To: Chemistry 344
From: Cynthia J. Jameson

Never mind that the physics behind how computers and TV sets work depends on an understanding of the quantum behavior of electrons. As we have seen in Chemistry 344, the fundamental nature of all of chemistry, the structure of molecules, the empirical periodicity of properties as described by the Periodic Table, the characterization of individual molecules by their spectra (transitions between energy states), and so on, requires quantum mechanics. Unfortunately, we did not have time to show that the empirical laws of thermodynamics, and rates of reactions, as well as chemical equilibrium constants can be arrived at starting with molecular quantum states and using statistical theory. Nevertheless, I hope that by the end of the semester, I have enticed you to see Chemistry through the lens of principles of quantum mechanics.

Let me just leave you with one philosophical bit. There is something more profound that the wavefunctions and probability description that is inherent in the QM description that quantum mechanics does for us. "By introducing uncertainty and probability into the equations, quantum mechanics does away once and for all with the predictive clockwork of Newtonian determinism. If the universe operates, at the deepest level, in a genuinely unpredictable and indeterministic way, then we are given back our free will, and we can after all make our own decisions and our own mistakes."*

*M. White and J. Gribbin, "Stephen Hawking: A Life in Science"

Chemistry 344

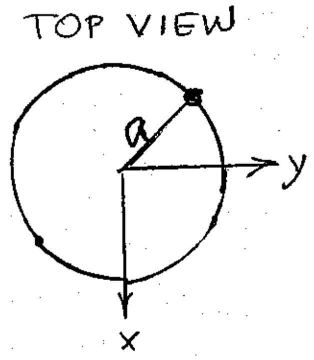
Final Exam ANSWERS
Dec. 10, 2002

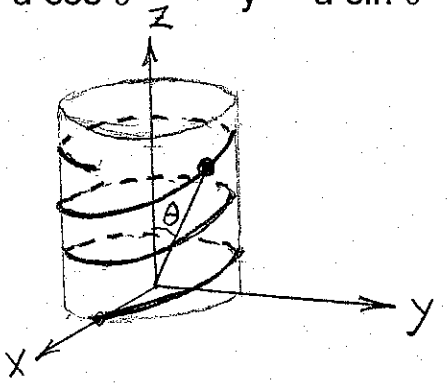
Look at the entire exam first, then decide which problems are easiest for you to start with

1. The helix is a very important structure for biochemistry. At least some parts of important biological macromolecules have helical structure. In Problem Set 5 you could interpret the variation of the wavelength of the three bands in the ultraviolet spectrum of series of compounds containing aromatic rings by using the simple model of a particle on a circle. It turns out that many qualitative aspects of the optical rotation spectra of helical systems can be interpreted entirely by using only the electron on a helix model system. Let us see how to start. We have solved several Schrödinger equations in only one variable, for a particle on a circle, as well as a particle on a line along the x axis. Now let us consider the case which is sort of a combination of the two, that is, we take the line and wrap it on the outside of a right circular cylinder to form a helix.

A particle of mass M is constrained to move along a right-handed helix consisting of t turns (shown below). The radius of the helix is a and the pitch of the helix (the distance between successive turns) is $b2\pi$. The position of the electron anywhere on the helix is given by:

$$x = a\cos\theta \qquad y = a\sin\theta \qquad z = b\theta$$





Since there are t turns, at the bottom end of the helix $\theta = 0°$
and at the top end of the helix $\theta = t(2\pi)$.

For a free particle constrained to move on this helix of t turns, we specify that
$V(x,y,z)$ = constant = 0 <u>on the helix</u> and $V = \infty$ everywhere else. Obviously a complicated V!
The kinetic energy of this single particle is of course, still given by

$$\text{K.E.} = p_x^2/2M + p_y^2/2M + p_z^2/2M$$

We replace the individual components of linear momentum by the corresponding quantum mechanical operators,

$(p_x)_{op} = \frac{\hbar}{i}\frac{\partial}{\partial x}$	$(p_y)_{op} = \frac{\hbar}{i}\frac{\partial}{\partial y}$	$(p_z)_{op} = \frac{\hbar}{i}\frac{\partial}{\partial z}$

Therefore, in terms of x,y and z, the Hamiltonian operator for this particle is

$$\mathcal{H} = \frac{-\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)$$

As we have already found in other simple systems such as the particle on a circle, it is possible to make use of a change in coordinate system to simplify the form of the Schrödinger equation that needs to be solved. For the particle on a circle, we changed coordinates from the set (x,y) into the set (R,ϕ). Since the radius R of the circle is a constant we solved a Schrödinger equation in ϕ only.

For the *particle on the helix*, instead of having the operators and the eigenfunctions in terms of three variables (x,y,z), we can use a transformation to the new coordinates (a,b,θ) defined above: $x = a\cos\theta$ $y = a\sin\theta$ $z = b\,\theta$

By varying a, b, and θ one could sweep all of 3-D space, but for the helix, a and b are constants. Thus, our operators and eigenfunctions can be written in terms of only one variable, θ. In other words, to locate the particle on the helix, we only need to know the value of θ. We express the derivatives with respect to x,y,z in terms of the derivatives with respect to a, b, and θ, and since a and b are constants for the helix, we afterwards leave out all derivatives $\partial^n/\partial a^n$, $\partial^n/\partial b^n$ from the Hamiltonian, that is, we can do the following:

$$\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 \Rightarrow (a^2+b^2)^{-1}\,\partial^2/\partial\theta^2 \text{ for } a \text{ and } b \text{ are constants}$$

Thus, in terms of θ, the <u>Schrödinger equation</u> to be solved is
(write the equation explicitly in terms of a, b, and θ):

$$\left[\frac{-\hbar^2}{2M}\cdot\left(\frac{1}{a^2+b^2}\right)\frac{\partial^2}{\partial\theta^2} + 0\right]\Psi(\theta) = E\,\Psi(\theta)$$

Examine the above Schrödinger equation for this system, and figure out what kind of function will satisfy this equation. Remember that this system is similar in some way to the particle on a line along the x axis from 0 to L, except that here the line is wound around the outside surface of a right circular cylinder.

Try $\Psi(\theta)$ of the form: $A\sin(k\theta) + B\cos(k\theta)$

$$\frac{\partial}{\partial\theta} A\sin(k\theta) = k\cos k\theta$$

$$\frac{\partial^2}{\partial\theta^2} A\sin(k\theta) = k^2(-\sin k\theta)$$

Substitute it into the Schrödinger equation and <u>establish whether it can satisfy the equation</u>.

$$\frac{-\hbar^2}{2M(a^2+b^2)}\frac{\partial^2}{\partial\theta^2}\left[A\sin(k\theta) + B\cos(k\theta)\right] \overset{?}{=} E\left[A\sin(k\theta) + B\cos(k\theta)\right]$$

$$\frac{-\hbar^2}{2M(a^2+b^2)}\left[A\cdot -k^2\sin(k\theta) + B\cdot -k^2\cos(k\theta)\right] \overset{?}{=} E\left[A\sin(k\theta) + B\cos(k\theta)\right]$$

$$+\frac{k^2\hbar^2}{2M(a^2+b^2)}\left[A\sin(k\theta) + B\cos(k\theta)\right] = E\left[A\sin(k\theta) + B\cos(k\theta)\right]$$

YES it satisfies the equation

What are the conditions that a function describing the state of this physical system (the single particle of mass M on the helix) has to meet in order to be an acceptable description? Hint: The particle is not allowed to exist beyond either end of the helix.

In general	Explicitly, for this system*
State function has to be: a) FINITE	since sin is between 1 and −1, cos is between 1 and −1, the function is always finite.
b) CONTINUOUS	since $\Psi = 0$ at $\theta < 0$ i.e. negative values of θ (particle cannot exist beyond this end of the helix), to be continuous, $\Psi(\theta = 0) \overset{must}{=} 0 = A\sin(k\theta) + B\cos(k\theta)$ since for any k, $\sin(k \cdot 0) = 0$, we only have to set $B = 0$ to make $\Psi(\theta = 0) = 0$ $\therefore \Psi(\theta) = A\sin k\theta$
	since $\Psi = 0$ at $\theta > t2\pi$ (particle cannot exist beyond this end of the helix), to be continuous $\Psi(\theta = t2\pi) = A\sin(kt2\pi) \overset{must}{=} 0$ Can only happen if $2kt$ = integer = 1, 2, 3, ··n
c) SINGLE-VALUED	This is satisfied $\Psi(\theta) = A\sin(\frac{n}{2t}\theta)$ have only one value for any point on the helix and we have also made it single-valued at $\theta = 0$ and $\theta = t2\pi$

*That is, apply each of the requirements of acceptable state functions in mathematical terms specific to this system (in terms of the constants *a*, *b*, *t*, and the variable θ).

Calculate the energy eigenvalues of this system in terms of the constants *a*, *b*, *t*

We already found that $\frac{k^2\hbar^2}{2M(a^2+b^2)} = E$ and $2kt = 1, 2, 3, \ldots n$ integer

or $k = \frac{n}{2t}$

Thus, $$E = \frac{(n/2t)^2\hbar^2}{2M(a^2+b^2)} = \frac{n^2\hbar^2}{8M(a^2+b^2)t^2}$$

Specify the conditions that must be satisfied by the quantities appearing in your expression for the energy eigenvalue.

n must be an integer 1, 2, 3, ...

n cannot be zero because this would make sin zero for all θ.

Normalize the function that satisfies the above conditions:

$$\int_0^{t2\pi} A^2 \sin^2\left(\frac{n}{2t}\theta\right) d\theta = 1 \qquad A^2\left[\frac{1}{2}\theta - \frac{1}{4\frac{n}{2t}}\sin\left(\frac{n}{t}\theta\right)\right]_0^{t2\pi} = 1$$

$$A^2\left[\frac{1}{2}t2\pi\right] = 1 \qquad A = \frac{1}{\sqrt{t\pi}}$$

Summarize: Explicitly write the 3 lowest energy eigenvalues and corresponding normalized eigenfunctions below:

quantum number	Energy eigenvalue	Eigenfunction
$n=1$	$\hbar^2/8M(a^2+b^2)t^2$	$\frac{1}{\sqrt{t\pi}}\sin\left(\frac{\theta}{2t}\right)$
$n=2$	$\hbar^2/2M(a^2+b^2)t^2$	$\frac{1}{\sqrt{t\pi}}\sin\left(\theta/t\right)$
$n=3$	$9\hbar^2/8M(a^2+b^2)t^2$	$\frac{1}{\sqrt{t\pi}}\sin\left(\frac{3\theta}{2t}\right)$

In this coordinate system, the z component of linear momentum is

$$(p_z)_{op} = (\hbar/i)\, b\, (a^2+b^2)^{-1}\, \partial/\partial\theta$$

For the system of a particle on a helix, determine whether $(p_z)_{op}$ commutes with $\mathcal{H}$

$$[p_{z_{op}}, \mathcal{H}] = \left[\frac{\hbar b}{i(a^2+b^2)}\frac{d}{d\theta}, \frac{-\hbar^2}{2M(a^2+b^2)}\frac{d^2}{d\theta^2}\right] = 0$$

yea they commute

What are the constraints, if any, on simultaneously measuring the energy and the z component of linear momentum for this system? Explain.

none $\quad \sigma_{p_z}\cdot\sigma_E \geq \frac{1}{2}\left\langle\frac{[p_z,\mathcal{H}]}{i}\right\rangle \quad$ Since $[p_z,\mathcal{H}]=0$ the product of standard deviations in measurements of p_z and E is ≥ 0

There are no theoretical limits

Calculate the expected average value of the outcomes of measurements of p_z on this system in its lowest energy state.

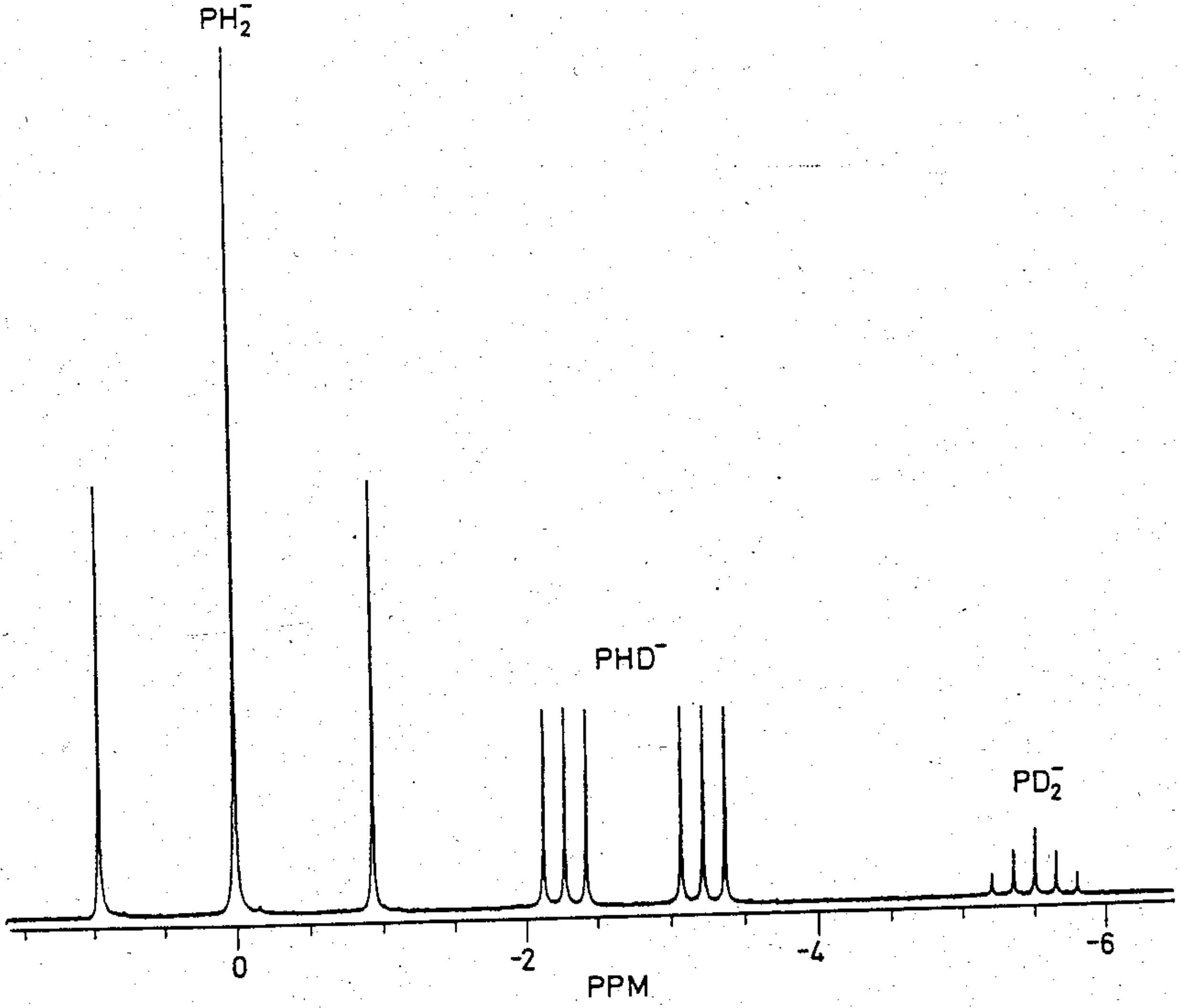
a real function

$$\langle p_z\rangle = \int_0^{t2\pi}\frac{1}{\sqrt{t\pi}}\sin\left(\frac{\theta}{2t}\right)\underbrace{\frac{\hbar}{i}\frac{b}{a^2+b^2}\frac{d}{d\theta}}_{\text{operator}}\frac{1}{\sqrt{t\pi}}\sin\left(\frac{\theta}{2t}\right)d\theta$$

$$= \frac{1}{t\pi}\frac{\hbar}{i}\frac{b}{a^2+b^2}\int_0^{t2\pi}\sin\left(\frac{\theta}{2t}\right)d\left(\sin\frac{\theta}{2t}\right) = 0$$

$$\int_{\sin(0)}^{\sin\pi} x\,dx = \left.\frac{x^2}{2}\right]_0^0 = 0$$

2. In field-free space the states having different z components of spin angular momentum are degenerate in energy. When placed in a magnetic field along the z direction, the formerly degenerate states become separated in energy on the order of several hundred MHz.
The ^{13}C NMR spectrum of $CDCl_3$ shows 3 equally spaced peaks of equal intensity. On the other hand, the NMR spectrum of the ^{31}P nucleus in a solution containing PH_2^-, PHD^-, and PD_2^- ions is shown below:
Nuclear spins are I = ½ for H, 1 for D, ½ for ^{31}P, ½ for ^{13}C



Using angular momentum properties and separation of variables, devise a concrete explanation of the observed intensities

The PH_2^- intensities are 1:2:1

2 protons of spin $\frac{1}{2}$. Each can have z component of angular momentum $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. Add the z components to get

$(+\frac{1}{2} + \frac{1}{2})\hbar = \hbar$ one of this 1

$(+\frac{1}{2} - \frac{1}{2})\hbar = 0$ two (degenerate) 2

$(-\frac{1}{2} + \frac{1}{2})\hbar = 0$

$(-\frac{1}{2} - \frac{1}{2})\hbar = -\hbar$ one of this 1

These are the states of the two protons, as seen by the ^{31}P nucleus

The PHD^- intensities are 1:1:1 and 1:1:1

one proton $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$ angular momentum z component

one deuteron $\hbar$, 0, $-\hbar$

they combine

$+\frac{1}{2}\hbar$ $\hbar$ 1

$+\frac{1}{2}\hbar$ 0 1

$+\frac{1}{2}\hbar$ $-\hbar$ 1

$-\frac{1}{2}\hbar$ $\hbar$ 1

$-\frac{1}{2}\hbar$ 0 1

$-\frac{1}{2}\hbar$ $-\hbar$ 1

These are the individual states (6 of them) of the proton + deuteron system as seen by the ^{31}P nucleus

The PD_2^- intensities are 1:2:3:2:1

2 deuterons, add z components

$(1 + 1)\hbar = 2\hbar$ one of this 1

$(1 + 0)\hbar = 1\hbar$ degen. two of these 2

$(1 - 1)\hbar = 0\hbar$

$(0 + 1)\hbar = 1\hbar$ degenerate three of these 3

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

$(0 - 1)\hbar = -1\hbar$ degenerate two of these 2

$(-1 + 1)\hbar = 0\hbar$

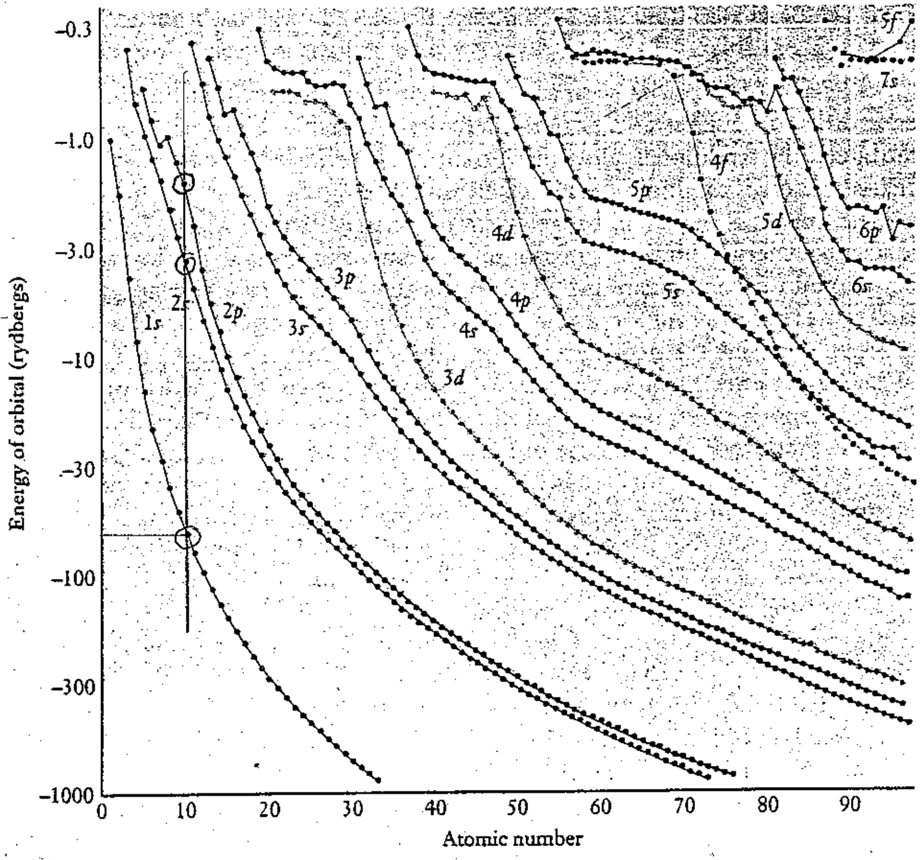
$(-1 + 0)\hbar = -1\hbar$

$(-1 - 1)\hbar = -2\hbar$ one of this 1

These are the states of the two deuterons as seen by the ^{31}P nucleus

Degeneracies give rise to multiple transitions falling on same frequency. thus, intensity pattern arises.

3. The orbital energies of the first 97 elements, based on photoelectron spectroscopy experiments, are shown below from a Freshman chemistry textbook (Oxtoby, Gillis and Nachtrieb): Note the logarithmic energy scale. One rydberg is 13.6057 eV.



You have seen the photoelectron spectrum of Ar in Problem Set 11 and calculated the expected peaks. Pick element 10 (Ne) from this figure. Write down the electronic configuration of the ion that is produced for each of the **3** peaks that are observed for Ne:

label	Electronic configuration
1S	$(1S)^1\ (2S)^2\ (2p)^6$
2S	$(1S)^2\ (2S)^1\ (2p)^6$
2p	$(1S)^2\ (2S)^2\ (2p)^5$

Using Slater's approximation, calculate the energy of the most energetic peak in the photoelectron spectrum of Ne. Compare your answer with the value in the figure.

Energy = E(Ne$^+$ ion) − E(Ne atom)

$(1S)^1(2S)^2(2p)^6$ $\quad$ $(1S)^2(2S)^2(2p)^6$

$E_i = -\frac{Z_{eff_i}}{n_i}$ rydberg for each electron

$$E(\text{Ne}^+\text{ion}) = \left[\frac{(10)^2}{1^2} + \frac{(10-0.35\times7-0.85)^2}{2^2}\times8\right]\left[-\frac{e^2}{2a_0}\right] = -(100+89.78)\text{ rydberg} = -189.78\text{ rydberg}$$

$$E(\text{Ne atom}) = \left[\frac{(10-0.30)^2}{1^2}\times2 + \frac{(10-0.35\times7-0.85\times2)^2}{2^2}\times8\right]\left[\frac{-e^2}{2a_0}\right] = (188.18+68.445) = -256.62\text{ rydberg}$$

$\Delta E = -189.78 - (-256.62) = 66.84$ rydberg

experimental value of binding energy of 1s electron is in agreement with this (as well as the log scale can be read!)

4. Write down the electronic configurations for the Li, N, and F atoms.

	# e	electronic configuration
Li	3	$(1s)^2(2s)^1$
N	7	$(1s)^2(2s)^2(2p)^3$
F	9	$(1s)^2(2s)^2(2p)^5$

Assuming that the ordering of the orbital energies for these molecules are the same, write down the <u>electronic configurations</u> expected for the Li_2, N_2 and F_2 diatomic molecules.

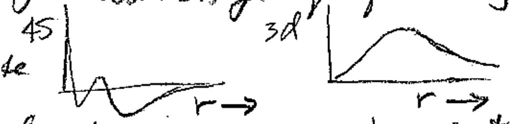
	# e	electronic configuration
Li_2	6	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2$
N_2	14	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p_z)^2(\pi_g 2p_{x,y})^4$
F_2	18	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p_z)^2(\pi_g 2p_{x,y})^4(\pi_u^* 2p_{x,y})^4$

The Pauli exclusion principle states that the total wavefunction of an atom or molecule has to be antisymmetric with respect to interchange of any two indistinguishable fermions (particles having half-integer spin) and symmetric with respect to interchange of any two indistinguishable bosons (particles with integer spins). The spins of the most abundant isotopes in the above molecules are: I=1/2 for ^{19}F, I = 1 for ^{14}N, and I=3/2 for ^{7}Li nuclei. Supposing someone took the spectra of the above molecules and did not identify which molecular species the Raman spectra belonged to, is it possible to determine whether or not the molecules are homonuclear diatomics rather than heteronuclear diatomics, if you were shown the Raman spectra ($v' \leftarrow v''$: $1 \leftarrow 0$, for example) of the molecules without identification? <u>Explain.</u>

Yes can tell if homonuclear or heteronuclear. Alternation of intensities will not occur in heteronuclear diatomics since the two nuclei can not be exchanged in the latter.

Alternation of intensities (1:3 in F_2, 3:6 in $^{14}N_2$ for example) comes from <u>only one set</u> of nuclear spin functions (either symmetric or antisymmetric) can go with J even, the other set can only go with J = odd, since $Y_{JM}(\theta,\phi)$ rotational functions change signs according to $(-1)^J$.

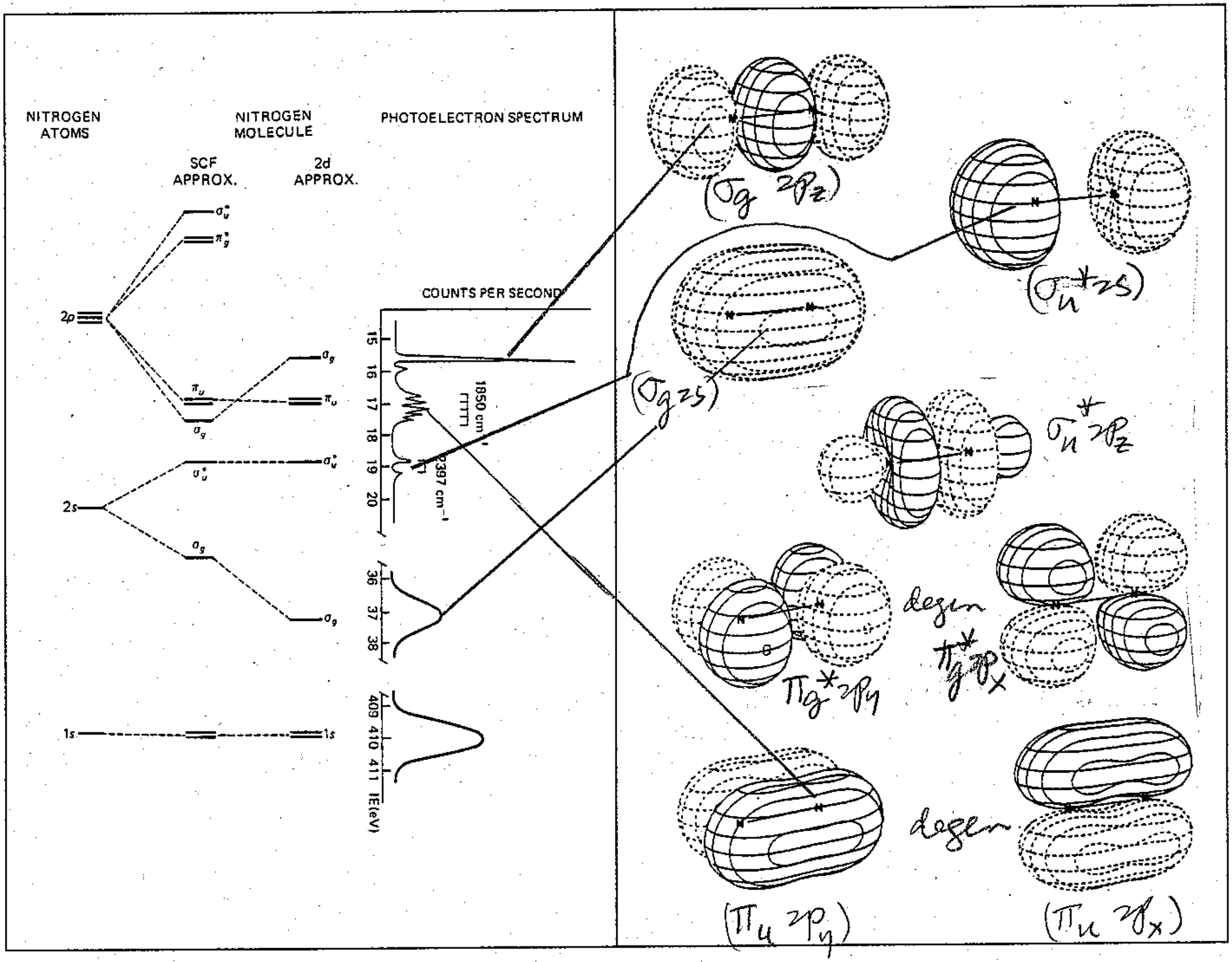
5. With what you have learned in Chemistry 344, it is now possible for you to derive or explain from first principles some facts you had learned in earlier chemistry classes. For each of the following which you would have learned in Chemistry 112, provide a quantitative explanation that is based on quantum mechanics, using mathematical equations as needed, starting from first principles.

Within a group in the Periodic Table, bond lengths in diatomic molecules usually increase with increasing atomic number Z. Thus, bond lengths increase in the series F_2 to Cl_2 to Br_2 to I_2.	In the Born-Oppenheimer separation of electronic and nuclear motion we solve the electronic motion Schrödinger eqn, for stationary nuclei $\left(\frac{-\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_i Z_A e^2/r_i - \sum_i Z_B e^2/r_i + \sum_i \sum_j \frac{e^2}{r_{ij}} + \frac{e^2}{R_{AB}}\right) \Psi(\vec{r}_1, ..) = U(R_{AB}) \Psi(\vec{r}_1, ..)$ $U(R_{AB})$ lowest eigenvalues of this equation has a minimum at that value of R_{AB} where $+e^2/R_{AB}$ is compensated by the electronic energy. This minimum corresponds to the equilibrium bond length. How the electronic energy changes with Z_{AB} depends on the core orbitals as well as the valence orbitals. The number of electrons and the n of the core increases in going from F to Cl to Br to I.
The tendency of an atom to donate or accept electrons in a chemical bond is indicated by the value of the electronegativity, which in the Mulliken definition is proportional to $(IE_1+EA)/2$. The electronegativity of F is greater than that of O.	Both IE_1 and EA can be calculated for the ground state configurations of the atom and the ions $IE_1 \equiv E(+ion) - E(atom)$ $EA \equiv E(atom) - E(-ion)$ E(+ion) and E(-ion) for their ground state configs can be calculated using self-consistent field or approximately by Slater rules. $(IE_1 + EA) = E(+ion) - E(-ion)$ We expect to find $[E(F^+) - E(F^-)] > [E(O^+) - E(O^-)]$
As orbitals are filled in order of increasing energies, in going from Ar to K the 4s orbital is filled first, before the 3d. On the other hand, Sc upon ionization to produce Sc^+ ion, loses the electron from the 4s rather than the 3d.	Because of the finite probability of finding the electron in a 4s orbital inside of the region where there is a high probability of finding the electron in a 3d there is incomplete screening of the nuclear charge by the inner core as far as the 4s electron is concerned, whereas the 3d does not have this advantage.  Ionization on the other hand, compared two energies E(+ion) and E(atom), with different screening in the two configurations.
Excited lithium atoms emit light strongly at a wavelength of 671 nm. This emission predominates when Li atoms are excited in a flame.	Li ground electronic configuration, the product of one-electron functions: $\psi_{1s}(1) \psi_{1s}(2) [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \cdot \psi_{2s}(3)\alpha(3)$, for example, (actually there are 3! terms with alternating signs) in $(1s)^2(2s)^1$. The excited electronic configuration corresponding to $(1s)^2(2p)^1$ in a flame, leads to states $^2P_{3/2}$, $^2P_{1/2}$ upon spin-orbit coupling. These states are connected to the ground $^2S_{1/2}$ state by an energy gap that is 671 nm (red), in the same way that in problem 7(b) the $^2P_{3/2}$, $^2P_{1/2}$ states of

Na atom drop to the $^2S_{1/2}$ state, emitting the two yellow lines, also seen as yellow emission for Na in flames.

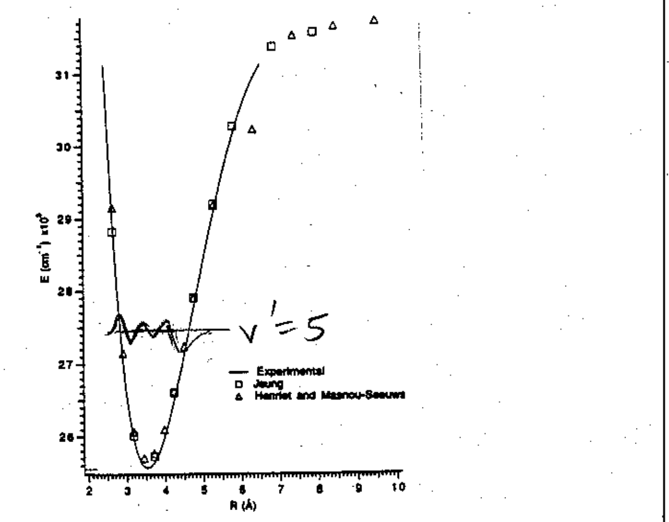
7. Spectroscopy provides a means by which we identify the compounds that we have made by organic or inorganic synthesis, provides a means by which we determine the composition of mixtures in quantitative analytical chemistry, provides a means by which we identify interstellar matter. That each molecule has a distinct fingerprint absorption/emission spectrum in each region of the electromagnetic spectrum comes about because of the following fundamental reason: Each molecule has a unique Hamiltonian which leads to a unique set of energy eigenfunctions and eigenvalues, between which set of energy states, transitions can be induced by light. The transitions that are "allowed" by the symmetry of the molecule and the symmetry of its eigenfunctions are the only ones that can be observed under absorption and emission. Demonstrate your understanding of the energy eigenfunctions and eigenvalues of a molecule by answering the following spectroscopy questions:

(a) Below we see the molecular orbital energies of N_2 molecule can be related to its photoelectron spectrum [in which one electron is kicked off by a photon, leaving an ion; various ionization energies are found, just as in atoms (problem 3 of this exam)]. The one-electron functions (molecular orbitals) for N_2 molecule are shown on the right, in randomized order! Draw a line connecting the orbitals on the right to the peaks in the spectrum on the left:

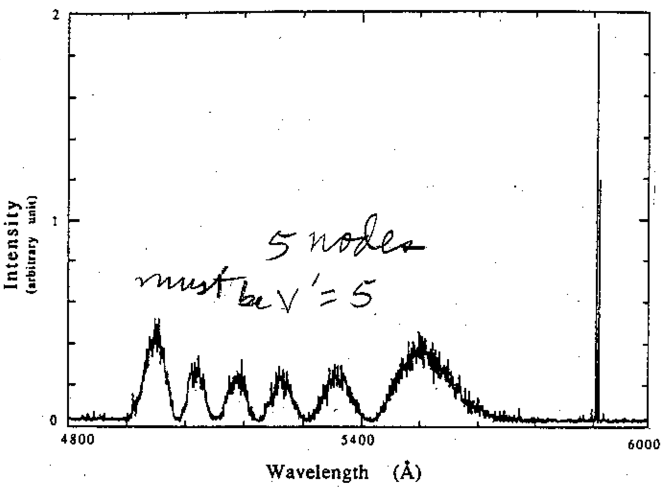


(b) The ground electronic configuration of Na_2 molecule is $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_g)^4(1\pi_u^*)^4(3\sigma_g)^2(4\sigma_g(3s))^2$. The excited electronic configuration $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_g)^4(1\pi_u^*)^4(3\sigma_g)^2(4\sigma_g(3s))^1(5\sigma_g(4s))^1$ gives a bound state $2\ {}^3\Sigma_g^+$, as can be seen from the plot of the U(R). The electronic transitions from the bound state of Na_2 molecule $2\ {}^3\Sigma_g^+$ to the free (that means, the molecule dissociates into free Na atoms after it gets there) a ${}^3\Sigma_u^+$ state of Na_2 is shown below. A particular vibrational state V′ of the excited $2\ {}^3\Sigma_g^+$ state was prepared by a pump laser and the emitted light from that prepared state to the lower free a${}^3\Sigma_u^+$ (″) state was collected. Identify the V′ and draw the vibrational level and vibrational eigenfunction on the U(R) plot below.

U(R) of the excited $2\ {}^3\Sigma_g^+$ state



Spectrum bound $2\ {}^3\Sigma_g^+ \rightarrow$ free a ${}^3\Sigma_u^+$



5 nodes
must be $V' = 5$

Identify electronic configurations of the two Na atoms that the above U(R) plot would approach if extrapolated well beyond 10 Å. Hint: Look at the molecular electronic configuration.

one is $(1s)^2(2s)^2(2p)^6(3s)$ ground state Na atom the other is $(1s)^2(2s)^2(2p)^6(4s)$ excited Na atom

The dissociative a${}^3\Sigma_u^+$ state of Na_2 gives rise to one excited and one ground state Na atom. When the excited Na atom gives up its excitation, it produces the characteristic double yellow D lines that one sees in a flame test for Na in elemental analysis. These two yellow lines are seen in the spectrum at the right hand side at wavelength 5890 and 5896 Å with one peak more intense than the other. Explain why the longer wavelength peak of the yellow doublet is less intense than the shorter wavelength peak in the atomic emission spectrum of excited Na atom. Hint: Consider the electronic configurations of the excited Na atom and the ground electronic state Na atom and remember that angular momentum vectors add.

$(4s)$ eventually drops to $(3p)$ $(\Delta l = \pm 1)$

$\ldots(3p)^1$ configuration has $l=1$, $s=\frac{1}{2}$ $\rightarrow$ $j = 3/2$ or $1/2$ Terms are ${}^2P_{\textcircled{3/2}}$ and ${}^2P_{\textcircled{1/2}}$

$m_l = 0, \pm 1$ $m_s = \pm\frac{1}{2}$

add to $\underbrace{m_j = \tfrac{3}{2}\ \tfrac{1}{2}\ -\tfrac{1}{2}\ -\tfrac{3}{2}}\ \tfrac{1}{2}\ -\tfrac{1}{2}$

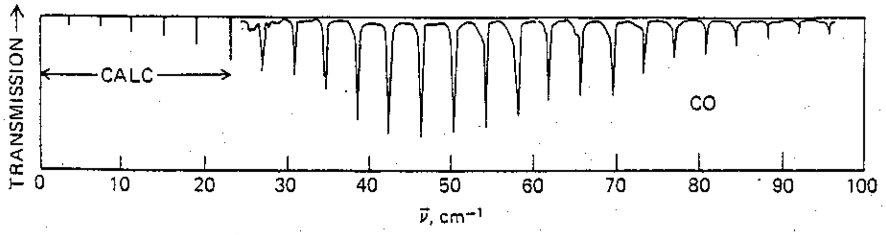
4 state here more intense

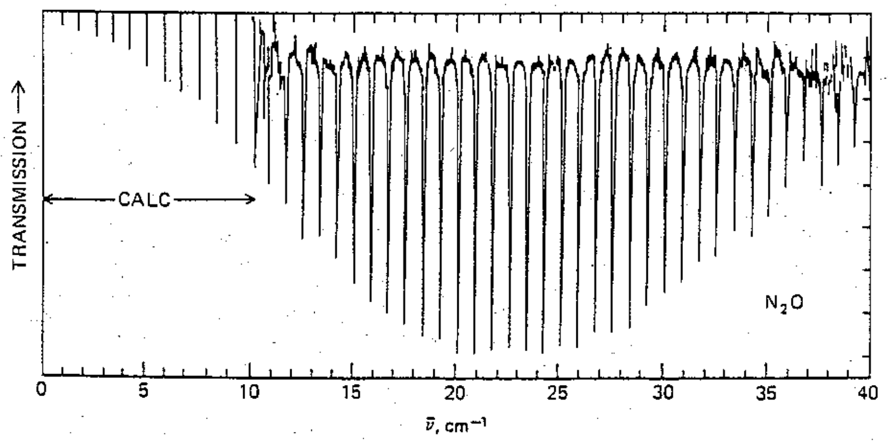
2 states less intense

both drop into

$l=0$ $s=\frac{1}{2}$ $\ldots(3s)$ ${}^2S_{1/2}$ ground state

(c) The microwave spectra of CO molecule and NNO molecules are shown below:





Which specific spectroscopic constants can be obtained from each of these spectra~~(s)~~? Determine the equation that provides the frequency of each peak (the calculated peaks are shown in those regions where the spectrometer was not operational). You may neglect D_e which is obviously very small in these cases.

same electronic and same vibrational state (ground for both)

$E' - E'' = (B_e - \frac{1}{2}\alpha_e)J'(J'+1) - (B_e - \frac{1}{2}\alpha_e)J''(J''+1)$ for $\Delta J = 1$ (absorption)

or $J' = J''+1$

$\Delta E = h\nu = (B_e - \frac{1}{2}\alpha_e)\left[(J''+1)(J''+2) - J''(J''+1)\right] = (B_e - \frac{1}{2}\alpha_e)2J''$

What is the frequency spacing (between adjacent peaks) equal to?

since $h\nu = (B_e - \frac{1}{2}\alpha_e)2J''$ and $J'' = 0, 1, 2, 3, \ldots$

the frequency spacing is $2(B_e - \frac{1}{2}\alpha_e)$

Why is the frequency spacing so much larger in CO than in NNO?

$B_e = \frac{\hbar^2}{2\boxed{I}}$ moment of inertia is larger for NNO (atoms are farther out from center of mass)

therefore B_e is smaller for NNO than CO.

8. Assume that you have solved the hydrogen-like atom problem and know all the eigenfunctions and eigenvalues in terms of the number of positive charges in the nucleus.

(a) What is the hamiltonian for the motion of nuclei and electrons in the He atom?

$$\mathcal{H}_{all} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\hbar^2}{2M_N}\nabla_N^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \quad \text{where } Z = 2$$

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

(b) After the motion of the center of mass of the atom has been separated out, what is the hamiltonian for the electronic motion in the He atom?

$$\mathcal{H}_{elec} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \quad \text{where } Z = 2$$

(c) If we simply neglect the electron-electron repulsion in the above hamiltonian, what would the Schrödinger equation for the electronic motion in the He atom be?

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}\right)\Psi(\vec{r}_1, \vec{r}_2) = E\,\Psi(\vec{r}_1, \vec{r}_2)$$

when $Z = 2$

(d) What are the eigenvalues and eigenfunctions of the above Schrödinger equation?

$E = E_1 + E_2 = \left(-\frac{Z^2}{n_1^2} - \frac{Z^2}{n_2^2}\right)\frac{e^2}{2a_0}$ where $Z = 2$ eigenvalues

eigenfunctions are $\Psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1)\cdot\psi(\vec{r}_2)$ but need to antisymmetrize and include spin

where $\psi(\vec{r}_1) = R_{n_1 l_1}(r_1)\cdot Y_{l_1 m_1}(\theta_1, \phi_1)$ and $\psi(\vec{r}_2) = R_{n_2 l_2}(r_2)\cdot Y_{l_2 m_2}(\theta_2, \phi_2)$

these are hydrogen-like functions exactly.

(e) If instead of total neglect of electron-electron repulsion, we use Slater's approximation, what would be the effective Hamiltonian for the He atom?

$$\mathcal{H}_{Slater} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - Z_{eff}^{(1)}\frac{e^2}{r_1} - Z_{eff}^{(2)}\frac{e^2}{r_2}$$

(f) If we use Slater's approximation for the He atom, what would be the electronic configuration of the ground state? Calculate the ground state energy of the He atom under this approximation.

$(1s)^2$

$$E_{ground} = -\frac{(2-0.30)^2}{1^2}\left(\frac{e^2}{2a_0}\right) \times 2 = -78.64\,\text{eV}$$

(g) If we use Slater's approximation for the He atom, what would be the electronic configuration of the first excited state?

$(1s)(2s)$

(h) If we use Slater's approximation for the He atom, what would be the energy difference between the first excited state and the ground state? Calculate your answer in terms of $(e^2/2a_0)$ which is 13.6 eV.

$$E(1s2s) - E(1s^2) = \left\{-\left[\frac{2^2}{1^2} + \frac{(2-0.85)^2}{2^2}\right] - - \left[\frac{(2-0.30)^2}{1^2}\cdot 2\right]\right\}\frac{e^2}{2a_0}$$

$$= (-4.3306 + 5.78)(13.6\text{eV})$$

$$= 1.4494\,\frac{e^2}{2a_0} = 19.72\text{ eV}$$

9. In each of the following cases, state the particular principle (don't just name it), or the definition that has been applied in order to arrive at your answer.

The set of functions $\{\Psi_1(\phi), \Psi_2(\phi), \Psi_3(\phi), \Psi_4(\phi), \ldots\}$ are eigenfunctions of the operator $(\hbar/i)\partial/\partial\phi$ where ϕ is an angle that ranges from 0 to 2π and the particle is restricted to the circle $x^2 + y^2 = R^2$ in the xy plane and $x = R\cos\phi$ and $y = R\sin\phi$.

(a) What is the general form of the functions $\{\Psi_1, \Psi_2, \Psi_3, \Psi_4, \ldots\}$? **Note**: these subscripts are merely running labels to distinguish one function from another in the complete list, not necessarily parameters or quantum numbers. You will choose the identity of the functions and order the functions in your own way, according to your own choices below.

Answer	Statement of Principle
$Ae^{im\phi}$ are the functions that satisfy the equation $\frac{\hbar}{i}\frac{\partial}{\partial\phi}\Psi(\phi) = a\Psi(\phi)$ ↖ a constant.	The only possible values which a single measurement of an observable associated with operator can yield are the eigenvalues of the ~~equation~~: $\hbar/i\,\partial/\partial\phi\,\Psi(\phi) = a\,\Psi(\phi)$ where $\Psi(\phi)$ is the eigenfunction

(b) Normalize each function

Answer	Statement of Principle
$\int_0^{2\pi} A^* e^{-im\phi}\cdot Ae^{im\phi}d\phi = 1$ $= A^2\int_0^{2\pi} d\phi = A^2\cdot 2\pi = 1$ $\therefore A = \frac{1}{\sqrt{2\pi}}$	Ψ is said to be normalized if $\int_{\text{all space}} \Psi^*\Psi\, d\tau = 1$

(c) What are the restrictions on the parameters that are involved in each of the eigenfunctions?

Answer	Statement of Principle
$\Psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$ must be equal to $\frac{1}{\sqrt{2\pi}} e^{im(\phi + \text{integer } 2\pi)}$ $e^{im\phi} = e^{im(\phi + 2\pi)} = e^{im\phi} \cdot e^{im2\pi}$ This requires that $e^{im2\pi} = 1$ $\cos(m2\pi) + i\sin(m2\pi) = 1$ occurs only for $m = 0, \pm 1, \pm 2, \ldots$	Functions which describe the state of a physical system must be single-valued.

(d) Now that you have identified the functions and the parameters involved in them, what are the eigenvalues of the operator $(\hbar/i)\partial/\partial\phi$ corresponding to the first four eigenfunctions Ψ_1, Ψ_2, Ψ_3, Ψ_4 in the list? Write the function down and then the eigenvalue for it.

Answer	Statement of Principle
Ψ_1: $\frac{1}{\sqrt{2\pi}}$, 0 $\frac{\hbar}{i}\frac{\partial}{\partial\phi} e^{im\phi} = \frac{\hbar}{i}(im) e^{im\phi} = +m\hbar e^{im\phi}$ eigenvalue is $m\hbar$ Ψ_2: $\frac{1}{\sqrt{2\pi}} e^{i\phi}$, $\hbar$ Ψ_3: $\frac{1}{\sqrt{2\pi}} e^{-i\phi}$, $-\hbar$ Ψ_4: $\frac{1}{\sqrt{2\pi}} e^{2i\phi}$, $2\hbar$	The only possible values that a single measurement of an observable associated with (this) operator can yield are the eigenvalues a of the equation $\frac{\hbar}{i}\frac{\partial}{\partial\phi}\Psi(\phi) = a\Psi(\phi)$

(e) If the physical system is found in the state described by the function Ψ_2 (whose identity is as you have specified it above) what would be the outcomes of four measurements of the property whose operator is $(\hbar/i)\partial/\partial\phi$?

Answer	Statement of Principle
Ψ_2: $\frac{1}{\sqrt{2\pi}} e^{i\phi}$ (1) $\hbar$ (2) $\hbar$ (3) $\hbar$ (4) $\hbar$	The only possible values that any single measurement of an observable associated with the operator can yield are the eigenvalues. Since this is an eigenstate, it has a unique eigenvalue. Every outcome is the same.

(f) If the physical system is found in the state described by function Ψ_2, as you have specified it above, what would be the outcomes of any four measurements of the property whose operator is $-(\hbar^2/2\mu R^2)\partial^2/\partial\phi^2$?

Answer	Statement of Principle
Ψ_2: $\frac{1}{\sqrt{2\pi}} e^{i\phi}$ (1) $+\frac{\hbar^2}{2\mu R^2} \cdot 1^2$ (2) same (3) same (4) same	Ψ_2 is also an eigenfunction of $-\frac{\hbar^2}{2\mu R^2}\frac{\partial^2}{\partial\phi^2}$, thus it has a unique eigenvalue, every outcome gives this eigenvalue $+\frac{\hbar^2}{2\mu R^2} 1^2$

$$\frac{\partial^2}{\partial\phi^2} e^{im\phi} = (im)^2 e^{im\phi}$$

(g) If the physical system is found in the state described by function $\Psi = (1/\sqrt{5})(2\Psi_2 + \Psi_4)$, as you have specified these functions above, determine the <u>average value</u> of the measurements of the observable whose operator is $(\hbar/i)\partial/\partial\phi$? Write down <u>a typical set of measurement outcomes</u>, as they would appear in your lab notbook.

Answer	Statement of Principle
$\Psi: \frac{1}{\sqrt{5}}(2\psi_2+\psi_4)$. We can see this is already normalized since $\left(\frac{2}{\sqrt{5}}\right)^2+\left(\frac{1}{\sqrt{5}}\right)^2=1$ average = $\int_0^{2\pi}\frac{1}{\sqrt{5}}(2\psi_2+\psi_4)^*\underbrace{\frac{\hbar}{i}\frac{\partial}{\partial\phi}\frac{1}{\sqrt{5}}(2\psi_2+\psi_4)}_{\downarrow}d\phi$ $\left(\frac{2}{\sqrt{5}}\cdot 1\hbar\psi_2+\frac{1}{\sqrt{5}}\cdot 2\hbar\psi_4\right)$ average = $\frac{2^2}{5}\cdot 1\hbar\int\psi_2^*\psi_2\,d\phi+\frac{1^2}{5}\cdot 2\hbar\int\psi_4^*\psi_4\,d\phi$ $=\left[\frac{4}{5}(1)+\frac{1}{5}(2)\right]\hbar = 1.2\hbar$ Typical outcomes: $\hbar, \hbar, \hbar, \hbar, 2\hbar$ one out of 5 outcomes is $2\hbar$	If a system is in a state represented by Ψ then the average of a sequence of measurements of an observable associated with the operator $\left(\frac{\hbar}{i}\frac{\partial}{\partial\phi}\right)$ is given by the integral $\frac{\int_0^{2\pi}\Psi^*\frac{\hbar}{i}\frac{\partial}{\partial\phi}\Psi\,d\phi}{\int_0^{2\pi}\Psi^*\Psi\,d\phi}$ Normalized functions $\int_0^{2\pi}\psi_2^*\psi_2\,d\phi=1$, $\int_0^{2\pi}\psi_4^*\psi_4\,d\phi=1$

(g) Determine whether or not it is theoretically possible to find for this physical system that both the observables described in (e) and (f) are measured with zero standard deviation for both observables at the same time.

Answer	Statement of Principle
yes since $\partial/\partial\phi$ commutes with $\partial^2/\partial\phi^2$ the theoretical limit of the product of the two standard deviations is zero.	uncertainty principle states that the standard deviations of measurements of any two observables is related to the expectation value of the commutator between their operators. $\sigma_A \cdot \sigma_B \geq \frac{1}{2}\left\langle \frac{[A_{op}, B_{op}]}{i} \right\rangle$