Quantum Monte Carlo

Variational Monte Carlo

goal: obtain variational energy without computing integrals →
freedom in type of wave function

$$E = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\int \Phi^* \hat{H} \Phi \, dr}{\int \Phi^* \Phi \, dr} =$$

$$= \frac{\int \Phi^* \Phi \left(\Phi^{-1} \hat{H} \Phi \right) dr}{\int \Phi^* \Phi \, dr} = \frac{\int |\Phi(r)|^2 \left(\Phi^{-1} \hat{H} \Phi \right) dr}{\int |\Phi(r)|^2} =$$

$$= \int E_{local}(r) \cdot P(r) \, dr$$

$$P(r) = \frac{|\Phi(r)|^2}{\int |\Phi(r)|^2 dr}$$

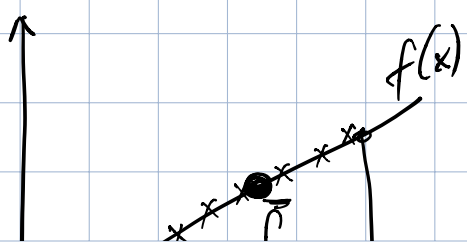
probability density

$$E_{local}(r) = \frac{\hat{H} \Phi(r)}{\Phi(r)}$$

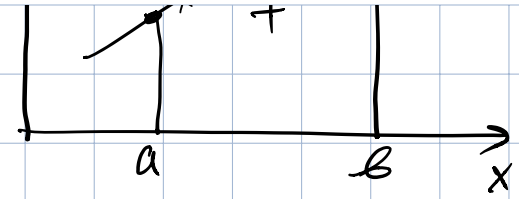
local energy

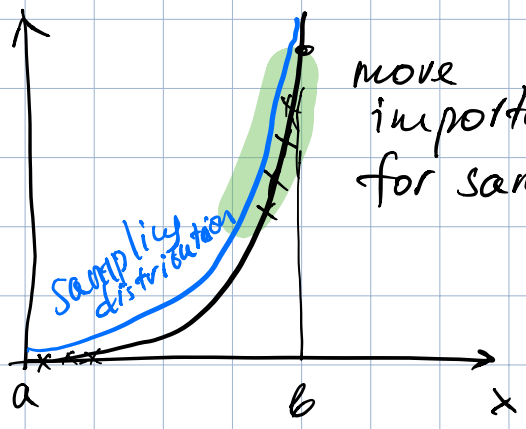
dimensionality of problem: $3N_{elec}$
numerically very hard

Metropolis algorithm



$$\frac{\sum_i^N f(i)}{N} (b-a) = I$$





move important for sampling

Classical energy of a system

$$E = \int \varepsilon P(\varepsilon) d\varepsilon =$$

$$= \sum_{i=1}^{N\,states} \varepsilon_i P_i =$$

$$= \frac{\sum_{i=1}^{N} \varepsilon_i e^{-\varepsilon_i / k_B T}}{\sum_i e^{-\varepsilon_i / k_B T}}$$

state i, ε_i

do move, state j, ε_j

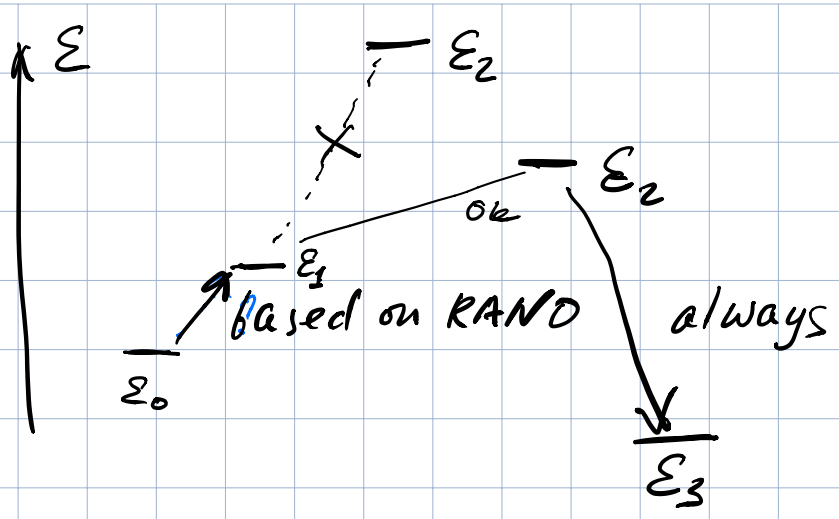
$e^{-(\varepsilon_j - \varepsilon_i)/k_B T}$ compare with random number $\{0, \ldots 1\}$

if $\varepsilon_j < \varepsilon_i \rightarrow$ accept the move

if $\varepsilon_j > \varepsilon_i$, $e^{-(\varepsilon_j - \varepsilon_i)/k_B T} > RAND$

$\rightarrow$ accept the move,

else reject the move



$$E = \frac{1}{N_{points}} \sum_{i=1}^{N_{points}} E_{local}(r_i)$$

Errors: 1) statistical error ~ amount of sampling

2) trial wave function

↓

based on Slater determinants, multiplied by Jastrow factor

$$\Psi(r) = e^{J(r)} \sum_{sd} c_{sd} \Phi_{sd}(r)$$

↖ Slater determ.

$$J(r) = \sum_{i}^{N_{elec}} \chi(r_{ij}) + \sum_{i>j}^{N_{elec}} u(r_i, r_j)$$

↑ nuclei-el. interactions

↑ el.-el. correlation

$\Psi(r, p)$ ← parameters

orbital coefs, weights for SD, γ params

need to optimize parameters to obtain the lowest energy

Diffusion Monte Carlo

$$i\frac{\partial \Phi(r,t)}{\partial t} = \hat{H}\Phi(r,t)$$

$it \to \tau$ τ – imaginary time

$$-\frac{\partial \Phi(r,\tau)}{d\tau} = \hat{H}\Phi(r,\tau)$$

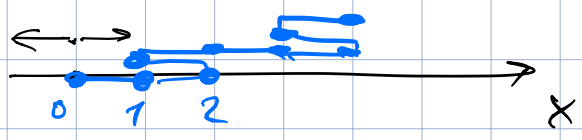
(for a free electron, no V):

$$\frac{\partial \Phi(r,\tau)}{\partial \tau} = \frac{1}{2}\nabla^2\Phi(r,\tau) \leftarrow \text{diffusion eq-n}$$

$$\frac{\partial \Phi(r,\tau)}{\partial \tau} = \frac{1}{2}\nabla^2\Phi(r,\tau) - V(r)\Phi(r,\tau)$$

generalized diff. eqn

can be solved by random walk



$$\Phi(r,\tau) = \sum_k c_k \Psi_k(r,\tau) = \sum_k c_k \Psi_k(r) e^{-E_k\tau}$$

higher energy states will decay faster,

$$\lim_{\tau \to \infty} \Phi(r, \tau) = c_0 \Psi_0 e^{-E_0 \tau}$$

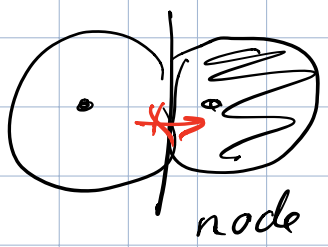
this will disappear if E is set to E_0

→ get Ψ_0 and E_0 !

Main problem: requirement of antisymmetry of w.f.

nodes have zero probability

need guiding w.f. ~ trial w.f. with correct nodal structure



walkers cannot cross nodes

Scaling ~ $N_{occ}^2 \cdot N_{basis}$, but large prefactors

Hard to compute forces