7.2: Classical Light–Matter Interactions

Classical Plane Electromagnetic Waves

As a starting point, it is helpful to first summarize the classical description of electromagnetic fields. A derivation of the plane wave solutions to the electric and magnetic fields and vector potential is described in the appendix in Section 6.6.

Maxwell's equations describe electric ($\overline{E}$) and magnetic fields ($\overline{B}$); however, to construct a Hamiltonian, we must use the time-dependent interaction **potential** (rather than a field). To construct the potential representation of $\overline{E}$ and $\overline{B}$, you need a vector potential $\overline{A}(\overline{r},t)$, and a scalar potential $\varphi(\overline{r},t)$. For electrostatics we normally think of the field being related to the electrostatic potential through $\overline{E}=-\nabla\varphi$, but for a field that varies in time and in space, the electrodynamic potential must be expressed in terms of both $\overline{A}$ and φ.

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

$$-\overline{\nabla}^2\overline{A}(\overline{r},t)+\frac{1}{c^2}\frac{\partial^2\overline{A}(\overline{r},t)}{\partial t^2}=0 \tag{7.2.1}$$

and

$$\overline{\nabla}\cdot\overline{A}=0 \tag{7.2.2}$$

This wave equation for the vector potential gives a plane wave solution for charge free space and suitable boundary conditions:

$$\overline{A}(\overline{r},t)=A_0\hat{\varepsilon}\,e^{i(\overline{k}\cdot\overline{r}-\omega t)}+A_0^*\hat{\varepsilon}\,e^{-i(\overline{k}\cdot\overline{r}-\omega t)} \tag{7.2.3}$$

This describes the wave oscillating in time at an angular frequency ω and propagating in space in the direction along the wave vector $\overline{k}$, with a spatial period $\lambda=2\pi/|\overline{k}|$. Writing the relationship between k, ω, and λ in a medium with index of refraction n in terms of their values in free space:

$$k=nk_0=\frac{n\omega_0}{c}=\frac{2\pi n}{\lambda_0} \tag{7.2.4}$$

The wave has an amplitude A_0, which is directed along the polarization unit vector $\overline{k}$. Since $\overline{\nabla}\cdot\overline{A}=0$, we see that $\overline{k}\cdot\hat{\mathcal{E}}=0$ or $\overline{k}\perp\hat{\mathcal{E}}$. From the vector potential we can obtain $\overline{E}$ and $\overline{B}$

$$\overline{E}=-\frac{\partial\overline{A}}{\partial t} \tag{7.2.5}$$

$$=i\omega A_0\hat{\varepsilon}\left(e^{i(\overline{k}\cdot\overline{r}-\omega t)}-e^{-i(\overline{k}\cdot\overline{r}-\omega t)}\right) \tag{7.2.6}$$

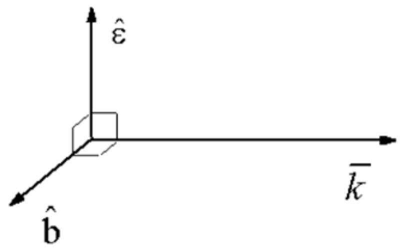
$$\overline{B}=\overline{\nabla}\times\overline{A} \tag{7.2.7}$$

$$=i(\overline{k}\times\hat{\varepsilon})A_0\left(e^{i(\overline{k}\cdot\overline{r}-\omega t)}-e^{-i(\overline{k}\cdot\overline{r}-\omega t)}\right) \tag{7.2.8}$$

If we define a unit vector along the magnetic field polarization as

$$\hat{b}=(\overline{k}\times\hat{\varepsilon})/|\overline{k}|=\hat{k}\times\hat{\mathcal{E}}, \tag{7.2.9}$$

we see that the wave vector, the electric field polarization and magnetic field polarization are mutually orthogonal $\hat{k}\perp\hat{\varepsilon}\perp\hat{b}$.



Also, by comparing Equation 7.2.3 and 7.2.6 we see that the vector potential oscillates as $\cos(\omega t)$, whereas the electric and magnetic fields oscillate as $\sin(\omega t)$. If we define

$$\frac{1}{2}E_0 = i\omega A_0 \tag{7.2.10}$$

$$\frac{1}{2}B_0 = i|k|A_0 \tag{7.2.11}$$

then,

$$\overline{E}(\overline{r},t) = |E_0|\,\hat{\varepsilon}\,\sin(\overline{k}\cdot\overline{r}-\omega t) \tag{7.2.12}$$

$$\overline{B}(\overline{r},t) = |B_0|\,\hat{b}\,\sin(\overline{k}\cdot\overline{r}-\omega t) \tag{7.2.13}$$

Note that

$$E_0/B_0 = \omega/|k| = c. \tag{7.2.14}$$

We will want to express the amplitude of the field in a manner that is experimentally accessible. The intensity I, the energy flux through a unit area, is most easily measured. It is the time-averaged value of the *Poynting vector*

$$I = \langle\overline{S}\rangle = \frac{1}{2}\varepsilon_0 c E_0^2 \quad \left(\mathrm{W/m^2}\right) \tag{7.2.15}$$

An alternative representation of the amplitude that is useful for describing quantum light fields is the energy density

$$U = \frac{I}{c} = \frac{1}{2}\varepsilon_0 E_0^2 \quad \left(\mathrm{J/m^3}\right) \tag{7.2.16}$$

Classical Hamiltonian for radiation field interacting with charged particle

Now, we obtain a classical Hamiltonian that describes charged particles interacting with a radiation field in terms of the vector potential. Start with Lorentz force on a particle with charge q:

$$\overline{F} = q(\overline{E}+\overline{v}\times\overline{B}) \tag{7.2.17}$$

Here 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:

$$F_x = q\left(E_x + v_y B_z - v_z B_y\right) \tag{7.2.18}$$

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

$$F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt}\left(\frac{\partial U}{\partial v_x}\right) \tag{7.2.19}$$

Using the relationships that describe $\overline{E}$ and $\overline{B}$ in terms of $\overline{A}$ and φ (Equations 7.2.10 and 7.2.11), inserting into Equation 7.2.18, and working it into the form of Equation 7.2.19, we can show that

$$U = q\varphi - q\overline{v}\cdot\overline{A} \tag{7.2.20}$$

This is derived elsewhere[4] and is readily confirmed by replacing it into Equation 7.2.19. Now we can write a Lagrangian in terms of the kinetic and potential energy of the particle

$$L = T - U \tag{7.2.21}$$

$$= \frac{1}{2}m\bar{v}^2 + q\bar{v}\cdot\overline{A} - q\varphi \tag{7.2.22}$$

The classical Hamiltonian is related to the Lagrangian as

$$H = \bar{p}\cdot\bar{v} - L \tag{7.2.23}$$

$$= \bar{p}\cdot\bar{v} - \frac{1}{2}m\bar{v}^2 - q\bar{v}\cdot\overline{A} - q\varphi \tag{7.2.24}$$

Recognizing

$$\bar{p} = \frac{\partial L}{\partial \bar{v}} = m\bar{v} + q\overline{A} \tag{7.2.25}$$

we write

$$\bar{v} = \frac{1}{m}(\bar{p} - q\overline{A}) \tag{7.2.26}$$

Now substituting Equations 7.2.26 into Equation 7.2.24, we have

$$H = \frac{1}{m}\bar{p}\cdot(\bar{p} - q\overline{A}) - \frac{1}{2m}(\bar{p} - q\overline{A})^2 - \frac{q}{m}(\bar{p} - q\overline{A})\cdot A + q\varphi \tag{7.2.27}$$

$$= \frac{1}{2m}[\bar{p} - q\overline{A}(\bar{r},t)]^2 + q\varphi(\bar{r},t) \tag{7.2.28}$$

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

We can write a Hamiltonian for a single particle in a bound potential V_0 in the absence of an external field as

$$H_0 = \frac{\bar{p}^2}{2m} + V_0(\bar{r}) \tag{7.2.29}$$

and in the presence of the EM field,

$$H = \frac{1}{2m}(\bar{p} - q\overline{A}(\bar{r},t))^2 + V_0(\bar{r}) \tag{7.2.30}$$

Expanding we obtain

$$H = H_0 - \frac{q}{2m}(\bar{p}\cdot\overline{A} + \overline{A}\cdot\bar{p}) + \frac{q^2}{2m}|\overline{A}(\bar{r},t)|^2 \tag{7.2.31}$$

Generally the last term which goes as the square of A is small compared to the cross term, which is proportional to first power of A. This term should be considered for extremely high field strength, which is non-perturbative and significantly distorts the potential binding molecules together, i.e., when it is similar in magnitude to V_0. 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:

$$H = H_0 + V(t) \tag{7.2.32}$$

with

$$V(t) = \frac{q}{2m}(\bar{p}\cdot\overline{A} + \overline{A}\cdot\bar{p}). \tag{7.2.33}$$

Readings

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4. Merzbacher, E., Quantum Mechanics. 3rd ed.; Wiley: New York, 1998.
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6. Schatz, G. C.; Ratner, M. A., Quantum Mechanics in Chemistry. Dover Publications: Mineola, NY, 2002; pp. 82-83.