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With 307 Figures

Springer-Verlag
Berlin Heidelberg New York Tokyo

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Preface

An exciton is an electronic excitation wave consisting of an electron-hole pair which propagates in a nonmetallic solid. Since the pioneering research of Frenkel, Wannier and the Pohl group in the 1930s, a large number of experimental and theoretical studies have been made. Due to these investigations the exciton is now a well-established concept and the electronic structure has been clarified in great detail.

The next subjects for investigation are, naturally, dynamical processes of excitons such as excitation, relaxation, annihilation and molecule formation and, in fact, many interesting phenomena have been disclosed by recent works. These excitonic processes have been recognized to be quite important in solid-state physics because they involve a number of basic interactions between excitons and other elementary excitations. It is the aim of this quasi monograph to describe these excitonic processes from both theoretical and experimental points of view.

To discuss and illustrate the excitonic processes in solids, we take a few important and well-investigated insulating crystals as playgrounds for excitons on which they play in a manner characteristic of each material. The selection of the materials is made in such a way that they possess some unique properties of excitonic processes and are adequate to cover important interactions in which excitons are involved. In each material, excitonic processes are described in detail from the experimental side in order to show the whole story of excitons in a particular material. Part of this book is devoted to the theoretical description of the excitonic processes which play particularly important roles in the materials chosen in this book but are not necessarily restricted to these materials. The theory is presented in a general fashion so as to cover a variety of phenomena which have been of recent interest.

It should be remarked that, although this book has been written through the cooperation of five authors, the main contribution to Chap. 3 was made by Ueta, Chaps. 5 and 6 by Kanzaki, Chaps. 7, 8, and 9 by Kobayashi, Chaps. 1 and 4 by Toyozawa and Chap. 2 by Hanamura.

The authors wish to express their gratitude to all of their colleagues for collaboration and discussions at various stages of their researches on excitons. One of the authors (MU) would like to acknowledge the assistance of Prof. T. Itoh and Dr. Y. Nozue in completing the manuscript. The authors thank the original authors of the figures used in this book who kindly gave permission to reproduce them. Thanks are also due to the Physical Society of Japan, The American Physical Society, The Institute of Physics, Progress of Theoretical

Tokyo and Sendai 1984

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Contents

1. Introduction

This first chapter introduces the basic concept of an exciton as an elementary excitation in a many-electron system of an insulator. Various kinds of interaction associated with translational and internal motions of this composite particle, such as electron-hole Coulomb and exchange interactions, spin-orbit interactions and interatomic or intermolecular overlap and dipole-dipole energies, are described with particular attention to their interplay and to their reflection in the optical spectra. The coupled mode of light and electronic polarization waves, whose quanta are a photon and an exciton, respectively, is described in terms of a polariton picture, whereby the optical response of the bulk is related to that of the surface, with additional boundary conditions in the case of spatial dispersion. This chapter provides the conceptual basis for more dynamical aspects of the excitons to be described in later chapters.

1.1 The Ground State of Many-Body Systems and the Modes of Excitation

Which kind of ground state is preferred by a system consisting of a great number of like particles interacting with each other has always been a matter of fundamental interest; yet a question difficult to answer in a general way. The ground state should be a perfectly ordered state in the sense of the third law of thermodynamics that the entropy of a macroscopic system approaches zero with vanishing temperature [1.1]. Two typical ways of perfect ordering are a periodic array in r-space and condensation in k-space. The former is preferred when the interparticle interaction dominates the kinetic energy – atoms (except He) and molecules form crystalline lattices while low-density electrons form a Wigner lattice. The latter is preferred in the opposite situation – outer electrons in a solid are Fermi-condensed in the Bloch band because of their large interatomic transfer energy and the small pseudopotential from atoms and other electrons, while ^{4}He atoms, the lightest closed-shell atoms, become Bose-condensed in k-space. It should be noted, however, that many-particle systems in general can take ground states with much more varied and intriguing features [1.2] than the two limiting situations mentioned above.

Once the ground state is known, the excited states are next to be considered. We have two aims in doing this. Firstly, the responses of the system to small

external fields are described in terms of virtual and/or real excitations of the system. Secondly, if the assumed ground state is an approximate or an inappropriate one, one has to consider mixing of some of the excited states to get the true ground state. This state may turn out to be significantly different from the one initially conceived, perhaps eventually involving symmetry breaking such as in super-structure formation.

The modes of low-lying excitations of a many-particle system can be classified into individual and collective excitations [1.3, 4]. The individual excitation in r-space is exemplified by the formation of a Frenkel defect in the perfect crystal lattice, while that in k-space is typified by the excitation of an electron across the Fermi energy (metal) or the band gap (insulator). The collective motions can have arbitrarily small amplitude within the classical mechanics, and the potential energy for such small displacements of collective coordinates from their equilibrium points can be approximated by a quadratic form, diagonalization of which gives a set of non interacting harmonic oscillators each with angular frequency ω_j. . By quantizing them, one finds that the low-lying excited states of the collective motions can be described in terms of an integral number n_j of energy quanta $\hbar\omega_j$ for each mode j:

$$E = \sum_j n_j \hbar\omega_j \qquad (n_j = 0, 1, 2, \ldots) . \tag{1.1}$$

This system behaves as though it consists of an assemblage of noninteracting fictitious particles with energy $\hbar\omega_j$ ($j = 1, 2, \ldots$), which are called the elementary excitations. For example, a collective oscillation of atoms in solids is a lattice vibration, whose energy quantum is called a phonon. The collective oscillation of charge density in a system consisting of mobile electrons and ions (e.g., a metal and an ionized gas) is known as a plasma oscillation with a plasmon for its energy quantum. The deviation of spin orientation from its ordered state in a magnetic material propagates from site to site as a wave, which is called a spin wave; its energy quantum being a magnon.

The collective motions are not completely independent of the individual motions; on the contrary, the former are superpositions of the latter. The former claim their own significance as better eigenmodes of motion in the many-particle system than the latter, when the interparticle interaction is not small. To be more exact, the interaction can be partly incorporated, as a sort of average, into the effective field (e.g., the Hartree-Fock field for the electrons in the Bloch band) which acts upon the particles themselves thus governing their individual motion. The fluctuating part of the interaction is responsible for the collective motion on the one hand and for the interparticle correlation on the other. For example, the plasma oscillation in the Fermi-degenerate electrons in a metal has a much higher frequency than the individual excitations (whose energy range starts from zero) across the Fermi energy although the former is nothing but a superposition of the latter; the long-range fluctuating part of the Coulomb repulsion gives rise to the plasma oscillation and at the same time to the interelectron correlation which amounts to a screening of the repulsion into a short-range one [1.3].

1.2 Electronic Excitation in Insulators and the Wannier-Mott Exciton

The situation is different in insulators in which the individual electronic excitations have a lower bound ε_g – the band-gap energy. Let us assume the conduction (c) and valence (v) bands to be parabolic with isotropic effective masses m_e and m_h with a minimum and maximum, respectively, at $k = 0$:

$$\varepsilon_c(k) = \varepsilon_c(0) + \frac{\hbar^2 k^2}{2m_e} ,$$

$$\varepsilon_v(k) = \varepsilon_c(0) - \varepsilon_g - \frac{\hbar^2 k^2}{2m_h} .$$

(1.2)

One can then write the energy for one-electron excitation: $(v, k - K) \rightarrow (c, k)$ as [1.5]

$$\varepsilon_c(k) - \varepsilon_v(k - K) = \varepsilon_g(K) + \frac{\hbar^2 k'^2}{2\mu} \equiv E(k, K) ,$$

(1.3)

$$\varepsilon_g(K) \equiv \varepsilon_g + \frac{\hbar^2 K^2}{2M} , \quad \text{where}$$

$$M = m_e + m_h , \quad \mu^{-1} = m_e^{-1} + m_h^{-1} ,$$

(1.4)

$$k' \equiv k - \frac{m_e}{M} K .$$

(1.5)

Here K and k' represent the wave vectors for the translational (center-of-mass) and the relative motions, respectively, of the electron in the conduction band (e) and the hole in the valence band (h), as is obvious from their associated masses M and μ (reduced mass) given by (1.4).

The Coulomb potentials from all the nuclei and other electrons have been incorporated into the periodic potential with which we solve for the one electron states $\varepsilon_c(k), \varepsilon_v(k), \ldots$ self-consistently, assuming the ground state in which electrons fill the core and the valence bands. In the excited state (1.3) where we have a pair of e and h, there should be attractive Coulomb and repulsive exchange interactions between them. The former is given by $-e^2/\epsilon r$ if the e–h distance $r \equiv |r_e - r_h|$ is large compared to the lattice constant a_0, since the crystal lattice consisting of electrons and nuclei can then be regarded quasi-macroscopically as a polarizable medium specified by a dielectric constant ϵ [1.6]. From (1.3), the e–h relative motion is subject to the Schrödinger equation $(k' \rightarrow -i\nabla_r)$ [1.7]

$$\left(-\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{e^2}{\epsilon r} \right) \psi_\lambda(r) = \varepsilon_\lambda \psi_\lambda(r)$$

(1.6)

of the hydrogen atom type, which has the discrete and continuous eigenvalues

$$\varepsilon_{nlm} = - \frac{E^b_{ex}}{n^2} \quad (n = 1, 2, \ldots) ,$$

$$\varepsilon_{klm} = + \frac{\hbar^2 k^2}{2\mu} .$$

(1.7)

The e–h binding energy E^b_{ex} and the effective Bohr radius a_B in the $1s$ ($n = 1$, $l = m = 0$) state are given by rescaling those of the hydrogen atom (H):

$$E^b_{ex} = Ry = \frac{\mu e^4}{2\epsilon^2 \hbar^2} = \frac{e^2}{2\epsilon a_B} = \frac{\hbar^2}{2\mu a_B^2} = \frac{1}{\epsilon^2} \left(\frac{\mu}{m_0} \right) R_H ,$$

(1.8)

$$a_B = \frac{\epsilon \hbar^2}{\mu e^2} = \epsilon \left(\frac{m_0}{\mu} \right) a_H ,$$

(1.9)

where m_0 is the true mass of an electron.

The excitation energy, with the e–h Coulomb attraction taken into account, is then given by

$$E_{\lambda,K} = \varepsilon_g(K) + \varepsilon_\lambda$$

(1.10)

since the translational wave vector K remains a constant of motion. The discrete state $\lambda = (n, l, m)$ represents a bound pair of e and h which is called an exciton. The whole spectrum of an e–h pair excitation is shown schematically in Fig. 1.1 as a function of K. Since the wave vector of a photon in this region of excitation energy is negligibly small compared to the reciprocal lattice vector, only those
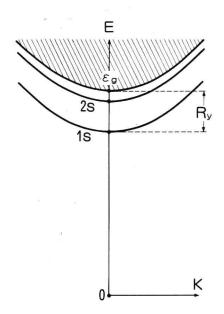

Fig. 1.1. Excitation energy of an e–h pair as a function of translational wave vector K

excited states with $K = 0$ contribute to the optical absorption spectra, which therefore consists of a series of discrete lines followed by the ionization continuum.

The above description of an exciton is based on two approximations: the effective mass approximation [the neglection of terms higher than quadratic in (1.2)] [1.7] and the dielectric continuum model for Coulomb screening (the use of macroscopic ε). They are justified only when $a_B \gg a_0$. Such an exciton is specifically called a Wannier-Mott exciton. This situation is well realized in narrow-gap semiconductors which usually have large $\epsilon(\gg 1)$ and small $\mu(\ll m_0)$.

1.3 The Frenkel Exciton

With narrow Bloch bands and hence with large effective masses m_e and m_h as in molecular crystals (small intermolecular overlapping), and/or with a smaller dielectric constant ϵ as realized in large band gap crystals, the relative motion wavefunction $\psi_\lambda(r)$ of the lowest exciton may be so localized that e and h are almost located on the same atom or molecule. One can then consider the exciton to be the intraatomic or intramolecular excitation energy which propagates through the lattice with wave vector K. This was in fact the model of an exciton as first conceived by *Frenkel* [1.8].

Let us consider, for simplicity, N identical molecules, each with one spinless electron, arrayed in a crystal lattice. We denote by Φ_n the Slater determinant of the electronic configuration in which only the nth molecule at R_n is in the excited state $a_c(r_n - R_n)$ with excitation energy ε, all other molecules (n') being in the ground state: $a_v(r_{n'} - R_{n'})$. Due to the intermolecular interactions, the excitation energy can propagate from site to site, resulting in the eigenstate:

$$\Psi_K = N^{-1/2} \sum_n [\exp(iK \cdot R_n)] \Phi_n , \tag{1.11}$$

similar in form to the tight-binding model for a one-electron Bloch state. In contrast to the latter case, however, the excitation energy can be transferred even without the intermolecular overlap: the Coulomb interaction $v_{nm} = e^2/|r_n - r_m|$ between the electrons on the nth and the mth molecules gives the matrix element

$$(\Phi_n^{cv} v_{nm} \Phi_m^{cv}) = \int dr_n \int dr_m a_c^*(r_n - R_n) a_v^*(r_m - R_m)$$

$$\times \frac{e^2}{|r_n - r_m|} a_v(r_n - R_n) a_c(r_m - R_m) \equiv w(R_{nm}) , \tag{1.12}$$

under the assumption of intermolecular orthogonality. The multiple expansion of v_{nm} gives the dipole-dipole interaction

$$H_{nm} \sim D(R_{nm}) = \frac{|\mu|^2}{R_{nm}^3} - \frac{3|\mu \cdot R_{nm}|^2}{R_{nm}^5} , \qquad (n \neq m) \tag{1.13}$$

to be predominant at long distances $R_{nm} = |R_n - R_m|$, where μ is the intramolecular transition dipole moment:

$$\mu = \int a_c^*(r)(-er)a_v(r)\,dr\ . \tag{1.14}$$

The energy of the Frenkel exciton state (1.11) is then given by

$$E_K = \varepsilon + \sum_{n(\neq 0)} D(R_n)\exp(-iK\cdot R_n) \equiv \varepsilon + D_K\ . \tag{1.15}$$

Replacing the sum over distant molecules by integrals, as is justified for $Ka_0 \ll 1$, one finds

$$D_K \approx \text{const.} - \frac{4\pi}{3}N_0\left(|\mu|^2 - 3\frac{|\mu\cdot K|^2}{K^2}\right)\ , \tag{1.16}$$

where N_0 is the number of molecules per unit volume. Equation (1.16) is singular at $K = 0$; the longitudinal exciton $(K\|\mu)$ has higher energy than the transverse one $(K\perp\mu)$ by $4\pi N_0\mu^2$. This difference originates from the depolarizing electric field due to the longitudinal component of the electronic polarization wave. The exciton is nothing but a quantum of this classical polarization wave.

1.4 The General Case

We have so far considered the simplest systems in the two limiting situations $(a \gtrless a_0)$. In the realistic case, we have first to consider the spin and orbital degeneracies of the bands which we denote by $\nu, \nu', \ldots$ and $\mu, \mu', \ldots$ for the conduction and the valence bands, respectively. Secondly, we have to introduce a discrete function $F(R_l)$ for the e–h relative motion with finite spatial extension. An exciton state with translational wave vector K can then be written as

$$\Psi_{\lambda K} = N^{-1/2}\sum_m\sum_l\sum_\nu\sum_\mu[\exp(iK\cdot R_m)]\,F_{\lambda K}^{\nu\mu}(R_l)\,\Phi_{m+l,m}^{\nu,\mu}\ , \tag{1.17}$$

$$\sum_\nu\sum_\mu\sum_l|F^{\nu\mu}(R_l)|^2 = 1\ , \tag{1.18}$$

where $\Phi_{n,m}^{\nu,\mu}$ denotes the Slater determinant of the configuration in which the electron in the atomic or Wannier state $a_\mu(r - R_m)$ is excited into $a_\nu(r - R_n)$. The associated Bloch states

$$\psi_k(r) = N^{-1/2}\sum_m[\exp(ik\cdot R_m)]a_\mu(r - R_m) \tag{1.19}$$

constitute the one-electron energy matrix for the degenerate valence band:

$$\varepsilon_{\mu\mu'}(k)\ , \tag{1.20}$$

and the same for the conduction bands.