DUE BEFORE WORKSHOP 4 - May 26th

Write a report addressing the following problems. All computational exercises must be completed in Fortran. Submit a **PDF** of your report via Blackboard, along with any Fortran files, input and output files, gnuplot scripts, and anything else required to run your programs and replicate your results in a separate zipped directory.

Marking: There are ten marks in total. One mark is for presentation (readability, figure formatting etc), and the remaining nine marks will be split unevenly amongst the problems. For each problem half the available marks are for the implementation, and the other half are for the discussion of theory and explanation of results wherever appropriate.

Problem 1 - Quantum harmonic oscillator (6 marks)

Consider an electron in a quantum harmonic oscillator, with potential

$$V(x) = \frac{1}{2}\omega^2 x^2. \tag{1}$$

Use either the the shooting-bisection or Numerov-Cooley method to calculate the wave functions $\psi_n(x)$ and corresponding energies E_n of the quantum harmonic oscillator for $n = 0$, 1, 2, and 3. For simplicity, take $\omega = 1$, and use Hartree atomic units ($m_e = \hbar = 1$).

If you choose to use the Numerov-Cooley method, you may wish to write a general subroutine which inputs the potential on a grid and performs the Numerov iteration (one subroutine each for the forwards and backwards cases), so you can re-use it for problem 2. You will also need to find a suitable way of choosing the matching point x_m which guarantees $\psi^\mathrm{L}(x_\mathrm{m})$ and $\psi^\mathrm{R}(x_\mathrm{m})$ are nonzero.

Benefits to choosing each approach:

Shooting-bisection: Easier to understand and implement

Numerov-Cooley: You can reuse the forward-iteration Numerov subroutine for Problem 2

Include the following in your report:

- Discussion of any relevant theory
- Figures comparing the wave functions and energies to the analytical solutions, showing convergence as the grid spacing δx is decreased. The two methods converge at different rates so find a few suitable δx values to demonstrate the point well.
- A table showing the Energies for each n (rows) and δx (columns). Include a column for the analytical energies.
- A table showing the number of iterations required to reach convergence for each n and δx.

Extension (optional): implement both methods and compare the number of iterations required to reach convergence with each one.

Problem 2 - Dissociative wave functions for H_2^+ (3 marks)

Modify your vibrational wave function code from the previous assignment to also calculate dissociative wave functions for the $2p\sigma_u$ state of H_2^+ using Numerov's method. Read in the appropriate parameters to construct a grid similar to the R grid but containing values of the kinetic-energy release (0 to 30 eV will be sufficient), and use Numerov's method to calculate the wave function for each energy

$$E = E_\mathrm{k} + D, \tag{2}$$

where $D \equiv \epsilon(\infty)$ is the asymptotic energy of the potential-energy curve. You will need to store the wave functions in a matrix similar to before with each column being a wave as a function of R. Determine what you will have to do to account for the nuclear reduced mass in the Numerov iteration (you should

see you do not need to change the Numerov subroutine and just need to modify the energy and potential you pass to it).

Since we use atomic units for the calculations you will need to convert your E_k grid to Hartrees (divide by 27.21136) first, then convert back to eV when printing the KER distribution to file so you can plot it as a function of energy in eV.

For a fairly course E_k grid (so you don't have to write a huge matrix to file), print out the dissociative wave functions so you can plot them against the $2p\sigma_u$ potential-energy curve like the figure in the slides.

Use the Franck-Condon approximation to estimate the normalised kinetic-energy-release distributions:

$$\frac{\mathrm{d}\sigma_{f,iv_i}}{\mathrm{d}E_\mathrm{k}} \approx \left|\langle \nu_{fE_\mathrm{k}} | \nu_{iv_i} \rangle\right|^2 \tag{3}$$

and print them to file as a function of E_k for each initial vibrational level v_i in the $1s\sigma_g$ state.

Include the following in your report:

- Discussion of any relevant theory
- A figure of a few different dissociative wave functions in the $2p\sigma_u$ PEC, shifted to show their energy
- Figures of the kinetic-energy-release distributions for scattering on the $v_i = 0$, 3, 6, and 9 levels of the $1s\sigma_g$ state.

Extension (optional): at high incident energies the R-dependent $2p\sigma_u$ excitation cross section can be well approximated by

$$\sigma_{f,i}(R) \propto R^2. \tag{4}$$

Implement this in your code as well and normalise the resulting KER distribution. How does this compare with the Franck-Condon approximation?