OPTICAL PROCESSES IN SOLIDS

It is known from theory and from comparison with experiment that optical spectra and their lineshapes can tell us much about the microscopic motion of the constituent particles of matter – electrons and nuclei.

A unifying element that links the apparently diverse phenomena observed in optical processes is the dielectric dispersion of matter. It describes the response of matter to incoming electromagnetic waves and charged particles, and thus predicts their behavior in the self-induced field of matter, known as polariton and polaron effects. The energies of phonon, exciton and plasmon, quanta of the collective motions of charged particles constituting the matter, are also governed by the dielectric dispersion. Since the latter is a functional of the former, one can derive useful relations for their self-consistency. The nonlinear response to laser light inclusive of multiphoton processes, and excitation of atomic inner shells by synchrotron radiation, are also described in the same context.

Within the validity of the configuration coordinate model, photo-induced lattice relaxation and chemical reaction are described in terms of the interaction modes. Applying these arguments equally to both ground and relaxed excited states, one obtains a novel and global perspective on structural phase transitions as well as on the nature of interatomic bonds.

The book will be of value to graduate students and researchers in solid state physics, physical chemistry, materials science and biochemistry.

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CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town,
Singapore, São Paulo, Delhi, Mexico City

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521556057

First published 2003

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication Data
Toyozawa, Yutaka, 1926–
Optical processes in solids / Yutaka Toyozawa.
p. cm.
Includes bibliographical references and index.
ISBN 0 521 55447 0 – ISBN 0 521 55605 8 (pbk.)
1. Solids – Optical properties. I. Title.
QC176.8. O6 T69 2003
530.4′12–dc21 2002067409

ISBN 978-0-521-55447-3 Hardback
ISBN 978-0-521-55605-7 Paperback

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Preface

Light is the most important medium of recognition in human life, as is obvious from the prominent role of vision among the five human senses. In its most naive form, one can recognize by light the position and shape of an object on the one hand and its color on the other. From the time that light was revealed to be a type of waveform, these two functions have been ascribed to the *spatially* and *temporally* oscillating factors of the wave, and have been applied to the diffraction study of the microscopic *structures* of matter and the spectroscopic study of microscopic *motions* in matter, respectively. It was Maxwell who revealed light to be an electromagnetic wave, which could be deduced from his fundamental equations for an electromagnetic field in a vacuum (Chapter 1).

Einstein, in his theory of relativity, incorporated three-dimensional space and one-dimensional time into a four-dimensional spacetime coordinate system on the basis of his Gedanken experiment with light as a standard signal for communication between observers. In contradistinction to the Newtonian equation of motion, the Maxwell equations survived this revolution of physics, proving themselves to be invariant against Lorentz transformation among different coordinate systems in relative motion. Thus, light acquired the position of universality governing the space-time framework itself, something more than an unknown and intangible medium which was once called "the ether".

Another important role of light in the history of physics is the spectral distribution of a radiation field in thermal equilibrium with matter. Planck's *working hypothesis* introduced ad hoc to remove the deviation of the prediction of classical mechanical theory from observation, together with the empirical constant h now called by his name, turned out to be a doorway to the discovery of quantum mechanics (Chapter 2). The first step beyond Planck was made by Einstein who explained the Franck–Hertz experiment on photoelectrons through his hypothesis of a *quantum of light* – a photon as it is now called – which was a *model substantiating* Planck's working hypothesis but was in a sense also a revival of Newton's corpuscular model of light discarded long before. Compton explicitly associated *momentum* as well as *energy* to this hypothetical *particle* in conformity with the well-known energy–momentum relationship in the electromagnetic *wave*, and successfully explained his X-ray electron scattering experiment by applying the energy–momentum conservation law to two colliding particles. The success of two *apparently contradicting* models – wave and particle – depending upon the phenomena to be explained, was increasingly embarrassing to the physicists of that time.

What was found with light (wave $\rightarrow$ particle) took place with an electron in the opposite direction (particle $\rightarrow$ wave). Thus, de Broglie advocated that an electron with momentum p and energy E behaves like a wave with wave number $k = p/\hbar$ and angular frequency $\omega = E/\hbar$, the relation advocated by Einstein and Compton for a quantum of light. Shortly afterwards, Schrödinger presented his famous *wave equation* on the basis of this idea.

Another approach to quantum mechanics had been prepared by Bohr. He succeeded in explaining the series of lines in the spectrum of a hydrogen atom by assuming that the angular momentum of the orbital motion of an electron around a proton takes only integral multiples of $\hbar$ and that the spectral lines correspond to the energy *difference* between these quantized stationary states. The *correspondence principle* he advocated, that the notion of the *transition* energy between (not the energies themselves of) the stationary states corresponds to the frequency of *classical* motion (as will most clearly be seen with a harmonic oscillator in Section 2.2), paved the way towards the discovery of *matrix mechanics* due to Heisenberg, which was soon proved to be equivalent to Schrödinger's wave mechanics.

In this way, the interplay of radiation field and material particle, together with the wave–particle duality common to them, was the most important motivation driving classical physics towards the discovery of quantum mechanics. Atomic and molecular spectroscopy played the role of confirming quantum mechanics to the extremity of accuracy, particularly in the early days of its application.

Subsequent application of spectroscopic methods to condensed matter, which will be the main subject of the present book, opened an extremely fertile area of study which had never been expected, partly because light played the role of not only *probing* but sometimes *changing* the nature of the interatomic bonds of condensation – evolving from a *spectator* to a *participator*. First of all, light revealed the individual (Chapter 7) and collective (Chapters 5 and 8) motions of the constituent charged particles of matter which interact with various strengths and over different ranges. These motions are excited by electromagnetic waves, and the coefficient of the linear part of the response can be described in terms of the *dielectric constant* or conductivity *as a function of frequency* (Chapter 6). Even the *motion* of a charged particle and the *effective interaction* between charged particles within matter as the dielectric medium can be described in terms of a dielectric function (Section 6.5; Chapters 8 and 9). The great difference in the rapidity of motion between electrons and nuclei allows us to apply the adiabatic approximation to describe their correlated motions (Chapter 4), providing the *configuration coordinate model with interaction mode* as a powerful tool to describe intuitively the rearrangement of nuclear positions after optical transition of (i) electrons in a molecule, or (ii) localized electrons in solids, inclusive of their photostructural *changes* and photochemical *reactions* (Chapter 13) – the light is here a participator in changing the nature of the interatomic bond. The way the dynamics of interacting collective excitations is reflected in typical optical spectra can be described systematically (Chapters 10, 11, and 12). Such studies turn out to be quite useful in judging what is going on in the microscopic world from a glance at the spectra – the light is here a spectator. The reader will find that the importance of the role of light as a participator increases in the order Chapter 11 through to Chapter 13.

On the basis of all that has been established in the main part of the book, the author presents in the last chapter (Chapter 14) a *tentative* scenario for the origin of life and its evolution, as a small contribution from physical science to a highly interdisciplinary problem yet unsolved. According to this scenario, solar radiation is a "creator" of life, far beyond being a mere participator.

The problems covered by this book are so diverse that presentation of some common viewpoints or intuitive models is desirable in order to describe them in a unified way and to correlate them in a plausible way. As such, we will take the dielectric description on the one hand and the configuration coordinate model with interaction mode (which can be extended to describe a phase transition) on the other (as already mentioned) – which are the two main features characterizing the book. At the same time, in a particular chapter we will refer not only to preceding but also to subsequent chapters in correlating the underlying physics and in showing instructive examples. In fact, such a style has already been taken in this preface. Also, we have tried to include many examples of comparison between theories and experiments which are considered to be of particular importance in the spectroscopic studies. Explanations are given in as intuitive a way as possible, sometimes with unavoidable lengthy mathematical expressions which can be skipped by readers with insufficient time. In fact, we have put more emphasis on the conceptual aspects than on mathematical derivations. The author hopes that this method of presentation will not only lead readers to a deeper understanding but will also encourage them to further creative thinking.

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Acknowledgments

The author is much indebted to the Research Institute for Fundamental Physics of Kyoto University, the Institute for Solid State Physics of the University of Tokyo and the Physics Department of Chuo University, where the basic ideas underlying this book were developed. His particular thanks are due to the late Professor R. Kubo for many useful suggestions and continual encouragement. It is his great pleasure to acknowledge helpful conversations and interactions with many colleagues in the field: Professors Masaharu Inoue, K. S. Song, E. Hanamura, K. Cho, Y. Onodera, H. Sumi, A. Sumi, A. Kotani, K. Nasu. V. Hizhnyakov, Y. Kayanuma, Y. Shinozuka, S. Abe, M. Schreiber and many others not mentioned here. The author has been happy to learn a great deal from experimental physicists, including Professors H. Kanzaki, K. Kobayashi, T. Koda, T. Goto and K. Kan'no, who revealed many of the intriguing mechanisms of nature.

The author acknowledges with thanks the excellent cooperation he received from the staff of Cambridge University Press, in particular to Dr. Simon Capelin, the publishing director for physical sciences, for his encouragement and generous consideration of the time needed for the completion of the manuscript, and to Dr. Brian Watts, the copy editor, for laboriously converting the incomplete manuscript into a form useful for a broader area of readers. Finally, his thanks are due to Asako Toyozawa for her encouragement and help throughout this endeavor.

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Principal symbols

A	Einstein's A coefficient; amplitude (Chapter 5)
A_{a}	electron affinity of an acceptor
$\boldsymbol{A}(\boldsymbol{r})$	vector potential
a	microscopic length, such as orbital radius
a_{ex}	exciton radius
$a(\boldsymbol{r})$	Wannier function
a_0	lattice constant
$a, a^\dagger$	annihilation, creation operator of a fermion
B	Einstein's B coefficient; half-width of a band
$\boldsymbol{B}$	magnetic flux density
b	reciprocal lattice
$b, b^\dagger$	annihilation, creation operator of a boson
C	elastic constant
c	light velocity
c_ℓ	longitudinal sound velocity
c_0	light velocity in vacuum
D	amplitude of local energy fluctuation
$\boldsymbol{D}$	electric flux density
d	dimensionality
E	energy
E_0	energy of zero-phonon line
E_{a}	energy of peak (center) of absorption band
E_{e}	energy of peak (center) of emission band
E_{R}	relaxation energy
$\boldsymbol{E}$	electric field
$\boldsymbol{e}\,(\boldsymbol{r})$	microscopic electric field (Section 6.3)
e	absolute value of the electronic charge

e, e^*	effective charge of ion (Chapter 5)
$\boldsymbol{e}$	unit vector for polarization of light
$F(E)$, $F_a(E)$	absorption spectrum
$F_e(E)$	emission spectrum
$f(t)$	generating function
f	oscillator strength; force constant
$\boldsymbol{f}$	force density
g	degree of degeneracy; coupling constant
g_s, g_ℓ	short- and long-range coupling constants,
H, h	Hamiltonian
$\boldsymbol{H}$	magnetic field
I_d	ionization energy of a donor
i, j, k	(suffix) rectangular component
i, j, k	(suffix) particle numbering
$\mathbb{i}$, $\mathbb{j}$, $\mathbb{k}$	unit vectors along three rectangular axes
$\boldsymbol{J}$	electric current density
$\boldsymbol{j}(\boldsymbol{r})$	operator for microscopic electric current density
K	kinetic energy
$\boldsymbol{K}$, $\boldsymbol{k}$, $\boldsymbol{q}$	wave vector
k_B	Boltzmann constant
L	macroscopic length
L_T	thermal energy density (Chapter 1)
ℓ	(suffix) longitudinal; long range
l	azimuthal quantum number (ℓ in Chapter 12 only)
$\boldsymbol{l}$	orbital angular momentum
ℓ, m, n	state- or site-numbering; directional cosines
M	atomic mass
M_r	atomic reduced mass (Chapter 5)
m	electron mass; magnetic quantum number
m_e	electron effective mass
m_h	hole effective mass
m_{ex} $(= m_e + m_h)$	exciton mass
m_r $[= (m_e^{-1} + m_h^{-1})^{-1}]$	exciton reduced mass
N	total number
N_0	number density
n	principal quantum number
n $(\equiv b^\dagger b, \equiv a^\dagger a)$	number operator (for boson, or fermion)
$n(\omega)$	refractive index
$O(\ldots)$	of the order of ...

p, $\boldsymbol{p}$, $\boldsymbol{P}$	momentum of a particle
$\boldsymbol{P}(\boldsymbol{r})$	electric polarization density
p_{e} $[\equiv m_{\mathrm{h}}/(m_{\mathrm{e}}+m_{\mathrm{h}})]$; p_{h} $[\equiv m_{\mathrm{e}}/(m_{\mathrm{e}}+m_{\mathrm{h}})]$	fractional distances of an electron and a hole from their center-of-mass coordinate
Q	point charge (Chapter 6)
q, $\boldsymbol{q}$, Q	position coordinate of a particle
Ry	Rydberg energy
$\boldsymbol{r}$	position in space
s	(suffix) short range
s	mode index; spin; steepness index (Section 10.6)
$\boldsymbol{s}$	spin angular momentum
$s(\omega)$	spectral coupling (coupling function)
S	coupling strength; total spin
T	absolute temperature
t	(suffix) transverse; triplet
t	time; interatomic transfer energy
U, V	potential energy
V	macroscopic volume
v	velocity; potential energy
W	rate of a process (Section 6.6)
$W_{\mathrm{g,e}}(q)$	adiabatic potential of ground or excited state
$w(\omega)$	spectral density of energy (Chapter 3)
$w(q)$; w_ℓ	Boltzmann distribution
x, y, z	rectangular coordinates
Z	partition function
α	polaron coupling constant
$\beta(\equiv 1/k_{\mathrm{B}}T)$	reciprocal temperature in units of reciprocal energy
γ	decay rate $(= 2\Gamma/\hbar)$; non-adiabaticity parameter (Section 9.4)
2Γ	level width (see Σ)
Δ	level shift (see Σ); displacement (Chapter 4); exchange energy (Section 8.5); ℓ-t splitting (Section 8.6); exciton energy difference in mixed crystal (Section 8.7)
$\Delta(\boldsymbol{r})$	dilation field
$\boldsymbol{\nabla} \equiv (\partial/\partial x, \partial/\partial y, \partial/\partial z)$	gradient operator
ε	one-electron energy,

ε_g	bandgap energy
ε_μ	normally occupied level (Chapters 8, 12)
ε_ν	normally unoccupied level (Chapters 8, 12)
$\epsilon; \epsilon(\omega)$	dielectric constant; dielectric function
$\epsilon_0 \equiv \epsilon(\infty)$	dielectric constant of vacuum
ϵ_e	electronic dielectric constant
$\epsilon_s \equiv \epsilon(0)$	static dielectric constant
λ	wavelength; mode of photons specified by $(\boldsymbol{k}, \boldsymbol{e})$ (Chapter 3); spin–orbit coupling constant; quantum number for internal states of an exciton
$\Lambda(\boldsymbol{r})$	locator (Chapter 6)
μ	magnetic permeability
μ_0	magnetic permeability of vacuum
$\boldsymbol{\mu}$	electric dipole moment
ν	frequency; number of nearest neighbors; number of p-holes in an atom (Section 13.1)
ρ	charge density; density matrix (Chapter 2); mass density (Chapter 5); number density (Chapter 6)
$\rho(E)$	density of states (per energy)
$\prod$	product
$\sum$	summation
$\varSigma\,(= \varDelta + i\varGamma)$	self-energy
σ	electric conductivity; steepness coefficient (Urbach rule); number of atoms in unit cell
τ	relaxation time; lifetime; other characteristic time
χ	electric susceptibility
$\varOmega, \omega\ (\equiv 2\pi\nu)$	angular frequency; energy (in Sections 11.2–11.7 only)
ω_t, ω_ℓ	angular frequencies of transverse, longitudinal optical modes lattice vibrations
$(\hbar)\omega_{nm}$	(with two suffixes) $\equiv E_n - E_m$ (without $\hbar$ in Sections 11.2–11.7)
$d\varOmega$	differential solid angle
$\varXi$	deformation potential constant
$\boldsymbol{\xi}(\boldsymbol{\eta}, \boldsymbol{\zeta})$	displacement of an atom (Chapter 5)
ζ	chemical shift (Section 12.2)
$\varPhi, \Psi, \phi, \psi$	wave function
$\phi(\boldsymbol{r}), \varPhi(\boldsymbol{r})$	scalar potential
$\mathrm{Tr}(A)$	trace: sum of diagonal elements
$[A, B]_- \equiv AB - BA$	commutator

$[A, B]_+ \equiv AB + BA$	anticommutator
$\langle A \rangle$	quantum-mechanical expectation value
$\langle\langle A \rangle\rangle$	thermodynamic average
$\overline{\overline{A}}$	tensor of the second rank; renormalized quantity (in Chapter 10 only)
$\boldsymbol{A} \cdot \boldsymbol{B}$	scalar product
$\boldsymbol{A} \times \boldsymbol{B}$	vector product