Radiative and nonradiative decay rates of a molecule close to a metal particle of complex shape

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(Received 13 April 2004; accepted 24 August 2004)

We present a model to evaluate the radiative and nonradiative lifetimes of electronic excited states of a molecule close to a metal particle of complex shape and, possibly, in the presence of a solvent. The molecule is treated quantum mechanically at Hartree–Fock (HF) or density-functional theory (DFT) level. The metal/solvent is considered as a continuous body, characterized by its frequency dependent local dielectric constant. For simple metal shapes (planar infinite surface and spherical particle) a version of the polarizable continuum model based on the integral equation formalism has been used, while an alternative methodology has been implemented to treat metal particles of arbitrary shape. In both cases, equations have been numerically solved using a boundary element method. Excitation energies and nonradiative decay rates due to the energy transfer from the molecule to the metal are evaluated exploiting the linear response theory (TDHF or TDDFT where TD—time dependent). The radiative decay rate of the whole system (molecule + metal/solvent) is calculated, still using a continuum model, in terms of the response of the surrounding to the molecular transition. The model presented has been applied to the study of the radiative and nonradiative lifetimes of a lissamine molecule in solution (water) and close to gold spherical nanoparticles of different radius. In addition, the influence of the metal shape has been analyzed by performing calculations on a system composed by a coumarin-type molecule close to silver aggregates of complex shape. © 2004 American Institute of Physics. [DOI: 10.1063/1.1806819]

I. INTRODUCTION

It is well known that the presence of a metal body can strongly affect the response properties of a molecule placed in its close proximity.1 Molecular optical properties are probably the most significative example of how strong the metal influence can be: this is the main cause, for example, of the well-known surface enhanced Raman scattering (SERS),2 for which enhancement factors of more than ten orders of magnitude has been reported.3 The metal influence is responsible also for many other surface enhanced (SE) optical effects,2 such as second harmonic (SE) generation, SE two-photon absorption, or SE fluorescence. Nevertheless, as far as concerns the excited state properties, the presence of the metal can have an opposite effect and it is responsible, in many cases, for a decrease of the molecular responses. This result is due to the fact that the excitation energy of the molecule can be efficiently transferred to the metal body (for example, via a resonant energy transfer, or RET, or via the formation of a charge transfer state) and can undergo, inside this medium, several dissipation processes.

With this work we present a model to treat radiative and nonradiative decay rates of a molecule close to a metal particle of arbitrary shape, thus allowing the study of different kinds of interesting physical systems. In fact, both the fluorescence enhancement and the fluorescence quenching are the basis of many recent experimental works and technological developments, starting from RET (Refs. 4 and 5) and fluorescence hyperquenching near spherical (or quasispherical) nanoparticles and arriving to fluorescence enhancement near fractal aggregates6,7 or near the tip of a scanning near-field optical microscope (SNOM).8–10

Many of the models used to treat these effects consider the molecule as a polarizable pointlike dipole:11–14 nevertheless, for metal-molecule distances less than few nanometers (a situation that often occurs in many experimental situations) this approximation can be too rough and a quantum mechanical (QM) description of the whole molecule would be instead necessary. On the other side, for many of the physical systems of interest the metal shape is one of the most important factors and a proper description of this aspect is compulsory. For both these reasons we have formulated a method that treats the molecule at a high level of accuracy and at the same time can explicitly consider metal particle of complex shape.

The paper is organized as follows: in Sec. II we present the main features of the proposed QM model to calculate...
radiative and nonradiative lifetimes for a molecule placed near a metal particle. In Sec. III a comparison with experimental results is reported together with an investigation on the importance of the metal shape and of the geometrical configuration of the system (position, orientation, and distance of the molecule with respect to the metal surface) in the enhancement or decrease of the molecular response.

II. THEORY

The starting point of the present work is the theoretical model that has been recently proposed\textsuperscript{15,16} for the calculation of dynamic response properties of a molecule in close proximity to metal bodies and possibly in the presence of a solvent. This model is based on a hierarchical principle: the main part of the system under study is treated using a high level of accuracy while the remaining objects are treated only considering the features important in the interaction with the interesting part. Thus, the molecule, that in the studied phenomena has the main role, is treated at a quantum mechanical level (Hartree–Fock, HF, or within the density-functional theory, DFT), whereas the metal (and the solvent, if present) is considered as a continuous body characterized by its response properties to electric fields, both the ones imposed on the system from outside and the ones arising from the molecular charge distribution.

In the previous works,\textsuperscript{16} only semi-infinite metals with planar (possibly rough) surfaces were considered. In the present work, we extend the theory of Ref. 16 by considering nanoparticles of complex shape. In particular, we model the metal as a sphere or as a complex body of irregular geometry, obtained as the union of different interlocking spheres. The metal response to the electric fields has been described using the same assumptions used previously: the metal behaves as a perfect conductor for static fields and as a dielectric for time dependent fields. In the latter case, the frequency dependent permittivity experimentally measured is used, possibly modified to take into account quantum size effects (in particular, the reduced mean free path of the metal electrons in the nanoparticle) on the response of the metal body.

The solvent is described as a continuum dielectric which occupies all the space free from the metal specimen and the molecular shaped cavity hosting the molecule. The metal-molecule and solvent-molecule interactions have been treated through the polarizable continuum model (PCM),\textsuperscript{17,18} implemented in two complementary versions. Considering the metal/solvent as continuous media and exploiting classical electrodynamic treatments it is possible to describe the interaction between the molecule and the surrounding (metal/solvent) in terms of the interaction of the molecule with an apparent surface charge density spread only on the system interfaces. In this way the original three-dimensional problem is reduced to a simpler two-dimensional problem defined only at the boundaries of the system. The set of equations that determine the apparent surface density have been numerically solved by a boundary element method (BEM).\textsuperscript{16} In this respect, our model can be so referred to the apparent surface charge methods (Ref. 18) widely used in continuum solvation models.

In previous works,\textsuperscript{16} we described a procedure to calculate metal induced nonradiative decay rates based on time dependent DFT (TDDFT) or time dependent HF (TDHF) in the random phase approximation-like formulation.\textsuperscript{20} In the present work, this procedure will be extended to more complex metal shapes (as said above). Moreover, we will also present the theory for the calculation of metal-induced radiative decay rate, again in the TDDFT/TDHF framework, that was not present in our previous works on the subject.

In the next few sections, we shall discuss how to calculate the apparent charges mentioned above for (complex-shaped) nanoparticles and how the radiative and nonradiative metal-induced lifetimes are computed. We shall also describe a method to calculate the dynamic polarizability of complex shape nanoparticles that will be useful in rationalizing some of the numerical results obtained in the Numerical Applications section.

A. The calculation of the apparent charges: Spherical particles

As said above, the total electrostatic potential acting on the molecule due to the metal/solvent polarization is calculated from a set of apparent charges placed on the interfaces of the system. These charges (evaluated, in this case, by considering the dynamic dielectric response of metal and solvent) also appear in the equations that determine excitation energies and lifetimes, as discussed in Secs. II C and II D.

The apparent surface charges can be obtained by exploiting two different methodologies. For simple shapes it is more useful and time saving to exploit the integral equation formalism (IEF) version of the PCM model [IEF-PCM (Ref. 21)], already applied to the study of excitation energies and lifetimes of a molecule close to a metal planar infinite surface.\textsuperscript{16} With this procedure, the metal-molecule and solvent-molecule interactions are reduced to the interaction with a fictitious charge density spread on the molecular cavity surface only.

To exploit this procedure for a given system, it is necessary (and sufficient) to know (at least numerically) the expression of the Green’s function $G^E$ characteristic of the region of space external to the molecular cavity for that system. In particular, it is possible to find an analytical expression of $G^E$ for a spherical particle (see the Appendix).

This extends the previous works,\textsuperscript{16} focused on planar surfaces, since it introduces the possibility to directly control an important physical parameter: the sphere radius. We also note that, because of the nanometer dimension of the system, a quasistatic treatment is sufficient in most cases, instead of the full electrodynamic one. In addition, as for the metallic planar surface, also for the spherical particle it is possible to obtain an analytical expression for the Green’s function in the case of a nonlocal response for the metal.\textsuperscript{22} We note, however, that, at the present stage of the work, we have chosen to focus on the description of the effects related to the metal shape: the nonlocal response of the metal will be introduced in the model in future works.
B. The calculation of the apparent charges: Complex-shaped particles

With the purpose of treating systems characterized by a complex and arbitrary shape, for which it is not available, numerically or analytically, a Green’s function, here we have chosen to revert to the original version of the PCM (Refs. 17 and 18) also known as DPCM (where D stands for dielectric).

Based on elementary electrostatic considerations, this version of the PCM treats explicitly all the different interfaces present in the system: in the case under study, these interfaces are the surface of the metal body and, in case of the presence of a solvent, the molecular cavity. This model has been already used in previous works for the characterization of metal-molecule interactions. As for IEF, the resulting equations are numerically solved by a BEM, discretizing all the surfaces. For the generation of the metal specimen, an algorithm similar to the one defined for the molecular cavity is used: the metal body is built as the union of interlocking spheres of arbitrary radius and position. Playing with these two parameters and the total number of spheres generated, it is possible to control the exact shape of the metal surface and to reproduce several systems.

The main equation to be solved to calculate the apparent charges spread on all the interfaces is of the form

$$\mathbf{D} \mathbf{A}^{-1} \mathbf{q} = \mathbf{E}_n^0,$$

where $\mathbf{A}$ is the diagonal matrix of the tessera areas, $\mathbf{D}$ is the characteristic matrix of DPCM (Ref. 17), and $\mathbf{E}_n^0$ is the component normal to the tesserae surfaces of the electric field generated by the solvated molecule.

C. Excitation energies and nonradiative lifetimes

For the sake of brevity, we do not present here the derivation of the expressions for the nonradiative lifetimes and excitation energies from the TD-DFT equations, since such derivation has been already given in Ref. 16. It is sufficient to recall that the metal/solvent effects are taken into account by including in the TD equations a polarization term $K_{\text{pol}}^{\text{tot}}(\omega)$ which can be written as

$$K_{\text{pol}}^{\text{tot}}(\omega) = \sum_i q_w(s, \{ \psi_u^s \psi_t \} | V(s, \{ \psi_u^s \psi_t \})).$$

In Eq. (2), $V(s, \{ \psi_u^s \psi_t \})$ is the electrostatic potential generated by the distribution of charge $\psi_u^s \psi_t$ (where $\psi_u$ and $\psi_t$ are molecular orbitals) at the point $s$, on the cavity surface. $q_w(s, \{ \psi_u^s \psi_t \})$ is the apparent charge placed in $s$ due to the metal/solvent polarization induced by $\psi_u^s \psi_t$ and calculated exploiting the methodologies resumed in the previous sections. These charges are evaluated considering the response of the metal at the frequency $\omega$. Since such a response is described by a complex dielectric constant, the charges are complex and $K_{\text{pol}}^{\text{tot}}(\omega)$ is complex as well. Thus, also the poles of the response function are complex. We associated their real part to the excitation energies (such as for purely real response function), and their imaginary part with the metal-induced nonradiative decay rate $\Gamma_{\text{Met}}^{\text{nonrad}}$ (i.e., to the nonradiative lifetimes $\tau_{\text{Met}}^{\text{nonrad}} = 1/\Gamma_{\text{Met}}^{\text{nonrad}}$).

We would also like to recall that the lifetimes so obtained are related, strictly speaking, to the absorption process and not to the emission one, i.e., we are considering the transition between the ground state and an excited state, not vice versa. Due to the presence of the metal solvent surrounding, this is just an approximation; nevertheless, it has been already noted that, in general (and this is the case of the systems analyzed in the numerical section), the importance of the presence of the metal/solvent on the molecular transition density is quite limited and it can in many cases be neglected.

D. Radiative lifetimes

Besides the nonradiative process, that has been analyzed above, another way of dissipating the molecular excitation energy is the radiative one. The molecular excited state of interest may undergo processes of fluorescence. In Ref. 16, the radiative processes were considered by reverting on the classical electrodynamics model by Chance, Prock, and Silbey. In the present work, we present a methodology to calculate radiative lifetimes within the same model used for the computations of nonradiative lifetimes. Thus, both radiative and nonradiative decay rates are calculated in a coherent way, taking explicitly into account the presence of the metal and the solvent surrounding the molecule. The fluorescence rate for an isolated molecule can be written as

$$\Gamma_{\text{rad}} = \frac{4 \omega^3}{3 \hbar c^3} |\tilde{\mu}_{K0}|^2,$$

where $\omega$ is the fluorescence frequency corresponding to the transition under study (it corresponds to the real part of the pole of the response function) and $\tilde{\mu}_{K0}$ is the molecular transition dipole between the excited state $K$ and the ground state. When the whole system, instead of the single molecule, is considered, the transition dipole $\tilde{\mu}_{K0}^{\text{tot}}$ must be used instead of $\tilde{\mu}_{K0}$ and the refraction index $n_1$ of the medium in which emission takes place has to be inserted in the numerator of Eq. (3). Following a theoretical approach similar to the one exploited to describe the effects of an applied electric field on a solvated molecule (see Refs. 16 and 25) it is possible to write $\tilde{\mu}_{\text{tot}}$ (let us omit the indication of electronic states for simplicity) as

$$\tilde{\mu}_{\text{tot}} = \tilde{\mu}_{\text{tot}}^0 + \tilde{\mu},$$

where $\tilde{\mu}_{\text{tot}}^0$ is the transition dipole moment of the molecule in the complex environment while $\tilde{\mu}$ is the dipole induced in the metal/solvent by the molecular transition. Such an induced dipole moment can be obtained from the knowledge of the PCM characteristic matrix $\mathbf{D}$ and of the electrostatic potential generated by the transition charge density $\mathbf{V}^{\text{tr}}$. Indeed, the interaction between the dipole induced by the molecule on the metal/solvent and an external field $\mathbf{E}^{\text{ex}}$ can be rewritten in terms of the interaction between the charge induced by the external field on the metal/solvent and the molecular electrostatic potential $\mathbf{V}^{\text{tr}}$.

$$-\tilde{\mu} \cdot \mathbf{E}^{\text{ex}} = \mathbf{q}^{\text{ex}} \mathbf{V}^{\text{tr}},$$
where the charge $\mathbf{q}^{ex}$ induced by the external field are given by Eq. (1), namely,

$$\mathbf{q}^{ex} = \mathbf{D}^{-1}(\mathbf{E}^{ex}, \hat{n}) \label{e5}$$

In Eq. (6) $\hat{n}$ contains the direction of the unit vectors perpendicular to the tesserae surface.

Thus, exploiting Eqs. (5) and (6), the $i$th component of the induced dipole can be written as

$$\mu^i = -\frac{\partial (\mathbf{q}^{ex} \mathbf{V}^{tr})}{\partial E^{ex}_i} = -\frac{\partial \mathbf{q}^{ex}}{\partial E^{ex}_i} \mathbf{V}^{tr} = -(\mathbf{A}^{-1} \mathbf{n}) \mathbf{V}^{tr} \label{e6}$$

E. The metal polarizability

Similarly to what has been done to obtain the dipole induced on the metal particle by the molecular transition, it is possible to calculate the response of the metal particle alone. This kind of calculation can be easily done still exploiting the DPCM procedure as follows.

The elements of the metal polarizability tensor can be written as

$$\alpha^{ij}_m = \frac{\partial \mu^{ex}_i}{\partial E^{ex}_j} \label{e7}$$

where $\mu^{ex}_i$ and $E^{ex}_j$ are the components, respectively, of the electric dipole induced on the metal particle and of the external electric field acting on the particle. In a similar way to what has been done in the preceding section, the metal induced dipole can be written in term of a set of apparent charges as

$$\mu^{ex}_m = \sum_{n \in m} q_n \mathbf{r}_n = \mathbf{q}^{ex} \mathbf{r} \label{e8}$$

where the summation is only on the tesserae belonging to the metal and the array of vectors $\mathbf{r}$ contains the positions of the metallic tesserae. Then, using Eqs. (8) and (9), the metal polarizability can be obtained as

$$\alpha^{ij}_m = \frac{\partial \mathbf{q}^{ex}}{\partial E^{ex}_j} \mathbf{r}_j = (\mathbf{A}^{-1} \mathbf{n}) \mathbf{r}_j \label{e9}$$

with all the matrices ($\mathbf{D}$, $\mathbf{n}$, $\mathbf{r}$, etc.) defined only for tesserae belonging to the metal surface.

### III. NUMERICAL APPLICATIONS

Numerical applications can be of different types: first of all, it is necessary to estimate the numerical precision of the results obtained with the method proposed, varying the internal parameters; in addition, and this is one of the aims of our work, it is possible to address real systems and compare theoretical results with the experimental ones; finally, for all those cases for which experiments are not yet available, it is possible to use the model proposed to theoretically estimate the behavior of the system. All these applications will be analyzed in the following sections.

#### A. Computational details

The theory presented in Sec. II has been implemented in a local version of the Gaussian suite of programs. Calculations have been made using different molecules: while in the comparison with experiments and for theoretical studies of realistic system complex molecules (lissamine and coumarin) have been used, for testing the model numerical stability a simpler system has been chosen. With the purpose of repeating a great number of rapid calculations, we have chosen to use a formaldehyde molecule, placed with the main axis perpendicular to the metal surface and with the oxygen atom the closest to the metal. For this small system, the calculation have been made at the HF level, using the 6-31G basis set. On the contrary, for the other calculations a DFT level of theory has been considered, exploiting the B3LYP hybrid functional and using the 6-31+G* basis set.

For calculations in solution, we built a cavity around the molecule done by interlocking spheres centered on atoms. The radii of the spheres are obtained by multiplying by a cavity size factor ($\alpha = 1.2$) the radii specific of the atoms (1.2 Å for H not linked to C atoms, 1.7 Å for C, 1.9 Å for CH$_2$ group, 1.56 Å for O, 1.6 Å for N, and 1.8 Å for S). In addition, spheres have been added, if necessary, to simulate the solvent excluded volume. As for the solvent, for all the calculations we considered water, characterized by a static dielectric constant $\varepsilon_0$ of 78.39 and an optical dielectric constant $\varepsilon_{op}$ of 1.776.

For the metallic part of the system only silver and gold have been considered, with the aim of remaining as close as possible to the most common experimental situations. The values for the dielectric constant of the metals at the different frequencies considered in our calculations have been taken from the handbook of Palik:

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Re($\varepsilon_{op}$)</th>
<th>Im($\varepsilon_{op}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400.0</td>
<td>-3.773</td>
<td>0.6747</td>
</tr>
<tr>
<td>413.3</td>
<td>-4.422</td>
<td>0.7301</td>
</tr>
<tr>
<td>427.5</td>
<td>-5.082</td>
<td>0.7232</td>
</tr>
<tr>
<td>442.8</td>
<td>-5.735</td>
<td>0.7536</td>
</tr>
<tr>
<td>459.2</td>
<td>-6.377</td>
<td>0.7402</td>
</tr>
<tr>
<td>476.9</td>
<td>-7.381</td>
<td>0.7181</td>
</tr>
<tr>
<td>495.9</td>
<td>-8.278</td>
<td>0.7488</td>
</tr>
<tr>
<td>516.6</td>
<td>-9.408</td>
<td>0.7982</td>
</tr>
<tr>
<td>539.1</td>
<td>-10.546</td>
<td>0.8385</td>
</tr>
</tbody>
</table>

For the metallic part of the system only silver and gold have been considered, with the aim of remaining as close as possible to the most common experimental situations. The values for the dielectric constant of the metals at the different frequencies considered in our calculations have been taken from the handbook of Palik:

#### B. Comparison between different numerical approaches: IEF and DPCM for a spherical particle

Numerical tests, not reported here, have confirmed the stability of the method with respect to changes in the most important parameters and the convergence of the results with those obtained with simpler models for which an analytical expression is available.

Here we report, instead, another important test: the comparison between the two different numerical procedures we
have described in Sec. II (namely, the IEF-PCM and the here developed DPCM) to compute the apparent charges. With respect to the IEF-PCM, which has been already tested in details for metallic planar surfaces, the procedure based on DPCM has more numerical sources of possible instability: the ones coming from the tessellation of the molecular cavity, that are also present in the IEF case, plus the ones characteristic of the metallic part of the system. Thus, the agreement of the results obtained with the two procedures is an implicit check for the stability of the proposed method.

For the case of a perfectly spherical metal particle, both methods can be exploited and the results can be directly compared. The system chosen for this comparison is composed by a formaldehyde molecule placed in proximity of a silver sphere with a radius of 50 Å. Calculations have been performed both in vacuo and in solvent (water) and the first two excited singlets have been examined. In each case, two different distances (3 Å and 8 Å) between the metal and the molecule have been used. The wavelength for which response of the system has been calculated is 520 nm, with the purpose of considering a spectral region in which the metal behaves in a known and characteristic way. This choice has been made without considering the real molecular transition wavelengths of formaldehyde: at this stage of the calculation, in fact, it is not necessary that the results have a direct physical meaning, since this is only an analysis of numerical accuracy.

The results, reported in Tables II and III, show a very good agreement between the two procedures especially for calculations in solution, for which the differences between IEF-PCM and DPCM are negligible if compared with the ones due to the different tessellations of the molecular cavity (a step common to both procedures and to PCM for homogeneous solutions).

### TABLE II. Electrostatic interaction free energy $\Delta G^e$ obtained from the difference between the free energy of the molecule interacting with the dielectric surrounding (metal) and the energy of the isolated molecule. Energies ($E_1$ and $E_2$) and radiative decay rates ($\Gamma_{\text{rad}}^{\text{Met}}$) for the two lowest singlet excited states of a formaldehyde molecule in vacuum and interacting with a silver spherical particle of radius $r = 5$ nm. Calculations have been performed with the IEF-PCM procedure and with the DPCM one. In both cases two distances ($D = 0.3$ nm and $D = 0.8$ nm) between the molecule and the metal surface have been considered.

<table>
<thead>
<tr>
<th>$\Delta G^e$ (kcal/mol)</th>
<th>Excited state : 1</th>
<th>Excited state : 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_1$ (eV)</td>
<td>$\Gamma_{\text{rad}}^{\text{Met}}$ (1/s)</td>
</tr>
<tr>
<td>Without metal</td>
<td>⋯</td>
<td>4.1094</td>
</tr>
<tr>
<td>DPCM ($D = 0.8$ nm)</td>
<td>$-1.44 \times 10^{-2}$</td>
<td>4.1099</td>
</tr>
<tr>
<td>IEFPCM ($D = 0.8$ nm)</td>
<td>$-1.51 \times 10^{-2}$</td>
<td>4.1099</td>
</tr>
<tr>
<td>DPCM ($D = 0.3$ nm)</td>
<td>$-1.80 \times 10^{-2}$</td>
<td>4.1174</td>
</tr>
<tr>
<td>IEFPCM ($D = 0.3$ nm)</td>
<td>$-1.83 \times 10^{-2}$</td>
<td>4.1175</td>
</tr>
</tbody>
</table>

### TABLE III. Electrostatic interaction free energy $\Delta G^e$ obtained from the difference between the free energy of the molecule interacting with the dielectric surrounding (metal+solvent) and the energy of the isolated molecule. Energies ($E_1$ and $E_2$) and nonradiative decay rates ($\Gamma_{\text{nonrad}}^{\text{Met}}$) for the two lowest singlet excited states of a formaldehyde molecule in solution (water) and interacting with a silver spherical particle of radius $r = 5$ nm. $N_{\text{Tes.}}$ values correspond to the approximate number of tesserae generated for each sphere used for building the molecular cavity. Calculations have been performed with the IEF-PCM procedure and with the DPCM one. Only the values obtained for a metal-molecule distance $D = 0.8$ nm are reported.

<table>
<thead>
<tr>
<th>$N_{\text{Tes.}}$</th>
<th>$\Delta G^e$ (kcal/mol)</th>
<th>Excited state : 1</th>
<th>Excited state : 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_1$ (eV)</td>
<td>$\Gamma_{\text{nonrad}}^{\text{Met}}$ (1/s)</td>
<td>$E_2$ (eV)</td>
</tr>
<tr>
<td>Without metal</td>
<td>200</td>
<td>$-3.724$</td>
<td>4.2570</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>$-3.719$</td>
<td>4.2567</td>
</tr>
<tr>
<td>DPCM</td>
<td>200</td>
<td>$-3.724$</td>
<td>4.2570</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>$-3.719$</td>
<td>4.2567</td>
</tr>
<tr>
<td>IEF-PCM</td>
<td>200</td>
<td>$-3.724$</td>
<td>4.2570</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>$-3.719$</td>
<td>4.2567</td>
</tr>
</tbody>
</table>
immersed in a dielectric representing the solvent and considers metal particles of spherical shape and characterized by a local response.

The system under study is the one resumed in Fig. 1: the lissamine molecule is attached to the metal particle via a thioether group and the distance between the principal three-ring system of the molecule and the metal surface is almost equal to 1 nm. The fluorescence signal coming from the molecule is at a wavelength $\lambda_{em} = 595$ nm and it is greatly influenced by the presence of the metal particle. The presence of a surface plasmon peak for the gold sphere at a wavelength of 520 nm has been experimentally observed.

We note that as here effects on the response properties due to the specific chemical interactions between the molecule and the metal (for example, possible chemical bonds between the molecule and the metal or formations of charge transfer states, or more in general, and in analogy with SERS, the “chemical effects”) are not considered, the system reported in Fig. 2(a) is, in the limit of our method, equivalent to the real lissamine. The study of the lowest molecular transitions of the system in water, without the metal, shows that such transitions mainly involve the condensed three-ring aromatic system and only marginally the fourth aromatic ring. Because of this, it seems to be useless to treat the whole molecule under study and thus, instead of considering the whole lissamine molecule, a simplified model system, named “Antra,” has been considered (see Fig. 2).

The calculations we have done on this system and on the reference system (in the following named “Lissa”) in gas phase and in solution (but without the metal) are resumed, respectively, in Tables IV and V.

The results reported in the two tables clearly show that the Antra model represents a reliable substitute of the by far more computationally expensive system Lissa both in gas phase and in solution.

In order to reduce the effects of all the intrinsic inaccuracies of the model (still present for a molecule in vacuum or in solution and without the metal) and to limit the consequence of using a molecule different from the experimental one, the calculated value of the molecular radiative decay rate without the metal but in the presence of the solvent has been scaled to the one experimentally found and all the results obtained with the metal, both for radiative and nonradiative processes, have been multiplied by this scaling factor. In addition, the whole nonradiative lifetimes, that include both the contribution from the metal-molecule interaction and the contribution from other possible processes ($\Gamma_{nonrad} = \Gamma_{nonrad, Met} + \Gamma_0^{nonrad}$), has been calculated approximating the latter term ($\Gamma_0^{nonrad}$) with the experimental value of the nonradiative lifetimes obtained for the system without the metal [$\Gamma_{nonrad,Exp} = 0.43 \times 10^9$ s$^{-1}$ (Ref. 4)].

To reproduce the experimental results, we have chosen to use the geometrical configuration of the different parts of the system as reported in Ref. 4. Thus, the model molecule has been placed with the three-ring system $\approx$ 1 nm far from the metal surface and oriented as shown in Fig. 1.

The results corresponding to this system are reported in Figs. 3 and 4 for the radiative and the nonradiative decay rate, respectively.

As far as concerns the radiative decay rate, the results we have obtained and the ones obtained in Ref. 4 with the GN model are quite similar; they show qualitative agreement with the experimental data but they quantitatively differ from the experiments, especially for the largest values of the metal radii. On the contrary, exploiting either the DPCM or the IEF-PCM procedures outlined above, the nonradiative decay rates are almost one order of magnitude closer to the experimental results than those obtained using the GN method.4 However, the results are still one order of magnitude far from

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$\lambda$ (nm)</th>
<th>Osc. St.</th>
<th>$\Gamma_{rad}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lissa</td>
<td>3.0426</td>
<td>408</td>
<td>0.4233</td>
</tr>
<tr>
<td>Antra</td>
<td>3.0228</td>
<td>410</td>
<td>0.1738</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$\lambda$ (nm)</th>
<th>Osc. St.</th>
<th>$\Gamma_{rad}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.</td>
<td>2.084</td>
<td>595</td>
<td>…</td>
</tr>
<tr>
<td>Lissa</td>
<td>2.8235</td>
<td>439</td>
<td>0.7196</td>
</tr>
<tr>
<td>Antra</td>
<td>2.8374</td>
<td>436</td>
<td>0.7344</td>
</tr>
</tbody>
</table>
the discrepancies between the calculated values are probably due to numerical errors, since they are less intense for the IEF based procedure.

There are several possible effects that may be the cause of the discrepancies between the calculated values (both with the model presented in this paper and with the GN model) and the experimental ones. For example, both the theoretical models do not take into account nonlocal metal response effects and “chemical effects.” Moreover, results have been obtained considering only one of the possible geometrical configurations of the system, while other molecular orientations and values of the metal-molecule distance could be considered.

As far as concerns the nonlocal behavior of the metal, it has been recently shown that using different kinds of nonlocal dielectric constants can either increase or decrease the nonradiative molecular decay rates with respect to what obtained using a local response for the metal body. In particular, it has been calculated that the use of the hydrodynamic dielectric constant decreases the nonradiative decay rates for a molecule close to an infinite planar surface (see Ref. 16). On the other side, exploiting for the same system the more complex and reliable Lindhard–Mermin dielectric constant, that takes into account nonlocal effects omitted in the hydrodynamic theory (in particular, the excitation of electron-hole pairs), one obtains an increase of the nonradiative decay rates. Thus, it is difficult to predict the effect of nonlocality on the calculated decay rates. If we assume for the spherical particle a behavior similar to the one reported for the planar surface, it seems that by describing in a proper way the nonlocal behavior of the metal, the agreement between theoretical and experimental results becomes worse, contrary to what suggested in Ref. 4.

Similarly, taking into account the chemical effects, such as the formation of a charge transfer state between the metal and the molecule, would further increase the deviation of the theoretical values from the experimental ones, since these phenomena represent new ways for the molecule to undergo a nonradiative decay.

Another factor which could be tested is the inclusion of quantum size effect in the description of the dielectric constant. For the dimensions of the systems under study, the main correction is that due to the variation in the electron mean free path with respect to the bulk metal. This effect has not been considered in the results reported in Figs. 3 and 4; as a matter of fact, it can be included in the model as shown in Ref. 15 but the variation we obtain is just a slight increase of both the radiative and the nonradiative decays for the smallest particles.

In order to explore the effects of the relative metal-molecule geometry, calculations have been performed on the same system, but varying the geometrical parameters and the relative metal-molecule configuration. Results obtained for different values of the metal-molecule distance are resumed in Table VI, while the radiative and nonradiative decay rate obtained considering an orientation of the molecule perpendicular to the metal surface are reported in Table VII.

### Table VI. Radiative and nonradiative decay rates for the lissamine molecule (model Antra) as a function of the distance between the three ring aromatic system and the metal surface. The values reported have been obtained for a metal radius of 100 Å. [The correction for the electron mean free path has been taken into account (Ref. 15)].

<table>
<thead>
<tr>
<th>Distance (Å)</th>
<th>7.0</th>
<th>8.0</th>
<th>9.0</th>
<th>10.0</th>
<th>10.5</th>
<th>13.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^\text{rad}$ (s$^{-1}$)</td>
<td>$4.41\times10^7$</td>
<td>$3.76\times10^7$</td>
<td>$3.20\times10^7$</td>
<td>$2.59\times10^7$</td>
<td>$2.50\times10^7$</td>
<td>$1.64\times10^7$</td>
</tr>
<tr>
<td>$\Gamma^\text{nonrad}$ (s$^{-1}$)</td>
<td>$6.02\times10^{11}$</td>
<td>$4.24\times10^{11}$</td>
<td>$3.73\times10^{11}$</td>
<td>$2.78\times10^{11}$</td>
<td>$2.71\times10^{11}$</td>
<td>$1.69\times10^{11}$</td>
</tr>
</tbody>
</table>
The variations of the decay rates with respect to these geometrical parameters are large: thus, a statistical averaging of the quantities examined, that takes into account all the possible configurations of the system, can be important and it can be suggested as an element to consider in future developments. In addition, differently to all the other sources of discrepancies (such as charge transfer effects or the molecular orientation), increasing the value of the metal-molecule distance makes possible to improve the agreement with the calculated results: it is sufficient to consider a chromophore placed at a distance of \( \sim 20 \) Å from the metal surface to obtain results in almost quantitative agreement with the experimental ones. Thus, it is possible that the experimental values refer, for example, to a system in which the molecule is attached to a nonmetallic layer covering the gold spheres. Another possibility is that the measured signal came from lissamine molecules close to the metal particle but not directly attached to it, maybe placed on a second molecular layer. In fact in our calculations we have seen that an hypothetical second layer presents a slower de-excitation rate, which may dominate the experimental measure.

### D. Lifetimes and quantum yields of a coumarin dye near complex metal nanoparticles

In addition to the dimension of the metal particle, the model has been used to test the influence of the metal shape on the excited state properties, with the purpose of finding suitable configurations that enhance or decrease such properties. As far as we know, no experimental results are available about this subject and we have, thus, decided to consider an arbitrary system, trying to remain as general as possible. In particular, in this section we shall examine the influence of a complex shaped metal particle on the excited state properties of a coumarin-type molecule. The test molecule chosen for this series of calculation is derived from the coumarin 1, although its structure is attached to a nonmetallic layer covering the gold spheres. Two different orientations of the coumarin molecule with respect to the metal surface have been used: since the molecular transition dipole moment is oriented along the main axis of the aromatic two-ring system, a configuration with the transition dipole perpendicular and one with the dipole tangent to the metal surface have been considered.

Calculations have been performed considering silver as the metal (the correction for the electron mean free path has been taken into account\(^{15}\)) and using three different shapes for the particle: these have been generated as the union of two or three spheres of radius equal to \( 50 \) Å.

Let us now pass to analyze the three different aggregates separately, starting from the simplest one.

#### 1. Two-sphere aggregate

The first aggregate that we have analyzed is the one composed by two identical interlocking silver spheres with centers placed at a distance of \( 50 \) Å (i.e., equal to their radius).

To have a more immediate analysis of the effects of the metal aggregate on the decay of coumarin, in Fig. 6 we have plotted the coumarin fluorescence quantum yield \( \Phi_{\text{fl,Met}} \) for two different orientations: one (a) in which its transition dipole moment is directed perpendicular to the metal surface and one (b) in which the same moment is tangent to the metal surface.

We recall that the fluorescence quantum yield \( \Phi_{\text{fl,Met}} \) of a molecule near the metal particle is defined as

\[
\Phi_{\text{fl,Met}} = \frac{\Gamma_{\text{rad,fl}}}{\Gamma_{\text{rad,fl}} + \Gamma_{\text{nonrad,fl}} + \Gamma_{\text{nonrad,Met}}} \tag{11}
\]

where \( \Gamma_{\text{rad,fl}} \) and \( \Gamma_{\text{nonrad,fl}} \) are the quantities already examined in previous sections, while \( \Gamma_{\text{nonrad,Met}} \) refer to all the nonradiative processes not related to the presence of the metal body. Starting form the knowledge of the fluorescence quantum yield for the molecule in solution without the metal (obtained, for example, from experimental results)

\[
\Phi_{\text{fl,0}} = \frac{\Gamma_{\text{rad,fl,0}}}{\Gamma_{\text{rad,fl,0}} + \Gamma_{\text{nonrad,fl,0}}} \tag{12}
\]

and considering for \( \Gamma_{\text{rad,fl,0}} \) the expression reported in Eq. (3), it is easy to find an indicative estimate for \( \Gamma_{\text{nonrad,fl,0}} \). For the case under study, using the experimental values of \( \Phi_{\text{fl,0}} = 0.055 \) for the coumarin 1 in water (as reported in Ref. 30) and the already mentioned value of \( \Gamma_{\text{rad,fl,0}} = 10^8 \text{ s}^{-1} \), a magnitude of \( \Gamma_{\text{nonrad,fl,0}} = 10^8 \text{ s}^{-1} \) is obtained. As will be clear in

### TABLE VII. Radiative and nonradiative decay rates for the lissamine molecule (model Antra) as a function of the orientation of the three ring aromatic system with respect to the metal surface. The values reported have been obtained for a metal radius of 100 Å and for a metal-molecule distance of 10 Å. [The correction for the electron mean free path has been taken into account (Ref. 15)].

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Tangent</th>
<th>Perpendicular</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{\text{rad}} ) ( (s^{-1}) )</td>
<td>( 2.59 \times 10^7 )</td>
<td>( 3.22 \times 10^7 )</td>
</tr>
<tr>
<td>( \Gamma_{\text{nonrad}} ) ( (s^{-1}) )</td>
<td>( 2.78 \times 10^{11} )</td>
<td>( 2.50 \times 10^{12} )</td>
</tr>
</tbody>
</table>
the following, this value is much lower than the calculated nonradiative decay rates due to the metal, $\Gamma_{\text{nonrad}, \text{Met}}$.

Due to the symmetry of the system, the grid of points used to plot the quantum yield has been obtained considering quadrants of spheres having the same center of one of the two spheres forming the aggregate but with larger radii: namely, the points used have distances from the metal surface of 7, 14, 28, and 56 Å, respectively. The quantum yields calculated in this way are reported for both orientations in Fig. 6. A color scale has been used to represent the results (blue: low yields, red: high yields), and the positions of the molecule for which the calculations have been performed are indicated with white squares (the color in the rest of the space is obtained from linear interpolation of the calculated results). The depicted values show the characteristic behavior of RET processes, with a quenching of the molecular fluorescence near the metal particle and a gradual recovery of the normal quantum yield in solution as the molecule-metal distance increases. On the other side, a strong dependence from the molecular orientation and position is observed: in the case of the perpendicular orientation [Fig. 6(a)], the different behavior as a function of the different molecular locations (along the particle main axis or on the $X = 0$ line) is evident. In particular, it seems that the quenching effects of the metal are longer ranged along the main axis than along the $X = 0$ line. Moreover, the fluorescence quenching for the tangent orientation [Fig. 6(b)] is bigger than for the perpendicular one [Fig. 6(a)] at all the considered coumarin-metal distances.

To better understand where this orientation dependence comes from, we discuss here the behavior of the two decay rates (radiative and nonradiative) separately. The influence of the orientation of the molecule with respect to the metal particle seems to be only of secondary importance on the calculation of nonradiative decay rates: in fact, we obtain results showing a strong dependence only on the metal-molecule distance (with a decrease of two orders of magnitude, from $10^{12}$ to $10^{10}$ s$^{-1}$, passing from a metal-molecule distance of 5 Å to a distance of 50 Å).

On the contrary, the radiative decay rate strongly depends on the orientation of the molecule. In particular, when the molecular transition dipole moment is oriented along the main axis of the metal particle, the radiative decay rate is largely increased with respect to the case without the metal. By contrast, when the molecular dipole is directed along the second orientation considered (orthogonal to the metal particle main axis) the radiative decay rate is decreased in proximity of the metal. In both cases, for metal-molecule distances greater than 50 Å the influence of the metal on the radiative process becomes almost negligible.

These opposite results for the two different orientations can be explained in terms of the imaginary and real components of the polarizability tensor of the metal aggregate [see Eq. (10)]. These components are reported in Figs. 7 and 8, respectively.

As it can be seen from the graphs, a typical resonance behavior is found around 460 nm for the diagonal component along the main axis of the metal particle (the $x$ component in the coordinate system used for the calculation), i.e., exactly in the region of the coumarin fluorescence emission ($\sim$ 465 nm). This resonance is due to the excitation of a surface plasmon of the complex shaped metal particle, and the fre-
frequency of such resonance is the result of the combination of the values of the frequency dependent permittivity of the metal and the shape of the aggregate. The surface plasmon excited at this frequency is that having charge density oscillations along the main axis of the particle, since the resonance behavior is observed for the diagonal polarizability component oriented along this axis. Clearly, such a resonance will have a great influence on the molecular decay rates. Indeed, when the molecular transition dipole moment is oriented along the main axis of the metal particle, we observe an increase of two orders of magnitude in the radiative decay rate with respect to the case without the metal (~\(10^6\) s\(^{-1}\)) for a metal molecule distance of 5 Å versus ~\(10^8\) s\(^{-1}\) for the molecule alone in water; this is due to the large contribution of the metal (~\(\mu\) of Eq. (7)) to the total transition dipole \(\mu_{\text{tot}}\). The same effect cannot be found for the other orientation as, in this case, the real part of the polarizability diagonal components to be considered (\(yz\) and \(zz\)) are out of resonance and negative. Thus the induced dipole is opposite (and comparable in magnitude) to that of the molecule, the transition dipole \(\mu_{\text{tot}}\) is smaller than the molecular one and the radiative decay rate decreases.

2. Linear three-sphere aggregate

The second kind of aggregate that we have considered is the one composed by three spherical particles, the centers of which are placed on a straight line at a distance of 50 Å. This particular shape has been chosen in order to try to maximize the enhancement of the molecular fluorescence: it has been already tested (see Ref. 15) that, for a linear configuration of the metal spheres, increasing the number of spheres gives an enhancement of the strength of the metallic plasmon resonances along the main axis of the aggregate. However, by changing the aspect ratio of the nanoparticle, also the frequency of the surface plasmon resonance will change. Indeed, we have found that even if the elements of the polarizability calculated with Eq. (10) are greater, in general, than the ones calculated for the previous aggregate (about twice the ones reported in Figs. 7 and 8), the plasmon resonance has its peak quite redshifted from the molecular fluorescence wavelength (\(\lambda_{\text{Met}} = 540\) nm). The effects of these two phenomena (redshifting of the plasmon resonance and increasing of the resonance strength) almost annihilate each other at the wavelength of coumarin fluorescence emission (\(\approx 465\) nm); the value of \(|\alpha_{xx}\text{Met}|\) for the three-sphere aggregate (\(\approx 7 \times 10^5\) a.u.) at this wavelength is similar to that for the two-sphere aggregate (\(\approx 9 \times 10^6\) a.u.). However, while in the case of the two-sphere aggregate \(\alpha_{xx}\text{Met}\) at 465 nm is almost purely imaginary (see Figs. 7 and 8), for the three-sphere case \(\alpha_{xx}\text{Met}\) has real and imaginary parts of comparable magnitude (Re[\(\alpha_{xx}\text{Met}\])\(\approx -5 \times 10^5\) a.u. and Im[\(\alpha_{xx}\text{Met}\])\(\approx 5 \times 10^5\) a.u.). The negative sign of Re[\(\alpha_{xx}\text{Met}\]) means that the real part of the dipole induced in the metal particle oscillates with a phase, which is opposite to that of the molecular transition dipole (i.e., it is negative when the molecular dipole is positive and vice versa). This creates a peculiar nonmonotonic trend for the radiative decay rate as a function of the distance for the molecule (radial orientation of the transition dipole) moving along the direction of the aggregate main axis. Such trend is documented in Fig. 9, where the values of radiative decay rate is depicted by exploiting a color scale. The minimum of the radiative decay rate along the direction of the particle main axis is clearly visible at a metal-molecule distance of about 30 Å. Such minimum occurs when the out-of-phase dipole induced in the metal (whose value depends on the molecule-metal distance) compensates for the molecular transition dipole, giving a very small total dipole.

The resulting quantum yields for both the orientations are reported in Fig. 10.

The peculiar nonmonotonic trends of the radiative rate for the radial molecular orientation is not transferred to the corresponding quantum yield [Fig. 10(a)] that shows instead a monotonic behavior as a function of the metal-molecule distance. The reason of such difference is that in determining the quantum yield, the monotonic behavior of the nonradiative decay rate (not shown) prevails on the nonmonotonic one of the radiative rate. Note that differently from the two-
3. Triangular three-sphere aggregate

Finally, we analyzed a more complex aggregate, obtained from three spheres placed on the vertex of an equilateral triangle of sides equal to the spheres radius (50 Å). This particle does not show the cylindrical symmetry characteristic of the two previous shapes and, for this reason, not just a two-dimensional plane but the whole three-dimensional volume outside the metal must be considered. For the same reason, only the first molecular orientation with respect to the metal surface has an univocal definition and, thus, can be reported and analyzed in a simple way.

An analysis of the metal response shows that the two diagonal components of the polarizability that lie on the metal particle plane (the one containing the centers of the spheres) are equal. They have a resonance at the wavelength \( \lambda_{\text{M}Nil} = 450 \text{ nm} \) close to the one of the two spheres reported in Figs. 7 and 8. These components of the polarizability should be equal due to the symmetry of the aggregate and the fact that they are indeed equal in our calculations is a further proof of the quality of the implemented numerical treatment.

As expected, the radiative decay rate is enhanced for the molecule placed near the three vertices of the triangle while only a low fluorescence quenching is reported for the molecule placed on the vertices of the triangle.

IV. CONCLUSIONS

In this paper we have presented a methodology to evaluate the influence of a metal particle of complex shape on the decay rates of an excited molecule in its close proximity. With respect to other alternative theories, the one outlined in this paper makes it possible to characterize the molecular response at an accurate QM level, paying attention to both the radiative and the nonradiative processes. At the same time, the proposed model has a large flexibility in the definition of the shape of the metal body and thus it allows us to consider a large class of systems and to compare to many different experiments.

The preliminary comparisons with experimental results show that the model is in qualitative agreement with the experiments but there are still sources of inaccuracy. The causes of these discrepancies have been shortly analyzed. Some of the effects neglected in the present work, in particular, the nonlocal behavior of the metal body, can be included in the theory and will be part of future developments.

The decay rates and the quantum yields of coumarine close to nanoparticles have been studied as a function of various geometrical parameters of the system (the molecule position and orientation, the shape of the nanoparticle). We found that when the transition dipole of the molecule is perpendicular to the particle surface, quantum yields are quite sensitive to the molecule position relative to the particle. We remark that for the systems considered in the present article, only quenching of the fluorescence was observed: for such small nanoparticles, we did not observe “hot spots” able to enhance the molecular fluorescence. Remarkably, a kind of “cold spot” for the radiative decay rate was instead observed for the linear three-sphere aggregate at about 30 Å from the metal surface. The presence of such behavior at the proper molecular emission frequency is related to the complex shape of the aggregate that allows to modulate the surface plasmon resonances.
The work we have presented is a first step to model complex systems. Starting from what has been shown above, it is possible to consider metallic aggregates bigger and more complex than the ones examined. In fact, according to the hierarchical principle exploited in the theoretical section, a large metallic aggregate can be decomposed in the region closest to the molecule (the most important one), that can be treated with the model discussed in this paper, and the remainder of the aggregate that can be described with a more approximate method (such as a coarse-grained discrete dipole approximation, or DDA). As it has been done for SERS near fractal aggregates, using this approach it is possible to exploit the implemented method to calculate enhancement factors for the fluorescence of a molecule in close proximity of a metallic fractal aggregate. Also the effects of metallic fractal surfaces on excited states properties can be analyzed starting from what reported in this paper.

The complex system composed by the metallic tip of a SNOM interacting with a single molecule also be treated by the model presented in this work. For this system it is possible to include in the QM molecular equations only the metal part closest to the molecule and to describe the remaining part of the tip using, for example, the DDA model. In this case, due to the macroscopic dimension of the considered device, a whole electrodynamic treatment, instead of exploiting a quasistatic approximation, would be necessary. In addition, in order to reproduce experimental situations, the description of the dielectric surrounding must include the medium on which the molecule is deposited. We reserve such studies for future communications.

APPENDIX: GREEN’S FUNCTION FOR A SPHERICAL PARTICLE

Let us consider a system constituted by a metallic spherical particle of radius $a$ and dielectric constant $\varepsilon_{\text{met}}$ placed on the origin of coordinates and surrounded by a solvent of dielectric constant $\varepsilon_{\text{sol}}$. The Green’s function for the space external to the sphere can be written, in terms of Legendre’s functions $P_n(\cos \theta)$, as (Ref. 31)

$$G^E(\vec{r},\vec{r}') = \frac{1}{\varepsilon_{\text{sol}}} \frac{1}{|\vec{r}-\vec{r}'|} + \sum_{n=0}^{\infty} \frac{1}{\varepsilon_{\text{sol}}^n d^{n+1}} a^{2n+1} c^{n+1} \left[ \frac{n (\varepsilon_{\text{sol}} - \varepsilon_{\text{met}})}{n \varepsilon_{\text{sol}} + (n+1) \varepsilon_{\text{met}}} \right] P_n(\cos \theta), \tag{A1}$$

where $\vec{r} = c\hat{r}$, $\vec{r}' = d\hat{r}'$ and $\theta$ is the angle between $\vec{r}$ and $\vec{r}'$. Equation (A1) reduces to the simpler expression

$$G^E(\vec{r},\vec{r}') = \frac{1}{\varepsilon_{\text{sol}}} \frac{1}{|\vec{r}-\vec{r}'|} \left[ \frac{a}{d} \right] - \frac{a}{d^2} \frac{\partial^2}{\partial r^2} + \frac{a}{d|\vec{r}|} \right], \tag{A2}$$

when the metal behaves as a perfect conductor (i.e., for $\varepsilon_{\text{met}} \rightarrow \infty$).

The series that appear in the second member of Eq. (A1) must be truncated to a finite order $N$ for the numerical calculation. For evaluating the best procedure to calculate $G^E$ it is necessary to consider one by one all the different possible situations.
(a) For $d \gg a$ (or $c \gg a$) the contribution to $G^E$ due to the presence of the sphere becomes small and the error due to the truncation of the series becomes small too; each term of the series is, in fact, at least $a/d$ times less than the previous one. Thus, analyzing the quantity $(a/d)^n$ it is possible to define a criterion for choosing the number of terms $N$ to include in the expression.

(b) On the other side, for $r$ and $r'$ very close to the metal ($(d-a)/a \approx 0, (c-a)/a \approx 0$) the problem reduces to the case of a planar infinite surface, and the almost exact Green’s function is that of the infinite metal plane

$$G^E(r,r') = \frac{1}{\epsilon_{\text{sol}} |r-r'|} \left[ \frac{1}{\epsilon_{\text{met}} + \epsilon_{\text{sol}}} \right] \frac{1}{|\bar{r} - \hat{R}(r')|},$$

(A3)

where $\bar{R}(r')$ is the symmetric of $r'$ with respect to the metallic plane. The difference between the two Green’s functions can be evaluated by expressing the second quantity in the right side of Eq. (A3) in terms of Legendre’s functions and by subtracting its contribution from the series of Eq. (A1). For the cases examined ($(d-a)/a \approx 0$) the terms of the series arising from this subtraction are small and the truncation error is small too.

(c) The intermediate situations have been referred, in the present work, to the closest of the two extreme cases considered above. In such intermediate situations, the number of series terms to be summed can be quite large, and the calculation of $G^E$ can become computationally demanding. Note, however, that in realistic applications we are often in the case $d-a/a \ll 1$ (i.e., metallic particles much larger than the molecule and the metal-molecule distance). Although it has not been implemented in present work, an alternative expression can be exploited: it is possible to show that

$$\sum_{n=0}^{N} \frac{1}{\epsilon_{\text{sol}}^n} \left[ \frac{1}{(n+1)} \frac{1}{\epsilon_{\text{met}}^n} \right] P_n(\cos \theta)$$

$$= \frac{\epsilon_{\text{sol}} - \epsilon_{\text{met}}}{\epsilon_{\text{sol}} + \epsilon_{\text{met}}} \left[ \frac{a}{d} \frac{\partial}{\partial r} \right]$$

$$- \frac{\epsilon_{\text{sol}}}{\epsilon_{\text{sol}} + \epsilon_{\text{met}}} \int_0^{\pi} \left( \frac{\partial}{\partial x} \right)^2 \left( \frac{\epsilon_{\text{met}}(\epsilon_{\text{sol}} + \epsilon_{\text{met}})}{\|r-x\|^2} \right) \frac{1}{\|r-x\|^2} \, dx.$$

(A4)

In Eq. (A4), the series is divided in two different contributions, the first arising from an “image charge,” similar to the one obtained in the case of a conductor sphere, and the second one arising from a continuous linear distribution of charge. Thus, the series is transformed in an integral that can be numerically calculated.