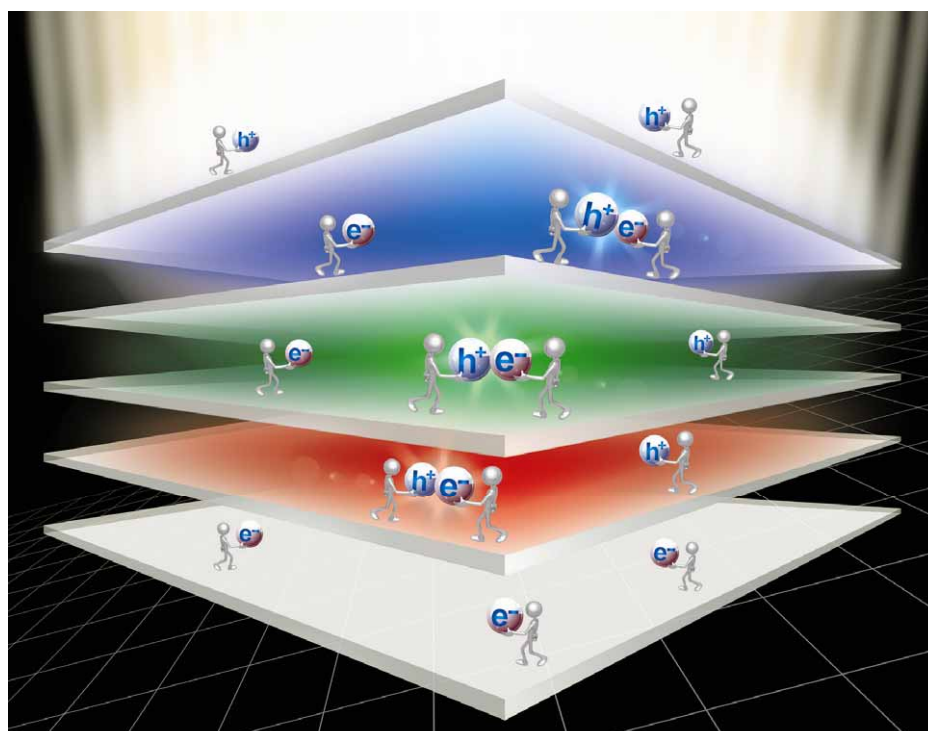


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Physical theory of excitons in conducting polymers†

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In this *tutorial review*, we cover the solid state physics approach to electronic and optical properties of conducting polymers. We attempt to bring together languages and advantages of the solid state theory for polymers and of the quantum chemistry for monomers. We consider polymers as generic one-dimensional semiconductors with features of strongly correlated electronic systems. Our model combines the long range electron-hole Coulomb attraction with a specific effect of strong intra-monomer electronic correlations, which results in effective intra-monomer electron-hole repulsion. Our approach allows to go beyond the single-chain picture and to compare excitons for polymers in solutions and in films. The approach helps connecting such different questions as shallow singlet and deep triplet excitons, stronger binding of interchain excitons in films, crossings of excitons' branches, $1/N$ energies shifts in oligomers. We describe a strong suppression of the luminescence from free charge carriers by long-range Coulomb interactions. Main attention is devoted to the most requested in applications phenyl based polymers. The specifics of the benzene ring monomer give rise to existence of three possible types of excitons: Wannier-Mott, Frenkel and intermediate ones. We discuss experimental manifestations of various excitons and of their transformations. We touch effects of the time-resolved self-trapping by libron modes leading to formation of torsion polarons.

1. Introduction: Conjugated polymers on the borderline of solid state and molecular sciences

Since its launching more than three decades ago,^{1–3} the science of conducting polymers has been looking for its place as an interdisciplinary field, or being itself the playground in disputes between fundamental science and applications, chemistry and

physics, molecular and condensed matter physics, quantum chemistry and solid state theory.

In this review we outline advantages of applying knowledge and experience of the solid state theory. We consider conducting polymers as one-dimensional semiconductors with features of strongly correlated electronic systems. We can bring together a large distance motion of electron-hole (e-h) pairs governed by the long range Coulomb attraction, and intra-molecular electronic correlations resulting in intra-monomer short-range repulsion. The picture of a one-dimensional semiconductor underlines universal laws for optical thresholds.

Theory of traditional semiconductors was able to elaborate the tiniest details recovered in experiments and demanded in applications. For half a century, all was done based on limited

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Serguei Brazovskii and Natasha Kirova

Serguei Brazovskii and Natasha Kirova are a couple of physicists who share their family life as well as collaborating at work. Both graduated from the Moscow Institute for Physics and Technology in 1969. Till the early 1990's they were working in the Soviet Union: S.B. at the Landau Institute, and N.K. in research on micro-electronics. Then they worked in various leading centers (Grenoble and Orsay, universities of Montpellier and Angers in France, Weitzman Inst. in Israel, Los Alamos and Brookhaven Nat. Labs. in US, Universities of Tokyo and Kyoto in Japan). In 1998 they settled in France; both are now leading researchers of the CNRS at Orsay. S.B. and N.K. made a highly recognized contribution to the theory of conducting polymers in the early 1980's; the studies were particularly stimulating for the emerging optics of these materials. They invented ideas of confinement of solitons and gave exact solutions of realistic models. The outcome was the notion of polarons, bipolarons, twistons. Now S.B. and N.K. are working on electronic crystals and plastic ferroelectricity.

information on gaps, their locations in the momentum space and the effective masses at the bands edges. The major theoretical tool was the method of the effective mass, finalized by Kohn and Luttinger and applied very successively from kinetics to optical properties.^{4,5} With arrival of the numerical power, a challenge was taken to determine the phenomenological parameters from the first principles.⁶ One lesson is that electronic interactions play a very important role in determining the parameters. Another lesson is that these interactions do not harm applications of an effective band theory. Still, in conjugated polymers, the elementary units—monomers are much more complicated than Si atoms and we may worry on appearance of some special effects, as we shall indeed see.

On this way we meet the front of the molecular science moving in the opposite direction—from isolated molecules to their chains. This wave, totally dominating today,⁷ carries on ideas and conjectures of molecules and their loosely packed-Van der Waals-crystals, and the language of the quantum chemistry. But the remarkable computational power, which was so successful to recover detailed molecular spectra, cannot withstand well the challenge of big systems composed with well known but strongly hybridized units.

At this point, the two sciences have the possibility to meet, recognize each other and fruitfully crosslink. This opportunity is almost missed due to lack of information, motivation and because of cultural and even linguistic differences. This article reviews our attempts to take the best of the two worlds; they were performed since 1998 with the review at an intermediate stage,⁸ and the final formulation.^{9–11} In most general terms, the major advice of the solid state theory, and the theoretical physics in general, is to look for divisions of scales (in energy, space, time), make transfers among scales and use methods adequate to each scale instead of a uniform attack. We shall try to give examples here.

2. Excitons *versus* excitations

2.1 Excitons for applications

There are two main goals in applications of conducting polymers: photovoltaic cells and light emitting diodes—LED.^{12,13} Both rely upon excited states created by the light or emitting it, but in a different way: exploiting either unbound charge carriers—electrons (e) in LUMO states and holes (h) in HOMO states, or their neutral bound states—the excitons. The photovoltaic deals with conversion of light into electric current; it requires creating, under illumination, of unbound e–h pairs and needs to prevent their binding to the exciton with an imminent recombination. Long range Coulomb attraction tends to bind the pairs into shallow excitons which need to be ionized by temperature or voltage.

In LED, the currents of electrons and holes are injected from contacts; when the carriers meet each other, there is a need to bind them into a light emitting exciton. Recombination of excitons produces the light, their ionization reduces the efficiency. Notice nevertheless that in traditional semiconducting LED and lasers, the light is emitted mostly by recombination of unbound particles—simply because the weak excitons are ionized at the room temperature.

Effects of excitons' formation are very essential—positively for the LED and negatively for the photovoltaic cell; and for both types of applications it is necessary to understand the nature, the nomenclature, the hierarchy of the excitons.

2.2 Excitons—semantic and proprietary conflicts

While the conjugated polymers have already been used in optical applications and are even commercialized, there is still no consensus on the nature of the light emitting excitons. Sharp discussions of the late 1990's were kindly forgotten but without reaching a consensus. Thus, the estimations for excitons' binding energies E_b in phenyl-based polymers were spread over the range of values 0.1–0.9 eV: from quite weak to very strong effects. Later on, a value of 0.4 eV became more quoted, but as a compromise rather than being established experimentally or theoretically. A substantial body of experimental and theoretical work has emerged supporting each of the extremes,^{7,14–22} and resolution of these issues remains as a fundamental challenge. Recall for comparison that in semiconductors used in optical devices the binding energy is truly small –0.01 eV in silicon and even smaller in GaAs.^{4,5} Then the excitons are ionized at the room temperature leaving the LEDs to work by recombination of free e–h pairs, sometimes at the defects serving as recombination centers. But at low temperatures of, say 20 K, most of luminescence goes *via* the now stabilized excitons. This important dilemma has not even been sufficiently addressed in polymers.

However drastic the divergence, the question is not only about numbers, but the very nature of excitons and of all the related physics. The disagreements are directly related to a question of which approach is adequate for conducting polymers: either the molecular physics, determined by the size quantization with emphasis upon separate levels,^{7,14,22} or the solid state physics operating with continuous spectra.^{8–11,18,19}

First of all, we need to translate through the division of languages. Within molecular physics, and quantum chemistry as its theoretical basis, any excitation above the ground state of a molecule is an exciton. In solid state physics, the delocalized, current conducting excitations are formed by pairs of independent single particles (electrons and holes) while the term exciton is reserved only for their bound state confined well within the exciton size—an effective “Bohr radius”.

In a finite system, an oligomer composed with N monomers, all levels are quantized (see Fig. 1, left) and may be accessed individually, usually named following the molecular spectroscopy convention as ${}^m\text{A}_g$, ${}^n\text{B}_u$, *etc.* For long polymer chains, the features computed for small systems mostly evolve into pairs of states with quasi-momenta \mathbf{k} . These single-particle states form continuous bands where separate levels cannot be distinguished. The continuous bands are separated by gaps E_g originating structureless valence and conducting bands as heritors of the molecular HOMO and LUMO states. Optical transitions between these bands also form continuous absorption band at $\hbar\omega \geq E_g$ which is complemented by a deeper series of split-off bound states—the excitons. These bands and levels are the universal properties of long chains, and they do not depend on N when it is sufficiently large. The problem of computational approach, as we discussed earlier,⁸

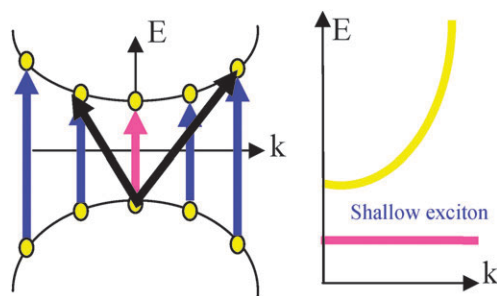


Fig. 1 Transitions into intramolecular excited states for the finite system (left, pictured for a $N = 5$ oligomer), and the structureless absorption band formation with the split off excitonic level (right). E and k are the energy and quasi momentum correspondingly.

is that non universal features of size-quantized levels, extracted from calculations are doable²² for small $N = 2,3$ (with great efforts extended⁷ up to $N = 5$) are interpreted as generic features applicable in polymers.²² This is the origin for the conjecture of so high binding energies.

The solid state physics knows two limiting types of excitons:^{23–25} the Wannier-Mott exciton is a loosely bound e–h pair; the strongly bound Frenkel exciton is practically localized within one monomer, and the constituent electron and hole lose their identity. A wonder of typical conducting polymers is that both types do coexist in their chains; these are the one-dimensional intrachain excitons.⁸ Moreover, there are also specific to polymeric films interchain excitons (also called polaron pairs, excimers),^{19,20} where the electron and the hole are bound by the long range Coulomb attraction while residing on different, usually neighboring, chains. These excitons are mostly created in LED, at least as intermediate steps.

The most efficient light emission is expected to come from what is called the “primary exciton”; usually it is expected to be the intra-chain exciton with a lowest energy and the odd parity (that is allowed for an intensive-dipole emission and absorption of a photon). Curiously, in films the inter-chain exciton may capture this role as we shall discuss below.

The nomenclature is further complicated when spins are taken into account. The spin states of excitons, singlet S or triplet T , are better preserved than in usual semiconductors because of small spin–orbit interactions in polymers which are normally composed with light atoms. The S – T conversion is a big issue in LED because nominally the number of triplets is 3 times higher than that of singlets, and only the spin singlets are allowed to emit the light.

A popular view is that triplet excitons are strongly bound, by ~ 1 eV, which was thought to speak in favor of very strong correlations, short localization and against any band picture.²² We shall see that differently: the triplet excitons, indeed relatively deep, are located at energies dictated by the scale of the band theory, namely effective Rydberg as given by the effective mass derived from the band picture and the dielectric constant of the media. What is special is that it is the intrachain singlet exciton which is strongly affected by electronic correlations. Namely its energy is pushed up by the peculiar intra-monomer repulsion between the electron and the hole—a counterintuitive statement keeping in mind the long range Coulomb attraction.

2.3 Polarons—another semantic problem

A further complication comes from local adjustments of the polymer’s backbone to the electronic state which results in formation of e/h polarons and polaron–excitons. While these effects may take place already in usual semiconductors, they are more common and more pronounced in conducting polymers. The endorsement comes from a general easiness of forming self-trapped states in 1D systems, and particularly from existence of soft modes related to mutual rotations of monomers, see *e.g.* ref. 28.

The term polaron, as well as the exciton, is also the source of semantic discrepancies leading sometimes to misunderstanding of the underlying physics. In the molecular school of conducting polymers, the polarons P^- or P^+ are the single-charged states of monomers;⁷ they are allowed for quantum or activated transfers to neighboring neutral sites, hence for carrying the current. The name “polaron” hints to the polarization of the whole electronic system (both π and σ) of the molecule when it accepts the charge (takes or gives up one electron). The next ingredient, which is now detectable experimentally, is the following adaptation of the atomic positions;⁷ this effect is closer to the view of polarons in the solid state physics. For the last, the name has been invented²⁶ in 1940’s to describe self-trapping of electrons interacting with optically active lattice modes in “polar” crystals, like the common NaCl. The name became used for any type of selftrapping for either electrons or excitons²⁷ and as such it has been brought to the science of conducting polymers by the present authors.^{28,29} Particular spectral features associated to polarons and their generalizations (bipolarons, exciton-polaron)^{28–31} became the cornerstone to identify the nature of states in doped polymers.^{1,2} The principle difference for long chains, following the solid state physics wisdom, is that electronic states are not geometrically confined as in molecules, they are delocalized with a vanishing probability $\sim 1/N$ to affect any single monomer, then the polarization or the lattice adaptation would be negligible except the sufficiently heavy doping. So there would be no trace of the original molecular polaron. But what may happen, according to the solid state theory, is that the lattice and the added electron or the hole form a self-localized state where the lattice deforms to build a potential well strong enough that the energy gain from residing the electron into the split-off local state exceeds the energy cost to create such a well. For usual 3D or even 2D materials it is possible only for polar crystals thanks to the long range Coulomb forces. But for 1D system the effect is allowed in any case which is one reason for common existence of polarons. Still, two more ingredients have to be remembered: 1. Polarons are the objects distributed over many monomers. 2. The polaron energy gain must well exceed the frequency of the involved vibrations. In the phenyl based polymers which we address here there are only the libron modes which satisfy the condition (2.) of the “strong coupling”. Hence the torsion nature of polarons which is rarely recognized.^{31–33} The polaronic effect strongly reduces the mobility of charge carriers, hence a practical recommendation to lock the libronic degrees of freedom, as it happens in ladder-type polymers. If the carriers in polymers are indeed the intra-monomer polarons, then the low mobility would

eliminate advantages with respect to molecular crystals used in OLEDs and the materials lose their attractiveness in applications.

2.4 Excitons versus band-to-band transitions

In a long polymeric chain, the excited unbound electron and hole are free carriers derived from conducting (LUMO) and valence (HOMO) bands, respectively. For distant particles, the total energy is just the sum of energies of the electron (E_e) and the hole (E_h) which gives the value of the HOMO–LUMO gap: $E_g = E_e + E_h$. The single-particle gap E_g defines the threshold of the photoconductivity. At a finite distance R , the Coulomb attraction reduces the energy below E_g giving rise to the energy

$$E(R) = E_e + E_h = E_g - \frac{e^2}{\epsilon R}$$

Here ϵ is an effective dielectric susceptibility of the media (taken here isotropic for simplicity), $e > 0$ is the value of the electron charge, $-e$. At small R , the attraction is opposed by the faster growing kinetic energy $\sim 1/(mR^2)$ and finally the branch is stabilized at the exciton energy

$$E_{\text{ex}} = E_e + E_h - E_b, E_b \propto \frac{e^2}{\epsilon R_{\text{ex}}} \propto \frac{me^4}{\epsilon^2 \hbar^2}$$

The energy of the primary exciton $E_{\text{ex}} < E_g$ gives the optical gap which lies below the gap E_g for the photoconductivity.

The question may be asked, if we should be concerned about excitons in LED? At first sight, it seems sufficient to consider the direct recombination of free injected electrons and holes as it takes place mostly in semiconducting LED and lasers. But it happens that the Coulomb attraction (contrary to a common naïve picture) reduces the probability for the recombination of the unbound electron and hole. But binding of these pairs into the exciton does favor the recombination. Indeed, within the classical picture, the recombination probability w is proportional to the time $\tau_{\text{rec}} = a/v$ for the electron and the hole, moving with a relative velocity v , to overlap at the monomer of a length a . We can make the estimations based only on the energy conservation law.¹¹

With no account of the Coulomb interaction

$$\frac{\mu v^2}{2} = E - E_g; \tau_{\text{rec}}^0 = \frac{a\sqrt{\mu}}{\sqrt{E - E_g}} \quad (2.1)$$

with proper account of the Coulomb attraction

$$\frac{\mu v^2}{2} - \frac{e^2}{\epsilon a} = E - E_g; \tau_{\text{rec}} = \frac{a\sqrt{\mu}}{\sqrt{E - E_g + e^2/\epsilon a}} \quad (2.2)$$

In the above formulas, a is the monomer size, μ is the effective mass ($1/\mu = 1/m_e + 1/m_h$), v is the e–h relative velocity; E is the e–h pair energy. The first, oversimplified expression (2.1) corresponds to the usually assumed density of states (DOS) singularity near the band bottom in one-dimensional case ($D = 1$). The second, corrected, expression (2.2) takes into account of what is called in optics of semiconductors the “final state interaction”. The free particles are thermalized at a room temperature T , so the energy is $E - E_g \sim T \sim 30$ meV while the onsite kinetic energy reaches $e^2/\epsilon a \sim 1$ eV. We see that the

Coulomb interaction drastically diminishes the overlap time τ_{rec} . The approaching electron and hole accelerate to an extent that they pass by without enough time for the recombination.

When a relatively loose bound electron-hole pair—the Wannier-Mott exciton with a radius $R_{\text{ex}} \gg a$ is formed, the energy does not reach the value as high as $e^2/\epsilon a$ being stabilized at an intermediate value $e^2/\epsilon R_{\text{ex}}$. So, formation of excitons increases the yield of the light emission. We shall present an adequate quantum picture of these effects below in Section 7.

3. Realities of conducting polymers

Most of the recent activity in physics and applications of conjugated polymers is devoted to phenyl-based polymers thanks to their ability to emit light in the optical range of about 2 eV. The main block of the polymer chain is the benzene ring, pure or modified (see Fig. 2).

All important physics of conjugated systems comes from the so called π -electrons; their atomic wave functions are oriented perpendicular to the ring plane. In the neutral benzene molecule, there are 6 π -electrons (one per carbon atom) which are delocalized over the ring. Firstly recall the picture which ignores the, actually strong, intra-ring interactions among electrons. The eigenstates of non-interacting electrons (molecular orbitals) at the isolated benzene ring are pairs of levels from π and π^* shells at $E = \pm T = \pm 2.4$ eV.³⁴ Each level is degenerate between odd u and even g states, their parity is taken with respect to the polymer axis.

$$g_l = \frac{1}{\sqrt{3}} \cos \frac{\pi l}{3}; u_l = \frac{1}{\sqrt{3}} \sin \frac{\pi l}{3}; l = 0, 1, \dots, 5$$

Within this approximation, there are four totally degenerate excitations at $2T \approx 4.8$ eV, half of them is optically active, see Fig. 3. The degeneracy is further multiplied if the spin is taken into account.

Actually, the electronic correlations are quite strong to split the degeneracy over a remarkably broad range (see Fig. 3, right): the four spin-singlet transitions form one doublet at 6.76 eV and two singlets, at 5.96 eV and 4.71 eV.³⁴ The true excitation energies are higher than one of the exciting molecular orbitals, and hence the e–h interaction energy is positive. This corresponds to the effective on-site e–h repulsion—in contrast to the long range attraction, which comes from the complex many-electronic correlations at the benzene ring. As we shall see, these effects become very important for excitons in the polymer chain.^{8,11,35}

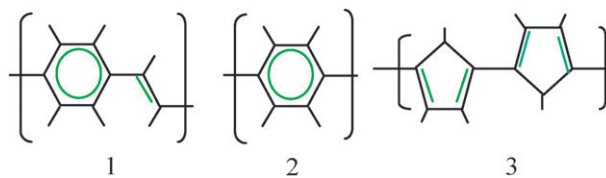


Fig. 2 Basic structure of the most studied optically active polymers: 1—poly(paraphenylene vinylene) (PPV), 2—poly(paraphenylene) (PPP), 3—polypyrrole or polythiophene.

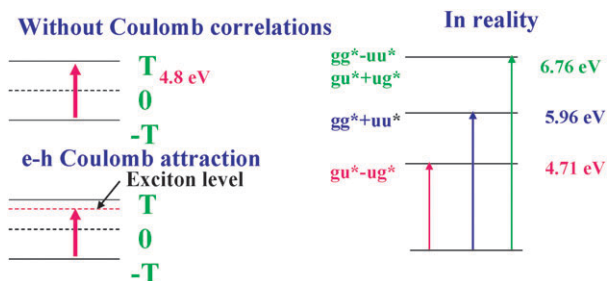


Fig. 3 Excited levels of the benzene molecule in a model of free π -electrons (left) and in reality (right).

In the polymer chain the odd (u, u^*) states have the zero amplitude at the connection points ($l = 0, 3$). They do not hybridize with each other, hence do not acquire a band dispersion and finally form the flat bands L, L^* . The even states (g, g^*) are hybridized, thus forming strongly dispersive bands D, D^* , see Fig. 4.

In the basis of molecular orbitals, the state at 6.0 eV and one of the components of the doublet at 6.8 eV have a composite structure of uu^* and gg^* excitations with opposite interferences: $gg^* \pm uu^*$. When g, g^* states become the delocalized D, D^* states, only the uu^* component is left in the new exciton LL^* . Hence we can interpolate its energy between 6.0 and 6.8 eV, say at 6.4 eV

As an example we consider the band structure for the phenyl-based polymer—the PPV. This polymer is the most studied and the most processible for applications. In addition to the phenyl (benzene) rings, the PPV chain contains also the vinyl dimers providing the linkage between the rings (see Fig. 5).

Electronic energy bands in this polymer can be viewed as originating from the intra-ring electronic levels at $\pm T$ and $\pm 2T$, as well as from vinyl dimer levels at $\pm T_1$. We shall use standard values for hopping integrals between adjacent atoms within the ring $T = 2.4$ eV, within the dimer $T_1 = 2.6$ eV, and between them $t = 2.1$ eV, see Fig. 5A. Within this tight-binding model, the analytical solution can be found, providing the spectrum and the transitions intensities.⁸ The obtained gap is too low, so robust Coulomb corrections need to be included by displacing of all D, D^*, L, L^* bands by ± 0.6 eV—that can be viewed as a ionization potential. The resulting band structure is presented in Fig. 6. The bands L_1, L_1^* , are flat, originating from the u, u^* states of the phenyl ring, while the dispersion of D_1, D_1^* is notably high. The especially strong

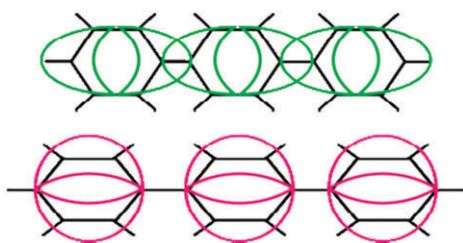


Fig. 4 Formation of dispersive (upper panel) and flat (lower panel) bands in the polymer chain based on phenyl (benzene) ring starting from g and u molecular orbitals of the ring.

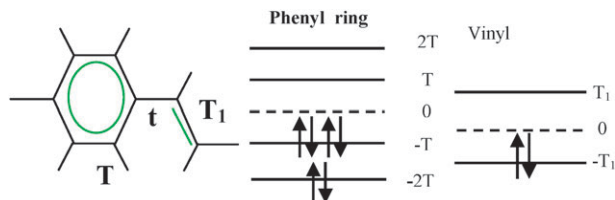


Fig. 5 Left-phenylene-vinylene monomer unit. center and right-energy levels for molecular orbitals of the phenyl and the vinyl.

hybridization in PPV, and hence the low gap, is an apparent result of the resonance between T levels of the ring and T_1 levels of the dimer.

There are several important consequences from this band picture, see ref. 8 for more details and comparison with experiments:

- The delocalization is well demonstrated by the dispersion of bands D_1, D_1^* ;
- The effective mass is surprisingly small $m \approx 0.1 m_e$, which leads to the solid-state physics of highly mobile particles, shallow bound states, *etc*;
- Dispersionless L states at higher energy determine part of the observed photoinduced features. In terms of semiconductors, their creation corresponds to a kind of photo-doping;
- Delocalization breaks the scheme of intra-ring correlations. The states responsible for the highest intra-ring excitation ≈ 6 eV, now contribute to the lowest on-chain excitation ≈ 2 eV. This is one of the effects of the level inversion.⁸

The band picture naturally allows for three different excitons.⁸

Exciton 1 (EX1) corresponds to a weakly bound state of delocalized electron and hole in HOMO and LUMO bands D_l and D_l^* . This 1D Wannier-Mott exciton is well described within the effective mass approximation. Recall that E_{b1} strongly depends on the dielectric susceptibility ϵ , and a notable feature is that here $\epsilon = \epsilon_{\perp}$ is the susceptibility perpendicular to the chain, and it depends on (and hence is tunable by) the matrix, packing, film density, solvents, *etc*. Hence E_{b1} is not an intrinsic property of the polymer chain but also a property of the medium (solution, film). That is

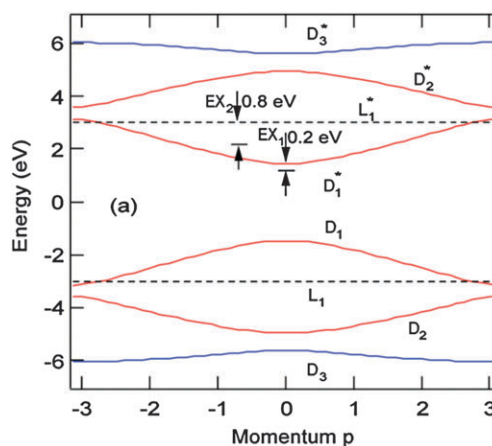


Fig. 6 Band structure and excitons for PPV chain.

very important to remember since this exciton is the most important one for the visible range optics.

Exciton 2 (EX2) corresponds to a more tightly bound state of $D_1L_1^* + L_1D_1^*$. Now the non dispersive electron L_1^* or hole L_1 plays the role of an immobile Coulomb center (similarly to donors or acceptors in semiconductors), which binds the delocalized particle from the band D_1 (D_1^*) of the opposite sign. With twice higher effective mass of the internal motion μ with respect to the EX1, the radius of the EX2 is reduced to values of the order of 3–4 unit cells; then the dispersion of the dielectric susceptibility ε (it always decreases at short distances) may reduce it to be even shorter. This exciton is of higher energy by some 3 eV in comparison with the EX1 and normally it lies above the conduction gap. But one can predict circumstances where this order changes and the EX2 descends below the gap. The crossing can be identified because of different polarizations of the excitons with respect to the chain axis,³⁶ or in EELS (electron energy loss spectroscopy) experiments³⁷ which allow for an access to the exciton's motion.

Exciton 3 (EX3) corresponds to the intra- and inter-ring bound state of the non dispersive electron and hole. The lowest $L_1L_1^*$ state is localized within one ring, being related to the u, u^* states of the electron and the hole near $\pm T$. This is a true Frenkel exciton but even that is essentially modified in the chain in comparison with the one for an isolated monomer as we have discussed above.

In the following we shall deal only with the exciton EX1. To determine the energies and effective radii, we have to take into account the peculiarities of the allowed motion of the electron and the hole forming the exciton. Namely, in a conducting polymer, electron and hole can move only along the chain, being either both on one chain or on the neighboring ones. The long range Coulomb potential has the form:

$$V_C = \frac{e^2}{\varepsilon \sqrt{x^2/\varepsilon_{\parallel} + r^2/\varepsilon_{\perp}}}, \varepsilon = \varepsilon_{\perp} \sqrt{\varepsilon_{\parallel}} \quad (3.1)$$

Here x and ε_{\parallel} are the coordinate and the dielectric constant along the chain direction, r and ε_{\perp} are the coordinate and the dielectric constant perpendicular to the polymer chain. Keeping in mind the one-dimensional motion of the particles forming the exciton, we can estimate the exciton binding energy E_b variation:

$$-E_b = \left\langle \frac{e^2}{\varepsilon_{\perp}|x|} \right\rangle - \left\langle \frac{p^2}{2\mu} \right\rangle$$

hence

$$E_b = \frac{e^2}{\varepsilon_{\perp} R_b} \ln \frac{R_b}{a} - \frac{\hbar^2}{2\mu R_b^2} \quad (3.2)$$

Here p is the momentum of the reciprocal motion, a is a minimal distance (the monomer size for the on-chain exciton or the interchain spacing for the interchain exciton correspondingly). Finding the extreme over R_b , we obtain the parameters R_b and E_b of the lowest intra-chain exciton

(primary, 1Bu exciton in notations of molecular spectroscopy)

$$R_b = R^* \frac{1}{\ln(R_b/a)}; E_b = E^* \ln^2(R_b/a) \quad (3.3)$$

The characteristic energy E^* and the radius R^* are

$$E^* = \frac{\mu e^4}{\varepsilon_{\perp}^2 \hbar^2} = \frac{2}{\varepsilon_{\perp}^2 m_e} E_{Ry} \quad (3.4)$$

$$R^* = \frac{\varepsilon_{\perp} \hbar^2}{\mu e^2} = \varepsilon_{\perp} \frac{m_e}{\mu} a_B \quad (3.5)$$

where m_e is the bare electron mass, \hbar is the Planck constant, $a_B = 0.5 \text{ \AA}$ is the Bohr radius and $E_{Ry} = 13.6 \text{ eV}$. The logarithmic enhancement of the binding energy is coming from the one-dimensional nature of the exciton in conducting polymers which makes a difference with usual, 3D semiconductors.³⁸ It can be understood to be primarily the effect of the electric field—the “capacitance” of the cigar-shaped distribution of charges. For a similar reason, the binding energy of the intra-chain excitons in the polymer depends on the dielectric susceptibility perpendicular to the chain and not on the longitudinal one, which is a sadly frequent mistake.³⁹

The long-range Coulomb interaction originates also a series of higher excitons filling the energy interval between $E_b < E_g$ and E_g . Their localization radii and binding energies are given nearly as the Hydrogen series $E_n = E^*/(2n^2)$, $n = 1, 2, \dots$. The conducting polymers are never clean enough to resolve this staircase except for maybe $n = 1$; it will be seen as a broadening of the conduction gap E_g .

4. Merging the band picture with strong intra-monomer correlations

In the polymer, both the intra-ring Coulomb interactions and the delocalization lift the degeneracy of the molecular orbitals of the benzene ring, but in a completely different way: knowing that allows us to choose the adequate efficient approximation.

Within the exciton, the hole and the electron experience quantum oscillations in the mutually attractive Coulomb potential $-e^2/\varepsilon|x|$. Also, there are strong multi-particle electronic correlations, but they can still be reduced to easily treatable parameters. Namely, effects of these correlations decay as $1/x^3$ or faster, so their average, in a 1D system, converges to smallest distances of the order of the monomer unit a , and only therein it is sufficient to take them into account.^{10,11} As we have briefly discussed above, these impact interaction is equivalent to adding the intra-monomer repulsive potential U_0 , as shown in Fig. 7.

The value U_0 can be estimated from the already available experimental or numerical results, or reasonably guessed from the information on isolated monomer molecule. Since U_0 depends on the overlap between the quantum state of the delocalized e–h pair and correlated intra-molecular states, then it is different for singlet and triplet excitons: $U_0 \rightarrow U_{S,T}$. At large x , the electron-hole pair exists in the $D_1D_1^*$ form which greatly benefits from the band delocalization. But meeting each other within the same monomer, at $x \sim a$ the pair finds itself in the least favorable configuration which

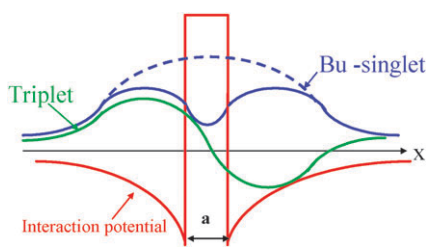


Fig. 7 Interaction potential and wave functions of singlet and triplet excitons. Notice the dip for the B1u exciton in compare to the simple maximum at $U_0 = 0$ (dashed line).

energy costs 6–6.8 eV for singlet excitation (while only 3.6 eV for the triplet one). Hence we arrive at the rather large value for U_S (~ 3.2 eV) and a moderate one for U_T (~ 1.2 eV). Another way to estimate U_S and U_T comes from universal computational and experimental observations for $1/L$ size dependences of E_{ex} on the oligomer length L .^{7,40,41} Apparently, oligomers have been studied in the length window of being long enough to neglect the size quantization shift $\sim 1/L^2$ and short enough for the state to be squeezed in compare to the equilibrium exciton radius $R_{\text{ex}} > L$. Then we are left just with $\delta E_b \approx U_0 \psi^2(0) \sim U_0/L$ which both explains the dependence and provides a mean to determine U_0 .^{10,11,35} *e.g.* we extract $U_S \approx 3.6$ eV from experimental data⁴⁰ and larger $U_S \approx 4.2$ eV (with expected smaller $U_T \approx 1.2$ eV) from data.⁷

Notice the inversion of the picture with respect to a conventional wisdom:^{18,22} local electronic correlations provide the *repulsive* interaction strongly reducing the binding energy; only the long range Coulomb interaction is attractive and prone to originate bound states. The repulsion of the correlational origin is smaller for triplet excitons; hence their energy and the radius are most characteristic for the semiconducting Wannier-Mott exciton which is due only to the long range Coulomb attraction. The role of the long range Coulomb interaction cannot be elucidated in typical numerical modeling of short (usually 3, rarely 5) oligomers. The effect of correlational repulsion was inevitably missed since the numerical quantum problem of several rings forces to sacrifice the accuracy below the level necessary to describe correctly the single benzene ring. Following discussion in the Introduction, we face here a clear example of necessity and fruitfulness of the scales division.

Now we are armed to give a final picture of shallow excitons. The wave function $\psi(x)$ for the reciprocal motion and the binding energy E_b are determined by the equation

$$\left(\frac{p^2}{2\mu} - \frac{e^2}{\epsilon_{\perp}|x|} + U_0 a \delta(x) + E_b \right) \psi(x) = 0 \quad (4.1)$$

Its approximate explicit solution¹⁰ yields the following results. For the $1B_u$ exciton (the wave function of the reciprocal motion $\psi(x)$ is even), E_b is expressed approximately *via* the exciton radius R :

$$E_b = E^* \left(\log \frac{R}{a} - \epsilon_{\perp} \frac{a}{a_B} \frac{U_0}{2E_{Ry}} \right)^2 \quad (4.2a)$$

where R is to be determined self-consistently by the equation

$$\epsilon_{\perp} \frac{m_0}{2\mu} \frac{a_B}{R} = \log \frac{R}{a} - \epsilon_{\perp} \frac{a}{a_B} \frac{U_0}{2E_{Ry}} \quad (4.2b)$$

Apparently, the intra-monomer repulsion U_0 suppresses the binding energy of the exciton increasing its radius R . The same time, there is no repulsion for higher excited states for which the wave function is zero at $x = 0$ *i.e.* when the particles meet at the same monomer. This effect can even lead to the level crossing of optically allowed B_u and forbidden A_g excitons.^{10,11}

5. Inter-chain excitons

For Wannier-Mott large radius excitons, on the side of long range Coulomb forces, there is almost no difference between the exciton formed at one and at neighboring chains. The correction comes only from the change in the eqn (3.3) of the cut-off parameter $a \rightarrow d$ —the inter-chain distance. (It may be appropriate to notice here that logarithmic dependencies are so much appreciated in theoretical physics just because of so weak dependence of cutoff parameters which are always ill-defined.) But there is a big difference with respect to the intra-ring correlations, which are accounted for *via* the effective intra-monomer repulsion U_0 . This repulsive interaction disappears for the inter-chain exciton which then does not experience the drastic suppression of the intra-chain one. The energies of the singlet and the triplet interchain excitons should be close, and comparable with the energy of the triplet intrachain exciton. The binding energies were given by eqn (3.3) for the inter-chain exciton and by eqn (4.2 a,b) for the intra-chain one.

The weak inter-chain electronic hybridization will strongly reduce the light emitting intensity. Thus for the inter-chain excitons, we expect a curious coincidence of a rather high binding energy (~ 0.4 eV) and a low luminescence intensity.

The bound on-chain singlet pair, experiencing the highest effect of the on-site repulsion, shows the weakest binding. That explains observation of the shallow resonance revealed in electro-absorption experiments.⁹ The stronger bound inter-chain exciton presents for geminate e–h pairs a fast efficient sink to longer leaving states.^{42,43} This readily explains the delayed fluorescence as well as its sensitivity to the magnetic field.^{44,45} Indeed, for interchain excitons the S-T splitting will be negligible allowing for an easy cross-linking thus facilitating contribution of triplet excitons to the luminescence—a big issue in applications.

We expect that for the films there are three channels for the geminate recombination. Fast emission comes from very shallow intra-chain Coulomb excitons, which are resolved from the band edge only in the high electric field.^{9,35} It will be followed by the red-shifted luminescence from the secondary inter-chain exciton which will decay at longer time scales of the fluorescence.^{46,47} Finally, the on-chain triplet pairs which are excited states of the lowest energy and of the longest life time may travel far away to find deep traps in regions with lower ϵ (fibrils' surface, split-off single chains) to give a strongly red-shifted phosphorescence.

The above picture is in accordance with experiments on transient photoluminescence and photoinduced absorption

in MEH-PPV under high hydrostatic pressure.^{48,49} Under pressure, the photoluminescence is red-shifted and loses intensity. Recall that under pressure the torsion angle between the benzene rings along the polymer chain should decrease, so the intrachain hopping integral increases, the band dispersion also increases, hence the HOMO–LUMO gap decreases (by ~ 0.5 eV for the case of PPV, which is the right order of magnitude), hence the red shift of the photoluminescence. Also, the decrease of the interchain distances enhances the interchain electronic hybridization, increasing the probability of the optical emission from the interchain excitons.

There also exists another direct possibility to compare the binding energies of intra- and inter-chain excitons revealed by photo- and electroluminescence.

There is a tendency to explain the photoluminescence spectra of PPV polymers as the intra-chain pure electronic transition and the vibronic progression.⁵⁰ The experimental values of the energies of vibrational phonon modes in PPV are 41 meV (330 cm^{-1}), 144 meV (1160 cm^{-1}), 188 meV (1518 cm^{-1}).⁵¹ Vibronic replica have been observed for photoconductivity spectra with equal energy separation between the peaks, 0.19 eV.⁹ The shape of photoluminescence and electroluminescence spectra can be decomposed into three peaks (2.45 eV, 2.3 eV, 2.15 eV) with the distance about 0.15 eV. The small peak at 2.45 eV is interpreted as band-to-band electron-hole recombination and 2.3 eV and 2.15 eV are the main and first phonon assistant exciton recombination transitions. Notice, that for the case of direct gap the phonon assistant exciton recombination transition should have lower intensity with respect to the pure exciton recombination. This does coincide with the data for photoluminescence, namely, the main part comes from 2.3 eV, and the ratio of integrated intensities of the higher to lower peak is 1.1. But for the electroluminescence the main peak comes from 2.15 eV, and the corresponding ratio is 0.38. So, either we accept that phonon assistant recombination is higher than the direct one, or there is another explanation. Our point of view is the following.

In the case of steady-state measurements, both electro- and photoluminescence are originated from recombination of intra- and interchain excitons and from a smaller contribution of band-to-band transitions. In experiments on the steady state photoluminescence, the pumping and the probes are continuous. The geminate intra-chain excitons can either

recombine giving rise to the photoluminescence or dissociate into free electron and hole. These free particles diffuse, jumping also between chains; soon they form the inter-chain excitons and then recombine. Finally in the steady state photoluminescence spectrum of films, two lines should be present, being originated by the intra- and interchain excitons. Notice that in the case of steady state experiments, contrary to time resolved ones, the contribution coming from the intra-chain and inter-chain excitons annihilation should be comparable.

In the case of the electro-luminescence, free electrons and holes are injected from opposite contacts of OLED. In the course of diffusion, electrons and holes meet each other, thus forming the excitons. The two types of excitons give again the two different lines in the photoluminescence spectrum. But now the major part should come from the inter-chain excitons. In Fig. 8 we present the data on electro- and photoluminescence of PPV from ref. 31. Each peak can be decomposed into two centered around 2.15 eV and 2.3 eV. For the photoluminescence the main part comes from 2.3 eV and for the electroluminescence from 2.15 eV. We explain this in a way that the lower peak corresponds to the inter-chain exciton, and the higher one—to the intra-chain exciton. Integrating the areas, we obtain the following ratios for the inter-chain/intra-chain excitons: 0.92 for the photo-luminescence and 2.65 for the electro-luminescence.

The arguments against our interpretation could be that there is the same form of the photoluminescence in the film and solution. But as it was pointed out²⁰ actually in all solutions there is a part of chain aggregates. This is clearly seen in time resolved photoinduced absorption.^{20,21} In spite of the fact that in the solution of DSB-oligomer the absorption spectra reveal the spectra in PPV polymer, the time resolved photoinduced absorption measurements indicate that three PA peaks have the same time constant in oligomers solution, but it is not the case of the MEH-PPV in solution.

Notice that the role of the interchain excitons (polaron pairs, excimers in another language) in the photoinduced absorption was already pointed out.²⁰ The changes in luminescence and photoinduced absorption under pressure, which favorise the creation of interchain excitons were first presented⁴⁸ up to 50 kbar and this year in experiments up to 100 kbar.⁴⁹

6. Field-induced exciton dissociation

The fine structure of the absorption edge, and consequently of the luminescent states, have been elucidated by experiments on photoconductivity which resolve the shallow excitonic peak in the external electric field F . The most striking observation is the appearance of a narrow peak in the photocurrent spectrum I_{photo} at $F > 10^5\text{ V cm}^{-1}$. The exciton emergence just below the absorption edge, and its efficient dissociation by the field, clearly signify the shallow, large radius bound state, see Fig. 9.

Relatively long-lived states can exist if their energy is below the barrier shown in the Fig. 10. At strong fields the primary and all higher excitons would be destroyed, so that all states will be delocalized. Hence, the photoconductivity will depend on F only *via* the carriers' mobility. For the experimentally

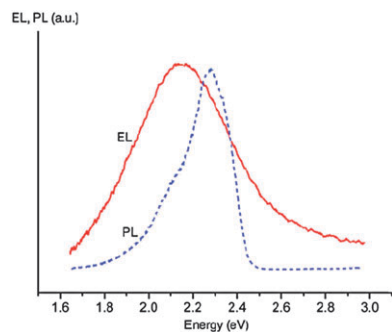


Fig. 8 Steady state electro- and photo luminescence in PPV, courtesy D. Lee.⁵²

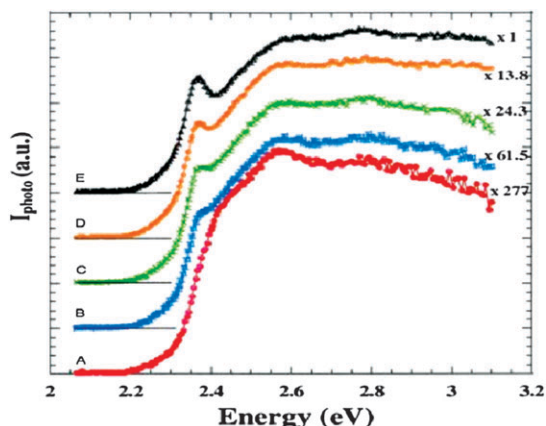


Fig. 9 Photocurrent excitation spectra in PPV at various external fields F . A: $0.4 \times 10^5 \text{ V cm}^{-1}$, B: $0.8 \times 10^5 \text{ V cm}^{-1}$, C: $1.2 \times 10^5 \text{ V cm}^{-1}$, D: $0.4 \times 10^5 \text{ V cm}^{-1}$, E: $4 \times 10^5 \text{ V cm}^{-1}$. The normalization factors of the curves are indicated on the right.

significant region of intermediate fields, all higher states $n \neq 0$ lie above the barrier, hence they are broken by the field.

We see the exciton peak followed by the exponential (tunneling!) increase towards the kink corresponding to the onset of the single-particle gap. The corresponding potential is shown at Fig. 10. It shows a well at small x , which is separated from the unbinding region by a barrier $U_b = 2e\sqrt{eF/\epsilon_\perp}$ with a top at $x = -\sqrt{e/\epsilon_\perp F}$.

But the primary 1B_u exciton is preserved within a finite lifetime $\tau \sim \Gamma^{-1}$ determined by the tunneling probability Γ through the barrier. This escape probability is given as⁹

$$\Gamma = \frac{E_b}{\hbar} \exp\left(-\frac{4E_b^{3/2}\mu^{1/2}}{3e\hbar F}\right)$$

The above equation provides the field dependence of the photoconductivity due to the cold ionization of the exciton. It describes the main field dependence of the peak in photoconductivity. The fitting parameter $E_b \sim 0.1 \text{ eV}$ quantitatively agree with the results based on the band picture described above. For $F = 10^5 \text{ V cm}^{-1}$ we obtain $\tau \approx 3 \times 10^{-13} \text{ s}$.

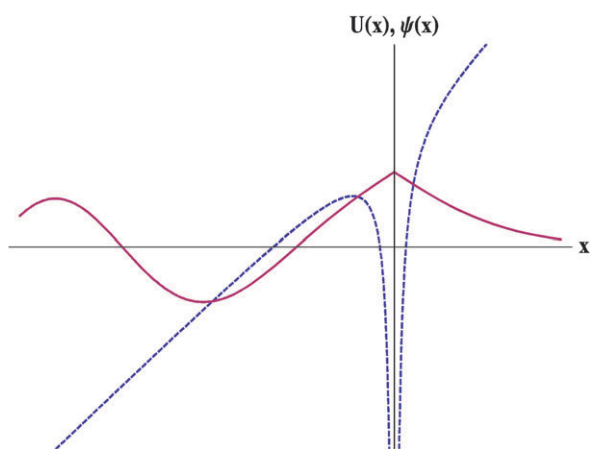


Fig. 10 The potential U (dashed line) and the wave function (solid line) of the primary exciton at the presence of the external electric field.

7. Unbound states: Quasi-classical approximation

Contrary to photoconductivity, the absorption α is not essentially affected by the electric field. It is worth discussing this in view of confusions between the excitonic peak and the band-to-band edge threshold. In spite of a relatively small contribution to the total intensity (see below), higher excitonic levels determine the band edge profile.^{9,10} Smearing these transitions to the continuous spectrum, we obtain a flat shape $\alpha \approx \text{const}$ at $E = E_g$ instead of the usually expected DOS singularity $(E - E_g)^{-1/2}$ with a sharp abrupt below E_g .

For the long-range Coulomb interaction, the quasiclassical (WKB) approximation correctly reproduces a sequence $\sim 1/n^2$ of excitonic states, while missing the primary exciton. In the WKB approximation, the local motion is controlled by the action S related to the classical momentum P :

$$p = \frac{ds}{dx} = \sqrt{\mu\left(\frac{e^2}{\epsilon_\perp|x|} + E - E_g\right)} \quad (7.1)$$

For the bound states $E - E_g = -E_{bn}$, the quasi-classical quantization is given by the integration between turning points $\pm x_n = \pm e^2/(\epsilon_\perp E_{bn})$:

$$2\pi\hbar n = 2 \int_{-x_n}^{x_n} p dx = \pi\hbar \sqrt{\frac{E^*}{E_{bn}}} \quad (7.2)$$

hence $E_{bn} = E^*/4n^2$. The normalized excitonic wave functions are:

$$\psi_{n-s,c} = \frac{A_n}{\sqrt{p}} \left(\sin\frac{S}{\hbar}, \cos\left(\frac{S}{\hbar} - \gamma\right) \right) \quad (7.3)$$

where the phase shift γ of $\psi_{n-c,c}$ comes from the on-site repulsion U_0 and

$$A_n^2 = \frac{2\epsilon\sqrt{\mu E_{bn}^3}}{\pi e^2} \quad (7.4)$$

The absorption coefficient for the x -polarized optical transition to the n th allowed excitonic state is:

$$\alpha_{\text{ex}}^n = C[\psi_n(0)]^2 = \frac{2}{\pi} C \frac{\alpha^{1/2}}{n^3 a_B^{3/2}} \quad (7.5)$$

where $C = \text{const} \sim M_{\text{bb}}^2$ and M_{bb} is the dipole matrix element between the basic wave functions, which is the same as for the band-to-band absorption.^{9,10}

The ratio of the absorption α_{ex} arising from all higher excitonic states to primary exciton absorption is $\alpha_{\text{ex}}/\alpha_{1B_u} = (a_B/a_B^*)^{3/2} \approx 0.1$.

In spite of the relatively small contribution to the total intensity, the higher excitonic levels determine the band edge profile. Smearing these transitions to the continuous spectrum, we obtain $\alpha_{\text{ex}} \sim a^{1/2}/(E^* a_B^*)^{3/2} = \text{const}$.

By continuity, this non-zero value should also be preserved for $E > E_g$: this expectation is different from both the model

of non-interacting particles which gives the band edge singularity and from the model of short-range interactions, where the bleaching suppresses the intensity at E_g to zero. So, what happens with the traditionally expected singularity $\alpha \sim (E - E_g)^{-1/2}$ above the edge? The unbound states are the plane waves at large distances; at shorter ones they show a dip due to the increasing velocity as we have discussed qualitatively. The normalized wave function can be written as

$$\psi = \psi_E = \frac{2}{\sqrt{L}} \left(\frac{E - E_g}{E - E_g + e^2/\epsilon_{\perp}|x|} \right)^{1/4} \cos\left(\frac{S}{\hbar} - \gamma\right) \quad (7.6)$$

Its magnitude is suppressed at small x as $|\psi|^2 \sim x^{1/2}$ which comes from the faster motion near $x = 0$. Eqn (7.1) shows that while on average $\langle P \rangle \approx [\mu(E - E_g)]^{1/2}$, at the origin $P(0) \sim (\mu E^* a^*/a) \gg \langle P \rangle$. The excitation probability $w_{\text{ex}}(E)$ is suppressed at low energies as $w_{\text{ex}}(E) \sim (E - E_g)^{1/2}$. This suppression exactly compensates for the diverging factor of the density of states $dn/dE \sim (E - E_g)^{-1/2}$.

Finally, for the band-to-band absorption, we obtain:

$$\alpha_{\text{B-B}} \approx \frac{2}{\pi\hbar} C \frac{a^{1/2}}{a_{\text{B}}^{*3/2} E^*} \quad (7.7)$$

Note that the singularity $1/(E - E_g)^{1/2}$ is rounded at the energy scale $e^2/\epsilon a$, which is several times $\sim a_{\text{B}}^*/a$ larger than the exciton binding scale. The absorption saturates at the band edge, thus meeting the averaged absorption from the high excitonic series below the edge. The crossover happens at an energy $E_{\text{C}}^* \sim E^* a_{\text{B}}^*/a \sim E_{\text{b}}$, for that estimation we have exploited the numerical feature: the enhancement factors a_{B}^*/a for E^* and $\ln^2(R/a)$ for the primary exciton are numerically similar.

In summary, the optical absorption increases from high energy values, saturates above the band edge at the scale of the binding energy and continues as a kind of a plateau through the edge down to the excitonic level; then, after a dip, it sharply increases at $E = E_g - E_{\text{b}}$. Since the law $(E_g - E)^{-1/2}$ at $E > E_g$ became limited to high enough values, it can be shadowed by a systematic increase of the band-to-band matrix elements across the total D–D* band, as found in [5]. The edge singularity is then dominated by the exciton alone.

We can extend this analysis to include the electric field F to obtain:¹⁰

$$\begin{aligned} \alpha_{\text{B-B}}(F) &= C |\psi_E(0)|^2 \frac{dn}{dE} \\ &\approx \frac{2}{\pi\hbar} C \sqrt{\frac{\mu}{E - E_g - Fa + e^2/\epsilon_{\perp}a}} \\ &\rightarrow \frac{1}{\pi} C \frac{a^{1/2}}{a_{\text{B}}^{*3/2} E^*} \left(1 - \frac{F a^2}{F^* a_{\text{B}}^2} \right) \end{aligned}$$

which reduces to the law in eqn (7.10) at $F = 0$ plus correction $\sim -F$ corresponding to the Franz–Keldysh effect.

The small exciton binding energy in PPV revealed directly by the high-field conductivity experiments⁹ indicates that the e–e interaction is of the long-range nature, compatible with a ‘band model’ approach to the electronic excitations. Our analysis indicates that whenever the sharp optical features are observed (stimulated emission, high field photoconductivity),

they come from the well-ordered, highly conjugated fraction of the polymer. In these regions, the physics is dominated by the band picture and the consequent long-range bound states, which lead to narrow shallow excitons. The excitons also dominate at the onset of the direct absorption, while being smeared by contributions from less ordered regions, most probably by variations of ϵ . A practical consequence is that these contemporary materials still have high potential for improving their quality and applications.

8. Polaronic effects

Major properties of delocalized states and excitations depend on inter-ring transfer integrals t , which are subject to lattice distortion. Various kinds of bond stretching and bond angle twisting may be involved in deformations of t . In contrast to the polyacetylene where the gap is of a spontaneous origin due to the Peierls effect,^{2,28} in phenyl based polymers all distortions of bond lengths and bond angles involving σ electrons are small because of their high stiffness. The main effect of the lattice relaxation originates from the soft mode of phenyl rings rotation around the chain axis—the librons. The significance of librations and the related polaronic effects have been noted,³¹ exploited³² and discovered independently.³³ (There is a particular significance of the chain’s twisting for carriers’ mobility in the crystalline polyacetylene.⁵³)

The intra-chain hopping integral t between monomers depends on a mutual orientation of the nearest rings by the angle θ as $t = t_0 \cos\theta$. The equilibrium angle is determined by competition of two different effects: the repulsion of C–H dipoles tends to arrange the rings in perpendicular planes when $\theta = 90^\circ$, while the hybridization of π -electrons applies a restoring force to keep the rings in one plane $\theta = 0$. As a result of this compromise, the ring planes form angles of $\theta \approx 20^\circ$ for PPV chain and $\theta \approx 30^\circ$ for PPP chain. In principle, each electronic excitation experiences a shift due to the lattice relaxation, with formation of polarons as an extreme case. Within the polaron, the chain becomes more planar, t increases and the gap decreases locally.

The effect may well account for the time dependent features of the optical spectra in femto-second experiments, *e.g.* the red shift of the absorption edge (0.5 eV is the upper estimate from the dispersion relation⁸) and the blue shift in photoinduced absorption. The time-dependence gives the characteristic time $\tau \sim 0.1$ ps of the selflocalized state formation which well corresponds to the inverse frequency of librons. This is also the origin of the difference in estimates of the peak position, coming from steady state and timer resolved PA studies.^{9,21} The same effect is provided by doping or pressure as it recently has been shown experimentally.^{48,49} On the contrary, the temperature activates the libron motion and the gap increases with temperature.

9. Comparison with other schemes

Debates on the nature of the excitons have been centered on points important to applications:

(i.) A delocalized (band) picture against the one of localized molecular transitions;

(ii.) Nature of emissive excitons as weakly bound delocalized (Wannier–Mott) ones against the one of tightly bound localized (Frenkel) excitons.

Evidences for small exciton binding energies came predominantly from charge transport and injection experiments and the electro-luminescence.^{14–16} In these measurements, the energy difference between separated charged excitations (free electrons and holes or corresponding polarons) and the neutral emissive excitons has been established at ~ 0.1 – 0.2 eV in several PPV derivatives.¹⁵ Evidence for large exciton binding energies were based predominantly on nonlinear optical measurements such as electro-absorption and photo-induced absorption (PA).^{16,21,22} It became clear that for resolution of this dilemma the whole picture of linear and nonlinear optical probes in the whole frequency range should be involved. However instead of clarifying the picture, the complex studies resulted in several different, sometimes incompatible scenarios.

For these big multi-electronic interacting systems, any quantitative method is expected to give a noticeable inaccuracy. Numeric methods do not help much: the first principle quantum chemistry does not go beyond one monomer and already for oligomers truncated methods are exploited,^{7,22} which was known to give inadequate results for the single ring.³⁴ Even if one cannot rely upon a good quantitative agreement among various approaches, a qualitative similarity might at least be expected. Instead, several existing pictures^{8,18,22} remained incompatible leading to different assignments of optical features. Quantitative disagreements concerning the binding energy of the primary emitting exciton is drastic with conceptual consequences for applications. Estimates of the binding energy E vary from ~ 0.9 eV²² to ~ 0.1 eV.^{8,10} Studies devoted to linear optics disagree on the origin of the second absorption peak near 3.6 eV which was guessed to be originated *e.g.* from finite size effects,^{7,22} or from symmetry-breaking due to side group substitution.^{18,19} There was no consensus also on nonlinear properties. They have been interpreted on the basis of the size-quantized states,²² as an evidence for formations of bipolarons,⁵⁴ polaron pairs, eximers, exiplexes.^{19,20} As we have discussed in the Section 2, some discrepancies, *e.g.* in binding energy, come from a lack of correspondence between different terminologies.

On the theory side, there were two main branches: computational and analytical.

The *computational studies* derive essential optical features from the size quantization for oligomers. They are divided into two groups with conclusions so different that they may be assigned to different definitions rather than to results:

1. Advanced full-scale quantum chemistry calculations are practically limited to single monomers with side groups, or to dimers.⁷

2. Adjustable models of π -electronic sub-shells which allow extension of the size to the important five-ring oligomers but not yet to the polymer limit, give the binding energy 0.9 eV.²²

Analytical studies invoke the coexistence of localized and delocalized states, which is a special feature of phenyl-based polymers. Among them one can also distinguish two different branches:

- A1. The picture of excitons exploiting the language of and derived from the molecular spectroscopy of the isolated

phenyl ring.^{18,19} Emphasizing the intra-molecular scheme, one underestimates the inter-monomer hybridization of electrons, and it becomes necessary to enforce it by hand to reach agreement with experiments. Hence the large, unreal values of transfer integrals have to be taken as adjustable parameters:¹⁸ more than 3 eV, in comparison with the standard 2.2–2.4 eV.

- A2. The band picture of delocalized electronic states exploiting a solid state physics band theory language relevant to polymers and long oligomers with dominating delocalization of electrons;^{8–10} it yields small binding energy for the unrelaxed intra-chain exciton (~ 0.1 eV) and moderate 0.2–0.3 eV for the polaron–exciton and for the inter-chain exciton. This theory, having been reviewed in this article, is consistent only because of merging the notions of physics of semiconductors and of the exact monomer spectroscopy.

Our main point is that the scales of ~ 6 eV for transition energies of the isolated phenyl ring (benzene molecule) are reduced in polymers so strongly down to the scale ~ 2.4 eV is due to effect of strong electronic delocalization; this fact alone directs us towards the band picture. The common attempts to build a strongly localized exciton to gain the Coulomb attraction will oppositely face the losses of the kinetic energy. This will not allow to go below the conduction (HOMO–LUMO) gap $E_g \approx 2$ – 3 eV, but oppositely will push the total exciton energy upwards the high intra-molecular values, *i.e.* 4.8–6.8 eV for singlet and 3.6 eV for triplet exciton.

Fortunately, the nature provides us with necessary criteria to choose the adequate picture. The lowest transitions in the benzene molecule and in a polymer chain are formed with different π sub-shells, LD*–DL* and DD*, correspondingly. Thus, observing a sequence of bands coinciding with the one for intra-molecular excitations would call for local approaches.^{7,18,22} This can happen sometimes for less important polymers with weakly bridged rings (*e.g.*, orthogonally twisted, like in PTP) and correspondingly large gaps, above 4 eV (4.7 eV is the energy of the lowest intra-ring singlet excitation). However, the apparent observation of the opposite band sequence, corresponding to the intra-molecular hybridization with DD* rather than DL*, LD* being the lowest ones, justifies the electronic band picture as our starting point with the primacy of electronic delocalization. More comparison can be found.⁸

10. Conclusions: Views backwards and forward

Science of conducting polymers provides a unique workshop where the molecular and the solid state physics immanently meet and are bound to recognize each other and merge. Such an alliance took place in the past: recall the cross-disciplinary impacts brought by L. Pauling, W. Kohn, P. Fulde, by A. J. Heeger, A. MacDiarmid and H. Shirakava, by R. Friend *et al.*; chemical dreams of the generic physicist W. Little gave rise to all our activities. Recall the discovery of organic superconductors by the chemist K. Bechgaard and physicist D. Jerome, and raised at another level by correspondingly E. Yagubskii and I. Shchegolev *et al.*; in this field, from the beginning and till nowadays, the most refined physics and chemistry go

hand-to-hand. Recall first years of the polymer science in early 1980's, when it was dominated by the solid state physics and its theory. That was too biased and naturally the pendulum moved to the opposite, from solid state to molecular spectroscopy, from condensed matter theory to quantum chemistry. We are staying here for too long, nearly quarter of a century, and the whole generation of scientists have been formed not possessing our common language.

In this review, we have tried to demonstrate that none of the sciences is able alone to deal with the interdisciplinary complexity of electronic and optical properties of conjugated polymers. Our preferable physics of semiconductors was not prepared to deal with on-site electronic correlations which suddenly rise from corrections to dominating effects; it can never advise on what kind of the monomers modifications will give a desirable color of emitted light or improve stability. The molecular approach meets the dead end keeping a picture of size-quantized small systems in circumstances of continuous spectra, long-range excitons and polarons. The physical quantities and even the very interpretations of experiments are not settled even within the approaches, and the meanings of concepts differ among the sciences. The contrast is striking on both sides: the tiniest optical features have been identified both in band semiconductors and in molecular crystals of, sometimes, the same monomers which behave so mysteriously being polymerized.

What kind of perspective do we see? It looks most plausible that interpolational schemes, like the phenomenology of semiconductors on one side or PPP-like models of finite p-electronic subsystems on another side cannot work properly alone. We need a theorists' beloved division of scales where the full-rank quantum chemistry, together with the experimental spectroscopy of monomers, is used as the source of exact local parameters. Then the solid state physics comes at the scale of many monomers adapting the wisdom of the science of semiconductors. We were able to demonstrate an efficiency of this approach thanks to the provision of the exact theory of the benzene ring; such information is rarely available without recognition of the request. We dare to think that this review will articulate the appeal for the reconciliation which already has been voiced in our articles.

Lost integration and the need to reverse it can be noticed already on a larger scale of the whole science of synthetic metals. One can easily see it by analyzing the history of our widest forum—the ICSM conferences. The CDWs have been expelled in the early 1980's; organic metals and polymers coexist with no interaction. Result is that wonders of optics in polymers stay ill known to other sciences (the nonlinear and femto-second methods are coming only now). The polymers are not aware of very common density waves, particularly of the new wave of observations of the charge ordering and the related Mott transition. That should certainly work at least in the polyaniline and in heavily doped polymers. A very useful example comes from discovery of the gigantic ferroelectric signal related to the charge ordering in quasi-1D organic conductors TMTTF, and beyond,^{55,56} see the review.⁵⁷ The non-interpreted signatures were known since the mid 1980's but the resolution came only through synergetic of theory of polymers, permittivity methods sharpened for sliding

CDWs and the NMR in organic metals. The loop is going to be closed by transferring the gained understanding back to polymers.^{57,58} Then the cross-fertilization will open a new perspective in science and applications of conducting polymers.

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