Problem Set PS02

ISSUED: 1/17/02 **Due: 1/24/02**

Prof. Darin J. Ulness Name ____________________

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. Write out all the spherical harmonics for $l = 0, 1, 2$. Verify that there are $2l+1$ distinct spherical harmonics for each l that you worik out.
2. Verify that for the spherical harmonics you wrote out in the previous problem,

$$Y_{l,-m} = (-1)^m Y^*_{l,m}$$

Exercises

3. Calculate $\delta\phi = \sqrt{\langle \phi^2 \rangle - \langle \phi \rangle^2}$.
4. Are the eigenfunctions of the particle on a ring Hamiltonian also eigenfunctions of the z-component of the angular momentum operator, $\hat{L}_z$? If so, what are the eigenvalues?
5. Benzene absorbs light at about 265nm. Where would we predict benzene to absorb if we treated the π-electrons as particles on a ring (radius 1.3Å)? What is the %error?
6. Derive a relationship between the energy levels for a particle on a ring (radius R) and a particle in a box having the length equal to the circumference of the ring.
7. The Hamiltonian which governs the quantum behavior of a *particle on a sphere* is exactly the same as the Hamiltonian for general rotations (Eq. (12.85) of the notes).
   (a) Draw an energy level diagram for a particle on a sphere. Verify that the degeneracy of the energy levels is given by $g = 2l + 1$.
   (b) Draw the spectrum for a particle on a sphere.
   (c) Comment on how the spectrum changes with changing mass and the radius of a the sphere
   (d) Draw the wavefunctions for $l = 2$, $m = 0$ on the wooden ball I provide. Draw the nodes in regular pencil and then color in red the regions where the wavefunction is positive and color in blue the regions where the wavefunction is negative. (Hints: 1; it helps to plot the wavefunctions on a piece of paper first and then identify where the nodes are and 2; both these wavefunctions have no ϕ dependence so all of your nodes should be along latitude lines and none should be along longitude lines.) You might find the first computer problem useful.
8. The moment of inertia for N_2O is 6.649×10^{-46}kg m^2. Determine the rotational quantum number for a N_2O molecule with rotational energy equal to thermal energy at 298K. Treat N_2O as a rigid rotor.

Conceptual Problems

9. Order the following molecules according to the increasing rotational constant ($\triangle E_{0\to 1}$): O_2, N_2, CO_2, CS_2

Computer Problems

10. Download the MATHEMATICA notebook dealing with a particle on a sphere. This program plots the probability density, $|Y_{l,m}|^2$, for finding the a particle on the surface of the sphere. Plot the functions corresponding to quantum number $l = 0, 1, 2, 3$. You only need to use positive values of m.

11. Consider a 2D harmonic oscillator described by the Hamiltonian operator:

$$\hat{H} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{M\omega^2}{2}\left(x^2 + y^2\right).$$

(a) Use the separation of variables method to express the corresponding wavefunctions in terms the 1D harmonic oscillator wavefunctions. Set all constants to 1 and plot the first nine wavefunctions and probability distributions.

(b) Draw the energy level diagram for the 2D harmonic oscillator.

(c) This problem can also be solved in polar coordinates. Here since $r^2 = x^2 + y^2$, the Hamiltonian can be written as

$$\hat{H} = \hat{T}_{\text{radial}} + \hat{L}_z^2 + \frac{M\omega^2 r^2}{2}.$$

Since the Hamiltonian is a sum of radial part and an angular the wavefunction can be written as a product state

$$\psi = R(r)\,\Phi(\phi).$$

The angular part is simply the particle on sphere problem so

$$\Phi_m(\phi) = \sqrt{\frac{1}{2\pi}} e^{im\phi}$$

To find the radial part one must solve a very difficult differential equation which we will not attempt. If we were to solve it we would get

$$R_p(r) = C_{p,m} r^{|m|} e^{-\frac{M\omega r^2}{2\hbar}} {}_1F_1\left(-p; |m|+1; \frac{M\omega r^2}{2\hbar}\right)$$

where $p = 0, 1, 2, \cdots$ is the radial quantum number, $C_{p,m}$ is the normalization constant and ${}_1F_1()$ is the confluent hypergeometric function (which MATHEMATICA knows as `Hypergeometric1F1[a,b,z]`). Assemble the wavefunction $\psi_{p,m}$ and plot several of the corresponding probability distributions.

(d) The energy levels in terms of the radial and angular quantum numbers is

$$E_{p,m} = \hbar\omega(|m| + 1 + 2p).$$

Draw the energy level diagram for the 2D oscillator (it better be the same as in part B). How are the radial and angular quantum numbers related to the Cartesian quantum numbers?

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(1)

Out[22]//MatrixForm=

$$\begin{pmatrix} \frac{1}{2\sqrt{\pi}} \\ \frac{1}{2} e^{-i\phi}\sqrt{\frac{3}{2\pi}}\,\mathrm{Sin}[\theta] \\ \frac{1}{2}\sqrt{\frac{3}{\pi}}\,\mathrm{Cos}[\theta] \\ -\frac{1}{2} e^{i\phi}\sqrt{\frac{3}{2\pi}}\,\mathrm{Sin}[\theta] \\ \frac{1}{4} e^{-2i\phi}\sqrt{\frac{15}{2\pi}}\,\mathrm{Sin}[\theta]^2 \\ \frac{1}{2} e^{-i\phi}\sqrt{\frac{15}{2\pi}}\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta] \\ \frac{1}{4}\sqrt{\frac{5}{\pi}}\,(-1+3\,\mathrm{Cos}[\theta]^2) \\ -\frac{1}{2} e^{i\phi}\sqrt{\frac{15}{2\pi}}\,\mathrm{Cos}[\theta]\,\mathrm{Sin}[\theta] \\ \frac{1}{4} e^{2i\phi}\sqrt{\frac{15}{2\pi}}\,\mathrm{Sin}[\theta]^2 \end{pmatrix}
\begin{matrix} l=0, m=0 \\ m=-1 \\ m=0 \;\; \} \; l=1 \\ m=1 \\ m=-2 \\ m=-1 \\ m=0 \;\; \} \; l=2 \\ m=1 \\ m=2 \end{matrix}$$

(2) yes this is true for (1)

(3) $\langle \phi^2 \rangle = \frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi}\,\phi^2 e^{im\phi}\,d\phi = \frac{1}{2\pi}\int_0^{2\pi}\phi^2 d\phi = \frac{1}{2\pi}\frac{\phi^3}{3}\Big|_0^{2\pi} = \frac{4\pi^2}{3}$

$\langle \phi \rangle = \frac{1}{2\pi}\int_0^{\pi} e^{-im\phi}\,\phi\, e^{im\phi}\,d\phi = \frac{1}{2\pi}\int \phi\, d\phi = \frac{1}{2\pi}\frac{\phi^2}{2}\Big|_0^{2\pi} = \pi$

$\delta\phi = \sqrt{\frac{4\pi^2}{3} - (\pi)^2} = \sqrt{\frac{1}{3}\pi^2} = \boxed{\frac{\pi}{\sqrt{3}}}$

(4) $\hat{L}_z = -i\hbar \frac{d}{d\phi}$ $\quad \hat{L}_z \frac{1}{\sqrt{2\pi}} e^{im\phi} = \frac{-i\hbar}{\sqrt{2\pi}}\frac{d}{d\phi} e^{im\phi}$

$= \frac{m\hbar}{\sqrt{2\pi}} e^{im\phi}$

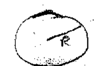
eigenvalue

(5) 6 π elect so HOMO: m=1, LUMO: m=2

$\Delta E = \frac{(2m+1)h^2}{8\pi^2 m_e R^2} = \frac{3\,(6.63\times10^{-34}\,\mathrm{Js})^2}{8(3.14159)^2(9.1095\times10^{-31})(1.3\times10^{-10}\,\mathrm{m})^2} = 1.08\times10^{-18}$

$\lambda = \frac{hc}{\Delta E} = 183$ nm -34.68 error

(6)



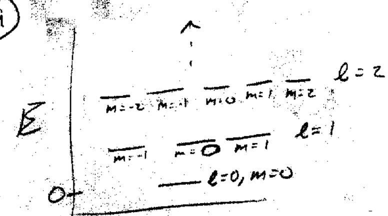
$a = 2\pi R$ $\quad E_n = \frac{n^2h^2}{8Ma^2} = \frac{n^2h^2}{8M4\pi^2R^2} = \frac{n^2h^2}{(4)8\pi^2 I}$

$E_m = \frac{m^2h^2}{8\pi^2 I}$

$E_m = 4E_n$ when $n=m$ but E_m is 2 fold degenerate.

(7)

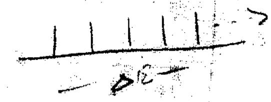
(a)



(b) $E_l = \frac{l(l+1)h^2}{8\pi^2 I}$

$\Delta E_l = \frac{(l+1)(l+2)h^2}{8\pi^2 I} - \frac{l(l+1)h^2}{8\pi^2 I}$

$= \frac{(l+1)h^2}{8\pi^2 I}$



(c) m↑ ΔE↓
R↑ ΔE↓

(d) wooden balls

(8) $kT = 4.11\times10^{-21}\,\mathrm{J} = \frac{l(l+1)h^2}{8\pi^2 I}$

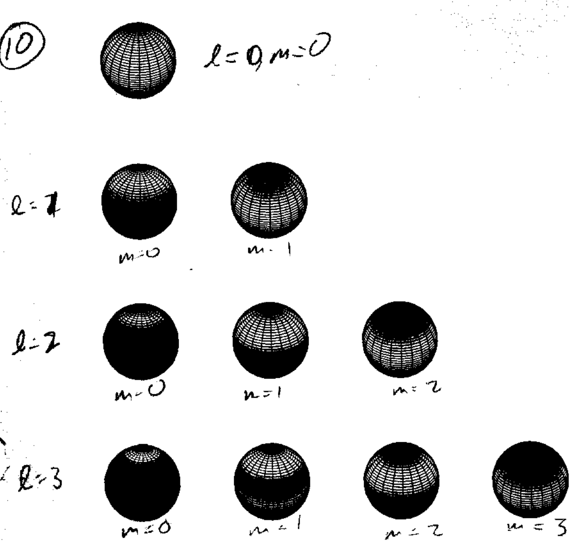
$\Rightarrow l(l+1) = \frac{8(3.14159)^2(6.649\times10^{-46}\,\mathrm{kg\,m^2})(4.11\times10^{-21}\,\mathrm{J})}{(6.63\times10^{-34}\,\mathrm{Js})^2} = 490.86$

$l^2 + l - 490.86 = 0 \Rightarrow l = \frac{1\pm\sqrt{1+4(490.86)}}{2} = \frac{1\pm44.3}{2} = 22.6$

$l = 22$ or 23

(9) CS_2, CO_2, O_2, N_2

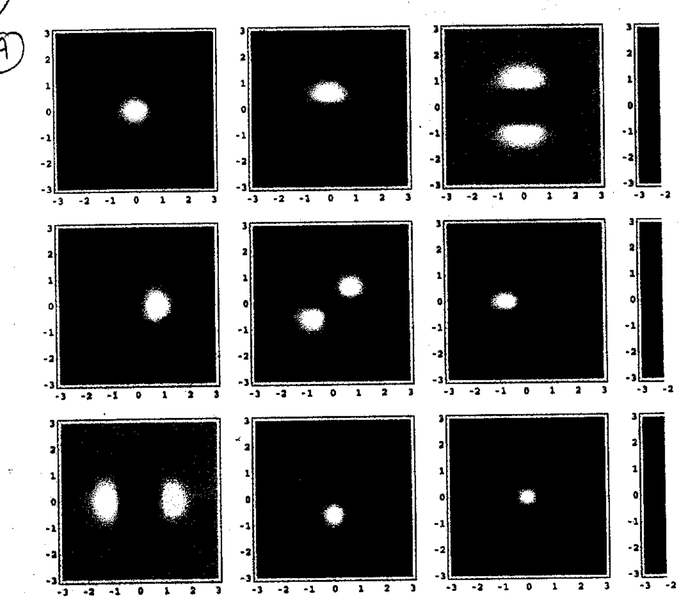
(10)



2d_HO1.nb

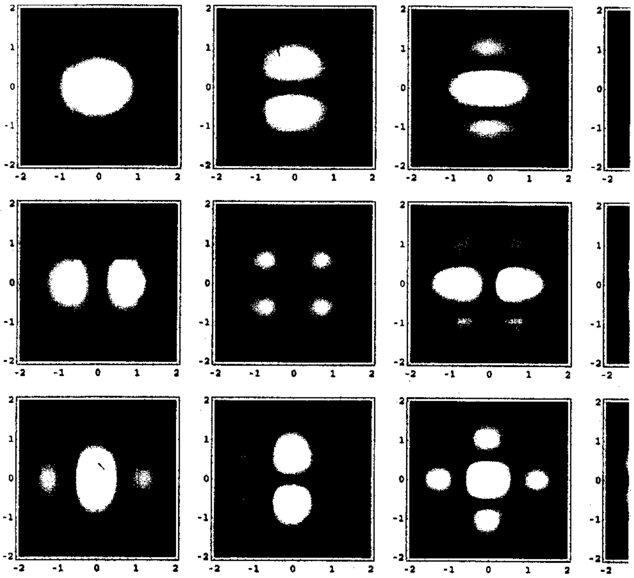
(11)

(A)



11 cont

(b)



$E_{n_x n_y} = \hbar\omega(n_x + n_y + 1)$

E

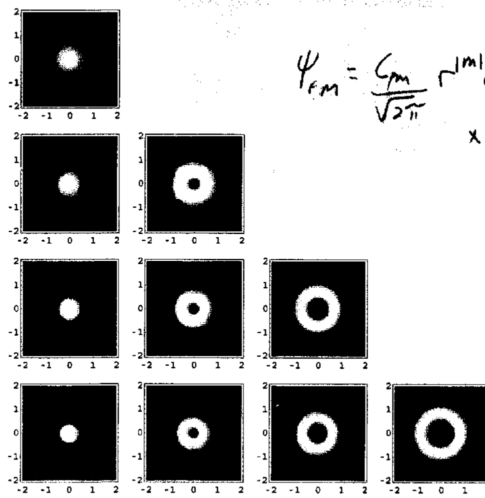
ψ_{11} ψ_{02} ψ_{20} $E = 3\hbar\omega$

ψ_{01} ψ_{10} $E = 2\hbar\omega$

ψ_{00} $E = \hbar\omega$

11 cont

(c)



$\psi_{pm} = \frac{C_{pm}}{\sqrt{2\pi}} r^{|m|} e^{-\frac{M\omega r^2}{2\hbar}} {}_1F_1(-p; |m|+1; \ldots) \times e^{im\phi}$

(d)

E

p=1 m=0 p=0 m=-1 p=0 m=1 $E = 3\hbar\omega$

m=-1 m=1 p=0 $E = 2\hbar\omega$

p=0, m=0 $E = \hbar\omega$

$\boxed{2p + |m| = n_x + n_y}$ relation between QN's