Lecture 1

Matter - field interactions.

* EM field
* electric dipole Hamiltonian
* selection rules.

* ceiba
* course participants.
* course outline ← logins

* <u>Derivation of the electric dipole Hamiltonian</u>

We aim to cover basic principles of time-dependent spectroscopy. In the 6 lectures, The style will be informal, so please just raise your hands if you have any questions, I also recognize that everyone's background is a bit different, so don't feel hesitate if you want to to cover some basics.
↑ more.

To begin with, in this lecture we will derive the Hamiltonian that describe light-matter interaction in the semiclassical approximation ⟹ interaction of a molecule with a classical electromagnetic field :

$$H_{int}(t) = -\hat{\mu} \cdot \vec{E}(t) .$$

dipole operator ⟶ (pointing to $\hat{\mu}$)

elec. field ⟶ (pointing to $\vec{E}(t)$)

To reach this Hamiltonian, we need :

① Maxwell equations. (classical electromagnetic field).

② quantum molecular Hamiltonian ← how the field interacts with molecules

③ dipole approximation ← molecule much smaller than wavelength.

✱ Maxwell's equation in vacuum.

Let's start with free electromagnetic wave, of course, this is described by the Maxwell's equation (no current, no electric charge).

$\nabla \times A = \begin{pmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{pmatrix}$

↙ divergence.

① $\nabla \cdot \vec{E} = 0$.   Gauss's law

② curl $\nabla \cdot \vec{B} = 0$ Gauss's law for magnetism.

③ $\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$ Faraday's law of induction.

④ $\nabla \times \vec{B} = \mu_0 \cdot \varepsilon_0 \cdot \frac{\partial \vec{E}}{\partial t}$ Ampère's law.

Note that the equations describe $\vec{E}$ & $\vec{B}$, in total 6 variables ← they are not independent, very often, Maxwell's equation is written in the alternative form:

scalar potential (electrostatic).
vector potential

$$\vec{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \vec{A}}{\partial t}$$

$$\vec{B} = \nabla \times \vec{A}$$

$\vec{A}$ is in the direction of $\vec{E}$

Transformation

$A \rightarrow A + \nabla \phi$ ← gauge transformation

$\{\phi, \vec{A}\}$ reduce the number of variables to 4,

and ②① & ③ of the Maxwell's eq.

are automatically satisfied. The problem is,

real physical observables

for a given $\vec{E}$ & $\vec{B}$, ϕ & $\vec{A}$ are not

uniquely determined. To obtain a consistent

physical description, we need to add an additional

constraint (like set up a coordinate), called

choosing a gauge. Here we choose the

Coulomb gauge : $\nabla \cdot \vec{A} = 0$.

In this case, plugging the "potential" representation.

of $\vec{E}$ & $\vec{B}$ into ① & ④ of the Maxwell eq.,

we obtain, in free space (no charge).

Laplace's eq.   no charge, no electric

$$\nabla^2 \phi = 0 \qquad \therefore \phi = \text{constant} \to 0. \qquad \text{field}$$

$$\nabla^2 \vec{A} = \frac{1}{c} \nabla \left(\frac{\partial \phi}{\partial t} \right) + \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2}$$

$=0$.

The second equation is a classical

wave equation for free electromagnetic wave.

$$\nabla^2 \vec{A} = \frac{1}{c^2} \frac{\partial^2 \vec{A}}{\partial t^2}$$

The plane wave solution to this is well

known : $\vec{A}(\vec{r},t) = \vec{A_0} \cdot \left[e^{i(\vec{k}\cdot\vec{r} - \omega t)} + c.c. \right]$

complex conjugate.

easy to verify by plugging into

$\Rightarrow$ freely propagating plane wave.

Note that $\vec{A_0}$ is defined in the direction of

$\vec{A_0} \parallel \vec{\epsilon}$

the electric field. Also, $\vec{k}$ is $\perp$ to $\vec{A}$:

Coulomb gauge

$$\nabla \cdot \vec{A} = 0 = -i \, \vec{k} \cdot \vec{A_0} \cdot \sin(\vec{k}\cdot\vec{r} - \omega t).$$

$\therefore \vec{k} \cdot \vec{A_0} = 0$ at all times. $\leftarrow \therefore \vec{k} \perp \vec{\epsilon}$

$\hat{\epsilon} = \frac{\vec{A_0}}{A_0}$

$$\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} = -\frac{\omega}{c} A_0 \cdot \hat{\epsilon} \cdot \sin(\vec{k}\cdot\vec{r} - \omega t)$$

finally, $\vec{B} = \nabla \times \vec{A} = -A_0 (\vec{k} \times \hat{\epsilon}) \cdot \sin(\vec{k}\cdot\vec{r} - \omega t). \leftarrow \therefore \vec{k} \perp \vec{B}$

$\vec{B} \perp \vec{\epsilon}$
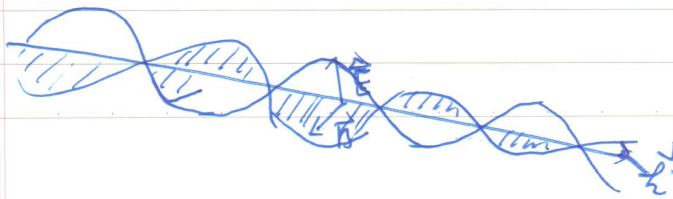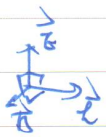
* Charge - EM interactions.

Now, a classical particle with charge q interacts with
a EM field through:

vector potential modifies the momentum

$$H = \frac{1}{2m} \left(\vec{p} - \frac{q}{c} \vec{A} \right)^2 + V(\vec{r})$$

momentum of the particle $\quad \vec{A} = \vec{A}(\vec{r}, t) \quad$ other potential of the particle

see Jackson or C-T.

We can now write down the quantum

Hamiltonian via the quantum - classical correspence:

In the x-representation:

$$\hat{H} = \frac{1}{2m} \left(-i\hbar \nabla - \frac{q}{c} \vec{A} \right)^2 + V(\vec{r})$$

$$H_0$$

$$= \boxed{\frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r})} + \frac{i\hbar q}{2mc} \left(\nabla \cdot \vec{A} + \vec{A} \nabla \right) + \frac{q^2}{2mc^2} \vec{A}^2$$

∴ vector field interaction Hamiltonian

← normally very small, so perturbation theory is good.

$$V = \frac{i\hbar q}{2mc} \cdot \left(\nabla \vec{A} + \vec{A} \cdot \nabla \right) + \frac{q^2}{2mc^2} \vec{A}^2 \quad \text{too small for weak fields}$$

Coulomb gauge

Note $\nabla \cdot \vec{A} \Rightarrow \nabla \cdot \left(\vec{A} \cdot \psi(\vec{r}) \right) = \left(\nabla \cdot \vec{A} \right) \psi(\vec{r}) + \left(\vec{A} \cdot \nabla \right) \psi(\vec{r})$

$\quad = 0$

momentum operator of the particle.

depends on

$[\vec{A}, \hat{P}] \neq 0$

since

$\vec{A} = \vec{A}(\vec{r})$

units ∴ $V = -\frac{q}{mc} \cdot \left(\vec{A} \bullet \hat{P} \right)$

coupled sources to light particle $\quad$ not commute

timeless

✱ Electric dipole approximation.

$$V = \frac{-q}{2mc} A_0 \cdot \hat{\mathbb{C}} e^{i(\vec{k}\cdot\vec{r} - \omega t)} \cdot \hat{\varepsilon} \cdot \hat{p} + c.c.$$

since magnetude of $|\vec{k}| \sim \frac{2\pi}{\lambda}$ ← wave length $\sim$ 500 nm for optical light.

$|\vec{r}|$: size of molecule $\sim$ 0.5 nm.

field ↓

molecule.

∴ $\vec{k}\cdot\vec{r} << 1$ ⇒ $e^{i\vec{k}\cdot\vec{r}} \approx 1$

← flat field
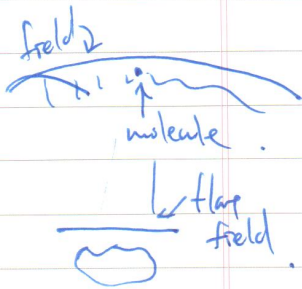
. We can consider $e^{i\vec{k}\cdot\vec{r}} \approx 1$ ← long wavelength, ← independence of $\vec{r}$ now!!

point-dipole approx.

all scalar field variables now

∴ $V \approx \frac{-q\cdot A_0}{mc} \cdot A_0 \cdot \hat{\varepsilon} \cdot e^{-i\omega t} + c.c.$

$= \frac{\pi E_0 c}{2\pi\hbar}$

$H_0 = \frac{-p^2}{2m} + V(\vec{x})$ Note that $\hat{p}$ is usually not easy to

∴ $[H_0, r] = \frac{-i\hbar\hat{p}}{m}$ evaluate, in the x-representation. But we

can apply the trick :

$$[H_0, r] = \frac{-i\hbar}{m}\hat{p} \quad \Rightarrow \quad \hat{p} = \frac{m}{-i\hbar}[H_0, r]$$

∴ we can easily evaluate matrix element
of V in the eigenstates of H_0 :

$$H_0 |k\rangle = \mathcal{E}_k |k\rangle, \quad H_0 |l\rangle = \mathcal{E}_l |l\rangle$$

In weak field,

$$V_{kl} = \mp q \, \vec{E}_0 \cdot \hat{\varepsilon} \cdot \sin(\omega t) \cdot \frac{1}{\hbar} \langle k| (H_0 \hat{r} - \hat{r} \cdot H_0) |l\rangle$$

$$\underbrace{\omega_{kl} = \frac{\mathcal{E}_l - \mathcal{E}_k}{\hbar}}_{} \qquad = \vec{E}(t)$$

$$= - \underbrace{\boxed{\frac{\omega_{kl}}{\omega}}}_{\simeq 1} \cdot \langle k| q \, i\vec{r} |l\rangle \cdot \boxed{\mp \vec{E}_0 \cdot \hat{\varepsilon} \cdot \sin(\omega t)}$$

due to resonance condition will
be always true for quantized field.

EM field induces transition between H_0 eigen states!!

$\not\Rightarrow$ In the weak-field limit, the electric field induce couplings between $\boxed{\text{eigenstates of } H_0}$

For a system with many charged particles :

$$H = H_0 + H_{int}(t)$$

$$H_{int} = - \hat{\mu} \cdot \vec{E}(t)$$

← reference at center of the molecule

$$\hat{\mu} \equiv \sum_i q_i \cdot \hat{r}_i \quad \leftarrow \text{"dipole"}$$

① $\hat{\mu}_{kl}$ does not change due to a shift in coordinate, because $|k\rangle, |l\rangle$ orthogonal.

② induces transitions between eigen states of H_0, because V actually contains "energy" H_0 operator :
$\Rightarrow$ photons "measure" energy eigen states of molecules.

Summary of approximations / conditions :

① free space   , matter   , field

② quantum particle , classical EM field

  ∗ no photons
  ∗ no spontaneous emission.
  ∗ no quantized field effect.
  ∗ no field retarded effect.

③ weak field ⟸ drops $\vec{A}^2$ terms, this is

  okay even for normal intense laser $\leftarrow \frac{q^2}{m c^2}$

  because light-matter interactions are
  intrinsically weak.

④ electric dipole approximation
  (long field wavelength, small molecule).

⑤ field - frequency independent response .
  ⌃ actually this is always true ~

⟹ light matter interactions are important !!

* Selection rules.

Now we have established <u>that</u> photon induces transitions between eigenstates of H_0. so, what is $\hat{H_0}$: molecular Hamiltonian.

$$\hat{H_0} = \sum_{i=1}^{M} \frac{\hat{P_i}^2}{2M_c} + \sum_{i=1}^{N} \frac{\hat{P_c}^2}{2M_e} + \ldots\ldots$$

It is actually more informative to represent the molecular Hamiltonian in Born-Oppenheimer approximation:

$$\hat{H_0} = -\sum_i \frac{\hbar^2}{2M_c} \vec{\nabla}_{\vec{R_i}}^2 + E(\{\vec{R_\sigma}\})$$

$$\hat{H}(\vec{R_i}) \psi_e(\{\vec{r_i}\}) = E(\{\vec{R_c}\}) \cdot \psi_e(\{\vec{r_\sigma}\}).$$

This can go further :

$$\hat{H_0} = \hat{H}_{molecule} = \hat{H}_{tr} + \hat{H}_{rot} + \hat{H}_{vib} + \hat{H}_e$$

wave function $= \psi_e \times \psi_{tr} \times \psi_{rot} \times \psi_{vib}.$

for diatomic molecules :   "PES"

To specify a transition, we need to

state the initial state & the final state.

↛ each requires several quantum numbers !!

$\underset{elec}{\downarrow}$ $\underset{\substack{rot. \\ free rotor, JM.}}{\downarrow}$

$\psi_e \cdot \psi_v \cdot \psi_{JM} \longrightarrow \psi_{e'} \cdot \psi_{v'} \cdot \psi_{J'M'}$

$\underset{\substack{vib. \\ H.O.}}{\uparrow}$

a complete
state.

$|1\rangle \longrightarrow |2\rangle$

Gen General rule is that for the transition to occur, the off-diagonal matrix element.

$$\sum_{i=1}^{M} z_i \cdot \hat{R}_i \cdot e + \sum_{i=1}^{N} \hat{r}_i \cdot e$$ this is key.

$$\textbf{①} \quad \mu_{12} = \langle 1 | \hat{\mu} | 2 \rangle \qquad \hat{M}_N \qquad \hat{M}_e$$

transition dipole

$$= \langle e, \nu, JM | \hat{\mu} | e', \nu', J'M' \rangle .$$

(we will go back to this next week)

✳ rotational spectroscopy (microwave ...).

In this case, $e' = e$, $\nu' = \nu$

$$\therefore \quad \mu_{12} = \iiint \psi_e^* \psi_\nu^* \psi_{JM}^* \cdot \hat{\mu} \cdot \psi_e \psi_\nu \psi_{JM'} \cdot d\tau_e \, d\tau_{vib} \, d\tau_{rot}$$

define $\rightarrow$

(Same elec. & vib. states)

$$\hat{\mu}_0 = \iint \psi_e^* \psi_\nu^* \cdot \hat{\mu} \cdot \psi_e \psi_\nu \cdot d\tau_e \, d\tau_{vib}$$

permanent dipole moment of a molecule in the electronic & vibrational states

this look like γ_i^0, i.e. $\vec{z}$.

$$\therefore \mu_{12} = \int \psi_{JM}^* \cdot \hat{\mu}_0 \cdot \psi_{J'M'} \cdot d\tau_{rot}$$

{ for μ_{12} to : ① the molecule has permanent dipole ⇐ Gross selection rule.

② $\Delta J = \pm 1$, $\Delta M = 0$ ⇐ specific selection rule.

↑ Selection rules!!

✱ Vibrational spectroscopy (ignore rotational states).

$$v \rightarrow v'$$

same state

$$\int \psi_e^* \cdot \hat{\mu} \cdot \psi_e \cdot d\tau_e \Leftarrow \text{electronic permanent dipole}$$

$$\mu_{12} = \int \psi_v^* \cdot \mu_0^{(e)} \cdot \psi_v \cdot d\tau_{vib}$$

nuclear position

Note that $\mu_0^{(e)}$ is a function of x (B-O approximation),

at equilibrium position.

$$\therefore \quad \mu_0^{(e)} = \mu_0 + \left(\frac{\partial \mu}{\partial x}\right)\bigg|_{x=0} \cdot x + \frac{1}{2}\left(\frac{\partial^2 \mu_0}{\partial x^2}\right)_{x=0} \cdot x^2 + \dots$$

Ignore these : Condon approximation

i.e. curvature not affected by vib. motion.

$$\therefore \quad \mu_{12} = \mu_0 \cdot \int \psi_v^* \psi_{v'} \cdot d\tau + \left(\frac{\partial \mu}{\partial x}\right)\bigg|_{x=0} \cdot \int \psi_{v'}^* \cdot x \cdot \psi_v \cdot d\tau$$

$$\hat{b} + b$$

$\therefore$ selection rules:

electron density distribution

① Gross : $\left(\frac{\partial \mu}{\partial x}\right)\bigg|_{x=0} \neq 0$, i.e. dipole moment changes with the vibrational coordinate.
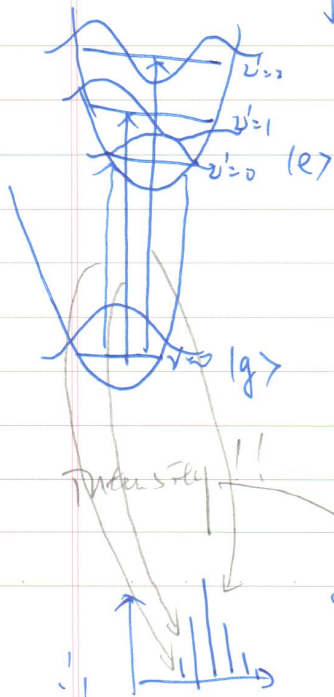
② Specific : $\delta v = \pm 1$

$\Rightarrow$ vibrational absorption occurs at a single frequency

$\int \delta E = \hbar \omega_0$

forbidden.

We won't go further (electronic spectroscopy...),

but the general rules are the same.

The transition dipole between two states

are crucial to induce transition between

them. In fact, one can even derive that.

transition probability

absorption efficiency (i.e. rate) B $\propto |\mu_{12}|^2$.

With this in ~~mind~~ ~~mind~~ mind, it is possible to

describe many stationary spectrum. for example :

for $|g, \nu=0\rangle \longrightarrow |e, \nu'=n\rangle$. (can

be ignored

$-\sum_i e \cdot \hat{r}_i + \sum_i e z_i \hat{R}_i$

$\mu_{12} = \iint \Psi_g^* \Psi_{\nu=0}^* \cdot \hat{\mu} \cdot \Psi_e \cdot \Psi_{\nu'=n} \cdot d\tau_e d\tau_{vib}.$

$\underbrace{}_{\mu_{ge}}$ overlap

$= \int \Psi_g^* \hat{\mu} \cdot \Psi_e \cdot d\tau_e \cdot \int \Psi_{\nu=0}^* \cdot \Psi_{\nu'=n} \cdot d\tau_{vib}$

$= \mu_{ge} \cdot \langle \Psi_{\nu=0} | \Psi_{\nu'=n} \rangle$ F-C factor.

$\therefore$ transition prob. $|\mu|^2 \approx |\mu_{ge}|^2 \cdot |\langle \Psi_{\nu=0} | \Psi_{\nu'=n} \rangle|^2$