

6. INTERACTION OF LIGHT AND MATTER

6.1. Introduction

One of the most important topics in time-dependent quantum mechanics is the description of spectroscopy, which refers to the study of matter through its interaction with electromagnetic radiation. Classically, light–matter interactions are a result of an oscillating electromagnetic field resonantly interacting with charged particles in the matter, most often bound electrons. We observe these processes either through changes to the light induced by the matter, such as absorption or emission of new light fields, or by light-induced changes to the matter, such as ionization and photochemistry. By studying such processes as a function of the control variables for the light field (amplitude, frequency, polarization, phase, etc.), we can deduce properties of the samples.

The term “spectroscopy” comes from the Latin “spectron” for *spirit* or *ghost* and the Greek “σκοπειν” for *to see*. These roots are telling because in molecular spectroscopy you use light to interrogate matter, but you actually never see the molecules, only their influence on the light. Different types of spectroscopy give you different perspectives. This indirect contact with the microscopic targets means that the interpretation of spectroscopy requires a model, whether it is stated or not. Modeling and laboratory practice of spectroscopy are dependent on one another, and spectroscopy is only as useful as its ability to distinguish different models. This makes an accurate theoretical description of the underlying physical process governing the interaction of light and matter important.

Quantum mechanically, we will treat spectroscopy as a perturbation induced by the light which acts to couple quantum states of the charged particles in the matter, as we have discussed earlier. Our starting point is to write a Hamiltonian for the light–matter interaction, which in the most general sense would be of the form

$$H = H_M + H_L + H_{LM} \quad (6.1)$$

Although the Hamiltonian for the matter may be time-dependent, we will treat the Hamiltonian for the matter H_M as 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 begin with a semiclassical treatment of the problem, which describes the matter quantum mechanically and the light field classically. We assume that a light field described by a time-dependent vector potential acts on the matter, but the matter does not influence the light. (Strictly, energy conservation requires that any change in energy of the matter be matched with an equal and opposite change in the light field.) For the moment, 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 for the system that is

$$\begin{aligned} H &\approx H_M + H_{LM}(t) \\ &= H_0 + V(t) \end{aligned} \quad (6.2)$$

which we can solve in the interaction picture. We will derive an explicit expression for the Hamiltonian H_{LM} in the Electric Dipole Approximation. Here, we will derive a Hamiltonian for the light–matter interaction, starting with the force experienced by a charged particle in an electromagnetic field, developing a classical Hamiltonian for this interaction, and then substituting quantum operators for the matter:

$$\begin{aligned} p &\rightarrow -i\hbar\hat{\nabla} \\ x &\rightarrow \hat{x} \end{aligned} \quad (6.3)$$

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

6.2. 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. Also, it is helpful to review this material in Jackson¹ or Cohen-Tannoudji et al.²

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

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.

gauge—that allows us to uniquely describe the wave. Choosing a gauge such that $\varphi = 0$ (Coulomb gauge) leads to a unique description of \bar{E} and \bar{B} :

$$-\bar{\nabla}^2 \bar{A}(\bar{r}, t) + \frac{1}{c^2} \frac{\partial^2 \bar{A}(\bar{r}, t)}{\partial t^2} = 0 \quad (6.4)$$

$$\bar{\nabla} \cdot \bar{A} = 0 \quad (6.5)$$

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

$$\bar{A}(\bar{r}, t) = A_0 \hat{\varepsilon} e^{i(\bar{k} \cdot \bar{r} - \omega t)} + A_0^* \hat{\varepsilon} e^{-i(\bar{k} \cdot \bar{r} - \omega t)} \quad (6.6)$$

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

$$k = nk_0 = \frac{n\omega_0}{c} = \frac{2\pi n}{\lambda_0} \quad (6.7)$$

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}

$$\begin{aligned} \bar{E} &= -\frac{\partial \bar{A}}{\partial t} \\ &= i\omega A_0 \hat{\varepsilon} \left(e^{i(\bar{k} \cdot \bar{r} - \omega t)} - e^{-i(\bar{k} \cdot \bar{r} - \omega t)} \right) \end{aligned} \quad (6.8)$$

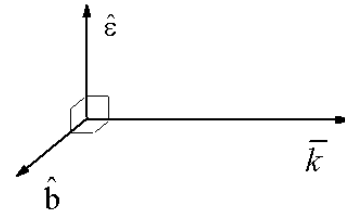
$$\begin{aligned} \bar{B} &= \bar{\nabla} \times \bar{A} \\ &= i(\bar{k} \times \hat{\varepsilon}) A_0 \left(e^{i(\bar{k} \cdot \bar{r} - \omega t)} - e^{-i(\bar{k} \cdot \bar{r} - \omega t)} \right) \end{aligned} \quad (6.9)$$

If we define a unit vector along the magnetic field polarization as $\hat{b} = (\bar{k} \times \hat{\varepsilon})/|\bar{k}| = \hat{k} \times \hat{\varepsilon}$, 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 eqs. (6.6) and (6.8) 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

$$\frac{1}{2} E_0 = i\omega A_0 \quad (6.10)$$

$$\frac{1}{2} B_0 = i|k| A_0 \quad (6.11)$$



then,

$$\bar{E}(\bar{r}, t) = |E_0| \hat{\epsilon} \sin(\bar{k} \cdot \bar{r} - \omega t) \quad (6.12)$$

$$\bar{B}(\bar{r}, t) = |B_0| \hat{b} \sin(\bar{k} \cdot \bar{r} - \omega t) \quad (6.13)$$

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

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

$$\bar{S} = \epsilon_0 c^2 \bar{E} \times \bar{B} \quad (6.14)$$

$$I = \langle \bar{S} \rangle = \frac{1}{2} \epsilon_0 c E_0^2 \quad (\text{W/m}^2) \quad (6.15)$$

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

$$U = \frac{I}{c} = \frac{1}{2} \epsilon_0 E_0^2 \quad (\text{J/m}^3) \quad (6.16)$$

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 force³ on a particle with charge q :

$$\bar{F} = q(\bar{E} + \bar{v} \times \bar{B}) \quad (6.17)$$

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

$$F_x = q(E_x + v_y B_z - v_z B_y) \quad (6.18)$$

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

$$F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt} \left(\frac{\partial U}{\partial v_x} \right) \quad (6.19)$$

Using the relationships that describe \bar{E} and \bar{B} in terms of \bar{A} and φ (eqs. (6.10) and (6.11), inserting into eq. (6.18), and working it into the form of eq. (6.19), we can show that

$$U = q\varphi - q\bar{v} \cdot \bar{A} \quad (6.20)$$

³ See Schatz and Ratner, pp. 82–83.

This is derived elsewhere⁴ and is readily confirmed by replacing it into eq. (6.19).

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

$$L = T - U \quad (6.21)$$

$$L = \frac{1}{2} m \bar{v}^2 + q \bar{v} \cdot \bar{A} - q\phi \quad (6.22)$$

The classical Hamiltonian is related to the Lagrangian as

$$\begin{aligned} H &= \bar{p} \cdot \bar{v} - L \\ &= \bar{p} \cdot \bar{v} - \frac{1}{2} m \bar{v}^2 - q \bar{v} \cdot \bar{A} - q\phi \end{aligned} \quad (6.23)$$

Recognizing
$$\bar{p} = \frac{\partial L}{\partial \bar{v}} = m \bar{v} + q \bar{A} \quad (6.24)$$

we write
$$\bar{v} = \frac{1}{m} (\bar{p} - q \bar{A}) \quad (6.25)$$

Now substituting eq. (6.25) into eq. (6.23), we have

$$H = \frac{1}{m} \bar{p} \cdot (\bar{p} - q \bar{A}) - \frac{1}{2m} (\bar{p} - q \bar{A})^2 - \frac{q}{m} (\bar{p} - q \bar{A}) \cdot \bar{A} + q\phi \quad (6.26)$$

$$H = \frac{1}{2m} [\bar{p} - q \bar{A}(\bar{r}, t)]^2 + q\phi(\bar{r}, t) \quad (6.27)$$

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

$$H_0 = \frac{\bar{p}^2}{2m} + V_0(\bar{r}) \quad (6.28)$$

and in the *presence* of the EM field,

$$H = \frac{1}{2m} (\bar{p} - q \bar{A}(\bar{r}, t))^2 + V_0(\bar{r}) \quad (6.29)$$

Expanding we obtain
$$H = H_0 - \frac{q}{2m} (\bar{p} \cdot \bar{A} + \bar{A} \cdot \bar{p}) + \frac{q^2}{2m} |\bar{A}(\bar{r}, t)|^2 \quad (6.30)$$

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.,

⁴ Cohen-Tannoudji et al. App. III, p. 1492.

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/cm², 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:

$$H = H_0 + V(t) \quad (6.31)$$

$$V(t) = \frac{q}{2m} (\bar{p} \cdot \bar{A} + \bar{A} \cdot \bar{p}) \quad (6.32)$$

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; Appendix III.
2. Jackson, J. D., *Classical Electrodynamics*. 2nd ed.; John Wiley and Sons: New York, 1975.
3. McHale, J. L., *Molecular Spectroscopy*. 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999.
4. Merzbacher, E., *Quantum Mechanics*. 3rd ed.; Wiley: New York, 1998.
5. Sakurai, J. J., *Modern Quantum Mechanics, Revised Edition*. Addison-Wesley: Reading, MA, 1994.
6. Schatz, G. C.; Ratner, M. A., *Quantum Mechanics in Chemistry*. Dover Publications: Mineola, NY, 2002; pp. 82-83.

6.3. 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:

$$\bar{p} = -i\hbar\bar{\nabla} \quad (6.33)$$

$$V(t) = \frac{i\hbar}{2m} q (\bar{\nabla} \cdot \bar{A} + \bar{A} \cdot \bar{\nabla}) \quad (6.34)$$

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

$$\begin{aligned} V(t) &= \frac{i\hbar q}{m} \bar{A} \cdot \bar{\nabla} \\ &= -\frac{q}{m} \bar{A} \cdot \hat{p} \end{aligned} \quad (6.35)$$

We can generalize eq. (6.35) for the case of multiple charged particles, as would be appropriate for interactions involving a molecular Hamiltonian:

$$V(t) = - \sum_j \frac{q_j}{m_j} \bar{A}(\bar{r}_j, t) \cdot \hat{p}_j \quad (6.36)$$

$$V(t) = - \sum_j \frac{q_j}{m_j} \left[A_0 \hat{\epsilon} \cdot \hat{p}_j e^{i(\bar{k} \cdot \bar{r}_j - \omega t)} + A_0^* \hat{\epsilon} \cdot \hat{p}_j^\dagger e^{-i(\bar{k} \cdot \bar{r}_j - \omega t)} \right] \quad (6.37)$$

Under most of the circumstances we will encounter, we can neglect the wave vector dependence of the interaction potential. This applies if the wavelength of the field is much larger than the dimensions of the molecules we are interrogating, i.e., $(\lambda \rightarrow \infty) (|k| \rightarrow 0)$. To see this, let's define r_0 as the center of mass of a molecule and expand about that position:

$$\begin{aligned} e^{i\bar{k} \cdot \bar{r}_i} &= e^{i\bar{k} \cdot \bar{r}_0} e^{i\bar{k} \cdot (\bar{r}_i - \bar{r}_0)} \\ &= e^{i\bar{k} \cdot \bar{r}_0} e^{i\bar{k} \cdot \delta \bar{r}_i} \end{aligned} \quad (6.38)$$

For interactions with UV, visible, and infrared radiation, wavelengths are measured in hundreds to thousands of nanometers. This is orders of magnitude larger than the dimensions that describe charge distributions in molecules ($\delta \bar{r}_i = \bar{r}_i - \bar{r}_0$). Under those circumstances $|k| \delta r_i \ll 1$, and setting $\bar{r}_0 = 0$ means that $e^{i\bar{k} \cdot \bar{r}} \rightarrow 1$. This is known as the electric dipole approximation. Implicit in this is also the statement that all molecules within a macroscopic volume experience an interaction with a spatially uniform, homogeneous electromagnetic field.

Certainly there are circumstances where the electric dipole approximation is poor. In the case where the wavelength of light is on the same scale as molecular dimensions, the light will now have to interact with spatially varying charge distributions, which will lead to scattering of the light and interferences between the scattering between different spatial regions. We will not concern ourselves with this limit further.

We also retain the spatial dependence for certain other types of light-matter interactions. For instance, we can expand eq. (6.38) as

$$e^{i\bar{k} \cdot \bar{r}_i} \approx e^{i\bar{k} \cdot \bar{r}_0} \left[1 + i\bar{k} \cdot (\bar{r}_i - \bar{r}_0) + \dots \right] \quad (6.39)$$

We retain the second term for quadrupole transitions: charge distribution interacting with gradient of electric field and magnetic dipole (Section 6.7).

Now, using $A_0 = iE_0/2\omega$, we write eq. (6.35) as

$$V(t) = \frac{-iqE_0}{2m\omega} \left[\hat{\epsilon} \cdot \hat{p} e^{-i\omega t} - \hat{\epsilon} \cdot \hat{p} e^{i\omega t} \right] \quad (6.40)$$

$$\begin{aligned} V(t) &= \frac{-qE_0}{m\omega} (\hat{\epsilon} \cdot \hat{p}) \sin \omega t \\ &= \frac{-q}{m\omega} (\bar{E}(t) \cdot \hat{p}) \end{aligned} \quad (6.41)$$

or for a collection of charged particles (molecules):

$$V(t) = - \left(\sum_j \frac{q_j}{m_j} (\hat{\epsilon} \cdot \hat{p}_j) \right) \frac{E_0}{\omega} \sin \omega t \quad (6.42)$$

This is the interaction Hamiltonian in the electric dipole approximation.

In eq. (6.39), the second term must be considered in certain cases, where variation in the vector potential over the distance scales of the molecule must be considered. This will be the case when one describes interactions with short wavelength radiation, such as x-rays. Then the scattering of radiation by electronic states of molecules and the interference between transmitted and scattered field are important. The second term is also retained for electric quadrupole transitions and magnetic dipole transitions, as described in the appendix in Section 6.7. Electric quadrupole transitions require a gradient of electric field across the molecule, and is generally an effect that is $\sim 10^{-3}$ of the electric dipole interaction.

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

$$w_{k\ell} = \frac{\pi}{2\hbar} |V_{k\ell}|^2 \left[\delta(E_k - E_\ell - \hbar\omega) + \delta(E_k - E_\ell + \hbar\omega) \right] \quad (6.43)$$

which depends on the matrix elements for the Hamiltonian in eq. (6.42). Note in first-order perturbation matrix element calculations one uses unperturbed wavefunctions. Thus, we evaluate the matrix elements of the electric dipole Hamiltonian using the eigenfunctions of H_0 :

$$V_{k\ell} = \langle k | V_0 | \ell \rangle = \frac{-qE_0}{m\omega} \langle k | \hat{\epsilon} \cdot \hat{p} | \ell \rangle \quad (6.44)$$

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

$$[\hat{r}, \hat{H}_0] = \frac{i\hbar\hat{p}}{m} \quad (6.45)$$

This expression gives

$$\begin{aligned} \langle k | \hat{p} | \ell \rangle &= \frac{m}{i\hbar} \langle k | \hat{r} \hat{H}_0 - \hat{H}_0 \hat{r} | \ell \rangle \\ &= \frac{m}{i\hbar} (\langle k | \hat{r} | \ell \rangle E_\ell - E_k \langle k | \hat{r} | \ell \rangle) \\ &= im\omega_{k\ell} \langle k | \hat{r} | \ell \rangle. \end{aligned} \quad (6.46)$$

So we have

$$V_{k\ell} = -iqE_0 \frac{\omega_{k\ell}}{\omega} \langle k | \hat{\boldsymbol{\varepsilon}} \cdot \vec{r} | \ell \rangle \quad (6.47)$$

or for many charged particles

$$V_{k\ell} = -iE_0 \frac{\omega_{k\ell}}{\omega} \langle k | \hat{\boldsymbol{\varepsilon}} \cdot \sum_j q_j \hat{\mathbf{r}}_j | \ell \rangle \quad (6.48)$$

The matrix element can be written in terms of the dipole operators, which describes the spatial distribution of charges,

$$\hat{\boldsymbol{\mu}} = \sum_j q_j \hat{\mathbf{r}}_j \quad (6.49)$$

We can see that it is the quantum analog of the classical dipole moment, which describes the distribution of charge density ρ in the molecule:

$$\vec{\mu} = \int d\vec{r} \vec{r} \rho(\vec{r}) \quad (6.50)$$

The strength of interaction between light and matter is given by the matrix element in the dipole operator,

$$\mu_{fi} \equiv \langle f | \vec{\mu} \cdot \hat{\boldsymbol{\varepsilon}} | i \rangle \quad (6.51)$$

which is known as the transition dipole moment. In order that we have absorption, the part $\langle f | \boldsymbol{\mu} | i \rangle$, which is a measure of change of charge distribution between $|f\rangle$ and $|i\rangle$, should be non-zero. In other words, the incident radiation has to induce a change in the charge distribution of matter to get an effective absorption rate. This matrix element is the basis of selection rules based on the symmetry of the matter charge eigenstates. The second part, namely the electric field polarization vector says that the electric field of the incident radiation field must project onto the matrix elements of the dipole moment between the final and initial states of the charge distribution.

Then the matrix elements in the electric dipole Hamiltonian are

$$V_{k\ell} = -iE_0 \frac{\omega_{k\ell}}{\omega} \mu_{kl} \quad (6.52)$$

This expression allows us to write in a simplified form the well-known interaction potential for a dipole in a field:

$$V(t) = -\vec{\mu} \cdot \vec{E}(t) \quad (6.53)$$

Note that we have reversed the order of terms because they commute.

This leads to an expression for the rate of transitions between quantum states induced by the light field:

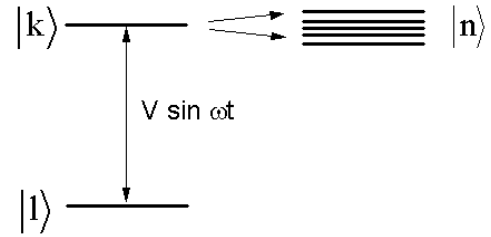
$$\begin{aligned}
w_{k\ell} &= \frac{\pi}{2\hbar} |E_0|^2 \frac{\omega_{k\ell}^2}{\omega^2} |\bar{\mu}_{k\ell}|^2 \left[\delta(E_k - E_\ell - \hbar\omega) + (E_k - E_\ell + \hbar\omega) \right] \\
&= \frac{\pi}{2\hbar^2} |E_0|^2 |\bar{\mu}_{k\ell}|^2 \left[\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right]
\end{aligned} \tag{6.54}$$

In essence, eq. (6.54) is an expression for the absorption and emission spectrum since the rate of transitions can be related to the power absorbed from or added to the light field. More generally, we would express the spectrum in terms of a sum over all possible initial and final states, the eigenstates of H_0 :

$$w_{fi} = \sum_{i,f} \frac{\pi}{\hbar^2} |E_0|^2 |\mu_{fi}|^2 \left[\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega) \right] \tag{6.55}$$

6.4. Relaxation and Line-broadening

Let's describe absorption to a state that is coupled to a continuum. What happens to the probability of absorption if the excited state decays exponentially?



We can start with the first-order expression

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{k\ell}t} V_{k\ell}(t) \tag{6.56}$$

where we make the approximation $b_\ell(t) \approx 1$. We can add irreversible relaxation to the description of b_k using our earlier expression for the relaxation of $b_k(t) = \exp[-\bar{w}_{nk}t/2 - i\Delta E_k t/\hbar]$. In this case, we will neglect the correction to the energy $\Delta E_k = 0$, so

$$\frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{i\omega_{k\ell}t} V_{k\ell}(t) - \frac{\bar{w}_{nk}}{2} b_k \tag{6.57}$$

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

$$\begin{aligned}
\frac{\partial}{\partial t} b_k &= \frac{-i}{\hbar} e^{i\omega_{k\ell}t} \sin \omega t V_{k\ell} - \frac{\bar{w}_{nk}}{2} b_k(t) \\
&= \frac{E_0 \omega_{k\ell}}{2i\hbar\omega} \left[e^{i(\omega_{k\ell}+\omega)t} - e^{i(\omega_{k\ell}-\omega)t} \right] \bar{\mu}_{k\ell} - \frac{\bar{w}_{nk}}{2} b_k(t)
\end{aligned} \tag{6.58}$$

The solution to the differential equation

$$\dot{y} + ay = b e^{i\alpha t} \tag{6.59}$$

is

$$y(t) = A e^{-at} + \frac{b e^{i\alpha t}}{a + i\alpha} \tag{6.60}$$

$$b_k(t) = A e^{-\bar{\omega}_{nk}t/2} + \frac{E_0 \bar{\mu}_{k\ell}}{2i\hbar} \left[\frac{e^{i(\omega_{k\ell} + \omega)t}}{\bar{\omega}_{nk}/2 + i(\omega_{k\ell} + \omega)} - \frac{e^{i(\omega_{k\ell} - \omega)t}}{\bar{\omega}_{nk}/2 + i(\omega_{k\ell} - \omega)} \right] \quad (6.61)$$

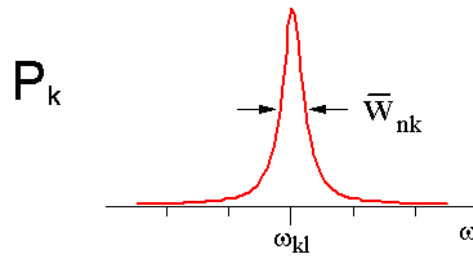
Let's look at absorption only, in the long time limit:

$$b_k(t) = \frac{E_0 \bar{\mu}_{k\ell}}{2\hbar} \left[\frac{e^{i(\omega_{k\ell} - \omega)t}}{\omega_{k\ell} - \omega - i\bar{\omega}_{nk}/2} \right] \quad (6.62)$$

For which the probability of transition to k is

$$P_k = |b_k|^2 = \frac{E_0^2 |\mu_{k\ell}|^2}{4\hbar^2} \frac{1}{(\omega_{k\ell} - \omega)^2 + \bar{\omega}_{nk}^2 / 4} \quad (6.63)$$

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



The FWHM line width gives the relaxation rate from k into the continuum n . Also the line width is related to the system rather than the manner in which we introduced the perturbation. The line width or line shape is an additional feature that we interpret in our spectra, and commonly originates from irreversible relaxation or other processes that destroy the coherence first set up by the light field.

6.5. Absorption Cross Section

The rate of absorption induced by a monochromatic electromagnetic field is

$$w_{k\ell}(\omega) = \frac{\pi}{2\hbar^2} |E_0(\omega)|^2 |\langle k | \hat{\epsilon} \cdot \bar{\mu} | \ell \rangle|^2 \delta(\omega_{k\ell} - \omega) \quad (6.64)$$

The rate is clearly dependent on the strength of the field. The variable that you can most easily measure is the intensity I , the energy flux through a unit area, which is the time-averaged value of the Poynting vector, S :

$$S = \epsilon_0 c^2 (\bar{E} \times \bar{B}) \quad (6.65)$$

$$I = \langle S \rangle = \frac{1}{2} \epsilon_0 c E_0^2 \quad (6.66)$$

Using this we can write

$$w_{k\ell} = \frac{4\pi}{3\epsilon_0 c \hbar^2} I(\omega) |\langle k | \bar{\mu} | \ell \rangle|^2 \delta(\omega_{k\ell} - \omega) \quad (6.67)$$

where I have also made use of the uniform distribution of polarizations applicable to an isotropic field: $|\bar{E}_0 \cdot \hat{x}| = |\bar{E}_0 \cdot \hat{y}| = |\bar{E}_0 \cdot \hat{z}| = \frac{1}{3} |E_0|^2$.

Now let's relate the rates of absorption to a quantity that is directly measured, an absorption cross section α :

$$\begin{aligned} \alpha &= \frac{\text{total energy absorbed per unit time}}{\text{total incident intensity (energy / unit time / area)}} \\ &= \frac{\hbar\omega w_{k\ell}}{I} \end{aligned} \quad (6.68)$$

Note α has units of cm^2 . The golden rule rate for absorption also gives the same rate for stimulated emission. Given two levels $|m\rangle$ and $|n\rangle$,

$$\begin{aligned} w_{nm} &= w_{mn} \\ \therefore (\alpha_A)_{nm} &= (\alpha_{SE})_{mn} \end{aligned} \quad (6.69)$$

We can now use a phenomenological approach to calculate the change in the intensity of incident light, I , due to absorption and stimulated emission passing through a sample of length L . Given that we have a thermal distribution of identical non-interacting particles with quantum states such that the level $|m\rangle$ is higher in energy than $|n\rangle$:

$$\frac{dI}{dx} = -N_n \alpha_A I + N_m \alpha_{SE} I \quad (6.70)$$

$$\frac{dI}{I} = -(N_n - N_m)\alpha dx \quad (6.71)$$

Here N_n and N_m are population of the upper and lower states, but expressed as population densities (cm^{-3}). Note that I and α are both functions of the frequency of the incident light. If N is the molecular density,

$$N_n = N \left(\frac{e^{-\beta E_n}}{Z} \right) \quad (6.72)$$

Integrating eq. (6.71) over a path length L , we have

$$\begin{aligned} T = \frac{I}{I_0} &= e^{-\Delta N \alpha L} \\ &\approx e^{-N \alpha L} \end{aligned} \quad (6.73)$$

We see that the transmission of light through the sample decays exponentially as a function of path length. $\Delta N = N_n - N_m$ is the thermal population difference between states. The second expression in eq. (6.73) comes from the high-frequency approximation applicable to optical spectroscopy. Equation (6.73) can also be written in terms of the familiar Beer–Lambert Law:

$$A = -\log \frac{I}{I_0} = \epsilon CL \quad (6.74)$$

where A is the absorbance and C is the sample concentration in $mol L^{-1}$, which is related to the number density via Avagadro's number N_A ,

$$C[mol L^{-1}] = \frac{N[cm^{-3}]}{1000 N_A} \quad (6.75)$$

In eq. (6.74), the characteristic molecular quantity that describes the sample's ability to absorb the light is ϵ , the molar decadic extinction coefficient, given in $L mol^{-1} cm^{-1}$. With these units, we see that we can equate ϵ with the cross section as

$$\epsilon = \frac{N_A \alpha}{2303} \quad (6.76)$$

In the context of sample absorption characteristics, our use of the variable α for cross section should not be confused with another use as an absorption coefficient with units of cm^{-1} that is equal to $N\alpha$ in eq. (6.73).

These relationships also allow us to obtain the magnitude of the transition dipole matrix element from absorption spectra by integrating over the absorption line shape.^{5,6}

$$\begin{aligned} |\mu_{if}|^2 &= \frac{6\epsilon_0\hbar^2 2303c}{N_A n} \int \frac{\epsilon(\nu)}{\nu} d\nu \\ &= (108.86 \text{ L mol}^{-1} \text{ cm}^{-1} \text{ D}^{-2})^{-1} \int \frac{\epsilon(\nu)}{\nu} d\nu \end{aligned} \quad (6.77)$$

Here the absorption line shape is expressed in molar decadic units and the frequency in wavenumbers.

Readings

1. Herzberg, G., *Molecular Spectra and Molecular Structure: Infrared and Raman of Polyatomic Molecules*. Prentice-Hall: New York, 1939; Vol. II, p. 261.
2. McHale, J. L., *Molecular Spectroscopy*. 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999.

⁵ McHale, J. L., *Molecular Spectroscopy*. 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999.

⁶ Herzberg, G., *Molecular Spectra and Molecular Structure: Infrared and Raman of Polyatomic Molecules*. Prentice-Hall: New York, 1939; Vol. II, p. 261.

6.6. Appendix: Review of Free Electromagnetic Field

Here we review the derivation of the vector potential for the plane wave in free space. We begin with Maxwell's equations (SI):

$$\bar{\nabla} \cdot \bar{B} = 0 \quad (6.78)$$

$$\bar{\nabla} \cdot \bar{E} = \rho / \epsilon_0 \quad (6.79)$$

$$\bar{\nabla} \times \bar{E} = -\frac{\partial \bar{B}}{\partial t} \quad (6.80)$$

$$\bar{\nabla} \times \bar{B} = \mu_0 \bar{J} + \epsilon_0 \mu_0 \frac{\partial \bar{E}}{\partial t} \quad (6.81)$$

Here the variables are: \bar{E} , electric field; \bar{B} , magnetic field; \bar{J} , current density; ρ , charge density; ϵ_0 , electrical permittivity; μ_0 , magnetic permittivity. We are interested in describing \bar{E} and \bar{B} in terms of a vector and scalar potential, \bar{A} and ϕ .

Next, let's review some basic properties of vectors and scalars. Generally, vector field \bar{F} assigns a vector to each point in space. The divergence of the field

$$\bar{\nabla} \cdot \bar{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} \quad (6.82)$$

is a scalar. For a scalar field ϕ , the gradient

$$\nabla \phi = \frac{\partial \phi}{\partial x} \hat{x} + \frac{\partial \phi}{\partial y} \hat{y} + \frac{\partial \phi}{\partial z} \hat{z} \quad (6.83)$$

is a vector for the rate of change at one point in space. Here $\hat{x}^2 + \hat{y}^2 + \hat{z}^2 = \hat{r}^2$ are unit vectors. Also, the curl

$$\bar{\nabla} \times \bar{F} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ F_x & F_y & F_z \end{vmatrix} \quad (6.84)$$

is a vector whose x , y , and z components are the circulation of the field about that component.

Some useful identities from vector calculus that we will use are

$$\bar{\nabla} \cdot (\bar{\nabla} \times \bar{F}) = 0 \quad (6.85)$$

$$\nabla \times (\nabla \phi) = 0 \quad (6.86)$$

$$\nabla \times (\bar{\nabla} \times \bar{F}) = \bar{\nabla} (\bar{\nabla} \cdot \bar{F}) - \bar{\nabla}^2 \bar{F} \quad (6.87)$$

We now introduce a vector potential $\bar{A}(\bar{r}, t)$ and a scalar potential $\varphi(\bar{r}, t)$, which we will relate to \bar{E} and \bar{B} . Since $\bar{\nabla} \cdot \bar{B} = 0$ and $\bar{\nabla} \cdot (\bar{\nabla} \times \bar{A}) = 0$, we can immediately relate the vector potential and magnetic field

$$\bar{B} = \bar{\nabla} \times \bar{A} \quad (6.88)$$

Inserting this into eq. (6.80) and rewriting, we can relate the electric field and vector potential:

$$\bar{\nabla} \times \left[\bar{E} + \frac{\partial \bar{A}}{\partial t} \right] = 0 \quad (6.89)$$

Comparing eqs. (6.89) and (6.86) allows us to state that a scalar product exists with

$$\bar{E} = \frac{\partial \bar{A}}{\partial t} - \nabla \varphi \quad (6.90)$$

So summarizing our results, we see that the potentials \bar{A} and φ determine the fields \bar{B} and \bar{E} :

$$\bar{B}(\bar{r}, t) = \bar{\nabla} \times \bar{A}(\bar{r}, t) \quad (6.91)$$

$$\bar{E}(\bar{r}, t) = -\bar{\nabla} \varphi(\bar{r}, t) - \frac{\partial}{\partial t} \bar{A}(\bar{r}, t) \quad (6.92)$$

We are interested in determining the classical wave equation for \bar{A} and φ . Using eq. (6.91), differentiating eq. (6.92), and substituting into eq. (6.81), we obtain

$$\bar{\nabla} \times (\bar{\nabla} \times \bar{A}) + \epsilon_0 \mu_0 \left(\frac{\partial^2 \bar{A}}{\partial t^2} + \bar{\nabla} \frac{\partial \varphi}{\partial t} \right) = \mu_0 \bar{J} \quad (6.93)$$

Using eq. (6.87),

$$\left[-\bar{\nabla}^2 \bar{A} + \epsilon_0 \mu_0 \frac{\partial^2 \bar{A}}{\partial t^2} \right] + \bar{\nabla} \left(\bar{\nabla} \cdot \bar{A} + \epsilon_0 \mu_0 \frac{\partial \varphi}{\partial t} \right) = \bar{\mu}_0 \bar{J} \quad (6.94)$$

From eq. (6.90), we have

$$\bar{\nabla} \cdot \bar{E} = -\frac{\partial \bar{\nabla} \cdot \bar{A}}{\partial t} - \bar{\nabla}^2 \varphi \quad (6.95)$$

and using eq. (6.79),

$$\frac{-\partial \bar{\nabla} \cdot \bar{A}}{\partial t} - \bar{\nabla}^2 \varphi = \rho / \epsilon_0 \quad (6.96)$$

Notice from eqs. (6.91) and (6.92) that we only need to specify four field components (A_x, A_y, A_z, φ) to determine all six \bar{E} and \bar{B} components. But \bar{E} and \bar{B} do not uniquely determine \bar{A} and φ . So we can construct \bar{A} and φ in any number of ways without changing \bar{E} and \bar{B} . Notice that if we change \bar{A} by adding $\bar{\nabla} \chi$ where χ is any function of \bar{r} and t , this will not change \bar{B} ($\nabla \times (\nabla \cdot B) = 0$). It will change E by $(-\frac{\partial}{\partial t} \bar{\nabla} \chi)$, but we can change φ to

$\varphi' = \varphi - (\partial\chi/\partial t)$. Then \bar{E} and \bar{B} will both be unchanged. This property of changing representation (gauge) without changing \bar{E} and \bar{B} is gauge invariance. We can define a gauge transformation with

$$\bar{A}'(\bar{r}, t) = \bar{A}(\bar{r}, t) + \bar{\nabla} \cdot \chi(\bar{r}, t) \quad (6.97)$$

$$\varphi'(\bar{r}, t) = \varphi(\bar{r}, t) - \frac{\partial}{\partial t} \chi(\bar{r}, t) \quad (6.98)$$

Up to this point, A' and φ' are undetermined. Let's choose a χ such that:

$$\bar{\nabla} \cdot \bar{A} + \varepsilon_0 \mu_0 \frac{\partial \varphi}{\partial t} = 0 \quad (6.99)$$

which is known as the Lorentz condition. Then from eq. (6.93):

$$-\nabla^2 \bar{A} + \varepsilon_0 \mu_0 \frac{\partial^2 \bar{A}}{\partial t^2} = \mu_0 \bar{J} \quad (6.100)$$

The right hand side of this equation can be set to zero when no currents are present.

From eq. (6.96), we have:

$$\varepsilon_0 \mu_0 \frac{\partial^2 \varphi}{\partial t^2} - \nabla^2 \varphi = \frac{\rho}{\varepsilon_0} \quad (6.101)$$

Equations (6.100) and (6.101) are wave equations for \bar{A} and φ . Within the Lorentz gauge, we can still arbitrarily add another χ ; it must only satisfy eq. (6.99). If we substitute eqs. (6.97) and (6.98) into eq. (6.101), we see

$$\nabla^2 \chi - \varepsilon_0 \mu_0 \frac{\partial^2 \chi}{\partial t^2} = 0 \quad (6.102)$$

So we can make further choices/constraints on \bar{A} and φ as long as it obeys eq. (6.102).

We now choose $\varphi = 0$, the Coulomb gauge, and from eq. (6.99) we see

$$\bar{\nabla} \cdot \bar{A} = 0 \quad (6.103)$$

So the wave equation for our vector potential when the field is far currents ($J = 0$) is

$$-\bar{\nabla}^2 \bar{A} + \varepsilon_0 \mu_0 \frac{\partial^2 \bar{A}}{\partial t^2} = 0 \quad (6.104)$$

The solutions to this equation are plane waves:

$$\bar{A} = \bar{A}_0 \sin(\omega t - \bar{k} \cdot \bar{r} + \alpha) \quad (6.105)$$

where α is a phase. \bar{k} is the wave vector which points along the direction of propagation and has a magnitude

$$k^2 = \omega^2 \mu_0 \varepsilon_0 = \omega^2 / c^2 \quad (6.106)$$

Since $\bar{\nabla} \cdot \bar{A} = 0$ (eq. (6.103)), $-\bar{k} \cdot \bar{A}_0 \cos(\omega t - \bar{k} \cdot \bar{r} + \alpha) = 0$, therefore

$$\bar{k} \cdot \bar{A}_0 = 0 \quad (6.107)$$

So the direction of the vector potential is perpendicular to the direction of wave propagation ($\bar{k} \perp \bar{A}_0$). From eqs. (6.91) and (6.92), we see that for $\varphi = 0$:

$$\bar{E} = -\frac{\partial \bar{A}}{\partial t} = -\omega \bar{A}_0 \cos(\omega t - \bar{k} \cdot \bar{r} + \alpha) \quad (6.108)$$

$$\bar{B} = \bar{\nabla} \times \bar{A} = -(\bar{k} \times \bar{A}_0) \cos(\omega t - \bar{k} \cdot \bar{r} + \alpha) \quad (6.109)$$

Here the electric field is parallel with the vector potential, and the magnetic field is perpendicular to the electric field and the direction of propagation ($\bar{k} \perp \bar{E} \perp \bar{B}$). The Poynting vector describing the direction of energy propagation is $\bar{S} = \epsilon_0 c^2 (\bar{E} \times \bar{B})$ and its average value, the intensity, is $I = \langle S \rangle = \frac{1}{2} \epsilon_0 c E_0^2$.

6.7. Appendix: Magnetic Dipole and Electric Quadrupole Transitions⁷

The second term in the expansion in eq. (6.39) leads to magnetic dipole and electric quadrupole transitions, which we will describe here. The interaction potential is

$$V^{(2)}(t) = -\frac{q}{m} \left[iA_0 (\hat{\epsilon} \cdot \bar{p})(\bar{k} \cdot \bar{r}) e^{-i\omega t} - iA_0^* (\hat{\epsilon} \cdot \bar{p})(\bar{k} \cdot \bar{r}) e^{i\omega t} \right] \quad (6.110)$$

We can use the identity

$$\begin{aligned} (\hat{\epsilon} \cdot \bar{p})(\bar{k} \cdot \bar{r}) &= \hat{\epsilon} \cdot (\bar{p}\bar{r}) \cdot \bar{k} \\ &= \frac{1}{2} \hat{\epsilon} \cdot (\bar{p}\bar{r} - \bar{r}\bar{p}) \bar{k} + \frac{1}{2} \hat{\epsilon} \cdot (\bar{p}\bar{r} + \bar{r}\bar{p}) \bar{k} \end{aligned} \quad (6.111)$$

to separate $V(t)$ into two distinct light-matter interaction terms:

$$V^{(2)}(t) = V_{mag}^{(2)}(t) + V_Q^{(2)}(t) \quad (6.112)$$

$$V_{mag}^{(2)}(t) = \frac{-iq}{2m} \hat{\epsilon} \cdot (\bar{p}\bar{r} - \bar{r}\bar{p}) \cdot \bar{k} (A_0 e^{-i\omega t} + A_0^* e^{i\omega t}) \quad (6.113)$$

$$V_Q^{(2)}(t) = \frac{-iq}{2m} \hat{\epsilon} \cdot (\bar{p}\bar{r} + \bar{r}\bar{p}) \cdot \bar{k} (A_0 e^{-i\omega t} + A_0^* e^{i\omega t}) \quad (6.114)$$

where the first $V_{mag}^{(2)}$ gives rise to magnetic dipole transitions, and the second $V_Q^{(2)}$ leads to electric quadrupole transitions.

⁷ Baym, G., *Lectures On Quantum Mechanics*. Westview Press: New York, 1990.

For the notation above, $\overline{p\mathbf{r}}$ represents an outer product (tensor product $\overline{p} \cdot \overline{\mathbf{r}}$), so that

$$\hat{\boldsymbol{\varepsilon}} \cdot (\overline{p\mathbf{r}}) \cdot \overline{\mathbf{k}} = \begin{pmatrix} \varepsilon_x & \varepsilon_y & \varepsilon_z \end{pmatrix} \begin{pmatrix} p_x r_x & p_x r_y & p_x r_z \\ p_y r_x & p_y r_y & p_y r_z \\ p_z r_x & p_z r_y & p_z r_z \end{pmatrix} \begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix} \quad (6.115)$$

This expression is meant to imply that the component of r that lies along k can influence the magnitude of p along $\boldsymbol{\varepsilon}$. Alternatively this term could be written $\sum_{a,b=x,y,z} \varepsilon_a (p_a r_b) k_b$.

These interaction potentials can be simplified and made more intuitive. Considering first eq. (6.113), we can use the vector identity $(\overline{A} \times \overline{B}) \cdot (\overline{C} \times \overline{D}) = (\overline{A} \times \overline{C}) \cdot (\overline{B} \times \overline{D}) - (\overline{A} \times \overline{D}) \cdot (\overline{B} \times \overline{C})$ to show

$$\begin{aligned} \frac{1}{2} \hat{\boldsymbol{\varepsilon}} \cdot (\overline{p\mathbf{r}} - \overline{\mathbf{r}p}) \cdot \overline{\mathbf{k}} &= \frac{1}{2} [(\hat{\boldsymbol{\varepsilon}} \cdot \overline{p})(\overline{\mathbf{r}} \cdot \overline{\mathbf{k}}) - (\hat{\boldsymbol{\varepsilon}} \cdot \overline{\mathbf{r}})(\overline{p} \cdot \overline{\mathbf{k}})] = \frac{1}{2} [(\overline{\mathbf{k}} \cdot \hat{\boldsymbol{\varepsilon}}) \cdot (\overline{\mathbf{r}} \times \overline{p})] \\ &= \frac{1}{2} (\overline{\mathbf{k}} \times \hat{\boldsymbol{\varepsilon}}) \cdot \overline{\mathbf{L}} \end{aligned} \quad (6.116)$$

For electronic spectroscopy, $\overline{\mathbf{L}}$ is the orbital angular momentum. Since the vector $\overline{\mathbf{k}} \times \hat{\boldsymbol{\varepsilon}}$ describes the direction of the magnetic field $\overline{\mathbf{B}}$, and since $A_0 = B_0/2ik$,

$$V_{md}^{(2)}(t) = \frac{-q}{2m} \overline{\mathbf{B}}(t) \cdot \overline{\mathbf{L}} \quad \overline{\mathbf{B}}(t) = \overline{B}_0 \cos \omega t \quad (6.117)$$

$\overline{\mathbf{B}} \cdot \overline{\mathbf{L}}$ more generally is $\overline{\mathbf{B}} \cdot (\overline{\mathbf{L}} + 2\overline{\mathbf{S}})$ when considering the spin degrees of freedom. In the case of an electron,

$$\frac{q\overline{\mathbf{L}}}{m} = \frac{2c}{\hbar} \beta \overline{\mathbf{L}} = \frac{2c}{\hbar} \overline{\boldsymbol{\mu}}_{mag} \quad (6.118)$$

where the Bohr magneton $\beta = \sum_i e\hbar/2m_i c$, and $\overline{\boldsymbol{\mu}}_{mag} = \beta \overline{\mathbf{L}}$ is the magnetic dipole operator. So we have the form for the magnetic dipole interaction

$$V_{mag}^{(2)}(t) = -\frac{c}{\hbar} \overline{\mathbf{B}}(t) \cdot \overline{\boldsymbol{\mu}}_{mag} \quad (6.119)$$

For electric quadrupole transitions, one can simplify eq. (6.114) by evaluating matrix elements for the operator $(\overline{p\mathbf{r}} + \overline{\mathbf{r}p})$. Using the identity eq. (6.45), we can show

$$\overline{p\mathbf{r}} + \overline{\mathbf{r}p} = \frac{im}{\hbar} [[H_0, \overline{\mathbf{r}}] \overline{\mathbf{r}} - \overline{\mathbf{r}} [\overline{\mathbf{r}}, H_0]] = \frac{-im}{\hbar} [\overline{\mathbf{r}} \overline{\mathbf{r}}, H_0] \quad (6.120)$$

and

$$V_Q^{(2)}(t) = \frac{-q}{2\hbar} \hat{\boldsymbol{\varepsilon}} \cdot [\overline{\mathbf{r}} \overline{\mathbf{r}}, H_0] \cdot \overline{\mathbf{k}} (A_0 e^{-i\omega t} + A_0^* e^{i\omega t}) \quad (6.121)$$

Here $\overline{\mathbf{r}} \overline{\mathbf{r}}$ is an outer product of vectors. For a system of many charges (i), we define the quadrupole moment, a traceless second rank tensor

$$\begin{aligned}\bar{\bar{Q}} &= \sum_i q_i \bar{r} \otimes \bar{r} \\ Q_{mn} &= \sum_i q_i (3r_{mi} \cdot r_{ni} - r_i^2 \delta_{mn}) \quad m, n = x, y, z\end{aligned}\tag{6.122}$$

Now, using $A_0 = E_0/2i\omega$, eq. (6.121) becomes

$$V(t) = -\frac{1}{2i\hbar\omega} \bar{E}(t) \cdot \left[\bar{\bar{Q}}, H_0 \right] \cdot \hat{k} \quad \bar{E}(t) = \bar{E}_0 \cos \omega t\tag{6.123}$$

Since the matrix element $\langle k | [Q, H_0] | \ell \rangle = \hbar\omega_{k\ell} \bar{\bar{Q}}_{k\ell}$, we can write the electric quadrupole transition moment as

$$\begin{aligned}V_{k\ell} &= \frac{iE_0\omega_{k\ell}}{2\omega} \langle k | \hat{\epsilon} \cdot \bar{\bar{Q}} \cdot \hat{k} | \ell \rangle \\ &= \frac{iE_0\omega_{k\ell}}{2\omega} \bar{\bar{Q}}_{k\ell}\end{aligned}\tag{6.124}$$