NEW PATHS FOR QUANTUM CHEMISTRY

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MOTIVATION

Electronic structure is the key issue behind materials properties, those of atoms, molecules and solids. 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 also suffer from laborious or **insufficient description of many-body effects** and they are **restricted to zero-Kelvin temperature** and **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

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

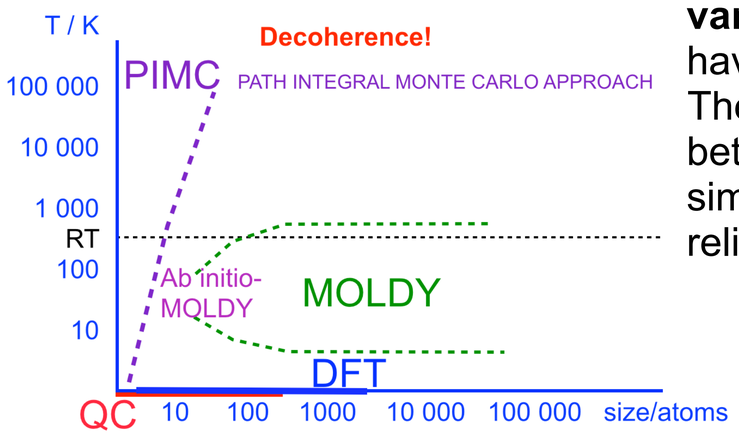
τDMC

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

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

This is the conventional **Diffusion Monte Carlo** (DMC) with a great history and benchmarking various quantum systems.

"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, *e.g.* S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys*. **58**,1200 (1980); J. P. Perdew and A. Zunger, *Phys. Rev. B*. **23**, 5048 (1981).



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 $T > 0$, *i.e.* NVT ensemble Free energy minimum!

We have studied several small atoms and molecules to settle the nonadiabatic coupling of nuclei and electrons and the **roles of quantum and thermal dynamics.** The most prominent thermal effect is **dissociation–recombination reaction** [3].

Most recently, static and dynamic electric **multipole (hyper)polarizabilities** including rovibrational effects, and also, **van der Waals coefficients** have been evaluated [4 i–ii]. Thermal effects on interactions between **quantum dots** were simulated to establish thermal reliability of related devices [4 iii].

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

RTPI

$$K = \int \exp(iS)\; Dx(t) \longrightarrow K = C\, \exp(i\phi)$$

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

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

tDMC

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 may also lead to practical **solutions to the fermion sign problem.** For proof-of-concept studies and demonstrations see the reference 5.

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

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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

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