

Quantum auto-ionization of molecular excitons and photovoltaic conversion

V. A. Bendetskii⁺, E. I. Kats^{*×1)}

⁺*Institute of Problems of Chemical Physics of the RAS, 142432 Chernogolovka, Russia*

^{*}*Landau Institute for Theoretical Physics of the RAS, 142432 Chernogolovka, Russia*

[×]*Moscow Institute of Physics and Technology, 141700 Dolgoprudny, Russia*

Submitted 14 November 2014

This paper explores a novel way of charge separation (auto-ionization) of molecular excitons, by quantum tunneling through nano-size $p-n$ junction. This mechanism can dominate the standard one (i.e., when Frenkel exciton is ionized at donor or acceptor impurity sites) for very short, nano-size, $p-n$ junction, where the junction electric field can be strong for relatively small (on the order of 1 V) voltage drop. Within a simple one-dimensional model for the depletion region of the $p-n$ junction (donor and acceptor reservoirs connected by a short molecular wire) we compute the quantum yield Y_b for the tunneling exciton auto-ionization in the “bulk” of the depletion region. For modern organic photo-sensitive materials with $p-n$ junction size on the order of 10–20 nm, Y_b could be close to 1. Such a high efficiency of the charge separation (one of the main factor entering figure of merit, indicating how good are photovoltaic conversion cells) makes this new mechanism potentially very perspective for the applications.

DOI: 10.7868/S0370274X1501004X

Background. Organic semiconductors (like phthalocyanines, doped-fullerenes, and some other photo-sensitive compounds) already long time attract attention of scientists (see, e.g., [1–4]) as potentially perspective materials for solar cell applications. Usually for conventional micron size $p-n$ junction, in the lowest energy state, the electron and the hole (forming the neutral Frenkel exciton) are localized on the same molecular site. Quantum dynamics of such excitons can not lead to charge transfer. Charge separation may occur only when diffusing Frenkel exciton meets the impurity site. Main difficulty for a practical application of such mechanism for photovoltaic conversion is that light absorption in organic semiconductors is related to intramolecular state transitions (to contrast with inter-band transitions in conventional inorganic solid state materials). Charge transfer by excitons, created by these intramolecular transitions, is related to a very low efficiency process of charge separation. Much research performed in order to enhance the efficiency of charge separation failed because there are conceptual restrictions for such processes in conventional (macroscopic size) heterojunctions. The matter is that ionization of the excitons requires some additional energy which can be taken from thermal phonons. The probability of the corresponding

processes is very small in organic semiconductors. However, and this is the main point of our work, there is one more way for free charge carrier formation. Namely, the exciton auto-ionization through the intermediate (appearing at higher energy) charge transfer exciton states (where the $e-h$ pairs are smeared over many sites). Unfortunately, the probability of requiring quantum tunneling processes is very low for a standard macroscopic size $p-n$ junction.

From the experimental point of view the situation turns out less desperate. Recent progress in nanotechnology [5–7] allows to design nano-size heterojunctions randomly or regularly spaced in photo-sensitive organic materials. However despite the undoubted relevance of a such approach, it suffers from some major drawbacks that limit the practical perspective of the applications. Theoretical estimations [5–7] show that even for the $p-n$ junction size, 20–30 nm, comparable with the localized exciton characteristic diffusion length ($l_e \simeq \sqrt{D_e \tau_e}$, which is on the order of 10 nm for a typical life time $\tau_e \simeq 10^{-10}$ s and diffusion coefficient $D_e \simeq 10^{-2}$ cm²/s), the best expected efficiency for all known photo-sensitive organic materials is still smaller than that for the standard solid-state inorganic systems.

In our paper we would like to take a fresh look at the theoretical estimations made for the nano-size $p-n$ junctions in organic photo-sensitive materials. We are

¹⁾e-mail: efim.i.kats@gmail.com

discussing a novel way (overlooked in previous considerations) of charge separation (ionization) of molecular excitons, by quantum tunneling through the depletion region of the p - n junction. For the nano-size system this tunneling auto-ionization can lead to much more efficient charge separation than that realized outside the depletion region (at its boundaries within our model, i.e., by “surface” charge separation). Indeed intrinsic internal voltage through the p - n junction is determined by characteristic impurity (donor and acceptor) levels spacing. It is independent of the junction length L . Therefore bulk (by the tunneling ionization) charge separation processes exponentially small (over the parameter l_e/L) for the conventional macroscopic size heterojunctions, can at $L \simeq l_e$ become comparable with the surface (i.e., at the junction boundaries) exciton ionization processes. These very short heterojunctions in photo-sensitive organic materials could be still promising candidates for the efficient charge separation processes needed for solar cells. Writing our paper we hope to motivate new experimental and advanced theoretical studies of the nano-size p - n junctions in organic photo-sensitive molecules.

Of course no miracles and not everything is so cloudless. To get efficient bulk charge separation is not sufficient to produce very short p - n junction. The length L of the junction has to be larger than electron and hole Debye screening lengths ($r_D^{(e)}$, $r_D^{(h)}$). The condition to be satisfied reads as

$$l_e > L > \{r_D^{(e)} + r_D^{(h)}\}, \quad (1)$$

where in self-evident notations

$$r_D^{(e)}(r_D^{(h)}) = \left(\frac{\kappa_0 k_B T}{8\pi e^2 n_0^{(e,h)}} \right)^{1/2} \quad (2)$$

with $n_0^{(e,h)}$ being the concentration of the main charge carriers (electrons or holes) in the heavily doped regions, and $\kappa_0 \simeq 3-4$ is dielectric permeability. For typical in photo-sensitive organic materials [5–7] parameters (impurity ionization energy 0.2 eV, impurity concentration 10^{19} cm^{-3}), charge carrier concentration $n_0^{(e,h)}$ could be as large as 10^{17} cm^{-3} and it gives $r_D^{(e,h)} \simeq 5 \text{ nm}$.

Organic photo-sensitive materials we are talking about are formed by flat-shaped molecules packed into layers with relatively weak interlayer coupling. Therefore, it seems naturally to start theoretical investigation with one dimensional model for the p - n junction. While the effects related to realistic three dimensional molecular packing and impurity configurations may lead to certain changes, it is not expected to radically alter

the picture we are studying here. Although pure mathematically our one dimensional case is simpler, but all essential ingredients and difficulties (e.g., competition between exciton tunneling and diffusion) are already there.

Charge separation in one dimensional model for the nano-size p - n junction. With all said above in mind we model the p - n junction by one dimensional finite length L chain of photo-sensitive molecules placed in the sites 1, 2, ..., N of the chain (where $N = L/l_0$ with l_0 being the lattice period; in what follows, unless opposite will be said we use l_0 as a unit of the distance). The chain is supposed to be under a constant electric field which models the p - n junction intrinsic internal field. It is convenient to write down the model Hamiltonian in terms of the localized at the molecular sites wave functions. The exciton (electron-hole pair) wave function can be characterized by the sites n^+ , n^- where the hole and the electron respectively are localized. One can easily see that the quantum dynamics of the exciton center of mass is separated from the relative electron-hole motion we are only interested in. Then, diagonal matrix elements of the Hamiltonian depend only on $n = |n^+ - n^-|$ and read as

$$V(n) = \langle n^+, n^- | H | n^-, n^+ \rangle = \begin{cases} -V_1(1/n) - V_2(n/N), & n \geq 1, \\ -V_0, & n = 0. \end{cases} \quad (3)$$

Here $n = 0$ corresponds to the localized state of the molecular (Frenkel) exciton (the bound state energy is $-V_0$), and $n = 1, 2, \dots, N$ elements determine characteristic distance of the charge separation in the exciton ($-V_1/n$ term simulates the electron-hole Coulomb attraction, and $-V_2n/N$ term models the intrinsic p - n junction electric field), V_0 is the exciton complete ionization energy, and naturally $V_0 > V_1$.

We take into account only the nearest neighbors hopping and then, the non-diagonal matrix elements are written in the following form

$$\langle n^+, n^- | H | n^- \pm 1, n^+ \pm 1 \rangle = \epsilon_n \quad (4)$$

and

$$\begin{aligned} \langle n^+, n^- | H | n^-, n^+ \pm 1 \rangle &\equiv \epsilon_+, \\ \langle n^+, n^- | H | n^- \pm 1, n^+ \rangle &\equiv \epsilon_-. \end{aligned} \quad (5)$$

The matrix elements ϵ_0 (and ϵ_n with $n = 1, 2, \dots$ for electron-hole separation distance n) for the exciton (i.e., e and h in block) transfer are determined by the probabilities of the transitions between HOMO (highest

occupied molecular orbitals) and LUMO (lowest unoccupied molecular orbitals) states [7]. For the localized Frenkel exciton ϵ_0 (inverse hopping time) in organic photo-sensitive molecules is typically $\epsilon_0 \simeq l_0^2/D_e \simeq (0.01-0.03)$ eV. On the contrary, the elements ϵ_{\pm} (the widths of the valence and conduction bands respectively) are determined by the nearest sites hopping probabilities either for electron or for hole moving separately. In the natural situation $\epsilon_{\pm} > \epsilon_n$, and as we mentioned already the uncharged exciton center of mass motion is separated from the relative (in opposite directions) movements of the electron and of the hole.

Transforming the site localized basis into propagating wave basis (with the wave vector k and given $e-h$ separation distance n)

$$\psi_k(n) = \frac{1}{N^{1/2}} \sum_{n^+, n^-} \exp[ik(n^+ - n^-)] |n^+, n^-\rangle, \quad (6)$$

the matrix elements (3), (4) are

$$\langle \psi_k(n) | H | \psi_k^*(n) \rangle = V(n) + \sum_{n^+, n^-} \epsilon_n \exp[ik(n^+ + n^-)], \quad (7)$$

and

$$\begin{aligned} \langle \psi_k(n) | H | \psi_k^*(n \pm 1) \rangle &= \epsilon_+ \exp(\pm k) + \epsilon_- \exp(\mp k) \equiv \\ &\equiv \epsilon_k \exp(i\delta_k), \end{aligned} \quad (8)$$

where following [8] and [9] to take into account electron-hole asymmetry (i.e., $\epsilon_+ \neq \epsilon_-$) and to get more compact expression we introduce

$$\begin{aligned} \epsilon_k &= (\epsilon_+^2 + \epsilon_-^2 + 2\epsilon_+\epsilon_- \cos k)^{1/2}; \\ \delta_k &= \tan^{-1} \left(\frac{\epsilon_+ - \epsilon_-}{\epsilon_+ + \epsilon_-} \tan k \right). \end{aligned} \quad (9)$$

In the basis of the wave functions (6) with the matrix elements (8), (9) in hands we derive the following set of finite difference equations (for the coefficients $a_k(n)$) of the system wave function expansion over the basis functions (6) which determines the energy eigen values E_{λ} of the molecular exciton

$$[V_k(n) - E_{\lambda}]a_k(n) = \epsilon_k [a_k(n-1) + a_k(n+1)], \quad (10)$$

where λ numerates the eigen states of the exciton within the $p-n$ junction. This deceptively simple set of the finite difference equations can be solved analytically [8] only for $V_2 = 0$ (neglecting the intrinsic $p-n$ junction electric field). One can prove [10] that there is one eigen value of the three-diagonal determinant of the set (10) with the corresponding wave vector k in each interval

$$\frac{\pi\lambda}{N+1} < k < \frac{\pi[\lambda + (1/2)]}{N+1}, \quad \lambda = 1, \dots, N, \quad (11)$$

therefore for $N \gg 1$, $k \propto 1/N$. The inequality (11) allows us to approximate ϵ_k in (9) replacing $k \simeq \pi\lambda/(N+1)$. In this approximation the spectrum of the charge transfer exciton depending on the value of λ can be divided into two parts, namely discrete and quasi continuous parts. The discrete part is formed for $V_1/(2\epsilon_k) \geq \lambda \geq 1$, whereas for $V_1/(2\epsilon_k) < \lambda \leq N$ the spectrum is quasi-continuous one:

$$E_{\lambda} = \begin{cases} -\{(V_1/\lambda)^2 + 4\epsilon_k^2 \cos^2[\pi\lambda/(N+1)]\}^{1/2}, \\ 1 \leq \lambda \leq V_1/(2\epsilon_k), \\ 2\epsilon_k \cos[\pi\lambda/(N+1)], V_1/(2\epsilon_k) < \lambda \leq N. \end{cases} \quad (12)$$

In the upper panel in Fig. 1 we compare the results of the analytical (12) calculations and numerical computation

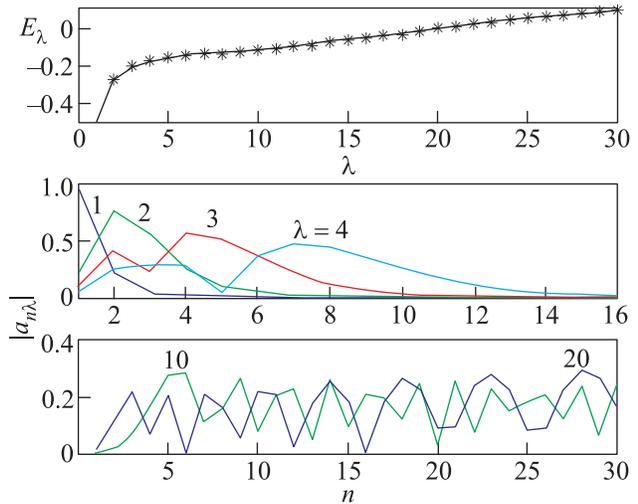


Fig. 1. Upper panel – the exciton eigen-value spectrum E_{λ} (dots on the curve are computed by numeric diagonalization of the Hamiltonian matrix); middle panel – the absolute values of the site amplitudes for a given n and $\lambda = 1, 2, 3, 4$; lower panel – the quasi-continuous spectrum ($\lambda = 10, 20$, $N = 30$, $V_1 = 0.3$ eV, and $\epsilon_+ + \epsilon_- = 0.04$ eV)

(by the standard Matlab software to solve the finite difference equations (10)) of E_{λ} for $V_2 = 0$. The spectrum of charge transfer excitons ($n = 1, 2, \dots$) found numerically is almost coinciding with its analytical counterpart. Since typically $V_1 \gg (\epsilon_+ + \epsilon_-)$ in the lowest states $\lambda = 1$, the electron and hole are localized at the nearest neighbor sites ($n = 1$). This state can be approximated by the independent of wave vector k level with the average energy

$$\bar{E}_1 = \left[\left(V_1 - \frac{V_2}{N} \right)^2 + \epsilon_+^2 + \epsilon_-^2 \right]^{1/2}. \quad (13)$$

For $\lambda = 1$ the amplitudes of the states with $n > 1$ are small over the parameter $(\epsilon_+ + \epsilon_-)/V_1$ (see the middle panel in the Fig. 1). Upon increase of λ the exciton is smeared over larger and larger number of sites and eventually at $\lambda > V_1/(\epsilon_+ + \epsilon_-)$ the wave functions are delocalized over all sites (see the lower panel in the Fig. 1).

For $V_2 \neq 0$ one has to rely on numerics. In Fig. 2 we present the results of the computations assuming mirror

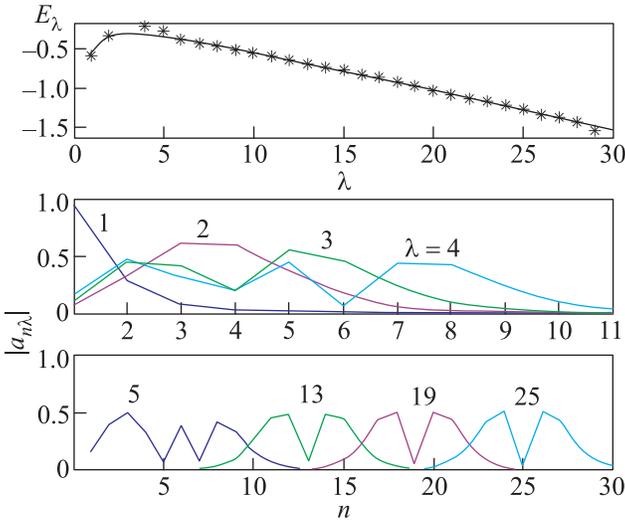


Fig. 2. Upper panel – the exciton eigen-value spectrum E_λ , for $V_1 = 0.5$ eV, $V_2 = 1.5$ eV, $\epsilon_- + \epsilon_+ = 0.06$ eV, and $N = 30$; middle panel – the absolute values of the site amplitudes for a given n and $\lambda = 1, 2, 3, 4, 5$; lower panel – the quasi-continuous spectrum ($\lambda = 7, 13, 19, 25$)

reflection boundary condition $a_{N+1} = 0$ at the end of the chain. The lowest energy state $\lambda = 1$ is well approximated by the Eq. (13). Its wave function is localized at the nearest neighbor sites, similarly to the case with $V_2 = 0$. Since the diagonal matrix elements (3) are larger than the non-diagonal ones (4), the energy eigen values in the classically accessible region, $n > NV_1/V_2$ only weakly depend on ϵ_k . The wave functions of such states are spread over approximately $4N(\epsilon_- + \epsilon_+)/V_2$ sites.

Results and conclusion. To calculate the efficiency of the exciton auto-ionization (quantum yield) we have to solve the same set of the Eqs. (10) but to replace the mirror reflection boundary condition, by the requirement of the continuity for the tunneling probability density flow (so-called Zeldovich boundary conditions [11]). In the intrinsic electric field of the p - n junction there is potential barrier with its width NV_1/V_2

and height $2\sqrt{V_1V_2/N}$ separating the lowest energy level $\lambda = 1$ from the quasi-continuum spectrum. In the quasi-classical approximation the tunneling probability through this barrier

$$P = \exp(-2S/\hbar); \quad (14)$$

$$S = \frac{2}{3} \sqrt{\frac{V_1}{\epsilon_+ + \epsilon_-}} [(\eta + 1)E(\xi) - 2K(\xi)],$$

where $\eta \equiv NV_1/V_2$, $\xi = \sqrt{1 - 1/\eta}$, and $K(\xi)$, $E(\xi)$ are complete elliptical integrals of the 1-st and 2-d order correspondingly. Up to evident change of the parameters the same quasi-classical expression (14) can be used to calculate the Frenkel ($n = 0$) exciton ionization probability. Namely

$$P_e = \exp(-2S_e/\hbar); \quad (15)$$

$$S_e = \frac{2}{3} \sqrt{\frac{V_0}{\epsilon_0}} [(\eta + 1)E(\xi_0) - 2K(\xi_0)]$$

with $\eta_0 \equiv NV_0/V_2$, $\xi_0 = \sqrt{1 - 1/\eta_0}$.

Comparing the expressions (14) and (15) we conclude that for nano-size p - n junction, one may not separate quantum dynamics of the molecular exciton from its auto-ionization (charge separation). When diagonal and non-diagonal matrix elements are on the same order ($4(\epsilon_+ + \epsilon_-)/V_0 \simeq 1$) the exciton eigenfunctions are spread over many sites. Then the bands E_λ are overlapped, and therefore the localized exciton states are mixed with the charge transfer states. Created either by light absorption or by electric pumping, molecular exciton ($n = 0$) decays with characteristic time $\hbar/(\epsilon_+ + \epsilon_-)$ into the stationary states smeared over all sites of the short p - n junction. In the intrinsic electric field of the junction these stationary states are mixed with the band states of the charge carriers (electrons and holes). This is the essence of the new “bulk” (within nano-size p - n junction depletion region) photoeffect, we investigate in this work. The bulk p - n junction photoeffect can lead to a high efficiency of the charge separation process. Its quantum yield Y_b is determined by the probability to ionize the molecular exciton during its life time τ_e . From (15) we find

$$Y_b = \frac{\omega_e \tau_e P_e}{1 + \omega_e \tau_e P_e}, \quad (16)$$

where $\omega_e \simeq \epsilon_0/\hbar$ is approximately characteristic inverse nearest neighbor hopping time of the exciton. Unfortunately, although the bulk photoeffect quantum yield can be close to 1, the less efficient standard “surface” ionization remains the main mechanism of the exciton

ionization if light is absorbed in the heavily doped regions outside of the depletion region. The matter is that in the heavily doped regions, characteristic exciton diffusion length is much larger than average distance between donor or acceptor impurity positions. Then strong Debye screening reduces considerably Coulomb interaction, and no chance for the exciton to achieve the bulk depletion region of the $p-n$ junction before its ionization. Luckily modern technological tendency in photoelectric devices [6] is to reduce the sizes of strongly doped regions. Therefore we hope that proposed in our work, bulk mechanism of the exciton charge separation can be realized, and our predictions can be checked. To illustrate our results we compute the bulk photoeffect quantum yield as a function of the $p-n$ junction size N (see Fig. 3).

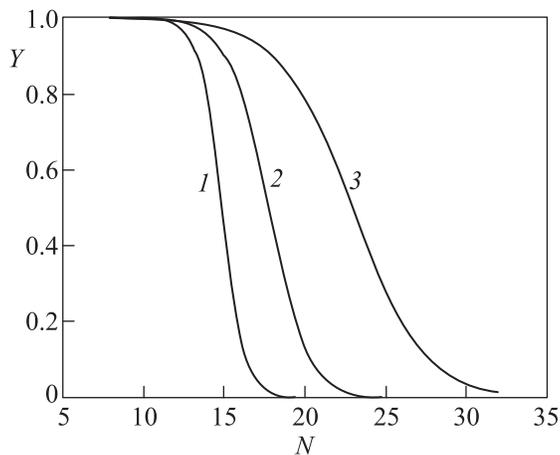


Fig. 3. The quantum yield Y_b for the bulk photoeffect (dependence on the number of photo-sensitive molecules within the $p-n$ junction). $\tau_e V_1/\hbar = 100$, $V_2 = 1.0$ eV, and $V_1/(\epsilon_+ + \epsilon_-) = 2, 3, 5$ for the curves 1, 2, 3 respectively

Because the tunneling probability (15) depends exponentially on N , Y_b is also very sharp function of the $p-n$ junction size. It is worth to note that the acceptable size of the junction could be increased if the exciton ionization energy V_0 is reduced. Another way is to increase the $p-n$ junction intrinsic potential jump V_2 and the width of the charge carrier bands ϵ_{\pm} . Having in mind solar energy conversion (the optimal photon energy 1.2–1.7 eV), we estimate $Y_b \simeq 1$ for $V_2 \simeq (1.2-1.5)$ eV, $V_0 \leq 0.4$ eV, $(\epsilon_+ + \epsilon_-)/V_0 \geq 0.05$, and the $p-n$ junction size ≤ 15 nm ($N \leq 35$). These parameters are not terribly different from already achiev-

able in a program to design the efficient photovoltaic devices [7].

In summary, we have proposed a new mechanism for molecular exciton auto-ionization. Physics behind is quite transparent. It does not require e or h recombination at the impurity sites. For a very short (but still larger than the Debye screening lengths (2)) $p-n$ junction, relatively large intrinsic electric field strongly enhances quantum tunneling and leads to the mixing of the exciton states with different n . It is worth to noting to the point that conceptually related approach of electromagnetic field stimulated ionization in semiconductors developed long ago by Keldysh [12] requires much higher fields $\geq 10^7$ V/cm. Additional theoretical and experimental efforts are needed to check whether our concept can be useful for practical applications for solar to electrical energy conversion. Our main aim in this work is to attract potential researchers to this challenging problem.

E.I. Kats acknowledges the RFBR support through the grant # 13-02-00120.

-
1. D. Kearns and M. Calvin, J. Chem. Phys. **29**, 950 (1958).
 2. V. A. Benderskii, N. N. Usov, and M. I. Fedorov, Proceedings of the USSR Academy of Sciences (in Russian, Doklady Chemistry) **183**, 1117 (1968).
 3. M. I. Fedorov and V. A. Benderskii, Phys. Tech. Semicond. (in Russian FTP) **4**, 1403 (1970); Phys. Tech. Semicond. **4**, 2007 (1970).
 4. A. K. Ghosh, D. L. Morel, T. Feng, R. F. Shaw, and C. A. Rowe, Jr., J. Appl. Phys. **45**, 230 (1974).
 5. P. Sullivan, A. Daraud, I. Hancox, N. Beaumont, G. Mirri, J. H. R. Tucker, R. A. Hatton, M. Shipman, and T. S. Jones, Adv. Energy Mater. **7**, 352 (2011).
 6. Y. Shinmura, M. Kubo, N. Ishiyama, T. Kaji, and M. Hiramoto, AIP Adv. **2**, 032145 (2013).
 7. *Organic Solar Cells*, ed. by W. C. H. Choy, Springer, London (2013).
 8. R. E. Merrifield, J. Chem. Phys. **34**, 1835 (1961).
 9. V. A. Benderskii, L. A. Blumenfeld, and D. A. Popov, J. Structural Chemistry (in Russian) **7**, 370 (1966).
 10. V. A. Benderskii and E. I. Kats, JETP **116**, 1 (2013).
 11. A. I. Baz, Ya. B. Zeldovich, and A. M. Perelomov, Scattering, *Reaction in Non-Relativistic Quantum Mechanics* (in Russian), Nauka, Moscow (1971).
 12. L. V. Keldysh, JETP **20**, 1307 (1965).