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Introductory Mathematics for Quantum Chemistry

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I. SYNOPSIS

Since much of the mathematics needed for quantum chemistry is not covered in the first two years of calculus, a short introduction to those methods is presented here. Elegance has been eschewed in the Einstein spirit.

II. ORTHOGONAL FUNCTIONS

A. Dirac Notation

The notation employed in beginning discussions of quantum chemistry becomes cumbersome when the complexity of problems increase and the need to see struc-

ture in equations dominates. Dirac introduced a notation which eliminates the ever-redundant ψ from discourse. He defined a wave function as a ket.

The ket is defined as ‘ $|index \rangle \equiv \psi$ ’, where ‘index’ is some human chosen index or indicator whose purpose is to label the state (or the function) under discussion. For a particle in a box, a potential ket is

$$\psi_n(x) = |n \rangle \equiv N_n \sin\left(\frac{n\pi x}{L}\right) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (2.1)$$

where the domain is $0 \leq x \leq L$, N_n is a normalization constant, and ‘n’ is a quantum number, i.e., an index chosen by us.

For the hydrogen atom, an appropriate ket might be

$$\psi_{n=3,\ell=1,m_\ell=-1}(\rho, \vartheta, \phi) = |3, 1, -1 \rangle = N_{3,1,1} \rho(4 - \rho) e^{-\rho} \sin \vartheta e^{-i\phi} \quad (2.2)$$

which is a 3p electron’s state (ρ) is a dimensionless radius.

A harmonic oscillator might have an appropriate ket of the form

$$\psi_3(x) = |3 \rangle = N_3 (8\beta^3 x^3 - 12\beta x) e^{-\beta^2 x^2/2} \quad (2.3)$$

i.e., the ket notation allows us to indicate inside the funny delimiters the essential characteristics of the involved wavefunction without extraneous elements which might distract attention from the overall viewpoint being propounded!

B. The Dot Product

Returning to the hydrogen atom, the following ‘vector’

$$\langle 3, 1, -1 | = N_{3,1,1} \rho(4 - \rho) e^{-\rho} \sin \vartheta e^{+i\phi} \quad (2.4)$$

which is the complex conjugate of the original wave function [1], is known as a ‘bra’ vector, and the notation

$$\langle 3, 1, -1 | 3, 1, -1 \rangle = 1 \quad (2.5)$$

is a shorthand for

$$\int_{\text{all space}} \psi_{3,1,-1}^* \psi_{3,1,-1} d\tau = 1 \quad (2.6)$$

(i.e., the normalization equation, required so that the probability of finding the electron somewhere is 1, certain(!)), which itself is shorthand for the complicated three-dimensional integral, usually display is spherical polar coordinates.

One sees that constructing the ‘bra’/‘ket’ [2] consists of two separate concepts, making the ‘bra’ from the ‘ket’ by using the complex conjugate, juxtaposing the two in the proper order, and integrating over the appropriate domain. The analogy of this process is the dot product of elementary vector calculus, and it is here where we get our mental images of the processes described.

In three space, x , y , and z , we have unit vectors $\hat{i}, \hat{j}, \hat{k}$, so that an arbitrary vector as:

$$\vec{R}_1 = X\hat{i} + Y\hat{j} + Z\hat{k}$$

could be re-written as

$$|R_1 \rangle = X|i \rangle + Y|j \rangle + Z|k \rangle$$

In this space, one doesn’t integrate over all space, one adds up over all components, thus

$$\langle R_1 | R_1 \rangle = \vec{R}_1 \cdot \vec{R}_1 = X^2 + Y^2 + Z^2$$

since $|i \rangle$ is orthogonal (“perpendicular”) to $|j \rangle$ and $|k \rangle$, etc..

In the same sense,

$$|arb\rangle = \sum_n c_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (2.7)$$

where $|arb\rangle$ is an arbitrary state. This is our normal entry point for Fourier Series.

Before we go there, let us re-introduce orthogonality, i.e.,

$$\langle n|m\rangle = 0 = \int_{domain} \psi_n^* \psi_m d\tau; \quad m \neq n \quad (2.8)$$

where the domain is problem specific, as is the volume element $d\tau$. This orthogonality is the analog of the idea that

$$\hat{i} \cdot \hat{j} = 0$$

as an example in normal vector calculus.

III. FOURIER SERIES

A. Particle in a Box vis-a-vis Fourier Series

The normal introduction to orthogonal functions is via Fourier Series, but in the context of quantum chemistry, we can re-phrase that into the Particle in a Box solution to the Schrödinger Equation, i.e.,

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + 0\psi = E\psi \quad (3.1)$$

in the box (domain) $0 \leq x \leq L$. The solutions are known to be

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} = |n\rangle \quad (3.2)$$

where n is an integer greater than zero, and L remains the size of the box.

Now, a Fourier Series is an expansion of a function (periodic) over the same (repeated) domain as above, in the form

$$|function\rangle = \sum_i c_i |i\rangle = \sum_i c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \quad (3.3)$$

(where we changed index for no particular reason from n to i , other than to remind you that the index is a dummy variable). The question is, what is the optimal, best, nicest, etc., etc., etc., value for each of the c_i in this expansion?

B. A Minimum Error Approximation

To answer this question, we look for a measure of error between the function and the expansion. To do this we

define a truncated expansion:

$$S_m = \sum_{i=0}^{i=m} c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \quad (3.4)$$

where, contrary to the particle in a box, we have employed the $i=0$ particle in a box basis function. Now, we form an error at the point x :

$$|function\rangle - S_m(x) = err(x) \quad (3.5)$$

and notice that if we added up this error for every value of x in the domain $0 \leq x \leq L$ we would be approaching the concept we desire, a measure of the error, the difference between the function and its approximation, the truncated series.

But, you say, sometimes the error ($err(x)$) is positive, and sometimes its negative, depending on circumstances. We want a measure which counts either effect properly, and the answer is to define a new error

$$(|function\rangle - S_m(x))^2 = ERR(x) \equiv [err(x)]^2 \quad (3.6)$$

where clearly, the l.h.s. is positive definite, and therefore can not give rise to fortuitous cancelation.

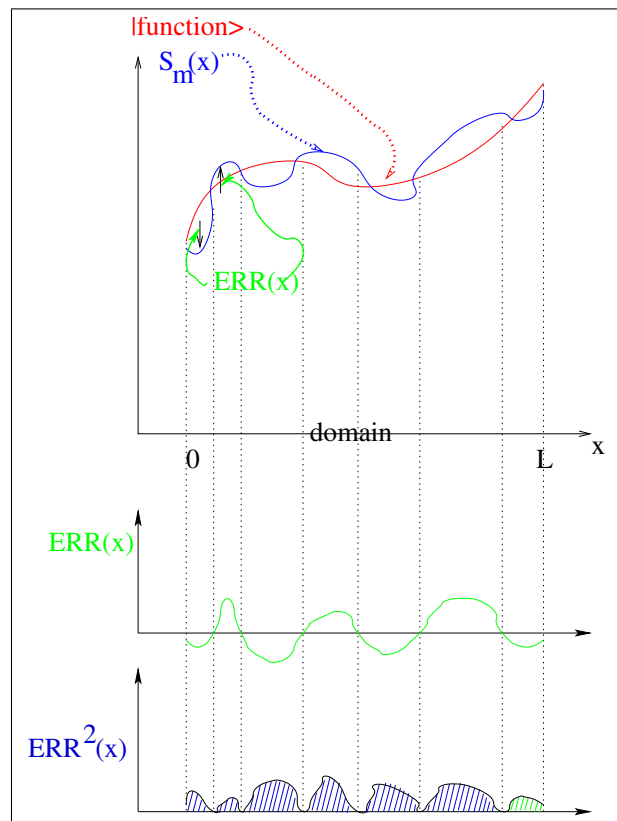


FIG. 1: Error involved in approximating a function.

So, adding up $ERR(x)$ at each point x in the domain, we have

$$\int_0^L (|function\rangle - S_m(x))^2 dx = \int_0^L ERR(x) dx \equiv ERROR_m \quad (3.7)$$

$ERROR_m$ is now a positive definite number which measures the error committed in truncating the approximate

series at m . We re-write this explicitly to show that summation:

$$\int_0^L \left(|function\rangle - \sum_{i=0}^m c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \right)^2 dx = \int_0^L ERR(x) dx \equiv ERROR_m \quad (3.8)$$

and form the partial

$$\frac{\partial ERROR_m}{\partial c_j} \quad (3.9)$$

holding all other c_i constant, where $i = 0 \dots j \dots m$, which is

$$\frac{\partial ERROR_m}{\partial c_j} = -2 \left\{ \int_0^L \left(|function\rangle - \sum_{i=0}^m c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \right) \sqrt{\frac{2}{L}} \sin \frac{j\pi x}{L} dx \right\} \quad (3.10)$$

which we set equal to zero. This means that we are searching for that value of c_j which makes the ERROR an extremum (of course, we want a minimum). This leads to the equation

$$\int_0^L \left\{ |function\rangle - \left(\sin \frac{j\pi x}{L} \right) \right\} dx = \int_0^L \left\{ \left(\sum_{i=0}^m c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \right) \sin \frac{j\pi x}{L} \right\} dx \quad (3.11)$$

and, since one can exchange summation and integration, one has

$$\int_0^L |function\rangle \left(\sin \frac{j\pi x}{L} \right) dx = \sum_{i=0}^m \int_0^L \left(c_i \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \right) \sin \frac{j\pi x}{L} dx \quad (3.12)$$

But the right hand side of this equation simplifies because the sines are orthogonal to each other over this domain, so the r.h.s. becomes

$$\int_0^L |function\rangle \left(\sin \frac{j\pi x}{L} \right) dx = c_j \int_0^L \left(\sqrt{\frac{2}{L}} \sin \frac{j\pi x}{L} \right) \sin \frac{j\pi x}{L} dx \quad (3.13)$$

since the only survivor on the r.h.s. is the $i = j$ term.

$$c_j = \frac{\int_0^L |function\rangle \left(\sin \frac{j\pi x}{L} \right) dx}{\int_0^L \left(\sqrt{\frac{2}{L}} \sin \frac{j\pi x}{L} \right) \sin \frac{j\pi x}{L} dx} \quad (3.14)$$

Multiplying top and bottom by $\sqrt{2/L}$ one has

$$c_j = \frac{\langle function | j \rangle}{\langle j | j \rangle} \quad (3.15)$$

which is fairly cute in its compactness. Of course, if $|j\rangle$ is normalized (as it is in our example) then

$$c_j = \langle function | j \rangle \quad (3.16)$$

which is even more compact!

C. Completeness

What if we wanted to approximate a function of the form

$$\sin \frac{7\pi x}{L} \quad (3.17)$$

and $i=7$ were omitted from the summations (Equation 3.3), i.e., the summation ran past this particular harmonic. It would look like:

$$\dots + c_6 \sin \frac{6\pi x}{L} + c_8 \sin \frac{8\pi x}{L} + \dots$$

Clearly, since each sine is orthogonal to every other sine, the seventh sine ($\sin \frac{7\pi x}{L}$) would have no expansion in this series, i.e., each c_i would be zero! We can not

leave out any term in the series, i.e., it must be complete, before one can assert that one can expand any function in terms of these sines (and cosines, if need be). Said another way,

$$\sin \frac{7\pi x}{L} \neq c_0 + c_1 \sin \frac{1\pi x}{L} + c_2 \sin \frac{2\pi x}{L} + \dots$$

since the one term on the r.h.s which is needed, was, by assumption, absent!

IV. LADDER OPERATORS

A. Laddering in the Space of the Particle in a Box

We start by remembering the trigonometric definition of the sine of the sum of two angles, i.e.,

$$\sin(\alpha + \beta) = \sin \alpha \cos \beta + \cos \alpha \sin \beta \quad (4.1)$$

We seek an operator, M^+ which takes a state $|n\rangle$ and ladders it up to the next state, i.e., $|n+1\rangle$. Symbolically, we define the operator through the statement

$$M^+|n\rangle \rightarrow |n+1\rangle \quad (4.2)$$

and we will require the inverse, i.e.,

$$M^-|n\rangle \rightarrow |n-1\rangle \quad (4.3)$$

where the down ladder operator is lowering us from n to $n-1$.

One sees immediately that there is a lower bound to the ladder, i.e., that one can not ladder down from the lowest state, implying

$$M^-|lowest\rangle = 0 \quad (4.4)$$

B. Form of the UpLadder Operator

What must the form of M^+ be, in order that it function properly? Since

$$\sin \left(\frac{(n+1)\pi x}{L} \right) = \cos \left(\frac{\pi x}{L} \right) \sin \frac{n\pi x}{L} + \cos \left(\frac{n\pi x}{L} \right) \sin \left(\frac{\pi x}{L} \right)$$

One has, defining the up-ladder operator M^+

$$M^+ \left(\sin \left(\frac{n\pi x}{L} \right) \right) \rightarrow \sin \left(\frac{(n+1)\pi x}{L} \right) = \cos \left(\frac{\pi x}{L} \right) \sin \frac{n\pi x}{L} + \sin \left(\frac{\pi x}{L} \right)$$

which looks like

$$M^+|n\rangle \rightarrow \cos \left(\frac{\pi x}{L} \right) |n\rangle + \left(\frac{L}{n\pi} \right) \sin \left(\frac{\pi x}{L} \right) \frac{\partial |n\rangle}{\partial x} = |n+1\rangle$$

The $\frac{L}{n\pi}$ takes out the constant generated by the partial derivative.

What this is saying is that there is an operator, M^+ , which has a special form involving a multiplier function and a partial derivative, whose total effect on an eigenfunction is to “ladder” it from n to $n+1$.

$$M^+ = \cos \left(\frac{\pi x}{L} \right) + \left(\frac{L}{n\pi} \right) \sin \left(\frac{\pi x}{L} \right) \frac{\partial}{\partial x}$$

written as an operator.

C. The DownLadder Operator

We need the down operator also, i.e.,

$$\sin \left(\frac{(n-1)\pi x}{L} \right) = \cos \left(\frac{\pi x}{L} \right) \sin \frac{n\pi x}{L} - \sin \left(\frac{\pi x}{L} \right) \cos \frac{n\pi x}{L}$$

making use of the even and odd properties of cosines and sines, respectively.

$$M^-|n\rangle \rightarrow \cos \left(\frac{\pi x}{L} \right) |n\rangle - \left(\frac{L}{n\pi} \right) \sin \left(\frac{\pi x}{L} \right) \frac{\partial |n\rangle}{\partial x} \rightarrow |n-1\rangle$$

$$M^- = \cos \left(\frac{\pi x}{L} \right) - \left(\frac{L}{n\pi} \right) \sin \left(\frac{\pi x}{L} \right) \frac{\partial}{\partial x}$$

D. Ladder Operators in the Operator Representation

Stated another way, in the traditional position-momentum language, one has

$$M^+ = \cos \frac{\pi x}{L} - \left(\frac{L}{n\pi} \right) \sin \frac{\pi x}{L} \frac{p_x}{i\hbar} \quad (4.5)$$

$$M^- = \cos \frac{\pi x}{L} + \left(\frac{L}{n\pi} \right) \sin \frac{\pi x}{L} \frac{p_x}{i\hbar} \quad (4.6)$$

E. Ladder Operators and the Hamiltonian

We need to show that this ladder operator works properly with the Hamiltonian, i.e.,

$$\frac{p_x^2}{2m} \equiv H_{op} \quad (4.7)$$

and to do this we assume

$$H_{op}|n\rangle = \epsilon|n\rangle$$

and ask what happens when we operate from the left with M^+ (for example). We obtain

$$M^+ H_{op}|n\rangle = \epsilon M^+|n\rangle \quad (4.8)$$

where we want to exchange the order on the l.h.s. so that we can ascertain what the eigenvalue of the operator $M^+|n\rangle$, i.e., we need the commutator of the Hamiltonian with the ladder operator,

$$[H_{op}, M^+] \equiv H_{op}M^+ - M^+H_{op}$$

Remembering that

$$[p_x, x] = -i\hbar$$

one forms

$$[H_{op}, M^+] = \left(\frac{p_x^2}{2m}\right) \left(\cos\frac{\pi x}{L} + \left(\frac{L}{n\pi}\right) \sin\frac{\pi x}{L} \frac{\partial}{\partial x}\right) - \left(\cos\frac{\pi x}{L} + \left(\frac{L}{n\pi}\right) \sin\frac{\pi x}{L} \frac{\partial}{\partial x}\right) \left(\frac{p_x^2}{2m}\right) \quad (4.9)$$

F. Some Precursor Commutators

First, one needs $[p_x, \cos\frac{\pi x}{L}]$,

$$[p_x, \cos\frac{\pi x}{L}] \equiv -i\hbar \frac{\partial}{\partial x} \cos\left(\frac{\pi x}{L}\right) - \cos\left(\frac{\pi x}{L}\right) \left(-i\hbar \frac{\partial}{\partial x}\right) \quad (4.10)$$

which works out to be

$$[p_x, \cos\frac{\pi x}{L}] = i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) = p_x \cos\frac{\pi x}{L} - \cos\frac{\pi x}{L} p_x \quad (4.11)$$

or, in the most useful form for future work:

$$p_x \cos\left(\frac{\pi x}{L}\right) = \cos\left(\frac{\pi x}{L}\right) p_x + i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) \quad (4.12)$$

One needs the same commutator involving the appropriate sine also:

$$[p_x, \sin\left(\frac{\pi x}{L}\right)] = -i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) = p_x \sin\left(\frac{\pi x}{L}\right) - \sin\left(\frac{\pi x}{L}\right) p_x = p_x \cos\left(\frac{\pi x}{L}\right) p_x + i\hbar \frac{\pi}{L} [p_x \sin\left(\frac{\pi x}{L}\right)] - \cos\left(\frac{\pi x}{L}\right) p_x^2 \quad (4.13)$$

$$= \left(i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) + \cos\left(\frac{\pi x}{L}\right) p_x\right) p_x + i\hbar \frac{\pi}{L} [p_x \sin\left(\frac{\pi x}{L}\right)] - \cos\left(\frac{\pi x}{L}\right) p_x^2$$

i.e.,

$$\begin{aligned} &= i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + \cos\left(\frac{\pi x}{L}\right) p_x^2 + i\hbar \frac{\pi}{L} \left[\sin\left(\frac{\pi x}{L}\right) p_x - i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right)\right] - \cos\left(\frac{\pi x}{L}\right) p_x^2 \\ &= i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + i\hbar \frac{\pi}{L} \left[\sin\left(\frac{\pi x}{L}\right) p_x - i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right)\right] \end{aligned}$$

$$p_x \sin\left(\frac{\pi x}{L}\right) = \sin\left(\frac{\pi x}{L}\right) p_x - i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) \quad (4.14)$$

Next, one needs $[p_x^2, \cos\left(\frac{\pi x}{L}\right)]$ (and its sine equivalent).

$$[p_x^2, \cos\left(\frac{\pi x}{L}\right)] = p_x^2 \cos\left(\frac{\pi x}{L}\right) - \cos\left(\frac{\pi x}{L}\right) p_x^2 \quad (4.15)$$

$$= p_x p_x \cos\left(\frac{\pi x}{L}\right) - \cos\left(\frac{\pi x}{L}\right) p_x^2$$

which we re-write, factoring, as

$$= p_x \left(\cos\left(\frac{\pi x}{L}\right) p_x + i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right)\right) - \cos\left(\frac{\pi x}{L}\right) p_x^2$$

which we re-write as

$$[p_x^2, \cos\left(\frac{\pi x}{L}\right)] = 2i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right)$$

$$p_x^2 \cos\left(\frac{\pi x}{L}\right) = 2i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) + \cos\left(\frac{\pi x}{L}\right) p_x^2$$

Now one needs $[p_x^2, \sin\left(\frac{\pi x}{L}\right)]$

$$[p_x^2, \sin\left(\frac{\pi x}{L}\right)] = p_x^2 \sin\left(\frac{\pi x}{L}\right) - \sin\left(\frac{\pi x}{L}\right) p_x^2 \quad (4.16)$$

$$= p_x \left(p_x \sin\left(\frac{\pi x}{L}\right) \right) - \sin\left(\frac{\pi x}{L}\right) p_x^2$$

$$= p_x \left(\sin\left(\frac{\pi x}{L}\right) p_x - i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) \right) - \sin\left(\frac{\pi x}{L}\right) p_x^2$$

which we re-write as

$$= \left(p_x \sin\left(\frac{\pi x}{L}\right) \right) p_x - i\hbar \frac{\pi}{L} \left[p_x \cos\left(\frac{\pi x}{L}\right) \right] - \sin\left(\frac{\pi x}{L}\right) p_x^2$$

$$= \left(\sin\left(\frac{\pi x}{L}\right) p_x - i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) \right) p_x - i\hbar \frac{\pi}{L} \left[p_x \cos\left(\frac{\pi x}{L}\right) \right] - \sin\left(\frac{\pi x}{L}\right) p_x^2$$

$$= -i\hbar \frac{\pi}{L} \left(\cos\left(\frac{\pi x}{L}\right) p_x \right) - \left[i\hbar \frac{\pi}{L} p_x \cos\left(\frac{\pi x}{L}\right) \right]$$

i.e.,

$$= -i\hbar \frac{\pi}{L} \left(\cos\left(\frac{\pi x}{L}\right) p_x \right) - \left[i\hbar \left(\frac{\pi}{L}\right) \left(\cos\frac{\pi x}{L} p_x + i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) \right) \right]$$

$$[p_x^2, \sin\left(\frac{\pi x}{L}\right)] = -2i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \sin\left(\frac{\pi x}{L}\right)$$

$$p_x^2 \sin\left(\frac{\pi x}{L}\right) = -2i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \sin\left(\frac{\pi x}{L}\right) + \sin\left(\frac{\pi x}{L}\right) p_x^2$$

We had, in Equation 4.8 the following,

$$M^+ H_{op} |n\rangle = \epsilon M^+ |n\rangle$$

which we now wish to reverse. We need the commutator of the Hamiltonian with the UpLadder Operator [3].

$$[H_{op}, M^+] = \frac{p_x^2}{2m} \left(\cos\left(\frac{\pi x}{L}\right) - \frac{L}{n\pi} \left\{ \sin\left(\frac{\pi x}{L}\right) \right\} \frac{p_x}{i\hbar} \right) - M^+ H_{op}$$

which becomes

$$[H_{op}, M^+] = \frac{p_x^2}{2m} \cos\left(\frac{\pi x}{L}\right) - \frac{p_x^2}{2m} \frac{L}{n\pi} \left\{ \sin\left(\frac{\pi x}{L}\right) \right\} \frac{p_x}{i\hbar} - M^+ H_{op} \quad (4.17)$$

expanding,

$$[H_{op}, M^+] = \frac{1}{2m} p_x^2 \cos\left(\frac{\pi x}{L}\right) - \frac{1}{2m} \frac{L}{n\pi} \left\{ p_x^2 \sin\left(\frac{\pi x}{L}\right) \right\} \frac{p_x}{i\hbar} - M^+ H_{op}$$

and using the previously obtained commutators,

$$\begin{aligned}
[H_{op}, M^+] &= \frac{1}{2m} \left\{ 2i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) + \cos\left(\frac{\pi x}{L}\right) p_x^2 \right\} \\
&- \frac{1}{2m} \frac{L}{n\pi} \left\{ -2i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) p_x - \hbar^2 \left(\frac{\pi}{L}\right)^2 \sin\left(\frac{\pi x}{L}\right) + \sin\left(\frac{\pi x}{L}\right) p_x^2 \right\} \frac{p_x}{i\hbar} - M^+ H_{op}
\end{aligned} \tag{4.18}$$

which expands, at first, to

$$\begin{aligned}
[H_{op}, M^+] &= \frac{1}{2m} \left\{ 2i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) \right\} \\
&- \frac{1}{2m} \frac{L}{n\pi} \left\{ -2i\hbar \frac{\pi}{L} \cos\left(\frac{\pi x}{L}\right) p_x - \hbar^2 \left(\frac{\pi}{L}\right)^2 \sin\left(\frac{\pi x}{L}\right) \right\} \frac{p_x}{i\hbar}
\end{aligned} \tag{4.19}$$

$$\begin{aligned}
[H_{op}, M^+] &= \frac{1}{2m} \left\{ 2i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) \right\} \\
&+ \frac{1}{2m} \frac{1}{n} \left\{ -2 \cos\left(\frac{\pi x}{L}\right) p_x - \frac{\hbar}{i} \left(\frac{\pi}{L}\right) \sin\left(\frac{\pi x}{L}\right) \right\} p_x
\end{aligned} \tag{4.20}$$

$$2m[H_{op}, M^+] = 2i\hbar \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) - \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) p_x^2 - \frac{1}{n} \frac{\hbar}{i} \left(\frac{\pi}{L}\right) \sin\left(\frac{\pi x}{L}\right) p_x \tag{4.21}$$

$$2m[H_{op}, M^+] = \left(2i\hbar + \frac{1}{n} \frac{\hbar}{i} \right) \frac{\pi}{L} \sin\left(\frac{\pi x}{L}\right) p_x + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) + \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) p_x^2 \tag{4.22}$$

$$2m[H_{op}, M^+] = i\hbar \left(2i\hbar + \frac{1}{n} \frac{\hbar}{i} \right) \frac{\pi}{L} \left\{ \sin\left(\frac{\pi x}{L}\right) \frac{p_x}{i\hbar} \right\} + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) + \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) p_x^2 \tag{4.23}$$

and substituting for $\left\{ \sin\left(\frac{\pi x}{L}\right) \frac{p_x}{i\hbar} \right\}$ one has

$$2m[H_{op}, M^+] = \hbar^2 (1 + 2n) \left(\frac{\pi}{L}\right)^2 \left\{ M^+ - \cos\left(\frac{\pi x}{L}\right) \right\} + \hbar^2 \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) + \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) p_x^2 \tag{4.24}$$

$$[H_{op}, M^+] = \hbar^2 \frac{(1 + 2n)}{2m} \left(\frac{\pi}{L}\right)^2 \left\{ M^+ - \cos\left(\frac{\pi x}{L}\right) \right\} + \hbar^2 \frac{1}{2m} \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) + \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) \frac{p_x^2}{2m} \tag{4.25}$$

$$[H_{op}, M^+] = \hbar^2 \frac{(1 + 2n)}{2m} \left(\frac{\pi}{L}\right)^2 \left\{ M^+ \right\} - \hbar^2 \frac{(1 + 2n)}{2m} \left(\frac{\pi}{L}\right)^2 \left\{ \cos\left(\frac{\pi x}{L}\right) \right\} + \hbar^2 \frac{1}{2m} \left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) + \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) \frac{p_x^2}{2m} \tag{4.26}$$

$$[H_{op}, M^+] = \hbar^2 \frac{(1 + 2n)}{2m} \left(\frac{\pi}{L}\right)^2 \left\{ M^+ \right\} + \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (2n) \cos\left(\frac{\pi x}{L}\right) + \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) H_{op} \tag{4.27}$$

1. Alternative Formulation

$$\frac{\partial^2}{\partial x^2} \left(\cos\left(\frac{\pi x}{L}\right) + \frac{L}{n\pi} \sin\left(\frac{\pi x}{L}\right) \frac{\partial}{\partial x} \right) f =$$

$$\begin{aligned}
\frac{\partial}{\partial x} \left(\cos \left(\frac{\pi x}{L} \right) \frac{\partial}{\partial x} - \frac{\pi}{L} \sin \left(\frac{\pi x}{L} \right) + \frac{L}{n\pi} \sin \left(\frac{\pi x}{L} \right) \frac{\partial^2}{\partial x^2} + \frac{1}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial}{\partial x} \right) f = \\
- \frac{\pi}{L} \sin \left(\frac{\pi x}{L} \right) \frac{\partial f}{\partial x} + \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2 f}{\partial x^2} \\
- \left(\frac{\pi}{L} \right)^2 \cos \left(\frac{\pi x}{L} \right) f - \frac{\pi}{L} \sin \left(\frac{\pi x}{L} \right) \frac{\partial f}{\partial x} \\
+ \frac{1}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2 f}{\partial x^2} + \frac{L}{n\pi} \sin \left(\frac{\pi x}{L} \right) \frac{\partial^3 f}{\partial x^3} \\
- \frac{\pi}{nL} \sin \left(\frac{\pi x}{L} \right) \frac{\partial f}{\partial x} + \frac{1}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2 f}{\partial x^2}
\end{aligned} \tag{4.28}$$

So the commutator would be:

$$\begin{aligned}
\frac{\partial^2}{\partial x^2} \left(\cos \left(\frac{\pi x}{L} \right) + \frac{L}{n\pi} \sin \left(\frac{\pi x}{L} \right) \frac{\partial}{\partial x} \right) f - \left(\cos \left(\frac{\pi x}{L} \right) + \frac{L}{n\pi} \sin \left(\frac{\pi x}{L} \right) \frac{\partial}{\partial x} \right) \frac{\partial^2 f}{\partial x^2} = \\
- \frac{2\pi}{L} \sin \left(\frac{\pi x}{L} \right) \frac{\partial f}{\partial x} \\
- \left(\frac{\pi}{L} \right)^2 \cos \left(\frac{\pi x}{L} \right) f \\
+ \frac{2}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2 f}{\partial x^2} \\
- \frac{\pi}{nL} \sin \left(\frac{\pi x}{L} \right) \frac{\partial f}{\partial x}
\end{aligned} \tag{4.29}$$

or

$$= \left(-\frac{2\pi}{L} - \frac{\pi}{nL} \right) \sin \left(\frac{\pi x}{L} \right) \frac{\partial}{\partial x} - \left(\frac{\pi}{L} \right)^2 \cos \left(\frac{\pi x}{L} \right) + \frac{2}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2}{\partial x^2} \tag{4.30}$$

$$= \left(-\frac{2\pi}{L} - \frac{\pi}{nL} \right) \frac{n\pi}{L} \left(M^+ - \cos \left(\frac{\pi x}{L} \right) \right) - \left(\frac{\pi}{L} \right)^2 \cos \left(\frac{\pi x}{L} \right) + \frac{2}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2}{\partial x^2} \tag{4.31}$$

$$-\frac{2m}{\hbar^2} [H, M^+] = - \left(\frac{\pi}{L} \right)^2 (2n-1) \left(M^+ - \cos \left(\frac{\pi x}{L} \right) \right) - \left(\frac{\pi}{L} \right)^2 \cos \left(\frac{\pi x}{L} \right) + \frac{2}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2}{\partial x^2} \tag{4.32}$$

$$-\frac{2m}{\hbar^2} [H, M^+] = - \left(\frac{\pi}{L} \right)^2 (2n+1) M^+ + \left(\frac{\pi}{L} \right)^2 (2n) \cos \left(\frac{\pi x}{L} \right) + \frac{2}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2}{\partial x^2} \tag{4.33}$$

$$[H, M^+] = -\frac{\hbar^2}{2m} \left(- \left(\frac{\pi}{L} \right)^2 (2n+1) M^+ + \left(\frac{\pi}{L} \right)^2 (2n) \cos \left(\frac{\pi x}{L} \right) + \frac{2}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\partial^2}{\partial x^2} \right) \tag{4.34}$$

$$[H, M^+] = -\frac{\hbar^2}{2m} \left(- \left(\frac{\pi}{L} \right)^2 (2n+1) M^+ + 2n \left(\frac{\pi}{L} \right)^2 \cos \left(\frac{\pi x}{L} \right) \right) - \frac{2}{n} \cos \left(\frac{\pi x}{L} \right) \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \tag{4.35}$$

$$H|n\rangle = \epsilon_n |n\rangle$$

and, operating from the left with M^+ one has

$$M^+ H|n\rangle = \epsilon_n M^+ |n\rangle = \epsilon_n |n+1\rangle$$

and since $[H, M^+] = HM^+ - M^+H$, one has

$$HM^+|n\rangle - [H, M^+]|n\rangle = \epsilon_n|n+1\rangle$$

$$H|n+1\rangle - [H, M^+]|n+1\rangle = \epsilon_n|n+1\rangle$$

$$H|n+1\rangle + \frac{\hbar^2}{2m} \left(-\left(\frac{\pi}{L}\right)^2 (2n+1)M^+ + 2n\left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) \right) |n\rangle + \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} |n\rangle = \epsilon_n|n+1\rangle$$

$$H|n+1\rangle + \frac{\hbar^2}{2m} \left(-\left(\frac{\pi}{L}\right)^2 (2n+1)M^+ + 2n\left(\frac{\pi}{L}\right)^2 \cos\left(\frac{\pi x}{L}\right) \right) |n\rangle - \frac{2}{n} \cos\left(\frac{\pi x}{L}\right) \epsilon_n|n\rangle = \epsilon_n|n+1\rangle$$

$$H|n+1\rangle + \frac{\hbar^2}{2m} \left(-\left(\frac{\pi}{L}\right)^2 (2n+1)M^+ + \left[2n\left(\frac{\pi}{L}\right)^2 - \frac{4m}{n\hbar^2} \epsilon_n \right] \cos\left(\frac{\pi x}{L}\right) \right) |n\rangle = \epsilon_n|n+1\rangle$$

$$H|n+1\rangle + \frac{\hbar^2}{2m} \left(-\left(\frac{\pi}{L}\right)^2 (2n+1)M^+ \right) |n\rangle + \left[2n\left(\frac{\pi}{L}\right)^2 - \frac{4m}{n\hbar^2} \epsilon_n \right] \cos\left(\frac{\pi x}{L}\right) |n\rangle = \epsilon_n|n+1\rangle$$

$$H|n+1\rangle + \frac{\hbar^2}{2m} \left(-\left(\frac{\pi}{L}\right)^2 (2n+1) \right) |n+1\rangle + \left[2n\left(\frac{\pi}{L}\right)^2 - \frac{4m}{n\hbar^2} \epsilon_n \right] \cos\left(\frac{\pi x}{L}\right) |n\rangle = \epsilon_n|n+1\rangle$$

$$H|n+1\rangle + \left[2n\left(\frac{\pi}{L}\right)^2 - \frac{4m}{n\hbar^2} \epsilon_n \right] \cos\left(\frac{\pi x}{L}\right) |n\rangle = \epsilon_n|n+1\rangle + \frac{\hbar^2}{2m} \left(\left(\frac{\pi}{L}\right)^2 (2n+1) \right) |n+1\rangle$$

From this we conclude that, if the elements in square brackets cancelled perfectly, $M^+|n+1\rangle$ would be an eigenfunction, i.e., if

$$+ \left[2n\left(\frac{\pi}{L}\right)^2 - \frac{4m}{n\hbar^2} \epsilon_n \right] = 0 \quad (4.36)$$

i.e.,

$$\epsilon_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2}$$

then

$$H|n+1\rangle = \left(\epsilon_n + \frac{\hbar^2}{2m} \left(\left(\frac{\pi}{L}\right)^2 (2n+1) \right) \right) |n+1\rangle$$

Sines and cosines form a complete orthonormal set, suitable for Fourier Series expansion, where ‘ortho’ means that each member is orthogonal to every other member, and ‘normal’ means that one can normalize them (if one wishes). There are other such sets, and each of them shows up in standard Quantum Chemistry, so each needs to be addressed separately.

V. HERMITE POLYNOMIALS

The relevant Schrödinger Equation is

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial z^2} \psi + \frac{k}{2} z^2 \psi = E\psi \quad (5.1)$$

where k is the force constant (dynes/cm) and μ is the reduced mass (grams). Cross multiplying, one has

$$\frac{\partial^2}{\partial z^2} \psi - \frac{k\mu}{\hbar^2} z^2 \psi = -\frac{2\mu}{\hbar^2} E\psi \quad (5.2)$$

which would be simplified if the constants could be suppressed. To do this we change variable, from z to something else, say x , where $z = \alpha x$. Then

$$\frac{\partial}{\partial z} = \frac{\partial x}{\partial z} \frac{\partial}{\partial x} = \frac{1}{\alpha} \frac{\partial}{\partial x}$$

so

$$\left(\frac{1}{\alpha^2} \right) \frac{\partial^2}{\partial x^2} \psi - \frac{k\mu}{\hbar^2} \alpha^2 x^2 \psi = -\frac{2\mu}{\hbar^2} E\psi \quad (5.3)$$

and

$$\frac{\partial^2}{\partial x^2} \psi - \frac{k\mu}{\hbar^2} \alpha^4 x^2 \psi = -\alpha^2 \frac{2\mu}{\hbar^2} E\psi \quad (5.4)$$

which demands that we treat

$$1 = \frac{k\mu}{\hbar^2} \alpha^4$$

$$\alpha = \left(\frac{1}{\frac{k\mu}{\hbar^2}} \right)^{1/4} = \left(\frac{\hbar^2}{k\mu} \right)^{1/4}$$

With this choice, the differential equation becomes

$$\frac{\partial^2 \psi}{\partial x^2} - x^2 \psi = -\epsilon \psi \quad (5.5)$$

where

$$\epsilon = \frac{2\alpha^2 \mu E}{\hbar^2} = \frac{2\sqrt{\frac{\hbar^2}{k\mu}} \mu E}{\hbar^2} = \frac{2E\sqrt{\frac{\mu}{k}}}{\hbar}$$

A. A Guessed Solution

The easiest solution to this differential equation is

$$e^{-\frac{x^2}{2}}$$

which leads to $\epsilon = 1$ and

$$E = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}}$$

B. Laddering up on the Guessed Solution

Given

$$\psi_0 = |0\rangle = e^{-\frac{x^2}{2}}$$

with $\epsilon = 1$, it is possible to generate the next solution by using

$$N^+ = -\frac{\partial}{\partial x} + x \quad (5.6)$$

as an operator, which ladders up from the ground (n=0) state to the next one (n=1) To see this we apply N^+ to ψ_0 obtaining

$$N^+ \psi_0 = N^+ |0\rangle = \left(-\frac{\partial}{\partial x} + x \right) e^{-\frac{x^2}{2}} = -(-x) \psi_0 + x \psi_0 = 2x e^{-x^2/2} = \psi_1 = |1\rangle \quad (5.7)$$

Doing this operation again, one has

$$N^+ \psi_1 = N^+ |1\rangle = \left(-\frac{\partial}{\partial x} + x \right) 2x e^{-\frac{x^2}{2}} = (-2 + 4x^2) e^{-x^2/2} \quad (5.8)$$

etc., etc., etc..

where $H(x)$ is going to become a Hermite polynomial. One then has

$$\frac{d\psi}{dx} = -x e^{-x^2/2} H(x) + e^{-x^2/2} \frac{dH(x)}{dx}$$

C. Generating Hermite's differential equation

Assuming

$$\psi = e^{-x^2/2} H(x)$$

and

$$\frac{d^2 \psi}{dx^2} = -e^{-x^2/2} H(x) + x^2 e^{-x^2/2} H(x) - 2x e^{-x^2/2} \frac{dH(x)}{dx} + e^{-x^2/2} \frac{d^2 H(x)}{dx^2}$$

From Equation 5.5 one has,

$$\frac{\partial^2}{\partial x^2} \psi - x^2 \psi = -e^{-x^2/2} H(x) - 2x e^{-x^2/2} \frac{dH(x)}{dx} + e^{-x^2/2} \frac{d^2 H(x)}{dx^2} = -\epsilon e^{-x^2/2} H(x) \quad (5.9)$$

or

$$-H(x) - 2x \frac{dH(x)}{dx} + \frac{d^2 H(x)}{dx^2} = -\epsilon H(x) \quad (5.10)$$

which we re-write in normal lexicographical order

$$\frac{d^2 H(x)}{dx^2} - 2x \frac{dH(x)}{dx} - (1 - \epsilon) H(x) = 0 \quad (5.11)$$

D. An alternative solution scheme

Starting with

$$\frac{dy}{dx} + 2xy = 0 \quad (5.12)$$

one has

$$\frac{dy}{y} = -2xdx$$

so, integrating each side separately, one has

$$\ln y = -x^2 + \ln C$$

or, inverting the logarithm,

$$y = Ce^{-x^2}$$

We now differentiate Equation 5.12, obtaining

$$\frac{d^2y}{dx^2} + 2\frac{d(xy)}{dx} = \frac{d^2y}{dx^2} + 2x\frac{dy}{dx} + 2y\frac{dx}{dx} = \frac{d^2y}{dx^2} + 2x\frac{dy}{dx} + 2y = 0; n = 0 \quad (5.13)$$

Doing this again, i.e., differentiating this (second) equation (Equation 5.13), one has

$$\frac{d\frac{d^2y}{dx^2}}{dx} + \frac{d2x\frac{dy}{dx}}{dx} + 2\frac{dy}{dx} = \frac{d^2\left(\frac{dy}{dx}\right)}{dx^2} + 2x\frac{d\left(\frac{dy}{dx}\right)}{dx} + 4\left(\frac{dy}{dx}\right) = 0; n = 1$$

which is the same equation, (but with a 4 multiplier of the last term) applied to the first derivative of y . Take the derivative again:

$$\frac{d\left(\frac{d^2\frac{dy}{dx}}{dx^2} + 2x\frac{d\frac{dy}{dx}}{dx} + 4\frac{dy}{dx}\right)}{dx} = 0$$

i.e.,

$$\frac{d^2\left(\frac{d^2y}{dx^2}\right)}{dx^2} + 2x\frac{d\left(\frac{d^2y}{dx^2}\right)}{dx} + 6\left(\frac{d^2y}{dx^2}\right) = 0$$

$$\frac{d^2f(x)}{dx^2} + 2x\frac{df(x)}{dx} + 6f(x) = 0; n = 2$$

$f(x)$ has the form $g(x)e^{-x^2}$ where $g(x)$ is a polynomial in x .

$$\frac{d^2g(x)e^{-x^2}}{dx^2} + 2x\frac{dg(x)e^{-x^2}}{dx} + 2(n+1)g(x)e^{-x^2} = 0$$

i.e.,

$$(g''(x) - 4xg'(x) - 2g(x) + 4x^2g(x) + 2xg'(x) - 4x^2g(x) + 2(n+1)g(x))e^{-x^2} = 0$$

or

$$g''(x) - 2xg'(x) + 2ng(x) = 0$$

and we had (see Equation 5.11)

$$H''(x) - 2xH'(x) - (1 - \epsilon)H(x) = 0$$

which leads to

$$2n = -1 + \epsilon$$

i.e.,

$$\epsilon = 1 + 2n = \frac{2E\sqrt{\mu/k}}{\hbar}$$

i.e.,

$$E = \hbar(n + 1/2)\sqrt{\frac{k}{\mu}}$$

E. Frobenius Method

The most straight forward technique for handling the Hermite differential equation is the method of Frobenius. We assume a power series Ansatz (ignoring the indicial equation argument here), i.e.,

$$\psi = \sum_{i=0} a_i x^i$$

and substitute this into Equation 5.11, obtaining

$$\begin{aligned}\frac{\partial^2 \psi}{\partial x^2} &= \sum_{i=2} i(i-1)a_i x^{i-2} \\ -2x \frac{\partial \psi}{\partial x} &= -2 \sum_{i=1} i a_i x^i \\ (\epsilon - 1)\psi &= (\epsilon - 1) \sum_i a_i x^i = 0\end{aligned}$$

i.e.,

$$\begin{aligned}\frac{\partial^2 \psi}{\partial x^2} &= 2(1)a_2 + (3)(2)a_3 x + (4)(3)a_4 x^2 + \dots \\ -2x \frac{\partial \psi}{\partial x} &= -2a_1 x^1 - 2a_2 x^2 - 2a_3 x^3 - \dots \\ (\epsilon - 1)\psi &= (\epsilon - 1)a_0 + (\epsilon - 1)a_1 x + (\epsilon - 1)a_2 x^2 - \dots = 0\end{aligned}$$

which leads to

$$(3)(2)a_3 + (\epsilon - 1)a_1 - 2a_1 = 0 \text{ (odd)}$$

$$(4)(3)a_4 - 2a_2 + (\epsilon - 1)a_2 = 0 \text{ (even)}$$

$$(5)(4)a_5 - 2a_3 + (\epsilon - 1)a_3 = 0 \text{ (odd)}$$

etc., which shows a clear distinction between the even and the odd powers of x . We can solve these equations sequentially.

We obtain

$$a_3 = \frac{2 + 1 - \epsilon}{(3)(2)} a_1$$

$$a_4 = \frac{2 + 1 - \epsilon}{(4)(3)} a_2 = \left(\frac{2 + 1 - \epsilon}{(4)(3)} \right) \left(\frac{1 - \epsilon}{(2)(1)} \right)$$

i.e.,

$$a_4 = \left(\frac{(3 - \epsilon)(1 - \epsilon)}{(4)(3)(2)(1)} \right)$$

etc..

This set of even (or odd) coefficients leads to a series which itself converges unto a function which grows to positive infinity as x varies, leading one to require that the series be terminated, becoming a polynomial.

We leave the rest to you and your textbook.

VI. LEGENDRE POLYNOMIALS

A. From Laplace's Equation

There are so many different ways to introduce Legendre Polynomials that one searches for a path into this subject most suitable for chemists.

Consider Laplace's Equation:

$$\nabla^2 \chi = \frac{\partial^2 \chi}{\partial x^2} + \frac{\partial^2 \chi}{\partial y^2} + \frac{\partial^2 \chi}{\partial z^2} = 0 \quad (6.1)$$

which is a partial differential equation for $\chi(x, y, z)$. For our purposes, the solutions can be obtained by guessing, starting with $\chi = 1$, and proceeding to $\chi = x$, $\chi = y$ and $\chi = z$. It takes only a little more imagination to obtain $\chi = xy$ and its associates $\chi = yz$ and $\chi = xz$. It takes just a little more imagination to guess $\chi = x^2 - y^2$, but once done, one immediately guesses its two companions $\chi = x^2 - z^2$ and $\chi = y^2 - z^2$.

Reviewing, there was one simple (order 0) solution, three not so simple, but not particularly difficult solutions (of order 1) and six slightly more complicated solutions of order 2. Note that the first third-order solution one might guess would be $\chi = xyz!$

If one looks at these solutions, knowing that they are quantum mechanically important, the 1, x , y , and z solutions, accompanied by the xy , xz , yz , and $x^2 - y^2$ solutions suggest something having to do with wave functions, where the first function (1) is associated in some way with s-orbitals, the next three (x , y , and z) are associated with p-orbitals, and the next (of order 2) are associated with d-orbitals. If all this is true, the perceptive student will wonder where is the d_{z^2} orbital, the fifth one, and how come there are six functions of order two listed, when, if memory serves correctly, there are 5 d-orbitals! Ah.

$$(y^2 - z^2) + (x^2 - y^2)$$

can be rewritten as

$$(y^2 - z^2) + (x^2 - y^2) + (z^2 - z^2)$$

which is

$$x^2 + y^2 + z^2 - 3z^2$$

or as

$$r^2 - 3z^2$$

which combines the last two (linearly dependent) solutions into one, the one of choice, which has been employed for more than 50 years as the d_{z^2} orbital.

In Spherical Polar Coordinates, these solutions become

$$\begin{aligned}
1 &\Leftrightarrow 1 \\
x &\Leftrightarrow r \sin \vartheta \cos \phi \\
y &\Leftrightarrow r \sin \vartheta \sin \phi \\
z &\Leftrightarrow r \cos \vartheta \\
xy &\Leftrightarrow r \sin \vartheta \cos \phi r \sin \vartheta \sin \phi = r^2 \sin^2 \vartheta \cos \phi \sin \phi \\
xz &\Leftrightarrow r \sin \vartheta \cos \phi r \cos \vartheta = r^2 \sin \vartheta \cos \vartheta \cos \phi \\
yz &\Leftrightarrow r \sin \vartheta \sin \phi r \cos \vartheta = r^2 \sin \vartheta \cos \vartheta \sin \phi \\
x^2 - y^2 &\Leftrightarrow r^2 \sin^2 \vartheta \cos^2 \phi - r^2 \sin^2 \vartheta \sin^2 \phi = r^2 (\sin^2 \vartheta [\cos^2 \phi - \sin^2 \phi]) \\
r^2 - 3z^2 &\Leftrightarrow r^2 - 3r^2 \cos^2 \vartheta = r^2 (1 - 3 \cos^2 \vartheta) \\
&\vdots
\end{aligned} \tag{6.2}$$

Now, Laplace's equation in spherical polar coordinates is

$$\nabla^2 \chi = \frac{1}{r^2} \frac{\partial r^2 \frac{\partial \chi}{\partial r}}{\partial r} + \frac{1}{r^2 \sin^2 \vartheta} \left[\sin \vartheta \frac{\partial \sin \vartheta \frac{\partial \chi}{\partial \vartheta}}{\partial \vartheta} + \frac{\partial^2 \chi}{\partial \phi^2} \right] = 0 \tag{6.3}$$

Next, we notice that our earlier solutions were all of the form

$$\chi = r^\ell \mathcal{Y}_{\ell, m_\ell}(r, \vartheta, \phi) \tag{6.4}$$

where ℓ specifies the order, 0, 1, 2, etc., and the function of angles is dependent on this order, and on another quantum number as yet unspecified. Substituting this form into the spherical polar form of Laplace's equation results in a new equation for the angular parts alone, which we know from our previous results. We substitute Equation 6.4 into Equation 6.3 to see what happens, obtaining

$$\begin{aligned}
\nabla^2 r^\ell \mathcal{Y}_{\ell, m_\ell} &= \frac{1}{r^2} \frac{\partial r^2 \frac{\partial r^\ell \mathcal{Y}_{\ell, m_\ell}}{\partial r}}{\partial r} \\
&+ \frac{1}{r^2 \sin^2 \vartheta} \left[\sin \vartheta \frac{\partial \sin \vartheta \frac{\partial r^\ell \mathcal{Y}_{\ell, m_\ell}}{\partial \vartheta}}{\partial \vartheta} + \frac{\partial^2 r^\ell \mathcal{Y}_{\ell, m_\ell}}{\partial \phi^2} \right] \\
&= 0
\end{aligned}$$

which, by the nature of partial differentiation, becomes

$$\begin{aligned}
\nabla^2 r^\ell \mathcal{Y}_{\ell, m_\ell} &= \mathcal{Y}_{\ell, m_\ell} \frac{1}{r^2} \frac{\partial r^2 \frac{\partial r^\ell}{\partial r}}{\partial r} \\
&+ r^\ell \frac{1}{r^2 \sin^2 \vartheta} \left[\sin \vartheta \frac{\partial \sin \vartheta \frac{\partial \mathcal{Y}_{\ell, m_\ell}}{\partial \vartheta}}{\partial \vartheta} + \frac{\partial^2 \mathcal{Y}_{\ell, m_\ell}}{\partial \phi^2} \right] = 0 \tag{6.5}
\end{aligned}$$

and the first term in Equation 6.5 is

$$\frac{1}{r^2} \frac{\partial r^2 \frac{\partial r^\ell}{\partial r}}{\partial r} = \frac{1}{r^2} \ell(\ell+1) r^\ell \tag{6.6}$$

so, substituting into Equation 6.5 we obtain

$$\nabla^2 r^\ell \mathcal{Y}_{\ell, m_\ell} = \ell(\ell+1) r^{\ell-2} \mathcal{Y}_{\ell, m_\ell} + r^{\ell-2} \frac{1}{\sin^2 \vartheta} \left[\sin \vartheta \frac{\partial \sin \vartheta \frac{\partial \mathcal{Y}_{\ell, m_\ell}}{\partial \vartheta}}{\partial \vartheta} + \frac{\partial^2 \mathcal{Y}_{\ell, m_\ell}}{\partial \phi^2} \right] = 0 \tag{6.7}$$

which, of course, upon cancelling common terms, gives

$$\ell(\ell+1) \mathcal{Y}_{\ell, m_\ell} + \frac{1}{\sin^2 \vartheta} \left[\sin \vartheta \frac{\partial \sin \vartheta \frac{\partial \mathcal{Y}_{\ell, m_\ell}}{\partial \vartheta}}{\partial \vartheta} + \frac{\partial^2 \mathcal{Y}_{\ell, m_\ell}}{\partial \phi^2} \right] = 0 \tag{6.8}$$

Laplace's Equation in Spherical Polar Coordinates on the unit sphere, i.e. Legendre's Equation!

What then are these angular solutions we found?

$$\begin{aligned}
 \ell &= 0; 1 \\
 \ell &= 1; \sin \vartheta \cos \phi \\
 \ell &= 1; \sin \vartheta \sin \phi \\
 \ell &= 1; \cos \vartheta \\
 \ell &= 2; \sin^2 \vartheta \cos \phi \sin \phi \\
 \ell &= 2; \sin \vartheta \cos \vartheta \cos \phi \\
 \ell &= 2; \sin \vartheta \cos \vartheta \sin \phi \\
 \ell &= 2; (\sin^2 \vartheta [\cos^2 \phi - \sin^2 \phi]) \\
 \ell &= 2; (1 - 3 \cos^2 \vartheta) \\
 &\vdots
 \end{aligned} \tag{6.9}$$

and if you check back concerning their origin, you will see where the Hydrogenic Orbitals naming pattern comes from for s , p and d orbitals.

These functions have been written in “real” form, and they have “complex” (not complicated) forms which allow a different simplification:

$$\begin{aligned}
 1s &\Leftrightarrow \ell = 0; 1 \\
 2p_x &\Leftrightarrow \ell = 1; \sin \vartheta \frac{e^{i\phi} + e^{-i\phi}}{2} \\
 2p_y &\Leftrightarrow \ell = 1; \sin \vartheta \left(\frac{e^{i\phi} - e^{-i\phi}}{2i} \right) \\
 2p_z &\Leftrightarrow \ell = 1; \cos \vartheta \\
 3d_{xy} &\Leftrightarrow \ell = 2; \sin^2 \vartheta \left(\frac{e^{i\phi} + e^{-i\phi}}{2} \right) \left(\frac{e^{i\phi} - e^{-i\phi}}{2i} \right) \\
 3d_{xz} &\Leftrightarrow \ell = 2; \sin \vartheta \cos \vartheta \frac{e^{i\phi} + e^{-i\phi}}{2} \\
 3d_{yz} &\Leftrightarrow \ell = 2; \sin \vartheta \cos \vartheta \left(\frac{e^{i\phi} - e^{-i\phi}}{2i} \right) \\
 3d_{x^2-y^2} &\Leftrightarrow \ell = 2; \left(\sin^2 \vartheta \left[\left(\frac{e^{i\phi} + e^{-i\phi}}{2} \right)^2 - \left(\frac{e^{i\phi} - e^{-i\phi}}{2i} \right)^2 \right] \right) \\
 3d_{z^2} &\Leftrightarrow \ell = 2; (1 - 3 \cos^2 \vartheta) \\
 &\vdots
 \end{aligned} \tag{6.10}$$

Once they have been written in imaginary form, we can create intelligent linear combinations of them which illuminate their underlying structure. Consider $2p_x + i2p_y$ which becomes

$$\sin \vartheta e^{i\phi}$$

(employing DeMoivre’s theorem) aside from irrelevant constants. Next consider $2p_x - i2p_y$ which becomes

$$\sin \vartheta e^{-i\phi}$$

We have a trio of functions

$$\begin{aligned}
 2p_{m_\ell=-1} &= \sin \vartheta e^{-i\phi} \\
 2p_{m_\ell=0} &= \cos \vartheta \\
 2p_{m_\ell=+1} &= \sin \vartheta e^{+i\phi}
 \end{aligned} \tag{6.11}$$

$$\tag{6.12}$$

which correspond to the m_ℓ values expected of p-orbitals.

You will see that the same “trick” can be applied to d_{xz} and d_{yz} .

Finally, the same trick, almost, can be applied to d_{xy} and $d_{x^2-y^2}$ with the $m_\ell = 0$ value reserved for d_{z^2} , all by itself.

B. From the Hydrogen Atom

Perhaps the next best place to introduce Spherical Harmonics and Legendre Polynomials is the Hydrogen Atom, since its eigenfunctions have angular components which are known to be Legendre Polynomials.

The Schrödinger Equation for the H-atom is

$$-\frac{\hbar^2}{2m_e}\nabla^2|n, \ell, m_\ell\rangle - \frac{Ze^2}{r}|n, \ell, m_\ell\rangle = E_n|n, \ell, m_\ell\rangle \quad (6.13)$$

We know that this equation is variable separable, in

the sense that

$$|n, \ell, m_\ell\rangle = R_{n,\ell}(r)\mathcal{Y}_{\ell,m_\ell}(\vartheta, \phi)$$

Here, $R_{n,\ell}$ is the radial wave function, and $\mathcal{Y}_{\ell,m_\ell}$ is the angular wave function (a function of two variables), Since

$$\nabla^2 = \frac{1}{r^2}\frac{\partial^2}{\partial r^2} + \frac{1}{r^2\sin^2\vartheta}\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\phi^2}\right]$$

$$\nabla^2|n, \ell, m_\ell\rangle = \nabla^2 R_{n,\ell}(r)\mathcal{Y}_{\ell,m_\ell}(\vartheta, \phi) = \frac{\mathcal{Y}}{r^2}\frac{\partial r^2}{\partial r} + \frac{R}{r^2\sin^2\vartheta}\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\phi^2}\right]$$

which means that the Schrödinger Equation has the form

$$-\frac{\hbar^2}{2m_e}\left\{\frac{\mathcal{Y}}{r^2}\frac{\partial r^2}{\partial r} + \frac{R}{r^2\sin^2\vartheta}\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\phi^2}\right]\right\} - \frac{Ze^2}{r}R\mathcal{Y} = E_n R\mathcal{Y}$$

Dividing through by $R_{n,\ell}\mathcal{Y}_{\ell,m_\ell}$ (abbreviated as $R\mathcal{Y}$) we have

$$-\frac{\hbar^2}{2m_e}\left\{\frac{1}{Rr^2}\frac{\partial r^2}{\partial r} + \frac{1}{r^2\mathcal{Y}\sin^2\vartheta}\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\phi^2}\right]\right\} - \frac{Ze^2}{r} = E_n$$

Multiplying through by r^2 shows that the expected variable separation has resulted in a proper segregation of the angles from the radius.

$$\frac{1}{R}\frac{\partial r^2}{\partial r} + \underbrace{\frac{1}{\mathcal{Y}\sin^2\vartheta}\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\phi^2}\right]}_{\text{pure function of angles}} + \frac{2mZe^2r}{\hbar^2} = -\frac{2m}{\hbar^2}E_nr^2$$

We can see this by noting that the underbracketed part of this last equation is a pure function of angles, with no radius explicitly evident.

It is now standard to obtain (recover?) the equation (6.8)

$$\frac{1}{\mathcal{Y}\sin^2\vartheta}\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\phi^2}\right] = -\ell(\ell+1) \quad (6.14)$$

where the minus sign (which is essentially arbitrary) is demanded by convention.

Cross multiplying by \mathcal{Y} , one has

$$\frac{1}{\sin^2\vartheta}\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\phi^2}\right] = -\ell(\ell+1)\mathcal{Y} \quad (6.15)$$

which is written in traditional eigenfunction/eigenvalue form.

C. Another Form for the Legendre Differential Equation

A change of variables can throw this equation (Equation 6.15) into a special form, which is sometimes illumi-

nating. We write

$$\mu = \cos\vartheta$$

and

$$\frac{\partial\mu}{\partial\vartheta} = -\sin\vartheta = -\sqrt{1-\cos^2\vartheta} = -\sqrt{1-\mu^2}$$

so

$$\frac{\partial}{\partial\vartheta} = \left(\frac{\partial\mu}{\partial\vartheta}\right)\frac{\partial}{\partial\mu}$$

which is, substituting into Equation 6.15

$$\frac{\partial}{\partial\vartheta} = \left(-\sqrt{1-\mu^2}\right)\frac{\partial}{\partial\mu}$$

$$\frac{1}{(1-\mu^2)} \left[\sqrt{1-\mu^2} \sqrt{1-\mu^2} \frac{\partial \sqrt{1-\mu^2} \sqrt{1-\mu^2} \frac{\partial \mathcal{Y}}{\partial \mu}}{\partial \mu} + \frac{\partial^2 \mathcal{Y}}{\partial \phi^2} \right] = -\ell(\ell+1)\mathcal{Y} \quad (6.16)$$

where the $\ell(\ell+1)$ form is a different version of a constant, looking ahead to future results!

$$\left[\frac{\partial \left((1-\mu^2) \frac{\partial \mathcal{Y}}{\partial \mu} \right)}{\partial \mu} + \frac{\partial^2 \mathcal{Y}}{\partial \phi^2} \right] = -\ell(\ell+1)\mathcal{Y} \quad (6.17)$$

where

$$\mathcal{Y}_{\ell, m_\ell}(\vartheta, \phi) = e^{\pm i m_\ell \phi} S_{\ell, m_\ell}(\vartheta)$$

For $m_\ell = 0$ we have

$$\left[\frac{\partial \left((1-\mu^2) \frac{\partial S_{\ell, 0}}{\partial \mu} \right)}{\partial \mu} \right] = -\ell(\ell+1)S_{\ell, 0} \quad (6.18)$$

i.e., Legendre's equation.

D. Schmidt Orthogonalization

We assume polynomials in μ^n and seek orthonormal combinations which can be generated starting with a constant ($n=0$) term. Then the normalization integral

$$\langle 0|0 \rangle = \int_{+1}^{-1} \psi_0^2 d\mu = 1$$

[4] implies that

$$|0 \rangle = \sqrt{\frac{1}{2}}$$

We now seek a function $|1 \rangle$ orthogonal to $|0 \rangle$ which itself is normalizable. We have

$$0 = \langle 1|0 \rangle = \int_{+1}^{-1} \psi_1 \sqrt{\frac{1}{2}} d\mu$$

which has solution $\psi_1 = N_1 x$. Normalizing, we have

$$\langle 1|1 \rangle = \int_{+1}^{-1} \psi_1^2 d\mu = 1 = \int_{+1}^{-1} N_1^2 \mu^2 d\mu$$

which yields

$$1 = N_1^2 \frac{2}{3}$$

i.e.,

$$|1 \rangle = \sqrt{\frac{3}{2}} x$$

To proceed, we need to generate a function $|2 \rangle$ which is not only normalizable but orthogonal to $|0 \rangle$ and $|1 \rangle$.

$$\langle 2|0 \rangle = \int_{+1}^{-1} \psi_2 \sqrt{\frac{1}{2}} d\mu = 0$$

and

$$\langle 2|1 \rangle = \int_{+1}^{-1} \psi_2 \sqrt{\frac{2}{3}} \mu d\mu = 0$$

where $|2 \rangle$ is a polynomial of order 2 in μ , i.e.,

$$\psi_2 = |2 \rangle = a\mu^2 + b$$

Substituting, we have

$$\langle 2|0 \rangle = \int_{+1}^{-1} (a\mu^2 + b) \sqrt{\frac{1}{2}} d\mu = 0$$

and

$$\langle 2|1 \rangle = \int_{+1}^{-1} (a\mu^2 + b) \sqrt{\frac{3}{2}} \mu d\mu = 0$$

We obtain two equations in two unknowns, a and b ,

$$\sqrt{\frac{1}{2}} \left(\frac{2a}{3} + 2b \right) = 0$$

and the other integral vanishes automatically. i.e.,

$$\frac{a}{3} + b = 0$$

i.e., $a = -3b$ so

$$|2 \rangle = -3b\mu^2 + b$$

in unnormalized form. Normalizing gives

$$\langle 2|2 \rangle = \int_{+1}^{-1} (-3b\mu^2 + b)^2 d\mu = 1$$

i.e.,

$$\langle 2|2 \rangle = b^2 \int_{+1}^{-1} (-3\mu^2 + 1)^2 d\mu = 1$$

which gives

$$b = \sqrt{\frac{1}{\int_{+1}^{-1} (-3\mu^2 + 1)^2 d\mu}}$$

where, of course, we recognize the sign ambiguity in this result.

One can continue forever with this Schmidt Orthogonalization, but the idea is clear, and there are better ways, so why continue?

E. Frobenius Solution to Legendre's Equation

We start a Frobenius solution without worrying about the technical details of the indicial equation, and just assert that the proposed solution Ansatz will be

$$S_{\ell,0}(\mu) = y(\mu) = \sum_{n=0}^{\infty} c_n \mu^n = c_0 + c_1 \mu + c_2 \mu^2 + \dots \quad (6.19)$$

which we substitute into the differential equation:

$$\frac{\partial \left((1 - \mu^2) \frac{\partial y(\mu)}{\partial \mu} \right)}{\partial \mu} = -\ell(\ell + 1)y(\mu) \quad (6.20)$$

which leads to

$$\frac{\partial \left(\frac{\partial y(\mu)}{\partial \mu} \right)}{\partial \mu} - \frac{\partial \left(\mu^2 \frac{\partial y(\mu)}{\partial \mu} \right)}{\partial \mu} + \ell(\ell + 1)y(\mu) = 0 \quad (6.21)$$

$$\frac{\partial^2 y(\mu)}{\partial \mu^2} - \mu^2 \frac{\partial^2 y(\mu)}{\partial \mu^2} - 2\mu \frac{\partial y(\mu)}{\partial \mu} + \ell(\ell + 1)y(\mu) = 0 \quad (6.22)$$

so that when we feed the Ansatz into this differential equation we obtain

$$\begin{aligned} & (2)(1)c_2 + (3)(2)c_3\mu + (4)(3)c_4\mu^2 + (5)(4)c_5\mu^3 \dots \\ & - \mu^2 ((2)(1)c_2 + (3)(2)c_3\mu + (4)(3)c_4\mu^2 + (5)(4)c_5\mu^3 \dots) \\ & - 2\mu (c_1 + (2)c_2\mu + (3)c_3\mu^2 + (4)c_4\mu^3 + \dots) \\ & + \ell(\ell + 1) (c_0 + c_1\mu + c_2\mu^2 + c_3\mu^3 + \dots) = 0 \end{aligned} \quad (6.23)$$

$$\begin{aligned} & (2)(1)c_2 + (3)(2)c_3\mu + (4)(3)c_4\mu^2 + (5)(4)c_5\mu^3 \dots \\ & - (2)(1)c_2\mu^2 - (3)(2)c_3\mu^3 - (4)(3)c_4\mu^4 - (5)(4)c_5\mu^5 - \dots \\ & - 2c_1\mu - 2(2)c_2\mu^2 - 2(3)c_3\mu^3 - 2(4)c_4\mu^4 - \dots \\ & + \ell(\ell + 1)c_0 + \ell(\ell + 1)c_1\mu + \ell(\ell + 1)c_2\mu^2 + \ell(\ell + 1)c_3\mu^3 + \dots = 0 \end{aligned} \quad (6.24)$$

which, in standard Frobenius form, we separately equate to zero (power by power) to achieve the appropriate recursion relationships. Note that there is an even and an odd set, based on starting the c_0 or c_1 , which correspond to the two arbitrary constants associated with a second order differential equation. We obtain

$$\begin{aligned} & (2)(1)c_2 + \ell(\ell + 1)c_0 = 0 \\ & + (3)(2)c_3\mu - 2c_1\mu + \ell(\ell + 1)c_1\mu = 0 \\ & + (4)(3)c_4\mu^2 - (2)(1)c_2\mu^2 - 2(2)c_2\mu^2 + \ell(\ell + 1)c_2\mu^2 = 0 \\ & (5)(4)c_5\mu^3 - (3)(2)c_3\mu^3 - 2(3)c_3\mu^3 + \ell(\ell + 1)c_3\mu^3 = 0 \\ & - (4)(3)c_4\mu^4 - 2(4)c_4\mu^5 + \dots \text{ etc} = 0 \end{aligned}$$

$$\begin{aligned} & (2)(1)c_2 + \ell(\ell + 1)c_0 = 0 \\ & + (3)(2)c_3 - 2c_1 + \ell(\ell + 1)c_1 = 0 \\ & + (4)(3)c_4 - (2)(1)c_2 - 2(2)c_2 + \ell(\ell + 1)c_2 = 0 \\ & (5)(4)c_5 - (3)(2)c_3 - 2(3)c_3 + \ell(\ell + 1)c_3 = 0 \\ & - (4)(3)c_4\mu^4 - 2(4)c_4\mu^5 \text{ etc} + \dots = 0 \end{aligned} \quad (6.25)$$

$$\begin{aligned} & (2)(1)c_2 = -\ell(\ell + 1)c_0 \\ & + (3)(2)c_3 = (2 - \ell(\ell + 1))c_1 \\ & + (4)(3)c_4 = ((2)(1) + 2(2) - \ell(\ell + 1))c_2 \\ & (5)(4)c_5 = ((3)(2) + 2(3) - \ell(\ell + 1))c_3 \\ & - (4)(3)c_4\mu^4 - 2(4)c_4\mu^5 \text{ etc} + \dots = 0 \end{aligned} \quad (6.26)$$

$$\begin{aligned} c_2 &= -\frac{\ell(\ell + 1)}{2!}c_0 \\ c_3 &= -\frac{(2\ell + (\ell + 1))}{(3)(2)}c_1 \\ c_4 &= -\frac{(-(2)(1) - 2(2) + \ell(\ell + 1))}{(4)(3)}c_2 \\ c_5 &= -\frac{((3)(2) - 2(3) + \ell(\ell + 1))}{(5)(4)}c_3 \\ & \text{etc.} \end{aligned} \quad (6.27)$$

which we re-write in terms of c_0 and c_1 only, i.e.,

$$\begin{aligned} c_2 &= -\frac{\ell(\ell + 1)}{2!}c_0 \\ c_3 &= -\frac{(2 + \ell(\ell + 1))}{(3)(2)}c_1 + \\ c_4 &= -\left(\frac{((2)(1) - 2(2) + \ell(\ell + 1))}{(4)(3)} \right) \left(-\frac{\ell(\ell + 1)}{2!} \right) c_0 \\ c_5 &= -\left(\frac{((3)(2) - 2(3) + \ell(\ell + 1))}{(5)(4)} \right) \left(-\frac{(2 + \ell(\ell + 1))}{(3)(2)} \right) c_1 \end{aligned} \quad (6.28)$$

so $S_{\ell,0}(\mu) = f_1 c_0 + f_2 c_1$ where f_1 and f_2 are power series based on the above set of coefficients. For an even series, declare $c_1 = 0$ and choose an ℓ value which truncates the

power series into a polynomial. Do the opposite for an odd solution.

F. Rodrigue's Formula

Rodrique's formula is

$$S_{\ell,0} \rightarrow P_{\ell}(\mu) = \frac{1}{2^{\ell}\ell!} \frac{d^{\ell}(\mu^2 - 1)^{\ell}}{d\mu^{\ell}}$$

where Legendre's Equation is

$$(1 - \mu^2) \frac{d^2 P_{\ell}(\mu)}{d\mu^2} - 2\mu \frac{dP_{\ell}(\mu)}{d\mu} + \ell(\ell + 1)P_{\ell}(\mu) = 0$$

To show this, we start by defining

$$g_{\ell} \equiv (\mu^2 - 1)^{\ell}$$

and find that

$$\frac{dg_{\ell}}{d\mu} = 2\mu\ell(\mu^2 - 1)^{\ell-1}$$

and

$$\frac{d^2 g_{\ell}}{d\mu^2} = 2\ell(\mu^2 - 1)^{\ell-1} + 4\mu^2\ell(\ell - 1)(\mu^2 - 1)^{\ell-2}$$

We now form (construct)

$$\begin{aligned} (1 - \mu^2) \frac{d^2 g_{\ell}}{d\mu^2} &= -2\ell(\mu^2 - 1)^{\ell} - 4\mu^2\ell(\ell - 1)(\mu^2 - 1)^{\ell-1} \\ 2(\ell - 1)\mu \frac{dg_{\ell}}{d\mu} &= 4\mu^2\ell(\ell - 1)(\mu^2 - 1)^{\ell-1} \\ + 2\ell g_{\ell} &= 2\ell(\mu^2 - 1)^{\ell} \end{aligned} \quad (6.29)$$

The r.h.s. of this equation set adds up to zero, and one obtains on the left:

$$A(\mu) = (1 - \mu^2) \frac{d^2 g_{\ell}}{d\mu^2} + 2(\ell - 1)\mu \frac{dg_{\ell}}{d\mu} + 2\ell g_{\ell} = 0 \quad (6.30)$$

Defining the l.h.s of this equation as $A(\mu)$, we form

$$\frac{dA(\mu)}{d\mu} = \left[(1 - \mu^2) \frac{d^3}{d\mu^3} - 2\mu \frac{d^2}{d\mu^2} + 2(\ell - 1)\mu \frac{d}{d\mu} + 2(\ell - 1) \frac{d}{d\mu} + 2\ell \frac{d}{d\mu} \right] g_{\ell}$$

$$= \left[(1 - \mu^2) \frac{d^2}{d\mu^2} - (2\ell - 4)\mu \frac{d}{d\mu} + (4\ell - 2)\mu \right] \frac{dg_{\ell}}{d\mu}$$

$$\frac{d^2 A(\mu)}{d\mu^2} = \left[(1 - \mu^2) \frac{d^2}{d\mu^2} - (2\ell - 6)\mu \frac{d}{d\mu} + (6\ell - 6)\mu \right] \frac{d^2 g_{\ell}}{d\mu^2}$$

$$\frac{d^3 A(\mu)}{d\mu^3} = \left[(1 - \mu^2) \frac{d^2}{d\mu^2} - (2\ell - 8)\mu \frac{d}{d\mu} + (8\ell - 12)\mu \right] \frac{d^3 g_{\ell}}{d\mu^3}$$

Continuing, one notices that the changing coefficients are regular in their appearance, so that the following table, which summarizes the pattern of coefficients,

$\kappa = 1$	$2\ell - 4 = 2\ell - 2 * (\kappa + 1)$	$4\ell - 2 = (3 + \kappa)\ell - 2 * \kappa$	$= 6$ if $\ell = 1$
$\kappa = 2$	$2\ell - 6 = 2\ell - 2 * (\kappa + 1)$	$6\ell - 6 = (3 + \kappa)\ell - 2 * \kappa$	$= 6$ if $\ell = 2$
$\kappa = 3$	$2\ell - 8 = 2\ell - 2 * (\kappa + 1)$	$8\ell - 12 = (3 + \kappa)\ell - 2 * \kappa$	$= 12$ if $\ell = 3$
\vdots	\vdots	\vdots	\vdots
$\kappa = \ell$	$2\ell - 2 * (\ell + 1) = 2$	$8\ell - 12 = (3 + \ell)\ell - 2 * \ell$	$= \ell(\ell + 1)$

leads to generalization by which one finally obtains

$$\frac{\partial^{\ell} A(x)}{\partial \mu^{\ell}} = \left[(1 - \mu^2) \frac{\partial^2}{\partial \mu^2} - 2\mu \frac{\partial}{\partial \mu} + \ell(\ell + 1) \right] \frac{g_{\ell}(\mu)}{d\mu^{\ell}} \quad (6.31)$$

so, if

$$\frac{d^{\ell} g_{\ell}}{d\mu^{\ell}} \equiv KP_{\ell}(\mu)$$

with K constant, then

$$P_\ell(\mu) = \frac{1}{K} \frac{\partial d^\ell g_\ell}{d\mu^\ell} = \frac{1}{K} \frac{d^\ell(\mu^2 - 1)^\ell}{d\mu^\ell}$$

Here,

$$2^\ell \ell!$$

is chosen for K's value to make the normalization automatic.

G. Generating Function for Legendre Polynomials

The technically correct generating function for Legendre polynomials is via the equation

$$\frac{1}{\sqrt{1-2xu+u^2}} = \sum_0^\infty P_n(x)u^n \quad (6.32)$$

$$\frac{1}{(1-2xu+u^2)^{1/2}} = 1 - (1/2)(u^2 - 2xu) + \frac{(1/2)((1/2)+1)}{2!}(u^2 - 2xu)^2 - \frac{(1/2)((1/2)+1)((1/2)+2)}{3!}(u^2 - 2xu)^3 + \dots$$

which we now re-arrange in powers of u (in the mode required by Equation 6.32), obtaining

$$\frac{1}{(1-2xu+u^2)^{1/2}} = 1 - \frac{u^2}{2} + xu + \frac{(3/4)}{2!}(u^4 - 4xu^3 + 4x^2u^2) - \frac{(1/2)(3/2)(5/2)}{3!}(u^2 - 2xu)^3 + \dots$$

1. Alternative Generating Function Method

Another method of introducing Legendre Polynomials is through the generating function. Since this method is very important in Quantum Mechanical computations concerning poly-electronic atoms and molecules, it is worth our attention. When one considers the Hamiltonian of the Helium Atom's electrons, one has

$$-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \quad (6.33)$$

where r_{12} is the distance between electron 1 and electron 2, i.e., it is the electron-electron repulsion term. We examine this term in this discussion. We can write this electron-electron repulsion term as

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \vartheta}} \quad (6.34)$$

Here, we expand the denominator using the binomial theorem,

$$\frac{1}{(1+y)^m} = 1 - my + \frac{m(m+1)}{2!}y^2 - \frac{m(m+1)(m+2)}{3!}y^3 + \dots$$

where $m = \frac{1}{2}$ and the series converges when $y < 1$. Notice that it is an alternating series. Identifying $y = u^2 - 2xu$ we have

where r_1 and r_2 are the distances from the nucleus to electrons 1 and 2 respectively. ϑ is the angle between the vectors from the nucleus to electron 1 and electron 2. It is required that we do this in two domains, one in which $r_1 > r_2$ and one in which $r_2 > r_1$. This is done for convergence reasons (vide infra). For the first case, we define

$$\zeta = \frac{r_2}{r_1}$$

so that $\zeta < 1$, and Equation 6.34 becomes

$$\frac{1}{r_{12}} = \frac{1}{r_1} \frac{1}{\sqrt{1 + \zeta^2 - 2\zeta \cos \vartheta}} \quad (6.35)$$

which we now expand in a power series in $\cos \vartheta$ (which will converge while $\zeta < 1$). We have

$$\frac{1}{r_1} \frac{1}{\sqrt{1 + \zeta^2 - 2\zeta \cos \vartheta}} = \frac{1}{r_1} \left(1 + \frac{1}{1!} \frac{d \left(\frac{1}{\sqrt{1 + \zeta^2 - 2\zeta \cos \vartheta}} \right)}{d \cos \vartheta} \Big|_{\cos \vartheta=0} + \frac{1}{2!} \frac{d^2 \left(\frac{1}{\sqrt{1 + \zeta^2 - 2\zeta \cos \vartheta}} \right)}{d \cos \vartheta^2} \Big|_{\cos \vartheta=0} \cos^2 \vartheta + \dots \right) \quad (6.36)$$

It is customary to change notation from $\cos \vartheta$ to μ , so

$$\frac{1}{r_{12}} = \frac{1}{r_1} \frac{1}{\sqrt{1 + \zeta^2 - 2\zeta\mu}} \quad (6.37)$$

which we now expand in a power series in μ (which will converge while $\zeta < 1$). We have

$$\frac{1}{r_1} \frac{1}{\sqrt{1 + \zeta^2 - 2\zeta\mu}} = \frac{1}{r_1} \left(1 + \frac{1}{1!} \frac{d\left(\frac{1}{\sqrt{1 + \zeta^2 - 2\zeta\mu}}\right)}{d\mu} \Big|_{\mu=0} \mu + \frac{1}{2!} \frac{d^2\left(\frac{1}{\sqrt{1 + \zeta^2 - 2\zeta\mu}}\right)}{d\mu^2} \Big|_{\mu=0} \mu^2 + \dots \right) + \quad (6.38)$$

which we leave in this form, ready to evaluate and equate to earlier versions of this expansion.

H. The Expansion of a Finite Dipole in Legendre Polynomials

There is yet another way to see Legendre Polynomials in action, through the expansion of the potential energy of point dipoles. To start, we assume that we have a dipole at the origin, with its positive charge (q) at $(0,0,-a/2)$ and its negative charge ($-q$) at $(0,0,+a/2)$, so that

the “bond length” is “ a ”, and therefore the “dipole moment” is “ qa ”.

At some point $P(x, y, z)$, located (also) at r, ϑ, ϕ , we have that the potential energy due to these two point charges is

$$U(x, y, z, a) = \frac{-q}{\sqrt{x^2 + y^2 + (z - a/2)^2}} + \frac{q}{\sqrt{x^2 + y^2 + (z + a/2)^2}}$$

which is just Coulomb’s law.

If we expand this potential energy as a function of “ a ”, the “bond distance”, we have

$$U(x, y, z, a) = U(x, y, z, 0) + \frac{1}{1!} \frac{dU}{da} \Big|_{a=0} a + \frac{1}{2!} \frac{d^2U}{da^2} \Big|_{a=0} a^2 + \frac{1}{3!} \frac{d^3U}{da^3} \Big|_{a=0} a^3 + \dots$$

All we need do, now, is evaluate these derivatives. We have, for the first

$$\frac{1}{1!} \frac{dU}{da} \Big|_{a=0} = q \left(- \left[- \left(\frac{1}{2} \right) \frac{2(z - a/2)(-1/2)}{(x^2 + y^2 + (z - a/2)^2)^{3/2}} \right] + \left[- \left(\frac{1}{2} \right) \frac{2(z + a/2)(1/2)}{(x^2 + y^2 + (z + a/2)^2)^{3/2}} \right] \right)$$

which is, in the limit $a \rightarrow 0$,

$$q \left(- \frac{z}{r^3} \right)$$

so, we have, so far,

$$U(x, y, z, a) = 0 - qa \left(\frac{z}{r^3} \right) + \dots = -qa \left(\frac{\cos \vartheta}{r^2} \right) + \dots$$

i.e., to the dipolar form.

For the second derivative, we take the derivative of the first derivative:

$$\frac{1}{2!} \frac{d^2U}{da^2} \Big|_{a=0} = -q \frac{1}{2 \times 2!} \left(\frac{d\left(\left[\frac{(z - a/2)}{(x^2 + y^2 + (z - a/2)^2)^{3/2}} \right] + \left[\frac{(z + a/2)}{(x^2 + y^2 + (z + a/2)^2)^{3/2}} \right] \right)}{da} \right)$$

which equals zero. The next term gives

$$q \frac{\cos \vartheta (3 - 5 \cos^2 \vartheta)}{8r^4} a^3$$

and so it goes.

I. Alternative Formulations for Angular Momentum Operators

To proceed, it is of value to inspect the angular momentum operator in terms of angles rather than Cartesian coordinates.

Remember that

$$\begin{aligned}x &= r \sin \vartheta \cos \phi \\y &= r \sin \vartheta \sin \phi \\z &= r \cos \vartheta\end{aligned}$$

We start with a feast of partial derivatives:

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \sin \vartheta \cos \phi \quad (6.39)$$

$$\left(\frac{\partial r}{\partial y}\right)_{x,z} = \sin \vartheta \sin \phi \quad (6.40)$$

$$\left(\frac{\partial r}{\partial z}\right)_{x,y} = \cos \vartheta \quad (6.41)$$

$$\left(\frac{\partial \vartheta}{\partial x}\right)_{y,z} = \frac{\cos \vartheta \cos \phi}{r} \quad (6.42)$$

$$\left(\frac{\partial \vartheta}{\partial y}\right)_{x,z} = \frac{\cos \vartheta \sin \phi}{r} \quad (6.43)$$

$$\left(\frac{\partial \vartheta}{\partial z}\right)_{x,y} = -\frac{\sin \vartheta}{r} \quad (6.44)$$

and finally

$$\left(\frac{\partial \phi}{\partial x}\right)_{y,z} = -\frac{\sin \phi}{r \sin \vartheta} \quad (6.45)$$

$$\left(\frac{\partial \phi}{\partial y}\right)_{x,z} = \frac{\cos \phi}{r \sin \vartheta} \quad (6.46)$$

$$\left(\frac{\partial \phi}{\partial z}\right)_{x,y} = 0 \quad (6.47)$$

which we employ on the defined x-component of the angular momentum, thus

$$L_x \equiv yp_z - zp_y = -i\hbar \sin \vartheta \sin \phi \frac{\partial}{\partial z} - \left(-i\hbar \cos \vartheta \frac{\partial}{\partial y}\right)$$

where

$$\begin{aligned}\frac{\partial}{\partial z} &= \left(\frac{\partial r}{\partial z}\right)_{x,y} \frac{\partial}{\partial r} + \left(\frac{\partial \vartheta}{\partial z}\right)_{x,y} \frac{\partial}{\partial \vartheta} + \left(\frac{\partial \phi}{\partial z}\right)_{x,y} \frac{\partial}{\partial \phi} \\ &= (\cos \vartheta) \frac{\partial}{\partial r} + \left(\frac{\sin \vartheta}{r}\right) \frac{\partial}{\partial \vartheta} + (0) \frac{\partial}{\partial \phi}\end{aligned}$$

and

$$\begin{aligned}\frac{\partial}{\partial y} &= \left(\frac{\partial r}{\partial y}\right)_{x,z} \frac{\partial}{\partial r} + \left(\frac{\partial \vartheta}{\partial y}\right)_{x,z} \frac{\partial}{\partial \vartheta} + \left(\frac{\partial \phi}{\partial y}\right)_{x,z} \frac{\partial}{\partial \phi} \\ &= (\sin \vartheta \sin \phi) \frac{\partial}{\partial r} + \left(\frac{\cos \vartheta \sin \phi}{r}\right) \frac{\partial}{\partial \vartheta} + \left(\frac{\cos \phi}{r \sin \vartheta}\right) \frac{\partial}{\partial \phi}\end{aligned}$$

and parenthetically,

$$\begin{aligned}\frac{\partial}{\partial x} &= \left(\frac{\partial r}{\partial x}\right)_{y,z} \frac{\partial}{\partial r} + \left(\frac{\partial \vartheta}{\partial x}\right)_{y,z} \frac{\partial}{\partial \vartheta} + \left(\frac{\partial \phi}{\partial x}\right)_{y,z} \frac{\partial}{\partial \phi} \\ &= (\sin \vartheta \cos \phi) \frac{\partial}{\partial r} + \left(\frac{\cos \vartheta \cos \phi}{r}\right) \frac{\partial}{\partial \vartheta} + \left(-\frac{\sin \phi}{r \sin \vartheta}\right) \frac{\partial}{\partial \phi}\end{aligned}$$

so,

$$\begin{aligned}L_x \equiv yp_z - zp_y &= -i\hbar r \sin \vartheta \sin \phi \left((\cos \vartheta) \frac{\partial}{\partial r} + \left(-\frac{\sin \vartheta}{r}\right) \frac{\partial}{\partial \vartheta} \right) \\ &\quad - \left(-i\hbar r \cos \vartheta \left((\sin \vartheta \sin \phi) \frac{\partial}{\partial r} + \left(\frac{\cos \vartheta \sin \phi}{r}\right) \frac{\partial}{\partial \vartheta} + \left(\frac{\cos \phi}{r \sin \vartheta}\right) \frac{\partial}{\partial \phi} \right)\right)\end{aligned} \quad (6.48)$$

At constant r, the partial with respect to r loses mean-

ing, and one has

$$\begin{aligned}\frac{L_x}{-i\hbar} &= r \sin \vartheta \sin \phi \left(+ \left(-\frac{\sin \vartheta}{r}\right) \frac{\partial}{\partial \vartheta} \right) \\ &\quad - \cos \vartheta \left(\left(\frac{\cos \vartheta \sin \phi}{r}\right) \frac{\partial}{\partial \vartheta} + \left(\frac{\cos \phi}{r \sin \vartheta}\right) \frac{\partial}{\partial \phi} \right)\end{aligned} \quad (6.49)$$

which leads to (combining the ϑ partial derivative terms and cancelling the r terms)

$$L_x = i\hbar \left(\sin\phi \frac{\partial}{\partial\vartheta} + \frac{\cos\vartheta \cos\phi}{\sin\vartheta} \frac{\partial}{\partial\phi} \right) \quad (6.50)$$

and similar arguments lead to

$$L_y = i\hbar \left(\cos\phi \frac{\partial}{\partial\vartheta} - \frac{\cos\vartheta \sin\phi}{\sin\vartheta} \frac{\partial}{\partial\phi} \right) \quad (6.51)$$

$$L_z = i\hbar \frac{\partial}{\partial\phi} \quad (6.52)$$

with

$$L^2 = -\hbar^2 \left(\frac{1}{\sin^2\vartheta} \left[\frac{\partial \sin\vartheta}{\partial\vartheta} \frac{\partial}{\partial\vartheta} + \frac{\partial^2}{\partial\phi^2} \right] \right) \quad (6.53)$$

We see that the operator associated with Legendre's Equation (multiplied by a constant) has emerged, meaning that Legendre Polynomials and angular momentum are intimately associated together.

J. Ladder Operator for Angular Momentum

Defining

$$L^+ = L_x + iL_y$$

and

$$L^- = L_x - iL_y$$

and knowing

$$L_x L_y - L_y L_x = (yp_z - zp_y)(zp_x - xp_z) - (zp_x - xp_z)(yp_z - zp_y)$$

which is

$$\begin{aligned} &= yp_z zp_x - yp_z xp_z - zp_y zp_x + zp_y xp_z - zp_x yp_z \\ &\quad + zp_x zp_y + xp_z yp_z - xp_z zp_y = yp_z zp_x \end{aligned}$$

which is, reordering:

$$\begin{aligned} &= yp_z zp_x - zp_x yp_z - yp_z xp_z + xp_z yp_z \\ &\quad - zp_y zp_x + zp_x zp_y + zp_y xp_z - xp_z zp_y \end{aligned}$$

which is, cancelling:

$$\begin{aligned} &= yp_z zp_x - zp_x yp_z + zp_y xp_z - xp_z zp_y \\ &= yp_x (p_z z - zp_z) + xp_y (zp_z - p_z z) \\ &= yp_x (-i\hbar) + xp_y (i\hbar) \\ &= i\hbar (xp_y - yp_x) = i\hbar L_z = [L_x, L_y] \end{aligned}$$

that

$$[L_x, L_y] = i\hbar L_z \quad (6.54)$$

$$[L_y, L_z] = i\hbar L_x \quad (6.55)$$

$$[L_z, L_x] = i\hbar L_y \quad (6.56)$$

and knowing

$$[L_x, L^+] = L_x(L_x + iL_y) - (L_x + iL_y)L_x$$

which is, expanding:

$$\begin{aligned} &= L_x L_x + iL_x L_y - L_x L_x - iL_y L_x \\ &= L_x L_x - L_x L_x + i(L_x L_y - L_y L_x) \\ &= +i(i\hbar L_z) \\ &= -\hbar L_z \end{aligned}$$

we derive that

$$[L_x, L^+] = -\hbar L_z \quad (6.57)$$

$$[L_y, L^+] = \hbar L_z \quad (6.58)$$

$$[L_z, L^+] = \hbar L^+ \quad (6.59)$$

and its companion

$$[L_z, L^-] = -\hbar L^- \quad (6.60)$$

This last equation tell us that L^+ ladders us up, and L^- ladders us down on L_z components. If

$$L_z |> = \text{something} |>$$

then

$$L^- L_z | \rangle = \text{something} L^- | \rangle$$

or

$$[L_z L^- + \hbar] | \rangle = \text{something} L^- | \rangle$$

$$L_z L^- | \rangle = (\text{something} - \hbar) L^- | \rangle$$

which means that where ever we were, we are now lower by \hbar .

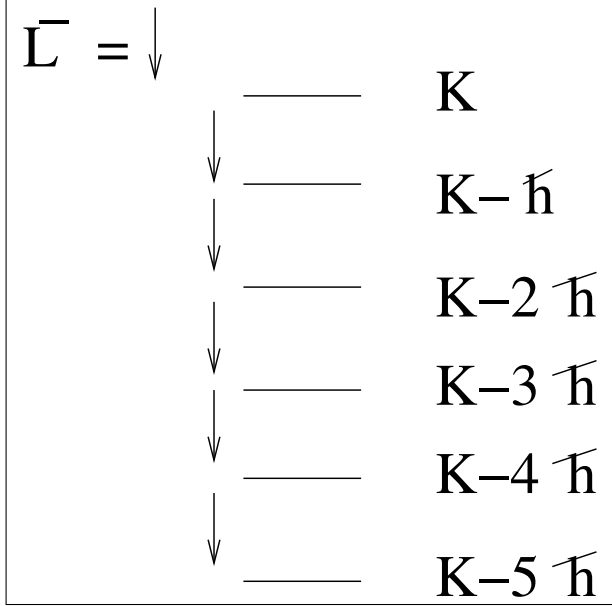


FIG. 2: Laddering Down on the z-component of angular momentum

Next, we need an expression for $L^+ L^-$, not the commutator. It is:

$$\begin{aligned} L^+ L^- &= (L_x + iL_y)(L_x - iL_y) \\ &= L_x^2 + L_y^2 + i(L_y L_x - L_x L_y) \end{aligned}$$

or

$$= L_x^2 + L_y^2 + L_z^2 + i(L_y L_x - L_x L_y) - L_z^2$$

or

$$= L_x^2 + L_y^2 + L_z^2 + i(-i\hbar L_z) - L_z^2$$

i.e.

$$L^+ L^- = L^2 + \hbar L_z - L_z^2$$

and repeating this for the other order, one has

$$L^- L^+ = L^2 - \hbar L_z - L_z^2$$

If

$$L_z | \rangle = K \hbar | \rangle$$

with no intentional restriction on the value of K, and

$$L^2 | \rangle = K' \hbar^2 L^+ | \rangle \quad (6.61)$$

$$L^- L^+ | \rangle + \hbar L_z | \rangle + L_z^2 | \rangle = K' \hbar^2 | \rangle$$

If this particular ket is the highest one, $|hi\rangle$, then laddering up on it must result in destruction, so we have

$$+\hbar L_z |hi\rangle + L_z^2 |hi\rangle = K' \hbar^2 |hi\rangle$$

$$+(hi)\hbar^2 |hi\rangle + (hi)^2 \hbar^2 |hi\rangle = K' \hbar^2 |hi\rangle$$

which means that

$$+(hi) + (hi)^2 = K'$$

while, working down from the low ket one has

$$L^+ L^- |lo\rangle - \hbar L_z |lo\rangle + L_z^2 |lo\rangle = K' \hbar^2 |lo\rangle$$

which is

$$-(lo)\hbar^2 L_z |lo\rangle + (lo)^2 \hbar^2 |lo\rangle = K' \hbar^2 |lo\rangle$$

i.e.,

$$-(lo) + (lo)^2 = K'$$

which means

$$-(lo) + (lo)^2 = K' = +(hi) + (hi)^2 = (lo)((lo) - 1) = (hi)((hi) + 1)$$

which can only be true if $(lo) = -(hi)$. Say $(hi) = 7$, then $K' = 7*8$ and $-7(-7-1)$ which is the same! Note that

if $(hi) = 7.1$ then (lo) can not be achieved by stepping down integral multiples of \hbar .

VII. LAGUERRE POLYNOMIALS

The radial equation for the H-atom is

$$-\frac{\hbar^2}{2\mu} \left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} \right] R(r) - \frac{Ze^2}{r} R(r) = ER(r)$$

which we need to bring to dimensionless form before proceeding (text book form). Cross multiplying, and defining $\epsilon = -E$ we have

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} \right] R(r) + \frac{2\mu Ze^2}{\hbar^2 r} R(r) - \frac{2\mu\epsilon}{\hbar^2} R(r) = 0$$

and where we are going to only solve for states with $\epsilon > 0$, i.e., negative energy states.

Defining a dimensionless distance, $\rho = \alpha r$ we have

$$\frac{d}{dr} = \frac{d\rho}{dr} \frac{d}{d\rho} = \alpha \frac{d}{d\rho}$$

so that the equation becomes

$$\alpha^2 \left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \frac{\ell(\ell+1)}{\rho^2} \right] R(\rho) + \frac{2\mu Ze^2 \alpha}{\hbar^2 \rho} R(\rho) - \frac{2\mu\epsilon}{\hbar^2} R(\rho) = 0$$

which is, upon dividing through by α^2 ,

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \frac{\ell(\ell+1)}{\rho^2} \right] R(\rho) + \frac{2\mu Ze^2}{\hbar^2 \rho \alpha} R(\rho) - \frac{2\mu\epsilon}{\hbar^2 \alpha^2} R(\rho) = 0$$

Now, we choose α as

$$\alpha^2 = \frac{2\mu\epsilon}{\hbar^2}$$

so

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \frac{\ell(\ell+1)}{\rho^2} \right] R(\rho) + \frac{2\mu Ze^2}{\rho\epsilon} R(\rho) - R(\rho) = 0 \quad (7.1)$$

To continue, we re-start our discussion with Laguerre's differential equation:

$$x \frac{d^2 y}{dx^2} + (1-x) \frac{dy}{dx} + \alpha y = 0 \quad (7.2)$$

To show that this equation is related to Equation 7.1 we differentiate Equation 7.2

$$\frac{d \left(x \frac{d^2 y}{dx^2} + (1-x) \frac{dy}{dx} + \alpha y = 0 \right)}{dx} \quad (7.3)$$

which gives

$$y'' + xy''' - y' + (1-x)y'' + \alpha y' = 0$$

which is

$$xy''' + (2-x)y'' + (\alpha-1)y' = 0$$

or

$$\left(x \frac{d^2}{dx^2} + (2-x) \frac{d}{dx} + (\alpha-1) \right) \frac{dy}{dx} = 0 \quad (7.4)$$

Doing it again (differentiating), we obtain

$$\frac{d(xy''' + (2-x)y'' + (\alpha-1)y') = 0}{dx}$$

which leads to

$$y''' + xy'''' - y'' + (2-x)y''' + (\alpha-1)y'' = 0$$

which finally becomes

$$\left(x \frac{d^2}{dx^2} + (3-x) \frac{d}{dx} + (\alpha-2) \right) \frac{d^2 y}{dx^2} = 0 \quad (7.5)$$

Generalizing, we have

$$\left(x \frac{d^2}{dx^2} + (k+1-x) \frac{d}{dx} + (\alpha-k) \right) \frac{d^k y}{dx^k} = 0 \quad (7.6)$$

VIII. PART 2

Consider Equation 7.1

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} R(\rho) - \frac{\ell(\ell+1)}{\rho^2} \right] R(\rho) + \frac{2\mu Ze^2}{\hbar^2 \rho \alpha} R(\rho) - R(\rho) = 0 \quad (8.1)$$

if we re-write it as

$$\left[\rho \frac{d^2}{d\rho^2} + 2 \frac{d}{d\rho} - \frac{\ell(\ell+1)}{\rho} \right] R(\rho) + \frac{2\mu Ze^2}{\hbar^2 \alpha} R(\rho) - \rho R(\rho) = 0 \quad (8.2)$$

(for comparison with the following):

$$xy'' + 2y' + \left(n - \frac{k-1}{2} - \frac{x}{4} - \frac{k^2-1}{4x} \right) y = 0 \quad (8.3)$$

Notice the similarity if $\rho \sim x$, i.e., powers of x , x^{-1} etc.,

$$\frac{2\mu Ze^2}{\hbar^2 \alpha} \Leftrightarrow n - \frac{k-1}{2} \quad (8.4)$$

$$\rho \Leftrightarrow \frac{x}{4} \quad (8.5)$$

$$\frac{k^2-1}{4x} \Leftrightarrow \frac{\ell(\ell+1)}{\rho} \quad (8.6)$$

We force the asymptotic form of the solution $y(x)$ to be exponentially decreasing, i.e.,

$$y = e^{-x/2} x^{(k-1)/2} v(x) \quad (8.7)$$

and “ask” what equation $v(x)$ solves. We do this in two steps, first assuming

$$y = e^{-x/2}w(x)$$

and then assuming that $w(x)$ is

$$w = x^{(k-1)/2}v(x)$$

So, assuming the first part of Equation 8.7, we have

$$y'(x) = \frac{k-1}{2}x^{(k-3)/2}w(x) + x^{(k-1)/2}w'(x)$$

and

$$y''(x) = \frac{k-1}{2} \frac{k-3}{2} x^{(k-5)/2} w(x) + \frac{k-1}{2} x^{(k-3)/2} w'(x) + \frac{k-1}{2} x^{(k-3)/2} w'(x) + x^{(k-1)/2} w''(x) = 0$$

which we now substitute into Equation 8.3 to obtain

$$\begin{aligned} xy'' &= \frac{k-1}{2} \frac{k-3}{2} x^{(k-3)/2} w(x) + (k-1)x^{(k-1)/2} w'(x) + x^{(k+1)/2} w''(x) \\ 2y' &= 2 \frac{k-1}{2} x^{(k-3)/2} w(x) + 2x^{(k-1)/2} w'(x) \\ ny &= nx^{(k-1)/2} w(x) \\ -\frac{k-1}{2} y &= -\frac{k-1}{2} x^{(k-1)/2} w \\ -\frac{x}{4} y &= -\frac{x^{(k+1)/2}}{4} w \\ -\frac{k^2-1}{4x} y &= -\frac{k^2-1}{4} x^{(k-3)/2} w \rightarrow 0 \end{aligned} \tag{8.8}$$

or

$$xw'' + (k+1)w' + \left(n - \frac{k-1}{2} - \frac{x}{4}\right)w = 0 \tag{8.9}$$

IX.

Now we let

$$w = e^{-x/2}v(x)$$

(as noted before) to obtain

$$w' = -\frac{1}{2}e^{-x/2}v + e^{-x/2}v'$$

$$w'' = \frac{1}{4}e^{-x/2}v - e^{-x/2}v' + e^{-x/2}v''$$

so, substituting into Equation 8.8 we have

$$\begin{aligned} xw'' &= e^{-x/2} \left(\frac{x}{4}v - xv' + xv'' \right) \\ (k+1)w' &= e^{-x/2} \left(-\frac{k+1}{2}v + (k+1)v' \right) \\ \left(n - \frac{k-1}{2} - \frac{x}{4} \right) w &= e^{-x/2} \left(n - \frac{k-1}{2} - \frac{x}{4} \right) v \end{aligned} \tag{9.1}$$

$$= 0 \tag{9.2}$$

so, v solves Equation 7.6 if $\alpha = n$. Expanding the r.h.s. of Equation 9.1 we have

$$\frac{x}{4}v - \frac{x}{4}xv'' + (k+1-x)v' + \left(n - \frac{k-1}{2} - \frac{k+1}{2} \right) v = 0$$

i.e.,

$$xv'' + (k+1-x)v' + (n-k)v = 0$$

which is Equation 7.6, i.e.,

$$v = \frac{d^k y}{dx^k}$$

and

$$y = e^{-x/2} x^{(k-1)/2} \frac{d^k y^*}{dx^k}$$

or

$$w'' = \frac{1}{4} e^{-x/2} v - e^{-x/2} v' + e^{-x/2} v''$$

so, substituting into Equation 8.8 we have

$$\begin{aligned} xw'' &= e^{-x/2} \left(\frac{x}{4} v - xv' + xv'' \right) \\ (k+1)w' &= e^{-x/2} \left(-\frac{k+1}{2} v + (k+1)v' \right) \\ \left(n - \frac{k-1}{2} - \frac{x}{4} \right) w &= e^{-x/2} \left(n - \frac{k-1}{2} - \frac{x}{4} \right) v \quad (9.3) \\ &= 0 \quad (9.4) \end{aligned}$$

so, v solves Equation 7.6 if $\alpha = n$. Expanding the r.h.s. of Equation 9.3 we have

$$\frac{x}{4} v - \frac{x}{4} + xv'' + (k+1-x)v' + \left(n - \frac{k-1}{2} - \frac{k+1}{2} \right) v = 0$$

i.e.,

$$xv'' + (k+1-x)v' + (n-k)v = 0$$

which is Equation 7.6, i.e.,

$$v = \frac{d^k y}{dx^k}$$

and

$$y = e^{-x/2} x^{(k-1)/2} \frac{d^k y^*}{dx^k}$$

or

$$R(\rho) = e^{-\rho/2} \rho^{(k-1)/2} L_{n^*}^k(\rho)$$

where y^* and $R(\rho)$ are solutions to Laguerre's Equation of degree n . Wow.

X. PART 3

Now, all we need do is solve Laguerre's differential equation.

$$xy'' + (1-x)y' + \gamma y = 0$$

where γ is a constant (to be discovered). We let

$$y = \sum_{\lambda=0}^? a_{\lambda} x^{\lambda}$$

and proceed as normal

$$\begin{aligned} xy'' &= 2a_2x + (3)(2)a_3x^2 + (4)(3)a_4x^3 + \dots \\ +y' &= (2)a_2x + (3)a_3x^2 + (4)a_4x^3 + \dots \\ -xy' &= -a_2x - (2)a_2x^2 - (3)a_3x^3 - \dots \\ +\gamma y &= \gamma a_0 + \gamma a_1x + \gamma a_2x^2 + \dots = 0 \quad (10.1) \end{aligned}$$

which yields

$$\begin{aligned} a_1 &= -\gamma a_0 \\ a_2 &= \frac{1-\gamma}{4} a_1 \\ a_3 &= \frac{2-\gamma}{9} a_2 \\ a_4 &= \frac{3-\gamma}{16} a_3 \end{aligned} \quad (10.2)$$

or, in general,

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

which means

$$\begin{aligned} a_1 &= -\frac{\gamma}{1} a_0 \\ a_2 &= -\frac{(1-\gamma)\gamma}{(4)(1)} a_0 \\ a_3 &= -\frac{(2-\gamma)(1-\gamma)\gamma}{(9)(4)(1)} a_0 \\ a_4 &= -\frac{(3-\gamma)(2-\gamma)(1-\gamma)\gamma}{(16)(9)(4)(1)} a_0 \\ &\dots \end{aligned} \quad (10.3)$$

which finally is

$$a_j = -\frac{\prod_{k=0}^{j-1} (k-\gamma)}{\prod_{k=1}^j (k^2)} a_0$$

and

$$a_{j+1} = -(j-\gamma) \frac{\prod_{k=0}^{j-1} (k-\gamma)}{(j+1)^2 \prod_{k=1}^j (k^2)} a_0 = \frac{j-\gamma}{(j+1)^2} a_j$$

which implies that

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

as $j \rightarrow \infty$. This is the behaviour of $y = e^x$, which would overpower the previous Ansatz, so we must have truncation through an appropriate choice of γ (i.e., $\gamma = n^*$).

XI.

If γ were an integer, then as j increased, and passed into γ we would have a zero numerator in the expression

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

and all higher a 's would be zero (i.e., not a power series but a polynomial instead)! But

$$\alpha^2 = \frac{2\mu\epsilon}{\hbar^2} = -\frac{2\mu E}{\hbar^2}$$

so, from Equation 8.6 we have

$$\frac{k^2 - 1}{4} = \ell(\ell + 1)$$

$$k^2 - 1 = 4\ell^2 + 4\ell$$

$$k = 2\ell + 1$$

so

$$\frac{k^2 - 1}{2} = \frac{2\ell + 1 - 1}{2} = \ell$$

and therefore Equation 8.3 tells us that

$$\left(n^* - \frac{k-1}{2}\right) = n^* - \ell = \frac{2\mu Z e^2}{\hbar^2 \alpha}$$

implies

$$\alpha = \frac{2\mu Z e^2}{\hbar^2 (n^* - \ell)^2}$$

$$\alpha^2 = -\frac{2\mu E}{\hbar^2} = \frac{\mu Z^2 e^4}{\hbar^4 (n^* - \ell)^2}$$

i.e.,

$$E = -\frac{\mu Z^2 e^4}{2\hbar^2 (n^* - \ell)^2}$$

[1] the only thing that happens in making the complex conjugate is that each i is changed to $-i$ (and each $-i \rightarrow i$).
[2] the 'bracket', hah, hah.

[3] notice the rewriting into momentum language!
[4] The limits correspond to $\vartheta = 0$ to $\vartheta = \pi$