Averages continued:

Free energy calculations

- cannot express directly as average.

Free energy differences

Thermodynamic integration

option ① $\left.\frac{\partial F}{\partial V}\right|_{N,T} = -p$ or $\frac{\partial F/T}{\partial 1/T} = E$ etc...

$$\Delta F = \int_{V_0}^{V_1} dV\,(-p)$$

option ② $F = -\frac{1}{\beta}\log Z$ Overlapping distribution method

$Z_1 = \cdots \int \exp(-\beta U_1)$ ← reference system

$Z_0 = \cdots \int \exp(-\beta U_0)$

$$\log \frac{Z_1}{Z_0} = -(\beta_1 F_1 - \beta_0 F_0) = \log \frac{\int \exp(-\beta(U_1 - U_0) - \beta U_0)}{\int \exp(-\beta U_0)}$$

$$= \log \left\langle \exp\left[-\beta(U_1 - U_0)\right] \right\rangle_{\text{system 0}}.$$

- only works if dists overlap sufficiently otherwise: need a chain of differences

umbrella sampling

option ③ acceptance ratio

etc....

Chemical potential

particle insertion

$$Z = \underbrace{\frac{V^N}{\Lambda^{dN} N!}}_{Z_{ideal}} \int ds \exp(-\beta U)$$ ← reference to ideal gas

$$F = -\frac{1}{\beta}\log Z = F_{ideal} + F_{excess}.$$

$$\mu = F(N+1) - F(N)$$

$$\mu = -\frac{1}{\beta}\left(Z_{ideal}(N+1) - Z_{ideal}(N)\right) = \frac{1}{\beta}\frac{\int ds^{N+1} \exp(-\beta U)}{\int ds^N \exp(-\beta U)}$$

analytically known

$= \mu_{ideal} + \mu_{excess}.$

$$\mu_{excess} = -\frac{1}{\beta}\log \int ds \left(\exp(-\beta \Delta U)\right)$$ (not) adding a particle at a random location

Transport coefficients: Green-Kubo (autocorrelation functions)

Quantum Monte Carlo

- Variational QMC — use variational principle to find ground state
- Diffusion QMC — reformulate SE into diffusion eq.
- Path-Integral QMC — path Integral → classical partition function

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$-i\hbar \frac{d}{dt}\psi = \mathcal{H}\psi$ (Schrödinger Eq.)

$E_i \phi_i = \mathcal{H}_i \phi_i$

energy expectation value

$$E[\psi] = \frac{\int dx\, \psi^*(x)\, \mathcal{H}\, \psi(x)}{\int dx\, \psi^*(x)\, \psi(x)}$$

variational principle: small change $\epsilon\,\delta\psi$

We have an eigenstate if $\delta E = E[\psi+\epsilon\delta\psi] - E[\psi] = 0 + O(\epsilon^2)$

⇒ we parameterise ψ and look for where this is the case.

"trial" function ψ_T — not in MC sense

in principle need ∞ basis set

example: linear orthogonal basis set χ_p $\quad \psi_T = \sum_p c_p \chi_p$

$$E[\psi] = \frac{\sum_{pq} c_p^* c_q H_{pq}}{\sum_{pq} c_p^* c_q \delta_{pq}} = E_i \qquad H_{pq} = \langle \chi_p | H | \chi_q \rangle$$

$$\frac{\partial}{\partial c_p^*} E_i : \quad \sum_{pq} c_p^* c_q \delta_{pq} = \sum_q E_i \delta_{pq} c_q = \sum_q H_{pq} c_q$$

eigenvalue equation. expensive to solve

hey: choose a small basis set that can describe ϕ_i well.

other option: nonlinear parametrisation

example harmonic oscillator: $\mathcal{H} = \frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2$

trial function $\psi_T^\alpha = \exp(-\alpha x^2)$ (solution for gs: $\alpha = \frac{1}{2}$)

$$\mathcal{H}\psi_T = \tfrac{1}{2}x^2 + \tfrac{1}{2}\left[(-2\alpha x)^2 - 2\alpha\right]\psi_T = \left[x^2\left(\tfrac{1}{2} - 2\alpha^2\right) + \alpha\right]\psi_T$$

Do gaussian integral:

$$E[\psi_T] = \frac{1}{4\alpha}\left(\tfrac{1}{2} - 2\alpha^2\right) + \alpha = \frac{1}{8\alpha} + \frac{1}{2}\alpha$$

$$\frac{\partial E}{\partial \alpha} = -\frac{1}{8\alpha^2} + \frac{1}{2} \quad \Rightarrow \alpha = \frac{1}{2}$$

Not always easy to parameterise so that exact solution is there. hence we look at local $E_L = \frac{\mathcal{H}\psi}{\psi}$

$\text{var}(E) = \langle (E_L - E)^2 \rangle = \frac{\int \psi^* (\mathcal{H} - E)^2 \psi}{\int \psi^* \psi}$ 0 if exact, $\neq 0$ otherwise

harmonic $= \frac{(1-4\alpha^2)^2}{32\alpha^2}$

How can MC help speed this up?

$\psi(X)$ ← typically high-dimensional variable

⇒ MC integration (cheaper in high d than with grid)

How to generate the correct distribution? $(\psi_T \psi_T)$

Using Metropolis-like algorithm

(complicated space, try different random initial conditions)

① random walker(s) position X

② random increment ΔX $\quad p(\rightarrow) = p(\leftarrow)$

③ $\left[\frac{\psi_T(X+\Delta X)}{\psi_T(X)}\right]^2 = p$

accept with prob $\min(1, p)$

detailed balance etc..

$\psi_T(X)^2 \min(1,p) = \psi(X+\Delta X)^2 \min(1, \frac{1}{p})$ ok!

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problem: what if $\mathcal{H}$ diverges (because V diverges)?

f.e $\frac{1}{r}$ coulomb. if ψ_T is finite sometimes: trouble with $\langle E \rangle$ here ϕ^2 vanishes, so must construct trial functions with correct structure

called "cusp condition"

Fermions: Slater determinant to get correct pauli things

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to find minimum, we need $\frac{dE}{d\alpha}$, so calculating $\langle E \rangle$ is inefficient

analytical derivative of $\frac{\mathcal{H}\psi}{\psi}$

$\frac{dE}{d\alpha} = 2\left(\left\langle E_L \frac{d\log\psi_T}{d\alpha}\right\rangle - \langle E \rangle \left\langle \frac{d\log\psi_T}{d\alpha}\right\rangle\right)$

$\alpha \rightarrow \alpha - \alpha \frac{dE}{d\alpha}$ will be exercise

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- trial wave function major restriction, could miss important physics
- can be used to impose physically sensible restrictions such as fermion anti-symmetry etc.