PC5215, Numerical Recipes with Applications, Lab 2 (Due Tuesday, 10 Oct 2023)

1. Using the polynomial interpolation Python code polint.py of "Numerical Recipes in C", compute and then plot a curve for x in the interval [-1, 4], passing through exactly the points (x,y) = (-1, 1.25), (1, 2), (2,3), (4,0) with a cubic polynomial. For plotting, you can use Origin, or the plotting function in MATLAB, or even Python itself (need import matplotlib). Label the axis, mark the points with circles and the interpolated curve with solid line.

2. Implement the Romberg integration method in Python [following the "Numerical Recipes" code qromb(), trapzd.py and polint.py], and compute the integral:

$$\int_0^2 x^4 \ln\left(x+\sqrt{x^2+1}\right) dx.$$

Here ln means natural logarithm (base e). Use different parameters (such as the number of iterations JMAX, and convergence criteria EPS), compare the results. What is your most accurate estimation of the integral you can get? Give an error estimate of the answers. Compare with the exact answer. You can obtain exact answer with a symbolic integration system, such as *Mathematica*, and evaluate to high accuracy (say 16 digits).

3. The quantum Hamiltonian of a hydrogen molecule H_2 with two fixed protons and two moving electrons is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_{A1}} - \frac{e^2}{4\pi\varepsilon_0 r_{B1}} - \frac{e^2}{4\pi\varepsilon_0 r_{A2}} - \frac{e^2}{4\pi\varepsilon_0 r_{B2}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}},$$

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. We assume that the two protons are located at 3D 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). 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 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 Bohr radius. Note that the wave function is not normalized to 1.

Estimate numerically lower bounds to the hydrogen molecule bonding energy by evaluating the 6-dimensional integral through a Monte Carlo method with the Metropolis algorithm,

$$E(r_{AB}) = \frac{\left\langle \Psi \mid \hat{H} \mid \Psi \right\rangle}{\left\langle \Psi \mid \Psi \right\rangle} \ .$$

To apply the Metropolis algorithm, one writes the expectation value of the Hamiltonian as an average of some effect local energy $E(x_1,y_1,z_1,x_2,y_2,z_2)$ with respect to $|\Psi|^2$ as the probability distribution. It is best for numerical accuracy that the kinetic energy terms from the two Laplacians should be computed analytically first. For internal computer calculation, it is best to use atomic units ($\hbar$=1,e=1,m=1,$4\pi\varepsilon_0$=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}.

[For background, read any quantum mechanics textbooks, or Chapter 2 of "Molecular Modelling, principles and applications", by Andrew R. Leach.]