

Chapter 8

Light emission and optical interactions in nanoscale environments

The scope of this chapter is to discuss optical interactions between nanoscale systems and the properties of the emitted radiation. This is different to Chapter ?? where we considered the focusing and confinement of free propagating radiation. To link the two topics it is also necessary to understand how focused light interacts with nanoscale matter. This is a difficult task since it depends on the particular material properties, the shape of the investigated objects and also on the strength of interaction. Nevertheless, there are issues that can be discussed from a more or less general point of view.

At the heart of nano-optics are light-matter interactions on the nanometer scale. Optical interactions with nanoscale matter are encountered in various fields of research. For example, the activity of proteins and other macromolecules is followed by optical techniques, optically excited single molecules are used to probe their nano-environment and optical interactions with semiconductor nanostructures (quantum wells/wires/dots) are actively investigated because of their technological promise as nanocomposite materials or quantum coherent devices. Furthermore, various nanometric structures are encountered in near-field optics as tiny light sources.

To rigorously understand light-matter interactions we need to invoke quantum electrodynamics (QED). There are many textbooks that provide a good understanding of optical interactions with atoms or molecules and we especially recommend the books in Refs. [1-3]. Since nanometer scale structures are often too complex to be solved rigorously by QED we prefer to stick to classical theory and invoke the results of QED in a phenomenological way. Of course, the results obtained in this way have to be validated, but as long as there is no experimental contradiction we are save to

use this approach. A classical description is often more intuitive because of its simpler formalism but also because it is closer to our perception.

8.1 The multipole expansion

In this section we will consider an arbitrary ‘piece of matter’ which is small compared to the wavelength of light and which we will designate by *particle*. Although small compared to the wavelength, this particle consists of many atoms or molecules. On a macroscopic scale the charge density ρ and current density \mathbf{j} can be treated as continuous functions of position. However, atoms and molecules are made of discrete charges which are spatially separated. Thus, the microscopic structure of matter is not considered in the macroscopic Maxwell equations. The macroscopic fields are local spatial averages over microscopic fields.

In order to derive the potential energy for a microscopic system we have to give up the definitions of the electric displacement \mathbf{D} and the magnetic field \mathbf{H} and consider only the field vectors \mathbf{E} and \mathbf{B} in the empty space between a set of discrete charges q_n . We thus replace $\mathbf{D} = \epsilon_o \mathbf{E}$ and $\mathbf{B} = \mu_o \mathbf{H}$ in Maxwell’s equations [c.f. Eqs. (??)- (??)] and set

$$\rho(\mathbf{r}) = \sum_n q_n \delta[\mathbf{r} - \mathbf{r}_n], \quad (8.1)$$

$$\mathbf{j}(\mathbf{r}) = \sum_n q_n \dot{\mathbf{r}}_n \delta[\mathbf{r} - \mathbf{r}_n], \quad (8.2)$$

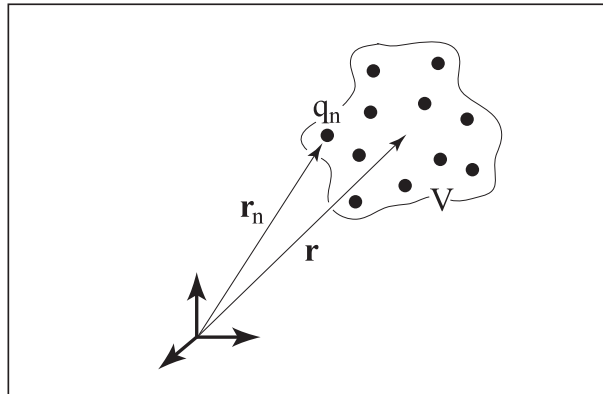


Figure 8.1: In the microscopic picture, optical radiation interacts with the discrete charges q_n of matter. The collective response of the charges with coordinates \mathbf{r}_n can be described by a multipole expansion with origin \mathbf{r} .

where \mathbf{r}_n denotes the position vector of the n-th charge and $\dot{\mathbf{r}}_n$ its velocity. The total charge and current of the particle is obtained by a volume integration over ρ and \mathbf{j} .

To derive the polarization and magnetization of the charge distribution we consider the total current density as defined in Eq. (??)

$$\mathbf{j} = \frac{d\mathbf{P}}{dt} + \nabla \times \mathbf{M} . \quad (8.3)$$

We ignored the contribution of the source current \mathbf{j}_s which generates the incident field \mathbf{E}_{inc} since it is not part of the considered particle. Furthermore, we incorporated the conduction current \mathbf{j}_c into the polarization current. To solve for \mathbf{P} we apply the operator $\nabla \cdot$ to both sides of Eq. (8.3). The last term on the right side vanishes because of $\nabla \cdot \nabla \times = 0$ and the term on the left can be related to the time derivative of the charge density through the continuity equation for charge (??). We then obtain

$$\rho = -\nabla \cdot \mathbf{P} . \quad (8.4)$$

If the particle is not charge neutral we need to add the net charge density to the right side. Using Eq. (8.1) for the charge density it is possible to solve for \mathbf{P} as [1]

$$\mathbf{P}(\mathbf{r}) = \sum_n q_n \mathbf{r}_n \int_0^1 \delta[\mathbf{r} - s\mathbf{r}_n] ds . \quad (8.5)$$

Together with the current density in Eq. (8.2) this expression can be introduced into Eq. (8.3). It is then possible to solve for \mathbf{M} as [1]

$$\mathbf{M}(\mathbf{r}) = \sum_n q_n \mathbf{r}_n \times \dot{\mathbf{r}}_n \int_0^1 s \delta[\mathbf{r} - s\mathbf{r}_n] ds . \quad (8.6)$$

To calculate the potential energy of the particle in the incident field we first consider fixed charges, i.e. the charge distribution is not induced by the incident field. Instead, the charge distribution is determined by the atomic and interatomic potentials. Of course, the particle is polarizable but for the moment we consider this to be a secondary effect. The important point is that on a microscopic scale the particle does have a permanent polarization and magnetization. On a macroscopic scale it can lose this permanent magnetization and polarization because the microscopic properties get averaged out. Thus, the importance of permanent polarization and magnetization depends on the size and properties of the particle. This is what makes the mesoscopic size range so challenging.

We now consider the interaction between a discrete charge distribution and an electromagnetic field. The incident field in the absence of the charge distribution is denoted as \mathbf{E}_{inc} . The electric potential energy of the *permanent* microscopic charge distribution is determined as [4]

$$V_E = - \int_V \mathbf{P} \cdot \mathbf{E}_{inc} dV = - \sum_n q_n \int_0^1 \mathbf{r}_n \cdot \mathbf{E}_{inc}(s\mathbf{r}_n) ds . \quad (8.7)$$

Next, we expand the electric field \mathbf{E}_{inc} in a Taylor series with origin at the center of the particle. For convenience we choose this origin at $\mathbf{r}=0$ and obtain

$$\mathbf{E}_{inc}(s\mathbf{r}_n) = \mathbf{E}_{inc}(0) + [s\mathbf{r}_n \cdot \nabla] \mathbf{E}_{inc}(0) + \frac{1}{2!} [s\mathbf{r}_n \cdot \nabla]^2 \mathbf{E}_{inc}(0) + \dots \quad (8.8)$$

This expansion can now be inserted into Eq. (8.7) and the integration over s can be carried out. Then, the electrical potential energy expressed in terms of the multipole moments of the charges becomes

$$V_E = -\sum_n q_n \mathbf{r}_n \cdot \mathbf{E}_{inc}(0) - \sum_n \frac{q_n}{2!} \mathbf{r}_n \cdot [\mathbf{r}_n \cdot \nabla] \mathbf{E}_{inc}(0) - \sum_n \frac{q_n}{3!} \mathbf{r}_n \cdot [\mathbf{r}_n \cdot \nabla]^2 \mathbf{E}_{inc}(0) - \dots \quad (8.9)$$

The first term is recognized as the *electric dipole interaction*

$$V_E^{(1)} = -\boldsymbol{\mu} \cdot \mathbf{E}_{inc}(0), \quad (8.10)$$

with the electric dipole moment defined as

$$\boldsymbol{\mu} = \sum_n q_n \mathbf{r}_n. \quad (8.11)$$

The next higher term in Eq. (8.9) is the *electric quadrupole interaction* which can be written as

$$V_E^{(2)} = -[\overset{\leftrightarrow}{\mathbf{Q}} \nabla] \cdot \mathbf{E}_{inc}(0), \quad (8.12)$$

with the electric quadrupole moment defined as

$$\overset{\leftrightarrow}{\mathbf{Q}} = \frac{1}{2} \sum_n q_n \mathbf{r}_n \mathbf{r}_n, \quad (8.13)$$

where $\mathbf{r}_n \mathbf{r}_n$ denotes the outer product. Therefore, $\overset{\leftrightarrow}{\mathbf{Q}}$ becomes a tensor of rank two.* Since $\nabla \cdot \mathbf{E}_{inc} = 0$ we can subtract any multiple of $\nabla \cdot \mathbf{E}_{inc}$ from Eq. (8.12). We can therefore rewrite Eq. (8.12) as

$$V_E^{(2)} = -\frac{1}{2} [(\overset{\leftrightarrow}{\mathbf{Q}} - A \bar{\mathbf{I}}) \nabla] \cdot \mathbf{E}_{inc}(0), \quad (8.14)$$

with an arbitrary constant A which commonly is chosen as $A = (1/3) |\mathbf{r}_n|^2$ because it generates a traceless quadrupole moment. Thus, we can also define the quadrupole moment as

$$\overset{\leftrightarrow}{\mathbf{Q}} = \frac{1}{2} \sum_n q_n \left[\mathbf{r}_n \mathbf{r}_n - \frac{\bar{\mathbf{I}}}{3} |\mathbf{r}_n|^2 \right]. \quad (8.15)$$

We avoid writing down the next higher multipole orders but we note that the rank of every next higher multipole increases by one.

*If we denote the cartesian components of \mathbf{r}_n by (x_{n1}, x_{n2}, x_{n3}) we can write Eq. (8.12) as $V_E^{(2)} = -(1/2) \sum_{i,j} [\sum_n q_n x_{ni} x_{nj}] [\partial/\partial x_i E_j(0)]$.

The dipole interaction is determined by the electric field at the center of the charge distribution whereas the quadrupole interaction is defined by the electric field gradients at the center. Thus, if the electric field is sufficiently homogeneous over the dimensions of the particle, the quadrupole interaction vanishes. This is why in small systems of charge, such as atoms or molecules, often only the dipole interaction is considered. This *dipole approximation* leads to the standard selection rules encountered in optical spectroscopy. However, the dipole approximation is not necessarily sufficient for nanoscale particles because of the larger size compared to an atom. Furthermore, if the particle interacts with an optical near-field it will experience strong field gradients. This increases the importance of the quadrupole interaction and modifies the standard selection rules. Thus, the strong field gradients encountered in near-field optics have the potential to excite usually forbidden transitions in larger quantum systems and thus extend the capabilities of optical spectroscopy.

A similar multipole expansion can be performed for the magnetic potential energy V_M . The lowest order term is the *magnetic dipole interaction*

$$V_M^{(1)} = -\mathbf{m}_d \cdot \mathbf{E}_{inc}(0) , \quad (8.16)$$

with the magnetic dipole moment defined as

$$\mathbf{m}_d = \sum_n (q_n/2m_n) \mathbf{r}_n \times (m_n \dot{\mathbf{r}}_n) . \quad (8.17)$$

The magnetic moment is often expressed in terms of the angular momenta $\mathbf{I}_n = m_n \mathbf{r}_n \times \dot{\mathbf{r}}_n$, where m_n denotes the mass of the n-th particle. We avoid deriving higher order magnetic multipole terms since the procedure is analogous to the electric case.

So far we considered the polarization and magnetization of a charge distribution that is *not* affected by the incident electromagnetic field. However, it is clear that the incident radiation will act on the charges and displace them from their unperturbed positions. This gives rise to an induced polarization and magnetization. The interaction of the incident field \mathbf{E}_{inc} with the particle causes a change $d\mathbf{P}$ in the polarization \mathbf{P} . The change in the electric potential energy dV_E due to this interaction is

$$dV_E = - \int_V \mathbf{E}_{inc} \cdot d\mathbf{P} dV . \quad (8.18)$$

To calculate the total induced electric potential energy $V_{E,ind}$ we have to integrate dV_E over the polarization range $\mathbf{P}_p \dots \mathbf{P}_{p+i}$, where \mathbf{P}_p and \mathbf{P}_{p+i} are the initial value and final values of the polarization. We now assume that the interaction between the field and the particle is *linear* so we can write $\mathbf{P} = \varepsilon_o \chi \mathbf{E}_{inc}$. In this case we find for the total differential $d(\mathbf{P} \cdot \mathbf{E}_{inc})$

$$d(\mathbf{P} \cdot \mathbf{E}_{inc}) = \mathbf{E}_{inc} \cdot d\mathbf{P} + \mathbf{P} \cdot d\mathbf{E}_{inc} = 2 \mathbf{E}_{inc} \cdot d\mathbf{P} , \quad (8.19)$$

and the induced potential energy becomes

$$V_{E,ind} = -\frac{1}{2} \int_V \left[\int_{\mathbf{P}_p}^{\mathbf{P}_{p+i}} d(\mathbf{P} \cdot \mathbf{E}_{inc}) \right] dV . \quad (8.20)$$

Using $\mathbf{P}_{p+i} = \mathbf{P}_p + \mathbf{P}_i$ we finally obtain

$$V_{E,ind} = -\frac{1}{2} \int_V \mathbf{P}_i \cdot \mathbf{E}_{inc} dV . \quad (8.21)$$

This result states that the induced potential energy is smaller than the permanent potential energy by a factor 1/2. The other 1/2 portion is related to the work needed to build up the polarization from zero to \mathbf{P}_i . For $\mathbf{P}_i > 0$ regions of high electric fields cause an attracting force on polarizable objects (laser tweezers).

A similar derivation can be performed for the induced magnetization \mathbf{M}_i and its associated energy. The interesting outcome is that objects with $\mathbf{M}_i > 0$ are repelled from regions of high magnetic fields. This finding underlies the phenomenon of eddy-current damping. However, at optical frequencies induced magnetizations are practically zero.

8.2 The classical particle-field Hamiltonian

So far we have been concerned with the potential energy of a particle in an external electromagnetic field. However, for a fundamental understanding of the interaction of a particle with the electromagnetic field we require to know the total energy of the system consisting of particle and field. This energy remains conserved; the particle can borrow energy from the field (absorption) or it can donate energy to it (emission). The total energy corresponds to the classical Hamiltonian H which constitutes the Hamiltonian operator \hat{H} encountered in quantum mechanics. For particles consisting of many charges, the Hamiltonian soon becomes a very complex function: it depends on the mutual interaction between the charges, their kinetic energies and the exchange of energy with the external field.

To understand the interaction between a particle and an electromagnetic field we first consider a single point-like particle with mass m and charge q . Later we generalize the situation to systems consisting of multiple charges and with finite size. The Hamiltonian for a single charge in an electromagnetic field is found by first deriving a Lagrangian function $L(\mathbf{r}, \dot{\mathbf{r}})$ which satisfies the Lagrange-Euler equation

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) - \frac{\partial L}{\partial q} = 0, \quad q = x, y, z . \quad (8.22)$$

Here, $\mathbf{q} = (x, y, z)$ and $\dot{\mathbf{q}} = (\dot{x}, \dot{y}, \dot{z})$ denote the coordinates of the charge and the velocities, respectively.[†] To determine L , we first consider the (nonrelativistic) equation of motion for the charge

$$\mathbf{F} = \frac{d}{dt} [m\dot{\mathbf{r}}] = q(\mathbf{E} + \dot{\mathbf{r}} \times \mathbf{B}) , \quad (8.23)$$

and replace \mathbf{E} and \mathbf{B} by the vector potential \mathbf{A} and scalar potential ϕ according to

$$\mathbf{E}(\mathbf{r}, t) = -\frac{\partial}{\partial t} \mathbf{A}(\mathbf{r}, t) - \nabla\phi(\mathbf{r}, t) \quad (8.24)$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) . \quad (8.25)$$

Now we consider the vector-components of Eq. (8.23) separately. For the x-component we obtain

$$\begin{aligned} \frac{d}{dt} [m\dot{x}] &= -q \left[\frac{\partial\phi}{\partial x} + \frac{\partial A_x}{\partial t} \right] + q \left[\dot{y} \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) - \dot{z} \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) \right] \\ &= \frac{\partial}{\partial x} [-q\phi + q(A_x\dot{x} + A_y\dot{y} + A_z\dot{z})] - q \left[\frac{\partial A_x}{\partial t} + \dot{x} \frac{\partial A_x}{\partial x} + \dot{y} \frac{\partial A_y}{\partial y} + \dot{z} \frac{\partial A_z}{\partial z} \right] . \end{aligned} \quad (8.26)$$

Identifying the last expression in brackets with dA_x/dt (total differential) and rearranging terms, the equation above can be written as

$$\frac{d}{dt} [m\dot{x} + qA_x] - \frac{\partial}{\partial x} [-q\phi + q(A_x\dot{x} + A_y\dot{y} + A_z\dot{z})] = 0 . \quad (8.27)$$

This equation has almost the form of the Lagrange-Euler equation (8.22). Therefore, we seek a Lagrangian of the form

$$L = -q\phi + q(A_x\dot{x} + A_y\dot{y} + A_z\dot{z}) + f(x, \dot{x}) , \quad (8.28)$$

with $\partial f/\partial x = 0$. With this choice, the first term in Eq. (8.22) leads to

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) = \frac{d}{dt} \left[qA_x + \frac{\partial f}{\partial \dot{x}} \right] . \quad (8.29)$$

This expression has to be identical with the first term in Eq. (8.27) which leads to $\partial f/\partial \dot{x} = m\dot{x}$. The solution $f(x, \dot{x}) = m\dot{x}^2/2$ can be substituted into Eq. (8.28) and, after generalizing to all degrees of freedom, we finally obtain

$$L = -q\phi + q(A_x\dot{x} + A_y\dot{y} + A_z\dot{z}) + \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) , \quad (8.30)$$

which can be written as

$$L = -q\phi + q\mathbf{v} \cdot \mathbf{A} + \frac{m}{2} \mathbf{v} \cdot \mathbf{v} . \quad (8.31)$$

[†]It is a convention of the Hamiltonian formalism to designate the generalized coordinates by the symbol q . Here, it should not be confused with the charge q .

To determine the Hamiltonian H we first calculate the the canonical momentum $\mathbf{p} = (\mu_x, \mu_y, \mu_z)$ conjugate to the coordinates $\mathbf{q} = (x, y, z)$ according to $p_i = \partial L / \partial \dot{q}_i$. The canonical momentum turns out to be

$$\mathbf{p} = m\mathbf{v} + q\mathbf{A} , \quad (8.32)$$

which is the sum of mechanical momentum $m\mathbf{v}$ and field momentum $q\mathbf{A}$. According to Hamiltonian mechanics, the Hamiltonian is derived from the Lagrangian according to

$$H(\mathbf{q}, \mathbf{p}) = \sum_i [p_i \dot{q}_i - L(\mathbf{q}, \dot{\mathbf{q}})] , \quad (8.33)$$

in which all the velocities \dot{q}_i have to be expressed in terms of the coordinates q_i and conjugate momenta p_i . This is easily done by using Eq. (8.32) as $\dot{q}_i = p_i/m - qA_i/m$. Using this substitution in Eqs. (8.30) and (8.33) we finally obtain

$$H = \frac{1}{2m} [\mathbf{p} - q\mathbf{A}]^2 + q\phi . \quad (8.34)$$

This is the Hamiltonian of a *free* charge q with mass m in an external electromagnetic field. The first term renders the kinetic mechanical energy and the second term the potential energy of the charge. Notice, that the derivation of L and H is independent of gauge, i.e. we did not imply any condition on $\nabla \cdot \mathbf{A}$. Using Hamilton's canonical equations $\dot{q}_i = \partial H / \partial p_i$ and $\dot{p}_i = -\partial H / \partial q_i$ it is straightforward to show that the Hamiltonian in Eq. (8.34) reproduces the equations of motion stated in Eq. (8.23).

The Hamiltonian of Eq. (8.34) is not yet the total Hamiltonian H_{tot} of the system "charge+field" since we did not include the energy of the electromagnetic field. Furthermore, if the charge is interacting with other charges, as in the case of an atom or a molecule, we must take into account the interaction between the charges. In general, the total Hamiltonian for a system of charges can be written as

$$H_{tot} = H_{particle} + H_{rad} + H_{int} . \quad (8.35)$$

Here, H_{rad} is the Hamiltonian of the radiation field in the absence of the charges and $H_{particle}$ is the Hamiltonian of the system of charges (particle) in the absence of the electromagnetic field. The interaction between the two systems is described by the interaction Hamiltonian H_{int} . Let us determine the individual contributions.

The particle Hamiltonian $H_{particle}$ is determined by a sum of the kinetic energies $\mathbf{p}_n \cdot \mathbf{p}_n / (2m_n)$ of the N charges and the potential energies $V(\mathbf{r}_m, \mathbf{r}_n)$ between the charges (intramolecular potential), i.e.,

$$H_{particle} = \sum_{n,m} \left[\frac{\mathbf{p}_n \cdot \mathbf{p}_n}{2m_n} + V(\mathbf{r}_m, \mathbf{r}_n) \right] , \quad (8.36)$$

where the n -th particle is specified by its charge q_n , mass m_n , and coordinate \mathbf{r}_n . Notice, that $V(\mathbf{r}_m, \mathbf{r}_n)$ is determined in the absence of the external radiation field. This term is solely due to the Coulomb interaction between the charges. H_{rad} is defined by integrating the electromagnetic energy density W of the radiation field [Eq. (??)] over all space as[‡]

$$H_{rad} = \frac{1}{2} \int [\varepsilon_o E^2 + \mu_o^{-1} B^2] dV, \quad (8.37)$$

where $E^2 = |\mathbf{E}|^2$ and $B^2 = |\mathbf{B}|^2$. It should be noted, that the inclusion of H_{rad} is essential for a rigorous quantum electrodynamical treatment of light-matter interactions. This term ensures that the system consisting of particles and fields is conservative; it permits the interchange of energy between the atomic states and the states of the radiation field. Spontaneous emission is a direct consequence of the inclusion of H_{rad} and cannot be derived by semiclassical calculations in which H_{rad} is not included. Finally, to determine H_{int} we first consider each charge separately. Each charge contributes to H_{int} a term which can be derived from Eq. (8.34) as

$$H - \frac{\mathbf{p} \cdot \mathbf{p}}{2m} = -\frac{q}{2m} [\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}] + \frac{q^2}{2m} \mathbf{A} \cdot \mathbf{A} + q\phi. \quad (8.38)$$

Here, we subtracted the kinetic energy of the charge from the classical ‘particle-field’ Hamiltonian since this term is already included in $H_{particle}$. Using $\mathbf{p} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p}$ and then summing the contributions of all N charges in the system we can write H_{int} as[§]

$$H_{int} = \sum_n \left[-\frac{q_n}{m_n} \mathbf{A}(\mathbf{r}_n, t) \cdot \mathbf{p}_n + \frac{q_n^2}{2m_n} \mathbf{A}(\mathbf{r}_n, t) \cdot \mathbf{A}(\mathbf{r}_n, t) + q_n \phi(\mathbf{r}_n, t) \right]. \quad (8.39)$$

In the next section we will show that H_{int} can be expanded into a multipole series similar to our previous results for V_E and V_M .

8.2.1 Multipole expansion of the interaction Hamiltonian

The Hamiltonian expressed in terms of the vector potential \mathbf{A} and scalar potential ϕ is not unique. This is caused by the freedom of gauge, i.e. if the potentials are replaced by new potentials $\tilde{\mathbf{A}}$, $\tilde{\phi}$ according to

$$\mathbf{A} \rightarrow \tilde{\mathbf{A}} + \nabla\chi \quad \text{and} \quad \phi \rightarrow \tilde{\phi} - \partial\chi/\partial t, \quad (8.40)$$

[‡]This integration leads necessarily to an infinite result which caused difficulties in the development of the quantum theory of light. Renormalization procedures are needed to overcome these problems.

[§]In quantum mechanics, the canonical momentum \mathbf{p} is converted to an operator according to $\mathbf{p} \rightarrow -i\hbar\nabla$ (Jordan rule) which turns also H_{int} into an operator. \mathbf{p} and \mathbf{A} commute only if the Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$) is adopted.

with $\chi(\mathbf{r}, t)$ being an arbitrary gauge function, Maxwell's equations remain unaffected. This is easily seen by introducing the above substitutions in the definitions of \mathbf{A} and ϕ [Eqs. (8.24) and (8.25)]. To remove the ambiguity caused by the freedom of gauge we need to express H_{int} in terms of the original fields \mathbf{E} and \mathbf{B} . To do this, we first expand the electric and magnetic fields in a Taylor series with origin $\mathbf{r} = 0$ [c.f. Eq. (8.8)]

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}(0) + [\mathbf{r} \cdot \nabla] \mathbf{E}(0) + \frac{1}{2!} [\mathbf{r} \cdot \nabla]^2 \mathbf{E}(0) + \dots \quad (8.41)$$

$$\mathbf{B}(\mathbf{r}) = \mathbf{B}(0) + [\mathbf{r} \cdot \nabla] \mathbf{B}(0) + \frac{1}{2!} [\mathbf{r} \cdot \nabla]^2 \mathbf{B}(0) + \dots, \quad (8.42)$$

and introduce these expansions in the definitions for \mathbf{A} and ϕ [Eqs. (8.24) and (8.25)]. The task is now to find an expansion of \mathbf{A} and ϕ in terms of \mathbf{E} and \mathbf{B} such that the left and right hand sides of Eqs. (8.24) and (8.25) are identical. These expansions have been determined by Barron and Gray as [6]

$$\phi(\mathbf{r}) = \phi(0) - \sum_{i=0}^{\infty} \frac{\mathbf{r} [\mathbf{r} \cdot \nabla]^i}{(i+1)!} \cdot \mathbf{E}(0), \quad \mathbf{A}(\mathbf{r}) = \sum_{i=0}^{\infty} \frac{[\mathbf{r} \cdot \nabla]^i}{(i+2)!} \mathbf{B}(0) \times \mathbf{r}. \quad (8.43)$$

Inserting into the expression for H_{int} in Eq. (8.39) leads to the so-called *multipolar interaction Hamiltonian*

$$H_{int} = q_{tot} \phi(0, t) - \boldsymbol{\mu} \cdot \mathbf{E}(0, t) - \mathbf{m} \cdot \mathbf{B}(0, t) - [\overset{\leftrightarrow}{\mathbf{Q}} \nabla] \cdot \mathbf{E}(0, t) - \dots, \quad (8.44)$$

in which we used the following definitions

$$q_{tot} = \sum_n q_n, \quad \boldsymbol{\mu} = \sum_n q_n \mathbf{r}_n, \quad \mathbf{m} = \sum_n (q_n/2m_n) \mathbf{r}_n \times \tilde{\mathbf{p}}_n, \quad \overset{\leftrightarrow}{\mathbf{Q}} = \sum_n (q_n/2) \mathbf{r}_n \mathbf{r}_n, \quad (8.45)$$

q_{tot} is the total charge of the system, $\boldsymbol{\mu}$ denotes the total electric dipole moment, \mathbf{m} the total magnetic dipole moment, and $\overset{\leftrightarrow}{\mathbf{Q}}$ the total electric quadrupole moment. If the system of charges is charge neutral, the first term in H_{int} vanishes and we are left with an expansion which looks very much like the former expansion of the potential energy $V_E + V_M$. However, the two expansions are *not* identical! First, the new magnetic dipole moment is defined in terms of the canonical momenta $\tilde{\mathbf{p}}_n$ and not by the mechanical momenta $m_n \dot{\mathbf{r}}_n$.[¶] Second, the expansion of H_{int} contains a term nonlinear in $\mathbf{B}(0, t)$ which is nonexistent in the expansion of $V_E + V_M$. The nonlinear term arises from the term $\mathbf{A} \cdot \mathbf{A}$ of the Hamiltonian and is referred to as the diamagnetic term. It reads as

$$\sum_n (q_n^2/8m_n) [\mathbf{r}_n \times \mathbf{B}(0, t)]^2. \quad (8.46)$$

[¶]A gauge transformation also transforms the canonical momenta. Therefore, the canonical momenta $\tilde{\mathbf{p}}_n$ are different from the original canonical momenta \mathbf{p}_n .

Our previous expressions for V_E and V_M have been derived by neglecting retardation and assuming weak fields. In this limit, the nonlinear term in Eq. (8.46) can be neglected and the canonical momentum can be approximated by the mechanical momentum.

The multipolar interaction Hamiltonian can easily be converted to an operator by simply applying Jordan's rule $\mathbf{p} \rightarrow -i\hbar\nabla$ and replacing the fields \mathbf{E} and \mathbf{B} by the corresponding electric and magnetic field operators. However, this is beyond the present scope. Notice, that the Hamiltonian H_{int} in Eq. (8.44) is gauge independent. The gauge affects H_{int} only when the latter is expressed in terms of \mathbf{A} and ϕ but not when it is represented by the original fields \mathbf{E} and \mathbf{B} . The first term in the multipolar Hamiltonian of a charge neutral system is the dipole interaction which is identical to the corresponding term in V_E . In most circumstances, it is sufficiently accurate to reject the higher terms in the multipolar expansion. This is especially true for farfield interactions where the magnetic dipole and electric quadrupole interaction are roughly two orders of magnitude weaker than the electric dipole interaction. Therefore, standard selection rules for optical transitions are based on the electric dipole interaction. However, in strongly confined optical fields as encountered in near-field optics, higher-order terms in the expansion of H_{int} can become important and the standard selection rules can be violated. Finally, it should be noted, that the multipolar form of H_{int} can also be derived from Eq. (8.39) by a unitary transformation [7]. This transformation, commonly referred to as the *Power-Zienau-Woolley* transformation, plays an important role in quantum optics [3].

We have established that to first order any neutral system of charges (particle), that is smaller than the wavelength of the interacting radiation, can be viewed as a dipole. In the next section we will consider its radiating properties.

8.3 The radiating electric dipole

The current density due to a distribution of charges q_n with coordinates \mathbf{r}_n and velocities $\dot{\mathbf{r}}_n$ has been given in Eq. (8.2). We can develop this current density in a Taylor series with origin \mathbf{r}_o which is typically at the center of the charge distribution. If we keep only the lowest order term we find

$$\mathbf{j}(\mathbf{r}, t) = \frac{d}{dt}\boldsymbol{\mu}(t)\delta[\mathbf{r} - \mathbf{r}_o], \quad (8.47)$$

with the dipole moment

$$\boldsymbol{\mu}(t) = \sum_n q_n[\mathbf{r}_n(t) - \mathbf{r}_o]. \quad (8.48)$$

The dipole moment is identical with the definition in Eq. (8.11) for which we had $\mathbf{r}_o = 0$. We assume a harmonic time-dependence which allows us to write the current den-

sity as $\mathbf{j}(\mathbf{r}, t) = \text{Re}\{\mathbf{j}(\mathbf{r}) \exp(-i\omega t)\}$ and the dipole moment as $\boldsymbol{\mu}(t) = \text{Re}\{\boldsymbol{\mu} \exp(-i\omega t)\}$. Eq. (8.47) can then be written as

$$\mathbf{j}(\mathbf{r}) = -i\omega \boldsymbol{\mu} \delta[\mathbf{r} - \mathbf{r}_o]. \quad (8.49)$$

Thus, to lowest order, any current density can be thought of as an oscillating dipole with origin at the center of the charge distribution.

8.3.1 Electric dipole fields in a homogeneous space

In this section we will derive the fields of a dipole representing the current density of a small charge distribution located in a homogeneous, linear and isotropic space. The fields of the dipole can be derived by considering two oscillating charges q of opposite sign, separated by an infinitesimal vector $d\mathbf{s}$. In this physical picture the dipole moment is given by $\boldsymbol{\mu} = qd\mathbf{s}$. However, it is more elegant to derive the dipole fields using the Green's function formalism developed in Section ???. There, we have derived the so-called volume integral equations [c.f. Eqs. (??) and (??)]

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_o + i\omega \mu \mu_o \int_V \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \mathbf{j}(\mathbf{r}') dV', \quad (8.50)$$

$$\mathbf{H}(\mathbf{r}) = \mathbf{H}_o + \int_V [\nabla \times \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}')] \mathbf{j}(\mathbf{r}') dV'. \quad (8.51)$$

$\vec{\mathbf{G}}$ denotes the dyadic Green's function and $\mathbf{E}_o, \mathbf{H}_o$ are the fields in the absence of the current \mathbf{j} . The integration runs over the source volume specified by the coordinate \mathbf{r}' . If we introduce the current from Eq. (8.49) into the last two equations and assume that all fields are produced by the dipole we find

$$\mathbf{E}(\mathbf{r}) = \omega^2 \mu \mu_o \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o) \boldsymbol{\mu}, \quad (8.52)$$

$$\mathbf{H}(\mathbf{r}) = -i\omega [\nabla \times \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o)] \boldsymbol{\mu}. \quad (8.53)$$

Hence, the fields of an arbitrarily oriented electric dipole located at $\mathbf{r} = \mathbf{r}_o$ are determined by the Green's function $\vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o)$. As mentioned earlier, each column vector of $\vec{\mathbf{G}}$ specifies the electric field of a dipole whose axis is aligned with one of the coordinate axes. For a homogeneous space, $\vec{\mathbf{G}}$ has been derived as

$$\vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o) = \left[\vec{\mathbf{I}} + \frac{1}{k^2} \nabla \nabla \right] G(\mathbf{r}, \mathbf{r}_o), \quad G(\mathbf{r}, \mathbf{r}_o) = \frac{\exp(ik|\mathbf{r} - \mathbf{r}_o|)}{4\pi|\mathbf{r} - \mathbf{r}_o|}. \quad (8.54)$$

where $\vec{\mathbf{I}}$ is the unit dyad and $G(\mathbf{r}, \mathbf{r}_o)$ the scalar Green's function. It is straightforward to calculate $\vec{\mathbf{G}}$ in the major three coordinate systems. In a Cartesian system $\vec{\mathbf{G}}$ can be written as

$$\vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o) = \frac{\exp(ikR)}{4\pi R} \left[\left(1 + \frac{ikR - 1}{k^2 R^2} \right) \vec{\mathbf{I}} + \frac{3 - 3ikR - k^2 R^2}{k^2 R^2} \frac{\mathbf{R}\mathbf{R}}{R^2} \right], \quad (8.55)$$

where R is the absolute value of the vector $\mathbf{R} = \mathbf{r} - \mathbf{r}_o$ and $\mathbf{R}\mathbf{R}$ denotes the outer product of \mathbf{R} with itself. Eq. (8.55) defines a symmetric 3×3 matrix

$$\vec{\mathbf{G}} = \begin{bmatrix} G_{xx} & G_{xy} & G_{xz} \\ G_{xy} & G_{yy} & G_{yz} \\ G_{xz} & G_{yz} & G_{zz} \end{bmatrix}, \quad (8.56)$$

which, together with Eqs. (8.52) and (8.53), determines the electromagnetic field of an arbitrary electric dipole $\boldsymbol{\mu}$ with Cartesian components μ_x, μ_y, μ_z . The tensor $[\nabla \times \vec{\mathbf{G}}]$ can be expressed as

$$\nabla \times \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o) = \frac{\exp(ikR)}{4\pi R} \frac{k(\mathbf{R} \times \vec{\mathbf{I}})}{R} \left(i - \frac{1}{kR} \right), \quad (8.57)$$

where $\mathbf{R} \times \vec{\mathbf{I}}$ denotes the matrix generated by the cross-product of \mathbf{R} with each column vector of $\vec{\mathbf{I}}$.

The Green's function $\vec{\mathbf{G}}$ has terms in $(kR)^{-1}$, $(kR)^{-2}$ and $(kR)^{-3}$. In the *farfield*, for which $R \gg \lambda$, only the terms with $(kR)^{-1}$ survive. On the other hand, the dominant terms in the *near-field*, for which $R \ll \lambda$, are the terms with $(kR)^{-3}$. The terms with $(kR)^{-2}$ dominate the *intermediate field* at $R \approx \lambda$. To distinguish these three ranges it is convenient to write

$$\vec{\mathbf{G}} = \vec{\mathbf{G}}_{NF} + \vec{\mathbf{G}}_{IF} + \vec{\mathbf{G}}_{FF}, \quad (8.58)$$

where the near-field (G_{NF}), intermediate field (G_{IF}) and farfield (G_{FF}) Green's functions are given by

$$\vec{\mathbf{G}}_{NF} = \frac{\exp(ikR)}{4\pi R} \frac{1}{k^2 R^2} [-\vec{\mathbf{I}} + 3\mathbf{R}\mathbf{R}/R^2], \quad (8.59)$$

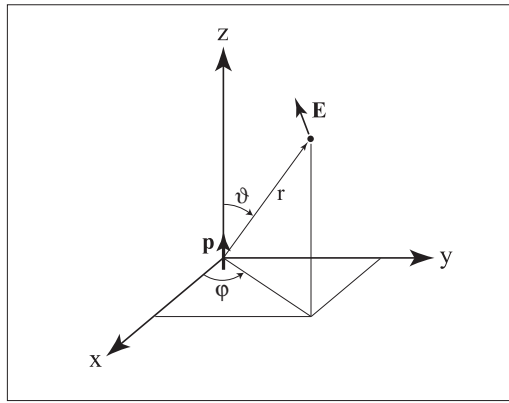


Figure 8.2: The fields of a dipole are most conveniently represented in a spherical coordinate system (r, ϑ, φ) in which the dipole points along the z -axis ($\vartheta=0$).

$$\vec{\mathbf{G}}_{IF} = \frac{\exp(ikR)}{4\pi R} \frac{i}{kR} [\vec{\mathbf{I}} - 3\mathbf{R}\mathbf{R}/R^2] , \quad (8.60)$$

$$\vec{\mathbf{G}}_{FF} = \frac{\exp(ikR)}{4\pi R} [\vec{\mathbf{I}} - \mathbf{R}\mathbf{R}/R^2] . \quad (8.61)$$

Notice that the intermediate field is 90° out of phase with respect to the near- and farfield.

Because the dipole is located in a homogeneous environment, all three dipole orientations lead to fields which are identical upon suitable frame rotations. We therefore choose a coordinate system with origin at $\mathbf{r} = \mathbf{r}_o$ and a dipole orientation along the dipole axis, i.e. $\boldsymbol{\mu} = |\boldsymbol{\mu}| \mathbf{n}_z$ (c.f. Fig. 8.2). It is most convenient to represent the dipole fields in spherical coordinates $\mathbf{r} = (r, \vartheta, \varphi)$ and in spherical vector components $\mathbf{E} = (E_r, E_\vartheta, E_\varphi)$. In this system the field components E_φ and H_r, H_ϑ are identical to zero and the only non-vanishing field components are

$$E_r = \frac{|\boldsymbol{\mu}| \cos \vartheta}{4\pi\epsilon_o\epsilon} \frac{\exp(ikr)}{r} k^2 \left[\frac{2}{k^2 r^2} - \frac{2i}{kr} \right] , \quad (8.62)$$

$$E_\vartheta = \frac{|\boldsymbol{\mu}| \sin \vartheta}{4\pi\epsilon_o\epsilon} \frac{\exp(ikr)}{r} k^2 \left[\frac{1}{k^2 r^2} - \frac{i}{kr} - 1 \right] , \quad (8.63)$$

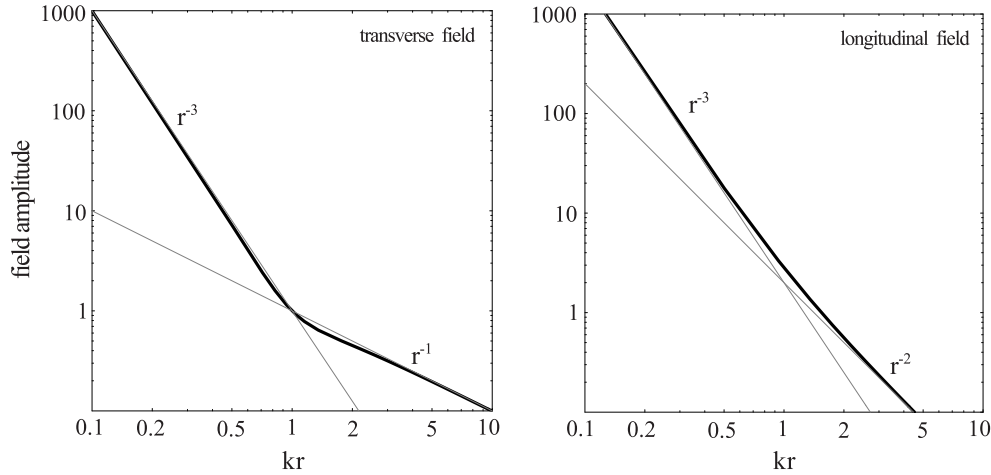


Figure 8.3: Radial decay of the dipole's transverse and longitudinal fields. The curves correspond to the absolute value of the expressions in brackets of Eqs. (8.62) and (8.63), respectively. While both the transverse and the longitudinal field contribute to the near-field, only the transverse field survives in the farfield. Notice, that the intermediate field with $(kr)^{-2}$ does not really show up for the transverse field. Instead the near-field dominates for $(kr) < 1$ and the far-field for $(kr) > 1$.

$$H_\varphi = \frac{|\boldsymbol{\mu}| \sin \vartheta}{4\pi\epsilon_o\epsilon} \frac{\exp(ikr)}{r} k^2 \left[-\frac{i}{kr} - 1 \right] \sqrt{\frac{\epsilon_o\epsilon}{\mu_o\mu}} . \quad (8.64)$$

The fact that E_r has no farfield term ensures that the field in the farfield is purely transverse. Furthermore, since the magnetic field has no terms in $(kr)^{-3}$ the near-field is dominated by the electric field. Thus, close to the origin of the dipole the magnetic field strength is much smaller than the electric field strength which justifies a quasi-electrostatic consideration.

So far we have considered a dipole which oscillates harmonically in time, i.e. $\boldsymbol{\mu}(t) = \text{Re}\{\boldsymbol{\mu} \exp(-i\omega t)\}$. Therefore, the electromagnetic field is monochromatic and oscillates at the same frequency. Although it is possible to generate any time-dependence by a superposition of monochromatic fields (Fourier transformation), it is of advantage for ultrafast applications to have the full time dependence available. The fields of a dipole $\boldsymbol{\mu}(t)$ with arbitrary time dependence can be derived by using the time-dependent Green's function. In a non-dispersive medium it is easier to introduce the explicit time dependence by using the substitutions

$$\exp(ikr) k^m \boldsymbol{\mu} = \exp(ikr) \left[\frac{in}{c} \right]^m (-i\omega)^m \boldsymbol{\mu} \rightarrow \left[\frac{in}{c} \right]^m \frac{d^m}{dt^m} \boldsymbol{\mu}(t - nr/c) , \quad (8.65)$$

where n denotes the (dispersionfree) index of refraction^{||} and $(t - nr/c)$ is the retarded time. With this substitution, the dipole fields read as

$$E_r(t) = \frac{\cos \vartheta}{4\pi\epsilon_o\epsilon} \left[\frac{2}{r^3} + \frac{n}{c} \frac{2}{r^2} \frac{d}{dt} \right] |\boldsymbol{\mu}(t - nr/c)| , \quad (8.66)$$

^{||}A dispersion-free index of refraction different from one is an approximation since it violates causality.

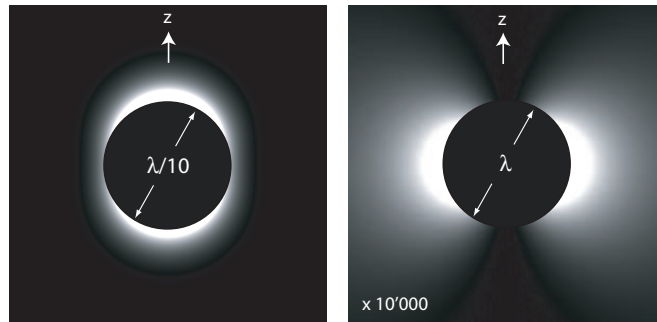


Figure 8.4: Electric energy density outside a fictitious sphere enclosing a dipole $\boldsymbol{\mu} = \mu_z$. (a) Close to the dipole's origin the field distribution is elongated along the dipole axis (near-field). (b) At larger distances the field spreads transverse to the dipole axis (farfield).

$$E_{\vartheta}(t) = \frac{\sin \vartheta}{4\pi\epsilon_o\epsilon} \left[\frac{1}{r^3} + \frac{n}{c} \frac{1}{r^2} \frac{d}{dt} + \frac{n^2}{c^2} \frac{1}{r} \frac{d^2}{dt^2} \right] |\boldsymbol{\mu}(t - r n/c)|, \quad (8.67)$$

$$H_{\varphi}(t) = \frac{\sin \vartheta}{4\pi\epsilon_o\epsilon} \sqrt{\frac{\epsilon_o\epsilon}{\mu_o\mu}} \left[\frac{n}{c} \frac{1}{r^2} \frac{d}{dt} + \frac{n^2}{c^2} \frac{1}{r} \frac{d^2}{dt^2} \right] |\boldsymbol{\mu}(t - r n/c)|. \quad (8.68)$$

We see that the farfield is generated by the acceleration of the charges which constitute the dipole moment. Similarly, the intermediate field and the near-field are generated by the speed and the position of the charges, respectively.

8.3.2 Dipole radiation

It can be shown (see Problem 8.3) that only the farfield of the dipole contributes to the net energy transport. The Poynting vector $\mathbf{S}(t)$ associated with the farfield can be calculated by retaining only the r^{-1} terms in the dipole fields. We obtain

$$\mathbf{S}(t) = \mathbf{E}(t) \times \mathbf{H}(t) = \frac{1}{16\pi^2\epsilon_o\epsilon} \frac{\sin^2 \vartheta}{r^2} \frac{n^3}{c^3} \left[\frac{d^2}{dt^2} |\boldsymbol{\mu}(t - r n/c)| \right]^2 \mathbf{n}_r. \quad (8.69)$$

The radiated power P can be determined by integrating $\mathbf{S}(t)$ over a closed spherical surface as

$$P(t) = \int_{\partial V} \mathbf{S} \cdot \mathbf{n} da = \frac{1}{4\pi\epsilon_o\epsilon} \frac{2n^3}{3c^3} \left[\frac{d^2 |\boldsymbol{\mu}(t)|}{dt^2} \right]^2, \quad (8.70)$$

where we have shrunk the radius of the sphere to zero to get rid of the retarded time. The average radiated power for a harmonically oscillating dipole turns out to be

$$\bar{P} = \frac{|\boldsymbol{\mu}|^2}{4\pi\epsilon_o\epsilon} \frac{n^3\omega^4}{3c^3}, \quad (8.71)$$

which could have been also calculated by integrating the time-averaged Poynting vector $\langle \mathbf{S} \rangle = (1/2) \text{Re}\{\mathbf{E} \times \mathbf{H}^*\}$, \mathbf{E} and \mathbf{H} being the dipole's complex field amplitudes given by Eqs. (8.62)-(8.64). We find that the radiated power scales with the fourth power of the frequency. To determine the normalized radiation pattern we calculate the power $\bar{P}(\vartheta, \varphi)$ radiated into an infinitesimal unit solid angle $d\Omega = \sin \vartheta d\vartheta d\varphi$ and divide by the total radiated power \bar{P}

$$\frac{\bar{P}(\vartheta, \varphi)}{\bar{P}} = \frac{3}{8\pi} \sin^2 \vartheta. \quad (8.72)$$

Most of the energy is radiated perpendicular to the dipole moment and there is no radiation at all in direction of the dipole.

Although we have considered an arbitrary time-dependence for the dipole we will restrict ourselves in the following to the time harmonic case. It is straightforward to account for dispersion when working with time-harmonic fields and arbitrary time-dependences can be introduced by using Fourier transforms.

8.3.3 Rate of energy dissipation in inhomogeneous environments

According to Poynting's theorem [c.f. Eq. (??)] the radiated power of any current distribution with a harmonic time dependence in a linear medium has to be identical to the rate of energy dissipation dW/dt given by

$$\frac{dW}{dt} = -\frac{1}{2} \int_V \operatorname{Re}\{\mathbf{j}^* \cdot \mathbf{E}\} dV, \quad (8.73)$$

V being the source volume. It is important to notice that \mathbf{j} is not the total current density. Instead, it represents the source current \mathbf{j}_s which generates the fields, or, a loss current \mathbf{j}_c which is associated with thermal losses. In either way, \mathbf{j} represents both energy sources and energy sinks. If we introduce the dipole's current density from Eq. (8.49) we obtain the important result

$$\boxed{\frac{dW}{dt} = \frac{\omega}{2} \operatorname{Im}\{\boldsymbol{\mu}^* \cdot \mathbf{E}(\mathbf{r}_o)\}}, \quad (8.74)$$

where the field \mathbf{E} is evaluated at the dipole's origin \mathbf{r}_o . This equation can be rewritten in terms of the Green's function by using Eq. (8.52) as

$$\frac{dW}{dt} = \frac{\omega^3 |\boldsymbol{\mu}|^2}{2c^2 \varepsilon_o \varepsilon} \left[\mathbf{n}_\mu \cdot \operatorname{Im}\{\vec{\mathbf{G}}(\mathbf{r}_o, \mathbf{r}_o; \omega)\} \cdot \mathbf{n}_\mu \right], \quad (8.75)$$

with \mathbf{n}_μ being the unit vector in direction of the dipole moment. At first sight it seems not possible to evaluate Eq. (8.74) since $\exp(ikR)/R$ appears to be infinite at $\mathbf{r}=\mathbf{r}_o$. As we shall see this is not the case. We first note that due to the dot product between $\boldsymbol{\mu}$ and \mathbf{E} we need only to evaluate the component of \mathbf{E} in direction of $\boldsymbol{\mu}$. Choosing $\boldsymbol{\mu} = |\boldsymbol{\mu}| \mathbf{n}_z$ we calculate E_z as

$$E_z = \frac{|\boldsymbol{\mu}|}{4\pi \varepsilon_o \varepsilon} \frac{e^{ikR}}{R} \left[k^2 \sin^2 \vartheta + \frac{1}{R^2} (3 \cos^2 \vartheta - 1) - \frac{ik}{R} (3 \cos^2 \vartheta - 1) \right]. \quad (8.76)$$

Since the interesting part is the field at the origin of the dipole, the exponential term is expanded into a series [$\exp(ikR) = 1 + ikR + (1/2)(ikR)^2 + (1/6)(ikR)^3 + \dots$] and the limiting case $R \rightarrow 0$ is considered. Thus,

$$\frac{dW}{dt} = \lim_{R \rightarrow 0} \frac{\omega}{2} |\boldsymbol{\mu}| \operatorname{Im}\{E_z\} = \frac{\omega |\boldsymbol{\mu}|^2}{8\pi \varepsilon_o \varepsilon} \lim_{R \rightarrow 0} \left\{ \frac{2}{3} k^3 + R^2(\dots) + \dots \right\} = \frac{|\boldsymbol{\mu}|^2}{12\pi} \frac{\omega}{\varepsilon_o \varepsilon} k^3, \quad (8.77)$$

which is identical with Eq. (8.71). Thus, Eq. (8.74) leads to the correct result despite of the apparent singularity at $R=0$.

The importance of Eq. (8.74) becomes obvious if we consider an emitting dipole in an inhomogeneous environment such as an atom in a cavity or a molecule in a superlattice. The rate at which energy is released can still be calculated by integrating the

Poynting vector over a surface enclosing the dipole emitter. However, to do this, we need to know the electromagnetic field everywhere on the enclosing surface. Because of the inhomogeneous environment, this field is not equal to the dipole field alone! Instead, it is the self-consistent field, i.e. the field \mathbf{E} generated by the superposition of the dipole field \mathbf{E}_o and the scattered field \mathbf{E}_s from the environment. Thus, to determine the energy dissipated by the dipole we first need to determine the electromagnetic field everywhere on the enclosing surface. However, by using Eq. (8.74) we can do the same job by only evaluating the total field at the dipole's origin \mathbf{r}_o . It is convenient to decompose the electric field at the dipole's position as

$$\mathbf{E}(\mathbf{r}_o) = \mathbf{E}_o(\mathbf{r}_o) + \mathbf{E}_s(\mathbf{r}_o), \quad (8.78)$$

where \mathbf{E}_o and \mathbf{E}_s are the primary dipole field and the scattered field, respectively. Introducing Eq. (8.78) into Eq. (8.74) allows us to split the rate of energy dissipation $P = dW/dt$ into two parts. The contribution of \mathbf{E}_o has been determined in Eq. (8.71) and Eq. (8.77) as

$$P_o = \frac{|\boldsymbol{\mu}|^2}{12\pi} \frac{\omega}{\varepsilon_o \varepsilon} k^3, \quad (8.79)$$

which allows us to write for the normalized rate of energy dissipation

$$\boxed{\frac{P}{P_o} = 1 + \frac{6\pi\varepsilon_o\varepsilon}{|\boldsymbol{\mu}|^2} \frac{1}{k^3} \text{Im}\{\boldsymbol{\mu}^* \cdot \mathbf{E}_s(\mathbf{r}_o)\}}. \quad (8.80)$$

Thus, the change of energy dissipation depends on the *secondary field* of the dipole. This field corresponds to the dipole's own field emitted at a former time. It arrives at the position of the dipole after it has been scattered in the environment.

8.3.4 Radiation reaction

An oscillating charge produces electromagnetic radiation. This radiation not only dissipates the energy of the oscillator but it also influences the motion of the charge. This back-action is called radiation damping or radiation reaction. With the inclusion of the reaction force \mathbf{F}_r the equation of motion for an undriven harmonic oscillator becomes

$$m\ddot{\mathbf{r}} + \omega_o^2 m\mathbf{r} = \mathbf{F}_r, \quad (8.81)$$

where $\omega_o^2 m = c$ is the linear spring constant. According to Eq. (8.70) the average rate of energy dissipation is

$$P(t) = \frac{1}{4\pi\varepsilon_o} \frac{2}{3c^3} \left[\frac{d^2 |\boldsymbol{\mu}(t)|}{dt^2} \right]^2 = \frac{q^2}{6\pi\varepsilon_o c^3} (\ddot{\mathbf{r}} \cdot \ddot{\mathbf{r}}). \quad (8.82)$$

Integrated over a certain time period $T = [t_1 .. t_2]$, this term must be equal to the work exerted on the oscillating charge by the radiation reaction force. Thus,

$$\int_{t_1}^{t_2} \left[\mathbf{F}_r \cdot \dot{\mathbf{r}} + \frac{q^2 (\ddot{\mathbf{r}} \cdot \dot{\mathbf{r}})}{6\pi\epsilon_0 c^3} \right] dt = 0. \quad (8.83)$$

After integrating the second term by parts we obtain

$$\int_{t_1}^{t_2} \left[\mathbf{F}_r \cdot \dot{\mathbf{r}} - \frac{q^2 (\dot{\mathbf{r}} \cdot \ddot{\mathbf{r}})}{6\pi\epsilon_0 c^3} \right] dt + \frac{q^2 (\ddot{\mathbf{r}} \cdot \dot{\mathbf{r}})}{6\pi\epsilon_0 c^3} \Big|_{t_1}^{t_2} = 0. \quad (8.84)$$

For short time-intervals $T \rightarrow 0$, the integrated term goes to zero and consequently the remaining integrand has to vanish, i.e.

$$\mathbf{F}_r = \frac{q^2 \ddot{\mathbf{r}}}{6\pi\epsilon_0 c^3}, \quad (8.85)$$

which is the *Abraham-Lorentz formula* for the radiation reaction force. The equation of motion (8.81) now becomes

$$\ddot{\mathbf{r}} - \frac{q^2}{6\pi\epsilon_0 c^3 m} \ddot{\mathbf{r}} + \omega_o^2 \mathbf{r} = 0. \quad (8.86)$$

Assuming that the damping introduced by the radiation reaction force is negligible, the solution becomes $\mathbf{r}(t) = \mathbf{r}_o \exp[-i\omega_o t]$ and hence $\ddot{\mathbf{r}} = -\omega_o^2 \mathbf{r}$. Thus, for small damping, we obtain

$$\ddot{\mathbf{r}} + \gamma_o \dot{\mathbf{r}} + \omega_o^2 \mathbf{r} = 0, \quad \gamma_o = \frac{1}{4\pi\epsilon_0} \frac{2q^2 \omega_o^2}{3c^3 m}. \quad (8.87)$$

This equation corresponds to an undriven Lorentzian atom model with transition frequency ω_o and linewidth γ_o . A more rigorous derivation shows that radiation reaction not only affects the damping of the oscillator due to radiation but also the oscillator's effective mass. This additional mass contribution is called the *electromagnetic mass* and it is the source of many controversies [8].

Due to radiation damping the undriven oscillator will ultimately come to rest. However, the oscillator interacts with the vacuum field which keeps the oscillator alive. Consequently, a driving term accounting for the fluctuating vacuum field \mathbf{E}_o has to be added to the right hand side of Eq. (8.87). The fluctuating vacuum field compensates the dissipation of the oscillator. Such fluctuation-dissipation relations will be discussed in Chapter ???. In short, to preserve an equilibrium between the oscillator and the vacuum, the vacuum must give rise to fluctuations if it takes energy from the oscillator (radiation damping). It can be shown that spontaneous emission is the result of both radiation reaction *and* vacuum fluctuations [8].

Finally, let us remark that radiation reaction is an important ingredient to obtain the correct result for the *optical theorem* in the dipole limit [9], i.e. for a particle that is described by a polarizability α . In this limit, an incident field polarizes the particle and induces a dipole moment $\boldsymbol{\mu}$ which in turn radiates a scattered field. According to the optical theorem, the extinct power (sum of scattered and absorbed power) can be expressed by the field scattered in the forward direction. However, it turns out that in the dipole limit the extinct power is identical with the absorbed power and hence light scattering is not taken into account! The solution to this dilemma is provided by the radiation reaction term in Eq. (8.85) and is analyzed in more detail in Problem 8.5. In short, the particle not only interacts with the external driving field but also with its own field causing a phase-lag between the induced dipole oscillation and the driving electric field oscillation. This phase-lag recovers the optical theorem and is responsible for light scattering in the dipole limit.

8.4 Spontaneous decay

Before Purcell's analysis in 1946, spontaneous emission was considered a radiative intrinsic property of atoms or molecules [10]. Purcell's work established that the spontaneous decay rate of a magnetic dipole placed in a resonant electronic device can be enhanced compared to the free space decay rate. Thus, it can be inferred that the environment in which the atoms are embedded modifies the radiative properties of the atoms. In order to experimentally observe this effect a physical device with dimensions on the order of the emission wavelength λ is needed. Since most of the atomic transitions occur in or near the visible spectral range, the modification of spontaneous decay was not an obvious fact. Drexhage investigated the effect of planar interfaces on the spontaneous decay rate of molecules [11] and the enhancement of the atomic decay rates in a cavity was verified by Goy *et al.* [12]. Kleppner observed that the decay of excited atoms can also be inhibited by a cavity [13]. Another novel structure, the photonic crystal (optical structure with a periodic dielectric function) was first conceived by Yablonovitch and John, as a system to control radiative properties [14, 15]. Photonic crystals exhibit forbidden photonic bandgaps which may inhibit the decay of an excited atomic system. Related potential applications are thresholdless lasers, perfect mirrors, wave guides bending light by 90 degrees without loss, etc. [16]. Changes of molecular decay rates have also been observed in near-field optical microscopy since molecules near optical probes experience a modified density of states [17]. Recently, it was also demonstrated that non-radiative energy transfer between adjacent molecules (Förster transfer) can be modified by an inhomogeneous environment [18].

In the theory of atom-field interaction there are two physically distinctive regimes,

namely, the strong and weak coupling regimes. The two regimes are distinguished on basis of the atom-field coupling constant which is estimated as

$$\kappa = \frac{\mu}{\hbar} \sqrt{\frac{\hbar \omega_o}{2\epsilon_o V}}, \quad (8.88)$$

where ω_o is the atomic transition frequency, μ the dipole matrix element, and V the volume of the cavity. Strong coupling satisfies the condition $\kappa \gg \gamma_{cav}$, γ_{cav} being the photon decay rate inside the cavity. In the strong coupling regime only quantum electrodynamics (QED) can give an accurate description of atom-field interactions. For example, the emission spectrum of an atom inside a cavity with a high quality factor ($Q \rightarrow \infty$) exhibits two distinct peaks[19, 20]. On the other hand, in the weak-coupling regime ($\kappa \ll \gamma_{cav}$) it has been shown that QED and classical theory give the same results for the *modification* of the spontaneous emission decay rate by inhomogeneous environments. Classically, the modification of the spontaneous decay rate is generated by the scattering of the atomic field in the environment, whereas in the QED picture, the decay rate is partly stimulated by vacuum field fluctuations, the latter being a function of the environment.

8.4.1 QED of spontaneous decay

In this section we derive the spontaneous emission rate γ for a two-level quantum system located at $\mathbf{r} = \mathbf{r}_o$. Spontaneous decay is a pure quantum effect and requires a QED treatment. This section is intended to put classical treatments into the proper context. We consider the combined ‘*field+system*’ states and calculate the transitions from the excited state $|i\rangle$ with energy E_i to a set of final states $|f\rangle$ with identical energies E_f (see Fig. 8.5). The final states differ only by the mode \mathbf{k} of the radiation field.** The derivation presented here is based on the Heisenberg picture. An equivalent derivation is presented in Appendix ??.

According to Fermi’s Golden Rule γ is given by

$$\gamma = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f | \hat{H}_I | i \rangle \right|^2 \delta(\omega_i - \omega_f) \quad (8.89)$$

where $\hat{H}_I = -\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}}$ is the interaction Hamiltonian in the dipole approximation. Notice, that all ω_f are identical. Using the expression for \hat{H}_I we can substitute as follows

$$\left| \langle f | \hat{H}_I | i \rangle \right|^2 = \langle f | \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}} | i \rangle^* \langle f | \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}} | i \rangle = \langle i | \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}} | f \rangle \langle f | \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}} | i \rangle. \quad (8.90)$$

Let us represent the electric field operator $\hat{\mathbf{E}}$ at $\mathbf{r} = \mathbf{r}_o$ as [2]

$$\hat{\mathbf{E}} = \sum_{\mathbf{k}} \left[\mathbf{E}_{\mathbf{k}}^+ \hat{a}_{\mathbf{k}}(t) + \mathbf{E}_{\mathbf{k}}^- \hat{a}_{\mathbf{k}}^\dagger(t) \right], \quad (8.91)$$

** \mathbf{k} is not to be confused with the wavevector. It is a label denoting a specific mode which in turn is characterized by the polarization vector and the wavevector.

where

$$\hat{a}_{\mathbf{k}}^\dagger(t) = \hat{a}_{\mathbf{k}}^\dagger(0) \exp(i\omega_{\mathbf{k}}t), \quad \hat{a}_{\mathbf{k}}(t) = \hat{a}_{\mathbf{k}}(0) \exp(-i\omega_{\mathbf{k}}t). \quad (8.92)$$

Here, $\hat{a}_{\mathbf{k}}(0)$ and $\hat{a}_{\mathbf{k}}^\dagger(0)$ are the annihilation and creation operators, respectively. The sum over \mathbf{k} refers to summation over all modes. $\omega_{\mathbf{k}}$ denotes the frequency of mode \mathbf{k} . The spatially dependent complex fields $\mathbf{E}_{\mathbf{k}}^+ = (\mathbf{E}_{\mathbf{k}}^-)^*$ are the positive and negative frequency parts of the complex field $\mathbf{E}_{\mathbf{k}}$. For a two-level atomic system with the ground state $|g\rangle$ and the excited state $|e\rangle$, the dipole moment operator $\hat{\boldsymbol{\mu}}$ can be written as

$$\hat{\boldsymbol{\mu}} = \boldsymbol{\mu} [\hat{r}^+ + \hat{r}], \quad \text{with } \hat{r}^+ = |e\rangle\langle g| \text{ and } \hat{r} = |g\rangle\langle e|. \quad (8.93)$$

In this notation, $\boldsymbol{\mu}$ is simply the transition dipole moment which is assumed to be real, i.e. $\langle g|\hat{\boldsymbol{\mu}}|e\rangle = \langle e|\hat{\boldsymbol{\mu}}|g\rangle$. Using the expressions for $\hat{\mathbf{E}}$ and $\hat{\boldsymbol{\mu}}$, the interaction Hamiltonian takes on the form

$$-\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}} = -\sum_{\mathbf{k}} \boldsymbol{\mu} \cdot \left[\mathbf{E}_{\mathbf{k}}^+ \hat{r}^+ \hat{a}_{\mathbf{k}}(t) + \mathbf{E}_{\mathbf{k}}^- \hat{r} \hat{a}_{\mathbf{k}}^\dagger(t) + \mathbf{E}_{\mathbf{k}}^+ \hat{r} \hat{a}_{\mathbf{k}}(t) + \mathbf{E}_{\mathbf{k}}^- \hat{r}^+ \hat{a}_{\mathbf{k}}^\dagger(t) \right]. \quad (8.94)$$

We now define the initial and final state of the combined system ‘*field+atom*’ as

$$|i\rangle = |e, \{0\}\rangle = |e\rangle |\{0\}\rangle \quad (8.95)$$

$$|f\rangle = |g, \{1\omega_{\mathbf{k}'}\}\rangle = |g\rangle |\{1\omega_{\mathbf{k}'}\}\rangle, \quad (8.96)$$

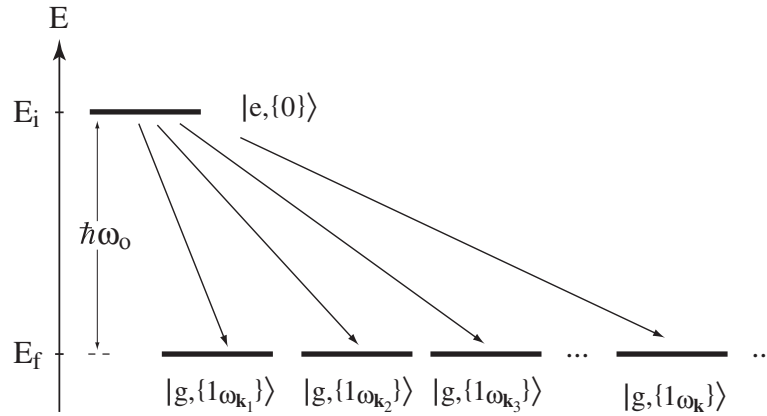


Figure 8.5: Transition from an initial state $|i\rangle = |e, \{0\}\rangle$ to a set of final states $|f\rangle = |g, \{1\omega_{\mathbf{k}}\}\rangle$. All the final states have the same energy. The difference of initial and final energies is $(E_i - E_f) = \hbar\omega_o$. The states are products of atomic states ($|e\rangle$ or $|g\rangle$) and single-photon states ($|\{0\}\rangle$ or $|\{1\omega_{\mathbf{k}}\}\rangle$). The number of distinct final single-photon states is defined by the partial local density of states $\rho_{\mu}(\mathbf{r}_o, \omega_o)$, with \mathbf{r}_o being the origin of the two-level system.

respectively. Here, $|\{0\}\rangle$ denotes the zero-photon state, and $|\{1_{\omega_{\mathbf{k}'}}\}\rangle$ designates the one-photon state associated with mode \mathbf{k}' and frequency $\omega_o = (E_e - E_g)/\hbar$, E_e and E_g being the energies of excited state and ground state, respectively. Thus, the final states in Eq. (8.89) are associated with the different modes \mathbf{k}' . Operating with $\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}}$ on state $|i\rangle$ leads to

$$\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}} |i\rangle = \boldsymbol{\mu} \cdot \sum_{\mathbf{k}} \mathbf{E}_{\mathbf{k}}^{-} e^{i\omega_{\mathbf{k}} t} |g, \{1_{\omega_{\mathbf{k}}}\}\rangle, \quad (8.97)$$

where we used $\hat{a}_{\mathbf{k}}^{\dagger}(0) |\{0\}\rangle = |\{1_{\omega_{\mathbf{k}}}\}\rangle$. Operating with $\langle f|$ gives

$$\langle f| \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}} |i\rangle = \boldsymbol{\mu} \cdot \sum_{\mathbf{k}} \mathbf{E}_{\mathbf{k}}^{-} e^{i\omega_{\mathbf{k}} t} \langle g, \{1_{\omega_{\mathbf{k}'}}\} | g, \{1_{\omega_{\mathbf{k}}}\}\rangle, \quad (8.98)$$

where we used $\hat{a}_{\mathbf{k}}(0) |\{1_{\omega_{\mathbf{k}}}\}\rangle = \{0\}$. A similar procedure leads to

$$\langle i| \hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{E}} |f\rangle = \boldsymbol{\mu} \cdot \sum_{\mathbf{k}} \mathbf{E}_{\mathbf{k}}^{+} e^{-i\omega_{\mathbf{k}} t} \langle g, \{1_{\omega_{\mathbf{k}}}\} | g, \{1_{\omega_{\mathbf{k}'}}\}\rangle. \quad (8.99)$$

The matrix elements can now be introduced into Eq. (8.90) and Eq. (8.89). Expressing the sum over the final states as a sum over the modes \mathbf{k}' the transition rate becomes

$$\begin{aligned} \gamma = \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}} \sum_{\mathbf{k}''} [\boldsymbol{\mu} \cdot \mathbf{E}_{\mathbf{k}''}^{+} \mathbf{E}_{\mathbf{k}}^{-} \cdot \boldsymbol{\mu}] e^{i(\omega_{\mathbf{k}} - \omega_{\mathbf{k}''})t} \times \\ \sum_{\mathbf{k}'} \langle g, \{1_{\omega_{\mathbf{k}'}}\} | g, \{1_{\omega_{\mathbf{k}'}}\}\rangle \langle g, \{1_{\omega_{\mathbf{k}'}}\} | g, \{1_{\omega_{\mathbf{k}}}\}\rangle \delta(\omega_{\mathbf{k}'} - \omega_o). \end{aligned} \quad (8.100)$$

Because of orthogonality, the only nonvanishing terms are those for which $\mathbf{k}' = \mathbf{k}'' = \mathbf{k}$ which leads to the simple expression

$$\gamma = \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}} [\boldsymbol{\mu} \cdot (\mathbf{E}_{\mathbf{k}}^{+} \mathbf{E}_{\mathbf{k}}^{-}) \cdot \boldsymbol{\mu}] \delta(\omega_{\mathbf{k}} - \omega_o). \quad (8.101)$$

Here, $\mathbf{E}_{\mathbf{k}}^{+} \mathbf{E}_{\mathbf{k}}^{-}$ denotes the outer product, i.e. the result is a 3×3 matrix. For later purposes it is convenient to rewrite this expression in terms of normal modes $\mathbf{u}_{\mathbf{k}}$ defined as

$$\mathbf{E}_{\mathbf{k}}^{+} = \sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\varepsilon_o}} \mathbf{u}_{\mathbf{k}}, \quad \mathbf{E}_{\mathbf{k}}^{-} = \sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\varepsilon_o}} \mathbf{u}_{\mathbf{k}}^*. \quad (8.102)$$

Because the delta function imposes $\omega_{\mathbf{k}} = \omega_o$ the decay rate can be written as

$$\boxed{\gamma = \frac{2\omega}{3\hbar\varepsilon_o} |\boldsymbol{\mu}|^2 \rho_{\mu}(\mathbf{r}_o, \omega_o), \quad \rho_{\mu}(\mathbf{r}_o, \omega_o) = 3 \sum_{\mathbf{k}} [\mathbf{n}_{\mu} \cdot (\mathbf{u}_{\mathbf{k}} \mathbf{u}_{\mathbf{k}}^*) \cdot \mathbf{n}_{\mu}] \delta(\omega_{\mathbf{k}} - \omega_o)} \quad (8.103)$$

where we introduced the *partial local density of states* $\rho_{\mu}(\mathbf{r}_o, \omega_o)$ which will be discussed in the next section. The dipole moment has been decomposed as $\boldsymbol{\mu} = \mu \mathbf{n}_{\mu}$

with \mathbf{n}_μ being the unit vector in direction of $\boldsymbol{\mu}$. The above equation for γ is our main result. The delta-function in the expression suggests that we need to integrate over a finite distribution of final frequencies. However, even for a single final frequency, the apparent singularity introduced through $\delta(\omega_{\mathbf{k}} - \omega_o)$ is compensated by the normal modes whose magnitude tends to zero for a sufficiently large mode volume. In any case, it is convenient to get rid of these singularities by representing $\rho_\mu(\mathbf{r}_o, \omega_o)$ in terms of the Green's function instead of normal modes.

8.4.2 Spontaneous decay and Green's dyadics

We aim at deriving an important relationship between the normal modes $\mathbf{u}_{\mathbf{k}}$ and the dyadic Green's function $\vec{\mathbf{G}}$. Subsequently, this relationship is used to express the spontaneous decay rate γ and to establish an elegant expression for the local density of states. While we suppressed the explicit position-dependence of $\mathbf{u}_{\mathbf{k}}$ in the previous section for notational convenience, it is essential in the current context to carry all the arguments along. The normal modes defined in the previous section satisfy the wave-equation

$$\nabla \times \nabla \times \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}) - \frac{\omega_{\mathbf{k}}^2}{c^2} \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}) = 0 \quad (8.104)$$

and they fulfill the orthogonality relation

$$\int \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}) \cdot \mathbf{u}_{\mathbf{k}'}^*(\mathbf{r}, \omega_{\mathbf{k}'}) d^3 \mathbf{r} = \delta_{\mathbf{k}\mathbf{k}'}, \quad (8.105)$$

where the integration runs over the entire mode volume. $\delta_{\mathbf{k}\mathbf{k}'}$ is the Kronecker delta and $\vec{\mathbf{I}}$ the unit dyad. We now expand the Green's function $\vec{\mathbf{G}}$ in terms of the normal modes as

$$\vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}}(\mathbf{r}', \omega) \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}), \quad (8.106)$$

where the vectorial expansion coefficients $\mathbf{A}_{\mathbf{k}}$ have yet to be determined.

We recall the definition of the Green's function [c.f. Eq. (??)]

$$\nabla \times \nabla \times \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}'; \omega) - \frac{\omega^2}{c^2} \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}'; \omega) = \vec{\mathbf{I}} \delta(\mathbf{r} - \mathbf{r}'). \quad (8.107)$$

To determine the coefficients $\mathbf{A}_{\mathbf{k}}$ we substitute the expansion for $\vec{\mathbf{G}}$ and obtain

$$\sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}}(\mathbf{r}', \omega) \left[\nabla \times \nabla \times \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}) - \frac{\omega^2}{c^2} \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}) \right] = \vec{\mathbf{I}} \delta(\mathbf{r} - \mathbf{r}'). \quad (8.108)$$

Using Eq. (8.104) we can rewrite the latter as

$$\sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}}(\mathbf{r}', \omega) \left[\frac{\omega_{\mathbf{k}}^2}{c^2} - \frac{\omega^2}{c^2} \right] \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}) = \vec{\mathbf{I}} \delta(\mathbf{r} - \mathbf{r}'). \quad (8.109)$$

Multiplying on both sides with $\mathbf{u}_{\mathbf{k}'}^*$, integrating over the mode volume and making use of the orthogonality relation leads to

$$\mathbf{A}_{\mathbf{k}'}(\mathbf{r}', \omega) \left[\frac{\omega_{\mathbf{k}'}^2}{c^2} - \frac{\omega^2}{c^2} \right] = \mathbf{u}_{\mathbf{k}'}^*(\mathbf{r}', \omega_{\mathbf{k}}). \quad (8.110)$$

Substituting this expression back into Eq. (8.106) leads to the desired expansion for $\vec{\mathbf{G}}$ in terms of the normal modes

$$\vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{\mathbf{k}} c^2 \frac{\mathbf{u}_{\mathbf{k}}^*(\mathbf{r}', \omega_{\mathbf{k}}) \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}})}{\omega_{\mathbf{k}}^2 - \omega^2}, \quad (8.111)$$

To proceed we make use of the following mathematical identity which can be easily proved by complex contour integration

$$\lim_{\eta \rightarrow 0} \text{Im} \left\{ \frac{1}{\omega_{\mathbf{k}}^2 - (\omega + i\eta)^2} \right\} = \frac{\pi}{2\omega_{\mathbf{k}}} [\delta(\omega + \omega_{\mathbf{k}}) - \delta(\omega - \omega_{\mathbf{k}})]. \quad (8.112)$$

Multiplying on both sides with $\mathbf{u}_{\mathbf{k}}^*(\mathbf{r}, \omega_{\mathbf{k}}) \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}})$ and summing over all \mathbf{k} yields

$$\text{Im} \left\{ \lim_{\eta \rightarrow 0} \sum_{\mathbf{k}} \frac{\mathbf{u}_{\mathbf{k}}^*(\mathbf{r}, \omega_{\mathbf{k}}) \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}})}{\omega_{\mathbf{k}}^2 - (\omega + i\eta)^2} \right\} = \frac{\pi}{2} \sum_{\mathbf{k}} \frac{1}{\omega_{\mathbf{k}}} \mathbf{u}_{\mathbf{k}}^*(\mathbf{r}, \omega_{\mathbf{k}}) \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}) \delta(\omega - \omega_{\mathbf{k}}) \quad (8.113)$$

where we dropped the term $\delta(\omega + \omega_{\mathbf{k}})$ because we are concerned only with positive frequencies. By comparison with Eq. (8.111), the expression in brackets on the left

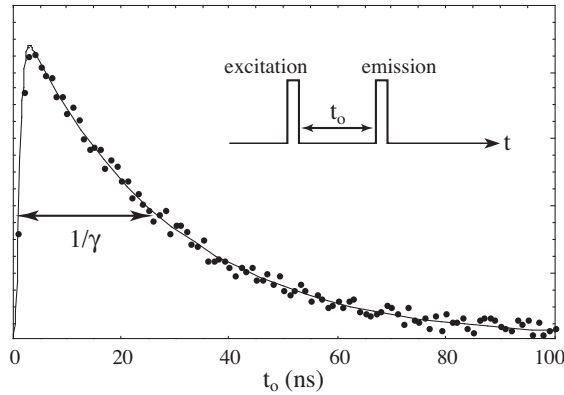


Figure 8.6: Radiative decay rate γ of the $2P_{1/2}$ state of Li . The time interval t_0 between an excitation pulse and the subsequent photon count is measured and plotted in a histogram. The $1/e$ width of the exponential distribution corresponds to the lifetime $\tau = 1/\gamma = 27.1$ ns. For $t_0 \rightarrow 0$ the distribution falls to zero because of the finite response time of the photon detector.

hand side can be identified with the Green's function evaluated at its origin $\mathbf{r} = \mathbf{r}'$. Furthermore, the delta function on the right hand side restricts all values of $\omega_{\mathbf{k}}$ to ω which allows us to move the first factor out of the sum. We therefore obtain the important relationship

$$\text{Im}\left\{\vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}; \omega)\right\} = \frac{\pi c^2}{2\omega} \sum_{\mathbf{k}} \mathbf{u}_{\mathbf{k}}^*(\mathbf{r}, \omega_{\mathbf{k}}) \mathbf{u}_{\mathbf{k}}(\mathbf{r}, \omega_{\mathbf{k}}) \delta(\omega - \omega_{\mathbf{k}}). \quad (8.114)$$

We now set $\mathbf{r} = \mathbf{r}_o$ and $\omega = \omega_o$ and rewrite the decay rate γ and the partial local density of states ρ_{μ} in Eq. (8.103) as rewritten as

$$\gamma = \frac{2\omega_o}{3\hbar\epsilon_o} |\boldsymbol{\mu}|^2 \rho_{\mu}(\mathbf{r}_o, \omega_o), \quad \rho_{\mu}(\mathbf{r}_o, \omega_o) = \frac{6\omega_o}{\pi c^2} \left[\mathbf{n}_{\mu} \cdot \text{Im}\left\{\vec{\mathbf{G}}(\mathbf{r}_o, \mathbf{r}_o; \omega_o)\right\} \cdot \mathbf{n}_{\mu} \right] \quad (8.115)$$

This formula is the main result of this section. It allows us to calculate the spontaneous decay rate of a two-level quantum system in an arbitrary reference system. All there is needed is the knowledge of the Green's dyadic for the reference system. The Green's dyadic is evaluated at its origin which corresponds to the location of the atomic system. From a classical viewpoint this is equivalent to the electric field previously emitted by the quantum system and now arriving back at its origin. The mathematical analogy of the quantum and the classical treatments becomes now obvious when comparing Eq. (8.115) and Eq. (8.75). The latter is the classical equation for energy dissipation based on Poynting's theorem.

We have expressed γ in terms of the partial local density of states ρ_{μ} which corresponds to the number of modes per unit volume and frequency, at the origin \mathbf{r} of the (pointlike) quantum system, into which a photon with energy $\hbar\omega_o$ can be released during the spontaneous decay process. In the next section we discuss some important aspects of ρ_{μ} .

8.4.3 Local density of states

In situations where the transitions of the quantum system have no fixed dipole axis \mathbf{n}_{μ} and the medium is isotropic and homogeneous, the decay rate is averaged over the various orientations leading to (see problem 8.6)

$$\left\langle \mathbf{n}_{\mu} \cdot \text{Im}\left\{\vec{\mathbf{G}}(\mathbf{r}_o, \mathbf{r}_o; \omega_o)\right\} \cdot \mathbf{n}_{\mu} \right\rangle = \frac{1}{3} \text{Im}\left\{ \text{Tr}[\vec{\mathbf{G}}(\mathbf{r}_o, \mathbf{r}_o; \omega_o)] \right\}. \quad (8.116)$$

Substituting into Eq. (8.115), we find that in this case the partial local density of states ρ_{μ} becomes identical with the *total local density of states* ρ defined as

$$\rho(\mathbf{r}_o, \omega_o) = \frac{2\omega_o}{\pi c^2} \text{Im}\left\{ \text{Tr}[\vec{\mathbf{G}}(\mathbf{r}_o, \mathbf{r}_o; \omega_o)] \right\} = \sum_{\mathbf{k}} |\mathbf{u}_{\mathbf{k}}|^2 \delta(\omega_{\mathbf{k}} - \omega_o), \quad (8.117)$$

where $Tr[.]$ denotes the trace of the tensor in brackets. ρ corresponds to the total number of electromagnetic modes per unit volume and unit frequency at a given location \mathbf{r}_o . In practice, ρ has little significance because any detector or measurement relies on the translation of charge carriers from one point to another. Defining the axis between these points as \mathbf{n}_μ it is obvious that ρ_μ is of much greater practical significance as it also enters the well known formula for spontaneous decay.

As shown earlier in section 8.3.3, the imaginary part of $\vec{\mathbf{G}}$ evaluated at its origin is not singular. For example, in free space ($\vec{\mathbf{G}}=\vec{\mathbf{G}}_o$) we have (see problem 8.7)

$$\left[\mathbf{n}_\mu \cdot \text{Im} \left\{ \vec{\mathbf{G}}_o(\mathbf{r}_o, \mathbf{r}_o; \omega_o) \right\} \cdot \mathbf{n}_\mu \right] = \frac{1}{3} \text{Im} \left\{ \text{Tr}[\vec{\mathbf{G}}_o(\mathbf{r}_o, \mathbf{r}_o; \omega_o)] \right\} = \frac{\omega_o}{6\pi c}. \quad (8.118)$$

where no orientational averaging has been performed. It is the symmetric form of $\vec{\mathbf{G}}_o$ which leads to this simple expression. Thus, ρ and ρ_μ take on the well-known value of

$$\rho_o = \frac{\omega_o^2}{\pi^2 c^3}. \quad (8.119)$$

which is the density of electromagnetic modes as encountered in blackbody radiation. The free-space spontaneous decay rate turns out to be

$$\boxed{\gamma_o = \frac{\omega_o^3 |\boldsymbol{\mu}|^2}{3\pi\epsilon_o \hbar c^3}}, \quad (8.120)$$

where $\boldsymbol{\mu} = \langle g | \hat{\boldsymbol{\mu}} | e \rangle$ denotes the transition dipole matrix element.

To summarize, the spontaneous decay rate is proportional to the partial local density of states which depends on the atomic dipole axis defined by the two atomic states involved in the transition. Only in homogeneous environments or after orientational averaging can ρ_μ be replaced by the total local density of states. This explains why a change in the environmental conditions can change the spontaneous decay rate.

8.5 Classical lifetimes and decay rates

We now derive the classical picture of spontaneous decay by considering an undriven harmonically oscillating dipole. As the dipole oscillates it radiates energy according to Eq. (8.70). As a consequence, the dipole dissipates its energy into radiation and its dipole moment decreases. We are interested in calculating the time τ after which the dipole's energy decreases to $1/e$ of its initial value.

8.5.1 Homogeneous environment

The equation of motion for an undriven harmonically oscillating dipole is [c.f. Eq. (8.87)]

$$\frac{d^2}{dt^2} \boldsymbol{\mu}(t) + \gamma_o \frac{d}{dt} \boldsymbol{\mu}(t) + \omega_o^2 \boldsymbol{\mu}(t) = 0. \quad (8.121)$$

The natural frequency of the oscillator is ω_o and its damping constant is γ_o . The solution for $\boldsymbol{\mu}$ is

$$\boldsymbol{\mu}(t) = \text{Re} \left\{ \boldsymbol{\mu}_o e^{-i\omega_o \sqrt{1 - (\gamma_o^2/4\omega_o^2)} t} e^{-\gamma_o t/2} \right\}. \quad (8.122)$$

Because of losses introduced through γ_o the dipole forms a non-conservative system. The damping rate not only attenuates the dipole strength but also produces a shift in resonance frequency. In order to be able to define an average dipole energy \bar{W} at any instant of time we have to make sure that the oscillation amplitude stays constant over one period of oscillation. In other words, we require

$$\gamma_o \ll \omega_o. \quad (8.123)$$

The average energy of a harmonic oscillator is the sum of the average kinetic and potential energy. At time t this average energy reads as^{††}

$$\bar{W}(t) = \frac{m}{2q^2} [\omega_o^2 \mu^2(t) + \dot{\mu}^2(t)] = \frac{m\omega_o^2}{2q^2} |\boldsymbol{\mu}_o|^2 e^{-\gamma_o t}, \quad (8.124)$$

where m is the mass of the particle with charge q . The *lifetime* τ_o of the oscillator is defined as the time for which the energy decayed to $1/e$ of its initial value at $t=0$. We simply find

$$\tau_o = 1/\gamma_o. \quad (8.125)$$

We now turn to the rate of energy loss due to radiation. The average radiated power P_o in free space at time t is [c.f. Eq. (8.71)]

$$P_o(t) = \frac{|\boldsymbol{\mu}(t)|^2}{4\pi\epsilon_o} \frac{\omega_o^4}{3c^3}. \quad (8.126)$$

Energy conservation requires that the decrease in oscillator energy must equal the energy losses, i.e.

$$\bar{W}(t=0) - \bar{W}(t) = q_i \int_0^t P_o(t') dt', \quad (8.127)$$

where we introduced the so-called *intrinsic quantum yield* (c.f. Section 8.5.4). This parameter has a value between zero and one and indicates the fraction of the energy-loss associated with radiation. For $q_i = 1$, all of the oscillator's dissipated energy is

^{††}This is easily derived by setting $\mu = qx$, $\omega_o^2 = c/m$ and using the expressions $m\dot{x}^2/2$ and $cx^2/2$ for the kinetic and potential energy, respectively.

transformed to radiation. It is now straight forward to solve for the decay rate. We introduce Eq. (8.124) and Eq. (8.126) into the last equation and obtain

$$\gamma_o = q_i \frac{1}{4\pi\epsilon_o} \frac{2q^2\omega_o^2}{3m c^3}, \quad (8.128)$$

which is identical to Eq. (8.87). γ_o is the classical expression for the atomic decay rate and through Eq. (8.125) also for the atomic lifetime. It depends on the oscillation frequency and the particle's mass and charge. The higher the index of refraction of the surrounding medium is, the shorter the lifetimes of the oscillator will be. γ_o can easily be generalized to multiple particle systems by summing over the individual charges q_n and masses m_n . At optical wavelengths we obtain a value for the decay rate of $\gamma_o \approx 2 \cdot 10^{-8} \omega_o$ which is in the *MHz* regime. The quantum mechanical analog of the decay rate [c.f. Eq. (8.120)] can be arrived at by replacing the oscillator's initial average energy $m\omega_o^2|\mu_o|^2/(2q^2)$ by the lowest energy of a quantum oscillator $\hbar\omega_o/2$. At the same time, the classical dipole moment has to be associated with the transition dipole matrix element between two atomic states.

In the treatments so far, we have assumed that the atom is locally surrounded by vacuum ($n=1$). For an atom placed in a dielectric medium there are two corrections that need to be performed: 1) the bulk dielectric behavior has to be accounted for by a dielectric constant, and 2) the local field at the dipole's position has to be corrected. The latter arises from the depolarization of the dipole's microscopic environment which influences the dipole's emission properties. The resulting correction is similar to the Clausius-Mossotti relation but more sophisticated models have been put forth recently.

The Lorentzian lineshape function

Spontaneous emission is well represented by an undriven harmonic oscillator. Although the oscillator acquires its energy through an exciting local field, the phases of excitation and emission are uncorrelated. Therefore, we can envision spontaneous emission as the radiation emitted by an undriven harmonic oscillator whose dipole moment is restored by the local field whenever the oscillator has lost its energy to the radiation field. The spectrum of spontaneous emission by a single atomic system is well described by the spectrum of the emitted radiation of an undriven harmonic oscillator. In free space, the electric farfield of a radiating dipole is calculated as [c.f. Eq. (8.67)]

$$E_\vartheta(t) = \frac{\sin \vartheta}{4\pi\epsilon_o} \frac{1}{c^2} \frac{1}{r} \frac{d^2}{dt^2} |\mu(t-r/c)|, \quad (8.129)$$

where r is the distance between observation point and the dipole origin. The spectrum $\hat{E}_\vartheta(\omega)$ can be calculated as [c.f. Eq. (??)]

$$\hat{E}_\vartheta(\omega) = \frac{1}{2\pi} \int_{r/c}^{\infty} E_\vartheta(t) e^{i\omega t} dt. \quad (8.130)$$

Here, we set the lower integration limit to $t=r/c$ because the dipole starts emitting at $t=0$ and it takes the time $t=r/c$ for the radiation to propagate to the observation point. Therefore $E_\vartheta(t < r/c) = 0$. Inserting the solution for the dipole moment from Eq. (8.122) and making use of $\gamma_o \ll \omega_o$ we obtain after integration

$$\hat{E}_\vartheta(\omega) = \frac{1}{2\pi} \frac{|\boldsymbol{\mu}| \sin\vartheta \omega_o^2}{8\pi\epsilon_o c^2 r} \left[\frac{\exp(i\omega r/c)}{i(\omega + \omega_o) - \gamma_o/2} + \frac{\exp(i\omega r/c)}{i(\omega - \omega_o) - \gamma_o/2} \right]. \quad (8.131)$$

The energy radiated into the unit solid angle $d\Omega = \sin\vartheta d\vartheta d\varphi$ is calculated as

$$\frac{dW}{d\Omega} = \int_{-\infty}^{\infty} I(\mathbf{r}, t) r^2 dt = r^2 \sqrt{\frac{\epsilon_o}{\mu_o}} \int_{-\infty}^{\infty} |E_\vartheta(t)|^2 dt = 4\pi r^2 \sqrt{\frac{\epsilon_o}{\mu_o}} \int_0^{\infty} |\hat{E}_\vartheta(\omega)|^2 d\omega, \quad (8.132)$$

where we applied Parseval's theorem and used the definition of the intensity $I = \sqrt{\epsilon_o/\mu_o} |E_\vartheta|^2$ of the emitted radiation. The total energy per unit solid angle $d\Omega$ and per unit frequency interval $d\omega$ can now be expressed as

$$\boxed{\frac{dW}{d\Omega d\omega} = \frac{1}{4\pi\epsilon_o} \frac{|\boldsymbol{\mu}|^2 \sin^2\vartheta \omega_o^2}{4\pi^2 c^3 \gamma_o^2} \left[\frac{\gamma_o^2/4}{(\omega - \omega_o)^2 + \gamma_o^2/4} \right]}. \quad (8.133)$$

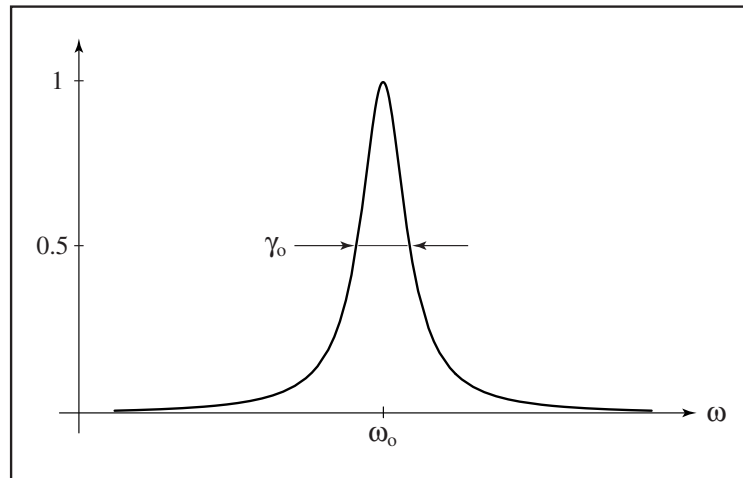


Figure 8.7: Lorentzian lineshape function as defined by the expression in brackets in Eq. (8.133).

The spectral shape of this function is determined by the expression in the brackets known as the *Lorentzian lineshape function*. The function is shown in Fig. 8.7. The width of the curve measured at half its maximum height is equal to γ_o , and integrated over the entire spectral range its value is $\pi\gamma_o/2$. Integrating Eq. (8.133) over all frequencies and all directions leads to the totally radiated energy

$$W = \frac{|\boldsymbol{\mu}|^2}{4\pi\epsilon_o} \frac{\omega_o^4}{3c^3\gamma_o}. \quad (8.134)$$

This value is equal to the average power \bar{P} radiated by a driven harmonic oscillator divided by the decay rate γ_o (c.f. Eq. (8.71)).

8.5.2 Inhomogeneous environment

In an inhomogeneous environment, a harmonically oscillating dipole left to itself will experience its own field as a driving force. This driving field is the field that arrives back to the oscillator after it has been scattered in the environment. If we ignore radiation reaction, the equation of motion is

$$\frac{d^2}{dt^2}\boldsymbol{\mu}(t) + \gamma_o \frac{d}{dt}\boldsymbol{\mu}(t) + \omega_o^2\boldsymbol{\mu}(t) = \frac{q^2}{m}\mathbf{E}_s(t), \quad (8.135)$$

with \mathbf{E}_s being the secondary local field. We expect that the interaction with \mathbf{E}_s will cause a shift of the resonance frequency and a modification of the decay rate. Therefore, we use the following trial solutions for dipole moment and driving field

$$\boldsymbol{\mu}(t) = \text{Re} \left\{ \boldsymbol{\mu}_o e^{-i\omega t} e^{-\gamma t/2} \right\}, \quad \mathbf{E}_s(t) = \text{Re} \left\{ \mathbf{E}_o e^{-i\omega t} e^{-\gamma t/2} \right\}. \quad (8.136)$$

γ and ω are the new decay rate and resonance frequency, respectively. The two trial solutions can be inserted into Eq. (8.135). As before, we assume that γ is much smaller than ω [c.f. Eq. (8.123)] which allows us to reject terms in γ^2 . Furthermore, we assume that the interaction with the field \mathbf{E}_s is weak. In this limit the last term on the left hand side of Eq. (8.135) is always larger than the driving term on the right hand side. Using the expression for γ_o from Eq. (8.128) we obtain

$$\boxed{\frac{\gamma}{\gamma_o} = 1 + q_i \frac{6\pi\epsilon_o}{|\boldsymbol{\mu}_o|^2} \frac{1}{k^3} \text{Im}\{\boldsymbol{\mu}_o^* \cdot \mathbf{E}_s(\mathbf{r}_o)\}}. \quad (8.137)$$

Since \mathbf{E}_s is proportional to $\boldsymbol{\mu}_o$, the dependence on the magnitude of the dipole moment cancels out. Besides the introduction of q_i , Eq. (8.137) is identical with Eq. (8.80) for the rate of energy dissipation in inhomogeneous environments. Thus, for $q_i=1$ we find the important relationship

$$\boxed{\frac{\gamma}{\gamma_o} = \frac{P}{P_o}}. \quad (8.138)$$

This equation can be verified by expressing the radiated power in terms of the average energy $\bar{W}(t)$ given in Eq. (8.124). With the help of Eq. (8.127) we find

$$\frac{P}{P_o} = \frac{\gamma}{\gamma_o} e^{-(\gamma-\gamma_o)t}, \quad (8.139)$$

where we assumed that the intrinsic quantum yield remains unaffected by the inhomogeneous environment. Besides the exponential time dependence the last two equations are the same. The exponential function can be expanded in powers of its argument and for sufficiently small times only the lowest order term, which is equal to one, is retained. This verifies, that Eq. (8.138) is fulfilled for sufficiently small times. In Section 8.6.2 Eq. (8.138) will be used to derive energy transfer from one nanosystem to another.

Eq. (8.137) can be adapted to describe the (normalized) spontaneous emission rate of a quantum system. In this case the classical dipole represents the quantum mechanical transition dipole matrix element from the excited to the ground state. The decay rate of the excited state is equal to the spontaneous emission rate $P/(\hbar\omega)$, where $\hbar\omega$ is the photon energy. Eq. (8.80) provides a simple means to calculate lifetime variations of atomic systems in arbitrary environments. In fact, this formula has been used by different authors to describe fluorescence quenching near planar interfaces and the achieved agreement to experiment is excellent (c.f. Fig. 8.8).

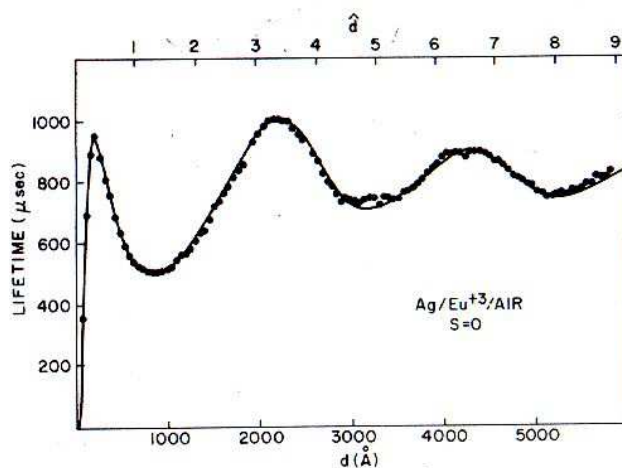


Figure 8.8: Comparison of classical theory and experimental data of molecular lifetimes in inhomogeneous environments. In the experiment, a layer of Eu^{3+} ions is held by fatty acid spacers of variable thickness close to a silver surface (data after Drexhage [21]). The calculated curve is due to Chance et al. [22].

8.5.3 Frequency shifts

The inhomogeneous environment not only influences the lifetime of the oscillating dipole but also causes a frequency shift $\Delta\omega = \omega - \omega_o$ of the emitted light. An expression for $\Delta\omega$ can be derived by inserting Eq. (8.136) into Eq. (8.135). The resulting expression for $\Delta\omega$ reads as

$$\Delta\omega = \omega \left[1 - \sqrt{1 - \frac{1}{\omega^2} \left[\frac{q^2}{m|\boldsymbol{\mu}_o|^2} \operatorname{Re}\{\boldsymbol{\mu}_o^* \cdot \mathbf{E}_s\} + \frac{\gamma\gamma_o}{2} - \frac{\gamma\gamma}{4} \right]} \right]. \quad (8.140)$$

After expanding the square root to first order and neglecting the quadratic terms in γ , the expression for the normalized frequency shift reduces to

$$\frac{\Delta\omega}{\gamma_o} = q_i \frac{3\pi\epsilon_o}{|\boldsymbol{\mu}_o|^2} \frac{1}{k^3} \operatorname{Re}\{\boldsymbol{\mu}_o^* \cdot \mathbf{E}_s\}. \quad (8.141)$$

For molecular fluorescence the frequency shift is very small, in the range of the radiative linewidth. The latter follows from Heisenberg's uncertainty principle as follows: The average time t that is available to 'measure' the excited state is $\langle t \rangle = \tau_o$. From the width in energy of the transition $\Delta E = \Delta\omega\hbar$ and Heisenberg's uncertainty $\Delta E \langle t \rangle \approx \hbar$ it follows that $\Delta\omega \approx \tau_o^{-1}$. Thus, a typical radiative lifetime of $\tau_o \approx 10 \text{ nsec}$ corresponds to a width of $\Delta\lambda \approx 2 \cdot 10^{-3} \text{ nm}$.

For molecules close to planar interfaces, the frequency shift varies as h^{-3} , h being the height of the molecule, and reaches its maximum near the surface plasmon frequency. The dependence on h^{-3} suggests that the observation of the frequency shift should be possible for small h . Yet, this is not the case because for small h also the linewidth increases. A shift in the range of $\Delta\lambda \approx 20 \text{ nm}$ was experimentally observed for small dipolar scatterers (silver islands) close to a silver layer [23]. In this configuration the dipolar scatterers were excited close to their resonance frequency leading to a highly enhanced polarizability. At cryogenic temperatures, the linewidths of molecules become very narrow and the frequency shifts can be well resolved.

Notice again, that since \mathbf{E}_s is proportional to $\boldsymbol{\mu}_o$, the dependence on the magnitude of the dipole moment in Eq. (8.141) cancels out.

8.5.4 Quantum yield

The excitation energy of a molecule or any other quantum system can be dissipated either radiatively or non-radiatively. Radiative relaxation is associated with the emission of a photon whereas non-radiative relaxation can have various pathways such as the coupling to vibrations, energy transfer to the environment, or quenching by other molecules. Often it is desired to generate conditions that maximize the radiative

output of a quantum system. A useful measure for this output is the *quantum yield* defined as

$$Q = \frac{\gamma_r}{\gamma_r + \gamma_{nr}}, \quad (8.142)$$

where γ_r and γ_{nr} are the radiative and non-radiative decay rates, respectively. In a homogeneous environment, Q is identical to the intrinsic quantum yield q_i defined in Section 8.5.1. However, γ_r and γ_{nr} are functions of the local environment and thus are affected by inhomogeneities. A particular environment can either increase or decrease the overall quantum yield Q .

To determine the quantum yield in a particular environment it is necessary to divide the total decay rate in Eq. (8.137) into a radiative and a non-radiative part

$$\gamma = \gamma_r + \gamma_{nr}. \quad (8.143)$$

The two contributions can be determined by calculating the balance between radiation emitted to the farfield and radiation absorbed in the environment P_{abs} . As an example, near a noble metal surface, the quantum yield of a normally weakly fluorescent molecule can be increased or decreased, depending on the distance between molecule and surface. For distances larger than $\approx 5nm$, the presence of the metal surface tends to increase γ_r whereas for shorter distances the molecule will predominantly dissipate its excitation energy non-radiatively to the metal thereby increasing γ_{nr} (fluorescence quenching).

8.6 Dipole-dipole interactions and energy transfer

So far we have discussed the interaction of a nanometric system with its macroscopic environment. In this section we will focus on the interaction between two particles (atoms, molecules, quantum dots, ..). These considerations are important for the understanding of delocalized excitations (excitons), energy transfer between particles, and collective phenomena. We will assume that the internal structure of a particle is not affected by the interactions. Therefore, processes such as electron transfer and molecular binding are not considered and the interested reader is referred to texts on physical chemistry [24].

8.6.1 Multipole expansion of the Coulombic interaction

Let us consider two separate particles **A** and **B** which are represented by the charge densities ρ_A and ρ_B , respectively. For simplicity, we only consider nonretarded interactions. In this case, the Coulomb interaction energy between the systems **A** and **B** reads as

$$V_{AB} = \frac{1}{4\pi\epsilon_0} \iint \frac{\rho_A(\mathbf{r}') \rho_B(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} dV' dV'' . \quad (8.144)$$

If we assume that the the extent of the charge distributions ρ_A and ρ_B is much smaller than their separation R we may expand V_{AB} in a multipole series with respect to the center of mass coordinates \mathbf{r}_A and \mathbf{r}_B . The first few multipole moments of the charge

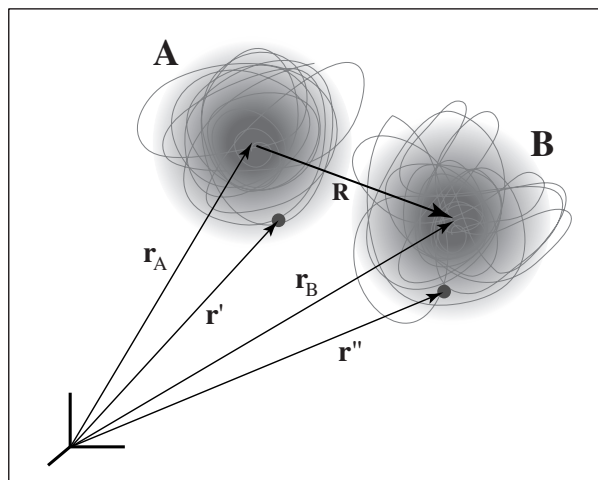


Figure 8.9: Interaction between two particles **A** and **B** which are represented by their charge distributions.

distribution ρ_A are determined as

$$q_A = \int \rho_A(\mathbf{r}') dV' \quad (8.145)$$

$$\boldsymbol{\mu}_A = \int \rho_A(\mathbf{r}') (\mathbf{r}' - \mathbf{r}_A) dV' \quad (8.146)$$

$$\overleftrightarrow{\mathbf{Q}}_A = \int \rho_A(\mathbf{r}') \left[3(\mathbf{r}' - \mathbf{r}_A)(\mathbf{r}' - \mathbf{r}_A) - \overleftrightarrow{\mathbf{I}} |\mathbf{r}' - \mathbf{r}_A|^2 \right] dV', \quad (8.147)$$

and similar expressions hold for the charge distribution ρ_B . With these multipole moments we can express the interaction potential as

$$V_{AB}(\mathbf{R}) = \frac{1}{4\pi\epsilon_0} \left[\frac{q_A q_B}{R} + \frac{q_A \boldsymbol{\mu}_B \cdot \mathbf{R}}{R^3} - \frac{q_B \boldsymbol{\mu}_A \cdot \mathbf{R}}{R^3} + \frac{R^2 \boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B - 3(\boldsymbol{\mu}_A \cdot \mathbf{R})(\boldsymbol{\mu}_B \cdot \mathbf{R})}{R^5} + \dots \right] \quad (8.148)$$

where $\mathbf{R} = \mathbf{r}_B - \mathbf{r}_A$. The first term in the expansion is the charge-charge interaction. It is only non-zero if both charge distributions carry a net charge. Charge-charge interactions span over long distances since the distance dependence is only R^{-1} . The next two terms are charge-dipole interactions. They require that at least one particle carries a net charge. These interactions decay as R^{-2} and are therefore of shorter range than the charge-charge interaction. Finally, the fourth term is the dipole-dipole interaction. It is the most important interaction among neutral particles. This term gives rise to van der Waals forces and to Förster energy transfer. The dipole-dipole interaction decays as R^{-3} and depends strongly on the dipole orientations. The next higher expansion terms are the quadrupole-charge, quadrupole-dipole, and quadrupole-quadrupole interactions. These are usually of much shorter range and therefore we do not list them explicitly. It has to be emphasized that the potential V_{AB} only accounts for interactions mediated by the near-field of the two dipoles. Inclusion of the intermediate field and the farfield gives rise to additional terms. We will include these terms in the derivation of energy transfer between particles.

8.6.2 Energy transfer between two particles

Energy transfer between individual particles is a photophysical process which is encountered in various systems. Probably the most important example is radiationless energy transfer between light-harvesting proteins in photosynthetic membranes [25]. In these systems, the photoenergy absorbed by chlorophyll molecules has to be channelled over longer distances to a protein called the reaction center. This protein uses the energy in order to perform a charge separation across the membrane surface. Energy transfer is also observed between closely arranged semiconductor nanoparticles [26] and it is the basis for fluorescence resonance energy transfer (FRET) studies of biological processes [27].

Energy transfer between individual particles can be understood within the same quasi-classical framework as developed in Section 8.5.1. The system to be analyzed is shown in Fig. 8.10. Two uncharged particles **D** (donor) and **A** (acceptor) are characterized by a set of discrete energy levels. We assume that initially the donor resides in an excited state with energy $E_D = \hbar\omega_o$. We are interested in calculating the rate $\gamma_{D \rightarrow A}$ of energy transfer from donor to acceptor. The transition dipole moments of donor and acceptor are denoted as $\boldsymbol{\mu}_D$ and $\boldsymbol{\mu}_A$, respectively, and \mathbf{R} is the vector from donor to acceptor. The corresponding unit vectors are \mathbf{n}_D , \mathbf{n}_A , and \mathbf{n}_R , respectively. Our starting point is Eq. (8.138) which connects the quantum mechanical picture with the classical picture. In the current context this equation reads as

$$\frac{\gamma_{D \rightarrow A}}{\gamma_o} = \frac{P_{D \rightarrow A}}{P_o}. \quad (8.149)$$

Here, $\gamma_{D \rightarrow A}$ is the energy transfer rate from donor to acceptor and γ_o is the donor's decay rate in the absence of the acceptor [c.f. Eq. (8.129)]. Similarly, $P_{D \rightarrow A}$ is the donor's energy per unit time which is absorbed by the acceptor, and P_o is the energy per unit time released from the donor in the absence of the acceptor. P_o can be written as [c.f. Eq. (8.71)]

$$P_o = \frac{|\boldsymbol{\mu}_D|^2 n(\omega_o)}{12\pi \epsilon_o c^3} \omega_o^4. \quad (8.150)$$

Classically, we envision the donor to be a dipole radiating at the frequency ω_o and the acceptor to be an absorber at ω_o . Both systems are embedded in a medium with index of refraction $n(\omega_o)$. Since the expressions of γ_o and P_o are known, we only need to determine $P_{D \rightarrow A}$.

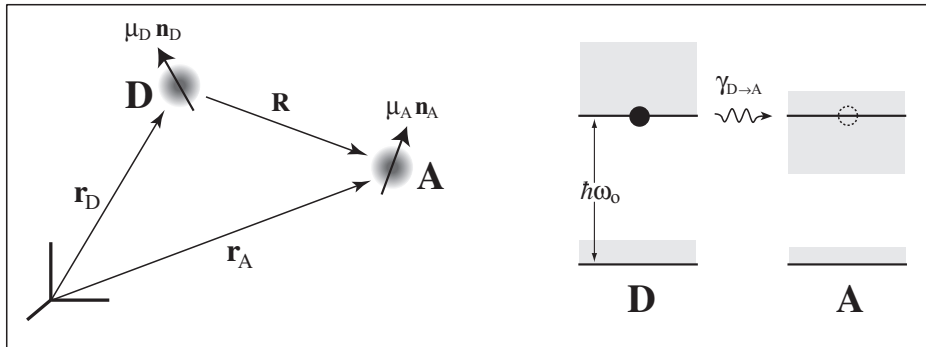


Figure 8.10: Energy transfer between two particles **D** (donor) and **A** (acceptor). Initially, the donor is in its excited state whereas the acceptor is in its ground state. The transition rate $\gamma_{D \rightarrow A}$ depends on the relative orientation of the transition dipole moments and the distance R between donor and acceptor.

According to Poynting's theorem the power transferred from donor to acceptor is [c.f. Eq. (8.73)]

$$P_{D \rightarrow A} = -\frac{1}{2} \int_{V_A} \text{Re}\{\mathbf{j}_A^* \cdot \mathbf{E}_D\} dV. \quad (8.151)$$

Here, \mathbf{j}_A is the current density associated with the charges of the acceptor and \mathbf{E}_D is the electric field generated by the donor. In the dipole approximation, the current density reads as $\mathbf{j}_A = -i\omega_o \boldsymbol{\mu}_A \delta(\mathbf{r} - \mathbf{r}_A)$ and Eq. (8.151) reduces to

$$P_{D \rightarrow A} = \frac{\omega_o}{2} \text{Im}\{\boldsymbol{\mu}_A^* \cdot \mathbf{E}_D(\mathbf{r}_A)\}. \quad (8.152)$$

It is important to realize that the acceptor's dipole moment $\boldsymbol{\mu}$ is not a permanent dipole moment. Instead, it is a transition dipole moment induced by the donor's field. In the linear regime we may write

$$\boldsymbol{\mu}_A = \overleftrightarrow{\alpha}_A \mathbf{E}_D(\mathbf{r}_A), \quad (8.153)$$

where $\overleftrightarrow{\alpha}_A$ is the acceptor's polarizability tensor. The dipole moment can now be substituted in Eq. (8.152) and if we assume that the acceptor can only be polarized in direction of a fixed axis given by the unit vector \mathbf{n}_A in direction of $\boldsymbol{\mu}_A$, i.e. $\overleftrightarrow{\alpha}_A = \alpha_A \mathbf{n}_A \mathbf{n}_A$, the power transferred from donor to acceptor can be written as

$$P_{D \rightarrow A} = \frac{\omega_o}{2} \text{Im}\{\alpha_A\} \left| \mathbf{n}_A \cdot \mathbf{E}_D(\mathbf{r}_A) \right|^2. \quad (8.154)$$

This result demonstrates that energy absorption is associated with the imaginary part of the polarizability. Furthermore, because $\boldsymbol{\mu}_A$ is an induced dipole, the absorption rate scales with the square of the electric field projected on the dipole axis. It is convenient to express the polarizability in terms of the absorption cross-section σ defined as

$$\sigma(\omega_o) = \frac{\langle P(\omega_o) \rangle}{I(\omega_o)}, \quad (8.155)$$

where $\langle P \rangle$ is the absorbed power by the acceptor averaged over all absorption dipole orientations, and I_o is the incident intensity. In terms of the electric field \mathbf{E}_D , the absorption cross-section can be expressed as

$$\sigma(\omega_o) = \frac{(\omega_o/2) \text{Im}\{\alpha(\omega_o)\} \langle |\mathbf{n}_p \cdot \mathbf{E}_D|^2 \rangle}{(1/2) (\varepsilon_o/\mu_o)^{1/2} n(\omega_o) |\mathbf{E}_D|^2} = \frac{\omega_o}{3} \sqrt{\frac{\mu_o}{\varepsilon_o}} \frac{\text{Im}\{\alpha(\omega_o)\}}{n(\omega_o)}. \quad (8.156)$$

Here, we used the orientational average of $\langle |\mathbf{n}_p \cdot \mathbf{E}_D|^2 \rangle$ which is calculated as

$$\langle |\mathbf{n}_p \cdot \mathbf{E}_D|^2 \rangle = \frac{|\mathbf{E}_D|^2}{4\pi} \int_0^{2\pi} \int_0^\pi [\cos^2 \theta] \sin \theta d\theta d\phi = \frac{1}{3} |\mathbf{E}_D|^2, \quad (8.157)$$

where θ is the angle enclosed by the dipole axis and the electric field vector. Thus, in terms of the absorption cross-section, the power transferred from donor to acceptor can be written as

$$P_{D \rightarrow A} = \frac{3}{2} \sqrt{\frac{\varepsilon_o}{\mu_o}} n(\omega_o) \sigma_A(\omega_o) \left| \mathbf{n}_A \cdot \mathbf{E}_D(\mathbf{r}_A) \right|^2. \quad (8.158)$$

The donor's field \mathbf{E}_D evaluated at the origin of the acceptor \mathbf{r}_A can be written in terms of the free space Green's function $\vec{\mathbf{G}}$ as [c.f. Eq. (8.52)]

$$\mathbf{E}_D(\mathbf{r}_A) = \omega_o^2 \mu_o \vec{\mathbf{G}}(\mathbf{r}_D, \mathbf{r}_A) \boldsymbol{\mu}_D. \quad (8.159)$$

The donor's dipole moment can be represented as $\boldsymbol{\mu}_D = |\boldsymbol{\mu}_D| \mathbf{n}_D$ and the frequency dependence can be substituted as $k = (\omega_o/c) n(\omega_o)$. Furthermore, for later convenience we define the function

$$T(\omega_o) = 16\pi^2 k^4 R^6 \left| \mathbf{n}_A \cdot \vec{\mathbf{G}}(\mathbf{r}_D, \mathbf{r}_A) \mathbf{n}_D \right|^2, \quad (8.160)$$

where $R = |\mathbf{r}_D - \mathbf{r}_A|$ is the distance between donor and acceptor. Using Eqs. (8.158)-(8.160) together with Eq. (8.150) in the original equation 8.149 we obtain for the normalized transfer rate from donor to acceptor

$$\frac{\gamma_{D \rightarrow A}}{\gamma_o} = \frac{9c^4}{8\pi R^6} \frac{\sigma_A(\omega_o)}{n^4(\omega_o) \omega_o^4} T(\omega_o). \quad (8.161)$$

In terms of the Dirac delta function this equation can be rewritten as

$$\frac{\gamma_{D \rightarrow A}}{\gamma_o} = \frac{9c^4}{8\pi R^6} \int_0^\infty \frac{\delta(\omega - \omega_o) \sigma_A(\omega)}{n^4(\omega) \omega^4} T(\omega) d\omega. \quad (8.162)$$

We notice that the normalized frequency distribution of the donor emission is given by

$$\int_0^\infty \delta(\omega - \omega_o) d\omega = 1. \quad (8.163)$$

Since the donor emits over a range of frequencies we need to generalize the distribution as

$$\int_0^\infty f_D(\omega) d\omega = 1, \quad (8.164)$$

with $f_D(\omega)$ being the donor's normalized emission spectrum in a medium with index $n(\omega)$. Thus, we finally obtain the important result

$$\boxed{\frac{\gamma_{D \rightarrow A}}{\gamma_o} = \frac{9c^4}{8\pi R^6} \int_0^\infty \frac{f_D(\omega) \sigma_A(\omega)}{n^4(\omega) \omega^4} T(\omega) d\omega}. \quad (8.165)$$

The transfer rate from donor to acceptor depends on the spectral overlap of the donor's emission spectrum f_D and the acceptor's absorption cross-section. Notice

that f_D has units of ω^{-1} whereas the units of σ_A are m^2 . In order to understand the orientation dependence and the distance dependence of the transfer rate we need to evaluate the function $T(\omega)$. Using the definition in Eq. (8.160) and inserting the free space dyadic Green's function from Eq. (8.55) we obtain

$$T(\omega) = (1 - k^2 R^2 + k^4 R^4) (\mathbf{n}_A \cdot \mathbf{n}_D)^2 + (9 + 3k^2 R^2 + k^4 R^4) (\mathbf{n}_R \cdot \mathbf{n}_D)^2 (\mathbf{n}_R \cdot \mathbf{n}_A)^2 + (-6 + 2k^2 R^2 - 2k^4 R^4) (\mathbf{n}_A \cdot \mathbf{n}_D) (\mathbf{n}_R \cdot \mathbf{n}_D) (\mathbf{n}_R \cdot \mathbf{n}_A), \quad (8.166)$$

where \mathbf{n}_R is the unit vector pointing from donor to acceptor. $T(\omega)$ together with Eq. (8.165) determine the energy transfer rate from donor to acceptor for arbitrary dipole orientation and arbitrary separations. Fig. 8.11 shows the normalized distance dependence of $T(\omega)$ for 3 different relative orientations of \mathbf{n}_D and \mathbf{n}_A . At short distances R , $T(\omega)$ is constant and the transfer rate in Eq. (8.165) decays as R^{-6} . For large distances R , $T(\omega)$ scales in most cases as R^{-4} and the transfer rate decays as R^{-2} .

In many situations the dipole orientations are not known and the transfer rate $\gamma_{D \rightarrow A}$ has to be determined by a statistical average over many donor-acceptor pairs. The same applies to one single donor-acceptor pair subject to random rotational diffusion. We therefore replace $T(\omega)$ by its orientational average $\langle T(\omega) \rangle$. The calculation

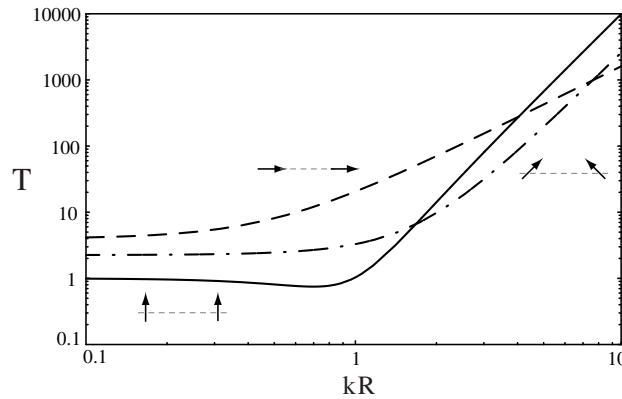


Figure 8.11: Dependence of the function $T(\omega)$ on the distance R between donor and acceptor for different dipole orientations. In all cases, the short distance behavior ($kR \ll 1$) is constant. Therefore the short distance transfer rate $\gamma_{D \rightarrow A}$ scales as R^{-6} . The long distance behavior ($kR \gg 1$) depends on the relative orientation of donor and acceptor. If the dipoles are aligned, $T(\omega)$ scales as $(kR)^2$ and $\gamma_{D \rightarrow A}$ decays as R^{-4} . In all other cases, the long distance behavior of $T(\omega)$ shows a $(kR)^4$ dependence and $\gamma_{D \rightarrow A}$ decays as $(kR)^{-2}$.

is similar to the procedure encountered before [c.f. Eq. (8.157)] and gives

$$\langle T(\omega) \rangle = \frac{2}{3} + \frac{2}{9}k^2R^2 + \frac{2}{9}k^4R^4. \quad (8.167)$$

The transfer rate decays very rapidly with distance between donor and acceptor. Therefore, only distances $R \ll 1/k$, where $k = 2\pi n(\omega)/\lambda$, are experimentally significant and the terms scaling with R^2 and R^4 in $T(\omega)$ can be neglected. In this limit, $T(\omega)$ is commonly denoted as κ^2 and the transfer rate can be expressed as

$$\frac{\gamma_{D \rightarrow A}}{\gamma_o} = \left[\frac{R_o}{R} \right]^6, \quad R_o^6 = \frac{9c^4\kappa^2}{8\pi} \int_0^\infty \frac{f_D(\omega) \sigma_A(\omega)}{n^4(\omega) \omega^4} d\omega, \quad (8.168)$$

where κ^2 is given by

$$\kappa^2 = [\mathbf{n}_A \cdot \mathbf{n}_D - 3(\mathbf{n}_R \cdot \mathbf{n}_D)(\mathbf{n}_R \cdot \mathbf{n}_A)]^2. \quad (8.169)$$

The process described by Eq. (8.168) is known as Förster energy transfer. It is named after Th. Förster who first derived this formula in 1946 in a slightly different form [28]. The quantity R_o is called the Förster radius and it indicates the efficiency of energy transfer between donor and acceptor. For $R = R_o$ the transfer rate $\gamma_{D \rightarrow A}$ is equal to the decay rate γ_o of the donor in absence of the acceptor. R_o is typically in the range of 2..9nm [29]. Notice that the refractive index $n(\omega)$ of the environment (solvent) is included in the definition of R_o . The Förster radius therefore has different values for different solvents. The literature is not consistent about the usage of $n(\omega)$ in R_o . A discussion can be found in Ref. [30]. The factor κ^2 has a value in the range $\kappa^2 = [0..4]$. The relative orientation of donor and acceptor is often not known and the orientational average

$$\langle \kappa^2 \rangle = \frac{2}{3} \quad (8.170)$$

is adopted for κ^2 .

In the limit of Förster energy transfer only the nonradiative near-field term in Eq. (8.167) is retained. For distances $kR \gg 1$ the transfer becomes radiative and scales with R^{-2} . In this limit we only retain the last term in Eq. (8.167). The result is identical with the quantum electrodynamical calculation by Andrews and Juzeliunas [31]. In the radiative limit the donor emits a photon and the acceptor absorbs the same photon. However, the probability for such an event is extremely small. Besides the R^{-6} and the R^{-2} terms we also find an intermediate term which scales as R^{-4} . The inclusion of this term is important for distances $kR \approx 1$.

Recently, it has been demonstrated that the energy transfer rate is modified in an inhomogeneous environment such as in a microcavity [32]. This modification follows directly from the formalism outlined in this section: the inhomogeneous environment has to be accounted for by a modified Green's function $\vec{\mathbf{G}}$ which not only alters the donor's decay rate γ_o but also the transfer rate $\gamma_{D \rightarrow A}$ through Eq. (8.160). Using the here developed formalism it is possible to calculate energy transfer in an arbitrary environment.

Example: Fluorescence resonance energy transfer (FRET)

In order to illustrate the derived formulas for energy transfer we shall calculate the fluorescence from a donor molecule and an acceptor molecule attached to specific sites of a protein. Such a configuration is encountered in studies of protein folding and molecular binding [33]. For the current example we choose *fluorescein* as the donor molecule and *Alexa Fluor 532* as the acceptor molecule. At room temperatures the emission and absorption spectra of donor and acceptor can be well fitted by a superposition of Gaussian distribution functions of the form

$$\sum_{n=1}^N A_n e^{-(\lambda - \lambda_n)^2 / \Delta \lambda_n^2} . \quad (8.171)$$

For the two dye molecules we obtain good fits with only two Gaussians ($N=2$). The parameters for the donor emission spectrum f_D are [$A_1 = 2.52 fs$, $\lambda_1 = 512.3 nm$, $\Delta \lambda_1 = 16.5 nm$; $A_2 = 1.15 fs$, $\lambda_2 = 541.7 nm$, $\Delta \lambda_2 = 35.6 nm$] and those for the acceptor absorption spectrum σ_A are [$A_1 = 0.021 nm^2$, $\lambda_1 = 535.8 nm$, $\Delta \lambda_1 = 15.4 nm$; $A_2 =$

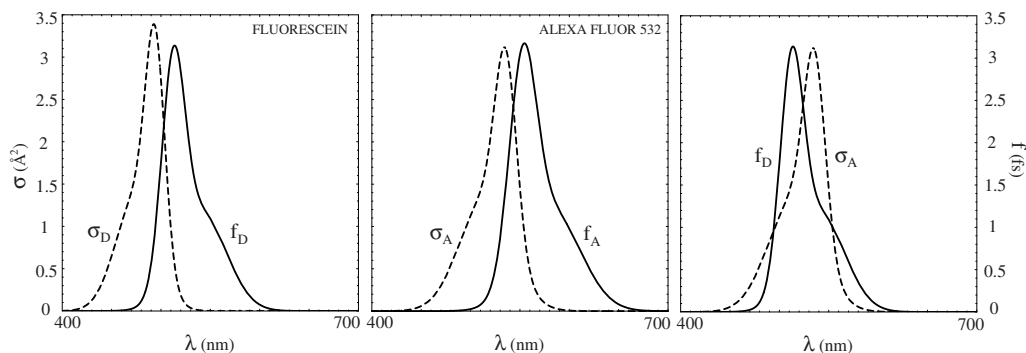


Figure 8.12: Absorption and emission spectra of donor (fluorescein) and acceptor (Alexa Fluor 532) fitted with a superposition of two Gaussian distribution functions. The figure on the right shows the overlap between f_D and σ_A which determines the value of the Förster radius.

$0.013nm^2$, $\lambda_2=514.9nm$, $\Delta\lambda_2=36.9nm$]. The fitted absorption and emission spectra are shown in Fig. 8.12. The third figure shows the overlap of the donor emission spectrum and the acceptor absorption spectrum. In order to calculate the transfer rate we adopt the orientational average of κ^2 from Eq. (8.167). For the index of refraction we choose $n=1.33$ (water) and we ignore any dispersion effects. Thus, the Förster radius is calculated as

$$R_o = \left[\frac{3c}{32\pi^4 n^4} \int_0^\infty f_D(\lambda) \sigma_A(\lambda) \lambda^2 d\lambda \right]^{1/6} = 6.3nm, \quad (8.172)$$

where we substituted ω by $2\pi c/\lambda$.* In air ($n=1$) the Förster radius would be $R_o = 7.6nm$ which indicates that the local medium has a strong influence on the transfer rate.

In order to experimentally measure energy transfer the donor molecule has to be promoted into its excited state. We choose an excitation wavelength of $\lambda_{exc}=488nm$ which is close to the peak of fluorescein absorption of $\lambda=490nm$. At λ_{exc} the acceptor absorption is a factor of four lower than the donor absorption. The non-zero absorption cross-section of the acceptor will lead to a background acceptor fluorescence signal. With the help of spectral filtering it is possible to experimentally separate the fluorescence emission from donor and acceptor. Energy transfer from donor to acceptor is then observed as a decrease of the donor's fluorescence intensity and as an increase of the acceptor's fluorescence intensity. The energy transfer efficiency E

*Notice that in the λ -representation the emission spectrum needs to be normalized as $2\pi c \int_0^\infty f_D(\lambda)/\lambda^2 d\lambda = 1$.

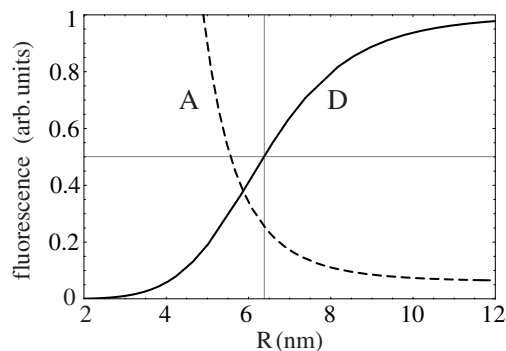


Figure 8.13: Fluorescence intensity of donor and acceptor as a function of their separation R . The donor emission drops to one half at the distance $R=R_o$. The acceptor fluorescence increases as R^{-6} and saturates at a value determined by the acceptor's excited state lifetime.

is usually defined as the relative change of the donor's fluorescence emission

$$E = \frac{P_o}{P_o + P_{D \rightarrow A}} = \frac{1}{1 + (\gamma_o/\gamma_{D \rightarrow A})} = \frac{1}{1 + (R/R_o)^6} . \quad (8.173)$$

Fig. 8.13 illustrates the change of donor and acceptor fluorescence as a function of their separation R . It is assumed that the absorption cross-section of the acceptor is sufficiently small at the excitation wavelength λ_{exc} . At the distance $R = R_o$ the emission of the donor drops to one half. The fluorescence intensity of the acceptor increases as R^{-6} and it saturates at a level determined by the lifetime of the acceptor's excited state.

In single molecule experiments it is important to know the orientation of donor and acceptor. Depending on the relative orientation the value of κ^2 can vary in the range $\kappa^2 = [0..4]$. It is common practice to adopt the averaged value of $\kappa^2 = 2/3$. However, this might affect the conclusions drawn on basis of experimental data. In addition to measurements of the transfer efficiency E it is necessary to determine the orientation of the donor and acceptor dipoles in three dimensions.

8.7 Delocalized excitations (strong coupling)

The theory of Förster energy transfer assumes that the transfer rate from donor to acceptor is smaller than the vibrational relaxation rate. This ensures that once the energy is transferred to the acceptor, there is little chance of a backtransfer to the donor.

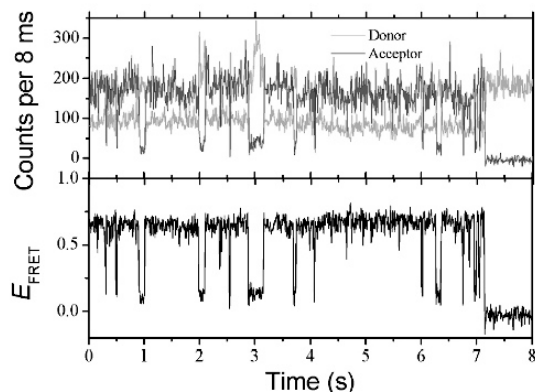


Figure 8.14: Time trajectory of donor and acceptor fluorescence and corresponding FRET efficiency for a donor-acceptor pair attached to a four-way DNA (Holliday) junction. The data indicates that the DNA structure is switching back and forth between two conformations. From Ref. [34].

However, if the dipole-dipole interaction energy is larger than the energy associated with vibrational broadening of the electronic excited states a delocalized excitation of donor and acceptor is more probable. In this so called *strong coupling* regime it is not possible to distinguish between donor and acceptor and one must view the pair as one system, i.e. the excitation becomes delocalized over the pair of particles. If the uncoupled eigenstates of donor and acceptor are $|\Phi_D\rangle$ and $|\Phi_A\rangle$, respectively, then the coupled eigenstates become $[|\Phi_D\rangle \pm |\Phi_A\rangle]/\sqrt{2}$. In this section we discuss strong coupling between a pair of particles A and B , but the analysis can be extended to larger systems such as *J-aggregates* which are chains of strongly coupled molecules. There is no adequate classical theory and we have to use the principles of quantum mechanics.

We consider two particles A and B which are represented by two-level systems. In the absence of any interactions between the two particles the ground state and eigenvalue of A are denoted as $|A\rangle$ and E_A , respectively, and for the excited state we use $|A^*\rangle$ and E_A^* (c.f. Fig. 8.15). Similar notation is used for the eigenstates and eigenvalues of B . To solve the coupled system exactly, we could proceed by defining four states $|AB\rangle, |A^*B\rangle, |AB^*\rangle, |A^*B^*\rangle$ which satisfy the Schrödinger equation of the uncoupled system

$$[\hat{H}_A + \hat{H}_B]|\phi_n\rangle = e_n |\phi_n\rangle . \quad (8.174)$$

Here, $|\phi_n\rangle$ is any of the defined four states and E_n denotes the eigenvalue associated with this state, i.e. $e_n \in [(E_A + E_B), (E_A^* + E_B), (E_A + E_B^*), (E_A^* + E_B^*)]$. After introducing interaction terms between the four states, the Schrödinger equation of the coupled system becomes

$$[\hat{H}_A + \hat{H}_B + \hat{V}_{int}]|\Phi_n\rangle = E_n |\Phi_n\rangle , \quad (8.175)$$

where \hat{V}_{int} is the interaction Hamiltonian, $|\Phi_n\rangle$ are the new eigenstates and E_n the new eigenvalues. To determine the eigenstates $E_n = \langle \Phi_n | \hat{H}_A + \hat{H}_B + \hat{V}_{int} | \Phi_n \rangle$ we can now expand the new eigenstates in terms of the old eigenstates as

$$|\Phi_n\rangle = a_n |AB\rangle + b_n |A^*B\rangle + c_n |AB^*\rangle + d_n |A^*B^*\rangle , \quad (8.176)$$

and diagonalize the Hamiltonian $[\hat{H}_A + \hat{H}_B + \hat{V}_{int}]$ using standard procedures.

The problem of this rigorous approach is the lack of information of the coupling terms that lead to V_{int} . These terms are defined by the combined system of particles A and B . They only approximately correspond to the interparticle interaction potentials V_{AB} in Eq. (8.148). V_{int} could be determined by first rigorously solving the Schrödinger equation of the combined system of particles and then trying to decouple the unperturbed Hamiltonians from the system. But this is a difficult task. To better understand this subtle point let us consider a system made of two electrons, two neutrons and two protons. The resulting element is known as Helium (He^4). If the particles are equally divided into two separate systems we obtain two Deuterium

atoms (D). It is quite evident, that it is challenging to view He^4 as two interacting deuterium atoms.

Since the exact parameters of a coupled system are not known *a priori* it is favorable to describe the interaction between two particles in terms of their unperturbed parameters. In this picture, the interaction between two particles can be viewed as a perturbation of the two isolated particles. In particular, if we assume that the dipole moments of particle A and particle B are known, the interaction between the two particles can be described in terms of the interparticle interaction potentials V_{AB} in Eq. (8.148). Assuming that the two particles are charge neutral, the leading term in the interaction becomes the dipole-dipole interaction.

Using first order non-degenerate perturbation theory [35], we write for the states of the ground state $|0\rangle$ and the doubly excited state $|A^*B^*\rangle$ of the coupled system

$$|0\rangle = |AB\rangle = |A\rangle|B\rangle \quad (8.177)$$

$$|2\rangle = |A^*B^*\rangle = |A^*\rangle|B^*\rangle \quad (8.178)$$

and obtain the following first-order corrected energy eigenstates

$$E_0 = E_A + E_B + \langle 0|V_{AB}|0\rangle \quad (8.179)$$

$$E_2 = E_{A^*} + E_{B^*} + \langle 2|V_{AB}|2\rangle . \quad (8.180)$$

Thus, the coupling between A and B gives rise to a displacement of the ground state energy and the energy of the doubly excited state. For the singly excited states $|1^+\rangle$ and $|1^-\rangle$ we cannot proceed in the same way. If the particles A and B were identical, the unperturbed singly excited states $|A^*B\rangle$ and $|AB^*\rangle$ would be degenerate. Even if the two particles are not identical, non-degenerate perturbation theory can only be applied if the energy separation of the unperturbed states,

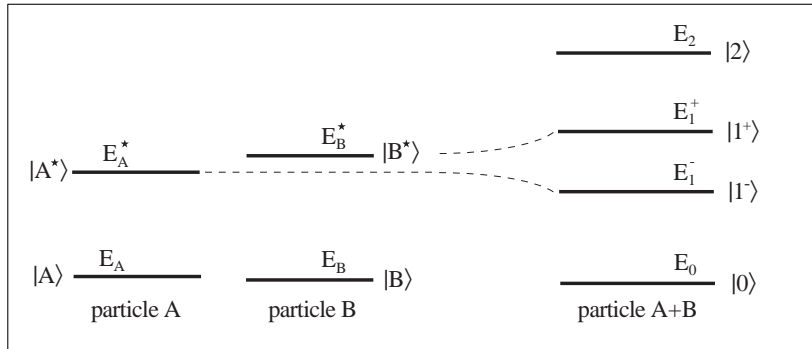


Figure 8.15: Coherent interaction between two particles A and B . In the resonant limit, the excitation becomes delocalized over the two particles.

$\Delta E = |(E_A^* + E_B) - (E_A + E_B^*)|$, is much bigger than the strength of the perturbations $\langle A^*B | V_{AB} | AB^* \rangle$ and $\langle AB^* | V_{AB} | A^*B \rangle$. If this is not the case, degenerate perturbation theory has to be applied even to a non-degenerate system. Therefore, we define the states $|1^+\rangle$ and $|1^-\rangle$ of the coupled system as a linear combination of the unperturbed states

$$|1^+\rangle = \cos \alpha |A^*B\rangle + \sin \alpha |AB^*\rangle = \cos \alpha |A^*\rangle |B\rangle + \sin \alpha |A\rangle |B^*\rangle \quad (8.181)$$

$$|1^-\rangle = \sin \alpha |A^*B\rangle - \cos \alpha |AB^*\rangle = \sin \alpha |A^*\rangle |B\rangle - \cos \alpha |A\rangle |B^*\rangle, \quad (8.182)$$

where α is an arbitrary coefficient to be determined later. The states $|1^+\rangle$ and $|1^-\rangle$ have to satisfy the Schrödinger equations

$$[\hat{H}_A + \hat{H}_B + V_{AB}] |1^+\rangle = E_1^+ |1^+\rangle \quad (8.183)$$

$$[\hat{H}_A + \hat{H}_B + V_{AB}] |1^-\rangle = E_1^- |1^-\rangle, \quad (8.184)$$

To facilitate notation we introduce the following abbreviations

$$W_{A^*B} = \langle A^*B | V_{AB} | A^*B \rangle, \quad W_{AB^*} = \langle AB^* | V_{AB} | AB^* \rangle \quad (8.185)$$

Inserting $|1^+\rangle$ from Eq. (8.181) into Eq. (8.183) and operating from the left with $\langle 1^+ |$ we obtain

$$E_1^+ = \sin^2 \alpha [E_A + E_{B^*} + W_{AB^*}] + \cos^2 \alpha [E_{A^*} + E_B + W_{A^*B}] + 2 \sin \alpha \cos \alpha \operatorname{Re} \{ \langle A^*B | V_{AB} | AB^* \rangle \}. \quad (8.186)$$

We made use of the fact that \hat{H}_A operates only on the states of particle A and \hat{H}_B operates only on the states of particle B . We also applied the orthogonality relations $\langle A|A\rangle = 1$, $\langle A^*|A\rangle = 0$, $\langle B|B\rangle = 1$, and $\langle B^*|B\rangle = 0$. Furthermore, since V_{AB} is a Hermitian operator we have $[\langle AB^* | V_{AB} | A^*B \rangle]^* = \langle A^*B | V_{AB} | AB^* \rangle$, with $[\dots]^*$ denoting the complex conjugate. The energy E^- is derived in a similar way as

$$E_1^- = \cos^2 \alpha [E_A + E_{B^*} - W_{AB^*}] + \sin^2 \alpha [E_{A^*} + E_B + W_{A^*B}] - 2 \sin \alpha \cos \alpha \operatorname{Re} \{ \langle A^*B | V_{AB} | AB^* \rangle \}. \quad (8.187)$$

The energy levels E^+ and E^- depend on the coefficient α which can be determined by requiring orthogonality between the states $|1^+\rangle$ and $|1^-\rangle$. Operating with $\langle 1^- |$ on Eq. (8.183) and making use of $\langle 1^- | 1^+ \rangle = 0$ leads to the condition

$$\langle 1^- | \hat{H}_A + \hat{H}_B + V_{AB} | 1^+ \rangle = 0 \quad (8.188)$$

from which we derive

$$\tan 2\alpha = \frac{2 \operatorname{Re} \{ \langle A^*B | V_{AB} | AB^* \rangle \}}{[E_{A^*} + E_B + W_{A^*B}] - [E_A + E_{B^*} + W_{AB^*}]}. \quad (8.189)$$

The coefficient α can have any value in the range $[0.. \pi/2]$ depending on the strength of interaction between particles A and B . A better insight is gained by considering

the two limiting cases of $\alpha = 0$ ($\alpha = \pi/2$) and $\alpha = \pi/4$.

For $\alpha = 0$, the singly excited states reduce to $|1^+\rangle = |A^*B\rangle$ and $|1^-\rangle = -|AB^*\rangle$. Thus, in state $|1^+\rangle$ the excitation is entirely localized on particle A whereas in state $|1^-\rangle$ the excitation is localized on particle B . The energy eigenvalues become

$$E_1^+ = [E_{A^*} + E_B + W_{A^*B}] \quad (\alpha=0) \quad (8.190)$$

$$E_1^- = [E_A + E_{B^*} + W_{A^*B}] \quad (\alpha=0). \quad (8.191)$$

There is no energy level splitting if A and B are identical particles. The interaction gives only rise to a level shift by an amount of W_{A^*B} .

The situation is similar for the case $\alpha = \pi/2$ for which the roles of A and B are simply reversed. The singly excited states become $|1^+\rangle = |AB^*\rangle$ and $|1^-\rangle = |A^*B\rangle$ and the energy eigenvalues are

$$E_1^+ = [E_A + E_{B^*} + W_{AB^*}] \quad (\alpha=\pi/2) \quad (8.192)$$

$$E_1^- = [E_{A^*} + E_B + W_{AB^*}] \quad (\alpha=\pi/2) \quad (8.193)$$

If the nominator of Eq. (8.189) goes to infinity or if the denominator goes to zero we obtain the limiting case of $\alpha = \pi/4$. For this so-called resonant case the excitation is distributed equally over both particles and the energy eigenvalues read as

$$E_1^+ = \frac{1}{2} [E_A + E_{A^*} + E_B + E_{B^*} + W_{AB^*} + W_{A^*B}] + \operatorname{Re} \{ \langle A^*B | V_{AB} | AB^* \rangle \} \quad (\alpha=\pi/4) \quad (8.194)$$

$$E_1^- = \frac{1}{2} [E_A + E_{A^*} + E_B + E_{B^*} + W_{AB^*} + W_{A^*B}] - \operatorname{Re} \{ \langle A^*B | V_{AB} | AB^* \rangle \} \quad (\alpha=\pi/4) \quad (8.195)$$

This delocalized excitation is also denoted as *exciton* and the regime for which $\alpha \approx \pi/4$ is called the *strong coupling* regime. Delocalized excitation is always achieved if particles A and B are identical. In general, we have to require that

$$\operatorname{Re} \{ \langle A^*B | V_{AB} | AB^* \rangle \} \gg \frac{1}{2} ([E_{A^*} + E_B + W_{A^*B}] - [E_A + E_{B^*} + W_{AB^*}]). \quad (8.196)$$

Our analysis shows that the interaction between two identical particles leads to a level splitting of the singly excited states. In case of many interacting particles, the multiple splitting of the singly excited states will lead to an energy band (exciton band). Delocalized excitation is based on a coherent superposition of states. The time required to establish this coherence is on the order of $\tau_c = \hbar/V_{AB}$. Vibronic coupling can easily destroy the coherence within a few picoseconds. As a result, the excitation becomes localized and incoherent energy transfer between particles (Förster energy transfer) becomes more probable. In general, strong coupling in a system can only be

established if τ_c is larger than vibrational relaxation times τ_{vib} .

As an illustration of strong coupling, Fig. 8.16 shows the level splitting of two *InAs* quantum dots separated by a *GaAs* barrier of variable thickness. The peaks correspond to the emission of the ground state exciton (s-shell) and first excited state exciton (p-shell). At large separations, only one ground state emission line is seen, but as the barrier thickness is decreased the emission line splits. The same is true for the first excited state exciton although only the lower energy level is shown. In these experiments, low excitation powers were used to prevent the excitation of multiexcitons.

8.7.1 Entanglement

The concept of entanglement is becoming increasingly important in the context of quantum information theory. The concept is adopted from the German "*verschränkter Zustand*" and was first introduced by Schrödinger [37]. It refers to a combined state of two systems (e.g. the singly excited states encountered in the previous section) that cannot be written as a product of the individual states. More qualitatively, entanglement refers to the degree of 'quantum memory' in a system. There exist different definitions for the degree of entanglement but we restrict the discussion to the so-

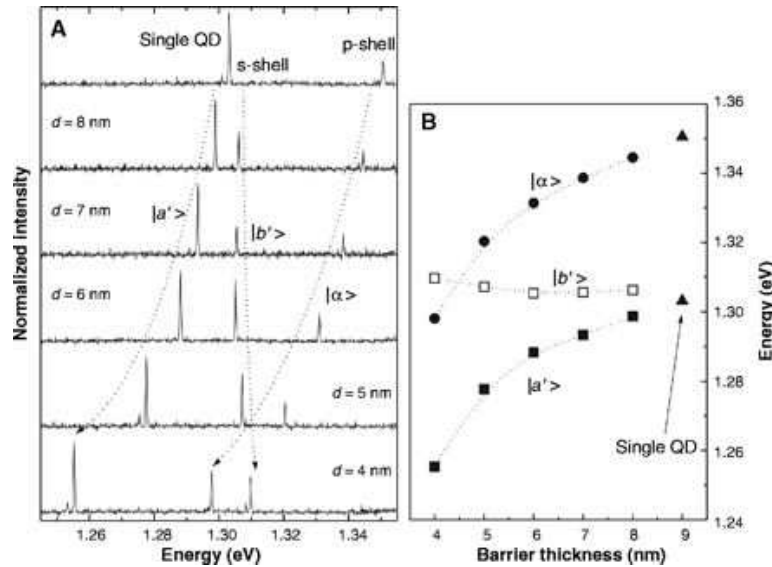


Figure 8.16: Level splitting of two *InAs* quantum dots separated by a *GaAs* barrier. (A) Emission spectra at $T \approx 60K$ for varying dot separation d . (B) Corresponding energy level diagram. From Ref. [36].

called *Schmidt decomposition* applicable to pure states [38].

Entanglement refers to a joint property of *two* systems A and B , a so-called bipartite system. Each system is characterized by its eigenstates, i.e. $|A_n\rangle$ and $|B_m\rangle$ with $n = 1, 2, \dots, N$ and $m = 1, 2, \dots, M$. A and B are called *qubits* if $N = M = 2$. The combined system of $A+B$ has its own eigenstates $|\Psi_i\rangle$ which can be arbitrarily superimposed and which define the density matrix

$$\hat{\rho} = |\Psi\rangle\langle\Psi|. \quad (8.197)$$

Because $|\Psi\rangle$ can be expressed in terms of $|A_n\rangle$ and $|B_m\rangle$ we define the *reduced* density matrices $\hat{\rho}_A$ and $\hat{\rho}_B$ as

$$\begin{aligned} \hat{\rho}_A &= \text{Tr}_B [\hat{\rho}] = \sum_m \langle B_m | \hat{\rho} | B_m \rangle \\ \hat{\rho}_B &= \text{Tr}_A [\hat{\rho}] = \sum_n \langle A_n | \hat{\rho} | A_n \rangle, \end{aligned} \quad (8.198)$$

where 'Tr' stands for trace. A given (normalized) state $|\Psi\rangle$ is called *separable* if all but one of the eigenvalues λ_i of the reduced density matrix $\hat{\rho}_A$ are zero. It can be shown that $\hat{\rho}_B$ has the same eigenvalues and so it suffices to consider only one of the reduced matrices. Notice that the sum of all λ_i is equal to one. If $|\Psi\rangle$ is *not* separable the state is called entangled and the degree of entanglement is defined by the *Grober-Rzazewski-Eberly* number [39]

$$K = \left[\sum_i \lambda_i^2 \right]^{-1}, \quad (8.199)$$

which is always larger or equal than one and smaller or equal than the total number of nonzero eigenvalues.

As an example, let us discuss the state

$$|1^+\rangle = \cos\alpha |A^*B\rangle + \sin\alpha |AB^*\rangle \quad (8.200)$$

encountered in the previous section. This is a state of the combined system of A ($|A\rangle, |A^*\rangle$) and B ($|B\rangle, |B^*\rangle$). Thus, $N = M = 2$. The density matrix $\hat{\rho}$ is calculated as

$$\begin{aligned} \hat{\rho} &= [\cos\alpha |A^*B\rangle + \sin\alpha |AB^*\rangle] [(\cos\alpha)^* \langle A^*B| + (\sin\alpha)^* \langle AB^*|] \\ &= \cos^2\alpha |A^*B\rangle \langle A^*B| + \sin^2\alpha |AB^*\rangle \langle AB^*| + \\ &\quad \sin\alpha \cos\alpha |A^*B\rangle \langle AB^*| + \sin\alpha \cos\alpha |AB^*\rangle \langle A^*B| \end{aligned} \quad (8.201)$$

and the reduced density matrix $\hat{\rho}_A$ becomes

$$\hat{\rho}_A = \cos^2\alpha |A^*\rangle \langle A^*| + \sin^2\alpha |A\rangle \langle A| = \begin{bmatrix} \cos^2\alpha & 0 \\ 0 & \sin^2\alpha \end{bmatrix}, \quad (8.202)$$

where we have made use of the orthonormality of $|B\rangle$ and $|B^*\rangle$. Because the off-diagonal elements are zero the eigenvalues are $\lambda_1 = \sin^2\alpha$, $\lambda_2 = \cos^2\alpha$ and the *Grobe-Rzazewski-Eberly* number becomes

$$K = \frac{1}{\sin^4\alpha + \cos^4\alpha} \quad (8.203)$$

Thus, the state $|1^+\rangle$ is separable if $\alpha = 0$ or $\alpha = \pi/2$. For angles in between the state is entangled. For $\alpha = \pi/4$ the state is maximally entangled ($K = 2$) and is called a *Bell state*. This is consistent with our discussion in the previous section where we determined that for $\alpha = \pi/4$ the excitation is equally distributed over the two particles (resonant case) and that the strongest coupling is achieved in this case. Finally, it should be noted that the Schmidt decomposition works only for pure states and that different procedures have to be applied to mixed states.

Problems

Problem 8.1 Derive the potential energy V for a system of two charges $q, -q$ in an external field \mathbf{E}, \mathbf{H} . The charges are separated by a vector \mathbf{s} with $s = |\mathbf{s}| \ll \lambda$. Calculate first the force $\mathbf{F} = (m_1 + m_2)\ddot{\mathbf{r}}$ acting on the two charges and expand \mathbf{F} in a Taylor series with origin \mathbf{r} at the center of the two charges. Retain only the lowest order in the expansion. Then, derive V for the two cases of

1. Permanent dipole moment $\boldsymbol{\mu}$.
2. Induced dipole moment $\boldsymbol{\mu} = \alpha\mathbf{E}$.

Problem 8.2 Derive the farfield Green's function $\vec{\mathbf{G}}_{FF}$ in spherical coordinates and Cartesian vector components. Calculate the radiation pattern $P(\vartheta, \varphi)/P$ for a dipole $\boldsymbol{\mu}$ which encloses an angle α with the z -axis.

Problem 8.3 Proof that the near-field and farfield terms of a dipole in free space do not contribute to radiation.

Problem 8.4 Calculate the interaction energy between two dipoles given by $V = -\boldsymbol{\mu}_1 \cdot \mathbf{E}_2(\mathbf{r}_1) - \boldsymbol{\mu}_2 \cdot \mathbf{E}_1(\mathbf{r}_2)$. $\mathbf{E}_1(\mathbf{r}_2)$ is the field of dipole $\boldsymbol{\mu}_1$ evaluated at the position \mathbf{r}_2 of dipole $\boldsymbol{\mu}_2$. Similarly, $\mathbf{E}_2(\mathbf{r}_1)$ is the field of dipole $\boldsymbol{\mu}_2$ evaluated at the position \mathbf{r}_1 of dipole $\boldsymbol{\mu}_1$. Separate the near-field, intermediate-field, and farfield interactions.

Problem 8.5 In section 8.3.4 it was pointed out that radiation reaction is necessary to account for light scattering from particles that are treated in the dipole limit. In this exercise we derive a correction for the particle polarizability α in order to be consistent with the optical theorem.

1. The radiation reaction force \mathbf{F}_r defines a self-field \mathbf{E}_{self} according to $\mathbf{F}_r = q\mathbf{E}_{\text{self}}$. Express Eq. (8.85) in terms of the dipole moment $\boldsymbol{\mu} = q\mathbf{r}$ and represent the associated self-field in frequency domain, i.e. find $\mathbf{E}_{\text{self}}(\omega)$.
2. The dipole $\boldsymbol{\mu}$ is induced by the local field consisting of the external field \mathbf{E}_o and the self-field \mathbf{E}_{self} according to $\boldsymbol{\mu} = \alpha(\omega)[\mathbf{E}_o + \mathbf{E}_{\text{self}}]$. On the other hand, the self-field itself is induced by the external field \mathbf{E}_o . Show that in order to relate the dipole only to the external field the polarizability has to be expressed in terms of an effective polarizability given by

$$\alpha_{\text{eff}}(\omega) = \alpha(\omega) + i \frac{(\omega/c)^3}{6\pi\epsilon_o} \alpha^2(\omega). \quad (8.204)$$

When applied to the optical theorem, the first term in α_{eff} leads to absorption whereas the second term defines scattering. The inconsistency of the optical theorem in the dipole limit is also discussed in Problem ??.

Problem 8.6 The partial local density of states ρ_μ depends on the orientation of the unit vector \mathbf{n}_μ . Show that by averaging \mathbf{n}_μ over all orientations, ρ_μ becomes identical with the total density of states ρ . It suffices to show that

$$\langle \mathbf{n}_\mu \cdot \text{Im}\{\vec{\mathbf{G}}\} \cdot \mathbf{n}_\mu \rangle = \frac{1}{3} \text{Im}\{Tr[\vec{\mathbf{G}}]\} .$$

Problem 8.7 In free-space, the partial local density of states ρ_μ is identical to the total density of states ρ . To show this, proof that

$$[\mathbf{n}_\mu \cdot \text{Im}\{\vec{\mathbf{G}}_o\} \cdot \mathbf{n}_\mu] = \frac{1}{3} \text{Im}\{Tr[\vec{\mathbf{G}}_o]\} ,$$

where $\vec{\mathbf{G}}_o$ is the free-space dyadic.

Problem 8.8 A molecule with emission dipole moment in direction of the x-axis is scanned in the x, y plane. A spherical gold particle ($\varepsilon = -7.6 + 1.7i$) with radius $r_o = 10\text{nm}$ is placed above the x, y plane. The emission wavelength is $\lambda = 575\text{nm}$ (*DiI* molecule). The center of the particle is located at the fixed position $(x, y, z) = (0, 0, 20\text{nm})$.

1. Calculate the normalized decay rate γ/γ_o as a function of x, y . Neglect retardation effects and draw a contour plot. What is the minimum value of γ/γ_o ? How does the quenching rate scale with the sphere radius r_o ?
2. Repeat the calculation for a dipole oriented in direction of the z -axis.

Problem 8.9 Two molecules, *fluorescein* (donor) and *alexa green 532* (acceptor), are located in a plane centered between two perfectly conducting surfaces separated by the distance d . The emission spectrum of the donor (f_D) and the absorption spectrum of the acceptor (σ_A) are approximated by a superposition of two Gaussian distribution functions. Use the fit parameters from Section 8.6.2.

1. Determine the Green's function for this configuration.
2. Calculate the decay rate γ_o of the donor in the absence of the acceptor.
3. Determine the transfer rate $\gamma_{D \rightarrow A}$ as a function of the separation R between donor and acceptor. Assume random dipole orientations.
4. Plot the Förster radius R_o as a function of the separation d .

Problem 8.10 Prove Eq. 8.189 by following the steps in Section 8.7.

Problem 8.11 Consider the state

$$|\Psi\rangle = \beta_1 |1^+\rangle + \beta_2 |1^-\rangle ,$$

where $|1^+\rangle$ and $|1^-\rangle$ are defined by Eqs. (8.181) and (8.182), respectively. Assume that $|1^+\rangle$ and $|1^-\rangle$ are maximally entangled states ($\alpha = \pi/4$) and investigate the separability of $|\Psi\rangle$ as a function of β_1 and β_2 . Can superpositions of entangled states be unentangled? Determine the *Grobe-Rzazewski-Eberly* number.

Problem 8.12 Systems A and B are three-level systems with the states $|-1\rangle$, $|0\rangle$, and $|1\rangle$. Determine the combined, maximally entangled state(s).

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