Quantum Mechanics

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Chapter 5

The Hydrogen Atom

So far

1. TDSE (the Time-Dependent Schrödinger Equation)

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right]\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

2. TISE (the Time-Independent Schrödinger Equation)

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$

3. The Relation between Ψ and ψ

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

Terminology

$\psi(x)$ is an **eigenfunction**.
E is an **eigenvalue**.

Here is a more familiar example.

$$\begin{bmatrix} 0 & 2 \\ 0 & 2 \end{bmatrix}\begin{bmatrix} 1 \\ 1 \end{bmatrix} = \begin{bmatrix} 2 \\ 2 \end{bmatrix} = 2\begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ is an eigenvector for $\begin{bmatrix} 0 & 2 \\ 0 & 2 \end{bmatrix}$ with an eigenvalue 2.

We have not really tried any real system yet. But, we need to carry out a real computation for a real system for an experimental confirmation of the correctness of the Schrödinger Equation

One of the simplest systems is a hydrogen atom.

However, this poses a couple of difficulties since (1) two particles are involved now and also since (2) it is no longer one-dimensional, but three-dimensional.

(1) 2 partilces instead of 1

Let M be the mass of the nucleus and m the mass of the electron. The nucleus and the electron are moving about their fixed center of mass. But, introduction of the reduced mass μ given by

$$\mu = \frac{Mm}{M+m}$$

solves this problem. In particular, for a hydrogen atom,

$$\mu = \left(\frac{M}{m+M}\right) m \approx m$$

and we can simply use m instead of μ.

(2) Three-dimensional

The classical energy equation is

$$\frac{p^2}{2\mu} + V = E$$

or

$$\frac{1}{2\mu}\left(p_x^2 + p_y^2 + p_z^2\right) + V(x, y, z) = E.$$

We want to transform this into a three-dimensional Schrödinger Equation.
Our solution, the wavefunction, now depends on four variables x, y, z, and t.

$$\Psi(x, t) \Longrightarrow \Psi(x, y, z, t)$$

Here are the operator correspondences we are going to use.

$$p_x \Longleftrightarrow -i\hbar\frac{\partial}{\partial x} \qquad p_y \Longleftrightarrow -i\hbar\frac{\partial}{\partial y} \qquad p_z \Longleftrightarrow -i\hbar\frac{\partial}{\partial z} \qquad E \Longleftrightarrow i\hbar\frac{\partial}{\partial t}$$

Of course, this means we have the following.

$$p_x^2 = -\hbar^2\frac{\partial^2}{\partial x^2} \qquad p_y^2 = -\hbar^2\frac{\partial^2}{\partial y^2} \qquad p_z^2 = -\hbar^2\frac{\partial^2}{\partial z^2}$$

Therefore,

$$\frac{p^2}{2\mu} = \frac{p_x^2 + p_y^2 + p_z^2}{2\mu} = \frac{1}{2\mu}\left[-\hbar^2\frac{\partial^2}{\partial x^2} + \left(-\hbar^2\frac{\partial^2}{\partial y^2}\right) + \left(-\hbar^2\frac{\partial^2}{\partial z^2}\right)\right] = \frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right).$$

On the other hand, the potential energy is now a function of x, y, and z as below.

$$V = V(x, y, z) = \frac{-e^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}}$$

We now have the following Time-Independent Schrödinger Equation in three domensions.

$$\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x, y, z, t) + V(x, y, z)\Psi(x, y, z, t) = i\hbar\frac{\partial\Psi(x, y, z, t)}{\partial t}$$

Let us introduce a Laplacian operator or "*del squared*" ∇^2 defined by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

This simplifies the equation to the following form.

$$\frac{-\hbar}{2\mu}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t};$$

where

$$V = V(x, y, z) \qquad \text{and} \qquad \Psi = \Psi(x, y, z, t).$$

Now let

$$\Psi(x, y, z, t)\ \psi(x, y, z)e^{-iEt/\hbar}.$$

Then, we get the Time-Independent Schrödinger Equation.

$$\frac{-\hbar^2}{2\mu}\nabla^2\psi(x, y, z) + V(x, y, z)\psi(x, y, z) = E\psi(x, y, z)$$

As it turned out, it is easier to solve this equation in spherical (polar) coordinates, where (x, y, z) are replaced by (r, θ, ϕ).
Note that in pure math books θ and ϕ are usually switched.

Since a hydrogen atom possesses spherical symmetry, this is a better coordinate system.

Right away, $V(x, y, z)$ simplifies as follows.

$$V(x, y, z) = \frac{-e^2}{4\pi\varepsilon_0 \sqrt{x^2 + y^2 + z^2}} = \frac{-e^2}{4\pi\varepsilon_0 r} = V(r, \theta, \varphi)$$

In fact, the potential energy only depends on the distance from the origin.

$$V(r, \theta, \varphi) = \frac{-e^2}{4\pi\varepsilon_0 r} = V(r)$$

Of course,

$$\psi(x, y, z) \Longrightarrow \psi(r, \theta, \varphi).$$

This means that we have to convert $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ to another equivalent operator expressed as derivatives with respect to r, θ, and φ.
Then, we will have

$$\frac{-\hbar^2}{2\mu}\nabla^2\psi(r, \theta, \varphi) + V(r)\psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi).$$

The answer is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial\varphi^2},$$

and we can see that ∇^2 appears far more complicated in the spherical coordinates.

How is it done? We begin with the three relations between (x, y, z) and (r, θ, φ).

$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases}$$

We can see how $\frac{\partial^2}{\partial x^2}$ etc. can be converted. What we should do is to keep using chain rules and relations like $\frac{\partial x}{\partial r} = \sin\theta\cos\varphi$. But, the actual operation is quite tedious.

Let us prove a part of this conversion.

Consider a one-variable function $\psi(r)$ for $r = \sqrt{x^2 + y^2 + z^2}$.
Since

$$\frac{\partial\psi}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial\psi}{\partial r} = \frac{x}{\sqrt{x^2 + y^2 + z^2}}\frac{\partial\psi}{\partial r} = \frac{x}{r}\frac{\partial\psi}{\partial r}$$

and

$$\frac{\partial r}{\partial x} = \frac{1}{2}\left(x^2 + y^2 + z^2\right)^{-1/2} \cdot 2 = \frac{x}{r},$$

we have

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial}{\partial x}\left(\frac{x}{r}\frac{\partial\psi}{\partial r}\right) = \frac{\partial}{\partial x}\left(x \cdot \frac{1}{r}\frac{\partial\psi}{\partial r}\right) = \frac{\partial x}{\partial x}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right)+x\frac{\partial}{\partial x}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right) = \frac{1}{r}\frac{\partial\psi}{\partial r}+x\frac{\partial r}{\partial x}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right)$$

$$= \frac{1}{r}\frac{\partial\psi}{\partial r} + x \cdot \frac{x}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right) = \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{x^2}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right).$$

Similarly,

$$\frac{\partial^2\psi}{\partial y^2} = \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{y^2}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right)$$

and

$$\frac{\partial^2\psi}{\partial z^2} = \frac{1}{r}\frac{\partial\psi}{\partial r} + \frac{z^2}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right).$$

Therefore,

$$\nabla^2\psi = \frac{3}{r}\frac{\partial\psi}{\partial r}+\frac{x^2 + y^2 + z^2}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right) = \frac{3}{r}\frac{\partial\psi}{\partial r}+r\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi}{\partial r}\right) = \frac{3}{r}\frac{\partial\psi}{\partial r}+r\left(-\frac{1}{r^2}\frac{\partial\psi}{\partial r} + \frac{1}{r}\frac{\partial^2\psi}{\partial r^2}\right)$$

$$= \frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{\partial^2\psi}{\partial r^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right).$$

In order to get other parts, try $\psi = \psi(\varphi)$ and $\psi = \psi(\theta)$.

In preparation for the rest of the course as well as your career as a physicist or just as someone who needs to understand and use physics, please do get used to the spherical coordinates. For example, the volume element

$$dxdydz$$

becomes

$$r^2 dr \sin\theta d\theta d\varphi \qquad \text{or} \qquad -r^2 dr d(\cos\theta) d\varphi$$

in spherical coordinates.

Let us pause for a minute here, take a deep breath, and summarize what we have achieved so far to clearly understand where we are now. (as well as, "hopefully", where we are heading)

1. Due to the spherical symmetry inherent in the hydrogen atom, we made a decision to use the spherical coordinates as opposed to the familiar Cartesian coordinates. In particular, this simplifies the expression for the potential energy greatly. It is now a function only of the radial distance between the electron and the proton nucleus.

$$V(x, y, z) = V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$$

2. However, a rather heavy trade-off was the conversion of ∇^2 to the equivalent expression in the spherical coordinates. The conversion process is cumbersome, and the resulting expression is far less palatable.

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

We are now ready to solve the Time-Independent Schrödinger Equation in spherical coordinates given by

$$\frac{-\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\varphi) + V(r)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi).$$

We will resort to the separation of variables technique yet one more time. So, consider ψ as a product of three single variable functions of r, θ, and φ respectively.

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$$

Then, the Time-Independent Schrödinger Equation is

$$\left[\frac{-\hbar^2}{2\mu}\nabla^2_{(r,\theta,\varphi)} + V(r)\right]R(r)\Theta(\theta)\Phi(\varphi) = ER(r)\Theta(\theta)\Phi(\varphi).$$

Let us write it out in its full glory and start computing!

$$\frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial(R\Theta\Phi)}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial(R\Theta\Phi)}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2(R\Theta\Phi)}{\partial\varphi^2}\right] + V(r)R(r)\Theta(\theta)\Phi(\varphi)$$

$$= ER(r)\Theta(\theta)\Phi(\varphi)$$

$$\Longrightarrow \frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\Theta\Phi\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}R\Phi\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}R\Theta\right]+V(r)R\Theta\Phi$$

$$= \frac{-\hbar^2}{2\mu}\left[\Theta\Phi\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{r^2\sin\theta}R\Phi\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}R\Theta\frac{\partial^2\Phi}{\partial\varphi^2}\right]+V(r)R\Theta\Phi$$

$$= \frac{-\hbar^2}{2\mu}\left[\Theta\Phi\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{r^2\sin\theta}R\Phi\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{r^2\sin^2\theta}R\Theta\frac{d^2\Phi}{d\varphi^2}\right]+V(r)R\Theta\Phi$$

$$= ER(r)\Theta(\theta)\Phi(\varphi)$$

Now, multiply through by

$$\frac{-2\mu}{\hbar^2}\cdot r^2\sin^2\theta\frac{1}{R\Theta\Phi}.$$

$$\frac{-\hbar^2}{2\mu}\cdot\frac{-2\mu}{\hbar^2}r^2\sin^2\theta\frac{1}{R\Theta\Phi}\left[\Theta\Phi\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{r^2\sin\theta}R\Phi\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{r^2\sin^2\theta}R\Theta\frac{d^2\Phi}{d\varphi^2}\right]$$

$$+V(r)R\Theta\Phi\frac{-2\mu}{\hbar^2}r^2\sin^2\theta\frac{1}{R\Theta\Phi} = ER\Theta\Phi\cdot\frac{-2\mu}{\hbar^2}r^2\sin^2\theta\frac{1}{R\Theta\Phi}$$

$$\Longrightarrow \frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}+\frac{-2\mu}{\hbar^2}r^2\sin^2\theta V(r) = \frac{-2\mu}{\hbar^2}r^2 sin^2\theta E$$

$$\Longrightarrow \frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = -\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{2\mu}{\hbar^2}r^2\sin^2\theta\,[E-V(r)]$$

The LHS (lefthand side) is a function of φ, and the RHS (righthand side) is a function of r and θ. And the equality holds for all values of r, θ, and φ. Therefore, both sides have to equal a constant. For later convenience, we denote this by $-m_l^2$. So, we have

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = -m_l^2$$

or

$$\frac{d^2\Phi}{d\varphi^2} = -m_l^2\Phi.$$

But, this also means

$$-\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta\,[E - V(r)] = -m_l^2$$

Dividing through by $\sin^2\theta$,

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{2\mu}{\hbar^2}r^2\,[E - V(r)] = -\frac{m_l^2}{\sin^2\theta}$$

$$\Longrightarrow \frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}r^2\,[E - V(r)] = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

The LHS depends on r, and the RHS is a function of θ. Since the equality holds for any values of r and θ, both sides have to be a constant. Denote that constant by $l(l+1)$ to get

$$\frac{-1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_l^2\Theta}{\sin^2\theta} = l(l+1)\Theta$$

and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\,[E - V(r)]\,R = l(l+1)\frac{R}{r^2}.$$

We have now reduced the problem to that of solving the following three equations each in one variable.

$$\frac{d^2\Phi}{d\varphi^2} = -m_l^2\Phi \tag{5.1}$$

$$\frac{-1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_l^2\Theta}{\sin^2\theta} = l(l+1)\Theta \tag{5.2}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\,[E - V(r)]\,R = l(l+1)\frac{R}{r^2} \tag{5.3}$$

5.1 The Solutions for Φ

The easiest to solve is equation 5.1.

$$\frac{d^2\Phi}{d\varphi^2} = -m_l^2\Phi$$

So,

$$\Phi(\varphi) = e^{im_l\varphi}.$$

Consider single-valuedness.

$$\Phi(0) = \Phi(2\pi) \Longrightarrow e^{i\cdot m_l\cdot 0} = e^{i\cdot m_l\cdot 2\pi} \Longrightarrow 1 = e^{im_l\cdot 2\pi} = \cos(m_l 2\pi) + i\sin(m_l 2\pi)$$

Now, let $m_l = a + bi$ for $(a, b \in \mathbb{R})$.

$$|1| = \left|e^{im_l 2\pi}\right| = \left|e^{i(a+bi)2\pi}\right| = \left|e^{ia2\pi}\right|\left|e^{-b2\pi}\right|$$

$$\left|e^{-b2\pi}\right| = e^{-b2\pi} = 1$$

$$2\pi b = 0 \Longrightarrow b = 0$$

It is now obvious that m_l is a real number and

$$|m_l| = 0, 1, 2, 3, 4, \ldots\ldots.$$

For each value of m_l, there is a corresponding solution

$$\Phi_{m_l}(\varphi) = e^{im_l\varphi}.$$

The numbers m_l are known as quantum numbers.

Now we need to solve equations 5.2 and 5.3.

5.2 The Solutions for Θ

Equation 5.2 is known as the angular equation.

$$-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_l^2\Theta}{\sin^2\theta} = l(l+1)\Theta$$

Note that

$$d\cos\theta = -\sin\theta d\theta.$$

So,

$$\frac{-1}{\sin\theta}\frac{d}{d\theta} = \frac{d}{d\cos\theta},$$

and

$$\sin\theta\frac{d}{d\theta} = \sin\theta\frac{d}{\frac{d\cos\theta}{-\sin\theta}} = -\sin^2\theta\frac{d}{d\cos\theta} = -(1-\cos^2\theta)\frac{d}{d\cos\theta}$$

This suggests that 5.2 can be simplified if we let $z = \cos\theta$. Since,

$$\frac{d}{d\cos\theta}\left(-(1-\cos^2\theta)\frac{d\Theta}{d\cos\theta}\right) + \frac{m_l^2\Theta}{1-\cos^2\theta} = l(l+1)\Theta,$$

we have

$$\frac{d}{dz}\left(-(1-z^2)\frac{d\Theta}{dz}\right) + \frac{m_l^2\Theta}{1-z^2} = l(l+1)\Theta$$

$$\implies \frac{d}{dz}\left((1-z^2)\frac{d\Theta}{dz}\right) + \left(l(l+1) - \frac{m_l^2}{1-z^2}\right)\Theta = 0$$

At the time Schrödinger was solving his equation for the hydrogen atom, this was already a well-known differential equation, and the solutions are called the associated Legendre functions denoted $\Theta_{lm_l}(z)$. This is related to a better known set of functions called the Legendre polynomials denoted $P_l(z)$. The fact is the relation is as follows.

$$\Theta_{lm_l}(z) = (1-z^2)^{|m_l|/2}\frac{d^{|m_l|}P_l(z)}{dz^{|m_l|}}$$

Our first job is to prove this.

Now $P_l(z)$ is a solution to

$$(1-z^2)\frac{d^2P_l}{dz^2} - 2z\frac{dP_l}{dz} + l(l+1)P_l = 0.$$

Differentiate both sides with respect to z to obtain

$$-2z\frac{d^2P_l}{dz^2} + (1-z^2)\frac{d^3P_l}{dz^3} - 2\frac{dP_l}{dz} - 2z\frac{d^2P_l}{dz^2} + l(l+1)\frac{dP_l}{dz}$$

$$= (1-z^2)\frac{d^3P_l}{dz^3} - 4z\frac{d^2P_l}{dz^2} + \left((l(l+1)-2)\frac{dP_l}{dz}\right) = 0$$

Try $\frac{d}{dz}$ again.

$$-2\frac{d^2P_l}{dz^2} - 2z\frac{d^3P_l}{dz^3} - 2z\frac{d^3P_l}{dz^3} + (1-z^2)\frac{d^4P_l}{dz^4} - 2\frac{d^2P_l}{dz^2} - 2\frac{d^2P_l}{dz^2} - 2z\frac{d^3P_l}{dz^3} + l(l+1)\frac{d^2P_l}{dz^2}$$

$$= (1-z^2)\frac{d^4P_l}{dz^4} - 6z\frac{d^3P_l}{dz^3} + (l(l+1)-6)\frac{d^2P_l}{dz^2} = 0$$

Suppose we get

$$(1-z^2)\frac{d^{k+2}P_l}{dz^{k+2}} - 2(k+1)z\frac{d^{k+1}P_l}{dz^{k+1}} + (l(l+1)-k(k+1))\frac{d^k}{dz^k}P_l = 0$$

after differentiating k times.
Now apply $\frac{d}{dz}$ one more time.

$$-2z\frac{d^{k+2}P_l}{dz^{k+2}}+(1-z^2)\frac{d^{k+3}P_l}{dz^{k+3}}-2(k+1)\frac{d^{k+1}P_l}{dz^{k+1}}-2(k+1)z\frac{d^{k+2}P_l}{dz^{k+2}}+(l(l+1)-k(k+1))\frac{d^{k+1}P_l}{dz^{k+1}}$$

$$= (1-z^2)\frac{d^{(k+1)+2}P_l}{dz^{(k+1)+2}}-2((k+1)+1)z\frac{d^{(k+2)+1}P_l}{dz^{(k+2)+1}}+(l(l+1)-(k+1)((k+1)+1)\frac{d^{k+1}P_l}{dz^{k+1}} = 0$$

So, by mathematical induction,

$$(1-z^2)\frac{d^{k+2}}{dz^{k+2}}P_l - 2(k+1)z\frac{d^{k+1}P_l}{dz^{k+1}} + (l(l+1)-k(k+1))\frac{d^kP_l}{dz^k} = 0$$

when we apply $\frac{d^k}{dz^k}$.

On the other hand, consider

$$\Theta_{lm_l} = (1-z^2)^{|m_l|/2}\Gamma(z)$$

and substitute this into

$$\frac{d}{dz}\left((1-z^2)\frac{d\Theta}{dz}\right) + \left(l(l+1) - \frac{m_l^2}{1-z^2}\right)\Theta = 0.$$

We have the following lengthy computation.

$$\frac{d}{dz}\left((1-z^2)\frac{d}{dz}(1-z^2)^{k/2}\Gamma\right) + \left(l(l+1) - \frac{k^2}{1-z^2}\right)(1-z^2)^{k/2}\Gamma$$

$$= -2z\frac{d}{dz}((1-z^2)^{k/2}\Gamma) + (1-z^2)\frac{d^2}{dz^2}((1-z^2)^{k/2}\Gamma) + \left(l(l+1) - \frac{k^2}{1-z^2}\right)(1-z^2)^{k/2}\Gamma$$

$$= -2z\left(\frac{k}{2}(1-z^2)^{(k/2-1)}(-2z)\Gamma + (1-z^2)^{k/2}\frac{d\Gamma}{dz}\right)$$

$$+(1-z^2)\frac{d}{dz}\left(\frac{k}{2}(1-z^2)^{(k/2-1)}(-2z)\Gamma + (1-z^2)^{k/2}\frac{d\Gamma}{dz}\right)+\left(l(l+1)-\frac{k^2}{1-z^2}\right)(1-z^2)^{k/2}\Gamma$$

$$= -2z\left(kz(1-z^2)^{(k/2-1)}\Gamma + (1-z^2)^{k/2}\frac{d\Gamma}{dz}\right)$$

$$+(1-z^2)\left[\frac{k}{2}(k/2-1)(1-z^2)^{(k/2-2)}(-2z)(-2z)\Gamma + \frac{k}{2}(1-z^2)^{(k/2-1)}(-2)\Gamma\right.$$

$$\left.+\frac{k}{2}(1-z^2)^{(k/2-1)}(-2z)\frac{d\Gamma}{dz} + \frac{k}{2}(1-z^2)^{(k/2-1)}(-2z)\frac{d\Gamma}{dz} + (1-z^2)^{k/2}\frac{d^2\Gamma}{dz^2}\right]$$

$$+\left(l(l+1)-\frac{k^2}{1-z^2}\right)(1-z^2)^{k/2}\Gamma$$

$$= 2kz^2(1-z^2)^{(k/2-1)}\Gamma - 2z(1-z^2)^{k/2}\frac{d\Gamma}{dz}$$

$$+(1-z^2)\left[2kz^2\left(\frac{k}{2}-1\right)(1-z^2)^{(k/2-2)}\Gamma - k(1-z^2)^{(k/2-1)}\Gamma\right.$$

$$\left.-kz(1-z^2)^{(k/2-1)}\frac{d\Gamma}{dz} - kz(1-z^2)^{(k/2-1)}\frac{d\Gamma}{dz} + (1-z^2)^{k/2}\frac{d^2\Gamma}{dz^2}\right]$$

$$+\left(l(l+1)-\frac{k^2}{1-z^2}\right)(1-z^2)^{k/2}\Gamma = 0$$

Multiplying through by $(1-z^2)^{-k/2}$,

$$\frac{2kz^2}{1-z^2}\Gamma - 2z\frac{d\Gamma}{dz}$$

$$+(1-z^2)\left[2kz^2\left(\frac{k}{2}-1\right)(1-z^2)^{-2}\Gamma - k(1-z^2)^{-1}\Gamma - kz(1-z^2)^{-1}\frac{d\Gamma}{dz} - kz(1-z^2)^{-1}\frac{d\Gamma}{dz} + \frac{d^2\Gamma}{dz^2}\right]$$

$$+\left(l(l+1)-\frac{k^2}{1-z^2}\right)\Gamma$$

$$= \frac{2kz^2}{1-z^2}\Gamma - 2z\frac{d\Gamma}{dz} + 2kz^2\left(\frac{k}{2}-1\right)(1-z^2)^{-1}\Gamma - k\Gamma - kz\frac{d\Gamma}{dz} - kz\frac{d\Gamma}{dz} + (1-z^2)\frac{d^2\Gamma}{dz^2} + \left(l(l+1)-\frac{k^2}{1-z^2}\right)\Gamma$$

$$= (1-z^2)\frac{d^2\Gamma}{dz^2} + (-2kz-2z)\frac{d\Gamma}{dz} + \left[l(l+1) + \frac{2kz^2 + 2kz^2\left(\frac{k}{2}-1\right) - k^2}{1-z^2} - k\right]\Gamma$$

$$= (1-z^2)\frac{d^2\Gamma}{dz^2} - 2(k+1)z\frac{d\Gamma}{dz} + \left[l(l+1) + \frac{k^2z^2 - k^2}{1-z^2} - k\right]\Gamma$$

$$= (1-z^2)\frac{d^2\Gamma}{dz^2} - 2(k+1)z\frac{d\Gamma}{dz} + \left[l(l+1) - k^2 - k\right]\Gamma = 0.$$

So, we have shown

$$(1-z^2)\frac{d^2\Gamma}{dz^2} - 2(k+1)z\frac{d\Gamma}{dz} + [l(l+1) - k(k+1)]\,\Gamma = 0$$

or

$$(1-z^2)\frac{d^2\Gamma}{dz^2} - 2(|m_l|+1)z\frac{d\Gamma}{dz} + [l(l+1) - |m_l|\,(|m_l|+1)]\,\Gamma = 0.$$

Comparing this with

$$(1-z^2)\frac{d^{k+2}}{dz^{k+2}}P_l - 2(k+1)z\frac{d^{k+1}P_l}{dz^{k+1}} + (l(l+1) - k(k+1))\frac{d^kP_l}{dz^k} = 0,$$

we conclude

$$\Theta_{lm_l} = (1-z^2)^{|m_l|/2}\frac{d^{|m_l|}P_l}{dz^{|m_l|}}.$$

It remains to solve

$$(1-z^2)\frac{d^2P_l}{dz^2} - 2z\frac{dP_l}{dz} + l(l+1)P_l = 0$$

for P_l.

Try

$$P_l(z) = \sum_{k=0}^{\infty} a_k z^k.$$

We get a recursion relation as before.

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

Also as before, we do not want an infinite series; that is, we want the series to terminate after a finite number of terms. So, $l = 0, 1, 2, 3, \ldots$ give acceptable

solutions.
We get

$$P_0 = 1, P_1 = z, P_2 = 1 - 3z^2, P_3 = 3z - 5z^3, \ldots.$$

So, the corresponding $\Theta_{lm_l}s$ are

$$\Theta_{00} = 1, \quad \Theta_{10} = z, \quad \Theta_{1\pm1} = (1-z^2)^{1/2}, \quad \Theta_{20} = 1-3z^2, \quad \Theta_{2\pm1} = (1-z^2)^{1/2}z, \quad \Theta_{2\pm2} = 1-z^2,$$

and so on, and the like.

Note that $P_l(z)$ is an lth degree polynomial. Therefore, for each l, we have

$$m_l = -l, \quad -l+1, \quad \ldots, \quad 0, \quad \ldots, \quad l-1, \quad l.$$

We now have Θ and Φ.

5.3 The Radial Function R

The general radial equation for a one-eletron atom is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right]R = l(l+1)\frac{R}{r^2}.$$

We will only solve this for $Z = 1$ or for a hydrogen atom.

Let us first invoke some substitutions to put it in a more manageable, after the fact it is, form.

$$\beta^2 = \frac{2\mu E}{\hbar} \quad (\beta > 0)$$

$$\rho = 2\beta r$$

$$\gamma = \frac{\mu e^2}{4\pi\varepsilon_0\hbar^2\beta}$$

With this substitution, we get

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

As $\rho \to \infty$

$$R(\rho) \approx e^{-\rho/2}.$$

So, write

$$R(\rho) = e^{-\rho/2} F(\rho),$$

and substitute this into the radial equation to get

$$\frac{d^2F}{d\rho^2} + \left(\frac{2}{\rho} - 1\right)\frac{dF}{d\rho} + \left[\frac{\gamma - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right] F = 0.$$

Once again, we will try a series solution with

$$F(\rho) = \rho^s \sum_{k=0}^{\infty} a_k \rho^k \quad (a_0 \neq 0, \quad s \geq 0);$$

where the conditions on a_0 and s are in place to prevent F from blowing up at the origin.

After substituting this sum into the differential equation, we get

$$\left\{ \begin{array}{l} s(s+1) - l(l+1) = 0 \quad \text{and} \\ a_{j+1} = \frac{s+j+1-\gamma}{(s+j+1)(s+j+2)-l(l+1)} a_j \end{array} \right\}$$

The first equality gives $s = l$ and $s = -(l+1)$. But, $s = -(l+1)$ should be rejected as $s \geq 0$.

The second equality

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

indicates that

$$\gamma = j + l + 1 = n \ \ \text{(Call this } n.\text{)}$$

assures termination of the series after a finite number of terms. Hence,

$$n = l + 1, l + 2, l + 3, \cdots$$

as j goes from 0 to ∞ with $l = 0, 1, 2, 3, \ldots$.

Now recall

$$\beta^2 = \frac{2\mu E}{\hbar^2}$$

and

$$\gamma = \frac{\mu e^2}{4\pi\varepsilon_0\hbar^2\beta}.$$
$$\|$$
$$n$$

So,

$$E_n = -\frac{\mu e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} \qquad n = 1, 2, 3, \cdots.$$

Putting it all together, we get

$$R_{nl}(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\varphi) = \Psi_{nlm_l}(r, \theta, \varphi);$$

where

$$\Phi_{m_l}(\varphi) = e^{im_l\varphi} \quad |m_l| = 0, 1, 2, 3, \cdots,$$

$$\Theta_{lm_l}(\theta) = \sin^{|m_l|}\theta F_{l|m_l|}(\cos\theta),$$

and

$$R_{nl}(r) = e^{-r/na_0}\left(\frac{r}{a_0}\right)^2 G_{nl}\left(\frac{r}{a_0}\right).$$

Here,

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2},$$

$$F_{l|m_l|}$$

is a polynomial in $\cos\theta$, and

$$G_{nl}\left(\frac{r}{a_0}\right)$$

is a polynomial in r/a_0.

Recall that we have

$$|m_l| = 0, 1, 2, 3, \cdots,$$

$$l = |m_l|, |m_l| + 1, \cdots, |m_l| + 3, \cdots,$$

and

$$n = l + 1, l + 2, l + 3, \cdots.$$

This can be reorganized as follows.

$$n = 1, 2, 3, 4, \cdots$$

$$l = 0, 1, 2, \cdots, n - 1$$

$$m_l = -l, -l + 1, \cdots, 0, \cdots, +l$$

The first number n is associated with $R(r)$ and is called the principal quantum number. The second number l is associated with $\Theta(\theta)$ and is called the orbital quantum number. Finally, the number m_l is called the magnetic quantum number which is asoociated with $\Phi(\varphi)$. In addition to these, we also have a spin quantum number m_s, which we have no time to discuss.

About The Final Examination

1. 07/04/2005, 10:30 → 12:00
2. Open lecture notes, open homework (no copies): I will check these in the first 10 minutes.
3. Can't use a calculator, but will never need it.
4. Examples of topics to be covered
   (a) The Step Potential
   (b) The Infinite Square Well
   (c) The Simple Harmonic Oscillator
   (d) The Hydrogen Atom: You don't have to solve any differential equation.
   (e) Series Solutions
5. You should know the following.
   (a) Know how to use continuity conditions.
   (b) Know how to interpret Ψ.
   (c) Know how to compute expectation values.
6. **Show all your work. Include the intermediate steps.**