Comments on the classical theory of energy transfer. II. Extension to higher multipoles and anisotropic media*

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The classical electromagnetic theory of the fluorescence emission and energy transfer in layered systems is extended to describe magnetic dipole and electric quadrupole radiation and anisotropic media. A general formulation is developed for energy transfer from various emitter types and orientations to isotropic acceptors. The description is exact within the classical framework and requires none of the usual assumptions as to the nature of the acceptor layer. The theory is further extended to describe one- and two-dimensional acceptors and electric dipole radiation in an anisotropic medium. The latter case is the actual situation in the fatty-acid layer experiments. The coupling to the surface plasmon modes of the acceptor is discussed as it relates to the various systems described here.

I. INTRODUCTION

In a previous paper1 we have discussed energy transfer from an emitting electric dipole to an absorbing medium. This paper is an extension of that work to magnetic dipole and electric quadrupole emitters and to anisotropic media. Interest in these systems stems largely from the work of Kuhn and co-workers,2-4 who utilized the fatty-acid-monolayer assembly technique to examine the distance dependence of energy transfer. Their theoretical descriptions of the problem were limited to weakly absorbing media, an approximation which is valid in most of the experimental situations investigated. As in the previous paper,1 our description is exact within the framework of classical electromagnetic theory and requires no assumptions as to the nature of the absorbing media. We will also consider here the effect of the optical anisotropy of the fatty-acid layers which has been largely ignored in previous work, including our own.

In Sec. II results are presented for the interaction of electric dipole, magnetic dipole, and electric quadrupole radiation with an isotropic absorbing medium. The medium containing the emitter is restricted to a nonabsorbing half-space. The absorbing medium is described as a single layer of finite thickness. Energy transfer formulas are derived for the two limiting cases of very small and very large layer thicknesses.

In Sec. III, we discuss briefly the effect on energy transfer and surface plasmon coupling when an electric dipole is embedded in an anisotropic, nonabsorbing medium. In Sec. IV we describe energy transfer from an electric dipole to anisotropic media. Specifically, we consider one- and two-dimensional conductors as acceptors.

II. ISOTROPIC ABSORBING MEDIA

The interaction of an emitting electric dipole with an absorbing half-space (mirror) has been described by a number of authors.1,5-8 We have recently extended the theory to describe electric dipole radiation near a number of different mirror configurations.1,9,10 Here we use basically the same approach extended to magnetic dipole and electric quadrupole emission. The Hertz vectors are constructed by matching the appropriate boundary conditions at each interface. The decay rate is then calculated as the time rate of change of the energy of the oscillating charge distribution. Specific details of the derivation relevant to the present discussion will be published elsewhere11; here we will present only the results with emphasis on the energy transfer region.

The decay rate constant (normalized to unity in the absence of the acceptor) may be written as one general equation for the systems to be considered here (Fig. 1):

\[ b = 1 + A_{1} \Im \int_{0}^{\infty} \left( B_{\alpha} + C_{\alpha} \right) \exp(-2\hat{d}_1) \, \frac{du}{\hbar} \]

where \( q \) is the quantum yield of the emitting state, \( \hat{d}_1 \) is the normalized distance (\( \hat{d}_1 = \frac{2\pi \epsilon_{1}^{\frac{1}{2}}}{\lambda} \)), and from the

FIG. 1. Geometry of the problem. The emitter is an electric dipole, a magnetic dipole, or an electric quadrupole. Regions 1 and 3 are half-spaces. The normal to the interfaces is the z direction.
TABLE I. Parameters for Eq. (1).

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Orientation</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric dipole</td>
<td>z</td>
<td>−1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>x, y</td>
<td>½</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>isotropic</td>
<td>½</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Magnetic dipole</td>
<td>z</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>x, y</td>
<td>½</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>isotropic</td>
<td>½</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Electric quadrupole</td>
<td>z</td>
<td>−½</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>x, y, z</td>
<td>½</td>
<td>(1 − u 2)/u 2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>isotropic</td>
<td>½</td>
<td>(1 − 2a 2)/u 2</td>
<td>1</td>
</tr>
</tbody>
</table>

a Obtained as (β 2 + 2β 1)/3.
b Obtained as (β 2 + 2β 1 + 2β 0)/5.

emitter to the mirror, μ = sin θ (where θ is the angle of incidence for the emitted ray), and I 2 = −i(ε′/ε 1 − u 2)/2. ε′ and ε″ are the reflectivities of the mirror system for the electric field of the incident ray polarized parallel and perpendicular, respectively, to the plane of incidence. Restricting ourselves to the geometry illustrated in Fig. 1, we have

\[ \mathbf{R} = (R_{d2} + R_{d6} \exp(-2\mathbf{d}_z))(1 + R_{d2}R_{d6} \exp(-2\mathbf{d}_z))^{-1}, \]

where \( \mathbf{d}_z \) is the normalized layer thickness (\( \mathbf{d}_z = 2\pi\mathbf{d}_L/\lambda \)) and a superscript \( \bullet \), \( i \) is understood for \( \mathbf{R} \) and each \( \mathbf{R} \). The quantities \( R_{d2} \) and \( R_{d6} \) are the reflectivities of the individual interfaces. For example, for the first interface, we have

\[ R_{d2} = (\varepsilon_i\mathbf{l}_2 − \varepsilon_e\mathbf{l}_1)/(\varepsilon_i\mathbf{l}_2 + \varepsilon_e\mathbf{l}_1), \]

and

\[ R_{d6} = (\mathbf{l}_1 − \mathbf{l}_2)/(\mathbf{l}_1 + \mathbf{l}_2). \]

The dielectric constants are defined in terms of the real and imaginary parts of the refractive indices (\( n_f \), \( K_f \)) at the emission wavelength λ:

\[ \varepsilon_f = n_f^2 − K_f^2 + i2n_fK_f. \]

The remaining quantities \( A \), \( B \), and \( C \) take on different values for different emitters. Their values are shown in Table I for various emitters and a complete set of orientations. The electric dipole results have been presented previously for the \( z \) orientation.

Equation (1) and Table I yield results which are valid at all values of the distances, \( \mathbf{d}_1 \), and \( \mathbf{d}_2 \). In this paper we are concerned primarily with the energy transfer region, i.e., the small distance (small \( \mathbf{d}_1 \)) regime. We will consider two limiting cases:

Case 1 \( \mathbf{d}_2 \gg 1 \gg \mathbf{d}_1 \).

Case 2 \( \mathbf{d}_2 \ll \mathbf{d}_1 \).

Cases 1 and 2 are set up for the description of energy transfer to a single mirror and to a thin film, respectively. If we add the condition \( n_a = n_1 = n_2 \gg K_f \) under Case 2, we may compare our results to those derived by Kuhn\(^3\) using a different approach. In deriving all Case 2 formulas we will assume \( n_1 = n_2 \).

Using Eq. (1) together with the results of Table I, we may calculate the energy transfer rate constant \( \beta_{ET} \) as

\[ \beta_{ET} = \lim_{\mathbf{d}_1 \to 0} b \]

The results are

**Electric Quadrupole**

Case 1 \( \beta_{ET} = \left( \frac{q_2}{d_2^3} \right) \left( \frac{\varepsilon_1 n_f K_f}{\varepsilon_i} \right) \left( \frac{4\varepsilon_i^2 + 1}{\varepsilon_i + 1} \right) \)

Case 2 \( \beta_{ET} = \left( \frac{2q_2}{d_2^4} \right) \left[ \frac{\varepsilon_i n_f K_f}{\varepsilon_i} \left( 1 + \frac{\varepsilon_i^2}{\varepsilon_i + 1} \right) \right] \)

**Magnetic Dipole**

Case 1 \( \beta_{ET} = \left( \frac{q_2}{d_2^4} \right) \left( \frac{n_f K_f}{\varepsilon_i} \right) \left( \frac{\varepsilon_i}{\varepsilon_i + 1} \right) \)

Case 2 \( \beta_{ET} = \left( \frac{15q_2}{d_2^4} \right) \left( \frac{n_f K_f}{\varepsilon_i} \right) \left( 1 + \frac{\varepsilon_i^2}{\varepsilon_i + 1} \right) \)

The quantities \( \theta_1 \) and \( \theta_2 \) are orientational parameters and are given in Table II. \( \theta_1 \) derives from \( \theta_1^* \) in Eq. (1) while \( \theta_2 \) originates from \( \theta_1^* \).

We,\(^1\) as well as Morawitz and Philpott,\(^5\) have pointed out previously that the short range field of the electric dipole couples to the surface plasmon modes of the metal according to the dispersion relation

\[ \varepsilon_1 + \varepsilon_2 = 0. \]

This coupling is also evident in all the Case 1 results.

**TABLE II. Energy transfer parameters.**

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Orientation</th>
<th>( \theta_1^* )</th>
<th>( \theta_2^* )</th>
<th>( \theta_{DP}(\text{Kuhn}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric dipole</td>
<td>z</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>x, y</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>isotropic</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Magnetic dipole</td>
<td>z</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>x, y</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>isotropic</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Electric quadrupole</td>
<td>z</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td></td>
<td>x, y, z</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td></td>
<td>isotropic</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\( ^a \) For insertion in Eqs. (7)–(12) (isotropic acceptor).

\( ^b \) From Refs. 2 and 3 for the case \( n_a = n_1 = n_2 \gg K_f \) with acceptor transition dipoles oriented randomly in \( xy \) plane.

\( ^c \) Obtained as \( (\beta_2 + 2\beta_0)/3 \).

\( ^d \) Obtained as \( (\beta_2 + 2\beta_0 + 2\beta_1)/5 \).

with the exception of the perpendicular (z) orientation of the magnetic dipole; in that case, there is no coupling, since the radiation field contains no component normal to the mirror surface.

In Case 2, we show no surface plasmon coupling because of the restriction \( d_2 \ll d_1 \). At larger values of the distance ratio \( d_3/d_1 \), surface plasmon coupling is evident as is shown in Ref. (1) for electric dipole radiation.

The results for an electric dipole given in Table II may be compared directly with those of Kuhn\(^2\) in the limit of weak absorbers, \( n_2 = n_1 = n_{g} > K_{g} \). As we pointed out previously,\(^1\) they are in agreement. For magnetic dipoles and electric quadrupoles Kuhn treats only the case where the transition moments of the acceptor lie (randomly) in the xy plane. This restriction has no effect on \( \theta_{g} \), since \( d_{g} \) has no z component. However, from geometrical considerations \( \theta_{g} \) is reduced a factor of 2 by this restriction to a two-dimensional acceptor. It is also reduced by a factor of 2 if the acceptor transition moments are oriented only in the z direction. Table II lists Kuhn’s values\(^12\) for \( \theta_{g} \) (acceptor transition moments in xy plane) which should be related to our results as \( \theta_{g} = \frac{1}{2} \theta_{g} + \theta_{d} \). We have agreement in all cases except the xy and yz quadrupoles, where the previous results\(^5\) are \( \frac{2}{3} \) smaller than ours. We repeated the calculations using Kuhn’s method for both two-dimensional and isotropic acceptors and for all cases shown in Table II. We find \( \theta_{2d} = \frac{1}{2} \theta_{g} + \theta_{d} \) and \( \theta_{iso} = \theta_{g} + \theta_{d} \) as required by the earlier discussion. We conclude that the previous results are in error for these two cases. We want to emphasize, however, that the error is of little consequence numerically, since it ends up being raised to the \( \frac{1}{2} \) power, and does not affect any of the conclusions in Refs. (2–4).

Before leaving this section, a few additional comments are in order concerning the weak absorber limiting case. It is now clear that, to apply Kuhn’s formulation\(^15\) to an experimental system, it is not sufficient that the acceptor layer absorb weakly at the emission frequency of the donor—an experimental condition which could be satisfied, for example, by simply making the acceptor layer thinner. The acceptor layer must intrinsically be a weak absorber. In the case of dye acceptors this can be accomplished, if necessary, by diluting the dye layer itself. In the case of highly absorbing metals as acceptors, however, the previous formulation\(^5\) does not apply, no matter how thin the layer.

### III. ELECTRIC DIPOLE EMBEDDED IN ANISOTROPIC MEDIUM

In this section, we will consider the situation where the emitter (electric dipole) is embedded in an anisotropic dielectric of the form \( n_{g} = n_{e} \neq n_{s} \). This system is of interest, because it describes the actual experimental situation in all the fatty acid-layer experiments.\(^13\) For example, the frequently used CdC\(_2\) layers have ordinary and extraordinary refractive indices given by \( n_{g} = 1.52 \) and \( n_{e} = 1.59 \),\(^13\) Drexhage has already shown, in a radiation zone calculation, that this anisotropy can have a considerable effect on the angular distribution of fluorescence emission.\(^13\) We will consider here the effect on the lifetime of an emitting dipole with emphasis on energy transfer and surface plasmon coupling.

The setup of the problem is similar to that described earlier here and in other publications.\(^7\) In this case, we use Clemmow’s plane wave spectrum approach\(^14\) for the description of dipole radiation in an anisotropic medium. The resulting decay rate constants are

\[
b_{1} = \frac{3}{2} \left( \frac{\varepsilon_{g}}{\varepsilon_{e}} \right)^{1/2} \frac{1}{2} \int_{0}^{\pi} R_{12}^{\text{I}} \exp \left( -2 \pi d_{1} \right) u^{2} du / \int_{1}^{1}, \quad (14)
\]

and

\[
b_{1, 2} = \frac{3}{4} \left( \frac{\varepsilon_{g}}{\varepsilon_{e}} \right)^{3/2} \int_{0}^{\pi} \left( \frac{\varepsilon_{g}}{\varepsilon_{e}} \right)^{1/2} R_{12}^{\text{I}} \exp \left( -2 \pi d_{1} \right) u^{2} du / \int_{1}^{1}, \quad (15)
\]

In the earlier definitions of \( R_{12} \), \( d_{1} \) and \( I_{0} \) it is necessary to replace \( \varepsilon_{g} \) with \( \varepsilon_{g}^{1/2} \), \( \varepsilon_{e} \), and \( \varepsilon_{e} \), respectively. Though we have only treated the single mirror case, we believe that our earlier double-mirror analysis of the lifetime variations in the Eu\(^{3+}\)/mirror systems\(^5\) will be affected very little by including the anisotropy of the fatty-acid layers. The principal correction will be a few percent change in the quantum yield derived from the data fit.

Since many energy transfer experiments have been conducted using these fatty acid layers, the short distance behavior is also important. Taking the limiting case as \( d_{1} \rightarrow 0 \) for Eqs. (14) and (16), we find

\[
b_{d} = \left( \frac{3}{2} \right) \left( \frac{\varepsilon_{g}^{1/2} K_{g}}{2 d_{1}^{2}} \right), \quad (17)
\]

and

\[
b_{d} = \left( \frac{3}{4} \right) \left( \frac{\varepsilon_{g}^{1/2}}{} \right), \quad (18)
\]

Again the correction factor is in the order of \( 1 - n_{g}/n_{e} \), and, therefore, only a few percent error is made by neglecting the anisotropy. However, it is important to emphasize that the ordinary ray refractive index \( n_{g} \) determines the distance scaling, i.e., the relationship between \( d_{1} \) and the experimental distance determined by the number of deposited fatty-acid layers.

We note that surface plasmon coupling also occurs in these systems. The resonance condition is simply modified to \( \varepsilon_{g} \left( \varepsilon_{g} \varepsilon_{e} \right)^{1/2} \approx 0 \). Our earlier prediction\(^9\) for the wavelength at which this resonance would occur in the fatty-acid/silver system would be changed only slightly in light of this new result.

TABLE III. Energy transfer parameters for a one-dimensional acceptor.

<table>
<thead>
<tr>
<th>Dipole orientation</th>
<th>$A$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>$\cos^2 \phi$</td>
<td>$3/2^3$</td>
</tr>
<tr>
<td>$y$</td>
<td>$\sin^2 \phi$</td>
<td>$3/2^3$</td>
</tr>
<tr>
<td>$z$</td>
<td>$1$</td>
<td>$3/2^2$</td>
</tr>
<tr>
<td>isotropic</td>
<td>$\frac{3}{8}$</td>
<td>$1/2^4$</td>
</tr>
</tbody>
</table>

*The $x$ direction is the absorbing direction.

**IV. ANISOTROPIC ABSORBING MEDIA**

There is presently a great deal of interest in the characterization of materials whose electronic properties are pseudo-one-dimensional. Examples are TTF-TCNQ and other charge transfer salts, and the polydiacylenes. In this section we will address the problem of energy transfer from a fluorescing probe to a one- or two-dimensional conductor.

We take as a model of the conductor an anisotropic absorbing medium with dielectric function described by a tensor whose principal axes are parallel to the $x$, $y$, and $z$ axes of Fig. 1. The $xy$ plane defines the interface between the isotropic medium containing the dipole and the absorbing medium. As a probe we have chosen an electric dipole emitter which is placed at a distance $d$ from the interface. We have derived the solution to that problem for all distances, although for simplicity we will present only the short distance (i.e., energy transfer) limit. In describing the medium we take one axis to be unique and let the other two have the same tensor component. With the unique component complex and the other two components real, or vice versa, we can describe a one- or two-dimensional conductor.

First we consider a one-dimensional conductor along the $x$ direction, i.e., $\epsilon_y$ is complex and $\epsilon_x$ and $\epsilon_z$ are real and equal. The energy transfer rate constant for the emitting dipole near the surface can be written

$$b_{ET} = \frac{3q/2d^2}{4} \text{Im} \langle R \rangle,$$  \hspace{1cm} (19)

where

$$\langle R \rangle = \frac{1}{\pi} \int_0^{2\pi} \epsilon_x \left( \epsilon_x - \epsilon_y \right) \cos^2 \phi \left( \epsilon_x + \epsilon_z \right) \frac{1}{\epsilon_x + \epsilon_z} \epsilon_z d\phi.$$  \hspace{1cm} (20)

The factor $A$ depends only on dipole orientation and is given in Table III. We note that, in contrast to the description of an isotropic absorber, $\langle R \rangle$ cannot be made arbitrarily large at some wavelength by making the denominator approach zero. For a one-dimensional conductor there is, then, no resonance effect comparable to that with surface plasmon coupling to an isotropic conductor. With the same formulation, if $\epsilon_x$ is real and $\epsilon_y$ and $\epsilon_z$ are complex, then we have the description of a dipole interacting with a two-dimensional conductor whose plane of conduction is perpendicular to the $x$ axis. For the same reason we note that a resonance effect is not predicted.

As in Sec. II, we may consider the limiting case of a weak absorber, i.e., $n_1 = n_2 = n_3 = n_i$, $K_x = n_i$. Equation (19) then reduces to

$$b_{ET} = \frac{3q}{2d^2} \left( \frac{K_x}{n_i} \right),$$  \hspace{1cm} (21)

where the geometrical factor $\theta$ is given in Table III.

Finally, we consider the case of a two-dimensional conductor whose conducting planes are parallel to the interface ($xy$ plane), i.e., $\epsilon_x$ and $\epsilon_y$ are equal and complex and $\epsilon_z$ is real. Note that this system is analogous to Kuhn's usual restriction to acceptor transition moments randomly oriented in the $xy$ plane. Our result for this case is

$$b_{ET} = \frac{3q}{2d^2} \left( \frac{\epsilon_x n_i K_x}{1 + \epsilon_x \epsilon_y} \right),$$  \hspace{1cm} (22)

where $\theta$ has the value $\frac{3}{8}$, $\frac{3}{4}$, or $1$ for dipoles oriented in $z$, in the $xy$ plane, or isotropically. Because we have cylindrical symmetry in this case, no averaging over $\phi$ is necessary. Since $\epsilon_z$ is real, the denominator cannot approach zero and again there are no resonance effects. If we consider the one-dimensional case where $\epsilon_z$ is the only complex component, it is only necessary to replace $n_i K_x$ with $n_i K_i$ in Eq. (22). This observation and a comparison of Eq. (22) with Eq. (7) illustrates the point made earlier in the discussion of the $\theta$ parameter: When the transition moments of the acceptors are restricted to the $xy$ plane or to the $x$ direction and if only $\theta^2$ results in energy transfer (electric dipoles and quadrupoles), the energy transfer rate constant is reduced by a factor of 2 relative to the isotropic case.

Kuhn has considered many of these configurations for thin-film acceptors in the weak absorber limit. We have considered explicitly only the single mirror case here. However, we have repeated the derivations using Kuhn's method for both thin films and single mirrors as weak absorbers. We find agreement with Kuhn's expressions and, in the single mirror case, with Eq. (21) and the weak absorber limit of Eq. (22).

**V. CONCLUSIONS**

We have derived lifetime and energy transfer formulas for electric dipoles, magnetic dipoles, and electric quadrupoles situated near an absorbing medium or film in a layered configuration. The results are generally in agreement with those of Kuhn for weakly absorbing media but are sufficiently general to describe any isotropic absorber, including metals. We also discuss anisotropic media for electric dipole radiation only. The effect of the anisotropy of the fatty-acid layers on the emission lifetime and on energy transfer is shown to be relatively small. Formulas are derived, however, which will allow correction for this effect in future energy transfer experiments. Finally, one- and two-dimensional acceptors are considered. We show that some of the interesting resonance effects predicted for isotropic absorbers are not present in these systems.

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1R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. 62,
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2245 (1975).


11R. Chance, A. Prock, and R. Silbey (to be published). A fuller description of some of the derivations discussed here will be contained in a review article in preparation. Further details are available on request.

12We have converted Kuhn's expressions to our notation; his expression for the absorbance of the layer is given in our notation as $A_s = 2K^2 d/n\pi$.


