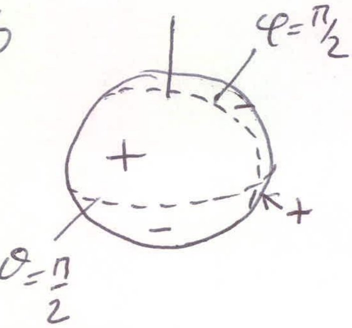
Examination AMF - 21 Dec 2012 (1)

I Knowledge of course

(1) $\mathrm{Re}\, Y_2^1(\theta,\varphi) = -\sqrt{\frac{5}{8\pi}} \cos\theta \sin\theta \cos\phi$



$\mathrm{Re}(Y_2^1) = 0$ for $\theta = \frac{\pi}{2}$, $\theta = 0$, $\phi = \frac{\pi}{2}$

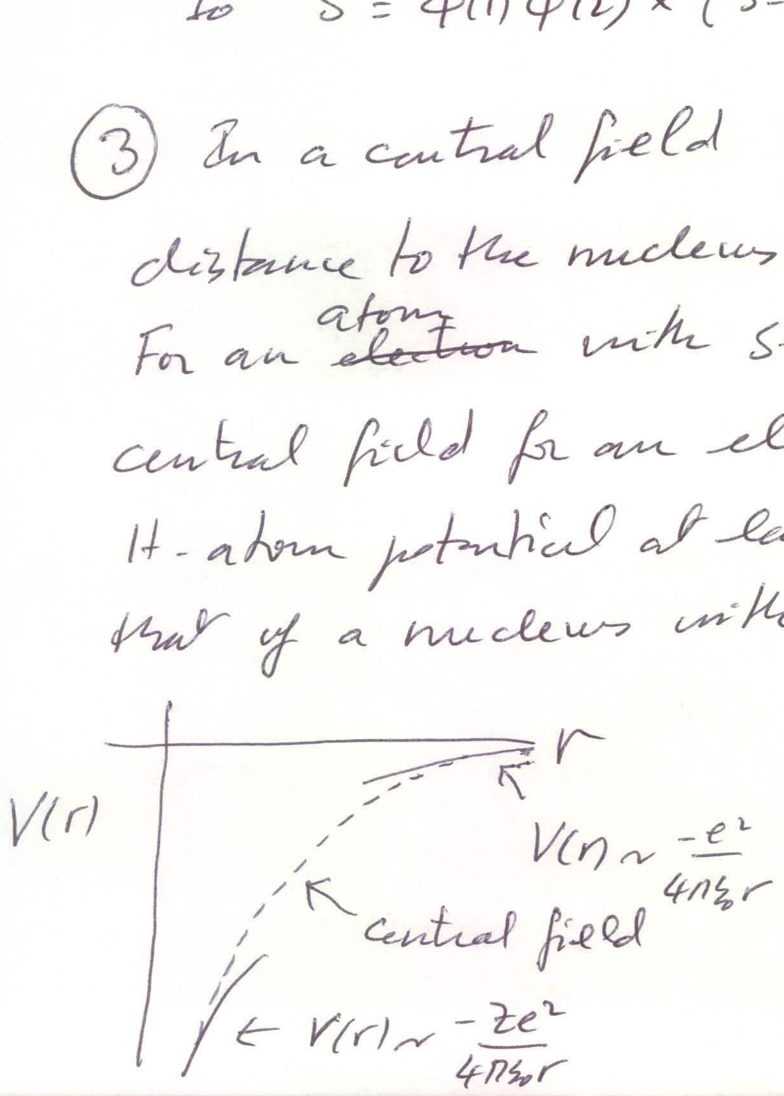
(it's a d-wavefc.)

(2) Slater determinant with $\phi(1)\alpha(1)$

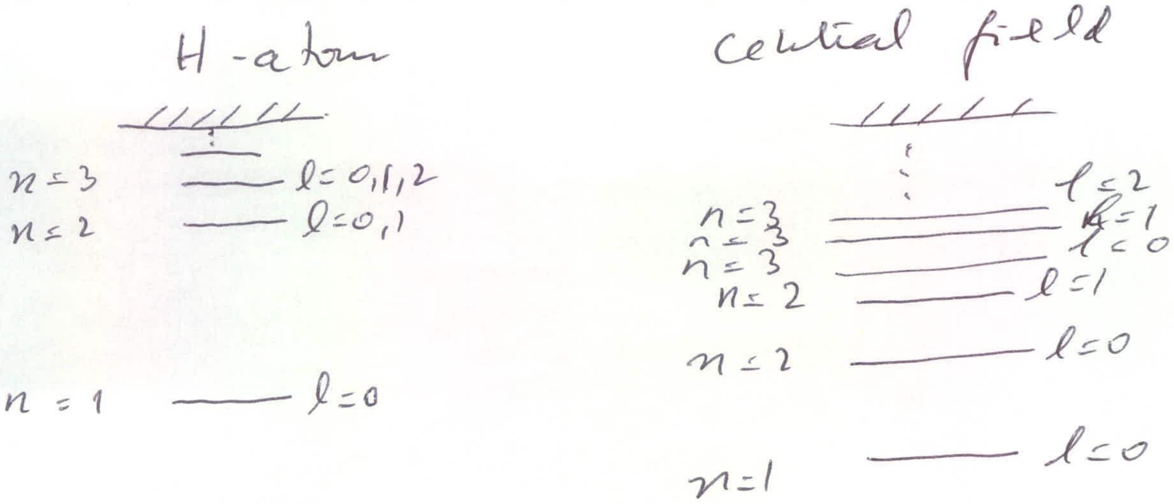
$$S = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi(1)\alpha(1) & \phi(2)\alpha(2) \\ \phi(1)\beta(1) & \phi(2)\beta(2) \end{vmatrix} = \phi(1)\phi(2)\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(1)\beta(1))$$

so $S = \phi(1)\phi(2) \times |S=0, M_S=0\rangle$ singlet spin.

(3) In a central field $V(r)$ depends only on the distance to the nucleus, not on any angles. For an ~~electron~~ atom with several electrons, the central field for an electron resembles a H-atom potential at large r, but resembles that of a nucleus with Z + charges for r <<.



For a given n, all l-states are degenerate in a Coulomb potential, but the lower-l numbers are stabilized in this field.



(4) Balmer series of H $n \geq 2 \rightarrow n=2$

Transition energy $\left| -\frac{E_I}{n^2} - \left(-\frac{E_I}{2^2}\right) \right| = E_I \left(\frac{1}{4} - \frac{1}{n^2} \right)$

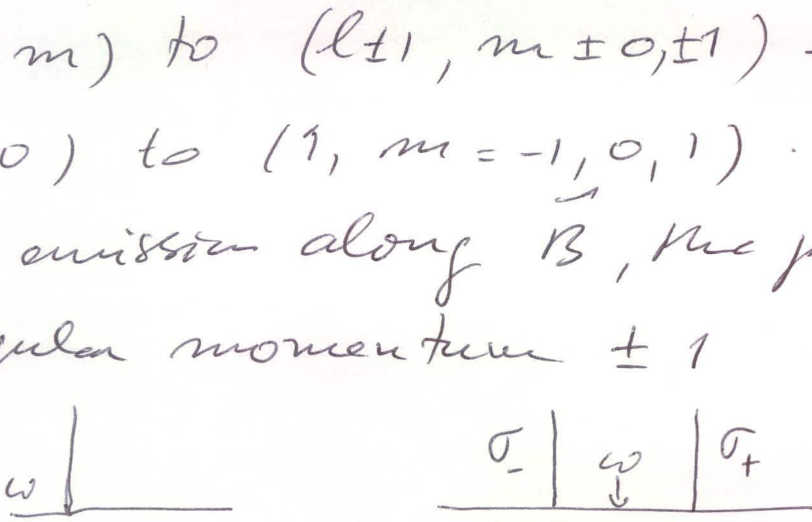
Red-most transition is for $n=3$: $E_I \left(\frac{1}{4} - \frac{1}{9} \right)$

Next one for $n=4$: $E_I \left(\frac{1}{4} - \frac{1}{16} \right) = \frac{3}{16} E_I$

$$\frac{\lambda_4}{\lambda_3} = \frac{E_3}{E_4} = \frac{5/36}{3/16} = \frac{20}{27} \qquad \lambda_4 = \frac{20}{27} \times 656.3 = 486.1 \text{ nm}$$

(5) Normal Zeeman effect = transitions from (l, m) to $(l \pm 1, m \pm 0, \pm 1)$. For example $(0,0)$ to $(1, m = -1, 0, 1)$.

For emission along B, the photon carries angular momentum ± 1



The polarization are circular right or left (σ_+ and σ_-) but π is absent.

6) In the Born-Oppenheimer approximation, the nuclei are left immobile to solve the electronic Schrödinger problem $\rightarrow$ $\Psi_i(\vec{R}, \vec{r})$, where $\vec{R}$ is a <u>parameter</u>. The electronic energy $E_i(\vec{R})$ is the potential in which the nuclei will move to solve the nuclear Schrödinger problem in a second step $\rightarrow$ $\chi_{iv}(\vec{R})$.

B.-O. applies for large nuclear mass, when the energy differences between electronic states is much larger than nuclear vibrational energies.

7) H_2 has 2 electrons. We build the molecular orbital from 1s atomic orbitals of H

$\sigma_g^2 (1s)(1s)$ - Term: ${}^1\Sigma_g^+$ ($S=0$; $+ \rightarrow$ symm/mirror; $g \rightarrow$ even)

8) CO_2 has σ and pi bonds between C and O.

O=C=O (linear)

Vibration modes $3N-5 = 4$

2 mode are stretching of C=O, 2 are bending of O=C=O angle

i) ←O=C=O→

ii) ←O=$\vec{C}$=O←

iii) $\overset{\uparrow}{O}=\underset{\downarrow}{C}=\overset{\uparrow}{O}$

iv) $\overset{\nearrow}{O}=\underset{\swarrow}{C}=\overset{\nearrow}{O}$

i) inactive in IR; ii) $\vec{\mu}$ O=C=O →; iii) O=C=O, ↓ $\vec{\mu}$; iv) $\vec{\mu}$ O=C=O ↗

9 Rotational constant B from

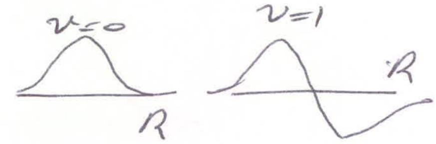
$$E_K = \frac{\hbar^2}{2I} K(K+1) \quad \text{with} \quad B = \frac{\hbar^2}{2I}, \quad I = MR^2$$

(M reduced nuclear mass, R distance between nuclei)

If the nuclei are not fixed, R^2 may vary, and B averages all R values.

For an oscillator $\langle R^2 \rangle > \langle R \rangle^2$ and

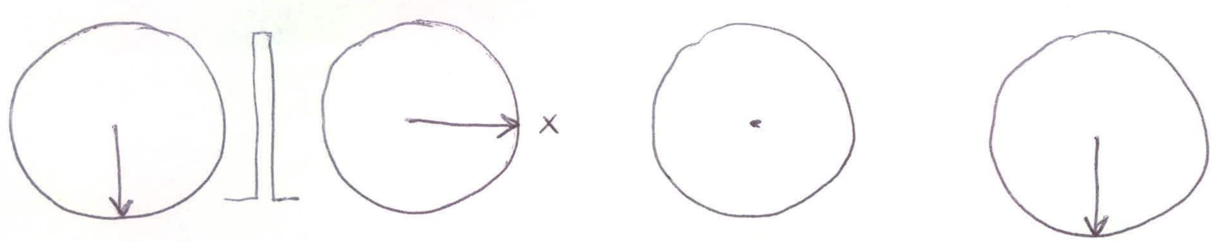
$\langle R^2 \rangle_{v=1} > \langle R^2 \rangle_{v=0}$ because



moreover anharmonicity shifts the centre of the $v=1$ function away from the minimum

10 Bloch vector

after $\pi/2$ pulse



$t=0^-$	$t=0^+$	$t_a \gg T_2$	$t_b \gg T_1$
$\begin{bmatrix} 0 \\ 0 \\ -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 0 \\ \frac{1}{2} \\ 0 \end{bmatrix}$	$\begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 0 \\ 0 \\ -\frac{1}{2} \end{bmatrix}$

II Problems

A Terms of the Ar^+ ion

ⓐ Lowest energy configuration is obtained by removing one of the 2p electron:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ \underline{3p^5}$$

ⓑ Ar^+ excited has: $1s^2\ 2s^2\ 2p^6\ \underline{3p^4\ 4s}$

Total number of states: 2 for 4s, for $3p^4$ choose 2 orbitals among 6: $\frac{6\times5}{2} = 15$.
Thus $15\times2 = 30$ possible states of this config.

ⓒ Allowed terms for $3p^4$ are as for $3p^2$:

^1D, ^3P, ^1S - with total j $\quad J = \begin{cases} L+S \\ \vdots \\ |L-S| \end{cases}$

$^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1S_0$

We now have to combine with a spin-$\frac{1}{2}$ in shell 4s:

$^1D_2 \rightarrow \ ^2D_{5/2}, \ ^2D_{3/2} \qquad 6+4 \qquad = 2\times5$

$$^3P + ^2S \rightarrow \left\{ \begin{array}{lll} ^4P & ^4P_{5/2}, \ ^4P_{3/2}, \ ^4P_{1/2} & 6+4+2 \\ & & \\ ^2P & ^2P_{3/2}, \ ^2P_{1/2} & 4+2 \end{array} \right\} 2\times9$$

$^1S_0 \rightarrow \ ^2S_{1/2} \qquad 2 \qquad = 2\times1$

$\overline{}$

30 states.

(d) Hund's rules

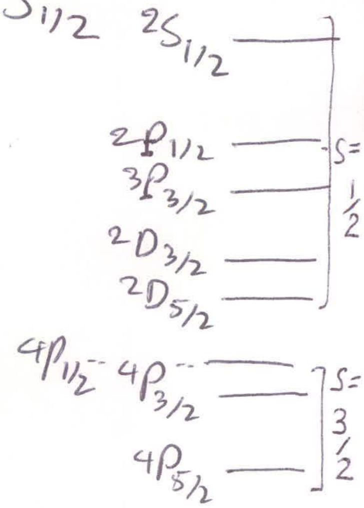
i) largest $2S+1$ lowest

ii) largest L lowest

iii) largest J lowest for less than half-filled

$$^4P_{5/2},\ ^4P_{3/2},\ ^4P_{1/2},\ ^2D_{5/2},\ ^2D_{3/2},\ ^2P_{3/2},\ ^2P_{1/2},\ ^2S_{1/2}$$

$$\longrightarrow\ E \nearrow\ \longrightarrow$$



B Magnetic resonance with J-coupling

(a) Basis $\{|++\rangle, |+-\rangle, |-+\rangle, |--\rangle\} \equiv \{|\varepsilon_1, \varepsilon_2\rangle\}$

dimension $4 = 2\times 2$

$$H_{z1} = \omega_0 \begin{pmatrix} \hbar/2 & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} \quad \text{for spin 1}$$

$$H_z = \frac{\hbar\omega_0}{2} \begin{array}{c} \begin{array}{cccc} |++\rangle & |+-\rangle & |-+\rangle & |--\rangle \end{array} \\ \begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 \end{bmatrix} \end{array} \begin{array}{c} \\ |++\rangle \\ |+-\rangle \\ |-+\rangle \\ |--\rangle \end{array}$$

(b) $$W = \Omega(S_{1x} + S_{2x}) = \frac{\hbar\Omega}{2} \begin{bmatrix} \boxed{\begin{matrix} 0 & 1 \\ 1 & 0 \end{matrix}} & \begin{matrix} 1 & 0 \\ 0 & 1 \end{matrix} \\ \begin{matrix} 1 & 0 \\ 0 & 1 \end{matrix} & \boxed{\begin{matrix} 0 & 1 \\ 1 & 0 \end{matrix}} \end{bmatrix}$$

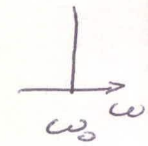
Transitions from

$|++\rangle$ to $|-+\rangle$ and $|+-\rangle$ $\Big\}$ $\underline{8}$ matrix elements

$|--\rangle$ to $|-+\rangle$ and $|+-\rangle$

energies exchanged are the Bohr energies

$E_{++} - E_{+-}, \dots \; : \; \pm \omega_0$ -

Only one line at ω_0 appears in the spectrum 

(c) $V = A\left(S_{1x} S_{2x} + S_{1y} S_{2y} + S_{1z} S_{2z}\right)$

$$S_{1x} = \frac{1}{2}\left(S_{1+} + S_{1-}\right) \qquad S_{1y} = \frac{1}{2i}\left(S_{1+} - S_{1-}\right)$$

$$S_{1x} S_{2x} + S_{1y} S_{2y} = \frac{1}{4}\left(S_{1+} + S_{1-}\right)\left(S_{2+} + S_{2-}\right) - \frac{1}{4}\left(S_{1+} - S_{1-}\right)\left(S_{2+} - S_{2-}\right)$$

$$= \frac{1}{4}\left(S_{1-} S_{2+} + S_{1+} S_{2-} + S_{1-} S_{2+} + S_{1+} S_{2-}\right)$$

$$= \frac{1}{2}\left(S_{1+} S_{2-} + S_{1-} S_{2+}\right)$$

$$V = A\left[\frac{1}{2}\left(S_{1+} S_{2-} + S_{1-} S_{2+}\right) + S_{1z} S_{2z}\right]$$

matrices of S_{1+} : $\frac{\hbar}{2}\left\{\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + i \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}\right\} = \frac{\hbar}{2}\begin{bmatrix} 0 & 2 \\ 0 & 0 \end{bmatrix}$

$$S_{1-} = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

$$S_{1+} S_{2-} = \hbar^2 \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$S_{1+} S_{2-} |-+\rangle = |+-\rangle \hbar^2$

$S_{1+} S_{2-} |+ \varepsilon_2\rangle = 0$

$S_{1+} S_{2-} |\varepsilon_1 -\rangle = 0$

$$S_{1-} S_{2+} = \hbar^2 \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$S_{1z} S_{2z}$ is diagonal $= \frac{\hbar^2}{4}\begin{bmatrix} 1 & & & \\ & -1 & & \\ & & -1 & \\ & & & 1 \end{bmatrix}$

$$V = A\left[S_{1z} S_{2z} + \frac{1}{2}\left(S_{1+} S_{2-} + S_{1-} S_{2+}\right)\right] = \frac{\hbar^2}{4} A \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

V couples only $|+-\rangle$ and $|-+\rangle$ - We diagonalize it by choosing the new basis vector

$$\frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right) \equiv |10\rangle$$

(notations: $|S, M_S\rangle$)

and

$$\frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right) \equiv |00\rangle$$

The diagonal eigenvalues of V are now:

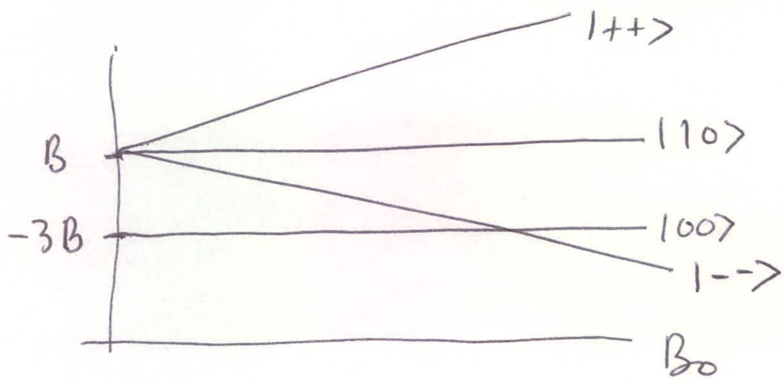
$$\frac{\hbar^2 A}{4}(-1 \pm 2) = \frac{\hbar^2 A}{4} \text{ and } -3\frac{\hbar^2 A}{4}$$

$$V = \frac{\hbar^2 A}{4} \begin{array}{c} \begin{matrix} |{++}\rangle & |10\rangle & |00\rangle & |{--}\rangle \end{matrix} \\ \begin{bmatrix} 1 & & & 0 \\ & 1 & & \\ & & -3 & \\ 0 & & & 1 \end{bmatrix} \end{array} \qquad H_z + V = \begin{bmatrix} \hbar\omega_0 + \frac{\hbar^2 A}{4} & & & 0 \\ & \frac{\hbar^2 A}{4} & & \\ & & -3\frac{\hbar^2 A}{4} & \\ 0 & & & -\hbar\omega_0 + \frac{\hbar^2 A}{4} \end{bmatrix}$$

or

$$H_z + V = \hbar \begin{bmatrix} \omega_0 + B & & & \\ & B & & \\ & & -3B & \\ & & & -\omega_0 + B \end{bmatrix} \quad \text{with } B = \frac{\hbar A}{4}$$

(d)



magnetic resonance for ω = Bohr frequencies

$|{++}\rangle \rightarrow |10\rangle$: ω_0

$\quad |00\rangle$: $\omega_0 + 4B$

$\quad |{--}\rangle$: $2\omega_0$

$|10\rangle \rightarrow |00\rangle$: $4B$

$\quad |{--}\rangle$: ω_0

$|00\rangle \rightarrow |{--}\rangle$: $\omega_0 - 4B$

(e) matrix elements of W:

couples only $|++\rangle$ to $(|+-\rangle, |-+\rangle)$ or to $(|1,0\rangle, |00\rangle)$

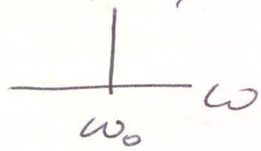
$|--\rangle$ " "

$\langle ++|W|10\rangle = \frac{\hbar\Omega}{2}(1+1) = \hbar\Omega$ (similar for $|--\rangle$)

$\langle ++|W|00\rangle = \frac{\hbar\Omega}{2}(1-1) = 0$

Thus W couples only $|++\rangle$ to $|10\rangle$ and $|--\rangle$ to $|10\rangle$.

Only 2 transitions are left, at ω_0. There is still one line!



The perturbation W is symmetric in the exchange of the 2 spins. Therefore, it cannot connect a symmetric to an antisymmetric state.

Singlet to triplet transitions are forbidden in a magnetic resonance spectrum.