▸▸▸ PROJECT FOR SECTION 14.3

The Hydrogen Atom

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The hydrogen atom was one of the most important unsolved problems in physics at the beginning of the twentieth century. With just one proton and one electron, it provided the simplest possible example that had to be explained by any atomic model. The classical picture was that of an electron orbiting around the proton due to electrical attraction. This hypothesis was inconsistent, however, because to move around the proton, the electron needs to accelerate. Any accelerated charged particle radiates electromagnetic waves. Over time, then, the electron should lose kinetic energy and eventually collapse toward the nucleus of the atom. To make matters even more puzzling, it was known from spectroscopic data that hydrogen gas emits light of very specific wavelengths, the so-called spectral lines. Moreover, the spectral lines that could be observed in the visible range satisfy an empirical formula first described by J. J. Balmer in 1885. If the wavelength is denoted by λ, then the spectral lines of what is now called the Balmer series are defined by

$$\frac{1}{\lambda} = R_H\left(\frac{1}{4} - \frac{1}{k^2}\right),\ k = 3, 4, 5, \ \ldots \tag{1}$$

where R_H is a constant for which the best empirical value is $10{,}967{,}757.6 \pm 1.2\ \text{m}^{-1}$.

Any reasonable atomic model not only had to explain the stability of the hydrogen atom, but also had to produce an explanation for spectral lines with frequencies satisfying this formula. The first such model was proposed by Niels Bohr in 1913, using an ingenious combination of classical arguments and two "quantum postulates." Bohr assumed that the electron is restricted to move in orbits with "quantized" angular momentum—that is, integer multiples of a given constant. See Figure 1. Moreover, the atom emits energy in the form of electromagnetic waves only when the electron jumps from one fixed orbit to another. The frequencies of these waves are then given by Planck's formula, $\Delta E = \hbar\nu$, where ΔE is the energy difference between the orbits and $\hbar$ is Planck's constant.

Try to reproduce Bohr's steps by working Problems 1–3.

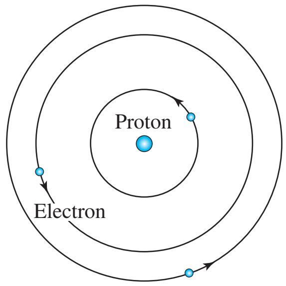

Figure 1 Bohr planetary model of the hydrogen atom: In this model, one electron can occupy only certain orbits around a nucleus consisting of one proton.

Related Problems

1. Suppose, as shown in Figure 1, the electron has mass m and charge $-e$ and moves in a circular orbit of radius r around the proton, which has charge e and a much greater mass. Use the classical formulas for the electric force for point charges to deduce that the total mechanical energy (kinetic plus potential) for the electron in this orbit is

$$E = -\frac{e^2}{8\pi\varepsilon_0 r}, \tag{2}$$

where ε_0 is the permittivity of space. Further, deduce that the classical angular momentum for this orbit is

$$L = \sqrt{\frac{me^2 r}{4\pi\varepsilon_0}}. \tag{3}$$

2. Now let us use Bohr's first postulate: Assume that the angular momentum is of the form $L = n\hbar$, where $n = 1, 2, \ldots$. Substitute this expression into equation (3) and find an expression for the orbital radius r as a function of n. Insert this function into equation (2) to obtain an expression for the quantized energy levels of the hydrogen atom.

3. We are now ready to use Bohr's second postulate. Suppose that an electron makes a transition from the energy level E_k to the energy level E_n, for integers $k > n$. Use the formula $\Delta E = \hbar\nu$ and the relation $\lambda\nu = c$ (where c is the speed of light) to deduce that the wavelength emitted by this transition is

$$\frac{1}{\lambda} = \frac{me^4}{8\hbar^3\varepsilon_0^2 c}\left(\frac{1}{n^2} - \frac{1}{k^2}\right). \tag{4}$$

Put $n = 2$ in equation (4) and conclude that this gives the Balmer series with $R_H = \frac{me^4}{h^3\varepsilon_0^2 c}$. Now do a literature search for the values of the physical constants appearing in this formula and compute R_H. Is your value comparable with the empirical value? Finally, replace m by the reduced mass $\frac{mM}{m + M}$ (where M is the mass of the proton) and be impressed by the remarkable accuracy of this result.

Despite its obvious success, the Bohr model had the feature of stretching the classical theory as far as it could go and then supplementing it by ad hoc quantum postulates where necessary. This state of affairs was rightly considered to be unsatisfactory and inspired physicists to develop a much more comprehensive theory of atomic phenomena, giving rise to quantum mechanics. At its core rests a partial differential equation proposed by Erwin Schrödinger in 1926 in a paper suggestively entitled "Quantization as an Eigenvalue Problem." The time-independent Schrödinger equation for a physical system of mass m subject to a potential $V(\mathbf{x})$ is

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{x}) + V(\mathbf{x})\Psi(\mathbf{x}) = E\Psi(\mathbf{x}), \qquad (5)$$

where ∇^2 is the Laplacian operator and E is the (scalar) value for the total energy of the system in the stationary state $\Psi(\mathbf{x})$. Here $\mathbf{x} = (x, y, z)$ represents a point in the three-dimensional position space. The correct interpretation of the function $\Psi(\mathbf{x})$ involves subtle probabilistic arguments. For our problem, it suffices to say that $\Psi(\mathbf{x})$ contains all the information that can be physically obtained about the system in consideration. Our purpose now, in the spirit of Schrödinger's original paper, is to try to obtain the energy levels E_n for the hydrogen atom as the possible values of energy for which equation (5) admits a solution.

Now try working the next problem.

4. Because the potential energy $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$ depends only on the radius r, it is natural for this problem to consider spherical coordinates (r, θ, ϕ) defined by the equations

$$x = r\sin\theta\cos\phi, \quad y = r\sin\theta\sin\phi, \quad z = r\cos\theta.$$

Begin by writing down equation (5) in these coordinates [recall the expression for the Laplacian operator in spherical coordinates in (2) of Section 14.3]. Now use separation of variables with $\Psi(\mathbf{x}) = R(r)\Theta(\theta)\Phi(\phi)$ to show that the radial component $R(r)$ satisfies

$$R'' + \frac{2}{r}R' + \frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)R = -k\frac{2m}{\hbar^2 r^2} \qquad (6)$$

where k is a constant.

In the solution of Problem 4 you should have found that the separation of variables technique splits the Schrödinger equation into two parts: one depending solely on r and the other depending only on θ and ϕ. Each of these parts must be equal to a constant, which we called k. If we were to pursue the solution of the angular part (the one involving θ and ϕ), we would find that k is a quantum number related to the angular momentum of the atom. For the remainder of this project, we will consider the case $k = 0$, corresponding to states with zero angular momentum.

At this point work Problems 5–7.

5. Put $k = 0$ in equation (6) and consider its limit as $r \to \infty$. Show that e^{-Cr}, where

$$C = \sqrt{-\frac{2mE}{\hbar^2}} \qquad (7)$$

is a solution for this limiting equation.

6. Based on the previous exercise, consider a general solution of the form $R(r) = f(r)e^{-Cr}$ for an analytic function $f(r)$. By analyticity, the function $f(r)$ possesses a series expansion

$$f(r) = a_0 + a_1 r + a_2 r^2 + \cdots$$

Substitute this series into equation (6) (with $k = 0$) and deduce that the coefficients a_j satisfy the recursive relation

$$a_j = 2\frac{jC - B}{j(j+1)}a_{j-1}, \quad j = 1, 2, \ldots, \qquad (8)$$

where $B = \frac{me^2}{4\pi\varepsilon_0\hbar^2}$

7. Show that the limit of equation (8) for large values of j is $a_j = \frac{2C}{j+1}a_{j-1}$, which is the power series for the function e^{2Cr}. Conclude that the only way to have the function $R(r)$ decaying to zero as r becomes large is for the power series for $f(r)$ to terminate after a finite number of terms. Finally, observe that this happens if and only if $nC = B$ for some integer n.

Our final problem in this project will produce the energy levels of the hydrogen atom as a consequence of the work done so far. You should observe that, this time around, the existence of quantized energy levels did not have to be postulated, but rather followed from the mathematical analysis of Schrödinger's equation.

While the derivation steps are more difficult than those followed by Bohr, it should be clear to you that the elimination of Bohr's ad hoc quantization axioms was a significant achievement by Schrödinger, for which he was awarded the Nobel Prize in physics in 1933.

8. Use the condition expressed in the previous exercise and the formulas obtained for C and B to conclude that the allowed energies for the hydrogen atom in a state with zero angular momentum are

$$E_n = -\frac{me^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} \tag{9}$$

which should coincide with the energy levels that you found for the Bohr atom in Problem 2.