Physics Days 2023 - Physics makes dreams come true

PATH INTEGRAL APPROACH TO QUANTUM DYNAMICS AND EIGENSTATES

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MOTIVATION

Electronic structure is the key issue behind materials properties, those of atoms, molecules and solids, in all phases. The conventional approaches target on finding either the wave function or the density of the many-electron system. Both of these approaches have their pros and cons, and consequently, somewhat different subfields of applications.

The conventional approaches suffer from laborious or **insufficient description of many-body effects**, they are **restricted to zero-Kelvin temperature,** and also, **restricted to Born–Oppenheimer approximation**.

FEYNMAN PATH INTEGRALS

Feynman path integrals (PI) provide an alternative approach to quantum theory, and also, derivation of Schrödinger equation [1]. Furthermore, with the PI the time evolution of the wave function or the density matrix can be simulated [1,2], and also, stationary eigenstates and energies can be found.

Path integral approaches heal the before mentioned deficiencies of conventional *ab initio* methods.

Below, playing with the real and imaginary time, like:

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

DMC

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

τDMC

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

Everywhere real and positive! Thus, probability interpretation and ”simulation of diffusion”

This is the conventional **Diffusion Monte Carlo** (DMC).

”Ground State of the Electron Gas” by Ceperley D.M. and Alder B.J., Phys. Rev. Lett. **45**, 566–569 (1980) leading to LDA parametrizations

PATH INTEGRALS IN IMAGINARY AND REAL TIME

PIMC

$$\rho(x) = \int \exp(-S[0,\beta])\; Dx(\tau)$$

”period” $\beta = \tau_b - \tau_a = \frac{1}{k_B T}$

Quantum statistical physics at finite temperature $\mathrm{T} > 0$, *i.e.* NVT ensemble Free energy minimum!

Most recently, static and dynamic electric **multipole (hyper)polarizabilities** including rovibrational effects, and also, **van der Waals coefficients** have been evaluated [4 i–iv].

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

RTPI

$$K = \int \exp(iS)\; Dx(t)$$
$$S[x_a,x_b] = \int_{t_a}^{t_b} L_x dt$$

The first real time path integral approach to find the wave function of electrons

tDMC

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

Complex function! Novel ”real time diffusion Monte Carlo” approach

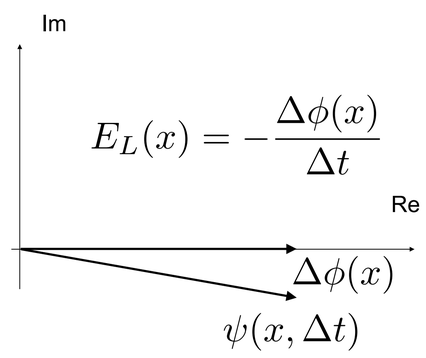
These approaches simulate coherent **time evolution in real time** or **stationary eigenstates** from incoherent time evolution. This might also lead to practical **solutions to the fermion sign problem,** see reference 5.

Everything, Everywhere, All at Once and All the Time!

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

QUANTUM DYNAMICS

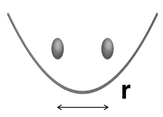
Coherent dyamics:
The modulus ”vector” rotates on complex plane with increasing phase leading to the dynamics of the wave function.

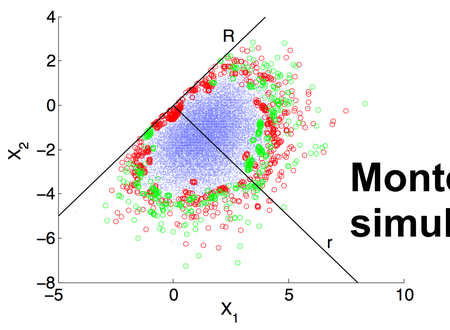


Incoherent dyamics:
The rotating modulus ”vector” is projected stepwise onto the real axis finally leading to the real wave function of one of the eigenstates.

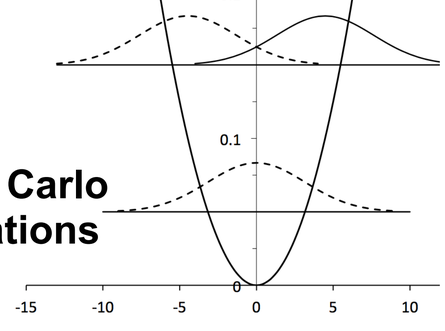
EIGENSTATES

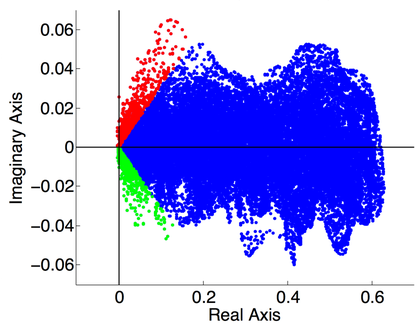
Hooke’s atom: Two electrons confined with a harmonic potential: Many-body problem

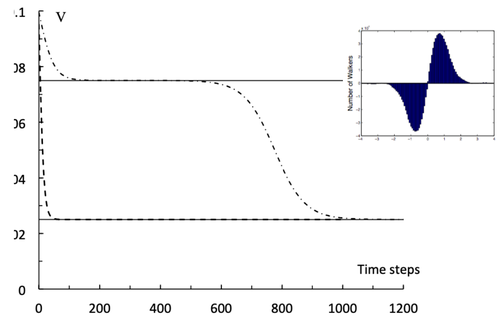




Monte Carlo simulations







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For more references see http://www.tut.fi/semiphys/ *or pick up the ones you want from* http://iki.fi/trantala/paths *or request from* Tapio.T.Rantala@iki.fi