PHYS4070/PHYS7270 – Due date: 19/04/2021 10:00am

Assignment 3 - Hydrogen-like atoms: calculation of wavefunctions, energies, and expectation values

Help: Rm 6-427, Mon 1-2pm, Tues & Wed, 2-3pm; b.roberts@uq.edu.au

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1 Background

The Schrödinger equation for a model hydrogen-like atom is:

$$\left(-\frac{\hbar}{2m_e}\nabla^2 + V(r)\right)\psi_{nlm}(r,\theta,\phi) = \varepsilon_n\,\psi_{nlm}(r,\theta,\phi), \tag{1}$$

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}, \tag{2}$$

where m_e is the electron mass, and ∇^2 is the Laplacean in spherical coordinates. Our problem is to find the wavefunctions and energies of a hydrogenlike atom (that is, an ion with a single electron only). You may choose any ion, including neutral hydrogen. This will place us in good stead to consider more complex atomic systems in the near future.

2 Problems

1. Re-write equation (1) using atomic units ($e \to e\sqrt{4\pi\epsilon_0}$, $r \to r/a_B$, $mass \to mass/m_e$, so that $\hbar = m_e = |e| = 1$, $c = 1/\alpha \approx 137$), and use the separation of variables

   $$\psi_{nlm}(\boldsymbol{r}) = R_{nl}(r)Y_{lm}(\theta,\phi) = \frac{P_{nl}(r)}{r}Y_{lm}(\theta,\phi)$$

   to find the "radial Schrodinger equation" for $P(r)$ of the form

   $$H_{\text{radial}}P_{nl}(r) = \varepsilon_n P_{nl}(r) \tag{3}$$

   (you do not need to present working). [You may consult textbook: W. R. Johnson, *Atomic Structure Theory*, Chapter 2, available as pdf from library]

2. There are many ways to solve the equation (3); we will use perhaps the simplest. Find and encode a scheme to turn the radial differential equation into a matrix eigenvalue problem, using the "hard boundary value" condition. Make sure you appropriately avoid the problem occurring at $V(0)$. You will have to decide appropriate initial/final radial coordinates to use, and ensure you use a sufficiently small step-size δr – justify your choices. Keep in mind the typical radius for an atomic orbital scales like $r_{\text{typical}} \sim a_B n^2/Z$.

   - You may want to write a simple class to store the $N \times N$ square matrix. (Note that to use lapack, the matrix must use contiguous memory – we cannot define a "vector of vectors" or a pointer-to-pointers style 2D array.)

   Solve the Schrodinger equation using lapack for $l = 0, 1$ (s and p states). The radial Hamiltonian matrix is real and symmetric, so we can use the routine *dsyev*.

   - You should wrap the call to lapack in its own function (possibly in a separate c++ file)
   - Documentation: http://www.netlib.org/lapack/explore-html/

3. The exact analytical binding energies for a hydrogenlike atom (in given approximation) are

$$\varepsilon_n = -\frac{Z^2}{2n^2}\,(2R_y)$$

($R_y \approx 13\,\mathrm{eV}$ is the Rydberg constant – $2R_y = 1$ in atomic units). Compare the first few eigenvalues to the analytic solution. At some point, the calculated energies will stop matching – we will see why below. Try to ensure that we have good agreement up to at least $n = 5$ – you may need to "go back" to question 3 and increase the maximum radial coordinate and/or number of steps.

4. Normalise the wavefunctions (eigenvectors), and plot the radial part of the normalised probability distribution for the electron in $n = 1, 2, 3$ for $l = 0$.

   - You may want to write a function (or functions) to perform integrals of the form $\int P_a(r)P_b(r)\,f(r)\,\mathrm{d}r$, where $f(r)$ is some function of r
   - To plot: use gnuplot. Write the relevant data to a text file, and read the text file using gnuplot. You may either include a bash script in you code to do this, or just include the plots within your report
   - You can use atomic units

5. Calculate the expectation values $\langle |r| \rangle$ and $\langle |r|^{-1} \rangle$ for the first few n for $l = 0, 1$ (Note that $n_{\min} = l + 1$). Compare them to the analytical formulas:

$$\langle r \rangle_{nl} = \frac{a_B}{2Z}[3n^2 - l(l+1)] \tag{4}$$

$$\langle r^{-1} \rangle_{nl} = \frac{Z}{a_B n^2} \tag{5}$$

   What happens as the expectation value $\langle r \rangle$ becomes comparable to the chosen maximum radial coordinate? Comment on the link to the energy "problem" that arose in question 3. Note that $\langle r \rangle$ is the expectation value of $|r|$ – the wavefunction extends significantly beyond this value.

6. When we solved the matrix eigenvalue problem, we obtained an entire spectrum of states (solutions to Schrodinger equation). The number of states we obtain will be equal to the dimension of the matrix – which is equal to the number of steps between $r_{\min}$ and $r_{\max}$. From the completeness relation of quantum mechanics, we should be able to write:

$$\langle a|r^2|a\rangle = \sum_m \langle a|r|m\rangle\langle m|r|a\rangle, \tag{6}$$

   where $r = |\boldsymbol{r}|$ is a scalar. Our set of solutions should, in theory, be complete. We may use (6) to test this. Calculate the left- and right-hand-side of Eq. (6) for the first few states (n=1,2,3) for $l = 0$ [i.e., $|a\rangle = |1s\rangle, |2s\rangle, |3s\rangle$]. In the sum over m, observe what happens when we use only the first $10, 100, 500$ etc. states in the summation. You will likely notice that you get better agreement if you drop the last $\sim 10\%$ or so states from the sum – this is normal, and is due to inaccuracies in the numerical approximations (caused by unphysical "hard" boundary condition). Do we need to include other values of l in the sum over m? If not, why?

   That we have managed to form such a complete set of states is important – it is very useful to have an (approximately) complete, *finite* set of states (which includes the discretised continuum). We can use these as a basis for perturbation theory.

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7. In Equation (1), the electron mass m_e appears in the kinetic energy operator. This assumes the nucleus is entirely stationary, which is valid in the $M_{\text{nucleus}} \to \infty$ limit. To correct for this, m_e should be replaced by the reduced mass. Re-do Question 3 using the reduced mass (for whichever isotope of chosen atom you like) – how much difference does it make? (Hint: proton-electron mass ratio is $m_p/m_e \approx 1836$)

3 Submission

Submit your report and your source code via the git submission server. Create a new directory as03 under your student user name, e.g. s1234567/as03/, and upload all the files listed:

- Your report (as a pdf) that must cover all of the tasks and be written in a professional style
- Your source code. You may organise the files however you wish – for readability, you may want to split your functions across several files
- A bash script that compiles the code and shows the plots (using gnuplot).
- Any other files needed for the bash script to produce and present the assignment data.

4 Hints for solving eigenvalue problem with lapack

The Hamiltonian matrix is a real symmetric matrix. Solve this matrix eigenvalue problem by calling `dsyev` (a lapack function) in your C++ code. `dsyev` is used to solve the eigenvalue problem for a symmetric matrix. You need to provide `dsyev` the dimension and the elements of the target matrix. The `dsyev` function will return you the eigenvalues and eigenvectors of the target matrix. Documentation for lapack is here: http://www.netlib.org/lapack/explore-html/

To form the matrix eigenvalue problem, you need to define the boundary (r_{min} and r_{max}), the number of steps (N_{step}), and thus the step size, $\delta r = \frac{r_{\text{max}} - r_{\text{min}}}{N_{\text{step}} - 1}$, so that the function $P(r)$ goes to zero at the endpoints.

Energy eigenvalues, radial wavefunctions, and radial probability distribution function: Solve the eigenvalue problems with your final input parameters. You will get “all” energy eigenvalues and eigenfunctions that can be defined in the size of the system you constructed. You will need to determine the correct ones to use.