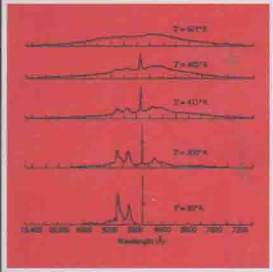

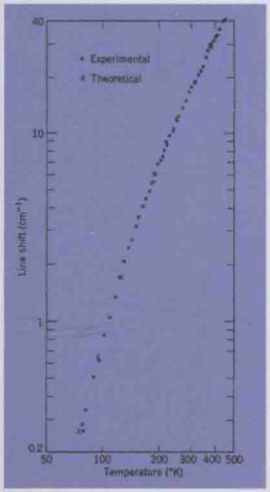

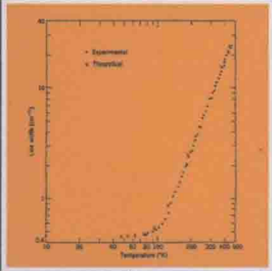

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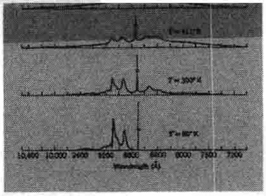

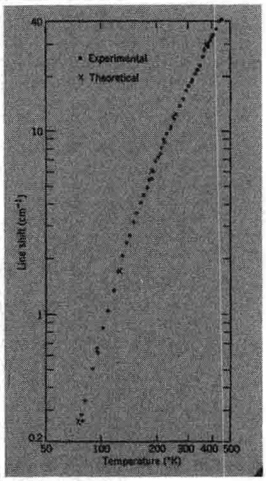

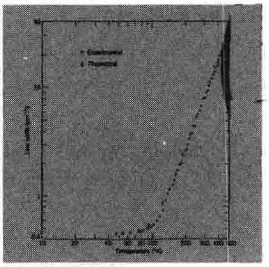

# Optical Interactions in Solids

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"Il fare un libro è meno che niente,
se il libro fatto non rifà la gente."

To Rita, John, Daniel and Claudia

"Fici 'sti quattru chiacchiri
—e sai comu li fici—
sulu pri fari ridiri
'na pennula d'amici."

# Preface to the Second Edition

The appearance of the second edition of this book is due to my belief that *Optical Interactions in Solids* may continue to be useful to students and researchers in the field of solid-state spectroscopy by providing them with a theoretical background and to the encouragement I have received from several colleagues and from Ms. Yubing Zhai, Editor of World Scientific. The preparation of this edition has given me the opportunity to correct most (I hope) of the misprints and mistakes of the first edition. I want to thank the people who pointed them out to me, in particular Dr. Freek Suijver. I want also to acknowledge the assistance received from Mr. Alvin Chong, Editor of World Scientific in Singapore.

Much of what follows is reported from the preface to the first edition of the book. As one of the workers in the fields of absorption and emission spectroscopy of solids I have tried to express my understanding of the basic mathematic tools and physics involved in these fields of research: the choice of the different subjects has been determined by the needs that at one time or another have been part of my experience.

This book is not intended to be a work in quantum mechanics or group theory; as a matter of fact it presupposes the equivalent of one year of study of quantum mechanics. No previous knowledge of group theory, however, is required. The content of this work could be the subject of a two-term graduate course in solid-state spectroscopy.

*Optical Interactions in Solid* is divided into twenty one chapters. In the first chapter quantum mechanics is developed from certain basic postulates, the fundamental concepts are enunciated, and basic tools, such as time-independent and time-dependent perturbation theories, are elaborated.

In the second chapter group theory is developed with particular reference to symmetries in crystals. This treatment does not presuppose any previous knowledge of group theory.

In Chapter 3 the connection between group theory and quantum mechanics is examined. This, I think, may be one of the peculiar aspects of this work, for group theory is introduced from the beginning before any example of physical systems is presented. Quantum mechanics and group theory are then used *at the same time*, and the connections examined are fully exploited throughout the rest of the book.

In Chapter 4 the hydrogen atom is considered, which may seem to be a repetition, for this simple system is covered in many books on quantum mechanics. The introduction of this example will familarize the reader with group theory even in the treatment of simple systems in which no use of it has ever been made. It is important to point out in this context how many group theoretical concepts are unknowingly applied by physicists in the treatment of their problems. The purpose of this chapter is to uncover the group theoretical aspects of some of these treatments so that the reader may become fully conscious of their potentialities.

In Chapter 5 the theory of complex atoms is examined, and here too group theory is used to derive many of the results of atomic spectroscopy.

The basic problems in the evaluation of energy levels of ions in crystals and the role played by crystal symmetries are investigated in Chapter 6. The crystalline hypothesis is introduced and a formal classification of weak, medium, and strong field is introduced. It is pointed out here that, although this classification may resemble different physical situations, the three cases of weak, medium, and strong field may be considered as *schemes* that a worker could choose independently, according to his own particular approach to the problem. These schemes can actually be developed from a purely mathematical point of view.

The three schemes and their relevance to magnetic ions in crystals are examined in Chapters 7, 8, and 9.

In Chapter 10 the effects of covalent bonding on the energy levels of magnetic ions in crystals are studied and a comparison is made between the molecular orbital and crystalline field approaches. The theory of molecular orbitals is then formally established to provide a background for the understanding of some aspects of absorption spectroscopy (charge transfer spectra) described in Chapter 19.

The second part of the book begins with Chapter 11 with the quantum theory of the radiation field. Chapter 12 follows with a formal treatment of molecular vibrations, and Chapter 13 describes a quantum mechanical treatment of thermal vibrations in crystals.

Next, Chapter 14 deals with the interaction of ionic systems with the radiation field. The basic mechanisms involved in the absorption and emission of radiation are examined.

The subject of Chapter 15 is the Judd-Ofelt theory that considers the probability of radiative transitions of rare earth ions in solids.

Chapter 16 deals with the interaction of ionic systems in solids with the lattice vibrations. The effects of thermal vibrations on the positions and widths of spectral lines are also treated.

Chapter 17 is devoted to the study of vibrational-electronic, or vibronic, transitions, i.e. of those processes that involve the contemporary emission or absorption of a photon and the absorption or emission of one or more phonons.

Chapter 18 contains a treatment of the subject of energy transfer among ions in solids.

Chapter 19 reports the fundamental problems in the evaluation of the absorption spectra of magnetic ions in crystals, as does Chapter 20 with regard to the fluorescence spectra of the same systems.

Finally, in Chapter 21, elements of laser theory are presented with emphasis on the essential features and basic schemes of laser systems.

I would like to acknowledge the help I have received in the preparation of this second edition from Professors John Collins and Xuesheng Chen of Wheaton College, Drs. Norman Barnes and Brian Walsh of NASA, Dr. Kailash Mishra of Sylvania-OSRAM, and Dr. Freek Suijver of Philips Research.

*Baldassare Di Bartolo*
Chestnut Hill, Massachusetts
August 2009

# Contents

## Chapter 1

# Elements of Quantum Mechanics

### 1. Review of Classical Mechanics

Let us assume that we have a system with $N$ degrees of freedom, and represented by $N$ generalized coordinates $q_1, q_2 \dots q_N$.

In the Lagrangian formulation the equations of motion are given by the following $N$ second-order differential equations:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0. \tag{1.1}$$

The Lagrangian $L$, for conservative systems, is defined as

$$L(q_i, \dot{q}_i) = T - V, \tag{1.2}$$

where $T$ = kinetic energy and $V$ = potential energy. For a one-coordinate conservative system $q_i = x$ and

$$L = \frac{1}{2}m\dot{x}^2 - V(x) \tag{1.3}$$

and (1.1) reduces to

$$m\ddot{x} = -\frac{\partial V}{\partial x}. \tag{1.4}$$

An example of a nonconservative system is given by a particle with a charge $q$ in an electromagnetic field. The Lagrangian is given by

$$L = T - q\phi + \frac{q}{c}\mathbf{v} \cdot \mathbf{A}, \tag{1.5}$$

$\phi$ being the scalar and $\mathbf{A}$ the vector potential of the field. In fact,

$$\begin{aligned} \frac{d}{dt}\frac{\partial L}{\partial \dot{x}} &= m\ddot{x} + \frac{q}{c}\frac{dA_x}{dt} \\ \frac{\partial L}{\partial x} &= -q\left[\frac{\partial \phi}{\partial x} - \frac{\partial}{\partial x}\left(\frac{1}{c}\mathbf{v} \cdot \mathbf{A}\right)\right]. \end{aligned}$$

Then we have the vector equation

$$m\ddot{\mathbf{r}} = q\left[-\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}\left(\frac{1}{c}\mathbf{v}\cdot\mathbf{A}\right) - \frac{1}{c}\frac{d\mathbf{A}}{dt}\right]. \tag{1.6}$$

Taking into account

$$\begin{aligned} \mathbf{v}\times(\boldsymbol{\nabla}\times\mathbf{A}) &= \boldsymbol{\nabla}(\mathbf{v}\cdot\mathbf{A}) - (\mathbf{v}\cdot\boldsymbol{\nabla})\mathbf{A} \\ \frac{d\mathbf{A}}{dt} &= \frac{\partial\mathbf{A}}{\partial t} + (\mathbf{v}\cdot\boldsymbol{\nabla})\mathbf{A}, \end{aligned}$$

we transform (1.6) into

$$\begin{aligned} m\ddot{\mathbf{r}} &= q\left[-\boldsymbol{\nabla}\phi - \frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} - \frac{1}{c}\mathbf{v}\times(\boldsymbol{\nabla}\times\mathbf{A})\right] \\ &= q\left[\mathbf{E} + \frac{1}{c}(\mathbf{v}\times\mathbf{B})\right] \end{aligned} \tag{1.7}$$

since the fields are expressed by

$$\begin{aligned} \mathbf{E} &= -\boldsymbol{\nabla}\phi - \frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}, \\ \mathbf{B} &= \boldsymbol{\nabla}\times\mathbf{A}. \end{aligned} \tag{1.8}$$

The right side of (1.7) expresses the Lorentz force; (1.5) is then proved.

A different formulation of the equations of motion is given by the Hamilton's equations which are derived in the following way.

We define as *generalized momenta* the quantities

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \tag{1.9}$$

and as Hamiltonian of the system the following function:

$$H = \sum_i p_i\dot{q}_i - L = H(p_i, q_i, t). \tag{1.10}$$

Differentiating (1.10), we get

$$\begin{aligned} dH &= \sum_i \left(\frac{\partial H}{\partial q_i}dq_i + \frac{\partial H}{\partial p_i}dp_i\right) + \frac{\partial H}{\partial t}dt \\ &= \sum_i \left(p_i d\dot{q}_i + \dot{q}_i dp_i - \frac{\partial L}{\partial q_i}dq_i - \frac{\partial L}{\partial \dot{q}_i}d\dot{q}_i\right) - \frac{\partial L}{\partial t}dt \\ &= \sum_i \left(\dot{q}_i dp_i - \frac{\partial L}{\partial q_i}dq_i\right) - \frac{\partial L}{\partial t}dt \\ &= \sum_i (\dot{q}_i dp_i - \dot{p}_i dq_i) - \frac{\partial L}{\partial t}dt. \end{aligned} \tag{1.11}$$

Then we get the canonical or Hamilton's equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}; \quad \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}. \tag{1.12}$$

The kinetic energy is in general given by

$$T = \sum_{ij} \alpha_{ij} \dot{q}_i \dot{q}_j, \qquad (\alpha_{ij} = \alpha_{ji}), \tag{1.13}$$

and

$$\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} = 2T. \tag{1.14}$$

If the system is conservative ($L = T - V$) we get

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial T}{\partial \dot{q}_i}. \tag{1.15}$$

Then

$$H = \sum_i p_i \dot{q}_i - L = \sum_i \left( \dot{q}_i \frac{\partial T}{\partial q_i} - L \right) = T + V. \tag{1.16}$$

Let us now consider the Hamiltonian of a charged particle in an electromagnetic field. The generalized momentum is given by

$$\begin{aligned} p_i &= \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial T}{\partial \dot{q}_i} + \frac{q}{c} \frac{\partial}{\partial \dot{q}_i} (\mathbf{v} \cdot \mathbf{A}) \\ &= \frac{\partial T}{\partial \dot{q}_i} + \frac{q}{c} A_i = m v_i + \frac{q}{c} A_i. \end{aligned} \tag{1.17}$$

Then from (1.17) and (1.5) we get

$$\begin{aligned} H &= \sum_i (p_i \dot{q}_i - L) = \sum_i \left( \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i \right) - \left( T - q\phi + \frac{q}{c} \mathbf{v} \cdot \mathbf{A} \right) \\ &= \sum_i \left[ \left( \frac{\partial T}{\partial \dot{q}_i} + \frac{q}{c} A_i \right) \dot{q}_i \right] - \left( T - q\phi + \frac{q}{c} \mathbf{v} \cdot \mathbf{A} \right) \\ &= \sum_i \left[ \frac{\partial T}{\partial \dot{q}_i} \dot{q}_i \right] - T + q\phi \\ &= T + q\phi = \frac{1}{2} m v^2 + q\phi. \end{aligned} \tag{1.18}$$

We have

$$\frac{1}{2} m v^2 = \frac{1}{2} \frac{(m\mathbf{v})^2}{m} = \frac{1}{2} \frac{[\mathbf{p} - (q/c)\mathbf{A}]^2}{m},$$