The Separation of Variables

START LECTURE 18 (THE LEFT OVERS FROM LAST TIME) 7-23-09

IN DIFF EQN LANGUAGE

TDSE $\longrightarrow$ TISE

COMES FROM SEPARATING VARIABLES

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\,\psi(x,t) = i\hbar\frac{d}{dt}\psi(x,t)$$

$$\psi(x,t) = f(x)\,g(t)$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}(f\cdot g) + V(x)(f\cdot g) = i\hbar\frac{d}{dt}(f\cdot g)$$

$$g\left(-\frac{\hbar^2}{2m}\right)\frac{d^2f}{dx^2} + g\,V(x)\,f = f(i\hbar)\frac{dg}{dt}$$

$$\frac{1}{f\cdot g}$$

$$\frac{-\frac{\hbar^2}{2m}\frac{d^2f}{dx^2}}{f} + \frac{V(x)\,f}{f} = \frac{(i\hbar)\frac{dg}{dt}}{g} = E_n$$

$$\ell \quad \frac{dg}{dt} = \frac{E_n}{i\hbar}\,g = \frac{-iE_n}{\hbar}\,g$$

$$g(t) = e^{-iE_n t/\hbar}$$

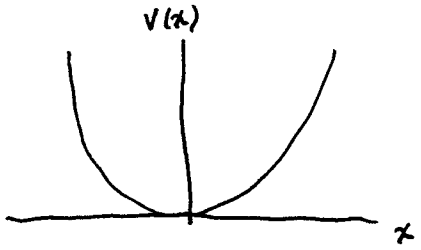
LEFT WITH TISE

$$H\,|\psi_n\rangle = E_n\,|\psi_n\rangle$$

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

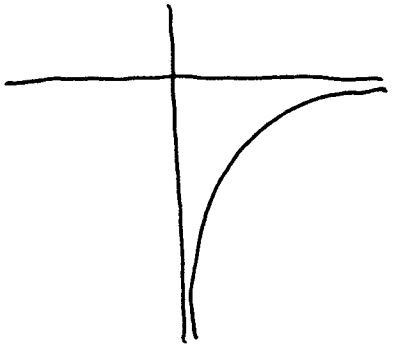
in 3d ∇^2

different $V(x)$'s



SHO

$V(x) \sim x^2$



$V(r) \sim \frac{1}{r}$

IMPORTANT TECHNIQUE # 137

SEPARATION OF VARIABLES

$$Y_{\ell m}(\theta, \varphi) = f_{\ell m}(\theta)\, g_{\ell m}(\varphi)$$

$$L_z |\ell, m\rangle = m\hbar\, |\ell, m\rangle$$

$$-i\hbar \frac{\partial}{\partial \varphi}\left(f_{\ell m}(\theta)\, g_{\ell m}(\varphi)\right) = m\hbar \left(f_{\ell m}(\theta)\, g_{\ell m}(\varphi)\right)$$

$$-i\hbar\, \cancel{f_{\ell m}(\theta)}\, \frac{\partial g_{\ell m}(\varphi)}{\partial \varphi} = m\hbar\, \cancel{f_{\ell m}(\theta)}\, g_{\ell m}(\varphi)$$

$$\frac{\partial g}{\partial \varphi} = i m g \quad \Rightarrow \quad g = e^{i m \varphi}$$

so it separates

and it does not depend on ℓ

Chapter 10 The Hydrogen Atom

There are many good reasons to address the hydrogen atom beyond its historical significance. Though hydrogen spectra motivated much of the early quantum theory, research involving the hydrogen remains at the cutting edge of science and technology. For instance, transitions in hydrogen are being used in 1997 and 1998 to examine the constancy of the fine structure constant over a cosmological time scale[2]. From the view point of pedagogy, the hydrogen atom merges many of the concepts and techniques previously developed into one package. It is a particle in a box with spherical, soft walls. Finally, the hydrogen atom is one of the precious few realistic systems which can actually be solved analytically.

The Schrodinger Equation in Spherical Coordinates

In chapter 5, we separated time and position to arrive at the time independent Schrodinger equation which is

$$\mathcal{H}\left|E_i\right> = E_i\left|E_i\right>, \tag{10-1}$$

where E_i are eigenvalues and $\left|E_i\right>$ are energy eigenstates. Also in chapter 5, we developed a one dimensional position space representation of the time independent Schrodinger equation, changing the notation such that $E_i \to E$, and $\left|E_i\right> \to \psi$. In three dimensions the Schrodinger equation generalizes to

$$\boxed{\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi,}$$

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where ∇^2 is the Laplacian operator. Using the Laplacian in spherical coordinates, the Schrodinger equation becomes

$$\boxed{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi + V(r)\psi = E\psi.} \tag{10-2}$$

In spherical coordinates, $\psi = \psi(r,\theta,\phi)$, and the plan is to look for a variables separable solution such that $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$. We will in fact find such solutions where $Y(\theta,\phi)$ are the spherical harmonic functions and $R(r)$ is expressible in terms of associated Laguerre functions. Before we do that, interfacing with the previous chapter and arguments of linear algebra may partially explain why we are proceeding in this direction.

Complete Set of Commuting Observables for Hydrogen

Though we will return to equation (10–2), the Laplacian can be expressed

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right). \tag{10-3}$$

Compare the terms in parenthesis to equation 11–33. The terms in parenthesis are equal to $-\mathcal{L}^2/\hbar^2$, so assuming spherical symmetry, the Laplacian can be written

$$\boxed{\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2},}$$

[2] Schwarzschild. "Optical Frequency Measurement is Getting a Lot More Precise," Physics Today 50(10) 19–21 (1997).

and the Schrodinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{\mathcal{L}^2}{r^2\hbar^2}\right)+V(r)\right]\psi=E\psi. \qquad (10-4)$$

Assuming spherical symmetry, which we will have because a Coulomb potential will be used for $V(r)$, we have complicated the system of chapter 11 by adding a radial variable. Without the radial variable, we have a complete set of commuting observables for the angular momentum operators in $\mathcal{L}^2$ and $\mathcal{L}_z$. Including the radial variable, we need a minimum of one more operator, if that operator commutes with both $\mathcal{L}^2$ and $\mathcal{L}_z$. The total energy operator, the Hamiltonian, may be a reasonable candidate. What is the Hamiltonian here? It is the group of terms within the square brackets. Compare equations (10–1) and (10–4) if you have difficulty visualizing that. In fact,

$$\boxed{\left[\mathcal{H},\,\mathcal{L}^2\right]=0, \qquad \text{and} \qquad \left[\mathcal{H},\,\mathcal{L}_z\right]=0,}$$

commute

so the Hamiltonian is a suitable choice. The complete set of commuting observables for the hydrogen atom is $\mathcal{H}$, $\mathcal{L}^2$, and $\mathcal{L}_z$. We have all the eigenvalue/eigenvector equations, because the time independent Schrodinger equation is the eigenvalue/eigenvector equation for the Hamiltonian operator, *i.e.*, the the eigenvalue/eigenvector equations are

$$\boxed{\begin{aligned}\mathcal{H}\,|\psi>&=E_n|\psi>,\\ \mathcal{L}^2|\psi>&=l(l+1)\hbar^2|\psi>,\\ \mathcal{L}_z|\psi>&=m\hbar|\psi>,\end{aligned}}$$

simultaneous

eigenvalue

eigenvector

where we subscripted the energy eigenvalue with an n because that is the symbol conventionally used for the energy quantum number (per the particle in a box and SHO). Then the solution to the problem is the eigenstate which satisfies all three, denoted $|n,l,m>$ in abstract Hilbert space. The representation in position space in spherical coordinates is

$$\boxed{<r,\theta,\phi|n,l,m>=\psi_{nlm}(r,\theta,\phi).}$$

Example 10–1: Starting with the Laplacian included in equation (10–2), show the Laplacian can be express as equation (10–3).

$$\begin{aligned}\nabla^2&=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\\ &=\frac{1}{r^2}\left(2r\frac{\partial}{\partial r}+r^2\frac{\partial^2}{\partial r^2}\right)+\frac{1}{r^2\sin\theta}\left(\cos\theta\frac{\partial}{\partial\theta}+\sin\theta\frac{\partial^2}{\partial\theta^2}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\\ &=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}+\frac{1}{r^2\tan\theta}\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\\ &=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2}+\frac{1}{\tan\theta}\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right),\end{aligned}$$

which is the form of equation (10–3).

Example 10–2: Show $\left[\mathcal{H},\,\mathcal{L}^2\right]=0$.

$$\left[\mathcal{H},\,\mathcal{L}^2\right]=\mathcal{H}\,\mathcal{L}^2-\mathcal{L}^2\,\mathcal{H}$$

$$= \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2} \right) + V(r) \right] \mathcal{L}^2 - \mathcal{L}^2 \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2} \right) + V(r) \right]$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\mathcal{L}^2 - \frac{\hbar^2}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}^2 + \frac{\hbar^2}{2m}\frac{\mathcal{L}^4}{r^2\hbar^2} + \frac{\hbar^2}{2m}V(r)\mathcal{L}^2$$

$$+\frac{\hbar^2}{2m}\mathcal{L}^2\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}^2\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\frac{\mathcal{L}^4}{r^2\hbar^2} - \frac{\hbar^2}{2m}\mathcal{L}^2 V(r)$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\mathcal{L}^2 - \frac{\hbar^2}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}^2 + \frac{\hbar^2}{2m}V(r)\mathcal{L}^2 + \frac{\hbar^2}{2m}\mathcal{L}^2\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}^2\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\mathcal{L}^2 V(r)$$

where the third and seventh terms in $\mathcal{L}^4$ sum to zero. The spherical coordinate representation of $\mathcal{L}^2$ is

$$\mathcal{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right)$$

and has angular dependence only. The partial derivatives with respect to the radial variable act only on terms without radial dependence. Partial derivatives with respect to angular variables do not affect the potential which is a function only of the radial variable. Therefore, the order of the operator products is interchangeable, and

$$\left[\mathcal{H},\, \mathcal{L}^2 \right] = -\frac{\hbar^2}{2m}\mathcal{L}^2\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2m}\mathcal{L}^2\frac{2}{r}\frac{\partial}{\partial r} + \frac{\hbar^2}{2m}\mathcal{L}^2 V(r) + \frac{\hbar^2}{2m}\mathcal{L}^2\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}^2\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\mathcal{L}^2 V(r) = 0.$$

Instead of the verbal argument, we could substitute the angular representation of $\mathcal{L}^2$, form the 18 resultant terms, explicitly interchange nine of them, and get the same result.

Example 10–3: Show $\left[\mathcal{H},\, \mathcal{L}_z \right] = 0$.

$$\left[\mathcal{H},\, \mathcal{L}_z \right] = \mathcal{H}\,\mathcal{L}_z - \mathcal{L}_z\,\mathcal{H}$$

$$= \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2} \right) + V(r) \right] \mathcal{L}_z - \mathcal{L}_z \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2} \right) + V(r) \right]$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\mathcal{L}_z - \frac{\hbar^2}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}_z + \frac{\hbar^2}{2m}\frac{\mathcal{L}^2\,\mathcal{L}_z}{r^2\hbar^2} + \frac{\hbar^2}{2m}V(r)\mathcal{L}_z$$

$$+\frac{\hbar^2}{2m}\mathcal{L}_z\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}_z\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\frac{\mathcal{L}_z\,\mathcal{L}^2}{r^2\hbar^2} - \frac{\hbar^2}{2m}\mathcal{L}_z V(r)$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}\mathcal{L}_z - \frac{\hbar^2}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}_z + \frac{\hbar^2}{2m}V(r)\mathcal{L}_z + \frac{\hbar^2}{2m}\mathcal{L}_z\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}_z\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\mathcal{L}_z V(r)$$

where the third and seventh terms in $\mathcal{L}^2\,\mathcal{L}_z$ sum to zero because we already know those two operators commute. The spherical coordinate representation of $\mathcal{L}_z$ is

$$\mathcal{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

and has angular dependence only. Again there are no partial derivatives which affect any term of the other operator, or the potential $V(r)$, in any of the operator products. Therefore, the order of the operator products is interchangeable, and

$$\left[\mathcal{H},\, \mathcal{L}_z \right] = -\frac{\hbar^2}{2m}\mathcal{L}_z\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2m}\mathcal{L}_z\frac{2}{r}\frac{\partial}{\partial r} + \frac{\hbar^2}{2m}\mathcal{L}_z\,V(r) + \frac{\hbar^2}{2m}\mathcal{L}_z\frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m}\mathcal{L}_z\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^2}{2m}\mathcal{L}_z V(r) = 0.$$

Separating Radial and Angular Dependence

In this and the following three sections, we illustrate how the angular momentum and magnetic moment quantum numbers enter the symbology from a calculus based argument. In writing equation (10–2), we have used a representation, so are no longer in abstract Hilbert space. One of the consequences of the process of representation is the topological arguments of linear algebra are obscured. They are still there, simply obscured because the special functions we use are orthogonal, so can be made orthonormal, and complete, just as bras and kets in a dual space are orthonormal and complete. The primary reason to proceed in terms of a position space representation is to attain a position space description. One of the by–products of this chapter may be to convince you that working in the generality of Hilbert space in Dirac notation can be considerably more efficient. Since we used topological arguments to develop angular momentum in the last chapter, and arrive at identical results to those of chapter 11, we rely on connections between the two to establish the meanings of of l and m. They have the same meanings within these calculus based discussions.

As noted, we assume a variables separable solution to equation (10–2) of the form

$$\boxed{\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi).} \tag{10 – 5}$$

An often asked question is "How do you know you can assume that?" You do not know. You assume it, and if it works, you have found a solution. If it does not work, you need to attempt other methods or techniques. Here, it will work. Using equation (10–5), equation (10–2) can be written

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\boxed{R(r)\,Y(\theta,\phi)} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\boxed{R(r)\,Y(\theta,\phi)}$$

$$+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\boxed{R(r)\,Y(\theta,\phi)} - \frac{2m}{\hbar^2}\Big[V(r)-E\Big]\boxed{R(r)\,Y(\theta,\phi)} = 0$$

$$\Rightarrow\quad Y(\theta,\phi)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) + R(r)\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi)$$

$$+R(r)\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi) - \frac{2m}{\hbar^2}\Big[V(r)-E\Big]R(r)\,Y(\theta,\phi) = 0.$$

Dividing the equation by $R(r)\,Y(\theta,\phi)$, multiplying by r^2, and rearranging terms, this becomes

$$\left\{\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) - \frac{2mr^2}{\hbar^2}\Big[V(r)-E\Big]\right\}$$ **depends only on r**

depends only on angles $$+\left[\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi) + \frac{1}{Y(\theta,\phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi)\right] = 0.$$

The two terms in the curly braces depend only on r, and the two terms in the square brackets depend only upon angles. With the exception of a trivial solution, the only way the sum of the groups can be zero is if each group is equal to the same constant. The constant chosen is known as the **separation constant**. Normally, an arbitrary separation constant, like K, is selected and then you solve for K later. In this example, we are instead going to stand on the shoulders of

=> they must be constants

some of the physicists and mathematicians of the previous 300 years, and make the enlightened choice of $l(l+1)$ as the separation constant. It should become clear l is the angular momentum quantum number introduced in chapter 11. Then

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2mr^2}{\hbar^2}\Big[V(r) - E\Big] = l(l+1) \qquad (10-6)$$

which we call the **radial equation**, and

$$\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi) + \frac{1}{Y(\theta,\phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi) = -l(l+1), \qquad (10-7)$$

which we call the **angular equation**. Notice the signs on the right side are opposite so they do, in fact, sum to zero.

The Angular Equation

The solutions to equation (10–7) are the spherical harmonic functions, and the l used in the separation constant is, in fact, the same used as the index l in the spherical harmonics $Y_{l,m}(\theta,\phi)$. In fact, it is the angular momentum quantum number. But where is the index m? How is the magnetic moment quantum number introduced? To answer these questions, remember the spherical harmonics are also separable, *i.e.*, $Y_{l,m}(\theta,\phi) = f_{l,m}(\theta)\,g_m(\phi)$. We will use such a solution in the angular equation, without the indices until we see where they originate. Using the solution $Y(\theta,\phi) = f(\theta)\,g(\phi)$ in equation (10–7),

$$\frac{1}{f(\theta)\,g(\phi)\,\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\boxed{f(\theta)\,g(\phi)} + \frac{1}{f(\theta)\,g(\phi)\,\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\boxed{f(\theta)\,g(\phi)} = -l(l+1)$$

$$\Rightarrow \quad \frac{1}{f(\theta)\,\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f(\theta) + \frac{1}{g(\phi)\,\sin^2\theta}\frac{\partial^2}{\partial\phi^2}g(\phi) = -l(l+1).$$

Multiplying the equation by $\sin^2\theta$ and rearranging,

only on theta

$$\frac{\sin\theta}{f(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f(\theta) + l(l+1)\,\sin^2\theta + \frac{1}{g(\phi)}\frac{\partial^2}{\partial\phi^2}g(\phi) = 0.$$

only on phi

The first two terms depend only on θ, and the last term depends only on ϕ. Again, the only non–trivial solution such that the sum is zero is if the groups of terms each dependent on a single variable is equal to the same constant. Again using an enlightened choice, we pick m^2 as the separation constant, so

$$\frac{\sin\theta}{f(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)f(\theta) + l(l+1)\,\sin^2\theta = m^2, \qquad (10-8)$$

$$\boxed{\frac{1}{g(\phi)}\frac{d^2}{d\phi^2}g(\phi) = -m^2,} \qquad (10-9)$$

and that is how the magnetic moment quantum number is introduced. Again, (10–8) and (10–9) need to sum to zero so the separation constant has opposite signs on the right side in the two equations.

The Azimuthal Angle Equation

The solution to the azimuthal angle equation, equation (10–9), is

$$g(\phi) = e^{im\phi} \quad \Rightarrow \quad \boxed{g_m(\phi) = e^{im\phi},} \tag{10 – 10}$$

where the subscript m is added to $g(\phi)$ because it is now clear there are as many solutions as there are allowed values of m.

Example 10–4: Show $g_m(\phi) = e^{im\phi}$ is a solution to equation (10–9).

$$\frac{d^2}{d\phi^2} g_m(\phi) = \frac{d^2}{d\phi^2} e^{im\phi} = \frac{d}{d\phi}(im)e^{im\phi} = (im)^2 e^{im\phi} = -m^2 g_m(\phi).$$

Using this in equation (10–9),

$$\frac{1}{g(\phi)} \frac{d^2}{d\phi^2} g(\phi) = -m^2 \quad \Rightarrow \quad \frac{1}{g(\phi)}\Big(- m^2 g_m(\phi)\Big) = -m^2 \quad \Rightarrow \quad -m^2 = -m^2,$$

therefore $g_m(\phi) = e^{im\phi}$ is a solution to equation (10–9).

The Polar Angle Equation

This section is a little more substantial than the last. Equation (10–8) can be written

$$\boxed{\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d}{d\theta}\right) f(\theta) + l(l+1)\, \sin^2\theta\, f(\theta) - m^2\, f(\theta) = 0.}$$

Evaluating the first term,

$$\begin{aligned}
\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d}{d\theta}\right) f(\theta) &= \sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\, f(\theta)}{d\theta}\right) \\
&= \sin\theta \left(\cos\theta \frac{d\, f(\theta)}{d\theta} + \sin\theta \frac{d^2\, f(\theta)}{d\theta^2}\right) \\
&= \sin^2\theta \frac{d^2\, f(\theta)}{d\theta^2} + \sin\theta\, \cos\theta \frac{d\, f(\theta)}{d\theta}.
\end{aligned}$$

Using this, equation (10–8) becomes

$$\sin^2\theta \frac{d^2\, f(\theta)}{d\theta^2} + \sin\theta\, \cos\theta \frac{d\, f(\theta)}{d\theta} + l(l+1)\, \sin^2\theta\, f(\theta) - m^2\, f(\theta) = 0. \tag{10 – 11}$$

We are going to change variables using $x = \cos\theta$, and will comment on this substitution later. We then need the derivatives with respect to x vice θ, so

$$\frac{d\, f(\theta)}{d\theta} = \frac{d\, f(x)}{dx}\frac{dx}{d\theta} = \frac{d\, f(x)}{dx}\big(- \sin\theta\big) = - \sin\theta \frac{d\, f(x)}{dx},$$

and

$$\begin{aligned}\frac{d^2 f(\theta)}{d\theta^2} &= \frac{d}{d\theta}\left(-\sin\theta\,\frac{d\,f(x)}{dx}\right) = -\cos\theta\,\frac{d\,f(x)}{dx} - \sin\theta\,\frac{d}{d\theta}\,\frac{d\,f(x)}{dx}\\ &= -\cos\theta\,\frac{d\,f(x)}{dx} - \sin\theta\,\frac{d}{dx}\,\frac{dx}{d\theta}\,\frac{d\,f(x)}{dx} = -\cos\theta\,\frac{d\,f(x)}{dx} - \sin\theta\,\frac{d}{dx}\Big(-\sin\theta\Big)\frac{d\,f(x)}{dx}\\ &= -\cos\theta\,\frac{d\,f(x)}{dx} + \sin^2\theta\,\frac{d^2 f(x)}{dx^2}.\end{aligned}$$

Substituting just the derivatives in the equation (10–11),

$$\sin^2\theta\left(\sin^2\theta\frac{d^2 f(x)}{dx^2} - \cos\theta\,\frac{d\,f(x)}{dx}\right) + \sin\theta\cos\theta\left(-\sin\theta\frac{d\,f(x)}{dx}\right) + l(l+1)\sin^2\theta f(x) - m^2 f(x) = 0,$$

which gives us an equation in both θ and x, which is not formally appropriate. This is, however, an informal text, and it becomes difficult to keep track of the terms if all the substitutions and reductions are done at once. Dividing by $\sin^2\theta$, we get

$$\sin^2\theta\,\frac{d^2 f(x)}{dx^2} - \cos\theta\,\frac{d\,f(x)}{dx} - \cos\theta\,\frac{d\,f(x)}{dx} + l(l+1)\,f(x) - \frac{m^2}{\sin^2\theta}f(x) = 0.$$

The change of variables is complete upon summing the two first derivatives, using $\cos\theta = x$, and $\sin^2\theta = 1 - \cos^2\theta = 1 - x^2$, which is

$$\boxed{\left(1 - x^2\right)\frac{d^2 f(x)}{dx^2} - 2x\,\frac{d\,f(x)}{dx} + l(l+1)\,f(x) - \frac{m^2}{1 - x^2}f(x) = 0.}$$

This is the **associated Legendre equation**, which reduces to **Legendre equation** when $m = 0$. The function has a single argument so there is no confusion if the derivatives are indicated with primes, and the associated Legendre equation is often written

$$\left(1 - x^2\right) f''(x) - 2x\,f'(x) + l(l+1)\,f(x) - \frac{m^2}{1 - x^2}f(x) = 0,$$

and becomes the Legendre equation,

$$\left(1 - x^2\right) f''(x) - 2x\,f'(x) + l(l+1)\,f(x) = 0,$$

when $m = 0$. The solutions to the associated Legendre equation are the associated Legendre polynomials discussed briefly in the last section of chapter 11. To review that in the current context, associated Legendre polynomials can be generated from Legendre polynomials using

$$P_{l,m}(x) = (-1)^m\sqrt{(1 - x^2)^m}\,\frac{d^m}{dx^m}P_l(x),$$

where the $P_l(x)$ are Legendre polynomials. Legendre polynomials can be generated using

$$P_l(x) = \frac{(-1)^l}{2^l l!}\,\frac{d^l}{dx^l}(1 - x^2)^l.$$

The use of these generating functions was illustrated in example 11–26 as intermediate results in calculating spherical harmonics.

The first few Legendre polynomials are listed in table 10–1. Our interest in those is to generate associated Legendre functions. The first few associated Legendre polynomials are listed in table 10–2.

symmetry around z-axis (m = 0)

$P_0(x) = 1$	$P_3(x) = \frac{1}{2}\left(5x^3 - 3x\right)$
$P_1(x) = x$	$P_4(x) = \frac{1}{8}\left(35x^4 - 30x^2 + 3\right)$
$P_2(x) = \frac{1}{2}\left(3x^2 - 1\right)$	$P_5(x) = \frac{1}{8}\left(63x^5 - 70x^3 + 15x\right)$

Table $10-1$. The First Six Legendre Polynomials.

Legendre Polynomials

no symmetry around z-axis

$P_{0,0}(x) = 1$	$P_{2,0}(x) = \frac{1}{2}\left(3x^2 - 1\right)$
$P_{1,1}(x) = -\sqrt{1-x^2}$	$P_{3,3}(x) = -15\left(\sqrt{1-x^2}\right)^3$
$P_{1,0}(x) = x$	$P_{3,2}(x) = 15x\left(1-x^2\right)$
$P_{2,2}(x) = 3\left(1-x^2\right)$	$P_{3,1}(x) = -\frac{3}{2}\left(5x^2-1\right)\sqrt{1-x^2}$
$P_{2,1}(x) = -3x\sqrt{1-x^2}$	$P_{3,0}(x) = \frac{1}{2}\left(5x^3 - 3x\right)$

Table $10-2$. The First Few Associated Legendre Polynomials.

Spherical Harmonics

Two comment concerning the tables are appropriate. First, notice $P_l = P_{l,0}$. That makes sense. If the Legendre equation is the same as the associated Legendre equation with $m = 0$, the solutions to the two equations must be the same when $m = 0$. Also, many authors will use a positive sign for all associated Legendre polynomials. This is a different choice of phase. We addressed that following table 11–1 in comments on spherical harmonics. We choose to include a factor of $(-1)^m$ with the associated Legendre polynomials, and the sign of all spherical harmonics will be positive as a result.

Finally, remember the change of variables $x = \cos\theta$. That was done to put the differential equation in a more elementary form. In fact, a dominant use of associated Legendre polynomials is in applications where the argument is $\cos\theta$. One example is the generating function for spherical harmonic functions,

$$Y_{l,m}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{l,m}(\cos\theta)\, e^{im\phi} \qquad m \geq 0, \tag{10-10}$$

and

$$Y_{l,-m}(\theta,\phi) = Y^*_{l,m}(\theta,\phi), \qquad m < 0,$$

where the $P_{l,m}(\cos\theta)$ are associated Legendre polynomials. If we need a spherical harmonic with $m < 0$, we will calculate the spherical harmonic with $m = \left|m\right|$, and then calculate the adjoint.

To summarize the last three sections, we separated the angular equation into an azimuthal and a polar portion. The solutions to the azimuthal angle equation are exponentials including the magnetic moment quantum number in the argument. The solutions to the polar angle equation are the associated Legendre polynomials, which are different for each choice of orbital angular momentum and magnetic moment quantum number. Both quantum numbers are introduced into

the respective differential equations as separation constants. Since we assumed a product of the two functions to get solutions to the azimuthal and polar parts, the solutions to the original angular equation (10–7) are the products of the two solutions $P_{l,m}(\cos\theta)\, e^{im\phi}$. These factors are included in equation (10–10). All other factors in equation (10–12) are simply normalization constants. The products $P_{l,m}(\cos\theta)\, e^{im\phi}$ are the spherical harmonic functions, the alternating sign and radical just make the orthogonal set orthonormal.

Associated Laguerre Polynomials and Functions

The azimuthal equation was easy, the polar angle equation a little more substantial, but you will likely percieve the solution to the radial equation as plain, old heavy! There is no easy way to do this. Our approach will be to relate the radial equation to the associated Laguerre equation, for which the associated Laguerre functions are solutions. A popular option to solve the radial equation is a power series solution, for which we will refer you to Griffiths[3], or Cohen–Tannoudji[4].

Laguerre polynomials are solutions to the Laguerre equation

$$x\, L_j^{''}(x) + \big(1 - x\big)\, L_j^{'}(x) + j\ L_j(x) = 0.$$

The first few Laguerre polynomials are listed in table 10–3.

$$\begin{aligned}
L_0(x) &= 1 \\
L_1(x) &= -x + 1 \\
L_2(x) &= x^2 - 4x + 2 \\
L_3(x) &= -x^3 + 9x^2 - 18x + 6 \\
L_4(x) &= x^4 - 16x^3 + 72x^2 - 96x + 24 \\
L_5(x) &= -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120 \\
L_6(x) &= x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720
\end{aligned}$$

Table $10-3$. The First Seven Laguerre Polynomials.

Laguerre polynomials of any order can be calculated using the generating function

$$L_j(x) = e^x\, \frac{d^j}{dx^j}\, e^{-x}\, x^j.$$

The Laguerre polynomials do not form an orthogonal set. The related set of **Laguerre functions**,

$$\phi_j(x) = e^{-x/2} L_j(x) \qquad (10-13)$$

is orthonormal on the interval $0 \le x < \infty$. The Laguerre functions are not solutions to the Laguerre equation, but are solutions to an equation which is related.

Just as the Legendre equation becomes the associated Legendre equation by adding an appropriate term containing a second index, the associated Laguerre equation is

$$x\, L_j^{k''}(x) + \big(1 - x + k\big)\, L_j^{k'}(x) + j\ L_j^k(x) = 0, \qquad (10-14)$$

[3] Griffiths, *Introduction to Quantum Mechanics* (Prentice Hall, Englewood Cliffs, New Jersey, 1995), pp. 134–141.

[4] Cohen–Tannoudji, Diu, and Laloe, *Quantum Mechanics* (John Wiley & Sons, New York, 1977), pp. 794–797.

which reduces to the Laguerre equation when $k = 0$. The first few associated Laguerre polynomials are

$L_0^0(x) = L_0(x)$	$L_0^2(x) = 2$
$L_1^0(x) = L_1(x)$	$L_3^0(x) = L_3(x)$
$L_1^1(x) = -2x + 4$	$L_3^1(x) = -4x^3 + 48x^2 - 144x + 96$
$L_0^1(x) = 1$	$L_2^3(x) = 60x^2 - 600x + 1200$
$L_2^0(x) = L_2(x)$	$L_3^3(x) = -120x^3 + 2160x^2 - 10800x + 14400$
$L_2^1(x) = 3x^2 - 18x + 18$	$L_3^2(x) = -20x^3 + 300x^2 - 1200x + 1200$
$L_2^2(x) = 12x^2 - 96x + 144$	$L_1^3(x) = -24x + 96$
$L_1^2(x) = -6x + 18$	$L_0^3(x) = 6$

Table $10-4$. Some Associated Laguerre Polynomials.

Notice $L_j^0 = L_j$. Also notice the indices are all non–negative, and either index may assume any integral value. We will be interested only in those associated Laguerre polynomials where $k < j$ for hydrogen atom wave functions.

Associated Laguerre polynomials can be calculated from Laguerre polynomials using the generating function

$$L_j^k(x) = \big(-1\big)^k \frac{d^k}{dx^k} L_{j+k}(x).$$

Example 10–5: Calculate $L_3^1(x)$ starting with the generating function.

We first need to calculate $L_4(x)$, because

$$L_j^k(x) = \big(-1\big)^k \frac{d^k}{dx^k} L_{j+k}(x) \quad \Rightarrow \quad L_3^1(x) = \big(-1\big)^1 \frac{d^1}{dx^1} L_{3+1}(x) = -\frac{d}{dx} L_4(x).$$

Similarly, if you want to calculate L_3^2, you need to start with L_5, and to calculate L_4^3, you need to start with L_7. So using the generating function,

$$\begin{aligned}
L_4(x) &= e^x \frac{d^4}{dx^4} e^{-x} x^4 \\
&= e^x \frac{d^3}{dx^3}\Big(-e^{-x}x^4 + e^{-x}\,4x^3\Big) \\
&= e^x \frac{d^2}{dx^2}\Big(e^{-x}x^4 - e^{-x}\,4x^3 - e^{-x}\,4x^3 + e^{-x}\,12x^2\Big) = e^x \frac{d^2}{dx^2}\Big(e^{-x}x^4 - e^{-x}\,8x^3 + e^{-x}\,12x^2\Big) \\
&= e^x \frac{d}{dx}\Big(-e^{-x}x^4 + e^{-x}\,4x^3 + e^{-x}\,8x^3 - e^{-x}\,24x^2 - e^{-x}\,12x^2 + e^{-x}\,24x\Big) \\
&\qquad\qquad = e^x \frac{d}{dx}\Big(-e^{-x}x^4 + e^{-x}\,12x^3 - e^{-x}\,36x^2 + e^{-x}\,24x\Big) \\
&= e^x\Big(e^{-x}x^4 - e^{-x}\,4x^3 - e^{-x}\,12x^3 + e^{-x}\,36x^2 + e^{-x}\,36x^2 - e^{-x}\,72x - e^{-x}\,24x + e^{-x}\,24\Big) \\
&= e^x e^{-x}\Big(x^4 - 16x^3 + 72x^2 - 96x + 24\Big) \\
&= x^4 - 16x^3 + 72x^2 - 96x + 24,
\end{aligned}$$

per table 10–4. Then to get $L_3^1(x)$,

$$\begin{aligned} L_3^1 &= -\frac{d}{dx}\, L_4(x) \\ &= -\frac{d}{dx}\big(x^4 - 16x^3 + 72x^2 - 96x + 24\big) \\ &= -\big(4x^3 - 48x^2 + 144x - 96\big) \\ &= -4x^3 + 48x^2 - 144x + 96, \end{aligned}$$

per table 10–3.

Associated Laguerre polynomials are not orthogonal but **associated Laguerre functions** of the type

$$\Phi_j^k(x) = e^{-x/2} x^{k/2} L_j^k(x)$$

are orthogonal on the interval $0 \le x < \infty$, so can be made an orthonormal set. Again, the $\Phi_j^k(x)$ are not solutions to the associated Laguerre equation but are solutions to a related equation.

We are specifically interested in a slightly different associated Laguerre function than the usual first choice indicated above, *i.e.*, we are interested in

$$y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x). \qquad (10-15)$$

These are also not solutions to the associated Laguerre equation, but they are solutions to

$$y_j^{k''}(x) + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2}\right) y_j^k(x) = 0. \qquad (10-16)$$

The reason for our interest in (10–16) and its solutions (10–15), is that equation (10–16) is a form of the radial equation, so the radial functions $R(r)$ we seek are $R_{n,l}(r) = A\, y_n^l(r)$, where A is simply a normalization constant.

Example 10–6: Show equation (10–15) satisfies equation (10–16).

Unlike some of the toy problems given as examples, this example is a critical connection...unless you take our word for it, and then you should skip this. We are going to use the result of this example as a direct link to the solution of the radial equation. We are going to simplify the notation to minimize clutter, and will explain as we go.

To attain the second derivative, we need the first derivative, and use the notation

$$y = e^{-x/2} x^{(k+1)/2} v,$$

for equation (10–15) where $v = L_j^k(x)$, because the indices do not change and only serve to add clutter, and we can remember the independent variable is x. The first derivative is

$$\begin{aligned} y' &= -\frac{1}{2} e^{-x/2} x^{(k+1)/2} v + e^{-x/2}\left(\frac{k+1}{2}\right) x^{(k-1)/2} v + e^{-x/2} x^{(k+1)/2} v' \\ &= \left[-\frac{1}{2} v + \left(\frac{k+1}{2x}\right) v + v'\right] e^{-x/2} x^{(k+1)/2} \\ \Rightarrow \quad \left(e^{x/2} x^{-(k+1)/2}\right) y' &= -\frac{1}{2} v + \frac{k+1}{2x}\, v + v'. \end{aligned}$$

Notice we adjusted the second term on the right to do the factoring. Using the same adjustment technique, will factor these terms out of the second derivative as we go. These are also factors common to equation (10–15). Since the right side of equation (10–16) is zero, after we substitute the second derivative and the function into (10–16), we will simplify the equation by dividing the equation by common factors, therefore, none of the common factors will enter into the final solution. The exponentials and powers still need to be considered in differentiation, but their inverses will appear on the left and only the terms which have impact will appear on the right. Proceeding....

$$\left(e^{x/2}x^{-(k+1)/2}\right)\, y'' = \frac{1}{4}v - \frac{1}{2}\frac{k+1}{2x}\, v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}\, v + \frac{k+1}{2x}\,\frac{k-1}{2x}\, v + \frac{k+1}{2x}\, v' - \frac{1}{2}\, v' + \frac{k+1}{2x}\, v' + v''.$$

Substituting the second derivative and the function into equation (10–16),

$$y'' + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2}\right) y = 0,$$

and dividing by the common factor of $e^{-x/2}x^{(k+1)/2}$, the remaining terms are

$$\left(\frac{1}{4}v - \frac{1}{2}\frac{k+1}{2x}\, v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}\, v + \frac{k+1}{2x}\,\frac{k-1}{2x}\, v + \frac{k+1}{2x}\, v' - \frac{1}{2}\, v' + \frac{k+1}{2x}\, v' + v''\right)$$

$$+\left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2}\right) v = 0$$

$$\Rightarrow \quad v'' + \cancel{\frac{1}{4}}v - \frac{1}{2}\frac{k+1}{2x}\, v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}\, v + \cancel{\frac{k^2-1}{4x^2}}\, v + \frac{k+1}{2x}\, v' - \frac{1}{2}\, v' + \frac{k+1}{2x}\, v'$$

$$-\cancel{\frac{1}{4}}v + \frac{2j+k+1}{2x}\, v - \cancel{\frac{k^2-1}{4x^2}}\, v = 0$$

$$\Rightarrow \quad v'' - \cancel{\frac{k+1}{4x}}\, v - \frac{1}{2}v' - \cancel{\frac{k+1}{4x}}\, v + \frac{k+1}{x}\, v' - \frac{1}{2}\, v' + \frac{j}{x}\, v + \cancel{\frac{k+1}{2x}}\, v = 0$$

$$\begin{aligned}
&\Rightarrow \quad v'' - v' + \frac{k+1}{x}\, v' + \frac{j}{x} = 0 \\
&\Rightarrow \quad x\, v'' - x\, v' + (k+1)\, v' + j\, v = 0 \\
&\Rightarrow \quad x\, v'' + (1 - x + k)\, v' + j\, v = 0 \qquad (10-17)
\end{aligned}$$

which is the associated Laguerre equation. Since $v = L_j^k(x)$, and the $L_j^k(x)$ are solutions to the associated Laguerre equation, equation (10–17) is equivalent to

$$x\, L_j^{k''}(x) + \left(1 - x + k\right) L_j^{k'}(x) + j\; L_j^k(x) = 0,$$

which is the associated Laguerre, which we know to be a true statement, so

$$\begin{aligned}
y &= e^{-x/2}x^{(k+1)/2}v \\
&= e^{-x/2}x^{(k+1)/2}L_j^k(x)
\end{aligned}$$

are solutions to equation (10–16).

The Reduced Mass

Equation (10–2) describes a single particle in a central potential. The hydrogen atom is a two body problem, and the potential is not central but is dependent upon the distance between the nucleus and the electron. Were we able to anchor the nucleus to a stationary location we could designate an origin, equation (10–2) would be an accurate description. This is not possible, but we can reach a similar end by picturing the center of mass being anchored to a fixed location. If we use the **reduced mass** in place of the electron mass,

$$\boxed{\mu = \frac{m_p\, m_e}{m_p + m_e},}$$

the radial coordinate r accurately describes the distance between the nucleus and the electron. The effect in equation (10–2) is cosmetic; where there was an m representing m_e, it is replaced by μ. Because the proton is about 1836 times more massive than the electron, the reduced mass is nearly identically the electron mass. Many authors simply retain the electron mass. Since the center of mass is not actually anchored, a second set of coordinates is required to track the center of mass using this scheme. This consideration and other details of reducing a two particle problem to a one particle problem are adequately covered in numerous texts, including Chohen–Tannoudji[5], Levine[6], and many classical mechanics texts.

Solution of the Radial Equation

The radial equation (10–6) using the reduced mass and the Coulomb potential, $V(r) = -e^2/r$, is

$$\begin{aligned}
&\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2\mu r^2}{\hbar^2}\Big[-\frac{e^2}{r} - E\Big] - l(l+1) = 0 \\
\Rightarrow\quad &\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2\mu r^2}{\hbar^2}\Big[-\frac{e^2}{r} - E\Big]R(r) - l(l+1)\,R(r) = 0 \\
\Rightarrow\quad &\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) + \Big[\frac{2\mu r^2}{\hbar^2}\frac{e^2}{r} + \frac{2\mu r^2}{\hbar^2}E - l(l+1)\Big]R(r) = 0. \qquad (10-18)
\end{aligned}$$

The plan is to get (10–18) into a form comparable to equation (10–16), and we already know the solutions are equation (10–15). We will be able to glean additional information by comparing the equations term by term. The energy levels of the hydrogen atom and the meaning of the indices of the associated Laguerre polynomials, which will be quantum numbers for the hydrogen atom, will come from the comparison of individual terms.

We will make three substitutions to get the last equation into the form of equation (10–16). The first is

$$y(r) = r\,R(r) \quad\Rightarrow\quad R(r) = \frac{y(r)}{r}. \qquad (10-19)$$

[5] Cohen–Tannoudji, Diu, and Laloe, *Quantum Mechanics* (John Wiley & Sons, New York, 1977), pp. 784–788.

[6] Levine, *Quantum Chemistry* (Allyn and Bacon, Inc., Boston, Massachusetts, 1983), pp. 101–106.

Making this substitution in the first term and evaluating the derivatives

$$\begin{aligned}
\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) &= \frac{d}{dr}\left(r^2\frac{d}{dr}\right)\left(r^{-1}\right)y(r) \\
&= \frac{d}{dr}\,r^2\left[\left(-r^{-2}\right)y(r)+\left(r^{-1}\right)\frac{d\,y(r)}{dr}\right] \\
&= \frac{d}{dr}\left[-y(r)+r\,\frac{d\,y(r)}{dr}\right] \\
&= -\frac{d\,y(r)}{dr}+\frac{d\,y(r)}{dr}+r\,\frac{d^2\,y(r)}{dr^2} \\
&= r\,\frac{d^2\,y(r)}{dr^2}.
\end{aligned}$$

The substitution serves to eliminate the first derivative. We would have both a first and second derivative if we had evaluated the first term using $R(r)$. With this and the substitution of equation (10–19), equation (10–18) becomes

$$r\,\frac{d^2\,y(r)}{dr^2}+\left[\frac{2\mu r e^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E-l(l+1)\right]\frac{y(r)}{r}=0$$

$$\Rightarrow\quad \frac{d^2\,y(r)}{dr^2}+\left[\frac{2\mu e^2}{r\,\hbar^2}+\frac{2\mu E}{\hbar^2}-\frac{l(l+1)}{r^2}\right]y(r)=0.$$

The second substitution is essentially to simplify the notation, and is

$$\left(\frac{\epsilon}{2}\right)^2=-\frac{2\mu E}{\hbar^2} \tag{10 – 20}$$

where the negative sign on the right indicates we are looking for bound states, states such that $E<0$, so including the negative sign here lets us have an ϵ which is real. The last equation becomes

$$\frac{d^2\,y(r)}{dr^2}+\left[\frac{2\mu e^2}{r\,\hbar^2}-\frac{\epsilon^2}{4}-\frac{l(l+1)}{r^2}\right]y(r)=0.$$

The third substitution is a change of variables, and notice it relates radial distance and energy through equation (10-20),

$$x=r\epsilon\quad\Rightarrow\quad r=\frac{x}{\epsilon}, \tag{10 – 21}$$

$$\Rightarrow\quad dr=\frac{dx}{\epsilon}\quad\Rightarrow\quad \frac{d^2\,y(r)}{dr^2}=\frac{d}{dr}\frac{d\,y(r)}{dr}=\epsilon\frac{d}{dx}\,\epsilon\frac{d\,y(x)}{dx}=\epsilon^2\frac{d^2\,y(x)}{dx^2},$$

so our radial equation becomes

$$\epsilon^2\frac{d^2\,y(x)}{dx^2}+\left[\frac{2\mu e^2\epsilon}{x\,\hbar^2}-\frac{\epsilon^2}{4}-\epsilon^2\frac{l(l+1)}{x^2}\right]y(x)=0$$

$$\Rightarrow\quad \frac{d^2\,y(x)}{dx^2}+\left[-\frac{1}{4}+\frac{2\mu e^2}{\hbar^2\epsilon x}-\frac{l(l+1)}{x^2}\right]y(x)=0, \tag{10 – 22}$$

and equation (10–22) is equation (10–16) where

$$l(l+1)=\frac{k^2-1}{4}, \tag{10 – 23}$$

and

$$\frac{2\mu e^2}{\hbar^2\epsilon} = \frac{2j+k+1}{2}, \qquad (10-24)$$

Per example 10–6, the solutions are equation (10–15),

$$y_j^k(x) = e^{-x/2}x^{(k+1)/2}L_j^k(x).$$

Eigenenergies from the Solution of the Radial Equation

Equation (10–23) tells us $k = 2l+1$.

Example 10–7: Show $k = 2l+1$.

Equation (10–23) is

$$\begin{aligned}
\frac{k^2-1}{4} &= l(l+1) \\
\Rightarrow \quad k^2 &= 4l(l+1)+1 \\
&= 4l^2+4l+1 \\
&= \left(2l+1\right)^2 \\
\Rightarrow \quad & \boxed{k = 2l+1.}
\end{aligned}$$

We are going to take what appears to be a slight diversion to evaluate a particular set of factors in equation (10–24), $\hbar^2/\mu e^2$, which recurs repeatedly. Going back to the old quantum theory, this is called the Bohr radius, that is

$$a_0 = \frac{\hbar^2}{\mu e^2} = 0.529\,\text{Å}. \qquad (10-25)$$

We want to express lengths in terms of the Bohr radius because it is a natural length for the hydrogen atom.

Example 10–8: Show $a_0 = 0.529\,\text{Å}$, using both the electron mass and the reduced mass.

This example is intended to illustrate three simple things. First, $a_0 = 0.529\,\text{Å}$, second is to work out the CGS units for e^2, and then to show the electron mass is a very good approximation to the reduced mass in hydrogen. The electrostatic force in MKS and CGS systems is defined

$$\frac{1}{4\pi\epsilon_0}\frac{e^2_{\text{MKS}}}{r^2} = F = \frac{e^2_{\text{CGS}}}{r^2}$$

$$\begin{aligned}
\Rightarrow \quad e^2_{\text{CGS}} &= \frac{e^2_{\text{MKS}}}{4\pi\epsilon_0} = \left(1.602\times10^{-19}\,C\right)^2\left(8.988\times10^9\,N\cdot m^2/C^2\right) \\
&= 2.307\times10^{-28}\,N\cdot m^2 = 2.307\times10^{-19}\,dyne\cdot cm^2 \\
&= 2.307\times10^{-19}\,erg\cdot cm = 14.42\,eV\cdot\text{Å}.
\end{aligned}$$

So

$$a_0 = \frac{\hbar^2}{m_e e^2} = \frac{1}{4\pi^2}\frac{(hc)^2}{m_e c^2 e^2} = \frac{1}{4\pi^2}\frac{(1.240\times10^4\,eV\cdot\text{Å})^2}{(0.5110\times10^6\,eV)(14.42\,eV\cdot\text{Å})} = 0.5286\,\text{Å}.$$

The reduced mass is

$$\mu = \frac{m_p\, m_e}{m_p + m_e} = \frac{1.673 \times 10^{-24}}{1.673 \times 10^{-24} + 9.110 \times 10^{-28}} m_e = 0.9995\, m_e,$$

$$\Rightarrow \quad \frac{\hbar^2}{\mu e^2} = \frac{\hbar^2}{0.9995 m_e e^2} = \frac{0.5286\,\text{Å}}{0.9995} = 0.5288\,\text{Å}.$$

There is 0.03% difference between the electron mass and reduced mass values. Many authors simply use the electron mass and it yields a good approximation. The CGS value of e^2 can be mysterious for those who have worked primarily in MKS units. By the way, the square root $e = 3.797\,(eV \cdot \text{Å})^{1/2}$ can be a convenient way to express the charge on the electron in CGS units.

Equation (10–24) gives us the eigenenergies of the hydrogen atom, but requires some development. Since $k = 2l + 1$,

$$\frac{2j + k + 1}{2} = \frac{2j + (2l + 1) + 1}{2} = j + l + 1.$$

From the discussion on associated Laguerre polynomials, the indices j and k are non–negative. The sum $j + l + 1$ can, therefore, assume any integer values of 1 or greater. We are going to rename it n, or

$$n = j + l + 1. \tag{10 – 26}$$

The new integer index n is known as the **principal quantum number**. Using the principal quantum number, it follows that the eigenenergies of the hydrogen atom are

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{13.6\, eV}{n^2}, \tag{10 – 27}$$

where the quantity $13.6\, eV$ is called the Rydberg, usually denoted R or Ry. The ground state energy is $E_0 = -13.6\, eV$ when $n = 1$. It is often convenient to express excited state energies in terms of the ground state energy.

Example 10–9: Show equation (10–27) follows from equation (10–24).

$$\frac{2\mu e^2}{\hbar^2 \epsilon} = \frac{2j + k + 1}{2}$$

$$\Rightarrow \quad j + l + 1 = n = \frac{2\mu e^2}{\hbar^2 \epsilon}$$

$$\Rightarrow \quad \epsilon = \frac{2\mu e^2}{\hbar^2 n}$$

$$\Rightarrow \quad \epsilon^2 = \frac{4\mu^2 e^4}{\hbar^4 n^2}.$$

Substituting equation (10–20) to eliminate ϵ and insert energy,

$$-4\frac{2\mu E}{\hbar^2} = \frac{4\mu^2 e^4}{\hbar^4 n^2}$$

$$\Rightarrow \quad E = -\frac{\mu^2 e^4 \hbar^2}{2\mu\hbar^4 n^2} = -\left(\frac{\mu e^2}{\hbar^2}\right)^2 \frac{\hbar^2}{2\mu n^2}$$

$$\Rightarrow \quad E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2}.$$

Inserting numerical values,

$$\begin{aligned} E_n &= -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{1}{4\pi^2}\frac{(hc)^2}{2(\mu c^2)a_0^2 n^2} \\ &= -\frac{1}{4\pi^2}\frac{(1.24\times 10^4\, eV\cdot \text{Å})^2}{2(0.511\times 10^6\, eV)(0.529\,\text{Å})^2 n^2} = -\frac{13.6\, eV}{n^2}, \end{aligned}$$

so eigenenergies do follow from the solution of the radial equation.

SPHERICAL COORDINATES

$$\nabla^2\Phi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Phi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Phi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2} = 0$$

$$\Phi(r,\theta,\varphi) = R(r)P(\theta)Q(\varphi)$$

$$\frac{1}{r^2R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{r^2P\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) + \frac{1}{r^2Q\sin^2\theta}\frac{d^2Q}{d\varphi^2} = 0$$

multiply with $r^2\sin^2\theta$:

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{P}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) = -\frac{1}{Q}\frac{d^2Q}{d\varphi^2}$$

The left-hand side depends only on r and θ, while the right-hand side depends only on ϕ. Thus the two sides must be a constant, m^2.

$$\frac{d^2Q}{d\varphi^2} + m^2Q = 0 \quad ; \quad Q(\varphi) \sim e^{\pm im\varphi} \quad ; \quad m = 0,1,2\ldots$$

Note: If the physical problem limits ϕ to a restricted range m can be a non-integer.

Now we return to the left-hand side and rearrange the terms:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = -\frac{1}{P\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) + \frac{m^2}{\sin^2\theta}$$

The new left-hand side depends only on r and the right-hand side on only θ. Thus, they must be a constant, $l(l+1)$.

We get

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

and

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)+\left[l(l+1)-\frac{m^2}{\sin^2\theta}\right]P=0$$

To solve the first, we make the ansatz: $R=Ar^{\alpha}$ and obtain the two solutions r^{l} and $r^{-(l+1)}$. The general solution is then

$$\boxed{R_l(r)=A_l r^l+B_l\frac{1}{r^{l+1}}}$$

For the polar-angle function $P(\theta)$ it is customary to make the substitution

$$\cos\theta\to x\quad;\quad -\frac{1}{\sin\theta}\frac{d}{d\theta}\to\frac{d}{dx}$$

This gives

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{dP}{dx}\right]+\left[l(l+1)-\frac{m^2}{1-x^2}\right]P=0$$

We will first limit ourselves to axial or azimuthal symmetry.

Axial symmetry

$$\boxed{\left(1-x^2\right)\frac{d^2P}{dx^2}-2x\frac{dP}{dx}+l(l+1)P=0}$$ *Legendre's equation*

Note that if x=±1 are excluded from the problem l may be non-integer.

The solution is the *Legendre polynomial* of order l: $P_l(\cos\theta)$

Thus we have the general solution to Laplace's equation in spherical coordinates for the special case of axial symmetry as:

$$\boxed{\Phi(r,\theta)=\sum_{l=0}^{\infty}\left[A_l r^l+B_l\frac{1}{r^{l+1}}\right]P_l(\cos\theta)}$$

Legendre Polynomial

The Legendre polynomials can be obtained from

$$\boxed{P_l(x)=\frac{1}{2^l\,l!}\frac{d^l}{dx^l}\left(x^2-1\right)^l}$$ *Rodrigues' formula*

or from the *generating function*

$$F(x,\mu)=\frac{1}{\left(1-2x\mu+\mu^2\right)^{1/2}}=\sum_{l=0}^{\infty}\mu^l P_l(x)$$

or from *recursion relations* such as:

$$(l+1)P_{l+1}(x)=(2l+1)xP_l(x)-lP_{l-1}(x)$$

or

$$\left(1-x^2\right)\frac{dP_l}{dx}=-lxP_l(x)+lP_{l-1}(x)$$

The polynomials form a *complete, orthogonal set* of functions in the domain $-1 \le x \le 1$ $(0 \le \theta \le \pi)$

$$f(x) = \sum_{l=0}^{\infty} A_l P_l(x)$$

$$A_l = \frac{2l+1}{2} \int_{-1}^{1} f(x) P_l(x) dx$$

General case, no axial symmetry.

In this case we have in general a non-zero m value and the differential equation for P is more elaborate. The Legendre polynomials are replaced by the *associated Legendre polynomials*, $P_l^m(\cos\theta)$. For a given l-value there are $2l+1$ possible m-values: $m = 0, \pm 1, \pm 2,, \pm 3, \ldots$

There is a more general *Rodrigues' formula* for these functions:

$$P_l^m(x) = \frac{(-1)^m}{2^l\, l!}\left(1-x^2\right)^{m/2}\frac{d^{l+m}}{dx^{l+m}}\left(x^2-1\right)^l \quad ; \quad (-l \le m \le +l)$$

For any given m the functions $P_l^m(\cos\theta)$ and $P_{l'}^m(\cos\theta)$ are orthogonal and the associated Legendre polynomials for a fixed m form a complete set of functions in the variable x.

The product of $P_l^m(x)$ and $e^{im\varphi}$ forms a complete set for the expansion of an arbitrary function on the surface of a sphere. These functions are called *spherical harmonics*.

$$\boxed{Y_l^m(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}P_l^m(\cos\theta)e^{im\varphi}}$$

They are orthonormal

$$\int_{4\pi} Y_l^m(\theta,\varphi)Y_{l'}^{m'}{}^*(\theta,\varphi)d\Omega$$
$$= \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta Y_l^m(\theta,\varphi)Y_{l'}^{m'}{}^*(\theta,\varphi) = \delta_{ll'}\delta_{mm'}$$

complete set of orthonormal functions on the sphere

$$f(\theta,\varphi)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}C_l^m Y_l^m(\theta,\varphi)$$

and

$$C_l^m=\int_{4\pi} f(\theta,\varphi)Y_l^m{}^*(\theta,\varphi)d\Omega$$

| f > = sum sum C(l,m) | l, m >

dot with < theta, phi |

C(l,m) = <l, m | f >

The general solution to Laplace's equation in terms of spherical harmonics is

$$\Phi(r,\theta,\varphi)=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\left[A_l^m r^l+B_l^m\frac{1}{r^{l+1}}\right]Y_l^m(\theta,\varphi)$$

separation in other coordinate systems

In the *Annals of Mathematics* for April, 1934, I derive the conditions for the Stäckel result in such a form that I have been able to determine all the real type forms so that the space with the fundamental form

$$ds^2 = H_1^2 dx_1^2 + H_2^2 dx_2^2 + H_3^2 dx_3^2 \tag{4}$$

is euclidean, and I have shown that they satisfy the condition (3). These forms and the relation between the coordinates x_i and cartesian coordinates are as follows:

$$H_i = 1, \text{ cartesian;} \tag{I}$$

$$H_1 = H_2 = 1,\ H_3 = x_1, \text{ cylindrical polar coordinates;} \tag{II}$$

$$H_1 = 1,\ H_2 = x_1,\ H_3 = x_1 \sin x_2, \text{ polar coordinates;} \tag{III}$$

$$H_1^2 = 1,\ H_2^2 = H_3^2 = a^2 (\cosh 2x_2 - \cos 2x_3),$$
$$\text{elliptic cylinder coordinates;}$$
$$x = x_1;\ y = a \cosh x_2 \cos x_3,\ z = a \sinh x_1 \sin x_3; \tag{IV}$$

$$H_1^2 = 1,\ H_2^2 = H_3^2 = x_1^2 x_3^2,$$
$$\text{parabolic cylinder coordinates;}$$
$$x = x_1,\ y = x_2^2 - x_3^2,\ z = x_2 x_3; \tag{V}$$

$$H_1^2 = 1,\ H_2^2 = H_3^2 = x_1^2[k^2 cn^2(x_2, k) + k'^2 cn^2(x_3, k')],$$
$$k^2 + k'^2 = 1,\ x = x_1 dn(x_2, k) sn(x_3, k'),$$
$$y = x_1 sn(x_2, k) dn(x_3, k'),\ z = x_1 cn(x_2, k) cn(x_3, k'); \tag{VI}$$

$$H_1^2 = H_3^2 = x_1^2 + x_3^2,\ H_2^2 = x_1^2 x_3^2,$$
$$\text{parabolic coordinates,}$$
$$x = x_1 x_3 \cos x_2,\ y = x_1 x_3 \sin x_2,\ z = \tfrac{1}{2}(x_1^2 - x_3^2); \tag{VII}$$

$$H_1^2 = H_3^2 = a^2 (\sinh^2 x_1 + \sin^2 x_3),$$
$$H_2^2 = a^2 \sinh^2 x_1 \sin^2 x_3,$$
$$\text{prolate spheroidal coordinates,}$$
$$x = \sinh x_1 \sin x_3 \cos x_2,\ y = a \sinh x_1 \sin x_3 \sin x_2,$$
$$z = a \cosh x_1 \cos x_2; \tag{VIII}$$

$$H_1^2 = H_3^2 = a^2 (\cosh^2 x_1 - \sin^2 x_3),$$
$$H_2^2 = a^2 \cosh^2 x_1 \sin^2 x_3,$$
$$\text{oblate spheroidal coordinates,}$$
$$x = a \cosh x_1 \sin x_3 \cos x_2,\ y = a \cosh x_1 \sin x_3 \sin x_2,$$
$$2 = a \sinh x_1 \cos x_3; \tag{IX}$$

$$H_i^2 = (x_i - x_j)(x_i - x_k)/f(x_i),$$
$$f(x_i) = 4(\alpha - x_i)(\beta - x_i)(\gamma - x_i),\ (i, j, k \neq),$$
$$\text{confocal ellipsoidal coordinates;} \tag{X}$$

$$H_i^2 = (x_i - x_j)(x_i - x_k)/f(x_i),$$
$$f(x_i) = 4(a - x_i)(b - x_i),\ (i, j, k \neq),$$
$$\text{confocal parabolic coordinates,}$$
$$x = (x_1 + x_2 + x_3 - a - b)/2,$$
$$y^2 = (a - x_1)(a - x_2)(a - x_3)/(b - a)$$
$$z^2 = (b - x_1)(b - x_2)(b - x_3)/(a - b),\ x_1 > b > x_2 > a > x_3. \tag{XI}$$

In each case the coordinate surfaces consist of confocal quadrics including the cases when one or more families consist of planes. All such systems yield solutions and only these. Consequently the only orthogonal systems of coordinates in which the three-dimensional Schrödinger equation can be solved by separation of the variables are the above types.

LUTHER PFAHLER EISENHART

Fine Hall,
Princeton, New Jersey,
February 24, 1934.

On the Inversion of Doublets in Alkali-Like Spectra

In a recent paper[1] we considered the effect of the polarization of the core on the doublet separations in alkali-like spectra. We are indebted to Professor Van Vleck for pointing out to us that such an effect may be formulated as a third order perturbation in a systematic application of perturbation theory. If H is the Hamiltonian the third order correction to the energy of the state i is

$$\delta E_i = -\Sigma_{jj'} \frac{H_{ij} H_{jj'} H_{j'i}}{(H_{ii} - H_{jj})(H_{ii} - H_{j'j'})}. \tag{1}$$

A careful examination shows that, for our case, and for both the coupling schemes which we considered for the excited core states, the terms in (1) reduce to those calculated by us. But whereas (1) is clearly independent of the representation chosen for the excited core states, our results, based on two different assumptions for this representation, differed by a factor of two. We have found that in the table of doublet separations on p. 646 the values given for terms arising from triplet parents are incorrect: the coefficients of ξ_1 for these three doublets should all be reduced by a factor of three. When this is done, and the corresponding correction is made in Table III, the result, on the assumption of LS coupling, reduces to $\delta E = -(F_0 G/E_0^2)\xi_1 - 2(fG + gF_0)/3E_0$, in complete agreement with that given on p. 648 for the other coupling scheme considered.

MELBA PHILLIPS

Department of Physics,
University of California,
February 22, 1934.

[1] Melba Phillips, Phys. Rev. **44**, 644 (1933).

Artificial Radioactivity Produced by Deuton Bombardment

Following the discovery by I. Curie and F. Joliot[1] that radionitrogen is formed when boron is bombarded with alpha-particles, it seemed probable, as they in fact suggest, that this new radioactive element might be formed by bombarding carbon with high speed protons and deutons. Indeed, in the light of our recent experiments in which

[1] Curie and Joliot, Nature **133**, 201 (1934).

4.5. The Nature of the Spherical Eigenfunctions

It is instructive to examine the energy eigenfunctions that arise from the separation of variables in spherical coordinates because, as will be discussed, the hydrogen atom problem can also be solved using separation of variables in parabolic coordinates. (In fact, it can also be solved in spheroidal coordinates,[7] but this solution is of limited use.) This separability of the Schrödinger equation in more than one coordinate system is indicative of the additional symmetry that leads to the accidental degeneracy, that is, symmetry beyond the spherical symmetry of any central potential. This additional symmetry manifests itself by permitting separability in parabolic coordinates. It should be clear that the spatial symmetry of a central potential is the symmetry that permits separation of variables in spherical coordinates for any central potential.

The complete energy eigenfunctions in spherical coordinates, sometimes referred to as spherical eigenfunctions or "orbital" eigenfunctions, are

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\,Y_{\ell m}(\theta,\phi) \tag{4.30}$$

The probability density is, as usual, $|\psi|^2$. The angular part of ψ is the spherical harmonics (see Section 2.6),

$$Y_{\ell m}(\theta,\phi) = P_{\ell m}(\theta)\cdot\exp(im\phi) \tag{4.31}$$

where the $P_{\ell m}(\theta)$ are the associated Legendre functions. Upon taking the absolute square, the ϕ-dependence disappears. The probability density is therefore cylindrically symmetric about the z-axis. Now $|\psi|^2$ represents the probability per unit volume so that $|\psi|^2$ multiplied by the volume element is the probability of finding the electron somewhere in the volume element. Thus, the probability density (multiplied by the electronic charge) is the charge density of a given eigenstate. A convenient way to depict the charge density is by using a density plot in which the regions of the highest density of dots are the locations at which the electron would be more likely to be found. FIGURE 4.3 is such a plot for the $n = 4$, $\ell = 2$, $m = 0$ state.

The cylindrical symmetry discussed above is apparent. In contrast with the charge densities that will be obtained using parabolic coordinates it should be noted that the charge distribution for orbital eigenstates is symmetric about the xy-plane.

4.6. Separation of the Schrödinger Equation in Parabolic Coordinates

We follow the same procedure to effect the separation of variables in parabolic coordinates that was used to separate the Schrödinger equation in spherical coordinates. The treatment is standard and can be found in the books by Bethe and Salpeter,[3] Landau and Lifshitz,[8] and by Schiff.[4] The relationship between

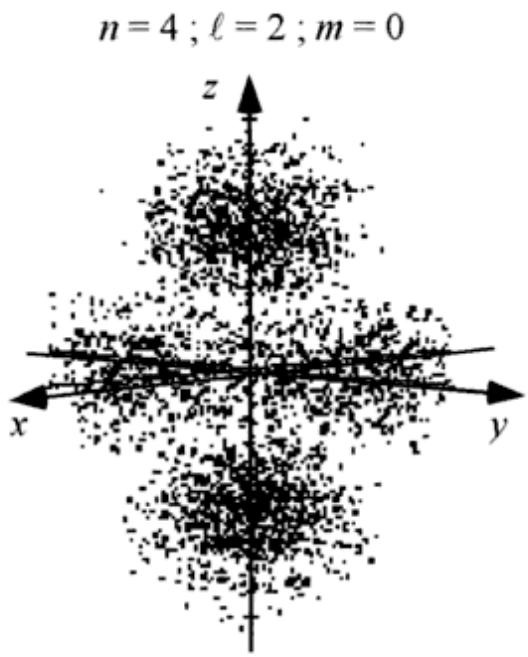

FIGURE 4.3. Density plot of the spherical wave function indicated. The maximimum on each axis is 50 a.u.

parabolic coordinates and spherical coordinates is given by the following transformation equations.

$$\begin{aligned} \xi &= r - z = r\,(1 - \cos\theta) \\ \eta &= r + z = r\,(1 + \cos\theta) \\ \phi &= \phi \end{aligned} \tag{4.32}$$

The angular coordinate ϕ is seen to be the same azimuthal angle as in spherical coordinates. This coordinate defines position with respect to the x-axis of a point in the xy-plane. The surfaces of constants ξ and η are paraboloids of revolution about the z-axis as shown in FIGURE 4.4.

The Coulomb potential in parabolic coordinates in SI units is

$$V\,(\xi, \eta) = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{2}{\xi + \eta}\right) \tag{4.33}$$

Using the Laplacian operator in parabolic coordinates,[1] the Schrödinger equation is

$$\begin{aligned} &\left(-\frac{\hbar^2}{2m_e}\right)\left(\frac{4}{\xi+\eta}\right)\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial\psi\,(\xi,\eta,\phi)}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial\psi\,(\xi,\eta,\phi)}{\partial\eta}\right)\right] \\ &\quad + \frac{1}{\xi\eta}\frac{\partial^2\psi\,(\xi,\eta,\phi)}{\partial\phi^2} - \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{2}{\xi+\eta}\right)\psi\,(\xi,\eta,\phi) = E\psi\,(\xi,\eta,\phi) \end{aligned} \tag{4.34}$$

To separate this equation we let

$$\psi(\xi, \eta, \phi) = f(\xi)g(\eta)\Phi(\phi) \tag{4.35}$$

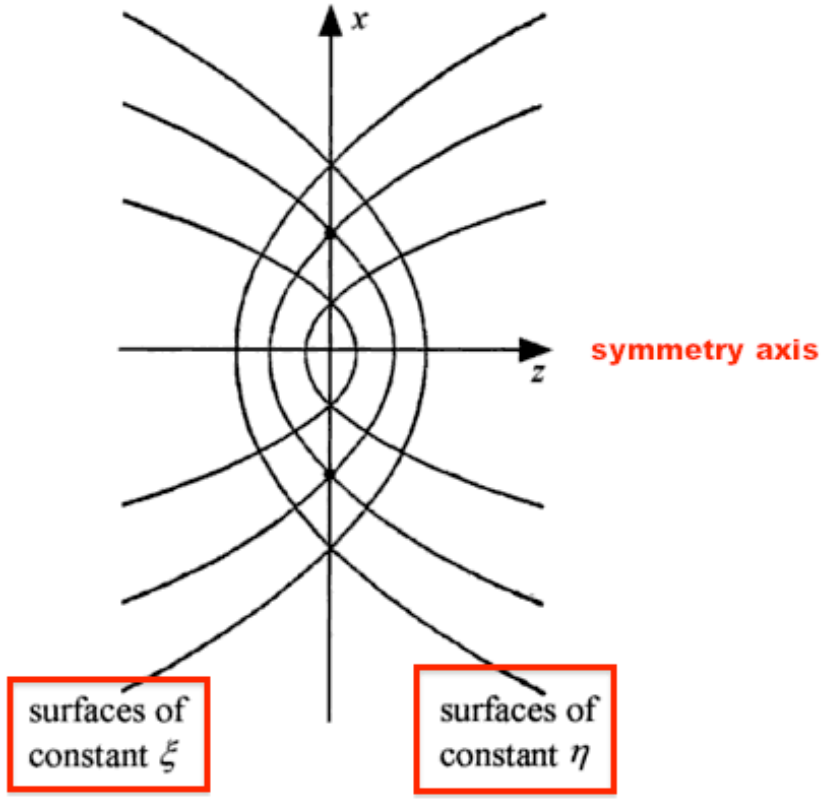

FIGURE 4.4. Parabolic coordinates and their relation to other coordinate systems.

After a considerable amount of algebra we obtain

$$F(\xi, \eta) = -\frac{1}{\Phi(\phi)} \frac{d^2\Phi(\phi)}{d\phi^2} = -m^2 \tag{4.36}$$

where the function $F(\xi, \eta)$ does not contain ϕ and m^2 is a separation constant that has been judiciously chosen to be the same azimuthal (magnetic) quantum number that represents the z-component of the angular momentum. This equation obviously leads to the same solution that was obtained in spherical coordinates for the Φ part of the wave function

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi) \quad m = 0, \pm 1, \pm 2, \ldots \tag{4.37}$$

The remaining equation, $F(\xi, \eta) = -m^2$, can also be separated. We obtain

$$\frac{1}{f(\xi)} \frac{d}{d\xi}\left(\xi \frac{df(\xi)}{d\xi}\right) - \frac{m^2}{4\xi} - \frac{m_e|E|}{2\hbar^2}\xi + \frac{m_e}{\hbar^2} \cdot \left(\frac{e^2}{4\pi\varepsilon_0}\right) = -\left[\frac{1}{g(\eta)} \frac{d}{d\eta}\left(\eta \frac{dg(\eta)}{d\eta}\right) - \frac{m^2}{4\eta} - \frac{m_e|E|}{2\hbar^2}\eta\right] \tag{4.38}$$

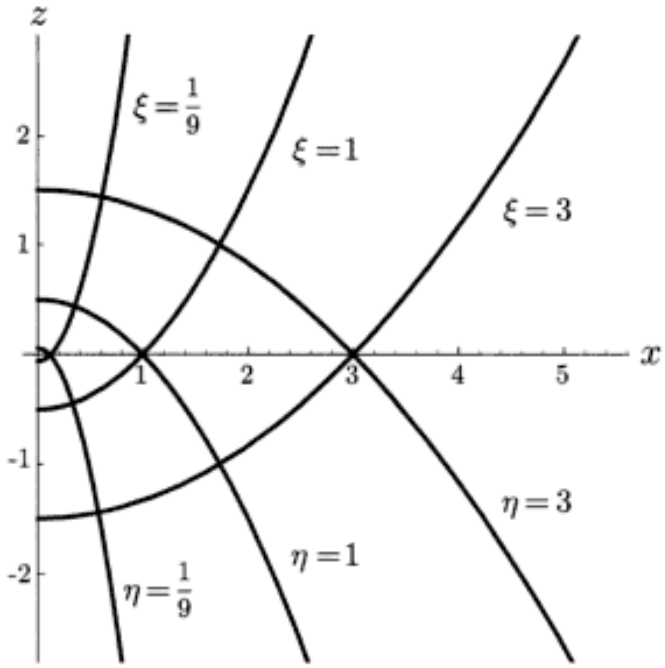

FIGURE 2.9. The coordinate curves $\xi = \text{const.}$, $\eta = \text{const.}$ of the parabolic coordinate system in the half-plane where $\varphi = 0$ are parabolas.

2.6. Special Topic: Parabolic Coordinates

The Schrödinger equation for the hydrogen atom also separates in parabolic coordinates. This observation is important because it remains true in the presence of an additional constant electric field in the z-direction (*Stark effect*).

The parabolic coordinates of a point (x, y, z) in $\mathbb{R}^3$ are given by (ξ, η, φ), where

$$\begin{aligned} \xi &= r + z = r(1 + \cos\vartheta), & x &= \sqrt{\xi\eta}\,\cos\varphi, \\ \eta &= r - z = r(1 - \cos\vartheta), & y &= \sqrt{\xi\eta}\,\sin\varphi, \\ \varphi &= \varphi, & z &= (\xi - \eta)/2. \end{aligned} \tag{2.115}$$

Here, (r, ϑ, φ) are the spherical coordinates of the point (x, y, z). The coordinates ξ and η are non-negative, and φ is the familiar azimuthal angle. The parabolic coordinate system is an orthogonal, right-handed system. Hence, the coordinate curves meet at right angles. Figure 2.9 shows a few coordinate curves in the half-plane where $\varphi = 0$ (the xz-plane). The coordinate surfaces with constant ξ or η are obtained by rotating the corresponding parabolas of Figure 2.9 about the z-axis. In Figure 2.10, we see the coordinate surfaces for $\xi = 1$ and $\eta = 1$.

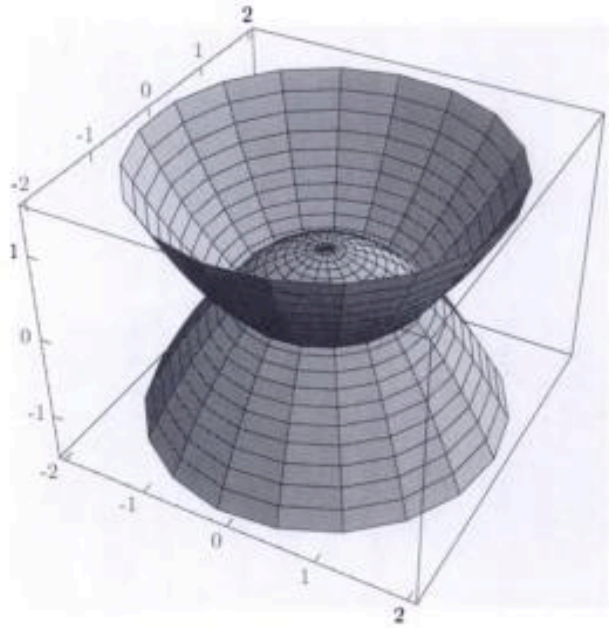

FIGURE 2.10. The surfaces with $\xi = 1$ (upper paraboloid) and $\eta = 1$ (lower paraboloid) are obtained by rotating the corresponding parabolas of Figure 2.9 about the z-axis.

The unit vectors along the coordinate lines are given by

$$\mathbf{e}_\xi = \sqrt{\frac{\eta}{\xi+\eta}} \begin{pmatrix} \cos\varphi \\ \sin\varphi \\ \sqrt{\xi/\eta} \end{pmatrix}, \quad \mathbf{e}_\eta = \sqrt{\frac{\xi}{\xi+\eta}} \begin{pmatrix} \cos\varphi \\ \sin\varphi \\ -\sqrt{\eta/\xi} \end{pmatrix}, \quad \mathbf{e}_\varphi = \begin{pmatrix} -\sin\varphi \\ \cos\varphi \\ 0 \end{pmatrix}.$$

The gradient in parabolic coordinates reads

$$\nabla = 2\mathbf{e}_\xi \sqrt{\frac{\xi}{\xi+\eta}} \frac{\partial}{\partial\xi} + 2\mathbf{e}_\eta \sqrt{\frac{\eta}{\xi+\eta}} \frac{\partial}{\partial\eta} + \mathbf{e}_\varphi \frac{1}{\sqrt{\xi\eta}} \frac{\partial}{\partial\varphi}. \tag{2.116}$$

From this it is not difficult to obtain the expression for the Coulomb Hamiltonian (2.39) in parabolic coordinates

$$H = -\frac{2}{\xi+\eta}\left(\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right) - \frac{1}{2\xi\eta}\frac{\partial^2}{\partial\varphi^2} - \frac{2}{\xi+\eta}. \tag{2.117}$$

The stationary Schrödinger equation $(H - E)\psi = 0$ can be separated by writing

$$\psi(\xi,\eta,\varphi) = N\, f(\xi)\, g(\eta)\, \mathrm{e}^{\mathrm{i}m\varphi}, \tag{2.118}$$

whence

$$w = F\left(-n, 2l+\frac{3}{2}, \xi\right),$$

where n must be a non-negative integer. We consequently find as the energy levels the infinite set of equidistant values

$$E_n = \hbar\sqrt{(B/2m)}[4n+2+\sqrt{\{(2l+1)^2+8mA/\hbar^2\}}],\ n = 0, 1, 2, \ldots.$$

§37. Motion in a Coulomb field (parabolic coordinates)

The separation of the variables in Schrödinger's equation written in spherical polar coordinates is always possible for motion in any centrally symmetric field. In the case of a Coulomb field, the separation of the variables is also possible in what are called *parabolic coordinates*. The solution of the problem of motion in a Coulomb field in terms of parabolic coordinates is useful in investigating a number of problems where a certain direction in space is distinctive; for example, for an atom in an external electric field (see §77).

The parabolic coordinates ξ, η, ϕ are defined by the formulae

$$\left.\begin{aligned} x &= \sqrt{(\xi\eta)}\cos\phi, \quad y = \sqrt{(\xi\eta)}\sin\phi, \quad z = \tfrac{1}{2}(\xi-\eta), \\ r &= \sqrt{(x^2+y^2+z^2)} = \tfrac{1}{2}(\xi+\eta), \end{aligned}\right\} \tag{37.1}$$

or conversely

$$\xi = r+z, \quad \eta = r-z, \quad \phi = \tan^{-1}(y/x); \tag{37.2}$$

ξ and η take values from 0 to ∞, and ϕ from 0 to 2π. The surfaces $\xi =$ constant and $\eta =$ constant are paraboloids of revolution about the z-axis, with focus at the origin. This system of coordinates is orthogonal. The element of length is given by the expression

$$(\mathrm{d}l)^2 = \frac{\xi+\eta}{4\xi}(\mathrm{d}\xi)^2+\frac{\xi+\eta}{4\eta}(\mathrm{d}\eta)^2+\xi\eta(\mathrm{d}\phi)^2, \tag{37.3}$$

and the element of volume is

$$\mathrm{d}V = \tfrac{1}{2}(\xi+\eta)\mathrm{d}\xi\mathrm{d}\eta\mathrm{d}\phi. \tag{37.4}$$

From (37.3) we have the Laplacian operator

$$\Delta = \frac{4}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right)+\frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right]+\frac{1}{\xi\eta}\frac{\partial^2}{\partial\phi^2}. \tag{37.5}$$

Schrödinger's equation for a particle in an attractive Coulomb field with $U = -1/r = -2/(\xi+\eta)$ is

3d isotropic harmonic oscillator: Cartesian nx ny nz, and Spherical n, L2, and Lz

2d isotropic harmonic oscillator: Cartesian nx and ny, and Polar n and Lz

Physics 6320/7320

M 1 November 2010

Isotropic Harmonic Oscillator

Ref. Zettili §6.2.4, §6.3.4

1 Separation in two different coordinate systems

For some problems the Schrödinger equation can be separated in more than one coordinate system. In these cases it turns out that there is some "dynamical" symmetry in the problem. That is, an additional symmetry beyond the "geometrical" symmetries such as translations, rotations, and inversions, which lead to conserved quantities such as momentum, angular momentum and parity. Corresponding to the additional symmetry is an additional conservation law and an additional degeneracy.

A well-known example is the non-relativistic hydrogen atom, which can be separated in both spherical and parabolic coordinates, and in which there is an "accidental" degeneracy in the orbital quantum number. That is, the energy depends on n but not on l. The same situation occurs in the isotropic harmonic oscillator, which can be separated in both rectangular and spherical coordinates. In ***both*** the Coulomb and the oscillator problems the classical orbit is a closed ellipse, and there are many orbits with the same energy but different angular momentum.

2 Separation in rectangular coordinates

This is very simple. We have $H = K + V$ with

$$\begin{aligned} K = \frac{p^2}{2m} &= \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \\ V = \frac{1}{2}m\omega^2 r^2 &= \frac{1}{2}m\omega^2(x^2 + y^2 + z^2) \end{aligned}$$

so that $H = H_x + H_y + H_z$ with each term being the hamiltonian for a one-dimensional harmonic oscillator. Thus there are three uncoupled equations. The results for the eigenfunctions and eigenvalues are

$$\psi_{n_x,n_y,n_z}(x,y,z) = X_{n_x}(x)\, Y_{n_y}(y)\, Z_{n_z}(z) \tag{1}$$

$$E_n = (n_x + \tfrac{1}{2})\hbar\omega \;+\; (n_y + \tfrac{1}{2})\hbar\omega \;+\; (n_z + \tfrac{1}{2})\hbar\omega \tag{2}$$

$$= \left(n + \frac{3}{2}\right)\hbar\omega\,; \quad n = n_x + n_y + n_z = 0, 1, 2, \cdots \tag{3}$$

Degeneracy

The energy E_n depends on only one integer, but the wavefunction depends on three. For example there are six states with energy E_2. If we label each state by the set of three numbers (n_x, n_y, n_z), then the six states with n=2 are

$$(2,0,0),\ (0,2,0),\ (0,0,2), \quad \text{and} \quad (1,1,0),\ (1,0,1),\ (0,1,1)\,.$$

Zettili (p 439) shows that the degree of degeneracy for the energy level given by the quantum number n is

$$g_n = \frac{1}{2}(n+1)(n+2)\,. \tag{4}$$

OVER

2d anisotropic harmonic oscillator

cartesian and parabolic

order differential operators. Hamiltonians that can be expressed as bilinear combinations of these operators will leave invariant any finite-dimensional representation space of the symmetry algebra and as a result, the corresponding part of their spectra can be computed through a finite-matrix eigenvalue problem. In one dimension, more specifically, one uses the su(2) realization

$$T^0 = -j + z\frac{\partial}{\partial z}, \qquad T^+ = 2jz - z^2\frac{\partial}{\partial z}, \qquad T^- = \frac{\partial}{\partial z}, \qquad [T^0, T^\pm] = \pm T^\pm, \qquad [T^+, T^-] = 2T^0. \tag{1}$$

which for j as emi-integer, entails a $(2j+1)-$dimensional representation over the space spanned by the monomials $1, z, \ldots, z^{2j}$. One then takes for Hamiltonians

$$\tilde{H} = \sum_{a,b=0,\pm} C_{ab} T^a T^b + \sum_{a=0,\pm} C_a T^a . \tag{2}$$

Through a similarity transformation and possibly, a change of variable $x = x(z)$, these Hamiltonians can be cast in the form $-\frac{1}{2}\frac{d^2}{dx^2} + V(x)$ and a list of quasi-exactly solvable Schrödinger operators is thus obtained. We may remark that exactly solvable systems result if the parameter j does not appear in the Hamiltonian. This happens for instance in the case of the Morse potential $V(x) = A(e^{-2ax} - 2e^{-x})$ which plays an important rôle in molecular physics. The simplest example of a quasi-exactly solvable problem in one dimension is provided by the anharmonic oscillator with potential $V(x) = \frac{1}{2}\omega^2 x^6 - 2\beta\omega^2 x^4 + [2\beta^2\omega^2 - \omega(4j + \frac{3}{2})]x^2$. This system, as it turns out, is related to the two-dimensional anisotropic oscillator with Hamiltonian $H = -\frac{1}{2}(p_1^2 + p_2^2) + \frac{1}{2}\omega^2[x_1^2 + 4(x_2 - \beta)^2]$, $p_i = -i\frac{\partial}{\partial x_i}$ $i = 1, 2$. Indeed, owing to the higher symmetry of the Hamiltonian, the Schrödinger equation $H\psi(x_1, x_2) = E\psi(x_1, x_2)$ separates in parabolic coordinates as well in Cartesian coordinates[3]. We shall see that when parabolic coordinates are used, the separated equations coincide exactly with the one-dimensional equation associated to the anharmonic oscillator with potential $V(x)$.

We take great pleasure in dedicating this paper to Franco Iachello who has so brilliantly applied algebraic methods to domains as diverse as nuclear, high energy, atomic, and molecular physics. We hope that he will find interesting the occurrence of quadratic algebras in quantum mechanics. Let us also recall that Professor Iachello himself studied (among others) the dynamical symmetries of the Morse Hamiltonian[5]. He has shown that these can be traced back to the su(2) symmetry of the two-dimensional isotropic harmonic oscillator Schrödinger equation. In this case, one separates the variables in polar coordinates and after a change of variables, identifies the radial part as the Schrödinger equation for the particle in the one-dimensional Morse potential. It is in close analogy with this approach that the relation between the quasi-exactly anharmonic oscillator and the two-dimensional anisotropic oscillator with a 2 to 1 frequency ratio is established here.

The remainder of the paper is organized as follows. We first set our notation and identify the accidental degenaracies of a generalized 2-d anisotropic oscillator. We then present the quadratic dynamical algebra and show how the dynamics is resolved by constructing the representations of this algebra. We indicate in particular how the degeneracies are explained in this framework. Finally, we make the connection between the 2-d anisotropic oscillator and the quasi-exactly solvable anharmonic oscillator. Conclusions follow.

THE GENERALIZED 2-D ANISOTROPIC OSCILLATOR

We shall be considering a two-dimensional quantum system with Hamiltonian

$$H = H_1 + H_2 , \tag{3}$$

where

$$H_1 = \frac{1}{2}(p_1^2 + \omega^2 x_1^2) + \frac{1}{8}(\alpha^2 - 1)\frac{1}{x_1^2} , \tag{4a}$$

$$H_2 = \frac{1}{2}\left[(p_2^2 + 4\omega^2(x_2 - \beta)^2\right] , \tag{4b}$$

$p_i = -i\frac{\partial}{\partial x_i}$, $i = 1, 2$, and $\alpha, \beta, \omega \in R$. In the special case $\alpha = 1$, H governs the dynamics of an anisotropic oscillator with a 2 to 1 frequency ratio.

It will be convenient to introduce the annihilation and creation operators

$$a_1 = \frac{1}{\sqrt{2\omega}}(\omega x_1 + ip_1), \qquad a_1^\dagger = \frac{1}{\sqrt{2\omega}}(\omega x_1 - ip_1), \tag{5a}$$

$$a_2 = \sqrt{2\omega}\left[(x_2 - \beta) + \frac{i}{2\omega}p_2)\right] , \qquad a_2^\dagger = \sqrt{2\omega}\left[(x_2 - \beta) - \frac{i}{2\omega}p_2)\right] , \tag{5b}$$

that satisfy the commutation relations

$$[a_k, a_l^\dagger] = k\delta_{kl} \qquad [a_k, a_l] = [a_k^\dagger, a_l^\dagger] = 0 \quad k, l = 1, 2 . \tag{6}$$

In terms of these operators,

$$\frac{H_1}{\omega} = a_1^\dagger a_1 + \frac{1}{4}(\alpha^2 - 1)(a_1 + a_1^\dagger)^{-2} + \frac{1}{2} , \tag{7a}$$

$$\frac{H_2}{\omega} = a_2^\dagger a_2 + 1 . \tag{7b}$$

The spectrum of $H = H_1 + H_2$ is easily obtained by separating the Schrödinger equation in Cartesian coordinates. With $\psi(x_1, x_2) = \phi(x_1)\chi(x_2)$, the equation $H\psi = E\psi$ amounts to $H_1\phi(x_1) = E_1\phi(x_1)$ and $H_2\chi(x_2) = E_2\chi(x_2)$ with $E = E_1 + E_2$. We recognized in H_2, the Hamiltonian of a 1-d harmonic oscillator; its eigenfunctions are of the form $< x_2|n_2 > \propto < x_2|(a_2^\dagger)^{n_2}|0 >$ and have energy $E_2 = 2n_2 + 1$. The eigenvalues of H_1 can be determined by exploiting the conformal symmetry of this operator. Indeed, define the operators

$$\begin{aligned} B_1^+ &= (a_1^\dagger)^2 - \frac{1}{4}(\alpha^2 - 1)(a_1 + a_1^\dagger)^{-2} \\ &= a_1^\dagger(a_1 + a_1^\dagger) - \frac{H_1}{\omega} + \frac{1}{2} \end{aligned} \tag{8a}$$

$$B_1^- = (B_1^+)^\dagger . \tag{8b}$$

Clearly,

$$[H_1, B_1^\pm] = \pm 2\omega B_1^\pm . \tag{9}$$

It is also straightforward to check that

$$B_1^\pm B_1^\mp = \left[(\frac{H_1}{\omega} \mp 1) + \frac{|\alpha|}{2}][(H_1 \mp 1) - \frac{\alpha}{2}\right] , \tag{10}$$

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Superintegrability on the two-dimensional hyperboloid. II

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one separates in 4 coord systems
the other separates in 2

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This work is devoted to the investigation of the quantum mechanical systems on the two-dimensional hyperboloid which admits separation of variables in at least two coordinate systems. Here we consider two potentials introduced in a paper of C. P. Boyer, E. G. Kalnins, and P. Winternitz [J. Math. Phys. **24**, 2022 (1983)], which have not yet been studied. We give an example of an interbasis expansion and work out the structure of the quadratic algebra generated by the integrals of motion. © *1999 American Institute of Physics*. [S0022-2488(99)00505-8]

I. INTRODUCTION

Superintegrable systems on the two-dimensional hyperboloid were introduced and developed in Refs. 1–3. In distinction to the cases of two-dimensional Euclidean space and the two-sphere the classification of superintegrable systems on the hyperboloid is difficult. To date only the four potentials studied in Ref. 3 and two more listed in Ref. 1 are known. In the present paper two potentials are considered, which were constructed in Ref. 1 but have not previously been investigated. These potentials both have only a finite number of bound states. At this point we have treated all the potentials that arise by restriction from Hermitean hyperbolic space. We follow the approach of Ref. 3, which contains an introduction and motivation.

The two-dimensional hyperboloid is characterized via the Cartesian coordinates $\omega_0, \omega_1, \omega_2$ where $\omega_0^2-\omega_1^2-\omega_2^2=1$, $\omega_0>1$. The requirement $\omega_0>1$ means that we consider only the upper sheet of the double-sheet hyperboloid. Throughout this paper we will consider the Schrödinger equation on the hyperboloid in the form ($\hbar=m=1$)

$$H\Psi\equiv(-\tfrac{1}{2}\Delta_{\mathrm{LB}}+V)\Psi=E\Psi, \tag{1}$$

where V is a potential function and the Laplace–Beltrami operator Δ_{LB} is written as

$$\Delta_{\mathrm{LB}}=K_3^2+K_2^2-M_1^2. \tag{2}$$

Here K_3, K_2, M_1 generate the Lie algebra so(2,1) (Refs. 4 and 5):

$$K_3=\omega_0\partial_{\omega_1}+\omega_1\partial_{\omega_0},\quad K_2=\omega_0\partial_{\omega_2}+\omega_2\partial_{\omega_0},\quad M_1=\omega_1\partial_{\omega_2}-\omega_2\partial_{\omega_1}, \tag{3}$$

and

$$[K_3,K_2]=M_1,\quad [K_2,M_1]=-K_3,\quad [K_3,M_1]=K_2. \tag{4}$$

The Schrödinger equation (1) for $V=0$ separates in nine coordinate systems.[2] Introduction of a potential breaks the symmetry and, in general, reduces the number of coordinate systems permitting separability, usually to zero. We consider the following two potentials (see Table I), constructed in Ref. 1, for which (1) is superintegrable.

in 3d

THREE STANDARD COORDINATE SYSTEMS

CARTESIAN x, y, z

SPHERICAL r, θ, φ

CYLINDRICAL ρ, θ, z

∇^2 LOOKS DIFFERENT!

SOLUTIONS ARE DIFFERENT

OF COURSE, YOU CAN USE ANY COORDINATE SYSTEM

"IF THE BOUNDARY CONDITIONS ARE NOT SEPARABLE, MOST LIKELY WE ARE HOSED."

$\longrightarrow$ NEXT PAGE

http://quantumrelativity.calsci.com/Physics/EandM7.html

If the boundary conditions are not separable, most likely we're hosed

Generally speaking, if the boundary conditions are separable, there's a good chance the solution is separable. If the boundary conditions are not separable, most likely we're hosed.

This is Bessel's equation. The solutions are Bessel functions, Neumann functions, and Hankel functions, and we've officially entered Graduate Student Hell.

http://www.urbandictionary.com/define.php?term=hosed

IN 3d $\nabla^2 V = 0$

SEPARATES IN $11 + 2 = 13$ COORD SYSTEMS

$V(x, y, z) = X(x)\, Y(y)\, Z(z)$ CARTESIAN

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

$V(r, \theta, z) = R(r)\, \Theta(\theta)\, Z(z)$ CYLINDRICAL

ONE EQN FOR EACH COORD

$$\frac{d^2 X}{dx^2} = c_1 X$$

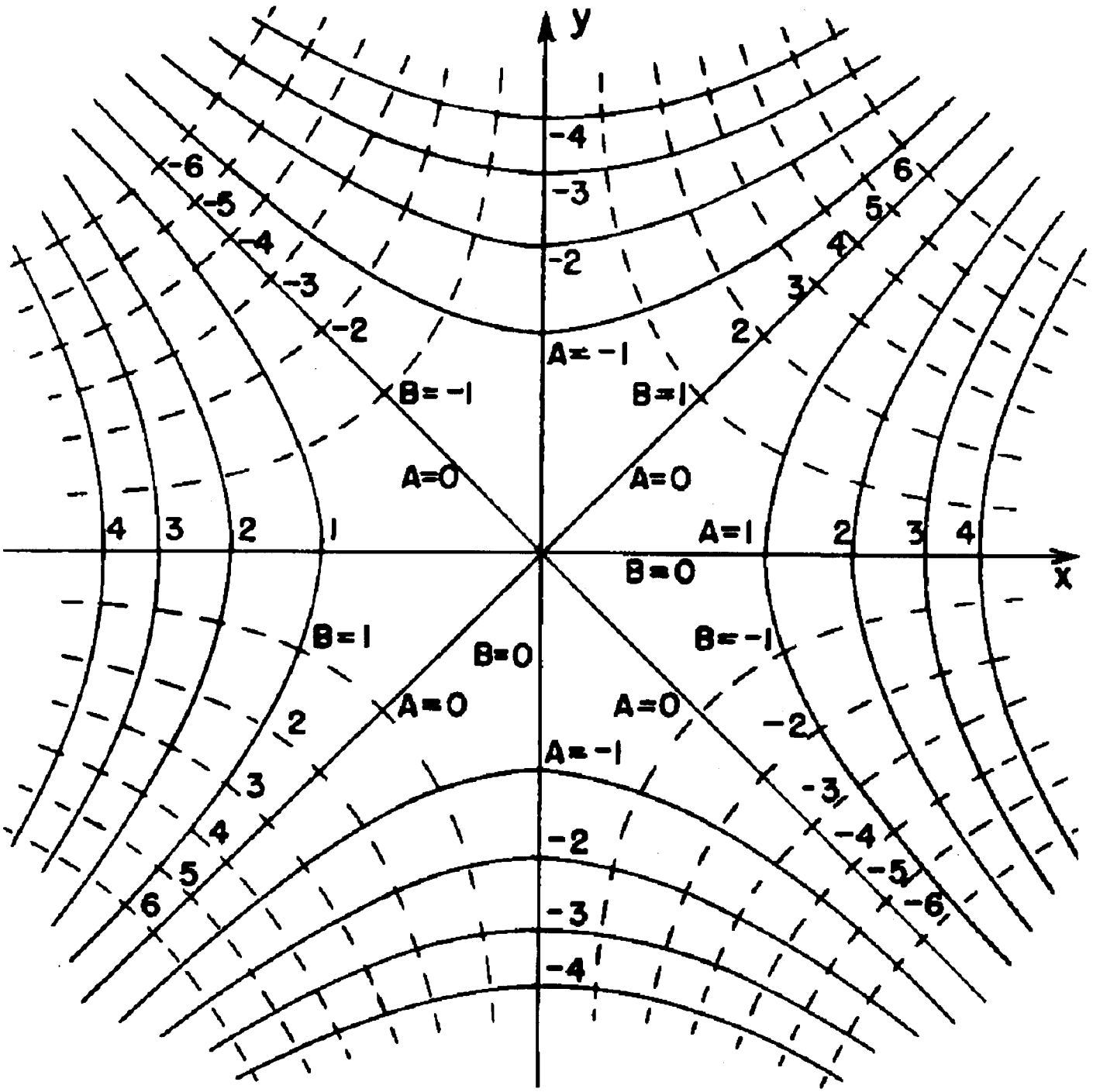
$$\frac{d^2 Y}{dy^2} = c_2 Y$$

$$\frac{d^2 Z}{dz^2} = c_3 Z$$

$$c_1 + c_2 + c_3 = 0$$

Coordinate System	Variables	Solution Functions
Cartesian	$X(x)\,Y(y)\,Z(z)$	exponential functions, circular functions, hyperbolic functions
circular cylindrical	$R(r)\,\Theta(\theta)\,Z(z)$	Bessel functions, exponential functions, circular functions
conical		ellipsoidal harmonics, power
ellipsoidal	$\Lambda(\lambda)\,M(\mu)\,N(\nu)$	ellipsoidal harmonics
elliptic cylindrical	$U(u)\,V(v)\,Z(z)$	Mathieu function, circular functions
oblate spheroidal	$\Lambda(\lambda)\,M(\mu)\,N(\nu)$	Legendre polynomial, circular functions
parabolic		Bessel functions, circular functions
parabolic cylindrical		parabolic cylinder functions, Bessel functions, circular functions
paraboloidal	$U(u)\,V(v)\,\Theta(\theta)$	circular functions
prolate spheroidal	$\Lambda(\lambda)\,M(\mu)\,N(\nu)$	Legendre polynomial, circular functions
spherical	$R(r)\,\Theta(\theta)\,\Phi(\phi)$	Legendre polynomial, power, circular functions

Laplace's equation can be solved by separation of variables in all 11 coordinate systems that the Helmholtz differential equation can. The form these solutions take is summarized in the table above. In addition to these 11 coordinate systems, separation can be achieved in two additional coordinate systems by introducing a multiplicative factor. In these coordinate systems, the separated form is


y
x
A=-1
A=0
A=1
B=-1
B=1
B=0
-4
-3
-2
2
3
4
5
6
-6
-5
-4
-3
-2
4
3
2
1
2
3
4
-2
-3
-4
-5
-6
6
5
4
3
2
-2
-3
-4

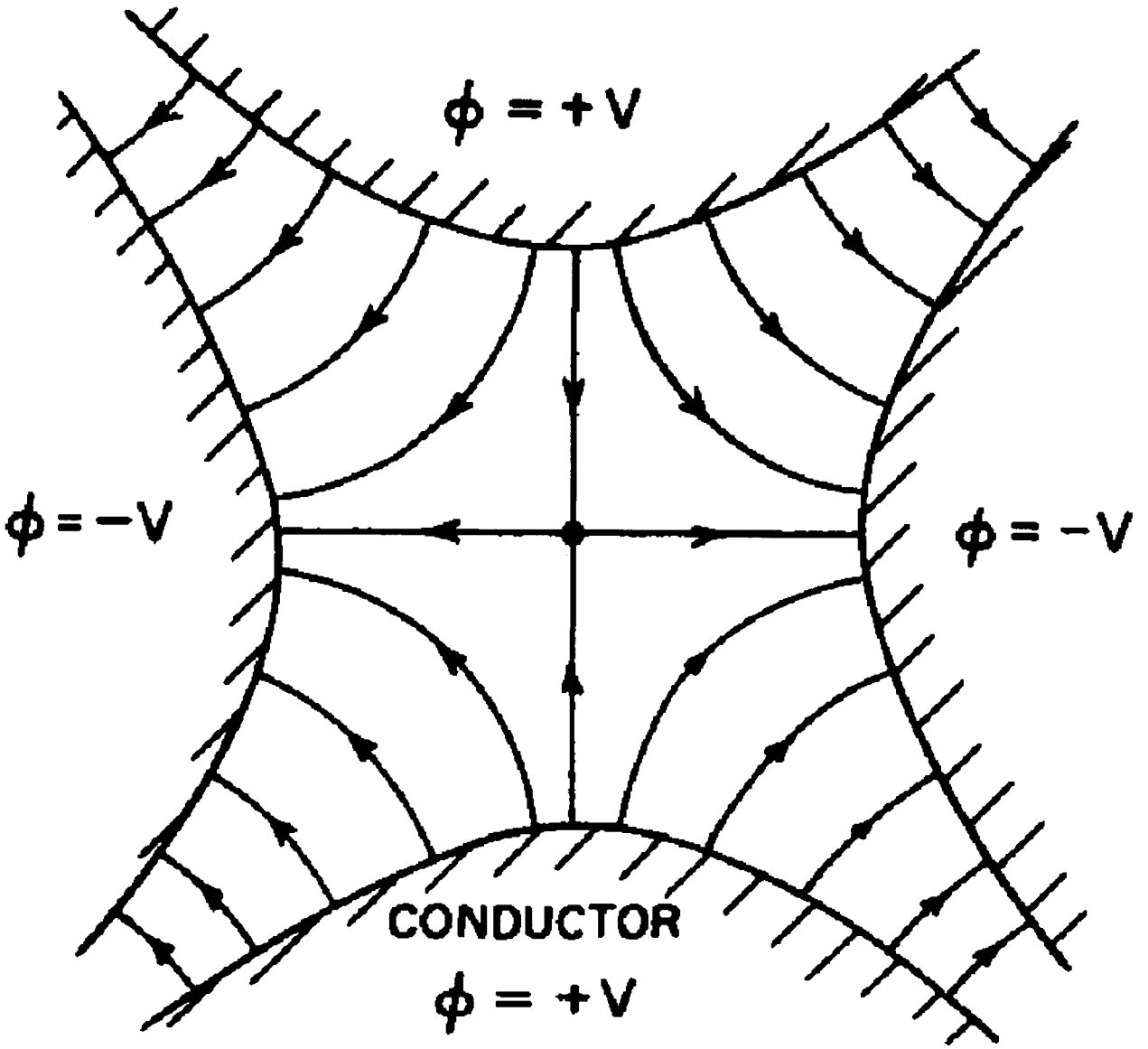


Fig. 7–3. The field in a quadrupole lens.

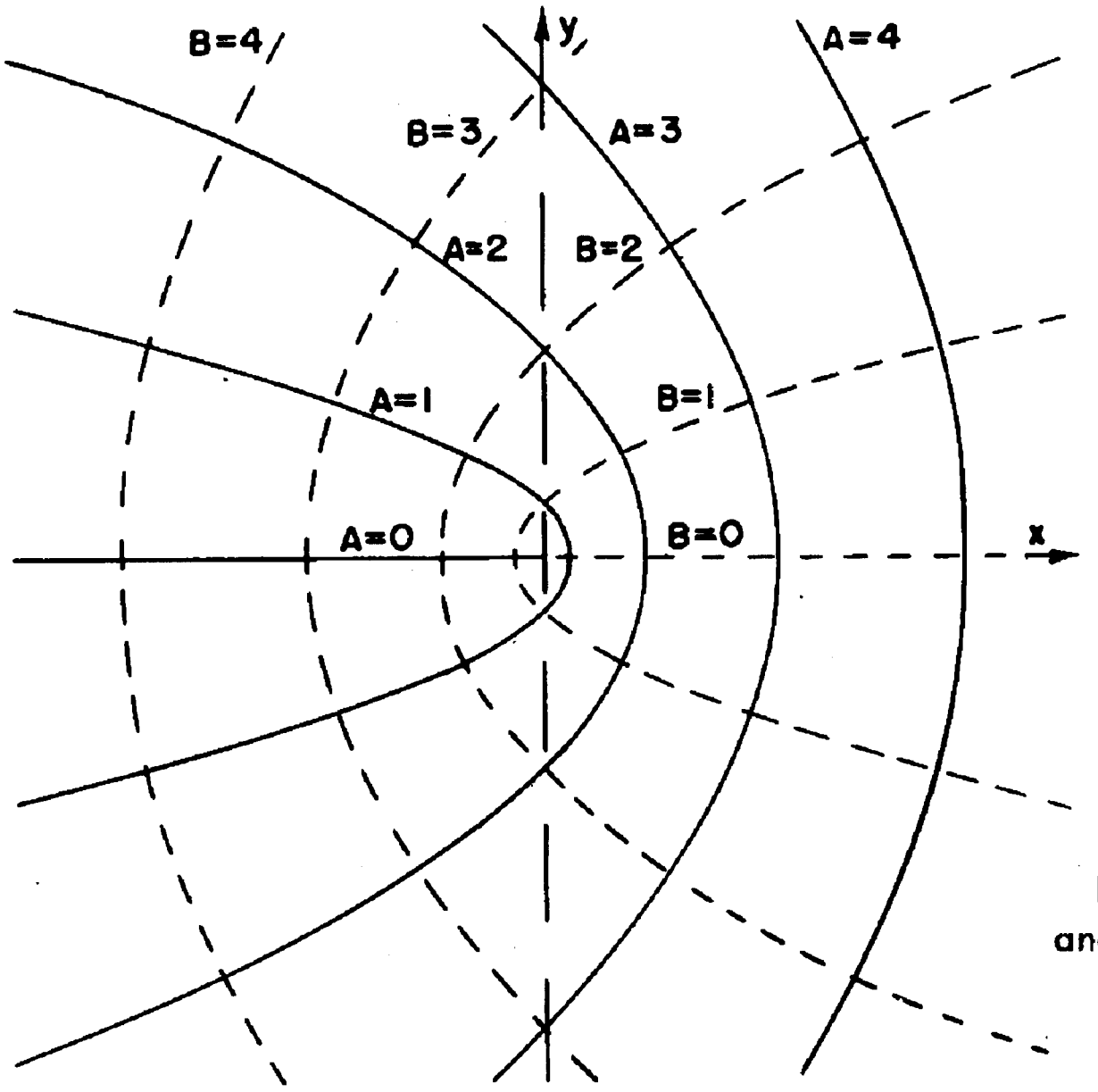


Fig. 7–4.
and $V(x, y)$ f

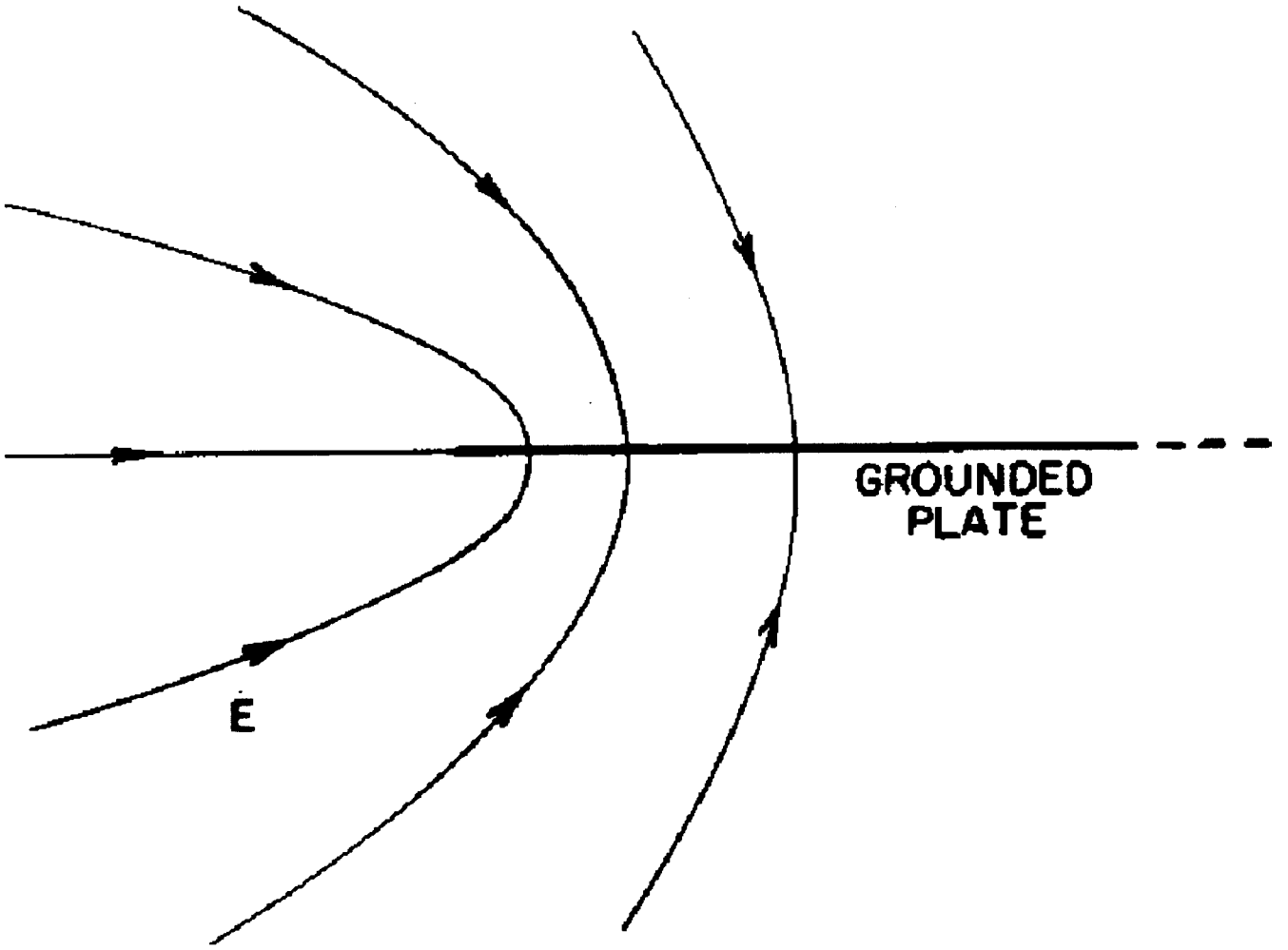


Fig. 7–5. The electric field near the edge of a thin grounded plate.

HYDROGEN PART ONE

SO FAR, SINGLE PARTICLE WAVEFCNS

$$\psi(\vec{r}, t)$$

HYDROGEN ATOM HAS 2 PARTICLES

$$\psi(\vec{r}_1, \vec{r}_2, t)$$

where proton is

where electron is

H ATOMS COME IN LUMPS

$$\int |\psi(\vec{r}_1, \vec{r}_2, t)|^2 \, d^3r_1 \, d^3r_2 = 1$$

CALLED SINGLE PARTICLE BASIS

$$\langle \vec{r}_1, \vec{r}_2 | \psi(t) \rangle = \psi(\vec{r}_1, \vec{r}_2, t)$$

need operators

$$\vec{r}_{1\,op} \rightarrow \vec{r}_1 \qquad \vec{p}_{1\,op} \rightarrow -i\hbar \nabla_1$$

$$\vec{r}_{2\,op} \rightarrow \vec{r}_2 \qquad \vec{p}_{2\,op} \rightarrow -i\hbar \nabla_2$$

CAN GENERALIZE TO N PARTICLES

$\rightarrow$ 3N degrees of freedom + time

SCHRODINGER EQUATION TDSE

$$H|\psi\rangle = i\hbar \frac{d}{dt}|\psi\rangle$$

$$H = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + V(\vec{r}_1, \vec{r}_2)$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}_1^{\,2} - \frac{\hbar^2}{2m}\vec{\nabla}_2^{\,2} + V(\vec{r}_1, \vec{r}_2)\right]\psi(\vec{r}_1, \vec{r}_2, t)$$

$$= i\hbar \frac{d}{dt}\psi(\vec{r}_1, \vec{r}_2, t)$$

$\Rightarrow$ 7 DIMENSIONAL DIFF EQ

(3N+1) DIM

I DON'T WANT TO SOLVE 7d DIFF EQ!

BREAK PROBLEM INTO PIECES...

WHOLE PROBLEM $\rightarrow$ CENTER-OF-MASS $\rightarrow$ x, y, z

WHOLE PROBLEM $\rightarrow$ RELATIVE MOTION $\rightarrow$ r, θ, φ

CHANGE VARIABLES

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \qquad \text{relative}$$

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \qquad \text{center of mass}$$

$$\frac{m_1 \cdot m_2}{m_1 + m_2} = \mu \qquad \text{REDUCED MASS}$$

$$m_1 + m_2 = M \qquad \text{TOTAL MASS}$$

$$\left[-\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{\hbar^2}{2M} \vec{\nabla}_R^2 + V(\vec{r}) \right] \varphi(\vec{r}, \vec{R}, t)$$

$$= i\hbar \frac{d}{dt} \varphi(\vec{r}, \vec{R}, t)$$

SEPARATE THIS EQN: $\varphi(\vec{r}, \vec{R}, t) = f(\vec{R}, t)\, g(\vec{r}, t)$

$\Rightarrow$ POSSIBLE BECAUSE $\vec{R}$ does not appear in V

$$\left[-\frac{\hbar^2}{2\mu} \vec{\nabla}_r^2 - \frac{\hbar^2}{2M} \vec{\nabla}_R^2 + V(\vec{r}) \right] f \cdot g$$

$$= i\hbar \frac{d}{dt} (f \cdot g)$$

$$\frac{1}{\cancel{f \cdot g}} \cancel{f(\vec{R},t)} \left[-\frac{\hbar^2}{2\mu} \vec{\nabla}_r^2 + V(\vec{r}) - i\hbar \frac{d}{dt} \right] g(\vec{r},t)$$

depends only on $\vec{r}, t$

$$= \frac{1}{f \cdot \cancel{g}} \cancel{g(\vec{r},t)} \left[\frac{\hbar^2}{2M} + i\hbar \frac{d}{dt} \right] f(\vec{R},t)$$

depends only on $\vec{R}, t$

~~$f(\vec{R},t)$ = prob density~~

$f(\vec{R},t) =$ prob amplitude that cm is at $\vec{R}$ at time t

$g(\vec{r},t) =$ prob amplitude that separation is $\vec{r}$ at time t

SEPARATED EQUATIONS 7d $\nearrow$ 3 + 1 CM 8d!
$\searrow$ 3 + 1 RRL

TDSE R:
$$\left[-\frac{\hbar^2}{2M}\vec{\nabla}_R^2\right] f(\vec{R},t) = i\hbar\frac{d}{dt} f(\vec{R},t)$$

3d free particle

$$f(\vec{R},t) = e^{i(\vec{P}\cdot\vec{R} - (P^2/2M)t)/\hbar}$$

CM eigenstates

TDSE r:
$$\left[-\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 + V(\vec{r})\right] q(\vec{r},t) = i\hbar\frac{d}{dt} q(\vec{r},t)$$

SEPARATE TIME DEPENDENCE

$$q(\vec{r},t) = \varphi(\vec{r})\, h(t)$$

$$\cancel{h(t)\left[-\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 + V(\vec{r})\right]\varphi_n(\vec{r}) =}$$

$$\frac{1}{\cancel{h}\varphi_n} h(t)\left[-\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 + V(\vec{r}) - i\hbar\frac{d}{dt}\right]\varphi_n(\vec{r})$$

$$\frac{1}{h\cancel{\varphi_n}}\cancel{\varphi_n(\vec{r})}\left[i\hbar\frac{d}{dt}\right]h(t)$$

SEPARATION CONSTANT E_n

energy eigenvalue = separation constant.

$$\frac{1}{\varphi_n}\left[-\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 + V(\vec{r})\right]\varphi_n(\vec{r}) = E_n$$

$$E_n = \frac{1}{h(t)}\left[i\hbar\frac{dh}{dt}\right]$$

$$\frac{dh}{dt} = -i\frac{E_n}{\hbar}h$$

$$h(t) = e^{-iE_n t/\hbar}$$

$$\left[-\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 + V(\vec{r})\right]\varphi_n(\vec{r}) = E_n\,\varphi_n(\vec{r})$$

3d TISE for relative motion

SO, THE ENERGY EIGENSTATES ARE

$$\psi_n(\vec{r},\vec{R},t) = f(\vec{R},t)\,g(\vec{R},t)$$

$$= e^{i(\vec{P}\cdot\vec{R} - (P^2/2m))t/\hbar}\,\varphi_n(\vec{r})\,e^{-iE_n t/\hbar}$$

HARD JOB IS FINDING φ_n's

TISE

$$\left[-\frac{\hbar^2}{2\mu} \vec{\nabla}^2 + V(\vec{r}) \right] \varphi_n(\vec{r}) = E_n \varphi_n(\vec{r})$$

SPECIAL CASE

central potential $\quad V(\vec{r}) = V(r) = -\dfrac{e^2}{r}$ HYDROGEN

$-\dfrac{Ze^2}{r}$ HYDROGEN-LIKE

$V(r)$ is spherically symmetric $\Rightarrow$ $\vec{L}$ is conserved

SEPARATE AGAIN

$$\varphi_n(\vec{r}) = R(r)\,\Omega(\theta,\varphi)$$

$$\left[-\frac{\hbar^2}{2\mu} \vec{\nabla}^2 + V(r) \right] R(r)\,\Omega(\theta,\varphi)$$

$$= E_n R(r)\,\Omega(\theta,\varphi)$$

$$-\frac{\hbar^2}{2\mu}\nabla^2 = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{1}{r^2}\left\{ \frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \right\} \right]$$

$$= -\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2} r + \frac{L^2}{2\mu r^2}$$

$$H = -\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2} r + \frac{\vec{L}^2}{2\mu r^2} + V(r)$$

coupled system of eigenequations

$$H\,\varphi_{n\ell m}(\vec{r}) = E_n\,\varphi_{n\ell m}(\vec{r})$$

$$L^2\,\varphi_{n\ell m}(\vec{r}) = \ell(\ell+1)\hbar^2\,\varphi_{n\ell m}(\vec{r})$$

$$L_z\,\varphi_{n\ell m}(\vec{r}) = m\hbar\,\varphi_{n\ell m}(\vec{r})$$

we already solved the L^2, L_z problem

$$\varphi_{n\ell m}(\vec{r}) = R_n(r)\,Y_{\ell m}(\theta,\varphi)$$

$$\left[-\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2} r - \frac{e^2}{r}\right] R_n Y_{\ell m}$$

$$+ \left[\frac{L^2}{2\mu r^2}\right] R_n Y_{\ell m} = E_n R_n Y_{\ell m}$$

$$\ell(\ell+1)\hbar^2$$

NEW TISE

$$\left[-\frac{\hbar^2}{2\mu r}\frac{\partial^2}{\partial r^2} r - \frac{e^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} \right] R_n = E_n R_n$$

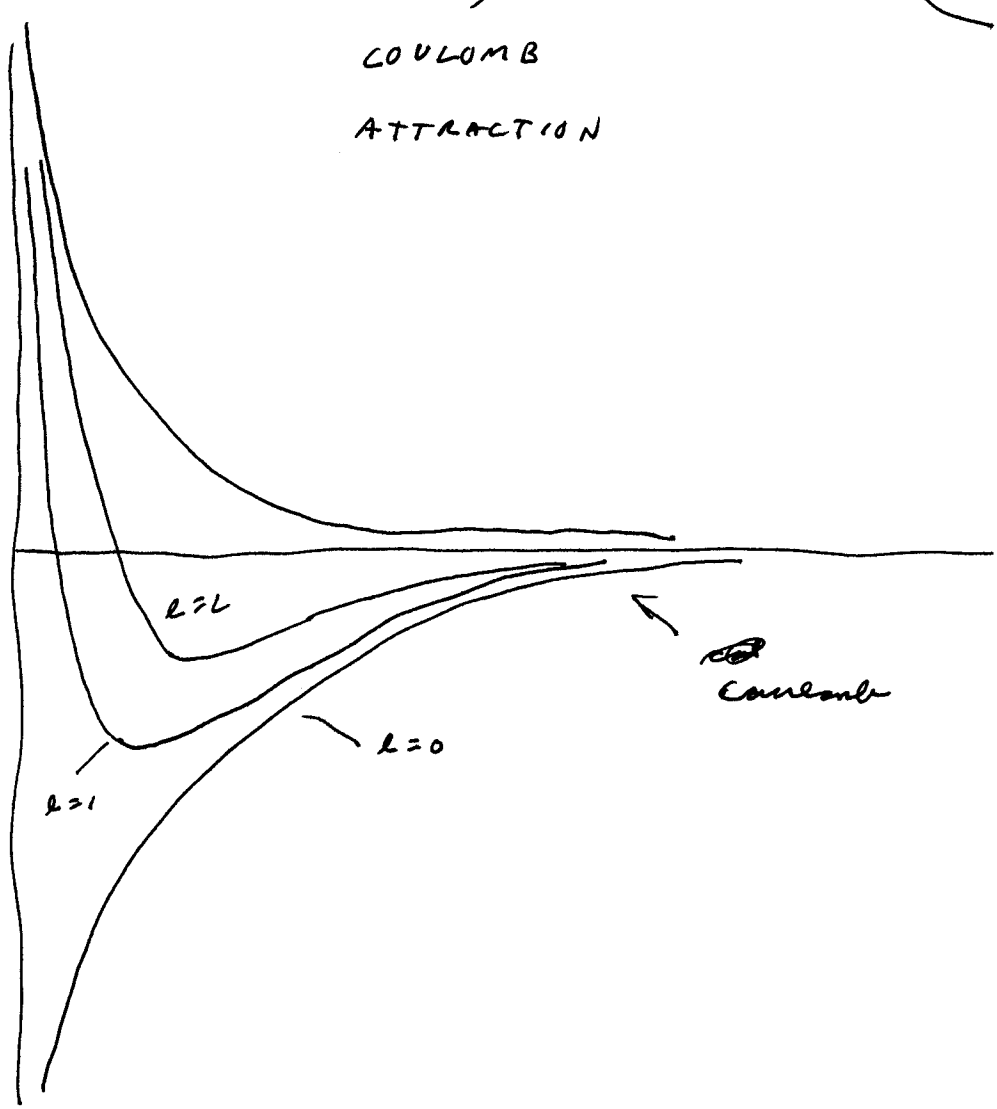
1d PROBLEM

WITH EFFECTIVE POTENTIAL

$$V_{eff}(r) = -\frac{e^2}{r} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}$$

COULOMB ATTRACTION

CENTRIFUGAL ~~POTENTIAL~~ BARRIER



START TO SOLVE

make equation dimensionless $r \to \rho$

length $\quad a_0 = \dfrac{\hbar^2}{me^2}$ BOHR RADIUS $= 0.52\,\text{Å}$

$$\rho = r/a_0$$

energy $\quad E_0 = \dfrac{\hbar^2}{2ma_0^2} = 13.6\ ev$ RYDBERG

$E \to \lambda^2$

$$\lambda^2 = E_n/E_0$$

$$\frac{2ma_0^2}{\hbar^2}\left[-\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{e^2}{r}\right]R_{nl} = E_n R_{nl}$$

$$r \times \left[-\frac{a_0^2}{r}\frac{\partial^2}{\partial r^2}r + \left(\frac{a_0^2}{r^2}\right)l(l+1) - \frac{2me^2}{\hbar^2}\frac{a_0^2}{r}\right]R_{nl} = \lambda^2 R_{nl}$$

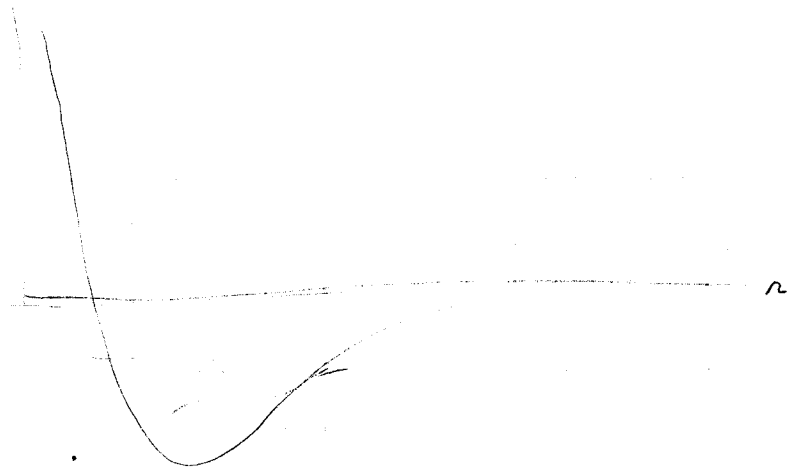
$$-\frac{\partial^2}{\partial\left(\frac{r}{a_0}\right)^2} + \frac{l(l+1)}{\rho^2} - \left(\frac{2}{a_0}\right)\left(\frac{a_0^2}{r}\right)$$

$$\frac{2}{\rho}$$

$S \equiv r R_{nl}$

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \lambda^2\right]S(\rho) = 0$$

Bound states



$r \to 0 \qquad V \to \infty \qquad \Rightarrow \qquad \psi \to 0$

$r \to \infty \qquad V \to 0 \qquad \Rightarrow \qquad \psi \sim e^{-\alpha r}.$

$\rho \to \infty$

$$\frac{d^2 S}{d\rho^2} - \left[\cancelto{0}{\frac{\ell(\ell+1)}{\rho^2}} + \cancelto{0}{\frac{2}{\rho}} - \lambda^2 \right] S = 0$$

$$S = A e^{-\lambda\rho} + \cancelto{0}{B e^{+\lambda\rho}}$$

$$S(\rho) = e^{-\lambda\rho} \, Y(\rho)$$

separate again

$$\frac{d^2}{d\rho^2}\left[e^{-\lambda\rho} Y(\rho) \right] - \left[\frac{\ell(\ell+1)}{\rho^2} + \frac{2}{\rho} - \lambda^2 \right] \left[e^{-\lambda\rho} Y(\rho) \right] = 0$$

$$\frac{d}{d\rho}\left[-\lambda e^{-\lambda\rho} y + e^{-\lambda\rho}\frac{dy}{d\rho}\right]$$

$$+\lambda^2 e^{-\lambda\rho} y \underbrace{- \lambda e^{-\lambda\rho}\frac{dy}{d\rho} - \lambda e^{-\lambda\rho}\frac{dy}{d\rho}}_{-2\lambda \ldots} + e^{-\lambda\rho}\frac{d^2y}{d\rho^2}$$

$$\cancel{e^{-\lambda\rho}}\left[\frac{d^2}{d\rho^2} - 2\lambda\frac{d}{d\rho} + \cancel{\lambda^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \cancel{\lambda^2}\right] y(\rho) = 0$$

want to solve this equation such that $\psi(r) \to 0$ as $r \to 0$

$$y(\rho) = \rho^m \sum_{n=0}^{\infty} c_n \rho^n = \sum_{n=0}^{\infty} c_n \rho^{n+m}$$

insures

$\psi(r) \to 0$ as $r \to 0$.

$$\frac{dy}{d\rho} = \frac{d}{d\rho}\left[\sum c_n \rho^{n+m}\right] = \sum (n+m)\, c_n \rho^{(n+m-1)}$$

$$\frac{d^2y}{d\rho^2} = \frac{d}{d\rho}\left[\sum (n+m)\, c_n \rho^{(n+m-1)}\right] = \sum_{n=0}^{\infty} (n+m)(n+m-1)\, c_n \rho^{n+m-2}$$

lowest power of ρ is $(m-2)$ TH.

$$(\cancel{n}^{0}+m)(\cancel{n}^{0}+m-1)\, c_0\, \rho^{m-2} - \frac{l(l+1)}{\rho^2}\, c_0\, \rho^{m}$$

$$[m(m-1) - l(l+1)]\, c_0 = 0 \qquad \Rightarrow \quad m = l+1$$

$$\text{or} \quad m = -l$$

coefficient of the $(n+m-2)$ TH TERM

$$\sum_{n=0}^{\infty} (n+m)(n+m-1)\, c_n\, \rho^{n+m-2} - 2\lambda (n+m)\, c_n\, \rho^{n+m-1}$$

$$+ \frac{2}{\rho}\, c_n\, \rho^{(n+m)-1} - \frac{l(l+1)}{\rho^2}\, c_n\, \rho^{(n+m)-2} = 0$$

$$[(n+m)(n+m-1) - l(l+1)]\, c_n + [-2\lambda(n-1+m) + 2]\, c_{n-1} = 0$$

$l = m-1$

$$[(n+l+1)(n+l) - l(l+1)]\, c_n = 2[(n+l)\lambda - 1]\, c_{n-1}$$

$$n[n+2l+1]\, c_n = 2[(n+l)\lambda - 1]\, c_{n-1}$$

$$\boxed{c_n = \frac{2[(n+l)\lambda - 1]}{n[n+2l+1]}\, c_{n-1}}$$

special values of λ terminate series

TWO CONDITIONS

1) POLYNOMIAL STARTS WITH ρ^{l+1} finite $\psi(0)$

2) POLYNOMIAL STOPS WITH ρ^{n+l} finite energy.

eigenenergies

$$c_n = \frac{2\left[(n+\ell)\lambda - 1\right]}{n(n+2\ell+1)} c_{n-1}$$

$$(n+\ell)\lambda - 1 = 0$$

$$\lambda = \left(\frac{1}{n+\ell}\right) = \frac{1}{(j+\ell)}$$

energy $\quad \lambda^2 = \frac{E_n}{E_0}$

$$E_n = \frac{1}{(j+\ell)^2} E_0$$

$$\boxed{E_n = \frac{1}{n^2} E_0}$$

$$\psi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\, Y_{\ell m}(\theta, \varphi) = \frac{e^{-\lambda\rho}}{a_0 \rho} Y_{n\ell}(\rho)\, Y_{\ell m}(\theta, \varphi)$$

$$= N \; e^{-\rho/n} \left[\frac{Y_{n\ell}(\rho)}{\rho}\right] Y_{\ell m}(\theta, \varphi)$$

Y goes from $\ell \ldots n$

$[\;]$ goes from $\ell-1 \ldots n-1$