

PC5215, Numerical Recipes with Applications, Lab 3

Due Thursday, 23 Oct 2025

1. The quantum Hamiltonian of a hydrogen molecule H_2 with two fixed protons A and B and two moving electrons 1 and 2 is given by

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} - \frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 r_{AB}},$$

where m is the mass of the electron, ϵ_0 is the dielectric constant of vacuum, e is the magnitude of the electron charge, \hbar is the reduced Planck constant. ∇_1^2 is the 3D Laplacian for electron 1, and ∇_2^2 for electron 2. The first two terms are the kinetic energies, and the rest are Coulomb energies. We assume that the two protons are located at fixed vector positions $\mathbf{r}_A = (0,0,0)$ and $\mathbf{r}_B = (r_{AB}, 0, 0)$, and the two electrons are at $\mathbf{r}_1 = (x_1, y_1, z_1)$ and $\mathbf{r}_2 = (x_2, y_2, z_2)$; they are the dynamic variables of the electron positions in a 6-dimensional space. The distance is defined by $r_{\alpha\beta} = |\mathbf{r}_\alpha - \mathbf{r}_\beta|$, where α or β can be A, B, 1 or 2. In the simplest possible approximation for the electron wave function, we use the atomic orbital of the ground-state hydrogen atom in the symmetrized form,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi(r_{A1})\varphi(r_{B2}) + \varphi(r_{A2})\varphi(r_{B1}), \quad \varphi(r) = e^{-r/a_0}$$

where a_0 is the Bohr radius. Note that the wave function is not normalized to 1.

- Compute the explicit expression of ∇_1^2 acting on the wave function ψ . This expression is needed in part c.
- Without actually performing any calculation, what should be the answer for the energy in part c, if the distance between two protons r_{AB} is infinity? Hint: think of a hydrogen atom H in isolation.
- Based on the variational principle, estimate numerically lower bounds to the hydrogen molecule H_2 bonding energy by evaluating the 6-dimensional integral through a Monte Carlo method with the Metropolis algorithm,

$$E(r_{AB}) = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \int d\mathbf{r}_1 d\mathbf{r}_2 P(\mathbf{r}_1, \mathbf{r}_2) E_L(\mathbf{r}_1, \mathbf{r}_2).$$

To apply the Metropolis algorithm, one writes the expectation value of the Hamiltonian as an average of some effective local energy $E_L(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\Psi} \hat{H} \Psi$ with respect to $P \propto |\Psi|^2$ as the probability distribution. It is best for numerical accuracy that the kinetic energy terms from the two Laplacians should be computed analytically first, as asked in part a. For internal computer calculation, it is best to use atomic units ($\hbar=1, e=1, m=1, 4\pi\epsilon_0=1$). Outline your method, and report the results in conventional units of ångström (for distance r_{AB} between two protons) and eV (for energy). Make a plot of energy (with error bars) vs. r_{AB} . As Monte Carlo for each data point is computationally intensive, you should sample about 20 points for r_{AB} in the proper range, while each Monte Carlo point should be as long as possible, say 10^5 steps.

[For background, read Chapter 2 of “Molecular Modelling, principles and applications”, by Andrew R. Leach.]