Chap 3. Light-Matter Interaction

- **Electromagnetic wave** [SR 5.2] (outline)

  1. Maxwell Eq with vector ($\mathbf{A}$) and scalar (ϕ) potentials

  2. Vacuum (no charge, no current) $\rho = 0, \mathbf{i} = 0$, Coulomb gauge $\nabla\mathbf{A} = 0$

  3. $\Rightarrow$ $\boxed{\text{Wave Eq}: \dfrac{1}{c^2}\dfrac{\partial^2 \mathbf{A}}{\partial t^2} = \nabla^2\mathbf{A} \Rightarrow \text{Plane wave } \mathbf{A} = A_0\varepsilon\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)}$

  4. (Energy from fields amplitude) = (Photon density)$\times$(Energy quantum)
     $$\Rightarrow A_0 = 2c(2\pi\hbar N/\omega V)^{1/2}$$

- **"Minimal" Electromagnetic Interaction** (charged particles)

  $$H = \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}\right)^2 + q\phi \qquad \left[\begin{array}{l}\rightarrow \text{ classical eq of motion with} \\ \underline{\text{Lorenz force}}\ \mathbf{F} = q(\mathbf{E} + \mathbf{v}\times\mathbf{B}/c)\end{array}\right]$$

  Using : $\mathbf{p} \rightarrow i\hbar\nabla$, $\nabla\cdot\mathbf{A} = 0$ (Coulomb gauge)

  $$H = H_0 + V, \qquad V = -\frac{q}{mc}(\mathbf{A}\cdot\mathbf{p}) + \frac{q^2}{2mc^2}\mathbf{A}\cdot\mathbf{A}$$

  ("weak-field approximation" neglects the 2nd term [SR 5.3.3])

- **Absorption and Emission Spectra** (1st order processes)

$$V = -\frac{q}{mc}(\mathbf{A} \cdot \mathbf{p}) = -\frac{q}{mc}A_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t)\varepsilon \cdot \mathbf{p}$$

$$\equiv U(\mathbf{k})e^{-i\omega t} + U(-\mathbf{k})e^{i\omega t} \qquad \left[U(\mathbf{k}) \equiv -\frac{qA_0}{2mc}e^{i\mathbf{k}\cdot\mathbf{r}}\varepsilon \cdot \mathbf{p}\right]$$

(periodic interaction)

Fermi's golden-rule : $|m\rangle \to |k\rangle$

$$\Rightarrow \qquad w_{km} = \frac{2\pi}{\hbar}|U_{km}(\mathbf{k})|^2 \delta(E_k - E_m - \hbar\omega) \qquad \text{(Absorption)}$$

$$+\frac{2\pi}{\hbar}|U_{km}(-\mathbf{k})|^2 \delta(E_k - E_m + \hbar\omega) \qquad \text{(Emission)}$$

(Absorption or Emission $\Leftarrow$ sign of $E_k - E_m$)

Dipole Approximation (long wavelength)

Visible lights (electronic transitions) :

$$\lambda = 400 \sim 700 \text{ nm} \gg \text{dimension of molecules}$$

(even longer wavelength for infrared and microwave lights)

$$\Rightarrow e^{i\mathbf{k}\cdot\mathbf{r}} \simeq 1 \quad (|\mathbf{k}| = 2\pi/\lambda)$$

Then,
$$U_{km} \simeq -\frac{qA_0}{2mc}\langle k|\varepsilon \cdot \mathbf{p}|m\rangle$$

Using :
$$\mathbf{p} = \frac{im}{\hbar}[H_0, \mathbf{r}]$$

$$\left[[H_0, \mathbf{r}_i] = [\sum_I \frac{\mathbf{P}_I^2}{2M_I} + \sum_j \frac{\mathbf{p}_j^2}{2m} + V(\mathbf{r}, \mathbf{R}), \mathbf{r}_i] \right.$$
$$\left. = \frac{1}{2m}[\mathbf{p}_i^2, \mathbf{r}_i] = \frac{\hbar}{im}\mathbf{p}_i \right]$$

$$U_{km} = -\frac{qA_0}{2mc}\frac{im}{\hbar}\varepsilon \cdot \langle k|[H_0, \mathbf{r}]|m\rangle = -\frac{qA_0}{2mc}\frac{im}{\hbar}\varepsilon \cdot \langle k|\mathbf{r}|m\rangle(E_k - E_m)$$

From the δ functions in w_{km} , $E_k - E_m = \pm\hbar\omega$ (+ : absorption, − : emission)

$$\Rightarrow U_{km} = \mp\frac{iA_0\omega}{2c}\varepsilon \cdot \langle k|q\mathbf{r}|m\rangle \qquad \propto \text{transition dipole moment}$$

So far, we have treated one particle (with charge q).

By considering <u>all nuclei and electrons</u> in molecular systems,

$$V = -\frac{1}{c}\mathbf{A} \cdot \left(\sum_I \frac{Z_I}{M_I}\mathbf{P}_I - \frac{e}{m}\sum_i \mathbf{p}_i\right)$$

We arrive at (*Note : all calculations were linear*)

$$U_{km} = \mp\frac{iA_0\omega}{2c}\varepsilon \cdot \langle k|\left(\sum_I Z_I\mathbf{R}_I - e\sum_i \mathbf{r}_i\right)|m\rangle = \mp\frac{iA_0\omega}{2c}\varepsilon \cdot \mu_{km}$$

μ_{km} : transition dipole of the molecular system

(Note : in [SR 5.4] only electrons are considered, but we should include nuclei to treat IR spectra etc.)

• **Simpler derivation of U_{km}** [SR 5.5.2]

We get the same U_{km} (more easily) starting from $\underline{V = -\mu \cdot \mathbf{E}}$ with

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} = \frac{\omega}{c}A_0\varepsilon \sin(\mathbf{k} \cdot \mathbf{r} - \omega t) = \frac{\omega A_0}{2ic}\varepsilon(e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} - e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)})$$

(Coulomb gauge $\nabla\phi = 0$)

Density of states of photon field

Having specified the states ($|m\rangle \rightarrow |k\rangle$) of the molecular system, we still need to <u>sum over the photon field states</u>

$$w_{\text{abs/em}}(m \rightarrow k) = \int w_{km} \rho_{\text{photon}}(\hbar\omega) d(\hbar\omega)$$

Insert w_{km} of page 2 :

$$w_{\text{abs}}(m \rightarrow k) = \frac{2\pi}{\hbar} |U_{km}(\mathbf{k})|^2 \rho_{\text{photon}}(E_k - E_m)$$

$$w_{\text{em}}(m \rightarrow k) = \frac{2\pi}{\hbar} |U_{km}(-\mathbf{k})|^2 \rho_{\text{photon}}(E_m - E_k)$$

- **Calculation of $\rho_{\text{photon}}(\hbar\omega)$**

1. Number of states N in wave vector $\mathbf{k}$: $dN = (\frac{L}{2\pi})^3 d\mathbf{k}$
   $$\left[\begin{array}{l} \text{Periodic boundary condition in length } L : \\ \quad e^{ik_x(x+L)} = e^{ik_x x} \Rightarrow k_x L = 2\pi n_x \; (n_x = 0, \pm 1, \pm 2, \cdots) \end{array} \right]$$

2. Use polar coordinate $d\mathbf{k} = k^2 dk d\Omega$ and $k = \omega/c$: $dN = \dfrac{V}{(2\pi)^3} \dfrac{\omega^2}{c^3} d\omega d\Omega$

3. $d\rho_{\text{photon}}(\hbar\omega) = \dfrac{dN}{d(\hbar\omega)} = \dfrac{V}{(2\pi c)^3}\dfrac{\omega^2}{\hbar}d\Omega$ $\quad\begin{bmatrix}\text{(Differential) density of photon}\\\text{states having } \mathbf{k} \text{ directed to } d\Omega\end{bmatrix}$

Thus, (differential) emission rate toward $d\Omega$:

$$\frac{dw_{\text{em}}(m \to k)}{d\Omega} = \frac{2\pi}{\hbar}|U_{km}|^2\frac{d\rho_{\text{photon}}(E_k - E_m)}{d\Omega} = \frac{N\omega^3}{2\pi\hbar c^3}|\varepsilon \cdot \mu_{km}|^2$$

$$\left[\text{used } |U_{km}| = (A_0\omega/2c)|\varepsilon \cdot \mu_{km}|,\ \ A_0 = 2c(2\pi\hbar N/\omega V)^{1/2},\ \ \hbar\omega = E_k - E_m\right]$$

- $|\varepsilon \cdot \mu_{km}| = |\mu_{km}|\sin\theta$ $\qquad$ ($\theta \equiv$ angle between $\mathbf{k}$ and μ_{km})

- Integration over the solid angle $d\Omega$ $\qquad\left[\int d\Omega \sin^2\theta = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta \sin^2\theta = \frac{8\pi}{3}\right]$

$$\Rightarrow \boxed{\begin{array}{l}\text{Total emission rate}\\[4pt]\quad w_{\text{em}}(m \to k) = \dfrac{4N}{3\hbar}\left(\dfrac{\omega}{c}\right)^3|\mu_{km}|^2\end{array}}$$

- However, it is not correct to have $w_{\text{em}} \to 0$ for $N \to 0$, since in reality, we have "spontaneous emissions".

- To remedy this, we just need to replace N by $N + 1$, which is indeed justified via quantization of radiation (photon) field.

- Quantization of radiation field :   Photon state $|n\rangle = \dfrac{1}{\sqrt{n!}}(b^{\dagger})^{n}|0\rangle$

$$\langle n-1|b|n\rangle = \sqrt{n} \qquad \langle n+1|b^{\dagger}|n\rangle = \sqrt{n+1}$$
     (absorption)   (emission)

$\langle 1|b^{\dagger}|0\rangle = 1 \neq 0 \Rightarrow$ spontaneous emission into the photon vacuum is possible.

(On the other hand, we have no "spontaneous absorption" since $b|0\rangle = 0$)

- **Natural lifetime of excited states**   of an excited state $|m\rangle$

  $\Leftarrow$ summing over all $|k\rangle$ in lower energy $E_k < E_m$:

$$\frac{1}{\tau_{\text{rad}}(E_m)} = \sum_{E_k < E_m} w_{\text{em}}(m \to k)|_{N=0} = \sum_{E_k < E_m} \frac{4}{3\hbar}\left(\frac{|\omega_{km}|}{c}\right)^{3}|\mu_{km}|^{2}$$

- **Rate of photo-absorption**   (Similarly to the emission case)

$$w_{\text{abs}}(m \to k) = \frac{4}{3\hbar}N\left(\frac{\omega}{c}\right)^{3}|\mu_{km}|^{2}$$

$[w_{\text{abs}} \to 0$ as $N \to 0$: no "spontaneous absorption" $]$

Miscellaneous

- **Einstein's A and B factors** [SR 5.4.6]

Photon field density of states (or energy)

- SR uses that for quantized plane-wave (temperature independent)

- Many others use black-body Planck distribution (temperature dependent) or discuss without explicit form of the density of states. (Indeed, the A, B factors are defined from the <u>photon-field independent part</u> of the transition rate.)

- **Oscillator strength**

$$f_{km} \equiv \frac{2m\omega}{3\hbar e^2} |\mu_{km}|^2 \quad \text{(dimensionless)}$$

Defined as relative intensity to

$n = 0 \rightarrow 1$ transition of 3D harmonic oscillator (which gives $f = 1$ ... (*)).

$\left[\begin{array}{l} \text{Exercise : Derive (*) via the following two routes:} \\ \text{1. Using creation-annihilation operator} \\ \text{2. Carrying out Gaussian integration of the wavefunctions representation} \end{array}\right]$

Answer :   (3D H.O. $H = \frac{1}{2m}\mathbf{p}^2 + \frac{m\omega^2}{2}|\mathbf{x}|^2$, $\lambda \equiv m\omega/\hbar$)

1. $b = (m\omega/2\hbar)^{1/2}(x+ip/m\omega)$, $b^\dagger = (m\omega/2\hbar)^{1/2}(x-ip/m\omega) \Rightarrow x = (m\omega/2\hbar)^{1/2}(b+b^\dagger)/2$

   Using $b|n\rangle = \sqrt{n}|n-1\rangle$, $b^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \Rightarrow \langle 1|x|0\rangle = (\hbar/2m\omega)^{1/2}$

   Thus, $|\langle 1|e\mathbf{r}|0\rangle|^2 = 3 \times \frac{\hbar e^2}{2m\omega}$ (where $3\times$ from x, y, z components)

2. $\phi_0 = (\lambda/\pi)^{1/4}\exp(-\lambda x^2/2)$, $\phi_1 = \sqrt{2\lambda}(\lambda/\pi)^{1/4}x\exp(-\lambda x^2/2)$

   $\Rightarrow \int dx\,\phi_0 x\phi_1 = \sqrt{2/\pi}\lambda \int dx\,x^2 e^{-\lambda x^2} = \cdots$

• **Correspondence with experiments**

Beer-Lambert Law : $I_l = I_0 e^{-\alpha C l}$ $\begin{bmatrix} \alpha \ ... \ \text{absorption coefficient} \\ C \ ... \ \text{molar concentration} \end{bmatrix}$

Integrated absorbance $\mathcal{A} \equiv \int \alpha(\nu)d\nu$

Considering the decay of photon field energy, we get (skipping details)

$$\boxed{\mathcal{A} = \frac{h\bar{\nu}_{km}}{c}LB = \frac{4\pi^2\bar{\nu}_{km}L}{3\hbar c}|\mu_{km}|^2}$$
     B ... Einstein's B-coeff.
     L ... Avogadro number

$\bar{\nu}_{km}$ ... central peak frequency of the $|m\rangle \to |k\rangle$ absorption band

(or in the derivation, representative ν when approximating $\int \frac{\alpha(\nu)}{\nu}d\nu \simeq \frac{1}{\bar{\nu}}\int \alpha(\nu)d\nu$)

- **1st correction to long-wavelength approx.** [SR 5.4.8]

Dipole Approx : $e^{i\mathbf{k}\cdot\mathbf{r}} \simeq 1$ $(|\mathbf{k}| = 2\pi/\lambda)$

To 1st-order : $e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + \mathbf{k}\cdot\mathbf{r} + \cdots$

$$U_{km} = -\frac{eA_0}{2mc}\langle k|e^{i\mathbf{k}\cdot\mathbf{r}}\varepsilon\cdot\mathbf{p}|m\rangle$$

$$\simeq \underbrace{-\frac{iA_0\omega_{km}}{2c}\varepsilon\cdot\mu_{km}}_{\text{(dipole approx.)}} - \frac{i}{2}\underbrace{A_0(\mathbf{k}\times\varepsilon)}_{\mathbf{H}}\cdot M_{km} + \frac{1}{4e}\underbrace{\frac{A_0\omega_{km}}{c}}_{\mathbf{E}}\varepsilon\cdot Q_{km}\cdot\mathbf{k}$$

- $\mathbf{M} = \frac{e}{2mc}(\mathbf{r}\times\mathbf{p})$ ... magnetic dipole

- $Q_{ij} = (er_i)(er_j)$ ... electric quadrupole tensor $(r_i = x, y, z)$

Symmetry :

- $\mu \sim x, y, z$,   • $\mathbf{M} \sim R_x, R_y, R_z$, (rotation)   • $\mathbf{Q} \sim xy, x^2$, etc.

$\Rightarrow$ different symmetry for each term

Franck-Condon Factor

Molecular wavefunction (adiabatic approx.)

$$\Phi_{\varepsilon,\nu}(r,R) \simeq \chi_{\varepsilon,\nu}(R)\varphi_{\varepsilon}(r;R)$$

$$\begin{bmatrix} \text{Quantum number} \\ \varepsilon \ ... \ \text{electronic} \\ \nu \ ... \ \text{nuclear} \end{bmatrix}$$

Transition dipole for $(\varepsilon,\nu) \to (\varepsilon',\nu')$:

$$\mu_{\varepsilon'\nu',\varepsilon\nu} \quad = \int dR \int dr \chi_{\varepsilon'\nu'} \varphi_{\varepsilon'} \mu \chi_{\varepsilon\nu} \varphi_{\varepsilon} = \int dR \chi_{\varepsilon'\nu'} \underbrace{\left\{ \int dr \varphi_{\varepsilon'} \mu \varphi_{\varepsilon} \right\}}_{\equiv \tilde{\mu}_{\varepsilon'\varepsilon}(R)} \chi_{\varepsilon\nu}$$

$$= \langle \chi_{\varepsilon'\nu'} | \tilde{\mu}_{\varepsilon'\varepsilon}(R) | \chi_{\varepsilon\nu} \rangle$$

Expand $\tilde{\mu}$ around a (particular) nuclear configuration R_0

(usually minimum of the adiabatic potential)

$$\tilde{\mu}_{\varepsilon'\varepsilon}(R) = \tilde{\mu}_{\varepsilon'\varepsilon}(R_0) + \left(\frac{\partial \tilde{\mu}_{\varepsilon'\varepsilon}}{\partial R} \right)_{R=R_0} (R - R_0) + \cdots$$

Then,

$$\mu_{\varepsilon'\nu',\varepsilon\nu} = \tilde{\mu}_{\varepsilon'\varepsilon}(R_0) \cdot \underbrace{\langle \chi_{\varepsilon'\nu'} | \chi_{\varepsilon\nu} \rangle}_{\text{(Franck-Condon factor)}} + \text{(non-Condon terms)}$$

$$\left[\begin{array}{c} \text{In many cases, large Franck-Condon overlap at "vertical transitions"} \\ \Leftrightarrow \text{Nuclei don't move during fast electronic transitions} \\ \text{(semi-classical interpretation)} \end{array} \right]$$

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