Chapter 1  The Hydrogen Spectrum

The hydrogen atom and its spectrum treated in this chapter are of special interest in atomic spectroscopy because only for the hydrogen atom can the Schrödinger and Dirac equations be solved analytically. So-called hydrogenlike approximations are widely used in the theory of atomic spectra.

1.1 Schrödinger's Equation for the Hydrogen Atom

1.1.1 Energy Levels

The problem of the relative motion of an electron (mass: \(m\), charge: \(-e\)) and a nucleus (mass: \(M\), charge: \(Ze\)) reduces, as is well known, to the problem of the motion of a particle with an effective mass \(\mu = mM/(m + M) \approx m\) in a Coulomb field of \(-Ze^2/r\). The Schrödinger equation for a particle in the field \(-Ze^2/r\) has the form

\[
\left( \frac{\hbar^2}{2\mu} \Delta + E + \frac{Ze^2}{r} \right) \psi = 0.
\]  

The wave function \(\psi\), which is the solution of this equation, describes the stationary state with a definite value of the energy \(E\). In the case of a centrally symmetric field the angular momentum is conserved. Because of that, we shall consider stationary states which are characterized by definite values of the quantities \(E\), the square of the angular momentum, and the \(z\) component of the angular momentum. The wave functions \(\psi\) of these stationary states are eigenfunctions of the operators \(I^2\) and \(I_z\) and must therefore satisfy the equations

\[
I^2\psi = l(l + 1) \psi, \tag{1.2}
\]
\[
I_z\psi = m\psi, \tag{1.3}
\]

where \(l(l + 1)\) and \(m\) are eigenvalues of the operators \(I^2\) and \(I_z\). We recall that in quantum mechanics the square of the angular momentum can only take a discrete series of values \(\hbar^2(l + 1)\), where \(\hbar = h/2\pi\); \(h\) is Planck's constant, and also \(l = 0, 1, 2, \ldots\). In exactly the same way, the \(z\) component of the momentum can have the values \(\hbar m\), \(m = 0, \pm 1, \pm 2, \ldots\) with the additional condition \(|m| \leq l\).

For brevity, we shall henceforth speak of the angular momentum \(l\) and the \(z\) component of the angular momentum \(m\), meaning the angular momentum...
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whose square is equal to $\hbar^2(l + 1)$ and whose $z$ component equals $\hbar m$.

Let us seek the solution of (1.1) in the form

$$\psi = R(r) Y_{lm}(\theta, \phi),$$  \hspace{1cm} (1.4)

where $Y_{lm}(\theta, \phi)$ is the spherical harmonic. The radial part $R(r)$ satisfies the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr}\right) - \frac{l(l+1)}{r^2} R + \frac{2\mu}{\hbar^2} \left( E + \frac{Ze^2}{r} \right) R = 0.$$  \hspace{1cm} (1.5)

If $E > 0$, this equation has finite and continuous solutions for any value of $E$ and $l$. If $E < 0$, such solutions are possible only at certain discrete values of energy

$$E = -\frac{1}{2} \frac{Z^2 \mu e^4}{n^2 \hbar^2},$$  \hspace{1cm} (1.6)

where $n$ is an integer, and also $n \geq l + 1$. The number $n$ is called the principal quantum number. For a given value of $n$, the quantum number $l$ can take the values $0, 1, 2, \ldots n-1$. To each value of $l$ there correspond $(2l + 1)$ states, differing by the values of the quantum number $m$, which is usually called the magnetic quantum number. The energy of an atom in the state $nlm$ is uniquely determined by the principal quantum number and does not depend on $l$ or $m$.

Thus, for a particle in a Coulomb field the energy levels are $n^2$-fold degenerate. There are $n^2 = 1 + 3 + 5 + \ldots + 2n - 1$ states differing in the quantum numbers $l$ and $m$. The independence of $m$ for the energy has a simple physical meaning.

In a central field, all directions in space are equivalent, and therefore the energy cannot depend on the spatial orientation of the angular momentum. The independence of $l$ is a specific property of the Coulomb field and does not occur in the general case of a centrally symmetric field. The energy level diagram of the hydrogen atom corresponding to (1.6) is shown in Fig. 1.1.

In spectroscopy it is usual to denote states corresponding to the values $l = 0, 1, 2, \ldots$ by letters of the Latin alphabet

$$s, p, d, f, g, h, i, k \ldots$$

Thus the state $n = 1, l = 0$ is denoted $1s$, the state $n = 2, l = 1$ is denoted $2p$, and so on. So the state $1s$ relates to the level $n = 1$, the states $2s, 2p$ relate to the level $n = 2$, the states $3s, 3p, 3d$ relate to the level $n = 3$, and so on.

If we neglect the difference between the reduced mass $\mu = m(1 - m/M)$ and the electron mass $m$, which is approximately $m/2000$, we obtain $E_n = - (me^4/\hbar^2) Z^2/2n^2$. The quantity $me^4/\hbar^2 = 4.304 \times 10^{-11}$ ergs ($\approx 27.07$ eV) is taken as the atomic unit of energy. The Rydberg unit of energy $Ry = me^4/2\hbar^2$ is also used in spectroscopy; hence $E_n = - RyZ^2/n^2$.

For ionization of the hydrogen atom, i.e., for the detachment of an electron from the nucleus, it is necessary to impart to the atom the energy $|E_n - E_1| = \mu e^4/2\hbar^2$. This quantity is called the ionization energy (or ionization potential