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Preliminaries of the Interaction of Light with Matter

Influencing the dynamics of atomic and molecular systems, the goal of quantum control, requires exposing the system to an external perturbation to alter its state. The most widely applied approaches use controllable incident external radiation as the source of this perturbation. In this chapter we introduce some of the fundamental concepts of the interaction of radiation with matter. The treatment assumes a classical electromagnetic field interacting with a quantized molecule, and is intended as a summary of the relevant equations used in the early parts of this book. (A summary of the symbols used throughout the book is provided in the Appendix.) A detailed derivation of these equations, starting from fundamentals, is provided in Chapter 9. Further development, in terms of quantized electromagnetic fields, is discussed in Section 10.1.

Consider a material system comprising a set of particles of mass m_i and charge q_i at positions $\boldsymbol{r}_i$ that is interacting with an incident classical electric field $\boldsymbol{E}(\boldsymbol{r}, t)$. Here $\boldsymbol{r}$ denotes the spatial coordinates, and t denotes time. The Hamiltonian H of the system, at time t, is then given by

$$H(t) = H_M + H_{MR}(t) \, . \tag{1.1}$$

where H_M denotes the Hamiltonian of the material and $H_{MR}(t)$ describes its interaction with an incident external radiation field. The former is of the form

$$H_M = \sum_j \frac{-\hbar^2}{2m_j} \nabla_j^2 + V_C \, , \tag{1.2}$$

where ∇_j^2 is the Laplacian associated with the coordinates of the jth particle, and V_C is the Coulomb potential between the particles. The $H_{MR}(t)$ term is given below in Eq. (1.5).

Given the Hamiltonian $H(t)$, then, in accord with standard quantum mechanics [3], the dynamical evolution of the wave function $\Psi(t)$ describing the motion of the system in the presence of the field $\boldsymbol{E}(\boldsymbol{r}, t)$ is given by the solution to the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = H(t)\Psi(t) = \left[H_M + H_{MR}(t)\right] \Psi(t) \, . \tag{1.3}$$

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In general, $\boldsymbol{E}(\boldsymbol{r}, t)$ is comprised of modes that are described by plane waves with directions of propagation $\boldsymbol{k}$, unit vectors $\hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}}$ describing the polarizations, frequencies $\omega_{\boldsymbol{k}}$, and complex amplitudes $A_{\boldsymbol{k}}$.

Specifically,

$$\boldsymbol{E}(\boldsymbol{r}, t) = i \sum_{\boldsymbol{k}} k \hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}} \left\{ A_{\boldsymbol{k}} \exp\left(-i\omega_{\boldsymbol{k}} t + i\boldsymbol{k} \cdot \boldsymbol{r}\right) - A_{\boldsymbol{k}}^{*} \exp\left(i\omega_{\boldsymbol{k}} t - i\boldsymbol{k} \cdot \boldsymbol{r}\right) \right\} . \tag{1.4}$$

In the traditional case, where one can neglect the variation of the incident electric field over the size of the material, and assuming that the electric field propagates along the z direction, $H_{MR}(t)$ is given by

$$H_{MR}(t) = -\boldsymbol{d} \cdot \boldsymbol{E}(z, t) , \tag{1.5}$$

where $\boldsymbol{d}$ is the molecular dipole moment,

$$\boldsymbol{d} \equiv \sum_{j} q_j \boldsymbol{r}_j , \tag{1.6}$$

and where the center of mass of the material is positioned at z.

When considering a coherent *pulse* of light, it is necessary to superimpose a collection of plane waves, as in Eq. (1.4). We adopt the reasonable simplifying assumption that all the modes of the pulse propagate in the same (z) direction and that all the pulse modes have the same polarization direction $\hat{\boldsymbol{\epsilon}}$. We can therefore eliminate the integration over the $\hat{\boldsymbol{k}}$ directions and write Eq. (1.4) (in an infinite volume) as

$$\begin{aligned}\boldsymbol{E}(z, t) &= \hat{\boldsymbol{\epsilon}} \int_{0}^{\infty} d\omega \left\{ \epsilon(\omega) \exp\left[i\omega \left(\frac{z}{c} - t \right) \right] + \epsilon^{*}(\omega) \exp\left[-i\omega \left(\frac{z}{c} - t \right) \right] \right\} \\ &\equiv \boldsymbol{E}_{+}(\tau) + \boldsymbol{E}_{-}(\tau) \equiv \boldsymbol{E}(\tau) = \hat{\boldsymbol{\epsilon}} \int_{-\infty}^{\infty} d\omega \epsilon(\omega) \exp(-i\omega\tau) .\end{aligned} \tag{1.7}$$

Here, $\epsilon(\omega) \equiv ikA_k/c$, and τ is the so-called "retarded time",

$$\tau \equiv t - \frac{z}{c} . \tag{1.8}$$

Each mode amplitude in Eq. (1.7) is a complex number,

$$\epsilon(\omega) = |\epsilon(\omega)| \exp[i\phi(\omega)] , \tag{1.9}$$

where $\phi(\omega)$ are frequency-dependent phases. The fact that $\boldsymbol{E}(z, t)$ is real ensures that $\epsilon(-\omega) = \epsilon^{*}(\omega)$, and hence that

$$\phi(-\omega) = -\phi(\omega) , \quad |\epsilon(-\omega)| = |\epsilon(\omega)| . \tag{1.10}$$

As discussed in later chapters, the phase $\phi(\omega)$ plays a central role in coherent control theory. However, individual phase values depend on an (arbitrary) definition of the origin of time and space. Therefore only the relative phases, which are the only phase factors that can actually be measured, are of any consequence physically.

Equation (1.7) describes a pulse of *coherent* light, where $\boldsymbol{E}(z, t)$ is represented by an analytic function of time. In cases of partially coherent light, either the phase or amplitude acquires a random component and an analytic expression for $\boldsymbol{E}(z, t)$ no longer exists. Appropriate descriptions of partially incoherent light interacting with molecules are provided in Section 6.5.