UNOFFICIAL SOLUTIONS BY TheLongCat

B3: QUANTUM, ATOMIC AND MOLECULAR PHYSICS

TRINITY TERM 2015

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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)

(a) In a multi-e$^-$ atom, the Hamiltonian of the system is:

$$\hat{H} = \sum_i \left[\frac{\hat{\mathbf{p}}_i^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 \hat{r}_i} + \sum_{J>i} \frac{e^2}{4\pi\epsilon_0 \hat{r}_{ij}} \right]$$

where the first two terms are kineic energy and potential energy under tha Coulomb potential due to the nuclues. The last term is the mutual repulsion between e$^-$.

Introduce a central field $S(r_i)$ such that $\hat{H} = \hat{H}_{\mathrm{CF}} + \Delta\hat{H}_{\mathrm{RE}}$, where:

$$\hat{H}_{\mathrm{CF}} = \sum_i \left[\frac{\hat{\mathbf{p}}_i^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 \hat{r}_i} + S(r_i) \right] \quad \text{is the central field Hamiltonian}$$

$$\Delta\hat{H}_{\mathrm{RE}} = \sum_i \left[\sum_{J>i} \frac{e^2}{4\pi\epsilon_0 \hat{r}_{ij}} - S(r_i) \right] \quad \text{is the residual electrostatic Hamiltonian}$$

With a proper choice of $S(r)$, $\Delta\hat{H}_{\mathrm{RE}} \ll \hat{H}_{\mathrm{CF}}$ and thus the atom may be diagonalised into $|\Psi_{\mathrm{atom}}\rangle = |\psi_1\rangle + |\psi_2\rangle + \ldots + |\psi_n\rangle$ where $|\psi_i\rangle$ is the wavefunction of the ith e$^-$.

This then leads to the concept of configuration where the eigenstates are perturbed by $\Delta\hat{H}_{\mathrm{RE}}$, i.e. $\hat{H}\,|\Psi_{\mathrm{atom}}\rangle = (E_1 + E_2 + \ldots + E_n)\,|\Psi_{\mathrm{atom}}\rangle$.

$\Delta\hat{H}_{\mathrm{RE}}$ being an internal interaction, conserves the total angular momentum $\mathbf{L}$ with modifying the individual angular momentum $\mathbf{l}_i$. This gives rise to a term where a configuration may possess different values of L and S, causing splitting.

Furthermore, the spin-orbit interaction $\Delta\hat{H}_{\mathrm{SO}}$ means that within a term, further splitting may occur due to different possible values of $\mathbf{J} = \mathbf{L} + \mathbf{S}$. This arises from the fact that:

$$\begin{aligned}
\Delta\hat{H}_{\mathrm{SO}} &= \beta_1 \langle \mathbf{l}_1 \cdot \mathbf{s}_1 \rangle + \beta_2 \langle \mathbf{l}_2 \cdot \mathbf{s}_2 \rangle + \ldots \\
\xRightarrow{\text{Wigner-Eckart}} \Delta\hat{H}_{\mathrm{SO}} &= \beta_1 \frac{\langle \mathbf{l}_1 \cdot \mathbf{L} \rangle}{L^2} \mathbf{L} \cdot \mathbf{S} \frac{\langle \mathbf{s}_1 \cdot \mathbf{S} \rangle}{S^2} + \ldots \\
&= \beta_{\mathrm{SO}} \mathbf{L} \cdot \mathbf{S} \\
\Rightarrow \Delta E_{\mathrm{SO}} &= \frac{\beta_{\mathrm{SO}}}{2} \left[J(J+1) - L(L+1) - S(S+1) \right]
\end{aligned}$$

The labelling of eigenstates with $|LM_LSM_S\rangle$ or $|LSJM_J\rangle$ is called the LS coupling scheme. It warrants the assumption that $\hat{H}_{\mathrm{CF}} \gg \Delta\hat{H}_{\mathrm{RE}} \gg \Delta\hat{H}_{\mathrm{SO}}$ so that the perturbation is done successively via term and then level.

From before,

$$\begin{aligned}
\Delta E_{\mathrm{SO}}(J) &= \frac{\beta_{\mathrm{SO}}}{2} \left[J(J+1) - L(L+1) - S(S+1) \right] \\
\Delta E_{\mathrm{SO}}(J-1) &= \frac{\beta_{\mathrm{SO}}}{2} \left[(J-1)J - L(L+1) - S(S+1) \right] \\
\Delta E_{\mathrm{SO}}(J-2) &= \frac{\beta_{\mathrm{SO}}}{2} \left[(J-2)(J-1) - L(L+1) - S(S+1) \right]
\end{aligned}$$

$$\begin{aligned}\frac{\Delta E_{\text{SO}}(J)-\Delta E_{\text{SO}}(J-1)}{\Delta E_{\text{SO}}(J-1)-\Delta E_{\text{SO}}(J-2)} &= \frac{J(J+1)-(J-1)J}{(J-1)J-(J-2)(J-1)} \\ &= \frac{\cancel{J^2}+J-\cancel{J^2}+J}{J^2-J-J^2+3J-2} \\ &= \frac{J}{J-1}\end{aligned}$$

This is the interval rule and is an indicator of how good LS coupling is in describing the energy levels.

(b) Config $5s5l$:

$$\begin{matrix} L=l \\ S=0,1 \end{matrix} \longrightarrow \text{Term} \begin{matrix} {}^1L \\ {}^3L \end{matrix} \longrightarrow \text{Level} \begin{matrix} {}^1L_l \\ {}^3L_{l+1} \\ {}^3L_l \\ {}^3L_{l-1} \end{matrix}$$

In the triplet,

$$\begin{aligned}\Delta E(l+1)-\Delta E(l) &= 35\,045\,\text{cm}^{-1}-35\,022\,\text{cm}^{-1} \\ &= 23\,\text{cm}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta E(l)-\Delta E(l-1) &= 35\,022\,\text{cm}^{-1}-35\,007\,\text{cm}^{-1} \\ &= 15\,\text{cm}^{-1}\end{aligned}$$

Interval rule:

$$\begin{gathered}\frac{l+1}{l} = \frac{23}{15} \simeq \frac{3}{2} \\ \Rightarrow l = 2\end{gathered}$$

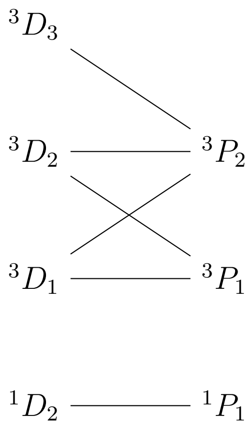
So the four levels are ${}^1D_2$, ${}^3D_3$, ${}^3D_2$, ${}^3D_1$.

(c) Electric dipole selection rules:

$$\begin{matrix} 1\ \text{e}^-\ \text{jumpps} & \Delta L = 0, \pm 1\ (0 \nrightarrow 0) \\ \Delta n = \text{any} & \Delta S = 0 \\ \Delta l = \pm 1 & \Delta J = 0, \pm 1\ (0 \nrightarrow 0) \\ & \Delta M_J = 0, \pm 1\ (0 \nrightarrow 0 \iff \Delta J = 0) \end{matrix}$$

Try $5s5d \to 5s5p$:

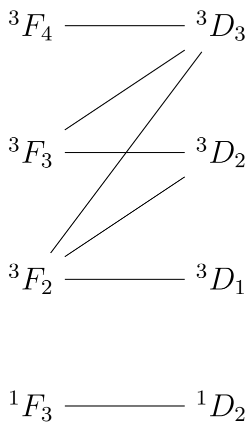
Allowed transitions:



so a total of 6 lines!

What about $5s5d \to 5s5f$?

Levels: $^3F_4$, $^3F_3$, $^3F_2$, $^1F_3$



so 7 lines but not observed, hence $5s5p$ is the correct config.

2. (DRAFT)

(a) $A_J\mathbf{I}\cdot\mathbf{J}$: spin-spin interaction between the nucleus and the e$^-$, this is the alignment of nuclear spin under the magnetic field due to the e$^-$ motion and intrinsic magnetic moment.

$g_J\mu_\mathrm{B}\mathbf{J}\cdot\mathbf{B}_\mathrm{ext}$: external magnetic field Hamiltonian. This is the alignment of total electronic angular momentum with the external field due to the e$^-$ motion and intrinsic magnetic moment.

$g_J\mu_\mathrm{N}\mathbf{I}\cdot\mathbf{B}_\mathrm{ext}$: external magnetic field Hamiltonian, similar to the electronic one above but this is the interaction between nuclear spin and external field.

Weak magnetic field means that $g_J\mu_\mathrm{B}\mathbf{J}\cdot\mathbf{B}_\mathrm{ext} + g_J\mu_\mathrm{N}\mathbf{I}\cdot\mathbf{B}_\mathrm{ext} \gg A_J\mathbf{I}\cdot\mathbf{J}$, i.e. the external interaction is much weaker than the hyperfine interaction.

Strong field means the opposite, where the external interaction is much stronger than the hyperfine interaction.

In weak field, the external Hamiltonian acts as a perturbation on top of the hyperfine interaction, which conserves total angular momentum F, making it a good quantum number.

Wigner-Eckart theorem then states $\mathbf{J}\to\mathbf{J}\cdot\mathbf{F}/F^2\mathbf{F}$ and $\mathbf{I}\to\mathbf{I}\cdot\mathbf{J}/F^2\mathbf{F}$ so:

$$\hat{H}_F = A_J\mathbf{I}\cdot\mathbf{J} + g_J\mu_\mathrm{B}\frac{\mathbf{J}\cdot\mathbf{F}}{F^2}\mathbf{F}\cdot\mathbf{B} - g_I\mu_\mathrm{N}\frac{\mathbf{I}\cdot\mathbf{F}}{F^2}\mathbf{F}\cdot\mathbf{B}$$

$$\Rightarrow E_F = \frac{A_J}{2}[\dots] + g_J\mu_\mathrm{B}\frac{J(J+1)+\frac{1}{2}[F(F+1)-J(J+1)-I(I+1)]}{F(F+1)}M_FB + \underbrace{\dots}_{\substack{\text{negligible}\\ \text{as } \mu_\mathrm{N}\ll\mu_\mathrm{B}}}$$

So hyperfine level is split by:

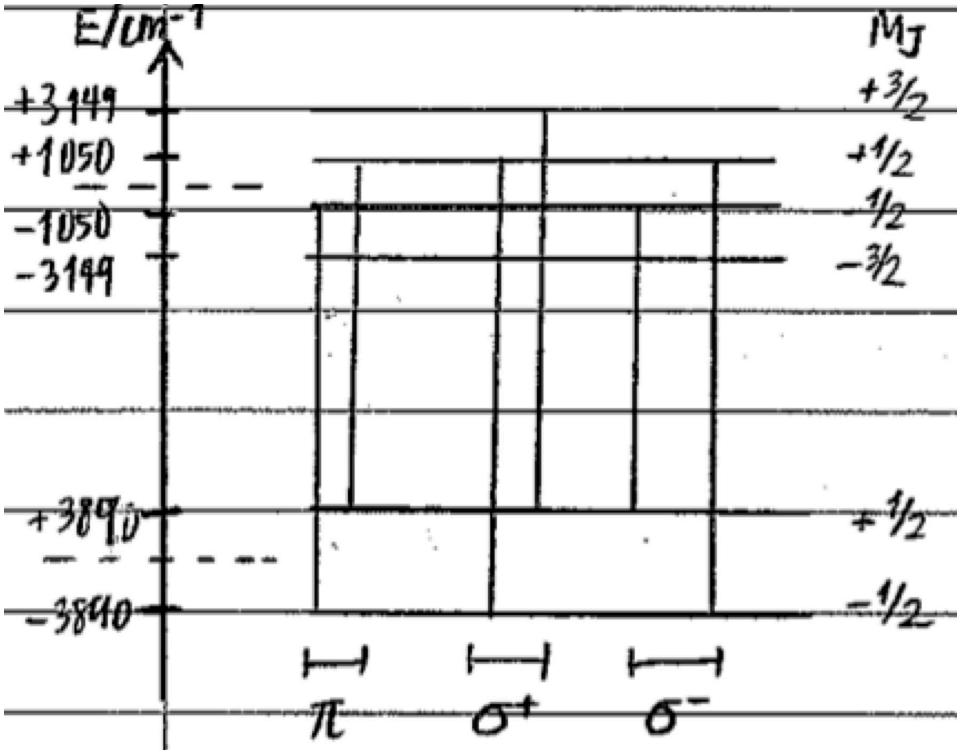
$$\Delta E_F = \underbrace{g_J\left[\frac{1}{2}+\frac{1}{2}\frac{J(J+1)-I(I+1)}{F(F+1)}\right]}_{g_F}\mu_\mathrm{B}BM_F$$

(b) For ^{39}K at ground state with config $4s$, available term: $L=0$, $S=1/2\to{}^2S\Rightarrow$ level $^2S_{1/2}$.

$$\begin{aligned}
&\mu_\mathrm{B}\mathbf{L}\cdot\mathbf{B} + g_s\mu_\mathrm{B}\mathbf{S}\cdot\mathbf{B}\\
&\to\mu_\mathrm{B}\left[\frac{\mathbf{L}\cdot\mathbf{J}}{J^2}\mathbf{J}\cdot\mathbf{B} + g_s\frac{\mathbf{S}\cdot\mathbf{J}}{J^2}\mathbf{J}\cdot\mathbf{B}\right]\\
&\to\mu_\mathrm{B}\frac{\cancel{L(L+1)}+\frac{1}{2}[J(J+1)-L(L+1)-S(S+1)]+2S(S+1)+\frac{1}{2}\times2[J(J+1)-\cancel{L(L+1)}-S(S+1)]}{J(J+1)}\mathbf{B}\cdot\mathbf{J}\\
&\Rightarrow g_J = \frac{3}{2}-\frac{L(L+1)-S(S+1)}{2J(J+1)}\\
&\quad = \frac{3}{2}-\frac{-\frac{1}{2}(\frac{3}{2})}{2(\frac{1}{2})(\frac{3}{2})} = 2
\end{aligned}$$

Total possible values of $F = |I - J|, ..., (I + J) = 1, 2$.

$$g_F(F = 1) = g_J \cdot \frac{1}{2}\left[1 + \frac{\frac{1}{2}(\frac{3}{2}) - \frac{3}{2}(\frac{5}{2})}{1(2)}\right] = -\frac{1}{2}$$
$$g_F(F = 2) = g_J \cdot \frac{1}{2}\left[1 + \frac{\frac{1}{2}(\frac{3}{2}) - \frac{3}{2}(\frac{5}{2})}{2(3)}\right] = \frac{1}{2}$$



(c) Electric dipole selection rules:

- $\Delta n =$ any
- $\Delta l = \pm 1 \leftarrow$ violated!

Try magnetic dipole:

- $\Delta n = \Delta l = 0$
- $\Delta F = 0, \pm 1$ $(0 \nrightarrow 0)$
- $\Delta M_F = 0, \pm 1$ $(0 \nrightarrow 0 \iff \Delta F = 0)$

Since $|g_F|$ is identical across the two levels, some transitions share the same frequency. So in total there are $\underbrace{N(0 \text{ gaps})}_{1} + \underbrace{N(1 \text{ gap})}_{3} + \underbrace{N(2 \text{ gaps})}_{3} = 7$ lines.

When observed along the magnetic field, only the σ radiation may be observed (σ^+ and σ^-), but there will still be 7 lines as explained above.

4. (DRAFT)

(a) **(TO EXPAND)** In X-ray transitions, holes are introduced in inner shell e^- and the resulting radiation from the hole transition is X-ray.

Transition energy:

$$E_{nm} = hcR_\infty \left[\frac{(Z-\sigma_n)^2}{n^2} - \frac{(Z-\sigma_m)^2}{m^2} \right]$$

The form of the energy resembles the hydrogenic energy level as the inner shell e^- are symmetric, causing the system to be largely central.

The parameters σ_n and σ_m are the shielding term that quantifies the effect of shielding by other inner shell e^-. For K shell, $\sigma \simeq 2$.

The K_α radiation is the transition from K shell to L shell ($n = 1 \to 2$).

K absorption edge?