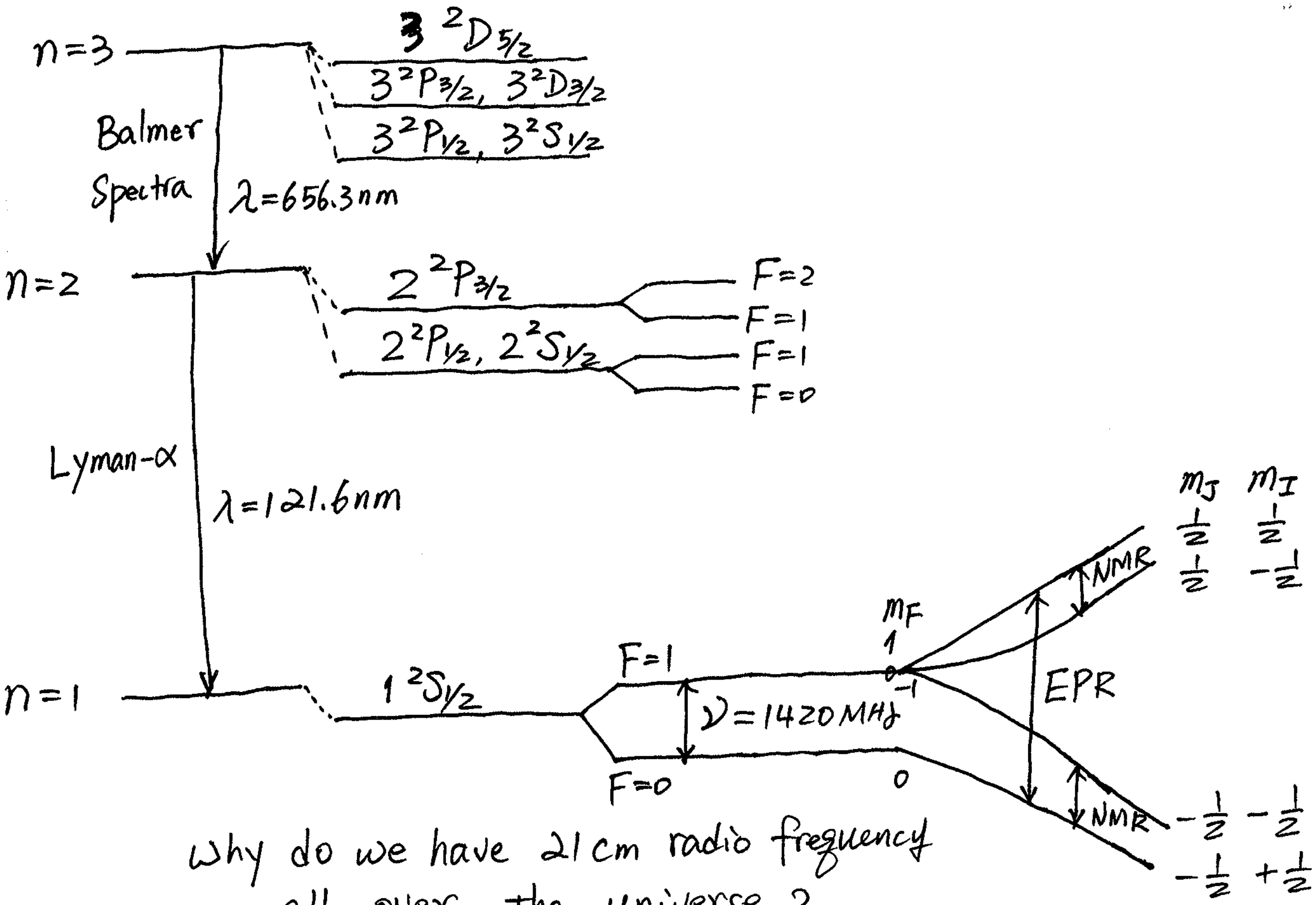
Chapter 6. Radiative Transitions

§6.1 Introduction

By now, we finished the study of atomic structure using QM theory and methods — deriving eigenvalues and eigenstates of energy of an atom, under different internal and external interactions. We now understand, e.g., the hydrogen energy structure, and how we obtain certain wavelength spectral lines:



why do we have 21 cm radio frequency all over the universe?

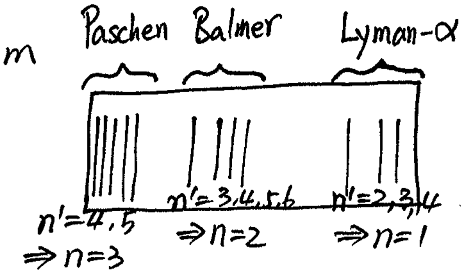
① Lyman-α transition: 121.6cm (Solar flux)

② Balmer spectra, Hα = 656.3nm

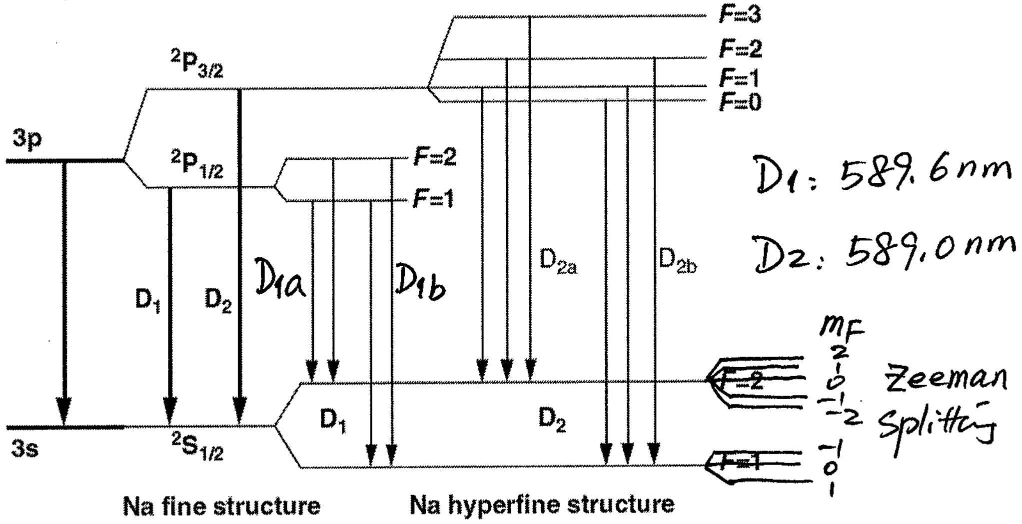
③ Hyperfine transition: F=1 ↔ F=0, λ=21cm

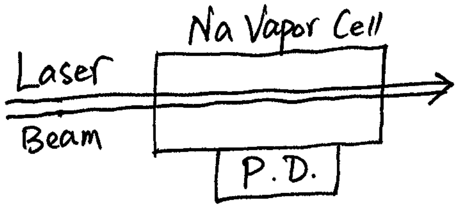
④ NMR: Zeeman splitting / transition, EPR

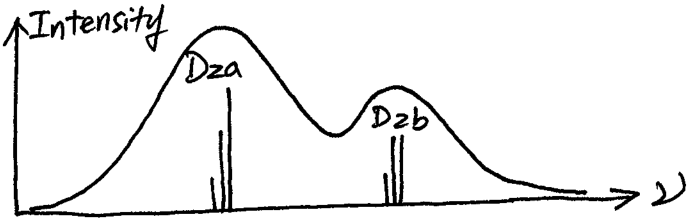
⑤ Stark effect.



Another Example: Na







We now understand why Na D_2 lines have fine (D_{2a} and D_{2b}) and hyperfine (3 lines for D_{2a} and 3 lines for D_{2b}) structures.

D1: 589.6 nm } (in air) 589.7558 } (in vacuum)
D2: 589.0 nm } 589.1583 }

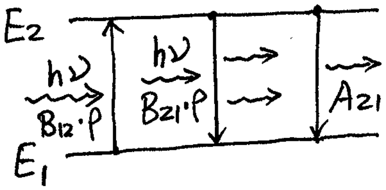
But we haven't touched why certain transitions have certain strength (why one is stronger than another) and why some transitions don't occur, e.g., $F=3 \not\leftrightarrow F=1$.

Also, why some lines are linearly polarized.

These questions will be answered by radiative transition theory that we will address below.

§6.2. Absorption, Stimulated Emission, and Spontaneous Emission

From atomic structure theory, we know atoms have discrete energy levels. Assume an atom has two energy levels E_1 and E_2 (again, energy levels mean the eigenstates of $\hat{H}_0$), and is brought into a thermal radiation field.



① Absorption (Stimulated / induced absorption)

$$\frac{dP_{12}(t)}{dt} = \overset{\curvearrowright}{B_{12}}\rho(\nu) \quad \text{Einstein } B \text{ coefficient}$$

where $\frac{dP_{12}(t)}{dt}$ is the absorption probability per unit time, i.e., the probability per second that an atom will absorb a photon, $\rho(\nu)$ is the spectral energy density of the radiation field.

Note: There is no such thing called A_{12}! Only A_{ki}, no A_{ik}!

k — upper level
i — lower level

② Stimulated emission:

$$\frac{dP_{21}^{st}(t)}{dt} = B_{21}\rho(\nu) \quad \text{Einstein } B \text{ coefficient}$$

③ Spontaneous emission:

$$\frac{dP_{21}^{sp}(t)}{dt} = A_{21} \quad \text{Einstein } A \text{ coefficient}$$

A_{21} is also called the spontaneous transition probability per unit time.

Note: Transition probability $P_{12}(t)$ and $P_{21}(t)$ are the probability that an atom will absorb or emit a photon at time t. From the definition of probability, transition probability must be in between 0 and 1 (i.e; $0 \le P_{12}(t) \le 1$, $0 \le P_{21}(t) \le 1$) and dimensionless.

Because Quantum transition can happen very fast (on the order of 10s ns), it is more meaningful in spectroscopy field to study the transition probability per unit time $\frac{dP_{12}(t)}{dt}$ and $\frac{dP_{21}(t)}{dt}$, which is the probability per second that an atom will absorb or emit a photon. The unit of $\frac{dP_{12}(t)}{dt}$ and $\frac{dP_{21}(t)}{dt}$ is s^{-1} (s — second).

So it is not surprising that A_{21} is usually around $10^8 s^{-1}$.
To be accurate, $\frac{dP_{12}(t)}{dt}$ and $\frac{dP_{21}(t)}{dt}$ should be called the transition probability per unit time. But people usually just brief them as the transition probability. We must be aware of the differences.
This is why we call A_{21} as the spontaneous transition probability per unit time.

④ Relationship among Einstein coefficients A_{21}, B_{12}, and B_{21}:
At thermal equilibrium, atomic population on each energy level is given by Maxwell-Boltzmann distribution law:

$$N_i = N \frac{g_i}{Z} e^{-E_i/k_B T}$$

where E_i is the energy level, k_B is the Boltzmann constant, T is the temperature, N is the total atomic population:

$$N = \sum_i N_i .$$

Z is the normalization factor:

$$Z = \sum_i g_i e^{-E_i/k_B T}$$

where g_i is the statistical weight: $g_i = 2J_i + 1$ (J_i is the total angular momentum). g_i gives the number of degenerate sublevels of the energy level E_i.

At thermal equilibrium, total photon number of the radiation field will not change, total number of atoms will not change, and the number of atoms on each state will not change. Thus,

$$\frac{dN_2}{dt} = \frac{dN_1}{dt} = 0.$$

$$\Rightarrow \frac{dN_2}{dt} = N_1 \cdot B_{12} \cdot \rho - N_2 \cdot B_{21}\rho - N_2 \cdot A_{21} = 0$$

$$\Rightarrow [B_{21}\rho + A_{21}]\, N_2 = B_{12}\,\rho\, N_1$$

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-(E_2-E_1)/k_BT} = \frac{g_2}{g_1} e^{-h\nu/k_BT}, \qquad \nu = \frac{E_2-E_1}{h}$$

$$= \frac{B_{12}\,\rho}{B_{21}\rho + A_{21}}$$

$$\Rightarrow B_{21}\frac{g_2}{g_1} e^{-h\nu/k_BT}\rho + A_{21}\frac{g_2}{g_1} e^{-h\nu/k_BT} = B_{12}\rho$$

$$\Rightarrow \rho = \frac{A_{21}\cdot \frac{g_2}{g_1} e^{-h\nu/k_BT}}{B_{12} - B_{21}\frac{g_2}{g_1} e^{-h\nu/k_BT}}$$

$$= \frac{A_{21}/B_{21}}{\frac{B_{12}}{B_{21}}\cdot\frac{g_1}{g_2} e^{h\nu/k_BT} - 1}$$

Recall Planck's law: $\rho(\nu) = \frac{8\pi h\nu^3}{c^3}\,\frac{1}{e^{h\nu/k_BT}-1}$

Since both equations are valid for any arbitrary T and ν,

$$\Rightarrow \left.\begin{array}{l} A_{21}/B_{21} = \frac{8\pi h\nu^3}{c^3} \\ \frac{B_{12}}{B_{21}}\cdot\frac{g_1}{g_2} = 1 \end{array}\right\} \Rightarrow \left\{\begin{array}{l} A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21} \\ B_{12}\cdot g_1 = B_{21}\cdot g_2 . \end{array}\right.$$

If $g_1 = g_2$, then we have $B_{12} = B_{21}$, and $\frac{N_2}{N_1} = \frac{B_{12}\rho}{B_{21}\rho + A_{21}}$.

Considering A_{21}, we will always have $N_2 < N_1$ — consistent with Maxwell-Boltzmann distribution.

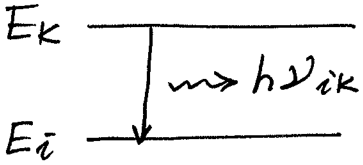
The number of modes per unit volume and per freq. interval:

$$n(\nu) = 8\pi\nu^2/c^3$$

$$\therefore \frac{A_{21}}{n(\nu)} = B_{21}\cdot h\nu . \longrightarrow$$ The spontaneous emission per mode is equal to the stimulated emission that is triggered by 1 photon.

The ratio of $\frac{\text{Stimulated}}{\text{Spontaneous}}$ emission rate in an arbitrary mode is equal to the number of photons in this mode.

⑤ Emission and Absorption Spectra.



If somehow, the atoms/molecules are in excited states, they can emit photons with $h\nu_{ik} = E_K - E_i$, where E_K – upper level, E_i – lower level.

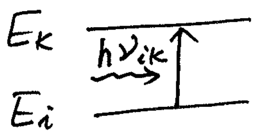
If we use instruments to record the emitted photon spectrum, we may see something like :

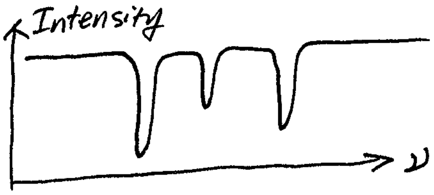
— This is called emission spectra.

If on the other hand, atoms are in ground states, when some continuous radiation (e.g., thermal radiation) passes through the atoms, the atoms may absorb photons at $\nu_{ik} = (E_K - E_i)/n$

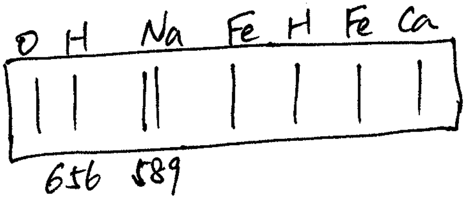
Thus, the received radiation will have less power at these resonance frequencies, appearing as dark lines in spectra.

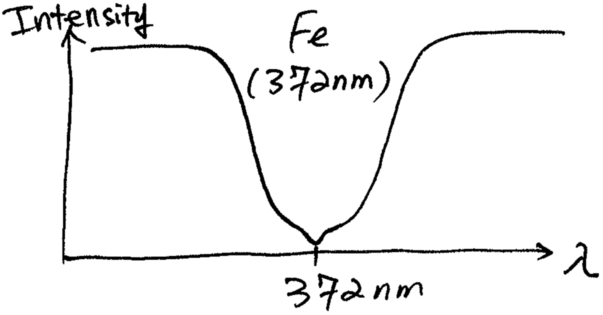
— This is called absorption spectra.





Example: Fraunhofer lines in the Solar spectrum:





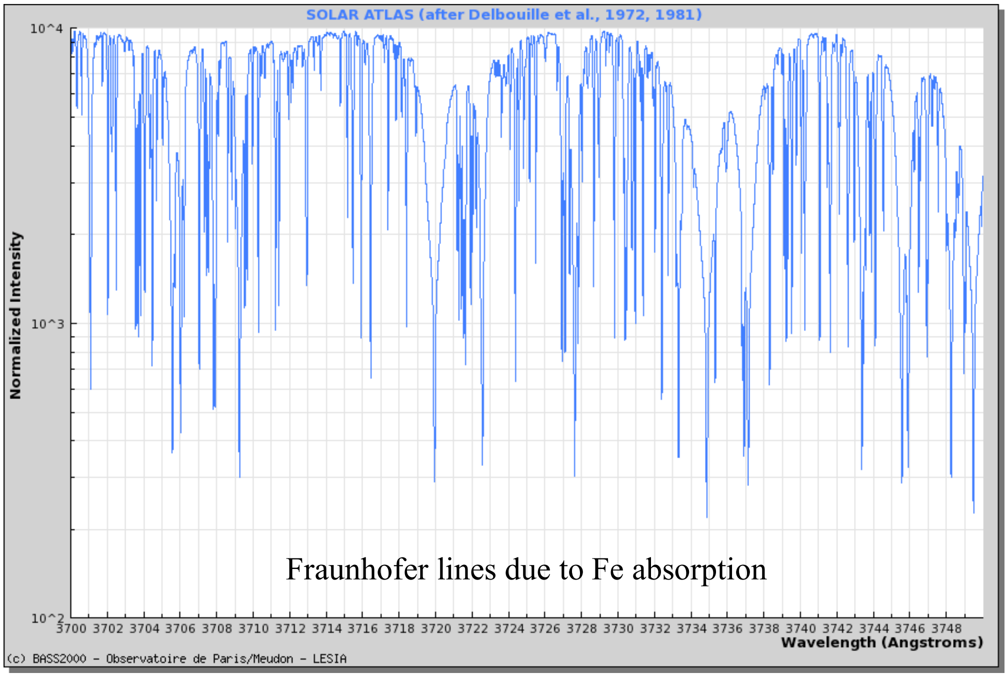
⇒ resulting in much lower solar background at Fraunhofer lines than at wavelength without an absorption line.

⇒ Lidar (resonance) can take advantage of this!

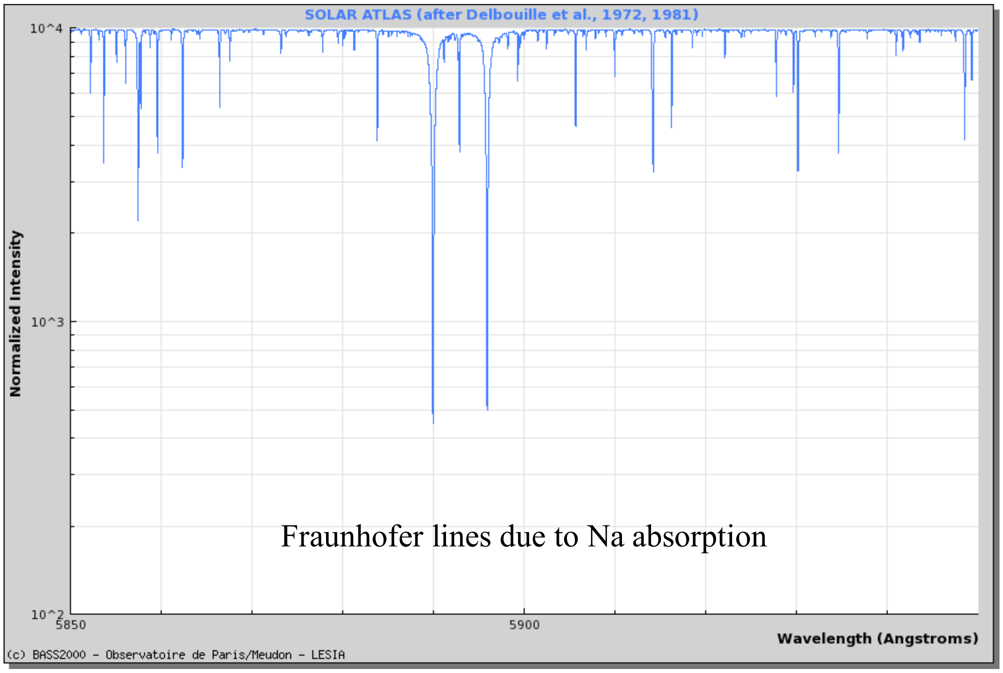
Fraunhofer lines are a set of spectral lines observed as dark features (absorption lines) in the optical spectrum of the sun by the German physicist Joseph Von Fraunhofer (1787–1826).

Fraunhofer Lines in Solar Spectrum

The following website can be used to look at the solar spectrum and numerous Fraunhofer lines
http://bass2000.obspm.fr/solar_spect.php?PHPSESSID=b1fb4b5e30286b1698ae5b2f330b3318

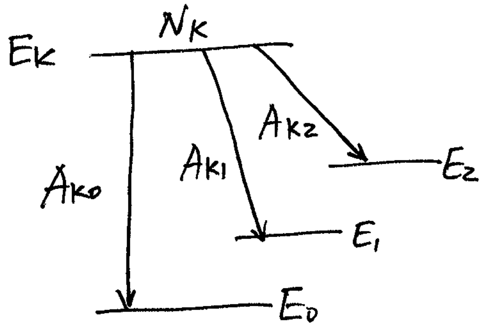


Fraunhofer lines due to Fe absorption



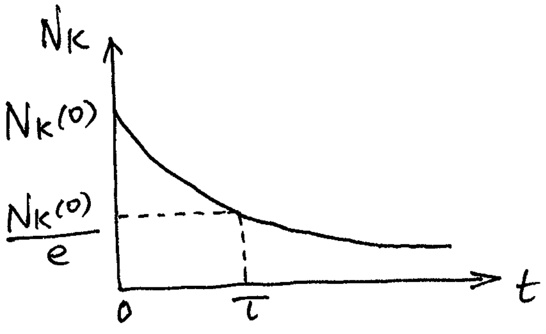
Fraunhofer lines due to Na absorption

⑥ Lifetime: Radiative lifetime and Effective Lifetime



The probability P_{Ki} that an excited atom in the level E_K makes a transition to a lower level E_i by spontaneous emission of a fluorescence quantum $h\nu_{Ki} = E_K - E_i$ is related to the Einstein coefficient A_{Ki} by

$$\frac{dP_{Ki}}{dt} = A_{Ki}$$



The total transition probability from the upper energy level E_K is

$$A_K = \sum_i A_{Ki}.$$

$$\frac{dN_K}{dt} = -A_{K0}N_K - A_{K1}N_K - A_{K2}N_K$$
$$= -(A_{K0} + A_{K1} + A_{K2})N_K$$
$$= -A_K N_K$$

$$\Rightarrow N_K(t) = N_K(0)\,e^{-A_K t}. \qquad N_K(0) = N_K(t=0)$$

At $\tau_K = \frac{1}{A_K}$, we have $N_K(t) = \frac{N_K(0)}{e}$.

Thus, τ_K is the mean radiative lifetime, caused by the spontaneous emission: $\tau_K = \frac{1}{A_K} = \frac{1}{\sum_i A_{Ki}}$.

Besides spontaneous emission, an energy level E_K can be depopulated by stimulated emission transitions and by collision-induced radiationless transitions. The overall effect is to reduce the lifetime of an atom staying in E_K.

Collision: $\frac{dP_{Ki}^{Collision}}{dt} = \bar{v} N_B \sigma_{Ki}^{Col}$, where N_B - density of collision partner B; σ_{Ki}^{Coll} - collision cross-section.

Stimulated: $\frac{dP_{Ki}^{St}}{dt} = \rho(\nu_{Ki}) B_{Ki} [N_K - \frac{g_K}{g_i} N_i]$

$\Rightarrow$ mean effective lifetime: $\frac{1}{\tau_K^{eff}} = \sum_i [A_{Ki} + \rho(\nu_{Ki}) B_{Ki} (N_K - N_i \frac{g_k}{g_i}) + N_B \sigma_{Ki}^{Coll} \bar{v}]$.

§6.3. Transition Probabilities: Statement of the Problem

Above we introduce the Einstein A and B coefficients phenomenologically to describe the absorption and emission phenomena. However, to quantitatively describe the transition phenomena, we must understand this transition concept from QM frame-work. What is transition probability in QM?

(1) Transition is a change of state of an atom with time, i.e., the atom (regarded as a QM system) changes its state from one eigenstate to another.

— The eigenstates and eigenvalues of Hamiltonian operator are solved by solving the energy eigenvalue equation, i.e., the time-independent Schrödinger equation.

— The evolution of state with time is described by the time-dependent Schrödinger equation. Therefore, the transition problem should be solved in the frame work of QM Schrödinger equation.

(2) Without radiation field, the atom is usually in one of its energy eigenstates. Transition involves changing the atomic state from one eigenstate to another — essentially the atomic state becomes a superposition of eigenstates. Thus, the atom has certain probability to be in another eigenstate.

Let us keep the above two points in mind and solve the time-dependent Schrödinger equation to derive transition probability.

Consider a physical system with Hamiltonian $\hat{H}_0$. The eigenvalues and eigenstates of $\hat{H}_0$ are denoted by E_n and $|\varphi_n\rangle$:

$$\hat{H}_0 |\varphi_n\rangle = E_n |\varphi_n\rangle \qquad (1)$$

Assume that $\hat{H}_0$ is <u>not</u> explicitly time-dependent. Thus, its eigenstates are stationary states given by

$$|\Phi_n(t)\rangle = |\varphi_n\rangle e^{-iE_nt/\hbar} \qquad (2)$$

which satisfies the Schrödinger equation:

$$i\hbar \frac{d}{dt} |\Phi_n(t)\rangle = \hat{H}_0 |\Phi_n(t)\rangle . \qquad (3)$$

The solution of stationary states is obtained as the following:

Since $\hat{H}_0$ is not explicitly dependent on time, we can use separation of variables and write $|\Phi_n(t)\rangle = T(t)|\varphi_n\rangle$, where $T(t)$ is a time factor and $|\varphi_n\rangle$ does not depend on t.

Substitute $|\Phi_n(t)\rangle = T(t)|\varphi_n\rangle$ into the Schrödinger equation:

$$i\hbar \frac{dT(t)}{dt} |\varphi_n\rangle = T(t)\hat{H}_0 |\varphi_n\rangle = T(t) E_n |\varphi_n\rangle$$

$$\Rightarrow i\hbar \frac{dT(t)}{dt} = T(t) E_n$$

$$\Rightarrow T(t) = T_0 e^{-iE_nt/\hbar}$$

$$\therefore |\Phi_n(t)\rangle = T_0 |\varphi_n\rangle e^{-iE_nt/\hbar}$$

Since at $t=0$, $|\Phi(t=0)\rangle = |\varphi_n\rangle$, $\Rightarrow T_0 = 1$

$$\therefore |\Phi_n(t)\rangle = |\varphi_n\rangle e^{-iE_nt/\hbar}$$

At $t=0$, a perturbation is applied to the system. The Hamiltonian operator of the system then becomes:

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t) \qquad (4)$$

Before the perturbation is added, the system is assumed to be initially in the stationary state $|\Phi_i\rangle$, an eigenstate of $\hat{H}_0$ with eigenvalue E_i.

Starting at $t=0$ when the perturbation is applied, the system evolves:

① The state $|\Phi_i\rangle$ is no longer (in general) an eigenstate of the perturbed Hamiltonian $\hat{H}(t)$.

② The state evolves to be the superposition of several eigenstates of $\hat{H}_0$. So there will be probability $P_{if}(t)$ of finding the system in another eigenstate $|\Phi_f\rangle$ of $\hat{H}_0$ at time t.

In other words, the perturbation causes the system to make transitions between the stationary states of the unperturbed system:

$$|\Phi_i\rangle \longrightarrow |\Phi_f\rangle.$$

The evolution of state $|\psi(t)\rangle$ with time is determined by the Schrödinger equation: $i\hbar \dfrac{d|\psi(t)\rangle}{dt} = \hat{H}(t)|\psi(t)\rangle \qquad (5).$

Since the stationary states of $\hat{H}_0$ form an orthonormal, complete basis, the state $|\psi(t)\rangle$ can be expanded on this basis:

$$|\psi(t)\rangle = \sum_n C_n(t)|\Phi_n(t)\rangle. \qquad (6)$$

The initial condition of $|\psi(t)\rangle$ is

$$|\psi(t=0)\rangle = |\Phi_i\rangle. \qquad (7)$$

Since $|\psi(t)\rangle$ is a superposition of the stationary states of $\hat{H}_0$, there will be probability to find the system in another stationary state $|\Phi_f\rangle$ which is different from the initial state $|\Phi_i\rangle$.

According to QM, this probability is given by:

$$P_{if}(t) = |\langle \Phi_f | \psi(t)\rangle|^2 = |C_f(t)|^2 \qquad (8)$$

$P_{if}(t)$ means the probability of finding the system in the state $|\Phi_f\rangle$ at time t when evolving from the initial state $|\Phi_i\rangle$. Thus, $P_{if}(t)$ is the transition probability of the system from the initial state $|\Phi_i\rangle$ to the final state $|\Phi_f\rangle$ at time t and under Hamiltonian operator $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$.

Therefore, the problem becomes how to solve the Schrödinger equation (5) to derive the coefficient $C_f(t)$. Substitute Eqs. (4) and (6) into Eq. (5):

$$i\hbar \sum_n \left(|\Phi_n(t)\rangle \frac{dC_n(t)}{dt}\right) + i\hbar \sum_n \left(C_n(t) \frac{\partial}{\partial t} |\Phi_n(t)\rangle\right) \qquad (9)$$
$$= \sum_n \left(C_n(t) \hat{H}_0 |\Phi_n(t)\rangle\right) + \sum_n \left(C_n(t) \hat{H}'(t) |\Phi_n(t)\rangle\right)$$

Recall Eq. (3): $i\hbar \frac{\partial}{\partial t} |\Phi_n(t)\rangle = \hat{H}_0 |\Phi_n(t)\rangle$, we can cancel the 2nd term on the left with the 1st term on the right of Eq. (9). Thus, we obtain:

$$i\hbar \sum_n \left(|\Phi_n(t)\rangle \frac{dC_n(t)}{dt}\right) = \sum_n \left(C_n(t) \hat{H}'(t) |\Phi_n(t)\rangle\right) \quad (10)$$

Use $\langle \Phi_f(t)| = |\Phi_f(t)\rangle^* = e^{iE_f t/\hbar} \langle \varphi_f|$ to time both sides of Eq. (10), we obtain:

$$i\hbar \sum_n \left(\langle \Phi_f | \Phi_n \rangle \frac{d C_n(t)}{dt} \right) = \sum_n \left(C_n(t) \langle \Phi_f | \hat{H}' | \Phi_n(t) \rangle \right) \quad (11)$$

Recall $\langle \Phi_m | \Phi_n \rangle = e^{i(E_m - E_n)t/\hbar} \langle \varphi_m | \varphi_n \rangle = e^{i(E_m-E_n)t/\hbar} \delta_{mn} = \delta_{mn}$ (12)

$\therefore$ Eq. (11) becomes :

$$i\hbar \frac{d\, C_f(t)}{dt} = \sum_n \left[C_n(t)\, e^{i(E_f - E_n)t/\hbar} \langle \varphi_f | \hat{H}' | \varphi_n \rangle \right]$$

$$= \sum_n \left[C_n(t)\, e^{i\omega_{fn} t} H'_{fn} \right] \quad (13)$$

where $\omega_{fn} \equiv (E_f - E_n)/\hbar$ (14)

$H'_{fn} \equiv \langle \varphi_f | \hat{H}' | \varphi_n \rangle$ (15)

Note that from Schrödinger equation (5) to Eq. (13), it is an exact derivation. So Eq. (13) is equivalent to Eq. (5). In other words, Eq. (13) is another form of Schrödinger Equation. To derive the transition probability $P_{if}(t) = |C_f(t)|^2$, we need to solve Eq. (13) to obtain $C_f(t)$.

It is usually difficult to solve Eq. (13) exactly, except a few occasions. ① In our class, we will introduce the exact solution for a special case — a two-level system that we will obtain the Rabi oscillation and Rabi frequency. ② Then we will introduce the time-dependent perturbation theory to solve the equation with approximations for general cases. ③ Armed with these knowledges, we will then go to the full Quantum Treatment of the Radiative Transitions.

§6.4. Semi-Classical Description of Transition Probabilities for 2-level System

① Semiclassical Description:

$\hat{H}_0 = \hat{H}_a$ (the atom is described by QM)

$\vec{E} = \vec{E}_0 \cos(\omega t - kz)$ (the radiation is described by a classical EM wave)

$\hat{H}' = \hat{\vec{p}}\cdot\vec{E} = \hat{\vec{p}}\cdot\vec{E}_0 \cos\omega t$ (the interaction between the atom and the radiation field is the dipole approximation $\hat{\vec{p}} = -e\hat{\vec{r}}$)

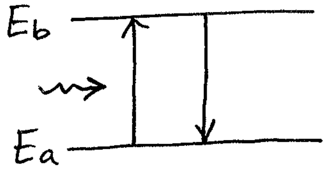
Thus, $\hat{H} = \hat{H}_0 + \hat{H}'$ as the total Hamiltonian operator.

Phenomenologically introduce A_{ki} for the spontaneous emission.

By solving the Schrödinger equation $i\hbar \dfrac{\partial|\psi(t)\rangle}{\partial t} = \hat{H}(t)\,|\psi(t)\rangle$ as described above, we can derive Einstein B coefficients B_{12} and B_{21}. But the spontaneous emission A_{21} is added phenomenologically. Only QED, i.e, the Quantization of the radiation field can naturally include the spontaneous emission.

② Weak-Field Approximation for 2-Level System.

Let us consider a 2-level atomic system, with $\hat{H}_0$ eigenstates $|\varphi_a\rangle$ and $|\varphi_b\rangle$ and eigenvalues of energy E_a and E_b. The system state $|\psi(t)\rangle$ can be expressed as the superposition of these two states:



$$|\psi(t)\rangle = a(t)\,|\varphi_a\rangle e^{-iE_a t/\hbar} + b(t)\,|\varphi_b\rangle e^{-iE_b t/\hbar} \tag{16}$$

Going through the same process as we did in Section 6.3, we will come to Eq. (13). Thus, for the 2-level system, the Schrödiger equation Eq.(13) gives us the following equations:

$$\begin{cases} i\hbar \dfrac{d\,a(t)}{dt} = a(t)\, e^{i\omega_{aa}t}\langle \varphi_a|\hat{H}'|\varphi_a\rangle + b(t)\,e^{i\omega_{ab}t}\langle\varphi_a|\hat{H}'|\varphi_b\rangle \\ i\hbar \dfrac{d\,b(t)}{dt} = a(t)\,e^{i\omega_{ba}t}\langle\varphi_b|\hat{H}'|\varphi_a\rangle + b(t)\,e^{i\omega_{bb}t}\langle\varphi_b|\hat{H}'|\varphi_b\rangle \end{cases}$$

Since $\omega_{aa} = (E_a - E_a)/\hbar = 0$, $\omega_{ab} = (E_a - E_b)/\hbar$,

$$\therefore \begin{cases} \dot{a}(t) = -\dfrac{i}{\hbar}\left[a(t)\,H'_{aa} + b(t)\,H'_{ab}\,e^{i(E_a-E_b)t/\hbar}\right] \\ \dot{b}(t) = -\dfrac{i}{\hbar}\left[a(t)\,H'_{ba}\,e^{i(E_b-E_a)t/\hbar} + b(t)\,H'_{bb}\right] \end{cases} \tag{17}$$

$$\because\ \hat{H}' = \hat{\vec{P}}\cdot\vec{E} = -e\hat{\vec{r}}\cdot\vec{E} = \hat{H}(\hat{\vec{r}})$$

$$\therefore \langle\varphi_a|\hat{H}'|\varphi_b\rangle = -eE\langle\varphi_a|\hat{\vec{r}}|\varphi_b\rangle, \quad \langle\varphi_a|\hat{H}'|\varphi_a\rangle = H'_{aa}$$

Since $\hat{\vec{r}}$ has odd parity, $\langle\varphi_a|\hat{\vec{r}}|\varphi_a\rangle = \langle\varphi_b|\hat{\vec{r}}|\varphi_b\rangle = 0$

We define the atomic dipole matrix element:

$$D_{ab} \equiv D_{ba} \equiv -e\langle\varphi_a|\hat{\vec{r}}|\varphi_b\rangle \tag{18}$$

$\Omega_{ab} = D_{ab}E_0/\hbar = \Omega_{ba}$ is called the Rabi frequency. (18b)

$$\therefore \begin{cases} \dot{a}(t) = -\dfrac{i}{\hbar}\, b(t)\cdot E_0\,\dfrac{e^{i\omega t}+e^{-i\omega t}}{2}\,D_{ab}\,e^{i\omega_{ab}t/\hbar} \\ \qquad = -\dfrac{i}{2}\,\Omega_{ab}\cdot b(t)\left[e^{i(\omega_{ab}-\omega)t} + e^{i(\omega_{ab}+\omega)t}\right] \\ \dot{b}(t) = -\dfrac{i}{2}\,\Omega_{ab}\cdot a(t)\left[e^{-i(\omega_{ab}-\omega)t} + e^{-i(\omega_{ab}+\omega)t}\right] \end{cases} \tag{19}$$

If decay into other levels is neglected, then the relation

$$|a(t)|^2 + |b(t)|^2 = 1 \tag{20}$$

must hold at all times t.

Suppose at $t=0$, the atoms are in the lower state E_a,

$\therefore\ a(0)=1,\ b(0)=0$ — initial conditions (21)

Assume the radiation field E_0 is sufficiently small so that for times $t<T=\frac{1}{\Omega_{ab}}$, the population of E_b remains small compared with that of E_a, i.e., $|b(t<T)|^2 \ll 1$. — Weak-field approximation (22)

Under this weak-field condition, we can solve Eq.(19) by an iterative procedure starting with $a^{(0)}(t)=1$, $b^{(0)}(t)=0$. This iterative procedure is to put lower order $a^{(n-1)}(t)$ and $b^{(n-1)}(t)$ into the Eq.(19) for the higher order $\dot{a}^{(n)}(t)$ and $\dot{b}^{n}(t)$. In the 1st order appr.

$$\begin{cases} \dot{a}^{(1)}(t) = -\frac{i}{2}\Omega_{ab}\, b^{(0)}(t)\left[e^{i(\omega_{ab}-\omega)t} + e^{i(\omega_{ab}+\omega)t}\right] = 0 \\ \dot{b}^{(1)}(t) = -\frac{i}{2}\Omega_{ab}\, a^{(0)}(t)\left[e^{-i(\omega_{ab}-\omega)t} + e^{-i(\omega_{ab}+\omega)t}\right] \\ \qquad\quad = \frac{i}{2}\Omega_{ab}\left[e^{i(\omega_{ba}-\omega)t} + e^{i(\omega_{ba}+\omega)t}\right] \end{cases} \quad (23)$$

From initial condition, we obtain the solution to the 1st order approximation:

$$\begin{cases} a(t) = a^{(0)}(t) + a^{(1)}(t) = a^{(0)}(t) = 1 \\ b(t) = b^{(0)}(t) + b^{(1)}(t) = \frac{\Omega_{ab}}{2}\left[\frac{e^{i(\omega_{ba}-\omega)t}}{\omega_{ba}-\omega} + \frac{e^{i(\omega_{ba}+\omega)t}}{\omega_{ba}+\omega}\right] \end{cases} \quad (24)$$

For the 1st term, noticeable absorption occurs only if ω is close to ω_{ba}, i.e., in the optical frequency range: $|\omega_{ba}-\omega| \ll \omega_{ba}$. The 2nd term $(\omega_{ba}+\omega)$, is small compared to the 1st term, and may be neglected. — Rotating-wave approximation.

In the rotating-wave approximation, the probability $|b(t)|^2$ that finding the system is in the upper level E_b at time t is

$$|b(t)|^2 = \left(\frac{\Omega_{ab}}{2}\right)^2 \left[\frac{\sin(\omega_{ba}-\omega)t/2}{(\omega_{ba}-\omega)/2}\right]^2. \quad (25)$$

Since the initial condition is that all atoms are in the lower level E_a, $|b(t)|^2$ gives the transition probability for the atom to go from E_a to E_b during the time t: $P_{ab}(t) = |b(t)|^2$.

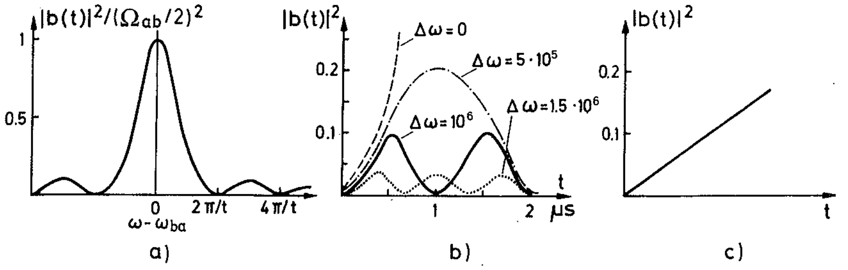


Fig. 2.18. (**a**) Normalized transition probability as a function of the detuning $(\omega-\omega_{ba})$ in the rotating-wave approximation; (**b**) probability of a transition to the upper level as a function of time for different detuning; (**c**) $|b(t)|^2$ under broadband excitation and weak fields

Since $\lim\limits_{x\to 0}\frac{(\sin xt)^2}{x^2} = t^2$, the transition probability at resonance $(\omega\to\omega_{ba})$ is given by

$$|b(t)|^2_{\omega=\omega_{ba}} = \left(\frac{\Omega_{ab}}{2}\right)^2 t^2, \qquad (26)$$

which increases proportionally with t^2. Note that the conclusion from above derivation is only valid under the following conditions:

$$|b(t)|^2 \ll 1, \text{ i.e., } \Omega_{ab}^2 t^2 \ll 1 \text{ or } t \ll T = \frac{\hbar}{D_{ab}E_0} = \frac{1}{\Omega_{ab}}. \qquad (27)$$

This small-signal approximation only holds if the maximum interaction time T of the field with the atom is restricted to $t \ll T$. Recall Heisenbergy uncertainty principle, the spectral analysis of a wave with the finite detection time T gives the spectral width $\Delta\omega \approx \frac{1}{T}$. Thus, we cannot assume monochromaticity, but have to take into account the frequency distribution of the interaction term.

③. Transition Probabilities with Broad-Band Excitation.

Let us consider a radiation source with broad bandwidth. Instead of using a single frequence $\vec{E}=\vec{E_0}\cos\omega t$, we introduce the spectral energy density $\rho(\omega)$ within the frequency range of the absorption line for the radiation field. We can generalize Eq. (25) to include the interaction of broadband radiation with our two-level system by integrating Eq. (25) over all frequencies ω of the radiation field. This yields the total transition probability $P_{ab}(t)$

Within the time t, if $\vec{D}_{ab} \parallel \vec{E}_0$:

$$P_{ab}(t) = \int |b(t)|^2 d\omega = \frac{(D_{ab})^2}{2\varepsilon_0 \hbar^2} \int \rho(\omega) \left[\frac{\sin(\omega_{ba}-\omega)t/2}{(\omega_{ba}-\omega)/2} \right]^2 d\omega . \quad (28)$$

For thermal light source or broadband laser, $\rho(\omega)$ varies slowly over the absorption line profile, so it is essentially constant over the frequency range where the Sinc function is large. So,

$$\rho(\omega) \longrightarrow \rho(\omega_{ba}) .$$

Also, consider the integration: $\displaystyle\int_{-\infty}^{+\infty} \frac{\sin^2(xt)}{x^2} dx = 2\pi t.$ (29)

For broadband excitation, the transition probability for the time interval between 0 and t is then given by

$$P_{ab}(t) = \frac{\pi}{\varepsilon_0 \hbar^2} D_{ab}^2 \rho(\omega_{ba}) t . \quad (30)$$

Note that this probability is linearly dependent on t. Thus, for broadband excitation, the transition probability per unit time

$$\frac{d}{dt} P_{ab}(t) = \frac{\pi}{\varepsilon_0 \hbar^2} D_{ab}^2 \rho(\omega_{ba}) \quad (31)$$

becomes independent of time !

To compare this result with the Einstein coefficient B_{ab} introduced phenomenologically in Section 6.2, we must take into account that the blackbody radiation is isotropic, while the EM wave used in above derivation propages into one direction. In case of the isotropic radiation, the interaction term $D_{ab}^2 \rho(\omega_{ba})$ has to be divided by a factor of 3. Thus,

$$\frac{d P_{ab}(t)}{dt} = \frac{\pi}{3\varepsilon_0 \hbar^2} \rho(\omega_{ba}) D_{ab}^2 = \rho(\omega_{ba}) \underset{\substack{\uparrow \\ \text{Einstein B coefficient}}}{B_{ab}} \quad (32)$$

Therefore, the Einstein B coefficient is given by

$$B^{\omega}_{ab} = \frac{\pi}{3\varepsilon_0 \hbar^2} D^2_{ab} \qquad (33).$$

Considering the definition of Dab (Eq. (18)), the Einstein Coefficient B_{ik} of induced absorption $E_i \rightarrow E_k$ becomes

$$B^{\omega}_{ik} = \frac{\pi e^2}{3\varepsilon_0 \hbar^2} \langle \varphi_i | \hat{\vec{r}} | \varphi_k \rangle, \quad B^{\nu}_{ik} = B^{\omega}_{ik}/2\pi \qquad (34).$$

The Einstein Coefficient B_{ik} for the transition $E_i \rightarrow E_k$ between two degenerate levels $|i\rangle$ and $|k\rangle$ is therefore

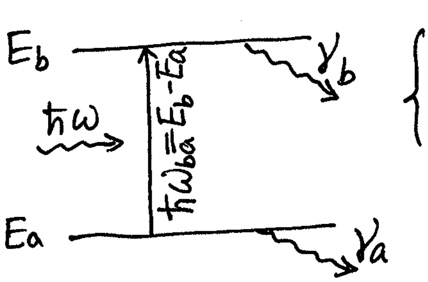
$$B_{ik} = \frac{\pi}{3\varepsilon_0 \hbar^2} \frac{1}{g_i} \sum_{m=1}^{g_i} \sum_{n=1}^{g_k} |D_{i_m k_n}|^2 = \frac{\pi}{3\varepsilon_0 \hbar^2 g_i} S_{ik}. \quad (35)$$

Here the line strength $S_{ik} = \sum_{m=1}^{g_i} \sum_{n=1}^{g_k} |D_{i_m k_n}|^2 = |D_{ik}|^2$.

④ Phenomenological Inclusion of Decay Phenomena

Above derivation is made on a "closed" or "isolated" 2-level system, i.e., $|a\rangle$ and $|b\rangle$ are not coupled with any other levels. Such system does not exist, because the states $|a\rangle$ and $|b\rangle$ are not only coupled by transition induced by the external radiation field, but also decay by spontaneous emission or by other relaxation processes such as collision-induced transitions, to couple with other energy levels.

We can include these decay phenomena in our formulas by adding phenomenological decay terms to Eq. (19), which can be expressed by the decay constants γ_a and γ_b. A rigorous treatment requires QED, i.e., quantization of the radiation field.



Two-level system with open decay channels into other levels interacting with an EM field.

$$\begin{cases} \dot{a}(t) = -\frac{1}{2}\gamma_a a(t) + \frac{i}{2}\Omega_{ab}\, e^{-i(\omega_{ba}-\omega)t}\, b(t) \\ \dot{b}(t) = -\frac{1}{2}\gamma_b b(t) + \frac{i}{2}\Omega_{ab}\, e^{+i(\omega_{ba}-\omega)t}\, a(t) \end{cases} \qquad (36)$$

Note: Eq.(36) is obtained under the rotating-wave approximation (i.e., the $(\omega_{ba}+\omega)$ term is neglected) for single frequency (ω) radiation field excitation.

When the radiation field amplitude E_0 is sufficiently small, we can use the weak-signal approximation, i.e.,

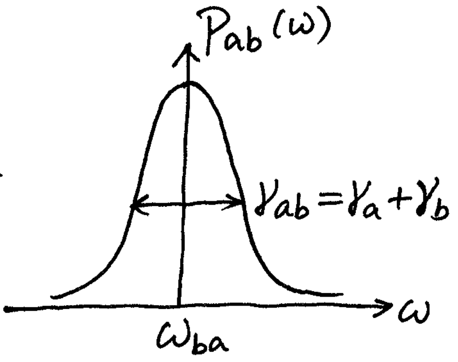
$$|a(t)|^2 = 1, \quad |b(t)|^2 \ll 1, \quad \text{and} \quad aa^* - bb^* \simeq 1. \qquad (37)$$

Thus, the transition probability for single frequency (ω) radiation field excitation and decay/relaxation is

$$P_{ab}(\omega) = |b(t,\omega)|^2 = \int \gamma_{ab}\, e^{-\gamma_{ab}t}\, |b(t)|^2\, dt$$
$$= \frac{1}{2}\, \frac{\Omega_{ab}^2}{(\omega_{ba}-\omega)^2 + \left(\frac{1}{2}\gamma_{ab}\right)^2} \qquad (38)$$

where $\gamma_{ab} = \gamma_a + \gamma_b$.

This $P_{ab}(\omega)$ is a Lorentzian line profile with a full width at half maximum γ_{ab}. $\Rightarrow$



⑤ Interaction with Strong Fields

When intense laser beams are used for the excitation of atomic transitions, the weak-field approximation is no longer valid. Therefore, we introduce Rabi's strong-field theory for 2-level system.

We consider a monochromatic field of frequency ω and start from Eq. (19) for the probability amplitudes in the rotating-wave approximation:

$$\begin{cases} \dot{a}(t) = \frac{i}{2}\Omega_{ab}\, e^{-i(\omega_{ba}-\omega)t}\, b(t) \\ \dot{b}(t) = \frac{i}{2}\Omega_{ab}\, e^{+i(\omega_{ba}-\omega)t}\, a(t) \end{cases} \qquad (39)$$

Insert the trial solution: $a(t) = e^{i\mu t}$ into Eq. (39).

$$b(t) = \frac{2}{i\Omega_{ab}} e^{i(\omega_{ba}-\omega)t} \cdot i\mu\, e^{i\mu t} = \frac{2\mu}{\Omega_{ab}} e^{i(\omega_{ba}-\omega+\mu)t}$$

$$\Rightarrow \frac{2\mu\, i(\omega_{ba}-\omega+\mu)}{\Omega_{ab}} e^{i(\omega_{ba}-\omega+\mu)t} = \frac{i\Omega_{ab}}{2} e^{i(\omega_{ba}-\omega+\mu)t}$$

$$\Rightarrow 2\mu(\omega_{ba}-\omega+\mu) = \Omega_{ab}^2/2 \Rightarrow \mu^2 + (\omega_{ba}-\omega)\mu - \Omega_{ab}^2/4 = 0$$

$$\Rightarrow \mu_{1,2} = -\frac{1}{2}(\omega_{ba}-\omega) \pm \frac{1}{2}\sqrt{(\omega_{ba}-\omega)^2 + \Omega_{ab}^2} \qquad (40)$$

The general solutions for the amplitudes a and b are then

$$\begin{cases} a(t) = C_1 e^{i\mu_1 t} + C_2 e^{i\mu_2 t} \\ b(t) = (2/\Omega_{ab})\, e^{i(\omega_{ba}-\omega)t}\left(C_1\mu_1 e^{i\mu_1 t} + C_2\mu_2 e^{i\mu_2 t}\right) \end{cases} \qquad (41)$$

With the initial conditions $a(0)=1$ and $b(0)=0$,

$$C_1 + C_2 = 1 \quad \text{and} \quad C_1\mu_1 = -C_2\mu_2$$

$$\Rightarrow C_1 = -\frac{\mu_2}{\mu_1-\mu_2}, \quad C_2 = \frac{\mu_1}{\mu_1-\mu_2}.$$

Define $\Omega \equiv \mu_1 - \mu_2 = \sqrt{(\omega_{ba}-\omega)^2 + \Omega_{ab}^2} = \sqrt{(\omega_{ba}-\omega)^2 + (\vec{D}_{ab}\vec{E}_0/\hbar)^2}$ (42)

Ω is called the general Rabi "flopping frequency" for the nonresonant case $\omega \neq \omega_{ba}$.

∴ The probability amplitude

$$b(t) = i(\Omega_{ab}/\Omega)\, e^{i(\omega_{ba}-\omega)t/2} \sin(\Omega t/2) \qquad (43)$$

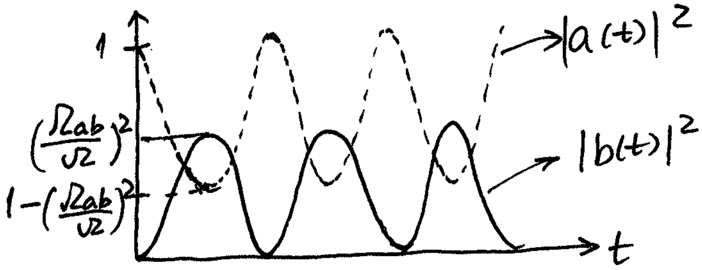
The probability of finding the system in level E_b is

$$|b(t)|^2 = (\Omega_{ab}/\Omega)^2 \sin^2(\Omega t/2) \qquad (44)$$

The probability of finding the system in level E_a is

$$|a(t)|^2 = 1 - |b(t)|^2 = 1 - (\Omega_{ab}/\Omega)^2 \sin^2(\Omega t/2) \qquad (45).$$

Eq.(44) and Eq.(45) show that the system oscillates with the frequency Ω between the levels E_a and E_b.



At resonance $\omega = \omega_{ba}$, $\Omega \longrightarrow \Omega_{ab} = D_{ab} E_0/\hbar$.

* Ω_{ab} is the Rabi flopping frequency for the resonance case $\omega = \omega_{ba}$, also called Rabi frequency.

At resonance $\omega = \omega_{ba}$,

$$\begin{cases} |a(t)|^2 = \cos^2(\Omega_{ab} t/2) \\ |b(t)|^2 = \sin^2(\Omega_{ab} t/2) \end{cases} \qquad (46)$$

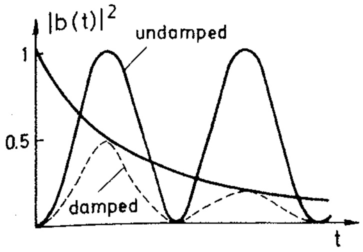


Fig. 2.20. Population probability $|b(t)|^2$ of the levels E_b altering with the Rabi flopping frequency due to the interaction with a strong field. The resonant case is shown without damping and with damping due to decay channels into other levels. The decaying curve represents the factor $\exp[-(\gamma_{ab}/2)t]$

On resonance, $|a(t)|^2$ and $|b(t)|^2$ oscillate between 0 and 1 sequentially. This means all atoms transit between E_a and E_b periodically, going from all on E_a to all on E_b, and vice versa.

We now include the damping terms γ_a and γ_b, and obtain the $\boxed{\gamma = \gamma_a - \gamma_b}$ transition probability

$$|b(t)|^2 = \frac{\Omega_{ab}^2\, e^{-\gamma_{ab} t/2}\, [\sin(\Omega t/2)]^2}{(\omega_{ba} - \omega)^2 + (\gamma/2)^2 + \Omega_{ab}^2} . \qquad (47)$$

This is the damped oscillation with the damping constant $\frac{1}{2}\gamma_{ab} = (\gamma_a + \gamma_b)/2$, with the Rabi flopping frequency

$$\Omega = \sqrt{(\omega_{ba} - \omega + \tfrac{1}{2}\gamma)^2 + \Omega_{ab}^2} . \qquad (48)$$

The spectral profile of the transition probability Eq. (47) is Lorentzian.

§6.5. Transition Probability for General Cases:
Time-Dependent Perturbation Theory

(1). Time-Dependent Perturbation Theory

The approximation method is valid under the condition of

$$\hat{H}'(t) \ll \hat{H}_0 \qquad (49).$$

Thus, the $\hat{H}'$ can be treated as a perturbation to $\hat{H}_0$ states.

We write $C_n(t)$ in the expansion of many orders of approximations:

$$C_n(t) = C_n^{(0)}(t) + C_n^{(1)}(t) + C_n^{(2)}(t) + \cdots \qquad (50).$$

The initial conditions for solving the Schrödinger equation is that at $t=0$, $|\psi(0)\rangle \equiv |\psi(t=0)\rangle = |\Phi_i(t=0)\rangle = |\varphi_i\rangle$. (51)

From Eq. (6), we have:

$$C_f(t=0) = \langle \Phi_f(t=0) | \psi(0)\rangle = \langle \Phi_f | \Phi_i \rangle = \delta_{fi} \qquad (52)$$

Substitute Eq. (50) into the Schrödinger Eq. (13), we obtain

$$i\hbar \frac{dC_f^{(0)}(t)}{dt} + i\hbar \frac{dC_f^{(1)}(t)}{dt} + i\hbar \frac{dC_f^{(2)}(t)}{dt} + \cdots$$

$$= \sum_n C_n^{(0)}(t)\, e^{i\omega_{fn}t} H'_{fn} \qquad (53)$$

$$+ \sum_n C_n^{(1)}(t)\, e^{i\omega_{fn}t} H'_{fn}$$

$$+ \sum_n C_n^{(2)}(t)\, e^{i\omega_{fn}t} H'_{fn} + \cdots$$

We then set equal the terms of same order approximation on both sides of the equation (53). Note: Since $\hat{H}' \ll \hat{H}_0$, H'_{fn} is already a first order approximation. Considering $C_n^{(0)}(t)$ is the zeroeth-order approximation of the coefficient $C_n(t)$, the first term on the right side of Eq. (53) is already a first order approximation. Therefore, there is <u>no</u> zeroeth-order term on the right side of Eq. (53). So we have:

$$\begin{cases} i\hbar \dfrac{dC_f^{(0)}(t)}{dt} = 0 & (54) \\ i\hbar \dfrac{dC_f^{(1)}(t)}{dt} = \sum\limits_n C_n^{(0)}(t)\, e^{i\omega_{fn}t}\, H'_{fn} & (55) \\ i\hbar \dfrac{dC_f^{(2)}(t)}{dt} = \sum\limits_n C_n^{(1)}(t)\, e^{i\omega_{fn}t}\, H'_{fn} & (56) \\ \cdots\cdots \end{cases}$$

From Eq. (54), we get $C_f^{(0)}(t) = \text{Constant}$ (57)

From the initial condition Eq. (51), $C_f(t=0) = \delta_{fi}$

Since $\hat{H}'(t=0) = 0$, we have $\begin{cases} C_f^{(r)}(t=0) = 0, & (r \geq 1) \\ C_f^{(0)}(t=0) = \delta_{fi}. \end{cases}$

Considering Eq. (57), we have

$$\begin{cases} C_f^{(0)}(t) = C_f^{(0)}(t=0) = \delta_{fi} & (58). \\ C_n^{(0)}(t) = \delta_{ni} \end{cases}$$

Substitute Eq. (58) into Eq. (55), we have

$$i\hbar \frac{d C_f^{(1)}(t)}{dt} = e^{i\omega_{fi} t} H'_{fi}(t) \quad (59).$$

The equation can be integrated to give

$$C_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{fi} t'} H'_{fi}(t') dt' \quad (60).$$

Since the final state $|\Phi_f\rangle$ is different from the initial state $|\Phi_i\rangle$, from Eq. (58), we have $C_f^{(0)}(t) = 0$. (61).

Therefore, by taking the first order approximation, we get

$$C_f(t) = C_f^{(0)}(t) + C_f^{(1)}(t)$$

$$= \frac{1}{i\hbar} \int_0^t e^{i\omega_{fi} t'} H'_{fi}(t') dt' \quad (62).$$

From our discussion above about the transition probability and Eq. (8), the transition probability from $|\Phi_i\rangle$ to $|\Phi_f\rangle$ under $\hat{H}'(t)$ perturbation is given by

$$P_{if}(t) = |C_f(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{fi} t'} H'_{fi}(t') dt' \right|^2. \quad (63).$$

In spectroscopy, we usually use a term called transition rate, which is defined as the transition probability in unit time, i.e.,

$$W_{if}(t) = \frac{d P_{if}(t)}{dt} = \frac{d}{dt} |C_f(t)|^2 \quad (64)$$

$$= \frac{1}{\hbar^2} \frac{d}{dt} \left| \int_0^t e^{i\omega_{fi} t'} H'_{fi}(t') dt' \right|^2.$$

Note: from the point of view of time-dependent perturbation theory, after integratig Eq. (60) to obtain $C_f^{(1)}(t)$, $C_f^{(1)}(t)$ can be substituted into the 2nd order equation (56) to derive $C_f^{(2)}(t)$. This procedure can go on to higher order approximations $C_f^{(r)}(t)$.

Then $C_f(t) = \sum_r C_f^{(r)}(t)$, (65)

so the transition probability $P_{if}(t) = |C_f(t)|^2$.

transition rate: $W_{if}(t) = \frac{d P_{if}(t)}{dt} = \frac{d |C_f(t)|^2}{dt}$

The time-dependent perturbation theory, like Eqs. (63) and (64), gives the general equation for transition probability. We need to derive the matrix element $H'_{fi} \equiv \langle \varphi_f | \hat{H}' | \varphi_i \rangle$, which depends on ① the perturbation $\hat{H}'$ and ② the eigenstates $|\varphi_f\rangle$ and $|\varphi_i\rangle$.

(2) For radiation absorption and transition, we care about the periodic perturbation (i.e., sinusoidal perturbation like EM waves):

$$\hat{H}' = \hat{F} \cos\omega t = \frac{\hat{F}}{2}\left(e^{i\omega t} + e^{-i\omega t}\right) \qquad (66)$$

where W is a time-independent operator, and ω is a constant angular flequency of the EM wave. Substitute Eq. (66) into Eq. (62):

$$C_f(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{fi}t'} H'_{fi}(t')\,dt'$$

$$= \frac{F_{fi}}{2i\hbar}\int_0^t e^{i\omega_{fi}t'}\left(e^{i\omega t'} + e^{-i\omega t'}\right)dt' \qquad (67)$$

$$= \frac{F_{fi}}{2i\hbar}\int_0^t \left[e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'}\right]dt'$$

$$= -\frac{F_{fi}}{2\hbar}\left[\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi}+\omega} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi}-\omega}\right]$$

Therefore, under the sinusoidal perturbation, the transition probability is given by

$$P_{if}(t) = |C_f(t)|^2 = \frac{|F_{fi}|^2}{4\hbar^2}\left|\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi}+\omega} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi}-\omega}\right|^2 \qquad (68)$$

$$\boxed{F_{fi} = \langle \varphi_f | \hat{F} | \varphi_i \rangle}$$

Eq. (68) reveals the resonance nature of the transition probability:

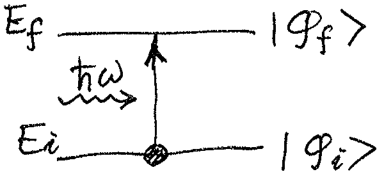
Case 1: When $\omega \approx \omega_{fi}$, the 2nd term on the right side of Eq. (68) is much larger than the first term:

$$A_- = \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi}-\omega} = i e^{i(\omega_{fi}-\omega)t/2} \frac{\sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)/2} \qquad (69)$$

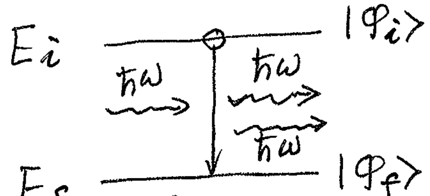
Case 2: When $\omega \approx -\omega_{fi}$, the first term becomes dominant

$$A_+ = \frac{e^{i(\omega_{fi}+\omega)t} - 1}{2} = i e^{i(\omega_{fi}+\omega)t/2} \frac{\sin[(\omega_{fi}+\omega)t/2]}{(\omega_{fi}+\omega)/2} \qquad (70).$$

Let us choose $\omega \geq 0$ all the time, then Case 1, $\omega_{fi} \approx \omega > 0$, means $E_f > E_i$, i.e., the atom absorbs a photon and makes a transition from the lower level $|\varphi_i\rangle$ to the higher level $|\varphi_f\rangle$



Case 1



Case 2

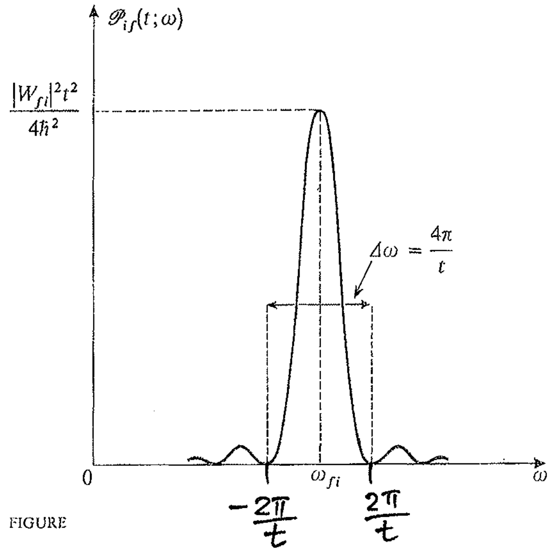
Case 2, $\omega_{fi} \approx -\omega < 0$, means $E_f < E_i$, i.e., the atom goes from the higher level $|\varphi_i\rangle$ to the lower level $|\varphi_f\rangle$ by stimulatedly emitting a photon.

When ω is far away from $\pm\omega_{fi}$, the transition probability is very small. Thus, the transitions we care about are a resonance phenomenon.

Therefore, when $\omega \approx \omega_{fi}$, we only take A_- term, and when $\omega \approx -\omega_{fi}$, we only take A_+ term. Thus, the transition probability is given by

$$P_{if}(t) = \frac{|F_{fi}|^2}{4\hbar^2} \frac{\sin^2[(\omega_{fi} \pm \omega) t/2]}{[(\omega_{fi} \pm \omega)/2]^2}, \qquad (71)$$

where "+" for $\omega \approx -\omega_{fi}$ (emission) and "−" for $\omega \approx \omega_{fi}$ (absorption).



FIGURE

Variation, with respect to ω, of the first-order transition probability $\mathscr{P}_{if}(t;\omega)$ associated with a sinusoidal perturbation of angular frequency ω; t is fixed. When $\omega \simeq \omega_{fi}$, a resonance appears whose intensity is proportional to t^2 and whose width is inversely proportional to t.

An example for $\omega \approx \omega_{fi}$ (absorption) case is shown in above figure for fixed time t. This clearly shows the resonant nature of the transition probability: The probability reaches the maximum when $\omega = \omega_{fi}$. As we move away from ω_{fi}, the transition probability decreases, going to zero for $|\omega - \omega_{fi}| = 2\pi/t$. When $|\omega - \omega_{fi}|$ continues to increase, the probability oscillates between a much smaller value $\frac{|W_{fi}|^2}{\hbar^2(\omega - \omega_{fi})^2}$ and zero.

(3) The resonance width $\Delta\omega$ can be approximately defined as the distance between the two zeros of $P_{if}(t)$ about $\omega = \omega_{fi}$.

$$\Delta\omega \approx \frac{4\pi}{t} \qquad (72)$$

⇒ The larger the time t, the smaller this width.

Eq. (72) presents a certain analogy with the time-energy uncertainty relation. Assume that we want to measure the energy difference $E_f - E_i = \hbar\omega_{fi}$ by applying a sinusoidal perturbation of angular frequency ω to the system, and varying ω so as to detect the resonance. If the perturbation acts during a time t, the uncertainty ΔE on the value $E_f - E_i$ will be of the order of

$$\Delta E = \hbar \Delta\omega \approx \frac{\hbar}{t} 4\pi .$$

$\therefore \quad \Delta E \cdot t > \hbar$. This recalls the time-energy uncertainty relation: $\quad \Delta E \cdot \Delta t \geqslant \frac{\hbar}{2}$.

Note: here, the t is the time of measurements. Since the measurement time t is not infinite, it will cause uncertainty of the energy level E_f. When no perturbation presents, due to the spontaneous emission A_{21}, the lifetime — the time interval of the free evolution of the atom — is finite, the energy level E_f (higher than ground state) has uncertainty: $\quad \Delta E_f \cdot \tau \geqslant \frac{\hbar}{2}$. (73)

Thus, the spontaneously emitted spectral lines have certain width for resonance $\Delta\omega = \frac{\Delta E_f}{\hbar} \geqslant \frac{1}{2\tau}$, which also results in the natural linewidth for absorption.

Note: Above approximation is valid under the condition:

$$\Delta\omega = |\omega - \omega_{fi}| << 2\omega_{fi}$$

Thus, $\Delta t = t \gg \frac{1}{\omega_{fi}} \simeq \frac{1}{\omega}$ is required condition.

(4) When t is large enough ($t \to \infty$), Eq.(71) takes the limit of

$$\lim_{t\to\infty} \frac{\sin^2[(\omega_{fi} \pm \omega)t/2]}{[(\omega_{fi} \pm \omega)/2]^2} = \pi t\, \delta[(\omega_{fi} \pm \omega)/2] \qquad (74)$$

Recall $\delta(ax) = \frac{1}{a}\delta(x)$, (75)

then Eq.(74) becomes: $\lim_{t\to\infty} \frac{\sin^2[(\omega_{fi} \pm \omega)t/2]}{[(\omega_{fi} \pm \omega)/2]^2} = 2\pi t\, \delta(\omega_{fi} \pm \omega)$ (76)

From Eq.(71),

$$\therefore\ P_{if}(t) = \frac{\pi t}{2\hbar^2} |F_{fi}|^2 \delta(\omega_{fi} \pm \omega) \qquad (77)$$

The transition rate:

$$W_{if}(t) = \frac{d P_{if}(t)}{dt} = \frac{\pi}{2\hbar^2} |F_{fi}|^2 \delta(\omega_{fi} \pm \omega)$$

$$= \frac{\pi}{2\hbar} |F_{fi}|^2 \delta(E_f - E_i \pm \hbar\omega) \qquad (78)$$

$$\boxed{\text{Note: } \delta(ax) = \frac{1}{a}\delta(x),\ \therefore\ \delta\left(\frac{E_f - E_i}{\hbar} \pm \omega\right) = \hbar\, \delta(E_f - E_i \pm \hbar\omega)}$$

This further exhibits the resonance feature of radiation absorption and emission.

(5) Limits of the first-order calculation:

The first-order approximation can cease to be valid when the time becomes too large. This can be seen from two examples:

① From Eq.(71), at resonance $\omega = \pm\omega_{fi}$, the transition probability

$$P_{if}(t) = \frac{|F_{fi}|^2}{4\hbar^2} t^2 \qquad (79)$$

Note: $\frac{\sin^2 x}{x^2} = 1$ when $x = 0$, $\therefore\ \frac{\sin^2[(\omega_{fi} \pm \omega)t/2]}{[(\omega_{fi} \pm \omega)/2]^2} = t^2$ @ $\omega = \pm\omega_{fi}$

② From Eq. (77), at resonance $\omega = \pm\omega_{fi}$,

$$P_{if}(t) = \frac{\pi t}{2\hbar^2}|F_{fi}|^2 \qquad (80)$$

Both Eq. (79) and Eq. (80) become infinite when $t \to \infty$, which is absurd, since a probability can never be greater than 1.

In practice, for the first-order approximation to be valid at resonance, the probability in Eqs. (79) or (80) must be much smaller than 1, i.e.,

$$t \ll \frac{\hbar}{|F_{fi}|} \qquad (81)$$

Indeed, for this theory to be meaningful, it is necessary to have another condition to be matched:

$$t \gg \frac{1}{|\omega_{fi}|} \qquad (82)$$

Thus, for the 1st-order approximation to be valid, the conditions below must be matched:

$$\frac{1}{|\omega_{fi}|} \ll t \ll \frac{\hbar}{|F_{fi}|} \qquad (83).$$

i.e., $$\frac{1}{\hbar|\omega_{fi}|} = \frac{1}{|E_f - E_i|} \ll \frac{1}{|F_{fi}|} \qquad (84)$$

The energy difference $|E_f - E_i| = \hbar|\omega_{fi}|$ must be much larger than the matrix element $|F_{fi}|$.

To show precisely why the inequality Eq. (81) and Eq. (82) is related to the validity of the first-order approximation, it would be necessary to calculate the higher-order correction and to examine under what conditions they are negligible. It turns the inequality Eq. (81) is a necessary condition, but not rigorously sufficient.

The problem of calculating the transition probability when t does not satisfy Eq. (81) can be found in the complement C_{XIII} in the book "Quantum Mechanics" Volume Two by Claude Cohen-Tannoudji (Nobel Laureat), in which an approximation of a different method is used — the secular approximation. Of course, higher-order perturbation theory can also be used.

(6) Non-monochromatic Radiation Field Excitation:

Above we only consider monochromatic waves. When the radiation has certain linewidth (bandwidth), i.e., not a single sinusoidal wave any more, we can take Fourier transform on the radiation field:

$$\hat{H}'(t) = \int_{-\infty}^{+\infty} \hat{H}'(\omega)\, e^{-i\omega t}\, d\omega , \qquad (85)$$

where $\hat{H}'(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \hat{H}'(t)\, e^{i\omega t}\, dt$.

is the amplitude of monochromatic wave with angular frequency ω in the Fourier transform of $\hat{H}'(t)$.

Thus, the matrix element $\hat{H}'_{fi}(t) \equiv \langle \varphi_f | \hat{H}'(t) | \varphi_i \rangle$ is given by

$$H'_{fi}(t) = \int_{-\infty}^{+\infty} H'_{fi}(\omega)\, e^{-i\omega t}\, d\omega. \qquad (86)$$

$$\therefore C_f(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{fi}t'} \cdot H'_{fi}(t')\, dt'$$

$$= \frac{1}{i\hbar}\int_0^t e^{i\omega_{fi}t'}\, dt' \int_{-\infty}^{+\infty} H'_{fi}(\omega)\, e^{-i\omega t}\, d\omega$$

$$= \frac{1}{i\hbar}\int_{-\infty}^{+\infty} d\omega\, H'_{fi}(\omega)\, 2\pi\, \delta(\omega_{fi}-\omega)$$

$$= \frac{2\pi}{i\hbar} H'_{fi}(\omega_{fi}) \qquad (87)$$

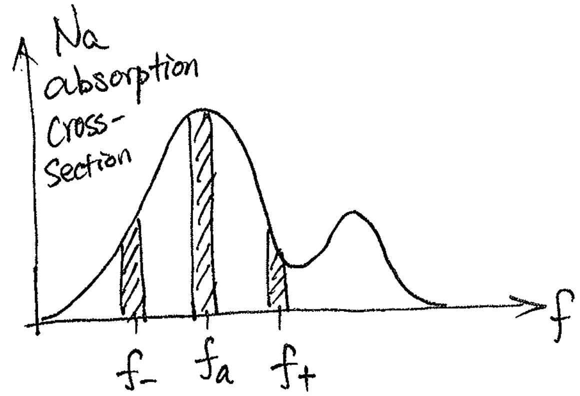
$$\therefore P_{if}(t) = |C_f(t)|^2 = \frac{4\pi^2}{\hbar^2}\,|H'_{fi}(\omega_{fi})|^2 \qquad (88)$$

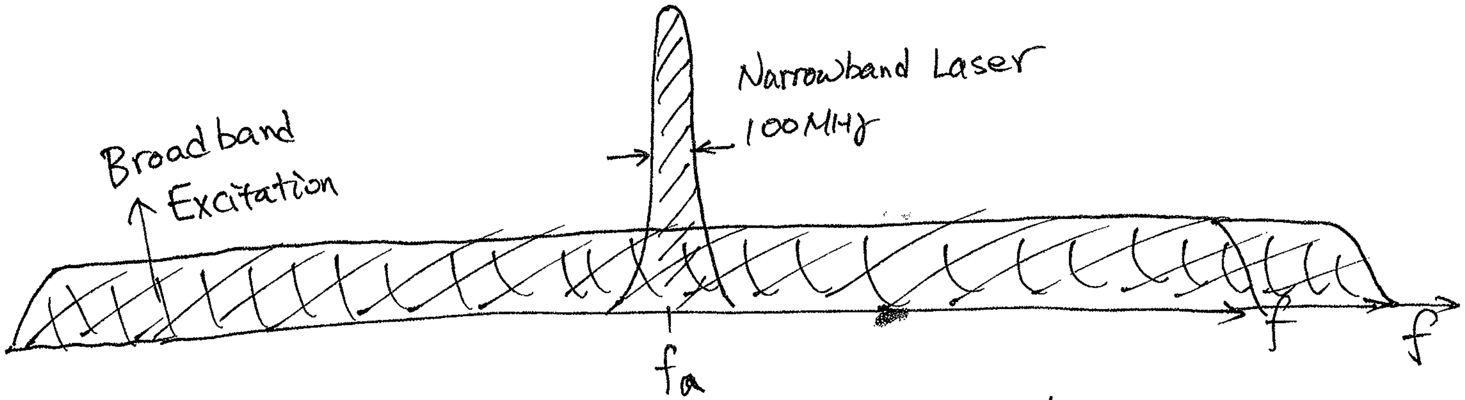
Therefore, the transition probability is proportional to the matrix element $|H'_{fi}(\omega_{fi})|^2$, $\hat{H}'_{fi}(t)$'s component at angular frequency ω_{fi}. This makes lots of sense, because for a broad-band excitation, the useful energy is only the energy at the frequency of Bohr frequency ω_{fi}. Energy at other frequencies is useless.

Example: in Na lidar application, we want ~100 MHz narrow-band laser light @ 3 frequencies. The available power is ~ 1.5 W. Now somebody can produce 10W power @ 589 nm but with 5 GHz linewidth. The useful power is about $\frac{100\text{ MHz}}{5\text{ GHz}} \times 10\text{W} = \frac{1}{50} \times 10\text{W} = 0.2\text{W}$

For 100 MHz laser @ 3-freq, useful power $\frac{1.5\text{W}}{3} = 0.5\text{W}$.

— The narrowband is better!!!





Why do we want to waste energy/power at the frequencies where we can't have resonance?

— Narrowband Laser is better!!!

§6.6. Full Quantum Treatment of Radiative Transitions

The good reference books for this subject are

① "The Quantum Theory of Light" by Rodney Loudon

② "Atomic Spectra and Radiative Transitions" by Igor I. Sobelman

The good reference books for Perturbation Theory are

① "Quantum Mechanics" by L. D. Landau

② "Quantum Mechanics" by Claude Cohen-Tannoudji

As we have described in the earlier sections, the semi-classical theory can describe the stimulated/induced absorption and emission very well, but cannot naturally include the spontaneous emission. In the semi-classical theory, the radiation field strengths $\vec{E}$ and $\vec{B}$ are treated as classical variables, while the atoms are treated quantum-mechanically. Quantization conditions on the energy of the radiation field were used to derive Planck's law, but the concept of photons has played a small role in the subsequent theory. This semi-classical theory provides the correct theoretical expressions for a wide range of quantities.

The most complete description of the radiation field must be sought in quantum-mechanical terms, where the field observables $\hat{\vec{E}}$ and $\hat{\vec{B}}$ are represented by operators. This full quantum treatment is applied to the electromagnetic field. We obtain expressions for the operators that represent the various field observables and we describe the various kinds of field state that can be envisaged in the quantum picture. Quantization introduces characteristic quantum-mechanical effects into the properties of the radiation field.

1. Quantization of the Radiation Field

(1) Potential theory for the classical EM field

The quantum theory of the radiation field has many similarities with the classical theory. The field vectors in quantum theory must be taken as operators instead of the algebraic quantities of classical theory, but both theories are based on Maxwell's equations. It is not possible to derive the quantum theory from the classical equations, but the transition to quantum mechanics can be accomplished most easily if the equations of classical EM theory are first put into a suitably suggestive form. The first task here is to cast the classical equations in a form where the harmonic-oscillator dependence of the field variables is suitable for conversion to quantum mechanics.

Maxwell's Equations for EM field in nonmagnetic medium:

$$\begin{cases} \nabla \times \vec{E} = -\partial \vec{B}/\partial t \\ \frac{1}{\mu_0} \nabla \times \vec{B} = \varepsilon_0 (\partial \vec{E}/\partial t) + \vec{J} \\ \varepsilon_0 \nabla \cdot \vec{E} = \sigma \\ \nabla \cdot \vec{B} = 0 \end{cases}$$

where σ and $\vec{J}$ ar the charge and current densities, respectively.

The quantization procedure is facilitated if the classical Maxwell equations are re-expressed in terms of the scalar and vector potentials, ϕ and $\vec{A}$, respectively. In terms of scalar potential ϕ and vector potential $\vec{A}$,

$$\begin{cases} \vec{E} = -\nabla\phi - \frac{\partial \vec{A}}{\partial t} & (89) \\ \vec{B} = \nabla \times \vec{A} & (90) \end{cases}$$

where $\nabla \times \nabla\phi \equiv 0$, i.e., ϕ is a scalar function.

If the potentials are known, Eqs. (89) and (90) enable $\vec{E}$ and $\vec{B}$ to be found. The potentials can be determined by the followings

$$\begin{cases} \nabla(\nabla\cdot\vec{A})-\nabla^2\vec{A}+\frac{1}{c^2}\frac{\partial}{\partial t}\nabla\phi+\frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t}=\mu_0\vec{J} & (91) \\ -\varepsilon_0\nabla^2\phi-\varepsilon_0\nabla\cdot(\partial\vec{A}/\partial t)=\sigma & (92) \end{cases}$$

where $\nabla\times\nabla\times\vec{A}\equiv\nabla(\nabla\cdot\vec{A})-\nabla^2\vec{A}$.

It is possible to simplify the equations by the imposition of some additional conditions on the potentials $\vec{A}$ and ϕ. It is important to realize that Eqs. (89) and (90) do not completely specify the forms of the potentials $\vec{A}$ and ϕ. The potentials $\vec{A}$ and ϕ can be varied, within certain limits, without any resulting change in the observable fields $\vec{E}$ and $\vec{B}$. This kind of transformation is called "gauge" tranformation. It should be emphasized that $\vec{E}$ and $\vec{B}$, the physically measurable fields, do not depend in any way on the choice of gauge for $\vec{A}$ and ϕ. However, the freedom of choice provided by gauge invariance can often be used to obtain considerable simplifications in the calculation of $\vec{E}$ and $\vec{B}$.

(2) The Coulomb Gauge

The EM field is said to be in the Coulomb gauge when the vector potential satisfies the condition

$$\nabla\cdot\vec{A}=0 \qquad (93).$$

For a field specified originally by a pair of potentials $\vec{A_0}$ and ϕ_0, it is alway possible to transform to the Coulomb gauge by a gauge transformation like

$$\begin{cases} \vec{A}=\vec{A_0}-\nabla\theta \\ \phi=\phi_0+(\partial\theta/\partial t) \end{cases} \qquad (94)$$

Under Coulomb transformation, Eqs. (91) and (92) are simplified to

$$\begin{cases} -\nabla^2\vec{A} + \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} + \frac{1}{c^2}\frac{\partial}{\partial t}\nabla\phi = \mu_0\vec{J} & (95) \\ -\nabla^2\phi = \sigma/\varepsilon_0 & (96) \end{cases}$$

According to Helmholtz' theorem, any vector field can be written as a sum of two components, one of which has zero divergence and the other of which has zero curl. For the case of the current density $\vec{J}$, the sum is

$$\vec{J} = \vec{J}_T + \vec{J}_L, \qquad (97)$$

where $\nabla\cdot\vec{J}_T = 0$, $\nabla\times\vec{J}_L = 0$

J_T and J_L are the transverse and longitudinal components, respectively.

Thus, Eq. (95) can be simplified to

$$-\nabla^2\vec{A} + \frac{1}{c^2}\frac{\partial^2\vec{A}}{\partial t^2} = \mu_0\vec{J}_T \qquad (98).$$

in considering $\vec{J}_L = \varepsilon_0\nabla\partial\phi/\partial t$.

The solution of Eq. (98) is

$$\vec{A}(\vec{r},t) = \frac{\mu_0}{4\pi}\int\frac{\vec{J}_T(\vec{r}\,',t')}{|\vec{r}-\vec{r}\,'|}d^3\vec{r}\,' \qquad (99)$$

Where

$$t' = t - |\vec{r}-\vec{r}\,'|/c \qquad (100)$$

The vector potential $\vec{A}$ at position $\vec{r}$ and time t thus includes explicitly the effect of the finite velocity of light in delaying the arrival at $\vec{r}$ of the influence of the current at a distant point $\vec{r}\,'$. An observer at $\vec{r}$ can have a knowledge of the current distribution at $\vec{r}\,'$ only as it existed at the retarded time t' given by Eq. (100).

The scalar potential ϕ can be obtained from Eq. (96):

$$\phi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int\frac{\sigma(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3\vec{r}\,' \qquad (101)$$

The electric field vector $\vec{E}$ can also be divided into transverse and longitudinal parts: $\vec{E} = \vec{E}_T + \vec{E}_L$ (102)

where $\nabla \cdot \vec{E}_T = \nabla \times \vec{E}_L = 0$ (103).

Thus,

$$\begin{cases} \vec{E}_T = -\partial \vec{A}/\partial t, & (104) \\ \vec{E}_L = -\nabla \phi & (105) \end{cases}$$

The magnetic field vector $\vec{B}$ is entirely transverse accordg to the Maxwell equation $\nabla \cdot \vec{B} = 0$.

The great advantage of the Coulomb gauge, for the problem of the radiation field and its interaction with charges and current, lies in the separation of the field equations and Maxwell's equations into two distinct parts. The longitudinal part is associated with the scalar potential ϕ:

$$\begin{cases} \nabla \cdot \vec{E}_L = -\nabla^2 \phi = \sigma/\varepsilon_0 & (106) \\ \vec{J}_L = -\varepsilon_0 \partial \vec{E}_L/\partial t & (107) \end{cases}$$

The longitudinal equations describe the fields arising from the charges, as determined by the equations of electrostatics.

The transverse part is associated with the vector potential $\vec{A}$:

$$\begin{cases} \nabla \times \vec{E}_T = -\partial \vec{B}/\partial t \\ \frac{1}{\mu_0} \nabla \times \vec{B} = \varepsilon_0 (\partial \vec{E}_T/\partial t) + \vec{J}_T \\ \nabla \cdot \vec{E}_T = 0 \\ \nabla \cdot \vec{B} = 0 \end{cases} \quad (108)$$

The transverse equations describe EM waves, which are influenced only by $\vec{J}_T$.

The separation of the equations into a static part (longitudinal) associated with the charge density and a dynamic part (transverse) associated with the EM waves is a formal consequence of the Coulomb gauge condition.

(3) The free classical field

If a region of space where $\vec{J}_T = 0$, and hence

$$-\nabla^2 \vec{A} + \frac{1}{c^2}\frac{\partial^2 \vec{A}}{\partial t} = 0, \qquad (109)$$

the field in such a region of space is said to be free.

The quantization of the EM field proceeds by the replacement of the classical vector potential $\vec{A}$ by a quantum-mechanical operator $\hat{\vec{A}}$. The final manipulation on the classical field leads to a form of the classical equations in which the transition to quantum Mechanics is straightforward.

Let us consider a cubic region of space of side L, merely as a region of space without any real boundaries. We take running waves and subject them to periodic boundary conditions. Thus, the vector potential in the "cavity" can be expanded in a Fourier series:

$$\vec{A} = \sum_{\vec{K}} \{ \vec{A}_K(t) \exp(i\vec{K}\cdot\vec{r}) + \vec{A}_K^*(t) \exp(-i\vec{K}\cdot\vec{r}) \} \qquad (110)$$

where the components of the wavevector $\vec{K}$ take the values

$$K_x = 2\pi N_x/L, \quad K_y = 2\pi N_y/L, \quad K_z = 2\pi N_z/L, \qquad (111)$$

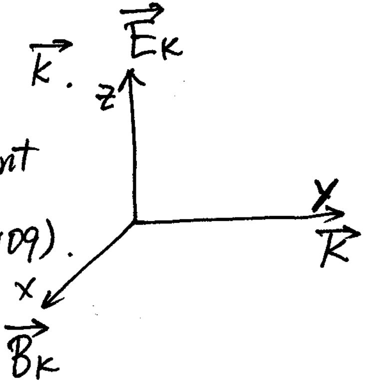
with $N_x, N_y, N_z = 0, \pm 1, \pm 2, \pm 3, \cdots$

The wave vector $\vec{K} = \frac{2\pi}{L}(N_x \hat{i} + N_y \hat{j} + N_z \hat{k})$. The Coulomb gauge condition Eq. (93) is satisfied if

$$\vec{K}\cdot\vec{A}_K(t) = \vec{K}\cdot\vec{A}^*(t) = 0 \qquad (112)$$

There are two independent directions of $\vec{A}_K(t)$ for each $\vec{K}$. The different Fourier components of $\vec{A}$ are independent and must separately satisfy the field equation Eq.(109). Thus,

$$K^2 \vec{A}_K(t) + \frac{1}{c^2}\frac{\partial^2 \vec{A}_K(t)}{\partial t^2} = 0 \qquad (113)$$



and $\vec{A}_K^*(t)$ satisfies the same equation.

The Fourier coefficients therefore satisfy the simple-Harmonic equation: $\left(\partial^2 \vec{A}_K(t)/\partial t^2\right) + \omega_K^2 \vec{A}_K(t) = 0$ (114)

where $\omega_K = c \cdot k$ (115)

The solution of Eq.(114) can be taken as

$$\vec{A}_K(t) = \vec{A}_K \exp(-i\omega_K t) . \qquad (116)$$

Thus, the complete vector potential becomes

$$\vec{A} = \sum_K \left[\vec{A}_K \exp(-i\omega_K t + i\vec{K}\cdot\vec{r}) + \vec{A}_K^{*} \exp(i\omega_K t - i\vec{K}\cdot\vec{r}) \right]. \qquad (117)$$

The cycle-averaged energy content of a single mode $\vec{K}$ is

$$\bar{\mathcal{E}}_K = \frac{1}{2}\int_{cavity} \left(\varepsilon_0 \overline{\vec{E}_K^2} + \frac{1}{\mu_0} \overline{\vec{B}_K^2} \right) dV \qquad (118)$$

where the bars denote a cycle average, and $\vec{E}_K$ and $\vec{B}_K$ are the electric and magnetic fields associated with the mode. Thus,

$$\begin{cases} \vec{E}_K = -\frac{\partial \vec{A}_K}{\partial t} = i\omega_K \left[\vec{A}_K \exp(-i\omega_K t + i\vec{K}\cdot\vec{r}) - \vec{A}_K^{*} \exp(i\omega_K t - i\vec{K}\cdot\vec{r}) \right] & (119) \\ \vec{B}_K = \nabla \times \vec{A}_K = i\vec{K} \times \left[\vec{A}_K \exp(-i\omega_K t + i\vec{K}\cdot\vec{r}) - \vec{A}_K^{*} \exp(i\omega_K t - i\vec{K}\cdot\vec{r}) \right], & (120) \end{cases}$$

(If $\vec{K}$ is along y-axis, $\vec{E}_K$ is along z-axis, then $\vec{B}_K$ is in x-axis.)

Substitute Eqs.(119) and (120) into Eq.(118), the energy

$$\bar{\mathcal{E}}_K = 2\varepsilon_0 V \omega_K^2 \vec{A}_K \cdot \vec{A}_K^{*} \qquad (121)$$

where $V = L^3$.

The mode variables $\vec{A}_K$ and $\vec{A}_K^{*}$ can be replaced by a generalized mode "position" coordinate Q_K and mode "momentum" P_K in accordance with the transformations

$$\vec{A}_K = (4\varepsilon_0 V \omega_K^2)^{-1/2} (\omega_K Q_K + iP_K) \vec{e}_K \qquad (122)$$

$$\vec{A}_K^{*} = (4\varepsilon_0 V \omega_K^2)^{-1/2} (\omega_K Q_K - iP_K) \vec{e}_K \qquad (123)$$

The coordinates Q_K and P_K are scalar quantities, the directional properties of $\vec{A}_K$ and $\vec{A}_K^*$ having been separated by the introduction of a unit polarization vector $\vec{e}_K$ for the mode. Thus, the single-mode energy

$$\bar{\mathcal{E}}_K = \frac{1}{2}(P_K^2 + \omega_K^2 Q_K^2) \qquad (124).$$

This is precisely the usual form of the energy of a classical harmonic oscillator. The problem of the vector potential associated with a cavity mode has been made formally equivalent to a classical harmonic-oscillator problem. The complete classical Hamiltonian for the cavity is formed by taking a sum over $\vec{K}$, and the two independent directions of $\vec{e}_K$ of the single mode-expression Eq.(124).

(4) The quantum-mechanical harmonic oscillator

The EM field is quantized by converting Q_K and P_K into quantum-mechanical position and momentum operators $\hat{\vec{q}}_K$ and $\hat{\vec{P}}_K$.

The QM Hamiltonian for a 1-D harmonic oscillator of unit mass is

$$\hat{H} = \frac{1}{2}(\hat{p}^2 + \omega^2 \hat{q}^2) \qquad (125)$$

where $\hat{p}$ and $\hat{q}$ obey the usual commutation relation:

$$[\hat{q}, \hat{p}] = i\hbar \qquad (126)$$

Define a pair of operators $\hat{a}$ and $\hat{a}^+$ to replace $\hat{q}$ and $\hat{p}$.

$$\hat{a} = (2\hbar\omega)^{-\frac{1}{2}}(\omega\hat{q} + i\hat{p}) \qquad (127)$$

$$\hat{a}^+ = (2\hbar\omega)^{-\frac{1}{2}}(\omega\hat{q} - i\hat{p}) \qquad (128)$$

Thus,
$$\hat{q} = (\hbar/2\omega)^{\frac{1}{2}}(\hat{a} + \hat{a}^+) \qquad (129)$$

$$\hat{p} = -i(\hbar\omega/2)^{\frac{1}{2}}(\hat{a} - \hat{a}^+) \qquad (130)$$

The operators $\hat{a}$ and $\hat{a}^+$ are called the destruction and creation operators for the harmonic oscillator. They do not, however, represent observables of the harmonic oscillator.

From Eqs. (127–128), we have

$$\begin{aligned}\hat{a}^+\hat{a} &= (2\hbar\omega)^{-1}(\hat{p}^2+\omega^2\hat{q}^2+\underbrace{i\omega\hat{q}\hat{p}-i\omega\hat{p}\hat{q}}_{i\omega[\hat{q},\hat{p}]=-\hbar\omega}) \\ &= (\hbar\omega)^{-1}(\hat{H}-\tfrac{1}{2}\hbar\omega) \qquad (131)\end{aligned}$$

Similarly, $\hat{a}\hat{a}^+ = (\hbar\omega)^{-1}(\hat{H}+\frac{1}{2}\hbar\omega)$ (132)

Thus, the commutator of the new operators is

$$[\hat{a},\hat{a}^+] = \hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = 1 \qquad (133)$$

From Eq. (132), we obtain $\hat{H} = \hbar\omega(\hat{a}^+\hat{a}+\frac{1}{2})$ (134)

The operator $\underline{\underline{\hat{a}^+\hat{a}}}$ is called the number operator of the oscillator, and we denote it as $\hat{n} \equiv \hat{a}^+\hat{a}$. (135)

Let $|n\rangle$ be an energy eigenstate of the harmonic oscillator with eigenvalue E_n. The eigenvalue equation is

$$\hat{H}|n\rangle = \hbar\omega(\hat{a}^+\hat{a}+\tfrac{1}{2})|n\rangle = E_n|n\rangle \qquad (136)$$

Multiply both sides from the left by $\hat{a}^+$

$$\hbar\omega(\hat{a}^+\hat{a}^+\hat{a}+\tfrac{1}{2}\hat{a}^+)|n\rangle = E_n\hat{a}^+|n\rangle \qquad (137)$$

Utilizing Eq. (133), Eq. (137) becomes

$$\hbar\omega(\hat{a}^+\hat{a}\hat{a}^+-\hat{a}^++\tfrac{1}{2}\hat{a}^+)|n\rangle = E_n\hat{a}^+|n\rangle, \qquad (138)$$

which can be re-arranged as

$$\hbar\omega(\hat{a}^+\hat{a}+\tfrac{1}{2})\hat{a}^+|n\rangle = (E_n+\hbar\omega)\hat{a}^+|n\rangle = \hat{H}\hat{a}^+|n\rangle \qquad (139)$$

The last equation again has the form of an energy eigenvalue equation. It shows that the state $\hat{a}^+|n\rangle$ is an eigenstate of the harmonic oscillator with eigenvalue $E_n + \hbar\omega$.

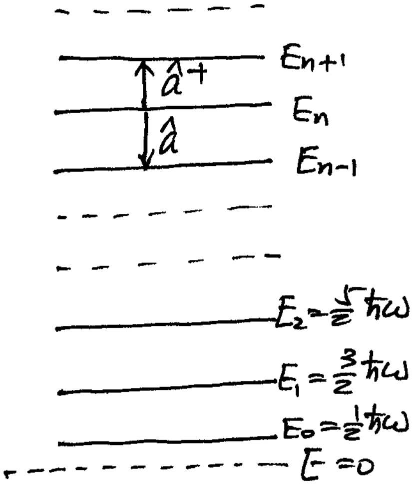
We define the new eigenstate and eigen value as

$$\begin{cases} |n+1\rangle = \hat{a}^+ |n\rangle & (140) \\ E_{n+1} = E_n + \hbar\omega & (141) \end{cases}$$

Thus, Eq. (139) can be written as

$$\hat{H} |n+1\rangle = E_{n+1} |n+1\rangle \qquad (142)$$

These results show that, given a harmonic-oscillator energy level E_n, there exists another level $\hbar\omega$ above the first. The energy levels thus form an equally-spaced ladder. As in classical mechanics, there is no maximum energy restriction for the harmonic oscillator, and the ladder of levels extends upwards to infinity.



The lower end of the ladder can be investigated by multiplication of Eq. (136) from the left by $\hat{a}$. We obtain

$$\hat{H}\hat{a}|n\rangle = (E_n - \hbar\omega)\hat{a}|n\rangle \qquad (143)$$

Thus, the state $\hat{a}|n\rangle$ is an energy eigenstate with eigenvalue $E_n - \hbar\omega$. We define

$$|n-1\rangle = \hat{a}|n\rangle \qquad (144)$$

$$E_{n-1} = E_n - \hbar\omega \qquad (145)$$

So $\hat{H}|n-1\rangle = E_{n-1}|n-1\rangle$. (146)

The ladder of energy levels thus extends downwards with equal steps $\hbar\omega$. However, the ladder must have a lower end because the oscillator kinetic and potential energies are positive quantities, and the eigenvalues are not allowed to be negative.

Let $|0\rangle$ be the ground state with energy E_0. Eq. (143) gives, for the ground state,
$$\hat{H}\,\hat{a}\,|0\rangle = (E_0 - \hbar\omega)\,\hat{a}\,|0\rangle \qquad (147)$$
Since by hypothesis, there is no eigenstate of lower energy than the ground state, the only solution of Eq. (147) consistent with this physical interpretation is
$$\hat{a}\,|0\rangle = 0 \qquad (148)$$
The ground-state condition can be used to determine E_0, since Eq. (136) for the groundstate becomes
$$\begin{aligned}\hat{H}\,|0\rangle &= \hbar\omega(\hat{a}^+\hat{a} + \tfrac{1}{2})|0\rangle \\ &= \hbar\omega\hat{a}^+(\hat{a}\,|0\rangle) + \tfrac{1}{2}\hbar\omega|0\rangle \\ &= 0 + \tfrac{1}{2}\hbar\omega|0\rangle\end{aligned}$$
$$\therefore\quad \hat{H}\,|0\rangle = \tfrac{1}{2}\hbar\omega|0\rangle = E_0\,|0\rangle \qquad (149)$$
Thus, the energy eigenvalue $E_0 = \frac{1}{2}\hbar\omega \qquad (150)$

The energy eigenvalues for the harmonic oscillator are
$$E_n = (n + \tfrac{1}{2})\,\hbar\omega. \qquad (151)$$
As shown in the Figure on page II 151, $\hat{a}$ and $\hat{a}^+$ destroy or create a quantum $\hbar\omega$ in the oscillator's excitation energy, and thus producing a step down or up the ladder. The states $|n\rangle$ are simultaneous eigenstates of $\hat{H}$ and $\hat{n}$:
$$\hat{n}\,|n\rangle = \hat{a}^+\hat{a}\,|n\rangle = n\,|n\rangle \qquad (152)$$
The eigenvalue of $\hat{n}$ indicates the number of quanta $\hbar\omega$ excited above the oscillator ground state.

To normalize the eigenstate $|n\rangle$, i.e., to make

$$\langle n-1|n-1\rangle = \langle n|n\rangle = \langle n+1|n+1\rangle = 1 \qquad (153)$$

let us consider the effect of these conditions on Eq. (144). Insert a number factor e_n. $e_n|n-1\rangle = \hat{a}\,|n\rangle$

$$\langle n-1|e_n^* e_n|n-1\rangle = \langle n|\hat{a}^+\hat{a}|n\rangle = n\langle n|n\rangle = n$$

$$\Rightarrow |e_n|^2 = n \quad \Rightarrow \quad e_n = \sqrt{n}\,.$$

Thus, $\hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle \qquad (154)$

Similarly, $\hat{a}^+|n\rangle = \sqrt{n+1}\,|n+1\rangle. \qquad (155)$

Different energy eigenstates of the harmonic oscillators are orthogonal and the only non-vanishing matrix elements of $\hat{a}$ and $\hat{a}^+$ are those of the types

$$\langle n-1|\hat{a}|n\rangle = \sqrt{n} \qquad (156)$$

$$\langle n+1|\hat{a}^+|n\rangle = \sqrt{n+1} \qquad (157)$$

Every Hermitian operator $\hat{o}$ has matrix elements that satisfy the condition $\langle i|\hat{o}|j\rangle = \langle j|\hat{o}|i\rangle^* \qquad (158)$

It is clear that $\hat{a}$ and $\hat{a}^+$ are not Hermitian operators, and according to the general principles of QM, they cannot represent observable quantities. However, their property of destroying or creating a quantum of energy, when applied to an energy eigenstate of the oscillator is easily appreciated in a physical sense. Next, we will use $\hat{a}$ and $\hat{a}^+$ to quantize the radiation field.

(5) Quantization of the Field

The EM field is now quantized by the association of a quantum-mechanical harmonic oscillator with each mode $\vec{k}$ of the radiation field. The mode to which a quantum-mechanical operator refers is indicated by a subscript. $\hat{a}_k^+$ and $\hat{a}_k$ are the operators that creat and destroy a quantum of energy $\hbar\omega_k$ in the cavity EM-field mode of wavevector $\vec{k}$. These quanta are the photons of wavevector $\vec{k}$; the number of photons $\vec{k}$ excited in the cavity is determined by the eigenvalue n_k of the appropriate number operator $\hat{n}_k = \hat{a}^+\hat{a}$, and has possible values $0, 1, 2, \cdots$. The excitation level of a cavity mode $\vec{k}$ is determined by its eigenstate $|n_k\rangle$. The creation, destruction, and number operators for mode $\vec{k}$ applied to $|n_k\rangle$ obey the following rules:

$$\hat{a}_k |n_k\rangle = \sqrt{n_k}\, |n_k - 1\rangle \quad , \quad \hat{a}|0\rangle = 0 . \tag{159}$$

$$\hat{a}_k^+ |n_k\rangle = \sqrt{n_k + 1}\, |n_k + 1\rangle \tag{160}$$

$$\hat{n}_k |n_k\rangle = n_k |n_k\rangle \tag{161}$$

The states of the total radiation field in the cavity can be specified by the numbers of photons $n_{k_1}, n_{k_2}, n_{k_3}, \cdots$ excited in the complete set of cavity modes $\vec{k_1}, \vec{k_2}, \vec{k_3}, \cdots$.

In counting the normal modes, it must be remembered that for each wavevector $\vec{k}$, there are two independent directions of the mode polarization $\vec{e}_k$. Here we let the single symbol $\vec{k}$ stand for both the wavevector and polarization of a mode. With this convention, the phrase "a particular normal mode $\vec{k}$" implies that both the wavevector and polarization of the mode are specified.

A state of the total field can be written as $|n_{k1}, n_{k2}, n_{k3}, \cdots\rangle$ and is specified by a string of numbers. Since the different cavity modes are independent, the state of the total field can be written as a product of the states of the individual modes

$$|n_{k1}, n_{k2}, n_{k3}, \cdots\rangle = |n_{k1}\rangle |n_{k2}\rangle |n_{k3}\rangle \cdots . \qquad (162)$$

The states of the individual cavity modes will always be assumed normalized, and it follows that the total state of the field is also normalized. An operator that refers to a particular normal mode $\vec{K}_i$ affects only the photons in that particular mode, for example,

$$\hat{a}^{+}_{ki} |n_{k1}, n_{k2}, n_{k3}, \cdots, n_{ki}, \cdots\rangle = \sqrt{n_{ki}+1}\, |n_{k1}, n_{k2}, \cdots, n_{ki}+1, \cdots\rangle \qquad (163)$$

Sometimes, we denote the states of the total field by the short-hand

$$|\{n_k\}\rangle = |n_{k1}\rangle |n_{k2}\rangle |n_{k3}\rangle \cdots \qquad (164)$$

The symbols $\{n_k\}$ here denote the complete set of numbers that specify the excitation levels of all the harmonic oscillators associated with the cavity modes. There is always an infinite numbers of oscillators. The $|\{n_k\}\rangle$ form a complete set of states for the EM field in the cavity when every member n_{ki} of the set $\{n_k\}$ is allowed to take on the values zero and all the positive integers.

The classical vector potential $\vec{A}_k$ and $\vec{A}^*_k$ for cavity mode $\vec{K}$ expressed in term of P_k and Q_k by Eqs. (122) and (123) are converted into quantum-mechanical operators expressed in terms of $\hat{P}_k$ and $\hat{q}_k$:

$$\vec{A}_k = (4\varepsilon_0 V \omega_k^2)^{-1/2} (\omega_k Q_k + i P_k) \vec{e}_k \longrightarrow$$
$$(4\varepsilon_0 V \omega_k^2)^{-1/2} (\omega_k \hat{q}_k + i \hat{P}_k) \hat{\vec{e}}_k = (\hbar / 2\varepsilon_0 V \omega_k)^{\frac{1}{2}} \hat{a}_k \hat{\vec{e}}_k \qquad (165)$$

$$\vec{A}^*_k = (4\varepsilon_0 V \omega_k^2)^{-1/2} (\omega_k Q_k - i P_k) \vec{e}_k \longrightarrow$$
$$(4\varepsilon_0 V \omega_k^2)^{-1/2} (\omega_k \hat{q}_k - i \hat{p}_k) \hat{\vec{e}}_k = (\hbar / 2\varepsilon_0 V \omega_k)^{\frac{1}{2}} \hat{a}^{+}_k \hat{\vec{e}}_k \qquad (166)$$

The relationships given by Eqs. (127) and (128) have been used above.

The transition from classical to quantum mechanics thus consists of the replacement of the classical fourier coefficients $\vec{A}_k$ and $\vec{A}_k^*$ by the destruction operator $\hat{a}_k$ and the creation operator $\hat{a}_k^+$, multiplied by a numerical factor and a unit vector. The quantum-mechanical expression for the total vector potential is obtained by substitution of Eqs. (165) and (166) into Eq. (117):

$$\hat{\vec{A}} = \sum_k (\hbar/2\varepsilon_0 V\omega_k)^{1/2}\,\hat{\vec{e}}_k\left\{\hat{a}_k \exp(-i\omega_k t + i\vec{k}\cdot\hat{\vec{r}}) + \hat{a}_k^+ \exp(i\omega_k t - i\vec{k}\cdot\hat{\vec{r}})\right\} \tag{167}$$

The corresponding results for the electric and magnetic field operators $\hat{\vec{E}}_k$ and $\hat{\vec{B}}_k$ associated with mode $\vec{k}$ are obtained by making similar substitutions in Eqs. (119) and (120):

$$\hat{\vec{E}}_k = i(\hbar\omega_k/2\varepsilon_0 V)^{1/2}\,\hat{\vec{e}}_k\left\{\hat{a}_k \exp(-i\omega_k t + i\vec{k}\cdot\hat{\vec{r}}) - \hat{a}_k^+ \exp(i\omega_k t - i\vec{k}\cdot\hat{\vec{r}})\right\} \tag{168}$$

$$\hat{\vec{B}}_k = i(\hbar/2\varepsilon_0 V\omega_k)^{1/2}\,\vec{k}\times\hat{\vec{e}}_k\left\{\hat{a}_k \exp(-i\omega_k t + i\vec{k}\cdot\hat{\vec{r}}) - \hat{a}_k^+ \exp(i\omega_k t - i\vec{k}\cdot\hat{\vec{r}})\right\}. \tag{169}$$

The operators for the total transverse electric and magnetic fields are

$$\hat{\vec{E}}_T = \sum_k \hat{\vec{E}}_k, \qquad \hat{\vec{B}} = \sum_k \hat{\vec{B}}_k \tag{170}$$

The field energy becomes $\bar{\mathcal{E}}_k = \frac{1}{2}\int_{\text{cavity}} \langle n_k|\,\varepsilon_0 \hat{\vec{E}}_k\cdot\hat{\vec{E}}_k + \frac{1}{\mu_0}\hat{\vec{B}}_k\cdot\hat{\vec{B}}_k\,|n_k\rangle\, dV.$

It can be proven that $\bar{\mathcal{E}}_k = (n_k + \frac{1}{2})\hbar\omega_k$. (171)

The Hamitonian operator for the total EM field in the cavity is

$$\hat{H}_f = \sum_k \hbar\omega_k(\hat{a}_k^+\hat{a}_k + \tfrac{1}{2}) \tag{172}$$

The total energy of the radiation for cavity state $|\{n_k\}\rangle$ is

$$\bar{\mathcal{E}} = \sum_k \bar{\mathcal{E}}_k = \sum_k (n_k + \tfrac{1}{2})\hbar\omega_k. \tag{173}$$

2. Radiative Transition Probabilities

Radiative transitions are to deal with the interaction between an atom and a radiation field. Armed with the quantized radiation field, here let us treat the radiative transitions with full quantum mechanics, i.e., a quantized atom interacts with a quantized radiation field.

When the atom and the radiation field have interaction, the total Hamiltonian operator is given by

$$\hat{H} = \hat{H}_a + \hat{H}_f + \hat{H}_{int} \qquad (174)$$

where $\hat{H}_a$, $\hat{H}_f$, and $\hat{H}_{int}$ are the Hamiltonian operators of the atom, the radiation field, and the interaction. The idea behind the total Hamiltonian operator $\hat{H}$ is that the atom and the radiation field are treated as a whole system, and both are described by quantum mechanics.

$$\hat{H}_a = \sum_i \frac{\hat{\vec{P}}_i^{\,2}}{2\mu} + U \qquad (175)$$

$$\hat{H}_f = \sum_k \hbar\omega_k \left(\hat{a}_k^+ \hat{a}_k + \frac{1}{2}\right) \qquad (176)$$

where $\sum_i$ is to take sum for all electrons inside the atom, U includes all interactions that determine the atomic state, like the Coulomb interaction between the nucleus and electrons, electrostatic interaction between electrons, spin-orbit coupling, nuclear spin-electron coupling, and constant external field influence, etc. $\hat{a}_k^+$ is the creation operator, $\hat{a}_k$ is the annihilation operator (also called destruction operator).

Assume $\hat{H}_a$ has eigenstates $|a\rangle$ and $|b\rangle$:

$$\hat{H}_a|a\rangle = E_a|a\rangle, \quad \hat{H}_a|b\rangle = E_b|b\rangle. \qquad (177)$$

$\hat{H}_f$ has eigenstates $|n_{k\lambda}\rangle$ and $|n_{k\lambda}\pm 1\rangle$

$$\hat{H}_f|n_{k\lambda}\rangle = (n_{k\lambda}+\tfrac{1}{2})\hbar\omega_{k\lambda}|n_{k\lambda}\rangle \qquad (178)$$

$$\hat{H}_f|n_{k\lambda}\pm 1\rangle = (n_{k\lambda}\pm 1+\tfrac{1}{2})\hbar\omega_{k\lambda}|n_{k\lambda}\rangle$$

Note that both $\hat{H}_a$ and $\hat{H}_f$ are independent of time.

Let $\quad \hat{H}_0 = \hat{H}_a + \hat{H}_f \qquad (179)$

$$|A\rangle = |a\rangle|n_{k\lambda}\rangle = |a, n_{k\lambda}\rangle \qquad (180)$$

$$|B\rangle = |b\rangle|n_{k\lambda}\pm 1\rangle = |b, n_{k\lambda}\pm 1\rangle \qquad (181)$$

Note: The reason that we can write $|A\rangle$ and $|B\rangle$ as Eqs.(180-181) is that $\hat{H}_a$ and $\hat{H}_f$ are independent of each other.

Thus, we have

$$\hat{H}_0|A\rangle = [E_a + (n_{k\lambda}+\tfrac{1}{2})\hbar\omega_{k\lambda}]|A\rangle = E_A|A\rangle \qquad (182)$$

$$\hat{H}_0|B\rangle = [E_b + (n_{k\lambda}\pm 1+\tfrac{1}{2})\hbar\omega_{k\lambda}]|B\rangle = E_B|B\rangle \qquad (183)$$

where $\quad E_A \equiv E_a + (n_{k\lambda}+\tfrac{1}{2})\hbar\omega_{k\lambda} \qquad (184)$

$\qquad E_B \equiv E_b + (n_{k\lambda}\pm 1+\tfrac{1}{2})\hbar\omega_{k\lambda} \qquad (185)$

From Eqs.(182) and (183), we know the eigenstates

$$|\psi_A(t)\rangle = |A\rangle e^{-iE_At/\hbar}, \quad |\psi_B(t)\rangle = |B\rangle e^{-iE_Bt/\hbar} \qquad (186)$$

satisfy the Schrödinger equation:

$$i\hbar\frac{d}{dt}|\psi_N(t)\rangle = \hat{H}_0|\psi_N(t)\rangle, \quad N=A,B \qquad (187)$$

The total Hamiltonian operator $\hat{H}$ is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{int} \qquad (188)$$

The idea is to treat $\hat{H}_{int}$ as a time-dependent perturbation to $\hat{H}_0$, and then use perturbation theory (1st order) to derive the transition probability. Similar to what we did in the semi-classical theory, the initial conditions are

$$C_A(0) = 1, \quad C_{N\neq A}(0) = 0, \text{ i.e., the system is at } |\psi_A^{(t=0)}\rangle \qquad (189)$$

For Schrödinger equation $i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)$, (190)

the state $|\psi(t) = \sum_N C_n(t)|\psi_N(t)\rangle$ (191)

The probability of the system in state $|\psi_B(t)\rangle$ at time t is given by $|C_B(t)|^2$

Similar to the derivation we did in semi-classical theory,

$$i\hbar \frac{d}{dt} C_B^{(1)}(t) = C_A^{(0)}(t)\, e^{i(E_B - E_A)t/\hbar} \langle B|\hat{H}_{int}|A\rangle$$

$$\Rightarrow i\hbar \frac{d}{dt} C_B^{(1)}(t) = e^{i(E_B - E_A)t/\hbar} \langle B|\hat{H}_{int}|A\rangle. \qquad (192)$$

$$\therefore C_B^{(1)}(t) = \frac{1}{i\hbar}\int_0^t e^{i(E_B - E_A)t/\hbar} \langle B|\hat{H}_{int}|A\rangle\, dt \qquad (193)$$

Therefore, the transition probability from $|A\rangle$ to $|B\rangle$ is

$$P_{A\to B}(t) = |C_B(t)|^2 = |C_B^{(1)}(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t e^{i(E_B - E_A)t/\hbar} \langle B|\hat{H}_{int}|A\rangle dt\right|^2 \qquad (194)$$

The transition probability per unit time:

$$W_{A\to B}(t) = \frac{d P_{A\to B}(t)}{dt} = \frac{1}{\hbar^2}\frac{d}{dt}\left|\int_0^t e^{i(E_B - E_A)t/\hbar} \langle B|\hat{H}_{int}|A\rangle\right|^2 \qquad (195)$$

To derive the transition probability, we must write out the interaction Hamiltonian operator $\hat{H}_{int}$. For the entire system of the atom interacting with the radiation field, another way to write the total Hamiltonian $\hat{H}$ is

$$\hat{H} = \hat{H}_f + \sum_i \left\{ \frac{[\vec{\hat{P}}_i - e\vec{\hat{A}}(t)]^2}{2\mu} - \frac{e}{\mu}\vec{\hat{S}}_i \vec{\hat{B}} \right\} + U \qquad (196)$$

where $\vec{\hat{S}}_i \cdot \vec{\hat{B}}$ represents the interaction of the spin magnetic moment of the electron with the oscillating magnetic field of the plane wave.

Eq.(196) can be further derived to

$$\hat{H} = \hat{H}_f + \underbrace{\left(\sum_i \frac{\vec{\hat{P}}_i^{\,2}}{2\mu} + U\right)}_{\hat{H}_a} - \sum_i \left(\frac{e}{\mu}\vec{\hat{P}}_i \cdot \vec{\hat{A}} + \frac{e}{\mu}\vec{\hat{S}}_i\cdot\vec{\hat{B}} - \frac{e^2}{2\mu}(\vec{\hat{A}}(t))^2\right) \qquad (197)$$

$$\therefore \quad \hat{H}_{int} = -\sum_i \left[\frac{e}{\mu}\vec{\hat{P}}_i \cdot \vec{\hat{A}}(t) + \frac{e}{\mu}\vec{\hat{S}}_i\cdot\vec{\hat{B}} - \frac{e^2}{2\mu}(\vec{\hat{A}}(t))^2\right] \qquad (198)$$

The first two terms in Eq.(198) depend on $\vec{\hat{A}}$ linearly, and the third one depends on it quadratically. With normal light sources, the intensity is sufficiently low that the effect of the $\vec{\hat{A}}^2$ term can be neglected.

To compare the 1st and the 2nd terms, $\vec{\hat{S}}$ is on the order of $\hbar$, $\vec{\hat{B}}$ is of the order of kA. Thus, $(k = 2\pi/\lambda)$ (p is momentum)

$$\frac{\vec{\hat{S}}_i\cdot\vec{\hat{B}}}{\vec{\hat{P}}_i\cdot\vec{\hat{A}}} \simeq \frac{\hbar k A_0}{p A_0} = \frac{\hbar k}{p}$$

$\hbar/p$ is, at most, of the order of atomic dimension (Bohr radius $\underset{0.5\,\text{Å}}{\underset{\parallel}{a_0}}$)

$k = 2\pi/\lambda$, $\therefore$

$$\frac{\vec{\hat{S}}_i\cdot\vec{\hat{B}}}{\vec{\hat{P}}_i\cdot\vec{\hat{A}}} \simeq \frac{a_0}{\lambda} \ll 1 \qquad (199)$$

The large inequality comes from the fact light wavelength is ~100nm or more for most cases we study.

Thus, $$\frac{e^2}{2\mu}\hat{\vec{A}}^2(t) \ll \frac{e}{\mu}\hat{\vec{S}}_i\cdot\hat{\vec{B}} \ll \frac{e}{\mu}\hat{\vec{P}}_i\cdot\vec{B} \qquad (200)$$

Let us only consider the $\hat{\vec{P}}_i\cdot\hat{\vec{A}}(t)$ term for now:

$$\hat{H}_{int} = -\sum_i\left[\frac{e}{\mu}\hat{\vec{P}}_i\cdot\hat{\vec{A}}(t)\right] \qquad (201)$$

Substitute Eq. (167) into Eq. (201),

$$\hat{H}_{int} = -\sum_i\sum_k\frac{e}{\mu}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\left(\hat{\vec{e}}_k\cdot\hat{P}_i\right)\left\{\hat{a}_k e^{-i\omega_k t+i\vec{k}\cdot\hat{\vec{r}}} + \hat{a}_k^{+} e^{i\omega_k t-i\vec{k}\cdot\hat{\vec{r}}}\right\} \qquad (202)$$

Some complication occurs here. Since we define the atom and the radiation field as an entire system, the interactions between them are regarded as internal interaction. Because no external interaction is introduced, the entire system energy (the atom + the radiation field) should be conservative. This means that the total Hamiltonian $\hat{H}$ is independent of time in the representation $\{\psi_N(t)=|N\rangle e^{-iE_N t/\hbar},\ N=A, B, \cdots\}$

Since $\hat{H}_a$ and $\hat{H}_f$ are independent of time, $\hat{H}_{int}$ should be turned into time-independent operator, i.e., set $t=0$:

$$\hat{H}_{int} = -\frac{e}{\mu}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\left(\hat{\vec{e}}_k\cdot\hat{\vec{P}}\right)\left\{\hat{a}_k e^{i\vec{k}\cdot\hat{\vec{r}}} + \hat{a}_k^{+} e^{-i\vec{k}\cdot\hat{\vec{r}}}\right\} \qquad (203)$$

Note: Here we only consider single electron atom and single mode radiation field to simplify the $\hat{H}_{int}$ to Eq. (203).

This is called Schrödinger representation (or picture), i.e., operators are independent of time, but all time-dependence is included in the state vector.

Appendix: Schrödinger, Heisenberg, and Interaction Representation

These are three different ways to handle the time factor.

(1) Schrödinger Representation (Picture)

All observable operators are independent of time.

The time factors are included only in the state vectors.

For example, when we use $\{\psi_N = |N\rangle e^{-iE_N t/\hbar},\ N=A,B,\cdots\}$ as the Representation, we are working in the Schrödinger Representation.

This is because $\hat{H} = \hat{H}_a + \hat{H}_f + \hat{H}_{int}$ all operators are time-independent, and $e^{-iE_N t/\hbar} = e^{-i(\hat{H}_a + \hat{H}_f)t/\hbar}$ includes all time dependence factors.

(2) Heisenberg Representation (Picture)

All state vectors are independent of time,

Time factors are included only in the operators.

Heisenberg representation is opposite to Schrödinger representation.

(3) Interaction Representation (Picture)

Schrödinger and Heisenberg Representations are two extremes, While the Interaction Representation is in the middle — Part of time factors are included in the state vector, and other part of time factors are included in the operators.

For example, in the semi-classical theory, we use

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \left(\hat{H}_0 + \hat{H}'(t)\right) |\psi(t)\rangle$$

where $\hat{H}_0$ is time-independent, but both $\hat{H}'(t)$ and $|\psi(t)\rangle$ are time-dependent. All representations are equivalent, i.e., giving the same results, but they can make problems simplified.

Since $\hat{H}_{int}$ is time-independent, we can obtain from the 1st order perturbation equation Eq. (193) the coefficient $C_B^{(1)}(t)$:

$$C_B^{(1)}(t) = \frac{1}{i\hbar}\cdot\frac{1}{i(E_B-E_A)/\hbar}\langle B|\hat{H}_{int}|A\rangle e^{i(E_B-E_A)t/\hbar}\Big|_0^t$$

$$= \frac{-1}{\hbar}\,\frac{e^{i(E_B-E_A)t/\hbar}-1}{(E_B-E_A)/\hbar}\,\langle B|\hat{H}_{int}|A\rangle \qquad (204)$$

Since

$$\frac{e^{i(E_B-E_A)t/\hbar}-1}{(E_B-E_A)/\hbar} = e^{i(E_B-E_A)t/2\hbar}\,\frac{\sin[(E_B-E_A)t/2\hbar]}{(E_B-E_A)/2\hbar} \qquad (205)$$

∴ The transition probability from $|A\rangle \rightarrow |B\rangle$ is (Eq. (194))

$$P_{A\to B} = |C_B(t)|^2 = |C_B^{(1)}(t)|^2 = \frac{|\langle B|\hat{H}_{int}|A\rangle|^2}{\hbar^2}\,\frac{\sin^2[(E_B-E_A)t/2\hbar]}{[(E_B-E_A)/2\hbar]^2} \qquad (206)$$

Since

$$\lim_{t\to\infty}\frac{\sin^2[(E_B-E_A)t/2\hbar]}{[(E_B-E_A)/2\hbar]^2} = \pi t\,\delta[(E_B-E_A)/2\hbar]$$

$$\boxed{\delta(ax) = \frac{1}{a}\delta(x)} \qquad = 2\pi\hbar t\,\delta(E_B-E_A) \qquad (207)$$

Thus, for large t,

$$P_{A\to B} = \frac{2\pi t}{\hbar}|\langle B|\hat{H}_{int}|A\rangle|^2\,\delta(E_B-E_A) \qquad (208)$$

From Eqs. (184) and (185), we have

$$E_B - E_A = [E_b + (n_k \pm 1 + \tfrac{1}{2})\hbar\omega_k] - [E_a + (n_k + \tfrac{1}{2})\hbar\omega_k]$$

$$= E_b - E_a \pm \hbar\omega_k$$

$$\therefore\ P_{A\to B} = \frac{2\pi t}{\hbar}|\langle B|\hat{H}_{int}|A\rangle|^2\,\delta(E_b - E_a \pm \hbar\omega_k) \qquad (209)$$

The transition probability per unit time is

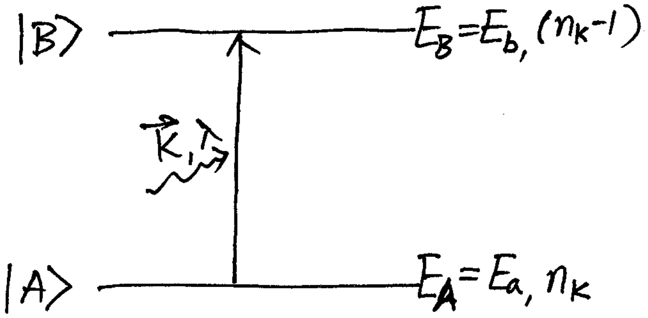
$$W_{A\to B} = \frac{dP_{A\to B}}{dt} = \frac{2\pi}{\hbar}|\langle B|\hat{H}_{int}|A\rangle|^2\delta(E_b - E_a \pm \hbar\omega_k) \quad (210)$$

Again, as we stated in the semi-classical theory, Eqs. (209) and Eq. (210) are valid only for conditions of

$$\frac{\hbar}{|E_b - E_a|} \ll t \ll \frac{\hbar}{|\langle B|\hat{H}_{int}|A\rangle|} \quad (211)$$

Now let us analyze the transition in two different processes: absorption and emission.

(1) For absorption, the initial state is the lower state $|a\rangle$ with n_k photons; the final state is the upper state $|b\rangle$ with $(n_k - 1)$ photons. From Eq. (203)



$$\langle B|\hat{H}_{int}|A\rangle = \langle b, n_k - 1|\hat{H}_{int}^{(-)}|a, n_k\rangle$$

$$= -\frac{e}{\mu}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\langle n_k - 1|\hat{a}_k|n_k\rangle \cdot \langle b|\hat{e}_k \cdot \hat{p}\, e^{i\vec{k}\cdot\hat{r}}|a\rangle$$

$$= -\frac{e}{\mu}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\sqrt{n_k}\,\langle b|\hat{\vec{e}}_k \cdot \hat{\vec{p}}\, e^{i\vec{k}\cdot\hat{\vec{r}}}|a\rangle \quad (212)$$

Substitute Eq. (212) into Eq. (210),

$$W_{A\to B} = \frac{2\pi}{\hbar}\frac{e^2}{\mu^2}\frac{\hbar}{2\varepsilon_0 V\omega_k} n_k |\langle b|\hat{\vec{e}}_k \cdot \hat{\vec{p}}\, e^{i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2 \delta(E_b - E_a - \hbar\omega_k)$$

$$= \frac{\pi e^2 n_k}{\mu^2 \varepsilon_0 V\omega_k}|\langle b|\hat{\vec{e}}_k \cdot \hat{\vec{p}}\, e^{i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2 \delta(E_b - E_a - \hbar\omega_k) \quad (213)$$

This is absorption probability per unit time, i.e., absorption rate for atom with single mode radiation field.

(2) For emission, initial state $|a, n_k\rangle$, final state $|b, n_k+1\rangle$.

Similarly, $\langle B|\hat{H}_{int}|A\rangle = \langle b, n_k+1|\hat{H}^{(+)}_{int}|a, n_k\rangle$

$$= -\frac{e}{\mu}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\,\langle n_k+1|\hat{a}_k^{+}|n_k\rangle\langle b|\hat{\vec{e}}_k\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle$$

$$= -\frac{e}{\mu}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\,\sqrt{n_k+1}\,\langle b|\hat{\vec{e}}_k\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle \qquad (214)$$

$$\therefore\ W_{A\to B} = \frac{2\pi}{\hbar}\,\frac{e^2}{\mu^2}\cdot\frac{\hbar}{2\varepsilon_0 V\omega_k}(n_k+1)|\langle b|\hat{\vec{e}}_k\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2\delta(E_b-E_a+\hbar\omega_k)$$

$$= \frac{\pi e^2(n_k+1)}{\mu^2\varepsilon_0 V\omega_k}|\langle b|\hat{\vec{e}}_k\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2\delta(E_b-E_a+\hbar\omega_k) \qquad (215)$$

This is the emission probability per unit time., i.e., the emission rate for atom interacting with single mode radiation field.

Note: Eq.(215) has a term that is independent of photon number n_k. This is to say even when there is no radiation field, there is still emission — Spontaneous emission.

$$W^{sp}_{A\to B} = \frac{\pi e^2}{\mu^2\varepsilon_0 V\omega_k}|\langle b|\hat{\vec{e}}_k\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2\delta(E_b-E_a+\hbar\omega_k) \qquad (216)$$

$$W^{st}_{A\to B} = \frac{\pi e^2 n_k}{\mu^2\varepsilon_0 V\omega_k}|\langle b|\hat{\vec{e}}_k\cdot\hat{\vec{P}}e^{\mp i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2\delta(E_b-E_a\pm\hbar\omega_k) \qquad (217)$$

sp — spontaneous, st — stimulated.

Above we obtain the transition probability per unit time for an atom interacting with single mode radiation field. When the radiation field contains multiple modes, the transition rate should be the integration result of the number of modes that can interact with the atom times the single mode transition rate. In a unit solid angle $d\Omega$, the mode number is given by

$$dN = \frac{V\omega_k^2}{(2\pi)^3\hbar c^3}\,d\Omega\, dE \qquad (218)$$

where E is energy. We use Eq.(218) to time Eq.(213) and Eq.(215), and then integrate over dE. Because of the δ function in Eqs.(213) and (215), only certain energy of the radiation field is choosen, who satisfies the resonance conditions given by the δ function; (We use emission Eq.(215) as an example here)

$$\int W_{A\to B}\cdot dN = \int \frac{\pi e^2(\bar{n}_{k\lambda}+1)}{\mu^2\varepsilon_0 V\omega_k}\,\frac{V\omega_k^2}{(2\pi)^3\hbar c^3}\left|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle\right|^2 d\Omega$$

$$\cdot\,\delta(E_b-E_a+\hbar\omega_k)\,dE$$

$$= \frac{e^2\omega_k(\bar{n}_{k\lambda}+1)}{8\pi^2\mu^2\varepsilon_0\hbar c^3}\left|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle\right|^2 d\Omega$$

Note: We use $\bar{n}_{k\lambda}$ (the mean number of photons of given polarization in the interval of wave vectors $\vec{k}\to\vec{k}+d\vec{k}$) to represent the photon number, $\omega_k = \omega_{ab} = |E_a-E_b|/\hbar = \omega$. Thus, we obtain the transition rate under multi-mode radiation field:

$$dW_{em} = \frac{e^2\omega\,(\bar{n}_{k\lambda}+1)}{8\pi^2\mu^2\varepsilon_0\hbar c^3}\left|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle\right|^2 d\Omega \qquad (219)$$

$$dW_{ab} = \frac{e^2\omega\,\bar{n}_{k\lambda}}{8\pi^2\mu^2\varepsilon_0\hbar c^3}\left|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle\right|^2 d\Omega \qquad (220)$$

Here, dW corresponds to $d\Omega$ (the unit solid angle).

Thus, under multi-mode radiation field, the spontaneous emission rate is

$$dW_{sp} = \frac{e^2\omega}{8\pi^2\mu^2\varepsilon_0\hbar c^3}|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2 d\Omega \qquad (221)$$

The stimulated emission and absorption rates are

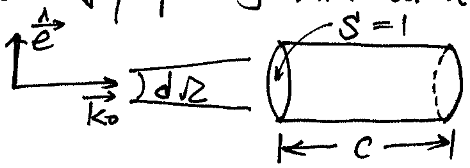
$$dW_{st} = \frac{e^2\omega\,\bar{n}_{k\lambda}}{8\pi^2\mu^2\varepsilon_0\hbar c^3}|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}e^{\mp i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2 d\Omega \qquad (222)$$

Note: The spontaneous and stimulated emission (absorption) rates contain the same matrix element $|\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}e^{-i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2$. Therefore, if this matrix element is zero, then both spontaneous and stimulated emission rates and absorption rates are zero, i.e., such transition is not possible. On the other hand, if this matrix element is non-zero, then spontaneous, stimulated emission and absorption rates are non-zero.

Sometimes it is more convenient to express the photon number $\bar{n}_{k\lambda}$ in terms of the intensity of radiation. The intensity is : ① Light power on unit area

or ② Energy flux density

or ③ Light energy passing unit area in unit time



$V = S\cdot c\cdot\Delta t = 1\cdot c\times 1 = c$

$$I_{k\lambda}\,d\omega\,d\Omega = \frac{\omega^2 c\,\bar{n}_{k\lambda}\hbar\omega}{(2\pi c)^3}d\omega\,d\Omega \qquad (223)$$

$$\Rightarrow \quad \bar{n}_{k\lambda} = \frac{(2\pi)^3 c^2}{\hbar\omega^3} I_{k\lambda} \qquad (224)$$

$$\therefore\ dW_{st} = \frac{\pi e^2 I_{k\lambda}}{\mu^2 \varepsilon_0 \hbar^2 \omega^2 c} \left| \langle b | \hat{\vec{e}}_{k\lambda} \cdot \hat{\vec{P}}\, e^{\mp i \vec{k}\cdot\hat{\vec{r}}} | a \rangle \right|^2 d\Omega \qquad (225)$$

With Eqs. (221), (222), and (225), we obtain the transition probability per unit time expressions. Now we need to derive the matrix element. For $e^{i\vec{k}\cdot\hat{\vec{r}}}$ term in these equations, because the radiation field wavelength λ is much longer than the atom dimension,

$$\vec{k}\cdot\vec{r} = \frac{2\pi r}{\lambda} \ll 1 .$$

Thus, we can expand $e^{i\vec{k}\cdot\hat{\vec{r}}}$ as

$$e^{i\vec{k}\cdot\hat{\vec{r}}} = 1 + i\vec{k}\cdot\hat{\vec{r}} - \frac{(\vec{k}\cdot\hat{\vec{r}})^2}{2!} + \cdots \qquad (226)$$

When taking different order of approximation, we obtain:

$e^{i\vec{k}\cdot\hat{\vec{r}}} \approx 1$ — electric dipole transition

$i\vec{k}\cdot\hat{\vec{r}}$ — $\begin{cases}\text{magnetic dipole transition}\\ \text{electric quadrapole transition.}\end{cases}$

3. Electric Dipole Transition (Electric Dipole Radiation)

When taking $e^{i\vec{k}\cdot\hat{\vec{r}}} \simeq 1$, Eqs. (221), (222), and (225) give the transition rate for electric dipole transition, called E_1 transition. It is the transition between electron states, e.g., from the ground state to excited states. Electron states are the different states formed by different electron configuration. For example,

$$\left.\begin{array}{l}\text{Na ground state is } 1S^2 2S^2 2p^6 3S^1. \\ \text{Na first excited state is } 1S^2 2S^2 2p^6 3p^1\end{array}\right\} \text{ i.e., electron configuration}$$

changes from $3S \rightarrow 3p$ for the electric dipole transition from the ground state to the 1st excited state.

For E_1 transition,

$$\langle b| \hat{\vec{e}}\cdot\hat{\vec{p}}\, e^{i\vec{k}\cdot\vec{r}} |a\rangle = \langle b| \hat{\vec{e}}\cdot\hat{\vec{p}} |a\rangle \qquad (227)$$

Note: We remove "$k\lambda$" under $\hat{\vec{e}}$ subscript for convenience.

To replace the operator $\hat{\vec{p}}$ with the operator $\hat{\vec{r}}$, we use the commutation relationship: $[x, P_x] = i\hbar$, $[x, P_y] = [x, P_z] = 0$

It is not difficult to obtain

$$[x, P_x^2] = 2i\hbar P_x \qquad (228)$$

Thus,

$$[\hat{\vec{r}}, \hat{H}_a] = \frac{i\hbar}{\mu}\hat{\vec{p}}, \qquad (229)$$

Where $\hat{H}_a = \frac{\hat{\vec{p}}^2}{2\mu}$. This will be a homework to prove Eqs. (228) (229).

Thus,

$$\begin{aligned}\langle b|\hat{\vec{p}}|a\rangle &= \frac{\mu}{i\hbar}\langle b|\hat{\vec{r}}\hat{H}_a - \hat{H}_a\hat{\vec{r}}|a\rangle \\ &= \frac{\mu}{i\hbar}(E_a - E_b)\langle b|\hat{\vec{r}}|a\rangle \\ &= i\mu\omega_{ba}\langle b|\hat{\vec{r}}|a\rangle \qquad (230)\end{aligned}$$

where $\omega_{ba} = (E_b - E_a)/\hbar$.

The matrix element can now be written in terms of $\hat{\vec{r}}$ operator

$$
\begin{aligned}
|\langle b|\hat{\vec{e}}\cdot\hat{\vec{p}}\,e^{i\vec{k}\cdot\hat{\vec{r}}}|a\rangle|^2 &\approx |\langle b|\hat{\vec{e}}\cdot\hat{\vec{p}}|a\rangle|^2 = |\hat{\vec{e}}\cdot\langle b|\hat{\vec{p}}|a\rangle|^2 \\
&= \mu^2\omega^2|\hat{\vec{e}}\cdot\langle b|\hat{\vec{r}}|a\rangle|^2 \\
&= \mu^2\omega^2|\langle b|\hat{\vec{e}}\cdot\hat{\vec{r}}|a\rangle|^2 \qquad (231)
\end{aligned}
$$

Substitute Eq.(231) into Eq.(221) and Eq.(225), we obtain the transition probability per unit time:

$$
\begin{aligned}
dW_{sp} &= \frac{e^2\omega^3}{8\pi^2\varepsilon_0\hbar c^3}|\langle b|\hat{\vec{e}}\cdot\hat{\vec{r}}|a\rangle|^2 \\
&= \frac{\omega^3}{8\pi^2\varepsilon_0\hbar c^3}|\langle b|\hat{\vec{e}}\cdot\hat{\vec{d}}|a\rangle|^2 \qquad (232)
\end{aligned}
$$

$$
\begin{aligned}
dW_{st} &= \frac{\pi e^2 I_{k\lambda}}{\varepsilon_0\hbar^2 c}|\langle b|\hat{\vec{e}}\cdot\hat{\vec{r}}|a\rangle|^2 \\
&= \frac{\pi I_{k\lambda}}{\varepsilon_0\hbar^2 c}|\langle b|\hat{\vec{e}}\cdot\hat{\vec{d}}|a\rangle|^2 \qquad (233)
\end{aligned}
$$

Note: We define the electric dipole moment of the atom as

$$\hat{\vec{d}} = -e\hat{\vec{r}} \qquad (234)$$

where e is the electron charge, $\hat{\vec{r}}$ is the electron position relative to the nucleus (i.e., mass center).

Note: In electric dipole transition, the electric dipole moment $\hat{\vec{d}}$ used in the transition probability is the induced electric dipole moment. The permanent electric dipole moment of an atom is always zero, i.e., $\langle\hat{\vec{d}}\rangle \equiv \langle\psi_m|-e\hat{\vec{r}}|\psi_m\rangle = 0$. This is because $\hat{\vec{r}}$ is antisymmetric, the mean value is zero for any electron orbits. The instantaneous electric dipole moment is nonzero.

(1) Selection Rules derived from 3J-Symbols and Reduced Matrix Elements

To illustrate the selection rules for different kinds of transition, it is important to introduce 3J-symbol and reduced matrix element of "Group Theory". A close inspection of the line intensity, polarization, and angular distribution of emitted and absorbed radiation has to take into account of the orientation of the atoms with respect to a specified direction, called the quantization axis. Therefore, we describe the atomic energy levels $|a\rangle$ and $|b\rangle$ by sets of quantum numbers:

$$(\alpha_a, J_a, M_a) \quad \text{and} \quad (\alpha_b, J_b, M_b)$$

where J stands for the total angular momentum of the electron, M stands for J's projection onto the quantization axis. All other quantum numbers are respesented as a whole by α.

With this representation, the spontaneous transition probability per unit time per unit solid angle is

$$d W_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b) = \frac{\omega^3}{8\pi^2 \varepsilon_0 \hbar c^3} \left| \langle \alpha_b J_b M_b | \hat{e} \cdot \vec{d} \, | \alpha_a J_a M_a \rangle \right|^2 d\Omega \qquad (235)$$

The stimulated emission /absorption rate is

$$d W_{st}(\alpha_a J_a M_a \to \alpha_b J_b M_b) = \frac{\pi I_{k\Omega}}{\varepsilon_0 \hbar^2 c} \left| \langle \alpha_b J_b M_b | \hat{e} \cdot \vec{d} \, | \alpha_a J_a M_a \rangle \right|^2 \qquad (236).$$

where the matrix element $\langle \alpha_b J_b M_b | \hat{e} \cdot \vec{d} \, | \alpha_a J_a M_a \rangle$ represents the transition from state $|\alpha_a J_a M_a\rangle$ to state $|\alpha_b J_b M_b\rangle$.

This matrix element can be separated into a product of two factors: a "geometrical factor" describing the orientation of the atom, and an "intrinsic factor" which depends on the radiative coupling of the two energy states.

According to Wigner- Eckart theorem, $\left(\hat{\vec{e}}\cdot\hat{\vec{d}} = \sum_{q} e_q^{*} d_q,\ q=1,0,-1\right)$

$$\langle \alpha_b J_b M_b | d_q | \alpha_a J_a M_a \rangle = (-1)^{J_b - M_b} \begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix} \langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle \tag{237}$$

where $\begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix}$ is called the "3J- symbol", depending on M_b, M_a; $q = M_b - M_a$. These factors can be expressed by the CG coefficients (Clebsch- Gordan), which describe the coupling of angular momenta for a system initially in a state (J_a, M_a). The photon transfers an angular momentum of $1\hbar$ with projection $m\hbar$ $(m=0,\pm1)$ and brings the atomic system into another state (J_b, M_b).

The second factor $\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle$ is called the "reduced matrix element". It is independent of the atomic orientation, and gives the "physical part" of the transition probability. The reduced matrix element depends on the atomic wave function $\psi_i(\alpha_a J_a)$ and $\psi_f(\alpha_b J_b)$ in the coordinate frame of the atom.

From the properties of 3J- symbol (CG coefficients), the Conditions for non zero matrix elements are

$$\Delta J = 0, \pm 1, \quad J_a + J_b \geq 1; \quad \Delta M = 0, \pm 1 \tag{238}$$

where $\Delta J = J_b - J_a$, $\Delta M = M_b - M_a$.

There are the so-called selection rules for E_1 transitions.

When considering other quantum numbers, we have

$$\Delta S = 0; \quad \Delta L = 0, \pm 1, \quad L_a + L_b \geq 1 \tag{239}$$

(for single electron, $\Delta l = \pm 1$)

In addition, the parity of the initial and final states must be opposite, i.e., parity must change.

Furthermore, there is no limitation on the principal quantum number change, i.e., Δn can be arbitrary: $\Delta n = 0$ and $\Delta n \neq 0$

The combination of above four conditions forms the selection rules for the electric dipole (E_1) transitions. Below is a table copied from the book " Atomic and Laser Spectroscopy " by Corney.

TABLE 7.1.

Selection rules for single photon transitions in atomic spectra

Rule	Electric dipole	Magnetic dipole	Electric quadrupole
1.	$\Delta J = 0, \pm 1$ $(0 \nleftrightarrow 0)$	$\Delta J = 0, \pm 1$ $(0 \nleftrightarrow 0)$	$\Delta J = 0, \pm 1, \pm 2$ $(0 \nleftrightarrow 0;\ \frac{1}{2} \nleftrightarrow \frac{1}{2};\ 0 \nleftrightarrow 1)$
2.	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1$	$\Delta M = 0, \pm 1, \pm 2$
3.	Parity change	No parity change	No parity change
4.	One electron jump $\Delta l = \pm 1$	No electron jump $\Delta l = 0,\ \Delta n = 0$	One or no electron jump $\Delta l = 0, \pm 2$
5.	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
6.	$\Delta L = 0, \pm 1$ $(0 \nleftrightarrow 0)$	$\Delta L = 0$	$\Delta L = 0, \pm 1, \pm 2$ $(0 \nleftrightarrow 0;\ 0 \nleftrightarrow 1)$

When hyperfine structures are involved, the additional selection rules are:

$$\Delta F = 0, \pm 1, \quad F = 0 \nleftrightarrow F = 0 \qquad (240)$$

$$\Delta M_F = 0, \pm 1$$

for both E_1 and M_1 transitions.

(2) Intensity, Polarization, and Angular Distribution of Zeeman Spectral Lines

Without external magnetic field, same J but different M levels are degenerate. However, the transition gives polarized light, which enables the discrimination of different components although freqs are the same.

Let us consider in a certain ΔJ transition, the ~~three~~ components $\Delta M = 0, \pm 1$. This will give polarization and angular distribution.

For $\Delta M = 0$, i.e., $M_b = M_a$, $q = 0$, $\hat{\vec{e}}_0 = \hat{\vec{e}}_z$,

$$\langle \alpha_b J_b M_b | \hat{\vec{e}} \cdot \hat{\vec{r}} | \alpha_a J_a M_a \rangle = \hat{\vec{e}}_z^{\,*} \langle \alpha_b J_b M_b | \overset{z}{\boxed{r_z}} | \alpha_a J_a M_a \rangle . \qquad (241)$$

Radiation propagates in $\vec{k}_0$ direction, and its polarization $\vec{e}_1$ and $\vec{e}_2$ are shown as Figure. $\vec{e}_1$ is in the plane of $(\vec{k}_0, \vec{z})$.

$\therefore$ $e_{1z} = \sin\theta$, $\qquad e_{2z} = 0$. $\Rightarrow$ linear polarization

$\therefore$ $dW_{sp}(\alpha_a J_a M \to \alpha_b J_b M)$

$$= \frac{e^2 \omega^3}{4\pi\varepsilon_0 \, 2\pi\hbar c^3} |\langle \alpha_b J_b M | z | \alpha_a J_a M \rangle|^2 \sin^2\theta \, d\Omega . \qquad (242)$$

For $\Delta M = \pm 1$,

$$\langle \alpha_b J_b M_b | \hat{\vec{e}} \cdot \vec{r} | \alpha_a J_a M_a \rangle = \vec{e}_{\pm 1}^{\,*} \langle \alpha_b J_b M | r_{\pm 1} | \alpha_a J_a M \mp 1 \rangle$$
$$= \frac{1}{\sqrt{2}} (e_x \mp i e_y) \langle \alpha_b J_b M | \frac{X \pm iY}{\sqrt{2}} | \alpha_a J_a M \mp 1 \rangle \qquad (243)$$

$$\left.\begin{array}{l} e_{1x} = -\cos\theta, \quad e_{1y} = 0 \\ e_{2x} = 0, \quad e_{2y} = -1. \end{array}\right\} \Rightarrow \text{circular polarization.}$$

$$\therefore dW_{sp}(\alpha_a J_a M \to \alpha_b J_b M\pm1)$$
$$= \frac{e^2\omega^3}{4\pi\varepsilon_0\, 2\pi\hbar c^3} \left| \langle \alpha_b J_b M\pm1 | \frac{x \pm iy}{\sqrt{2}} | \alpha_a J_a M \rangle \right|^2 \times \frac{1}{2}(1+\cos^2\theta)\, d\Omega . \qquad (244)$$

Assume we can distinguish $\Delta M = 0, \pm1$ components. The observed intensity of the fluorescence emitted into the direction θ against the quantization axis is determined by the product of the angular transition rate of individual atom dW_{sp} and the number density of atoms on the initial state $|\alpha_a J_a M_a\rangle$: (at a far distance $\rho \gg \lambda$)

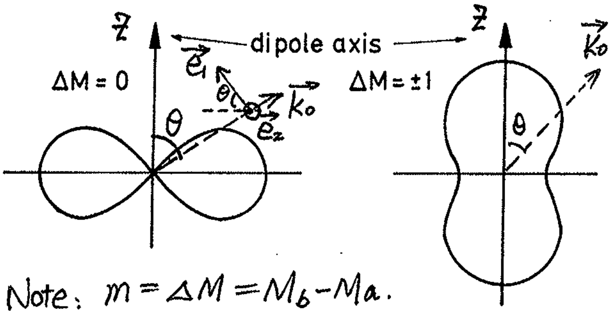
$$I(\theta)d\Omega = N(\alpha_a J_a M_a) \cdot dW_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b)$$
$$= \frac{d\Omega \cdot e^2\omega^4}{2\varepsilon_0 c^3 4\pi\rho^2} N(\alpha_a J_a M_a) \left| \langle \alpha_b J_b \| \vec{r} \| \alpha_a J_a \rangle \right|^2 * \left| \begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix} \right|^2 * \begin{cases} \frac{1}{2}(1+\cos^2\theta) & \text{for } q = \pm1 \\ \sin^2\theta & \text{for } q = 0 \end{cases} \qquad (245)$$

This is the intensity for specific transition from $|\alpha_a J_a M_a\rangle \longrightarrow |\alpha_b J_b M_b\rangle$ in unit solid angle.

The $dW_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b)$ is the angular transition rate for this specific transition between different Zeeman sublevels.

The angle factor
$$\begin{cases} \frac{1}{2}(1+\cos^2\theta) & \text{for } q = \pm1 \\ \sin^2\theta & \text{for } q = 0 \end{cases} \qquad (246)$$
gives the angular distribution of Zeeman components, shown as the following figure.

Angular Distribution of radiation for E_1 transition $\Delta M = 0, \pm 1$



Note: $m = \Delta M = M_b - M_a$.

Figure. Angular distribution of the fluorescence emitted on transitions $\Delta M = 0, \pm 1$ between the zeeman components $|\alpha_a J_a M_a\rangle \longrightarrow |\alpha_b J_b M_b\rangle$.

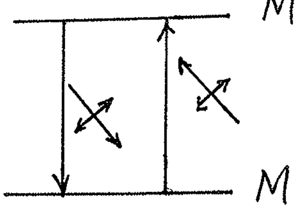
Above figure shows the angular distribution for $\Delta M = 0$ and $\Delta M = \pm 1$ transitions. The polarization characteristics of the emitted fluorescence are different for the two cases.

For $\Delta M = 0$, i.e., $M_b = M_a$. $(m=0)$,

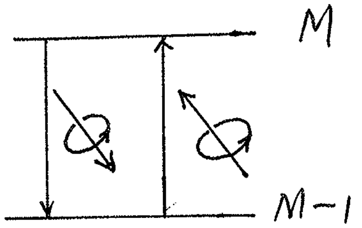
the emitted or absorbed photon is linearly polarized radiation, and its polarization direction is $\vec{e}_1$.

For $\Delta M = \pm 1$,

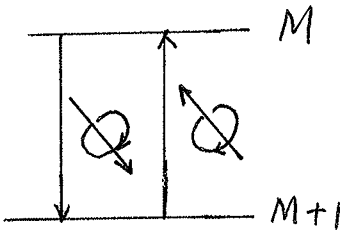
the emitted or absorbed photon is circularly polarized radiation.



Linear Polarization



Circular Polarization
(left)



Circular polarization
(right)

(3) ΔJ Transition Probabilities and Einstein Coefficients

Above we discussed the transition probabilities for the Zeeman components of certain ΔJ transition. Now let us take a look at the total transition probability of the ΔJ transition and the spectral line intensity.

First, let us investigate the spontaneous emission problem. All three transitions of $\Delta M = 0, \pm 1$ are possible, and all directions of radiation are also possible. To obtain the total transition probability, let us integrate dW_{sp} over all possible directions:

$$\Delta M = 0, \quad W_{sp}(\alpha_a J_a M \to \alpha_b J_b M) = \int dW_{sp}(\alpha_a J_a M \to \alpha_b J_b M)$$

$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} \begin{pmatrix} J_b & 1 & J_a \\ -M & 0 & M \end{pmatrix}^2 |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \qquad (247)$$

$$\Delta M = \pm 1, \quad W_{sp}(\alpha_a J_a M \mp 1 \to \alpha_b J_b M) = \int dW_{sp}(\alpha_a J_a M \mp 1 \to \alpha_b J_b M)$$

$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} \begin{pmatrix} J_b & 1 & J_a \\ -M & \pm 1 & M \mp 1 \end{pmatrix}^2 |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \qquad (248)$$

These are the transition probability per unit time (in all solid angles) of each Zeeman component.

Second, let us derive the total transition probability of the ΔJ transition, i.e., including all Zeeman components. For the initial level J_a, it has many M_a sub-levels. For each M_a sub-level, it has maximum 3 transitions to the final state J_b $(\Delta M = 0, \pm 1)$. Thus, the total transition probability from M_a to lower state J_b is given by

$$\sum_{M_b} W_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b)$$

$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \sum_{M_b} \begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix}^2$$

(249)

Using the following relationship of $3j$-symbols,

$$\sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \frac{1}{2j_3+1} \delta(j_3, j_3') \delta(m_3, m_3') \qquad (250)$$

We have

$$\sum_{M_b} \begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a \end{pmatrix}^2 = \frac{1}{2J_a+1} \qquad (251)$$

Thus, Eq. (249) can be further derived as

$$\sum_{M_b} W_{sp}(\alpha_a J_a M_a \to \alpha_b J_b M_b) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} |\langle \alpha_b J_b \| \vec{d} \| \alpha_a J_a \rangle|^2 \frac{1}{2J_a+1} \qquad (252)$$

Note: Eq. (252) is independent of M_a !!! This means that the transition probability from any one M_a of J_a to lower states is equal! We also have another "surprising" conclusion: The Eq. (252) also gives the total transition probability from $\alpha_a J_a \to \alpha_b J_b$:

$$W_{sp}(\alpha_a J_a \to \alpha_b J_b) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^3} \cdot \frac{1}{2J_a+1} |\langle \alpha_b J_b \| \vec{d} \| \alpha_a J_a \rangle|^2 \qquad (253)$$

Since for any single atom, it can only be in one M_a sub-level. So its total transition rate W_{sp} is given by Eq. (253). We should <u>not</u> multiply it by the degeneracy of J_a level $(2J_a+1)$.

When there is no external magnetic field, Zeeman components of the $\alpha_a J_a \to \alpha_b J_b$ transition own the same transition frequency. If we don't distinguish polarization, then only one spectral line is observed for $\alpha_a J_a \to \alpha_b J_b$ transition. If we assume each M_a sub-levels are homogeneously excited, and the population on each M_a is N_M, then the total population on J_a is

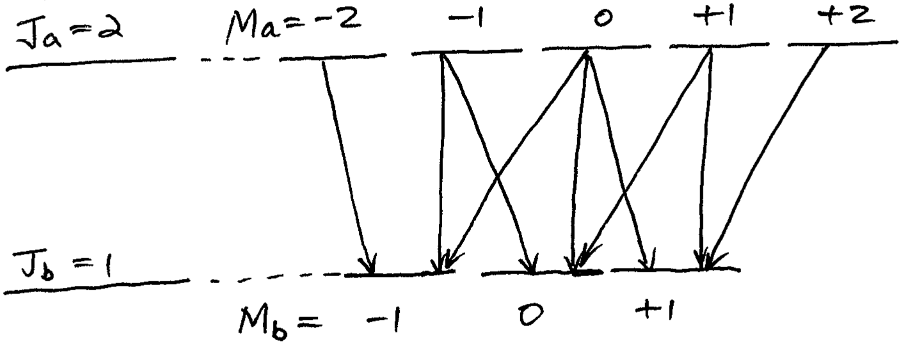
$$N_{J_a} = (2J_a+1) N_M = g_{J_a} N_M, \quad g_{J_a} = 2J_a+1 \qquad (253)$$

Thus, the $\alpha_a J_a \rightarrow \alpha_b J_b$ spectral line intensity is

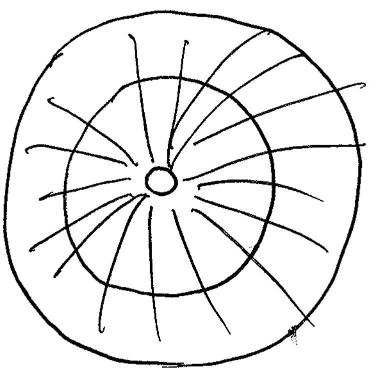
$$I \propto N_{J_a} W_{sp}(\alpha_a J_a \rightarrow \alpha_b J_b)\hbar\omega = g_{J_a} N_M W_{sp}(\alpha_a J_a \rightarrow \alpha_b J_b)\hbar\omega . \quad (254)$$

For angular distribution and polarization of $\alpha_a J_a \rightarrow \alpha_b J_b$ transition analysis, we need to start from Eqs. (242) and (244). For any arbitrary angle θ, add the contributions from all Zeeman components together. We skip the procedure here. The results are that the radiation intensity is independent of θ angle, so the radiation is isotropic and non-polarized. This is required by the physics — a space without external magnetic / electric field should be isotropic. In such a space, a group of atoms that are excited homogeneously are also isotropic. The decay from each M_a sub-levels cannot have different speed — but the same spontaneous emission rate, i.e., no single orientation would show dominant feature. Thus, the radiation field from the group of atoms is also isotropic — the radiation is not dependent on angular direction. Of course, if the group of atoms are not homogeneously excited, but M_a sublevels are selectively excited, then the isotropic properties are no longer valid.

Example:



Spontaneous emission is isotropic !



For stimulated transitions (emission and absorption), the situation is more complicated. Usually we shine a radiation field onto the atoms from one direction, and sometimes the radiation is polarized.

① If the incident light is polarized and can distinguish Zeeman components, also no optical pumping effect, then we should start from Eq. (225) $\left(dW_{st} = \frac{\pi e^2 I_{k\lambda}}{\mu^2 \varepsilon_0 \hbar^2 \omega^2 c} |\langle b| \hat{\vec{e}} \cdot \hat{\vec{P}} |a\rangle|^2 d\Omega \right)$, and derive equations similar to the spontaneous cases Eqs. (242) and (244)

$$\Delta M = 0, \quad dW_{st} (\alpha_a J_a M \to \alpha_b J_b M)$$
$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\pi^2}{\hbar^2 c} I_{k\lambda} |\langle \alpha_b J_b M | d_z | \alpha_a J_a M \rangle|^2 \sin^2\theta \, d\Omega \quad (255)$$

$$\Delta M = \pm 1, \quad dW_{st} (\alpha_a J_a M \mp 1 \to \alpha_b J_b M)$$
$$= \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\pi^2}{\hbar^2 c} I_{k\lambda} \left| \langle \alpha_b J_b M | \frac{1}{\sqrt{2}} (d_x \pm i d_y) | \alpha_a J_a M \mp 1 \rangle \right|^2$$
$$\cdot \frac{1}{2} (1 + \cos^2\theta) \, d\Omega \quad (256)$$

② If the incident light is non-polarized, then we will observe the total ΔJ transitions — ΔJ spectral line. Since the spontaneous emission from $\alpha_a J_a \to \alpha_b J_b$ is isotropic and non-polarized, the opposition process — absorption $\alpha_b J_b — \alpha_a J_a$ is isotropic, i.e., No matter which direction the radiation is incident, the stimulated transition probability should be the same. Therefore we can utilize the isotropic field results obtained above to derive the transition probability for non-polarized radiation interacting with atoms:

$$I_{k\lambda} = \frac{c}{2} \rho(\omega)$$

We define $E_a > E_b$, i.e., a level is higher than b level.

Thus, for stimulated absorption:

$$dW_{st}(\alpha_b J_b \to \alpha_a J_a) = \frac{1}{4\pi\varepsilon_0}\cdot\frac{4\pi^2}{3\hbar^2}\rho(\omega)\frac{1}{2J_b+1}\left|\langle\alpha_a J_a \| \hat{\vec{d}} \| \alpha_b J_b\rangle\right|^2 d\Omega \qquad (257)$$

for stimulated emission:

$$dW_{st}(\alpha_a J_a \to \alpha_b J_b\rangle = \frac{1}{4\pi\varepsilon_0}\frac{4\pi^2}{3\hbar^2}\rho(\omega)\frac{1}{2J_a+1}\left|\langle\alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a\rangle\right|^2 d\Omega \qquad (258)$$

Einstein A and B coefficients are obtained in isotropic radiation field, which corresponds to the total ΔJ transition (includ'g all Zeeman components).

Thus, $$A_{a\to b} = W_{sp}(\alpha_a J_a \to \alpha_b J_b) = \frac{1}{4\pi\varepsilon_0}\cdot\frac{4\omega^3}{3\hbar c^3}\frac{1}{2J_a+1}\left|\langle\alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a\rangle\right|^2 \qquad (259)$$

$$B_{a\to b}\rho(\omega) = W_{st}(\alpha_a J_a \to \alpha_b J_b)$$
$$= \frac{1}{4\pi\varepsilon_0}\cdot\frac{4\pi^2}{3\hbar^2}\rho(\omega)\frac{1}{2J_a+1}\left|\langle\alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a\rangle\right|^2 \qquad (260)$$

$$B_{b\to a}\rho(\omega) = W_{st}(\alpha_b J_b \to \alpha_a J_a)$$
$$= \frac{1}{4\pi\varepsilon_0}\cdot\frac{4\pi^2}{3\hbar^2}\rho(\omega)\frac{1}{2J_b+1}\left|\langle\alpha_a J_a \| \hat{\vec{d}} \| \alpha_b J_b\rangle\right|^2 \qquad (261)$$

From Eqs. (259–261), we obtain

$$A_{a\to b} = \frac{\hbar\omega^3}{\pi^2 c^3}B_{a\to b}, \qquad g_a B_{a\to b} = g_b B_{b\to a} \qquad (262)$$

where $g_a = 2J_a + 1$, $g_b = 2J_b + 1$.

(4) Oscillator strength, Line Strength, and A_{ki}

Equation (254) gives the Spectral line intensity for spontaneous emission $\alpha_a J_a \to \alpha_b J_b$:

$$I(\alpha_a J_a \to \alpha_b J_b) \propto N(\alpha_a J_a)\, W_{sp}(\alpha_a J_a \to \alpha_b J_b)\, \hbar\omega$$

$$\propto N_M \frac{4\omega^3}{3\hbar c^3} \cdot \frac{1}{4\pi\varepsilon_0} \cdot \hbar\omega\, |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \qquad (263)$$

Note: $N_{J_a} = N(\alpha_a J_a) = g_a N_M = (2J_a+1) N_M$. $\left.\right\} \Rightarrow$ Thus, the $(2J_a+1)$

$W_{sp}(\alpha_a J_a \to \alpha_b J_b) \propto \frac{1}{2J_a+1}$

factor is Cancelled out.

Thus, the line intensity I is independent of quantum number J_a, but proportional to the square of the matrix element.

We define the line strength $S(J_a \to J_b)$ as

$$S(J_a \to J_b) \equiv |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \qquad (264)$$

$$\text{Symmetry} \Rightarrow S(J_a \to J_b) = S(J_b \to J_a) \qquad (265)$$

We define the oscillator strength (f value) as

$$f(J_a \to J_b) = \frac{2\mu}{3\hbar e^2} \cdot \frac{\omega_{ba}}{2J_a+1} |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2$$

$$= \frac{2\mu}{3\hbar e^2} \cdot \frac{\omega_{ba}}{2J_a+1} S(J_a \to J_b) \qquad (266)$$

where $\omega_{ba} = (E_b - E_a)/\hbar$, $\mu = \frac{m_e M}{m_e + M}$. $\qquad (267)$

For emission, $\omega_{ba} < 0$, $\therefore f_{ki} < 0$ $\qquad$ k — upper

i — lower.

For absorption, $\omega_{ab} > 0$, $\therefore f_{ik} > 0$.

$$f(J_b \to J_a) = \frac{2\mu}{3\hbar e^2} \frac{\omega_{ab}}{2J_b+1} |\langle \alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a \rangle|^2 \qquad (268)$$

$$= \frac{2\mu}{3\hbar e^2} \cdot \frac{\omega_{ab}}{2J_b+1} S(J_b \to J_a)$$

$$\because\ S(J_a \rightarrow J_b) = S(J_b \rightarrow J_a)$$

$$\therefore\ -(2J_a+1)\, f(J_a \rightarrow J_b) = (2J_b+1)\, f(J_b \rightarrow J_a)$$

i.e., $$-g_k f_{ki} = g_i f_{ik} \qquad (269)$$

Compare Eq. (259) with Eqs. (266) and (268), we have

$$A_{ki} = \frac{e^2 \omega_{ki}^2}{2\pi \varepsilon_0 \mu c^3} (-f_{ki})$$

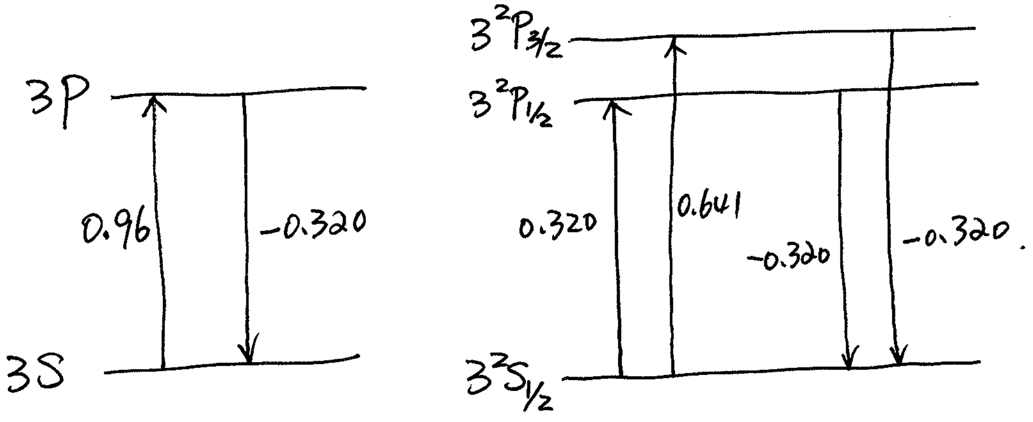
$$= \frac{e^2 \omega_{ki}^2}{2\pi \varepsilon_0 \mu c^3} \frac{g_i}{g_k} f_{ik} \qquad (270)$$

$$\therefore\ f_{ik} = \frac{2\pi \varepsilon_0 \mu c^3}{e^2 \omega_{ki}^2} \frac{g_k}{g_i} A_{ki} \qquad (271)$$

Regard $\mu \approx m_e$, and $\omega_{ki} = 2\pi \frac{c}{\lambda}$

$$\therefore\ f_{ik} = \frac{\varepsilon_0 m_e c \lambda^2}{2\pi e^2} \cdot \frac{g_k}{g_i} \cdot A_{ki} \qquad (272)$$

Remember, absorption oscillator strength is positive, and the emission oscillator strength is negative.



Oscillator strength f for Na $3P \leftrightarrow 3S$ transitions

Note: $$\sum_{J_b} f(J_a \rightarrow J_b) = 1 \qquad (273)$$

$$\begin{cases} 3S \rightarrow 3P & 0.96 \\ 3S \rightarrow 4P & 0.0153 \\ 3S \rightarrow 5P & 0.0025, \cdots \end{cases}$$

i.e., all transitions from J_a (including absorption and emission) have the sum of oscillator strengths to be 1 for single electron transition.

4. Magnetic Dipole Transition and Electric Quadrapole Transition

$$e^{i\vec{k}\cdot\hat{\vec{r}}} = 1 + i\vec{k}\cdot\hat{\vec{r}} - \frac{(\vec{k}\cdot\hat{\vec{r}})^2}{2!} + \cdots$$

When we consider the 2nd term $i\vec{k}\cdot\hat{\vec{r}}$ and the $\frac{e}{\mu}\hat{\vec{S}}_i\cdot\vec{B}$ term in equation (198), we will obtain the interaction between the radiation field and the atomic magnetic dipole moment, and the atomic quadrapole moment electric.

Since the transition probability $\propto$ the square of matrix element,

$$dW_{sp}^{(M_1, E_2)} \propto dW_{sp}^{(E_1)}\cdot(kr)^2$$

$$\therefore \frac{dW_{sp}^{(M_1,E_2)}}{dW_{sp}^{(E_1)}} \propto (kr)^2 = \left(\frac{2\pi a_0}{\lambda}\right)^2 \approx 10^{-6}. \qquad (274)$$

$\therefore$ M_1, E_2 transition probability is much smaller than E_1.

Considering $i\vec{k}\cdot\hat{\vec{r}}$ term,

$$\langle b|\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}e^{\pm i\vec{k}\cdot\hat{\vec{r}}}|a\rangle \longrightarrow \langle b|\pm i\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}\,\vec{k}\cdot\hat{\vec{r}}|a\rangle$$

$$i\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}\,\vec{k}\cdot\hat{\vec{r}} = i\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{P}}\hat{\vec{r}}\cdot\vec{k}$$

$$= \frac{1}{2}i\hat{\vec{e}}_{k\lambda}\cdot(\hat{\vec{P}}\hat{\vec{r}} - \hat{\vec{r}}\hat{\vec{P}})\cdot\vec{k} + \frac{1}{2}i\hat{\vec{e}}_{k\lambda}\cdot(\hat{\vec{P}}\hat{\vec{r}} + \hat{\vec{r}}\hat{\vec{P}})\cdot\vec{k}$$

$$\equiv \underset{\substack{\uparrow \\ \text{Asymmetry operator} \\ \downarrow \\ M_1 \text{ Transition}}}{\hat{O}_A} + \underset{\substack{\nwarrow \\ \text{Symmetry operator} \\ \downarrow \\ E_2 \text{ Transition}}}{\hat{O}_S} \qquad (275)$$

(1) Magnetic Dipole (M_1) Transition

Because $(\hat{\vec{A}} \times \hat{\vec{B}}) \cdot (\hat{\vec{C}} \times \hat{\vec{D}}) = (\hat{\vec{A}} \cdot \hat{\vec{C}})(\hat{\vec{B}} \cdot \hat{\vec{D}}) - (\hat{\vec{A}} \cdot \hat{\vec{D}})(\hat{\vec{B}} \cdot \hat{\vec{C}})$

$$\therefore \hat{O}_A = \frac{i}{2} \hat{\vec{e}}_{k\lambda} \cdot (\hat{\vec{P}}\hat{\vec{r}} - \hat{\vec{r}}\hat{\vec{P}}) \cdot \hat{\vec{K}}$$

$$= \frac{i}{2} [(\hat{\vec{e}}_{k\lambda} \cdot \hat{\vec{P}})(\hat{\vec{r}} \cdot \hat{\vec{K}}) - (\hat{\vec{e}}_{k\lambda} \cdot \hat{\vec{r}})(\hat{\vec{P}} \cdot \hat{\vec{K}})]$$

$$= \frac{i}{2} (\hat{\vec{K}} \times \hat{\vec{e}}_{k\lambda}) \cdot (\hat{\vec{r}} \times \hat{\vec{P}}) \qquad \hat{\vec{K}} = \hat{\vec{K}}_0 \frac{\omega}{c} = \hat{\vec{K}}_0 \frac{2\pi}{\lambda}$$

$$= \frac{i\omega}{2c} (\hat{\vec{K}}_0 \times \hat{\vec{e}}_{k\lambda}) \cdot \hat{\vec{L}} \qquad \hat{\vec{r}} \times \hat{\vec{P}} = \hat{\vec{L}}$$

$$= -i \frac{\mu\omega}{ec} (\hat{\vec{K}}_0 \times \hat{\vec{e}}_{k\lambda}) \cdot \hat{\vec{\mu}}_L \tag{276}$$

where $$\hat{\vec{\mu}}_L = -\frac{e\hbar}{2m_e}\sqrt{L(L+1)} = -\frac{e}{2m_e} g_L \hat{\vec{L}} = -\frac{e}{2\mu} g_L \hat{\vec{L}} \tag{277}$$

is the orbital magnetic moment of the electron. $(g_L = 1)$

$\hat{\vec{K}}_0 \times \hat{\vec{e}}_{k\lambda}$ is the unit vector along the magnetic field $\hat{\vec{B}}$.

From Eq. (203), we obtain the interaction Hamiltonian operator:

$$\hat{H}_{int} = \frac{e}{\mu} \sqrt{\frac{\hbar}{2\varepsilon_0 V\omega}}\, \hat{O}_A (\hat{a}_{k\lambda} - \hat{a}^+_{k\lambda})$$

$$= -\frac{i\omega}{c} \sqrt{\frac{\hbar}{2\varepsilon_0 V\omega}}\, (\hat{\vec{K}}_0 \times \hat{\vec{e}}_{k\lambda}) \cdot \hat{\vec{\mu}}_L (a_{k\lambda} - \hat{a}^+_{k\lambda})$$

Eq. (169) →

$$= - \hat{\vec{B}}(\hat{\vec{r}}) \cdot \hat{\vec{\mu}}_L \tag{278}$$

The $\frac{e}{\mu} \hat{\vec{S}}_i \cdot \hat{\vec{B}}$ term gives the interaction between electron spin magnetic moment and the radiation field. Through some algorithm, we obtain the Hamoltonian operator for M_1 transition:

$$\hat{H}_{int} = - \hat{\vec{B}}(\hat{\vec{r}}) \cdot \hat{\vec{\mu}} \tag{279}$$

where $\hat{\vec{\mu}}$ is the total magnetic dipole moment, including the electron orbital, electron spin, and nuclear spin contributions.

This is very similar to the electric dipole interaction:

$$\hat{H}_{int} = -\hat{\vec{E}}(\hat{\vec{r}})\cdot\hat{\vec{d}} \qquad (280)$$

Therefore, we can use similar derivation procedure to obtain the transition probability per unit time per solid angle:

$$dW_{sp} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{\omega^3}{2\pi\hbar c^5}\left|(\hat{\vec{k}}_0\times\hat{\vec{e}}_{k\lambda})\cdot\langle b|\hat{\vec{\mu}}|a\rangle\right|^2 d\Omega \qquad (281)$$

$$dW_{st} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{4\pi^2}{\hbar^2 c^3} I_{k\lambda}\left|(\hat{\vec{k}}_0\times\hat{\vec{e}}_{k\lambda})\cdot\langle b|\hat{\vec{\mu}}|a\rangle\right|^2 d\Omega \qquad (282)$$

When not considering hyperfine structure, $\langle b|\hat{\vec{\mu}}|a\rangle$ can be written as $\langle \alpha_b L_b S_b J_b M_b|\hat{\vec{\mu}}|\alpha_a L_a S_a J_a M_a\rangle$

$$= (-1)^{J_b-M_b}\begin{pmatrix} J_b & 1 & J_a \\ -M_b & q & M_a\end{pmatrix}\langle \alpha_b L_b S_b J_b \| \hat{\vec{\mu}} \| \alpha_a L_a S_a J_a\rangle \qquad (283)$$

where $\langle \alpha_b L_b S_b J_b \| \hat{\vec{\mu}} \| \alpha_a L_a S_a J_a\rangle = -\frac{e}{2\mu}\langle \alpha_b L_b S_b J_b \| \hat{\vec{L}} + 2\hat{\vec{S}} \| \alpha_a L_a S_a J_a\rangle$ (284)

The selection rules are

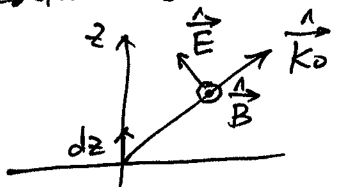
$$\Delta\alpha = 0 \ (\text{i.e., } \Delta n = 0), \quad \Delta L = 0, \quad \Delta S = 0$$
$$\Delta J = 0, \pm 1, \quad J_a + J_b \geq 1; \quad \Delta M = 0, \pm 1; \text{ no parity change.} \qquad (285)$$

When hyperfine structure is involved, additional selection rules are

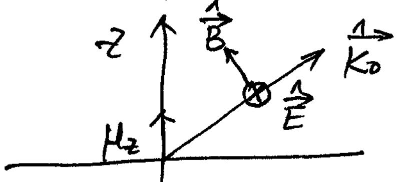
$$\Delta F = 0, \pm 1, \quad F_a + F_b \geq 1 \ (\text{i.e., } F=0 \not\leftrightarrow F=0)$$
$$\Delta m_F = 0, \pm 1. \qquad (286)$$

M_1 transitions only occur between fine structure or hyperfine structure (because $\Delta n = 0$), resulting in low transition frequency, ~ radio- or microwave frequency, and A_{ki} is small.

The angular distribution of M_1 radiation is similar to E_1 transition, but the polarization is different from E_1. For $\Delta M = 0$, see the figure below:



E_1 transition
$(\hat{\vec{d}} \cdot \hat{\vec{E}})$



M_1 transition
$(\hat{\vec{\mu}} \cdot \hat{\vec{B}})$

For E_1: $\vec{E}$ is in the plane of $(\hat{\vec{k}}_0, d_z)$

For M_1: $\vec{B}$ is in the plane of $(\hat{\vec{k}}_0, \mu_z)$, but $\vec{E}$ is perpendicular to this plane.

From $E_1 \to M$, the following transformation:

$$\hat{\vec{d}} \to \hat{\vec{\mu}}, \quad \hat{\vec{E}} \to \hat{\vec{B}}, \quad \hat{\vec{B}} \to -\hat{\vec{E}} \qquad (287).$$

After integrating through all possible directions,

$$W_{sp}(\alpha_a J_a \to \alpha_b J_b) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^5} \cdot \frac{1}{2J_a+1} \left| \langle \alpha_b J_b \| \hat{\vec{\mu}} \| \alpha_a J_a \rangle \right|^2 \qquad (288)$$

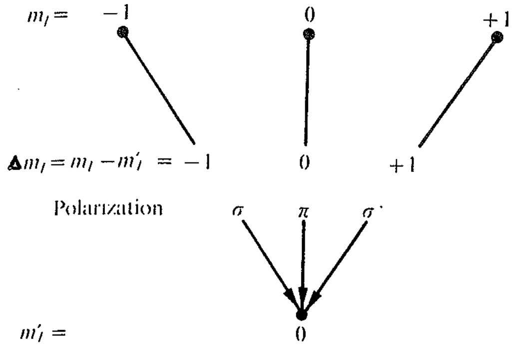
$$W_{st}(\alpha_a J_a \to \alpha_b J_b) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\pi^2}{3\hbar^2 c^2} \rho(\omega) \frac{1}{2J_a+1} \left| \langle \alpha_b J_b \| \hat{\vec{\mu}} \| \alpha_a J_a \rangle \right|^2 \qquad (289)$$

Polarization of Electric Dipole Transitions and Magnetic Dipole Transitions

(1) Polarization of Electric Dipole Transitions (E_1 Transitions)

$\Delta M = 0$, π-polarization (linear polarization)

$\Delta M = \pm 1$, σ-polarization (circular polarization)



Selection rules for magnetic quantum number m_l and polarization of electric dipole radiation (E_1) observed in the direction $\theta=0$.

(2) Polarization of Magnetic Dipole Transitions (M_1 transitions)

$\Delta M = \pm 1$, π-polarization (linear polarization for $\vec{E}$)

$\Delta M = 0$, σ-polarization (circular polarization for $\vec{E}$)

Selection rules for magnetic dipole transitions between hyperfine levels belonging to states with the same electronic angular momentum J (M_1) Transition

Static magnetic field $\underline{B}$	π-polarization ($\underline{B}_1 \perp \underline{B}$)	σ-polarization ($\underline{B}_1 \parallel \underline{B}$)
Weak	$\Delta M_F = \pm 1$	$\Delta M_F = 0$
Weak	$\Delta F = 0, \pm 1$	$\Delta F = \pm 1$
Strong	$\Delta M_J = \pm 1$	$\Delta M_J = 0$
Strong	$\Delta M_I = 0$	$\Delta M_I = 0$

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"Atomic and Laser Spectroscopy"

(2) Electric Quadrapole Transitions (E_2)

$$\hat{O}_s = \frac{i}{2}\hat{\vec{e}}_{k\lambda}\cdot(\hat{\vec{p}}\hat{\vec{r}}+\hat{\vec{r}}\hat{\vec{p}})\cdot\hat{\vec{k}} \qquad (290)$$

$$\because \ \hat{\vec{p}} = \frac{i\mu}{\hbar}[\hat{H}_a, \hat{\vec{r}}]$$

$$\therefore \ \hat{O}_s = -\frac{\mu}{2\hbar}\hat{\vec{e}}_{k\lambda}\cdot\{[\hat{H}_a,\hat{\vec{r}}]\hat{\vec{r}}+\hat{\vec{r}}[\hat{H}_a,\hat{\vec{r}}]\}\cdot\hat{\vec{k}}$$

$$= -\frac{\mu}{2\hbar}\hat{\vec{e}}_{k\lambda}\cdot[\hat{H}_a, \hat{\vec{r}}\hat{\vec{r}}]\cdot\hat{\vec{k}} \qquad (291)$$

$$\therefore \ \langle b|\hat{O}_s|a\rangle = -\frac{\mu}{2\hbar}(E_b-E_a)\hat{\vec{e}}_{k\lambda}\cdot\langle b|\hat{\vec{r}}\hat{\vec{r}}|a\rangle\cdot\hat{\vec{k}}$$

$$= -\frac{\mu\omega}{2}\hat{\vec{e}}_{k\lambda}\cdot\langle b|\hat{\vec{r}}\hat{\vec{r}}|a\rangle\cdot\hat{\vec{k}} \qquad (292)$$

Since $\hat{\vec{e}}_{k\lambda}\cdot\langle b|r^2\delta_{ij}|a\rangle\cdot\hat{\vec{k}} = \langle b|r^2\delta_{ij}|a\rangle\hat{\vec{e}}_{k\lambda}\cdot\hat{\vec{k}} = 0$ (293)

then in Eq.(292), we can replace $\hat{\vec{r}}\hat{\vec{r}}$ with $\hat{\vec{r}}\hat{\vec{r}} - r^2\delta_{ij}/3$

Define $\hat{Q} \equiv \hat{\vec{r}}\hat{\vec{r}} - \frac{1}{3}r^2\delta_{ij}$ (294),

then $\hat{Q}$ is the electric quadrapole of the atom.

$$\langle b|\hat{Q}|a\rangle = -\frac{\mu\omega}{2}\hat{\vec{e}}_{k\lambda}\cdot\langle b|\hat{Q}|a\rangle\cdot\hat{\vec{k}}$$

$$= -\frac{\mu\omega^2}{2c}\hat{\vec{e}}_k\cdot\langle b|\hat{Q}|a\rangle\cdot\hat{\vec{k}}_0 \qquad (295).$$

$\nearrow$ unit vector

The interaction Hamiltonian operator is

$$\hat{H}_{int} = \frac{e}{\mu}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega}}\,\hat{O}_s\,(\hat{a}_{k\lambda}-\hat{a}_{k\lambda}^{+})$$

$$= -\frac{e\omega}{2c}\sqrt{\frac{\hbar\omega}{2\varepsilon_0 V}}\,(\hat{\vec{e}}_{k\lambda}\cdot\hat{Q}\cdot\hat{\vec{k}}_0)(\hat{a}_{k\lambda}-\hat{a}_{k\lambda}^{+}) \qquad (296)$$

Regarding Eq.(296) as perturbation, we can use time-dependent perturbation theory to derive the transition probability, angular distribution, and polarization of E_2 transition.

Here we only analyze the selection rules.

$$\langle b | \hat{\vec{e}}_{k\lambda} \cdot \hat{Q} \cdot \hat{\vec{k}}_0 | a \rangle = \hat{\vec{e}}_{k\lambda} \cdot \langle b | Q | a \rangle \cdot \hat{\vec{k}}_0$$

$$\langle \alpha_b L_b S_b J_b M_b | Q^{(2)}_q | \alpha_a L_a S_a J_a M_a \rangle$$

$$= (-1)^{J_b - M_b} \begin{pmatrix} J_b & 2 & J_a \\ -M_b & q & M_a \end{pmatrix} \langle \alpha_b L_b S_b J_b \| Q^{(2)} \| \alpha_a L_a S_a J_a \rangle$$

The selection rules are

$\Delta L = 0, \pm 1, \pm 2, \quad L_a + L_b \geqslant 2; \quad \Delta S = 0$

$\Delta J = 0, \pm 1, \pm 2, \quad J_a + J_b \geqslant 2, \quad \Delta M = 0, \pm 1, \pm 2$

No parity change.

For hyperfine structure, add : $\Delta I = 0$.

* Example for E_2 and M_1 transitions: Oxygen atom OI.

OI ground state electron configuration: $1S^2 2S^2 2P^4$.

p^4 configuration has very similar atomic state terms as p^2.

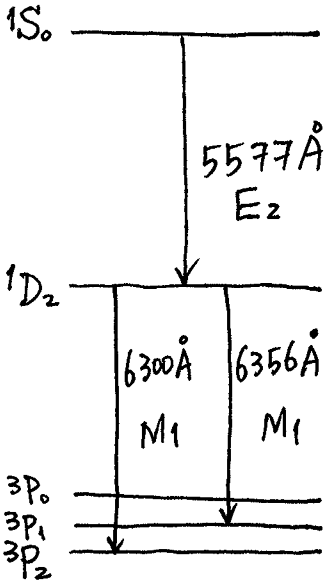
$$p^2: \left.\begin{array}{l} s_1 = \frac{1}{2},\ s_2 = \frac{1}{2} \Rightarrow S = 0,\ 1 \\ l_1 = 1,\ l_2 = 1 \Rightarrow L = 0, 1, 2 \end{array}\right\} {}^1S_0,\ {}^1D_2,\ {}^3P_{0,1,2} \text{ for equivalent electrons.}$$

According to Hund's rule, the ground state term is the term of maximum multiplicity, i.e., the term ^3P.

As the p shell is less than half filed in this p^2 configuration, the levels $J=0, 1, 2$ are arranged in normal order, i.e., the level $J=0$ is the lowest level. Thus, $^3P_0$ is the ground state for p^2.

As for p^4, the p shell is more than half filled, the level $J=0, 1, 2$ are arranged in reverse order, i.e., $J=2$ is the lowest. Thus, $^3P_2$ is the ground state for p^4 configuration.

From above analysis, we know the ground state of OI is 2^3P_2.



Atomic Oxygen (OI) Ground States

There is no E_1 transition between $^1S_0$ and $^1D_2$ to ^3P states, because $\Delta S \neq 0$. Therefore, $^1S_0$ and $^1D_2$ are both metastable states.

However, there are "famous" transitions between them due to E_2 and M_1 transitions.

From $^1S_0 \rightarrow {}^1D_2$, the famous green line 557.7 nm Airglow OI 5577 Å line is originating here! Since $\Delta L = 2, \Delta J = 2$, this is an E_2 transition.

As from $^1D_2 \rightarrow {}^3P$, because $^1D_2$ actually contains $^3P_2$ wave function, it is M_1 transitions:

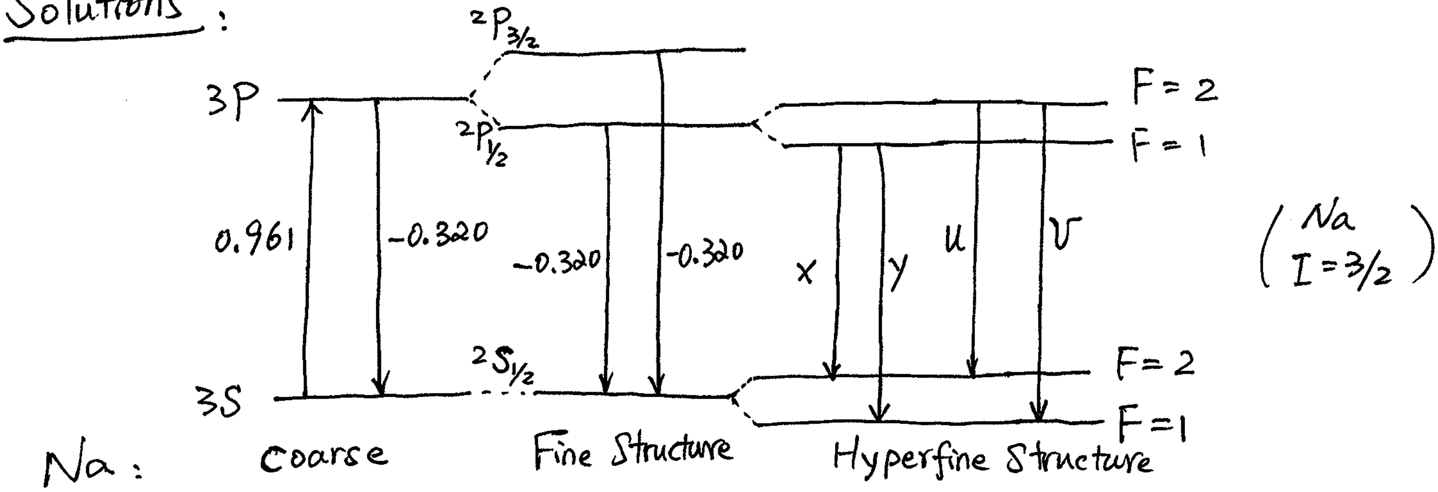
$$^3P_2 \rightarrow {}^3P_2, \text{ and } {}^3P_2 \rightarrow {}^3P_1$$

Corresponding to the famous double red lines 6300 Å and 6356 Å.

Example #1 for Radiative Transition Probability Computation

Problem: Given that Na $f(3S \to 3P) = 0.961$, find the transition probability of the four hyperfine components of D_1 line.

Solutions:



Na oscillator strength $f(3S \to 3P) = 0.961$.

From $-g_{La} f(La \to Lb) = g_{Lb} f(Lb \to La)$, we get

$$f(3P \to 3S) = -\frac{g_{3S}}{g_{3P}} f(3S \to 3P)$$

$$= -\frac{2\times 0+1}{2\times 1+1} \times 0.961 = -\frac{1}{3} \times 0.961$$

$$= -0.320$$

From $f(La \to Lb) = \sum_{Jb} f(Ja \to Jb)$, we obtain

$$f(3P \to 3S) = f(3^2P_{1/2} \to 3^2S_{1/2}) = f(3^2P_{3/2} \to 3^2S_{1/2})$$

$$\therefore\ f(3^2P_{1/2} \to 3^2S_{1/2}) = f(3^2P_{3/2} \to 3^2S_{1/2}) = -0.320.$$

D_1 line is the transition from $3^2P_{1/2} \to 3^2S_{1/2}$. Due to the nuclear spin of Na $I = 3/2$, there are hyperfine structures in $3^2P_{1/2}$ and $3^2S_{1/2}$. According to the selection rules, $\Delta F = 0, \pm 1$, so there are 4 hyperfine components in the D_1 spectral line, as illustrated in the above figure.

Let $x = f(3^2P_{1/2}, F=1 \rightarrow 3^2S_{1/2}, F=2)$

$y = f(3^2P_{1/2}, F=1 \rightarrow 3^2S_{1/2}, F=1)$

$u = f(3^2P_{1/2}, F=2 \rightarrow 3^2S_{1/2}, F=2)$

$v = f(3^2P_{1/2}, F=2 \rightarrow 3^2S_{1/2}, F=1)$

As the frequency difference among these 4 hyperfine lines are small, we treat them as the same frequency $\omega = 2\pi\nu = 2\pi\frac{c}{\lambda}$.

Since $f(J_a \rightarrow J_b) = \sum_{F_b} f(F_a \rightarrow F_b)$, we have

$$f(3^2P_{1/2} \rightarrow 3^2S_{1/2}) = x + y = u + v = -0.320.$$

$$f(F_a \rightarrow F_b) = \frac{2\mu\omega}{3\hbar e^2}\cdot\frac{1}{2F_a+1}|\langle\alpha_b J_b I_b F_b \| \hat{\vec{d}} \| \alpha_a J_a I_a F_a\rangle|^2.$$

From Group theory,

$$\langle\alpha_b J_b I_b F_b \| \hat{\vec{d}} \| \alpha_a J_a I_a F_a\rangle$$
$$= (-1)^{J_a+I_a+F_a+1}\delta_{I_bI_a}\sqrt{(2F_a+1)(2F_b+1)}\begin{Bmatrix} F_b & 1 & F_a \\ J_a & I_a & J_b \end{Bmatrix}\langle\alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a\rangle$$

$$\therefore f(F_a \rightarrow F_b) = \frac{2\mu\omega}{3\hbar e^2}\cdot\frac{\delta^2_{I_bI_a}}{2F_a+1}(2F_a+1)(2F_b+1)\begin{Bmatrix} F_b & 1 & F_a \\ J_a & I_a & J_b \end{Bmatrix}^2|\langle\alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a\rangle|^2$$

Lect $c = \frac{2\mu\omega}{3\hbar e^2}|\langle\alpha_b J_b \| \hat{\vec{d}} \| \alpha_a J_a\rangle|^2$

$$\therefore f(F_a \rightarrow F_b) = c\cdot\delta^2_{I_bI_a}\cdot(2F_b+1)\begin{Bmatrix} F_b & 1 & F_a \\ J_a & I_a & J_b \end{Bmatrix}^2$$

For x component, $J_a = \frac{1}{2}$, $I_a = \frac{3}{2}$, $F_a = 1$, $J_b = \frac{1}{2}$, $I_b = \frac{3}{2}$, $F_b = 2$

$$\therefore x = c\cdot 1\cdot(2\times 2+1)\begin{Bmatrix} 2 & 1 & 1 \\ \frac{1}{2} & \frac{3}{2} & \frac{1}{2} \end{Bmatrix}^2 = c\times 5\times\left(\frac{1}{2\sqrt{3}}\right)^2 = \frac{5}{12}c.$$

Similarly,

$$y = c\cdot 1\cdot(2\times 1+1)\begin{Bmatrix} 1 & 1 & 1 \\ \frac{1}{2} & \frac{3}{2} & \frac{1}{2} \end{Bmatrix}^2 = c\times 3\times\left(-\frac{1}{6}\right)^2 = \frac{1}{12}c.$$

$$u = c\cdot 1\cdot(2\times 2+1)\begin{Bmatrix} 2 & 1 & 2 \\ \frac{1}{2} & \frac{3}{2} & \frac{1}{2} \end{Bmatrix} = c\times 5\times\left(\frac{1}{2\sqrt{5}}\right)^2 = \frac{1}{4}c = \frac{3}{12}c$$

$$v = c\cdot 1\cdot(2\times 1+1)\begin{Bmatrix} 1 & 1 & 2 \\ \frac{1}{2} & \frac{3}{2} & \frac{1}{2} \end{Bmatrix} = c\times 3\times\left(\frac{1}{2\sqrt{3}}\right)^2 = \frac{1}{4}c = \frac{3}{12}c$$

$\therefore\ x : y : u : v = 5 : 1 : 3 : 3$

Substitute this into the above equation $x+y = u+v = -0.320$

$$\left\{\begin{matrix} x+y = -0.320 \\ u+v = -0.320 \end{matrix}\right\} \Rightarrow \begin{aligned} x &= \frac{5}{6}\times(-0.320) = -0.267 \\ y &= \frac{1}{6}\times(-0.320) = -0.053 \\ u &= \frac{1}{2}\times(-0.320) = -0.160 \\ v &= \frac{1}{2}\times(-0.320) = -0.160 \end{aligned}$$

The spontaneous transition probability per unit time is given by

$$W_{sp}(\alpha_a J_a I_a F_a \to \alpha_b J_b I_b F_b) = \frac{e^2\omega^2}{2\pi\varepsilon_0\mu c^3}\left[-f(F_a\to F_b)\right] \quad \text{(in SI unit)}$$

$$= \frac{-2\pi e^2}{\varepsilon_0 \mu c \lambda^2} f(F_a\to F_b)$$

$$= \frac{-2\pi\times(1.6\times10^{-19})^2\ f(F_a\to F_b)}{8.854\times10^{-12}\times 9.1\times10^{-31}\times 3\times10^{8}\times(589.6\times10^{-9})^2}$$

$$= 6.65\times10^{-5}\,\frac{\left[-f(F_a\to F_b)\right]}{\lambda^2}$$

$$= -1.914\times10^{8} f(F_a\to F_b) = 1.914\times10^{8}\,|f(F_a\to F_b)|$$

$\therefore\ W_{sp}(3^2P_{1/2}, F=1 \to 3^2S_{1/2}, F=2) = 1.914\times10^8\times|x| = 1.914\times10^8\times0.267 = 0.511\times10^8\,s^{-1}$

$W_{sp}(3^2P_{1/2}, F=1 \to 3^2S_{1/2}, F=1) = 1.914\times10^8\times|y| = 1.914\times10^8\times0.053 = 0.101\times10^8\,s^{-1}$

$W_{sp}(3^2P_{1/2}, F=2 \to 3^2S_{1/2}, F=2) = 1.914\times10^8\times|u| = 0.306\times10^8\,s^{-1}$

$W_{sp}(3^2P_{1/2}, F=2 \to 3^2S_{1/2}, F=1) = 1.914\times10^8\times|v| = 0.306\times10^8\,s^{-1}$.

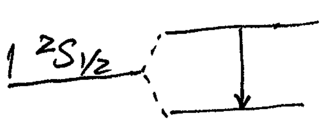
$\therefore$ The ratio of transition probability is $5:1:3:3$.

The ratio of spectral intensity is $5\times(2F_{a_1}+1) : 1\times(2F_{a_1}+1) : 3\times(2F_{a_2}+1)$
$: 3\times(2F_{a_2}+1) = 5\times3 : 1\times3 : 3\times5 : 3\times5 = 5:1:5:5$.

Example #2 for Radiative Transition Probability Calculation

Problem: Find the transition probability of $F=1 \rightarrow 0$ transition (spontaneous emission) within the ground state ${}^2S_{1/2}$ of hydrogen.

Solutions. H:



$\ell = 0,\ s = 1/2,\ j = \frac{1}{2}$

$I = \frac{1}{2},\ \therefore F = 1, 0.$

The transition between $F = 1 \leftrightarrow 0$ of the hyperfine structure of the ground state is a magnetic dipole transition (M_1).

The transition probability per unit time per unit solid angle is

$$dW_{sp}(F=1\rightarrow 0) = \frac{1}{4\pi\varepsilon_0}\frac{\omega^3}{2\pi\hbar c^5}\left|(\vec{k}_0\times\vec{e}_{k\lambda})\cdot\langle\alpha_b J_b I_b F_b\|\hat{\vec{\mu}}\|\alpha_a J_a I_a F_a\rangle\right|^2\cdot d\Omega$$

Integrating over all possible directions, i.e., 4π solid angle, the total spontaneous transition probability per unit time is

$$W_{sp}(F=1\rightarrow 0) = \frac{1}{4\pi\varepsilon_0}\cdot\frac{4\omega^3}{3\hbar c^5}\cdot\frac{1}{2F_a+1}\left|\langle\alpha_b J_b I_b F_b\|\hat{\vec{\mu}}\|\alpha_a J_a I_a F_a\rangle\right|^2$$

The magnetic dipole moment for hyperfine structure is (Note: $|\hat{\vec{J}}| = \sqrt{J(J+1)}\,\hbar$, $|\hat{\vec{I}}| = \sqrt{I(I+1)}\,\hbar$)

$$\hat{\vec{\mu}} = \hat{\vec{\mu}}_J + \hat{\vec{\mu}}_I = -\mu_B g_J\sqrt{J(J+1)} + \mu_B g_I'\sqrt{I(I+1)}$$

$$= -\frac{e}{2m_e}\left(g_J\hat{\vec{J}} - g_I'\hat{\vec{I}}\right) = -\mu_B\left(g_J\hat{\vec{J}} - g_I'\hat{\vec{I}}\right)$$

$$\therefore W_{sp}(F_a=1\rightarrow F_b=0) = \frac{1}{4\pi\varepsilon_0}\cdot\frac{4\omega^3}{3\hbar c^5}\cdot\frac{\mu_B^2}{2F_a+1}\left|\langle\alpha_b J_b I_b F_b\|\, g_J\hat{\vec{J}} - g_I'\hat{\vec{I}}\,|\alpha_a J_a I_a F_a\rangle\right|^2$$

$$\langle\alpha_b J_b I_b F_b\|\hat{\vec{J}}\|\alpha_a J_a I_a F_a\rangle$$

$$= (-1)^{J_b+I_b+F_a+1}\,\delta_{I_b I_a}\sqrt{(2F_a+1)(2F_b+1)}\begin{Bmatrix} F_b & 1 & F_a \\ J_a & I_a & J_b\end{Bmatrix}\langle J_b\|\hat{\vec{J}}\|J_a\rangle$$

$$= (-1)^{J_b+I_b+F_a+1}\,\delta_{I_b I_a}\sqrt{(2F_a+1)(2F_b+1)}\begin{Bmatrix} F_b & 1 & F_a \\ J_a & I_a & J_b\end{Bmatrix}\sqrt{(2J_a+1)(J_a+1)J_a}\;\delta_{J_a J_b}$$

$$= (-1)^{\frac{1}{2}+\frac{1}{2}+1+1}\times 1\times\sqrt{(2\times 1+1)(2\times 0+1)}\times\begin{Bmatrix} 0 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{Bmatrix}\times\sqrt{(2\times\tfrac{1}{2}+1)(\tfrac{1}{2}+1)\tfrac{1}{2}}\times 1$$

$$= (-1)\times\sqrt{3}\times\frac{1}{\sqrt{6}}\times\sqrt{\frac{3}{2}} = -\frac{\sqrt{3}}{2}$$

$$\langle \alpha_b J_b I_b F_b \| \hat{\vec{I}} \| \alpha_a J_a I_a F_a \rangle$$

$$= (-1)^{J_b+I_a+F_b+1}\, \delta_{J_b J_a} \sqrt{(2F_a+1)(2F_b+1)} \begin{Bmatrix} F_b & 1 & F_a \\ I_a & J_b & I_b \end{Bmatrix} \langle I_b \| \hat{\vec{I}} \| I_a \rangle$$

$$= (-1)^{J_b+I_a+F_b+1}\, \delta_{J_b J_a} \sqrt{(2F_a+1)(2F_b+1)} \begin{Bmatrix} F_b & 1 & F_a \\ I_a & J_b & I_b \end{Bmatrix} \sqrt{(2I_a+1)(I_a+1)I_a}\, \delta_{I_b I_a}.$$

$$= (-1)^{\frac{1}{2}+\frac{1}{2}+0+1} \times 1 \times \sqrt{(2\times1+1)(2\times0+1)} \times \begin{Bmatrix} 0 & 1 & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{Bmatrix} \times \sqrt{(2\times\frac{1}{2}+1)(\frac{1}{2}+1)\frac{1}{2}} \times 1$$

$$= 1 \times 1 \times \sqrt{3} \times \frac{1}{\sqrt{6}} \times \sqrt{\frac{3}{2}} = \frac{\sqrt{3}}{2}$$

$$\therefore \langle \alpha_b J_b I_b F_b \| g_J \hat{\vec{J}} - g_I' \hat{\vec{I}} \| \alpha_a J_a I_a F_a \rangle$$

$$= -\frac{\sqrt{3}}{2} g_J - \frac{\sqrt{3}}{2} g_I' = -\frac{\sqrt{3}}{2}(g_J + g_I')$$

$$g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} = 1 + \frac{\frac{1}{2}\times\frac{3}{2}+\frac{1}{2}\times\frac{3}{2}-0\times1}{2\times\frac{1}{2}\times\frac{3}{2}} = 2$$

$$g_I' = g_I \cdot \frac{m_e}{M_p} = \frac{5.58}{1836} = 0.003$$

$$\therefore W_{sp}(F_a=1 \to F_b=0) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{4\omega^3}{3\hbar c^5} \cdot \frac{\mu_B^2}{2F_a+1} \left[-\frac{\sqrt{3}}{2}(g_J+g_I)\right]^2$$

$$= \frac{(2\pi\nu)^3}{3\pi\varepsilon_0\hbar c^5} \cdot \frac{e^2\hbar^2}{4m_e^2} \cdot \frac{1}{2F_a+1} \cdot \frac{3}{4} \cdot (g_J+g_I)^2$$

$$= \frac{\pi^2\nu^3 e^2\hbar}{2\varepsilon_0 c^5 m_e^2} \cdot \frac{1}{2F_a+1} \cdot (g_J+g_I)^2.$$

$$= \frac{3.14^2 \times (1420\times10^6)^3 \times (1.6\times10^{-19})^2 \times 6.626\times10^{-34}/2\pi}{2\times 8.854\times10^{-12} \times (3\times10^8)^5 \times (9.1\times10^{-31})^2} \cdot \frac{1}{2\times1+1} \cdot (2+0.003)^2$$

$$= 2.85\times10^{-15}\ s^{-1}$$

Such small transition probability comes from two aspects:

① M_1 transition

② Low frequency $\nu = 1420$ MHz.