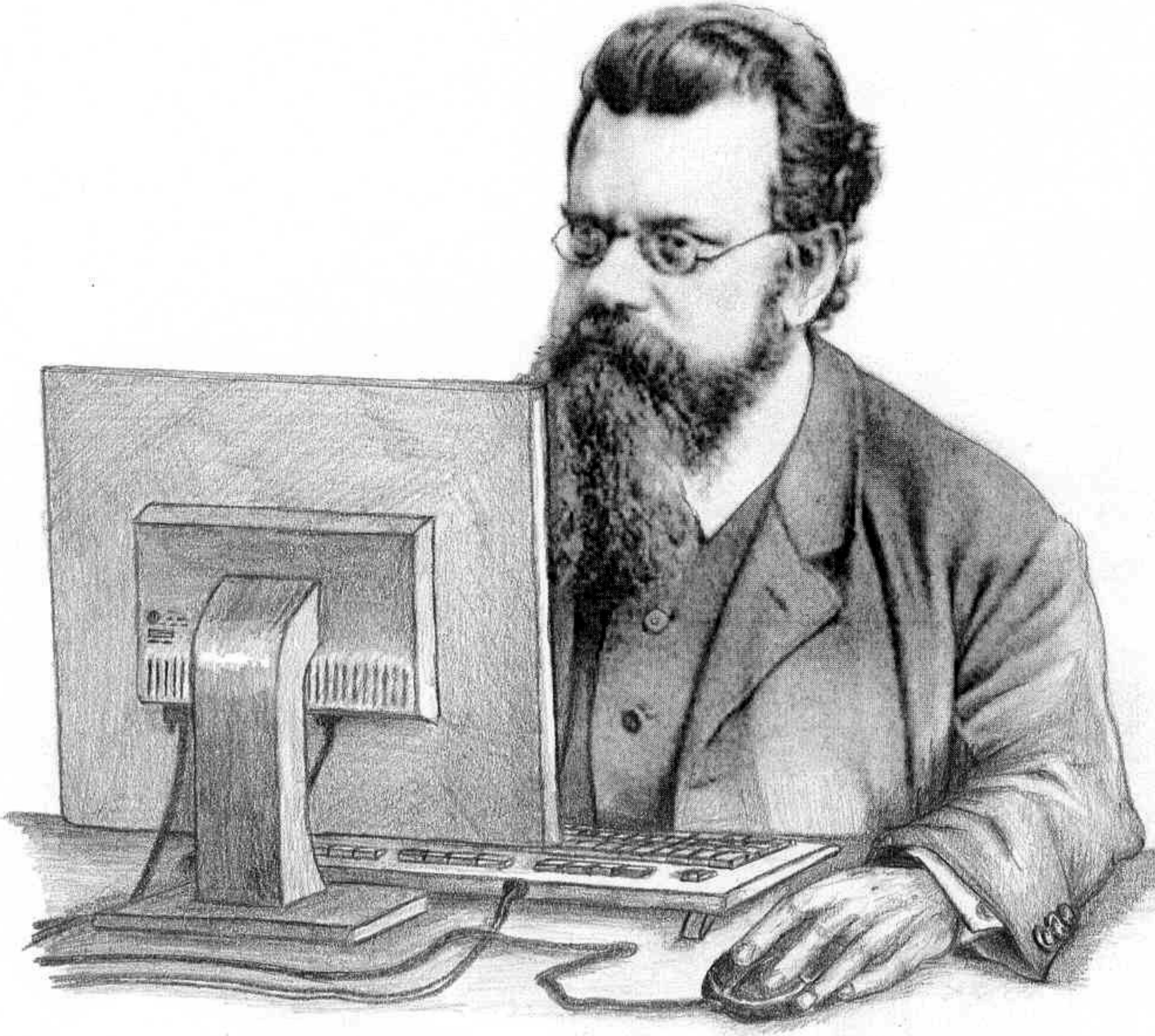
What we are interested in?

- Ergodic hypothesis: ensemble average equal to time average

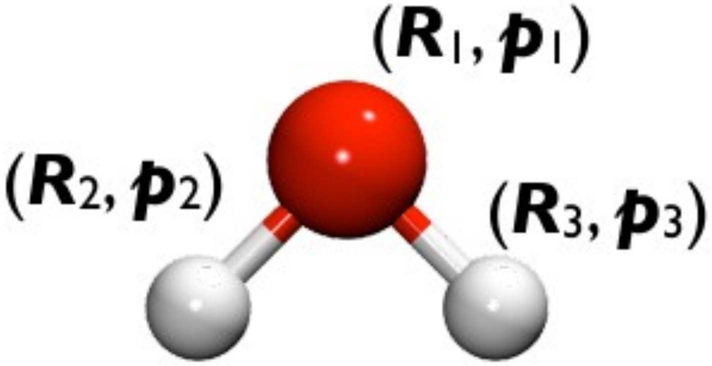
$$\langle A \rangle = \frac{1}{T}\int_0^T dt' A(p(t'), R(t'))$$

$$\langle A(0)B(t) \rangle = \frac{1}{T}\int_0^T dt' A(t')B(t+t')$$



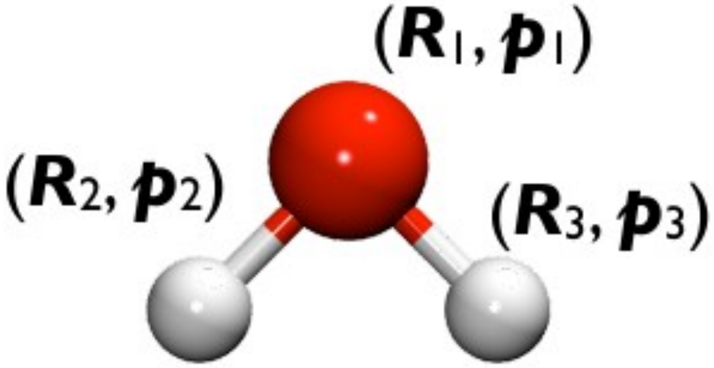


Integrating Newton’s EOM



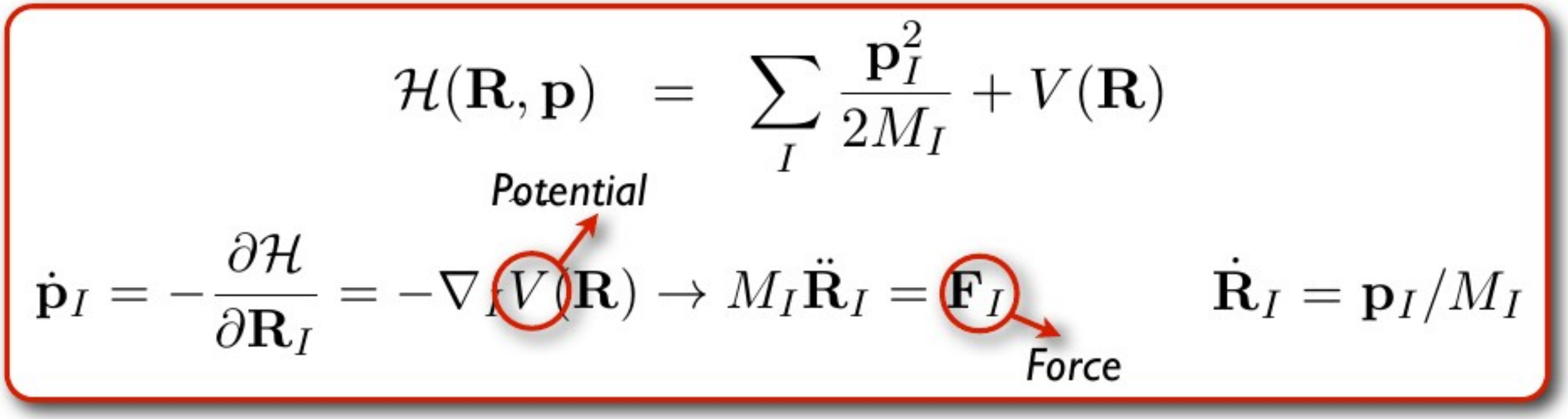
1. Assign initial $\boldsymbol{R}$ (positions) and $\boldsymbol{p}$ (momenta)

Integrating Newton’s EOM



1. Assign initial ***R*** (positions) and ***p*** (momenta)

2. Evolve (numerically) Newton's equations of motion for a discrete time increment (requires evaluation of the forces)



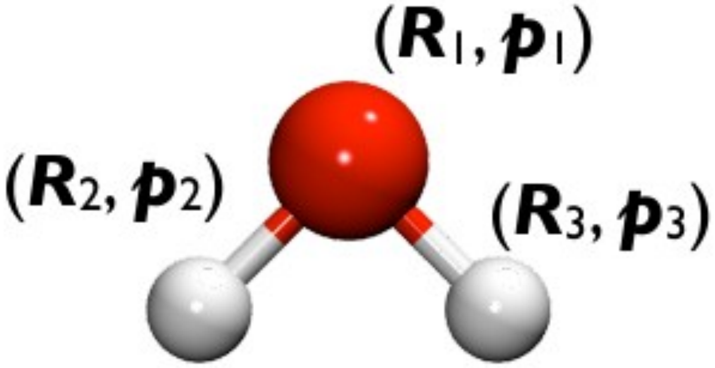
$$\mathcal{H}(\mathbf{R},\mathbf{p}) \quad = \quad \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R})$$

Potential

$$\dot{\mathbf{p}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I} = -\nabla V(\mathbf{R}) \rightarrow M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I \qquad \dot{\mathbf{R}}_I = \mathbf{p}_I / M_I$$

Force

Integrating Newton's EOM

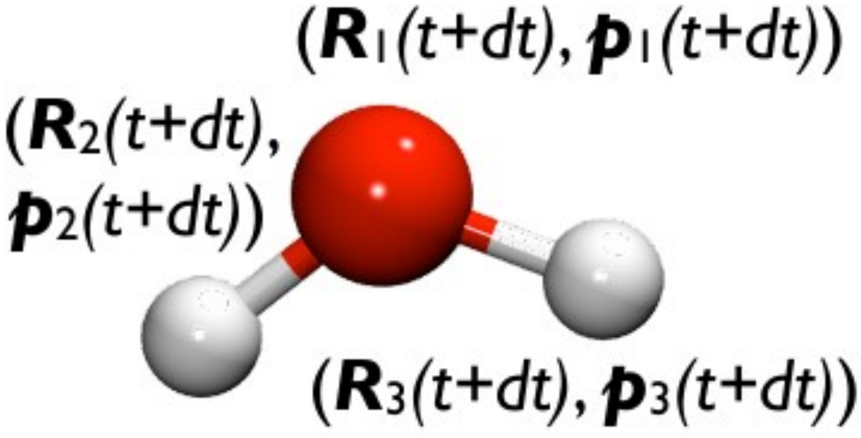


1. Assign initial ***R*** (positions) and ***p*** (momenta)

2. Evolve (numerically) Newton's equations of motion for a discrete time increment (requires evaluation of the forces)

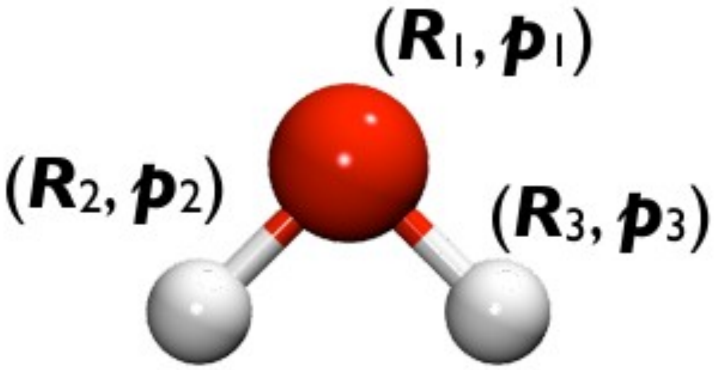
$$\mathcal{H}(\mathbf{R}, \mathbf{p}) \quad = \quad \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R})$$

$$\dot{\mathbf{p}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I} = -\nabla \overset{\text{Potential}}{V}(\mathbf{R}) \rightarrow M_I \ddot{\mathbf{R}}_I = \underset{\text{Force}}{\mathbf{F}_I} \qquad \dot{\mathbf{R}}_I = \mathbf{p}_I / M_I$$



3. Assign new positions and momenta

Integrating Newton’s EOM



1. Assign initial ***R*** (positions) and ***p*** (momenta)

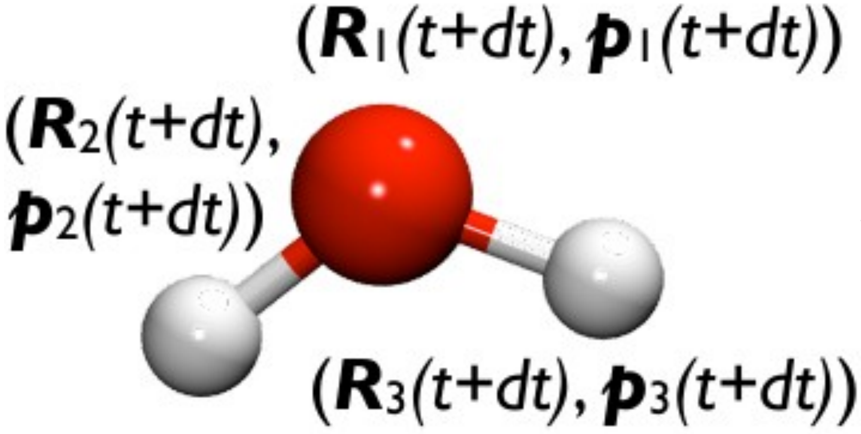
2. Evolve (numerically) Newton's equations of motion for a discrete time increment (requires evaluation of the forces)

$$\mathcal{H}(\mathbf{R},\mathbf{p}) \quad = \quad \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R})$$

Potential

$$\dot{\mathbf{p}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I} = -\nabla V(\mathbf{R}) \rightarrow M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I \qquad \dot{\mathbf{R}}_I = \mathbf{p}_I / M_I$$

Force



3. Assign new positions and momenta

Verlet's Algorithm

- First shot: Taylor expansion of *R*

$$R(t+\Delta t) = R(t) + \frac{p(t)}{m}\Delta t + \frac{\overset{\text{Force}}{\dot{p}(t)}}{2m}\Delta t^2 + \dddot{R}(t)\frac{\Delta t^3}{3!} + O(\Delta t^4)$$

Verlet’s Algorithm

- First shot: Taylor expansion of *R*

$$R(t+\Delta t) = R(t) + \frac{p(t)}{m}\Delta t + \frac{\overset{\text{Force}}{\boxed{\dot{p}(t)}}}{2m}\Delta t^2 + \overset{\text{Error } O(\Delta t^3)}{\cancel{\dddot{R}(t)\frac{\Delta t^3}{3!} + O(\Delta t^4)}}$$

- Simple truncation of the Taylor expansion is a bad idea
- The naive „forward Euler“ algorithm is
  - not time reversible
  - does not conserve phase space volume
  - does not conserve energy
- Use Verlet’s algorithm instead

Verlet's Algorithm

- First shot: Taylor expansion of *R*

$$\begin{array}{l}
R(t+\Delta t) = R(t) + \frac{p(t)}{m}\Delta t + \frac{\overset{\text{Force}}{\boxed{\dot{p}(t)}}}{2m}\Delta t^2 + \dddot{R}(t)\frac{\Delta t^3}{3!} + O(\Delta t^4) \\
R(t-\Delta t) = R(t) - \frac{p(t)}{m}\Delta t + \frac{\dot{p}(t)}{2m}\Delta t^2 - \dddot{R}(t)\frac{\Delta t^3}{3!} + O(\Delta t^4) \quad \mathbf{+} \\
\hline
R(t+\Delta t) + R(t-\Delta t) = 2R(t) + \frac{\dot{p}(t)}{m}\Delta t^2 + \boxed{O(\Delta t^4)}\ \text{Error}
\end{array}$$

$$R(t+\Delta t) \approx 2R(t) - R(t-\Delta t) + \frac{\dot{p}(t)}{m}\Delta t^2$$

Verlet Algorithm

Velocity-Verlet Algorithm

$$\boldsymbol{R}_I(t+\Delta t) = \boldsymbol{R}_I(t) + \Delta t \times \dot{\boldsymbol{R}}_I(t) + \frac{\Delta t^2}{2M_I}\boldsymbol{F}_I(t)$$

Calculate $\boldsymbol{F}_I(t+\Delta t)$

$$\dot{\boldsymbol{R}}_I(t+\Delta t) = \dot{\boldsymbol{R}}_I(t) + \frac{\Delta t}{2M_I}\left[\boldsymbol{F}_I(t) + \boldsymbol{F}_I(t+\Delta t)\right]$$

- Simple and efficient: Only $\boldsymbol{F}_I(t)$, no higher derivatives required
- Explicitly time reversible
- Symplectic, i.e. conserves phase space volume

Excellent long time stability ⇒ Energy conservation

Liouville Formalism

- Define phase space vector $\boldsymbol{\Gamma} = (\boldsymbol{R}, \boldsymbol{P})$ and commutator

$$\{\boldsymbol{A}, \boldsymbol{H}\} = \frac{\partial \boldsymbol{A}}{\partial \boldsymbol{R}} \frac{\partial \boldsymbol{H}}{\partial \boldsymbol{P}} - \frac{\partial \boldsymbol{A}}{\partial \boldsymbol{P}} \frac{\partial \boldsymbol{H}}{\partial \boldsymbol{R}}$$

- Hamilton's equations of motion

$$\frac{d\boldsymbol{\Gamma}}{dt} = \{\boldsymbol{\Gamma}, \mathcal{H}\} \equiv 0$$

- Define propagator $\hat{\mathcal{L}}$ such that

$$i\hat{\mathcal{L}}\boldsymbol{\Gamma} = \{\boldsymbol{\Gamma}, \mathcal{H}\}$$

- Symplectic algorithm via $\dot{\boldsymbol{\Gamma}} = 0 \Rightarrow$

$$\boldsymbol{\Gamma}(t) = e^{i\hat{\mathcal{L}}t}\boldsymbol{\Gamma}(0)$$

Lyapunov Instability

- It's impossible to determine initial conditions: $\Delta \boldsymbol{R} \times \Delta \boldsymbol{P} \sim \hbar$
- Finite numerical accuracy of the integrator as well as $\Phi(\boldsymbol{R})$
- Even worse: The Lyapunov instability

  $$\left| \boldsymbol{R}(t) - \boldsymbol{R}'(t) \right| \approx \epsilon \times e^{\lambda t}$$

  suggests an exponential dependence on them
- I.e. even knowing $\Phi(\boldsymbol{R})$ exactly still causes an $e^{\lambda t}$ divergence

Neither possible nor desirable to calculate exact trajectories

Molecular Dynamics

- Microcanonical (NVE) ensemble: Number of particles, Volume, and total Energy are conserved
    - Natural ensemble to simulate molecular dynamics (follows directly from Hamilton's equation of motion

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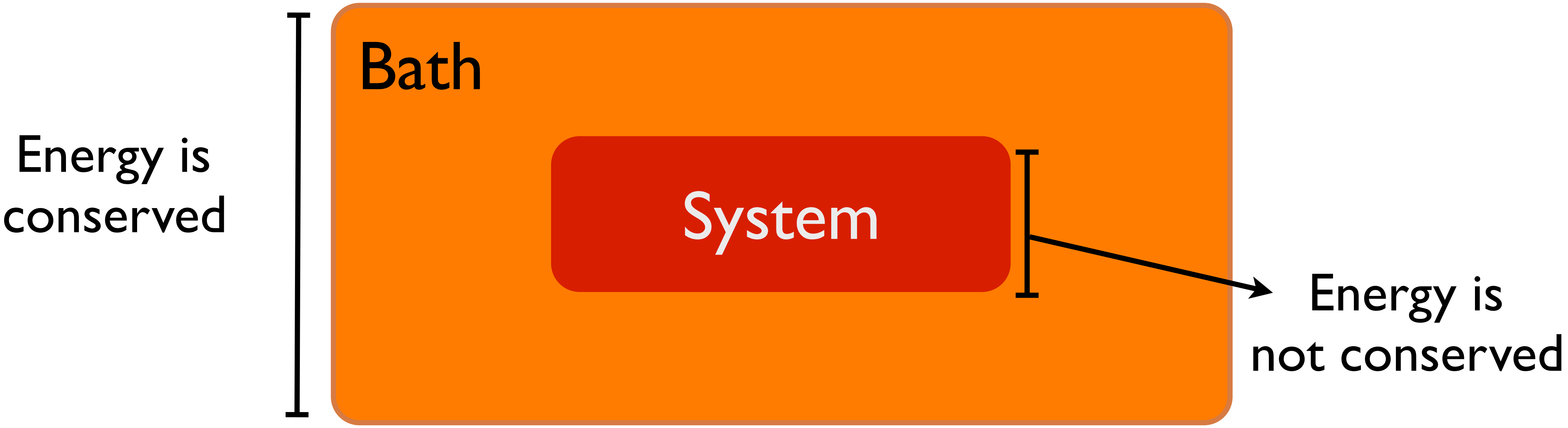
  - System in contact with a heat bath (discussed later on)

The Canonical Ensemble

- The idea: couple the system to a thermostat (heat bath)
- Interesting because:
  - Experiments are usually done at constant temperature
  - Better modeling of conformational changes



Bath

System

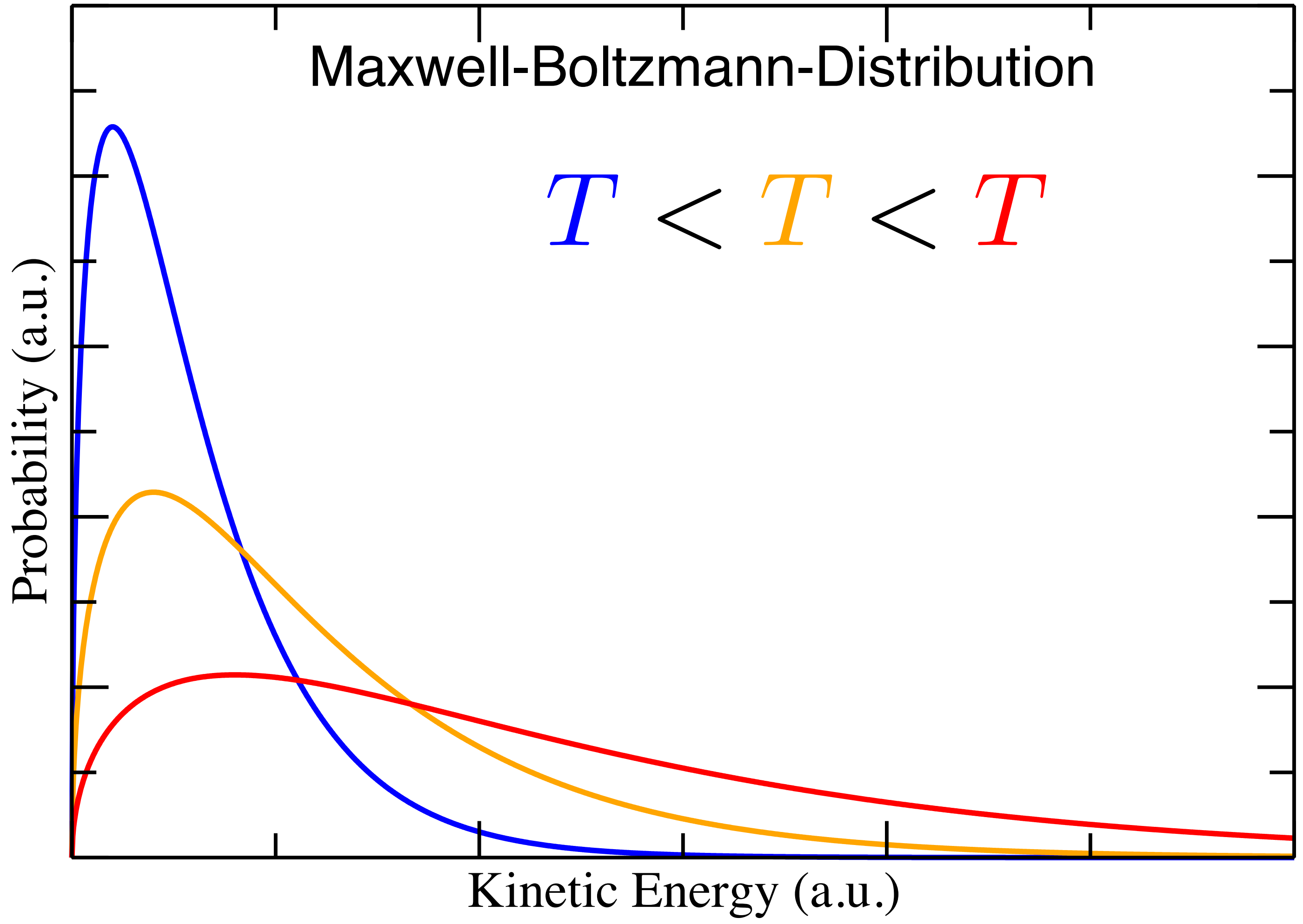
Energy is conserved

Energy is not conserved

Maxwell Distribution

Probability distribution of the kinetic energy:

$$P(E_{kin}) \propto \exp(-E_{kin}/k_B T)$$



kinetic energy: $p^2/2M$

$$\langle T \rangle = \frac{2\langle E_{kin} \rangle}{3Nk_B}$$

# of particles

Thermostats: First Ideas

- Temperature rescaling: Berendsen “thermostat”
  - Rescale velocities by a factor containing the ratio of target and instant temperature
  - Does not sample the canonical ensemble (wrong temperature distribution)
  - “Flying ice-cube” effect: rotations and translations acquire high E_{kin} and vibrations are frozen

H. J. C. Berendsen, *et al. J. Chem. Phys.* **81** 3684 (1984)

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H. J. C. Berendsen, *et al. J. Chem. Phys.* **81** 3684 (1984)

- Simple stochastic idea: Andersen thermostat
  - At each n^{th} time-step, replace velocity of a random particle by one drawn from a Maxwell-Boltzmann distribution at target temperature
  - Not very efficient, no conserved quantity
  - Very sensitive on *n*

H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980)

Stochastic Velocity Rescaling

G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).

Combine concepts from velocity rescaling (fast!) with concepts from stochastic thermostats (accurate!)

Target temperature follows a stochastic differential equation:

$$\frac{dT}{\bar{T}} = \underset{\text{Temperature rescaling}}{\boxed{\left[1 - \frac{T(t)}{\bar{T}}\right]\frac{dt}{\tau}}} - \underset{\text{White noise}}{\boxed{2\sqrt{\frac{T(t)}{3\bar{T}N\tau}}\,\xi(t)}}$$

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Temperature rescaling

White noise

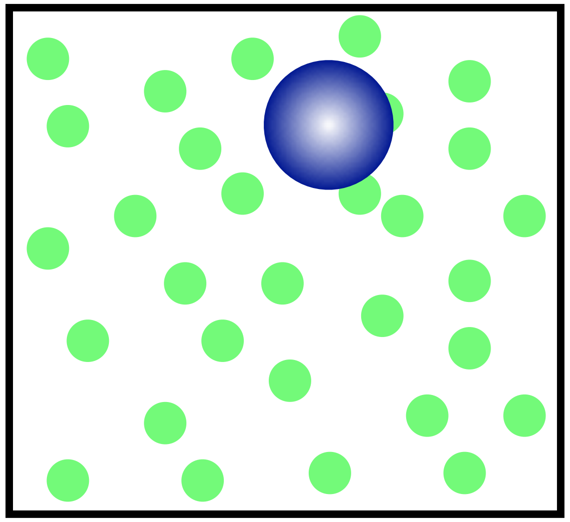
- Very successful thermostat, weakly dependent on relaxation time τ
- Pseudo-Hamiltonian is conserved

Bussi, Parrinello, *Phys. Rev. E* **75**, 056707 (2007)

Newton vs. Langevin

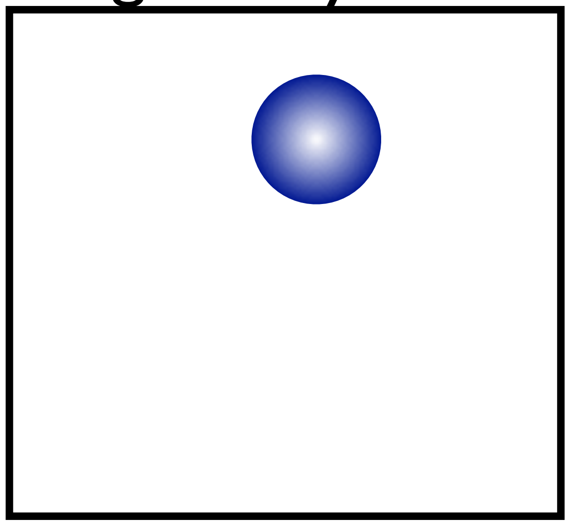
Heavy(er) body in a solvent (or gas)

Newtonian dynamics



$$\mathbf{F}_I = -\nabla_{\mathbf{R}_I} V$$

Langevin dynamics



$$\mathbf{F}_I = \underbrace{-\gamma \dot{\mathbf{R}}_I}_{\text{friction}} + \underbrace{\xi(t)}_{\text{random force}}$$

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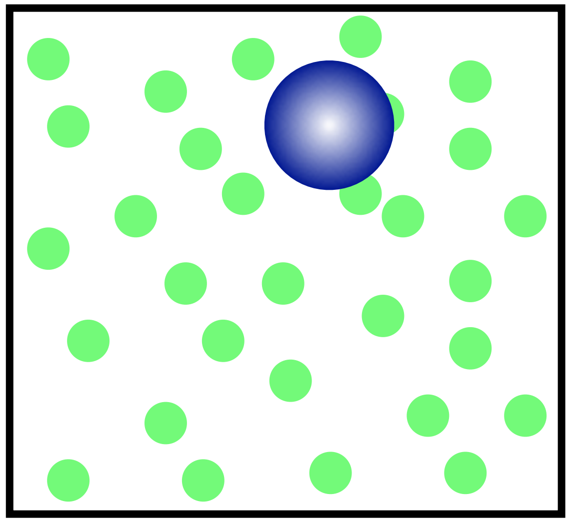

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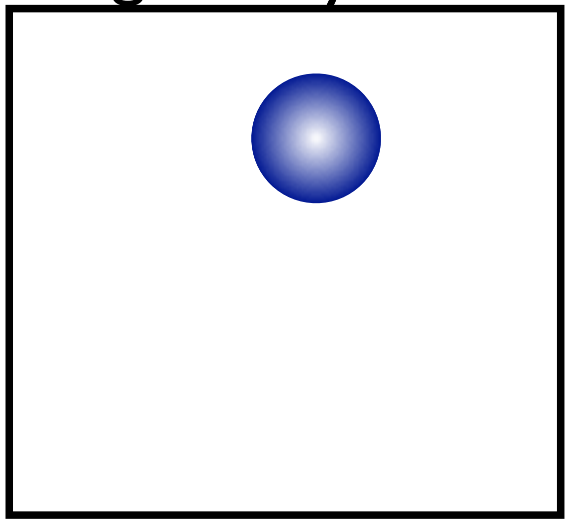

$$\mathbf{F}_I = -\gamma\dot{\mathbf{R}}_I + \xi(t)$$

friction

random force

- In thermal equilibrium, drag of the friction and kicks of the random noise balance each other - Fluctuation Dissipation Theorem (FDT)

$$\langle\xi(t)\xi(0)\rangle = 2k_B T\gamma\delta(t)$$

No memory of past times
No frequency dependence (white noise)

Langevin Thermostat

S. A. Adelman and J. D. Doll, *J. Chem. Phys.* **64**, 2375 (1976).

Model dynamics via the Langevin equation:

$$\boxed{M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I} - \boxed{\gamma_I \dot{\mathbf{R}}_I + \xi(t)}$$

Original system　　Friction and White Noise

$$\langle \xi(t)\xi(0) \rangle = 2k_B T \gamma \delta(t)$$

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Original system Friction and White Noise

$$\langle \xi(t)\xi(0)\rangle = 2k_B T\gamma\delta(t)$$

- Sensitive on γ
  - For systems spanning a wide range of frequencies, how to achieve the “best” critical damping?
- Disturbs dynamics considerably

Colored Noise Thermostat

M. Ceriotti, G. Bussi, M. Parrinello, *JCTC* **2010**, 6, 1170-1180 (**http://gle4md.org/index.html**)

Extremely flexible class of thermostats based on the Generalized Langevin Equation (GLE)

- Markovian (no memory) process in high dimensions

$$\begin{pmatrix}\dot{p}\\ \dot{\mathbf{s}}\end{pmatrix} = \boxed{\begin{pmatrix}-V'(R)\\ 0\end{pmatrix}} - \boxed{\mathbf{A}_p\begin{pmatrix}p\\ \mathbf{s}\end{pmatrix} + \mathbf{B}_p\left(\boldsymbol{\xi}\right)}$$

extra fictitious degrees of freedom

Original system

Friction and White Noise

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extra fictitious degrees of freedom

Original system

Friction and White Noise

- Non-Markovian process for the system (integrating out ***s***):

$$\dot{p} = F - \int_{-\infty}^{t} d\tau\, K(t-\tau)\, p(\tau) + \zeta(t)$$

Memory Kernel

Colored Noise

Fluctuation Dissipation: $H(t) = \langle \zeta(t)\zeta(0)\rangle = k_B T K(t)$

Colored Noise Thermostat

M. Ceriotti, G. Bussi, M. Parrinello, *JCTC* **2010**, 6, 1170-1180 (**http://gle4md.berlios.de/**)

- Input matrices $\mathbf{A}_p$ (and $\mathbf{C}_p$), connected by:

$$\mathbf{A}_p\mathbf{C}_p + \mathbf{C}_p\mathbf{A}_p^T = \mathbf{B}_p\mathbf{B}_p^T$$

covariance matrix

- However, flexible:
  - For canonical sampling, $\mathbf{C}_p = \mathbf{1} k_B T$ and FDT is obeyed
  - For other samplings one can break FDT
- What can you model?
  - Nuclear quantum effects, excitation of single modes
  - Make "*Path Integral Molecular Dynamics*" computationally cheaper *Ceriotti, Manolopoulos, Parinello, JCP 134, 084104 (2011)*

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- Isothermic-Isobaric (NPT) ensemble: Number of particles, Pressure, and Temperature are conserved

Isobaric-Isothermic MD

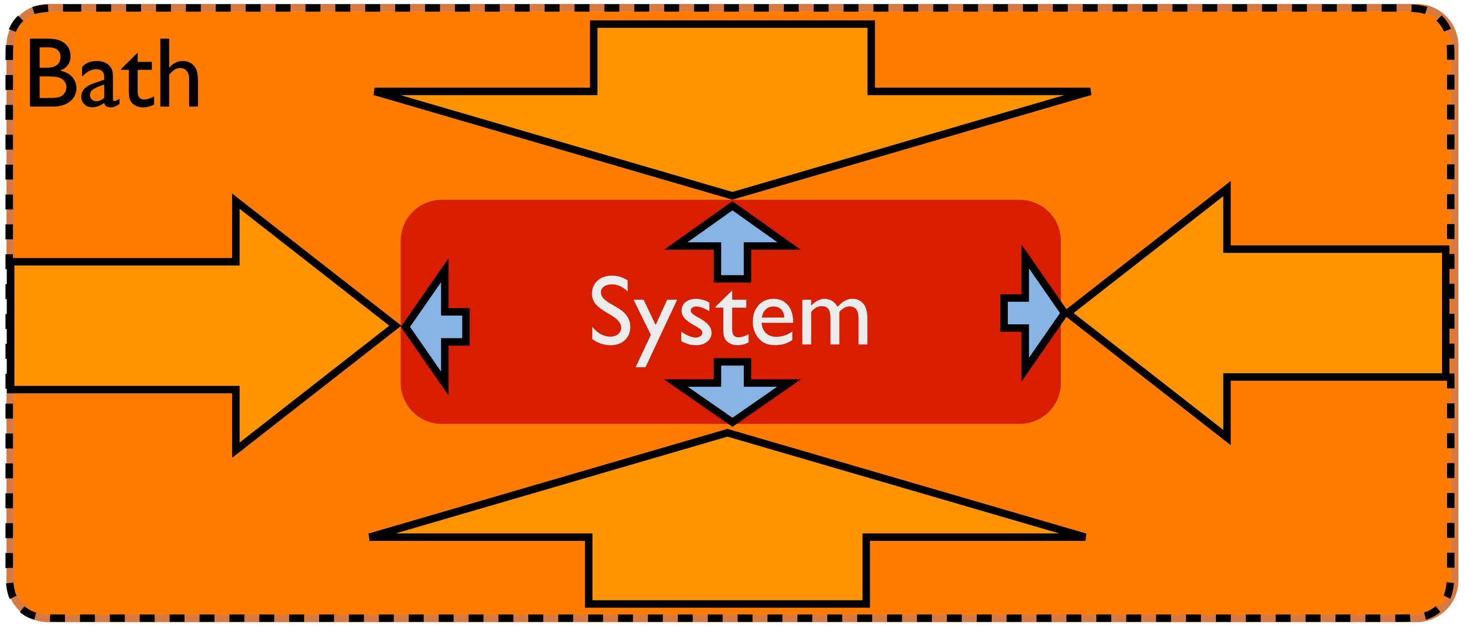
- Definition of instantaneous pressure:

$$P = \frac{2}{3V}(E_{\mathrm{kin}} - \Xi) \qquad \boldsymbol{\Xi} = \sum_{ij} \mathbf{R}_{ij}(\nabla_{\mathbf{R}_{ij}} U) = -V\boldsymbol{\sigma}$$

Stress Tensor

- Similar schemes as thermostats: pressure rescaling, extended Lagrangian, stochastic pressure rescaling
  Parinello and Rahman, J. Appl. Phys 52, 7182 (1981);
  Bussi, Zykova-Timan, Parrinello, J. Chem. Phys. 130, 074101 (2009)

- Use thermostat together with a barostat to control pressure and temperature



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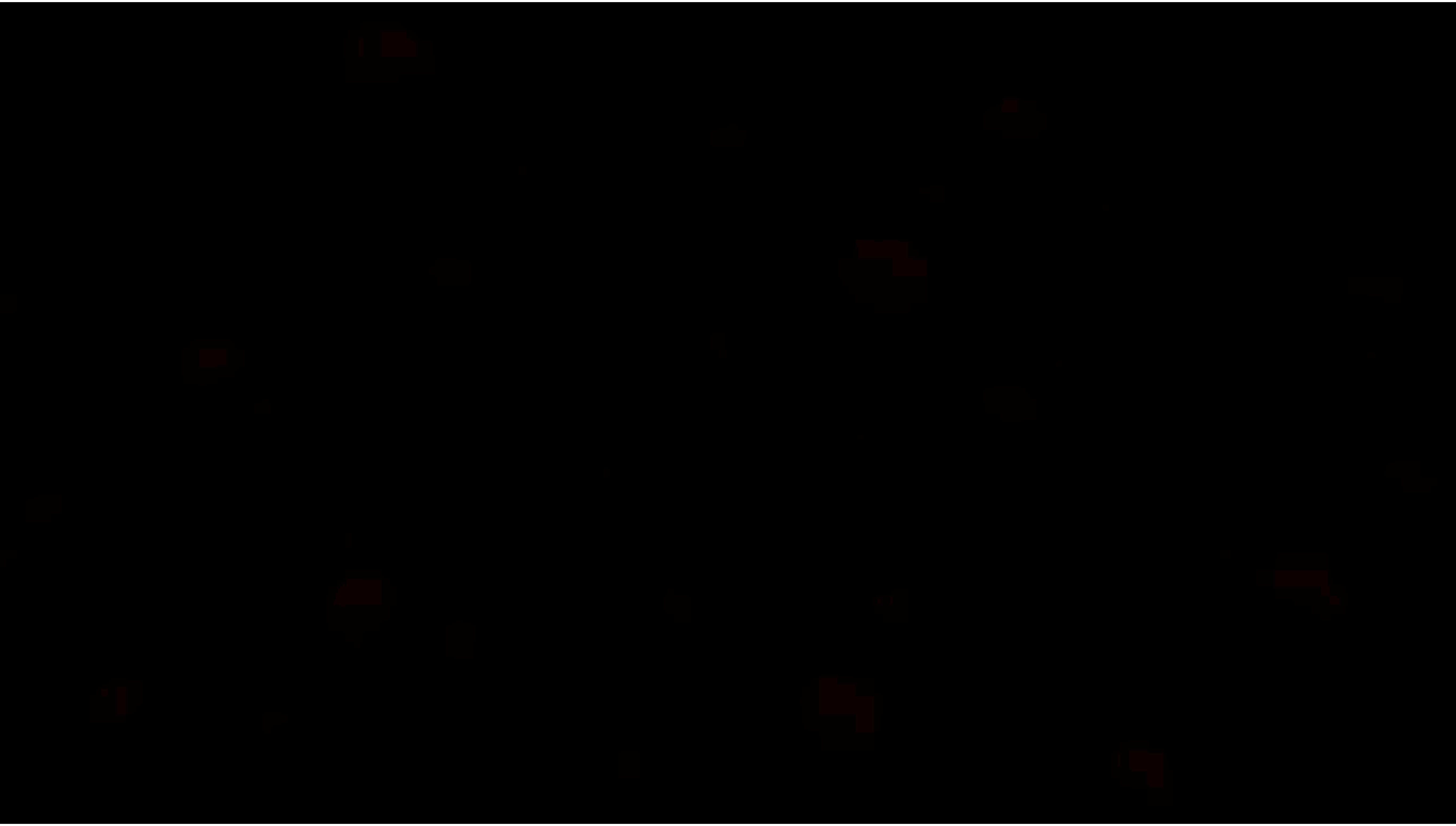
"Computer experiment": equilibrate system and measure

Molecular Dynamics



Electrons

Nuclei	Classical	Quantum Mechanical
Classical	Molecular Dynamics (MD)	Ab-Initio MD (AIMD)
Quantum Mech.	Path-Integral MD (PIMD)	Ab-Initio PIMD (AI-PIMD)

$$\mathcal{H}_e(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R}) = \varepsilon(\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})$$

$$M_I\ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I}\left[\varepsilon(\boldsymbol{R}) + V_{KK}(\boldsymbol{R})\right]$$

Born-Oppenheimer MD

$$\Phi(\boldsymbol{R}) = E_{\mathsf{KS}}^{\mathsf{DFT}}\big[\{\psi_i\};\boldsymbol{R}\big] + E_{II}(\boldsymbol{R}) = E\big[\{\psi_i\};\boldsymbol{R}\big]$$

Born-Oppenheimer Lagrangian

$$\mathcal{L}_{\mathsf{BO}}\big(\{\psi_i\};\boldsymbol{R},\dot{\boldsymbol{R}}\big) \quad = \quad \frac{1}{2}\sum_{I=1}^{N} M_I \dot{\boldsymbol{R}}_I^2 - \min_{\{\psi_i\}} \, E\big[\{\psi_i\};\boldsymbol{R}\big]\,\Big|_{\{\langle\psi_i|\psi_j\rangle=\delta_{ij}\}}$$

The forces are obtained by solving the Euler-Lagrange equation

$$\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{\boldsymbol{R}}_I} \quad = \quad \frac{\partial\mathcal{L}}{\partial\boldsymbol{R}_I}$$

Born-Oppenheimer MD

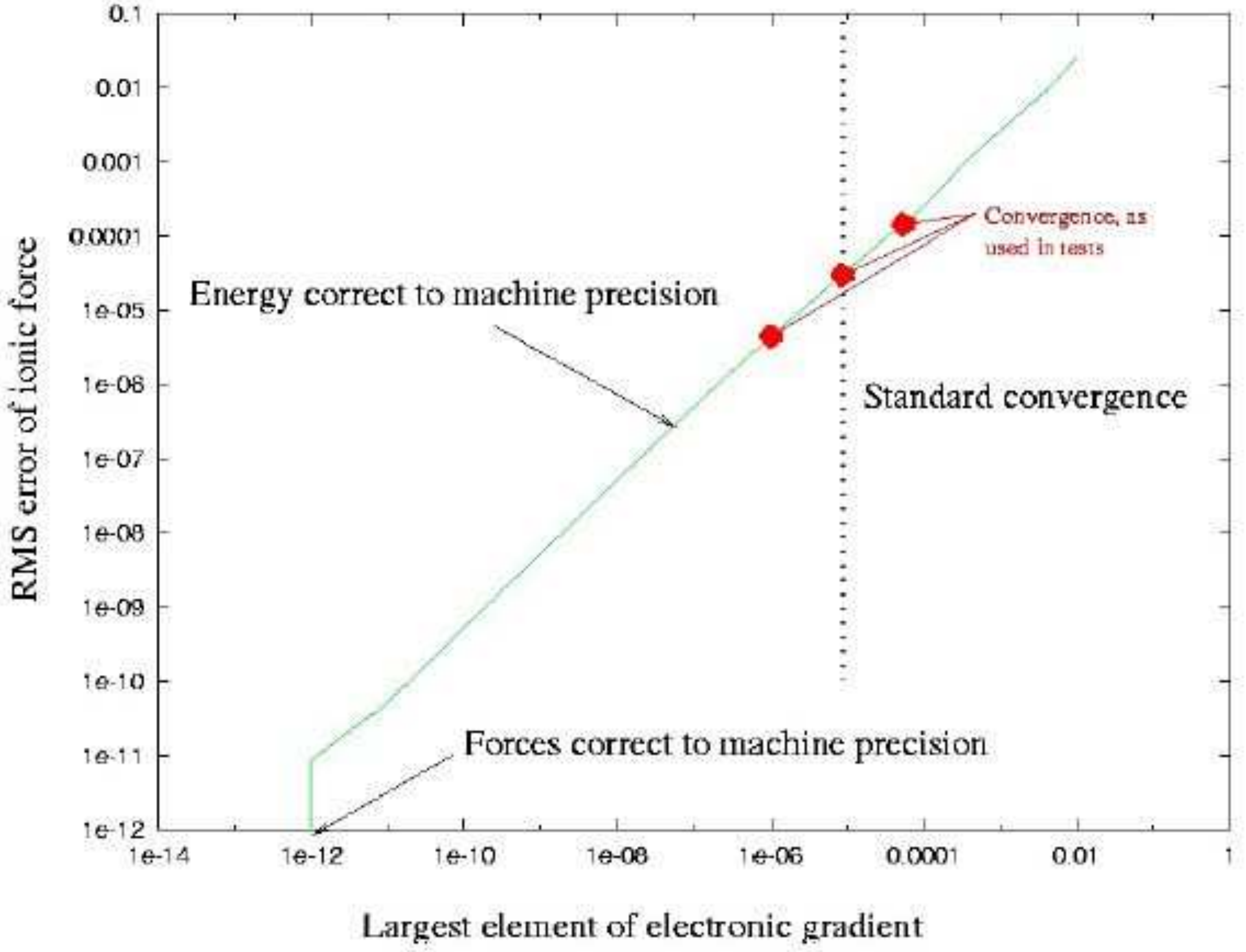
$$
\begin{aligned}
M_I \ddot{\boldsymbol{R}}_I &= -\nabla_{\boldsymbol{R}_I} \left[\min_{\{\psi_i\}} E\big[\{\psi_i\}; \boldsymbol{R}_I\big] \Big|_{\{\langle\psi_i|\psi_j\rangle=\delta_{ij}\}} \right] \\
&= -\frac{\partial E}{\partial \boldsymbol{R}_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial \boldsymbol{R}_I} \langle \psi_i \mid \psi_j \rangle \\
&- \quad 2 \sum_i \frac{\partial \langle \psi_i |}{\partial \boldsymbol{R}_I} \left[\frac{\partial E\big[\{\psi_i\}; \boldsymbol{R}_I\big]}{\partial \langle \psi_i |} - \sum_j \Lambda_{ij} | \psi_j \rangle \right]
\end{aligned}
$$

If and only if $\langle\psi_i|$ is an eigenfunction, then

$$
M_I \ddot{\boldsymbol{R}}_I = -\frac{\partial E}{\partial \boldsymbol{R}_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial \boldsymbol{R}_I} \langle \psi_i \mid \psi_j \rangle
$$

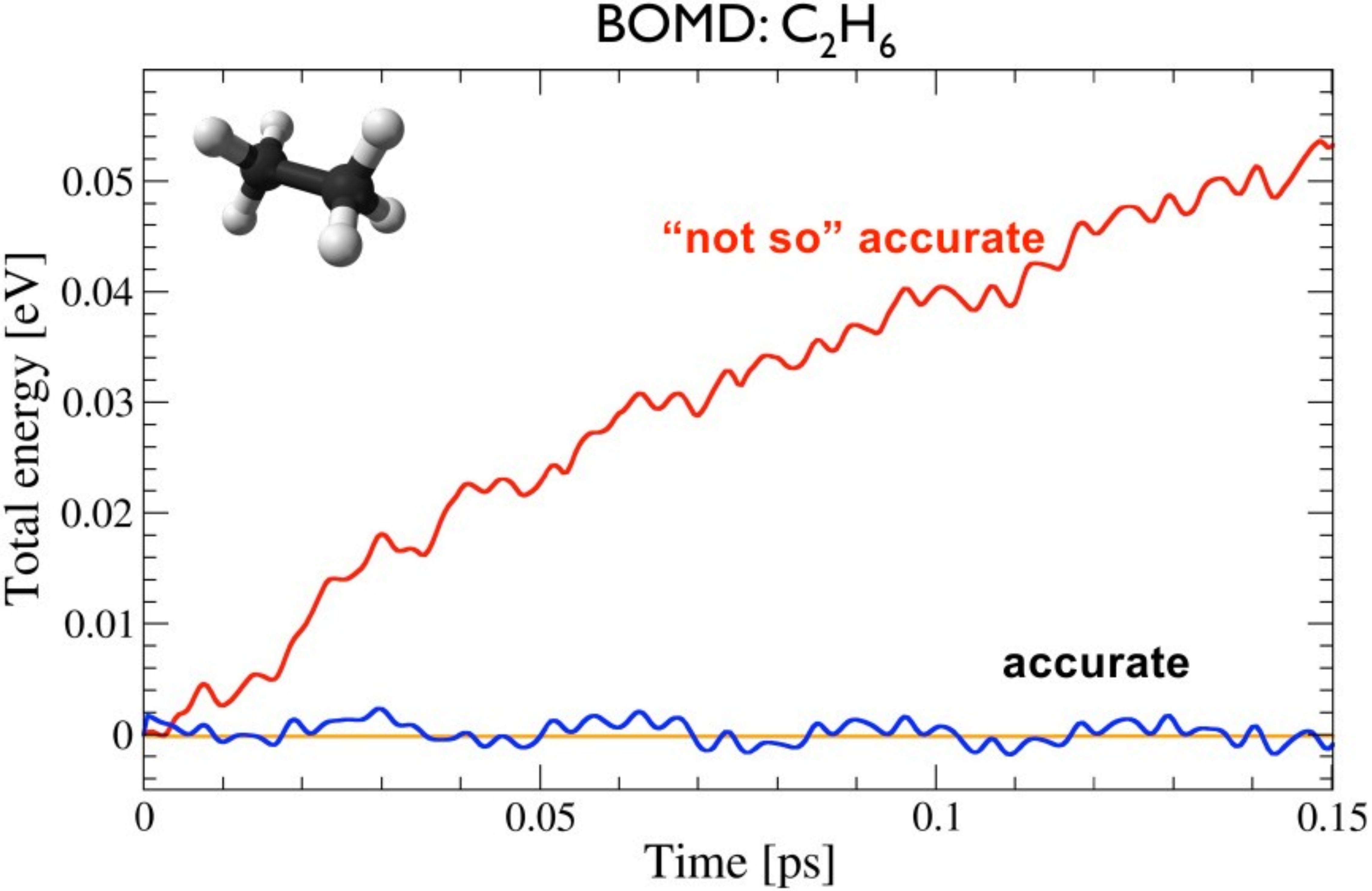
However, in general the HF-Theorem can not be assumed

Born-Oppenheimer MD



May be good enough to optimize the geometry, but not for AIMD

Born-Oppenheimer MD



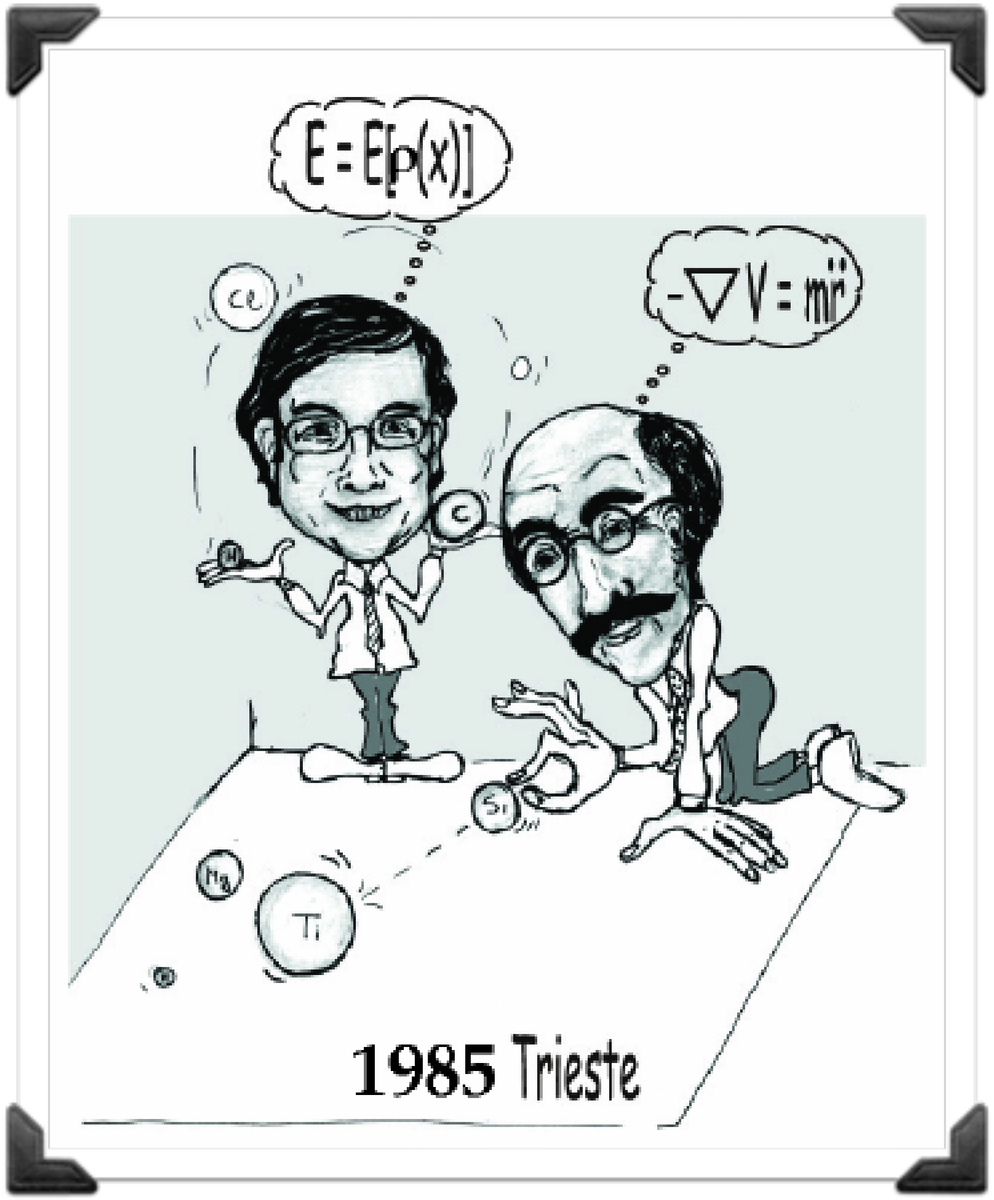
Born-Oppenheimer MD

- Large integration time steps
- Potential energy on the BO surface
- Expensive optimization of the WF required
- Very stringent SCF convergence requirement

However: $>> 10^5$ electronic structure calculations are required

Car-Parrinello MD

Car-Parrinello MD



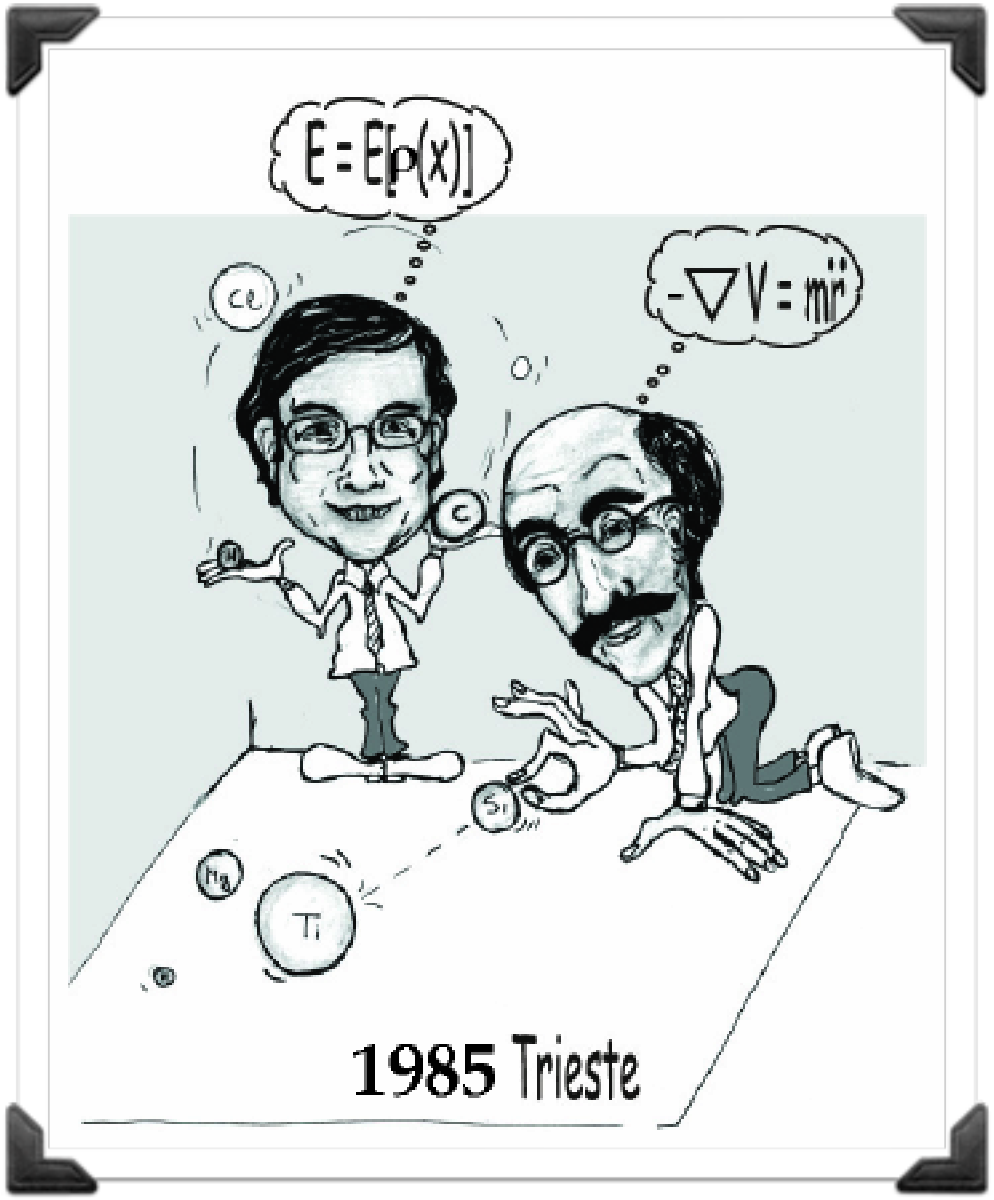
$$\mathcal{L}_{\mathrm{CP}}\big(\{\psi_i\};\boldsymbol{R},\dot{\boldsymbol{R}}\big) = \frac{1}{2}\mu\sum_i\langle\dot{\psi}_i|\dot{\psi}_i\rangle + \frac{1}{2}\sum_{I=1}^{N} M_I\dot{\boldsymbol{R}}_I^2 - E\big[\{\psi_i\};\boldsymbol{R}\big] + \sum_{i,j}\Lambda_{ij}\big(\langle\psi_i|\psi_j\rangle - \delta_{ij}\big)$$

$$\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{\boldsymbol{R}}_I} = \frac{\partial\mathcal{L}}{\partial\boldsymbol{R}_I}$$

$$\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\langle\dot{\psi}_i|} = \frac{\partial\mathcal{L}}{\partial\langle\psi_i|}$$

R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985)

Car-Parrinello MD



$$
\begin{aligned}
M_I \ddot{\mathbf{R}}_I &= -\nabla_{\mathbf{R}_I} \left[E\left[\{\psi_i\};\mathbf{R}\right] \Big|_{\{\langle\psi_i|\psi_j\rangle=\delta_{ij}\}} \right] \\
&= -\frac{\partial E}{\partial \mathbf{R}_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle\psi_i|\psi_j\rangle \\
\mu \ddot{\psi}_i(\boldsymbol{r},t) &= -\frac{\delta E}{\delta\langle\psi_i|} + \sum_j \Lambda_{ij} |\psi_j\rangle \\
&= -\hat{H}_e \langle\psi_i| + \sum_j \Lambda_{ij} |\psi_j\rangle
\end{aligned}
$$

R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985)

Car-Parrinello MD

Beside that it circumvent the SCF cycle, what is so clever about it?

- If μ is sufficiently small, the electrons adiabatically follow the ions
- In this case the metastable state can be sustained and $\ddot{\psi}_i \simeq 0$

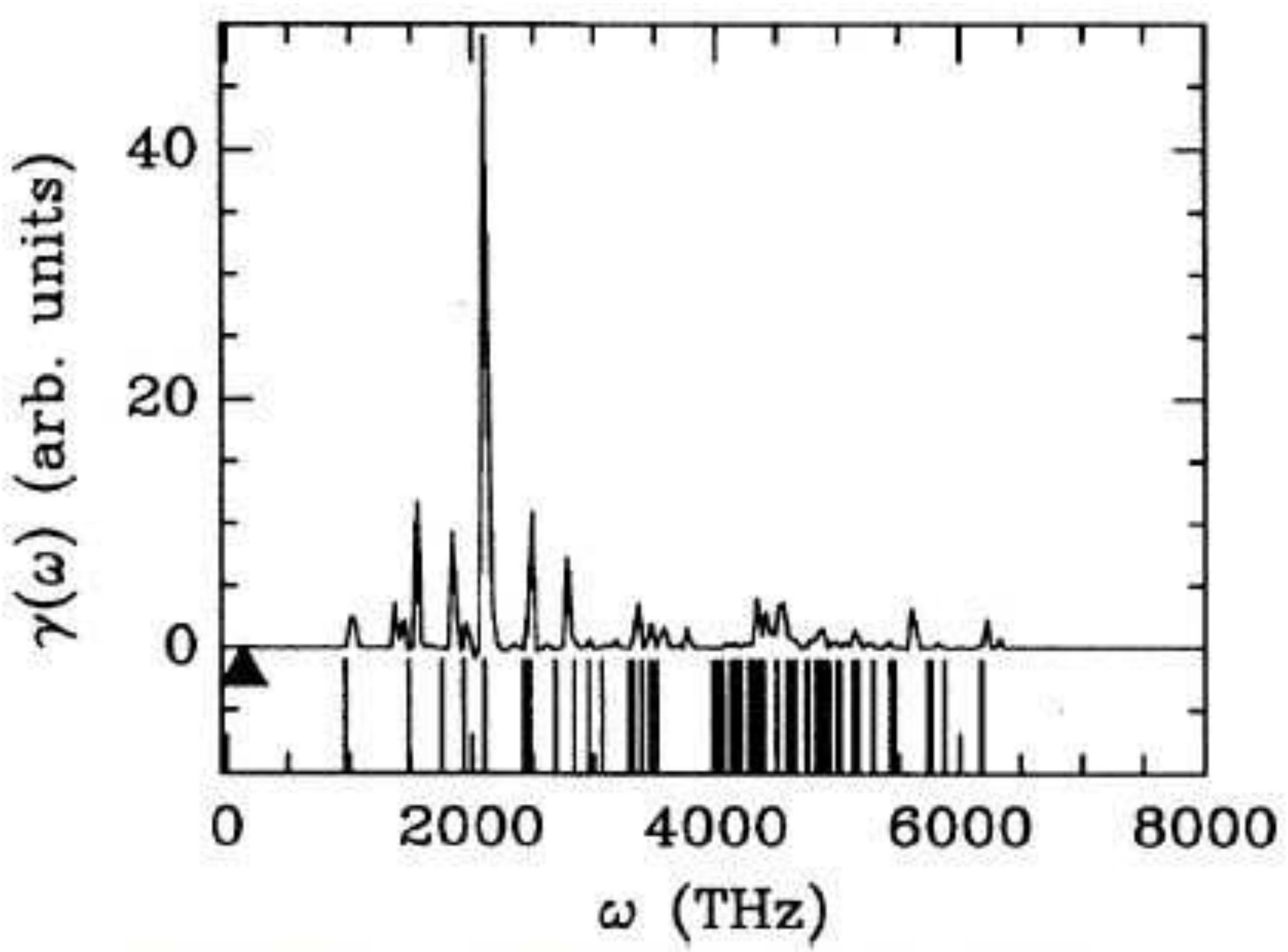
$$\frac{\partial E\left[\{\psi_i\};\boldsymbol{R}_I\right]}{\partial\langle\psi_i|} - \sum_j \Lambda_{ij}|\psi_j\rangle \simeq 0$$

- I.e. on ionic timescales the electron oscillations averages out $\Rightarrow \langle\psi_i|$ is an eigenfunction of $\mathcal{H}_e^{\text{CP}}$, thus the HF-Theorem holds
- Energies & Forces are NOT on the BO surface, but are consistent

$$\frac{d}{dt}\left\{\mathcal{H}_{\text{BO}} + \frac{1}{2}\mu\sum_{i=1}^{M}\langle\dot{\psi}_i \mid \dot{\psi}_i\rangle\right\} = \frac{d\mathcal{H}_{\text{CP}}}{dt} = 0$$

Car-Parrinello MD

Vibrational spectra of electrons and ions do not overlap

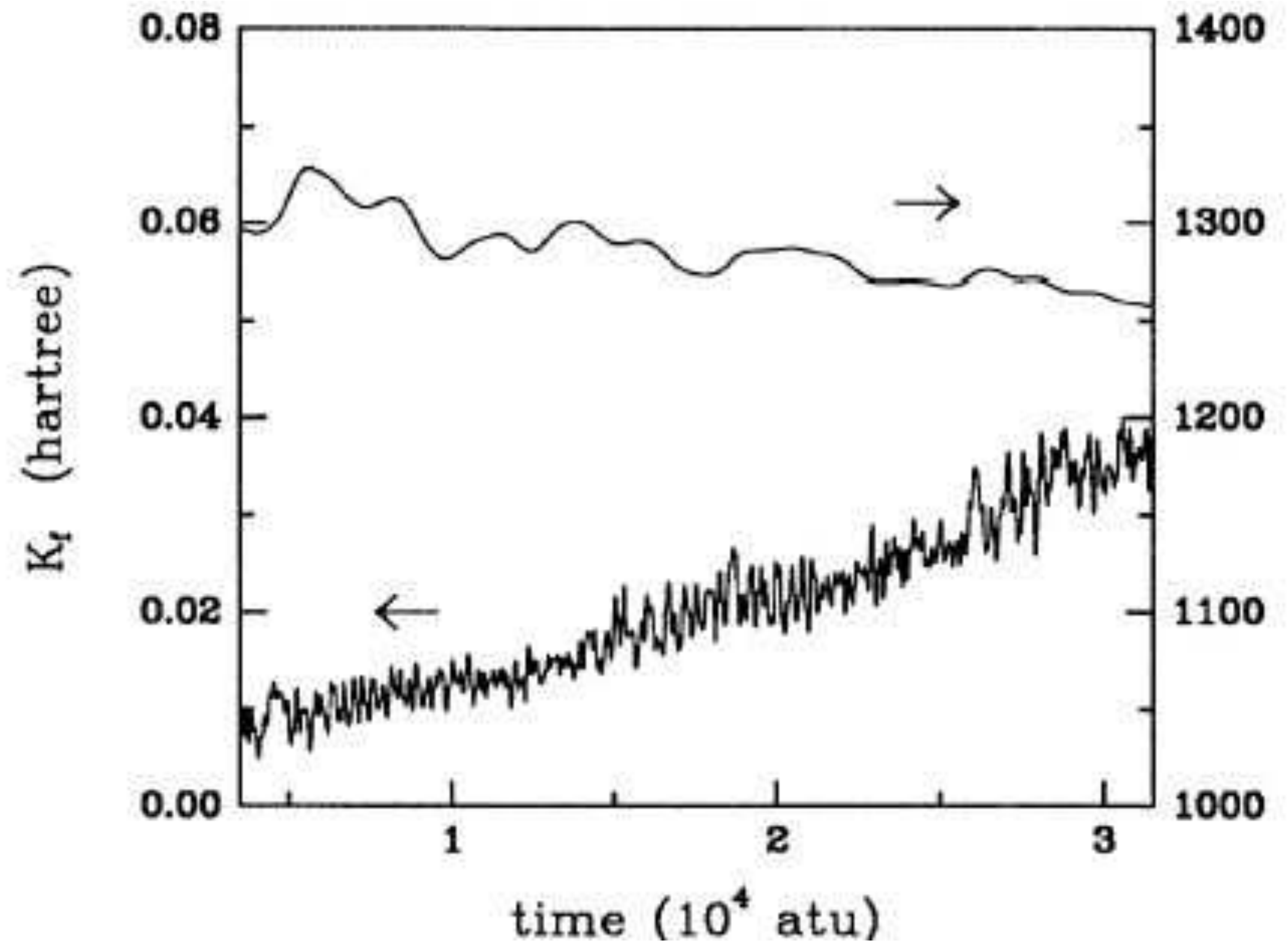


Triangle = highest ionic frequency

$$f^{e}(\omega) = \int_{t=0}^{\infty} \cos(\omega t) \sum_{i} \langle \dot{\psi}_i(t) | \dot{\psi}_i(0) \rangle \, dt$$

Car-Parrinello MD

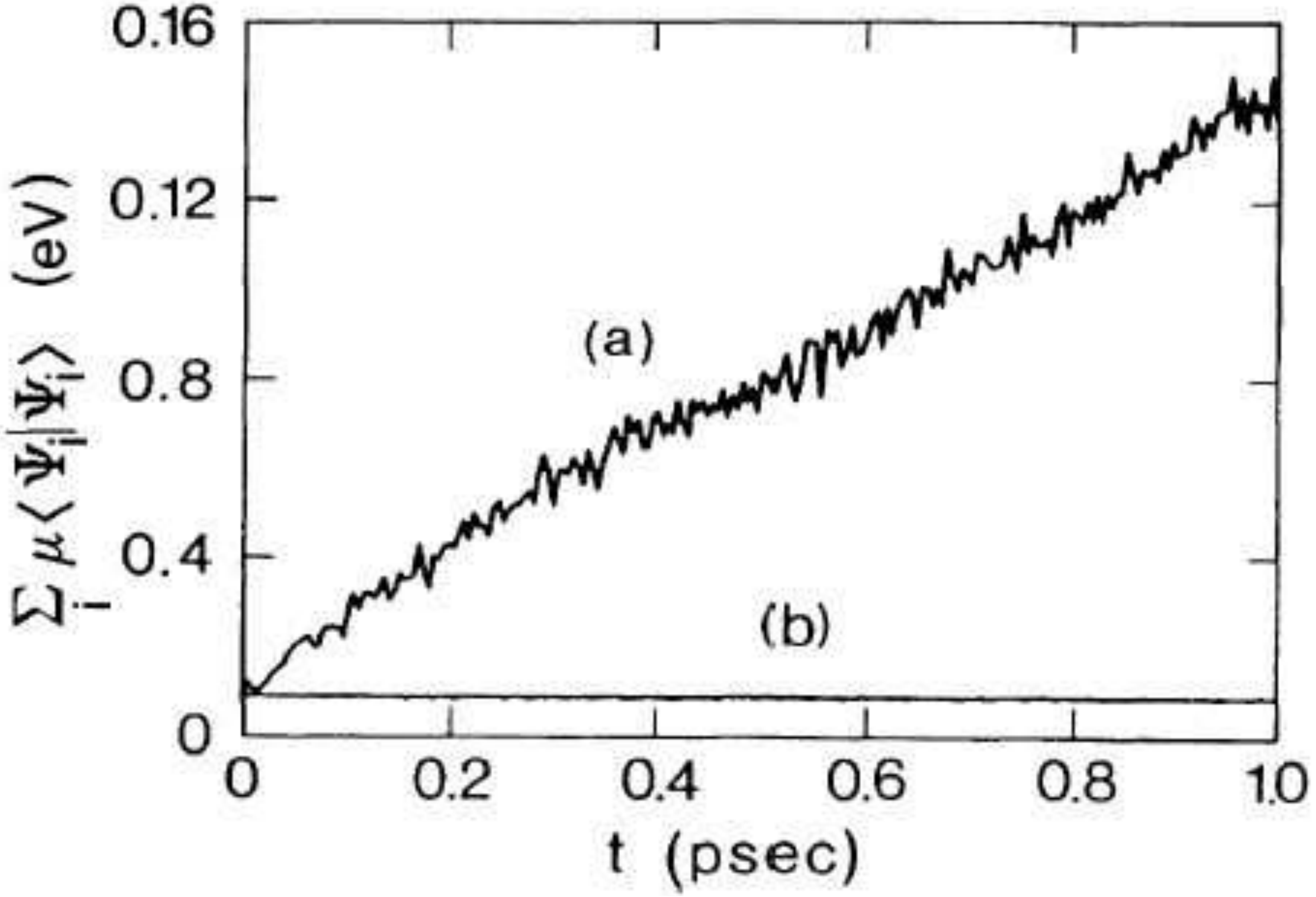
Vacancy in a hot 64-atom Si cell



Car-Parrinello MD

64 atoms of molten aluminum

- (a): Without thermostat
- (b): With thermostat



Car-Parrinello MD

Principal task of μ: Coupling between $\dot{\boldsymbol{R}}_I$ and $\dot{\psi}_i$

$$|\psi_\mu(\boldsymbol{r},t) - \psi_0(\boldsymbol{r},t)| \leq C\sqrt{\mu}$$

$$\Delta t_{\max} \propto \sqrt{\frac{\mu}{\Delta E_{gap}}}$$

- μ acts as a continuous slider between speed and accuracy
- Typically, the timestep is $\sim 5\times - 10\times$ smaller than in BOMD
- Depends on the application if either CPMD or BOMD is to favor
- Metals are problematic: Finite electron temperature or thermostats

Desirable to eliminate μ!

BOMD vs. CPMD

	BOMD	CPMD
Energy Conservation	fair	excellent
Iterative Optimization	yes	no
Exactly on the BO-Surface	yes	no
Integration time-step	large	small
Metals and small band-gap	possible	difficult

Second-Generation CPMD

$$\begin{aligned}
M_I \ddot{\boldsymbol{R}}_I &= -\nabla_{\boldsymbol{R}_I} \left[\min_{\{\psi_i\}} E\left[\{\psi_i\}; \boldsymbol{R}_I\right] \Big|_{\{\langle\psi_i|\psi_j\rangle=\delta_{ij}\}} \right] \\
&= -\frac{\partial E}{\partial \boldsymbol{R}_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial \boldsymbol{R}_I} \langle \psi_i \mid \psi_j \rangle \\
&- \quad 2 \sum_i \frac{\partial \langle \psi_i |}{\partial \boldsymbol{R}_I} \left[\frac{\partial E\left[\{\psi_i\}; \boldsymbol{R}_I\right]}{\partial \langle \psi_i |} - \sum_j \Lambda_{ij} |\psi_j\rangle \right]
\end{aligned}$$

T. D. Kühne, WIREs Comput. Mol. Sci. **4**, 391 (2014)

Second-Generation CPMD

$$
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\end{aligned}
$$

$$
\frac{d^2}{d\tau^2}|\psi_i(\boldsymbol{r},\tau)\rangle = -\frac{\delta E_{\textsf{NSC}}}{\delta\langle\psi_i(\boldsymbol{r},\tau)|} - \gamma\omega\frac{d}{d\tau}|\psi_i(\boldsymbol{r},\tau)\rangle + \sum_j \Lambda_{ij}|\psi_j(\boldsymbol{r},\tau)\rangle
$$

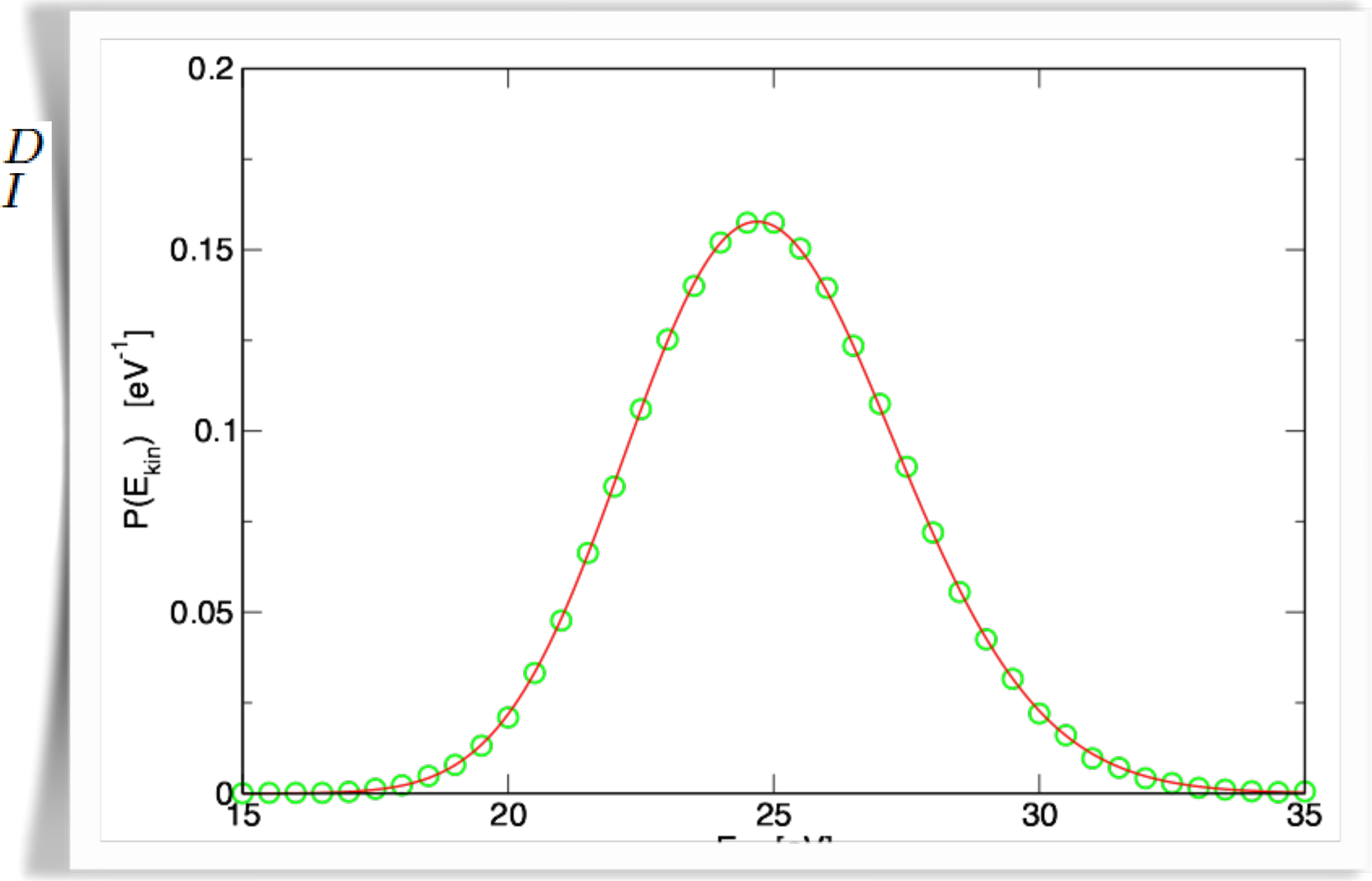
T. D. Kühne and E. Prodan, Annals of Physics **391**, 120 (2018)

Second-Generation CPMD

$$\begin{aligned} M_I \ddot{\boldsymbol{R}}_I &= \underbrace{\boldsymbol{F}_I^{BO} - \gamma_D M_I \dot{\boldsymbol{R}}_I}_{} + \boldsymbol{\Xi}_I^D \\ &= \boldsymbol{F}_I^{PC} + \boldsymbol{\Xi}_I^D \end{aligned}$$

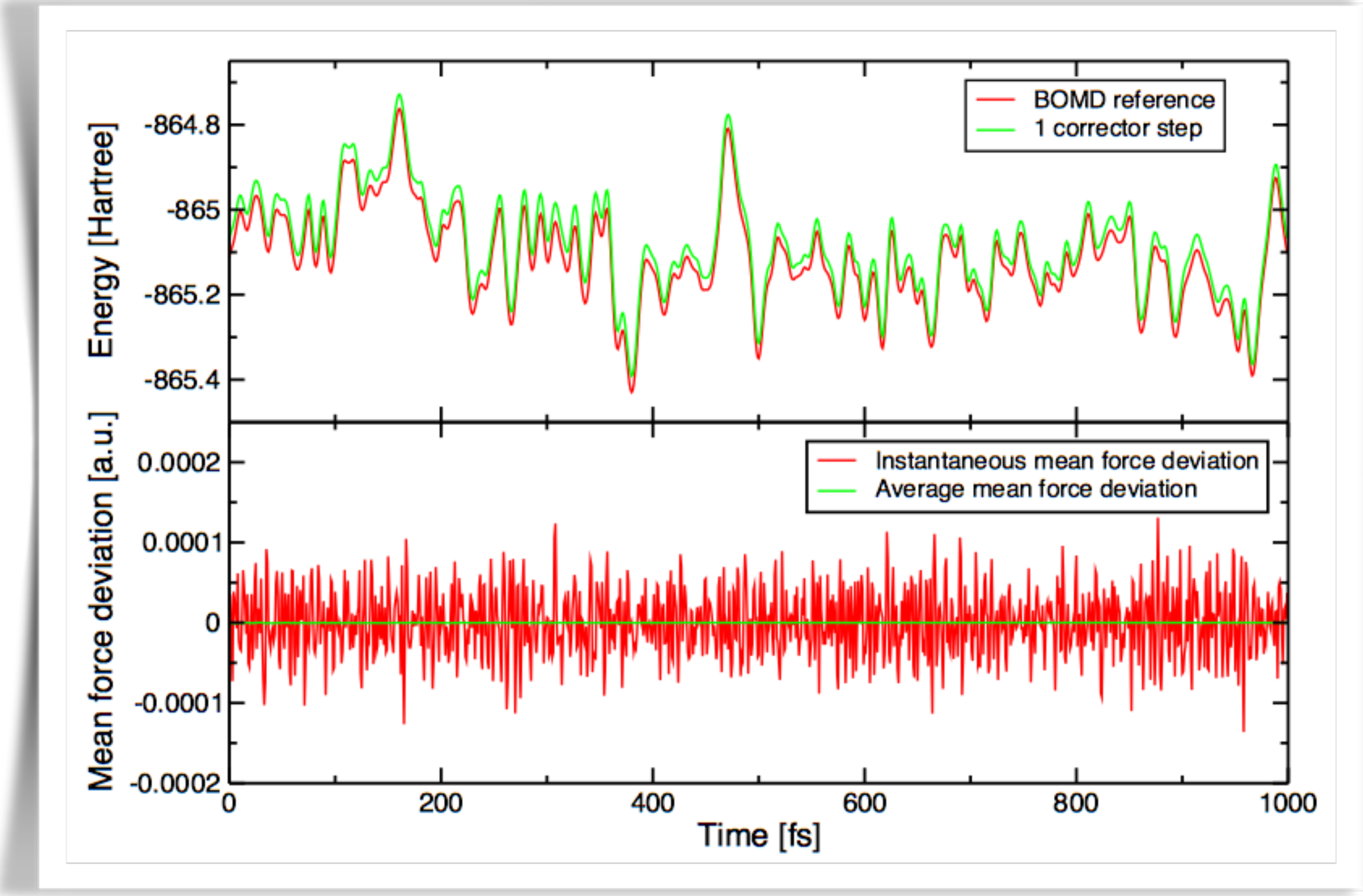
$$\left\langle \boldsymbol{\Xi}_I^D(0)\, \boldsymbol{\Xi}_I^D(t) \right\rangle = 2\gamma_D M_I k_B T \delta(t)$$

$$\left\langle \tfrac{1}{2} M_I \dot{\boldsymbol{R}}_I^2 \right\rangle = \tfrac{3}{2} k_B T$$



T. D. Kühne, M. Krack, F. Mohamed and M. Parrinello, Phys. Rev. Lett. **98**, 066401 (2007)

Second-Generation CPMD



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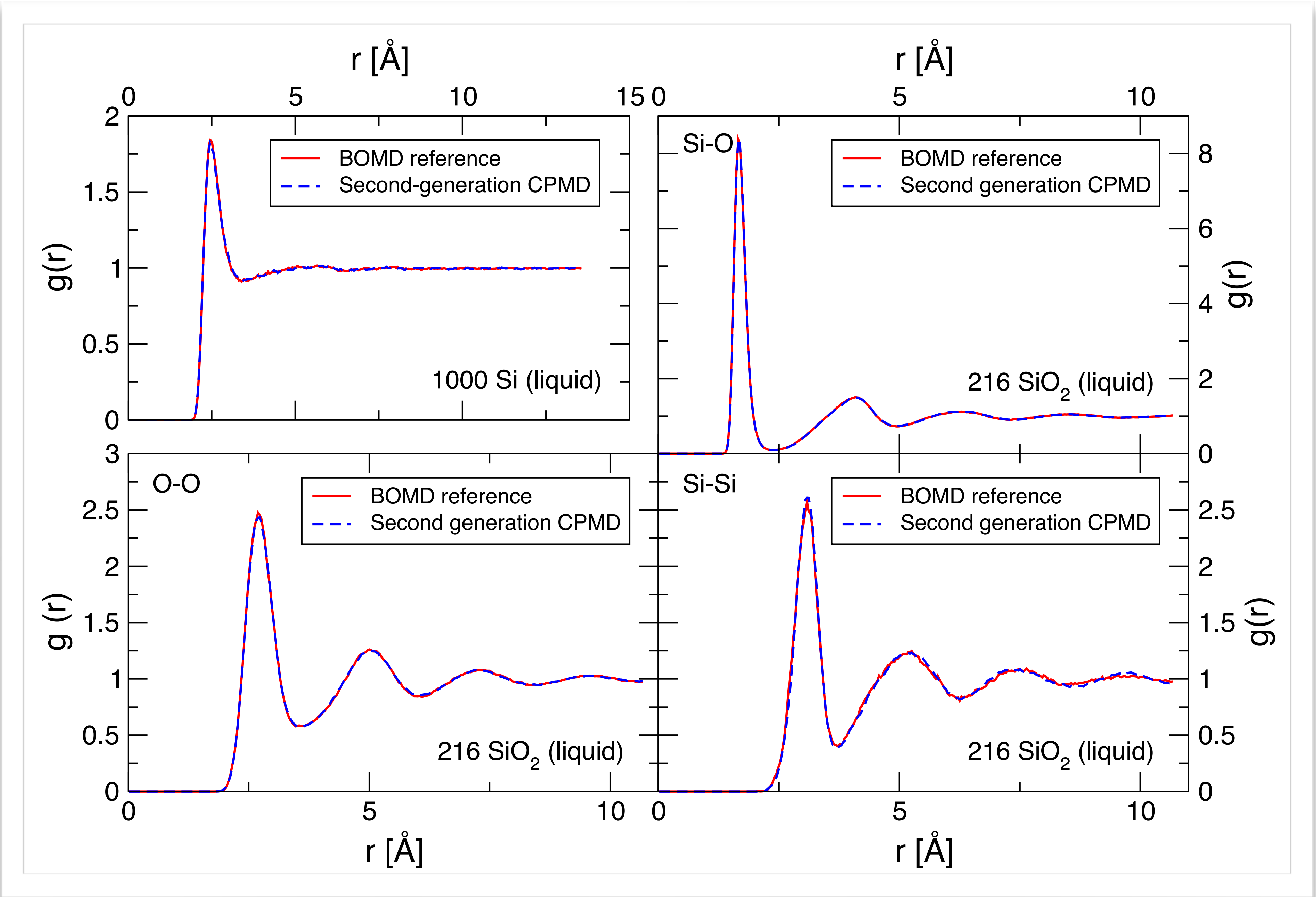

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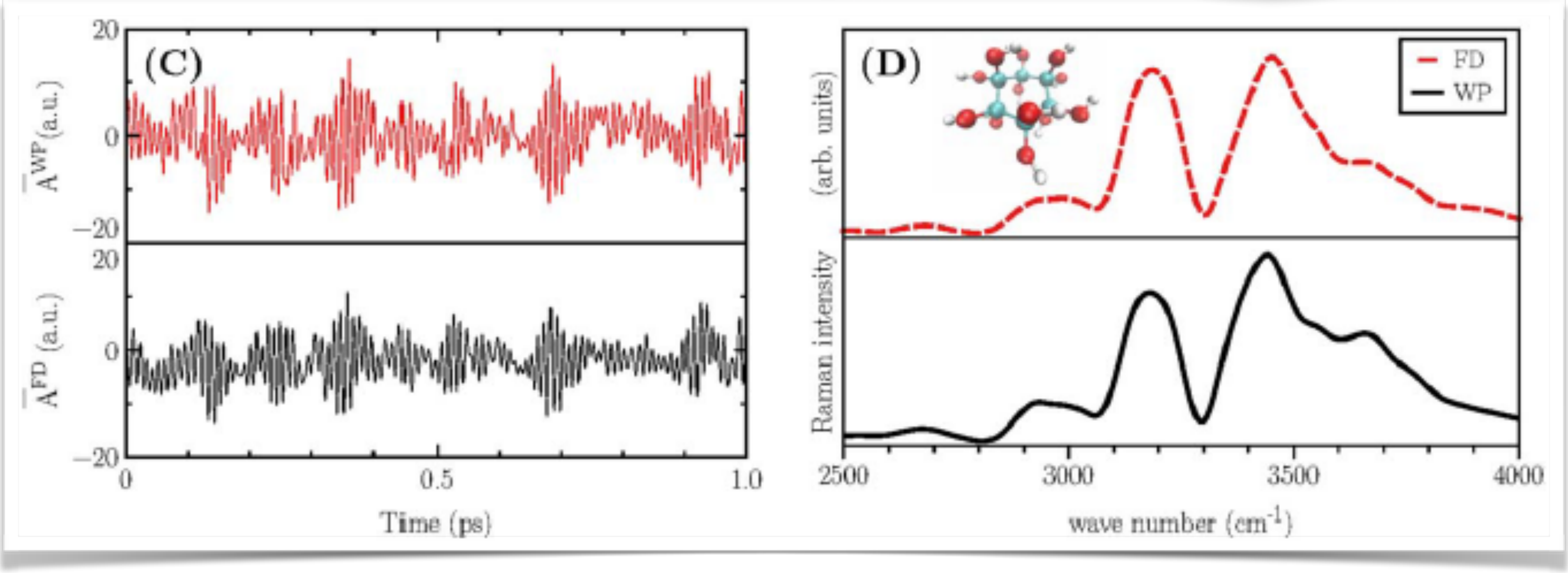
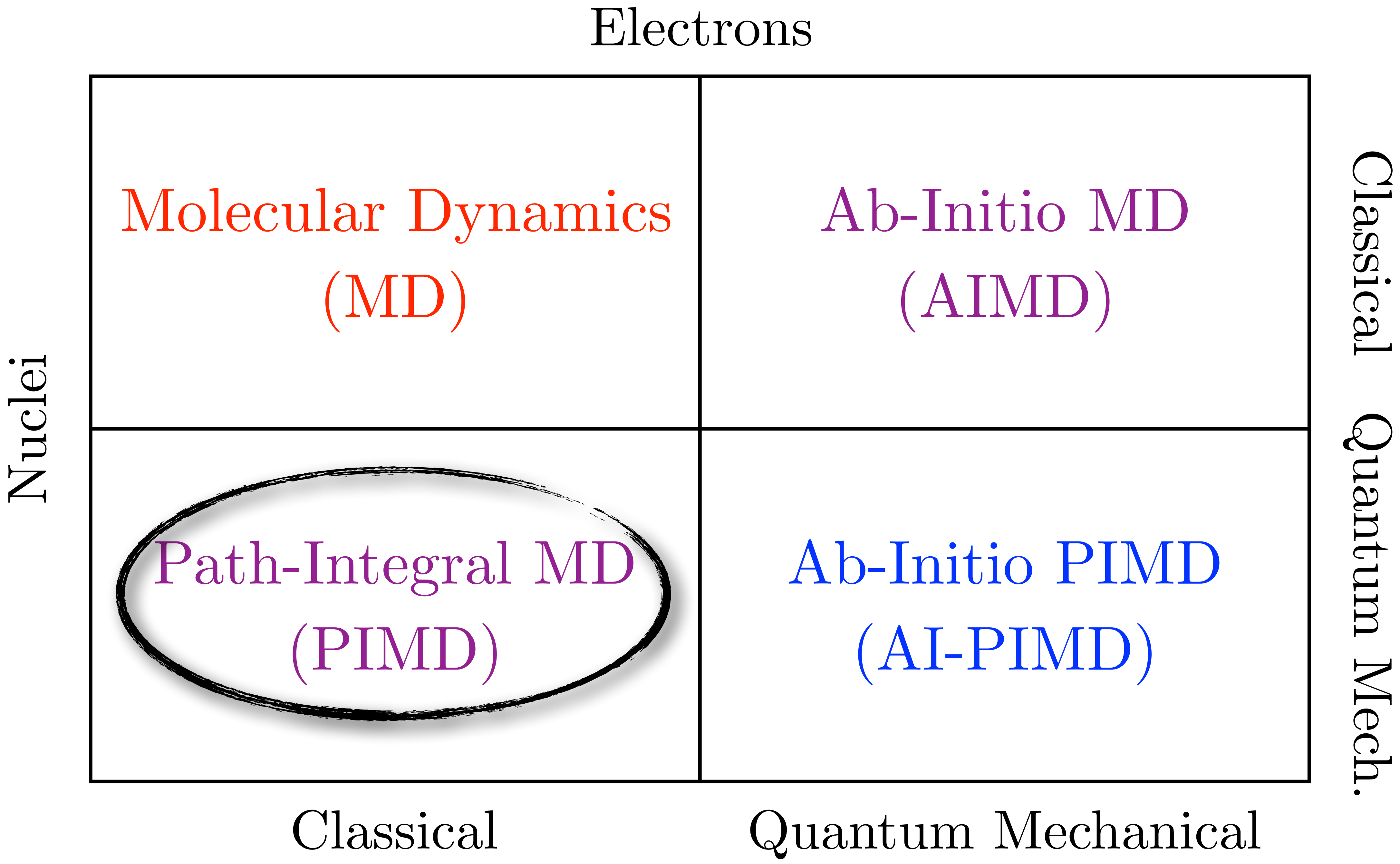
„On-the-fly“ Spectroscopy

$$w_n(\mathbf{r}-\mathbf{R}) = \frac{V}{(2\pi)^3}\int_\Omega d\mathbf{k}\, e^{i\mathbf{k}\cdot\mathbf{R}} \sum_{m=1}^{J} U_{mn}^{(\mathbf{k})}\psi_m^{(\mathbf{k})}(\mathbf{r})$$

$$S_n = \langle w_n|\mathbf{r}^2|w_n\rangle - \langle w_n|\mathbf{r}|w_n\rangle^2 \Rightarrow \boxed{A_n = \beta S_n^3}$$



P. Partovi-Azar and T. D. Kühne, J. Comp. Chem. **36**, 2188 (2015)



Nuclei \ Electrons	Classical	Quantum Mechanical
Classical	Molecular Dynamics (MD)	Ab-Initio MD (AIMD)
Quantum Mech.	Path-Integral MD (PIMD)	Ab-Initio PIMD (AI-PIMD)

$$\varepsilon(\boldsymbol{R}) + V_{KK}(\boldsymbol{R}) \approx \sum_I v_1(\boldsymbol{R}_I) + \sum_{I<J} v_2(\boldsymbol{R}_I, \boldsymbol{R}_J) + \ldots$$

$$\left[\mathcal{H}_K(\boldsymbol{R}) + \varepsilon(\boldsymbol{R})\right] \chi(\boldsymbol{R}) = E\chi(\boldsymbol{R})$$

Importance of NQE

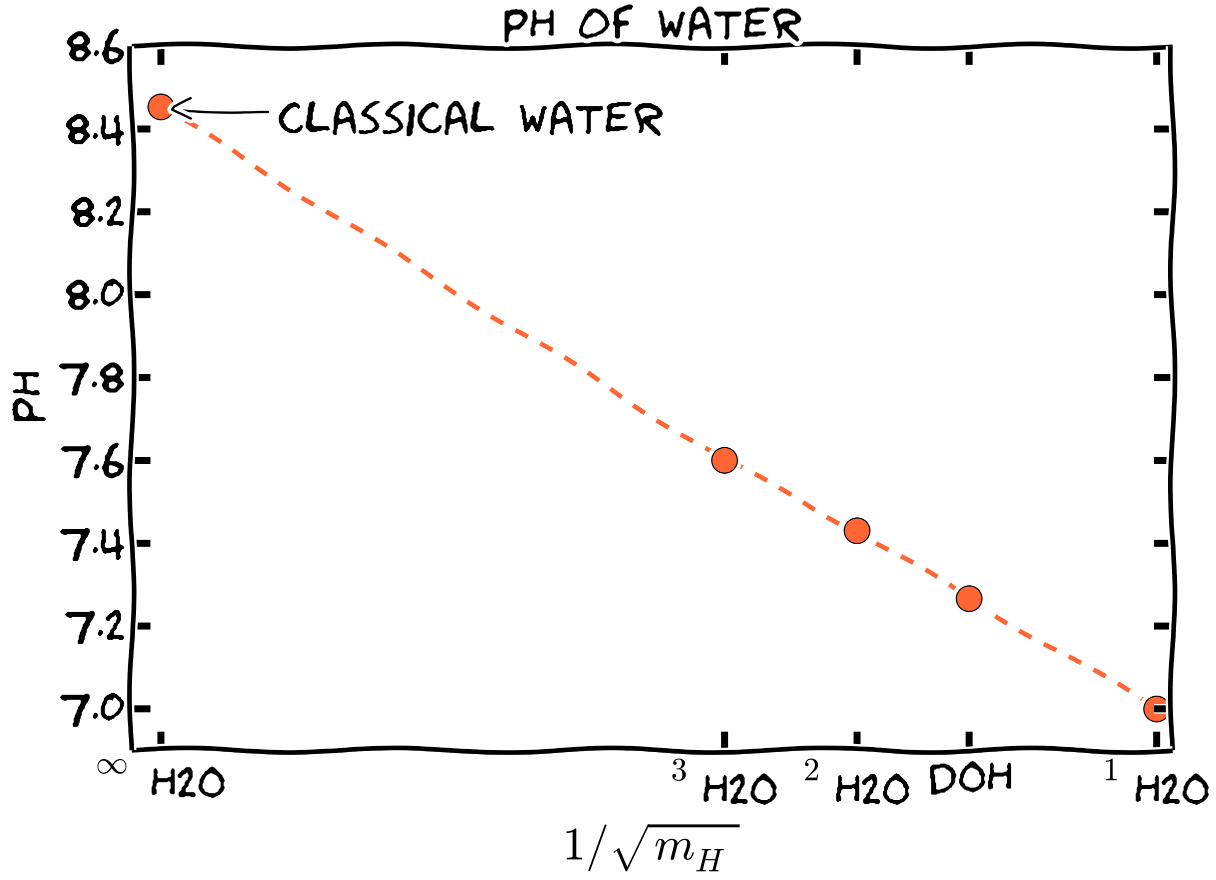
- Classically the average value of the kinetic energy follows equipartition (Boltzmann operator factorizes) and is given by

$$\langle K \rangle = \frac{3Nk_BT}{2}$$

- In quantum mechanics, Boltzmann operator does not factorize (because momentum and position do not commute). E.g. for a system of harmonic oscillators:

$$\langle K^{harm}_{qm} \rangle = \sum_i \frac{\hbar\sqrt{k_i}}{4\sqrt{m_i}} \coth\left(\frac{\beta\hbar\sqrt{k_i}}{2\sqrt{m_i}}\right)$$

mass dependence

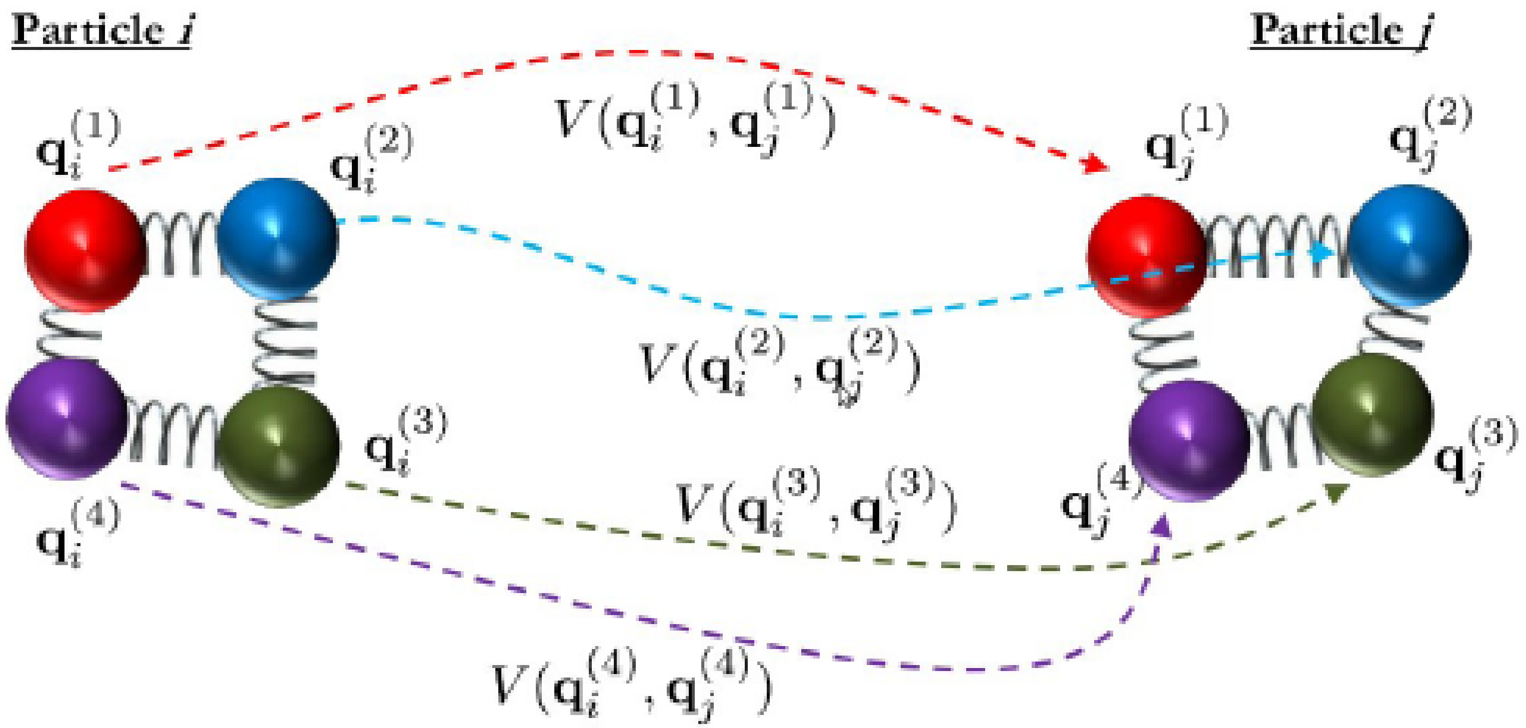


Path-Integral MD

$$Z = \mathrm{Tr}\left[e^{-\beta \mathcal{H}}\right] = \mathrm{Tr}\left[\left(e^{-\beta_n \mathcal{H}_n}\right)^n\right], \text{ mit } \beta_n = \frac{\beta}{n}$$

$$= \lim_{n\to\infty} \left(\tfrac{1}{2\pi\hbar}\right)^n \int d^n q \int d^n p \; e^{-\beta_n H_n}, \text{ mit}$$

$$H_n = \sum_{I=1}^{N} \sum_{j=1}^{n} \left[\underbrace{\frac{\boldsymbol{P}_I^{2\,(j)}}{2M_I}}_{E_{kin}^{(j)}} + \underbrace{\frac{M_I}{2}\omega_n^2 \left(\boldsymbol{R}_I^{(j)} - \boldsymbol{R}_I^{(j-1)}\right)^2}_{\text{Harmonic springs between beads}} \right] + \sum_{j=1}^{n} \underbrace{V\left(\boldsymbol{R}_1^{(j)}, ..., \boldsymbol{R}_N^{(j)}\right)}_{V_{ext}^{(j)}}$$

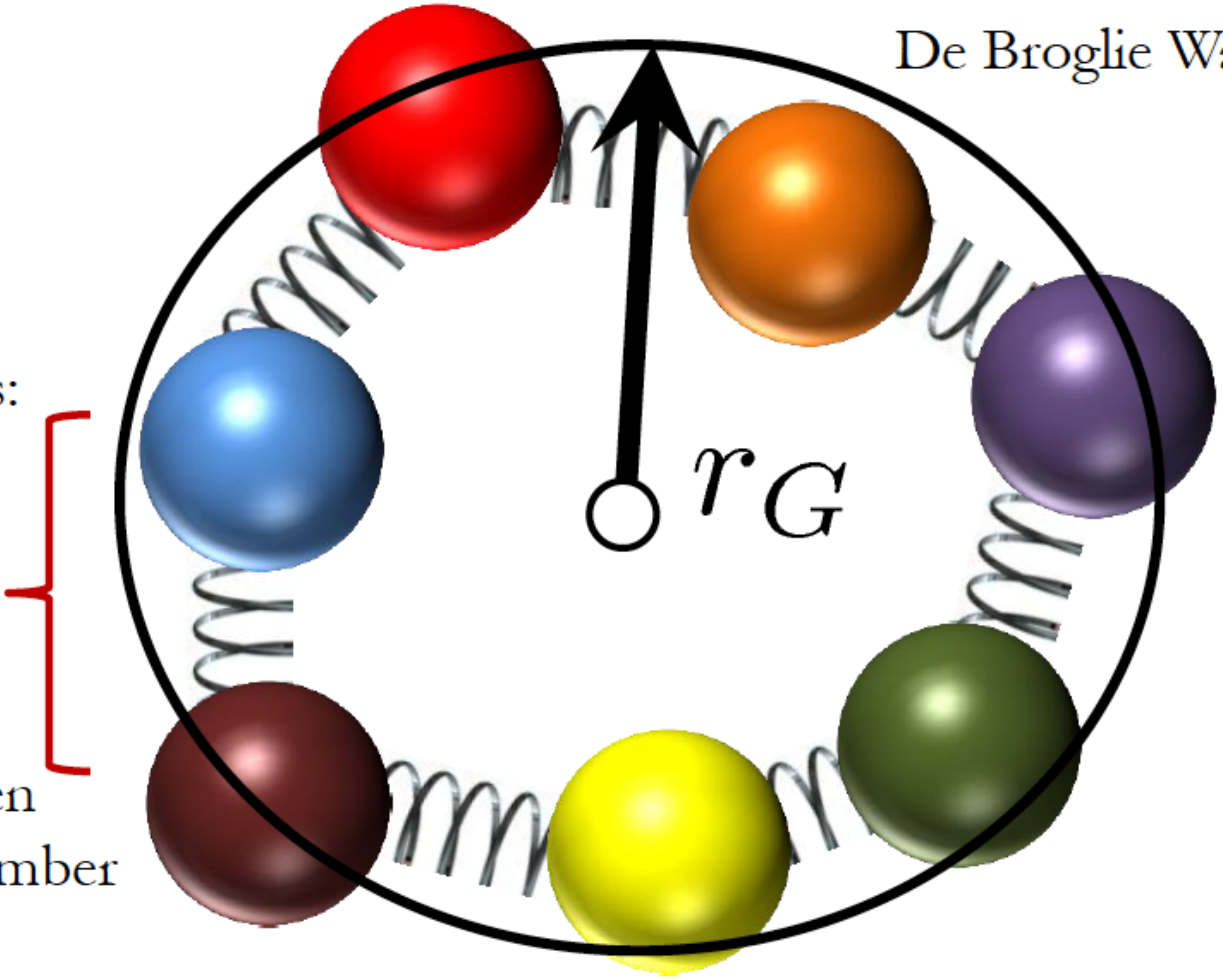


Path-Integral MD

- **Radius of gyration** – the spread in imaginary time. For a free particle the root mean square radius of gyration is:

$$\langle r_G^2(T)\rangle^{1/2} = \frac{\Lambda(T)}{\sqrt{8\pi}} \qquad \Lambda(T) = \frac{h}{\sqrt{2\pi m k_\mathrm{B} T}}$$

De Broglie Wavelength of the particle.



- **Bead to bead distance.** For a free particle the average is:

$$\sqrt{\frac{\beta\hbar^2}{nm}}$$

Note: distance between beads decreases as number of beads increases.

- **Centroid:** The centre of the polymer.

$$q_c = \frac{1}{n}\sum_{k=1}^{n} q_k$$

Ring-Polymer MD

Path Integral MD uses ring polymer trajectories to estimate static averages of the form:

$$\langle A \rangle = \frac{1}{Z}\mathrm{Tr}[e^{-\beta \hat{H}}\hat{A}]$$

However, many important quantities are given by dynamic averages:

Time correlation function

$$c_{AB}(t) = \mathrm{Tr}[e^{-\beta \hat{H}}\hat{A}(0)\hat{B}(t)]$$

Diffusion coefficient

$$D(T) = \frac{1}{3}\int_0^\infty c_{\mathbf{v}\cdot\mathbf{v}}(t)\,dt$$

velocity

IR spectrum (dipole adsorption cross section)

$$n(\omega)\alpha(\omega) = \frac{\pi\omega}{3\hbar c V \epsilon_0}(1 - e^{-\beta\hbar\omega})C_{\mu\cdot\mu}(\omega)$$

$$C_{\mu\cdot\mu}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t}c_{\mu\cdot\mu}(t)\,dt$$

dipole

PIMD does NOT give access to real time propagation (momenta are fictitious)

Ring-Polymer MD

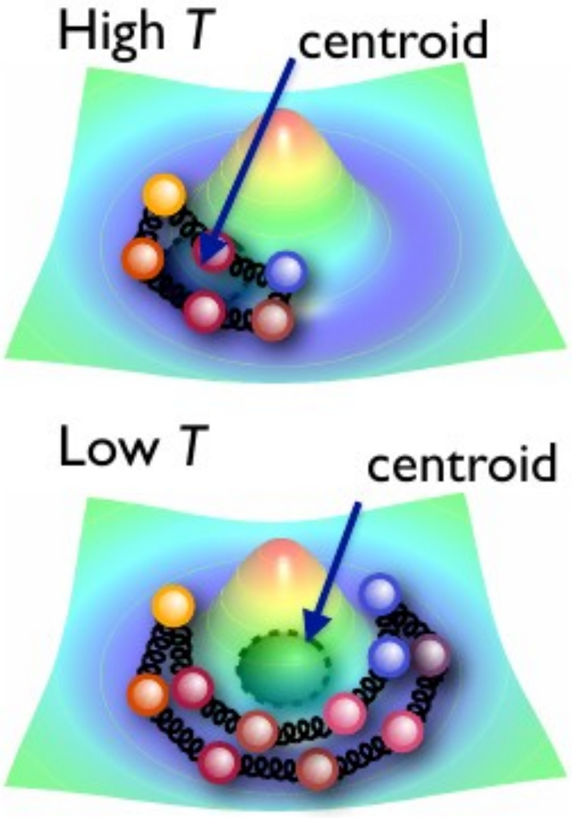
PIMD does NOT give access to real time propagation.
However, by normal mode transformation of free ring-polymer modes:

$$H_0 = \sum_j^N \sum_{s=0}^{n-1} \left[\frac{\tilde{\mathbf{p}}_s^j}{2(m^j)'} + \frac{1}{2} m^j \omega_s^2 (\tilde{\mathbf{q}}_s^j)^2 \right] \quad \begin{aligned} \omega_s &= 2\omega_n \sin(s\pi/n) \\ \omega_n &= n k_b T/\hbar \end{aligned}$$

$s=0 \Rightarrow$ centroid mode; $s \neq 0 \Rightarrow$ internal modes

Ring polymer molecular dynamics (RPMD) [1]
Masses of the beads are the real masses
Problem: beads frequencies resonate with physical frequencies

Centroid MD (CMD) [2]
Centroid moves in the effective potential generated by the internal modes of the ring
Beads have small masses: need for a special thermostat
Problem: curvature problem



[1] Craig and Manolopoulos, JCP ***121****, 3368 (2004)*
[2] Cao and Voth, JCP ***100****, 5093 (1994)*

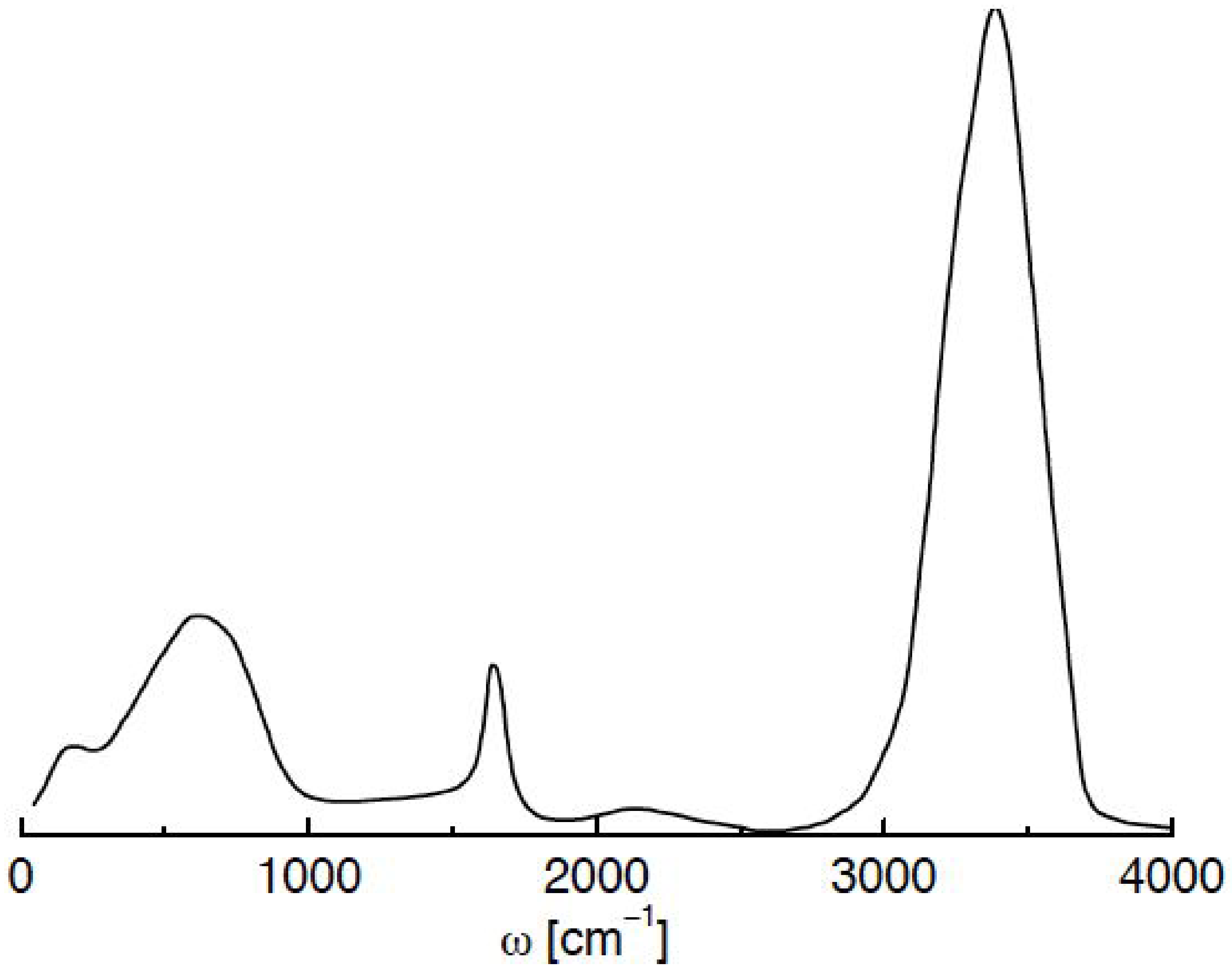
Electrons

Nuclei	Classical	Quantum Mechanical
Classical	Molecular Dynamics (MD)	Ab-Initio MD (AIMD)
Quantum Mech.	Path-Integral MD (PIMD)	Ab-Initio PIMD (AI-PIMD)

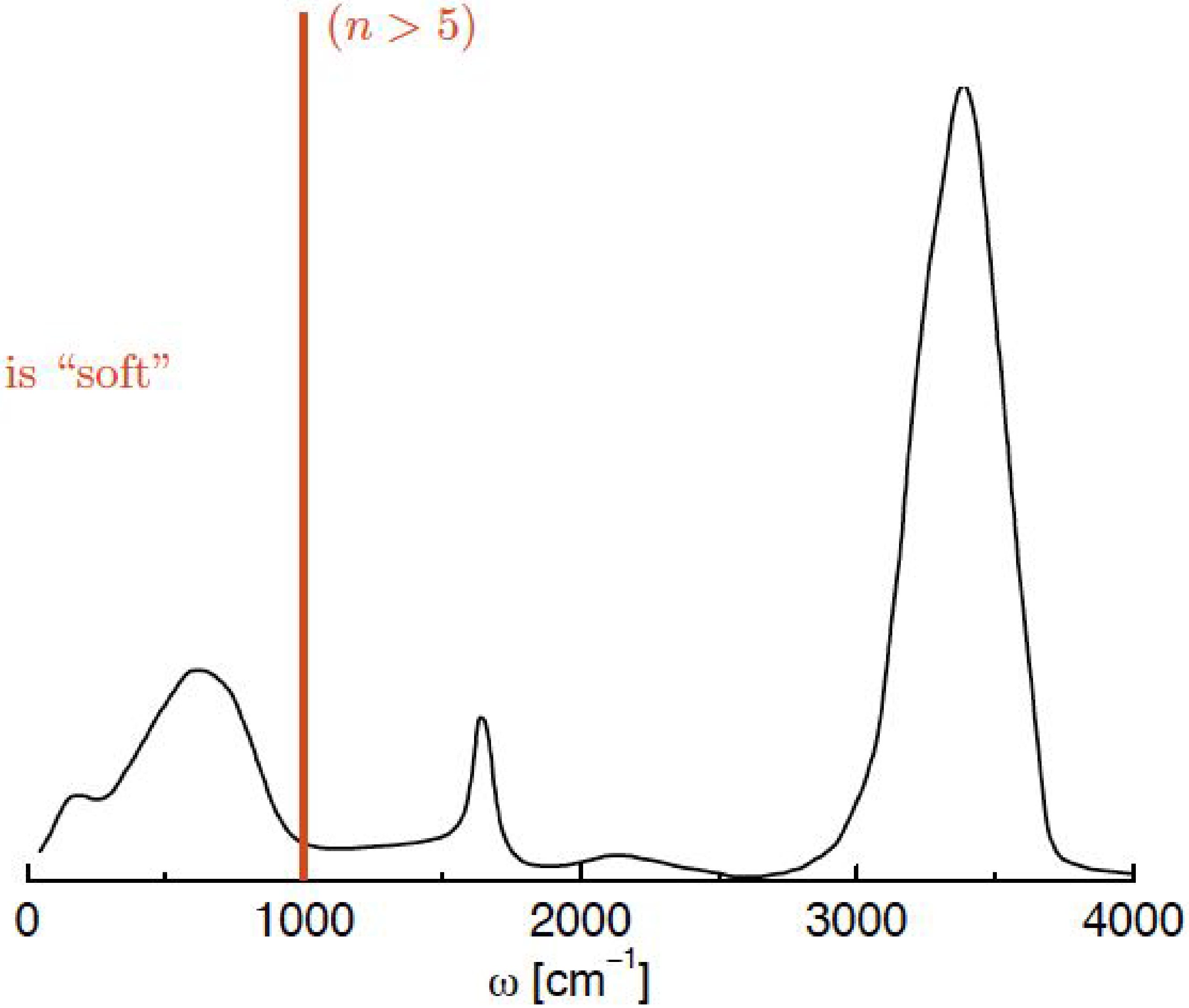
$$\mathcal{H}_e(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R}) = \varepsilon(\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})$$

$$\left[\mathcal{H}_K(\boldsymbol{R}) + \varepsilon(\boldsymbol{R})\right]\chi(\boldsymbol{R}) = E\chi(\boldsymbol{R})$$

Ring Polymer Contraction



Ring Polymer Contraction

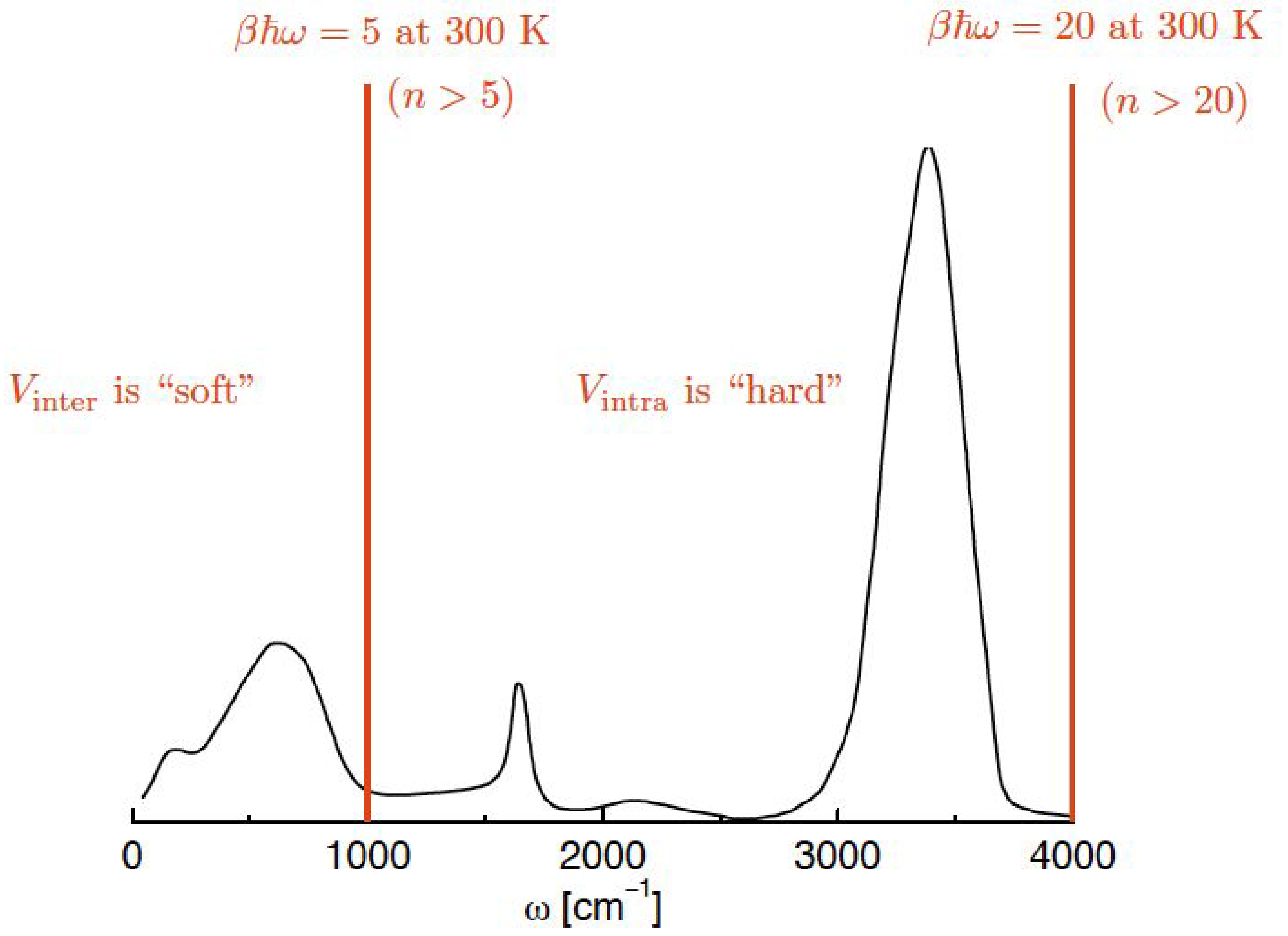


$\beta\hbar\omega = 5$ at 300 K

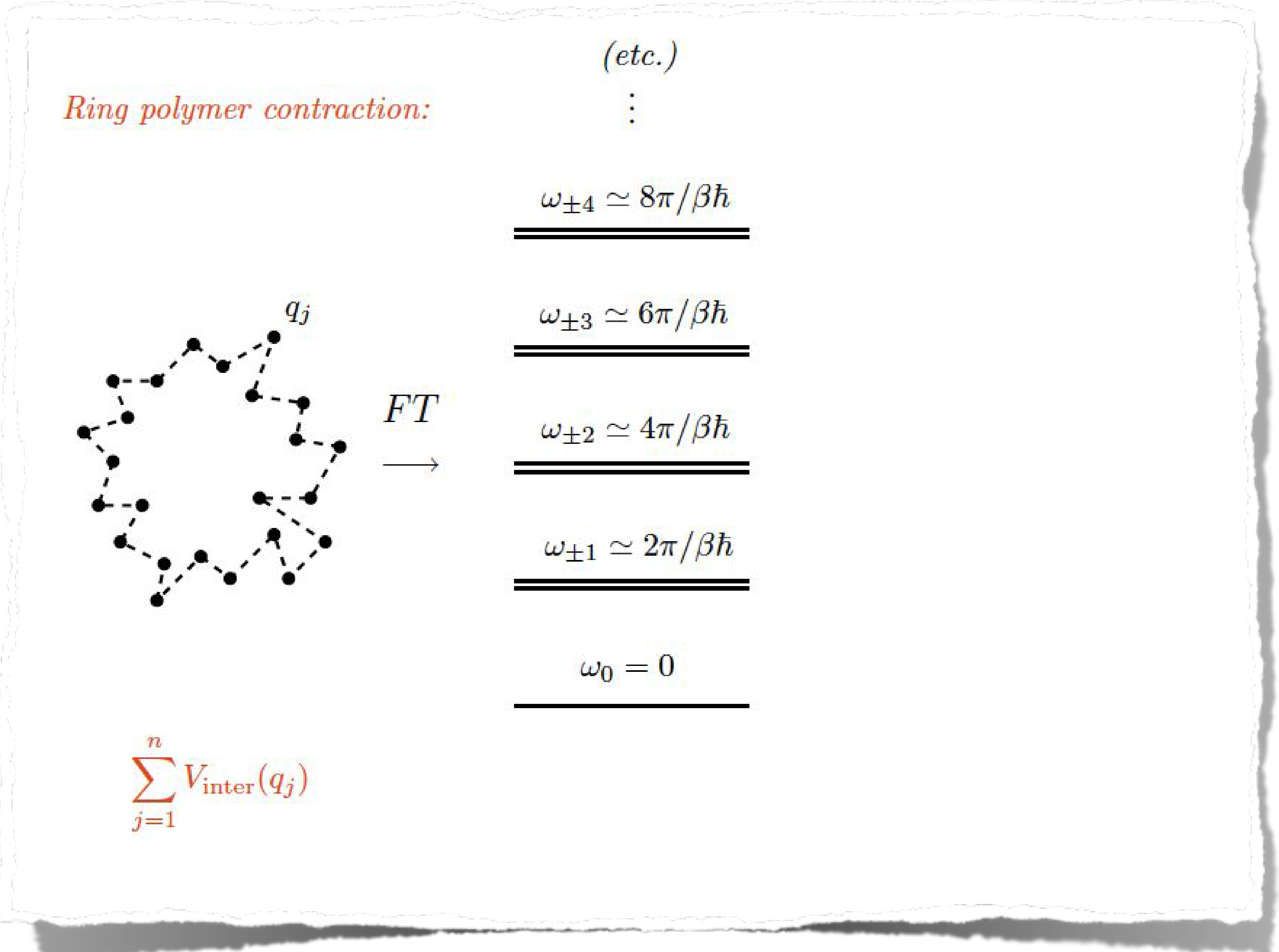
$(n > 5)$

V_{inter} is “soft”

Ring Polymer Contraction

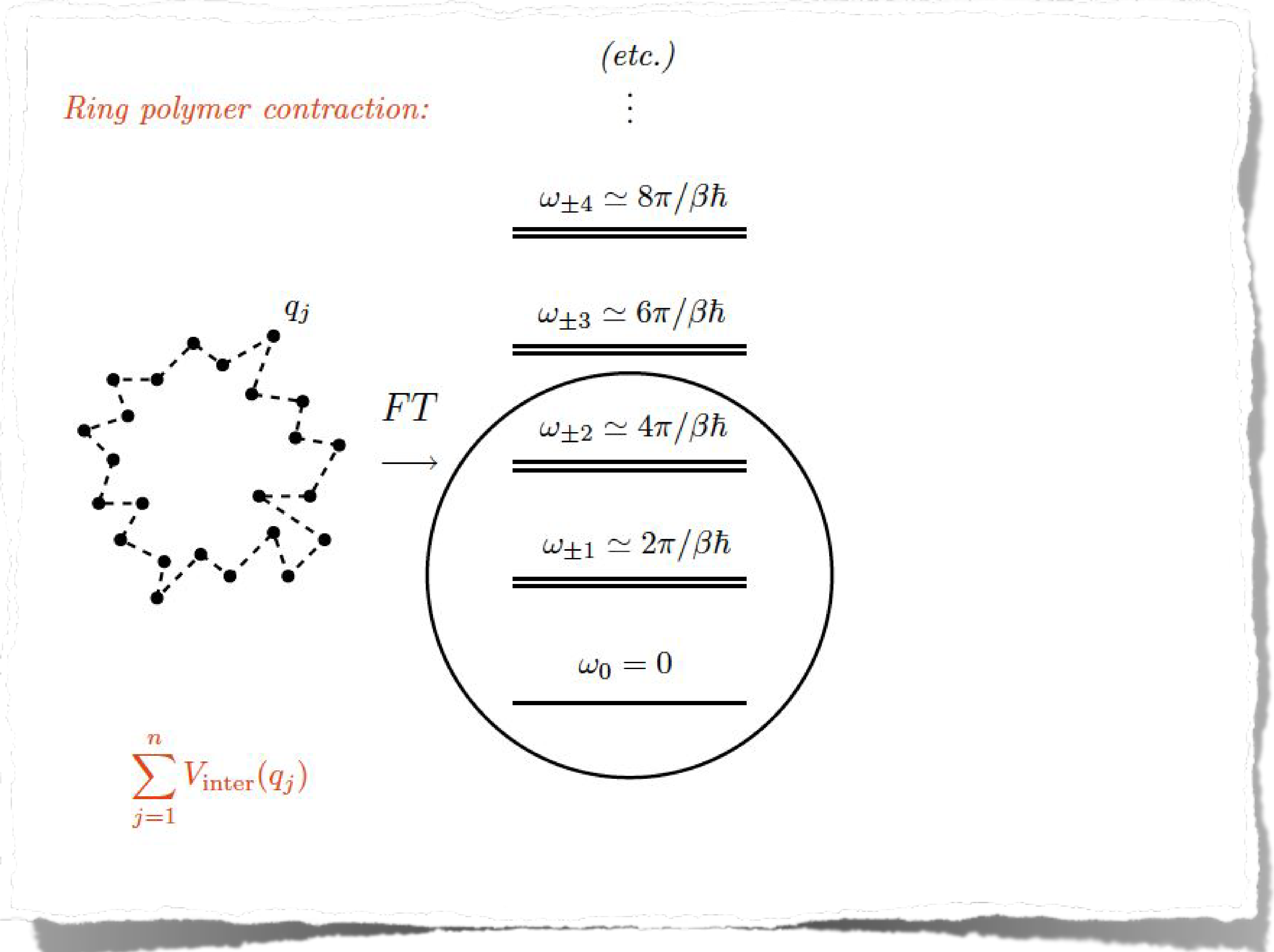


Ring Polymer Contraction



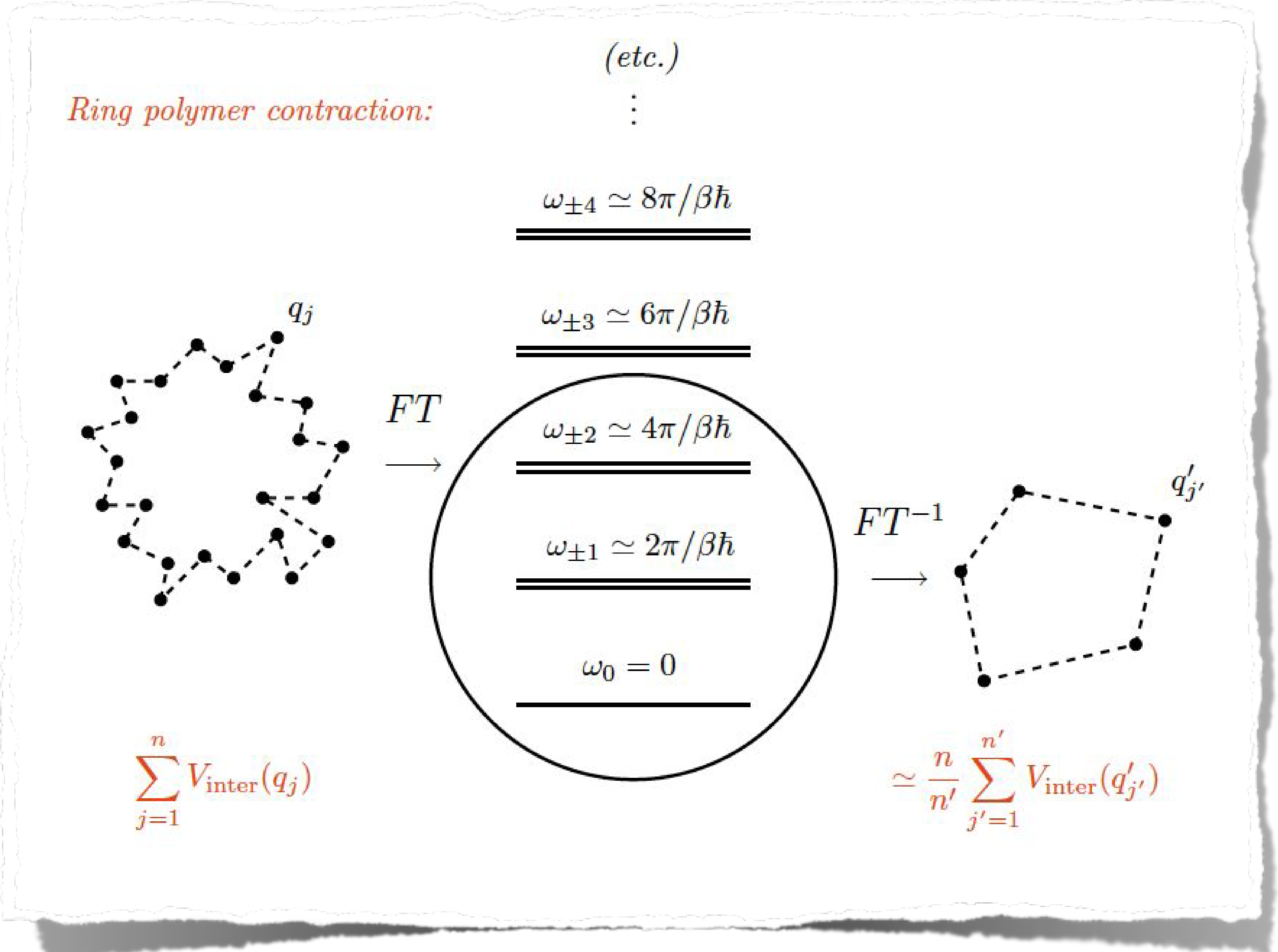
T. E. Markland and D. E. Manolopoulos, J. Chem. Phys. **129**, 024105 (2008)

Ring Polymer Contraction



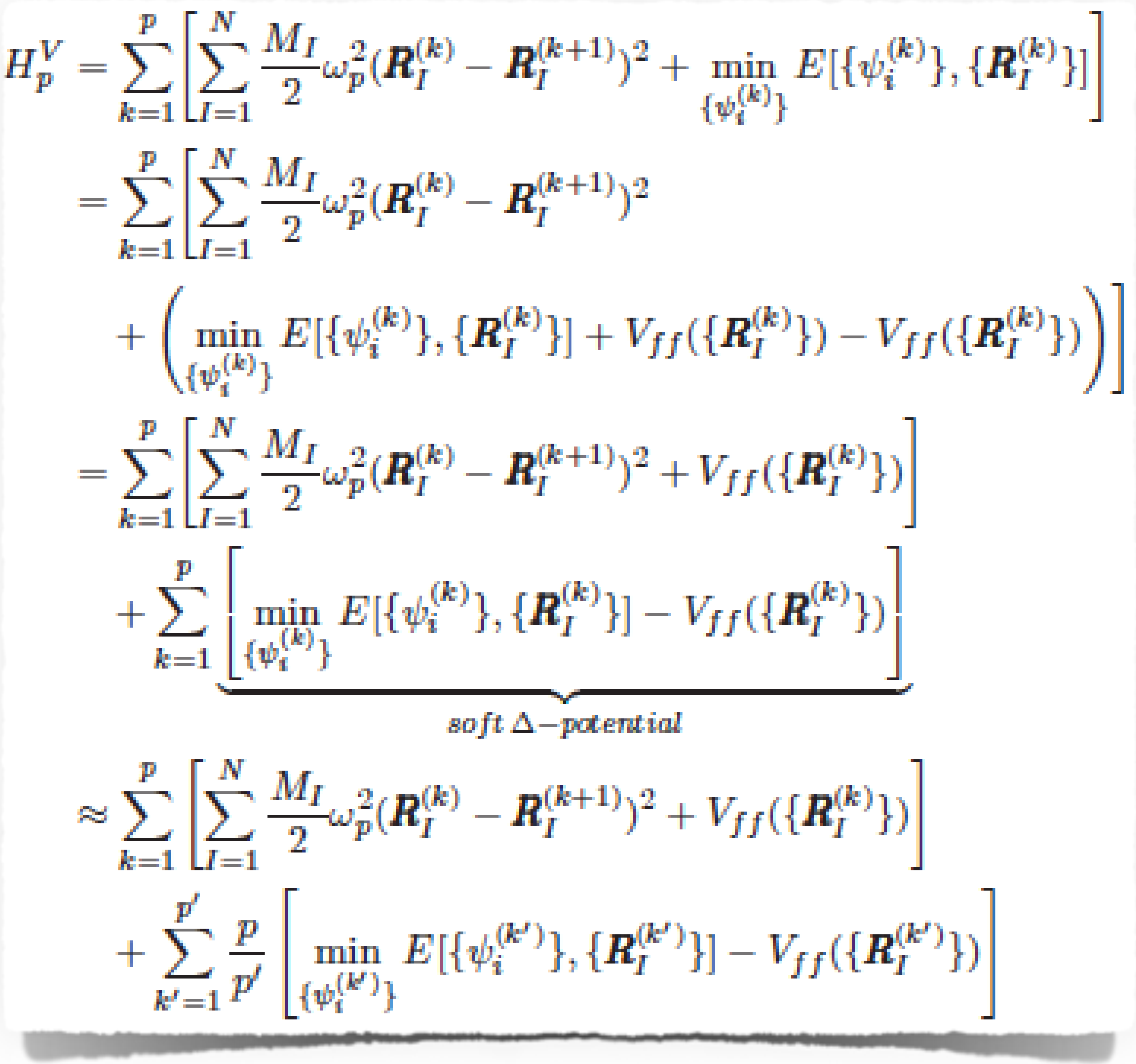
T. E. Markland and D. E. Manolopoulos, J. Chem. Phys. **129**, 024105 (2008)

Ring Polymer Contraction



T. E. Markland and D. E. Manolopoulos, J. Chem. Phys. **129**, 024105 (2008)

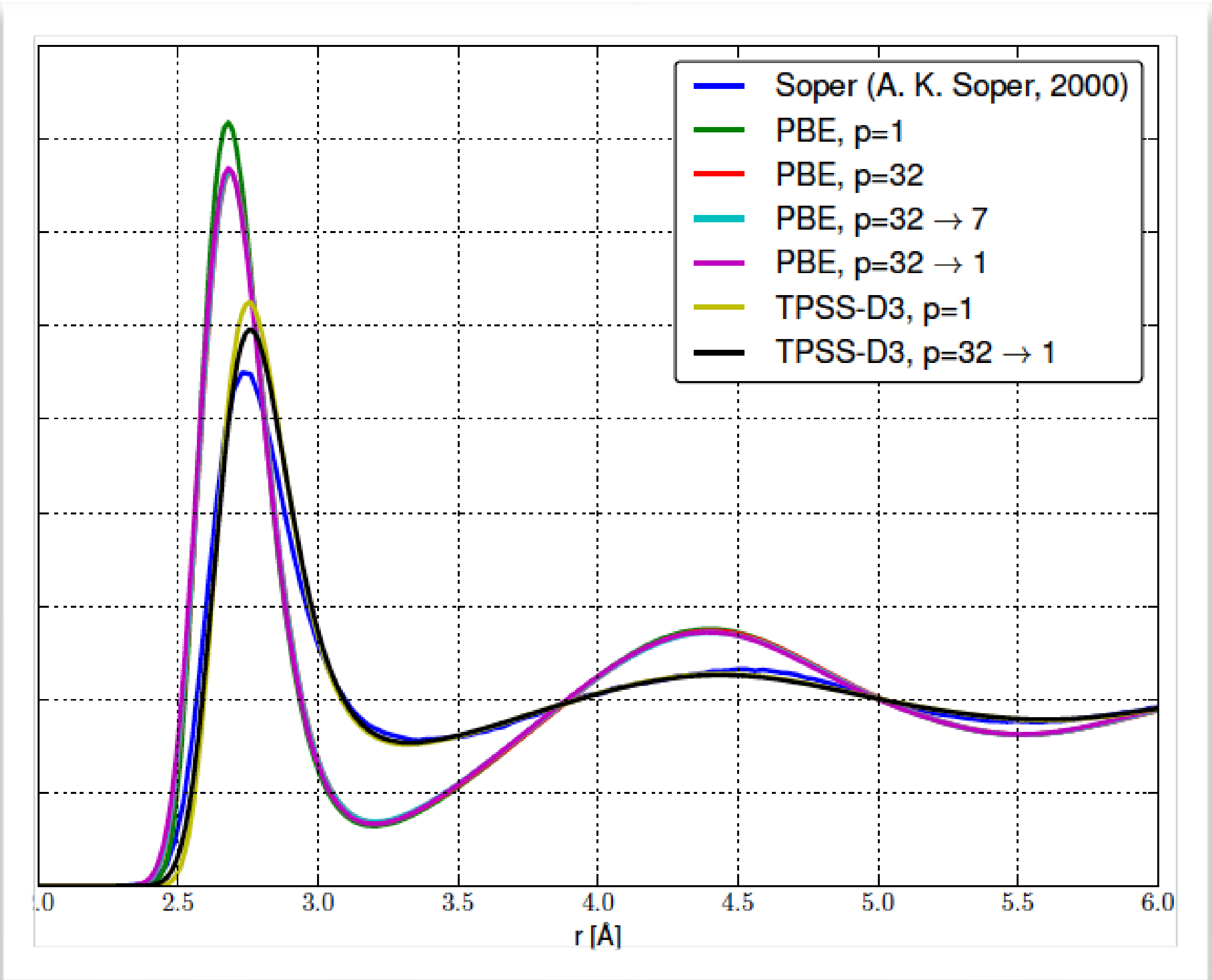
Quantum-RPC

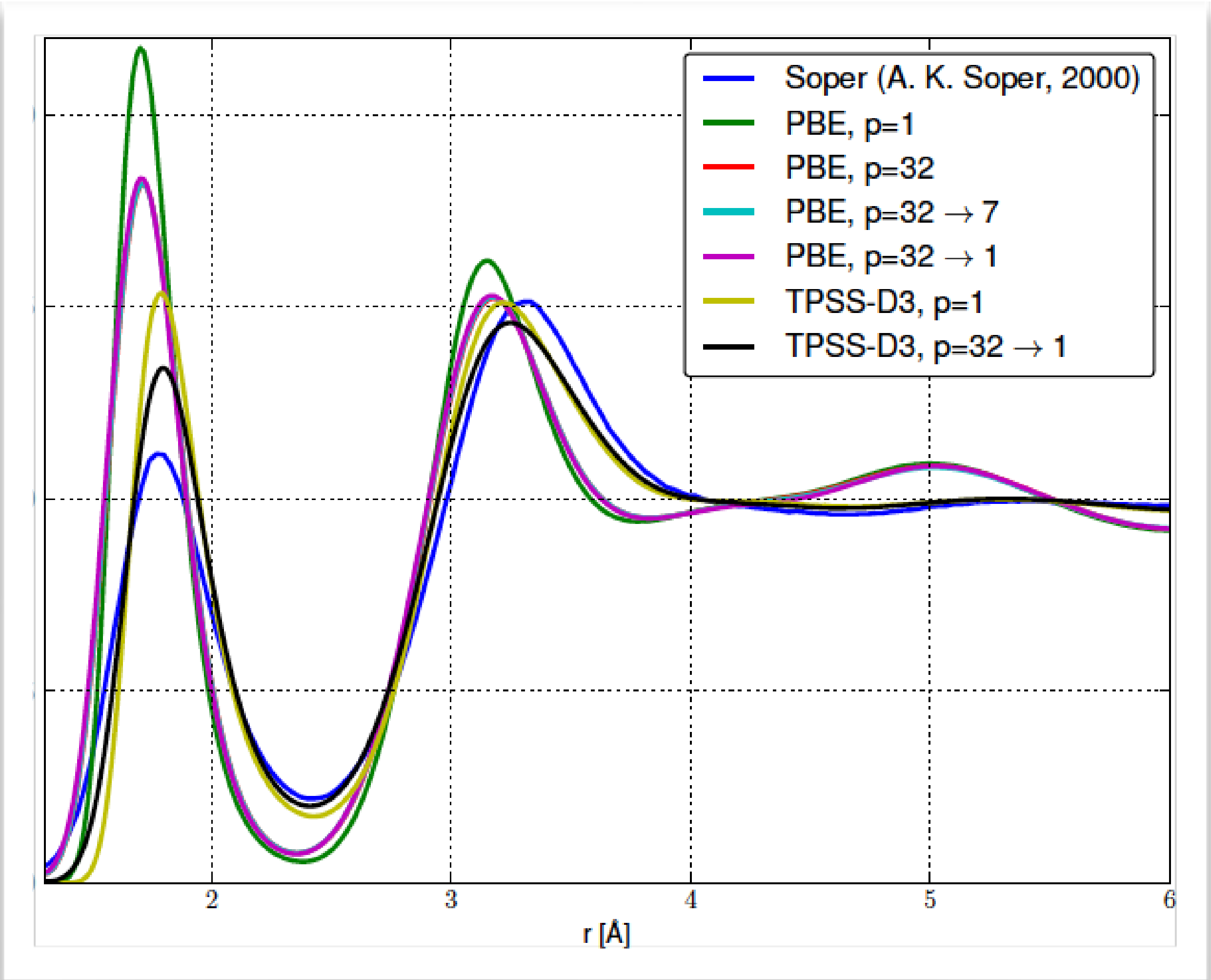


$$
\begin{aligned}
H_p^V &= \sum_{k=1}^{p}\left[\sum_{I=1}^{N}\frac{M_I}{2}\omega_p^2(\boldsymbol{R}_I^{(k)}-\boldsymbol{R}_I^{(k+1)})^2 + \min_{\{\psi_i^{(k)}\}} E[\{\psi_i^{(k)}\},\{\boldsymbol{R}_I^{(k)}\}]\right] \\
&= \sum_{k=1}^{p}\left[\sum_{I=1}^{N}\frac{M_I}{2}\omega_p^2(\boldsymbol{R}_I^{(k)}-\boldsymbol{R}_I^{(k+1)})^2\right. \\
&\quad \left. + \left(\min_{\{\psi_i^{(k)}\}} E[\{\psi_i^{(k)}\},\{\boldsymbol{R}_I^{(k)}\}] + V_{ff}(\{\boldsymbol{R}_I^{(k)}\}) - V_{ff}(\{\boldsymbol{R}_I^{(k)}\})\right)\right] \\
&= \sum_{k=1}^{p}\left[\sum_{I=1}^{N}\frac{M_I}{2}\omega_p^2(\boldsymbol{R}_I^{(k)}-\boldsymbol{R}_I^{(k+1)})^2 + V_{ff}(\{\boldsymbol{R}_I^{(k)}\})\right] \\
&\quad + \underbrace{\sum_{k=1}^{p}\left[\min_{\{\psi_i^{(k)}\}} E[\{\psi_i^{(k)}\},\{\boldsymbol{R}_I^{(k)}\}] - V_{ff}(\{\boldsymbol{R}_I^{(k)}\})\right]}_{soft\ \Delta-potential} \\
&\approx \sum_{k=1}^{p}\left[\sum_{I=1}^{N}\frac{M_I}{2}\omega_p^2(\boldsymbol{R}_I^{(k)}-\boldsymbol{R}_I^{(k+1)})^2 + V_{ff}(\{\boldsymbol{R}_I^{(k)}\})\right] \\
&\quad + \sum_{k'=1}^{p'}\frac{p}{p'}\left[\min_{\{\psi_i^{(k')}\}} E[\{\psi_i^{(k')}\},\{\boldsymbol{R}_I^{(k')}\}] - V_{ff}(\{\boldsymbol{R}_I^{(k')}\})\right]
\end{aligned}
$$

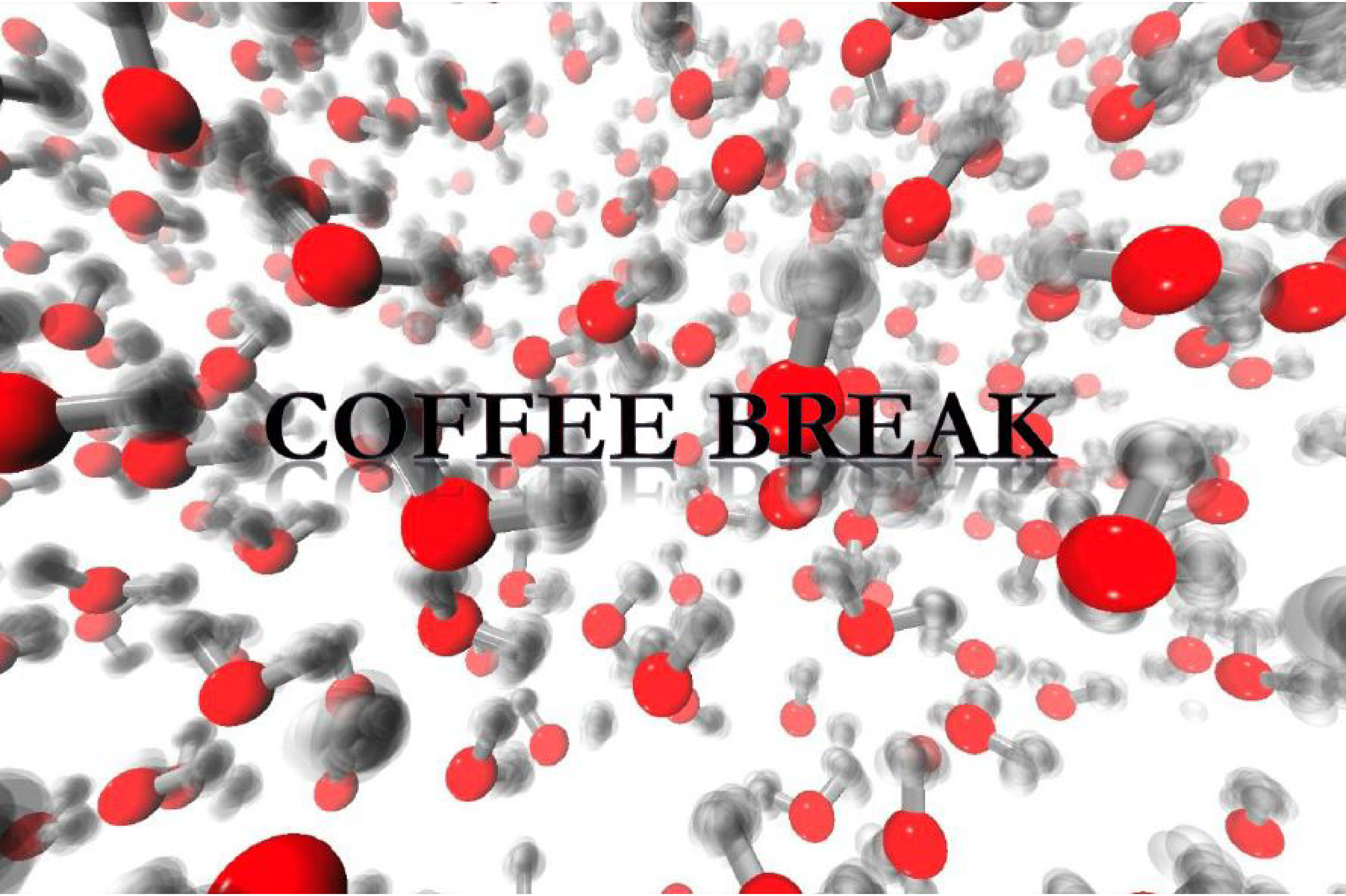
C. John, T. Spura, S. Habershon and T. D. Kühne, Phys. Rev. E **93**, 043305 (2016)

Water: Quo Vadis DFT?





C. John, T. Spura, S. Habershon and T. D. Kühne, Phys. Rev. E **93**, 043305 (2016)



COFFEE BREAK