PATH INTEGRAL PERSPECTIVE TO QUANTUM MECHANICS AND QUANTUM CHEMISTRY

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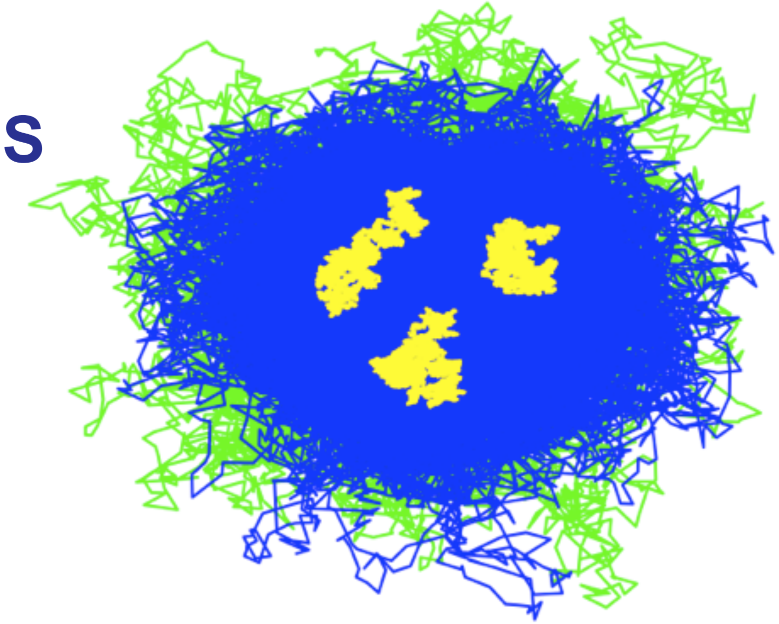
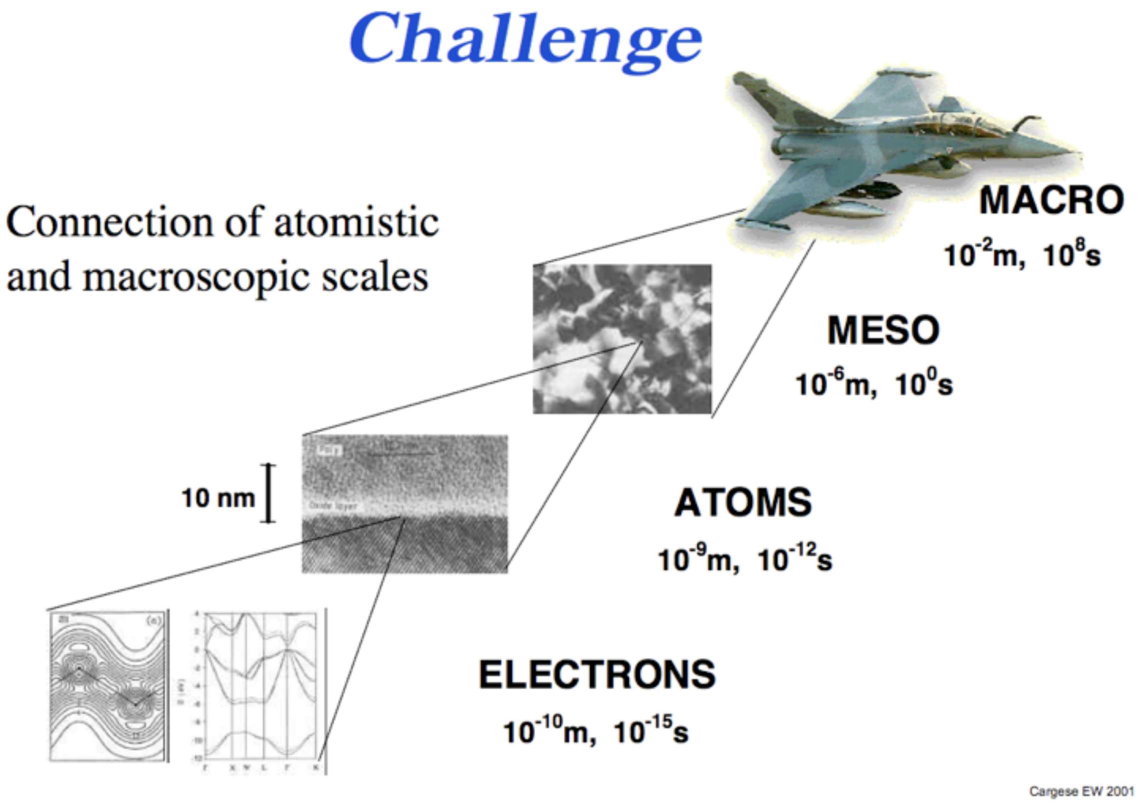


PROPERTIES OF MATTER

Where do properties of materials arise from?

- mechanical
- thermal
- electrical
- optical
- ...



ELECTRONIC STRUCTURE !

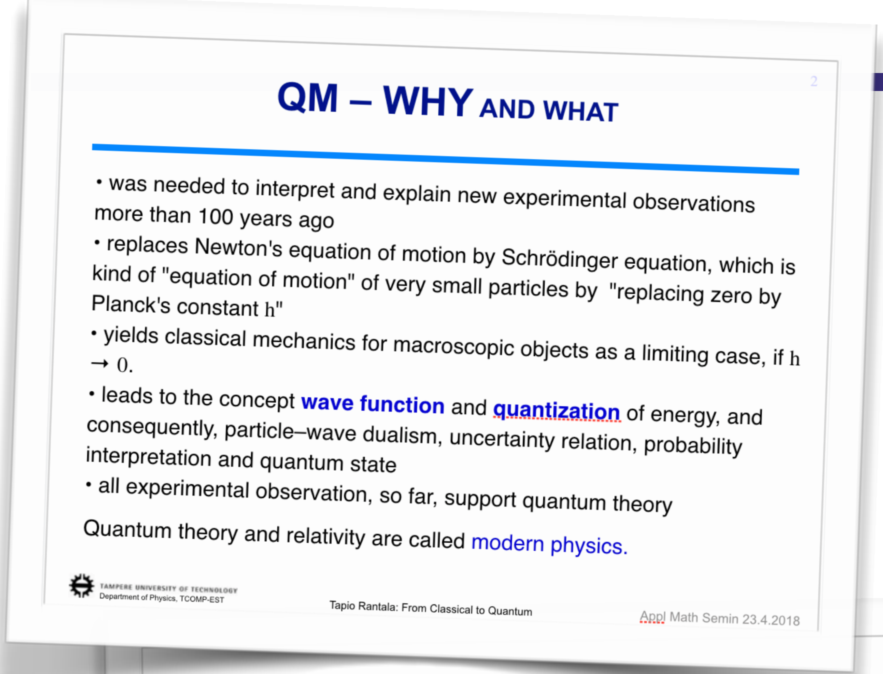
MOTIVATION FOR METHOD DEVELOPMENT

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.**
- are typically good for **stationary states, only.**

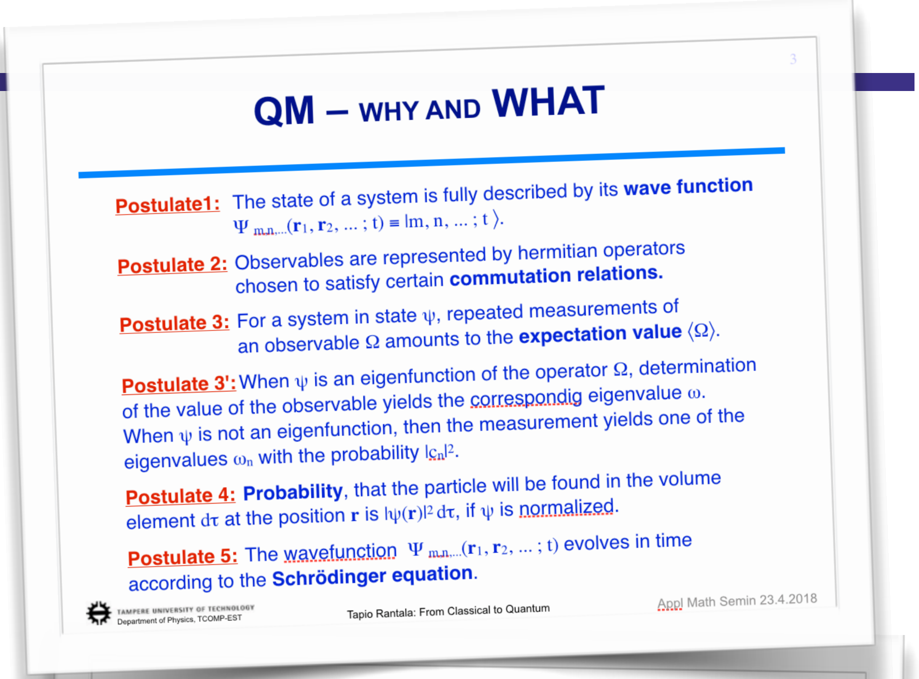
QUANTUM MECHANICS
THE CONVENTIONAL APPROACH



QM – WHY AND WHAT

- was needed to interpret and explain new experimental observations more than 100 years ago
- replaces Newton's equation of motion by Schrödinger equation, which is kind of "equation of motion" of very small particles by "replacing zero by Planck's constant h"
- yields classical mechanics for macroscopic objects as a limiting case, if $h \to 0$.
- leads to the concept **wave function** and **quantization** of energy, and consequently, particle–wave dualism, uncertainty relation, probability interpretation and quantum state
- all experimental observation, so far, support quantum theory

Quantum theory and relativity are called modern physics.



QM – WHY AND WHAT

Postulate1: The state of a system is fully described by its **wave function** $\Psi_{m,n,...}(\mathbf{r}_1, \mathbf{r}_2, \ldots ; t) \equiv |m, n, \ldots ; t\rangle$.

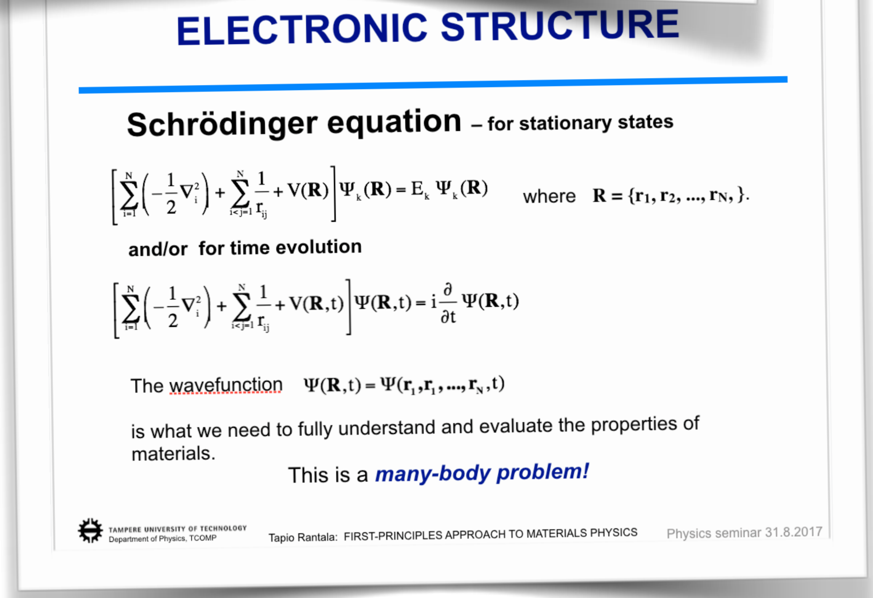
Postulate 2: Observables are represented by hermitian operators chosen to satisfy certain **commutation relations.**

Postulate 3: For a system in state ψ, repeated measurements of an observable Ω amounts to the **expectation value** $\langle\Omega\rangle$.

Postulate 3': When ψ is an eigenfunction of the operator Ω, determination of the value of the observable yields the correspondig eigenvalue ω. When ψ is not an eigenfunction, then the measurement yields one of the eigenvalues ω_n with the probability $|c_n|^2$.

Postulate 4: **Probability**, that the particle will be found in the volume element $d\tau$ at the position $\mathbf{r}$ is $|\psi(\mathbf{r})|^2\, d\tau$, if ψ is normalized.

Postulate 5: The wavefunction $\Psi_{m,n,...}(\mathbf{r}_1, \mathbf{r}_2, \ldots ; t)$ evolves in time according to the **Schrödinger equation**.



ELECTRONIC STRUCTURE

Schrödinger equation – for stationary states

$$\left[\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2\right)+\sum_{i<j=1}^{N}\frac{1}{r_{ij}}+V(\mathbf{R})\right]\Psi_k(\mathbf{R})=E_k\,\Psi_k(\mathbf{R}) \qquad \text{where} \quad \mathbf{R}=\{\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,\}.$$

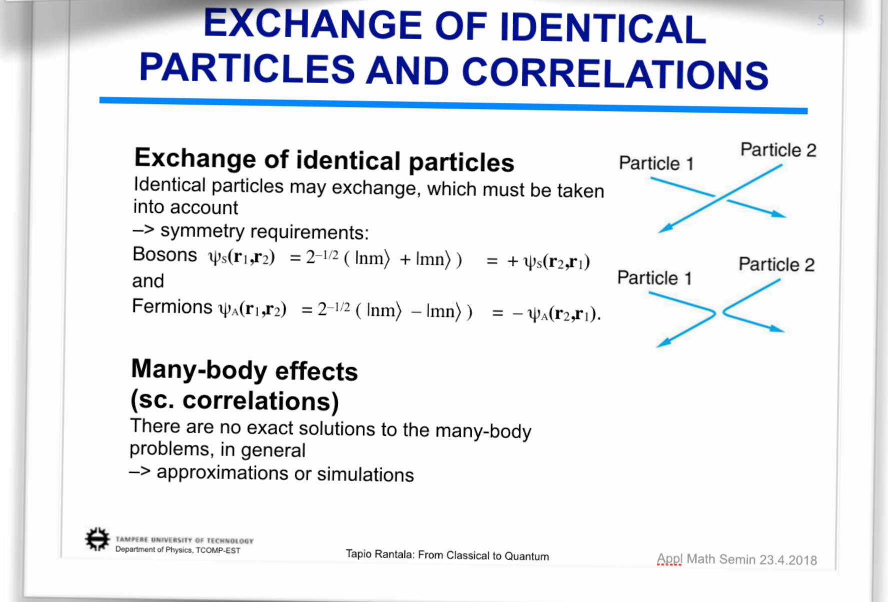
and/or for time evolution

$$\left[\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2\right)+\sum_{i<j=1}^{N}\frac{1}{r_{ij}}+V(\mathbf{R},t)\right]\Psi(\mathbf{R},t)=i\frac{\partial}{\partial t}\Psi(\mathbf{R},t)$$

The wavefunction $\Psi(\mathbf{R},t)=\Psi(\mathbf{r}_1,\mathbf{r}_1,\ldots,\mathbf{r}_N,t)$

is what we need to fully understand and evaluate the properties of materials.

This is a ***many-body problem!***



EXCHANGE OF IDENTICAL PARTICLES AND CORRELATIONS

Exchange of identical particles

Identical particles may exchange, which must be taken into account
–> symmetry requirements:
Bosons $\psi_S(\mathbf{r}_1,\mathbf{r}_2) = 2^{-1/2}\,(\,|nm\rangle + |mn\rangle\,) = +\psi_S(\mathbf{r}_2,\mathbf{r}_1)$
and
Fermions $\psi_A(\mathbf{r}_1,\mathbf{r}_2) = 2^{-1/2}\,(\,|nm\rangle - |mn\rangle\,) = -\psi_A(\mathbf{r}_2,\mathbf{r}_1)$.

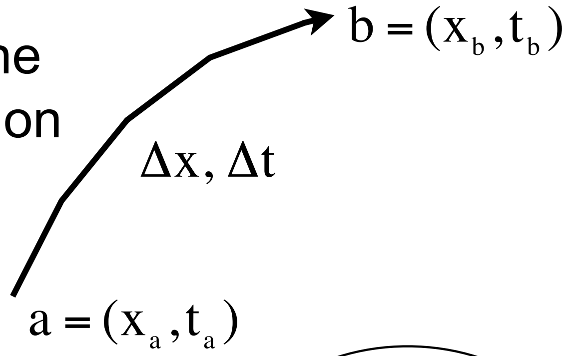
Many-body effects (sc. correlations)

There are no exact solutions to the many-body problems, in general
–> approximations or simulations

PATH INTEGRAL APPROACH:
1. CLASSICAL PATH AND QUANTUM PATHS

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

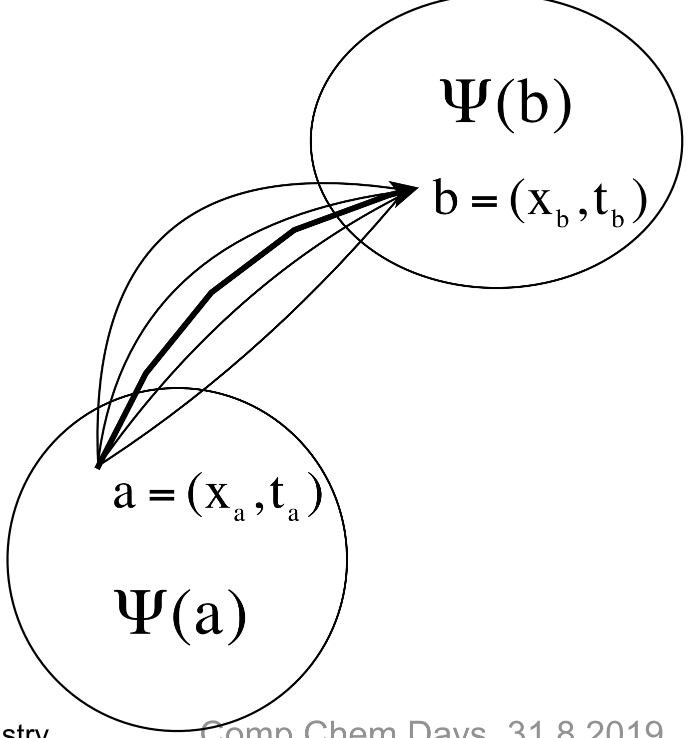


$$S=\int_{t_a}^{t_b} L(\dot{x},x,t)\,dt,$$ where the Lagrangian $L=T-V$.

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

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

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



PATH INTEGRAL APPROACH:
2. QUANTUM PATHS AND PROBABILITY

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

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

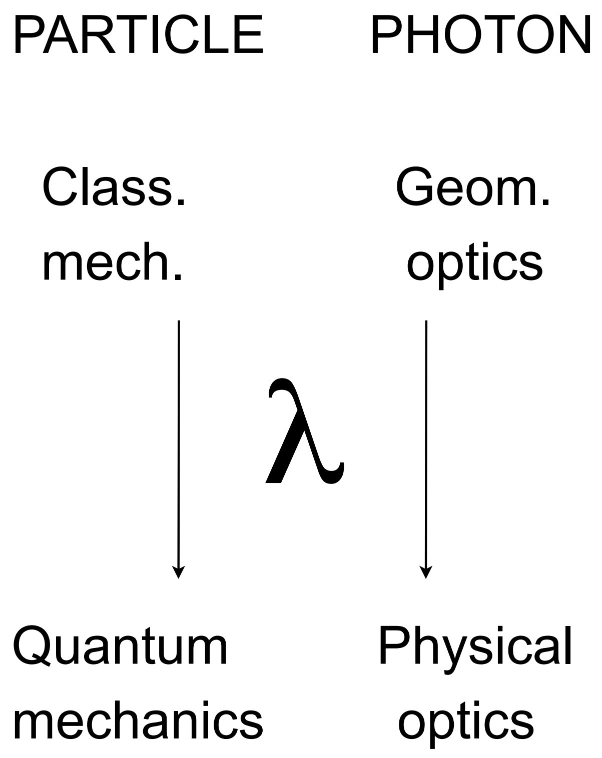
the absolute square of the probability amplitude K.

The probability amplitude is the sum over all oscillating phase factors ϕ (or interference) of the paths x_{ab} as

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

where the phase is proportional to the exponential of the action

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

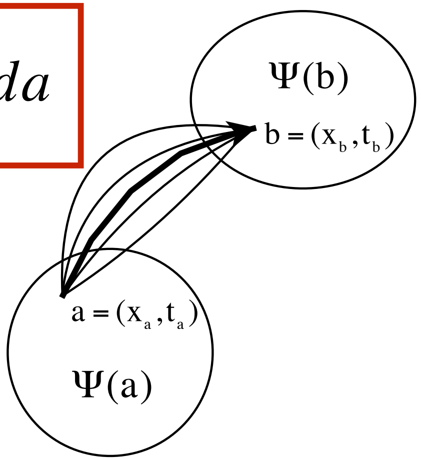


PATH INTEGRAL APPROACH:
3. PATH INTEGRAL

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

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

$$\boxed{\Psi(b) = \int K(b,a)\Psi(a)\,da}$$



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 Schrödinger equation in space and time $\{x_b, t_b\}$.

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

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

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

PATH INTEGRAL APPROACH:
4. 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

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

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

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

Note! The wave function does not exist in finite temperature!

Decoherence!

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 APPROACH:
5. 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 $\frac{\partial\rho(b,a)}{\partial\beta} = -H_b\,\rho(b,a)$. Cf. $\frac{\partial K(b,a)}{\partial t_b} = -\frac{i}{\hbar}H_b\,K(b,a)$

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

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

PATH INTEGRAL APPROACH:
6. MC 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.

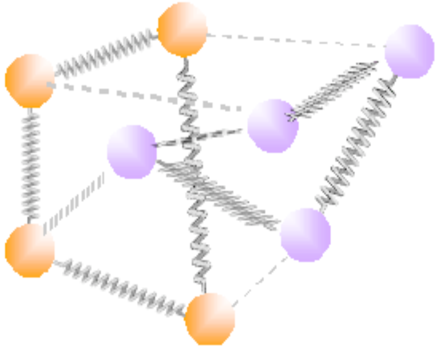
Thus, we can write

Decoherence!

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

where

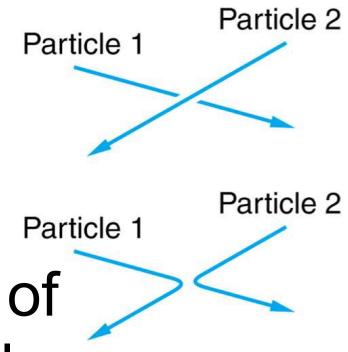
$$\tau = \beta / M , \quad \beta = \frac{1}{kT}$$



and M is called the Trotter number.

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

EXCHANGE AND CORRELATION

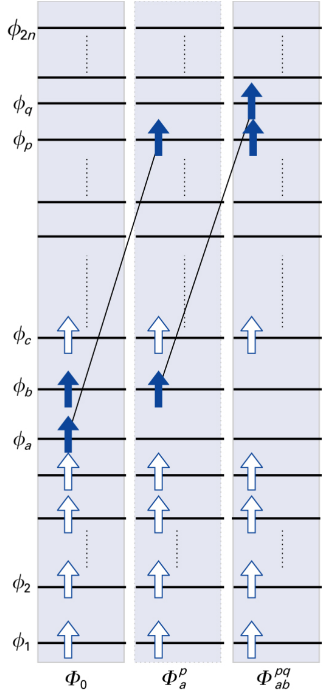


From one-electron picture to many-fermion description:

- fermionic wave function ⟶ Slater determinant of one-electron orbitals:

$$\Phi\,(1,2,...,N) = (1/N!)^{1/2} \begin{vmatrix} \varphi_a(1) & \varphi_b(1) & ... & \varphi_N(1) \\ \varphi_a(2) & \varphi_b(2) & ... & \varphi_N(2) \\ : & : & & : \\ : & : & & : \\ \varphi_a(N) & \varphi_b(N) & ... & \varphi_N(N) \end{vmatrix} = (1/N!)^{1/2}\,\mathrm{det}\,|\,\varphi_a(1)\,\varphi_b(2)\,...\,\,\varphi_N(N)\,|$$

- Many-body effects or correlations by configuration mixing or CI:



<u>9.6. Configuration interaction (CI)</u> *QTMN, 2018 179*

The exact N electron many-body wavefunction can be written as

$$\Psi = C_0\Phi_0 + \Sigma_{a,p}\, C_a^p\Phi_a^p + \Sigma_{a<b,p<q}\, C_{ab}^{pq}\Phi_{ab}^{pq} + \Sigma_{a<b<c,p<q<r}\, C_{abc}^{pqr}\Phi_{abc}^{pqr} + \dots ,$$

i.e., as a linear combination of the Slater determinants.

Note! The one-electron picture is becomes lost, now!

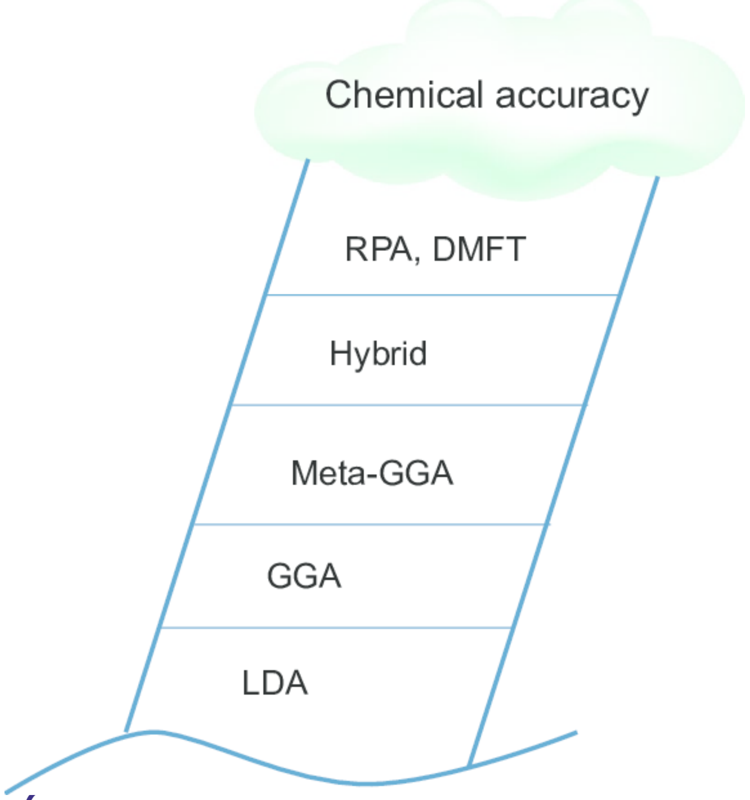
EXCHANGE AND CORRELATION (DFT)

$$E_{xc} = E_x + E_c$$

$$V_{xc} = V_x + V_c$$

$$\mathrm{E}[\rho] = -\frac{\hbar^2}{2\mathrm{m}} \sum_{\mathrm{i}}^{\mathrm{n}} \int \psi_{\mathrm{i}}^*(\mathbf{r})\, \nabla_{\mathrm{i}}^2\, \psi_{\mathrm{i}}^*(\mathbf{r})\, \mathrm{d}\mathbf{r} - \sum_{\mathrm{I}}^{\mathrm{N}} \int \frac{\mathrm{Z_I\, e^2}}{4\pi\varepsilon_0\, \mathrm{r_I}}\, \rho(\mathbf{r})\, \mathrm{d}\mathbf{r} + \frac{1}{2} \int\!\!\int \frac{\mathrm{e}^2\, \rho(\mathbf{r}_{\mathrm{i}})\, \rho(\mathbf{r}_{\mathrm{j}})}{4\pi\varepsilon_0\, \mathrm{r_{ij}}}\, \mathrm{d}\mathbf{r}_{\mathrm{i}}\, \mathrm{d}\mathbf{r}_{\mathrm{j}} + \mathrm{E_{xc}}[\rho]\,,$$

Jacob's ladder for exchange and correlation:



Chemical accuracy

RPA, DMFT

Hybrid

Meta-GGA

GGA

LDA

$$\mathrm{f} = -\frac{\hbar^2}{2\mathrm{m}} \nabla_{\mathrm{i}}^2 - \sum_{\mathrm{I}}^{\mathrm{N}} \frac{\mathrm{Z_I\, e^2}}{4\pi\varepsilon_0\, \mathrm{r_I}} + \frac{1}{2} \int \frac{\mathrm{e}^2\, \rho(\mathbf{r}_{\mathrm{j}})}{4\pi\varepsilon_0\, \mathrm{r_{ij}}}\, \mathrm{d}\mathbf{r}_{\mathrm{j}} + \mathrm{V_{xc}}[\rho]$$

$$\mathrm{f}\, \psi_{\mathrm{i}} = \varepsilon_{\mathrm{i}}\, \psi_{\mathrm{i}}$$

$$\mathrm{V_{xc}}[\rho] = \frac{\delta \mathrm{E_{xc}}[\rho]}{\delta\rho}\,.$$

Only E_x for HEG, and thus for LDA, is known analytically. The rest of the **exchange and correlation functionals** are increasingly better approximations for climbing up the Jacob's ladder to the heaven of chemical accuracy.

SOFTWARE: DFT

ACADEMIC/COMMERCIAL CODES:

- PlaneWave basis

VASP (Vienna Ab-initio Simulation Package)

CASTEP

abinit.org

- localized (atomic) basis

DMol^3

siesta

PBC ↕ finite

TURBOMOLE GmbH

Gaussian.com

- Real-space grid

GPAW!

PBC and finite

ASE: abinit Asap Dacapo EMT GPAW! siesta VASP

- (Gromacs for molecular dynamics)

PATH INTEGRALS IN IMAGINARY AND REAL TIME

$$H\psi(x,\tau) = \frac{\partial\psi(x,\tau)}{\partial\tau} \qquad \xleftarrow{\tau = it} \qquad H\psi(x,t) = \mathrm{i}\frac{\partial\psi(x,t)}{\partial t}$$

$$\psi(x,\tau) = \int G(x,\tau;x_a,\tau_a)\psi(x_a,\tau_a)dx_a \qquad \psi(x,t) = \int K(x,t;x_a,t_a)\psi(x_a,t_a)\mathrm{d}x_a$$

PATH INTEGRAL APPROACHES

τDMC

The conventional Diffusion Monte Carlo (DMC)

$$G = G_{\mathrm{diff}}G_{\mathrm{B}}$$
$$G_{\mathrm{diff}} = C_1 \exp(-\Delta x^2/2\tau)$$
$$G_{\mathrm{B}} = C_2 \exp[-(\bar{V} - E_T)\tau]$$

everywhere real and positive !

PIMC

$$\rho = \int \exp(-S)\ Dx(\tau)$$

Quantum statistical physics in equilibrium at temperature T > 0, $\tau_b - \tau_a = \beta = 1/k_B T$

RTPI

$$K = \int \exp(iS)\ Dx(t)$$

$$S[x_b,x_a] = \int_{t_a}^{t_b} L_x dt$$

tDMC

$$K = C\ \exp(i\phi)$$

complex function !

Coherent time evolution in real time and stationary eigenstates from incoherent evolution

Feynman–Hibbs, *Quantum Mechanics and Path Integrals,* (McGraw-Hill, 1965)

QUANTUM MONTE CARLO (QMC)

What?

Stochastic method for working out quantum many-body problems, like **finding the electronic structure** of materials from first-principles, *i.e., ab initio.*

Why?

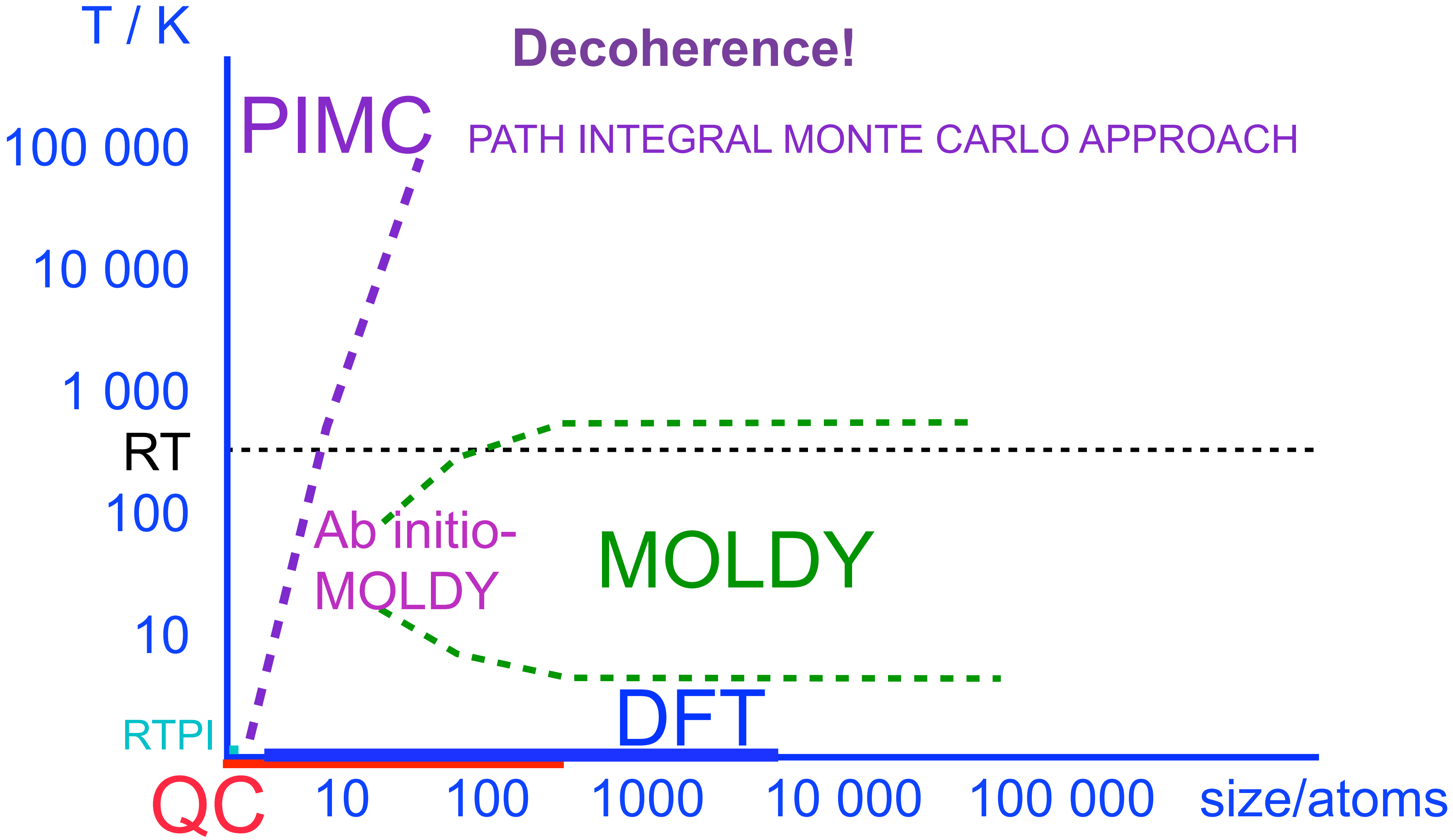
- Transparent account of **many-body effects**, *i.e.* correlations, typically included **exactly within numerical accuracy**
- Systematic way to improve accuracy
- Allows easy way beyond Born–Oppenheimer approximation
- Allows quantum dynamics
- Allows nonzero temperature
- Allows even chemical reactions

All from first-principles!

QUANTUM / CLASSICAL APPROACHES TO DYNAMICS

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

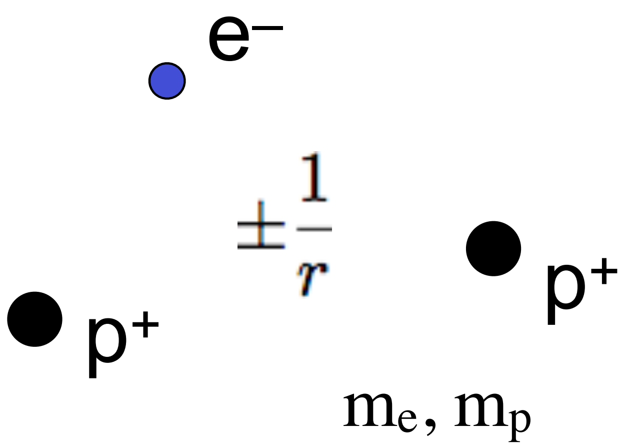
SIZE AND TEMPERATURE SCALES

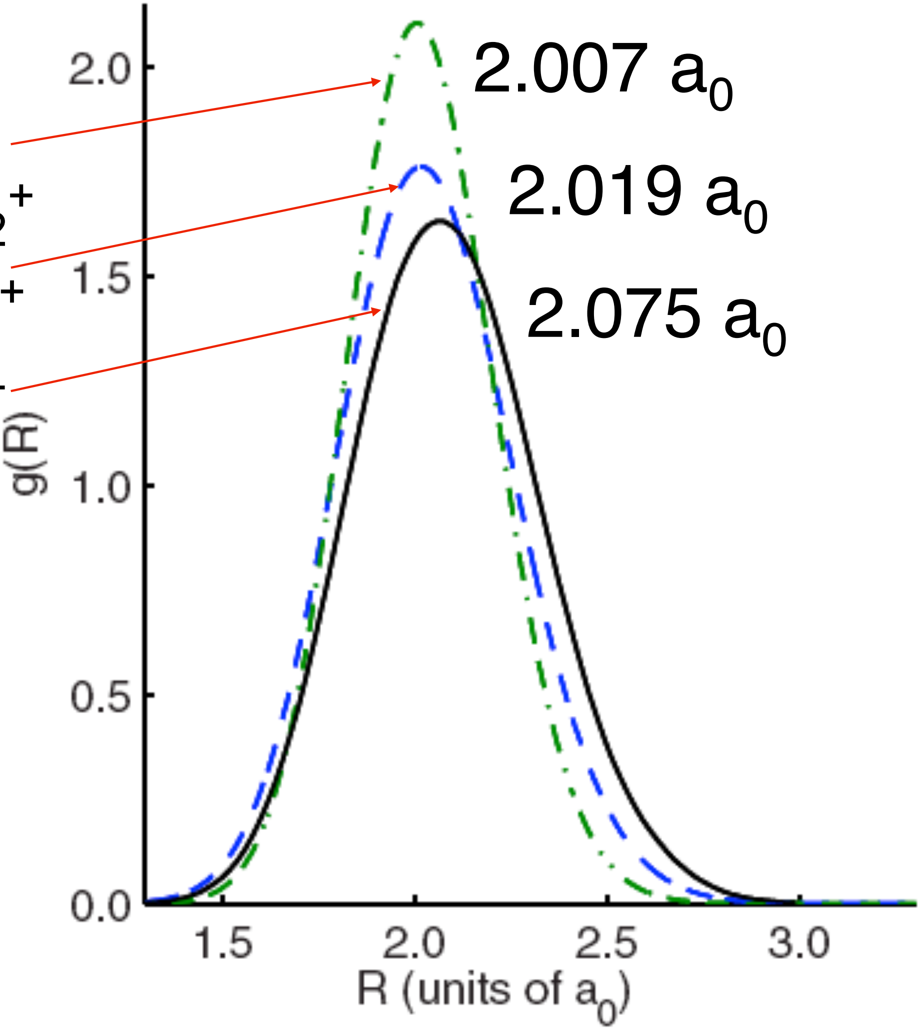


SIMPLE TEST CASES, FIRST: H ATOM, H_2^+ AND D_2^+ MOLECULES

Hydrogen atom: R_H / R_∞

Molecules:
- Adiabatic nuclear dynamics, D_2^+
  isotope effect: H_2^+
- All quantum particles H_2^+



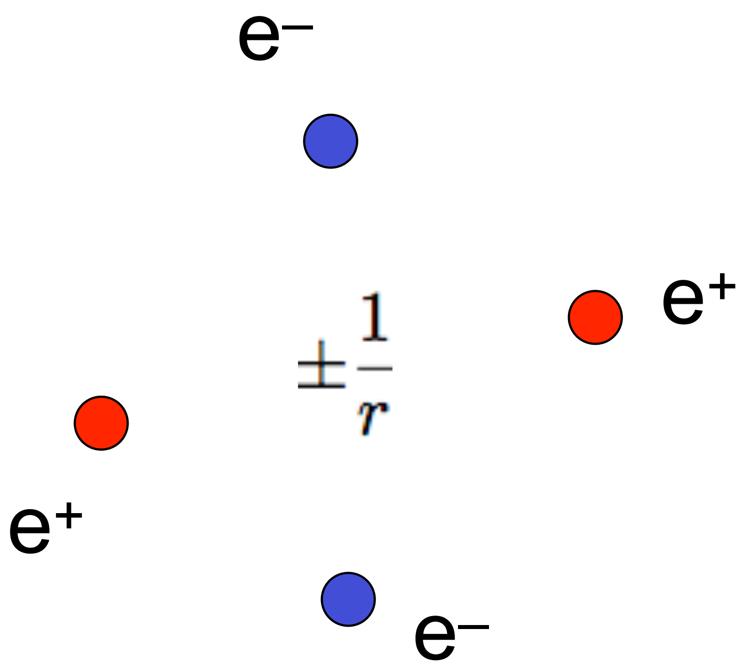


DIPOSITRONIUM Ps_2

- Pair approximation and matrix squaring
- Bisection moves
- Virial estimator for the kinetic energy
- same average ”time step” for all temperatures

$$\langle \tau \rangle = \beta/M = 0.015,\ M \approx 10^5$$

$$M = 2^{17} \ldots 2^{14}$$



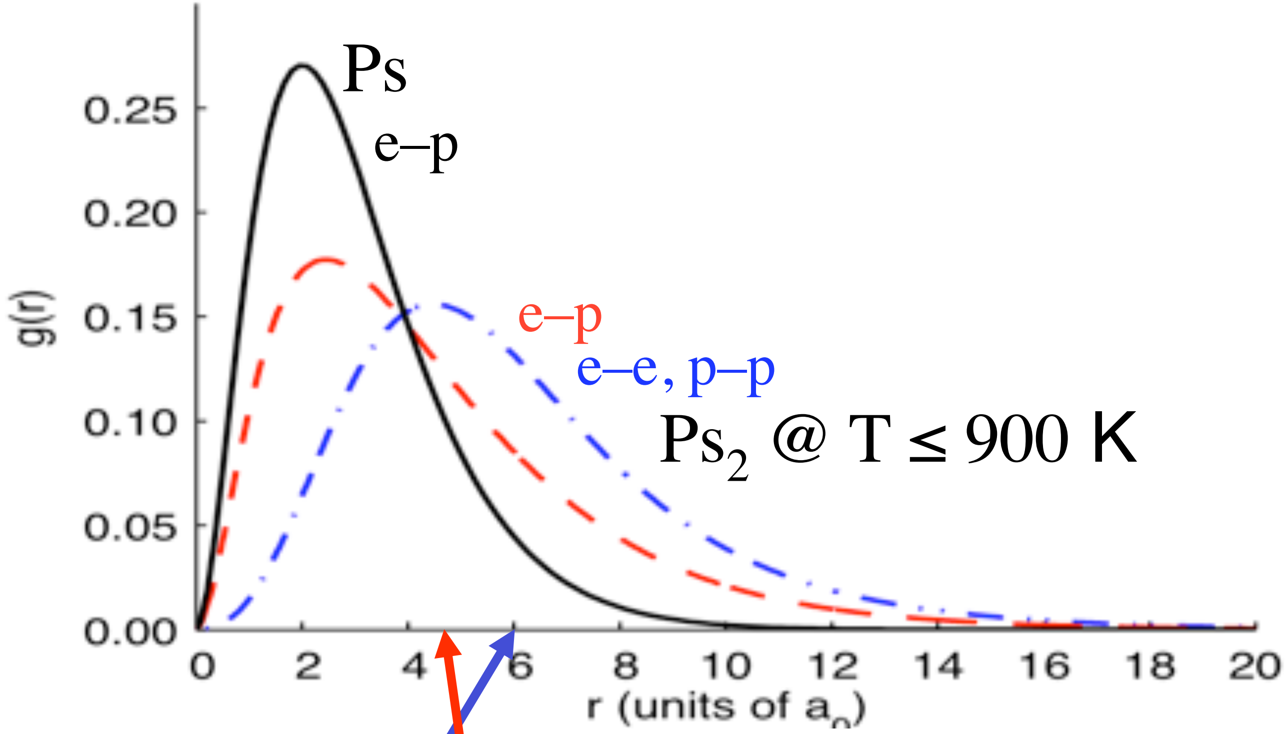
Ps$_2$ @ 0K – 900K

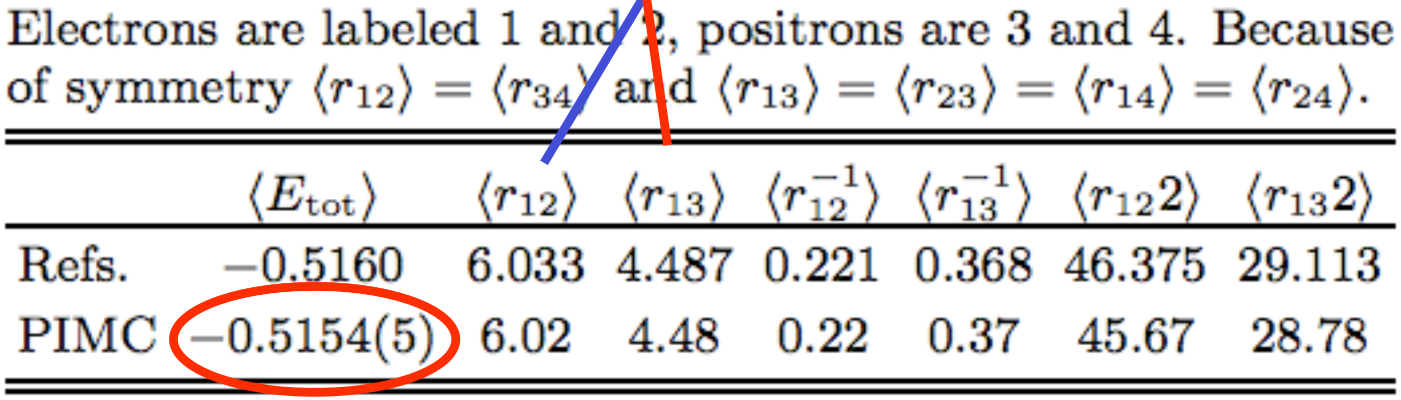
We find:

- $E_{Ps} = -0.250$
- $E_{Ps_2} = -0.5154$
- $E_D = 0.0154$

  ≈ 0.435 eV

  $:\approx 5000$ K





Electrons are labeled 1 and 2, positrons are 3 and 4. Because of symmetry $\langle r_{12}\rangle = \langle r_{34}\rangle$ and $\langle r_{13}\rangle = \langle r_{23}\rangle = \langle r_{14}\rangle = \langle r_{24}\rangle$.

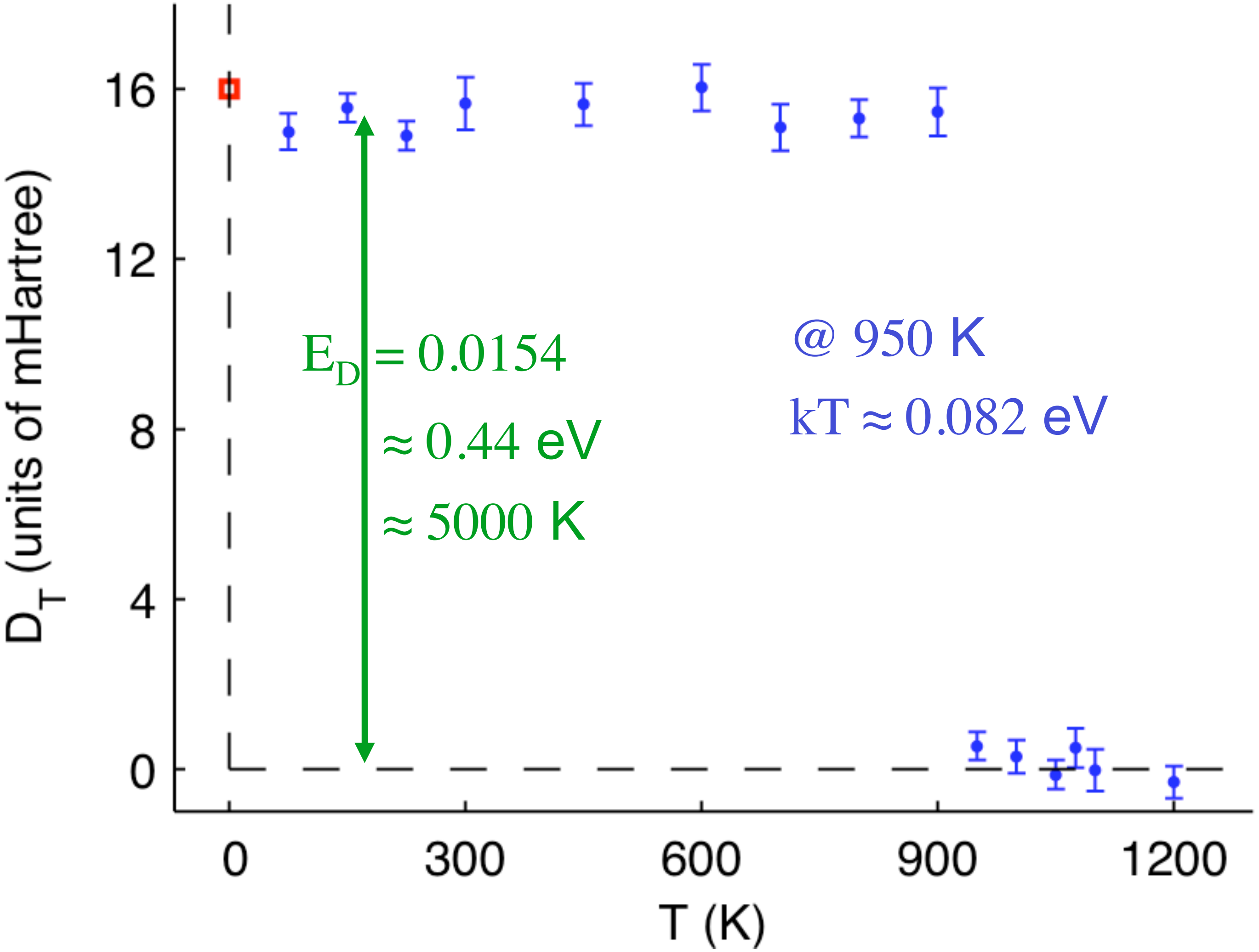
		$\langle E_{\text{tot}}\rangle$	$\langle r_{12}\rangle$	$\langle r_{13}\rangle$	$\langle r_{12}^{-1}\rangle$	$\langle r_{13}^{-1}\rangle$	$\langle r_{12}2\rangle$	$\langle r_{13}2\rangle$
Ps$_2$ @ T = 0 K	Refs.	−0.5160	6.033	4.487	0.221	0.368	46.375	29.113
T ≤ 900 K	PIMC	−0.5154(5)	6.02	4.48	0.22	0.37	45.67	28.78

APPARENT DISSOCIATION ENERGY

Dissociation energy from the equilibrium total energies as

$$D_T = 2\,E_{Ps} - E_{Ps2}$$

Low density limit !



$E_D = 0.0154$

≈ 0.44 eV

≈ 5000 K

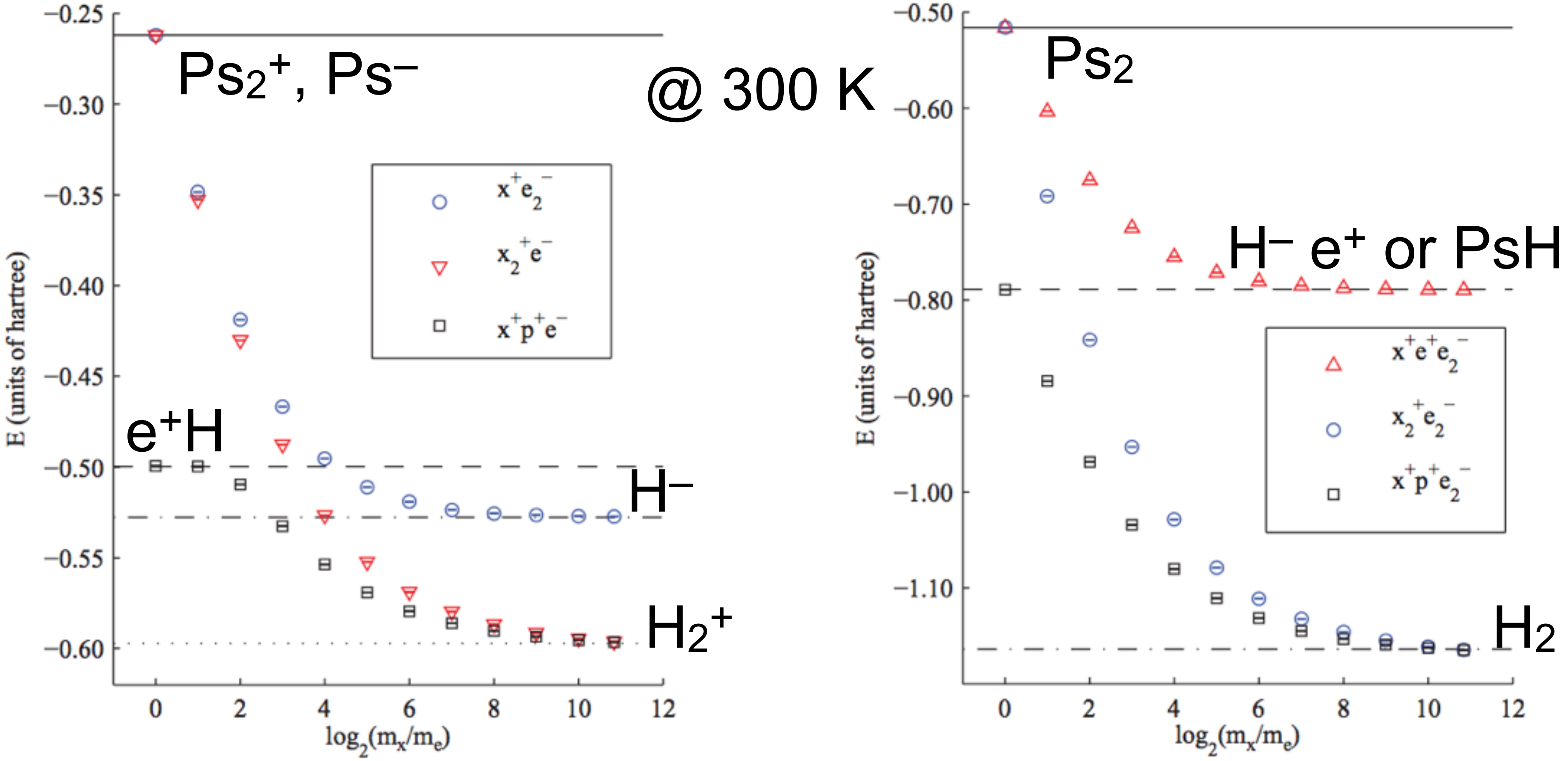
@ 950 K

$kT \approx 0.082$ eV

SMALL LIGHT NUCLEI MOLECULES:

ELECTRONS, PROTONS AND POSITRONS

3-particle and 4-particle ”molecules”

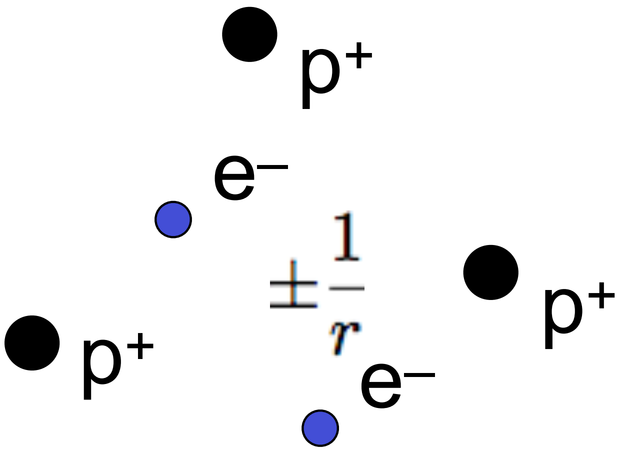


Kylänpää, TTR and D.M. Ceperley, PRA **86**, 052506 (2012)

H_3^+ MOLECULE

Quantum statistical physics 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.



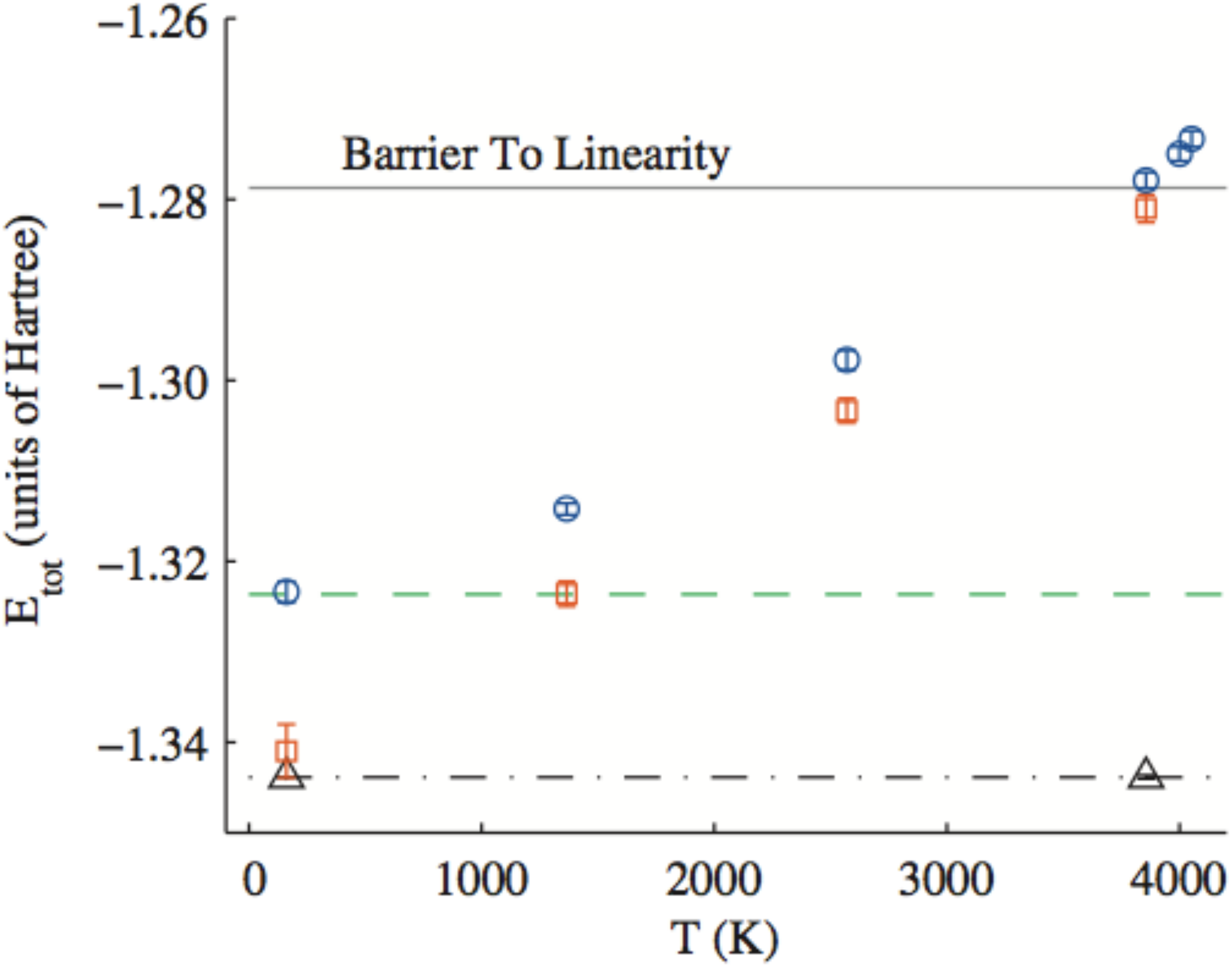
m_e, m_p

***Ab initio* or first-principles!**

H_3^+ TOTAL ENERGY:

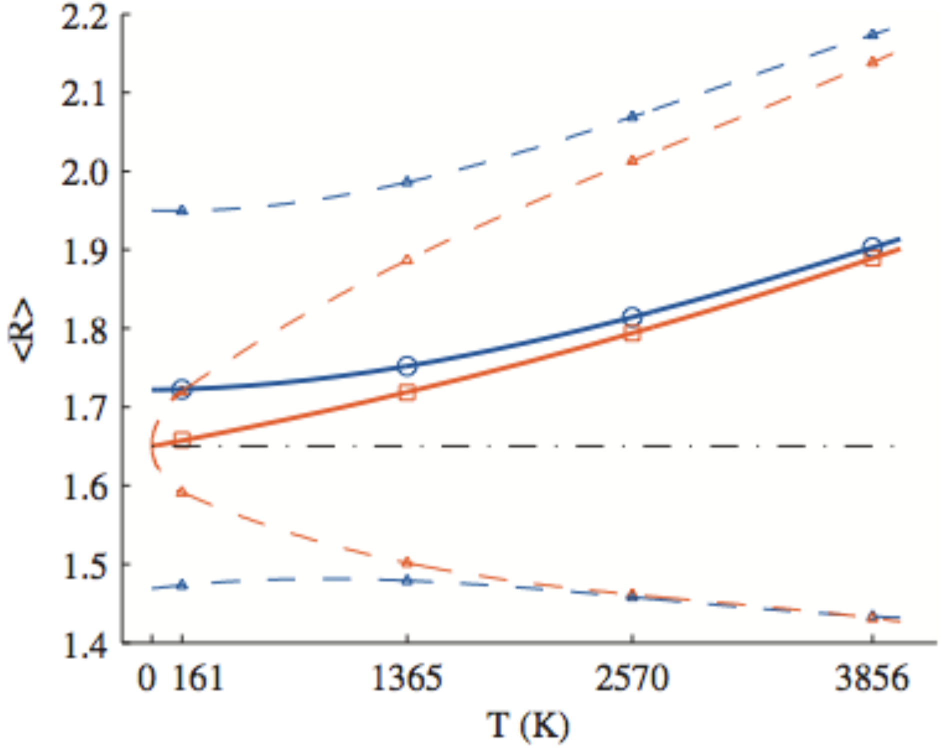
FINITE NUCLEAR MASS AND ZERO-POINT ENERGY

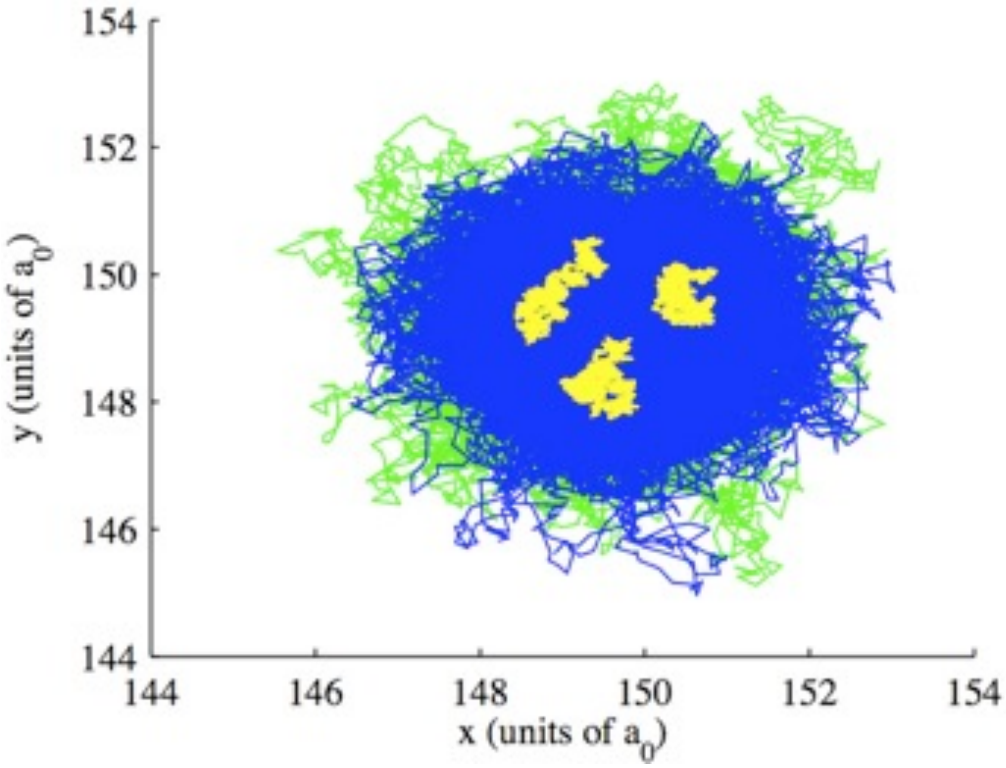
Total energy of the H_3^+ ion up to the dissociation temperature. Born–Oppenheimer approximation, classical nuclei and quantum nuclei.



H_3^+ 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}.

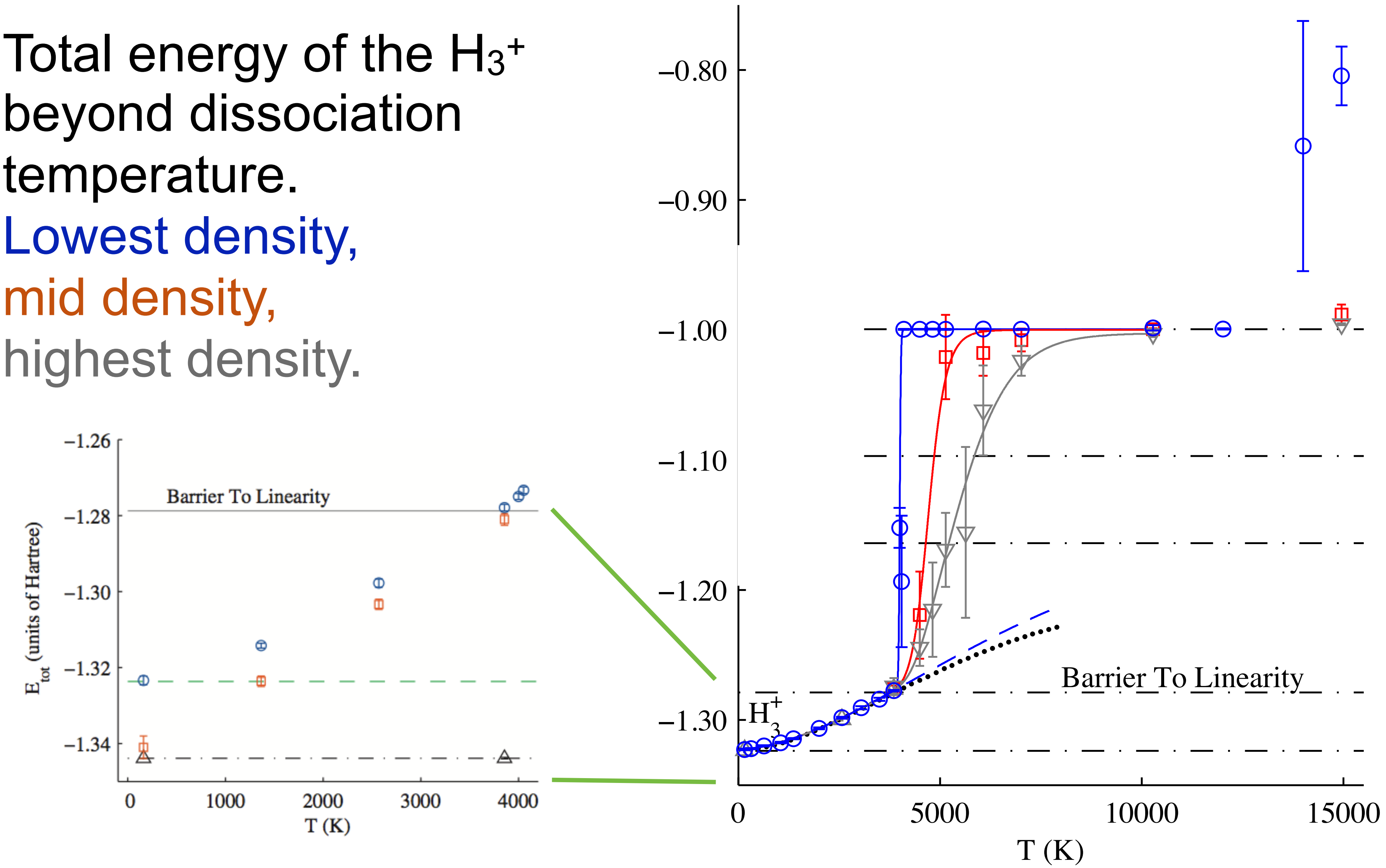
H_3^+ ENERGETICS AT HIGH TEMPERATURES

Total energy of the H_3^+ beyond dissociation temperature.

Lowest density,

mid density,

highest density.



COMPOSITIONS

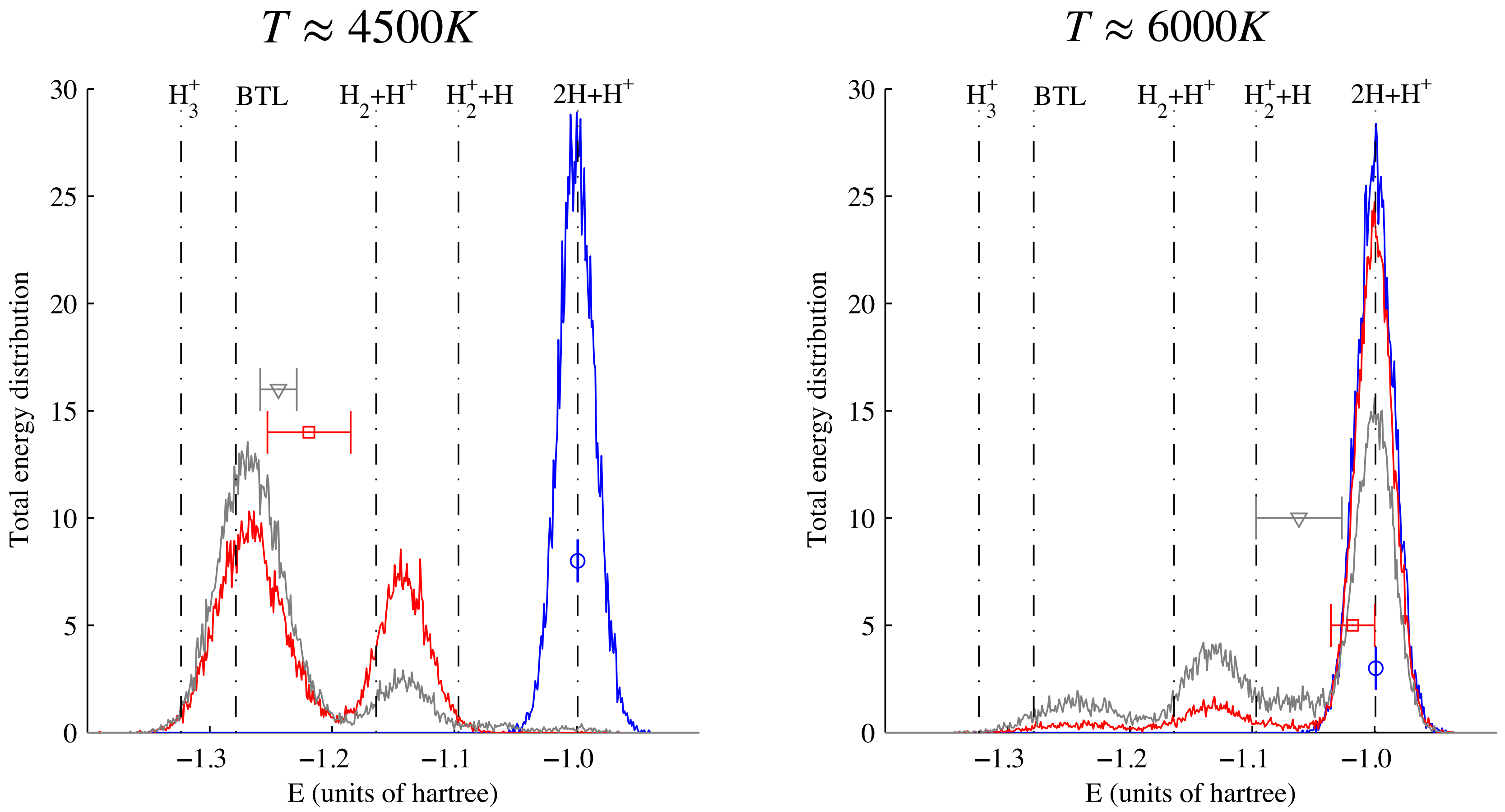


Figure 5.9: Simulation total energy distributions. (LEFT) $T \approx 4498.2$ K, (RIGHT) $T \approx 6070.3$ K. Notations are taken from Fig. 5.8.

PARTITION FUNCTION

Numerical integration of

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

gives the partition function.
We use the initial condition $Z(0) = 0$.

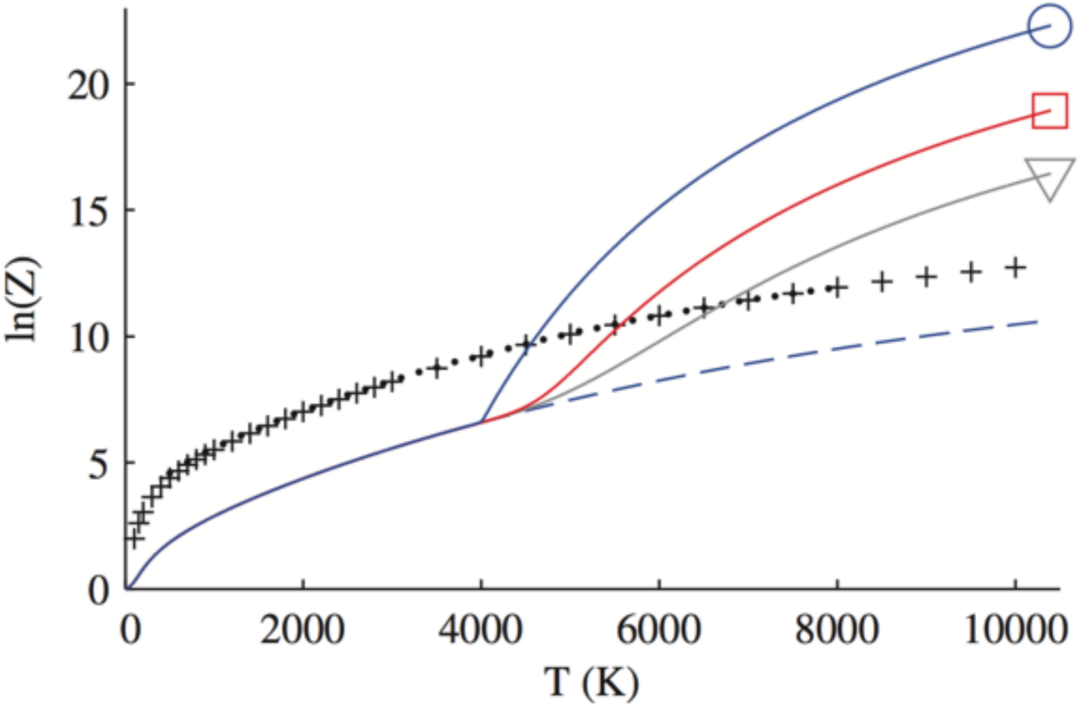
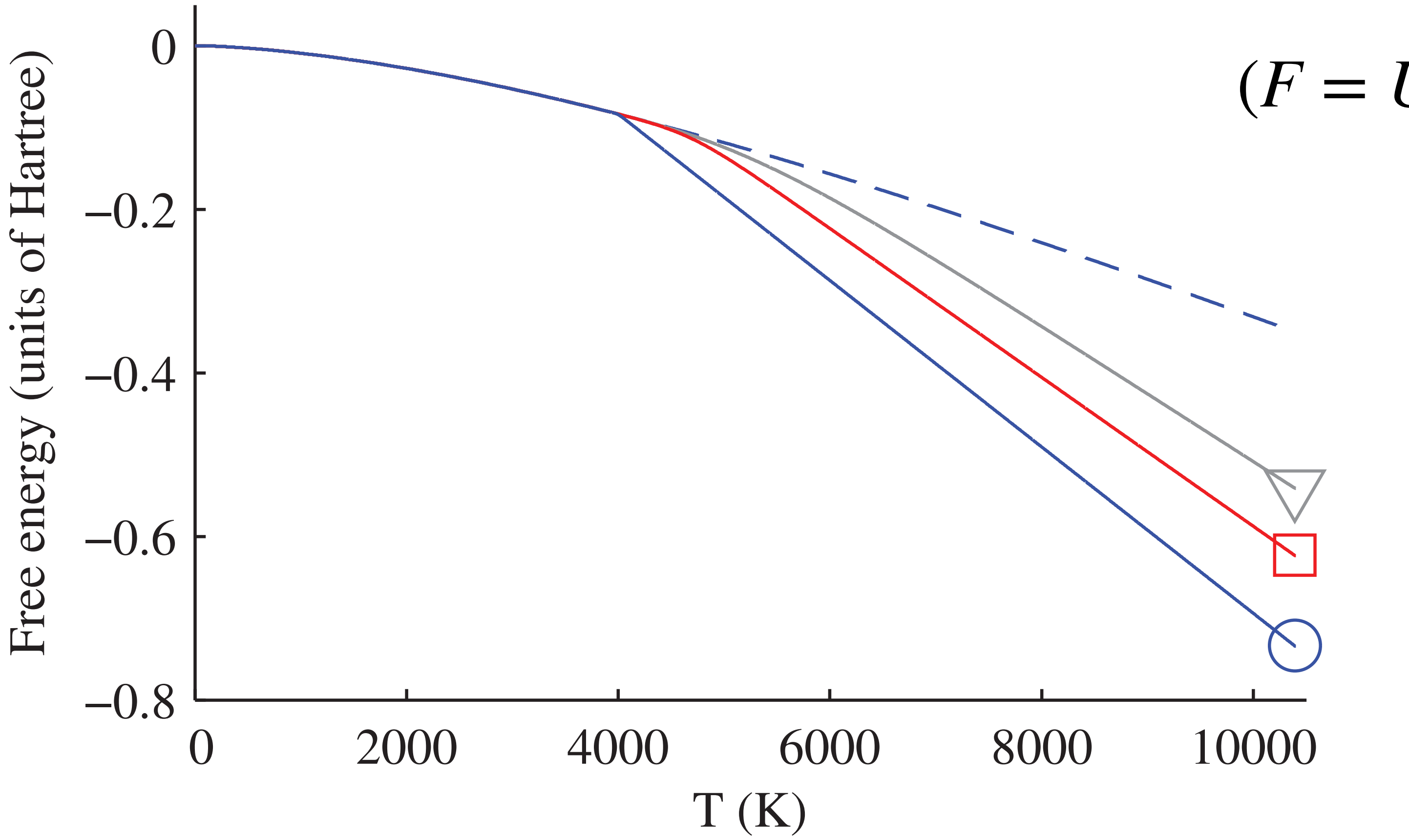


FIG. 3. The molecular NVT ensemble $\ln Z(T)$ from the energetics in Fig. 1 with the same notations. The blue solid line below 4000 K and its extrapolation (dashed line) are from Eq. (9), whereas the curves for three densities are from Eq. (10). The $\ln Z(T)$ data (black pluses) and the fit (black dots) 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



$(F = U - TS)$

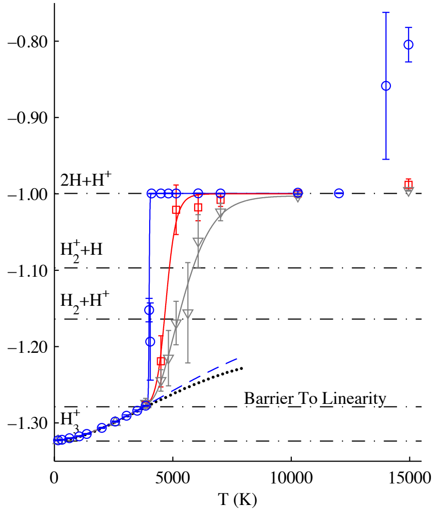


FIG. 4. Helmholtz free energy from Eq. (5) in the units of Hartree. Notations are the same as in Fig. 3.

ENTROPY

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

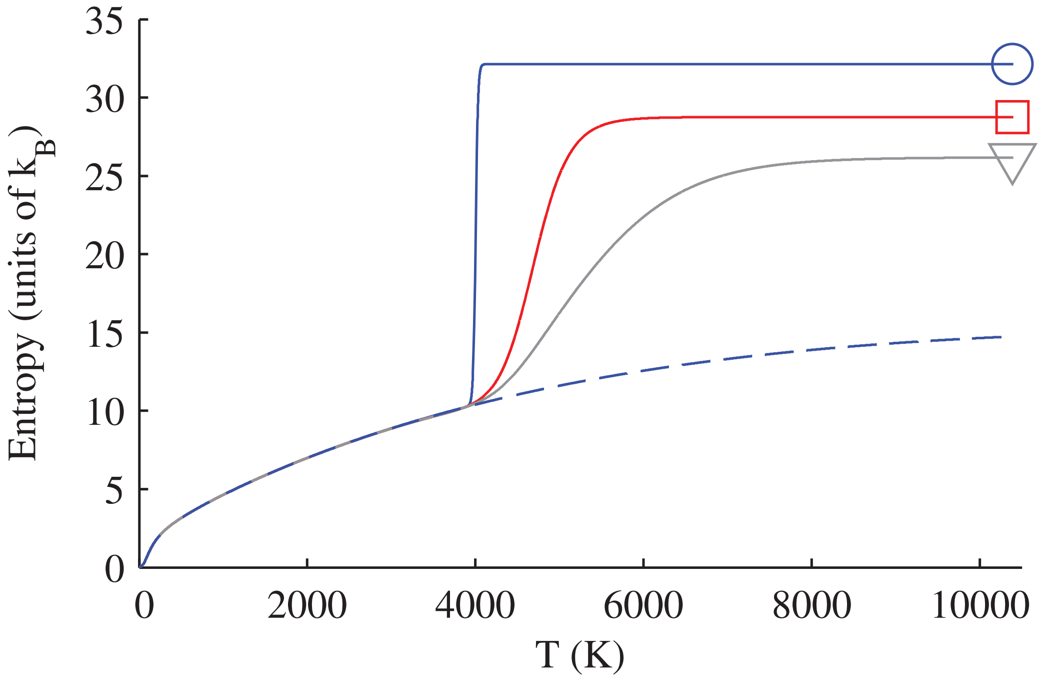


FIG. 5. Entropy from Eq. (11) in the units of k_B. Notations are the same as in Fig. 3.

MOLECULAR HEAT CAPACITY

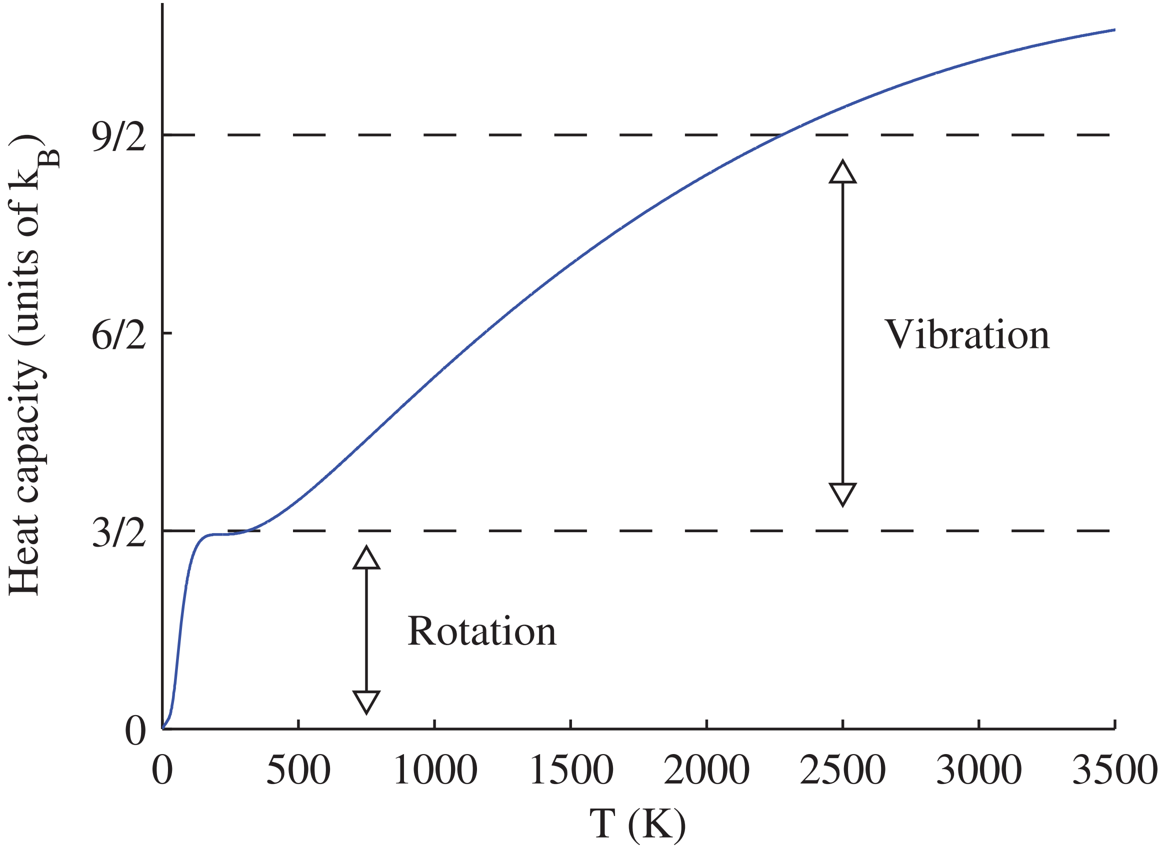
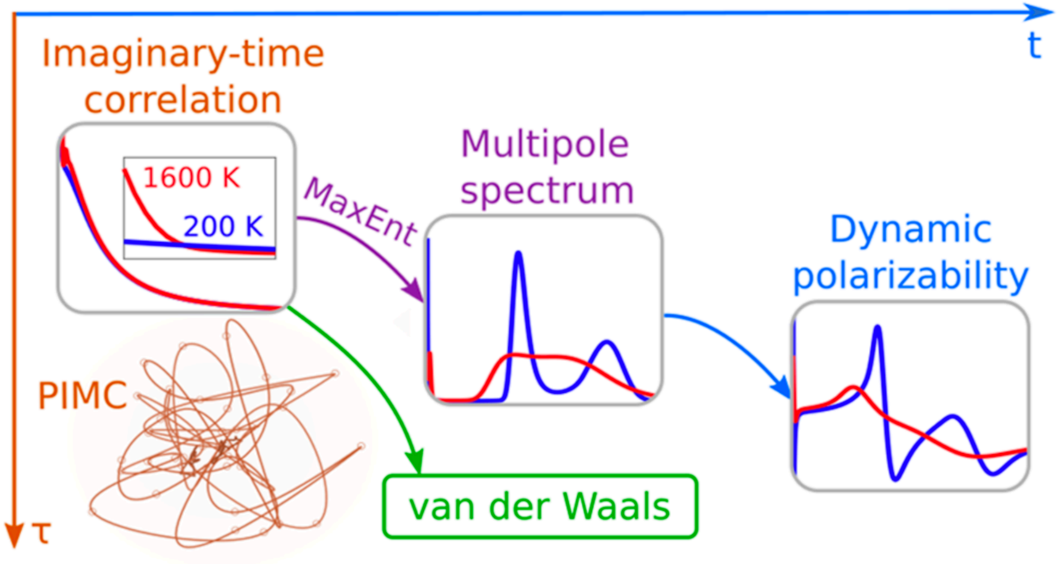


FIG. 6. Molecular heat capacity as a function of temperature calculated using the analytical model of this work. The values on the y-axis are given in units of the Boltzmann constant k_B.

DYNAMIC POLARIZABILITIES

Response to the external electric field with zero-field estimator operators



$$V^{AB}(r) = -\frac{C_6^{AB}}{r^6} - \frac{C_8^{AB}}{r^8} - \frac{C_{10}^{AB}}{r^{10}} - \dots$$

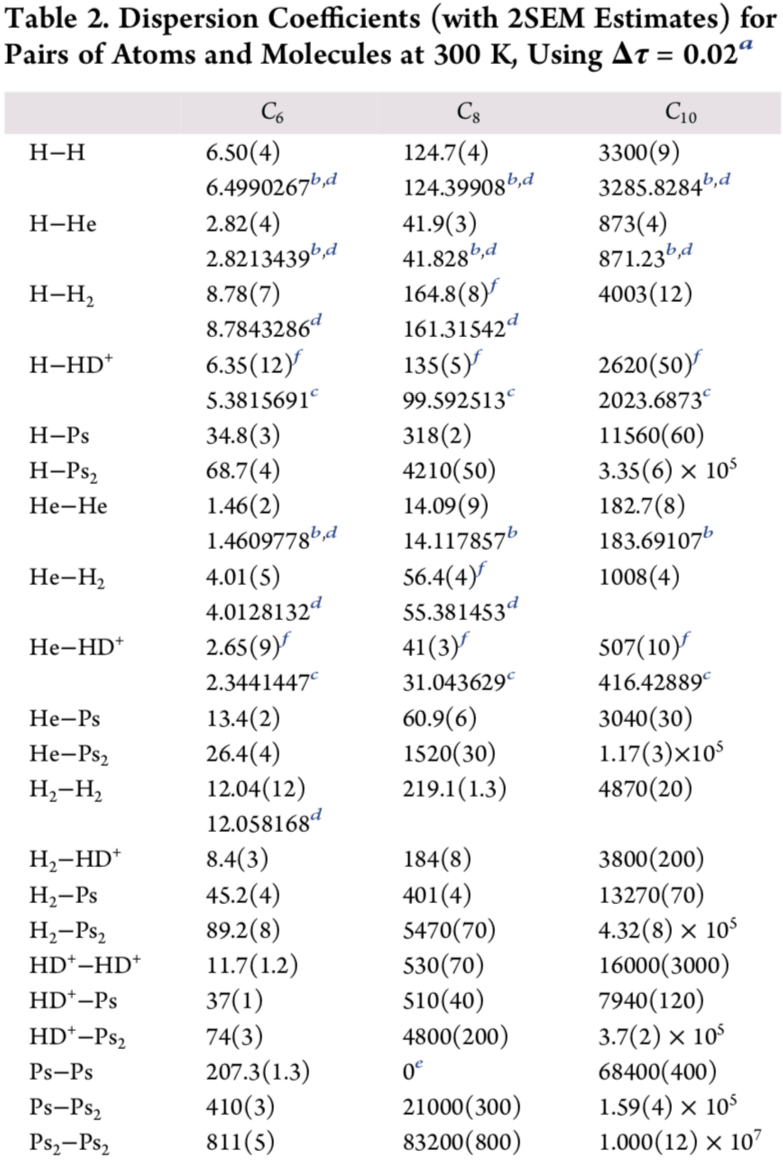


Table 2. Dispersion Coefficients (with 2SEM Estimates) for Pairs of Atoms and Molecules at 300 K, Using $\Delta\tau = 0.02^{a}$

	C_6	C_8	C_{10}
H–H	6.50(4)	124.7(4)	3300(9)
	$6.4990267^{b,d}$	$124.39908^{b,d}$	$3285.8284^{b,d}$
H–He	2.82(4)	41.9(3)	873(4)
	$2.8213439^{b,d}$	$41.828^{b,d}$	$871.23^{b,d}$
H–H_2	8.78(7)	$164.8(8)^{f}$	4003(12)
	8.7843286^{d}	161.31542^{d}	
H–HD^+	$6.35(12)^{f}$	$135(5)^{f}$	$2620(50)^{f}$
	5.3815691^{c}	99.592513^{c}	2023.6873^{c}
H–Ps	34.8(3)	318(2)	11560(60)
H–Ps_2	68.7(4)	4210(50)	$3.35(6) \times 10^5$
He–He	1.46(2)	14.09(9)	182.7(8)
	$1.4609778^{b,d}$	14.117857^{b}	183.69107^{b}
He–H_2	4.01(5)	$56.4(4)^{f}$	1008(4)
	4.0128132^{d}	55.381453^{d}	
He–HD^+	$2.65(9)^{f}$	$41(3)^{f}$	$507(10)^{f}$
	2.3441447^{c}	31.043629^{c}	416.42889^{c}
He–Ps	13.4(2)	60.9(6)	3040(30)
He–Ps_2	26.4(4)	1520(30)	$1.17(3)\times10^5$
H_2–H_2	12.04(12)	219.1(1.3)	4870(20)
	12.058168^{d}		
H_2–HD^+	8.4(3)	184(8)	3800(200)
H_2–Ps	45.2(4)	401(4)	13270(70)
H_2–Ps_2	89.2(8)	5470(70)	$4.32(8) \times 10^5$
HD^+–HD^+	11.7(1.2)	530(70)	16000(3000)
HD^+–Ps	37(1)	510(40)	7940(120)
HD^+–Ps_2	74(3)	4800(200)	$3.7(2) \times 10^5$
Ps–Ps	207.3(1.3)	0^{e}	68400(400)
Ps–Ps_2	410(3)	21000(300)	$1.59(4) \times 10^5$
Ps_2–Ps_2	811(5)	83200(800)	$1.000(12) \times 10^7$

THANK YOU!

For more details see **http://iki.fi/trantala/paths**

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Polarizabilities

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