

Computational Quantum Mechanics

From Fourier Grid Hamiltonian Method to Quantum Monte Carlo

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Abstract

While quantum mechanics can accurately describe our universe, the equation governing the quantum system is too complicated to be soluble through human analysis. To apply this great theory to real world scenarios, such as in the investigation of electronic structure or in the prediction of complex system in atomic scale, we have to resort to computational approach. In this report, I will present a brief history in the development of computational quantum mechanics. Then I will focus on two well-known approaches, the Fourier grid Hamiltonian method and Quantum Monte Carlo. Fourier grid Hamiltonian method is accurate and general with the cost of bad scalability, while Quantum Monte Carlo method can solve many-body quantum system very efficiently under certain restriction. To have hands-on experience in predecessor's achievement, I have implemented these methods using C++ completely from scratch. The codes are publicly available on [GitHub](#). I have applied my implementation on several real world situations. The results show well agreement with experimental and analytical results. Furthermore, it can easily apply to convoluted situations where finding analytical solution is strenuous and burdensome. Together, the results demonstrate the correctness and the usefulness of computational quantum mechanics.

1 Introduction

“The general theory of quantum mechanics is now almost complete, [...] the difficulty is that the exact application of these laws leads to equations much **too complicated to be soluble**. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed.”

— P.A.M. Dirac, 1929 [4].

As early as 1929, three years after the birth of quantum mechanics, P.A.M. Dirac observed that the fundamental physical law describing the microscopic world is near its completion. However, it is very difficult to exactly solve for the equation (the Dirac equation, or the Schrodinger equation, in the non-relativistic region) even for a single-particle system. Because the power of physics lies in its great prediction ability, it is very important to find approximation method to solve for any realistic physical systems. In this project, I will take on P.A.M. Dirac’s great vision, and introduce several achievements over the past 80 years. To gain better understanding to predecessors’ accomplishment, I decided to write C++ codes that approaches the goal posed by P.A.M. Dirac. I will introduce more on how to use my codes in the later content.

1.1 The Challenge We Face

In the following content, I will only consider the (general) Schrodinger’s equation, i.e. I will assume all particles are moving at speed much lower than the light speed. This is applicable in many fields, such as in chemistry, material science and solid-state physics as mentioned in Dirac’s paper on many-electron system [4]. Particularly, we will consider the following equation under Dirac’s notation:

$$\hat{H}|\psi\rangle = i\hbar \frac{\partial}{\partial t}|\psi\rangle, \quad (1)$$

where $|\psi\rangle$ is the complete description of our physical system (which can be single-body or many-body) and \hat{H} is the Hamiltonian operator. We can easily compare this to the canonical equation of motion in classical mechanics:

$$\frac{\partial H}{\partial \mathbf{q}} = -\frac{d\mathbf{p}}{dt}, \quad \frac{\partial H}{\partial \mathbf{p}} = \frac{d\mathbf{q}}{dt}, \quad (2)$$

where \mathbf{q} is the canonical coordinate and \mathbf{p} is the canonical momentum.

Classically, for a system with s -dimensional canonical coordinate, we only need $2s$ real number to store the entire information of the physical system, i.e. \mathbf{q}, \mathbf{p} . However quantum-mechanically, we need a s -dimensional complex function to store the information of the physical system, the difficulty increases drastically. The situation is even more strenuous, because in quantum mechanics, knowing the evolution of physical state (or $|\psi\rangle$) is often not very interesting. We are generally more interested in solving the following equation (the time-independent general Schrodinger equation):

$$\hat{H}|\psi\rangle = E|\psi\rangle, \quad (3)$$

where E : the energy eigenvalue is not known beforehand and is fundamentally very important. This problem is even more difficult than the previous one, because we have to deal with a (s -dim complex function) \times (s -dim complex function) eigenvalue problem.

1.2 A Little Bit of History

Even solving the 1D Schrodinger equations is difficult, so right after the discovery of the equation in 1926, Wentzel, Kramers, and Brillouin developed the so-called WKB approximation (for details, please see [18]) to approximately solve for the eigenstate and eigenenergy of 1D Schrodinger

equations. This approximation is valid only when \hbar can be assumed to be very small, so it is also called the semi-classical approximation.

Another well-known approach with a similar flavor is also developed, the Rayleigh-Schrodinger perturbation theory [19], again right after the advent of Schrodinger's 1926 paper. In many systems, the perturbation theory can be very successful and is used even till today. For example, in 2011, a group of Japanese scientist [1] has calculated the electron's magnetic moment using perturbation theory up to tenth-order and found very good agreement with the experiment (to eleventh decimal places).

However, perturbation method is invalid for many realistic systems, which happens quite often in quantum chemistry. To handle non-perturbative system, several different theory for designing accurate model have been proposed. These types of method have become increasingly popular after the birth of electronic computer. And is now widely used in helping us design drugs, superconductors, calculating the electronic structure of molecules, or predicting the phase transition behavior.

Among the various computational methods, a popular and successful approach is known as the density functional theory. It is used to calculate the ground state property of many-electron system. The theory is built upon the two famous Hohenberg-Kohn theorem [10] proposed in 1964:

1. The ground state property of N -electron system is uniquely determined by the electron density (which simplifies the $3N$ -dim wave function to a 3-dim real function).
2. The correct ground state electron density (satisfying the constraint that its integration over space must equal to N) minimizes the energy functional (energy functional is the energy expectation for the corresponding wave function).

The proof of the theorem is simple and straightforward (simply using *reductio ad absurdum* in the original paper [10]), but the implication is very powerful.

In the next year, Walter Kohn continue to work on this subject and publish another ground-breaking paper called the "Self-Consistent Equations Including Exchange and Correlation Effects" [12], also known as the Kohn-Sham equation. Originally, the electrons will interact with each other, thus the wave function can not be solved separately for different electrons. In the paper, they showed that the N -electron ground state wave function can be constructed by the wave function of N independent particles moving in an effective potential, the Kohn-Sham potential. The computational simplification led to many great insights, which enables successors to design essential tools for electronic materials and molecular structure (for more details see [16]). Even after 50 years, density functional theory remains to be a useful and wide-used approach, e.g. see last year's publication on Physical Review Letter [14] or this year's publication on Nature Review Materials [11]. Due to his development of density functional theory, Kohn was awarded the 1998 Nobel prize in chemistry.¹

1.3 Alternative Path to Fulfilling Dirac's Vision

Despite the success of density functional theory, there are still applications where density functional theory fails miserably. For example, due to the band-gap problem, density functional theory may predict a number of known insulator (e.g., the Mott insulator) as metallic (see page 190 in [15]). This breakdown is not because of the theory itself. The problem arises because we do not know the exact form of Kohn-Sham potential, which have to be approximated, e.g. using local density approximation (LDA) or generalized gradient approximations (GGA). As noted in a publication at Science in 2008 [3], a systematic approach for constructing the potential that are universally applicable is a hard problem and has remained elusive.

¹https://www.nobelprize.org/nobel_prizes/chemistry/laureates/1998/

As a results, methods that treat the problem more directly is desired, i.e. solving the quantum mechanical equation directly without resorting to fictitious equation that require approximations that sometimes work, but sometimes don't. In this project, I will follow the more direct approach to fulfill Dirac's vision. The booming of this new line of work actually happens much after the development of density functional theory. This may be due to the recent advancement of computing power that makes the direct approach very useful and attractive. To summarize, I will introduce the simple yet influential Fourier Grid Hamiltonian method in Section 2; the more advanced Quantum Monte Carlo in Section 3; and gives concluding remarks in Section 4.

2 Fourier Grid Hamiltonian Method

Around 1980, as the computing power of electronic computer starts to take off, scientist begin to apply direct method in solving low dimensional Schrodinger equation. Among them, a well-known and influential method, called the Spectral method [6], is developed by Feit et al. in 1982 to solve for the time-dependent Schrodinger equation, which has now accumulated nearly 3,000 citations. Latter, in 1984, Kosloff and Tal-Ezer [21] improved the original formulation to solve the time-dependent Schrodinger equation (equivalent to propagating the wave function) more accurately and efficiently, and renamed it as the Fourier method. Finally, in 1989, Marston et al. proposed the Fourier Grid Hamiltonian Method [13] to solve the time-independent Schrodinger equation (equivalent to finding the eigenfunctions and the corresponding eigenenergy).

2.1 Method Description

In the original paper [13], the authors only solve the 1D problem. I think 1D is too restricted, so I have generalize the method to handle 2D problem (some care has to be taken). Furthermore, I have applied a computational trick to reduce the time complexity of their original method, which will be described later.

We first consider the 1D one-body Schrodinger equation, which can be written as:

$$\hat{H}|\psi\rangle \equiv \left(\frac{\hat{P}^2}{2m} + V(\hat{X}) \right) |\psi\rangle = E|\psi\rangle,$$

where \hat{P} is the momentum operator, and \hat{X} is the position operator. We now consider the position eigenket and the momentum eigenket, denoted by

$$\begin{aligned} |x'\rangle \text{ with } \hat{X}|x'\rangle &= x'|x'\rangle, \langle x''|x'\rangle = \delta(x'' - x'). \\ |k'\rangle \text{ with } \hat{P}|k'\rangle &= \hbar k'|k'\rangle, \langle k''|k'\rangle = \delta(k'' - k'). \end{aligned}$$

The following useful identity relates the two eigenkets:

$$\langle k'|x'\rangle = \frac{1}{\sqrt{2\pi}} \exp(-ik'x').$$

Therefore we have

$$\begin{aligned} \langle x|\hat{H}|x'\rangle &= \langle x|\frac{\hat{P}^2}{2m}|x'\rangle + \langle x|V(\hat{X})|x'\rangle, \\ &= \int_{-\infty}^{\infty} dk' \int_{-\infty}^{\infty} dk'' \langle x|k'\rangle \langle k'|\frac{\hat{P}^2}{2m}|k''\rangle \langle k''|x'\rangle + V(x')\delta(x - x'), \\ &= \int_{-\infty}^{\infty} dk' \int_{-\infty}^{\infty} dk'' \frac{(\hbar k')^2}{2m} \langle x|k'\rangle \delta(k' - k'') \langle k''|x'\rangle + V(x')\delta(x - x'), \\ &= \int_{-\infty}^{\infty} dk' \frac{(\hbar k')^2}{2m} \langle x|k'\rangle \langle k'|x'\rangle + V(x')\delta(x - x'), \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk' T_{k'} \exp(ik'(x - x')) + V(x')\delta(x - x'), \end{aligned}$$

where $T_{k'}$ is defined as $\frac{(\hbar k')^2}{2m}$. Note that I used the closure relation in the second equality:

$$\int_{-\infty}^{\infty} dk' |k'\rangle \langle k'| = \hat{1}.$$

Also we have

$$\hat{H}|\psi\rangle = E|\psi\rangle \implies \langle x|H|\psi\rangle = E\langle x|\psi\rangle \implies \int_{-\infty}^{\infty} dx' \langle x|\hat{H}|x'\rangle \psi(x') = E\psi(x),$$

where I have used the fact that $\langle x|\psi\rangle = \psi(x)$. Notice right hand side look very much like the eigenvalue problem in standard linear algebra.

Let us now generalize everything into 2D, we would have

$$\hat{H} = \frac{\hat{P}_x^2 + \hat{P}_y^2}{2m} + V(\hat{X}, \hat{Y}),$$

and

$$\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \langle x, y|\hat{H}|x', y'\rangle \psi(x', y') = E\psi(x, y). \quad (4)$$

Similarly, $\langle x, y|\hat{H}|x', y'\rangle$ can be expressed as

$$\frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dk' \int_{-\infty}^{\infty} dl' (T_{k'} + T_{l'}) e^{i(k'(x-x') + l'(y-y'))} + V(x', y') \delta(x - x') \delta(y - y'), \quad (5)$$

which can be derived similar to 1D, but using the following identities:

$$\begin{aligned} \langle x'', y''|x', y'\rangle &= \delta(x'' - x') \delta(y'' - y'), \\ \langle k'', l''|k', l'\rangle &= \delta(k'' - k') \delta(l'' - l'), \\ \langle k', l'|x', y'\rangle &= \frac{1}{2\pi} \exp(-i(k'x' + l'y')). \end{aligned}$$

Before discretizing everything, a useful property of the desired eigenfunction is stated in Proposition 1.

Proposition 1. Eigenfunction can always taken to be real.

Proof. From Equation 5, we can see that $\langle x, y|\hat{H}|x', y'\rangle$ is always real, because V is a real function and the infinite integral is also real. And since \hat{H} is Hermitian, the eigenenergy will always be a real number. Combining these with Equation 4, we can see that if $\psi(x, y)$ satisfy the equation, then $\text{Re}[\psi(x, y)]$ and $\text{Im}[\psi(x, y)]$ also satisfy the equation. Therefore we can always assume that the desired eigenfunction is a real function. \square

Our next step is to discretize everything because computer can not really deal with infinite dimensional objects. The idea is simply to consider a finite grid of points (for simplicity, I will consider a uniform grid centered at the origin). Mathematically, it can be described as follows:

$$\begin{aligned} |x, y\rangle, \forall x, y \in \mathbb{R} &\mapsto |x_i, y_j\rangle, \forall i, j \in \{-n, \dots, 0, \dots, n\}. \\ |k, l\rangle, \forall k, l \in \mathbb{R} &\mapsto |k_i, l_j\rangle, \forall i, j \in \{-n, \dots, 0, \dots, n\}. \end{aligned}$$

where $x_i = i\Delta x, y_j = j\Delta x, k_i = i\Delta k, l_j = j\Delta k, \forall i, j$. And $N \equiv 2n + 1$. Basically it is a N -by- N grid, where N must be an odd number. Because the size of the grid is $N\Delta x$, the largest wave length is $N\Delta x$, which is equivalent to saying the smallest wave number $\Delta k = 2\pi/N\Delta x$. So we only have two discretization parameters: n and Δx . Under discretization, we also have to do the following modification:

$$\int_{-\infty}^{\infty} \mapsto \sum_{i=-n}^n \Delta x, \quad \delta(x_i - x_j) \mapsto \frac{1}{\Delta x} \delta_{ij}.$$

Therefore Equation 4 can be rewritten as

$$\Delta x^2 \sum_{i=-n}^n \sum_{j=-n}^n \langle x_p, y_q | \hat{H} | x_i, y_j \rangle \psi(x_i, y_j) = E \psi(x_p, y_q).$$

If we consider $\psi(x_i, y_j)$ as an N^2 -dim vector $\vec{\psi}$, and regard $\Delta x^2 \langle x_p, y_q | \hat{H} | x_i, y_j \rangle$ as an N^2 -by- N^2 matrix $[H]$, then the above equation is essentially an eigenvalue equation,

$$[H] \vec{\psi} = E \vec{\psi}.$$

The final ingredient would be to calculate the matrix element $\Delta x^2 \langle x_p, y_q | \hat{H} | x_i, y_j \rangle$. One choice is to directly discretize Equation 5. However, I found a modification that can improve numerical stability giving more accurate energy eigenvalues. Instead of doing a double integral, we first analytically perform one of the integration to yield

$$\frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dk' \int_{-\infty}^{\infty} dl' T_{k'} e^{i(k'(x-x') + l'(y-y'))} = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk' T_{k'} e^{i(k'(x-x'))} \delta(y-y').$$

Then we apply discretization using the right hand side when calculating kinetic energy contribution, so

$$\begin{aligned} \langle x_p, y_q | \hat{H} | x_i, y_j \rangle &= \frac{1}{2\pi} \sum_{m=-n}^n \Delta k T_{k_m} e^{i(k_m(x_p-x_i))} \frac{1}{\Delta x} \delta_{qj} \\ &+ \frac{1}{2\pi} \sum_{m=-n}^n \Delta k T_{k_m} e^{i(k_m(y_q-y_j))} \frac{1}{\Delta x} \delta_{pi} + V(x_i, y_j) \frac{1}{\Delta x^2} \delta_{pi} \delta_{qj}. \end{aligned} \quad (6)$$

Next we use the relation that $\Delta k = 2\pi/N\Delta x$ to obtain

$$\Delta x^2 \langle x_p, y_q | \hat{H} | x_i, y_j \rangle = \frac{1}{N} \sum_{m=-n}^n T_{k_m} (e^{i(k_m(x_p-x_i))} \delta_{qj} + e^{i(k_m(y_q-y_j))} \delta_{pi}) + V(x_i, y_j) \delta_{pi} \delta_{qj}.$$

Recall that $T_k = \frac{(\hbar k)^2}{2m}$, so $T_k = T_{-k}$, and we can use $e^{ix} + e^{-ix} = 2 \cos(x)$ to get

$$\begin{aligned} \Delta x^2 \langle x_p, y_q | \hat{H} | x_i, y_j \rangle &= \frac{1}{N} \sum_{m=0}^n 2T_{k_m} (\cos(k_m(x_p-x_i)) \delta_{qj} + \cos(k_m(y_q-y_j)) \delta_{pi}) \\ &+ V(x_i, y_j) \delta_{pi} \delta_{qj}. \end{aligned} \quad (7)$$

Notice that a naive construction of $[H]$ would require $O((N^2 \times N^2) \times N)$ computations², because there are $(N^2 \times N^2)$ entries and each require roughly N computation if Equation 7 is explicitly used. In the paper, they proposed to use FFT to speed up the process resulting in $O(N^4 \log N)$. However, I found that by a simple pre-computation we can decrease the total computations to $O(N^4)$, and is actually much easier to implement than FFT. For more details, please see my C++ code `FGH/FourierGridH.cpp`.

2.2 Code Usage

My design principle is to be as easily understandable as possible. The main purpose is to give the readers a more realistic experience to past achievements. Because for most people, coding things out is very different than simply knowing the concept. You can find all the codes on [GitHub](#)³.

For Fourier grid Hamiltonian method, you can find all the codes in the `FGH/` folder, including:

²I am using the big-O notation developed by Landau here.

³Or you can simply copy this link: <https://goo.gl/gdJ3Rn>

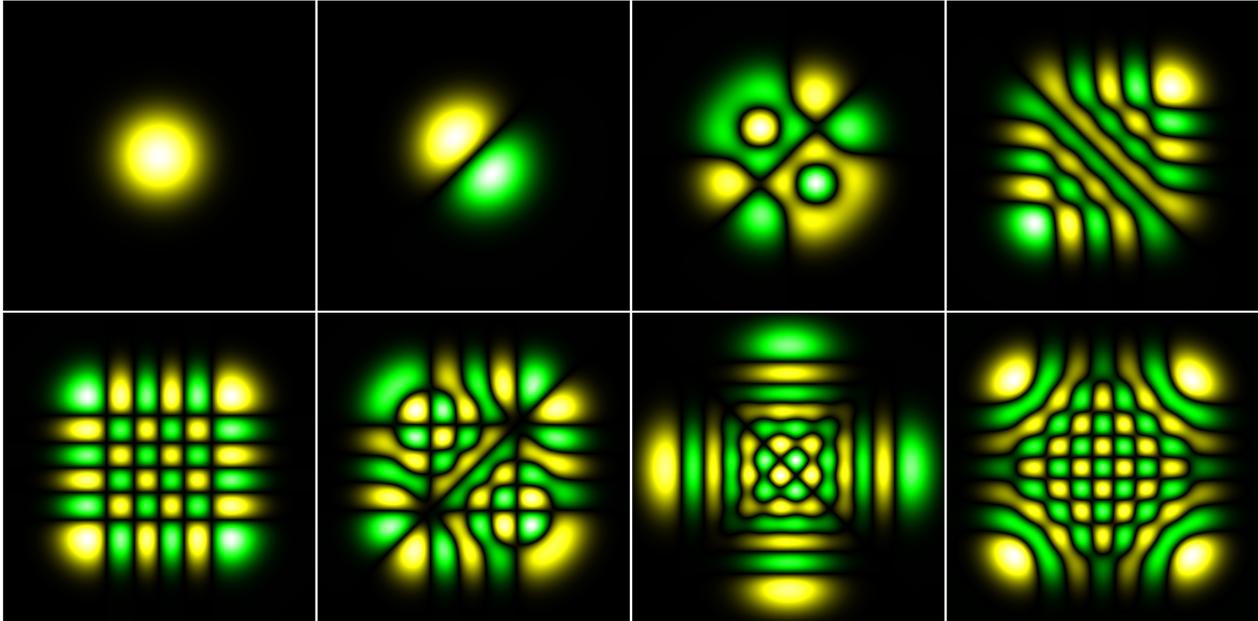


Figure 1: Selected eigenstates for 2D SHO

1. `FourierGridH.cpp`: This is the main body for Fourier grid Hamiltonian method. The method can solve for the eigenfunctions and eigen-energies of any desired potential. You simply need to change the function: `potential2D()`. Some parameters can also be tuned at the top few lines of the `main()` function.
2. `Eigen/`: To do efficient linear algebra operations, such as eigen-decomposition, I have used the C++ library Eigen [9] in `FourierGridH.cpp`. It is self-contained, and you don't need to download any software (which is very convenient).
3. `Plot_eigenstate.m`: This is a Matlab code for visualizing the output from `FourierGridH.cpp`. The output from `FourierGridH.cpp` is a lot of numbers that are hard to understand. Therefore I wrote this Matlab code to help visualize the numbers.
4. `RemoveWhiteSpace.m`: I have export the visualization in `Plot_eigenstate.m` to png files. However, there are some flaws in Matlab's export functionality (it creates a lot of white margin at the edge). This code is used to fix the flaws.

So after changing to your desired potential and parameters, you only need to type

```
g++ FourierGridH.cpp -o FourierGridH
```

to create the executable file `FourierGridH`. Then by typing

```
./FourierGridH
```

the eigen-energy will be outputted to the screen from ground state to more excited states. And a file named `top_eigenstates.txt` storing the eigenfunctions will also be created. (the number of states depends on your parameter) Now, to visualize your result, change the parameters in `Plot_eigenstate.m` to be the same as `FourierGridH.cpp`. Then simply run the Matlab code. A lot of interesting pictures will be created in the `FGH/` folder, including the potential and the beautiful excited energy eigenstates.

2.3 Some Results

In this subsection, I will present some results solved using my implementation. Let us first consider a very simple situation: the 2D simple harmonic oscillator. This problem can be solved analytically,

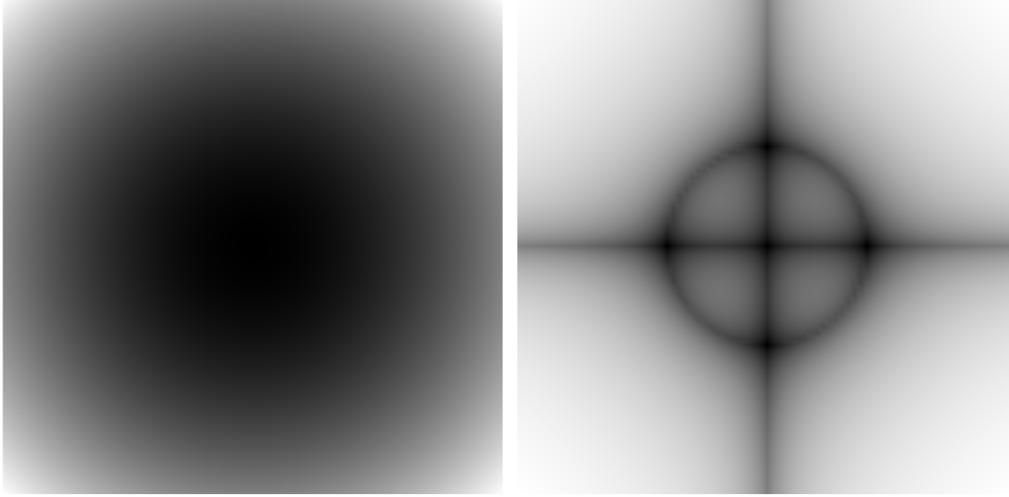


Figure 2: Potential visualization for SHO (left) and a special potential (right)

so it can serve as a check on whether the method is doing correctly or not. Recall that by using ladder operator (for more details, see page 90 in [17]), we can find that the energy eigenvalues are

$$E_{n,m} = (n + \frac{1}{2})\hbar\omega + (m + \frac{1}{2})\hbar\omega = (n + m + 1)\hbar\omega, \forall n, m \in \mathbb{N} \cup \{0\},$$

where $\omega = \sqrt{k/m}$. In my implementation, I am using $k = m = \hbar = 1$, and by running the code, we find the first 10 energy eigenvalues to be

$$1.0000, 2.0000, 2.0000, 3.0000, 3.0000, 3.0000, 4.0000, 4.0000, 4.0000, 4.0000,$$

which agrees very well with the analytical solution.

In Figure 1, we present some selected eigenstates visualization using my Matlab implementation. (For the lowest 150 excited states, please refer to this [dropbox folder](#)⁴) Note that in Section 2.1, we have prove that the eigenfunctions can always taken to be real. Therefore we can use 1D color to visualize the wave function. Green color corresponds to the positive value, while yellow is negative (black is zero). Due to the intrinsic grid discretization of wave function, the original figure is very bulky, therefore I have perform some smoothing technique to create better visualization. As you can see, even for the well-known simple harmonic oscillator, high energy eigenstates can still look very strange and interesting.

The power of Fourier grid Hamiltonian method lies in it's ability to handle arbitrary potential. Here I consider a special potential similar to putting positive charge along x, y -axis and along $r = 1$ circle. The potential can be seen in Figure 2, where darker color means lower potential. Some selected eigenstates can be seen in Figure 3 (For the lowest 150 excited states, please refer to this [dropbox folder](#)⁵).

Before getting into more complicated method, let me summarize the advantage of using Fourier grid Hamiltonian method.

1. It is very general: There are no restriction on the potential form, and it can solve for very high energy eigenstate.
2. It is very accurate: The energy value it obtain is very accurate. And is basically the most accurate method to date.

⁴Or you can simply copy this link: <https://goo.gl/PP5vNZ>

⁵Or you can simply copy this link: <https://goo.gl/lnhQGO>

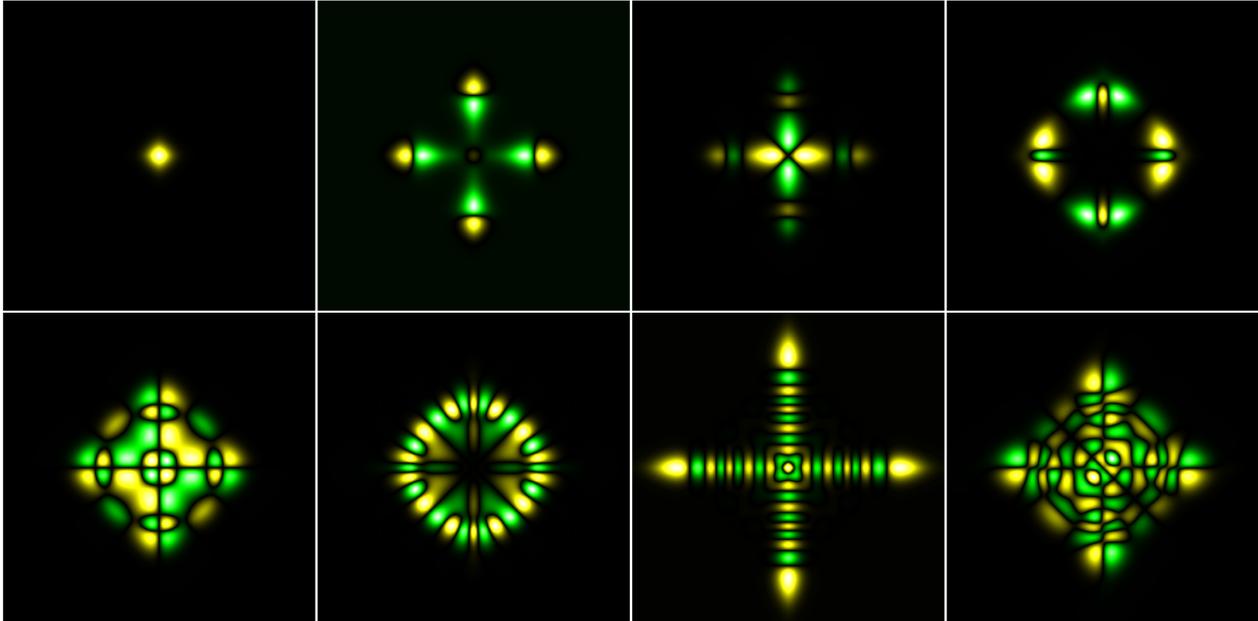


Figure 3: Selected eigenstates for the special potential

It looks like a very nice method, but the problem is it does not scale well. Notice that it solves the problem by discretizing the s -dim wave function ψ into N^s grid points (in my 2D case, $s = 2$). So the total time complexity is $O(N^{3s})$ due to eigenvalue decomposition of a $N^s \times N^s$ matrix.

Now let us consider the electron structure of H_2 molecule under Born-Oppenheimer approximation (i.e. nucleus is fixed), we would have $s = 6$. For a very coarse grid with $N = 21$, we would need about $21^{18} \approx 10^{24}$ computations to apply Fourier grid Hamiltonian method, which would take about 3×10^7 years for an ordinary PC to finish it. Even a super computer (about 1000000 faster than ordinary PC) would still take about 30 years to finish it. This is completely unacceptable. Nevertheless, Fourier grid Hamiltonian method is very useful in low-dimensional setting.

3 Quantum Monte Carlo

In the previous section, we discussed about the Fourier grid Hamiltonian method. It is very powerful, and can compute very high energy eigenstate that are hard to imagine before the computation. However, the major drawback is that it has bad scalability when applying to many-body system. In this section, I will present a more advanced technique, the "Quantum Monte Carlo" method [2, 8], that is able to efficient solve for many-body system under certain condition. The conditions are listed as follow, which will be used later to derive an efficient solver for the difficult N-body problem.

1. We only solve for the ground state wave function: This condition is the same as the Nobel-prize-winning density functional theory introduced in Section 1.2. Note that in many applications, people are mostly interested in the ground state property of the quantum system. Thus it is valuable to consider only the ground state.
2. The ground state wave function has the same sign everywhere: In Proposition 1, we have shown that the eigenfunction can always taken to be real. Furthermore, when ground state is considered, the wave function generally has the same sign everywhere. For example, in Hydrogen atom or in simple harmonic oscillator. But it is not the case for Fermion system, because it's wave function must be antisymmetric. Since it greatly complicates the problem, I will not dive into this in detail.

These are the condition for the standard Quantum Monte Carlo method, the "Diffusion Monte Carlo" method that I will be presenting. There are other variants with different conditions and different applications. For example, it is possible to extend the method to calculate the density matrix of the quantum system in finite temperature [20].

3.1 Method Description

Recall that our story started from Dirac's great vision in the difficulty and the usefulness of solving the equation governing quantum systems. It is surprising that the origin of this method also dates back to Dirac. The story begins at 1933, in another of his legendary paper, "The Lagrangian in Quantum Mechanics" [5]. In Equation 9, page 68 (the fifth page of his paper), he made the following mysterious remark:

$$(q_{t+dt}|q_t) \text{ corresponds to } \exp[iLdt/\hbar], \quad (8)$$

where q_t is the canonical coordinates of the system in time t , and L is the classical Lagrangian $T - V$. This is the core relation we will be using in developing quantum Monte Carlo method. However, Dirac did not state clearly on what "corresponds to" mean and this relation was left unnoticed until 1948.

About 15 years later, Richard Feynman accidentally encountered this interesting statement. He was invigorated by it and later developed the very well known path integral formulation of quantum mechanics in his 1948 paper: "Space-time approach to non-relativistic quantum mechanics" [7]. The basic idea is that we can use an integration over infinitely many paths to compute the time propagation of wave function. The contribution of each path is a unit modular complex number,

$$e^{iS/\hbar}, \text{ where } S = \int (T - U)dt \text{ is the classical action corresponding to the path.}$$

Let us now present the correct equation for Relation 8. We consider an N particle system in d -dimensional space, each with mass m_i . The Hamiltonian operator is

$$\hat{H} = \hat{K} + \hat{V} = \left(\sum_{i=1}^N \sum_{j=1}^d \frac{\hat{P}_{ij}^2}{2m_i} \right) + V(\hat{r}_{11}, \dots, \hat{r}_{Nd}),$$

where \hat{P}_{ij} is the momentum operator on i -th particle's j -th dimension, and \hat{r}_{ij} is the position operator on i -th particle's j -th dimension. In the following context, I will use a short hand notation for the position of the N particles

$$\vec{R} = [\vec{r}_1, \dots, \vec{r}_N] \in \mathbb{R}^{dN}.$$

Then the correct form for Relation 8 based on Feynman's path integral formulation is

$$\psi(\vec{R}, t + dt) = \alpha \int d\vec{R}' \exp\left(\frac{i}{\hbar}Ldt\right) \psi(\vec{R}', t), \quad (9)$$

where ψ is the N -body wave function, the integration is taken over the whole space and $L = T(\vec{R}, \vec{R}', dt) - V(\vec{R})$ with

$$\alpha = \prod_{i,j} \sqrt{\frac{m_i}{2\pi\hbar i dt}} \text{ and } T(\vec{R}, \vec{R}', dt) = \sum_{ij} \frac{1}{2} m_i \left(\frac{r_{ij} - r'_{ij}}{dt} \right)^2.$$

Note that we are only considering straight lines rather than some arbitrary paths. This is because for infinitesimal time interval, any path can be regarded as a straight line. For completeness, I have presented my own derivation for Equation 9 in Appendix A.

With this powerful tool at hand, we are ready to dive into the idea of Quantum Monte Carlo (QMC). The basic ingredients for this method are

1. Propagation in Imaginary Time to Generate Ground State.
2. Wave Function as Unnormalized Probability Density Function.
3. Gaussian Random Walk due to Kinetic Energy Contribution.
4. Death and Birth Process due to Potential Energy Contribution.

In the following content, I will be adding the ingredients one-by-one to derive the intellectually interesting QMC method. Along the way, I will refer to the two conditions presented in the beginning of Section 3.

Let us first define the energy eigenfunctions to be $\phi_n(\vec{R}), \forall n = 0, 1, \dots, \infty$, with their corresponding energy eigenvalues $E_0 < E_1 < E_2 < \dots$ arranged in increasing order. By Sturm-Liouville theory, we can decompose any initial wave function as

$$\psi(\vec{R}, 0) = \sum_{n=0}^{\infty} c_n \phi_n(\vec{R}).$$

By Schrodinger's equation, we then have

$$\psi(\vec{R}, t) = \sum_{n=0}^{\infty} c_n \phi_n(\vec{R}) \exp\left(-\frac{i}{\hbar} E_n t\right). \quad (10)$$

If we define $\tau = it$, and propagate in τ , the imaginary time, rather than t , we obtain

$$\psi(\vec{R}, \tau) = \sum_{n=0}^{\infty} c_n \phi_n(\vec{R}) \exp\left(-\frac{E_n}{\hbar} \tau\right) = \exp\left(-\frac{E_0}{\hbar} \tau\right) \sum_{n=0}^{\infty} c_n \phi_n(\vec{R}) \exp\left(-\frac{E_n - E_0}{\hbar} \tau\right).$$

Therefore, for sufficiently large τ , we find that

$$\exp\left(\frac{E_0}{\hbar} \tau\right) \psi(\vec{R}, \tau) \rightarrow c_0 \phi_0(\vec{R}), \quad (11)$$

only the ground state remains if $c_0 \neq 0$. Recall that this is our target, the ground state wave function of the N-body quantum system. This is the basic idea of QMC's first ingredient, also known as the Wick rotation of time. Similarly, we can apply Wick rotation of time on Equation 9 to obtain

$$\psi(\vec{R}, \tau + d\tau) = \left(\prod_{i,j} \sqrt{\frac{m_i}{2\pi\hbar d\tau}} \right) \int d\vec{R}' \exp\left(-\frac{d\tau}{\hbar} \left(V(\vec{R}) + \sum_{ij} \frac{1}{2} m_i \left(\frac{r_{ij} - r'_{ij}}{d\tau} \right)^2 \right)\right) \psi(\vec{R}', \tau), \quad (12)$$

Note that due to the dt in $T(\vec{R}, \vec{R}', dt)$, we now have the same sign for both T and V .

The next ingredient is to consider the wave function, a complex function, as an unnormalized probability density function. This is not the same as Born's interpretation of treating $\psi^* \psi$ as the probability density function. We are treating the wave function itself as the probability density function. But why is such interpretation valid? Let us justify this interpretation by looking at Equation 12. We see that everything is positive, therefore if $\psi(\vec{R}', \tau)$ is positive everywhere, so will $\psi(\vec{R}', \tau + d\tau)$. Thus by starting with a positive wave function, we can ensure that the wave function at any later time (imaginary time) will always be positive everywhere. Hence we can regard the wave function as an unnormalized probability density function with different normalization constant at different time. This also leads to the second restriction for using QMC. By Proposition 2, we see that c_0 will vanish if the ground state wave function does not have the same sign everywhere. And we require $c_0 \neq 0$ to find the ground state wave function, thus we arrived at the second restriction stated at the beginning.

Proposition 2. If we start with a positive wave function $\psi(\vec{R}, 0)$, then $c_0 \neq 0$ if and only if the ground state wave function has the same sign everywhere.

Proof. If the ground state has the same sign everywhere, we can see that

$$c_0 = \int d\vec{R} \phi_0^*(\vec{R})\psi(\vec{R}, 0) \neq 0.$$

For the other direction, if $c_0 \neq 0$, then by Equation 11 and using the fact that $\psi(\vec{R}, \tau)$ is positive everywhere for all τ , we can see that the ground state wave function must have the same sign everywhere. \square

If we regard $\psi(\vec{R}, \tau)$ as an unnormalized probability density function (PDF), we can sample finite points $\vec{R}_k \in \mathbb{R}^{dN}$ from the wave function using the following PDF

$$\rho(\vec{R}) = \frac{\psi(\vec{R}, \tau)}{\int d\vec{R}' \psi(\vec{R}', \tau)}.$$

For sufficiently large τ , by applying Equation 11, we found that the finite points \vec{R}_k are equivalent to those sampled from the ground state wave function

$$\rho(\vec{R}) = \frac{\phi_0(\vec{R})}{\int d\vec{R}' \phi_0(\vec{R}')} = \frac{\psi(\vec{R}, \tau)}{\int d\vec{R}' \psi(\vec{R}', \tau)}. \quad (13)$$

This is because $\psi(\vec{R}, \tau)$ is proportional to $\phi_0(\vec{R})$ for sufficiently large τ . Thus the density of the sampled points is the ground state wave function itself. So the problem now is how to sample from $\psi(\vec{R}, \tau)$? This is where path integral formulation comes into play. The process is like mathematical induction, we assume that we are able to sample from $\psi(\vec{R}, \tau)$, then we construct a way to sample from $\psi(\vec{R}, \tau + d\tau)$. We first rewrite Equation 12 as follows

$$\psi(\vec{R}, \tau + d\tau) = \exp\left(-\frac{d\tau}{\hbar}V(\vec{R})\right) \int d\vec{R}' \prod_{ij} \frac{1}{\sqrt{2\pi\sigma_i}} \exp\left(-\frac{1}{2}\left((r_{ij} - r'_{ij})/\sigma_i\right)^2\right) \psi(\vec{R}', \tau), \quad (14)$$

where $\sigma_i = \sqrt{\hbar d\tau/m_i}$. We first neglect the contribution of $V(\vec{R})$ and focus on

$$\psi(\vec{R}, \tau + d\tau) = \int d\vec{R}' \prod_{ij} \frac{1}{\sqrt{2\pi\sigma_i}} \exp\left(-\frac{1}{2}\left((r_{ij} - r'_{ij})/\sigma_i\right)^2\right) \psi(\vec{R}', \tau). \quad (15)$$

We can easily see that the right hand side contains a Gaussian distribution with standard deviation σ_i for different dimensions (corresponding to different particles). A second look on the equation give us a surprising way to sample points from $\psi(\vec{R}, \tau + d\tau)$. We simply sample a point \vec{R} from $\psi(\vec{R}, \tau)$ and apply a one step Gaussian random walk to the sampled point. More precisely, we sample a vector $\Delta\vec{R} \in \mathbb{R}^{dN}$ from a high-dimensional zero mean Gaussian distribution with the correct covariance matrix (constructed using σ_i). Then the point $\vec{R} + \Delta\vec{R}$ can be seen to be sampled from $\psi(\vec{R}, \tau + d\tau)$. This is the third ingredient of QMC, Gaussian random walk, due to the kinetic energy contribution in the Hamiltonian.

For the final ingredient of QMC, we have to take the potential into account. Before doing so, let us review the algorithm that we have designed up until now. At $\tau = 0$, we sampled a finite number of points (e.g. 10000 points) from an arbitrary positive function (e.g. Dirac's delta function). To be consistent with other literature, let's call the points replicas. And at each time point, we apply one step of Gaussian random walk on the 10000 replicas. Note that replicas do not exist physically, they are propagating in imaginary time and use wave function itself as the probability density function. Now we are ready to add in the final ingredient of QMC. In the previous algorithm, we have neglected $\exp\left(-\frac{d\tau}{\hbar}V(\vec{R})\right)$ in Equation 14. The potential energy contribution can be added by giving the replicas the ability to reproduce and die. At each time step, we do the following

1. Perform Gaussian random walk for each replicas independently.

2. Calculate the average value \bar{V} of the potential $V(\vec{R})$ for the living replicas.
3. For each replica, sample a discrete value X from either

$$\lfloor \exp(-\frac{d\tau}{\hbar}(V(\vec{R}) - \bar{V})) \rfloor \text{ or } \lfloor \exp(-\frac{d\tau}{\hbar}(V(\vec{R}) - \bar{V})) \rfloor + 1,$$

with expectation value $= \exp(-\frac{d\tau}{\hbar}(V(\vec{R}) - \bar{V}))$.

4. If $X = 0$, then the replica dies. If $X = 1$, the replica continue to lives. If $X > 1$, the replica reproduce $X - 1$ offsprings at the same location and continue to live.

As you can see, replicas wandering at places with lower potential will reproduce more, while replicas at higher potential will die with higher probability. Together, the density of the replicas is proportional to $\exp(-\frac{d\tau}{\hbar}(V(\vec{R}) - \bar{V})) \times$ (Equation 15). Because \bar{V} is a constant, the density is also proportional to Equation 14. Therefore we can regard the replicas to be sampled from $\psi(\vec{R}, \tau + d\tau)$, which is exactly the target we aim to do at the beginning. The use of \bar{V} is only to ensure that the replica number is roughly constant throughout the Quantum Monte Carlo process. However using \bar{V} can still lead to unstable number of replicas. After some trial and error, I found that instead of using \bar{V} , we can use the following

$$\tilde{V} \equiv \bar{V} + K * \left(1 - \frac{\text{current number of replicas}}{\text{initial number of replicas}}\right),$$

where K is a constant roughly in between $1 \sim 10$. This does not change the underlying physics since the use of \bar{V} is also an arbitrary choice.

After the long journey, we finally arrived at the complete algorithm. Initially, we throw a large number of replicas into the empty space. Then at each time step, we perform a Gaussian random walk followed by a birth and death process for each replicas. After a large number of time steps, the replicas can now be seen to be sampled from the ground state wave function. Then, we can start accumulating the position of each replicas for the following time steps. The accumulated density distribution is proportional to the ground state wave function. And all the ground state property can be computed from the distribution. I found visualization to be a very good way to learn and understand a subject. Therefore, I have designed a dynamical visualization, and have uploaded to [YouTube](#)⁶. In the video, I demonstrated the QMC computation process when calculating the ground state wave function for a wizard-hat potential. See Figure 4 for static visualization. This visualization can be reproduced using my codes given in `bump_potential` folder.

As an example, we can calculate the ground state energy through the distribution of the replicas. After propagating for a few thousands of time steps (so ground state is obtained), E_0 is simply the average of the potential $V(\vec{R})$ for the living replicas. This procedure can be justified by Proposition 3 and Equation 13.

Proposition 3. Let K be the number of living replicas, each with position \vec{R}_k , then

$$\frac{1}{K} \sum_k V(\vec{R}_k) \approx \int V(\vec{R}) \frac{\phi_0(\vec{R})}{\int \phi_0(\vec{R}') d\vec{R}'} d\vec{R} = \frac{\int V(\vec{R}) \phi_0(\vec{R}) d\vec{R}}{\int \phi_0(\vec{R}') d\vec{R}'} = E_0.$$

Proof. Since ϕ_0 is the ground state wave function,

$$\begin{aligned} E_0 \phi_0(\vec{R}) &= \left(\sum_{ij} -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial r_{ij}^2} + V(\vec{R}) \right) \phi_0(\vec{R}). \\ \implies \int E_0 \phi_0(\vec{R}) d\vec{R} &= \int \left(\sum_{ij} -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial r_{ij}^2} + V(\vec{R}) \right) \phi_0(\vec{R}) d\vec{R}. \end{aligned}$$

⁶Or you can simply copy this link: <https://youtu.be/tgJXdQFXmN0>

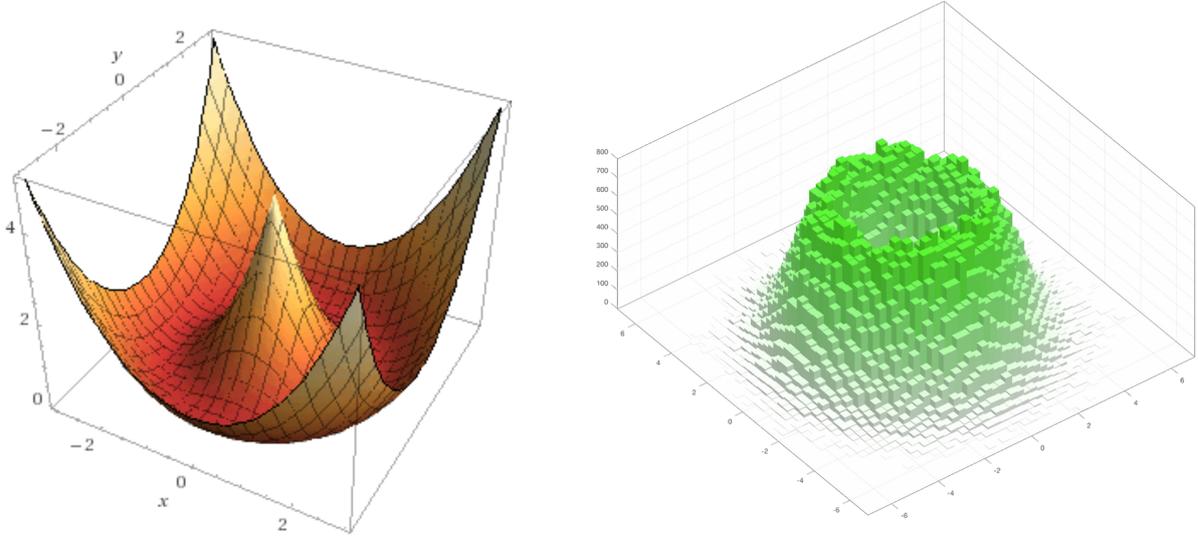


Figure 4: Visualization of Quantum Monte Carlo calculation on a wizard-hat potential.

Let us suppose that $\frac{\partial}{\partial r_{ij}} \phi_0(\vec{R})$ is zero if any coordinate is infinity, which is physically correct when considering bound system. Therefore

$$\sum_{i,j} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial r_{ij}^2} \phi_0(\vec{R}) dr_{11} \dots dr_{Nd} = 0.$$

Thus we have

$$E_0 \int \phi_0(\vec{R}) d\vec{R} = \int V(\vec{R}) \phi_0(\vec{R}) d\vec{R}.$$

□

3.2 Code Usage

Similar to Section 2.2, the codes are publicly available on [GitHub](#)⁷. The codes for QMC can be found in `QMC/` folder. QMC is very versatile, it can handle different number of particles in any dimensional space. Thus different visualization method has to be used accordingly. Some of the problems are even very hard to visualize, for example three particles in 3D SHO. Therefore I have created several different folders, each corresponds to a different situation.

The basic usage is very simple, which holds for all the folders. In the terminal, simply type

```
g++ -std=c++0x QMC.cpp -o QMC; ./QMC
```

It will automatically compile and run. After waiting several seconds, the ground state energy will be shown on the screen. Two txt files will be created, `walkerN.txt` stores the number of replicas in each time step, and `QMC_system.txt` stores the position \vec{R} of each replica at each time step. For the format of `QMC_system.txt`, please see the function `void export_QMC_system()` in `QMC.cpp`. If `Plot_QMC.m` is available in the folder, you can run it in Matlab to create a visualization of the results in `QMC_system.txt`.

3.3 Some examples

Let me now present some examples obtain using my code `QMC.cpp`. I have calculated the ground state energy for three different scenarios: (1) three particles in 3D simple harmonic oscillator; (2)

⁷Or you can simply copy this link: <https://goo.gl/gdJ3Rn>

Table 1: Comparison of my QMC calculation with analytical or experimental results.

Scenario	Simulated ground state energy	True ground state energy
3 Particles in 3D SHO	$4.498019 \pm 0.028470 \hbar\omega$	$9 * \frac{1}{2} \hbar\omega$
Hydrogen Atom	$-13.755569 \pm 0.253150 \text{ eV}$	-13.606 eV
Hydrogen Molecule	$-31.957334 \pm 0.423355 \text{ eV}$	-31.675 eV ⁸

hydrogen atom; (3) hydrogen molecule. The ground state energy for these scenarios are known through analytical calculation or experimental measurement. A comparison between the QMC computation and the known ground state energy is shown in Table 1. We can see that the simulated results agree well with the true ground state energy using only a few thousands of replicas. Note that for three particles in 3D SHO, we would have a 9D wave function, which can not be solved by Fourier grid Hamiltonian method, but can easily be solve using QMC.

To demonstrate the power of QMC, I have also designed some artificial molecules. I placed the nuclei at certain places with an electron orbiting around each nucleus. I then used the Born-Oppenheimer approximation to calculate the wave function of the electrons. Finally, I computed the electron density iso-surface in Matlab. The visualizations are shown in Figure 5. I have visualized two iso-surface for each artificial molecule, the lower density is colored grey, while the higher density is colored blue. It should be clear, where the nuclei are placed. To reproduce the results, please refer to folders `sqaure_molecule/` and `tetrahedron_molecule/`.

An important note is that even though I refer to them as electrons and nuclei, it only means their interaction potential follows the same form as electrons and nuclei. The electrons are not treated as Fermions in this simulation. They are actually electron-like Bosons. It is actually very difficult to use quantum Monte Carlo method in Fermion system. The problem is deeply rooted in any Quantum Monte-Carlo based approach (see [22]).

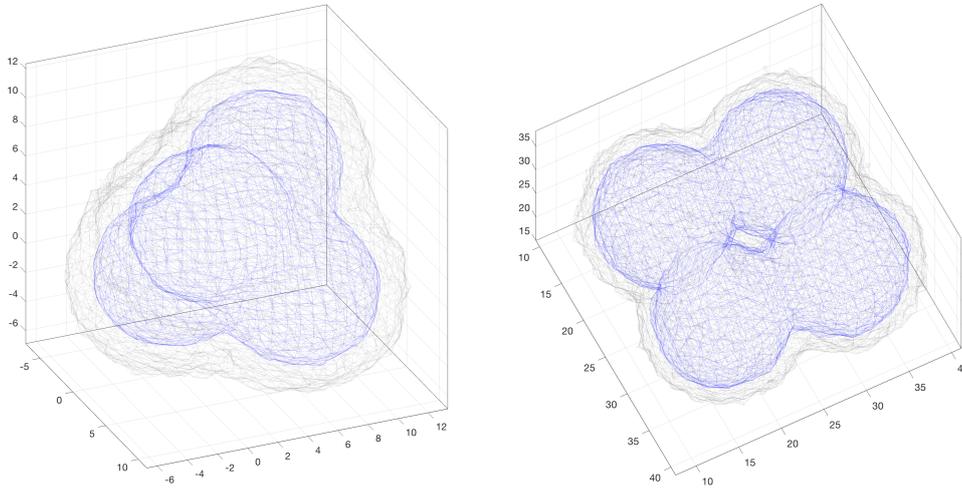


Figure 5: Visualization of the density iso-surface of artificial molecules.

4 Conclusion

Starting from Dirac's prophetic vision, we have walk through two well-known methods to solve any quantum system. The first method, Fourier grid Hamiltonian method is very powerful and accurate but is only applicable for small system. However, as human has strong analytical ability,

⁸The value is obtained from <http://www.millsian.com/summarytables/SummaryTables022709S.pdf> through experimental measurement.

we are able to manually reduce the dimensionality of the system. Then the reduced system can be solved very accurately using FGH. As a result, this straightforward method has continue to contribute in real world applications even till now.

On the other hand, quantum Monte-Carlo method can easily scale to multi-particle system. The beauty of this method is that it is embarrassingly parallel, if you have 1000 cores, you can easily speed it up to ≈ 1000 times. In many parallel algorithms, we often only gain ≈ 500 times speed-up due to communication cost between different cores. As there is no free lunch, the computational benefit comes with certain restrictions. The first restriction is that it can only calculate ground state property. It is favorable if we can remove this restriction and scientists have continue to pursue in this direction. However, for the second restriction, it is basically impossible to apply QMC on Fermion system. It has been shown theoretically that solving Fermion system using QMC is NP-hard, i.e. we would need a non-deterministic Turing machine to solve the problem in polynomial time (see [22]). Nevertheless the theoretical results holds only to standard QMC. For example, density functional theory has already been successfully apply to Fermion system. It would be very interesting if we can combine these two methods to obtain a more powerful computational algorithm to fulfill Dirac's vision.

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Appendices

A Derivation of N-Body Path Integral Formulation

For completeness, I will present my own derivation of Feynman’s path integral formulation for N-body systems in d-dimensional space using simple ideas. In the following context, I will use a short hand notation for the position of the N particles

$$\vec{R} = [\vec{r}_1, \dots, \vec{r}_N] \in \mathbb{R}^{dN}.$$

Similar to 1D case, we have the following completeness relation,

$$\int |\vec{R}\rangle \langle \vec{R}| d\vec{R} = \hat{1}, \quad (16)$$

where the integral is taken over the entire space.

By using general Schrodinger’s equation 2, we have

$$\hat{H}|\psi, t\rangle = i\hbar \frac{|\psi, t + dt\rangle - |\psi, t\rangle}{dt} \implies |\psi, t + dt\rangle = \left(\hat{1} - \frac{i}{\hbar} \hat{H} dt\right) |\psi, t\rangle.$$

We then decompose Hamiltonian to kinetic and potential contributions, $\hat{H} = \hat{K} + \hat{V}$, thus

$$\hat{1} - \frac{i}{\hbar} \hat{H} dt = \hat{1} - \frac{i}{\hbar} (\hat{K} + \hat{V}) dt = \left(\hat{1} - \frac{i}{\hbar} \hat{V} dt\right) \left(\hat{1} - \frac{i}{\hbar} \hat{K} dt\right),$$

by neglecting second order infinitesimal quantity dt^2 . Therefore we have

$$\langle \vec{R} | \psi, t + dt \rangle = \langle \vec{R} | \left(\hat{1} - \frac{i}{\hbar} \hat{V} dt\right) \left(\hat{1} - \frac{i}{\hbar} \hat{K} dt\right) | \psi, t \rangle.$$

Using the natural assumption that \hat{V} depends only on \vec{R} , note that this also includes interaction force between different bodies, we have

$$\begin{aligned} \left(\hat{1} + \frac{i}{\hbar} \hat{V} dt\right) |\vec{R}\rangle &= \left(1 + \frac{i}{\hbar} V(\vec{R}) dt\right) |\vec{R}\rangle \implies \\ \langle \vec{R} | \psi, t + dt \rangle &= \left(1 - \frac{i}{\hbar} V(\vec{R}) dt\right) \langle \vec{R} | \left(\hat{1} - \frac{i}{\hbar} \hat{K} dt\right) | \psi, t \rangle. \end{aligned}$$

Neglecting the second order infinitesimal quantity dt^2 again, we get

$$\langle \vec{R} | \psi, t + dt \rangle = e^{-\frac{i}{\hbar} V(\vec{R}) dt} \langle \vec{R} | e^{-\frac{i}{\hbar} \hat{K} dt} | \psi, t \rangle. \quad (17)$$

Now we only need to focus on the kinetic part. Using Equation 16, we have

$$\langle \vec{R} | e^{-\frac{i}{\hbar} \hat{K} dt} | \psi, t \rangle = \int d\vec{R}' \langle \vec{R} | e^{-\frac{i}{\hbar} \hat{K} dt} | \vec{R}' \rangle \langle \vec{R}' | \psi, t \rangle. \quad (18)$$

Next we need to calculate $\langle \vec{R} | e^{-\frac{i}{\hbar} \hat{K} dt} | \vec{R}' \rangle$. The first observation is that

$$\hat{K} = \sum_{i=1}^N \sum_{j=1}^d \frac{\widehat{P}_{ij}^2}{2m_i} \implies e^{-\frac{i}{\hbar} \hat{K} dt} = \int d\vec{P} d\vec{P}' | \vec{P}' \rangle \langle \vec{P}' | \exp\left(-\frac{i}{\hbar} \sum_{ij} \frac{\widehat{P}_{ij}^2}{2m_i}\right) | \vec{P} \rangle \langle \vec{P} |,$$

where \vec{P} is a short-hand notation for the momentum of the N particles

$$\vec{P} = [\vec{p}_1, \dots, \vec{p}_N] \in \mathbb{R}^{dN}.$$

Because $|\vec{P}\rangle$ is the eigenstate for $\widehat{P}_{ij}, \forall i = 1 \dots N, j = 1 \dots d$, we have

$$e^{-\frac{i}{\hbar} \hat{K} dt} = \int d\vec{P} | \vec{P} \rangle \exp\left(-\frac{i}{\hbar} \sum_{ij} \frac{P_{ij}^2}{2m_i}\right) \langle \vec{P} |.$$

Recalling that

$$\langle \vec{R} | \vec{P} \rangle = \langle \vec{r}_1, \dots, \vec{r}_N | \vec{p}_1, \dots, \vec{p}_N \rangle = \frac{1}{\sqrt{2\pi\hbar}^{Nd}} \exp\left(\frac{i}{\hbar} \sum_{ij} p_{ij} r_{ij}\right),$$

we get

$$\langle \vec{R} | e^{-\frac{i}{\hbar} \hat{K} dt} | \vec{R}' \rangle = \frac{1}{(2\pi\hbar)^{Nd}} \int d\vec{P} \exp\left(-\frac{i}{\hbar} \sum_{ij} \frac{P_{ij}^2}{2m_i} + \frac{i}{\hbar} \sum_{ij} p_{ij} (r_{ij} - r'_{ij})\right).$$

After some simple integration (since we can treat all i, j independently), we obtain

$$\langle \vec{R} | e^{-\frac{i}{\hbar} \hat{K} dt} | \vec{R}' \rangle = \frac{1}{(2\pi\hbar)^{Nd}} \prod_{i,j} \sqrt{\frac{2\pi\hbar m_i}{idt}} \exp\left(\frac{i}{\hbar} dt \cdot \frac{1}{2} m_i \left(\frac{r_{ij} - r'_{ij}}{dt}\right)^2\right).$$

With some reorganization, we get

$$\langle \vec{R} | e^{-\frac{i}{\hbar} \hat{K} dt} | \vec{R}' \rangle = \prod_{i,j} \sqrt{\frac{m_i}{2\pi\hbar i dt}} \exp\left(\frac{i}{\hbar} dt \cdot \frac{1}{2} m_i \left(\frac{r_{ij} - r'_{ij}}{dt}\right)^2\right).$$

Notice that the phase in the exponential is proportional to the classical kinetic energy times dt . Thus we can rewrite them as

$$\langle \vec{R} | e^{-\frac{i}{\hbar} \hat{K} dt} | \vec{R}' \rangle = \alpha \exp\left(\frac{i}{\hbar} dt \cdot T(\vec{R}, \vec{R}', dt)\right),$$

where we use the following definitions

$$\alpha = \prod_{i,j} \sqrt{\frac{m_i}{2\pi\hbar i dt}} \quad \text{and} \quad T(\vec{R}, \vec{R}', dt) = \sum_{ij} \frac{1}{2} m_i \left(\frac{r_{ij} - r'_{ij}}{dt}\right)^2.$$

Combining with Equation 17, 18, we get

$$\langle \vec{R} | \psi, t + dt \rangle = \alpha \int d\vec{R}' \exp\left(\frac{i}{\hbar} dt \cdot (T(\vec{R}, \vec{R}', dt) - V(\vec{R}))\right) \langle \vec{R}' | \psi, t \rangle. \quad (19)$$

This is the infinitesimal path integral formulation I have been using in the main text. We can use the same derivation on $|\psi, t + dt\rangle$ again to obtain $|\psi, t + 2dt\rangle$. And by applying infinite many times, we arrive at the original finite time path integral formulation.

$$\langle \vec{R}_f | \psi, t_f \rangle \propto \int_{\text{all path ending at } \vec{R}_f} \mathcal{D}[\vec{R}(t)] \exp\left(\frac{i}{\hbar} \int_{t_i}^{t_f} dt (T - V)\right) \langle \vec{R}_i | \psi, t_i \rangle,$$

where \vec{R}_i is the starting configuration (not fixed) of the path.