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# B2: III. QUANTUM, ATOMIC AND MOLECULAR PHYSICS

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**TRINITY TERM 2013**

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*Disclaimer: due to its unofficial nature, the author does not warrant the accuracy of the presented solutions in any form. However, the author is happy to discuss the typos and errors should one arises.*

**Turn over as you please – we are NOT under exam conditions here.**

**1. (DRAFT)**

| | Fine structure | Hyperfine structure |
|---|---|---|
| Physical origin | Spin-orbit interaction between $e^-$ moment and transformed field | Spin-spin interaction due to intrinsic magnetic moments of nucleus and $e^-$ |
| Coupling | $\lvert LSJM_J\rangle$ | $\lvert IJFM_F\rangle$ where $\hat{\mathbf{F}} = \hat{\mathbf{I}} + \hat{\mathbf{J}}$ |
| Relative strength | 1 | $\dfrac{m_e}{m_p} \sim 10^{-3}$ |

(a) In $IJ$ coupling scheme, the total atomic-nuclear angular momentum:

$$\hat{\mathbf{F}}^2 = \left(\hat{\mathbf{I}} + \hat{\mathbf{J}}\right)^2$$
$$\Rightarrow \mathbf{I}\cdot\mathbf{J} = \frac{1}{2}\left[\hat{\mathbf{F}}^2 - \hat{\mathbf{I}}^2 - \hat{\mathbf{J}}^2\right]$$

For eigenstates $\lvert IJFM_F\rangle$, we then have:

$$E_F = \langle \hat{H}_{\text{hf}} \rangle$$
$$E_F = \frac{A}{2}\left(F(F+1) - I(I+1) - J(J+1)\right)$$

The good quantum numbers in this scheme are $I$, $J$, $F$ and $M_F$.

(b) Now find $\Delta E_{\text{hf}}$:

$$\begin{aligned}\Delta E_{\text{hf}} &= E_F - E_{F-1} \\ &= \frac{A}{2}\left[F(F+1) - I(I+1) - J(J+1) - (F-1)F + I(I+1) + J(J+1)\right] \\ &= \frac{A}{2}\left[F^2 + F - F^2 + F\right] \\ &= AF\end{aligned}$$

Level ${}^2S_{1/2}$ has $J = 1/2$, hydrogen has $I = 1/2 \Rightarrow F = 0$ or $1$.

So:

$$\begin{aligned}\Delta E(F=0) &= \frac{A}{2}\left[0(1) - \frac{1}{2}\left(\frac{3}{2}\right) - \frac{1}{2}\left(\frac{3}{2}\right)\right] \\ &= -\frac{3A}{4} \\ &= -\frac{3}{4}\left(\frac{\mu_0}{4\pi}\right)\left(\frac{g_I \mu_B \mu_N}{1/2}\right)\frac{8}{3}\frac{1}{a_0^3} \\ &= -\frac{3}{4}\underbrace{\left(5.89\times10^{-6}\,\text{eV}\right)}_{1.425\times10^{9}\,\text{Hz}=4.749\,\text{m}^{-1}} \\ &= -1.069\times10^{9}\,\text{Hz} \\ &= -1.069\times10^{3}\,\text{MHz} \\ &= -3.562\,\text{m}^{-1} = -0.035\,62\,\text{cm}^{-1}\end{aligned}$$

$$
\begin{aligned}
\Delta E(F=1) &= \frac{A}{2}\left[1(2) - \frac{1}{2}\left(\frac{3}{2}\right) - \frac{1}{2}\left(\frac{3}{2}\right)\right] \\
&= \frac{A}{4} \\
&= 3.562 \times 10^{8}\,\mathrm{Hz} \\
&= 356.2\,\mathrm{MHz} \\
&= 1.187\,\mathrm{m}^{-1} = 0.0187\,\mathrm{cm}^{-1}
\end{aligned}
$$

Since no $\mathrm{e}^-$ has any transition, this is not an electric dipole transition (in fact it's magnetic dipole).

(c) $A_{10} \sim 1/\tau \sim \Delta\omega_n$ where $\Delta\omega_n$ is natural broadening, $\tau$ is the decay time.

Typically in lab, we would have Doppler broadening: $\Delta\omega/\omega \sim v/c$

Equipartition theorem tells us:

$$
\begin{aligned}
&\frac{1}{2}mv^2 = 3k_\mathrm{B}T \\
&\Rightarrow v = \sqrt{\frac{6k_\mathrm{B}T}{m}} \\
&\Rightarrow \frac{\Delta\omega}{\omega} \sim 1.658 \times 10^{-5} \quad \text{for } T \sim 500\,\mathrm{K} \\
&\Delta\omega = 2.36 \times 10^{4}\,\mathrm{Hz} \gg A_{10}
\end{aligned}
$$

So without eliminating such broadening, it would be difficult to resolve such transition.

(d) $5d^2 6s\ {}^4F_{9/2}$ has $J = \frac{9}{2}$.

Since there are an even (8) number of splitting, $F$ is an integer $\Rightarrow$ $I$ is a half-integer.

Also the Interval Rule:

$$
\begin{aligned}
\Delta E_F - \Delta E_{F-1} &= AF \\
\Rightarrow \frac{\Delta E_F - \Delta E_{F-1}}{\Delta E_{F-1} - \Delta E_{F-2}} &= \frac{F}{F-1}
\end{aligned}
$$

| $\Delta E$ (MHz) | $\Delta E - \Delta E_0$ (MHz) | Ratio $\dfrac{\Delta E - \Delta E_0}{\Delta E' - \Delta E}$ |
|---|---|---|
| 0 | N/A | N/A |
| 2312.87 | 2312.87 | N/A |
| 4334.02 | 2021.15 | $8/7$ |
| 6075.97 | 1741.95 | $7/6$ |
| 7528.28 | 1452.31 | $6/5$ |
| 8688.88 | 1160.60 | $5/4$ |
| 9568.19 | 879.31 | $4/3$ |

So $F$ ranges from 2 to 9:

$$\begin{cases} I + J = 9 \\ I - J = 2 \end{cases}$$
$$\Rightarrow 2I = 11$$
$$I = \frac{11}{2}$$

So we have:

$$A = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{g_I \mu_\mathrm{B} \mu_\mathrm{N}}{{}^{11}\!/_{2}}\right)\frac{8}{3}\frac{57}{(6a_0)^3}$$

Also:

$$\Delta E_{F=9} - \Delta E_{F=8} = 9A = 2312.87\,\mathrm{MHz}$$
$$A = 256.99\,\mathrm{MHz} = 1.703 \times 10^{-25}\,\mathrm{J}$$

Lastly:

$$g_I \mu_\mathrm{N} = \frac{4\pi \cdot {}^{11}\!/_{2} \cdot 3 \cdot (6a_0)^3 \Delta E}{\mu_0 \mu_\mathrm{B} 8 \cdot 57} = 2.127 \times 10^{-25}\,\mathrm{J\,T^{-1}}$$

but the Interval Rule assumes that $IJ$ coupling is good.

**2. (DRAFT)**

(a) Note that the e$^-$ are indistinguishable, therefore it follows an exchange symmetry and thus $\hat{p}^2\phi = \phi$ where $\hat{p}$ is the parity operator.

The definition of $\hat{p}$ implies that $\hat{p}\phi = \pm\phi$ and thus $\phi$ may be either symmetric or antisymmetric.

Since e$^-$ are fermions, they are antisymmetric under $\hat{p}$, however we may write $\phi = \phi_{\text{space}}\phi_{\text{spin}}$ so we have 2 cases:

1. Symmetric $\phi_{\text{space}}$, antisymmetric $\phi_{\text{spin}}$; and
2. Antisymmetric $\phi_{\text{space}}$, symmetric $\phi_{\text{spin}}$.

Therefore a normalised spatial wavefunction should look like this:

$$\phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[u_A(\mathbf{r}_1 u_B(\mathbf{r}_2)) + u_B(\mathbf{r}_1)u_A(\mathbf{r}_2)\right]$$

For aligned spin ($S = 1$), we have antisymmetric spatial *phi*:

$$\begin{aligned}\langle\phi|\left(\mathbf{r}_1 - \mathbf{r}_2\right)^2|\phi\rangle &= \frac{1}{2}\int \left[u_A^*(\mathbf{r}_1)u_B^*(\mathbf{r}_2) - u_B^*(\mathbf{r}_1)u_A^*(\mathbf{r}_2)\right] \\ &\qquad\qquad (\mathbf{r}_1 - \mathbf{r}_2)^2 \\ &\qquad\qquad \left[u_A(\mathbf{r}_1)u_B(\mathbf{r}_2) - u_B(\mathbf{r}_1)u_A(\mathbf{r}_2)\right]\ \mathrm{d}^3\mathbf{r}_1\ \mathrm{d}^3\mathbf{r}_2 \\ &= \frac{1}{2}\left(2I - 2K\right) \\ &= I - K\end{aligned}$$

where

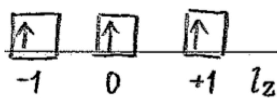
$$\begin{aligned}I &= \int |u_A(\mathbf{r}_1)|^2\,|u_B(\mathbf{r}_2)|^2\,(\mathbf{r}_1 - \mathbf{r}_2)^2\,\mathrm{d}^3\mathbf{r}_1\ \mathrm{d}^3\mathbf{r}_2 \\ J &= \int u_A^*(\mathbf{r}_1)u_A(\mathbf{r}_2)u_B^*(\mathbf{r}_2)u_B(\mathbf{r}_1)\,(\mathbf{r}_1 - \mathbf{r}_2)\,\mathrm{d}^3\mathbf{r}_1\ \mathrm{d}^3\mathbf{r}_2\end{aligned}$$

(b) Since aligned spins have larger separation, it has lower energy than antialigned spins. This means that a configuration is split into different terms with differing $S$.

Since electrical dipole transition forbids change in $S$, this effectively means that there exists groups of lines close together with scale greater than spin-orbit splitting.

However, intercombination lines are possible with non-electric-dipole transitions, e.g. magnetic dipole.

For this ground state, we may invoke Hund's rules:




So the e$^-$ arrange to give net nil orbital angular momentum, $L = 0$.

For phosphorous, the Aufbau principle gives config $1s^2 2s^2 2p^6 3s^2 3p^3 \Rightarrow$ ground state term $^4S$.

**4. (DRAFT)**

(a) The natural width of a transition is the homogeneous broadening due to the intrinsic lifetime associated with the transition itself. This may be illustrated by considering the Uncertainty Principle: $\Delta E \Delta t \geq \hbar/2$

Thus:

$$\Delta E \sim \Delta\omega \sim \frac{1}{\Delta t}$$

For a gas phase amplifier, Doppler broadening and pressure broadening are the major contributions to the overall broadening – at higher temperatures the average speed of the atoms increases, increasing both Doppler and pressure broadenings. For larger density the pressure broadening will increase as the mean free path decreases.

Rate equations:

$$\begin{aligned}
\frac{\mathrm{d}N_{\mathrm{e}}}{\mathrm{d}t} &= \Gamma - \frac{N_{\mathrm{e}}}{\tau_{\mathrm{e}}} \\
\frac{\mathrm{d}N_m}{\mathrm{d}t} &= \frac{N_{\mathrm{e}}}{\tau_{\mathrm{e}}} - \frac{N_m}{\tau_m} \\
\frac{\mathrm{d}N_g}{\mathrm{d}t} &= \frac{N_m}{\tau_m} - \Gamma
\end{aligned}$$

At steady state:

$$\begin{aligned}
N_{\mathrm{e}} &= \Gamma\tau_{\mathrm{e}} \\
\frac{N_{\mathrm{e}}}{\tau_{\mathrm{e}}} &= \frac{N_m}{\tau_m} \\
N_m &= \Gamma\tau_m
\end{aligned}$$

So:

$$\begin{aligned}
N_{\mathrm{e}} &= \frac{N_g - N_{\mathrm{e}}}{\hbar\omega_{\mathrm{L}}}\sigma_{ge} I_L \tau_{\mathrm{e}} \\
&= \frac{N - N_m - 2N_{\mathrm{e}}}{\hbar\omega_{\mathrm{L}}}\sigma_{ge} I_L \tau_{\mathrm{e}} \\
&= \frac{N - (\tau_m/\tau_{\mathrm{e}} + 2)N_{\mathrm{e}}}{\hbar\omega_{\mathrm{L}}}\sigma_{ge} I_L \tau_{\mathrm{e}}
\end{aligned}$$

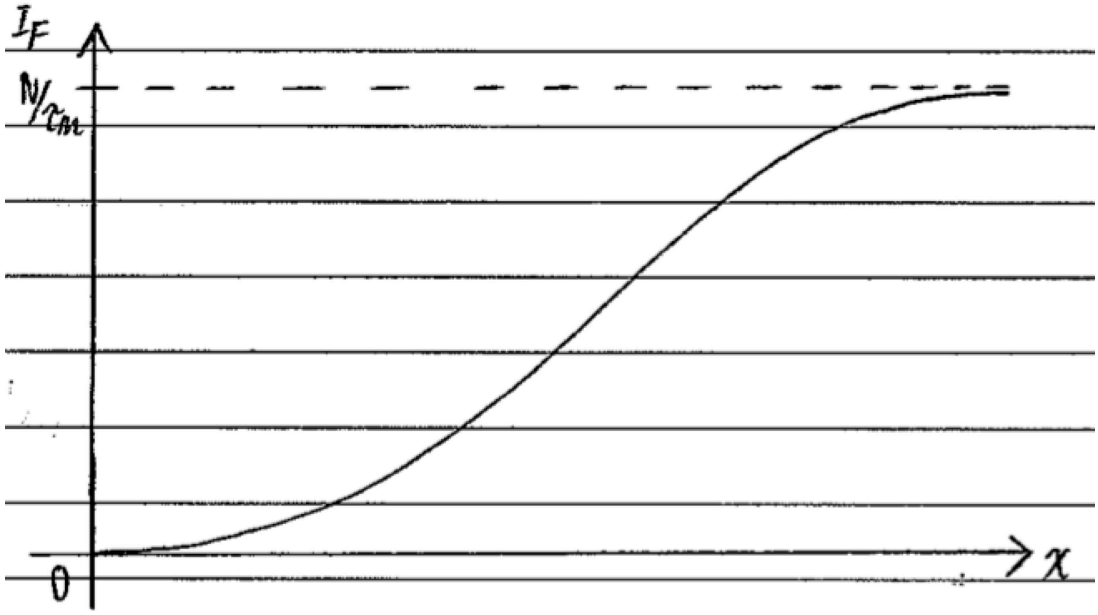
$$
\begin{aligned}
\Rightarrow \left(\hbar\omega_{\mathrm{L}} + \frac{\tau_m}{\tau_{\mathrm{e}}} + 2\right) N_{\mathrm{e}} - N \\
N_{\mathrm{e}} &= N\left[\frac{\hbar\omega_{\mathrm{L}}}{\sigma_{ge} I_L \tau_{\mathrm{e}}} + \frac{\tau_m}{\tau_{\mathrm{e}}} + 2\right]^{-1} \\
&= N \frac{\sigma_{ge} I_L \tau_{\mathrm{e}}}{\hbar\omega_{\mathrm{L}} + \sigma_{ge} I_L \tau_m \tau_{\mathrm{e}} + 2\sigma_{ge} I_L \tau_m} \\
&= N \frac{\tau_{\mathrm{e}}}{\tau_m} \frac{\sigma_{ge} I_L}{\frac{\hbar\omega_{\mathrm{L}}}{\tau_m} + \sigma_{ge} I_L(\tau_{\mathrm{e}} + 2)} \\
&= N \frac{\tau_{\mathrm{e}}}{\tau_m} \frac{\dfrac{\sigma_{ge} I_L \tau_m}{\hbar\omega_{\mathrm{L}}}}{1 + \dfrac{\sigma_{ge} I_L \tau_m}{\hbar\omega_{\mathrm{L}}}(\tau_{\mathrm{e}} + 2)}
\end{aligned}
$$

Hence $x = \dfrac{\sigma_{ge} I_L \tau_m}{\hbar\omega_{\mathrm{L}}}$, $\dfrac{\tau_R}{\tau_m} = \tau_{\mathrm{e}} + 2 \Rightarrow \tau_R = \tau_m(\tau_{\mathrm{e}} + 2)$. And:

$$
I_F \propto \frac{N_{\mathrm{e}}}{\tau_{\mathrm{e}}} = \frac{N}{\tau_m} \cdot \frac{x}{1 + x\left(\dfrac{\tau_R}{\tau_m}\right)}
$$

For $\tau_m \gg \tau_{\mathrm{e}}$, $\tau_R \simeq \tau_m$:

$$
\frac{N_{\mathrm{e}}}{\tau_{\mathrm{e}}} = \frac{N}{\tau_m} \cdot \frac{x}{1 + x}
$$




When $x$ is not small, $I_p$ so the broadening is of width $1/\tau_m$ instead. In intermediate regime, the broadening is of width $\frac{x}{\tau_m\left(1_x\left(\frac{\tau_R}{\tau_m}\right)\right)}$.