4.1 Diagonal Matrix Elements for the nmr $H_0$
Find the diagonal matrix elements for $H_0$ (the nmr Hamiltonian without spin coupling) for the 3 spin, same nuclei for each spin, same environment, situation. That is, the $A_3$ situation. Use as your basis set the functions $|\alpha \alpha \alpha\rangle$, $|\alpha \alpha \beta\rangle$, $|\alpha \beta \beta\rangle$, etc.

4.2 Diagonal Matrix Elements for the nmr $H_0$
Find the diagonal matrix elements for $H_0$ (the nmr Hamiltonian without spin coupling) for the 3 spin, three different nuclei, situation. That is, the AMX situation. Use as your basis set the functions $|\alpha \alpha \alpha\rangle$, $|\alpha \alpha \beta\rangle$, $|\alpha \beta \beta\rangle$, etc.

4.3 Diagonal Matrix Elements for the nmr $H_1$
Find the diagonal matrix elements for $H_1$ (the nmr Hamiltonian term for spin coupling) for the system in problem 1.

4.4 Off-Diagonal Matrix Elements for the nmr $H_1$
Find the non-zero off-diagonal matrix elements for $H_1$ (the nmr Hamiltonian term for spin coupling) for the system in problem 1.

4.5 Solving the Matrix for an NMR Problem
For the case in problem 1, with $\nu_0 = 100$, $\sigma = 0.1$, and $J = 1$, set up the matrix and solve for the eigenvalues and eigenvectors.

4.6 Sorting the States of the NMR Problem According to Total Nuclear Spin
Make a plot of the energy levels for the last problem with the vertical scale being energy and the horizontal scale being the total nuclear spin. HINT: Patience in working your way through this.

4.7 Allowed Transitions in NMR
Find the allowed transitions for the energy levels found in problem 5
### 4.8 Matrix Elements in a Four Nuclear Spin System

You are dealing with a four spin nuclear system, three of which are equivalent (called an AB\textsubscript{3} system). You are building the matrix representation of the Hamiltonian. If the first spin in the list is that due to the nucleus A (that is, in long hand, the function is $|\alpha_A \alpha_B \alpha_B \beta_B\rangle$), find the following matrix elements

\[
\langle \alpha \alpha \alpha \beta | H_0 + H_1 | \alpha \alpha \beta \alpha \rangle \\
\langle \alpha \alpha \beta \beta | H_0 + H_1 | \alpha \alpha \beta \alpha \rangle \\
\langle \alpha \alpha \beta \beta | H_0 + H_1 | \alpha \alpha \beta \beta \rangle
\]

### 4.9 Transitions in NMR

A transition between levels in nmr is proportional to

\[
\left( \langle m | \sum I_x | n \rangle \right)^2
\]

Use a three spin system to show that this integral is zero if $\sum I_z(i)$ in $\langle m \rangle$ minus $\sum I_z(i)$ in $|n\rangle$ is not equal to $\pm 1$. In this expression, $i$ is an index that runs over all nuclei. HINTS: (1) You don’t need Mathematica, nor do you need to evaluate what $I_x$ does between levels. (2) Try for $\langle m \rangle$ and $|n\rangle$ levels that violate the rule and you will quickly see the answer. (3) Note $\langle \alpha | I_x | \beta \rangle$ is not zero and $\langle \alpha | I_z | \alpha \rangle$ is.

### 4.10 Parve on a Pole

A parve is on a pole that extends from 0 to 1 in the x direction. The potential is 15 units (with $\hbar$ and $m$ both set equal to one) from $x = 0$ to $x = 0.3$. Elsewhere, on the pole, the potential is zero. Further, the potential is infinity at $x < 0$ and at $x > 1$. Find the energy for the lowest two energy levels for this parve using at least two methods.

### 4.11 Parve on Pole Wave Function

Make a plot of the wave function for the second energy level in the last problem and briefly discuss what you see.

### 4.12 Harmonic Oscillator Energy Levels

Find the energy associated with a harmonic oscillator function with $n = 3$. Giving the answer is not sufficient; I want you to show the math that establishes the value. HINT: You may work in “q space” if you wish.

### 4.13 Harmonic Oscillator Recursion Formula

In the harmonic oscillator we use a recursion expression that relates the $(n + 2)$th coefficient to the nth. At some value of $n$, say $n_{\text{max}}$, we say:

\[
a_{n+2} = \frac{2n + 1 - K}{(n + 2)(n + 1)} a_n = 0.
\]

Why?
4.14 *Harmonic Oscillator Recursion Formula*
Use the recursion formula for a harmonic oscillator to find the relative values of $a_7$, $a_5$, and $a_3$ in terms of $a_1$ for the $K = 15$ level.

4.15 *HMO Theory*
Use the Hückel M.O. treatment to find the energy levels and wave functions in 1.

4.16 *Eigenvalue/Eigenvector Problem*
Use matrix methods to show that the HOMO of the last problem is an eigenfunction of the Hamiltonian.

4.17 *HMO Theory*
Use the Hückel M.O. treatment to find the energy levels and the wave functions in 2.

4.18 *M.O.s in Benzyl Radical*
What does the singly occupied level in the benzyl radical (2) look like?

4.19 *Stern Gerloch Experiment*
A Cr atom has a $^7S$ ground state. If a beam of Cr atoms is passed through an inhomogeneous magnetic field aligned along the z axis, it will be split into a number of different beams. How many?

4.20 *Stern Gerloch Experiment*
If one of the exit beams from the last problem is passed through a similar magnetic field aligned in the x direction, it again is split. If we isolate one of the beams emerging from the x magnet, can we now say we know the projection of the spin in both the z and x directions? Explain.

4.21 *Measurement in Quantum Mechanics*
Complete the following sentence: “When we make a measurement of the energy of a single isolated quantum system, we always get as an answer one of the . . . .”
4.22  *Coupled and Uncoupled States*
For an \( f_2 \) configuration (the \( \ell \) of each electron is 3) I claim the linear combination of uncoupled states
\[
\frac{1}{\sqrt{2}}(|3^+ 2^-\rangle - |3^- 2^+\rangle)
\]
is an eigenfunction of \( L^2 \), the square of the total orbital angular momentum. Determine if this is true and find the eigenvalue.

4.23  *The Rigid Rotor*
Find the wave function for a rigid rotor with quantum numbers \( \ell = 1, m = 1 \).

4.24  *The Rigid Rotor*
Plot the spatial probability for the function in the last problem.

4.25  *The Rigid Rotor*
Determine the expectation value of \( \theta \) for the wave function in problem 23.

4.26  *The Rigid Rotor*
Determine the expectation value of \( \phi \) for the wave function in problem 23.

4.27  *The Rigid Rotor*
Justify your answers to the last two problems on the basis of the probability function (problem 24).

4.28  *Commutator Properties*
Evaluate the commutator \([\ell_+, \ell_-]\).

4.29  *Empirical Proof of Commutation Property*
Show that the commutator \([\ell_+, \ell_-]\) operating on \(|1^+\rangle\) from a \( d_1 \) configuration gives the same result as the answer to the last problem does when operating on the same function. I.e., prove that your commutator answer is correct.

4.30  *Conceptual Question to be Answered without Notes*
The wave function for a parve on a pole is:

4.31  *Conceptual Question to be Answered without Notes*
The energy of a parve on a pole is:

4.32  *Conceptual Question to be Answered without Notes*
In a harmonic oscillator: \( a_+ |4\rangle = \)

4.33  *Conceptual Question to be Answered without Notes*
In a harmonic oscillator: \( \langle 0|a_+a_-|0\rangle = \)
4.34 Conceptual Question to be Answered without Notes
In a rigid rotor: \( \langle 1 \ 1 | \ell_z | 2 \ 1 \rangle = \)

4.35 Conceptual Question to be Answered without Notes
In a rigid rotor: \( \langle 2 \ 1 | \ell^2 | 2 \ 1 \rangle = \)

4.36 Conceptual Question to be Answered without Notes
In a rigid rotor: \( \ell_+ | 2 \ 2 \rangle = \)

4.37 Conceptual Question to be Answered without Notes
In a rigid rotor: \( \ell_+ | 2 \ -2 \rangle = \)

4.38 Conceptual Question to be Answered without Notes
In a harmonic oscillator, where H is the appropriate Hamiltonian: \( H | n \rangle = \)

4.39 Conceptual Question to be Answered without Notes
In a hydrogen atom: \( \langle 2 \ 1 \ 0 | 2 \ 1 -1 \rangle = \)

4.40 Conceptual Question to be Answered without Notes
In perturbation theory, the first order correction to the energy of the function with quantum number n is given by (HINT: Dirac notation is best.)

4.41 Conceptual Question to be Answered without Notes
Crucial to the development of perturbation theory is the expansion of a wavefunction. Write the equation (in Dirac notation) for the expansion of \( |0_1 \rangle \), which is the first order perturbed wave function:

4.42 Conceptual Question to be Answered without Notes
In variational theory, you take three major steps. These are: (each can be answered in just a couple of words).

4.43 Conceptual Question to be Answered without Notes
Show in a “vector diagram” (drawn with lengths of vectors indicated) the state of a hydrogen atom, \( |3 \ 2 \ 0 \rangle \).

4.44 Conceptual Question to be Answered without Notes
Indicate on a vector diagram the result of \( \ell^- |3 \ 2 \ 2 \rangle \).

4.45 Conceptual Question to be Answered without Notes
Sketch the radial wave function for the hydrogen atom wave function \( |2 \ 1 \ 0 \rangle \).

4.46 Conceptual Question to be Answered without Notes
Sketch the angular wave function for the hydrogen atom wave function \( |3 \ 0 \ 0 \rangle \).
4.47  Conceptual Question to be Answered without Notes
The following matrix is produced in a degenerate perturbation theory problem.

\[
\begin{pmatrix}
1.0 & 0.2 & 0.4 & 0.0 \\
0.2 & 0.4 & 0.0 & 0.0 \\
0.4 & 0.0 & 1.2 & 0.0 \\
0.0 & 0.0 & 0.0 & 1.0 \\
\end{pmatrix}
\]

What can you say about one of the eigenfunctions in the solution to this matrix equation?

4.48  Conceptual Question to be Answered without Notes
In degenerate perturbation theory, what can you say about the matrix elements \( H_{n,m} \) and \( H_{m,n} \)? Why is your statement correct?

4.49  Variational Theory
Let the Hamiltonian for a modified harmonic oscillator be (in q language):

\[
-\frac{\delta^2}{\delta q^2} + q^2 + 0.1q^4
\]

In these terms Schrödinger’s equation reads

\[ H\psi = K\psi \]

where \( K = \frac{2E}{\hbar\omega} \). Let’s guess that a wave function for this system is

\[ \psi = \phi_0 + b\phi_2 \]

where \( \phi_0 \) and \( \phi_2 \) are the ground and second excited state wave functions for a normal harmonic oscillator, that is, the values corresponding to \( n = 0 \) and \( n = 2 \); and \( b \) is a constant to be determined. Find the best possible energy for this guessed wave function.

4.50  Variational Theory
Plot the wave function from the last problem.

4.51  Hückel MO Theory
Find the energy levels under the Hückel approximation for benzocyclobutadiene, \( \text{C}_8\text{H}_6 \).

4.52  Hückel MO orbital
What does the highest filled m.o. (HOMO) in problem 51 look like?

4.53  Hückel MO orbital
What does the lowest empty m.o. (LUMO) in problem 51 look like?
4.54 **Harmonic Oscillator Wave Function**
Give the wave function for \( n = 12 \) for the harmonic oscillator (working in "q language" is OK).

4.55 **Hydrogen Atom Wave Function**
Give the wave function for \( n = 4, \ell = 0, m = 0 \), for the hydrogen atom.

4.56 **Rigid Rotor Wave Function**
Give the wave function for \( \ell = 4, m = 2 \), for the rigid rotor.

4.57 **Spherical Coordinates**
What do you have to do to integrate the square of a function (as in the procedure to normalize) when using spherical coordinates.

4.58 **Two Dimensional Harmonic Oscillator**
For a two dimensional harmonic oscillator with equal force constants in the two directions, Schrödinger’s equation (written in terms of the dimensionless parameters \( q = \sqrt{\frac{m\omega}{\hbar}} x \) and \( r = \sqrt{\frac{m\omega}{\hbar}} y \)) is

\[
-\frac{\partial^2}{\partial q^2} \psi - \frac{\partial^2}{\partial r^2} \psi + (q^2 + r^2)\psi = K\psi
\]

where \( K = 2 \frac{E}{(\hbar\omega)} \). Show that the function

\[
\psi = \exp\left[-\frac{q^2}{2}\right]\exp\left[-\frac{r^2}{2}\right]
\]

is a solution.

4.59 **Two Dimensional Harmonic Oscillator**
For the wave function given in the last problem, determine the energy.

4.60 **Two Dimensional Harmonic Oscillator**
Plot the function in problem 58.

4.61 **Two Dimensional Harmonic Oscillator**
Examine the form of the wave function given in problem 58 and suggest a suitable form for a wave function of greater energy.

4.62 **Two Dimensional Harmonic Oscillator**
Determine the energy of your wave function in the last problem.

4.63 **Two Dimensional Harmonic Oscillator**
Plot the function from problem 61.
Two Dimensional Harmonic Oscillator

Make a plot of the probability of observing the 2-d harmonic oscillator at a point \([q, r]\) as a function of \(q\) and \(r\) for your excited wave function. HINTS: (1) This is not asking for anything unusual, just a plot of probability versus \(q\) and \(r\). (2) The Mathematica command 

\[
\text{PlotRange -> \{\{x lowest, x highest\}, \{y lowest, y highest\}, \{z lowest, z highest\}\}}
\]

is useful if Mathematica chooses to cut off the tops of your wave functions. It goes within the [ ..] of the Plot3D command.

Commutation

Give the values of the following commutators:

\[
[\ell_z, \ell_x] = \\
[\ell_x, \ell^2] =
\]

Commutation

Evaluate by expansion of \(a_+ = \frac{1}{\sqrt{2}}(q - \frac{\partial}{\partial q})\) and \(a_- = \frac{1}{\sqrt{2}}(q + \frac{\partial}{\partial q})\) the commutator \([a_+, a_-]\). HINTS: These “a” are ladder operators for the harmonic oscillator and \(q\) is the dimensionless parameter associated with the same. Also, remember that \(\partial/\partial q\) is not a momentum operator, but that \((\hbar \delta q/\partial q)\) is.

Commutation

Define an operator \(n = a_+ a_-\). Evaluate the commutator \([n, a_+]\).

Commutation

Is the commutator \([H, L^2]\) zero? Comment on the relevance of your answer in quantum mechanics. \(L\) and \(H\) refer to multielectron operators.

Parve on a Sheet

For a parve on a sheet with each side of length = 1, find the energy difference between the \(n = (n_x, n_y) = (1, 1)\) level and the \(n = (2, 3)\) level.

Parve on a Sheet

For a parve on a sheet with each side of length = 1, find the energy difference between the \(n = (n_x, n_y) = (1, 1)\) level and the \(n = (3, 2)\) level.

Perturbed Parve on a Sheet

Use perturbation theory to find the energy of the \(n = (1, 1)\) level if a perturbation given below is applied:

\[
V = (5xy) \text{ for } 0.0 \leq x \leq 0.67, \text{ all } y \\
V = 0 \text{ for } x > 0.67, \text{ all } y
\]

HINT: Be sure your potential is a function of the \(x\) times \(y\) product in the appropriate range.
4.72 *Perturbed Parve on a Sheet*
Find the first order perturbation for a parve on a sheet in the level \( n = (2,3) \) if the perturbation is as in the last problem.

4.73 *Perturbed Parve on a Sheet*
Plot the “good” linear combination of degenerate functions for the last problem and justify its shape.

4.74 *Hydrogen Atom Wave Functions*
The \(|2 1 1 \rangle\) and \(|2 1 -1 \rangle\) wave functions for a hydrogen atom are, respectively:

\[
\sqrt{\frac{1}{(64\pi)}\left(\frac{1}{a_0}\right)^{5/2}\sin[\theta]\exp[i\phi]\exp[-r/(2a_0)]}
\]

\[
\sqrt{\frac{1}{(64\pi)}\left(\frac{1}{a_0}\right)^{5/2}\sin[\theta]\exp[-i\phi]\exp[-r/(2a_0)]}
\]

where \(a_0\) is the Bohr radius, a real number greater than zero (and, if fact, equal to 0.5219 Å). Show that \(|2 1 1 \rangle\) is normalized.

4.75 *Hydrogen Atom Wave Functions*
Show that \(|2 1 1 \rangle\) and \(|2 1 -1 \rangle\) (from problem 74) are orthogonal.

4.76 *Hydrogen Atom Wave Functions*
Show that the linear combination of \(|2 1 1 \rangle\) and \(|2 1 -1 \rangle\) (from problem 74) is a function that we might call \(|2p_x\rangle\). HINT: Use the appropriate conversion of \((\exp[i\phi] + \exp[-i\phi])\) and show that your answer “points” as a \(p_x\) orbital does.

4.77 *Hydrogen Atom Wave Functions*
Find the expectation value of \(x^2\) for the function \(|2p_x\rangle\)–see problem 76.

4.78 *Hydrogen Atom Wave Functions*
Find the expectation value of \(y^2\) for the function \(|2p_x\rangle\)–see problem 76.

4.79 *Hydrogen Atom Wave Functions*
Rationalize the difference in your answers to the last two problems.

4.80 *Uncoupled States*
Build a table for the \(d^3\) configuration that includes only the top three rows (top three \(L_z\) values and the leftmost two columns (top two \(S_z\) values).

4.81 *Coupled and Uncoupled States*
For a \(d^2\) configuration, the coupled state:

\(|cL S M_L M_S \rangle = |c 3 1 2 1 \rangle\)

is equal to the uncoupled state \(|u 2^+ 0^+ \rangle\) (where the numbers are the \(m_\ell\) values and the superscripts are the \(m_s\) values). Find the linear combination of uncoupled state(s) that is the coupled state \(|c 3 1 2 0 \rangle\).
4.82  **Coupled and Uncoupled States**
The uncoupled states in the $M_L = 2$ and $M_S = 0$ box of the chart for the $d^2$ configuration are:

$$|f1⟩ = |u2^+ 0_d⟩$$
$$|f2⟩ = |u1^+ 1_d⟩$$
$$|f3⟩ = |u2^- 1_d⟩$$

Determine the matrix elements in the $L^2$ matrix for these uncoupled states.

4.83  **Coupled State and Uncoupled States**
Show that the uncoupled state $|m_{ls1} m_{ls2} m_{ls3}⟩ = |u2^+ 2^- 1_d⟩$ for a $d^3$ configuration is the coupled state $|cL S L_z S_z⟩ = |5 1/2 5 1/2⟩ = |c^2L^2 S^2 1/2⟩ = |c^2H 5 1/2⟩$.

4.84  **Matrix Representation**
In Dirac notation three rigid rotor functions are $|1 1⟩$, $|1 0⟩$, and $|1 -1⟩$. We can represent these three states as column vectors $[1, 0, 0]$, $[0, 1, 0]$, and $[0, 0, 1]$, respectively. Find the matrix that represents $\ell_z$.

4.85  **Matrix Representation**
For the system defined in the last problem, find the matrix that represents $\ell_x$.

4.86  **Matrix Representation**
From the results of the last two problems, show that the matrices that represent $\ell_z$ and $\ell_x$ can be put into a commutator, $[\ell_z, \ell_x]$ and will give the same result we get with the operators directly. HINT: The matrix corresponding to $\ell_y$ in this basis set is:

$$\begin{pmatrix}
0 & -\frac{\hbar}{\sqrt{2}} & 0 \\
\frac{\hbar}{\sqrt{2}} & 0 & -\frac{\hbar}{\sqrt{2}} \\
0 & \frac{\hbar}{\sqrt{2}} & 0
\end{pmatrix}$$

4.87  **Russell-Saunders States and Hund’s Third Rule**
Find the ground Russell-Saunders state with spin-orbit coupling using Hund’s third rule for the $d^5$ configuration and understand why there is no need for a condition ”if the shell is exactly half-filled ...” HINT: Do not try to build the entire table; use a short cut.

4.88  **Russell-Saunders States**
Show, using the “table” (or “chart”) method, that the uncoupled state $|u1^+ 0^+ - 1^+_d⟩$ of a N atom surely belongs to the multielectronic $^4S$ state. Give your logic.

4.89  **Coupled and Uncoupled States**
For the system in problem 88 write the coupled state that corresponds to the uncoupled state $|u1^+ 0^+ - 1^+_d⟩$ in the language of $|c L S L_z S_z⟩$. 
4.90  **Coupled and Uncoupled States**
Find the coupled state \( |c \ 0 \ 0 \ 0 \rangle \)—see the last two problems—in terms of its uncoupled state(s).

4.91  **Stern-Gerlach Experiment**
If you pass a beam of nitrogen atoms in their ground state through an inhomogeneous magnetic field (i.e., a modified Stern-Gerlach experiment), what splitting pattern will you find? Explain.

4.92  **Pauli Matrices**
I want you to “represent” the \( S_z \) intrinsic angular momentum operator for the nitrogen atom in the \( ^4S \) state. Come up with the appropriate column vectors and build the matrix that corresponds to (represents) \( S_z \). Show that your method works. HINT: Make sure you have the right number of vectors and hence the right dimension for them.

4.93  **Harmonic Oscillator**
Look up Schrödinger’s equation for the harmonic oscillator in “q” language. Carry out the appropriate operations (in Mathematica so that I can follow them) to find the value of the eigenvalue that we called in class “K”. Use the eigenfunction
\[
\frac{105 - 840q^2 + 840q^4 - 224q^6 + 16q^8 e^{-q^2/2}}{24\sqrt{70\pi}^{1/4}}
\]

4.94  **Finite Matrix Method**
Use the finite matrix method to find the energy of the lowest energy level of a parve on a pole of length one when there is a v-shaped potential: The potential decreases linearly from \( V=200 \) at \( x=0 \) to \( V=0 \) at \( x=0.5 \), then increases linearly from the \( V=0.5 \) value of 0 to \( V=200 \) at \( x=1.0 \). Let \( \hbar \) and \( m \) be unity. Plot the wave function for your answer.

4.95  **Making Sense of Quantum Wave Functions**
Comment on the plot in your answer to the last problem compared to the ground state of a parve on a pole without potential energy.

4.96  **NMR Matrix Elements**
This problem concerns the hydrogen nmr system AB, two non-equivalent nuclei (in therefore, different chemical environments) that can “couple” to each other with a coupling constant \( J \). The Hamiltonian matrix for this system in the basis set \( |\alpha \alpha\rangle \), \( |\alpha \beta\rangle \), \( |\beta \alpha\rangle \), and \( |\beta \beta\rangle \) (and in that order), where the first entry is for nucleus A and the second for nucleus B, is given here:
\[
\begin{pmatrix}
-n_0 \left( 1 - \frac{1}{2} \sigma_A - \frac{1}{2} \sigma_B \right) + \frac{1}{4} J & 0 & 0 & 0 \\
0 & ? & \frac{1}{4} J & 0 \\
0 & \frac{1}{4} J & n_0 \left( \frac{1}{2} \sigma_A - \frac{1}{2} \sigma_B \right) - \frac{1}{4} J & 0 \\
0 & 0 & 0 & n_0 \left( 1 - \frac{1}{2} \sigma_A - \frac{1}{2} \sigma_B \right) + \frac{1}{4} J
\end{pmatrix}
\]
Can you prove that all entries in the first row (except for \(\alpha \alpha \hat{H}_0 + \hat{H}_1 \alpha \alpha\)) should be zero? Please do so.

**4.97 NMR Matrix Elements**
Fill in the two missing entries in the matrix of the last problem. Give your work or your logic in doing so.

**4.98 Determining NMR Energy Levels**
Determine the energy levels for this AB system in the last two problems in terms of the four parameters, \(\nu_0, \sigma_A, \sigma_B,\) and \(J.\)

**4.99 Allowedness in NMR**
Determine if the transition from the lowest eigenvalue you obtained in the last problem (most negative) to the next lowest is allowed. HINT: If you have a bunch of constants in your wave functions, just name them to simplify things.

**4.100 Duh?**
We defined \(a_+\) in q language as \(\frac{1}{\sqrt{2}}(q - \partial / \partial q)\) and similarly for \(a_-\). Show that the sum of these is proportional to q. HINT: Duh?

**4.101 Allowedness in a Harmonic Oscillator**
In a harmonic oscillator, the intensity of a transition between two levels \(n\) and \(m\) is proportional to the square of the matrix element, \(\langle n | q | m \rangle.\) Using your result from the last problem, show that this matrix element is zero unless \(m = n \pm 1.\) HINT: Just put in the equivalence of q and then slowly and calmly expand that matrix element.

**4.102 Parve on Pole Eigenfunctions**
Show for a parve on a pole running between \(x = -1\) and \(x = 1\) that \(\cos[\pi x/2], \sin[\pi x/2]\) and \(\sin[\pi x]\) are all eigenfunctions of the Hamiltonian. Give the eigenvalues. HINT: Let \(\hbar\) and \(m\) be unity.

**4.103 Parve on Pole Wave Functions**
Which of the functions in problem 102 are valid wave functions for this pole? Explain.

**4.104 Orthogonality of Functions**
Show that the functions from problem 102, \(\cos[\pi x/2]\) and \(\sin[\pi x]\), are orthogonal.

**4.105 Coupled and Uncoupled State**
This problem concerns an atom in an \(d^3\) configuration. What are the uncoupled kets characterized by \(M_L\) (or \(L_z\)) = 3 and \(M_S\) (or \(S_z\)) = 1/2?

**4.106 Coupled and Uncoupled States**
For the system in problem 105, to what coupled state (\(|C L S L_z S_z\rangle\)) does the uncoupled ket \(|u 2^+ 1^+ 0^+\rangle\) belong?
4.107 Coupled and Uncoupled States
For the system in problem 105, find the linear combination of uncoupled kets that is equal to the coupled ket, \( \mid C, 3 \frac{3}{2} 3 \frac{1}{2} \rangle \)

4.108 \( L^2 \) Matrix
For an atom with the configuration \( d^3 \), construct the partial matrix for the uncoupled states with \( L_z = 4 \) and \( S_z = 1/2 \) for the operator \( L^2 \).

4.109 Eigenvalues and Eigenfunctions
Find the eigenvalues and eigenvectors for the matrix of the last problem. HINT: If your answers don’t make sense, you can obtain partial credit by explaining why.

4.110 Understanding of Coupled States
Explain what you could do to check the answer you got for the eigenvectors in the last problem. You don’t have to do it, just tell me what you could do.

4.111 The NMR matrix
Evaluate the following matrix elements for an nmr system with four nuclei with spin \( = 1/2 \) in two environments, A and B. In the ket the first two symbols are for the spin of the nuclei in environment A and the last two are for those in environment B. \( \hat{H}_0 \) is the chemical shift operator and \( \hat{H}_1 \) is the spin coupling operator. HINT: There are three coupling constants, \( J_{AA} \), \( J_{AB} \), and \( J_{BB} \).

\[
\langle \alpha \alpha \beta \mid \hat{H}_0 + \hat{H}_1 \mid \alpha \alpha \beta \rangle \\
\langle \alpha \beta \beta \mid \hat{H}_0 + \hat{H}_1 \mid \alpha \alpha \beta \rangle 
\]

4.112 Superposition
We have a one-dimensional system prepared in a state described by the wave function
\[
\psi = x(1 - 5x + 4x^2)
\]
This system is then placed in a parve on a pole system (of unit length) with potential equal to zero on the pole and infinite outside the pole. What is the expectation value of the energy? HINT: Let \( \hbar \) and \( m \) be equal to 1.

4.113 Probability of an Answer
Find the probability that a measurement of the energy of the state given in the last problem with a parve on a pole system will yield a value of 19.739 energy units.

4.114 Expectation Value
Find the expectation value of \( x \) for the wave function of problem 112.
4.115  *Solving Quantum Problems*
Find the energy of the ground state and the first excited state for an oscillator with a (total) potential of $2(1 - e^{-0.3q})^2$ (obviously in “q” language).

4.116  *Plotting Wave Functions*
Plot each of your answers from the last problem.

4.117  *Comparison of Wave Functions*
For the ground state function in the last problem, prove there is a distortion relative to a normal harmonic oscillator. Offer a rationalization of this distortion.

4.118  *Perturbation Theory*
This problem concerns a parve on a pole with a perturbation defined in Mathematica language as follows:

$$
tv[x_] := 0; \quad x < 0.4;

tv[x_] := 30(x - 0.4); \quad 0.4 \leq x \leq 0.5;

tv[x_] := 3 - 30(x - 0.5); \quad 0.5 < x \leq 0.6;

tv[x_] := 0; \quad x \geq 0.6;
$$

HINT: Let $\hbar$ and $m$ be unity. Find the perturbation energy (to first order) of the ground state wave function.

4.119  *Perturbation Theory*
Find the perturbation energy (to first order) of the first excited wave function for the system in the last problem.

4.120  *Perturbation Theory*
Qualitatively tell me why the two numbers in the last two problems differ and account for their relative magnitude.