QuantumMonteCarlo Methods

The energy of a many electron system(n-electron)in the state Ψ**(x_1,x_2,……………,x_{3n}**)is given by the value of 3n-dimensional integral–the so called expectation value of the Hamiltonian.

$$\langle E\rangle = \frac{\int \Psi^* H\Psi d\tau}{\int \Psi^*\Psi d\tau} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (24.1)$$

Ψ is the antisymmetric many electron wave function the square of which (i.e. **$|\Psi|^2$)** gives the probability density **at a point** in the 3n-dimensional space. Supposing for the moment that Ψ is known, the 3n-dimensional integral in (1) has to be evaluated and that is no mean task. The evaluation of the many dimensional integral can be facilitated by invoking the Monte-Carlo method.

Let us assume that we have randomly sampled N-points in the whole of the variable space (N large)and at each such point (**i**) the integral $[(\int\Psi^*H\Psi)/\ (\int\Psi^*\Psi)]$ has the value I_i. We can approximate the right hand side of equation (1) as,

$$\frac{\int \Psi^* H\Psi d\tau}{\int \Psi^*\Psi d\tau} = \frac{1}{N}\sum_{i=1}^{N}(\frac{\Psi^*}{\Psi^*})(\frac{H\Psi}{\Psi}) = \frac{1}{N}\sum_{i=1}^{N}(E)_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (24.2)$$

If Ψ is an exact eigenfunction of H, $H\Psi/\Psi$ is a constant that represents the exact energy of the system in the state Ψ at any point ‘i’ in the space of the integration variables. However, for approximate **Ψ,$(H\Psi/\Psi)_I$**would represent only the local energy (εi) which would vary with the point on (i)of the sampling point. In the limit of an infinite number of sampling point (i.e. N $\rightarrow\infty$),the expression **in equation 2** would yield the exact energy E.Since in practice,only a finite numberof sampling points can be used, we must find a suitable weighting function with which the local energy εi must be weighted to produce a satisfactory value of the **many dimensional integral of eqn.1.** If turns out that the a suitable weighting function is provided by the probability density that $|\Psi|^2$represents, as will be clear from thefollowingdemonstration;

$$\langle E\rangle = \frac{\int \Psi^* H\Psi d\tau}{\int \Psi^*\Psi d\tau} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (24.3)$$

$$= \frac{\int \Psi^* \Psi (\frac{H\Psi}{\Psi}) d\tau}{\int \Psi^* \Psi d\tau} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(24.4)}$$

$$= (\int|\Psi|^2(H\Psi/\Psi)\, d\tau) / (\int|\Psi|^2 d\tau) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(24.5)}$$

$$= \int P(r_1 \ldots\ldots\ldots\ldots r_n)\, \varepsilon_1(r_1 \ldots\ldots r_n)\, d\tau \ldots\ldots\ldots\ldots\ldots\ldots \text{(24.6)}$$

where,

$$\mathbf{E_1}(r_1 \ldots r_n) = \frac{(H\Psi(r_1 \ldots\ldots\ldots r_n))}{\Psi(r_1 \ldots\ldots r_n)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(24.7)}$$

is the local energy of the n-electron system for the given configuration,

$$P\,(r_1 \ldots r_n) = (|\Psi|^2) / (\int (|\Psi|^2 d\tau) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(24.8)}$$

is the probability density at the given point in the 3n-dimensional space, E is then given by the integral over the local energy$\varepsilon_1(r_1 \ldots\ldots r_n)$weighted by the probability density $P(r_1 \ldots\ldots r_n)$.If the N sampling points are chosen randomly by a Metropolis algorithm weighted by the probability density, we have,

$$E = \int P(r_1, r_2, \ldots\ldots, r_n)\varepsilon_1(r_1, r_2, \ldots\ldots\ldots, r_n) d\tau \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(24.9)}$$

$$= \frac{1}{N}\sum_{i=1}^{N} \varepsilon_1(r_1^{(i)} \ldots\ldots r_n^{(i)}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(24.10)}$$

which is just the average of the local energies at all the sampling points generated. The resulting algorithm has become known as the **variational** Quantum Monte Carlo method **(QMC).**

There is a variant of the QMC called the diffusion Monte Carlo. The idea here is to write down the time dependent Schrodinger equation in imaginary time. t′=it, where‘t’is the real time once we do that we have,

$$i\frac{h}{2\pi}\frac{\partial\psi(x,t)}{\partial t} = H\psi(x,t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(24.11)}$$

transformed into,

$$-\frac{h}{2\pi}\frac{\partial\psi(x.t)}{\partial t'} = H\psi(x,t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(24.12)}$$

Since,

$$H = -\frac{h^2}{8\pi^2 m}\nabla^2 + V(x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (24.13)$$

We have, (with $\frac{h}{2\pi}$ =1, m=1)

$$\frac{\partial\psi}{\partial t'} = \frac{1}{2}\nabla^2\psi(x,t) - V(x)\psi(x,t) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (24.14)$$

Which is nothing but a generalized diffusion equation in imaginary time (t′)? The unknown Ψ(x,t) can be expressed as a suppression of the eigen state **ϕ_k(x)**of H with energy **eigen value** E_k.

Then,

$$\psi(x,t) = \sum_k a_k\phi_k(x,\tau) \quad (24.15)$$

$$= \sum_k a_k\phi_k(x)\exp(-iE_k t)$$

$$= \sum_k a_k\phi_k \exp(-E_k t')\text{ , } \textbf{with}\ it = t' \, (24.16)$$

If we now take the long (imaginary) time limit (t′ →∞),we can immediately see that Ψ(x,t) exponentially decays to the state of the lowest energy(the higher energy states decay much faster)so that only the ground state ϕ_0(x) survives in the long t ′limit. **So** one can adopt a random-walk approach to solve the diffusion equation (cf) (generate Ψ(x,t) by random walk) and recover the ground **state o**f the many particle system. However, there are formidable difficulties that arise from the fact that Ψ (r_1……..r_n) must be an antisymmetric wave function (antisymmetric with respect to permutation of the space-spin coordinates of any pair of electrons). That means there are regions of space where Ψ is positive and there are regions where it is negative which in turn demands that there are 3n-1 dimensional surfaces in the space of the electronic variables where the wave function becomes zero. These surfaces define the so called nodes of the wave function where the probability of finding the system is just zero. In QMC one must be careful to sample the non-**nodal** regions more frequently and nodal regions far less frequently. To do that a guiding function must be there to determine how the space should be sampled in conformity with the antisymmetry requirement of a many Fermion wave function. This is a **serious** drawback.

One way to achieve the objective in the diffusion MonteCarlo has been to use the Hartree-Fock wave function as the guiding function that fixes the **nodal** structure to start with (fixed-node MC). In fixed node diffusion Monte Carlo the nodal structure is fixed by the guiding function and it recovers the best wave function consistent with that **noda**l structure. In case, the nodal structure provided by the guiding function matches with that of the exact one ,the exact ground state wavefunction and the energy are recovered.

In the variational QMC, the guiding function is constructed by multiplying the HF wave- function with a correction function that produces the electron-electron and electron-nucleus cusp **condition** with adequate accuracy. One then optimizes the parameters present in the correlation function so that energy is minimized. The computational labour in QMC method scales as N^3 (N is the number of basis function)good enough forit to be competitive with the coupled cluster method, but at least two order of magnitude more expensive compared to the HF or the DFT methods.QMCin all its variants continues to attract attention of the researches even today.