TRANSFER OF ELECTRONS OR HOLES BETWEEN LOCALIZED STATES. APPLICATION TO POLYMER ELECTRIC CONDUCTIVITY

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Abstract

Basing on the quantum transport formalizm a formula for the irreversible transfer of charged particles has been introduced by us recently. This formula is expected to be suitable for the theoretical description of the electron or hole transfer between quantum dots, other nanoparticles, molecules, and so on. We discuss shortly the main physical properties of the formula. We also demonstrate the use of the formula for the theoretical analysis of the electronic physical properties of some electrically conductive polymers.

Keywords: Electron transfer, electron-phonon interaction, quantum nanostructures, transfer rate formula, polymer conductivity

1. INTRODUCTION

The transfer of the charged particles, like electrons or holes, between nanoparticles like quantum dots, nanoparticles in colloid solution, molecules, and so on, has been regarded as an important phenomenon [1]. Similarly, the transfer of the electronic excitation, or an exciton, between the nanoparticles, is regarded to play an important effect, like in the photosynthesis. The transfer of the charged particles has been traditionally treated recently with help of the theory introduced by R. Marcus [2]. This theory for the charged particles and another such theory for electronic excitation energy transfer [3], were in fact built on using the interaction of the electronic subsystem of the nanoparticle with the vibrations of the atomic lattice of the nanostructure. So, the Förster's theory of resonance transfer [3] utilizes the optical emission spectral data and absorption spectra of the nanoparticles, broadened due to the exciton-phonon interaction. In the case of the Marcus theory of the electron transfer the important role is played by the introduction of a certain macroscopic fluctuating parameter, which presence in the theory should provide a vehicle for how to circumvent the question of the energy conservation between the particle state entering the transfer reaction and and the state when the system is leaving the reaction of the electron transfer. We have developed an effort recently to obtain similar transfer rate formulas using a more detailed microscopic approach [4], building on the use of the multiple scattering of the transferred electron, or exciton, scattered on the atomic vibrations of the lattices of both the nanoparticles entering the transfer process reaction. We show that the theory of the transfer can be built in a similar formal way for the electrons and also for the excitons, providing that the excitonic particle operator commutation relations are simple enough so as to be represented by fermionic commutation relations, as may happen in cases of sufficiently simple systems of two nanoparticles between which the exciton is considered to be transferred.

The multiple scattering of electron or exciton on lattice phonons can be viewed to be only an approximation from the point of view of the eventual more complete or full theory, taking into account the complicated situation in the simple systems of interacting electrons and phonons [5]. This approximation only means that we expect that the scattering electron or exciton has a sufficiently long mean free path before it looses its phase. We may perhaps expect this to be met in the quantum dots samples like those of GaAs quantum dots grown in the Stranski-Krastanow mode. On the other hand we might expect that in say a pair of nanoparticles made of the anthracene material, the mean free path of electron or exciton already in a single nanoparticle is regarded as so short [6] that we would rather not expect an electron to make coherent multiple scattering acts in such a nanostructure.

In this paper we briefly characterize the formula for the transfer and some of its main propeties. There are perhaps many areas of application of the transfer theory of electronic charge or excitation energy. We shall concentrate our attention on the application of the present theoretical approach in the theoretical analysis of experimental data measured recently on a certain class of bulk polymer materials. In order that we simplify the language, let us say that although the electric current in those polymers is very likely transferred by hole particles, we simply speak here about the electrons only.

2. CHARACTERISTIC PROPERTIES OF THE FORMULA FOR THE ELECTRONIC TRANSFER

Although our theoretical approach makes it possible to develop the transfer rate formula on the same grounds for the electronic charge transfer as well as for the exciton energy transfer, we shall confine ourselves to the case of the electronic transfer only. We shall not present the derivation of the formula from the Hamiltonian of the system of the nanoparticles, we instead give directly the resulting formula. It should be only emphasized that the formula for the electronic transfer was derived upon using the so called Lang-Firsov transformation to include into account exactly the significant electron-phonon interaction. The resulting Hamiltonian of the system was then simplified to neglect certain feature of the coherence between quantum mechanical systems of the source nanoparticle on one hand, and the target nanoparticles on the other. This approximation, which is discussed in more detail in the reference [4], is supposed to be a standard approximation included already in both the traditional theoretical transfer papers [2, 3]. In the present work the electron-phonon interaction is included in an approximation which goes beyond the limits of the finite order of the perturbation calculation, namely, the electron-phonon interaction is included in the self-consistent Born approximation. With using the nonequilibrium Green's functions, together with the standard approximations for obtaining the quantum transport equation [7], we arrive (see also [4]) at the quantum transport formula for the electron transfer between two quantum quasi-zero-dimensional (Q0D) nanostructures, where $C_{\pm}^{(i)}=\int_{-\infty}^{\infty}\sigma_1(E)\sigma_0(E\pm E_{LO,i})dE$, while the spectral densities σ_i of the both states i = 0, 1, are obtained from the electronic retarded Green's functions with using the standard formula $\sigma_i(E)=-\frac{1}{\pi}\operatorname{Im}G_i^{(r)}(E)$. The symbol $\mathcal{A}_{\mathbf{q}_i}^{i}$ gives the coupling constant of the electron coupling to the bulk mode of the phonons with the wave vector q_i, while the factor Φ is the form factor allowing us to use the bulk electron-phonon interaction operator in the quantum nanostructure of given geometrical shape [4]. In the formula (1) N_0, N_1 are the electronic occupation numbers of the source and target states i = 0, 1. The Bose-Einstein distribution function for the optical phonons with energy $E_{LO,i}$, in the i-th nanoparticle, is $\nu_{LO,i}$. The parameter t characterizes the quantum mechanical Hermitian operator of the reversible tunneling of the electron between the two nanoparticles between which we consider the irreversible electronic transfer process.

$$\frac{dN_1}{dt}=\frac{2\pi}{\hbar}\sum_i\sum_{\mathbf{q}_i}\left(\frac{t}{E_{LO,i}}\right)^2\left|\mathcal{A}_{\mathbf{q}_i}^{(i)}\Phi(i,i,\mathbf{q}_i)\right|^2$$
$$\times\Big[\big(N_1(1-N_0)+\nu_{LO,i}(N_1-N_0)\big)C_-^{(i)}-\big(N_0(1-N_1)+\nu_{LO,i}(N_0-N_1)\big)C_+^{(i)}\Big]\ , \qquad (1)$$

The retarded electronic Green's function of the system is given by the electronic self-energy M_m calculated from the equation (2):

$$M_n(E) = \sum_{\substack{m=0 \\ m \neq n}}^{1} U_{nm} \left\{ \frac{1 - N_m + \nu_{LO}}{E - E_m - E_{LO} - M_m(E - E_{LO}) + i0_+} + \right. \qquad (2)$$

$$\left. + \frac{N_m + \nu_{LO}}{E - E_m + E_{LO} - M_m(E + E_{LO}) + i0_+} \right\}, \qquad m = 0,1.$$

Let us now summarize some of the significant properties of the formula for the electron transfer. Thanks to the approximation to the electronic self-energy the formula can be applied to any choice of the single energies of the electron at the two localized sites. The reason is that the self-consistent Born approximation corresponds to the multiple scattering of the electron, due to which multiphonon states of the vibrational modes are excited. These multiphonon states can be seen as similar to the coherent phonon states which are known to have a continuum of their energy. In the case of the electron transfer this multiple scattering mechanism plays a similar role as the fluctuating macroscopic parameter introduced earlier with great intuition by R. Marcus [2]. In the case of the exciton scattering the present formulation allows one to obtain the transfer formula [4] to be possibly applied also in transfer processes which might be already outside the limits of the applicability of the traditional Förster's resonant transfer formula, which is restricted to the assumption of the nearly resonant transfer processes.

Besides the general properties of the formula (1) there are also other its properties which are manifested when the formula is applied to a more specific physical situation. In the next section the transfer rate formula is shown in aplication to the electric conduction of certain conductive polymers.

3. ELECTRIC CONDUCTION OF POLYMERS

Some polymers, like those based on poly(thiophene)s, display an electric conductivity [8]. Basing on the analysis of their electric conduction it might be suitable to imagine a mechanism of their electric conductivity to be like an electronic transfer between localized sites under the influence of the applied electric field. If we knew the distribution of the sites in the polymer, in which the conduction electron can be localized, and the quantum mechanical operators of the electron tunneling between the sites, we could try to develop the theoretical description of the electric conductivity along these lines. Instead of this we better confine ourselves to a much simpler task, namely we try to represent the whole polymer by just a single pair of neighboring localized sites. We are going to test the application of the formula (1) within this simple picture.

We imagine that there is an average occupation n_{tot} equal on all the localized sites. We represent the individual localized sites by a single CdSe cubic quantum dot, in which we consider only one bound state which can be occupied by single electron. In this way we can use a well defined localized state of electron and its coupling with optical phonon modes. The electron-phonon coupling in the polymer is substituted here by the coupling of the electron to the phonons inside the individual quantum dot. Because the pair of the quantum dots is coupled to the rest of the polymer, we assume that the chosen occupation of the two sites is constant in time and maintained at the level of n_{tot}. We assume that the pair of quantum dots is subject to an applied electric field which intensity is directed from the target quantum dot to the source quantum dot, so that the electric field moves the electronic charge from the source to the target. We simulate the effect of the applied electric field simply by introducing the energy difference $\Delta E = E_1 - E_0$ between the electronic state at the target state, E_1, and the electron energy at the source quantum dot E_0, as an input parameter in the numerical calculation.

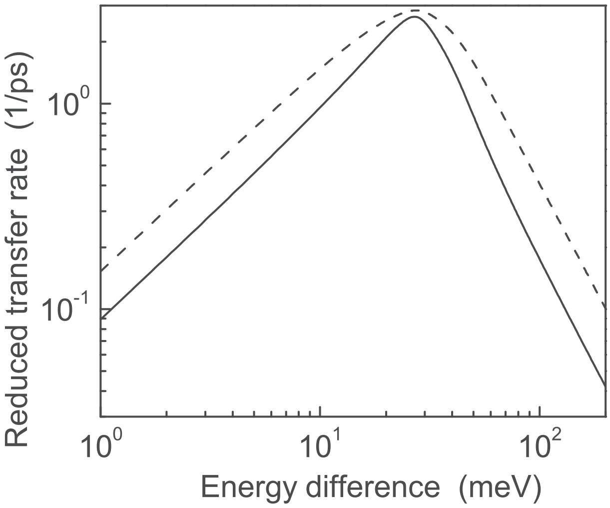

Figure 1 Reduced transfer rate plotted against the energy difference between the sites

In **Figure 1** we plot the reduced transfer rate of the electron from the source state (no. 0) to the targer state (no. 1). The reduced rate means here that the rate given by the transfer rate formula is devided by the average occupation of the both states 0 and 1. We sometimes use the quantity of the reduced transfer rate because this quantity is closely related to the electron mobility [4]. The full curve in **Figure 1** gives the transfer rate for the equal occupation of the both sites, each chosen as 0.05 of electron per the site. This curve shows us the important property of the formula. We see the effect of the negative differential conductivity in the polymer. This calculated effect can be compared with a similar effect found in experiment measured in polymers [9]. The comparison of the theory and experiment shows us that the effect of the negative differential conductivity can be caused by the nonadiabatic manifestation of the interaction between the electrons and the vibrations of the atomic lattice. Let us note that the maximum of the negative differential conductivity peak is found at such energy difference between the two sites which corresponds to the energy of the optical phonons (25 meV in CdSe). The observed maximum is due to the excitation of an optical phonon with which the conduction electron is assumed to interact in the present model.

In order to understand more the shape of the dependence of the electric conductivity of our model of the polymer, as it depends on the applied electric field, we compared the conductivity with the equally populated sites with a different case, in which the occupation of the sites fluctuates between the two distributions of the electronic density among the two sites, namely with the occupation $N_0 = 0.095, N_1 = 0.005$ and the occupation $N_1 = 0.095, N_0 = 0.005$. We assume that each of these two occupation of the sites occurs with 50 % probability. Note that on average the occupation of the sites is again 0.05 of electron per site. The result of the numerical evaluation of the reduced transfer rate is presented by the dash curve in **Figure 1**. We see that the negative differential conductivity peak of the displayed dependence becomes broader when the occupation of the sites fluctuates between two inhomogeneous distributions of the electronic charge. Let us remark that the use of the transfer rate formula assumes that the changes of the electronic distribution are supposed to occur with sufficiently low frequency in time, because the formula is derived inder the assumption that the electronic distribution $N_i, i = 0,1$ changes slowly as compared to the rapidity of the transfer process (see [4] and the references cited in).

4. CONCLUSION

We discuss the formula for the irreversible electronic transport of electrons between two quasi-zero-dimensional nanostructures and briefly characterize its general properties, among which we emphasize the property allowing the formula to be applicable to cases when electron is transferred between states with different energies. Another property of the present transfer rate is that for sufficiently simple situations in the physical systems under study the formula has a similar formal structure for the transfer of electrons and for the transfer of excitons. When applied to the electric conductivity of some conducting polymers the formula shows the property of negative differential conductivity. The formula also allows to analyze the behavior of the electric conduction under a significant occurence of the fluctuations in the electronic distributions among the localized sites in the polymer.

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