Quantum Systems

• Introduction

Simulating Quantum Systems? Indistinguishable, x and p_x cannot be specified simultaneously (no Molecular Dynamics), etc.

How about obtain *probability function*: $P(x,t) = |\Psi(x,t)|^2$?

But to solve the diffusion equation:

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2} \ ,$$

is very time consuming!

It is even worse for $P(x_1, x_2, \cdots, x_N, t)$.

Recall Random Walk Solution of the diffusion equation, there is a hope!

- **QM Review**

$$\int_{-\infty}^{\infty} dx|\Psi(x,t)|^2 = 1 \ .$$

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

Physical quantities have corresponding operators. The expectation or average value of an observer A is given by

$$< A >= \int dx\Psi^*(x,t)A_{op}\Psi(x,t) \ , \qquad A_{op} = \hat{A} \ .$$

If $V(x,t)$ is time-independent, then there exist *stationary solutions*:

$$\Psi(x,t) = \phi(x)Exp[-iEt/\hbar] \ ,$$

and

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\phi(x) = E\phi(x) \ .$$

In general,

$$\Psi(x,t) = \sum_n c_n\phi_n(x)e^{-iE_nt/\hbar} \ ,$$

and

$$c_n = \int dx\phi_n^*(x)\Psi(x,0) \ .$$

- **Bound State Solutions**

  $\phi_n(x)$ and $d\phi_n(x)/dx$ should be: continuous, finite for all x, bounded for large x, single valued.

  For symmetric potential $V(x) = V(-x)$, $\phi(x)$ has definite parity $\rightarrow \phi(-x) = \phi(x)$ or $\phi(-x) = -\phi(x)$.

  Program eigen in BASIC separately distributed.

  Example: a square well potential with

  unit: $\hbar = 1;\ m = 1$.

Euler-Cromer Algorithm:

1. Divide $a < x < b$ into intervals of width Δx. Let $x_s = a + s\Delta x$, where s is an integer. Thus $\phi_s = \phi(x_s)$ and $\phi_s^{'} = \phi^{'}(x_s)$.
2. Specify the parity of $\phi(x)$. For even parity, choose $\phi(0) = 1$ and $\phi^{'}(0) = 0$; For odd parity, choose $\phi(0) = 0$ and $\phi^{'}(0) = 1$.
3. Guess a value for E (important, calls for intuition).
4. Compute $\phi_{s+1}^{'}$ and ϕ_{s+1} by using the algorithm:

$$\phi_{s+1}^{'} = \phi_s^{'} + \phi_s^{''}\Delta x$$

$$\phi_{s+1} = \phi_s + \phi_{s+1}^{'}\Delta x \ .$$

5. Iterate $\phi(x)$ with increasing x until it diverges.
6. Vary E and repeat steps (4) & (5). Find E_0 such that
   (i) when $E < E_0$, $\phi(x)$ diverges with decreasing E;
   (ii) when $E > E_0$, $\phi(x)$ diverges with increasing E.

Note, it is impossible to obtain a numerical solution for $\phi(x)$ that does not diverge at sufficiently large x. (Why?)

How to guess and obtain several eigenvalues?

- **Time-Dependent Schodinger Equation**

Let $t_n = t_0 + n\Delta t,\ x_s = a + s\Delta x$, then

Explicit scheme: (unstable!)

$$\frac{\Psi(x_s, t_{n+1}) - \Psi(x_s, t_n)}{\Delta t} =$$

$$\frac{\Psi(x_{s+1}, t_n) - 2\Psi(x_s, t_n) + \Psi(x_{s-1}, t_n)}{(\Delta x)^2} \ .$$

Implicit scheme:

$$\frac{\Psi(x_s, t_{n+1}) - \Psi(x_s, t_n)}{\Delta t} =$$

$$\frac{\Psi(x_{s+1}, t_{n+1}) - 2\Psi(x_s, t_{n+1}) + \Psi(x_{s-1}, t_{n+1})}{(\Delta x)^2} \ .$$

Visscher's scheme:

$$\Psi(x,t) = R(x,t) + iI(x,t) \ ,$$

$$\frac{dR(x,t)}{dt} = HI(x,t), \qquad \frac{dI(x,t)}{dt} = -HR(x,t) \ .$$

Thus, use the half-step method, one gets

$$R(x, t + \Delta t) = R(x,t) + HI(x, t + \frac{1}{2}\Delta t)\Delta t$$

$$I(x, t + \frac{3}{2}\Delta t) = I(x, t + \frac{1}{2}\Delta t) - HR(x,t)\Delta t \ .$$

Probability function (conserved quantity):

$$P(x,t) = R(x,t)^2 + I(x,t+\frac{1}{2}\Delta t)I(x,t-\frac{1}{2}\Delta t)$$

$$P(x,t+\frac{1}{2}\Delta t) = R(t+\Delta t)R(x,t) + I(x,t+\frac{1}{2}\Delta t)^2 \ .$$

This algorithm is stable if

$$\frac{-2\hbar}{\Delta t} \leq V \leq \frac{2\hbar}{\Delta t} - \frac{2\hbar^2}{(m\Delta x)^2} \ .$$

How to get $R(x,t=0)$ and $I(x,t=\frac{1}{2}\Delta t)$?

Program TDSE in BASIC separately distributed.

- **Variational Methods**

  Variational Principle: for any trial wave function Ψ,

  $$< H >= E[\Psi] = \frac{\int dx \Psi^*(x) H \Psi(x)}{\int dx \Psi^*(x) \Psi(x)} \geq E_0 \ ,$$

  where E_0 is the exact ground state energy of the system.

  The choice of Ψ depends on your physics insights.

  $E[\Psi]$ could have many parameters.

  The integration could either be done analytically or numerically.

  The integrals are *multidimensional* $\rightarrow$
  Monte Carlo Integration.

Importance sampling is essential, rewrite

$$E[\Psi] = \frac{\int dx \Psi^2(x) E_L(x)}{\int dx \Psi^2(x)} \ ,$$

where E_L is called the *local energy*

$$E_L = \frac{H\Psi(x)}{\Psi(x)} \ . \quad (wieghted\ average)$$

Thus, we have the estimate of $E[\Psi]$

$$E[\Psi] = \lim_{n \to \infty} \sum_{i=1}^{n} E_L(x_i) \ ,$$

where n is the number of times that x is sampled from Ψ^2.

However, in general, it is not always possible to use the inverse transform method to generate a nonuniform distribution mimic probability $\Psi^2(x)$.

The solution: *Metropolis algorithm.*

- **Random Walk Quantum Monte Carlo**

Diffusion and Branching Processes

Let $\tau = it/\hbar$ and rewrite the S-equation for a free particle

$$\frac{\partial \Psi(x,\tau)}{\partial \tau} = \frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,\tau)}{\partial x^2} - V(x)\Psi(x,\tau) \ .$$

Diffusion process: the first term, $D = \hbar^2/2m$;

Branching process: the second term,

decreasing(increasing) for $-(+)$.

It is $\Psi \Delta x$ and not $\Psi^2 \Delta x$ which corresponds to the probability distribution of random walkers.

Thus one requires that Ψ be nonnegative!

The general solution of S-equation is

$$\Psi(x,\tau) = \sum_n c_n \phi_n(x) e^{-E_n \tau} \longrightarrow c_0 \phi_0(x) e^{-E_0 \tau} \ .$$

The population of walkers will eventually decay to zero unless $E_0 = 0$. We measure E_0 from an arbitrary reference energy V_{ref} (steady).

Estimation of E_0:

$$E_0 = < V >= \frac{\Sigma\, n_i V(x_i)}{\Sigma\, n_i}$$

$$n_i \ : \ number\ of\ walkers\ at\ x_i\ at\ time\ \tau\ .$$

Algorithm:

1. Place N_0 walkers at the initial set of positions x_i.
2. Compute the reference energy $V_{ref} = \Sigma_i\, V_i/N_0$.
3. Randomly move a walker to the right or left by a fixed step length Δs, such that $(\Delta s)^2 = 2D\Delta\tau$. ($D = 1/2$ in units such that $\hbar = m = 1$.)
4. Compute $\Delta V = V(x) - V_{ref}$ and a random number r of (0,1). If $\Delta V > 0$ and $r < \Delta V \Delta\tau$, remove the walker. If $\Delta V < 0$ and $r < -\Delta V \Delta\tau$, add another walker at x. Otherwise, just leave the walker at x. Assume $\Delta\tau << 1$.

5. Repeat steps 3 and 4 for each of the N_0 walkers and compute the mean potential energy and the actual number of random walkers. The new reference potential is given by

$$V_{ref} = < V > - \frac{a}{N_0 \Delta\tau}(N - N_0) \ ,$$

where N is the new number of random walkers and $< V >$ is their mean potential energy.

6. Repear steps 3-5 until the estimates of the ground state energy $< V >$ have reached a steady state value with only random fluctuations.

Program qmwalk (in BASIC, separately distributed) implements this algorithm for the harmonic oscillator potential.

- **Diffusion QMC**

  An improvement of the random walk algorithm.

  Green's function (propagator):

  $$\Psi(x',\tau) = \int dx G(x',x,\tau)\Psi(x,0) \ .$$

  $$\frac{\partial G}{\partial \tau} = -(H-V)G \ .$$

  $$G(\tau) = e^{-(H-V)\tau} \ .$$

  Let

  $$G_{diff} \equiv e^{-T\Delta\tau} \ , \qquad G_{branch/2} \equiv e^{-\frac{1}{2}(V-V_{ref})\Delta\tau} \ .$$

  Then

  $$\begin{aligned} G(\tau) &\approx G_{branch/2} G_{diff} G_{branch/2} \\ &\equiv e^{-\frac{1}{2}(V-V_{ref})\Delta\tau} e^{-T\Delta\tau} e^{-\frac{1}{2}(V-V_{ref})\Delta\tau} \ , \end{aligned}$$

  and

  $$\begin{aligned} \frac{\partial G_{diff}}{\partial \tau} &= -T G_{diff} \\ \frac{\partial G_{branch/2}}{\partial \tau} &= (V_{ref}-V) G_{branch/2} \ . \end{aligned}$$

  Solutions are (symmetric in x and x'): $D \equiv \hbar^2/2m$,

  $$\begin{aligned} G_{diff}(x',x,\Delta\tau) &= (4\pi D\Delta\tau)^{-1/2} e^{-(x'-x)^2/4D\Delta\tau} \\ G_{branch/2} &= e^{-\left(\frac{1}{2}[V(x)+V(x')]-V_{ref}\right)\Delta\tau} \ . \end{aligned}$$

An example of diffusion QMC in one-dimension:

1. Begin with a set of N_0 walkers. Positions of the walkers are continuous. Put more walkers in the region where the wave function is known to be large.

2. Choose one walker and displace it from x to x'. The new position is chosen from a Gaussian distribution with a variance $2D\Delta\tau$ and zero mean. This change corresponds to the diffusion process.

3. Weight the configuration x' by

$$w(x \to x', \Delta\tau) = e^{-\left(\frac{1}{2}[V(x)+V(x')]-V_{ref}\right)\Delta\tau} .$$

   This change corresponds to the branching process. We make an integer number of copies that is equal on the average to the number w, e.g.,
   INT[w+rand(0,1)], could be 0 (termination).

4. Repeats steps 2 and 3 for all members of the ensemble, thereby creating a new ensemble at a later time $\Delta\tau$. One iteration of the ensemble is equivalent to

$$\Psi(x,\tau) = \int dx G(x,x',\Delta\tau)\Psi(x,\tau-\Delta\tau)$$

5. The quantity of interest $\Psi(x',\tau)$ will be independent of the original ensemble $\Psi(x,0)$ if a sufficient number of MC steps are taken. We must ensure that $N(\tau)$ is kept close to the desired number N_0.

The previous RW algorithm is an approximation to the current one.

Once more, we can use importance sampling to make RWQMC more efficient. The idea is to use an initial guess $\Psi_T(x)$ for the wave function to guide the walkers toward the more important regions of $V(x)$.

Let $f(x,\tau) = \Psi(x,\tau)\Psi_T(x,\tau)$, we have

$$\frac{\partial f}{\partial \tau} = D\frac{\partial^2 f}{\partial x^2} - D\frac{\partial\left[fF(x)\right]}{\partial x} - [E_L(x) - V_{ref}]f \ ,$$

where

$$F(x) = \frac{2}{\Psi_T}\frac{\partial \Psi_T}{\partial x} \ ,$$

and

$$E_L(x) = \frac{H\Psi_T}{\Psi_T} = V(x) - \frac{D}{\Psi_T}\frac{\partial^2 \Psi_T}{\partial x^2} \ .$$

1. Replace $(x - x')^2$ by $(x - x' - D\Delta\tau F(x))^2$ in G_{diff}.
2. Use the Metropolis algorithm for accepting the new position of a walker. The acceptance probability p is given by

$$p = \frac{|\Psi_T(x')|^2 G_{diff}(x, x', \Delta\tau)}{|\Psi_T(x)|^2 G_{diff}(x', x, \Delta\tau)} \ .$$

- **Path Integral Quantum Monte Carlo**

  Will be discussed in Quantum Monte Carlo Weeks