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Excitations in Organic Solids

VLADIMIR M. AGRANOVICH



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Excitations in Organic Solids

Vladimir M. Agranovich

The University of Texas at Dallas

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PREFACE

The fundamental concept of an exciton as an uncharged electronic excitation is an essential part of the modern physics of solids and is now widely used for the explanation of many optical properties such as the absorption and dispersion of light and luminescence. The exciton is also important as a participant in phenomena such as photoemission, photoconductivity, and the photovoltaic effect. There is more than one type of exciton, and in crystals, the type of chemical bonding determines the model of the exciton to be used for the explanation of optical properties. The most widely used are the Frenkel exciton for organic crystals in which the intermolecular bonding is mainly of the weak van der Waals type, and the Wannier–Mott exciton, which is important in inorganic semiconductors, where the bonding is ionic or covalent, and is strong. A descriptive picture of the Frenkel exciton would be that of a electron–hole pair confined to one molecule, constituting an electronically excited molecular state that can transfer between the crystal lattice cells from one molecule to another by virtue of the weak intermolecular interactions; the Wannier–Mott exciton can be depicted as a mobile Coulomb–bonded electron–hole pair of wider separation. In molecular crystals there are also the important charge–transfer excitons, in which the hole–electron pairs are located at neighboring molecules of the crystal. These excited states play an important role in processes of charge separation.

It is worthy to mention that low–temperature spectroscopy of organic molecular crystals originated in the classical experiments carried out in the late 1920s by Pringsheim and Kronenberger¹ (1), also Obreimov and de Haas (2). At that time only the Bloch band scheme for electronic states in crystals was known. This concept predicted very broad absorption bands, in contradiction to the narrow lines observed in the cited experiments. It is known that I. V. Obreimov called this problem to the attention of Ya. J. Frenkel and it was in the 1931 paper of Frenkel (3), where the concept of the exciton in molecular crystals was formulated for the first time. The name "exciton" was introduced by Frenkel in 1936 (4). Following the introduction of the exciton concept, a series of important and puzzling spectroscopical observations using polarized light were reported by Obreimov and Prikhotko (5) the interpretation of which was made by Davydov (6). He rationalized the polarization of the lines in these absorption and fluorescence spectra, which involved what is now referred to as "Davydov splitting". A classical review of experiments on excitons in organic crystals is given in the book by Broude, Rashba and Sheka (7). We have to mention also the well known earlier published books by Hochstrasser(8), Craig and Walmsley (9), Davydov(10), Pope and Swenberg (11), and also in addition the many excellent review papers

¹See the references at the end of Preface.

which I used in this book and which constitute a vast reservoir of information on the properties of molecular crystals.

During the last fifteen to twenty years there has been developed considerable expertise in nanotechnology. Efforts have been devoted to the growth not only bulk but also of crystalline organic layered structures. Improvement in the technique of molecular beam deposition has led to a variety of good quality organic thin films, multilayered structures and heterostructures based on molecular solids, as well as on the combination of organic and inorganic semiconductors. The possibility of growing specially designed systems incorporating different organic crystalline materials with even more flexibility than for multiple quantum wells based on inorganic semiconductors alone, opened a promising field of research from the point of view of fundamental as well as applied physics. The advent of such a new class of organic and inorganic based crystalline materials with potentially important electro-optical linear and nonlinear properties, represents a challenge to scientists to understand their possible advantages in comparison with the usual organic and inorganic materials. And in the recently discovered new types of organic opto-electronic devices such as organic light-emitting diodes (OLEDs) and organic solar cells and in the photogeneration of carriers, the excitons play a decisive role. This has greatly increased interest in the study of properties of excitations in organic materials among scientists working not only in the field of physics, but also in chemistry and biology. For this reason in this book I describe not only the fundamentals of Frenkel exciton and polariton theory in organic crystals but also I consider the electronic excitations and electronic energy transfer in different nanostructures (quantum wells, quantum wires and quantum dots), at interfaces, in multilayers and in microcavities.

The proposed book is an updated English translation of the author's book "Theory of Excitons", published in 1968 (Publishing House Nauka, Moscow, in Russian). It was widely used in USSR and in other countries where students and scientists were able to read Russian. In this new English edition 5 old chapters have been included and updated, and 10 new chapters that contain discussions of new phenomena were added. The title of the book has been changed to reflect the new subject matter that has been added. Among the new chapters are those devoted to hybrid Frenkel-Wannier-Mott excitons in nanostructures, polaritons in organic microcavities including hybrid microcavities, new concept for LED, the mixing of Frenkel and charge-transfer excitons in organic quasi one-dimensional crystals, excitons and polaritons in one and two-dimensional crystals, surface electronic excitations, optical biphonons and Fermi resonance by polaritons.

It is known that excitons and polaritons in general have properties that can be considered within the framework of electrodynamics of continuous media. These properties were described in a monograph by V. M. Agranovich and V. L. Ginzburg ("Crystal Optics with Spatial Dispersion, and Excitons", Springer, 1984) where we used a mainly phenomenological approach. In the present book I provide a microscopical theory of excitations in organic solids and nanostruc-

tures, and only in some cases resort to the use of a phenomenological approach. As I have mentioned above, I concentrate attention on the Frenkel and charge-transfer excitons. However, many results presented in this book as, for example, the polariton theory, are quite general and can be used for all types of excitons. I hope that this book will be useful for scientists working on the field of photo-physics and photochemistry of organic solids, and for students who are entering this field.

In the book I have used theoretical and experimental results developed by many authors. However, here I would like to thank my former students and collaborators who worked with me in the studies of organic solids in the Institute of Physics and Power Engineering, Obninsk, and in the Institute of Spectroscopy, Troitsk. These include Yuri Konobeev, Oleg Dubovsky, Vratslav Toshich, Vladimir Kravtsov, Valery Rupasov, Vladimir Yudson, Tamara Leskova, Irina Talanina, Anatoly Malshukov, Ivan Lalov, Anatoly Kamchatnov, Yuri Lozovik, Boris Antonyuk, Anvar Zakhidov, Yuri Gartstein, Sergei Kiselev, Denis Basko and Masha Litinskaia.

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Dallas, Moscow

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INTRODUCTION

Molecules, atoms, ions, and electrons in condensed medias are constitutive units of the material. Because of the strong interaction between those particles they lose their individual properties. They are replaced by quasiparticles, the quantum of collective motions of condensed materials, that play a fundamental role in modern solid state physics.

At the present time we know a number of quasiparticles in crystals, each of them playing role in explaining specific physical properties of crystals. Excitons, the main topic of the present book, are examples of such particles, and they appear as a result of the quantum mechanical treatment of the collective properties of electrons in crystals.

The foundation of excitons theory was formulated by Frenkel, Peierls and Wannier (1)–(5) more than 70 years ago. After that time the theory has been enriched by many new aspects. The theory has also been exposed to continuous experimental verification, which has confirmed the role of excitons in such processes as absorption of light, luminescence and energy transfer, photochemical processes, etc. Before we examine the experiments, which illustrate the presence and the role of excitons in crystals, we will briefly describe the basic models of excitons, which are mostly used in the interpretation of experimental results.

The first exciton model was proposed by Frenkel (1), (2) in 1930. Frenkel excitons (FE) are mostly observed in molecular crystals.

As is known, crystals are defined as molecular when the interaction between different molecules is much smaller than the interaction between atoms and electrons within the molecule. In consequence, the molecules in such crystals preserve some individual properties. Therefore, in the zeroth approximation, the lowest electronic excited state of the crystal can be considered as a state in which one molecule is excited, and the others in their ground state. As a consequence of the translational symmetry and of the intermolecular interaction, the localization of the excited molecule is not stable, and the excitation energy will be transferred from one molecule to another, propagating like a wave through the crystal.²

Let Ψ be the wavefunction of the above described excited state of the crystal, satisfying the stationary Schrödinger equation

$$\hat{H}\Psi = E\Psi, \quad (1.1)$$

where \hat{H} is the crystal Hamiltonian and E the corresponding eigenvalue. Since the Hamilton operator is invariant under application of the translation sub-

²The theory of Frenkel excitons will be given in Chapt. 2 and Chapt. 3.

group of the crystal, including all translations which transform the crystal lattice into itself, the eigenfunction Ψ can be chosen as an eigenfunction of any translation operator. In this case for the eigenfunction we have (see, for example, Lyubarsky (6))

$$T_{\mathbf{m}}\Psi = e^{-i\mathbf{k}\mathbf{m}}\Psi, \quad (1.2)$$

where $T_{\mathbf{m}}$ is the translation operator, \mathbf{m} an integer-valued lattice vector, and \mathbf{k} the wavevector from the first Brillouin zone. Different eigenfunctions Ψ correspond to different eigenvalues of the operator $T_{\mathbf{m}}$. Therefore they can be characterized by the wavevector \mathbf{k} . Consequently, the exciton energy will also depend on the wavevector \mathbf{k} and the above conclusion does not need the use of a specific model of the exciton; it results in the translational symmetry of the crystal only. One of the fundamental problems of an accurate microscopic theory of excitons consists in the determination of the energies $E(\mathbf{k})$ and the wavefunctions $\Psi_{\mathbf{k}}$.

For the considered electronic states the wavevector \mathbf{k} is a continuous quantum number characterizing the eigenfunction Ψ . Together with this quantum number the state Ψ can be also characterized by a set s of discrete quantum numbers, so that $\Psi \equiv \Psi_{\mathbf{k}s}$. Making use of the notion of quasiparticles we can say that in the crystal in the state $\Psi_{\mathbf{k}s}$ there is a one quasiparticle of type s , having quasimomentum \mathbf{k} and the energy $E_s(\mathbf{k}) - E_0$, E_0 being the crystal ground state energy.

Just such a type of quasiparticle was named by Frenkel an exciton. For a given and fixed value of the quantum number s the exciton energy $E_s(\mathbf{k})$ becomes a continuum-valued function of \mathbf{k} within the s th energy band, and, in general, $E_s(\mathbf{k}) \neq E_{s'}(\mathbf{k})$ for $s \neq s'$.

Note that in an ideal crystal any stationary state is characterized by a value \mathbf{k} , which determines the change of the wavefunction by the translation operation (see eqn 1.2). However, this \mathbf{k} is not always the one continuous quantum number characterizing the state of the crystal. If we consider a crystal with free electrons and holes, the state of the crystal is characterized by two continuous quantum numbers \mathbf{k}_1 and \mathbf{k}_2 , where \mathbf{k}_1 is the quasimomentum of the electron, and \mathbf{k}_2 is the quasimomentum of the hole. Thus, the two continuous quantum numbers correspond to the state when we have not one, but two quasiparticles in the crystal.

The electron and the hole in the crystal attract themselves and can create a bound state. Obviously, the Frenkel exciton corresponds to the situation when the electron and the hole in a bound state are localized in the same lattice cell (the same molecule). Therefore the Frenkel excitons are also called small-radius excitons. When the radius of the electron-hole bound state is much larger than the lattice constant, the corresponding quasiparticle is called a Wannier-Mott exciton, or a large-radius exciton. Let us consider the latter in more detail.

Assume that a dielectric crystal has one electron in the conduction band with effective mass m_e , and one hole in the valence band with effective mass m_h . If we assume that the interaction between the electron and the hole is given by the

Coulomb potential $V(r) = -e^2/\epsilon r$, where ϵ is the static dielectric constant,³ and r is the distance between the electron and the hole, the Schrödinger equation for the electron–hole system will have the form⁴

$$\left(-\frac{\hbar^2}{2m_e}\Delta_e - \frac{\hbar^2}{2m_h}\Delta_h - \frac{e^2}{\epsilon r}\right)\Psi = E\Psi. \quad (1.3)$$

This is the Schrödinger equation for a hydrogen-like atom. The solution for $E < 0$, i.e. for the bound states, has the form

$$\Psi_{n\ell m, \mathbf{k}} = e^{i\mathbf{k}\mathbf{R}}F_{n\ell m}(r), \quad (1.4)$$

where \mathbf{R} is the electron–hole pair center-of-mass coordinate, $F_{n\ell m}(r)$ is the hydrogen–like atom eigenfunction with effective charge $Ze = e/\epsilon$, n, ℓ, m are the principal, the angular and the magnetic quantum numbers, respectively, and $\hbar\mathbf{k}$ is the quasimomentum which describes the motion of the electron–hole pair as a whole entity. The energy corresponding to the state (1.4) is given by the expression

$$E_n(\mathbf{k}) = -\frac{\mu e^4}{2\hbar^2\epsilon^2 n^2} + \frac{\hbar^2 k^2}{2(m_e + m_h)}, \quad \text{where} \quad \mu = \left(\frac{1}{m_e} + \frac{1}{m_h}\right)^{-1}. \quad (1.5)$$

The zero value of the energy (1.5) coincides with the bottom of the conduction band and its absolute value for $\mathbf{k} = 0$ is equal to the binding energy of the electron and the hole in the exciton. The relatively simple relation between the Wannier–Mott exciton energy does not hold when the electron–hole interaction is treated more accurately (see (8)), and becomes a relation of a more general type.

Expanding the exciton energy $E_s(\mathbf{k})$ in powers of \mathbf{k} around the point $\mathbf{k} = 0$, we obtain in crystals with inversion symmetry

$$E_s(\mathbf{k}) = E_s(0) + \frac{\hbar^2}{2m_{ij}^*}k_i k_j + \dots, \quad (1.6)$$

where m_{ij}^* is the tensor of the effective mass of exciton in the s th energy band:

$$m_{ij}^* = \hbar^2 \left\{ \frac{\partial^2 E_s(k)}{\partial k_i \partial k_j} \right\}_{k=0}^{-1}. \quad (1.7)$$

If $E_s(\mathbf{k})$ only depends on the absolute value of \mathbf{k} , then $m_{ij}^* = m^* \delta_{ij}$, where

$$m^* = \hbar^2 \left\{ \frac{d^2 E_s(k)}{dk^2} \right\}_{k=0}^{-1}. \quad (1.8)$$

Depending on the shape of $E_s(k)$ the effective mass can be positive or negative.

³This type of electron–hole interaction is possible only for values r large compared to the lattice constant.

⁴The theory of Wannier–Mott excitons and, in particular, the limits of validity of eqn (1.3), can be found, for instance, in the textbook by Knox (8) and the review article by Haken (19).