

Lecture 7. Fundamentals of Atomic Spectra 2/7/06

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I. Introduction

* Last week we talked about atomic structure; how atomic energy levels ~~are~~ are determined by the interactions within an atomic system and by interactions of atom with external static field (i.e., DC field - direct current)

* Today we will talk about how an atom can transit from one stationary state to another under the influence of ~~external~~ radiation or perturbation (i.e., external AC field) (alternating current)

* The ^{common} method to study transition is called perturbation theory.

II. Perturbation Theory

This is a commonly used method in quantum mechanics, because most eigenvalue equations and Schrödinger equations ~~cannot~~ cannot be solved analytically if all interactions are put in the equations at the same time.

In Many Cases, the interactions have different orders of magnitude. When the small quantities are neglected, the problem may be simpler to ~~to~~ have exact solutions. In such cases, perturbation theory can be used: the first step is to solve

Skip this section → go to time-dependent perturbation
 1. For time-independent perturbations → energy shift & splitting (2)

$$H = H_0 + \hat{V} \quad (1) \quad \begin{array}{l} H_0 - \text{unperturbed operator} \\ \hat{V} - \text{perturbation} \end{array}$$

Condition: $\hat{V} \ll H_0$

If eigenfunctions for H_0 are known, $H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$ (2)
 We want to find approximate solution of the equation:

$$\hat{H} |\psi\rangle = (H_0 + \hat{V}) |\psi\rangle = E |\psi\rangle \quad (3)$$

To solve this equation, we expand ψ in terms of $\psi_n^{(0)}$

$$|\psi\rangle = \sum_m C_m |\psi_m^{(0)}\rangle \quad (4)$$

$$\begin{aligned} (H_0 + \hat{V}) \sum_m C_m |\psi_m^{(0)}\rangle &= E \sum_m C_m |\psi_m^{(0)}\rangle \\ \Rightarrow \sum_m C_m (E_m^{(0)} + \hat{V}) |\psi_m^{(0)}\rangle &= \sum_m C_m E |\psi_m^{(0)}\rangle \quad (5) \end{aligned}$$

$\langle \psi_k^{(0)} |$ times the equation:

$$\begin{aligned} \sum_m C_m E_m^{(0)} \langle \psi_k^{(0)} | \psi_m^{(0)} \rangle + \sum_m C_m \langle \psi_k^{(0)} | \hat{V} | \psi_m^{(0)} \rangle \\ = \sum_m C_m E \langle \psi_k^{(0)} | \psi_m^{(0)} \rangle \end{aligned}$$

$$\langle \psi_k^{(0)} | \psi_m^{(0)} \rangle = \delta_{km} \Rightarrow C_k E_k^{(0)} + \sum_m C_m \langle \psi_k^{(0)} | \hat{V} | \psi_m^{(0)} \rangle = C_k E$$

$$\langle \psi_k^{(0)} | \hat{V} | \psi_m^{(0)} \rangle = V_{km} \Rightarrow (E - E_k^{(0)}) C_k = \sum_m C_m V_{km} \quad (6)$$

Since we do not know the coefficients C_m , we can't just calculate E from the above equation. We must seek the values of the coefficients C_m and the energy E in the following form:

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots, \quad C_m = C_m^{(0)} + C_m^{(1)} + C_m^{(2)} + \dots \quad (7)$$

$E^{(1)}$ and $C_m^{(1)}$ are of the same order of smallness as \hat{V} ,

$E^{(2)}$ and $C_m^{(2)}$ are of the second order of smallness, and so on.

Let's consider the first-order terms. Assume originally the system is in the n th eigen state, $|\psi_n^{(0)}\rangle$ with $E_n^{(0)}$

i.e.,
$$\begin{cases} C_n^{(0)} = 1, \\ C_m^{(0)} = 0, \text{ for } m \neq n \end{cases}$$

$$C_n^{(0)} = \delta_{nm}$$

Substitute
$$E = E_n^{(0)} + E_n^{(1)}$$

$$\begin{cases} C_k = C_k^{(0)} + C_k^{(1)} \end{cases}$$

The idea behind this is that after the time-independent perturbation, the eigenvalue is still close to the original $E_n^{(0)}$ but with small corrections.

into Eq. (6)

$$(E_n^{(0)} + E_n^{(1)} - E_n^{(0)}) (C_n^{(0)} + C_n^{(1)}) = \sum_m (C_m^{(0)} + C_m^{(1)}) V_{nm}$$

$$C_m^{(0)} = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$$

$$E_n^{(1)} (1 + C_n^{(1)}) = V_{nn} + \sum_m C_m^{(1)} V_{nm}$$

$$E_n^{(1)} + E_n^{(1)} C_n^{(1)} = V_{nn} + \sum_m C_m^{(1)} V_{nm} \rightarrow \text{2nd order term}$$

Only retain the 1st order terms, then we have:

The coefficients $C_k^{(1)}$

$$E_n^{(1)} = V_{nn} = \langle \psi_n^{(0)} | \hat{V} | \psi_n^{(0)} \rangle \quad (8)$$

for $k \neq n$,
$$(E_n^{(0)} + E_n^{(1)} - E_k^{(0)}) C_k^{(1)} = \sum_m V_{km} C_m^{(1)} + V_{kn} C_n^{(0)}$$

$C_k^{(0)} = 0$
 $C_m^{(0)} = 0 (m \neq n)$

retain first-order only

$$[E_n^{(0)} - E_k^{(0)}] C_k^{(1)} = V_{kn}$$

$$\Rightarrow C_k^{(1)} = \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} \quad \text{for } k \neq n. \quad (9)$$

* $C_n^{(1)}$ is still arbitrary. It must be chosen so that the function $|\psi_n\rangle = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle$ is normalized up to the first order.

$$\Rightarrow C_n^{(1)} = 0. \Rightarrow |\psi_n\rangle = \sum_m [C_m^{(0)} + C_m^{(1)}] |\psi_m^{(0)}\rangle$$

$$= |\psi_n^{(0)}\rangle + \sum_m C_m^{(1)} |\psi_m^{(0)}\rangle = |\psi_n^{(0)}\rangle + \sum_m \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle \quad (10)$$

i.e., $|\psi_n^{(1)}\rangle = \sum_m' \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$ (11) \rightarrow orthogonal to $\psi_n^{(0)}$ ④

Therefore, the new eigenstate ψ_n is a superposition of the original eigen-states ~~$\{\psi_k^{(0)}\}$~~ $\{\psi_k^{(0)}\}$, though $|\psi_n^{(0)}\rangle$ still dominates the new eigenstate.

In other words, with perturbation \hat{V} , the original eigenstates $\{|\psi_k^{(0)}\rangle\}$ are not eigenstates any more. The new eigenstates corresponding to $\hat{H} = \hat{H}_0 + \hat{V}$ can be expressed as a superposition of the original state.

New eigenstates: $|\psi_n\rangle = |\psi_n^{(0)}\rangle + \sum_m' \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$, (Prime means $m \neq n$)

Corresponding eigenvalues: $E_n = E_n^{(0)} + V_{nn}$.

$|\langle \psi_n | \psi_n \rangle|^2 = |\langle \psi_n^{(0)} + \psi_n^{(1)} | \psi_n^{(0)} + \psi_n^{(1)} \rangle|^2$

$$= |\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle|^2 + \underbrace{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}_{=0} + \underbrace{\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle}_{=0} + |\langle \psi_n^{(1)} | \psi_n^{(1)} \rangle|^2$$

$|V_{mn}| \ll |E_n^{(0)} - E_m^{(0)}|$ \rightarrow 2nd order of smallness.

Let us consider 2nd order approximation.

Substitute $E = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$

$\begin{cases} E = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} \\ C_k = C_k^{(0)} + C_k^{(1)} + C_k^{(2)} \end{cases}$

into Eq. (6) and exam

2nd order terms only:

$$[E_n^{(0)} + E_n^{(1)} + E_n^{(2)} - E_k^{(0)}] [C_k^{(0)} + C_k^{(1)} + C_k^{(2)}] = \sum_m V_{km} [C_m^{(0)} + C_m^{(1)} + C_m^{(2)}]$$

for $k = n$:
 $C_n^{(0)} = 1$

$$[E_n^{(1)} + E_n^{(2)}] [1 + C_n^{(1)} + C_n^{(2)}] = V_{nn} (1 + C_n^{(1)} + C_n^{(2)}) + \sum_m' V_{nm} [C_m^{(1)} + C_m^{(2)}]$$

2nd order

terms: $E_n^{(1)} C_n^{(1)} + E_n^{(2)} = V_{nn} C_n^{(1)} + \sum'_m V_{nm} C_m^{(1)}$

(5)

recall $E_n^{(1)} = V_{nn}$, $\therefore E_n^{(2)} = \sum'_m V_{nm} C_m^{(1)}$

$$C_m^{(1)} = \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} = \sum'_m \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}$$

~~to obtain~~ $|\psi_n\rangle = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle$ ~~that Eq (4)~~

We need to derive $C_m^{(2)}$ for all m .

~~to obtain~~

See Landau's book PP. 135-136 for

derivation of the 2nd order wavefunction, and third order $E_n^{(3)}$.

2. For time-dependent perturbation, \rightarrow transition (6)

* For time-~~independent~~ independent perturbation, we do corrections to the system eigenvalues and eigenstates, since the energy corresponding to $\hat{H} = \hat{H}_0 + \hat{V}$ is still conserved, so there are still stationary state.

* For time-dependent perturbation, \hat{H} is time-dependent, so the energy is not conserved, and there are no stationary states.
$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

* The problem becomes approximately calculating the wave function or state of the perturbed system from the stationary states of the unperturbed system. In other words, the new state will be the superposition of the stationary states, and allows the transition from one state to another.

* Let $\{|\psi_k^{(0)}\rangle\}$ be the stationary states of the unperturbed system, including the time factor $e^{-iE_k^{(0)}t/\hbar}$.

$$\hat{H}_0 |\psi_k^{(0)}\rangle = E_k^{(0)} |\psi_k^{(0)}\rangle$$

$$\text{or: } i\hbar \frac{\partial}{\partial t} |\psi_k^{(0)}\rangle = \hat{H}_0 |\psi_k^{(0)}\rangle \quad (2.1)$$

An arbitrary solution to unperturbed equation (2.1) can be written as a superposition of $\{|\psi_k^{(0)}\rangle\}$:

$$|\psi\rangle = \sum_k a_k |\psi_k^{(0)}\rangle \quad (2.2)$$

We shall seek the solution of the perturbed equation:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = (\hat{H}_0 + \hat{V}(t)) |\psi\rangle \quad (2.3)$$

In the form of a sum: $|\psi\rangle = \sum_k a_k(t) |\psi_k^{(0)}\rangle \quad (2.4)$

Notice the difference: now the coefficients are functions of time.

Substitute Eq. (2.4) into Eq. (2.3) :

$$\begin{aligned}
 & i\hbar \sum_k a_k(t) \frac{\partial |\psi_k^{(0)}\rangle}{\partial t} + i\hbar \sum_k \frac{da_k(t)}{dt} |\psi_k^{(0)}\rangle \\
 & = \sum_k a_k(t) (\hat{H}_0 + \hat{V}) |\psi_k^{(0)}\rangle \\
 \Rightarrow & \sum_k a_k(t) \hat{H}_0 |\psi_k^{(0)}\rangle + i\hbar \sum_k \frac{da_k(t)}{dt} |\psi_k^{(0)}\rangle \\
 & = \sum_k a_k(t) \hat{H}_0 |\psi_k^{(0)}\rangle + \sum_k a_k(t) \hat{V} |\psi_k^{(0)}\rangle \quad (2.4)
 \end{aligned}$$

$\langle \psi_k^{(0)} |$ times the equation and recall $\langle \psi_m^{(0)} | \psi_k^{(0)} \rangle = \delta_{mk}$

We have $i\hbar \frac{da_m(t)}{dt} = \sum_k a_k(t) V_{mk}(t)$ (2.5)

Here, $V_{mk}(t) = \langle \psi_m^{(0)} | \hat{V} | \psi_k^{(0)} \rangle = V_{mk} e^{i(E_m^{(0)} - E_k^{(0)})t/\hbar}$ (2.6)

are the matrix elements of the perturbation.

Note: because $\hat{V}(t)$ depends on time, V_{mk} itself is a function of time

$V_{mk}(t)$ also includes the time factor $e^{i\omega_{mk}t}$, $\omega_{mk} = \frac{E_m^{(0)} - E_k^{(0)}}{\hbar}$

We assume that before the time-dependent perturbation \hat{V} is applied to the system, the unperturbed system is in the ~~state~~ ^{initial} stationary state $|\psi_n^{(0)}\rangle$, so

$$\begin{cases} a_n^{(0)} = 1 \\ a_k^{(0)} = 0 \text{ for } k \neq n \end{cases} \quad (2.7)$$

To find the first approximation, we seek a_k in the form

of $a_k = a_k^{(0)} + a_k^{(1)}$. Substituting $a_k = a_k^{(0)}$ on the right-hand side of equation (2.5) which already contains the small quantities V_{mk} , i.e., keep the 1st order terms on

both sides: $i\hbar \frac{da_k^{(1)}}{dt} = a_n^{(0)}(t) V_{kn}(t) = V_{kn}(t)$ (2.8)

To show ^{to} which unperturbed state the correction is made, we introduce the 2nd suffix in the a_n , and write

$$\psi_n = \sum_k a_{kn}(t) \psi_k^{(0)} \quad (2.9)$$

The $a_{kn}^{(1)}$ can be obtained by integrating Eq. (2.8):

$$\begin{aligned} a_{kn}^{(1)} &= -\frac{i}{\hbar} \int V_{kn}(t) dt \\ &= -\frac{i}{\hbar} \int V_{kn} e^{i\omega_{kn}t} dt \end{aligned} \quad (2.10)$$

This determines the state in the first approximation:

$$\psi = \psi_n^{(0)} + \sum_k a_{kn}^{(1)}(t) \psi_k^{(0)}$$

Therefore, under the perturbation $\hat{V}(t)$, the system is no longer in the n th stationary state, but in the superposition of ~~several~~ (unperturbed) stationary states, which gives the basis for the system to pass from one initial stationary state to any other — the transition.

* Let us consider a ~~few~~ example: \leftarrow

(Transitions under a perturbation acting for a finite time)

$\hat{V}(t)$ acts only during some finite interval of time

(i.e., $V(t)$ vanishes as $t \rightarrow \pm\infty$).

Let the system be in the n th stationary state before the perturbation ($t \rightarrow -\infty$). At any subsequent instant,

the state of the system will be determined by the function

$$\psi = \sum_k a_{kn}(t) \psi_k^{(0)}$$

To the 1st order approximation,

(9)

$$\begin{cases} a_{kn} = a_{kn}^{(1)} = -\frac{i}{\hbar} \int_{-\infty}^t V_{kn} e^{i\omega_{kn}t} dt & \text{for } k \neq n \\ a_{nn} = 1 + a_{nn}^{(1)} = 1 - \frac{i}{\hbar} \int_{-\infty}^t V_{nn} dt & \text{~~for } k = n \end{cases} \quad (2.11)~~$$

The limits of integration in Eq (2.11) are taken so that as $t \rightarrow -\infty$, all $\begin{cases} a_{kn}^{(1)} \\ a_{nn}^{(1)} \end{cases}$ tend to zero.

After the perturbation has ceased to act (or in the limit $t \rightarrow +\infty$), the coefficient a_{kn} take constant values $a_{kn}(\infty)$ and the system is in the state ~~ψ~~

(no more change with time)

$$|\psi\rangle = \sum_k a_{kn}(\infty) |\psi_k^{(0)}\rangle$$

Which again satisfies the unperturbed ~~eigenvalue~~ ^(Schrödinger) equation, but is different from the original state $|\psi_n^{(0)}\rangle$.

According to the general rule, the squared modulus of the coefficient $a_{kn}(\infty)$ determines the probability for the system to have an energy $E_k^{(0)}$, i.e., to be in the k th stationary state.

Thus, under the action of the perturbation, the system may pass from its initial stationary state to any other. The probability of a transition from the initial (i th) to the final (f th) stationary state is

$$W_{fi} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{+\infty} V_{fi} e^{i\omega_{fi}t} dt \right|^2 \quad (2.12)$$

When ~~the~~ perturbation is not small, V_{fi} becomes $\langle \psi_f | \hat{V} | \psi_i^{(0)} \rangle$
 eigenstate for \rightarrow new \hat{H}
 eigenstate for \hat{H}_0 \leftarrow

III. Atomic Transition. (郑乐民“原子结构与原子光谱” ⑩)

If a physical system is set up in a certain stationary state, it will remain in that stationary state so long as it is not acted upon by outside forces. With the interaction from external EM fields, it is liable to cease to be in one stationary state and to make a transition to another.

1. Transition probability
 To derive the transition probability, we should consider the "atom + radiation field" as an entire system, and its total Hamiltonian is given by

$$\hat{H} = \hat{H}_{\text{radiation}} + \hat{H}_{\text{atom}} + \hat{H}_{\text{interaction}}. \quad (3.1)$$

$\hat{H}_{\text{radiation}}$ is the Hamiltonian operator for radiation field,

\hat{H}_{atom} is the Hamiltonian operator for atom,

and $\hat{H}_{\text{interaction}}$ is the Hamiltonian operator for the interaction between the atom and the radiation.

Quantum Theory of radiation

$$(3.2) \quad \left\{ \begin{aligned} \hat{H}_{\text{radiation}} &= \sum_k \hbar \omega_k (a_k^\dagger a_k + 1/2) \\ \hat{H}_{\text{atom}} &= \sum_i \hat{p}_i^2 / 2\mu + U \\ \hat{H}_{\text{interaction}} &= \frac{e}{\hbar c} \vec{A} \cdot \vec{p} + \frac{e^2}{2\hbar c^2} \vec{A}^2 \end{aligned} \right.$$

\vec{A} : vector potential
 $\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t}$
 $\vec{B} = \nabla \times \vec{A}$

creation operator annihilation operator
 reduced mass vector potential atom momentum

Usually, the radiation field is not very strong, so only the 1st term in \hat{H}_{int} is considered.

$$(3.3) \quad \left\{ \begin{aligned} \hat{H}' &= \frac{e}{\hbar c} \vec{A} \cdot \vec{p} \\ \hat{H}_0 &= \hat{H}_{\text{radiation}} + \hat{H}_{\text{atom}} \end{aligned} \right.$$

be a perturbation to

Then we can use the time-dependent perturbation theory to calculate the transition probability. We will not go through such calculation, but only give the results. ①

The results of the interaction between atom and radiation field are that the atom will transit from one energy level to another.

Assume:	initial state	final state
Atom	$ a\rangle$	$ b\rangle$
radiation field	$ n_{k\lambda}\rangle$	$ n_{k\lambda}\pm 1\rangle$
	↑	
(number of photons with wave vector \vec{k} and energy polarization)		
Entire System	$ A\rangle = a\rangle n_{k\lambda}\rangle$ $= a, n_{k\lambda}\rangle$	$ B\rangle = b\rangle n_{k\lambda}\pm 1\rangle$ $= b, n_{k\lambda}\pm 1\rangle$

From the perturbation theory, the transition probability in unit time from $|A\rangle$ to $|B\rangle$ is given by

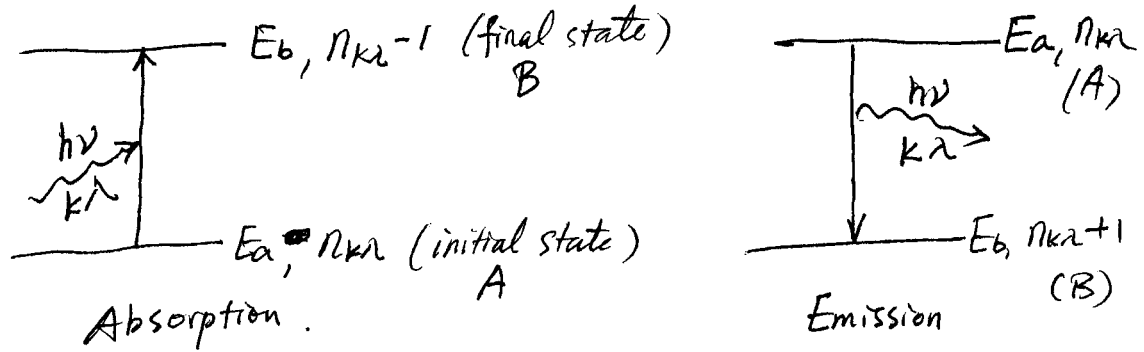
$$\frac{dP_{A \rightarrow B}}{dt} = W_{A \rightarrow B} = \frac{2\pi}{\hbar} |\langle B | \hat{H}' | A \rangle|^2 \delta(E_B - E_A) \quad (3.4)$$

$$(3.5) \begin{cases} \hat{H}_{\text{atom}} |a\rangle = E_a |a\rangle, \quad \hat{H}_{\text{atom}} |b\rangle = E_b |b\rangle \\ \hat{H}_{\text{rad}} |n_{k\lambda}\rangle = n_{k\lambda} h\nu |n_{k\lambda}\rangle, \quad \hat{H}_{\text{rad}} |n_{k\lambda}\pm 1\rangle = (n_{k\lambda}\pm 1) h\nu |n_{k\lambda}\pm 1\rangle \end{cases} \quad \begin{matrix} \text{Energy} \\ \text{Conservative} \end{matrix}$$

1) For absorption process, initial state is a ground state with atom energy E_a , and photon number $n_{k\lambda}$; final state is an excited state with atom energy E_b and photon number of $n_{k\lambda}-1$.

$$\begin{aligned} W_{A \rightarrow B} &= \frac{2\pi}{\hbar} |\langle B | \hat{H}' | A \rangle|^2 \delta(E_B - E_A) \\ &= \frac{2\pi}{\hbar} |\langle B | \hat{H}' | A \rangle|^2 \delta(E_b - h\nu_k - E_a) \end{aligned} \quad (3.6)$$

(12)



$$\begin{aligned} \langle B | \hat{H}' | A \rangle &= \langle b, n_{k\lambda}-1 | \hat{H}'^{(+)} | a, n_{k\lambda} \rangle \\ &= \frac{e}{\mu} \sqrt{\frac{2\pi\hbar}{V\omega_k}} \sqrt{n_{k\lambda}} \langle b | \vec{e}_{k\lambda} \cdot \vec{p} e^{-i\vec{k}\cdot\vec{r}} | a \rangle \quad (3.7) \end{aligned}$$

Substitute ~~the~~ Eq. (3.7) into Eq. (3.6), we get

$$\left(\frac{CGSE}{\text{unit}} \right) W_{ab} = \frac{4\pi^2 e^2}{\mu^2 V \omega_k} n_{k\lambda} |\langle b | \vec{e}_{k\lambda} \cdot \vec{p} e^{-i\vec{k}\cdot\vec{r}} | a \rangle|^2 \delta(E_b - E_a - \hbar\omega_k) \quad (3.8)$$

(2) For emission process, initial state is an excited state with atomic energy of E_a and photon number of $n_{k\lambda}$; the final state is a ground state with atomic energy of E_b and photon number of $n_{k\lambda}+1$.

$$\begin{aligned} W_{A \rightarrow B} &= \frac{2\pi}{\hbar} |\langle B | \hat{H}' | A \rangle|^2 \delta(E_B - E_A) \\ &= \frac{2\pi}{\hbar} |\langle B | \hat{H}'^{(+)} | A \rangle|^2 \delta(E_b + \hbar\omega_k - E_a) \quad (3.9) \end{aligned}$$

$$\begin{aligned} \langle B | \hat{H}' | A \rangle &= \langle b, n_{k\lambda}+1 | \hat{H}'^{(+)} | a, n_{k\lambda} \rangle \\ &= \frac{e}{\mu} \sqrt{\frac{2\pi\hbar}{V\omega_k}} \sqrt{n_{k\lambda}+1} \langle b | \vec{e}_{k\lambda} \cdot \vec{p} e^{-i\vec{k}\cdot\vec{r}} | a \rangle \quad (3.10) \end{aligned}$$

Substitute Eq. (3.10) into Eq. (3.9), we obtain

$$W_{em} = \frac{4\pi^2 e^2}{\mu^2 V \omega_k} (n_{k\lambda}+1) |\langle b | \vec{e}_{k\lambda} \cdot \vec{p} e^{-i\vec{k}\cdot\vec{r}} | a \rangle|^2 \delta(E_b - E_a + \hbar\omega_k) \quad (3.11)$$

Where $\vec{e}_{k\lambda}$ is the unit vector for ^{photon} polarization direction

Eqs. (3.8) and (3.11) give the ^{transition} ~~probability~~ ^{special} of the system ⁽¹³⁾ ~~also~~ absorbing or emitting a photon with k, λ properties. In other words, it describes the interaction ~~results~~ of atom with single mode radiation field.

* In reality, there may be many modes in the radiation field. Assume in a solid angle $d\Omega$ (within a narrow freq. range), there are many modes, which all can interact with the atom. Then the transition probability should be multiplied by the number of modes. The photon number $n_{k\lambda}$ should be replaced by an average $\bar{n}_{k\lambda}$:

$$dN = \frac{V}{(2\pi)^3 \hbar c^3} \omega^2 d\Omega dE. \quad (\omega_k \rightarrow \omega) \quad (3.12)$$

Therefore, we have a generalized expression of transition probability

$$dW_{em} = \frac{e^2 \omega}{2\pi \mu^2 \hbar c^3} (\bar{n}_{k\lambda} + 1) |\langle b | \vec{e}_{k\lambda} \cdot \vec{p} e^{-i\vec{k} \cdot \vec{r}} | a \rangle|^2 d\Omega \quad (3.13)$$

$$dW_{ab} = \frac{e^2 \omega}{2\pi \mu^2 \hbar c^3} \bar{n}_{k\lambda} |\langle b | \vec{e}_{k\lambda} \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}} | a \rangle|^2 d\Omega. \quad (3.14)$$

* Note: In Eq. (3.13), there is a term that is independent of the photon number of radiation field ($\bar{n}_{k\lambda}$). It means that even without the external resonance radiation field, there is still emission. This is the spontaneous emission, and its transition probability is

$$dW_{sp} = \frac{e^2 \omega}{2\pi \mu^2 \hbar c^3} |\langle b | \vec{e}_{k\lambda} \cdot \vec{p} e^{-i\vec{k} \cdot \vec{r}} | a \rangle|^2 d\Omega \quad (3.15)$$

The rest of Eq. (3.13) gives the stimulated emission transition probability.

(4)

Therefore, the stimulated transition (emission or absorption) probability can be written as

$$dW_{st} = \frac{e^2 \omega \bar{n}_{k\alpha}}{2\pi \mu^2 \hbar c^3} |\langle b | \vec{e}_{k\alpha} \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}} | a \rangle|^2 d\Omega. \quad (3.16)$$

If we express $\bar{n}_{k\alpha}$ through ~~energy~~ $I_{k\alpha}$ (energy flux density or light intensity): $\bar{n}_{k\alpha} = \frac{(2\pi)^3 c^2}{\hbar \omega^3} I_{k\alpha}$, (3.17)

then we have:

$$dW_{st} = \frac{(2\pi)^2 e^2}{\mu^2 \hbar^2 \omega^2 c} I_{k\alpha} |\langle b | \vec{e}_{k\alpha} \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}} | a \rangle|^2 d\Omega. \quad (3.18)$$

* ~~Eqs.~~ Eqs. (3.15) and (3.16) give the expressions ~~for~~ for spontaneous emission and stimulated transition probability transitions.

To obtain the final number, we need to compute the

matrix element $|\langle b | \vec{e}_{k\alpha} \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}} | a \rangle|^2$.

Notice ~~the~~ $e^{i\vec{k} \cdot \vec{r}}$ term, since light $\lambda \gg \overset{\circ}{A}$ (atom),

$\vec{k} \cdot \vec{r} \ll 1$, Thus, $e^{i\vec{k} \cdot \vec{r}}$ can be expanded as

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

When $e^{i\vec{k} \cdot \vec{r}} = 1$, it is for the electric dipole transition,

When considering the second term $i\vec{k} \cdot \vec{r}$,

it is the magnetic dipole transition

and electric quadrupole transition.

\vec{r} is the vector of electron relative to center of mass

* Eqs. (3.8) and (3.11) also indicate the condition for a radiation field to cause transition is that $\hbar \omega_k = |E_b - E_a|$.

2. Selection Rules

(i) Electric - Dipole (E1) Transition

$$e^{i\vec{k}\cdot\vec{r}} \approx 1, \Rightarrow \langle b | \vec{e} \cdot \vec{p} e^{i\vec{k}\cdot\vec{r}} | a \rangle \approx \langle b | \vec{e} \cdot \vec{p} | a \rangle$$

\vec{p} can be exchanged to \vec{r} using the commutation relation:

$$[\vec{r}, \hat{H}_{\text{atom}}] = \frac{i\hbar}{\mu} \vec{p} \Rightarrow \vec{p} = \frac{\mu}{i\hbar} [\vec{r}, \hat{H}_{\text{atom}}]$$

$$\begin{aligned} \therefore \langle b | \vec{p} | a \rangle &= \frac{\mu}{i\hbar} \langle b | \vec{r} \hat{H}_{\text{atom}} - \hat{H}_{\text{atom}} \vec{r} | a \rangle \\ &= \frac{\mu}{i\hbar} (E_a - E_b) \langle b | \vec{r} | a \rangle \\ &= i\mu \omega_{ba} \langle b | \vec{r} | a \rangle, \end{aligned}$$

$$\text{where } \omega_{ba} = \frac{E_b - E_a}{\hbar}$$

$$\begin{aligned} \therefore |\langle b | \vec{e} \cdot \vec{p} e^{i\vec{k}\cdot\vec{r}} | a \rangle|^2 &= |\vec{e} \cdot \langle b | \vec{p} | a \rangle|^2 \\ &= \mu^2 \omega^2 |\vec{e} \cdot \langle b | \vec{r} | a \rangle|^2 \\ &= \mu^2 \omega^2 |\langle b | \vec{e} \cdot \vec{r} | a \rangle|^2 \end{aligned}$$

Define atomic electric dipole $\vec{d} = -e\vec{r}$ ← vector of electron to center of mass
electron charge

Then we get the transition probability:

$$\begin{aligned} dW_{sp} &= \frac{e^2 \omega^3}{2\pi \hbar c^3} |\langle b | \vec{e} \cdot \vec{r} | a \rangle|^2 d\Omega \\ &= \frac{\omega^3}{2\pi \hbar c^3} |\langle b | \vec{e} \cdot \vec{d} | a \rangle|^2 d\Omega \end{aligned}$$

$$\begin{aligned} dW_{st} &= \frac{4\pi e^2}{\hbar^2 c} I_{\omega} |\langle b | \vec{e} \cdot \vec{r} | a \rangle|^2 d\Omega \\ &= \frac{4\pi^2}{\hbar^2 c} I_{\omega} |\langle b | \vec{e} \cdot \vec{d} | a \rangle|^2 d\Omega \end{aligned}$$

Selection rules can be derived from the properties of $\langle b | \vec{e} \cdot \vec{d} | a \rangle$. We skip the procedure, but only give the results: for electric-dipole transition (E_1) (16)

(1) Δn is arbitrary ($\neq 0$, and $= 0$)

(2) $\Delta S = 0$

(3) $\Delta L = 0, \pm 1$, $L_a + L_b \geq 1$ but $L=0 \leftrightarrow L=0$
(for single ~~atom~~ electron atom, $\Delta l = \pm 1$, i.e., $\Delta l \neq 0$)

(4) $\Delta J = 0, \pm 1$, $J_a + J_b \geq 1$, but $J=0 \leftrightarrow J=0$

(5) $\Delta M_J = 0, \pm 1$

(6) Parity must be opposite between initial and final states

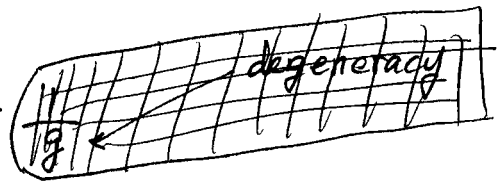
(7) $\Delta F = 0, \pm 1$, but $F=0 \leftrightarrow F=0$

(8) $\Delta M_F = 0, \pm 1$

* Einstein A and B coefficients:

$$A = W_{sp} = \frac{4\omega^3}{3hc^3} |\langle b | \vec{d} | a \rangle|^2$$

$$B = \frac{4\pi^2}{3h} |\langle b | \vec{d} | a \rangle|^2, \quad B \cdot \rho(\omega) = W_{st}$$



Where W_{sp} and W_{st} are the total transition probabilities for spontaneous emission and stimulated transitions in all directions.

(2) Magnetic-Dipole Transition (M1)

(7)

$$e^{i\vec{k}\cdot\vec{r}} \cong 1 + i\underline{\vec{k}\cdot\vec{r}} + \dots$$

Selection rules for M₁ transition

(1) $\Delta n = 0$

(2) $\Delta L = 0$

(3) $\Delta S = 0$

(4) $\Delta J = 0, \pm 1$ but $J=0 \not\leftrightarrow J=0$

(5) $\Delta M_J = 0, \pm 1$

(6) $\Delta F = 0, \pm 1$ but $F=0 \leftrightarrow F=0$

(7) $\Delta M_F = 0, \pm 1,$

(8) no parity change

(3) Electric - Quadrupole Transition (E_2)

(18)

$$\hat{O}_S = \frac{1}{2} i \vec{e}_{\kappa} \cdot (\vec{P} \vec{r} + \vec{r} \vec{P}) \cdot \vec{K}$$

$Q \equiv \vec{r} \vec{r} - \frac{1}{3} r^2 \delta_{ij}$ is the electric-quadrupole of atom

Selection rules for E_2 transition:

1. Δn

2. ~~#~~ $\Delta S = 0$

($L=0 \leftrightarrow L=1$)

3. $\Delta L = 0, \pm 1, \pm 2,$

($L=0 \leftrightarrow L=0$)
 $\leftarrow L_a + L_b \geq 2$

4. $\Delta J = 0, \pm 1, \pm 2,$

~~#~~ $J_a + J_b \geq 2$

5. $\Delta M_J = 0, \pm 1, \pm 2$

6. $\Delta F = 0, \pm 1, \pm 2,$ $F_a + F_b \geq 2$

7. $\Delta M_F = 0, \pm 1, \pm 2$

8. No parity change

3. Oscillator strength, ~~and~~ photon polarization & Light Intensity ⁽¹⁹⁾

(1) A commonly used term in transition probability discussion is oscillator strength, or f -value.

For $\alpha_a J_a \rightarrow \alpha_b J_b$ transition, f is defined as

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

The relationship between f and spontaneous transition probability

$$\text{is: } \omega_{sp}(\alpha_b J_b, \alpha_a J_a) = \frac{2\omega^2 e^2}{\mu c^3} |f(J_a \rightarrow J_b)|^2$$

— This is in CGSE unit. $(\frac{1}{4\pi\epsilon_0})$

For the relationship in the international unit, (PP. 199 Book)

$$f_{ik} = \frac{\epsilon_0 m_e c \lambda^2}{2\pi e^2} \cdot \frac{g_k}{g_i} A_{ki}$$

where A_{ki} is the spontaneous emission rate (s^{-1})

$$\boxed{f_{ik} > 0, \text{ absorption; } f_{ik} < 0, \text{ emission}}$$

$$\sum_{J_b} f(J_a \rightarrow J_b) = 1$$

i.e., from a state J_a , the sum of oscillator strength for all transitions (including emission and absorption) oscillator strength is 1, for single electron transition. If ~~more~~ N electrons are involved in transitions,

$$\sum_{J_b} f(J_a \rightarrow J_b) = N$$

$$A_{ki} = \omega_{sp} = \frac{e^2 \omega_{kb}^3}{3\pi \epsilon_0 \hbar c^3} \frac{1}{g_k} |\langle \alpha_b J_b || \vec{d} || \alpha_a J_a \rangle|^2$$

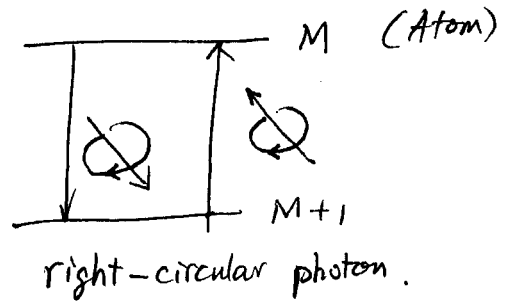
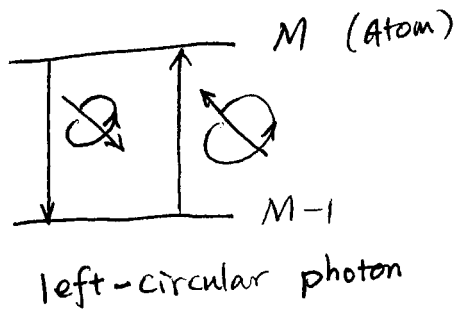
← degeneracy $g_k = 2J_k + 1$

(2) Photon polarization vs. ΔM .

In a ΔJ transition (or ΔF), three components of $\Delta M = 0, \pm 1$ ~~result in~~ result in different polarizations:

$\Delta M = 0$, linear polarization

$\Delta M = \pm 1$ circular polarization.



From angular momentum conservation

$(\text{Photon Spin}) + (\text{atom spin}) = \text{constant}$.

right-circular polarization photon spin (\hat{z}) = $-\hbar$

left " " " " = $+\hbar$

Emission from $M \rightarrow M-1$, it needs the photon to be $+\hbar$,

i.e., $\underbrace{M+0}_{\text{No photon}} = M-1 + \underbrace{1}_{+\hbar} \text{ photon (left-circular)}$

(3) Light intensity emitted by atoms

For degenerate states / levels, spontaneous emission probability

$$A_{ki} = \frac{e^2 \omega_{ki}^3}{3\pi \epsilon_0 \hbar c^3} \frac{1}{g_k} \sum_{m_k m_i} |\langle i m_i | \vec{r} | k m_k \rangle|^2$$

Population of atoms obey the Boltzmann distribution

$$\frac{N_k}{N} = \frac{g_k e^{-E_k/k_B T}}{\sum_i g_i e^{-E_i/k_B T}}$$

where N is total population,
k_B - Boltzmann Constant
T - temperature

g_k and g_i are the degeneracy.

g_k = 2J_k+1 or 2F_k+1 for hyperfine structure
↓
for fine structure

Between two levels, $\frac{N_k}{N_i} = \frac{g_k}{g_i} e^{(E_i - E_k)/k_B T}$
 $= \frac{g_k}{g_i} e^{-(E_k - E_i)/k_B T}$

The higher the E_k, the less population.

Light intensity: $I_{ki} = \frac{N_k V \hbar \omega_{ki} A_{ki}}{4\pi}$

where V is volume of the source

$$\omega_{ki} = (E_k - E_i)/\hbar$$

Regarding oscillator strength in degenerate levels,

(f_{ik} > 0) $f_i f_{ik} = -g_k f_{ki} \equiv f_f$ (f_{ki} < 0)

Therefore, we have the equation on PP.199 of the textbook

$$f_{ik} = \frac{\epsilon_0 m_e c d^2}{2\pi e^2} \cdot \frac{g_k}{g_i} A_{ki}$$

IV. Spectroscopy

(22)

What we concern here is the width and shape of spectral lines from atom and laser (light) interaction.

1. Natural linewidth

The uncertainty principle tells us:

$$\Delta E \cdot \Delta t = \hbar \quad (4.1)$$

$$\Rightarrow \hbar \Delta \omega \cdot \Delta t = \hbar \Rightarrow \Delta \omega = \frac{1}{\Delta t}$$

$$\therefore \Delta \nu = \frac{\Delta \omega}{2\pi} = \frac{1}{2\pi \cdot \Delta t} \quad (4.2)$$

It means that those energy levels of an atom, which have finite radiative lifetimes, cannot be considered to be infinitely sharp. The energy level has certain width, given by Eq. (4.2).

* The radiative lifetime is defined as below:

Let us consider an assembly of atoms in which $N_k(0)$ atoms per unit volume are ~~excite~~ in the excited state k at time $t=0$. In general, these atoms will decay by spontaneous emission to a number of lower levels i . In absence of collision depopulation, the population density in level k decreases at a rate given by

$$-\frac{dN_k}{dt} = N_k \sum_i' A_{ki}, \quad (4.3)$$

where prime indicates that it ~~extends~~ sums only over those levels that have lower energy than that of k .

$$\therefore N_k(t) = N_k(0) \exp[-t/\tau_k], \quad (4.4)$$

where $\tau_k = \frac{1}{\sum_i' A_{ki}}$ is the radiative lifetime.

$$\rightarrow (4.5)$$

* The half-width of the energy level k is determined by the radiative lifetime:

$$\Gamma_k = \Delta\omega_k = \Delta E_k / \hbar = 1/\tau_k = \sum_i' A_{ki} \quad (4.6)$$

where A_{ki} are the transition probabilities of the allowed electric dipole transitions from level k to all possible lower levels, i .

* Since in general both the upper and lower levels of an electric dipole transition have finite lifetimes, the uncertainty in the frequency of the emitted photons must include the uncertainty in the energy of both the upper and the lower levels. The frequency distribution of spectral line was obtained QM-ly by Weisskopf and Wigner [1930]. The result is a Lorentzian curve:

$$I_{ki}(\omega) = I_0 \frac{\Gamma_{ki}/2\pi}{(\omega_0 - \omega_{ki})^2 + \Gamma_{ki}^2/4} \quad (4.7)$$

where I_0 is the peak intensity,

$$\text{FWHM} = \Delta\omega_{1/2} = \Gamma_{ki} = \Gamma_k + \Gamma_i = \sum_j' A_{kj} + \sum_h' A_{ih} \quad (4.8)$$

Normally, a typical transition has $\tau_k \approx 10^{-8}$ s.

Therefore, the natural linewidth

$$\Delta\nu_{\text{natural}} = \frac{\Gamma_{ki}}{2\pi} \approx \frac{10^8}{2\pi} = 16 \text{ MHz}$$

$$= \frac{1}{2\pi\tau_k}$$

For Na $^2P_{3/2}$, $\tau_k = 1.623 \times 10^{-8}$ s. $\therefore \Delta\nu_{\text{natural}}^{\text{Na}} = \frac{1}{2\pi \times 1.623 \times 10^{-8}}$

For Fe, $\tau_k = 6.1 \times 10^{-8}$ s, $\Rightarrow \Delta\nu_{\text{natural}}^{\text{Fe}} = 2.6 \text{ MHz} = 9.8 \text{ MHz}$.

2. Collision broadening of spectral lines. (24)

* Although an isolated atom will emit a spectral line of finite width, in any real source, an atom will be subjected to the interaction forces of neighbouring atoms, ions, molecules. These collisions will perturb the state of the radiating atom so lead to a broadening of the line which is often ~~gr~~ greater than its natural linewidth. This is called collision broadening, also called pressure broadening, as the increase in the linewidth is a function of the density of the perturbing species.

* We do not go in details for this, but the collision's effect is to shorten the radiative lifetime of atom.

So a shorter lifetime τ will be resulted. Then the line-width of the spectral line is still

given by
$$\Gamma = \frac{1}{\tau}, \quad (4.9)$$

and the line shape is still a Lorentzian shape:

$$I_{ki}(\omega) = I_0 \frac{\Gamma/2\pi}{(\omega - \omega_{ki})^2 + (\Gamma/2)^2} \quad (4.10)$$

3. Doppler broadening.

Doppler shift: $\omega = \omega_0 \left(1 - \frac{\vec{v} \cdot \vec{r}}{c}\right) = \omega_0 \left(1 - \frac{v_z}{c}\right)$

Maxwell distribution:

$$P(v_z) dv_z = \sqrt{\frac{M}{2\pi k_B T}} \exp\left[-\frac{M v_z^2}{2 k_B T}\right] dv_z$$

Relationship: $v_z = \frac{\omega_0 - \omega}{\omega_0} c \Rightarrow dv_z = -\frac{c}{\omega_0} d\omega$

$$P(\omega) d\omega \propto P(v_z) dv_z = \sqrt{\frac{M}{2\pi k_B T}} \exp\left[-\frac{M (\omega_0 - \omega)^2 c^2}{2 \omega_0^2 k_B T}\right] \cdot \frac{c}{\omega_0} d\omega$$

Let $\sigma = \sqrt{\frac{\omega_0^2 k_B T}{M c^2}} = \frac{\omega_0}{c} \sqrt{\frac{k_B T}{M}}$

$$\therefore P(\omega) d\omega = \frac{1}{\sqrt{2\pi} \sigma} \exp\left[-\frac{(\omega_0 - \omega)^2}{2 \sigma^2}\right] d\omega$$

— This is a Gaussian shape.

This is called Doppler Broadening.

Notice that the Doppler shift is a function of radial velocity while the Doppler broadening is a function of temperature. This is the basis for Doppler lidars to measure wind and temp.

4. Voigt Profile

Among the broadening discussed above, there are two different types of broadening: the homogeneous broadening and the inhomogeneous broadening.

- (1) Homogeneous broadening: natural linewidth, collision broadening, and saturation broadening. Essentially, they are caused by limited radiative lifetime of atoms. So, they can be represented by an effective lifetime τ , and $\Gamma = \frac{1}{\tau}$.

The lineshape is a Lorentzian function:

$$I(\omega) = I_0 \frac{\Gamma/2\pi}{(\omega - \omega_0)^2 + (\Gamma/2)^2}$$

$$\therefore \Delta\omega_{\text{FWHM}} = \Gamma = \frac{1}{\tau} \text{ same for all atoms.}$$

- (2) Inhomogeneous broadening: Doppler broadening, Essentially, they are caused by the different central frequency shifts of different atoms. The overall lineshape is a superposition of the different spectral lines from different atoms. — Therefore, inhomogeneous.

When atoms' motions are random, the lineshape is given by a Gaussian function:

$$I(\omega) = \frac{I_0}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(\omega_0 - \omega)^2}{2\sigma^2}\right]$$

where σ is the rms width of the Gaussian peak.

$$\text{FWHM} = \sigma \sqrt{8 \ln 2}$$

(27)

(3) Convolution of Lorentzian and Gaussian

These broadenings are presented at the same time. So, the overall lineshape is an ~~convolution~~ ^{integration} of the Lorentzian and Gaussian distributions:

$$I(\omega) = \int_{-\infty}^{+\infty} L(\omega' - \omega) G(\omega, \omega_0) d\omega'$$

$$\omega' = \omega_0 \left(1 - \frac{v^2}{c^2}\right)$$



When $\Gamma \ll \sigma$, the convolution turns to be a Gaussian shape.

(4) Effect of laser lineshape

Use a Gaussian to simulate a laser lineshape,

Then the measured spectral lineshape is a convolution of laser lineshape with atomic lineshape

$$G_1 \otimes G_2 \Rightarrow G \text{ with } \sigma = \sqrt{\sigma_L^2 + \sigma_A^2}$$