

# Modal Approach to the Theory of Energy Transfer Mediated by a Metallic Nanosphere

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**Abstract.** Theoretically, the presence of a metallic nanoparticle enhances the intermolecular energy transfer. We calculate this enhancement factor with a modal approach pertaining analytical results in the case of a nanosphere. We calculate the Green's function of the system relying on the spectral properties of the electrostatic operator, fully known for spherical geometry. In contrast to other treatments, the present calculations are straightforward for any molecular orientation giving modal information about the response of the system. Numerical calculations and further discussions are also provided.

**Key-words:** Plasmonics; boundary integral equation method; electrostatic operator; finite element method; Förster resonance energy transfer.

## 1. Introduction

Energy transfer, especially the resonance energy transfer (RET) between a donor molecule and a near by acceptor molecule, plays an important role in many aspects of photophysical and photochemical processes like photosynthesis and light harvesting [1,2], photovoltaics [3], biomolecular structure and fluorescence probing [1,4-6], biosensing [7]. The main transfer mechanism of these processes obviously depends on the distance between the donors and the acceptors. Thus, when the distance is less than 2 nm the mechanism depends on the molecular orbital overlap hence, the treatment is quantum mechanical [2, 8]. Moreover, within this range of distances the energy transfer enters the competition with the electron transfer process. On the other hand, when distances are between 2 and 10 nm the electrostatic dipole-dipole interaction enables a nonradiative energy transfer by the Förster resonance energy transfer (FRET) [2, 9]. Alternatively, the radiative mechanism plays a role when the distances between donors and acceptors are comparable or greater than the wavelength of the incoming radiation [10].

FRET is a weak process because it is inverse proportional to the sixth power of the separation distance. Hence, an enhancement is often desired in various applications like in the long-range energy transfer between fluorescent centers [11]. The enhancement is obtained by plasmonic effect through the coupling between light and the collective excitations of the free electrons in metals. Plasmonic effects of surface plasmon polaritons (occurring on the interfaces between metals and dielectrics) and localized surface plasmons (around metallic nanoparticles) are shown by strong fields and field confinements below diffraction limit which can be utilized in sensing and biosensing applications [12]. Strong fields lead to strong coupling of light with atomic and atom-like systems [13-15].

FRET enhancement has been studied in planar metallic structures [16] and in variously shaped nanoparticles: spheres and spheroids [17], nanodiscs [18] and nanorods [19]. When it is possible analytical treatments of a physical process can provide valuable insights of the process. Analytical approaches of plasmonic enhancement of FRET were used in [17] for spheres and spheroids, for shelled spheres in [20] and for spheroids in [21]. For example Shishodia et al. used the Bergman's approach [22], which has the disadvantage of operators defined in the whole space [20].

In our work we use a method closely related [23-26]. It is also an operator method, but the operators are defined on surfaces rather than the whole space. Our method allows the calculation of a Green's function that permits easy calculations the system response to any kind of stimulus [27]. The Green's function exhibits a modal decomposition of the response and it has been used in spectroscopies like electron energy loss spectroscopy (EELS) or scanning near-field optical microscopy (SNOM), but it hasn't been used in FRET problems [27]. In the present work we apply the Green's function method to estimate the FRET enhancement. The approach is based on the fact that for spherical nanoparticles all spectral properties of the surface operators are known [28], hence an analytical expression of the boundary Green's function is provided. It will be further shown that the boundary Green's function allows easy calculations for any orientation of donors and acceptors. In addition to that, the terms associated with plasmonic enhancement can be easily identified in the expressions of the FRET enhancement factor. In a recent conference paper [29] we tackled the same problem. However, the approach is a bit different here, mostly by setting the problem in a broader context and explicitly calculating the boundary Green's function. The paper has the following structure: in section 2 we present the calculation model for plasmonic enhancement of FRET; in section 3 we present the description of plasmonic enhancement of FRET by the boundary Green's function, which allows a modal decomposition; in section 4, for a nanosphere we calculate its boundary Green's function and its plasmonic enhancement of FRET; in the last section, section 5, we present some numerical results, the discussions, and the concluding remarks.

## 2. The model for plasmonic enhancement of FRET

Energy transfer by FRET is governed by the electrostatic dipole-dipole interaction, which provides an expression for rate transfer of the following form [2, 9, 10, 30]:

$$k_{ET} = \frac{\eta_D}{\tau_D} \frac{9000k^2 \ln 10}{128\pi^5 n^4 N_A} \frac{1}{R^6} \int \frac{\varepsilon(\nu)I(\nu)}{\nu^4} d\nu. \quad (1)$$

In Eq. (1)  $\eta_D$  and  $\tau_D$  are respectively fluorescence quantum yield of the donor and donor emission lifetime,  $k$  is an orientation factor of the dipoles associated with the donor and the acceptor,

$N_A$  is the Avogadro number,  $n$  is the refraction index of the host medium,  $R$  is separation distance between donor and acceptor,  $\nu$  is wavenumber, while the integral is the spectral overlap between absorption coefficient of the acceptor  $\varepsilon(\nu)$  and the normalized emission spectrum of the donor  $I(\nu)$ . Nonetheless, the Förster theory based on Eq. (1) has several shortcomings, a few of which were mentioned above, like the range of validity (between 2 and 10 nm). Below 2 nm the point-dipole approximation is not valid anymore; also other quantum mechanical processes may become relevant like the electron transfer between donor and acceptor [2,8,10]. For distances comparable with the light wavelength radiative processes are needed to be considered [10,30]. In addition, the quantum nature of light may be also considered. Moreover, FRET is based on weak coupling and index of refraction may be inhomogeneous. Many of these limitations as well as the plasmon enhanced FRET have been considered in recent works where the quantum nature of the donors, acceptors, and radiation has been considered [30]. The expression reads:

$$k_{QET} = \frac{\eta_D}{\tau_D} \frac{9000 \ln 10}{128 \pi^5 N_A} \int \frac{\varepsilon(\nu) I(\nu)}{\nu^4} \left| \frac{\mathbf{e}_A \cdot \mathbf{E}^D(\mathbf{r}_A, \nu)}{d_D} \right|^2 d\nu. \quad (2)$$

In the last term of right hand side,  $\mathbf{e}_A$  is the direction of the acceptor dipole, located at  $\mathbf{r}_A$ ,  $\mathbf{E}^D$  is the field created by the donor with a classical dipole strength  $d_D$  at acceptor site. The information about dipole orientation factor, distance dependence as well as about the refraction index of the medium is embedded in this term. However, the plasmon enhanced factor is still calculated by classical electrodynamics means.

Below it is provided the method used in the electrostatic approximation by which we can calculate the plasmonic enhancement factor of FRET. Thus both the donor (D) and the acceptor (A) are associated with point-like dipoles,  $\mathbf{d}_D$  and  $\mathbf{d}_A$ , respectively, whose the energy transfer is governed by the dipole-dipole interaction [2,9,10]. The energy transfer and eventually its enhancement regard D and A as time-harmonic point-like dipoles interacting with each other directly or via the metallic nanoparticle (Fig. 1) [17,21]. The electrostatic potential contains four terms:

$$\Phi(\mathbf{r}) = \Phi_A(\mathbf{r}) + \Phi_D(\mathbf{r}) + \Phi_{A_{ind}}(\mathbf{r}) + \Phi_{D_{ind}}(\mathbf{r}). \quad (3)$$

The first and the second term are the electric potentials generated by A and D, while the other two terms are the electric potentials generated by the charge induced on the nanoparticle by the two dipoles A and D. The electric field at the acceptor site is:

$$\mathbf{E}_A = -\nabla [\Phi_D(\mathbf{r}_A) + \Phi_{D_{ind}}(\mathbf{r}_A) + \Phi_{A_{ind}}(\mathbf{r}_A)], \quad (4)$$

which gives an interaction energy for the acceptor in the presence of both the donor and the nanoparticle of the following form:

$$U_A = -\mathbf{d}_A \cdot \mathbf{E}_A = U_{AD} + U_{AD_{ind}} + U_{AA_{ind}}. \quad (5)$$

The plasmonic enhancement factor of the FRET process is thus defined simply as [17,21]:

$$|A|^2 = \left| 1 + \frac{U_{AD_{ind}}}{U_{AD}} \right|^2. \quad (6)$$

### 3. Description of the plasmonic enhancement of FRET by the boundary Green's function

In the electrostatic (nonretarded) approximation the total electric field  $\mathbf{E}$  is the sum of the electric field  $\mathbf{E}_{free}$  of the imposed free charge  $\rho_{free}(\mathbf{r}, \omega)$  and the field of the induced charge due to the presence of the nanoparticle  $\mathbf{E}_{bound}$ . It is assumed that the free charge distribution is placed in a medium of dielectric permittivity  $\epsilon_0$ , outside the nanoparticle of dielectric permittivity  $\epsilon_1$ , and has temporal evolution of the form  $\exp(j\omega t)$ . Accordingly all the electric fields  $\mathbf{E}_{free}$ ,  $\mathbf{E}_{bound}$ , and  $\mathbf{E}$  have an associated electrostatic potential, *i. e.*,  $\mathbf{E}_{free} = -\nabla\Phi_{free}$ ,  $\mathbf{E}_{bound} = -\nabla\Phi_{bound}$ , and the total electric field  $\mathbf{E} = -\nabla\Phi$ , such that the electrostatic potential in the presence of the nanoparticle has the form [23-27]:

$$\Phi(\mathbf{r}, \omega) = \Phi_{free}(\mathbf{r}, \omega) + \Phi_{bound}(\mathbf{r}, \omega) \quad (7)$$

with

$$\Phi_{free}(\mathbf{r}, \omega) = \int \frac{1}{\epsilon_0} G_{free}(\mathbf{r}, \mathbf{r}') \rho_{free}(\mathbf{r}', \omega) d\mathbf{r}' \quad (8)$$

and

$$\Phi_{free}(\mathbf{r}, \omega) = \int_{\Sigma} G_{free}(\mathbf{r}, \mathbf{r}') \sigma(\mathbf{r}', \omega) d\Sigma_{r'}. \quad (9)$$

The first integral is a volume integral in whole space, while the second integral is on the surface  $\Sigma$  that bounds the nanoparticle. The charge density  $\sigma(\mathbf{r}, \omega)$  induced on the surface of the nanoparticle is [23-26]:

$$\sigma(\mathbf{r}, \omega) = \sum_k \frac{1}{\frac{1}{2\lambda} - \chi_k} u_k(\mathbf{r}) \langle v_k | \mathbf{n} \cdot \mathbf{E}_{free} \rangle, \quad (10)$$

where  $\lambda = (\epsilon_1 - \epsilon_0)/(\epsilon_1 + \epsilon_0)$  with  $\epsilon_1$  and  $\epsilon_0$  being eventually  $\omega$ -dependent,  $u_k$  and  $\chi_k$  are the eigenfunctions and the eigenvalues of the electrostatic operator defined on  $\Sigma$  of the nanoparticle as [23-27]

$$\hat{M}[\sigma] = - \int_{\mathbf{r}' \in \Sigma} \sigma(\mathbf{r}') \frac{\partial}{\partial n_r} G_{free}(\mathbf{r}, \mathbf{r}') d\Sigma_{r'} \quad (11)$$

and  $\langle v_k | \mathbf{n} \cdot \mathbf{E}_{free} \rangle$  are the scalar products between the corresponding eigenfunctions  $v_k$  of the adjoint operator  $M^\dagger$  and the dot product  $\mathbf{n} \cdot \mathbf{E}_{free}$ , with  $\mathbf{n}$  the normal to the surface  $\Sigma$  of the nanoparticle. In Eqs. (8), (9), and (11)

$$G_{free}(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad (12)$$

is the free-space Green's function. It is well known [23-26] that  $u_k$  and  $v_k$  are bi-orthonormal, *i.e.*,  $\langle v_k | u_j \rangle = \delta_{ij}$  and the  $v_k$  are obtained from  $u_k$  by

$$v_k(\mathbf{r}) = \int_{\mathbf{r}' \in \Sigma} u_k(\mathbf{r}') G_{free}(\mathbf{r}, \mathbf{r}') d\Sigma_{r'}. \quad (13)$$

We can define a new Green's function  $G_{bound}(\mathbf{r}, \mathbf{r}', \omega)$ , which is a boundary Green's function that describes the response of the system to imposed free charge  $\rho_{free}(\mathbf{r}, \omega)$ , such that the total electric potential is then given by [23-27]

$$\Phi(\mathbf{r}, \omega) = \int \frac{1}{\epsilon_0} G_{free}(\mathbf{r}, \mathbf{r}') \rho_{free}(\mathbf{r}', \omega) d\mathbf{r}' + \int G_{bound}(\mathbf{r}, \mathbf{r}', \omega) \rho_{free}(\mathbf{r}', \omega) d\mathbf{r}'. \quad (14)$$

Combining Eqs. (7), (9), (10), (12), (13), and (14) one can obtain the expression of boundary Green's function as [27]

$$G_{bound}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{\epsilon_0} \sum_k \frac{1}{\frac{1}{2\lambda} - \chi_k} \phi_k(\mathbf{r}) \tilde{\phi}_k(\mathbf{r}'), \quad (15)$$

where

$$\phi_k(\mathbf{r}') = \int_{\mathbf{r}' \in \Sigma} u_k(\mathbf{r}') G_{free}(\mathbf{r}, \mathbf{r}') d\Sigma_{r'} \quad (16)$$

is the single-layer potential generated by the charge density  $u_k$  and

$$\tilde{\phi}_k(\mathbf{r}) = \int_{\mathbf{r}' \in \Sigma} v_k(\mathbf{r}') \frac{\partial}{\partial \mathbf{n}_{r'}} G_{free}(\mathbf{r}, \mathbf{r}') d\Sigma_{r'} \quad (17)$$

is the double-layer potential of the dipole density  $v_k$ . We note here that  $G_{bound}(\mathbf{r}, \mathbf{r}', \omega)$  provides a modal decomposition of the response. Moreover, it can take a manifestly symmetric form in  $\mathbf{r}$  and  $\mathbf{r}'$ , in which  $\tilde{\phi}_k$  is replaced by  $\phi_k$  [27], however the calculation of the boundary Green's function in its manifestly symmetric form requires the proper normalization of  $u_k$  by their bi-orthogonality with  $v_k$ .

#### 4. The boundary Green's function of a nanosphere and the calculation of plasmonic enhancement of FRET

In order to calculate the boundary Green's function one needs the knowledge of spectral properties of the electrostatic operator (11) and of its adjoint, namely  $\chi_k$ ,  $u_k$ , and  $v_k$ . There are several shapes having the associated electrostatic operators with well established spectral properties [28]. One of these shapes is sphere, whose free-space Green's function (12) has a separated form in spherical coordinates given by

$$G_{free}(\mathbf{r}, \mathbf{r}') = \sum_{l,m} \frac{1}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}(\theta, \varphi), \quad (18)$$

where  $Y_{lm}(\theta, \varphi)$  are the spherical harmonics and  $r_{<}$  and  $r_{>}$  represent the minimum and respectively the maximum of the pair  $(r, r')$ . The form given by Eq. (18) is a well-known expression found in any textbook treating classical electrodynamics [31]. What has been less known is the fact that this separated form allows the calculations of both the eigenfunctions and the eigenvalues of (11) for spherical shape [28]. Although for sphere the electrostatic operator is symmetric, the eigenfunctions  $u_k$ , and  $v_k$  are not identical (they differ by a constant) since they are related by Eq. (13). Thus, for a sphere of radius  $a$  one has

$$u_{lm}(\theta, \varphi) = \sqrt{\frac{2l+1}{a^3}} Y_{lm}(\theta, \varphi), \quad (19)$$

$$v_{lm}(\theta, \varphi) = \sqrt{\frac{1}{(2l+1)a}} Y_{lm}(\theta, \varphi), \quad (20)$$

and

$$\chi_l = \frac{1}{2(2l+1)}. \quad (21)$$

Now it is straightforward to calculate the boundary Green's function for a spherical particle by combining Eqs. (15)-(21). Its expression is given by

$$G_{bound}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{\varepsilon_0} \sum_{l,m} \frac{\varepsilon_1 - \varepsilon_0}{l\varepsilon_1 + (l+1)\varepsilon_0} \frac{l}{2l+1} \frac{a^{2l+1}}{r^{l+1}r'^{l+1}} Y_{lm}(\theta, \varphi) Y_{lm}^*(\theta', \varphi'). \quad (22)$$

We easily see that the boundary Green's function is symmetric in  $r$  and  $r'$ , even though Eq. (15) does not show it manifestly.

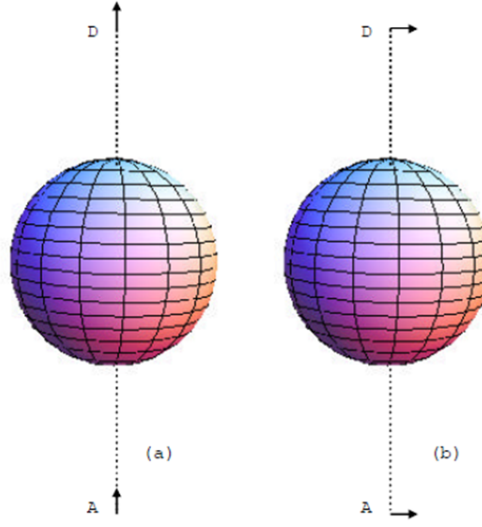
Formally, the charge density of a dipole of strength  $\mathbf{d}$  located at  $\mathbf{r}'$  is  $\rho_d(\mathbf{r}) = \mathbf{d} \cdot \nabla_{\mathbf{r}'} \delta(r - r')$ . Now we are able to find the electric potential generated by a dipole  $\mathbf{d}_D$  located at  $\mathbf{r}_D$  due to the presence of a sphere of radius  $a$  centered at origin as

$$\Phi_{D_{ind}}(\mathbf{r}, \omega) = \frac{-1}{\varepsilon_0} \sum_{l,m} \frac{\varepsilon_1 - \varepsilon_0}{l\varepsilon_1 + (l+1)\varepsilon_0} \frac{l}{2l+1} \frac{a^{2l+1}}{r'^{l+1}} Y_{lm}(\theta, \varphi) \mathbf{d}_D \cdot \nabla_{\mathbf{r}'} \left( \frac{Y_{lm}^*(\theta', \varphi')}{r'^{l+1}} \right) \Bigg|_{r'=r_d}. \quad (23)$$

Finally the interaction energy between a donor dipole  $\mathbf{d}_D$  located at  $\mathbf{r}_D$  and an acceptor dipole  $\mathbf{d}_A$  located at  $\mathbf{r}_A$  due to the presence of a sphere is given by the following

$$U_{AD_{ind}} = \frac{1}{\varepsilon_0} \sum_{l,m} \frac{\varepsilon_0 - \varepsilon_1}{l\varepsilon_1 + (l+1)\varepsilon_0} \frac{l}{2l+1} \frac{a^{2l+1}}{2l+1} \mathbf{d}_A \cdot \nabla_{\mathbf{r}} \left( \frac{Y_{lm}(\theta', \varphi')}{r'^{l+1}} \right) \Bigg|_{r=r_a} \mathbf{d}_D \cdot \nabla_{\mathbf{r}'} \left( \frac{Y_{lm}^*(\theta', \varphi')}{r'^{l+1}} \right) \Bigg|_{r'=r_d}. \quad (24)$$

Equation (24) applies for any locations and orientations of donor and acceptor molecules and as far as we know it has not been encountered in the literature. In the following we apply expression (24) to the dipole settings shown in Fig. 1.



**Fig. 1.** Arrangement geometries of the donor (D) and the acceptor (A) in the close proximity of a spherical metallic nanoparticle: (a) aligned and normal to surface dipoles, and (b) parallel and tangent to surface dipoles.

## 5. Numerical results, discussions, and concluding remarks

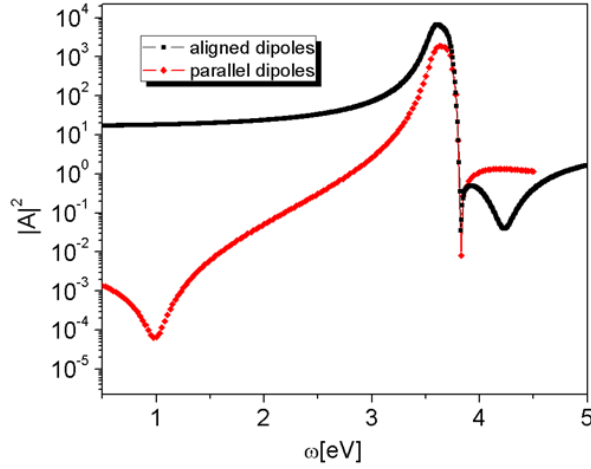
The donors (D) in Fig. 1 have spherical coordinates  $r = r_D$ ,  $\theta = 0$ ,  $\varphi = 0$ , while the acceptors (A) have the coordinates  $r = r_A$ ,  $\theta = \pi$ , and  $\varphi = 0$ . We recall that the gradient in spherical coordinates has the following expression:  $\nabla = \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \mathbf{e}_\varphi \frac{1}{r \sin(\theta)} \frac{\partial}{\partial \varphi}$ , where  $\mathbf{e}_r$ ,  $\mathbf{e}_\theta$  and  $\mathbf{e}_\varphi$  are the local and orthogonal unit vectors [31]. Moreover, the donor dipole is oriented along  $\mathbf{e}_r$  in Fig. 1(a) and along  $\mathbf{e}_\theta$  in Fig. 1(b). Similarly the acceptor is aligned with  $-\mathbf{e}_r$  in Fig.1(a) and aligned with  $-\mathbf{e}_\theta$  in Fig. 1(b). Now direct calculations lead us to the plasmonic enhancement factor of the FRET process for dipole arrangements shown in Fig. 1(a) of the form [20, 29]

$$|A|^2 = \left| 1 + \frac{(r_A + r_D)^2}{2a^3} \sum_l (-1)^{l+1} \frac{l(l+1)^2 (\epsilon_1 - \epsilon_0)}{l\epsilon_1 + (l+1)\epsilon_0} \left( \frac{a^2}{r_A r_D} \right)^{l+2} \right|^2 \quad (25)$$

while the plasmonic enhancement factor of the FRET process for dipole arrangements shown in Fig. 1(b) takes the following form

$$|A|^2 = \left| 1 + \frac{(r_A + r_D)^2}{2a^3} \sum_{l,m} \frac{(\epsilon_1 - \epsilon_0)}{l\epsilon_1 + (l+1)\epsilon_0} \frac{l}{2l+1} \times \left( \frac{a^2}{r_A r_D} \right)^{l+2} \frac{dY_{lm}(\theta, \varphi)}{d\theta} \Big|_{\theta=\pi, \varphi=0} \frac{dY_{lm}^*(\theta, \varphi)}{d\theta} \Big|_{\theta=0, \varphi=0} \right|^2 \quad (26)$$

We have several observations. First, Eq. (25) exhibits only  $m = 0$  for the whole sum regarding  $l$  and  $m$  indices. On the other hand, careful inspection of Eq. (26) will show that only terms



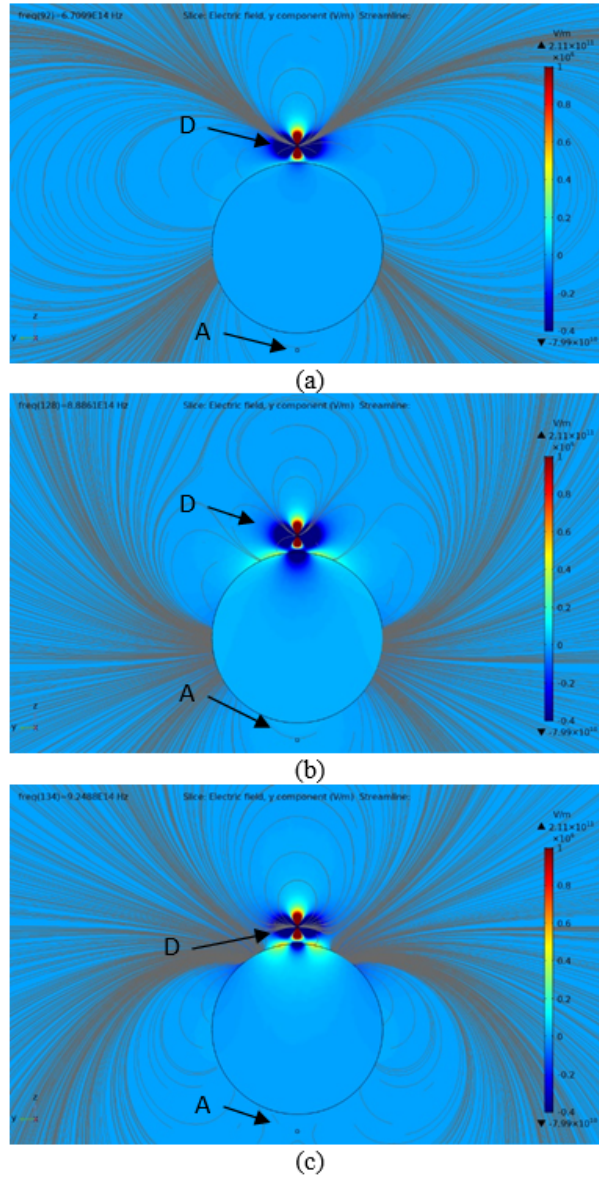
**Fig. 2.** The plasmonic enhancement factor of FRET for both arrangement geometries of the donor and the acceptor. The aligned dipole geometry (Fig. 1(a)) is plotted with black line with squares and the parallel geometry (Fig. 1 (b)) is plotted with red line with diamonds.

with  $m = \pm 1$  are different from 0, because only spherical harmonics that has only  $\sin(\theta)$  will survive. This can be further shown and Eq. (26) can be further worked out by using some recurrence relations for the derivative of associated Legendre polynomials which are part of spherical harmonics [32]. Also, apparently, due to the factor  $(l+1)^2$  in Eq. (25) and the factor  $1/(2l+1)$  in Eq. (26), the enhancement factor of FRET for aligned dipoles seems to be higher. Numerical estimations performed below prove our last observation.

In order to estimate numerically the plasmonic enhancement factor  $|A|^2$  we consider a spherical nanoparticle with 25 nm radius, made of silver whose dielectric function is described by a Drude model of the form  $\epsilon_1(\omega) = \epsilon_0(\epsilon_\infty - \omega_p^2/(\omega(\omega + i\delta)))$  having the following parameters:  $\epsilon_\infty = 5$ ,  $\omega_p = 9.5$ , eV, and  $\delta = 0.15$  eV. The donor as well as the acceptor molecules is placed at 5 nm from nanosphere surface. The computed enhancement factors as function of frequency (in eV) are shown in Fig. 2 for both dipole arrangements. The plasmonic enhancement factors of FRET have maximum values of about 6700 at 3.6 eV for aligned dipole configuration and of about 1900 at 3.65 eV for parallel dipole configuration. These calculations are consistent with other recent calculations of FRET enhancement for these two dipole arrangements [30]. The authors, who used a fully retarded numerical scheme, have also noticed a shift of the maximum of FRET enhancement from the dipole resonance to the quadrupole one, findings that are consistent with our results [30].

To understand the role of the spherical nanoparticle in FRET enhancement we show the electric field streamlines along  $y$ -component, along the dipole orientations depicted in Fig. 1 (b). The frequencies are chosen at 2.78 eV (off-resonance), 3.65 eV (on resonance) and at 3.83 eV (at the common dip). In the off-resonance regime, Fig. 3 (a), the nanosphere behaves as a dipole, but due to the dipole arrangement it screens the dipole field at acceptor site. The situation is different from that of the aligned arrangement, where there is an enhancement due to the sphere induced dipole (see our previous conference paper [29]). In the on-resonance regime, Fig. 3 (b), the role of the nanosphere is radically changed. The donor and the nanosphere become a very large, common, and extended dipole that enhances the electric field at the acceptor site. However, at the





**Fig. 3.** Electric field y-component streamlines at three frequencies: (a) 2.78 eV; (b) 3.65 eV; and (c) 3.83 eV. The dipole arrangement is parallel.

frequency of the dip (3.83 eV, the same for any dipole arrangement) the nanosphere effectively screens the donor dipole since some of the field lines end up on the sphere. We will discuss this issue elsewhere since it is related to the spectral properties of the electrostatic operator for spherical shape.

To conclude this work, we calculated analytically and analyzed numerically the enhancement of intermolecular resonance energy transfer in the presence of a spherical metallic nanoparticle. We calculated a boundary Green's function that straightforwardly provides the plasmonic enhancement factor of the FRET and its modal decomposition. In contrast to other previous works, our approach seems to be more direct since it makes use of spectral properties of the electrostatic operator for spherical geometry. Our numerical calculations show that at large plasmonic enhancement factors the donor and the nanoparticle become both a large and extended dipole that enhances the FRET process.

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