UNOFFICIAL SOLUTIONS BY TheLongCat

B3. QUANTUM, ATOMIC AND MOLECULAR PHYSICS

TRINITY TERM 2016

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

1. (DRAFT)

(a) $3d\ {}^2D_{5/2}$

configuration of the e^-

level: ${}^{2S+1}L_J$ where $2S+1$ is the spin degeneracy
L: S, P, D, F, ... is the total orbital angular momentum
J is the total electronic angular momentum

Large transition amplitude corresponds to the electric dipole transition, which has the following selection rules:

$$\text{Config} \begin{cases} \Delta n = \text{any} \\ 1\ e^- \text{ transition} \\ \Delta l = \pm 1 \end{cases} \qquad \text{Term} \begin{cases} \Delta L = 0, \pm 1 (0 \nrightarrow 0) \\ \Delta S = 0 \end{cases}$$

$$\text{Level} \begin{cases} \Delta J = 0, \pm 1 (0 \nrightarrow 0) \\ \Delta M_J = 0, \pm 1 (0 \nrightarrow 0 \text{ iff } \Delta J = 0) \end{cases}$$

Origin of electronic configuration:

Recall that for a multi-e^- atom,

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

and by introducing a central field $S(r)$, we may write $\hat{H} = \hat{H}_{\text{CF}} + \Delta\hat{H}_{\text{RE}}$ where $\hat{H}_{\text{CF}} = \sum_i \left[\frac{\hat{\mathbf{p}}_i^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 \hat{r}_i} + S(r_i) \right]$ and $\Delta\hat{H}_{\text{RE}} = \sum_i \left[-S(r_i) + \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 \hat{r}_{ij}} \right]$. The wavefunction of the atom may then be written as $\psi_{1s} + \psi_{2s} + \ldots$ and these are electronic configuration.

(b) Ca^+ ground config by Aufbau principle: $1s^2 2s^2 2p^6 3s^2 3p^6 4s$

$\Rightarrow L = 0$, $S = 1/2 \Rightarrow$ Term: ${}^2S \Rightarrow$ Level: ${}^2S_{1/2}$

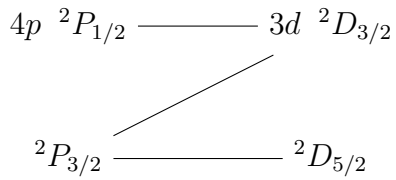
Try excited state $3d$, $L = 2$, $S = 1/2 \Rightarrow$ Term: ${}^2D \Rightarrow$ Levels: ${}^2D_{3/2}$, ${}^2D_{5/2}$

$4p$ has term ${}^2P \Rightarrow$ Levels: ${}^2P_{1/2}$, ${}^2P_{3/2}$

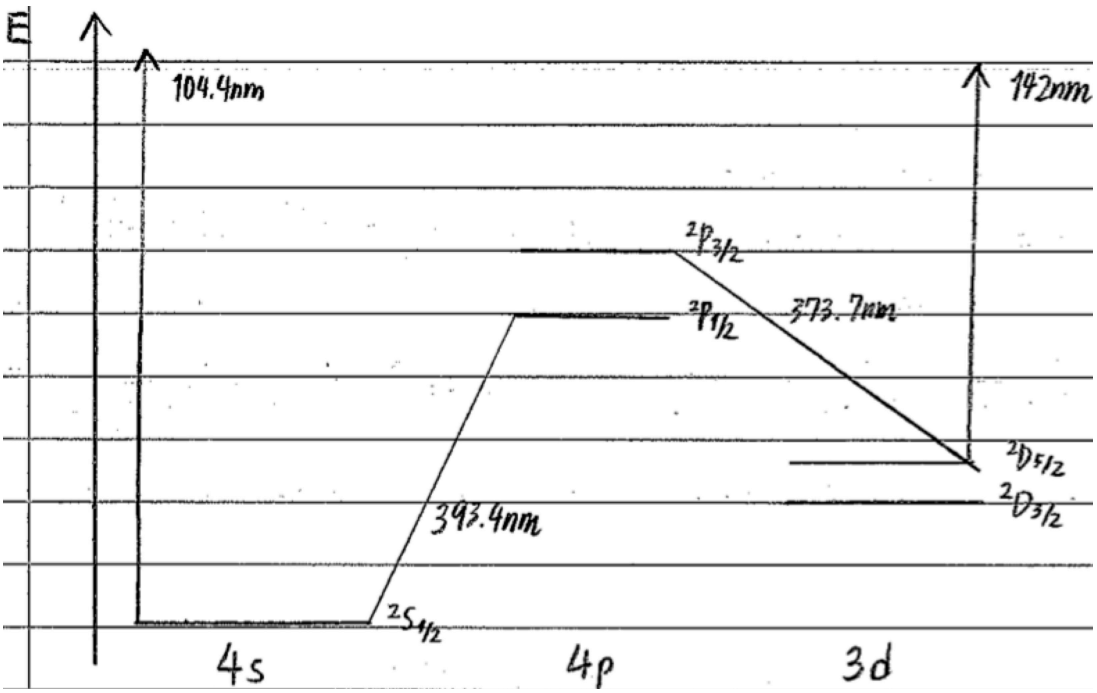
Recall the electric dipole selection rules above, we then have the following transitions:

$4s\ {}^2S_{1/2}$ ——— $4p\ {}^2P_{1/2}$

$4s\ {}^2S_{1/2}$ ——— ${}^2P_{3/2}$

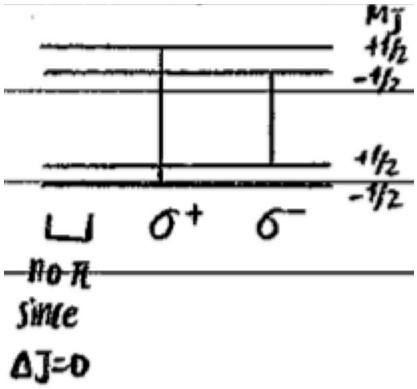


So the doublets are due to the transitions between levels.



The third line is due to the spin-orbit coupling that introduces fine structure splitting.

(c) For 393.4 nm transition, we may observe π and σ radiation perpendicular to the field.



So there should be 2 lines.

2. (DRAFT)

(a) Addition of angular momentum:

$$\begin{aligned}\hat{\mathbf{J}} &= \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 \\ \Rightarrow \hat{J}^2 &= \hat{J}_1^2 + \hat{J}_2^2 + 2\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 \\ \Rightarrow 2\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 &= \frac{1}{2}\left[\hat{J}^2 - \hat{J}_1^2 - \hat{J}_2^2\right]\end{aligned}$$

So:

$$\begin{aligned}\hat{H} &= A\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 \\ \Rightarrow \langle E \rangle &= A\left\langle \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 \right\rangle \\ &= \frac{A}{2}\left[J(J+1) - J_1(J_1+1) - J_2(J_2+1)\right]\end{aligned}$$

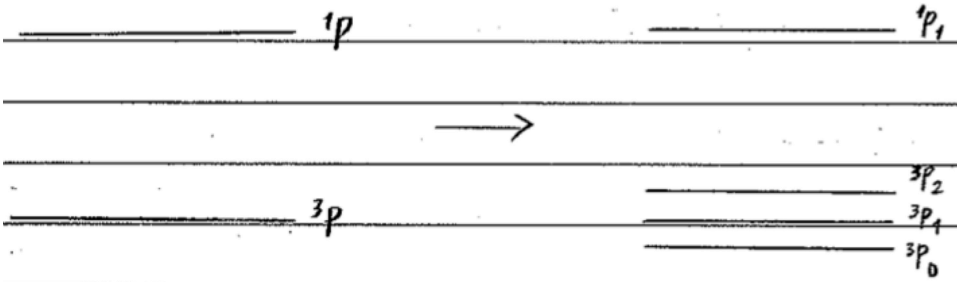
for eigenstates $|JJ_1J_2M_J\rangle$.

Then:

$$\begin{aligned}E(J) - E(J-1) = \frac{A}{2}\big[&J(J+1) - J_1(J_1+1) - J_2(J_2+1) \\ &(J-1)J - J_1(J_1+1) - J_2(J_2+1)\big] \\ = \frac{A}{2}\left[J^2 + J - J^2 + J\right] &= AJ\end{aligned}$$

(b) The interval rule is a property of LS coupling scheme. In this scheme, it is assumed that $\hat{H}_{\text{CF}} \gg \Delta\hat{H}_{\text{RE}} \gg \Delta\hat{H}_{\text{SO}}$ where $\hat{H}_{\text{CF}}$ is a central field Hamiltonian under central field approximation, $\Delta\hat{H}_{\text{RE}}$ is the residual electrostatic interaction, $\Delta\hat{H}_{\text{SO}}$ is the spin-orbit interaction.

For example, for calcium we have excited config $4s4p$ with terms ^1P, ^3P which then have levels $^1P_1$, $^3P_0$, $^3P_1$, $^3P_2$.



(c) Hyperfine Hamiltonian:

$$\hat{H}_{\text{hfs}} = -g_I\mu_{\text{N}}\hat{\mathbf{I}} \cdot \hat{\mathbf{B}}_{\text{e}}$$

$\mathbf{B}_{\text{e}}$ is the magnetic field due to the motion and intrinsic magnetic moment of the e^-. Since the magnetic moment of an $e^- \propto \hat{\mathbf{l}} + g_s\hat{\mathbf{s}}$ where $\hat{\mathbf{l}}$ is orbital angular momentum and $\hat{\mathbf{s}}$ is spin. We expect $\hat{\mathbf{B}}_{\text{e}} \propto \hat{\mathbf{J}}$ by the Wigner-Eckart theorem.

Hence $\hat{H}_{\text{hfs}} = A\hat{\mathbf{I}} \cdot \hat{\mathbf{J}}$, since this is an internal interaction, the total angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$ is conserved, making it a good quantum number and diagonalising $\hat{H}_{\text{hfs}}$ with $|IJFM_F\rangle$, similar to LS coupling.

(d) **(TO EXPAND)** The frequencies of hyperfine transitions are the energy differences between each hyperfine level and the reference level. Similar to LS coupling, we then have the Interval Rule where $\Delta E(F) - \Delta E(F-1) = AF$:

$$\Rightarrow \frac{\Delta E(F) - \Delta E(F-1)}{\Delta E(F-1) - \Delta E(F-2)} = \frac{F}{F-1}$$
$$\Rightarrow \frac{\Delta E(F) - \Delta E(F+1)}{\Delta E(F+1) - \Delta E(F+2)} = \frac{F}{F+1}$$

We may then find F from the data, and with the knowledge of J at ground state and the hint of whether I is integer/half-integer from the mass number, we may find the nuclear spin I. With knowledge of $\mathbf{B}_\text{e}$ we may also find the nuclear g-factor.

^{55}Mn peaks: 0, 72, 145, 217.3, 289.7, 362.1 MHz

^{56}Mn peaks: 0, 85, 141, 197.4, 253.8, 310.2 MHz

Ratios of ΔE (^{55}Mn):

$$0.497,\ 0.667,\ 0.750,\ 0.800$$
$$\simeq \frac{1}{2}, \frac{2}{3}, \frac{3}{4}, \frac{4}{5}$$

So F ranges from 1 to 6.

$$\begin{cases} I + J = 6 \\ |I - J| = 1 \end{cases}$$
$$\Rightarrow 2I = 7 \quad \text{or} \quad 2I = 5$$
$$\Rightarrow I = \frac{7}{2} \quad \text{or} \quad I = \frac{5}{2}$$
$$\Rightarrow J = -\frac{1}{2}\ \text{(unphysical!)} \quad \text{or} \quad J = \frac{1}{2}$$

For ^{56}Mn, the ratios are:

$$0.603,\ 0.714,\ 0.777,\ 0.818$$
$$\simeq \frac{3/2}{5/2}, \frac{5/2}{7/2}, \frac{7/2}{9/2}, \frac{9/2}{11/2}$$

So F ranges from $\frac{3}{2}$ to $\frac{11}{2}$.

$$\begin{cases} I + J = \frac{11}{2} \\ |I - J| = \frac{3}{2} \end{cases}$$
$$\Rightarrow I = \frac{7}{2} \quad \text{or} \quad I = 2$$
$$\Rightarrow J = 2\ \text{(unphysical!)} \quad \text{or} \quad J = \frac{7}{2}$$

But since the mass number is even, we have I as an integer so $I = 2$.

(e) From before, $A\mathbf{J} = -g_I \mu_\mathrm{N} \hat{\mathbf{I}} \cdot \hat{\mathbf{B}}_\mathrm{e}$ so the ratio of A gives the ratio of g_I:

$$\begin{aligned} \Delta E_{55}(1) - \Delta E_{55}(2) &= -A_{55}(2) \\ \Delta E_{56}\left(\frac{3}{2}\right) - \Delta E_{56}\left(\frac{5}{2}\right) &= -A_{56}\left(\frac{5}{2}\right) \\ \Rightarrow \frac{A_{55}}{A_{56}} &= \frac{g_{I,55}}{g_{I,56}} \\ &= \frac{4}{5} \cdot \frac{72}{85} = 0.678 \end{aligned}$$

3. (DRAFT)

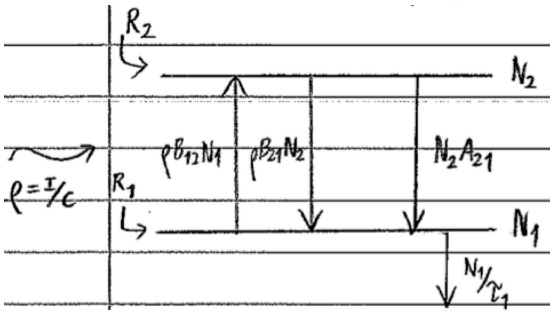
(a) A 3-level laser has its metastable level close to the ground level, making them essentially the same state. A 4-level laser, however, has a distinguishable metastable term at typical temperature range.

Example of 3-level laser: He-Ne

Example of 4-level laser: Nd:YAG

Both lasers operate by pumping the ground state population to an unstable upper state, which then immediately decays into the upper lasing state. After lasing the decayed population decays spontaneously back to the ground state.

The pump rate of 3-level laser is proportional to the difference in population if both ground and unstable states. At thermal equilibrium, the population will be roughly the same, making pumping difficult. In contrast, 4-level lasers do not suffer from this and thus may operate at lower power continuously.



In the absence of radiation, the rate equations read:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = R_2 - N_2 A_{21}$$
$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = R_1 + N_2 A_{21} - \frac{N_1}{\tau_1}$$

At thermal equilibrium,

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = \frac{\mathrm{d}N_1}{\mathrm{d}t} = 0$$
$$\Rightarrow N_2 = \frac{R_2}{A_{21}}$$
$$N_1 = R_1\tau_1 + R_2\tau_1$$

$$\begin{aligned} N^* &= N_2 - \frac{g_2}{g_1}N_1 \\ &= \frac{R_2}{A_{21}} - \frac{g_2}{g_1}(R_1\tau_1 + R_2\tau_1) \\ &= R_2\left[\frac{1}{A_{21}} - \frac{g_2}{g_1}\tau_1\right] \end{aligned}$$

for $R_1 = 0$.

Now in the presence of radiation:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = R_2 + \rho B_{12} N_1 - \rho B_{21} N_2 - A_{21} N_2$$
$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = R_1 - \rho B_{12} N_1 + \rho B_{21} N_2 + A_{21} N_2 - \frac{N_1}{\tau_1}$$

where ρ is spectral energy density, B is Einstein's B coefficient.

Change in number of photons in a volume element $A\,\mathrm{d}z$ (assuming narrowband so $\rho \to \rho g_H \delta\omega$ where $g_H(\omega - \omega_0)$ is homogeneous broadening function, $\delta\omega$ is the width of the input frequency):

$$\Delta N_\gamma = \left[\rho B_{21} N_2 - \rho B_{12} N_1\right] g_H \delta\omega A\,\mathrm{d}z$$

Energy change to the beam:

$$\mathrm{d}I \cancel{A} \cancel{\delta\omega} = \Delta N_\gamma \cdot \omega_L = \left[\rho B_{21} N_2 - \rho B_{12} N_1\right] g_H \cancel{\delta\omega} \cancel{A}\,\mathrm{d}z \cdot \hbar\omega_L$$
$$\frac{\mathrm{d}I}{\mathrm{d}z} = \underbrace{\left[N_2 - \frac{g_2}{g_1} N_1\right]}_{N^*} \underbrace{B_{21} g_H \frac{\hbar\omega_L}{c}}_{\sigma_{21}} I$$

where ω_L is the lasing frequency, $\rho = I/c$ and $B_{12} g_1 = g_2 B_{21}$.

Now rewrite the rate equations with N^*, σ_{21} and I:

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = R_2 - N^* \sigma_{21} \frac{I}{\hbar\omega_L} - A_{21} N_2$$
$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = R_1 + N^* \sigma_{21} \frac{I}{\hbar\omega_L} + A_{21} N_2 - \frac{N_1}{\tau_1}$$

At thermal equilibrium,

$$N_2 = \frac{R_2}{A_{21}} - \frac{N^* \sigma_{21} I}{A_{21} \hbar\omega_L}$$
$$N_1 = R_1 \tau_1 + N^* \sigma_{21} \frac{I}{\hbar\omega_L} \tau_1 + A_{21} N_2 \tau_1$$

Substitute N_2, N_1 into N^*:

$$N^* = \left(1 - \frac{g_2}{g_1} \tau_1 A_{21}\right) \left[\frac{R_2}{A_{21}} - N^* \sigma_{21} \frac{I}{\hbar\omega_L} \frac{1}{A_{21}}\right] - R_1 \tau_1 - N^* \sigma_{21} \frac{I}{\hbar\omega_L} \tau_1$$
$$\Rightarrow N^*(I) = \frac{N^*(0)}{1 + \dfrac{I}{I_s}}$$

where

$$N^*(0) = \left[1 - \frac{g_2}{g_1} \tau_1 A_{21}\right] \cdot \frac{R_2}{A_{21}} - R_1 \tau_1$$
$$= R_2 \left(\frac{1}{A_{21}} - \frac{g_2}{g_1} \tau_1\right) - R_1 \tau_1$$

and

$$\begin{aligned} I_s &= \left[\sigma_{21}\frac{1}{\hbar\omega_L}\frac{1}{A_{21}}\left(1-\frac{g_2}{g_1}\tau_1 A_{21}\right)+\sigma_{21}\frac{1}{\hbar\omega_L}\tau_1\right]^{-1} \\ &= \left[\sigma_{21}\frac{1}{\hbar\omega_L}\underbrace{\left(\tau_1+\frac{1}{A_{21}}+\frac{g_2}{g_1}\tau_1\frac{1}{A_{21}}\right)}_{\tau_R}\right]^{-1} \\ &= \frac{\hbar\omega_L}{\sigma_{21}\tau_R} \end{aligned}$$

is the saturation intensity.

Beam growth $^{\mathrm{d}I}/_{\mathrm{d}z} = \alpha(I)I$ where

$$\alpha(I) = N^*(I)\sigma_{21} = \frac{\alpha(0)}{1+\dfrac{I}{I_s}}$$

with

$$\begin{aligned} \alpha(0) &= N^*(0)\sigma_{21} \\ &= R_2\sigma_{21}\left(\frac{1}{A_{21}}-\frac{g_2}{g_1}\tau_1\right)-R_1\sigma_{21}\tau_1 \end{aligned}$$

the null intensity gain coefficient.

So:

$$\begin{aligned} \frac{1}{I}+\frac{1}{I_s}\,\mathrm{d}I &= \alpha(0)\,\mathrm{d}z \\ \ln\left(\frac{I}{I_0}\right)+\frac{I-I_0}{I_s} &= \alpha(0)z \end{aligned}$$

For $I \gg I_s$, the second term dominates and so $I = I_0 + \alpha(0)I_s z$ and the beam growth is linear as the medium is saturated.

(b) For $\sigma_{21} = 4\times10^{-15}\,\mathrm{cm}^2$, $R_2 = 5\times10^{19}\,\mathrm{s}^{-1}\,\mathrm{cm}^{-3}$, $R_1 = 0$, $A_{21} = 3\times10^6\,\mathrm{s}^{-1}$, $g_2 = 5$, $g_1 = 3$, $\tau_1 = 2\times10^{-8}\,\mathrm{s} \to \alpha(0) = 0.06$.

Similarly for $A_{21} = 3\times10^6\,\mathrm{s}^{-1}$, $g_2 = 3$, $\tau_1 = 3\times10^{-7}\,\mathrm{s}$, $g_1 = 1 \to \alpha(0) = -0.113$

4. (DRAFT)

(a) Substituting $\Psi(\mathbf{r},t)$ into the TDSE:

$$\begin{aligned} i\hbar\frac{\partial\Psi}{\partial t} &= \hat{H}\Psi \\ \Rightarrow i\hbar\dot{c}_1\psi_1 e^{-\frac{iE_1t}{\hbar}} + i\hbar c_1\psi_1\left(-i\frac{E_1}{\hbar}\right)e^{-\frac{iE_1t}{\hbar}} & \\ +i\hbar\dot{c}_2\psi_2 e^{-\frac{iE_2t}{\hbar}} + i\hbar c_2\psi_2\left(-i\frac{E_2}{\hbar}\right)e^{-\frac{iE_2t}{\hbar}} &= E_1c_1\psi_1e^{-\frac{iE_1t}{\hbar}} + E_2c_2\psi_2e^{-\frac{iE_2t}{\hbar}} \\ &\quad + \hat{V}\left[c_1\psi_1e^{-\frac{iE_1t}{\hbar}} + c_2\psi_2e^{-\frac{iE_2t}{\hbar}}\right] \end{aligned}$$

$\times\psi_2^*$ and integrate over position to get:

$$\begin{aligned} i\hbar\dot{c}_2e^{-\frac{iE_2t}{\hbar}} + \cancel{E_2c_2\psi_2e^{-\frac{iE_2t}{\hbar}}} &= \cancel{E_2c_2\psi_2e^{-\frac{iE_2t}{\hbar}}} \\ &\quad + \langle 2|\hat{V}|1\rangle c_1e^{-\frac{iE_1t}{\hbar}} + \langle 2|\hat{V}|2\rangle c_2e^{-\frac{iE_2t}{\hbar}} \\ \Rightarrow \dot{c}_2(t) &= -\frac{i}{\hbar}\langle 2|\hat{V}|1\rangle e^{i\omega_0t}c_1(t) - \frac{i}{\hbar}\langle 2|\hat{V}|2\rangle c_2(t) \end{aligned}$$

where $\omega_0 = (E_2 - E_1)/\hbar$.

Now:

$$\begin{aligned} \hat{V}(t) &= ex\mathcal{E}\cos\omega t \\ \Rightarrow V_{ij} &= \langle i|\hat{V}|j\rangle \\ \Rightarrow V_{21} &= \langle 2|ex\mathcal{E}\cos\omega t|1\rangle \\ &= \hbar\Omega\cos\omega t \end{aligned}$$

where $\hbar\Omega = \langle 2|ex\mathcal{E}|1\rangle$ is the Rabi frequency.

In addition, $V_{22} = \langle 2|ex\mathcal{E}\cos\omega t|2\rangle = 0$ as electric dipole transition requires the state to change.

Approximating $c_1 \simeq 1$, we have:

$$\begin{aligned} \dot{c}_2 &= -i\Omega e^{i\omega_0t}\cos\omega t \\ &= -\frac{i\Omega}{2}\left[\frac{e^{i(\omega_0+\omega)t} + e^{i(\omega_0-\omega)t}}{2}\right] \\ \Rightarrow c_2(t) &= \int_0^t \dot{c}_2(t')\,\mathrm{d}t' \\ &= -\frac{i\Omega}{2}\left[\frac{e^{i(\omega_0+\omega)t}}{i(\omega_0+\omega)} + \frac{e^{i(\omega_0-\omega)t}}{i(\omega_0-\omega)}\right]_{t=0}^{t} \end{aligned}$$

Typically for optical transition, we may invoke rotating wave approximation as $\omega + \omega_0 \gg |\omega - \omega_0|$. So we may ignore the term with $\omega + \omega_0$ since the fraction vanishes, physically this corresponds to the behaviour that the atom could not catch up with the high frequency

mode.

$$\begin{aligned}
\Rightarrow c_2(t) &\simeq -\frac{i\Omega}{2}\left[\frac{e^{i(\omega_0-\omega)t}-1}{i(\omega_0-\omega)}\right] \\
&= -\frac{i\Omega}{2(\omega_0-\omega)}e^{i\frac{\omega_0-\omega}{2}t}\left[\frac{e^{i\frac{\omega_0-\omega}{2}t}-e^{-i\frac{\omega_0-\omega}{2}t}}{2i}\right]\cdot 2 \\
&= -\frac{i\Omega}{\delta}e^{i\delta/2 t}\sin^2\left(\frac{\delta}{2}t\right) \quad \text{where } \delta=\omega_0-\omega \\
|c_2(t)|^2 &= \left(\frac{\Omega}{\delta}\right)^2\sin^2\left(\frac{\delta}{2}t\right)
\end{aligned}$$

For a broadband radiation, the energy density is given by:

$$\begin{aligned}
\hbar\Omega &= \langle 2|\, e\sqrt{\frac{2\rho\delta\omega}{\epsilon_0}}x\,|1\rangle \\
\Rightarrow \Omega &= e\sqrt{\frac{2\rho\delta\omega}{\epsilon_0}}\,\langle 2|\, x\,|1\rangle \\
\Omega^2 &= e^2\left(\frac{2\rho\delta\omega}{\epsilon_0}\right)|\langle 2|\, x\,|1\rangle|^2
\end{aligned}$$

Replacing $\delta\omega$ with integral, the limits assume that the response range is narrow enough such that $\rho \simeq \rho(\omega_0)$ for all ω:

$$\begin{aligned}
\Rightarrow |c_2(t)|^2 &= \int_{-\infty}^{\infty}\frac{2e^2\rho(\omega_0)}{4\epsilon_0}\,|\langle 2|\, x\,|1\rangle|^2\left[\frac{\sin^2\left(\frac{\delta}{2}t\right)}{\left(\frac{\delta}{2}\right)^2}\right]\mathrm{d}\omega \\
&= \frac{2e^2\rho(\omega_0)}{4\epsilon_0}\,|\langle 2|\, x\,|1\rangle|^2\cdot 2\pi t \\
&= \frac{\pi e^2\rho(\omega_0)}{\epsilon_0}\,|\langle 2|\, x\,|1\rangle|^2\cdot t
\end{aligned}$$

Transition probability:

$$\begin{aligned}
\rho B_{12} &= \frac{|c_2(t)|^2}{t} \\
B_{12} &= \frac{\pi e^2}{\epsilon_0}\,|\langle 2|\, x\,|1\rangle|^2 \\
&= \frac{\pi e^2}{3\epsilon_0}\,|\langle 2|\, x\,|1\rangle|^2
\end{aligned}$$

by isotropy and Einstein assumes incoherent radiation.