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Resonance interaction between two atomic dipoles separated by the surface of a dielectric nanosphere

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Studied within the framework of both classical and quantum-mechanical approaches is the resonance interaction between two atomic dipoles one of which is located inside a dielectric microsphere and the other near its outer surface. The dispersion equation of this system is found. The analysis of this equation in a quasistatic approximation has shown that the behavior of the eigenfrequencies depends in a complex manner on the parameters of the system, and that exact resonance can be achieved, provided the parameters are suitably selected. Based on the solutions of the above equation, relationships are found between the energy-transfer rate and the system parameters. It is demonstrated that as the inside atom approaches the surface of the microsphere, resonance excitation transfer from one atom to the other can take place. Similar results are obtained when using the quantum-mechanical density matrix to define the atomic interaction. The results obtained can be of use in implementing selective microscopy with a nanometer-high spatial resolution.
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I. INTRODUCTION

The development of nanoscience and nanotechnology has made it possible to study the interaction of atoms and molecules with nanostructures (nanotips, nanoprobes, etc.), using for the most part scanning force microscopy (see, for example, Ref. [1]). Of special interest is the study of resonance interactions, that potentially may help achieve a spatial resolution at an atomic-molecular level simultaneously with spectral resolution (or, in other words, chemical selectivity). To illustrate, the authors of Ref. [2] suggested a nanometer-resolution scanning optical microscopy technique involving the resonance excitation of fluorescence in the sample from a single-atom-excited center on the surface of a nanotip. This is essentially a combination of three techniques: scanning-force microscopy, near-field optical microscopy [3], and fluorescence resonant energy transfer (FRET) [4,5].

It has been known at the same time that the emission characteristics of a dipole (emission frequency and rate) suffer substantial modifications in microstructures of a size on the order of the optical wavelength λ (the so-called cavity QED effects [6]). Specifically this is true in the case of an atom inside or near a dielectric microsphere with a radius a of the order of λ [7]. Moreover, in the vicinity of a microsphere with a radius of $a \ll \lambda$, there may take place a change in the selection rules for the radiation, so that the quadrupole radiation probability will increase $(\lambda/a)^2$ times, approaching the dipole radiation probability [8]. The question therefore naturally arises as to what part can be played by such effects in the near-field FRET microscopy technique [2] that should involve the Förster resonance excitation transfer from a donor on the nanotip surface to an acceptor on the surface of interest (or vice versa).

The problem of resonance energy transfer in the vicinity of a plane interface was considered in Refs. [9–11]. The authors of Ref. [12] considered the influence of curvature effects upon the van der Waals interaction, and, in Ref. [13], an investigation was started into the process of resonance energy transfer between an oscillator located inside a microsphere modeling a nanotip and another oscillator close to the outer surface of the microsphere.

The use of a microsphere as the model of a nanotip is justified because the processes under consideration are local and sensitive to local curvature. If we need to consider a more general problem, including excitation of a donor and collection of fluorescent light, the use of a cone with a smoothed edge as a nanotip model is necessary. The point is that processes of excitation and registration are due to the photons propagation over distances exceeding the wavelength. As a result the global nanotip geometry comes into play. Within the spherical model of a nanotip we found [13] approximate analytical expressions for energy transfer between radialy oriented classical dipoles. In the present work, we will continue with the study of this problem within the spherical model, and find the equations describing the energy transfer for the arbitrary orientation of dipole momentum within classical as well as quantum mechanics. The solutions of the obtained equations are found analytically and numerically.

Generally speaking, the energy-transfer process should be analyzed within the framework of quantum mechanics [4]. However, in the case of homogeneous space, the final results for the energy-transfer rate prove independent of Planck's constant, and can be obtained within the framework of the

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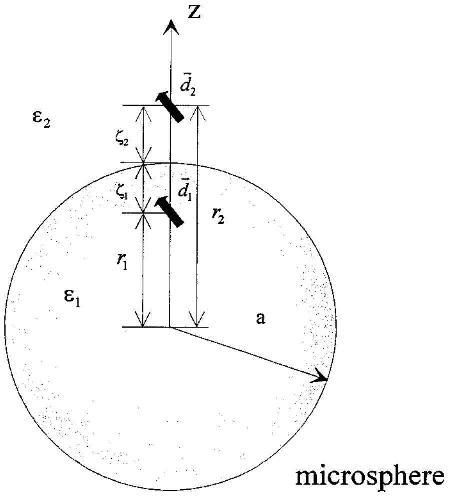

FIG. 1. Geometry of the problem.

purely classical approach [4,14]. In our case, the presence of the interface leads, generally speaking, to the occurrence of purely quantum corrections to the shifts of the partial frequencies [15], which in the case of microspheres turn out to be [16] of a higher order of smallness ($1/\zeta^2$) in comparison with the dipole interaction ($1/\zeta^3$) as the atoms approach the surface ($\zeta \rightarrow 0$). (Here ζ is the distance from the atom to the surface of the microsphere.) The plan of the rest of the work is as follows. In Sec. II, the equations describing the interaction between two oscillators in the presence of a dielectric microsphere are analyzed with due regard for delay effects, and the corresponding dispersion equation is derived. In Sec. III, the dispersion equation is simplified as applied to the quasistatic case of nanometer-scale dielectric spheres, the behavior of the eigenfrequencies is examined as a function of the mutual arrangement of atoms and the size of the microsphere, and conditions necessary for the occurrence of exact resonance in the system are found. In Sec. IV, the electronic excitation energy-transfer process is studied within the framework of the classical approach, and, in Sec. V, the process is investigated within the framework of an approach based on the quantum-mechanical density matrix. In Sec. VI, the results obtained are analyzed, and the quantum-mechanical and classical approaches are compared. The geometry of the problem is illustrated in Fig. 1.

II. GENERAL EQUATIONS. THE DYNAMICS OF COUPLED OSCILLATORS SEPARATED BY A SPHERICAL INTERFACE

In the absence of interaction between the dipoles themselves and between the dipoles and the spherical interface, the equations of motion of the dipoles treated as classical oscillators have the form

$$m_1(\delta\ddot{\mathbf{r}}_1 + \gamma_1 \delta\dot{\mathbf{r}}_1 + \omega_1^2 \delta\mathbf{r}_1) = 0,$$
$$m_2(\delta\ddot{\mathbf{r}}_2 + \gamma_2 \delta\dot{\mathbf{r}}_2 + \omega_2^2 \delta\mathbf{r}_2) = 0. \tag{1}$$

In the above equations, m_i, γ_i, and ω_i are the parameters characterizing an individual atomic dipole in a boundless medium with the appropriate dielectric constant ε_i, and $\delta\mathbf{r}_i$ are the displacements of the moving charges relative to their equilibrium position. Note that since the atomic oscillators are located in matter, their oscillation frequencies and linewidths differ substantially from their counterparts for isolated atoms, the linewidths being, as a rule, much in excess of the radiative linewidth γ_i^R in free space. In deriving Eqs. (1), we have disregarded the positional oscillations of the dipoles (nuclei). Note that the oscillation amplitude of the moving charge in an atomic dipole is of the order of the Bohr radius (0.053 nm), and so it can be neglected within the framework of the nanometer scale of interest to us (Rydberg atoms being an exclusion).

Equations (1) change materially if account is taken of the field reflected from the interface and the field emitted by the other dipole:

$$m_1(\delta\ddot{\mathbf{r}}_1 + \gamma_1 \delta\dot{\mathbf{r}}_1 + \omega_1^2 \delta\mathbf{r}_1) = e[\mathbf{E}_1^R(\mathbf{r}_1,t) + \mathbf{E}_2^T(\mathbf{r}_1,t)], \tag{2}$$
$$m_2(\delta\ddot{\mathbf{r}}_2 + \gamma_2 \delta\dot{\mathbf{r}}_2 + \omega_2^2 \delta\mathbf{r}_2) = e[\mathbf{E}_2^R(\mathbf{r}_2,t) + \mathbf{E}_1^T(\mathbf{r}_2,t)].$$

In these equations, e is the charge of the oscillating particle, and $\mathbf{E}_i^{T,R}(\mathbf{r}_j)$ is the total (T) or only the reflected (R) field due to the ith dipole in the position of the jth dipole.

Assuming that the oscillation direction remains unchanged with time, each one of Eq. (2) can additionally be multiplied in a scalar fashion by the unit oscillation direction vector $n_i = \mathbf{d}_i/d_i = \delta\mathbf{r}_i/\delta r_i$, as a result of which the equations describing the change of the dipole moment will take on the forms

$$(\ddot{d}_1 + \gamma_1 \dot{d}_1 + \omega_1^2 d_1) = \frac{e^2}{m_1}[\mathbf{n}_1 \cdot \mathbf{E}_1^R(\mathbf{r}_1) + \mathbf{n}_1 \cdot \mathbf{E}_2^T(\mathbf{r}_1)], \tag{3}$$
$$(\ddot{d}_2 + \gamma_2 \dot{d}_2 + \omega_2^2 d_2) = \frac{e^2}{m_2}[\mathbf{n}_2 \cdot \mathbf{E}_2^R(\mathbf{r}_2) + \mathbf{n}_2 \cdot \mathbf{E}_1^T(\mathbf{r}_2)].$$

Assuming that all the quantities vary in proportion to $e^{-i\omega t}$, and expressing the fields in terms of the appropriate Green functions, i.e., $\mathbf{n}_i \cdot \mathbf{E}_j = \mathbf{n}_i \overleftrightarrow{G} \mathbf{n}_j d_j$, we obtain the following equations:

$$(-\omega^2 - i\gamma_1\omega + \omega_1^2)d_1 = \frac{e^2}{m_1}[\mathbf{n}_1 \cdot \overleftrightarrow{G}_1^R(\mathbf{r}_1,\omega) \cdot \mathbf{n}_1 d_1 + \mathbf{n}_1 \cdot \overleftrightarrow{G}_2^T(\mathbf{r}_1,\omega) \cdot \mathbf{n}_2 d_2], \tag{4}$$
$$(-\omega^2 - i\gamma_2\omega + \omega_2^2)d_2 = \frac{e^2}{m_2}[\mathbf{n}_2 \cdot \overleftrightarrow{G}_1^T(\mathbf{r}_2,\omega) \cdot \mathbf{n}_1 d_1 + \mathbf{n}_2 \cdot \overleftrightarrow{G}_2^R(\mathbf{r}_1,\omega) \cdot \mathbf{n}_2 d_2],$$

whose consistency condition gives us the dispersion equation of the system:

$$\begin{vmatrix} -\omega^2-\mathbf{i}\gamma_1\omega+\omega_1^2-\dfrac{\mathbf{e}^2}{m_1}\,\mathbf{n}_1\cdot\overleftrightarrow{G}_1^R(\mathbf{r}_1,\omega)\cdot\mathbf{n}_1 & -\dfrac{\mathbf{e}^2}{m_1}\,\mathbf{n}_1\cdot\overleftrightarrow{G}_2^T(\mathbf{r}_1,\omega)\cdot\mathbf{n}_2 \\ -\dfrac{\mathbf{e}^2}{m_2}\,\mathbf{n}_2\cdot\overleftrightarrow{G}_1^T(\mathbf{r}_2,\omega)\cdot\mathbf{n}_1 & -\omega^2-\mathbf{i}\gamma_2\omega+\omega_2^2-\dfrac{\mathbf{e}^2}{m_2}\,\mathbf{n}_2\cdot\overleftrightarrow{G}_2^R(\mathbf{r}_1,\omega)\cdot\mathbf{n}_2 \end{vmatrix}=0. \tag{5}$$

If we solve this equation for ω and find the eigenfrequencies $\Omega_{1,2}$, we then can easily find all the characteristics of the system.

To solve dispersion equation (5), one must know the expressions for the fields on the right-hand side. The expressions for the additional reflected fields were found in Refs. [7, 17] to be as follows:

$$\mathbf{n}_2\cdot\overleftrightarrow{G}_2^R(\mathbf{r}_2,\omega)\cdot\mathbf{n}_2=ik_0^3\sqrt{\varepsilon_2}\left\{\sum_{l=1}^{\infty}\beta_l^{2,\mathrm{ext}}l(l+1)(2l+1)\left(\frac{h_l^{(1)}(\tilde{r}_2)}{\tilde{r}_2}\right)^2 n_{2,r}^2+\sum_{l=1}^{\infty}(l+1/2)\left[\alpha_l^{2,\mathrm{ext}}(h_l^{(1)}(\tilde{r}_2))^2\right.\right.$$
$$\left.\left.+\beta_l^{2,\mathrm{ext}}\left(\frac{d(\tilde{r}_2h_l^{(1)}(\tilde{r}_2))}{\tilde{r}_2d\tilde{r}_2}\right)^2[n_{2,\theta}^2+n_{2,\varphi}^2]\right]\right\} \tag{6}$$

$$\mathbf{n}_1\cdot\overleftrightarrow{G}_1^R(\mathbf{r}_1,\omega)\cdot\mathbf{n}_1=ik_0^3\sqrt{\varepsilon_1}\left\{n_{1,r}^2\sum_{l=1}^{\infty}\alpha_l^{1,\mathrm{int}}l(l+1)(2l+1)\,\frac{j_l^2(\tilde{r}_1)}{\tilde{r}_1^2}+[n_{1,\vartheta}^2+n_{1,\varphi}^2]\sum_{l=1}^{\infty}(l+1/2)\left[\beta_l^{1,\mathrm{int}}j_l^2(\tilde{r}_1)+\alpha_l^{1,\mathrm{int}}\,\frac{(\tilde{r}_1j_l(\tilde{r}_1))'^2}{\tilde{r}_1^2}\right]\right\} \tag{7}$$

$$\beta_l^{1,\mathrm{int}}=\frac{\varepsilon_1[z_2h_l^{(1)}(z_2)]'h_l^{(1)}(z_1)-\varepsilon_2[z_1h_l^{(1)}(z_1)]'h_l^{(1)}(z_2)}{\varepsilon_2[z_1j_l(z_1)]'h_l^{(1)}(z_2)-\varepsilon_1[z_2h_l^{(1)}(z_2)]'j_l(z_1)}\,, \tag{8}$$

$$\alpha_l^{1,\mathrm{int}}=\frac{[z_2h_l^{(1)}(z_2)]'h_l^{(1)}(z_1)-[z_1h_l^{(1)}(z_1)]'h_l^{(1)}(z_2)}{[z_1j_l(z_1)]'h_l^{(1)}(z_2)-[z_2h_l^{(1)}(z_2)]'j_l(z_1)}\,, \tag{9}$$

$$\beta_l^{2,\mathrm{ext}}=-\frac{\varepsilon_1\,\dfrac{d}{dz_2}\,[z_2j_l(z_2)]j_l(z_1)-\varepsilon_2\,\dfrac{d}{dz_1}\,[z_1j_l(z_1)]j_l(z_2)}{\varepsilon_1\,\dfrac{d}{dz_2}\,[z_2h_l^{(1)}(z_2)]j_l(z_1)-\varepsilon_2\,\dfrac{d}{dz_1}\,[z_1j_l(z_1)]h_l^{(1)}(z_2)}\,, \tag{10}$$

$$\alpha_l^{2,\mathrm{ext}}=-\frac{\dfrac{d}{dz_2}\,[z_2j_l(z_2)]j_l(z_1)-\dfrac{d}{dz_1}\,[z_1j_l(z_1)]j_l(z_2)}{\dfrac{d}{dz_2}\,[z_2h_l^{(1)}(z_2)]j_l(z_1)-\dfrac{d}{dz_1}\,[z_1j_l(z_1)]h_l^{(1)}(z_2)}\,, \tag{11}$$

where $z_i=k_0a\sqrt{\varepsilon_i}$, $\tilde{r}_i=r_ik_0\sqrt{\varepsilon_i}$, $k_0=\omega/c$.

The expressions for the fields describing the delayed interaction between the dipoles can be found using the approaches presented in Refs. [7, 17], and by virtue of the reciprocity theorem [18]

$$\mathbf{n}_2\cdot\overleftrightarrow{G}_1^T(\mathbf{r}_2,\omega)\cdot\mathbf{n}_1=\mathbf{n}_1\cdot\overleftrightarrow{G}_2^T(\mathbf{r}_1,\omega)\cdot\mathbf{n}_2 \tag{12}$$

it is sufficient to find any one of these expressions. When the orientations and positions of the dipoles are random, these expressions are cumbersome, and therefore here for brevity we will analyze only the case where the dipoles are arranged along a single line passing through the center of the microsphere. In that case, the interaction of the dipoles with the identical orientations ($\mathbf{n}_1=\mathbf{n}_2=\mathbf{n}$) will be defined by the expression

$$\mathbf{n}_2\cdot\overleftrightarrow{G}_1^T(\mathbf{r}_2,\omega)\cdot\mathbf{n}_1=\mathbf{n}_1\cdot\overleftrightarrow{G}_2^T(\mathbf{r}_1,\omega)\cdot\mathbf{n}_2=\frac{ik_0}{\sqrt{\varepsilon_2}}\sum_{l=1}^{\infty}l(l+1)(2l+1)\beta_l^{1,\mathrm{ext}}\,\frac{h_l^{(1)}(\tilde{r}_2)j_l(\tilde{r}_1)}{r_2r_1}\,n_r^2$$
$$+ik_0^3\sqrt{\varepsilon_2}\sum_{l=1}^{\infty}(l+1/2)\alpha_l^{1,\mathrm{ext}}h_l^{(1)}(\tilde{r}_2)j_l(\tilde{r}_1)[n_\theta^2+n_\varphi^2]$$
$$+\frac{ik_0}{\sqrt{\varepsilon_2}}\sum_{l=1}^{\infty}(l+1/2)\beta_l^{1,\mathrm{ext}}\,\frac{[\tilde{r}_2h_l^{(1)}(\tilde{r}_2)][\tilde{r}_1j_l(\tilde{r}_1)]'}{r_2r_1}\,[n_\theta^2+n_\varphi^2]. \tag{13}$$

In the above expression, the coefficients for the passage of the field due to the external dipole into the microsphere have the forms

$$\alpha_l^{1,\mathrm{ext}}=\frac{i}{z_2}\,\frac{1}{\dfrac{d}{dz_2}\,[z_2h_l^{(1)}(z_2)]j_l(z_1)-\dfrac{d}{dz_1}\,[z_1j_l(z_1)]h_l^{(1)}(z_2)},\tag{14}$$

$$\beta_l^{1,\mathrm{ext}}=\frac{i\varepsilon_2}{z_2}\,\frac{1}{\varepsilon_1\,\dfrac{d}{dz_2}\,[z_2h_l^{(1)}(z_2)]j_l(z_1)-\varepsilon_2\,\dfrac{d}{dz_1}\,[z_1j_l(z_1)]h_l^{(1)}(z_2)}.\tag{15}$$

III. QUASISTATIC APPROXIMATION

Generally speaking, to determine the energy-transfer rate, it is necessary to analyze exact dispersion equation (6). But in our case of small microspheres, one may first consider a quasistatic electric-field approximation wherein no allowance is made for delay. In that case, the dispersion equation describing the dynamics of the atomic dipoles is substantially simplified. In the case of radially oriented dipoles (head to tail geometry), this equation may be represented in the form

$$(\omega^2+i\gamma_1\omega-\tilde{\omega}_1^2)(\omega^2+i\gamma_2\omega-\tilde{\omega}_2^2)=g_1g_2f_{12}^{\mathrm{rad}^2},\tag{16}$$

where the partial frequencies $\tilde{\omega}_1$ and $\tilde{\omega}_2$ are defined by the expressions

$$\begin{aligned}\tilde{\omega}_1^2&=\omega_1^2-g_1f_{11}^{\mathrm{rad}}(x_1),\\ \tilde{\omega}_2^2&=\omega_2^2-g_2f_{22}^{\mathrm{rad}}(x_2).\end{aligned}\tag{17}$$

Here $x_1=r_1/a$, $x_2=a/r_2$, $g_i=e^2/m_ia^3$ are the coupling coefficients and

$$f_{11}^{\mathrm{rad}}(x_1)=-\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1x_1^2}\sum_{n=1}^{\infty}x_1^{2n}\,\frac{n^2(n+1)}{\varepsilon_1n+\varepsilon_2(n+1)},\tag{18}$$

$$\begin{aligned}f_{12}^{\mathrm{rad}}(x_1,x_2)&=f_{21}^{\mathrm{rad}}(x_1,x_2)\\ &=\frac{x_2^2}{x_1}\sum_{n=1}^{\infty}(x_1x_2)^n\,\frac{n(n+1)(2n+1)}{\varepsilon_1n+\varepsilon_2(n+1)},\end{aligned}\tag{19}$$

$$f_{22}^{\mathrm{rad}}(x_2)=\frac{(\varepsilon_1-\varepsilon_2)}{\varepsilon_2}\,x_2^4\sum_{n=1}^{\infty}x_2^{2n}\,\frac{n(n+1)^2}{\varepsilon_1n+\varepsilon_2(n+1)}.\tag{20}$$

In the case of tangential orientation of the dipoles (sandwich geometry), we have

$$(\omega^2+i\gamma_1\omega-\tilde{\omega}_1^2)(\omega^2+i\gamma_2\omega-\tilde{\omega}_2^2)=g_1g_2f_{12}^{\tan^2},\tag{21}$$

where the partial frequencies are given by the relations

$$\begin{aligned}\tilde{\omega}_1^2&=\omega_1^2-g_1f_{11}^{\tan}(x_1),\\ \tilde{\omega}_2^2&=\omega_2^2-g_2f_{22}^{\tan}(x_2).\end{aligned}\tag{22}$$

Here

$$f_{11}^{\tan}(x_1)=-\frac{\varepsilon_1-\varepsilon_2}{2\varepsilon_1x_1^2}\sum_{n=1}^{\infty}x_1^{2n}\,\frac{n(n+1)^2}{\varepsilon_1n+\varepsilon_2(n+1)},\tag{23}$$

$$\begin{aligned}f_{12}^{\tan}(x_1,x_2)&=f_{21}^{\tan}(x_1,x_2)\\ &=-\frac{x_2^2}{2x_1}\sum_{n=1}^{\infty}(x_1x_2)^n\,\frac{n(n+1)(2n+1)}{\varepsilon_1n+\varepsilon_2(n+1)},\end{aligned}\tag{24}$$

$$f_{22}^{\tan}(x_2)=\frac{(\varepsilon_1-\varepsilon_2)}{2\varepsilon_2}\,x_2^4\sum_{n=1}^{\infty}x_2^{2n}\,\frac{n^2(n+1)}{\varepsilon_1n+\varepsilon_2(n+1)}.\tag{25}$$

To solve dispersion Eqs. (16) or (21), it is necessary to calculate sums (18)–(20). Generally speaking, these sums are expressed in terms of hypergeometric functions whose exact calculation is somewhat difficult to make. However, for any rational ε's, these sums can be expressed in terms of elementary functions. In the case of heavy glass ($\varepsilon_1=3$, $\varepsilon_2=1$), which will be analyzed, we have [19]

$$\sum_{k=0}^{\infty}\frac{x^{4k+1}}{4k+1}=\frac{1}{2}\left[\arctan(x)+\ln\left(\frac{1+x}{1-x}\right)^{1/2}\right],\tag{26}$$

and the above sums of interest to us can be expressed in terms of the derivatives of this function.

An important feature of the quasistatic approximation used is the fact that here the interactions of the dipoles with the reflected waves and with each other are independent of frequency (no microsphere resonances [20–22] are excited), and so the dispersion equation has four roots (two with positive real parts and another two with negative real parts). From physical considerations, these roots must have negative imaginary parts corresponding to damping. But in our case a situation is possible where one of the normal modes ceases to be oscillating. One can easily see that this occurs as the external atom approaches the surface of the microsphere in the vicinity of the point, at which the free term in dispersion equations (16) or (21) changes sign, i.e., at the point defined by the equation

$$[\omega_1^2-g_1f_{11}^{\mathrm{rad}}(x_1)][\omega_2^2-g_2f_{22}^{\mathrm{rad}}(x_2)]=g_1g_2f_{12}^{\mathrm{rad}^2}.\tag{27}$$

At this point one of the solutions of dispersion equations (16) or (21) goes to zero, and the system becomes unstable in the neighborhood of this point. Physically this means that the interaction of the oscillating charge with its "mirror-reflection" counterpart proves stronger than the intraatomic interaction. In this region, our approximation becomes inadequate, and one must take account of the atomic structure of the interface.

The involved behavior of the system under consideration is due largely to the fact that the partial frequencies are dependent on the position of the dipoles, and differ substantially from the partial frequencies of the same dipoles in free space:

$$\tilde{\omega}_1^2=\omega_1^2-g_1 f_{11}^{\mathrm{rad}}\left(\frac{r_1}{a}\right)>\omega_1^2 \tag{28}$$

$$\tilde{\omega}_2^2=\omega_2^2-g_1 f_{22}^{\mathrm{rad}}\left(\frac{a}{r_2}\right)<\omega_2^2, \tag{29}$$

and so the condition for the equality of the partial frequencies will depend not only on the frequencies of the oscillators, but also on their position. As the atoms draw closer to the interface, the partial frequencies always fall off resonance.

In the case of weak damping, the solution of the dispersion equation can easily be written in explicit form:

$$\Omega_{\pm}=\left(\frac{\tilde{\omega}_1^2+\tilde{\omega}_2^2\pm\sqrt{(\tilde{\omega}_1^2-\tilde{\omega}_2^2)^2+4g_1g_2f_{12}^2}}{2}\right)^{1/2}. \tag{30}$$

When the oscillator frequencies are equal, i.e., $\omega_1=\omega_2=\omega_0$, expression (30) is even more simple:

$$\begin{aligned}\Omega_{\pm}&=\left(\omega_0^2-\frac{g_1f_{11}+g_2f_{22}\mp\sqrt{(g_1f_{11}-g_2f_{22})^2+4g_1g_2f_{12}^2}}{2}\right)^{1/2}\\&\approx\omega_0-\frac{g_1f_{11}+g_2f_{22}\mp\sqrt{(g_1f_{11}-g_2f_{22})^2+4g_1g_2f_{12}^2}}{4\omega_0},\end{aligned} \tag{31}$$

but even these simple expressions show that the relationships between the eigenfrequencies of the system and the absolute and relative positions of the dipoles are fairly complex, the coefficients f_{ij} being dependent on the same parameters. Nevertheless, the analysis of the case of negligibly small damping [Eq. (30)] allows one to conclude that it is impossible in the given case to attain exact resonance in the system, i.e., the eigenfrequencies will never coincide, no matter what the parameters of the problem.

To make numerical calculations, we will measure all the frequencies and linewidths involved in terms of some linewidth $\gamma^*=3.14\times10^{13}\ \mathrm{s}^{-1}$, and take the dimensionless coefficients to be equal:

$$\tilde{g}_1=\frac{e^2}{m_1a^3\gamma^{*2}}=\tilde{g}_2=\frac{e^2}{m_2a^3\gamma^{*2}}; \tag{32}$$

that is, we will assume that the masses of the oscillating charges are the same.

Note that if the charge and mass of an oscillating particle are expressed in terms of the radiative linewidth

$$\gamma_i^R=\frac{2e^2}{3c^3}\frac{\omega_i^2}{m_i} \tag{33}$$

(we take it that the transition oscillator force is equal to unity), the expressions for the dimensionless coupling coefficients can be reduced to the form

$$\tilde{g}_1=\tilde{g}_2=\frac{3}{2}\frac{\gamma^R}{\left(\dfrac{\omega_1+\omega_2}{2}\right)^2}\frac{c^3}{\alpha^3\gamma^{*2}}, \tag{34}$$

where γ^R is some effective radiative linewidth. In our numerical calculations, we assume that $\gamma^R/\gamma^*=10^{-4}$.

Figure 2 shows the solutions of the dispersion equation as a function of the position of the acceptor at such problem parameters as maximize the equalization of the frequencies. One can easily see the intensification of frequency splitting (‘‘line repulsion’’), going in line with the increase of the dipole-dipole interaction, and the vanishing of one of the normal modes at $z_2\approx0.5$ nm. The dashed line in the figure shows the solution of the dispersion equation in the case of a

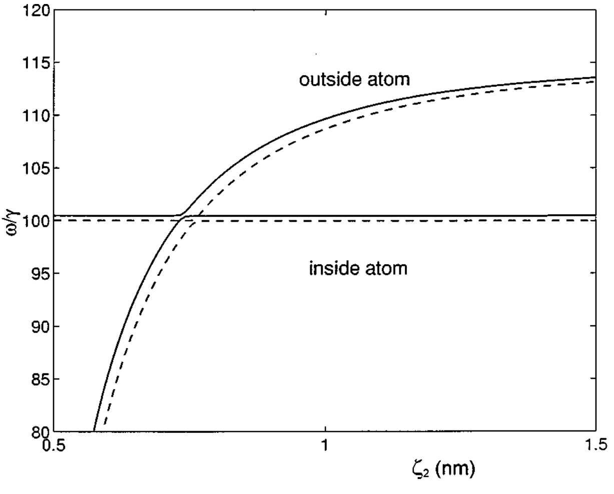

FIG. 2. Eigenfrequencies as a function of the position of the acceptor ζ_2 in the case of partial frequencies resonance (radial orientation; $\omega_1/\gamma^*=100$, $\omega_2/\gamma^*=115$, $\gamma_1/\gamma^*=\gamma_2/\gamma^*=1$, $a=4.75$ nm, and $\zeta_1=7.4$ nm). One can easily see the ‘‘line repulsion,’’ going in line with the increase of the dipole-dipole interaction, and the vanishing of one of the normal modes at $\zeta_2\approx0.5$ nm. The dashed line shows the eigenfrequencies in the case of a plane interface. Comparing between these curves allows one to conclude that the solutions of the dispersion equations in the given case behave qualitatively alike.

plane interface. Comparing between these curves allows one to conclude that the solutions of the dispersion equations in the given case behave qualitatively alike.

More complex relationships will occur if we consider the damping of the oscillators. In that case, it is possible to demonstrate that there exist conditions under which the partial frequencies are not equal, and the force of interaction between the oscillators is such that exact resonance occurs in the system. If we fix the atoms in some random positions and select their frequencies to satisfy the equations

$$\omega_1^2=\frac{1}{4}\,\gamma_1^2+g_1 f_{11}^{\mathrm{rad}}(x_1)+\frac{4g_1g_2 f_{12}^{\mathrm{rad}^2}(x_1,x_2)}{(\gamma_1-\gamma_2)^2},$$

$$\omega_2^2=\frac{1}{4}\,\gamma_2^2+g_2 f_{22}^{\mathrm{rad}}(x_2)+\frac{4g_1g_2 f_{12}^{\mathrm{rad}^2}(x_1,x_2)}{(\gamma_1-\gamma_2)^2}, \tag{35}$$

the solutions of the dispersion equation will become degenerate. If we assume that $\Omega_i=-i(\overline{\gamma_i}/2)+\overline{\omega_i}$, then

$$\overline{\gamma_1}=\overline{\gamma_2}=\frac{\gamma_1+\gamma_2}{2},$$

$$\overline{\omega_1^2}=\overline{\omega_2^2}=\tfrac{1}{2}[\omega_1^2-g_1 f_{11}^{\mathrm{rad}}(x_1)+\omega_2^2-g_2 f_{22}^{\mathrm{rad}}(x_2)-\tfrac{1}{4}(\gamma_1-\gamma_2)^2]. \tag{36}$$

Figure 3 shows the solutions of the dispersion equation as a function of the position of the external atom at a certain choice of the problem parameters providing for the occurrence of exact resonance when the second atom is 2 nm distant from the surface of the microsphere. It can be seen from this figure that as the second atom approaches the microsphere, no frequency repulsion takes place at first, and it is only the imaginary parts of the solutions that change, until they coincide completely at the point of resonance. Once resonance is reached, the frequencies rapidly move apart.

When one of the parameters of the system changes, the latter falls off resonance. Figure 4 shows the behavior of the eigenfrequencies and linewidths as the frequency of the external atom (in free space) rises from $\omega_2/\gamma^*=114$ to $\omega_2/\gamma^*=116$ (the dashed lines represent the partial frequencies $\tilde{\omega}_{1,2}$). In that case, all the dependencies are of monotonic character: as the external (acceptor) atom draws closer to the surface of the microsphere, its frequency and the linewidth of the internal atom increase, whereas the frequency of the internal atom and the linewidth of the acceptor atom decrease. At very small distances (not shown in the figure), the oscillatory condition of the internal atom vanishes altogether.

A different situation occurs when the dimensionless frequency of the external atom drops from $\omega_2/\gamma^*=114.1$ to $\omega_2/\gamma^*=112$ (Fig. 5) (the dashed lines represent the partial frequencies $\tilde{\omega}_{1,2}$). In that case, the monotonic behavior of the atomic frequencies as a function of the position of the external atom persists (though the frequency of the external atom becomes decreasing, and that of the internal one increasing). As for the linewidths, their behavior is not monotonic, so that after having drawn closer in the region of resonance, they start approaching their initial values.

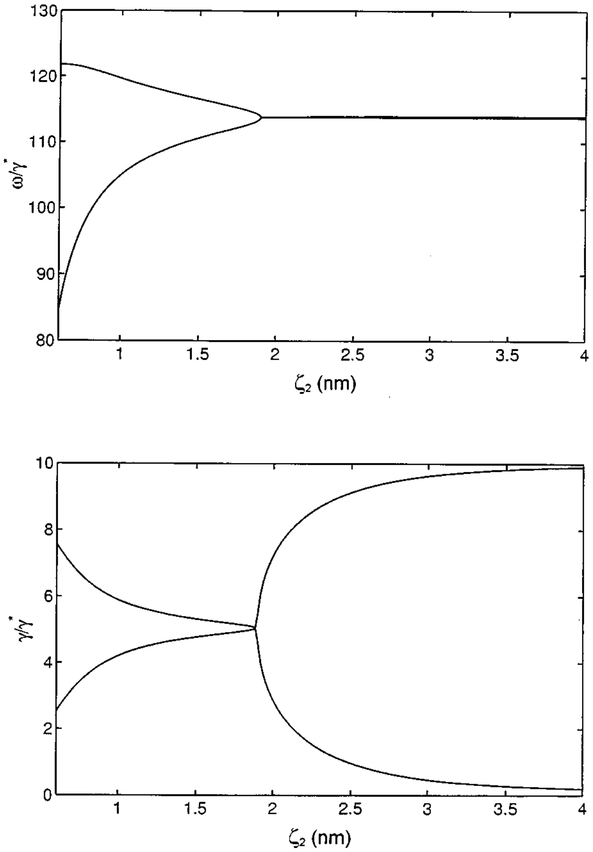

FIG. 3. Eigenfrequencies as a function of the position of the acceptor ζ_2 in the case of exact resonance (radial orientation; $\omega_1/\gamma^*=100$, $\omega_2/\gamma^*=114.1$, $\gamma_1/\gamma^*=0.1$, $\gamma_2/\gamma^*=10$, $a=1$ nm, and $\zeta_1=1$ nm). It can be seen from this figure that as the second atom approaches the microsphere, no frequency repulsion takes place at first, and it is only the imaginary parts of the solutions that change until they coincide completely at the point of resonance. Once resonance is reached, the frequencies rapidly move apart.

Up to now we have considered the case of radially oriented dipoles (head to tail geometry), but the situation with the tangential orientation of the dipoles, i.e., when the oscillation direction is normal to the radius (sandwich geometry), is exactly the same. In that case, there take place the same effects, the only difference being that the interaction force decreases and the resonance occurs at closer distances to the surface of the microsphere. Figure 6 illustrates the behavior of the atomic frequencies and linewidths at the same system parameters as in the case of radial dipole orientation. It can be seen that exact resonance in this case occurs when the external atom comes within some 1.4 nm of the microsphere; i.e., at smaller distances from the surface of the latter (in the case of radial orientation, resonance occurs at a distance of around 2.1 nm from the surface of the microsphere).

IV. ENERGY TRANSFER BETWEEN THE OSCILLATORS (CLASSICAL THEORY)

With the solutions of the dispersion equation known, one can easily find all the characteristics of the classical system. To illustrate, the oscillation equation of the second oscillator

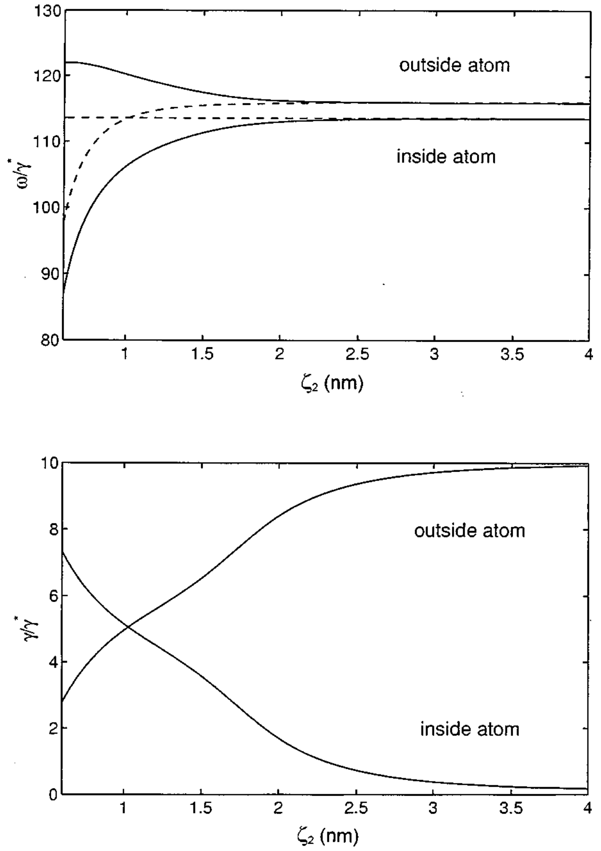

FIG. 4. Eigenfrequencies as a function of the position of the acceptor ζ_2 near exact resonance (radial orientation; $\omega_1/\gamma^* = 100$, $\omega_2/\gamma^* = 116$, $\gamma_1/\gamma^* 0.1$, $\gamma_2/\gamma^* = 10$, $a = 1$ nm, and $\zeta_1 = 1$ nm). In that case, all the dependencies are of monotonic character: as the external (acceptor) atom draws closer to the surface of the microsphere, its frequency and the linewidth of the internal atom increase, whereas the frequency of the internal atom and the linewidth of the acceptor atom decrease. At very small distances (not shown), the oscillatory condition of the internal atom vanishes altogether. The dashed lines correspond to no interaction case, i.e., to partial frequencies.

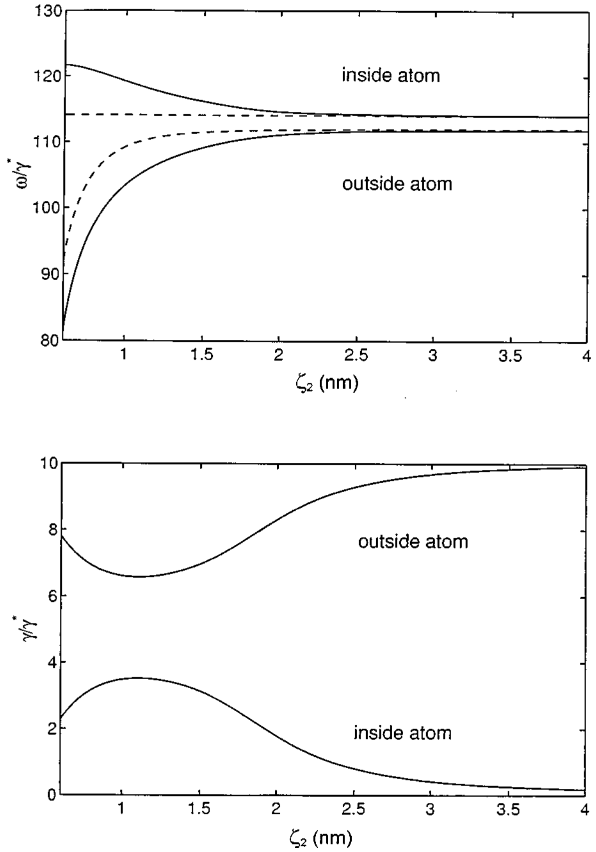

FIG. 5. Eigenfrequencies as a function of the position of the acceptor ζ_2 near exact resonance (radial orientation; $\omega_1/\gamma^* = 100$, $\omega_2/\gamma^* = 112$, $\gamma_1/\gamma^* = 0.1$, $\gamma_2/\gamma^* = 10$, $a = 1$ nm, and $\zeta_1 = 1$ nm). In that case, the monotonic behavior of the atomic frequencies as a function of the position of the external atom persists (though the frequency of the external atom becomes decreasing and that of the internal one, increasing). The dashed lines correspond to no interaction case, i.e., to partial frequencies. As for the linewidths, their behavior is not monotonic, so that after having drawn closer in the region of resonance, they start to approach their initial values.

(acceptor) may be described by the equation

$$d_2(t) = e^{-\bar{\gamma}_1 t/2}[c_1 \sin(\bar{\omega}_1 t) + c_2 \cos(\bar{\omega}_1 t)] + e^{-\bar{\gamma}_2 t/2}[c_3 \sin(\bar{\omega}_2 t) + c_4 \cos(\bar{\omega}_2 t)] \tag{37}$$

in the case where the system is off exact resonance, and by the equation

$$d_2(t) = e^{-\bar{\gamma} t/2}[c_1 \sin(\bar{\omega} t) + c_2 \cos(\bar{\omega} t)] + e^{-\bar{\gamma} t/2} t[c_3 \sin(\bar{\omega} t) + c_4 \cos(\bar{\omega} t)] \tag{38}$$

at exact resonance (when it is the eigenfrequencies and not partial frequencies that coincide). In the above equations, $\Omega = -i(\bar{\gamma}/2) + \bar{\omega}$. The coefficients c_i can be readily found if we assume that it is only the first oscillator that is excited at the initial instant $t = 0$ $[d_1(0) = 1,\ \dot{d}_1(0) = 0]$, while the second is at rest $[d_2(0) = 0,\ \dot{d}_2(0) = 0]$. In the general case, the resultant expressions for these coefficients are rather cumbersome, and therefore we will only give them for the case of weak damping (nonresonance case):

$$c_1 = c_3 = 0; \quad c_2 = -c_4 = \frac{g_2 f_{12}}{(\Omega_2^2 - \Omega_1^2)}. \tag{39}$$

In the case of resonance, we have (arbitrary damping)

$$c_1 = \frac{g_2 f_{12}(3\bar{\gamma} - 2\gamma_2)}{4\bar{\omega}^3}, \quad c_2 = 0,$$
$$c_3 = \frac{g_2 f_{12}}{2\bar{\omega}}, \quad c_4 = -\bar{\omega} c_1. \tag{40}$$

It is only natural to take the ratio between the energy of the second oscillator and the initial energy of the first oscillator as a measure of excitation of the second oscillator:

$$\eta_2 = \frac{E_2(t)}{E_1(0)} = \frac{m_2(\dot{x}_2^2 + \omega_2^2 x_2^2)}{m_1(\omega_1^2 x_1^2(0))} \approx 2\frac{\overline{x_2^2}}{x_1^2(0)}. \tag{41}$$

The overscored symbol in Eq. (41) denotes averaging over high frequency.

Substituting expression (37) into Eq. (41), and averaging, we obtain the following expression for the measure of exci-

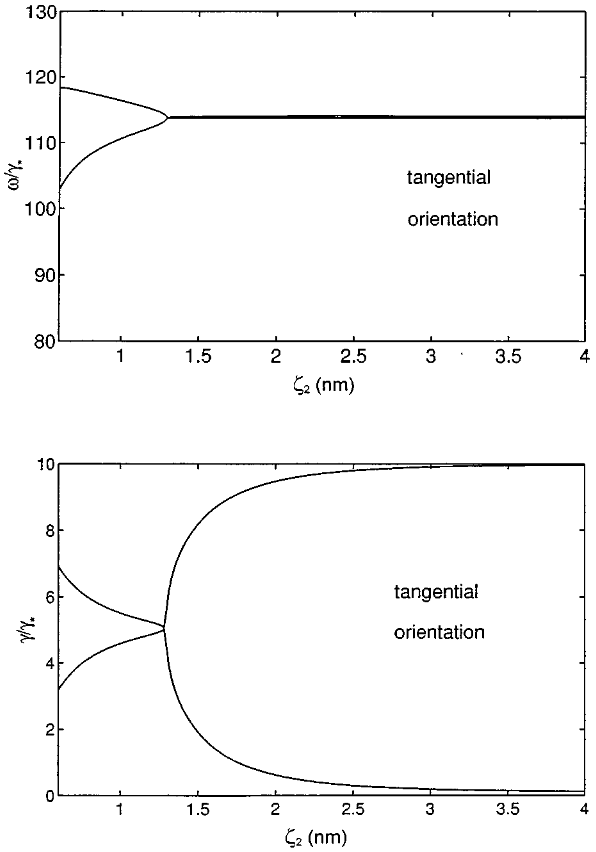

FIG. 6. Eigenfrequencies as a function of the position of the acceptor ζ_2 in the case of exact resonance (tangential orientation; $\omega_1/\gamma^*=100$, $\omega_2/\gamma^*=114.2$, $\gamma_1/\gamma^*=0.1$, $\gamma_2/\gamma^*=10$, $a=1$ nm, and $\zeta_1=1$ nm).

tation of the second oscillator in the nonresonance case, which only includes low-frequency terms:

$$\eta_2=(c_1^2+c_1^2)e^{-\overline{\gamma}_1 t}+(c_3^2+c_4^2)e^{-\overline{\gamma}_2 t}+2e^{-(\overline{\gamma}_2+\overline{\gamma}_1)t/2}\{(c_1c_4-c_2c_3)\sin[(\overline{\omega}_1-\overline{\omega}_2)t]+(c_1c_3+c_2c_4)\cos[(\overline{\omega}_1-\overline{\omega}_2)t]\}. \tag{42}$$

In the case of resonance, it is necessary to substitute expression (38) into Eq. (41), to obtain

$$\eta_2^{\text{reson}}=e^{-\overline{\gamma}t}[(c_1+c_3t)^2+(c_2+c_4t)^2]. \tag{43}$$

The behavior of expressions (42) and (43) as a function of time is governed by the ratio between the frequency difference and damping. Where damping is small in comparison with the difference between the eigenfrequencies, expressions (39) hold true, and we obtain the following simple expression for the degree of excitation of the second oscillator:

$$\eta_2=\left(\frac{2g_2f_{12}}{(\Omega_2^2-\Omega_1^2)}\right)^2\sin^2[(\Omega_1-\Omega_2)t/2]. \tag{44}$$

In the case of resonance, we have

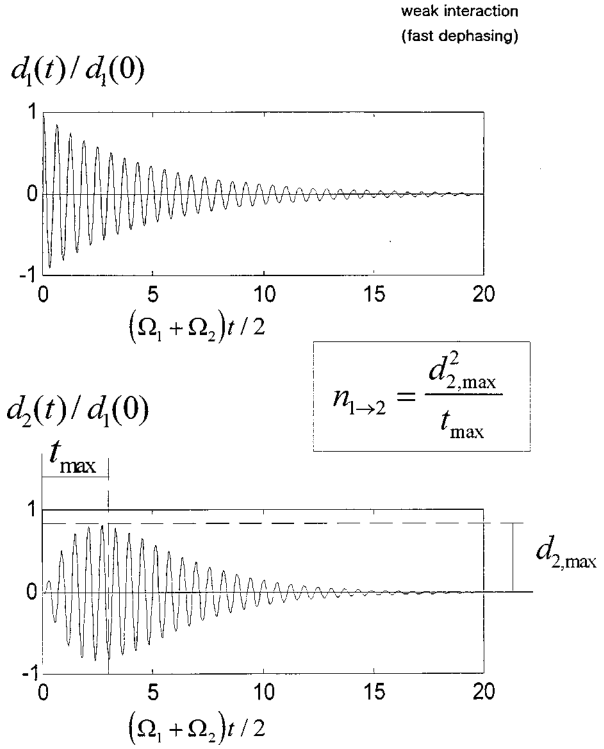

FIG. 7. Resonance energy-transfer illustration.

$$\eta_2^{\text{res}}=\left(\frac{g_2f_{12}}{4\overline{\omega}^3}\right)^2e^{-\overline{\gamma}t}[(3\overline{\gamma}-2\gamma_2+2\overline{\omega}^2t)^2+(3\overline{\gamma}-2\gamma_2)^2\overline{\omega}^2t^2]. \tag{45}$$

There are no beats in this case.

In any case, the energy of the second oscillator treated as a function of time has at least one maximum (see Fig. 7). This circumstance allows us to define, according to Ref. [4], the energy-transfer rate (or excitation probability for the second particle) as the ratio between the maximum degree of excitation and the time it takes for excitation to reach its maximum, i.e.,

$$n_{1\to 2}=\frac{\eta_{2,\max}}{t_{\max}}. \tag{46}$$

In the case of weak damping (strong interaction), we have

$$\eta_{2,\max}=\left(\frac{2g_2f_{12}}{(\Omega_2^2-\Omega_1^2)}\right)^2, \tag{47}$$

$$t_{\max}=\frac{\pi}{|\Omega_1-\Omega_2|}, \tag{48}$$

and, for the energy-transfer rate (excitation probability), we obtain the expression

$$n_{1\to 2}=\frac{1}{\pi}\left(\frac{2g_2f_{12}}{(\Omega_2^2-\Omega_1^2)}\right)^2|\Omega_1-\Omega_2|. \tag{49}$$

In the case of strong interaction, i.e., when the amplitude of the second dipole (acceptor) is equal to that of the first dipole (donor), the energy-transfer rate between the atomic dipoleswill only be governed by the maximum time $t_{\max}$ (see, for example, Ref. [23]):

$$n_{1\to 2}^{\mathrm{res}}=\left|\frac{\Omega_2-\Omega_1}{\pi}\right|. \tag{50}$$

Expressions (49) and (50) agree fully with the results obtained by Förster [4]. In the case of exact resonance [see Eq. (45)], the time it takes for the oscillation amplitude of the second oscillator to reach its maximum is defined by the expressions

$$t_{\max}^{\mathrm{reson}}=\frac{\overline{\omega}[A-2\overline{\gamma}(3\overline{\gamma}-2\gamma_2)]+\sqrt{(\overline{\omega}A)^2+(3\overline{\gamma}-2\gamma_2)^2}}{\overline{\gamma}\overline{\omega}A},\quad A=(2\overline{\omega})^2+(3\overline{\gamma}-2\gamma_2)^2, \tag{51}$$

and the energy-transfer rate is given by

$$n_{1\to 2}^{\mathrm{reson}}=\frac{\eta_2^{\mathrm{reson}}(t_{\max}^{\mathrm{reson}})}{t_{\max}^{\mathrm{reson}}}=\left(\frac{g_2f_{12}}{4\overline{\omega}^3}\right)^2\frac{2\overline{\omega}^2A[\overline{\omega}A+\sqrt{(\overline{\omega}A)^2+(3\overline{\gamma}-2\gamma_2)^2}]}{\overline{\gamma}\{\overline{\omega}[A-2\overline{\gamma}(3\overline{\gamma}-2\gamma_2)]+\sqrt{(\overline{\omega}A)^2+(3\overline{\gamma}-2\gamma_2)^2}\}}\,e^{-\overline{\gamma}t_{\max}^{\mathrm{reson}}}. \tag{52}$$

V. ENERGY TRANSFER BETWEEN THE OSCILLATORS (QUANTUM THEORY)

In Sec. IV, we found energy-transfer rates in the classical approximation. Similar results can also be obtained in the case of quantum mechanics if we restrict ourselves to the analysis of two-level donor and acceptor atoms. Indeed, for the three states of our two-level systems [24], if we introduce the density matrix

$$\langle 1|=\varphi_1'\varphi_2;\langle 2|=\varphi_2'\varphi_1;\langle 3|=\varphi_2\varphi_1 \tag{53}$$

(where the prime denotes an excited state), the general equation for the density matrix will assume the forms

$$\begin{aligned}
\dot{\rho}_{11}&=\frac{1}{i\hbar}(V_{12}\rho_{21}-V_{21}\rho_{12})-\gamma_1\rho_{11},\\
\dot{\rho}_{22}&=-\frac{1}{i\hbar}(V_{12}\rho_{21}-V_{21}\rho_{12})-\gamma_2\rho_{22},\\
\dot{\rho}_{12}&=\frac{1}{i\hbar}V_{12}(\rho_{22}-\rho_{12})-\Gamma_{12}\rho_{12}+\frac{\Delta E}{i\hbar}\rho_{12},\\
\dot{\rho}_{21}&=\frac{1}{i\hbar}V_{21}(\rho_{11}-\rho_{22})-\Gamma_{12}\rho_{21}-\frac{\Delta E}{i\hbar}\rho_{21},\\
&\rho_{11}+\rho_{22}+\rho_{33}=1.
\end{aligned} \tag{54}$$

Here $V_{12}=\langle 1|V|2\rangle$ is the interaction energy matrix element. $\Delta E=(E_1'-E_1)-(E_2'-E_2)$, and γ_1, γ_2, and Γ_{12} are the longitudinal and transverse relaxation rates. It is not very difficult to understand that one should use ΔE as the difference between the partial frequencies with due regard for the interaction with the microsphere:

$$\Delta E=(\tilde{\omega}_1-\tilde{\omega}_2)\hbar=\Delta\tilde{\omega}\hbar, \tag{55}$$

where the partial frequencies $\tilde{\omega}_1$ and $\tilde{\omega}_2$ are defined by expressions (17) in the case of radial orientation, and by expressions (22) in the case of tangential orientation.

To find the interaction energy matrix element as applied to our problem, we write down the classical system's Lagrangian corresponding to equations of motion (3) without damping:

$$\begin{aligned}
L&=L_1+L_2+L_{\mathrm{int}},\\
L_1&=\frac{m_1(\dot{d}_1^2-\tilde{\omega}_1^2d_1^2)}{2},\\
L_2&=\frac{m_2(\dot{d}_2^2-\tilde{\omega}_2^2d_2^2)}{2},\\
L_{\mathrm{int}}&=\frac{e^2}{a^3}f_{12}(x_1x_2)d_1d_2.
\end{aligned} \tag{56}$$

One can see from this Lagrangian that the interaction energy matrix element is given by the expression

$$V_{12}=\left\langle 1\left|-\frac{L_{\mathrm{int}}}{e^2}\right|2\right\rangle=-f_{12}(x_1,x_2)\frac{(d_1)_{eg}(d_2)_{ge}}{a^3}, \tag{57}$$

where we mean either radial or tangential components of the transition dipole moment matrix elements. The density matrix dynamics thus proves to be fully determinate.

The detailed analysis of all the conditions of the system of equations (54) is the subject of an individual investigation. Nevertheless, one can find, without solving this system in explicit form, the quantity

$$\begin{aligned}
n_{12}&=\left[\int_0^\infty\rho_{11}(t)dt\right]^{-1}-\gamma_1\\
&=\frac{2|V_{12}|^2/(\Gamma_{12}\hbar^2)}{1+[\Delta E/(\Gamma_{12}\hbar)]^2+2|V_{12}|^2/(\Gamma_{12}\gamma_2\hbar^2)},
\end{aligned} \tag{58}$$

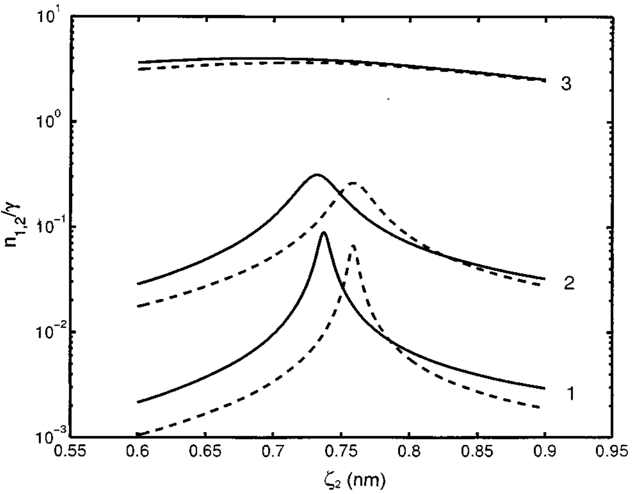

FIG. 8. Resonance energy-transfer rate (49) as a function of acceptor position ζ_2 (radial orientation; the dashed curve corresponds to the plane interface between the dipoles). $1-\zeta_1=7.4$ nm, $2-\zeta_1=4.4$ nm, $3-\zeta_1=1.4$ nm, $\omega_1/\gamma^*=100$, $\omega_2/\gamma^*=115$, $\gamma_1/\gamma^*=\gamma_2/\gamma^*=1$, and $a=4.75$ nm. Here the energy-transfer rate curve corresponding to the case where the first (inside) atom is closer to the opposite side of the microsphere ($\zeta_1=7.4$ nm) is of resonance character. If the inside atom is close to the center of the microsphere ($\zeta_1=4.4$ nm), the resonance effect diminishes, though the total energy-transfer rate increases on account of the atoms drawing closer together. If the inside atom is located near the surface of the microsphere ($\zeta_1=1.4$ nm), the resonance effect practically vanishes, but the total energy-transfer rate reaches its maximum, the atoms being the closest to each other. The dashed lines in this figure indicate energy-transfer rates corresponding to a plane interface. Note that the point at hand is the resonance of the partial frequencies and a relatively weak damping. The occurrence of exact resonance does not mean that the energy-transfer rate will be of resonance character. This is especially true in the case of real systems where the acceptor atom features a strong damping.

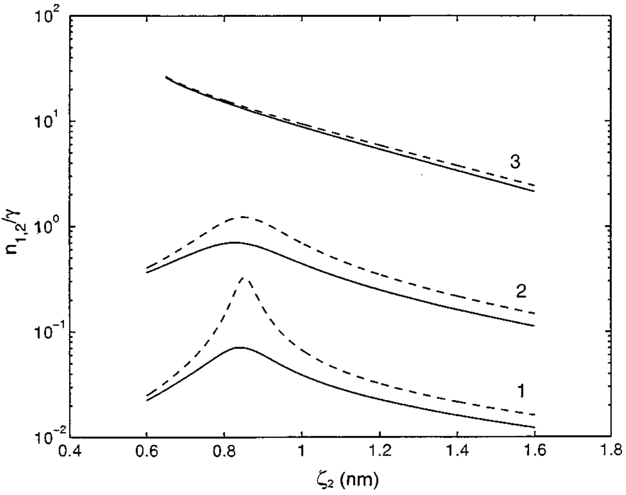

FIG. 9. Resonance energy-transfer rate as a function of acceptor position ζ_2 [radial orientation; the solid curve corresponds to the computer calculations; the dashed curve corresponds to the analytical solution (49)]. $1-\zeta_1=4.3$ nm, $2-\zeta_1=2.4$ nm, $3-\zeta_1=0.5$ nm, $\omega_1/\gamma^*=100$, $\omega_2/\gamma^*=110$, $\gamma_1/\gamma^*=\gamma_2/\gamma^*=1$, and $a=4.75$ nm. In the case of strong interaction (the top curve), one can see a good agreement between the analytical formula and the exact calculation. As the interaction weakens (as the donor atom moves away from the surface of the microsphere; see the central and bottom curves), the discrepancy between the results increases, although the analytical formula correctly describes all the qualitative characteristic features.

which can be treated as the generalized energy-transfer rate [25].

Expressing the squared dipole moment matrix elements in terms of the oscillator frequencies by means of the relation

$$|\mathbf{d}_{i,eg}|^2=\frac{\hbar e^2}{2m_i\omega_i}f_i, \tag{59}$$

and assuming that the oscillator forces f_i are equal to unity, we obtain the following expression for the squared matrix element:

$$|V_{12}|^2=f_{12}^{\mathrm{rad}^2}\frac{\hbar^2 g_1 g_2}{4\omega_1\omega_2}. \tag{60}$$

Substituting the above expression into Eq. (58), we obtain the final expression for the energy-transfer rate in the vicinity of a curved surface:

$$n_{1,2}=\frac{(f_{12}^{\mathrm{rad}})^2\,\dfrac{g_1g_2}{2\omega_1\omega_2\Gamma_{12}}}{1+\left(\dfrac{\Delta\tilde{\omega}}{\Gamma_{12}}\right)^2+f_{12}^{\mathrm{rad}^2}\,\dfrac{g_1g_2}{2\omega_1\omega_2\Gamma_{12}\gamma_2}}, \tag{61}$$

where

$$\Delta\tilde{\omega}=\sqrt{\omega_1^2-g_1f_{11}^{\mathrm{rad}}(x_1)}-\sqrt{\omega_2^2-g_2f_{22}^{\mathrm{rad}}(x_2)}. \tag{62}$$

The above expression in this form does not depend on Planck's constant.

It should be emphasized once more that being the exact characteristic of system (54), expression (61) provides an adequate description only in the case of strong damping in the second system.

VI. RESULTS AND DISCUSSION

To find the energy-transfer rate, it is sufficient to substitute the eigenfrequency values found into expressions (49) or (52), or else find exact expressions for the coefficients c_i, and then use expression (42) (see Fig. 7) to find the energy-transfer rate numerically. In the quantum-mechanical case, use can be made of expression (61).

Figure 8 shows the rate of energy exchange between the oscillators [see expression (49)] as a function of the position of the outer atom (the dashed line corresponds to a plane interface between the dipoles) for various positions of the inner atom. In our case of a microsphere with a radius of 4.75 nm, of resonance character is the energy-transfer rate curve corresponding to the case where the first (inside) atom

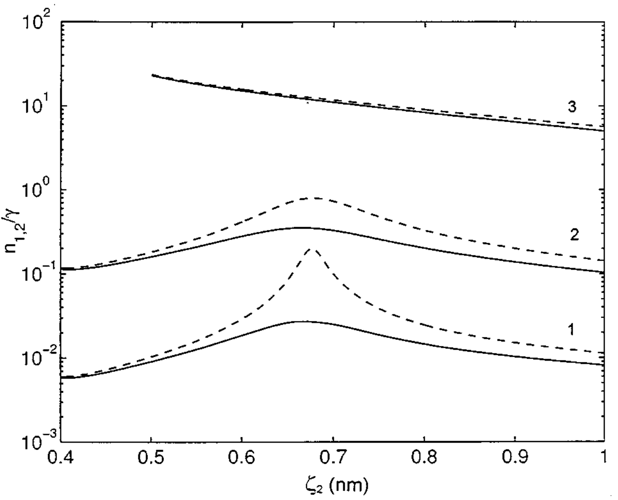

FIG. 10. Resonance energy-transfer rate as a function of acceptor position ζ_2 [tangential orientation; solid line corresponds to the computer simulation, the dashed curve corresponds to the analytical solution (49)]: $1-\zeta_1=4.3$ nm, $2-\zeta_1=2.4$ nm, $2-\zeta_1=0.5$ nm, $\omega_1/\gamma^*=100$, $\omega_2/\gamma^*=110$, $\gamma_1/\gamma^*=\gamma_2/\gamma^*=1$, and $a=4.75$ nm. Note that all the effects occur at closer distances to the surface of the microsphere in comparison with case of radial orientation.

is closer to the opposite side of the microsphere ($z_1=7.4$ nm). If the inside atom is close to the center of the microsphere ($z_1=4.4$ nm), the resonance effect diminishes, though the total energy-transfer rate increases on account of the atoms drawing closer together. If the inside atom is located near the surface of the microsphere ($z_1=1.4$ nm) the resonance effect practically vanishes, but the total-energy-transfer rate reaches its maximum, the atoms being closest to each other. The dashed lines in this figure indicate the energy-transfer rates corresponding to a plane interface. As one can see, the qualitative features in the plane case are generally retained, but with the parameters fixed (the position of the acceptor fixed) the energy-transfer rates may differ substantially between the plane and spherical cases; for the lower curve, this difference may be as great as an order of magnitude. Note that the point in hand is the resonance of the partial frequencies and a relatively weak damping. The occurrence of exact resonance does not mean that the energy-transfer rate will be of resonance character. This is especially true in the case of real systems where the acceptor atom features a strong damping.

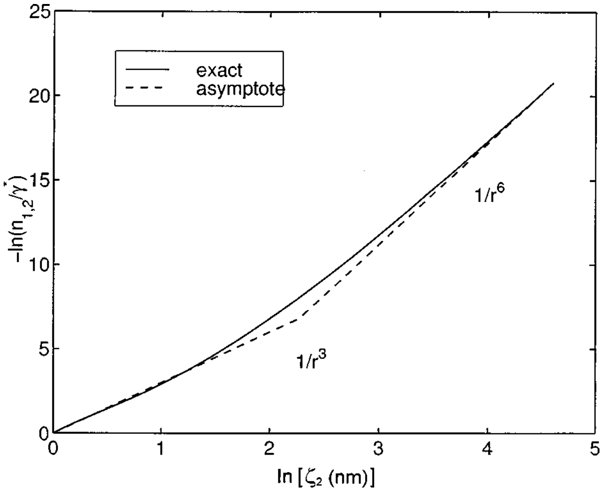

FIG. 11. Resonance energy-transfer rate as a function of acceptor position ζ_2 (radial orientation; log-log scale; the dashed curves correspond to the different decreasing law). $\omega_1/\gamma^*=100$, $\omega_2/\gamma^*=110$, $\gamma_1/\gamma^*=\gamma_2/\gamma^*=1$, $a=4.75$ nm, and $\zeta_1=2.4$ nm. It is seen from this figure that Forster's $1/r^6$ law only starts to be obeyed after $r\geqslant 20$ nm, while it is the law $1/r^3$ (!) that is more appropriate up to a distance of 3 nm.

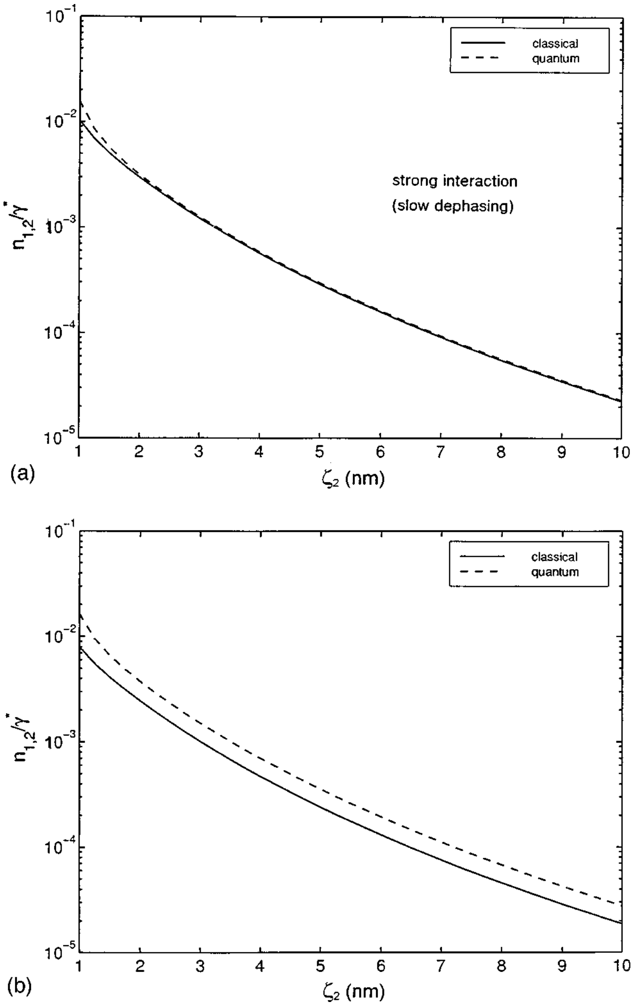

FIG. 12. Resonance energy-transfer rate (61) as a function of acceptor position ζ_2 (radial orientation; the solid line corresponds to the quantum calculation; the dashed curve corresponds to the classical calculation.) $\gamma_2/\gamma^*=\Gamma_{12}/\gamma^*=7$ (a) and $\gamma_2/\gamma^*=\Gamma_{12}/\gamma^*=10$ (b), and $\omega_1/\gamma^*=100$, $\omega_2/\gamma^*=115$, $\gamma_1/\gamma^*=0.1$, $a=4.75$ nm, and $\zeta_1=4.4$ nm.

Analytical formula (49) for the energy-transfer rate is derived on the assumption that the coupling between the oscillators is strong and their damping is weak, and it is convenient for qualitative analysis purposes. In the case of weaker interaction, the damping effects may become important, so that one has to find the energy-transfer rate numerically within the framework of the definition given above. Figure 9 presents the results of such computer calculations for various mutual arrangements of the oscillators (the solid curve), and the results of computations by the formula obtained on the assumption of weak damping (strong coupling) (the dashed curve). In the case of strong interaction (the top curve), one can see a good agreement between the analytical formula and the exact calculation. As the interaction weakens [as the donor atom moves away from the surface of the microsphere, (the central and bottom curves)], the discrepancy between the results increases, although the analytical formula correctly describes all the qualitative characteristic features.

In the case of tangential orientation of the atomic dipoles (Fig. 10), the situation remains generally the same, although all the effects occur at closer distances to the surface of the microsphere, 0.7 nm instead of the 0.9 nm characteristic of the radial dipole orientation.

It is well known that, according to Förster, the energy-transfer rate in a homogeneous substance decreases as the sixth power of the interatomic distance. The only question now arises: How does the presence of a dielectric microsphere affect this law? In any case, the effect of the microsphere must be substantial, for a change in the distance between the dipoles causes to vary not only the force of coupling between them, but their oscillation frequencies as well. Figure 11 shows, on a log-log scale, the energy-transfer rate as a function of the position of the second atom. It is seen from this figure that the law $1/r^6$ only starts to be obeyed after $r \geqslant 20$ nm, while it is the law $1/r^3$ (!) that is more appropriate up to an distance of 3 nm. This circumstance is very important to the understanding of the operation of the scanning FRET microscope [5].

In the preceding sections, we have presented both classical and quantum mechanical approaches to the determination of the electronic excitation transfer rate. This naturally raises the question as to the agreement between these two approaches. One can expect beforehand that the results will be close, there being no dependence on Planck's constant in the quantum-mechanical expression (61). However, the quantum-mechanical result includes the transverse relaxation rate, and so no exact coincidence can be expected between the results. Nevertheless, as can be seen from Fig. 12(a), a very good agreement can take place in some region of the problem parameters. Where the parameter values are outside this region, some discrepancy arises, but the behavior of the system remains qualitatively the same (especially at great distances from the microsphere) [Fig. 12(b)].

VII. CONCLUSION

A theoretical investigation is conducted in the present work into the processes of resonance energy transfer from a donor atom to an acceptor atom in the presence of a spherical interface between them. The model used is a system of two atomic dipoles, one residing inside a dielectric microsphere and the other in the vicinity of its outer surface, interacting through the intermediary of electromagnetic field. The dispersion equation of this system is found with due regard for delay effects. The analysis of this dispersion equation in a quasistatical approximation shows that, by appropriately selecting the problem parameters, one can attain both partial-frequency and exact resonances. Electronic excitation transfer rates in the case of both classical and quantum-mechanical dipole dynamics are found on the basis of the dispersion equation solutions obtained. It is demonstrated that the classical and quantum-mechanical calculations yield qualitatively similar results. This agreement also proves very good quantitatively at a certain choice of the problem parameters.

It is demonstrated that as the inside atom approaches the surface of the microsphere, the dipole-dipole interaction grows stronger and the rate of excitation transfer from one atom to the other increases materially. The relationship between the transfer rate and the position of the outside atom (acceptor) at not very strong dampings features a resonant maximum near the surface of the microsphere. As the distance between the acceptor atom and the surface of the microsphere grow larger, the transfer rate decreases first as $1/r^3$ and then, at farther distances, as $1/r^6$, which agrees with the results obtained by Förster.

It is appropriate to emphasize that because of smallness of microsphere ($a \ll 1$) its resonances (whispering gallery modes) [20–22] cannot be excited here. The resonances we found are due to variation of partial frequencies of atomic oscillators. In the case of large microspheres ($a \geqslant 1$) it is possible to excite its resonances (whispering gallery modes) [20–22], and in the case of strong coupling our system will be analogous to system of three coupled oscillators. The results of the investigation of this case will be presented in a separate publication.

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