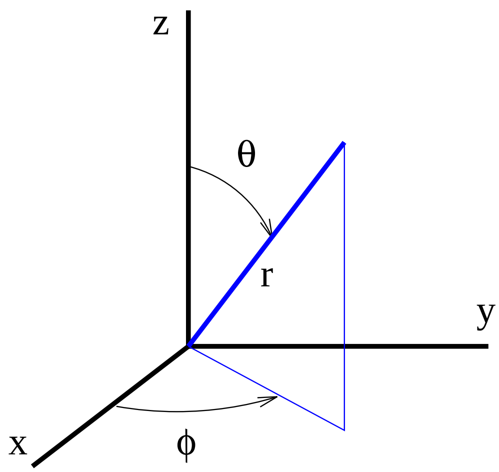

Figure 1: Definition sketch for spherical coordinates.

1 Orbital Angular Momentum and the Hydrogen Atom

Conservative central forces exhibit a potential energy which is a function of radius only in spherical coordinates (see figure 1). The Hamiltonian for a particle of mass M subject to a central potential, $U(r)$, is

$$H = -\frac{\hbar^2}{2M}\nabla^2 + U(r), \tag{1}$$

Using the spherical coordinate form of the Laplacian, the Schrödinger equation becomes

$$\begin{aligned}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) &+ \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) \\ &+ \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2M[E-U(r)]}{\hbar^2}\psi = 0.\end{aligned} \tag{2}$$

1.1 Separation of Variables

Though of considerable complexity, this equation may be solved by separation of variables. Assuming that $\psi = R(r)\Theta(\theta)\Phi(\phi)$, the above equation becomes

$$
\frac{1}{r^2 R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{r^2\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{r^2\sin^2\theta\Phi}\frac{d^2\Phi}{d\phi^2} + \frac{2M[E-U(r)]}{\hbar^2} = 0. \tag{3}
$$

We note that all ϕ dependence is confined to the third term of equation (3), which means that $(d^2\Phi/d\phi^2)/\Phi$ is constant. This constant must be negative in order for Φ to be periodic in ϕ, as is required by spherical coordinates. Calling it $-m^2$, the Φ equation becomes

$$
\frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0, \tag{4}
$$

with the solutions

$$
\Phi = \exp(\pm im\phi). \tag{5}
$$

In order to satisfy periodic boundary conditions in ϕ, m must take on only integral values, as in the case of the two-dimensional harmonic oscillator.

Multiplying equation (3) by r^2 leaves us with

$$
\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left\{\frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{m^2}{\sin^2\theta}\right\} + \frac{2M[E-U(r)]r^2}{\hbar^2} = 0. \tag{6}
$$

All θ dependence is now confined to within the curly brackets while all r dependence is outside, so the content of these brackets must be constant. Taking λ as the separation parameter, we find

$$
\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{m^2\Theta}{\sin^2\theta} = -\lambda\Theta \tag{7}
$$

and

$$
\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \lambda R + \frac{2M[E-U(r)]r^2 R}{\hbar^2} = 0. \tag{8}
$$

1.2 Orbital Angular Momentum States

Let us perform a change of variables on the Θ equation (7). Defining $z = \cos\theta$, so that $\sin\theta d\theta = -d\cos\theta = -dz$, this equation can be written

$$(1-z^2)\frac{d}{dz}\left[(1-z^2)\frac{d\Theta}{dz}\right] + [\lambda(1-z^2) - m^2]\Theta = 0. \tag{9}$$

This equation has two types of solutions:

$$\Theta_1 = a + bz + cz^2 + \ldots \qquad \Theta_2 = \eta(a + bz + cz^2 + \ldots), \quad \eta \equiv (1-z^2)^{1/2}. \tag{10}$$

Some examples of solutions of the first type are as follows: $\Theta = 1$ requires that $|m| = \lambda = 0$, while $\Theta = z$ forces $|m| = 0$ and $\lambda = 2$. $\Theta = z^2 - 1/3$ leads to $|m| = 0$ and $\lambda = 6$, while $\Theta = 1 - z^2$ results in $|m| = 2$ and $\lambda = 6$. Solutions of the second type include $\Theta = \eta$, which requires $|m| = 1$ and $\lambda = 2$, while $\Theta = \eta z$ leads to $|m| = 1$ and $\lambda = 6$.

Figure 2 summarizes these results. The quantum number λ takes the form $l(l+1)$ where l is an integer. Furthermore, m can take on the values $-l, -l+1, \ldots, l-1, l$. There are $2l+1$ of these m states for each allowed value of l. As we will prove later, the two quantum numbers l and m represent the orbital angular momentum state of a particle in a central potential. In particular, $[l(l+1)]^{1/2}\hbar$ is the magnitude of the angular momentum vector, while $m\hbar$ is the z-component of angular momentum.

1.3 Hydrogen Atom

Let us now return to the radial equation (8), substituting $l(l+1)$ for λ and the Coulomb potential for $U(r)$:

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - l(l+1)R + \frac{2M}{\hbar^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r}\right)r^2 R = 0, \tag{11}$$

where M is now specifically the mass of the electron.[1] This equation may be reduced to non-dimensional form as follows: First, notice that the combination $\alpha = e^2/(4\pi\epsilon_0\hbar c)$ is dimensionless, where c is the speed of light. This

[1]More accurately, $M^{-1} = M_e^{-1} + M_p^{-1}$ where M_e is the electron mass and M_p is the proton mass. M is called the *reduced mass* of the electron-proton system. See any mechanics text for further explanation.

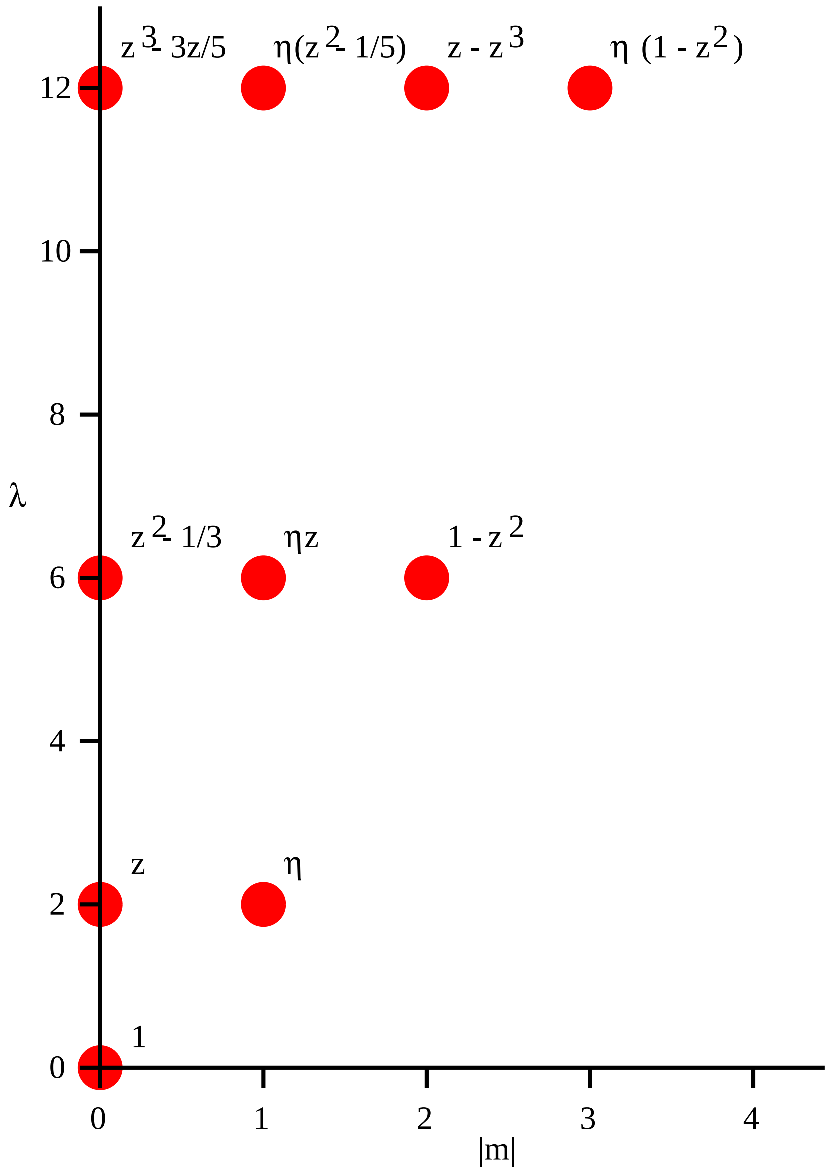

Figure 2: Plot of three-dimensional angular momentum states and associated Θ wave functions. Recall that $\eta = (1 - z^2)^{1/2}$ and $z = \cos\theta$.

combination of parameters is called the *fine structure constant* and takes on the value $7.272\times10^{-3} \approx 1/137$. It is a fundamental measure of the strength of the electromagnetic force in elementary particle interactions. The coefficient of R may therefore be written

$$\frac{2MEr^2}{\hbar^2} + \frac{2\alpha Mcr}{\hbar}. \tag{12}$$

Note that this entire coefficient is itself dimensionless, so the combination $a_0 = \hbar/(Mc\alpha)$ must have the dimensions of length. This length is called the *Bohr radius*, and it has the value $a_0 = 5.31 \times 10^{-11}$ m. This turns out to be the approximate radius of the hydrogen atom in its ground state.

The combination $MEa_0^2/\hbar^2 = E/(Mc^2\alpha^2)$ is dimensionless, so $E_0 \equiv Mc^2\alpha^2 = 4.37 \times 10^{-18}$ J $= 27$ eV is a fundamental energy scale for the hydrogen atom.

Performing the nondimensionalizing transformations $r/a_0 \to r$ and $E/E_0 \to E$, the radial equation for the hydrogen atom becomes

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - l(l+1)R + 2(Er^2 + r)R = 0 \tag{13}$$

in nondimensional form.

Solutions to this equation take the form

$$R(r) = \exp(-\beta r)(a + br + cr^2 + \ldots) \tag{14}$$

where β, a, b, and c are constants.[2] For instance, the ground state solution has $\beta = 1$, $a = 1$, $b = c = \ldots = 0$, $l = 0$, and $E = -1/2$. It turns out that the allowed energies are

$$E_n = -\frac{E_0}{2n^2}, \quad n = 1, 2, 3, \ldots, \tag{15}$$

where n is called the *principal quantum number* of the hydrogen atom. Furthermore, l can take on the values $0, 1, 2, \ldots, n-1$. Thus, as in the two-dimensional harmonic oscillator, only a limited number of angular momentum states are allowed for each energy. We label the full wave functions by the subscripted quantum numbers, $\psi_{nlm}(r, \theta, \phi)$.

[2]There is another set of solutions which blow up at the origin. However, they are of no interest because they are unphysical.

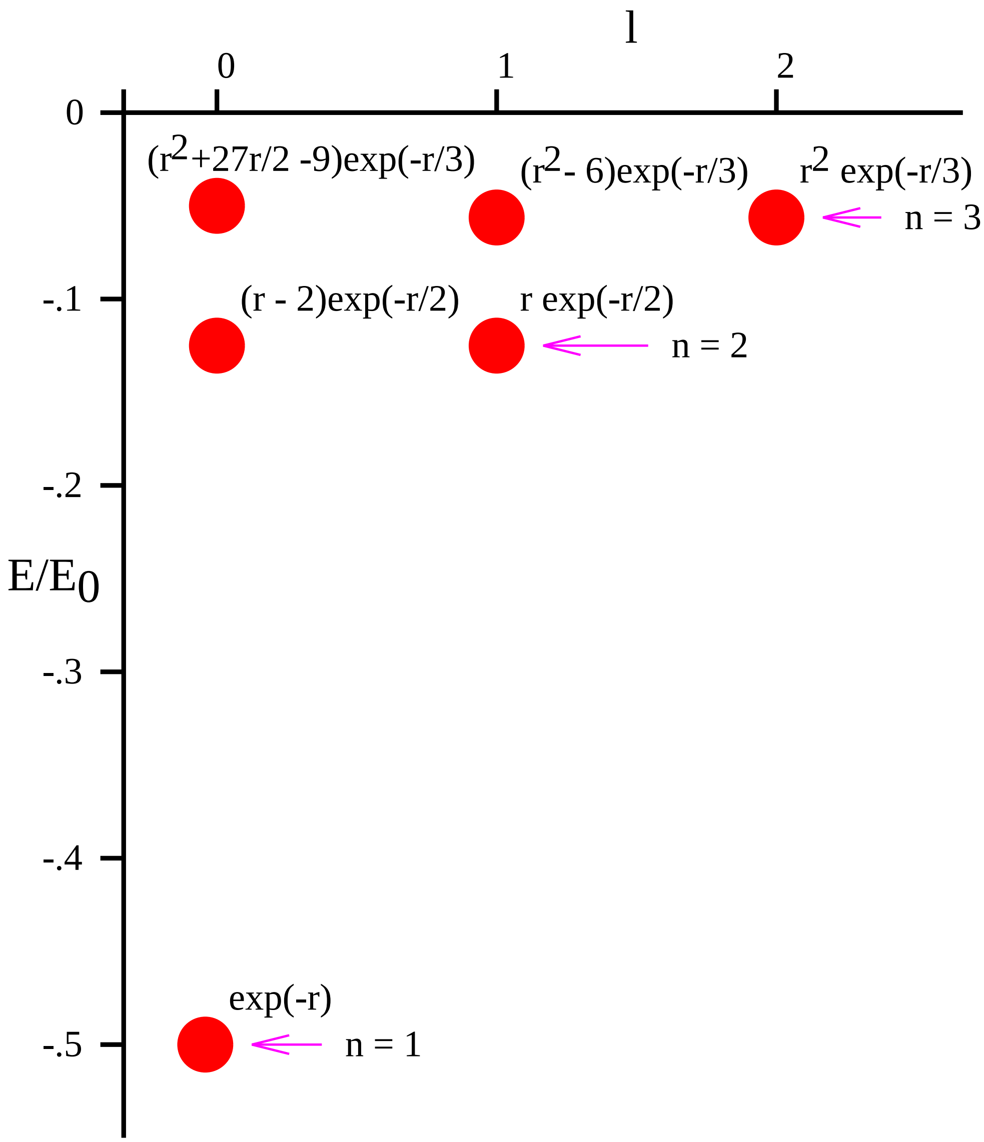

Figure 3: Plot of hydrogen atom energy states. The horizontal axis is the angular momentum quantum number l and the vertical axis is the scaled energy. The formulas represent the radial wave functions $R(r)$ associated with each state.