Chemistry 331 **Assignment #8** (due* Monday 30 November, in class)

**this assignment is optional* (you lose no marks if you don't hand it in – happy studying)

Q1. A two-dimensional rotor in the *x-y* plane is described by the wave function $\psi_m(\phi) = \sqrt{\frac{1}{2\pi}}\, e^{im\phi}$

a) The only permissable values of m are … −3, −2, −1, 0, 1, 2, 3, … Why?

b) Show $\psi_m(\phi)$ is normalized.

c) Give the average value of ϕ.

d) Use the $\hat{L}_z = -i\hbar\partial/\partial\phi$ operator to show the angular momentum of the rotor is $mh/2\pi$.

[7] **e)** Use the angular moment of the rotor to show the energy of the rotor is $m^2h^2/8\pi^2\mu r^2$.

f) Rotors described by the wave functions $\psi_{-2}(\phi)$ and $\psi_2(\phi)$ have exactly the same energy but have different rotational states. Explain.

g) Show the de Broglie wavelength of the rotor is $2\pi r/m$.

Q2. The transition dipole moment for a molecule absorbing or emitting a photon and changing from rotational state ℓ, m to rotational state ℓ', m' in three dimensions is

$$(\mu_z)_{\ell m,\ell' m'} = \mu N_{\ell m} N_{\ell' m'} \int_0^{2\pi} e^{i(m-m')\phi} d\phi \int_{-1}^{1} \left[\frac{\ell - |m| + 1}{2\ell + 1} P_{\ell+1}^{|m|} + \frac{\ell + |m|}{2\ell + 1} P_{\ell-1}^{|m|} \right] P_{\ell'}^{|m'|}(x)\, dx$$

[3] Use this result to derive <u>three</u> selection rules for microwave spectroscopy. *Hints*: μ is the electric dipole moment of the molecule and the $P_\ell^m(x)$ Legendre polynomials are orthogonal.

Q3. World War II led to huge advances in microwave technology. Why? [1]

Q4. If a mug of tea or coffee is warmed up in a microwave oven, the coffee or tea gets hot, but the mug
[1] remains relatively cool. Why?

Q5. In the 1960s, research teams at Bell Labs were developing ultra-sensitive microwave receivers for high-speed radio communication. (*No fiber optic cables back then!*) When the receiver antennas were pointed
[1] at the sky, a strange background microwave signal was detected. What is the source of this signal? *Hint*: Arno Penzias and Robert Wilson won the 1978 Nobel Physics Prize for solving this problem.

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Q6. The Boltzmann distribution we've used previously suggests the probability of finding a molecule in energy level E_ℓ is proportional to $\exp(-E_\ell / kT)$. But the probability a molecule is in rotational energy
[1] level E_ℓ is proportional to $(2\ell+1)\exp(-E_\ell / kT)$. Why the difference?

Q7. The energy levels of a diatomic molecule rotating in 3 dimensions are

$$E_\ell = \ell(\ell+1)B \qquad\qquad \ell = 0,\ 1,\ 2,\ 3,\ \ldots$$

[2] B is the rotational constant $\quad B = \dfrac{h^2}{8\pi^2 I} = hc\tilde{B}$

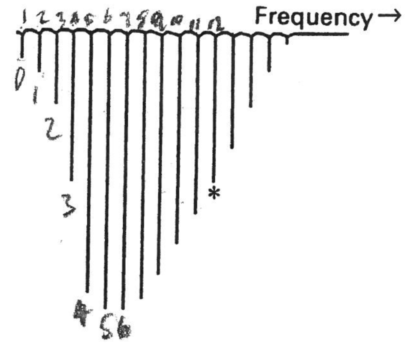
At temperature T, show the most probable value of quantum number ℓ is

$$\ell_{\text{mp}} = \sqrt{\frac{kT}{2B}} - \frac{1}{2}$$

Q8. The diagram below shows the microwave absorption spectrum for ^{12}CO ($\tilde{B} = 1.9313\ \text{cm}^{-1}$).

[2] **a)** Give the initial ℓ value and the final ℓ value for the labeled (*) frequency.

b) Estimate the temperature of the gas.



Q9. High-resolution microwave spectroscopy is used for the most precise measurements of chemical bond lengths. For example, spectroscopic data give $10.5912\ \text{cm}^{-1}$ for the rotational constant

$$\tilde{B} = \frac{h}{8\pi^2 c I}$$

[1] of $H^{35}Cl$ molecules. Calculate a precise bond length of the molecule. *Hint*: $I = \mu r^2$ *Data*:

$h = 6.626070 \times 10^{-34}$ J s $\qquad m_H = 1.673534 \times 10^{-27}$ kg $\qquad m_{35Cl} = 5.806719 \times 10^{-26}$ kg
$c = 2.997924 \times 10^{10}$ cm s^{-1}

Q10. How rapidly are the nuclei moving in a rotating molecule? Calculate the speed of the H nuclei in a
[1] rotating H_2 molecule with $\ell = 1$. Use 0.07414 nm for the bond length r.

Chem 331 <u>Assignment #8</u>

Q1 2-dimensional rotor in the x-y plane is described by the wave function

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

with $m = 0, \pm 1, \pm 2, \pm 3, \ldots$

a) why are the allowed values of m integers?

$\psi_m(\phi)$ must be single-valued

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}\left[\cos(m\phi) + i\sin(m\phi)\right]$$

and $\psi_m(\phi) = \psi_m(\phi + 2\pi)$

(trigonometry: $\cos(\alpha+\beta) = \cos(\alpha)\cos(\beta) - \sin(\alpha)\sin(\beta)$)

$$\cos[m(\phi+2\pi)] = \cos(m\phi)\cos(m2\pi) - \sin(m\phi)\sin(m2\pi)$$

$$= \cos(m\phi)(1) - \sin(m\phi)(0)$$

$\cos[m(\phi+2\pi)] = \cos(m\phi)$ only if $m = \ldots, -2, -1, 0, 1, 2, \ldots$

similarly, $\sin[m(\phi+2\pi)] = \sin(m\phi)$

only if $m = \ldots, -2, -1, 0, 1, 2, \ldots$

b) is $\psi_m(\phi)$ normalized?

$$\int_0^{2\pi} \psi_m^*(\phi)\,\psi_m(\phi)\,d\phi = \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} e^{-im\phi} \frac{1}{\sqrt{2\pi}} e^{im\phi}\,d\phi$$

$$= \frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi + im\phi}\,d\phi = \frac{1}{2\pi}\int_0^{2\pi} e^{0}\,d\phi$$

$$= \frac{1}{2\pi}\int_0^{2\pi} d\phi = \frac{1}{2\pi}(2\pi - 0) = 1 \qquad \text{(yes)}$$

c) average ϕ value?

$$\langle\phi\rangle = \int_0^{2\pi} \phi\, P(\phi)\,d\phi = \int_0^{2\pi} \phi\,\psi_m^*(\phi)\,\psi_m(\phi)\,d\phi$$

$$= \int_0^{2\pi} \phi \frac{1}{\sqrt{2\pi}} e^{-im\phi} \frac{1}{\sqrt{2\pi}} e^{im\phi}\,d\phi$$

$$= \frac{1}{2\pi}\int_0^{2\pi} \phi\,d\phi = \frac{1}{2\pi}\left(\frac{\phi^2}{2}\right)\Big|_0^{2\pi}$$

$$= \frac{1}{2\pi}\left(\frac{4\pi^2}{2} - 0\right)$$

$$\boxed{\langle\phi\rangle = \pi}$$

d) angular momentum of the rotor?

$$\hat{L}_z \psi_m(\phi) = -\frac{ih}{2\pi} \frac{\partial \psi_m(\phi)}{\partial \phi}$$

$$= -\frac{ih}{2\pi} \frac{\partial}{\partial \phi} \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

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

$$\hat{L}_z \psi_m(\phi) = \left(m \frac{h}{2\pi} \right) \psi_m(\phi)$$

eigenvalue $m \frac{h}{2\pi} = m\hbar$ is the z-angular momentum of the rotor

e) the energy of the rotor is "all kinetic"

$$E_m = T_m = \frac{L_z^2}{2I}$$

(analogous to $\frac{p_x^2}{2\pi}$ for linear momentum)

$$\boxed{E_m = \frac{m^2 \hbar^2}{2I}}$$

$I = \mu r^2 =$ moment of inertia

f) rotors described by the wave functions $\psi_{-2}(\phi)$ and $\psi_2(\phi)$ have <u>identical energies</u>

$$E_{\pm 2} = \frac{4\hbar^2}{2I}$$

but <u>different angular momentum</u>

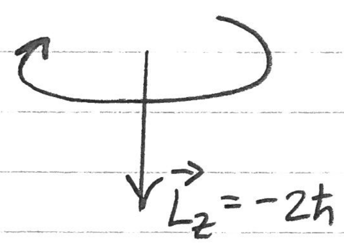
$-2\hbar$ or $2\hbar$

$(m=-2)$ $(m=2)$

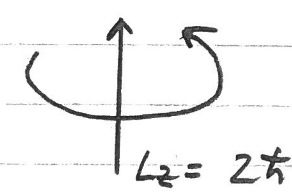
clockwise rotation

counter-clockwize rotation

$m=-2$



$m=2$



g) de Broglie wavelength $\lambda_m = \dfrac{h}{P_m}$ ← <u>linear</u> momentum

$$E_m = T_m = \frac{m^2\hbar^2}{2I} = \frac{P_m^2}{2\mu}$$

$$P_m^2 = \frac{m^2\hbar^2}{2I}2\mu = \frac{m^2\hbar^2}{\mu r^2}\mu \qquad P_m = \frac{m\hbar}{r}$$

$$\lambda_m = \frac{h}{P_m} = \frac{h}{m\hbar/r} = \frac{h}{m\frac{h}{2\pi r}} = \frac{2\pi r}{m} = \frac{\text{circumference}}{m}$$

for a "standing" wave

Q2 a rotation transition from state l, m to state l', m' is possible if the transition dipole moment is not zero

this requires:

i) $\boxed{\mu \neq 0}$ the molecule must have a permanent electric dipole moment

ii) because the Legendre polynomials are orthogonal $\Rightarrow$ $l' = l+1$ or $l' = l-1$

iii) " $m' = m$

Q3 huge advances in microwave technology in WWII to develop radar for locating ships and aircraft, navigation, proximity fuses, fire control

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Q4 freely rotating water molecules absorb more microwave radiation and heat up more quickly than the solid ceramic mug.

Q5 Cosmic Microwave Background Radiation!
photons from the "big-bang" birth of the universe expanded adiabatically and cooled to a few degrees K

Q6 a 3-dimensional rotor with quantum number l has $\underline{2l+1}$ different states with identical energy $E_l = l(l+1)\hbar^2/(2\mu r^2)$

the probability of finding a rotor in energy level E_l is proportional to

$$P_l \propto \underbrace{(2l+1)}_{\text{degeneracy}} e^{-E_l/kT}$$

larger degeneracy $\Longrightarrow$ higher probability of being in energy level E_l

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Q7 $$P_l = k \underbrace{(2l+1)}_{\substack{\text{increases} \\ P_l}} \underbrace{e^{-Bl(l+1)/kT}}_{\substack{\text{decreases} \\ P_l}}$$ (k is a normalization constant)

maximum P_l when:

$$\frac{dP_l}{dl} = 0 = \frac{d}{dl} k(2l+1)e^{-Bl(l+1)/kT}$$

$$0 = ke^{-Bl(l+1)/kT}\left[-(2l+1)\frac{B}{kT}(2l+1) + 2\right]$$

$$(2l+1)^2 = \frac{2kT}{B} \qquad 2l+1 = \sqrt{\frac{2kT}{B}} \qquad l = \sqrt{\frac{kT}{2B}} - \frac{1}{2}$$

Q8 a) first (lowest frequency line) $l=0$ to $l=1$

⋮

12th line (labeled) $l=11$ to $l=12$

b) max intensity for $l=5$ to $l=6$
and $l=6$ to $l=7$

suggests most probable l value is about $l_{mp}=5.5$

$$l_{mp} = \sqrt{\frac{kT}{2B}} - \frac{1}{2}$$

$$\left(l_{mp} + \frac{1}{2}\right)\sqrt{\frac{2B}{k}} = \sqrt{T} \qquad T = \left(l_{mp} + \frac{1}{2}\right)^2 \frac{2B}{k}$$

$\tilde{B} = 1.9313\ \text{cm}^{-1}$ $\qquad B = hc\tilde{B}$
(in Joules)

$$B = (6.626\times10^{-34}\ \text{J s})(2.998\times10^{10}\ \text{cm s}^{-1})(1.9313\ \text{cm}^{-1})$$

$$B = 3.836\times10^{-23}\ \text{J}$$

$$T = \left(5.5+\frac{1}{2}\right)^2 \frac{2(3.836\times10^{-23}\ \text{J})}{1.381\times10^{-23}\ \text{J K}^{-1}}$$

$$\boxed{T = 200\ \text{K}}$$

remote sensing applications

Q9 accurate bond length of $H^{35}Cl$

$$\tilde{B} = \frac{h}{8\pi^2 c I} = \frac{h}{8\pi^2 c \mu r^2}$$

$$r = \sqrt{\frac{h}{8\pi^2 c \mu \tilde{B}}}$$

reduced mass $\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}}$

$\mu = 1.626653 \times 10^{-27}$ kg

$$= \sqrt{\frac{6.626070 \times 10^{-34}}{8\pi^2 (2.997924 \times 10^{10})(1.626653 \times 10^{-27})(10.5912)}}$$

$$\boxed{r = 1.274685 \times 10^{-10} \text{ m}}$$

Q10 for a H_2 molecule with $l = 1$

$$\left(\mu = \frac{m_p m_p}{m_p + m_p} = \frac{m_p}{2}\right)$$

$$E_1 \left(\begin{matrix}\text{all} \\ \text{kinetic}\end{matrix}\right) = l(l+1)B = 1(1+1)\frac{h^2}{8\pi^2 \mu r^2}$$

$$E_1 = \frac{2(6.626 \times 10^{-34})^2}{8\pi^2 \frac{1.6735 \times 10^{-27}}{2}(0.07414 \times 10^{-9})^2} = 2.418 \times 10^{-21} \text{ J}$$

$$E_1 = \frac{1}{2} m_p v_p^2 + \frac{1}{2} m_p v_p^2 = m v_p^2$$

v_p = proton speed (2 protons in H_2)

$$v_p = \sqrt{\frac{E_1}{m_p}} = \sqrt{\frac{2.418 \times 10^{-21} \text{ J}}{1.6735 \times 10^{-27} \text{ kg}}} = \boxed{1,202 \ \frac{m}{s}}$$