FEYNMAN PATH INTEGRAL APPROACH TO QUANTUM DYNAMICS
AND QUANTUM MONTE CARLO

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http://www.tut.fi/semiphys

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    - **NOVEL FEATURES AND DEMONSTRATIONS**

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MOTIVATION

Electronic structure is the key concept in materials properties and related phenomena:
for mechanical, thermal, electrical, optical, and also,
for dynamics of electrons.

Conventional *ab initio* / first-principles type methods
- suffer from laborious description of electronic **correlations** (CI, MCHF, CC, DFT-functionals).
- typically ignore nuclear (quantum) dynamics and non-adiabatic coupling of electron–nuclei dynamics (**Born–Oppenheimer approximation**)
    —> *ab initio* MOLDY.
- give the **zero-Kelvin description, only**, though more realistic temperatures might be relevant.
- are typically good for **stationary states, only**.

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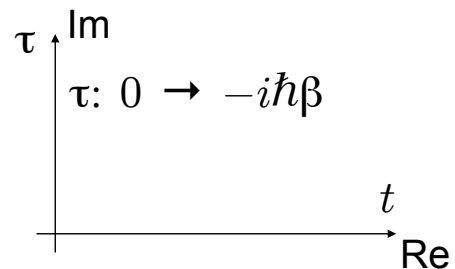
PATH INTEGRAL APPROACH TO QUANTUM MECHANICS

$$H\psi(x,t) = i\frac{\partial\psi(x,t)}{\partial t}$$

$$\psi(x,t) = \int K(x,t;x_a,t_a)\psi(x_a,t_a)\mathrm{d}x_a$$

$$K(x_b,t_b;x_a,t_a) = \int_{x_a}^{x_b} \exp(iS[x_b,x_a])\mathcal{D}x(t)$$

Real Time Path Integrals (RTPI):
Time evolution in real time

$$\psi(x,t) = \sum_{n=0}^{\infty} C_n\phi_n(x)\exp[-iE_n t]$$

Stationary states from incoherent RTPI

τ | Im

$\tau: 0 \rightarrow -i\hbar\beta$

t / Re

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PATH INTEGRAL APPROACH TO QUANTUM MECHANICS

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

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

$$K(x_b,t_b;x_a,t_a) = \int_{x_a}^{x_b} \exp(iS[x_b,x_a])\mathcal{D}x(t) \qquad \rho(x_b,\tau_b;x_a,\tau_a) = \int_{x_a}^{x_b} \exp(-S[x_b,x_a])\mathcal{D}x(\tau)$$

Real Time Path Integrals (RTPI):
Time evolution in real time

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

$$\psi(x,t) = \sum_{n=0}^{\infty} C_n\phi_n(x)\exp[-iE_n t] \qquad \psi(x,\tau) = \sum_{n=0}^{\infty} C_n\phi_n(x)\exp[-E_n\tau]$$

Stationary states from incoherent RTPI

Diffusion Monte Carlo (DMC)

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PATH INTEGRAL APPROACH TO QUANTUM MECHANICS

There is nothing but dynamics and all possible paths contribute with a complex phase. Path integral (sum over all paths) gives the probability amplitude, the wave function.

in real time
(t)

in imaginary time
($t = -i\hbar\beta$)

Time evolution in real time
& stationary states
(RTPI)

Quantum statistical physics
in equilibrium with
temperature T, $\beta = 1/k_B T$
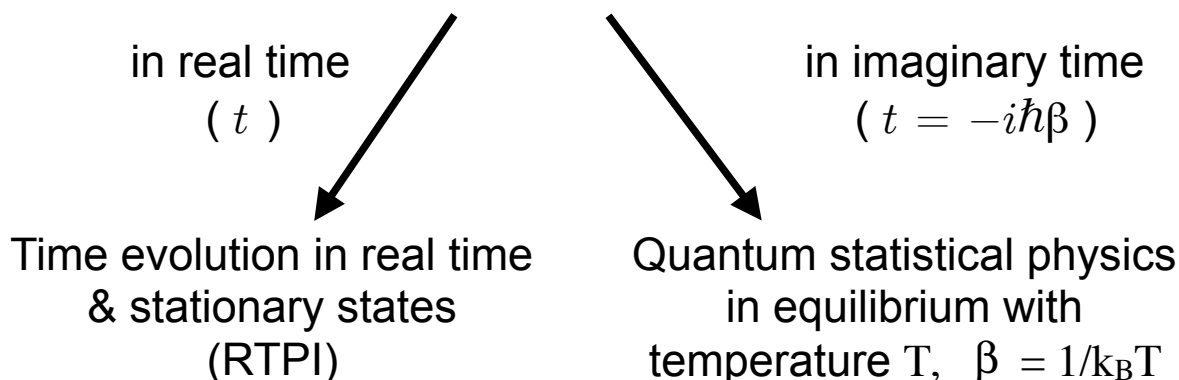
Feynman–Hibbs, *Quantum Mechanics and Path Integrals,* (McGraw-Hill, 1965)
Feynman R.P., Rev. Mod. Phys. **20**, 367–387 (1948)
Feynman R.P., *Statistical Mechanics* (Westview, Advance Book Classics, 1972)

<u>REAL TIME</u> PATH INTEGRAL APPROACH TO <u>COHERENT</u> QUANTUM DYNAMICS

$$H\psi(x,t) = i\frac{\partial \psi(x,t)}{\partial t}$$
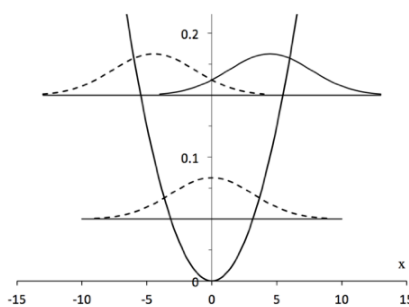
$$\psi(x,t) = \int K(x,t;x_a,t_a)\psi(x_a,t_a)\mathrm{d}x_a$$

$$K(x_b,t_b;x_a,t_a) = \int_{x_a}^{x_b} \exp(iS[x_b,x_a])\mathcal{D}x(t)$$

Glauber state evolution in a regular grid
with different kernels and time steps.

Short time kernel or Trotter kernel

$$K(x_b,x_a;\Delta t) \approx \left[\frac{m}{2\pi i\hbar\Delta t}\right]^{D/2} \exp\left[\frac{i}{\hbar}(\frac{m}{2\Delta t}(x_b-x_a)^2 - \frac{\Delta t}{2}(V(x_a)+V(x_b))\right]$$

Monte Carlo grid to:
- avoid artificial interferences
- sample the space continuously
- allow adaptation along time evolution – **the walkers**
  and walker distribution

I. Ruokosenmäki and TTR,
Numerical path integral approach to quantum dynamics and stationary states, Communications in Computational Physics **18**, 91 (15).

<u>REAL TIME</u> PATH INTEGRAL APPROACH TO <u>INCOHERENT</u> PROPAGATION

Coherent propagation and zero reference shift

$$\psi(x,t) = \int K(x,t;x_a,t_a)\psi(x_a,t_a)\mathrm{d}x_a$$

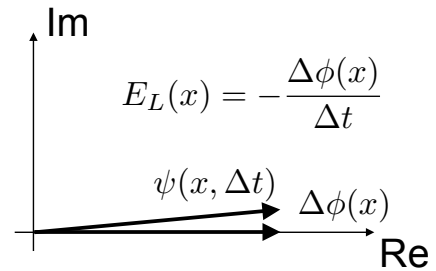$$\psi(x,\Delta t) = \sum_{n=0}^{\infty} C_n\phi_n(x)\exp[-\mathrm{i}(E_n-E_T)\Delta t]$$

with small angle approximation

$$\psi(x,\Delta t) \approx \sum_{n=0}^{\infty} C_n\phi_n(x)\{1-[(E_n-E_T)\Delta t]^2/2 - \mathrm{i}[(E_n-E_T)\Delta t]\}$$

Incoherent propagation: ignore the very small imaginary part

$$\psi_\mathrm{R}(x,\Delta t) = \sum_{n=0}^{\infty} C_n\phi_n(x)\{1-[(E_n-E_T)\Delta t]^2/2\}$$

This is simulation of quantum Zeno effect as $\Delta t \rightarrow 0$, i.e., keeping the system in its observable real state – or finding the eigenstate closest to E_T, the same way as DMC finds the ground state.   Cool, isn't it!

Im

$$E_L(x) = -\frac{\Delta\phi(x)}{\Delta t}$$

$\psi(x,\Delta t)$ $\Delta\phi(x)$

$\Delta\phi(x)$

Re

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ONE DIMENSIONAL HOOKE'S ATOM: SEPARATION OF COORDINATES

The two electron dynamics with Cartesian coordinates x_1 and x_2 can be separated to relative internal and center-of-mass motions with coordinates $r = x_1-x_2$ and $R = (x_1+x_2)/2$, respectively. The latter motion is harmonic oscillation.   Strong Coulomb correlation in the internal one dimensional dynamics leads to $\psi(r) = 0$ and allows discontinuity of ψ at $r = 0$.
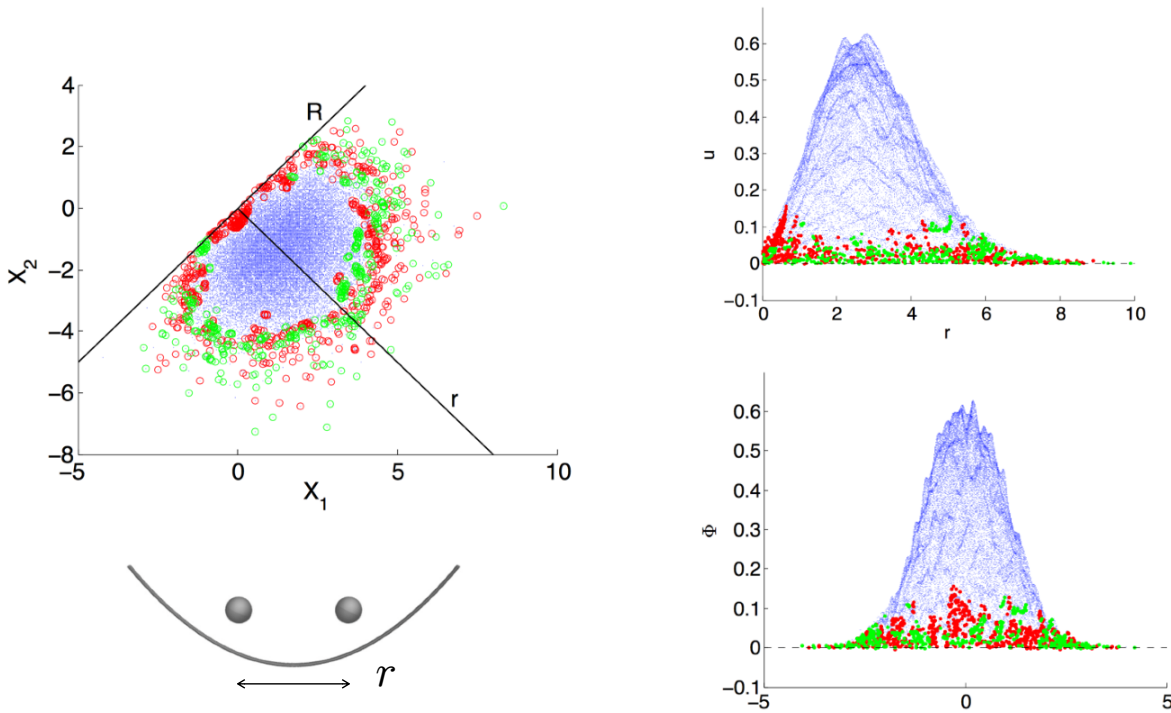
Figure 1: Ground state wave function of internal dynamics, exact (dashed) [4] and from perturbation theory (red).
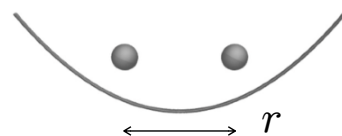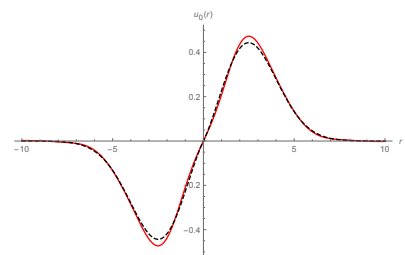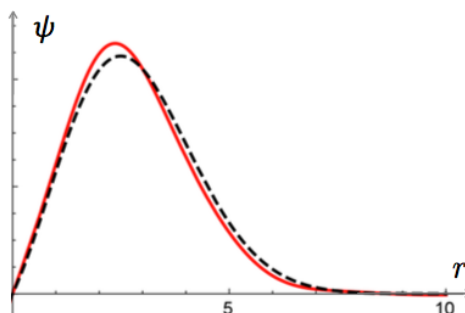
$$H(x_1,x_2) = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}\omega^2 x_1^2 + \frac{1}{2}\omega^2 x_2^2 + \frac{1}{|x_1-x_2|}$$

$$H(r,R) = -\frac{1}{2\mu}\nabla_r^2 + \frac{1}{2}\mu\omega^2 r^2 + \frac{1}{|r|} - \frac{1}{2M}\nabla_R^2 + \frac{1}{2}M\omega^2 R^2 \equiv H_r + H_R$$
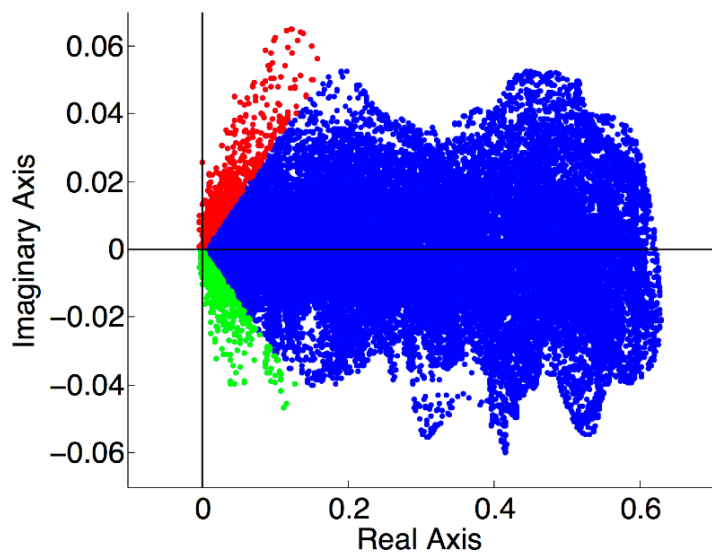
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1D HOOKE'S ATOM:
GROUND STATE WAVE FUNCTION

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1D HOOKE'S ATOM:
PHASE OF THE WAVE FUNCTION

Total energy is calcu-
lated as the average
of the phase of the
complex walker am-
plitudes.

Figure 3: Snap shot of
walker complex values after
a short time step, rotated
back to real axis. Walker
color coding is the same as
in Fig. 2.

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1D HOOKE'S ATOM: RTPI AND DMC

Diffusion Monte Carlo (DMC) method is acknowledged as the standard high accuracy reference for ground state simulations. We find that accuracy of RTPI is comparable, but with more computational efforts.

Combined DMC and RTPI turns out as a novel method with new features.

Figure 4: Snap shot of DMC walker distribution as histogram, compared to the exact wave function.
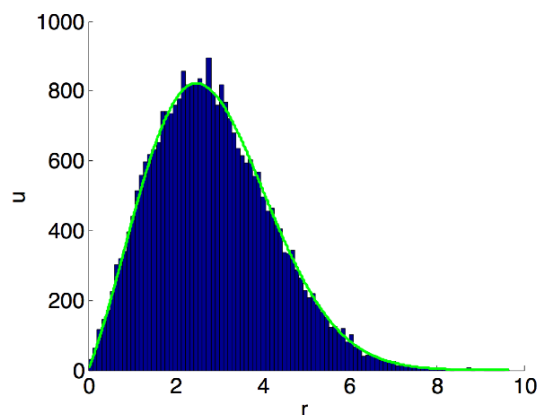
I. Ruokosenmäki et al., *Numerical path integral solution to strong Coulomb correlation in one dimensional Hooke's atom*, submitted to CPC, (arXiv:1510.02230).

PATH INTEGRALS IN <u>IMAGINARY TIME</u>

Feynman path integral in imaginary time evaluates the **mixed state density matrix**

$$\rho(R(0), R(\beta)) = \int_{R(0)}^{R(\beta)} e^{-S(R(\tau))} \mathcal{D}R(\tau)$$

The **partition function** is obtained as

Note! There is no wave function!

$$Z(\beta) = \mathrm{Tr}\,\rho,$$

where

$$\beta = 1 / k_B T$$

and $S[R]$ is the action of the path $R(0) \dashrightarrow R(\beta)$ for the imaginary time period β.

NVT ENSENBLE QUANTUM STATISTICAL MECHANICS

Thus, we have the quantum statistical mechanics and the concepts of NVT ensemble

- finite temperature, $T > 0$ $\qquad \beta = \dfrac{1}{k_B T}$
- density matrix $\qquad \hat{\rho}(\beta) = \mathrm{e}^{-\hat{S}}$
  action $\qquad \hat{S}(\beta) = \beta \hat{H} = \beta(\hat{T} + \hat{V})$
- partition function $\qquad Z = \mathrm{Tr}(\hat{\rho})$
- expectation values $\qquad \langle \hat{A} \rangle = \mathrm{Tr}(\hat{\rho}\hat{A})/Z$

- **Note! this is all exact, so far!**

Feynman–Hibbs, *Quantum Mechanics and Path Integrals,* (McGraw-Hill, 1965)
Feynman R.P., *Statistical Mechanics* (Westview, Advance Book Classics, 1972)

DISCRETIZING THE PATH ...

With the primitive approximation and Trotter expansion

$$\rho(\mathbf{r}_0, \mathbf{r}_M; \beta) = \int \rho(\mathbf{r}_0, \mathbf{r}_1; \beta/M)...\rho(\mathbf{r}_{M-1}, \mathbf{r}_M; \beta/M)\mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2...\mathrm{d}\mathbf{r}_{M-1}$$

where M is the Trotter number and

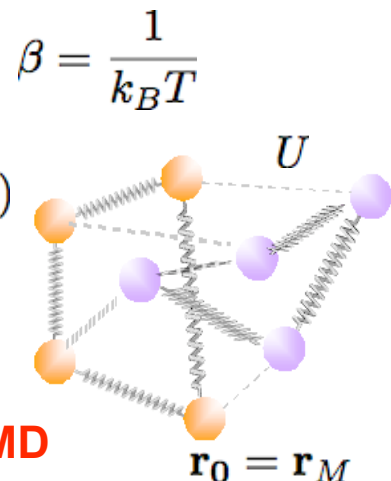With short enough $\tau = \beta/M$ $\qquad \beta = \dfrac{1}{k_B T}$

the action

$$S(\beta) = \frac{m_e}{\hbar^2}\frac{M}{2\beta}(\mathbf{r}_i - \mathbf{r}_{i+1})^2 + U(\mathbf{r}_i, \mathbf{r}_{i+1}; \beta)$$

approaches that of free particle
as the potential function

$$U(\mathbf{r}_i, \mathbf{r}_{i+1}; \tau) \propto \tau.$$

Note!
This is not sc. PIMD
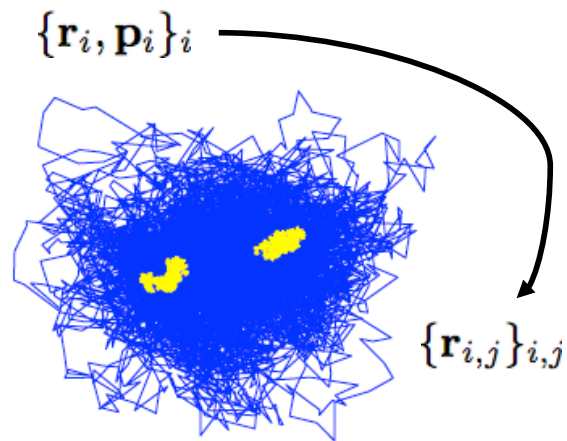
U

$\mathbf{r}_0 = \mathbf{r}_M$

... FOR 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

$\{\mathbf{r}_i, \mathbf{p}_i\}_i$

$\{\mathbf{r}_{i,j}\}_{i,j}$

Metropolis N. *et al.*, J. Chem. Phys. **21**, 1087, (1953).
Ceperley D.M., Rev. Mod. Phys. **67**, 279, (1995)

PATH INTEGRAL MONTE CARLO (PIMC)

An *ab initio* electronic structure approach with novel features:
- FIXED FINITE TEMPERATURE, NVT ENSEMBLE
- NO BORN–OPPENHEIMER APPROXIMATION
- FULL ACCOUNT OF CORRELATION, the van der Waals interaction, for example!
- Evaluation of EXCHANGE INTERACTION suffers from *Fermion Sign Problem!*
- **SIMULATION OF EQUILIBRIUM DISSOCIATION–RECOMBINATION REACTION**

QUANTUM DOTS IN QCA

- ## Finite temperature and electron delocalization effects
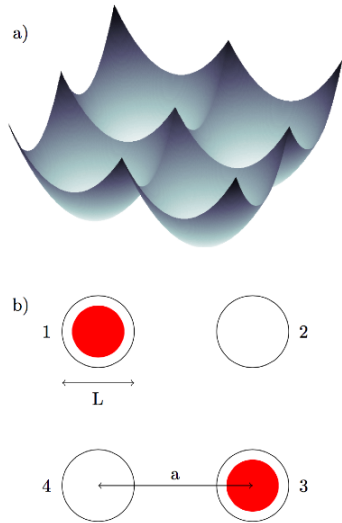

a)

b)

1 ● 2 ○

L

4 ○ 3 ●

a

FIG. 1. (a) A visualization of harmonic confinement potential of our QCA cell model. (b) Schematic picture of an ideal QCA setup, where the two electrons occupy either "0" bit (sites 1 & 3) or "1" bit (sites 2 & 4). The site separation a and QD size L are marked.
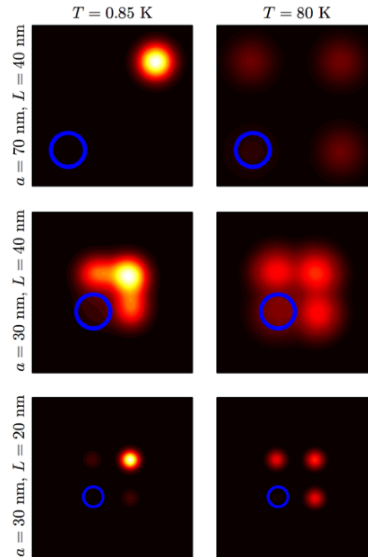
$T = 0.85$ K $T = 80$ K

$a = 70$ nm, $L = 40$ nm
$a = 30$ nm, $L = 40$ nm
$a = 30$ nm, $L = 20$ nm

FIG. 3. The density distribution of one electron is plotted according to the reference electron (blue circle) at $T = 0.85$ K (left) and $T = 80$ K (right) with different separation distances and QD sizes. The normalization is the same in both temperatures.
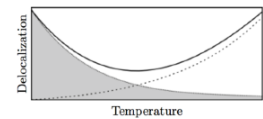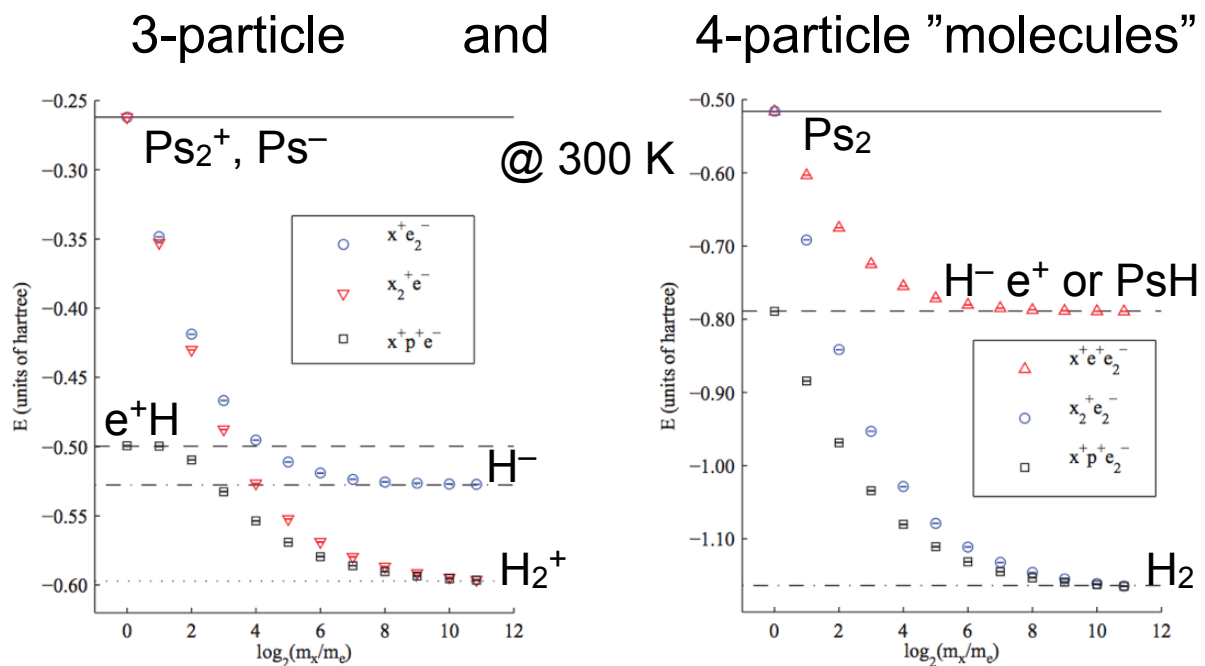
FIG. 6. A schematic separation of the total delocalization (solid line) to thermal part (dashed) and quantum mechanical part (dotted) as functions of temperature. The gray area causes the difference in fidelity between full quantum and classical data.

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SMALL LIGHT NUCLEI MOLECULES:
ELECTRONS, PROTONS AND POSITRONS

3-particle   and   4-particle "molecules"

@ 300 K

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

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DIPOSITRONIUM Ps$_2$

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

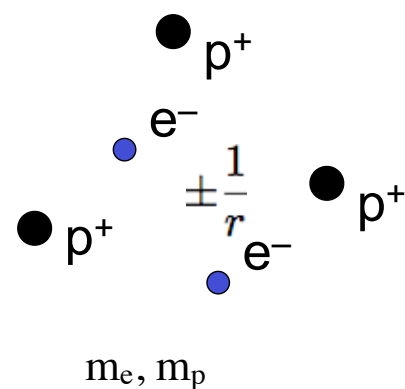$$\langle \tau \rangle = \beta/M = 0.015, \, M \approx 10^5$$

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

e$^-$

e$^+$

$\pm\dfrac{1}{r}$

e$^+$

e$^-$
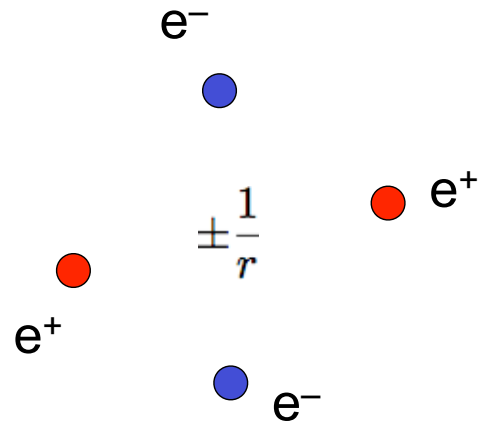
H$_3$$^+$ MOLECULE

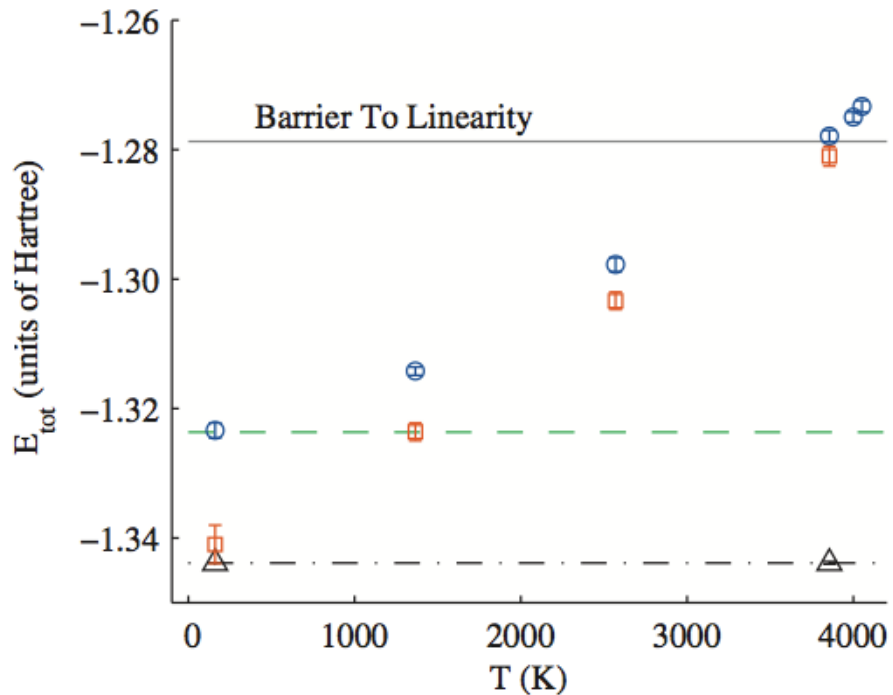Quantum statistical physics of two electrons and three nuclei (five-particle system) as a function of temperature:
  - Structure and energetics:
    - quantum nature of nuclei
    - pair correlation functions, contact densities, ...
    - dissociation temperature
  - Comparison to the data from conventional quantum chemistry.

p$^+$

e$^-$

$\pm\dfrac{1}{r}$

p$^+$

p$^+$

e$^-$

m_e, m_p

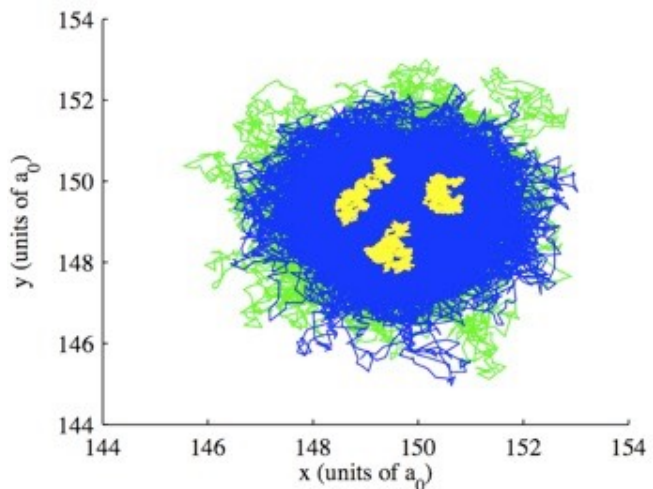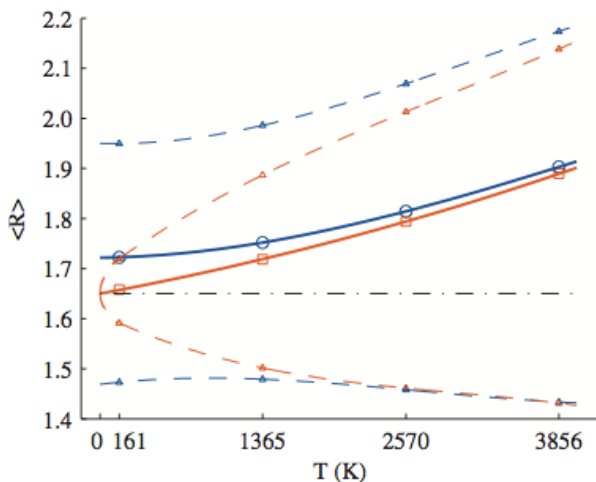***Ab initio* or first-principles!**

H₃⁺ TOTAL ENERGY:
FINITE NUCLEAR MASS AND ZERO-POINT ENERGY

Total energy
of the H₃⁺ ion
up to the
dissociation
temperature.
Born–
Oppenheimer
approximation,
classical
nuclei and
quantum
nuclei.

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H₃⁺ MOLECULAR GEOMETRY AT
LOW TEMPERATURE: ZERO-POINT MOTION
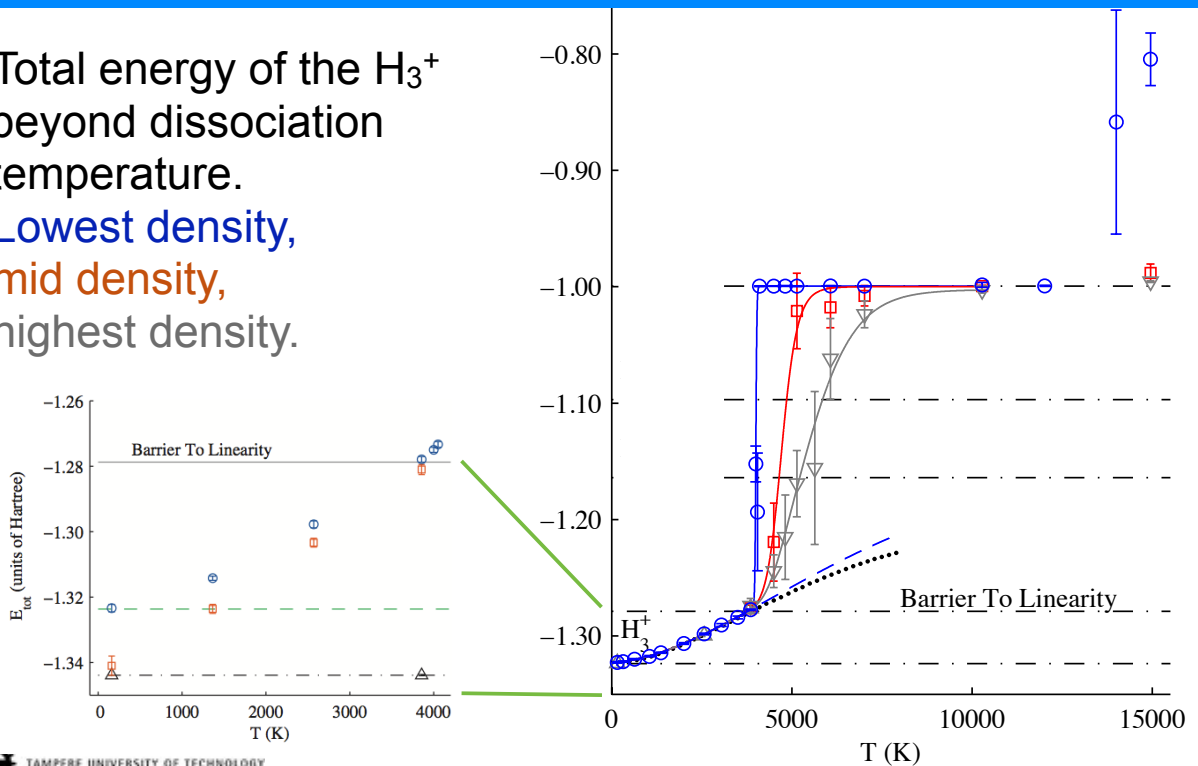
Internuclear distance.
Quantum nuclei, classical
nuclei, with FWHM

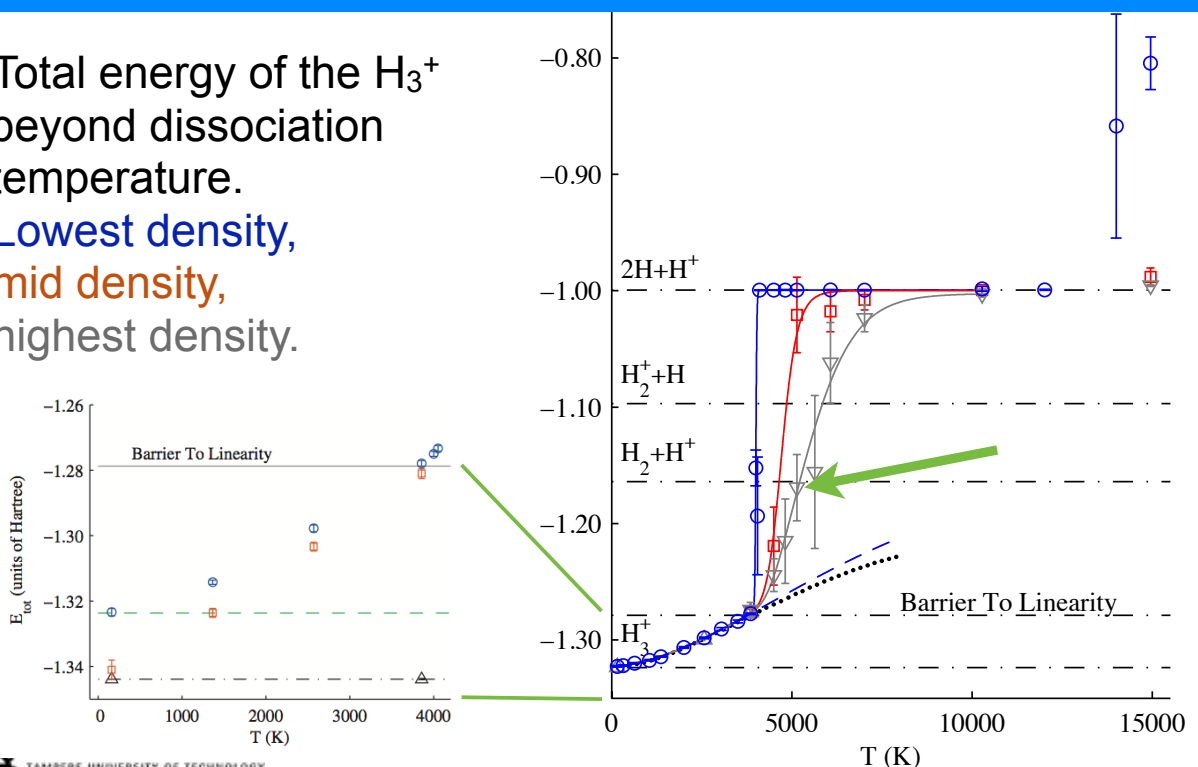Snapshot from simulation,
projection to xy-plane. Trotter
number 2¹⁶.

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H₃⁺ ENERGETICS AT HIGH TEMPERATURES

Total energy of the H₃⁺ beyond dissociation temperature.

Lowest density,

mid density,

highest density.

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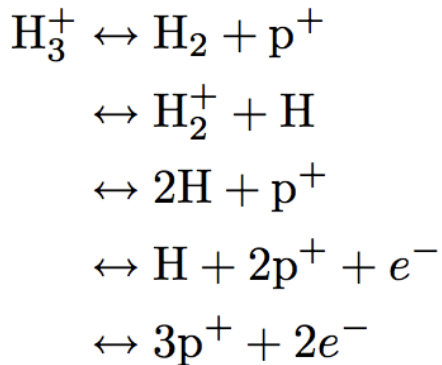
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H₃⁺ ENERGETICS AT HIGH TEMPERATURES: DISSOCIATION–RECOMBINATION

Total energy of the H₃⁺ beyond dissociation temperature.

Lowest density,

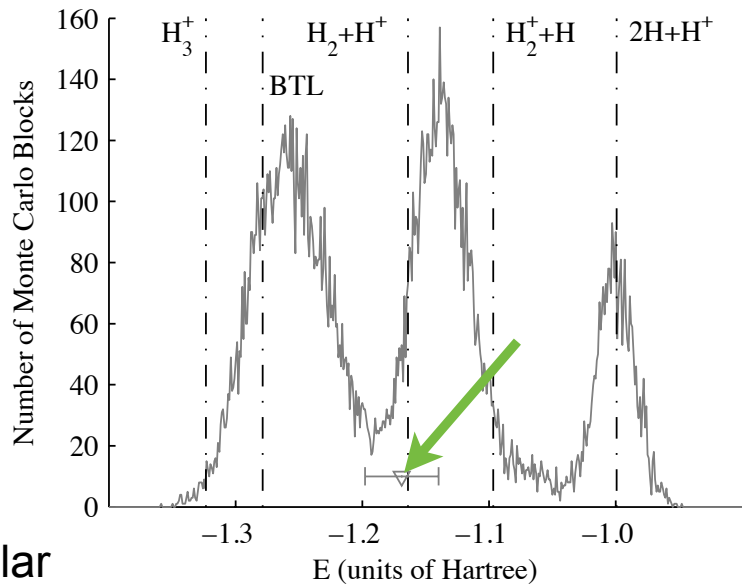mid density,

highest density.

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DISSOCIATION–RECOMBINATION EQUILIBRIUM REACTION

The molecule and its fragments:

$$H_3^+ \leftrightarrow H_2 + p^+$$
$$\leftrightarrow H_2^+ + H$$
$$\leftrightarrow 2H + p^+$$
$$\leftrightarrow H + 2p^+ + e^-$$
$$\leftrightarrow 3p^+ + 2e^-$$

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

The equilibrium composition of fragments at about 5000 K.

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PARTITION FUNCTION

Numerical integration of

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

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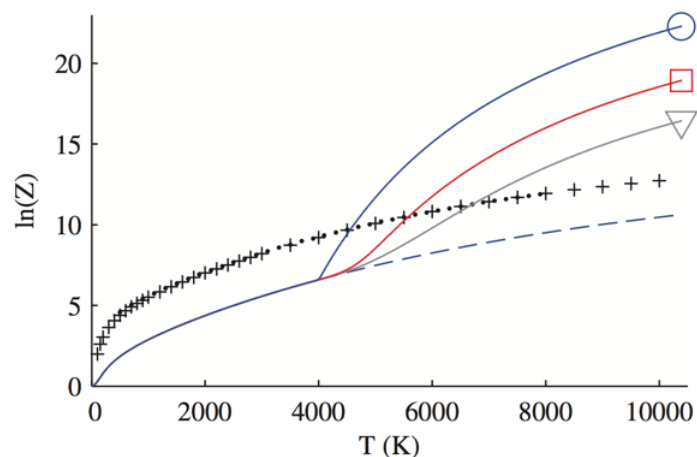We use the initial condition $Z(0) = 0$.

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).

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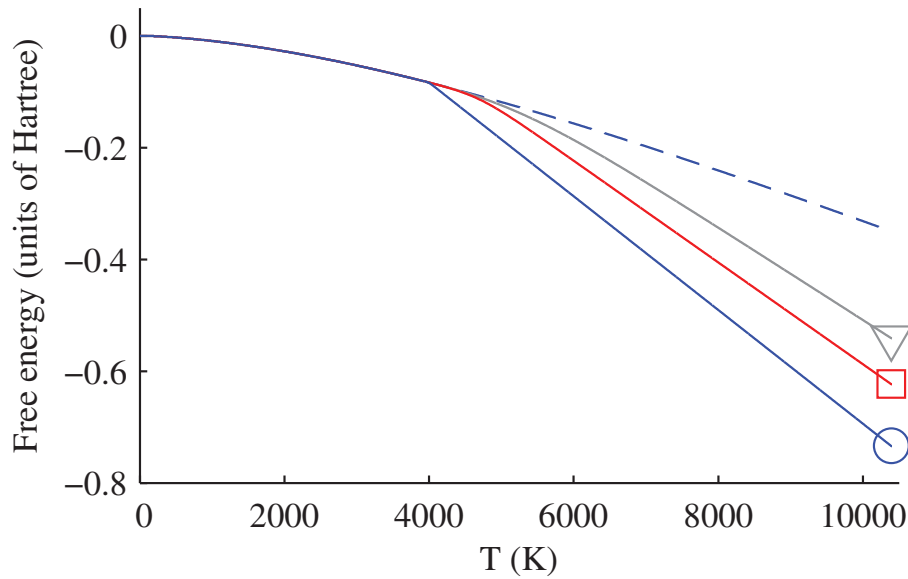
FREE ENERGY

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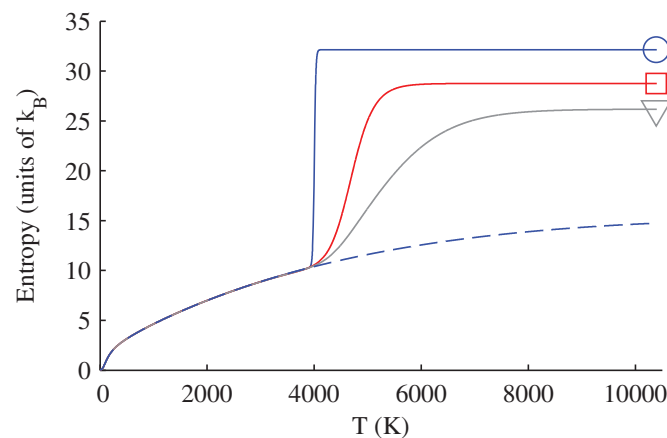
ENTROPY

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

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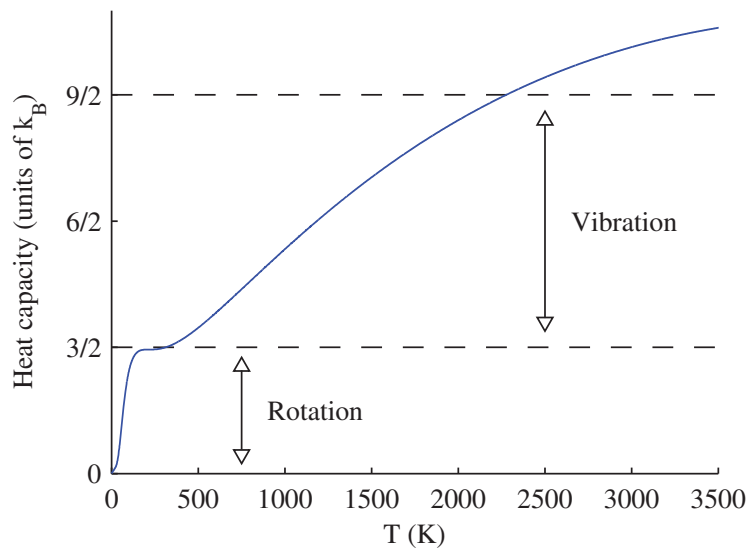
MOLECULAR HEAT CAPACITY

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.

THANK YOU!

For more details see   http://www.tut.fi/semiphys

1. Ilkka Kylänpää, PhD Thesis (Tampere University of Technology, 2011)
2. Ilkka Kylänpää and Tapio T. Rantala, Phys. Rev. A **80**, 024504, (2009) and
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Ps$_2$

H$_3$$^+$