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1 Project 1

1.1 Project 1 - Part 1

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

Targeting an energy scale $\epsilon = \hbar\omega$, a new length scale x^* is defined:

$$x^* = \frac{x}{\sqrt{\frac{\hbar}{m\omega}}} \rightarrow x = x^*\sqrt{\frac{\hbar}{m\omega}}$$

$$dx^* = \frac{dx}{\sqrt{\frac{\hbar}{m\omega}}} \rightarrow \frac{dx^*}{dx} = \frac{1}{\sqrt{\frac{\hbar}{m\omega}}} = \sqrt{\frac{m\omega}{\hbar}}$$

$$\frac{d}{dx} = \frac{d}{dx^*}\left(\frac{dx^*}{dx}\right) = \frac{d}{dx^*}\sqrt{\frac{m\omega}{\hbar}}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{d^2}{dx^{*2}}\left(\sqrt{\frac{m\omega}{\hbar}}\right)^2\right] + \frac{1}{2}m\omega^2\left[x^{*2}\left(\sqrt{\frac{m\omega}{\hbar}}\right)^2\right]$$

$$\hat{H} = -\frac{\hbar\omega}{2}\frac{d^2}{dx^{*2}} + \frac{\hbar\omega}{2}x^{*2}$$

Dividing the Halitonian with the targeted energy scale $\epsilon = \hbar\omega$ and defining the dimensionless Hamiltonian:

$$\hat{H}^* = \frac{\hat{H}}{\epsilon} = -\frac{\hbar\omega}{2\epsilon}\frac{d^2}{dx^{*2}} + \frac{\hbar\omega}{2\epsilon}x^{*2}$$

$$\hat{H}^* = -\frac{1}{2}\frac{d^2}{dx^{*2}} + \frac{1}{2}x^{*2}$$

1.2 Project 1 - Part 2

1.2.1 Probability Densities

E_0: 0.500000097134011 E_1: 1.500000139284624 E_2: 2.500001117282008

1.2.2 Ensemble Energy, Heat Capacity Derivation

Given the energy of the harmonic oscillator is:

$$E_n = (n + \frac{1}{2})$$

The analytical form of partition function Z of a 1D harmonic oscillator can be evaluated using a geometric sum:

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})} = e^{\frac{-\beta}{2}} \sum_{n=0}^{\infty} e^{-\beta n}$$

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r}, \quad \text{for } |r| < 1$$

$$Z = \frac{e^{-\beta/2}}{1 - e^{-\beta}}$$

Then, the ensemble energy can be evaluated:

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \qquad C_v = \frac{\partial \langle E \rangle}{\partial T}$$

$$\ln Z = \ln \left(\frac{e^{-\beta/2}}{1 - e^{-\beta}} \right) = \frac{-\beta}{2} - \ln \left(1 - e^{-\beta} \right)$$

$$-\frac{\partial}{\partial \beta} \left[\frac{-\beta}{2} - \ln \left(1 - e^{-\beta} \right) \right] = \frac{1}{2} + \frac{e^{-\beta}}{1 - e^{-\beta}} = \frac{1}{2} + \frac{1}{e^\beta - 1}$$

Then the heat capacity:

$$\frac{d\langle E \rangle}{dT} = \frac{d\langle E \rangle}{dx} \cdot \frac{dx}{dT} = \left(-\frac{e^x}{(e^x - 1)^2} \right) \cdot \left(-\frac{1}{T^2} \right) \quad \text{with} \quad x = \frac{1}{T}$$

$$C(T) = \frac{e^{1/T}}{T^2 (e^{1/T} - 1)^2}$$

Setting $k_B = 1$ gives the analytical forms:

$$\langle E \rangle = \frac{1}{2} + \frac{1}{e^{1/T} - 1}$$

$$C(T) = \frac{e^{1/T}}{T^2 (e^{1/T} - 1)^2}$$

1.3 Project 1 Part 3

1.3.1 See Code

1.4 Project 1 Part 4

Plotting both the ensemble energies and heat capacities for analytical forms of the quantum harmonic oscillator and for the simulated classical harmonic oscillator across several temperatures shows the breakdown of the quantum partition funciton when $T < 1.0$. The plot also shows the recovery of the classical partition function when $T > 1.0$.

2 Project 2

2.1 Project 2 Part 1

2.1.1 See Code

2.2 Project 2 Part 2

2.2.1 DIIS implementation

2.2.2 See Code

The DIIS implementation is slightly faster in both tests and consistently takes fewer iterations in the H2O test case.

2.3 Project 2 part 3

2.4 Project 2 Part 4

The Moorse Potential and LJ potentials have the correct energy dissociation behaviors, which RHF cannot reproduce due to the lack of spin characterization of the spacial orbitals. With the adjusted parameters from the HF calculation, the Moorse Potential fits well. However, the LJ-potential decays much rapidly, which is expected from the r^{-6} decay. For the LJ-Potential, an arbitrary shift parameter had to be fit to match the bottom of the well to the bonding energy minima.

One possible way to improve the potential is to add additional hyperparameters and try to fit to the Hartree Fock potential energy curve.

3 Project 3

3.1 Project 3 Part 1

The Ensemble energy can be derived from path integral formulation of the quantum partition function:

$$Z = \int_{x(0)=x}^{x(\beta\hbar)=x} D(x(\tau))e^{-S(x(\tau))}, \text{ where } \quad S = \beta \sum_{n=0}^{k-1} \left[\frac{mk(x_n - x_{n+1})^2}{2\beta^2\hbar^2} + \frac{V(x_n)}{k} \right]$$

$$\text{and} \quad \int D(x(\tau)) = \lim_{k \to \infty} \left(\frac{km}{2\pi\beta\hbar^2} \right)^{kd/2} \prod_{n=0}^{k-1} \int dx_n$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln[Z] = \frac{kd}{2\beta} - \sum_{n=0}^{k-1} \left[\frac{mk(x_n - x_{n+1})}{2\beta^2 \hbar^2} - \frac{V(x_n)}{k} \right]$$

This can be approximated with the Virial Estimator:

$$\langle E \rangle = \frac{1}{k} \sum_{n=0}^{k-1} \left[\langle V(x_n) \rangle + \frac{1}{2} \left\langle x_n \frac{d}{dx_n}[V(x_n)] \right\rangle \right]$$

Substituting the Morse Potential into the Virial Estimator form:

$$V(r) = D_e (1 - e^{-\alpha(r - r_{eq})})^2 - D_e$$

$$\frac{\partial V(r)}{\partial r_{eq}} = 2aD_e e^{-a(r - r_{eq})} \left(1 - e^{-a(r - r_{eq})} \right)$$

$$\langle E \rangle = \frac{1}{k} \sum_{n=0}^{k-1} \left[\langle (D_e(1 - e^{-\alpha(r_n - r_{eq})})^2 - D_e) \rangle + \frac{1}{2} \left\langle r_n 2aD_e e^{-a(r_n - r_{eq})} \left(1 - e^{-a(r_n - r_{eq})} \right) \right\rangle \right]$$

$$\langle E \rangle = \frac{1}{k} \sum_{n=0}^{k-1} \left[D_e \left(1 - e^{-a(r_n - r_{eq})} \right)^2 - D_e + aD_e r_n e^{-a(r_n - r_{eq})} \left(1 - e^{-a(r_n - r_{eq})} \right) \right]$$

3.2 Project 3 Part 2

3.2.1 See Code

3.3 Project 3 Part 3

Translatin the whole ring polymer keeps springs between the beads unchanged, therefore the kinetic energy remains the same. The difference in energy comes from the displaced position in the potenteial term:

$$\Delta E = \frac{1}{k} \sum_{n=0}^{k-1} [V(r_n + \delta r_n) - V(r_n)k]$$

$$\text{where} \quad r_n = e_n - h_n$$

The energy difference is then substituted into the Metropolis condition:

$$e^{-\beta \Delta E} = e^{-\beta \frac{1}{k} \sum_{n=0}^{k-1} [V(r_n + \delta r_n) - V(r_n)k]}$$

4

3.3.1 See Code

3.4 Project 3 Part 4

3.4.1 $T = 1000K$

Virial Estimator Energy: -4.923008678736133 +/- 0.09299213115055376

3.4.2 $T = 2000K$

Virial Estimator Energy: -2.3682754221264912 +/- 0.3004361114166225

4 Project 4

4.1 Project 4 Part 1 - Part 3

4.1.1 See Code

4.2 Project 4 Part 4 - Part 5

T*	$\rho\sigma^3$	System state after 20τ simulation runs, starting from an initial FCC solid configuration	System state after 20τ simulation runs, starting from an initial liquid configuration
0.6	1.0	Solid	Semi-Liquid (almost Liquid)
0.7	1.0	Solid	Semi-Liquid (almost Liquid)
0.8	0.9	Semi-Solid	Liquid
0.8	0.9	Semi-Solid	Liquid
0.9	0.9	Semi-Liquid	Liquid
0.9	0.8	Liquid	Liquid

Starting initially with the FCC structure gives the correct final atom configurations and radial distribution functions with increasing temperatures and decreasing pressures from solid FCC phase to the liquid phase. Starting from the liquid phase, or a distantly spaced simple cubic lattice, all phases end up in the liquid phase with a very small semi-liquid behavior at the highest densities and lowest temperatures.

The cause of this is likely the initial starting condition. The first five condition start with an unusually high potential energy followed by an immediate response of increased kinetic energy. The initial atom distances in the simple cubic lattice was scaled by the box length / n_sides and a scaling hyperparamter was used to increase the initial distance in the simple cubic lattice to minimize the initial potenetial energy. Despite the significant improved form exploding gradients and non-interacting atoms, finding a balance remains difficult. Some possible ways to address this is to introduce dampening hyperparameters or cutoffs to both the velocity and the potential to prevent exploding graidents. Radial density plots and Energy plots are shown below.

One possible way to determine the solid liquid bounary, is to devlop code that quantifies the organization/disorder of particles, such as the Lindemann index. Simulating and determing such quantifier across varying temperature and pressure with both solid and liquid phase initializations, the set of conditions at which the quantifier is identical for both phase is the solid-liquid boundary.

4.2.1 FCC Initialized Simulation Visualizations

4.2.2 Liquid Initialized Simulation Visualizations

4.3 Project 4 Part 6

4.3.1 See Code