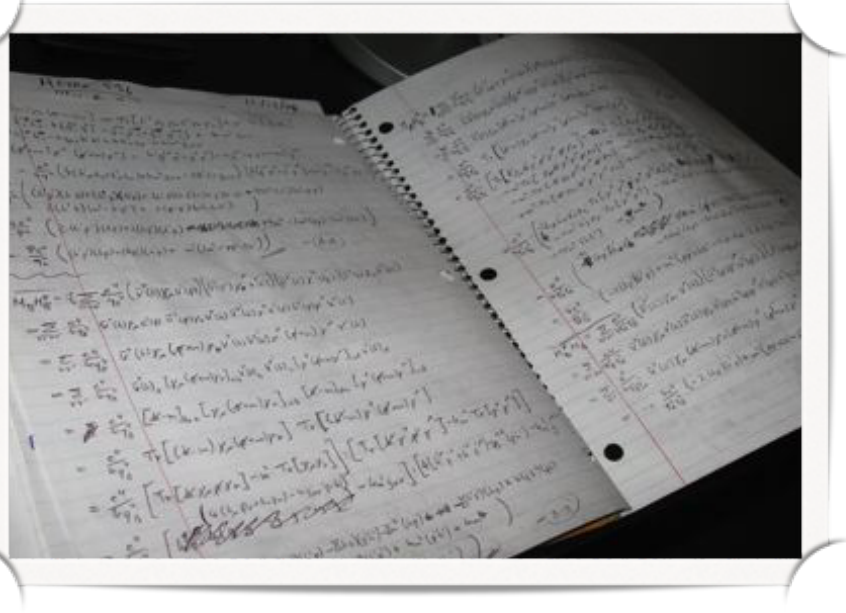
Ab-Initio Path-Integral Molecular Dynamics

Thomas D. Kühne
Chair of Theoretical Chemistry
Dynamics of Condensed Matter

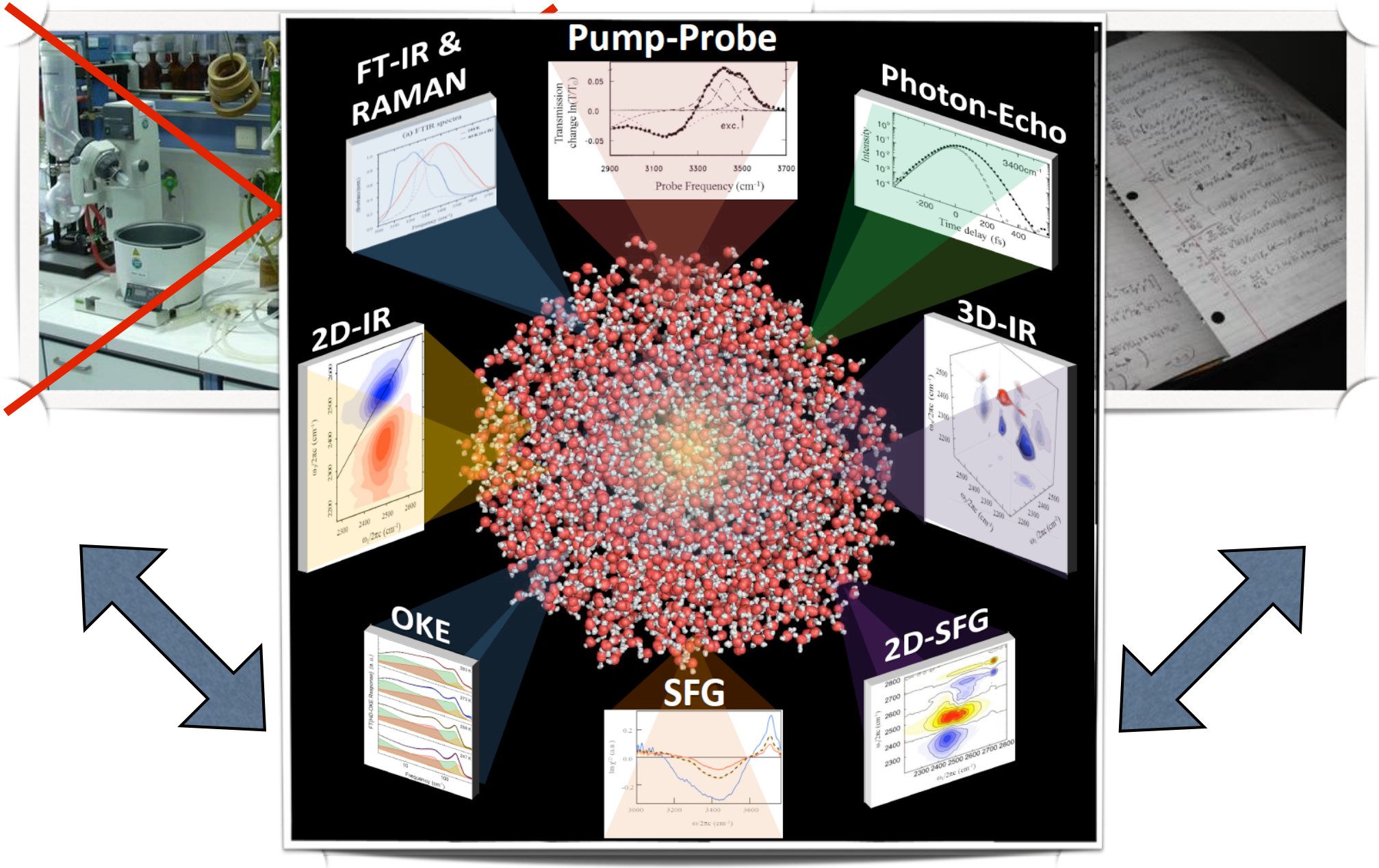
UNIVERSITÄT PADERBORN
Die Universität der Informationsgesellschaft

The Virtual Chemistry Lab

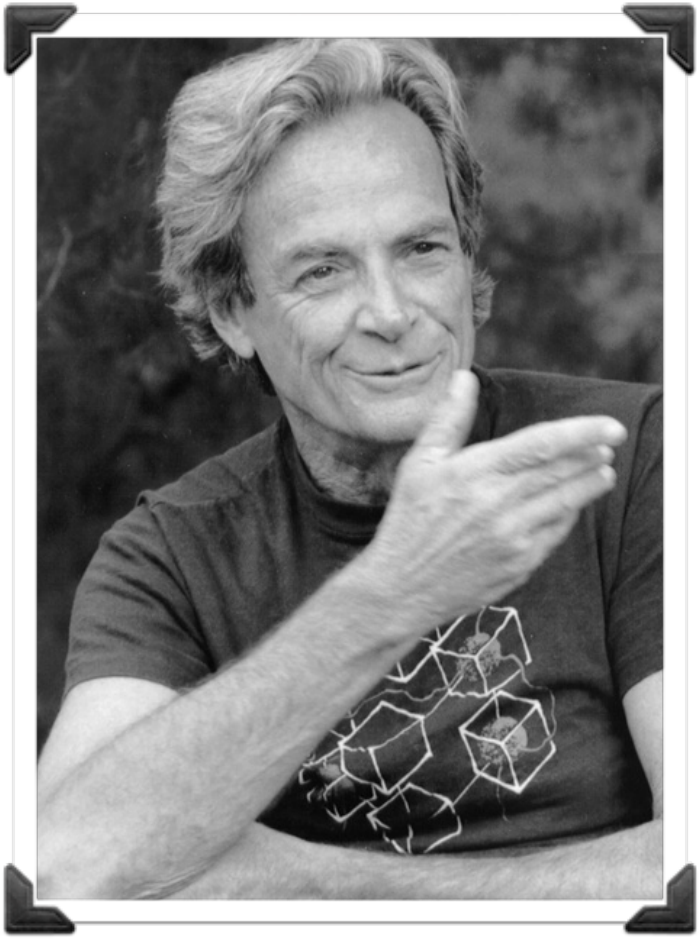
The Virtual Chemistry Lab



The Virtual Chemistry Lab



The Virtual Chemistry Lab



„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“

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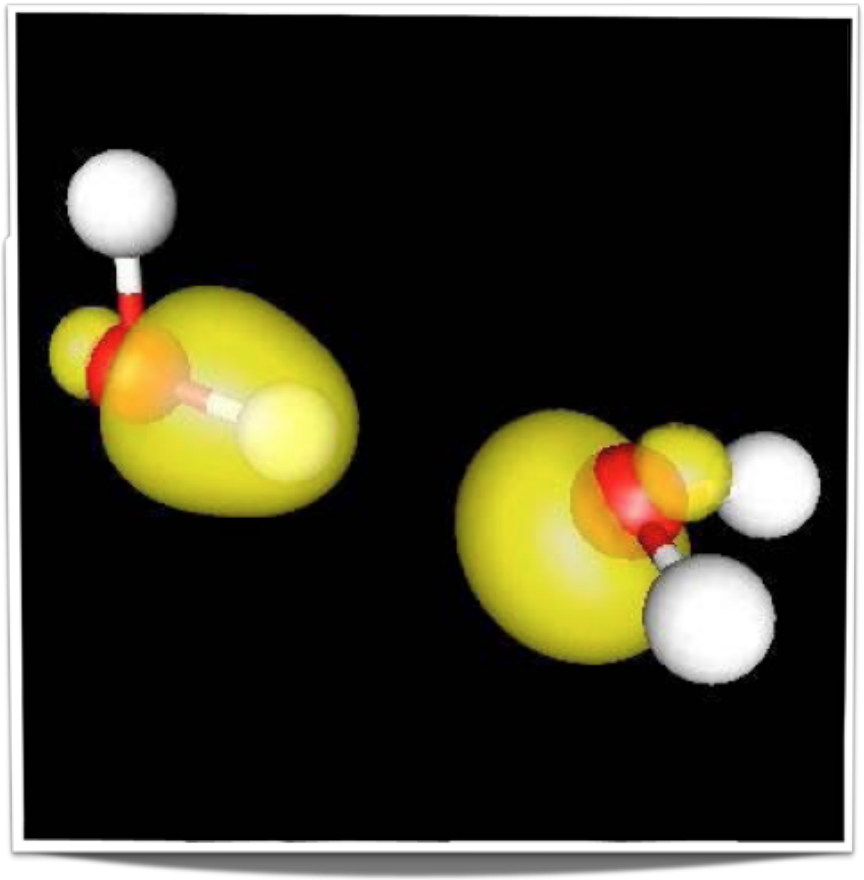

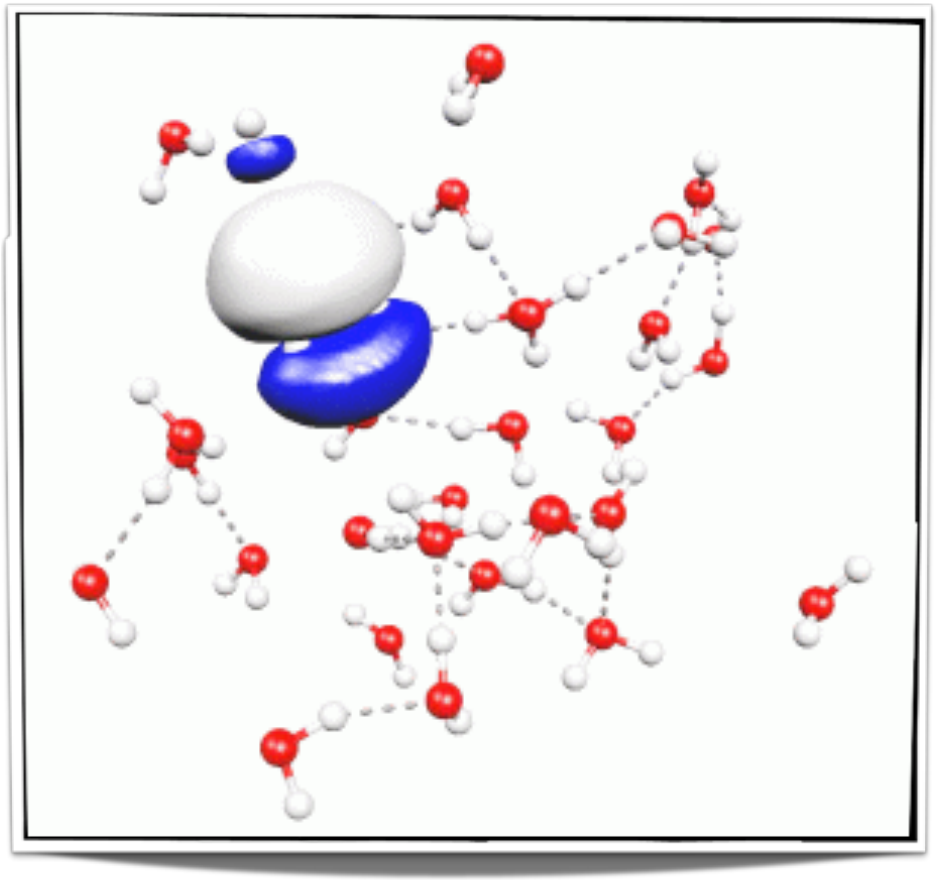

Quantum mechanical description is essential

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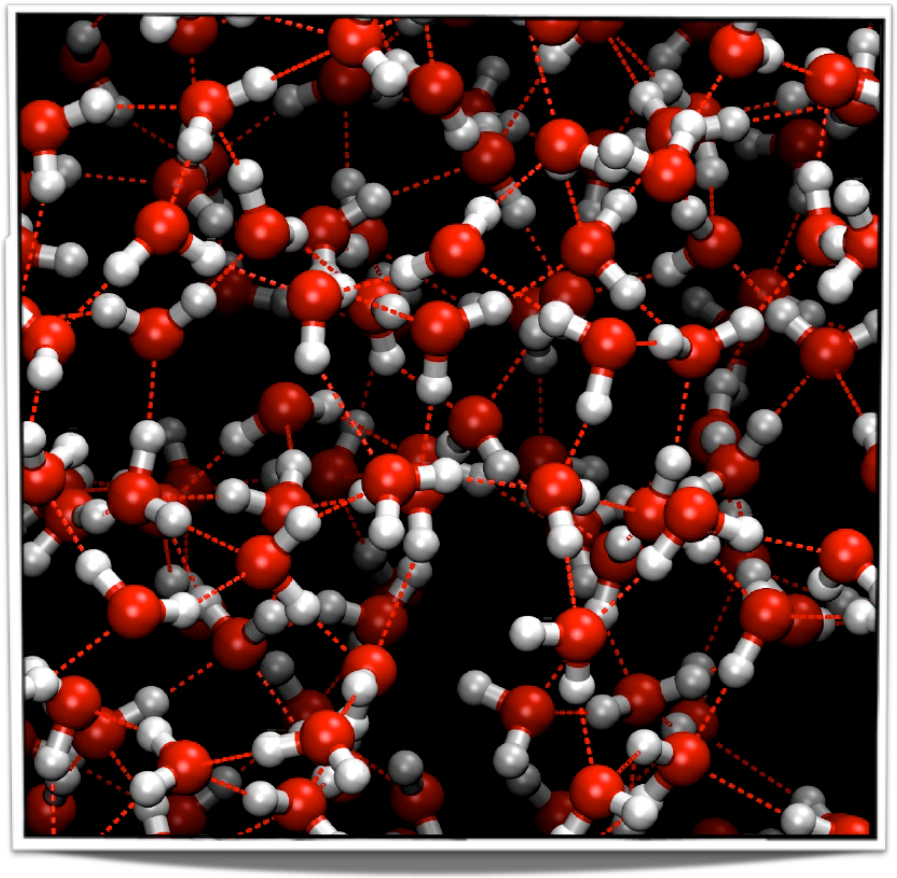

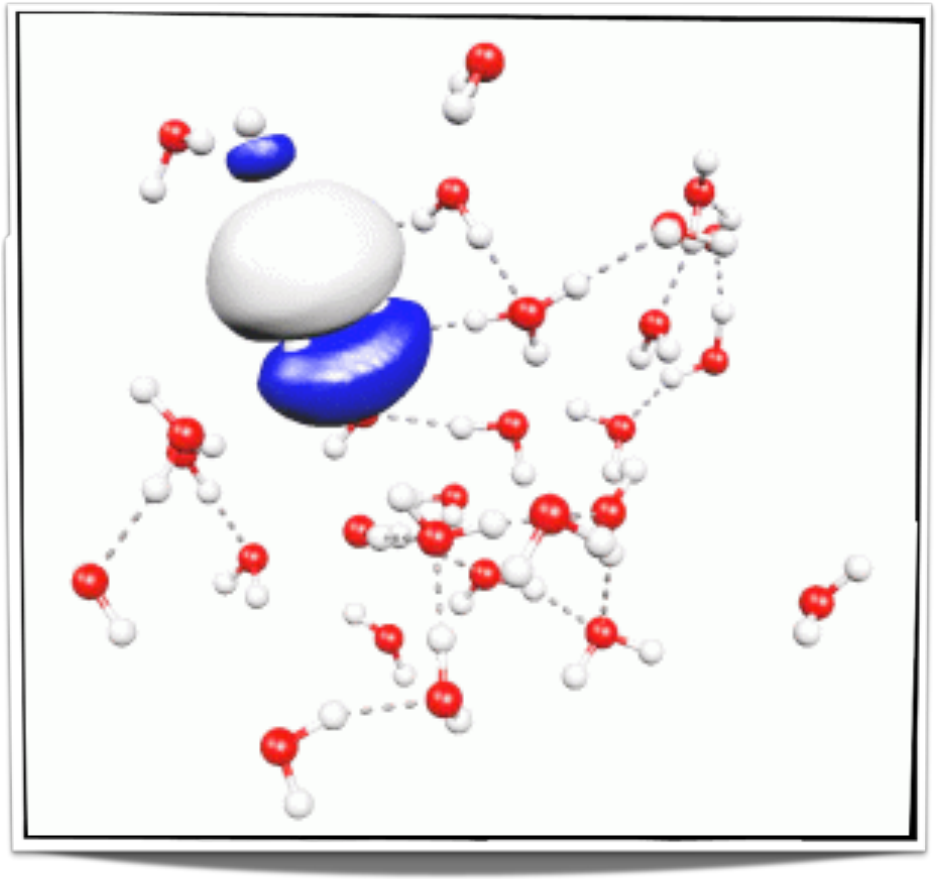

Dynamics is indispensable

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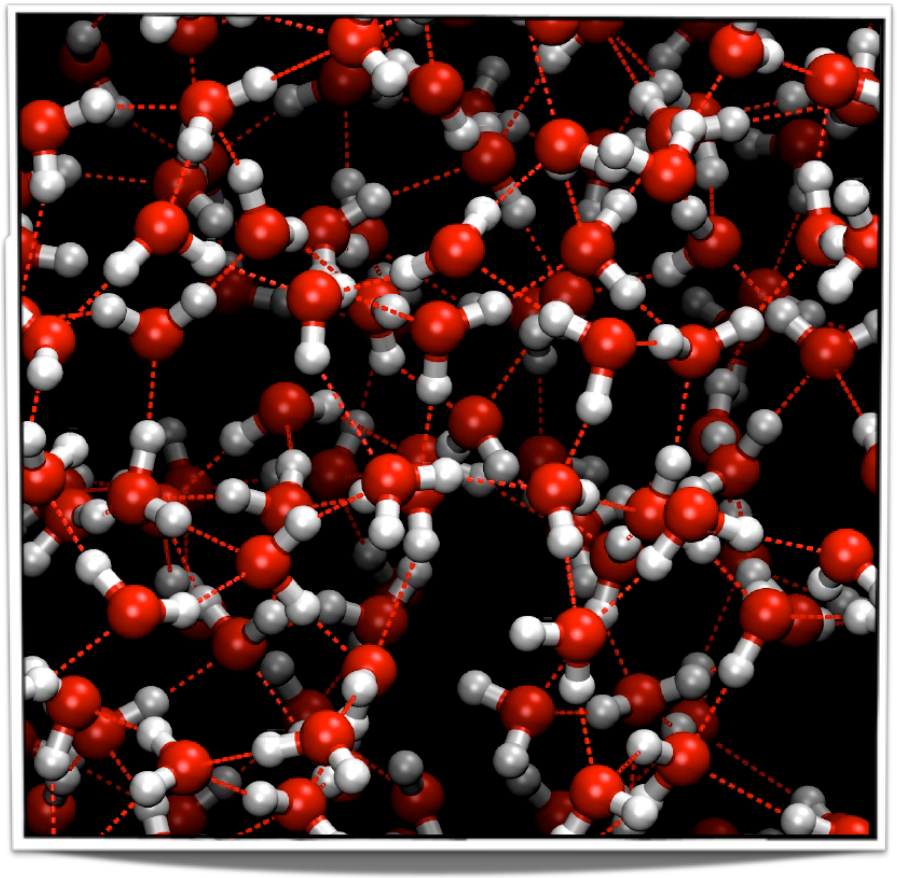
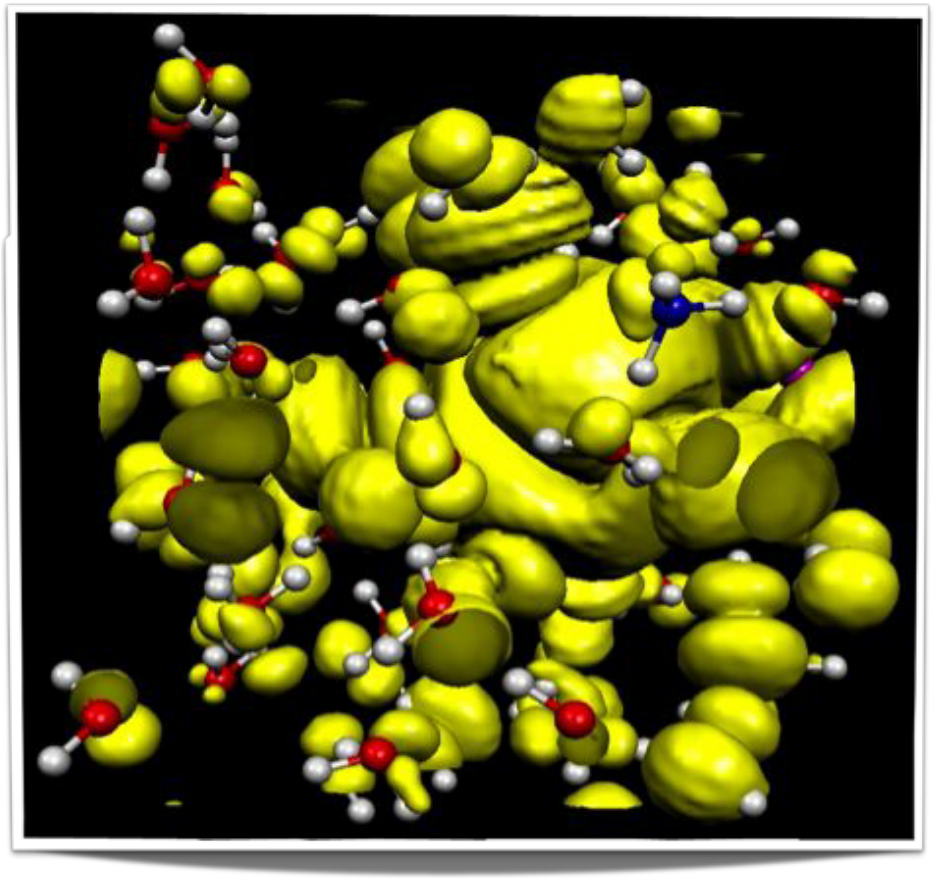
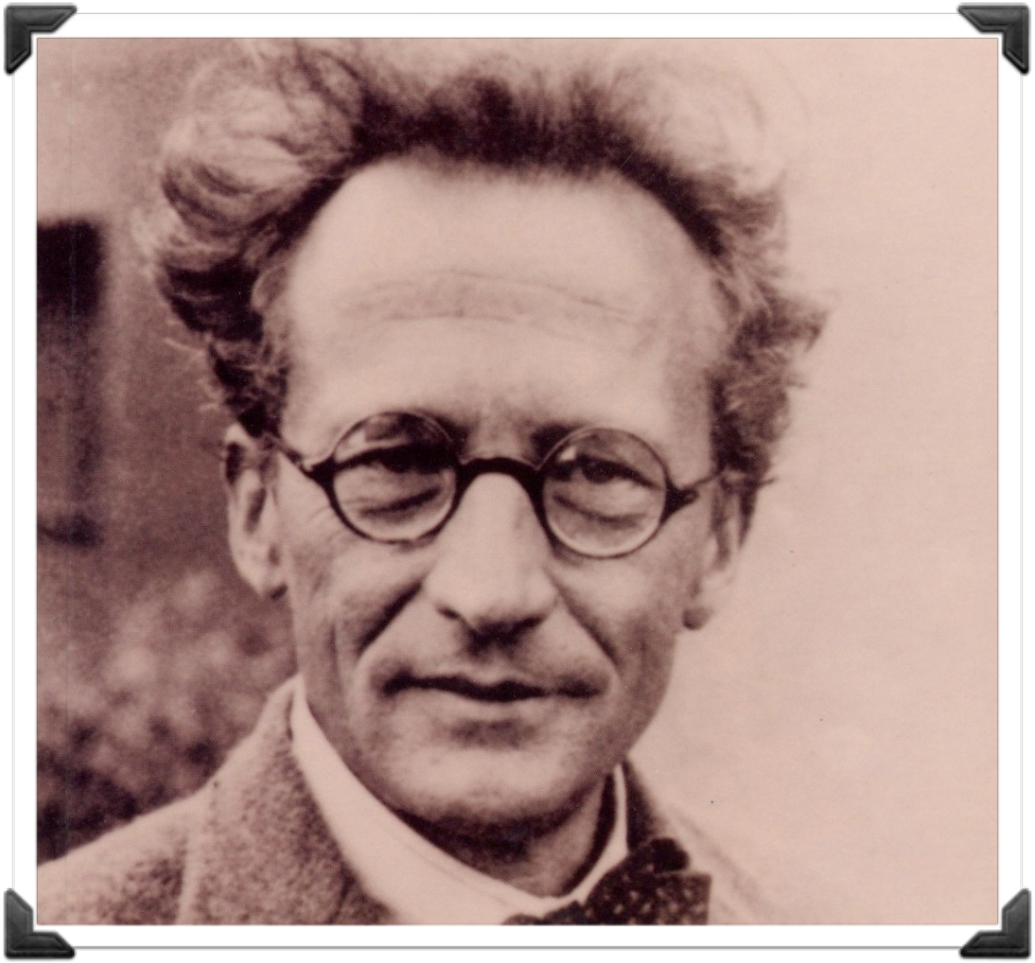


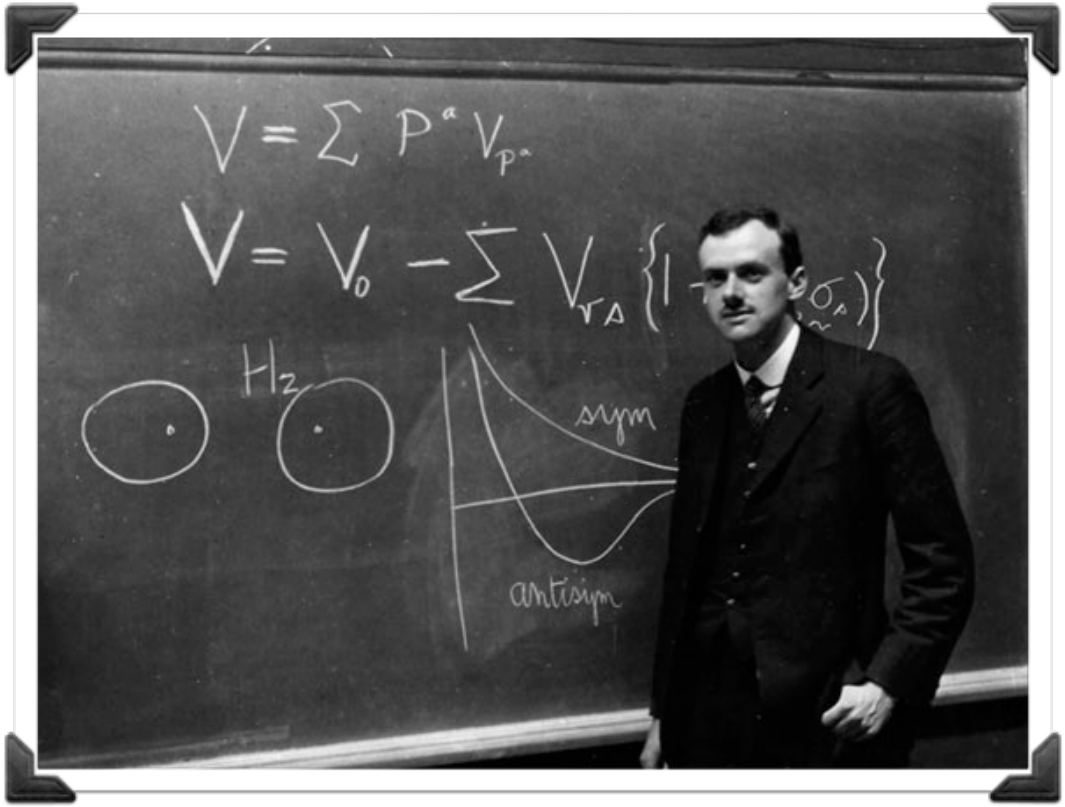


Dynamics & QM on large length and time scales

Schrödinger Equation



Schrödinger Equation

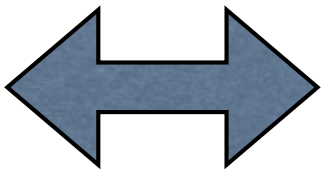


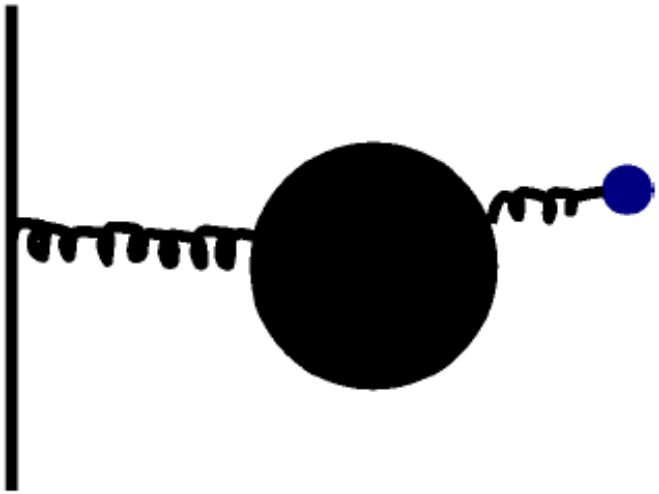
„... hence it would be desirable to develop practical approximation schemes for the application of quantum mechanics“

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

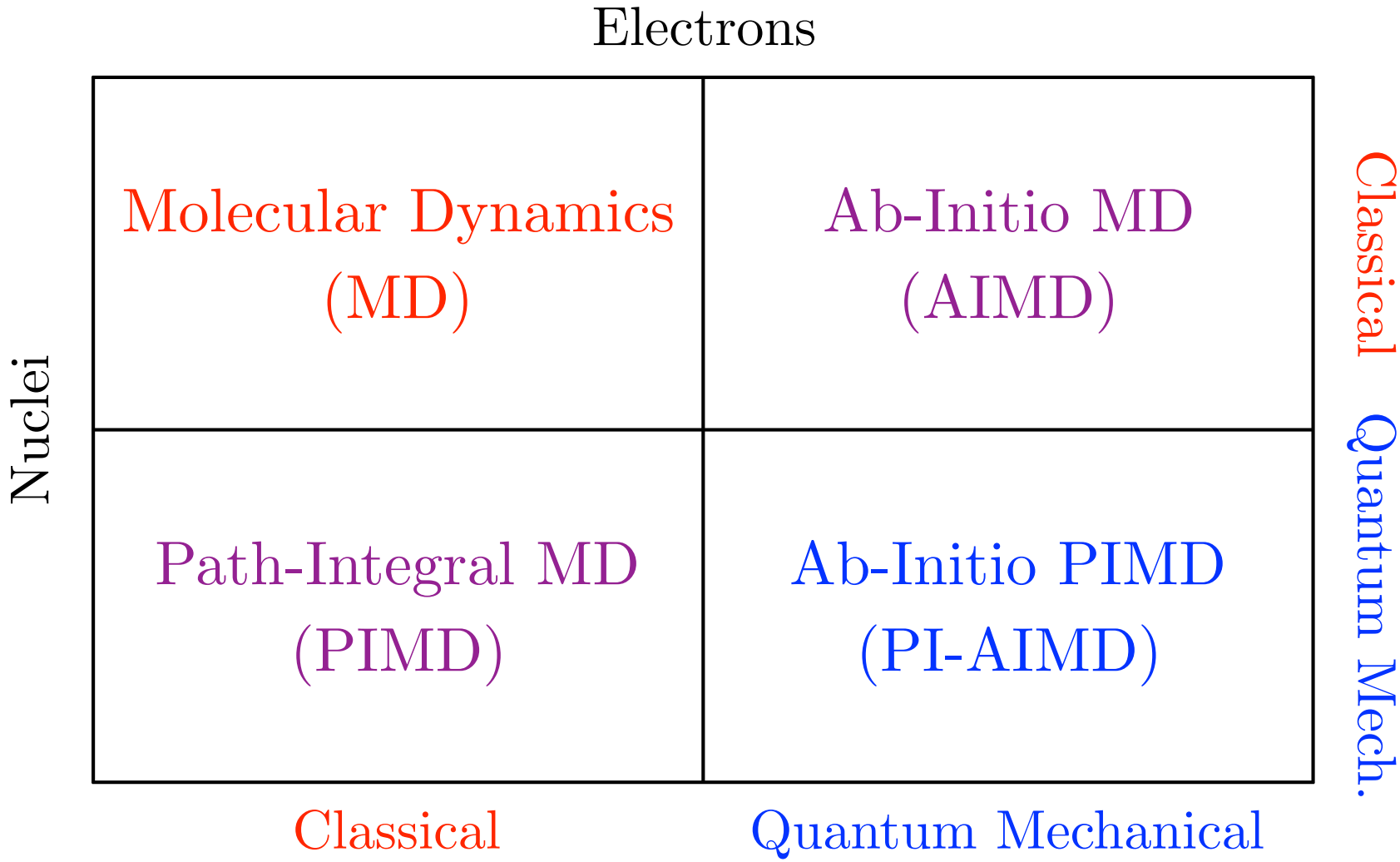
$$\mathcal{H}(\boldsymbol{r},\boldsymbol{R}) = \mathcal{H}_e(\boldsymbol{r};\boldsymbol{R}) + \mathcal{H}_K(\boldsymbol{R}) \;\;\&\;\; \nabla^2_{\boldsymbol{R}_I}\chi(\boldsymbol{R}) >> \nabla^2_{\boldsymbol{R}_I}\psi(\boldsymbol{r};\boldsymbol{R})$$

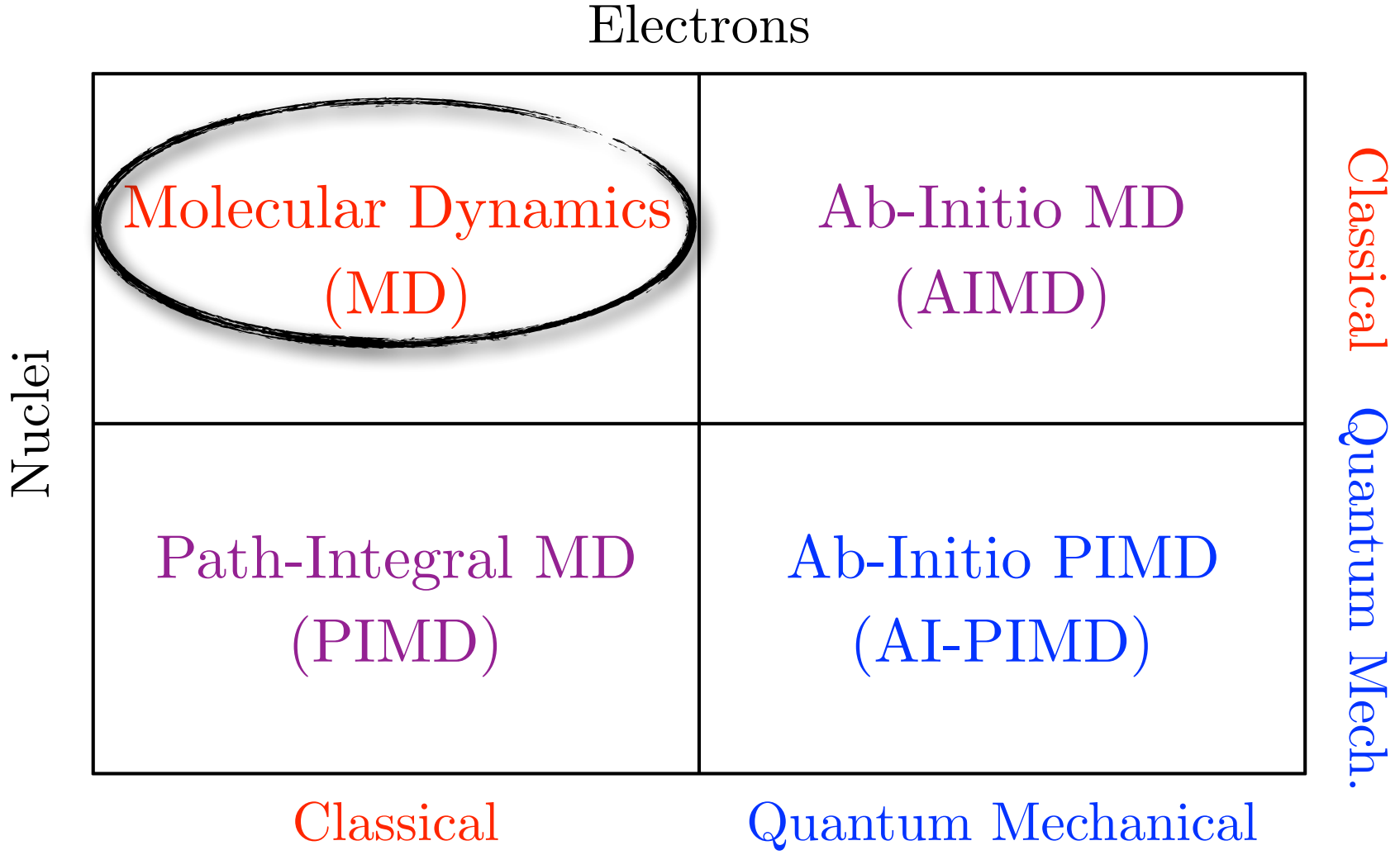
$$\frac{\mathcal{H}_e(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})}{\psi(\boldsymbol{r};\boldsymbol{R})} = E - \frac{\mathcal{H}_K(\boldsymbol{R})\chi(\boldsymbol{R})}{\chi(\boldsymbol{R})} = \varepsilon(\boldsymbol{R})$$

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

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

Born-Oppenheimer





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

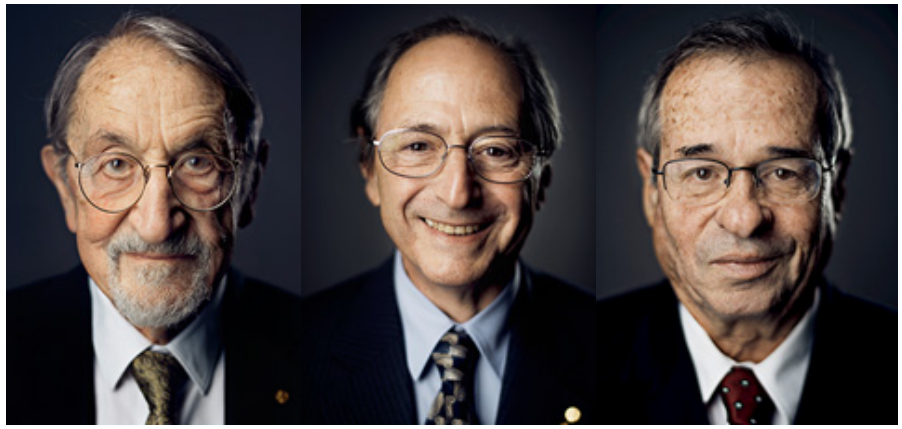
$$M_I \ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I} \left[\varepsilon(\boldsymbol{R}) + V_{KK}(\boldsymbol{R})\right]$$

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

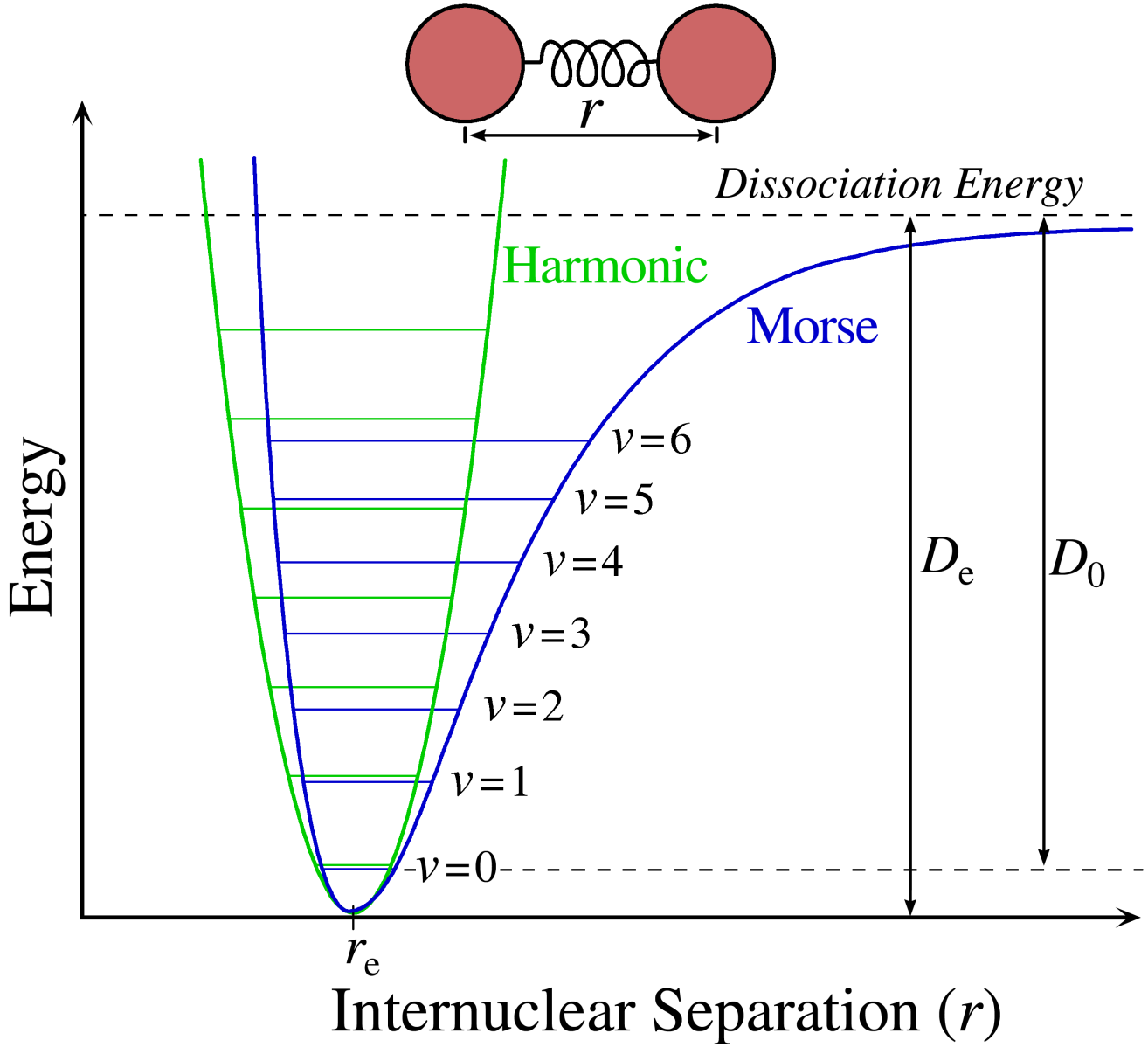


Martin Karplus Michael Levitt Arieh Warshel

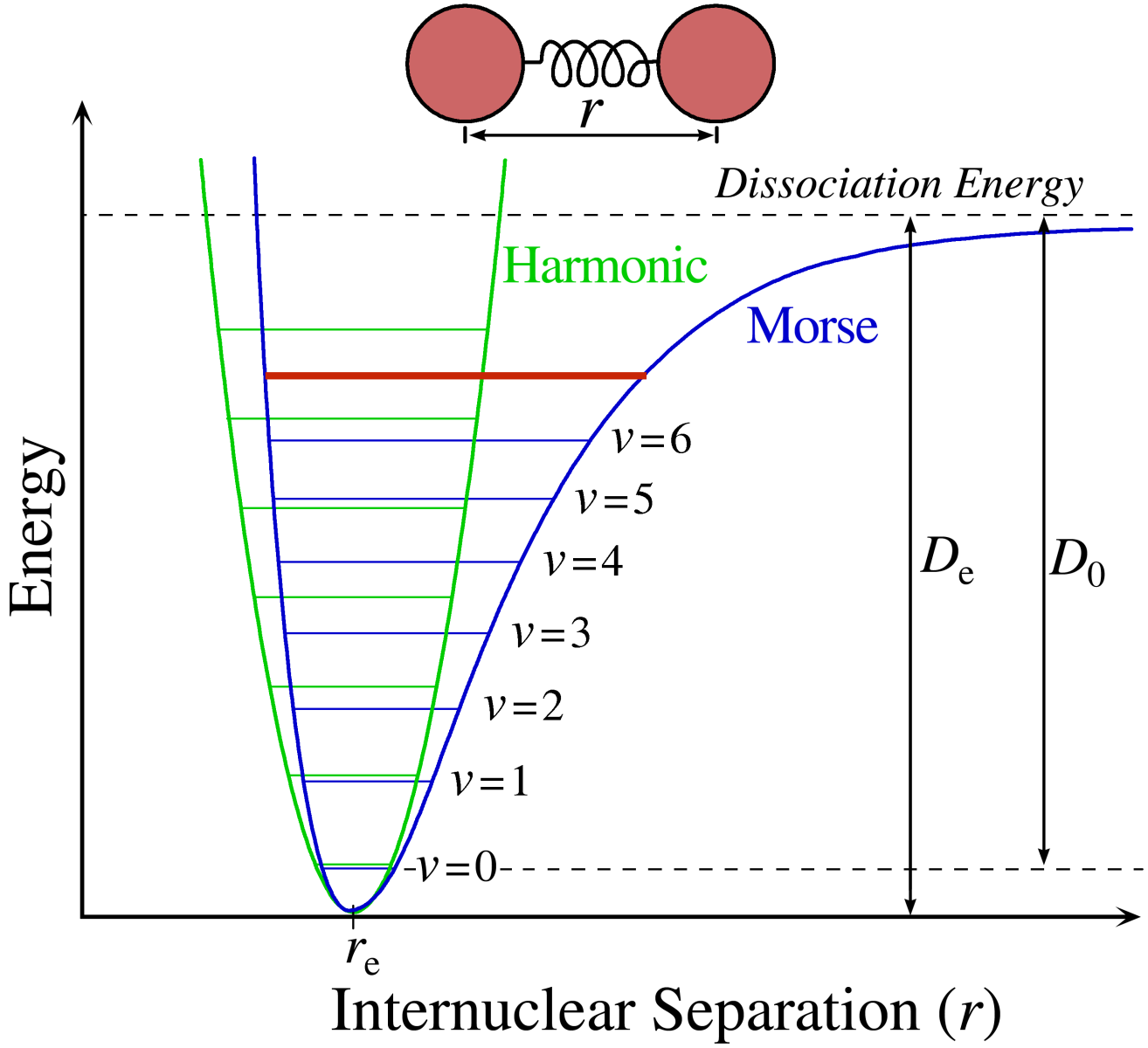
1. Alder, B. J. and Wainwright, T. E. *J. Chem. Phys.* **27**, 1208 (1957)
2. Alder, B. J. and Wainwright, T. E. *J. Chem. Phys.* **31**, 459 (1959)
3. Rahman, A. *Phys. Rev.* **A136**, 405 (1964)
4. Stillinger, F. H. and Rahman, A. *J. Chem. Phys.* **60**, 1545 (1974)
5. McCammon, J. A., Gelin, B. R.,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

What MD is NOT!

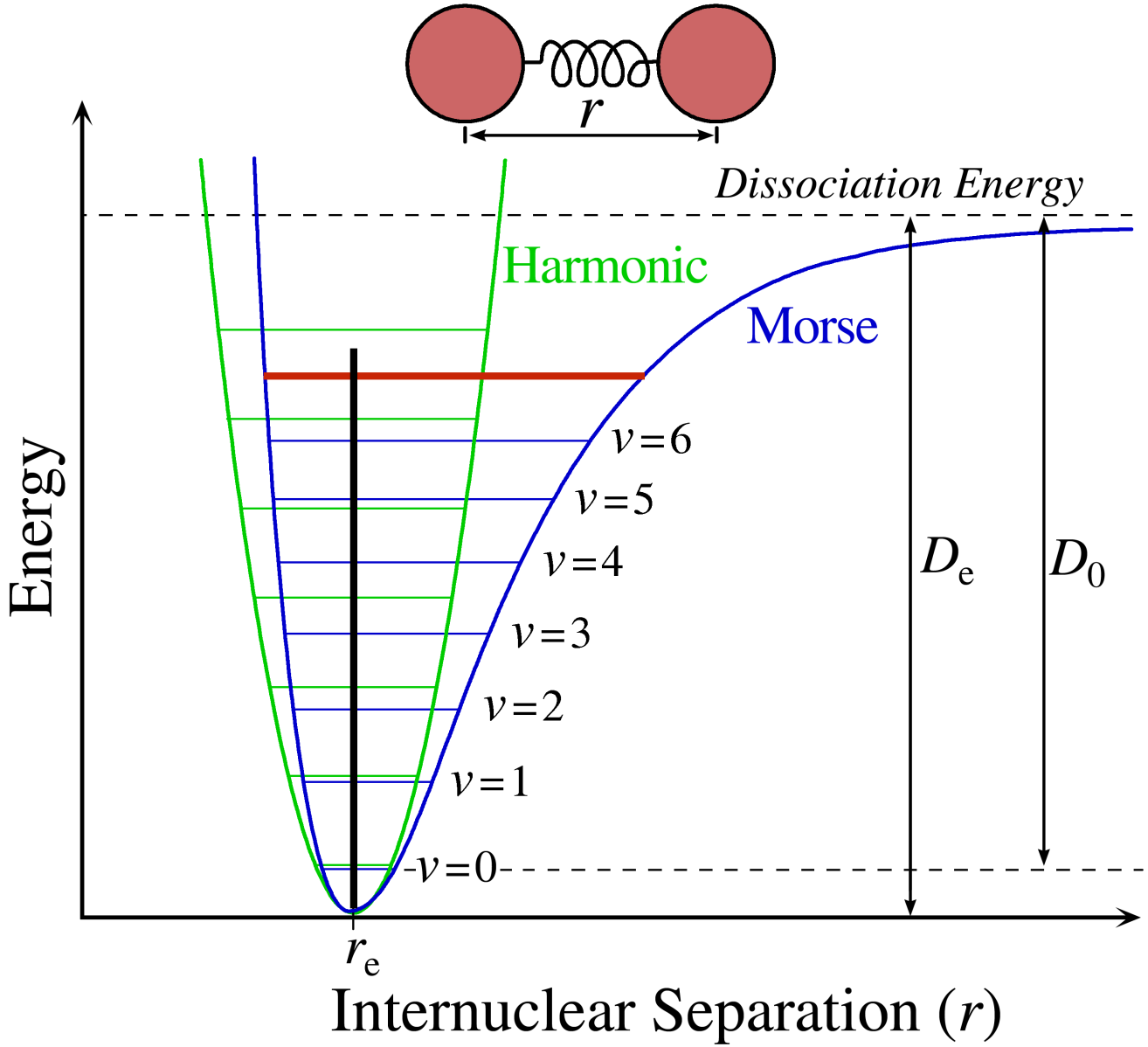
The Essence of MD



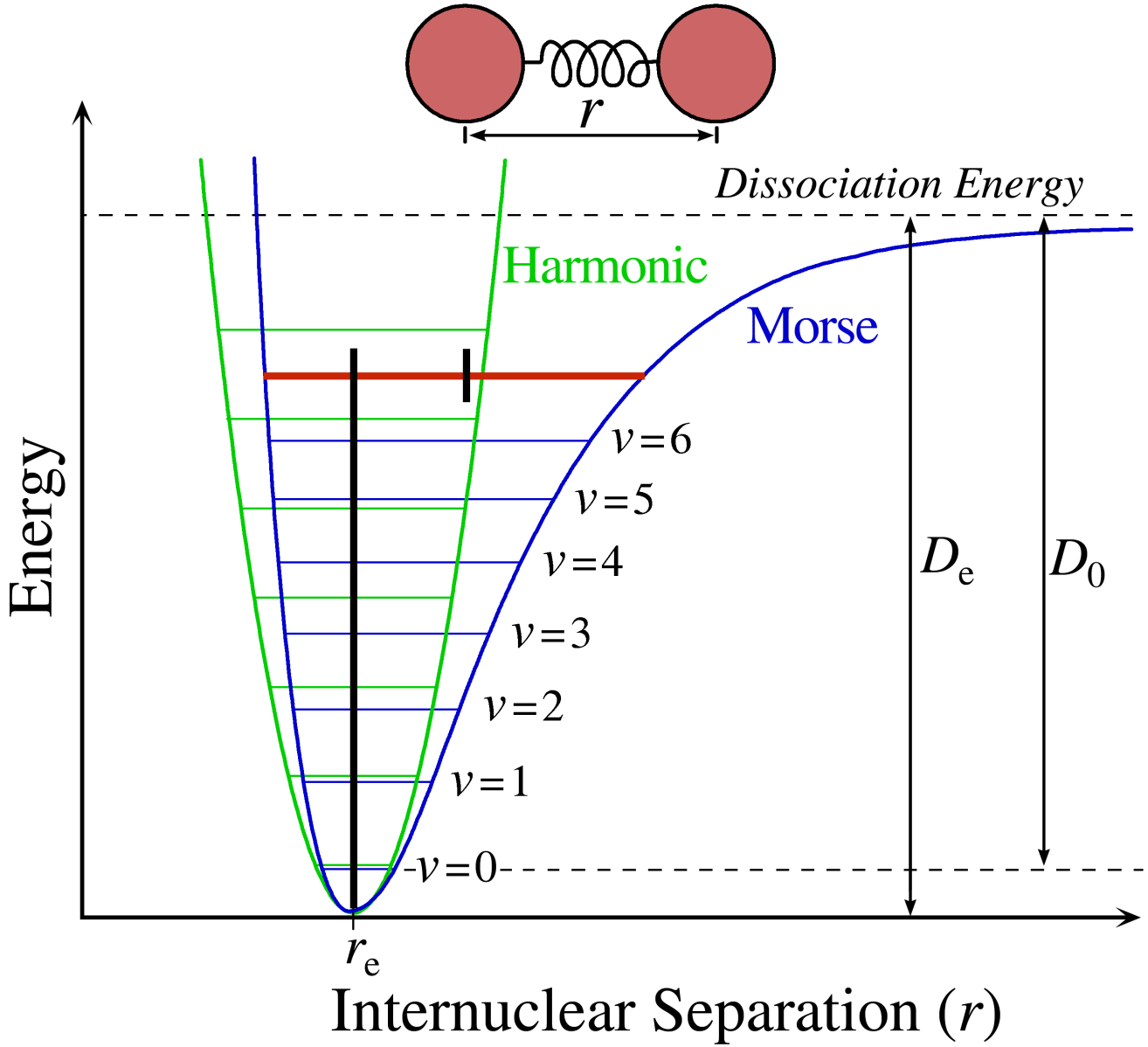
The Essence of MD



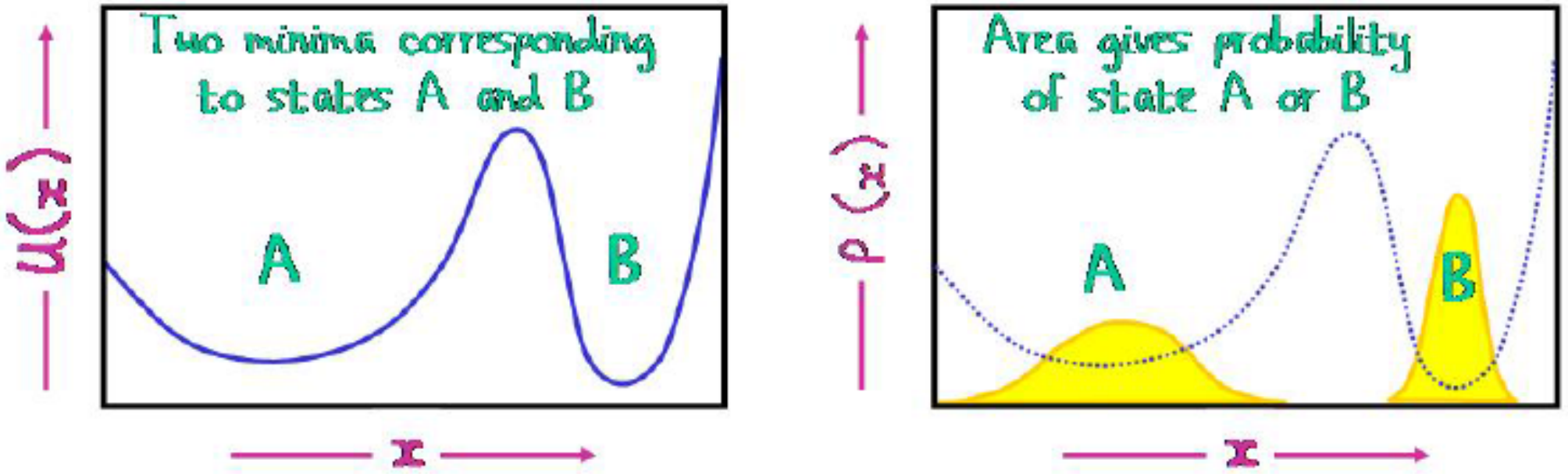
The Essence of MD



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!

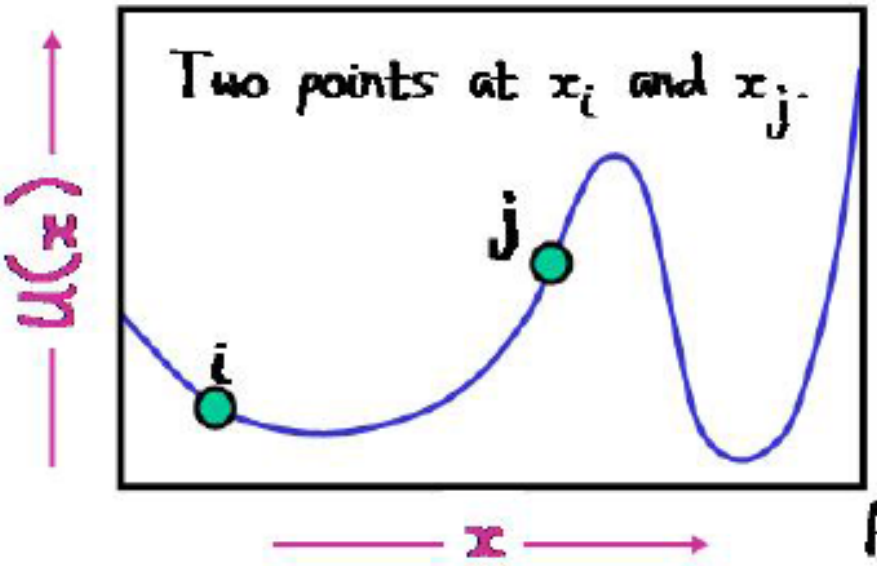
- Analytic determination of Z is generally impossible!
- Evaluating Z at random points is not accurate enough!
- Approximating Z at nuclear ground-state only valid for T=0 K!
- Calculation of P(x) by MD/MC requires unlimited computer time!

- Computing rel. probability is easy:

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

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

$$\frac{P(x_i)}{P(x_j)} = e^{-\frac{U(x_i) - U(x_j)}{k_b T}}$$



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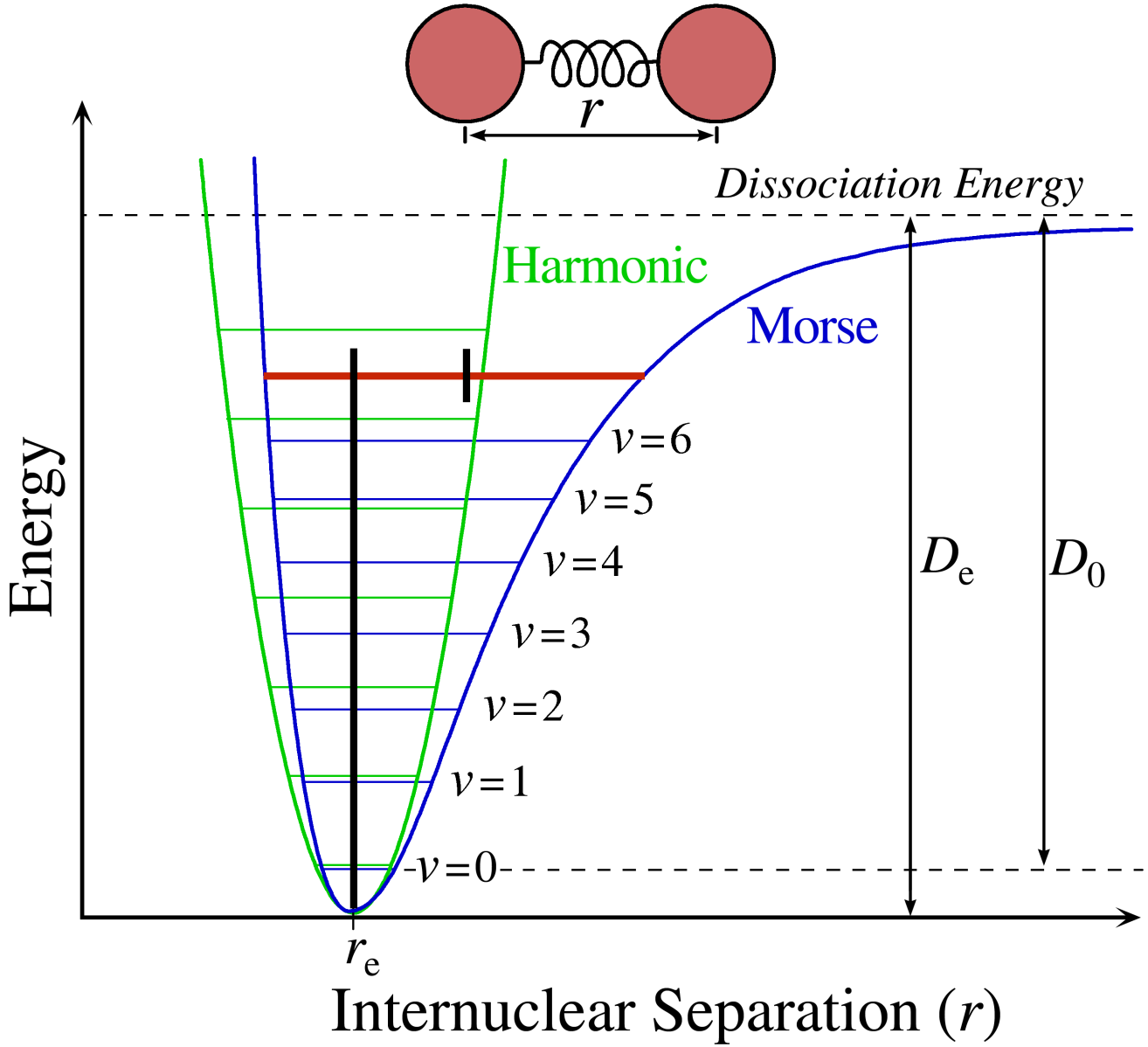

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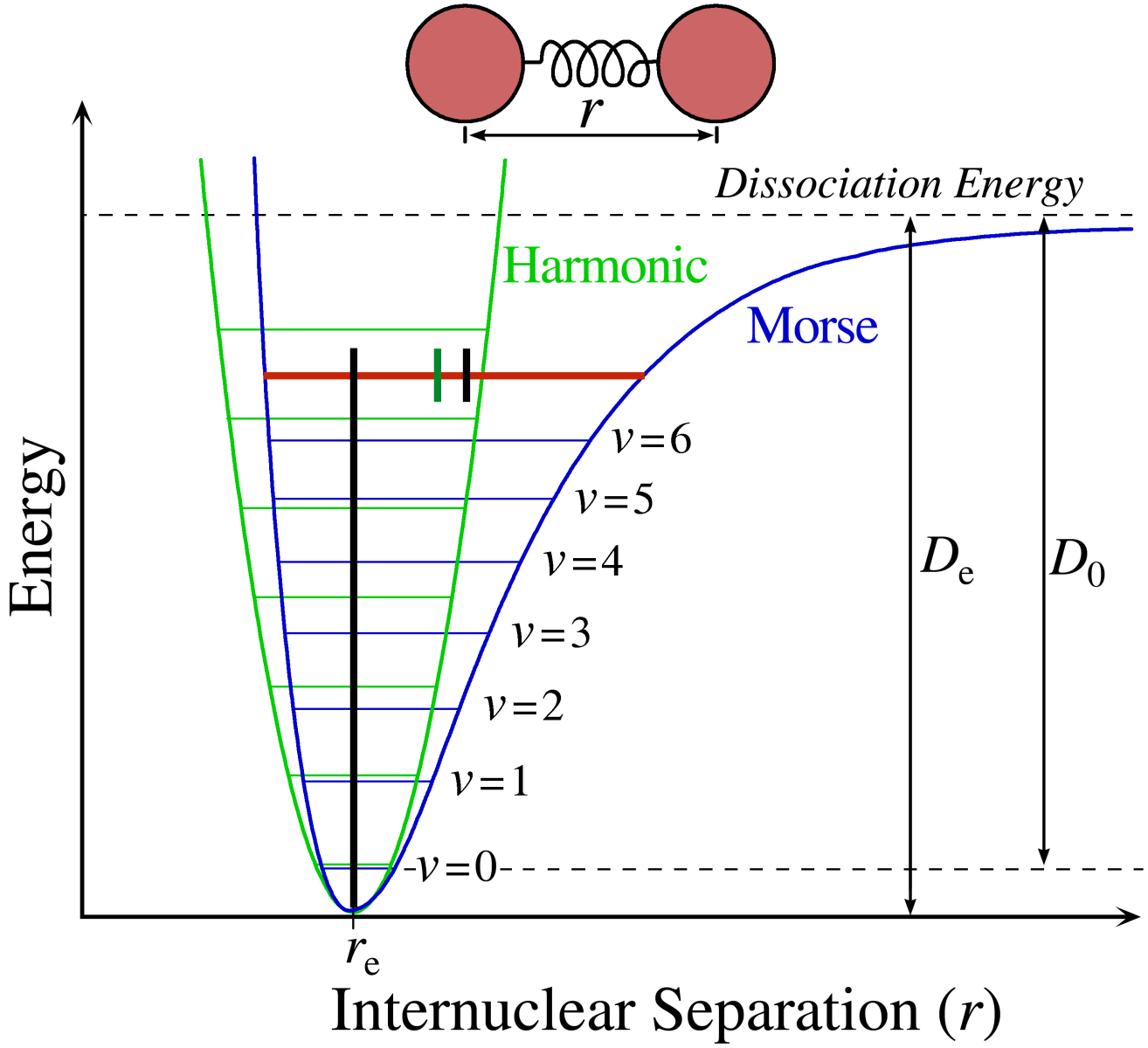
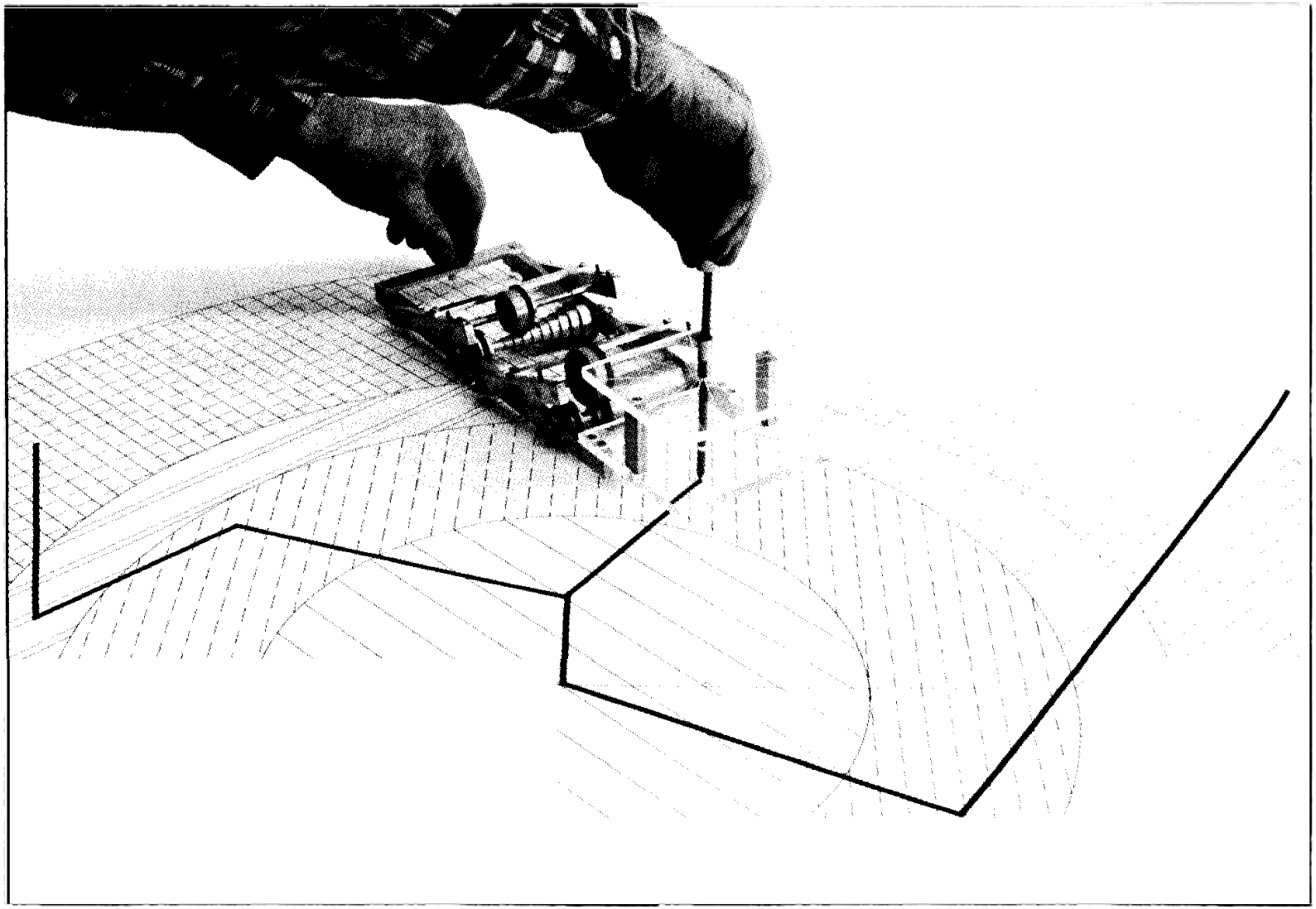
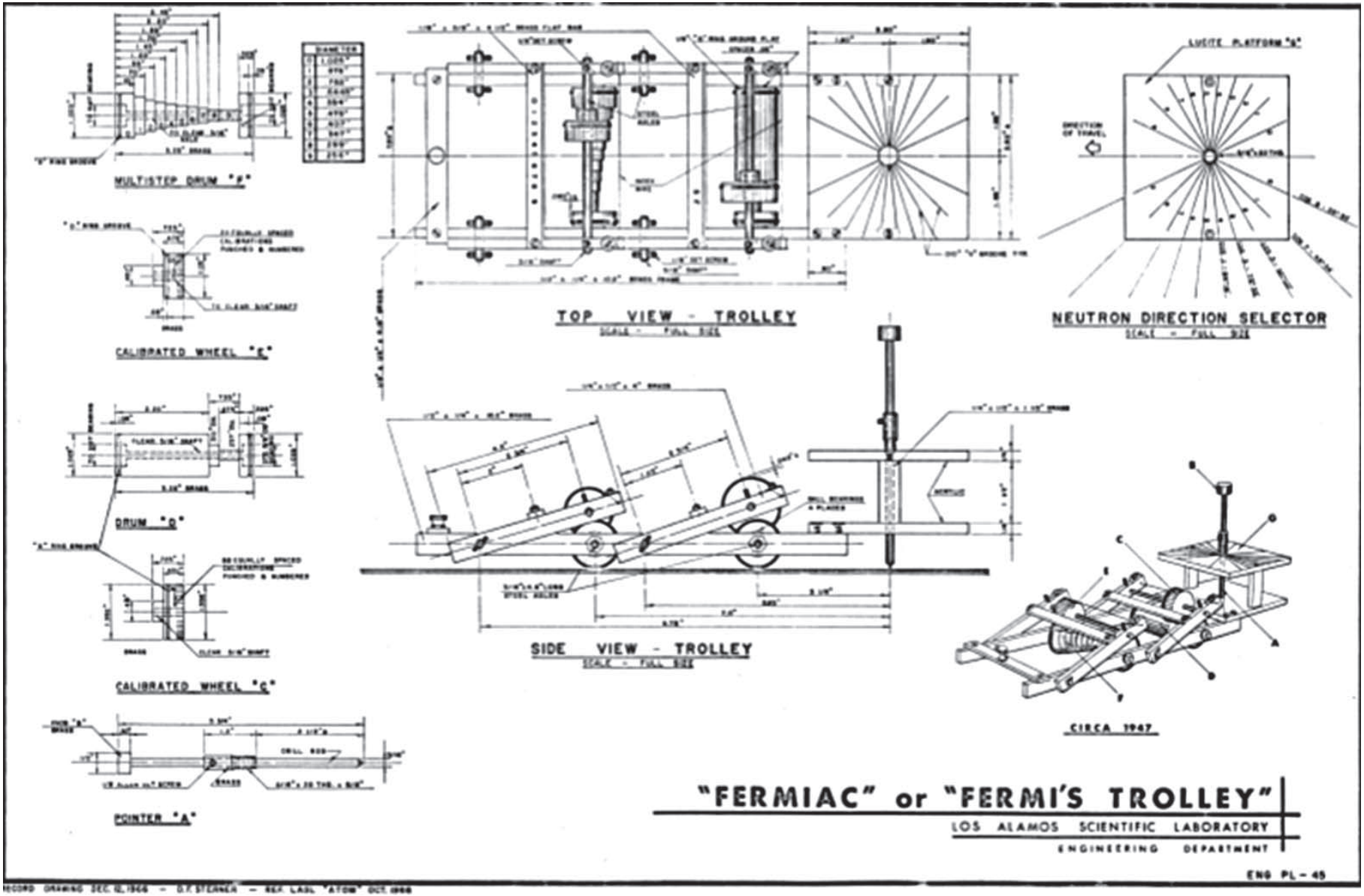


Monte Carlo



Monte Carlo


MULTISTEP DRUM "F"
CALIBRATED WHEEL "E"
DRUM "D"
CALIBRATED WHEEL "C"
POINTER "A"
TOP VIEW - TROLLEY
SCALE - FULL SIZE
SIDE VIEW - TROLLEY
SCALE - FULL SIZE
LUCITE PLATFORM "B"
NEUTRON DIRECTION SELECTOR
SCALE - FULL SIZE
CIRCA 1947
"FERMIAC" or "FERMI'S TROLLEY"
LOS ALAMOS SCIENTIFIC LABORATORY
ENGINEERING DEPARTMENT
ENG PL - 45

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 $\frac{P(x_i)}{P(x_j)} = e^{-\frac{U(x_i)-U(x_j)}{k_b T}}$

• Instead, we would like to sample *a priori* from the Boltzmann distribution and weight the configurations equally, i.e.

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

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

• 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.

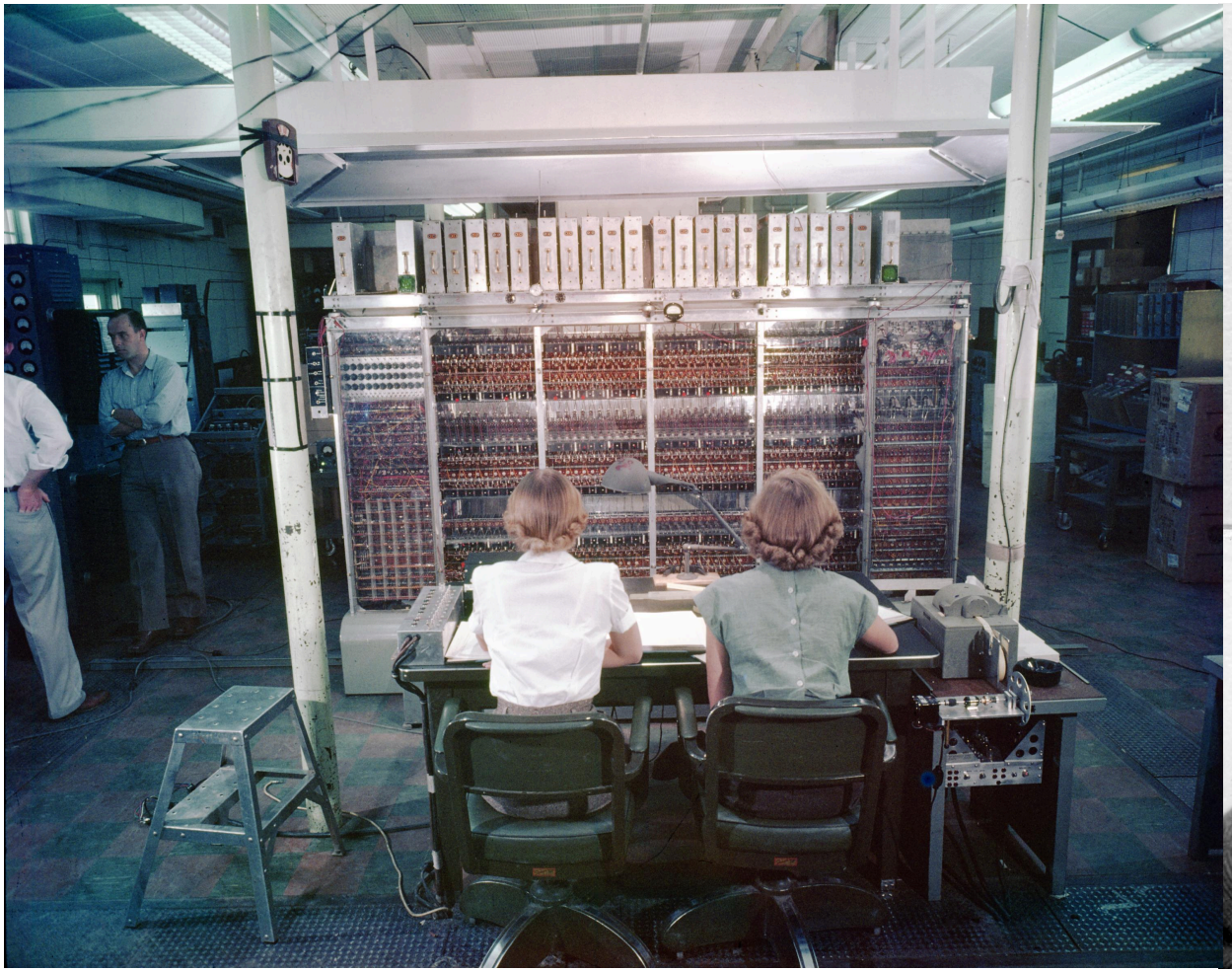
I. INTRODUCTION

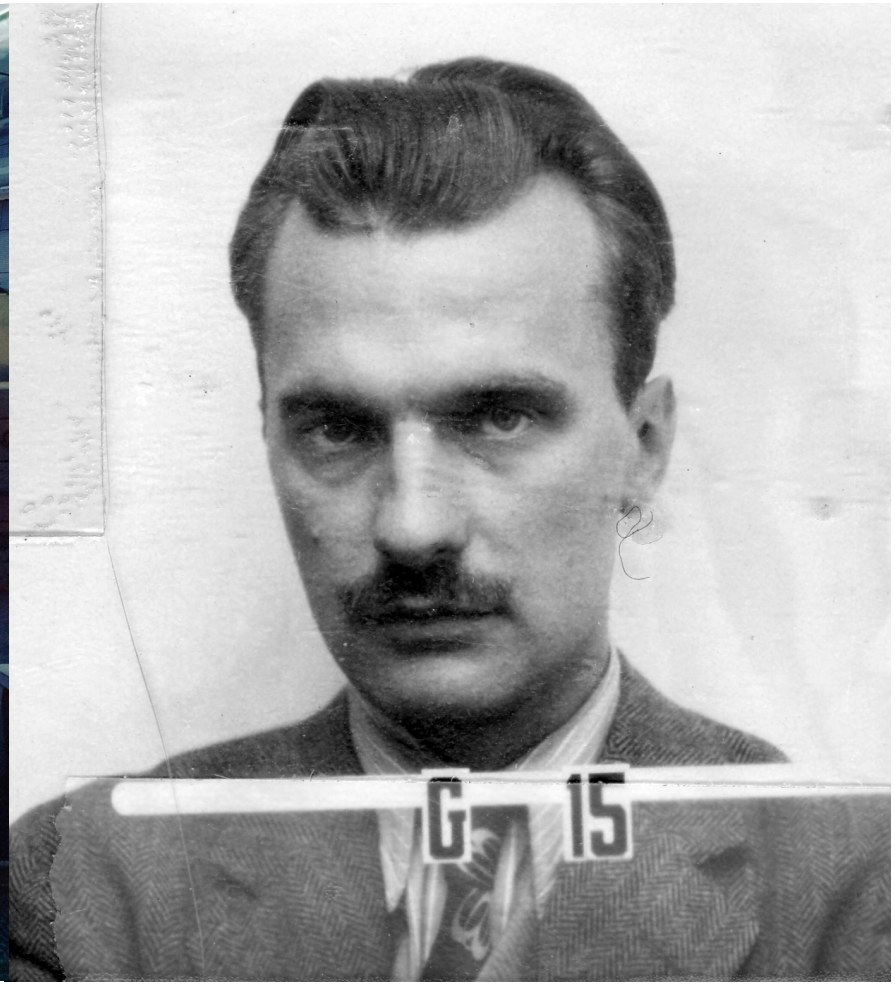
THE purpose of this paper is to describe a general method, suitable for fast electronic computing machines, of calculating the properties of any substance which may be considered as composed of interacting individual molecules. Classical statistics is assumed,

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

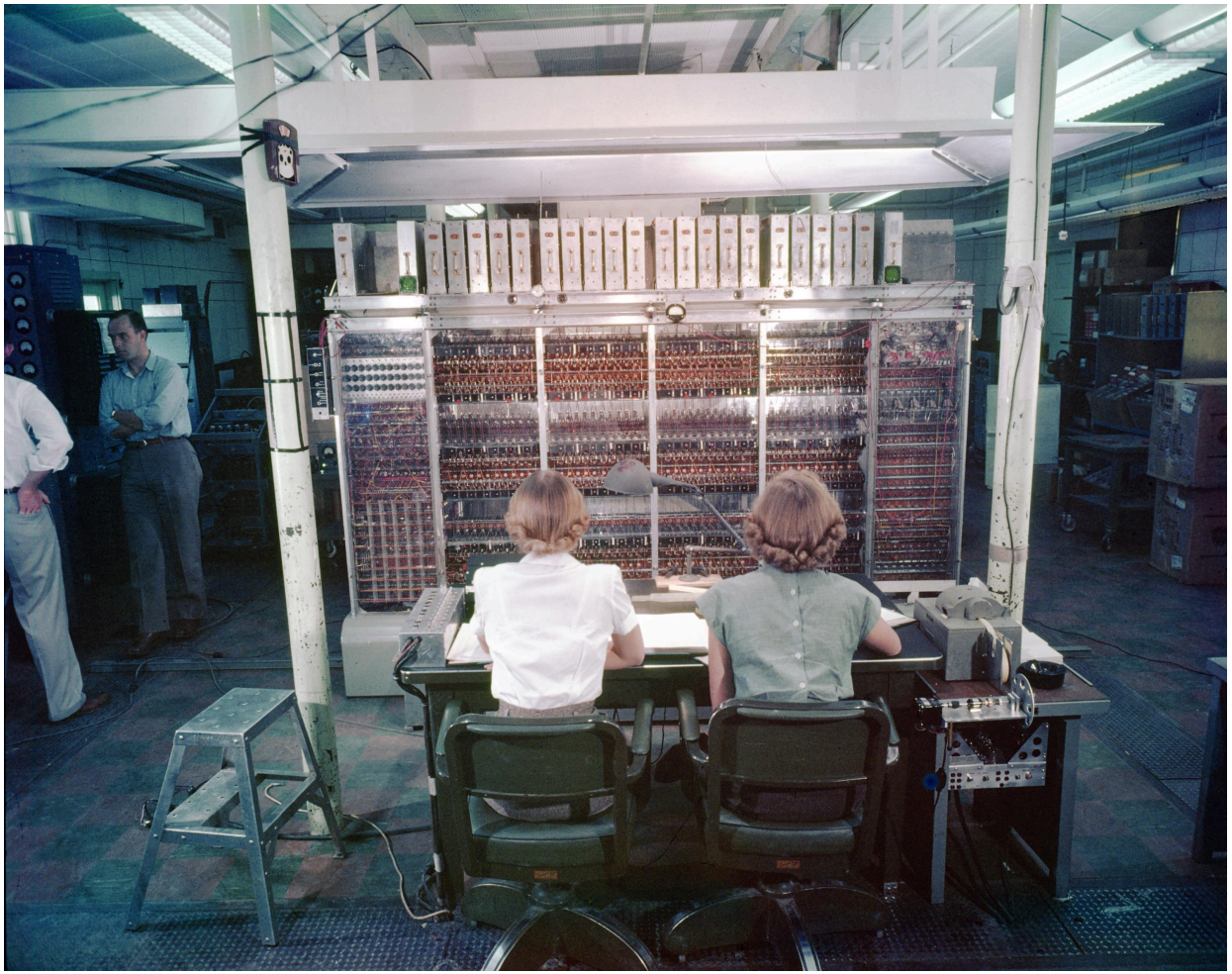
In order to reduce the problem to a feasible size for numerical work, we can, of course, consider only a finite number of particles. This number N may be as high as several hundred. Our system consists of a square† con-

Monte Carlo & MANIAC





Monte Carlo & MANIAC



Now, Teller was not one to let Fermi leave him behind. Anything Fermi could do, he could do too. So Teller also became a student of Nick's and learned how to program the MANIAC. When he came back to Chicago—he was on the faculty then—not to be outdone by Fermi he announced that he would give a colloquium on the subject of computers. But when the colloquium notice appeared, it didn't convey exactly the impression he had intended. It read,

Edward Teller

The MANIAC

What we are interested in?

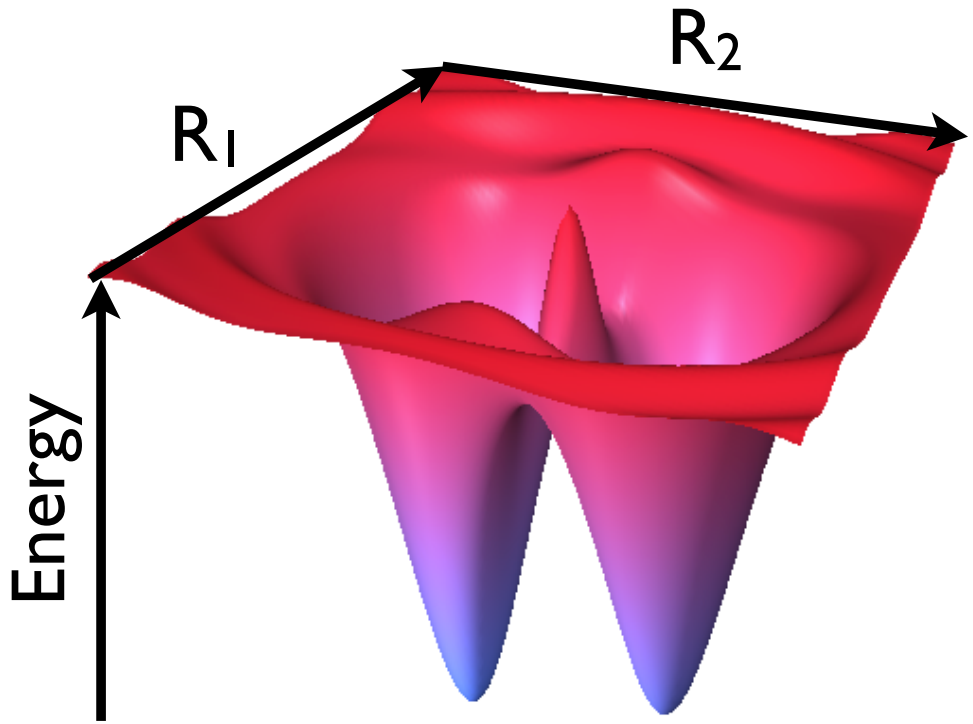
- Thermodynamic ensemble properties:

Partition Function

Hamiltonian

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

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



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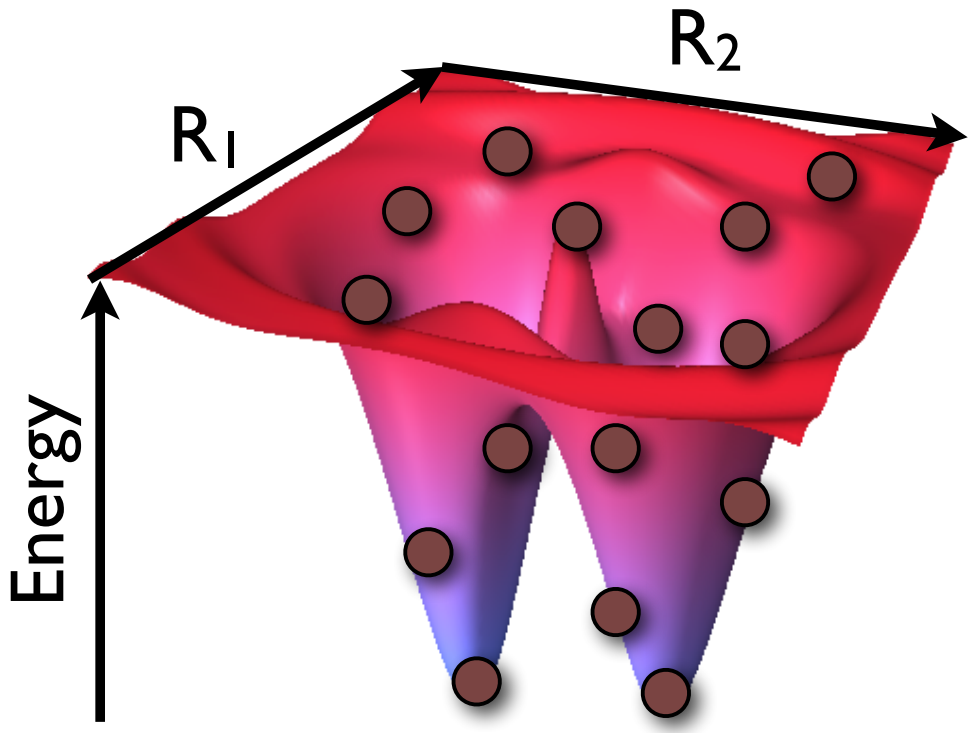
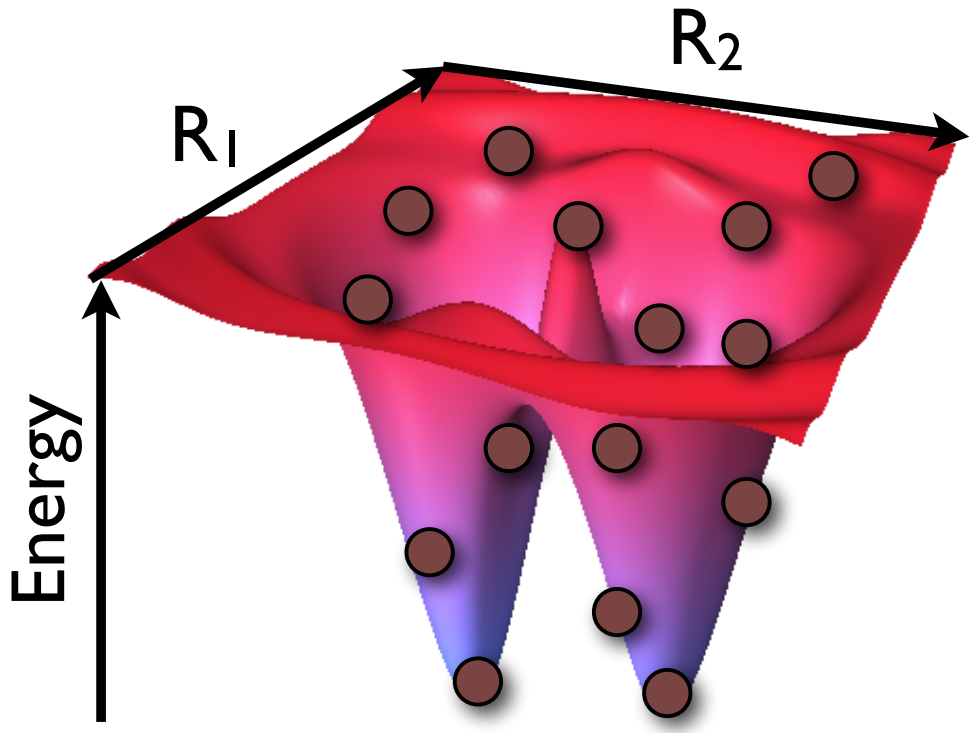


What we are interested in?

- Ergodic hypothesis: ensemble average equal to time average

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

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

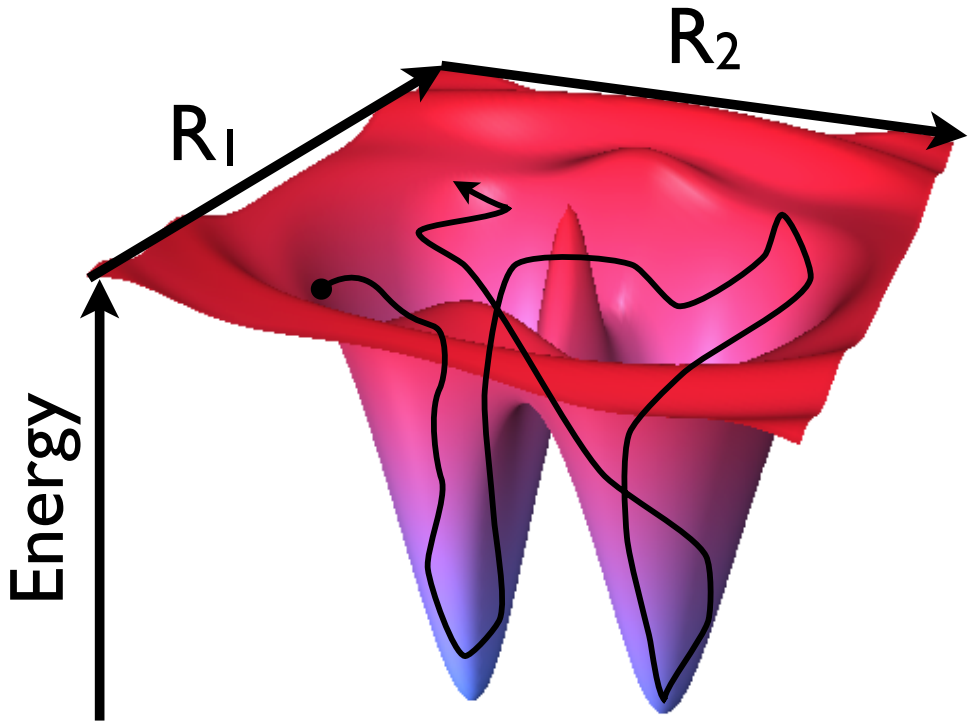


What we are interested in?

- Ergodic hypothesis: ensemble average equal to time average

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

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



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

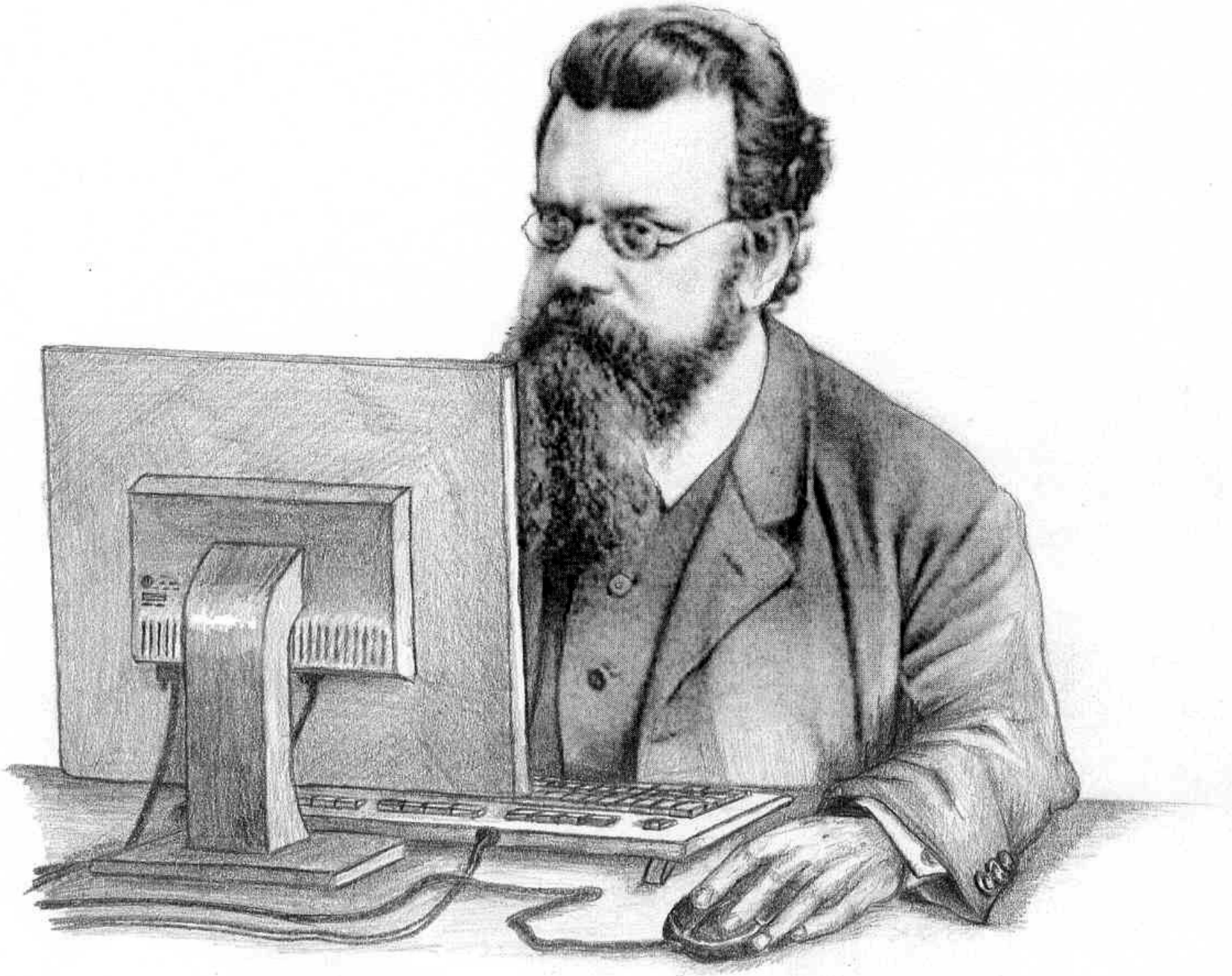
PHYSICAL REVIEW VOLUME 136, NUMBER 2A 19 OCTOBER 1964

Correlations in the Motion of Atoms in Liquid Argon*

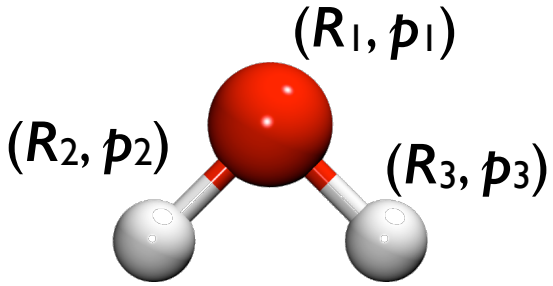
A. RAHMAN
Argonne National Laboratory, Argonne, Illinois
(Received 6 May 1964)

A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon

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

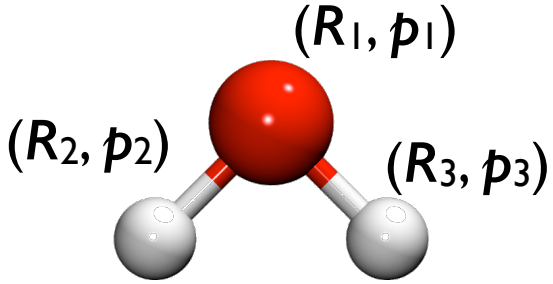


Integrating Newton's EOM



1. Assign initial R (position) and p (momenta)

Integrating Newton's EOM



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

2. Evolve (numerically) Newton's equation of motion for a finite time increment

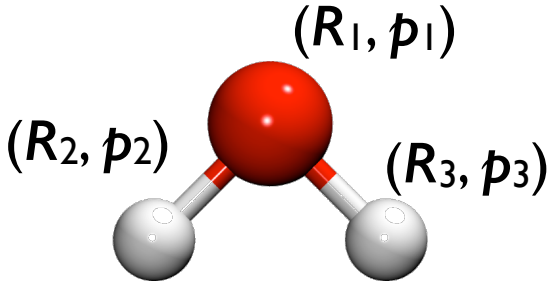
$$\mathcal{H}(\mathbf{R},\mathbf{p}) = \sum_I \frac{\mathbf{p}_I^2}{2M_I} + V(\mathbf{R})$$

Potential

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

Force

Integrating Newton's EOM



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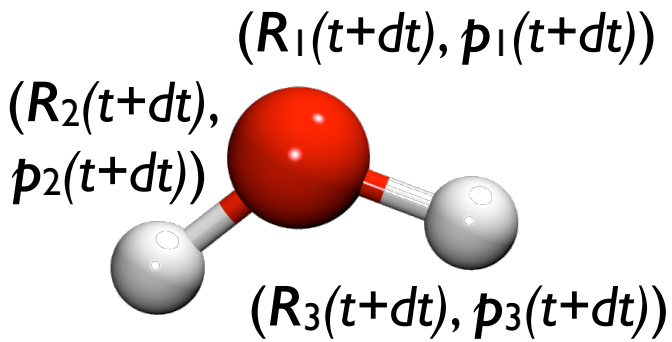
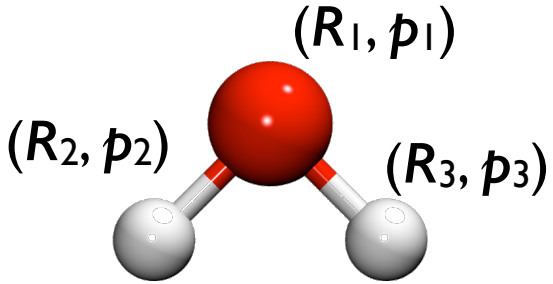


3. Assign new position and momenta

Integrating Newton's EOM



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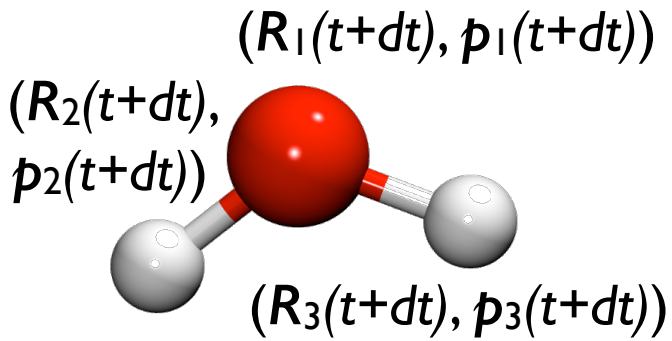
Force



3. Assign new position and momenta

Euler's Algorithm

- First shot: Taylor expansion of *R*

Force

Error $O(\Delta t^3)$

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

Euler's Algorithm

- First shot: Taylor expansion of *R*

Force

Error $O(\Delta t^3)$

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

- 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*

Force

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

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

$$R(t+\Delta t) + R(t-\Delta t) = 2R(t) + \frac{\dot{p}(t)}{m}\Delta t^2 + O(\Delta t^4)$$

Error

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

Verlet Algorithm

"Verlet" is also symplectic: conserves dp∧dR and the form of Hamilton's equations

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 $\Rightarrow$ Energy conservation

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

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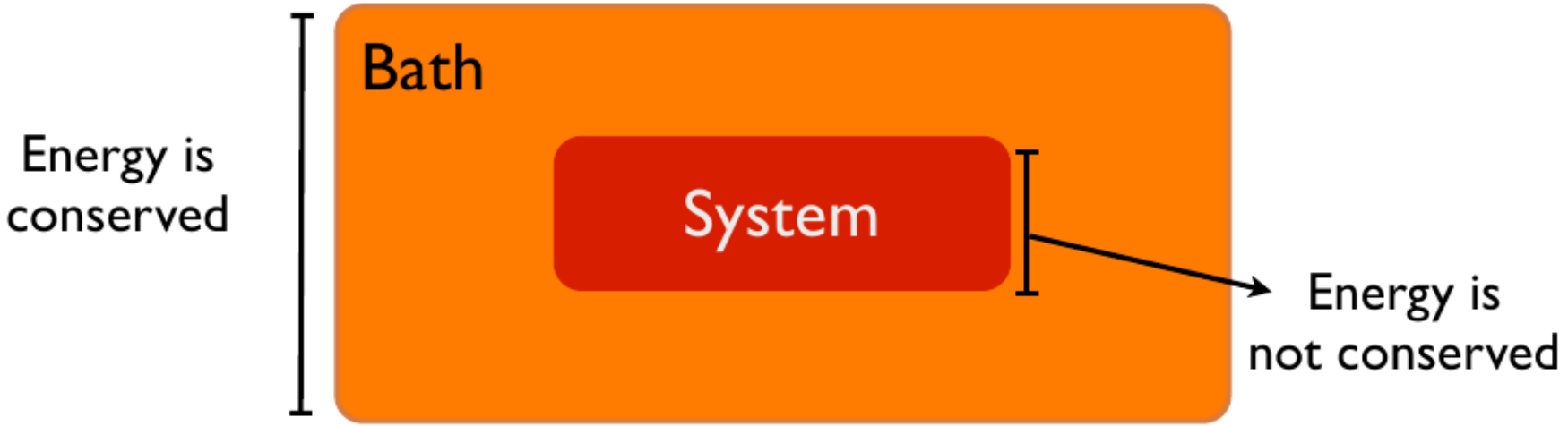
    - System in contact with a heat bath (discussed later on)

The Canonical Ensemble

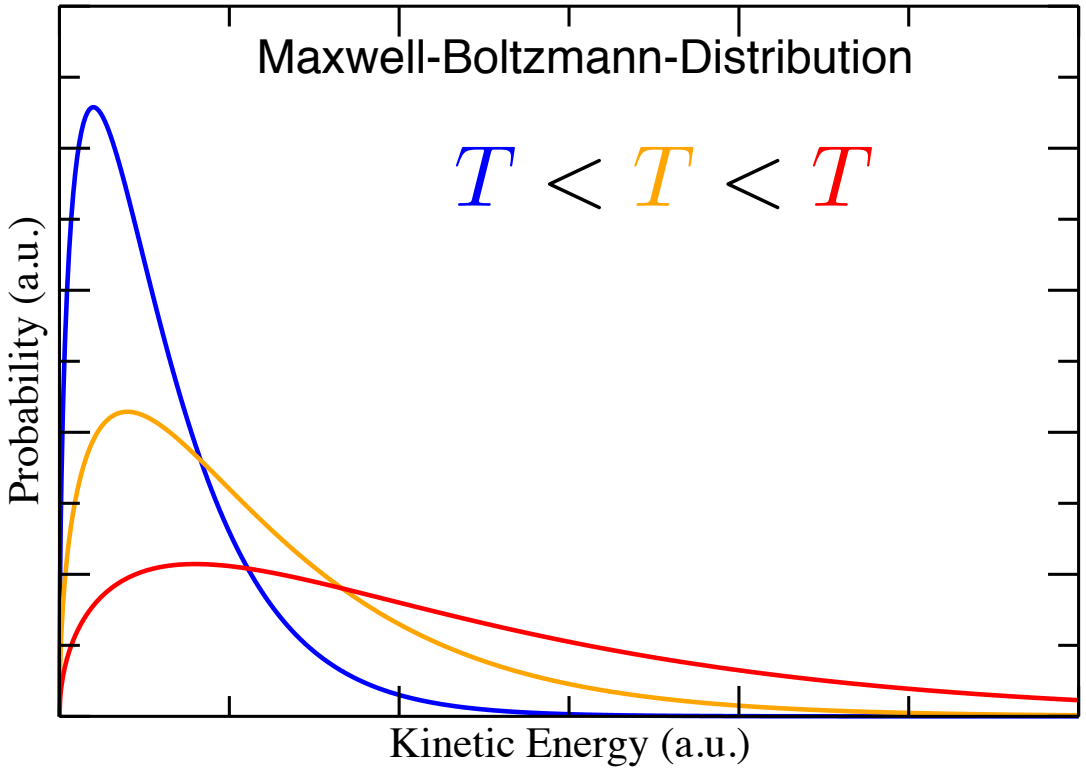
- The idea: couple the system to a thermostat (heat bath)
- Interesting because:
  - Experiments are usually done at constant temperature
  - Better modeling of conformational changes



Maxwell Distribution

Probability distribution of the kinetic energy:

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



kinetic energy: $p^2/2M$

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

# 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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- 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:

$$\frac{dT}{\bar{T}} = \left[1 - \frac{T(t)}{\bar{T}}\right]\frac{dt}{\tau} + 2\sqrt{\frac{T(t)}{3\bar{T}N\tau}}\xi(t)$$

Temperature rescaling

White noise

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Temperature rescaling

White noise

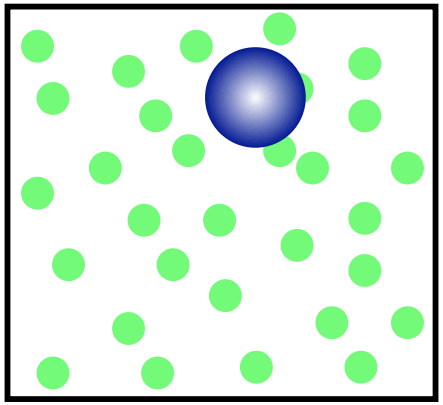
- Very successful thermostat, weakly dependent on relaxation time τ
- Pseudo-Hamiltonian is conserved

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

Newton vs. Langevin

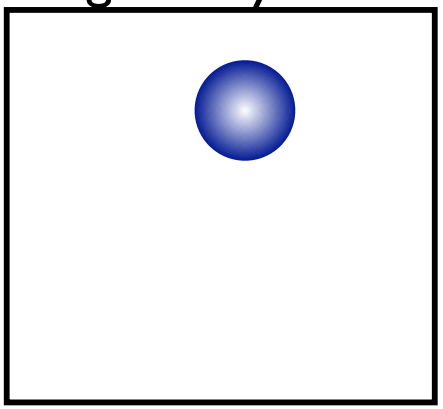
Heavy(er) body in a solvent (or gas)

Newtonian dynamics



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

Langevin dynamics



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

friction

random force

Newton vs. Langevin

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

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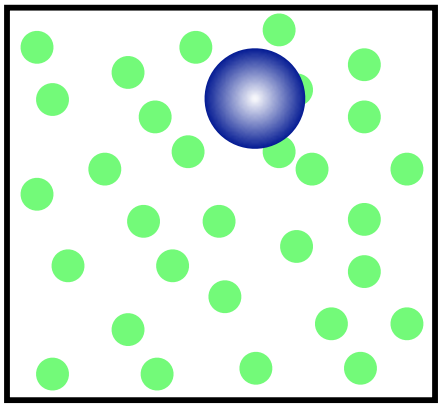

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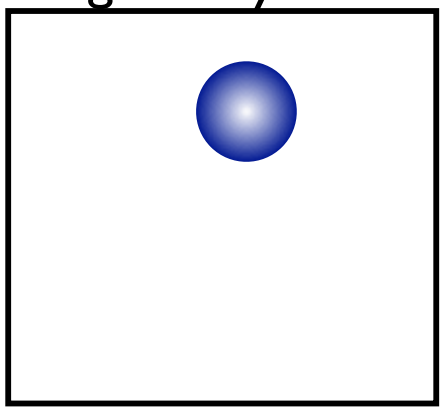

$$\mathbf{F}_I = -\gamma \dot{\mathbf{R}}_I + \xi(t)$$

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:

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

Original system — Friction and White Noise

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Original system — Friction and White Noise

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

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

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

Isobaric-Isothermic MD

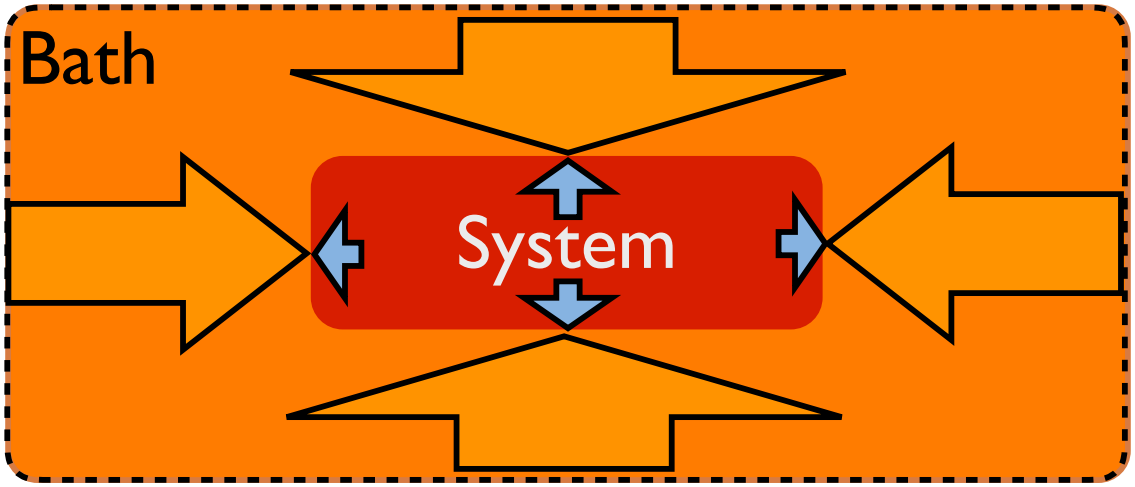
- Definition of instantaneous pressure:

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

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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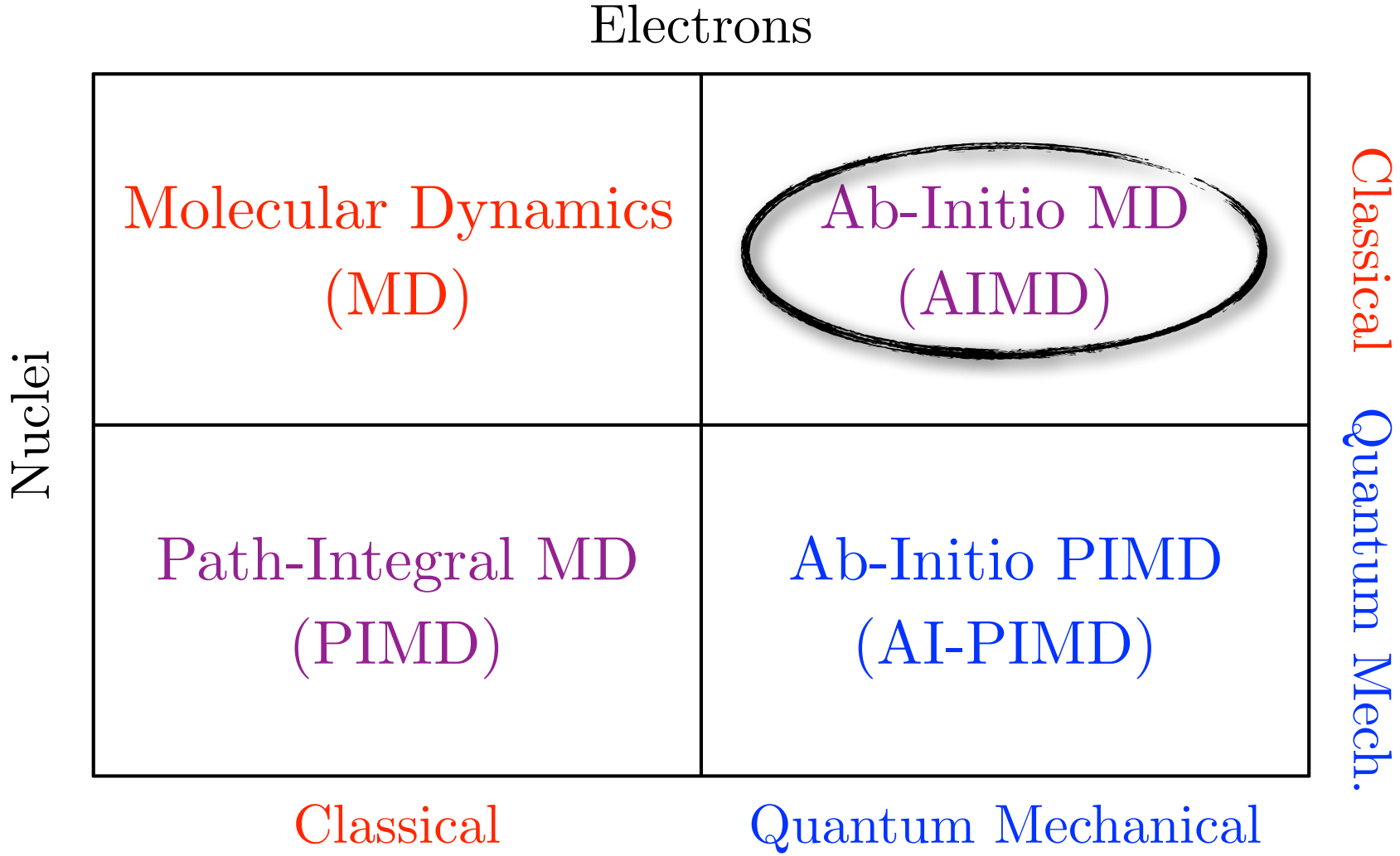
"Computer experiment": equilibrate system and measure



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

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

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

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

The forces are obtained by solving the Euler-Lagrange equation

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

Born-Oppenheimer MD

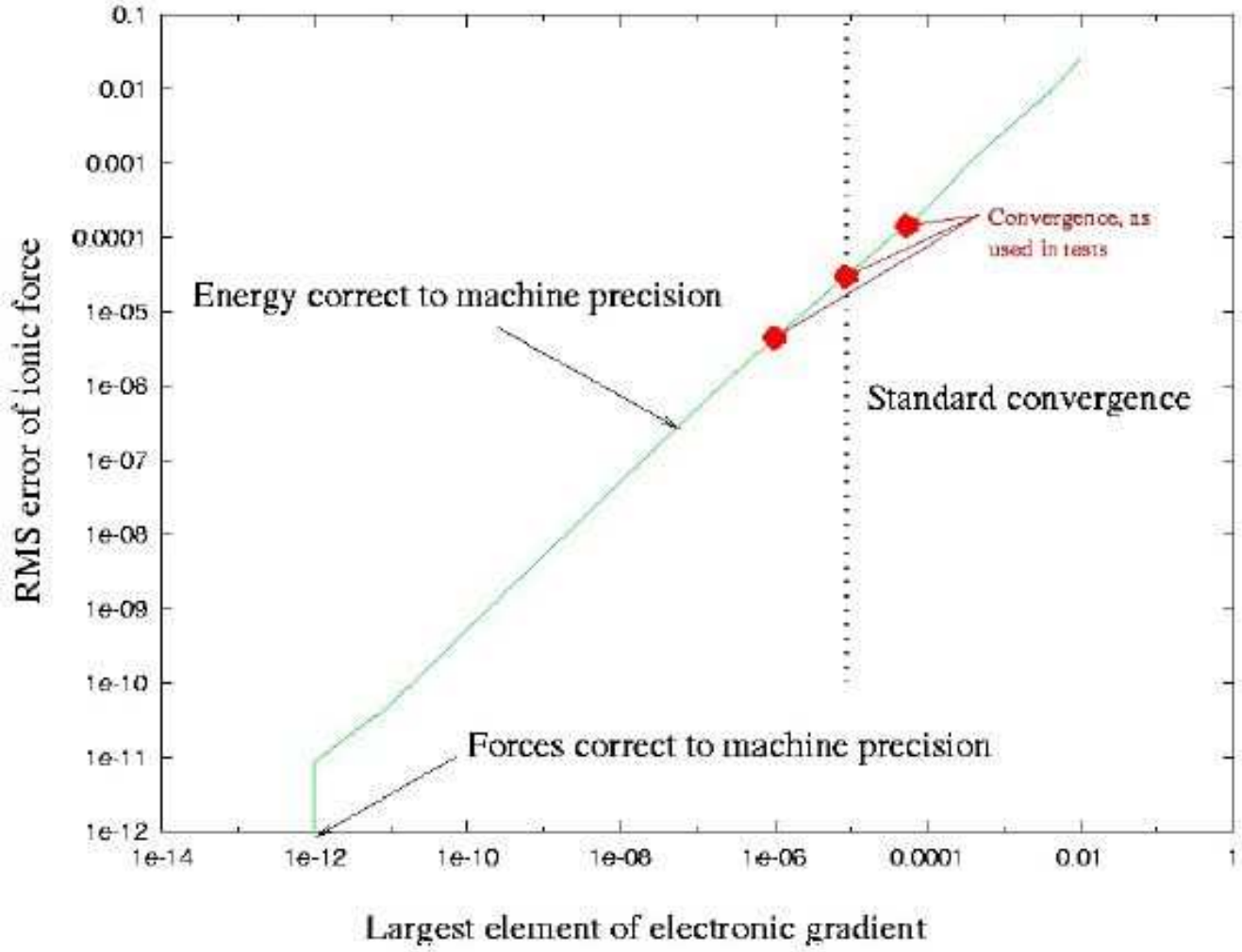
$$
\begin{aligned}
M_I \ddot{\boldsymbol{R}}_I &= -\nabla_{\boldsymbol{R}_I} \left[\min_{\{\psi_i\}} E\big[\{\psi_i\}; \boldsymbol{R}_I\big] \,\Big|_{\{\langle\psi_i|\psi_j\rangle = \delta_{ij}\}} \right] \\
&= -\frac{\partial E}{\partial \boldsymbol{R}_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial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

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

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

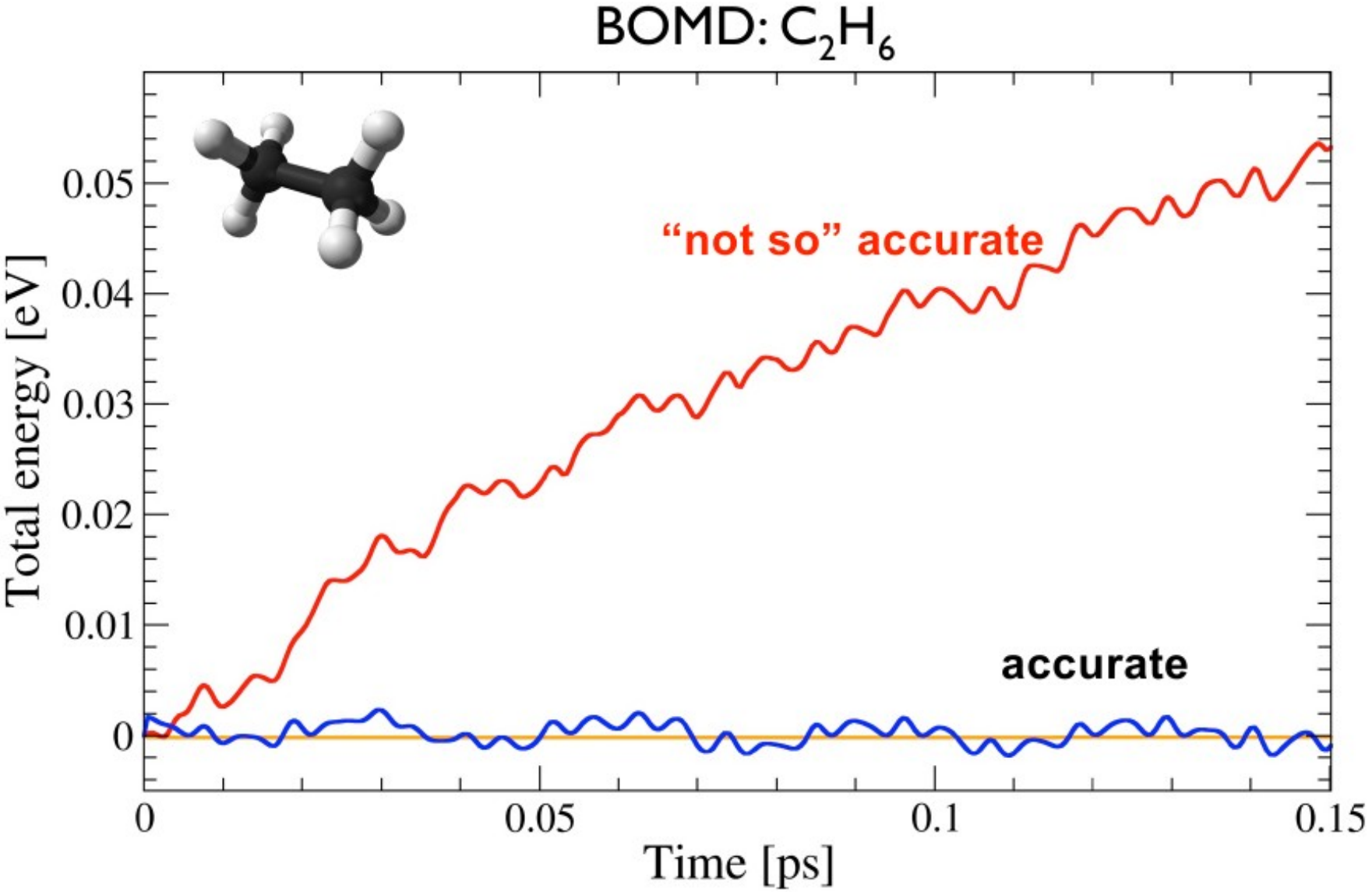
However, in general the HF-Theorem can not be assumed

Born-Oppenheimer MD



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

Born-Oppenheimer MD



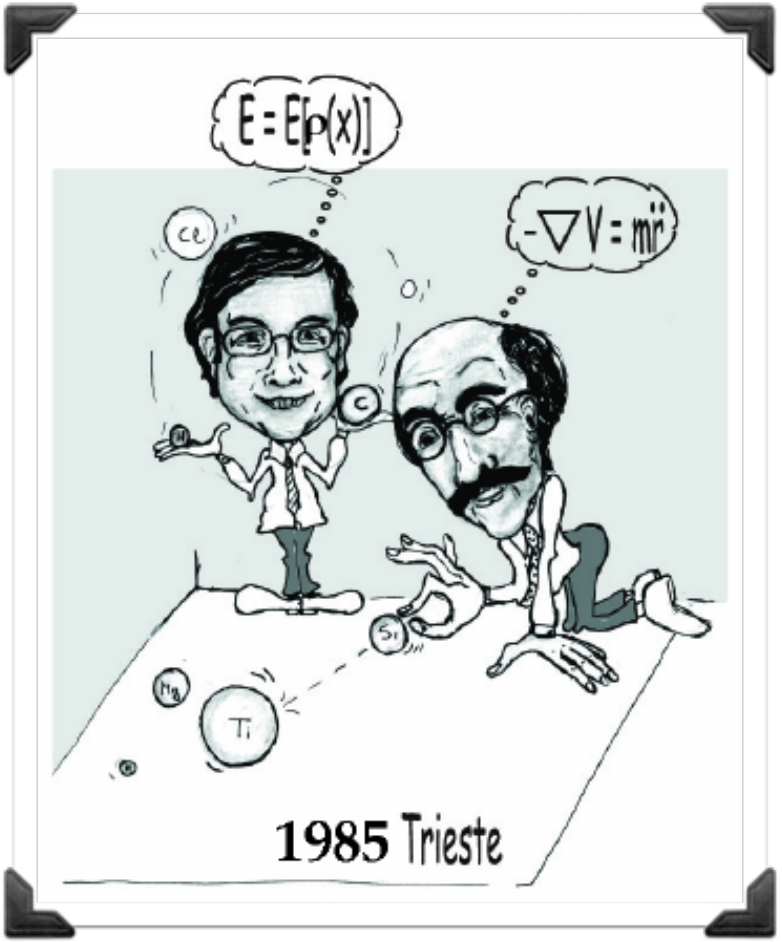
Born-Oppenheimer MD

- 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



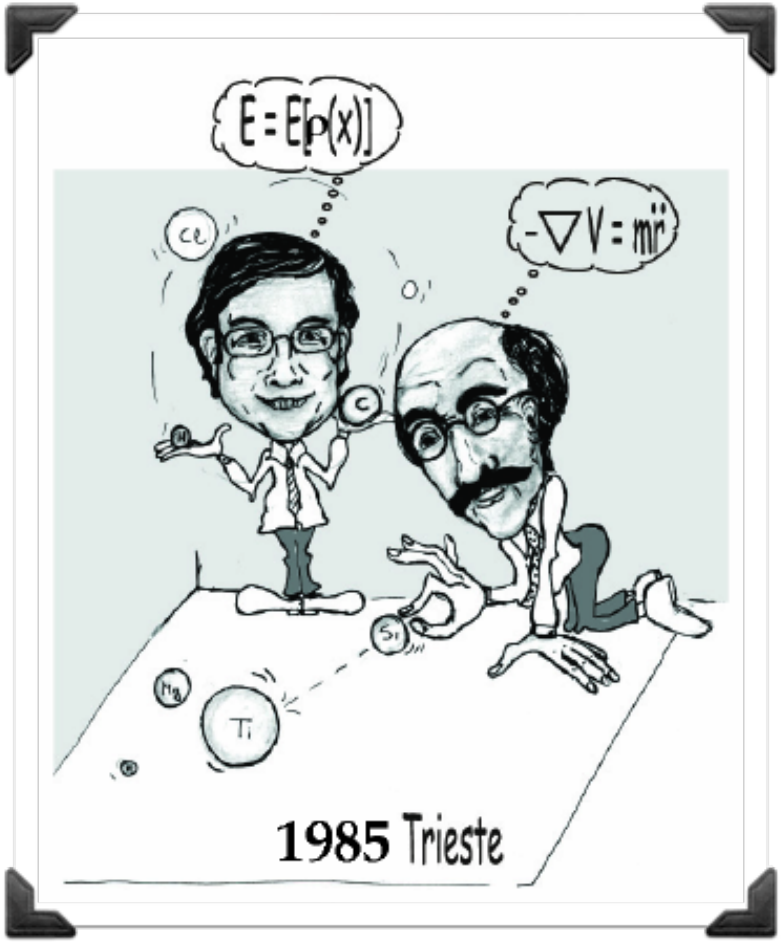
$$\mathcal{L}_{\mathrm{CP}}\big(\{\psi_i\};\boldsymbol{R},\dot{\boldsymbol{R}}\big) = \frac{1}{2}\mu\sum_i\langle\dot\psi_i|\dot\psi_i\rangle + \frac{1}{2}\sum_{I=1}^{N} M_I\dot{\boldsymbol{R}}_I^2 - E\big[\{\psi_i\};\boldsymbol{R}\big] + \sum_{i,j}\Lambda_{ij}\big(\langle\psi_i|\psi_j\rangle - \delta_{ij}\big)$$

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

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

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

Car-Parrinello MD



$$M_I \ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} \left[E\big[\{\psi_i\};\mathbf{R}\big] \Big|_{\{\langle\psi_i|\psi_j\rangle=\delta_{ij}\}} \right]$$

$$= -\frac{\partial E}{\partial \mathbf{R}_I} + \sum_{i,j} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle\psi_i|\psi_j\rangle$$

$$\mu \ddot{\psi}_i(\boldsymbol{r},t) = -\frac{\delta E}{\delta \langle\psi_i|} + \sum_j \Lambda_{ij}|\psi_j\rangle$$

$$= -\hat{H}_e\langle\psi_i| + \sum_j \Lambda_{ij}|\psi_j\rangle$$

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 $\ddot{\psi}_i \simeq 0$

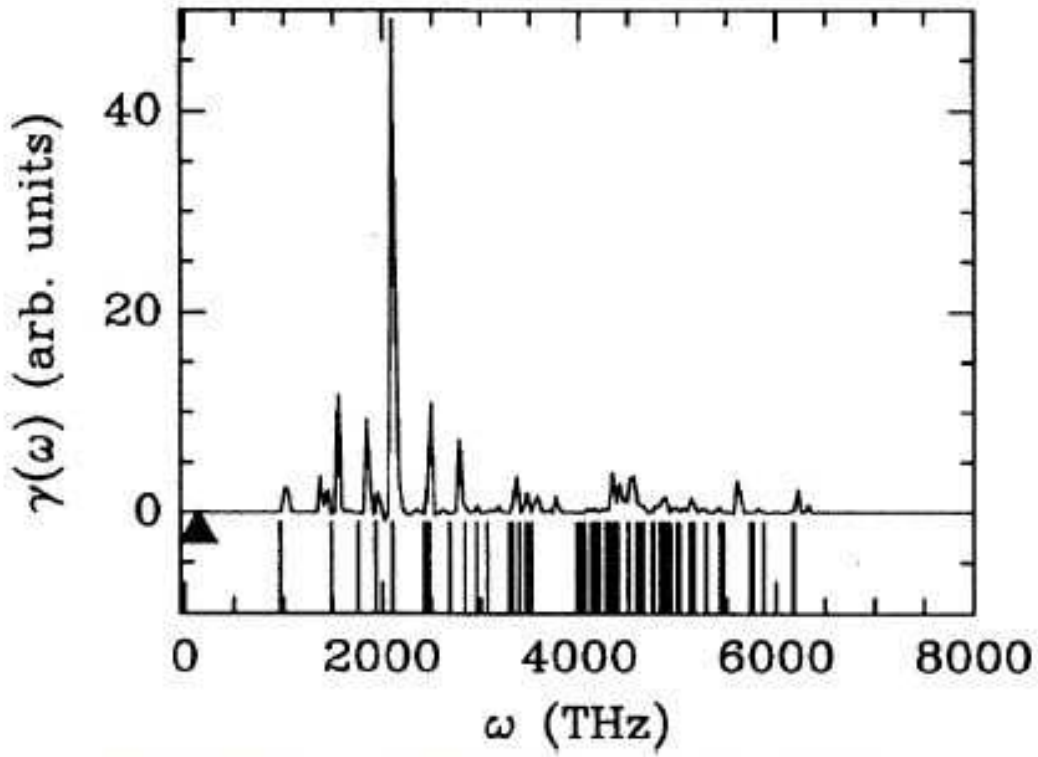
$$\frac{\partial E\left[\{\psi_i\}; \boldsymbol{R}_I\right]}{\partial \langle \psi_i |} - \sum_j \Lambda_{ij} |\psi_j\rangle \simeq 0$$

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

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

Car-Parrinello MD

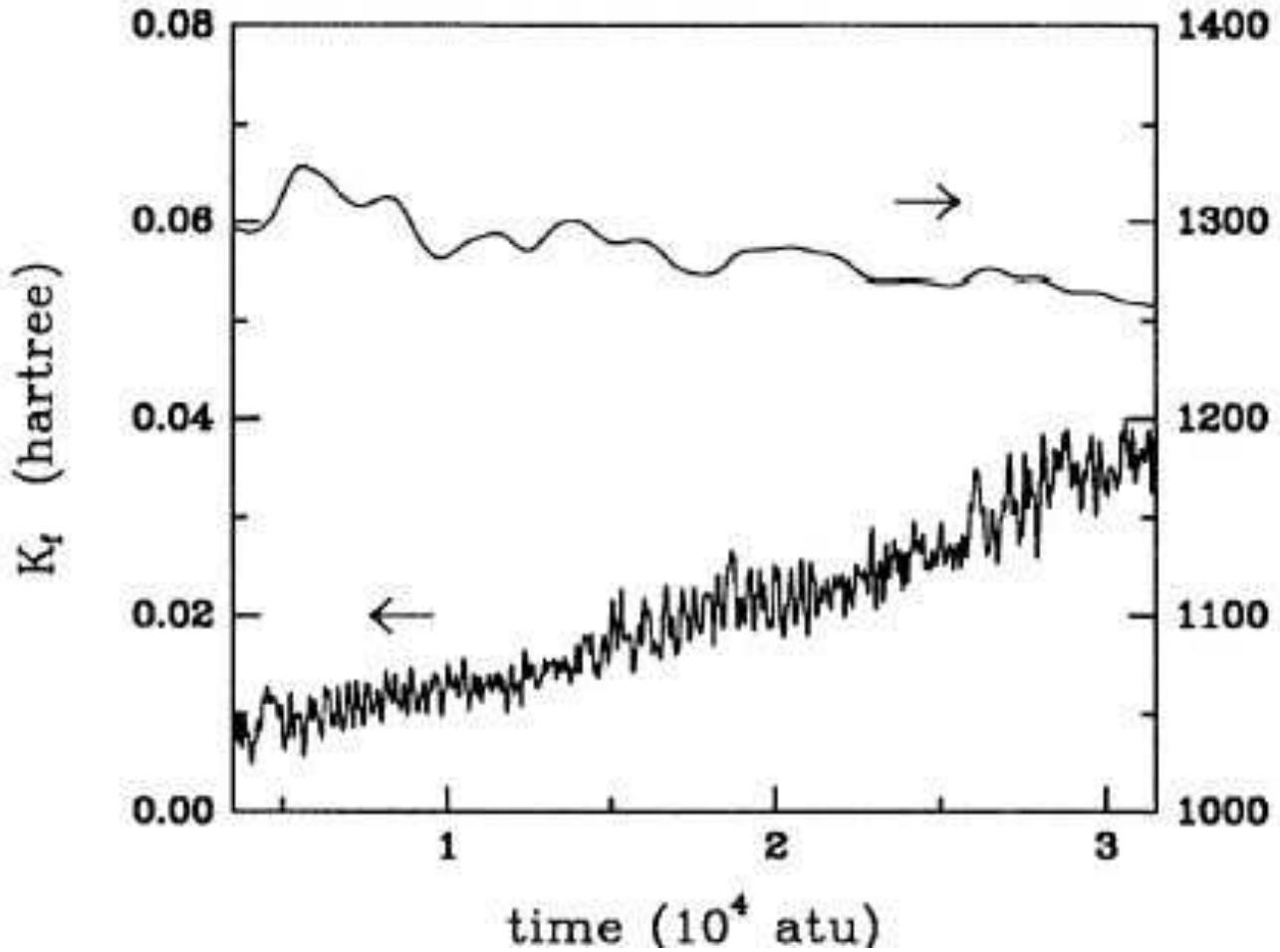
Vibrational spectra of electrons and ions do not overlap



Triangle = highest ionic frequency

Car-Parrinello MD

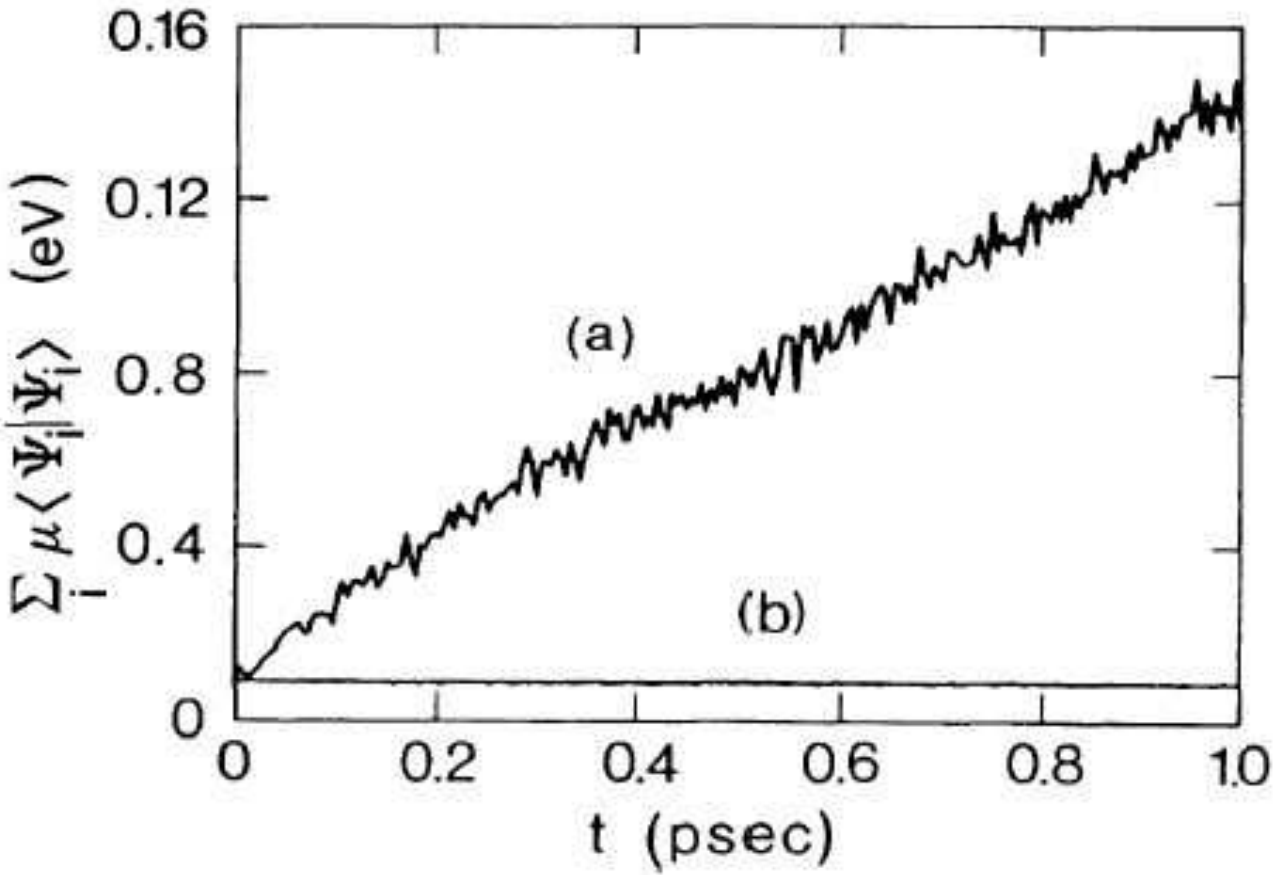
Vacancy in a hot 64-atom Si cell



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

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

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

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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 \\
&- 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}
$$

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

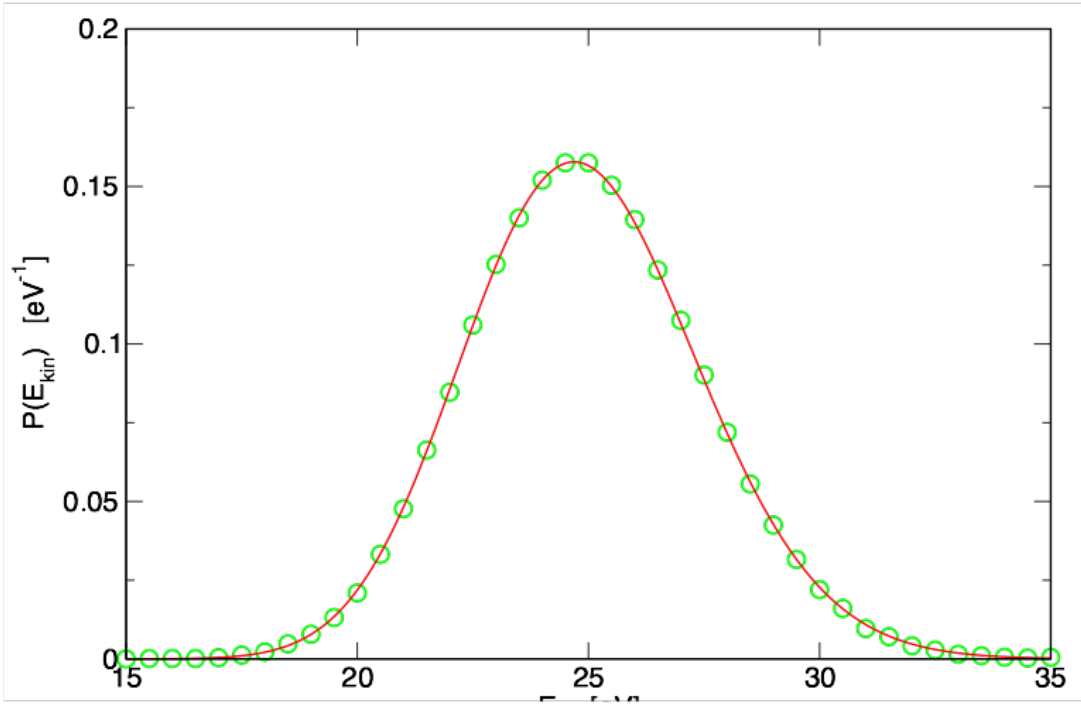
T. D. Kühne and E. Prodan, Annals of Physics **391**, 120 (2018)

Second-Generation CPMD

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

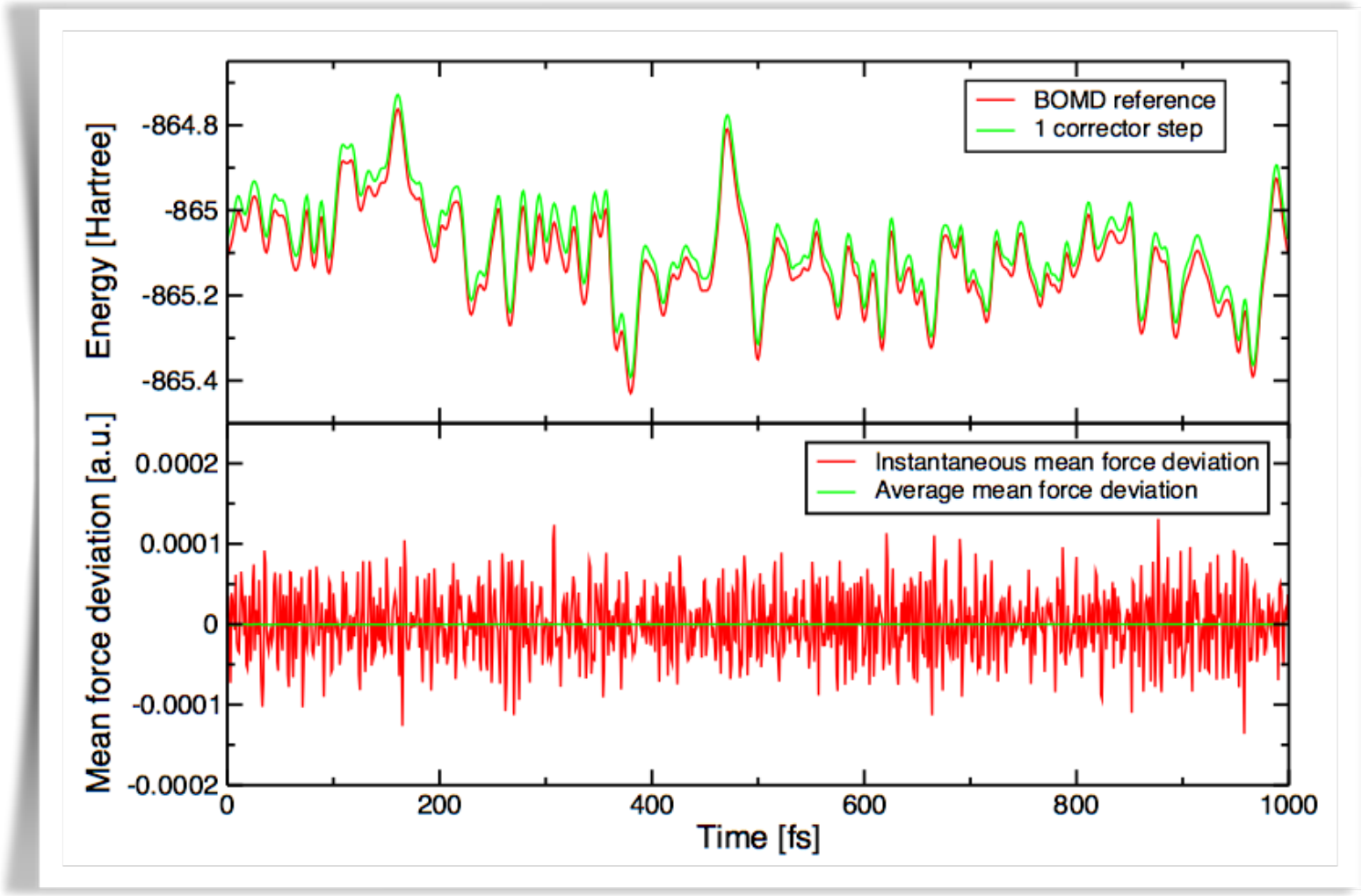
$$
\left\langle \Xi_I^D(0)\, \Xi_I^D(t) \right\rangle = 2\gamma_D M_I k_B T \delta(t)
$$

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



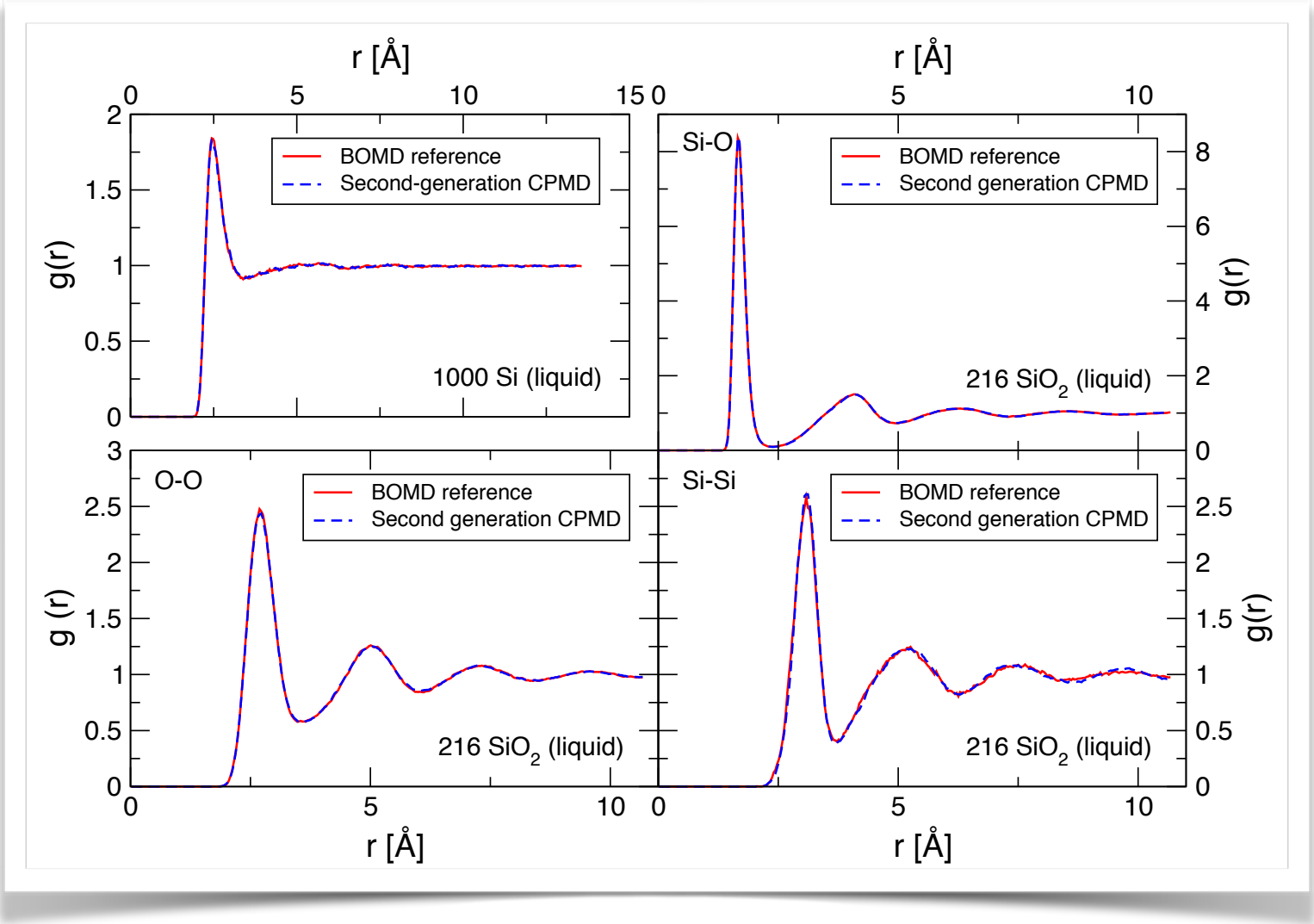
T. D. Kühne, M. Krack, F. Mohamed and M. Parrinello, Phys. Rev. Lett. **98**, 066401 (2007)

Second-Generation CPMD



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

Second-Generation CPMD

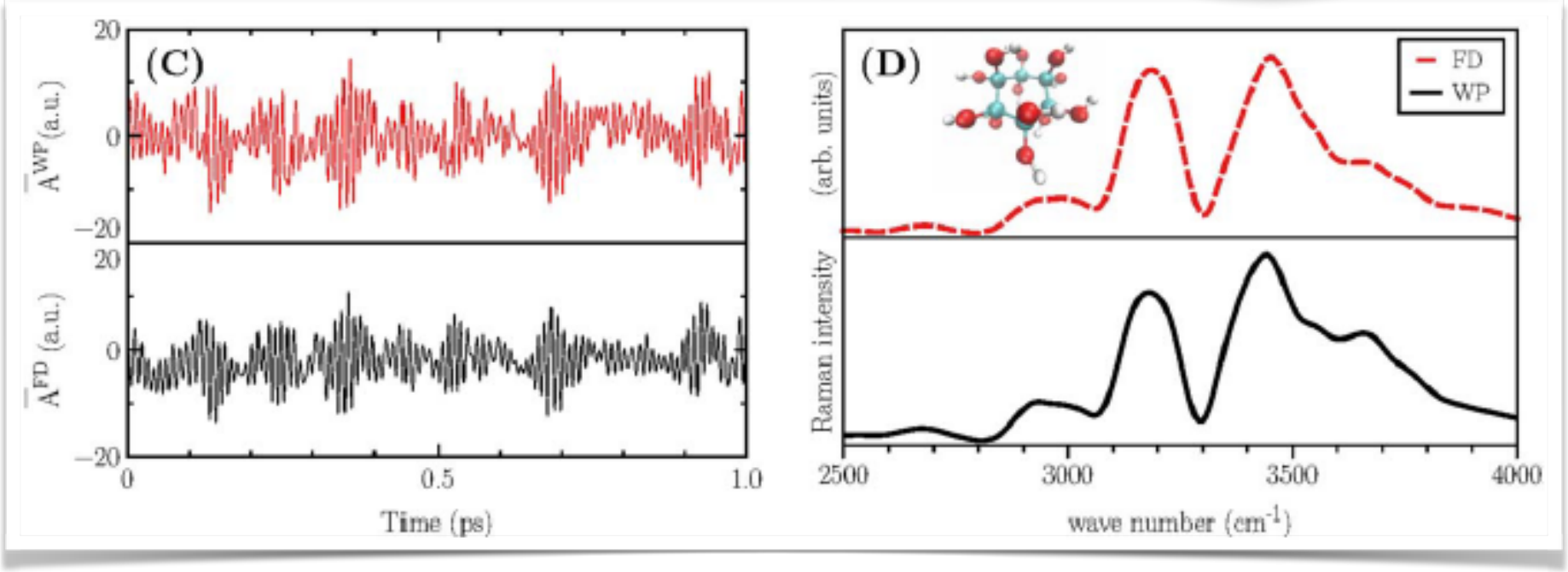


T. D. Kühne, M. Krack, F. Mohamed and M. Parrinello, Phys. Rev. Lett. **98**, 066401 (2007)

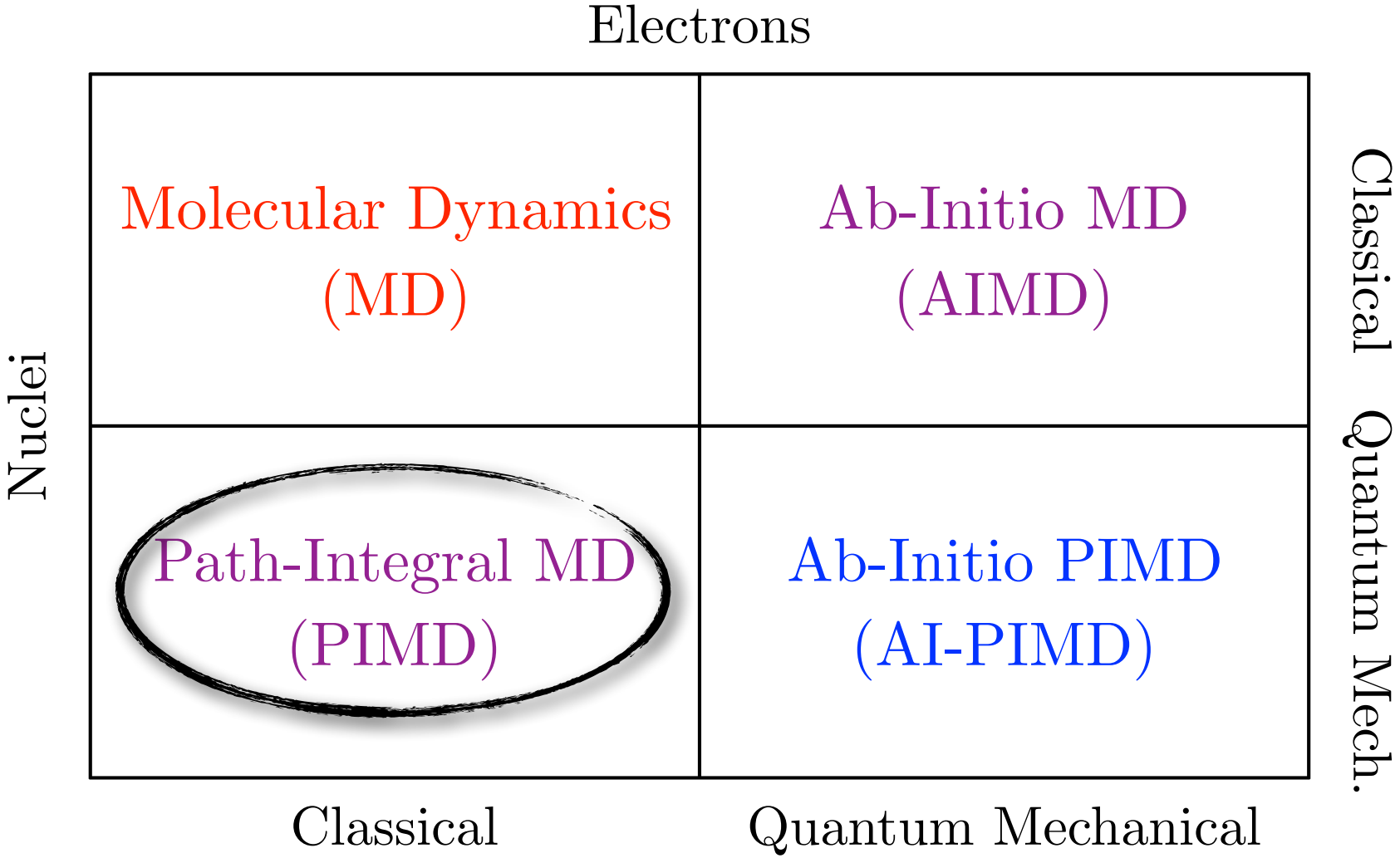
„On-the-fly“ Spectroscopy

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

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



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



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

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

Importance of NQE

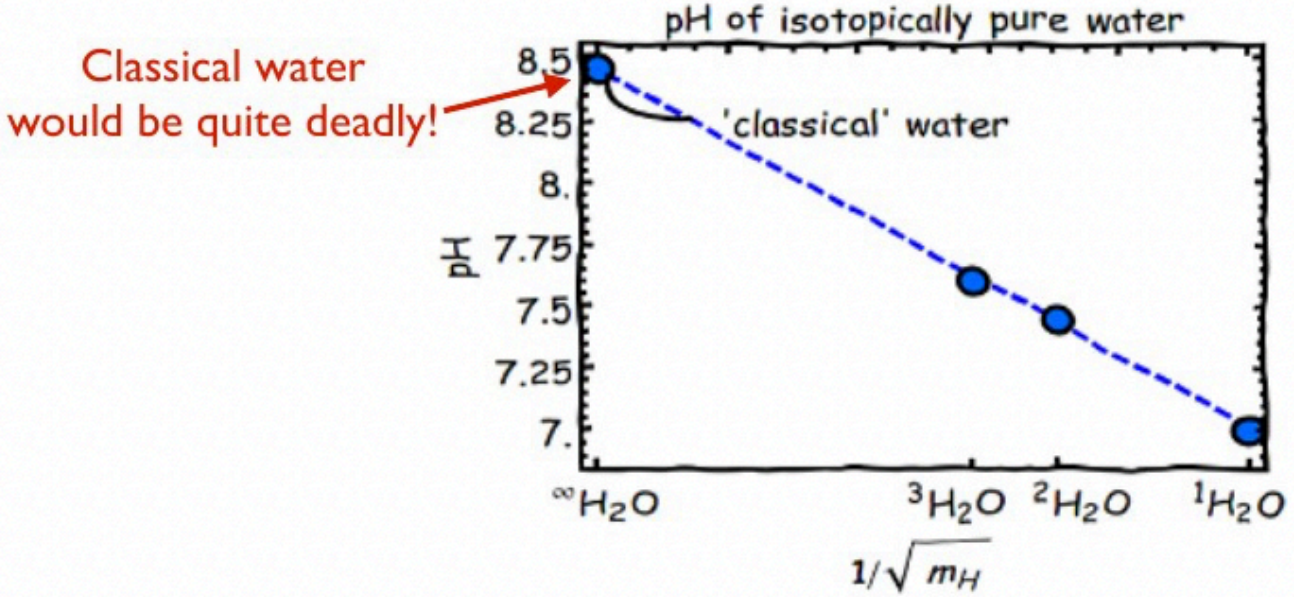
- Classically the average value of the kinetic energy follows equipartition (Boltzmann operator factorizes) and is given by

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

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

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

mass dependence

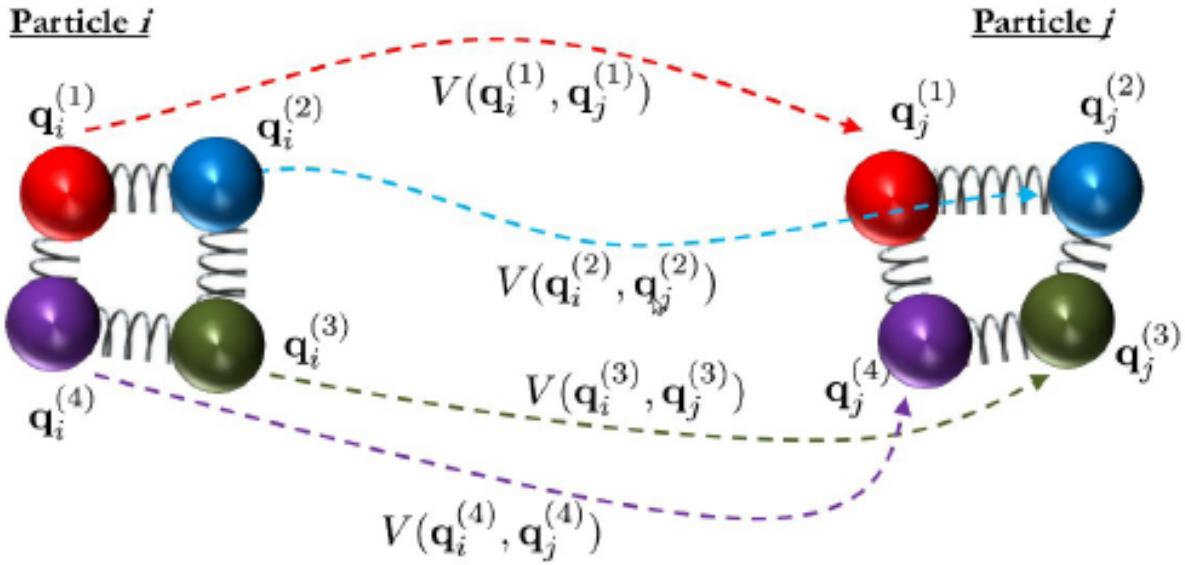


Path-Integral MD

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

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

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

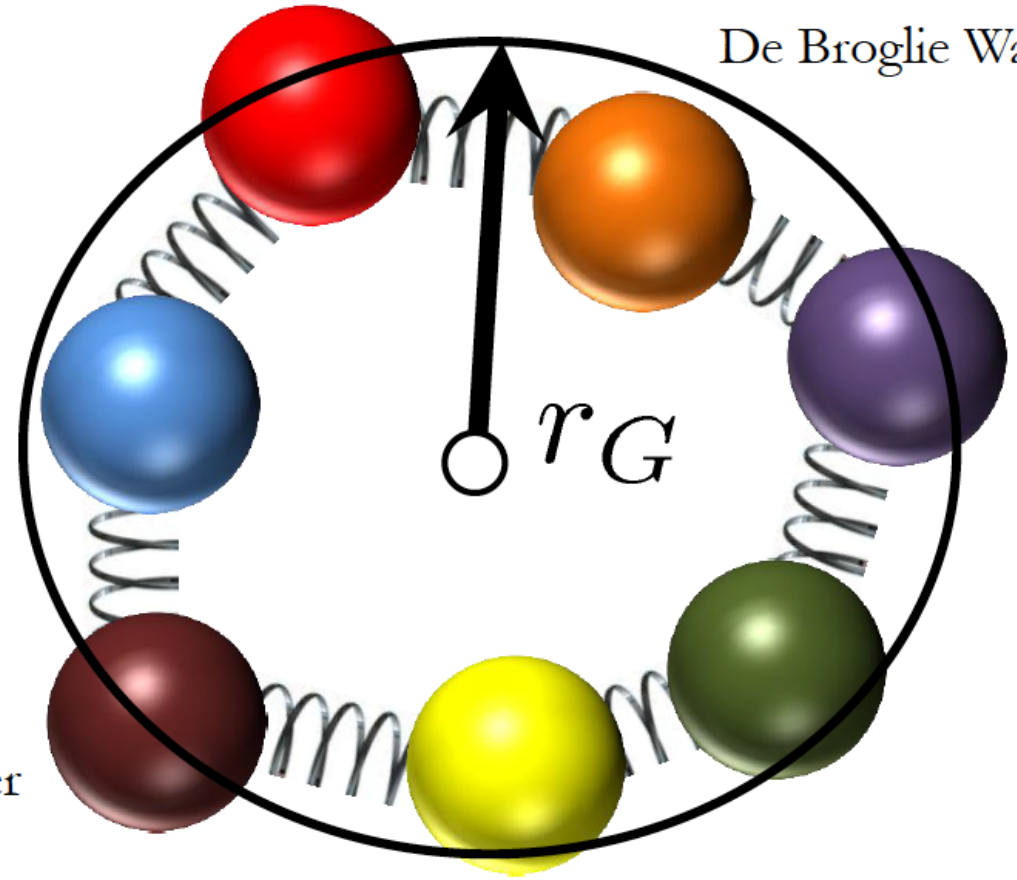


Path-Integral MD

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

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

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

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

$\mathbf{v}$: velocity

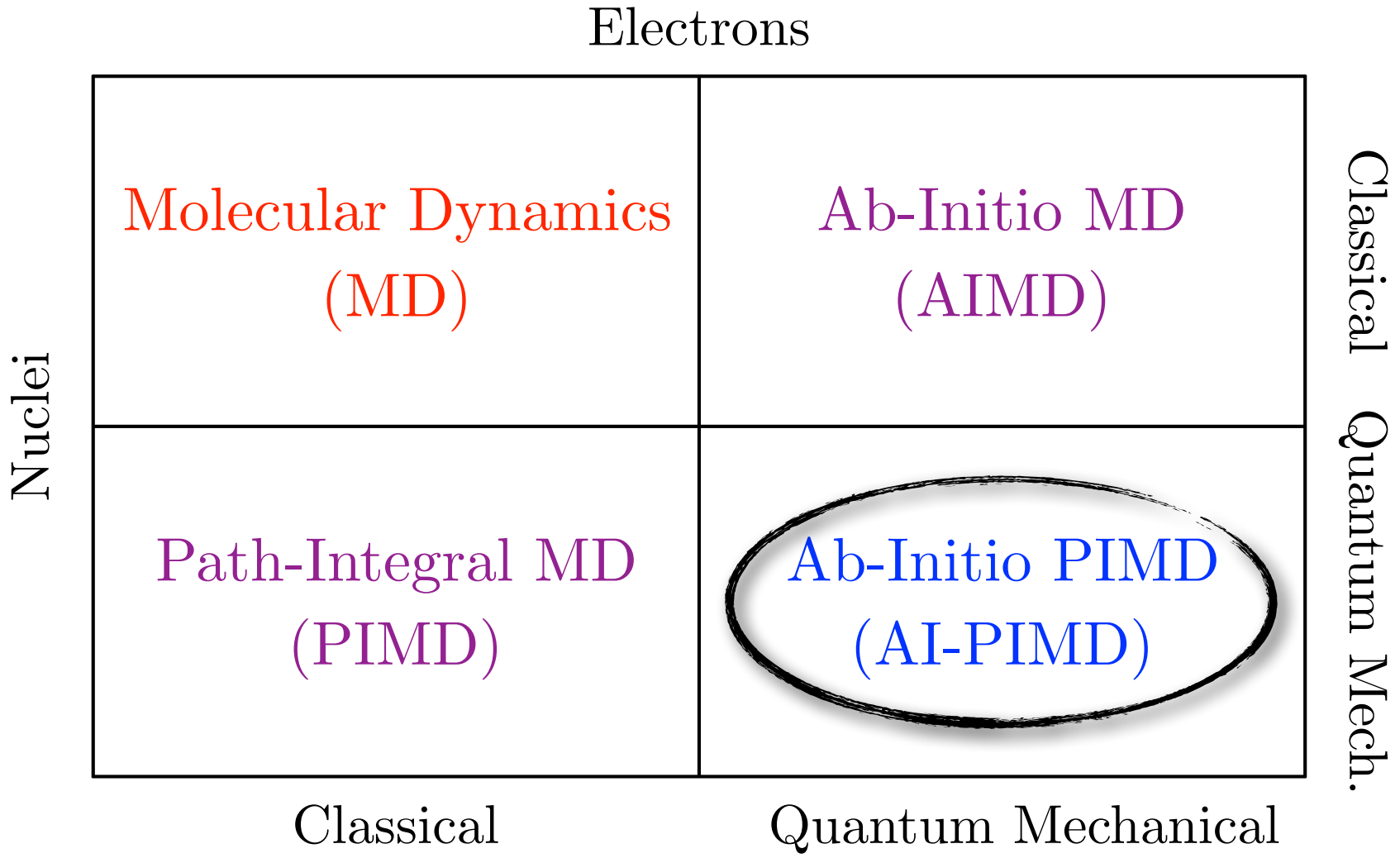
IR spectrum (dipole adsorption cross section)

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

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

μ: dipole

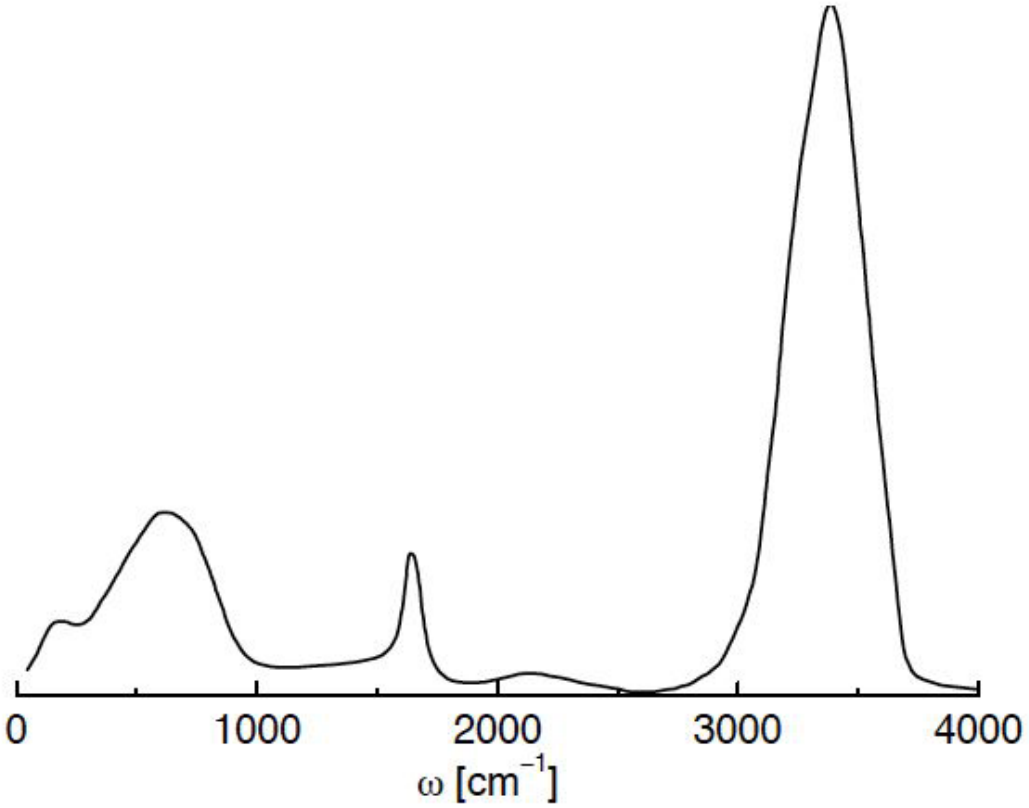
PIMD does NOT give access to real time propagation (momenta are fictitious)



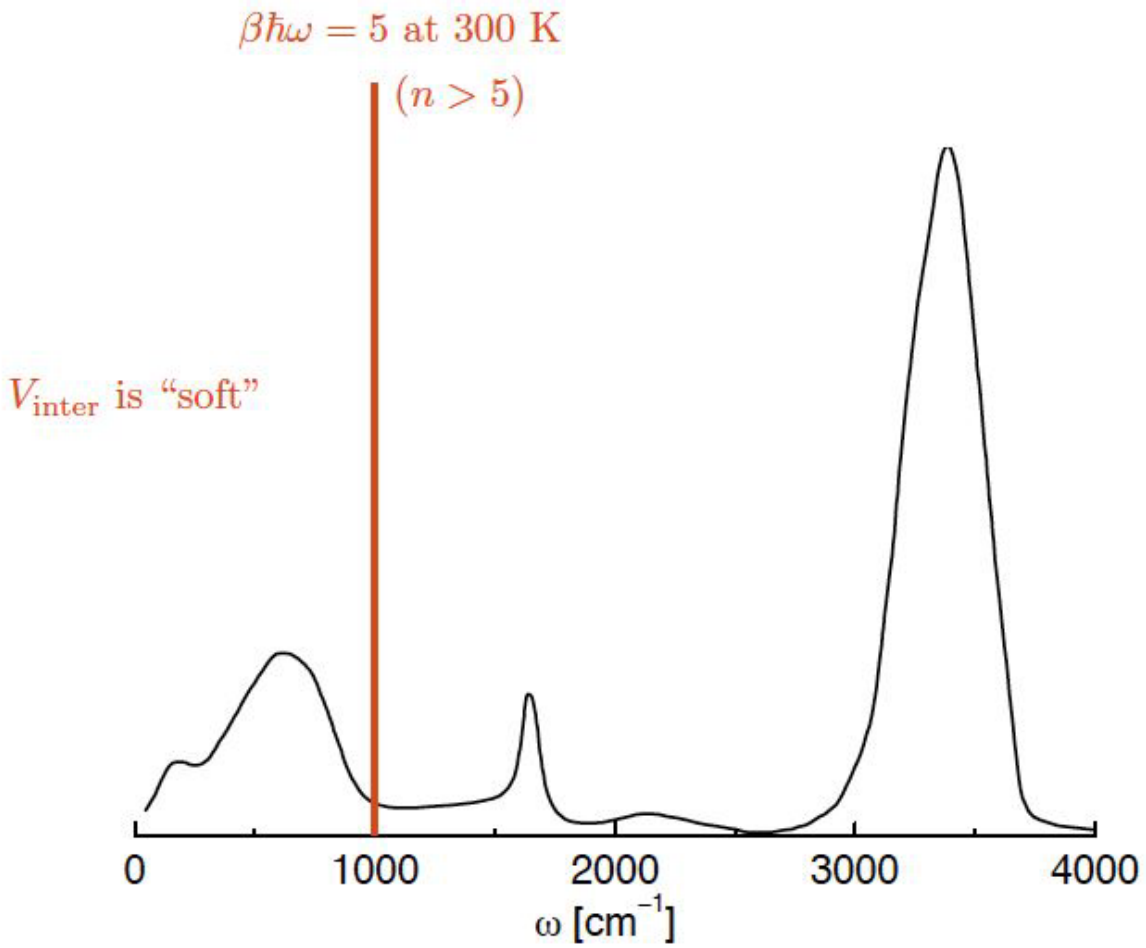
$$\mathcal{H}_e(\boldsymbol{r};\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R}) = \varepsilon(\boldsymbol{R})\psi(\boldsymbol{r};\boldsymbol{R})$$

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

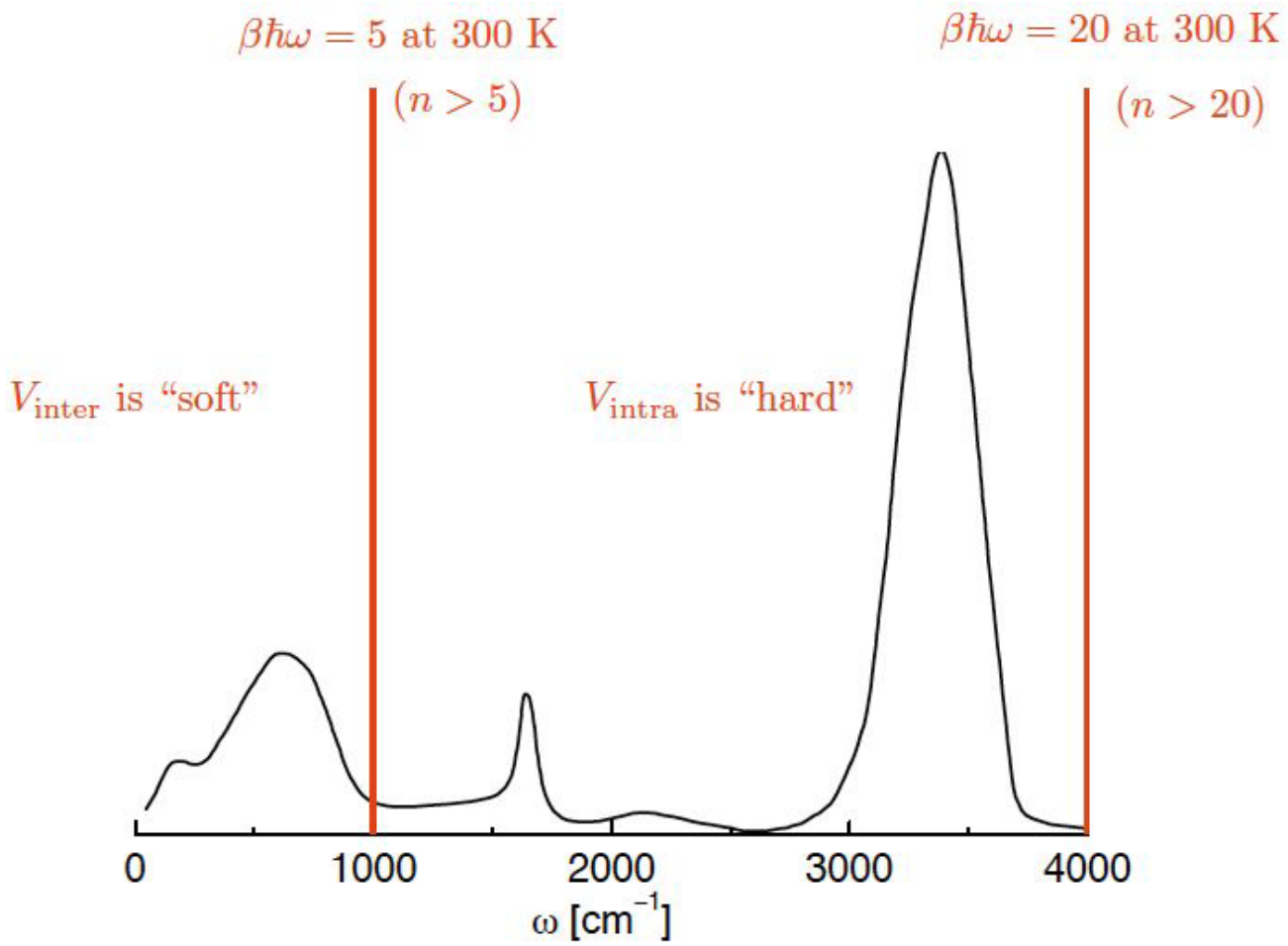
Ring Polymer Contraction



Ring Polymer Contraction

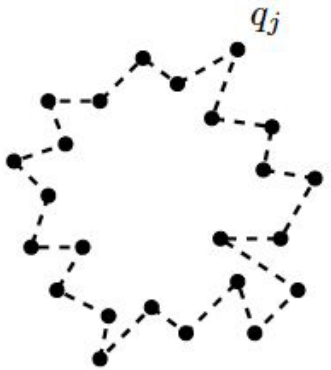


Ring Polymer Contraction



Ring Polymer Contraction

Ring polymer contraction:



$$\sum_{j=1}^{n} V_{\text{inter}}(q_j)$$

$FT \longrightarrow$

(etc.)

$\vdots$

$\omega_{\pm 4} \simeq 8\pi/\beta\hbar$

$\omega_{\pm 3} \simeq 6\pi/\beta\hbar$

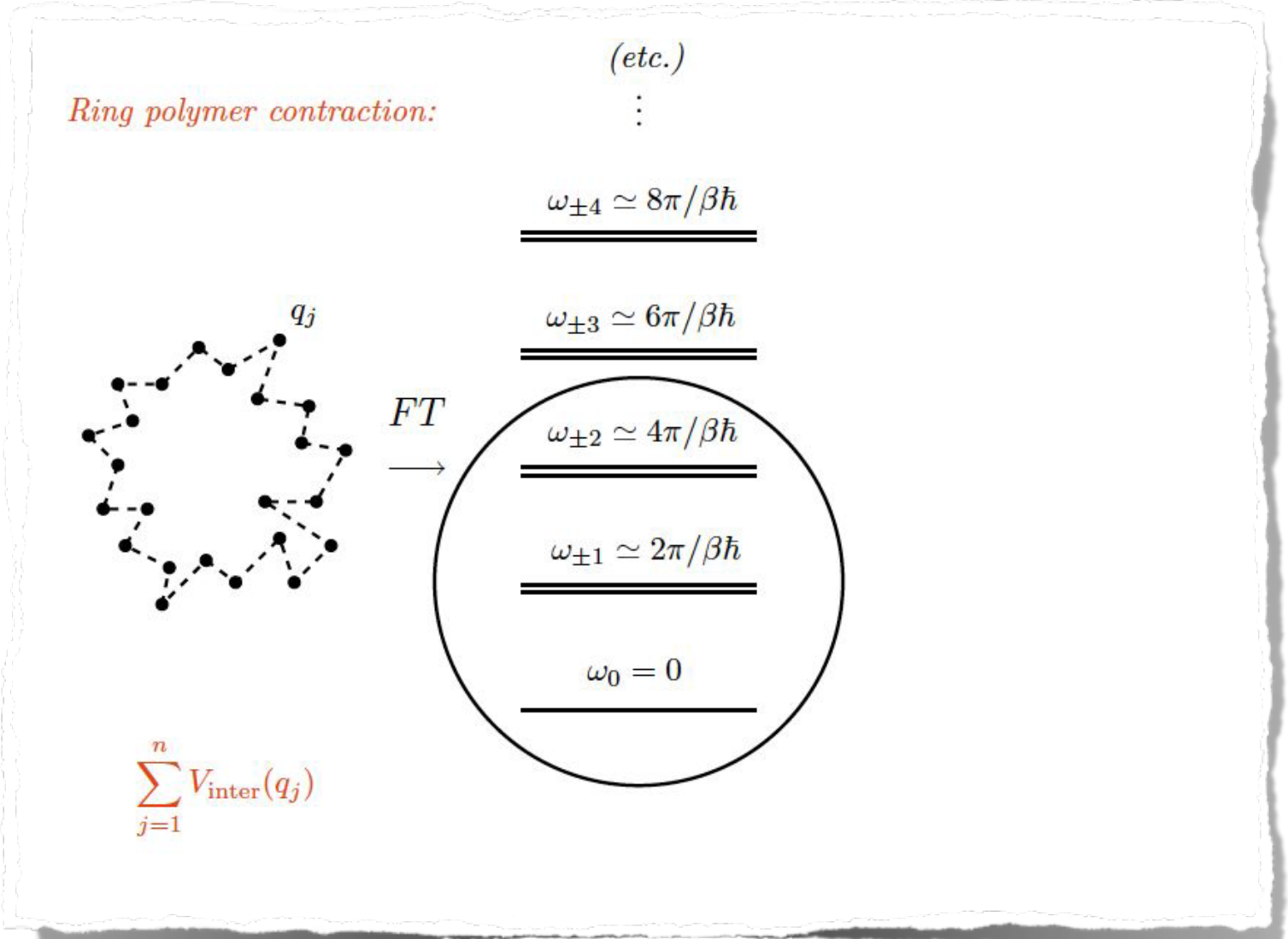
$\omega_{\pm 2} \simeq 4\pi/\beta\hbar$

$\omega_{\pm 1} \simeq 2\pi/\beta\hbar$

$\omega_0 = 0$

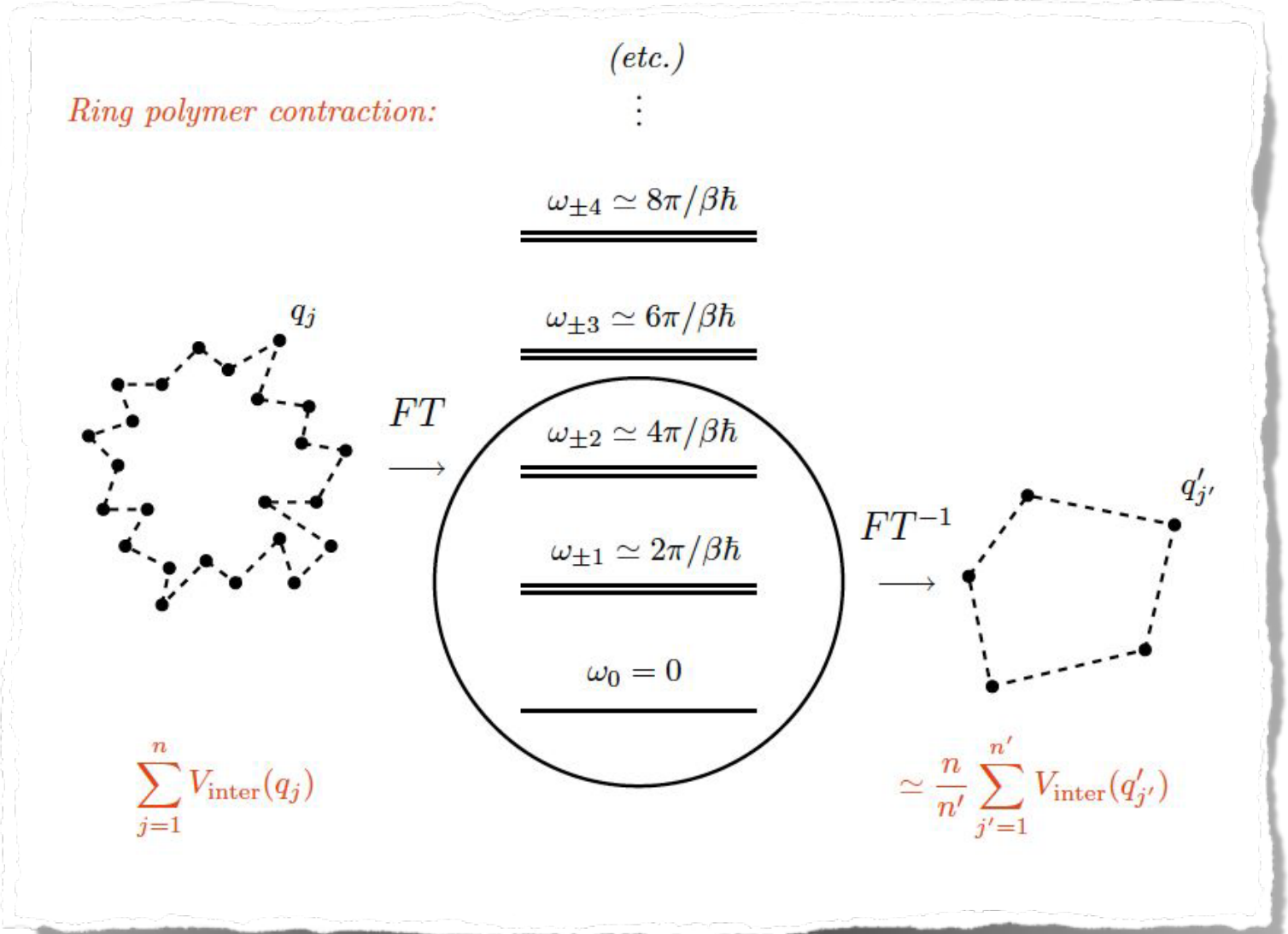
T. E. Markland and D. E. Manolopoulos, J. Chem. Phys. **129**, 024105 (2008)

Ring Polymer Contraction



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

Ring Polymer Contraction



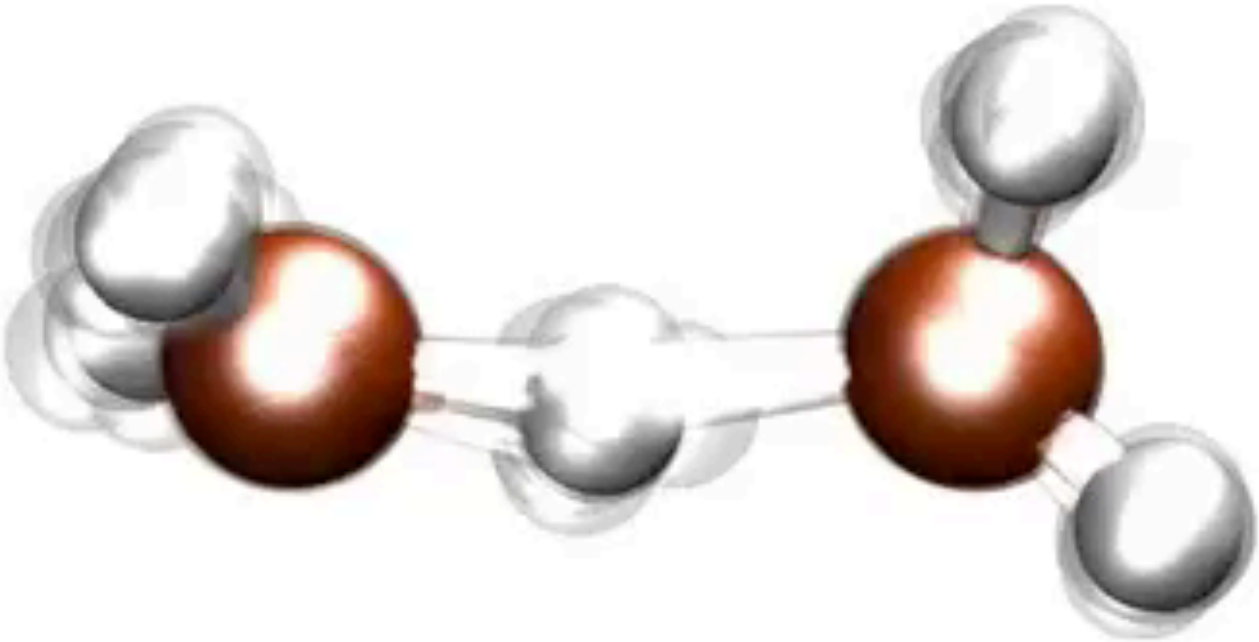
T. E. Markland and D. E. Manolopoulos, J. Chem. Phys. **129**, 024105 (2008)

Quantum-RPC

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

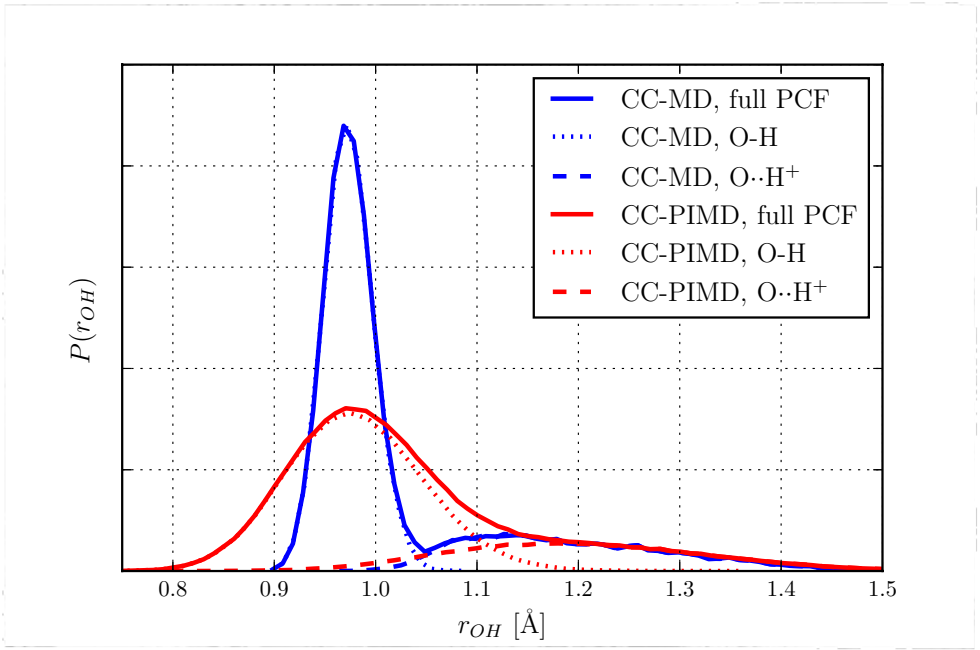
C. John, T. Spura, S. Habershon and T. D. Kühne, Phys. Rev. E **93**, 043305 (2016)

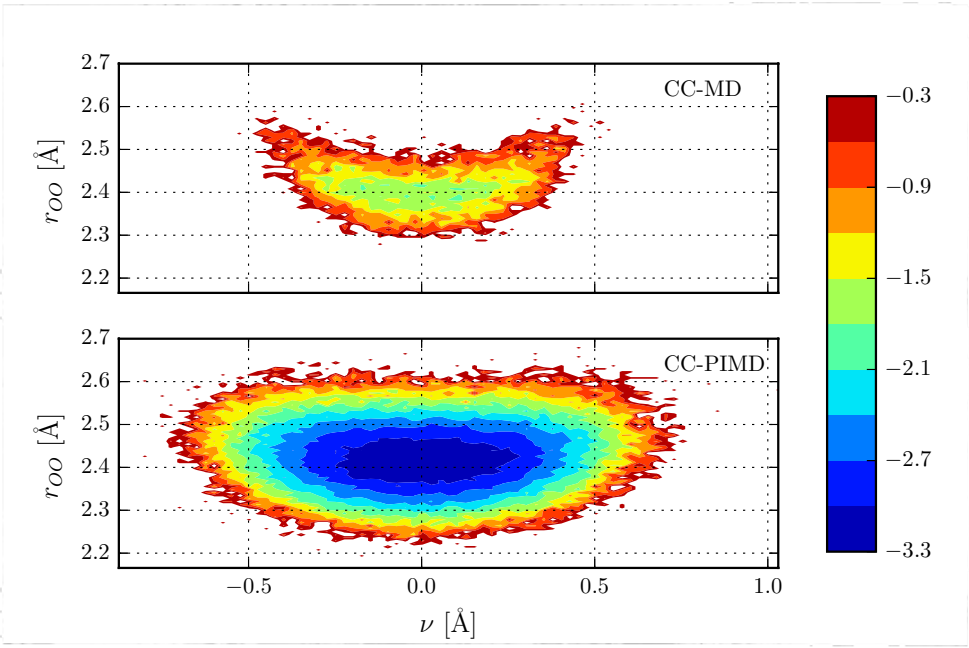
Coupled Cluster-RPMD



T. Spura, H. Elgabarty and T. D. Kühne, Phys. Chem. Chem. Phys. **17**, 14355 (2015)

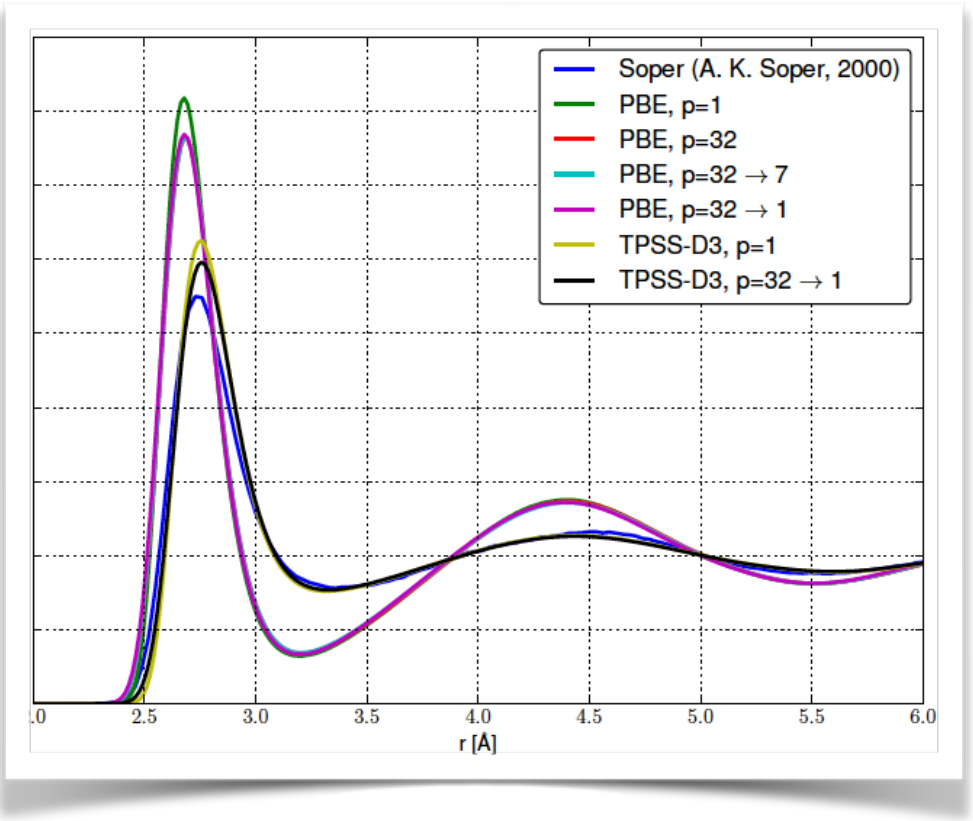
Coupled Cluster-RPMD

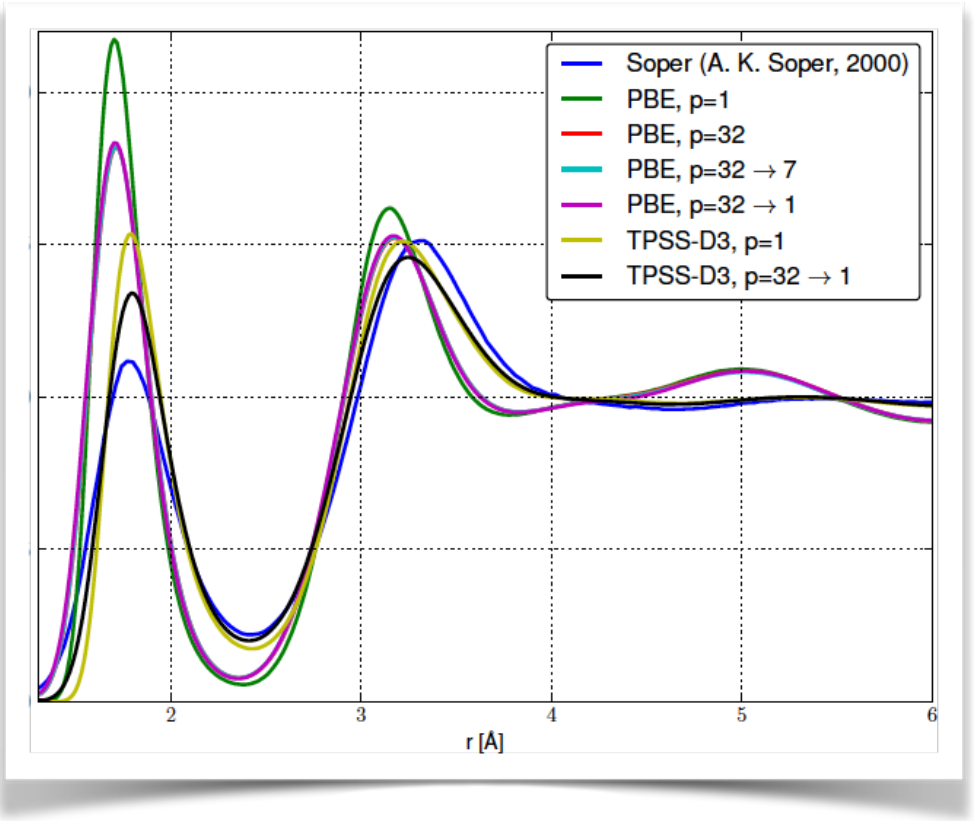




T. Spura, H. Elgabarty and T. D. Kühne, Phys. Chem. Chem. Phys. **17**, 14355 (2015)

Water: Quo Vadis DFT?





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


COFFEE BREAK