

Optical transitions in semiconductor nanostructures

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Abstract

Employing the Maxwell equations and conventional boundary conditions for the radiation field on the nanostructure interfaces, we compute the radiative spontaneous decay rate of optical transitions in spherical semiconductor nanocrystals, core–shell nanocrystals and nanostructures comprising more than one shell. We also show that the coupling between optical transitions localized in the shell of core–shell nanocrystals and radiation field is determined by both conventional electro-multipole momenta and electro-multipole “inverse” momenta. The latter are proportional to the core radius even for interband transitions that should result in very strong optical transitions.

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1. Introduction

The radiative spontaneous decay rate, Γ , of an optical transition of frequency ω and dipole momentum d in a point-like emitter, such as an atom or a molecule, embedded into a dielectric host of permittivity ε is described by well-known expression [1] (speed of light $c = 1$):

$$\Gamma = \frac{4}{3}\omega^3 d^2 \sqrt{\varepsilon}. \quad (1.1)$$

However, in the case of colloidal semiconductor nanocrystals experiments show an essential depression of the decay compared to the value determined by Eq. (1.1).

To explain this depression, Wehrenberg, Wang, and Guyot-Sionnest [2] noted that the above expression, derived for point-like emitters, does not take into account the local field effect, or the screening of the radiation field inside a nanocrystal of finite size. If a spherical nanocrystal of permittivity ε_1 is embedded into a dielectric host of permittivity ε_2 , the internal electric field (inside the nanocrystal) \mathbf{E}_{int} is weaker, if $\varepsilon_1 > \varepsilon_2$, in comparison with the external field \mathbf{E}_{ext} in the host [1]:

$$\mathbf{E}_{\text{int}} = \frac{3}{2 + \varepsilon_1/\varepsilon_2} \mathbf{E}_{\text{ext}}. \quad (1.2)$$

Therefore, the expression (1.1) should be replaced by:

$$\Gamma = \frac{4}{3}\omega^3 d^2 \left(\frac{3}{2 + \varepsilon_1/\varepsilon_2} \right)^2 \sqrt{\varepsilon_2}. \quad (1.3)$$

The estimates of radiative lifetime done with Eq. (1.3) for PbSe and CdSe nanocrystals [2] show a good agreement with experimental data. However, the expression (1.2) is derived under assumption that the field variation is small on the nanocrystal size scale, while the radiation field exhibits obviously a strong angular dependence [3]. For example, the intensity of light, I , emitted

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by an electric dipole polarized along the Z -axis is varied as $I \sim \sin^2 \theta$, where θ is the angle between the direction of emission and the Z -axis. It is clear also that Eq. (1.3) should be essentially modified in the case of core–shell nanocrystals and nanostructures comprising more than one shell.

Therefore, employing the Maxwell equations and conventional boundary conditions for the radiation field on nanostructure interfaces, we compute in this Letter the radiative spontaneous decay rate of optical transitions in bare semiconductor nanocrystals, core–shell nanocrystals and nanostructures comprising more than one shell. We also show that the coupling of optical transitions localized in the shell of core–shell nanocrystals to the radiation field is determined by both conventional electro-multipole momenta and electro-multipole “inverse” momenta. The latter are proportional to the core radius even for interband transitions that should result in very strong optical transitions.

2. Maxwell equations

The Maxwell equations for the Fourier components of the electric, $\mathbf{E}_\omega(\mathbf{r})$, and magnetic, $\mathbf{H}_\omega(\mathbf{r})$, fields are written as:

$$\text{curl } \mathbf{E}_\omega(\mathbf{r}) = i\omega \mathbf{H}_\omega(\mathbf{r}), \quad (2.1)$$

$$\text{curl } \mathbf{H}_\omega(\mathbf{r}) = -i\omega \varepsilon(r) \mathbf{E}_\omega(\mathbf{r}), \quad (2.2)$$

$$\text{div } \mathbf{E}_\omega(\mathbf{r}) = 0, \quad (2.3)$$

$$\text{div } \mathbf{H}_\omega(\mathbf{r}) = 0. \quad (2.4)$$

In the simplest case of a bare nanocrystal of radius R_1 and permittivity ε_1 embedded in a host of permittivity ε_2 , the dielectric function $\varepsilon(r)$ in the above equations has obviously the form:

$$\varepsilon(r) = \begin{cases} \varepsilon_1, & r < R_1, \\ \varepsilon_2, & r > R_1. \end{cases} \quad (2.5)$$

In more general problem of a core–shell nanocrystal with the core of radius R_1 and permittivity ε_1 and the shell of radius R_2 and permittivity ε_2 embedded in a host of permittivity ε_3 , we obviously have:

$$\varepsilon(r) = \begin{cases} \varepsilon_1, & r < R_1, \\ \varepsilon_2, & R_1 < r < R_2, \\ \varepsilon_3, & r > R_2. \end{cases} \quad (2.6)$$

Finally, the dielectric function of the nanostructure comprising two shells is written as:

$$\varepsilon(r) = \begin{cases} \varepsilon_1, & r < R_1, \\ \varepsilon_2, & R_1 < r < R_2, \\ \varepsilon_3, & R_2 < r < R_3, \\ \varepsilon_4, & r > R_4, \end{cases} \quad (2.7)$$

where ε_1 is the core permittivity, ε_2 and ε_3 are the permittivities of the shells of the thicknesses $\Delta_1 = R_2 - R_1$ and $\Delta_2 = R_3 - R_2$, respectively, while ε_4 is the permittivity of the host.

For the scalar, $\Phi_\omega(\mathbf{r})$, and vector, $\mathbf{A}_\omega(\mathbf{r})$, potentials:

$$\mathbf{H}_\omega(\mathbf{r}) = \text{curl } \mathbf{A}_\omega(\mathbf{r}), \quad (2.8)$$

$$\mathbf{E}_\omega(\mathbf{r}) = -\nabla \Phi_\omega(\mathbf{r}) + i\omega \mathbf{A}_\omega(\mathbf{r}), \quad (2.9)$$

related by the Lorenz gauge:

$$-i\omega \varepsilon(r) \Phi_\omega(\mathbf{r}) + \text{div } \mathbf{A}_\omega(\mathbf{r}) = 0 \quad (2.10)$$

the Maxwell equations take the form:

$$\Delta \Phi_\omega(\mathbf{r}) + \omega^2 \varepsilon(r) \Phi_\omega(\mathbf{r}) = 0, \quad (2.11)$$

$$\Delta \mathbf{A}_\omega(\mathbf{r}) + \omega^2 \varepsilon(r) \mathbf{A}_\omega(\mathbf{r}) = 0, \quad (2.12)$$

where Δ stands for the Laplace operator.

The coupling of electronic transitions to the radiation field is expressed in terms of the potentials:

$$V = \int d^3 \mathbf{r} [\rho(\mathbf{r}) \Phi_\omega(\mathbf{r}) + \mathbf{j} \cdot \mathbf{A}_\omega(\mathbf{r})], \quad (2.13)$$

where ρ and \mathbf{j} are the densities of charge and current in the nanocrystal, respectively. The integration in the above equation is performed over the volume of the electron localization.

3. Radiation field

3.1. Field inside the core

Since the field inside the core, $r < R_1$, must be nonsingular at the origin of the spherical polar coordinate system, $r = 0$, we can solve Eqs. (2.11) and (2.12) employing the Fourier transform of the potentials:

$$\Phi_\omega(\mathbf{k}) = \int d^3\mathbf{r} \Phi_\omega(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}, \quad \mathbf{A}_\omega(\mathbf{k}) = \int d^3\mathbf{r} \mathbf{A}_\omega(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}.$$

Then, these equations take the form:

$$[k^2 - \omega^2 \varepsilon_1(\omega)] \Phi_\omega(\mathbf{k}) = 0, \quad (3.1)$$

$$[k^2 - \omega^2 \varepsilon_1(\omega)] \mathbf{A}_\omega(\mathbf{k}) = 0. \quad (3.2)$$

There are two types of solutions of the above equations—electric and magnetic—with the quantum numbers: frequency ω , angular momentum j , and projection thereof m . For the electric type the potentials are found to be:

$$\Phi_{\omega jm}^{(e)}(\mathbf{k}) = \frac{a}{n_1} \delta(k - k_1) C Y_{jm}(\mathbf{n}), \quad (3.3)$$

$$\mathbf{A}_{\omega jm}^{(e)}(\mathbf{k}) = a \delta(k - k_1) [\mathbf{Y}_{jm}^{(e)}(\mathbf{n}) + C \mathbf{n} Y_{jm}(\mathbf{n})], \quad (3.4)$$

while for the magnetic type they are given by:

$$\Phi_{\omega jm}^{(m)}(\mathbf{k}) = 0, \quad (3.5)$$

$$\mathbf{A}_{\omega jm}^{(m)}(\mathbf{k}) = a \delta(k - k_1) \mathbf{Y}_{jm}^{(m)}(\mathbf{n}). \quad (3.6)$$

Here,

$$k_1(\omega) = \omega \sqrt{\varepsilon_1(\omega)} = \omega n_1(\omega)$$

is the wavevector in the core, $n_1(\omega) = \sqrt{\varepsilon_1(\omega)}$ is the refractive index of the core, $\mathbf{n} = \mathbf{k}/k$ is the unit vector along the wavevector direction, a and C are arbitrary constants. The spherical harmonic functions $Y_{jm}(\mathbf{n})$ and the spherical vectors $\mathbf{Y}_{jm}^{(\alpha)}(\mathbf{n})$, where $\alpha = e, m, l$ stands respectively for the electric, magnetic, and longitudinal types, are defined in Ref. [3]. The expressions (3.3)–(3.6) generalize well-known vacuum solutions [3] to the case of a medium with the refractive index $n \neq 1$.

In this Letter, we restrict our computations to the case of the electric multipole radiation. Therefore, hereafter we use the potentials of the electric type (3.3) and (3.4) omitting the upper index (e). Making use of Eqs. (2.8) and (2.9) we find for the magnetic and electric fields inside the core:

$$\mathbf{H}_{\omega jm}(\mathbf{k}) = i a k_1 \delta(k - k_1) \mathbf{Y}_{jm}^{(m)}(\mathbf{n}), \quad (3.7)$$

$$\mathbf{E}_{\omega jm}(\mathbf{k}) = i a \omega \delta(k - k_1) \mathbf{Y}_{jm}^{(e)}(\mathbf{n}). \quad (3.8)$$

The fields in \mathbf{r} -space are found by the inverse Fourier transform. For the scalar potential we have:

$$\Phi_{\omega jm}(\mathbf{r}) = i^j a C \frac{\omega k_1}{2\pi^2} g_j(k_1 r) Y_{jm}\left(\frac{\mathbf{r}}{r}\right), \quad (3.9)$$

where the spherical Bessel functions are defined as:

$$g_j(z) = \sqrt{\frac{\pi}{2z}} J_{j+1/2}(z)$$

and $J_{j+1/2}(z)$ are the Bessel functions of semi-integer order. The magnetic and electric fields are found to be:

$$\mathbf{H}_{\omega jm}(\mathbf{r}) = i^{j+1} a \frac{k_1^3}{2\pi^2} g_j(k_1 r) \mathbf{Y}_{jm}^{(m)}\left(\frac{\mathbf{r}}{r}\right), \quad (3.10)$$

$$\mathbf{E}_{\omega jm}(\mathbf{r}) = \mathbf{E}_{\omega jm}^\perp(\mathbf{r}) + \mathbf{E}_{\omega jm}^\parallel(\mathbf{r}), \quad (3.11)$$

where

$$\mathbf{E}_{\omega jm}^\perp(\mathbf{r}) = i^j a \frac{\omega k_1^2}{2\pi^2} \frac{1}{2j+1} [-j g_{j+1}(k_1 r) + (j+1) g_{j-1}(k_1 r)] \mathbf{Y}_{jm}^{(e)}\left(\frac{\mathbf{r}}{r}\right), \quad (3.12)$$

$$\mathbf{E}_{\omega jm}^\parallel(\mathbf{r}) = i^j a \frac{\omega k_1}{2\pi^2} \sqrt{j(j+1)} \frac{g_j(k_1 r)}{r} \mathbf{Y}_{jm}^{(l)}\left(\frac{\mathbf{r}}{r}\right) \quad (3.13)$$

are respectively the transverse and longitudinal components.

3.2. Field outside the nanocrystal core

Let us now find the solutions of the electric type outside the core, $r > R_1$. The general solutions for the scalar potential and magnetic field are convenient to write in the form:

$$\Phi_{\omega jm}(\mathbf{r}) = i^j C \frac{\omega k_2}{2\pi^2} [B_1 g_j(k_2 r) + B_2 y_j(k_2 r)] Y_{jm} \left(\frac{\mathbf{r}}{r} \right), \quad (3.14)$$

$$\mathbf{H}_{\omega jm}(\mathbf{r}) = i^{j+1} \frac{k_2^3}{2\pi^2} [B_1 g_j(k_2 r) + B_2 y_j(k_2 r)] \mathbf{Y}_{jm}^{(m)} \left(\frac{\mathbf{r}}{r} \right), \quad (3.15)$$

where $k_2 = \omega \sqrt{\varepsilon_2} = \omega n_2$, B_1 and B_2 are arbitrary coefficients to be found from boundary conditions, and $y_j(k_2 r)$ are the spherical Neumann functions defined as:

$$y_j(z) = (-1)^{n+1} \sqrt{\frac{\pi}{2z}} J_{-(j+1/2)}(z).$$

In the core, the requirement of nonsingularity at the point $r = 0$ leads to $B_2 = 0$, because the spherical Neumann functions $y_j(kr)$ are singular at $r = 0$. Inserting the expression for the magnetic field (3.15) into the Maxwell equation (2.2) we find for the transverse and longitudinal components of the electric field:

$$\mathbf{E}_{\omega jm}^{\perp}(\mathbf{r}) = i^j \frac{\omega k_2^2}{2\pi^2} \frac{1}{2j+1} \{ B_1 [-j g_{j+1}(k_2 r) + (j+1) g_{j-1}(k_2 r)] + B_2 [-j y_{j+1}(k_2 r) + (j+1) y_{j-1}(k_2 r)] \} \mathbf{Y}_{jm}^{(e)} \left(\frac{\mathbf{r}}{r} \right), \quad (3.16)$$

$$\mathbf{E}_{\omega jm}^{\parallel}(\mathbf{r}) = i^j \frac{\omega k_2}{2\pi^2} \sqrt{j(j+1)} \frac{B_1 g_j(k_2 r) + B_2 y_j(k_2 r)}{r} \mathbf{Y}_{jm}^{(l)} \left(\frac{\mathbf{r}}{r} \right). \quad (3.17)$$

For a bare nanocrystal in a host, the above expressions describe the radiation field inside the host, $r > R$. In the core-shell geometry they describe the radiation field in the shell, $R_1 < r < R_2$. While the field in the host is obviously given by:

$$\mathbf{H}_{\omega jm}(\mathbf{r}) = i^{j+1} \frac{k_3^3}{2\pi^2} [C_1 g_j(k_3 r) + C_2 y_j(k_3 r)] \mathbf{Y}_{jm}^{(m)} \left(\frac{\mathbf{r}}{r} \right), \quad (3.18)$$

$$\mathbf{E}_{\omega jm}^{\perp}(\mathbf{r}) = i^j \frac{\omega k_3^2}{2\pi^2} \frac{1}{2j+1} \{ C_1 [-j g_{j+1}(k_3 r) + (j+1) g_{j-1}(k_3 r)] + C_2 [-j y_{j+1}(k_3 r) + (j+1) y_{j-1}(k_3 r)] \} \mathbf{Y}_{jm}^{(e)} \left(\frac{\mathbf{r}}{r} \right), \quad (3.19)$$

$$\mathbf{E}_{\omega jm}^{\parallel}(\mathbf{r}) = i^j \frac{\omega k_3}{2\pi^2} \sqrt{j(j+1)} \frac{C_1 g_j(k_3 r) + C_2 y_j(k_3 r)}{r} \mathbf{Y}_{jm}^{(l)} \left(\frac{\mathbf{r}}{r} \right), \quad (3.20)$$

where $k_3 = \omega \sqrt{\varepsilon_3} = \omega n_3$, C_1 and C_2 are arbitrary coefficients to be found from boundary conditions on the shell–host interface.

4. Boundary conditions

To find arbitrary coefficients in the above expressions for the radiation field, one must employ conventional boundary conditions derived from the Maxwell equations. The following field components must be continuous across the nanocrystal–host interface, $r = R$, in bare nanocrystals:

- (1) transverse component of the magnetic field: $\mathbf{H}(r = R - 0) = \mathbf{H}(r = R + 0)$;
- (2) transverse component of the electric field: $\mathbf{E}^{\perp}(r = R - 0) = \mathbf{E}^{\perp}(r = R + 0)$; and
- (3) longitudinal component of the electric displacement vector $\mathbf{D} = \varepsilon \mathbf{E}$: $\varepsilon_1 \mathbf{E}^{\parallel}(r = R - 0) = \varepsilon_2 \mathbf{E}^{\parallel}(r = R + 0)$;

or on the core–shell, $r = R_1$, and shell–host, $r = R_2$, interfaces in core–shell nanocrystals. Note that here we defined the transverse and longitudinal components with respect to the direction of the radius-vector \mathbf{r} . Since the vector \mathbf{r} is perpendicular to the nanocrystal surface, a vector transverse to \mathbf{r} is tangential to the surface, and vice versa a longitudinal vector is normal to the surface.

4.1. Bare nanocrystals

For bare nanocrystals the boundary conditions on the nanocrystal–host interface result in the following equations:

$$a k_1^3 g_j(k_1 R) = k_2^3 [B_1 g_j(k_2 R) + B_2 y_j(k_2 R)], \quad (4.1)$$

$$ak_1^2[-jg_{j+1}(k_1R) + (j+1)g_{j-1}(k_1R)] = k_2^2\{B_1[-jg_{j+1}(k_2R) + (j+1)g_{j-1}(k_2R)] + B_2[-jy_{j+1}(k_2R) + (j+1)y_{j-1}(k_2R)]\}. \quad (4.2)$$

It is easy to see that the third boundary condition is equivalent to the first one. The above equations provide us two relations between three unknown coefficients a , B_1 and B_2 . The third relation will be derived from the normalization condition of the radiation field. Thus, the boundary conditions (4.1) and (4.2) together with the normalization condition completely determine the field inside and outside a bare nanocrystal.

The above equations are valid at an arbitrary nanocrystal radius R . In what follows, we assume that $k_1R \ll 1$ and $k_2R \ll 1$. Even for nanocrystals of large radius, $R \sim 10$ nm, and the refractive index $n_1 \sim 5$, as in lead salt semiconductors, the factor $k_1R \ll 1$ in the visible and near-IR frequency ranges. Thus, one can use the above inequalities practically for all nanocrystals and optical transitions.

At $k_1R \ll 1$ and $k_2R \ll 1$, the functions $g_{j+1} \ll g_{j-1}$ and $y_{j-1} \ll y_{j+1}$ and can be omitted. Then, Eqs. (4.1) and (4.2) are reduced to:

$$g_j(k_2R)B_1 + y_j(k_2R)B_2 = a\left(\frac{\varepsilon_1}{\varepsilon_2}\right)^{3/2} g_j(k_1R), \quad (4.3)$$

$$(j+1)g_{j-1}(k_2R)B_1 - jy_{j+1}(k_2R)B_2 = a(j+1)\frac{\varepsilon_1}{\varepsilon_2}g_{j-1}(k_1R). \quad (4.4)$$

Making use of the asymptotic expressions for the spherical Bessel and Neumann functions at small distances:

$$g_n(z) = \frac{z^n}{(2n+1)!!}, \quad z \ll 1, \quad (4.5)$$

$$y_n(z) = -\frac{(2n-1)!!}{z^{n+1}}, \quad z \ll 1, \quad (4.6)$$

we find the following relations between the coefficients B_1 and B_2 outside the nanocrystal and the coefficient a inside the nanocrystal:

$$B_1 = \frac{a}{2j+1} \left[(j+1) + j\frac{\varepsilon_1}{\varepsilon_2} \right] \left(\frac{n_1}{n_2} \right)^{j+1}, \quad (4.7)$$

$$B_2 = \frac{j+1}{2j+1} \frac{a}{(2j-1)!!(2j+1)!!} \frac{\varepsilon_1}{\varepsilon_2} \left(1 - \frac{\varepsilon_1}{\varepsilon_2} \right) (k_1R)^{j-1} (k_2R)^{j+2}. \quad (4.8)$$

As it must be expected, at $\varepsilon_1 = \varepsilon_2$ the coefficient B_2 vanishes, $B_2 = 0$, while the coefficient B_1 becomes equal to a , $B_1 = a$.

The expression (4.7) is convenient to rewrite as:

$$a = \left(\frac{n_2}{n_1} \right)^{j+1} S_j B_1, \quad (4.9)$$

where we introduced the screening factor for the field harmonic with the angular momentum j :

$$S_j = \frac{2j+1}{(j+1) + j\varepsilon_1/\varepsilon_2} \quad (4.10)$$

describing the local field effect inside the nanocrystal. Despite the radiation field is strongly nonuniform, the screening factor for the dipole and only for the dipole harmonic:

$$S_1 = \frac{3}{2 + \varepsilon_1/\varepsilon_2} \quad (4.11)$$

coincides with the screening factor for a uniform electric field as assumed in Eq. (1.2).

Although B_2 is much smaller than B_1 , in the boundary equations it stands at the spherical Neumann functions growing up at small distances as $(k_2r)^{-(j+1)}$. But, at large distances from the nanocrystal ($k_2r \gg 1$), the spherical Bessel and Neumann functions are of the same order. Therefore, at large distances one can neglect the terms with the Neumann functions in the expressions (3.15)–(3.17). Then they take the form:

$$\mathbf{H}_{\omega jm}(\mathbf{r}) = i^{j+1} B_1 \frac{k_2^2}{2\pi^2} \frac{\sin(k_2r - \pi j/2)}{r} \mathbf{Y}_{jm}^{(m)}\left(\frac{\mathbf{r}}{r}\right), \quad (4.12)$$

$$\mathbf{E}_{\omega jm}^\perp(\mathbf{r}) = -i^j B_1 \frac{\omega k_2}{2\pi^2} \frac{\cos(k_2r - \pi j/2)}{r} \mathbf{Y}_{jm}^{(e)}\left(\frac{\mathbf{r}}{r}\right), \quad (4.13)$$

while the longitudinal component of the electric field vanishes as $1/r^2$.

4.2. Core–shell nanocrystals

In the case of core–shell nanocrystals, Eqs. (4.7) and (4.8) relate the coefficients B_1 and B_2 inside the nanocrystal shell, $R_1 < r < R_2$, and the coefficient a inside the core, $r < R_1$. The boundary conditions on the shell–host interface, $r = R_2$, result in the following equations:

$$k_3^3 [B_1 g_j(k_2 R_2) + B_2 y_j(k_2 R_2)] = k_3^3 [C_1 g_j(k_3 R_2) + C_2 y_j(k_3 R_2)], \quad (4.14)$$

$$k_2^2 \{ B_1 [-j g_{j+1}(k_2 R_2) + (j+1) g_{j-1}(k_2 R_2)] + B_2 [-j y_{j+1}(k_2 R_2) + (j+1) y_{j-1}(k_2 R_2)] \} \\ = k_3^2 \{ C_1 [-j g_{j+1}(k_3 R_2) + (j+1) g_{j-1}(k_3 R_2)] + C_2 [-j y_{j+1}(k_3 R_2) + (j+1) y_{j-1}(k_3 R_2)] \}. \quad (4.15)$$

Together with the boundary conditions (4.1) and (4.2) on the core–shell interface ($r = R_1$) the above equation compose the full system of the boundary conditions for core–shell nanocrystals.

Since $k_3 R_2 \ll 1$, we find:

$$g_j(k_3 R_2) C_1 + y_j(k_3 R_2) C_2 = \left(\frac{\varepsilon_2}{\varepsilon_3} \right)^{3/2} [g_j(k_2 R_2) B_1 + y_j(k_2 R_2) B_2], \quad (4.16)$$

$$(j+1) g_{j-1}(k_3 R_2) C_1 - j y_{j+1}(k_3 R_2) C_2 = \frac{\varepsilon_2}{\varepsilon_3} [(j+1) g_{j-1}(k_2 R_2) B_1 - j y_{j+1}(k_2 R_2) B_2]. \quad (4.17)$$

Employing again the asymptotic expressions for spherical Bessel and Neumann functions we then derive the following relations between the coefficients B_1 and B_2 inside the shell and the coefficients C_1 and C_2 in the host:

$$C_1 = \frac{1}{2j+1} \frac{\varepsilon_2}{\varepsilon_3} \left[(j+1) \left(\frac{n_2}{n_3} \right)^{j-1} + j \left(\frac{n_2}{n_3} \right)^{j+1} \right] B_1 + \frac{j}{2j+1} \frac{\varepsilon_2}{\varepsilon_3} \left(1 - \frac{\varepsilon_2}{\varepsilon_3} \right) \frac{(2j-1)!!(2j+1)!!}{(k_2 R_2)^{j+2} (k_3 R_2)^{j-1}} B_2, \quad (4.18)$$

$$C_2 = \frac{j+1}{2j+1} \left(1 - \frac{\varepsilon_2}{\varepsilon_3} \right) \frac{\varepsilon_2}{\varepsilon_3} \frac{(k_3 R_2)^{j+2} (k_2 R_2)^{j-1}}{(2j-1)!!(2j+1)!!} B_1 + \frac{1}{2j+1} \left(\frac{n_3}{n_2} \right)^j \left[(j+1) \frac{\varepsilon_2}{\varepsilon_3} + j \right] B_2. \quad (4.19)$$

Inserting now the expressions (4.7) and (4.8), we find the relation between the coefficients C_1 and a :

$$a = \left(\frac{n_3}{n_1} \right)^{j+1} W_j C_1, \quad (4.20)$$

where we introduced the screening factor:

$$W_j = \frac{(2j+1)^2}{(j+1 + j \frac{\varepsilon_1}{\varepsilon_2})(j+1 + j \frac{\varepsilon_2}{\varepsilon_3}) + j(j+1)(1 - \frac{\varepsilon_1}{\varepsilon_2})(1 - \frac{\varepsilon_2}{\varepsilon_3}) \left(\frac{R_1}{R_2} \right)^{2j+1}} \quad (4.21)$$

describing the screening of the radiation field in the core of a core–shell nanocrystal. For the dipole harmonic the above expression is slightly simplified:

$$W_1 = \frac{9}{(2 + \frac{\varepsilon_1}{\varepsilon_2})(2 + \frac{\varepsilon_2}{\varepsilon_3}) + 2(1 - \frac{\varepsilon_1}{\varepsilon_2})(1 - \frac{\varepsilon_2}{\varepsilon_3}) \left(\frac{R_1}{R_2} \right)^3}. \quad (4.22)$$

Again, despite the radiation field is strongly nonuniform, the screening for the dipole harmonic is the same as in the case of the uniform field. The latter was derived in Ref. [1] for the particular case $\varepsilon_1 = \varepsilon_3 = 1$.

Finally, inserting Eq. (4.20) into Eqs. (4.7), (4.8) we find the relations between the coefficients B_1 , B_2 and C_1 :

$$B_1 = \left(\frac{n_3}{n_2} \right)^{j+1} \frac{W_j}{S_j} C_1, \quad (4.23)$$

$$B_2 = \frac{j+1}{2j+1} \frac{W_j}{(2j-1)!!(2j+1)!!} \left(\frac{n_3}{n_1} \right)^{j+1} \frac{\varepsilon_1}{\varepsilon_2} \left(1 - \frac{\varepsilon_1}{\varepsilon_2} \right) (k_1 R_1)^{j-1} (k_2 R_1)^{j+2} C_1. \quad (4.24)$$

Since C_2 is much smaller C_1 , at large distances one can neglect the terms with the Neumann functions in the expressions (3.18) and (3.19). Then, these expressions take the form:

$$\mathbf{H}_{\omega jm}(\mathbf{r}) = i^{j+1} C_1 \frac{k_3^2}{2\pi^2} \frac{\sin(k_3 r - \pi j/2)}{r} \mathbf{Y}_{jm}^{(m)} \left(\frac{\mathbf{r}}{r} \right), \quad (4.25)$$

$$\mathbf{E}_{\omega jm}^\perp(\mathbf{r}) = -i^j C_1 \frac{\omega k_3}{2\pi^2} \frac{\cos(k_3 r - \pi j/2)}{r} \mathbf{Y}_{jm}^{(e)} \left(\frac{\mathbf{r}}{r} \right), \quad (4.26)$$

while the longitudinal component of the electric field vanishes as $1/r^2$.

5. Normalization condition

In radiation problems, the field harmonics are normalized by the condition [3]:

$$\frac{1}{4\pi} \int d^3\mathbf{r} [\varepsilon(\mathbf{r}) \mathbf{E}_{\omega'j'm'}^*(\mathbf{r}) \cdot \mathbf{E}_{\omega jm}(\mathbf{r}) + \mathbf{H}_{\omega'j'm'}^*(\mathbf{r}) \cdot \mathbf{H}_{\omega jm}(\mathbf{r})] = \omega\delta(\omega - \omega')\delta_{jj'}\delta_{mm'}, \quad (5.1)$$

where the dielectric function $\varepsilon(\mathbf{r})$ is defined by Eqs. (2.5), (2.6) or (2.7). Here, we do not account for dissipation of radiation energy assuming that imaginary parts of all permittivities are sufficiently small, and therefore, the dissipation terms can be omitted in the normalization condition.

Since the field harmonics are normalized to the δ -function, the integral on the left side is determined only by the asymptotic behavior of the field harmonics at large distances $r \rightarrow \infty$ [4], and does not depend on the field behavior inside the nanocrystal. Therefore, to compute the above integral, one can employ the asymptotic expressions for the field at large distances in the host and, correspondingly the host permittivity.

Using Eqs. (4.12) and (4.13) for the case of a bare nanocrystal, we find:

$$B_1 = \frac{4\pi^2}{(\omega n_2)^{3/2}}. \quad (5.2)$$

Inserting this expression into Eq. (4.8), we finally derive for the coefficient a :

$$a = \frac{4\pi^2}{(\omega n_2)^{3/2}} \left(\frac{n_2}{n_1}\right)^{j+1} S_j. \quad (5.3)$$

In the case of a core–shell nanocrystal, employing Eqs. (4.25) and (4.26) we derived:

$$C_1 = \frac{4\pi^2}{(\omega n_3)^{3/2}}. \quad (5.4)$$

This expression together with Eqs. (4.20), (4.23) and (4.24) completely determine the radiation field inside the core:

$$a = \frac{4\pi^2}{(\omega n_3)^{3/2}} \left(\frac{n_3}{n_1}\right)^{j+1} W_j \quad (5.5)$$

and inside the shell of core–shell nanocrystal:

$$B_1 = \frac{4\pi^2}{(\omega n_3)^{3/2}} \left(\frac{n_3}{n_2}\right)^{j+1} \frac{W_j}{S_j}, \quad (5.6)$$

$$B_2 = \frac{4\pi^2}{(\omega n_3)^{3/2}} \frac{j+1}{2j+1} \frac{W_j}{(2j-1)!!(2j+1)!!} \left(\frac{n_3}{n_1}\right)^{j+1} \frac{\varepsilon_1}{\varepsilon_2} \left(1 - \frac{\varepsilon_1}{\varepsilon_2}\right) (k_1 R_1)^{j-1} (k_2 R_1)^{j+2}. \quad (5.7)$$

6. Coupling to optical transitions

Although the field gauge is already fixed by Eq. (2.8), the potentials of the electric type still contain an arbitrary constant C . If one chooses

$$C = -\sqrt{\frac{j+1}{j}}, \quad (6.1)$$

then the vector potential of the field harmonic with the angular momentum j contains only the spherical Bessel functions of the order $j+1$ [3], and hence, it falls down at small distances as $g_{j+1}(k_1 r) \sim (k_1 r)^{j+1}$. Therefore, in nanocrystals of radius $R \ll 1/k_1$, the contribution of the second (current) term into the nanocrystal–field coupling (2.11) is smaller than the first (charge) term by the factor $k_1 R \ll 1$, while its contribution into the decay rate is obviously smaller by the factor $(k_1 R)^2 \ll 1$. Even for nanocrystals of large radius, $R \sim 10$ nm, and the refractive index, $n_1 \sim 5$, as in lead salt semiconductors, the factor $(k_1 R)^2 \sim 10^{-2}–10^{-3}$. Thus, as well for point-like emitters, practically for all nanocrystals, the exact expression (2.12) for the nanocrystal–field coupling is reduced to:

$$V = \int d^3\mathbf{r} \rho(\mathbf{r}) \Phi_{\omega jm}(\mathbf{r}). \quad (6.2)$$

6.1. Coupling to optical transitions in the core

In Eq. (6.2) the integration is performed over the vicinity of the electron localization. Coupling to optical transitions in bare nanocrystals or to transitions localized in the core of core–shell nanocrystals is obviously determined by the scalar potential inside the core and the integration in Eq. (6.2) is extended over the nanocrystal core only.

Inserting the expression (3.3) for the scalar potential into Eq. (6.2) and employing the asymptotic expression (4.5) for the spherical Bessel functions at small distances, we find:

$$V = -i^j \sqrt{\frac{(2j+1)(j+1)}{\pi j}} \frac{\omega^{j+\frac{1}{2}} n_2^{j-\frac{1}{2}}}{(2j+1)!!} S_j Q_{jm}, \quad (6.3)$$

where:

$$Q_{jm} = \sqrt{\frac{4\pi}{2j+1}} \int d^3 \mathbf{r} \rho(\mathbf{r}) r^j Y_{jm}\left(\frac{\mathbf{r}}{r}\right) \quad (6.4)$$

are 2^j -pole electrical momenta [3].

In the case of core–shell nanocrystals, analogous computations result in:

$$V = -i^j \sqrt{\frac{(2j+1)(j+1)}{\pi j}} \frac{\omega^{j+\frac{1}{2}} n_3^{j-\frac{1}{2}}}{(2j+1)!!} W_j Q_{jm}. \quad (6.5)$$

The multipole momenta Q_{jm} , as they are defined in Eq. (6.4), are controlled by the power behavior of the spherical Bessel functions on small distances, $g_j \sim (kr)^j$, and by the absence of the term with the singular Neumann functions $y_j \sim (kr)^{-(j+1)}$ in the expression (3.9) for the scalar potential inside the core. In the shell, radiation field contains also the Neumann functions that significantly modify the coupling the radiation field to electronic transitions localized in the shell.

6.2. Coupling to optical transitions in the shell

In the case of electronic transitions localized in the shell of core–shell nanocrystals, the integration in the general expression (6.2) is performed over the volume of the shell, while the scalar potential is given by Eq. (3.14). Inserting the expression (3.14), (5.6) and (5.7) into Eq. (6.2), we then derive:

$$V = -i^j \sqrt{\frac{(2j+1)(j+1)}{\pi j}} \frac{\omega^{j+\frac{1}{2}} n_3^{j-\frac{1}{2}}}{(2j+1)!!} \left[\frac{W_j}{S_j} Q_{jm} + \frac{j+1}{2j+1} \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right) W_j P_{jm} \right], \quad (6.6)$$

where the “inverse” electro-multipole momenta P_{jm} are found to be:

$$P_{jm} = \sqrt{\frac{4\pi}{2j+1}} R_1^{2j+1} \int d^3 \mathbf{r} \rho(\mathbf{r}) \frac{1}{r^{j+1}} Y_{jm}\left(\frac{\mathbf{r}}{r}\right). \quad (6.7)$$

The inverse momenta describe the coupling of an optical transition localized in the shell to the radiation field component proportional to the spherical Neumann function in the general expression (3.14). They are obviously absent in the expression (6.3) for the coupling in the core, because the field in the core contains only the spherical Bessel function with the power asymptotic behavior at small distances.

7. Radiative decay rate

In the second order of the perturbation theory, the radiative decay rate of an optical transition is given by the expression [3]:

$$\Gamma = 2\pi |V|^2 \quad (7.1)$$

provided that the field harmonics are normalized to the δ -function as in Eq. (5.1).

As well as in the case of atomic optical transitions [3], due to the small factor $(kR)^2 \ll 1$ the decay rate of electro-dipole transition, if it is not forbidden by selection rules, essentially exceeds the decay rates of multipole ($j \geq 2$) transitions. For the same reason, we do not consider here coupling to the radiation field of the magnetic type. Therefore, here we consider the decay rate due to coupling to the electro-dipole harmonic of the radiation field, $j = 1$, only. It should be also emphasized that for intraband transitions between the electron states with the angular momenta $l = 0$ and $l = 1$ (SP transitions), all electric and magnetic momenta, except the electro-dipole one, vanish due to selection rules. Therefore, for SP transitions, our computations for the electro-dipole radiation are exact and complete.

7.1. Optical transitions in the core

For the transitions localized in the core, the coupling is determined by the momenta Q_{jm} only. At $j = 1$, they are related to the dipole momentum [3] of electronic system in the core:

$$Q_{10} = id_z; \quad Q_{1,\pm 1} = \mp \frac{i}{\sqrt{2}}(d_x \pm id_y). \quad (7.2)$$

Therefore, the decay rate, is found to be:

$$\Gamma = 2\pi |V|^2 = \frac{4}{3} \omega^3 d^2 \left(\frac{3}{2 + \varepsilon_1/\varepsilon_2} \right)^2 \sqrt{\varepsilon_2}. \quad (7.3)$$

Correspondingly, the decay rate of a transition with the dipole momentum d in the core of a core–shell nanocrystal is given by:

$$\Gamma = \frac{4}{3} \omega^3 d^2 \left[\frac{9}{\left(2 + \frac{\varepsilon_1}{\varepsilon_2}\right) \left(2 + \frac{\varepsilon_2}{\varepsilon_3}\right) + 2 \left(1 - \frac{\varepsilon_1}{\varepsilon_2}\right) \left(1 - \frac{\varepsilon_2}{\varepsilon_3}\right) \left(\frac{R_1}{R_2}\right)^3} \right]^2 \sqrt{\varepsilon_3}, \quad (7.4)$$

where the expression in the square brackets is the screening factor W_1 for the field in the core of a core–shell nanocrystal.

In core–shell nanostructures with a relatively thick shell, $\Delta = R_2 - R_1 > R_1$, the geometry factor $\sigma = (R_1/R_2)^3 \ll 1$. Therefore, the term in the denominator of the expression (4.22) proportional to σ can be omitted. Then, the screening factor W_1 is reduced to the product of two screening factors S_1 :

$$W_1 \sim S_1(\varepsilon_1/\varepsilon_2) S_1(\varepsilon_2/\varepsilon_3) = \frac{3}{2 + \frac{\varepsilon_1}{\varepsilon_2}} \frac{3}{2 + \frac{\varepsilon_2}{\varepsilon_3}} \quad (7.5)$$

describing “subsequent” screening of the field in the shell and then in the core of a core–shell nanocrystals. In the opposite limiting case of a relatively thin shell, $\Delta \ll R_1$, the contribution of the shell becomes small, and the screening factor W_1 is reduced, as it must be expected, to the factor S_1 :

$$W_1 \sim S_1(\varepsilon_1/\varepsilon_3) = \frac{3}{2 + \frac{\varepsilon_1}{\varepsilon_3}} \quad (7.6)$$

describing the screening of the radiation field in a bare nanocrystal in a host of permittivity ε_3 .

Finally, we present here the expression for the decay rate of an optical dipole transition in a semiconductor core of a nanostructure having two shells. The dielectric function of the structure is given in Eq. (2.7). Solving the Maxwell equation with the boundary condition on three interfaces $r = R_1$, $r = R_2$ and $r = R_3$, we find:

$$\Gamma = \frac{4}{3} \omega^3 d^2 |G|^2 \sqrt{\varepsilon_4}, \quad (7.7)$$

where the screening factor G is given by:

$$G = 27 \left[\left(2 + \frac{\varepsilon_1}{\varepsilon_2}\right) \left(2 + \frac{\varepsilon_2}{\varepsilon_3}\right) \left(2 + \frac{\varepsilon_3}{\varepsilon_4}\right) + 2 \left(1 - \frac{\varepsilon_1}{\varepsilon_2}\right) \left(1 - \frac{\varepsilon_2}{\varepsilon_3}\right) \left(2 + \frac{\varepsilon_3}{\varepsilon_4}\right) \left(\frac{R_1}{R_2}\right)^3 \right. \\ \left. + 2 \left(2 + \frac{\varepsilon_1}{\varepsilon_2}\right) \left(1 - \frac{\varepsilon_2}{\varepsilon_3}\right) \left(1 - \frac{\varepsilon_3}{\varepsilon_4}\right) \left(\frac{R_2}{R_3}\right)^3 + 2 \left(1 - \frac{\varepsilon_1}{\varepsilon_2}\right) \left(1 + 2 \frac{\varepsilon_2}{\varepsilon_3}\right) \left(1 - \frac{\varepsilon_3}{\varepsilon_4}\right) \left(\frac{R_1}{R_3}\right)^3 \right]^{-1}. \quad (7.8)$$

Again, in nanostructures with relatively thick shells, so that $(R_1/R_2)^3 \ll 1$ and $(R_2/R_3)^3 \ll 1$, the factor G is reduced to the product of three S -factors:

$$G \sim S(\varepsilon_1/\varepsilon_2) S(\varepsilon_2/\varepsilon_3) S(\varepsilon_3/\varepsilon_4) = \frac{3}{2 + \frac{\varepsilon_1}{\varepsilon_2}} \frac{3}{2 + \frac{\varepsilon_2}{\varepsilon_3}} \frac{3}{2 + \frac{\varepsilon_3}{\varepsilon_4}}. \quad (7.9)$$

While, in nanostructures with thin shells, the screening factor G is reduced to the S -factor:

$$G \sim S(\varepsilon_1/\varepsilon_4) = \frac{3}{2 + \frac{\varepsilon_1}{\varepsilon_4}}. \quad (7.10)$$

7.2. Optical transitions in the shell

The radiative decay rate of electronic transition localized in the shell of core–shell nanocrystals is found from Eq. (7.1), where the coupling V is given by Eq. (6.6):

$$\Gamma = \frac{4}{3}\omega^3 \left[\frac{W_j}{S_j} Q_{jm} + \frac{j+1}{2j+1} \left(\frac{\varepsilon_1}{\varepsilon_2} - 1 \right) W_j P_{jm} \right]^2 \sqrt{\varepsilon_3}. \quad (7.11)$$

The appearance of the multipole momenta Q_{jm} in the expression (6.3) for the coupling to optical transitions localized in the core is quite obvious. The density of the coupling in Eq. (6.2) is the product of the density of charge and the scalar potential. In the core, due to the requirement of nonsingularity at the point $r = 0$, the scalar potential (3.9) contains only the spherical Bessel functions with the power behavior at small distances, $g_j(k_1 r) \sim (k_1 r)^j$. Therefore, the momenta Q_{jm} have the form:

$$Q_{jm} \sim e \langle r^j \rangle, \quad (7.12)$$

where $\langle r^j \rangle$ is the average value of the powers r^j with the distribution function $\rho(\mathbf{r})$. In this sense, Q_{jm} are really the momenta of the electron density in the core.

The situation is drastically changed for electrons localized in the shell. In the shell, the scalar potential (3.14) contains both Bessel and Neumann functions. The latter grow up at small distances, $y_j \sim -r^{j+1}$, therefore, besides the momenta of the electron density in the shell Q_{jm} , the coupling (6.6) contains also the inverse momenta P_{jm} (6.7), which have the form:

$$P_{jm} \sim e R_1^{2j+1} \left\langle \frac{1}{r^{j+1}} \right\rangle \quad (7.13)$$

and can be treated as inverse momenta of the electron density in the shell. They obviously have the same dimension (charge $\times \text{cm}^j$) as the momenta Q_{jm} , but proportional to the power of core radius R_1 even in the case of interband transitions, which are basically determined by the Bloch functions of an electron in the valence and conduction bands insensitive to the geometry of a nanocrystal. That can obviously result to very strong optical transitions in shells of core–shell nanocrystals.

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