1 Introduction

2 Configuration Interaction Methods

3 Møller-Plesset Perturbation Theory

4 Coupled Cluster Methods

5 Quantum Monte Carlo Methods

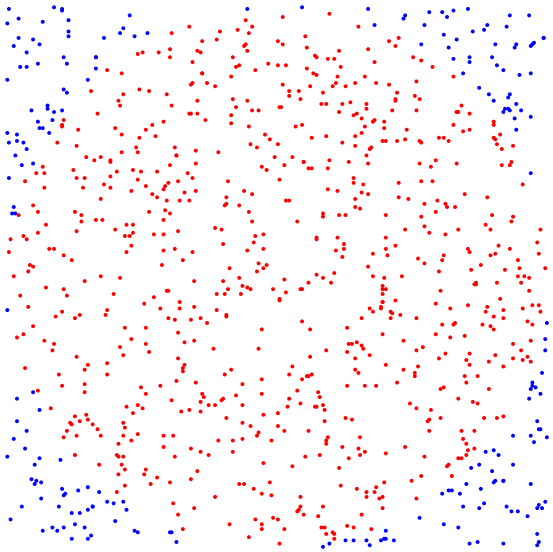
6 Summary

Monte Carlo (MC) method

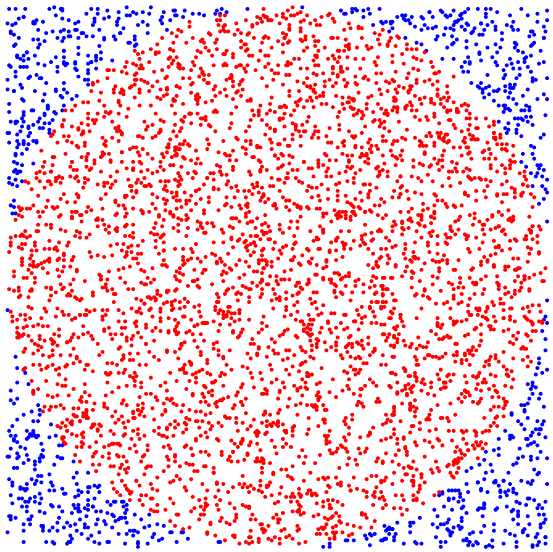
- Monte Carlo is a numerical integration method
- It is used in problems where it is too difficult or impossible to obtain analytical expressions or the dimensionality of the integral is large
- The method consists in repeating random sampling many times to obtain numerical results:
  $\Rightarrow$ this is a non-deterministic or stochastic method.
- MC converges as $N^{-1/2}$ where N is the number of MC step
- In 1946, **Stanislaw Ulam** was the first mathematician to dignify this approach with a name, in honor of his uncle having a little issue with gambling
- **Nicolas Metropolis** also made important contributions (Metropolis algorithm)

Monte Carlo computation of π

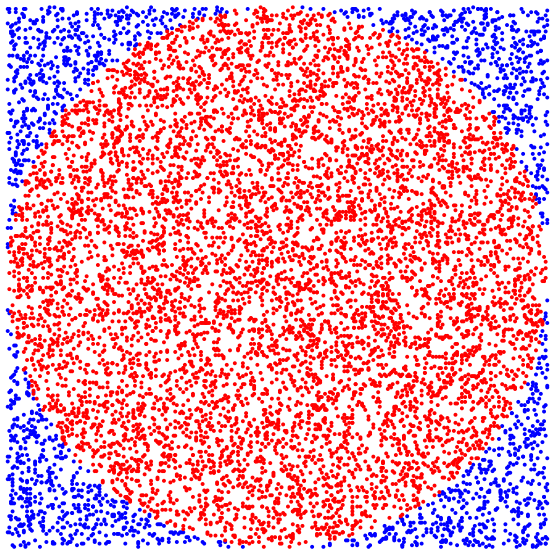
$$\int_{-1}^{1}\int_{-1}^{1} f(x,y)\,dx\,dy = \pi \qquad \text{with} \qquad f(x,y) = \begin{cases} 1, & x^2+y^2 \leq 1, \\ 0, & \text{otherwise.} \end{cases}$$



$$\pi \approx \frac{774}{1000} = 3.096$$



$$\pi \approx \frac{3962}{5000} = 3.1696$$



$$\pi \approx \frac{7948}{10000} = 3.1792$$

```
      program pi
c     Declare variables
      implicit none
      integer seed,i,n
      double precision one,four,x,y,r,res
c     Input data
      one=1.0d0
      four=4.0d0
      seed=19082016
      res=0.0d0
      n=100000
c     Initialize random number generator
      call srand(seed)
c     Start loop
      do i=1,n
c       Get two random numbers
        x=rand(0)
        y=rand(0)
c       Calculate the radius
        r=x**2+y**2
c       Increment result if in circle
        if(r.le.1) res=res+one
      enddo
c     Print the result
      print*,'MC estimate of pi = ',four*res/dble(n)
      print*,'Exact value of pi = ',four*atan(one)
c     End of the program
      return
      end
```

Variational Monte Carlo (VMC)

- Within quantum chemistry, VMC is used to obtain expectation values (mainly energies)
- In VMC, the expectation value of the Hamiltonian with respect to a trial wave function Ψ_T is obtained using a stochastic integration technique
- The VMC energy is an upper bound to the exact ground state energy

$$\boxed{E_{\text{VMC}} = \frac{\int \Psi_T(\boldsymbol{r})\, \mathbf{H}\, \Psi_T(\boldsymbol{r})\, d\boldsymbol{r}}{\int \Psi_T(\boldsymbol{r})^2\, d\boldsymbol{r}} = \frac{\int \frac{\mathbf{H}\, \Psi_T(\boldsymbol{r})}{\Psi_T(\boldsymbol{r})} \Psi_T(\boldsymbol{r})^2\, d\boldsymbol{r}}{\int \Psi_T(\boldsymbol{r})^2\, d\boldsymbol{r}} = \frac{\int E_L(\boldsymbol{r}) \Psi_T(\boldsymbol{r})^2\, d\boldsymbol{r}}{\int \Psi_T(\boldsymbol{r})^2\, d\boldsymbol{r}}}$$

where

$$E_L(\boldsymbol{r}) = \frac{\hat{H}\, \Psi_T(\boldsymbol{r})}{\Psi_T(\boldsymbol{r})} \quad \text{is the local energy}$$

Diffusion Monte Carlo (DMC)

Time-dependent Schrödinger equation written in imaginary time:

$$\boxed{\frac{\partial \Phi(\boldsymbol{r},\tau)}{\partial \tau} = (\mathbf{H} - S)\Phi(\boldsymbol{r},\tau)}$$

- For $\tau \to \infty$, the solution is the exact ground state wave function $\Phi(\boldsymbol{r})$
- DMC generates **configurations** (or **walkers**) distributed according to the density $\rho(\boldsymbol{r},\tau) = \Psi_T(\boldsymbol{r})\,\Phi(\boldsymbol{r},\tau)$

$$\boxed{\frac{\partial \rho(\boldsymbol{r},\tau)}{d\tau} = \underbrace{\frac{1}{2}\nabla^2 \rho(\boldsymbol{r},\tau)}_{\textbf{diffusion}} + \underbrace{\nabla \cdot [F(\boldsymbol{r})\rho(\boldsymbol{r},\tau)]}_{\textbf{drift}} - \underbrace{[E_L(\boldsymbol{r}) - E_T]\,\rho(\boldsymbol{r},\tau)}_{\textbf{branching}}}$$

where

$$F(\boldsymbol{r}) = \frac{\nabla \Psi_T(\boldsymbol{r})}{\Psi_T(\boldsymbol{r})} \quad \text{is the quantum force}$$

If $\Psi_T(\boldsymbol{r})$ has exact **nodes**, DMC energy = exact energy (fixed-node error)

Congratulations!

You have survived Part III of Chem3208!

Next time, you will talk about

Density-functional theory

with Andrew Gilbert