Exam 1

Chemistry 539
Wednesday, October 12, 2011

Your Name:

This is the mid term exam. You can use your notes or a textbook but cannot discuss anything with other students. You have 1 hour to complete the exam. Write ALL your derivations , especially if you wish to get partial credit.

Question 1 (10 points)

Construct the matrix representation of the operators S^2, S_z, and S_x for spin S=3/2 in the basis set defined by its projections, m_s. **Hint:** Use algebraic relations for these operators to derive the corresponding 4×4 matrices.

$$\hat{S}^2 = \frac{15}{4}\hbar^2 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}; \hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

$$\hat{S}_+ = \hbar \begin{pmatrix} 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}; \hat{S}_- = \hbar \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & \sqrt{3} \\ 0 & 0 & 0 & 0 \end{pmatrix}; \hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_+\right)$$

Question 2 (30 points)

Dipole moment of HCl molecule is 1.05 D (1 electron$\times 1\,\text{Å}$=4.8 D) and the bond length is $1.274\,\text{Å}$. Take m(^{1}H) = 1.007825 amu and m(^{35}Cl) = 34.96885 amu

Can the state J=2 radiatively go into the states J=1, J=0?

What is the energy of photon emiited for J=1 → J=0 transition?

What is the radiative lifetime of J=1 state?

Reminder: The Einstein coefficients A and B are: $A_{i\to f} = \frac{16\pi^3}{3\varepsilon_o hc^3}\nu_{fi}^3|\mu_{if}|^2$

Spherical harmonics $Y_l^m(\theta,\varphi) = (-1)^m\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\,e^{im\varphi}P_l^m(\cos\theta)$:

1) The selection rules allow only J=2→ J=1 transition, while J=2↛ J=1 is forbidden

2) Expressed in wavenumbers, $\nu_{1\to 0} = 2B = 2\frac{16.8576314}{1.5900(amu\,\text{Å}^2)}\,\text{cm}^{-1} = 21.205\,\text{cm}^{-1}$

where the moment of inertia was calculated : $I = \frac{1.007825\times 34.96885}{1.007825+34.96885}1.274^2 = 1.5900 amu\,\text{Å}^2$

3) First, the numeric value for:

$$A_{i\to f} = \frac{16\pi^3}{3\varepsilon_o hc^3}\nu_{fi}^3|\mu_{if}|^2 = b\frac{32\pi^3}{3\times137}(21.205)^3 3\times10^{10}\times10^{-16}\left(\frac{1.05}{4.8}\right)^2 = b3.3043\times10^{-3}s$$

where the coefficient b should be on the order of unity and evaluates just the angular part of the integral for the transition moment. The transition corresponds to tilting the dipole moment μ_o to change its rotational state.

$$\vec{\mu} = \mu_o\left(\vec{e}_x\sin\theta\cos\varphi + \vec{e}_y\sin\theta\sin\varphi + \vec{e}_z\cos\theta\right)$$

The states involved are:

$$Y_0^0(\theta,\varphi) = \sqrt{\frac{1}{4\pi}}\,; Y_1^0(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}(\cos\theta); Y_1^1(\theta,\varphi) = -\sqrt{\frac{3}{8\pi}}e^{i\varphi}\sin\theta$$

Let us choose the light polarization along z axis. Then only the z projection of μ_{if} needs to be evaluated. The answer should not vary if we chose x or y instead.

$$\frac{1}{\mu_o}\langle Y_1^0|\mu_z|Y_0^0\rangle = \frac{\sqrt{3}}{4\pi}\int d\cos\theta\times\cos^2\theta\int d\varphi = \frac{1}{\sqrt{3}} => \frac{\mu_z^2}{\mu_o^2} = \frac{1}{3} = b$$

$A_{J=1\to J=0} = 1.1\times10^{-3}s$ or $\tau_{J=1\to J=0} = 900s$ - very sloooooow process.

Question 3 (10 points)

How many cycles of light are in a 10 fs (0.01ps) pulse of light of nominal frequency corresponding to λ= 600nm? How long (in space) is this pulse? How precisely can this light's wavelength be specified? Is it enough to distinguish red and green?

$$l\sim c\Delta t\sim3\times10^8 m/s * 10^{-14}s = 3\times10^{-6}m$$

$$\Delta E\Delta t\sim h => \Delta\nu\Delta t\sim1 => \Delta\lambda\sim\lambda^2\frac{\Delta\nu}{c}\sim\frac{\lambda^2}{l} = \frac{(600\times10^{-9})^2}{3\times10^{-6}} = 1.2\times10^{-7}m = 120nm$$

Thus it spreads from ~540 nm and 660 nm, barely enough to make the distinction between green and red.

Question 4 (20 points)

Identify point symmetry groups for the following molecules

Molecule	Point Group
CH_3Cl	C_{3v}
CH_4	T_d
CO_2	$D_{\infty h}$
$H_2C{=}C{=}CH_2$	D_{2d}
C_6H_6	D_{6h}
H-C≡N	$C_{\infty v}$
trans dichloroethylene	C_{2h}
cis dichloroethylene	C_{2v}
PF_3	C_{3v}
NH_3	C_{3v}

Question 5 (25 points)

Identify molecules with observable microwave transitions and sketch their microwave spectra (neglect centrifugal distortion). $B_e = \frac{\hbar^2}{2\mu r_e^2} = \frac{16.8576314}{\mu r_e^2 (amu\,\text{Å}^2)}\ \text{cm}^{-1}$

Molecule	Symmetric top? What kind?	*Estimate B
H_2	linear	no μw
$H_2C{=}CH_2$	-	no μw
C_6H_6	oblate top	no μw
C_{60}	spherical top	no μw
CH_4	spherical top	no μw
HCl	linear	**
CH_3Cl	prolate top	**
$H_2C{=}C{=}CH_2$	prolate top	no μw
trans dichloroethylene	-	no μw

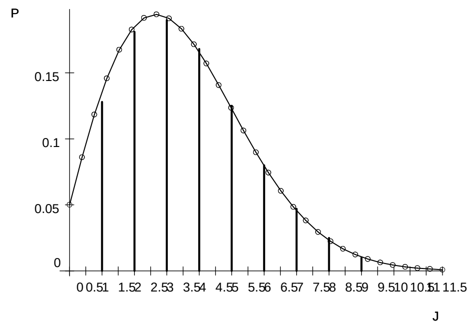
*- Estimate B **only for the molecules that do show rotational spectra**. Otherwise, indicate ' no μw absorption'. Take the bond lengths very approximately. Describe or sketch the microwave spectra at room temperature in the gas phase with indication of the splitting(s) and approximate relative intensities.

**- the spectra without centrifugal distortion should have equally spaced lines with 2B and intensities reaching maximum at $J_{max} \sim \sqrt{\frac{kT}{2B}} - 1/2$

2B for HCl for estimated above 21.2cm^{-1}

The moment of inertia I_B for CH_3Cl can be estimated as $\frac{m_{CH_3} \cdot m_{Cl}}{m_{CH_3} \cdot m_{Cl}} R_{CCl}^2 \sim \frac{15 \cdot 35}{50} 1.77^2 =$

$32.9\, amu\, \text{Å}^2$ i.e. $2B = 2\frac{16.8576314}{32.9} \sim 1\, \text{cm}^{-1}$



Question 6 (5 points)

In how many lines will the transition 4 <–3 in microwave absorption of HCl split in the electric field ?

Selection rules are $\Delta M_J = 0, \pm 1$. In electric field the degeneracy is lifted with respect to $|M_J|$. Thus transititons from :

$J = 3, M_J = 0 \rightarrow J = 4, M_J = 0, \pm 1$ - 2 lines.

$J = 3, M_J = \pm 1 \rightarrow J = 4, M_J = 0, \pm 1, \pm 2$ - 3 lines.

$J = 3, M_J = \pm 2 \rightarrow J = 4, M_J = \pm 1, \pm 2, \pm 3$ - 3 lines.

$J = 3, M_J = \pm 3 \rightarrow J = 4, M_J = \pm 2, \pm 3, \pm 4$ - 3 lines.

Total - 11 lines

'Cheating' Sheet

Postulates:

1) $\int \Psi^*(\vec{r},t)\Psi(\vec{r},t)d\tau = 1$

2) For every **observable** → **Hermitian operator** in QM. $x \to \hat{x}$; $p_x \to \ \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$.

3) For any observable A: $\hat{A}\psi_k = \lambda_k\psi_k$ and any

$$\Psi = \sum_k c_k\psi_k \Leftrightarrow |\Psi >= \left(\sum_k\right)|k >< k|\Psi >.$$

4) $\langle A\rangle \equiv \frac{<\Psi|\hat{A}|\Psi>}{<\Psi|\Psi>} = \frac{\int \Psi^*\hat{A}\Psi d\tau}{\int \Psi^*\Psi d\tau} = \int \Psi^*\hat{A}\Psi d\tau$ (if $<\Psi|\Psi>= 1$);

$$\langle A\rangle = \sum_k \lambda_k|c_k|^2 = \left(\sum_k\right)\lambda_k|< k|\Psi >|^2$$

5) Time dependent Schrödinger equation: $i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \hat{H}\Psi(\vec{r},t)$,

where nonrelativistic **Hamiltonian**: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$

For time independent $V(x)$:

$\hat{H}\psi_n(x) = E_n\psi_n(x)$
$\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar}$

1D systems:

PIB:

$\|n >= \psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$	$E_n = \frac{n^2h^2}{8mL^2}$

HO:

$\|n >= \psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{n!2^n}}H_n(\xi)e^{-\xi^2/2}$	$\omega = \sqrt{\frac{k}{m}}$; $\xi = \sqrt{\frac{m\omega}{\hbar}}\,x$
$E_n = (n+\frac{1}{2})\hbar\omega = (n+\frac{1}{2})h\nu$	$\nu = \frac{\omega}{2\pi}$
$\hat{a} = \sqrt{\frac{m\omega\hbar}{2}}\,x + i\sqrt{\frac{1}{2\hbar m\omega}}\,\hat{p}$; $\hat{a}^+ = \sqrt{\frac{m\omega\hbar}{2}}\,x - i\sqrt{\frac{1}{2\hbar m\omega}}\,\hat{p}$	
$\hat{a}\|n >= \sqrt{n}\,\|n >$; $\hat{a}^+\|n >= \sqrt{n+}\,\|n+1 >$	

ψ_0	$(\frac{1}{\pi})^{1/4}e^{-\xi^2/2}$
ψ_1	$(\frac{4}{\pi})^{1/4}\xi e^{-\xi^2/2}$
ψ_2	$\frac{2\xi^2-1}{\sqrt[4]{4\pi}}e^{-\frac{1}{2}\xi^2}$
ψ_3	$\frac{2\xi^3-3\xi}{\sqrt{3}\,\sqrt[4]{\pi}}e^{-\frac{1}{2}\xi^2}$

POR:

$\psi_n(\varphi) = \sqrt{\frac{1}{2\pi}}\,e^{in\varphi}$	$E_n = \frac{n^2\hbar^2}{2I}$	$I = \sum m_ir_i^2\left(\frac{m_1m_2}{m_1+m_2}R_e^2\right.$ for diatomic$\left.\right)$

3D systems:

Hamiltonian in spherical coordinates:

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right] + V(r)$$

Angular momentum (and spin):

$\vec{L} =$	$-i\hbar[\vec{\mathbf{r}} \times \vec{\nabla}]$	
$\hat{L}^2 =$	$\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 =$	$\frac{-\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$
$\hat{L}_z =$	$\frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$	$= -i\hbar\frac{\partial}{\partial\varphi}$
$\hat{L}_x =$	$\frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$	$= i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cos\varphi\cot\theta\frac{\partial}{\partial\varphi}\right)$
$\hat{L}_y =$	$\frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$	$= i\hbar\left(\sin\varphi\cot\theta\frac{\partial}{\partial\varphi} - \cos\varphi\frac{\partial}{\partial\theta}\right)$
$\hat{L}_\pm =$	$L_x \pm iL_y$	$= \pm\hbar e^{\pm i\varphi}\left(\frac{\partial}{\partial\theta} \pm i\cot\theta\frac{\partial}{\partial\varphi}\right)$

$\hat{L}^2 = (L_+L_- + L_z^2 - \hbar L_z)$
$\hat{L}^2\|l,m> = \hbar^2 l(l+1)\|l,m>$
$\hat{L}_z\|l,m> = \hbar m\|l,m>$
$\hat{L}_\pm\|l,m> = \hbar\sqrt{l(l+1) - m(m\pm1)}\,\|l,m\pm1>$

Y_0^0	$\sqrt{1/4\pi}$
Y_1^0	$\sqrt{\frac{3}{4\pi}}\cos\theta$
$Y_1^{\pm1}$	$\sqrt{\frac{3}{8\pi}}e^{\pm i\varphi}\sin\theta$
Y_2^0	$\sqrt{\frac{5}{\pi}}\frac{3\cos^2\theta-1}{4}$
$Y_2^{\pm1}$	$\sqrt{\frac{15}{2\pi}}e^{\pm i\varphi}\sin 2\theta$
$Y_2^{\pm2}$	$\sqrt{\frac{15}{32\pi}}e^{\pm 2i\varphi}\sin^2\theta$

Linear Combinations:	Names
Y_0^0	s
Y_1^0	p_z
$\frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1})$	p_x
$\frac{1}{i\sqrt{2}}(Y_1^1 - Y_1^{-1})$	p_y

Linear Combinations:	Names
Y_2^0	d_{z^2}
$\frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1})$	d_{xz}
$\frac{1}{i\sqrt{2}}(Y_2^1 - Y_2^{-1})$	d_{yz}
$\frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2})$	$d_{x^2-y^2}$
$\frac{1}{i\sqrt{2}}(Y_2^2 - Y_2^{-2})$	d_{xy}

Hydrogen-like atom: $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$

$\psi_{nlm}(r,\theta,\varphi) = R_{nl}Y_l^m(\theta,\varphi) = \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+1)!]^3}}\,e^{-Zr/na}\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na}\right)Y_l^m(\theta,\varphi)$	$E_n = -\frac{1}{2n^2}\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}$

R_{10}	$2(\frac{Z}{a})^{3/2}e^{-Zr/a}$
R_{20}	$(\frac{Z}{2a})^{3/2}(2-\frac{Zr}{a})e^{-Zr/2a}$
R_{21}	$\frac{1}{\sqrt{3}}(\frac{Z}{2a})^{3/2}(\frac{Zr}{a})e^{-Zr/2a}$
R_{30}	$\frac{2}{81\sqrt{3}}(\frac{Z}{a})^{3/2}\left(27\text{-}18\frac{Zr}{a}+2\frac{Z^2r^2}{a^2}\right)e^{-\frac{Zr}{3a}}$
R_{31}	$\frac{4}{81\sqrt{6}}(\frac{Z}{a})^{3/2}(\frac{Zr}{a})(6-\frac{Zr}{a})e^{-Zr/3a}$
R_{32}	$\frac{4}{81\sqrt{30}}(\frac{Z}{a})^{3/2}(\frac{Zr}{a})^2e^{-Zr/3a}$

$$\frac{s+1}{n^2}<r^s>-(2s+1)a<r^{s-1}>+\frac{s}{4}\left((2l+1)^2-s^2\right)a^2<r^{s-2}$$

Constants :

Electron charge	e	$1.602177\times10^{-19}\,\mathrm{C}$
Planck's constant	h	$6.6260755\times10^{-34}\,\mathrm{J\cdot s}$
Electron mass	m_e	$9.1093897\times10^{-31}\,\mathrm{kg}$ or $0.511\,\mathrm{MeV}$
Proton mass	m_p	$1.672623\times10^{-27}\,\mathrm{kg}$ or $938.27\,\mathrm{MeV}$
Speed of light	c	$2.997924\times10^{8}\,m/\mathrm{s}$
Bohr radius	$a_0=\hbar^2\frac{4\pi\varepsilon_0}{me^2}$	$0.52918\times10^{-10}\,\mathrm{m}$
Rydberg constant	$R_\infty=\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$	$2.17987\times10^{-18}\,\mathrm{J}$ or $3.28984\times10^{15}\,\mathrm{Hz}$
Hartree energy	$E_h=2R_\infty$	$4.35975\times10^{-18}\,\mathrm{J}$ or $27.2114\,\mathrm{eV}$
Fine-structure constant	$\alpha=\frac{e^2}{2\varepsilon_0hc}$	$7.29735\times10^{-3}=1/137.04$
Boltzmann constant	k	$1.380658\times10^{-23}\,\mathrm{J\cdot K^{-1}}$
Bohr magneton	μ_B	$9.274\times10^{-24}\,\mathrm{J/T}$
Nuclear magneton	μ_N	$5.051\times10^{-27}\,\mathrm{J/T}$
Mag. permeability of free space	μ_o	$1.25664\times10^{-6}N\bullet A^{-2}$
Permeability of free space	$\varepsilon_o=1/c^2\mu_o$	$8.854187817\times10^{-12}F/m$
Avogadro's number	N_A	$6.0221367\times10^{23}\,\mathrm{mol^{-1}}$

Virial theorem: for $V(x)=ax^s, < K >= \frac{s}{2} < V >$