QUANTUM AND THERMAL MOTION IN MOLECULES FROM FIRST-PRINCIPLES

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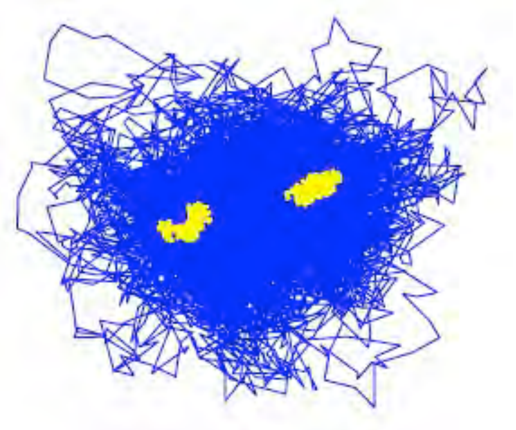

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  - ~~STRONG CORRELATION~~ SOME THERMOCHEMISTRY

MOTIVATION

Electronic structure is the key quantity to materials properties and related phenomena: Mechanical, thermal, electrical, optical,... .

Conventional *ab initio* / first-principles type methods

- suffer from laborious description of electron–electron correlations (CI, MCHF, DFT-functionals)
- typically ignore nuclear quantum and thermal dynamics and coupling of electron–nuclei dynamics (Born–Oppenheimer approximation)
- give the zero-Kelvin description, only.

PATH-INTEGRAL DESCRIPTION OF QUANTUM DYNAMICS

Time evolution of the wave function is laborious and ”challenging”:

- **path sampling**
- **interference of paths**
- **. . .**

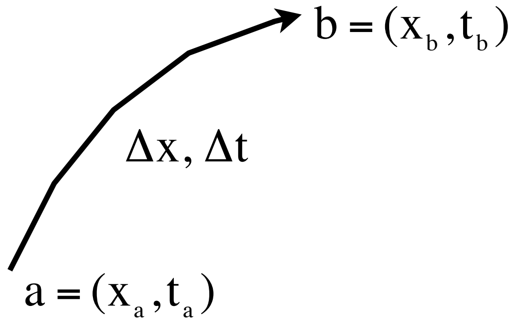
Propagation in imaginary time is in better control. It can be used as formulation quantum statistical physics, and thus, finding the <u>finite temperature electronic structure.</u>

Feynman–Hibbs, *Quantum Mechanics and Path Integrals,* (McGraw-Hill, 1965)
Feynman R.P., Rev. Mod. Phys. **20**, 367–387 (1948)
Feynman R.P., *Statistical Mechanics* (Westview, Advance Book Classics, 1972)

CLASSICAL PATH

Let us consider particle dynamics from a to b.

Lagrangian formulation of classical mechanics for finding the path/trajectory leads to equations of motion from minimization (extremum) of action



$$S = \int_{t_a}^{t_b} L(\dot{x}, x, t)\,dt,$$ where the Lagrangian $L = T - V$.

$$\delta S = 0 \quad \Rightarrow \quad \frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = 0 \quad \Rightarrow \quad -\frac{\partial V}{\partial x} = m\ddot{x}$$

For example, the classical action of the free-particle is

$$S = \frac{1}{2} m \left(\frac{\Delta x}{\Delta t}\right)^2 \Delta t = \frac{1}{2} m \frac{(x_b - x_a)^2}{(t_b - t_a)}.$$

QUANTUM PATH

Usually, the most probable quantum path is the classical one, but other paths contribute, too, with a certain probability. Quantum probability of the particle propagation from a to b is

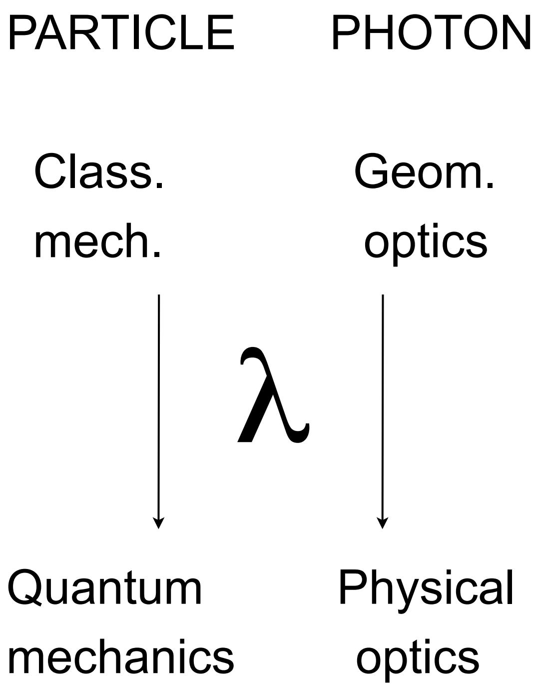
$$P(b,a) = |K(b,a)|^2 ,$$

the absolute square of the probability amplitude K. The probability amplitude is the sum over all oscillating phase factors ϕ of the paths x_{ab} as

$$K(b,a) = \sum_{\text{all } x_{ab}} \phi[x_{ab}]$$

where the phase is proportional to the action

$$\phi[x(t)] = A \times \exp\left(\frac{i}{\hbar} S[x(t)]\right)$$



PARTICLE

PHOTON

Class. mech.

Geom. optics

λ

Quantum mechanics

Physical optics

PATH-INTEGRAL

Now, let us define the sum over all paths as a path-integral

$$K(b,a) = \int_a^b e^{(i/\hbar)S[b,a]} \, \mathcal{D}x(t).$$

We call this ”kernel” or ”propagator” or ”Green’s function”.

In terms of stationary eigenstates it can be written as

$$K(b,a) = \sum_n \phi_n^*(a)\phi_n(b)\, e^{-(i/\hbar)E_n(t_b - t_a)}$$

The kernel satisfies the free-particle Schrödinger equation in space-time $\{x_b, t_b\}$.

For example, the free-particle propagator takes now the form

$$K_0(b,a) = \left(\frac{m}{2\pi i\hbar(t_b - t_a)}\right)^{1/2} \exp\left(\frac{im(x_b - x_a)^2}{2\hbar(t_b - t_a)}\right).$$

MIXED STATE DENSITY MATRIX

Considering all states $\phi_n(x)$ of the particle, for the probability $p(x)$ of finding the particle/system in configuration space at x, we have

$$P(x) = \sum_n p_n(x) = \frac{1}{Z} \sum_n \phi_n^*(x) \phi_n(x)\, e^{-\beta E_n}.$$

$$\beta = \frac{1}{kT}$$

Now, define the mixed state density matrix (in position presentation)

$$\rho(x', x) = \sum_n \phi_n^*(x') \phi_n(x)\, e^{-\beta E_n}.$$

$$(\ \rho(\beta) = e^{-\beta H}\ )$$

Thus, we find

$$P(x) = \frac{1}{Z} \rho(x, x)$$

and normalization implies

$$Z = \int \rho(x, x)\, dx = \mathrm{Tr}(\rho).$$

Expectation values evaluated from

$$\langle A \rangle = \mathrm{Tr}(\rho A) / Z$$

PATH-INTEGRAL EVALUATION OF DENSITY MATRIX

Now, compare

$$\rho(x',x) = \sum_n \phi_n^*(x')\phi_n(x)\, e^{-\beta E_n}$$

and

$$K(b,a) = \sum_n \phi_n^*(a)\phi_n(b)\, e^{-(i/\hbar)E_n(t_b - t_a)}$$

in equilibrium (time independent hamiltonian) and $t_b > t_a$.

Replacing $(t_b - t_a) = u$ by $-i\hbar\beta$ or $\beta = i(t_b - t_a)/\hbar$ (imaginary time period)

we obtain $\rho(b,a)$, for which $\dfrac{\partial\rho(b,a)}{\partial\beta} = -H_b\,\rho(b,a)$. Cf. $\dfrac{\partial K(b,a)}{\partial t_b} = -\dfrac{i}{\hbar} H_b\, K(b,a)$

for a time independent hamiltonian. Thus, we can evaluate the density matrix from a path-integral similarly

$$\rho(x_b, x_a; \beta) = \int_{\text{all } x(u)} e^{(-i/\hbar)S[\beta,0]}\, \mathcal{D}x(u),$$

where the imaginary time action is

$$S[x(u);\beta,0] = \int_0^b \left[\frac{m}{2}\dot{x}^2(u) + V(x(u))\right] du.$$

MONTE CARLO SAMPLING OF IMAGINARY TIME PATHS

For the density operator we can write

$$\rho(\beta) = e^{-\beta H} = e^{-\beta/2H} e^{-\beta/2H},$$

if the kinetic and potential energies in the hamiltonian

$$H = T + V$$

commute. This becomes exact at the limit of imaginary time period goes to zero, the high temperature limit, because the potential energy approaches constant in position representation for each imaginary time step.

Thus, we can write

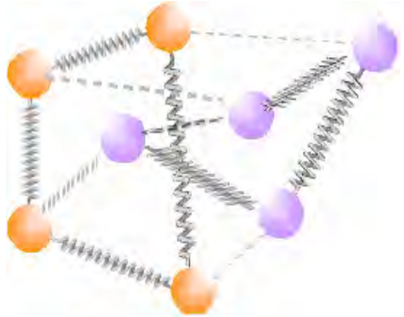
$$\rho(r_0, r_M; \beta) = \iiint \rho(r_0, r_1; \tau)\rho(r_1, r_2; \tau) \ldots \rho(r_{M-1}, r_M; \tau)\, dr_1 dr_2 \ldots dr_{M-1},$$

where

$$\tau = \beta / M, \qquad \beta = \frac{1}{kT}$$

and M is called the Trotter number.

This allows numerical sampling of the imaginary time paths with a Monte Carlo method.



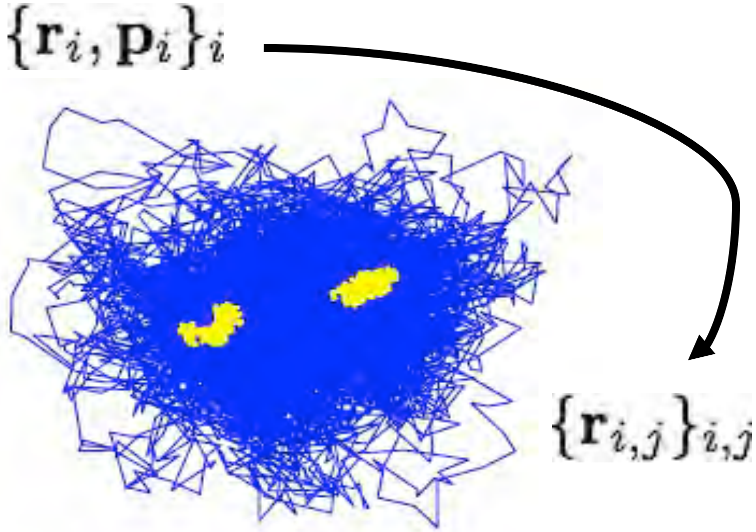
EVALUATION WITH MONTE CARLO

Monte Carlo allows straightforward numerical procedure for evaluation of multidimensional integrals.

Metropolis Monte Carlo

- NVT (equilibrium) ensemble
- now yields mixed state density matrix with almost classical transparency

Metropolis N. et al., J. Chem. Phys. **21**, 1087, (1953).



Ceperley D.M., Rev. Mod. Phys. **67**, 279, (1995) and in *Monte Carlo and ...*
(Eds. K. Binder and G. Ciccotti, Editrice Compositori, Bologna, Italy 1996)
Storer R.G., J. Math. Phys. 9, 964, (1968)

A-FEW-QUANTUM-PARTICLES SYSTEMS

- **A COUPLE OF ELECTRONS IN QUANTUM DOTS**
  - M. Leino & TTR, Physica Scripta **T114**, 44 (2004)
  - M. Leino & TTR, Few Body Systems **40**, 237 (2007)
- **HYDROGEN ATOMS ON Ni SURFACE**
  - M. Leino, J. Nieminen & TTR, Surf. Sci. **600**,1860 (2006)
  - M. Leino, I. Kylänpää & TTR, Surf. Sci. **601**, 1246 (2007)
- **ELECTRONS AND NUCLEI QUANTUM DYNAMICS**
  - I. Kylänpää, M. Leino & TTR, PRA **76**, 052508 (2007)
  - ➡ I. Kylänpää, TTR, J.Chem.Phys. **133**, 044312 (2010)
  - ➡ I. Kylänpää, TTR, J.Chem.Phys. **135**, 104310 (2011)
- **THREE AND FOUR PARTICLE MOLECULES**
  - I. Kylänpää, TTR, PRA **80**, 024504, (2009)
  - I. Kylänpää, TTR and DM. Ceperley, PRA **86**, 052506, (2012)

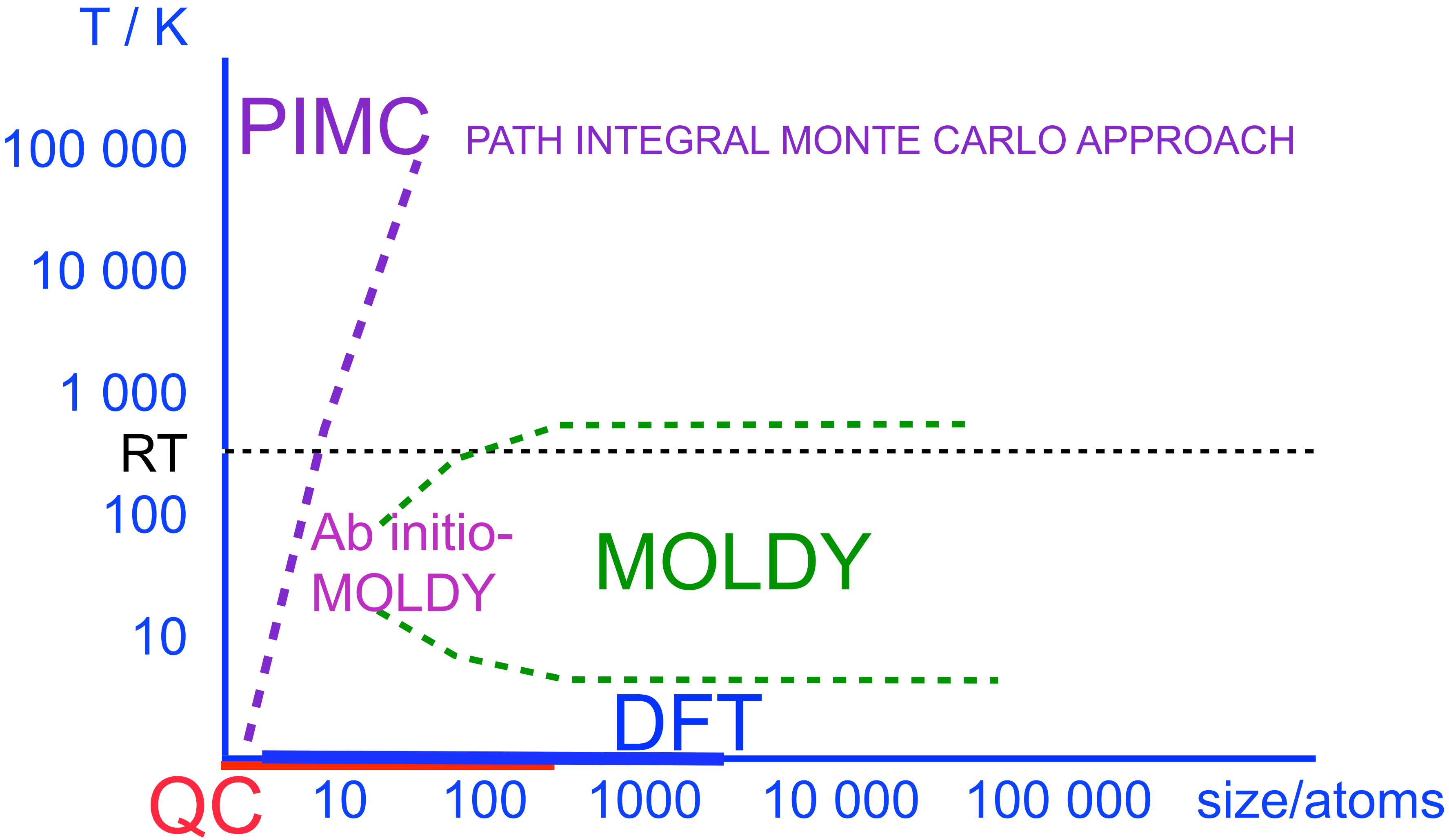
QUANTUM STATISTICAL PHYSICS PATH INTEGRAL MONTE CARLO APPROACH

An *ab initio* electronic structure approach with

- FULL ACCOUNT OF CORRELATION, the van der Waals interaction, for example!
- TEMPERATURE DEPENDENCE
- BEYOND BORN–OPPENHEIMER APPROXIMATION
- INTERPRETATION OF EQUILIBRIUM DISSOCIATION REACTION

- Without the exchange interaction, now

SIZE AND TEMPERATURE SCALES



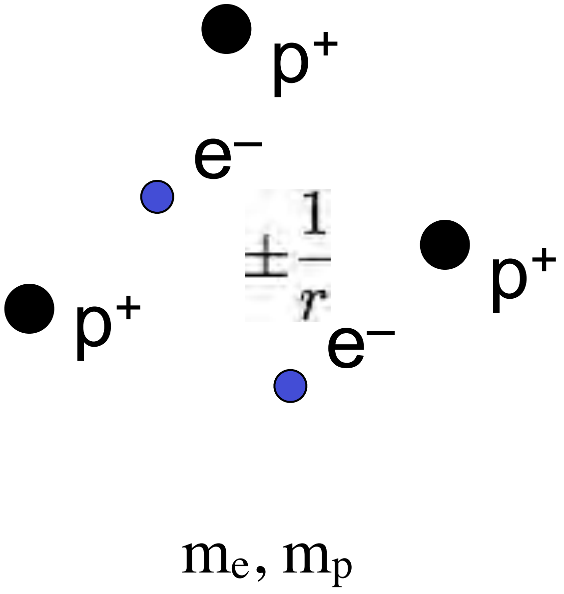
QUANTUM / CLASSICAL APPROACHES TO DYNAMICS

time dependent	**MOLECULAR DYNAMICS**	**Wave packet approaches**	**!**	**TDDFT**	**Car–Parrinello and *ab initio* MOLDY**
T > 0 equilibrium	**Metropolis Monte Carlo**	**Rovibrational approaches**	**!**		
T = 0	**Molecular mechanics**		**DMC**	***ab initio* Quantum Chemistry / DFT / semiemp.**	
electronic dyn.:			**Q**	**Q**	**Q**
nuclear dyn.:	**Classical**	**Q**	**Q**		**Classical**

H_3^+ MOLECULE

Quantum statistics of two electrons and three nuclei (five-particle system) as a function of temperature:

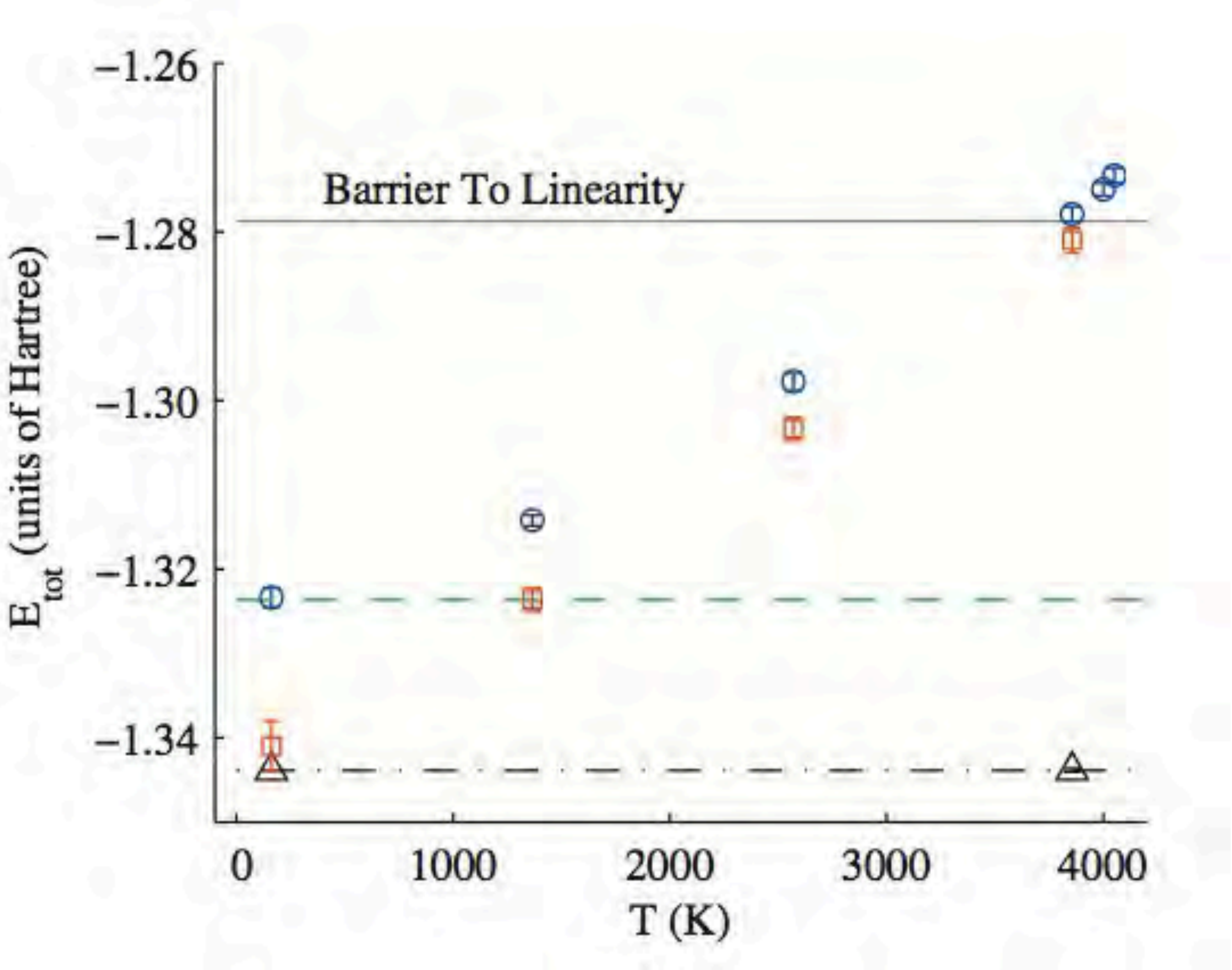
- Structure and energetics:
  - quantum nature of nuclei
  - pair correlation functions, contact densities, ...
  - dissociation temperature
- Comparison to the data from conventional quantum chemistry.



TOTAL ENERGY:

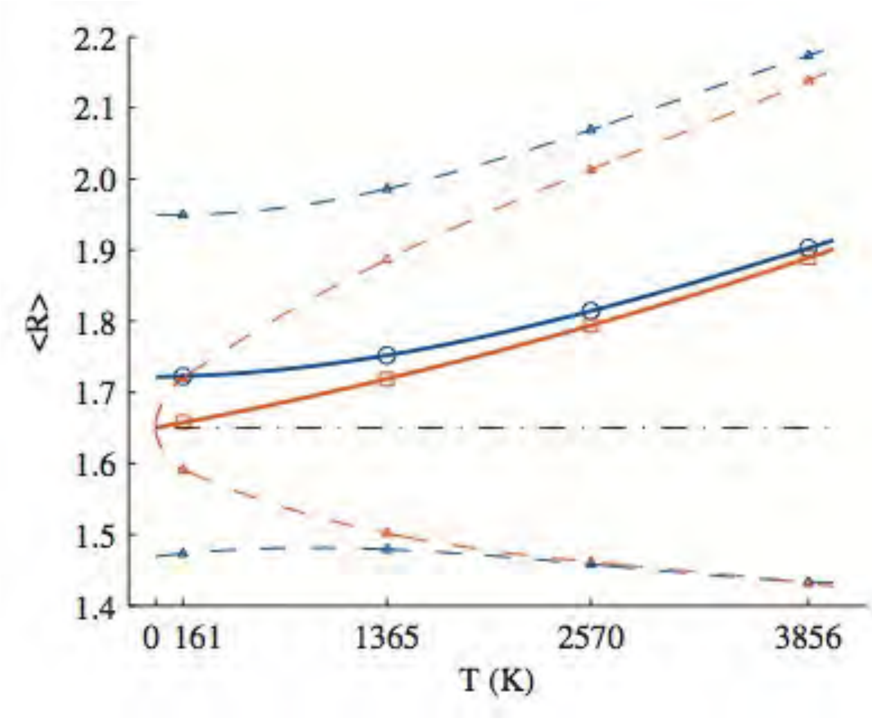
FINITE NUCLEAR MASS AND ZERO-POINT ENERGY

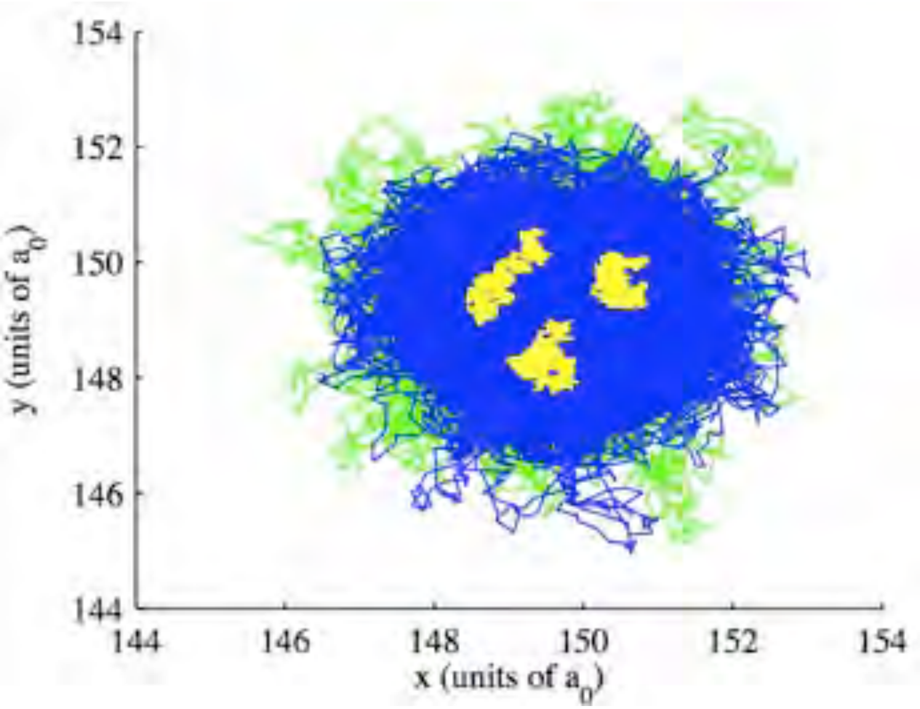
Total energy of the H_3^+ ion up to the dissociation temperature. Born–Oppenheimer approximation, classical nuclei and quantum nuclei.



MOLECULAR GEOMETRY AT LOW TEMPERATURE: ZERO-POINT MOTION

Internuclear distance.
Quantum nuclei, classical nuclei, with FWHM



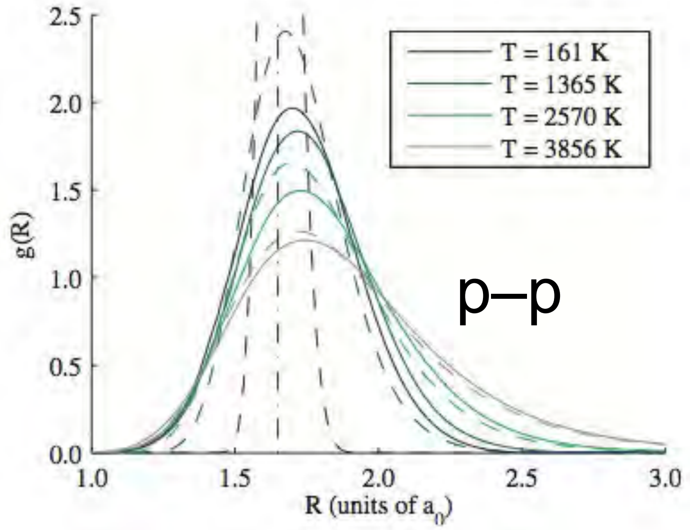


Snapshot from simulation, projection to xy-plane. Trotter number 2^{16}.

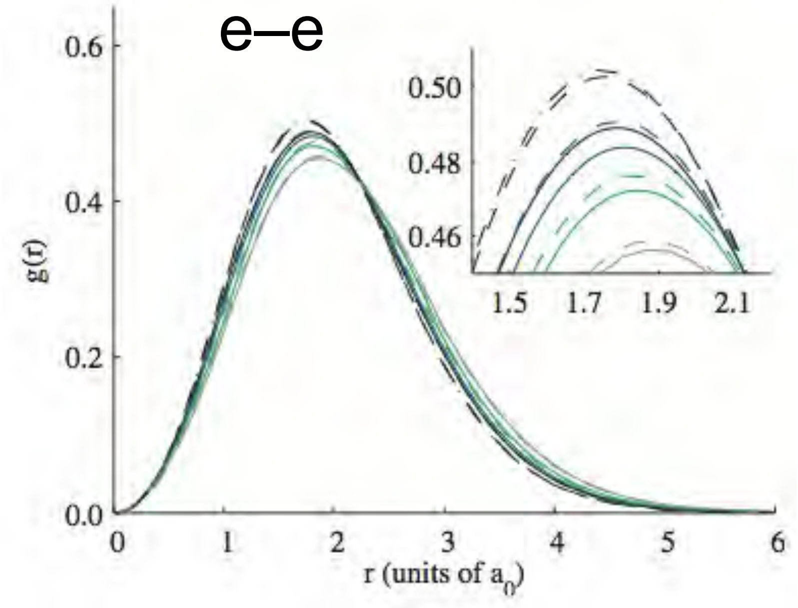
PARTICLE–PARTICLE CORRELATIONS:

ELECTRON–NUCLEI COUPLING

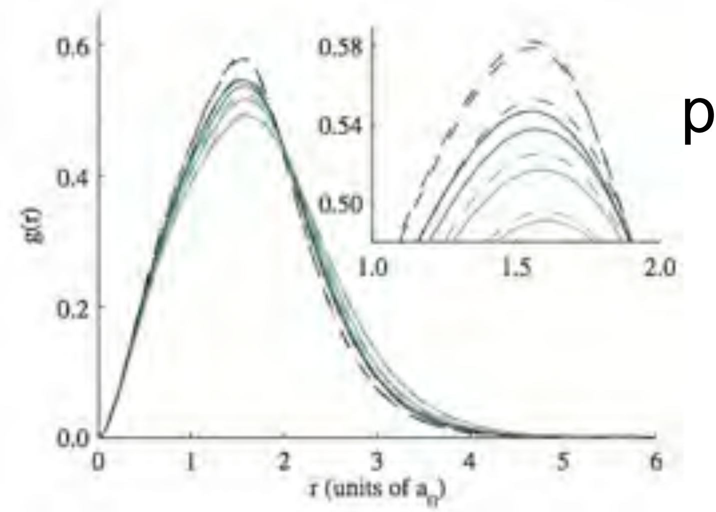
Pair correlation functions. Quantum p (solid), classical p (dashed) and Born–Oppenheimer (dash-dotted).



p–p



e–e



p–e

ENERGETICS AT HIGH TEMPERATURES:

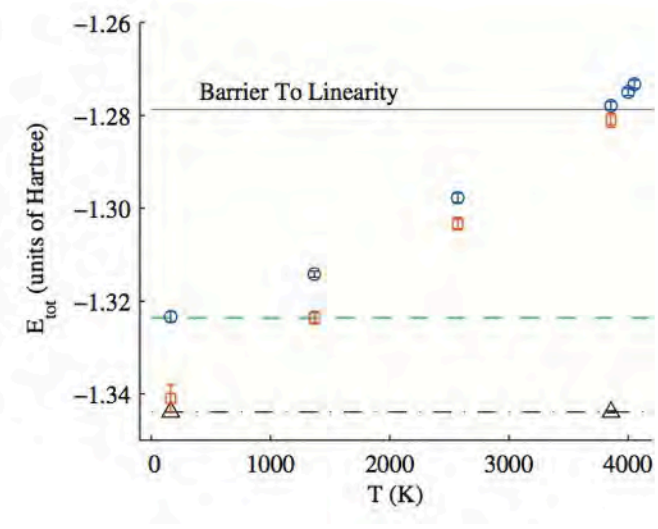
DISSOCIATION–RECOMBINATION

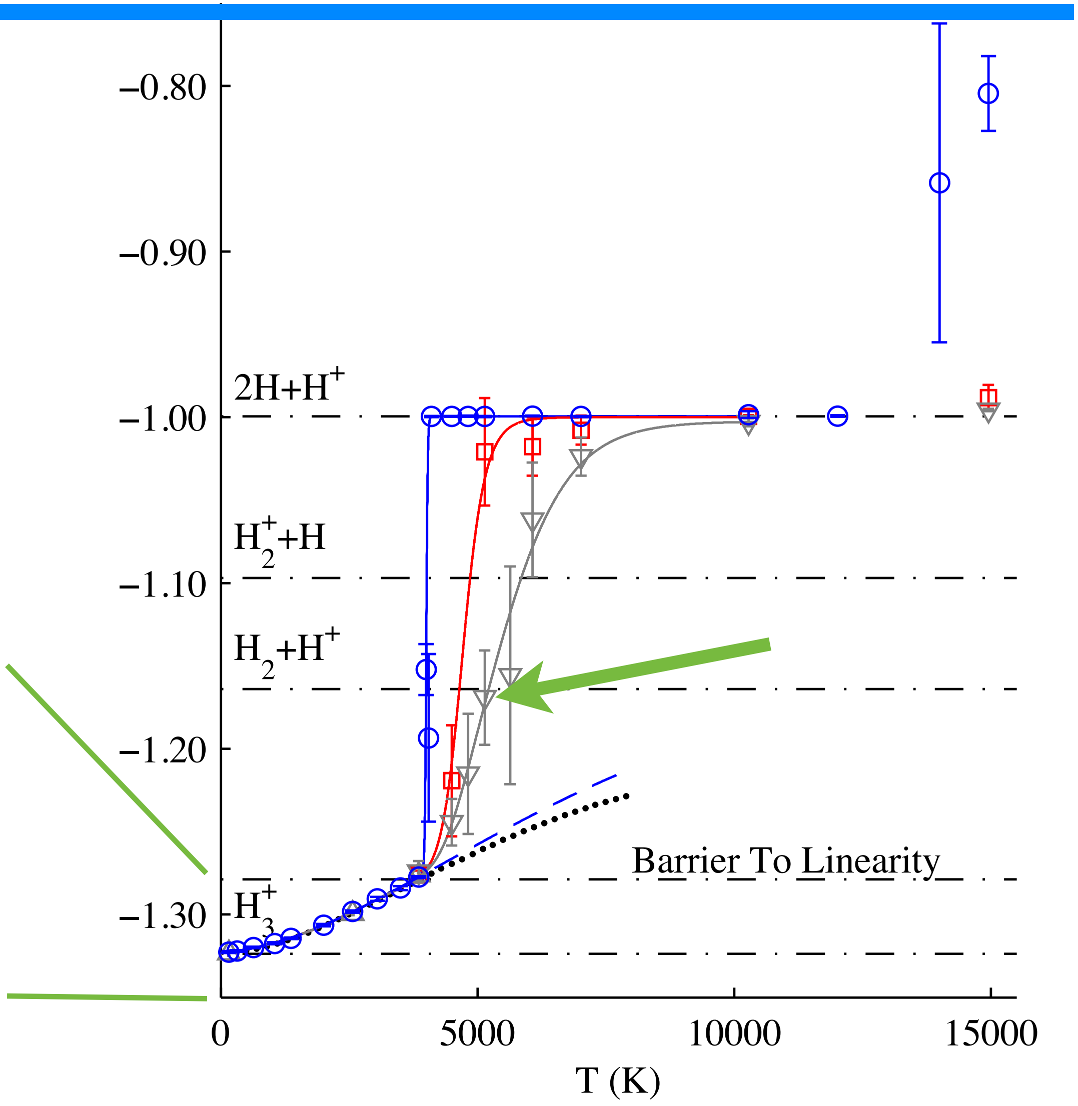
Total energy of the H_3^+ beyond dissociation temperature.

Lowest density,

mid density,

highest density



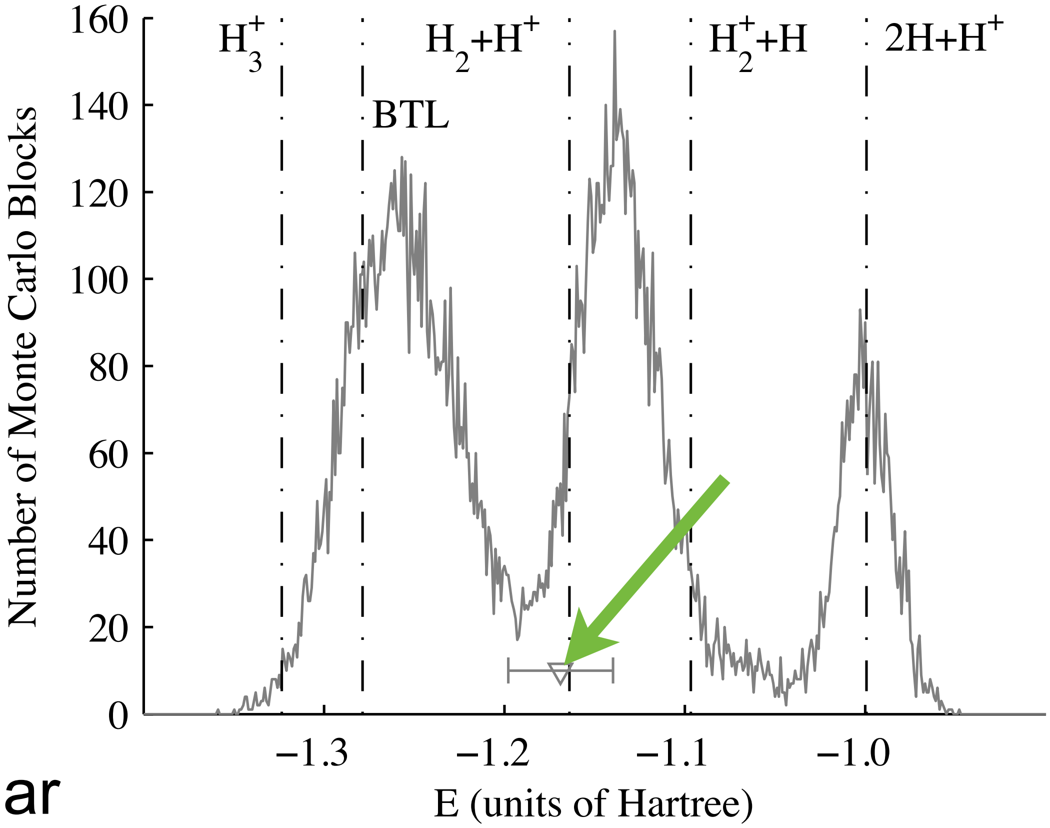


DISSOCIATION–RECOMBINATION EQUILIBRIUM REACTION

The molecule and its fragments:

$$\begin{aligned} H_3^+ &\leftrightarrow H_2 + p^+ \\ &\leftrightarrow H_2^+ + H \\ &\leftrightarrow 2H + p^+ \\ &\leftrightarrow H + 2p^+ + e^- \\ &\leftrightarrow 3p^+ + 2e^- \end{aligned}$$

We also evaluate molecular free energy, entropy and heat capacity!



The equilibrium composition of fragments at about 5000 K.

SOME THERMODYNAMICS

Expected total energy or internal energy is

$$\langle E \rangle = U = -\frac{1}{Z}\frac{\partial(Z)}{\partial\beta} \quad \text{and} \quad Z = \sum_n e^{-\beta E_n} = e^{-\beta F} \quad \text{or} \quad F = -\frac{1}{\beta}\ln Z \qquad \left(\beta = \frac{1}{kT}\right)$$

All standard thermodynamic quantities and relations can be derived from the partition function Z or free energy F.

$$\frac{\partial F}{\partial V} = -P$$

$$\frac{\partial F}{\partial T} = -S$$

$$F = U - TS$$

$$dU = -PdV + dQ$$

$$dQ = TdS$$

$$\langle E \rangle = U = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} = kT^2\frac{\partial(\ln Z)}{\partial T} = \frac{\partial(\beta F)}{\partial\beta}.$$

PARTITION FUNCTION

Numerical integration of

$$\ln Z(T) = \ln Z(T_1) + \int_{T_1}^{T} \frac{\langle E \rangle}{k_B T^2}\, dT$$

gives the partition function.

We use the boundary condition $Z(0) = 1$.

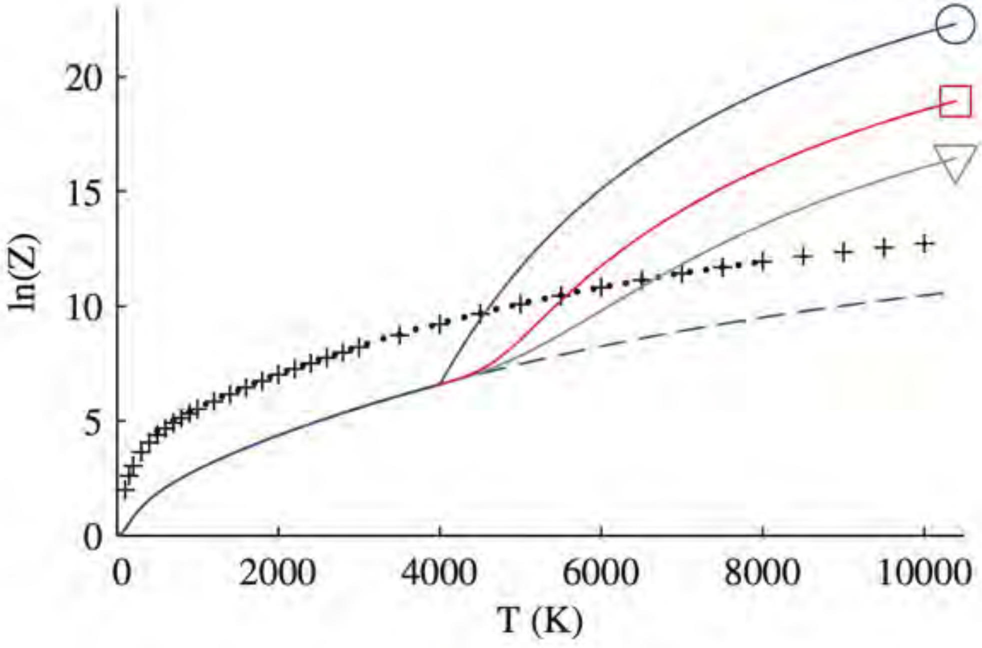


FIG. 3. The molecular NVT ensemble $\ln Z(T)$ from the energetics in Fig. 1 with the same notations. The blue solid line below 4000 K and its extrapolation (dashed line) are from Eq. (9), whereas the curves for three densities are from Eq. (10). The $\ln Z(T)$ data (black pluses) and the fit (black dots) of Ref. 2 are also shown. The black dots have the same zero energy as the partition function of this work (see text).

FREE ENERGY

$$F = -\frac{1}{\beta}\ln Z$$

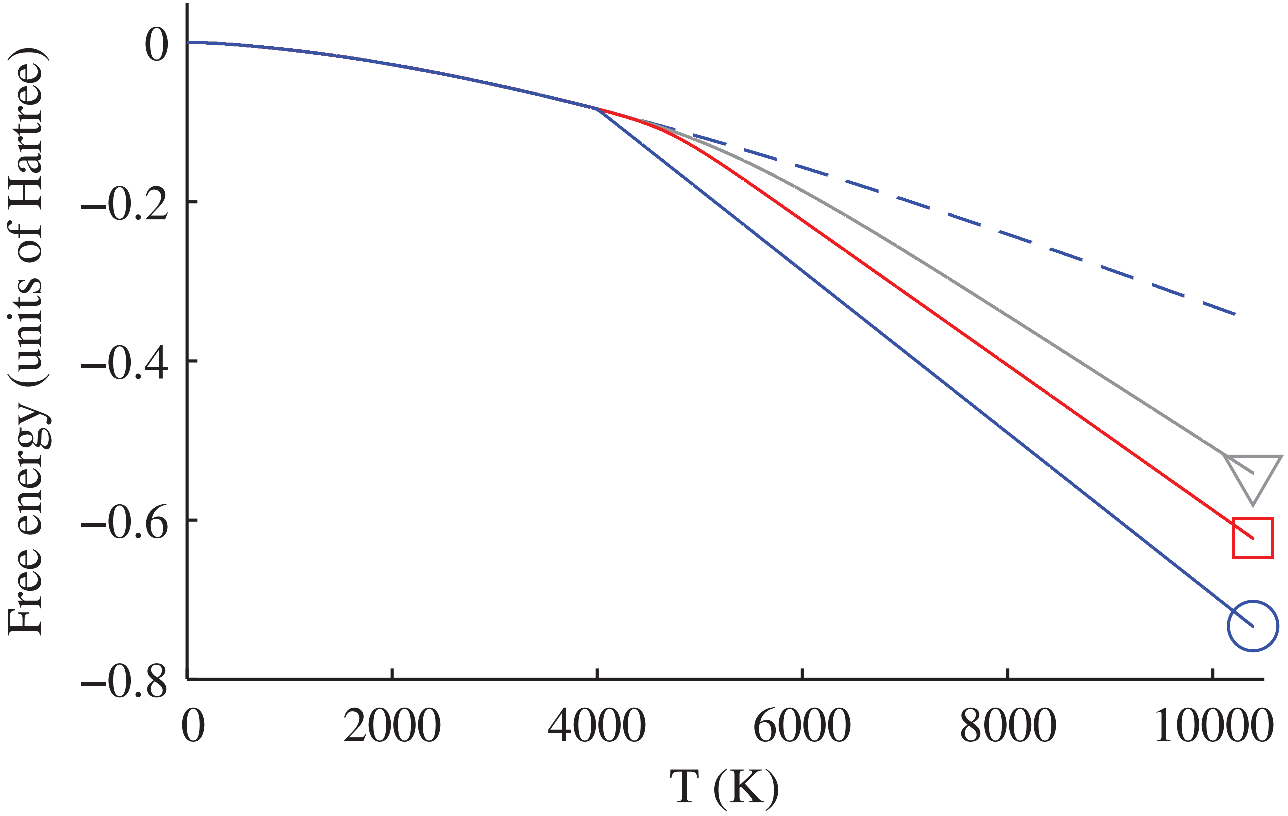


FIG. 4. Helmholtz free energy from Eq. (5) in the units of Hartree. Notations are the same as in Fig. 3.

ENTROPY

$$S = \frac{U - F}{T}, \qquad (11)$$

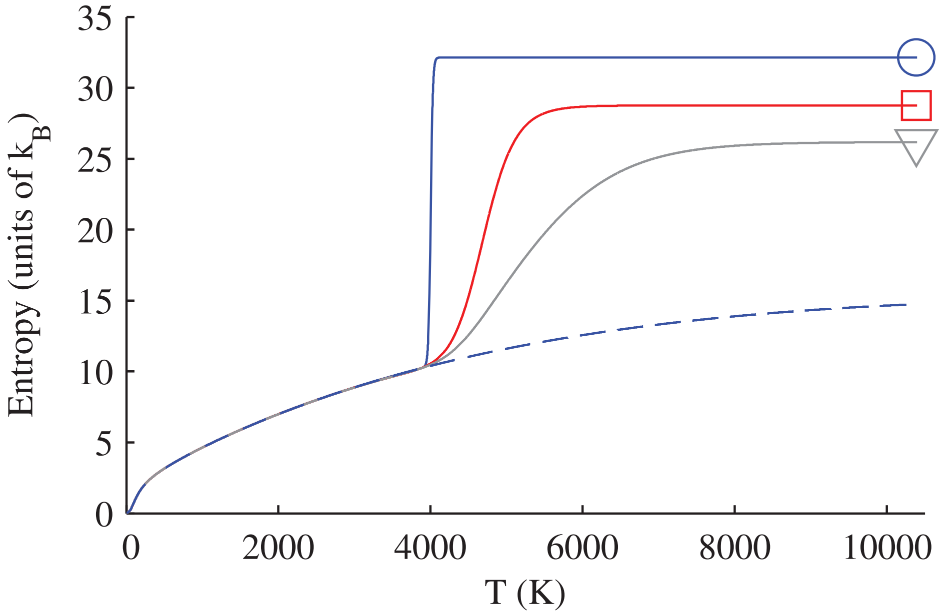


FIG. 5. Entropy from Eq. (11) in the units of k_B. Notations are the same as in Fig. 3.

MOLECULAR HEAT CAPACITY

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

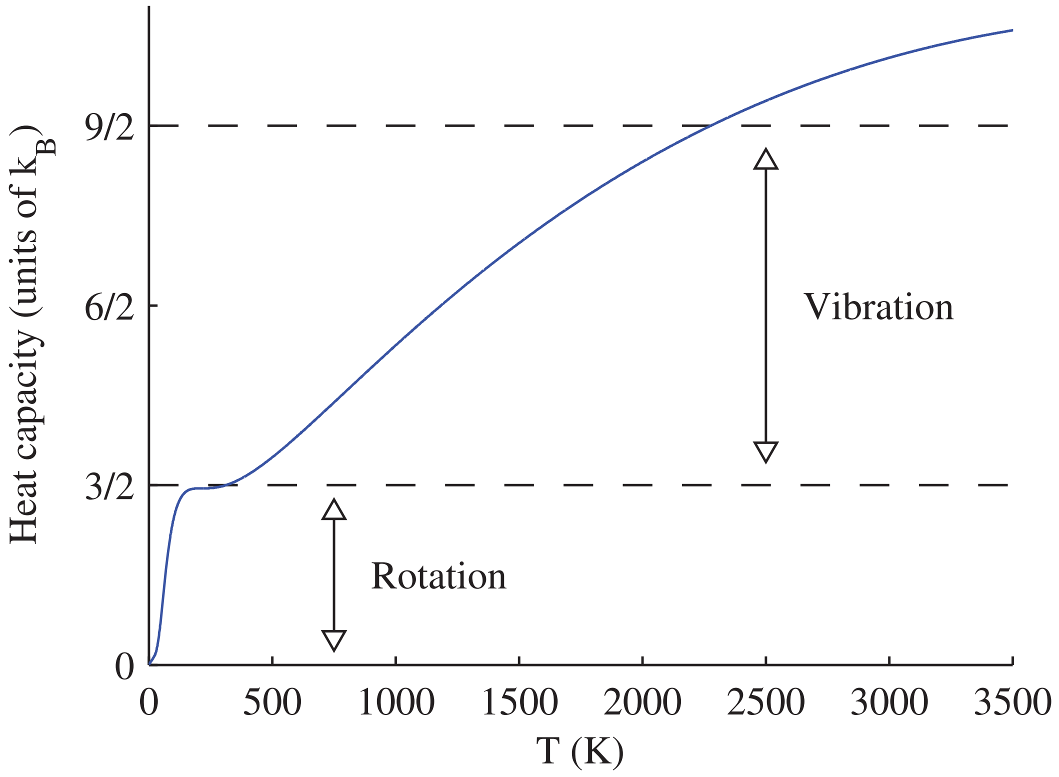
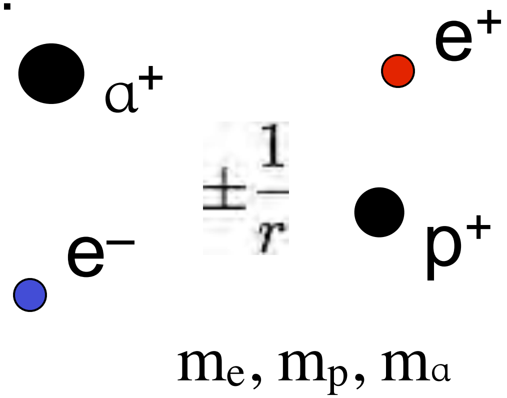


FIG. 6. Molecular heat capacity as a function of temperature calculated using the analytical model of this work. The values on the y-axis are given in units of the Boltzmann constant k_B.

SOME FINAL NOTES AND THOUGHTS

- Dynamics is always present in molecules and all the constituent particles participate:
  - in zero Kelvin and
  - in finite temperature
- In finite temperature
  - there are no stable molecules
  - classical dynamics emerge



Essay title: **Ehrenfest theorem and decoherence**

Instruction: Find definition/explanation of both from the literature and compare these two as a way from quantum mechanics to classical mechanics