

\mathbf{r}_o which is typically at the center of the charge distribution [1]. If we keep only the lowest order term we find

$$\mathbf{j}(\mathbf{r}, t) = \frac{d}{dt} \mathbf{p}(t) \delta[\mathbf{r} - \mathbf{r}_o], \quad (3.24)$$

with the dipole moment

$$\mathbf{p}(t) = \sum_n q_n [\mathbf{r}_n(t) - \mathbf{r}_o]. \quad (3.25)$$

The dipole moment is identical with the definition in Eq. 3.15 for which we had $\mathbf{r}_o = 0$. We assume a time harmonic time-dependence which allows us to write the current density as $\mathbf{j}(\mathbf{r}, t) = \text{Re}\{\mathbf{j}(\mathbf{r}) \exp(-i\omega t)\}$ and the dipole moment as $\mathbf{p}(t) = \text{Re}\{\mathbf{p} \exp(-i\omega t)\}$. Eq. 3.24 can then be written as

$$\mathbf{j}(\mathbf{r}) = -i\omega \mathbf{p} \delta[\mathbf{r} - \mathbf{r}_o]. \quad (3.26)$$

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

3.2.1 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 $\mathbf{p} = qd\mathbf{s}$. However, it is more elegant to derive the dipole fields using the Green's function formalism developed in Section 1.3. There, we have derived the so-called volume integral equations (c.f. Eq. 1.60 and Eq. 1.61)

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_o + i\omega \mu \mu_o \int_V \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}') \mathbf{j}(\mathbf{r}') dV', \quad (3.27)$$

$$\mathbf{H}(\mathbf{r}) = \mathbf{H}_o + \int_V [\nabla \times \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}')] \mathbf{j}(\mathbf{r}') dV'. \quad (3.28)$$

$\vec{\mathbf{G}}$ 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. 3.26 into the last two equations and assume that all fields are produced by the dipole we find

$$\mathbf{E}(\mathbf{r}) = \omega^2 \mu \mu_o \int_V \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o) \mathbf{p}, \quad (3.29)$$

$$\mathbf{H}(\mathbf{r}) = -i\omega [\nabla \times \vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o)] \mathbf{p}. \quad (3.30)$$

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

$$\vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o) = \left[\vec{\mathbf{I}} + \frac{1}{k^2} \nabla \nabla \right] G(\mathbf{r}, \mathbf{r}_o), \quad G(\mathbf{r}, \mathbf{r}_o) = \frac{\exp(ik|\mathbf{r} - \mathbf{r}_o|)}{4\pi|\mathbf{r} - \mathbf{r}_o|}. \quad (3.31)$$

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

$$\vec{\mathbf{G}}(\mathbf{r}, \mathbf{r}_o) = \frac{\exp(ikR)}{4\pi R} \left[\left(1 + \frac{ikR - 1}{k^2 R^2} \right) \vec{\mathbf{I}} + \frac{3 - 3ikR - k^2 R^2}{k^2 R^2} \frac{\mathbf{R}\mathbf{R}}{R^2} \right], \quad (3.32)$$

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. 3.32 defines a symmetric 3×3 matrix

$$\vec{\mathbf{G}} = \begin{bmatrix} G_{xx} & G_{xy} & G_{xz} \\ G_{xy} & G_{yy} & G_{yz} \\ G_{xz} & G_{yz} & G_{zz} \end{bmatrix}, \quad (3.33)$$

which, together with Eqs. 3.29 and 3.30, determines the electromagnetic field of an arbitrary electric dipole \mathbf{p} with Cartesian components p_x, p_y, p_z .

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

$$\vec{\mathbf{G}} = \vec{\mathbf{G}}_{NF} + \vec{\mathbf{G}}_{IF} + \vec{\mathbf{G}}_{FF}, \quad (3.34)$$

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

$$\vec{\mathbf{G}}_{NF} = \frac{\exp(ikR)}{4\pi R} \frac{1}{k^2 R^2} [-\vec{\mathbf{I}} + 3\mathbf{R}\mathbf{R}/R^2], \quad (3.35)$$

$$\vec{\mathbf{G}}_{IF} = \frac{\exp(ikR)}{4\pi R} \frac{i}{kR} [\vec{\mathbf{I}} - 3\mathbf{R}\mathbf{R}/R^2], \quad (3.36)$$

$$\vec{\mathbf{G}}_{FF} = \frac{\exp(ikR)}{4\pi R} [\vec{\mathbf{I}} - \mathbf{R}\mathbf{R}/R^2]. \quad (3.37)$$

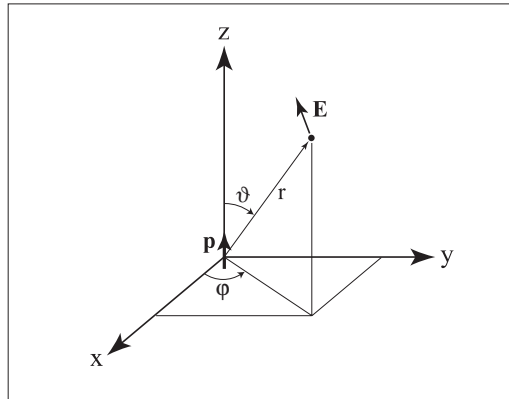


Figure 3.2: The fields of a dipole are most conveniently represented in a spherical coordinate system (r, ϑ, φ) in which the dipole points along the z -axis ($\vartheta = 0$).

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. $\mathbf{p} = p\mathbf{n}_z$ (c.f. Fig. 3.2). 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

$$E_r = \frac{p \cos \vartheta}{4\pi\epsilon_o\epsilon} \frac{\exp(ikr)}{r} k^2 \left[\frac{2}{k^2 r^2} - \frac{2i}{kr} \right], \quad (3.38)$$

$$E_\vartheta = \frac{p \sin \vartheta}{4\pi\epsilon_o\epsilon} \frac{\exp(ikr)}{r} k^2 \left[\frac{1}{k^2 r^2} - \frac{i}{kr} - 1 \right], \quad (3.39)$$

$$H_\varphi = \frac{p \sin \vartheta}{4\pi\epsilon_o\epsilon} \frac{\exp(ikr)}{r} k^2 \left[-\frac{i}{kr} - 1 \right] \sqrt{\frac{\epsilon_o\epsilon}{\mu_o\mu}}. \quad (3.40)$$

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.

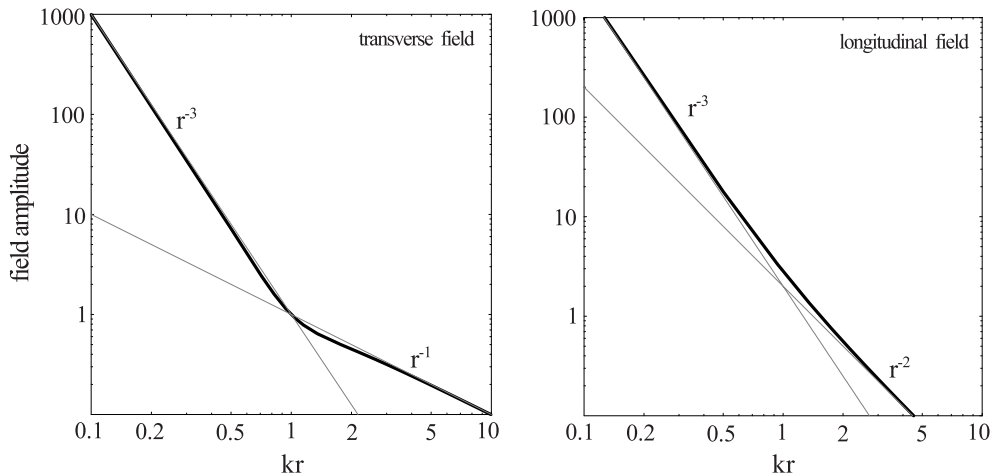


Figure 3.3: Radial decay of the dipole's transverse and longitudinal fields. The curves correspond to the absolute value of the expressions in brackets of Eq. 3.38 and Eq. 3.39, respectively. While both the transverse and the longitudinal field contribute to the near-field, only the transverse field 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 $(kr) > 1$.

So far we have considered a dipole which oscillates harmonically in time, i.e. $\mathbf{p}(t) = \text{Re}\{\mathbf{p} \exp(-i\omega t)\}$. 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 $\mathbf{p}(t)$ with arbitrary time dependence can be derived by using the time-dependent Green's function. In a nondispersive medium it is easier to introduce the explicit time dependence by using the substitutions

$$\exp(ikr) k^m \mathbf{p} = \exp(ikr) \left[\frac{in}{c} \right]^m (-i\omega)^m \mathbf{p} \rightarrow \left[\frac{in}{c} \right]^m \frac{d^m}{dt^m} \mathbf{p}(t - rn/c) , \quad (3.41)$$

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

$$E_r(t) = \frac{\cos \vartheta}{4\pi\epsilon_o\epsilon} \left[\frac{2}{r^3} + \frac{n}{c} \frac{2}{r^2} \frac{d}{dt} \right] p(t - rn/c) , \quad (3.42)$$

$$E_\vartheta(t) = \frac{\sin \vartheta}{4\pi\epsilon_o\epsilon} \left[\frac{1}{r^3} + \frac{n}{c} \frac{1}{r^2} \frac{d}{dt} + \frac{n^2}{c^2} \frac{1}{r} \frac{d^2}{dt^2} \right] p(t - rn/c) , \quad (3.43)$$

$$H_\varphi(t) = \frac{\sin \vartheta}{4\pi\epsilon_o\epsilon} \sqrt{\frac{\epsilon_o\epsilon}{\mu_o\mu}} \left[\frac{n}{c} \frac{1}{r^2} \frac{d}{dt} + \frac{n^2}{c^2} \frac{1}{r} \frac{d^2}{dt^2} \right] p(t - rn/c) . \quad (3.44)$$

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.

3.2.2 Dipole radiation

It can be shown (see Problem 3.3) 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

$$\mathbf{S}(t) = \mathbf{E}(t) \times \mathbf{H}(t) = \frac{1}{16\pi^2\epsilon_o\epsilon} \frac{\sin^2 \vartheta}{r^2} \frac{n^3}{c^3} \left[\frac{d^2}{dt^2} p(t - rn/c) \right]^2 \mathbf{n}_r . \quad (3.45)$$

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

$$P(t) = \int_{\partial V} \mathbf{S} \cdot \mathbf{n} da = \frac{1}{4\pi\epsilon_o\epsilon} \frac{2n^3}{3c^3} \left[\frac{d^2 p(t)}{dt^2} \right]^2 , \quad (3.46)$$

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

$$\bar{P} = \frac{p^2}{4\pi\epsilon_o\epsilon} \frac{n^3\omega^4}{3c^3} , \quad (3.47)$$

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. 3.38-3.40. 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}

$$\frac{\bar{P}(\vartheta, \varphi)}{\bar{P}} = \frac{3}{8\pi} \sin^2\vartheta. \quad (3.48)$$

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.

3.2.3 Rate of energy dissipation in inhomogeneous environments

According to Poynting's theorem (c.f. Eq. 1.36) 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

$$\frac{dW}{dt} = -\frac{1}{2} \int_V \text{Re}\{\mathbf{j}^* \cdot \mathbf{E}\} dV, \quad (3.49)$$

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}_e 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. 3.26 we obtain the important result

$$\boxed{\frac{dW}{dt} = \frac{\omega}{2} \text{Im}\{\mathbf{p}^* \cdot \mathbf{E}(\mathbf{r}_o)\}}, \quad (3.50)$$

where the field \mathbf{E} is evaluated at the dipole's origin \mathbf{r}_o . At first sight this seems not possible to evaluate 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 \mathbf{p} and \mathbf{E} we need only to evaluate the component of \mathbf{E} in direction of \mathbf{p} . Since we chose $\mathbf{p}=p\mathbf{n}_z$ we calculate E_z as

$$E_z = \frac{p}{4\pi\epsilon_o\epsilon} \frac{e^{ikR}}{R} \left[k^2 \sin^2\vartheta + \frac{1}{R^2} (3\cos^2\vartheta - 1) - \frac{ik}{R} (3\cos^2\vartheta - 1) \right]. \quad (3.51)$$

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,

$$\frac{dW}{dt} = \lim_{R \rightarrow 0} \frac{\omega}{2} p \text{Im}\{E_z\} = \frac{\omega p^2}{8\pi\epsilon_o\epsilon} \lim_{R \rightarrow 0} \left\{ \frac{2}{3} k^3 + R^2(\dots) + \dots \right\} = \frac{p^2}{12\pi} \frac{\omega}{\epsilon_o\epsilon} k^3, \quad (3.52)$$

which is identical with Eq. 3.47. Thus, Eq. 3.50 leads to the correct result despite of the apparent singularity at $R=0$.

The importance of Eq. 3.50 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. 3.50 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

$$\mathbf{E}(\mathbf{r}_o) = \mathbf{E}_o(\mathbf{r}_o) + \mathbf{E}_s(\mathbf{r}_o) , \quad (3.53)$$

where \mathbf{E}_o and \mathbf{E}_s are the primary dipole field and the scattered field, respectively. Introducing Eq. 3.53 into Eq. 3.50 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. 3.47 and Eq. 3.52 as

$$P_o = \frac{p^2}{12\pi} \frac{\omega}{\varepsilon_o \varepsilon} k^3 , \quad (3.54)$$

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

$$\boxed{\frac{P}{P_o} = 1 + \frac{6\pi\varepsilon_o\varepsilon}{p^2} \frac{1}{k^3} \text{Im}\{\mathbf{p}^* \cdot \mathbf{E}_s(\mathbf{r}_o)\}} . \quad (3.55)$$

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.

3.2.4 Classical lifetimes and decay rates

Let us consider an undriven harmonically oscillating dipole. As the dipole oscillates it radiates energy according to Eq. 3.46. 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.

Homogeneous environment

The equation of motion for an undriven harmonically oscillating dipole is²

$$\frac{d^2}{dt^2} \mathbf{p}(t) + \gamma_o \frac{d}{dt} \mathbf{p}(t) + \omega_o^2 \mathbf{p}(t) = 0 . \quad (3.56)$$

The natural frequency of the oscillator is ω_o and its damping constant is γ_o . The solution for \mathbf{p} is

$$\mathbf{p}(t) = \text{Re} \left\{ \mathbf{p}_o e^{-i\omega_o \sqrt{1 - (\gamma_o^2/4\omega_o^2)} t} e^{-\gamma_o t/2} \right\} . \quad (3.57)$$

²We ignore radiation reaction, i.e. the effect of the dipole's radiated field on itself.

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

$$\gamma \ll \omega_o . \quad (3.58)$$

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 ³

$$\bar{W}(t) = \frac{m}{2q^2} [\omega_o^2 p^2(t) + \dot{p}^2(t)] = \frac{m\omega_o^2}{2q^2} |\mathbf{p}_o|^2 e^{-\gamma_o t} , \quad (3.59)$$

where m is the mass of the particle with charge q . For a system with several particles we have to sum the individual energies. 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

$$\tau_o = 1/\gamma_o . \quad (3.60)$$

We now turn to the rate of energy loss due to radiation. The average radiated power P_o at time t is (c.f. Eq. 3.47)

$$P_o(t) = \frac{p^2(t)}{4\pi\epsilon_o\epsilon} \frac{n^3\omega_o^4}{3c^3} . \quad (3.61)$$

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

$$\bar{W}(t=0) - \bar{W}(t) = q_i \int_0^t P_o(t') dt' , \quad (3.62)$$

where we introduced the so-called *intrinsic quantum yield* q_i . This parameter has a value between zero and one and indicates the fraction of energy losses associated with radiation. For $q_i = 1$, all the oscillator energy is transformed to radiation. It is now straight forward to solve for the decay rate. We introduce Eq. 3.59 and Eq. 3.61 into the last equation and obtain

$$\boxed{\gamma_o = q_i \frac{n^3}{4\pi\epsilon_o\epsilon} \frac{2q\omega_o^2}{3m c^3}} \quad (\text{classical}) . \quad (3.63)$$

This is the classical formula for the atomic decay rate and through Eq. 3.60 also for the atomic lifetime. It depends on the oscillation frequency and the oscillating particle's mass and charge. We see that 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 . The quantum mechanical analog of the decay rate (c.f. Appendix ??) can be arrived at by replacing the oscillator's initial average energy $m\omega_o^2|\mathbf{p}_o|^2/(2q^2)$ by the lowest energy of a quantum oscillator $\hbar\omega_o/2$. Thus,

$$\boxed{\gamma_o = q_i \frac{n^3}{4\pi\epsilon_o\epsilon} \frac{4|\mathbf{p}_o|^2\omega_o^3}{3\hbar c^3}} \quad (\text{quantum}) . \quad (3.64)$$

³This is easily derived by setting $p = qx$, $\omega_o^2 = c/m$ and using the expressions $m\dot{x}^2/2$ and $cx^2/2$ for the kinetic and potential energy, respectively.

Here, \mathbf{p}_o refers to the transition dipole matrix element between two atomic states. While the last equation is correct for empty space $n=1$ it requires some correction in dielectric media. This correction is related to the local field at the dipole's position. Depolarization of the dipole's microscopic environment influences its emission properties. The resulting correction is similar to the Clausius-Mossotti relation.

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

$$\frac{d^2}{dt^2}\mathbf{p}(t) + \gamma_o \frac{d}{dt}\mathbf{p}(t) + \omega_o^2 \mathbf{p}(t) = \frac{q^2}{m} \mathbf{E}_s(t) , \quad (3.65)$$

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

$$\mathbf{p}(t) = \text{Re} \left\{ \mathbf{p}_o e^{-i\omega t} e^{-\gamma t/2} \right\} , \quad \mathbf{E}_s(t) = \text{Re} \left\{ \mathbf{E}_o e^{-i\omega t} e^{-\gamma t/2} \right\} . \quad (3.66)$$

γ and ω are the new decay rate and resonance frequency, respectively. The two trial solutions can be inserted into Eq. 3.65. As before, we assume that γ is much smaller than ω (c.f. Eq. 3.58) 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. 3.65 is always larger than the driving term on the right hand side, or

$$\omega^2 \mathbf{p}_o \ll \frac{q^2}{m} \mathbf{E}_o . \quad (3.67)$$

With these approximations and the classical expression for the 'undisturbed' decay rate γ_o from Eq. 3.63 we obtain

$$\boxed{\frac{\gamma}{\gamma_o} = 1 + q_i \frac{6\pi\epsilon_o\epsilon}{|\mathbf{p}_o|^2} \frac{1}{k^3} \text{Im}\{\mathbf{p}_o^* \cdot \mathbf{E}_s(\mathbf{r}_o)\}} . \quad (3.68)$$

Since \mathbf{E}_s is proportional to \mathbf{p}_o , the dependence on the magnitude of the dipole moment cancels out. Besides the introduction of q_i , Eq. 3.68 is identical with Eq. 3.55 for the rate of energy dissipation in inhomogeneous environments. Thus, for $q_i = 1$ we find the important relationship

$$\frac{\gamma}{\gamma_o} = \frac{P}{P_o} . \quad (3.69)$$

This equation can be verified by expressing the radiated power in terms of the average energy $\bar{W}(t)$ given in Eq. 3.59. With the help of Eq. 3.62 we find

$$\frac{P}{P_o} = \frac{\gamma}{\gamma_o} e^{-(\gamma-\gamma_o)t} , \quad (3.70)$$

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. 3.69 is fulfilled for sufficiently small times.

Eq. 3.68 can be adapted to describe the (normalized) spontaneous emission rate of a quantum system (c.f. Appendix ??). In this case the classical dipole represents the quantum mechanical transition dipole matrix element from the excited to the ground state (see Appendix ??). 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. 3.55 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. 3.4).

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 Eqs. 3.66 into Eq. 3.65. The resulting expression for $\Delta\omega$ reads as

$$\Delta\omega = \omega \left[1 - \sqrt{1 - \frac{1}{\omega^2} \left[\frac{q^2}{m |\mathbf{p}_o|^2} \operatorname{Re}\{\mathbf{p}_o^* \cdot \mathbf{E}_s\} + \frac{\gamma\gamma_o}{2} - \frac{\gamma\gamma}{4} \right]} \right]. \quad (3.71)$$

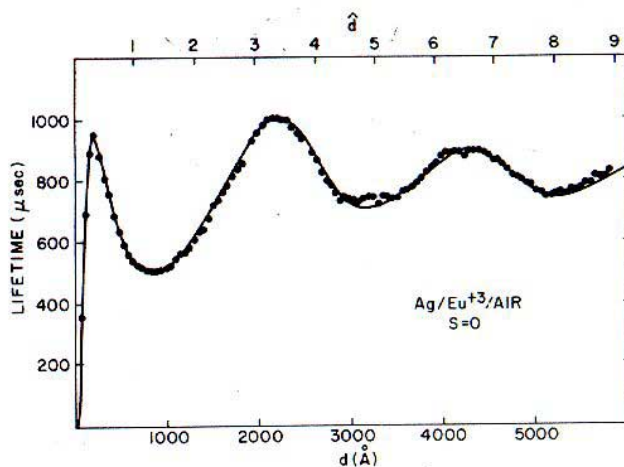


Figure 3.4: Comparison of classical theory and experimental measurements of molecular lifetimes in inhomogeneous environments. In the experiment, a layer of Eu^{3+} ions is held by fatty acid spacers of variable thickness close to a silver surface (data after Drexhage [6]). The calculated curve is due to Chance et al. [7] (used with no permission yet!).

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

$$\boxed{\frac{\Delta\omega}{\gamma_o} = q_i \frac{3\pi\varepsilon_o\varepsilon}{|\mathbf{p}_o|^2} \frac{1}{k^3} \operatorname{Re}\{\mathbf{p}_o^* \cdot \mathbf{E}_s\}} \quad (3.72)$$

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 [8]. In this configuration the dipolar scatterers were excited close to their resonance frequency leading to a highly enhanced polarizability. At cryogenic temperatures, the linewidths are very narrow and the frequency shifts can be well resolved.

Notice again, that since \mathbf{E}_s is proportional to \mathbf{p}_o , the dependence on the magnitude of the dipole moment in Eq. 3.72 cancels out.