# Contents

# Chapter 5

# The Hydrogen Atom

We picture the hydrogen atom as a proton and an electron bound together. It is the simplest of all atoms. To describe this system we start with a vector $\vec{r}_p$ to represent the position of the proton and $\vec{r}_e$ to represent the position of the electron. The Hamiltonian for this system is:

$$H = \frac{p_p^2}{2m_p} + \frac{p_e^2}{2m_e} + V(\mathbf{r_e}, \mathbf{r_p}) \tag{5.1}$$

The two particles interact via the Coulomb force which depends only on the distance between them, so that:

$$H = \frac{p_p^2}{2m_p} + \frac{p_e^2}{2m_e} + V(|\mathbf{r_e} - \mathbf{r_p}|) \tag{5.2}$$

## 5.1 The reduced mass and the separation of the two-body problem

In classical mechanics the two-body problem is solved by reducing it to two independent problems, one for the motion of the center of mass and one for the relative motion of the two particles. The same reduction works in quantum mechanics. Define the relative vector and the center of mass vector:

$$\vec{r} = \vec{r}_e - \vec{r}_p, \qquad \vec{R} = \frac{m_p\vec{r}_p + m_e\vec{r}_e}{M} \tag{5.3}$$

where:

$$M \equiv m_p + m_e \tag{5.4}$$

The inverse of these relations is:

$$\vec{r}_e = \vec{R} + \frac{m_p}{M}\vec{r}, \qquad \vec{r}_p = \vec{R} - \frac{m_e}{M}\vec{r} \tag{5.5}$$

As $m_p/m_e \to \infty$, the center of mass coincides with the position of the proton: $\vec{r}_e \to \vec{R} + \vec{r}$, and $\vec{r}_p \to \vec{R}$.

We will denote the components of the two vectors by $\mathbf{R} = (X, Y, Z)$ and $\mathbf{r} = (x, y, z)$.

For central forces the Schrödinger Equation is:

$$\left(\frac{p_p^2}{2m_p} + \frac{p_e^2}{2m_e} + V(r)\right)\psi(\vec{r}_e, \vec{r}_p) = E_T\psi \tag{5.6}$$

where $r$ is the magnitude of $\vec{r}$, i.e. the distance between the two particles. $E_T$ is the total energy of the two-body system.

We can solve the Schrödinger Equation with $\psi = F(X, Y, Z)G(x, y, z)$. Then:

$$\begin{aligned}\frac{\partial\psi}{\partial x_p} &= G\frac{\partial F}{\partial X}\frac{\partial X}{\partial x_p} + F\frac{\partial G}{\partial x}\frac{\partial x}{\partial x_p} \\ &= \frac{m_p}{M}G\frac{\partial F}{\partial X} - F\frac{\partial G}{\partial x}\end{aligned}$$

Differentiating again:

$$\frac{\partial^2\psi}{\partial x_p^2} = \frac{m_p^2}{M^2}G\frac{\partial^2 F}{\partial X^2} - 2\frac{m_p}{M}\frac{\partial F}{\partial X}\frac{\partial G}{\partial x} + F\frac{\partial^2 G}{\partial x^2}$$

Similarly:

$$\frac{\partial^2\psi}{\partial x_e^2} = \frac{m_e^2}{M^2}G\frac{\partial^2 F}{\partial X^2} + 2\frac{m_e}{M}\frac{\partial F}{\partial X}\frac{\partial G}{\partial x} + F\frac{\partial^2 G}{\partial x^2}$$

Combining these:

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial x_e^2} - \frac{\hbar^2}{2m_p}\frac{\partial^2\psi}{\partial x_p^2} = -\frac{\hbar^2}{2}\left(\frac{m_e + m_p}{M^2}G\frac{\partial^2 F}{\partial X^2} + \left(\frac{1}{m_e} + \frac{1}{m_p}\right)F\frac{\partial^2 G}{\partial x^2}\right)$$

Defining the **reduced mass**, $\mu$:

$$\frac{1}{\mu} \equiv \frac{1}{m_e} + \frac{1}{m_p}$$

so that:

$$\mu = \frac{m_e m_p}{m_e + m_p} \tag{5.7}$$

we get:

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial x_e^2}-\frac{\hbar^2}{2m_p}\frac{\partial^2\psi}{\partial x_p^2}=-\frac{\hbar^2}{2M}G\frac{\partial^2 F}{\partial X^2}-\frac{\hbar^2}{2\mu}F\frac{\partial^2 G}{\partial x^2}$$

The equations for $y$ and $z$ are identical. The time-independent Schrödinger Equation is:

$$-\frac{\hbar^2}{2M}G\nabla_R^2 F-\frac{\hbar^2}{2\mu}F\nabla_r^2 G=(E_T-V(r))FG \tag{5.8}$$

where:

$$\nabla_R^2\equiv\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2},\qquad \nabla_r^2\equiv\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2},$$

Dividing by $FG$:

$$-\frac{\hbar^2}{2M}\frac{1}{F}\nabla_R^2 F-\frac{\hbar^2}{2\mu}\frac{1}{G}\nabla_r^2 G+(V(r)-E_T)=0 \tag{5.9}$$

The first term depends only the c.m. coordinates and the rest depends on the relative coordinates. Thus each part must separately be a constant:

$$-\frac{\hbar^2}{2M}\frac{1}{F}\nabla_R^2 F=E^* \tag{5.10}$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{G}\nabla_r^2 G+(V(r)-E_T)=-E^* \tag{5.11}$$

or:

$$-\frac{\hbar^2}{2M}\nabla_R^2 F=E^* F \tag{5.12}$$

$$-\frac{\hbar^2}{2\mu}\nabla_r^2 G+V(r)G=(E_t-E^*)G\equiv EG \tag{5.13}$$

The vector $\vec{R}$ represents the center of mass of the atom. The function $F(\vec{R})$ is the wave function for a free particle of energy $E^*$, a problem that we have already solved. The second equation is an equivalent one-body problem for a particle of mass $\mu$ with energy $E$, moving under the influence of a central potential $V(r)$.

## 5.2 Solution of the Effective One-body Problem for the Hydrogen Atom

Replacing $G$ with the familiar symbol $\psi(\vec{r})$, its solution is:

$$\psi(\mathbf{r}) = \frac{1}{r} u(r) Y_l^m(\theta, \phi),$$

where $u(r)$ satisfies the equation:

$$\frac{d^2 u}{dr^2} + \left( \frac{-l(l+1)}{r^2} + \frac{2\mu(E - V(r))}{\hbar^2} \right) u = 0 \tag{5.14}$$

Using the Coulomb potential to describe the electron-proton force:

$$V = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} = -\frac{k_e}{r} \tag{5.15}$$

$$\frac{d^2 u}{dr^2} + \left[ \frac{2\mu E}{\hbar^2} + \frac{2\mu k_e}{\hbar^2 r} - \frac{l(l+1)}{r^2} \right] u = 0 \tag{5.16}$$

Defining $\kappa^2 \equiv \frac{-2\mu E}{\hbar^2}$:

$$\frac{d^2 u}{dr^2} - \kappa^2 \left[ 1 - \frac{2\mu k_e}{\hbar^2 \kappa (\kappa r)} + \frac{l(l+1)}{(\kappa r)^2} \right] u = 0 \tag{5.17}$$

Defining the variable $\rho = \kappa r$ and defining:

$$\rho_0 \equiv \frac{2\mu k_e}{\hbar^2 \kappa} \tag{5.18}$$

$$\frac{d^2 u}{d\rho^2} - \left[ 1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u = 0 \tag{5.19}$$

At very large $\rho$:

$$\frac{d^2 u}{d\rho^2} - u = 0 \tag{5.20}$$

which has the solution, $e^{\pm\rho}$. To obtain a wave-function that can be normalized, we must discard the divergent solution.

Near the origin, the Schrödinger Equation reduces to:

$$\frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2} u = 0 \tag{5.21}$$

if we try try $u = \rho^n$, we see that:

$$n(n-1)\rho^{n-2} = l(l+1)\rho^{n-2} \tag{5.22}$$

which works for $n = l+1$ or $n = -l$. As usual we discard the singular solution and choose $u \approx \rho^{l+1}$ near the origin.

We can incorporate both of these special cases into the solution by defining:

$$u = \rho^{l+1} e^{-\rho} v(\rho) \tag{5.23}$$

We can substitute this form into the Schrödinger Equation once we calculate:

$$\frac{du}{d\rho} = (l+1)\rho^l e^{-\rho} v(\rho) - \rho^{l+1} e^{-\rho} v(\rho) + \rho^{l+1} e^{-\rho} \frac{dv}{d\rho} \tag{5.24}$$

$$\frac{d^2u}{d\rho^2} = l(l+1)\rho^{l-1} e^{-\rho} v(\rho) - (l+1)\rho^l e^{-\rho} v(\rho) + (l+1)\rho^l e^{-\rho} \frac{dv}{d\rho} \tag{5.25}$$

$$-(l+1)\rho^l e^{-\rho} v(\rho) + \rho^{l+1} e^{-\rho} v(\rho) - \rho^{l+1} e^{-\rho} \frac{dv}{d\rho} \tag{5.26}$$

$$+(l+1)\rho^l e^{-\rho} \frac{dv}{d\rho} - \rho^{l+1} e^{-\rho} \frac{dv}{d\rho} + \rho^{l+1} e^{-\rho} \frac{d^2v}{d\rho^2} \tag{5.27}$$

$$\frac{d^2u}{d\rho^2} = \left[l(l+1)\rho^{l-1} - (l+1)\rho^l - (l+1)\rho^l + \rho^{l+1}\right] e^{-\rho} v(\rho) \tag{5.28}$$

$$+\left[(l+1)\rho^l - \rho^{l+1} + (l+1)\rho^l - \rho^{l+1}\right] e^{-\rho} \frac{dv}{d\rho} + \rho^{l+1} e^{-\rho} \frac{d^2v}{d\rho^2} \tag{5.29}$$

$$\frac{d^2u}{d\rho^2} = \left[\frac{l(l+1)}{\rho^2} - 2\frac{(l+1)}{\rho} + 1\right] \rho^{l+1} e^{-\rho} v(\rho) \tag{5.30}$$

$$+2\left[\frac{(l+1)}{\rho} - 1\right] \rho^{l+1} e^{-\rho} \frac{dv}{d\rho} + \rho^{l+1} e^{-\rho} \frac{d^2v}{d\rho^2} \tag{5.31}$$

Substitution into the D.E. results in:

$$\frac{d^2v}{d\rho^2} + 2\left[\frac{(l+1)}{\rho} - 1\right] \frac{dv}{d\rho} + \left[\frac{l(l+1)}{\rho^2} - 2\frac{(l+1)}{\rho} + 1\right] v = \tag{5.32}$$

$$= \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right] v \tag{5.33}$$

$$\frac{d^2v}{d\rho^2} + 2\left[\frac{(l+1)}{\rho} - 1\right] \frac{dv}{d\rho} + \frac{\rho_0 - 2(l+1)}{\rho} v = 0 \tag{5.34}$$

$$\rho\frac{d^2v}{d\rho^2} + 2\left[(l+1) - \rho\right]\frac{dv}{d\rho} + \left[\rho_0 - 2(l+1)\right]v = 0 \tag{5.35}$$

We can solve for $v$ using a power series, $v = \sum_{j=0}^{\infty} a_j\rho^j$. By substitution:

$$\sum_j j(j-1)a_j\rho^{j-1} + 2(l+1)\sum_j ja_j\rho^{j-1} - 2\sum_j ja_j\rho^j$$

$$+\left[\rho_0 - 2(l+1)\right]\sum_j a_j\rho^j = 0 \tag{5.36}$$

$$\sum_j j[j-1+2(l+1)]a_j\rho^{j-1} + \left[\rho_0 - 2(l+1) - 2j\right]\sum_j a_j\rho^j = 0 \tag{5.37}$$

$$\sum_{j=1}^{\infty} j[j+2l+1)]a_j\rho^{j-1} + \left[\rho_0 - 2(l+j+1)\right]\sum_j a_j\rho^j = 0 \tag{5.38}$$

Changing the index in the first sum:

$$\sum_{j=0}(j+1)[j+2l+2)]a_{j+1}\rho^j + \sum_{j=0}\left[\rho_0 - 2(l+j+1)\right]\ a_j\rho^j = 0 \tag{5.39}$$

Equating equal powers of $\rho^j$:

$$(j+1)[j+2l+2)]a_{j+1} = \left[2(l+j+1) - \rho_0\right]a_j \tag{5.40}$$

giving us finally the recursion relation:

$$a_{j+1} = \frac{2(l+j+1) - \rho_0}{(j+1)(j+2l+2)}a_j \tag{5.41}$$

Starting from an arbitrary $a_0$ we can build up all the remaining terms in the series. Let us check the behavior of this series at large $j$:

$$a_{j+1} = \frac{2}{j+1}a_j \tag{5.42}$$

This is the recursion formula for $e^{2\rho}$, which tells us that the function $v(\rho)$ will diverge like $e^{2\rho}$. When we multiply by the function $e^{-\rho}$, we are left with $e^{\rho}$. The solution blows up at infinity. As we are now accustomed to doing, we must find a way to truncate the infinite series into a polynomial. The coefficient $a_{j_{max}+1}$ will be 0 if we choose $\rho_0$ so that:

$$\rho_0 = 2(j_{max} + l + 1) \equiv 2n \tag{5.43}$$

Since the smallest possible value of $j_{max} = 0$ and the smallest possible value of $l$ is 0, it follows that $n = 1, 2, 3 \cdots \infty$. Recalling the definition of $\rho_0$ given in eqn. 5.18:

$$\frac{2\mu k_e}{\hbar^2 \kappa} = 2n \tag{5.44}$$

Squaring both sides, and recalling that $\kappa^2 = \frac{-2\mu E}{\hbar^2}$:

$$\frac{\mu^2 k_e^2}{\hbar^2(-2\mu E)} = n^2 \tag{5.45}$$

$$E = -\frac{\mu k_e^2}{2\hbar^2 n^2} \tag{5.46}$$

Substituting $k_e = \frac{e^2}{4\pi\epsilon_0}$:

$$E_n = -\left[\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \qquad n = 1, 2, 3, \cdots \tag{5.47}$$

where the lowest, or ground state, energy is:

$$E_1 = -\frac{\mu}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \tag{5.48}$$

It is convenient to write this as:

$$E_1 = -\frac{\mu c^2}{2}\left(\frac{e^2}{4\pi\epsilon_0 \hbar c}\right)^2 \tag{5.49}$$

where $\mu c^2$ is the 'reduced' rest mass energy of the electron, and the quantity in parentheses is dimensionless. For historical reasons, it is called the **fine structure constant**, and is given the symbol $\alpha$:

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = 1/137.01 \tag{5.50}$$

We will see later how it got its name. From a modern field theory point of view it is the dimensionless parameter characterizing the strength of the electromagnetic interaction.

The electron volt (eV) is the preferred unit of energy for atomic and subatomic physics. It is the energy acquired by a particle of charge $e$ when it falls through a potential difference of 1 Volt. In SI units the electron charge is e=1.6 $\times 10^{-19}$ Coulombs, and 1 eV=1.6 $\times 10^{-19}$ Joules. The rest mass of the electron is 0.511 MeV, from which we obtain:

$$E_1 = -13.6 \text{ eV} \tag{5.51}$$

The energy needed to free an electron bound in the ground state of the hydrogen atom is the same as would be acquired by an electron accelerated through a potential difference of 13.6 V.

The allowed energies are determined by a single quantum number, $n$. For any choice of $n$, we see from the requirement that $j_{max} \geq 0$, that $n \geq l+1$, so for any given $n$, $l \leq n-1$. For example, if $n = 3$, then the possible values of $l$ are $0,\ 1,\ 2$.

If we set $n = 2$ we get the first set of excited states of hydrogen, which are at:

$$E_2 = E_1/4 = -13.6/4 = -3.4 \text{ eV} \tag{5.52}$$

For $n = 2$, the possible values of $l$ are 0, and 1. The choice of $l = 1$ has three sub-states corresponding to $m = 0, \pm 1$, so altogether there are four states with $n = 2$.

Similarly, setting $n = 3$, we obtain a set of states with energy:

$$E_3 = E_1/9 = -1.5 \text{ eV} \tag{5.53}$$

For this set, $l = 0,\ 1,\ 2$. The total number of states with $n = 3$ is $1+3+5 = 9$.

Using the difference between ground state energy and zero energy as a scale, we see that the first excited state is a long way above the ground state, and the successively higher states are crowded more and more tightly into a very small energy range below E=0.

We have obtained the radial solutions as functions of the dimensionless variable $\rho = \kappa r$. The parameter $\kappa$ has the dimensions of an inverse length. The value of $\kappa$ depends on the energy. We can express it conveniently as the inverse of an integer multiple of a basic length, by writing:

$$\kappa^2 = \frac{-2\mu E}{\hbar^2} = \frac{-2\mu E_1}{\hbar^2 n^2} \tag{5.54}$$

$$\kappa^2 = \frac{\mu^2}{\hbar^4 n^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \tag{5.55}$$

$$\kappa = \left(\frac{\mu e^2}{4\pi\epsilon_0 \hbar^2}\right)\frac{1}{n} \equiv \frac{1}{na} \tag{5.56}$$

where:

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \tag{5.57}$$

If we set $\mu = m_e$, we obtain what is called the **Bohr radius**, $a_B = 5.29177\times 10^{-11}$ meters. We can now write $\kappa r$ as $\frac{r}{na}$.

When we combine the radial functions with the angular solutions, we obtain the complete wave-functions for all the energy states of the hydrogen atom:

$$\psi_{nlm} = R_{nl}(r)Y_l^m(\theta,\phi) \tag{5.58}$$

where the radial functions have the form:

$$u_{nl} = rR_{nl} \propto \rho^{l+1}e^{-\rho}v_{nl}(\rho) = (\frac{r}{na})^{l+1}e^{-r/na}v_{nl}(r/na)$$

where $v_{nl}(r/na)$ is a polynomial of order $j_{max} = n - l - 1$.

$$R_{nl} = C(\frac{r}{na})^l e^{-r/na}v_{nl}(r/na)$$

For $n = 1$, $l = 0$ and $j_{max} = 0$, and the result is simple:

$$\psi_{100} = R_{10}Y_0^0 = \frac{1}{\sqrt{4\pi}}R_{10}, \qquad R_{10} = Ce^{-r/a} \tag{5.59}$$

To normalize $R_{10}$:

$$1 = C^2\int_0^\infty e^{-2r/a}\ r^2\ dr = C^2\int_0^\infty\ e^{-u}\ (au/2)^2\ (a/2)du \tag{5.60}$$

$$1 = C^2(a^3/8)\int_0^\infty\ e^{-u}\ u^2\ du = C^2(a^3/4) \tag{5.61}$$

$$R_{10} = \frac{2}{\sqrt{a^3}}e^{-r/a} \tag{5.62}$$

and:

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}}e^{-r/a} \tag{5.63}$$

The polynomial $v_{nl}(\rho)$ can be expressed in terms of the associated Laguerre polynomials:

$$v_{nl}(\rho) = L_{n-l-1}^{2l+1}(2\rho) \tag{5.64}$$

The Laguerre polynomials are defined by:

$$L_q(x) \equiv e^x\left(\frac{d}{dx}\right)^q(e^{-x}x^q) \tag{5.65}$$

where $q$ is an integer. The associated Laguerre polynomials are defined by:

$$L^p_{q-p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \tag{5.66}$$

Setting $n - l - 1 = q - p$ and $p = 2l + 1$, so that $q = n - l - 1 + p = n - l - 1 + 2l + 1 = n + l$: the solutions are:

$$v_{nl} = L^{2l+1}_{n-l-1}(x) \equiv (-1)^{2l+1} \left(\frac{d}{dx}\right)^{2l+1} L_{n+l}(x) \tag{5.67}$$

Obtaining the associated Laguerre polynomial from the Laguerre polynomial is relatively simple, since we just do a series of differentiations on powers of $x$:

$$\frac{d^n x^m}{dx^n} = \frac{m!}{(m-n)!} x^{m-n}, \qquad m \geq n$$

Obtaining the Laguerre polynomial can be quite tedious.

Let's try it for $n = 3$, and $l = 1$:

$$L^{2l+1}_{n-l-1}(x) = (-1)^3 \left(\frac{d}{dx}\right)^3 L_4(x) \tag{5.68}$$

Using:

$$L_4(x) \equiv e^x \left(\frac{d}{dx}\right)^4 \left(e^{-x} x^4\right) \tag{5.69}$$

we see that we need to differentiate $e^{-x}x^4$ four times. The required successive derivatives are given in Table 5.1.

Thus, for $n = 3$ and $l = 2$:

$$L^{2l+1}_{n-l-1}(x) = -\left(\frac{d}{dx}\right)^3 L_4(x) = -(24x - 96) = 24(4 - x) \tag{5.70}$$

Then:

$$v_{31}(\rho) = L^{2l+1}_{n-l-1}(2\rho) = 48(2 - \rho) = 48(2 - \frac{r}{3a}) = 96(1 - \frac{r}{6a}) \tag{5.71}$$

Fortunately, tables of these polynomials are plentiful. If they weren't, there would be no particular advantage over the use of the recursion relations for $a_{j+1}/aj$:

$$a_{j+1} = 2\frac{l + j + 1 - n}{(j+1)(j + 2l + 2)} a_j \tag{5.72}$$

| | |
|---|---|
| $\frac{df}{dx}$ | $(4x^3 - x^4)e^{-x}$ |
| $\frac{d^2f}{dx^2}$ | $(x^4 - 8x^3 + 12x^2)e^{-x}$ |
| $\frac{d^3f}{dx^3}$ | $(-x^4 + 12x^3 - 36x^2 + 24x)e^{-x}$ |
| $\frac{d^4f}{dx^4}$ | $(x^4 - 16x^3 + 72x^2 - 96x + 24)e^{-x}$ |
| $L_4(x)$ | $x^4 - 16x^3 + 72x^2 - 96x + 24$ |
| $\frac{dL_4}{dx}$ | $4x^3 - 48x^2 + 144x - 96$ |
| $\frac{d^2L_4}{dx^2}$ | $12x^2 - 96x + 144$ |
| $\frac{d^3L_4}{dx^3}$ | $24x - 96$ |

Table 5.1: Derivatives of $x^4e^{-x}$

For our example of $n = 3$, $l = 1$:

$$aj + 1 = 2\frac{j-1}{(j+1)(j+4)}a_j \tag{5.73}$$

which gives:

$$a_1 = -\frac{1}{2}a_0$$

so:

$$v_{31}(\rho) = v_{31}(r/3a) = a_0(1 - \frac{r}{6a})$$

which is certainly less work.

There is another formula for the Laguerre polynomials, called the Rodriguez function, which is also simpler to use:

$$L^{2l+1}_{n-l-1} = \frac{1}{(n-l-1)!}x^{-(2l+1)}e^x\frac{d^{(n-l-1)}}{dx^{(n-l-1)}}\left(e^{-x}x^{n+l}\right)$$

For $n = 3$ we need to differentiate twice for $l = 0$ , once for $l = 1$, and not at all for $l = 2$.

Writing the wave-function in terms of the Laguerre polynomials:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}e^{-r/na}\left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)Y^m_l(\theta,\phi) \tag{5.74}$$

For the case, $n = 3$, and $l = 1$:

$$\psi_{31m} = \sqrt{\left(\frac{2}{3a}\right)^3\frac{1}{6[(4)!]^3}}e^{-r/3a}\left(\frac{2r}{3a}\right)L^3_1\left(\frac{2r}{3a}\right)Y^m_1(\theta,\phi) \tag{5.75}$$

$$\psi_{31m} = \left(\frac{2}{3a}\frac{1}{24}\right)^{3/2} \frac{1}{\sqrt{6}} \left(\frac{2r}{3a}\right) (-24(2r/3a) + 96) e^{-r/3a} Y_1^m(\theta,\phi) \tag{5.76}$$

$$\psi_{31m} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6}\frac{r}{a}\right) \left(\frac{r}{a}\right) e^{-r/3a} Y_1^m(\theta,\phi) \tag{5.77}$$

This formula provides us with three sub-states, for $m = 0,\ \pm 1$.

For $l = 0$ the wave-function peaks at $r = 0$. For $l > 0$ the radial part of the wave-function vanishes at the origin. The wave function becomes broader and broader in $r$ as $l$ increases, and the probability distribution for the electron extends farther and farther out.

The wave functions $\psi_{nlm}$ are all orthogonal:

$$\int \psi^*_{nlm}\ \psi_{n'l'm'}\ r^2\ \sin\theta\ dr\ d\theta\ d\phi = \delta_{nn'}\delta_{ll'}\delta mm' \tag{5.78}$$

What is the size of a hydrogen atom in its ground state?

$$\langle r \rangle = \int |\psi_{100}|^2 r\ r^2\ dr\ d\Omega = \int_0^\infty |R_{10}|^2\ r^3\ dr$$

$$= (4/a^3) \int_0^\infty e^{-2r/a} r^3\ dr = (4/a^3)(a/2)^4 \int_0^\infty e^{-u}\ u^3\ du$$

Using:

$$\iint_0^\infty e^{-u}\ u^n\ du = n!$$

$$\langle r \rangle = \frac{3a}{2} = 7.6 \times 10^{-11}\ \mathrm{m} \tag{5.79}$$

Likewise:

$$\langle r^2 \rangle = \int |\psi_{100}|^2 r^4\ dr\ d\Omega = \int_0^\infty |R_{10}|^2\ r^4\ dr =$$

$$= (4/a^3)(a/2)^5 \int e^{-u}\ u^4\ du = 3a^2 \tag{5.80}$$

$$\sigma_r^2 = 3a^2 - (9/4)a^2 = 3a^2/4, \qquad \sigma_r = \frac{\sqrt{3}a}{2} \tag{5.81}$$

## 5.3 The Hydrogen Spectrum

An isolated hydrogen atom in one of the energy eigenstates would persist forever in that state. However, there is no such thing as an isolated atom. In the laboratory the atom is generally part of a gas of atoms which interact frequently through collisions. Even in a very good vacuum there would be interactions with the walls of the container. External electric and magnetic fields can interact with the charged electron and proton. Even in outer space, the 3K background radiation left over from the big-bang can interact with the atom. In the laboratory, an electric discharge can be passed through a tube filled with hydrogen. The electric current interacts with the atoms to excite the gas to a system containing ions and atoms in excited states. The ions in this case would be free protons, which will recombine with free electrons to produce excited atoms. The excited atoms are then induced by collision processes and by interactions with the electromagnetic fields existing in the gas to emit energy and fall into lower energy states. Next term we will make a stab at calculating such transitions. In the meantime, let us accept that the transitions will occur. The energy released when an atom falls to a lower state will most commonly appear in the form of a quantum of light (electromagnetic field energy). The energy of an emitted photon will be:

$$E_\gamma = h\nu = \frac{hc}{\lambda} = E_i - E_f = -13.6(\frac{1}{n_i^2} - \frac{1}{n_f^2}) \tag{5.82}$$

In atomic spectroscopy, the spectrometers normally provide a direct measurement of the wave-length of the emitted light. We write:

$$\frac{1}{\lambda} = \frac{E_i - E_f}{\hbar c} = \frac{13.6}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \equiv R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{5.83}$$

here $R = 1.097 \times 10^7\ \mathrm{m}^{-1}$ is called the Rydberg constant. Parts of this formula were discovered empirically at the end of the $19^{th}$ century from close study of the experimental observations. In particular, the spectral lines were grouped into sets. The first one to be so ordered is obtained by setting $n_f = 2$ in the Rydberg formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{n_i^2}\right), \qquad n_i = 3, 4, \cdots \tag{5.84}$$

The longest wavelength in this series (called the Balmer series) is:

$$\frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36}R \tag{5.85}$$

$$\lambda \approx 0.7\ \mu = 7000A \tag{5.86}$$

The series ends at $\lambda = 4/R \approx 4000A$. These lines are all in the visible region, which is why the series was the first to be recognized. The spacing between lines grows steadily smaller as the wavelength decreases and most of the transitions are crowded up against the short wavelength limit, which is given by $n_i \to \infty$.

The Lyman series, obtained by setting $n_f = 1$, is in the ultraviolet region of the spectrum, and the Paschen series ($n_f = 3$) is in the infrared region.

## 5.4 Runge-Lenz-Laplace Vector

The degeneracy in $l$ for the hydrogen atom implies the existence of some symmetry other than the conservation of $\mathbf{L}$,(invariance under rotations). There is in fact another vector that is conserved. To obtain this for the classical problem, first note:

$$\mathbf{p} = m\dot{\mathbf{r}}$$

According to Newton's second law:

$$\dot{\mathbf{p}} = \mathbf{F}$$

For a central force the direction of the force is radial:

$$\dot{\mathbf{p}} = \vec{F}(\vec{r}) = f(r)\hat{r} = f(r)\frac{\mathbf{r}}{r} \tag{5.87}$$

Now:

$$\dot{\mathbf{p}} \times \mathbf{L} = \dot{\mathbf{p}} \times (\mathbf{r} \times \mathbf{p}) = f(r)\frac{1}{r}\mathbf{r} \times (\mathbf{r} \times \mathbf{p}) \tag{5.88}$$

$$= \frac{f(r)}{r}[\Big[\mathbf{r} \cdot \mathbf{p})\mathbf{r} - r^2\mathbf{p}\Big] \tag{5.89}$$

But:

$$\mathbf{r} \cdot \mathbf{p} = m\mathbf{r} \cdot \frac{d\mathbf{r}}{dt} = \frac{1}{2}m\frac{d\mathbf{r} \cdot \mathbf{r}}{dt} = mr\dot{r} \tag{5.90}$$

so:

$$\dot{\mathbf{p}} \times \mathbf{L} = \frac{f(r)}{r}\Big[mr\dot{r}\mathbf{r} - r^2\mathbf{p}\Big] = mf(r)r^2\left[\frac{\dot{r}\mathbf{r}}{r^2} - \frac{\dot{\mathbf{r}}}{r}\right] \tag{5.91}$$

$$= -mf(r)r^2\frac{d}{dt}\left(\frac{\mathbf{r}}{r}\right) \tag{5.92}$$

But, since $\mathbf{L}$ is a conserved vector for the central force problem:

$$\frac{d}{dt}(\mathbf{p} \times \mathbf{L}) = \dot{\mathbf{p}} \times \mathbf{L} = -mf(r)r^2\frac{d}{dt}\left(\frac{\mathbf{r}}{r}\right) \tag{5.93}$$

For the inverse square law $f = -k/r^2$ this reduces to:

$$\frac{d}{dt}(\mathbf{p} \times \mathbf{L}) = mk\frac{d}{dt}\left(\frac{\mathbf{r}}{r}\right) \tag{5.94}$$

which yields the immediate solution:

$$\mathbf{p} \times \mathbf{L} - mk\frac{\mathbf{r}}{r} = \mathbf{A} \tag{5.95}$$

where **A** is a fixed vector. It was first published by Laplace in 1799, independently discovered again by Hamilton in 1845, rediscovered by Runge in 1919, whose publication was discussed in a text book in 1925 by Lenz. It then received wide-spread application under the title the Runge-Lenz vector. It should properly be called the Laplace vector or the Laplace-Runge-Lenz vector.

We observe that:

$$\mathbf{A} \cdot \mathbf{L} = -mk\frac{\mathbf{r} \cdot \mathbf{L}}{r} = 0 \tag{5.96}$$

Thus **A** is orthogonal to and therefore independent of **L**. It lies in the plane of the orbit. We can observe that:

$$\mathbf{r} \times \mathbf{A} = \mathbf{r} \times (\mathbf{p} \times \mathbf{L}) = (\mathbf{r} \cdot \mathbf{L})\mathbf{p} - (\mathbf{r}\dot{\mathbf{p}})\mathbf{L} = -(\mathbf{r} \cdot \mathbf{p})\mathbf{L} \tag{5.97}$$

At the turning points $\mathbf{r}_t$of the orbit (where $r$ is either a minimum or a maximum), **p** and **r** are perpendicular, so that when $\mathbf{r} = \mathbf{r}_t$, $\mathbf{r} \cdot \mathbf{p} = 0$, and $\mathbf{r} \times \mathbf{A} = 0$. At both turning points **A** and **r** are collinear. Since **A** is a fixed vector in space, the turning points are fixed, and the orbits are closed. We can conclude that **A** is collinear with the major axis. We can find which direction it points by:

$$\mathbf{A} \cdot \mathbf{r} = Ar\cos\theta = \mathbf{r} \cdot (\mathbf{p} \times \mathbf{L}) - mkr = (\mathbf{r} \times \mathbf{p}) \cdot \mathbf{L} - mkr = l^2 - mkr \tag{5.98}$$

This scalar product is positive when $r$ has its minimum value (perihelion). The above equation can be written as:

$$Ar\cos\theta = l^2 - mkr \tag{5.99}$$

or:

$$\frac{1}{r} = \frac{mk}{l^2}\left(1 + \frac{A}{mk}\cos\theta\right) \tag{5.100}$$

which is the equation of an ellipse.

## 5.5 Appendix

## 5.6 Derivation of $L_x$ and $L_y$ in Spherical Coordinate

$$L_x = yp_z - zp_y = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

$$L_y = zp_x - xp_z = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

The Cartesian derivatives can be written in terms of derivatives in spherical coordinates using:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \mu}{\partial x}\frac{\partial}{\partial \mu} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \mu}{\partial y}\frac{\partial}{\partial \mu} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \mu}{\partial z}\frac{\partial}{\partial \mu} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi}$$

To evaluate this we have:

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = r\cos\theta$$

The derivatives with respect to $r$:

$$r^2 = x^2 + y^2 + z^2$$

$$\frac{\partial r}{\partial x} = \frac{x}{r} = \sin\theta\,\cos\phi$$

$$\frac{\partial r}{\partial y} = \frac{y}{r} = \sin\theta\,\sin\phi$$

$$\frac{\partial r}{\partial z} = \frac{z}{r} = \cos\theta$$

derivatives with respect to $\mu$:

$$\mu = z/r = \frac{z}{\sqrt{x^2+y^2+z^2}}$$

$$\frac{\partial \mu}{\partial x} = -\frac{zx}{r^3} = -\frac{\sin\theta\cos\theta\cos\phi}{r}$$
$$\frac{\partial \mu}{\partial y} = -\frac{zy}{r^3} = -\frac{\sin\theta\cos\theta\sin\phi}{r}$$
$$\frac{\partial \mu}{\partial z} = \frac{r^2 - z^2}{r^3} = \frac{\sin^2\theta}{r}$$

and derivatives with respect to $\phi$:

$$\tan\phi = y/x$$

$$\frac{\partial \phi}{\partial x} = -\frac{y\ \cos^2\phi}{x^2} = -\frac{\cos^2\phi\sin\theta\sin\phi}{r\sin^2\theta\cos^2\phi} = -\frac{\sin\phi}{r\sin\theta}$$
$$\frac{\partial \phi}{\partial y} = \frac{\cos^2\phi}{x} = \frac{\cos\phi}{r\sin\theta}$$
$$\frac{\partial \phi}{\partial z} = 0$$

Using these and carrying out the algebra:

$$L_x = \frac{\hbar}{i}\left(\sin\theta\sin\phi\frac{\partial}{\partial\mu} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$
$$L_y = -\frac{\hbar}{i}\left(\sin\theta\cos\phi\frac{\partial}{\partial\mu} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$
$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

## 5.7 Hamiltonian in terms of $L^2$

$$L^2 = (\vec{r}\times\vec{p})\cdot(\vec{r}\times\vec{p})$$

$$L^2 = \epsilon_{ijk}x_j p_k \epsilon_{ilm}x_l p_m = (\delta_{jl}\delta km - \delta_{jm}\delta_{kl})x_j p_k x_l p_m$$
$$= x_j p_k x_j p_k - x_j p_k x_k p_j = x_j(x_j p_k - i\hbar\delta_{jk})p_k - x_j(x_k p_k - 3i\hbar)p_j$$
$$= r^2p^2 - i\hbar x_j p_j - x_j x_k p_k p_j + 3i\hbar\vec{r}\cdot\vec{p}$$
$$= r^2p^2 + 2i\hbar\vec{r}\cdot\vec{p} - x_j x_k p_j p_k = r^2p^2 + 2i\hbar\vec{r}\vec{p}_r - x_j p_j x_k p_k - i\hbar\delta_{jk}x_j p_k$$
$$= r^2p^2 + 2i\hbar\vec{r}\vec{p}_r - (\vec{r}\cdot\vec{p})(\vec{r}\cdot\vec{p}) - i\hbar x_j p_j$$

$$= r^2p^2 + i\hbar\vec{r}\cdot\vec{p}) - (\vec{r}\cdot p)(\vec{r}\cdot\vec{p})$$

$$\vec{r}\cdot\vec{p} = rp_r$$

$$p_r = \frac{\hbar}{i}\frac{\partial}{\partial r}$$

$$[r, p_r] = i\hbar$$

$$L^2 = r^2p^2 + i\hbar rp_r - r^2p_r^2 + i\hbar rp_r = r^2p^2 + 2i\hbar rp_r - r^2p_r^2$$

so:

$$\frac{p^2}{2m} = \frac{p_r^2}{2m} - \frac{i\hbar}{mr}p_r + \frac{1}{2mr^2}L^2$$

$$H = \frac{p_r^2}{2m} - \frac{i\hbar}{mr}p_r + \frac{1}{2mr^2}L^2 + V(r)$$

The eigenfunction equation is:

$$H\psi = E\psi$$

The eigenfunctions, $\psi_{nlm}$, have the property that $L^2\psi_{nlm} = l(l+1)\hbar^2\psi_{nlm}$.

$$\left(r^2p_r^2 - 2i\hbar rp_r + l(l+1)\hbar^2 + 2m(V-E)r^2\right)\psi_{nlm} = 0$$

$$\left(-p_r^2 + 2i\hbar\frac{1}{r}p_r + 2m(E-V) - \frac{l(l+1)\hbar^2}{r^2}\right)\psi_{nlm} = 0$$

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{2m}{\hbar^2}(E-V) - \frac{l(l+1)}{r^2}\right)\psi_{nlm} = 0$$

Let $\psi_{nlm} = R_{nl}(r)Y_l^m(\theta,\phi)$:

$$\frac{\partial^2 R_{nl}}{\partial r^2} + \frac{2}{r}\frac{\partial R_{nl}}{\partial r} + \left(\frac{2m}{\hbar^2}(E-V) - \frac{l(l+1)}{r^2}\right)R_{nl} = 0$$