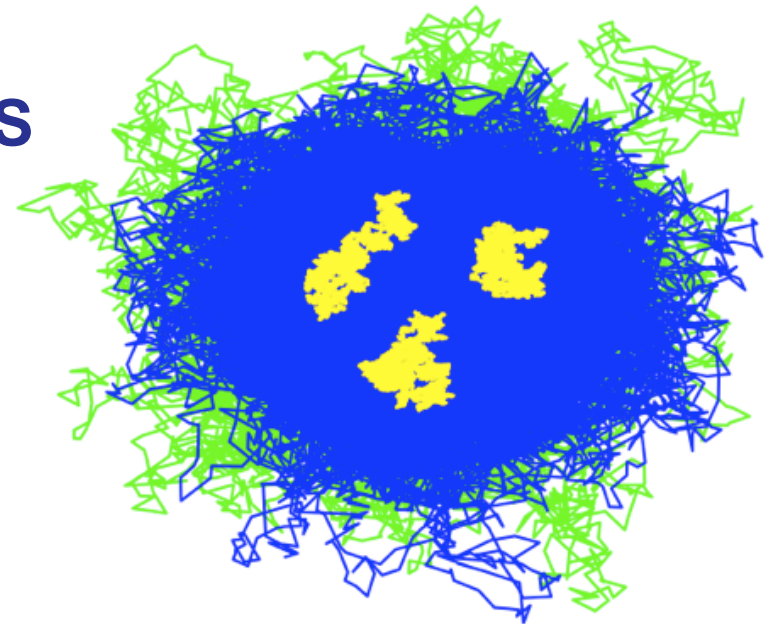


FEYNMAN PATH INTEGRAL APPROACHES TO ELECTRONIC STRUCTURE THEORY AND CALCULATIONS

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CONTENTS

- MOTIVATIONS
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 - IN REAL TIME, $T=0$
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- NUMERICAL ISSUES
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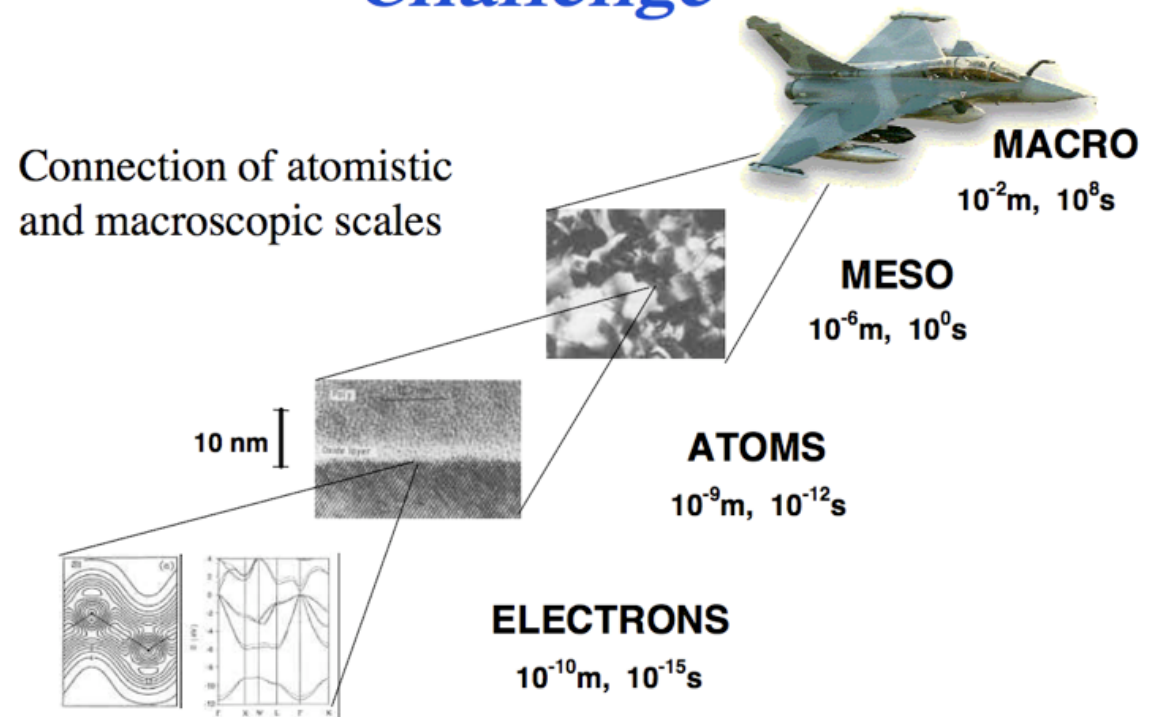


PROPERTIES OF MATTER

Where do properties of materials arise from?

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

Challenge



Cargese EW 2001

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

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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 $\hbar$ "
 - yields classical mechanics for macroscopic objects as a limiting case, if $\hbar \rightarrow 0$.
 - 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**.



Tapio Rantala: From Classical to Quantum

Appl Math Semin 23.4.2018

QM – WHY AND WHAT

- Postulate 1:** The state of a system is fully described by its **wave function** $\Psi_{m,n,\dots}(\mathbf{r}_1, \mathbf{r}_2, \dots; t) = |m, n, \dots; t\rangle$.
- 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 **corresponding eigenvalue** ω . When ψ is not an eigenfunction, then the measurement yields one of the eigenvalues ω_k with the probability $|\langle \omega_k | \psi \rangle|^2$.
- Postulate 4:** **Probability**, that the particle will be found in the volume element $d\mathbf{r}$ at the position $\mathbf{r}$ is $|\psi(\mathbf{r})|^2 d\mathbf{r}$, if ψ is **normalized**.
- Postulate 5:** The wavefunction $\Psi_{m,n,\dots}(\mathbf{r}_1, \mathbf{r}_2, \dots; t)$ evolves in time according to the **Schrödinger equation**.



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ELECTRONIC STRUCTURE

Schrödinger equation – for stationary states

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

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** $\Psi(\mathbf{R}, t) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)$

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

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



Tapio Rantala: FIRST-PRINCIPLES APPROACH TO MATERIALS PHYSICS

Physics seminar 31.8.2017

EXCHANGE OF IDENTICAL PARTICLES AND CORRELATIONS

Exchange of identical particles

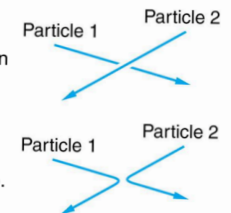
Identical particles may exchange, which must be taken into account

→ symmetry requirements:

Bosons $\psi_S(\mathbf{r}_1, \mathbf{r}_2) = 2^{-1/2} (|\ln m\rangle + |\ln n\rangle) = + \psi_S(\mathbf{r}_2, \mathbf{r}_1)$

and

Fermions $\psi_A(\mathbf{r}_1, \mathbf{r}_2) = 2^{-1/2} (|\ln m\rangle - |\ln n\rangle) = - \psi_A(\mathbf{r}_2, \mathbf{r}_1)$.



Many-body effects (sc. correlations)

There are no exact solutions to the many-body problems, in general

→ approximations or simulations



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PATH INTEGRAL APPROACH:

1. CLASSICAL PATH AND QUANTUM PATHS

Let us consider particle dynamics from a to b .

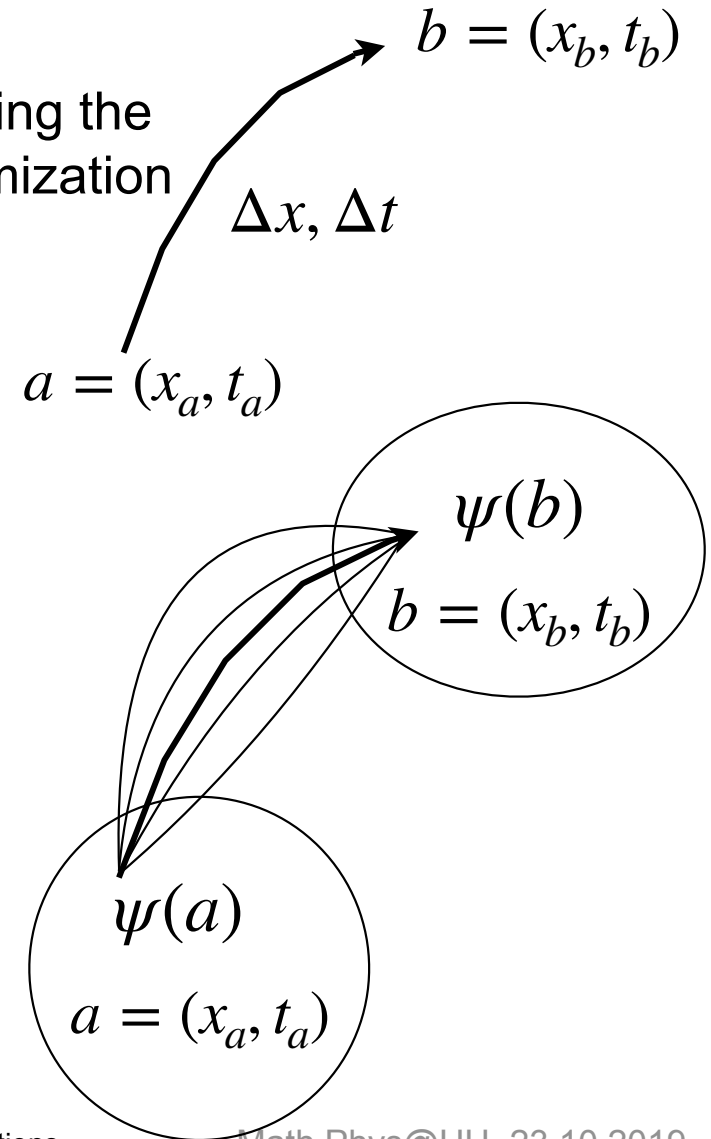
Lagrangian formulation of classical mechanics for finding the path/trajectory leads to equations of motion from minimization (extremum) of action

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

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

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

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

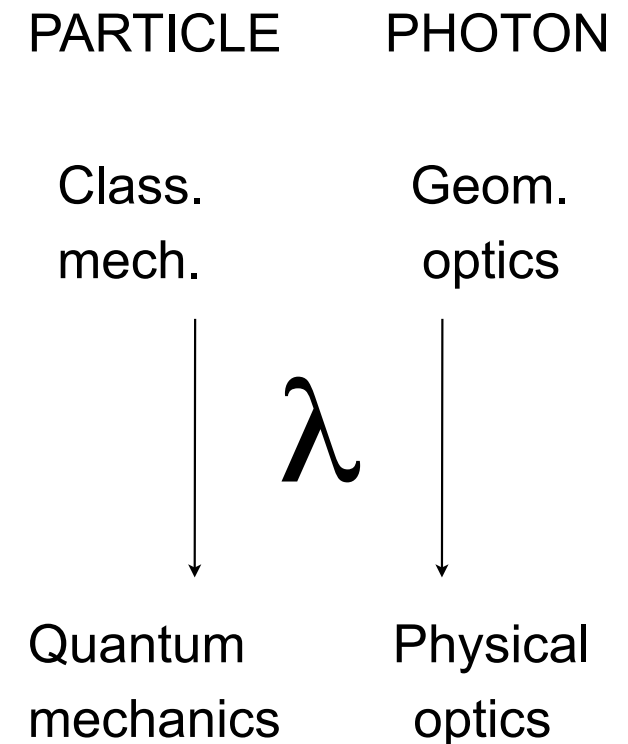
the absolute square of the probability amplitude K .

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 DYNAMICS (IN REAL TIME)

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

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

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

We call this "kernel" or "propagator" or "Green's function".

In terms of stationary eigenstates it can be written as

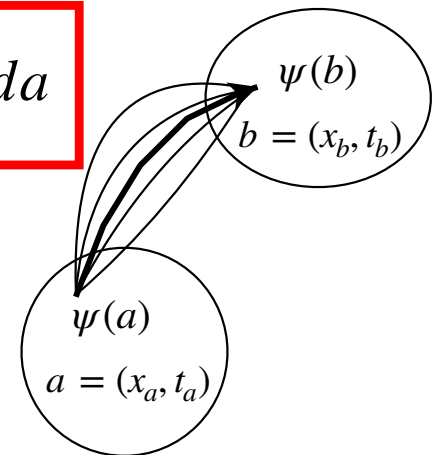
$$K(b,a) = \sum_n \phi_n^*(a) \phi_n(b) e^{-(i/\hbar)E_n(t_b - t_a)}$$

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

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

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

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

Thus, we find

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

and normalization implies

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

Expectation values evaluated from

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

PATH INTEGRAL APPROACH:

5. EQUILIBRIUM PATH INTEGRAL (IN IMAGINARY TIME)

Now, compare

$$\rho(x', x) = \sum_n \phi_n^*(x') \phi_n(x) e^{-\beta E_n} \quad \beta = \frac{1}{kT}$$

and

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

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

Decoherence!

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 (PIMC)

For the density operator we can write

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

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

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

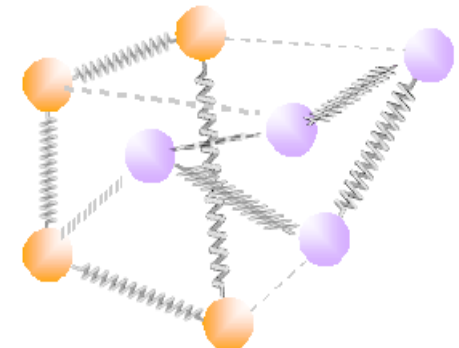
where

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

and M is called the Trotter number.

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

Decoherence!



EXCHANGE AND CORRELATION

From one-electron picture to many-fermion description:

- fermionic wave function $\longrightarrow$ Slater determinant of one-electron orbitals:

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

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

9.6. Configuration interaction (CI)

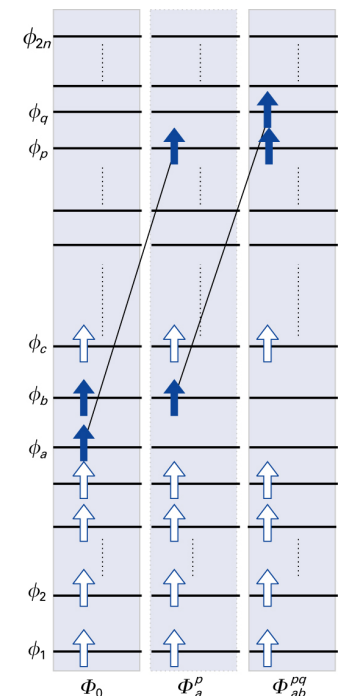
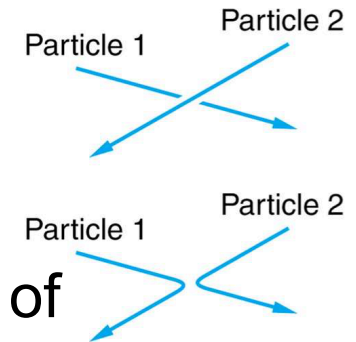
QTMN, 2018 179

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

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

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

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

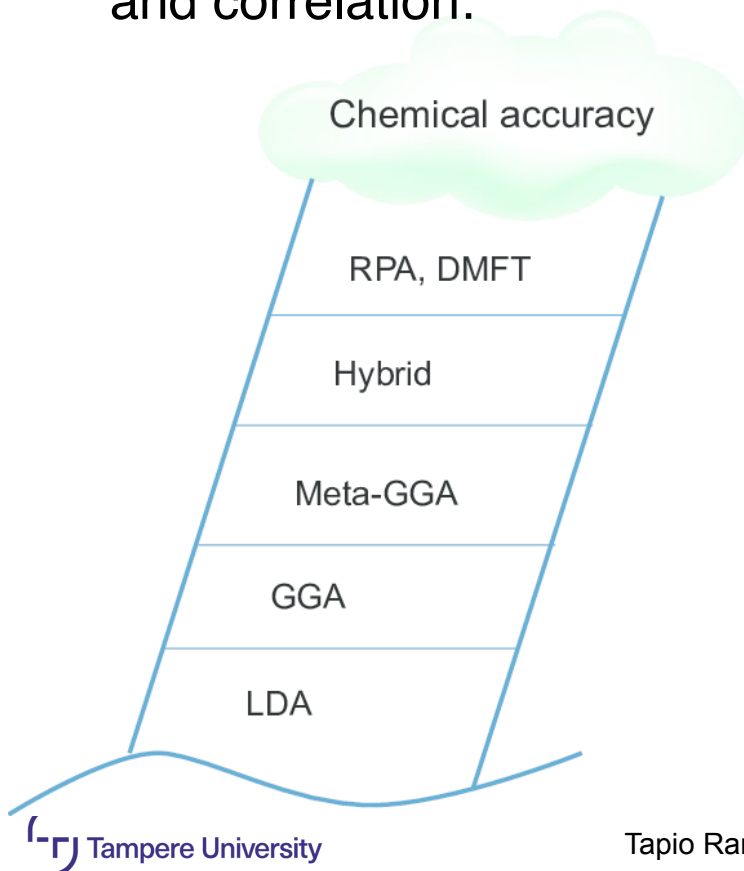


EXCHANGE AND CORRELATION (DFT)

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

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

Jacob's ladder for exchange and correlation:



$$E[\rho] = -\frac{\hbar^2}{2m} \sum_i^n \int \psi_i^*(\mathbf{r}) \nabla_i^2 \psi_i^*(\mathbf{r}) d\mathbf{r} - \sum_I^N \int \frac{Z_I e^2}{4\pi\epsilon_0 r_I} \rho(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \int \int \frac{e^2 \rho(\mathbf{r}_i) \rho(\mathbf{r}_j)}{4\pi\epsilon_0 r_{ij}} d\mathbf{r}_i d\mathbf{r}_j + E_{xc}[\rho],$$

$$f = -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_I^N \frac{Z_I e^2}{4\pi\epsilon_0 r_I} + \frac{1}{2} \int \frac{e^2 \rho(\mathbf{r}_j)}{4\pi\epsilon_0 r_{ij}} d\mathbf{r}_j + V_{xc}[\rho]$$

$$f \psi_i = \epsilon_i \psi_i$$

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

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



CASTEP

abinit.org

PBC

- localized (atomic) basis

DMol³



finite

- Real-space grid



TURBOMOLE GmbH



PBC and finite

ASE: *abinit* Asap Dacapo



EMT



- (Gromacs for molecular dynamics)

PATH INTEGRALS IN IMAGINARY AND REAL TIME

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

$$\leftarrow \tau = it$$

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

$$\psi(x, \tau) = \int G(x, \tau; x_a, \tau_a) \psi(x_a, \tau_a) dx_a$$

$$\psi(x, t) = \int K(x, t; x_a, t_a) \psi(x_a, t_a) dx_a$$

PATH INTEGRAL APPROACHES

τ DMC

The
conventional
Diffusion Monte
Carlo (DMC)

$$G = G_{\text{diff}} G_B$$

$$G_{\text{diff}} = C_1 \exp(-\Delta x^2 / 2\tau)$$

$$G_B = C_2 \exp[-(\bar{V} - E_T)\tau]$$

everywhere real
and positive !

PIMC

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

Quantum statistical
physics in
equilibrium at

temperature $T > 0$,

$$\tau_b - \tau_a = \beta = 1/k_B T$$

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

RTPI

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

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

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

tDMC

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

complex function !

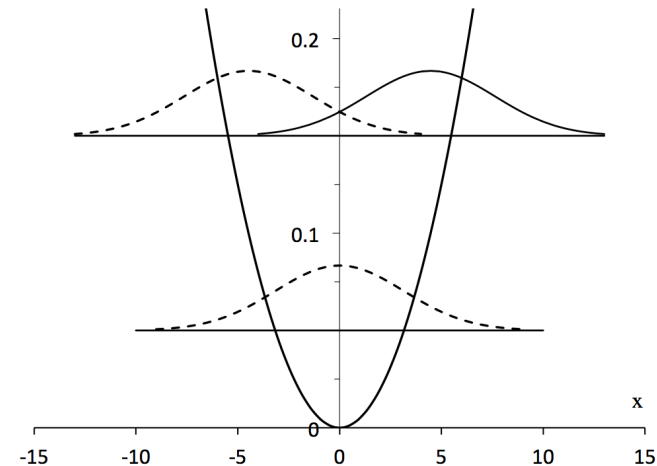
REAL TIME PATH INTEGRAL APPROACH TO COHERENT QUANTUM DYNAMICS

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

$$\psi(x, t) = \int K(x, t; x_a, t_a) \psi(x_a, t_a) dx_a$$

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



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

Short time kernel or Trotter kernel

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

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).

REAL TIME PATH INTEGRAL APPROACH TO INCOHERENT PROPAGATION

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Coherent propagation and zero reference shift

$$\psi(x, t) = \int K(x, t; x_a, t_a) \psi(x_a, t_a) dx_a$$

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

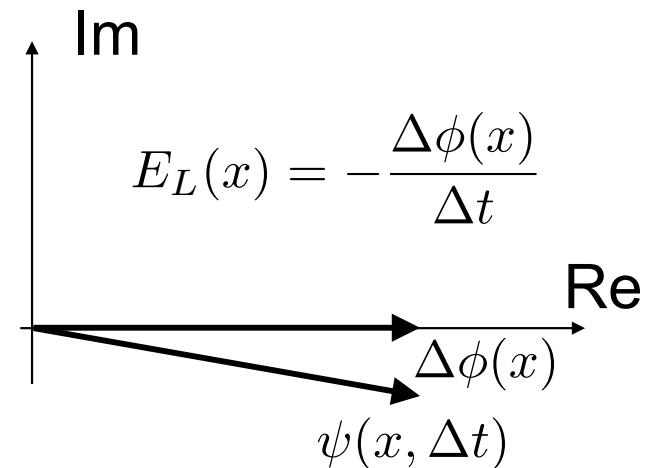
with small angle approximation

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

Incoherent propagation: ignore the very small imaginary part

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

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!



REAL-TIME DMC: POSITIVE PROBABILITIES

(tDMC)

Starting from the real time propagation of the many-body wave function

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

$$\begin{aligned} K(b, a) &= C \exp(i\phi) = C [\cos(\phi) + i \sin(\phi)] = C \left[\cos(\phi) + i \cos\left(\frac{\pi}{2} - \phi\right) \right] \\ &= C \left[\cos^2\left(\frac{\phi}{2}\right) - \sin^2\left(\frac{\phi}{2}\right) + i \left(\cos^2\left(\frac{\frac{\pi}{2} - \phi}{2}\right) - \sin^2\left(\frac{\frac{\pi}{2} - \phi}{2}\right) \right) \right] \\ &= K_+(b, a) - K_-(b, a) + iK_{+i}(b, a) - iK_{-i}(b, a) \end{aligned} \quad (2.5)$$

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

Thus, starting from four contributions to the wave function at a , we have four contributions at b .

and

$$\psi(a) = \psi_+(a) - \psi_-(a) + i\psi_{+i}(a) - i\psi_{-i}(a). \quad (2.6)$$

we get

$$\begin{aligned} \psi_+(b) &= \int_a K_+ \psi_+ dx_a + \int_a K_- \psi_- dx_a + \int_a K_{+i} \psi_{-i} dx_a + \int_a K_{-i} \psi_{+i} dx_a \\ \psi_-(b) &= \int_a K_+ \psi_- dx_a + \int_a K_- \psi_+ dx_a + \int_a K_{+i} \psi_{+i} dx_a + \int_a K_{-i} \psi_{-i} dx_a \\ \psi_{+i}(b) &= \int_a K_+ \psi_{+i} dx_a + \int_a K_- \psi_{-i} dx_a + \int_a K_{+i} \psi_+ dx_a + \int_a K_{-i} \psi_- dx_a \\ \psi_{-i}(b) &= \int_a K_+ \psi_{-i} dx_a + \int_a K_- \psi_{+i} dx_a + \int_a K_{+i} \psi_- dx_a + \int_a K_{-i} \psi_+ dx_a, \end{aligned} \quad (2.7)$$

This "diffusion" turns out to be fully delocalised in space.

Therefore, only a relevant part of space is considered.

and

$$\psi(b) = \psi_+(b) - \psi_-(b) + i\psi_{+i}(b) - i\psi_{-i}(b). \quad (2.8)$$

REAL-TIME DMC: NORMALISATION

Thus, starting from the ground state (gaussian), the (in)coherent propagation "normalised" into a finite domain keeps its shape . . .

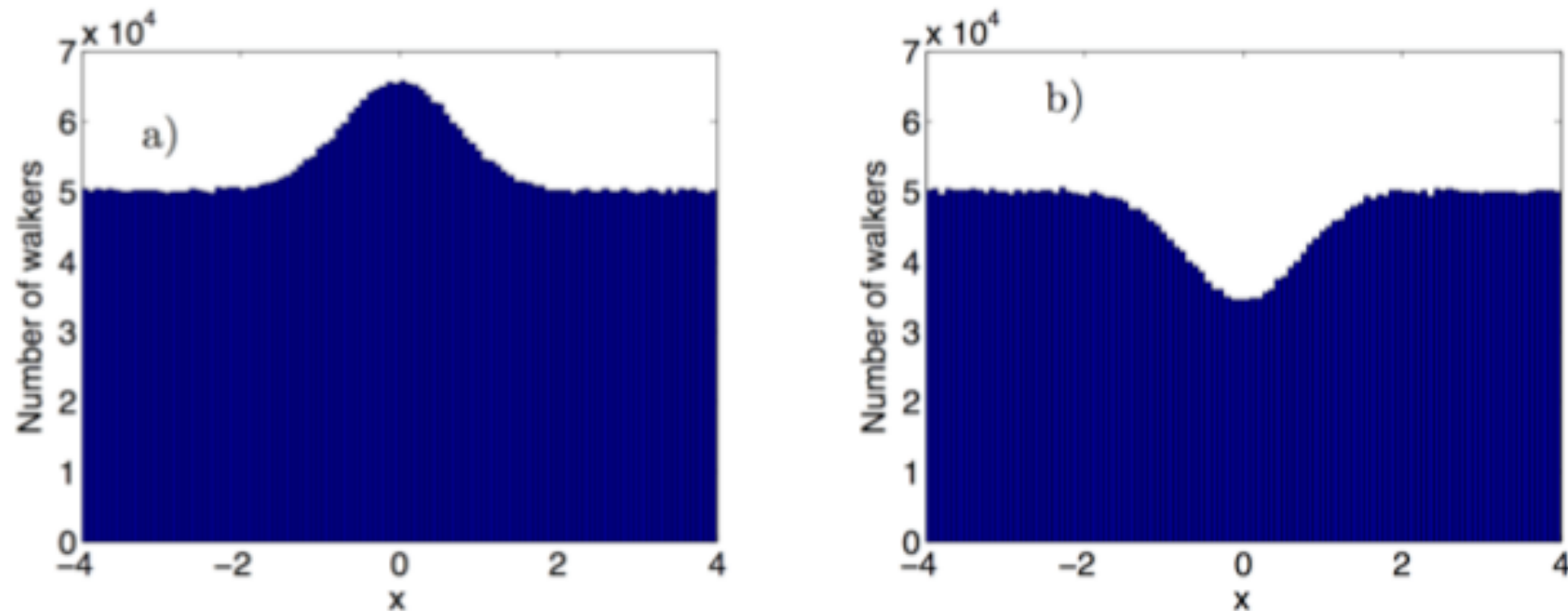


Figure 1: Distribution of a) positive and b) negative walkers ($\psi_+(b)$ and $\psi_-(b)$) after one time step $t = 0.1$ from gaussian real wave function $\psi_+(a)$ and $N(x_a) \approx 10^7$ walkers. Histogram bin width is 0.08.

REAL-TIME DMC: EXCITED STATES, NODES

Starting from an "arbitrary trial the incoherent (quantum Zeno) propagation can be used to find the closest eigenstate to a given energy.

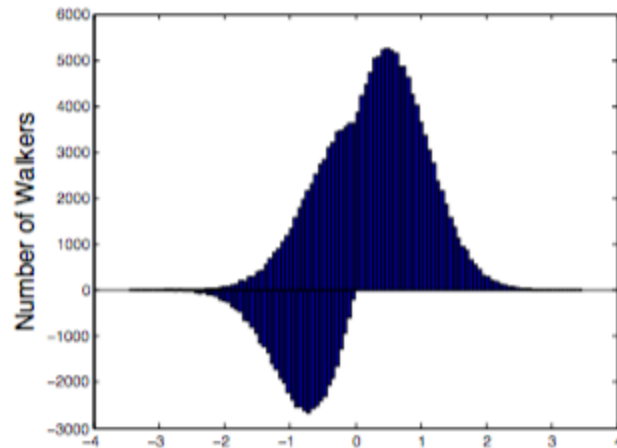


Figure 4: Positive ($N=150 \times 10^3$) and negative walkers ($N=50 \times 10^3$) of the superposition of 1st excited and the ground state ($N=100 \times 10^3$ each). Other notations are the same as in above figures.

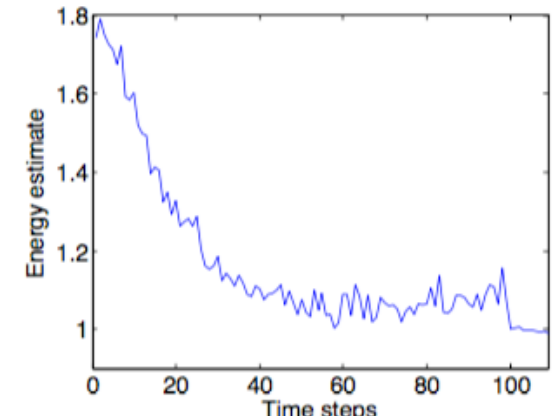


Figure 5: Estimated energy that demonstrates convergence starting from the superposition of the 1st excited state and ground state in incoherent tDMC ending to the ground state. The exact ground state eigenenergy is one, $E = 1$. $N \approx 10^6$, and $t = 0.1$ for the first 100 time steps and then $t = 0.8$.

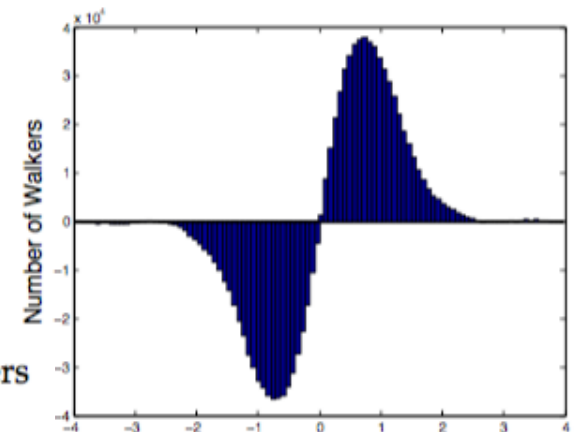


Figure 6: Distribution of positive ($N \approx 0.57 \times 10^6$) and negative ($N \approx 0.56 \times 10^6$) real walkers after the system has converged to its 1st excited state.

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*.

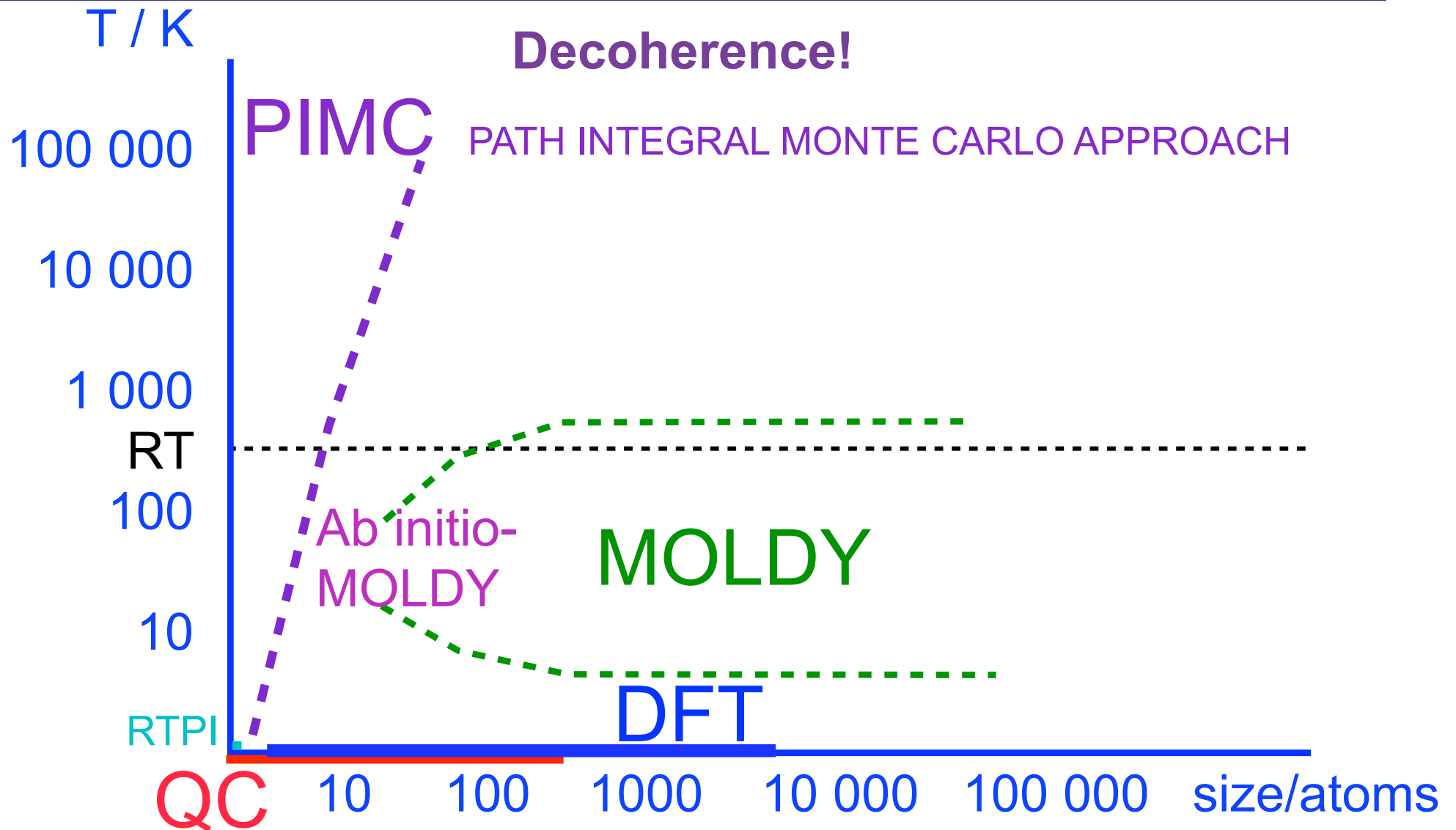
Why?

- 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	PIMC	PIMC	<i>ab initio</i> MOLDY
T = 0	Molecular mechanics	approaches	RTPI DMC VMC	<i>ab initio</i> Quantum Chemistry / DFT / semiemp.	
electronic dyn.: nuclear dyn.:			Q Q	Q	Q Class
	Class	Q			Class

SIZE AND TEMPERATURE SCALES

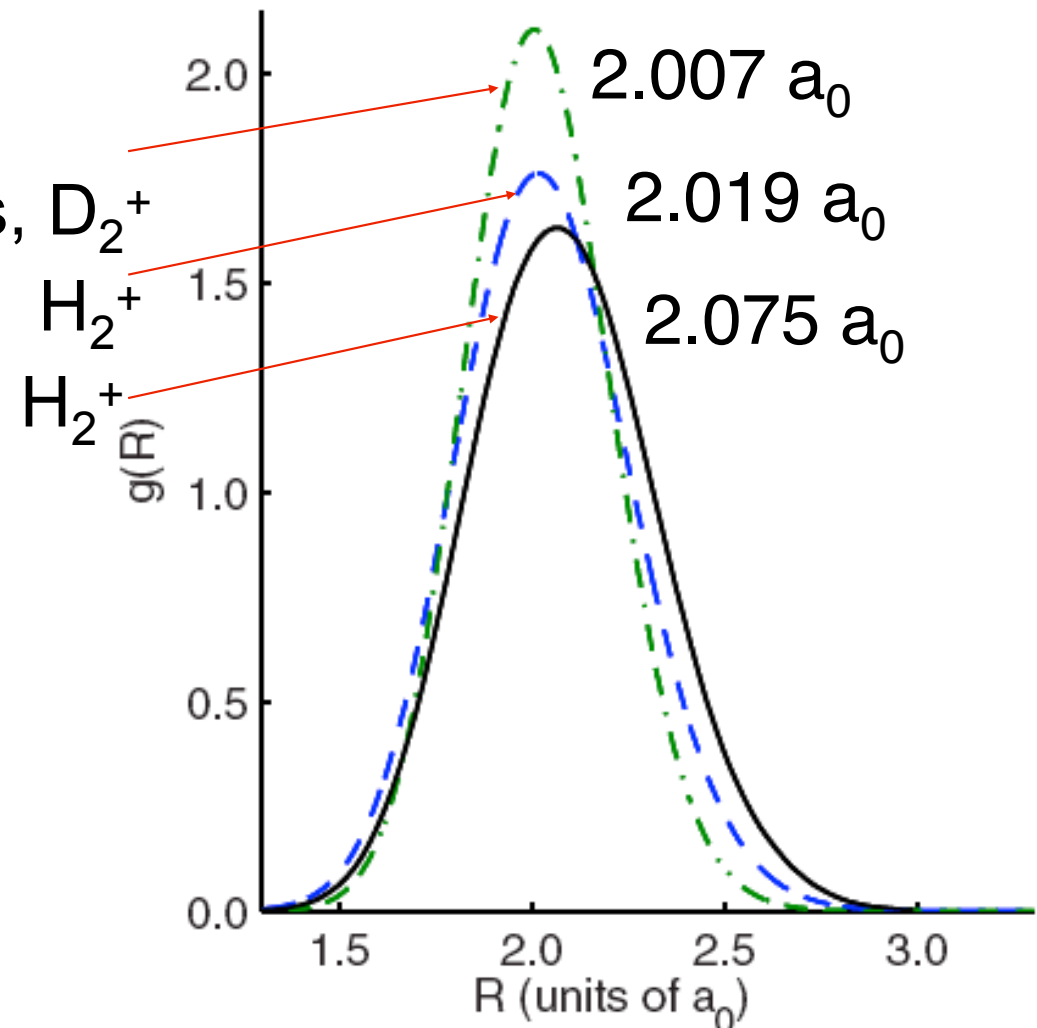
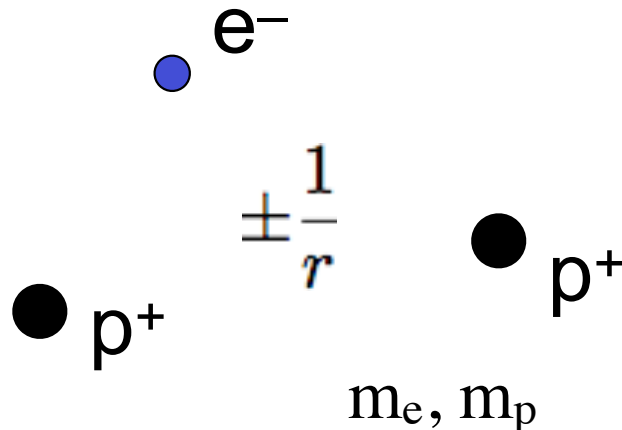


SIMPLE TEST CASES, FIRST: H ATOM, H_2^+ AND D_2^+ MOLECULES

Hydrogen atom: R_H / R_∞

Molecules:

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

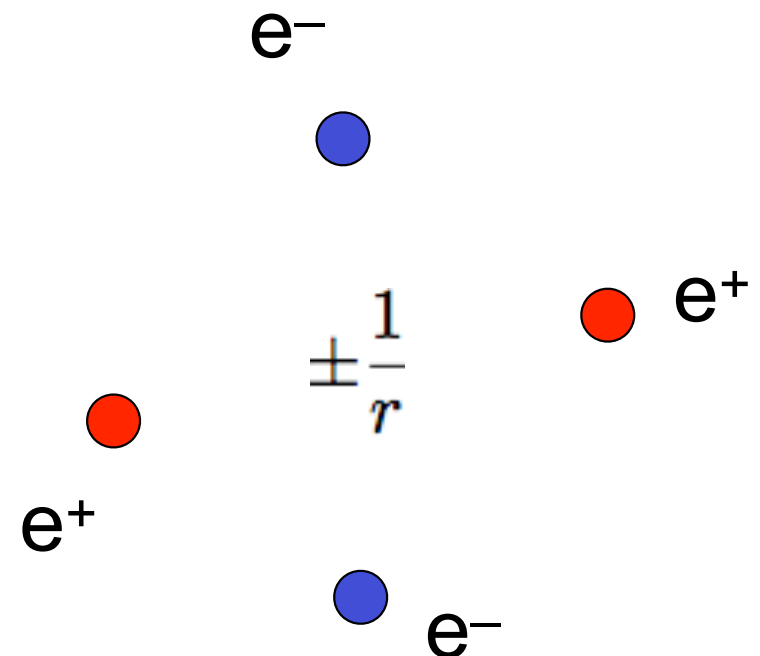


DIPOSITRONIUM Ps_2

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

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

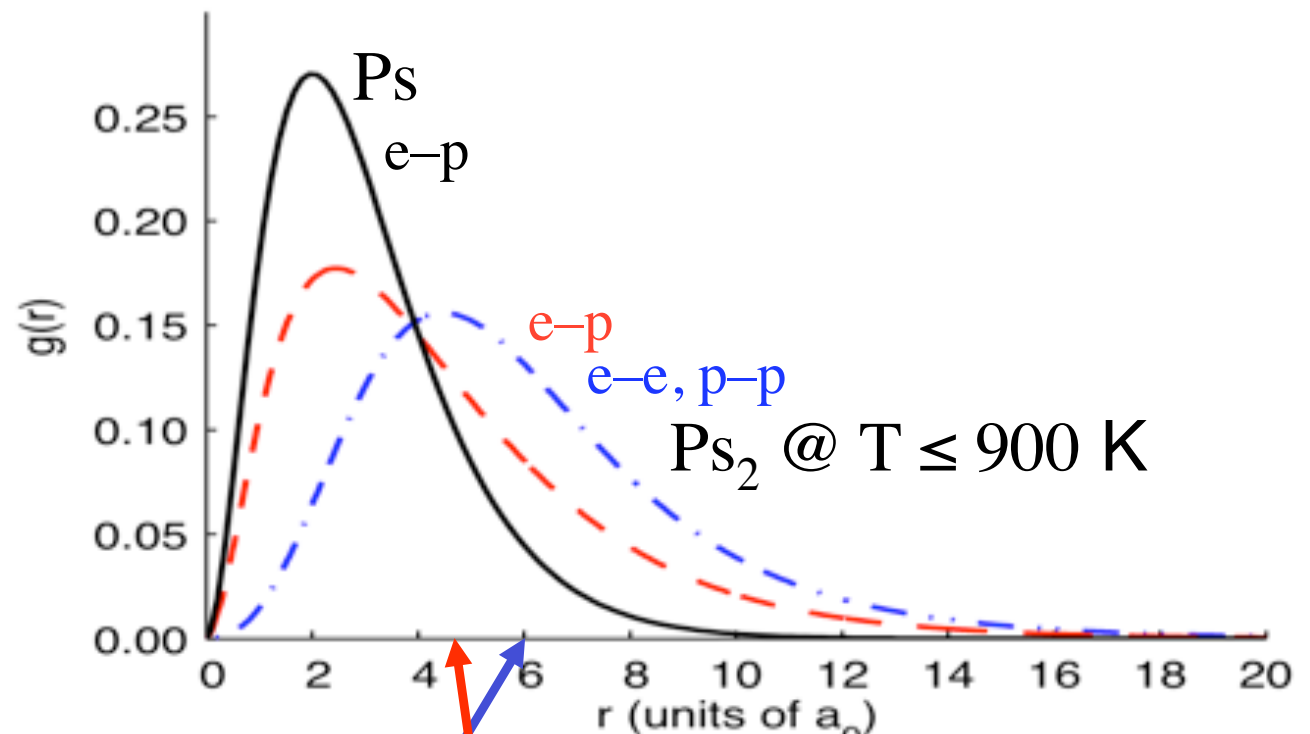
$$M = 2^{17} \dots 2^{14}$$



Ps₂ @ 0K – 900K

We find:

- $E_{\text{Ps}} = -0.250$
- $E_{\text{Ps}_2} = -0.5154$
- $E_{\text{D}} = 0.0154$
 $\approx 0.435 \text{ eV}$
 $\approx 5000 \text{ K}$



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

Ps₂ @ T = 0 K

T ≤ 900 K

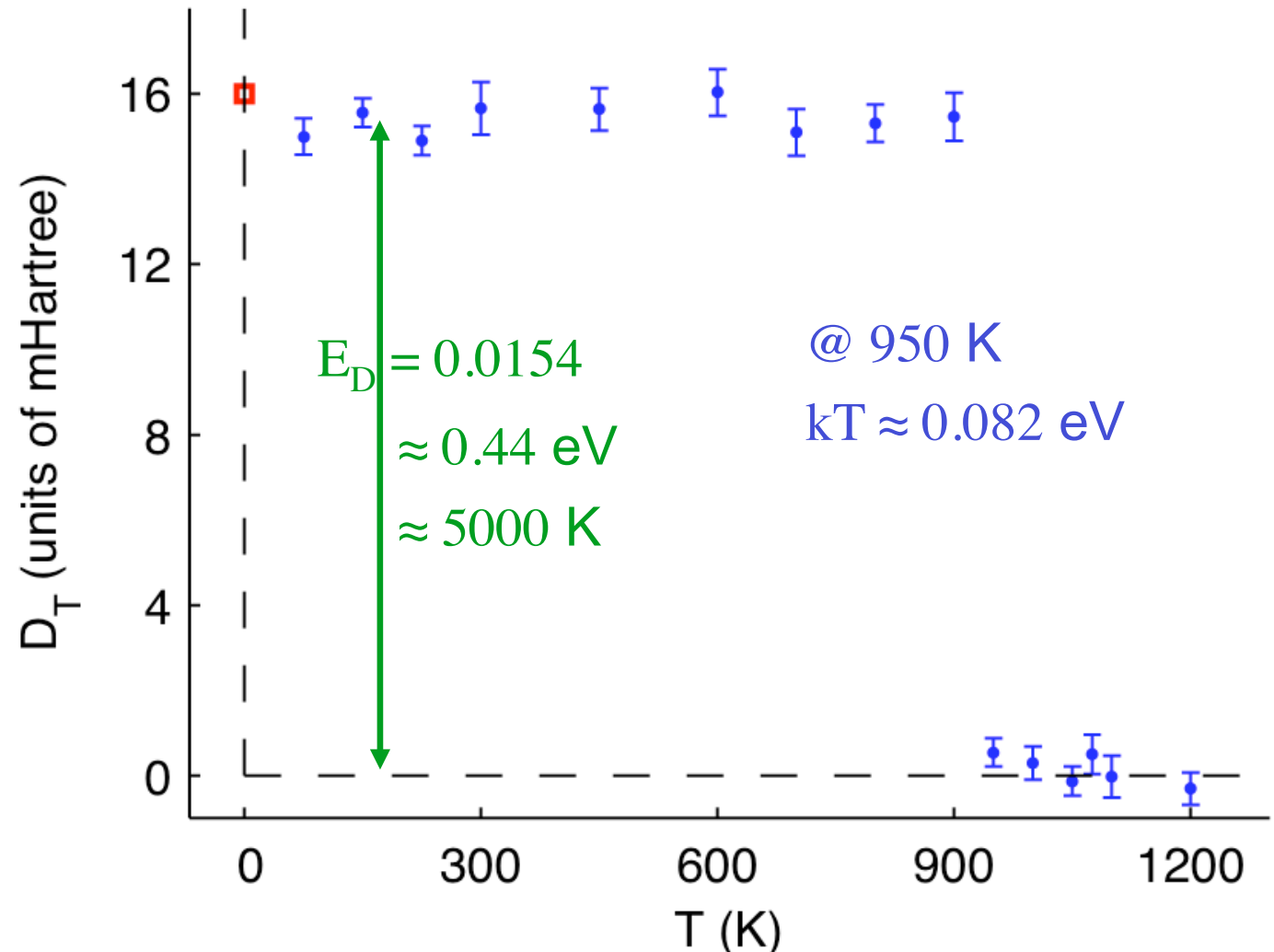
	$\langle E_{\text{tot}} \rangle$	$\langle r_{12} \rangle$	$\langle r_{13} \rangle$	$\langle r_{12}^{-1} \rangle$	$\langle r_{13}^{-1} \rangle$	$\langle r_{12}^2 \rangle$	$\langle r_{13}^2 \rangle$
Refs.	-0.5160	6.033	4.487	0.221	0.368	46.375	29.113
PIMC	-0.5154(5)	6.02	4.48	0.22	0.37	45.67	28.78

APPARENT DISSOCIATION ENERGY

Dissociation energy from the equilibrium total energies as

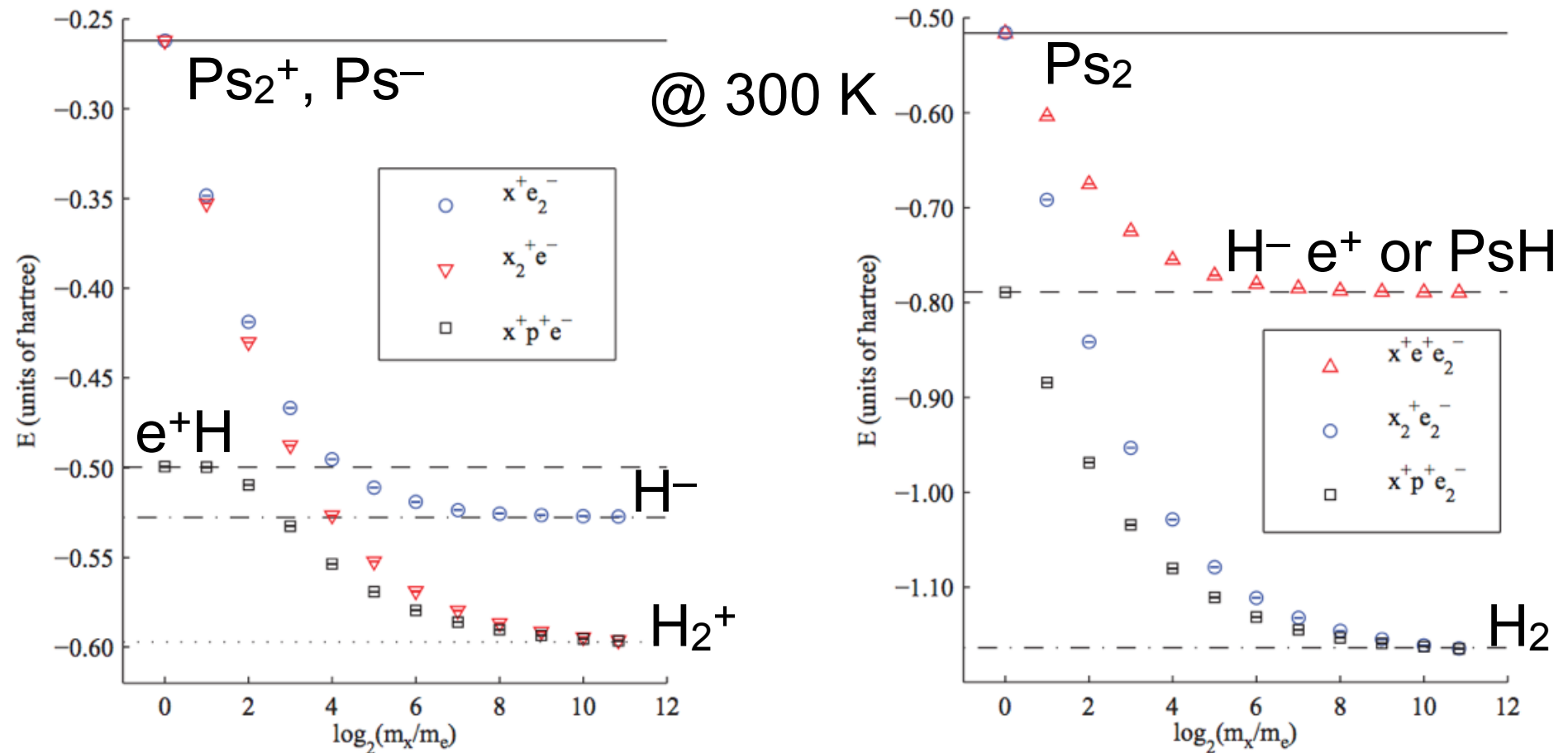
$$D_T = 2 E_{\text{Ps}} - E_{\text{Ps}^2}$$

Low density limit !



SMALL LIGHT NUCLEI MOLECULES: ELECTRONS, PROTONS AND POSITRONS

3-particle and 4-particle "molecules"

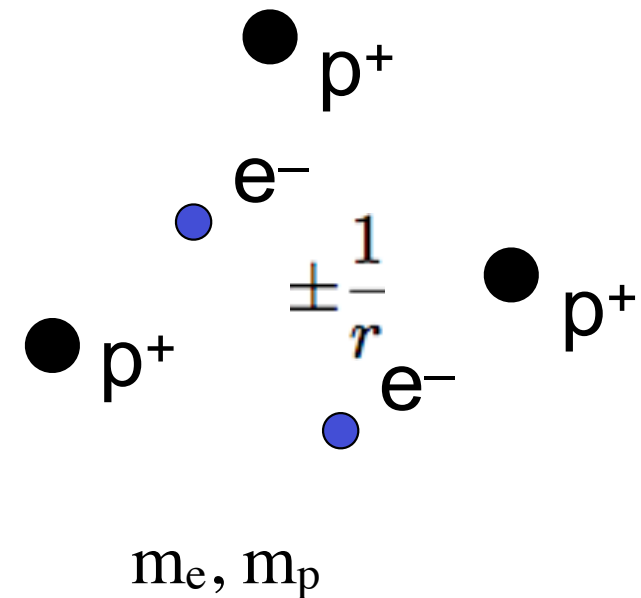


Kylänpää, TTR and D.M. Ceperley, PRA **86**, 052506 (2012)

H₃⁺ 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.

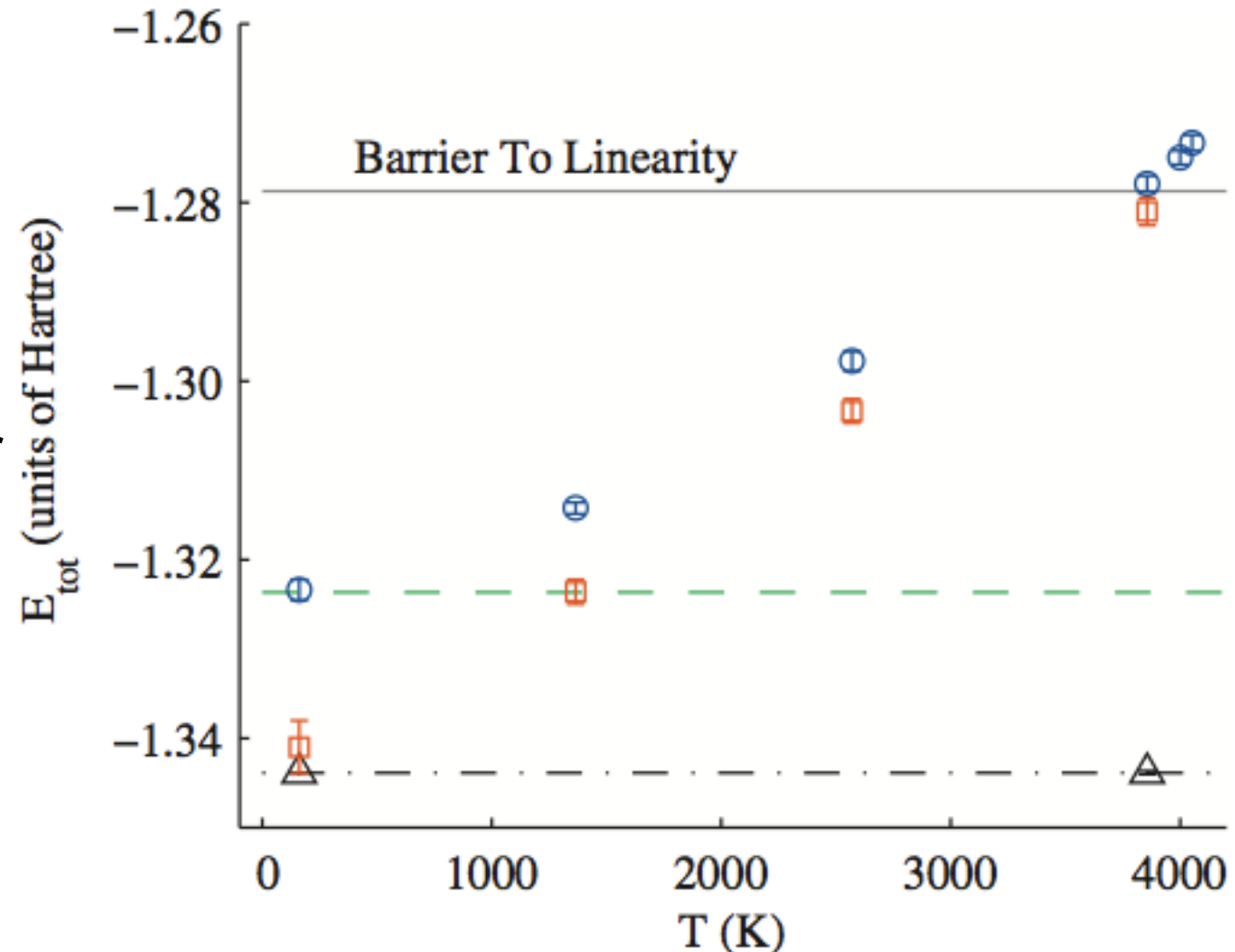


***Ab initio or
first-principles!***

H_3^+ TOTAL ENERGY:

FINITE NUCLEAR MASS AND ZERO-POINT ENERGY

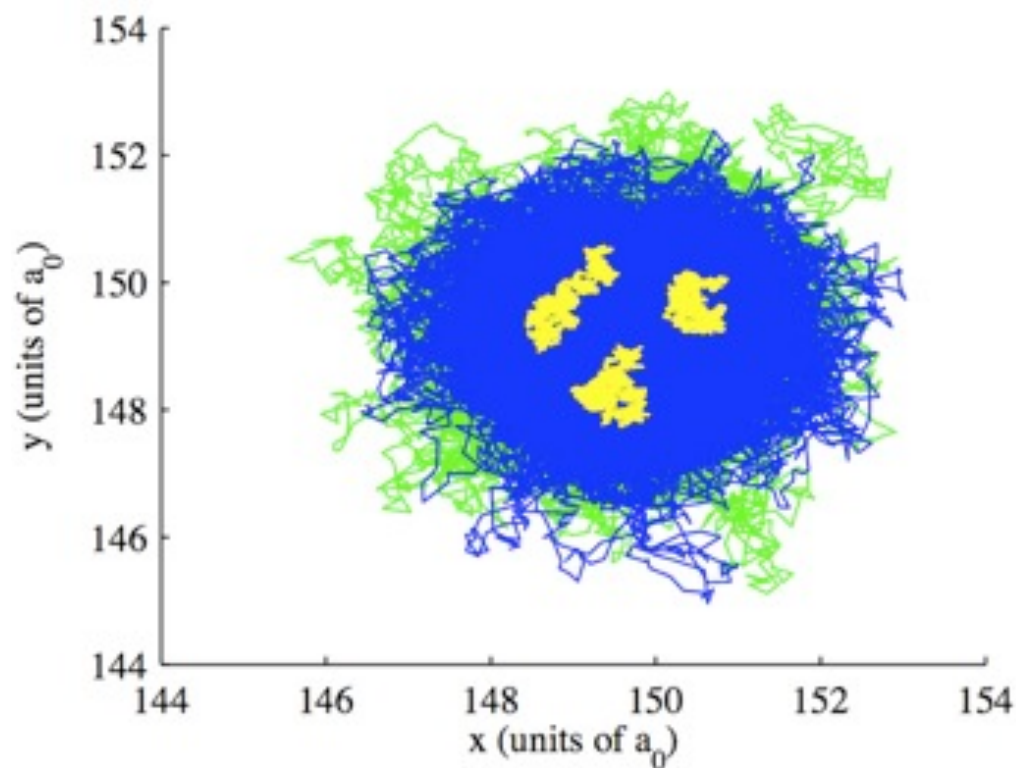
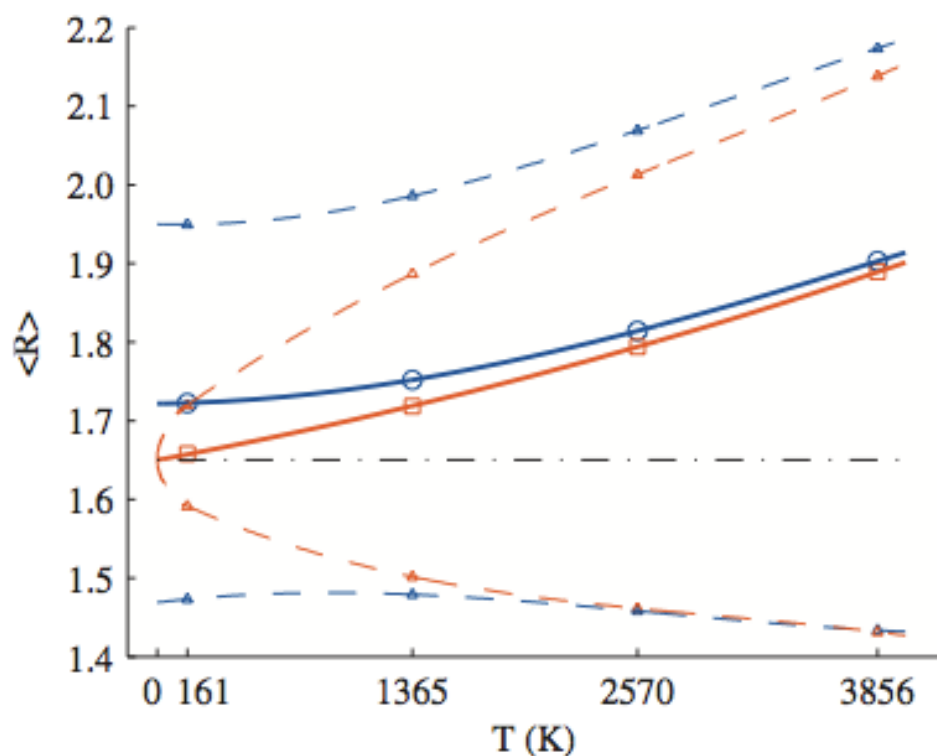
Total energy of the H_3^+ ion up to the dissociation temperature. Born–Oppenheimer approximation, **classical nuclei** and **quantum nuclei**.



H₃⁺ MOLECULAR GEOMETRY AT LOW TEMPERATURE: ZERO-POINT MOTION

Internuclear distance.

Quantum nuclei, classical nuclei, with FWHM

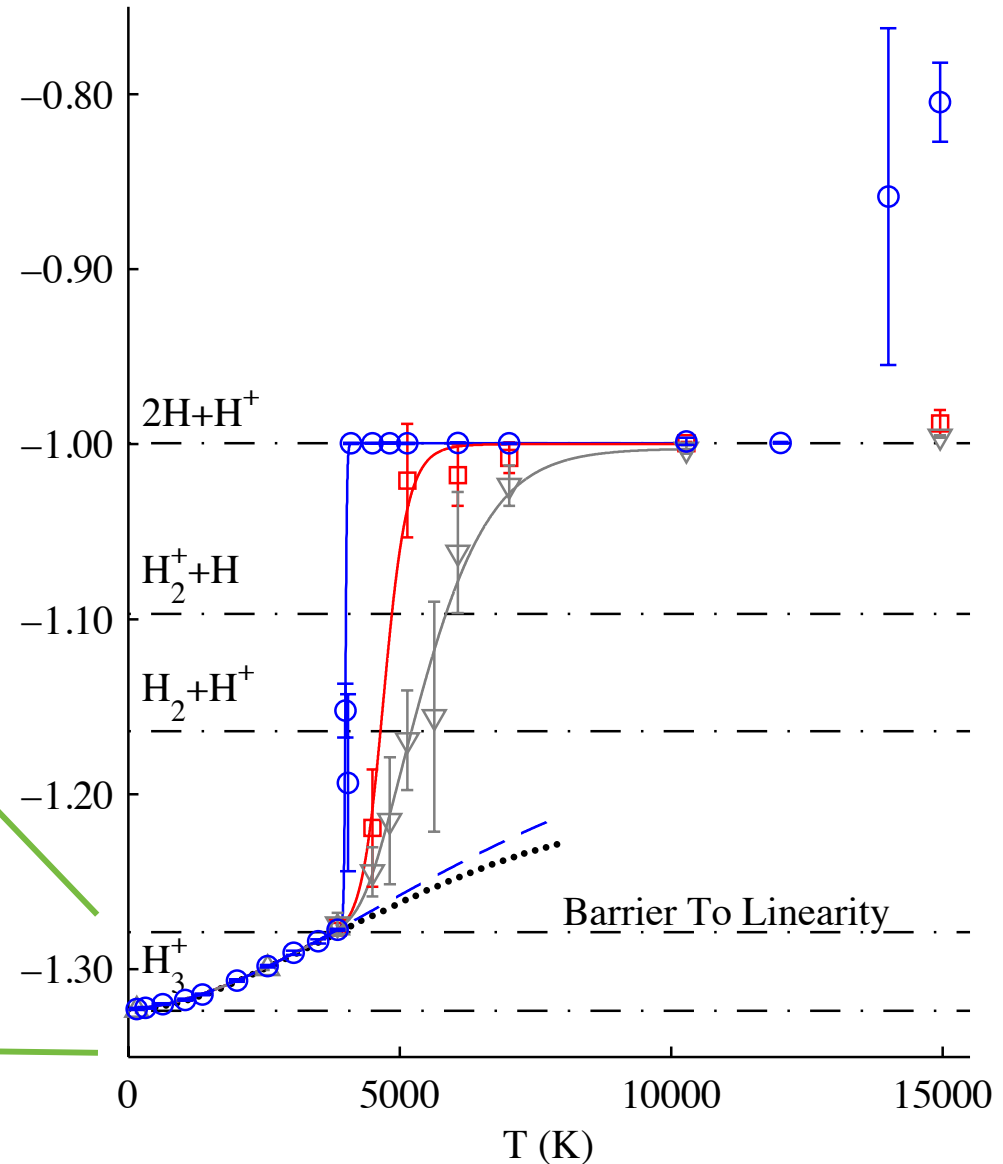
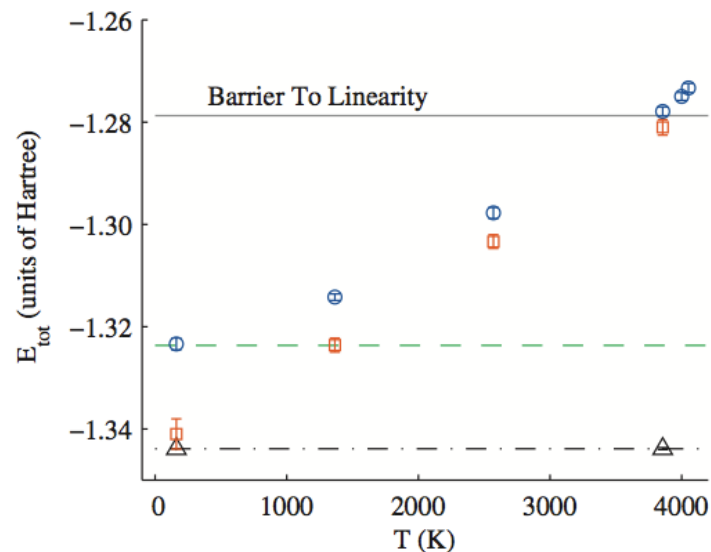


Snapshot from simulation, projection to xy-plane. Trotter number 2^{16} .

H_3^+ ENERGETICS AT HIGH TEMPERATURES

Total energy of the H_3^+ beyond dissociation temperature.

Lowest density,
mid density,
highest density.



COMPOSITIONS

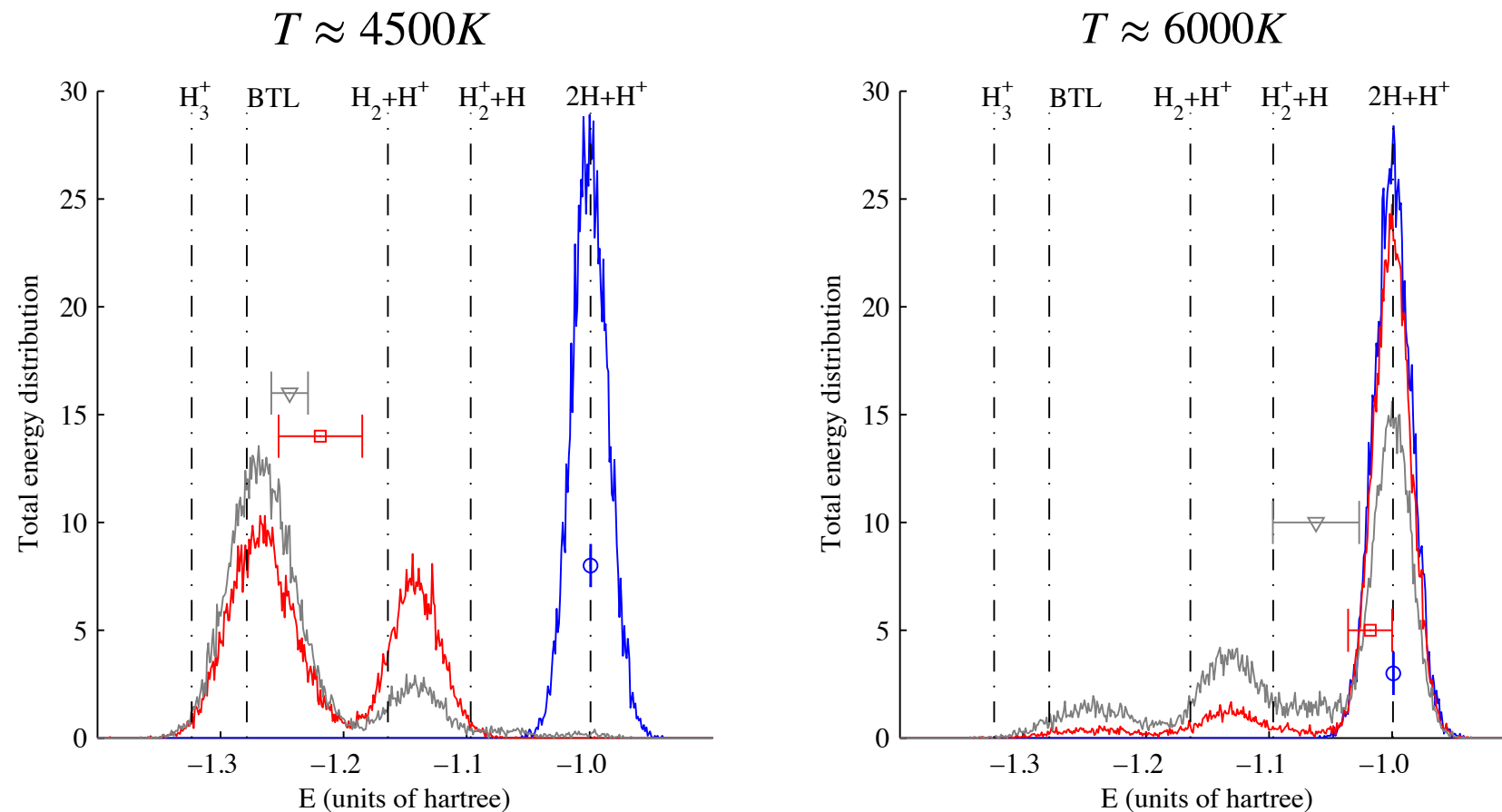


Figure 5.9: Simulation total energy distributions. (LEFT) $T \approx 4498.2\text{ K}$, (RIGHT) $T \approx 6070.3\text{ K}$. Notations are taken from Fig. 5.8.

PARTITION FUNCTION

Numerical integration
of

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

gives the partition
function.

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

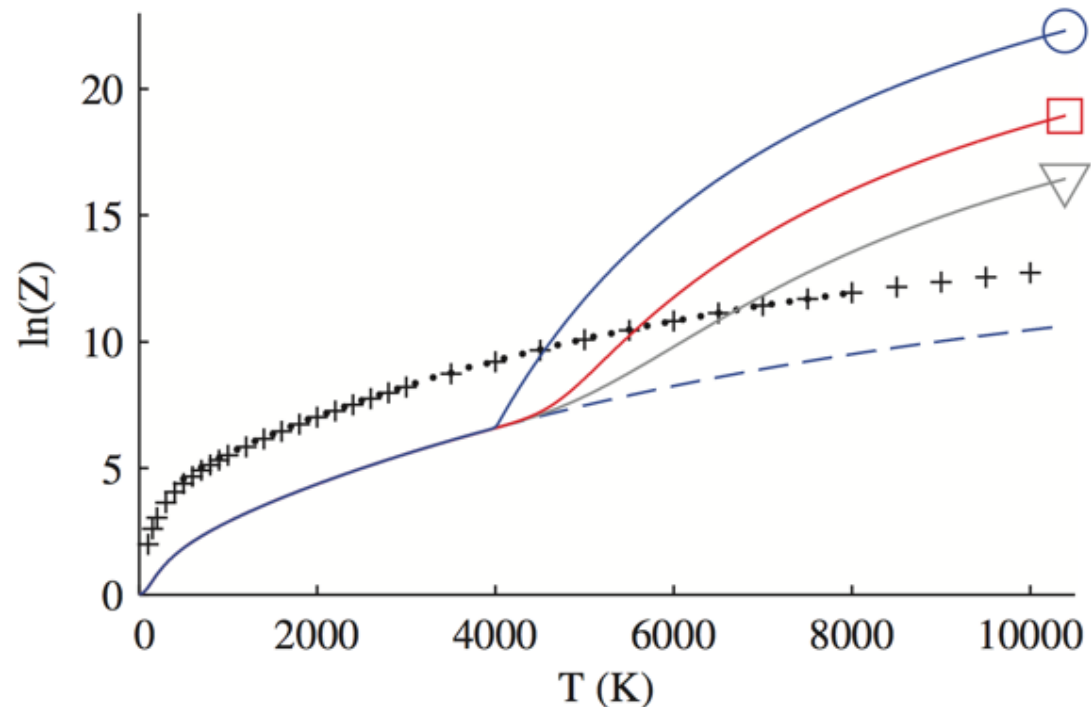


FIG. 3. The molecular NVT ensemble $\ln Z(T)$ from the energetics in Fig. 1 with the same notations. The blue solid line below 4000 K and its extrapolation (dashed line) are from Eq. (9), whereas the curves for three densities are from Eq. (10). The $\ln Z(T)$ data (black pluses) and the fit (black dots)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

FREE ENERGY

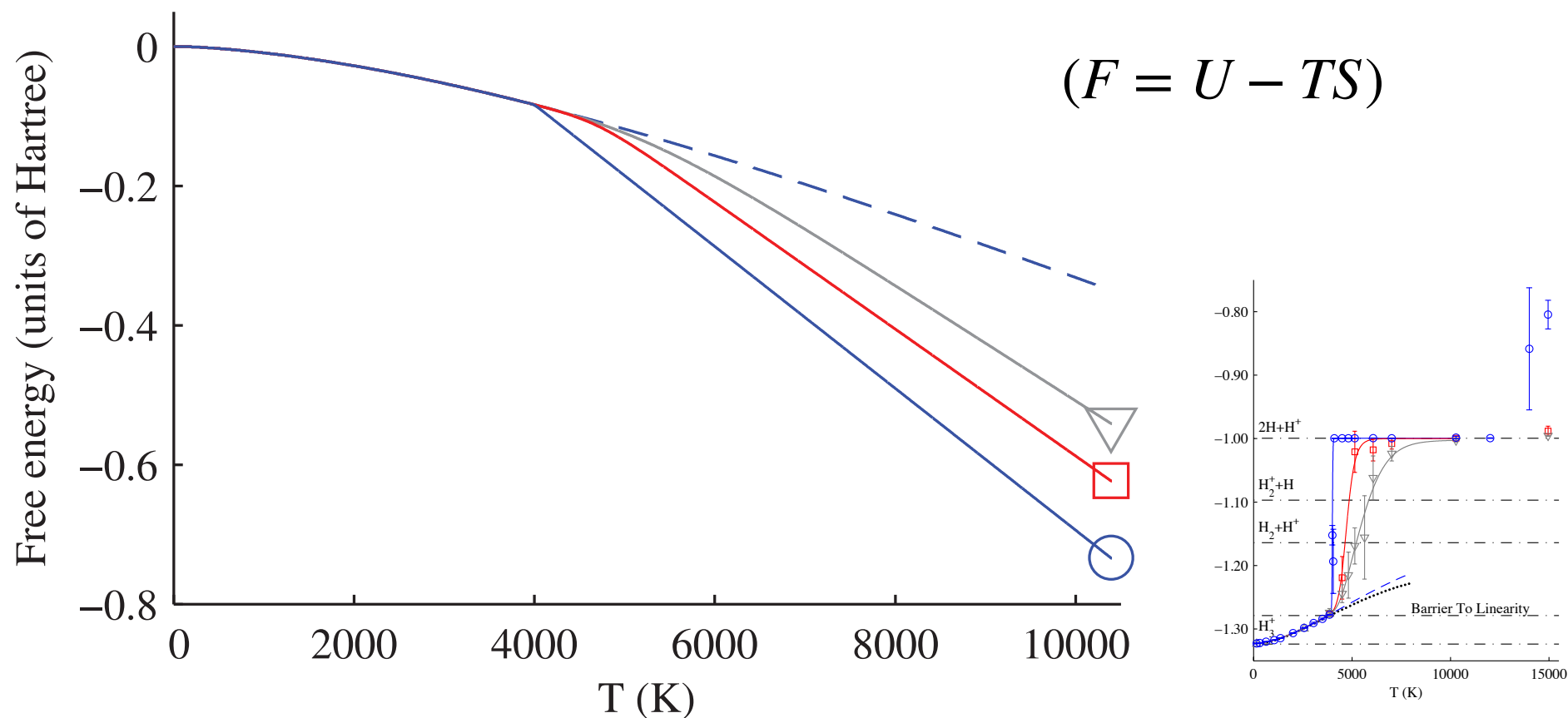


FIG. 4. Helmholtz free energy from Eq. (5) in the units of Hartree. Notations are the same as in Fig. 3.

ENTROPY

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

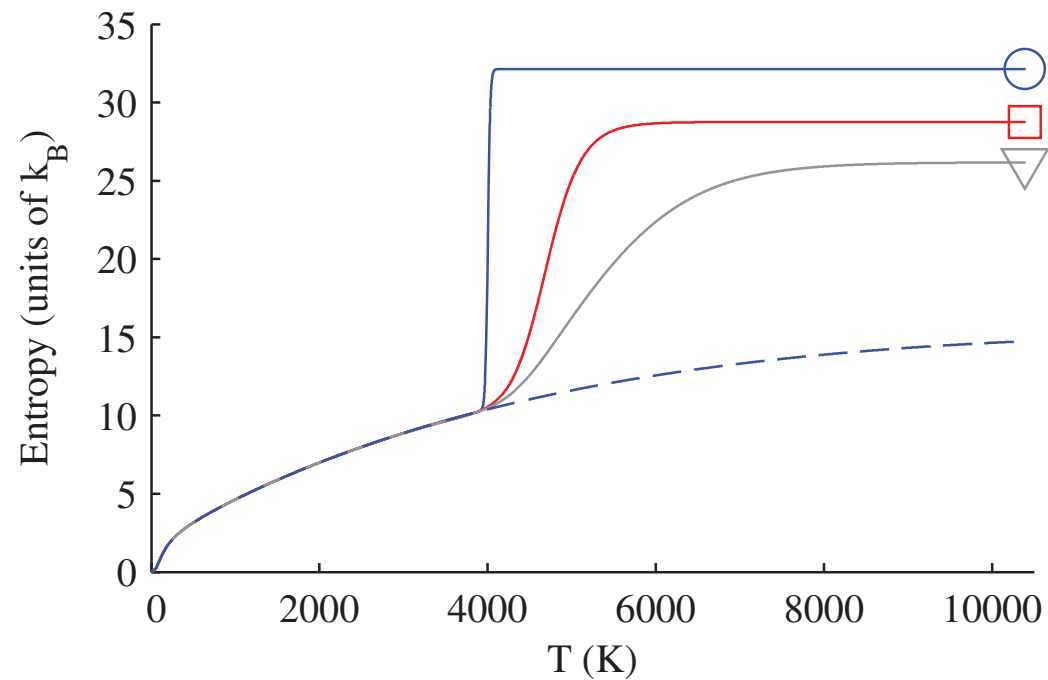


FIG. 5. Entropy from Eq. (11) in the units of k_B . Notations are the same as in Fig. 3.

MOLECULAR HEAT CAPACITY

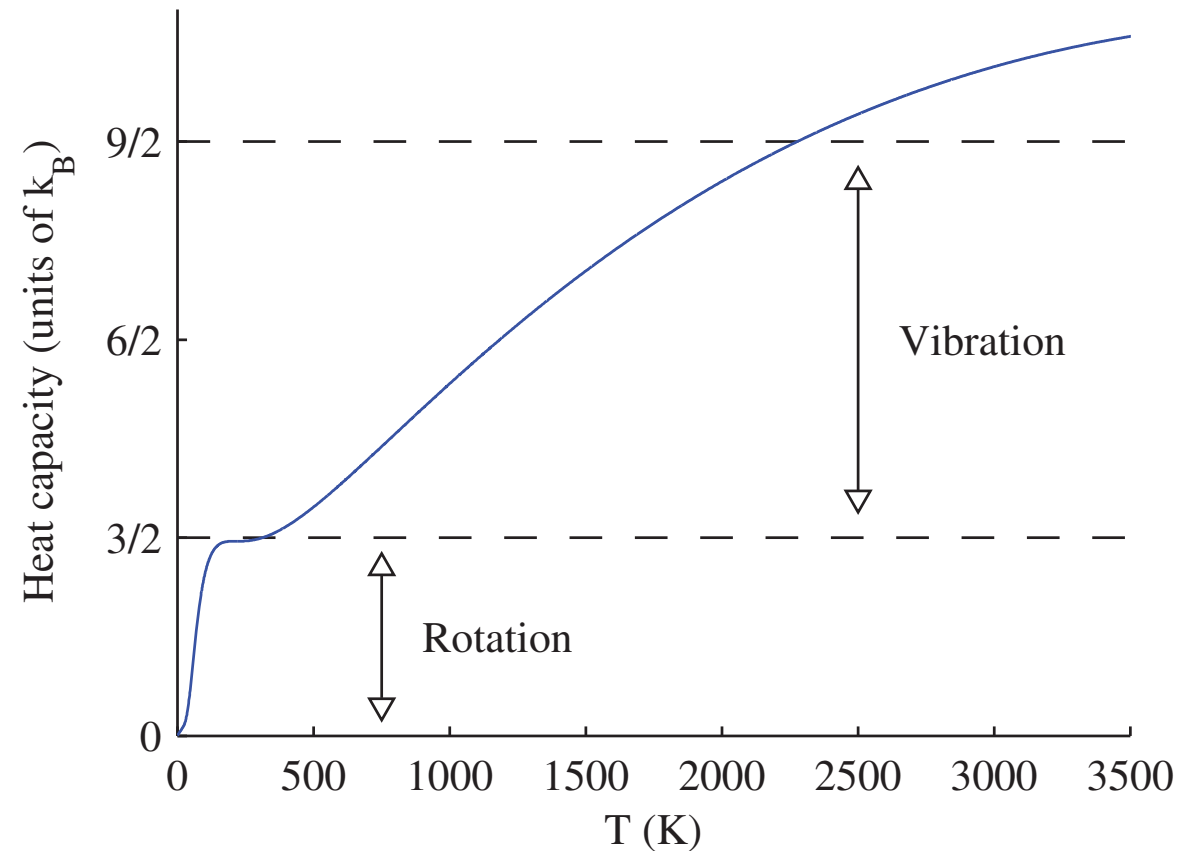
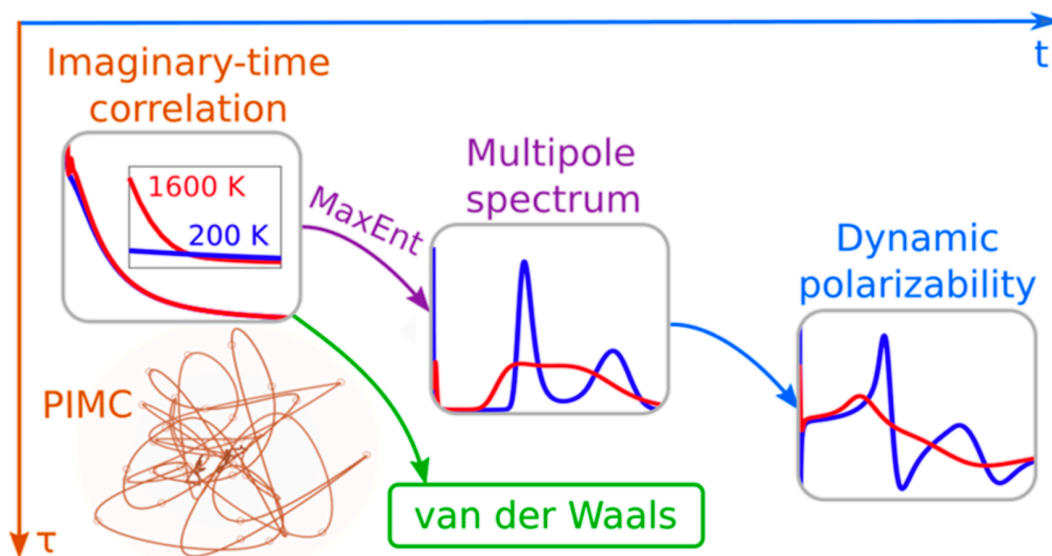


FIG. 6. Molecular heat capacity as a function of temperature calculated using the analytical model of this work. The values on the y-axis are given in units of the Boltzmann constant k_B .

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) 6.4990267 ^{b,d}	124.7(4) 124.39908 ^{b,d}	3300(9) 3285.8284 ^{b,d}
H-He	2.82(4) 2.8213439 ^{b,d}	41.9(3) 41.828 ^{b,d}	873(4) 871.23 ^{b,d}
H-H ₂	8.78(7) 8.7843286 ^d	164.8(8) ^f 161.31542 ^d	4003(12)
H-HD ⁺	6.35(12) ^f 5.3815691 ^c	135(5) ^f 99.592513 ^c	2620(50) ^f 2023.6873 ^c
H-Ps	34.8(3)	318(2)	11560(60)
H-Ps ₂	68.7(4)	4210(50)	3.35(6) × 10 ⁵
He-He	1.46(2) 1.4609778 ^{b,d}	14.09(9) 14.117857 ^b	182.7(8) 183.69107 ^b
He-H ₂	4.01(5) 4.0128132 ^d	56.4(4) ^f 55.381453 ^d	1008(4)
He-HD ⁺	2.65(9) ^f 2.3441447 ^c	41(3) ^f 31.043629 ^c	507(10) ^f 416.42889 ^c
He-Ps	13.4(2)	60.9(6)	3040(30)
He-Ps ₂	26.4(4)	1520(30)	1.17(3) × 10 ⁵
H ₂ -H ₂	12.04(12) 12.058168 ^d	219.1(1.3)	4870(20)
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) × 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) × 10 ⁵
Ps-Ps	207.3(1.3)	0 ^e	68400(400)
Ps-Ps ₂	410(3)	21000(300)	1.59(4) × 10 ⁵
Ps ₂ -Ps ₂	811(5)	83200(800)	1.000(12) × 10 ⁷

THANK YOU!

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

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Polarizabilities

ACKNOWLEDGEMENTS

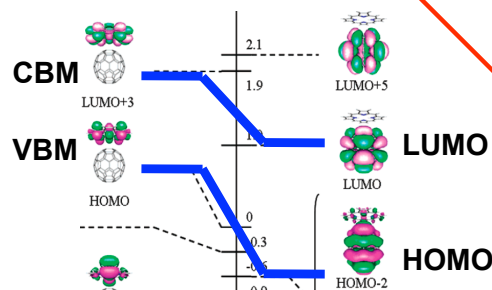
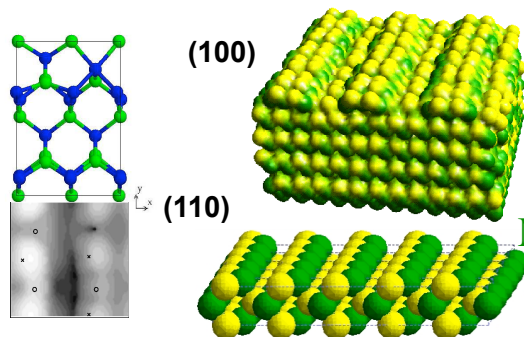
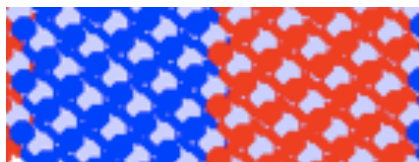
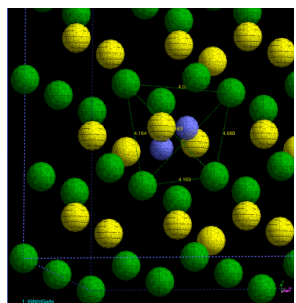
Markku Leino, Ilkka Kylänpää, Juha Tiihonen, Ilkka Ruokosenmäki (TUT)

Ilkka Kylänpää, David M. Ceperley (UIUC)

THEORETICAL AND COMPUTATIONAL MATERIALS PHYSICS @ TAMPERE

H-P. Komsa: PhD Thesis (2008)

Compound semiconductor physics



M. Kuisma: PhD Thesis (2014)

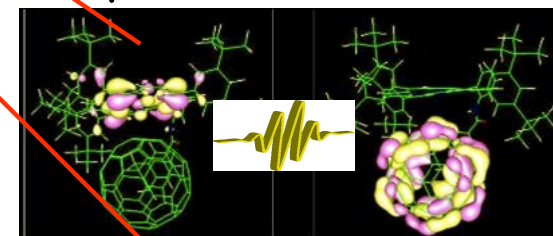


O. Cramariuc: PhD Thesis (2006)

(Bio)molecular

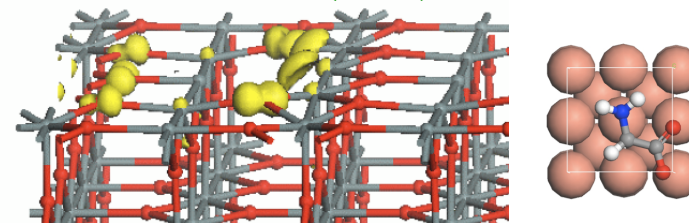
O. Kontkanen: PhD Thesis (2018)

(opto)electronics

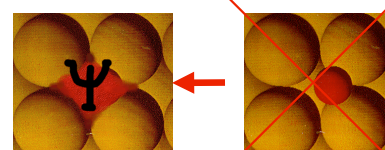


Surface science

M. Viitala: PhD Thesis (2012)



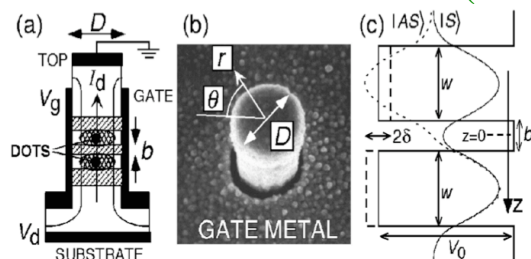
M. Mäki-Jaskari: PhD Thesis (2004)



M. Leino: PhD (2007)

Path-Integral Quantum Monte Carlo

I. Ruokosenmäki: PhD (2019)



J. Tiihonen: PhD (2019)

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