Hertentamen AMF 25 Febr. 2013

I Knowledge of course

1. Ground state and 2 first singlet + 2 first triplet excited states of He:

$1s^2$: $^1S_0$ ground

$1s\,2s$: $^1S_0$ singlet

$^3S_1$ Triplet (lower in energy)

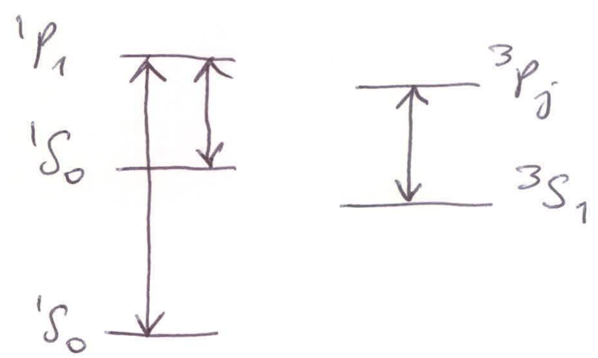
$1s\,2p$: $^1P_1$ singlet

^3P_j triplet $j = 0, 1, 2$

allowed if:

$\Delta S = 0$

$\Delta L = \pm 1$



2. Be $(Z=4)$ $1s^2\,2s^2$ $^1S_0$

B $(Z=5)$ $1s^2\,2s^2\,2p^1$ $^2P_{1/2}$

C $(Z=6)$ $1s^2\,2s^2\,2p^2$ $^3P_0$

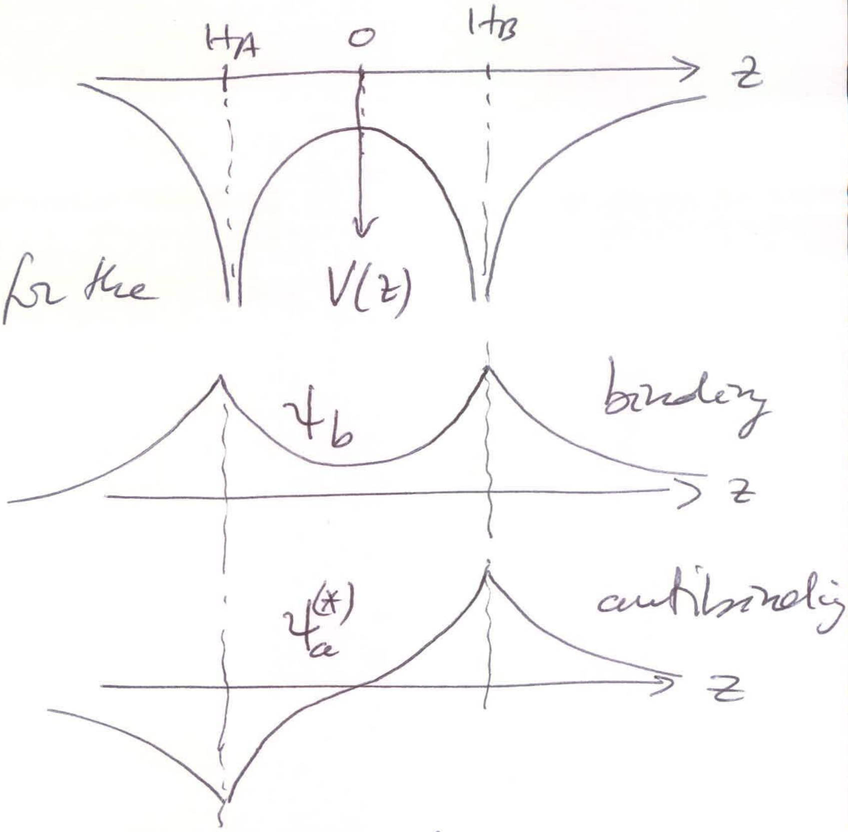
Less than half-filled : lowest j has lower energy.

3. Al $Z = 13$

Ground state $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^1$

4. H_2^+ mol. ion

Wavefunction of e^- on internuclear axis for the 2 lowest states:



$\psi_b(z) \simeq \psi_A(z) + \psi_B(z)$

$\psi_a^{(*)}(z) \simeq \psi_A(z) - \psi_B(z)$

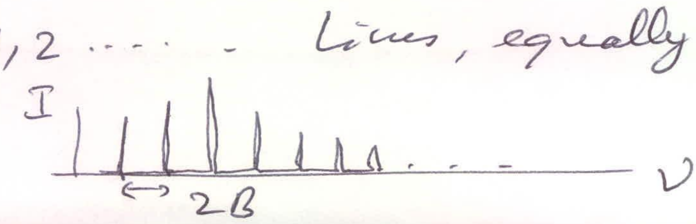
$\psi_b(z)$ is the wavefunction with the lowest energy, as deduced from perturbation theory of V_B for H-atom around H_A (and vice-versa).

5. energy spacing

electronic > vibrational > rotational

(the ratio is about $\sqrt{\frac{m_e}{M}}$).

6. Rotational transitions appear between levels $BK(K+1)$ with $\Delta K = \pm 1$. Therefore, in absorption $B(K+1)(K+2) - B(K+1)K = 2B(K+1)$ with $K = 0, 1, 2 \ldots\ldots$ Lines, equally spaced by $2B$



Here $2B \simeq 20\ cm^{-1}$ $\Rightarrow$ $B = 10\ cm^{-1}$

and $B = \frac{\hbar^2}{2J}$ J moment of inertia.

$$J = \frac{\hbar^2}{2B}.$$

7. Shells 1,2,3 are full - Shell four has the configur. $4s^2\ 4p\ 4d$ -

$4s^2$ is a closed sub-shell, thus we consider only the 2 electron $4p4d$. Pauli principle doesn't apply, so all combinations are allowed:

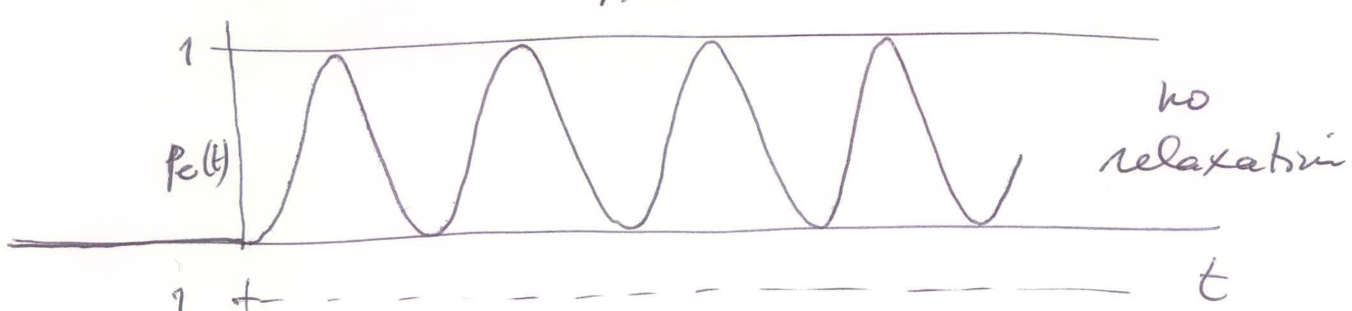
$2S+1 = 1$ (singlets) $L = 2-1,\ 2,\ 2+1$ $(1,2,3)$

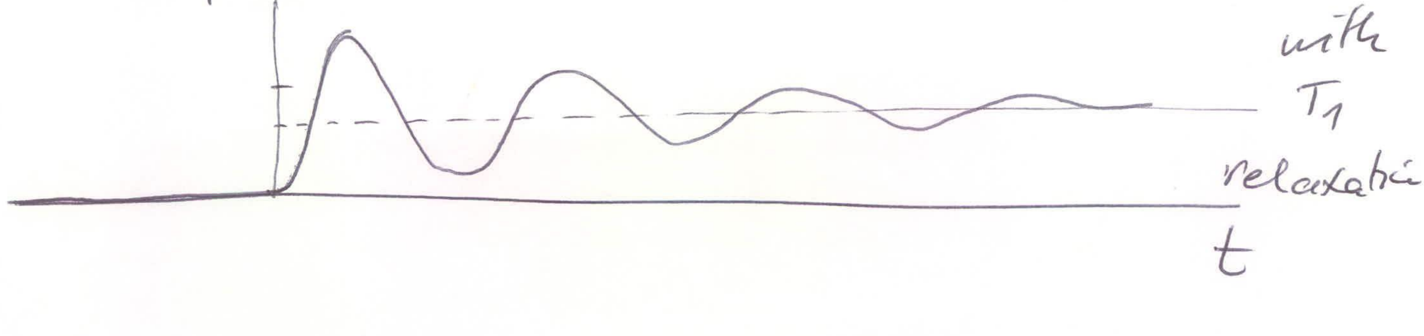
$2S+1 = 3$ (triplets) $L = 1,2,3$

$^1P,\ ^1D,\ ^1F,\ ^3P,\ ^3D,\ ^3F$ (<u>not</u> ground state).

The ground state has $4s^2 4p^2$ (term $^3P_0$).

8. Optical nutation: apply $\vec{E}_0 \cos\omega t$ at $t=0$



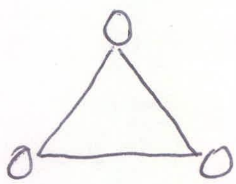


9. Population difference $p_g - p_e$ with

$$\frac{p_e}{p_g} = \exp\left(-\frac{h\nu}{k_B T}\right)$$ here $|p_e - p_g| \ll 1$ thus

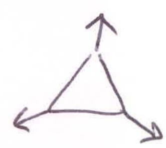
$$(p_g - p_e) \simeq p_g\left(1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right) \simeq \frac{1}{2} \cdot \frac{h\nu}{k_B T}$$

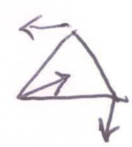
$$\frac{1}{2}\frac{h\nu}{k_B T} = \frac{1}{2}\frac{6.6\,10^{-34} \times 43.10^{6}}{1.38\,10^{-23} \times 300} = \frac{1}{2}\frac{43 \times 6.6}{4.4\,10^{-21}} \cdot 10^{-28} \simeq 3.3\,10^{-6}$$

10. 

number of modes $3N-6$ (not linear) $= 3$ modes of vibration.

All modes have to be <u>in-plane</u> motions because there are $3\times 2 \underbrace{-2}_{\text{2 transl.}} \underbrace{-1}_{\text{1 rotation}} = 3$ in-plane vibrations.

- symmetric mode 

- 2 degenerate antisymmetric modes 

[note: the 2 modes sketched are <u>not</u> orthogonal]

II Problem : Hyperfine structure

1. I nuclear angular mom. number

$\mathbb{I}^2$ has eigenvalues $I(I+1)\hbar^2$

I_z ——— $m_I \hbar$, $m_I = -I, -I+1, \dots I-1, I$.

Spin degeneracy $2I+1$.

^{133}Cs has $I = \frac{7}{2}$ $\quad I(I+1) = \frac{63}{4}$

$$m_I = -\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$$

$$2I+1 = 8.$$

2. $\vec{j} = \vec{l} + \vec{s}$, j total electronic ang. mom.

$\vec{F} = \vec{j} + \vec{I}$ $\quad F$ total atomic ang. mom.

(a) possible values of $F = |I-j|, |I-j|+1, \dots, I+j$.

degeneracy is $2F+1$ for each value of F.

(b) if $I+j$ is integer, the total degeneracy is a sum of odd integers:

$$2(I+j)+1 + 2[(I+j)-1]+1 + \dots + 2\{|I-j|\}+1 = N$$

but $2p+1 + 2(p-1)+1 + \dots + 1 = (p+1)^2$

Thus $N = (I+j+1)^2 - (|I-j|)^2 = (I+j+1-I+j)(I+j+1+I-j)$

$$= (2j+1)(2I+1)$$

Let us consider now the case $I+j$ = half-integer and assume $I \geq j$ (without loss of generality)

Set $I+j = p+\frac{1}{2}$

The sum of all degeneracies from $\frac{1}{2}$ to $I+j$ is :

$$2+4+\dots+2(I+j)+1 = 2(1+2+\dots+p+1) = (p+1)(p+2)$$

From $\frac{1}{2}$ to $|I-j|$, this sum is $(q+1)(q+2)$

if $|I-j| = q+\frac{1}{2}$.

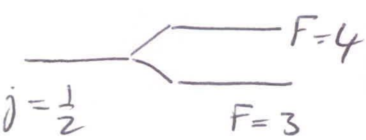
Thus $N = \text{Sum}(I+j) - \text{Sum}(|I-j|-1) = (p+1)(p+2) - q(q+1)$

$$= \underbrace{(I+j+\tfrac{1}{2})(I+j+\tfrac{3}{2})}_{(I+j)^2+2(I+j)+\frac{3}{4}} - \underbrace{(I-j-\tfrac{1}{2})(I-j+\tfrac{1}{2})}_{(I-j)^2-\frac{1}{4}} = (I+j)^2+2(I+j)+1 - (I-j)^2$$

$$N = 2I\times 2j+2I+2j+1 = (2I+1)(2j+1).$$

(c) ^{133}Cs has the config. of a rare gas (Xe) plus one e^- (it is an alkali). We may thus consider only that electron.

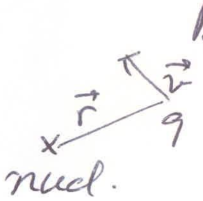
$I=\frac{7}{2}$, $j=\frac{1}{2}$ $\rightarrow$ $F = 4$ or 3



3. Biot-Savart law ; $\vec{B} = \frac{\mu_0}{4\pi} \cdot \frac{q\vec{v}\times\vec{R}}{R^3}$

Field created by the orbital ang. mom. of the electron at the nucleus' position : $\vec{R} = -\vec{r}$

$$\vec{B}_0 = -\frac{\mu_0}{4\pi}\frac{q\vec{v}\times\vec{r}}{r^3} = +\frac{\mu_0}{4\pi}\frac{q}{m}\frac{\vec{l}}{r^3} \quad \text{with } \vec{l} = m\vec{r}\times\vec{v}$$



$$H = -\vec{\mu}_I\cdot\vec{B}_0 = \frac{-\mu_0}{4\pi}\frac{q}{mr^3}\,\vec{l}\cdot\vec{\mu}_I$$

4. Spin magnetic moment

$$\vec{\mu}_s = -g_s \vec{s} \cdot \mu_B$$

$$\vec{B}_{el} = \vec{B}_0 + \vec{B}_s \qquad \vec{B}_s = \frac{\mu_0}{4\pi r^3}\left[-\vec{\mu}_s + 3\frac{\vec{\mu}_s \vec{r}}{r^2}\vec{r}\right]$$

$$H_{int} = -\vec{\mu}_I \cdot \vec{B}_{el} = -\vec{\mu}_I \cdot \left\{+\frac{\mu_0}{4\pi}\frac{q}{m}\frac{\vec{l}}{r^3} + \frac{\mu_0}{4\pi r^3}\left(-\vec{\mu}_s + 3\frac{\vec{\mu}_s \cdot \vec{r}}{r^2}\vec{r}\right)\right\}$$

$$= \vec{\mu}_I \cdot \left[\frac{-q}{m}\frac{\vec{l}}{r^3} + \frac{1}{r^3}\left(\vec{\mu}_s - 3\frac{\vec{\mu}_s \vec{r}}{r^2}\vec{r}\right)\right]\frac{\mu_0}{4\pi}$$

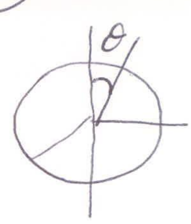
$$= \frac{\mu_0}{4\pi r^3}\cdot\frac{q}{m}\ \vec{\mu}_I \cdot \left[-\vec{l} + \frac{g_s}{2}\left(\vec{s} - \frac{3\vec{s}\cdot\vec{r}}{r^2}\vec{r}\right)\right]$$

5. Averaging the Hamiltonian close to 0 in perturb. theory, we get $\int 4\pi r^2 dr\, |\psi|^2 H(r)$

$$H(r) \sim r^{-3},\ |\psi|^2 \sim r^{2l} \Rightarrow \int r^{2-3+2l} dr = \int r^{2l-1} dr$$

converges for $l \geq 1$, but diverges for $l = 0$!

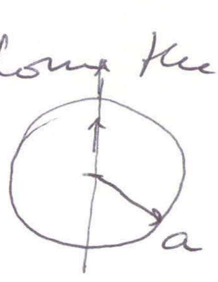
(a) Average of the dipole field outside the nucleus



angular integration:

$$\int d\varphi \sin\theta\, d\theta \cdot \underbrace{(1 - 3\cos^2\theta)}_{H_{int}} = 2\pi \int du\,(1 - 3u^2) = 0$$

(b) normal component of B continuous follows from the eq. $\vec{\nabla} \cdot \vec{B} = 0$ $\quad$ ($\text{div}\,\vec{B} = 0$)



$$\vec{B}_i = \vec{B}_{dipole} \text{ on axis at } r = a = \frac{+2\mu_I \mu_0}{4\pi a^3}$$

(c) The average interaction is 0 outside the sphere and constant inside because the magnetic field is uniform. Thus:

$$H_{int} = -\vec{\mu}_{el} \cdot \vec{B}_I = -\vec{\mu}_{el} \cdot \frac{2\mu_0 \vec{\mu}_I}{4\pi a^3} \times \frac{4\pi}{3} a^3 \delta(\vec{r})$$

$$= -\frac{1}{3} 2\mu_0 \vec{\mu}_{el} \cdot \vec{\mu}_I \delta = -\frac{2}{3} \mu_0 \vec{\mu}_s \vec{\mu}_I \delta(\vec{r})$$

because only $\vec{\mu}_s$ contributes to the magnetic moment of the electron ($\vec{\ell} = 0$).