2.1. Commutation
Two operators, \( a \) and \( b \), commute if
\[
ab = ba
\]

Does the pair of numbers acting as operators, \( a = 3 \) and \( b = 7 \), commute?
2.2. Commutation
If the two operators are such that they really do something to functions (unlike the rather boring thing that numbers do to functions), then to determine commutation you need to insert an arbitrary function to test. Let \( a = \frac{\partial}{\partial x} \) and \( b = \frac{\partial^2}{\partial x^2} \). Does this pair of operators commute? HINT: Devise symbols to aid yourself in solving this kind of problem. Let \( f \) be an arbitrary function of \( x \), then let \( \frac{\partial f}{\partial x} = f' \). You continue.

2.3. Commutation of Operators
Which of the following pairs of operators commute?
\[
\begin{align*}
\frac{\partial^2}{\partial x^2} \quad &\text{and} \quad x^2 \\
\frac{\partial}{\partial x} \quad &\text{and} \quad \frac{\partial}{\partial x} \\
\frac{\partial}{\partial x} \quad &\text{and} \quad \frac{\partial}{\partial y} \\
\left( \frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) \quad &\text{and} \quad \left( \frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right)
\end{align*}
\]
HINT: Don’t forget you need an arbitrary function to figure out commutation. In the case of two variables (the third and fourth problems) the function must be dependent on both variables.

2.4. Commutation of Matrices
Do the two matrices given below commute?
\[
\begin{pmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
1 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]
HINT: If you want to use M. to do this problem, remember that the matrix multiplication operator in M. is a period.

2.5. Operators
Operators change functions into new functions. Let’s consider the two operators, \( G \), which squares the function it operates on; so that \( G[f] = f^2 \); and as a second operator, \( J \), which takes the first derivative of a function with respect to \( x \), \( J[f] = \frac{df}{dx} \). What is the result of \( G \) on the function \( 2x^2 \)? What is the result of \( J \) on the function \( 2x^2 \)?

2.6. Linear Operators
Show that \( G \) (see the last problem) is not linear whereas \( J \) is. HINT: A linear operator, \( L \), has the properties \( L[cf] = c L[f] \) and \( L[f + g] = L[f] + L[g] \), where \( c \) is a constant and \( f \) and \( g \) are functions.

2.7. Review: Eigenvalues and Eigenvectors of Matrices
Find the eigenvalues and eigenvectors of the matrix
\[
\begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}
\]
HINT: This is an extraordinary easy problem in M.
2.8. **Review: Eigenvalues and Eigenvectors of Matrices**

Find the eigenvalues and eigenvectors of the matrix

\[
\begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\]

2.9. **Commutation Relationships**

Show by expansion and then condensation that the commutator

\[
\]

2.10. **Commutation Relationships**

Determine the value of the commutation relationship of the operators (in quantum mechanics): \([\hat{p}_x, \hat{x}]\).

2.11. **Hermitian Operators**

An operator, \(A\), is Hermitian if

\[
\int \psi^* (A\phi) dx = \int (A\psi)^* \phi dx
\]

Show that the operator \(\frac{\partial}{\partial x}\) is not Hermitian. That is, show that:

\[
\int \psi^* \frac{\partial}{\partial x} \phi dx \neq \int \phi \left[ \frac{\partial}{\partial x} \right]^* \psi^* dx
\]

**HINTS**: You should follow the procedure in class, using integration by parts in which you let the lhs of the equation above be the first term on the rhs of the equation below.

\[
\int \frac{\partial (fg)}{\partial x} dx = \int g \frac{\partial f}{\partial x} + \int f \frac{\partial g}{\partial x} dx
\]

2.12. **Hermitian Operators**

Show that the quantum operator corresponding to \(\hat{x}\hat{p}_x\hat{x}\) is Hermitian. That is, show that:

\[
\int \psi^* x \frac{\hbar}{i} \frac{\partial}{\partial x} x\phi dx = \int \phi \left[ \frac{\hbar}{i} \frac{\partial}{\partial x} x \right]^* \psi^* dx
\]

**HINTS**: You should follow the procedure in class, using integration by parts in which you let the lhs of the equation above be the first term on the rhs of the equation below.

\[
\int \frac{\partial (fg)}{\partial x} dx = \int g \frac{\partial f}{\partial x} + \int f \frac{\partial g}{\partial x} dx
\]

Also, think about incorporation of an \(x\), which is its own complex conjugate, into each of the \(\psi\) and \(\phi\); that is, to group the integral as

\[
\int (\psi^* x)^* \frac{\hbar}{i} \frac{\partial}{\partial x} (x\phi) dx
\]
2.13.  **Dirac Notation**  
You have a normalized POP wave function for \( n = 3 \), that is, \( \psi_3 = \sin[3 \pi x/L] \). Write the symbol for this state in *Dirac notation*. HINT: This and many of the following problems are very easy.

2.14.  **Dirac Notation**  
You have an un-normalized POP wave function for \( n = 5 \), that is, \( \psi_5 = \sin[5 \pi x/L] \). Write the equation for what you have to do to normalize this function in *Dirac notation*. HINT: Very easy problem.

2.15.  **Dirac Notation**  
The wave functions for the POP in level \( n = 3 \) and level \( n = 8 \) are orthogonal to each other. State this in Dirac notation. HINT: As in last problem.

2.16.  **Dirac Notation**  
For wave functions for the POP write each of the following three expressions in Dirac notation where the ket (and bra) are labeled by the quantum number, \( n \).

\[
<x> = \int \sqrt{2/L} \sin \left[ \frac{1\pi x}{L} \right] x \sqrt{2/L} \sin \left[ \frac{1\pi x}{L} \right] dx
\]

\[
< p^2 > = \int \sqrt{2/L} \sin \left[ \frac{3\pi x}{L} \right] \frac{1\pi x}{L} \sin \left[ \frac{3\pi x}{L} \right] \frac{d^2}{dx^2} \sqrt{2/L} \sin \left[ \frac{3\pi x}{L} \right] dx = 0
\]

HINT: This is a very easy problem; it is here just to get you to use Dirac notation. Don’t make it harder than it is.

2.17.  **Dirac Notation**  
Say you have a set of eigenfunctions, \( \phi_i \), of the Hermitian operator \( Q \) with different eigenvalues. Write that statement in Dirac notation.

2.18.  **Dirac Notation**  
You expand another wave function, \( \psi \) in terms of the functions of the last problem and the numbers \( c_i \). Write the statement of that expansion using Dirac notation. HINT: This is an easy problem.

2.19.  **Dirac Notation**  
Show that \( c_7 \) in the last problem is given by \( \langle 7 | \psi \rangle \). State clearly the postulate that you used to get to this conclusion if you didn’t do so in the last problem.

2.20.  **Expansion of a Wave Function and Dirac Notation**  
Given the expansion in problem 18, show that

\[
Q | \psi \rangle = c_1 q_1 | 1 \rangle + c_2 q_2 | 2 \rangle + c_3 q_3 | 3 \rangle + \ldots
\]

where the \( q_i \) are the eigenvalues of \( Q \) operating on the \( \phi_i \). Also write this in a more compact form using a summation sign.
2.21. **Expansion of a Wave Function and Dirac Notation**  
Given the equation in the last problem, show that  
\[ \langle \psi | Q | \psi \rangle = c_1^2 q_1 + c_2^2 q_2 + c_3^2 q_3 + \ldots \]
Also write this in a more compact form using a summation sign. What property of the \( \phi_i \) did you use to get this answer?

2.22. **Review of Harmonic Oscillator and Dirac Notation**  
Use M. to show that the wave functions for the harmonic oscillator with \( n = 0 \) and \( n = 2 \) are orthogonal to each other. Write the statement in Dirac notation for the fact that your wave functions are normalized.

2.23. **Dirac Notation and Hermitian Operators**  
Is the following equality true when \( O \) is a Hermitian operator?  
\[ \langle \psi | O | \phi \rangle = \langle \psi | O^* | \phi \rangle \]
HINTS: This is *our* usage of the arrow notation; you won’t find it elsewhere. Write the second Dirac statement in integral language and compare with the definition of a Hermitian operator.

2.24. **Dirac Notation and Hermitian Operators**  
Is the following equality true when \( O \) is a Hermitian operator?  
\[ \langle \psi | O | \phi \rangle = \langle O \psi | \phi \rangle \]

2.25. **Dirac Notation and Hermitian Operators**  
If \( O \) and \( P \) are Hermitian operators, use Dirac notation to show that  
\[ \langle \psi | PO | \phi \rangle = \langle OP \psi | \phi \rangle \]
Use Dirac notation in your derivation. HINT: This means that the operator \( (PO)^\dagger = O^\dagger P^\dagger \).

2.26. **Testing the Abstract**  
Using \( P = \hat{x}, O = \hat{p}^2_x, \phi \) as the POP wave function with \( n = 2 \), and \( \psi \) as the POP wave function with \( n = 1 \), show the result in the last equation gives what real integration shows. HINTS: (1) Of course you will have to change \( \hat{p}^2_x \) into the quantum mechanical operator equivalent. (2) Be sure you know what statements mean. Here \( \langle OP \psi | \phi \rangle \) means do \( P^* \) on \( \psi \), then do \( O^* \) on that result, then multiply the second result by \( \phi \) and integrate it.
2.27. Matrices as Operators
We will have the occasion later to use matrices as operators (Heisenberg’s original presentation of quantum mechanics was made using matrices; hence you sometimes see the name “matrix mechanics”). For a matrix to be Hermitian requires that \( A^\dagger = A \), where the “dagger” means to take the complex conjugate of the transpose of the matrix. To transpose the matrix means to rotate it about the upper left to lower right diagonal; clearly only square matrices can be Hermitian. Show that the matrix

\[
\begin{pmatrix}
1 & -i & 3 + 4i \\
- i & 3 & 1 \\
3 - 4i & 1 & 1
\end{pmatrix}
\]

is Hermitian. HINT: As you might expect, Mathematica has the ability to do both of these operations, with the command Transpose[...] and the command Conjugate[...]. So if you want \( A^\dagger \) from \( A \), you would issue the command Transpose[Conjugate[A]].

2.28. Matrices as Operators
The matrix given below is also Hermitian. Show that the product of this matrix and the one from problem 27 obey the rule in the HINT in problem 25.

\[
\begin{pmatrix}
0 & 1 & i \\
1 & 1 & 1 \\
-i & 1 & 0
\end{pmatrix}
\]

2.29. Hermitian Matrix
Is the matrix given below Hermitian?

\[
\begin{pmatrix}
0 & 1 & 0 \\
1 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\]

2.30. Hermitian Matrix
Is the matrix given below Hermitian?

\[
\begin{pmatrix}
0 & \frac{1}{\sqrt{2}} & 0 \\
\frac{-1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\
0 & \frac{-1}{\sqrt{2}} & 0
\end{pmatrix}
\]

2.31. Hermitian Operators and Dirac Notation
The contention is that the eigenvalues of a Hermitian matrix are real. Imagine we have the relationship

\[ A |c\rangle = \gamma |c\rangle \] (1)

Multiply this from the left with \( \langle c | \). Also take the complex conjugate of both sides of equation 1, multiply from the right with \( |c\rangle \), and show that

\[ \langle c | A^\dagger | c \rangle = \langle c | c \rangle \gamma^* \]

Now take advantage of the Hermitian property, \( A^\dagger = A \), and show that \( \gamma^* = \gamma \).
2.32. *Hermitian Matrices*
Show that the eigenvalues of the matrices in problems 27 and 28 are real. HINT: M.

2.33. *Hermitian Matrices*
Are the eigenvalues of the matrix in problem 30 real? HINT: M.

2.34. *Eigenvectors of a Hermitian Matrix*
Find the eigenvectors of the matrix in problem 28. Show by carrying out $A|c\rangle$, where $A$ is
the matrix of problem 28 and $|c\rangle$ is one of its eigenvectors, that you get an eigenvalue times
the eigenvector.

2.35. *Eigenvalues of Hermitian Matrix*
Construct a 4 x 4 Hermitian matrix with $i$ in it at least once and show that the eigenvalues
are real.

2.36. *Eigenvalues*
“The eigenvalues of Hermitian operators are [blank].”

2.37. *Hermitian Matrices*
Is the matrix given below Hermitian? Why or why not?

\[
\begin{pmatrix}
1 & i & 0 \\
i & 1 & 1 \\
0 & 1 & -1 \\
\end{pmatrix}
\]

Find the eigenvalues of this matrix.

2.38. *Hermitian Operators and Dirac Notation*
The contention is that the eigenfunctions (eigenvectors) of a Hermitian operator belonging
to different eigenvalues are orthogonal. Imagine we have the Hermitian operator $R$ and the
two eigenfunction/eigenvalue equations

\[
R|c\rangle = r|c\rangle \\
R|c'\rangle = p|c'\rangle
\]

where $r \neq p$. Multiply the first from the left with $\langle c'|$. Now take the complex conjugate of
the second equation and multiply it from the right by $|c\rangle$. Using the definition of Hermitian
operator, you can set

\[
\langle c'| R|c\rangle = \langle c'| R^\dagger|c\rangle
\]

and rearrange the result to get

\[
(r - p)\langle c'|c\rangle = 0
\]

Since $r \neq p$, what do you conclude?

2.39. *Hermitian Matrices*
Show that the eigenvectors of the matrices in problems 27 and 28 are orthogonal. HINT:
Don’t forget that $\langle c'|c\rangle$ requires a Conjugate[. . .].
2.40. Eigenfunctions

“The non-degenerate eigenfunctions of a Hermitian operator are [blank].” REMARK: We will show that even for degenerate functions they can be made to obey this rule.

2.41. Orthogonality and Dirac Notation

Suppose you have two normalized kets, \(|w\rangle\) and \(|x\rangle\), and suppose these two are not orthogonal; that is \(\langle w|x \rangle = k\), where \(k\) is real. Show that the sum of the two kets and the difference of the two kets are orthogonal.

2.42. Orthogonality and Dirac Notation

Given the functions, \(|f\rangle = 2|a\rangle - |b\rangle - |c\rangle\) and \(|g\rangle = 2|b\rangle - |a\rangle - |c\rangle\), show that \(|f\rangle\) and \(|g\rangle\) are not orthogonal if \(\langle i|j \rangle = \delta_{ij}\) for \(i\) and \(j = a, b, c\). HINT: \(\delta_{ij}\) is the Kronecker, or Dirac, delta; equal to 1 when \(i = j\), zero otherwise. Do this entire problem using Dirac notation.

2.43. Orthogonality and Dirac Notation

Find \(|g'\rangle\), the function that is orthogonal to \(|f\rangle\) of the last problem. HINT: Normalize \(|f\rangle\) and \(|g\rangle\) before you start.

2.44. Vector Space

Thinking about the bracket in Dirac notation as a dot product of vectors can be useful. (The virtual space in which these vectors exist is called Hilbert Space, but the analogies are reasonably good.) In vector language, the symbol \(\langle g|g \rangle\) represents the length of a vector. What would \(\langle j|g \rangle\) represent? HINT: Remember that

\[ \vec{j} \cdot \vec{g} = |j||g| \cos \theta \]

2.45. Schwartz Inequality

Use the vectors pictured in Figure 1 to establish that the Schwartz inequality, given below, is valid:

\[ \langle g|g \rangle \langle j|j \rangle \geq |\langle g|j \rangle|^2 \quad (2) \]
2.46. The Equality in the Schwartz Inequality
When does the “equal to” condition hold in the Schwartz inequality of the last problem?

2.47. Expectation Values of Hermitian Operators
Imagine you have the Hermitian operator $O$. Show that the expectation value for some function $\psi$, $\langle \psi | O | \psi \rangle$ is real. HINTS: Expand $\psi$ in terms of eigenfunctions of $O$; use Dirac notation.

2.48. Hermitian Operators
Show that if $O$ is Hermitian, then so is $Q$ where $Q = O - \langle O \rangle$. That is, you want to prove that
\[
\langle \psi | Q^\dagger Q | \psi \rangle = \langle \psi | Q | \psi \rangle
\]
HINT: Use Dirac notation and remember that $\langle O \rangle$ is just a number, a number you learned something about in the last problem.

2.49. Hermitian Operators
Define a new function $|\alpha\rangle = (O - \langle O \rangle) |\psi\rangle$ where $\langle O \rangle = \langle \psi | O | \psi \rangle$ and $|\beta\rangle = (P - \langle P \rangle) |\psi\rangle$ where $\langle P \rangle = \langle \psi | P | \psi \rangle$, where $O$ and $P$ are Hermitian. Show that $\langle \alpha | \alpha \rangle = \sigma_O^2$ and that $\langle \beta | \beta \rangle = \sigma_P^2$.

2.50. Useful Side Result
Let $q$ be any complex number, which you can write as $q = a + bi$. Show that
\[
|q|^2 = q q^* = a^2 + b^2 \geq b^2
\]
Then show from $q - q^*$ that $b$ also equals
\[
\frac{(q - q^*)}{2i}
\]
and therefore conclude that $|q|^2 \geq \left(\frac{(q - q^*)}{2i}\right)^2$.

2.51. Moving Toward the Uncertainty Principle
We want to apply the Schwartz Inequality (equation 2) to $\langle \alpha | \alpha \rangle \langle \beta | \beta \rangle$ of problem 49. To do so, we need $| \langle \alpha | \beta \rangle |^2$. Let $\langle \alpha | \beta \rangle$ be equal to the “$q$” of the last problem. Show then that
\[
| \langle \alpha | \beta \rangle |^2 \geq \left( \frac{\langle \alpha | \beta \rangle - \langle \beta | \alpha \rangle}{2i} \right)^2
\]

2.52. Even Closer to the Uncertainty Principle
Show by expansion of $\langle \alpha | \beta \rangle$ (see problem 49) that it is equal to $\langle O P \rangle - \langle O \rangle \langle P \rangle$. Get a similar expression for $\langle \beta | \alpha \rangle$. Then determine
\[
\left( \frac{\langle \alpha | \beta \rangle - \langle \beta | \alpha \rangle}{2i} \right)^2
\]
2.53. **The Generalized Uncertainty Principle**

Put your result from the last problem into the right hand side of the Schwartz Inequality (equation 2) and your result from problem 49 and obtain:

\[
\sigma_O^2 \sigma_P^2 \geq \left( \frac{\langle [O, P] \rangle}{2i} \right)^2
\]  

(3)

2.54. **Review**

What is the commutator of \( \hat{p}_x \) with \( \hat{x} \)?

2.55. **HUP in the Usual Formulation**

Put your result for \( [\hat{p}_x, \hat{x}] \) from the last problem into the generalized Heisenberg Uncertainty Principle, equation 3, as \( [O, P] \) and evaluate the answer for \( \sigma_p \sigma_x \), which will give you the usual expression for the HUP.

2.56. **Ladder Operator in q Language**

For a harmonic oscillator, define the operator

\[
a_+ = \frac{1}{\sqrt{\hbar \omega}} \left( \sqrt{m/2\omega} \hat{x} - \frac{i}{\sqrt{2m}} \hat{p}_x \right)
\]

Use \( q = (\sqrt{m\omega/\hbar})x \) and find the value of \( a_+ \) in terms of the parameter \( q \). Write a Mathematica underscore function for this operator so you can use it below. HINT: Be careful with the first term in the parenthesis. The square root symbol ends where it ends!

2.57. **Schrödinger’s Equation for the Harmonic Oscillator in q Language**

What is Schrödinger’s equation in q language for a harmonic oscillator? Show this expression is correct by evaluation of \( \hat{H} |3\rangle \), where \( |3\rangle \) is the eigenfunction for a harmonic oscillator with \( n = 3 \). HINT: Write a Mathematica underscore function for the Hamiltonian so you can use it below.

2.58. **A Mathematica Normalized Harmonic Oscillator Wave Function**

I think that a generalized underscore function for the harmonic oscillator wave function could be written:

\[
wf[n_,] := \text{Sqrt}[1/(\text{Integrate}[\text{HermiteH}[n, q]^2 \text{Exp}[-q^2/2]^2, \{q, -\text{Infinity}, \text{Infinity}\}])] \\
\text{HermiteH}[n, q] \text{Exp}[-q^2/2]
\]

Show that this is true (or false). What is the purpose of “Integrate” in the middle of that function? HINTS: (1) If I remember correctly, Mathematica Version 10 does not like the limits of integration of infinity for too large an “n”; the fix is to change those to numbers that are sufficiently large to define the limits of \( \psi \) going (effectively) to zero. (2) Also, the \( wf[n] \) function cannot be plotted as such, since it requires \( q \) to be \(-\infty\) in the integral, but \( q \) must be restricted to real values to get a plot. The work-around is to define some symbol, \( gg = wf[n] \), which defines a numerical thing in M., and then plot gg between whatever limits you wish.
2.59. **The Lowering Operator’s Result**

The contention is that the function \( |m\rangle = a_- |n\rangle \) is an eigenfunction of \( \hat{H} \) with an eigenvalue of \( n-1 \) (in q language). Use your M. derived operators (problems 56 and 57) to prove this for \( n = 5 \). HINT: You could use your underscore function from the last problem.

2.60. **Ladder Operator Commutation**

Use a pen and paper to find the commutator \([a_-, a_+]\) where the a’s are the harmonic oscillator ladder operators. HINT: This is much less messy to do in q language because you don’t have to carry around all the constants.

2.61. **Ladder Operator Commutation**

Use Mathematica defined operators to find the commutator \([a_+, a_-]\). HINT: Note that you operate on a arbitrary function to evaluate a commutator, then when finished remove that function. Also recall the issue is \((a_+ a_-)f - (a_- a_+)f\) and the evaluation of the second in M. is aminus[aplus[f]] if aminus and aplus are the names of underscore operators.

2.62. **Ladder Operator Evaluation**

Show using the equivalent of \( a_- \) in q language that \( a_- |2\rangle \) produces \( |1\rangle \), where all functions are eigenfunctions for the harmonic oscillator problem (obviously in “q” language). HINT: M. would be useful.

2.63. **Ladder Operator Manipulation and Dirac Notation**

Find the complete answer (use the results of the last problem to get coefficients) for the following operations:

\[
\begin{align*}
    a_+ |2\rangle \\
    a_- |2\rangle \\
    a_- |0\rangle \\
    a_+ a_- |2\rangle \\
    \langle 2|a_+|1\rangle \\
    \langle 7|a_+^3|4\rangle
\end{align*}
\]

2.64. **Ladder Operator on Wave Functions**

We showed in class that given any \( \psi \) for a harmonic oscillator that you can get the next one up by using the raising operator \( a_+ \); given that the \( n = 2 \) wave function is

\[
A(2q^2 - 1)e^{-q^2/2}
\]

find the \( n = 3 \) wave function. HINTS: (1) It would clearly be most convenient to use the raising operator in terms of q on these functions. (2) If you did problem 58, then you not only have this function, but you know “A”.
2.65.  

**Ladder Operator on Wave Functions**

This problem can be messy. I did it once earlier and made mistakes that took me a while to figure out because I was sloppy; but it is a good one to test your knowledge of how to do things, so do it if you like. But don’t do it without M. and be sure to set up your system so you can use a symbol for a wave function again since you have to use your net formula twice. Also I wrote this problem with the idea that you evaluate the operator by hand (or mind); if you use a M. underscore definition of $a_+$ and let M. do the evaluation, this whole problem become trivial. Enough of the preliminaries.

Take the expression given below for the wavefunction of a harmonic oscillator in the $n = 4$ state and use the operator $a_+$ three times (at once if you are doing it by hand: that is, evaluate $a_+^3$ in terms of $q$ and $\partial/\partial q$ before you operate) to produce the answer for $n = 7$. Then use the same expression to jump to $n = 10$. Plot $\psi_4, \psi_7,$ and $\psi_{10}$. See any trend?

Two more HINTS: When you expand $a_+^3$ don’t forget that $q$ and $\partial/\partial q$ do not commute. Use Simplify[... ] around your function to get the answers in a form where you can see the structure.

$$\psi_4 = \frac{(16q^4 - 48q^2 + 12)e^{-q^2/2}}{8\sqrt{6\pi^3}}$$

2.66.  

**Ladder Operator Manipulation**

Consider the operator $a_-a_+a_+$ on the $|0\rangle$ state of the harmonic oscillator. Group the two leftmost of those operators and replace them by an expression containing the commutator $[a_-, a_+]$ and expand the result. This will have the effect of moving the $a_-$ operator over to the right one step, leaving another term behind. HINT: Remember that you have derived the value of the commutator $[a_-, a_+]$ in problem 60.

2.67.  

**Ladder Operator Manipulation**

Repeat the process from the last problem again and you will have a term with $a_-$ operating on $|0\rangle$. What is the effect of this? What is $w$ in your total answer for $a_-a_+a_+ |0\rangle = w|0\rangle$? HINT: $w$ is not necessarily just a constant.

2.68.  

**Ladder Operator Manipulation**

Repeat the process begun in problem 66 with the operator $a_-a_+a_+a_+$. What is your answer for $w$ in the expression $a_-a_+a_+a_+ = w |0\rangle$? What would be the answer if you used the operator $a_-(a_+)^n$? HINT: You can (should, must?) use logic on this rather than math.

2.69.  

**Ladder Operator Manipulation**

You established in the last problem the value of $s$ in the equation

$$a_-(a_+)^n |0\rangle = s(a_+)^{n-1} |0\rangle$$

Now apply $a_-$ to both sides of this expression and evaluate the right hand side using the same tricks that you have just developed. Show that you get

$$a_-a_-(a_+)^n |0\rangle = s(s - 1)(a_+)^{n-2} |0\rangle$$

HINT: Rather than completely doing this mathematically, use logic.
2.70. Ladder Operator Manipulation
See if you can figure out what the number, g, will be on the right hand side of the equation if we do the following:

\[(a_-)^n(a_+)^n \langle 0 \rangle = g \langle 0 \rangle\]

HINT: See the last several problems.

2.71. Ladder Operator Manipulation
The following is not a proof–we did that in class–but makes reasonable sense in case you didn’t like the proof. From the last problem, we now know that

\[\langle 0 | a^a a^+ | 0 \rangle = g\]

and so we might postulate that

\[a_+ | n \rangle = \sqrt{n + 1} | n + 1 \rangle \quad (4)\]

and that

\[a_- | n \rangle = \sqrt{n} | n - 1 \rangle \quad (5)\]

Would these postulates account for the results we have thus far? Show this (symbolically) by operating on \(| 0 \rangle\) with the \(a_+ n\) times followed by doing the same for all the \(a_-\), and then multiply with \(| 0 \rangle\). We will use this result later for selection rules and perturbation theory.

2.72. Ladder Operator Coefficient
Determine using M. (which is very easy if you have defined operators and functions with underscore language (see problems 56 and 58) that

\[a_- | n \rangle = \sqrt{n} | n - 1 \rangle\]

and that

\[a_+ | n \rangle = \sqrt{n + 1} | n + 1 \rangle\]

2.73. Two Body Coordinates
Figure 2 gives the coordinate system used for a two body system. The center of mass is defined as the point between the atoms where \(m_A r_{AC} = m_B r_{BC}\). From the figure determine which mass is larger.

2.74. Two Body Coordinates
In Figure 2 we can say that the vector equation \(\vec{r} = r_{BC} + r_{AC}\) is true. Write similar equations expressing the relationship of the vectors \(\vec{r}, r_A, r_B\) on the one hand, and \(\vec{R}, r_A, \text{ and } r_{AC}\) on the other, and then, on one foot, the relationship between \(\vec{R}, r_B, \text{ and } r_{BC}\), leaving one poor foot behind.

2.75. Two Body Problem Resolution
You can use the last two equations of the last problem and the equation for the center of mass in problem 73 to rid the equations of \(r_{AC}\) and \(r_{BC}\). Then using the definition of the vector \(\vec{r}\) you can solve for \(r_A\) to get

\[r_A = \frac{m_B}{m_A + m_B} \vec{r} + \vec{R}\]

\[r_B = -\frac{m_A}{m_A + m_B} \vec{r} + \vec{R}\]

Providing you have established this (or believe it), in terms of what physical parameters (other than the obvious masses) have we been able to express the vectorial location of atoms A and B?
Figure 2: Coordinate System for the Diatomic Molecule AB. The point between atoms A and B is the center of mass.
2.76. Simplification of the Two Body Problem
The vector \( \vec{R} \) in the last problem simply measures the movement through space of the center of mass of the molecule, and hence is a translation of the molecule as a whole. How could we understand the quantum mechanics of that?

2.77. Simplification of the Two Body Problem
The vector \( \vec{r} \) in problem 75 is a measure of how the AB molecule rotates and vibrates. How are each of those reflected in changes in \( \vec{r} \)? What would be true of the vector \( \vec{r} \) if we decided to adopt a “rigid rotor” approximation? HINT: Your job is to interpret what is the meaning of what is quoted.

2.78. Angular Momentum
We can simplify our problem even further by defining the angular momentum of the molecule. Angular momentum in general is defined as the mass times the distance to center of rotation squared times the angular frequency. Express this for our AB molecule about the center of mass in terms of quantities in Figure 2.

2.79. Angular Momentum
We have for the angular momentum
\[
\Lambda = m_A r_{AC}^2 \omega + m_B r_{BC}^2 \omega
\]
where the \( r \) values are lengths of vectors. If you multiply both sides of this by the sum of the masses (and divide by \( \omega \)) and expand the terms, you end up with two terms of the form \( m_X r_{XC}^2 \), one with \( X = A \) and one with \( X = B \). Because of the definition of the center of mass, these two terms can be established as equal to each other. Show this.

2.80. Angular Momentum
The expression for the angular momentum is now:
\[
(m_A + m_B) \frac{\Lambda}{\omega} = m_A m_B (r_{AC}^2 + 2 r_{AC} r_{BC} + r_{BC}^2)
\]
where, of course \( r_{AC} \) and \( r_{BC} \) are the lengths of the corresponding vectors. Show that this can be written
\[
\Lambda = \frac{m_A m_B}{m_A + m_B} b_l^2 \omega
\]
where \( b_l \) is the bond length.

2.81. The Equation for a Single Rotating Body
The quantity
\[
\frac{m_A m_B}{m_A + m_B}
\]
is called the reduced mass, symbolized \( \mu \), and the angular momentum becomes
\[
\Lambda = \mu b_l^2 \omega
\]
(6)
Justify that this is the same as the momentum of a single body about a point in space. Of what mass? What is the conclusion of our development? “We can model the behavior of a rigid rotor as if . . . ”
Figure 3: The Relationship between Cartesian and Spherical Coordinates
2.82. Cartesian and Spherical Coordinates
Consult Figure 3 and convert the given Cartesian coordinates \([x, y, z]\) into spherical coordinates \([r, \theta, \phi]\). You should not need a calculator or M. \([1, 0, 0]; [0, 1, 0]; [0, 0, 1]; [1, 1, 0]\).

2.83. Cartesian and Spherical Coordinates
For each of the following convert the spherical coordinates \([r, \theta, \phi]\) into Cartesian coordinates \([x, y, z]\). You should not need a calculator or M. \([1, \pi/2, \pi/2]; [1, \pi, 0]; [1, \pi/2, 3\pi/2]\).

2.84. Cartesian and Spherical Coordinates
Find the expressions that relate \(x, y, z\) to \(r, \theta, \phi\); three equations. See Figure 3

2.85. Between Cartesian and Spherical Coordinates
For future problems we need the \(\partial s/\partial c\) where \(s\) is one of the spherical coordinates, \(r, \theta, \phi\); and \(c\) is one of the Cartesian coordinates \(x, y, z\). For instance, one quantity we might want is \(\partial \theta/\partial z\). To get this you could differentiate both sides of the equation \(z/r = \cos \theta\) with respect to \(z\), which would give you

\[
\frac{1}{r} + (-1)z \frac{1}{r^2} \frac{z}{r} = -\sin \theta \frac{\partial \theta}{\partial z}
\]

Prove this. Then show that this simplifies to \(\partial \theta/\partial z = -\sin \theta/r\).

2.86. Between Cartesian and Spherical Coordinates
Given that \(y/x = \sin \phi/\cos \phi\), show that \(\partial \phi/\partial z = 0\). HINT: For future reference, a table of these partials is given in Table 1.

<table>
<thead>
<tr>
<th>Partial Derivative</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\partial r/\partial x)</td>
<td>(x/r)</td>
</tr>
<tr>
<td>(\partial r/\partial y)</td>
<td>(y/r)</td>
</tr>
<tr>
<td>(\partial r/\partial z)</td>
<td>(z/r)</td>
</tr>
<tr>
<td>(\partial \theta/\partial x)</td>
<td>(\cos \theta \cos \phi/r)</td>
</tr>
<tr>
<td>(\partial \theta/\partial y)</td>
<td>(\cos \theta \sin \phi/r)</td>
</tr>
<tr>
<td>(\partial \theta/\partial z)</td>
<td>(-\sin \theta/r)</td>
</tr>
<tr>
<td>(\partial \phi/\partial x)</td>
<td>(-\sin \phi/(r \sin \theta))</td>
</tr>
<tr>
<td>(\partial \phi/\partial y)</td>
<td>(\cos \phi/(r \sin \theta))</td>
</tr>
<tr>
<td>(\partial \phi/\partial z)</td>
<td>(0)</td>
</tr>
</tbody>
</table>

Table 1: Values of Partial Derivatives \(\partial s/\partial c\)

2.87. Between Cartesian and Spherical Coordinates
Express the chain rule for \(\partial/\partial x\) in terms of the three \(\partial/\partial s\). Express your opinion of the mess we will get into with a second derivative, which we need in using whose equation?

2.88. Separation of Variables: Step One
Suppose you have an operator of the form \(G = \partial/\partial x + x^2 - \partial^2/\partial y^2 + y\) and an equation that says \(G \psi = \alpha \psi\), where \(\alpha\) is a constant. Put into this equation a guessed solution of the form \(\psi = \phi(x) \chi(y)\).
2.89. Separation of Variables: Step Two
Move any part of the function $\phi(x) \chi(y)$ from the last problem that is not affected by an operator “across” that operator. That is,

$$\frac{\partial}{\partial x} \phi(x) \chi(y) = \chi(y) \frac{\partial}{\partial x} \phi(x)$$

2.90. Separation of Variables: Step Three
Divide your result from the last problem by $\psi$ and simplify fractions.

2.91. Separation of Variables: Step Four
Using your answer from the last problem, move all terms involving $x$ or functions of $x$ onto one side of an equation and all terms involving $y$ or functions of $y$ onto the other. You can put $\alpha$, since it is just a constant, anywhere you like. This is a variables separable equation. It is a very common way of solving the SE; we did it when we separated space from time in the time dependent SE and we will do it again.

2.92. Separation of Variables
How many steps are there in a separation of variables approach? What are they?

2.93. Schrödinger’s Equation for a Parve on a Sheet
For a parve on a square sheet (a two dimensional problem) with the potential energy equal to zero on the sheet and infinity elsewhere, write Schrödinger’s equation.

2.94. Variable Separable Solution for a Parve on a Sheet
Assume a solution for $\psi$ for the parve on a sheet has the form $F(x)G(y)$; divide both sides of Schrödinger’s equation (from the last problem) by this pair, rearrange to get all $x$ dependencies on one side and all $y$ dependencies on the other, thereby showing that this is a variable separable problem.

2.95. Solving for the Energy of a Parve on a Sheet
Determine the $E$ and $\psi$ for the problem of a parve on a sheet–see the last two problems.

2.96. Plotting Wave Functions for a Parve on a Sheet
You might want to plot the answers for $\psi$ in the last problem for $n_x = 1$, $n_y = 2$, or maybe other values. The command for a three dimensional plot in M. is, for instance:

$$\text{Plot3D}[\sin[y] \sin[x], \{x, 0, 1\}, \{y, 0, 1\}]$$

2.97. The $\Phi$ Solution for a Rigid Rotar
What steps did we take to obtain the solution to the $\phi$ dependent part of the rigid rotor wave function?

$$\Phi = \frac{1}{2\pi} e^{im\phi} \quad (7)$$

where $m = 0, \pm 1, \pm 2, \pm 3, \ldots$
2.98. The Θ Solution for a Rigid Rotor
If you have a variables separated solution of the form
\[ f(\phi) = g(\theta) + e h(\theta) \]
where \( e \) is a constant, and you know that \( f(\phi) \) is \( -m^2 \), what are you going to do to get the solution that depends on \( \theta \)? HINT: Conceptual problem.

2.99. Legendre Polynomial
Use M. to generate the Legendre polynomial of \( \cos \theta \) for \( m = 0 \) and \( \ell = 2 \) (called \( n = 2 \) in M.). The command is
\[ \text{LegendreP}[2, \cos[\theta]] \text{ or LegendreP}[2, 0, \cos[\theta]] \]
HINT: You might call this function something—I’m calling it “f” in what follows—so that you can easily insert it into SE for \( \theta \).

2.100. Solving the θ Part of the Rigid Rotor
The \( \theta \) part of the SE operator for a rigid rotor, called \( \mathcal{O} \) in class, is:
\[ \left( \frac{1}{\sin[\theta]} \frac{\partial}{\partial \theta} \sin[\theta] \frac{\partial}{\partial \theta} - \frac{m^2}{\sin^2[\theta]} + \lambda \right) \]
Put in the value of “\( f \)” from the last problem (\( m = 0 \)) and show that this is indeed an eigenfunction of \( \mathcal{O} \). What is the eigenvalue? HINTS: You might want to write the \( \theta \) portion of SE as a M. underscore command (probably best as a function of both “\( f \)” and “\( m \)” so that you can use it again and again. Also, the M. command \text{Simplify}[\ldots] \) enclosing these kind of operations makes them easier to fathom.

2.101. Eigenfunctions of Θ SE for a Rigid Rotor
Use M. to generate the Legendre polynomial of \( \cos \theta \) for \( m = 0 \) and \( \ell = 3 \) (called \( n = 3 \) in M.). Show that it is also an eigenfunction of the operator given in the last problem. What is the eigenvalue?

2.102. Eigenvalues of the Rigid Rotor
Can you see a relationship between the eigenvalues of the last three problems? HINT: if you did problems with \( \ell = 4, 5, \) and \( 6 \) (as you should have if you need this hint, since M. makes it very easy) you would have obtained \( \lambda \) of 20, 30, and 42.

2.103. Eigenfunctions of Θ SE for a Rigid Rotor
Use M. to generate the Legendre polynomial of \( \cos \theta \) for \( m = 1 \) and \( \ell = 2 \) (called \( n = 2 \) in M.). Show that it is also an eigenfunction of the operator given in problem 100. What is the eigenvalue?

2.104. Eigenvalues of the Rigid Rotor
Do you see a relationship between the eigenvalue of the eigenfunction in the last problem, \( \Theta_{2,1} \), with that of the value for \( \Theta_{2,0} \) in problem 100?

2.105. Eigenvalues of the Rigid Rotor
How would you test you hypothesis from the last problem?
2.106. Normalizing the Rigid Rotor Wave Functions
Normalize the rigid rotor wave function composed of the Θ part and the Φ part for \( \ell = 0, m = 0 \). Also do \( \ell = 2, m = 1 \). HINTS: Remember the integral range to enclose space correctly for these is \( \sin \theta \, d\theta \, d\phi \) and pay attention to the limits of the integration. For double integrals in M. you have to write:

\[
\text{Integrate}[\text{function}, \{x, 0, 1\}, \{y, 0, 2\}]
\]

for the limits of integration of \( x \) (zero to one) and \( y \) (zero to two).

2.107. Normalized Spherical Harmonics
Show that the M. generated functions called spherical harmonics, \( Y_{00} \) and \( Y_{21} \) (which are obtained in M. with the command \( \text{SphericalHarmonicY}[...] \)) are the normalized functions from the last problem.

2.108. Spherical Harmonic Functions
Show that the spherical harmonic \( Y_{10} \) is orthogonal to \( Y_{11} \). That is, that

\[
\langle 1 \ 0 | 1 \ 1 \rangle = 0
\]

HINT: M. uses the command \( \text{SphericalHarmonicsY}[\ell, m, \theta, \phi] \) to generate the spherical harmonics.

2.109. Rigid Rotor Eigenvalues
For the rigid rotor, how many states are there with an eigenvalue of the operator \( \ell^2 \) of 2? Of 6? Of 20?

2.110. Rigid Rotor Eigenvalues
What can you say about the energy of the states in the last problem?

2.111. Angular Momentum
Classical angular momentum about the z axis is given by \( \ell_z = x \ p_y - y \ p_x \). Convert the right hand side of this expression to quantum mechanical form and evaluate it in terms of spherical coordinates. MANY HINTS: When you evaluate \( \partial/\partial x \) you have to expand that as

\[
\frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi}
\]

Use Table 1. Remember that \( \cos^2[\phi] + \sin^2[\phi] = 1 \). This is long, but just easy algebra with the table.

2.112. Eigenvalues of the Angular Momentum for the Rigid Rotor
We have the angular momentum about the z axis operator, \( \hat{\ell}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \). Show that the rigid rotor wave function, \( |3 \ 1 \rangle = \psi_{\ell=3,m=1} = Y_{31} \) is an eigenfunction of \( \hat{\ell}_z \). What is the eigenvalue? HINT: Remember you need both the \( \theta \) and the \( \phi \) functions, indeed the product of them, for this problem. That product is, by definition, the spherical harmonic.
2.113. **Angular Momentum Commutation**
Show by expanding the angular momentum operators that \([\ell_x, \ell_z] = -i\hbar \ell_y\). HINT: When you expand \(\ell_x\) and \(\ell_z\) in terms of \(x, y, z, p_x\), etc., you end up with eight terms. It is with the correct collection of these that simplifications occur. When you finish, be sure that you note the commutators with \(x, y,\) and \(z\) arranged in alphabetical order is always \(i\hbar\) times the missing one, and the commutators with \(x, y,\) and \(z\) arranged in reverse alphabetical order is always minus \(i\hbar\) times the missing one; or, just to add to the confusion, is \(-\left(\frac{\hbar}{2}\right)\) times the missing one in the former case and \(\left(\frac{\hbar}{2}\right)\) times the missing one in the latter.

2.114. **Commutation Properties**
Show that the commutator \([(a-b),(c-d)]\), when expanded, is equal to
\[
[a, c] - [a, d] - [b, c] + [b, d]
\]

2.115. **Angular Momentum Commutation**
Expand the commutator \([\ell_x^2, \ell_z]\). Then insert zero into that expanded expression in the form of
\[
\ell_x \ell_z \ell_x - \ell_z \ell_x \ell_x
\]
and show that this commutator is equal to
\[
-i\hbar (\ell_x \ell_y + \ell_y \ell_x) \quad (8)
\]

2.116. **Angular Momentum Commutation**
Expand the commutator \([\ell_y^2, \ell_z]\). Then insert zero into it in the same manner as in the last problem. Show that this commutator is equal to
\[
i\hbar (\ell_x \ell_y + \ell_y \ell_x) \quad (9)
\]

2.117. **Angular Momentum Commutation**
Show that \([\ell_z^2, \ell_z] = 0\).

2.118. **Angular Momentum Commutation**
Use your result from the last problem and equations 8 and 9 to show that \(\ell^2\), which is equal to \(\ell_x^2 + \ell_y^2 + \ell_z^2\), commutes with \(\ell_z\).

2.119. **Angular Momentum Commutation**
Use logic to determine the value of the commutator \([\ell^2, \ell_y]\).

2.120. **Angular Momentum Commutation**
Does \(\ell_z\) commute with \(\ell_y\)?

2.121. **Angular Momentum Commutation**
What commutes and what does not commute among the angular momentum operators?
2.122. **Angular Momentum Commutation**
If $\ell_+$ is defined as $\ell_x + i\ell_y$, find the commutator $[\ell_z, \ell_+]$.

2.123. **Angular Momentum Commutation**
If $\ell_+$ is defined as $\ell_x + i\ell_y$, show that $[\ell^2, \ell_+] = 0$.

2.124. **Actual Angular Momentum Operators**
I claim the operators for $\ell_x$ and $\ell_y$ are given by

\[
\ell_x = i\hbar \left( \sin[\phi] \frac{\partial}{\partial \theta} + \frac{\cos[\theta]}{\sin[\theta]} \cos[\phi] \frac{\partial}{\partial \phi} \right)
\]

\[
\ell_y = i\hbar \left( -\cos[\phi] \frac{\partial}{\partial \theta} + \frac{\cos[\theta]}{\sin[\theta]} \sin[\phi] \frac{\partial}{\partial \phi} \right)
\]

Show that $\ell_+$ operating on $Y_{20}$ gives some constant times $Y_{21}$.

2.125. **Actual Angular Momentum Operators**
The operator for $\ell^2$ is as follows:

\[
\ell^2 = -\hbar^2 \left[ \frac{1}{\sin[\theta]} \frac{\partial}{\partial \theta} \left( \sin[\theta] \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2[\theta]} \frac{\partial^2}{\partial \phi^2} \right]
\]

Show that $\ell^2 |31\rangle$ is an eigenfunction/eigenvalue problem. What is the eigenvalue? HINT: When I tried this I had to do some simplification by hand; I could not figure out why M. would not do it automatically.

2.126. **Actual Angular Momentum Operators**
Another way to get $\ell^2$ is to use the sum of the squares of the components, $\ell^2_i$, with $i$ running over $x$, $y$, and $z$. Try this on the spherical harmonic $Y_{31}$. HINT: Remember to do $\ell^2_x$ in M. (provided you have defined an underscore operator that I call $l_x$) you need

\[ l_x[l_x[func]] \]

2.127.
Assume that $|\ell\rangle$ is an eigenfunction of $\ell^2$ with eigenvalue $q$. Use the result of problem 123 to show that $\ell_+ |\ell\rangle$ is also an eigenfunction of $\ell^2$ with the same eigenvalue.

2.128. **Angular Momentum Operators**
What are the results of the following operations?

\[
\ell^2 |3, 2\rangle \\
\ell_z |3, 2\rangle \\
\ell_z |3, -3\rangle \\
\ell_+ |2, 1\rangle
\]
2.129. *Angular Momentum Matrix Elements*
Evaluate the following integrals (expressed in Dirac notation) without M.; that is, don’t use any math at all.

\[
\begin{align*}
\langle 2\ 1 | \ell_z | 2\ 1 \rangle \\
\langle 1\ 0 | \ell^2 | 1\ 0 \rangle \\
\langle 1\ 0 | \ell^2 | 1\ 1 \rangle \\
\langle 2\ 0 | \ell_+ \ell_- | 2\ -\ 2 \rangle \\
\langle 2\ p_x | \ell_z | 2\ p_x \rangle \\
\langle 1\ 1 | \ell_+ | 1\ 1 \rangle
\end{align*}
\]

2.130. *Diatomic Rotor Energy Levels*
For the diatomic rotor, determine the degeneracies in the energy levels as a function of the quantum number, \( \ell \).

2.131. *Review of Rotational Energy Levels*
How does the \( \lambda \) of our rigid rotor problem depend on the quantum number \( \ell \)?

2.132. *Moment of Inertia*
The equation for the angular momentum, equation 6, contains the expression \( \mu b l^2 \), which is the moment of inertia for a diatomic molecule, usually labeled I. What will be the units of I? Find the moment of inertia of CO if the bond length is 1.128Å. HINT: Be careful with units: You don’t want mole or mole\(^{-1} \) in your answer.

2.133. *Rotational Energy Levels*
The solution to the \( \theta \) dependent rigid rotor equation, problem 100, is in terms of \( \lambda \), which is proportional to the energy via the equation:

\[
\lambda = \frac{2IE}{\hbar^2}
\]
where I is the moment of inertia. Show that \( \lambda \) should be unitless.

2.134. *Rotational Energy Levels*
Spectroscopists often express their energy levels in terms of units of wave numbers, or reciprocal cm. This relationship comes from the Einstein relationship

\[
E = h\nu = hc\frac{1}{\lambda} = h\nu'c'
\]
where \( \nu' \) is the energy in reciprocal cm and \( c' \) is the speed of light in cm/sec. Show, using information in the last problem, that you can write

\[
\nu' = \frac{\ell(\ell + 1)h}{8\pi^2Ic'}
\]
HINT: This equation shows up so often in rotational spectra that the set of constants \( h/(8\pi^2Ic') \) is labeled \( \tilde{B} \).
2.135. **Diatomic Rotor Energy Distribution**

If $B$—see the last problem’s HINT—is $17 \text{ cm}^{-1}$ for some substance, find the ratio of the number of particles in level $\ell$ relative to those in the ground level at 300K for $\ell = 1$ to 10. HINTS: $kT$ is $210 \text{ cm}^{-1}$ at 300K; this sounds like a M. Table[...] exercise to me.

2.136. **Bond Distance Determination**

Rotational spectra offer a way to determine bond lengths. The pure rotational spectrum of $^{1}H^{35}Cl$ has lines at 83.2, 104.2, 124.3, 145.1, 165.7, 186.0, 206.2, and 226.3 $\text{ cm}^{-1}$. What is the distance between the H and the Cl? HINT: The hardest part of this problem is the units.

2.137. **Vector Diagram for Angular Momentum States**

Make a vector diagram for the $|3 \ m\rangle$ states. HINT: If you want to get fancy, the M. command Graphics[Arrow[{{0, 0}, {1, 1}}]] draws an arrow from the point {0, 0} to the point {1, 1}.

2.138. **Vector Diagram for Angular Momentum States**

Show on a vector diagram what $\ell_+ |3 \ 1\rangle$ looks like (ignoring constants).

2.139. **Vector Diagram for Angular Momentum States**

Make a “vector picture” of a system in the state $|2 \ 1\rangle$.

2.140. **Vector Diagram for Angular Momentum States**

Make a vector picture of the process $\ell_- |2 \ 1\rangle$.

2.141. **Effect of Raising and Lowering Operators**

Show that $\ell_- |\ell \ m\rangle$ is an eigenfunction of $\ell^2$ with eigenvalue of $\ell(\ell + 1)$ and is an eigenfunction of $\ell_z$ with eigenvalue of $(m - 1)\hbar$.

2.142. **Viewing Rotor (and H Atom) Probability Functions**

Here is the prescription to get M. to plot how the probability of finding a rotor at various $\theta$ and $\phi$ depends on those angles. (And, you will be pleased to find, these are the same answers that we will get for the position of the electron in a hydrogen atom as a function of $\theta$ and $\phi$)

It is useful to define a function so that you don’t have to keep typing SphericalHarmonicY all the time, as follows: Y[l_, m_, theta_, phi_]:= SphericalHarmonicY[l, m, theta, phi]. Then we can define the probability for a Y, say Y_{21}, as P21, which is $(2 \ 1 |2 \ 1\rangle$ by

$$ P_{21} = \text{Conjugate}[Y[2, 1, \theta, \phi]]*Y[2, 1, \theta, \phi] $$

Now you can plot with

SphericalPlot3D[Evaluate[P21], {theta, 0, Pi}, {phi, 0, 3 Pi/2}, Axes -> None, Boxed -> False, ViewPoint -> {1, -3, 2}]

The Axes and Boxed commands just make the picture clearer (at least to me). The ViewPoint command tells M. where you are standing. Note that the range of Phi is only from 0 to $3\pi/2$, which leaves a hole for you to see inside the surface. If you want to avoid this, change that value to $2\pi$. Look at several of the Conjugate[Y]*Y functions so that you are satisfied you know what they look like. Except for your amusement, I wouldn’t go past $\ell$ = 3.
2.143. **Mathematica Review**
What would M. do if you forgot the “Conjugate” in the definition of P21 in the last problem?

2.144. **Review**
If you have a wave function for a system, say $\psi$, how do you find the expectation value of the operator $O$?

2.145. **Rotor (and H Atom) Expectation Values**
Find the expectation value for $\phi$ for the wave function $Y_{11}$.

2.146. **Rotor (and H Atom) Probability Functions**
What is the probability of finding a rigid rotor in the $\ell = 1, m = 1$, state with a $\theta$ value of between 0 and $\pi/18$ and a $\phi$ value of between 0 and $2\pi/36$?

2.147. **Learning Quantum Mechanics**
When you finish a problem like the last one, ask yourself (1) WHERE is the range of $\theta$ between 0 and $\pi/18$ and of $\phi$ between 0 and $2\pi/36$? and (2) DOES that answer make sense to me? Did you?

2.148. **Rotor (and H Atom) Probability Functions**
Do the answers to problems 146 and ??? make sense given your knowledge of what this probability surface “looks like”?

2.149. **Linear Combination of Angular Momentum Eigenfunctions**
What is our rule about any linear combination of degenerate functions?

2.150. **Linear Combination of Angular Momentum Eigenfunctions**
Use our rule about any linear combination of degenerate functions to create a new function from equal amounts of the spherical harmonics $|2\ 2\rangle$ and $|2\ -2\rangle$. Show that this function is the familiar $d_{xy}$ (or perhaps $d_{x^2-y^2}$ depending on your combination) by mathematical manipulation and perhaps plotting in M.

2.151. **Review**
Assume that $\Psi$ is the time dependent wave function for a system, which has a ground state of $\Psi_g$ and an excited state of $\Psi_e$. We can write

$$\Psi = a_g \Psi_g + a_e \Psi_e$$

where the $a_i$ are (time dependent) coefficients, numbers. What is this called?

2.152. **Allowedness**
As we shall learn later in the course, after we have talked about perturbation theory, a transition from a ground state to an excited state under the influence of light can occur, is allowed, only (1) if the energy of the photon, $h\nu$, is equal to the energy difference of the two states, $E_e - E_g$; and (2) if the matrix element $\langle g | \mu | e \rangle \neq 0$. In this matrix element $\mu$ is the dipole moment of the molecule, a vector; and the bra and ket are the symbols for the ground and excited state. Express the three components of this vector, $\mu_x$, $\mu_y$, and $\mu_z$ in terms of the total vector length; use as variables only $\theta$ and $\phi$, our natural variables for spherical coordinates.
2.153. **Allowedness**
From the last problem we learned that a transition is allowed if \( \langle g | \mu_i | e \rangle \neq 0 \) for \( i = x \) or \( y \) or \( z \). [Strictly speaking, the intensity is proportional to the sum of the squares of these three.]

Determine if a transition is allowed from \( Y_{2,1} \) to \( Y_{4,1} \) with any of those dipole projections, or, as the pro would say, polarizations. HINT: I certainly would use \( M \). This and the next four problems are algebraically the same. You could do them with other students.

2.154. **Allowedness**
Is a rigid rotor transition allowed from \( Y_{1,0} \) to \( Y_{4,0} \)?

2.155. **Allowedness**
Is a rigid rotor transition allowed from \( Y_{1,0} \) to \( Y_{2,0} \)?

2.156. **Allowedness**
Is a rigid rotor transition allowed from \( Y_{2,1} \) to \( Y_{3,1} \)?

2.157. **Allowedness**
Is a rigid rotor transition allowed from \( Y_{2,0} \) to \( Y_{3,1} \)? HINT: Pay attention to the "sum of the squares" remark in problem 153.

2.158. **Allowedness**
Can you formulate a rule for allowed transitions in the rigid rotor from your answers to the last several problems? Suggestions are \( \Delta \ell = 2 \), \( \Delta m = 1 \), for instance. HINT: Would I give the right answer?

2.159. **Review**
What are the steps we take to do a separation of variables?

2.160. **Normalization of the \( R(r) \) and \( Y(\theta, \phi) \) Functions**
When we separate variables in the hydrogen atom problem, the separation is usually into a radial dependence, \( R(r) \), and an angular dependence, \( Y(\theta, \phi) \). Recall the integrating factor for spherical coordinates. It would seem logical to separate this such that the radial part had the \( r^2 \) dependence. What does that leave for the integrating factor for the angular part?

2.161. **Radial Wave Functions**
Plot the first four \( \ell = 0 \) radial wave functions such that you see the behavior at small \( r \) as well as to compare them over all significant \( r \) values.

\[
R_{1,0} = -\left( \frac{1}{a_0} \right)^{3/2} 2e^{-r/a_0}
\]
\[
R_{2,0} = \left( \frac{1}{2a_0} \right)^{3/2} 2 \left( 1 - \frac{r}{2a_0} \right) e^{-r/(2a_0)}
\]
\[
R_{3,0} = \frac{1}{27} \left( \frac{1}{3a_0} \right)^{3/2} 2 \left( 27 - 18r/a_0 + 2r^2/a_0^2 \right) e^{-r/(3a_0)}
\]
\[
R_{4,0} = \frac{1}{192} \left( \frac{1}{4a_0} \right)^{3/2} 2 \left( 192 - 144r/a_0 + 24r^2/a_0^2 - r^3/a_0^3 \right) e^{-r/(3a_0)}
\]
2.162. Radial Wave Function Orthogonality
Since the functions in the last problem are solutions to a SE, they must be orthogonal to each other. So, in this context, if I asked you why $R_{2,0}$ “waves”, what would your answer be? HINT: A non-mathematical problem about orthogonality. NOTE: Just as in the analytical solution to the harmonic oscillator, it is a power series that brings about the waviness.

2.163. Radial Wave Function Orthogonality
Show mathematically that $R_{1,0}$ and $R_{2,0}$ are indeed orthogonal.

2.164. Radial Wave Function Normality
Show in at least one case from problem 161 that the normalization constants are correct. Note in passing why these wave functions have the crazy units of inverse three halves power of distance. HINT: Pay attention to the integration factor as discussed in problem 160.

2.165. Expectation Value of $r$
Find the expectation value for $r$ for $R_{2,0}$.

2.166. Radial Wave Function Orthogonality
The form of $R_{n,1}$ wave functions are:

$$R_{2,1} = \frac{1}{\sqrt{3}} \left( \frac{1}{2a_0} \right)^{3/2} r \frac{r}{a_0} e^{-r/(2a_0)}$$
$$R_{3,1} = \frac{8}{54\sqrt{2}} \left( \frac{1}{3a_0} \right)^{3/2} \left( 6 - \frac{r}{a_0} \right) \left( \frac{r}{a_0} \right) e^{-r/(3a_0)}$$
$$R_{4,1} = \frac{\sqrt{5}}{160\sqrt{3}} \left( \frac{1}{4a_0} \right)^{3/2} \left( 80 - 20r/a_0 + r^2/a_0^2 \right) \left( r/a_0 \right) e^{-r/(4a_0)}$$

Show that $R_{2,1}$ is not orthogonal to $R_{1,0}$.

2.167. Radial Wave Function Orthogonality
And because $\langle R_{2,1}|R_{1,0} \rangle \neq 0$, why not? What is going on here?

2.168. Eigenvalue of a Radial Wave Function
Show that $R_{2,0}$ is an eigenfunction of the radial Hamiltonian. SE for the radial part has the form

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \partial / \partial r \left( r^2 \partial / \partial r \right) R_{2,0} - \frac{Z \hbar^2}{ma_0 r} R_{2,0} = ER_{2,0}$$

HINTS: The form of $R_{2,0}$ is in problem 161. For simplicity, let $Z = 1$.

2.169. Expectation Value of $r$ for Radial Wave Functions
Get together with some class mates and find the expectation value of $r$ for the 1s, 2s, 2p, 3s, 3p, and 3d wave functions. Draw comparisons between your values. HINT: The functions you need are in many books, at many sources on the web, and are scattered among the
2.170. **Expectation Value of \( r \) for Radial Wave Functions**

Show that the formula

\[
<r> = a_0 \frac{n^2}{2} \left( 3n^2 - \ell(\ell + 1) \right)
\]

gives the same answers that you got by integration (which, of course, is where it came from).

2.171. **Expectation Value**

Find the expectation value of \( z \) and \( z^2 \) for the hydrogen atom wave function with \( n = 1, \ell = 0, m = 0 \). HINT: Since the wave function is in terms of \( r, \theta \), and \( \phi \), you clearly need to express \( z \) that way.

2.172. **Expectation Value**

Does your result of the last problem make sense?

2.173. **Expectation Value**

Find the expectation value of \( x^2 \) for the hydrogen atom wave function with \( n = 3, \ell = 1, m = 1 \). HINT: Since the wave function is in terms of \( r, \theta \), and \( \phi \), you clearly need to express \( x^2 \) that way.

2.174. **Expectation Value**

Find the expectation value of \( z^2 \) for the hydrogen atom wave function with \( n = 3, \ell = 1, m = 1 \).

2.175. **Expectation Value**

Do the results of the last two problems make sense to you?

2.176. **Radial Wave Function for He**

Find the radial wave function for He\(^+\) and plot it (versus \( r \)) on the same scale as that for H. HINT: You will have to look up how \( a_0 \) depends on \( Z \), the nuclear charge.

2.177. **H Atom Spectrum**

Determine the wavelengths of the light emitted when a hydrogen atom drops from the 3p, 4p, and 5p levels to the 2s level. HINT: The permittivity of free space, \( 4\pi\varepsilon_0 \) is \( 1.126 \times 10^{-10} \) C\(^2\) J\(^{-1}\) m\(^{-1}\).
2.178. *Radial Probability Distributions*
The radial probability distribution is a plot of the probability of finding an electron at a given distance from the nucleus. It is constructed from $R_{n,l}$ squared (as is usual for a probability) but with multiplication by $4\pi r^2$ to account for the increase in the number of little volumes in which to find that probability as $r$ increases. Make radial distribution plots for 1s, 2s, 2p, 3p and 3d radial wave functions.

2.179. *Radial Probability Distributions*
Find the expectation value for the potential energy of an electron in the 2s radial wave function of the hydrogen atom. HINT: Your answer will be easier to interpret if you express $V$ in terms of $a_0$ and compare your result to the total energy.