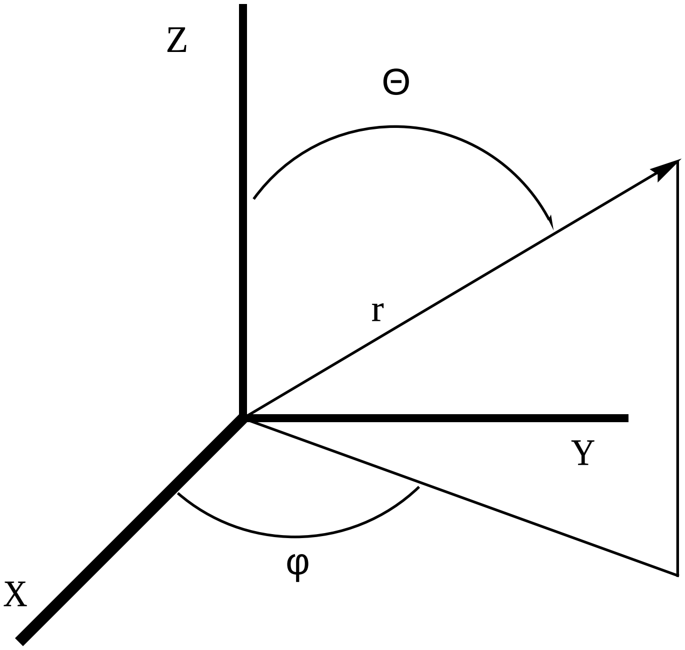
Problems and Solutions

Exercises, Problems, and Solutions

Section 1 Exercises, Problems, and Solutions

Review Exercises

1. Transform (using the coordinate system provided below) the following functions accordingly:



a. from cartesian to spherical polar coordinates
$3x + y - 4z = 12$
b. from cartesian to cylindrical coordinates
$y^2 + z^2 = 9$
c. from spherical polar to cartesian coordinates
$r = 2 \, \mathrm{Sin}\theta \, \mathrm{Cos}\varphi$

2. Perform a separation of variables and indicate the general solution for the following expressions:

a. $9x + 16y\dfrac{\partial y}{\partial x} = 0$

b. $2y + \dfrac{\partial y}{\partial x} + 6 = 0$

3. Find the eigenvalues and corresponding eigenvectors of the following matrices:

a. $\begin{bmatrix} -1 & 2 \\ 2 & 2 \end{bmatrix}$

b. $\begin{bmatrix} -2 & 0 & 0 \\ 0 & -1 & 2 \\ 0 & 2 & 2 \end{bmatrix}$

4. For the hermitian matrix in review exercise 3a show that the eigenfunctions can be normalized and that they are orthogonal.

5. For the hermitian matrix in review exercise 3b show that the pair of degenerate eigenvalues can be made to have orthonormal eigenfunctions.

6. Solve the following second order linear differential equation subject to the specified "boundary conditions":

$$\frac{d^2x}{dt^2} + k^2x(t) = 0 \text{ , where } x(t{=}0) = L, \text{ and } \frac{dx(t{=}0)}{dt} = 0.$$

<u>Exercises</u>

1. Replace the following classical mechanical expressions with their corresponding quantum mechanical operators.

a. K.E. = $\frac{mv^2}{2}$ in three-dimensional space.
b. $\mathbf{p} = m\mathbf{v}$, a three-dimensional cartesian vector.
c. y-component of angular momentum: $L_y = zp_x - xp_z$.

2. Transform the following operators into the specified coordinates:

a. $\mathbf{L}_x = \frac{\hbar}{i}\left\{ y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right\}$ from cartesian to spherical polar coordinates.

b. $\mathbf{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial \varphi}$ from spherical polar to cartesian coordinates.

3. Match the eigenfunctions in column B to their operators in column A. What is the eigenvalue for each eigenfunction?

Column A	Column B
i. $(1-x^2)\frac{d^2}{dx^2} - x\frac{d}{dx}$	$4x^4 - 12x^2 + 3$
ii. $\frac{d^2}{dx^2}$	$5x^4$
iii. $x\frac{d}{dx}$	$e^{3x} + e^{-3x}$
iv. $\frac{d^2}{dx^2} - 2x\frac{d}{dx}$	$x^2 - 4x + 2$
v. $x\frac{d^2}{dx^2} + (1-x)\frac{d}{dx}$	$4x^3 - 3x$

4. Show that the following operators are hermitian.

a. $\mathbf{P}_x$
b. $\mathbf{L}_x$

5. For the following basis of functions ($\Psi_{2p_{-1}}$, Ψ_{2p_0}, and $\Psi_{2p_{+1}}$), construct the matrix representation of the $\mathbf{L}_x$ operator (use the ladder operator representation of $\mathbf{L}_x$). Verify that the matrix is hermitian. Find the eigenvalues and corresponding eigenvectors. Normalize the eigenfunctions and verify that they are orthogonal.

$$\Psi_{2p_{-1}} = \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-zr/2a}\,\text{Sin}\theta\; e^{-i\varphi}$$

$$\Psi_{2p_o} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a}\right)^{5/2} re^{-zr/2a}\,\text{Cos}\theta$$

$$\Psi_{2p_1} = \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-zr/2a}\,\text{Sin}\theta\; e^{i\varphi}$$

6. Using the set of eigenstates (with corresponding eigenvalues) from the preceding problem, determine the probability for observing a z-component of angular momentum equal to $1\hbar$ if the state is given by the $\mathbf{L}_x$ eigenstate with $0\hbar$ $\mathbf{L}_x$ eigenvalue.

7. Use the following definitions of the angular momentum operators:

$$\mathbf{L}_x = \frac{\hbar}{i}\left\{ y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\},\ \mathbf{L}_y = \frac{\hbar}{i}\left\{ z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right\},$$

$$\mathbf{L}_z = \frac{\hbar}{i}\left\{ x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right\},\ \text{and } \mathbf{L}^2 = \mathbf{L}_x^2 + \mathbf{L}_y^2 + \mathbf{L}_z^2,$$

and the relationships:

$$[\mathbf{x},\mathbf{p}_x] = i\hbar,\ [\mathbf{y},\mathbf{p}_y] = i\hbar,\ \text{and } [\mathbf{z},\mathbf{p}_z] = i\hbar,$$

to demonstrate the following operator identities:

a. $[\mathbf{L}_x,\mathbf{L}_y] = i\hbar\ \mathbf{L}_z$,

b. $[\mathbf{L}_y,\mathbf{L}_z] = i\hbar\ \mathbf{L}_x$,

c. $[\mathbf{L}_z,\mathbf{L}_x] = i\hbar\ \mathbf{L}_y$,

d. $[\mathbf{L}_x,\mathbf{L}^2] = 0$,

e. $[\mathbf{L}_y,\mathbf{L}^2] = 0$,

f. $[\mathbf{L}_z,\mathbf{L}^2] = 0$.

8. In exercise 7 above you determined whether or not many of the angular momentum operators commute. Now, examine the operators below along with an appropriate given function. Determine if the given function is simultaneously an eigenfunction of both operators. Is this what you expected?

a. $\mathbf{L}_z$, $\mathbf{L}^2$, with function: $Y_0^0(\theta,\varphi) = \dfrac{1}{\sqrt{4\pi}}$.

b. $\mathbf{L}_x$, $\mathbf{L}_z$, with function: $Y_0^0(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$.

c. $\mathbf{L}_z$, $\mathbf{L}^2$, with function: $Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\ \mathrm{Cos}\theta$.

d. $\mathbf{L}_x$, $\mathbf{L}_z$, with function: $Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\ \mathrm{Cos}\theta$.

9. For a "particle in a box" constrained along two axes, the wavefunction $\Psi(x,y)$ as given in the text was :

$$\Psi(x,y) = \left(\frac{1}{2L_x}\right)^{\frac{1}{2}}\left(\frac{1}{2L_y}\right)^{\frac{1}{2}}\left[e^{\frac{in_x\pi x}{L_x}} - e^{\frac{-in_x\pi x}{L_x}}\right]\left[e^{\frac{in_y\pi y}{L_y}} - e^{\frac{-in_y\pi y}{L_y}}\right],$$

with n_x and n_y = 1,2,3, ... Show that this wavefunction is normalized.

10. Using the same wavefunction, $\Psi(x,y)$, given in exercise 9 show that the expectation value of $\mathbf{p}_x$ vanishes.

11. Calculate the expectation value of the $\mathbf{x}^2$ operator for the first two states of the harmonic oscillator. Use the v=0 and v=1 harmonic oscillator wavefunctions given below which are normalized such that $\int_{-\infty}^{+\infty}\Psi(x)^2dx = 1$. Remember that $\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$ and $\Psi_1 = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$.

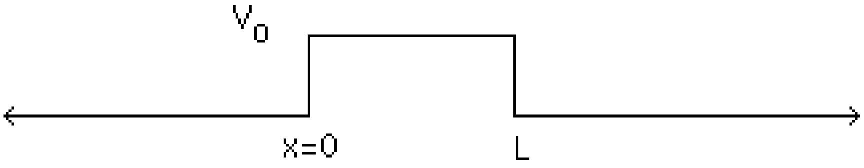
12. For each of the one-dimensional potential energy graphs shown below, determine:

a. whether you expect symmetry to lead to a separation into odd and even solutions,

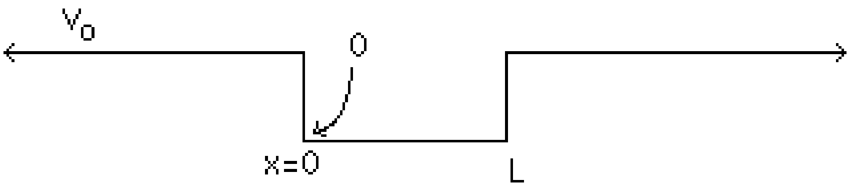
b. whether you expect the energy will be quantized, continuous, or both, and

c. the boundary conditions that apply at each boundary (merely stating that Ψ and/or $\frac{\partial\Psi}{\partial x}$ is continuous is all that is necessary).

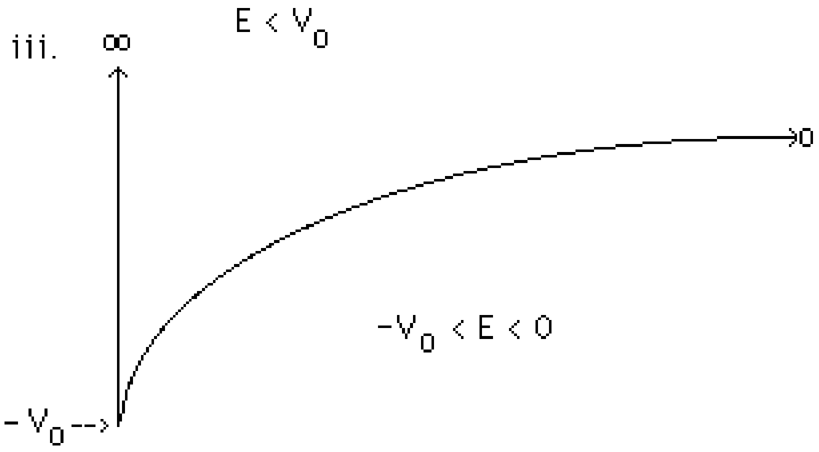
i.



ii.



iii.



13. Consider a particle of mass m moving in the potential:

$V(x) = \infty$	for	$x < 0$	Region I
$V(x) = 0$	for	$0 \le x \le L$	Region II
$V(x) = V (V > 0)$	for	$x > L$	Region III

a. Write the general solution to the Schrödinger equation for the regions I, II, III, assuming a solution with energy $E < V$ (i.e. a bound state).

b. Write down the wavefunction matching conditions at the interface between regions I and II and between II and III.

c. Write down the boundary conditions on Ψ for $x \to \pm\infty$.

d. Use your answers to a. - c. to obtain an algebraic equation which must be satisfied for the bound state energies, E.

e. Demonstrate that in the limit V → ∞, the equation you obtained for the bound state energies in d. gives the energies of a particle in an infinite box; $E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}$; $n = 1,2,3,\ldots$

Problems

1. A particle of mass m moves in a one-dimensional box of length L, with boundaries at x = 0 and x = L. Thus, $V(x) = 0$ for $0 \le x \le L$, and $V(x) = \infty$ elsewhere. The normalized eigenfunctions of the Hamiltonian for this system are given by $\Psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \mathrm{Sin}\frac{n\pi x}{L}$, with $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$, where the quantum number n can take on the values n=1,2,3,....

a. Assuming that the particle is in an eigenstate, $\Psi_n(x)$, calculate the probability that the particle is found somewhere in the region $0 \le x \le \frac{L}{4}$. Show how this probability depends on n.

b. For what value of n is there the largest probability of finding the particle in $0 \le x \le \frac{L}{4}$?

c. Now assume that Ψ is a superposition of two eigenstates, $\Psi = a\Psi_n + b\Psi_m$, at time t = 0. What is Ψ at time t? What energy expectation value does Ψ have at time t and how does this relate to its value at t = 0?

d. For an experimental measurement which is capable of distinguishing systems in state Ψ_n from those in Ψ_m, what fraction of a large number of systems each described by Ψ will be observed to be in Ψ_n? What energies will these experimental measurements find and with what probabilities?

e. For those systems originally in $\Psi = a\Psi_n + b\Psi_m$ which were observed to be in Ψ_n at time t, what state (Ψ_n, Ψ_m, or whatever) will they be found in if a second experimental measurement is made at a time t' later than t?

f. Suppose by some method (which need not concern us at this time) the system has been prepared in a nonstationary state (that is, it is not an eigenfunction of **H**). At the time of a measurement of the particle's energy, this state is specified by the normalized wavefunction $\Psi = \left(\frac{30}{L^5}\right)^{1/2} x(L-x)$ for $0 \le x \le L$, and $\Psi = 0$ elsewhere. What is the probability that a measurement of the energy of the particle will give the value $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$ for any given value of n?

g. What is the expectation value of **H**, i.e. the average energy of the system, for the wavefunction Ψ given in part f?

2. Show that for a system in a non-stationary state,

$\Psi = \sum_j C_j \Psi_j e^{-iE_j t/\hbar}$, the average value of the energy does not vary with time but the expectation values of other properties do vary with time.

3. A particle is confined to a one-dimensional box of length L having infinitely high walls and is in its lowest quantum state. Calculate: $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$, and $\langle p^2\rangle$. Using the definition $\Delta A = (\langle A^2\rangle - \langle A\rangle^2)^{1/2}$, to define the uncertainty , ΔA, calculate Δx and Δp. Verify the Heisenberg uncertainty principle that $\Delta x \Delta p \geq \hbar/2$.

4. It has been claimed that as the quantum number n increases, the motion of a particle in a box becomes more classical. In this problem you will have an oportunity to convince yourself of this fact.

a. For a particle of mass m moving in a one-dimensional box of length L, with ends of the box located at x = 0 and x = L, the classical probability density can be shown to be independent of x and given by $P(x)dx = \frac{dx}{L}$ regardless of the energy of the particle. Using this probability density, evaluate the probability that the particle will be found within the interval from x = 0 to $x = \frac{L}{4}$.

b. Now consider the quantum mechanical particle-in-a-box system. Evaluate the probability of finding the particle in the interval from x = 0 to $x = \frac{L}{4}$ for the system in its nth quantum state.

c. Take the limit of the result you obtained in part b as $n \rightarrow \infty$. How does your result compare to the classical result you obtained in part a?

5. According to the rules of quantum mechanics as we have developed them, if Ψ is the state function, and φ_n are the eigenfunctions of a linear, Hermitian operator, **A**, with eigenvalues a_n, $\mathbf{A}\varphi_n = a_n\varphi_n$, then we can expand Ψ in terms of the complete set of eigenfunctions of **A** according to $\Psi = \sum_n c_n\varphi_n$, where $c_n = \int \varphi_n^*\Psi \, d\tau$. Furthermore, the probability of making a measurement of the property corresponding to **A** and obtaining a value a_n is given by $|c_n|^2$, provided both Ψ and φ_n are properly normalized. Thus, $P(a_n) = |c_n|^2$. These rules are perfectly valid for operators which take on a discrete set of eigenvalues, but must be generalized for operators which can have a continuum of eigenvalues. An example of this latter type of operator is the momentum operator, $\mathbf{p}_x$, which has eigenfunctions given by $\varphi_p(x) = Ae^{ipx/\hbar}$ where p is the eigenvalue of the $\mathbf{p}_x$ operator and A is a normalization constant. Here p can take on any value, so we have a continuous spectrum of eigenvalues of $\mathbf{p}_x$. The obvious generalization to the equation for Ψ is to convert the sum over discrete states to an integral over the continuous spectrum of states:

$$\Psi(x) = \int_{-\infty}^{+\infty} C(p)\varphi_p(x)dp = \int_{-\infty}^{+\infty} C(p)Ae^{ipx/\hbar}dp$$

The interpretation of C(p) is now the desired generalization of the equation for the probability P(p)dp = úC(p)ú^{2}dp. This equation states that the probability of measuring the momentum and finding it in the range from p to p+dp is given by úC(p)ú^{2}dp. Accordingly, the probability of measuring p and finding it in the range from p_1 to p_2 is given by $\int_{p_1}^{p_2} P(p)dp = \int_{p_1}^{p_2} C(p)^*C(p)dp$. C(p) is thus the probability amplitude for finding the particle with momentum between p and p+dp. This is the <u>momentum representation</u> of the wavefunction. Clearly we must require C(p) to be normalized, so that $\int_{-\infty}^{+\infty} C(p)^*C(p)dp = 1$.

With this restriction we can derive the normalization constant A = $\frac{1}{\sqrt{2\pi\hbar}}$, giving a direct relationship between the wavefunction in coordinate space, Ψ(x), and the wavefunction in momentum space, C(p):

$$\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} C(p)e^{ipx/\hbar}dp \ ,$$

and by the fourier integral theorem:

$$C(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x)e^{ipx/\hbar}dx \ .$$

Lets use these ideas to solve some problems focusing our attention on the harmonic oscillator; a particle of mass m moving in a one-dimensional potential described by V(x) = $\frac{kx^2}{2}$.

a. Write down the Schrödinger equation in the coordinate representation.

b. Now lets proceed by attempting to write the Schrödinger equation in the momentum representation. Identifying the kinetic energy operator **T**, in the momentum representation is quite straightforward $\mathbf{T} = \frac{\mathbf{p}^2}{2m}$ = -
Error!. Writing the potential, V(x), in the momentum representation is not quite as straightforward. The relationship between position and momentum is realized in their commutation relation $[\mathbf{x},\mathbf{p}] = i\hbar$, or $(\mathbf{xp} - \mathbf{px}) = i\hbar$
This commutation relation is easily verified in the coordinate representation leaving **x** untouched (**x** = x·) and using the above definition for **p**. In the momentum representation we want to leave **p** untouched (**p** = p·) and define the operator **x** in such a manner that the commutation relation is still satisfied. Write the operator **x** in the momentum representation. Write the full Hamiltonian in the momentum representation and hence the Schrödinger equation in the momentum representation.

c. Verify that Ψ as given below is an eigenfunction of the Hamiltonian in the coordinate representation. What is the energy of the system when it is in this state?

Determine the normalization constant C, and write down the normalized ground state wavefunction in coordinate space.

$$\Psi(x) = C \exp\left(-\sqrt{mk}\,\frac{x^2}{2\hbar}\right).$$

d. Now consider Ψ in the momentum representation. Assuming that an eigenfunction of the Hamiltonian may be found of the form $\Psi(p) = C \exp(-\alpha p^2)$, substitute this form of Ψ into the Schrödinger equation in the momentum representation to find the value of α which makes this an eigenfunction of **H** having the same energy as $\Psi(x)$ had. Show that this $\Psi(p)$ is the proper fourier transform of $\Psi(x)$. The following integral may be useful:

$$\int_{-\infty}^{+\infty} e^{-\beta x^2}\mathrm{Cos}\,bx\,dx = \sqrt{\frac{\pi}{\beta}}\; e^{-b^2/4\beta}.$$

Since this Hamiltonian has no degenerate states, you may conclude that $\Psi(x)$ and $\Psi(p)$ represent the same state of the system if they have the same energy.

6. The energy states and wavefunctions for a particle in a 3-dimensional box whose lengths are L_1, L_2, and L_3 are given by

$$E(n_1,n_2,n_3) = \frac{h^2}{8m}\left[\left(\frac{n_1}{L_1}\right)^2 + \left(\frac{n_2}{L_2}\right)^2 + \left(\frac{n_3}{L_3}\right)^2\right] \text{ and}$$

$$\Psi(n_1,n_2,n_3) = \left(\frac{2}{L_1}\right)^{\frac{1}{2}}\left(\frac{2}{L_2}\right)^{\frac{1}{2}}\left(\frac{2}{L_3}\right)^{\frac{1}{2}}\ \mathrm{Sin}\left(\frac{n_1\pi x}{L_1}\right)\mathrm{Sin}\left(\frac{n_2\pi y}{L_2}\right)\mathrm{Sin}\left(\frac{n_3\pi z}{L_3}\right).$$

These wavefunctions and energy levels are sometimes used to model the motion of electrons in a central metal atom (or ion) which is surrounded by six ligands.

a. Show that the lowest energy level is nondegenerate and the second energy level is triply degenerate if $L_1 = L_2 = L_3$. What values of n_1, n_2, and n_3 characterize the states belonging to the triply degenerate level?

b. For a box of volume $V = L_1L_2L_3$, show that for three electrons in the box (two in the nondegenerate lowest "orbital", and one in the next), a lower total energy will result if the box undergoes a rectangular distortion ($L_1 = L_2 \neq L_3$). which preserves the total volume than if the box remains undistorted (hint: if V is fixed and $L_1 = L_2$, then $L_3 = \frac{V}{L_1^2}$ and L_1 is the only "variable").

c. Show that the degree of distortion (ratio of L_3 to L_1) which will minimize the total energy is $L_3 = \sqrt{2}\,L_1$. How does this problem relate to Jahn-Teller distortions? Why (in terms of the property of the central atom or ion) do we do the calculation with fixed volume?

d. By how much (in eV) will distortion lower the energy (from its value for a cube, $L_1 = L_2 = L_3$) if $V = 8$ Å^3 and $\frac{h^2}{8m} = 6.01 \times 10^{-27}$ erg cm^2. 1 eV = 1.6×10^{-12} erg

7. The wavefunction $\Psi = Ae^{-a|x|}$ is an exact eigenfunction of some one-dimensional Schrödinger equation in which x varies from $-\infty$ to $+\infty$. The value of a is: $a = (2\text{Å})^{-1}$. For

now, the potential V(x) in the Hamiltonian ($\mathbf{H} = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + V(x)$) for which $\Psi(x)$ is an eigenfunction is unknown.

a. Find a value of A which makes $\Psi(x)$ normalized. Is this value unique? What units does $\Psi(x)$ have?

b. Sketch the wavefunction for positive and negative values of x, being careful to show the behavior of its slope near x = 0. Recall that |x| is defined as:

$$|x| = \begin{matrix} x \text{ if } x > 0 \\ -x \text{ if } x < 0 \end{matrix}$$

c. Show that the derivative of $\Psi(x)$ undergoes a discontinuity of magnitude $2(a)^{3/2}$ as x goes through x = 0. What does this fact tell you about the potential V(x)?

d. Calculate the expectation value of |x| for the above normalized wavefunction (obtain a numerical value and give its units). What does this expectation value give a measure of?

e. The potential V(x) appearing in the Schrödinger equation for which $\Psi = Ae^{-a|x|}$ is an exact solution is given by $V(x) = \frac{\hbar^2 a}{m}\delta(x)$. Using this potential, compute the expectation value of the Hamiltonian ($\mathbf{H} = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + V(x)$) for your normalized wavefunction. Is V(x) an attractive or repulsive potential? Does your wavefunction correspond to a bound state? Is <H> negative or positive? What does the sign of <H> tell you? To obtain a numerical value for <H> use $\frac{\hbar^2}{2m} = 6.06 \times 10^{-28}$ erg cm^2 and 1eV = 1.6 x 10^{-12} erg.

f. Transform the wavefunction, $\Psi = Ae^{-a|x|}$, from coordinate space to momentum space.

g. What is the ratio of the probability of observing a momentum equal to $2a\hbar$ to the probability of observing a momentum equal to $-a\hbar$?

8. The π-orbitals of benzene, C_6H_6, may be modeled very crudely using the wavefunctions and energies of a particle on a ring. Lets first treat the particle on a ring problem and then extend it to the benzene system.

a. Suppose that a particle of mass m is constrained to move on a circle (of radius r) in the xy plane. Further assume that the particle's potential energy is constant (zero is a good choice). Write down the Schrödinger equation in the normal cartesian coordinate representation. Transform this Schrödinger equation to cylindrical coordinates where $x = r\cos\varphi$, $y = r\sin\varphi$, and z = z (z = 0 in this case).

Taking r to be held constant, write down the general solution, $\Phi(\varphi)$, to this Schrödinger equation. The "boundary" conditions for this problem require that $\Phi(\varphi) = \Phi(\varphi + 2\pi)$. Apply this boundary condition to the general solution. This results in the quantization of the energy levels of this system. Write down the final expression for the normalized wavefunction and quantized energies. What is the physical significance of these quantum numbers which can have both positive and negative values? Draw an energy diagram representing the first five energy levels.

b. Treat the six π-electrons of benzene as particles free to move on a ring of radius 1.40 Å, and calculate the energy of the lowest electronic transition. Make sure the Pauli principle is satisfied! What wavelength does this transition correspond to? Suggest some reasons why this differs from the wavelength of the lowest observed transition in benzene, which is 2600 Å.

9. A diatomic molecule constrained to rotate on a flat surface can be modeled as a planar rigid rotor (with eigenfunctions, $\Phi(\varphi)$, analogous to those of the particle on a ring) with fixed bond length r. At t = 0, the rotational (orientational) probability distribution is observed to be described by a wavefunction $\Psi(\varphi,0) = \sqrt{\frac{4}{3\pi}}\,\mathrm{Cos}^2\varphi$. What values, and with what probabilities, of the rotational angular momentum, $\left(-i\hbar\frac{\partial}{\partial\varphi}\right)$, could be observed in this system? Explain whether these probabilities would be time dependent as $\Psi(\varphi,0)$ evolves into $\Psi(\varphi,t)$.

10. A particle of mass m moves in a potential given by

$V(x,y,z) = \frac{k}{2}(x^2 + y^2 + z^2) = \frac{kr^2}{2}$.

a. Write down the time-independent Schrödinger equation for this system.

b. Make the substitution $\Psi(x,y,z) = X(x)Y(y)Z(z)$ and separate the variables for this system.

c. What are the solutions to the resulting equations for X(x), Y(y), and Z(z)?

d. What is the general expression for the quantized energy levels of this system, in terms of the quantum numbers n_x, n_y, and n_z, which correspond to X(x), Y(y), and Z(z)?

e. What is the degree of degeneracy of a state of energy $E = 5.5\hbar\sqrt{\frac{k}{m}}$ for this system?

f. An alternative solution may be found by making the substitution $\Psi(r,\theta,\varphi) = F(r)G(\theta,\varphi)$. In this substitution, what are the solutions for $G(\theta,\varphi)$?

g. Write down the differential equation for F(r) which is obtained when the substitution $\Psi(r,\theta,\varphi) = F(r)G(\theta,\varphi)$ is made. Do not solve this equation.

11. Consider an N_2 molecule, in the ground vibrational level of the ground electronic state, which is bombarded by 100 eV electrons. This leads to ionization of the N_2 molecule to form N_2^+. In this problem we will attempt to calculate the vibrational distribution of the newly-formed N_2^+ ions, using a somewhat simplified approach.

a. Calculate (according to classical mechanics) the velocity (in cm/sec) of a 100 eV electron, ignoring any relativistic effects. Also calculate the amount of time required for a 100 eV electron to pass an N_2 molecule, which you may estimate as having a length of 2Å.

b. The radial Schrödinger equation for a diatomic molecule treating vibration as a harmonic oscillator can be written as:

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)\right) + \frac{k}{2}(r - r_e)^2\Psi = E\,\Psi ,$$

Substituting $\Psi(r) = \frac{F(r)}{r}$, this equation can be rewritten as:

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}F(r) + \frac{k}{2}(r - r_e)^2F(r) = E\,F(r) .$$

The vibrational Hamiltonian for the ground electronic state of the N_2 molecule within this approximation is given by:

$$\mathbf{H}(N_2) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{k_{N_2}}{2}(r - r_{N_2})^2 ,$$

where r_{N_2} and k_{N_2} have been measured experimentally to be:

$$r_{N_2} = 1.09769\ \text{Å};\ k_{N_2} = 2.294 \times 10^6\,\frac{g}{sec^2} .$$

The vibrational Hamiltonian for the N_2^+ ion , however, is given by :

$$\mathbf{H}(N_2) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{k_{N_2^+}}{2}(r - r_{N_2^+})^2 ,$$

where $r_{N_2^+}$ and $k_{N_2^+}$ have been measured experimentally to be:

$$r_{N_2^+} = 1.11642\ \text{Å};\ k_{N_2^+} = 2.009 \times 10^6\,\frac{g}{sec^2} .$$

In both systems the reduced mass is $\mu = 1.1624 \times 10^{-23}$ g. Use the above information to write out the ground state vibrational wavefunctions of the N_2 and N_2^+ molecules, giving explicit values for any constants which appear in them. Note: For this problem use the "normal" expression for the ground state wavefunction of a harmonic oscillator. You need not solve the differential equation for this system.

c. During the time scale of the ionization event (which you calculated in part a), the vibrational wavefunction of the N_2 molecule has effectively no time to change. As a result, the newly-formed N_2^+ ion finds itself in a vibrational state which is not an eigenfunction of the new vibrational Hamiltonian, $\mathbf{H}(N_2^+)$. Assuming that the N_2 molecule was originally in its v=0 vibrational state, calculate the probability that the N_2^+ ion will be produced in its v=0 vibrational state.

12. The force constant, k, of the C-O bond in carbon monoxide is 1.87×10^6 g/sec^2. Assume that the vibrational motion of CO is purely harmonic and use the reduced mass μ = 6.857 amu.

a. Calculate the spacing between vibrational energy levels in this molecule, in units of ergs and cm^{-1}.

b. Calculate the uncertainty in the internuclear distance in this molecule, assuming it is in its ground vibrational level. Use the ground state vibrational wavefunction ($\Psi_{v=0}$), and calculate $\langle x\rangle$, $\langle x^2\rangle$, and $\Delta x = (\langle x^2\rangle - \langle x\rangle^2)^{1/2}$.

c. Under what circumstances (i.e. large or small values of k; large or small values of μ) is the uncertainty in internuclear distance large? Can you think of any relationship between this observation and the fact that helium remains a liquid down to absolute zero?

13. Suppose you are given a trial wavefunction of the form:

$$\varphi = \frac{Z_e^3}{\pi a_0^3} \exp\left(\frac{-Z_e r_1}{a_0}\right) \exp\left(\frac{-Z_e r_2}{a_0}\right)$$

to represent the electronic structure of a two-electron ion of nuclear charge Z and suppose that you were also lucky enough to be <u>given</u> the variational integral, W, (instead of asking you to derive it!):

$$W = \left(Z_e^2 - 2ZZ_e + \frac{5}{8} Z_e\right)\frac{e^2}{a_0} .$$

a. Find the optimum value of the variational parameter Z_e for an arbitrary nuclear charge Z by setting $\frac{dW}{dZ_e} = 0$. Find both the optimal value of Z_e and the resulting value of W.

b. The total energies of some two-electron atoms and ions have been experimentally determined to be:

Z = 1	H^-	-14.35 eV
Z = 2	He	-78.98 eV
Z = 3	Li^+	-198.02 eV
Z = 4	Be^{+2}	-371.5 eV
Z = 5	B^{+3}	-599.3 eV
Z = 6	C^{+4}	-881.6 eV
Z = 7	N^{+5}	-1218.3 eV
Z = 8	O^{+6}	-1609.5 eV

Using your optimized expression for W, calculate the estimated total energy of each of these atoms and ions. Also calculate the percent error in your estimate for each ion. What physical reason explains the decrease in percentage error as Z increases?

c. In 1928, when quantum mechanics was quite young, it was not known whether the isolated, gas-phase hydride ion, H^-, was stable with respect to dissociation into a hydrogen atom and an electron. Compare your estimated total energy for H^- to the ground state energy of a hydrogen atom and an isolated electron (system energy = -13.60 eV), and show that this simple variational calculation erroneously predicts H^- to be unstable. (More complicated variational treatments give a ground state energy of H^- of -14.35 eV, in agreement with experiment.)

14. A particle of mass m moves in a one-dimensional potential given by $\mathbf{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + a|x|$, where the absolute value function is defined by $|x| = x$ if $x \geq 0$ and $|x| = -x$ if $x \leq 0$.

a. Use the normalized trial wavefunction $\varphi = \left(\frac{2b}{\pi}\right)^{\frac{1}{4}} e^{-bx^2}$ to estimate the energy of the ground state of this system, using the variational principle to evaluate W(b).

b. Optimize b to obtain the best approximation to the ground state energy of this system, using a trial function of the form of φ, as given above. The numerically calculated exact ground state energy is $0.808616\ \hbar^{\frac{2}{3}}\ m^{-\frac{1}{3}}\ a^{-\frac{2}{3}}$. What is the percent error in your value?

15. The harmonic oscillator is specified by the Hamiltonian:

$$\mathbf{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2.$$

Suppose the ground state solution to this problem were unknown, and that you wish to approximate it using the variational theorem. Choose as your trial wavefunction,

$$\varphi = \sqrt{\frac{15}{16}}\ a^{-\frac{5}{2}}(a^2 - x^2) \quad \text{for } -a < x < a$$

$$\varphi = 0 \qquad\qquad \text{for } |x| \geq a$$

where a is an arbitrary parameter which specifies the range of the wavefunction. Note that φ is properly normalized as given.

a. Calculate $\int_{-\infty}^{+\infty} \varphi^*\mathbf{H}\varphi dx$ and show it to be given by:

$$\int_{-\infty}^{+\infty} \varphi^*\mathbf{H}\varphi dx = \frac{5}{4}\frac{\hbar^2}{ma^2} + \frac{ka^2}{14}.$$

b. Calculate $\int_{-\infty}^{+\infty} \varphi^*\mathbf{H}\varphi dx$ for $a = b\left(\frac{\hbar^2}{km}\right)^{\frac{1}{4}}$ with b = 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0, and plot the result.

c. To find the best approximation to the true wavefunction and its energy, find the minimum of $\int_{-\infty}^{+\infty} \varphi^*\mathbf{H}\varphi dx$ by setting $\frac{d}{da}\int_{-\infty}^{+\infty} \varphi^*\mathbf{H}\varphi dx = 0$ and solving for a. Substitute this value into the expression for $\int_{-\infty}^{+\infty} \varphi^*\mathbf{H}\varphi dx$ given in part a. to obtain the best approximation for the energy of the ground state of the harmonic oscillator.

d. What is the percent error in your calculated energy of part c. ?

16. Einstein told us that the (relativistic) expression for the energy of a particle having rest mass m and momentum p is $E^2 = m^2c^4 + p^2c^2$.

a. Derive an expression for the relativistic kinetic energy operator which contains terms correct through one higher order than the "ordinary" $E = mc^2 + \frac{p^2}{2m}$

b. Using the first order correction as a perturbation, compute the first-order perturbation theory estimate of the energy for the 1s level of a hydrogen-like atom (general Z). Show the Z dependence of the result.

$$\text{Note: } \Psi(r)_{1s} = \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(\frac{1}{\pi}\right)^{\frac{1}{2}} e^{-\frac{Zr}{a}} \text{ and } E_{1s} = -\frac{Z^2me^4}{2\hbar^2}$$

c. For what value of Z does this first-order relativistic correction amount to 10% of the unperturbed (non-relativistic) 1s energy?

17. Consider an electron constrained to move on the surface of a sphere of radius r. The Hamiltonian for such motion consists of a kinetic energy term only $\mathbf{H}_0 = \frac{\mathbf{L}^2}{2m_er_0^2}$, where $\mathbf{L}$ is the orbital angular momentum operator involving derivatives with respect to the spherical polar coordinates (θ,φ). $\mathbf{H}_0$ has the complete set of eigenfunctions $\psi^{(0)}_{lm} = Y_{l,m}(\theta,\varphi)$.

a. Compute the zeroth order energy levels of this system.

b. A uniform electric field is applied along the z-axis, introducing a perturbation $V = -e\varepsilon z = -e\varepsilon r_0\text{Cos}\theta$, where ε is the strength of the field. Evaluate the correction to the energy of the lowest level through second order in perturbation theory, using the identity

$$\text{Cos}\theta\, Y_{l,m}(\theta,\varphi) = \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}}\, Y_{l+1,m}(\theta,\varphi) + \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}}\, Y_{l-1,m}(\theta,\varphi) .$$

Note that this identity enables you to utilize the orthonormality of the spherical harmonics.

c. The electric polarizability α gives the response of a molecule to an externally applied electric field, and is defined by $\alpha = -\left.\frac{\partial^2E}{\partial^2\varepsilon}\right|_{\varepsilon=0}$ where E is the energy in the presence of the field and ε is the strength of the field. Calculate α for this system.

d. Use this problem as a model to estimate the polarizability of a hydrogen atom, where $r_0 = a_0 = 0.529$ Å, and a cesium atom, which has a single 6s electron with $r_0 \approx 2.60$ Å. The corresponding experimental values are $\alpha_H = 0.6668$ Å^3 and $\alpha_{Cs} = 59.6$ Å^3.

18. An electron moving in a conjugated bond framework can be viewed as a particle in a box. An externally applied electric field of strength ε interacts with the electron in a fashion described by the perturbation $V = e\varepsilon\left(x - \frac{L}{2}\right)$, where x is the position of the electron in the box, e is the electron's charge, and L is the length of the box.

a. Compute the first order correction to the energy of the n=1 state and the first order wavefunction for the n=1 state. In the wavefunction calculation, you need only compute the contribution to $\Psi^{(1)}_1$ made by $\Psi^{(0)}_2$. Make a rough (no calculation needed) sketch of $\Psi^{(0)}_1 + \Psi^{(1)}_1$ as a function of x and physically interpret the graph.

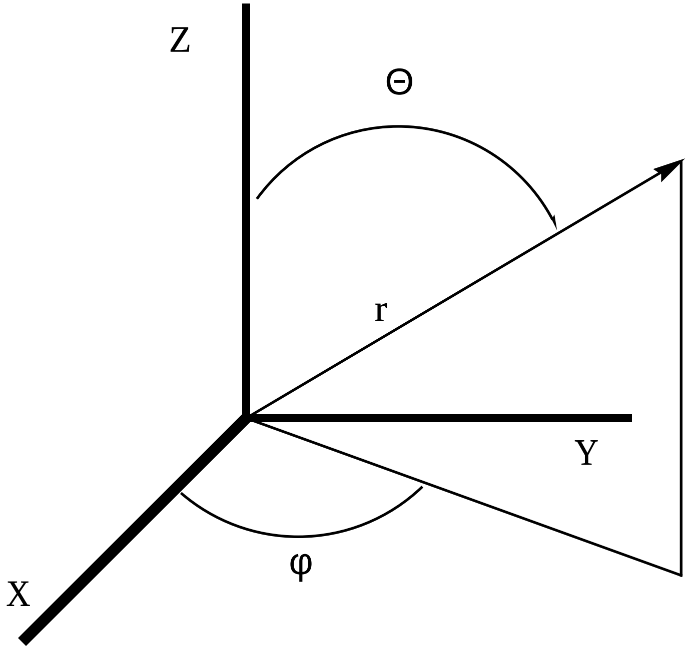
b. Using your answer to part a. compute the induced dipole moment caused by the polarization of the electron density due to the electric field effect $\mu_{\text{induced}} = -e\int \Psi^*\left(x - \frac{L}{2}\right)\Psi dx$. You may neglect the term proportional to ε^2 ; merely obtain the term linear in ε.

c. Compute the polarizability, α, of the electron in the n=1 state of the box, and explain physically why α should depend as it does upon the length of the box L. Remember that $\alpha = \left.\frac{\partial \mu}{\partial \varepsilon}\right|_{\varepsilon=0}$.

Solutions

Review Exercises

1. The general relationships are as follows:



$$x = r \, \mathrm{Sin}\theta \, \mathrm{Cos}\varphi \qquad r^2 = x^2 + y^2 + z^2$$

$$y = r \, \mathrm{Sin}\theta \, \mathrm{Sin}\varphi \qquad \mathrm{Sin}\theta = \frac{\sqrt{x^2 + y^2}}{\sqrt{x^2 + y^2 + z^2}}$$

$$z = r \, \mathrm{Cos}\theta \qquad \mathrm{Cos}\theta = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$\mathrm{Tan}\varphi = \frac{y}{x}$$

a. $3x + y - 4z = 12$

$3(r\mathrm{Sin}\theta\mathrm{Cos}\varphi) + r\mathrm{Sin}\theta\mathrm{Sin}\varphi - 4(r\mathrm{Cos}\theta) = 12$

$r(3\mathrm{Sin}\theta\mathrm{Cos}\varphi + \mathrm{Sin}\theta\mathrm{Sin}\varphi - 4\mathrm{Cos}\theta) = 12$

b. $x = r\mathrm{Cos}\varphi \qquad r^2 = x^2 + y^2$

$y = r\mathrm{Sin}\varphi \qquad \mathrm{Tan}\varphi = \frac{y}{x}$

$z = z$

$y^2 + z^2 = 9$

$r^2 \mathrm{Sin}^2\varphi + z^2 = 9$

c. $r = 2\mathrm{Sin}\theta\mathrm{Cos}\varphi$

$r = 2\left(\frac{x}{r}\right)$

$r^2 = 2x$

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

$x^2 - 2x + y^2 + z^2 = 0$

$x^2 - 2x + 1 + y^2 + z^2 = 1$

$(x - 1)^2 + y^2 + z^2 = 1$

2. a. $9x + 16y\frac{\partial y}{\partial x} = 0$

$16ydy = -9xdx$

$\frac{16}{2} y^2 = -\frac{9}{2} x^2 + c$

$16y^2 = -9x^2 + c'$

$\frac{y^2}{9} + \frac{x^2}{16} = c''$ (general equation for an ellipse)

b. $2y + \frac{\partial y}{\partial x} + 6 = 0$

$2y + 6 = -\frac{dy}{dx}$

$y + 3 = -\frac{dy}{2dx}$

$-2dx = \frac{dy}{y + 3}$

$-2x = \ln(y + 3) + c$

$c'e^{-2x} = y + 3$

$y = c'e^{-2x} - 3$

3. a. First determine the eigenvalues:

$$\det\begin{bmatrix} -1 - \lambda & 2 \\ 2 & 2 - \lambda \end{bmatrix} = 0$$

$(-1 - \lambda)(2 - \lambda) - 2^2 = 0$

$-2 + \lambda - 2\lambda + \lambda^2 - 4 = 0$

$\lambda^2 - \lambda - 6 = 0$

$(\lambda - 3)(\lambda + 2) = 0$

$\lambda = 3$ or $\lambda = -2$.

Next, determine the eigenvectors. First, the eigenvector associated with eigenvalue -2:

$$\begin{bmatrix} -1 & 2 \\ 2 & 2 \end{bmatrix}\begin{bmatrix} C_{11} \\ C_{21} \end{bmatrix} = -2\begin{bmatrix} C_{11} \\ C_{21} \end{bmatrix}$$

$-C_{11} + 2C_{21} = -2C_{11}$

$C_{11} = -2C_{21}$ (Note: The second row offers no new information, e.g. $2C_{11} + 2C_{21} = -2C_{21}$)

$C_{11}^2 + C_{21}^2 = 1$ (from normalization)

$(-2C_{21})^2 + C_{21}^2 = 1$

$4C_{21}^2 + C_{21}^2 = 1$

$5C_{21}^2 = 1$

$C_{21}^2 = 0.2$

$C_{21} = \sqrt{0.2}$, and therefore $C_{11} = -2\sqrt{0.2}$.

For the eigenvector associated with eigenvalue 3:

$$\begin{bmatrix} -1 & 2 \\ 2 & 2 \end{bmatrix} \begin{bmatrix} C_{12} \\ C_{22} \end{bmatrix} = 3 \begin{bmatrix} C_{12} \\ C_{22} \end{bmatrix}$$

$-C_{12} + 2C_{22} = 3C_{12}$

$-4C_{12} = -2C_{22}$

$C_{12} = 0.5C_{22}$ (again the second row offers no new information)

$C_{12}^2 + C_{22}^2 = 1$ (from normalization)

$(0.5C_{22})^2 + C_{22}^2 = 1$

$0.25C_{22}^2 + C_{22}^2 = 1$

$1.25C_{22}^2 = 1$

$C_{22}^2 = 0.8$

$C_{22} = \sqrt{0.8} = 2\sqrt{0.2}$, and therefore $C_{12} = \sqrt{0.2}$.

Therefore the eigenvector matrix becomes:

$$\begin{bmatrix} -2\sqrt{0.2} & \sqrt{0.2} \\ \sqrt{0.2} & 2\sqrt{0.2} \end{bmatrix}$$

b. First determine the eigenvalues:

$$\det \begin{bmatrix} -2 - \lambda & 0 & 0 \\ 0 & -1 - \lambda & 2 \\ 0 & 2 & 2 - \lambda \end{bmatrix} = 0$$

$$\det [-2 - \lambda] \ \det \begin{bmatrix} -1 - \lambda & 2 \\ 2 & 2 - \lambda \end{bmatrix} = 0$$

From 3a, the solutions then become -2, -2, and 3. Next, determine the eigenvectors. First the eigenvector associated with eigenvalue 3 (the third root):

$$\begin{bmatrix} -2 & 0 & 0 \\ 0 & -1 & 2 \\ 0 & 2 & 2 \end{bmatrix} \begin{bmatrix} C_{11} \\ C_{21} \\ C_{31} \end{bmatrix} = 3 \begin{bmatrix} C_{11} \\ C_{21} \\ C_{31} \end{bmatrix}$$

$-2\ C_{13} = 3C_{13}$ (row one)

$C_{13} = 0$

$-C_{23} + 2C_{33} = 3C_{23}$ (row two)

$2C_{33} = 4C_{23}$

$C_{33} = 2C_{23}$ (again the third row offers no new information)

$C_{13}^2 + C_{23}^2 + C_{33}^2 = 1$ (from normalization)

$0 + C_{23}^2 + (2C_{23})^2 = 1$

$5C_{23}^2 = 1$

$C_{23} = \sqrt{0.2}$, and therefore $C_{33} = 2\sqrt{0.2}$.

Next, find the pair of eigenvectors associated with the degenerate eigenvalue of -2. First, root one eigenvector one:

$-2C_{11} = -2C_{11}$ (no new information from row one)

$-C_{21} + 2C_{31} = -2C_{21}$ (row two)

$C_{21} = -2C_{31}$ (again the third row offers no new information)

$C_{11}^2 + C_{21}^2 + C_{31}^2 = 1$ (from normalization)

$C_{11}^2 + (-2C_{31})^2 + C_{31}^2 = 1$

$C_{11}^2 + 5C_{31}^2 = 1$

$C_{11} =$

$\sqrt{1 - 5C_{31}^2}$ (Note: There are now two equations with three unknowns.)

Second, root two eigenvector two:

$-2C_{12} = -2C_{12}$ (no new information from row one)

$-C_{22} + 2C_{32} = -2C_{22}$ (row two)

$C_{22} = -2C_{32}$ (again the third row offers no new information)

$C_{12}^2 + C_{22}^2 + C_{32}^2 = 1$ (from normalization)

$C_{12}^2 + (-2C_{32})^2 + C_{32}^2 = 1$

$C_{12}^2 + 5C_{32}^2 = 1$

$C_{12} =$

$\sqrt{1 - 5C_{32}^2}$ (Note: Again there are now two equations with three unknowns)

$C_{11}C_{12} + C_{21}C_{22} + C_{31}C_{32} = 0$ (from orthogonalization)

Now there are five equations with six unknowns.

Arbitrarily choose $C_{11} = 0$

$C_{11} = 0 = \sqrt{1 - 5C_{31}^2}$

$5C_{31}^2 = 1$

$C_{31} = \sqrt{0.2}$

$C_{21} = -2\sqrt{0.2}$

$C_{11}C_{12} + C_{21}C_{22} + C_{31}C_{32} = 0$ (from orthogonalization)

$0 + -2\sqrt{0.2}(-2C_{32}) + \sqrt{0.2}\, C_{32} = 0$

$5C_{32} = 0$

$C_{32} = 0$, $C_{22} = 0$, and $C_{12} = 1$

Therefore the eigenvector matrix becomes:

$$\begin{bmatrix} 0 & 1 & 0 \\ -2\sqrt{0.2} & 0 & \sqrt{0.2} \\ \sqrt{0.2} & 0 & 2\sqrt{0.2} \end{bmatrix}$$

4. Show: $<\varphi_1|\varphi_1> = 1$, $<\varphi_2|\varphi_2> = 1$, and $<\varphi_1|\varphi_2> = 0$

$<\varphi_1|\varphi_1> \overset{?}{=} 1$

$(-2\sqrt{0.2})^2 + (\sqrt{0.2})^2 \overset{?}{=} 1$

$4(0.2) + 0.2 \overset{?}{=} 1$

$0.8 + 0.2 \overset{?}{=} 1$

$1 = 1$

$\langle\varphi_2|\varphi_2\rangle \overset{?}{=} 1$

$(\sqrt{0.2})^2 + (2\sqrt{0.2})^2 \overset{?}{=} 1$

$0.2 + 4(0.2) \overset{?}{=} 1$

$0.2 + 0.8 \overset{?}{=} 1$

$1 = 1$

$\langle\varphi_1|\varphi_2\rangle = \langle\varphi_2|\varphi_1\rangle \overset{?}{=} 0$

$-2\sqrt{0.2}\,\sqrt{0.2} + \sqrt{0.2}\,\,2\sqrt{0.2} \overset{?}{=} 0$

$-2(0.2) + 2(0.2) \overset{?}{=} 0$

$-0.4 + 0.4 \overset{?}{=} 0$

$0 = 0$

5. Show (for the degenerate eigenvalue; $\lambda = -2$): $\langle\varphi_1|\varphi_1\rangle = 1$, $\langle\varphi_2|\varphi_2\rangle = 1$, and $\langle\varphi_1|\varphi_2\rangle = 0$

$\langle\varphi_1|\varphi_1\rangle \overset{?}{=} 1$

$0 + (-2\sqrt{0.2})^2 + (\sqrt{0.2})^2 \overset{?}{=} 1$

$4(0.2) + 0.2 \overset{?}{=} 1$

$0.8 + 0.2 \overset{?}{=} 1$

$1 = 1$

$\langle\varphi_2|\varphi_2\rangle \overset{?}{=} 1$

$1^2 + 0 + 0 \overset{?}{=} 1$

$1 = 1$

$\langle\varphi_1|\varphi_2\rangle = \langle\varphi_2|\varphi_1\rangle \overset{?}{=} 0$

$(0)(1) + (-2\sqrt{0.2})(0) + (\sqrt{0.2})(0) \overset{?}{=} 0$

$0 = 0$

6. Suppose the solution is of the form $x(t) = e^{\alpha t}$, with α unknown. Inserting this trial solution into the differential equation results in the following:

$$\frac{d^2}{dt^2} e^{\alpha t} + k^2 e^{\alpha t} = 0$$

$$\alpha^2 e^{\alpha t} + k^2 e^{\alpha t} = 0$$

$$(\alpha^2 + k^2)\, x(t) = 0$$

$$(\alpha^2 + k^2) = 0$$

$$\alpha^2 = -k^2$$

$\alpha = \sqrt{-k^2}$

$\alpha = \pm ik$

Solutions are of the form e^{ikt}, e^{-ikt}, or a combination of both: $x(t) = C_1e^{ikt} + C_2e^{-ikt}$.

Euler's formula also states that: $e^{\pm i\theta} = Cos\theta \pm iSin\theta$, so the previous equation for x(t) can also be written as:

$x(t) = C_1\{Cos(kt) + iSin(kt)\} + C_2\{Cos(kt) - iSin(kt)\}$

$x(t) = (C_1 + C_2)Cos(kt) + (C_1 + C_2)iSin(kt)$, or alternatively

$x(t) = C_3Cos(kt) + C_4Sin(kt)$.

We can determine these coefficients by making use of the "boundary conditions".

at $t = 0$, $x(0) = L$

$x(0) = C_3Cos(0) + C_4Sin(0) = L$

$C_3 = L$

at $t = 0$, $\frac{dx(0)}{dt} = 0$

$\frac{d}{dt}\, x(t) = \frac{d}{dt}(C_3Cos(kt) + C_4Sin(kt))$

$\frac{d}{dt}\, x(t) = -C_3kSin(kt) + C_4kCos(kt)$

$\frac{d}{dt}\, x(0) = 0 = -C_3kSin(0) + C_4kCos(0)$

$C_4k = 0$

$C_4 = 0$

The solution is of the form: $x(t) = L\ Cos(kt)$

Exercises

1. a. $K.E. = \frac{mv^2}{2} = \left(\frac{m}{m}\right)\frac{mv^2}{2} = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$

$K.E. = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$

$K.E. = \frac{1}{2m}\left\{\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{\hbar}{i}\frac{\partial}{\partial z}\right)^2\right\}$

$K.E. = \frac{-\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\}$

b. $\mathbf{p} = m\mathbf{v} = \mathbf{i}p_x + \mathbf{j}p_y + \mathbf{k}p_z$

$p = \left\{\mathbf{i}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) + \mathbf{j}\left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right) + \mathbf{k}\left(\frac{\hbar}{i}\frac{\partial}{\partial z}\right)\right\}$

where **i**, **j**, and **k** are unit vectors along the x, y, and z axes.

c. $L_y = zp_x - xp_z$

$L_y = z\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right) - x\left(\frac{\hbar}{i}\frac{\partial}{\partial z}\right)$

2. First derive the general formulas for $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$, $\frac{\partial}{\partial z}$ in terms of r,θ, and φ, and $\frac{\partial}{\partial r}$, $\frac{\partial}{\partial \theta}$, and $\frac{\partial}{\partial \varphi}$ in terms of x,y, and z. The general relationships are as follows:

$$x = r \,\mathrm{Sin}\theta \,\mathrm{Cos}\varphi \qquad r^2 = x^2 + y^2 + z^2$$

$$y = r \,\mathrm{Sin}\theta \,\mathrm{Sin}\varphi \qquad \mathrm{Sin}\theta = \frac{\sqrt{x^2 + y^2}}{\sqrt{x^2 + y^2 + z^2}}$$

$$z = r \,\mathrm{Cos}\theta \qquad \mathrm{Cos}\theta = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$\mathrm{Tan}\varphi = \frac{y}{x}$$

First $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$, and $\frac{\partial}{\partial z}$ from the chain rule:

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)_{y,z}\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial x}\right)_{y,z}\frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial x}\right)_{y,z}\frac{\partial}{\partial \varphi} ,$$

$$\frac{\partial}{\partial y} = \left(\frac{\partial r}{\partial y}\right)_{x,z}\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial y}\right)_{x,z}\frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial y}\right)_{x,z}\frac{\partial}{\partial \varphi} ,$$

$$\frac{\partial}{\partial z} = \left(\frac{\partial r}{\partial z}\right)_{x,y}\frac{\partial}{\partial r} + \left(\frac{\partial \theta}{\partial z}\right)_{x,y}\frac{\partial}{\partial \theta} + \left(\frac{\partial \varphi}{\partial z}\right)_{x,y}\frac{\partial}{\partial \varphi} .$$

Evaluation of the many "coefficients" gives the following:

$$\left(\frac{\partial r}{\partial x}\right)_{y,z} = \mathrm{Sin}\theta \,\mathrm{Cos}\varphi \,, \left(\frac{\partial \theta}{\partial x}\right)_{y,z} = \frac{\mathrm{Cos}\theta \,\mathrm{Cos}\varphi}{r} \,, \left(\frac{\partial \varphi}{\partial x}\right)_{y,z} = -\frac{\mathrm{Sin}\varphi}{r \,\mathrm{Sin}\theta} \,,$$

$$\left(\frac{\partial r}{\partial y}\right)_{x,z} = \mathrm{Sin}\theta \,\mathrm{Sin}\varphi \,, \left(\frac{\partial \theta}{\partial y}\right)_{x,z} = \frac{\mathrm{Cos}\theta \,\mathrm{Sin}\varphi}{r} \,, \left(\frac{\partial \varphi}{\partial y}\right)_{x,z} = \frac{\mathrm{Cos}\varphi}{r \,\mathrm{Sin}\theta} \,,$$

$$\left(\frac{\partial r}{\partial z}\right)_{x,y} = \mathrm{Cos}\theta \,, \left(\frac{\partial \theta}{\partial z}\right)_{x,y} = -\frac{\mathrm{Sin}\theta}{r} \,, \text{ and } \left(\frac{\partial \varphi}{\partial z}\right)_{x,y} = 0 \,.$$

Upon substitution of these "coefficients":

$$\frac{\partial}{\partial x} = \mathrm{Sin}\theta \,\mathrm{Cos}\varphi \frac{\partial}{\partial r} + \frac{\mathrm{Cos}\theta \,\mathrm{Cos}\varphi}{r}\frac{\partial}{\partial \theta} - \frac{\mathrm{Sin}\varphi}{r \,\mathrm{Sin}\theta}\frac{\partial}{\partial \varphi} ,$$

$$\frac{\partial}{\partial y} = \mathrm{Sin}\theta \,\mathrm{Sin}\varphi \frac{\partial}{\partial r} + \frac{\mathrm{Cos}\theta \,\mathrm{Sin}\varphi}{r}\frac{\partial}{\partial \theta} + \frac{\mathrm{Cos}\varphi}{r \,\mathrm{Sin}\theta}\frac{\partial}{\partial \varphi} , \text{ and}$$

$$\frac{\partial}{\partial z} = \mathrm{Cos}\theta \frac{\partial}{\partial r} - \frac{\mathrm{Sin}\theta}{r}\frac{\partial}{\partial \theta} + 0 \frac{\partial}{\partial \varphi} .$$

Next $\frac{\partial}{\partial r}$, $\frac{\partial}{\partial \theta}$, and $\frac{\partial}{\partial \varphi}$ from the chain rule:

$$\frac{\partial}{\partial r} = \left(\frac{\partial x}{\partial r}\right)_{\theta,\varphi}\frac{\partial}{\partial x} + \left(\frac{\partial y}{\partial r}\right)_{\theta,\varphi}\frac{\partial}{\partial y} + \left(\frac{\partial z}{\partial r}\right)_{\theta,\varphi}\frac{\partial}{\partial z} ,$$

$$\frac{\partial}{\partial\theta} = \left(\frac{\partial x}{\partial\theta}\right)_{r,\varphi}\frac{\partial}{\partial x} + \left(\frac{\partial y}{\partial\theta}\right)_{r,\varphi}\frac{\partial}{\partial y} + \left(\frac{\partial z}{\partial\theta}\right)_{r,\varphi}\frac{\partial}{\partial z}\text{ , and}$$

$$\frac{\partial}{\partial\varphi} = \left(\frac{\partial x}{\partial\varphi}\right)_{r,\theta}\frac{\partial}{\partial x} + \left(\frac{\partial y}{\partial\varphi}\right)_{r,\theta}\frac{\partial}{\partial y} + \left(\frac{\partial z}{\partial\varphi}\right)_{r,\theta}\frac{\partial}{\partial z}\,.$$

Again evaluation of the the many "coefficients" results in:

$$\left(\frac{\partial x}{\partial r}\right)_{\theta,\varphi} = \frac{x}{\sqrt{x^2+y^2+z^2}}\,,\ \left(\frac{\partial y}{\partial r}\right)_{\theta,\varphi} = \frac{y}{\sqrt{x^2+y^2+z^2}}\,,$$

$$\left(\frac{\partial z}{\partial r}\right)_{\theta,\varphi} = \frac{z}{\sqrt{x^2+y^2+z^2}}\,,\ \left(\frac{\partial x}{\partial\theta}\right)_{r,\varphi} = \frac{x\ z}{\sqrt{x^2+y^2}}\,,\ \left(\frac{\partial y}{\partial\theta}\right)_{r,\varphi} = \frac{y\ z}{\sqrt{x^2+y^2}}\,,$$

$$\left(\frac{\partial z}{\partial\theta}\right)_{r,\varphi} = -\sqrt{x^2+y^2}\,,\ \left(\frac{\partial x}{\partial\varphi}\right)_{r,\theta} = -y\,,\ \left(\frac{\partial y}{\partial\varphi}\right)_{r,\theta} = x\text{ , and }\left(\frac{\partial z}{\partial\varphi}\right)_{r,\theta} = 0$$

Upon substitution of these "coefficients":

$$\frac{\partial}{\partial r} = \frac{x}{\sqrt{x^2+y^2+z^2}}\frac{\partial}{\partial x} + \frac{y}{\sqrt{x^2+y^2+z^2}}\frac{\partial}{\partial y}$$
$$+ \frac{z}{\sqrt{x^2+y^2+z^2}}\frac{\partial}{\partial z}$$

$$\frac{\partial}{\partial\theta} = \frac{x\ z}{\sqrt{x^2+y^2}}\frac{\partial}{\partial x} + \frac{y\ z}{\sqrt{x^2+y^2}}\frac{\partial}{\partial y} - \sqrt{x^2+y^2}\frac{\partial}{\partial z}$$

$$\frac{\partial}{\partial\varphi} = -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y} + 0\frac{\partial}{\partial z}\,.$$

Note, these many "coefficients" are the elements which make up the Jacobian matrix used whenever one wishes to transform a function from one coordinate representation to another. One very familiar result should be in transforming the volume element dxdydz to $r^2\mathrm{Sin}\theta dr d\theta d\varphi$. For example:

$$\int f(x,y,z)dxdydz =$$

$$\int f(x(r,\theta,\varphi),y(r,\theta,\varphi),z(r,\theta,\varphi))\left|\begin{matrix}\left(\frac{\partial x}{\partial r}\right)_{\theta\varphi} & \left(\frac{\partial x}{\partial\theta}\right)_{r\varphi} & \left(\frac{\partial x}{\partial\varphi}\right)_{r\theta}\\ \left(\frac{\partial y}{\partial r}\right)_{\theta\varphi} & \left(\frac{\partial y}{\partial\theta}\right)_{r\varphi} & \left(\frac{\partial y}{\partial\varphi}\right)_{r\theta}\\ \left(\frac{\partial z}{\partial r}\right)_{\theta\varphi} & \left(\frac{\partial z}{\partial\theta}\right)_{r\varphi} & \left(\frac{\partial z}{\partial\varphi}\right)_{r\theta}\end{matrix}\right| dr d\theta d\varphi$$

a. $$\mathbf{L}_x = \frac{\hbar}{i}\left\{y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right\}$$

$$\mathbf{L}_x = \frac{\hbar}{i}\left(r\mathrm{Sin}\theta\mathrm{Sin}\varphi\left(\mathrm{Cos}\theta\frac{\partial}{\partial r} - \frac{\mathrm{Sin}\theta}{r}\frac{\partial}{\partial\theta}\right)\right)$$

$$-\frac{\hbar}{i}\left(r\mathrm{Cos}\theta\left(\mathrm{Sin}\theta\mathrm{Sin}\varphi\frac{\partial}{\partial r} + \frac{\mathrm{Cos}\theta\mathrm{Sin}\varphi}{r}\frac{\partial}{\partial\theta} + \frac{\mathrm{Cos}\varphi}{r\mathrm{Sin}\theta}\frac{\partial}{\partial\varphi}\right)\right)$$

$$\mathbf{L}_x = -\frac{\hbar}{i}\left(\mathrm{Sin}\varphi\frac{\partial}{\partial\theta} + \mathrm{Cot}\theta\mathrm{Cos}\varphi\frac{\partial}{\partial\varphi}\right)$$

b. $\mathbf{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi} = -i\hbar\frac{\partial}{\partial\varphi}$

$$\mathbf{L}_z = \frac{\hbar}{i}\left(-y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}\right)$$

3.

	B	B'	B''
i.	$4x^4 - 12x^2 + 3$	$16x^3 - 24x$	$48x^2 - 24$
ii.	$5x^4$	$20x^3$	$60x^2$
iii.	$e^{3x} + e^{-3x}$	$3(e^{3x} - e^{-3x})$	$9(e^{3x} + e^{-3x})$
iv.	$x^2 - 4x + 2$	$2x - 4$	2
v.	$4x^3 - 3x$	$12x^2 - 3$	$24x$

B(v.) is an eigenfunction of A(i.):

$(1-x^2)\frac{d^2}{dx^2} - x\frac{d}{dx}$ B(v.) =

$(1-x^2)(24x) - x(12x^2 - 3)$

$24x - 24x^3 - 12x^3 + 3x$

$-36x^3 + 27x$

$-9(4x^3 - 3x)$ (eigenvalue is -9)

B(iii.) is an eigenfunction of A(ii.):

$\frac{d^2}{dx^2}$ B(iii.) =

$9(e^{3x} + e^{-3x})$ (eigenvalue is 9)

B(ii.) is an eigenfunction of A(iii.):

$x\frac{d}{dx}$ B(ii.) =

$x(20x^3)$

$20x^4$

$4(5x^4)$ (eigenvalue is 4)

B(i.) is an eigenfunction of A(vi.):

$\frac{d^2}{dx^2} - 2x\frac{d}{dx}$ B(i) =

$(48x^2 - 24) - 2x(16x^3 - 24x)$

$48x^2 - 24 - 32x^4 + 48x^2$

$-32x^4 + 96x^2 - 24$

$-8(4x^4 - 12x^2 + 3)$ (eigenvalue is -8)

B(iv.) is an eigenfunction of A(v.):

$$x\frac{d^2}{dx^2} + (1-x)\frac{d}{dx}\ \mathrm{B(iv.)} =$$
$$x\,(2) + (1-x)\,(2x - 4)$$
$$2x + 2x - 4 - 2x^2 + 4x$$
$$-2x^2 + 8x - 4$$
$$-2(x^2 - 4x + 2)\quad \text{(eigenvalue is -2)}$$

4. Show that: $\int f^*\mathbf{A}g d\tau = \int g(\mathbf{A}f)^* d\tau$

a. Suppose f and g are functions of x and evaluate the integral on the left hand side by "integration by parts":

$$\int f(x)^*\left(-i\hbar\frac{\partial}{\partial x}\right)g(x)dx$$

$$\text{let } dv = \frac{\partial}{\partial x}\,g(x)dx \qquad \text{and} \qquad u = -i\hbar\, f(x)^*$$

$$v = g(x) \qquad du = -i\hbar\frac{\partial}{\partial x}\, f(x)^* dx$$

Now, $\int udv = uv - \int vdu$,

so:

$$\int f(x)^*\left(-i\hbar\frac{\partial}{\partial x}\right)g(x)dx = -i\hbar\, f(x)^* g(x) + i\hbar\int g(x)\frac{\partial}{\partial x}\, f(x)^* dx\ .$$

Note that in, principle, it is impossible to prove hermiticity unless you are given knowledge of the type of function on which the operator is acting. Hermiticity requires (as can be seen in this example) that the term $-i\hbar\, f(x)^* g(x)$ vanish when evaluated at the integral limits. This, in general, will occur for the "well behaved" functions (e.g., in bound state quantum chemistry, the wavefunctions will vanish as the distances among particles approaches infinity). So, in proving the hermiticity of an operator, one must be careful to specify the behavior of the functions on which the operator is considered to act. This means that an operator may be hermitian for one class of functions and non-hermitian for another class of functions. If we assume that f and g vanish at the boundaries, then we have

$$\int f(x)^*\left(-i\hbar\frac{\partial}{\partial x}\right)g(x)dx = \int g(x)\left(-i\hbar\frac{\partial}{\partial x}f(x)\right)^* dx$$

b. Suppose f and g are functions of y and z and evaluate the integral on the left hand side by "integration by parts" as in the previous exercise:

$$\int f(y,z)^*\left\{-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right\}g(y,z)dydz$$

$$= \int f(y,z)^*\left(-i\hbar\left(y\frac{\partial}{\partial z}\right)\right)g(y,z)dydz - \int f(y,z)^*\left(-i\hbar\left(z\frac{\partial}{\partial y}\right)\right)g(y,z)dydz$$

For the first integral, $\int f(z)^*\left(-i\hbar y\frac{\partial}{\partial z}\right)g(z)dz$,

$$\text{let } dv = \frac{\partial}{\partial z} g(z)dz \qquad u = -i\hbar\, y f(z)^*$$

$$v = g(z) \qquad du = -i\hbar\, y\frac{\partial}{\partial z} f(z)^* dz$$

so:

$$\int f(z)^*(-i\hbar y\frac{\partial}{\partial z})g(z)dz = -i\hbar\, y f(z)^* g(z) + i\hbar\, y\int g(z)\frac{\partial}{\partial z} f(z)^* dz$$

$$= \int g(z)\left(-i\hbar y\frac{\partial}{\partial z}f(z)\right)^* dz \ .$$

For the second integral, $\int f(y)^*\left(-i\hbar z\frac{\partial}{\partial y}\right)g(y)dy$,

$$\text{let } dv = \frac{\partial}{\partial y} g(y)dy \qquad u = -i\hbar\, z f(y)^*$$

$$v = g(y) \qquad du = -i\hbar\, z\frac{\partial}{\partial y} f(y)^* dy$$

so:

$$\int f(y)^*(-i\hbar z\frac{\partial}{\partial y})g(y)dy = -i\hbar\, z f(y)^* g(y) + i\hbar\, z\int g(y)\frac{\partial}{\partial y} f(y)^* dy$$

$$= \int g(y)\left(-i\hbar z\frac{\partial}{\partial y}f(y)\right)^* dy$$

$$\int f(y,z)^*\left\{-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right\}g(y,z)dydz$$

$$= \int g(z)\left(-i\hbar y\frac{\partial}{\partial z}f(z)\right)^* dz - \int g(y)\left(-i\hbar z\frac{\partial}{\partial y}f(y)\right)^* dy$$

$$= \int g(y,z)\left(-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)f(y,z)\right)^* dydz \ .$$

Again we have had to assume that the functions f and g vanish at the boundary.

5. $\mathbf{L}_+ = \mathbf{L}_x + i\mathbf{L}_y$

$\mathbf{L}_- = \mathbf{L}_x - i\mathbf{L}_y$, so

$\mathbf{L}_+ + \mathbf{L}_- = 2\mathbf{L}_x$, or $\mathbf{L}_x = \frac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-)$

$\mathbf{L}_+ Y_{l,m} = \sqrt{l(l+1) - m(m+1)}\,\hbar\ Y_{l,m+1}$

$\mathbf{L}_- Y_{l,m} = \sqrt{l(l+1) - m(m-1)}\,\hbar\ Y_{l,m-1}$

Using these relationships:

$\mathbf{L}_- \Psi_{2p_{-1}} = 0$, $\mathbf{L}_- \Psi_{2p_0} = \sqrt{2}\hbar\ \Psi_{2p_{-1}}$, $\mathbf{L}_- \Psi_{2p_{+1}} = \sqrt{2}\hbar\ \Psi_{2p_0}$

$\mathbf{L}_+ \Psi_{2p_{-1}} = \sqrt{2}\hbar\ \Psi_{2p_0}$, $\mathbf{L}_+ \Psi_{2p_0} = \sqrt{2}\hbar\ \Psi_{2p_{+1}}$, $\mathbf{L}_+ \Psi_{2p_{+1}} = 0$, and the following L_x matrix elements can be evaluated:

$$L_x(1,1) = \left\langle \Psi_{2p_{-1}} \middle| \tfrac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-) \middle| \Psi_{2p_{-1}} \right\rangle = 0$$

$$L_x(1,2) = \left\langle \Psi_{2p_{-1}} \middle| \tfrac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-) \middle| \Psi_{2p_0} \right\rangle = \frac{\sqrt{2}}{2}\hbar$$

$$L_x(1,3) = \left\langle \Psi_{2p_{-1}} \middle| \tfrac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-) \middle| \Psi_{2p_{+1}} \right\rangle = 0$$

$$L_x(2,1) = \left\langle \Psi_{2p_0} \middle| \tfrac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-) \middle| \Psi_{2p_{-1}} \right\rangle = \frac{\sqrt{2}}{2}\hbar$$

$$L_x(2,2) = \left\langle \Psi_{2p_0} \middle| \tfrac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-) \middle| \Psi_{2p_0} \right\rangle = 0$$

$$L_x(2,3) = \left\langle \Psi_{2p_0} \middle| \tfrac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-) \middle| \Psi_{2p_{+1}} \right\rangle = \frac{\sqrt{2}}{2}\hbar$$

$$L_x(3,1) = \left\langle \Psi_{2p_{+1}} \middle| \tfrac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-) \middle| \Psi_{2p_{-1}} \right\rangle = 0$$

$$L_x(3,2) = \left\langle \Psi_{2p_{+1}} \middle| \tfrac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-) \middle| \Psi_{2p_0} \right\rangle = \frac{\sqrt{2}}{2}\hbar$$

$$L_x(3,3) = 0$$

This matrix: $\begin{bmatrix} 0 & \frac{\sqrt{2}}{2}\hbar & 0 \\ \frac{\sqrt{2}}{2}\hbar & 0 & \frac{\sqrt{2}}{2}\hbar \\ 0 & \frac{\sqrt{2}}{2}\hbar & 0 \end{bmatrix}$, can now be diagonalized:

$$\begin{vmatrix} 0 - \lambda & \frac{\sqrt{2}}{2}\hbar & 0 \\ \frac{\sqrt{2}}{2}\hbar & 0 - \lambda & \frac{\sqrt{2}}{2}\hbar \\ 0 & \frac{\sqrt{2}}{2}\hbar & 0 - \lambda \end{vmatrix} = 0$$

$$\begin{vmatrix} 0 - \lambda & \frac{\sqrt{2}}{2}\hbar \\ \frac{\sqrt{2}}{2}\hbar & 0 - \lambda \end{vmatrix} (-\lambda) - \begin{vmatrix} \frac{\sqrt{2}}{2}\hbar & \frac{\sqrt{2}}{2}\hbar \\ 0 & 0 - \lambda \end{vmatrix} \left(\frac{\sqrt{2}}{2}\hbar\right) = 0$$

Expanding these determinants yields:

$$\left(\lambda^2 - \frac{\hbar^2}{2}\right)(-\lambda) - \frac{\sqrt{2}\hbar}{2}(-\lambda)\left(\frac{\sqrt{2}\hbar}{2}\right) = 0$$

$$-\lambda(\lambda^2 - \hbar^2) = 0$$

$$-\lambda(\lambda - \hbar)(\lambda + \hbar) = 0$$

with roots: $0, \hbar$, and $-\hbar$

Next, determine the corresponding eigenvectors:

For $\lambda = 0$:

$$\begin{bmatrix} 0 & \frac{\sqrt{2}}{2}\hbar & 0 \\ \frac{\sqrt{2}}{2}\hbar & 0 & \frac{\sqrt{2}}{2}\hbar \\ 0 & \frac{\sqrt{2}}{2}\hbar & 0 \end{bmatrix} \begin{bmatrix} C_{11} \\ C_{21} \\ C_{31} \end{bmatrix} = 0 \begin{bmatrix} C_{11} \\ C_{21} \\ C_{31} \end{bmatrix}$$

$\frac{\sqrt{2}}{2}\hbar\, C_{21} = 0$ (row one)

$C_{21} = 0$

$\frac{\sqrt{2}}{2}\hbar\, C_{11} + \frac{\sqrt{2}}{2}\hbar\, C_{31} = 0$ (row two)

$C_{11} + C_{31} = 0$

$C_{11} = -C_{31}$

$C_{11}^2 + C_{21}^2 + C_{31}^2 = 1$ (normalization)

$C_{11}^2 + (-C_{11})^2 = 1$

$2C_{11}^2 = 1$

$C_{11} = \frac{1}{\sqrt{2}}$, $C_{21} = 0$, and $C_{31} = -\frac{1}{\sqrt{2}}$

For $\lambda = 1\hbar$:

$$\begin{bmatrix} 0 & \frac{\sqrt{2}}{2}\hbar & 0 \\ \frac{\sqrt{2}}{2}\hbar & 0 & \frac{\sqrt{2}}{2}\hbar \\ 0 & \frac{\sqrt{2}}{2}\hbar & 0 \end{bmatrix} \begin{bmatrix} C_{12} \\ C_{22} \\ C_{32} \end{bmatrix} = 1\hbar \begin{bmatrix} C_{12} \\ C_{22} \\ C_{32} \end{bmatrix}$$

$\frac{\sqrt{2}}{2}\hbar\, C_{22} = \hbar\, C_{12}$ (row one)

$C_{12} = \frac{\sqrt{2}}{2}\, C_{22}$

$\frac{\sqrt{2}}{2}\hbar\, C_{12} + \frac{\sqrt{2}}{2}\hbar\, C_{32} = \hbar\, C_{22}$ (row two)

$\frac{\sqrt{2}}{2}\frac{\sqrt{2}}{2}\, C_{22} + \frac{\sqrt{2}}{2}\, C_{32} = C_{22}$

$\frac{1}{2}\, C_{22} + \frac{\sqrt{2}}{2}\, C_{32} = C_{22}$

$$\frac{\sqrt{2}}{2}\, C_{32} = \frac{1}{2}\, C_{22}$$

$$C_{32} = \frac{\sqrt{2}}{2} C_{22}$$

$$C_{12}^2 + C_{22}^2 + C_{32}^2 = 1 \quad \text{(normalization)}$$

$$\left(\frac{\sqrt{2}}{2}\, C_{22}\right)^2 + C_{22}^2 + \left(\frac{\sqrt{2}}{2} C_{22}\right)^2 = 1$$

$$\frac{1}{2}\, C_{22}^2 + C_{22}^2 + \frac{1}{2} C_{22}^2 = 1$$

$$2C_{22}^2 = 1$$

$$C_{22} = \frac{\sqrt{2}}{2}$$

$$C_{12} = \frac{1}{2}\ , C_{22} = \frac{\sqrt{2}}{2}\ , \text{ and } C_{32} = \frac{1}{2}$$

For $\lambda = -1\hbar$:

$$\begin{bmatrix} 0 & \frac{\sqrt{2}}{2}\hbar & 0 \\ \frac{\sqrt{2}}{2}\hbar & 0 & \frac{\sqrt{2}}{2}\hbar \\ 0 & \frac{\sqrt{2}}{2}\hbar & 0 \end{bmatrix} \begin{bmatrix} C_{13} \\ C_{23} \\ C_{33} \end{bmatrix} = -1\hbar \begin{bmatrix} C_{13} \\ C_{23} \\ C_{33} \end{bmatrix}$$

$$\frac{\sqrt{2}}{2}\, \hbar\, C_{23} = -\hbar\, C_{13} \quad \text{(row one)}$$

$$C_{13} = -\frac{\sqrt{2}}{2}\, C_{23}$$

$$\frac{\sqrt{2}}{2}\, \hbar\, C_{13} + \frac{\sqrt{2}}{2}\, \hbar\, C_{33} = -\hbar\, C_{23} \quad \text{(row two)}$$

$$\frac{\sqrt{2}}{2}\left(-\frac{\sqrt{2}}{2}\, C_{23}\right) + \frac{\sqrt{2}}{2}\, C_{33} = -C_{23}$$

$$-\frac{1}{2}\, C_{23} + \frac{\sqrt{2}}{2}\, C_{33} = -C_{23}$$

$$\frac{\sqrt{2}}{2}\, C_{33} = -\frac{1}{2}\, C_{23}$$

$$C_{33} = -\frac{\sqrt{2}}{2} C_{23}$$

$$C_{13}^2 + C_{23}^2 + C_{33}^2 = 1 \quad \text{(normalization)}$$

$$\left(-\frac{\sqrt{2}}{2}\, C_{23}\right)^2 + C_{23}^2 + \left(-\frac{\sqrt{2}}{2} C_{23}\right)^2 = 1$$

$$\frac{1}{2}\, C_{23}^2 + C_{23}^2 + \frac{1}{2} C_{23}^2 = 1$$

$$2C_{23}^2 = 1$$

$C_{23} = \frac{\sqrt{2}}{2}$

$C_{13} = -\frac{1}{2}$, $C_{23} = \frac{\sqrt{2}}{2}$, and $C_{33} = -\frac{1}{2}$

Show: $<\varphi_1|\varphi_1> = 1$, $<\varphi_2|\varphi_2> = 1$, $<\varphi_3|\varphi_3> = 1$, $<\varphi_1|\varphi_2> = 0$, $<\varphi_1|\varphi_3> = 0$, and $<\varphi_2|\varphi_3> = 0$.

$$<\varphi_1|\varphi_1> \overset{?}{=} 1$$

$$\left(\frac{\sqrt{2}}{2}\right)^2 + 0 + \left(-\frac{\sqrt{2}}{2}\right)^2 \overset{?}{=} 1$$

$$\frac{1}{2} + \frac{1}{2} \overset{?}{=} 1$$

$$1 = 1$$

$$<\varphi_2|\varphi_2> \overset{?}{=} 1$$

$$\left(\frac{1}{2}\right)^2 + \left(\frac{\sqrt{2}}{2}\right)^2 + \left(\frac{1}{2}\right)^2 \overset{?}{=} 1$$

$$\frac{1}{4} + \frac{1}{2} + \frac{1}{4} \overset{?}{=} 1$$

$$1 = 1$$

$$<\varphi_3|\varphi_3> \overset{?}{=} 1$$

$$\left(-\frac{1}{2}\right)^2 + \left(\frac{\sqrt{2}}{2}\right)^2 + \left(-\frac{1}{2}\right)^2 \overset{?}{=} 1$$

$$\frac{1}{4} + \frac{1}{2} + \frac{1}{4} \overset{?}{=} 1$$

$$1 = 1$$

$$<\varphi_1|\varphi_2> = <\varphi_2|\varphi_1> \overset{?}{=} 0$$

$$\left(\frac{\sqrt{2}}{2}\right)\left(\frac{1}{2}\right) + (0)\left(\frac{\sqrt{2}}{2}\right) + \left(-\frac{\sqrt{2}}{2}\right)\left(\frac{1}{2}\right) \overset{?}{=} 0$$

$$\left(\frac{\sqrt{2}}{4}\right) - \left(\frac{\sqrt{2}}{4}\right) \overset{?}{=} 0$$

$$0 = 0$$

$$<\varphi_1|\varphi_3> = <\varphi_3|\varphi_1> \overset{?}{=} 0$$

$$\left(\frac{\sqrt{2}}{2}\right)\left(-\frac{1}{2}\right) + (0)\left(\frac{\sqrt{2}}{2}\right) + \left(-\frac{\sqrt{2}}{2}\right)\left(-\frac{1}{2}\right) \overset{?}{=} 0$$

$$\left(-\frac{\sqrt{2}}{4}\right) + \left(\frac{\sqrt{2}}{4}\right) \overset{?}{=} 0$$

$$0 = 0$$

$$<\varphi_2|\varphi_3> = <\varphi_3|\varphi_2> \overset{?}{=} 0$$

$$\left(\frac{1}{2}\right)\left(-\frac{1}{2}\right) + \left(\frac{\sqrt{2}}{2}\right)\left(\frac{\sqrt{2}}{2}\right) + \left(\frac{1}{2}\right)\left(-\frac{1}{2}\right) \overset{?}{=} 0$$

$$\left(-\frac{1}{4}\right) + \left(\frac{1}{2}\right) + \left(-\frac{1}{4}\right) \overset{?}{=} 0$$

$$0 = 0$$

6. $$P_{2p_{+1}} = \left| \left\langle \varphi_{2p_{+1}} \middle| \psi^{0\hbar}_{L_x} \right\rangle \right|^2$$

$$\psi^{0\hbar}_{L_x} = \frac{1}{\sqrt{2}}\varphi_{2p_{-1}} - \frac{1}{\sqrt{2}}\varphi_{2p_{+1}}$$

$$P_{2p_{+1}} = \left| -\frac{1}{\sqrt{2}} \left\langle \varphi_{2p_{+1}} \middle| \varphi_{2p_{+1}} \right\rangle \right|^2 = \frac{1}{2} \quad \text{(or 50\%)}$$

7. It is useful here to use some of the general commutator relations found in Appendix C.V.

a. $[L_x,L_y] = [yp_z - zp_y, zp_x - xp_z]$
$= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z]$
$= [y,z]p_xp_z + z[y,p_x]p_z + y[p_z,z]p_x + yz[p_z,p_x]$
$- [y,x]p_zp_z - x[y,p_z]p_z - y[p_z,x]p_z - yx[p_z,p_z]$
$- [z,z]p_xp_y - z[z,p_x]p_y - z[p_y,z]p_x - zz[p_y,p_x]$
$+ [z,x]p_zp_y + x[z,p_z]p_y + z[p_y,x]p_z + zx[p_y,p_z]$

As can be easily ascertained, the only non-zero terms are: $[L_x,L_y] = y[p_z,z]p_x + x[z,p_z]p_y$

$= y(-i\hbar)p_x + x(i\hbar)p_y$

$= i\hbar(-yp_x + xp_y)$

$= i\hbar L_z$

b. $[L_y,L_z] = [zp_x - xp_z, xp_y - yp_x]$
$= [zp_x, xp_y] - [zp_x, yp_x] - [xp_z, xp_y] + [xp_z, yp_x]$
$= [z,x]p_yp_x + x[z,p_y]p_x + z[p_x,x]p_y + zx[p_x,p_z]$
$- [z,y]p_xp_x - y[z,p_x]p_x - z[p_x,y]p_x - zy[p_x,p_x]$
$- [x,x]p_yp_z - x[x,p_y]p_z - x[p_z,x]p_y - xx[p_z,p_y]$
$+ [x,y]p_xp_z + y[x,p_x]p_z + x[p_z,y]p_x + xy[p_z,p_x]$

Again, as can be easily ascertained, the only non-zero terms are:

$[L_y,L_z] = z[p_x,x]p_y + y[x,p_x]p_z$

$= z(-i\hbar)p_y + y(i\hbar)p_z$

$= i\hbar(-zp_y + yp_z)$

$= i\hbar L_x$

c. $[L_z,L_x] = [xp_y - yp_x, yp_z - zp_y]$
$= [xp_y, yp_z] - [xp_y, zp_y] - [yp_x, yp_z] + [yp_x, zp_y]$
$= [x,y]p_zp_y + y[x,p_z]p_y + x[p_y,y]p_z + xy[p_y,p_z]$
$- [x,z]p_yp_y - z[x,p_y]p_y - x[p_y,z]p_y - xz[p_y,p_y]$
$- [y,y]p_zp_x - y[y,p_z]p_x - y[p_x,y]p_z - yy[p_x,p_z]$
$+ [y,z]p_yp_x + z[y,p_y]p_x + y[p_x,z]p_y + yz[p_x,p_y]$

Again, as can be easily ascertained, the only non-zero terms are:

$[L_z,L_x] = x[p_y,y]p_z + z[y,p_y]p_x$

$= x(-i\hbar)p_z + z(i\hbar)p_x$

$= i\hbar(-xp_z + zp_x)$

$= i\hbar L_y$

d. $[L_x,L^2] = [L_x,L_x^2 + L_y^2 + L_z^2]$

$= [L_x,L_x^2] + [L_x,L_y^2] + [L_x,L_z^2]$

$= [L_x,L_y^2] + [L_x,L_z^2]$

$= [L_x,L_y]L_y + L_y[L_x,L_y] + [L_x,L_z]L_z + L_z[L_x,L_z]$

$= (i\hbar L_z)L_y + L_y(i\hbar L_z) + (-i\hbar L_y)L_z + L_z(-i\hbar L_y)$

$= (i\hbar)(L_zL_y + L_yL_z - L_yL_z - L_zL_y)$

$= (i\hbar)([L_z,L_y] + [L_y,L_z]) = 0$

e. $[L_y,L^2] = [L_y,L_x^2 + L_y^2 + L_z^2]$

$= [L_y,L_x^2] + [L_y,L_y^2] + [L_y,L_z^2]$

$= [L_y,L_x^2] + [L_y,L_z^2]$

$= [L_y,L_x]L_x + L_x[L_y,L_x] + [L_y,L_z]L_z + L_z[L_y,L_z]$

$= (-i\hbar L_z)L_x + L_x(-i\hbar L_z) + (i\hbar L_x)L_z + L_z(i\hbar L_x)$

$= (i\hbar)(-L_zL_x - L_xL_z + L_xL_z + L_zL_x)$

$= (i\hbar)([L_x,L_z] + [L_z,L_x]) = 0$

f. $[L_z,L^2] = [L_z,L_x^2 + L_y^2 + L_z^2]$

$= [L_z,L_x^2] + [L_z,L_y^2] + [L_z,L_z^2]$

$= [L_z,L_x^2] + [L_z,L_y^2]$

$= [L_z,L_x]L_x + L_x[L_z,L_x] + [L_z,L_y]L_y + L_y[L_z,L_y]$

$= (i\hbar L_y)L_x + L_x(i\hbar L_y) + (-i\hbar L_x)L_y + L_y(-i\hbar L_x)$

$= (i\hbar)(L_yL_x + L_xL_y - L_xL_y - L_yL_x)$

$= (i\hbar)([L_y,L_x] + [L_x,L_y]) = 0$

8. Use the general angular momentum relationships:

$J^2|j,m\rangle = \hbar^2 (j(j+1))|j,m\rangle$

$J_z|j,m\rangle = \hbar\, m|j,m\rangle$,

and the information used in exercise 5, namely that:

$\mathbf{L}_x = \frac{1}{2}(\mathbf{L}_+ + \mathbf{L}_-)$

$\mathbf{L}_+ Y_{l,m} = \sqrt{l(l+1) - m(m+1)}\,\hbar\, Y_{l,m+1}$

$\mathbf{L}_- Y_{l,m} = \sqrt{l(l+1) - m(m-1)}\,\hbar\, Y_{l,m-1}$

Given that:

$$Y_{0,0}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}} = |0,0\rangle$$

$$Y_{1,0}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\ \mathrm{Cos}\theta = |1,0>.$$

a. $\mathbf{L}_z|0,0> = 0$

$\mathbf{L}^2|0,0> = 0$

Since L^2 and L_z commute you would expect $|0,0>$ to be simultaneous eigenfunctions of both.

b. $\mathbf{L}_x|0,0> = 0$

$\mathbf{L}_z|0,0> = 0$

L_x and L_z <u>do not</u> commute. It is unexpected to find a simultaneous eigenfunction ($|0,0>$) of both ... for sure these operators do not have the same full set of eigenfunctions.

c. $\mathbf{L}_z|1,0> = 0$

$\mathbf{L}^2|1,0> = 2\hbar^2|1,0>$

Again since L^2 and L_z commute you would expect $|1,0>$ to be simultaneous eigenfunctions of both.

d. $\mathbf{L}_x|1,0> = \frac{\sqrt{2}}{2}\hbar\ |1,-1> + \frac{\sqrt{2}}{2}\hbar\ |1,1>$

$\mathbf{L}_z|1,0> = 0$

Again, L_x and L_z <u>do not</u> commute. Therefore it is expected to find differing sets of eigenfunctions for both.

9. For:

$$\Psi(x,y) = \left(\frac{1}{2L_x}\right)^{\frac{1}{2}}\left(\frac{1}{2L_y}\right)^{\frac{1}{2}}\left[e^{in_x\pi x/L_x} - e^{-in_x\pi x/L_x}\right]\left[e^{in_y\pi y/L_y} - e^{-in_y\pi y/L_y}\right]$$

$$<\Psi(x,y)|\Psi(x,y)> \overset{?}{=} 1$$

Let: $a_x = \frac{n_x\pi}{L_x}$, and $a_y = \frac{n_y\pi}{L_y}$ and using Euler's formula, expand the exponentials into Sin and Cos terms.

$$\Psi(x,y) = \left(\frac{1}{2L_x}\right)^{\frac{1}{2}}\left(\frac{1}{2L_y}\right)^{\frac{1}{2}} [\mathrm{Cos}(a_x x) + i\mathrm{Sin}(a_x x) - \mathrm{Cos}(a_x x) + i\mathrm{Sin}(a_x x)]\ [\mathrm{Cos}(a_y y) + i\mathrm{Sin}(a_y y) - \mathrm{Cos}(a_y y) + i\mathrm{Sin}(a_y y)]$$

$$\Psi(x,y) = \left(\frac{1}{2L_x}\right)^{\frac{1}{2}}\left(\frac{1}{2L_y}\right)^{\frac{1}{2}} 2i\mathrm{Sin}(a_x x)\ 2i\mathrm{Sin}(a_y y)$$

$$\Psi(x,y) = -\left(\frac{2}{L_x}\right)^{\frac{1}{2}}\left(\frac{2}{L_y}\right)^{\frac{1}{2}} \mathrm{Sin}(a_x x)\ \mathrm{Sin}(a_y y)$$

$$<\Psi(x,y)|\Psi(x,y)> = \int\left(-\left(\frac{2}{L_x}\right)^{\frac{1}{2}}\left(\frac{2}{L_y}\right)^{\frac{1}{2}}\mathrm{Sin}(a_x x)\ \mathrm{Sin}(a_y y)\right)^2 dxdy$$

$$= \left(\frac{2}{L_x}\right)\left(\frac{2}{L_y}\right)\int \mathrm{Sin}^2(a_x x)\ \mathrm{Sin}^2(a_y y)\ dxdy$$

Using the integral:

$$\int_0^{L} \mathrm{Sin}^2\frac{n\pi x}{L}\,dx = \frac{L}{2}\ ,$$

$$\langle\Psi(x,y)|\Psi(x,y)\rangle = \left(\frac{2}{L_x}\right)\left(\frac{2}{L_y}\right)\left(\frac{L_x}{2}\right)\left(\frac{L_y}{2}\right) = 1$$

10.

$$\langle\Psi(x,y)|p_x|\Psi(x,y)\rangle = \left(\frac{2}{L_y}\right)\int_0^{L_y}\mathrm{Sin}^2(a_y y)dy\left(\frac{2}{L_x}\right)\int_0^{L_x}\mathrm{Sin}(a_x x)\left(-i\hbar\frac{\partial}{\partial x}\right)\mathrm{Sin}(a_x x)dx$$

$$= \left(\frac{-i\hbar 2a_x}{L_x}\right)\int_0^{L_x}\mathrm{Sin}(a_x x)\mathrm{Cos}(a_x x)dx$$

But the integral:

$$\int_0^{L_x}\mathrm{Cos}(a_x x)\mathrm{Sin}(a_x x)dx = 0,$$

$$\langle\Psi(x,y)|p_x|\Psi(x,y)\rangle = 0$$

11. $$\langle\Psi_0|\mathbf{x}^2|\Psi_0\rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty}\left(e^{-\alpha x^2/2}\right)(\mathbf{x}^2)\left(e^{-\alpha x^2/2}\right)dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} 2\int_0^{+\infty} x^2 e^{-\alpha x^2}dx$$

Using the integral:

$$\int_0^{+\infty} x^{2n}\, e^{-\beta x^2}dx = \frac{1\cdot 3\cdots(2n-1)}{2^{n+1}}\left(\frac{\pi}{\beta^{2n+1}}\right)^{\frac{1}{2}}\ ,$$

$$\langle\Psi_0|\mathbf{x}^2|\Psi_0\rangle = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} 2\left(\frac{1}{2^2}\right)\left(\frac{\pi}{\alpha^3}\right)^{\frac{1}{2}}$$

$$\langle\Psi_0|\mathbf{x}^2|\Psi_0\rangle = \left(\frac{1}{2\alpha}\right)$$

$$\langle\Psi_1|\mathbf{x}^2|\Psi_1\rangle = \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty}\left(xe^{-\alpha x^2/2}\right)(\mathbf{x}^2)\left(xe^{-\alpha x^2/2}\right)dx$$

$$= \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} 2 \int_0^{+\infty} x^4 e^{-\alpha x^2/2} dx$$

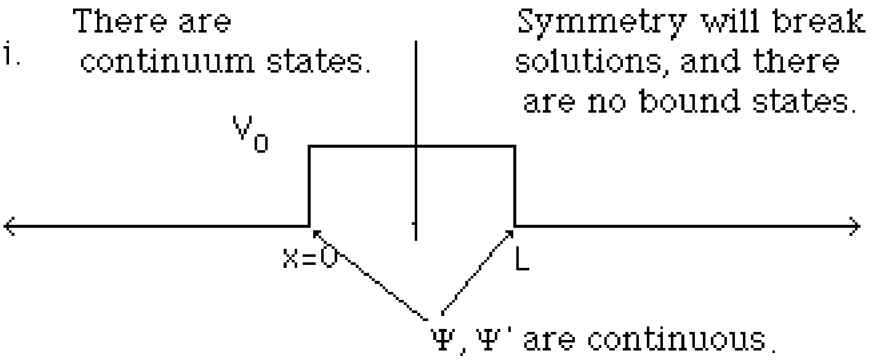
Using the previously defined integral:

$$<\Psi_1|\mathbf{x}^2|\Psi_1> = \left(\frac{4\alpha^3}{\pi}\right)^{\frac{1}{2}} 2 \left(\frac{3}{2^3}\right)\left(\frac{\pi}{\alpha^5}\right)^{\frac{1}{2}}$$

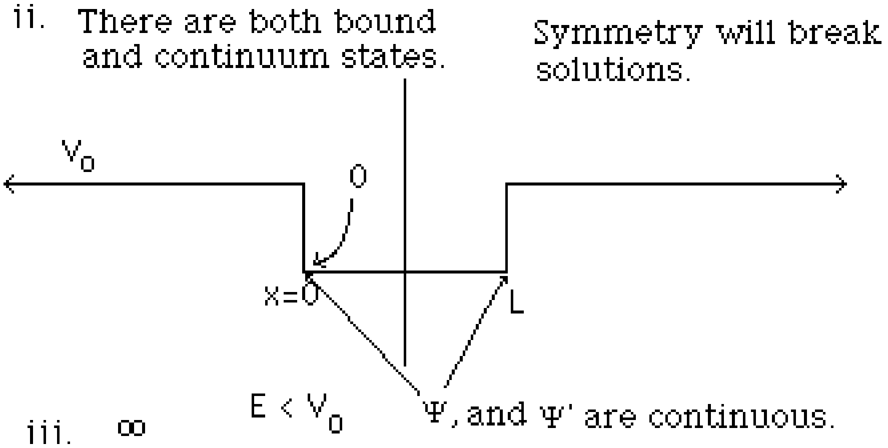
$$<\Psi_1|\mathbf{x}^2|\Psi_1> = \left(\frac{3}{2\alpha}\right)$$

12.

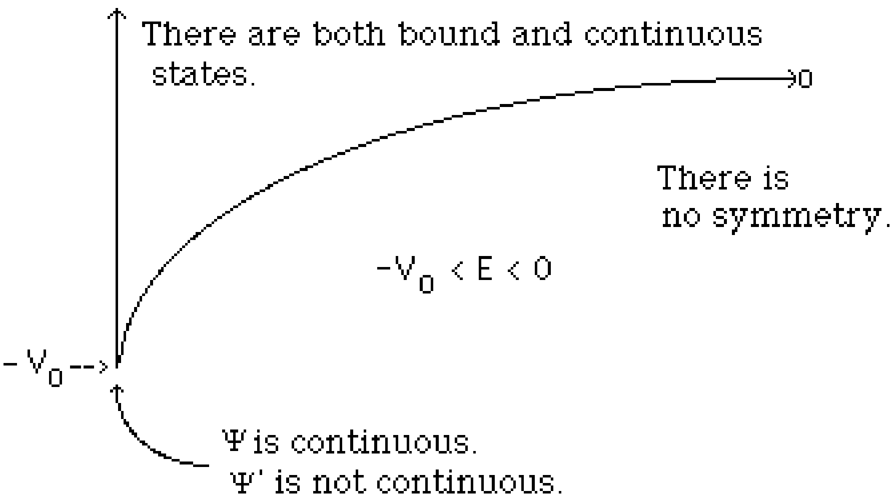
i.


There are
continuum states.
Symmetry will break
solutions, and there
are no bound states.
V_0
x=0
L
Ψ, Ψ' are continuous.

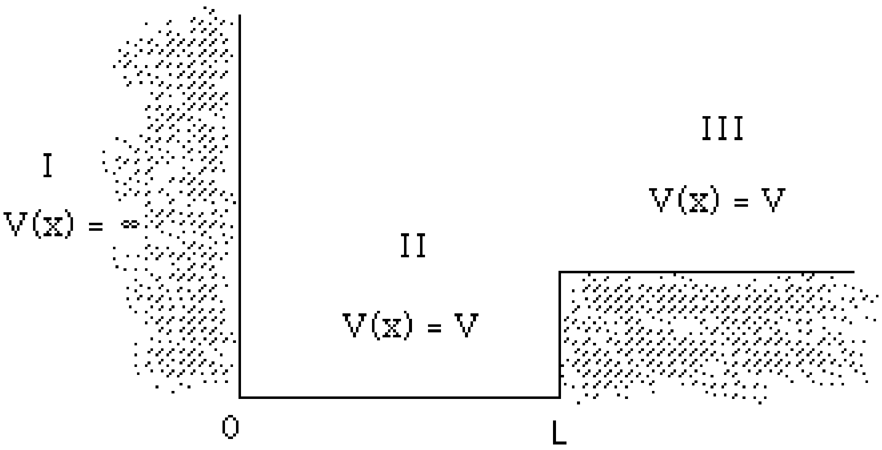
ii.


There are both bound
and continuum states.
Symmetry will break
solutions.
V_0
0
x=0
L
E < V_0
Ψ, and Ψ' are continuous.

iii.


∞
There are both bound and continuous
states.
0
There is
no symmetry.
$-V_0 < E < 0$
$-V_0$ -->
Ψ is continuous.
Ψ' is not continuous.

13.



a. $\Psi_{I}(x) = 0$

$$\Psi_{II}(x) = Ae^{i\sqrt{2mE/\hbar^2}\,x} + Be^{-i\sqrt{2mE/\hbar^2}\,x}$$

$$\Psi_{III}(x) = A'e^{i\sqrt{2m(V-E)/\hbar^2}\,x} + B'e^{-i\sqrt{2m(V-E)/\hbar^2}\,x}$$

b. I ↔ II

$\Psi_{I}(0) = \Psi_{II}(0)$

$$\Psi_{I}(0) = 0 = \Psi_{II}(0) = Ae^{i\sqrt{2mE/\hbar^2}\,(0)} + Be^{-i\sqrt{2mE/\hbar^2}\,(0)}$$

$0 = A + B$

$B = -A$

$\Psi'_{I}(0) = \Psi'_{II}(0)$ (this gives no useful information since $\Psi'_{I}(x)$ does not exist at x = 0)

II ↔ III

$\Psi_{II}(L) = \Psi_{III}(L)$

$$Ae^{i\sqrt{2mE/\hbar^2}\,L} + Be^{-i\sqrt{2mE/\hbar^2}\,L} = A'e^{i\sqrt{2m(V-E)/\hbar^2}\,L}$$
$$+ B'e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

$\Psi'_{II}(L) = \Psi'_{III}(L)$

$$A(i\sqrt{2mE/\hbar^2}\,)e^{i\sqrt{2mE/\hbar^2}\,L} - B(i\sqrt{2mE/\hbar^2}\,)e^{-i\sqrt{2mE/\hbar^2}\,L}$$
$$= A'(i\sqrt{2m(V-E)/\hbar^2}\,)e^{i\sqrt{2m(V-E)/\hbar^2}\,L}$$
$$- B'(i\sqrt{2m(V-E)/\hbar^2}\,)e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

c. as x → -∞, $\Psi_{I}(x) = 0$

as x → +∞, $\Psi_{III}(x) = 0$ $A' = 0$

d. Rewrite the equations for $\Psi_{I}(0) = \Psi_{II}(0)$, $\Psi_{II}(L) = \Psi_{III}(L)$, and $\Psi'_{II}(L) = \Psi'_{III}(L)$ using the information in 13c:

$B = -A$ (eqn. 1)

$$Ae^{i\sqrt{2mE/\hbar^2}\,L} + Be^{-i\sqrt{2mE/\hbar^2}\,L} = B'e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

(eqn. 2)

$$A(i\sqrt{2mE/\hbar^2}\,)e^{i\sqrt{2mE/\hbar^2}\,L} - B(i\sqrt{2mE/\hbar^2}\,)e^{-i\sqrt{2mE/\hbar^2}\,L}$$

$$= - B'(i\sqrt{2m(V-E)/\hbar^2}\,)e^{-i\sqrt{2m(V-E)/\hbar^2}\,L} \qquad \text{(eqn. 3)}$$

substituting (eqn. 1) into (eqn. 2):

$$Ae^{i\sqrt{2mE/\hbar^2}\,L} - Ae^{-i\sqrt{2mE/\hbar^2}\,L} = B'e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

$$A(\mathrm{Cos}(\sqrt{2mE/\hbar^2}\ L) + i\mathrm{Sin}(\sqrt{2mE/\hbar^2}\ L))$$

$$- A(\mathrm{Cos}(\sqrt{2mE/\hbar^2}\ L) - i\mathrm{Sin}(\sqrt{2mE/\hbar^2}\ L))$$

$$= B'e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

$$2Ai\mathrm{Sin}(\sqrt{2mE/\hbar^2}\ L) = B'e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

$$\mathrm{Sin}(\sqrt{2mE/\hbar^2}\ L) = \frac{B'}{2Ai}\,e^{-i\sqrt{2m(V-E)/\hbar^2}\,L} \qquad \text{(eqn. 4)}$$

substituting (eqn. 1) into (eqn. 3):

$$A(i\sqrt{2mE/\hbar^2}\,)e^{i\sqrt{2mE/\hbar^2}\,L} + A(i\sqrt{2mE/\hbar^2}\,)e^{-i\sqrt{2mE/\hbar^2}\,L}$$

$$= - B'(i\sqrt{2m(V-E)/\hbar^2}\,)e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

$$A(i\sqrt{2mE/\hbar^2}\,)(\mathrm{Cos}(\sqrt{2mE/\hbar^2}\ L) + i\mathrm{Sin}(\sqrt{2mE/\hbar^2}\ L))$$

$$+ A(i\sqrt{2mE/\hbar^2}\,)(\mathrm{Cos}(\sqrt{2mE/\hbar^2}\ L) - i\mathrm{Sin}(\sqrt{2mE/\hbar^2}\ L))$$

$$= - B'(i\sqrt{2m(V-E)/\hbar^2}\,)e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

$$2Ai\sqrt{2mE/\hbar^2}\ \mathrm{Cos}(\sqrt{2mE/\hbar^2}\ L)$$

$$= - B'i\sqrt{2m(V-E)/\hbar^2}\ e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

$$\mathrm{Cos}(\sqrt{2mE/\hbar^2}\ L) = - \frac{B'i\sqrt{2m(V-E)/\hbar^2}}{2Ai\sqrt{2mE/\hbar^2}}\ e^{-i\sqrt{2m(V-E)/\hbar^2}\,L}$$

$$\mathrm{Cos}(\sqrt{2mE/\hbar^2}\ L) = - \frac{B'\sqrt{V-E}}{2A\sqrt{E}}\ e^{-i\sqrt{2m(V-E)/\hbar^2}\,L} \qquad \text{(eqn. 5)}$$

Dividing (eqn. 4) by (eqn. 5):

$$\frac{\text{Sin}(\sqrt{2mE/\hbar^2}\ L)}{\text{Cos}(\sqrt{2mE/\hbar^2}\ L)} = \frac{B'}{2Ai}\,\frac{-2A\sqrt{E}}{B'\sqrt{V-E}}\,\frac{e^{-i\sqrt{2m(V-E)/\hbar^2}\ L}}{e^{-i\sqrt{2m(V-E)/\hbar^2}\ L}}$$

$$\text{Tan}(\sqrt{2mE/\hbar^2}\ L) = -\left(\frac{E}{V-E}\right)^{1/2}$$

e. As V → $+\infty$, $\text{Tan}(\sqrt{2mE/\hbar^2}\ L) \rightarrow 0$

So, $\sqrt{2mE/\hbar^2}\ L = n\pi$

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

Problems

1. a. $\Psi_n(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \text{Sin}\frac{n\pi x}{L}$

$P_n(x)dx = |\Psi_n|^2(x)\ dx$

The probability that the particle lies in the interval $0 \le x \le \frac{L}{4}$ is given by:

$$P_n = \int_0^{\frac{L}{4}} P_n(x)dx = \left(\frac{2}{L}\right)\int_0^{\frac{L}{4}} \text{Sin}^2\left(\frac{n\pi x}{L}\right)dx$$

This integral can be integrated to give (using integral equation 10 with $\theta = \frac{n\pi x}{L}$):

$$P_n = \left(\frac{L}{n\pi}\right)\left(\frac{2}{L}\right)\int_0^{\frac{n\pi}{4}} \text{Sin}^2\left(\frac{n\pi x}{L}\right)d\left(\frac{n\pi x}{L}\right)$$

$$P_n = \left(\frac{L}{n\pi}\right)\left(\frac{2}{L}\right)\int_0^{\frac{n\pi}{4}} \text{Sin}^2\theta d\theta$$

$$P_n = \frac{2}{n\pi}\left(-\frac{1}{4}\text{Sin}2\theta + \frac{\theta}{2}\right|_0^{\frac{n\pi}{4}}\Bigg)$$

$$= \frac{2}{n\pi}\left(-\frac{1}{4}\text{Sin}\frac{2n\pi}{4} + \frac{n\pi}{(2)(4)}\right)$$

$$= \frac{1}{4} - \frac{1}{2\pi n}\,\mathrm{Sin}\left(\frac{n\pi}{2}\right)$$

b. If n is even, $\mathrm{Sin}\left(\frac{n\pi}{2}\right) = 0$ and $P_n = \frac{1}{4}$.

If n is odd and n = 1,5,9,13, ... $\mathrm{Sin}\left(\frac{n\pi}{2}\right) = 1$

and $P_n = \frac{1}{4} - \frac{1}{2\pi n}$

If n is odd and n = 3,7,11,15, ... $\mathrm{Sin}\left(\frac{n\pi}{2}\right) = -1$

and $P_n = \frac{1}{4} + \frac{1}{2\pi n}$

The higher P_n is when <u>n = 3</u>. Then $P_n = \frac{1}{4} + \frac{1}{2\pi 3}$

$P_n = \frac{1}{4} + \frac{1}{6\pi} = 0.303$

c. $\Psi(t) = e^{\frac{-iHt}{\hbar}}\,[\,a\Psi_n + b\,\Psi_m] = a\Psi_n e^{\frac{-iE_n t}{\hbar}} + b\Psi_m e^{\frac{-iE_m t}{\hbar}}$

$H\Psi = a\Psi_n E_n e^{\frac{-iE_n t}{\hbar}} + b\Psi_m E_m e^{\frac{iE_m t}{\hbar}}$

$\langle\Psi|H|\Psi\rangle = |a|^2E_n + |b|^2E_m + a^*b e^{\frac{i(E_n-E_m)t}{\hbar}}\langle\Psi_n|H|\Psi_m\rangle$

$+ b^*a e^{\frac{-i(E_m-E_n)t}{\hbar}}\langle\Psi_m|H|\Psi_n\rangle$

Since $\langle\Psi_n|H|\Psi_m\rangle$ and $\langle\Psi_m|H|\Psi_n\rangle$ are zero,

$\langle\Psi|H|\Psi\rangle = |a|^2E_n + |b|^2E_m$ (note the time independence)

d. The fraction of systems observed in Ψ_n is $|a|^2$. The possible energies measured are E_n and E_m. The probabilities of measuring each of these energies is $|a|^2$ and $|b|^2$.

e. Once the system is observed in Ψ_n, it stays in Ψ_n.

f. $P(E_n) = \left|\langle\Psi_n|\Psi\rangle\right|^2 = |c_n|^2$

$$c_n = \int_0^L \sqrt{\frac{2}{L}}\,\mathrm{Sin}\left(\frac{n\pi x}{L}\right)\sqrt{\frac{30}{L^5}}\,x(L-x)dx$$

$$= \sqrt{\frac{60}{L^6}}\int_0^L x(L-x)\,\mathrm{Sin}\left(\frac{n\pi x}{L}\right)dx$$

$$= \sqrt{\frac{60}{L^6}}\left[L\int_0^L x\mathrm{Sin}\left(\frac{n\pi x}{L}\right)dx - \int_0^L x^2\mathrm{Sin}\left(\frac{n\pi x}{L}\right)dx\right]$$

These integrals can be evaluated from integral equations 14 and 16 to give:

$$c_n = \sqrt{\frac{60}{L^6}}\left[L\left(\frac{L^2}{n^2\pi^2}\mathrm{Sin}\left(\frac{n\pi x}{L}\right) - \frac{Lx}{n\pi}\mathrm{Cos}\left(\frac{n\pi x}{L}\right)\right)\Bigg|_0^L\ \right]$$

$$- \sqrt{\frac{60}{L^6}}\left[\left(\frac{2xL^2}{n^2\pi^2}\mathrm{Sin}\left(\frac{n\pi x}{L}\right) - \left(\frac{n^2\pi^2x^2}{L^2} - 2\right)\frac{L^3}{n^3\pi^3}\mathrm{Cos}\left(\frac{n\pi x}{L}\right)\right)\Bigg|_0^L\ \right]$$

$$c_n = \sqrt{\frac{60}{L^6}}\ \Bigg\{\frac{L^3}{n^2\pi^2}(\,\mathrm{Sin}(n\pi) - \mathrm{Sin}(0))$$

$$- \frac{L^2}{n\pi}(\,L\mathrm{Cos}(n\pi) - 0\mathrm{Cos}0)\ )$$

$$- \Bigg(\frac{2L^2}{n^2\pi^2}(\,L\mathrm{Sin}(n\pi) - 0\mathrm{Sin}(0))$$

$$- (\,n^2\pi^2 - 2)\frac{L^3}{n^3\pi^3}\mathrm{Cos}(n\pi)$$

$$+ \left(\frac{n^2\pi^2(0)}{L^2} - 2\right)\frac{L^3}{n^3\pi^3}\mathrm{Cos}(0)\Bigg)\Bigg\}$$

$$c_n = L^{-3}\sqrt{60}\ \Bigg\{-\frac{L^3}{n\pi}\mathrm{Cos}(n\pi) + (\,n^2\pi^2 - 2)\frac{L^3}{n^3\pi^3}\mathrm{Cos}(n\pi)$$

$$+ \frac{2L^3}{n^3\pi^3}\Bigg\}$$

$$c_n = \sqrt{60}\left(\frac{1}{n\pi}(-1)^n + (\,n^2\pi^2 - 2)\frac{1}{n^3\pi^3}(-1)^n + \frac{2}{n^3\pi^3}\right)$$

$$c_n = \sqrt{60}\left(\left(\frac{-1}{n\pi} + \frac{1}{n\pi} - \frac{2}{n^3\pi^3}\right)(-1)^n + \frac{2}{n^3\pi^3}\right)$$

$$c_n = \frac{2\sqrt{60}}{n^3\pi^3}\ )(\,-(-1)^n + 1)$$

$$|c_n|^2 = \frac{4(60)}{n^6\pi^6}\ )(\,-(-1)^n + 1)^2$$

If n is even then $c_n = 0$

If n is odd then $c_n = \frac{(4)(60)(4)}{n^6\pi^6} = \frac{960}{n^6\pi^6}$

The probability of making a measurement of the energy and obtaining one of the eigenvalues, given by:

$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$ is:

$P(E_n) = 0$ if n is even

$$P(E_n) = \frac{960}{n^6\pi^6} \text{ if n is odd}$$

g. $$\langle\Psi|H|\Psi\rangle = \int_0^L \left(\frac{30}{L^5}\right)^{\frac{1}{2}} x(L-x)\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\right)\left(\frac{30}{L^5}\right)^{\frac{1}{2}} x(L-x)dx$$

$$= \left(\frac{30}{L^5}\right)\left(\frac{-\hbar^2}{2m}\right)\int_0^L x(L-x)\left(\frac{d^2}{dx^2}\right)(xL-x^2)\,dx$$

$$= \left(\frac{15\hbar^2}{mL^5}\right)\int_0^L x(L-x)(-2)dx$$

$$= \left(\frac{30\hbar^2}{mL^5}\right)\int_0^L xL-x^2dx$$

$$= \left(\frac{30\hbar^2}{mL^5}\right)\left(L\frac{x^2}{2}-\frac{x^3}{3}\right)\Big|_0^L$$

$$= \left(\frac{30\hbar^2}{mL^5}\right)\left(\frac{L^3}{2}-\frac{L^3}{3}\right)$$

$$= \left(\frac{30\hbar^2}{mL^2}\right)\left(\frac{1}{2}-\frac{1}{3}\right)$$

$$= \frac{30\hbar^2}{6mL^2} = \frac{5\hbar^2}{mL^2}$$

2. $$\langle\Psi|H|\Psi\rangle = \sum_{ij} C_i^* e^{\frac{iE_it}{\hbar}} \langle\Psi_i|H|\Psi_j\rangle e^{\frac{-iE_jt}{\hbar}} C_j$$

Since $\langle\Psi_i|H|\Psi_j\rangle = E_j\delta_{ij}$

$$\langle\Psi|H|\Psi\rangle = \sum_j C_j^*C_jE_je^{\frac{i(E_j-E_j)t}{\hbar}}$$

$$\langle\Psi|H|\Psi\rangle = \sum_j C_j^*C_jE_j \text{ (not time dependent)}$$

For other properties:

$$\langle\Psi|A|\Psi\rangle = \sum_{ij} C_i^* e^{\frac{iE_it}{\hbar}} \langle\Psi_i|A|\Psi_j\rangle e^{\frac{-iE_jt}{\hbar}} C_j$$

<u>but,</u> $\langle\Psi_i|A|\Psi_j\rangle$ does not necessarily = $a_j\delta_{ij}$.

This is only true if [A,H] = 0.

$$\langle\Psi|A|\Psi\rangle = \sum_{ij} C_i^* C_j e^{\frac{i(E_i-E_j)t}{\hbar}} \langle\Psi_i|A|\Psi_j\rangle$$

Therefore, in general, other properties are time dependent.

3. For a particle in a box in its lowest quantum state:

$$\Psi = \sqrt{\frac{2}{L}}\,\mathrm{Sin}\left(\frac{\pi x}{L}\right)$$

$$\langle x\rangle = \int_0^L \Psi^* x \Psi dx$$

$$= \frac{2}{L}\int_0^L x\,\mathrm{Sin}^2\left(\frac{\pi x}{L}\right)dx$$

Using integral equation 18:

$$= \frac{2}{L}\left(\frac{x^2}{4} - \frac{xL}{4\pi}\mathrm{Sin}\left(\frac{2\pi x}{L}\right) - \frac{L^2}{8\pi^2}\mathrm{Cos}\left(\frac{2\pi x}{L}\right)\right)\Bigg|_0^L$$

$$= \frac{2}{L}\left(\frac{L^2}{4} - \frac{L^2}{8\pi^2}(\mathrm{Cos}(2\pi) - \mathrm{Cos}(0))\right)$$

$$= \frac{2}{L}\left(\frac{L^2}{4}\right)$$

$$= \frac{L}{2}$$

$$\langle x^2\rangle = \int_0^L \Psi^* x^2 \Psi dx$$

$$= \frac{2}{L}\int_0^L x^2\,\mathrm{Sin}^2\left(\frac{\pi x}{L}\right)dx$$

Using integral equation 19:

$$= \frac{2}{L}\left(\frac{x^3}{6} - \left(\frac{x^2L}{4\pi} - \frac{L^3}{8\pi^3}\right)\mathrm{Sin}\left(\frac{2\pi x}{L}\right) - \frac{xL^2}{4\pi^2}\mathrm{Cos}\left(\frac{2\pi x}{L}\right)\right)\Bigg|_0^L$$

$$= \frac{2}{L}\left(\frac{L^3}{6} - \frac{L^2}{4\pi^2}(L\mathrm{Cos}(2\pi) - (0)\mathrm{Cos}(0))\right)$$

$$= \frac{2}{L}\left(\frac{L^3}{6} - \frac{L^3}{4\pi^2}\right)$$

$$= \frac{L^2}{3} - \frac{L^2}{2\pi^2}$$

$$\langle p\rangle = \int_0^L \Psi^* p \Psi dx$$

$$= \frac{2}{L}\int_0^L \mathrm{Sin}\left(\frac{\pi x}{L}\right)\left(\frac{\hbar}{i}\frac{d}{dx}\right)\mathrm{Sin}\left(\frac{\pi x}{L}\right)dx$$

$$= \frac{2\hbar\pi}{L^2 i}\int_0^L \mathrm{Sin}\left(\frac{\pi x}{L}\right)\mathrm{Cos}\left(\frac{\pi x}{L}\right)dx$$

$$= \frac{2\hbar}{Li}\int_0^L \mathrm{Sin}\left(\frac{\pi x}{L}\right)\mathrm{Cos}\left(\frac{\pi x}{L}\right)d\left(\frac{\pi x}{L}\right)$$

Using integral equation 15 (with $\theta = \frac{\pi x}{L}$):

$$= \frac{2\hbar}{Li}\left(-\frac{1}{2}\mathrm{Cos}^2(\theta)\Big|_0^{\pi}\right) = 0$$

$$\langle p^2\rangle = \int_0^L \Psi^* p^2 \Psi dx$$

$$= \frac{2}{L}\int_0^L \mathrm{Sin}\left(\frac{\pi x}{L}\right)\left(-\hbar^2\frac{d^2}{dx^2}\right)\mathrm{Sin}\left(\frac{\pi x}{L}\right)dx$$

$$= \frac{2\pi^2\hbar^2}{L^3}\int_0^L \mathrm{Sin}^2\left(\frac{\pi x}{L}\right)dx$$

$$= \frac{2\pi\hbar^2}{L^2}\int_0^L \mathrm{Sin}^2\left(\frac{\pi x}{L}\right)d\left(\frac{\pi x}{L}\right)$$

Using integral equation 10 (with $\theta = \frac{\pi x}{L}$):

$$= \frac{2\pi\hbar^2}{L^2}\left(-\frac{1}{4}\mathrm{Sin}(2\theta) + \frac{\theta}{2}\right)\Big|_0^{\pi}$$

$$= \frac{2\pi\hbar^2}{L^2}\frac{\pi}{2} = \frac{\pi^2\hbar^2}{L^2}$$

$$\Delta x = \left(<x^2> - <x>^2\right)^{\frac{1}{2}}$$

$$= \left(\frac{L^2}{3} - \frac{L^2}{2\pi^2} - \frac{L^2}{4}\right)^{\frac{1}{2}}$$

$$= L\left(\frac{1}{12} - \frac{1}{2\pi^2}\right)^{\frac{1}{2}}$$

$$\Delta p = \left(<p^2> - <p>^2\right)^{\frac{1}{2}}$$

$$= \left(\frac{\pi^2\hbar^2}{L^2} - 0\right)^{\frac{1}{2}} = \frac{\pi\hbar}{L}$$

$$\Delta x\, \Delta p = \pi\hbar\left(\frac{1}{12} - \frac{1}{2\pi^2}\right)^{\frac{1}{2}}$$

$$= \frac{\hbar}{2}\left(\frac{4\pi^2}{12} - \frac{4}{2}\right)^{\frac{1}{2}}$$

$$= \frac{\hbar}{2}\left(\frac{\pi^2}{3} - 2\right)^{\frac{1}{2}}$$

Finally, $\frac{\hbar}{2}\left(\frac{\pi^2}{3} - 2\right)^{\frac{1}{2}} > \frac{\hbar}{2}\left(\frac{(3)^2}{3} - 2\right)^{\frac{1}{2}} = \frac{\hbar}{2}$

$$\Delta x\, \Delta p > \frac{\hbar}{2}$$

4. a. $\int_0^{L/4} P(x)dx = \int_0^{L/4} \frac{1}{L}dx = \frac{1}{L}\, x\Big|_0^{L/4}$

$$= \frac{1}{L}\frac{L}{4} = \frac{1}{4} = 25\%$$

$P_{\text{classical}} = \frac{1}{4}$ (for interval 0 - L/4)

b. This was accomplished in problem 1a. to give:

$$P_n = \frac{1}{4} - \frac{1}{2\pi n}\,\text{Sin}\left(\frac{n\pi}{2}\right)$$

(for interval 0 - L/4)

c. $\lim\limits_{n\to\infty} P_{\text{quantum}} = \lim\limits_{n\to\infty}\left(\frac{1}{4} - \frac{1}{2\pi n}\,\text{Sin}\left(\frac{n\pi}{2}\right)\right)$

$$\lim_{n\to\infty} P_{\text{quantum}} = \frac{1}{4}$$

Therefore as n becomes large the classical limit is approached.

5. a. The Schrödinger equation for a Harmonic Oscillator in 1-dimensional coordinate representation, $\mathbf{H}\,\Psi(x) = E_x\,\Psi(x)$, with the Hamiltonian defined as: $\mathbf{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$, becomes:

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\Psi(x) = E_x\Psi(x).$$

b. The transformation of the kinetic energy term to the momentum representation is trivial : $\mathbf{T} = \frac{\mathbf{p}_x^2}{2m}$. In order to maintain the commutation relation $[\mathbf{x},\mathbf{p}_x] = i\hbar$ and keep the **p** operator unchanged the coordinate operator must become $\mathbf{x} = i\hbar\frac{d}{dp_x}$. The Schrödinger equation for a Harmonic Oscillator in 1-dimensional momentum representation, $\mathbf{H}\,\Psi(p_x) = E_{p_x}\,\Psi(p_x)$, with the Hamiltonian defined as: $\mathbf{H} = \frac{1}{2m}p_x^2 - \frac{k\hbar^2}{2}\frac{d^2}{dp_x^2}$, becomes:

$$\left(\frac{1}{2m}p_x^2 - \frac{k\hbar^2}{2}\frac{d^2}{dp_x^2}\right)\Psi(p_x) = E_{p_x}\,\Psi(p_x).$$

c. For the wavefunction $\Psi(x) = C\exp\left(-\sqrt{mk}\,\frac{x^2}{2\hbar}\right)$,

let $a = \frac{\sqrt{mk}}{2\hbar}$, and hence $\Psi(x) = C\exp(-ax^2)$. Evaluating the derivatives of this expression gives:

$$\frac{d}{dx}\Psi(x) = \frac{d}{dx}C\exp(-ax^2) = -2axC\exp(-ax^2)$$

$$\frac{d^2}{dx^2}\Psi(x) = \frac{d^2}{dx^2}C\exp(-ax^2) = \frac{d}{dx}-2axC\exp(-ax^2)$$

$$= (-2axC)(-2ax\exp(-ax^2)) + (-2aC)(\exp(-ax^2))$$

$$= (4a^2x^2 - 2a)C\exp(-ax^2).$$

$\mathbf{H}\,\Psi(x) = E_x\,\Psi(x)$ then becomes:

$$\mathbf{H}\,\Psi(x) = \left(\frac{-\hbar^2}{2m}(4a^2x^2 - 2a) + \frac{1}{2}kx^2\right)\Psi(x).$$

Clearly the energy (eigenvalue) expression must be independent of x and the two terms containing x^2 terms must cancel upon insertion of a:

$$E_x = \frac{-\hbar^2}{2m}\left(4\left(\frac{\sqrt{mk}}{2\hbar}\right)^2 x^2 - 2\left(\frac{\sqrt{mk}}{2\hbar}\right)\right) + \frac{1}{2}kx^2$$

$$= \frac{-\hbar^2}{2m}\left(\frac{4mkx^2}{4\hbar^2}\right) + \frac{\hbar^2}{2m}\frac{2\sqrt{mk}}{2\hbar} + \frac{1}{2}kx^2$$

$$= -\frac{1}{2}kx^2 + \frac{\hbar\sqrt{mk}}{2m} + \frac{1}{2}kx^2$$

$$= \frac{\hbar\sqrt{mk}}{2m} .$$

Normalization of $\Psi(x)$ to determine the constant C yields the equation:

$$C^2 \int_{-\infty}^{+\infty} \exp\left(-\sqrt{mk}\,\frac{x^2}{\hbar}\right) dx = 1.$$

Using integral equation (1) gives:

$$C^2\, 2\left(\frac{1}{2}\right)\sqrt{\pi}\left(\left(\frac{\sqrt{mk}}{\hbar}\right)^{-\frac{1}{2}}\right) = 1$$

$$C^2 \left(\frac{\pi\hbar}{\sqrt{mk}}\right)^{\frac{1}{2}} = 1$$

$$C^2 = \left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{2}}$$

$$C = \left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{4}}$$

Therefore, $\Psi(x) = \left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(-\sqrt{mk}\,\frac{x^2}{2\hbar}\right)$.

d. Proceeding analogous to part c, for a wavefunction in momentum space $\Psi(p) = C \exp(-\alpha p^2)$, evaluating the derivatives of this expression gives:

$$\frac{d}{dp}\,\Psi(p) = \frac{d}{dp}\, C \exp(-\alpha p^2) = -2\alpha p C \exp(-\alpha p^2)$$

$$\frac{d^2}{dp^2}\,\Psi(p) = \frac{d^2}{dp^2}\, C \exp(-\alpha p^2) = \frac{d}{dp}\, -2\alpha p C \exp(-\alpha p^2)$$

$$= (-2\alpha pC)(-2\alpha p \exp(-\alpha p^2)) + (-2\alpha C)(\exp(-\alpha p^2))$$

$$= (4\alpha^2 p^2 - 2\alpha)\, C\exp(-\alpha p^2).$$

H $\Psi(p) = E_p\, \Psi(p)$ then becomes:

$$\mathbf{H}\,\Psi(p) = \frac{1}{2m}\,p^2 - \frac{k\hbar^2}{2}\,(4\alpha^2 p^2 - 2\alpha)\ \Psi(p)$$

Once again the energy (eigenvalue) expression corresponding to E_p must be independent of p and the two terms containing p^2 terms must cancel with the appropriate choice of α. We also desire our choice of α to give us the same energy we found in part c (in coordinate space).

$$E_p = \frac{1}{2m}\,p^2 - \frac{k\hbar^2}{2}\,(4\alpha^2 p^2 - 2\alpha)$$

Therefore we can find α either of two ways:

(1) $\frac{1}{2m}p^2 = \frac{k\hbar^2}{2}\,4\alpha^2p^2$, or

(2) $\frac{k\hbar^2}{2}\,2\alpha = \frac{\hbar\sqrt{mk}}{2m}$.

Both equations yield $\alpha = \left(2\hbar\sqrt{mk}\right)^{-1}$.

Normalization of Ψ(p) to determine the constant C yields the equation:

$$C^2\int_{-\infty}^{+\infty}\exp\left(-2\alpha p^2\right)\,dp = 1.$$

Using integral equation (1) gives:

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

$$C^2\sqrt{\pi}\left(2\left(2\hbar\sqrt{mk}\right)^{-1}\right)^{-\frac{1}{2}} = 1$$

$$C^2\sqrt{\pi}\left(\hbar\sqrt{mk}\right)^{\frac{1}{2}} = 1$$

$$C^2\left(\pi\hbar\sqrt{mk}\right)^{\frac{1}{2}} = 1$$

$$C^2 = \left(\pi\hbar\sqrt{mk}\right)^{-\frac{1}{2}}$$

$$C = \left(\pi\hbar\sqrt{mk}\right)^{-\frac{1}{4}}$$

Therefore, $\Psi(p) = \left(\pi\hbar\sqrt{mk}\right)^{-\frac{1}{4}}\exp\left(-p^2/(2\hbar\sqrt{mk})\right)$.

Showing that Ψ(p) is the proper fourier transform of Ψ(x) suggests that the fourier integral theorem should hold for the two wavefunctions Ψ(x) and Ψ(p) we have obtained, e.g.

$$\Psi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty}\Psi(x)e^{ipx/\hbar}dx \text{ , for}$$

$$\Psi(x) = \left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left(-\sqrt{mk}\,\frac{x^2}{2\hbar}\right) \text{ , and}$$

$$\Psi(p) = \left(\pi\hbar\sqrt{mk}\right)^{-\frac{1}{4}}\exp\left(-p^2/(2\hbar\sqrt{mk})\right).$$

So, verify that:

$$\left(\pi\hbar\sqrt{mk}\right)^{-\frac{1}{4}}\exp\left(-p^2/(2\hbar\sqrt{mk})\right)$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(-\sqrt{mk}\,\frac{x^2}{2\hbar}\right) e^{ipx/\hbar}\, dx \ .$$

Working with the right-hand side of the equation:

$$= \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{4}}\int_{-\infty}^{+\infty}\exp\left(-\sqrt{mk}\,\frac{x^2}{2\hbar}\right)\left(\mathrm{Cos}\left(\frac{px}{\hbar}\right)+ i\,\mathrm{Sin}\left(\frac{px}{\hbar}\right)\right)dx \ ,$$

the Sin term is odd and the integral will therefore vanish. The remaining integral can be evaluated using the given expression:

$$\int_{-\infty}^{+\infty} e^{-\beta x^2}\mathrm{Cos}\,bx\,dx = \sqrt{\frac{\pi}{\beta}}\; e^{-b^2/4\beta}$$

$$= \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{4}}\int_{-\infty}^{+\infty}\exp\left(-\frac{\sqrt{mk}}{2\hbar}\,x^2\right)\mathrm{Cos}\left(\frac{p}{\hbar}\,x\right)dx$$

$$= \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{4}}\left(\frac{2\pi\hbar}{\sqrt{mk}}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty}\exp\left(\left(-\frac{p^2}{\hbar^2}\right)\frac{2\hbar}{4\sqrt{mk}}\right)$$

$$= \left(\frac{\sqrt{mk}}{\pi\hbar}\right)^{\frac{1}{4}}\left(\frac{1}{\sqrt{mk}}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty}\exp\left(-\frac{p^2}{2\hbar\sqrt{mk}}\right)$$

$$= \left(\frac{\sqrt{mk}}{mk\pi\hbar}\right)^{\frac{1}{4}}\int_{-\infty}^{+\infty}\exp\left(-\frac{p^2}{2\hbar\sqrt{mk}}\right)$$

$$= \left(\hbar\pi\sqrt{mk}\right)^{-\frac{1}{4}}\int_{-\infty}^{+\infty}\exp\left(-\frac{p^2}{2\hbar\sqrt{mk}}\right) = \Psi(p)\text{Q.E.D.}$$

6. a. The lowest energy level for a particle in a 3-dimensional box is when $n_1 = 1$, $n_2 = 1$, and $n_3 = 1$. The total energy (with $L_1 = L_2 = L_3$) will be:

$$E_{total} = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2) = \frac{3h^2}{8mL^2}$$

Note that n = 0 is not possible. The next lowest energy level is when one of the three quantum numbers equals 2 and the other two equal 1:

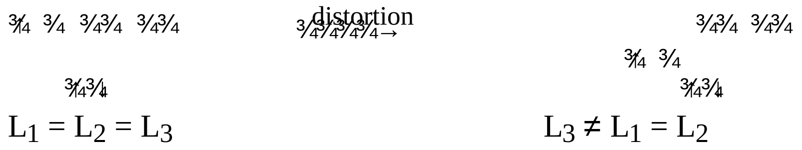
$n_1 = 1$, $n_2 = 1$, $n_3 = 2$
$n_1 = 1$, $n_2 = 2$, $n_3 = 1$
$n_1 = 2$, $n_2 = 1$, $n_3 = 1$.

Each of these three states have the same energy:

$$E_{total} = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2) = \frac{6h^2}{8mL^2}$$

Note that these three states are only degenerate if $L_1 = L_2 = L_3$.

b.



For $L_1 = L_2 = L_3$, $V = L_1L_2L_3 = L_1^3$,

$E_{total}(L_1) = 2\varepsilon_1 + \varepsilon_2$

$$= \frac{2h^2}{8m}\left(\frac{1^2}{L_1^2} + \frac{1^2}{L_2^2} + \frac{1^2}{L_3^2}\right) + \frac{1h^2}{8m}\left(\frac{1^2}{L_1^2} + \frac{1^2}{L_2^2} + \frac{2^2}{L_3^2}\right)$$

$$= \frac{2h^2}{8m}\left(\frac{3}{L_1^2}\right) + \frac{1h^2}{8m}\left(\frac{6}{L_1^2}\right) = \frac{h^2}{8m}\left(\frac{12}{L_1^2}\right)$$

For $L_3 \neq L_1 = L_2$, $V = L_1L_2L_3 = L_1^2L_3$, $L_3 = V/L_1^2$

$E_{total}(L_1) = 2\varepsilon_1 + \varepsilon_2$

$$= \frac{2h^2}{8m}\left(\frac{1^2}{L_1^2} + \frac{1^2}{L_2^2} + \frac{1^2}{L_3^2}\right) + \frac{1h^2}{8m}\left(\frac{1^2}{L_1^2} + \frac{1^2}{L_2^2} + \frac{2^2}{L_3^2}\right)$$

$$= \frac{2h^2}{8m}\left(\frac{2}{L_1^2} + \frac{1}{L_3^2}\right) + \frac{1h^2}{8m}\left(\frac{2}{L_1^2} + \frac{4}{L_3^2}\right)$$

$$= \frac{2h^2}{8m}\left(\frac{2}{L_1^2} + \frac{1}{L_3^2} + \frac{1}{L_1^2} + \frac{2}{L_3^2}\right)$$

$$= \frac{2h^2}{8m}\left(\frac{3}{L_1^2} + \frac{3}{L_3^2}\right) = \frac{h^2}{8m}\left(\frac{6}{L_1^2} + \frac{6}{L_3^2}\right)$$

In comparing the total energy <u>at constant volume</u> of the undistorted box ($L_1 = L_2 = L_3$) versus the distorted box ($L_3 \neq L_1 = L_2$) it can be seen that:

$$\frac{h^2}{8m}\left(\frac{6}{L_1^2} + \frac{6}{L_3^2}\right) \leq \frac{h^2}{8m}\left(\frac{12}{L_1^2}\right) \text{ as long as } L_3 \geq L_1.$$

c. In order to minimize the total energy expression, take the derivative of the energy with respect to L_1 and set it equal to zero. $\frac{\partial E_{total}}{\partial L_1} = 0$

$$\frac{\partial}{\partial L_1}\left(\frac{h^2}{8m}\left(\frac{6}{L_1^2} + \frac{6}{L_3^2}\right)\right) = 0$$

But since $V = L_1L_2L_3 = L_1^2L_3$, then $L_3 = V/L_1^2$. This substitution gives:

$$\frac{\partial}{\partial L_1}\left(\frac{h^2}{8m}\left(\frac{6}{L_1^2} + \frac{6L_1^4}{V^2}\right)\right) = 0$$

$$\left(\frac{h^2}{8m}\left(\frac{(-2)6}{L_1^3} + \frac{(4)6L_1^3}{V^2}\right)\right) = 0$$

$$\left(\frac{12}{L_1^3} + \frac{24L_1^3}{V^2}\right) = 0$$

$$\left(\frac{24L_1^3}{V^2}\right) = \left(\frac{12}{L_1^3}\right)$$

$$24L_1^6 = 12V^2$$

$$L_1^6 = \frac{1}{2}V^2 = \frac{1}{2}(L_1^2L_3)^2 = \frac{1}{2}L_1^4L_3^2$$

$$L_1^2 = \frac{1}{2}L_3^2$$

$$L_3 = \sqrt{2}\,L_1$$

d. Calculate energy upon distortion:

cube: $V = L_1^3$, $L_1 = L_2 = L_3 = (V)^{\frac{1}{3}}$

distorted: $V = L_1^2L_3 = L_1^2\sqrt{2}\,L_1 = \sqrt{2}\,L_1^3$

$$L_3 = \sqrt{2}\left(\frac{V}{\sqrt{2}}\right)^{\frac{1}{3}} \neq L_1 = L_2 = \left(\frac{V}{\sqrt{2}}\right)^{\frac{1}{3}}$$

$$\Delta E = E_{total}(L_1 = L_2 = L_3) - E_{total}(L_3 \neq L_1 = L_2)$$

$$= \frac{h^2}{8m}\left(\frac{12}{L_1^2}\right) - \frac{h^2}{8m}\left(\frac{6}{L_1^2} + \frac{6}{L_3^2}\right)$$

$$= \frac{h^2}{8m}\left(\frac{12}{V^{2/3}} - \frac{6(2)^{1/3}}{V^{2/3}} + \frac{6(2)^{1/3}}{2V^{2/3}}\right)$$

$$= \frac{h^2}{8m}\left(\frac{12 - 9(2)^{1/3}}{V^{2/3}}\right)$$

Since $V = 8\text{Å}^3$, $V^{2/3} = 4\text{Å}^2 = 4 \times 10^{-16}\ \text{cm}^2$, and $\frac{h^2}{8m} = 6.01 \times 10^{-27}$ erg cm^2:

$$\Delta E = 6.01 \times 10^{-27}\ \text{erg cm}^2\left(\frac{12 - 9(2)^{1/3}}{4 \times 10^{-16}\ \text{cm}^2}\right)$$

$$\Delta E = 6.01 \times 10^{-27}\ \text{erg cm}^2\left(\frac{0.66}{4 \times 10^{-16}\ \text{cm}^2}\right)$$

$$\Delta E = 0.99 \times 10^{-11}\ \text{erg}$$

$$\Delta E = 0.99 \times 10^{-11}\ \text{erg}\left(\frac{1\ \text{eV}}{1.6 \times 10^{-12}\ \text{erg}}\right)$$

$\Delta E = 6.19$ eV

7. a. $$\int_{-\infty}^{+\infty} \Psi^*(x)\Psi(x)\,dx = 1.$$

$$A^2 \int_{-\infty}^{+\infty} e^{-2a|x|}\,dx = 1.$$

$$A^2 \int_{-\infty}^{0} e^{2ax}\,dx + A^2 \int_{0}^{+\infty} e^{-2ax}\,dx = 1$$

Making use of integral equation (4) this becomes:

$$A^2\left(\frac{1}{2a} + \frac{1}{2a}\right) = \frac{2A^2}{2a} = 1$$

$A^2 = a$

$A = \pm\sqrt{a}$, therefore A is not unique.

$\Psi(x) = Ae^{-a|x|} = \pm\sqrt{a}\,e^{-a|x|}$

Since a has units of $Å^{-1}$, $\Psi(x)$ must have units of $Å^{-\frac{1}{2}}$.

b. $$|x| = \begin{cases} x \text{ if } x \geq 0 \\ -x \text{ if } x \leq 0 \end{cases}$$

$$\Psi(x) = \sqrt{a}\begin{cases} e^{-ax} \text{ if } x \geq 0 \\ e^{ax} \text{ if } x \leq 0 \end{cases}$$

Sketching this wavefunction with respect to x (keeping constant a fixed; a = 1) gives:

c. $$\frac{d\Psi(x)}{dx} = \sqrt{a}\begin{cases} -ae^{-ax} \text{ if } x \geq 0 \\ ae^{ax} \text{ if } x \leq 0 \end{cases}$$

$$\left.\frac{d\Psi(x)}{dx}\right|_{0+\varepsilon} = -a\sqrt{a}$$

$$\left.\frac{d\Psi(x)}{dx}\right|_{0-\varepsilon} = a\sqrt{a}$$

The magnitude of discontinuity is $a\sqrt{a} + a\sqrt{a} = 2a\sqrt{a}$ as x goes through x = 0. This also indicates that the potential V undergoes a discontinuity of ∞ magnitude at x = 0.

d. $$<|x|> = \int_{-\infty}^{+\infty} \Psi^*(x)|x|\Psi(x)\,dx$$

$$= (\sqrt{a}\,)^2 \int_{-\infty}^{0} e^{2ax}(-x)\ dx + (\sqrt{a}\,)^2 \int_{0}^{+\infty} e^{-2ax}(x)\ dx$$

$$= 2a\int_{0}^{\infty} e^{-2ax}(x)\ dx$$

Making use of integral equation (4) again this becomes:

$$= 2a\,\frac{1}{(2a)^2} = \frac{1}{2a} = \frac{1}{2(2\text{Å})^{-1}}$$

$$\langle|x|\rangle = 1\text{Å}$$

This expectation value is a measure of the average distance (|x|) from the origin.

e. $$\Psi(x) = \sqrt{a}\begin{Bmatrix} e^{-ax} \text{ if } x \geq 0 \\ e^{ax} \text{ if } x \leq 0 \end{Bmatrix}$$

$$\frac{d\Psi(x)}{dx} = \sqrt{a}\begin{Bmatrix} -ae^{-ax} \text{ if } x \geq 0 \\ ae^{ax} \text{ if } x \leq 0 \end{Bmatrix}$$

$$\frac{d^2\Psi(x)}{dx^2} = \sqrt{a}\begin{Bmatrix} a^2e^{-ax} \text{ if } x \geq 0 \\ a^2e^{ax} \text{ if } x \leq 0 \end{Bmatrix} = a^2\Psi(x)$$

$$\langle H\rangle = \left\langle \left(-\frac{\hbar}{2m}\frac{d^2}{dx^2} - \frac{\hbar^2 a}{m}\,\delta(x)\right) \right\rangle$$

$$\langle H\rangle = \int_{-\infty}^{+\infty} \Psi^*(x)\left(-\frac{\hbar}{2m}\,\frac{d^2}{dx^2}\right)\Psi(x)\ dx - \int_{-\infty}^{+\infty} \Psi^*(x)\left(\frac{\hbar^2 a}{m}\ \delta(x)\right)\Psi(x)\ dx$$

$$= -\frac{\hbar a^2}{2m}\int_{-\infty}^{+\infty} \Psi^*(x)\Psi(x)\ dx - \frac{\hbar^2 a}{m}\int_{-\infty}^{+\infty} \Psi^*(x)(\,\delta(x))\,\Psi(x)\ dx$$

Using the integral equation:

$$\int_{a}^{b} f(x)\delta(x-x_0)dx = \begin{Bmatrix} f(x_0) \text{ if } a<x_0<b \\ 0 \quad \text{otherwise} \end{Bmatrix}$$

$$\langle H\rangle = -\frac{\hbar a^2}{2m}(1) - \frac{\hbar^2 a}{m}(\sqrt{a})^2 = -\frac{3\hbar a^2}{2m}$$

$$= -3\ (6.06 \times 10^{-28}\ \text{erg cm}^2)\ (2 \times 10^{-8}\ \text{cm})^{-2}$$

$$= -4.55 \times 10^{-12}\ \text{erg}$$

$$= -2.84\ \text{eV}.$$

f. In problem 5 the relationship between $\Psi(p)$ and $\Psi(x)$ was derived:

$$\Psi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \Psi(x) e^{-ipx/\hbar} dx \; .$$

$$\Psi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \sqrt{a}\, e^{-a|x|} e^{-ipx/\hbar} dx \; .$$

$$\Psi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{0} \sqrt{a}\, e^{ax} e^{-ipx/\hbar} dx \; + \frac{1}{\sqrt{2\pi\hbar}} \int_{0}^{+\infty} \sqrt{a}\, e^{-ax} e^{-ipx/\hbar} dx \; .$$

$$= \sqrt{\frac{a}{2\pi\hbar}} \left(\frac{1}{a-ip/\hbar} + \frac{1}{a+ip/\hbar} \right)$$

$$= \sqrt{\frac{a}{2\pi\hbar}} \left(\frac{2a}{a^2+p^2/\hbar^2} \right)$$

g. $$\frac{\left|\Psi(p=2a\hbar)\right|^2}{\left|\Psi(p=-a\hbar)\right|^2} = \left[\frac{1/(a^2+(2a\hbar)^2/\hbar^2)}{1/(a^2+(-a\hbar)^2/\hbar^2)} \right]^2$$

$$= \left[\frac{1/(a^2+4a^2)}{1/(a^2+a^2)} \right]^2$$

$$= \left[\frac{1/(5a^2)}{1/(2a^2)} \right]^2$$

$$= \left[\frac{2}{5} \right]^2 = 0.16 = 16\%$$

8. a. $\mathbf{H} = \frac{-\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right\}$ (cartesian coordinates)

Finding $\frac{\partial}{\partial x}$ and $\frac{\partial}{\partial y}$ from the chain rule gives:

$$\frac{\partial}{\partial x} = \left(\frac{\partial r}{\partial x}\right)_y \frac{\partial}{\partial r} + \left(\frac{\partial \varphi}{\partial x}\right)_y \frac{\partial}{\partial \varphi} \; , \quad \frac{\partial}{\partial y} = \left(\frac{\partial r}{\partial y}\right)_x \frac{\partial}{\partial r} + \left(\frac{\partial \varphi}{\partial y}\right)_x \frac{\partial}{\partial \varphi} \; ,$$

Evaluation of the "coefficients" gives the following:

$$\left(\frac{\partial r}{\partial x}\right)_y = \mathrm{Cos}\varphi \; , \left(\frac{\partial \varphi}{\partial x}\right)_y = -\frac{\mathrm{Sin}\varphi}{r} \; ,$$

$$\left(\frac{\partial r}{\partial y}\right)_x = \mathrm{Sin}\varphi \; , \text{and} \; \left(\frac{\partial \varphi}{\partial y}\right)_x = \frac{\mathrm{Cos}\varphi}{r} \; ,$$

Upon substitution of these "coefficients":

$$\frac{\partial}{\partial x} = \mathrm{Cos}\varphi\frac{\partial}{\partial r} - \frac{\mathrm{Sin}\varphi}{r}\frac{\partial}{\partial\varphi} = -\frac{\mathrm{Sin}\varphi}{r}\frac{\partial}{\partial\varphi}\text{; at fixed r.}$$

$$\frac{\partial}{\partial y} = \mathrm{Sin}\varphi\frac{\partial}{\partial r} + \frac{\mathrm{Cos}\varphi}{r}\frac{\partial}{\partial\varphi} = \frac{\mathrm{Cos}\varphi}{r}\frac{\partial}{\partial\varphi}\text{; at fixed r.}$$

$$\frac{\partial^2}{\partial x^2} = \left(\frac{\mathrm{Sin}\varphi}{r}\frac{\partial}{\partial\varphi}\right)\left(\frac{\mathrm{Sin}\varphi}{r}\frac{\partial}{\partial\varphi}\right)$$

$$= \frac{\mathrm{Sin}^2\varphi}{r^2}\frac{\partial^2}{\partial\varphi^2} + \frac{\mathrm{Sin}\varphi\mathrm{Cos}\varphi}{r^2}\frac{\partial}{\partial\varphi}\text{ ; at fixed r.}$$

$$\frac{\partial^2}{\partial y^2} = \left(\frac{\mathrm{Cos}\varphi}{r}\frac{\partial}{\partial\varphi}\right)\left(\frac{\mathrm{Cos}\varphi}{r}\frac{\partial}{\partial\varphi}\right)$$

$$= \frac{\mathrm{Cos}^2\varphi}{r^2}\frac{\partial^2}{\partial\varphi^2} - \frac{\mathrm{Cos}\varphi\mathrm{Sin}\varphi}{r^2}\frac{\partial}{\partial\varphi}\text{ ; at fixed r.}$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\mathrm{Sin}^2\varphi}{r^2}\frac{\partial^2}{\partial\varphi^2} + \frac{\mathrm{Sin}\varphi\mathrm{Cos}\varphi}{r^2}\frac{\partial}{\partial\varphi} + \frac{\mathrm{Cos}^2\varphi}{r^2}\frac{\partial^2}{\partial\varphi^2} - \frac{\mathrm{Cos}\varphi\mathrm{Sin}\varphi}{r^2}\frac{\partial}{\partial\varphi}$$

$$= \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\text{ ; at fixed r.}$$

So, $\mathbf{H} = \frac{-\hbar^2}{2mr^2}\frac{\partial^2}{\partial\varphi^2}$ (cylindrical coordinates, fixed r)

$$= \frac{-\hbar^2}{2I}\frac{\partial^2}{\partial\varphi^2}$$

The Schrödinger equation for a particle on a ring then becomes:

$$H\Psi = E\Psi$$

$$\frac{-\hbar^2}{2I}\frac{\partial^2\Phi}{\partial\varphi^2} = E\Phi$$

$$\frac{\partial^2\Phi}{\partial\varphi^2} = \left(\frac{2IE}{\hbar^2}\right)\Phi$$

The general solution to this equation is the now familiar expression:

$$\Phi(\varphi) = C_1e^{-im\varphi} + C_2e^{im\varphi}\text{, where } m = \left(\frac{2IE}{\hbar^2}\right)^{\frac{1}{2}}$$

Application of the cyclic boundary condition, $\Phi(\varphi) = \Phi(\varphi+2\pi)$, results in the quantization of the energy expression: $E = \frac{m^2\hbar^2}{2I}$ where $m = 0, \pm1, \pm2, \pm3, \ldots$ It can be seen that the ±m values correspond to angular momentum of the same magnitude but opposite directions. Normalization of the wavefunction (over the region 0 to 2π) corresponding to + or - m will result in a value of $\left(\frac{1}{2\pi}\right)^{\frac{1}{2}}$ for the normalization constant.

$$\Phi(\varphi) = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} e^{im\varphi}$$

—— —— $\frac{(\pm4)^2\hbar^2}{2I}$

—— —— $\frac{(\pm3)^2\hbar^2}{2I}$

—— —— $\frac{(\pm2)^2\hbar^2}{2I}$

—— —— $\frac{(\pm1)^2\hbar^2}{2I}$

—— $\frac{(0)^2\hbar^2}{2I}$

b. $\frac{\hbar^2}{2m} = 6.06 \times 10^{-28}$ erg cm^2

$$\frac{\hbar^2}{2mr^2} = \frac{6.06 \times 10^{-28}\ \text{erg cm}^2}{(1.4 \times 10^{-8}\ \text{cm})^2}$$

$= 3.09 \times 10^{-12}$ erg

$\Delta E = (2^2 - 1^2)\ 3.09 \times 10^{-12}$ erg $= 9.27 \times 10^{-12}$ erg

but $\Delta E = h\nu = hc/\lambda$ So $\lambda = hc/\Delta E$

$$\lambda = \frac{(6.63 \times 10^{-27}\ \text{erg sec})(3.00 \times 10^{10}\ \text{cm sec}^{-1})}{9.27 \times 10^{-12}\ \text{erg}}$$

$= 2.14 \times 10^{-5}$ cm $= 2.14 \times 10^{3}$ Å

Sources of error in this calculation include:

i. The attractive force of the carbon nuclei is not included in the Hamiltonian.

ii. The repulsive force of the other π-electrons is not included in the Hamiltonian.

iii. Benzene is not a ring.

iv. Electrons move in three dimensions not one.

v. Etc.

9. $\Psi(\varphi,0) = \sqrt{\frac{4}{3\pi}}\ \text{Cos}^2\varphi.$

This wavefunction needs to be expanded in terms of the eigenfunctions of the angular momentum operator, $\left(-i\hbar\frac{\partial}{\partial\varphi}\right)$. This is most easily accomplished by an exponential expansion of the Cos function.

$$\Psi(\varphi,0) = \sqrt{\frac{4}{3\pi}}\left(\frac{e^{i\varphi} + e^{-i\varphi}}{2}\right)\left(\frac{e^{i\varphi} + e^{-i\varphi}}{2}\right)$$

$$= \left(\frac{1}{4}\right)\sqrt{\frac{4}{3\pi}}\left(e^{2i\varphi} + e^{-2i\varphi} + 2e^{(0)i\varphi}\right)$$

The wavefunction is now written in terms of the eigenfunctions of the angular momentum operator, $\left(-i\hbar\frac{\partial}{\partial\varphi}\right)$, but they need to include their normalization constant, $\frac{1}{\sqrt{2\pi}}$.

$$\Psi(\varphi,0) = \left(\frac{1}{4}\right)\sqrt{\frac{4}{3\pi}}\sqrt{2\pi}\left(\frac{1}{\sqrt{2\pi}}\,e^{2i\varphi} + \frac{1}{\sqrt{2\pi}}\,e^{-2i\varphi} + 2\frac{1}{\sqrt{2\pi}}\,e^{(0)i\varphi}\right)$$

$$= \left(\sqrt{\frac{1}{6}}\right)\left(\frac{1}{\sqrt{2\pi}}\,e^{2i\varphi} + \frac{1}{\sqrt{2\pi}}\,e^{-2i\varphi} + 2\frac{1}{\sqrt{2\pi}}\,e^{(0)i\varphi}\right)$$

Once the wavefunction is written in this form (in terms of the normalized eigenfunctions of the angular momentum operator having $m\hbar$ as eigenvalues) the probabilities for observing angular momentums of $0\hbar$, $2\hbar$, and $-2\hbar$ can be easily identified as the square of the coefficients of the corresponding eigenfunctions.

$$P_{2\hbar} = \left(\sqrt{\frac{1}{6}}\right)^2 = \frac{1}{6}$$

$$P_{-2\hbar} = \left(\sqrt{\frac{1}{6}}\right)^2 = \frac{1}{6}$$

$$P_{0\hbar} = \left(2\sqrt{\frac{1}{6}}\right)^2 = \frac{4}{6}$$

10. a. $\left(\frac{-\hbar^2}{2m}\right)\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z) + \frac{1}{2}k(x^2 + y^2 + z^2)\Psi(x,y,z)$

$= E\,\Psi(x,y,z)$.

b. Let $\Psi(x,y,z) = X(x)Y(y)Z(z)$

$$\left(\frac{-\hbar^2}{2m}\right)\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)X(x)Y(y)Z(z) + \frac{1}{2}k(x^2 + y^2 + z^2)X(x)Y(y)Z(z)$$

$= E\,X(x)Y(y)Z(z)$.

$$\left(\frac{-\hbar^2}{2m}\right)Y(y)Z(z)\frac{\partial^2X(x)}{\partial x^2} + \left(\frac{-\hbar^2}{2m}\right)X(x)Z(z)\frac{\partial^2Y(y)}{\partial y^2} + \left(\frac{-\hbar^2}{2m}\right)X(x)Y(y)\frac{\partial^2Z(z)}{\partial z^2} +$$

$$\frac{1}{2}kx^2X(x)Y(y)Z(z) + \frac{1}{2}ky^2X(x)Y(y)Z(z) + \frac{1}{2}kz^2X(x)Y(y)Z(z)$$

$= E\,X(x)Y(y)Z(z)$.

Dividing by $X(x)Y(y)Z(z)$ you obtain:

$$\left(\frac{-\hbar^2}{2m}\right)\left(\frac{1}{X(x)}\right)\frac{\partial^2X(x)}{\partial x^2} + \frac{1}{2}kx^2 + \left(\frac{-\hbar^2}{2m}\right)\left(\frac{1}{Y(y)}\right)\frac{\partial^2Y(y)}{\partial y^2} + \frac{1}{2}ky^2 + \left(\frac{-\hbar^2}{2m}\right)\left(\frac{1}{Z(z)}\right)\frac{\partial^2Z(z)}{\partial z^2} + \frac{1}{2}kz^2 = E.$$

Now you have each variable isolated:

$F(x) + G(y) + H(z) = \text{constant}$

So,

$$\left(\frac{-\hbar^2}{2m}\right)\left(\frac{1}{X(x)}\right)\frac{\partial^2X(x)}{\partial x^2} + \frac{1}{2}kx^2 = E_x \qquad \left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2X(x)}{\partial x^2} + \frac{1}{2}kx^2X(x) = E_xX(x),$$

$$\left(\frac{-\hbar^2}{2m}\right)\left(\frac{1}{Y(y)}\right)\frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{2}ky^2 = E_y \qquad \left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{2}ky^2Y(y) = E_yY(y),$$

$$\left(\frac{-\hbar^2}{2m}\right)\left(\frac{1}{Z(z)}\right)\frac{\partial^2 Z(z)}{\partial z^2} + \frac{1}{2}kz^2 = E_z \qquad \left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2 Z(z)}{\partial z^2} + \frac{1}{2}kz^2Z(z) = E_zZ(z),$$

and $E = E_x + E_y + E_z$.

c. All three of these equations are one-dimensional harmonic oscillator equations and thus each have one-dimensional harmonic oscillator solutions which taken from the text are:

$$X_n(x) = \left(\frac{1}{n!2^n}\right)^{\frac{1}{2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{\left(\frac{-\alpha x^2}{2}\right)} H_n(\alpha^{\frac{1}{2}} x)\ ,$$

$$Y_n(y) = \left(\frac{1}{n!2^n}\right)^{\frac{1}{2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{\left(\frac{-\alpha y^2}{2}\right)} H_n(\alpha^{\frac{1}{2}} y)\ , \text{ and}$$

$$Z_n(z) = \left(\frac{1}{n!2^n}\right)^{\frac{1}{2}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{\left(\frac{-\alpha z^2}{2}\right)} H_n(\alpha^{\frac{1}{2}} z)\ ,$$

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

d. $E_{n_x,n_y,n_z} = E_{n_x} + E_{n_y} + E_{n_z}$

$$= \left(\frac{\hbar^2 k}{\mu}\right)^{\frac{1}{2}}\left\{\left(n_x + \frac{1}{2}\right) + \left(n_y + \frac{1}{2}\right) + \left(n_z + \frac{1}{2}\right)\right\}$$

e. Suppose $E = 5.5\left(\frac{\hbar^2 k}{\mu}\right)^{\frac{1}{2}}$

$$= \left(\frac{\hbar^2 k}{\mu}\right)^{\frac{1}{2}}\left\{\left(n_x + n_y + n_z + \frac{3}{2}\right)\right\}$$

$$5.5 = \left(n_x + n_y + n_z + \frac{3}{2}\right)$$

So, $n_x + n_y + n_z = 4$. This gives rise to a degeneracy of 15. They are:

States 1-3			States 4-6			States 7-9		
n_x	n_y	n_z	n_x	n_y	n_z	n_x	n_y	n_z
4	0	0	3	1	0	0	3	1
0	4	0	3	0	1	1	0	3
0	0	4	1	3	0	0	1	3

States 10-12			States 13-15		
n_x	n_y	n_z	n_x	n_y	n_z
2	2	0	2	1	1
2	0	2	1	2	1
0	2	2	1	1	2

f. Suppose $V = \frac{1}{2}kr^2$ (independent of θ and φ)

The solutions $G(\theta,\varphi)$ are the spherical harmonics $Y_{l,m}(\theta,\varphi)$.

$$\text{g. } -\frac{\hbar^2}{2\mu r^2}\left(\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)\right) + \frac{1}{r^2\text{Sin}\theta}\frac{\partial}{\partial\theta}\left(\text{Sin}\theta\frac{\partial\Psi}{\partial\theta}\right)\right.$$

$$\left. + \frac{1}{r^2\text{Sin}^2\theta}\frac{\partial^2\Psi}{\partial\varphi^2}\right) + \frac{k}{2}(r - r_e)^2\Psi = E\,\Psi ,$$

If $\Psi(r,\theta,\varphi)$ is replaced by $F(r)G(\theta,\varphi)$:

$$-\frac{\hbar^2}{2\mu r^2}\left(\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial F(r)G(\theta,\varphi)}{\partial r}\right)\right) + \frac{F(r)}{r^2\text{Sin}\theta}\frac{\partial}{\partial\theta}\left(\text{Sin}\theta\frac{\partial G(\theta,\varphi)}{\partial\theta}\right)\right.$$

$$\left. + \frac{F(r)}{r^2\text{Sin}^2\theta}\frac{\partial^2 G(\theta,\varphi)}{\partial\varphi^2}\right) + \frac{k}{2}(r - r_e)^2F(r)G(\theta,\varphi) = E\,F(r)G(\theta,\varphi) ,$$

and the angle dependence is recognized as the L^2 angular momentum operator. Division by $G(\theta,\varphi)$ further reduces the equation to:

$$\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial F(r)}{\partial r}\right)\right) + \frac{J(J+1)\hbar^2}{2\mu r_e^2}F(r) + \frac{k}{2}(r - r_e)^2F(r) = E\,F(r) .$$

11. a. $\frac{1}{2}mv^2 = 100\text{ eV}\left(\frac{1.602\times 10^{-12}\text{ erg}}{1\text{ eV}}\right)$

$$v^2 = \left(\frac{(2)1.602\times 10^{-10}\text{ erg}}{9.109\times 10^{-28}\text{g}}\right)$$

$$v = 0.593\times 10^{9}\text{ cm/sec}$$

The length of the N_2 molecule is $2Å = 2\times 10^{-8}$ cm.

$$v = \frac{d}{t}$$

$$t = \frac{d}{v} = \frac{2\times 10^{-8}\text{ cm}}{0.593\times 10^{9}\text{ cm/sec}} = 3.37\times 10^{-17}\text{ sec}$$

b. The normalized ground state harmonic oscillator can be written (from both in the text and in exercise 11) as:

$$\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4}e^{-\alpha x^2/2}, \quad \text{where } \alpha = \left(\frac{k\mu}{\hbar^2}\right)^{\frac{1}{2}} \text{ and } x = r - r_e$$

Calculating constants;

$$\alpha_{N_2} = \left(\frac{(2.294\times 10^{6}\text{ g sec}^{-2})(1.1624\times 10^{-23}\text{ g})}{(1.0546\times 10^{-27}\text{ erg sec})^2}\right)^{\frac{1}{2}}$$

$$= 0.48966\times 10^{19}\text{ cm}^{-2} = 489.66\text{ Å}^{-2}$$

For N_2: $\Psi_0(r) = 3.53333Å^{-\frac{1}{2}}e^{-(244.83Å^{-2})(r-1.09769Å)^2}$

$$\alpha_{N_2^+} = \left(\frac{(2.009 \text{ x } 10^{6} \text{ g sec}^{-2})(1.1624 \text{ x } 10^{-23} \text{ g})}{(1.0546 \text{ x } 10^{-27} \text{ erg sec})^{2}}\right)^{\frac{1}{2}}$$

$$= 0.45823 \text{ x } 10^{19} \text{ cm}^{-2} = 458.23 \text{ Å}^{-2}$$

For N_2^+: $\Psi_0(r) = 3.47522\text{Å}^{-\frac{1}{2}} e^{-(229.113\text{Å}^{-2})(r-1.11642\text{Å})^2}$

c. $P(v=0) = \left| \langle \Psi_{v=0}(N_2^+) | \Psi_{v=0}(N_2) \rangle \right|^2$

Let $P(v=0) = I^2$ where I = integral:

$$I = \int_{-\infty}^{+\infty} (3.47522\text{Å}^{-\frac{1}{2}} e^{-(229.113\text{Å}^{-2})(r-1.11642\text{Å})^2}) \cdot$$

$$(3.53333\text{Å}^{-\frac{1}{2}} e^{-(244.830\text{Å}^{-2})(r-1.09769\text{Å})^2})dr$$

Let $C_1 = 3.47522\text{Å}^{-\frac{1}{2}}$, $C_2 = 3.53333\text{Å}^{-\frac{1}{2}}$,
$A_1 = 229.113\text{Å}^{-2}$, $A_2 = 244.830\text{Å}^{-2}$,
$r_1 = 1.11642\text{Å}$, $r_2 = 1.09769\text{Å}$,

$$I = C_1C_2 \int_{-\infty}^{+\infty} e^{-A_1(r-r_1)^2} e^{-A_2(r-r_2)^2} \, dr \, .$$

Focusing on the exponential:

$$-A_1(r-r_1)^2 - A_2(r-r_2)^2 = -A_1(r^2 - 2r_1r + r_1^2) - A_2(r^2 - 2r_2r + r_2^2)$$

$$= -(A_1 + A_2)r^2 + (2A_1r_1 + 2A_2r_2)r - A_1r_1^2 - A_2r_2^2$$

Let $A = A_1 + A_2$,
$B = 2A_1r_1 + 2A_2r_2$,
$C = C_1C_2$, and
$D = A_1r_1^2 + A_2r_2^2$.

$$I = C \int_{-\infty}^{+\infty} e^{-Ar^2 + Br - D} \, dr$$

$$= C \int_{-\infty}^{+\infty} e^{-A(r-r_0)^2 + D'} \, dr$$

where $-A(r-r_0)^2 + D' = -Ar^2 + Br - D$

$$-A(r^2 - 2rr_0 + r_0^2) + D' = -Ar^2 + Br - D$$

such that, $2Ar_0 = B$

$$-Ar_0^2 + D' = -D$$

and, $r_0 = \frac{B}{2A}$

$$D' = Ar_0^2 - D = A\frac{B^2}{4A^2} - D = \frac{B^2}{4A} - D \, .$$

$$I = C \int_{-\infty}^{+\infty} e^{-A(r-r_0)^2 + D'} \, dr$$

$$= Ce^{D'} \int_{-\infty}^{+\infty} e^{-Ay^2} \, dy$$

$$= Ce^{D'}\sqrt{\frac{\pi}{A}}$$

Now back substituting all of these constants:

$$I = C_1C_2\sqrt{\frac{\pi}{A_1 + A_2}} \exp\left(\frac{(2A_1r_1 + 2A_2r_2)^2}{4(A_1 + A_2)} - A_1r_1^2 - A_2r_2^2\right)$$

$$I = (3.47522)(3.53333)\sqrt{\frac{\pi}{(229.113) + (244.830)}}$$

$$\cdot \exp\left(\frac{(2(229.113)(1.11642) + 2(244.830)(1.09769))^2}{4((229.113) + (244.830))}\right)$$

$$\cdot \exp(-(229.113)(1.11642)^2 - (244.830)(1.09769)^2)$$

$I = 0.959$

$P(v=0) = I^2 = 0.92$

12. a. $E_\nu = \left(\frac{\hbar^2 k}{\mu}\right)^{\frac{1}{2}}\left(\nu + \frac{1}{2}\right)$

$\Delta E = E_{\nu+1} - E_\nu$

$$= \left(\frac{\hbar^2 k}{\mu}\right)^{\frac{1}{2}}\left\{\nu + 1 + \frac{1}{2} - \nu - \frac{1}{2}\right\} = \left(\frac{\hbar^2 k}{\mu}\right)$$

$$= \left(\frac{(1.0546 \times 10^{-27} \text{ erg sec})^2 (1.87 \times 10^6 \text{ g sec}^{-2})}{6.857 \text{ g} / 6.02 \times 10^{23}}\right)^{\frac{1}{2}}$$

$= 4.27 \times 10^{-13}$ erg

$$\Delta E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-27} \text{ erg sec})(3.00 \times 10^{10} \text{ cm sec}^{-1})}{4.27 \times 10^{-13} \text{ erg}}$$

$= 4.66 \times 10^{-4}$ cm

$$\frac{1}{\lambda} = 2150\ \text{cm}^{-1}$$

b. $\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$

$$\langle x\rangle = \langle \Psi_{v=0} | x | \Psi_{v=0} \rangle$$

$$= \int_{-\infty}^{+\infty} \Psi_0^* x \Psi_0 dx$$

$$= \int_{-\infty}^{+\infty} \left(\frac{\alpha}{\pi}\right)^{1/2} x e^{-\alpha x^2} dx$$

$$= \int_{-\infty}^{+\infty} \left(\frac{\alpha}{-\alpha^2\pi}\right)^{1/2} e^{-\alpha x^2} d(-\alpha x^2)$$

$$= \left(\frac{1}{\alpha\pi}\right)^{1/2} e^{-\alpha x^2} \Big|_{-\infty}^{+\infty} = 0$$

$$\langle x^2\rangle = \langle \Psi_{v=0} | x^2 | \Psi_{v=0} \rangle$$

$$= \int_{-\infty}^{+\infty} \Psi_0^* x^2 \Psi_0 dx$$

$$= \int_{-\infty}^{+\infty} \left(\frac{\alpha}{\pi}\right)^{1/2} x^2 e^{-\alpha x^2} dx$$

$$= 2\left(\frac{\alpha}{\pi}\right)^{1/2} \int_{0}^{+\infty} x^2 e^{-\alpha x^2} dx$$

Using integral equation (4) this becomes:

$$= 2\left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{1}{2^{1+1}\alpha}\right) \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$= \left(\frac{1}{2\alpha}\right)$$

$$\Delta x = (\langle x^2\rangle - \langle x\rangle^2)^{1/2} .= \left(\frac{1}{2\alpha}\right)$$

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

$$= \left(\frac{(1.0546 \times 10^{-27}\ \text{erg sec})^2}{4(1.87 \times 10^{6}\ \text{g sec}^{-2})(6.857\ \text{g} / 6.02 \times 10^{23})}\right)^{\frac{1}{4}}$$

$= 3.38 \times 10^{-10}$ cm = 0.0338Å

c. $$\Delta x = \left(\frac{\hbar}{2\sqrt{k\mu}}\right)^{\frac{1}{2}}$$

The smaller k and μ become, the larger the uncertainty in the internuclear distance becomes.

Helium has a small μ and small force between atoms. This results in a very large Δx. This implies that it is extremely difficult for He atoms to "vibrate" with small displacement as a solid even as absolute zero is approached.

13. a. $$W = \left(Z_e^2 - 2ZZ_e + \frac{5}{8}Z_e\right)\frac{e^2}{a_0}$$

$$\frac{dW}{dZ_e} = \left(2Z_e - 2Z + \frac{5}{8}\right)\frac{e^2}{a_0} = 0$$

$$2Z_e - 2Z + \frac{5}{8} = 0$$

$$2Z_e = 2Z - \frac{5}{8}$$

$Z_e = Z - \frac{5}{16} = Z - 0.3125$ (Note this is the shielding factor of one 1s electron to the other).

$$W = Z_e\left(Z_e - 2Z + \frac{5}{8}\right)\frac{e^2}{a_0}$$

$$W = \left(Z - \frac{5}{16}\right)\left(\left(Z - \frac{5}{16}\right) - 2Z + \frac{5}{8}\right)\frac{e^2}{a_0}$$

$$W = \left(Z - \frac{5}{16}\right)\left(-Z + \frac{5}{16}\right)\frac{e^2}{a_0}$$

$$W = -\left(Z - \frac{5}{16}\right)\left(Z - \frac{5}{16}\right)\frac{e^2}{a_0} = -\left(Z - \frac{5}{16}\right)^2\frac{e^2}{a_0}$$

$$= -(Z - 0.3125)^2(27.21)\ \text{eV}$$

b. Using the above result for W and the percent error as calculated below we obtain the following:

$$\%\text{error} = \frac{(\text{Experimental-Theoretical})}{\text{Experimental}} * 100$$

Z	Atom	Experimental	Calculated	% Error
Z = 1	H^-	-14.35 eV	-12.86 eV	10.38%
Z = 2	He	-78.98 eV	-77.46 eV	1.92%
Z = 3	Li^+	-198.02 eV	-196.46 eV	0.79%
Z = 4	Be^{+2}	-371.5 eV	-369.86 eV	0.44%

Z = 5	B^{+3}	-599.3 eV	-597.66 eV	0.27%
Z = 6	C^{+4}	-881.6 eV	-879.86 eV	0.19%
Z = 7	N^{+5}	-1218.3 eV	-1216.48 eV	0.15%
Z = 8	O^{+6}	-1609.5 eV	-1607.46 eV	0.13%

The ignored electron correlation effects are essentially constant over the range of Z, but this correlation effect is a larger percentage error at small Z. At large Z the dominant interaction is electron attraction to the nucleus completely overwhelming the ignored electron correlation and hence reducing the overall percent error.

c. Since -12.86 eV (H^-) is greater than -13.6 eV (H + e) this simple variational calculation erroneously predicts H^- to be unstable.

14. a.

$$W = \int_{-\infty}^{\infty} \varphi^* H \varphi dx$$

$$W = \left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-bx^2} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + a|x|\right) e^{-bx^2} dx$$

$$\frac{d^2}{dx^2} e^{-bx^2} = \frac{d}{dx}\left(-2bx\ e^{-bx^2}\right)$$

$$= (-2bx)\left(-2bx\ e^{-bx^2}\right) + \left(e^{-bx^2}\right)(-2b)$$

$$= \left(4b^2x^2\ e^{-bx^2}\right) + \left(-2b\ e^{-bx^2}\right)$$

Making this substitution results in the following three integrals:

$$W = \left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \left(-\frac{\hbar^2}{2m}\right) \int_{-\infty}^{\infty} e^{-bx^2}\ 4b^2x^2\ e^{-bx^2} dx\ +$$

$$\left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \left(-\frac{\hbar^2}{2m}\right) \int_{-\infty}^{\infty} e^{-bx^2}\ -2b\ e^{-bx^2} dx\ +$$

$$\left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-bx^2}\ a|x| e^{-bx^2} dx$$

$$= \left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \left(-\frac{2b^2\hbar^2}{m}\right) \int_{-\infty}^{\infty} x^2 e^{-2bx^2} dx + \left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \left(\frac{b\hbar^2}{m}\right) \int_{-\infty}^{\infty} e^{-2bx^2} dx +$$

$$\left(\frac{2b}{\pi}\right)^{\frac{1}{2}} a \int_{-\infty}^{\infty} |x| e^{-2bx^2} dx$$

Using integral equations (1), (2), and (3) this becomes:

$$= \left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \left(-\frac{2b^2\hbar^2}{m}\right) 2 \left(\frac{1}{2^2 2b}\right)\sqrt{\frac{\pi}{2b}} + \left(\frac{2b}{\pi}\right)^{\frac{1}{2}} \left(\frac{b\hbar^2}{m}\right) 2 \left(\frac{1}{2}\right)\sqrt{\frac{\pi}{2b}} +$$

$$\left(\frac{2b}{\pi}\right)^{\frac{1}{2}} a \left(\frac{0!}{2b}\right)$$

$$= \left(-\frac{b\hbar^2}{m}\right)\left(\frac{1}{2}\right) + \left(\frac{b\hbar^2}{m}\right) + \left(\frac{2b}{\pi}\right)^{\frac{1}{2}}\left(\frac{a}{2b}\right)$$

$$W = \left(\frac{b\hbar^2}{2m}\right) + a\left(\frac{1}{2b\pi}\right)^{\frac{1}{2}}$$

b. Optimize b by evaluating $\frac{dW}{db} = 0$

$$\frac{dW}{db} = \frac{d}{db}\left(\left(\frac{b\hbar^2}{2m}\right) + a\left(\frac{1}{2b\pi}\right)^{\frac{1}{2}}\right)$$

$$= \left(\frac{\hbar^2}{2m}\right) - \frac{a}{2}\left(\frac{1}{2\pi}\right)^{\frac{1}{2}} b^{-\frac{3}{2}}$$

So, $\frac{a}{2}\left(\frac{1}{2\pi}\right)^{\frac{1}{2}} b^{-\frac{3}{2}} = \left(\frac{\hbar^2}{2m}\right)$ or, $b^{-\frac{3}{2}} = \left(\frac{\hbar^2}{2m}\right)\frac{2}{a}\left(\frac{1}{2\pi}\right)^{-\frac{1}{2}} = \left(\frac{\hbar^2}{ma}\right)\sqrt{2\pi}$,

and, $b = \left(\frac{ma}{\sqrt{2\pi}\,\hbar^2}\right)^{\frac{2}{3}}$. Substituting this value of b into the expression for W gives:

$$W = \left(\frac{\hbar^2}{2m}\right)\left(\frac{ma}{\sqrt{2\pi}\,\hbar^2}\right)^{\frac{2}{3}} + a\left(\frac{1}{2\pi}\right)^{\frac{1}{2}}\left(\frac{ma}{\sqrt{2\pi}\,\hbar^2}\right)^{-\frac{1}{3}}$$

$$= \left(\frac{\hbar^2}{2m}\right)\left(\frac{ma}{\sqrt{2\pi}\,\hbar^2}\right)^{\frac{2}{3}} + a\left(\frac{1}{2\pi}\right)^{\frac{1}{2}}\left(\frac{ma}{\sqrt{2\pi}\,\hbar^2}\right)^{-\frac{1}{3}}$$

$$= 2^{-\frac{4}{3}} \pi^{-\frac{1}{3}} \hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{-\frac{1}{3}} + 2^{-\frac{1}{3}} \pi^{-\frac{1}{3}} \hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{-\frac{1}{3}}$$

$$= \left(2^{-\frac{4}{3}}\pi^{-\frac{1}{3}} + 2^{-\frac{1}{3}}\pi^{-\frac{1}{3}}\right)\hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{-\frac{1}{3}} = \frac{3}{2}(2\pi)^{-\frac{1}{3}}\hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{-\frac{1}{3}}$$

$$= 0.812889106\hbar^{\frac{2}{3}} a^{\frac{2}{3}} m^{-\frac{1}{3}}$$ in error = 0.5284% !!!!!

15. a. $\mathbf{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$

$\varphi = \sqrt{\frac{15}{16}}\, a^{-\frac{5}{2}}(a^2 - x^2)$ for $-a < x < a$

$\varphi = 0$ for $|x| \geq a$

$$\int_{-\infty}^{+\infty} \varphi^* \mathbf{H} \varphi \, dx$$

$$= \int_{-a}^{+a} \sqrt{\frac{15}{16}}\, a^{-\frac{5}{2}}(a^2 - x^2)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\sqrt{\frac{15}{16}}\, a^{-\frac{5}{2}}(a^2 - x^2)\, dx$$

$$= \left(\frac{15}{16}\right)a^{-5}\int_{-a}^{+a}(a^2 - x^2)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)(a^2 - x^2)\, dx$$

$$= \left(\frac{15}{16}\right)a^{-5}\int_{-a}^{+a}(a^2 - x^2)\left(-\frac{\hbar^2}{2m}\right)\frac{d^2}{dx^2}(a^2 - x^2)\, dx$$

$$+ \left(\frac{15}{16}\right)a^{-5}\int_{-a}^{+a}(a^2 - x^2)\frac{1}{2}kx^2(a^2 - x^2)\, dx$$

$$= \left(\frac{15}{16}\right)a^{-5}\int_{-a}^{+a}(a^2 - x^2)\left(-\frac{\hbar^2}{2m}\right)(-2)\, dx$$

$$+ \left(\frac{15}{32}\right)a^{-5}\int_{-a}^{+a}(kx^2)(a^4 - 2a^2x^2 + x^4)\, dx$$

$$= \left(\frac{15\hbar^2}{16m}\right)a^{-5}\int_{-a}^{+a}(a^2 - x^2)\, dx + \left(\frac{15}{32}\right)a^{-5}\int_{-a}^{+a} a^4kx^2 - 2a^2kx^4 + kx^6\, dx$$

$$= \left(\frac{5\hbar^2}{16m}\right) a^{-5}\left(a^2 x \Big|_{-a}^{a} - \frac{1}{3} x^3 \Big|_{-a}^{a} \right)$$

$$+ \left(\frac{15}{32}\right) a^{-5}\left(\frac{a^4 k}{3} x^3 \Big|_{-a}^{a} - \frac{2a^2 k}{5} x^5 \Big|_{-a}^{a} + \frac{k}{7} x^7 \Big|_{-a}^{a} \right)$$

$$= \left(\frac{5\hbar^2}{16m}\right) a^{-5}\left(2a^3 - \frac{2}{3} a^3 \right) + \left(\frac{15}{32}\right) a^{-5}\left(\frac{2a^7 k}{3} - \frac{4a^7 k}{5} + \frac{2k}{7} a^7 \right)$$

$$= \left(\frac{15}{16}\right) a^{-5}\left(\frac{4\hbar^2}{3m} a^3 + \frac{a^7 k}{3} - \frac{2a^7 k}{5} + \frac{k}{7} a^7 \right)$$

$$= \left(\frac{15}{16}\right) a^{-5}\left(\frac{4\hbar^2}{3m} a^3 + \left(\frac{k}{3} - \frac{2k}{5} + \frac{k}{7} \right) a^7 \right)$$

$$= \left(\frac{15}{16}\right) a^{-5}\left(\frac{4\hbar^2}{3m} a^3 + \left(\frac{35k}{105} - \frac{42k}{105} + \frac{15k}{105} \right) a^7 \right)$$

$$= \left(\frac{15}{16}\right) a^{-5}\left(\frac{4\hbar^2}{3m} a^3 + \left(\frac{8k}{105} \right) a^7 \right) = \frac{5\hbar^2}{4ma^2} + \frac{ka^2}{14}$$

b. Substituting $a = b\left(\frac{\hbar^2}{km}\right)^{\frac{1}{4}}$ into the above expression for E we obtain:

$$E = \frac{5\hbar^2}{4b^2 m}\left(\frac{km}{\hbar^2}\right)^{\frac{1}{2}} + \frac{kb^2}{14}\left(\frac{\hbar^2}{km}\right)^{\frac{1}{2}}$$

$$= \hbar\; k^{\frac{1}{2}}\; m^{-\frac{1}{2}} \left(\frac{5}{4} b^{-2} + \frac{1}{14} b^2 \right)$$

Plotting this expression for the energy with respect to b having values of 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 gives:

c. $E = \frac{5\hbar^2}{4ma^2} + \frac{ka^2}{14}$

$$\frac{dE}{da} = -\frac{10\hbar^2}{4ma^3} + \frac{2ka}{14} = -\frac{5\hbar^2}{2ma^3} + \frac{ka}{7} = 0$$

$$\frac{5\hbar^2}{2ma^3} = \frac{ka}{7} \text{ and } 35\hbar^2 = 2mka^4$$

So, $a^4 = \frac{35\hbar^2}{2mk}$, or $a = \left(\frac{35\hbar^2}{2mk}\right)^{\frac{1}{4}}$

Therefore $\varphi_{best} = \sqrt{\frac{15}{16}}\left(\frac{35\hbar^2}{2mk}\right)^{-\frac{5}{8}}\left(\left(\frac{35\hbar^2}{2mk}\right)^{\frac{1}{2}} - x^2\right)$,

and $E_{best} = \frac{5\hbar^2}{4m}\left(\frac{2mk}{35\hbar^2}\right)^{\frac{1}{2}} + \frac{k}{14}\left(\frac{35\hbar^2}{2mk}\right)^{\frac{1}{2}} = \hbar\; k^{\frac{1}{2}}\; m^{-\frac{1}{2}}\left(\frac{5}{14}\right)^{\frac{1}{2}}$.

d. $$\frac{E_{best} - E_{true}}{E_{true}} = \frac{\hbar\, k^{\frac{1}{2}}\, m^{-\frac{1}{2}} \left(\left(\frac{5}{14}\right)^{\frac{1}{2}} - 0.5 \right)}{\hbar\, k^{\frac{1}{2}}\, m^{-\frac{1}{2}}\, 0.5}$$

$$= \frac{\left(\frac{5}{14}\right)^{\frac{1}{2}} - 0.5}{0.5} = \frac{0.0976}{0.5} = 0.1952 = 19.52\%$$

16. a. $E^2 = m^2c^4 + p^2c^2.$

$$= m^2c^4\left(1 + \frac{p^2}{m^2c^2}\right)$$

$$E = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}}$$

$$\approx mc^2\left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \ldots\right)$$

$$= mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots)$$

Let $V = -\frac{p^4}{8m^3c^2}$

b. $E^{(1)}_{1s} = \langle \Psi(r)_{1s}{}^* \; V \; \Psi(r)_{1s} \rangle$

$$E^{(1)}_{1s} = \int \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(\frac{1}{\pi}\right)^{\frac{1}{2}} e^{-\frac{Zr}{a}} \left(\frac{p^4}{8m^3c^2}\right) \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(\frac{1}{\pi}\right)^{\frac{1}{2}} e^{-\frac{Zr}{a}} \, d\tau$$

Substituting $p = -i\hbar\nabla$, $d\tau = r^2dr\,\mathrm{Sin}\theta d\theta\, d\varphi$, and pulling out constants gives:

$$E^{(1)}_{1s} = \left(\frac{-\hbar^4}{8m^3c^2}\right)\left(\frac{Z}{a}\right)^3\left(\frac{1}{\pi}\right)\int_0^\infty e^{-\frac{Zr}{a}}\,\nabla^2\,\nabla^2\, e^{-\frac{Zr}{a}}\, r^2dr \int_0^\pi \mathrm{Sin}\theta d\theta \int_0^{2\pi} d\varphi\ .$$

The integrals over the angles are easy, $\int_0^{2\pi} d\varphi = 2\pi$ and $\int_0^{\pi} \mathrm{Sin}\theta d\theta = 2$.

The work remaining is in evaluating the integral over r. Substituting

$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}$ we obtain:

$$\nabla^2 e^{-\frac{Zr}{a}} = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} e^{-\frac{Zr}{a}} = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{-Z}{a} e^{-\frac{Zr}{a}} = \frac{-Z}{a}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 e^{-\frac{Zr}{a}}$$

$$= \frac{-Z}{a}\frac{1}{r^2}\left(\frac{\partial}{\partial r} r^2 e^{-\frac{Zr}{a}}\right) = \frac{-Z}{a}\frac{1}{r^2}\left(r^2 \frac{-Z}{a} e^{-\frac{Zr}{a}} + e^{-\frac{Zr}{a}} 2r\right)$$

$$= \frac{-Z}{a}\left(-\frac{Z}{a} + \frac{2}{r}\right) e^{-\frac{Zr}{a}} = \left(\left(\frac{Z}{a}\right)^2 - \frac{2Z}{ar}\right) e^{-\frac{Zr}{a}} .$$

The integral over r then becomes:

$$\int_0^\infty e^{-\frac{Zr}{a}} \nabla^2 \nabla^2 e^{-\frac{Zr}{a}} r^2 dr = \int_0^\infty \left(\left(\frac{Z}{a}\right)^2 - \frac{2Z}{ar}\right)^2 e^{-\frac{2Zr}{a}} r^2 dr$$

$$= \int_0^\infty \left(\left(\frac{Z}{a}\right)^4 - \frac{4}{r}\left(\frac{Z}{a}\right)^3 + \frac{4}{r^2}\left(\frac{Z}{a}\right)^2\right) r^2 e^{-\frac{2Zr}{a}} dr$$

$$= \int_0^\infty \left(\left(\frac{Z}{a}\right)^4 r^2 - 4\left(\frac{Z}{a}\right)^3 r + 4\left(\frac{Z}{a}\right)^2\right) e^{-\frac{2Zr}{a}} dr$$

Using integral equation (4) these integrals can easily be evaluated:

$$= 2\left(\frac{Z}{a}\right)^4\left(\frac{a}{2Z}\right)^3 - 4\left(\frac{Z}{a}\right)^3\left(\frac{a}{2Z}\right)^2 + 4\left(\frac{Z}{a}\right)^2\left(\frac{a}{2Z}\right)$$

$$= \left(\frac{Z}{4a}\right) - \left(\frac{Z}{a}\right) + 2\left(\frac{Z}{a}\right) = \left(\frac{5Z}{4a}\right)$$

So, $E^{(1)}_{1s} = \left(-\frac{\hbar^4}{8m^3c^2}\right)\left(\frac{Z}{a}\right)^3\left(\frac{1}{\pi}\right)\left(\frac{5Z}{4a}\right)4\pi = -\frac{5\hbar^4Z^4}{8m^3c^2a^4}$

Substituting $a_0 = \frac{\hbar^2}{m_e e^2}$ gives:

$$E^{(1)}_{1s} = -\frac{5\hbar^4Z^4m^4e^8}{8m^3c^2\hbar^8} = -\frac{5Z^4me^8}{8c^2\hbar^4}$$

Notice that $E_{1s} = -\frac{Z^2me^4}{2\hbar^2}$, so, $E_{1s}{}^2 = -\frac{Z^4m^2e^8}{4\hbar^4}$ and that $E^{(1)}_{1s} = \frac{5m}{2} E_{1s}{}^2$

c. $\frac{E^{(1)}_{1s}}{E_{1s}} = \left(-\frac{5Z^4me^8}{8c^2\hbar^4}\right)\left(-\frac{2\hbar^2}{Z^2me^4}\right) = 10\% = 0.1$

$$\frac{5Z^2e^4}{4c^2\hbar^2} = 0.1 \text{ , so, } Z^2 = \frac{(0.1)4c^2\hbar^2}{5e^4}$$

$$Z^2 = \frac{(0.1)(4)(3.00\text{x}10^{10})^2(1.05\text{x}10^{-27})^2}{(5)(4.8\text{x}10^{-10})^4}$$

$Z^2 = 1.50\text{x}10^3$
$Z = 39$

17. a. $$\mathbf{H}_0\, \psi_{lm}^{(0)} = \frac{\mathbf{L}^2}{2m_er_0^2}\, \psi_{lm}^{(0)} = \frac{\mathbf{L}^2}{2m_er_0^2}\, Y_{l,m}(\theta,\varphi)$$
$$= \frac{1}{2m_er_0^2}\, \hbar^2\, l(l+1)\, Y_{l,m}(\theta,\varphi)$$
$$E_{lm}^{(0)} = \frac{\hbar^2}{2m_er_0^2}\, l(l+1)$$

b. $V = -e\varepsilon z = -e\varepsilon r_0\text{Cos}\theta$

$$E_{00}^{(1)} = \langle Y_{00}|V|Y_{00}\rangle = \langle Y_{00}|-e\varepsilon r_0\text{Cos}\theta|Y_{00}\rangle$$
$$= -e\varepsilon r_0\langle Y_{00}|\text{Cos}\theta|Y_{00}\rangle$$

Using the given identity this becomes:

$$E_{00}^{(1)} = -e\varepsilon r_0\langle Y_{00}|Y_{10}\rangle\sqrt{\frac{(0+0+1)(0-0+1)}{(2(0)+1)(2(0)+3)}} + -e\varepsilon r_0\langle Y_{00}|Y_{-10}\rangle\sqrt{\frac{(0+0)(0-0)}{(2(0)+1)(2(0)-1)}}$$

The spherical harmonics are orthonormal, thus $\langle Y_{00}|Y_{10}\rangle = \langle Y_{00}|Y_{-10}\rangle = 0$, and $E_{00}^{(1)} = 0$.

$$E_{00}^{(2)} = \sum_{lm\neq 00} \frac{\left|\langle Y_{lm}|V|Y_{00}\rangle\right|^2}{E_{00}^{(0)} - E_{lm}^{(0)}}$$

$$\langle Y_{lm}|V|Y_{00}\rangle = -e\varepsilon r_0\langle Y_{lm}|\text{Cos}\theta|Y_{00}\rangle$$

Using the given identity this becomes:

$$\langle Y_{lm}|V|Y_{00}\rangle = -e\varepsilon r_0\langle Y_{lm}|Y_{10}\rangle\sqrt{\frac{(0+0+1)(0-0+1)}{(2(0)+1)(2(0)+3)}} + -e\varepsilon r_0\langle Y_{lm}|Y_{-10}\rangle\sqrt{\frac{(0+0)(0-0)}{(2(0)+1)(2(0)-1)}}$$

$$\langle Y_{lm}|V|Y_{00}\rangle = -\frac{e\varepsilon r_0}{\sqrt{3}}\langle Y_{lm}|Y_{10}\rangle$$

This indicates that the only term contributing to the sum in the expression for $E_{00}^{(2)}$ is when lm = 10 (l=1, and m=0), otherwise $\langle Y_{lm}|V|Y_{00}\rangle$ vanishes (from orthonormality). In quantum chemistry when using orthonormal functions it is typical to write the term $\langle Y_{lm}|Y_{10}\rangle$ as a delta function, for example $\delta_{lm,10}$, which only has values of 1 or 0; $\delta_{ij} = 1$ when $i = j$ and 0 when $i \neq j$. This delta function when inserted into the sum then eliminates the sum by "picking out" the non-zero component. For example,

$$\langle Y_{lm}|V|Y_{00}\rangle = -\frac{e\varepsilon r_0}{\sqrt{3}}\,\delta_{lm,10} \text{ ,so}$$

$$E_{00}^{(2)} = \sum_{lm\neq 00} \frac{e^2\varepsilon^2 r_0^2}{3}\,\frac{\delta_{lm,10}^{\;2}}{E_{00}^{(0)} - E_{lm}^{(0)}} = \frac{e^2\varepsilon^2 r_0^2}{3}\,\frac{1}{E_{00}^{(0)} - E_{10}^{(0)}}$$

$$E_{00}^{(0)} = \frac{\hbar^2}{2m_e r_0^2}\,0(0+1) = 0 \text{ and } E_{10}^{(0)} = \frac{\hbar^2}{2m_e r_0^2}\,1(1+1) = \frac{\hbar^2}{m_e r_0^2}$$

Inserting these energy expressions above yields:

$$E_{00}^{(2)} = -\frac{e^2\varepsilon^2 r_0^2}{3}\,\frac{m_e r_0^2}{\hbar^2} = -\frac{m_e e^2\varepsilon^2 r_0^4}{3\hbar^2}$$

c. $E_{00} = E_{00}^{(0)} + E_{00}^{(1)} + E_{00}^{(2)} + \ldots$

$$= 0 + 0 - \frac{m_e e^2\varepsilon^2 r_0^4}{3\hbar^2}$$

$$= -\frac{m_e e^2\varepsilon^2 r_0^4}{3\hbar^2}$$

$$\alpha = -\frac{\partial^2 E}{\partial^2 \varepsilon} = \frac{\partial^2}{\partial^2 \varepsilon}\left(\frac{m_e e^2\varepsilon^2 r_0^4}{3\hbar^2}\right)$$

$$= \frac{2m_e e^2 r_0^4}{3\hbar^2}$$

d. $$\alpha = \frac{2(9.1095\text{x}10^{-28}\text{g})(4.80324\text{x}10^{-10}\text{g}^{\frac{1}{2}}\text{cm}^{\frac{3}{2}}\text{s}^{-1})^2 r_0^4}{3(1.05459\text{x}10^{-27}\text{ g cm}^2\text{ s}^{-1})^2}$$

$\alpha = r_0^4\ 12598\text{x}10^6\text{cm}^{-1} = r_0^4\ 1.2598\text{Å}^{-1}$

$\alpha_H = 0.0987\ \text{Å}^3$

$\alpha_{Cs} = 57.57\ \text{Å}^3$

18. a. $V = e\varepsilon\left(x - \frac{L}{2}\right)$, $\psi_n^{(0)} = \left(\frac{2}{L}\right)^{\frac{1}{2}} \text{Sin}\left(\frac{n\pi x}{L}\right)$, and

$$E_n^{(0)} = \frac{\hbar^2\pi^2 n^2}{2mL^2}\ .$$

$$E_{n=1}^{(1)} = \left\langle \psi_{n=1}^{(0)}|V|\psi_{n=1}^{(0)}\right\rangle = \left\langle \psi_{n=1}^{(0)}\middle|e\varepsilon\left(x - \frac{L}{2}\right)\middle|\psi_{n=1}^{(0)}\right\rangle$$

$$= \left(\frac{2}{L}\right)\int_0^L \text{Sin}^2\left(\frac{\pi x}{L}\right) e\varepsilon\left(x - \frac{L}{2}\right)dx$$

$$= \left(\frac{2\varepsilon}{L}\right)\int_0^L \sin^2\left(\frac{\pi x}{L}\right)x\,dx - \left(\frac{2\varepsilon}{L}\right)\frac{L}{2}\int_0^L \sin^2\left(\frac{\pi x}{L}\right)dx$$

The first integral can be evaluated using integral equation (18) with $a = \frac{\pi}{L}$:

$$\int_0^L \sin^2(ax)x\,dx = \frac{x^2}{4} - \frac{x\sin(2ax)}{4a} - \frac{\cos(2ax)}{8a^2}\Bigg|_0^L = \frac{L^2}{4}$$

The second integral can be evaluated using integral equation (10) with $\theta = \frac{\pi x}{L}$ and $d\theta = \frac{\pi}{L}$ dx :

$$\int_0^L \sin^2\left(\frac{\pi x}{L}\right)dx = \frac{L}{\pi}\int_0^\pi \sin^2\theta\,d\theta$$

$$\int_0^\pi \sin^2\theta\,d\theta = -\frac{1}{4}\sin(2\theta) + \frac{\theta}{2}\Bigg|_0^\pi = \frac{\pi}{2}$$

Making all of these appropriate substitutions we obtain:

$$E^{(1)}_{n=1} = \left(\frac{2\varepsilon}{L}\right)\left(\frac{L^2}{4} - \frac{L}{2}\,\frac{L}{\pi}\,\frac{\pi}{2}\right) = 0$$

$$\Psi^{(1)}_{n=1} = \frac{\left\langle \Psi^{(0)}_{n=2}\middle|\varepsilon\left(x - \frac{L}{2}\right)\middle|\Psi^{(0)}_{n=1}\right\rangle}{E^{(0)}_{n=1} - E^{(0)}_{n=2}}\,\Psi^{(0)}_{n=2}$$

$$\Psi^{(1)}_{n=1} = \frac{\left(\frac{2}{L}\right)\int_0^L \sin\left(\frac{2\pi x}{L}\right)\varepsilon\left(x - \frac{L}{2}\right)\sin\left(\frac{\pi x}{L}\right)dx}{\frac{\hbar^2\pi^2}{2mL^2}\left(1^2 - 2^2\right)}\left(\frac{2}{L}\right)^{\frac{1}{2}}\sin\left(\frac{2\pi x}{L}\right)$$

The two integrals in the numerator need to be evaluated:

$$\int_0^L x\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)dx \ \text{, and} \ \int_0^L \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)dx \ .$$

Using trigonometric identity (20), the integral $\int x\cos(ax)dx = \frac{1}{a^2}\cos(ax) + \frac{x}{a}\sin(ax)$, and the integral $\int \cos(ax)dx = \frac{1}{a}\sin(ax)$, we obtain the following:

$$\int_0^L \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)dx = \frac{1}{2}\left[\int_0^L \cos\left(\frac{\pi x}{L}\right)dx - \int_0^L \cos\left(\frac{3\pi x}{L}\right)dx\right]$$

$$= \frac{1}{2}\left[\frac{L}{\pi}\sin\left(\frac{\pi x}{L}\right)\Big|_0^L - \frac{L}{3\pi}\sin\left(\frac{3\pi x}{L}\right)\Big|_0^L\right] = 0$$

$$\int_0^L x\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi x}{L}\right)dx = \frac{1}{2}\left[\int_0^L x\cos\left(\frac{\pi x}{L}\right)dx - \int_0^L x\cos\left(\frac{3\pi x}{L}\right)dx\right]$$

$$= \frac{1}{2}\left[\left(\frac{L^2}{\pi^2}\cos\left(\frac{\pi x}{L}\right) + \frac{Lx}{\pi}\sin\left(\frac{\pi x}{L}\right)\right)\Big|_0^L - \left(\frac{L^2}{9\pi^2}\cos\left(\frac{3\pi x}{L}\right) + \frac{Lx}{3\pi}\sin\left(\frac{3\pi x}{L}\right)\right)\Big|_0^L\right]$$

$$= \frac{L^2}{2\pi^2}(\cos(\pi) - \cos(0)) + \frac{L^2}{2\pi}\sin(\pi) - 0$$

$$- \frac{L^2}{18\pi^2}(\cos(3\pi) - \cos(0)) - \frac{L^2}{6\pi}\sin(3\pi) + 0$$

$$= \frac{-2L^2}{2\pi^2} - \frac{-2L^2}{18\pi^2} = \frac{L^2}{9\pi^2} - \frac{L^2}{\pi^2} = -\frac{8L^2}{9\pi^2}$$

Making all of these appropriate substitutions we obtain:

$$\Psi^{(1)}_{n=1} = \frac{\left(\frac{2}{L}\right)(e\varepsilon)\left(\frac{8L^2}{9\pi^2} - \frac{L}{2}(0)\right)}{\frac{-3\hbar^2\pi^2}{2mL^2}}\left(\frac{2}{L}\right)^{\frac{1}{2}}\sin\left(\frac{2\pi x}{L}\right)$$

$$\Psi^{(1)}_{n=1} = \frac{32mL^3e\varepsilon}{27\hbar^2\pi^4}\left(\frac{2}{L}\right)^{\frac{1}{2}}\sin\left(\frac{2\pi x}{L}\right)$$

Crudely sketching $\Psi^{(0)}_{n=1} + \Psi^{(1)}_{n=1}$ gives:

Note that the electron density has been pulled to the left side of the box by the external field!

b. $\mu_{\text{induced}} = -e\int \Psi^*\left(x - \frac{L}{2}\right)\Psi dx$, where, $\Psi = \left(\Psi^{(0)}_1 + \Psi^{(1)}_1\right)$.

$$\mu_{\text{induced}} = -e\int_0^L \left(\Psi^{(0)}_1 + \Psi^{(1)}_1\right)^*\left(x - \frac{L}{2}\right)\left(\Psi^{(0)}_1 + \Psi^{(1)}_1\right)dx$$

$$= -e\int_0^L \Psi^{(0)*}_1\left(x - \frac{L}{2}\right)\Psi^{(0)}_1 dx - e\int_0^L \Psi^{(0)*}_1\left(x - \frac{L}{2}\right)\Psi^{(1)}_1 dx$$

$$- e\int_0^L \psi_1^{(1)*}\left(x - \frac{L}{2}\right)\psi_1^{(0)}dx \;\; - e\int_0^L \psi_1^{(1)*}\left(x - \frac{L}{2}\right)\psi_1^{(1)}dx$$

The first integral is zero (see the evaluation of this integral for $E_1^{(1)}$ above in part a.) The fourth integral is neglected since it is proportional to ε^2. The second and third integrals are the same and are combined:

$$\mu_{induced} = -2e\int_0^L \psi_1^{(0)*}\left(x - \frac{L}{2}\right)\psi_1^{(1)}dx$$

Substituting $\psi_1^{(0)} = \left(\frac{2}{L}\right)^{\frac{1}{2}} \text{Sin}\left(\frac{\pi x}{L}\right)$ and $\psi_1^{(1)} = \frac{32mL^3e\varepsilon}{27\hbar^2\pi^4}\left(\frac{2}{L}\right)^{\frac{1}{2}} \text{Sin}\left(\frac{2\pi x}{L}\right)$, we obtain:

$$\mu_{induced} = -2e\frac{32mL^3e\varepsilon}{27\hbar^2\pi^4}\left(\frac{2}{L}\right)\int_0^L \text{Sin}\left(\frac{\pi x}{L}\right)\left(x - \frac{L}{2}\right)\text{Sin}\left(\frac{2\pi x}{L}\right)dx$$

These integrals are familiar from part a:

$$\mu_{induced} = -2e\frac{32mL^3e\varepsilon}{27\hbar^2\pi^4}\left(\frac{2}{L}\right)\left(\frac{8L^2}{9\pi^2}\right)$$

$$\mu_{induced} = \frac{mL^4e^2\varepsilon}{\hbar^2\pi^6}\,\frac{2^{10}}{3^5}$$

c. $\alpha = \left(\frac{\partial\mu}{\partial\varepsilon}\right)_{\varepsilon=0} = \frac{mL^4e^2}{\hbar^2\pi^6}\,\frac{2^{10}}{3^5}$

The larger the box (molecule), the more polarizable the electron density.

Section 2 Exercises, Problems, and Solutions

Review Exercises:

1. Draw qualitative shapes of the (1) s, (3) p and (5) d "tangent sphere" atomic orbitals (note that these orbitals represent only the angular portion and do not contain the radial portion of the hydrogen like atomic wavefunctions) Indicate with ± the relative signs of the wavefunctions and the position(s) (if any) of any nodes.

2. Define the symmetry adapted "core" and "valence" orbitals of the following systems:

   i. NH_3 in the C_{3v} point group,
   ii. H_2O in the C_{2v} point group,
   iii. H_2O_2 (cis) in the C_2 point group,
   iv. N in $D_{\infty h}$, D_{2h}, C_{2v}, and C_s point groups,

v. N_2 in $D_{\infty h}$, D_{2h}, C_{2v}, and C_s point groups.

3. Plot the radial portions of the 4s, 4p, 4d, and 4f hydrogen like atomic wavefunctions.

4. Plot the radial portions of the 1s, 2s, 2p, 3s, and 3p hydrogen like atomic wavefunctions for the Si atom using screening concepts for any inner electrons.

Exercises:

1. In quantum chemistry it is quite common to use combinations of more familiar and easy-to-handle "basis functions" to approximate atomic orbitals. Two common types of basis functions are the Slater type orbitals (STO's) and gaussian type orbitals (GTO's). STO's have the normalized form:

$$\left(\frac{2\zeta}{a_o}\right)^{n+\frac{1}{2}} \left(\frac{1}{(2n)!}\right)^{\frac{1}{2}} r^{n-1}\, e^{\left(\frac{-\zeta r}{a_o}\right)}\, Y_{l,m}(\theta,\varphi),$$

whereas GTO's have the form:

$$N\, r^l\, e^{\left(-\zeta r^2\right)}\, Y_{l,m}(\theta,\varphi).$$

Orthogonalize (using Löwdin (symmetric) orthogonalization) the following 1s (core), 2s (valence), and 3s (Rydberg) STO's for the Li atom given:

Li_{1s} $\zeta = 2.6906$

Li_{2s} $\zeta = 0.6396$

Li_{3s} $\zeta = 0.1503$.

Express the three resultant orthonormal orbitals as linear combinations of these three normalized STO's.

2. Calculate the expectation value of r for each of the orthogonalized 1s, 2s, and 3s Li orbitals found in Exercise 1.

3. Draw a plot of the radial probability density (e.g., $r^2[R_{nl}(r)]^2$ with R referring to the radial portion of the STO) versus r for each of the orthonormal Li s orbitals found in Exercise 1.

Problems:

1. Given the following orbital energies (in hartrees) for the N atom and the coupling elements between two like atoms (these coupling elements are the Fock matrix elements from standard *ab-initio* minimum-basis SCF calculations), calculate the molecular orbital energy levels and 1-electron wavefunctions. Draw the orbital correlation diagram for formation of the N_2 molecule. Indicate the symmetry of each atomic and molecular orbital. Designate each of the molecular orbitals as bonding, non-bonding, or antibonding.

$N_{1s} = -15.31^*$

$N_{2s} = -0.86^*$

$N_{2p} = -0.48^*$

N_2 σ_g Fock matrix*

$$\begin{bmatrix} -6.52 & & \\ -6.22 & -7.06 & \\ 3.61 & 4.00 & -3.92 \end{bmatrix}$$

N_2 π_g Fock matrix*

$$[0.28]$$

N_2 σ_u Fock matrix*

$$\begin{bmatrix} 1.02 & & \\ -0.60 & -7.59 & \\ 0.02 & 7.42 & -8.53 \end{bmatrix}$$

N_2 π_u Fock matrix*

$$[-0.58]$$

*The Fock matrices (and orbital energies) were generated using standard STO3G minimum basis set SCF calculations. The Fock matrices are in the orthogonal basis formed from these orbitals.

2. Given the following valence orbital energies for the C atom and H_2 molecule draw the orbital correlation diagram for formation of the CH_2 molecule (via a C_{2v} insertion of C into H_2 resulting in bent CH_2). Designate the symmetry of each atomic and molecular orbital in both their highest point group symmetry and in that of the reaction path (C_{2v}).

$C_{1s} = -10.91^*$ $\quad$ $H_2\ \sigma_g = -0.58^*$

$C_{2s} = -0.60^*$ $\quad$ $H_2\ \sigma_u = 0.67^*$

$C_{2p} = -0.33^*$

*The orbital energies were generated using standard STO3G minimum basis set SCF calculations.

3. Using the empirical parameters given below for C and H (taken from Appendix F and "The HMO Model and its Applications" by E. Heilbronner and H. Bock, Wiley-Interscience, NY, 1976), apply the Hückel model to ethylene in order to determine the valence electronic structure of this system. Note that you will be obtaining the 1-electron energies and wavefunctions by solving the <u>secular equation</u> (as you <u>always</u> will when the energy is dependent upon a set of linear parameters like the MO coefficients in the LCAO-MO approach) using the definitions for the matrix elements found in Appendix F.

C $\alpha_{2p\pi} = -11.4$ eV

C $\alpha_{sp^2} = -14.7$ eV

H $\alpha_s = -13.6$ eV

C-C $\beta_{2p\pi\text{-}2p\pi} = -1.2$ eV

C-C $\beta_{sp^2\text{-}sp^2} = -5.0$ eV

C-H $\beta_{sp^2\text{-}s} = -4.0$ eV

a. Determine the C=C (2pπ) 1-electron molecular orbital energies and wavefunctions. Calculate the $\pi \rightarrow \pi^*$ transition energy for ethylene within this model.

b. Determine the C-C (sp^2) 1-electron molecular orbital energies and wavefunctions.

c. Determine the C-H (sp^2-s) 1-electron molecular orbital energies and wavefunctions (note that appropriate choice of symmetry will reduce this 8x8 matrix down to 4 2x2 matrices; that is, you are encouraged to symmetry adapt the atomic orbitals before starting the Hückel calculation). Draw a qualitative orbital energy diagram using the HMO energies you have calculated.

4. Using the empirical parameters given below for B and H (taken from Appendix F and "The HMO Model and its Applications" by E. Heilbronner and H. Bock, Wiley-

Interscience, NY, 1976), apply the Hückel model to borane (BH_3) in order to determine the valence electronic structure of this system.

B $\alpha_{2p\pi}$ = -8.5 eV

B α_{sp^2} = -10.7 eV

H α_s = -13.6 eV

B-H $\beta_{sp^2\text{-}s}$ = -3.5 eV

Determine the symmetries of the resultant molecular orbitals in the D_{3h} point group. Draw a qualitative orbital energy diagram using the HMO energies you have calculated.

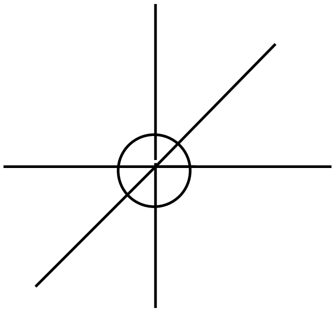
5. Qualitatively analyze the electronic structure (orbital energies and 1-electron wavefunctions) of PF_5. Analyze only the 3s and 3p electrons of P and the <u>one</u> 2p bonding electron of each F. Proceed with a D_{3h} analysis in the following manner:

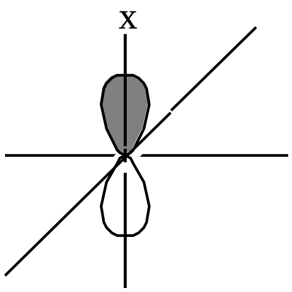
a. Symmetry adapt the top and bottom F atomic orbitals.
b. Symmetry adapt the three (trigonal) F atomic orbitals.
c. Symmetry adapt the P 3s and 3p atomic orbitals.
d. Allow these three sets of D_{3h} orbitals to interact and draw the resultant orbital energy diagram. Symmetry label each of these molecular energy levels. Fill this energy diagram with 10
"valence" electrons.

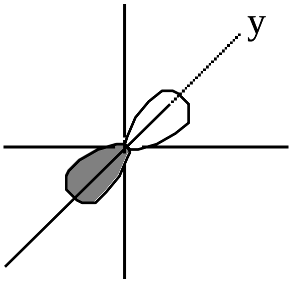
Solutions

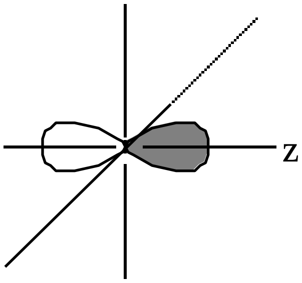
<u>Review Exercises</u>

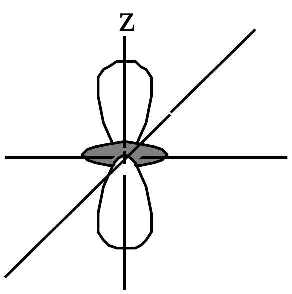
1.

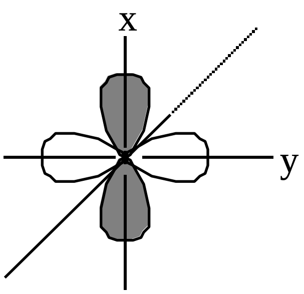


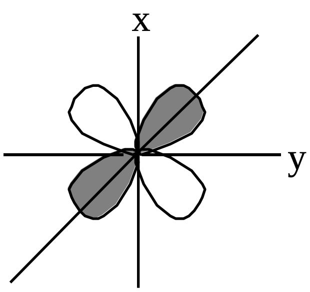


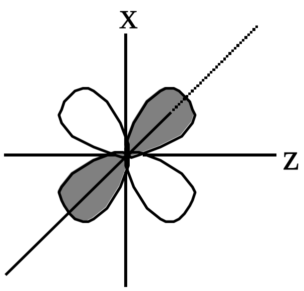


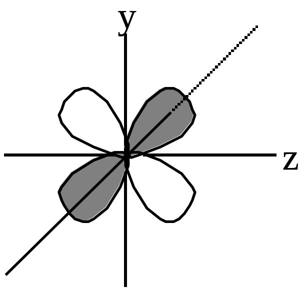












2. i.In ammonia the only "core" orbital is the N 1s and this becomes an a_1 orbital in C_{3v} symmetry. The N 2s orbitals and 3 H 1s orbitals become 2 a_1 and an e set of orbitals. The remaining N 2p orbitals also become 1 a_1 and a set of e orbitals. The total valence orbitals in C_{3v} symmetry are $3a_1$ and 2e orbitals.

2. ii. In water the only core orbital is the O 1s and this becomes an a_1 orbital in C_{2v} symmetry. Placing the molecule in the yz plane allows us to further analyze the remaining valence orbitals as: O $2p_z = a_1$, O $2p_y$ as b_2, and O $2p_x$ as b_1. The H 1s + H 1s combination is an a_1 whereas the H 1s - H 1s combination is a b_2.

=2. iii. Placing the oxygens of H_2O_2 in the yz plane (z bisecting the oxygens) and the (cis) hydrogens distorted slightly in +x and -x directions allows us to analyze the orbitals as follows. The core O 1s + O 1s combination is an a orbital whereas the O 1s - O 1s combination is a b orbital. The valence orbitals are: O 2s + O 2s = a, O 2s - O 2s = b, O $2p_x$ + O $2p_x$ = b, O $2p_x$ - O $2p_x$ = a, O $2p_y$ + O $2p_y$ = a, O $2p_y$ - O $2p_y$ = b, O $2p_z$ + O $2p_z$ = b, O $2p_z$ - O $2p_z$ = a, H 1s + H 1s = a, and finally the H 1s - H 1s = b.

2. iv. For the next two problems we will use the convention of choosing the z axis as principal axis for the $D_{\infty h}$, D_{2h}, and C_{2v} point groups and the xy plane as the horizontal reflection plane in C_s symmetry.

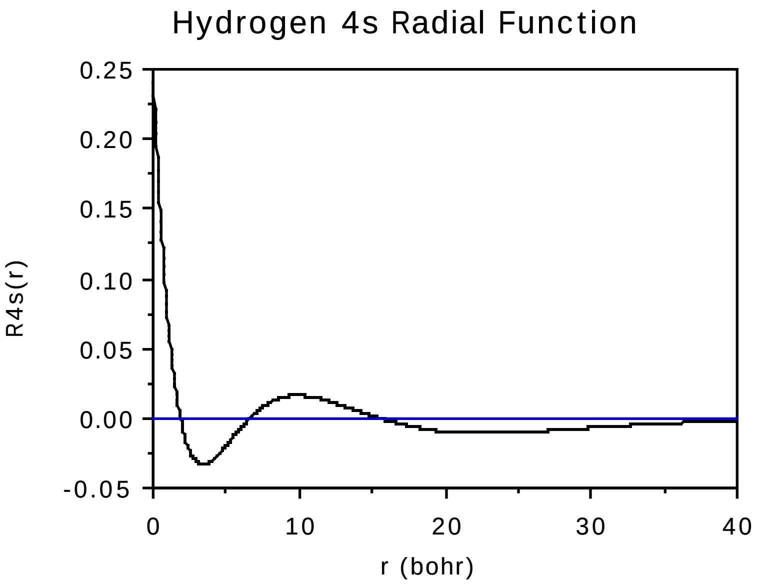
	$D_{\infty h}$	D_{2h}	C_{2v}	C_s
N 1s	σ_g	a_g	a_1	a'
N 2s	σ_g	a_g	a_1	a'
N $2p_x$	π_{xu}	b_{3u}	b_1	a'
N $2p_y$	π_{yu}	b_{2u}	b_2	a'
N $2p_z$	σ_u	b_{1u}	a_1	a''

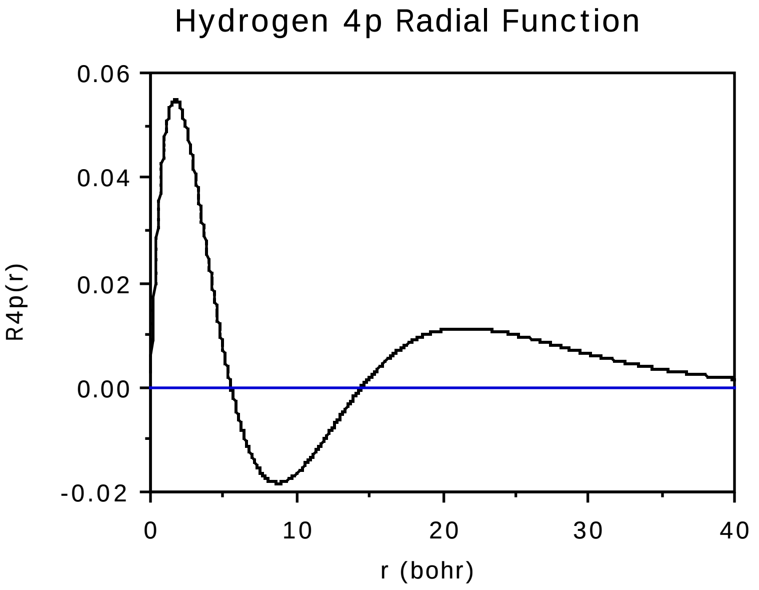
2. v. The Nitrogen molecule is in the yz plane for all point groups except the C_s in which case it is placed in the xy plane.

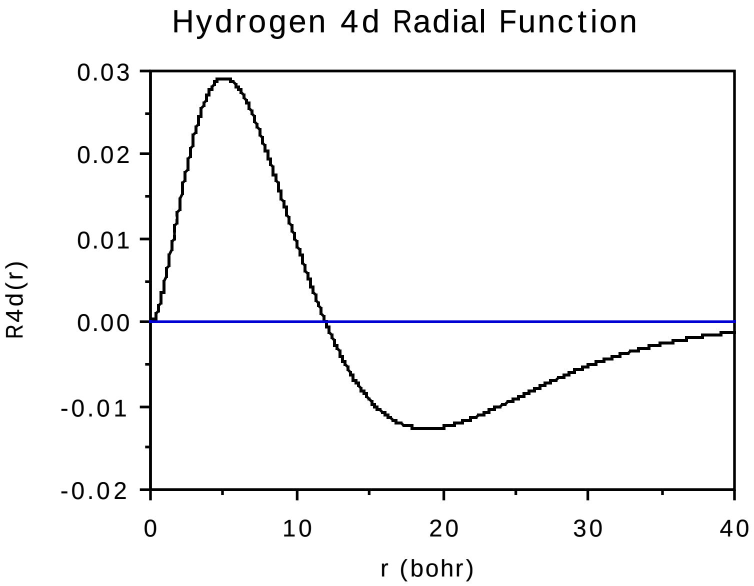
	$D_{\infty h}$	D_{2h}	C_{2v}	C_s
N 1s + N 1s	σ_g	a_g	a_1	a'
N 1s - N 1s	σ_u	b_{1u}	b_2	a'
N 2s + N 2s	σ_g	a_g	a_1	a'

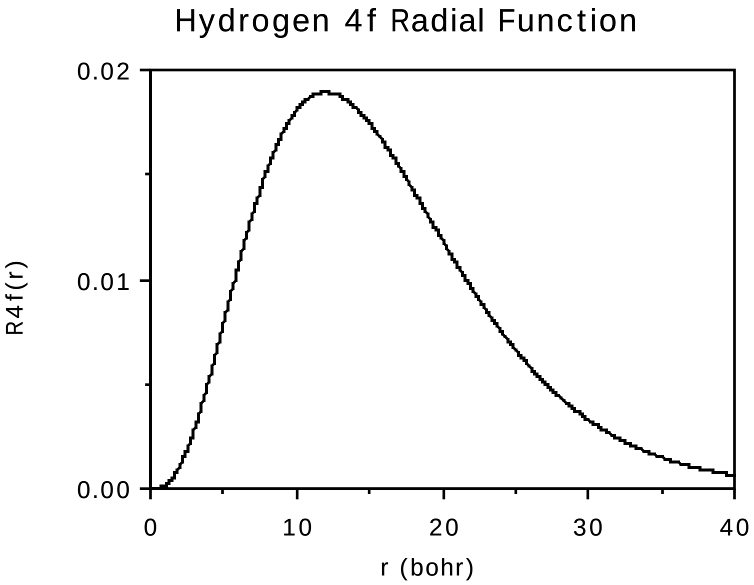
N 2s - N 2s	σ_u	b_{1u}	b_2	a'
N $2p_x$ + N $2p_x$	π_{xu}	b_{3u}	b_1	a'
N $2p_x$ - N $2p_x$	π_{xg}	b_{2g}	a_2	a'
N $2p_y$ + N $2p_y$	π_{yu}	b_{2u}	a_1	a'
N $2p_y$ - N $2p_y$	π_{yg}	b_{3g}	b_2	a'
N $2p_z$ + N $2p_z$	σ_u	b_{1u}	b_2	a''
N $2p_z$ - N $2p_z$	σ_g	a_g	a_1	a''

3.

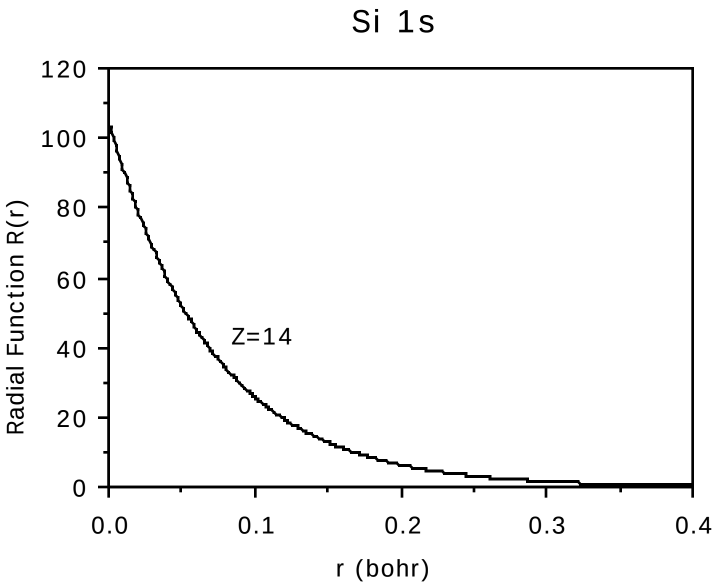

Hydrogen 4s Radial Function


Hydrogen 4p Radial Function


Hydrogen 4d Radial Function
R4d(r)
0.03
0.02
0.01
0.00
-0.01
-0.02
0
10
20
30
40
r (bohr)

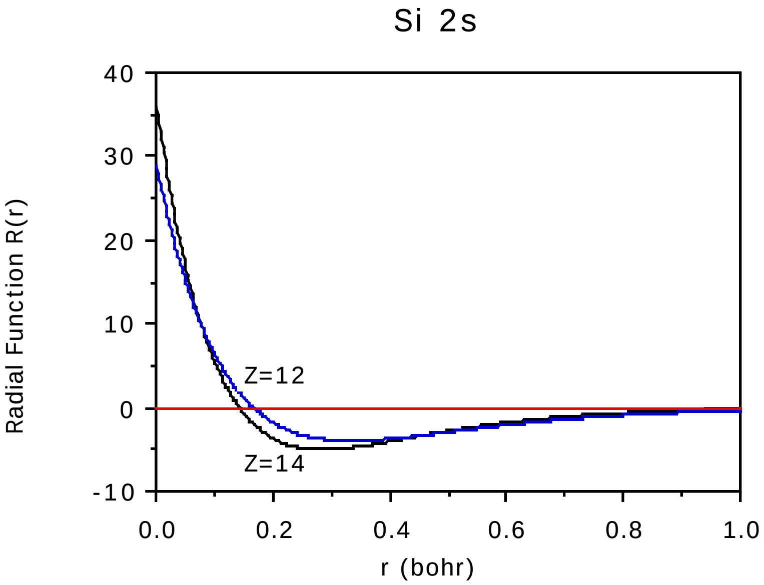

Hydrogen 4f Radial Function
R4f(r)
0.02
0.01
0.00
0
10
20
30
40
r (bohr)

4.



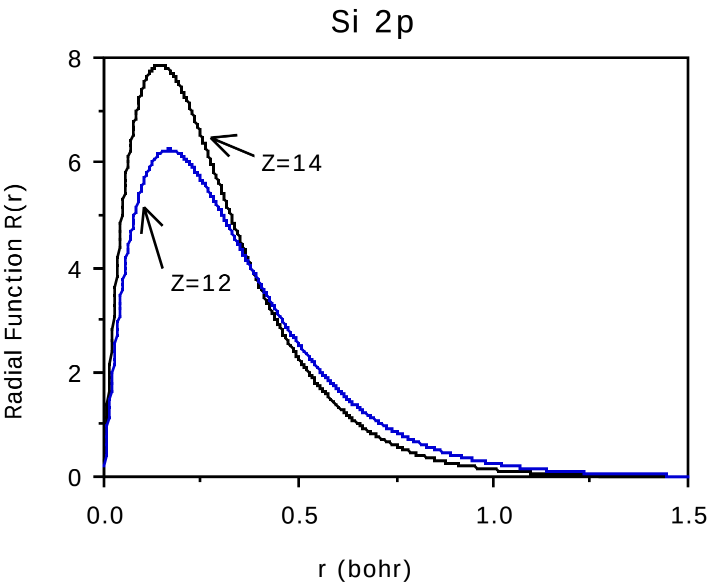
Si 1s

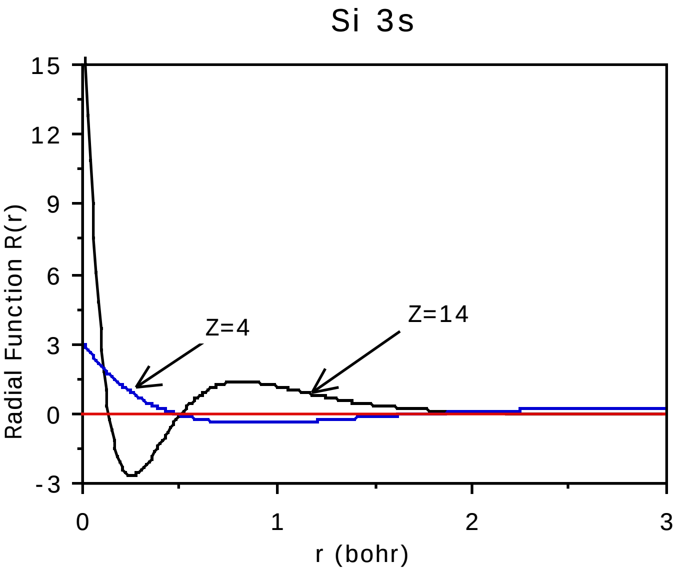
Radial Function R(r)
r (bohr)
Z=14
0
20
40
60
80
100
120
0.0
0.1
0.2
0.3
0.4

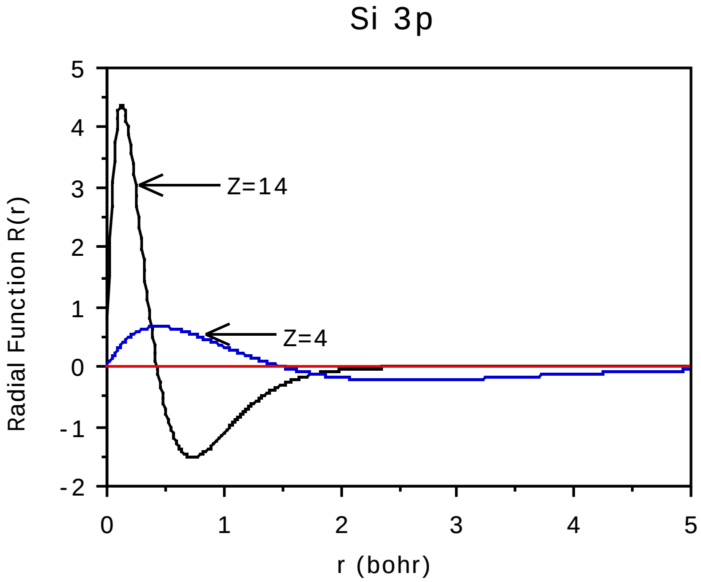


Si 2s

Radial Function R(r)
r (bohr)
Z=12
Z=14
-10
0
10
20
30
40
0.0
0.2
0.4
0.6
0.8
1.0


Si 2p
Radial Function R(r)
8
6
4
2
0
0.0
0.5
1.0
1.5
r (bohr)
Z=14
Z=12


Si 3s
Radial Function R(r)
15
12
9
6
3
0
-3
0
1
2
3
r (bohr)
Z=4
Z=14



Exercises

1. Two Slater type orbitals, i and j, centered on the same point results in the following overlap integrals:

$$S_{ij} = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \left(\frac{\zeta_i}{a_0}\right)^{n_i+\frac{1}{2}} \left(\frac{1}{(2n_i)!}\right)^{\frac{1}{2}} r^{(n_i-1)} e^{\left(\frac{\zeta_i r}{a_0}\right)} Y_{l_i,m_i}(\theta,\varphi)\cdot$$

$$\left(\frac{\zeta_j}{a_0}\right)^{n_j+\frac{1}{2}} \left(\frac{1}{(2n_j)!}\right)^{\frac{1}{2}} r^{(n_j-1)} e^{\left(\frac{\zeta_j r}{a_0}\right)} Y_{l_j,m_j}(\theta,\varphi)\cdot$$

$$r^2 \sin\theta\, dr\, d\theta\, d\varphi.$$

For these s orbitals l = m = 0 and $Y_{0,0}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$. Performing the integrations over θ and φ yields 4π which then cancels with these Y terms. The integral then reduces to:

$$S_{ij} = \left(\frac{\zeta_i}{a_0}\right)^{n_i+\frac{1}{2}} \left(\frac{1}{(2n_i)!}\right)^{\frac{1}{2}} \left(\frac{\zeta_j}{a_0}\right)^{n_j+\frac{1}{2}} \left(\frac{1}{(2n_j)!}\right)^{\frac{1}{2}} \int_0^{\infty} r^{(n_i-1+n_j-1)} e^{\left(\frac{(\zeta_i+\zeta_j)r}{a_0}\right)} r^2 dr$$

$$= \left(\frac{\zeta_i}{a_0}\right)^{n_i+\frac{1}{2}} \left(\frac{1}{(2n_i)!}\right)^{\frac{1}{2}} \left(\frac{\zeta_j}{a_0}\right)^{n_j+\frac{1}{2}} \left(\frac{1}{(2n_j)!}\right)^{\frac{1}{2}} \int_0^{\infty} r^{(n_i+n_j)} e^{\left(\frac{-(\zeta_i+\zeta_j)r}{a_0}\right)} dr$$

Using integral equation (4) the integral then reduces to:

$$S_{ij} = \left(\frac{\zeta_i}{a_0}\right)^{n_i+\frac{1}{2}} \left(\frac{1}{(2n_i)!}\right)^{\frac{1}{2}} \left(\frac{\zeta_j}{a_0}\right)^{n_j+\frac{1}{2}} \left(\frac{1}{(2n_j)!}\right)^{\frac{1}{2}} (n_i+n_j)\,! \left(\frac{a_0}{\zeta_i+\zeta_j}\right)^{n_i+n_j+1} .$$

We then substitute in the values for each of these constants:

for i=1; n=1, l=m=0, and $\zeta = 2.6906$

for i=2; n=2, l=m=0, and $\zeta = 0.6396$

for i=3; n=3, l=m=0, and $\zeta = 0.1503$.

Evaluating each of these matrix elements we obtain:

S_{11} = (12.482992)(0.707107)(12.482992)
(0.707107)(2.000000)(0.006417)
= 1.000000

$S_{21} = S_{12}$ = (1.850743)(0.204124)(12.482992)
(0.707107)(6.000000)(0.008131)
= 0.162673

S_{22} = (1.850743)(0.204124)(1.850743)
(0.204124)(24.000000)(0.291950)
= 1.000000

$S_{31} = S_{13}$ = (0.014892)(0.037268)(12.482992)
(0.707107)(24.000000)(0.005404)
= 0.000635

$S_{32} = S_{23}$ = (0.014892)(0.037268)(1.850743)
(0.204124)(120.000000)(4.116872)
= 0.103582

S_{33} = (0.014892)(0.037268)(0.014892)
(0.037268)(720.000000)(4508.968136)
= 1.000000

$$S = \begin{bmatrix} 1.000000 & & \\ 0.162673 & 1.000000 & \\ 0.000635 & 0.103582 & 1.000000 \end{bmatrix}$$

We now solve the matrix eigenvalue problem S U = λ U.

The eigenvalues, λ, of this overlap matrix are:

[0.807436 0.999424 1.193139] ,

and the corresponding eigenvectors, U, are:

$$\begin{bmatrix} 0.596540 & -0.537104 & -0.596372 \\ -0.707634 & -0.001394 & -0.706578 \\ 0.378675 & 0.843515 & -0.380905 \end{bmatrix} .$$

The $\lambda^{-\frac{1}{2}}$ matrix becomes:

$$\lambda^{-\frac{1}{2}} = \begin{bmatrix} 1.112874 & 0.000000 & 0.000000 \\ 0.000000 & 1.000288 & 0.000000 \\ 0.000000 & 0.000000 & 0.915492 \end{bmatrix}.$$

Back transforming into the original eigenbasis gives $S^{-\frac{1}{2}}$, e.g.

$$S^{-\frac{1}{2}} = U\lambda^{-\frac{1}{2}}U^T$$

$$S^{-\frac{1}{2}} = \begin{bmatrix} 1.010194 & & \\ -0.083258 & 1.014330 & \\ 0.006170 & -0.052991 & 1.004129 \end{bmatrix}$$

The old ao matrix can be written as:

$$C = \begin{bmatrix} 1.000000 & 0.000000 & 0.000000 \\ 0.000000 & 1.000000 & 0.000000 \\ 0.000000 & 0.000000 & 1.000000 \end{bmatrix}.$$

The new ao matrix (which now gives each ao as a linear combination of the original aos) then becomes:

$$C' = S^{-\frac{1}{2}}C = \begin{bmatrix} 1.010194 & -0.083258 & 0.006170 \\ -0.083258 & 1.014330 & -0.052991 \\ 0.006170 & -0.052991 & 1.004129 \end{bmatrix}$$

These new aos have been constructed to meet the orthonormalization requirement $C'^TSC' = 1$ since:

$$\left(S^{-\frac{1}{2}}C\right)^T S\, S^{-\frac{1}{2}}C = C^TS^{-\frac{1}{2}}S\, S^{-\frac{1}{2}}C = C^TC = 1\ .$$

But, it is always good to check our result and indeed:

$$C'^TSC' = \begin{bmatrix} 1.000000 & 0.000000 & 0.000000 \\ 0.000000 & 1.000000 & 0.000000 \\ 0.000000 & 0.000000 & 1.000000 \end{bmatrix}$$

2. The least time consuming route here is to evaluate each of the needed integrals first. These are evaluated analogous to exercise 1, letting χ_i denote each of the individual Slater Type Orbitals.

$$\int_0^\infty \chi_i\ r\ \chi_j r^2 dr = \langle r\rangle_{ij}$$

$$= \left(\frac{2\zeta_i}{a_0}\right)^{n_i+\frac{1}{2}}\left(\frac{1}{(2n_i)!}\right)^{\frac{1}{2}}\left(\frac{2\zeta_j}{a_0}\right)^{n_j+\frac{1}{2}}\left(\frac{1}{(2n_j)!}\right)^{\frac{1}{2}}\int_0^\infty r^{(n_i+n_j+1)}e^{\left(\frac{-(\zeta_i+\zeta_j)r}{a_0}\right)}dr$$

Once again using integral equation (4) the integral reduces to:

$$= \left(\frac{2\zeta_i}{a_0}\right)^{n_i+\frac{1}{2}}\left(\frac{1}{(2n_i)!}\right)^{\frac{1}{2}}\left(\frac{2\zeta_j}{a_0}\right)^{n_j+\frac{1}{2}}\left(\frac{1}{(2n_j)!}\right)^{\frac{1}{2}}(n_i+n_j+1)\,!\left(\frac{a_0}{\zeta_i+\zeta_j}\right)^{n_i+n_j+2}.$$

Again, upon substituting in the values for each of these constants, evaluation of these expectation values yields:

$<r>_{11}$ = (12.482992)(0.707107)(12.482992)
(0.707107)(6.000000)(0.001193)
= 0.557496

$<r>_{21} = <r>_{12}$ = (1.850743)(0.204124)(12.482992)
(0.707107)(24.000000)(0.002441)
= 0.195391

$<r>_{22}$ = (1.850743)(0.204124)(1.850743)
(0.204124)(120.000000)(0.228228)
= 3.908693

$<r>_{31} = <r>_{13}$ = (0.014892)(0.037268)(12.482992)
(0.707107)(120.000000)(0.001902)
= 0.001118

$<r>_{32} = <r>_{23}$ = (0.014892)(0.037268)(1.850743)
(0.204124)(720.000000)(5.211889)
= 0.786798

$<r>_{33}$ = (0.014892)(0.037268)(0.014892)
(0.037268)(5040.000000)(14999.893999)
= 23.286760

$$\int_0^\infty \chi_i \; r \; \chi_j r^2 dr = <r>_{ij} = \begin{bmatrix} 0.557496 & & \\ 0.195391 & 3.908693 & \\ 0.001118 & 0.786798 & 23.286760 \end{bmatrix}$$

Using these integrals one then proceeds to evaluate the expectation values of each of the orthogonalized aos, $\chi'_{n,}$ as:

$$\int_0^\infty \chi'_n \; r \; \chi'_n r^2 dr = \sum_{i=1}^{3}\sum_{j=1}^{3} C'_{ni}C'_{nj}<r>_{ij}\,.$$

This results in the following expectation values (in atomic units):

$$\int_0^\infty \chi'_{1s} \; r \; \chi'_{1s} r^2 dr = 0.563240 \text{ bohr}$$

$$\int_0^\infty \chi'_{2s}\ r\ \chi'_{2s} r^2 dr = 3.973199 \text{ bohr}$$

$$\int_0^\infty \chi'_{3s}\ r\ \chi'_{3s} r^2 dr = 23.406622 \text{ bohr}$$

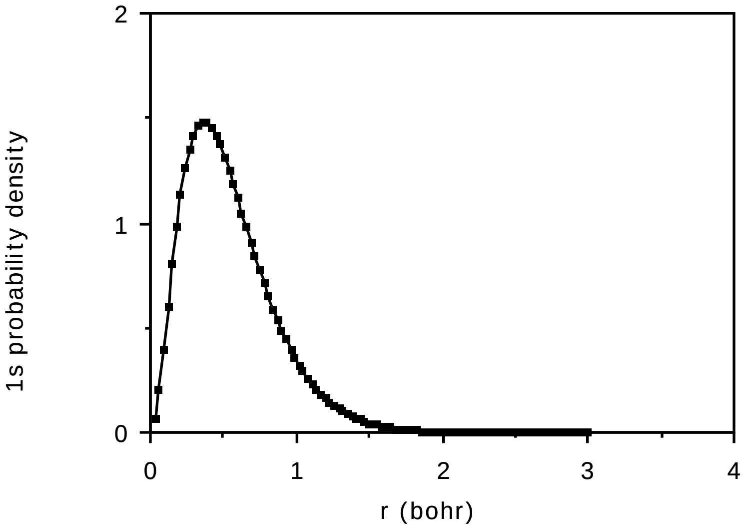
3. The radial density for each orthogonalized orbital, χ'_n, assuming integrations over θ and φ have already been performed can be written as:

$$\int_0^\infty \chi'_n \chi'_n r^2 dr = \sum_{i=1}^{3} \sum_{j=1}^{3} C'_{ni} C'_{nj} \int_0^\infty R_i R_j r^2 dr$$, where R_i and R_j are the radial portions of the individual Slater Type Orbitals, e.g.,

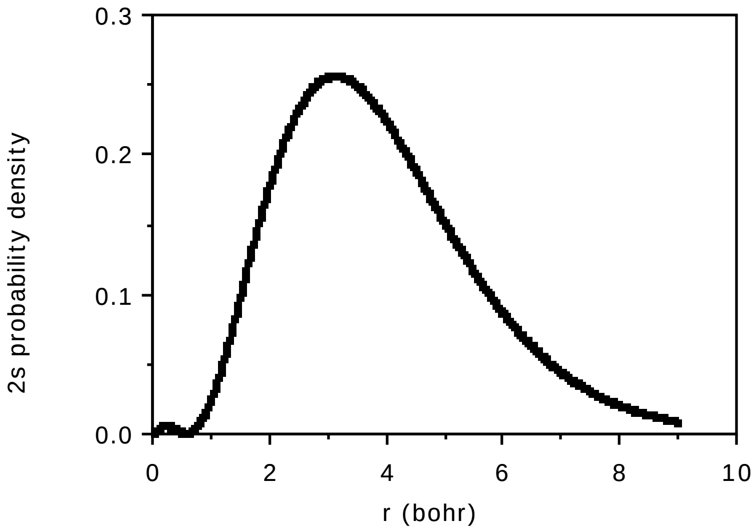
$$R_i R_j r^2 = \left(\frac{2\zeta_i}{a_0}\right)^{n_i+\frac{1}{2}} \left(\frac{1}{(2n_i)!}\right)^{\frac{1}{2}} \left(\frac{2\zeta_j}{a_0}\right)^{n_j+\frac{1}{2}} \left(\frac{1}{(2n_j)!}\right)^{\frac{1}{2}} r^{(n_i+n_j)} e^{\left(\frac{-(\zeta_i+\zeta_j)r}{a_0}\right)}$$

Therefore a plot of the radial probability for a given orthogonalized atomic orbital, n, will be : $\sum_{i=1}^{3} \sum_{j=1}^{3} C'_{ni} C'_{nj} R_i R_j r^2$ vs. r.

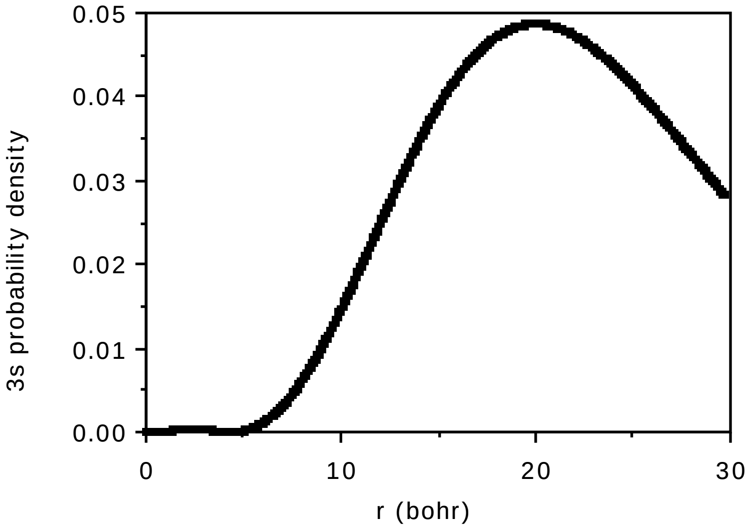
Plot of the orthogonalized 1s orbital probability density vs r; note there are no nodes.

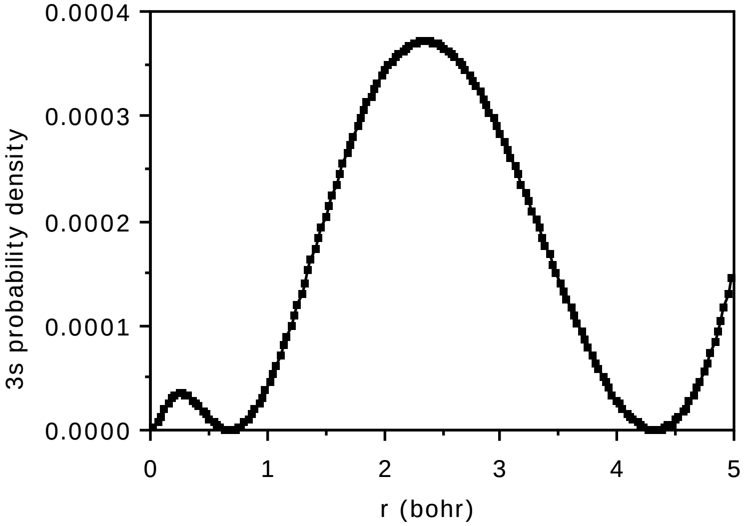


Plot of the orthogonalized 2s orbital probability density vs r; note there is one node.



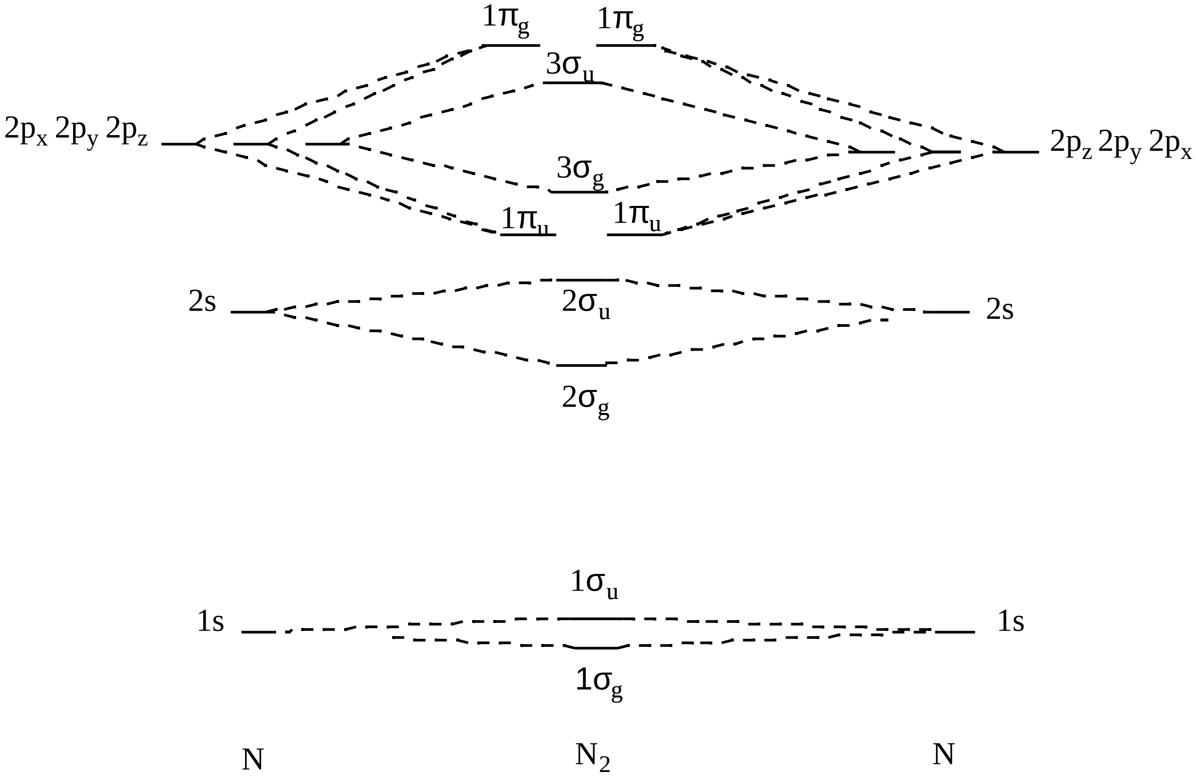
Plot of the orthogonalized 3s orbital probability density vs r; note there are two nodes in the 0-5 bohr region but they are not distinguishable as such. A duplicate plot with this nodal region expanded follows.





<u>Problems</u>

1.



The above diagram indicates how the SALC-AOs are formed from the 1s,2s, and 2p N atomic orbitals. It can be seen that there are $3\sigma_g$, $3\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $1\pi_{gx}$, and $1\pi_{gy}$ SALC-AOs. The Hamiltonian matrices (Fock matrices) are given. Each of these can be diagonalized to give the following MO energies:

$3\sigma_g$; -15.52, -1.45, and -0.54 (hartrees)

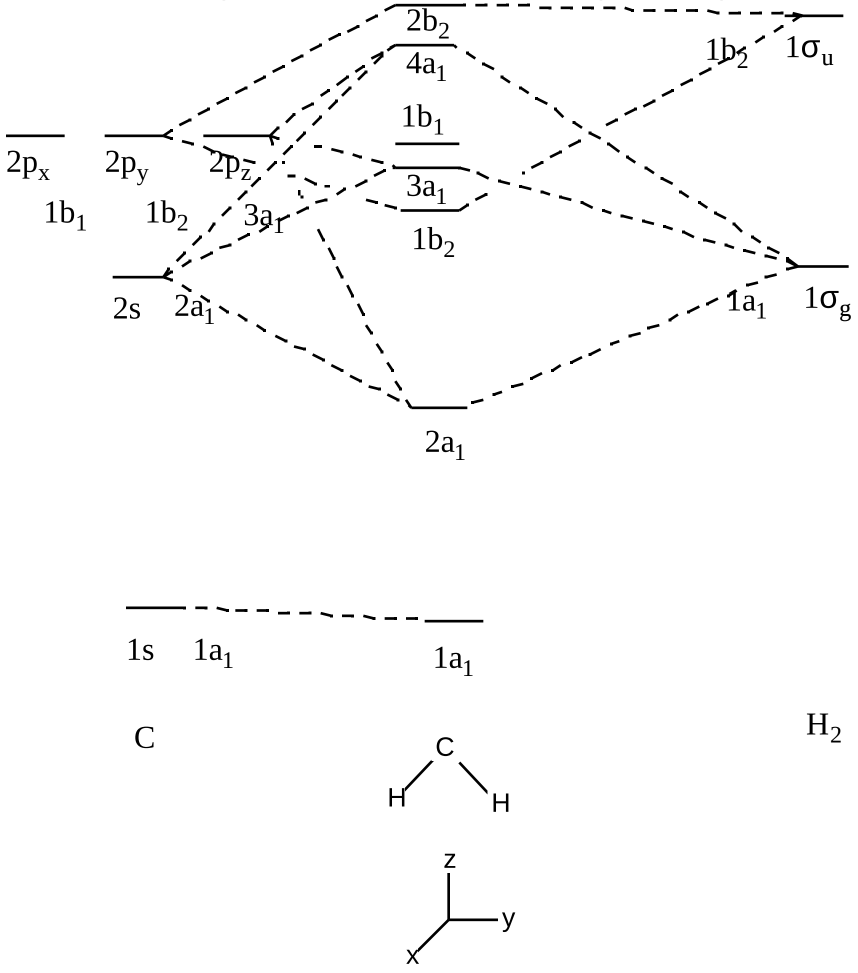
$3\sigma_u$; -15.52, -0.72, and 1.13

$1\pi_{ux}$; -0.58
$1\pi_{uy}$; -0.58
$1\pi_{gx}$; 0.28
$1\pi_{gy}$; 0.28

It can be seen that the $3\sigma_g$ orbitals are bonding, the $3\sigma_u$ orbitals are antibonding, the $1\pi_{ux}$ and $1\pi_{uy}$ orbitals are bonding, and the $1\pi_{gx}$ and $1\pi_{gy}$ orbitals are antibonding. The eigenvectors one obtains are in the orthogonal basis and therefore pretty meaningless.

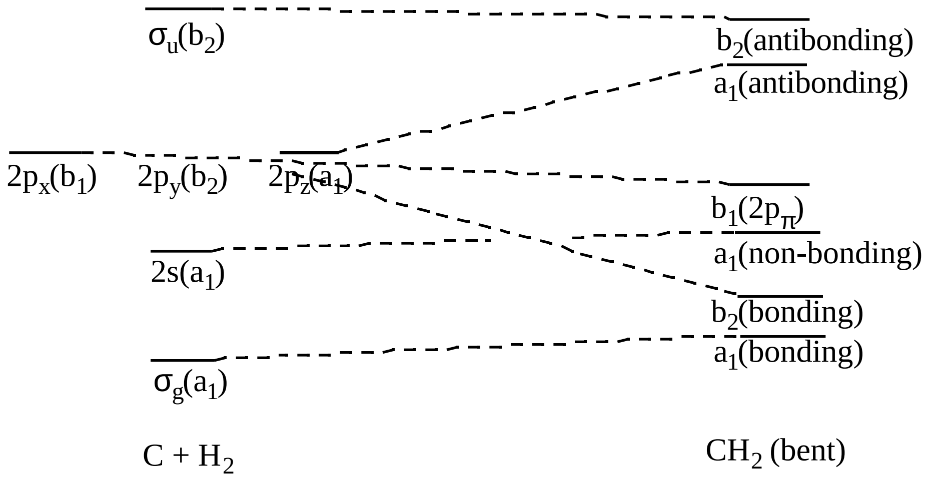
Back transformation into the original basis will generate the expected results for the $1e^-$ MOs (expected combinations of SALC-AOs).

2. Using these approximate energies we can draw the following MO diagram:

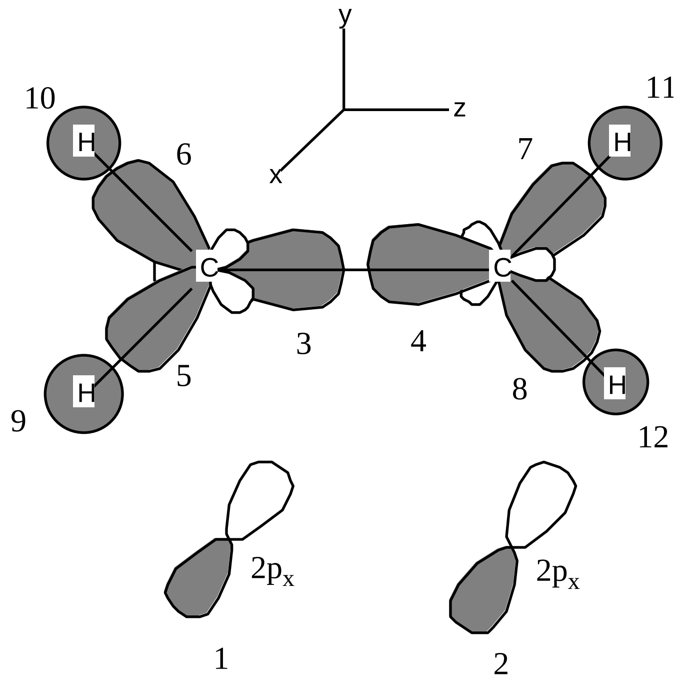


This MO diagram is <u>not</u> an orbital correlation diagram but can be used to help generate one. The energy levels on each side (C and H_2) can be "superimposed" to generate the left side of the orbital correlation diagram and the center CH_2 levels can be used to form the right side. Ignoring the core levels this generates the following orbital correlation diagram.

Orbital-correlation diagram for the reaction C + H_2 -----> CH_2 (bent)



3.



Using D_{2h} symmetry and labeling the orbitals (f_1-f_{12}) as shown above proceed by using the orbitals to define a reducible representation.which may be subsequently reduced to its irreducible components. Use projectors to find the SALC-AOs for these irreps.

3. a. The $2P_x$ orbitals on each carbon form the following reducible representation:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_{2p_x}	2	-2	0	0	0	0	2	-2

The number of irreducible representations may be found by using the following formula:

$$n_{irrep} = \frac{1}{g}\sum_R \chi_{red}(R)\chi_{irrep}(R) \ ,$$

where g = the order of the point group (8 for D_{2h}).

$$n_{A_g} = \frac{1}{8}\sum_R \Gamma_{2p_x}(R)\cdot A_g(R)$$

$$= \frac{1}{8}\{(2)(1)+(-2)(1)+(0)(1)+(0)(1)+$$
$$(0)(1)+(0)(1)+(2)(1)+(-2)(1)\} = 0$$

Similarly,

$n_{B_{1g}} = 0$
$n_{B_{2g}} = 1$
$n_{B_{3g}} = 0$
$n_{A_u} = 0$
$n_{B_{1u}} = 0$
$n_{B_{2u}} = 0$
$n_{B_{3u}} = 1$

Projectors using the formula:

$$P_{irrep} = \sum_R \chi_{irrep}(R)R\ ,$$

may be used to find the SALC-AOs for these irreducible representations.

$$P_{B_{2g}} = \sum_R \chi_{B_{2g}}(R)\ R\ ,$$

$$P_{B_{2g}}\ f_1 = (1)E\ f_1 + (-1)C_2(z)\ f_1 + (1)C_2(y)\ f_1 + (-1)C_2(x)\ f_1 +$$
$$(1)i\ f_1 + (-1)\sigma(xy)\ f_1 + (1)\sigma(xz)\ f_1 + (-1)\sigma(yz)\ f_1$$
$$= (1)\ f_1 + (-1)\ -f_1 + (1)\ -f_2 + (-1)\ f_2 +$$
$$(1)\ -f_2 + (-1)\ f_2 + (1)\ f_1 + (-1)\ -f_1$$
$$= f_1 + f_1 - f_2 - f_2 - f_2 - f_2 + f_1 + f_1$$
$$= 4f_1 - 4f_2$$

Normalization of this SALC-AO (and representing the SALC-AOs with φ) yields:

$$\int N(f_1 - f_2)N(f_1 - f_2)d\tau = 1$$

$$N^2\left(\int f_1f_1d\tau - \int f_1f_2d\tau - \int f_2f_1d\tau + \int f_2f_2d\tau\right) = 1$$

$$N^2(1 + 1) = 1$$

$$2N^2 = 1$$

$$N = \frac{1}{\sqrt{2}}$$

$$\varphi_{1b_{2g}} = \frac{1}{\sqrt{2}}(f_1 - f_2)\ .$$

The B_{3u} SALC-AO may be found in a similar fashion:

$$P_{B_{3u}}\ f_1 = (1)\ f_1 + (-1)\ -f_1 + (-1)\ -f_2 + (1)\ f_2 +$$
$$(-1)\ -f_2 + (1)\ f_2 + (1)\ f_1 + (-1)\ -f_1$$
$$= f_1 + f_1 + f_2 + f_2 + f_2 + f_2 + f_1 + f_1$$
$$= 4f_1 + 4f_2$$

Normalization of this SALC-AO yields:

$$\varphi_{1b_{3u}} = \frac{1}{\sqrt{2}}(f_1 + f_2) \ .$$

Since there are only two SALC-AOs and both are of different symmetry types these SALC-AOs are MOs and the 2x2 Hamiltonian matrix reduces to 2 1x1 matrices.

$$H_{1b_{2g},1b_{2g}} = \int \frac{1}{\sqrt{2}}(f_1 - f_2)H\frac{1}{\sqrt{2}}(f_1 - f_2)d\tau$$

$$= \frac{1}{2}\left(\int f_1Hf_1d\tau - 2\int f_1Hf_2d\tau + \int f_2Hf_2d\tau\right)$$

$$= \frac{1}{2}\left(\alpha_{2p\pi} - 2\beta_{2p\pi\text{-}2p\pi} + \alpha_{2p\pi}\right)$$

$$= \alpha_{2p\pi} - \beta_{2p\pi\text{-}2p\pi}$$

$$= -11.4 - (-1.2) = -10.2$$

$$H_{1b_{3u},1b_{3u}} = \int \frac{1}{\sqrt{2}}(f_1 + f_2)H\frac{1}{\sqrt{2}}(f_1 + f_2)d\tau$$

$$= \frac{1}{2}\left(\int f_1Hf_1d\tau + 2\int f_1Hf_2d\tau + \int f_2Hf_2d\tau\right)$$

$$= \frac{1}{2}\left(\alpha_{2p\pi} + 2\beta_{2p\pi\text{-}2p\pi} + \alpha_{2p\pi}\right)$$

$$= \alpha_{2p\pi} + \beta_{2p\pi\text{-}2p\pi}$$

$$= -11.4 + (-1.2) = -12.6$$

This results in a $\pi \rightarrow \pi^*$ splitting of 2.4 eV.

3. b. The sp^2 orbitals forming the C-C bond generate the following reducible representation:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_{Csp^2}	2	2	0	0	0	0	2	2

This reducible representation reduces to $1A_g$ and $1B_{1u}$ irreducible representations.

Projectors are used to find the SALC-AOs for these irreducible representations.

$$\begin{aligned} P_{A_g} f_3 &= (1)E\ f_3 + (1)C_2(z)\ f_3 + (1)C_2(y)\ f_3 + (1)C_2(x)\ f_3 + \\ &\quad (1)i\ f_3 + (1)\sigma(xy)\ f_3 + (1)\sigma(xz)\ f_3 + (1)\sigma(yz)\ f_3 \\ &= (1)\ f_3 + (1)\ f_3 + (1)\ f_4 + (1)\ f_4 + \\ &\quad (1)\ f_4 + (1)\ f_4 + (1)\ f_3 + (1)\ f_3 \\ &= 4f_3 + 4f_4 \end{aligned}$$

Normalization of this SALC-AO yields:

$$\varphi_{1a_g} = \frac{1}{\sqrt{2}}(f_3 + f_4) \ .$$

The B_{1u} SALC-AO may be found in a similar fashion:

$$\begin{aligned} P_{B_{1u}} f_3 &= (1)\ f_3 + (1)\ f_3 + (-1)\ f_4 + (-1)\ f_4 + \\ &\quad (-1)\ f_4 + (-1)\ f_4 + (1)\ f_3 + (1)\ f_3 \\ &= 4f_3 - 4f_4 \end{aligned}$$

Normalization of this SALC-AO yields:

$$\varphi_{1b_{3u}} = \frac{1}{\sqrt{2}}(f_3 - f_4) \ .$$

Again since there are only two SALC-AOs and both are of different symmetry types these SALC-AOs are MOs and the 2x2 Hamiltonian matrix reduces to 2 1x1 matrices.

$$H_{1a_g,1a_g} = \int \frac{1}{\sqrt{2}}(f_3 + f_4)H\frac{1}{\sqrt{2}}(f_3 + f_4)d\tau$$

$$= \frac{1}{2}\left(\int f_3Hf_3d\tau + 2\int f_3Hf_4d\tau + \int f_4Hf_4d\tau\right)$$

$$= \frac{1}{2}\left(\alpha_{sp^2} + 2\beta_{sp^2-sp^2} + \alpha_{sp^2}\right)$$

$$= \alpha_{sp^2} + \beta_{sp^2-sp^2}$$

$$= -14.7 + (-5.0) = -19.7$$

$$H_{1b_{1u},1b_{1u}} = \int \frac{1}{\sqrt{2}}(f_3 - f_4)H\frac{1}{\sqrt{2}}(f_3 - f_4)d\tau$$

$$= \frac{1}{2}\left(\int f_3Hf_3d\tau - 2\int f_3Hf_4d\tau + \int f_4Hf_4d\tau\right)$$

$$= \frac{1}{2}\left(\alpha_{sp^2} - 2\beta_{sp^2-sp^2} + \alpha_{sp^2}\right)$$

$$= \alpha_{sp^2} - \beta_{sp^2-sp^2}$$

$$= -14.7 - (-5.0) = -9.7$$

3. c. The C sp^2 orbitals and the H s orbitals forming the C-H bonds generate the following reducible representation:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_{sp^2-s}	8	0	0	0	0	0	0	8

This reducible representation reduces to 2A$_g$, 2B$_{3g}$, 2B$_{1u}$ and 2B$_{2u}$ irreducible representations.

Projectors are used to find the SALC-AOs for these irreducible representations.

$$P_{A_g} f_6 = (1)E\ f_6 + (1)C_2(z)\ f_6 + (1)C_2(y)\ f_6 + (1)C_2(x)\ f_6 + (1)i\ f_6 + (1)\sigma(xy)\ f_6 + (1)\sigma(xz)\ f_6 + (1)\sigma(yz)\ f_6$$

$$= (1)\ f_6 + (1)\ f_5 + (1)\ f_7 + (1)\ f_8 + (1)\ f_8 + (1)\ f_7 + (1)\ f_5 + (1)\ f_6$$

$$= 2f_5 + 2f_6 + 2f_7 + 2f_8$$

Normalization yields: $\varphi_{2a_g} = \frac{1}{2}(f_5 + f_6 + f_7 + f_8)$.

$$P_{A_g} f_{10} = (1)E\ f_{10} + (1)C_2(z)\ f_{10} + (1)C_2(y)\ f_{10} + (1)C_2(x)\ f_{10} + (1)i\ f_{10} + (1)\sigma(xy)\ f_{10} + (1)\sigma(xz)\ f_{10} + (1)\sigma(yz)\ f_{10}$$

$$= (1)\ f_{10} + (1)\ f_9 + (1)\ f_{11} + (1)\ f_{12} + (1)\ f_{12} + (1)\ f_{11} + (1)\ f_9 + (1)\ f_{10}$$

$$= 2f_9 + 2f_{10} + 2f_{11} + 2f_{12}$$

Normalization yields: $\varphi_{3a_g} = \frac{1}{2}(f_9 + f_{10} + f_{11} + f_{12})$.

$$P_{B_{3g}} f_6 = (1)\ f_6 + (-1)\ f_5 + (-1)\ f_7 + (1)\ f_8 + (1)\ f_8 + (-1)\ f_7 + (-1)\ f_5 + (1)\ f_6$$

$$= -2f_5 + 2f_6 - 2f_7 + 2f_8$$

Normalization yields: $\varphi_{1b_{3g}} = \frac{1}{2}(-f_5 + f_6 - f_7 + f_8)$.

$$P_{B_{3g}} f_{10} = (1)\ f_{10} + (-1)\ f_9 + (-1)\ f_{11} + (1)\ f_{12} +$$

$$(1)\ f_{12} + (-1)\ f_{11} + (-1)\ f_9 + (1)\ f_{10}$$
$$= -2f_9 + 2f_{10} - 2f_{11} + 2f_{12}$$

Normalization yields: $\varphi_{2b_{3g}} = \frac{1}{2}(-f_9 + f_{10} - f_{11} + f_{12})$.

$$P_{B_{1u}}\ f_6 = (1)\ f_6 + (1)\ f_5 + (-1)\ f_7 + (-1)\ f_8 +$$
$$(-1)\ f_8 + (-1)\ f_7 + (1)\ f_5 + (1)\ f_6$$
$$= 2f_5 + 2f_6 - 2f_7 - 2f_8$$

Normalization yields: $\varphi_{2b_{1u}} = \frac{1}{2}(f_5 + f_6 - f_7 - f_8)$.

$$P_{B_{1u}}\ f_{10} = (1)\ f_{10} + (1)\ f_9 + (-1)\ f_{11} + (-1)\ f_{12} +$$
$$(-1)\ f_{12} + (-1)\ f_{11} + (1)\ f_9 + (1)\ f_{10}$$
$$= 2f_9 + 2f_{10} - 2f_{11} - 2f_{12}$$

Normalization yields: $\varphi_{3b_{1u}} = \frac{1}{2}(f_9 + f_{10} - f_{11} - f_{12})$.

$$P_{B_{2u}}\ f_6 = (1)\ f_6 + (-1)\ f_5 + (1)\ f_7 + (-1)\ f_8 +$$
$$(-1)\ f_8 + (1)\ f_7 + (-1)\ f_5 + (1)\ f_6$$
$$= -2f_5 + 2f_6 + 2f_7 - 2f_8$$

Normalization yields: $\varphi_{1b_{2u}} = \frac{1}{2}(-f_5 + f_6 + f_7 - f_8)$.

$$P_{B_{2u}}\ f_{10} = (1)\ f_{10} + (-1)\ f_9 + (1)\ f_{11} + (-1)\ f_{12} +$$
$$(-1)\ f_{12} + (1)\ f_{11} + (-1)\ f_9 + (1)\ f_{10}$$
$$= -2f_9 + 2f_{10} + 2f_{11} - 2f_{12}$$

Normalization yields: $\varphi_{2b_{2u}} = \frac{1}{2}(-f_9 + f_{10} + f_{11} - f_{12})$.

Each of these four 2x2 symmetry blocks generate identical Hamiltonian matrices. This will be demonstrated for the B_{3g} symmetry, the others proceed analogously:

$$H_{1b_{3g},1b_{3g}} = \int \frac{1}{2}(-f_5 + f_6 - f_7 + f_8) H \frac{1}{2}(-f_5 + f_6 - f_7 + f_8) d\tau$$

$$= \frac{1}{4}\Big\{ \int f_5Hf_5d\tau - \int f_5Hf_6d\tau + \int f_5Hf_7d\tau - \int f_5Hf_8d\tau -$$
$$\int f_6Hf_5d\tau + \int f_6Hf_6d\tau - \int f_6Hf_7d\tau + \int f_6Hf_8d\tau +$$
$$\int f_7Hf_5d\tau - \int f_7Hf_6d\tau + \int f_7Hf_7d\tau - \int f_7Hf_8d\tau -$$
$$\int f_8Hf_5d\tau + \int f_8Hf_6d\tau - \int f_8Hf_7d\tau + \int f_8Hf_8d\tau \Big\}$$

$$= \frac{1}{4}\Big\{ \alpha_{sp^2} - 0 + 0 - 0 -$$
$$0 + \alpha_{sp^2} - 0 + 0 +$$
$$0 - 0 + \alpha_{sp^2} - 0 -$$
$$0 + 0 - 0 + \alpha_{sp^2} \Big\} = \alpha_{sp^2}$$

$$H_{1b_{3g},2b_{3g}} = \int \frac{1}{2}(-f_5 + f_6 - f_7 + f_8) H \frac{1}{2}(-f_9 + f_{10} - f_{11} + f_{12}) d\tau$$

$$= \frac{1}{4}\Big\{ \int f_5Hf_9d\tau - \int f_5Hf_{10}d\tau + \int f_5Hf_{11}d\tau - \int f_5Hf_{12}d\tau -$$

$$\int f_6Hf_9d\tau + \int f_6Hf_{10}d\tau - \int f_6Hf_{11}d\tau + \int f_6Hf_{12}d\tau +$$

$$\int f_7Hf_9d\tau - \int f_7Hf_{10}d\tau + \int f_7Hf_{11}d\tau - \int f_7Hf_{12}d\tau -$$

$$\int f_8Hf_9d\tau + \int f_8Hf_{10}d\tau - \int f_8Hf_{11}d\tau + \int f_8Hf_{12}d\tau \}$$

$$= \frac{1}{4}\{\beta_{sp^2-s} - 0 + 0 - 0 -$$

$$0 + \beta_{sp^2-s} - 0 + 0 +$$

$$0 - 0 + \beta_{sp^2-s} - 0 -$$

$$0 + 0 - 0 + \beta_{sp^2-s}\} = \beta_{sp^2-s}$$

$$H_{2b_{3g},2b_{3g}} = \int \frac{1}{2}(-f_9 + f_{10} - f_{11} + f_{12})H\frac{1}{2}(-f_9 + f_{10} - f_{11} + f_{12})d\tau$$

$$= \frac{1}{4}\{\int f_9Hf_9d\tau - \int f_9Hf_{10}d\tau + \int f_9Hf_{11}d\tau - \int f_9Hf_{12}d\tau -$$

$$\int f_{10}Hf_9d\tau + \int f_{10}Hf_{10}d\tau - \int f_{10}Hf_{11}d\tau + \int f_{10}Hf_{12}d\tau +$$

$$\int f_{11}Hf_9d\tau - \int f_{11}Hf_{10}d\tau + \int f_{11}Hf_{11}d\tau - \int f_{11}Hf_{12}d\tau -$$

$$\int f_{12}Hf_9d\tau + \int f_{12}Hf_{10}d\tau - \int f_{12}Hf_{11}d\tau + \int f_{12}Hf_{12}d\tau \}$$

$$= \frac{1}{4}\{\alpha_s - 0 + 0 - 0 -$$

$$0 + \alpha_s - 0 + 0 +$$

$$0 - 0 + \alpha_s - 0 -$$

$$0 + 0 - 0 + \alpha_s\} = \alpha_s$$

This matrix eigenvalue problem then becomes:

$$\begin{vmatrix} \alpha_{sp^2} - \varepsilon & \beta_{sp^2-s} \\ \beta_{sp^2-s} & \alpha_s - \varepsilon \end{vmatrix} = 0$$

$$\begin{vmatrix} -14.7 - \varepsilon & -4.0 \\ -4.0 & -13.6 - \varepsilon \end{vmatrix} = 0$$

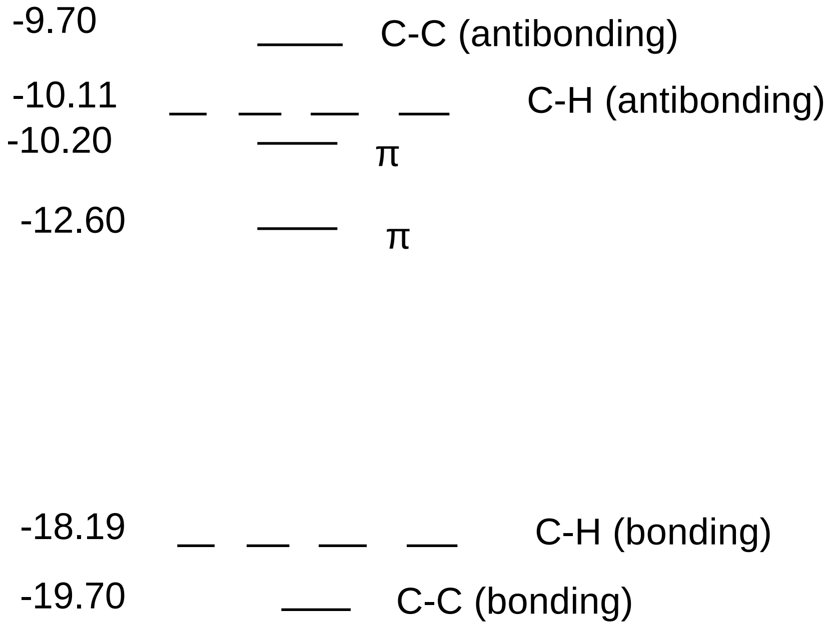
Solving this yields eigenvalues of:

$$| -18.19 \quad -10.11 |$$

and corresponding eigenvectors:

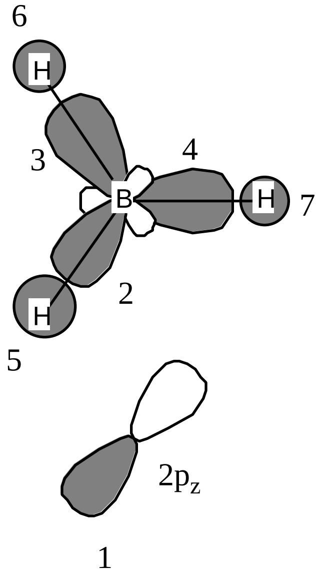
$$\begin{vmatrix} -0.7537 & -0.6572 \\ -0.6572 & 0.7537 \end{vmatrix}$$

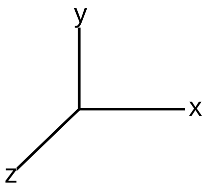
This results in an orbital energy diagram:



For the ground state of ethylene you would fill the bottom 3 levels (the C-C, C-H, and π bonding orbitals), with 12 electrons.

4.





Using the hybrid atomic orbitals as labeled above (functions f_1-f_7) and the D_{3h} point group symmetry it is easiest to construct three sets of reducible representations:

i. the B $2p_z$ orbital (labeled function 1)

ii. the 3 B sp^2 hybrids (labeled functions 2 - 4)

iii. the 3 H 1s orbitals (labeled functions 5 - 7).

i. The B $2p_z$ orbital generates the following irreducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{2p_z}	1	1	-1	-1	-1	1

This irreducible representation is A_2'' and is its own SALC-AO.

ii. The B sp^2 orbitals generate the following reducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{sp2}	3	0	1	3	0	1

This reducible representation reduces to $1A_1'$ and $1E'$
irreducible representations.
Projectors are used to find the SALC-AOs for these irreducible representations.
Define: C_3 = 120 degree rotation, C_3' = 240 degree rotation,
C_2 = rotation around f_4, C_2' = rotation around f_2, and
C_2 = rotation around f_3. S_3 and S_3' are defined analogous
to C_3 and C3' with accompanying horizontal reflection.
σ_v = a reflection plane through f_4, σ_v' = a reflection plane
through f_2, and σ_v'' = a reflection plane through f_3

$P_{A_1'}\, f_2 =$ $(1)E\, f_2 + (1)C_3\, f_2 + (1)C_3'\, f_2 +$
$(1)C_2\, f_2 + (1)C_2'\, f_2 + (1)C_2''\, f_2 +$
$(1)\sigma_h\, f_2 + (1)S_3\, f_2 + (1)S_3'\, f_2$
$(1)\sigma_v\, f_2 + (1)\sigma_v'\, f_2 + (1)\sigma_v''\, f_2$
$=$ $(1)f_2 + (1)f_3 + (1)f_4 +$
$(1)f_3 + (1)f_2 + (1)f_4 +$
$(1)f_2 + (1)f_3 + (1)f_4 +$
$(1)f_3 + (1)f_2 + (1)\sigma f_4$
$=$ $4f_2 + 4f_3 + 4f_4$

Normalization yields: $\varphi_{1a_1'} = \frac{1}{\sqrt{3}}(f_2 + f_3 + f_4)$.

$P_{E'}\, f_2 =$ $(2)E\, f_2 + (-1)C_3\, f_2 + (-1)C_3'\, f_2 +$
$(0)C_2\, f_2 + (0)C_2'\, f_2 + (0)C_2''\, f_2 +$
$(2)\sigma_h\, f_2 + (-1)S_3\, f_2 + (-1)S_3'\, f_2$
$(0)\sigma_v\, f_2 + (0)\sigma_v'\, f_2 + (0)\sigma_v''\, f_2$
$=$ $(2)f_2 + (-1)f_3 + (-1)f_4 +$
$(2)f_2 + (-1)f_3 + (-1)f_4 +$
$=$ $4f_2 - 2f_3 - 2f_4$

Normalization yields: $\varphi_{1e'} = \frac{1}{\sqrt{6}}(2f_2 - f_3 - f_4)$.

To find the second e' (orthogonal to the first), projection on f_3 yields $(2f_3 - f_2 - f_4)$ and projection on f_4 yields $(2f_4 - f_2 - f_3)$. Neither of these functions are orthogonal to the first, but a combination of the two $(2f_3 - f_2 - f_4) - (2f_4 - f_2 - f_3)$ yields a function which is orthogonal to the first.

Normalization yields: $\varphi_{2e'} = \frac{1}{\sqrt{2}}(f_3 - f_4)$.

iii. The H 1s orbitals generate the following reducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{sp2}	3	0	1	3	0	1

This reducible representation reduces to $1A_1'$ and $1E'$
irreducible representations.exactly like part ii. and in addition the projectors used to find the SALC-AOs for these irreducible representations.is exactly analogous to part ii.

$$\varphi_{2a_1'} = \frac{1}{\sqrt{3}}(f_5 + f_6 + f_7)$$

$$\varphi_{3e'} = \frac{1}{\sqrt{6}}(2f_5 - f_6 - f_7) \quad .$$

$$\varphi_{4e'} = \frac{1}{\sqrt{2}}(f_6 - f_7) \quad .$$

So, there are 1A$_2$'', 2A$_1$' and 2E' orbitals. Solving the Hamiltonian matrix for each symmetry block yields:

A$_2$'' Block:

$$H_{1a_{2'},1a_{2'}} = \int f_1 H f_1 d\tau$$

$$= \alpha_{2p\pi} \qquad = -8.5$$

A$_1$' Block:

$$H_{1a_{1'},1a_{1'}} = \int \frac{1}{\sqrt{3}}(f_2 + f_3 + f_4) H \frac{1}{\sqrt{3}}(f_2 + f_3 + f_4) d\tau$$

$$= \frac{1}{3}\Big\{ \int f_2Hf_2d\tau + \int f_2Hf_3d\tau + \int f_2Hf_4d\tau +$$

$$\int f_3Hf_2d\tau + \int f_3Hf_3d\tau + \int f_3Hf_4d\tau +$$

$$\int f_4Hf_2d\tau + \int f_4Hf_3d\tau + \int f_4Hf_4d\tau \Big\}$$

$$= \frac{1}{3}\Big\{ \alpha_{sp^2} + 0 + 0 +$$

$$0 + \alpha_{sp^2} + 0 +$$

$$0 + 0 + \alpha_{sp^2} \Big\} = \alpha_{sp^2}$$

$$H_{1a_{1'},2a_{1'}} = \int \frac{1}{\sqrt{3}}(f_2 + f_3 + f_4) H \frac{1}{\sqrt{3}}(f_5 + f_6 + f_7) d\tau$$

$$= \frac{1}{3}\Big\{ \int f_2Hf_5d\tau + \int f_2Hf_6d\tau + \int f_2Hf_7d\tau +$$

$$\int f_3Hf_5d\tau + \int f_3Hf_6d\tau + \int f_3Hf_7d\tau +$$

$$\int f_4Hf_5d\tau + \int f_4Hf_6d\tau + \int f_4Hf_7d\tau \Big\}$$

$$= \frac{1}{3}\Big\{ \beta_{sp^2\text{-}s} + 0 + 0 +$$

$$0 + \beta_{sp^2\text{-}s} + 0 +$$

$$0 + 0 + \beta_{sp^2\text{-}s} \Big\} = \beta_{sp^2\text{-}s}$$

$$H_{2a_{1'},2a_{1'}} = \int \frac{1}{\sqrt{3}}(f_5 + f_6 + f_7) H \frac{1}{\sqrt{3}}(f_5 + f_6 + f_7) d\tau$$

$$= \frac{1}{3}\Big\{ \int f_5Hf_5d\tau + \int f_5Hf_6d\tau + \int f_5Hf_7d\tau +$$

$$\int f_6Hf_5d\tau + \int f_6Hf_6d\tau + \int f_6Hf_7d\tau +$$

$$\int f_7 H f_5 d\tau \;+\; \int f_7 H f_6 d\tau \;+\; \int f_7 H f_7 d\tau \Big\}$$

$$= \frac{1}{3}\Big\{\alpha_s + 0 + 0 +$$

$$0 + \alpha_s + 0 +$$

$$0 + 0 + \alpha_s \Big\} = \alpha_s$$

This matrix eigenvalue problem then becomes:

$$\begin{vmatrix} \alpha_{sp^2} - \varepsilon & \beta_{sp^2\text{-}s} \\ \beta_{sp^2\text{-}s} & \alpha_s - \varepsilon \end{vmatrix} = 0$$

$$\begin{vmatrix} -10.7 - \varepsilon & -3.5 \\ -3.5 & -13.6 - \varepsilon \end{vmatrix} = 0$$

Solving this yields eigenvalues of:

$$\begin{vmatrix} -15.94 & -8.36 \end{vmatrix}$$

and corresponding eigenvectors:

$$\begin{vmatrix} -0.5555 & -0.8315 \\ -0.8315 & 0.5555 \end{vmatrix}$$

E' Block:

This 4x4 symmetry block factors to two 2x2 blocks: where one 2x2 block includes the SALC-AOs

$$\varphi_{e'} = \frac{1}{\sqrt{6}}(2f_2 - f_3 - f_4)$$

$$\varphi_{e'} = \frac{1}{\sqrt{6}}(2f_5 - f_6 - f_7)\ ,$$

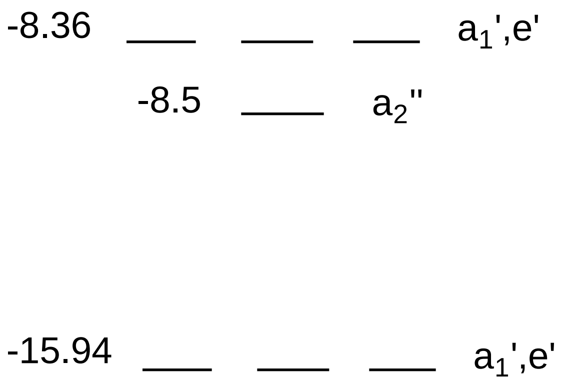
and the other includes the SALC-AOs

$$\varphi_{e'} = \frac{1}{\sqrt{2}}(f_3 - f_4)$$

$$\varphi_{e'} = \frac{1}{\sqrt{2}}(f_6 - f_7)\ .$$

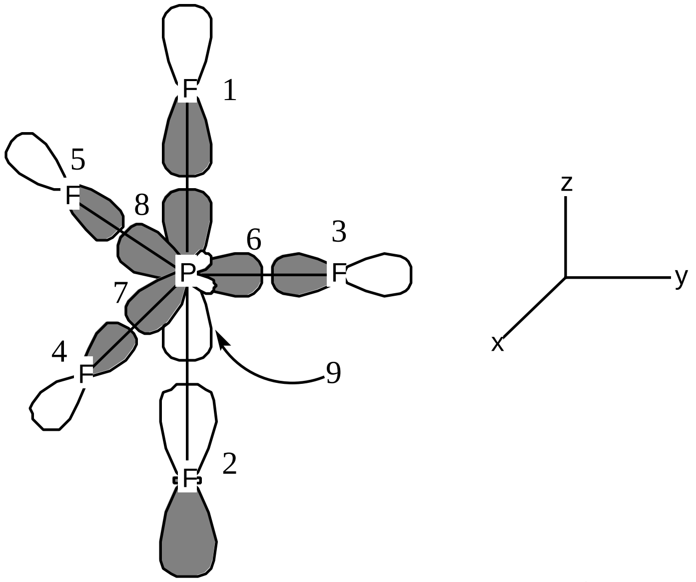
Both of these 2x2 matrices are identical to the A_1' 2x2 array and therefore yield identical energies and MO coefficients.

This results in an orbital energy diagram:



For the ground state of BH_3 you would fill the bottom level (B-H bonding), a_1' and e' orbitals, with 6 electrons.

5.



5. a. The two F p orbitals (top and bottom) generate the following reducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_p	2	2	0	0	0	2

This reducible representation reduces to $1A_1'$ and $1A_2''$ irreducible representations.

Projectors may be used to find the SALC-AOs for these irreducible representations.

$$\varphi_{a_1'} = \frac{1}{\sqrt{2}}(f_1 - f_2)$$

$$\varphi_{a_2''} = \frac{1}{\sqrt{2}}(f_1 + f_2)$$

5. b. The three trigonal F p orbitals generate the following reducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_p	3	0	1	3	0	1

This reducible representation reduces to $1A_1'$ and 1E' irreducible representations.

Projectors may be used to find the SALC-AOs for these irreducible representations (but they are exactly analogous to the previous few problems):

$$\varphi_{a_1'} = \frac{1}{\sqrt{3}}(f_3 + f_4 + f_5)$$

$$\varphi_{e'} = \frac{1}{\sqrt{6}}(2f_3 - f_4 - f_5)$$

$$\varphi_{e'} = \frac{1}{\sqrt{2}}(f_4 - f_5)\ .$$

5. c. The 3 P sp^2 orbitals generate the following reducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{sp^2}	3	0	1	3	0	1

This reducible representation reduces to $1A_1'$ and $1E'$ irreducible representations. Again, projectors may be used to find the SALC-AOs for these irreducible representations.(but again they are exactly analogous to the previous few problems):

$$\varphi_{a_1'} = \frac{1}{\sqrt{3}}(f_6 + f_7 + f_8)$$

$$\varphi_{e'} = \frac{1}{\sqrt{6}}(2f_6 - f_7 - f_8)$$

$$\varphi_{e'} = \frac{1}{\sqrt{2}}(f_7 - f_8)\ .$$

The leftover P p_z orbital generate the following irreducible representation:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{p_z}	1	1	-1	-1	-1	1

This irreducible representation is an A_2''

$$\varphi_{a_2''} = f_9.$$

Drawing an energy level diagram using these SALC-AOs would result in the following: