Project 3: Variational Quantum Monte Carlo

Key Topic: Monte Carlo integration

1 Introduction

This project is about solving the time-independent Schrödinger equation numerically. We will use this to find the ground state of a hydrogen molecule and evaluate the ground state energy, electron density, bond length, and bond dissociation energy. The method we will use is known as Variational Monte Carlo (VMC), a technique widely used in research today. Before we start, it is worth thinking about what would happen if we tried to apply the methods we learned in the course (based on discretising space) to solve the Schrödinger equation. For N particles in d dimensions, the wavefunction is a function of Nd variables $\psi(r_1, r_2, \ldots, r_N)$. Given this, we can calculate the memory needed to just *store* a wavefunction. Suppose we use 100 points along each dimension, and we save the wavefunction at each position with a 64-bit float. The total memory needed is 64×100^{Nd} bits. For example, a water molecule has 22 electrons, so this turns out to be (in 3D) 64×10^{132} bits, over 50 orders of magnitude greater than the number of atoms in the observable universe!

At room temperature, electrons are mostly in the lowest energy eigenstate. Therefore, the ground state contains most of the information you might want about a quantum system. Thankfully, this is quite a special state, as it minimises the expectation of the Hamiltonian,

$$\langle H \rangle = \frac{\int d^3r_1 \ldots d^3r_N \psi^*(r_1, \ldots, r_N) H \psi(r_1, \ldots, r_N)}{\int d^3r_1 \ldots d^3r_N \psi^*(r_1, \ldots, r_N) \psi(r_1, \ldots, r_N)}. \tag{1}$$

The idea is to write an ansatz - a guess of what the ground state wavefunction could be, in terms of some parameters θ: $\psi(r_1, \ldots, r_N) \equiv \psi(r_1, \ldots, r_N; \theta)$. Then, the expectation of the Hamiltonian becomes a function of the parameters θ, and nothing else. We can then find an approximation to the ground state wavefunction by minimising $\langle H \rangle$ with respect to θ.

1.1 Calculating $\langle H \rangle$

We will solve the integral in eq. 1 with Monte Carlo integration. Why do you think this is a good choice? What issues would Newton-Cotes methods face? From now on, we will abbreviate $\{r_1, \ldots, r_N\}$ as R, which is a vector of Nd entries. Starting with eq. 1, show analytically that the expectation value of the Hamiltonian $\langle H \rangle$ can be written as eq. 2.

$$\langle H \rangle \approx \frac{1}{N_s} \sum_{i=1}^{N_s} E_l(R^{(i)}), \qquad\qquad R^{(i)} \sim \rho(R) \tag{2}$$

where $R^{(i)}$ are random samples distributed by the normalised PDF $\rho(R)$, N_s is the number of random samples and $E_l(R)$ is known as the local energy,

$$\rho(R) = \frac{|\psi(R)|^2}{\int dR |\psi(R)|^2}, \tag{3}$$

$$E_l(R) = \frac{1}{\psi(R)} H \psi(R). \tag{4}$$

2 The 1D simple harmonic oscillator

To understand the variational method and Monte Carlo sampling, we first start with a toy model involving a single particle (N=1) in 1D, the simple harmonic oscillator. This question is about performing Monte Carlo

sampling to estimate the energy expectation value of any wavefunction. The Schrödinger equation for a simple harmonic oscillator in 1D, and a single electron is given by

$$\frac{-\hbar^2}{2m_e}\frac{d^2}{dx^2}\psi(x) + \frac{1}{2}m_e\omega^2 x^2\psi(x) = \mathcal{E}\psi(x), \tag{5}$$

where ψ is the wavefunction, $\mathcal{E}$ is the energy, m_e is the electron mass, $\hbar$ is the reduced Plank constant, and ω is the harmonic oscillator strength. What are the dimensions of each variable/constant? By using natural units, rewrite the Schrödinger equation in dimensionless form. The dimensionless Hamiltonian should then be

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2. \tag{6}$$

The exact eigenfunctions and eigenvalues of H are

$$\psi_n(x) = H_n(x)e^{-x^2/2}, \qquad\qquad E_n = n + \frac{1}{2}, \tag{7}$$

where H_n are the Hermite polynomials, the first few are

$$H_0(x) = 1, \tag{8}$$
$$H_1(x) = 2x, \tag{9}$$
$$H_2(x) = 4x^2 - 2, \tag{10}$$
$$H_3(x) = 8x^3 - 12x, \tag{11}$$
$$H_4(x) = 16x^4 - 48x^2 + 12. \tag{12}$$

2.1 The local energy

For the case of the 1D harmonic oscillator, the local energy is

$$E_l(x) = \frac{1}{\psi(x)}\left(-\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2\right)\psi(x) = -\frac{1}{2}\frac{1}{\psi}\frac{d^2}{dx^2}\psi(x) + \frac{1}{2}x^2. \tag{13}$$

The second term (corresponding to the potential) is easy to calculate, but the first term involves the second derivative of the wavefunction. This can be evaluated numerically with the finite difference method. Investigate the impact of step size on the numerical error of the finite difference scheme. How do different order approximations to the second derivative compare?

2.2 Verifying the energy of harmonic oscillator eigenstates

Verify numerically that the states ψ_n defined in eq. 7 have the correct energy expectation values. This is done by following these steps:

- Generate N_s random samples $x^{(i)}$ from $\rho(x)$ (see eq. 3). You may use the random number generation method of your choice, but explain why you chose that particular method. You must also demonstrate that your random sampling algorithm works as intended.

- Evaluate the local energy at the random points, $E_l(x^{(i)})$.

- Take the average of the local energies, following eq. 2.

3 The hydrogen atom

This question is about optimising the parameters of a trial wavefunction to find the ground state of a hydrogen atom. We still have a single particle ($N=1$), but in 3 dimensions. We will work under the Born-Oppenheimer

approximation: the hydrogen nucleus is treated as a fixed point particle at the origin, and only consider the electronic degrees of freedom. The dimensionless Hamiltonian for this system is

$$H = -\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{1}{r}, \tag{14}$$

where $r = \sqrt{x^2 + y^2 + z^2}$, and the wavefunction is now a function of 3 variables $\psi(x, y, z)$. We shall take the following parametrised ansatz,

$$\psi(x, y, z; \theta) = e^{-\theta r}, \tag{15}$$

where θ is a number to be found. Different values of θ define different wavefunctions with different energy expectation values; we seek the one that corresponds to the lowest energy state.

3.1 Finding the ground state of Hydrogen

Using any of the minimisation algorithms learnt in the course, minimise the energy expectation value of the Hamiltonian with respect to θ. The energy can be calculated as in the previous section (see eq. 2). The kinetic energy part of the local energy, $-\frac{1}{2\psi(\boldsymbol{R};\theta)}(\partial_x^2 + \partial_y^2 + \partial_z^2)\psi(\boldsymbol{R};\theta)$, now requires the sum of 3 second derivatives. Verify that your numerical implementation of the 3D Laplacian is correct. Also, verify that the random sampling from $\rho(\boldsymbol{R};\theta)$ works as intended with 3 variables. If needed, you may use the following expression for the gradient of $\langle H \rangle$ with respect to θ,

$$\partial_\theta \langle H \rangle \approx \frac{2}{N_s} \sum_{i=1}^{N_s} \left[\left(E_l(\boldsymbol{R}^{(i)}) - \langle H \rangle\right)\frac{\partial_\theta \psi(\boldsymbol{R}^{(i)}; \theta)}{\psi(\boldsymbol{R}^{(i)}; \theta)}\right] \qquad \boldsymbol{R}^{(i)} \sim \rho(\boldsymbol{R}; \theta), \tag{16}$$

where each symbol means the same as in eq. 2. A summary of the process is shown in section 5. Once you believe you have found the optimum value of θ, calculate the energy of the state keeping θ fixed. Why do you think this is necessary? At the optimum value of θ, the energy expectation value should be exactly -0.5. Plot the number density of the ground state projected to the $x - y$ plane. This is done by obtaining random samples $\boldsymbol{R}^{(i)}$ from $\rho(\boldsymbol{R}; \theta)$, discarding the z coordinate, and plotting a 2-dimensional histogram of the $(x^{(i)}, y^{(i)})$ generated. Different bin counts can be represented using different colours.

4 The hydrogen molecule

This question is about applying the techniques learnt in previous sections to tackle a more complicated problem: the hydrogen molecule (2 electrons and 2 nuclei in 3 dimensions). By optimising the wavefunction to find the ground state at different atomic separations, we will calculate some chemical properties of the molecule. The dimensionless Hamiltonian for 2 hydrogen nuclei located at $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ and 2 electrons in 3D is given by

$$H = -\frac{1}{2}\sum_{i=1}^{2}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) - \sum_{i=1}^{2}\sum_{j=1}^{2}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{q}_j|} + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + \frac{1}{|\boldsymbol{q}_1 - \boldsymbol{q}_2|}. \tag{17}$$

You may use the following ansatz for this system,

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2; \boldsymbol{\theta}) = \left[e^{-\theta_1(|\boldsymbol{r}_1 - \boldsymbol{q}_1| + |\boldsymbol{r}_2 - \boldsymbol{q}_2|)} + e^{-\theta_1(|\boldsymbol{r}_1 - \boldsymbol{q}_2| + |\boldsymbol{r}_2 - \boldsymbol{q}_1|)}\right]e^{-\frac{\theta_2}{1 + \theta_3 r_{12}}}, \tag{18}$$

where $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$.

4.1 Finding the ground state of H_2

Using the methods employed in previous parts, find the ground state energy and wavefunction for a range of atomic distances $|\boldsymbol{q}_1 - \boldsymbol{q}_2|$. For each atomic distance, plot the projected electron density. This is done by taking samples $\boldsymbol{R}^{(i)}$ from $\rho(\boldsymbol{R}; \boldsymbol{\theta})$, and adding both $(x_1^{(i)}, y_1^{(i)})$ and $(x_2^{(i)}, y_2^{(i)})$ to the 2D histogram. An example is shown below.
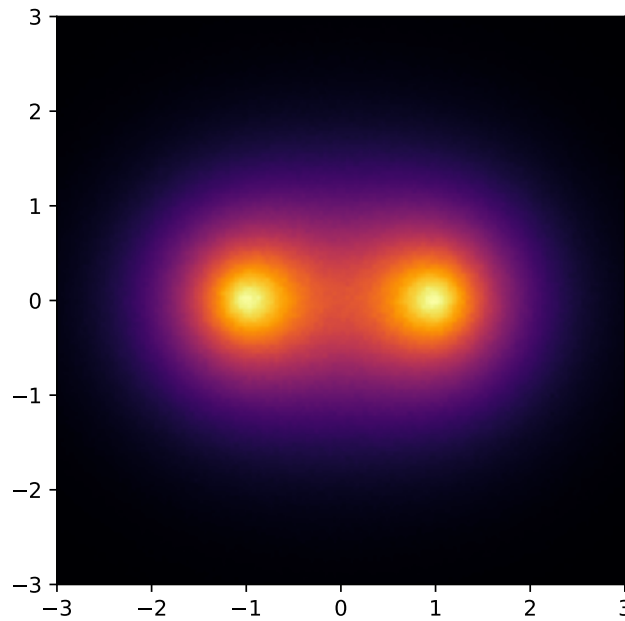
If we change the separation of the hydrogen nuclei, we will obtain different ground state energies: the ground state energy as a function of atomic separation will follow a Morse potential,

$$V_{\text{Morse}}(r) = D\left(1 - e^{-a(r-r_0)}\right)^2 - D + 2E_{\text{single}}, \tag{19}$$

where D, a and r_0 are fitting constants, and E_{single} is your calculated value of the ground state energy of a single hydrogen atom. Fit the ground state energies to the Morse potential. The bond length will then be the value obtained for r_0, and the bond dissociation energy (the energy needed to break a hydrogen bond) will be D. The experimental value for the bond length is about 1.4, and the bond dissociation energy is about 0.17 in these units. Briefly comment on how your numerical estimates compare to the experimental values.

5   Summary of optimisation

You can find below a flow chart summarising the optimisation process