Lecture 24

Light-Matter Interactions

Study Goal of This Lecture

- Time-dependent perturbation theory
- Interaction of radiation and matter
- Absorption and stimulated emission

24.1 Preface

Now we have learned that electronic structures of molecules can be "approximatelly" solved to yield various molecular properties, such as energy/ dipole moment/ vibration frequency $\cdots$ etc.

How do we observe/measure these properties? ⇒ Spectroscopy: our window into microscopic molecular world.

24.2 Why spectroscopy

We will turn our attention to various spectroscopic methods. As an elite college student, you should ask why. Why bother? and so what? Asking why and so what actually will help you to learn a subject, because these questions allow you to focus on keys of learning the subject, allow you to look at a broad field with a "big picture".

In this vein, I hope I can covince you that spectroscopic methods are our mechanics: a large part of QM was inspired, or even more previouly, was necessary by the advanced of spectroscopic methods. Without observation of black-body radiation and atomic spectrum, there won't be motivations for quantum mechanics!

Also keep in mind that "spectroscopy" is not the only subject that requires quantum chemistry. Chemical reactions, chemical dynamics, $\cdots$, a huge part of chemistry discipline requires quantum mechanic!! However, much of these will be covered in other courses. For example, bonding and transformation of chemical structure,(much of these involves the ideas of PESs defined by molecular wavefunctions at varying nuclear geometries.) will be covered in organic chemistry and inorganic chemistry as well. We won't even talk about the "instrumental" part of spectroscopy, which will be covered in analytical chemistry. The development of theory of spectroscopy requires using "time-dependent" quantum mechanics. Because, all spectroscopic techniques involve

1. Prepare the system in equilibrium.
2. Apply a "perturbation"(or more) to push the system out of equilibrium.
3. "Observe" while system relax and establish equilibrium again.

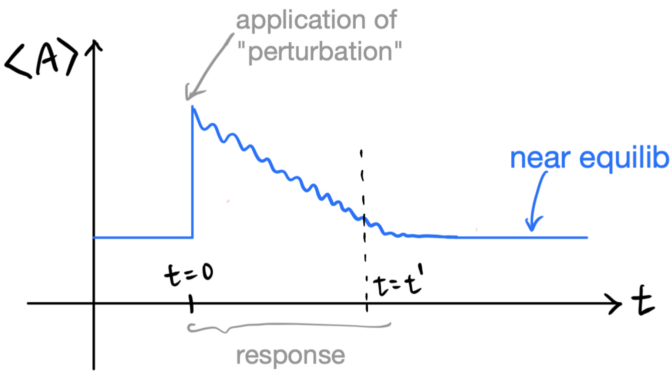

Figure 24.1: Using quantum mechanics to study spectroscopy.

We will briefly introduce time-dependent formalism that can be used to describe such responses. This is the so called time-dependent perturbation theory for quantum mechanics. Note that this advanced materials is meant to let you gain a underlying physical picture to pave the way for our later discussions. The derivation of these time-dependent perturbation theory part is optional and won't appear on the final exam. However, you need to know the results which are actually present in Silbey's textbook.

Recall the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{H}(t)\left|\psi(t)\right\rangle . \tag{24.1}$$

If $\hat{H}(t) = \hat{H}_0$ is time-independent and we know exactly it's eigenvalues and eigenfunctions

$$\hat{H}_0\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle , \tag{24.2}$$

H_0 is the molecular Hamiltonian.

then for any wavefunction $|\psi\rangle$ initially written as a superposition of $\{\phi_n\}$, we have

$$\left|\psi(0)\right\rangle = \sum_n C_n(0)\left|\phi_n\right\rangle \ \ \& \ \ \left|\psi(t)\right\rangle = \sum_n C_n(t)\left|\phi_n\right\rangle . \tag{24.3}$$

Plug it into TDSE

$$i\hbar\sum_n\frac{\partial C_n(t)}{\partial t}\left|\phi_n\right\rangle = \hat{H}_0\sum_n C_n(t)\left|\phi_n\right\rangle = \sum_n C_n(t)E_n\left|\phi(t)\right\rangle , \tag{24.4}$$

and operate $\langle\phi_m|$ from the left, we obtain

$$\begin{aligned} &i\hbar\sum_n\frac{\partial C_n(t)}{\partial t}\left\langle\phi_m|\phi_n\right\rangle = \sum_n C_n(t)E_n\left\langle\phi_m|\phi_n\right\rangle \\ &\Rightarrow i\hbar C_n(t) = E_n\frac{\partial C_n(t)}{\partial t} = E_nC_n(t),\ C_n(t) = C_n(0)e^{-\frac{iE_nt}{\hbar}} . \end{aligned} \tag{24.5}$$

Therefore

$$\left|\phi(t)\right\rangle = \sum_n C_n(0)e^{-\frac{iE_nt}{\hbar}}\left|\phi_n\right\rangle , \tag{24.6}$$

This is why it is called wave mechanics.

time-evolution is phase evolution, a superposition of interferencing waves! Note that if the system is initially prepared in a eigenstate, e.g. the ground state $|\phi_n\rangle$, then $C_n = 1$ and all $C_m = 0$ for $m \neq n$

$$\Rightarrow \left|\phi(t=0)\right\rangle = \left|\phi_n\right\rangle ,\ \left|\phi(t)\right\rangle = e^{-\frac{iE_nt}{\hbar}}\left|\phi_n\right\rangle . \tag{24.7}$$

Probability of finding the system remains in $|\phi_n\rangle$ is $|C_n(t)|^2 = 1 \Leftarrow$ always in the same state. And for any observable:

$$\left\langle\hat{A}\right\rangle = \langle\phi_n|e^{\frac{iE_nt}{\hbar}}\hat{A}e^{-\frac{iE_nt}{\hbar}}|\phi_n\rangle = \langle\phi_n|\hat{A}|\phi_n\rangle . \tag{24.8}$$

It is time-independent! Due to this, we say that the eigenstate of $\hat{H}_0$ are stationary states. That is not the case if an external perturbation is introduced.

24.3 Time-dependent perturbation theory(First order)

Now let's consider a perturbed Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}(t). \tag{24.9}$$

Again, $\hat{H}_0$ is exactly known. Since the eigenbasis of $\hat{H}_0$ still spans the whole space, we can write arbitrary wavefunctions as the superposition of $\{\phi_n\}$:

$$|\psi\rangle = \sum_n C_n(t)\,|\phi_n\rangle = \sum_n b_n(t) e^{-\frac{iE_n t}{\hbar}}\,|\phi_n\rangle. \tag{24.10}$$

Plug it into full Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\left(\sum_n b_n(t) e^{-\frac{iE_n t}{\hbar}}\right)|\phi_n\rangle = (\hat{H}_0 + \hat{V}(t))\sum_n b_n(t) e^{-\frac{iE_n t}{\hbar}}. \tag{24.11}$$

LHS:

$$\begin{aligned}
&i\hbar\sum_n \frac{\partial b_n(t)}{\partial t} e^{-\frac{iE_n t}{\hbar}}\,|\phi_n\rangle + i\hbar\sum_n b_n(t)\frac{\partial}{\partial t}\{e^{-\frac{iE_n t}{\hbar}}\,|\phi_n\rangle\}\\
&= i\hbar\sum_n \frac{\partial b_n(t)}{\partial t} e^{-\frac{iE_n t}{\hbar}}\,|\phi_n\rangle - i\cancel{\hbar}\sum_n b_n(t)\frac{iE_n}{\cancel{\hbar}} e^{-\frac{iE_n t}{\hbar}}\,|\phi_n\rangle\\
&= i\hbar\sum_n \frac{\partial b_n(t)}{\partial t} e^{-\frac{iE_n t}{\hbar}}\,|\phi_n\rangle + \sum_n b_n(t) E_n\,|\phi_n\rangle \times e^{-\frac{iE_n t}{\hbar}}.
\end{aligned} \tag{24.12}$$

RHS:

$$\begin{aligned}
&(\hat{H}_0 + \hat{V}(t))\sum_n b_n(t) e^{-\frac{iE_n t}{\hbar}}\\
&= \sum_n b_n(t) E_n e^{-\frac{iE_n t}{\hbar}}\,|\phi_n\rangle + \sum_n b_n(t) e^{-\frac{iE_n t}{\hbar}}\hat{V}(t)\,|\phi_n\rangle.
\end{aligned} \tag{24.13}$$

Therefore, we find that

$$i\hbar\sum_n \frac{\partial b_n(t)}{\partial t} e^{-\frac{iE_n t}{\hbar}}\,|\phi_n\rangle = \sum_n b_n(t) e^{-\frac{iE_n t}{\hbar}}\hat{V}(t)\,|\phi_n\rangle, \tag{24.14}$$

now, again, operate $\langle\phi_m|$ to check out $b_m(t)$,

$$i\hbar\sum_n \frac{\partial b_n(t)}{\partial t} e^{-\frac{iE_n t}{\hbar}}\delta_{mn} = \sum_n b_n(t) e^{-\frac{iE_n t}{\hbar}}\,\langle\phi_m|\hat{V}(t)|\phi_n\rangle, \tag{24.15}$$

$$i\hbar\frac{\partial b_m(t)}{\partial t} e^{-\frac{iE_n t}{\hbar}} = \sum_n b_n(t) e^{-\frac{iE_n t}{\hbar}}\,\langle\phi_m|\hat{V}(t)|\phi_n\rangle, \tag{24.16}$$

therefore,

$$\frac{\partial b_m(t)}{\partial t} = -\frac{i}{\hbar}\sum_n b_n(t)e^{\frac{i(E_m-E_n)t}{\hbar}} \langle\phi_m|\hat{V}(t)|\phi_n\rangle\,. \tag{24.17}$$

Up to now, we obtain an exact formula, but it can't be solved easily. Let's assume the system is initially prepared in a eigenstate of $\hat{H}_0$, $\{|\phi_k\rangle\}$. When $\hat{V}(t)$ is small and the time is short,

$$b_n(t) \simeq b_n(0) + \mathcal{O}\Big(\hat{V}_{nm}t\Big), \tag{24.18}$$

and note $b_n(0) = \delta_{nk}$, since we prepare it in state k. So we obtain

$$\frac{\mathrm{d}b_m(t)}{\mathrm{d}t} = -\frac{i}{\hbar}e^{\frac{i(E_m-E_n)t}{\hbar}} \langle\phi_m|\hat{V}(t)|\phi_k\rangle \tag{24.19}$$

$\langle\phi_m|\hat{V}(t)|\phi_k\rangle$ is the coupling from $|k\rangle$ to $|m\rangle$.

at time $t = t'$

$$b_m(t') \simeq \delta_{mk} - \frac{i}{\hbar}\int_0^{t'} e^{\frac{i(E_m-E_k)t}{\hbar}} \langle\phi_m|\hat{V}(t)|\phi_k\rangle\, dt. \tag{24.20}$$

This is the first order time-dependent perturbation theory. The population of finding the system at state $|\phi_m\rangle$ at time t' is then $P_m(t') \simeq |b_m(t)|^2$. Note that the rate of going from $|\phi_k\rangle \to |\phi_m\rangle$ is generally $\frac{\mathrm{d}}{\mathrm{d}t}P_m(t') \propto |\langle\phi_m|\hat{V}(t)|\phi_k\rangle|^2$ i.e. the square of the interaction introduced by the perturbation $\hat{V}(t)$, determines the transition rate.

24.4 Interaction of Radiation with Matter

Now let's apply this formula to study the behavior of molecules under the influence of a external electromagnetic field. Consider a linearly polarized light, it's electric field component is:

Look at classical version first.

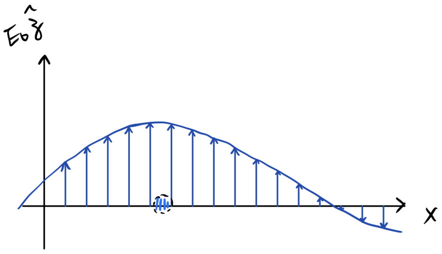

Figure 24.2: Electromagnetic field, $\vec{E}$ part.

We write the electric field as

$$\vec{E}(x,t) = \vec{E_0}\sin\Big(2\pi\nu t - 2\pi\frac{x}{\lambda}\Big). \tag{24.21}$$

The interaction Hamiltonian:

$$V(t) = -\vec{E_0}\sum_n q_i\vec{r_i}\sin\Big(2\pi\nu t - 2\pi\frac{x}{\lambda}\Big), \tag{24.22}$$

the above equation means sun over all electrons and nuclei. In general, the size of the molecule is much smaller than λ, therefore we can ignore the position dependency and define:

$$\vec{\mu} = \sum_i q_i\vec{r_i},\ \text{molecular dipole moment.} \tag{24.23}$$

Then $V(t)$ is

$$V(t) = -\vec{E_0}\vec{\mu}\sin(2\pi\nu t), \tag{24.24}$$

so

$$\begin{aligned}\hat{V}(t) &= -\hat{\mu}\vec{E_0}\sin(2\pi\nu t)\\ &= -\hat{\mu}\vec{E_0}\sin(\omega_0 t).\end{aligned} \tag{24.25}$$

ω_0 is angular frequency, and the whole term $\hat{V}(t)$ called molecular dipole interaction.

24.4.1 Resonant Transition

For our application here, it is sufficient to consider two levels system which are eigenstate of $\hat{H}_0$ with eigenvalue E_n & E_m.

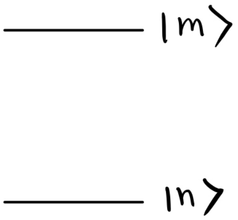

Figure 24.3: Two states(levels) of $\hat{H}_0$

For a system initially in $|n\rangle$ and making transition to $|m\rangle(m \neq n)$, we use the first order time-dependent perturbation theory to derive:

We define
$\omega_{mn} = \frac{E_m - E_n}{\hbar}$,
$\vec{\mu}_{mn} = \langle\phi_m|\hat{\mu}|\phi_n\rangle$,
$\vec{E} = \epsilon_0\hat{\epsilon}$.

$$
\begin{aligned}
b_m(t') &= -\frac{i}{\hbar}\int_0^{t'} e^{\frac{i}{\hbar}(E_m-E_n)t}\,\langle\phi_m|-\hat{\mu}\vec{E}_0\sin(\omega_0 t)|\phi_n\rangle\,dt \\
&= \frac{i}{\hbar}\vec{E}_0\,\langle\phi_m|\hat{\mu}|\phi_n\rangle\int_0^{t'} e^{\frac{i}{\hbar}(E_m-E_n)t}\times\frac{1}{2i}[e^{i\omega_0 t}-e^{-i\omega_0 t}]dt \\
&= \frac{\epsilon_0}{2\hbar}\vec{\mu}_{mn}\cdot\hat{\epsilon}\int_0^{t'}\Big[e^{i(\omega_{mn}+\omega_0)t}-e^{i(\omega_{mn}-\omega_0)t}\Big]dt \\
&= \frac{E_0}{2\hbar i}\vec{\mu}_{mn}\cdot\hat{\epsilon}\Big[\frac{e^{i(\omega_{mn}+\omega_0)t'}-1}{\omega_{mn}+\omega_0}-\frac{e^{i(\omega_{mn}-\omega_0)t'}-1}{\omega_{mn}-\omega_0}\Big].
\end{aligned}
\tag{24.26}
$$

The the two terms in Eq.24.26 are only significant when:

- **First term:**

  Max at $\omega_0 = -\omega_{mn}$, so $\omega_{mn} < 0$, $E_m < E_n$, $E_n = E_m + \hbar\omega_0$.

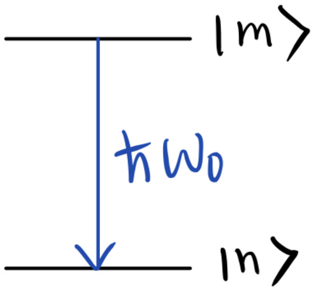

Figure 24.4: Stimulated emission.

This is **sitmulated emission**! or called anti-resonant term.

- **Second term:**

  Max at $\omega_0 = \omega_{mn}$, so $\omega_{mn} > 0$, $E_m > E_n$, $E_m = E_n + \hbar\omega_0$

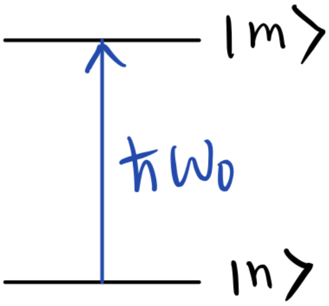

Figure 24.5: Absorption.

  This is **absorption**! or called resonant term.

We find that the significant transition occurs only when $\Delta E \simeq \hbar\omega_0$, so we called this **resonant transition**. And we also find that the rate for the two terms are the same($k_{n\to m} = k_{m\to n}$), this is the "detailed balance" between $|m\rangle \to |n\rangle$ and $|n\rangle \to |m\rangle$ transition.

In general, the transtion rate is described by the state-to-state version of the Fermi's Golden Rule:

Fermi's Golden Rule:

For $V_{nm}(t) = V_{nm}sin(\omega_0 t)$, the rate is determined by:

$$k_{m\to n} = \frac{2\pi}{\hbar}|V_{nm}|^2\delta(E_m - E_n \pm \hbar\omega_0), \tag{24.27}$$

where $|V_{nm}|^2$ is the square of coupling and $\delta(E_m - E_n \pm \hbar\omega_0)$ is the requirement of energy conservation.

This golden rule can be derived from the above result(i.e. derivation from $b_m(t')$) and it is important in describing transition rate, for those who are interested in, one can check the more advanced book(......) for more contents. (or we put the quantum dynamic handouts here for optional material?)

24.5 Appendix: Dirac Delta-function

Some students might be first time to see the Dirac delta function, we introduce it here if one don't understand its meaning.

24.5.1 Dirac Delta Function

$\delta(x)$ is the "Dirac δ-function", then it is defined as:

1.

$$\delta(x) = \begin{cases} +\infty & \text{if } x = 0, \\ 0 & \text{if } x \neq 0. \end{cases} \tag{24.28}$$

2.

$$\int_{-\infty}^{\infty} \delta(x) dx = 1. \tag{24.29}$$

3.

$$\int_{-\infty}^{\infty} f(x)\delta(x-a)dx = f(a). \tag{24.30}$$

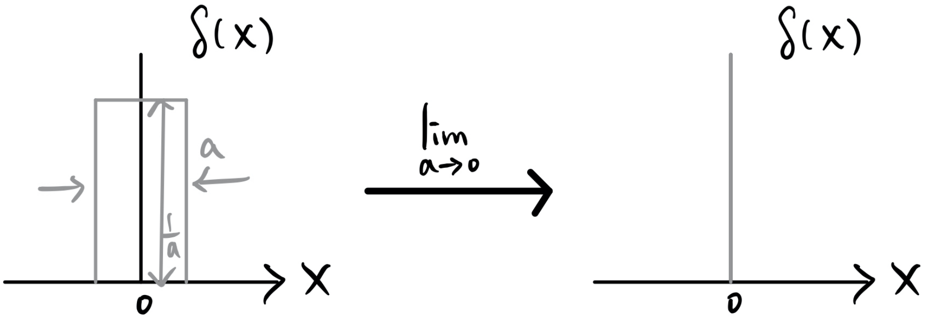

Figure 24.6: Dirac delta function