The Hydrogen Atom

13.1. The Eigenvalue Problem

We have here a two-body problem, of an electron of charge \(-e\) and mass \(m\), and a proton of charge \(+e\) and mass \(M\). By using CM and relative coordinates and working in the CM frame, we can reduce the problem to the dynamics of a single particle whose mass \(\mu = mM/(m + M)\) is the reduced mass and whose coordinate \(r\) is the relative coordinate of the two particles. However, since \(m/M \approx 1/2000\), as a result of which the relative coordinate is essentially the electron's coordinate and the reduced mass is essentially \(m\), let us first solve the problem in the limit \(M \to \infty\). In this case we have just the electron moving in the field of the immobile proton. At a later stage, when we compare the theory with experiment, we will see how we can easily take into account the finiteness of the proton mass.

Since the potential energy of the electron in the Coulomb potential

\[
\phi = e/r
\]

(13.1.1)
due to the proton is \(V = -e^2/r\), the Schrödinger equation

\[
\left\{ \frac{d^2}{dr^2} + \frac{2m}{\hbar^2} \left[ E + \frac{e^2}{r} - \frac{l(l+1)\hbar^2}{2mr^2} \right] \right\} U_{El} = 0
\]

(13.1.2)
determines the energy levels in the rest frame of the atom, as well as the wave functions\(^{\dagger}\)

\[
\psi_{Elm}(r, \theta, \phi) = R_{El}(r) Y^{m}_{l}(\theta, \phi) = \frac{U_{El}(r)}{r} Y^{m}_{l}(\theta, \phi)
\]

(13.1.3)

It is clear upon inspection of Eq. (13.1.2) that a power series ansatz will lead to a three-term recursion relation. So we try to factor out the asymptotic behavior.

\(^{\dagger}\) It should be clear from the context whether \(m\) stands for the electron mass or the \(z\) component of angular momentum.
We already know from Section 12.6 that up to (possibly fractional) powers of $r$ [Eq. (12.6.19)],

$$U_{EI} \sim \exp\left[-(2mW/\hbar^2)^{1/2}r\right] \quad (13.1.4)$$

where

$$W = -E$$

is the binding energy (which is the energy it would take to liberate the electron) and that

$$U_{EI} \sim r^{l+1} \quad (13.1.5)$$

Equation (13.1.4) suggests the introduction of the dimensionless variable

$$\rho = (2mW/\hbar^2)^{1/2}r \quad (13.1.6)$$

and the auxiliary function $v_{EI}$ defined by

$$U_{EI} = e^{-\rho} v_{EI} \quad (13.1.7)$$

The equation for $v$ is then

$$\frac{d^2v}{dp^2} - 2\frac{dv}{dp} + \left[\frac{e^2}{\rho} \frac{l(l+1)}{\rho^2}\right] v = 0 \quad (13.1.8)$$

where

$$\lambda = (2m/\hbar^2W)^{1/2} \quad (13.1.9)$$

and the subscripts on $v$ are suppressed. You may verify that if we feed in a series into Eq. (13.1.8), a two-term recursion relation will obtain. Taking into account the behavior near $\rho = 0$ [Eq. (13.1.5)] we try

$$v_{EI} = \rho^{l+1} \sum_{k=0}^{\infty} C_k \rho^k \quad (13.1.10)$$

and obtain the following recursion relation between successive coefficients:

$$\frac{C_{k+1}}{C_k} \rightarrow \frac{-e^2\lambda + 2(k+l+1)}{(k+l+2)(k+l+1)-l(l+1)} \quad (13.1.11)$$

The Energy Levels

Since

$$\frac{C_{k+1}}{C_k} \rightarrow \frac{2}{k \rightarrow \infty} \quad (13.1.12)$$