

8.3 Hydrogenic Atoms

Let us consider a one-electron atom having atomic number Z . We know that $Z = 1$ for the hydrogen atom (H). The charge on the nucleus is Ze and that on the electron is $-e$.

The potential energy due to the *attractive Coulomb interaction* between them is

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \quad \dots(8.26)$$

which depends only on the distance r between the nucleus and the electron and hence is spherically symmetric.

If m is the mass of the electron and M is the mass of the nucleus, then the reduced mass of the system is

$$\mu = \frac{mM}{m + M} \quad \dots(8.27)$$

Since the nuclear mass M is much larger than the electron mass m , the reduced mass μ is very close to m . That is, we shall consider the nucleus to be *stationary*.

The radial Equation (8.12) becomes

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m}{\hbar^2} \left[E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right] R(r) = 0 \quad \dots(8.28)$$

Since we are interested only in the energies associated with the relative motion, we may assume that we are working in the center-of-mass system, so that $E_R = 0$ and the total energy E is equal to the energy E_r of relative motion. Further, we shall be interested only in the bound state solutions and therefore, we shall consider $E < 0$.

In order to solve (8.28), it is convenient to introduce the dimensionless variable ρ and the dimensionless constant λ defined by

$$\rho = \left(-\frac{8mE}{\hbar^2} \right)^{1/2} r \quad \dots(8.29)$$

and

$$\lambda = \frac{Ze^2}{4\pi\epsilon_0 \hbar} \left(\frac{-m}{2E} \right)^{1/2} = Z\alpha \left(\frac{-mc^2}{2E} \right)^{1/2} \quad \dots(8.30)$$

where $\alpha = e^2/(4\pi\epsilon_0\hbar c) \approx 1/137$ is the well known fine-structure constant.

In terms of ρ and λ , Equation (8.28) becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] R(\rho) = 0 \quad \dots(8.31)$$

In order to solve this equation, we first examine the asymptotic behavior of $R(\rho)$. We note that as $\rho \rightarrow \infty$, Equation (8.31) reduces to

$$\frac{d^2R}{d\rho^2} - \frac{1}{4} R(\rho) = 0 \quad \dots(8.32)$$

The solutions of this equation are proportional to $e^{\pm \frac{\rho}{2}}$. Out of these only $e^{-\frac{\rho}{2}}$ is acceptable because $e^{\frac{\rho}{2}}$ becomes unbounded as $\rho \rightarrow \infty$. This suggests that the exact solution of (8.31) must be of the form

$$R(\rho) = e^{-\rho/2} F(\rho) \quad \dots(8.33)$$

Substitution into (8.31) gives the equation for $F(\rho)$ as

$$\rho^2 \frac{d^2F}{d\rho^2} + \rho(2 - \rho) \frac{dF}{d\rho} + [(\lambda - 1)\rho - l(l+1)] F(\rho) = 0 \quad \dots(8.34)$$

When $\rho = 0$, this equation yields

$$l(l+1) F(0) = 0$$

or $F(0) = 0$ for $l \neq 0$... (8.35)

The power series solution $F(\rho)$ of the form

$$F(\rho) = \sum_{k=0}^{\infty} a_k \rho^{s+k} \quad \dots(8.36)$$

Substituting into (8.34) and simplifying, we obtain

$$\sum_{k=0}^{\infty} a_k [(s+k)(s+k+1) - l(l+1)] \rho^k - \sum_{k=0}^{\infty} a_k [s+k+1 - \lambda] \rho^{k+1} = 0 \quad \dots(8.37)$$

For this equation to be valid, the coefficient of each power of ρ must vanish. Equating the coefficient of ρ^0 to zero gives

$$\begin{aligned}
& s(s+1) - l(l+1) = 0 \\
\text{or} & (s-l)(s+l+1) = 0 \\
\text{Thus,} & s = l \quad \text{or} \quad s = -(l+1) \quad \dots(8.38)
\end{aligned}$$

If we take $s = -(l+1)$, then the first term in the expansion (8.36) would be a_0/ρ^{l+1} , which tends to infinity $\rho \rightarrow 0$ as . Therefore, the acceptable value is $s = l$. Now, setting the coefficient of ρ^{k+1} in (8.37) equal to zero, we obtain

$$a_{k+1}[(s+k+1)(s+k+2) - l(l+1)] - a_k(s+k+1-\lambda) = 0$$

Putting $s = l$ and rearranging, we obtain the *recurrence relation*

$$a_{k+1} = \frac{k+l+1-\lambda}{(k+1)(k+2l+2)} a_k \quad \dots(8.39)$$

This relation determines the coefficients $a_1, a_2, a_3 \dots$ in terms of a_0 which can be arbitrary. In order to find the behavior of the series (8.36) for large values of k , we note that

$$\lim_{k \rightarrow \infty} \frac{a_{k+1}}{a_k} = \frac{1}{k}$$

This is similar to the asymptotic behavior of the expansion of the function e^ρ as shown below. We have

$$e^\rho = \sum_{k=0}^{\infty} c_k \rho^k$$

where

$$c_k = \frac{1}{k!}$$

Therefore,

$$\frac{c_{k+1}}{c_k} = \frac{k!}{(k+1)!} = \frac{1}{k+1}$$

So,

$$\lim_{k \rightarrow \infty} \frac{c_{k+1}}{c_k} = \frac{1}{k}$$

If the series (8.36) does not terminate, then $F(\rho)$ will behave as e^ρ and so, according to (8.33), $R(\rho)$ will behave as $e^{\rho/2}$, which diverges as $\rho \rightarrow \infty$. Since this is not acceptable, the series must terminate at some value of k , say n_r . This can be possible if we require that λ be equal to a positive integer n such that

$$\dots(8.40)$$

$$\lambda = n = n_r + l + 1$$

In that case a_{k+1} , and hence all higher coefficients, will be zero. Since both n_r and l can be positive integers or zero, it is clear that n can have only positive integral values. n_r is called the *radial quantum number* and n the *principal quantum number*. Note that for a given n the allowed values of l are $1, 2, \dots, n - 1$.

Energy Eigenvalues

Equations (8.30) and (8.40) give the bound-state energy eigenvalues

$$\begin{aligned} E_n &= -\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \\ &= -\frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2}, \quad n = 1, 2, 3, \dots \end{aligned} \quad \dots(8.41)$$

- This formula agrees exactly with the one obtained from the Bohr model.
(Energy of the Electron in the n th Bohr Orbit $E_n = -\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2}$)
- It was the most important early success of Schrödinger's theory because it could reproduce Bohr's formula from a general equation of motion.
- The calculations based on this formula explain the main features of the experimental spectrum of hydrogen.
- The agreement is not perfect and various corrections, especially for the fine structure arising from the *relativistic effects* and the *electron spin*, must be taken into account to obtain detailed agreement with the experiment.
- It may be noted that n may take all integral values from 1 to ∞ .
- The bound-state energy spectrum of a system held by the Coulomb force contains an infinite number of discrete energy levels.
- This is because the magnitude of the Coulomb potential decreases slowly at larger r . On the other hand, short-range forces have a finite number of bound states.

Degeneracy

$$E_n = -\frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2}$$

- The *energy eigenvalues* depend only the principal quantum number n .
- There is no dependence on l and m_l .

- The *eigenfunctions* for a hydrogenic atom are determined by the values of three quantum numbers n, l and m_l .
- For each energy level E_n there are more than one distinct state which have the same energy. This phenomenon is called **degeneracy**.

Let us find the total degeneracy of the energy level E_n . For a given value of n , the quantum number l may take any of the values $0, 1, \dots, n - 1$. For each value of l , the quantum number m_l may take any of the $(2l + 1)$ possible values $-l, -l + 1, \dots, 0, \dots, l - 1, l$. The total degeneracy of the level is therefore given by

$$\sum_{l=0}^n (2l + 1) = 2 \frac{n(n-1)}{2} + n = n^2$$

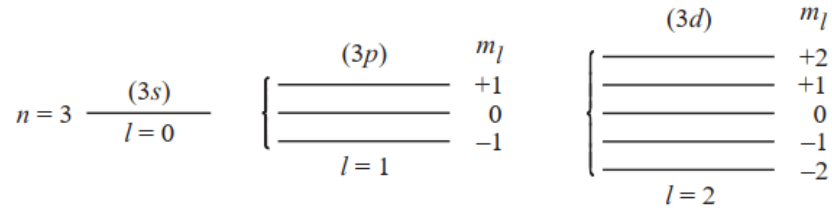
Electrons (also protons and neutrons) have an intrinsic angular momentum called **spin**, that makes them fall in two possible states but the energy of the hydrogen atom is independent of these states. As a result, the degeneracy of the atom is $2n^2$, not n^2 .

These levels are labelled by two symbols according to the standard **spectroscopic notation**. The first is a number which represents the principal quantum number n ; the second is a letter which indicates the value of the orbital angular momentum quantum number l according to the following scheme:

Value of l	0	1	2	3	4	5...
Letter	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h...</i>

According to this notation, the ground state ($n = 1, l = 0$) is a $1s$ state, the first excited state ($n = 2, l = 0, 1$) is four-fold degenerate, having one $2s$ state and three $2p$ states with $m_l = -1, 0, +1$, and so on, as shown in the figure. All the m_l -states corresponding to a particular value of l are drawn slightly apart to show their multiplicity, but they are degenerate.

$$n = 1 \quad \frac{(1s)}{l = 0} \quad n = 2 \quad \frac{(2s)}{l = 0} \quad \left\{ \begin{array}{l} \text{---} \\ \text{---} \\ \text{---} \end{array} \right. \begin{array}{l} (2p) \\ m_l \\ +1 \\ 0 \\ -1 \end{array} \\ l = 1$$



Radial Eigenfunctions

Let us now come back to the solution of (8.34).

$$R_{nl}(r) = - \left\{ \left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho)$$

L_{n+l}^{2l+1} Laguerre polynomials.

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-l-1-k)!(2l+1+k)!} \frac{\rho^k}{k!}$$

$$\rho = \left(\frac{-8mE_n}{\hbar^2} \right)^{1/2} r = \left(\frac{2Zme^2}{n(4\pi\epsilon_0)\hbar^2} \right) r = \left(\frac{2Z}{na_0} \right) r$$

a_0 being the radius of the first Bohr orbit for hydrogen:

$$a_0 = (4\pi\epsilon_0)\hbar^2/me^2$$