Methods and Applications in Fluorescence

Surface plasmon enhanced fluorescence: self-consistent classical treatment in the quasi-static limit

Dentcho A Genov
Department of Physics, Louisiana Tech University, PO Box 10348, Ruston, LA 71272, United States of America
E-mail: dgenov@latech.edu

Abstract
The problem of enhanced molecular emission in close proximity to dielectric and metallic interfaces is of great importance for many physical and biological applications. Here we present an exact treatment of the problem from the viewpoint of classical electromagnetism. Self-consistent analytical theory of the surface enhanced fluorescence (SEF) is developed for configurations consisting of an emitter in proximity to core–shell metal–dielectric nanoparticles. The dependence of the fluorescence enhancement on the excitation laser and fluorescence frequencies and distance of the emitter to the nanoparticle interface are studied. The developed theory predicts enhanced fluorescence at intermediate distances as well as emission quenching into non-radiative surface plasmon (SP) modes dominating the response for short distances. The conditions for optimal emission enhancement for two core–shell configurations are determined and a comparison to published experimental data is performed showing a good correspondence between theory and experiment. The developed model can be applied toward analyzes and optimizations of various applications related to SP enhance fluorescence spectroscopy.

1. Introduction
The fluorescence emission is a common marker for a wide variety of practical problems including fluorescence tagging related to bio-sensing and spectroscopic studies [1–5], dye and quantum dot lasers [6, 7], and electrochemistry [8]. When an emitter is placed in close proximity to a plasmonic interface enhanced emission is expected, a process also known as Purcell effect [9]. This effect is especially prominent in low-dimension metallic nanostructures [10] and has been extensively utilized to observe naturally weak radiation processes with enhanced sensitivity including surface enhanced fluorescence (SEF) and Raman spectroscopy [11–14]. Recently metal based meta-surfaces have been proposed and investigated for prospective applications in bio-sensing and temperature sensors [15–18]. Furthermore, applications in laser and nano-laser systems and as ultrafast light sources have been also considered [19–23].

The theoretical treatment of surface enhanced fluorescence (SEF) has a long history. Analytical models from the viewpoint of classical electromagnetic theory have been developed for semi-infinite metal interfaces [24, 25], spherical and spheroidal metal particles [26–29], dimers [30, 31] and embedded concentric spheres [32–34]. Studies based on the quantum electrodynamics approach have been also proposed and carried out in details [35–38]. Within the applicability of the linear response theory (weak coupling) the classical and quantum approaches have been shown to lead to similar results, with emission rates governed by competing radiative and non-radiative processes. It must be pointed out that the vast majority of presented theories consider the problem of a single dipole emitter with fixed dipole moment in the presence of metal structures. The general case in which the molecular dipole moment is self-consistently obtained through the molecular polarization and the local electromagnetic field consisting of the incident laser radiation (pump) and scattered field due to the nanostructures, is not well studied. To address this problem, in this paper we present, the first completely self-consistent model of core–shell nanoparticles in the present of point dipole emitters from the point view of classical electromagnetism.
The organization of the paper follows. In section 2, the classical electromagnetic theory of fluorescence emission enhancements of a single molecule placed next to a three-dimensional core–shell particle is presented. First, an approximate model in which the nanoparticle and emitter are treated as simple electric point dipoles is developed. The model properly predicts the fluorescence enhancement for emitters at sufficiently large distances from the nanoparticle. A complete, self-consistent multipole theory is then developed under the quasi-statics approximation. In section 3, the fluorescence emission enhancement is analyzed in term of the molecular-particle separation distance, filling fraction of the nanoparticle core–shell configuration and frequency of illumination/emission. Comparison between the theory and published experimental data is then provided showing excellent correspondence. The conclusions are finally drawn in section 4.

2. Theoretical description

The system under consideration is presented in figure 1 and consists of a single molecular emitter situated at a distance $R$ along the $+z$ axis from a core–shell metal-dielectric nanoparticle. The nanoparticle is positioned at the center of the coordinate system and has inner core radius $b$ and outer shell radius $a$. In the model the emitter-nanoparticle system is driven by an external arbitrary polarized time harmonic electric field $\mathbf{E}(t) = E_0 e^{-i\omega t}$ and the molecular emitter is modeled as a point dipole with dipole moment $\mathbf{p}_d(t) = \mathbf{p}_d(\omega) e^{-i\omega t}$. Neglecting the Stokes shift and restricting our analysis to the linear response theory we have $\mathbf{p}_d(\omega) = \alpha_d(\omega) \mathbf{E}_d(\omega)$, where $\mathbf{E}_d$ is the electric field amplitude at the position of the dipole excluding the dipole self-field. The molecular polarizability is represented through the Lorentz model and is given as $\alpha_d(\omega) = 4\pi\varepsilon_0 a_d^3 \mathcal{L}_d$, where $\mathcal{L}_d = \omega_d^2/(\omega_0^2 - \omega^2 - i\omega\gamma_d)$ is the molecular line shape function, $\omega_0$ is the fluorescence frequency, $\omega_{\gamma,d}$ is the damping frequency, and $a_d = (e^2/4\pi\varepsilon_0 m\omega_0^2)^{1/3} = (d^2/2\pi\varepsilon_0 \hbar \omega_0)^{1/3}$ is the effective molecular dipole radius related to the transition dipole moment $d = |2|\mu_0|\mathbf{E}_0|$. Provided the distance $R$ between nanoparticle and emitter satisfies the condition $\omega R \ll c$, the problem can be treated in the quasi-static approximation involving the corresponding quasi-static electrical potentials and fields. In what follows, the SEF response is first considered under the effective medium dipole-dipole approximation and then a closed form, self-consistent multipole theory is presented.

2.1. Coupled dipole-dipole approximation

If the distance between emitter and nanoparticle is sufficiently large $R \gg a$, we can consider the problem as a simple dipole-dipole system coupled to the incident laser radiation. Under this condition the nanoparticle is modeled as a point dipole situated at the center of the coordinate system (see figure 1(b)) having a dipole moment $\mathbf{p}_p(\omega) = \alpha_p(\omega) \mathbf{E}_p(\omega)$, with $\mathbf{E}_p$ being the electric field amplitude at the nanoparticle position excluding the particle self-field. The particle polarizability is $\alpha_p(\omega) = 4\pi\varepsilon_0 a_0^3 \mathcal{L}_p$, where $\mathcal{L}_p = (\varepsilon_\infty - \varepsilon_0)/(\varepsilon_\infty + 2\varepsilon_0)$ is the dipolar polarizability line shape function represented through the dipolar effective permittivity of the core–shell nanostructure [39, 40] given as

$$\varepsilon_\infty = \varepsilon_2 + \varepsilon_1 - 2p(\varepsilon_2 - \varepsilon_1)/2\varepsilon_2 + \varepsilon_1 + p(\varepsilon_2 - \varepsilon_1),$$

where $p = (b/a)^3$ is the core volume filling fraction. The electric fields at the positions of the particle and molecular emitter are then given by the coupled equations

$$\mathbf{E}_d = \mathbf{E}_0 + \frac{\alpha_p}{4\pi\varepsilon_0 R^3} (3(\hat{z} \cdot \mathbf{E}_p)\hat{z} - \mathbf{E}_p),$$

$$\mathbf{E}_p = \mathbf{E}_0 + \frac{\alpha_d}{4\pi\varepsilon_0 R^3} (3(\hat{z} \cdot \mathbf{E}_d)\hat{z} - \mathbf{E}_d).$$

Since the radiated power by the molecule is $P_d = \mu_0 \omega^4 |\alpha_d \mathbf{E}_0|^2/(12\pi c)$ the fluorescence emission...
The multipole coefficients depend on the incident electric field \( \vec{E}_0 = (E_{0,x}, E_{0,y}, E_{0,z}) \), distance between emitter and particle surface and the emitter dipole moment \( \vec{p}_d = (p_x, p_y, p_z) \) as

\[
I_{lm}^0 = \delta_{l,i} \left( \frac{\delta_{m,1} - \delta_{m,-1}}{2Y_{11}} \right) \\
+ E_{0,1} \left( \frac{\delta_{m,1} + \delta_{m,-1}}{2Y_{11}} - \frac{E_{0,0}}{Y_{0,1}} \right) \\
I_{lm}^d = -\frac{1}{4\pi \epsilon_0 R^{l+2}} \left( p_x \frac{\delta_{m,1} - \delta_{m,-1}}{2Y_{11}} + \frac{p_y}{2iY_{11}} \delta_{m,0} + p_z (l + 1) \delta_{m,0} \frac{Y_{0,1}}{Y_{0,0}} \right),
\]

where \( Y_{1,1} = \sqrt{(2l + 1)/4\pi} \), \( Y_{1,0} = Y_{1,0}/\sqrt{l(l + 1)} \) and \( \delta_{ji} \) is the Kronecker symbol. Substituting the potentials equation (5) in equation (4) and enforcing the boundary conditions at the nanoparticle surfaces closed form expressions for the remaining expansion coefficients can be obtained

\[
A_{lm} = \frac{\epsilon_2(2l + 1) (I_{lm}^0 + I_{lm}^d + D_{lm})}{\epsilon_2 + l(\epsilon_2 + \epsilon_1) + l(\epsilon_2 - \epsilon_1) p_l} \\
B_{lm} = \frac{(\epsilon_2 + l(\epsilon_2 + \epsilon_1)) (I_{lm}^0 + I_{lm}^d + D_{lm})}{\epsilon_2 + l(\epsilon_2 + \epsilon_1) + l(\epsilon_2 - \epsilon_1) p_l} \\
C_{lm} = p_l \frac{l(\epsilon_2 - \epsilon_1) (I_{lm}^0 + I_{lm}^d + D_{lm})}{\epsilon_2 + l(\epsilon_2 + \epsilon_1) + l(\epsilon_2 - \epsilon_1) p_l} \\
D_{lm} = -L_{pl} (I_{lm}^0 + I_{lm}^d),
\]

where \( p_l = p^{2l+1}/3 \), \( L_{pl} = (\tilde{\epsilon}_l - \epsilon_0)/(l\tilde{\epsilon}_l + (l + 1)\epsilon_0) \) is the polarizability line-shape function of the \( l \)-th multipole. The line-shape function depends on the mode specific effective permittivities [35]

\[
\tilde{\epsilon}_l = \frac{\epsilon_2 + l(\epsilon_2 + \epsilon_1) - l(\epsilon_2 - \epsilon_1) p_l}{\epsilon_2 + l(\epsilon_2 + \epsilon_1) + l(\epsilon_2 - \epsilon_1) p_l}.
\]

Note that equation (8) coincides with equation (1) for the dipolar response \( \tilde{\epsilon}_l = \epsilon_2 \) (\( l = 1 \)) as it should. To obtain self-consistently the induced dipole moment \( \vec{p}_l \) (determining the \( I_{lm}^d \) coefficients) one needs to find the electric field \( \vec{E}_d = -\nabla \phi_{nl} (\vec{r}) \) at the position of the dipole (excluding the emitter self-field) and relate it to the dipole moment using the linear response relationship \( \vec{p}_l = \alpha_d(\omega) \vec{E}_d \). A straightforward calculation is performed in appendix B with the components of the dipole moment given as

\[
\phi_0 (\vec{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} I_{lm}^0 r^l Y^m_l (\theta, \phi) \\
\phi_d (\vec{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} I_{lm}^d r^l Y^m_l (\theta, \phi) \\
\phi_{nl} (\vec{r}) = \phi_0 (\vec{r}) + \phi_d (\vec{r}) + \sum_{l=0}^{\infty} \sum_{m=-l}^{l} D_{lm} a^{2l+1} \frac{r^{2l+1}}{r^{l+1}} Y^m_l (\theta, \phi).
\]
\[ \begin{align*}
P_x &= \alpha_d E_{d,x} = \alpha_d \left( \frac{1 - \mu_p L_p}{1 - \mu_p \mu_d L_p \lambda_{d}^3} \right) E_{0,x}, \\
P_y &= \alpha_d E_{d,y} = \alpha_d \left( \frac{1 - \mu_p L_p}{1 - \mu_p \mu_d L_p \lambda_{d}^3} \right) E_{0,y}, \\
P_z &= \alpha_d E_{d,z} = \alpha_d \left( \frac{1 + 2 \mu_p L_p}{1 - 4 \mu_p \mu_d L_p \lambda_{d}^3 \lambda_{z}^3} \right) E_{0,z}
\end{align*} \]

where

\[ s_1 = \frac{1}{4} \sum_{l=1}^{\infty} \frac{L_p(l+1)}{L_p} \left( \frac{a}{R} \right)^{2l-2}, \]

\[ s_2 = \frac{1}{2} \sum_{l=1}^{\infty} \frac{L_p(l+1)}{L_p} \left( \frac{a}{R} \right)^{2l-2}. \]

Using equation (9) and averaging over the incident field polarizations the SEF factor follows as

\[ F = F_1 + F_1 = \frac{2}{3} \left( \frac{1 - \mu_p L_p}{1 - \mu_p \mu_d L_p \lambda_{d}^3} \right) \left( \frac{1 + 2 \mu_p L_p}{1 - 4 \mu_p \mu_d L_p \lambda_{d}^3 \lambda_{z}^3} \right), \]

where the contributions due to the external electric field components that are parallel (\( F_1 \)) and normal (\( F_1 \)) to the nanoparticle surface are identified separately. Since for \( R \gg a \) the two sums given in equation (10) approach unity, in this limit the fluorescence enhancement factor asymptotically approaches the dipole-dipole result equation (3) as it should. For \( R \ll a \), the factors \( s_1 \) and \( s_2 \) are no longer unity and describe the influence of higher order SP multipoles on the fluorescence emission. It must be noted that equation (11) also holds for particles consisting of multiple shells provided the effective permittivities \( \varepsilon_i \) are modified according to [40]. Furthermore to the best of my knowledge equation (11) provides the first exact self-consistent multi-mode treatment of molecular fluorescent enhancement due to core–shell nanostructures in the quasi-static case.

3. Results and discussion

In this section the fluorescence enhancement is studied for nanoparticles immersed in a rhodamine B (RhB) dye solution. This particular dye has been investigated extensively in the literature and its emission properties are readily obtained. In what follows the line shape function of the emitter is represented through the Lorentzian model with \( \omega_0 = 2.13 \text{ eV} \) and \( \omega_{v,d} = 0.16 \text{ eV} \) [42], while the metal particle permittivity \( \varepsilon_m \) is taken from Johnson and Christy [43]. In all calculations the laser excitation frequency is assumed to coincide with the emitter resonance frequency \( \omega = \omega_0 \), thus neglecting the Stokes shift which for RhB is small (\( \Delta \omega < 90 \text{ meV} \)). Under this condition the emitter line shape function is reduced to \( \mathcal{E}_d = i \omega_0 / \omega_{v,d} \) and for convenience the rendering \( \mu_d \mathcal{E}_d = i \left( \tilde{a}_d / R \right)^3 \) will be used with \( \tilde{a}_d = a_d (\omega_0 / \omega_{v,d})^{1/3} \) being the reduced molecular dipolar radius.

3.1. Single nanoparticle

In this section the SEF due to a single metal nanoparticle without a shell is studied. Since in this case we have \( \varepsilon_i = \varepsilon_2 = \varepsilon_1 = \varepsilon_m \), the sums in equation (10) can be solved explicitly and represented through the incomplete beta function as

\[ s_i = \frac{q ((2e + 1) + s) B(q, -2) - e B(q, -1)}{(e + 1) (1 - s)^s}, \]

\[ s_i = \frac{s_i}{2} + q B(q, -2) \frac{1}{2s}, \]

where \( e = \varepsilon_m / \varepsilon_0 \), \( s = (a / R)^3 \), and \( q = (e + 2) / (e + 1) \). To demonstrate the theory, the fluorescence enhancement of a single RhB molecule as function of the distance \( h = R - a \) to the nanoparticle surface is shown in figure 2. First we observe that the enhancement is rather weak having a maximal value of \( F_{\text{max}} = 3.13 \) for \( h = 0.8 \text{ nm} \). Such weak response is easy to explain by inspecting the emitter and particle dipolar polarization line-shape functions shown as an insert. For optimal enhancement the two line shapes must coincide. However, for the RhB molecule there is a considerable frequency mismatch between the two with the fluorescence radiation centered at \( \omega_0 = 2.13 \text{ eV} \) while the metal particle response manifests a resonant behavior at the corresponding surface plasmon (SP) frequency \( \omega_\text{sp} = 3.5 \text{ eV} \). In figure 2, the dipole-dipole theory according equation (3) is also included. As expected, this approximate result coincides with the exact only at sufficiently large separation distances and does not capture the effect of radiation quenching into higher order non-radiative SP multipoles at short distances. To better understand the behavior in close proximity to the particle surface, equation (12) can be expanded in terms of \( h / a < 1 \). In this limit the multipole correction factors can be simplified as

\[ \lim_{\hbar \to 0} s_i = \frac{(e + 2)}{(e + 1)} \left( \frac{a}{2h} \right)^3, \]

\[ \lim_{\hbar \to 0} s_j = \frac{s_j}{2}, \]

and the fluorescence enhancement has a simple asymptotic form

\[ \lim_{\hbar \to 0} F = \frac{3}{4} \left( \frac{2h}{a_d} \right)^6 \left[ 1 + \frac{1}{2} \left( \frac{8 + |e|^2}{|e|^2 + 2|e|^2} \right) \right]. \]

The above result shows explicitly that the emission suppression (quenching) is proportional to the sixth power of the emitter–particle distance and thus is only present at very short distances of the order of 1 nm. Finally, it is important to note that the fluorescence enhancement is driven predominantly by the
component of the electric field \( (E_z) \) that is perpendicular to the nanoparticle surface. This is expected since it is this field component that couples to the dominant dipolar SP mode.

### 3.2. Nanoparticles with a single shell

As discussed in the previous section optimal fluorescence enhancement can be achieved only if the metal nanoparticle SP resonance frequency coincides with the emitter excitation/fluorescence frequency. This requirement is difficult to satisfy for metal nanoparticles without a shell even if we chose different metals. Hence, one must instead consider particle with shell configurations; a metal-dielectric nanoparticle (MDNP) (the shell is dielectric) and a dielectric-metal nanoparticle (DMNP) (the shell is metallic). Setting the excitation frequency to coincide with that of the RhB emitter fixes the metal permittivity at \( \epsilon_m(\omega_0) = \epsilon'_m + i\epsilon''_m = -14.882 + 0.386i \) [43]. The effective permittivity of the system is then given by equation (1), with \( \epsilon_1 = \epsilon_m \) and \( \epsilon_2 = \epsilon_d \) for the MDNP and \( \epsilon_2 = \epsilon_m \) and \( \epsilon_1 = \epsilon_d \) for the DMNP. The nanoparticle dipolar polarizability line-shape functions \( \zeta_p \) of the two shell configurations can readily be calculated and is shown in figure 3. There is a clear resonance behavior provided the SP resonance condition \( \text{Re}(\epsilon(\omega_0, p)) = -2\epsilon_d \) is satisfied, which for small metal losses \( \epsilon''_m/|\epsilon'_m| \ll 1 \) can be solved for the optimal core filling fraction as

\[
P_{opt} = \frac{1}{2} \text{Re} \left( \frac{(\epsilon_2 + 2\epsilon_d)(2\epsilon_2 + \epsilon_d)}{(\epsilon_2 - \epsilon_d)(\epsilon_2 - \epsilon_1)} \right),
\]

Since \( 0 \leq P_{opt} \leq 1 \), this condition can be satisfied provided \( \epsilon_0 < \frac{1}{2}\epsilon_m |< \epsilon_d \) for the MDNP, and \( |\epsilon_m| > \max\left(\frac{1}{2}\epsilon_d, 2\epsilon_0\right) \) for the DMNP.

The SEF factor at the optimal core filling fraction equation (15) calculated as function of the distance between the molecule and particle surface is shown in figure 4. For the DMNP and MDNP configurations the sums in equation (10) no longer have solutions in simple functions and are obtained numerically. For each configuration we also consider three dielectric cases. The DMNP configuration provides higher fluorescence enhancement and increasing fluorescence with decreasing dielectric constant of the core. The opposite is found for the MDNP configuration. For both systems the observed trends are in agreement with figure 3 and the fluorescence enhancement is found to be substantially higher compared to the single metal particle studied in the previous section. If the dielectric permittivity is further increased so that \( \epsilon_d \rightarrow -\epsilon_m \) a cross over will be observed with the MDNP configuration now dominating. This is easy to check by solving equation (11) in the far zone, always from the quenching region, in which case for small metal losses one gets

\[
F_{DMNP} \approx 1 + \frac{9\epsilon^2_0}{2} \left( \frac{\epsilon_0 \epsilon'_m (\epsilon'_m - \epsilon_d)(2\epsilon'_m + \epsilon_d)}{\epsilon'_m (\epsilon'_m)^2 - \epsilon_d \epsilon_0 (\epsilon_2 + 2\epsilon_d)} \right)^2, \quad (\epsilon_d < -2\epsilon'_m)
\]

\[
F_{MDNP} \approx 1 + \frac{9\epsilon^2_0}{2} \left( \frac{\epsilon_0 (\epsilon'_m - \epsilon_d)(\epsilon'_m + 2\epsilon_d)}{\epsilon'_m (\epsilon'_m + \epsilon_0 (\epsilon_2 - 2\epsilon'_d}} \right)^2, \quad \left( \epsilon_d > -\frac{1}{2}\epsilon'_m \right).
\]

(16)
Inspection immediately leads to the cross over condition \( \epsilon_d = -\epsilon_{m} \) with the two SEF factors being identical. If the permittivity is further increased so that \( \epsilon_d \gg -\epsilon_{m} \), a saturation is observed with \( F_{\text{MDNP}} \rightarrow 1 + 18|\epsilon_d/\epsilon_m|^2 \). It must be noted that for the RhB emitter the cross over and saturation cannot be practically observed due to the absence of dielectric materials with such a large permittivity, hence the DMNP system represents the optimal configuration.

To complete the theoretical discussion we consider a general emitter with varying emission frequency \( \omega_0 \) equal to that of the excitation laser radiation. The results are presented in figure 5. All calculations have been performed at the corresponding optimal core filling fractions and separation distances. A strong frequency dependence of the maximal SEF is observed. The DMNP configuration presents stronger effect for low and moderate frequencies \( \omega_0 < 2 \text{ eV} \), while the MDNP is applicable only within a narrow frequency range \( 2 \text{ eV} < \omega_0 < 3.5 \text{ eV} \) in accordance with the applicability condition related to equation (15). The artificial cut-off for \( \omega_0 < 0.64 \text{ eV} \) is due to the absence of experimental data for the silver permittivity which is sourced from Johnson and Christy [43]. It must be noted that the observed decrease of the SEF factors for \( \omega_0 > 2 \text{ eV} \) is due to increased losses associated with interband transitions in the metal. Within this region both configurations provide similar SEF factors. Overall, the two core-shell configurations over performs the single metal nanoparticle case for all emitter frequencies. While the optimal core filling fraction, see figures 5(b) and (d), spans the entire possible range \( 0 < \rho_{\text{opt}} < 1 \), the optimal emitter-particle separation distance \( h_{\text{opt}} \) is found to be weakly dependent on the emission frequency and dielectric permittivity and is or the order of 1 nm. This can be verified by considering the short distance asymptotic equation (13), which under the substitution \( \epsilon \rightarrow \epsilon_2/\epsilon_0 \) holds even for the core–shell nanoparticles. Taking advantage of the small parameter \( h/a \ll 1 \) and working with equation (11) we obtain an approximated result for the optimal separation distance \( h_{\text{opt}} \approx \hat{a}_d \left| \left( \epsilon_2 - \epsilon_0 \right)/(\epsilon_2 + \epsilon_0) \right|^{1/3} \approx \hat{a}_d \). The maximal SEF can also be estimated and is found to follow closely the particle line shape-function at resonance \( F_{\text{max}} \approx \frac{3}{2} |\mathcal{L}_p(\omega_0, \rho_{\text{opt}})|^2 \). Typical molecular emitters have sizes ranging from 0.5 nm up to 2 nm (the PhB molecule has size 1.6 nm by 1.1 nm). It so happens that these molecular sizes nicely fall within the range where the SEF is maximal. Hence, surface immobilization techniques are preferable with optimization pursued not by changing the distance \( h \) but through varying the thickness of the shell \( d = a - b \), which is in fact what has been predominantly pursued experimentally. Finally, in figures 5(c)–(f) we compare the SEF factor calculated self-consistently and based on the traditional non self-consistent approach \((s_x = s_y = 0)\). For all cases and parameters used the self-consistent SEF factor is found to be weaker. This is expected due to the self-coupling of the dipolar radiation which tends to decrease the effective dipole moment according to equation (9).

### 3.3. Comparison to experiment - single shell

Before comparing the developed self-consistent SEF model to published experimental data it is important to identify the applicability constrains of the theory. As stated in the beginning of the paper, the developed model is based on the quasi-static approximation and the theory can only be applied for particle-emitter separation distances \( h < c/\omega \). For the rhodamine B
molecule this restriction translates to $h < 92$ nm, with the presented results (see figures (2)–(4)) being well within the applicability of the model. Furthermore, at higher separation distances where retardation effects start to dominate, the SEF factor is expected to be small in general due to the $\frac{1}{h^2}$ dependence of the power radiated by the dipole that is coupled to the particle. However, it is still worth considering the extension of the current work to include retardation. This can be achieved based on an extension of the quasi-effective medium theory \[40\] for 3D multi-layer magneto-dielectric systems, with the effective permittivity equation \[8\] now written as function of the wavevector. Additionally, when the metal particle size or shell thickness become of the order $2a \sim v_F/\omega$, where $v_F$ is the Fermi velocity, nonlocal elects will also be expected \[44-47\]. For silver and the particle size $2a = 30$ nm considered in this paper, we have $2a\omega/v_F \gg 1$ and nonlocal effects are expected to be weak. However, for smaller particles and thinner shells with $p < (v_F/2a\omega)^3$ (for MDNP) and $p > (1 - v_F/2a\omega)^3$ (for DMNP) non-local effects must be taken into account.

Within the constraints identified above next we compared the theory to available experimental data related to SEF due to core–shell nanoparticles. A review article of the current state of experimental research in the field can be found due to Yoon J et al \[48\]. The fluorescence enhancement for gold and silver-core silica-shell nanoparticles were studies for FAM (carboxyfluorescein) and CYe (cascade yellow) emitters at various spacer distances \[49\]. Optimal enhancement factor of $F = 6.8$ was measured for the FAM-labeled gold nanoparticles and $F = 12.5$ was recorded for Cye-labeled gold nanoparticles. Studies based on 120 nm gold-core silica spacer conjugated...
with mesoporous silica layer was carried for EiTC, FiTC and Rh B emitters in [50], demonstrating SEF factors ranging from 2 to 12 with optimal effects reached for 8 nm spacer thickness. Similar range of fluorescence enhancements for Ag-core silica-spacer nanoballs and nanobubbles have been demonstrated for Rh800 in [51]. The work by D Gontero et al [52] is probably the most complete study of the spacer thickness effect on the SEF. The authors synthesized 41.5 nm gold-core nanoparticles with silica spacer layers of 2 nm, 6–7 nm, 14 nm, 20 nm and 23–25 nm thicknesses. The fluorescence signal for RhB emitters linked to the silica surface were measured and compared to core-less silica shell nanoparticle. Due to the extensive data provided this particular study have been chosen to serve as a benchmark for testing the theory. A comparison between theory and experiment is shown in figure (6). In the calculations the PhB emitter were fixed at a distance of $h = 0.35$ nm (corresponding to half the molecule size) and the permittivities of gold $\varepsilon_4 = \varepsilon_m = -5.19 + 1.45i$, silica $\varepsilon_2 = 2.42$ and ethanol $\varepsilon_0 = 1.86$ at the excitation wavelength of 543 nm were sourced from the refractive index bank [53]. A published data for the permittivity of the gold-salt (sodium dicyanoaurate) of the reference ‘core-less’ system was not found but was kept as a parameter and varied within a reasonable range from 1 up to 3. The SEF factor was found to be weakly dependent on this parameter (see shaded region in figure (6)). Overall the theoretical predictions are consistent with the experimental data with the SEF factor initially increasing rapidly with the spacer thickness reaching a maximum value of 18.5 at 3 nm and then gradually decreasing. It must be noted that the silica spacer is not optimal for the PhB emitter. For the MDNP system optimal enhancement can be obtained for $p = p_{opt}$ given by equation (15) which requires that $\varepsilon_2 > \frac{1}{2}[\varepsilon_m] = 2.7$, with the permittivity of silica being substantially lower compared to this minimal requirement. To achieve higher SEF factors, new high refractive index dielectric coatings should be pursued by the SEF research community.

4. Conclusions

This paper presents a new self-constant analytical theory of molecular fluorescence enhancement due to metal-dielectric nanoparticles. Such self-consistent treatment of the problem has been so far lacking with the majority of already developed theories fixing the dipole moment of the emitter and thus do not consider the effect of back action of the particle on the emitter polarizability. The theory provides explicit insights related to the surface plasmon (SP) mechanism behind the phenomenon. Specifically, it shows that fluorescence due to emitters sufficiently far from the nanoparticle can be described as a simple dipole-dipole coupled system while at short distances emission is
quenched as result of coupling to higher-order non-radiative SP multipoles. The general condition for matching the emitter and nanoparticle line shape functions is derived leading to constrains to be imposed on the shell thickness. The core–shell nanoparticle configurations that provide optimal surface enhanced fluorescence (SEF) are identified for a rhodamine B (RhB) as well as for general emitter with unrestricted fluorescent frequency. Finally the theory is compared to published experimental data showing excellent correspondence. The presented self-consistent model can serve as a useful tool for fast theoretical estimates of the SEF enhancements in core–shell configurations and thus can help guide future experimental studies related to fluorescence spectroscopy and bio-sensing.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Appendix A: Potentials and spherical harmonics

To obtain a close form solution of equation (4) it is convenient to represent the incident and dipole potentials in spherical harmonics. For the incident potential it is straightforward to show by inspection that

\[ \phi_\text{inc}(\vec{r}) = -\vec{r} \cdot \vec{E}_\text{inc} = -r \sin(\theta) \times (E_{0_x,0} \cos(\phi) + E_{0_y,0} \sin(\phi)) \]

where the explicit form of the expansion coefficients \( p^\text{inc}_l(\theta, \phi) \) is given by equation (6). The dipole potential of the emitter has the traditional form

\[ \phi_\text{em}(\vec{r}) = \frac{\vec{p}_\text{em} \cdot (\vec{r} - \vec{R})}{4\pi \varepsilon_0 |\vec{r} - \vec{R}|^3} \]

\[ = \frac{\frac{p_x \cos(\phi) + p_y \sin(\phi)}{r \sin(\theta)} + \frac{r \cos(\theta) - \vec{R} \cos(\theta)}{4\pi \varepsilon_0 (r^2 - 2rR \cos(\theta) + R^2)^{3/2}}} \]

(A2)

where \( \vec{p}_\text{em} = (p_x, p_y) \) is the dipole moment and \( \vec{R} = R\hat{z} \). For \( r < R \) we implement the series expansion

\[ \frac{1}{\sqrt{r^2 + R^2 - 2rR \cos(\theta)}} \equiv \sum_{j=0}^{\infty} \frac{r^j}{R^{j+1}} p^\text{em}_{j}(\cos(\theta)), \]

(A3)
and write
\[
\frac{r \cos(\theta) - R}{(r^2 - 2rr \cos(\theta) + R^2)^{3/2}} = \frac{\partial}{\partial R} \left( \frac{1}{\sqrt{r^2 + R^2 - 2rr \cos(\theta)}} \right) = -\sum_{l=0}^{\infty} \frac{(l + 1)r^l}{R^{l+2}} P_l^0(\cos(\theta))
\]
\[
\frac{r \sin(\theta)}{(r^2 - 2rr \cos(\theta) + R^2)^{3/2}} = \frac{1}{R} \frac{\partial}{\partial \theta} \left( \frac{1}{\sqrt{r^2 + R^2 - 2rr \cos(\theta)}} \right) = -\sum_{l=0}^{\infty} \frac{r^l}{R^{l+2}} P_l^0(\cos(\theta)) > \quad (A4)
\]
Substituting equation (A4) in equation (A2) the dipole potential follows as
\[
\phi_d(\vec{r}) = -\frac{1}{4\pi\varepsilon_0} \sum_{l=0}^{\infty} \frac{r^l}{R^{l+2}} \left( (p_x \cos(\phi) + p_y \sin(\phi)) P_l^0(\cos(\theta)) + p_z (l + 1) P_l^0(\cos(\theta)) \right), \quad (A5)
\]
Recasting equation (A5) in spherical harmonics we arrive at
\[
\phi_d(\vec{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} I_{lm}^d r^l Y_l^m(\theta, \phi), \quad (A6)
\]

**Appendix B: Self-consistent field equations**

The electric field at the position of the molecular emitter (excluding the emitter self-field) is obtained from the corresponding potential
\[
\tilde{\phi}(\vec{r}) = \phi_{\text{em}}(\vec{r}) - \phi_d(\vec{r}) = \phi_d(\vec{r}) + \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{D_{lm} a^{l+1}}{r^{l+1}} Y_l^m(\theta, \phi). \quad (B1)
\]
Substituting the expansion coefficients equation (6) we obtain
\[
\tilde{\phi}(\vec{r}) = \phi_d(\vec{r}) - \sum_{l=1}^{\infty} \frac{L_{l,ai} a^{l+1}}{r^{l+1}} \left( (a_{1x} \cos(\phi) + a_{1y} \sin(\phi)) P_l^0(\cos(\theta)) \right) \nonumber \\
- (l + 1) a_{1z} P_l^0(\cos(\theta))), \quad (B2)
\]
where
\[
a_{1x} = \delta_{1,1} E_{0,x} - \frac{p_x}{4\pi\varepsilon_0 R^{l+2}}, \nonumber \\
a_{1y} = \delta_{1,1} E_{0,y} - \frac{p_y}{4\pi\varepsilon_0 R^{l+2}}, \nonumber \\
a_{1z} = \frac{1}{2} \delta_{1,1} E_{0,z} + \frac{p_z}{4\pi\varepsilon_0 R^{l+2}}. \quad (B3)
\]
The electric field then follows \( \vec{E} = -\nabla \tilde{\phi} = \vec{E}_0 + \vec{E}_r + \vec{E}_\theta + \vec{E}_\phi \), with the field components given as
\[
E_r = \sum_{l=1}^{\infty} \frac{(l + 1) L_{l,ai} a^{l+1}}{r^{l+2}} ((l + 1) a_{1z} P_l^0(\cos(\theta)) - (a_{1x} \cos(\phi) + a_{1y} \sin(\phi)) P_l^0(\cos(\theta)) \right) \nonumber \\
E_\theta = \sum_{l=1}^{\infty} \frac{L_{l,ai} a^{l+1}}{r^{l+2}} \left( (a_{1x} \cos(\phi) + a_{1y} \sin(\phi)) \frac{\partial P_l^0(\cos(\theta))}{\partial \theta} - (l + 1) a_{1z} \frac{\partial P_l^0(\cos(\theta))}{\partial \theta} \right), \quad (B4)
\]
\[
E_\phi = \sum_{l=1}^{\infty} \frac{L_{l,ai} a^{l+1}}{r^{l+2}} (a_{1y} \cos(\phi) - a_{1x} \sin(\phi)) \frac{P_l^0(\cos(\theta))}{\sin(\theta)}
\]
Using the asymptotic forms of the associated Legendre polynomials,

\[ \lim_{\theta \to 0} P_l^m(\cos(\theta)) = 1, \quad \lim_{\theta \to 0} \frac{\partial P_l^m(\cos(\theta))}{\partial \theta} = 0 \]

\[ \lim_{\theta \to 0} \frac{P_l^m(\cos(\theta))}{\sin(\theta)} = \lim_{\theta \to 0} \frac{\partial P_l^m(\cos(\theta))}{\partial \theta} = -\frac{l(l+1)}{2}, \]  

we can recast the electric field components equation (B4) as

\[ E_r = \sum_{l=1}^{\infty} \frac{(l+1)\mathcal{L}_{p,l}a^{l+1}}{\mathcal{R}^{l+2}} a_{l,z} \]

\[ E_\theta = -\sum_{l=1}^{\infty} \frac{l(l+1)\mathcal{L}_{p,l}a^{l+1}}{\mathcal{R}^{l+2}} (a_{l,x} \cos(\phi) + a_{l,y} \sin(\phi))' \]

\[ E_\phi = \sum_{l=1}^{\infty} \frac{l(l+1)\mathcal{L}_{p,l}a^{l+1}}{\mathcal{R}^{l+2}} (a_{l,x} \sin(\phi) - a_{l,y} \cos(\phi)) \]

Reversing to Cartesian coordinates we obtain

\[ E_d = E_\theta + E_r \hat{z} + (E_\theta \cos(\phi) - E_r \sin(\phi)) \hat{x} + (E_\theta \sin(\phi) + E_r \cos(\phi)) \hat{y} \]

\[ = E_\theta - \sum_{l=1}^{\infty} \frac{l(l+1)\mathcal{L}_{p,l}a^{l+1}}{\mathcal{R}^{l+2}} \left( \frac{a_{l,x} \hat{x} + a_{l,y} \hat{y}}{2} - \frac{l+1}{l} a_{l,z} \hat{z} \right). \]  

(B7)

Finally, substituting equation (B3) in equation (B7) and rearranging we end up with the governing equation of the emitter’s self-consistent dipole moment

\[ \vec{P}_d = \alpha_d \vec{E}_d = \alpha_d \left( 1 - \mu_p \mathcal{L}_{p} \right) E_{0,x} + \frac{\mu_p \mathcal{L}_{p} s_1}{4\pi \varepsilon_0 R^3} \hat{x} \]

\[ + \alpha_d \left( 1 - \mu_p \mathcal{L}_{p} \right) E_{0,y} + \frac{\mu_p \mathcal{L}_{p} s_1}{4\pi \varepsilon_0 R^3} \hat{y} \]

\[ + \alpha_d \left( 1 + 2\mu_p \mathcal{L}_{p} \right) E_{0,z} + \frac{\mu_p \mathcal{L}_{p} s_1}{\pi \varepsilon_0 R^3} \hat{z}, \]  

(B8)

where \( \mu_p = (a/R)^3 \), and the modal functions \( s_1 \) and \( s_2 \) are given by equation (10). From equation (B.9) the components of the self-consistent dipole moment are easily obtained and are given in equation (9).

**ORCID iDs**

Dentcho A Genov \( \text{https://orcid.org/0000-0002-6581-1651} \)

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