5.74 Introductory Quantum Mechanics II
Spring 2009

## 4.1. <u>INTERACTION OF LIGHT WITH MATTER</u>

One of the most important topics in time-dependent quantum mechanics for chemists is the description of spectroscopy, which refers to the study of matter through its interaction with light fields (electromagnetic radiation). Classically, light-matter interactions are a result of an oscillating electromagnetic field resonantly interacting with charged particles.  Quantum mechanically, light fields will act to couple quantum states of the matter, as we have discussed earlier.

Like every other problem, our starting point is to derive a Hamiltonian for the light-matter interaction, which in the most general sense would be of the form

$$H = H_M + H_L + H_{LM} \,. \tag{4.1}$$

The Hamiltonian for the matter $H_M$ is generally (although not necessarily) time independent, whereas the electromagnetic field $H_L$ and its interaction with the matter $H_{LM}$ are time-dependent. A quantum mechanical treatment of the light would describe the light in terms of photons for different modes of electromagnetic radiation, which we will describe later.

We will start with a common semiclassical treatment of the problem. For this approach we treat the matter quantum mechanically, and treat the field classically. For the field we assume that the light only presents a time-dependent interaction potential that acts on the matter, but the matter doesn't influence the light.  (Quantum mechanical energy conservation says that we expect that the change in the matter to raise the quantum state of the system and annihilate a photon from the field.  We won't deal with this right now).  We are just interested in the effect that the light has on the matter. In that case, we can really ignore $H_L$, and we have a Hamiltonian that can be solved in the interaction picture representation:

$$\begin{aligned} H &\approx H_M + H_{LM}\left(t\right) \\ &= H_0 + V\left(t\right) \end{aligned} \tag{4.2}$$

Here, we'll derive the Hamiltonian for the light-matter interaction, the Electric Dipole Hamiltonian. It is obtained by starting with the force experienced by a charged particle in an electromagnetic field, developing a classical Hamiltonian for this system, and then substituting quantum operators for the matter:

$$p \rightarrow -i\hbar \hat{\nabla}$$
$$x \rightarrow \hat{x}$$

(4.3)

In order to get the classical Hamiltonian, we need to work through two steps: (1) We need to describe electromagnetic fields, specifically in terms of a vector potential, and (2) we need to describe how the electromagnetic field interacts with charged particles.

## Brief summary of electrodynamics

Let's summarize the description of electromagnetic fields that we will use. A derivation of the plane wave solutions to the electric and magnetic fields and vector potential is described in the appendix. Also, it is helpful to review this material in Jackson[1] or Cohen-Tannoudji, et al.[2]

> Maxwell's Equations describe electric and magnetic fields $\left( \bar{E}, \bar{B} \right)$.

> To construct a Hamiltonian, we must describe the time-dependent interaction <u>potential</u> (rather than a field).

> To construct the potential representation of $\bar{E}$ and $\bar{B}$, you need a vector potential $\bar{A}\left( \bar{r}, t \right)$ and a scalar potential $\varphi\left( \bar{r}, t \right)$. For electrostatics we normally think of the field being related to the electrostatic potential through $\bar{E} = -\nabla \varphi$, but for a field that varies in time and in space, the electrodynamic potential must be expressed in terms of both $\bar{A}$ and $\varphi$.

> In general an electromagnetic wave written in terms of the electric and magnetic fields requires 6 variables (the *x,y,* and *z* components of *E* and *B*). This is an overdetermined problem; Maxwell's equations constrain these. The potential representation has four variables ( $A_x, A_y, A_z$ and $\varphi$ ), but these are still not uniquely determined. We choose a constraint – a representation or guage – that allows us to uniquely describe the wave. Choosing a gauge such that $\varphi = 0$ (Coulomb gauge) leads to a plane-wave description of $\bar{E}$ and $\bar{B}$:

$$-\bar{\nabla}^2 \bar{A}\left( \bar{r}, t \right) + \frac{1}{c^2} \frac{\partial^2 \bar{A}\left( \bar{r}, t \right)}{\partial t^2} = 0$$

(4.4)

$$\bar{\nabla} \cdot \bar{A} = 0$$

(4.5)

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[1] Jackson, J. D. *Classical Electrodynamics* (John Wiley and Sons, New York, 1975).
[2] Cohen-Tannoudji, C., Diu, B. & Lalöe, F. *Quantum Mechanics* (Wiley-Interscience, Paris, 1977), Appendix III.

This wave equation allows the vector potential to be written as a set of plane waves:

$$\bar{A}(\bar{r},t) = A_0\hat{\varepsilon}\,e^{i(\bar{k}\cdot\bar{r}-\omega t)} + A_0^*\hat{\varepsilon}\,e^{-i(\bar{k}\cdot\bar{r}-\omega t)}. \tag{4.6}$$

This describes the wave oscillating in time at an angular frequency $\omega$ and propagating in space in the direction along the wavevector $\bar{k}$, with a spatial period $\lambda = 2\pi/|\bar{k}|$. The wave has an amplitude $A_0$ which is directed along the polarization unit vector $\hat{\varepsilon}$. Since $\bar{\nabla}\cdot\bar{A}=0$, we see that $\bar{k}\cdot\hat{\varepsilon}=0$ or $\bar{k}\perp\hat{\varepsilon}$. From the vector potential we can obtain $\bar{E}$ and $\bar{B}$

$$\begin{aligned}
\bar{E} &= -\frac{\partial\bar{A}}{\partial t} \\
&= i\omega A_0\,\hat{\varepsilon}\left(e^{i(\bar{k}\cdot\bar{r}-\omega t)} - e^{-i(\bar{k}\cdot\bar{r}-\omega t)}\right)
\end{aligned} \tag{4.7}$$

$$\begin{aligned}
\bar{B} &= \bar{\nabla}\times\bar{A} \\
&= i\left(\bar{k}\times\hat{\varepsilon}\right)A_0\left(e^{i(\bar{k}\cdot\bar{r}-\omega t)} - e^{-i(\bar{k}\cdot\bar{r}-\omega t)}\right)
\end{aligned} \tag{4.8}$$

If we define a unit vector along the magnetic field polarization as $\hat{b}=\left(\bar{k}\times\hat{\varepsilon}\right)/|\bar{k}|=\hat{k}\times\hat{\varepsilon}$, we see that the wavevector, the electric field polarization and magnetic field polarization are mutually orthogonal $\hat{k}\perp\hat{\varepsilon}\perp\hat{b}$.

Also, by comparing eq. (4.6) and (4.7) we see that the vector potential oscillates as $cos(\omega t)$, whereas the field oscillates as $sin(\omega t)$. If we define
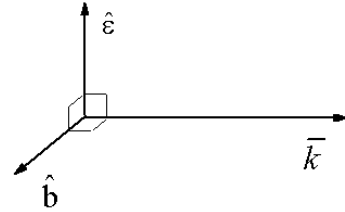
$$\frac{1}{2}E_0 = i\omega A_0 \tag{4.9}$$

$$\frac{1}{2}B_0 = i|\bar{k}|A_0 \tag{4.10}$$

then,

$$\bar{E}(\bar{r},t) = |E_0|\hat{\varepsilon}\sin\left(\bar{k}\cdot\bar{r}-\omega t\right) \tag{4.11}$$

$$\bar{B}(\bar{r},t) = |B_0|\hat{b}\sin\left(\bar{k}\cdot\bar{r}-\omega t\right). \tag{4.12}$$

Note, $E_0/B_0 = \omega/|\bar{k}| = c$.

## Classical Hamiltonian for radiation field interacting with charged particle

Now, let's find a classical Hamiltonian that describes charged particles in a field in terms of the vector potential. Start with Lorentz force[3] on a particle with charge $q$:

$$\overline{F} = q\left(\overline{E} + \overline{v} \times \overline{B}\right). \tag{4.13}$$

Here $\overline{v}$ is the velocity of the particle. Writing this for one direction ($x$) in terms of the Cartesian components of $\overline{E}$, $\overline{v}$ and $\overline{B}$, we have:

$$F_x = q\left(E_x + v_y B_z - v_z B_y\right). \tag{4.14}$$

In Lagrangian mechanics, this force can be expressed in terms of the total potential energy $U$ as

$$F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt}\left(\frac{\partial U}{\partial v_x}\right) \tag{4.15}$$

Using the relationships that describe $\overline{E}$ and $\overline{B}$ in terms of $\overline{A}$ and $\varphi$, inserting into eq. (4.14), and working it into the form of eq. (4.15), we can show that:

$$U = q\varphi - q\overline{v} \cdot \overline{A} \tag{4.16}$$

This is derived in CTDL,[4] and you can confirm by replacing it into eq. (4.15).

Now we can write a Lagrangian in terms of the kinetic and potential energy of the particle

$$L = T - U \tag{4.17}$$

$$L = \frac{1}{2}m\overline{v}^2 + q\overline{v} \cdot \overline{A} - q\varphi \tag{4.18}$$

The classical Hamiltonian is related to the Lagrangian as

$$\begin{aligned} H &= \overline{p} \cdot \overline{v} - L \\ &= \overline{p} \cdot \overline{v} - \tfrac{1}{2}m\overline{v}^2 - q\overline{v} \cdot \overline{A} - q\varphi \end{aligned} \tag{4.19}$$

Recognizing

$$\overline{p} = \frac{\partial L}{\partial \overline{v}} = m\overline{v} + q\overline{A} \tag{4.20}$$

we write

$$\overline{v} = \tfrac{1}{m}\left(\overline{p} - q\overline{A}\right). \tag{4.21}$$

Now substituting (4.21) into (4.19), we have:

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[3] See Schatz and Ratner, p.82-83.
[4] Cohen-Tannoudji, et al. app. III, p. 1492.

$$H = \tfrac{1}{m}\, \overline{p} \cdot \left( \overline{p} - q\overline{A} \right) - \tfrac{1}{2m} \left( \overline{p} - q\overline{A} \right)^2 - \tfrac{q}{m} \left( \overline{p} - q\overline{A} \right) \cdot A + q\varphi \tag{4.22}$$

$$H = \frac{1}{2m} \left[ \overline{p} - q\overline{A}\left( \overline{r}, t \right) \right]^2 + q\varphi\left( \overline{r}, t \right) \tag{4.23}$$

This is the classical Hamiltonian for a particle in an electromagnetic field. In the Coulomb gauge $\left( \varphi = 0 \right)$, the last term is dropped.

We can write a Hamiltonian for a collection of particles in the <u>absence</u> of a external field

$$H_0 = \sum_i \left( \frac{\overline{p}_i^{\,2}}{2m_i} + V_0\left( \overline{r}_i \right) \right). \tag{4.24}$$

and in the <u>presence</u> of the EM field:

$$H = \sum_i \left( \frac{1}{2m_i} \left( \overline{p}_i - q_i \overline{A}\left( \overline{r}_i \right) \right)^2 + V_0\left( r_i \right) \right). \tag{4.25}$$

Expanding:
$$H = H_0 - \sum_i \frac{q_i}{2m_i} \left( p_i \cdot \overline{A} + \overline{A} \cdot \overline{p}_i \right) + \sum_i \frac{q_i}{2m_i} \cancel{|A|^2} \tag{4.26}$$

Generally the last term is considered small compared to the cross term. This term should be considered for extremely high field strength, which is nonperturbative and significantly distorts the potential binding molecules together. One can estimate that this would start to play a role at intensity levels $>10^{15}$ W/cm$^2$, which may be observed for very high energy and tightly focused pulsed femtosecond lasers. So, for weak fields we have an expression that maps directly onto solutions we can formulate in the interaction picture:

$$H = H_0 + V\left( t \right) \tag{4.27}$$

$$V\left( t \right) = \sum_i \frac{q_i}{2m_i} \left( \overline{p}_i \cdot \overline{A} + \overline{A} \cdot \overline{p}_i \right). \tag{4.28}$$

## Quantum mechanical Electric Dipole Hamiltonian

Now we are in a position to substitute the quantum mechanical momentum for the classical. Here the vector potential remains classical, and only modulates the interaction strength.

$$\overline{p} = -i\hbar \overline{\nabla} \tag{4.29}$$

$$V(t) = \sum_i \frac{i\hbar}{2m_i} q_i \left( \overline{\nabla}_i \cdot \overline{A} + \overline{A} \cdot \overline{\nabla}_i \right) \tag{4.30}$$

We can show that $\overline{\nabla} \cdot \overline{A} = \overline{A} \cdot \overline{\nabla}$. Notice $\overline{\nabla} \cdot \overline{A} = \left( \overline{\nabla} \cdot \overline{A} \right) + \overline{A} \cdot \overline{\nabla}$ (chain rule). For instance, if we are operating on a wavefunction $\overline{\nabla} \cdot \overline{A} | \psi \rangle = \left( \overline{\nabla} \cdot \overline{A} \right) | \psi \rangle + \overline{A} \cdot \left( \overline{\nabla} | \psi \rangle \right)$. The first term is zero since we are working in the Coulomb gauge $\left( \overline{\nabla} \cdot \overline{A} = 0 \right)$. Now we have:

$$\begin{aligned} V(t) &= \sum_i \frac{i\hbar q_i}{m_i} \overline{A} \cdot \overline{\nabla}_i \\ &= -\sum_i \frac{q_i}{m_i} \overline{A} \cdot \overline{p}_i \end{aligned} \tag{4.31}$$

For a single charge particle our interaction Hamiltonian is

$$\begin{aligned} V(t) &= -\frac{q}{m} \overline{A} \cdot \overline{p} \\ &= -\frac{q}{m} \left[ A_0 \hat{\varepsilon} \cdot \overline{p} \, e^{i\left( \overline{k} \cdot \overline{r} - \omega t \right)} + \text{c.c.} \right] \end{aligned} \tag{4.32}$$

Under most circumstances, we can neglect the wavevector dependence of the interaction potential. If the wavelength of the field is much larger than the molecular dimension $(\lambda \to \infty)\left( |k| \to 0 \right)$, then $e^{i\overline{k} \cdot \overline{r}} \approx 1$. This is known as the electric dipole approximation.

We do retain the spatial dependence for certain types of light-matter interactions. In that case we define $r_0$ as the center of mass of a molecule and expand

$$\begin{aligned} e^{i\overline{k} \cdot \overline{r}_i} &= e^{i\overline{k} \cdot \overline{r}_0} \, e^{i\overline{k} \cdot \left( \overline{r}_i - \overline{r}_0 \right)} \\ &= e^{i\overline{k} \cdot \overline{r}_0} \left[ 1 + i\overline{k} \cdot \left( \overline{r}_i - \overline{r}_0 \right) + \dots \right] \end{aligned} \tag{4.33}$$

For interactions, with UV, visible, and infrared (but not X-ray) radiation, $|k| \left| \overline{r}_i - \overline{r}_0 \right| << 1$, and setting $\overline{r}_0 = 0$ means that $e^{i\overline{k} \cdot \overline{r}} \to 1$. We retain the second term for quadrupole transitions: charge distribution interacting with gradient of electric field and magnetic dipole.

Now, using $A_0 = iE_0 / 2\omega$, we write (4.32) as

$$V(t) = \frac{-iqE_0}{2m\omega} \left[ \hat{\varepsilon} \cdot \overline{p} \, e^{-i\omega t} - \hat{\varepsilon} \cdot \overline{p} \, e^{+i\omega t} \right] \tag{4.34}$$

$$V(t) = \frac{-qE_0}{m\omega}(\hat{\varepsilon} \cdot \overline{p})\sin \omega t$$

$$= \frac{-q}{m\omega}\left(\overline{E}(t) \cdot \overline{p}\right) \tag{4.35}$$

or for a collection of charged particles (molecules):

$$V(t) = -\left(\sum_i \frac{q_i}{m_i}(\hat{\varepsilon} \cdot \overline{p}_i)\right)\frac{E_0}{\omega}\sin \omega t \tag{4.36}$$

This is known as the electric dipole Hamiltonian (EDH).

## Transition dipole matrix elements

We are seeking to use this Hamiltonian to evaluate the transition rates induced by $V(t)$ from our first-order perturbation theory expression. For a perturbation $V(t) = V_0 \sin \omega t$ the rate of transitions induced by field is

$$w_{k\ell} = \frac{\pi}{2\hbar}|V_{k\ell}|^2\left[\delta(E_k - E_\ell - \hbar\omega) + \delta(E_k - E_\ell + \hbar\omega)\right] \tag{4.37}$$

Now we evaluate the matrix elements of the EDH in the eigenstates for $H_0$:

$$V_{k\ell} = \langle k|V_0|\ell\rangle = \frac{-qE_0}{m\omega}\langle k|\hat{\varepsilon} \cdot \overline{p}|\ell\rangle \tag{4.38}$$

We can evaluate the matrix element $\langle k|\overline{p}|\ell\rangle$ using an expression that holds for any one-particle Hamiltonian:

$$[\overline{r}, H_0] = \frac{i\hbar\overline{p}}{m}. \tag{4.39}$$

This expression gives

$$\langle k|\overline{p}|\ell\rangle = \frac{m}{i\hbar}\langle k|\overline{r}\,H_0 - H_0\,\overline{r}|\ell\rangle$$

$$= \frac{m}{i\hbar}\left(\langle k|\overline{r}|\ell\rangle E_\ell - E_k\langle k|\overline{r}|\ell\rangle\right) \tag{4.40}$$

$$= im\omega_{\ell k}\langle k|\overline{r}|\ell\rangle.$$

So we have

$$V_{k\ell} = -iqE_0 \frac{\omega_{\ell k}}{\omega}\langle k|\hat{\varepsilon} \cdot \overline{r}|\ell\rangle \tag{4.41}$$

or for a collection of particles

$$V_{k\ell} = -iE_0 \frac{\omega_{\ell k}}{\omega} \left\langle k \left| \hat{\varepsilon} \cdot \left( \sum_i q_i \bar{r}_i \right) \right| \ell \right\rangle$$

$$= -iE_0 \frac{\omega_{\ell k}}{\omega} \left\langle k \left| \hat{\varepsilon} \cdot \bar{\mu} \right| \ell \right\rangle \tag{4.42}$$

$$= -iE_0 \frac{\omega_{\ell k}}{\omega} \mu_{kl}$$

$\bar{\mu}$ is the dipole operator, and $\mu_{kl}$ is the transition dipole matrix element. We can see that it is the quantum analog of the classical dipole moment, which describes the distribution of charge density $\rho$ in the molecule:

$$\bar{\mu} = \int d\bar{r} \; \bar{r} \; \rho(\bar{r}). \tag{4.43}$$

These expressions allow us to write in simplified form the well known interaction potential for a dipole in a field:

$$V(t) = -\bar{\mu} \cdot \bar{E}(t) \tag{4.44}$$

Then the rate of transitions between quantum states induced by the electric field is

$$w_{k\ell} = \frac{\pi}{2\hbar} |E_0|^2 \frac{\omega_{k\ell}^2}{\omega^2} |\bar{\mu}_{kl}|^2 \left[ \delta(E_k - E_\ell - \hbar\omega) + (E_k - E_\ell + \hbar\omega) \right]$$

$$= \frac{\pi}{2\hbar^2} |E_0|^2 |\bar{\mu}_{kl}|^2 \left[ \delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right] \tag{4.45}$$

Equation (4.45) is an expression for the absorption spectrum since the rate of transitions can be related to the power absorbed from the field. More generally we would express the absorption spectrum in terms of a sum over all initial and final states, the eigenstates of $H_0$:

$$w_{fi} = \sum_{i,f} \frac{\pi}{\hbar^2} |E_0|^2 |\mu_{fi}|^2 \left[ \delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega) \right] \tag{4.46}$$

The strength of interaction between light and matter is given by the matrix element $\mu_{fi} \equiv \langle f | \bar{\mu} \cdot \hat{\varepsilon} | i \rangle$. The scalar part $\langle f | \mu | i \rangle$ says that you need a change of charge distribution between $|f\rangle$ and $|i\rangle$ to get effective absorption. This matrix element is the basis of selection rules based on the symmetry of the states. The vector part says that the light field must project onto the dipole moment. This allows information to be obtained on the orientation of molecules, and forms the basis of rotational transitions.

## Relaxation Leads to Line-broadening

Let's combine the results from the last two lectures, and describe absorption to a state that is coupled to a continuum. What happens to the probability of absorption if the excited state decays exponentially?
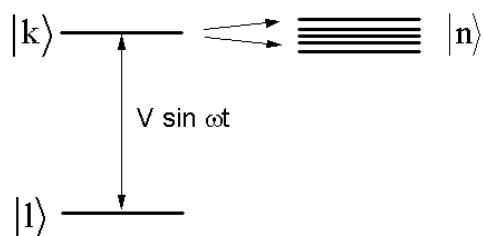


$|k\rangle$ relaxes exponentially

... for instance by coupling to continuum

$$P_k \propto \exp\left[-\overline{w}_{nk}t\right]$$

We can start with the first-order expression:

$$b_k = \frac{-i}{\hbar} \int_{t_0}^{t} d\tau \left\langle k |V| t\right\rangle \tag{4.47}$$

or equivalently

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{k\ell}t} V_{k\ell}(t) \tag{4.48}$$

We can add irreversible relaxation to the description of $b_k$, following our early approach:

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{k\ell}t} V_{k\ell}(t) - \frac{\overline{w}_{nk}}{2} b_k \tag{4.49}$$

Or using $V(t) = -iE_0 \overline{\mu}_{k\ell} \sin \omega t$

$$\frac{\partial}{\partial t} b_k = \frac{-i}{\hbar} e^{i\omega_{k\ell}t} \sin \omega t \, V_{k\ell} - \frac{\overline{w}_{nk}}{2} b_k(t)$$

$$= \frac{E_0 \omega_{k\ell}}{2i\hbar\omega} \left[ e^{i(\omega_{k\ell}+\omega)} - e^{i(\omega_{k\ell}-\omega)t} \right] \overline{\mu}_{k\ell} - \frac{\overline{w}_{nk}}{2} b_k(t) \tag{4.50}$$

The solution to the differential equation

$$\dot{y} + ay = b e^{i\alpha t} \tag{4.51}$$

is

$$y(t) = A e^{-at} + \frac{b e^{i\alpha t}}{a + i\alpha}. \tag{4.52}$$

$$b_k(t) = A\,e^{-\bar{w}_{nk}t/2} + \frac{E_0\,\bar{\mu}_{k\ell}}{2i\hbar}\left[\frac{e^{i(\omega_{k\ell}+\omega)t}}{\bar{w}_{nk}/2+i(\omega_{k\ell}+\omega)} - \frac{e^{i(\omega_{k\ell}-\omega)t}}{\bar{w}_{nk}/2+i(\omega_{k\ell}-\omega)}\right] \qquad (4.53)$$
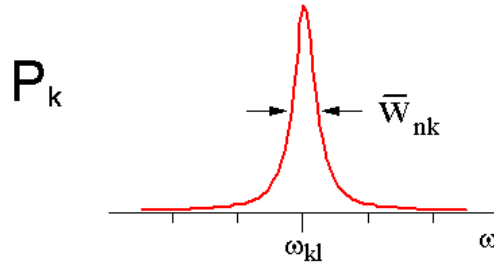
Let's look at absorption only, in the long time limit:

$$b_k(t) = \frac{E_0\bar{\mu}_{k\ell}}{2\hbar}\left[\frac{e^{i(\omega_{k\ell}-\omega)t}}{\omega_{k\ell}-\omega-i\bar{w}_{nk}/2}\right] \qquad (4.54)$$

For which the probability of transition to $k$ is

$$P_k = |b_k|^2 = \frac{E_0^2\,|\mu_{k\ell}|^2}{4\hbar^2}\,\frac{1}{(\omega_{k\ell}-\omega)^2+\bar{w}_{nk}^{\,2}/4} \qquad (4.55)$$

The frequency dependence of the transition probability has a Lorentzian form:



The linewidth is related to the relaxation rate from $k$ into the continuum $n$. Also the linewidth is related to the system rather than the manner in which we introduced the perturbation.