PHONONS AND RESONANCES IN SOLIDS

Baldassare Di Bartolo
Richard C. Powell

PHONONS AND RESONANCES IN SOLIDS

BALDASSARE DI BARTOLO

Department of Physics
Boston College
Chestnut Hill, Massachusetts

RICHARD C. POWELL

Department of Physics
Oklahoma State University
Stillwater, Oklahoma

PREFACE

The purpose of this book is to present a treatment of the thermal
vibrations of crystalline solids and of their effects on the
spectra of these materials. Crystalline solids present spectra
whose frequency distribution reflects the structure of their
energy levels. This structure becomes manifest in absorption
spectra every time the frequency of the incoming light is in
"resonance" with one of the energy levels of the system; in emis-
sion, the spectral distribution also reflects the energy spacings
of the system. It is also possible to derive spectral informa-
tion by using scattering experiments where the incoming photon or
neutron, by passing through the system, experiences a variation
of its energy in accordance with a quantum of excitation in the
solid.

In general, the energy levels of a solid may arise from a col-
lective excitation of all the atoms or from localized centers;
also, they can be determined mainly by the electrons or by the
thermal vibrations of the atoms. In general, excitations of dif-
ferent types (say, electronic or vibrational) occur in different
spectral regions, so that they may be studied separately; in some
other cases, for example, in the case of vibronic transitions,
both electronic and vibrational excitation play a role in the
radiative process.

In order to study the spectrum of a solid the researcher uses
probes (like a beam of light, a beam of neutrons) that interact
with the constituents of the crystal. Experimental investigations
may be directly pointing to the measurement of vibrations using
such varied techniques as infrared absorption, Raman and Brillouin
scattering, and neutron scattering. Other experiments may deal
with optical spectra, and be strongly affected by the presence of
thermal vibrations (to the point that they may even provide some
relevant information about these vibrations).

In other words, a researcher may face two different types of
problems:

1. He makes the thermal vibrations the object of his study.
    He uses spectroscopic techniques to investigate the phonon
    spectrum of the solid.
2. He wants to understand how thermal vibrations affect his
    results.

This book is addressed to both types of approaches to the re-
search in this field and may be of great interest not only to
researchers in the field of solid-state spectroscopy but also to
students and teachers of solid-state physics.

There are, of course, other thermal effects in solids that are
not closely related to spectral data and will not be treated here.
For example, thermal transport properties and interaction of pho-
nons with charge carriers in metals and semiconductors are two
areas that have been the subject of extensive investigation and
have already been treated in detail in the literature.

The present treatment proceeds along the following lines:

1. The Introduction (Chapter I) sets the stage for the entire
book by treating the Hamiltonian of a crystalline solid, intro-
ducing the adiabatic approximation, and considering the conse-
quences of this approximation on the role that symmetry plays.

2. Since solids are ordered arrays of atoms, their symmetry
properties are intimately related to their physical properties. A
study of the symmetries of crystals is then essential for an
understanding of their properties, in particular of their spectra.
This study is carried out in Chapters 2-4.

3. The thermal vibrations of a solid are the next subject of
this study. Both their theoretical treatment (Chapters 5 and 6)
and some of the experimental techniques used to investigate them
(Chapters 7 and 8) are considered.

4. The next subject of this study is the interaction of radi-
ation with matter (Chapter 9), which produces optical spectra in
the presence of impurities (Chapters 10 and 11) or infrared
absorption and Raman Scattering (Chapter 12), when the radiation
interacts with the vibrations of that solid.

The content of this book could be the subject of a two-term
graduate course on solid-state physics. It presupposes the
equivalent of one year of study of quantum mechanics. Although
group theory is used throughout the book, no previous knowledge
of this subject is required.

One of the authors (B. Di Bartolo) wishes to acknowledge the
help and assistance received from the Chairman of the Department
of Physics of Boston College, Professor R. L. Carovillano and the
benefit of discussions with his former graduate students, Dr.

CONTENTS

6. THERMODYNAMICS OF LATTICE VIBRATIONS 230

7. SCATTERING OF X-RAYS BY CRYSTALS 257

1

INTRODUCTION

1.1 THE HAMILTONIAN OF A CRYSTALLINE SOLID

A crystalline solid is an ordered array of atoms bound together. The Hamiltonian of such a system that includes n electrons and N nuclei is given by

$$H = \sum_{i=1}^{n} \frac{P_i^2}{2m} + \sum_{\alpha=1}^{N} \frac{P_\alpha^2}{2M_\alpha} + V(r_i, R_\alpha) \qquad (1.1.1)$$

where m is the mass of the electron, M_α is the mass of the αth nucleus, r_i is the position coordinate of the ith electron, P_i is the linear momentum of the ith electron, R_α is the position coordinate of the αth nucleus, and P_α is the linear momentum of the αth nucleus. Also

$$V(r_i, R_\alpha) = V_{ee} + V_{nn} + V_{ne} \qquad (1.1.2)$$

where

$$V_{ee} = \frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} \frac{e^2}{|r_i - r_j|}$$

$$V_{nn} = \frac{1}{2} \sum_{\substack{\alpha=1 \\ \alpha \neq \beta}}^{N} \sum_{\beta=1}^{N} \frac{e^2 Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}$$

$$V_{ne} = - \sum_{i=1}^{n} \sum_{\alpha=1}^{N} \frac{e^2 Z_\alpha}{|R_\alpha - r_i|}$$

The Schrödinger equation of the system is given by

$$H\Psi(r_i, R_\alpha) = E\Psi(r_i, R_\alpha) \qquad (1.1.3)$$

where the Hamiltonian operator H is expressed as follows:

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 - \frac{\hbar^2}{2} \sum_{\alpha=1}^{N} \frac{\nabla_\alpha^2}{M_\alpha} + V(r_i, R_\alpha) \qquad (1.1.4)$$

Therefore the eigenfunctions and the eigenvalues of the system are given by

$$-\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 \Psi - \frac{\hbar^2}{2} \sum_{\alpha=1}^{N} \frac{1}{M_\alpha} \nabla_\alpha^2 \Psi + V\Psi = E\Psi \qquad (1.1.5)$$

In order to solve the above Schrödinger equation we seek solutions of the type

$$\Psi(r_i, R_\alpha) = \phi(R_\alpha)\, \psi(r_i, R_\alpha) \qquad (1.1.6)$$

Using (1.1.6) in (1.1.5) we obtain, dropping the subscripts i and α,

$$-\frac{\hbar^2}{2m} \phi(R) \sum_{i=1}^{n} \nabla_i^2 \psi(r, R) - \frac{\hbar^2}{2} \sum_{\alpha=1}^{N} \frac{\nabla_\alpha^2}{M_\alpha} \phi(R)\, \psi(r, R)$$

$$+ V(r, R)\, \phi(R)\, \psi(r, R) = E\phi(R)\, \psi(r, R) \qquad (1.1.7)$$

But

$$\nabla_\alpha^2 \phi(R)\, \psi(r, R) = \phi(R)\, \nabla_\alpha^2 \psi(r, R) + \psi(r, R)\, \nabla_\alpha^2 \phi(R)$$

$$+ 2\nabla_\alpha \phi(R) \cdot \nabla_\alpha \psi(r, R) \qquad (1.1.8)$$

Then

$$-\sum_{\alpha=1}^{N} \frac{\hbar^2}{M_\alpha} \nabla_\alpha \phi(R) \cdot \nabla_\alpha \psi(r, R) - \sum_{\alpha=1}^{N} \frac{\hbar^2}{2M_\alpha} \phi(R)\, \nabla_\alpha^2 \psi(r, R)$$

$$- \psi(r, R) \sum_{\alpha=1}^{N} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 \phi(R) - \phi(R) \sum_{i=1}^{n} \frac{\hbar^2}{2m} \nabla_i^2 \psi(r, R)$$

$$+ V(r, R)\, \phi(R)\, \psi(r, R) = E\phi(R)\, \psi(r, R) \qquad (1.1.9)$$

We will assume that

$$\left| -\sum_{\alpha=1}^{N} \frac{\hbar^2}{M_\alpha} \left[\nabla_\alpha \phi \cdot \nabla_\alpha \psi + \frac{1}{2} \phi \nabla_\alpha^2 \psi \right] \right| \ll \left| -\psi \sum_{\alpha=1}^{N} \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 \phi \right| \quad (1.1.10)$$

We shall return to the validity of this assumption later. Because of (1.1.10), (1.1.9) becomes

$$-\frac{\hbar^2}{2} \frac{\psi}{\phi} \sum_{\alpha=1}^{N} \frac{1}{M_\alpha} \nabla_\alpha^2 \phi + \left[-\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 + V(\underset{\sim}{r},\underset{\sim}{R}) \right] \psi = E\psi . \quad (1.1.11)$$

The operator in the square brackets on the left-hand side of (1.1.11) represents the Hamiltonian for the system if the nuclei are assumed to be fixed in space. We call this Hamiltonian H_e:

$$H_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 + V(\underset{\sim}{r},\underset{\sim}{R}) \quad (1.1.12)$$

The corresponding eigenfunctions and eigenvalues are given by the Schrödinger equation,

$$-\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 \psi (\underset{\sim}{r},\underset{\sim}{R}) + V(\underset{\sim}{r},\underset{\sim}{R}) \psi(\underset{\sim}{r},\underset{\sim}{R}) = \epsilon(\underset{\sim}{R})\psi(\underset{\sim}{r},\underset{\sim}{R}) \quad (1.1.13)$$

Replacing (1.1.13) in (1.1.11) we obtain

$$-\frac{\hbar^2}{2} \sum_{\alpha=1}^{N} \frac{1}{M_\alpha} \nabla_\alpha^2 \phi(\underset{\sim}{R}) + \epsilon(\underset{\sim}{R}) \phi(\underset{\sim}{R}) = E\phi(\underset{\sim}{R}) \quad (1.1.14)$$

The solution of the Schrödinger equation (1.1.3) reduces then to the solution of the two equations (1.1.13) and (1.1.14); we now rewrite this solution with the proper subscripts as follows:

$$-\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 \psi_k(\underset{\sim}{r},\underset{\sim}{R}) + V(\underset{\sim}{r},\underset{\sim}{R}) \psi_k(\underset{\sim}{r},\underset{\sim}{R}) = \epsilon_k(\underset{\sim}{R}) \psi_k(\underset{\sim}{r},\underset{\sim}{R}) \quad (1.1.15)$$

$$-\frac{\hbar^2}{2} \sum_{\alpha=1}^{N} \frac{1}{M_\alpha} \nabla_\alpha^2 \phi_{kl}(\underset{\sim}{R}) + \epsilon_k(\underset{\sim}{R}) \phi_{kl}(\underset{\sim}{R}) = E_{kl}\phi_{kl}(\underset{\sim}{R}) \quad (1.1.16)$$

A stationary state of the system will be represented by the eigenfunction

$$\Psi_n(\underset{\sim}{r},\underset{\sim}{R}) = \psi_k(\underset{\sim}{r},\underset{\sim}{R})\phi_{kl}(\underset{\sim}{R}) \quad (1.1.17)$$

where $\psi_k(\underset{\sim}{r},\underset{\sim}{R})$ and $\phi_{kl}(\underset{\sim}{R})$ are eigenfunctions of the Hamiltonians

$$H_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{n} \nabla_i^2 + V(\underset{\sim}{r},\underset{\sim}{R}) \qquad (1.1.18)$$

and

$$H_v = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{N} \frac{\nabla_\alpha^2}{M_\alpha} + \varepsilon_k(\underset{\sim}{R}), \qquad (1.1.19)$$

respectively.

1.2   THE ADIABATIC APPROXIMATION

Let us consider now in detail equations (1.1.15) and (1.1.16). Equation (1.1.15) is an eigenvalue equation whose eigenfunctions represent the motion of the electrons in the crystal when the nuclei are kept fixed in space. The energy eigenvalues of (1.1.15) depend parametrically on the nuclear coordinates. Equation (1.1.16) is an eigenvalue equation whose eigenfunctions represent the motion of the nuclei in the crystal. In the Hamiltonian (1.1.19) for nuclear motion, the energy $\varepsilon_k(\underset{\sim}{R})$, which is a function of the nuclear coordinates regarded as parameters, plays the role of the potential energy for nuclear motion. This potential energy $\varepsilon_k(\underset{\sim}{R})$ is an eigenvalue of (1.1.15) and, as such, depends on the quantum number k. The eigenfunction $\phi(\underset{\sim}{R})$ also depends on k; however, k does not play the role of a quantum number for $\phi(R)$ even if it is used as one of its subscripts. Therefore the functions $\phi_{kl}(\underset{\sim}{R})$ and $\phi_{k'l}(\underset{\sim}{R})$ with $k' \neq k$ are *not* mutually orthogonal.

We now return to the approximation (1.1.10) and discuss its physical meaning. The implication of (1.1.10) is that the function $\psi(\underset{\sim}{r},\underset{\sim}{R})$, which represents the motion of the electrons, is a function that varies slowly with the nuclear coordinates, so that $|\nabla_\alpha \psi(\underset{\sim}{r},\underset{\sim}{R})|$ is much smaller than $|\nabla_\alpha \phi(\underset{\sim}{R})|$. In pictorial terms we may say that this is the case since the electrons, having much smaller masses than the nuclei, go through their orbits many times before the nuclei have shifted from their equilibrium position by any considerable distance.

In the light of this fact the approximation (1.1.10), which has allowed us to express the eigenstates of the system in the product form (1.1.6), is called the *adiabatic approximation*. It is also called sometimes the *Born-Oppenheimer approximation*.[1]

The implications of the adiabatic approximation are far reaching. We are now in the position of treating the electrons and the nuclei independently; we will, however, keep in mind that we are allowed to do so only within the limits of validity of the adiabatic approximation.

1.3 THE ROLE OF SYMMETRY

The quantum-mechanical treatment of a physical system implies generally the solution of a Schrödinger equation. This solution gives the energy eigenvalues and the eigenfunctions of the Hamiltonian. In general the eigenfunctions are degenerate; that is, several of them correspond to the same energy eigenvalue. The degeneracy and the transformation properties of the eigenfunctions are closely related to the symmetry properties of the Hamiltonian; indeed, both degeneracy and transformation properties can be derived from the knowledge of symmetries.

Before considering these symmetries for the case of a crystalline solid, it is worthwhile to review some basic concepts regarding coordinate transformations. In particular we are concerned with those transformations that leave the distance between two points unchanged. The most general transformation of this type can be expressed by the symbol $\{R|t\}$ and involves a rotational operation R followed by a translation t. A position vector x, when acted upon by $\{R|t\}$, becomes

$$x' = R\,x + t \qquad (1.3.1)$$

with

$$x'_1 = R_{11}x_1 + R_{12}x_2 + R_{13}x_3 + t_1$$

$$x'_2 = R_{21}x_1 + R_{22}x_2 + R_{23}x_3 + t_2 \qquad (1.3.2)$$

$$x'_3 = R_{31}x_1 + R_{32}x_2 + R_{33}x_3 + t_3$$

R is a 3 x 3 real orthogonal matrix: if its determinant is +1, the rotation is called *proper*; if its determinant is -1, the rotation is called *improper*.

A pure rotation is indicated by $\{R|0\}$ and a pure translation by $\{E|t\}$. The identity operation is represented by $\{E|0\}$.

If two operations $\{R_1|t'\}$ and $\{R_2|t''\}$ act in succession upon a vector x, the result is

$$x' = R_1 x + t' \qquad (1.3.3)$$