

FOUR-CENTER RESONANCE ENERGY TRANSFER IN RARE EARTH DOPED CRYSTALS

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The four-center resonance energy transfer in the framework of multipolar Hamiltonian formalism of interaction of the ions with the local transverse component of the electromagnetic field has been investigated. The structure of the transfer amplitude points to distinct transfer mechanisms. The particular case of rare-earth ions was considered when calculating the transition dipoles matrix elements.

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1. Introduction

When the absorption of light leads to electronic excitation, the associated energy is rapidly conveyed from the site of initial deposition to another. This phenomenon is well known in many areas of solid state physics and its distance dependence is important, for instance, in the detailed structural analysis of proteins [1,2]. When the energy transfer from donor to acceptor takes place between two chemically distinct species separated beyond wave function overlap, it has generally been considered as potentially involving two distinct mechanisms: at short distances, radiationless transfer with an inverse sixth power dependence on the donor-acceptor separation and at longer distances, radiative transfer identifiable with the well-known inverse square law. At intermediate distances, the dependence of transfer probability on donor-acceptor separation proved to be more complicated. The recent development of a unified theory of resonance energy transfer (RET), based on quantum electrodynamics, has identified these two mechanisms as the long- and short-range limit of a more general mechanism [3].

Besides the applications at the study of optical energy harvesting, solar energy conversion and photosynthesis [4], it is widely acknowledged that resonance energy transfer plays a highly important role in the photophysics of rare earth doped crystals (Pr^{3+}), used as solid-state laser media. The relative position of the rare earths energy levels generally affords excellent opportunities for the design of materials to invoke not only conventional RET, but also higher order effects.

The rare-earths have a number of unique features making them highly interesting as systems for quantum computing. The optical transitions considered here involve electrons situated in an inner shell, the f-shell, which is shielded from perturbations induced by the environment, the consequence being that the rare-earth ions have very narrow homogeneous linewidths. On the other hand, the exact frequencies of these transitions depend strongly on the surrounding electric fields. The remarkable combination of narrow homogeneous linewidths and large inhomogeneous broadening provides possibilities to address narrow individual frequency channels within a large frequency interval [6-8]. It gives the possibility for realization of a controlled dynamics, allowing implementation of n -bit quantum gates.

For the implementation of quantum computing in particular systems it is of great interest to compare the decay rates of the excited rare-earth states along different channels: radiative,

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nonradiative and phononic.

Firstly, collective process of RET was studied by Andrews for three centers [9,10].

The goal of the present work is to build up a systematic theory for four-center RET. There are several reasons for the interest in a collective RET process. One is that it may represent the multicenter energy pooling process. Any such process affords a means of promoting the acceptor site to a state higher in energy than any individual initially excited donor. Compared to a multistep process, it wouldn't be necessary for suitably placed intermediate energy levels of the acceptor. The collective RET also provides the possibility of exploiting the intrinsic dependence on the mutual orientation of the donors and the acceptor. As about the multiphoton excitation of the acceptor directly from the pump laser field, there is a greater probability of the photons to be captured by any separate donors in its vicinity [5].

In the section 2 we introduce the formalism of quantum electrodynamics, define the system Hamiltonian, classify the interaction diagrams and receive the general expression for the four-center transition probability amplitude in the sixth order of perturbation theory. In the section 3 we discuss the differences between the classes of diagrams, the structure of the probability amplitude, the possible associated phenomena. In the section 4 we point out to some specific properties of transition dipole matrix elements of rare-earths.

2. The multipolar formalism of interaction of the centers with the local transverse compound of the electromagnetic field

The goal of this section is to calculate the four-center transfer rate Γ . First, we need to compute the transfer probability amplitude and consequently to introduce it into the Fermi golden rule:

$$\Gamma = (2\pi / \hbar) |M_{fi}|^2 \rho \quad (1)$$

with ρ being the density of the acceptor final states. In the following we introduce the formalism of quantum electrodynamics (QED) in order to compute the matrix element connecting the initial state $|i\rangle$ to the final state $|f\rangle$.

Let the chemically identical donor molecules (D_1, D_2, D_3) begin in an already excited state $|1\rangle$ and progress to the electronic ground state $|0\rangle$. The acceptor molecule A evolves from the ground state $|0\rangle$ to the excited state $|1\rangle$ via transferal of the excitation energies of the tributaries (D_1, D_2, D_3). The resonance condition requires that $3E_{10}^d = E_{10}^a$, where E_{10}^d is the energy lost by a donor, and E_{10}^a that gained by the acceptor. Using the formalism of QED, the transfer results from the change of virtual photons associated with radiation modes $p = (\vec{p}, \lambda)$, where \vec{p} is the photon impulse, and λ denotes its polarization. The molecules coupled to several photonic propagators pass through virtual states that we will represent as a, b .

The full Hamiltonian for such a system can be written as:

$$H = \sum_{\xi=A, D_1, D_2, D_3} H^{(\xi)} + \sum_{\xi=A, D_1, D_2, D_3} H_{\text{int}}^{(\xi)} + H_{\text{rad}} \quad (2)$$

where $H^{(\xi)}$ is the Hamiltonian of the molecule ξ , H_{rad} the Hamiltonian of the electromagnetic field, and $H_{\text{int}}^{(\xi)}$ the molecule – local field coupling Hamiltonian with the transverse compound. In the electric dipole approximation the latter operator is given by:

$$H_{\text{int}}^{(\xi)} = -\varepsilon_0^{-1} \vec{\mu}(\xi) \vec{d}^{tr}(\vec{R}_\xi) \quad (3)$$

with $\vec{\mu}(\xi)$ being the electric dipole moment operator for the considered transition and \vec{R}_ξ the position vector of molecule ξ . The transverse electric displacement field operator $\vec{d}^{tr}(\vec{R})$ can be expressed in terms of a mode expansion:

$$\vec{d}^{tr}(\vec{R}) = \sum_p \left(\frac{\hbar c p \epsilon_0}{2V} \right)^{1/2} i[\vec{e}(p)a(p)e^{i\vec{p}\vec{R}} - \vec{e}^*(p)a^+(p)e^{-i\vec{p}\vec{R}}] \quad (4)$$

Here $\vec{e}(p)$ is the polarization vector, $a^+(a)$ the creation (annihilation) operators, and V the quantization volume.

The probability amplitude or matrix element between the initial state $|i\rangle$ and final state $|f\rangle$ is given by the sixth order of perturbation theory corresponding to the three photon creation and three photon annihilation events:

$$M_{fi} = \sum_{p,q,r,s,t} \frac{\langle f | H_{int} | p \rangle \langle p | H_{int} | q \rangle \langle q | H_{int} | r \rangle \langle r | H_{int} | s \rangle \langle s | H_{int} | t \rangle \langle t | H_{int} | i \rangle}{(E_i - E_p)(E_i - E_q)(E_i - E_r)(E_i - E_s)(E_i - E_t)} \quad (5)$$

where E_n is the energy of the state $|n\rangle$, which is of the form $|D_{1n}, D_{2n}, D_{3n}, A\rangle |rad_n\rangle$.

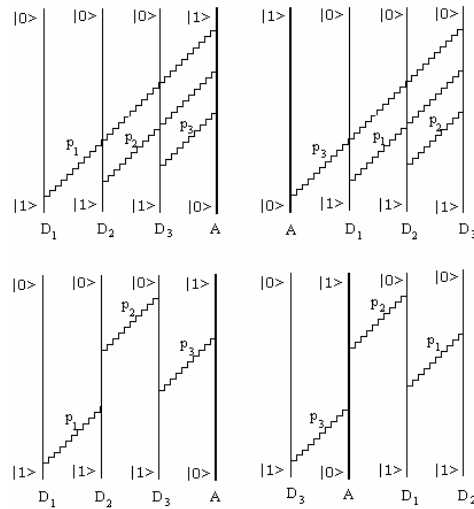


Fig 1. Example of diagrams, corresponding to different transfer mechanisms, generating the whole set of the intermediate states trough events permutation.

The sum in (5) is performed over the complete set of intermediate states that can be generated through permutation of the events in the diagrams represented, for example, in Fig. 1. They were obtained from topological reasons pointing to two different possibilities of connexion of molecular and photonic propagators. First, all three photonic propagators may be coupled, at one extremity, to a molecule propagator, arising formally as “acceptor”, and at the other extremity with the rest of molecule propagators, intervening here formally as “donors”. It is also possible that a molecule propagator, “donor”, is coupled to another, denoted “acceptor”, through a photon propagator and this subsystem is coupled in its turn to another similar one. In the latter case, we formally have two “acceptors” coupled each to two photons, so we may expect that the mechanism reduces to two three center interactions. Taking into account the distinctibility of the molecules we get four classes of diagrams of the first kind and twelve of the second, which are exemplified in the Fig. 1. Each one generates through permutation a class of $6! = 720$ diagrams. The entire set of complete states comprises 11520 diagrams. One may sum up the contributions of all diagrams

making a simple code in Mathematica, for instance. Finally one gets the following expression for the transfer probability amplitude:

$$M_{fi} = M^{(A)} + \sum_i M^{(D_i)} + \sum_{i,j} M_A^{(D_i, D_j)} + \sum_{i,j} M_{D_i}^{(A, D_j)} \quad (6)$$

where, for example:

$$\begin{aligned} M^{(A)} &= \mu_{i_1}^{01}(D_1)\mu_{i_2}^{01}(D_2)\mu_{i_3}^{01}(D_3)\alpha_{j_1 j_2 j_3}^{(3)(10)(A)}(-\omega, -\omega, -\omega)V_{i_1 j_1}(k, R_1)V_{i_2 j_2}(k, R_2)V_{i_3 j_3}(k, R_3) \\ M^{(D_1)} &= \mu_{i_1}^{01}(D_2)\mu_{i_2}^{01}(D_3)\mu_{i_3}^{10}(A)\alpha_{j_1 j_2 j_3}^{(3)(01)(D_1)}(-\omega, -\omega, 3\omega)V_{i_1 j_1}(k, R_{12})V_{i_2 j_2}(k, R_{13})V_{i_3 j_3}(3k, R_1) \\ M_A^{(D_2, D_3)} &= \mu_{i_1}^{01}(D_2)\mu_{i_2}^{01}(D_3)\alpha_{j_2 j_3}^{(2)(01)(D_1)}(2\omega, -\omega)\alpha_{j_3 j_1}^{(2)(10)(A)}(-\omega, -2\omega)V_{i_1 j_1}(k, R_2)V_{i_2 j_2}(k, R_{13})V_{i_3 j_3}(2k, R_1) \\ M_{D_2}^{(A, D_3)} &= \mu_{i_1}^{01}(A)\mu_{i_2}^{01}(D_3)\alpha_{j_2 j_3}^{(2)(01)(D_1)}(2\omega, -\omega)\alpha_{j_3 j_1}^{(2)(01)(D_2)}(-2\omega, 3\omega)V_{i_1 j_1}(3k, R_2)V_{i_2 j_2}(k, R_{13})V_{i_3 j_3}(2k, R_1) \end{aligned} \quad (7)$$

Here $\mu_i^{\alpha\beta}$ are the matrix elements of the transition dipole moments between the states $|\alpha\rangle$ and $|\beta\rangle$,

$\alpha_{ijk}^{(3)01}$ and $\alpha_{ijk}^{(3)01}$ are the two- and three-photon absorption tensors respectively:

$$\begin{aligned} \alpha_{ij}^{fi}(\bar{\omega}_1, \bar{\omega}_2) &= \sum_{\zeta} \left(\frac{\mu_i^{f\zeta} \mu_j^{\zeta i}}{E_{i\zeta} \pm \hbar\omega_1} + \frac{\mu_j^{f\zeta} \mu_i^{\zeta j}}{E_{i\zeta} \pm \hbar\omega_2} \right), \\ \alpha_{ij}^{fi}(\bar{\omega}_1, \bar{\omega}_2, \bar{\omega}_3) &= \sum_{\zeta} \left(\frac{\mu_i^{f\zeta} \alpha_{jk}^{(2)\zeta}(\bar{\omega}_3, \bar{\omega}_2)}{E_{i\zeta} \pm \hbar\omega_2 \pm \hbar\omega_3} + \frac{\mu_j^{f\zeta} \alpha_{ki}^{(2)\zeta}(\bar{\omega}_1, \bar{\omega}_3)}{E_{i\zeta} \pm \hbar\omega_1 \pm \hbar\omega_3} + \frac{\mu_k^{f\zeta} \alpha_{ij}^{(2)\zeta}(\bar{\omega}_2, \bar{\omega}_1)}{E_{i\zeta} \pm \hbar\omega_2 \pm \hbar\omega_1} \right) \end{aligned}$$

Above $V_{ij}(k, R)$ is the retarded electric-dipole potential of interaction according to Andrews:

$$V_{ij}(k, \vec{R}) = \frac{1}{4\pi\epsilon_0 R^3} [(\delta_{ij} - 3\hat{R}_i \hat{R}_j)(\cos kR + kR \sin kR) - (\delta_{ij} - \hat{R}_i \hat{R}_j)k^2 R^2 \cos kR] \quad (8)$$

In the short range, this coupling displays a R^{-3} distance dependence, though the terms linear and quadratic in kR increasingly modify the behavior as R increases. In practice, the term “short distance” indicates separations below 100 Å. The transfer rate Γ can be calculated substituting the matrix element (6) into the Fermi golden rule (1). If the resonance condition is satisfied only approximately, then RET proceeds only with the absorption or emission of phonons. The transfer rate (1) may be calculated using the same matrix element (6), but the calculus of ρ requires the consideration of the electron-phonon interaction. An efficient way to include the above contribution is the approximation of resonant electron-phonon interaction [11].

3. Distinct mechanisms. Differences

The classes of diagrams deduced in the previous section correspond to four distinct mechanisms, yet they can be grouped two by two according to their structure. The first two, represented in Fig. 2 are irreducible collective processes of the sixth order as it may be easily seen directly from the corresponding diagrams, as well as from the presence in $M^{(\xi)}$ of the three-photon absorption tensor. In the first case, the acceptor being coupled to the donors receives the excitation energy directly, in the second one, the coupling only with one donor, requires an accretive mechanism of transfer. We shall denote them irreducible direct (IR-D) and irreducible indirect mechanism (IR-IN). The last two are also sixth order mechanisms, but structurally reducible to two fourth order ones. The differences between them are the same as in the previous case. We shall call them reducible direct (R-D) and reducible indirect (R-IN) mechanisms.

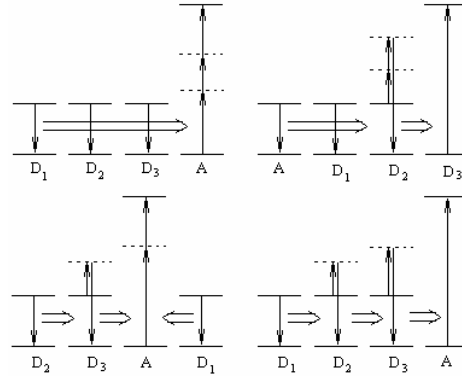


Fig. 2. Transfer mechanisms: IR and R denoting irreducible and reducible, D and IN – direct and indirect mechanisms respectively.

The D mechanism dominates in energy pooling phenomena from the donors to the acceptor. The IN mechanism prevails in sensitization processes. The dependence on the molecules mutual distances of each mechanism and the geometry of the transfer for significant probabilities is illustrated in Fig. 3, where each segment joining two centers represents the separation between them.

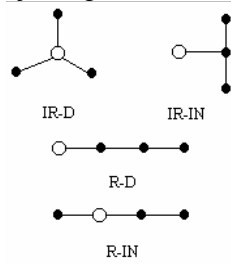


Fig. 3. Illustrated probability amplitude dependence on the distances between the centers.

4. The specific of rare-earths

The matrix elements of the dipole operator for the transitions of the f-shell PR^{3+} electrons give zero if their calculation is made in the framework of the same two-level atoms model. The transitions become possible due to the perturbations exerted by the above lying levels. Their theoretical computing is difficult and one applies a semi-empirical evaluation with the usage of Judd parameters [12]. Substituting the matrix elements (6) in (1) and taking the square power one gets, for a fixed mutual dipole orientation of the centers, the expressions of the square of the dipole moments $|\mu^{fi(\xi)}|^2$. We will classify the electronic states of the centers according to their point group symmetry. The initial and final states have the following form in the basis of the above mentioned representation:

$$|\alpha\rangle = \sum_{M_\alpha} a_{M_\alpha} |J_\alpha, M_\alpha\rangle \tag{9}$$

these matrix elements can be brought to the form:

$$\sum_{k=x,y,z} \sum_{M_f, M_i} \left| \langle J_f, M_f | \mu_k | J_i, M_i \rangle \right|^2 = \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle J_f || U^\lambda || J_i \rangle \right|^2 \tag{10}$$

where U^λ are the spherical irreducible tensors, Ω_λ are the Judd parameters and their value can be found in special tables, J_α is the dimension of the representation, M_α is the index of the energy levels degeneracy relatively the rotational symmetry, and α can take the values i or f .

5. Conclusion

In this work has been studied, for the most general case, the four-center resonance energy transfer. We analyzed the topological structure of the diagrams describing the phenomenon, identifying, thus, distinct mechanism of transfer according to the acceptor coupling to the donors and to the reducibility of the diagrams.

Compared to the three center resonance energy transfer [9,10] in the present case we met a reducible class of diagrams. The efficiency of the D mechanisms related to IN ones depends strongly on the relation between the mutual distances of the donors and of the acceptor-donor distances. For numerical applications we considered the computing of the Pr^{3+} dipole transition operator matrix elements using Judd parameters.

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