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.

Question 2 (5 points)

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

Question 3 (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 coefficient A : $A_{i\to f} = \frac{16\pi^3}{3\varepsilon_o hc^3}\nu_{fi}^3|\mu_{if}|^2$

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

Question 4 (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?

Question 5 (20 points)

Identify point symmetry groups for the following molecules

Molecule	Point Group
CH_3Cl	
CH_4	
CO_2	
$H_2C{=}C{=}CH_2$	
C_6H_6	
H-C≡N	
trans dichloroethylene	
cis dichloroethylene	
PF_3	
NH_3	

Question 6 (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		
$H_2C{=}CH_2$		
C_6H_6		
C_{60}		
CH_4		
HCl		
CH_3Cl		
$H_2C{=}C{=}CH_2$		
trans dichloroethylene		

*- Estimate B **only for the molecules that do show rotational spectra**. Otherwise, indicate ' no mw 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. **Neglect centrifugal distortion**

'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	$\left(\frac{1}{\pi}\right)^{1/4}e^{-\xi^2/2}$
ψ_1	$\left(\frac{4}{\pi}\right)^{1/4}\xi e^{-\xi^2/2}$
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):

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

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

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

$$\frac{s+1}{n^2}\langle r^s\rangle-(2s+1)a\langle r^{s-1}\rangle+\frac{s}{4}\left((2l+1)^2-s^2\right)a^2\langle r^{s-2}\rangle = 0$$

Constants :

Electron charge	e	1.602177×10^{-19} C
Planck's constant	h	6.6260755×10^{-34} J·s
Electron mass	m_e	9.1093897×10^{-31} kg or 0.511 MeV
Proton mass	m_p	1.672623×10^{-27} kg or 938.27 MeV
Speed of light	c	$2.997924\times10^{8}\,m$/s
Bohr radius	$a_0 = \hbar^2\frac{4\pi\varepsilon_0}{me^2}$	0.52918×10^{-10} m
Rydberg constant	$R_\infty = \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$	2.17987×10^{-18} J or 3.28984×10^{15} Hz
Hartree energy	$E_h = 2R_\infty$	4.35975×10^{-18} J or 27.2114 eV
Fine-structure constant	$\alpha = \frac{e^2}{2\varepsilon_0 hc}$	$7.29735\times10^{-3} = 1/137.04$
Boltzmann constant	k	1.380658×10^{-23} J·K^{-1}
Bohr magneton	μ_B	9.274×10^{-24} J/T
Nuclear magneton	μ_N	5.051×10^{-27} 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	6.0221367×10^{23} mol^{-1}