Understanding of Schrödinger Equations in Quantum Systems

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Project Duration: May'19 to June'19

Abstract

In this project we describe the different quantum systems and their properties. In the process we also analyse the different possible differential equations and their solutions. Most of the project we use Mathematica as a tool. The expressions of various functions are also studied and given in the Appendix.

Contents

1 Introduction

The quantum systems of the one-dimensional Linear Harmonic Oscillator and the Hydrogen Atom will be analysed and their solutions detailed before proceeding to more advanced quantum systems involving the use of Quantum Perturbation Theory. The text has been presented in such a manner that an undergraduate in physics who has completed a basic course in quantum mechanics will be able to easily understand the theory and work out the calculations as and when required. This text is also suitable for readers who just wish to look up certain calculations that are now fuzzy.

As we progress in our analysis, the emphasis will be on studying the properties of polynomial solutions that arise as a part of the total solution to quantum systems. Angular momentum algebra comes up naturally as a consequence of raising-lowering operator algebra applied to the system of one-dimensional Linear Harmonic Oscillator. The section on Spherical Harmonics is an essential prerequisite to the study of Hydrogen Atom.

2 The Linear Harmonic Oscillator

2.1 Schrödinger Equation for the Linear Harmonic Oscillator Potential

In linear harmonic oscillators we have a particle that experiences a force proportional but opposite to it's displacement from a fixed point in one dimension. Therefore, we have $F = -kx$ as the force considering origin as fixed point and the potential energy as $V(x) = \frac{1}{2}kx^2$.

The corresponding 1-D Schrödinger eigenvalue equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x) \tag{1}$$

Non-dimensionalizing the above equation using two dimensionless quantities

$$\lambda = \frac{2E}{\hbar\omega} \qquad \xi = \alpha x$$

where

$$\omega = \left(\frac{k}{m}\right)^{\frac{1}{2}} \qquad \alpha = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}$$

The equation becomes

$$\frac{d^2\psi(\xi)}{d\xi^2} + (\lambda - \xi^2)\psi(\xi) = 0 \tag{2}$$

We now analyse the equation in the asymptotic region of $|\xi| \to \infty$. For finite E, $\lambda << \xi^2$ and the equation simplifies to

$$\frac{d^2\psi(\xi)}{d\xi^2} = \xi^2\psi(\xi) \tag{3}$$

The asymptotic function therefore has the form $\quad \psi(\xi) = e^{\pm\frac{\xi^2}{2}}$. You can simply substitute to check this. The wave-function must be bounded everywhere, so we discard the positive sign in the exponent.

Asymptotic analysis therefore, suggests solutions of the form

$$\psi(\xi) = H(\xi)e^{-\frac{\xi^2}{2}} \tag{4}$$

where $H(\xi)$ does not affect the asymptotic behaviour of ψ.

Substituting 4 in 3 we get the **Hermite Equation**

$$\boxed{\frac{d^2H}{d\xi^2} - 2\xi\frac{dH}{d\xi} + (\lambda - 1)H = 0} \tag{5}$$

2.2 Potentials and Symmetry

The linear harmonic potential is special because of it's symmetric nature. This section will be about a few interesting consequences of this 'symmetry' in quantum mechanics.
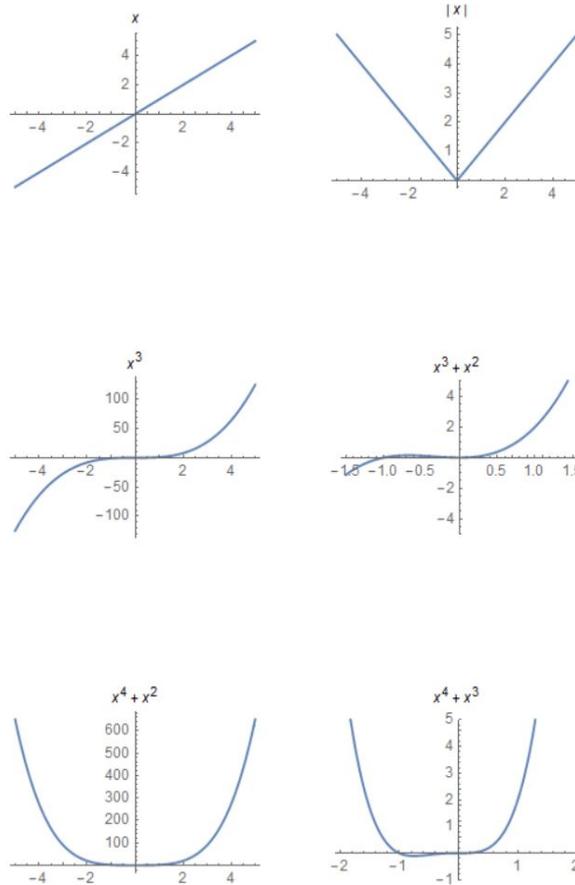
Figure 1: Graphs of some 1-D potentials

2.2.1 The Parity Operation

The 1-D Schrödinger eigenvalue equation is given by

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{6}$$

The operation of reflection through the origin, $x \to -x$ is called the parity operation. If the potential is symmetric, the Hamiltonian $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$ does not change when x is replaced with $-x$ and is said to be invariant under the parity operation.

Now, if we change the sign of x in 6 we get

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(-x)}{dx^2} + V(x)\psi(-x) = E\psi(-x) \tag{7}$$

and we realize that both $\psi(x)$ and $\psi(-x)$ are solutions to the same equation, with the same eigenvalue E.

2.2.2 Eigenfunctions with definite parity

An interesting consequence of our observations in section 2.2.1 is

Theorem: For a symmetric one-dimensional potential, the eigenfunctions of 1-D Schrödinger eigenvalue equation can always be *chosen* to have definite parity.

Let us detail a proof.

Case 1: The eigenvalue E is non-degenerate or in other words linearly independent eigenfunctions have distinct eigenvalues. Thus

$$\begin{aligned}
\psi(x) &= \alpha\psi(-x) \\
\implies \psi(-x) &= \alpha\psi(x) \\
\implies \psi(x) &= \alpha^2\psi(x)
\end{aligned} \tag{8}$$

We get $\alpha = \pm 1$ and therefore,

$$\psi(x) = \pm\psi(-x) \tag{9}$$

Therefore, $\psi(x)$ has a definite parity in case of the eigenfunctions being non-degenerate.

Case 2: The eigenvalue E is degenerate or in other words, at least two linearly independent eigenfunctions have the same eigenvalue.
(**Note:** n-fold degeneracy of an eigenvalue implies n linearly independent eigenfunctions have the same eigenvalue)

Let us assume that any one of degenerate eigenfunctions say $\psi(x)$ does not have a definite parity. But we can always write

$$\psi(x) = \psi_+(x) + \psi_-(x)$$

where

$$\begin{aligned}
\psi_+(x) &= \frac{1}{2}[\psi(x) + \psi(-x)] \tag{10} \\
\psi_-(x) &= \frac{1}{2}[\psi(x) - \psi(-x)] \tag{11}
\end{aligned}$$

A simple calculation will tell you that both $\psi_+(x)$ and $\psi_-(x)$ are eigenfunctions with eigenvalue E. Therefore, you can always find a set of n eigenfunctions (linearly independent of course) with definite parity for an n-fold degenerate eigenvalue.

This completes the proof.

Often this theorem largely simplifies calculations as we will see in the next section.

2.3 Hermite Polynomials

For solving the Hermite Equation, we expand $H(\xi)$ as a power series. For a parity symmetric potential, we know that the eigenfunctions can always be chosen to have a definite parity. Therefore, we have

$$\psi(\xi) = \pm\psi(-\xi) \Rightarrow H(\xi) = \pm H(-\xi)$$

from 4.

Even States

$$H(\xi) = \sum_{k=0}^{\infty} c_k \xi^{2k}$$

is substituted in 5 to get

$$\sum_{k=0}^{\infty} [2(k+1)(2k+1)c_{k+1} + (\lambda - 1 - 4k)c_{k+1}]\xi^{2k} = 0$$

For the equation to be satisfied each coefficient has to separately go to zero and therefore we get

$$c_{k+1} = \frac{4k+1-\lambda}{2(k+1)(2k+1)}c_k \tag{12}$$

We realize that $H(\xi)$ must be a polynomial that terminates in the variable ξ^2. Otherwise $\psi(\xi)$ does not have finite value for $|\xi| \to \infty$.

Let 2n be the highest power of the polynomial $H(\xi)$ then $c_n \neq 0$ and $c_{n+1} = 0$. Therefore

$$\lambda = 4n+1 \qquad n = 0, 1, 2, \ldots$$

Odd States

$$H(\xi) = \sum_{k=0}^{\infty} d_k \xi^{2k+1}$$

is substituted in 5 to get

$$d_{k+1} = \frac{4k+3-\lambda}{2(k+1)(2k+3)} d_k \tag{13}$$

(The calculations are similar to that for even states)

Let 2n+1 be the highest power of the polynomial $H(\xi)$ then $d_n \neq 0$ and $d_{n+1} = 0$. Therefore

$$\lambda = 4n + 3 \qquad n = 0, 1, 2, ...$$

Solving the Hermite Equation We will use mathematica as a tool. Since, it is a second order differential equation we need to specify two initial conditions.

They should be such that we get Physicist's Hermite Polynomials which look like

$$
\begin{aligned}
H_0(\xi) &= 1 \\
H_1(\xi) &= 2\xi \\
H_2(\xi) &= 4\xi^2 - 2 \\
H_3(\xi) &= 8\xi^3 - 12\xi \\
H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12
\end{aligned}
\tag{14}
$$

We observe that the coefficient of the highest power of ξ in $H_n(\xi)$ is 2^n. This fact is used to find coefficients of smaller order of the Hermite Polynomial taking $c_n = 2^n$ and evaluating $c_{n-1}, c_{n-2}, ...$ by substituting in recursion relations (7) or (8) depending on whether n is even or odd.

Here are the mathematica generated graphs.
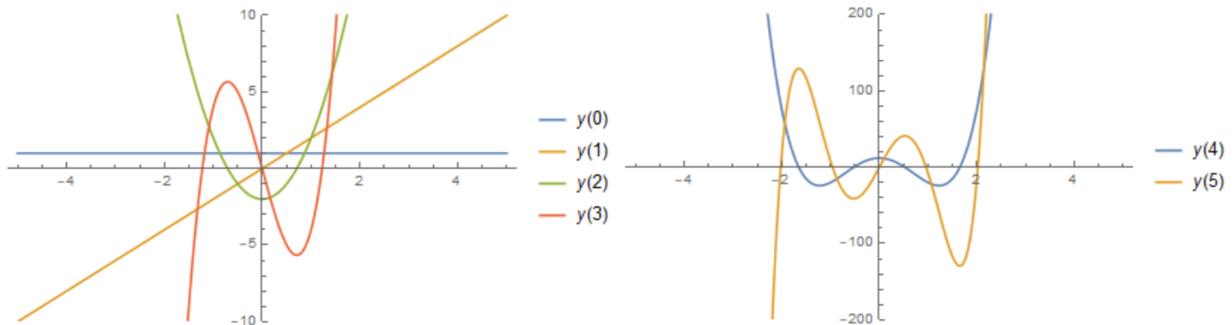
Figure 2: Hermite Polynomials

Note $y(n)$ is the same as $H_n(\xi)$.

Energy Levels

$$\lambda = 2n + 1 \qquad n = 0, 1, 2, ...$$

$$\lambda = \frac{2E}{\hbar\omega}$$

Therefore we get

$$E_n = \frac{(2n+1)}{2} \hbar\omega = (n + \frac{1}{2})h\nu$$

We get infinite discreet equally spaced energy levels.

$$E_{n+1} - E_n = h\nu$$

We have the **zero point energy** as

$$E_0 = \frac{\hbar\omega}{2}$$

This is a quantum phenomenon since a particle at rest with zero potential energy is prohibited by the Uncertainty Principle but is otherwise possible for a classical particle.

The final wave equation looks like
$$\psi_n(x) = N_n e^{-\frac{\alpha^2 x^2}{2}} H_n(\alpha x)$$
The coefficient N_n will be determined in the following section using a very different method.

2.3.1 Properties of Hermite Polynomials

1 One alternate definition of Hermite Polynomials in mathematics:

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n}$$

2 Generating Function of Hermite Polynomials $G(\xi, s) = e^{-s^2 + 2s\xi} = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n$

3 Recursion Relation Using G one can show that Hermite polynomials satisfy the recursion relation

$$H_{n+1}(\xi) - 2\xi H_n(\xi) + 2n H_{n-1}(\xi) = 0^{**} \tag{15}$$

4 Orthogonality The polynomials are orthogonal with respect to the weight function(measure) $w(x) = e^{-\frac{x^2}{2}}$. Thus, we have

$$\int_{-\infty}^{\infty} H_n(x) H_m(x) w(x) dx = 0 \quad , m \neq n$$

5 Completeness The Hermite polynomials form an orthogonal basis of the Hilbert space of functions satisfying

$$\int_{-\infty}^{\infty} |f(x)|^2 w(x) dx < \infty$$

in which the inner product is given by the integral

$$\langle f, g \rangle = \int_{-\infty}^{\infty} f(x) \overline{g(x)} w(x) dx$$

2.4 Raising and Lowering Operators

For those who are unfamiliar with Dirac's Bra and Ket notation, we first describe a short section on it. (The reader is advised to refer to any standard quantum mechanics textbook as a follow up if the notation is completely new)

2.4.1 Dirac's Bra and Ket Algebra

We will derive the final wave equation for Linear Harmonic Oscillator Potential using Dirac's Bra and Ket Algebra which is far more elegant than solving the Schrödinger Equation.

Few definitions and their consequences:

1 Scalar Product: If we have two square integrable functions ψ_1 and ψ_2 then their scalar product is given by

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^*(\mathbf{r}) \psi_2(\mathbf{r}) d\mathbf{r}$$

where the integration is over entire 'space'. Here $\langle \psi_1 |$ is called a bra while $| \psi_2 \rangle$ is called a ket. We'll list a few consequences of this definition.

    1.1 $\langle \psi_1 | \psi_2 \rangle = \langle \psi_2 | \psi_1 \rangle^*$ where the * denotes conjugate.

    1.2 $\langle \psi | \psi \rangle \geq 0$

    1.3 $\langle \psi | \psi \rangle = 1 \implies \psi$ is normalised.

2 What are these kets and bras? Kets are column vectors while bras are conjugate row vectors (or the conjugate transpose of ket vectors).

    2.1 $| \psi_1 \rangle = c | \psi_2 \rangle \implies \langle \psi_1 | = c^* \langle \psi_2 |$

    2.2 You can think of these ket vectors to be a part of some abstract vector space(spanned by a ket vector basis) while the corresponding bra vectors to be a part of a conjugate space satisfying relation 2.1.

Remark: This abstract 'space' that we keep talking about is a Hilbert Space. At this stage we don't need to confuse ourselves with it's definition. In quantum mechanics, wave functions sit inside a Hilbert Space.

3 Operators: An operator α (say) converts a bra or ket into a different bra or ket. We will only encounter **linear operators** which satisfy the condition

$$\alpha(c_1 |\psi_1\rangle + c_2 |\psi_2\rangle + ...) = c_1 \alpha |\psi_1\rangle + c_2 \alpha |\psi_2\rangle + ...$$

Some properties satisfied by operators:

3.1 Sum/Diff $(\alpha \pm \beta) |\psi\rangle = \alpha |\psi\rangle \pm \beta |\psi\rangle$

3.2 Associative Law $(\alpha + \beta) + \gamma = \alpha + (\beta + \gamma)$

3.3 Product $(\beta\alpha |\psi_a\rangle = \beta(\alpha |\psi_a\rangle)) = \beta |\psi_b\rangle$

4 Eigenvalue Equation: If operator satisfies

$$\alpha |\psi_n\rangle = \alpha_n |\psi_n\rangle$$

then α_n is an eigenvalue of the operator α corresponding to eigenfunction $|\psi_n\rangle$.

5 Observables: Any dynamical quantity that can be measured is an observable. Observables are assumed to be represented by linear operators. The eigenfunctions(or eigenkets if you wish) corresponding to the observable satisfy the following properties.

Orthogonality: The ψs satisfy

$$\langle\psi_n|\psi_m\rangle = c_{nm}\delta_{nm}$$

where c_{nm}'s are constants. The eigenfunctions can be normalized so that we can set $c_{nm} = 1$. We then say that the set of eigenfunctions is **orthonormal**.

Completeness: We'll represent ψs as ns for short.The ns form a complete set or we have the completeness condition

$$\sum_n |n\rangle \langle n| = I$$

Some important types of operators:

6 Adjoint Operator: We now have an idea that $|\psi\rangle$ is a column vector while $\langle\psi|$ is a conjugate row vector and operator α is a matrix. Adjoint operator $\alpha^\dagger$ of α is the **transpose conjugate** of the matrix α and satisfies condition

$$\langle\psi_1|\alpha^\dagger|\psi_2\rangle = \langle\psi_1|\alpha|\psi_2\rangle^*$$

An important property to list is when we change bras to kets or vice-versa.

$$\alpha |\psi_3\rangle = |\psi_4\rangle \implies \langle\psi_3| = \langle\psi_4| \alpha^\dagger \tag{16}$$

7 Hermitian Operator: If the operator A satisfies the condition

$$\langle\psi_1|A|\psi_2\rangle = \langle(A\psi_2)|\psi_1\rangle$$

then it is a Hermitian operator by definition. These operators are transpose conjugates of themselves! They also are a special class of linear operators representing observables that have real eigenvalues only (which is a direct consequence of the definition, proof outlined below).

(a) Taking $\psi_1 = \psi_2 = \psi_n$, $\langle\psi_n|A|\psi_n\rangle = a \langle\psi_n|\psi_n\rangle$

(b) $(A\psi_n)^* = a_n^* \psi_n^*$

(c) As a consequence of (b), we have $\langle(A\psi_n)|\psi_n\rangle = a_n^* \langle\psi_n|\psi_n\rangle$

Equating (a) and (c), we get

$$\boxed{a_n^* = a_n}$$

Therefore, a sufficient condition for operators to have real eigenvalues is for them to be Hermitian. But, this is not necessary a condition.

8 Unitary Operator: An operator U is unitary if it satisfies $UU^\dagger = 1$.

Also, U can be represented as $U = e^{iA}$ where A is a Hermitian operator.

2.4.2 Commutator Algebra for Operators

Commutator algebra for operators will be introduced here.

1. If A and B are operators then their commutator is defined as

$$[A, B] = AB - BA$$

and the operators are said to **commute** if

$$AB - BA = 0$$

2. The first example that comes to mind is $[x, p_x]$. We see that

$$[x, p_x] = [y, p_y] = [z, p_z] = i\hbar$$

3. Rest of the pairs commute. For example $[x, p_y] = 0, [x, y] = 0$. In the following sections we'll use commutator algebra everywhere.

2.4.3 Introduction to raising and lowering operators

The usefulness of these operators will be demonstrated for the linear harmonic oscillator case, but the method is very general. A few points are enlisted before the final result. We have the Hamiltonian

$$-\frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 = \hbar\omega(x\sqrt{\frac{m\omega}{2\hbar}} - ip_x\frac{1}{\sqrt{2m\hbar\omega}})(x\sqrt{\frac{m\omega}{2\hbar}} + ip_x\frac{1}{\sqrt{2m\hbar\omega}}) - \frac{1}{2}\hbar\omega$$

We have the extra $\frac{1}{2}\hbar\omega$ because x and p_x do not commute

1 Inspired by the above relation we introduce two operators, the raising and lowering (or the creation and annihilation) operators.

$$\boxed{a_\pm = x\sqrt{\frac{m\omega}{2\hbar}} \mp ip_x\frac{1}{\sqrt{2m\hbar\omega}}} \qquad (17)$$

a_+ and a_- are adjoints of each other (because x and p_x are Hermitian i.e. they are adjoints of themselves and so only i switches signs when we take $a_+^\dagger$)

2 Commutation relation

$$[a_-, a_+] = 1 \qquad (18)$$

3 From 17 and 18 we get

$$H = \hbar\omega(a_+a_- + \frac{1}{2})$$

4 From 17 we can see that

$$p_x = \frac{1}{i}\sqrt{\frac{m\hbar\omega}{2}}[a_- - a_+] \qquad (19)$$

and

$$x = \sqrt{\frac{\hbar}{2m\omega}}[a_- + a_+] \qquad (20)$$

5

$$[H, a_\pm] = \pm\hbar\omega a_\pm \qquad (21)$$

(Hint:For proving this result use 18)

6 Final Result If $|E\rangle$ is an eigenvector of H corresponding to eigenvalue E we have

$$H|E\rangle = E|E\rangle$$

and from 21

$$\begin{aligned} Ha_\pm|E\rangle &= (a_\pm H \pm \hbar\omega a_\pm)|E\rangle \\ &= (E \pm \hbar\omega)a_\pm|E\rangle \end{aligned} \qquad (22)$$

We see that $L_\pm f$ is an eigenfunction of H with new eigenvalue $\mu \pm \hbar$. Therefore, a_+ raises the value of E by $\hbar\omega$ while a_- lowers E by $\hbar\omega$.

We are moving along a "ladder" of states. Does this ladder have a lowest state?

Zero point energy using lowering operator   Since H only contains squares of operators p_x and x, the expectation value of H in any state cannot be negative, hence eigenvalues of H must be non-negative. Let E_0 be the smallest eigenvalue then

$$a_- \left| E_0 \right\rangle = 0$$

otherwise we will have a smaller eigenvalue for energy contrary to what we have assumed. If we operate Hamiltonian on E_0 we get

$$H \left| E_0 \right\rangle = (a_+ a_- + \frac{1}{2}\hbar\omega) \left| E_0 \right\rangle = \frac{1}{2}\hbar\omega \left| E_0 \right\rangle$$

So the zero point energy is $\frac{1}{2}\hbar\omega$ as we already obtained before!

Say a_+ is repeatedly operated on $\left| E_0 \right\rangle$ n times we raise the energy by $n\hbar\omega$. then eigenket $a_+^n \left| E_0 \right\rangle$ corresponds to energy

$$E_n = (n + \frac{1}{2})\hbar\omega \quad n = 0, 1, 2, ...$$

2.4.4   Trans-state Relations

$$a_- \left| n \right\rangle = c_n \left| n - 1 \right\rangle$$

Here a simpler notation for energy eigenstates has been used that is $\left| n \right\rangle = \left| E_n \right\rangle$. c_n or the normalisation constant is to be found.

When we change kets to bras according to the previous properties

$$\left\langle n \right| a_-^\dagger = c_n^* \left\langle n - 1 \right|$$

Combining the two equations we get

$$\left\langle n | a_+ a_- | n \right\rangle = \left\langle n | a_+ c_n | n - 1 \right\rangle = |c_n|^2 \left\langle n - 1 | n - 1 \right\rangle = |c_n|^2$$

$$\hbar\omega \left\langle n | a_+ a_- | n \right\rangle = \hbar\omega \left\langle n | n | n \right\rangle = n\hbar\omega$$

Therefore we get $|c_n| = \sqrt{n}$.

Let's derive another important relation. From previous result we have

$$a_- \left| n + 1 \right\rangle = \sqrt{n+1} \left| n \right\rangle \implies a_+ a \left| n + 1 \right\rangle = a_+ \sqrt{n+1} \left| n \right\rangle \implies \sqrt{n+1} \left| n + 1 \right\rangle = a_+ \left| n \right\rangle$$

Finally we have

$$
\begin{aligned}
a_- \left| n \right\rangle &= \sqrt{n} \left| n - 1 \right\rangle \\
a_+ \left| n \right\rangle &= \sqrt{n+1} \left| n + 1 \right\rangle
\end{aligned}
\tag{23}
$$

2.5   Normalisation constants using raising operator

N_0 can be easily obtained using normalisation integral involving just $e^{-\frac{\alpha^2 x^2}{2}}$ and we get

$$N_0 = \left(\frac{\alpha}{\sqrt{\pi}} \right)^{\frac{1}{2}}$$

We can now elegantly obtain not only N_n but also all of the eigenfunctions after ψ_0 using the raising operator.

From 23 we have

$$\left| \psi_{n+1} \right\rangle = \frac{1}{\sqrt{n+1}} a_+ \left| \psi_n \right\rangle$$

Substituting value of a_+ from 17 and making change of variable from x to ξ we get

$$\psi_{n+1}(\xi) = \frac{1}{[2(n+1)]^{\frac{1}{2}}} (\xi - \frac{d}{d\xi}) \psi_n(\xi)$$

Now from $\psi_0(\xi)$ we can get $\psi_1(\xi)$ as

$$\psi_1(\xi) = \left(\frac{\alpha}{2\sqrt{\pi}} \right)^{\frac{1}{2}} (2\xi) e^{-\frac{1}{2}\xi^2}$$

Generalizing,

$$N_n = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{\frac{1}{2}}$$

2.6 Expectation Values: Position and Momentum

The expectation or average value of a dynamical variable A (with respect to a system described by the wave function ψ) is given by

$$\langle A \rangle_\psi = \frac{\langle \psi | A | \psi \rangle}{\langle \psi | \psi \rangle} \tag{24}$$

When the wave functions are noramlized energy eigenfunctions of SHO and the dynamical variable is

1. **Position**: We have

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\, x\, \psi_n(x)$$

   Since $\psi_n^*(x)$ times $\psi_n(x)$ is even, the function inside the integral is odd. Therefore we get

$$\langle x \rangle = 0$$

2. **Momentum:** We have

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi_n^*(x)\, \frac{d}{dx}\left(\psi_n(x) \right)$$

   By replacing $x \to -x$ we realize that the function inside the integral is odd and we get

$$\langle p \rangle = 0$$

Theorem: A similar argument as above gives us

$$\langle x^{2n+1} \rangle = 0$$

2.7 Energy Eigenfunctions: The Final Expression

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{\frac{1}{2}} e^{-\frac{\alpha^2 x^2}{2}} H_n(\alpha x)$$

Mathematica generates these beautiful graphs for different values of n and $\alpha = 1$.
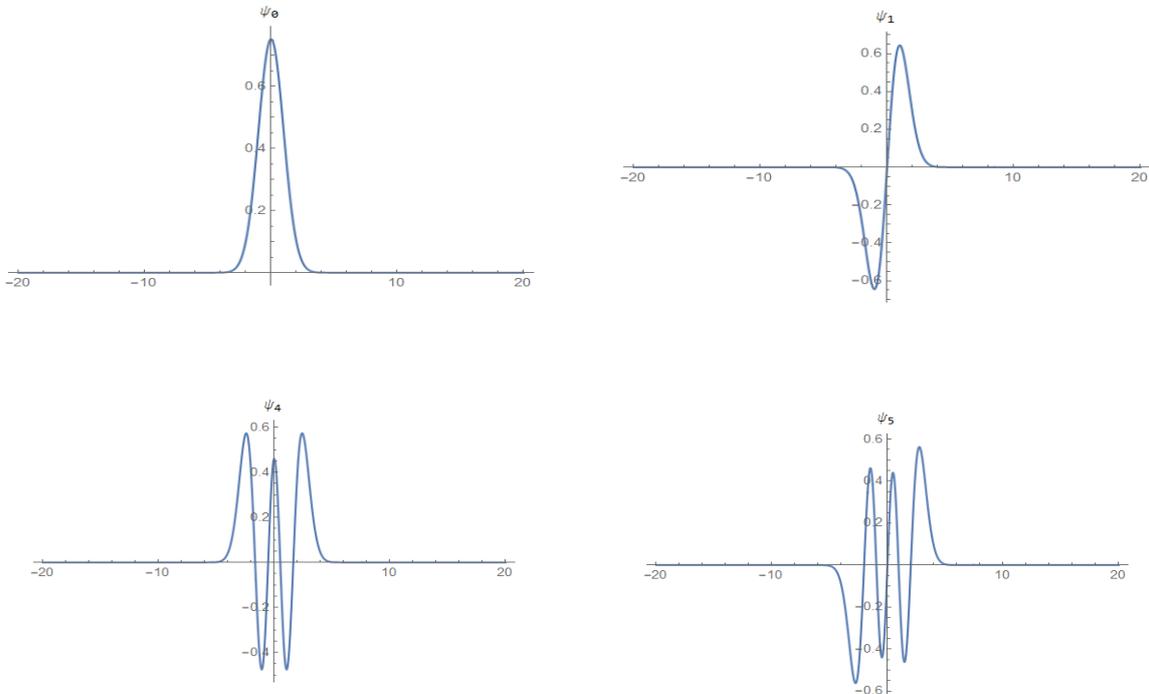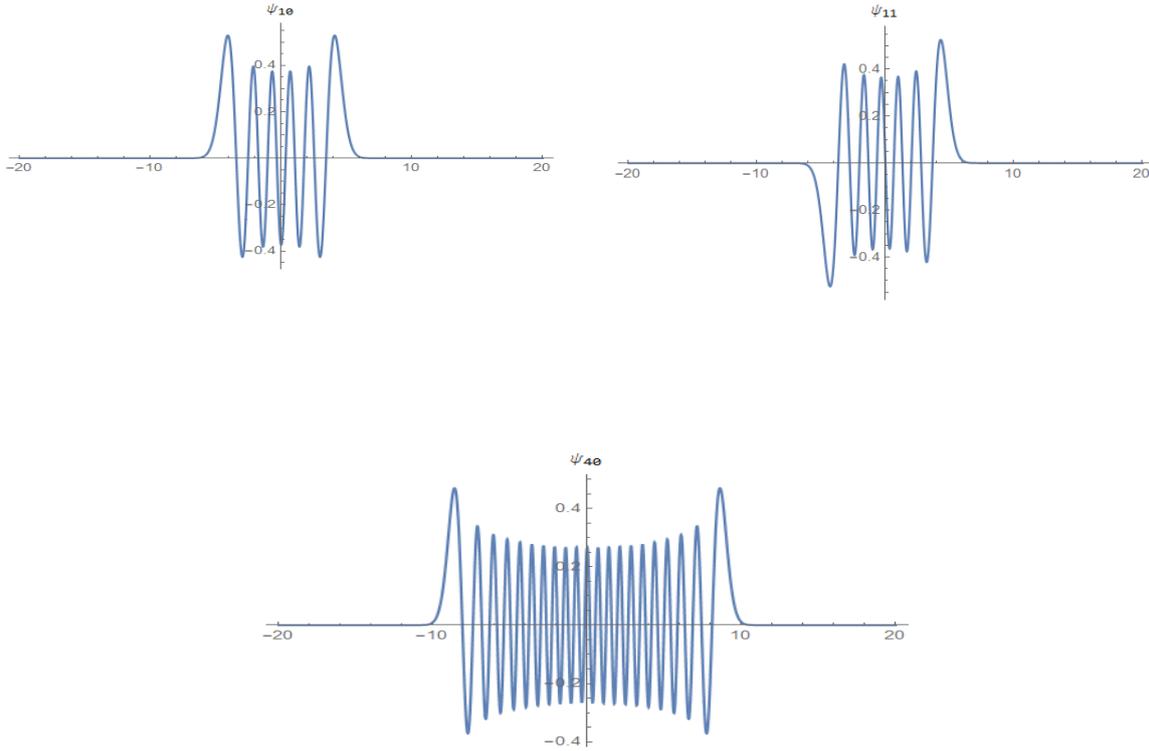
Figure 3: Energy eigenfunctions of the Linear Harmonic Oscillator

3 Angular Momentum Algebra

First we describe a short section introducing angular momentum algebra for readers who are new to this.

3.1 Introduction

- $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ is the angular momentum with respect to some origin.Converting these classical symbols into operators and evaluating the cross product we get L_x, L_y, L_z or th orbital angular momentum operators in the X,Y,Z directions respectively as

$$
\begin{aligned}
L_x &= yp_z - zp_y & (25)\\
L_y &= zp_x - xp_z & (26)\\
L_z &= xp_y - yp_x & (27)
\end{aligned}
$$

- They satisfy the commutation relations(using results of section 2.4.2)

$$
[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y \tag{28}
$$

or in short

$$
[L_i, L_j] = i\hbar \epsilon_{ijk} L_k \tag{29}
$$

(The ϵ_{ijk} is just the Levi-Civita symbol. It belongs to the set $\{-1, 0, 1\}$. If any of the indices are equal it becomes zero. If all indices are unequal and two of them are interchanged then it switches sign, interchanging twice makes it revert back. By convention $\epsilon_{123} = 1$)

- $[L^2, L] = 0$ where $L = L_x + L_y + L_z$.

This is an extremely important relation because it means we can find simultaneous eigenfunctions for L^2 and L_z(say).
These eigenfunctions are given by Spherical Harmonics represented by $Y_{lm}(\theta, \phi)$.

3.2 Eigenvalues of L^2 and L_z

Let the simultaneous eigenfunctions be called f for now. We then have

$$L^2 f = \eta f \tag{30}$$
$$L_z f = \mu f \tag{31}$$

Later on we'll use the standard notation Y instead of f.

Now introduce L_+ and L_- as

$$L_\pm = L_x \pm iL_y \tag{32}$$

We can prove that

$$[L_z, L_\pm] = \pm\hbar L_\pm$$

This is very similar to 21.

Therefore, L_+ raises the value of L_z by $\hbar$ while L_- lowers the value of L_z by $\hbar$ that is

$$L_z(L_\pm f) = (\mu \pm \hbar)(L_\pm f) \tag{33}$$

For a given value of η we again obtain a "ladder" of states. This ladder must have a top rung f_t because the z-component cannot exceed the total angular momentum's value.

$$L_+ f_t = 0$$

Let $\hbar l$ be the eigenvalue of L_z on the top rung.

$$L_z f_t = \hbar l f_t, \quad L^2 f_t = \eta f_t \tag{34}$$

Verifying that

$$L_\pm L_\mp = L^2 - L_z^2 \mp i(i\hbar L_z) \tag{35}$$

we can deduce

$$L^2 f_t = (L_- L_+ + L_z^2 + \hbar L_z)f_t = (0 + \hbar^2 l^2 + \hbar^2 l)f_t = \hbar^2 l(l+1)f_t \tag{36}$$

Therefore,

$$\eta = \hbar^2 l(l+1) \tag{37}$$

For the same reason that a top rung exists, we have a bottom rung for which

$$L_- f_b = 0$$

.

Let $\hbar l^*$ be the eigenvalue of L_z at the bottom rung. From (35) we can similarly deduce that

$$\eta = \hbar^2 l^*(l^* - 1) \tag{38}$$

From (37) and (38) we see that either $l^* = l + 1$ (which is clearly wrong since bottom rung would be higher than top) or else

$$l^* = -l \tag{39}$$

We realize that the eigenvalues $m\hbar$ of L_z vary with m going from $-l$ to l in integer steps. Let the number of steps be N.

$$l = -l + N \implies l = \frac{N}{2} \tag{40}$$

Observe that l can be *an integer or half integer*.

$$l = 0, \ \frac{1}{2}, \ 1, \ \frac{3}{2}, ... \tag{41}$$

For a given value of l there are $2l + 1$ values of m or $2l + 1$ "rungs" on the ladder!

Also, notice that the eigenfunctions (which we will derive in the section 4) are characterised by l and m.

$$\boxed{L_z f_l^m = \hbar m f_l^m, \quad L^2 f_l^m = \hbar^2 l(l+1)f_l^m} \tag{42}$$

13

3.3   Group Representations and SO(3)

This section is for advanced readers and can be omitted.

When you think angular momentum, you naturally also think of rotations. Maybe you think of a classical object spinning about its axis in empty space. Angular momentum classically as well as quantum mechanically is considered to be the *generator* of rotations.

Once we enter the realm of quantum mechanics, there comes the need to specify not just the orbital angular momentum of a particle, but also its spin angular momentum. We conveniently choose not to deal with spin of the particle in this text, though the algebra that spin operator follows is similar and is introduced in section 6. Before proceeding further, I suggest to read up on what 'groups' and 'homomorphisms' are in mathematics.

You must have studied rotations in 3-dimensions, where the coordinates (x, y, z) are transformed into a new set (x', y', z'). This transformation is produced by an appropriate 3×3 matrix determined by the rotation in question.

As an example consider a rotation about the z-axis by an angle θ which leaves the z coordinate unchanged. Simple calculations tell us

$$
\begin{aligned}
x' &= x\cos\theta - y\sin\theta \\
y' &= y\cos\theta + x\sin\theta \\
z' &= z
\end{aligned}
\tag{43}
$$

which is the same as saying,

$$
\begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}
$$

Therefore, a physical rotation about the z-axis through an angle θ is *represented* by the rotation matrix

$$
R(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}
\tag{44}
$$

For the particular angles 0, $2\pi/3$ and $4\pi/3$ we obtain the matrices $D(e)$, $D(g)$, $D(g^2)$ which *represent* elements of the cyclic group C_3.

$$
\begin{aligned}
D(e) = R(0) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
D(g) = R(2\pi/3) &= \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
D(g^2) = R(4\pi/3) &= \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\end{aligned}
\tag{45}
$$

One of the crucial properties that makes these matrices a 'representation' is $D(g^2) = (D(g))^2$. This should immediately remind you of homomorphisms!

Definition: A representation of dimension n of the abstract group G is defined as a **homomorphism** given by $D : G \mapsto GL(n, \mathbb{C})$, the group of non-singular $n \times n$ matrices with complex entries.

In other words, it is a mapping $g \mapsto D(g)$ preserving the group structure:

$$
D(g_1 g_2) = D(g_1)D(g_2)
\tag{46}
$$

Now you should be able to guess what equation 44 means. These rotation matrices belong to a more restricted 'subgroup' of $GL(n, \mathbb{C})$. Restricted because all the entries x, y, z are real while the matrix itself is orthogonal since the rotation leaves invariant the length of the vectors. Also, the matrices have a determinant equal to +1. The technical name of this group is $SO(3)$ or the special orthogonal group in three dimensions.

Notice that $SO(3)$ is not finite unlike C_3. It not only consists of rotations of finite order i.e. through an angle $2\pi/n$, but also of 'infinitesimal' rotations. It is the group of all proper rotations in 3-dimensions i.e. rotations through any arbitrary angle about an axis in the direction of some unit vector $\hat{n}$ (in 44 it was the

z-direction). $SO(3)$ therefore, belongs to the family of continuous or Lie groups.

For Lie groups, it is also useful to talk of their *infinitesimal generators* which form a structure called *Lie Algebra*. This is how the angular momentum operators L_x, L_y, L_z or the generators satisfying commutation relations arise in the context of the rotation group $SO(3)$.

Infinitesimal Generator(L_z) The generators of continuous (Lie) groups in a general representation D are introduced by elements infinitesimally near the identity element. For small θ we have a Taylor expansion that looks like

$$D(\theta) = \mathbb{I} - i\theta X + O(\theta^2) \tag{47}$$

which is equivalent to,

$$-iX = \left.\frac{dD(\theta)}{d\theta}\right|_{\theta=0} \tag{48}$$

X here is the *infinitesimal generator* and the i has been included in the expansion so that if the representation is unitary, the X will be a Hermitian operator.

On substituting $D(\theta) = R(\theta)$ (refer to 44) and evaluating at $\theta = 0$ we get

$$-iX_3 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{49}$$

The use of index 3 is to denote the z-direction.

Note: The most general definition of orbital angular momentum is as the generator of *spatial* rotations and for dimensional reasons we have

$$L_z = \hbar X_3 \tag{50}$$

We cannot stop here because two other generators exist for the x and y directions. You could use the same definitions as 47 to obtain X_1 and X_2, but to calculate L_x and L_y, I suggest the use of raising and lowering operators (a good exercise for advanced readers). We get

$$-iX_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \tag{51}$$

$$-iX_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \tag{52}$$

The structure formed by the infinitesimal generators X_i is known as an algebra. This algebra is a vector space since (complex) linear combinations of the X_i are generators too. When we also consider the binary operation of the commutator bracket i.e. $[X, Y]$ which satisfies the Jacobi Identity, it is called a Lie Algebra. The generators on the other hand satisfy 'commutation' relations which we have already come across. Simple but satisfying calculations tell us

$$-[X_1, X_2] = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = -iX_3$$
$$\implies [X_1, X_2] = iX_3 \tag{53}$$

Similarly for other cyclic permutations which we can summarize neatly as

$$[X_i, X_j] = i\epsilon_{ijk}X_k \tag{54}$$

For further reading refer to *Groups, Representations and Physics* by H.F. Jones. Most of the theory presented here has been borrowed from Chapters 3 and 6 of the book.

4 Spherical Harmonics

Spherical harmonics are defined as the eigenfunctions of the angular part of the Laplacian in three dimensions. The Laplacian appears frequently in physical equations (like the **Schrödinger equation**, the Heat equation, the Poisson equation,..) and therefore, the Spherical Harmonics are important for representing solutions that have physical significance.

We will study their most notable application in representing orbitals of the H-atom in section 5 while this section will cover solving for them as simultaneous eigenfunctions of the familiar operators L and L^2.

4.1 Operators in the Spherical Polar Coordinates

The calculations are a bit involved so the reader has to patiently solve for the relations.

- Some familiar relations:

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

  $\tan \theta = \frac{x^2 + y^2}{z^2}$

  $\tan \phi = \frac{y}{x}$

- Find $\frac{\partial r}{\partial x}, \frac{\partial \theta}{\partial x}, \frac{\partial \phi}{\partial x}, \frac{\partial r}{\partial y}, ...$ using the equations above.

- $L_z \psi(r, \theta, \phi) = i\hbar [x \frac{\partial \psi}{\partial y} - y \frac{\partial \psi}{\partial x}]$

  To convert to spherical coordinates we just split the partial derivatives.

  For example $\frac{\partial \psi}{\partial y} = \frac{\partial \psi}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial \psi}{\partial \theta}\frac{\partial \theta}{\partial y} + \frac{\partial \psi}{\partial \phi}\frac{\partial \phi}{\partial y}$ and so on.

  Similarly, for L_x, L_y.

We get

$$L_z = -i\hbar \frac{\partial}{\partial \phi} \tag{55}$$

$$L_y = i\hbar(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi}) \tag{56}$$

$$L_x = i\hbar(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi}) \tag{57}$$

- Finally solving for L^2

$$L^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2 [\frac{1}{\sin \theta}\frac{\partial}{\partial \theta}(\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta}\frac{\partial^2}{\partial^2 \phi^2}] \tag{58}$$

4.2 Eigenfunctions of L^2

To solve

$$L^2 Y(\theta, \phi) = \lambda \hbar^2 Y(\theta, \phi) \tag{59}$$

Y is a function of θ and ϕ only because operator L^2 does not contain terms in r!

Substituting 58 in 59 we get

$$\frac{1}{\sin \theta}\frac{\partial}{\partial \theta}(\sin \theta \frac{\partial Y}{\partial \theta}) + \frac{1}{\sin^2 \theta}\frac{\partial^2 Y}{\partial^2 \phi^2} + \lambda Y(\theta, \phi) = 0 \tag{60}$$

We try the method of separation of variables.

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

$$\therefore \frac{\sin^2 \theta}{\Theta}[\frac{1}{\sin \theta}\frac{\partial}{\partial \theta}(\sin \theta \frac{d\Theta}{d\theta}) + \lambda \Theta(\theta)] = -\frac{1}{\Phi(\phi)}\frac{d^2\Phi}{d\phi^2} \tag{61}$$

4.2.1 Solving for $\Phi(\phi)$

$$-\frac{1}{\Phi(\phi)}\frac{d^2\Phi}{d\phi^2} = m^2 \implies \Phi(\phi) \sim e^{im\phi}$$

For the wave function to be single valued(using concepts from complex analysis),

$$\Phi(\phi + 2\pi) = \Phi(\phi) \implies e^{2\pi mi} = 1$$

Therefore,

$$m = 0, \pm 1, \pm 2, ...$$

Normalization of $\Phi(\phi)$ gives

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi} \tag{62}$$

4.2.2 Solving for $\Theta(\theta)$

$$\frac{\sin^2\theta}{\Theta(\theta)}[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{d\Theta}{d\theta}) + \lambda\Theta(\theta)] = m^2$$
$$\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}(\sin\theta\frac{d\Theta}{d\theta}) + (\lambda - \frac{m^2}{\sin^2\theta})\Theta(\theta) = 0 \tag{63}$$

We make a change of variables $\cos\theta = \mu$ and $\Theta(\theta) = F(\mu)$. 63 becomes

$$\frac{d}{d\mu}[(1 - \mu^2)\frac{dF(\mu)}{d\mu}] + [\lambda - \frac{m^2}{1-\mu^2}]F(\mu) = 0 \tag{64}$$

Case I: m=0

$$\boxed{(1-\mu^2)\frac{d^2F(\mu)}{d\mu^2} - 2\mu\frac{dF(\mu)}{d\mu} + \lambda F(\mu) = 0} \tag{65}$$

This differential equation is called the **Legendre equation**. Since $\mu = 0$ is an ordinary point of this equation we can try power series solution of the form

$$F(\mu) = \sum_{k=0}^{\infty} a_k\mu^k$$

Substituting the power series into 65 we get

$$\sum_{k=0}^{\infty}[(k+1)(k+2)a_{k+2} + \lambda - k(k+1)a_k]\mu^k = 0$$

This equation is satisfied if the coefficient of each power of μ vanishes. We therefore get the recursion relation

$$a_{k+2} = \frac{k(k+1) - \lambda}{(k+1)(k+2)}a_k \tag{66}$$

Therefore we get

$$F(\mu) = a_0[1 + \frac{a_2}{a_0}\mu^2 + \frac{a_4}{a_0}\mu^4 + ...] + a_1[\mu + \frac{a_3}{a_1} + ...] \tag{67}$$

Note that $\lim_{k\to\infty}\frac{a_{k+2}}{a_k} = 1$ and therefore at $\mu = \pm 1$ the sequence clearly diverges. The series has to terminate.

Let l be the highest power of the polynomial then

$$\lambda = l(l+1) \tag{68}$$

as one obtained in section 3.2, but with a different method.

Now notice that for $\lambda = 0, 2, 6, ...$ one of the series will terminate at $a_l\mu^l$. For an even l, the odd series will **not** terminate and we set $a_1 = 0$ and vice versa. The two polynomial solutions (even and odd) are then called **independent** solutions.

Let $F(\mu) = P_l(\mu)$ and we take $l = 4$ as an example.

$$P_4(\mu) = a_0[1 - 10\mu^2 + \frac{70}{6}\mu^4]$$

a_0 is always chosen such that $\mathbf{P_l(1)} = \mathbf{1}$ and in the case of $l = 4$ comes out to be $\frac{3}{8}$.

Therefore,

$$\Theta_l(\theta) = N_\theta P_l(\cos\theta) \tag{69}$$

where the function is yet to be normalized.

4.2.3 Legendre Polynomials

$$
\begin{aligned}
P_0(\mu) &= 1 \\
P_1(\mu) &= \mu \\
P_2(\mu) &= \frac{1}{2}(3\mu^2 - 1) \\
P_3(\mu) &= \frac{1}{2}(5\mu^3 - 3\mu)
\end{aligned}
\tag{70}
$$

and so on.
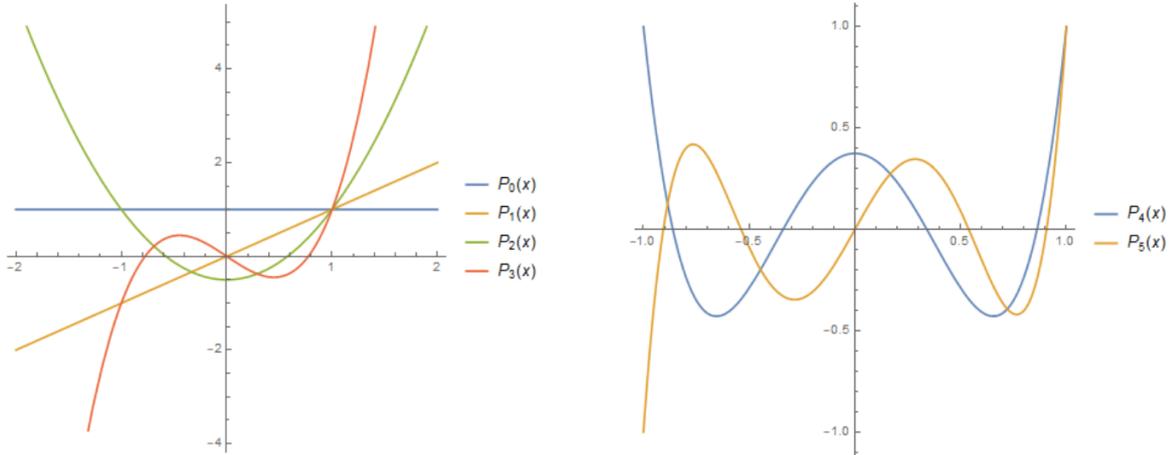
Figure 4: Legendre Polynomials

Some other properties of Legendre Polynomials are enlisted.

1. **Orthonormality** $\int_{-1}^{+1} P_l(\mu)P_{l'}(\mu)d\mu = \frac{2}{2l+1}\delta_{ll'}$

2. **Recurrence Relation** $P_l(\mu) = \frac{2l-1}{l}\mu P_{l-1}(\mu) - \frac{l-1}{l}P_{l-2}(\mu)$

3. **Completeness** Given any piecewise continuous function $f(x)$ with finitely many discontinuities in the interval $[-1, 1]$, the sequence of sums

$$f_n(x) = \sum_{l=0}^{n} a_l P_l(x)$$

converges in the mean to $f(x)$ as $n \to \infty$ provided we take

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

Our solution to 60 can now be written with subscripts as

$$Y_{lm}(\theta, \phi) = \Theta_l(\theta)\Phi_m(\phi) \tag{71}$$

and we now know

$$Y_{l,0} = \frac{1}{\sqrt{2\pi}}\Theta_l(\theta) = \left(\frac{2l+1}{4\pi}\right)^{\frac{1}{2}} P_l(\cos\theta)$$

where the normalization constant for $\Theta_l(\theta)$ comes from the orthonormality condition for Legendre Polynomials.

Case II: m $\neq$ 0

Let us define the *Associated Legendre function* $P_l^{|m|}(\mu)$ of degree $l(l = 0, 1, 2, ...)$ and order $|m| \leq l$ by the relation

$$P_l^{|m|}(\mu) = (1 - \mu^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{d\mu^{|m|}} P_l(\mu) \qquad |m| = 0, 1, 2, .. \tag{72}$$

Note for $m = 0$ we have $P_l^0(\mu) = P_l(\mu)$.

Differentiating m times the Legendre equation by substituting $\lambda = l(l + 1)$ we find that $P_l^{|m|}(\mu)$ satisfies the differential equation

$$[(1 - \mu^2)\frac{d^2}{d\mu^2} - 2\mu\frac{d}{d\mu} + l(l+1) - \frac{m^2}{1 - \mu^2}]P_l^{|m|}(\mu) = 0 \tag{73}$$

which is the same as 64.

Allowed values of m: Since $P_l(\mu)$ is of degree l, for $m > l$ we have $P_l^{|m|}(\mu) = 0$. Therefore, for a fixed value of l we get $(2l + 1)$ different values for m.

$$\boxed{m = -l, -l + 1, ..., l} \tag{74}$$

Some other properties of Associated Legendre Polynomials:

1. **Orthonormality** $\int_{-1}^{1} P_l^m(x)P_{l'}^m(x)dx = \frac{2(l+m)!}{(2l+1)(l-m)!}\delta_{ll'}$

2. **Completeness** They form a complete set too!

Spherical Harmonics:The Final Expression

We finally obtain the eigenfunctions of L^2 and L_z for non-negative m as

$$Y_{lm}(\theta, \phi) = (-1)^m [\frac{(2l+1)(l-m)!}{4\pi(l+m)!}]^{\frac{1}{2}} P_l^m(\mu)e^{im\phi} \tag{75}$$

and for negative m as

$$Y_{lm}(\theta, \phi) = (-1)^m Y_{l,-m}(\theta, \phi) \tag{76}$$

The phase convention adopted is the usual one.

$Y_{lm}(\theta, \phi)$ also form a complete set.

Illustrations of the real part of Spherical Harmonics for $l = 2$ using the 'SphericalPlot3D' function on mathematica are given on the next page.
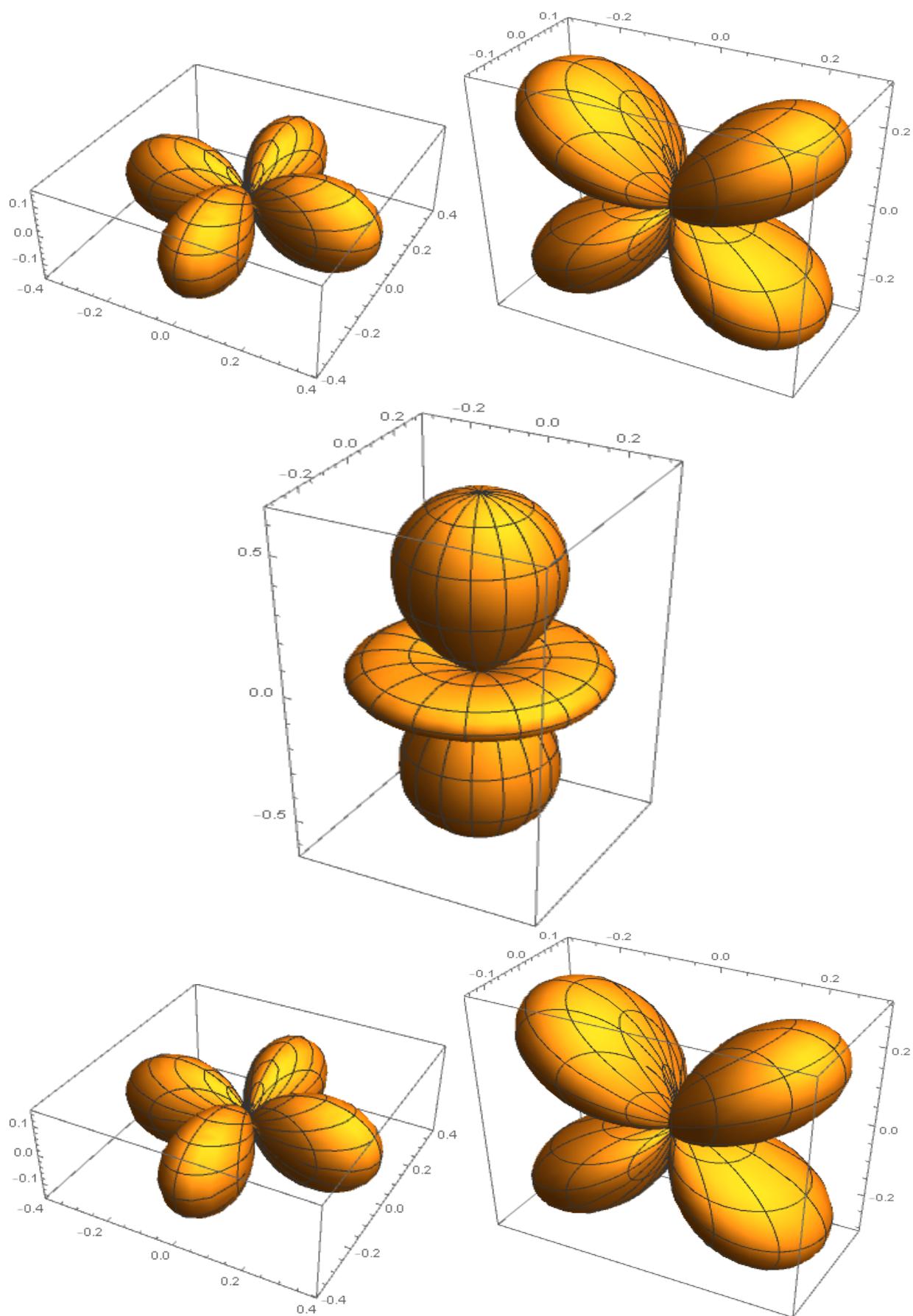
Figure 5: Real Spherical Harmonics for l=2
(We have clockwise from left: $m = -2, m = -1, m = 0, m = 1$ and $m = 2$)

5 The Hydrogen Atom

5.1 Central Potentials and the Schrödinger Equation

The nucleus of a hydrogen atom and the electron orbiting it interact by means of the Coulomb potential

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{77}$$

For a two-body problem like the Hydrogen atom problem, when we work with the centre of mass coordinates the Hamiltonian becomes

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{78}$$

where p is the relative momentum and μ is the reduced mass. r is of course the relative distance between the electron and the proton.

5.1.1 Hamiltonian and Commutators

Before just using 78 in our familiar time-independent Schrödinger Equation, we'll consider three things.

1. 78 when used in $H\psi = E\psi$, gives $\psi(\boldsymbol{r})$ which describes the internal motion of the atom and not how the hydrogen atom is moving as a whole.

$$\psi_{in}(\boldsymbol{r}, \boldsymbol{R}) = \psi(\boldsymbol{r})\Phi(\boldsymbol{R})$$

   $\Phi(\boldsymbol{R})$ which describes how the centre of mass is moving (where $\boldsymbol{R}$ represents the position of centre of mass) completes the time-independent Schrödinger equation's solution. $\Phi(\boldsymbol{R})$ turns out to be a **plane wave** describing the uniform translational motion of the Hydrogen Atom.

   (To understand where $\Phi(\boldsymbol{R})$ came from look at the derivation for 78)

2. $V(r)$ from before is Coulombic as well as **central** (i.e potential depends only on the **magnitude** of position vector $\mathbf{r}$) and therefore we can separate the Schrödinger equation in spherical polar coordinates.

   Using Hamiltonian in SPC,

$$H = \frac{-\hbar^2}{2\mu}[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) - \frac{L^2}{\hbar^2 r^2}]\,\psi(\boldsymbol{r}) + V(r,\theta,\phi)\,\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{79}$$

   This comes from

$$H = \frac{-\hbar^2}{2\mu}\nabla^2 + V(r,\theta,\phi) \tag{80}$$

$$\implies H = \frac{-\hbar^2}{2\mu}[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\phi^2}] + V(r,\theta,\phi) \tag{81}$$

   L^2 in SPC was talked about in the Spherical Harmonics section and recollect that it only depended on (θ, ϕ) and not on r. Also $V(r, \theta, \phi) = V(r)$. Therefore, 79 has solutions of the separable form

$$\boxed{\psi(\mathbf{r}) = R(r)Y(\theta, \phi)} \tag{82}$$

3. The Hamiltonian clearly commutes with L and L^2 i.e.

$$[H, L] = [H, L^2] = 0 \tag{83}$$

   Therefore we can find simultaneous eigenfunctions of H, L_z, L^2. In other words solutions to 79 will be eigenfunctions of L_z and L^2 too. We know that $Y_{lm}(\theta, \phi)$ are simultaneous eigenfunctions of L^2 and L_z. Therefore, 82 must look like

$$\psi_{Elm}(r) = R_{Elm}(r)Y_{lm}(\theta, \phi) \tag{84}$$

   $R(r)$ needs to be found and can therefore depend on all of E, l, m.

First encounter with V_{eff}: Substituting 84 into 79 and using $L^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi)$,

$$[(\frac{-\hbar^2}{2\mu}\frac{d^2}{dr^2} + 2\frac{d}{dr}) + V_{eff}(r)] R_{El}(r) = ER_{El}(r) \tag{85}$$

where

$$V_{eff}(r) = V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \tag{86}$$

Note: There is no dependence of R on m so we dropped that subscript.

5.1.2 Schrödinger Equation for the Hydrogen Atom

$$[-\frac{\hbar^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 r}]\psi(r) = E\psi(r) \tag{87}$$

Since the Coulomb potential is central, solutions of the above equation take the form

$$\psi_{Elm}(r) = R_{El}(r)Y_{lm}(\theta, \phi) \tag{88}$$

Taking

$$\boxed{u_{El}(r) = rR_{El}(r)} \tag{89}$$

we get

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{d^2 u_{El}(r)}{dr^2} + V_{eff}(r)\, u_{El}(r) = Eu_{El}(r)} \tag{90}$$

where again

$$V_{eff}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \tag{91}$$

Note that 90 is very similar to the 1-D time independent Schrödinger Equation.

5.1.3 Behaviour of $u_{El}(r)$ at the origin

Since $R_{El}(r) = r^{-1}u_{El}(r)$, for the radial function to be finite at the origin we must have

$$u_{El}(0) = 0$$

Therefore, for $u_{El}(r)$ near origin we have

$$u_{El}(r) \sim r^s, \quad s > 0$$

Substituting in 61 we get

$$\frac{\hbar^2}{2\mu}s(s-1) + \frac{l(l+1)\hbar^2}{2\mu} + V(r)r^2 = Er^2$$

As $r \to 0$ we get

$$s(s-1) = l(l+1)$$

.
Therefore, $\boxed{u_{El}(r) \sim r^{l+1}}$ near the origin.

Limiting Behaviour   Rewriting 90

$$\frac{d^2 u_{El}(r)}{dr^2} + \frac{2\mu}{\hbar^2}[E - V_{eff}(r)]u_{El}(r) = 0 \tag{92}$$

$V_{eff} \to 0$ when $r \to \infty$ and $u_{El}(r)$ will have oscillatory behaviour at infinity for $E > 0$. Therefore these are **scattering** or unbound states.
$u_{El}(r)$ will be an acceptable eigenfunction for any $E > 0$ and we have a continuous spectrum for $E > 0$.

5.2 Solutions for Bound States

Bound states here mean $E < 0$. We know $u_{El}(0) = 0$. Introducing dimensionless quantities

$$\rho = \left(-\frac{8\mu E}{\hbar^2}\right)^{\frac{1}{2}} r \tag{93}$$

$$\lambda = \frac{Ze^2}{4\pi\epsilon_0 \hbar}\left(-\frac{\mu}{2E}\right)^{\frac{1}{2}} \tag{94}$$

Using λ and ρ in 90 we get

$$[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}]u_{El}(\rho) = 0 \tag{95}$$

Asymptotic Analysis   As $\rho \to \infty$, $\rho^{-1}, \rho^{-2} \to 0$ and we have

$$[\frac{d^2}{d\rho^2} - \frac{1}{4}]u_{El}(\rho) = 0$$

Therefore $u_{El}(\rho) \sim e^{\pm\frac{\rho}{2}}$. Discarding $+\frac{\rho}{2}$ we have

$$u_{El}(\rho) = f(\rho)e^{-\frac{\rho}{2}} \tag{96}$$

where $f(\rho)$ does not affect the asymptotic behaviour of $u_{El}(\rho)$.
Substituting 96 into 95 we get

$$[\frac{d^2}{d\rho^2} - \frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho}]f(\rho) = 0 \tag{97}$$

Series expansion of $f(\rho)$

$$f(\rho) = \rho^{l+1}g(\rho) \tag{98}$$

where

$$g(\rho) = \sum_{k=0}^{\infty} c_k \rho^k$$

Putting 98 into 97 we get

$$[\rho\frac{d^2}{d\rho^2} + (2l + 2 - \rho)\frac{d}{d\rho} + (\lambda - l - 1)]g(\rho) = 0 \tag{99}$$

Using the expression for $g(\rho)$ we get

$$\sum_{k=0}^{\infty} [k(k+1) + (2l+2)(k+1)]c_{k+1} + (\lambda - l - 1)c_k \rho^k = 0$$

and hence the recursion relation

$$c_{k+1} = \frac{k + l + 1 - \lambda}{(k+1)(k+2l+2)}c_k \tag{100}$$

For large k, $\frac{c_{k+1}}{c_k} \sim \frac{1}{k}$ which are the coefficients of Taylor expansion of $\rho^p e^\rho$ which makes $u_{El}(\rho) \sim \rho^{l+1+p}e^{\frac{\rho}{2}}$ an unacceptable solution(p is some constant).
Therefore, series must terminate and $g(\rho)$ becomes a polynomial in ρ.

5.2.1   The Principal Quantum Number

Let the highest power of ρ appearing in $g(\rho)$ be n_r or the *radial quantum number* where $n_r = 0, 1, 2, ...$(since $k = 0, 1, 2, ..$). Therefore

$$c_{n_r+1} = 0 \implies \lambda = n_r + l + 1 \tag{101}$$

We introduce the **principal quantum number** n as

$$\boxed{n = n_r + l + 1} \qquad n = 1, 2, 3... \tag{102}$$

We know that $l = 0, 1, 2, ...$. But now that we have a dependence of l on n and n_r we have an upper bound (for $n_r = 0$).

$$\boxed{l = 0, 1, 2, ..., n-1} \tag{103}$$

5.2.2 Energy Eigenvalues

Putting n in place of λ

$$n = \frac{Ze^2}{4\pi\epsilon_0\hbar}\left(-\frac{\mu}{2E}\right)$$

$$E_n = \frac{\mu}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^2} \tag{104}$$

$$= -\frac{e^2}{4\pi\epsilon_0}a_\mu\frac{Z^2}{2n^2} \tag{105}$$

where

$$a_\mu = \frac{(4\pi\epsilon_0)\hbar^2}{\mu e^2} = \frac{m_e}{\mu}a_0$$

is the **modified Bohr radius** while a_0 is the Bohr radius.

From 102 we have n taking all integral values from 1 to ∞ and therefore, we have the bound state energy spectrum extending from E_1 (which is a finite non-zero value) to zero. Relate this fact with the magnitude of Coulomb potential falling of slowly at larger r.

The energy eigenvalues also depend only on the principal quantum number n and are therefore, are degenerate with respect to quantum numbers l and m. For each n, the orbital angular momentum quantum number may take on values 0,1,...,n-1 (refer 103), and for each value of l the magnetic quantum number m may take $(2l+1)$ possible values $-l, -l+1, ..., l$ (refer 74). The degree of degeneracy of E_n corresponding to eigenfunctions which are solutions of 87 is therefore given by

$$\sum_{l=0}^{n-1}(2l+1) = 2\frac{n(n-1)}{2} + n = n^2 \tag{106}$$

Another interesting point to be noted is that degeneracy with respect to quantum number m is present for any central potential $V(r)$ (as concluded at the end of section 5.1.1) but degeneracy with respect to l is characteristic of Coulomb potential.

5.2.3 Eigenfunctions for Bound States

Equation 99 is

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

We know the solutions to this equation are polynomials. To figure out how these polynomials look we first define the q th Laguerre Polynomial as

$$L_q(x) = e^x(\frac{d}{dx})^q(e^{-x}x^q) \tag{107}$$

which satisfies the differential equation

$$[\rho\frac{d^2}{d\rho^2} + (1-\rho)\frac{d}{d\rho} + q]L_q(\rho) = 0 \tag{108}$$

Define *Associated Laguerre Polynomials* as

$$L_q^p(\rho) = \frac{d^p}{d\rho^p}L_q(\rho) \tag{109}$$

Differentiating 108 p times, we find that L_q^p satisfies the differential equation

$$[\rho\frac{d^2}{d\rho^2} + (p+1-\rho)\frac{d}{d\rho} + (q-p)]L_q^p = 0$$

Comparing with equation 99 we realize that

$$g(\rho) = L_{n+l}^{2l+1}(\rho) \tag{110}$$

where $p = 2l+1$ and $q = \lambda - l - 1 + 2l + 1 = \lambda + l$.

This makes sense since the highest power of the Associated Laguerre Polynomial then becomes

$$q - p = \lambda - l - 1 = n_r$$

which agrees with our foregoing discussion.

5.2.4 Laguerre and Associated Laguerre Polynomials
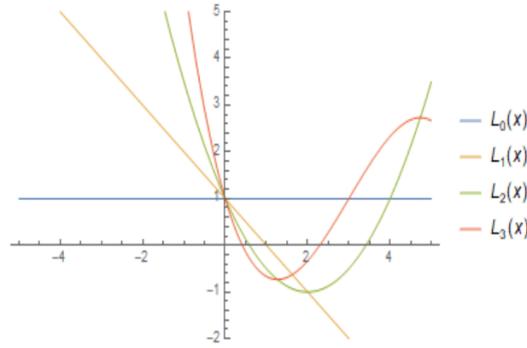
Figure 6: Laguerre Polynomials

For Laguerre Polynomials:

1 Generating Function Laguerre Polynomials may also be obtained using

$$U(\rho, s) = \frac{e^{\frac{-\rho s}{1-s}}}{1-s} = \sum_{q=0}^{\infty} \frac{L_q(\rho)}{q!} s^q, \quad |s| < 1$$

2 Recursion Relation Differentiating U with respect to s yields

$$L_{q+1}(\rho) - (\rho - 1 - 2q)L_q(\rho) + q^2 L_{q-1}(\rho) = 0^{**} \tag{111}$$

3 Orthogonality The polynomials are orthogonal with respect to the weight function(measure) $w(x) = e^{-x}$. Thus, we have

$$\int_0^\infty e^{-x} L_n(x) L_m(x) dx = 0, \quad m \neq n$$

For Associated Laguerre Polynomials:

1 Generating Function for Associated Laguerre Polynomials may be obtained by differentiating $U(\rho, s)$ p times with respect to ρ

$$U_p(\rho, s) = (-s)^p \frac{e^{\frac{-\rho s}{1-s}}}{(1-s)^p} = \sum_{q=0}^{\infty} \frac{L_q^p(\rho)}{q!} s^q, \quad |s| < 1$$

2 Orthogonality The polynomials are orthogonal with respect to the weight function(measure) $w(x) = x^p e^{-x}$. Thus, we have

$$\int_0^\infty x^p e^{-x} L_m^p L_n^p dx = 0, \quad m \neq n$$

3 Relation to Hermite Polynomials (Here Generalized Laguerre Polynomials $L_n^{(\alpha)}$ have been used)

$$\begin{array}{rcl} H_{2n}(x) & = & (-1)^n 2^{2n} n! L_n^{(-1/2)}(x^2) \\ H_{2n+1}(x) & = & (-1)^n 2^{2n+1} n! x L_n^{(1/2)}(x^2) \end{array} \tag{112}$$

5.3 The Radial Functions: Finally!

We can now to write

$$R_{nl} = N e^{\frac{-\rho}{2}} \rho^l L_{n+l}^{2l+1}(\rho) \tag{113}$$

The normalization constant can be determined using the normalization condition and the generating function for Associated Laguerre polynomials. It comes out as

$$N_{nl} = [\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}]^{\frac{1}{2}}$$

(**Note:** Here we have *Associated Laguerre Polynomials* according to our definition in 109)
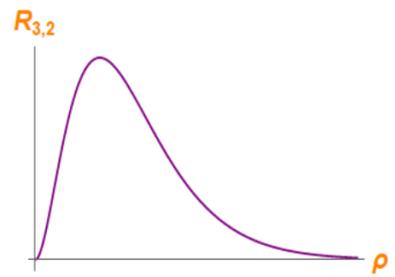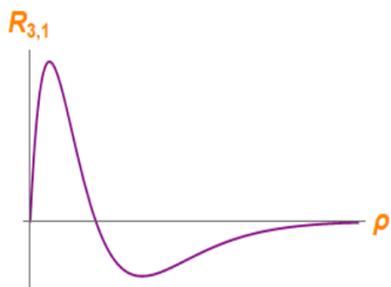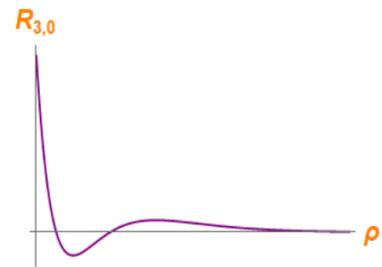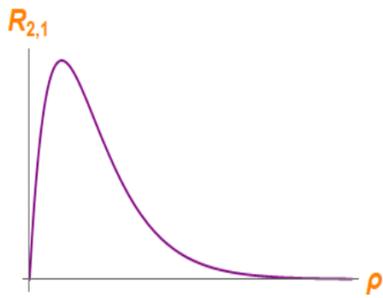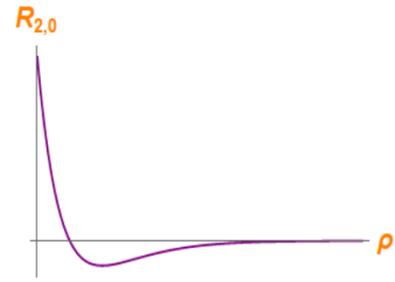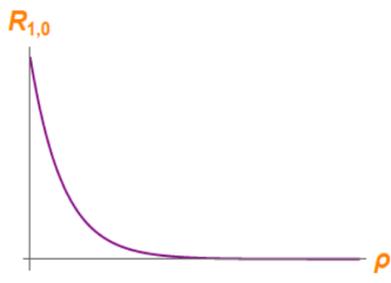
Figure 7: Radial Function Shapes of Hydrogen Atom

5.4 The Radial Distribution Functions
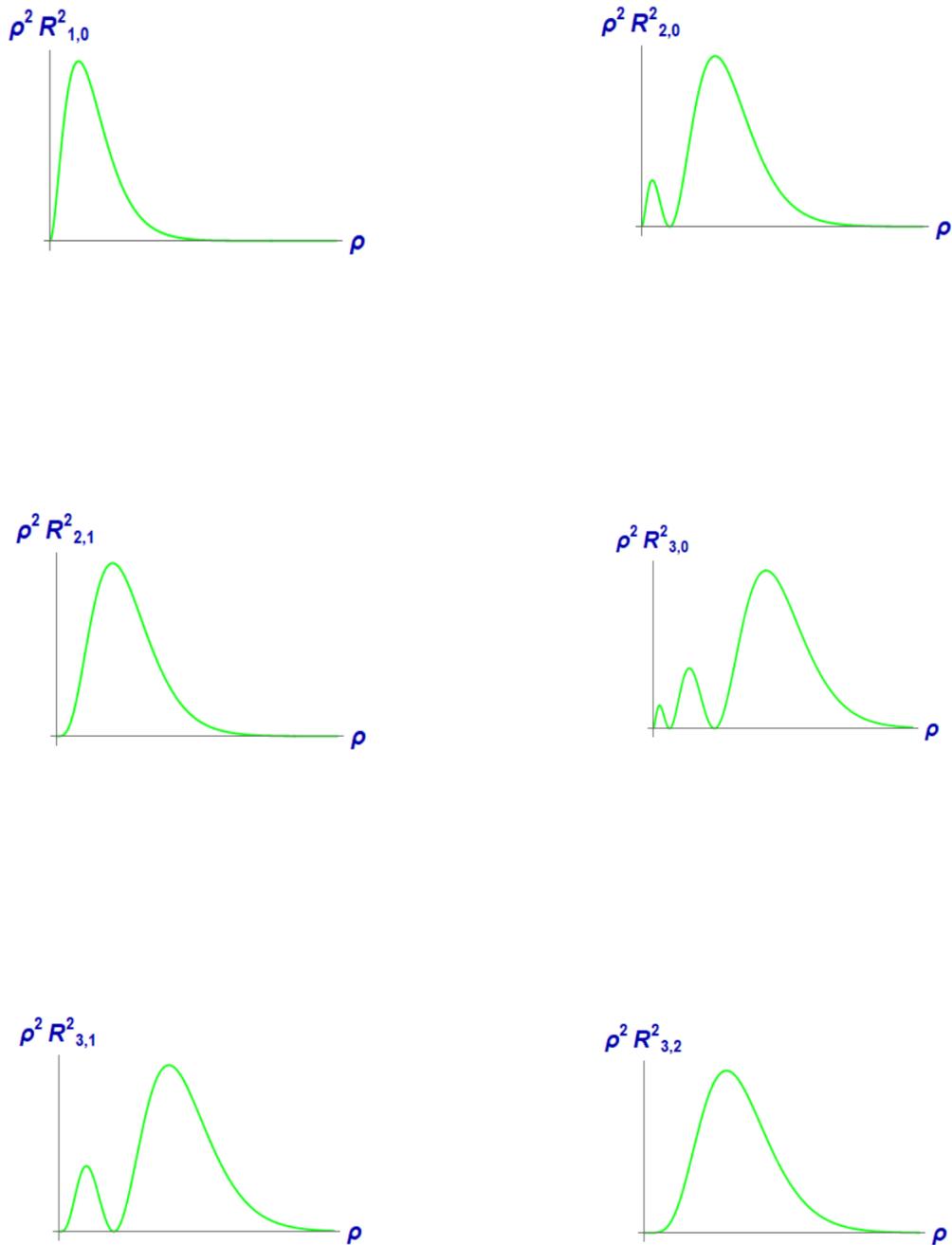
Figure 8: Radial Distribution Function Shapes of Hydrogen Atom

6 Addition of Angular Momenta and Clebsch-Gordon Coefficients

If you are unfamiliar with angular momentum algebra please refer to section 3 before proceeding.

6.1   General definition of Angular Momentum

A vector operator $\mathbf{J}$ is an angular momentum if its components are Hermitian operators satisfying commutation relations

$$[J_x, J_y] = i\hbar J_z, \quad [J_y, J_z] = i\hbar J_x, \quad [J_z, J_x] = i\hbar J_y \tag{114}$$

6.2   Ladder Operators and Commutator Relations

The relations can be derived in a very similar manner to section 3.

- $[J^2, J] = 0$

- Define the ladder operators as
$$J_\pm = J_x \pm J_y$$

- $[J_z, J_\pm] = \pm\hbar J_\pm$

- $[J_+, J_-] = 2\hbar J_z$

6.3   Clebsch-Gordon Coefficients

Consider two sets of angular momemtum operators J_1 and J_2.They can be say the angular momentum and spin angular momentum of an electron.
(We haven't talked about spin yet, but don't worry, it's just an angular momentum too!) By the previous definition
$$[J_{1_i}, J_{1_j}] = i\hbar\epsilon_{ijk}J_{1_k}, \quad [J_{2_i}, J_{2_j}] = i\hbar\epsilon_{ijk}J_{2_k}$$

Similar to section 3, the eigenvalue equations for $\mathbf{J_1}$ and $\mathbf{J_2}$ are

$$J_1^2 \left|j_1, m_1\right\rangle = j_1(j_1 + 1)\hbar^2 \left|j_1, m_1\right\rangle, \quad J_{1_z} \left|j_1, m_1\right\rangle = m_1\hbar \left|j_1, m_1\right\rangle, \quad -j_1 \le m_1 \le j_1 \tag{115}$$

$$J_2^2 \left|j_2, m_2\right\rangle = j_2(j_2 + 1)\hbar^2 \left|j_2, m_2\right\rangle, \quad J_{2_z} \left|j_2, m_2\right\rangle = m_2\hbar \left|j_2, m_2\right\rangle, \quad -j_2 \le m_2 \le j_2 \tag{116}$$

Define total angular momentum vector $\mathbf{J}$ as
$$\mathbf{J = J_1 + J_2}$$

Therefore, we get the operator
$$J^2 = J_x^2 + J_y^2 + J_z^2 = J_1^2 + J_2^2 + 2J_1 \cdot J_2$$

Few points to note:

- Each component of J_1 commutes with each component of J_2.
$$[J_{1_i}, J_{2_j}] = 0$$

- So, we have
$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k, \quad [J^2, J_z] = 0 \tag{117}$$

    proving that $\mathbf{J}$ is also an angular momentum.

- $[J_z, J_1^2] = [J_z, J_2^2] = 0$

- $[J^2, J_1^2] = [J^2, J_2^2] = 0$

- But,
$$[J^2, J_{1_z}] \ne 0$$

    and
$$[J^2, J_{2_z}] \ne 0$$

So, we cannot measure the quantum numbers m_1 and m_2 simultaneously with j. As we know m_1, m_2 can be measured simultaneously with j_1, j_2 and m_1, m_2 with j, m. These are two alternate groups of mutually commuting operators.

The first group is $(J_1^2, J_2^2, J_{1_z}, J_{2_z})$ and the second group is (J_1^2, J_2^2, J^2, J_z).The eigenvectors of each group can be denoted as $|j_1, j_2; m_1, m_2\rangle$ and $|j_1, j_2, j, m\rangle$.

For the first group $(J_1^2, J_2^2, J_{1_z}, J_{2_z})$ we have

$$
\begin{align}
J_1^2 |j_1, j_2; m_1, m_2\rangle &= j_1(j_1 + 1)\hbar^2 |j_1, j_2; m_1, m_2\rangle \tag{118}\\
J_2^2 |j_1, j_2; m_1, m_2\rangle &= j_2(j_2 + 1)\hbar^2 |j_1, j_2; m_1, m_2\rangle \tag{119}\\
J_{1_z} |j_1, j_2; m_1, m_2\rangle &= m_1\hbar |j_1, j_2; m_1, m_2\rangle \tag{120}\\
J_{2_z} |j_1, j_2; m_1, m_2\rangle &= m_2\hbar |j_1, j_2; m_1, m_2\rangle \tag{121}
\end{align}
$$

and for the second group (J_1^2, J_2^2, J^2, J_z):

$$
\begin{align}
J_1^2 |j_1, j_2, j, m\rangle &= j_1(j_1 + 1)\hbar^2 |j_1, j_2, j, m\rangle \tag{122}\\
J_2^2 |j_1, j_2, j, m\rangle &= j_2(j_2 + 1)\hbar^2 |j_1, j_2, j, m\rangle \tag{123}\\
J^2 |j_1, j_2, j, m\rangle &= j(j + 1)\hbar^2 |j_1, j_2, j, m\rangle \tag{124}\\
J_z |j_1, j_2, j, m\rangle &= m\hbar |j_1, j_2, j, m\rangle \tag{125}
\end{align}
$$

From (117), we can say that m can take $2j + 1$ values from $-j$ to j. Each set of eigenvectors are complete and mutually orthogonal,

$$
\sum_{m_1, m_2} |j_1, j_2; m_1, m_2\rangle \langle j_1, j_2; m_1, m_2| = 1 \tag{126}
$$

$$
\sum_{j, m} |j_1, j_2; j, m\rangle \langle j_1, j_2; j, m| = 1 \tag{127}
$$

Using $|j_1, j_2; m_1, m_2\rangle$ as basis we can write

$$
|j_1, j_2; j, m\rangle = \sum_{m_1, m_2} \langle j_1, j_2; j, m|j_1, j_2; m_1, m_2\rangle |j_1, j_2; m_1, m_2\rangle \tag{128}
$$

The problem of adding angular momenta reduces to finding $\langle j_1, j_2; j, m|j_1, j_2; m_1, m_2\rangle$ which are the *Clebsch-Gordon coefficients* denoted as $C(j_1, j_2, j, m; m_1, m_2)$.

We know $J_z = J_{1_z} + J_{2_z}$.

$$
(J_z - J_{1_z} - J_{2_z}) |j_1, j_2; j, m\rangle = 0
$$
$$
\implies \langle j_1, j_2; m_1, m_2|J_z - J_{1_z} - J_{2_z}|j_1, j_2; j, m\rangle = 0
$$
$$
\implies (m - m_1 - m_2) \langle j_1, j_2; m_1, m_2|j_1, j_2; j, m\rangle = 0 \tag{129}
$$

Therefore, $\langle j_1, j_2; m_1, m_2|j_1, j_2; j, m\rangle$ is zero unless $\boxed{m = m_1 + m_2}$

Two more useful and standard results related to the CG coefficients are stated without proof.

1 Range of j The maximum value of m is $max(m_1 + m_2)$ and so j_{max} is $m_1 + m_2$ too. The value of j_{min} turns out to be $|j_1 - j_2|$.

$$
|j_1 - j_2| \leq j \leq j_1 + j_2 \tag{130}
$$

2 Recursion Relation The CG coefficients obey

$$
\sqrt{(j \pm m)(j \mp m + 1)} \langle j_1, j_2; m_1, m_2|j_1, j_2; j, m \mp 1\rangle = \sqrt{(j_1 \mp m_1)(j_1 \pm m_1 + 1)} \langle j_1, j_2; m_1 \pm 1, m_2|j_1, j_2; j, m\rangle
$$
$$
+ \sqrt{(j_2 \mp m_2)(j_2 \pm m_2 + 1)} \langle j_1, j_2; m_1, m_2 \pm 1|j_1, j_2; j, m\rangle \tag{131}
$$

It is useful to work out a simple example say when $j_1 = 1/2, j_2 = 1/2$ before proceeding.
(Hint: Use any or all of the previous results and raising-lowering operator algebra when required)

7 Time Independent Perturbation Theory

The problems outlined in the previous section are very few of the problems in quantum mechanics that we can solve exactly. Approximation methods are used in nearly all the applications of the theory. We first address the problem of modifications in energy levels and eigenfunctions of a time-independent Hamiltonian when perturbation is applied.

7.1 Non-Degenerate Perturbation Theory

We are going to look at the *Rayleigh-Schrödinger Perturbation Theory* applied to systems with discreet energy levels.

$$H = H_0 + \lambda H' \tag{132}$$

where H_0 is the unperturbed Hamiltonian and $\lambda H'$ is a small perturbation. Therefore,

$$H_0 \psi_n^0 = E_n^0 \psi_n^0 \tag{133}$$

where the set of eigenfunctions ψ_n^0 is orthogonal and complete. The underlying assumption is of course that we do know the eigenvalues and eigenfunctions of the unperturbed Hamiltonian at least.

We would like to find the new eigenfunctions and eigenvalues that satisfy

$$H\psi_n = E_n \psi_n \tag{134}$$

The basic idea of perturbation theory is to assume that both the eigenvalues and eigenfunctions of H can be expanded in powers of the perturbation parameter λ.

$$E_n = \sum_{j=0}^{\infty} \lambda^j E_n^j \tag{135}$$

$$\psi_n = \sum_{j=0}^{\infty} \lambda^j E_n^j \tag{136}$$

where j can be called the order of perturbation while E_n^j and ψ_n^j are called the jth-order corrections to nth eigenvalue and eigenfunction respectively.

Substituting 135 and 136 into the Schrödinger equation 134 we have

$$(H_0 + \lambda H')(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + ...) = (E_n^0 + \lambda_n^1 + \lambda^2 E_n^2 + ...)(\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2) \tag{137}$$

Equating the powers of λ on both sides we get

$$H_0 \psi_n^0 = E_n^0 \psi_n^0 \tag{138}$$

$$H' \psi_n^0 + H_0 \psi_n^1 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0 \tag{139}$$

$$H' \psi_n^1 + H_0 \psi_n^2 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0 \tag{140}$$

and so on.

7.1.1 First Order Theory

For E_n^1, we premultiply 139 by ψ_n^{0*} and integrate over all coordinates which gives

$$\langle \psi_n^0 | H_0 | \psi_n^1 \rangle + \langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle \tag{141}$$

Since H_0 is Hermitian

$$\langle \psi_n^0 | H_0 | \psi_n^1 \rangle = \langle H_0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle \tag{142}$$

and thus we can cancel terms.

$$\therefore \boxed{\langle \psi_n^0 | H' | \psi_n^0 \rangle = E_n^1} \tag{143}$$

Remark: First order correction to the energy for non-degenerate energy level is just the expectation value of perturbation in the unperturbed state.

For wave-function ψ_n^1, we re-arrange 139 as

$$(H_0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0 \tag{144}$$

Since the set of ψ_n^0's are complete we can write

$$\psi_n^1 = \sum_{m \neq n} c_m^n \psi_m^0 \tag{145}$$

There wasn't a need to include $m = n$ in the sum, for if ψ_n^1 satisfies 145 then $\psi_n^1 + \alpha \psi_n^0$ does too for any constant α and we ca use this freedom to subtract the ψ_n^0 term.

Substituting 145 into 144 and using the fact that ψ_n^0 satisfies the unperturbed Schrödinger equation we have

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^n \psi_m^0 = -(H^{'} - E_n^1)\psi_n^0 \tag{146}$$

Taking inner product with ψ_l^0,

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^n \langle \psi_l^0 | \psi_m^0 \rangle = - \langle \psi_l^0 | H^{'} | \psi_n^0 \rangle + E_n^1 \langle \psi_l^0 | \psi_n^0 \rangle \tag{147}$$

If $l = n$ then $\langle \psi_l^0 | \psi_m^0 \rangle = 0$ and we recover 143.

If $l \neq n$ then

$$(E_m^0 - E_n^0) c_l^n = - \langle \psi_l^0 | H^{'} | \psi_n^0 \rangle \tag{148}$$

$$\therefore \boxed{c_m^n = \frac{\langle \psi_l^0 | H^{'} | \psi_n^0 \rangle}{(E_n^0 - E_m^0)}} \tag{149}$$

From this result and 145 we see that the sufficient condition for the applicability of Rayleigh-Schrödinger Perturbation Theory is

$$\left| \frac{\langle \psi_l^0 | H^{'} | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \right| << 1, \quad l \neq n \tag{150}$$

Notice that if two unperturbed states share the same energy we cannot use 149 and in that case we will need 'Degenerate Perturbation Theory' which we won't cover in this text. Also, first order theory gives surprisingly accurate energies but wave-functions shapes are very poor.

7.1.2 Second-Order Energies

Taking a similar approach as before, the inner product of second-order equation with ψ_n^0

$$\langle \psi_n^0 | H_0 \psi_n^2 \rangle + \langle \psi_n^0 | H^{'} \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$$

Again since H_0 is Hermitian:

$$\langle \psi_n^0 | H_0 \psi_n^2 \rangle = \langle H_0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle$$

we can cancel terms and we are left with:

$$E_n^2 = \langle \psi_n^0 | H^{'} | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle \tag{151}$$

But $\langle \psi_n^0 | \psi_n^1 \rangle = 0$ so

$$E_n^2 = \langle \psi_n^0 | H^{'} | \psi_n^1 \rangle = \sum_{m \neq n} c_m \langle \psi_n^0 | H^{'} | \psi_m^0 \rangle \tag{152}$$

Finally,

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_n^0 | H^{'} | \psi_m^0 \rangle|^2}{(E_n^0 - E_m^0)}} \tag{153}$$

We can calculate second-order correction to wave-function, the third-order correction to energy and so on but this is as far as it is useful to pursue this method.

7.2 Non-linear Oscillator Problem

As an example let us consider a non-linear oscillator whose Hamiltonian is

$$H = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 + ax^3 + bx^4 \qquad (154)$$

where

$$H^{'} = ax^3 + bx^4 \qquad (155)$$

and assumption is $b > 0$.
The first order correction in the nth state is therefore

$$E_n^1 = \int_{-\infty}^{\infty} (ax^3 + bx^4)|\psi_n^0(x)|^2 dx \qquad (156)$$

We know from section 2.6 that the first term in integral vanishes while the second term can be found by replacing x in terms of the raising and lowering operators (refer to equation 20). We get after some algebra:

$$\langle \psi_n^0 | x^4 | \psi_n^0 \rangle = \langle n | x^4 | n \rangle = \frac{3}{4\alpha^4}(2n^2 + 2n + 1) \qquad (157)$$

(Hint: You may need to use 23, orthogonality of distinct eigenfunctions and 18)

So the first order energy shift is

$$E_n^1 = \frac{3}{4}b\left(\frac{\hbar}{m\omega}\right)^2 (2n^2 + 2n + 1) \qquad (158)$$

Note that for a fixed value of b we have E_n^1 growing rapidly with n. To ensure the validity of the perturbation method, we need the magnitude of the correction term to be small compared to the spacing between energy levels so higher the value of n, smaller the value of parameter b for which reliable results may be obtained.
The **question** that can probably be addressed next is whether we can obtain these energy levels through a purely numerical approach rather than the use of perturbation theory.

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