Interaction of Light with Matter

We want to derive a Hamiltonian that we can use to describe the interaction of an electromagnetic field with charged particles: Electric Dipole Hamiltonian.

Semiclassical: matter treated quantum mechanically
Field: classical

Brief outline of electrodynamics: See nonlecture handout. Also, see Jackson, *Classical Electrodynamics*, or Cohen-Tannoudji, et al., Appendix III.

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

> For Hamiltonian, we require a potential.

> To construct a potential representation of $\bar{E}$ and $\bar{B}$, you need a vector potential $\bar{A}(\bar{r},t)$ and a scalar potential $\varphi(F,t)$.

> $\bar{A}$ and φ are mathematical constructs that can be written in various representations (gauges).

We choose a gauge such that $\varphi = 0$ (Coulomb gauge) which leads to plane-wave description of $\bar{E}$ and $\bar{B}$:

$$-\bar{\nabla}^2 \bar{A}(\bar{r},t) + \epsilon_0 \mu_0 \frac{\partial^2 \bar{A}(\bar{r},t)}{\partial t} = 0$$

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

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

$$\bar{A}(\bar{r},t) = A_0 \hat{\epsilon} e^{i(\bar{k}\cdot\bar{r}-\omega t)} + A_0^* \hat{\epsilon} e^{-i(\bar{k}\cdot\bar{r}-\omega t)} \qquad \text{(oscillates as } \cos\omega t\text{)}$$

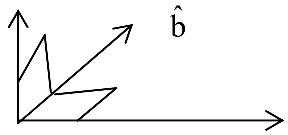
since $\bar{\nabla} \cdot \bar{A} = 0$, $\bar{k}\cdot\hat{\epsilon} = 0 \Rightarrow \bar{k} \perp \hat{\epsilon}$ where $\hat{\epsilon}$ is the polarization direction of the vector potential.

$$\bar{E} = -\frac{\partial \bar{A}}{\partial t} = i\omega A_0 \hat{\epsilon} e^{i(\bar{k}\cdot\bar{r}-\omega t)} + \text{c.c.} \qquad \text{(oscillates as } \sin\omega t\text{)}$$

$$\bar{B} = \bar{\nabla}\times\bar{A} = i\underbrace{(\bar{k}\times\bar{\epsilon})}_{\hat{b}|k|} A_0 e^{i(\bar{k}\cdot\bar{r}-\omega t)} + \text{c.c}$$

so we see that $\hat{k} \perp \hat{\in} \perp \hat{n}$

$\hat{\in}$ is the direction of the electric field polarization and
$\hat{n}$ is the direction of the magnetic field polarization.



We define $\frac{1}{2} E_0 = i\omega A_0$

$\frac{1}{2} B_0 = i|k| A_0 \qquad \left(\frac{E_0}{B_0} = \frac{\omega}{k} = c\right)$

$$\bar{E}(\bar{r}, t) = |E_0| \hat{\in} \sin(\bar{k} \cdot \bar{r} - \omega t)$$

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

Hamiltonian for radiation field interacting with charged particle

We will derive a Lagrangian for charged particle in field, then use it to determine classical Hamiltonian, then replace classical operators with quantum.

Start with Lorentz force on a charged particle:

$$F = q\left(\overline{E} + \overline{v} \times \overline{B}\right) \tag{1}$$

where $\dot{\overline{r}}$ is the velocity. In one direction (x), we have:

$$F_x = q\left(E_x + \dot{y}B_z - \dot{z}B_y\right) \tag{2}$$

The generalized force for the components of the force in the x direction in Lagrangian Mechanics is:

$$F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt}\left(\frac{\partial U}{\partial \dot{x}}\right) \tag{3}$$

U is the potential. Using our relationships for $\overline{E}$ and $\overline{B}$ in terms of A and φ in eq. (2) and working it into the form of eq. (3), we can show that:

$$U = q\varphi - q\dot{\overline{r}} \cdot A \tag{4}$$

See CTDL, app. III, p. 1492. Confirm by plugging into (3).

Now we can write a Lagrangian

$$L = T - U$$

$$= \tfrac{1}{2} m\dot{\overline{r}}^2 + q\dot{\overline{r}} \cdot A - q\varphi \tag{5}$$

Now the Hamiltonian is related to the Lagrangian at:

$$H = \overline{p} \cdot \dot{\overline{r}} - L$$

$$= \overline{p} \cdot \dot{\overline{r}} - \tfrac{1}{2} m\,\dot{\overline{r}}^2 - q\,\dot{\overline{r}} \cdot \overline{A} - q\varphi \tag{6}$$

$$\overline{p} = \frac{\partial L}{\partial \dot{\overline{r}}} = m\dot{\overline{r}} + q\overline{A} \quad \Rightarrow \quad \dot{\overline{r}} = \tfrac{1}{m}\left(\overline{p} - q\overline{A}\right) \tag{7}$$

Now substituting (7) into (6), we have:

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

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

This is the classical Hamiltonian for a particle of charge q in an electromagnetic field. So, in the Coulomb gauge $(\varphi = 0)$, we have the Hamiltonian for a collection of particles in the absence of a field:

$$H_0 = \sum_i \left(\frac{\bar{p}_i^2}{2m_i} + V_0(\bar{r}_i) \right)$$

and in the presence of the field:

$$H = \sum_i \left(\tfrac{1}{2m_i}\left(\bar{p}_i - q_i\bar{A}(\bar{r}_i)\right)^2 + V_0(r_i) \right)$$

Expanding:

$$H = H_0 - \sum_i \frac{q_i}{2m_i}\left(p_i\cdot\bar{A} + \bar{A}\cdot\bar{p}_i\right) + \sum_i \frac{q_i}{2m_i}\left|\bar{A}\right|^2$$

Generally the last term is considered small—energy of particles high relative to amplitude of potential—so we have:

$$H = H_0 + V(t)$$

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

Now we are in a position to substitute the quantum mechanical momentum for the classical:

$$\bar{p} = -i\hbar\bar{\nabla}$$ Matter: Quantum; Field (A): Classical

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

Notice $\bar{\nabla}\cdot\bar{A} = \left(\bar{\nabla}\cdot\bar{A}\right) + \bar{A}\cdot\bar{\nabla}$ (chain rule), but we are in the Coulomb gauge $\left(\bar{\nabla}\cdot\bar{A} = 0\right)$, so $\bar{\nabla}\cdot\bar{A} = \bar{A}\cdot\bar{\nabla}$

$$V(t) = \sum_i \frac{i\hbar q_i}{m_i} \bar{A} \cdot \bar{\nabla}_i$$
$$= -\sum_i \frac{q_i}{m_i} \bar{A} \cdot \bar{p}_i$$

For a single charge particle our interaction Hamiltonian is

$$V(t) = \frac{-q.}{m} \bar{A} \cdot \bar{p}$$

Using our plane-wave description of the vector potential:

$$V(t) = \frac{-q}{m}\left[A_0 \ \hat{\in} \cdot \bar{p} \ e^{i\left(\bar{k} \cdot \bar{r} - \omega t\right)} + \text{c.c.} \right]$$

Electric Dipole Approximation

If the wavelength of the field is much larger than the molecular dimension $(\lambda \to \infty)(|k| \to 0)$, then $e^{i\bar{k} \cdot \bar{r}} \to 1$.

If r_0 is the center of mass of a molecule:

$$e^{i\bar{k} \cdot \bar{r}_i} = e^{i\bar{k} \cdot \bar{r}_0} \ e^{i\bar{k} \cdot (\bar{r}_i - \bar{r}_0)}$$
$$= e^{i\bar{k} \cdot \bar{r}_0} \left[1 + i\bar{k} \cdot (\bar{r}_i - \bar{r}_0) + \ldots \right]$$

For UV, visible, infrared—not X-ray—$|k||\bar{r}_i - \bar{r}_0| << 1$, set $\bar{r}_0 = 0$ $\qquad e^{i\bar{k} \cdot \bar{r}} \to 1$.

We do retain higher-order terms to describe higher order interactions with the field.

Retain second term for quadrupole transition moment: charge distribution interacting with gradient of electric field and magnetic dipole.

Electric Dipole Hamiltonian

$$V(t) = \frac{-q}{m}\left[A_0\ \hat{\in}\cdot\bar{p}\ e^{-i\omega t} + c.c.\right]$$

Using $A_0 = \dfrac{iE_0}{2\omega}$

$$V(t) = \frac{-iqE_0}{2m\omega}\left[\hat{\in}\cdot\bar{p}\ e^{-i\omega t} - \hat{\in}\cdot\bar{p}\ e^{+i\omega t}\right]$$

$$V(t) = \frac{-qE_0}{m\omega}\left(\hat{\in}\cdot\bar{p}\right)\sin\omega t \qquad \text{Electric Dipole Hamiltonian}$$

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

or for a collection of charge particles (molecules):

$$V(t) = -\left(\sum_i \frac{q_i}{m_i}\left(\hat{\in}\cdot p_i\right)\right)\frac{E_0}{\omega}\sin\omega t$$

Harmonic Perturbation: Matrix Elements

For a perturbation $V(t) = V_0 \sin\omega t$ the rate of transitions induced by field is

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

Let's look at the matrix elements for the E.D.H.

$$V_{k\ell} = \left\langle k\left|V_0\right|\ell\right\rangle = \frac{qE_0}{m\omega}\left\langle k\left|\hat{\in}\cdot\bar{p}\right|\ell\right\rangle$$

Evaluate the bracket $\langle k|\bar{p}|\ell\rangle$ using $\left[\bar{r}, H_0\right] = \dfrac{i\hbar\bar{p}}{m}$

$$\langle k|\bar{p}|\ell\rangle = \frac{m}{i\hbar}\left\langle k\left|\bar{r}H_0 - H_0\bar{r}\right|\ell\right\rangle$$

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

$$\therefore V_{k\ell} = iqE_0\frac{\omega_{k\ell}}{\omega}\left\langle k\left|\hat{\in}\cdot\bar{r}\right|\ell\right\rangle$$

or for a collection of particles

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

$$= iE_0 \cancel{\frac{\omega_{k\ell}}{\omega}} \langle k | \hat{\in} \cdot \bar{\mu} | \ell \rangle$$

dipole moment

So we can write the electric dipole Hamiltonian as

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

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

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

$$\approx \frac{\pi}{\hbar^2} |E_0|^2 \left| \langle k | \bar{\mu} \cdot \hat{\in} | \ell \rangle \right|^2 \left[\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right]$$