Energy and Charge Transfer between Quasi-zero-dimensional Nanostructures

K. Král* and M. Menšík**

* Institute of Physics of Czech Academy of Sciences, v.v.i.
Na Slovance 2, 18221 Prague 8, Czech Republic, kral@fzu.cz
** Institute of Macromolecular Chemistry of Czech Academy of Science, v.v.i.
Heyrovského 2, 16206 Prague 6, Czech Republic, mensik@imc.cas.cz

ABSTRACT

Theory of the transfer of electronic excitation energy, or electronic charge, between quantum dots is presented. Kinetic equation describing this irreversible process is developed using quantum transport approach. The non-adiabatic property of the electron coupling to the atomic lattice vibrations is used. The applicability of the transfer approach to the case of the so called uphill or downhill transfers is shown. Theoretical approach is illustrated by numerical calculations showing the transfer between two quantum dots.

Keywords: exciton transfer, electron transfer, electron-phonon interaction, quantum dots, irreversible quantum transport.

1 INTRODUCTION

The process of the electronic charge transfer between two non-overlapping subsystems was some time ago solved theoretically by R. A. Marcus [1]. Using a somewhat different, though simple, an approach T. Förster ([2], see also ref. [3] for a later development) introduced his formula for the determination of the electronic excitation transfer rate in the form of an overlap of two excitonic spectral densities. Both the transfer theories used the Golden Rule formula for the treatment of the irreversible transport problem. Both theories appear to be well established and those who use them in applications, for example chemists, appreciate the relative ease of their use. The formula due to Marcus was recently subject to a criticism from the point of view of the energy conservation [4] during the charge transfer. The theory of Förster was basically formulated for the case of the so called resonance transfer, in which the excitation energies of the donor and that of the acceptor are sufficiently close to each other. In the experiments about the photosynthesis we can deal with the effect of the uphill energy transfer, in which the difference between the acceptor excitation energy and that of the donor subsystem [5] is quite large. Within the biological objects the uphill electron transfer reactions are regarded as existing [6]. Basing on the above given remarks the processes of the charge or energy transfer may deserve an additional attention.

The problem of the electronic energy relaxation was some time ago treated with using the electron-phonon interaction taken into account in an approximation going beyond the limits of the finite order perturbation calculation (see e. g. [7, 8]), treating the system under consideration as a two-level system with one fermion interacting with phonons. We are going to use a similar approach to the study of the electron or exciton transfer between two subsystems which are relatively well separated in space. Concerning such a two-level one fermion system some attempts were performed already to include the electron-phonon interaction in the electron/exciton transfer process (e. g. [9, 10]).

In this paper we present a version of the electron/exciton transfer theory in which the pure electronic transfer matrix element is treated as the weakest part of the interaction Hamiltonian of the whole system. The theory is developed for the case of the exciton transfer between two quantum dots. Similar steps of the derivation lead to the scheme suitable for electron or hole transfer between quantum dots.

2 THE HAMILTONIAN OF THE SYSTEM

We solve the simple case when each one of the quantum dots has its electronic ground state and one excited state. Using the exciton language we say that there is one exciton in the quantum dot no. i, $i = 0, 1$ when the quantum dot is in the electronic excited state. We restrict the physics of the whole system to the case when there is only one exciton in the whole system. With excitonic particle operators the Hamiltonian of the electronic system of two quantum dots is written as

$$H_e = E_0 c_0^+ c_0 + E_1 c_1^+ c_1, \qquad (1)$$

where c_0 is exciton annihilation operator in the quantum dot number 0. The quantities E_0 and E_1 are respectively the exciton energies at the quantum dots no. $0, 1$. These exciton energies can be generally different one from another. We shall formulate the exciton transfer theory for the case when the difference of the exciton energies is either zero or has any real value. The exciton can be assumed to be placed say at the quantum dot 0 at the beginning and we could wish to follow the process in

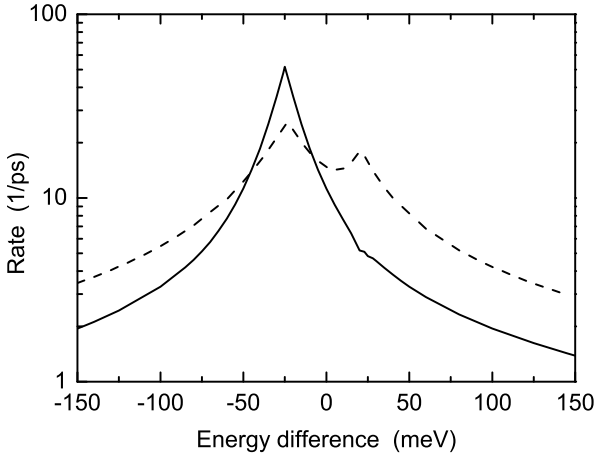

Figure 1: Exciton transfer rate between two quasi-zero-dimensional systems as dependent on the difference between the exciton energies on the two sites. Full line calculated at 50 K, dashed line at 300 K.

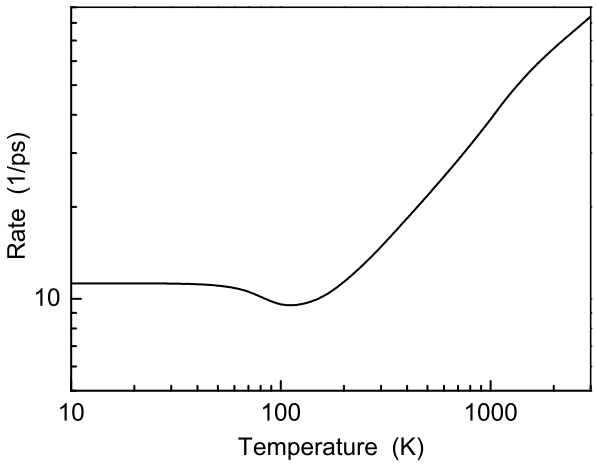

Figure 2: Dependence of the exciton transfer rate on temperature.

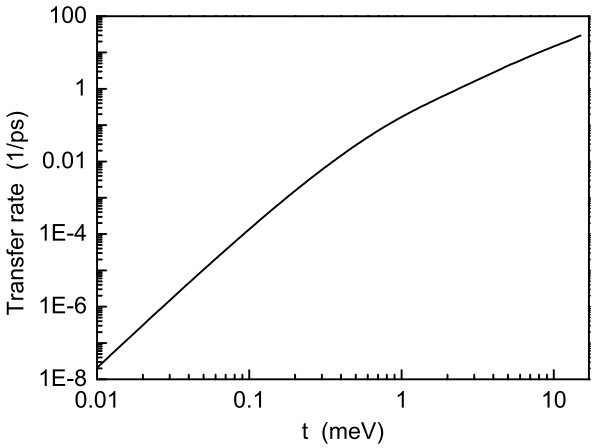

Figure 3: Dependence of the exciton transfer rate on parameter t of the pure electronic transfer mechanism.

which the exciton is being transferred in an irreversible way for this quantum dot to the other quantum dot with index 1. In the Förster's theory it is assumed the mechanism allowing for the pure exciton transfer of a matrix element of the coulomb electrostatic interaction, in particular its dipole-dipole part. In order to simplify the presentation of the results we will speak about a matrix element t allowing for the pure electronic part of the exciton transfer between the two quantum dots, leaving the details of the relation between the dipole-dipole interaction and the exciton transfer matrix element t to a later discussion. Formally the part of the total Hamiltonian responsible for the pure excitonic transfer between the dots is following:

$$H_t = t(c_0^+ c_1 + c_1^+ c_0). \tag{2}$$

As it is known, generally the exciton particle operators can obey rather complicated commutation relations. Because of the above given enumeration of the states of the electronic systems of the dots under consideration, and because we assume that the exciton is only one in the whole system, we can apply the fermion commutation relations for the exciton particle operators in the present case.

The interaction of the exciton with the oscillations of the atomic lattice will be included into the complete Hamiltonian, because the multiphonon states give us the possibility to deal with a continuum of energy [11]. Because in the present case we have only one orbital exciton state per quantum dot, we include only the transverse part of the exciton-phonon interaction. In this interaction the exciton occupying i-th dot couples to the intra-dot optical vibrations of this same i-th quantum dot:

$$H_{e-ph} = H_{e-ph,0} + H_{e-ph,1}, \tag{3}$$

in which the electron-phonon interaction in the i-th dot is

$$H_{e-ph,i} = \sum_{\mathbf{q}_i} A_{\mathbf{q}_i}^{(i)} \Phi(i,i,\mathbf{q}_i)(b_{\mathbf{q}_i} - b_{-\mathbf{q}_i}^+) c_i^+ c_i. \tag{4}$$

for i=0,1.

The symbol $\mathbf{q}_i$ denotes the $\mathbf{q}_i$-th bulk optical vibrational mode in the i-th quantum dot and $b_{\mathbf{q}_i}$ is the annihilation operator of the phonon in that vibrational mode. The summation includes all these modes in the particular quantum dot. Because of the lack of our knowledge of the values of the coupling constants giving the exciton-phonon interaction to the optical phonons of quantum dots we assume the functional form of the coupling operator to be identical with that of the electrons

in the lowest energy conduction band bound states in a quantum dot, neglecting in this way the hole-phonon scattering of the hole part of the excitonic particle. These effects are postponed to other studies. In the numerical calculations we use the material parameters of CdSe nanocrystal of cubic form with infinitely high potential wells. In H_i the quantity $A^{(i)}_{\mathbf{q}_i}$ is the coupling constant of the Fröhlich's coupling in the i-th dot and $\Phi(i,i,\mathbf{q}_i)$ is the form factor allowing for using the interaction operator in the i-th quantum dot [7, 8]. The Hamiltonian operator of the free phonons is $H_{ph} = H_{ph,0} + H_{ph,1}$, where

$$H_{ph,i} = \sum_{\mathbf{q}_i} E_{LO,i} b^+_{\mathbf{q}_i} b_{\mathbf{q}_i}, \tag{5}$$

is the free phonon Hamiltonian of the i-th dot. The symbol $E_{LO,i}$ is the energy of optical phonon in the i-th quantum dot. The total Hamiltonian then is $H = H_0 + H_1 + H_t$, where we denoted the Hamiltonian of the i-th dot as

$$H_i = E_i c^+_i c_i + H_{ph,i} + H_{e-ph,i}. \tag{6}$$

3 LANG-FIRSOV TRANSFORMATION

For example, the single dot Hamiltonian operator H_i, for the quantum dot with index i=0, reads

$$H_0 = E_0 c^+_0 c_0 + \sum_{\mathbf{q}_0} E_{LO,0} b^+_{\mathbf{q}_0} b_{\mathbf{q}_0} + H_{e-ph,0}. \tag{7}$$

This Hamiltonian shows that one can remove the exciton-phonon interaction from it by applying the well-known Lang-Firsov cannonical transformation [12]. This transformation transforms the original exciton operators c_i into new fermionic operators A_i. Upon making this transformation one observes that the innitial purely excitonic operator H_t gets a new form, which now depends on the new particle operators of the optical phonons $B_{\mathbf{q}_i}$. The new form $H^{(LF)}_t$ of the exciton transfer operator H_t can be written in the form

$$H^{(LF)}_t = tA^+_1 A_0 \exp\left[\sum_{\mathbf{q}_0} \gamma_{0\mathbf{q}_0}(B_{0\mathbf{q}_0} + B^+_{0,-\mathbf{q}_0})\right] \times \exp\left[-\sum_{\mathbf{q}_1} \gamma_{1\mathbf{q}_1}(B_{1\mathbf{q}_1} + B^+_{1,-\mathbf{q}_1})\right] + h.c. \tag{8}$$

As formula (8) shows, the applied Lang-Firsov transformation on one hand removes the interaction of the exciton with the intra-quantum dot vibrations, while on the other hand introduces a new operator, having the meaning of an inter-quantum dot exciton transfer combined with emissions or absorptions of a vibrational modes on either of the interacting quantum dots. We prefer to confine ourselves to the zero-th and the first orders of the expansion of the exponential functionsin powers of exciton-phonon interaction $\gamma_{i\mathbf{q}_i}$ in (8). It is important to underline that in the present theory of the exciton transfer we neglect completely the zero order term of this expansion, namely the interaction part

$$H^{(0)}_t = t\left(A^+_1 A_0 + A^+_0 A_1\right). \tag{9}$$

The complete neglecting of the interaction (9) means that we ignore a certain effect of coherence in the exciton transfer between the quasi-zero-dimensional subsystems. The neglecting of (9) corresponds to a similar approximation done by Förster [2] when making the derivation of his formula, and in fact such an approximation is actually understood to be performed by Marcus [1] in the course of the development of his approach to the electron transfer. After elaborating the details, one can see that the remaining new exciton-phonon coupling operator has only a longitudinal part of the interaction with the meaning that a phonon is emitted or absorbed while the exciton changes the quantum dot site. The corresponding details of the derivation of the present exciton transfer rate formula will be given elsewhere.

4 TRANSFER RATE

Upon performing the Lang-Firsov transformation we were able to change the transfer rate process to the problem of the fermion energy relaxation in the two-energy-level system with the electron-phonon interaction. The exciton transfer between two quantum dots is then transformed into the task of solving the problem of an irreversible transition of a fermion, or an electron, within the two-level system. The latter two-level system was suggested earlier to be solved in self-consistent Born (SCB) approximation to the electron-phonon interaction, in the present case to the interaction $H^{(LF)}_t$, see [7, 8]. The references [7, 8] contain a more detailed description of the solution of the two-level problem with using the nonequilibrium Green's functions and quantum kinetic equations.

The final result of the present work is the formula for the exciton transfer giving the rate of change of the mean occupation N_1 of the occupation of the state no. 1 providing that the occupations of the two states is N_0 and N_1, $N_0 + N_1 = 1$,

$$\frac{dN_1}{dt} = \tfrac{2\pi}{\hbar}\alpha_{01}\left[\left(N_1(1-N_0) + \nu_{LO}(N_1 - N_0)\right)C_- - \left(N_0(1-N_1) + \nu_{LO}(N_0 - N_1)\right)C_+\right], \tag{10}$$

in which α_{01} depends on coupling constant of the exciton-phonon coupling and the transfer coupling parameter t. Here $C_\pm$ are convolutions of two energy E dependent spectral densities of the two exciton states, $C_\pm = \int_{-\infty}^{\infty} \sigma_1(E)\sigma_0(E \pm E_{LO})dE$. The two spectral densities

are given by the nonequilibrium Green's functions calculated in the SCB approximation to the exciton self-energy. Note that although the present formula is similar to that developed by Förster in the presence of the convolution of the spectral densities, there is the difference in the mutual shift of the two spectral densities along the energy E parameter by the phonon energy in the present formula. The present approach gives the transfer rate for any difference between the two unperturbed exciton energies E_0 and E_1. The present approach gives the transfer rate for both the cases, downhill transfer and also for the uphill transfer.

5 NUMERICAL

The numerical calculations are performed for two interacting CdSe quantum dots of cubic shape with infinitely high potential walls. The exciton-phonon interaction was taken as identical with the coupling of Γ-valley conduction band electron of the dot with the CdSe optical phonons (Fröhlich's coupling). For the sake of simplicity, the energy difference ΔE between the unperturbed exciton energies on the two quantum dots is treated in the present model as an input parameter. Fig. 1 shows the exciton transfer rate to the quantum dot no. 1 for exciton originally occupying the site no. 0 for the difference between the exciton energies from interval -150 meV to +150 meV. The parameter t is chosen 10 meV in Fig. 1. We observe certain resonances to occur at energy differences close to optical phonon energies (25 meV).

Fig. 2 shows the temperature dependence of the exciton transfer rate between two quasi-zero-dimensional systems with equal exciton energies, and with t=10 meV. The exciton is assumed to occupy one site. The rate of the transfer to the other quantum dot is calculated. We see that near absolute zero of temperature the transfer rate is nonzero and temperature independent. We interpret this effect as being due to a correlation between the motion of the exciton the phonons, as given by the presently used self-consistent Born approximation to the exciton self-energy. In Fig. 3 we show the parameter t dependence of the exciton transfer rate between the quasi-zero-dimensional nanostructures in the state when the exciton fully occupies the original quantum dot site. The calculation is done at the temperature of 300 K and at equal exciton energies.

6 CONCLUSIONS

The theory presented uses the approximation in which the multiply scattering exciton leads to virtual multiphonon states, due to which the downhill and uphill processes may appear to be allowed in the off-shell transfer rate formula. We present the irreversible exciton transfer theory between two quasi-zero-dimensional nanostructures, which should be applicable not only for a resonance transfer but also for downhill and uphill transfer processes with any difference between the exciton unperturbed energies. It is straightforward to see that this transfer theory should equally well be applicable to the irreversible transfer of electron or a hole between two quasi-zero-dimensional subsystems.

The present paper deals with the transfer process which can be regarded as being incoherent in the sense similar to that ascribed usually to the well-known formula of Förster. This means that the pure electronic/excitonic transfer mechanism is not strong enough to cause any remarkable splitting of the electron/exciton eigenstate energies of the two interacting nanostructures.

ACKNOWLEDGEMENT

The authors acknowledge the support from the grants LH12236 and LD14011 of Ministry of Education of CR.

REFERENCES

[1] R. A. Marcus, Rev. Mod. Phys. 65, no. 3, 599-610, 1993.
[2] T. Förster, Ann. Physik 2, 55, 1948.
[3] S. Jang, Y.-J. Jung, R. J. Silbey, Chem. Phys. 275, 319-332, 2002.
[4] X.-Q. Zhu, and J.-D. Yang, J. Phys. Org. Chem. 26, 271-273, 2013.
[5] H.-W. Trissl, C. J. Law, and R. J. Cogdell, Biochimica et Biophysica Acta 1412, 149-172, 1999.
[6] A. Elbehti, G. Brasseur, and D. Lemesle-Meunier, J. of Bacteriology 182, no. 12, 3602-3606, 2000.
[7] K. Král, P. Zdeněk, and Z. Khás, IEEE Transact. on Nanotechnology 3, no. 1, 17-25, 2004.
[8] K. Král, P. Zdeněk, and Z. Khás, Surface Science 566-568, 321-326, 2004.
[9] K. Král and M. Menšík, "Inter-Molecular Electronic Transfer", *in* Colloidal Nanoparticles for Electronic Applications Light Emission, Detection, Photovoltaics and Transport, ed. by J. Steckel, N. Kotov, D. Norris, M. Bawendi, M. Kuno (Mater. Res. Soc. Symp. Proc. Volume 1207E, Warrendale, PA, 2010), 1207-N09-05.
[10] K. Král, M. Menšík, and Huibing Mao, e-J. Surf. Sci. Nanotech. 12, 11-17, 2014.
[11] N. Terzi, "Coherent Wavepackets of Phonons" *in* Collective excitations in solids, ed. by B. DiBartolo, NATO ASI Series, Series B (Plenum Press, New York, 1983), vol. 88, pp. 149182. Doi: 10.1007/978-1-4684-8878-4_4, ISBN 978-1-4684-8880-7(print).
[12] G. D. Mahan, Many-Particle Physics, 2nd ed., Plenum Press, New York, 1990.