# TICKLING THE MONTE CARLO TAIL

Introduction to forces in atoms!

Why want to do

Why DFT

Why QMC

$$\hat{H}\Psi = \underbrace{-\Psi\frac{\nabla^2}{2}\Psi}_{\text{what does this ?}} + \overbrace{\int V_{e-e}(r-r')\Psi^2(r,r')\,d^3r\,d^3r'}^{\substack{\text{smooth} \\ \text{pseudopotential}}} + \overbrace{\int V_{e-i}(r)\Psi^2(r)\,d^3r}^{\substack{\text{smooth, few } e^- \\ \text{pseudopotential}}} + \underbrace{V_{i-i}}_{\text{constant}}$$

To calculate energy

$$E = \frac{\int \Psi H \Psi}{\int \Psi\Psi}$$

many-body so use Monte Carlo integral.

But $\Psi H \Psi$ not constant so expensive, better to weight samples:

$$E = \int_{\Psi^2} \frac{H\Psi}{\Psi}\, d^3r \qquad \text{(Metropolis algorithm)}$$

Examine $H\Psi/\Psi$ carefully:

- If eigenstate constant
- If not eigenstate $\Psi \to 0$ but $H\Psi \neq 0$, so diverges

Monte Carlo: average + uncertainty that is $\sim N^{-1/2}$.

$$p(E) = \frac{dx}{dE} P(x)$$

$E = x^{-1}$

$x = E^{-1}$ $\quad P(x) = x^2 = E^{-2}$

$\frac{dx}{dE} = E^{-2}$

$$P(E) = E^{-2-2}$$
$$= E^{-4}$$


$$\sigma^2 = \int E^{-\beta} \cdot E^2 \cdot dE$$
$$= \int E^{2-\beta}\, dE$$
$$= \left[E^{3-\beta}\right]_{\text{FINITE}}^{\infty} \longrightarrow \text{need } \beta > 3$$

$$P(F) = \frac{dx}{dF} P(x)$$
$$= F^{-3/2} F^{-1}$$
$$= F^{-5/2}$$

$F = x^{-2}$

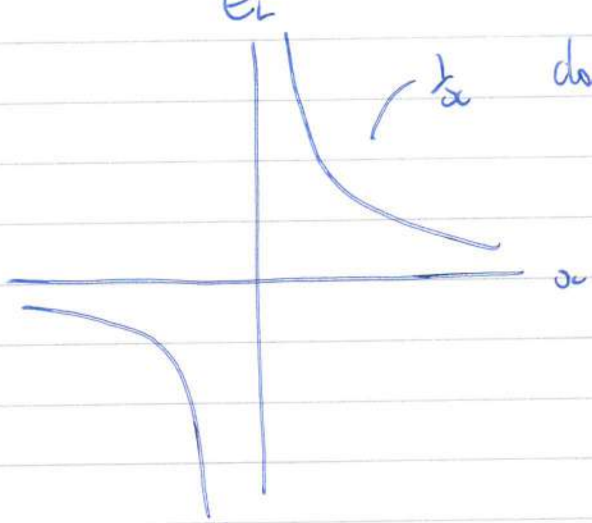
$x = F^{-1/2}$ $\quad P(x) = x^2 = F^{-1}$

$\frac{dx}{dF} = F^{-3/2}$

$$\sigma^2 = \int F^{-5/2} \cdot F^2 \cdot dF$$
$$= \int F^{-1/2}\, dF$$
$$= \left[F^{1/2}\right]_{\text{FINITE}}^{\infty} \rightarrow \text{diverge}$$

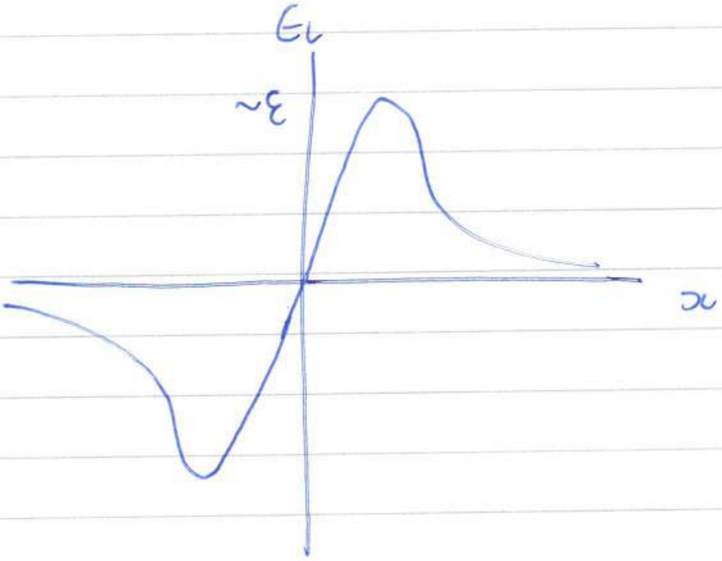
so cannot have uncertainty!

Method 1 : local energy softening :



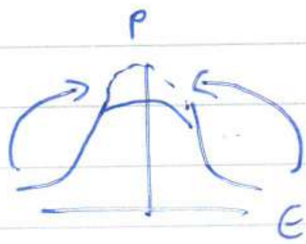

Try $E_L \longrightarrow \frac{E_L}{E_L^2/\varepsilon^2 + 1}$ so $E_L$ at small $E_L$ and

$$E_L \sim \frac{\varepsilon^2}{E_L} \quad \text{at large } E_L$$

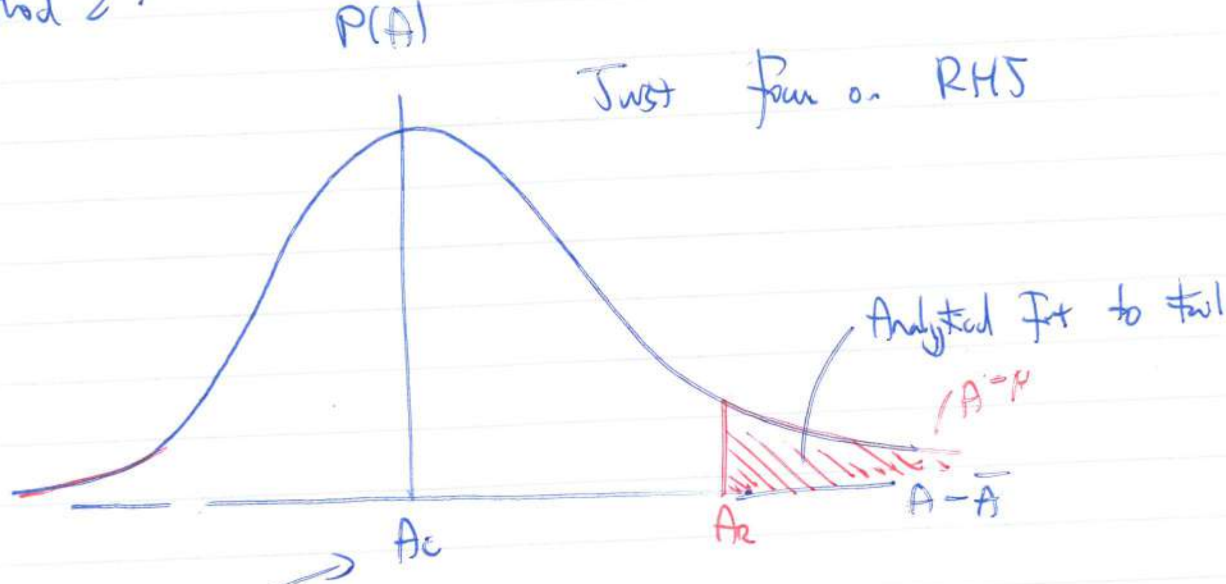



- Removes divergence
- Easy to do
- Reinforces average that may be incorrect

$$\frac{E_L - \bar{E}}{1 + (E_L - \bar{E})^2/\varepsilon^2}$$



Method 2:




Answer roughly independent of this variable.

$$\bar{A} = \frac{1}{M} \sum_{M > M_R} A^{(M)} + \sum_{n=0}^{n_R} C_n \int_{A_R}^{\infty} |A - A_c|^{-\mu - n\Delta} . A . dA$$

As before — Analytical

$$\gamma = \frac{1}{M-1} \sum \left| A^{(M)} - A_c \right|^2 + \sum_{n=0}^{n_R} C_n \int_{A_R}^{\infty} (A - A_c)^{-\mu - n\Delta} (A - \bar{A})^2 dA$$

As before — Analytical

Use knowledge of asymptotic form

Study the tail with the aid of the sample quintiles:

$$\int_{A^m}^{\infty} P(A)\,dA \approx q_m = \frac{m - \frac{1}{2}}{M}$$

with

$$P_A = \sum_{n=0}^{n_R} C_n \left|A - A_c\right|^{-\mu - n\Delta}$$

$$\sum_{n=0}^{n_R} \frac{C_n}{\mu + n\Delta - 1} \left|A^m - A_c\right|^{-\mu - n\Delta + 1} = q_m$$

$$\underbrace{q_m \left|A^m - A_c\right|^{\mu - 1}}_{y_m} = \sum_{n=0}^{n_R} \frac{C_n}{\mu + n\Delta - 1} \Big[\underbrace{\left|A^m - A_c\right|^{-\Delta}}_{x_m}\Big]^n$$

Try distribution

$$\frac{\mu \sin\frac{\pi}{\mu}}{2\pi} \frac{1}{1 + |A|^\mu}$$

Normalized
Expectation value of 0
Asymptote $A^{-\mu}$

Symmetry

$$C_{0L} = C_{0R}$$

Optimization

Minimize $$\frac{1}{M - n_R - 1} \sum_{m=1}^{M} \left|y_m - y(x_m)\right|^2.$$

All normally distributed