

Equivalence between the mechanical model and energy-transfer theory for the classical decay rates of molecules near a spherical particle

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In the classical modeling of decay rates for molecules interacting with a nontrivial environment, it is well known that two alternate approaches exist which include: (1) a mechanical model treating the system as a damped harmonic oscillator driven by the reflected fields from the environment; and (2) a model based on the radiative and nonradiative energy transfers from the excited molecular system to the environment. While the exact equivalence of the two methods is not trivial and has been explicitly demonstrated only for planar geometry, it has been widely taken for granted and applied to other geometries such as in the interaction of the molecule with a spherical particle. Here we provide a rigorous proof of such equivalence for the molecule-sphere problem via a direct calculation of the decay rates adopting each of the two different approaches. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4714498>]

INTRODUCTION

Ever since the pioneering work of Purcell,¹ it has been known that the lifetimes of any excited system are not intrinsic properties of the system but are variables depending on the interaction of the system with the environment. While the spontaneous decay rates of an isolated system are still intrinsic, the presence of the environment will induce (stimulate) the system to further decay at a rate different from that of the intrinsic decay of the system. In a quantum mechanical description of such phenomenon, one would resort to the modification of the density of photonic mode and excited states of the system, together with the application of time-dependent perturbation theory with the system-environment interaction treated as a perturbation to the system.² Alternatively, classical modeling of this induced decay is also possible and the results obtained for the reduced decay rates (i.e., normalized to the intrinsic rates) are known to be equivalent to those derived from a quantum mechanical approach.^{3,4}

Referring to the modified decay rates of a molecule in the vicinity of a dielectric/metallic surface as a specific example, one well-established simple classical approach is the driven-damped harmonic oscillator for the motion of the molecule with the induced decay being caused by the reflected field from the surface acting on the molecule.³ This so-called “mechanical model” is thus governed by the following equation of motion:

$$\ddot{p} + \gamma_0 \dot{p} + \omega_0^2 p = \frac{e^2}{m} E_R, \quad (1)$$

where p is the molecular dipole moment, e and m the electronic charge and mass, and ω_0 and γ_0 the intrinsic frequency and damping constant of the dipole, respectively. E_R is the field reflected from the surface acting back on the emitting dipole. Under the assumption $\gamma_0 \ll \omega_0$, the overall decay

rate in the presence of the surface can be obtained in the form (normalized to the intrinsic rate):^{3,5}

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3}{2k^3} \text{Im} \left(\frac{E_R}{p} \right), \quad (2)$$

where we have assumed that the molecule is located in vacuum and k is the wave number of the molecular emission. Note that we have also assumed the ideal case with the intrinsic quantum yield being unity.

On the other hand, the decay process of the molecule can also be accounted for by calculating the rate of energy transferred away from the excited molecule which can take place via the following two channels:^{6,7}

- (i) Radiative transfer with the energy radiated to infinity

$$\frac{\gamma^R}{\gamma_0} = \frac{3}{ck^4 p^2} \int_{(r \rightarrow \infty)} d\Omega r^2 \vec{S} \cdot \hat{n}, \quad (3)$$

and

- (ii) Nonradiative transfer with energy dissipated into the surrounding medium in the form of Joule heating

$$\frac{\gamma^{NR}}{\gamma_0} = \frac{3}{2ck^4 p^2} \int_V d\tau \sigma |\vec{E}|^2. \quad (4)$$

In Eqs. (3) and (4), $\vec{S} = (c/8\pi) \text{Re}(\vec{E} \times \vec{H}^*)$ is the time-averaged Poynting vector, c the speed of light in vacuum, V the volume of the medium and $\sigma = (ck/4) \text{Im} \epsilon$ is the conductivity of the medium which is proportional to the imaginary part of the dielectric function of the medium.

REVIEW OF LITERATURE ON THE EQUIVALENCE OF THE TWO METHODS

While from the viewpoint of conservation of energy, one would naturally expect the mechanical and energy-transfer

models to give the same results, i.e.,

$$\gamma = \gamma^R + \gamma^{NR}, \quad (5)$$

the proof of the equivalence of the two approaches has been demonstrated explicitly in the literature only for the case of simple planar geometry, via rather tedious calculations of the integrals in (3) and (4).^{3,6} For a surrounding medium of finite extent such as a spherical particle, it has been a very common practice in the literature to *assume* the validity of (5) and to apply it for various simplifications in the calculation of these induced decay rates. For example, while Ruppin⁷ has applied the energy-transfer method to calculate both the radiative and nonradiative rates for a dipole in the vicinity outside a sphere in a fully electrodynamic formulation, Chew⁸ has shown the equivalence between Ruppin's results and those from the mechanical model in the special case of a transparent sphere for which the nonradiative rates vanish identically, with extension to treat also the case when the molecular dipole is located inside the sphere. On the other hand, it has also been checked numerically for the general case of a metallic (absorptive) sphere that Eq. (5) is valid when both transfer rates exist.⁹ Moreover, even without having a rigorous proof of Eq. (5) for the general case established, it has been taken for granted and applied to decay rate calculations for dipole-sphere system in both the exact dynamic theory,¹⁰ and the long-wavelength quasi-static theory.¹¹⁻¹⁴ In the latter approximate theory, such assumption (i.e., validity of Eq. (5)) has been applied even in models with nonlocal dielectric response.¹⁵

Thus a rigorous proof of the validity of Eq. (5) for a dipole-sphere system will clarify most of the previous applications in the literature which were without justifications, and at the same time provide confidence for future study of decay rates using such an assumption. In the following, we shall provide an explicit proof of (5) for a dipole-sphere system via a direct calculation of the various rates as formulated using the exact electrodynamic theory. Hence, in parallel with the previous analysis for an extended (planar) geometry,^{3,6} our work will provide the corresponding explicit proof of (5) for a localized geometry, which at the same time extends the previous proof of Chew⁸ to the general case of a dissipative sphere.

PROOF OF EQUIVALENCE

Consider an oscillating dipole located at r in vacuum outside a homogeneous metallic sphere of radius a and dielectric function ε , we shall present our calculation of the various decay rates for each of the orthogonal dipole orientations relative to the sphere as follows (note that all the γ below denote normalized rates):

For radial dipoles

For the dipole oscillating along the radial direction, the overall decay rate obtained from the mechanical model (i.e., Eq. (2)) can be expressed as⁸⁻¹⁰

$$\gamma_{\perp} = 1 + \frac{3}{2} \operatorname{Re} \sum_{n=1}^{\infty} (2n+1)n(n+1)b_n [h_n(\rho)/\rho]^2, \quad (6)$$

where $\rho = kr = \omega r/c$ and $h_n(\rho)$ is the first kind spherical Hankel function. The Mie scattering coefficient b_n is defined by

$$b_n = \frac{[x_1 j_n(x_1)]' j_n(x) - \varepsilon [x j_n(x)]' j_n(x_1)}{\varepsilon [x h_n(x)]' j_n(x_1) - [x_1 j_n(x_1)]' h_n(x)}, \quad (7)$$

where $x = ka$, $x_1 = \sqrt{\varepsilon}ka$, and $j_n(x)$ is the spherical Bessel function.

On the other hand, from the energy-transfer theory, the radiative and nonradiative decay rates can be obtained in the following forms (via Eqs. (3) and (4)):⁷

$$\gamma_{\perp}^R = \frac{3}{2} \sum_{n=1}^{\infty} (2n+1)n(n+1) \frac{|j_n(\rho) + b_n h_n(\rho)|^2}{\rho^2}, \quad (8)$$

$$\gamma_{\perp}^{NR} = \frac{3}{2} k \operatorname{Im} \varepsilon \sum_{n=1}^{\infty} n(n+1) \frac{|\beta_n h_n(\rho)|^2}{r^2} \int_0^R [(n+1)|j_{n-1}(k_1 r')|^2 + n|j_{n+1}(k_1 r')|^2] r^2 dr', \quad (9)$$

respectively, where $k_1 = \sqrt{\varepsilon}k$, and

$$\beta_n = \sqrt{\varepsilon} \frac{[x h_n(x)]' j_n(x) - h_n(x)[x j_n(x)]'}{\varepsilon [x h_n(x)]' j_n(x_1) - h_n(x)[x_1 j_n(x_1)]'}. \quad (10)$$

Note that in Eq. (9), the integral has to be performed over the whole sphere to account for the nonradiative transfer via Joule heating of the sphere.

In order to verify the equivalence between the above two approaches, i.e., show that $\gamma_{\perp} = \gamma_{\perp}^R + \gamma_{\perp}^{NR}$, we first note that the integral for the nonradiative decay rate in Eq. (9) can be simplified using the following result:¹⁶

$$\int_0^a |j_n(k_1 r)|^2 r^2 dr = \frac{a}{k^2 \operatorname{Im} \varepsilon} I_n, \quad (11)$$

where $I_n = \operatorname{Im}[x_1^* j_{n-1}^*(x_1) j_n(x_1)]$. This result can be obtained from the following identity:¹⁷

$$\int_{r_1}^{r_2} j_n(pr) j_n(qr) r^2 dr = \frac{r^2}{p^2 - q^2} [q j_{n-1}(qr) j_n(pr) - p j_{n-1}(pr) j_n(qr)] \Big|_{r_1}^{r_2}, \quad (12)$$

and by setting $p = k_1$, $q = k_1^*$, $r_1 = 0$, and $r_2 = a$, respectively. Applying Eq. (11) to Eq. (9) leads to a simpler result for the nonradiative decay,

$$\gamma_{\perp}^{NR} = \frac{3x}{2\rho^2} \sum_{n=1}^{\infty} n(n+1) |\beta_n h_n(\rho)|^2 [(n+1)I_{n-1} + nI_{n+1}], \quad (13)$$

where no more integration is involved.

Now from Eqs. (6) and (8) we have

$$\gamma_{\perp} - \gamma_{\perp}^R = 1 - \frac{3}{2\rho^2} \sum_{n=1}^{\infty} n(n+1)(2n+1) \times [|h_n(\rho)|^2 (\operatorname{Re} b_n + |b_n|^2) - j_n^2(\rho)]. \quad (14)$$

The first term of the RHS of Eq. (14) can be eliminated by applying the following Bessel function identity¹⁷

$$\sum_{n=1}^{\infty} n(n+1)(2n+1) j_n^2(\rho) = 2\rho^2/3 \quad (15)$$

to Eq. (14), and thus obtain

$$\gamma_{\perp} - \gamma_{\perp}^R = -\frac{3}{2\rho^2} \sum_{n=1}^{\infty} n(n+1)(2n+1) \times |h_n(\rho)|^2 (\text{Re}b_n + |b_n|^2). \quad (16)$$

Note that the contributions of each multipole mode are separated in Eq. (16), and hence the problem now reduces to ver-

ify the equivalence between Eqs. (13) and (16) for each single multipole mode, i.e., to establish the following result:

$$x |\beta_n|^2 (\text{Re}b_n + |b_n|^2)^{-1} [(n+1)I_{n-1} + nI_{n+1}] = -(2n+1) \quad (17)$$

for each n . We first note that, after some algebra, the second and third terms of the LHS of Eq. (17) can be simplified to the following form using the definitions in Eqs. (7) and (10):

$$\frac{|\beta_n|^2}{\text{Re}b_n + |b_n|^2} = \frac{2ix[j_n(x)y_n'(x) - j_n'(x)y_n(x)]}{x_1^* j_n^*(x_1) j_n'(x_1) - x_1 j_n(x_1) [j_n^*(x_1)]' + |j_n(x_1)|^2 [(x_1^*)^2 - x_1^2] / |x_1|^2}. \quad (18)$$

On the other hand, using the following identities:¹⁷

$$j_{n-1}(x) + j_{n+1}(x) = \frac{2n+1}{x} j_n(x), \quad (19)$$

$$j_{n-1}(x) = j_n'(x) + \frac{n+1}{x} j_n(x), \quad (20)$$

and the definition of I_n given below Eq. (11), the last part of the LHS of Eq. (17) can be expressed as

$$[(n+1)I_{n-1} + nI_{n+1}] = i \frac{2n+1}{2} \left[x_1^* j_n^*(x_1) j_n'(x_1) - x_1 j_n(x_1) [j_n^*(x_1)]' + \frac{(x_1^*)^2 - x_1^2}{|x_1|^2} |j_n(x_1)|^2 \right]. \quad (21)$$

Substituting Eqs. (18) and (21) into Eq. (17), the LHS of Eq. (17) is reduced to

$$-(2n+1)x^2 [j_n(x)y_n'(x) - j_n'(x)y_n(x)]. \quad (22)$$

Hence using the following Wronskian relation for the spherical Bessel functions:¹⁸

$$x^2 [j_n(x)y_n'(x) - j_n'(x)y_n(x)] = 1, \quad (23)$$

the expression in (22) can be simplified and Eq. (17) (and hence Eq. (5)) is verified.

For tangential dipoles

In the case with a dipole oscillating along the tangential direction, the overall, radiative, and nonradiative decay rates can be expressed by the formulas^{7,8,10}

$$\gamma_{\parallel} = 1 + \frac{3}{4} \sum_{n=1}^{\infty} (2n+1) \left\{ a_n h_n^2(\rho) + b_n \left(\frac{[\rho h_n(\rho)]'}{\rho} \right)^2 \right\}, \quad (24)$$

$$\gamma_{\parallel}^R = \frac{3}{4} \sum_{n=1}^{\infty} (2n+1) \left\{ |j_n(\rho) + a_n h_n(\rho)|^2 + \frac{1}{\rho^2} |[\rho j_n(\rho)]' + b_n [\rho j_n(\rho)]'|^2 \right\}, \quad (25)$$

$$\gamma_{\parallel}^{NR} = \frac{3}{4} x \sum_{n=1}^{\infty} \left\{ (2n+1) |\alpha_n h_n(\rho)|^2 I_n + \left| \frac{\beta_n [\rho h_n(\rho)]'}{\rho} \right|^2 [(n+1)I_{n-1} + nI_{n+1}] \right\}, \quad (26)$$

respectively, where

$$a_n = \frac{[x j_n(x)]' j_n(x_1) - [x_1 j_n(x_1)]' j_n(x)}{[x_1 j_n(x_1)]' h_n(x) - [x h_n(x)]' j_n(x_1)}, \quad (27)$$

$$\alpha_n = \frac{[x j_n(x)]' h_n(x) - j_n(x) [x h_n(x)]'}{[x_1 j_n(x_1)]' h_n(x) - j_n(x_1) [x h_n(x)]'}. \quad (28)$$

As described in the previous case for radial dipoles, the overall decay rate is obtained by the mechanical model (Eq. (2)), while the radiative and nonradiative decay rates are derived from the energy transfer theory (Eqs. (3) and (4)). Note that the integrals for the nonradiative decay rate have again been carried out using Eq. (11).

Similarly, to establish Eq. (5) for this case, we first consider the quantity,

$$\gamma_{\parallel} - \gamma_{\parallel}^R = 1 - \frac{3}{4} \sum_{n=1}^{\infty} (2n+1) \left\{ j_n^2(\rho) + |h_n(\rho)|^2 (|a_n|^2 + \text{Re}a_n) + \left(\frac{[\rho j_n(\rho)]'}{\rho} \right)^2 + \left| \frac{[\rho h_n(\rho)]'}{\rho} \right|^2 (|b_n|^2 + \text{Re}b_n) \right\}. \quad (29)$$

Applying the following Bessel function identities:¹⁷

$$\sum_{n=1}^{\infty} (2n+1) \left\{ \frac{[\rho j_n(\rho)]'}{\rho} \right\}^2 = \frac{1}{3} + j_0^2(\rho), \quad (30)$$

$$\sum_{n=1}^{\infty} (2n+1) j_n^2(\rho) = 1 - j_0^2(\rho), \quad (31)$$

Eq. (29) can then be simplified to

$$\gamma_{\parallel} - \gamma_{\parallel}^R = -\frac{3}{4} \sum_{n=1}^{\infty} (2n+1) \left\{ |h_n(\rho)|^2 [|a_n|^2 + \text{Re}a_n] + \left| \frac{[\rho h_n(\rho)]'}{\rho} \right|^2 [|b_n|^2 + \text{Re}b_n] \right\}. \quad (32)$$

Again the contributions of each multipole mode are now separated and the problem is reduced to verifying the following relation:

$$\begin{aligned} x(2n+1) |\alpha_n h_n(\rho)|^2 I_n + x \left| \frac{\beta_n [\rho h_n(\rho)]'}{\rho} \right|^2 [(n+1)I_{n-1} + nI_{n+1}] \\ = -(2n+1) |h_n(\rho)|^2 [|a_n|^2 + \text{Re}a_n] - (2n+1) \left| \frac{[\rho h_n(\rho)]'}{\rho} \right|^2 \\ \times [|b_n|^2 + \text{Re}b_n]. \end{aligned} \quad (33)$$

Using the result in Eq. (17), we see that the second term in each of the two sides of Eq. (33) cancel with each other and (33) reduces to

$$x |\alpha_n|^2 I_n = -[|a_n|^2 + \text{Re}a_n]. \quad (34)$$

Substituting Eq. (27) into the RHS and Eq. (28) in the LHS of Eq. (34), it is straightforward to verify that Eq. (34) is indeed valid with each side equals to the following expression:

$$\frac{i}{2x} \frac{x_1 [j_n^*(x_1)]' j_n(x_1) - x_1 j_n^*(x_1) j_n'(x_1)}{|[x_1 j_n(x_1)]' h_n(x) - [x h_n(x)]' j_n(x_1)|^2}. \quad (35)$$

Hence, Eq. (5) is verified for the case of tangential dipoles.

DISCUSSION AND CONCLUSION

In the literature of classical modeling of “environment-induced” molecular decay rates over the last four decades, there have been two approaches: the mechanical oscillator model and the energy-transfer analysis. To our knowledge, the *explicit* demonstration of the equivalence of the two approaches has been established thus far only for the case of extended planar geometry.^{3,6} In our present work, we have demonstrated via direct calculations such equivalence also

holds for the most typical localized geometry—the sphere, which has been previously clarified only for a transparent (non-absorptive) sphere.⁸ In fact, from some general considerations as we discuss below, the general validity of Eq. (5) is expected to hold for any geometry and any dielectric medium as long as the response is linear, including possibly nonlocal dielectric response.

We want to stress that the validity of (5) is more than just conservation of energy as dictated by Poynting’s theorem. While the RHS does exhaust all the possible channels for transferring away the energy from the excited system (i.e., the molecule), the LHS obtained from a somewhat simplified damped-harmonic oscillator model is not expected to yield an exact result in general. In fact, the relative simple result in Eq. (2) is obtained only as an approximate result under the assumption that the linewidths are, in general, much smaller than the transition frequencies in the mechanical model.^{3,5}

However, from a more fundamental formulation using the general linear response theory based on the Fermi golden rule and the fluctuation-dissipation theorem, the result in Eq. (2) can indeed be shown to be exact and thus its validity is independent of the mechanical oscillator model.^{4,19–21} Furthermore, it is shown in Ref. 21 that by decomposing the dipole electric field into the transverse and longitudinal components, the application of the Poynting theorem indeed leads to Eq. (5) with each of the two components correspond to the radiative and nonradiative energy transfer, respectively. Hence, it is natural to expect, as a consequence, that Eq. (5) should hold for all geometry and dielectric response of the “environment” within the linear response approximation; and the previous works by Chance *et al.*^{3,6} together with our present work constitute *explicit* demonstration of its validity for each of an extended and a confined geometry of the environment. Furthermore, in case of an environment with nonlinear optical response, the equivalence between the two approaches as revealed from Eq. (5) will break down and the energy-transfer method will be the preferred approach without resorting to nonperturbative quantum transition theory.

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