A note on the green dyadic calculation of the decay rates for admolecules at multiple planar interfaces

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The Green dyadic formulation for calculating classical decay rates of admolecules at multiple planar interfaces first published by Chance, Prock and Silbey is reexamined. It is pointed out that, for the case of fluorescing molecules sandwiched between a system of super- and substrate interfaces, the original formalism requires significant modifications in order to lead to results consistent with those obtained from the Sommerfeld radiation theory. © *1999 American Institute of Physics.* [S0021-9606(99)70204-7]

I. INTRODUCTION

The study of molecular fluorescence at solid interfaces has been active for the last 2 decades since the first experimental works of Kuhn[1] and Drexhage[2] done in the early 1970's. Theoretically, it has been found that one of the most simple and direct approaches is to follow a phenomenological model solving the electrodynamics of an emitting molecular dipole in the vicinity of the interfaces. This model can provide both frequency shifts and decay rates for the admolecules (normalized to the free molecular decay rate), for example, yielding results in agreement with experimental results as well as quantum mechanical calculations. Among other contributors, Chance, Prock and Silbey (CPS) have cleverly applied the radiation antenna theory of Sommerfeld[3] to this problem and showed that classical electrodynamics alone can account for most of the experimental observations. A momentous review article[4] was compiled by CPS in the late 1970's summarizing the complete status of the subject at that time. Over the last 20 years, this article has often been quoted and used by people working in the field, experimentalists and theorists alike.[5] Application of this theory has also gone beyond fluorescence to other optical phenomena at interfaces as in Ref. 6 and 7. It is also in this review article that the Sommerfeld method[3] was first generalized to the case of multiple planar interfaces using the dyadic Green's function formulation. This generalization includes both cases (i) where the layer of fluorescent dyes is deposited on the top of a stratified multilayer system and (ii) where the layer is sandwiched between two such multilayer systems.

It is the purpose of this paper to point out that, in the original CPS formulation for case (ii) above, the choice of the dyadic eigenfunctions was not appropriately made and significant modifications are necessary to obtain a consistent Green dyadic theory for this case. The correct result will be presented in two different but equivalent formulations and will be shown to lead back to well-known results from the Sommerfeld theory for the simple case with the dyes sandwiched between only one superstrate and one substrate medium.

II. THE CPS FORMULATION

To be clear and self-contained, let us first recapitulate the main results from the CPS article.[4] For harmonic currents and fields, the dyadic Green formulation of Ref. 4 has the standard Green's function solution (in SI units):

$$\mathbf{E}(\mathbf{R})=i\omega\mu\int \mathbf{G}(\mathbf{R},\mathbf{R}')\cdot\mathbf{J}(\mathbf{R}')\,dV(\mathbf{R}'),\tag{1}$$

where μ is the magnetic permeability. For simplicity, we will consider in this paper only the case with one superstrate and one substrate confining the source in the gap as depicted in Fig. 1. More details on the case with a large number of layers and generalization to the case with gradient index media will be presented in a forthcoming paper.[8]

Let $\mathbf{G}_0$ denote the Green dyadic for the source field and $\mathbf{G}_i$ $(i=1,2,3)$ denote those for the scattered fields in the three media. Thus according to Ref. 4, one obtains[9]

$$\mathbf{G}_0(\mathbf{R},\mathbf{R}')=\frac{-1}{k_1^2}\hat{z}\hat{z}\,\delta(\mathbf{R}-\mathbf{R}')+\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}\begin{bmatrix}\mathbf{M}_{jn\lambda}(+h_1)\mathbf{M}'_{jn\lambda}(-h_1)+\mathbf{N}_{jn\lambda}(+h_1)\mathbf{N}'_{jn\lambda}(-h_1)\\ \mathbf{M}_{jn\lambda}(-h_1)\mathbf{M}'_{jn\lambda}(+h_1)+\mathbf{N}_{jn\lambda}(-h_1)\mathbf{N}'_{jn\lambda}(+h_1)\end{bmatrix}\begin{matrix}z\geqslant z'\\ z\leqslant z',\end{matrix}\tag{2}$$

$$\mathbf{G}_1(\mathbf{R},\mathbf{R}')=\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}\{[c_1\mathbf{M}_{jn\lambda}(-h_1)+c_1'\mathbf{M}_{jn\lambda}(h_1)]\mathbf{M}'_{jn\lambda}(h_1)$$
$$+[f_1\mathbf{N}_{jn\lambda}(-h_1)+f_1'\mathbf{N}_{jn\lambda}(h_1)]\mathbf{N}'_{jn\lambda}(h_1)\},\tag{3}$$

$$\mathbf{G}_2(\mathbf{R},\mathbf{R}')=\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\times\sum_{j=0}^{1}[c_2\mathbf{M}_{jn\lambda}(h_2)\mathbf{M}'_{jn\lambda}(h_1)+f_2\mathbf{N}_{jn\lambda}(h_2)\mathbf{N}'_{jn\lambda}(h_1)], \tag{4}$$

$$\mathbf{G}_3(\mathbf{R},\mathbf{R}')=\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\times\sum_{j=0}^{1}[c_3\mathbf{M}_{jn\lambda}(-h_3)\mathbf{M}'_{jn\lambda}(h_1)+f_3\mathbf{N}_{jn\lambda}(-h_3)\mathbf{N}'_{jn\lambda}(h_1)], \tag{5}$$

where $\mathbf{M}$ and $\mathbf{N}$ are given in cylindrical coordinates by:

$$\mathbf{M}_{jn\lambda}(h)=e^{ihz}\left[\frac{nJ_n(\lambda r)}{r}\sin\left(\frac{j\pi}{2}-n\varphi\right)\hat{r}-\frac{\partial J_n(\lambda r)}{\partial r}\times\cos\left(\frac{j\pi}{2}-n\varphi\right)\hat{\varphi}\right], \tag{6}$$

$$\mathbf{N}_{jn\lambda}(h)=\frac{e^{ihz}}{k}\left[ih\frac{\partial J_n(\lambda r)}{\partial r}\cos\left(\frac{j\pi}{2}-n\varphi\right)\hat{r}+inh\frac{J_n(\lambda r)}{r}\times\sin\left(\frac{j\pi}{2}-n\varphi\right)\hat{\varphi}+\lambda^2J_n(\lambda r)\cos\left(\frac{j\pi}{2}-n\varphi\right)\hat{z}\right], \tag{7}$$

with J_n the Bessel function of the first kind and $h_i(\lambda)=\sqrt{k_i^2-\lambda^2}$, where the square root is taken to have positive real part.

According to Ref. 4, requirement of continuity of transverse field components at interfaces $z=0$ and $z=z_0$ leads to the following systems where $e_j\equiv e^{ih_jz_0}$:

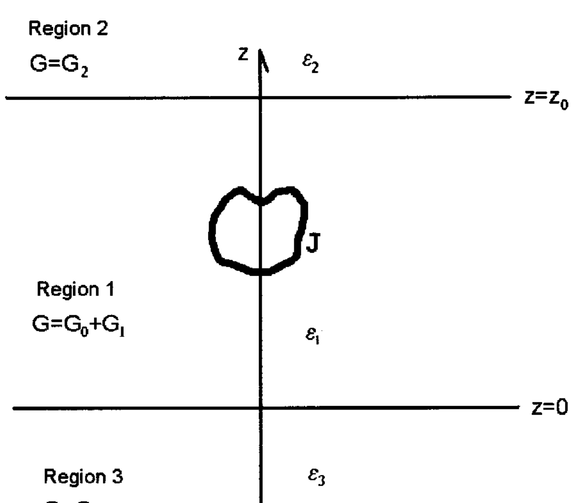

FIG. 1. Geometry of the problem.

$$\begin{bmatrix} 1 & 1 & 0 & -1 \\ -h_1 & h_1 & 0 & h_3 \\ \frac{1}{e_1} & e_1 & -e_2 & 0 \\ -\frac{h_1}{e_1} & h_1e_1 & -h_2e_2 & 0 \end{bmatrix}\begin{bmatrix} c_1 \\ c_1' \\ c_2 \\ c_3 \end{bmatrix}=\begin{bmatrix} -1 \\ h_1 \\ -e_1 \\ -h_1e_1 \end{bmatrix}, \tag{8}$$

or in matrix form $\mathbf{Ac}=\mathbf{r}_c$, and

$$\begin{bmatrix} -h_1/k_1 & h_1/k_1 & 0 & h_3/k_3 \\ k_1 & k_1 & 0 & -k_3 \\ \frac{-h_1}{k_1e_1} & h_1e_1/k_1 & -h_2e_2/k_2 & 0 \\ \frac{k_1}{e_1} & k_1e_1 & -k_2e_2 & 0 \end{bmatrix}\begin{bmatrix} f_1 \\ f_1' \\ f_2 \\ f_3 \end{bmatrix}=\begin{bmatrix} h_1/k_1 \\ -k_1 \\ -e_1h_1/k_1 \\ -e_1k_1 \end{bmatrix}, \tag{9}$$

or $\mathbf{Bf}=\mathbf{r}_f$. Solving Eqs. (8) and (9) yields the following:

$$\begin{pmatrix} c_1 \\ c_1' \\ f_1 \\ f_1' \end{pmatrix}=\begin{pmatrix} e_1^2R_{12}^{\perp}\frac{1+R_{13}^{\perp}}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}} \\ R_{13}^{\perp}\frac{1+e_1^2R_{12}^{\perp}}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}} \\ -R_{12}^{\parallel}\frac{e_1^2(1-R_{13}^{\parallel})}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}} \\ -R_{13}^{\parallel}\frac{(1-e_1^2R_{12}^{\parallel})}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}} \end{pmatrix}, \tag{10}$$

where

$$R_{ij}^{\parallel}\equiv\frac{\epsilon_ih_j-\epsilon_jh_i}{\epsilon_ih_j+\epsilon_jh_i}$$

and

$$R_{ij}^{\perp}\equiv\frac{h_i-h_j}{h_i+h_j}.$$

Note that sign errors in Eq. (3.34) of Ref. 4 are corrected in Eq. (10).

We have confirmed that the above results are in error by performing a numerical calculation of special cases. For example, the scattered electric field was calculated at the site of a vertical dipole located at the center of region 1, with values for the dielectric constants ϵ_1, ϵ_2, and ϵ_3 set arbitrarily. Next the values of ϵ_2 and ϵ_3 were interchanged. Results in the two cases differed, indicating that the analytical results in Eq. (10) are in error.

III. THE CORRECT SOLUTION

We shall present here two different approaches to the correct Green dyadic solution to the above problem.

A. Solution by expanding the solution space

In reviewing the problem, we found that Eqs. (8) and (9) do not satisfy the boundary conditions at the interfaces and that no solution could be found once the constraints of forms (3) (4), and (5) were imposed. A necessary remedy is enlargement of the solution space to the point where the boundary conditions can be satisfied. For instance, the expression for $\mathbf{G}_1$ contains dyadic products $\mathbf{M}_{jn\lambda}(-h_1)\mathbf{M}'_{jn\lambda}(+h_1)$ and $\mathbf{M}_{jn\lambda}(+h_1)\mathbf{M}'_{jn\lambda}(+h_1)$ but not $\mathbf{M}_{jn\lambda}(-h_1)\mathbf{M}'_{jn\lambda}(-h_1)$ and $\mathbf{M}_{jn\lambda}(+h_1)\mathbf{M}'_{jn\lambda}(-h_1)$ which are equally valid. It turns out that the correct solution from this approach has already been worked out in the electrical engineering literature.[10] The general solutions for the scattering fields are given by

$$\mathbf{G}_1(\mathbf{R},\mathbf{R}')\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}\{[c_1\mathbf{M}_{jn\lambda}(-h_1)+c'_1\mathbf{M}_{jn\lambda}(h_1)]\mathbf{M}'_{jn\lambda}(h_1)$$
$$+[a_1\mathbf{M}_{jn\lambda}(-h_1)+a'_1\mathbf{M}_{jn\lambda}(h_1)]\mathbf{M}'_{jn\lambda}(-h_1)+[f_1\mathbf{N}_{jn\lambda}(-h_1)+f'_1\mathbf{N}_{jn\lambda}(h_1)]\mathbf{N}'_{jn\lambda}(h_1)$$
$$+[b_1\mathbf{N}_{jn\lambda}(-h_1)+b'_1\mathbf{N}_{jn\lambda}(h_1)]\mathbf{N}'_{jn\lambda}(-h_1)\},\tag{11}$$

$$\mathbf{G}_2(\mathbf{R},\mathbf{R}')\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}[c_2\mathbf{M}_{jn\lambda}(h_2)\mathbf{M}'_{jn\lambda}(h_1)+f_2\mathbf{N}_{jn\lambda}(h_2)\mathbf{N}'_{jn\lambda}(h_1)+a_2\mathbf{M}_{jn\lambda}(h_2)\mathbf{M}'_{jn\lambda}(-h_1)$$
$$+b_2\mathbf{N}_{jn\lambda}(h_2)\mathbf{N}'_{jn\lambda}(-h_1)],\tag{12}$$

$$\mathbf{G}_3(\mathbf{R},\mathbf{R}')\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}[c_3\mathbf{M}_{jn\lambda}(-h_3)\mathbf{M}'_{jn\lambda}(h_1)+f_3\mathbf{N}_{jn\lambda}(-h_3)\mathbf{N}'_{jn\lambda}(h_1)$$
$$+a_3\mathbf{M}_{jn\lambda}(-h_3)\mathbf{M}'_{jn\lambda}(-h_1)+b_3\mathbf{N}_{jn\lambda}(-h_3)\mathbf{N}'_{jn\lambda}(-h_1)].\tag{13}$$

By imposing the appropriate boundary conditions, the expansion coefficients can finally be obtained as[10]

$$\mathbf{c}_s=\frac{1}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}\begin{bmatrix}e_1^2R_{12}^{\perp}R_{13}^{\perp}\\ R_{13}^{\perp}\\ \dfrac{e_1}{e_2}(1+R_{12}^{\perp})R_{13}^{\perp}\\ (1+R_{13}^{\perp})\end{bmatrix},$$

$$\mathbf{a}_s=\frac{1}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}\begin{bmatrix}e_1^2R_{12}^{\perp}\\ e_1^2R_{12}^{\perp}R_{13}^{\perp}\\ \dfrac{e_1}{e_2}(1+R_{12}^{\perp})\\ e_1^2R_{12}^{\perp}(1+R_{13}^{\perp})\end{bmatrix},$$

$$\mathbf{f}_s=\frac{1}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}\begin{bmatrix}e_1^2R_{12}^{\parallel}R_{13}^{\parallel}\\ -R_{13}^{\parallel}\\ \dfrac{-k_1e_1}{k_2e_2}(1-R_{12}^{\parallel})R_{13}^{\parallel}\\ \dfrac{k_1}{k_3}(1-R_{13}^{\parallel})\end{bmatrix},\tag{14}$$

$$\mathbf{b}_s=\frac{1}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}\begin{bmatrix}-e_1^2R_{12}^{\parallel}\\ e_1^2R_{12}^{\parallel}R_{13}^{\parallel}\\ \dfrac{k_1e_1}{k_2e_2}(1-R_{12}^{\parallel})\\ \dfrac{-k_1}{k_3}e_1^2R_{12}^{\parallel}(1-R_{13}^{\parallel})\end{bmatrix},$$

where

$$\mathbf{c}_s=\begin{bmatrix}c_1\\ c'_1\\ c_2\\ c_3\end{bmatrix},\quad \mathbf{a}_s=\begin{bmatrix}a_1\\ a'_1\\ a_2\\ a_3\end{bmatrix},\quad \mathbf{f}_s=\begin{bmatrix}f_1\\ f'_1\\ f_2\\ f_3\end{bmatrix},$$

and

$$\mathbf{b}_s=\begin{bmatrix}b_1\\ b'_1\\ b_2\\ b_3\end{bmatrix}.$$

Using the above solution, we can write out the Green's functions as

$$\mathbf{G}_1(\mathbf{R},\mathbf{R}')\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}\Bigg(\frac{1}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}$$
$$\times[e_1^2R_{12}^{\perp}\mathbf{M}^-(R_{13}^{\perp}\mathbf{M}^++\mathbf{M}^-)+R_{13}^{\perp}\mathbf{M}^+(\mathbf{M}^+$$
$$+e_1^2R_{12}^{\perp}\mathbf{M}^-)]+\frac{1}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}$$
$$\times[e_1^2R_{12}^{\parallel}\mathbf{N}^-(R_{13}^{\parallel}\mathbf{N}^+-\mathbf{N}^-)$$
$$+R_{13}^{\parallel}\mathbf{N}^+(e_1^2R_{12}^{\parallel}\mathbf{N}^--\mathbf{N}^+)]\Bigg),\tag{15}$$

$$\mathbf{G}_2(\mathbf{R},\mathbf{R}')\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}\left[\frac{1}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}\left(\frac{e_1}{e_2}(1+R_{12}^{\perp})\mathbf{M}(h_2)(\mathbf{M}^-+R_{13}^{\perp}\mathbf{M}^+)\right)\right.$$
$$\left.+\frac{1}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}\left(\frac{k_1e_1}{k_2e_2}(1-R_{12}^{\parallel})\mathbf{N}(h_2)(\mathbf{N}^--R_{13}^{\parallel}\mathbf{N}^+)\right)\right], \tag{16}$$

$$\mathbf{G}_3(\mathbf{R},\mathbf{R}')\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}\left[\frac{1}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}[(1+R_{13}^{\perp})\mathbf{M}(-h_3)(\mathbf{M}^++e_1^2R_{12}^{\perp}\mathbf{M}^-)]\right.$$
$$\left.+\frac{1}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}\left(\frac{k_1}{k_3}(1-R_{13}^{\parallel})\mathbf{N}(-h_3)(\mathbf{N}^+-e_1^2R_{12}^{\parallel}\mathbf{N}^-)\right)\right], \tag{17}$$

where $\mathbf{M}^{\pm}=\mathbf{M}'(\pm h_1)$ and $\mathbf{N}^{\pm}=\mathbf{N}'(\pm h_1)$. We have checked that the solution given by Eqs. (15)–(17) does satisfy the numerical test described above.

B. Solution by reassociation

An alternative approach, which might be called ''reassociation'', is to introduce explicitly the source $\mathbf{J}$ into the dyadic expansion. We replaced typical products such as $(\mathbf{MM}')\mathbf{J}$ with the equivalent product $\mathbf{M}(\mathbf{M}'\cdot\mathbf{J})$ reducing the product on the right to a complex scalar. An additional small step then leads to the realization that $c(\mathbf{MM}')\mathbf{J}$ can be replaced by $c\mathbf{M}$, where $\mathbf{M}'\cdot\mathbf{J}$ scalar has been absorbed into the c. We will see at the end that $\mathbf{J}$ can be factored from both sides of the resulting equations leading to expressions for $\mathbf{G}_i$ independent of the source, as they must be. Following the logic given above, we have:

$$\mathbf{G}_1(\mathbf{R},\mathbf{R}')\cdot\mathbf{J}\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}[c_1\mathbf{M}_{jn\lambda}(-h_1)+c_1'\mathbf{M}_{jn\lambda}(h_1)+f_1\mathbf{N}_{jn\lambda}(-h_1)+f_1'\mathbf{N}_{jn\lambda}(h_1)], \tag{18}$$

$$\mathbf{G}_2(\mathbf{R},\mathbf{R}')\cdot\mathbf{J}\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}[c_2\mathbf{M}_{jn\lambda}(h_2)+f_2\mathbf{N}_{jn\lambda}(h_2)], \tag{19}$$

$$\mathbf{G}_3(\mathbf{R},\mathbf{R}')\cdot\mathbf{J}\equiv\frac{i}{4\pi}\int_0^{+\infty}d\lambda\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\sum_{j=0}^{1}[c_3\mathbf{M}_{jn\lambda}(-h_3)+f_3\mathbf{N}_{jn\lambda}(-h_3)], \tag{20}$$

where the c and f coefficients are functions of current density $\mathbf{J}$ as well as position, j, n and λ. This approach allows us to work directly with electric and magnetic field values in applying the boundary conditions at the interfaces. The resulting eight equations decouple into two matrix systems:

$$\mathbf{Ac}=\{[-\mathbf{M}'(h_1)\quad h_1\mathbf{M}'(h_1)\quad -e_1\mathbf{M}'(-h_1)\quad -h_1e_1\mathbf{M}'(-h_1)]\cdot\mathbf{J}\}^t, \tag{21}$$

$$\mathbf{Bf}=\left[\left(\frac{h_1}{k_1}\mathbf{N}'(h_1)\quad -k_1\mathbf{N}'(h_1)\quad -\frac{h_1e_1}{k_1}\mathbf{N}'(-h_1)\quad -k_1e_1\mathbf{N}'(-h_1)\right)\cdot\mathbf{J}\right]^t, \tag{22}$$

where $\mathbf{A}$ and $\mathbf{B}$ are the same matrices defined above in Eqs. (8) and (9). The matrix solution of Eqs. (21) and (22) leads to:

$$\begin{bmatrix}c_1\\c_1'\\c_2\\c_3\end{bmatrix}=\frac{1}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}\begin{bmatrix}e_1^2R_{12}^{\perp}(R_{13}^{\perp}\mathbf{M}^++\mathbf{M}^-)\\R_{13}^{\perp}(\mathbf{M}^++e_1^2R_{12}^{\perp}\mathbf{M}^-)\\\frac{e_1}{e_2}(1+R_{12}^{\perp})(\mathbf{M}^-+R_{13}^{\perp}\mathbf{M}^+)\\(1+R_{13}^{\perp})(\mathbf{M}^++e_1^2R_{12}^{\perp}\mathbf{M}^-)\end{bmatrix}\cdot\mathbf{J}, \tag{23}$$

$$\begin{bmatrix}f_1\\f_1'\\f_2\\f_3\end{bmatrix}=\frac{1}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}\begin{bmatrix}e_1^2R_{12}^{\parallel}(R_{13}^{\parallel}\mathbf{N}^+-\mathbf{N}^-)\\R_{13}^{\parallel}(e_1^2R_{12}^{\parallel}\mathbf{N}^--\mathbf{N}^+)\\\frac{k_1e_1}{k_2e_2}(1-R_{12}^{\parallel})(\mathbf{N}^--R_{13}^{\parallel}\mathbf{N}^+)\\\frac{k_1}{k_3}(1-R_{13}^{\parallel})(\mathbf{N}^+-e_1^2R_{12}^{\parallel}\mathbf{N}^-)\end{bmatrix}\cdot\mathbf{J}. \tag{24}$$

We can now insert Eqs. (23) and (24) into Eqs. (18)–(20). Since an arbitrary $\mathbf{J}$ then appears on both sides of the result, we can factor out $\mathbf{J}$, yielding results in complete agreement with Eqs. (15)–(17). More details on this approach and the equivalence between the two methods will be provided in a forthcoming paper.[8]

IV. CALCULATION OF DECAY RATES

According to the classical phenomenological approach of CPS, the normalized decay rate of the admolecule can be obtained in terms of the imaginary part ($\Im$) of the reflected field at the dipole site as:

$$\hat{b}\equiv\frac{b}{b_0}=1+\frac{6\pi\epsilon_0qn_1^2}{p_0k_1^3}\Im(\mathbf{E}_0), \tag{25}$$

where q is the intrinsic quantum yield and $k_1=n_1\omega/c$, with n_1 the real refractive index of the medium containing the dipole. We show below that the dyadics given in Eqs. (15)–(17) can indeed lead back to the correct results for $\hat{b}$ for a molecule confined as in the geometry of Fig. 1.

We first consider the problem of a vertically oriented dipole with moment $p_0\hat{z}e^{-i\omega t}$ at the source position $d\hat{z}$ between two interfaces at $z=0$ and $z=s+d=z_0$. The current will be given by

$$\mathbf{J}=-i\omega p_0\hat{z}e^{-i\omega t}\delta(\mathbf{R}'-d\hat{z}). \tag{26}$$

Inserting this $\mathbf{J}$ into Eqs. (1) and using Eq. (15) yields

$$\begin{aligned}
\mathbf{E}_z^{\perp}(d\hat{z})&=\{\omega^2\mu_0\mu_1p_0e^{-i\omega t}\}\hat{z}\cdot\mathbf{G}_1(d\hat{z},d\hat{z})\hat{z}\\
&=\{\omega^2\mu_0\mu_1p_0e^{-i\omega t}\}\frac{i}{4\pi}\int_{\lambda=0}^{+\infty}\sum_{n=0}^{+\infty}\frac{2-\delta_n}{\lambda h_1(\lambda)}\\
&\quad\times\sum_{j=0,1}\hat{z}\cdot\left(\frac{1}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}[e_1^2R_{12}^{\parallel}\mathbf{N}^-(R_{13}^{\parallel}\mathbf{N}^+-\mathbf{N}^-)+R_{13}^{\parallel}\mathbf{N}^+(e_1^2R_{12}^{\parallel}\mathbf{N}^--\mathbf{N}^+)]\right)\hat{z}\,d\lambda\\
&=\{\omega^2\mu_0\mu_1p_0e^{-i\omega t}\}\frac{i}{4\pi}\int_{\lambda=0}^{+\infty}\frac{1}{\lambda h_1(\lambda)}\left\{\frac{1}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}\left[e_1^2R_{12}^{\parallel}\frac{\lambda^2}{e_dk_1}\left(R_{13}^{\parallel}\frac{e_d\lambda^2}{k_1}-\frac{\lambda^2}{e_dk_1}\right)\right.\right.\\
&\quad\left.\left.+R_{13}^{\parallel}\frac{e_d\lambda^2}{k_1}\left(e_1^2R_{12}^{\parallel}\frac{\lambda^2}{e_dk_1}-\frac{e_d\lambda^2}{k_1}\right)\right]\right\}d\lambda\\
&=\frac{i\omega^2\mu_0\mu_1p_0e^{-i\omega t}}{4\pi k_1^2}\int_{\lambda=0}^{+\infty}\frac{\lambda^3}{h_1(\lambda)}\frac{(2e_1^2R_{12}^{\parallel}R_{13}^{\parallel}-e_s^2R_{12}^{\parallel}-e_d^2R_{13}^{\parallel})}{(1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel})}d\lambda\\
&=\frac{p_0e^{-i\omega t}}{4\pi\epsilon_0\epsilon_1}\int_{\lambda=0}^{+\infty}\frac{\lambda^3}{[-ih_1(\lambda)]}\left(\frac{(1-R_{13}^{\parallel}e_d^2)(1-R_{12}^{\parallel}e_s^2)}{(1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel})}-1\right)d\lambda,
\end{aligned}\tag{27}$$

where $e_d=e^{idh_1(\lambda)}$ and $e_s=e^{ish_1(\lambda)}$ with $s+d=z_0$. We have also employed the identity:

$$\frac{2xy-x-y}{1-xy}=\frac{(1-x)(1-y)}{1-xy}-1.$$

Inserting Eq. (27) into Eq. (25), we obtain

$$\begin{aligned}
\hat{b}_{\perp}&=1+\frac{6\pi\epsilon_0qn_1^2}{p_0k_1^3}\Im\left[\frac{p_0}{4\pi\epsilon_0\epsilon_1}\int_{\lambda=0}^{+\infty}\frac{\lambda^3}{[-ih_1(\lambda)]}\right.\\
&\quad\left.\times\left(\frac{(1-R_{13}^{\parallel}e_d^2)(1-R_{12}^{\parallel}e_s^2)}{(1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel})}-1\right)d\lambda\right]\\
&=1-q+\frac{3q}{2k_1^3}\\
&\quad\times\Im\left[i\int_{\lambda=0}^{+\infty}\frac{\lambda^3}{h_1(\lambda)}\left(\frac{(1-R_{13}^{\parallel}e_d^2)(1-R_{12}^{\parallel}e_s^2)}{(1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel})}\right)d\lambda\right],
\end{aligned}\tag{28}$$

where we have used

$$\int_{\lambda=0}^{k}\frac{\lambda^3\,d\lambda}{\sqrt{k^2-\lambda^2}}=\frac{2}{3}k^3.$$

The result in Eq. (28) is equivalent to Eq. (2.47) of Ref. 4 using the transformation: $u=\lambda/k_1$. In the case of a trivial interface between regions 1 and 2, that is, $\epsilon_1=\epsilon_2$ implying $R_{12}^{\parallel}=0$, from Eq. (28) we have

$$\hat{b}_{\perp}=1-\frac{3q}{2k_1^3}\Im\left(i\int_{\lambda=0}^{+\infty}R_{13}^{\parallel}e_d^2\frac{\lambda^3\,d\lambda}{h_1(\lambda)}\right),$$

which is identical to Eq. (2.17) of Ref. 4.

We next consider the problem of a horizontally oriented dipole with moment $p_0\hat{x}e^{-i\omega t}$ at the source position $d\hat{z}$ between the same interfaces. The current density is then

$$\mathbf{J}=-i\omega p_0\hat{x}e^{-i\omega t}\delta(\mathbf{R}'-d\hat{z}). \tag{29}$$

Again, inserting $\mathbf{J}$ into Eq. (1) and integrating yields

$$E_x^{\parallel}(d\hat{z})=\{\omega^2\mu_0\mu_1p_0e^{-i\omega t}\}\hat{x}\cdot\mathbf{G}_1(d\hat{z},d\hat{z})\hat{x}. \tag{30}$$

To proceed further, we note that

$$\hat{x}\cdot\mathbf{M}^{\pm}(d\hat{z})=\begin{cases}\dfrac{\lambda}{2}e^{\pm ih_1d} & \text{if } n=1 \text{ and } j=1\\ 0 & \text{otherwise}\end{cases},$$

and

$$\hat{x}\cdot\mathbf{N}^{\pm}(d\hat{z})=\begin{cases}\dfrac{\pm i\lambda h_1}{2k_1}e^{\pm ih_1d} & \text{if } n=1 \text{ and } j=0\\ 0 & \text{otherwise}\end{cases},$$

Insertion of the above dot products into Eq. (15) yields

$$\hat{x}\cdot\mathbf{G}_1(d\hat{z},d\hat{z})\cdot\hat{x}=\frac{i}{8\pi}\int_{\lambda=0}^{+\infty}\left(\frac{1}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}(2e_1^2R_{12}^{\perp}R_{13}^{\perp}+e_s^2R_{12}^{\perp}+e_d^2R_{13}^{\perp})+\frac{h_1^2(\lambda)}{k_1^2(1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel})}(2e_1^2R_{12}^{\parallel}R_{13}^{\parallel}+e_s^2R_{12}^{\parallel}+e_d^2R_{13}^{\parallel})\right)\frac{\lambda\,d\lambda}{h_1(\lambda)}$$

$$=\frac{i}{8\pi k_1^2}\int_{\lambda=0}^{+\infty}\left[k_1^2\left(\frac{(e_s^2R_{12}^{\perp}+1)(e_d^2R_{13}^{\perp}+1)}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}-1\right)+h_1^2(\lambda)\left(\frac{(e_s^2R_{12}^{\parallel}+1)(e_d^2R_{13}^{\parallel}+1)}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}-1\right)\right]\frac{\lambda\,d\lambda}{h_1(\lambda)}, \tag{31}$$

where we have again used the identity:

$$\frac{2xy+x+y}{1-xy}=\frac{(x+1)(y+1)}{1-xy}-1.$$

Using $k_1^2=\omega^2\epsilon_0\epsilon_1\mu_0\mu_1$, we finally have

$$E_x^{\parallel}(d\hat{z})=\frac{p_0ie^{-i\omega t}}{8\pi\epsilon_0\epsilon_1}\int_{\lambda=0}^{+\infty}\left[k_1^2\left(\frac{(e_s^2R_{12}^{\perp}+1)(e_d^2R_{13}^{\perp}+1)}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}-1\right)+h_1^2(\lambda)\left(\frac{(e_s^2R_{12}^{\parallel}+1)(e_d^2R_{13}^{\parallel}+1)}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}-1\right)\right]\frac{\lambda\,d\lambda}{h_1(\lambda)}. \tag{32}$$

Inserting Eq. (32) into Eq. (25), we obtain

$$\hat{b}_{\parallel}=1+\frac{6\pi\epsilon_0qn_1^2}{p_0k_1^3}\Im\left\{\frac{p_0}{8\pi\epsilon_0\epsilon_1}\int_{\lambda=0}^{+\infty}\left[k_1^2\left(\frac{(e_s^2R_{12}^{\perp}+1)(e_d^2R_{13}^{\perp}+1)}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}-1\right)+h_1^2(\lambda)\left(\frac{(e_s^2R_{12}^{\parallel}+1)(e_d^2R_{13}^{\parallel}+1)}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}-1\right)\right]\frac{\lambda\,d\lambda}{[-ih_1(\lambda)]}\right\}$$

$$=1-q+\frac{3q}{4k_1^3}\Im\left\{\int_{\lambda=0}^{+\infty}\left[k_1^2\left(\frac{(e_s^2R_{12}^{\perp}+1)(e_d^2R_{13}^{\perp}+1)}{1-e_1^2R_{12}^{\perp}R_{13}^{\perp}}\right)+h_1^2(\lambda)\left(\frac{(e_s^2R_{12}^{\parallel}+1)(e_d^2R_{13}^{\parallel}+1)}{1-e_1^2R_{12}^{\parallel}R_{13}^{\parallel}}\right)\right]\frac{\lambda\,d\lambda}{[-ih_1(\lambda)]}\right\}, \tag{33}$$

where we have used

$$\int_{\lambda=0}^{k}\frac{(2k^2-\lambda^2)\lambda\,d\lambda}{\sqrt{k^2-\lambda^2}}=\frac{4}{3}k^3.$$

The result in Eq. (33) is equivalent to Eq. (2.48) of Ref. 4 using the transformation: $u=\lambda/k_1$. In the case of a trivial interface between regions 1 and 2, that is $\epsilon_1=\epsilon_2$, implying that $R_{12}^{\perp}=R_{12}^{\parallel}=0$, we have from Eq. (33)

$$\hat{b}_{\parallel}=1+\frac{3q}{4k_1^3}\Im\left(i\int_{\lambda=0}^{+\infty}e_d^2[k_1^2R_{13}^{\perp}+h_1^2(\lambda)R_{13}^{\parallel}]\frac{\lambda\,d\lambda}{h_1(\lambda)}\right),$$

which is identical to Eq. (2.29) of Ref. 4. Thus our Green dyadics in Eqs. (15)–(17) indeed reproduce the correct results for the decay rates obtained by the generalization of the Sommerfeld method.[4]

V. CONCLUSION

The dyadic Green's function solution to the double mirror problem in Ref. 4 was found to have a theoretical error. We have shown that the error can be corrected by extending and symmetrizing the solution form in order to satisfy boundary conditions as done in Ref. 10. Alternatively, reassociation of the dyadic product with current density leads to the same solution as can be seen by virtue of an isomorphism between formulations.[8] Finally, the corrected dyadic Green's function formulation can be used directly to calculate and verify decay rates calculated in Ref. 4 from the Sommerfeld theory for the case of an oscillating dipole positioned between interfaces. With either of the two approaches, generalization is straightforward to the case with an arbitrary number of multiple interfaces for both the substrate and superstrate.[8,10] In addition, the green dyadic formalism will also allow one to calculate an arbitrary source within the gap beyond that of an electric point dipole. The present formulation should be useful in these aspects.

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