

1. Introduction: Maxwell's Equations and Plane Waves

In what follows, we will consider the electrodynamic interaction of fluorescing molecules with an inhomogeneous environment. Although the absorption and emission of light is a thoroughly quantum-mechanical process, many aspects of this interaction can be studied within the so called semi-classical framework, which is based on Maxwell's electrodynamics. The core idea of this semi-classical approach is to handle the molecule as a classical oscillating electric dipole, which is an excellent approximation for most molecules of practical interest (corresponding to the fact the most electronic transitions involved in fluorescence are dipole transitions). All calculations of light absorption and emission are calculated by solving Maxwell's equations for the electromagnetic field in the presence of such a dipole. The term "semi" refers to the fact that the results of these calculations are then interpreted from a quantum-mechanical point of view.

Thus, from a technical point of view, what we have to deal with are Maxwell's equations, which read (in cgs units, which will be used throughout this tutorial)

$$\mathbf{div}(\epsilon\mathbf{E}) = 4\pi\rho$$

$$\mathbf{div}\mathbf{B} = 0$$

$$\mathbf{rot}\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}$$

$$\mathbf{rot}\left(\frac{\mathbf{B}}{\mu}\right) = \frac{1}{c}\frac{\partial(\epsilon\mathbf{E})}{\partial t} + \frac{4\pi}{c}\mathbf{j}$$

where \mathbf{E} and \mathbf{B} are the electric and magnetic field, ρ and \mathbf{j} are the electric charge and current density, ϵ and μ are the dielectric susceptibility and magnetic permeability of the medium, and c is the speed of light. For a singular dipole at the center of the coordinate system $\mathbf{r} = 0$ and oscillating with frequency ω , one has

$$\rho = 0 \quad \text{and} \quad \mathbf{j} = -i\omega\mathbf{p}\delta(\mathbf{r})\exp(-i\omega t),$$

with $\delta(\mathbf{r})$ Dirac's delta function in three dimensions, and \mathbf{p} the dipole amplitude vector. However, before we consider in detail the solution of Maxwell's equations for the dipole, we first consider their solutions for a source-free medium (no free charges and

currents), which are plane electromagnetic waves, and study the interaction of these plane waves with a planar discontinuity of the dielectric susceptibility of the medium. With other words, we study the interaction of plane electromagnetic waves with an interface. The results of these studies will be of fundamental importance for the subsequent considerations of the oscillating dipole and its interaction with such an interface. We seek the solution for the electromagnetic field within a source-free medium in the form of plane waves, $\mathbf{E}, \mathbf{B} \propto \exp(i\mathbf{k} \cdot \mathbf{r} - i\omega t)$, where \mathbf{k} and ω are the wave vector and oscillation frequency of the waves. For simplicity, we will always consider media with unity magnetic permeability, $\mu = 1$, which is in excellent approximation for most materials of practical interest. By direct insertion into Maxwell's equations a presented above, we find the relations

$$\mathbf{div} \epsilon \mathbf{E} = i\epsilon \mathbf{k} \cdot \mathbf{E} = 0$$

$$\mathbf{div} \mathbf{B} = \mathbf{k} \cdot \mathbf{B}$$

$$\mathbf{rot} \mathbf{E} = i\mathbf{k} \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} = \frac{i\omega}{c} \mathbf{B}$$

$$\mathbf{rot} \mathbf{B} = i\mathbf{k} \times \mathbf{B} = \frac{\epsilon}{c} \frac{\partial \mathbf{E}}{\partial t} = -\frac{i\epsilon\omega}{c} \mathbf{E}$$

These relations show, first at all, that \mathbf{E} , \mathbf{B} , and \mathbf{k} are mutually orthogonal one to another. Next, applying the rotor a second time to the third equation and using the first and last equation leads to

$$\mathbf{rot} \mathbf{rot} \mathbf{E} = -\mathbf{k} \times (\mathbf{k} \times \mathbf{E}) = k^2 \mathbf{E} = \frac{i\omega}{c} \mathbf{rot} \mathbf{B} = \frac{\epsilon\omega^2}{c^2} \mathbf{E}$$

thus defining the amplitude of the wave vector as $|\mathbf{k}| \equiv k = \sqrt{\epsilon} \omega/c \equiv n\omega/c$ (which is also called the dispersion relation), and relating the amplitude of the electric and magnetic field $|\mathbf{B}| = n|\mathbf{E}|$. Here, the so called index of refraction $n = \sqrt{\epsilon}$ was introduced.

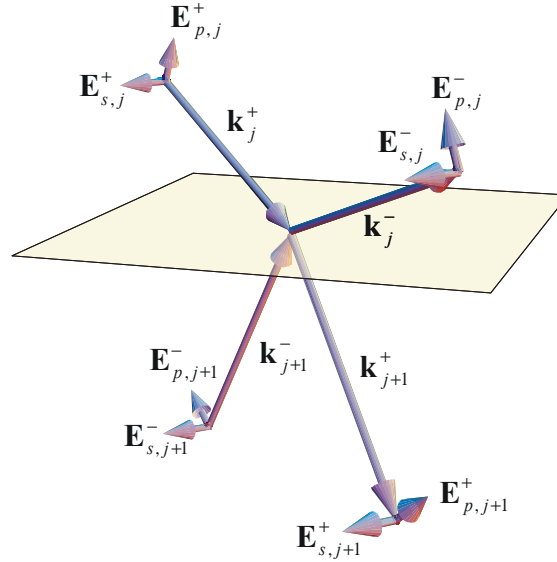
Thus, plane waves are indeed solutions of Maxwell's equations, as long as the relations $\mathbf{E} \perp \mathbf{B}$, $\mathbf{E} \perp \mathbf{k}$, $\mathbf{B} \perp \mathbf{k}$, $|\mathbf{B}| = n|\mathbf{E}|$ and $k = n\omega/c$ hold. As free variables we still have the electric field amplitude, \mathbf{E} , the oscillation frequency ω , and the propagation direc-

tion given by the unit vector $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$ (throughout the tutorial, we will use a hat for symbolizing unit vectors).

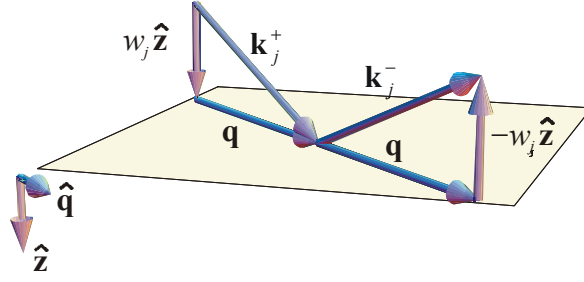
An important point is that the found plane wave solutions form a complete set of solutions: *any* solution of the electromagnetic field within a source-free homogeneous ($\epsilon = \text{const.}$) medium can be represented by a superposition of these plane waves. In subsequent chapters, we will learn of alternative complete systems of solutions that are more adapted to problems with cylindrical or spherical symmetry. The plane wave solutions, however, are perfect when studying problems involving only planar parallel interfaces, and the simplest problem that we will consider next is the interaction of a plane wave with a planar interface.

2. Plane Waves and Planar Boundaries: Fresnel's Relations

Let us consider the most general case of such plane waves at a planar interface dividing two media with index of refraction n_j and n_{j+1} . There are up to four interconnected plane waves (see figure below), denoted by \mathbf{E}_j^\pm and \mathbf{E}_{j+1}^\pm , where the subscript refers to the medium, and the \pm -sign to whether the wave travels into a positive direction (from medium j towards medium $j+1$) or into a negative direction (from $j+1$ towards j). If the electric field vectors are within the plane of the directions of wave propagation, the wave is called transversal electric (TE) or p -wave; if the electric field vectors are parallel to the boundary, the wave is called transversal magnetic (TM) or s -wave.



To get a connection between these four plane waves, we have to consider the boundary conditions. First of all, the plane waves represent periodic structures of the electric field in space. Along the boundary, the periodicity of the electric field on both sides of the boundary has to be the same. The periodicity is given by the projections of the wave vectors $\mathbf{k}_{j,j+1}^\pm$ onto the boundary. Let us denote these components of the $\mathbf{k}_{j,j+1}^\pm$ as \mathbf{q} , and the modulus of the component perpendicular to the boundary as $w_{j,j+1}$ (see figure below). Pay attention to the fact that \mathbf{q} is a two-dimensional vector within the plane of the boundary, and it is the same for all four plane waves, whereas $w_{j,j+1}$ has the same value on the same side of the boundary, but is different on different sides.



As we have seen in the preceding section, the lengths of the wave vectors are proportional to the index of refraction, $n_{j,j+1}$. Setting for convenience the length of the wave vector in vacuum to unity, we thus have the general relation

$$n_{j,j+1} = k_{j,j+1} = \sqrt{q^2 + w_{j,j+1}^2}.$$

Furthermore, the angle of incidence of the plane waves is given by

$$\sin \theta_{j,j+1} = q/n_{j,j+1},$$

which yields directly Snell's law of refraction because q is the same in all media.

Next, we take into account the boundary conditions for the electric field: The electric field components parallel to the boundary, as well as the products of the dielectric constant ($\epsilon_j = n_j^2$) with the components perpendicular to the boundary, have to be the same on both sides of the boundary.

Let us first consider the p -wave case. Simple geometry gives the components of the electric field parallel and perpendicular to the interface as $\pm w_j/n_j E_{p,j}^\pm$ and $q/n_j E_{p,j}^\pm$, respectively (the same holds for $j+1$). Thus, the boundary conditions can be written in a compact matrix form as:

$$\begin{pmatrix} w_j/n_j & -w_j/n_j \\ n_j & n_j \end{pmatrix} \begin{pmatrix} E_{p,j}^+ \\ E_{p,j}^- \end{pmatrix} = \begin{pmatrix} w_{j+1}/n_{j+1} & -w_{j+1}/n_{j+1} \\ n_{j+1} & n_{j+1} \end{pmatrix} \begin{pmatrix} E_{p,j+1}^+ \\ E_{p,j+1}^- \end{pmatrix}$$

where q was cancelled out. The inverse of the matrix on the l.h.s. is given by:

$$\begin{pmatrix} w_k/n_k & -w_k/n_k \\ n_k & n_k \end{pmatrix}^{-1} = \frac{1}{2w_k} \begin{pmatrix} n_k & w_k/n_k \\ -n_k & w_k/n_k \end{pmatrix}.$$

Thus, the connection between the electric field components is explicitly given by:

$$\begin{aligned} \begin{pmatrix} E_{p,j}^+ \\ E_{p,j}^- \end{pmatrix} &= \frac{1}{2} \begin{pmatrix} n_j/w_j & 1/n_j \\ -n_j/w_j & 1/n_j \end{pmatrix} \begin{pmatrix} w_{j+1}/n_{j+1} & -w_{j+1}/n_{j+1} \\ n_{j+1} & n_{j+1} \end{pmatrix} \begin{pmatrix} E_{p,j+1}^+ \\ E_{p,j+1}^- \end{pmatrix} \\ &= \frac{1}{2} \begin{pmatrix} w/n+n & -w/n+n \\ -w/n+n & w/n+n \end{pmatrix} \begin{pmatrix} E_{p,j+1}^+ \\ E_{p,j+1}^- \end{pmatrix} \end{aligned}$$

where the short-hand notation $w \equiv w_{j+1}/w_j$ and $n \equiv n_{j+1}/n_j$ is introduced.

Consider the special case of a plane wave incident from the j -side. Then, there will be no E_{j+1}^- component, but a reflected E_j^- and a transmitted E_{j+1}^+ component. We thus find

$$\begin{pmatrix} E_{p,j}^+ \\ E_{p,j}^- \end{pmatrix} = \frac{1}{2} \begin{pmatrix} w/n+n & -w/n+n \\ -w/n+n & w/n+n \end{pmatrix} \begin{pmatrix} E_{p,j+1}^+ \\ 0 \end{pmatrix},$$

and for the electric field amplitude in $j+1$:

$$\mathbf{E}_{p,j+1}^+ = \hat{\mathbf{e}}_{p,j+1}^+ \frac{2E_{p,j}^+}{w/n+n} = \hat{\mathbf{e}}_{p,j+1}^+ \frac{2n_j n_{j+1} w_j E_{p,j}^+}{n_j w_{j+1} + n_{j+1} w_1}$$

with $\hat{\mathbf{e}}_{p,j+1}^+ = \frac{w_{j+1} \hat{\mathbf{q}} - q \hat{\mathbf{z}}}{n_{j+1}}$ a unit vector along $\mathbf{E}_{p,j+1}^+$, where $\hat{\mathbf{q}}, \hat{\mathbf{z}}$ denote unit vectors

along \mathbf{q} and perpendicular to the boundary, respectively. Finally, the spatial field dependence is given by the exponential term $\exp(i\mathbf{q} \cdot \hat{\mathbf{n}} + iw_{j+1}z)$ where z is the coordinate perpendicular to the boundary, and \mathbf{r} the two-dimensional coordinate vector within the boundary plane. An important special case is when w_{j+1} becomes imaginary, leading to an evanescent wave on the $j+1$ -side. This happens if

$$w_{j+1}^2 = n_{j+1}^2 - q^2 = n_{j+1}^2 - (n_j^2 - w_j^2) < 0,$$

which shows that a condition for the emergence of an evanescent wave is $n_{j+1} < n_j$.

The angle of incidence for which $w_j = \sqrt{n_{j+1}^2 - n_j^2}$ is called the critical angle, where total reflection starts and evanescent waves emerge.

The reflection and transmission coefficients are defined as

$$R = \frac{E_{p,j}^-}{E_{p,j}^+} \quad \text{and} \quad T = \frac{E_{p,j+1}^+}{E_{p,j}^+}$$

so that we obtain:

$$R = \frac{n^2 - w}{n^2 + w} \quad \text{and} \quad T = \frac{2n}{n^2 + w}.$$

An important peculiarity of total internal reflection is the occurrence of a phase jump between incident and reflected wave, which can be seen by writing the electric field components $E_{p,j}^\pm$ as (see matrix equation for the boundary conditions above)

$$E_{p,j}^+ = \frac{1}{2} \left(\frac{w}{n} + n \right) E_{p,j+1}^+$$

$$E_{p,j}^- = \frac{1}{2} \left(-\frac{w}{n} + n \right) E_{p,j+1}^+$$

If w_{j+1} is purely imaginary, the factor in the brackets adds an additional phase ϕ^\pm to the $E_{p,j}^\pm$ components, with

$$\exp(i\phi^\pm) \propto \pm \frac{w}{n} + n$$

or

$$\tan \phi^\pm = \frac{\operatorname{Im} \left(\pm \frac{w}{n} + n \right)}{\operatorname{Re} \left(\pm \frac{w}{n} + n \right)} = \frac{\pm \operatorname{Im} w}{n^2},$$

so that

$$\Delta\phi = \phi^- - \phi^+ = \arctan \left(-\frac{\operatorname{Im} w}{n^2} \right) - \arctan \left(\frac{\operatorname{Im} w}{n^2} \right) = -2 \arctan \left(\frac{\operatorname{Im} w}{n^2} \right).$$

Very similar considerations hold for *s*-waves. Because all electric field vectors are now parallel to the interfaces, one uses a second boundary condition involving the continuity of the parallel component of the magnetic field across boundaries. For a plane wave

with electric field vector $\mathbf{E}_{s,j}$ parallel to the boundary, the parallel component of the magnetic field is given by $\hat{\mathbf{q}} \cdot (\hat{\mathbf{k}}_j \times \mathbf{E}_{s,j}) = w_j E_{s,j}$. Thus, the boundary conditions read:

$$\begin{pmatrix} 1 & 1 \\ w_j & -w_j \end{pmatrix} \begin{pmatrix} E_{s,j}^+ \\ E_{s,j}^- \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ w_{j+1} & -w_{j+1} \end{pmatrix} \begin{pmatrix} E_{s,j+1}^+ \\ E_{s,j+1}^- \end{pmatrix},$$

so that, with

$$\begin{pmatrix} 1 & 1 \\ w_j & -w_j \end{pmatrix}^{-1} = -\frac{1}{2w_j} \begin{pmatrix} -w_j & -1 \\ -w_j & 1 \end{pmatrix},$$

one finds

$$\begin{aligned} \begin{pmatrix} E_{s,j}^+ \\ E_{s,j}^- \end{pmatrix} &= \frac{1}{2} \begin{pmatrix} 1 & 1/w_j \\ 1 & -1/w_j \end{pmatrix} \begin{pmatrix} 1 & 1 \\ w_{j+1} & -w_{j+1} \end{pmatrix} \begin{pmatrix} E_{s,j+1}^+ \\ E_{s,j+1}^- \end{pmatrix} \\ &= \frac{1}{2} \begin{pmatrix} 1+w & 1-w \\ 1-w & 1+w \end{pmatrix} \begin{pmatrix} E_{s,j+1}^+ \\ E_{s,j+1}^- \end{pmatrix} \end{aligned}$$

The reflection and transmission coefficients at a single interface $(j, j+1)$ now are

$$R = \frac{1-w}{1+w} \quad \text{and} \quad T = \frac{2}{1+w},$$

and the phase jump under total reflection is $\Delta\phi = -2 \arctan(\text{Im } w)$, and we again employed the short-hand notation $w \equiv w_{j+1}/w_j$ and $n \equiv n_{j+1}/n_j$.

3. Oscillating electric dipole in a homogeneous environment

After our exceeding review of plane electromagnetic waves and their interaction with planar interfaces, let us now return to the electromagnetic field of a free electric dipole within a homogeneous environment.

Starting point of our considerations is the fourth of Maxwell's equations for a oscillating electric dipole at the coordinate system's origin, $\mathbf{r} = (0,0,0)$, thus

$$\mathbf{rot} \mathbf{B} = -\frac{i\omega\epsilon}{c} \mathbf{E} + \frac{4\pi}{c} \mathbf{j} = -\frac{i\omega\epsilon}{c} \mathbf{E} - \frac{4\pi i\omega}{c} \mathbf{p}\delta(\mathbf{r}).$$

Together with the third of Maxwell's equations, $\mathbf{rot} \mathbf{E} = (i\omega/c)\mathbf{B}$, this can be rewritten to

$$\mathbf{rot} \mathbf{rot} \mathbf{E} - \frac{\epsilon\omega^2}{c^2} \mathbf{E} = \frac{4\pi\omega^2}{c^2} \mathbf{p}\delta(\mathbf{r}).$$

Passing to Fourier space yields

$$-\mathbf{k} \times (\mathbf{k} \times \mathbf{E}) - \epsilon k_0^2 \mathbf{E} = (k^2 - \epsilon k_0^2) \mathbf{E} - \mathbf{k}(\mathbf{k} \cdot \mathbf{E}) = 4\pi k_0^2 \mathbf{p},$$

where the definition $k_0 = \omega/c$ was used. Multiplying both sides by \mathbf{k} gives a expression for $\mathbf{k} \cdot \mathbf{E}$:

$$\mathbf{k} \cdot \mathbf{E} = -\frac{4\pi}{\epsilon} \mathbf{k} \cdot \mathbf{p}$$

so that

$$\mathbf{E} = \frac{4\pi}{\epsilon(k^2 - \epsilon k_0^2)} [\epsilon k_0^2 \mathbf{p} - \mathbf{k}(\mathbf{k} \cdot \mathbf{p})]$$

when switching back from Fourier to direct space, \mathbf{E} is given by

$$\mathbf{E}(\mathbf{r}) = \frac{4\pi}{\epsilon} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{k^2 - \epsilon k_0^2} [\epsilon k_0^2 \mathbf{p} - \mathbf{k}(\mathbf{k} \cdot \mathbf{p})]$$

Representing \mathbf{k} in appropriately oriented spherical coordinates (k, η, ψ) so that

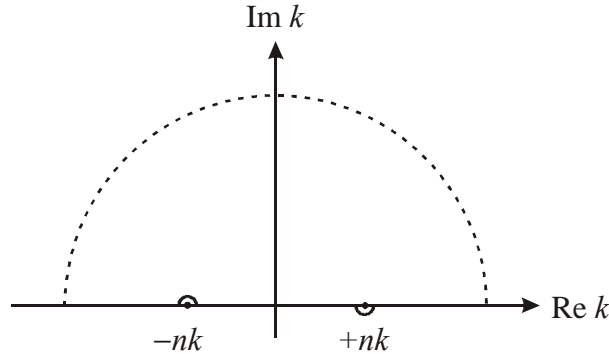
$\mathbf{k} \cdot \mathbf{r} = kr \cos\psi$, this result can be rewritten as

$$\begin{aligned}\mathbf{E}(\mathbf{r}) &= \frac{8\pi^2}{\varepsilon(2\pi)^3} \int_0^\infty dk k^2 \int_0^\pi d\psi \sin \psi \frac{\exp(ikr \cos \psi)}{k^2 - \varepsilon k_0^2} [\varepsilon k_0^2 \mathbf{p} - \mathbf{k}(\mathbf{k} \cdot \mathbf{p})] \\ &= \frac{1}{\varepsilon\pi} (\varepsilon k_0^2 + \mathbf{grad div}) \mathbf{p} \int_0^\infty dk k^2 \int_0^\pi d\psi \sin \psi \frac{\exp(ikr \cos \psi)}{k^2 - \varepsilon k_0^2},\end{aligned}$$

where the integration over η yielded a factor 2π . Let us next consider the integrals only. The integral over ψ can be taken directly, giving

$$\int_0^\infty dk k^2 \int_0^\pi d\psi \sin \psi \frac{\exp(ikr \cos \psi)}{k^2 - \varepsilon k_0^2} = \frac{1}{ir} \int_0^\infty dk k \frac{\exp(ikr) - \exp(-ikr)}{k^2 - \varepsilon k_0^2} = \frac{1}{ir} \int_{-\infty}^\infty dk k \frac{\exp(ikr)}{k^2 - \varepsilon k_0^2}.$$

The integration over k can be done in the complex k -plane, where the integration is closed in the upper half plane at infinity, and the integration is deformed in such a way as to exclude the pole $k = -\sqrt{\varepsilon}k_0$, taking into account that only outgoing waves with $k = +nk_0$ are physically reasonable. Thus, the integral is taken over the following closed path



Applying Cauchy's residue theorem we thus obtain

$$\frac{1}{ir} \int_{-\infty}^\infty dk k \frac{\exp(ikr)}{k^2 - \varepsilon k_0^2} = \frac{1}{ir} \oint_C dk k \frac{\exp(ikr)}{k^2 - \varepsilon k_0^2} = \pi \frac{\exp(ink_0 r)}{r},$$

or

$$\mathbf{E}(\mathbf{r}) = \frac{1}{\varepsilon} (\varepsilon k_0^2 + \mathbf{grad div}) \left[\mathbf{p} \frac{\exp(ink_0 r)}{r} \right].$$

Without restriction of generality, let us calculate the action of the differential operators in a spherical co-ordinate system (r, θ, ϕ) with its polar axis $\theta = 0$ oriented along \mathbf{p} .

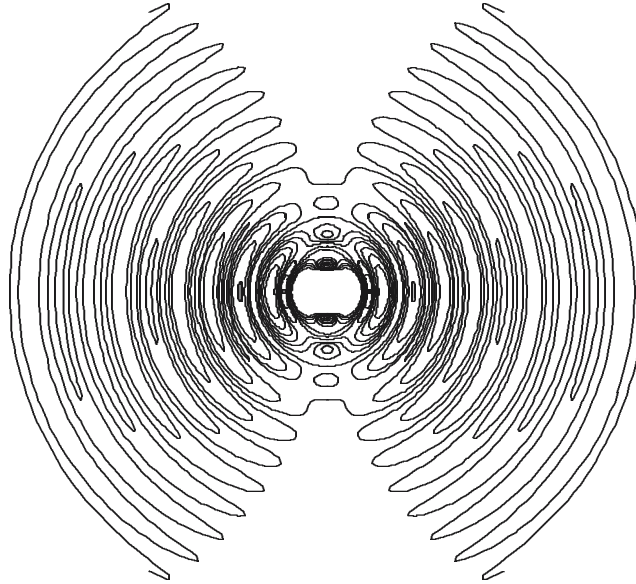
The we have (using in the following the abbreviation $k = nk_0$)

$$\begin{aligned} \mathbf{grad} \operatorname{div} \left[\mathbf{p} \frac{\exp(ikr)}{r} \right] &= \mathbf{grad} \left[\left(\frac{ik}{r} - \frac{1}{r^2} \right) (\mathbf{p} \cdot \hat{\mathbf{r}}) \exp(ikr) \right] \\ &= \left[\left(-\frac{k^2}{r} - \frac{2ik}{r^2} + \frac{2}{r^3} \right) (\mathbf{p} \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}} - \frac{1}{r} \hat{\mathbf{r}} \times (\hat{\mathbf{r}} \times \mathbf{p}) \left(\frac{ik}{r} - \frac{1}{r^2} \right) \right] \exp(ikr) \end{aligned}$$

or finally

$$\mathbf{E}(\mathbf{r}) = k_0^2 k \left[\left(-1 - \frac{3i}{kr} + \frac{3}{(kr)^2} \right) \hat{\mathbf{r}} (\hat{\mathbf{r}} \cdot \mathbf{p}) + \left(1 + \frac{i}{kr} - \frac{1}{(kr)^2} \right) \mathbf{p} \right] \frac{\exp(ikr)}{kr}.$$

This result describes the field of electromagnetic waves propagating away from the dipole's position (always remember that there is the factor $\exp(-i\omega t)$ present which we have all the time omitted). The next figure shows the contours of constant field amplitude $|\mathbf{E}(\mathbf{r})|$ for a vertical dipole orientation.



An interesting question is the angular distribution of energy radiation away from the dipole. The energy flux is given by the Poynting vector, $\mathbf{S} = (c/4\pi)\mathbf{E} \times \mathbf{B}$, or when using the complex-valued temporal Fourier amplitudes (as throughout this tutorial) and averaging over one oscillation period, by $\mathbf{S} = (c/8\pi)\operatorname{Re}(\mathbf{E} \times \mathbf{B}^*)$ (star always denotes complex conjugation). We can further simplify our considerations when taking into account that only components in \mathbf{S} that fall off with r^{-2} will contribute to energy transport towards infinity: anything that falls off faster cannot carry energy away, because

the area of dipole-enclosing spheres with radius r increases proportionally to r^2 . Thus, we have to consider only components proportional to r^{-1} in \mathbf{E} and \mathbf{B} , or

$$\mathbf{E}(\mathbf{r}) \sim k_0^2 k [\mathbf{p} - \hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{p})] \frac{\exp(ikr)}{kr}$$

and

$$\begin{aligned} \mathbf{B}(\mathbf{r}) &= \frac{1}{ik_0} \mathbf{rot} \mathbf{E}(\mathbf{r}) = \frac{1}{ik_0} \mathbf{rot} \frac{1}{\epsilon} (k^2 + \mathbf{grad} \mathbf{div}) \left[\mathbf{p} \frac{\exp(ikr)}{r} \right] \\ &= \frac{k_0}{i} \mathbf{rot} \left[\mathbf{p} \frac{\exp(ikr)}{r} \right] \sim \frac{k_0 k}{r} (\hat{\mathbf{r}} \times \mathbf{p}) \exp(ikr) \end{aligned}$$

so that for the far-field Poynting vector we obtain

$$\mathbf{S} \sim \frac{cnk_0^4}{8\pi r^2} [\mathbf{p} - \hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{p})] \times (\hat{\mathbf{r}} \times \mathbf{p}) = \frac{cnk_0^4}{8\pi r^2} \hat{\mathbf{r}} [p^2 - (\hat{\mathbf{r}} \cdot \mathbf{p})^2].$$

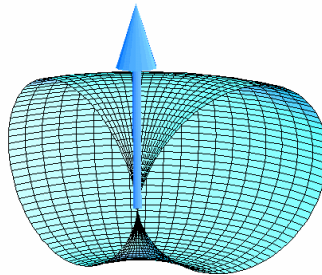
Thus, the radiation points away from the dipole's position, and has the angular distribution

$$\frac{d^2 S}{\sin \theta d\theta d\phi} = \frac{cnk_0^4 p^2}{8\pi} \sin^2 \theta.$$

The total power of emission is obtained by integrating over all angular directions,

$$S_{tot} = \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \frac{ck_0^2 p^2}{8\pi n} \sin^2 \theta = \frac{1}{3} cnk_0^4 p^2.$$

What do we learn from these results? The angular distribution of radiation of a dipole follows a simple $\sin^2 \theta$ -dependence, where θ is the angle between dipole orientation and radiation direction. This distribution is shown in the net figure.



Thus, there is no far-field energy transport along the direction of the dipole axis. The total emitted power is proportional to $k_0^4 \sim \lambda^{-4}$, thus inversely proportional to the fourth power of the wavelength. Because the electrodynamics of light scattering on dipoles follows a similar mathematics as developed here, we have recovered the well-known result that scattering intensity (scattering cross section) increases inversely proportional to the fourth power of the wavelength. Finally, we have the interesting result that the total power of emission depends also on the refractive index n of the embedding medium: This is the first encounter of the phenomenon that the dielectric properties of the environment can have a direct impact on the emission properties of a dipole (and thus on those of a fluorescing molecule).

Until now, we were only interested in the purely mathematical derivation of the electromagnetic field of an oscillating electric dipole. Now, it is time to stop and to consider the connection of the found results with the emission of a fluorescing molecule. Nearly all fluorescing molecules of practical interest are electric dipole emitters. Of course they are also quantum-mechanical entities in the sense that they are not emitting a continuous train of energy but emit their energy in quantized units, photons. These photons are characterized by their energy (which is directly connected with the oscillation frequency ω by $E = \hbar\omega$) and polarization (corresponding to the electric field vector orientation in our consideration). However, what does, for example, the angular distribution and total power of emission as derived above tell us about the single molecule's fluorescence? The angular distribution of emission, as derived above within the framework of Maxwell's electrodynamics for an oscillating dipole, corresponds to an angular probability distribution of photon emission: By repeatedly exciting a molecule and measuring the direction of subsequent photon emission, one obtains the same angular distribution as that calculated above. The total power of emission has a similar quantum-mechanical interpretation: The larger that value, the faster the energy is emitted away from the molecule, which means the shorter is the (average) lifetime of the excited state (fluorescence decay time). This correspondence between classical quantities such as angular distribution of radiation or total emission power, and quantum-mechanical quantities such as angular distribution of photon emission or lifetime of the excited state is the content of the so-called semi-classical approach to single molecule fluorescence, and is the basis of all further developments of this tutorial.

4. Förster Resonance Energy Transfer

In the conclusion of the preceding section, we considered the far-field emission of the dipole, neglecting the so called *near-field* components of the electric (and magnetic) field that fall off faster than r^{-1} . Here, we will concentrate on these near-field components, and we will study the action of an oscillating dipole onto another electric dipole causing the hopping of the energy from an optically excited molecule to an excitable molecule in its ground state (Förster Resonance Energy Transfer, or FRET).

Starting point is the r^{-3} -near-field part of electric field of the oscillating electric dipole (cf. with results of previous section):

$$\mathbf{E}_d(r) \approx [3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{p}_d) - \mathbf{p}_d] \frac{\exp(ikr)}{n^2 r^3}.$$

Here, the subscript d indicates that the quantities refer to a so-called *donor* molecule, which will act by its electromagnetic near-field on a suitable *acceptor* molecule, if there is so-called spectral overlap between the donor's frequency of emission and the acceptor's frequency of optical absorption.

The excitation rate of a potential acceptor molecule is given by the product of its absorption cross section and the number of (virtual) photons per area per second coming from the donor. This photon flux is calculated as the Poynting energy flux, proportional to $(nc/8\pi) \cdot E_d^2$ divided by the energy per photon λ/hc . Taking furthermore into account that the acceptor dipole excitation is proportional to the scalar product of acceptor dipole (\mathbf{p}_a) orientation and exciting electric field (\mathbf{E}_d) orientation, and that the macroscopically measured absorption cross section σ is averaged over all possible dipole orientations (and thus only 1/3 of its maximum value), one finds for the acceptor excitation rate k_a :

$$k_a = (3\sigma) \frac{nc}{8\pi} \frac{\lambda}{hc} |\hat{\mathbf{p}}_a \cdot \mathbf{E}_d|^2 \phi_d.$$

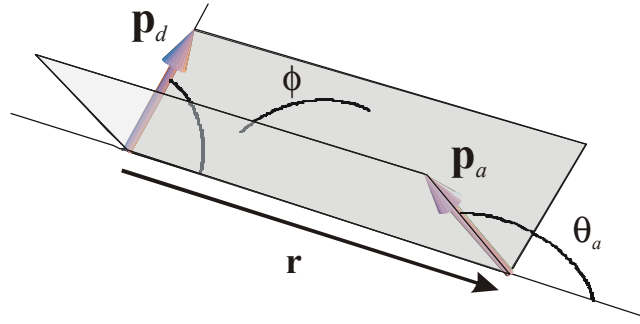
where ϕ_d is the donor's fluorescence quantum yield (the probability that the donor's energy is given away electromagnetically and not by e.g. molecular collisions). Inserting the explicit expression for \mathbf{E}_d yields

$$k_a = \frac{3\sigma\lambda p_d^2}{8\pi h} \frac{\phi_d}{n^3 r^6} |3(\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}_a)(\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}_d) - (\hat{\mathbf{p}}_a \cdot \hat{\mathbf{p}}_d)|^2 = \frac{3\sigma\lambda p_d^2}{8\pi h} \frac{\phi_d}{n^3 r^6} \kappa^2.$$

which defines the so called orientation factor κ as

$$\begin{aligned} \kappa^2 &= |3(\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}_a)(\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}_d) - (\hat{\mathbf{p}}_a \cdot \hat{\mathbf{p}}_d)|^2 \\ &= [3\cos\theta_a \cos\theta_d - \cos\phi]^2 \\ &= [2\cos\theta_a \cos\theta_d - \cos\phi \sin\theta_a \sin\theta_d]^2 \end{aligned}$$

Here, θ_a and θ_d are the angles between the donor and acceptor dipoles and the connecting vector \mathbf{r} , ϕ is the angle between the two dipoles, and ϕ the angle between the planes formed by the donor dipole and \mathbf{r} and the acceptor dipole and \mathbf{r} , see figure.



If the donor and acceptor can freely rotate, one obtains an averaged value for $\langle \kappa^2 \rangle$ as

$$\begin{aligned} \langle \kappa^2 \rangle &= \langle [2\cos\theta_a \cos\theta_d - \cos\phi \sin\theta_a \sin\theta_d]^2 \rangle \\ &= \langle 4\cos^2\theta_a \cos^2\theta_d - 4\cos\theta_a \cos\theta_d \cos\phi \sin\theta_a \sin\theta_d + \cos^2\phi \sin^2\theta_a \sin^2\theta_d \rangle \\ &= \frac{4}{9} + \frac{1}{2} \frac{4}{9} = \frac{2}{3} \end{aligned}$$

In the above equation for k_a , one has still the *a priori* unknown quantity p_d . It can be found by looking at the total energy emission of the free donor. From a quantum mechanical point of view, its energy is that of one photon, hc/λ . From an classical electromagnetic point of view, it is given by the emission rate of a dipole with amplitude p_d times the average lifetime of the donor's excited state, τ_d . Equaling both values yields:

$$\frac{hc}{\lambda} = \frac{1}{3} p_d^2 k_0^4 c n \tau_d$$

where k_0 is again the wave vector in vacuum. Thus, one finds

$$p_d^2 = \frac{3h}{2\pi k_0^3 n \tau_d} = \frac{3h}{2\pi k_0^3 n \tau_d}$$

and

$$k_a = \frac{3\sigma\lambda}{8\pi h} \frac{3h}{2\pi k_0^3 \tau_d n^4 r^6} \kappa^2 \phi_d = \frac{9\sigma}{8\pi k_0^4 \tau_d n^4 r^6} \kappa^2 \phi_d.$$

Until now, donor emission and acceptor excitation was assumed to happen at exactly one wavelength. The complete acceptor excitation rate has to be integrated over all wavelengths, leading to

$$k_{a,tot} = \frac{9}{8\pi(2\pi)^4 \tau_d n^4 r^6} \kappa^2 \phi_d \frac{\int d\lambda F_d(\lambda) \sigma(\lambda) \lambda^4}{\int d\lambda F_d(\lambda)}$$

where $F_d(\lambda)/\int d\lambda F_d(\lambda)$ is the normalized emission spectrum of the donor. The so called Förster radius is given by

$$R_0^6 = \frac{9\kappa^2}{8\pi(2\pi)^4 n^4} \phi_d \frac{\int d\lambda F_d(\lambda) \sigma(\lambda) \lambda^4}{\int d\lambda F_d(\lambda)},$$

so that

$$k_{a,tot} = \frac{1}{\tau_d} \left(\frac{R_0}{r} \right)^6.$$

Taking into account the relation between absorption cross section (in cm^2) and molar extinction ϵ (in l/cm/mol),

$$\sigma = \frac{10^3 \ln 10 \epsilon}{N_A} \approx \frac{2303}{N_A} \epsilon,$$

one finds the usual textbook expression for $k_{a,tot}$

$$k_{a,tot} = \frac{9000 \cdot \ln 10}{N_A 128\pi^5 n^4} \frac{\kappa^2 \phi_d}{\tau_d r^6} \frac{\int d\lambda F_d(\lambda) \epsilon_a(\lambda) \lambda^4}{\int d\lambda F_d(\lambda)}.$$

In practice, FRET can be measured by either intensity or lifetime measurements. The fluorescence intensity of the donor is given by the ratio

$$I_{da} \sim \frac{k_f}{k_f + k_{nr} + k_a},$$

where k_f and k_{nr} are the radiative (fluorescent) and non-radiative (e.g. molecular collision induced) transition rates of the free donor molecule from its excited to its ground state. The subscript da refers to the donor intensity in presence of the acceptor. The intensity of the acceptor is given directly by $I_a \sim \phi_a k_a$, where ϕ_a is the acceptor's fluorescence quantum yield. Thus, we find the relations

$$\frac{I_d - I_{da}}{I_d} = \frac{k_a}{k_f + k_{nr} + k_a} = \frac{r^6}{R_0^6 + r^6}$$

where I_d is the donor intensity at equal excitation and detection conditions, but in absence of the acceptor. If R_0 is known *a priori*, this relation can be used to infer the value of r from intensity measurements.

An alternative is to use lifetime measurements. As already mentioned, the fluorescence lifetime or lifetime of the excited state is the inverse of the total transition rate from the excited to the ground state. Thus, for the lifetimes τ_{da} and τ_d of the donor in presence and in absence of the acceptor we find the relation

$$\frac{\tau_d - \tau_{da}}{\tau_d} = \frac{k_a}{k_f + k_{nr} + k_a} = \frac{r^6}{R_0^6 + r^6},$$

which can again be used for determining r .

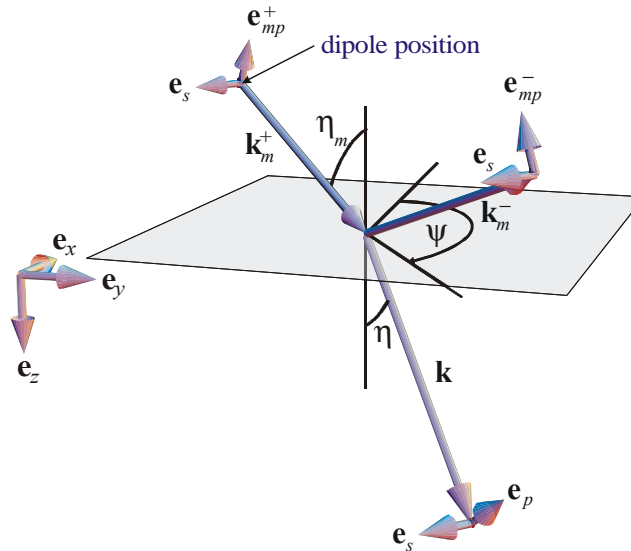
5. Fluorescing molecules on dielectric planar substrates

Until now, we have considered only an emitting molecule within a homogeneous environment or close to another absorbing molecule. Nonetheless, we have already seen that the properties of the molecule's environment, either represented by the refractive index of the embedding medium either by the optical-absorption capability of a nearby molecule, change the fundamental emission properties such as the excited state lifetime. Here, we will look closer onto this phenomenon, and more specifically, we will study the impact of the presence of a planar substrate on the molecule's emission properties.

When considering an oscillating dipole at position \mathbf{r}_0 over a surface, it is useful to go back to the integral representation of the free dipole as given in Section 3:

$$\mathbf{E}(\mathbf{r}) = \frac{4\pi}{\epsilon_m} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{\exp(i\mathbf{k} \cdot \mathbf{R})}{k^2 - \epsilon_m k_0^2} [\epsilon_m k_0^2 \mathbf{p} - \mathbf{k}(\mathbf{k} \cdot \mathbf{p})],$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}_0$, and the index m refers always to characteristics of the medium where the dipole is located. We will employ cylindrical coordinates with their z -axis perpendicular to the interface and pointing from the dipole towards the interface. The general geometry and several vectors used are shown in the following scheme.



Performing the integration along the wave vector component that is vertical to the interface, along a closed contour in the complex plane similar to that employed in Section 3, Cauchy's theorem yields

$$\mathbf{E} = \frac{i}{2\pi\epsilon_m} \int \frac{d^2\mathbf{q}}{w_m} [k_m^2 \mathbf{p} - \mathbf{k}_m^\pm (\mathbf{k}_m^\pm \cdot \mathbf{p})] \exp(i\mathbf{q} \cdot (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) + iw_m |z - z_0|),$$

where we have introduced cylindrical co-ordinates $\mathbf{R} = (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0, z - z_0)$ and $\mathbf{k}_m^\pm = (\mathbf{q}, \pm w_m)$, and the abbreviations $w_m = \sqrt{k_m^2 - q^2}$ and $k_m = \sqrt{\epsilon_m} k_0$ are used (w_m being value of the vertical \mathbf{k} -component at the pole of the integrand's denominator). The \pm -superscript in \mathbf{k}_m^\pm in accordance whether the target point \mathbf{r} is below or above the dipole's position, and the value of w_m has always non-negative imaginary part, corresponding to the fact that we admit only waves propagating away from the dipole, see also figure above. The found representation is the so called Weyl representation of the electric field of an oscillating dipole. This representation is perfectly suited to study the interaction of the dipole with a planar substrate at $z = 0$. Upon interaction, every plane wave in the Weyl representation is refracted and diffracted at the interface according to the formulas derived in Section 2.

Let us consider the case of a simple interface dividing the upper medium ($z < 0$) with dielectric constant ϵ_m from a lower medium ($z > 0$) with dielectric constant ϵ . Firstly, we separate the p - and s -waves within the Weyl representation above. Let us introduce two unit vectors \mathbf{e}_{mp}^+ and \mathbf{e}_s that are perpendicular to each other and to the wave vector \mathbf{k}_m , and with \mathbf{e}_s being parallel to the interface (cf. figure above). These unit vectors correspond to the polarizations of the p - and s -components of the plane wave propagating along \mathbf{k}_m and allow the recasting of the Weyl representation into the form

$$\mathbf{E} = \frac{ik_0^2}{2\pi} \iint \frac{d\mathbf{q}}{w_m} [\mathbf{e}_{mp}^\pm (\mathbf{e}_{mp}^\pm \cdot \mathbf{p}) + \mathbf{e}_s (\mathbf{e}_s \cdot \mathbf{p})] \exp[i\mathbf{q} \cdot (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) + iw_m |z - z_0|].$$

The unit vectors themselves have the explicit forms (in Cartesian co-ordinates, as shown in above figure)

$$\begin{aligned} \mathbf{e}_{mp}^+ &= (w_m \cos \psi, w_m \sin \psi, -q) / k_m = (\cos \psi \cos \eta_m, \sin \psi \cos \eta_m, -\sin \eta_m), \\ \mathbf{e}_s &= \mathbf{k}_m^+ \times \mathbf{e}_{mp}^+ / k_m = \mathbf{k}_m^- \times \mathbf{e}_{mp}^- / k_m = (-\sin \psi, \cos \psi, 0). \end{aligned}$$

Secondly, every plane wave in the above representation is reflected and transmitted at the interface, with reflection and transmission coefficients $R_{p,s}$ and $T_{p,s}$ for plane p - and s -waves that are given by (see Section 2)

$$R_p = \frac{w_m \epsilon - w \epsilon_m}{w_m \epsilon + w \epsilon_m}, R_s = \frac{w_m - w}{w_m + w},$$

and

$$T_p = \frac{2n_m n w_m}{w_m \epsilon + w \epsilon_m}, T_s = \frac{2w_m}{w_m + w}.$$

Now, it is straightforward to write down expressions for the electric fields transmitted through and reflected at the surface:

$$\mathbf{E}_T = \frac{ik_0^2}{2\pi} \iint \frac{d\mathbf{q}}{w_m} [\mathbf{e}_p T_p (\mathbf{e}_{mp}^+ \cdot \mathbf{p}) + \mathbf{e}_s T_s (\mathbf{e}_s \cdot \mathbf{p})] \exp[i\mathbf{q} \cdot (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) + iw_m |z_0| + iwz]$$

$$\mathbf{E}_R = \frac{ik_0^2}{2\pi} \iint \frac{d\mathbf{q}}{w_m} [\mathbf{e}_{mp}^- R_p (\mathbf{e}_{mp}^+ \cdot \mathbf{p}) + \mathbf{e}_s R_s (\mathbf{e}_s \cdot \mathbf{p})] \exp[i\mathbf{q} \cdot (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) + iw_m |z_0| - iwz]$$

where the additional unit vectors

$$\mathbf{e}_{mp}^- = (-w_m \cos \psi, -w_m \sin \psi, -q)/k_m = (-\cos \psi \cos \eta_m, -\sin \psi \cos \eta_m, -\sin \eta_m),$$

$$\mathbf{e}_p = (w \cos \psi, w \sin \psi, -q)/k = (\cos \psi \cos \eta, \sin \psi \cos \eta, -\sin \eta)$$

are defined. Please notice the negative sign in front of the exponential term iwz in the expression for the reflected field, showing that the reflected waves move away from the interface.

The next important quantity, after having obtained expressions for the electric field, is the *angular distribution of radiation* in both half spaces. For a propagating plane wave, $\mathbf{E}_k \exp(i\mathbf{k} \cdot \mathbf{r})$, propagating within a medium of refractive index n , the intensity of electromagnetic radiation into the direction \mathbf{k} is given by $S = (cn/8\pi)|\mathbf{E}_k|^2$. Thus, the intensity of the dipole radiation emitted into the upper half-space ($z < 0$) into a solid angle element $d\Omega^2 = (q/w_m k_m) dq d\phi$ along direction (\mathbf{q}, w) is proportional to

$$\begin{aligned} \frac{d^2 S_R}{d\Omega^2} &\propto n_m \left| \frac{k_0^2 k_m}{2\pi} \right|^2 \left\{ \left[\hat{\mathbf{e}}_{mp}^- (\hat{\mathbf{e}}_{mp}^- \cdot \mathbf{p}) + \hat{\mathbf{e}}_s (\hat{\mathbf{e}}_s \cdot \mathbf{p}) \right] + \left[\hat{\mathbf{e}}_{mp}^- R_p (\hat{\mathbf{e}}_{mp}^+ \cdot \mathbf{p}) + \hat{\mathbf{e}}_s R_s (\hat{\mathbf{e}}_s \cdot \mathbf{p}) \right] \exp(2i w_m |z_0|) \right\}^2 \\ &\propto n_m \left| \frac{k_0^2 k_m}{2\pi} \right|^2 \left\{ \left| \left[\hat{\mathbf{e}}_{mp}^- + R_p \hat{\mathbf{e}}_{mp}^+ \exp(2i w_m |z_0|) \right] \cdot \mathbf{p} \right|^2 + \left| \left[1 + R_s \exp(2i w_m |z_0|) \right] (\hat{\mathbf{e}}_s \cdot \mathbf{p}) \right|^2 \right\} \end{aligned}$$

The still unknown proportionality factor can be found by considering the limiting case that the upper and lower half space have the same refractive index, for which one has to recover the angular distribution of radiation of a free dipole (Section 3). Then,

$R_p = R_s \equiv 0$, and the above expression simplifies to

$$\frac{d^2 S_R}{d\Omega^2} \propto n_m \left| \frac{k_0^2 k_m}{2\pi} \right|^2 \left(\left| \hat{\mathbf{e}}_{mp}^- \cdot \mathbf{p} \right|^2 + \left| \hat{\mathbf{e}}_s \cdot \mathbf{p} \right|^2 \right) = n_m \left| \frac{k_0^2 k_m}{2\pi} \right|^2 \left[p^2 - (\hat{\mathbf{r}} \cdot \mathbf{p})^2 \right]$$

which should be identical to $\frac{cn_m k_0^4}{8\pi} \left[p^2 - (\hat{\mathbf{r}} \cdot \mathbf{p})^2 \right]$, so that the missing proportionality

factor is $c\pi/2k_m^2$, or

$$\frac{d^2 S_R}{d\Omega^2} = \frac{cn_m k_0^4}{8\pi} \left\{ \left| \left[\hat{\mathbf{e}}_{mp}^- + R_p \hat{\mathbf{e}}_{mp}^+ \exp(2i w_m |z_0|) \right] \cdot \mathbf{p} \right|^2 + \left| \left[1 + R_s \exp(2i w_m |z_0|) \right] (\hat{\mathbf{e}}_s \cdot \mathbf{p}) \right|^2 \right\}$$

By applying a similar line of reasoning for the angular distribution of radiation into the solid angle element $d\Omega^2 = (q/wk)dq d\phi$ in lower half space, we obtain

$$\frac{d^2 S_T}{d\Omega^2} = \frac{cnk_0^4}{8\pi} \left| \frac{w}{w_m} \right|^2 \left\{ \left| T_p \hat{\mathbf{e}}_{mp}^+ \cdot \mathbf{p} \right|^2 + \left| T_s \hat{\mathbf{e}}_s \cdot \mathbf{p} \right|^2 \right\} \exp[-2 \operatorname{Im}(w_m) |z_0|].$$

Notice the exponential term in the last expression: Even plane wave components with $\operatorname{Im}(w_m) > 0$, that are non-propagating and quickly decaying in upper half space (evanescent modes), can contribute to the far-field radiation in lower half-space. What is happening from a quantum-mechanical point of view is that virtual photons that are non-propagating in upper half-space tunnel through the gap between dipole and interface into the lower-half space where they are allowed to propagate. This can, of course, only happen if the refractive index of the lower half-space is larger than that of the upper half-space, so that there exist values of q where simultaneously $\operatorname{Im}(w) = 0$ and $\operatorname{Im}(w_m) > 0$.

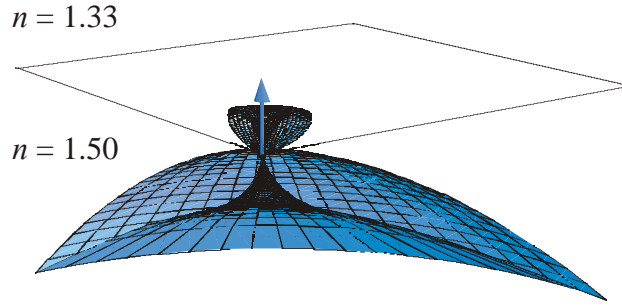
Let us next consider two limiting cases of dipole orientation: dipole orientation vertical, and dipole orientation parallel to the interface. In case of a vertical orientation we have $\mathbf{p} = p\hat{\mathbf{z}}$, so that

$$\frac{d^2 S_R}{d\Omega^2} = \frac{cn_m k_0^4}{8\pi} \left| \frac{qp}{k_m} \right|^2 \left| 1 + R_p \exp(2iw_m |z_0|) \right|^2$$

and

$$\frac{d^2 S_T}{d\Omega^2} = \frac{cnk_0^4}{8\pi} \left| \frac{qwp}{k_m w_m} \right|^2 |T_p|^2 \exp[-2\text{Im}(w_m)|z_0|].$$

The resulting angular distribution of radiation for a vertical dipole directly on a water/glass interface ($n_m = 1.33$, $n = 1.5$) is shown in the next figure.



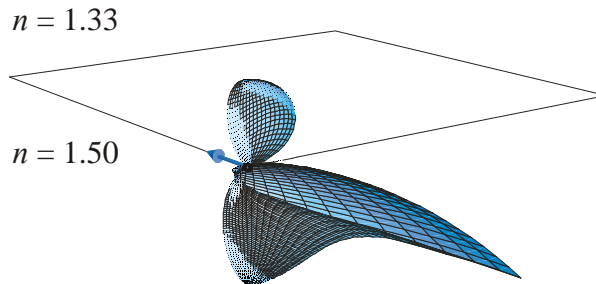
For the parallel dipole (along the direction $\phi = 0$) we have $\mathbf{p} = (p, 0, 0)$, and thus obtain

$$\frac{d^2 S_R}{d\Omega^2} = \frac{cn_m k_0^4 p^2}{8\pi} \left\{ \left| \frac{w_m}{k_m} \right|^2 \left| 1 - R_p \exp(2iw_m |z_0|) \right|^2 \cos^2 \phi + \left| 1 + R_s \exp(2iw_m |z_0|) \right|^2 \sin^2 \phi \right\}$$

and

$$\frac{d^2 S_T}{d\Omega^2} = \frac{cnk_0^4 p^2}{8\pi} \left| \frac{w}{w_m} \right|^2 \left\{ \left| \frac{w_m}{k_m} \right|^2 |T_p|^2 \cos^2 \phi + |T_s|^2 \sin^2 \phi \right\} \exp[-2\text{Im}(w_m)|z_0|].$$

The corresponding emission pattern is shown in the next figure.

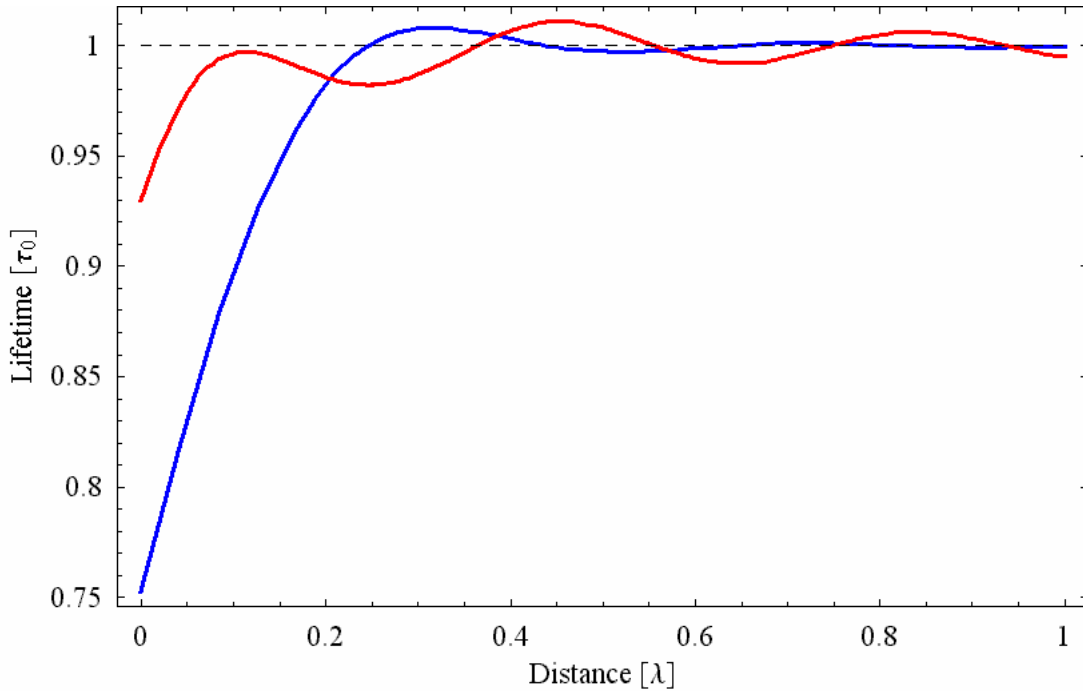


When integrating the derived angular distributions of radiation over all angles in both half-spaces, i.e.

$$S_{tot} = \int_0^{k_0 n_m} \frac{dq q}{k_m w_m} \int_0^{2\pi} d\phi \frac{d^2 S_R}{d\Omega^2} + \int_0^{k_0 n} \frac{dq q}{k w} \int_0^{2\pi} d\phi \frac{d^2 S_T}{d\Omega^2},$$

one calculates the *total* power of emission, S_{tot} . The ratio of that power to the total power of radiation of the free dipole in homogeneous medium with refractive index n_m then gives the inverse ratio of the fluorescence decay times in both cases.

The next figure shows the thus calculated dependence of the fluorescence lifetime for a dipole at a water/glass interface in dependence on its distance from silver surface interface.



The red line refers to a dipole oriented parallel, the blue line to a dipole oriented vertically to the surface.

6. Fluorescing molecules near planar metallic substrates

In the last Section, we considered the interaction of an emitting molecule with a dielectric substrate. In that case, no optical absorption of the emitted light took place. Thus, by integrating the far-field angular distribution of radiation over the whole solid angle of 4π , we were able to obtain the total power of emission of the dipole, which is inversely related to the fluorescence decay time. When considering the interaction with a metal (metal film or metallic half-space), the situation becomes more complicated. Metals have dielectric constants with non-zero imaginary part, leading to absorption of electromagnetic radiation within metallic bodies. Thus, the integral over the complete far-field radiation does no longer equal the total emission power of the dipole, because there is additional energy absorption within the metal. To obtain this total emission, one has to integrate the Poynting vector over a closed surface enclosing the dipole but no other absorbing material. In case of a dipole over a planar, possibly metallic substrate, one has thus to find the total energy emission into the lower half-space via the integral

$$S_- = \frac{c}{8\pi} \operatorname{Re} \int_{z=0} dA \hat{\mathbf{z}} \cdot (\mathbf{E} \times \mathbf{B}^*).$$

The electric field at $z = 0$ is given by either

$$\mathbf{E}_T = \frac{ik_0^2}{2\pi} \iint \frac{d\mathbf{q}}{w_m} [\mathbf{e}_p T_p (\mathbf{e}_{mp}^+ \cdot \mathbf{p}) + \mathbf{e}_s T_s (\mathbf{e}_s \cdot \mathbf{p})] \exp[i\mathbf{q} \cdot (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) + iw_m |z_0|]$$

or

$$\mathbf{E}_R = \frac{ik_0^2}{2\pi} \iint \frac{d\mathbf{q}}{w_m} [(\mathbf{e}_{mp}^+ + \mathbf{e}_{mp}^- R_p) (\mathbf{e}_{mp}^+ \cdot \mathbf{p}) + \mathbf{e}_s (1 + R_s) (\mathbf{e}_s \cdot \mathbf{p})] \exp[i\mathbf{q} \cdot (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) + iw_m |z_0|].$$

Both expressions will lead to the same result for the energy flux through the interface.

The corresponding magnetic fields are obtained by acting with the operator $k_0^{-1} \mathbf{rot}$ on the electric field expressions:

$$\mathbf{B}_T = \frac{ik_0^2 n}{2\pi} \iint \frac{d\mathbf{q}}{w_m} [\mathbf{e}_s T_p (\mathbf{e}_{mp}^+ \cdot \mathbf{p}) - \mathbf{e}_p T_s (\mathbf{e}_s \cdot \mathbf{p})] \exp[i\mathbf{q} \cdot (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) + iw_m |z_0|],$$

$$\mathbf{B}_R = \frac{ik_0^2 n_m}{2\pi} \iint \frac{d\mathbf{q}}{w_m} [\mathbf{e}_s (1 + R_p) (\mathbf{e}_{mp}^+ \cdot \mathbf{p}) - (\mathbf{e}_{mp}^+ + \mathbf{e}_{mp}^- R_s) (\mathbf{e}_s \cdot \mathbf{p})] \exp[i\mathbf{q} \cdot (\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) + iw_m |z_0|].$$

Thus, we obtain two alternative expressions for the total energy flux through the interface:

$$\begin{aligned} S_- &= \frac{ck_0^4}{32\pi^3} \operatorname{Re} \int \frac{d^2\mathbf{q}}{w_m} \int \frac{d^2\mathbf{q}'}{w_m'^*} \int d^2\tilde{\mathbf{n}} \frac{n_m^*}{k} [w(T_p \mathbf{e}_{mp}^+ \cdot \mathbf{p})(T_p' \mathbf{e}_{mp}' \cdot \mathbf{p}) \\ &\quad + w'^*(T_s \mathbf{e}_s \cdot \mathbf{p})(T_s' \mathbf{e}_s' \cdot \mathbf{p})] \exp[i(\mathbf{q} - \mathbf{q}')(\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) - \operatorname{Im}(w_m + w_m')|z_0|] \\ &= \frac{ck_0^4}{8\pi} \operatorname{Re} \int \frac{d^2\mathbf{q}}{|w_m|^2} \frac{n_m^*}{k} \left[w |T_p(\mathbf{e}_{mp}^+ \cdot \mathbf{p})|^2 + w'^* |T_s(\mathbf{e}_s \cdot \mathbf{p})|^2 \right] \exp[-2\operatorname{Im}(w_m)|z_0|] \end{aligned}$$

and

$$\begin{aligned} S_- &= \frac{ck_0^4}{32\pi^3} \operatorname{Re} \int \frac{d^2\mathbf{q}}{w_m} \int \frac{d^2\mathbf{q}'}{w_m'^*} \int d^2\tilde{\mathbf{n}} \frac{n_m^*}{k_m} [w_m(1 - R_p)(1 + R_p^*)(\mathbf{e}_{mp}^+ \cdot \mathbf{p})(\mathbf{e}_{mp}' \cdot \mathbf{p})^* + \\ &\quad + w_m'^*(1 + R_s)(1 - R_s^*)(\mathbf{e}_s \cdot \mathbf{p})(\mathbf{e}_s' \cdot \mathbf{p})^*] \exp[i(\mathbf{q} - \mathbf{q}')(\tilde{\mathbf{n}} - \tilde{\mathbf{n}}_0) - \operatorname{Im}(w_m + w_m')|z_0|] \\ &= \frac{ck_0^4}{8\pi} \operatorname{Re} \int \frac{d^2\mathbf{q}}{|w_m|^2} \frac{n_m^*}{k_m} \left[w_m(1 - R_p)(1 + R_p^*)|\mathbf{e}_{mp}^+ \cdot \mathbf{p}|^2 + \right. \\ &\quad \left. + w_m'^*(1 + R_s)(1 - R_s^*)|\mathbf{e}_s \cdot \mathbf{p}|^2 \right] \exp[-2\operatorname{Im}(w_m)|z_0|] \end{aligned}$$

In the above expressions, all primed variables refer to the integration variable \mathbf{q}' , and we used the well-known identity for Dirac's δ -function

$$\int d^2\tilde{\mathbf{n}} \exp[i\tilde{\mathbf{n}} \cdot (\mathbf{q} - \mathbf{q}')] = (2\pi)^2 \delta^2(\mathbf{q} - \mathbf{q}').$$

Both expressions obtained for S_- lead to exactly the same values, although that is not obvious when comparing them by sight.

Again, we consider the two limiting dipole orientations, vertically and parallel to the surface. We will present final results using the expression for S_- on the dipole side (involving reflection coefficients). This is especially advantageous if one considers multilayered substrates: all results remain valid, one has only to use the generalized reflection coefficients for the multilayer structure. Thus, for the vertical dipole, we obtain

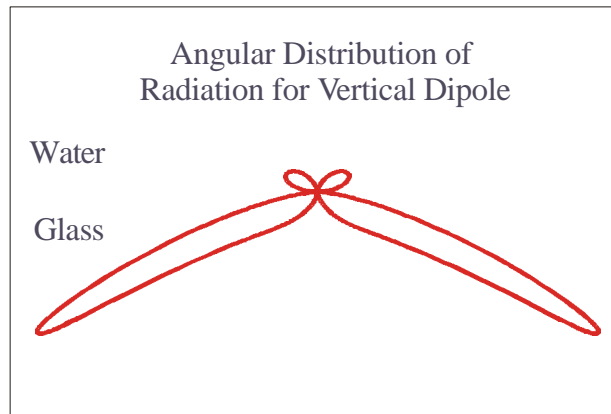
$$S_- = \frac{ck_0^4 p^2}{4} \operatorname{Re} \int \frac{dq}{|k_m w_m|^2} \frac{q^3 n_m^* w_m}{k_m} (1 - R_p)(1 + R_p^*) \exp[-2\operatorname{Im}(w_m)|z_0|]$$

Similarly, we find for the parallel dipole the result:

$$S_- = \frac{ck_0^4 p^2}{8} \operatorname{Re} \int dq \frac{qn_m^*}{|w_m^2|k_m} \cdot \left[\frac{|w_m^2|}{k_m^2} w_m (1 - R_p)(1 + R_p^*) + w_m^* (1 + R_s)(1 - R_s^*) \right] \exp[-2 \operatorname{Im}(w_m) |z_0|]$$

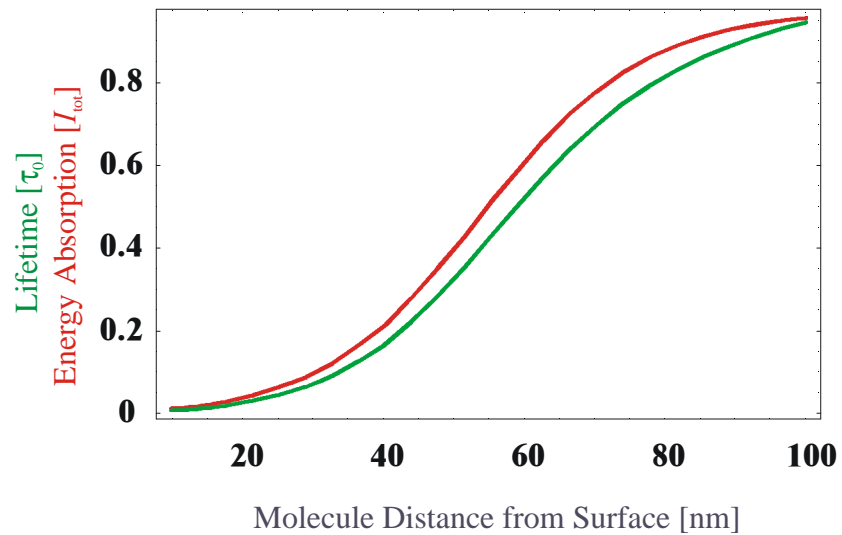
The usefulness of these results is that they allow for calculating the total emission power of the molecule into the substrate, and together with the total emission into the upper half-space as derived in the previous section, the yield information about the fluorescence lifetime of the molecule. Moreover, for a substrate with thin absorbing layers allowing light to tunnel through and radiate into the lower half-space, we have already derived the angular distribution of radiation into that half-space: The found expressions of the last Section remain valid as long as one uses the correct transmission coefficients for the absorbing substrate. These coefficients can be calculated exactly in the same way as for dielectric substrates, as was detailed in Section 2.

As an example let us consider the emission of a dipole near a water/glass interface that is covered by a thin (5 nm) film of silver ($n = 0.163 + i 4.07$). The next figure shows the calculated angular distribution of radiation both within the glass and the water for a vertically oriented dipole.



The dependence of the fluorescence decay time *and* the amount of energy absorbed by the metal for the same configuration shows the next figure. The energy absorption is calculated in the following way: firstly, one calculates the complete far-field emission via integrating the angular distribution of radiation over all directions; secondly, one calculates the total emission power of the dipole as the sum of the far-field radiation

into the upper half-space (water) plus the energy flux through the water/metal interface, using the expressions found above. The energy absorption is then given as the ratio of complete far-field radiation divided by total emission power. In the figure, the reference lifetime τ_0 is that of the free dipole in water.



7. Fluorescing molecules in beads and spherical cavities

Until now, we have studied only the interaction of fluorescing molecules with planar substrates. In this Section, we will extend our studies to problems with spherical symmetry, i.e. the interaction of dipole emitters with spherical beads and cavities. In Section 3, we have found a representation of the electric field (and thus indirectly also for the magnetic field) of the oscillating electric dipole in plane waves, which proved to be the corner-stone for handling all subsequent problems of dipole interactions with planar substrates. The same philosophy applies for other than planar geometries: For any given geometry, find a representation of the dipole field in an orthogonal function system corresponding to the given geometry. Unfortunately, there exist separable, complete, and orthogonal function systems only for a limited number of special co-ordinate systems, among the Cartesian, cylinder, spherical and ellipsoidal co-ordinates. In spherical co-ordinates, a complete orthonormal vector-valued function system is provided by the so-called vector spherical harmonics, which are defined in spherical co-ordinates (r, θ, ϕ) by

$$\mathbf{M}_{nm}^f(kr, \theta, \phi) = \sqrt{\frac{2n+1}{4\pi} \frac{(n-m)!}{(n+m)!}} \left[P_n^m \frac{im}{\sin \theta} \mathbf{e}_\theta - (P_n^{m+1} + m \cot \theta P_n^m) \mathbf{e}_\phi \right] f_n e^{im\phi}$$

$$\mathbf{N}_{nm}^f(kr, \theta, \phi) = \sqrt{\frac{2n+1}{4\pi} \frac{(n-m)!}{(n+m)!}} \left\{ \frac{n(n+1)}{kr} f_n P_n^m e^{im\phi} \mathbf{e}_r + \right.$$

$$\left. + \frac{1}{2} \left(\frac{f_n}{kr} + f_{n-1} - f_{n+1} \right) \left[(P_n^{m+1} + m \cot \theta P_n^m) \mathbf{e}_\theta + \frac{im}{\sin \theta} P_n^m \mathbf{e}_\phi \right] e^{im\phi} \right\}.$$

Here, P_n^m denote associated Legendre polynomials with argument $\cos \theta$, the f_n are spherical Bessel functions with argument kr , the \mathbf{e}_r , \mathbf{e}_θ , \mathbf{e}_ϕ are unit vectors along the co-ordinate lines, and the functional system is labeled by the integer indices (n, m) , $0 \leq n < \infty$, $-n \leq m \leq n$. The vector spherical harmonics constitute a complete set of orthogonal functions that fulfill the vector wave equation, namely $\Delta \mathbf{M} + k^2 \mathbf{M} = 0$, together with the zero-divergence condition $\mathbf{div} \mathbf{M} = 0$ (similarly for \mathbf{N}). When omitting the zero-divergence condition, there exists still a third class of functions to form a complete functional basis, which we will however not consider here. Thus, the functions \mathbf{M} and \mathbf{N} constitute a complete (within the space of zero-divergent functions)

orthonormal vector-valued function system in spherical co-ordinates similarly to the plane-wave function system in Cartesian co-ordinates which we met in Section 1. Additionally, the vector spherical harmonics are connected by the relations $\mathbf{rot} \mathbf{M} = k\mathbf{N}$ and $\mathbf{rot} \mathbf{N} = k\mathbf{M}$. The harmonics for negative values of m , $|m| \leq n$, are given by the complex conjugate expressions of $\mathbf{M}_{n|m|}^f$ and $\mathbf{N}_{n|m|}^f$.

Next, we have to find a representation of the dipole field in this function system. without proof, we state here only the final result which reads

$$\mathbf{E}(\mathbf{r}) = \sum_{n=1}^{\infty} \sum_{m=-n}^n [a_{nm} \mathbf{M}_{nm}^h(k\mathbf{r}) + b_{nm} \mathbf{N}_{nm}^h(k\mathbf{r})]$$

with the expansion coefficients

$$a_{nm} = \frac{4\pi i k k_0^2}{n(n+1)} \mathbf{p} \cdot \overline{\mathbf{M}_{nm}^j(k\mathbf{r}')} \quad \text{and} \quad b_{nm}^D = \frac{4\pi i k k_0^2}{n(n+1)} \mathbf{p} \cdot \overline{\mathbf{N}_{nm}^j(k\mathbf{r}')}.$$

Here, j and h stand for the spherical Bessel and Hankel functions $j(kr)$ and $h^1(kr)$. It is assumed that $r' < r$, else one has to interchange $j \leftrightarrow h$.

For practical purposes, several special dipole positions/orientations are of interest. Without loss of generality, we consider further only dipoles situated on the polar axis $\theta = 0$. If the dipole is oriented perpendicular to that axis along the direction $(\theta = \pi/2, \phi = 0)$, we have

$$a_{n,\pm 1} = \mp k k_0^2 \sqrt{\frac{\pi(2n+1)}{n(n+1)}} j_n(kr'),$$

$$b_{n,\pm 1} = -i k k_0^2 \sqrt{\frac{\pi(2n+1)}{n(n+1)}} \frac{\partial_{r'}(r' j_n(r'))}{kr'},$$

and if it is oriented along the polar axis $\theta = 0$, we find $a_{nm} \equiv 0$ and

$$b_{n,0} = i k_0^2 \sqrt{4\pi(2n+1)} \frac{j_n(kr')}{r'}.$$

With these expressions at hand, the further procedure of studying the interaction of the dipole with spherical objects is straightforward. As an example, let us consider a dipole within a metallic spherical cavity of inner radius R and thickness d as shown in the fig-

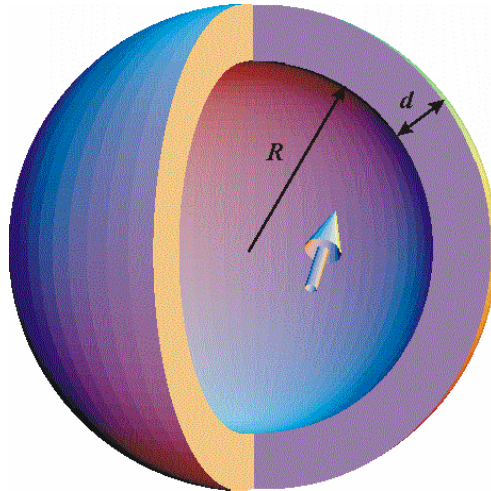
ure on the next page. Due to the interaction of the dipole field with the cavity, a reaction field is generated which can itself be expanded in vector spherical harmonics, on expansion for every of the three different media cavity core (c), shell (s), and environment (e)

$$\mathbf{E}_e = \sum_{n=1}^{\infty} \sum_{m=-n}^n [a_{nm}^{(e)} \mathbf{M}_{nm}^h(k_e \mathbf{r}) + b_{nm}^{(e)} \mathbf{N}_{nm}^h(k_e \mathbf{r})],$$

$$\mathbf{E}_s = \sum_{n=1}^{\infty} \sum_{m=-n}^n [a_{nm}^{(s,j)} \mathbf{M}_{nm}^j(k_s \mathbf{r}) + b_{nm}^{(s,j)} \mathbf{N}_{nm}^j(k_s \mathbf{r}) + a_{nm}^{(s,h)} \mathbf{M}_{nm}^h(k_s \mathbf{r}) + b_{nm}^{(s,h)} \mathbf{N}_{nm}^h(k_s \mathbf{r})],$$

$$\mathbf{E}_c = \sum_{n=1}^{\infty} \sum_{m=-n}^n [a_{nm}^{(c)} \mathbf{M}_{nm}^j(k_c \mathbf{r}) + b_{nm}^{(c)} \mathbf{N}_{nm}^j(k_c \mathbf{r})].$$

The $k_{e,s,c}$ are the three corresponding wave numbers of the three media, and if the dipole is e.g. o located within the core, one has obviously to use $k = k_c$ in the dipole-field expansion on the previous page. Notice the occurrence of the different Bessel/Hankel functions in the above expansion: Outside the cavity, only expanding wave traveling away from the cavity are admitted, thus asking for $h_n^1(k_e r)$; inside the core, the field has to remain finite, thus only $j_n(k_e r)$ are allowed; within the shell, both functions are admitted.



The eight unknown coefficients $a_{nm}^{(e)}$, $a_{nm}^{(s,j)}$, $a_{nm}^{(s,h)}$, $a_{nm}^{(c)}$, $b_{nm}^{(e)}$, $b_{nm}^{(s,j)}$, $b_{nm}^{(s,h)}$ and $b_{nm}^{(c)}$ in the above equations have to be found as solutions to the boundary conditions for the elec-

tric and magnetic field amplitudes, namely that the tangential components of the electric and magnetic fields are continuous across all boundaries. For every order n of the above expansions, this yields a total of eight linear algebraic equations for the eight unknown coefficients, which can be solved in a straightforward way. We won't give here the rather complex algebraic solution – in practice, one can use a numerical equation solver for doing the job.

Two quantities are of major interest when considering the molecule's fluorescence emission: the lifetime of its excited state, and the energy transmission through the metallic shell (i.e. the probability that the dipoles energy is emitted away from the cavity). For obtaining both values, one calculates the energy fluxes S_{in} and S_{out} through the inner and outer surface of the metallic layer. If there are no non-radiative transition channels from the excited to the ground state (unity fluorescence quantum yield), then the excited state lifetime is proportional to $1/S_{in}$. Moreover, the probability that the dipole's energy is radiated away from the cavity and is not absorbed within the metal layer is given by S_{out}/S_{in} .

Knowing the electric and magnetic field amplitudes allows calculating S_{in} and S_{out} by integrating the Poynting vector over the corresponding surfaces, i.e.

$$S_{in} = \frac{c}{8\pi} \operatorname{Re} \left[\int_{r=R} (\mathbf{E}_{in} \times \mathbf{B}_{in}^*) \cdot d\mathbf{A} \right]$$

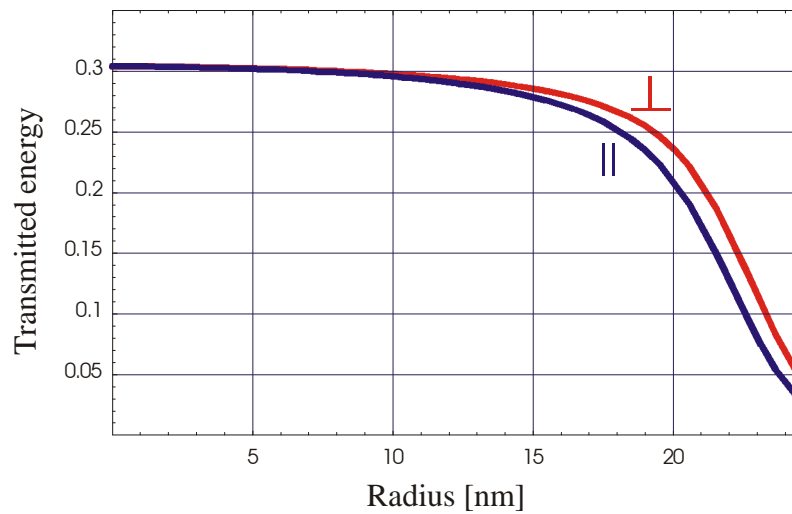
where $\mathbf{E}_{in} = \mathbf{E}_{dipole} + \mathbf{E}_c$. Analogously, one finds

$$S_{out} = \frac{c}{8\pi} \operatorname{Re} \left[\int_{r=R+d} (\mathbf{E}_e \times \mathbf{B}_e^*) \cdot d\mathbf{A} \right].$$

As before, the fluorescence lifetime of the molecule is inversely proportional to the total emission power, S_{in} , and the energy transmission through the metallic shell is given by S_{out}/S_{in} .

As a numerical example we consider a cavity with a polymeric core ($n = 1.5$) of 24 nm radius, surrounded by a silver shell ($n = 0.163 + i 4.07$) of 5 nm thickness, and immersed into a water solution ($n = 1.33$). The next figure shows the dependence of the optical transmission, S_{out}/S_{in} , on the dipole's position within the cavity for the two

principal dipole orientations, perpendicular (\perp) and along (\parallel) the line connecting the cavity's center with the dipole's position.



Similarly, the next figure shows the dependence of the fluorescence lifetime, using as reference lifetime τ_0 the lifetime of the same configuration but *without* the metallic shell (dipole within core in water).

