Lecture January 21

$$\mathbb{E}[H] = \frac{\int \psi_T^*(\vec{R};\vec{\alpha}) H(\vec{R}) \psi_T(\vec{R};\vec{\alpha}) \times d\vec{R}}{\int |\psi_T|^2 d\vec{R}}$$

$$P_T(\vec{R};\vec{\alpha}) = \frac{|\psi_T(\vec{R};\vec{\alpha})|^2}{\int |\psi_T|^2 d\vec{R}}$$

$$E_L(\vec{R};\vec{\alpha}) = \frac{1}{\psi_T} \hat{H} \psi_T(\vec{R};\vec{\alpha})$$

$$\vec{\alpha} = \{\alpha_0, \alpha_1, \ldots \alpha_m\}$$

$\vec{\alpha}$ = set of variational parameters

$$\mathbb{E}[H] = \mathbb{E}[E_L(\vec{\alpha})] = \int d\vec{R}\, P_T(\vec{R};\vec{\alpha})\, E_L(\vec{R};\vec{\alpha})$$

$$\simeq \frac{1}{M} \sum_{i=1}^{M} E_L(\vec{R}_i;\vec{\alpha})$$

Define $\Psi_T(\vec{R};\underline{\vec{\alpha}})$

— " — Hamiltonian

— " — Local energy

Develop a function for metropolis sampling and various averages.

How to structure a program

system

- wave functions
- Hamiltonian
- Local energy

→ project 1

if possible compute analytical expression for E_L

$E_L(\vec{R};\vec{\alpha}) =$

Solver

Metropolis sampling (p1 and p2)

Neural Net-works

- gradient descent
- other many-body methods

$$E_L(\vec{R};\alpha) =$$

$$\boxed{\frac{1}{\psi_T(\vec{R};\alpha)} H(\vec{R})\, \psi_T(\vec{R};\vec{\alpha})}$$

How do we define a trial wf?

Hydrogen atom

SE:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Zke^2}{r}\right)\psi(\vec{r}) = E\,\psi(\vec{r})$$

$$\psi(\vec{r}) = R(r)\, P_{ml}(\theta, \varphi)$$

$$x, y, z \Rightarrow r, \theta, \varphi \qquad r \in [0, \infty)$$
$$\theta \in [0, \pi]$$
$$\varphi \in [0, 2\pi]$$

Diff eq for r:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{d}{dr} r \frac{d}{dr}\right) + \frac{l(l+1)}{-r^2} - \frac{Zke^2}{r}\right] R(r) = E_r R(r)$$

$$l = 0$$

Local energy:

$$\left(\hbar = 1 \quad m = 1, \; ke^2 = 1\right)$$

$$\frac{1}{R(r)}\Big(\underbrace{-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr}}_{\text{kinetic energy}} \underbrace{-\frac{Z}{r}}_{\text{potential energy}}\Big)R(r)$$

$\frac{d^n}{dr}R(r)$ are finite for all r

$R(r)$ is finite for all r

$$\lim_{r\to 0}\frac{1}{R}\Big(-\frac{2}{r}\frac{dR}{dr} - \frac{Z}{r}R\Big) = 0$$

$$-\frac{2}{R(r)\cancel{r}}\frac{dR}{dr} = \frac{Z}{\cancel{r}}\frac{R}{R}$$

$$\frac{dR}{dr} = -\frac{Z}{2}R(r)$$

$$R(r) \propto e^{-r\alpha}$$

variational parameter.

what if $+\frac{Z}{r}$

$$R(r) \propto e^{+r\alpha}$$

How do we choose the step size?

Harmonic oscillator:

SE for the radial

of freedom:

$$R(r) = u(r)/r$$

$R(0) = \text{const}$ | $u(0) = 0$

$R(\infty) = 0$ | $u(\infty) = 0$

$\ell = 0$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u(r) + \frac{1}{2}m\omega^2 r^2 u(r)$$

$$= \varepsilon\, u(r)$$

Scale equations, make dimensionless

$\rho = \gamma r$ $\qquad [r] = \text{length}$

$\qquad [\gamma] = \text{length}^{-1}$

$r = \rho/\gamma$

$$-\frac{\hbar^2\gamma^2}{2m}\frac{d^2}{d\rho^2}u + \frac{1}{2}m\omega^2 \rho^2/\gamma^2\, u$$

$\times \frac{m}{\hbar^2\gamma^2} \Rightarrow \qquad = \varepsilon\, u$

$$-\frac{1}{2}\frac{d^2}{d\rho^2}u + \frac{1}{2}\frac{m^2\omega^2}{\hbar^2\gamma^4}\rho^2 u$$

$$= \tilde{\varepsilon}\cdot u$$

$$\tilde{\varepsilon} = \varepsilon\cdot m/\hbar^2\gamma^2$$

$$\frac{m^2\omega^2}{\hbar^2\gamma^4} = 1 \quad \Rightarrow$$

$$\gamma^2 = \frac{\hbar}{m\omega} \quad \Rightarrow$$

$$\boxed{\gamma} = \sqrt{\hbar/m\omega}$$

natural length scale.

natural units $\hbar = c = m = 1$

$$\gamma = \sqrt{\frac{1}{\omega}} \qquad \omega = 1$$

$\gamma = 1 \Rightarrow$ guess for step length

Metropolis algo =

simple Metropolis based on Markov chain theory.

Probability – $P_i(t)$

Transition probability $W(i \to j)$

stochastic matrix

$$\sum_j W_{ij} = \underline{1}$$

Largest Eigenvalue λ_{max}

$= \underline{1}$

Example

$$W = \begin{bmatrix} 1/3 & 1 & 2/3 \\ 0 & 0 & 1/3 \\ 2/3 & 0 & 0 \end{bmatrix}$$

$$\sum_i P_i(t) = \underline{1}$$

Markow - chain

$$\underline{P_i(t+\varepsilon)} = \sum_j W(j \to i) P_j(t)$$

~~known~~

have a model

$$P_i(t+\varepsilon) \to P_T(\vec{R};\alpha) = \frac{|\Psi_T(\vec{R};\alpha)|^2}{\int d\vec{R}\, |\Psi_T(\vec{R};\vec{\alpha})|^2}$$

Metropolis Test :

we accept new move

if $\quad w \in [0,1]$ (random number)

$$w \leq \frac{P_T(\vec{R}';\vec{\alpha})}{P_T(\vec{R};\vec{\alpha})}$$