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Spectroscopic properties of molecules interacting with small dielectric particles

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Appendix A. The isolated spheroid

In this appendix we derive expressions for the radiative decay rates and quantum yield for a small spheroidally shaped dielectric particle which is excited at its resonance frequency ω_1. We also derive an expression for the absorption cross section. In all cases we will limit our attention to the case where the dipole moment ~f the spheroid is parallel to the major axis. It is assumed that the particle size is small compared with the wavelength so that retardation effects may be neglected.

Assume the spheroid is excited in the longitudinal dipolar mode, described by the potential

$$\phi = \phi_0 P_1(\eta) \begin{cases} P_1(\zeta) & \zeta \prec \zeta_0 \\ \dfrac{Q_1(\zeta) P_1(\zeta_0)}{Q_1(\zeta_0)} & \zeta \succ \zeta_0 \end{cases}$$

where ϕ_0 denotes the amplitude of the excitation, (ζ, η) are prolate spheroidal coordinates, and ζ_0 denotes the surface of the spheroid. The functions p $P_1(\eta)$ and $Q_1(\zeta)$ are Legendre functions of the first and second kind, respectively. The electric field inside the spheroid is

$$\vec{E} = -\frac{\phi_0}{f}\hat{K}$$

where $f = (a^2 - b^2)^{\frac{1}{2}}$, a and b being the semi-major and semi-minor axes respectively and where $\hat{K}$ is a unit vector in the direction of the major axis. The field outside the spheroid is that of a dipole of moment $\vec{D}$, where

$$\vec{D} = \hat{K}\frac{f^2\phi_0}{3}\frac{\zeta_0}{Q_1(\zeta_0)}$$

as may be seen by examining the larger form of Eq. (A.l) using the relatlons $Q_1(\zeta) \to (3\zeta^2)^{-1}$ and $r \to f\zeta$:

$$\phi \to \frac{f^2\phi_0}{3}\frac{\zeta_0}{Q_1(\zeta_0)}\frac{z}{r^3} = \frac{\vec{D}\cdot\vec{r}}{r^3}$$

The radiated power from the spheroid is given classically by the formula

$$P_r = \frac{\omega_1^4 D^2}{3C^3}$$

Dividing this by the energy of a photon, $\hbar\omega_1$, yields the formula for the radiative decay rate

$$\Gamma_r = \frac{\omega_1^3}{27\hbar C^3}\frac{f^4|Q_0|^2\zeta_0^2}{[Q_1(\zeta_0)]^2}$$

This formula still depends on the normalization constant ϕ_0 which will be determined shortly.

The power that is dissipated into nonradiative modes is obtained from the Joule expression:

$$P_{nr} = \int d\vec{r}\,\frac{\sigma}{2}|E|^2$$

where σ is the conductivity of the spheroid $\left(\sigma = (\omega/4\pi)\times \operatorname{Im}\varepsilon\right)$ and the integral is taken over the particle's volume.

Since the volume of the spheroid is $v = 4\pi f^3\zeta_0\left(\zeta_0^2-1\right)/3$, we have

$$P_{nr} = \frac{2\pi\sigma f\zeta_0\left(\zeta_0^2-1\right)}{3}|\phi_0|^2$$

Again, dividing this by 'fitJ gives the non-radiative decay rate

$$\Gamma_{nr} = \frac{f}{6\hbar}\zeta_0(\zeta_0-1)|\phi_0|^2\operatorname{Im}\varepsilon$$

where we have used the relation $4\pi\sigma = \omega_1\operatorname{Im}\varepsilon, \varepsilon$ being the complex dielectric constant of the spheroid. This result again depends on the normalization constant ϕ_0.

We may qefine the quantum yield of the particle as the ratio of the radiative decay rate to the total decay rate

$$Y = \frac{\Gamma_r}{\Gamma_r+\Gamma_{nr}}$$

Substituting Eqs. (A.6) and (A.9) into (A.lO) results in

$$Y = \left[1+\frac{9}{2}\left(\frac{c}{\omega_1 f}\right)^3\operatorname{Im}\varepsilon\frac{\zeta_0^2-1}{\zeta_0}[Q_1(\zeta_0)]^2\right]^{-1}.$$

This may alternatively be written as

$$Y = \left[1+\frac{6\pi}{v}\left(\frac{c}{\omega}\right)^3\frac{\operatorname{Im}\varepsilon(\omega_1)}{|\varepsilon(\omega_1)-1|^2}\right]^{-1}.$$

The absorption cross-section may be obtained by putting the spheroid in an external field $\vec{E}_0$ and computing the power that the spheroid dissipates. The pote~tial for such a system is

$$\phi = \sum_n a_n P_n(\zeta) P_n(\eta), \qquad \zeta < \zeta_0$$
$$\phi = \sum_n b_n Q_n(\zeta) P_n(\eta) - E_0 f \zeta \eta, \qquad \zeta > \zeta_0$$

where ω is the frequency of the incident wave and where $\vec{E}_0$ is taken along the z-direction. The coefficients a_n and b_n are determined by matching the potential and normal electric field components at the surface. Only a_1, and b_1 are nonvanishing:

$$a_1 = -\frac{E_0 f}{\varepsilon + \bar{\varepsilon}_1} \frac{1}{(\zeta_0^2 - 1) Q_1(\zeta_0)}$$
$$b_1 = E_0 f \frac{(\varepsilon - 1)}{\varepsilon + \bar{\varepsilon}_1} \frac{\zeta_0}{Q_1(\zeta_0)}$$

where

$$\bar{\varepsilon}_1 = -\frac{\zeta_0 Q_1'(\zeta_0)}{Q_1(\zeta_0)} .$$

The dissipated power is computed as in Eq. (A.7) and is

$$P_a = -\frac{\omega}{6} \mathrm{Im}\left[\frac{1}{\varepsilon + \bar{\varepsilon}_1}\right] \frac{f^3 |E_0|^2 \zeta_0}{(\zeta_0^2 - 1)[Q_1(\zeta_0)]^2} .$$

Dividing by the incident flux $c|E_0|^2 / 8\pi$ gives the absorption cross section

$$\sigma_a = -\frac{4\pi\omega}{3c} \frac{\zeta_0 f^3}{(\zeta_0^2 - 1)[Q_1(\zeta_0)]^2} \mathrm{Im} \frac{1}{\varepsilon + \bar{\varepsilon}_1}$$

In this expression the "pole" where $\mathrm{Re}(\varepsilon + \bar{\varepsilon}_1)$ vanishes describes the absorption by the collective mode (or modes) of the system. The absorption cross section at that frequency is limited only by the imaginary part of ε.If we were to express the resonance denominator of Eq. (A.17) in a Breit-Wigner form we may interpret the damping constant as the nonradiative decay rate for the spheroid.[20] Thus

$$\sigma_a \propto \mathrm{Im} \frac{1}{\omega - \omega_1 + \frac{i}{2}\Gamma_{nr}}$$

where

$$\mathrm{Re}\, \varepsilon(\omega_1) + \hat{\varepsilon}_1 = 0$$

and

$$\Gamma_{nr} = 2\, \mathrm{Im}\, \varepsilon(\omega_1) \mathrm{Re} \frac{1}{\partial \varepsilon(\omega_1) / \partial \omega_1}$$

Equation (A.20) is the desired expression for the nonradiative decay rate.[22] It is independent of the size and shape of the particle.

Comparing Eq. (A.9) and (A.20) allows us to compute the normalization constant ϕ_0 that appears in Eq. (A.6):

$$|\phi_0| = \left[\frac{12\hbar}{f\zeta_0(\zeta_0^2-1)}\operatorname{Re}\left(\frac{\partial\omega_1}{\partial\varepsilon(\omega_1)}\right)\right]^{\frac{1}{2}}.$$

Thus the radiative decay rate is:

$$\Gamma_r = \frac{4}{9}\left(\frac{\omega_1 f}{c}\right)^3 \frac{\zeta_0}{(\zeta_0^2-1)[Q_1(\zeta_0)]^2}\operatorname{Re}\left[\frac{\partial\omega_1}{\partial\varepsilon(\omega_1)}\right],$$

corresponding to the dipole

$$D = \frac{1}{Q_1(\zeta_0)}\left[\frac{4\hbar f^3\zeta_0}{3(\zeta_0^2-1)}\operatorname{Re}\left(\frac{\partial\omega_1}{\partial\varepsilon(\omega_1)}\right)\right]^{\frac{1}{2}}.$$

Returning to the problem of a spheroid in an external field, we define also the generalized yield function

$$Y(\omega) = \frac{\sigma_r(\omega)}{\sigma_r(\omega)+\sigma_a(\omega)}.$$

The radiative cross-section $\sigma_r(\omega)$ is the ratio between the radiated power, P_r, associated with the induced dipole

$$D = \frac{f^2}{3}b_1,$$

[b_1 is given by Eq. (A.14)]and the incident flux. We find (using Eq. (A.5)

$$\sigma_r = \frac{8\pi}{3}\left(\frac{\omega}{c}\right)^4 \frac{f^6}{9}\left|\frac{\varepsilon-1}{\varepsilon+\bar{\varepsilon}_1}\right|^2\left[\frac{\zeta_0}{Q_1(\zeta_0)}\right]^2$$

and

$$Y(\omega) = \left[1-\frac{6\pi}{V}\left(\frac{c}{\omega}\right)^3\operatorname{Im}\frac{1}{\varepsilon(\omega)-1}\right]^{-1}$$

where V is the volume of the spheroid. Note that this result is independent of the shape of the spheroid. On resonance we have

$$Y(\omega_1) = Y$$

where Y was defined by Eq. (A.11).

Appendix B. Molecule near spheroid

Expressions for the radiative and nonradiative decay rates and quantum yield for a molecule near a spheroid are derived in this appendix. For simplicity the molecule is idealized as an oscillating point dipole located along the major axis. Two orientations of the dipole are to be considered:

perpendicular to the surface (⊥), and parallel to the surface (//). The spheroid is characterized by a semi-major axis a, and semi-minor axis b and a dielectic function $\varepsilon(\omega)$. The molecule is a distance d above the surface. We asSume that all relevant distances are small compared with the wave length of light so retardation efforts may be neglected.

a. The perpendicular orientation.

The potential associated with the spheroid-dipole system is given by

$$\phi = \begin{cases} \sum_n a_n P_n(\zeta) P_n(\eta) & \zeta < \zeta_0 \\ \sum_n b_n Q_n(\zeta) P_n(\eta) + \frac{\vec{\mu}\cdot(\vec{r}-\vec{r}_1)}{|\vec{r}-\vec{r}_1|^3} & \zeta > \zeta_0 \end{cases}$$

where a_n and b_n are to be determined from the boundary conditions. Here $\vec{r}_1 = (\vec{0}, d)$ is the position vector of the molecule. Using the expressions

$$\frac{\vec{\mu}\cdot(\vec{r}-\vec{r}_1)}{|\vec{r}-\vec{r}_1|^3} = \vec{\mu}\cdot\nabla_1 \frac{1}{|\vec{r}-\vec{r}_1|},$$

and

$$\frac{1}{|\vec{r}-\vec{r}_1|} = \frac{1}{f}\sum_n (zn+1) P_n(\zeta) Q_n(\zeta_1) P_n(\eta),$$

where $f = (a^2 - b^2)^{\frac{1}{2}}$, $\zeta_0 = a/f$ and $\zeta_1 = (a+d)/f$ we have

$$\frac{\vec{\mu}\cdot(\vec{r}-\vec{r}_1)}{|\vec{r}-\vec{r}_1|^3} = \frac{\mu}{f^2}\sum_n (2n+1) P_n(\zeta) Q_n'(\zeta_1) P_n(\eta)$$

This formula is valid in the domain $\zeta_0 \le \zeta < \zeta_1$.

Applying the boundary condition~ at the surface $\zeta = \zeta_0$ yields

$$a_n P_n(\zeta_0) = b_n Q_n(\zeta_0) + (2n+1)\frac{\mu}{f^2} P_n(\zeta_0) Q_n'(\zeta_1),$$

$$\varepsilon a_n P_n'(\zeta_0) = b_n Q_n'(\zeta_0) + (2n+1)\frac{\mu}{f^2} P_n'(\zeta_0) Q_n'(\zeta_1).$$

Using the expression for the Wronskian

$$Q_n(\zeta_0) P_n'(\zeta_0) - P_n(\zeta_0) Q_n'(\zeta_0) = (\zeta_0^2 - 1)^{-1}$$

we obtain

$$a_n = (2n+1)\frac{\mu}{f^2}\frac{1}{\varepsilon + \bar{\varepsilon}_n}\frac{Q_n'(\zeta_1)}{(\zeta_0^2 - 1)Q_n(\zeta_0)P_n'(\zeta_0)},$$

and

$$b_n = (2n+1)\frac{\mu}{f}\frac{1-\varepsilon}{\varepsilon + \bar{\varepsilon}_n}\frac{P_n(\zeta_0)Q_n'(\zeta_1)}{Q_n(\zeta_0)}$$

where

$$\bar{\varepsilon}_n = -\frac{P_n(\zeta_0)Q_n'(\zeta_0)}{Q_n(\zeta_0)P_n'(\zeta_0)}$$

The dipole moment of the system, D ($\perp$), is obtained by examining the asymptotic form of Φ:

$$\Phi \xrightarrow[r\to\infty]{} b_1 Q_1(\zeta)P_1(\eta) + \frac{\vec{\mu}\cdot\vec{r}}{r^3}$$

so

$$D(\perp) = \mu\left[1 + \frac{1-\varepsilon}{\varepsilon + \bar{\varepsilon}_1}\zeta_0\frac{Q_1'(\zeta_1)}{Q_1(\zeta_0)}\right].$$

The first term represents the contribution of the molecule and the second term is the contribution of the spheroid.

In the above analysis μ is regarded as the molecular dipole. In principle it consists of two parts -an intrinsic dipole and an induced dipole. The intrinsic dipole is what would be found for a totally isolated molecule and will be denoted by μ_0. The net molecular dipole may be expressed as:

$$\mu = \mu_0 + \alpha E_{loc},$$

where E_{loc} is the local field component due to the spheroid and α is the molecular polarizability. From Eq. (B .1) the local field is

$$\vec{E}_{loc} = -\frac{\hat{K}}{f}\sum_n b_n Q_n'(\zeta_1)$$

($\hat{K}$ is a unit vector in the ($\vec{o}$, d) direction) so we find

$$\mu = \frac{\mu_0}{1-\Delta(\perp)}$$

where

$$\Delta(\perp) = \frac{\alpha}{f^3}\sum_n (2n+1)\frac{\varepsilon - 1}{\varepsilon + \bar{\varepsilon}_n}\frac{P_n(\zeta_0)}{Q_n(\zeta_0)}[Q_n'(\zeta_1)]^2 .$$

We may regard the factor $(1-\Delta(\perp))^{-1}$ of Eq. (B.15) as the image enhancement factor. It is significant only close to the surface, in a region where the use of a classical approach and of the point dipole model for the molecule are questionable. Thus we may disregard $\Delta(\perp)$ in computing the actual decay rates, although our expressions will contain this .factor.

The radiated power is given by

$$P_r(\perp)=\frac{\omega^4[D(\perp)]^2}{3c^3}\ .$$

Dividing this by the photon energy yields the radiative decay rate

$$\Gamma_r(\perp)=\frac{\omega^3|\mu_0|^2}{3\hbar c^3|1-\Delta(\perp)|^2}\left|1+\frac{1-\varepsilon}{\varepsilon+\bar{\varepsilon}_1}\frac{\zeta_0 Q_1'(\zeta_1)}{Q_1(\zeta_0)}\right|^2\ .$$

In making the transition from the classical theory to the quantum theory one simply replaces μ_0 by the transition moment matrix element $\langle f|\mu_z|i\rangle$.

The nonradiative power is computed by evaluating the Joule heating in the spheroid

$$P_{nr}(\perp)=\frac{\sigma}{2}\int|E|^2\,d\vec{r}$$

which may be expressed as

$$P_{nr}(\perp)=\frac{\sigma}{2}\int dS\phi^*\frac{\partial\phi}{\partial\zeta}$$

where the integral is over the surface of the spheroid Inserting Eq. (8.1) in this and using $dS=2\pi f^2\left(\zeta_0^2-1\right)d\eta$ and

$$\int_{-1}^{1}d\eta P_n(\eta)P_m(\eta)=\frac{2}{2n+1}\delta_{nm}\ ,$$

yields

$$P_{nr}(\perp)=2\pi f\sigma\left(\zeta_0^2-1\right)\sum_n\frac{|a_n|^2}{2n+1}P_n(\zeta_0)P_n'(\zeta_0)\ ,$$

or

$$P_{nr}(\perp)=-\frac{\omega}{2f^3}\frac{1}{\zeta_0^2-1}\sum_n(2n+1)|\mu|^2\frac{P_n(\zeta_0)}{P_n'(\zeta_0)}\left[\frac{Q_n'(\zeta_1)}{Q_n(\zeta_0)}\right]^2\operatorname{Im}\frac{1}{\varepsilon+\bar{\varepsilon}_n}\ ,$$

or

$$\Gamma_{nr}(\perp)=-\frac{|\mu_0|^2}{2\hbar f^3\left(\zeta_0^2-1\right)|1-\Delta(\perp)|^2}\sum_n(2n+1)\frac{P_n(\zeta_0)}{P_n'(\zeta_0)}\left[\frac{Q_n'(\zeta_1)}{Q_n(\zeta_0)}\right]^2\operatorname{Im}\frac{1}{\varepsilon+\bar{\varepsilon}_n}\ .$$

It should be noted that the same expression for Γ_{nr} may be obtained by using an approach taken in other works, which considers a dipole moving in a local field produced by its surface image, by using the local field given by Eq. (B.14) . The quantum yield is given by

$$Y(\perp)=\frac{\Gamma_r(\perp)}{\Gamma_r(\perp)+\Gamma_{nr}(\perp)}.$$

The above expressions take simpler forms in the limit of a sphere (a=b) .The system dipole becomes

$$D(\perp)\to\mu\left[1+2\left(\frac{a}{r_1}\right)^3\frac{\varepsilon-1}{\varepsilon+2}\right],$$

where $r_1=a+d$. The radiative decay rate becomes

$$\Gamma_r(\perp)\to\frac{\omega^3|\mu_0|^2}{3\hbar c^3|1-\Delta(\perp)|^2}\left|1+2\left(\frac{a}{r_1}\right)^3\frac{\varepsilon-1}{\varepsilon+2}\right|^2$$

where $\Delta(\perp)$ is evaluated using the following asymptotic formulas

$$Q_n(\zeta_0)\xrightarrow[\zeta_0\to\infty]{}\frac{\sqrt{\pi}n!}{2^{n+1}\Gamma\left(n+\frac{3}{2}\right)\zeta_0^{n+1}}$$

$$P_n(\zeta_0)\xrightarrow[\zeta_0\to\infty]{}\frac{2^n\Gamma\left(n+\frac{1}{2}\right)\zeta_0^n}{\sqrt{\pi}n!}$$

Here Γ is the gamma function. Thus

$$\Delta(\perp)\to\frac{\alpha}{r_1^3}\sum_n\frac{\varepsilon-1}{\varepsilon+\frac{n+1}{n}}(n+1)^2\left(\frac{a}{r_1}\right)^{2n+1}$$

where $a=f\zeta_0$ is the sphere radius and $r_1=(a+d)=f\zeta_1$. The nonradiative decay rate becomes

$$\Gamma_{nr}(\perp)\to-\frac{|\mu_0|^2}{2\hbar a^3|1-\Delta(\perp)|^2}\sum_n(2n+1)\frac{(n+1)^2}{n}\mathrm{Im}\frac{1}{\varepsilon+\frac{n+1}{n}}\left(\frac{a}{r_1}\right)^{2n+4}$$

Next let us consider the limit of large spheres, $a>>d$, so that the sphere appears as a plane in the neighborhood of the molecule. In this limit the system dipole becomes

$$D(\perp)\to\mu\left[1+2\frac{\varepsilon-1}{\varepsilon+2}\right].$$

This result differs from that expected for a dipole near a flat plane

$$D_{plane}(\perp) = \mu\left[1+\frac{\varepsilon-1}{\varepsilon+1}\right].$$

However this difference is understandable. In deriving our result for a sphere we always assumed that $a << \lambda$, where λ is the wave length of light. Eq. (B.28) is for an infinite plane for which this assumption is not valid. The radiative decay rate based on Eq. (B.12") is

$$\Gamma_r(\perp) \to \frac{\omega^3|\mu_0|^2}{3\hbar c^3|1-\Delta(\perp)|^2}\left|1+2\frac{\varepsilon-1}{\varepsilon+2}\right|^2 .$$

Thus even when the dipole is very close to the surface, Γ_r is different from that obtained for a true plane, The nonradiative decay is obtained from Eq, (B,24') when $a \approx r_1$. Then the sum is dominated by contributions from large n, and

$$\Gamma_{nr}(\perp) \to -\frac{|\mu_0|^2}{4\hbar d^3}\frac{1}{|1-\Delta(\perp)|^2}\operatorname{Im}\frac{1}{\varepsilon+1} .$$

In Eqs. (B.18") and (B.24") $\Delta(\perp)$ is given by

$$\Delta(\perp) \to \frac{\alpha}{4d^3}\frac{\varepsilon-1}{\varepsilon+1} .$$

Equation (B.24") corresponds precisely to the nonradiative loss of a dipole near a plane surface.

b. The parallel orientation

Next let us consider the case of a dipole oriented parallel to the surface (in the x-direction) but still located along the major axis, The potential is now given by:

$$\Phi = \begin{cases} \sum_n a_n P_n^{(1)}(\zeta) P_n^{(1)}(\eta)\cos\phi & \zeta < \zeta_0 \\ \sum_n c_n Q_n^{(1)}(\zeta) P_n^{(1)}(\eta)\cos\phi + \dfrac{\mu x}{|\vec{r}-\vec{r}_1|^3} & \zeta > \zeta_0 \end{cases}$$

where $P_n^{(1)}$ and $Q_n^{(1)}$ are associated Legendre functions of the first and second kind, respectively. Using the expansion

$$\frac{1}{|\vec{r}-\vec{r}_1|} = -\frac{2}{f}\sum_{n=1}^{\infty}\frac{2n+1}{n^2(n+1)^2}P_n^{(1)}(\zeta)P_n^{(1)}(\eta)Q_n^{(1)}(\zeta_1)P_n^{(1)}(\eta_1)\cos\phi ,$$

which is valid when $\zeta_0 \le \zeta < \zeta_1$, we obtain an expansion for the dipolar potential

$$\frac{\mu x}{|\vec{r}-\vec{r}_1|^3} = \frac{2\mu}{f^2}\left[\frac{1-\eta_1^2}{\zeta_1^2-1}\right]^{\frac{1}{2}}\sum_n\frac{2n+1}{n^2(n+1)^2}P_n^{(1)}(\zeta)P_n^{(1)}(\eta)Q_n^{(1)}(\zeta_1)P_n^{(1)}(\eta_1)\cos\phi .$$

(Note that $\left(1-\eta_1^2\right)^{\frac{1}{2}} P_n'^{(1)}(\eta_1) \to n(n+1)/2$ as $\eta_1 \to 1$. Matching the boundary conditions yields equations for the coefficients c_n and a_n :

$$c_n Q_n^{(1)}(\zeta_0) + \frac{2n+1}{n(n+1)} \frac{\mu}{f^2} \frac{Q_n^{(1)}(\zeta_1) P_n^{(1)}(\zeta_0)}{\left(\zeta_1^2 - 1\right)^{\frac{1}{2}}} = a_n P_n^{(1)}(\zeta_0),$$

$$c_n Q_n^{(1)'}(\zeta_0) + \frac{2n+1}{n(n+1)} \frac{\mu}{f^2} \frac{Q_n^{(1)}(\zeta_1) P_n^{(1)'}(\zeta_0)}{\left(\zeta_1^2 - 1\right)^{\frac{1}{2}}} = \varepsilon a_n P_n^{(1)}(\zeta_0).$$

These equations may be inverted and simplified by making use of the Wronskian

$$P_n^{(1)}(\zeta_0) Q_n^{(1)'}(\zeta_0) - P_n^{(1)'}(\zeta_0) Q_n^{(1)}(\zeta_0) = \frac{n(n+1)}{\zeta_0^2 - 1}.$$

Thus

$$a_n = \frac{-\mu}{f^2} \frac{(2n+1) Q_n^{(1)}(\zeta_1)}{\left(\zeta_0^2 - 1\right)\left(\zeta_1^2 - 1\right)^{\frac{1}{2}} Q_n^{(1)}(\zeta_0) P_n^{(1)'}(\zeta_0)\left[\varepsilon + \bar{\varepsilon}_n^{(1)}\right]},$$

$$c_n \frac{\mu}{f^2} \frac{(2n+1)(1-\varepsilon) P_n^{(1)}(\zeta_0) Q_n^{(1)}(\zeta_1)}{n(n+1)\left(\zeta_1^2 - 1\right)^{\frac{1}{2}} Q_n^{(1)}(\zeta_0)\left[\varepsilon + \bar{\varepsilon}_n^{(1)}\right]},$$

$$\bar{\varepsilon}_n^{(1)} = -\frac{P_n^{(1)}(\zeta_0) Q_n^{(1)'}(\zeta_0)}{P_n^{(1)'}(\zeta_0) Q_n^{(1)}(\zeta_0)}.$$

The system dipole is obtained by examining the asymptotic form of the potential

$$\Phi \to c_1 Q_1^{(1)}(\zeta) P_1^{(1)}(\eta) \cos\phi + \frac{\mu x}{r^3}$$

so

$$D(//) = \mu\left[1 + \frac{(1-\varepsilon) P_1^{(1)}(\zeta_0) Q_1^{(1)}(\zeta_1)}{\left(\zeta_1^2 - 1\right)^{\frac{1}{2}} Q_1^{(1)}(\zeta_0)\left[\varepsilon + \bar{\varepsilon}_1^{(1)}\right]}\right].$$

The local field is determined from'Eq. (B.29) to be

$$\vec{E}_{loc} = \frac{\hat{i}}{f} \sum_{n=1}^{\infty} c_n Q_n'(\zeta_1) P_n'(1),$$

($\hat{i}$ being a unit vector in the x-dir.ection) so the total molecular dipole is related to its bare dipole by

$$\mu = \frac{\mu_0}{1 - \Delta(//)},$$

where

$$\Delta(//)=\frac{\alpha}{2f^3}\sum_{n=1}^{\infty}(2n+1)\frac{1-\varepsilon}{\varepsilon+\bar{\varepsilon}_n^{(1)}}\frac{P_n'(\zeta_0)}{Q_n'(\zeta_0)}\left[Q_n'(\zeta_1)\right]^2 .$$

The radiative decay rate is

$$\Gamma_r(//)=\frac{\omega^3|\mu_0|^2}{3\hbar c^3|1-\Delta(//)|^2}\left|1+\frac{1-\varepsilon}{\varepsilon+\bar{\varepsilon}_n^{(1)}}\frac{P_1^{(1)}(\zeta_0)Q_1^{(1)}(\zeta_1)}{\left(\zeta_1^2-1\right)^{\frac{1}{2}}Q_1^{(1)}(\zeta_0)}\right|^2 .$$

The nonradiative power is evaluated as in Eq. (B.19) and we obtain

$$P_{nr}(//)=\pi\sigma f\left(\zeta_0^2-1\right)\sum_n|a_n|^2\frac{n(n+1)}{2n+1}P_n^{(1)}(\zeta_0)P_n^{(1)'}(\zeta_0) ,$$

which yields the following expression for the decay rate

$$\Gamma_{nr}(//)=-\frac{|\mu_0|^2}{4\hbar f^3|1-\Delta(//)|^2\left(\zeta_0^2-1\right)\left(\zeta_1^2-1\right)}\sum_n n(n+1)(2n+1)\frac{P_n^{(1)}(\zeta_0)}{P_n^{(1)'}(\zeta_0)}\left[\frac{Q_n^{(1)}(\zeta_1)}{Q_n^{(1)}(\zeta_0)}\right]^2\mathrm{Im}\frac{1}{\varepsilon+\bar{\varepsilon}_n^{(1)}} .$$

In the sphere limit the above formulas simplify to

$$D(//)\to\mu\left[1-\frac{\varepsilon-1}{\varepsilon+2}\left(\frac{a}{r_1}\right)^3\right],$$

$$\Gamma_r(//)\to\frac{\omega^3|\mu_0|^2}{3\hbar c^3|1-\Delta(//)|^2}\left|1-\frac{\varepsilon-1}{\varepsilon+2}\left(\frac{a}{r_1}\right)^3\right|^2 ,$$

$$\Gamma_{nr}(//)\to-\frac{|\mu_0|^2}{4\hbar a^3}\frac{1}{|1-\Delta(//)|^2}\sum_n(n+1)(2n+1)\left(\frac{a}{r_1}\right)^{2n+4}\mathrm{Im}\frac{1}{\varepsilon+\frac{n+1}{n}} ,$$

and

$$\Delta(//)\to\frac{\alpha}{2a^3}\sum_{n=1}^{\infty}n(n+1)\frac{\varepsilon-1}{\varepsilon+\frac{n+1}{n}}\left(\frac{a}{r_1}\right)^{2n+4}$$

If we take the "plane" limit in which $a\approx r_1$, we obtain ,

$$D(//)\to\mu\left[1-\frac{\varepsilon-1}{\varepsilon+2}\right].$$

Appendix C. Particle in a lossless cavity.

Our goal in the present appendix is to obtain expressions for the radiative and nonradiative decay rates for a molecule inside a spheroidal cavity. The medium inside the cavity is assumed to have a real dielectric constant, while the medium outside the cavity may have a complex dielectric constant. We consider only one geometry here-that where the dipole lies along the major axis and is parallel to it.

Let the medium inside the cavity have dielectric constant ε_1 and that outside the cavity have dielectric constant ε_0. The cavity wall is defined by the surface $\zeta = \zeta_0$. The dipole is located on the surface $\zeta = \zeta_1$ where $\zeta_1 < \zeta_0$. The potential is

$$\Phi = \begin{cases} \sum_n b_n P_n(\zeta) P_n(\eta) + \dfrac{\vec{\mu}\cdot(\vec{r}-\vec{r}_1)}{\varepsilon_1 |\vec{r}-\vec{r}_1|^3} & \zeta < \zeta_0 \\ \sum_n c_n Q_n(\zeta) P_n(\eta) & \zeta > \zeta_0 \end{cases}$$

The potential of the dipole may be expanded as

$$\frac{\vec{\mu}\cdot(\vec{r}-\vec{r}_1)}{\varepsilon_1 |\vec{r}-\vec{r}_1|^3} = \frac{\mu}{\varepsilon_1 f^2} \sum_n (2n+1) P_n'(\zeta_1) Q_n(\zeta) P_n(\eta)$$

where now $\zeta_0 > \zeta > \zeta_1 > 1$.

We obtain the following equations for b_n and C_n :

$$b_n P_n(\zeta_0) + \frac{(2n+1)\mu}{\varepsilon_1 f^2} P_n'(\zeta_1) Q_n(\zeta_0) = C_n Q_n(\zeta_0),$$

$$\varepsilon_1 b_n P_n'(\zeta_0) + \frac{(2n+1)\mu}{f^2} P_n'(\zeta_1) Q_n'(\zeta_0) = \varepsilon_0 C_n Q_n'(\zeta_0).$$

Solving these gives

$$C_n = \frac{(2n+1)\mu}{f^2(\zeta_0^2 - 1)} \frac{P_n'(\zeta_1)}{P_n'(\zeta_0) Q_n(\zeta_0)} \frac{1}{\varepsilon_1 + \varepsilon_0 \bar{\varepsilon}_n},$$

where

$$\bar{\varepsilon}_n = -\frac{Q_n'(\zeta_0) P_n(\zeta_0)}{Q_n(\zeta_0) P_n'(\zeta_0)}.$$

The system dipole is obtained by examining theasymptotic potential

$$D = \frac{\varepsilon_0 C_1 f^2}{3},$$

or

$$D = \frac{\mu}{(\zeta_0^2 - 1) Q_1(\zeta_0) \left[\frac{\varepsilon_1}{\varepsilon_0} + \bar{\varepsilon}_1 \right]}.$$

The above formulas apply to the range $\eta_1 = 1,\ 1 \le \zeta_1 \le \zeta_0;\ a > |z| > f$. This corresponds to where z is the location of the molecule along the major axis. In considering the range $|z| < f$ one must use instead of Eq. (c.2) the following expansion

$$\frac{\vec{\mu} \cdot (\vec{r} - \vec{r}_1)}{\varepsilon_1 |\vec{r} - \vec{r}_1|^3} = \frac{\mu}{\varepsilon_1 f^2} \sum_n (2n+1) Q_n(\zeta) P_n(\eta) P_n'(\eta_1),$$

which corresponds to $\zeta_1 = 1$ and $-1 \le \eta_1 \le 1$. The system dipole is then still given by Eq. (c.8), so Eq. (c.8) is valid over the whole range $-a < z < a$.The radiative decay rate is given by

$$\Gamma_r(//) \to \frac{\omega^3}{3\hbar c^3} \frac{\varepsilon_0^{\frac{1}{2}} |\mu|^2}{(\zeta_0^2 - 1)^2 Q_1^2(\zeta_0)} \frac{1}{\left| \frac{\varepsilon_1}{\varepsilon_0} + \bar{\varepsilon}_1 \right|^2}.$$

The nonradiative power is

$$P_{nr} = \frac{\sigma_0}{2} \int |E|^2 d\tau$$

where the integral extends over the region outside the cavity.
This may be written as

$$P_{nr} = -2\pi f\sigma_0\left(\zeta_0^2 - 1\right)\sum_n \frac{\left|C_n\right|^2}{2n+1} Q_n\left(\zeta_0\right)Q_n'\left(\zeta_0\right).$$

This reduces to an expression for the nonradiative decay rate

$$\Gamma_{nr} = -\frac{\left|\mu\right|^2}{2\hbar f^3\left(\zeta_0^2 - 1\right)}\sum_n (2n+1)\frac{\left[P_n'(\varphi_1)\right]^2}{P_n\left(\zeta_0\right)P_n'\left(\zeta_0\right)} \mathrm{Im}\frac{1}{\varepsilon_1 + \varepsilon_0\bar{\varepsilon}_n},$$

where $\varphi_1 = \zeta_1$ if $\left|z\right| > f$ and $\varphi_1 = \eta_1$ if $\left|z\right| < f$.

The local field may be included by writing

$$\mu = \frac{\mu_0}{1-\Delta},$$

where

$$\Delta = \frac{-\alpha}{\varepsilon_0\varepsilon_1 f^3}\sum_n \frac{(2n+1)(\varepsilon_0 - \varepsilon_1)P_n(\varphi_1)P_n'(\varphi_1)Q_n'(\zeta_0)}{P_n'(\zeta_0)\left[\frac{\varepsilon_1}{\varepsilon_0} + \bar{\varepsilon}_1\right]}.$$

In the sphere limit the system dipole moment becomes

$$D \to \frac{3\mu}{2 + \frac{\varepsilon_1}{\varepsilon_0}}$$

and the radiative decay rate becomes

$$\Gamma_r \to \frac{3\omega^3}{\hbar C^3}\frac{\varepsilon_0^{\frac{1}{2}}\left|\mu\right|^2}{\left|\frac{\varepsilon_1}{\varepsilon_0} + 2\right|^2}.$$

Appendix D.

Here we derive the results (III.3) and (III.4) for the sphere potential in terms of the plasmon amplitudes b_{lm} and b_{lm}^*. To this end we start with the Hamiltonian for the sphere in the presence of a point charge q located at $\left(r_1, \theta_1, \phi_1\right)$:

$$H = H_s + qQ_s\left(r_1, \theta_1, \phi_1\right)$$

where H_s and ϕ_s are given by Eqs. (III.1) and (III.3) respectively. The equations of motion (Eq. (III.2) with H_s replaced by H) for the b_{lm} amplitudes are

$$b_{lm} = -i\omega_l b_{lm} - \frac{i}{\hbar} qG_{lm}\left(r_1, \theta_1, \phi_1\right) - \frac{1}{2}\gamma_l b_{lm},$$

where we have also added pheonoemnological damping terms $-\frac{1}{2}\gamma_l b_{lm}$. If $q = \hat{q}e^{i\omega t}$ we get the stationary solution $b_{lm}(t) = \hat{b}_{lm}\exp(-i\omega t)$ with

$$\hat{b}_{lm} = \frac{\hat{q} G^*_{lm}(r_1, \theta_1, \phi_1)}{\hbar\left(\omega - \omega_l + \frac{i}{2}\gamma_l\right)} .$$

Similarly with $b^*_{lm}(t) = \hat{b}^*_{lm} \exp(+i\omega t)$,

$$\hat{b}^*_{lm} = -\frac{\hat{q} G_{lm}(r_1, \theta_1, \phi_1)}{\hbar\left(\omega + \omega_l + \frac{i}{2}\gamma_l\right)} .$$

b^*_{lm} is thus smaller than b_{lm} and will be neglected. Eqs. (III.3} and (D.3} then yield

$$\phi_s(r, \theta, \phi) = \frac{q}{\hbar} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{G_{lm}(r, \theta, \phi) G^*_{lm}(r_1, \theta_1, \phi_1)}{\omega - \omega_l + \frac{i}{2}\gamma_l} .$$

This should be compared to the potential obtained from a conventional solution of the Laplace equation for a sphere polarized by a charge q. The resulting potential may be written as a sum $\phi = \phi_s + \phi_q$ where ϕ_q is the potential of q itself (i.e $\phi_q = q/|\vec{r} - \vec{r}_1|$) and where

$$\phi_s(r, \theta, \phi) = \frac{-4\pi q(\varepsilon - 1)}{a} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \frac{1}{\left(\varepsilon + \frac{l+1}{l}\right)(2l+1)} \frac{Y^*_{lm}(\theta_1, \phi_1) Y_{lm}(\theta, \phi)}{(r_1/a)^{l+1}} \begin{cases} \left(\frac{r}{a}\right)^{-l-1} & r > a \\ \left(\frac{r}{a}\right)^{l} & r < a \end{cases}$$

Next we use the expansion (analogous to Eqs. (A.18-20)):

$$\frac{\varepsilon - 1}{\left(\varepsilon + \frac{l+1}{l}\right)(2l+1)} \approx -\frac{1}{\left[l\varepsilon_1'(\omega_l)\left(\omega - \omega_l + \frac{i}{2}\gamma_l\right)\right]} ,$$

where ω_l satisfies $\varepsilon_1(\omega_l = -(l+1)/l)$ and where

$$\gamma_l = \frac{2\varepsilon_2(\omega_l)}{\varepsilon_1'(\omega_l)} ,$$

to get

$$\phi_s(r, \theta, \phi) = \frac{4\pi q}{a} \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[l\varepsilon_1'(\omega_l)\left(\omega - \omega_l + \frac{i}{2}\gamma_l\right)\right]^{-1} \frac{Y^*_{lm}(\theta_1, \phi_1) Y_{lm}(\theta, \phi)}{(r_1/a)^{l+1}} \begin{cases} \left(\frac{r}{a}\right)^{-l-1} & r > a \\ \left(\frac{r}{a}\right)^{l} & r < a \end{cases}$$

Comparing (D.5) with (D.9) we finally get Eq. (III.4).