UNOFFICIAL SOLUTIONS BY TheLongCat

B2: III. QUANTUM, ATOMIC AND MOLECULAR PHYSICS

TRINITY TERM 2012

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

1. **(DRAFT)**

(a) For a many-e^- system, its Hamiltonian may be written as:

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

where the last term is the inter-e^- repulsion.

We may choose a central potential:

$$\hat{H}_{\mathrm{CF}} = \sum_i \left[-\frac{Ze^2}{4\pi\epsilon_0\hat{r}_i} + S(\mathbf{r}_i) \right]$$

such that $\hat{H} = \hat{H}_{\mathrm{CF}} + \Delta\hat{H}\mathrm{RE}$ with

$$\Delta\hat{H}_{\mathrm{RE}} = \sum_i \left[\sum_{j>i} \frac{e^2}{4\pi\epsilon_0\hat{r}_{ij}} - S(\mathbf{r}_i) \right]$$

being the residual electrostatic interaction (i.e. non-central part of the overall potential).

For a good choice of $S(\mathbf{r}_i)$, $\Delta\hat{H}_{\mathrm{RE}} \ll \hat{H}_{\mathrm{CF}}$ and thus the system may be treated as a perturbed central force system. As $\Delta\hat{H}_{\mathrm{RE}}$ is an internal interaction, the overall orbital angular momentum should be conserved, making it a good quantum number. Similarly, S is also good since $\Delta\hat{H}_{\mathrm{RE}}$ does not depend on spins.

The labelling of eigenstates $|nlm_lsm_s\rangle \to |nLM_LSM_S\rangle$ is the LS coupling scheme.

(b) E-dipole selection rules:

1. Configuration
   $\Delta n = \text{any} \qquad \Delta l = \pm 1$

2. Term
   $\Delta L = \pm 1, 0(0 \nrightarrow 0) \qquad \Delta S = 0$

3. Level
   $\Delta J = 0, \pm 1(0 \nrightarrow 0) \qquad \Delta M_J = 0, \pm 1(0 \nrightarrow 0 \iff \Delta J = 0)$

Spin-orbit interaction:

$$\Delta\hat{H}_{\mathrm{SO}} = \beta\hat{\mathbf{l}}\cdot\hat{\mathbf{s}} \to \beta\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$$

$$\Rightarrow \langle\Delta E_{\mathrm{SO}}\rangle \to \beta\cdot\frac{1}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

where β is a constant of proportionality that depents on the orbital (radial ψ).

Energy difference between splittings:

$$\Delta E_{J,J-1} = \frac{1}{2}\beta\left[J(J+1)\cancel{-L(L+1)-S(S+1)} - (J-1)J\cancel{+L(L+1)+S(S+1)}\right]$$

$$= \frac{1}{2}\beta\left[2J\right]$$

$$\Delta E_{J-1,J-2} = \frac{1}{2}\beta \left[(J-1)J \cancel{-L(L+1)} \cancel{-S(S+1)} - (J-2)(J-1) \cancel{+L(L+1)} \cancel{+S(S+1)}\right]$$
$$= \frac{1}{2}\beta \left[\cancel{J^2} - J \cancel{-J^2} + 3J - 2\right]$$
$$= \frac{1}{2}\beta \left[2J - 2\right]$$

Hence the Interval Rule is true:

$$\frac{\Delta E_{J,J-1}}{\Delta E_{J-1,J-2}} = \frac{J}{J-1}$$

(c) Carbon ground state: $1s^2 2s^2 2p^2$

$$\begin{array}{c} L = 2 \\ S = 1 \text{ or } 0 \end{array} \xrightarrow{\text{terms}} \begin{array}{c} {}^3D \\ {}^1D \end{array} \xrightarrow{\text{levels}} \begin{array}{c} {}^3D_1, {}^3D_2, {}^3D_3 \\ {}^1D_2 \end{array}$$
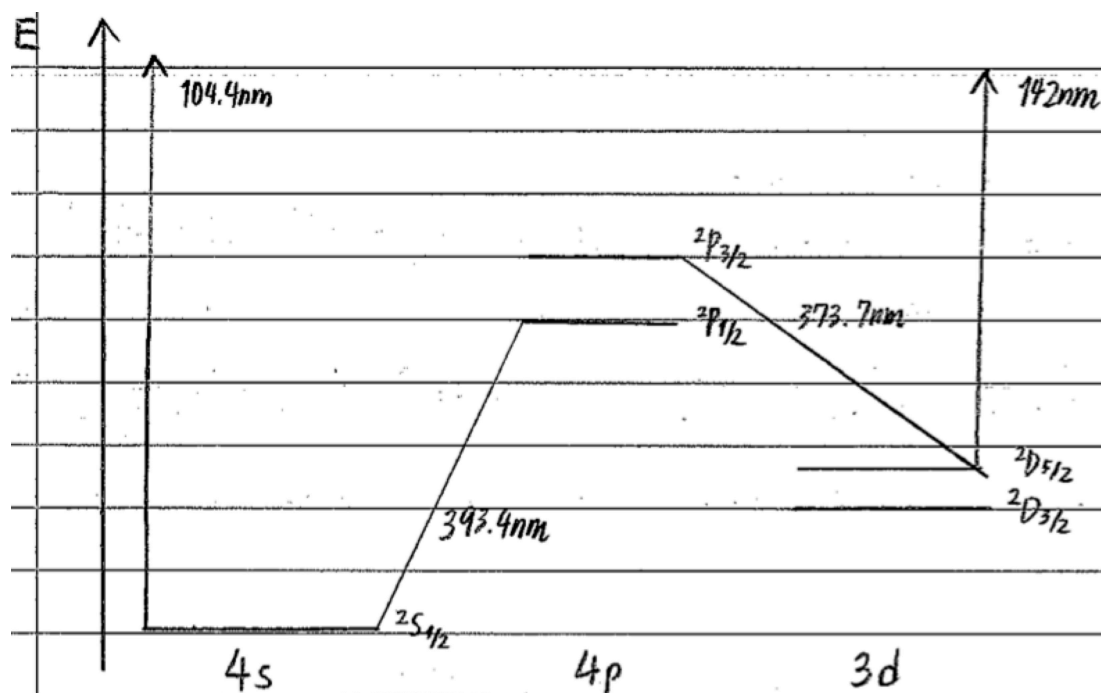
Excited state: $1s^2 2s^2 2p3s$

$$\begin{array}{c} L = 1 \\ S = 1 \text{ or } 0 \end{array} \rightarrow \begin{array}{c} {}^3P \\ {}^1P \end{array} \rightarrow \begin{array}{c} {}^3P_0, {}^3P_1, {}^3P_2 \\ {}^1P_1 \end{array}$$

Allowed transitions:

- ${}^3P_0 \rightarrow {}^3D_1 \qquad (\delta_{12} + \delta_{23} + \Delta)$
- ${}^3P_1 \rightarrow {}^3D_1 \qquad (\delta_{12} + \delta_{23} + \Delta + E_{01})$
- ${}^3P_1 \rightarrow {}^3D_2 \qquad (\delta_{23} + \Delta + \epsilon_{01})$
- ${}^3P_2 \rightarrow {}^3D_1 \qquad (\delta_{12} + \delta_{23} + \Delta + \epsilon_{01} + \epsilon_{12})$
- ${}^3P_2 \rightarrow {}^3D_2 \qquad (\delta_{23} + \Delta + \epsilon_{01} + \epsilon_{12})$
- ${}^3P_2 \rightarrow {}^3D_3 \qquad (\Delta + \epsilon_{01} + \epsilon_{12})$
- ${}^1P_1 \rightarrow {}^1D_2$

Sketch of the energy levels and transitions:

The only consistent arrangement is shown above in the diagram. Thus:

$$\delta_{23} = 2.914\,\text{cm}^{-1}$$
$$\delta_{12} = 24.049\,\text{cm}^{-1}$$
$$\Rightarrow \frac{\delta_{23}}{\delta_{12}} = 0.121$$

which does not follow the Interval Rule, so LS coupling is not very good here.

2. **(DRAFT)**

   (a) As X-ray transition involves core e^-, which have symmetric wavefunctions, the energy transition follows the Rydberg model where $E = -hcR_\infty Z^2/n^2$ it, however due to shielding, a parameter σ is added to represent its effect on reducing the effective potential.

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

   with σ being different for each n.

   (b) Conservation of energy gives $E_{\text{x-ray}} = E_{e^-} + T_{e^-}$ where E_{e^-} is the energy cost of ejecting the e^-, T_{e^-} is the kinetic energy of the e^-.

   $$\begin{aligned} E_{e^-} &= E_{\text{x-ray}} - T_{e^-} \\ &= 870\,\text{eV}, 48.5\,\text{eV}, 21.6\,\text{eV} \end{aligned}$$

   Further emission is due to the Auger effect, which causes electrons to be knocked off from the valence shell instead of photons.
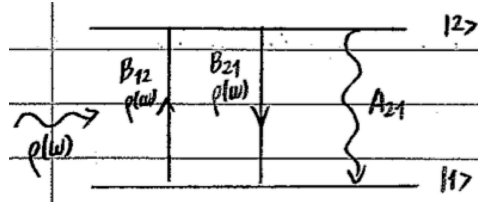
   Double ionisation is due to the Auger effect kicking more e^-.

   For L shell e^-,
   $$E = -hcR_\infty \frac{10^2}{2^2} = -340.15\,\text{eV}$$

   So the minimum energy required for X-ray generation is $340.15\,\text{eV}$.

3. (DRAFT)

(a) The Einstein coefficient are defined such that the following rate equations are satisfied:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = B_{12}\rho(\omega)N_1 - B_{21}\rho(\omega)N_2 - A_{21}N_2$$

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -\frac{\mathrm{d}N_2}{\mathrm{d}t}$$

where $\rho(\omega)$ is spectral energy density of the incoming radiation.

At thermal equilibrium, the population should satisfy Boltzmann distribution:

$$N_2 \propto g_2 e^{-\beta E_2} \qquad N_1 \propto g_1 e^{-\beta E_1}$$

where g_i is the degeneracy of state $|i\rangle$, E_i is its energy.

Hence:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1}e^{-\beta\hbar\omega_0}$$

where $\hbar\omega_0 = E_2 - E_1$.

Also at steady state,

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = 0$$

$$\Rightarrow B_{12}\rho(\omega)N_1 = B_{21}\rho(\omega)N_2 + A_{21}N_2$$

$$\Rightarrow \frac{N_2}{N_1} = \frac{B_{12}\rho(\omega)}{B_{21}\rho(\omega) + A_{21}}$$

Combining both expressions:

$$\frac{B_{12}\rho(\omega)}{B_{21}\rho(\omega) + A_{21}} = \frac{g_2}{g_1}e^{-\beta\hbar\omega_0}$$

$$\frac{g_1 B_{12}\rho(\omega)}{g_2 B_{21}\rho(\omega) + A_{21}g_2} = e^{-\beta\hbar\omega_0}$$

$$\frac{g_1 B_{12}\rho(\omega)}{g_2 B_{21}\rho(\omega) + g_2 A_{21}\cdot\frac{\pi^2 c^3}{\hbar\omega^3}(e^{\beta\hbar\omega_0} - 1)} = e^{-\beta\hbar\omega_0}$$

$$g_1 B_{12} = g_2 B_{21}e^{-\beta\hbar\omega_0} + g_2 A_{21}\cdot\frac{\pi^2 c^3}{\hbar\omega^3}\left(1 - e^{-\beta\hbar\omega_0}\right)$$

Since the relation must hold regardless of the temperature,

$$g_2 B_{21} = g_2 A_{21}\cdot\frac{\pi^2 c^3}{\hbar\omega^3}$$

$$\Rightarrow A_{21} = \frac{\hbar\omega^3 B_{21}}{\pi^2 c^3}$$

In addition:

$$g_1 B_{12} = g_2 A_{21} \cdot \frac{\pi^2 c^3}{\hbar \omega^3} = g_2 B_{21}$$

Since A_{21}, B_{12}, B_{21} all relate to the same levels, the lineshape is identical as Lorentzian.

(b) Homogeneous broadening refers to the spectral line broadening that is uniform throughout a sample, one example would be natural broadening which is a consequence of the uncertainty principle.

Inhomegeneous broadening refers to broadening that is sensitive towards a specific region/direction, i.e. there exists an asymmetry in the broadening. One example of this is Doppler broadening which is due to the particles' motion in the sample.

(c) Sketch of the setup:

$$B(x) = B_0 \frac{\cosh(x/\lambda)}{\cosh(t/\lambda)}$$

$B_0 \hat{\underline{z}}$

-t   0   t $\rightarrow x$
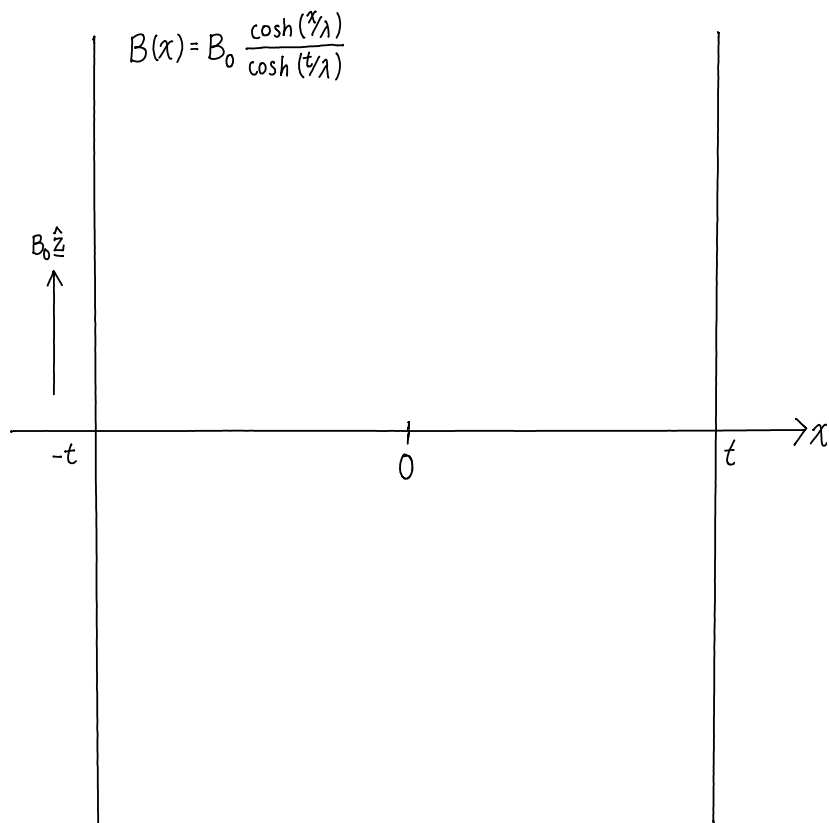
Find $N_\gamma / t \cdot \Omega \cdot A \cdot \nu$.

Known parameters:

$$t = 10^{-13}\,\text{s}$$

$$\Omega \simeq \pi\theta^2 = \pi\left(10^{-6}\,\text{rad}\right)^2 \quad \text{since } \theta \ll 1$$
$$= 3.142 \times 10^{-12}\,\text{sr}$$

$$A = \pi\left(\frac{d}{2}\right)^2$$
$$= \pi \cdot \frac{(300\,\mu\text{m})^2}{4} = 7.069 \times 10^{-8}\,\text{m}^2$$

$$\nu = \Delta\omega = \left(5 \times 10^{-3}\right)\left(\frac{8\,\text{keV}}{\hbar}\right) = 6.077 \times 10^{16}\,\text{s}^{-1}$$

So spectral brightness B:

$$B = \frac{10^{12}}{\left(10^{-13}\,\text{s}\right)\left(3.142 \times 10^{-12}\,\text{sr}\right)\left(7.069 \times 10^{-8}\,\text{m}^2\right)\left(6.077 \times 10^{16}\,\text{s}^{-1}\right)}$$
$$= 7.410 \times 10^{26}\,\text{sr}^{-1}\,\text{m}^{-2}$$

For blackbody,

$$\rho(\omega) = \frac{n\hbar\omega}{\nu}$$
$$= \frac{N_1\hbar\omega}{\nu A c t}$$
$$= \frac{\hbar\omega}{c} \cdot B\Omega$$
$$\Rightarrow B = \frac{\rho(\omega)c}{\hbar\omega\Omega}$$

Assuming isotropy, $\Omega = 4\pi\,\text{sr}$:

$$\Rightarrow \rho(\omega) = \frac{\hbar\omega B\Omega}{c} = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\beta\hbar\omega} - 1}$$
$$\Rightarrow e^{\beta\hbar\omega} = 1 + \frac{\omega^2 B\Omega}{\pi^2 c^2}$$
$$\frac{\hbar\omega}{k_\text{B}T} = \ln\left[1 + \frac{\omega^2 B\Omega}{\pi^2 c^2}\right]$$
$$T = \frac{\hbar\omega}{k_\text{B}\ln\left[1 + \frac{\omega^2 B\Omega}{\pi^2 c^2}\right]} = 8.367 \times 10^5\,\text{K}$$

4. (DRAFT)

(a) Hamiltonian of external magnetic interaction:

$$\hat{H}_z = -\boldsymbol{\mu} \cdot \mathbf{B}$$
$$= \left[g_s \mu_B \hat{\mathbf{s}} - \mu_B \hat{\mathbf{l}} \right] \cdot \mathbf{B}$$

In vector model, the component of $\mathbf{L}$, $\mathbf{S}$ perpendicular to $\mathbf{J}$ vanishes upon averaging so:

$$\langle E_z \rangle = \left[g_s \mu_B \langle \hat{\mathbf{s}} \rangle - \mu_B \langle \hat{\mathbf{l}} \rangle \right] \cdot \mathbf{B}$$
$$= \left[g_s \mu_B \left[\frac{\hat{\mathbf{S}} \cdot \hat{\mathbf{J}}}{\hat{\mathbf{J}}^2} \hat{\mathbf{J}} \right] - \mu_B \left[\frac{\hat{\mathbf{L}} \cdot \hat{\mathbf{J}}}{\hat{\mathbf{J}}^2} \hat{\mathbf{J}} \right] \right] \cdot \mathbf{B}$$
$$= g_J \mu_B \hat{\mathbf{J}} \cdot \mathbf{B}$$
$$= g_J \mu_B M_J B$$

where g_J is:

$$g_J = g_s \cdot \frac{\langle \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \rangle + \langle \hat{\mathbf{S}}^2 \rangle}{\langle \hat{\mathbf{J}}^2 \rangle} - \frac{\langle \hat{\mathbf{L}}^2 \rangle + \langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle}{\hat{\mathbf{J}}^2}$$
$$= g_s \frac{\frac{1}{2} \left[J(J+1) - L(L+1) - S(S+1) \right] + S(S+1)}{J(J+1)}$$
$$- \frac{L(L+1) + \frac{1}{2} \left[J(J+1) - L(L+1) - S(S+1) \right]}{J(J+1)}$$
$$= (g_s - 1) \frac{J(J+1) - L(L+1) - S(S+1)}{2J(J+1)} + \frac{g_s S(S+1) - L(L+1)}{J(J+1)}$$

(b) Normal Zeeman effect refers to an even splitting of energy levels under weak B field, which then leads to a degeneracy in transition lines and causing the observable lines be proportional to the splitting itself. This happens when either $S = 0$ or $L = 0$ in both levels.
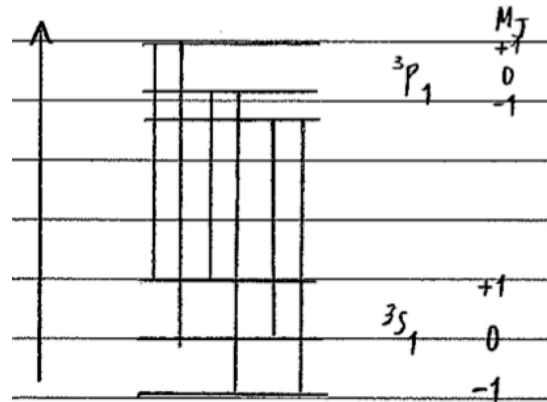
Anomalous Zeeman effect is the general case where g_J is dependent on J, this causes the levels splitting uneven and leads to a greater number of transition lines to be observed.
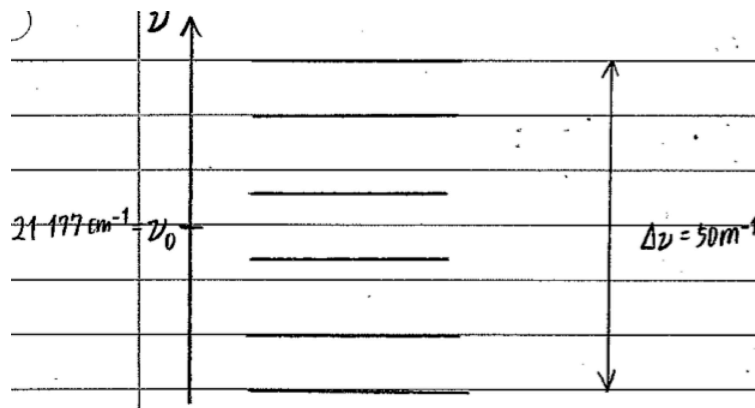
Transition: $^3P \to ?$, $S = 1$, $L = 1$, $J = 0, 1, 2$

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Dipole selection rules: $\Delta S = 0$, $\Delta L = \pm 1$, $\Delta J = 0, \pm 1$ ($0 \nrightarrow 0$), $\Delta M_J = 0, \pm 1$ ($0 \nrightarrow 0 \iff \Delta J = 0$)

Try $^3P \to {}^3S$ ($S = 1$, $L = 0$, $J = 0, 1$), and further consider $^3P_1 \to {}^3S_1$:

So 6 distinct lines!

For $^3P_1$, $J = 1$, $L = 1$, $S = 1$:

$$g_J = (g_s - 1)\frac{-2}{4} + \frac{g_s \cdot 2 - 2}{2}$$
$$= -\frac{1}{2}(g_s - 1) + (g_s + 1)$$
$$= \frac{g_s - 1}{2} \simeq \frac{1}{2} \quad \text{for } g_s \simeq 2$$

For $^3S_1$, $J = 1$, $L = 0$, $S = 1$:

$$g_J = (g_s - 1) \cdot 0 + \frac{g_s \cdot 2 - 0}{2}$$
$$= g_s \simeq 2$$

The difference between the highest and lowest line splits is then:

$$\Delta E_\nu = \mu_B B \left[1 \cdot \frac{1}{2} + 1 \cdot 2 \right]$$
$$hc\Delta\nu = \frac{3}{2}\mu_B B$$
$$\Rightarrow B = \frac{2hc}{3\mu_B}\Delta\nu$$
$$= 0.714\,\text{T}$$

Since Zeeman splitting is extremely fine, a high precision instrument such as a Fabry-Pérot étalon must be used.

Sketch of the apparatus: