Quasi-degenerate self-trapping in One-Dimensional Charge Transfer Exciton

Andrei S. Mishchenko$^{1,2}$ and Naoto Nagaosa$^{1,3}$

$^1$Correlated Electron Research Center, Tsukuba 305-0046, Japan
$^2$RRC ‘Kurchatov Institute’, 123182, Moscow, Russia
$^3$Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

The self-trapping by the nondiagonal particle-phonon interaction between two quasi-degenerate energy levels of excitonic system is studied. We propose this is realized in charge transfer exciton, where the directions of the polarization give the quasi-degeneracy. It is shown that this mechanism, unlike the conventional diagonal one, allows a coherence and resonance of the free and self-trapped states even in one-dimensional systems and a quantitative theory for the optical properties (light absorption and time-resolved luminescence) of the resonating states is presented. This theory gives a consistent resolution for the long-standing puzzles in quasi-one-dimensional compound A-PMDA.

PACS numbers: 71.38.+i, 78.66, 05.10.Ln

The charge transfer (CT) exciton in one-dimension (1D) attracts great interests due to its peculiar features, e.g., strong interaction with the phonons, magnons, and large nonlinearity in the optical responses. However the theoretical understanding of it is rather limited compared with that of Wannier and Frenkel excitons, because of its intermediate radius and strong coupling nature. E.g., although the prototypical compound Anthracene-PMDA (A-PMDA), which shows unusual vibronic structure in the optical spectra, is thoroughly experimentally investigated from 70-th till nowadays [1–8], even qualitative theoretical understanding it’s optical response is missing.

The most dramatic phenomenon which occurs at intermediate or strong coupling with the phonons is the self-trapping where the free (F) state of polaron with intermediate radius and strong coupling nature. E.g., strong interaction with the phonons, magnons, and the quasiparticle-phonon coupling (RTT) in 1D systems [9,10]. Although the RTT is prohibited by Rashba-Toyozawa theorem [11], two quasi-degenerate quasiparticle bands with interaction Hamiltonian (1)

\[ H = i \sum_{k,q} \sum_{i,j=1}^2 \sqrt{\gamma ij} \phi_{ij}(q) (b_q^\dagger - b_{-q}) c_{i,k-q}^\dagger c_{j,k} + h.c. \]  

(1)

Here \( c_{j,k} \) and \( b_q \) are annihilation operators for the quasiparticle of branch \( j \) with momentum \( k \) and for the phonon with momentum \( q \). One can restrict himself by one phonon mode since, even in case of the different symmetry of excitons, the same phonon branch contributes both to the diagonal and off-diagonal coupling and drop, without affecting the conclusions, the \( q \)-dependence \( (\phi_{ij}(q) \equiv 1) \) of the interaction for simplicity. The energy \( E_L \), the average number of phonons \( \bar{N} \equiv \langle \Psi_L | \sum_q b_q^\dagger b_q | \Psi_L \rangle \), and \( Z \)-factors of the \( n \)-phonon states

\[ Z(n) \equiv \sum_{i=1}^2 \sum_{q_1,..,q_n} | \alpha_i(q_1, ... ,q_n) |^2 \]

in phonon cloud of lowest zero-momentum eigenstate

\[ \Psi_L = \sum_{i=1}^2 \sum_{n=0}^\infty \sum_{q_1,..,q_n} \alpha_i(q_1, ... ,q_n) c_{i,q_1,..,q_n}^\dagger \prod_{q_{i}} b_{q_i}^\dagger | \text{vac} \rangle \]

(Here \( | \text{vac} \rangle \) is the vacuum state.) were calculated by the exact diagrammatic Monte Carlo technique [13] which was generalized in the present paper to the case of two-quasiparticle bands with interaction Hamiltonian (1). In
the vicinity of critical $\gamma_{12} \approx 0.2087$ the dependence of the energy $E_L$ on $\gamma_{12}$ rapidly changes, and the average number of phonons $N$ demonstrates sharp crossover to higher values (Fig. 1). Hence, according to $\{11\}$, the $F$-state, which is lowest for small values of nondiagonal interaction constant, resonates with the ST-state (see inset in Fig. 1) at $\gamma_{12}$ and ST-state is the lowest one for large values of $\gamma_{12}$ $[14]$. The system indeed undergoes crossover around the critical constant rather than a phase transition due to mixing of resonating eigenstates $[13]$.

**Strong-coupling limit model.** If the quasiparticle is exciton, one can study the optical transition between the ground state $G$ and the exciton-polaron states $\Psi_L$ with zero momentum (see Fig. 1). To study the optical properties we consider the case when the coexistence occurs in the strong coupling limit, i.e. when $\gamma_{12}^2 / \omega \gg \Delta$ and, therefore, the adiabatic approximation is justified $[10]$. In this case one can find for given lattice deformation $Q = \{Q_1, ..., Q_N\}$ ($N$ is the number of lattice modes) the adiabatic potential relieves $\epsilon_A(Q)$ ($A$ is the index of lower $l$ and upper $u$ sheet) and express the eigenfunctions $\psi_A(r, Q) = \alpha^{l}_{\Lambda}(Q) \phi_l(r) + \alpha^{u}_{\Lambda}(Q) \phi_u(r)$ in terms of the excitonic wave functions $\phi_l(r)$ for undistorted lattice $[11]$. In case of F-ST coexistence the lower sheet of the adiabatic potential contains two minima at different lattice distortions $Q^t$ ($t = F, ST$) which correspond to states with different lattice relaxation energy. When the minima are separated by large potential barrier one can neglect the $Q$-dependence of the electronic functions and introduce vibrational states $\chi^{(f)}_l(Q - Q^f) = \prod_{n=1}^{N} \chi^{f_n}_n(Q - Q^f_n)$ with quantum numbers $\{f_n\}$. The low lying eigenstates of the adiabatic approximation are

$$\psi^{(f)}_l(r, Q) = \psi_l(r, Q^f) \chi^{(f)}_l(Q - Q^f); \; t = F, ST,$$  

with the eigenvalues $E^{(f)}_l = \epsilon_l(Q^f) + \sum_{n=1}^{N} \omega_n^f (f_n + 1/2)$. The adiabatic basis $[2]$ is an approximate one due to nondiagonal matrix elements of nonadiabatic operator $[11]$. E.g., at critical $\gamma_{12}$ the ground state is already a mixture of weakly/strongly deformed states (inset in Fig. 1). However, the basis $[2]$ is valid when interaction constant is close enough to the critical value $\gamma_{12}$ to create two wells but far enough to neglect the mixing of F and ST sets.

**Spectrum of optical absorption.** The optical properties of A-PMDA give the evidence of the strong exciton-phonon interaction $[3]$. The low energy part of the absorption spectrum consists of the zero phonon line (ZPL) and a broad band with the full width at half maximum (FWHM) of around $100 \text{ cm}^{-1}$. Therefore, the optical response qualitatively remind lineshape of F-color centers absorption spectra which correspond to transitions between displaced oscillators $[17, 18]$. However, all attempts to interpret the optical properties of A-PMDA $[1, 4]$ encountered apparent contradictions with the model $[17, 18]$: (i) absorption and emission spectra can not be described as one series of the equidistant lines $[3]$; (ii) the value of Huang-Rhys parameter $S$, evaluated from the ratio of ZPL and total oscillator strength, is inconsistent with the intensity distribution of the broad band [E.g., the value $S = 4$ extracted from the oscillator strengths of ZPL leads to the estimate FWHM=$140 \text{ cm}^{-1}$. $[3]$].

These long-standing puzzles can be interpreted (such treatment has never been attempted due to the RTT) as response of the coexisting F and ST states. To calculate induced cross section $\sigma^{\text{abs}}(E)$ at energy $E$ of optical absorption which corresponds to transitions from the set $\psi^{(a)}_l(r, Q) = \phi_l(r) \chi^{(a)}_l(Q)$ of $\chi^{(a)}_l(Q)$ phonon states of ground electronic state $\phi_l(r)$ to the set of excited states in $[3]$ one has to average over initial states $\{\alpha\}$ and sum over final states in $[3]$. Using the standard
approach [19], defining the electronic dipole matrix elements $M_i = \int \mathcal{L}(\phi_i(r)) r \phi_i(r)$, and introducing an average optic phonon frequency $\tilde{\omega}$ one can take advantage of Huang-Rhys method [7] and obtain for zero temperature

$$\sigma_{\text{abs}}(E) = 4\pi^2 e^2/(3c) \langle E \rangle \sum_{i=F,ST} \mathcal{M}_i F_i^{\text{abs}}(E),$$

where

$$F_i^{\text{abs}}(E) = \frac{e^{-S_i} \int_0^\infty \frac{S_i^p}{p^3} \mathcal{S}(E - \epsilon_i(Q^p) - p\tilde{\omega}_i, \mathcal{T}_p^i)}{S_i} \left[ (M_i \alpha_i^j(Q^p))^* M_j \alpha_j^i(Q^p) \right]$$

(Here $S_i = (2N)^{-1} \omega_i \sum_{n=1}^N (Q_n^i)^2$ is the Huang-Rhys factor.) is the normalized shape function, and

$$\mathcal{M}_i = \int_{i,j} \left\langle (M_i \alpha_i^j(Q^p))^* M_j \alpha_j^i(Q^p) \right\rangle$$

is the weighting coefficient. Here $e$ and $c$ is electron charge and light velocity, $\langle E \rangle$ is the average energy of transitions, $\mathcal{S}(x, \mathcal{T}_p^i) = (\mathcal{T}_p^i/2\pi)(x^2 + \mathcal{T}_p^i/2)^{-1}$, and $\mathcal{T}_p^i$ is the spectroscopic linewidth. We note that for $T \neq 0$ one can also use approach [17] since the average is performed over the one well of the ground state [20].

The contradiction (i) in the optical absorption spectrum of A-PMDA is resolved when one note that experimental data [2] contain two series of satellites in absorption spectrum: one arises from the ZPL with the step $\tilde{\omega}_F \approx 27 \text{ cm}^{-1}$ ($0 - 29 - 55 - 83 - 111 \text{ cm}^{-1}$) and the second one (13 - 29 - 47 - 62 - 77 - 88 cm$^{-1}$) with the overtone $\tilde{\omega}_{ST} \approx 12 \text{ cm}^{-1}$ originates from the 13 cm$^{-1}$ satellite. The contradiction (ii) gains natural explanation since the spectrum is the superposition of the two contributions [3] from F and ST states with different parameters $S_F$ and $S_{ST}$ (Fig. 3).

**FIG. 3.** Comparison of light absorption experimental data (diamonds) with model curve (solid line) consisting of optic response of coexisting F (dashed line) and ST (dotted line) states with $S_F = 2.5$, $S_{ST} = 13.3$, and $M_F/M_{ST} = 0.82$. The onsets are $\epsilon_{ST}(Q^F,ST) = 18322/18334 \text{ cm}^{-1}$ and linewidths are $\mathcal{T}_{F,ST} = 2972 \text{ cm}^{-1}$ ($\mathcal{T}_{F,0} = 2.5 \text{ cm}^{-1}$).

**Luminescence from QDST states.** The main puzzle in luminescence spectra of A-PMDA is that although the pattern of satellites is symmetrically repeated in absorption and luminescence spectra, the intensity distribution of phonon sidebands is significantly different [10].

The experimental conditions of time-resolved luminescence spectroscopy are equivalent to the situation when at a moment $t = 0$ the system is excited to the upper sheet $U$ whereas F and ST wells are empty. The rates of the intrawell nonradiative processes are significantly larger than that of interwell ones $w_{U \rightarrow ST}$, $w_{U \rightarrow F}$ and $w_{ST \rightarrow F}$ (see Fig. 2), because successive relaxation of the system within one well does not demand many-phonon transitions whereas those are compulsory for the interwell jumps. Due to this first link of the "bottlenecks hierarchy" (BH), the states in one well can be treated as being in quasi-thermal equilibrium and only summary populations $P_U(t)$, $P_{ST}(t)$ and $P_F(t)$ have to be considered as dynamical variables with initial conditions $P_U(t = 0) = 1$ and $P_{ST}(t = 0) = P_F(t = 0) = 0$. The differential intensities $I_{U,ST,F}^{U,ST,F}$ (of luminescence can be expressed in terms of radiative rates $R_U$, $R_{ST}$, and $R_F$ as $I_{U,ST,F}^{U,ST,F}(t) = R_{U,ST,F} I_{U,ST,F} U_{ST,F}(t)$, and non time-resolved experimental setup is defined by total yields $I_{U,ST,F}^{U,ST,F} = R_{U,ST,F} \int_{0}^{\infty} P_{U,ST,F}(t)$.

The differential intensities $I_{U,ST,F}^{U,ST,F}$ of luminescence can be expressed in terms of radiative rates $R_U$, $R_{ST}$, and $R_F$ as $I_{U,ST,F}^{U,ST,F}(t) = R_{U,ST,F} I_{U,ST,F} U_{ST,F}(t)$, and non time-resolved experimental setup is defined by total yields $I_{U,ST,F}^{U,ST,F} = R_{U,ST,F} \int_{0}^{\infty} P_{U,ST,F}(t)$. The lattice distortion $Q^U$ in the upper sheet minimum and that for ST-minimum of the lower sheet almost coincide whereas the lattice relaxation $Q^F$ for the minimum $F$ differs significantly (such situation can be easily obtained in strong-coupling limit model), there is the second link of the BH $w_{U \rightarrow ST} \gg \{w_{U \rightarrow F} + w_{ST \rightarrow F}\}$, which is due to Franck-Condon suppression of nonradiative processes $U \leftrightarrow F$ and $ST \leftrightarrow F$. At low temperatures (when, e.g., ST state is metastable and the rates $w_{U \rightarrow ST}$, $w_{U \rightarrow F}$, and $w_{ST \rightarrow F}$ are negligibly small) the dynamics of the populations is reduced to the system of equations [21]

$$\dot{P}_U(t) = -(w_{U \rightarrow ST} + w_{U \rightarrow F}) P_U(t)$$

$$\dot{P}_{ST}(t) = -(w_{ST \rightarrow F} + R_{ST}) P_{ST}(t) + w_{U \rightarrow ST} P_U(t)$$

$$\dot{P}_F(t) = -R_F P_F(t) + w_{U \rightarrow F} P_U(t) + w_{ST \rightarrow F} P_{ST}(t).$$

The differential intensities of the luminescence from the states $T$ and $F$ are

$$I_{ST}(t) = \frac{R_{ST} w_{U \rightarrow ST}}{w_{ST \rightarrow F} - w_{U \rightarrow ST} - w_{U \rightarrow F}} \times \left[ e^{-(w_{U \rightarrow ST} + w_{U \rightarrow F})t} - e^{-(w_{ST \rightarrow F} + R_{ST})t} \right]$$

and

$$I_{F}(t) = R_F \left\{ \frac{(w_{U \rightarrow F} + D)}{(R_F - w_{U \rightarrow ST} - w_{U \rightarrow F})} \times \left[ e^{-(w_{U \rightarrow ST} + w_{U \rightarrow F})t} - e^{-R_F t} \right] + \frac{D}{(R_F - R_{ST} - w_{ST \rightarrow F})} \times \left[ e^{-R_F t} - e^{-(R_{ST} + w_{ST \rightarrow F})t} \right] \right\},$$

(6)
respectively. Here $\mathcal{D} = w_{U \rightarrow ST} w_{ST \rightarrow F}/(R_{ST} + w_{ST \rightarrow F} - w_{U \rightarrow F})$. Introducing the dimensionless quantities $\nu_{U \rightarrow F} = w_{U \rightarrow F} w_{ST \rightarrow U}/(w_{ST \rightarrow U} + w_{U \rightarrow F})$ and $\eta_{ST} = R_{ST}/w_{ST \rightarrow F}$ one obtain the integral yields as $Y_{ST} = \eta_{ST} \nu_{U \rightarrow ST} (1 + \eta_{ST})^{-1}$ and $Y_{F} = (1 + \eta_{ST} \nu_{U \rightarrow F}) (1 + \eta_{ST})^{-1}$, respectively. There are some domains of model parameters when one can observe vivid qualitative features. E.g., second link of the BH leads to relation $Y_{ST}/Y_{F} \geq 1$ provided the inequality $R_{ST} > w_{ST \rightarrow F}$ takes place. Therefore, due to specific BH of the relaxation processes it is possible that, e.g., the $F$ state is distinctly observed in the light absorption spectra but is almost not seen in the spectra of non-time-resolved luminescence. At the same time if criterion $R_{F} < R_{ST}$ is satisfied, at large times $t > R_{F}^{-1}$ the ratio of differential intensities $I_{ST}(t)/I_{F}(t) \ll 1$ is opposite. Note, that this relation implies that $M_{ST} > M_{F}$ because the rate of radiative processes is governed by the matrix elements $\langle \mathcal{E} \rangle$. Due to the first link of the BH at $T = 0$ only ground vibrational states of the wells $ST$ and $F$ are populated at a moment of radiative transition. Therefore, the many-well structure leaves intact Huang-Rhys approach since no average over the initial states is necessary. Hence, the differential spectrum of the luminescence is $\sigma(E, t) = I_{ST}(t) F_{ST}^{em}(E) + I_{F}(t) F_{F}^{em}(E)$. Here the emission normalized shape function $F_{F}^{em}(E)$ can be obtained from $\langle \mathcal{S} \rangle$ by replacing $-p \rightarrow p$ in the function $\mathcal{S}$. For the lineshape of non-time-resolved experiment one has to use integral yields $Y_{ST}$ and $Y_{F}$ instead of differential intensities $\langle \mathcal{E} \rangle$ and $\langle \mathcal{S} \rangle$. Note, that parameters $S_{F}$ and $S_{ST}$ are the same as in absorption experiment.

Finally, the difference between absorption and luminescence spectra pattern arises in A-PMDA due to the BH which manifests itself in the mirror image of sidebands coming from ST and F series in absorption and luminescence spectra, which relative intensities are different in two types of experiment. Moreover, due to the BH both $13 \text{ cm}^{-1}$ peak $\mathcal{S}$ and the whole broad structure $\mathcal{S}$ have inverse relative spectral weights in luminescence and absorption spectrum. More evidences can be found in experiments on time-resolved luminescence because proper fit (Fig. 3) of the experimental curve $\langle \mathcal{E} \rangle$ demands $M_{F}/M_{T} < 1$ in $\langle \mathcal{E} \rangle$, and, hence, criterion $R_{F} < R_{ST}$ is satisfied.

Conclusions. We have demonstrated that the coexistence of the F and ST states is possible even in 1D lattices, owing to the possibility of the QDST mechanism. When there are more than one electronic levels of a particle within the energy range of the lattice relaxation energy, F and ST states can coexist and even resonate. Hence, although the Rashba-Toyozawa theorem is not overthrown and remains valid within its domain of definition, there is the possibility of the coexisting of ST and F states in 1D systems. We have found several features which are unique for QDST states and can be checked in optical experiments. We have shown, that the QDST mechanism provides comprehensive description of the long-standing mystery of the optical properties of the quasi-1D compound A-PMDA.

We acknowledge M. Gonokami, B. V. Svidunov, and Y. Tokura for critical discussions. This work was supported by Priority Areas Grants and Grant-in-Aid for COE research from the Ministry of Education, Science, Culture and Sports of Japan, and RFBR 01-02-16508.

[1] D. Haarer, M. R. Philpott and H. Morawitz, J. Chem. Phys. 63, 5238 (1975).
[2] A. Brillante and M. R. Philpott, J. Chem. Phys. 72, 4019 (1980).
[3] D. Haarer, Chem. Phys. Lett. 27, 91 (1974).
[4] D. Haarer, J. Chem. Phys. 67, 4076 (1977).
[5] A. Elschner and G. Weiser, Chem. Phys. 98, 465 (1985).
[6] M. Kuwata-Gonokami et. al. Nature 367, 47 (1994).
[7] M. Kuwata-Gonokami, Springer Series in Solid-State sciences, Vol. 124, p. 171, Ed. by K. Nasu, Springer-Verlag, Berlin Heidelberg (1997).
[8] M. Kuwata-Gonokami, unpublished (1999).
[9] E. I. Rashba, Self-Trapping of Excitons, in Modern Problems in Condensed Matter Sciences, vol. 2, p.543, Ed. by V. M. Agranovich and A. A. Maradudin, North Holland, Amsterdam (1982).
[10] Exciton Processes in Solids by M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa and E. Hanamura, Springer-Verlag, Berlin (1986).
[11] K. A. Kikoin and A. S. Mishchenko, Sov. Phys. JETP 77, 828 (1993).
[12] A.S. Mishchenko, N.V. Prokof’ev, A. Sakamoto, and B.V. Svidunov, Phys. Rev. B 62, 6317 (2000).
[13] K. A. Kikoin and A. S. Mishchenko, J. Phys.; Condens Matt. 2, 6491 (1999).
[14] Our calculations for two- and three-dimensional cases show that the QDST phenomenon is possible for all dimensionalities.
[15] B. Gerlach and H. Löwen, Rev. Mod. Phys. 63, 63 (1991).
[16] I. B. Bersuker, The Jahn-Teller Effect, New York, IFI/Plenum (1983).
[17] K. Huang and A. Rhys, Proc. Roy. Soc. (London) A204, 406 (1950).
[18] R. C. O’Rourke, Phys. Rev. 91, 265 (1953).
[19] D. L. Dexter, Theory of the Optical Properties of Imperfections in Solids, in Solid State Physics, vol. 6, p. 353, Ed. by F. Seitz and D. Turnbull, New York and London, Academic Press (1958).
[20] Method $\langle \mathcal{E} \rangle$ is valid when the difference between phonon frequencies in F and ST states can be neglected. Otherwise expressions in ref. [13], which do not alter the gross features of $\langle \mathcal{E} \rangle$, are desirable for better fit.
[21] Here we neglect the radiative rate $\sim - R_{F} P_{F}(t)$ and the dissipation processes $\sim - P_{U,ST,F}(T)$ in the r.h.s. of the equations because this simplification leaves intact gross features of the luminescence and generalization is trivial.