

Homework 5: Monte Carlo Simulations

CHEM4050/5050 Fall 2025

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1 Monte Carlo Integration of the Overlap Integral between Two Hydrogen 2p Orbitals

In quantum chemistry, the overlap integral between atomic orbitals is fundamental for understanding molecular bonding and molecular orbital formation. In this assignment, you will calculate the overlap integral between two hydrogen 2p orbitals separated by a distance R along the z -axis using Monte Carlo integration. You will first use random sampling and then improve the efficiency of your calculation using importance sampling. Finally, you will plot the overlap integral as a function of R and interpret the change in sign of the overlap integral. The hydrogen atom's 2p orbital oriented along the z -axis is given by

$$\psi_{2p_z}(r, \theta) = \frac{1}{4\sqrt{2\pi}a_0^{3/2}} \left(\frac{r}{a_0}\right) \cos\theta e^{-r/(2a_0)} \quad (1)$$

where r is the radial distance, θ is the polar angle, and a_0 is the Bohr radius (set $a_0 = 1$ atomic unit for simplicity). The overlap integral $S(R)$ between two 2p orbitals located at positions $(0, 0, -R/2)$ and $(0, 0, R/2)$ along the z -axis is

$$S(R) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi_{2p_z}^*(x, y, z + R/2) \psi_{2p_z}(x, y, z - R/2) dx dy dz \quad (2)$$

1.1 Tasks

1.1.1 Define the Hydrogen 2p Orbital Function

- ☐ Convert the hydrogen atom's 2p orbital ψ_{2p_z} from polar coordinates (r, θ) to Cartesian coordinates (x, y, z) . *Hint:* Use $r = \sqrt{x^2 + y^2 + z^2}$ and $\cos\theta = z/r$.
- ☐ Write a Python function `psi_2p_z(x, y, z)` that computes $\psi_{2p_z}(x, y, z)$ at a given point.

1.1.2 Compute the Overlap Integral Using Random Sampling

- ☐ Set the separation distance $R = 2$ atomic units.
- ☐ Generate random points (x, y, z) within a cubic region $-L \leq x, y, z \leq L$, where L is large enough to capture significant contributions (*e.g.*, $L = 20$). *Hint:* Check the symmetry of the integrand about the center of the integration range.
- ☐ For each point, compute the integrand

$$\text{Integrand} = \psi_{2p_z}^*(x, y, z + R/2) \psi_{2p_z}(x, y, z - R/2) \quad (3)$$

- ☐ Estimate the overlap integral $S(R)$ using Monte Carlo integration

$$S(R) \approx V \times \langle \text{Integrand} \rangle \quad (4)$$

where $V = (2L)^3$ and $\langle \text{Integrand} \rangle$ is the average value over all sampled points.

- ☐ Perform the calculation for varying numbers of points $N = 10^2, 10^3, 10^4, 10^5, 10^6, 10^7, 10^8$.
- ☐ Plot the estimated $S(R)$ versus N on a logarithmic scale.
- ☐ Discuss the convergence of your results.

1.1.3 Improve Efficiency Using Importance Sampling

- ☐ Choose an importance sampling distribution $g(x, y, z)$ proportional to the absolute value of the integrand or similar in shape. *Hint:* Consider using a distribution based on the one we chose in Lecture 13.

- ☐ Modify your Monte Carlo integration code to sample from $g(x, y, z)$ instead of a uniform distribution.
- ☐ Adjust the integrand in your calculation by dividing by $g(x, y, z)$

$$S(R) \approx \frac{1}{N} \sum_{i=1}^N \frac{\psi_{2p_z}^*(x_i, y_i, z_i + R/2) \psi_{2p_z}(x_i, y_i, z_i - R/2)}{g(x_i, y_i, z_i)} \quad (5)$$

- ☐ Perform the calculation using the same N values as before.
- ☐ Plot the new estimates of $S(R)$ versus N .
- ☐ Compare the efficiency and convergence with the random sampling method.

1.1.4 Plot the Overlap Integral as a Function of Separation Distance

- ☐ Compute the overlap integral $S(R)$ for a range of separation distances R (e.g., $R = 0.5a_0$ to $R = 20a_0$ in increments of $0.5a_0$).
- ☐ Use the importance sampling method for these calculations with a fixed N (e.g., $N = 10^6$).
- ☐ Plot $S(R)$ versus R .
- ☐ Interpret the change in sign of $S(R)$ as R increases. *Hint:* Consider the symmetry and phase of the 2p orbitals and their overlap.

1.1.5 Analysis and Discussion

- ☐ Analyze your results and explain why importance sampling improves efficiency.
- ☐ Comment on the physical significance of the overlap integral and its dependence on R .

1.2 Submission Guidelines

- A Python script containing
 - ☐ Your functions for ψ_{2p_z} and both integration methods.
 - ☐ Adequate comments explaining your code.
- A Jupyter notebook containing your
 - ☐ Plots of $S(R)$ versus N for both methods.
 - ☐ Plot of $S(R)$ versus R .
 - ☐ Explanations, observations, and any conclusions drawn.
- Set a random seed (e.g., `np.random.seed(42)`) for reproducibility.

2 Graduate Supplement

In quantum chemistry, the calculation of kinetic energy matrix elements between atomic orbitals is essential for understanding molecular interactions and the formation of chemical bonds. In this assignment, you will compute both the diagonal and off-diagonal kinetic energy matrix elements between two hydrogen 1s orbitals separated by $R = 1.4$ Bohr radii (the equilibrium bond length of the hydrogen molecule H_2) along the z -axis. You will use Monte Carlo integration with both random sampling and importance sampling to perform these calculations. The hydrogen atom's normalized 1s orbital is given by

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad (6)$$

where $r = \sqrt{x^2 + y^2 + z^2}$ and a_0 is the Bohr radius (set $a_0 = 1$ atomic unit for simplicity). The Laplacian of the 1s orbital, which appears in the kinetic energy operator, is

$$\nabla^2 \psi_{1s}(r) = \frac{d^2}{dr^2} \psi_{1s}(r) + \frac{2}{r} \frac{d}{dr} \psi_{1s}(r) \quad (7)$$

The kinetic energy operator in atomic units is

$$\hat{T} = -\frac{1}{2} \nabla^2 \quad (8)$$

The kinetic energy matrix element between two orbitals ψ_i and ψ_j is

$$K_{ij} = \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \psi_j(\mathbf{r}) \right) d\mathbf{r} \quad (9)$$

2.1 Tasks

2.1.1 Define the Hydrogen 1s Orbital and its Laplacian

- ☐ Write a Python function `psi_1s(x, y, z, Z=1, a0=1)` that computes the normalized hydrogen 1s orbital at a given point. The quantity Z is the atomic number of the nucleus.
- ☐ Derive the expression for the Laplacian $\nabla^2 \psi_{1s}(r)$ in terms of r , and write a Python function `laplacian_psi_1s(x, y, z, Z=1, a0=1)` that computes it.

2.1.2 Compute the Diagonal Kinetic Energy Matrix Element Using Random Sampling

- ☐ The diagonal kinetic energy matrix element is

$$K_{ii} = \int \psi_{1s}(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \psi_{1s}(\mathbf{r}) \right) d\mathbf{r} \quad (10)$$

- ☐ Generate random points (x, y, z) within a cubic region large enough to capture significant contributions (e.g., $-L \leq x, y, z \leq L$ with $L = 7$).
- ☐ For each point, compute the integrand

$$\text{Integrand} = -\frac{1}{2} \psi_{1s}^*(x, y, z) \nabla^2 \psi_{1s}(x, y, z) \quad (11)$$

- ☐ Estimate K_{ii} using Monte Carlo integration

$$K_{ii} \approx V \times \langle \text{Integrand} \rangle \quad (12)$$

where $V = (2L)^3$.

- ☐ Perform the calculation for varying numbers of points $N = 10^2, 10^3, 10^4, 10^5, 10^6, 10^7, 10^8$.
- ☐ Record the estimated values of K_{ii} .
- ☐ Plot the estimated K_{ii} versus N on a logarithmic scale.
- ☐ Briefly discuss the convergence of your results.

2.1.3 Compute the Diagonal Kinetic Energy Matrix Element Using Importance Sampling

- ☐ Choose an importance sampling distribution $g(x, y, z)$ approximately proportional to $|\psi_{1s}(x, y, z)|^2$, the probability density of the 1s orbital.
- ☐ Since $\psi_{1s}(\mathbf{r})$ is spherically symmetric, consider using a Gaussian distribution for r .
- ☐ Sample x , y , and z from the Gaussian distribution
- ☐ Adjust the integrand by dividing by $g(x, y, z)$

$$K_{ii} \approx \frac{1}{N} \sum_{i=1}^N \frac{-\frac{1}{2} \psi_{1s}^*(x_i, y_i, z_i) \nabla^2 \psi_{1s}(x_i, y_i, z_i)}{g(x_i, y_i, z_i)} \quad (13)$$

- ☐ Use the same N values as before.
- ☐ Record the estimated values of K_{ii} .
- ☐ Plot the estimated K_{ii} versus N on a logarithmic scale.
- ☐ Compare the efficiency and convergence of importance sampling with random sampling.

2.1.4 Compute the Off-Diagonal Kinetic Energy Matrix Element Using Random Sampling

- ☐ The off-diagonal kinetic energy matrix element between two 1s orbitals centered at $\mathbf{R}/2$ and $-\mathbf{R}/2$ along the z -axis ($\mathbf{R} = (0, 0, 1.4)$) is

$$K_{ij} = \int \psi_{1s}^*(\mathbf{r} + \mathbf{R}/2) \left(-\frac{1}{2} \nabla^2 \psi_{1s}(\mathbf{r} - \mathbf{R}/2) \right) d\mathbf{r} \quad (14)$$

- ☐ Generate random points (x, y, z) within an appropriate region.
- ☐ For each point, compute the integrand

$$\text{Integrand} = -\frac{1}{2} \psi_{1s}^*(x, y, z + R_z/2) \nabla^2 \psi_{1s}(x, y, z - R_z/2) \quad (15)$$

where $R_z = 1.4$.

- ☐ Estimate K_{ij} using Monte Carlo integration.
- ☐ Use the same N values as before.
- ☐ Record the estimated values of K_{ij} .
- ☐ Plot the estimated K_{ij} versus N on a logarithmic scale.
- ☐ Briefly discuss the convergence of your results.

2.1.5 Compute the Off-Diagonal Kinetic Energy Matrix Element Using Importance Sampling

- ☐ Choose $g(x, y, z)$ that captures the regions where the product of the orbitals is significant.
- ☐ Since the orbitals are centered at different locations, consider a Gaussian distribution centered between them.
- ☐ Sample points (x, y, z) from $g(x, y, z)$.
- ☐ Adjust the integrand accordingly

$$K_{ij} \approx \frac{1}{N} \sum_{i=1}^N \frac{-\frac{1}{2} \psi_{1s}^*(x_i, y_i, z_i + R_z/2) \nabla^2 \psi_{1s}(x_i, y_i, z_i - R_z/2)}{g(x_i, y_i, z_i)} \quad (16)$$

- ☐ Use the same N values as before.
- ☐ Record the estimated values of K_{ij} .
- ☐ Plot the estimated K_{ij} *versus* N on a logarithmic scale.
- ☐ Compare the efficiency and convergence of importance sampling with random sampling.

2.2 Submission Guidelines

- ☐ A Python script containing
 - ☐ Your functions for $\psi_{1s}(x, y, z)$, $\nabla^2\psi_{1s}(x, y, z)$, and both integration methods.
 - ☐ Adequate comments explaining your code.
- ☐ A Jupyter notebook containing your
 - ☐ Plots of K_{ii} and K_{ij} versus N for both methods.
 - ☐ Explanations, observations, and any conclusions drawn.
- ☐ Set a random seed (*e.g.*, `np.random.seed(42)`) for reproducibility.

2.3 Hints

After you have analytically computed the derivatives involved in the Laplacian of ψ_{1s} , it's a good practice to verify your results using symbolic mathematics software. Tools like WolframAlpha or SymPy in Python can perform symbolic differentiation and simplify expressions for you.