Quantization principle

The present understanding of atom is provided by quantum physics and this has withstood the test of experiments so much so that atomic spectrum is known today to the precision of sixth decimal place. However, it is still useful to learn some details about old quantum theory that often helps us to make quick estimates of various physical quantities.

The quantization condition can be stated as follows: For every coordinate q that is a periodic function of time, the corresponding momentum coordinate p_q satisfies the condition

$$\oint p_q dq = nh \tag{1}$$

where $n = 1, 2, 3, \ldots$ takes integral values. For instance, if q is an angle coordinate in a plane that takes values $0 \leq q < 2\pi$, p_q will be the angular momentum for rotation in that plane. The physical consequence of this condition will be evident when we study Sommerfeld model where it is put to use.

Sommerfeld model

Bohr model assumes circular orbits for electrons around the nucleus. The radius of a circle is a constant. Thus we need only an angle measured from some fixed line to specify the position of the electron. We have already seen the drawbacks of Bohr's model, in spite of all its successes. To explain the spectrum of the H-atom better, Sommerfeld built a model

Figure 1: Circular and elliptic orbits

where orbits of electrons around the nucleus are assumed to be elliptic, much like the orbits of planets in solar system. In Bohr model, the circular orbits had only one periodic coordinate - the angle θ measured from a reference line as shown in fig(1a). The radius of the circle remains the same and we need no coordinate to represent the distance of the electron measured from the centre of the orbit. In an ellipse, however, it is not just the angle θ that keeps changing. Even the distance r to a point on the ellipse, measured from any point, keeps changing. But, as is clear from fig(1b), both the angle as well as the radius is periodic.

Sommerfeld imposed the quantization condition in eqn(1) for the coordinates θ and r. Taking up θ coordinate first, the momentum corresponding to a rotational motion that causes a change in θ is the angular momentum L.

$$\oint L \, d\theta = n_\theta h \tag{2}$$

The integral runs from $\theta = 0$ to $\theta = 2\pi$. The centrifugal force that causes this rotation is the electrostatic attraction between the nucleus and the electron. This force depends only on the distance from the nucleus to the electron and hence is a *central force*. For motion in central force potential, the angular momentum will be conserved and hence L will not change with time. The quantization condition becomes

$$L \int_0^{2\pi} d\theta = n_\theta h$$

$$\Rightarrow L = \frac{n_\theta h}{2\pi} = n_\theta \hbar \tag{3}$$

Here $n_\theta = 1, 2, 3, \ldots$. In terms of the angular momentum L the kinetic energy due to rotational motion is

$$K.E._{Rot} = \frac{L^2}{2mr^2} \tag{4}$$

Substituting, eqn(3) in eqn(4) the rotational kinetic energy for the electron in Sommerfeld model turns out to be

$$K.E._{Rot} = \frac{n_\theta^2 \hbar^2}{2mr^2} \tag{5}$$

with $n_\theta = 1, 2, 3, \ldots$, called the *azimuthal quantum number*. In an elliptical orbit, electron also has a translational kinetic energy due to the change in r coordinate

$$K.E._{Trans} = \frac{p_r^2}{2m} \tag{6}$$

From the quantization condition for the r coordinate

$$\oint p_r \, dr = n_r h \tag{7}$$

The total energy is conserved and is always the sum of kinetic and potential energies

$$E = K.E._{Trans} + K.E._{Rot} + P.E. = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r} \tag{8}$$

In terms of total energy we could express the momentum p_r as

$$p_r = \sqrt{2m\left(E - \frac{L^2}{2mr^2} + \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\right)} \tag{9}$$

Substituting the above in the quantization condition in eqn(7),

$$\oint \sqrt{2m\left(E - \frac{L^2}{2mr^2} + \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}\right)} \, dr = n_r h \tag{10}$$

The integral on the LHS depends on the ratio of the length of the semi-major axis a and the length of the the semi-minor axis $r = b$ of the ellipse. We will not explicitly evaluate the integral in eqn(10), but only write down the result. The integral gives us the condition

$$L\left(\frac{a}{b} - 1\right) = n_r h, \qquad n_r = 0, 1, 2, \ldots \tag{11}$$

Substituting the conditions in eqn(5) and eqn(11) into eqn(8) we get the n^{th} energy level to be

$$E_n = -\frac{mZ^2e^4}{8\epsilon_0^2 n^2 h^2} \tag{12}$$

where we have introduced *principal quantum number* $n = n_r + n_\theta$ that takes values $n = 1, 2, 3, \ldots$. It may be noted that, in the above we have taken the mass of electron m to be negligibly small compared to the mass of nucleus m_n. If we do not use this approximation, we must use the *reduced mass* $\mu = \frac{mm_n}{m+m_n}$ in place of m in eqn(12).

The spectrum of Sommerfeld model has many features that Bohr model did not have. Degeneracy of energy level is one such feature. For instance, it is clear that the same value of energy corresponding to, say, $n = 2$ can be achieved by having $n_r = 0, n_\theta = 2$ and $n_r = 1, n_\theta = 1$ level. Thus Sommerfeld model allows for the fine spectrum of H-atom which Bohr model could not explain.

A complete explanation of fine spectrum of Hydrogen requires the degeneracy of energy levels to be removed. Sommerfeld used a relativistic model wherein it was found that no degeneracy remained for the energy levels. The allowed values of energy explicitly depended on the principal quantum number n and the azimuthal quantum number n_θ as given below.

$$E_n = -\frac{mZ^2e^4}{8\epsilon_0^2 n^2 h^2}\left[1 + \frac{\alpha^2 Z^2}{n}\left(\frac{1}{n_\theta} - \frac{3}{4n}\right)\right] \tag{13}$$

Thus there is no degeneracy for the energy levels. Here $\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c}$ is a dimensionless constant, called *fine structure constant*, whose value is approximately $\frac{1}{137}$.

Sommerfeld model could explain the fine structure of H-atom with reasonable accuracy. Stability of the atom against a decay due to electromagnetic radiation was not explained. Furtherr, the experimental values of the frequencies of the fine spectrum were not the same as predicted by the model. Another drawback was that not all the fine spectral lines predicted by Sommerfeld model was actually found in experiment. This means that the electrons could not change their energy levels in all possible ways. The model also failed to provide the "selection rules" that explained the allowed transitions.

Vector atom model

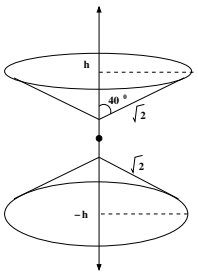

Figure 2: Vector representation for angular momentum value $l = 1$. Here $m = -1, 0, +1$.

The possible values of angular momentum of an electron in an atom are quantized, as seen in eqn(3) earlier. However a precise set of values of angular momentum are provided by

quantum mechanics. It is known that the magnitude of angular momentum vector $|\mathbf{L}|$ is allowed to take a set of values $\sqrt{l(l+1)}\hbar$ where the quantum number $l = 0, 1, 2, \ldots$. In addition to this, the L-component of the angular momentum L_z is also known to take values $m\hbar$, where the azimuthal (or magnetic) quantum number $m = -l, -l+1, \ldots, l-1, l$. Vector atom model provides a simple description for the possible angular momentum values of an atom as follows. The angular momentum vector is represented as a vector of magnitude $\sqrt{l(l+1)}\hbar$ that lies on the surface of a cone as shown in the figure. The vector subtends an angle $\cos^{-1}\left(\frac{m}{\sqrt{l(l+1)}}\right)$ with the Z-axis so that the Z-component of this vector is precisely $m\hbar$. Fig(2) shows demonstrates the vector model for $l = 1$.