HELLO!

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What I did...

During my degree thesis:

- AB initio calculation using an extremely localized orbital approach

During my PhD:

- QMC simulation of few body system including:

  - small clusters of noble gas

  - positron containing systems

...and what I am going to do

- Study of the metal-insulator transition

DMC and Time step bias

The most fundamental equation of DMC method is:

$$\boxed{\Psi_0 = \lim_{t\to\infty} e^{-tH}\Phi}$$

which can be recast as an integral equation of the form:

$$\Psi_0(x) = \lim_{t\to\infty} \int G(x,x',t)\Phi(x')dx'$$

Unfortunately $G(x,x',t)$ is not known exactly

$$\Downarrow$$

<u>Short time approximation</u>

$$\boxed{e^{-\tau(K+V)} = e^{-\tau K}e^{-\tau V} + \mathcal{O}(\tau)}$$

The Trotter-Suzuki theorem ensures that this approximation is correct.

Thanks to this approximation the action of the propagator can be simulated as a sequence of diffusive and braching steps.

Higher order factorizations

Why can this approximation be annoying?

- it requires extrapolation at low τ
- It does not allow the use of large time step (large variance)

To cope with these problems new factorizations have been proposed. The most widespread probably is:

$$e^{-\tau(K+V)} = e^{-\tau V/2} e^{-\tau K} e^{-\tau V/2} + \mathcal{O}(\tau^2)$$

This is a second order approximation in τ. Very recently Suzuki has proposed a new forth order approximation of the form :

$$e^{-\tau(K+V)} = e^{-\tau V/6} e^{-\tau K/2} e^{-\tau \tilde{U}} e^{-\tau K/2} e^{-\tau V/6} + \mathcal{O}(\tau^4)$$

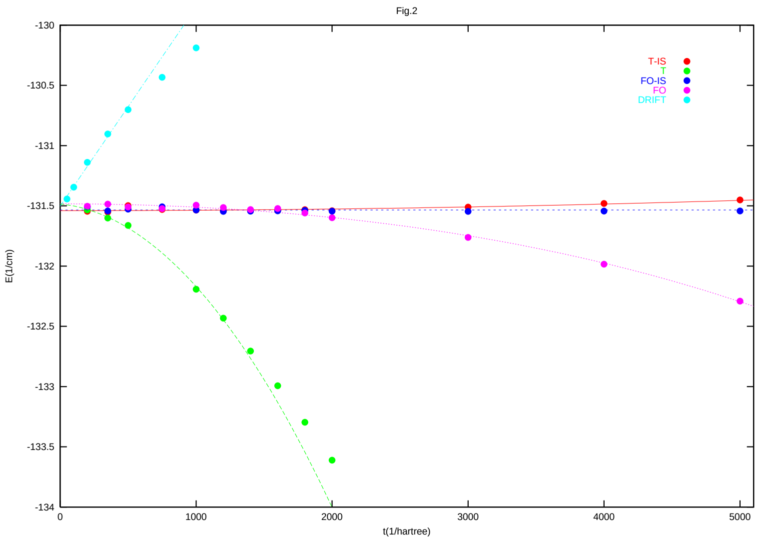
The main questions are:

- How implementing this factorization in a QMC code ?
- What the range of applicability of this factorization ?
- What about the prefactor in the error?

In order to answer to the other two questions we have initially applied the new propagator to the harmonic oscillator case. For this simple system an analytical answer is feasible. In particular, if a trial function of the form e^{cx^2} is chosen one has:

- II order propagator: $E(t) = 1/2 + \frac{2c-1}{48(1+2c)}t^2$
- IV order propagator: $E(t) = 1/2 + \frac{2c-1}{1728(1+2c)}t^4$
- IS-drift propagator: $E(t) = 1/2 + (\frac{c}{2} - c^2)t$

Calculation on physical system



Positronic systems

What QMC can do (now or, possibly, in the future)

- Bound state calculation on atom and molecules
- computation of scattering observables
- computation of annihilation rate and effective charge

The first point closely resemble molecular electronic calculation, with the only difference that only a little is known about wave-function of system containing positron.

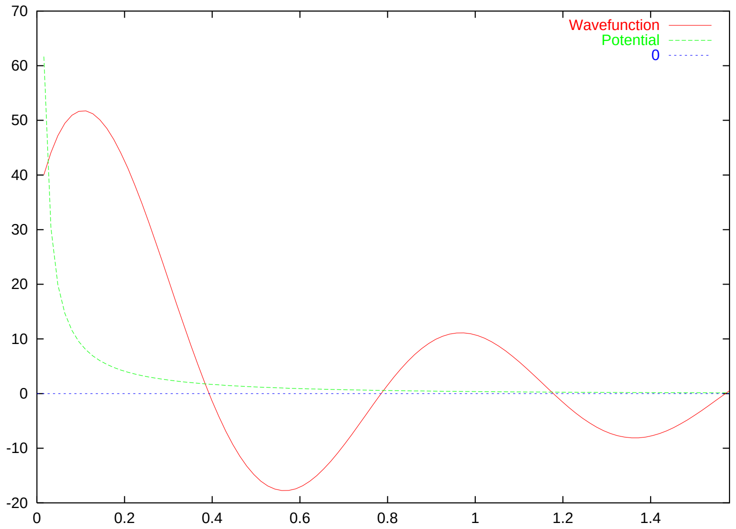
Second and third point need more care. In particular:

How can DMC work with continuum states ?

The straightforward solution is to convert the continuum problem in a discrete one....how ?

Scattering of a particle from a central potential

In this simple case one can reduce the problem in one dimension (the radial dimension)



When V=0 (no coulomb interactions) the exact form of the wave function is known:

$$\boxed{\Psi(r) = (\sin(kr) + b\cos(kr))/r}$$

with b arbitrary. Imposing a boundary condition has the effect to discretize the spectrum.

In QMC method is particularly simple imposing the condition $\Psi(R) = 0$.

Computing the S matrix

A three step reasoning leads now to the solution:

- Fixing a boundary condition determine the exact ground state solution with a specified energy E

- The internal energy determines the value of k in the external zone

- The external wave function is thus completely determined !

Because externally the wave function can be written as

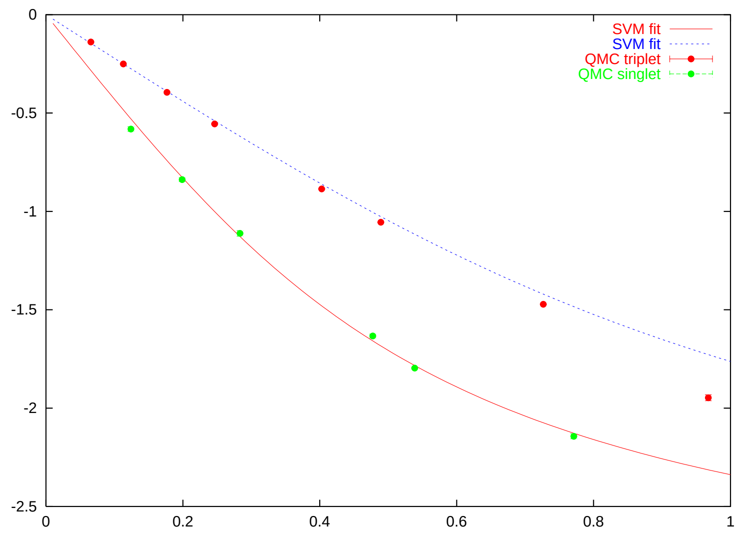
$$\boxed{e^{ikr} + \mathcal{S}e^{-ikr}}$$

where $\mathcal{S}$ is the scattering matrix (just a number in the single channel case), the scattering problem is completely solved being the knowledge of $\mathcal{S}$ enough to compute whatever else scattering observables.

Many Particle Problem

QMC becomes a competitive method when many body problems are treated.

Positronium scattering on hydrogen



Drawback

• Difficulty in treating scattering between systems supporting an overall bound state $\Rightarrow$ Monte Carlo methods for excited states

Future developments

• reactive scattering

• inelastic scattering

• developing of direct estimator for the cross section