

Quantum Theory of Solids

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SECOND REVISED PRINTING

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Preface

The object of this textbook is to present the central principles of the quantum theory of solids to theoretical physicists generally and to those experimental solid state physicists who have had a one year course in quantum mechanics. The book is intended for use in a one year graduate course, to follow a year of general education in the facts of solid state physics at the level at least of my earlier book *Introduction to Solid State Physics*, second edition. Much of the physical background to the theory is developed there, and it is hoped in the next edition to develop the physical interpretation up to the level needed here.

As far as possible I have tried to emphasize unifying principles. The first part of the book treats phonon, magnon, and electron fields and their interactions, culminating in the theory of superconductivity. The second part treats fermi surfaces and electron wavefunctions in metals, alloys, semiconductors, and insulators, with considerable attention to the theory of the important types of experiments which bear on our understanding. The third part deals with correlation functions and their application to time-dependent effects in solids, with a brief introduction to Green's functions. The order of the chapters, particularly within the second part, is not rigorously linear—I attempted to avoid an accumulation of material which did not challenge the imagination and participation of the reader. The first part of the book forms by itself a short course which has been observed to interest students of field theory and particle physics.

A number of important theoretical calculations in solid state physics are too long, intricate, fearsome, or tedious to present in full in a course; and a summary treatment often has no pedagogical value. To give several examples, the full theory of Bloch electrons in a magnetic field, by Blount, Roth, Wannier, Kohn, and others, has been omitted,

although a less complete treatment is included. Equally, the work of Soviet physicists and Luttinger on the Landau theory of the fermi gas is clearly beyond the scope of the book, together with a number of other many-body problems. The subject of the properties of paramagnetic ions in various environments appears to me to be too specialized for a general text. While writing it became abundantly clear that there is no level at which a textbook like this could aim to be a complete treatment of all major aspects of the theory of solids; the field is simply too vast. It is natural not to report several detailed subjects which are available in existing texts—thus the material on standard transport theory in the books by A. H. Wilson and J. Ziman is not repeated here; the discussion in Peierls of phonon interactions and the book by Abragam on nuclear magnetism are treatments so complete that it would be ridiculous to paraphrase them. I renounced an attempt to do everything by the method of Green's functions, for then the contents would be almost entirely inaccessible to experimentalists at the present time. Given an opportunity, many students will choose to write a term paper on an application of Green's functions to a many-body problem. The quantum theory of transport processes is not treated here. Fortunately, for many subjects excellent monographs exist, particularly in the monumental series *Solid State Physics—Advances in Research and Applications*, edited by F. Seitz and D. Turnbull, and in the *Encyclopedia of Physics—Handbuch der Physik* series. Details far beyond the scope of this text can be found in these and other specialized works.

This book contains problems and is a textbook; it is not a history of the development of the subject. I have actively tried as a matter of policy to avoid proper names, assignment of priority, and allocation of credit. Detailed references and names are given only when it would be positively clumsy to omit them, or when the work is too recent to have been included in reviews. An adequate bibliography would be as long as the text itself. Many lists of references are readily available in the *Advances* and in the *Handbuch* series. It is increasingly clear that many active research workers cannot find time both to write a text and to give full historical credit to all their colleagues responsible for the development of a large subject.

A number of very important results are developed in the problems to be found at the end of most chapters. It is urgently recommended that the problems be read over in conjunction with the text, and it would be vastly better for the reader to solve the problems.

A note on notation: $[,]$ = commutator; $\{ , \}$ = anticommutator; the symbols c, c^+ are usually reserved for fermion operators. The units

$\hbar = 1$ are employed throughout, but \hbar is sometimes restored to the final result. A Bloch function of wavevector \mathbf{k} is written as $|\mathbf{k}\rangle$. When convenient the volume Ω of the specimen is set equal to unity; N usually refers to the total number of particles and n to their concentration. The symbol Ψ usually denotes a field operator, and Φ usually denotes a state vector.

It is a pleasant duty to acknowledge here in part the wide assistance I have received. M. H. Cohen, W. A. Harrison, W. Kohn, H. Suhl, J. Friedel, A. Blandin, P. Argyres, B. Cooper, S. Silverstein, B. Dreyfus, J. W. Halley, G. Mahan, D. Mills, and F. Sheard have helpfully suggested improved treatments of various demonstrations. My colleague, J. Hopfield, alertly resolved innumerable apparent paradoxes which appeared during the writing. At Stanford, M. S. Sparks and his associates, including R. M. White, R. Adler, K. Nordtvedt, K. Motozaki, and I. Ortenberger, detected many lapses in the early versions of the manuscript. R. Peierls graciously agreed to share the title of his most useful book. The typing was done with perfection by Mrs. Eleanor Thornhill, without whose help few physics books would be written in Berkeley; Mrs. Sue Limoli kindly assisted with the proofs.

C. KITTEL

August 1963

Preface to the Second Revised Printing

The original preface suggested that "A number of very important results are developed in the problems...." Experience has shown that the problem solutions can be really useful both for self-study and as a supplement to lectures. Indeed, many of the results are too important to be left to the chance that the reader will take time off to work them out. It is fortunate that Professor C. Y. Fong offered to prepare an appendix giving the solutions to selected problems. He also made a number of typographic and algebraic corrections in the text itself. Thus the revised edition is defined by the original text, the solutions, and the corrections.

C. KITTEL

November 1986

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1 Mathematical introduction

It is convenient to gather together here a number of definitions and results which are utilized throughout the text.

RECIPROCAL LATTICE

We recall several important properties of the reciprocal lattice. The basis vectors \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* of the reciprocal lattice are defined in terms of the primitive basis vectors, \mathbf{a} , \mathbf{b} , \mathbf{c} of the direct lattice by the equations

$$(1) \quad \mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}; \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}; \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}};$$

this definition includes a factor 2π which is not usually present in the usual crystallographic definition followed by elementary texts. In treating the interaction of waves with periodic lattices we constantly encounter in the statements of wavevector conservation an additive term which is 2π times the crystallographic reciprocal lattice vector; thus we find it handy to include the 2π in the definition here. Otherwise our notation here is standard; the use of the asterisk superscript in no way implies "complex conjugate." All the basis vectors are real. We note that $\mathbf{a} \cdot \mathbf{a}^* = 2\pi$; $\mathbf{a} \cdot \mathbf{b}^* = 0$; etc.

By simple vector analysis it follows from (1) that

$$(2) \quad V_c^* = \frac{(2\pi)^3}{V_c},$$

where V_c^* is the volume of the primitive cell in the reciprocal lattice and $V_c = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ is the volume of the primitive cell in the direct lattice. We note that the conversion of wavevector sums to integrals involves

$$(3) \quad \sum_{\mathbf{k}} \rightarrow \frac{\Omega}{(2\pi)^3} \int d^3k = (N/V_c^*) \int d^3k,$$

where the direct volume Ω contains N primitive cells.

THEOREM. The vector $\mathbf{r}^*(hkl)$ to the point hkl of the reciprocal lattice is normal to the (hkl) plane of the direct lattice.

Proof: Note that

$$\frac{1}{h}\mathbf{a} - \frac{1}{k}\mathbf{b}$$

is a vector in the (hkl) plane of the direct lattice, by definition of the lattice indices. But

$$\begin{aligned} (4) \quad \mathbf{r}^* \cdot \left(\frac{1}{h}\mathbf{a} - \frac{1}{k}\mathbf{b} \right) &= (k\mathbf{a}^* + l\mathbf{b}^* + m\mathbf{c}^*) \cdot \left(\frac{1}{h}\mathbf{a} - \frac{1}{k}\mathbf{b} \right) \\ &= \mathbf{a}^* \cdot \mathbf{a} - \mathbf{b}^* \cdot \mathbf{b} = 0; \end{aligned}$$

therefore \mathbf{r}^* is normal to one vector in the plane. By the same argument \mathbf{r}^* is normal to the second vector

$$\frac{1}{h}\mathbf{a} - \frac{1}{l}\mathbf{b}$$

in the plane, and thus \mathbf{r}^* is normal to the plane.

THEOREM. The length of the vector $\mathbf{r}^*(hkl)$ is equal to 2π times the reciprocal of the spacing $d(hkl)$ of the planes (hkl) of the direct lattice.

Proof: If \mathbf{n} is the unit normal to the plane, then $h^{-1}\mathbf{a} \cdot \mathbf{n}$ is the interplanar spacing. Now

$$(5) \quad \mathbf{n} = \mathbf{r}^* / |\mathbf{r}^*|,$$

so that the spacing $d(hkl)$ is

$$(6) \quad d(hkl) = \frac{1}{h} \mathbf{n} \cdot \mathbf{a} = \frac{\mathbf{r}^* \cdot \mathbf{a}}{h |\mathbf{r}^*|} = \frac{2\pi}{|\mathbf{r}^*|}$$

We now go on to two important theorems about expansions of periodic functions.

THEOREM. A function $f(\mathbf{x})$ which is periodic with the period of the lattice may be expanded in a fourier series in the reciprocal lattice vectors \mathbf{G} .

Proof: Consider the series

$$(7) \quad f(\mathbf{x}) = \sum_{\mathbf{G}} a_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{x}};$$

to show that this is periodic with the period of the lattice we increase \mathbf{x} by a lattice vector:

$$(8) \quad \mathbf{x} \rightarrow \mathbf{x} + m\mathbf{a} + n\mathbf{b} + p\mathbf{c},$$

where m, n, p are integers. Then

$$(9) \quad f(\mathbf{x} + m\mathbf{a} + n\mathbf{b} + p\mathbf{c}) = \sum_{\mathbf{G}} a_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{x}} e^{i\mathbf{G} \cdot (m\mathbf{a} + n\mathbf{b} + p\mathbf{c})},$$

but

$$(10) \quad \mathbf{G} \cdot (m\mathbf{a} + n\mathbf{b} + p\mathbf{c}) = (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \cdot (m\mathbf{a} + n\mathbf{b} + p\mathbf{c}) \\ = 2\pi(hm + kn + lp),$$

which is just an integer times 2π , so that

$$(11) \quad f(\mathbf{x} + m\mathbf{a} + n\mathbf{b} + p\mathbf{c}) = f(\mathbf{x}),$$

and the representation (7) has the required periodicity.

THEOREM. If $f(\mathbf{x})$ has the periodicity of the lattice,

$$(12) \quad \int d^3x f(\mathbf{x}) e^{i\mathbf{K} \cdot \mathbf{x}} = 0,$$

unless \mathbf{K} is a vector in the reciprocal lattice.

Proof: This result is a direct consequence of the preceding theorem and is essentially a selection rule for interband ($\mathbf{G} \neq 0$) and intraband ($\mathbf{G} = 0$) transitions. By (7)

$$(13) \quad f(\mathbf{x}) = \sum_{\mathbf{G}} a_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{x}},$$

and

$$(14) \quad \int d^3x f(\mathbf{x}) e^{i\mathbf{K} \cdot \mathbf{x}} = \sum_{\mathbf{G}} a_{\mathbf{G}} \int d^3x e^{i(\mathbf{K} + \mathbf{G}) \cdot \mathbf{x}} = \Omega \sum_{\mathbf{G}} a_{\mathbf{G}} \Delta(\mathbf{K} + \mathbf{G}),$$

where Δ is the kronecker symbol; and Ω is the volume of the specimen; we also write $\Delta(\mathbf{K} + \mathbf{G})$ as $\delta_{\mathbf{K}, -\mathbf{G}}$.

FOURIER LATTICE SERIES

Consider the series

$$(15) \quad q_r = N^{-1/2} \sum_{\mathbf{k}} Q_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}.$$

We shall usually determine the allowed values of \mathbf{k} by the periodic boundary condition $q_{r+N} = q_r$, whence $e^{i\mathbf{k} \cdot N} = 1$; this condition is satisfied by $\mathbf{k} = 2\pi\mathbf{n}/N$, where \mathbf{n} is any integer. Only N values of \mathbf{n} give independent values of the N coordinates q_r . It is convenient to take N as even and to choose the values of \mathbf{n} as $0, \pm 1, \pm 2, \dots, \pm(\frac{1}{2}N - 1), \frac{1}{2}N$. We note that $\frac{1}{2}N$ and $-\frac{1}{2}N$ give identical values of $e^{i\mathbf{k} \cdot \mathbf{r}}$ for all \mathbf{r} , so that we need take only $\frac{1}{2}N$. The value $\mathbf{n} = 0$ or

$k = 0$ is associated with what is called the *uniform mode* in which all q_r are equal, independent of r .

THEOREM. Given (15), then

$$(16) \quad Q_k = N^{-1/2} \sum_s q_s e^{-iks}.$$

Proof: Substitute (16) in (15):

$$(17) \quad q_r = N^{-1} \sum_k q_s e^{ik(r-s)}.$$

If $s = r$, then the sum over k gives Nq_r , the desired result. If $s - r = \sigma$, some other integer,

$$(18) \quad \sum_n e^{iks} = \sum_n e^{i2\pi ns/N} = \sum_{n=0}^{N-1} e^{i2\pi ns/N} + \sum_{n=1}^{N-1} e^{-i2\pi ns/N} \\ = \sum_{n=0}^{N-1} e^{i2\pi ns/N} = \frac{1 - e^{i2\pi s}}{1 - e^{i2\pi s/N}} = 0$$

for $\sigma \neq 0$. Thus we have the orthogonality relation

$$(19) \quad \sum_k e^{ik(r-s)} = N \delta_{sr}.$$

This is the analog for discrete sums of the delta function representation

$$(20) \quad \int_{-\infty}^{\infty} e^{ikx} dk = 2\pi \delta(x).$$

Consider the series defined for $-\frac{1}{2}L < x < \frac{1}{2}L$:

$$(21) \quad q(x) = L^{-1/2} \sum Q_k e^{ikx},$$

where k is any integer times $2\pi/L$.

THEOREM. Given (21), then

$$(22) \quad Q_k = L^{-1/2} \int_{-1/2}^{1/2} d\xi q(\xi) e^{-ik\xi}.$$

Proof: Substitute (21) in (22):

$$(23) \quad Q_k = L^{-1} \sum_{k'} Q_{k'} \int d\xi e^{i(k'-k)\xi} = \sum_{k'} Q_{k'} \delta_{kk'} = Q_k,$$

because

$$\int_{-1/2}^{1/2} d\xi e^{i(k'-k)\xi} = \frac{2 \sin \frac{1}{2}(k' - k)L}{i(k' - k)} = 0,$$

except for $k = k'$.

THEOREM. The potential $1/|\mathbf{x}|$ may be expanded in a fourier series as

$$(24) \quad \frac{1}{|\mathbf{x}|} = \frac{4\pi}{\Omega} \sum_{\mathbf{q}} \frac{1}{q^2} e^{i\mathbf{q}\cdot\mathbf{x}},$$

where Ω is the volume of the crystal.

Proof: Following (22) consider, with $r = |\mathbf{x}|$,

$$(25) \quad \int d^3x \frac{e^{-\alpha r} e^{-i\mathbf{q}\cdot\mathbf{x}}}{r} = 2\pi \int r dr \int_{-1}^1 d\mu e^{-i\mathbf{q}'r\mu} e^{-\alpha r} \\ \cong \frac{2\pi}{iq'} \int_0^\infty dr (e^{-i(\mathbf{q}'-i\alpha)r} - e^{i(\mathbf{q}'+i\alpha)r}) = \frac{4\pi}{q'^2 + \alpha^2}.$$

On taking the limit $\alpha \rightarrow +0$ we obtain (24).

SUMMARY OF QUANTUM EQUATIONS ($\hbar = 1$)

$$(26) \quad i\psi = H\psi.$$

$$(27) \quad i\dot{F} = [F, H], \quad \text{for an operator } F.$$

$$(28) \quad [f(\mathbf{x}), \mathbf{p}] = i \frac{\partial}{\partial \mathbf{x}} f(\mathbf{x}); \quad \mathbf{p} = -i \text{grad} - \frac{e}{c} \mathbf{A}.$$

$$(29) \quad [f(\mathbf{x}), p_x^2] = 2i \frac{\partial f}{\partial x} p_x + \frac{\partial^2 f}{\partial x^2}.$$

$$(30) \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

$$(31) \quad \sigma^+ = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix}; \quad \sigma^- = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix}.$$

For the harmonic oscillator,

$$(32) \quad \langle n|x|n+1\rangle = (2m\omega)^{-1/2}(n+1)^{1/2}; \\ \langle n|p|n+1\rangle = -i(m\omega/2)^{1/2}(n+1)^{1/2}.$$

$$(33) \quad \text{Tr}\{A[B, C]\} = \text{Tr}\{[A, B]C\}; \quad \text{Tr}\{ABC\} = \text{Tr}\{CAB\}.$$

$$(34) \quad \lim_{\epsilon \rightarrow +0} \frac{1}{x \pm i\epsilon} = \mathcal{P} \frac{1}{x} \mp \pi i \delta(x); \quad \mathcal{P} \equiv \text{principal value}.$$

Transition rate:

$$(35) \quad W(n \rightarrow m) = 2\pi |\langle m|H'|n\rangle|^2 \delta(\epsilon_m - \epsilon_n).$$

Density of states per unit energy range, free electrons:

$$(36) \quad \rho_E = \frac{\Omega}{2\pi^2} (2m)^{3/2} \epsilon^{1/2}.$$

$$(37) \quad \int dx f(x) \delta(ax - y) = \frac{1}{|a|} f(y/a).$$

$$(38) \quad \delta(g(x)) = \sum_i \frac{1}{|g'(x_i)|} \delta(x - x_i),$$

where the x_i are the roots of $g(x) = 0$.

$$(39) \quad \int_{-\infty}^{\infty} dx e^{ixy} = 2\pi \delta(y).$$

For nondegenerate states,

$$(40) \quad |m\rangle^{(1)} = |m\rangle + \sum_k' \frac{|k\rangle \langle k| H' | m \rangle}{\epsilon_m - \epsilon_k};$$

$$\epsilon_m^{(2)} = \epsilon_m^{(0)} + \langle m | H' | m \rangle + \sum_k' \frac{|\langle m | H' | k \rangle|^2}{\epsilon_m - \epsilon_k}.$$

$$(41) \quad [AB, C] = A[B, C] + [A, C]B.$$

GENERAL TIME-DEPENDENT PERTURBATION THEORY

We consider the hamiltonian

$$(42) \quad H = H_0 + V,$$

where V is called the perturbation. Even when H_0 and V are independent of time, important results of perturbation theory appear more naturally from time-dependent theory than from the usual time-independent perturbation theory. We assume that the lowest eigenstate Φ of H can be derived from the unperturbed lowest eigenstate Φ_0 of H_0 by adiabatically switching on the interaction V in the time interval $-\infty$ to 0. This assumption is not necessarily always true, and in particular it fails if the perturbation causes one or more bound states to appear below a continuum. The assumption is called the *adiabatic hypothesis*. We shall use (only in this development) the notation $| \rangle$ to denote an eigenstate of H and $| \rangle_0$ to denote an eigenstate of H_0 . The unperturbed ground state is $|0\rangle_0$ and the exact ground state is $|0\rangle$. The same notation is used again at the end of Chapter 6 in the identical connection.

THEOREM. If E_0 is defined by

$$(43) \quad H_0 |0\rangle_0 = E_0 |0\rangle_0,$$

and ΔE by

$$(44) \quad (H_0 + V)|0\rangle = (E_0 + \Delta E)|0\rangle,$$

then the exact shift in the ground-state energy caused by the perturbation is

$$(45) \quad \boxed{\Delta E = \frac{\langle 0|V|0\rangle}{\langle 0|0\rangle}}.$$

Proof: The result (45) follows on subtracting

$$(46) \quad \langle 0|H_0|0\rangle = E_0\langle 0|0\rangle$$

from

$$(47) \quad \langle 0|H_0 + V|0\rangle = (E_0 + \Delta E)\langle 0|0\rangle.$$

Then

$$(48) \quad \langle 0|V|0\rangle = \Delta E\langle 0|0\rangle. \quad \text{Q.E.D.}$$

We now undertake to calculate $|0\rangle$. We replace V by

$$(49) \quad \lim_{s \rightarrow +0} e^{-s|t|}V, \quad s > 0.$$

This defines the process of adiabatic switching, in which the interaction is switched on slowly between $t = -\infty$ and $t = 0$. Between $t = 0$ and $t = \infty$ the interaction is switched off slowly. We shall in the following always understand that the limit $s \rightarrow +0$ is to be carried out.

We work with the perturbation in the interaction representation:

$$(50) \quad V(t) = e^{iH_0 t} V e^{-iH_0 t} e^{-s|t|},$$

so that the time-dependent Schrödinger equation has the form

$$(51) \quad i \frac{\partial \Phi}{\partial t} = V(t)\Phi,$$

with the boundary condition $\Phi(-\infty) = \Phi_0$. In the interaction representation

$$(52) \quad \Phi(t) = e^{iH_0 t} \Phi_s(t),$$

where Φ_s is in the Schrödinger representation. We confirm (51) by forming

$$(53) \quad i\dot{\Phi} = -H_0 e^{iH_0 t} \Phi_s + i e^{iH_0 t} \dot{\Phi}_s = V e^{iH_0 t} \Phi_s.$$