Radial Dipole Matrix Elements

January 15, 2020

Problem 1: Recall that the radial part of Schrödinger's equation for an electron orbiting a central point charge can be written as:

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{d}{dr}r\right)^2+\frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}\right]R_{nl}(r)=-ER_{nl}(r). \tag{1}$$

Here Z is the ionic stage ($Z=1$ for a neutral atom). For bound states the total (binding) energy has to be negative, so note that notation $E \geq 0$ in Eq. 1 following this convention.

Your objective over the following problems is to calculate the radial component of the dipole matrix element numerically, assuming no *a priori* knowledge of the solutions to the S.E.

(a) Let's first set up the equation we would like to solve. Show that by using $P_{nl}=rR_{nl}$ we can write this second order differential equation as a system of coupled first order differential equations:

$$\begin{aligned}\frac{dQ_{nl}}{d\rho}&=\left[\frac{E}{R_H}+\frac{l(l+1)}{\rho^2}-\frac{2Z}{\rho}\right]P_{nl},\\ \frac{dP_{nl}}{d\rho}&=Q_{nl},\end{aligned} \tag{2}$$

where ρ is in units of Bohr radii (a_0), and R_H is the Rydberg constant for hydrogen. Show your expressions for R_H and a_0.

(b) What are two reasons why we would go to the trouble of writing the S.E. in this way?

(c) Looking at this equation, describe why different isotopes of the same element are useful in determining the physical constants that make up R_H.

Problem 2: When solving this problem analytically, we would use Eq. 2 with the boundary conditions $P_{nl}(0)=P_{nl}(\infty)=0$. When solving this problem analytically, we determine the eigenfunctions P and corresponding eigenvalues E. However, for more complicated atoms we typically already know E through spectroscopic studies. As an alternative to the analytical method, we can use the known (measured) value of E for a given transition, and integrate numerically. However, this would over-constrain the problem, and so one of the boundary conditions must be dropped. This is known as the Coulomb approximation.

We will implement the Coulomb approximation by using known values of E and the b.c. at $\rho = \infty$ (or, in practice, a large value of ρ). The b.c. at ρ =0 is then dropped to avoid over-constraining the problem, and contributions to the integral near $\rho = 0$ are ignored.

(a) Write a program to numerically integrate Eq. 2 by stepping toward the origin from a large r asymptotic value. Plot the relevant wavefunctions and potentials for the 4p $\rightarrow$ 4d transition in hydrogen.

(b) The total dipole moment for a transition is given by $d_{12} = e\,\langle 1|\hat{r}|2\rangle$. What is the expression for the radial part of the dipole moment, using the notation from Problem 1? Your answer should be in the form of an integral involving $P(\rho)$ functions.

(c) Using you results from Problem 2(a) and the expression from Problem 2(b), calculate the radial dipole matrix element for the three cases where the smallest value of r_0 you use is $0.1\,a_0$, $0.5\,a_0$, and a_0. How sensitive is the numerical procedure to dropping the region near the origin? For hydrogen, the exact answer (assuming $\Delta n = 0$ and $\Delta l = 1$) is $d = 3/2n\sqrt{n^2 - l_>^2}$ where $l_>$ is the larger of the two states' l values. How do your results compare with the exact value?

Problem 3: Let's investigate a more complex atom.

(a) Use your program to calculate the radial matrix element for the 3p $\rightarrow$ 3d transition of Na. To truly feel like an atomic physicist, dig around in the included handout from the National Bureau of Standards: "Atomic Transition Probabilities - Sodium through Calcium" to find the data you need.

(b) Compare your solution with the value in that same handout noting that (in this case):

$$S = (2s+1)l_> d^2, \tag{3}$$

where d is the radial dipole matrix element.

Problem 4: This technique can also be used for atoms with multiple valence electrons. Consider the following transition in Pb:

$$6\text{p}7\text{s}\ {}^3P_1 \longrightarrow 6\text{p}7\text{p}\ {}^3D_1 \quad ; \quad \lambda = 1.06\,\mu\text{m} \tag{4}$$

(a) Write down all the quantum numbers (and their values) relevant to this transition.

(b) Calculate the radial dipole matrix element. The ${}^3P_1$-state has $E = 35\,287\,\text{cm}^{-1}$ and the ${}^3D_1$-state has $E = 44\,675\,\text{cm}^{-1}$. The ionization energy for Pb is $59\,821\,\text{cm}^{-1}$.