Ground state calculation with time averaged wave function

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1 Introduction

The most important computational problem in quantum mechanics is to find the ground state corresponding to some Hamiltonian operator $\hat{H}$. When done in the position representation, the quantum state is a wave function $\psi(\mathbf{x})$, where $\mathbf{x}$ is a vector containing the degrees of freedom of the system. This is usually what is done in quantum chemical calculations, even though the discrete spin variable is handled separately.

Common ways to find an approximate ground state include the variational method, and for atoms and molecules there are, e.g. the self-consistent field approximations and the density functional theory (DFT) ([1]).

One way to find an approximation to any wanted level of accuracy is the imaginary time propagation (ITP) scheme ([2]). If the initial state of a quantum system is

$$|\psi(0)\rangle = C_0 |0\rangle + C_1 |1\rangle + C_2 |2\rangle + \ldots, \tag{1}$$

where the state vectors $|k\rangle$ represent the k:th eigenstate of the Hamiltonian in order of increasing eigenvalue E_k, then the time evolved state $|\psi(t)\rangle$ at time t is

$$|\psi(t)\rangle = \hat{U}_t |\psi(0)\rangle = C_0 e^{-iE_0 t/\hbar} |0\rangle + C_1 e^{-iE_1 t/\hbar} |1\rangle + C_2 e^{-iE_2 t/\hbar} |2\rangle + \ldots, \tag{2}$$

where the operator $\hat{U}_t$ is the time evolution operator for time interval of length t (when the $\hat{H}$ doesn't have explicit time dependence, the operator $\hat{U}$ depends only on time interval and not the initial time).

Defining an imaginary time coordinate, $s = it$, the time evolution to positive direction of this coordinate is

$$|\psi(s)\rangle = \hat{U}_s |\psi(0)\rangle = C_0 e^{-E_0 s/\hbar} |0\rangle + C_1 e^{-E_1 s/\hbar} |1\rangle + C_2 e^{-E_2 s/\hbar} |2\rangle + \ldots \tag{3}$$

From this equation it can be seen that when s has large enough value, the components $|1\rangle, |2\rangle$ and so on will have become insignificant compared to the ground state component (except in the

unusual case where the ground state is degenerate, $E_0 = E_1$). This allows the calculation of the ground state in a way where the initial wave function $\Psi(x,0) = \langle \mathbf{x} | \psi(0) \rangle$ is positive real valued for all values of coordinates, and the function $\Psi(x,s)$ will also have only positive real values (if the system consists of several fermionic particles, negative wave function values can't be avoided even in the ground state, but that's a matter of another discussion). An advantage of this is that the problem is then just a normal diffusion equation problem and can be computed with Diffusion Monte Carlo ([3]) which can be parallelized for several processors. The calculation of evolution along real time axis is much more difficult to parallelize, but there have been attempts to do this by performing an analytical continuation of the QDMC result for $|\psi(s)\rangle$ to see what happens to the state when moving along real-valued time axis ([4]).

The program in this repository has been written with R language and the idea is to compute the ground state of a 1D quantum system in an unusual way where time evolution is calculated along real, instead of imaginary time axis. When the evolution of the state $|\psi(t)\rangle$ is known for a time interval of reasonable length, , the average state vector on that interval is computed as

$$
|\Phi(T)\rangle = \frac{1}{T} \int_0^T |\psi(t)\rangle dt
$$

$$
= \frac{1}{T} \left[C_0 \frac{i\hbar}{E_0} \left(e^{\frac{-iE_0 T}{\hbar}} - 1 \right) |0\rangle + C_1 \frac{i\hbar}{E_1} \left(e^{\frac{-iE_1 T}{\hbar}} - 1 \right) |1\rangle + C_2 \frac{i\hbar}{E_2} \left(e^{\frac{-iE_2 T}{\hbar}} - 1 \right) |2\rangle + \ldots \right]. \quad (4)
$$

The requirement for this to be the correct integration result is that none of the E_j have value 0 (the same as the requirement for the Hamiltonian to have an inverse $\hat{H}^{-1}$). But the integral exists even when there are zero eigenvalues, and eigenvalues can always be made non-zero with an additive constant in $V(x)$. As can be easily seen, this time average $|\Phi(T)\rangle$ contains less excited state components than the initial state $|\psi(0)\rangle$ because the multipliers of E_j^{-1} in front of each component $|j\rangle$ usually increase rapidly for increasing j. An exception is when the value of T is such that the multiplier $e^{-iE_0 T/\hbar} - 1$ happens to be zero. This occurs when T is an integer multiple of $2\pi\hbar/E_0$.

The idea in this ground state computation is that after finding $|\Phi(T)\rangle$ for a value of T far enough from the nearest multiple of $2\pi\hbar/E_0$, this time average $|\Phi(T)\rangle$ is set to be the initial state $|\psi(0)\rangle$ in a new iteration and this is evolved again to find a new average state on time interval of length T. After a few iterations the quantum state (wave function) can be converged to something near the ground state, as multipliers of E_j^{-n} have accumulated in front of each energy eigenstate component $|j\rangle$. Before performing the time averaging calculation to find $\Phi(x,T)$, each simulation first computes an accurate enough approximation for the ground state WF $\psi_0(x)$ by the more usual imaginary time propagation (ITP) method. The function $\Phi(x,T)$ on each time step is then plotted in the same image with the ITP result and the shape of the potential energy $V(x)$.

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2 Numerical discretization

All of the example problems included here are 1D quantum mechanics, which means that the time evolution is determined by the time dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) \tag{5}$$

,

and because dimensionless variables are needed for numerics, we set $m = \hbar = 1$

$$i\frac{\partial\Psi(x,t)}{\partial t} = -\frac{1}{2}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t). \tag{6}$$

When solving this for initial state $\Psi(x,0)$ and for time interval $t \in [0,T]$, direct explicit discretization by just changing the partial derivatives to difference quotients doesn't produce a result stable in accumulation of numerical errors or constancy of the norm of the wave function. But neither do classical point mass mechanics calculations usually even keep the total energy constant if it's just explicit finite difference, which is why the semi-implicit difference scheme of Ref. [5] is used here. The x- and t-axes are discretized and the wave function $\Psi(x,t)$ and potential energy $V(x)$ become a set of values Ψ_j^k and V_j given at discrete points (x_j, t_k). Then the time evolution is computed from

$$\Psi_j^{k+1} - \frac{i}{4}\Delta t\left(\frac{\Psi_{j+1}^{k+1} - 2\Psi_j^{k+1} + \Psi_{j-1}^{k+1}}{[\Delta x]^2}\right) + i\Delta t V_j = \Psi_j^k + \frac{i}{4}\Delta t\left(\frac{\Psi_{j+1}^k - 2\Psi_j^k + \Psi_{j-1}^k}{[\Delta x]^2}\right) - i\Delta t V_j, \tag{7}$$

which is a tridiagonal system of linear equations (on each time step) when it's this 1D version of the problem. When there are more dimensions where the particle is moving, the equivalent system is not tridiagonal but can be converted to one tridiagonal equation for each coordinate with operator splitting (this just requires a shorter time step to be accurate). The quantities $\Delta x = x_{j+1} - x_j$ and $\Delta t = t_{k+1} - t_k$ are the spatial and temporal step sizes.

The parameters for each simulation include the L_x, which is the lenght of the spatial interval $x \in [0, L]$ in which the evolution of the wave function is calculated, L_t which is the length of the time interval $t \in [0, L_t]$ and the number of discrete space and time steps are called n_x and n_t. These parameters are not necessarily the same in the time-average wave function part of the simulation and the imaginary time evolution part which the results are compared to.

3 Example cases

The examples in the included .r files are a quantum harmonic oscillator (quadratic potential), a $V(x) \propto (x - L/2)^4$ system (anharmonic oscillator) and a double well where there is a potential energy "barrier" in the middle of the domain.

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3.1 Quadratic potential

In this example, the potential energy function was (given in terms of dimensionless numbers) $V(x) = 2(x-3)^2$, the discretization parameters for the imaginary time propagation were $L_x = 6$, $L_t = 3$, $n_x = 120$, $n_t = 500$ and for the time average calculation they were $L_x = 6$, $L_t \approx 3\pi/2$, $n_x = 140$ and $n_t = 150$. The change of $|\Phi(x,t)|^2$ during four iterations is shown in the video file "Quadratic.mp4".

The initial state in both the ITP and time average simulation was the function

$$\Psi(x,0) = Ce^{-\frac{3}{2}(x-3)^2}, \tag{8}$$

where C is the appropriate normalization constant.

Images from first three iterations are shown in Fig. 1, and it is apparent that three iterations are enough in this case. Especially in the fourth image on the first row of this sequence it can be seen how around time $T = \pi$ the function $\Phi(x,T)$ "shatters" and looks more like an approximation to the 2nd excited state. This is exactly the time value $T = 2\pi\hbar/E_0$ where, as mentioned in the first section, the multiplier $e^{-\frac{iE_0T}{\hbar}} - 1$ in front of the $|0\rangle$ term of $\Phi(x,T)$ becomes zero.
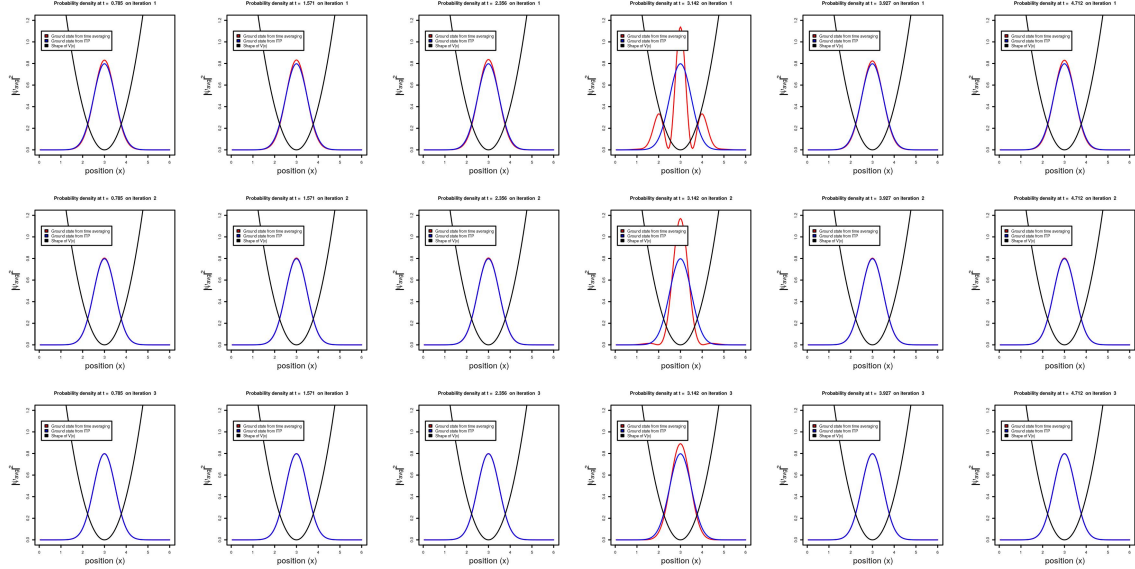

Fig. 1: Calculated time averaged wave function square modulus $|\Phi(x,T)|^2$ for various values of T during 3 iterations in the harmonic oscillator example, compared to the ground state found with ITP and with the shape of $V(x)$ shown in the same image.
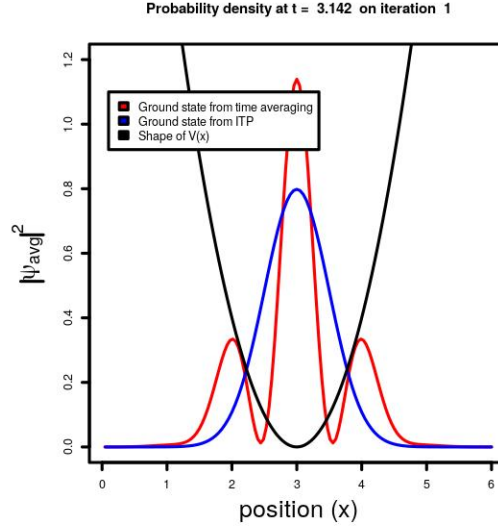
Probability density at t = 3.142 on iteration 1

Fig. 2: At around time $T = \pi$, the function $\Phi(x, T)$ temporarily becomes more like an approximation of 2nd excited state than one of the ground state.

3.2 Anharmonic oscillator

In this one, the parameters of the ITP part were $L_x = 6.0$, $L_t = 3.0$, $n_x = 120$ and $n_t = 500$. The parameters of time averaging part were $L_x = 6.0$, $L_t \approx \frac{3\pi}{2}$, $n_x = 140$ and $n_t = 150$. The potential energy function was $V(x) = 2(x-3)^4$ and the initial state was $\psi(x, 0) = C e^{-\frac{1}{2}(x-3)^2}$ with C the constant that normalizes this function.

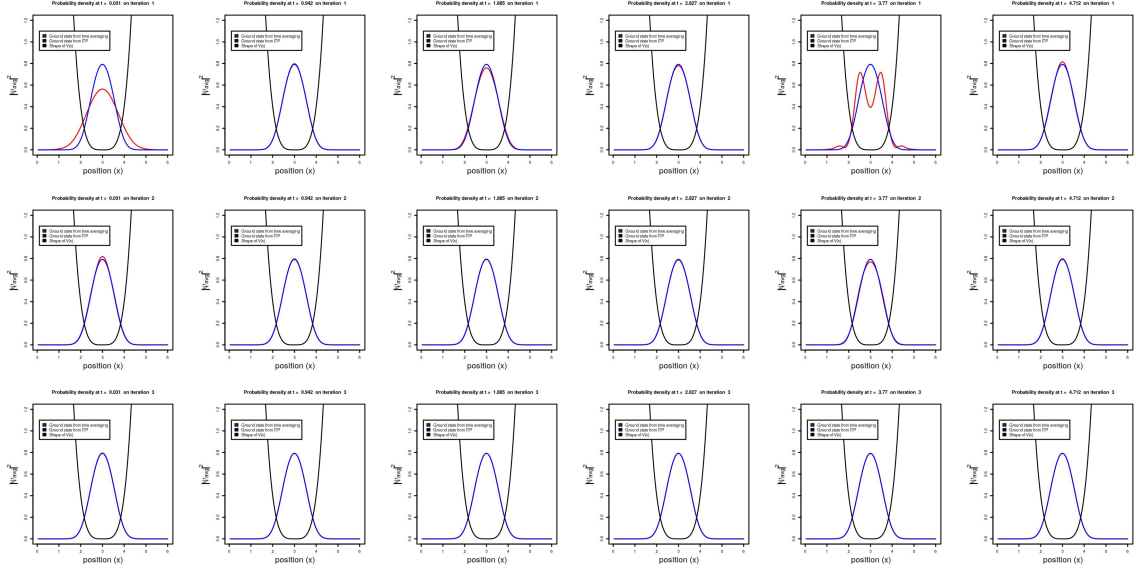An image sequence for the three first iterations is shown in Fig. 3.

Fig. 3: Calculated time averaged wave function square modulus $|\Phi(x,T)|^2$ for various values of T during 3 iterations in the quartic oscillator case, compared to the ground state found with ITP and with the shape of $V(x)$ shown in the same image.

Looking at the video file "Anharmonic.mp4", it seems that the breakdown of the wave function takes place at around $T = 3.74$, and there the function $\Phi(x,T)$ is not a good approximation at all for the ground state wave function.

3.3   Double well

This simulation has a potential well with two compartments and a barrier in between

$$V(x) = \begin{cases} 2.5, & \text{when } |x-3| < 0.5, \\ 0, & \text{when } 0.5 \leq |x-3| < 2 \\ 5, & \text{when } |x-3| \geq 2 \end{cases} , \tag{9}$$

and the discretization parameters and the initial state were identical to those in the previous example (anharmonic oscillator). An image set of the results is shown in Fig. 4.
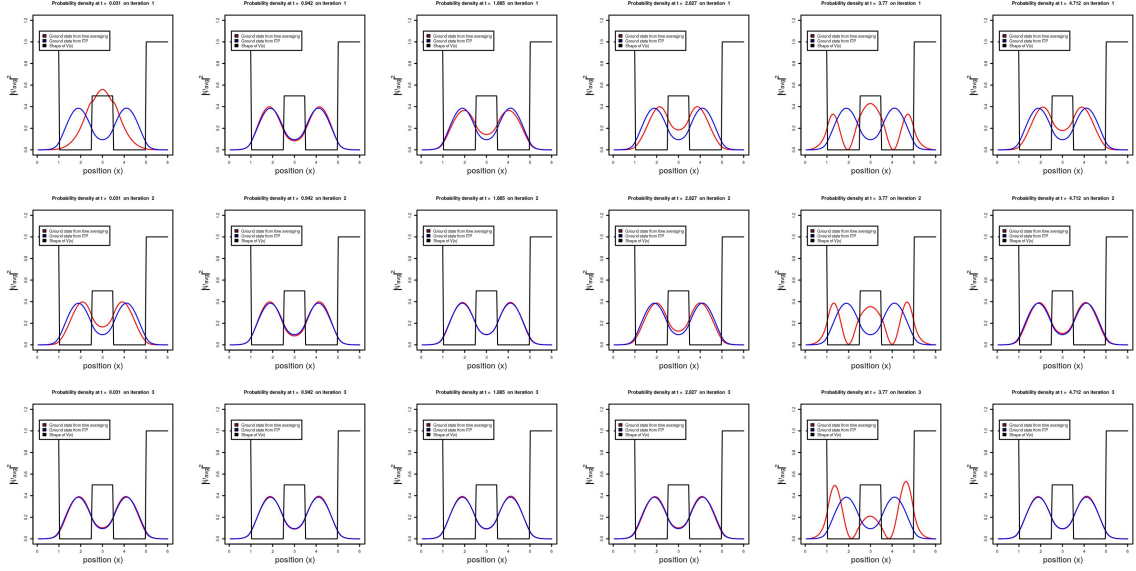
Fig. 4: Calculated time averaged wave function square modulus $|\Phi(x,T)|^2$ for various values of T during 3 iterations in the double well situation, compared to the ground state found with ITP and with the shape of $V(x)$ shown in the same image.

The time value when $\Phi(x,T)$ becomes a poor approximation for $\psi_0(x)$ seems to be about $T = 3.8$. You could expect both the ITP and time average calculation to converge more slowly to the ground state in the case of a double well, because the energy difference between the ground and 1st excited state is unusually small (with the ground state becoming almost degenerate for large barrier heights). However, this shouldn't be a problem unless the initial state is unsymmetrical and contains a significant 1st excited state component.

4   Discussion and possible improvements

It is possible that this calculation method can provide an approximation to the 2nd excited state in addition to the ground state. Doing this accurately would require making the timestep Δt adaptively much shorter when closing in to the time value $T = \frac{2\pi}{E_0}$. Then the $\Phi(x,T)$ could be taken to be an approximation of $\psi_2(x) = \langle x\,|2\rangle$ at the moment when it is most close to being orthogonal with the calculated ground state wave function.

The first excited state can be found by choosing the initial state $\psi(x,0)$ of first iteration so that it's an odd function about the midpoint $x = 3$, and with only one node (at $x = 3$). Then one would expect the shattering of $|\Phi(x,T)|^2$ to happen when $T = \frac{2\pi}{E_1}$ and the function $\Phi(x,T)$ would presumably be an approximation for the third excited state (which also has a wave function antisymmetric about $x = 3$) at that time value. The function $\Phi(x,T)$ can also be forced to remain odd about $x = 3$ during the simulation, applying a simple projection operator on each time step.

It is unclear whether this method has advantages over the usual ITP, as real time propagation can't be converted to parallelizable DMC and requires a complex valued wave function that takes twice as much bytes to store in computer's memory. However, if approximations to the excited states can be found from the same data that has been recorded when calculating the ground state, then it could be useful in some special situations.

One possible way to make the calculation faster could be to time average the function $\Phi(x,T)$ another time:

$$\Theta(x,T) = \frac{1}{T} \int\limits_0^T \Phi(x,T')dT', \tag{10}$$

but whether this improves the convergence rate has to be tested for a next version of this code.

If the conversion of initial state $\Psi(x,0)$ to average wave function $\Phi(x,T)$ is represented with an operator $\hat{A}(T)$, $\Phi(x,T) = \hat{A}(T)\Psi(x,0)$, then this operator can be converted to a neat and tidy form by writing the integral in (4) with the help of Riemann sum and evolution operator $\hat{U}(t)$:

$$\hat{A}(T)\Psi(x,0) = \lim_{n\to\infty} \left[\frac{1}{T} \sum_{m=0}^n \frac{T}{n} \hat{U}\left(\frac{mT}{n} \right) \right] \Psi(x,0) = \lim_{n\to\infty} \sum_{m=0}^n \left[\frac{1}{n} \exp\left(-\frac{imT\hat{H}}{n} \right) \right] \Psi(x,0)$$

$$= \left[\int\limits_0^1 \exp\left(-iqT\hat{H} \right) dq \right] \Psi(x,0) \quad (11)$$

In this, units where $\hbar = 1$ are used and the equation is for wave functions instead of abstract state vectors. The final result in this can also be written like

$$\left[\int\limits_0^1 \exp\left(-iqT\hat{H} \right) dq \right] \Psi(x,0) = \frac{i}{T} \hat{H}^{-1} \left[\exp\left(-iT\hat{H} \right) - 1 \right] \Psi(x,0) \tag{12}$$

where you immediately see that the inverse Hamiltonian $\hat{H}^{-1}$ there is why factors of E_j^{-1} appear in front of each term in (4), and also why all eigenvalues of $\hat{H}$ have to be non-zero for this to be the correct form of the result. Repeated application of $\hat{A}(T)$ on an initial state $\Psi(x,0)$ makes the wave function converge towards the ground state or some other low-lying energy eigenstate, depending on $\Psi(x,0)$ and the value of T. Actually this also holds for complex values of T if they are on the lower complex half-plane, $T \in \mathbb{C}$ and $\text{Im } T \leq 0$.

References

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[3] I. Kosztin, B. Faber and K. Schulten, *Introduction to the Diffusion Monte Carlo Method*, Am. J. Phys. **64**, 633 (1996), https://doi.org/10.1119/1.18168.

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