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# Numerical path integral solution to strong Coulomb correlation in one dimensional Hooke's atom

Ilkka Ruokosenmäki *, Hossein Gholizade, Ilkka Kylänpää, Tapio T. Rantala

*Department of Physics, Tampere University of Technology, Finland*

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ABSTRACT

We present a new approach based on real time domain Feynman path integrals (RTPI) for electronic structure calculations and quantum dynamics, which includes correlations between particles exactly but within the numerical accuracy. We demonstrate that incoherent propagation by keeping the wave function real is a novel method for finding and simulation of the ground state, similar to Diffusion Monte Carlo (DMC) method, but introducing new useful tools lacking in DMC. We use 1D Hooke's atom, a two-electron system with very strong correlation, as our test case, which we solve with incoherent RTPI (iRTPI) and compare against DMC. This system provides an excellent test case due to exact solutions for some confinements and because in 1D the Coulomb singularity is stronger than in two or three dimensional space. The use of Monte Carlo grid is shown to be efficient for which we determine useful numerical parameters. Furthermore, we discuss another novel approach achieved by combining the strengths of iRTPI and DMC. We also show usefulness of the perturbation theory for analytical approximates in case of strong confinements.



## 1. Introduction

Feynman path integral (PI) approach offers an intuitive description of quantum mechanics [1,2], where classical mechanics emerges transparently from disappearing wave nature of particles along with vanishing Planck constant. Therefore, it is robust in numerical calculations in cases close to classical ones, like molecular quantum dynamics in real time [3], but becomes more challenging and laborious for states of electrons, where the wave nature plays larger role. Furthermore, the PI presentation of stationary states also involves full time-dependent quantum dynamics, in contrast with the conventional solution of the time-dependent Schrödinger equation, where time evolution appears as simple change of the wave function phase, only.

We have already demonstrated that numerical solutions to stationary states and quantum dynamics of single electrons in one dimensional potentials can be reliably found, both in regular and Monte Carlo grids, by using real time path integral (RTPI) propagation [4]. We have also assessed the usefulness and accuracy of the Trotter kernel as compared to the exact kernels and pointed out the advantages of the Monte Carlo grid in avoiding spurious interference effects. For search and evaluation of the single particle eigenstates we found a novel approach based on the *incoherent propagation* [4], *i.e.*, collapsing the wave function to its real component after each short time step. This is the starting point of the present study.

RTPI approach can be expected to show most of its proficiency in simulation of many-electron systems, where correlation phenomena turn out to be in major role — the same way and partly for same reasons as it has been found to be with the more conventional path integral Monte Carlo (PIMC), simulation of the imaginary time propagation [5–8]. It may be pertinent to point out, that while PIMC simulation yields the finite temperature equilibrium description of the system of quantum particles, RTPI simulation finds the zero-Kelvin real time quantum dynamics. Furthermore, RTPI can also be used to find and simulate the eigenstates, as indicated above. Thus, for finding and simulation of the ground state, RTPI can be compared to the diffusion Monte Carlo (DMC) simulation [9]. Thus, combination of these two can be expected to offer novel features, which turns out to be the case.

To assess the performance of incoherent RTPI as compared with DMC we choose the Hooke's atom in one dimension as the test bench, presenting a case of an extremely strong correlation.

Three dimensional Hooke's atom is a helium-like system of two electrons with Coulomb repulsion, where electron–nucleus attraction is replaced by a confining parabolic or harmonic

* Corresponding author.
*E-mail addresses:* ilkka.ruokosenmaki@tut.fi (I. Ruokosenmäki), hossein.gholizadehkalkhoran@tut.fi (H. Gholizade), ilkka.kylanpaa@tut.fi (I. Kylänpää), Tapio.Rantala@tut.fi (T.T. Rantala).

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potential. It is one of the few non-trivial systems with exact solutions for certain strengths of confinement (harmonic force constant) [10], and therefore, it is a good test case for our new approach. As shown below, separation of the three dimensional problem in relative coordinates yields two problems, one of which is the one dimensional Hooke's atom once the angular momentum degrees of freedom are taken out. In one dimension, the Coulomb repulsion is strong enough to split the space to two independent domains defined by exchange of the electrons [11–14].

In this paper we will demonstrate the novel incoherent RTPI in finding the ground state of one dimensional Hooke's atom by using a Monte Carlo grid. We also analyze performance of the simulation by comparison with DMC simulation, and furthermore, discuss another new idea to combine the strengths of incoherent RTPI and DMC. Accuracy of the numerical approaches is analyzed by using analytical solutions and those from perturbation theory (PT), where relevant.

## 2. Ground state

Finding or simulation of the ground state is perhaps the most general problem to work out in dealing with quantum systems. Here, we present our novel approach to this based on the incoherent real time propagation [4] using the path integral formalism. First however, we briefly present the well known diffusion Monte Carlo (DMC) method [9] using imaginary time propagation, to be used as a reference. These both are numerical methods and the former one in its robust form also using Monte Carlo technique. For the specified test case, one dimensional Hooke's atom, we also compare with the analytical solutions, where available, and approximate solutions otherwise.

To keep notations simple, we use the atomic units, where $m_e = e = \hbar = 4\pi\epsilon_0 = 1$ throughout the paper, unless otherwise stated.

### 2.1. Imaginary time propagation: DMC

The time-dependent Schrödinger wave equation for the many-body wave function $\psi(x, t)$ is

$$\mathrm{i}\frac{\partial\psi(x,t)}{\partial t} = (H - E_T)\psi(x,t), \tag{1}$$

where $H$ is the hamiltonian, $x$ stands for all coordinates of particles in one or more spatial dimensions and $E_T$ is an arbitrary reference energy or shift of zero level. Now, by replacing the real time $t$ by imaginary time $\tau = it$, this becomes

$$-\frac{\partial\psi(x,\tau)}{\partial\tau} = (H - E_T)\psi(x,\tau), \tag{2}$$

which is of the form of a diffusion equation. Its solutions can be expressed in terms of eigenfunctions $\phi_n(x)$ of the hamiltonian as

$$\psi(x,\tau) = \sum_{n=0}^{\infty} C_n\phi_n(x)\exp[-(E_n - E_T)\tau]. \tag{3}$$

As Monte Carlo methods are useful for evaluation of integrals, the differential equation is transformed into an integral equation. This is done by using Green's function formalism [9] and we seek the solution of the form

$$\psi(x_b,\tau_b) = \int_a G(x_b,\tau_b;x_a,\tau_a)\psi(x_a,\tau_a)dx_a, \tag{4}$$

where $G(x_b, \tau_b; x_a, \tau_a)$ is the Green's function of the system, the position space representation of the time evolution operator $\exp[-(H - E_T)(\tau_b - \tau_a)]$.

The exact analytical form of the Green's function is rarely known, and therefore, it needs to be approximated. Use of the so called short time approximation [9] to separate the kinetic and potential energy contributions, $T$ and $V$, gives

$$\begin{aligned}\exp[-(H - E_T)\Delta\tau] &= \exp[-(T + V - E_T)\Delta\tau] \\ &\approx \exp[-T\Delta\tau]\exp[-(V - E_T)\Delta\tau].\end{aligned} \tag{5}$$

Since $T$ and $V$ do not commute, in general, this approximation is exact only in the limit $\Delta\tau \to 0$ but accurate for small $\Delta\tau$ for potentials bound from below [9].

The Green's function can be separated into two parts, kinetic and potential (or diffusion and branching),

$$G(x_b,\tau_b;x,\tau_a) \approx G_{\mathrm{diff}}(x_b,\tau_b;x,\tau_a)G_B(x_b,\tau_b;x,\tau_a). \tag{6}$$

As this Green's function satisfies the imaginary time Schrödinger equation, it gives one equation for both parts of the Green's equation with kinetic part satisfying diffusion equation and potential part satisfying rate equation. Solutions to these equations are well known, a Gaussian spreading in $\Delta\tau$ and an exponential function:

$$G_{\mathrm{diff}}(x_b,x_a;\Delta\tau) = (4\pi D\Delta\tau)^{-N/2}\exp[-(x_b - x_a)^2/4D\Delta\tau] \tag{7}$$

and

$$G_B(x_b,x_a;\Delta\tau) = \exp\left[-\left(\frac{1}{2}[V(x_a) + V(x_b)] - E_T\right)\Delta\tau\right], \tag{8}$$

where the diffusion constant is $D = \hbar^2/2m_e$ (=1/2 in atomic units for the electron).

With these equations one can simulate random-walk-with-branching procedure to find the imaginary time evolution. Carrying out the simulation iteratively with short enough time step $\Delta\tau$, large enough population of random walkers and adjusting the "trial energy" $E_T$ to keep the simulation stationary will finally converge to the ground state wave function distribution of walkers and trial energy as the corresponding energy eigenvalue.

We should note, that Diffusion Monte Carlo method is generally used with trial wave functions [9,15], which makes DMC a significantly more powerful tool than without, in which case it deals with the ground states, only. Trial wave functions enable studies of larger system sizes, finding the lowest energy states of given symmetries and use of sc. mixed estimators for evaluation of physical quantities. Also, use of wave function nodes, if available, allows simulation of excited states [16,17].

Here, we use the simple DMC without trial wave functions to compare the features of DMC and our iRTPI approach, and more importantly, to be able to consider combination of these two Monte Carlo methods as another novel approach.

### 2.2. Real time propagation: RTPI

For the real time dynamics of a quantum many-body system $\psi(x, t)$ we define the Feynman path integral as

$$K(x_b,t_b;x_a,t_a) = \int_{x_a}^{x_b}\exp(\mathrm{i}S[x_b,x_a])\mathcal{D}x(t), \tag{9}$$

where $S[x_b, x_a] = \int_{t_a}^{t_b} L_x dt$ is the action of the path $x(t)$ from $(x_a, t_a)$ to $(x_b, t_b)$ and $L_x$ is the corresponding Lagrangian [1,2]. This is the kernel (or real time Green's function) of the propagation.

Now, the time evolution of the wave function $\psi(x, t)$ (or probability amplitude), can be written as

$$\psi(x_b,t_b) = \int_a K(x_b,t_b;x_a,t_a)\psi(x_a,t_a)\mathrm{d}x_a, \tag{10}$$

where $t_a < t_b$. A more complete discussion about numerical time-dependent coherent PI solution for the full quantum dynamics is given elsewhere [4].

Now, we see the analogy of Eqs. (4) and (10), and the two propagators $G$ and $K$. The latter of these is complex, bringing in the phase and interference of paths, an additional complication to numerical approaches, called "numerical sign problem" [18].