Bose-Einstein Condensation of Excitons and Biexcitons

and Coherent Nonlinear Optics with Excitons

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BOSE–EINSTEIN CONDENSATION OF EXCITONS AND BIEXCITONS
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Bose–Einstein condensation of excitons is a unique effect in which the electronic states of a solid can self-organize to acquire quantum-phase coherence. The phenomenon is closely linked to Bose–Einstein condensation in other systems such as liquid helium and laser-cooled atomic gases. This is the first book to provide a comprehensive survey of this field, covering theoretical aspects as well as recent experimental work.

After setting out the relevant basic physics of excitons, the authors discuss exciton–phonon interactions as well as the behavior of biexcitons. They cover exciton phase transitions and give particular attention to nonlinear optical effects including the optical Stark effect and chaos in excitonic systems. The thermodynamics of equilibrium, quasi-equilibrium, and nonequilibrium systems are examined in detail.

The authors interweave theoretical and experimental results throughout the book and it will be of great interest to graduate students and researchers in semiconductor and superconductor physics, quantum optics, and atomic physics.

S.A. Moskalenko is Professor of Theoretical and Mathematical Physics of the Institute of Applied Physics of the Academy of Sciences of the Republic of Moldova. He has been a state prize winner of the Moldovan SSR, Laureate of the State Prize of the USSR in the field of Science and Technology, and a full member of the Academy of Sciences of the Republic of Moldova since 1992. He is the author of four books in Russian and many scientific articles.

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In memory of Prof. Yulya
S. Boyarskaya.
Soli Deo Gloria

Preface

The idea for this book grew out of the historic conference on Bose–Einstein Condensation in Trento, Italy, in 1993, which brought together many of the founders of theoretical and experimental research of excitons, as well as experts on Bose–Einstein condensation from many other fields, including astrophysics, nuclear theory, liquid helium, and superconductors. Especially important was the opportunity for Western and Russian researchers to participate together. The authors of this book first met at that time, and it became apparent to both of them that the fundamental works on Bose condensation of excitons remained scattered in the literature, and included many Eastern European publications not readily available in the West. This book is an attempt to bring together for the first time a coherent account of the great amount of theoretical and experimental work in this rapidly growing field.

In the years following that meeting, the theory of weakly interacting Bose systems has taken off, as experiments in new systems have started to pay off, following decades of emphasis on strongly interacting coherent systems. The accompanying table shows the four major areas of interest in coherent condensed matter systems today.

	Atomic systems	Solid systems
Strongly interacting	Liquid Helium-3 and Helium-4	BCS and Hi-T_c superconductors
Weakly interacting	Alkali vapors	Exciton and biexciton Gases

Each has its own appeal. Studies on atoms, including liquid Helium-3 and Helium-4 and the recent, exciting studies of hydrogen and alkali atoms in optical traps, have the appeal that the interactions between the atoms can be easily understood without extensive study of solid-state band structures. On the other hand, atomic condensates are necessarily a low temperature phenomenon, existing only at temperatures from 2 K down to a few nanokelvin. The solid-state phenomena of superconductors and excitonic condensates exist at much higher temperatures, possibly even at room temperature. Two effects exist in solid-state Bose systems which drive much of the research. First, charged bosons (e.g., Cooper pairs) can carry current, so that Bose condensates of charged bosons are superconductors. Several possibilities for novel charged bosons in solid-state systems are discussed in this book. Second, neutral bosons such as excitons typically couple directly to photons, so that coherence in the photon field can be maintained in the electronic states. This leads to a number of nonlinear optical effects, which are discussed at length in this volume. Excitons also couple directly to the crystal phonon states, so that an excitonic condensate can lead to novel acoustic effects.

The idea of the excitonic condensate appeared at the same time when the foundations of the theory of lasers, semiconductors, superconductors, and superfluids were being laid in the 1950s and 1960s. Much of the pioneering work was sponsored by the Academy of Sciences of the USSR, and involved the efforts of academicians such as N.N. Bogoliubov, A.S. Davydov, V.L. Ginzburg, L.V. Keldysh and R.V. Khohlov, and Prof. L.E. Gurevich. In 1982, the division of General Physics and Astronomy of the Academy of Sciences of the USSR listed the theory of high density excitons as one of the major achievements of multinational Soviet physics. S.A. Moskalenko was fortunate to be part of these discussions from the very start, starting with his graduate studies with Professor K.B. Tolpygo of the Kiev Institute of Physics, and wrote some of the earliest papers on the subject. The exciton condensate theory is, in a sense, a triumph of renormalization in quantum field theory. Starting with atoms, one can deduce the band structure of a solid and define a new vacuum equal to the ground state of the solid, in which the only particles are quasiparticles determined by the excitation spectrum of the solid, namely, free electrons, free holes, and lattice phonons. The Coulomb interaction between these electrons and holes leads to pairing into excitons. Starting with this new system of only excitons and phonons, one can move to a new vacuum which is the ground state of the exciton gas, and new quasiparticles appear as the excitations of the interacting exciton system. The beauty of the theory is that one needs to refer only occasionally to the underlying band structure, and in most cases the excitons can be viewed as weakly interacting bosons no different from atoms.

Much of the theoretical work discussed in this book comes from accomplishments of the Department of Theory of Semiconductors and Quantum Electronics of the Institute of Applied Physics (IAP) of the Academy of Sciences of Republic of Moldova, which was headed by S.A. Moskalenko for over 30 years from the time it was organized in 1964. Professor P.I. Khadzhi and Drs. A.I. Bobrysheva, I.V. Beloussov, M.I. Shmiglyuk, and V.R. Misko of this department contributed significantly to this book. Prof. A.H. Rotarv, Drs. M.F. Miglei, S.S. Russu, Yu.M. Shvera, V.A. Zalozh, E.S. Kiseleva, and many other former members of this department made important contributions to the theoretical works cited in the text. The contributions of S.A. Moskalenko to this book are based partially on his earlier books published by the Academy of Sciences of the Republic of Moldova, referred to in the text, and on lecture notes of the special course given from 1980 to 1994 to students of Moldova State University as well as at Uppsala State University in 1995 in connection with his collaboration with Prof. M.A. Liberman.

Our aim throughout the book has been to incorporate discussion of the experimental work with that of the theory. While the theory of excitonic condensates has progressed over the past 40 years, experiments did not begin to make substantial progress until the 1980s, coinciding with the developments of ultrafast laser spectroscopy and high-quality quantum heterostructures. As discussed in this book, there are two realms of experimental effort, the pursuit of spontaneous condensation of excitons in quasiequilibrium and the exploration of coherent effects which occur when a laser field couples directly to the excitonic states. The underlying theory is the same for both, and we have stressed this unity in the text.

Writing of this book would have been impossible without the support of the IAP of Moldova. Supplementary financial support was recieved from INTAS project 94-324. The work of S.A. Moskalenko was generously supported by his family, consisting entirely

of physicists. His wife, Professor Yu.S. Boyarskaya, was selflessly devoted to science and especially encouraged him to write this book. For the past three years, S.A. Moskalenko has written this book in her memory, and dedicates his work to her. The efforts of David Snoke have been supported by the National Science Foundation as part of Early Career Award DMR-9722239 and by the Research Corporation through its Cottrell Scholar program. Professors J.P. Wolfe, M. Cardona, G. Baym, Y.C. Chang, and D. Boyanovsky also provided significant support and feedback for this book.

Much remains to be done in this growing field, and we hope that this book will serve as an aid both to those newly entering in and to those already familiar with these topics.

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Contents

I

Introduction

1.1 What is an Exciton?

Many people seem to have trouble with the concept of an exciton. Is it "real" in the same sense that a photon or an atom is? Does the motion of an exciton correspond to the transport of anything real in a solid?

Simply put, an exciton is an electron and a hole held together by Coulomb attraction. Of course, for some people the idea of a "hole" is a difficult concept, so this may not help much. Nevertheless, a hole is a "real" particle and so is an exciton.[a] Modern solid-state theory [1, 2] gives equal footing to both free electrons and holes as charge carriers in a solid, exactly analogous to the way that electrons and positrons are both "real" particles, even though a positron can be seen as the absence of an electron in the negative-energy Dirac sea, i.e., a backwards-in-time-moving electron.

All excitons are *spatially compact.* The strong Coulomb attraction between the negatively charged electron and the positively-charged hole keeps them close together in real space, unlike Cooper pairs, which can have very long correlation lengths because of the weak phonon coupling between them. The sizes of excitons vary from the size of a single atom, e.g., approximately an angstrom up to several hundred angstroms, extending across thousands of lattice sites. Excitons are roughly divided into two categories based on their size. An exciton that is localized to a single lattice site is called a "Frenkel" exciton, after the pioneering work of Frenkel [3] on excitons in molecular crystals. Frenkel excitons appear most commonly in molecular crystals, polymers, and biological molecules, in which they are extremely important for understanding energy transfer. Excitons in the opposite limit, spanning many lattice sites, are known as "Wannier" excitons or "Wannier–Mott" excitons [4, 5]. These are typical in most semiconductors and are the main subject of this book. In between these two limits, there are excitons of intermediate size, which are described by the charge-transfer model.

In general, excitons can *move* through a solid. In the case of Frenkel excitons, this motion is viewed as hopping of both the electron and the hole from one atom to another. If an electron is excited from a valence shell of an atom into an excited state, it may then move

[a] In some of the literature, free electrons, holes, and excitons in a solid are called "quasiparticles," which carry "quasimomentum," to distinguish them from free particles in vacuum. This can lead to the impression that they are not "real," when actually all it means is that they are the fundamental quanta of a field with a renormalized energy spectrum. By this standard, even free electrons and positrons in vacuum may be called quasiparticles, since they have a renormalized energy spectrum compared with the bare electron and positron in quantum electrodynamics. In this volume, we reserve the term "quasiparticle" for elementary excitations of the many-electron and the many-exciton states.

into an unoccupied excited state of a nearby atom. The Coulomb repulsion of the electron on the valence electrons of the new atom will tend to push one of them into the hole left in the valence shell of the original atom when the electron was excited. This effectively causes the hole in the valence shell to follow the excited electron. Equivalently, one may say that the negatively charged excited electron attracts the positively charged hole in the valence band, taking it along to the new atom.

In the case of Wannier excitons, the picture is quite different. The underlying lattice of atoms is treated as a background field in which the electrons and the holes exist as free particles, and an exciton consists of an electron and a hole orbiting each other in this medium. To first order, the entire effect of the underlying atomic lattice on the excitons (or free electrons and holes) is taken into account by means of (1) the renormalized masses of the electron and hole, (2) the dielectric constant of the solid, and (3) scattering with phonons (quanta of vibration) and impurities.

The Wannier exciton is therefore essentially a Rydberg atom analogous to hydrogen or positronium. In the case of the hydrogen atom, the hydrogenic wave function consists of an atomic-orbital part multiplied by a plane-wave factor, $\exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)]$, where $\mathbf{k}=(m_0+m_P)\mathbf{v}/\hbar$ is the center-of-mass momentum. The energy spectrum for the bound pair is the Rydberg energy plus the kinetic energy associated with the center of mass,

$$E_H = \frac{-\mathrm{Ry}}{n^2} + \frac{\hbar^2 k^2}{2(m_0+m_P)},$$

where $n = 1, 2, \ldots,$ is the principal quantum number,

$$\mathrm{Ry} = \frac{e^2}{2a_0}$$

is the Rydberg energy, and

$$a_0 = \frac{\hbar^2}{e^2 m_r}$$

is the hydrogenic Bohr radius with reduced mass $m_r = m_0 m_P/(m_0+m_P)$. The situation in a semiconductor is analogous: an electron in the conduction band and a hole in the valence band bind together to form an exciton with center-of-mass wave vector $\mathbf{k}$ and total mass $m_{\mathrm{ex}} = m_e + m_h$. The factor e^2 in the definition of the Rydberg in a_0 is replaced by e^2/ϵ_0 (where ϵ_0 is the low-frequency dielectric constant of the solid) and the renormalized band masses m_e and m_h of the electron and the hole are used in place of the free-electron and the proton masses, giving

$$E_{\mathrm{ex}} = \frac{-e^2}{2a_{\mathrm{ex}}\epsilon_0 n^2} + \frac{\hbar^2 k^2}{2(m_e+m_h)}, \tag{1.1}$$

where

$$\mathrm{Ry}_{\mathrm{ex}} = \frac{e^2}{2\epsilon_0 a_{\mathrm{ex}}}, \tag{1.2}$$

$$a_{\mathrm{ex}} = \frac{\hbar^2 \epsilon_0}{e^2 m_r}, \tag{1.3}$$

Table 1.1. *Exciton parameters in various materials*

	ϵ_0	Binding energy (meV)	Approximate radius (Å)
KCl	4.6	580	3
CuCl	5.6	190	7
Cu_2O	7.1	150	7
Si	11.4	12	50
GaAs	13.1	4	150

where $m_r = m_e m_h/(m_e + m_h)$. The rescaling of the Coulomb interaction $e^2 \to e^2/\epsilon_0$ in Eqs. (1.1) to (1.3) implies that the binding energy of the exciton will be several orders of magnitude less than that of hydrogen or positronium. In the semiconductor Cu_2O, for example, which has relatively isolated conduction and valence bands, so that the electron and the hole masses very nearly equal the free-electron mass m_0, these equations imply a binding energy of 13.6 eV/$2\epsilon_0^2$, which for $\epsilon_0 = 7$ in Cu_2O implies $\text{Ry}_{\text{ex}} = 13.6\,\text{eV}/2 \times 49 =$ 0.138 eV, which is very close to the correct value of 0.100 eV, considering that we have used only one material parameter, the dielectric constant, without taking into account the band structure.[b] Table 1.1 gives a list of typical exciton binding energies and excitonic Bohr radii.

Despite the change of energy scale, the Wannier exciton still corresponds to the case of an electron and a hole orbiting each other in the background medium of the solid, exactly like a hydrogen or a positronium atom. The exciton as a whole will move in a straight line at constant momentum until it scatters with a phonon, an impurity, or another exciton, a free electron or a hole. Although the center-of-mass wave vector **k** now corresponds to a crystal momentum that is conserved only *modulo* a reciprocal lattice vector, Umklapp processes that lead to the nonconservation of crystal momentum occur for only high-energy scattering processes, i.e., at temperatures high compared with those of the excitonic Rydberg.

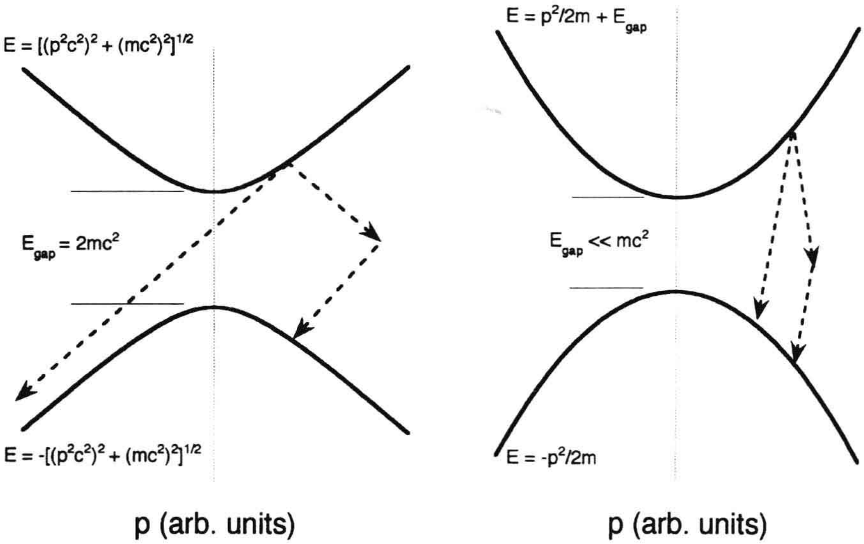
As a complex made of a particle and an antiparticle, excitons are in general *metastable*. Both Frenkel and Wannier excitons have a finite probability for the excited electron to recombine with the hole, leading to the emission of a photon. A typical "life cycle" for an exciton therefore goes as follows: (1) The exciton is created by absorption of a photon, (2) the exciton then moves through the solid, undergoing scattering processes, and (3) finally, the exciton recombines and emits a photon, possibly at some place in the solid quite distant from its creation point. Depending on the symmetries of the recombination processes and the experimental conditions, the lifetime of excitons can range from picoseconds up to milliseconds or longer. In general, the decay rate of an exciton is proportional to the square of the normalized electron–hole orbital wave function at zero separation, which for a hydrogenic Wannier exciton is $\varphi^2(0) = 1/(\pi a_{\text{ex}}^3)$, implying that smaller excitons and Frenkel excitons tend to decay faster.

In one sense, this property is also analogous to the case of positronium, which is a metastable state subject to recombination. Excitons couple to photons in a way different

[b] The excitonic Rydberg for the $n \geq 2$ states in Cu_2O is 100 meV, while the $n = 1$ ground-state binding energy is 150 meV because of central-cell corrections that arise because the size of the $n = 1$ exciton is comparable with the lattice constant. See Ref. 6.

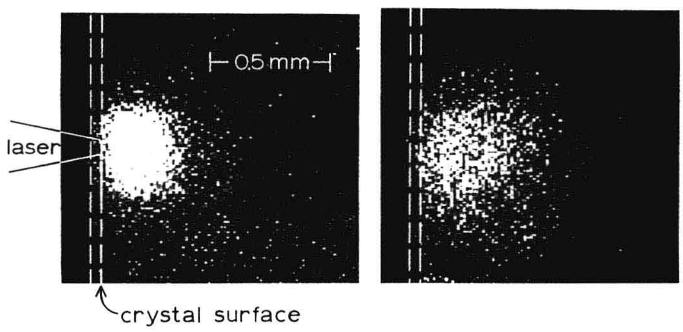
from positronium, however. Figure1.1 illustrates the two cases. By energy and momentum conservation, positronium cannot decay into a single photon; instead, it must decay into two back-to-back photons. The gap energy for excitons is much less than m_0c^2, however. Therefore, although a Wannier exciton can also decay by means of a two-photon process analogous to that of positronium, it can also be created by or decay into a single photon.

Figure 1.2 shows motion of excitons into a crystal of Cu_2O. In these time-resolved images, we can see the above-described characteristics of excitons. Excitons are created at the surface



(a) (b)

Figure 1.1. (a) Single-versus two-photon electron–positron recombination, (b) single-versus two-photon electron–hole recombination in a direct-gap semiconductor. Since $E_{gap} \ll mc^2$, these transitions are called "vertical" transitions, since the momentum of the hole is almost the same as the momentum of the electron.



(a) (b)

Figure 1.2. Time-resolved images of the paraexciton luminescence of Cu_2O at $T = 2$ K, obtained by x–y scanning of the crystal image across an entrance aperture of a spectrometer: (a) $t = 0.2$ μs after a 100-ns Ar^+ laser pulse is absorbed at the crystal surface, (b) $t = 0.6$ μs (from Ref. 7).

of the crystal by absorption of laser light; they then move into the crystal, scattering with phonons and each other. In general, those scattering processes lead to diffusion of the excitons into the solid. As they go, some of them recombine and emit photons, which are recorded in these images.

We note that the above "life cycle" for excitons has many possible exceptions. Excitons can be created not only by absorption of a photon, but by any process that produces excited electrons and holes, e.g., an electric field. Also, instead of recombining simply into photons, excitons may decay nonradiatively, leading ultimately to the emission of phonons, or by means of a combination of photons and phonons. Also, in some cases excitons may become stable, permanent excitons. The excitonic-insulator state, discussed briefly in Chapters 5 and 10, is one proposed mechanism for this, in which excitons can spontaneously form in a narrow-gap semiconductor. Another example is the case of self-trapped excitons, which can alter the band structure of a solid.

Excitons carry energy and momentum, but not mass or charge. One way of describing an exciton is as a "heavy and slow photon." The exciton can have wavelengths of tens of angstroms, compared with hundreds of nanometers for photons, but it has an energy of a few electron volts, comparable with photons. The coupling of photons to exciton states with very short wavelength leads to many of the potential applications of excitons. For example, one can imagine a photon effectively passing through an aperture of a size much less than the photon wavelength without diffraction – the photon can first be converted into an exciton, which stores the energy in the electronic states with short wavelength while passing through the aperture, and can then convert back into a photon on the other side. In payment for its short wavelength, an exciton moves at speeds far less than the speed of light in the medium, i.e., at speeds of the order of the thermal speeds for free electrons. The photon has been dressed with mass as it travels through the optical medium.

Although one can easily imagine passing light through an aperture smaller than the photon wavelength by converting it into excitons, the problem normally arises that the excitons move diffusively, so that the coherence of the light is lost. In the case of an excitonic Bose condensate, however, the excitons retain coherence or even acquire coherence spontaneously. This is the main topic of this book. As we will see, in many cases there is a continuous transition from coherent states of photons to coherent states of excitons. In other cases, however, coherence in the exciton states is quite distinct from coherence in the photon states.

The exciton is the fundamental quantum of excitation of a solid. This is true even for excitation well above the bandgap, in the electron–hole continuum; the absorption spectrum above the gap is strongly affected by the ionized-exciton wave function [8, 9]. Correlations persist between the excited electron and hole even in above-gap excitation of semiconductors until dephasing processes eliminate them [10].

The view of excitons as heavy photons is further illustrated by the "polariton" effect, which mixes the properties of excitons and photons. As seen in Fig. 1.1, the electron and the hole states couple directly by means of a single-photon transition, which means that the dispersion relation for photons in a solid intersects the dispersion relation for Wannier excitons. Depending on the strength of the coupling between photon and exciton states, the region of intersection may be strongly altered, leading to an anticrossing. Figure 1.3 shows a typical polariton dispersion. Polaritons in the region of intersection have mixed character, and, in general, there is no sharp distinction between a photon traveling in the medium and an exciton, other than the group velocity.