ACADEMIC PRESS

SOLID STATE REPRINTS

Electron Energy Bands in Solids

JOSEPH CALLAWAY

REPRINTED FROM SOLID STATE PHYSICS: ADVANCES IN RESEARCH AND APPLICATION

~~0481.1~~
~~C156e~~

5
7960948

0481.1
C156-

华南工学院
外国教材
中心图书室藏书

ELECTRON ENERGY BANDS IN SOLIDS

JOSEPH CALLAWAY

University of Miami
Coral Gables, Florida
presently *University of California*
Riverside, California

E7950948

ACADEMIC PRESS · New York and London

Copyright © 1958 by Academic Press Inc.
ALL RIGHTS RESERVED.
NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM, BY PHOTOSTAT, MICROFILM, OR ANY OTHER MEANS, WITHOUT WRITTEN PERMISSION FROM THE PUBLISHERS.

ACADEMIC PRESS INC.
111 Fifth Avenue, New York 3, New York

United Kingdom Edition published by
ACADEMIC PRESS INC. (LONDON) LTD.
Berkeley Square House, London W.1

ELECTRON ENERGY BANDS IN SOLIDS by Joseph Callaway was first published in SOLID STATE PHYSICS, Volume 7, edited by Frederick Seitz and David Turnbull, Academic Press Inc., 1958.

PRINTED IN THE UNITED STATES OF AMERICA

Electron Energy Bands
in Solids

Solid State Reprints

Articles originally published in SOLID STATE PHYSICS, edited by Frederick Seitz and David Turnbull, reprinted in separate volumes.

The Theory of Order-Disorder Transitions in Alloys
TOSHINOSUKE MUTO AND YUTAKA TAKAGI
Reprinted from Volume 1, 1955

Order-Disorder Phenomena in Metals
LESTER GUTTMAN
Reprinted from Volume 3, 1956 *in one volume*

The Elastic Constants of Crystals
H. B. HUNTINGTON
Reprinted from Volume 7, 1958

Ferroelectrics and Antiferroelectrics
WERNER KÄNZIG
Reprinted from Volume 4, 1957

Space Groups and Their Representations
G. F. KOSTER
Reprinted from Volume 5, 1957

Electron Energy Bands in Solids
JOSEPH CALLAWAY
Reprinted from Volume 7, 1958

Electronic Spectra of Molecules and Ions in Crystals
DONALD S. MCCLURE
Reprinted from Volumes 8 and 9, 1959

此为试读,需要完整PDF请访问: www.ertongbook.com

7960948

东南工学院
外国教材
中心图书室藏书

Contents

I. Introduction and General Theory

1. THE ENERGY BAND

A convenient assumption to make in beginning the discussion of the behavior of electrons in crystals is that we may consider the motion of only one particle in a periodic potential. This is an oversimplification, for one really has a many-electron problem. Moreover, real crystals are not perfectly periodic but contain imperfections. Some of the complications which arise because of the many-particle nature of the problem will be discussed in subsequent sections; a general treatment of the problem of imperfections is beyond the scope of this review. With this simplifying assumption mentioned above, Bloch proved that solutions of Schrödinger's equation have the form[1]

$$\psi_{\mathbf{k}} = u_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \tag{1.1}$$

in which $u_{\mathbf{k}}(\mathbf{r})$ is periodic in $\mathbf{r}$ with the periodicity of the potential. This theorem is a general consequence of translational symmetry. The wave functions are characterized by the wave number **k** which may be thought of as equivalent to the crystal momentum. The energy of a state $\psi_{\mathbf{k}}$ depends in a reasonably continuous fashion on the wave number. The relation between energy and wave number characterizes an energy band.

The simplifying assumptions made above could lead to the false im-

---

[1] F. Bloch, *Z. Physik* **52**, 555 (1928).

华南工学院
外国教材

7960948

pression that energy bands are found only in periodic structures. It is still useful to talk about energy bands in a disordered material provided the atoms are sufficiently close that the atomic wave functions of atoms on neighboring sites overlap. In such a case, one part of the material is, on the average, just like any other part, so that wave functions and energy values can still be characterized by a reasonably continuous dependence of energy on momentum. We will not expect however, that Eq. (1.1) will hold in such circumstances.

It should be apparent that the $E(\mathbf{k})$ relation is one of the most important properties of a material. It is involved in a basic way in any calculation of the electric, optical, or thermal characteristics of the substance. The calculation of $E(\mathbf{k})$ relations for actual materials is extremely complicated. Many considerations of electrical properties, for example, are based on extremely simplified models of the real band structure. Progress has been made, however, in determining energy bands in a number of the simpler metals and semiconductors. We shall describe, first of all, some of the general features of energy bands in periodic lattices, and will then discuss both theoretical and experimental results in materials which have been subject to detailed study. There will be no discussions of artificial models, such as the Kronig-Penney model, or of methods of calculation. For a survey of these topics, the reader is referred to the reviews by Reitz and by Slater.[2]

2. THE MANY-ELECTRON PROBLEM

The enormous number of particles involved in a typical solid makes direct solution of the Schrödinger equation completely impossible, and leads naturally to the development of a one-electron approximation. It is necessary, however, to relate the one-electron theory to the actual many-electron situation, and to estimate the corrections to the results of the one-body approximation. One might well wonder at first how a one-particle approximation can have any validity in the case of electrons which interact with reasonably strong and very long-range forces. Experience does convince us, however, that it is quite useful. We will examine the reason for this.

Suppose we have a set of one-particle wave functions believed to be appropriate to the problem. The best choice of these functions will be discussed in the next section. An antisymmetric N-body wave function can be found by taking N of the one-particle functions and forming a Slater determinant in the standard manner. Such an approximate wave function for the system will be called a model function in this article. If

---

[2] J. R. Reitz, *Solid State Physics* **1**, 1 (1955); J. C. Slater *in* "Handbuch der Physik," Vol. 19, p. 1. Springer, Berlin, 1956.

we construct all the possible N by N determinants out of the one-body functions, the result is a complete set of antisymmetric N-body functions in terms of which the real wave function of the system can be expanded.

It usually is convenient to choose the model functions to be eigenfunctions of a partial Hamiltonian which either does not include the interactions between particles at all, or includes only the average of these interactions. The model functions can then be considered as approximate, or unperturbed wave functions, for the system and the difference between the actual and model Hamiltonians can be treated as a perturbation. The actual machinery of this perturbation theory is quite complex and will not be discussed in detail here for the reason that the Coulomb interaction in metals (as well as many of the interactions of interest in nuclear physics) apparently leads to infinite results. Procedures have been devised which circumvent this difficulty.[3,4]

The question of principal concern to us is the relation between standard energy band theory and the many-body problem. It appears that much of the basic language of the theory is unchanged. W. Kohn has shown that the behavior of an extra electron or hole in an insulator can be described in some circumstances by an effective mass equation.[5] A more general approach would seem to be afforded by the work of Bethe, Gell-Mann, and Brueckner, etc.[3,4] The one-particle functions which are combined to form the model wave function of standard energy band theory satisfy Bloch's theorem and can be designated by the appropriate wave vector and band index. A model wave function can be characterized by specifying the one-particle states which are occupied. From a given model state, a real state can be constructed. The actual energy of the system can be associated with the model state from which the real state is derived. It may not be possible, however, to obtain all the real states in this way. In the model wave function of lowest actual energy E_0, the wave vectors of the occupied one-electron states will lie within some surface in **k** space. The excited states of interest to band theory are specified, in relation to the ground-state model function, by listing the wave vectors and spins of the previously occupied states which are now vacant (k_i') and the previously empty states now filled (k_i''). (Here $i = 1, \ldots \nu$, where ν is the number of excited particles or holes.) Let the real energy of an

---

[3] For a treatment of the general theory of the many-body problem see, for instance, H. Bethe, *Phys. Rev.* **103,** 1353 (1956), and the references contained therein.

[4] The Coulomb interaction is treated by M. Gell-Mann and K. A. Brueckner, *Phys. Rev.* **106,** 364 (1957); M. Gell-Mann, *Phys. Rev.* **106,** 369 (1957); K. Sawada, *Phys. Rev.* **106,** 372 (1957).

[5] W. Kohn, *Phys. Rev.* **105,** 509 (1957). For a general discussion of the many-body problem in solids see H. Haken, *Z. Naturforsch.* **9a,** 228 (1954).

excited state be E. Then we write (following Gell-Mann[4]):

$$E = E_0 + \Sigma_i[W(k_i'') - W(k_i')] + 0(\nu/N). \qquad (2.1)$$

The quantity $W(k_i'')$ is the difference in actual energy between the ground state (E_0) and a state containing $N + 1$ particles, the additional particle being (as far as the model wave function is concerned) in the previously unoccupied state k_i''. Here $W(k_i'')$ may be thought of as representing the complete interaction energy of one particle in the state k_i'' with the rest of the system, but it differs quantitatively from a similar quantity calculated in the Hartree-Fock approximation (see Section 3) because of the more accurate inclusion of the correlation between particle motions in this procedure. Similarly $W(k_i')$ is the difference in energy between the ground state and a state with N-1 particles, one particle being removed from the previously occupied state k_i'. In addition to the quantities $W(k)$, the energy of the excited N-body state must include terms containing the interaction between excited particles and between excited particles and holes. This interaction is of the order ν/N, and can be neglected if ν/N is small.

In more physical terms, the many-body system is capable of single-particle excitations, and also of other excitations, such as collective oscillations,[6] which are not described easily in a single-particle model and in which the interaction between the excited particles is important. The interesting single-particle excitations are those whose energy is low compared to a collective oscillation.

An energy band is specified by the function $W(k)$. A description of the many-body system in terms of energy bands will be meaningful formally when the excitation energy is not too large (less than is required to excite a collective oscillation) and as long as we are not concerned with the interactions between excited particles and between excited particles and holes. The energy bands defined in this way are the same as those obtained from the Hartree-Fock equations (3.1) when the more detailed treatment of the particle interactions is neglected. In general, however, there are quantitative differences arising from the more detailed treatment of particle interactions in $W(k)$.

Experimental results seem to indicate that the basic ideas of the one-particle approximation actually are applicable to metals.[7] A well-defined Fermi surface (the surface enclosing the occupied region of **k** space for the one-particle functions) exists in metals and its characteristics can be

---

[6] D. Pines, *Solid State Physics* **1,** 367 (1955). In a recent paper Nozières and Pines discussed the nature of the elementary excitations in solids. P. Nozières and D. Pines, *Phys. Rev.* **109,** 1062 (1958).

[7] N. F. Mott, *Nature* **178,** 1205 (1956).

determined. It also appears that many excitations of low-energy can be described conveniently in terms of a one-particle model. This is quite consistent with the point of view expressed in the foregoing. It should be possible, and it is a basic objective of band theory to determine the shape of the Fermi surface and to account quantitatively for the one-particle excitations by computing the function $W(k)$.

Similar successes of the one-particle model are observed in semiconductors. The reasons for success in this case are perhaps more obvious. In the first place, the number of holes and electrons involved in transport processes is usually very small, so that it is quite reasonable to neglect terms of the order ν/N. Second, because of the existence of a finite energy gap between filled and vacant states in the one-particle model, ordinary perturbation theory of the electron interaction is convergent.[8]

3. THE HARTREE-FOCK EQUATIONS

Although a theory for finding the exact energy to be associated with a model state exists, it has not yet been possible to make calculations for real systems. All existing calculations of energy bands are based on the use of one model function. The question then presents itself: what is the best choice of a model function? This can be determined by use of the variational principle. The best model function is that for which the expectation value of the energy is a minimum, subject to the conditions that the one-particle functions which compose it be orthonormal. We are lead in this way to an equation for the one-particle functions,[2] namely, the Hartree-Fock equations. Let such a one-particle function be $u_i(x_j)$. The equation is:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \Sigma_L \frac{Ze^2}{r_{iL}} + \Sigma_j \int |u_j(y)|^2 \frac{e^2}{|\mathbf{x}-\mathbf{y}|}\, d^3y\right] u_i(\mathbf{x}) - \Sigma_j \left(\int u_j^*(y) u_i(y) \frac{e^2}{|\mathbf{x}-\mathbf{y}|}\, d^3y\right) u_j(\mathbf{x}) = \epsilon_i u_i(\mathbf{x}). \quad (3.1)$$

In the second term on the left, r_{iL} is the distance between electron i and the nucleus L (assumed fixed). The sum runs over all the nuclei of the system. The third term expresses the average electrostatic potential of all the electrons of the system and the fourth term is the exchange interaction. In the approximation of Koopmans' theorem,[9] the energy parameter ϵ_i measures, the energy required to remove an electron in state i from the system. In other words it is the quantity $W(k)$ for the Hartree-Fock

---

[8] C. W. Ufford, *Phys. Rev.* **59**, 598 (1941).

[9] T. Koopmans, *Physica* **1**, 104 (1933).

此为试读，需要完整PDF请访问：www.ertongbook.com

approximation. The interpretation of this equation is discussed in the reviews by Reitz and Slater.[2]

The calculation of energy bands is based, in principle, on the Hartree-Fock equations. These equations form a quite complicated nonlinear integro-differential system. It is clear that numerical methods of solution must be employed. The usual procedure is the method of self-consistent fields. At the outset, values for the functions u_i are assumed. The integrals appearing in the equations are calculated with the use of the starting functions and the equations (which now have the standard Schrödinger form for a single particle) are solved for the eigenvalues ϵ_i and the function u_i. If the solutions agree, within assigned limits, with the functions assumed, the work is completed; if not, the process is repeated until such time as the results of the nth and $n + 1$ stages agree. The procedure is quite lengthy, and has been applied only to some of the simpler free atoms.[10]

In the case of a solid, there are two types of difficulties which stand in the way of obtaining a self-consistent field calculation. Assume that a choice of starting functions has been made, and the appropriate integrals have been evaluated. Then Eq. (2.1) can be written effectively as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_o(\mathbf{x}) + V_{ex}(\mathbf{x}) \right] u_i(\mathbf{x}) = \epsilon_i u_i(x) \tag{3.2}$$

where V_o and V_{ex} are ordinary and exchange potentials respectively. V_{ex} may depend on the state i under consideration. (See Section 4.) It is then necessary to solve (3.1) for a sufficiently large number of states that a reasonable idea of the band structure and wave functions can be obtained. This problem is more difficult than for free atoms because central symmetry does not prevail in solids. Thus the wave equation, in general, cannot be separated. Certain methods have been devised which will give good results, at least for some states. These methods are discussed in the review article of Reitz.[2]

Once the equations have been solved, the integrals must be re-evaluated and the process repeated until self-consistency has been achieved. This is quite difficult, in general, because it involves summing the charge distribution over all occupied states. In fact, the problem is so difficult that self-consistent calculations have not been completed for solids except possibly in the case of the alkali metals.

For the results to be meaningful, it is necessary that the potentials employed in (3.1) be reasonably close to those which would result from a self-consistent calculation. Physical arguments must be used.

[10] D. R. Hartree, "The Calculation of Atomic Structures." Wiley, New York, 1957.

It is apparent that the principal physical problem in a calculation band structure is the choice of an appropriate crystal potential. Some of the common approximations will be discussed in the next section. It is obvious immediately that those results which depend critically on the details of the potential used in a particular calculation must be viewed with some caution. Moreover it is important to determine the features of a calculation which are likely to be sensitive to the potential.

4. THE CRYSTAL POTENTIAL

Since the construction of a crystal potential is of crucial importance in a band calculation, it is desirable to discuss the various approximations in more detail. In Eq. (3.2) the crystal potential was separated into two parts; namely, an ordinary potential which is the sum of the nuclear attractions and the averaged electronic repulsions, and an exchange potential. The symmetry of the crystal permits us to calculate the potential within a single atomic cell. Consider first the ordinary potential. It is convenient to separate this into two parts; namely, the potential arising from the charge distribution in the particular cell, and that arising from all the other cells. Since the computation of these requires a knowledge of the charge distribution in the crystal, and hence the self-consistent solution of the problem, certain approximations are made.

Consider first the case of a monatomic crystal. Each cell is electrically neutral, so that we need to consider only one atom. In the solid state problem we usually are concerned only with the valence electrons. The core electron distributions on different atoms overlap very little, so that bands of negligible width are formed. Thus it is legitimate to regard the core electron distribution as the same in the solid and in the free atom. For this reason any information we may have about the distribution of the core electrons in the free atom is also relevant to the solid. Consider as examples the alkali metals, in which there is one electron outside a core of compact closed shells. Information regarding the core electron distribution may be obtained either from a self-consistent field calculation for the free ion, or from the spectroscopic data for the free atom. In the latter case, either an empirical potential can be constructed (see Section 12) or spectroscopic information can be used almost directly and explicit construction of a potential function can be avoided. For substances more complicated than the alkali metals, one generally must rely on self-consistent field calculations for the free atom in determining the core electron distribution. It is very unfortunate that self-consistent fields are available for less than half the atoms in the periodic table and that only a small number of the calculations that have been made include exchange.[11]

As a result of the assumptions which must be made concerning the

---

[11] Existing SCF calculations are listed by R. S. Knox, *Solid State Phys.* **4**, 413 (1957).

valence electron distribution, the construction of the crystal potential is uncertain. In the alkali metals, the Wigner-Seitz approximation (Section 10) allows us to avoid this difficulty by using the ionic potential. For more complicated materials, some assumption must be made explicitly. It is probably adequate in many metals to assume that the external electrons are uniformly distributed. This is not allowable for *d* electrons in the transition elements. In ionic crystals, one may assume free ions, and use the charge distribution appropriate to them. There is no clearly satisfactory procedure in valence semiconductors.

If the crystal being considered is not monatomic, there is the possibility of ionic character, for each atomic cell need not be electrically neutral. The potential within a particular cell will not be determined by the charge within the particular cell alone under these conditions. The rest of the lattice must be taken into account. This contribution can be estimated if the charges of the ions are known. The constant term in this potential can be determined easily from the lattice parameter, effective charge, and the Madelung constant. This "Madelung" potential is not actually constant in the unit cell; however, it has the symmetry of the lattice, so that it is reasonable to neglect all but the constant part for cubic crystals.

The determination of the exchange potential is still more uncertain. Fortunately, this potential usually is reasonably small compared with the ordinary potential and need not be determined with extreme accuracy. Actually, an exchange potential is defined only in reference to a particular state, and varies from state to state. For the function u_i we define:

$$V_{ex}{}^{i} = [u_i(\mathbf{x})]^{-1} \sum_{\substack{j \\ j \neq i}} \left(\int u_j{}^*(y) u_i(y) \frac{e^2}{|\mathbf{x} - \mathbf{y}|} \, d^3y \right) u_j(\mathbf{x}). \tag{4.1}$$

The sum runs only over states having the same spin as u_i. It usually is not practical to obtain different exchange potentials for all the electronic states of interest in a band calculation. Slater has proposed certain simplifying approximations which can be used to obtain an average exchange potential for all states.[12] A comparison of approximate exchange potentials has been given by Herman, Callaway, and Acton.[13] The most celebrated of these approximations replaces (4.1) by the exchange potential which would exist in a free electron gas having the same density, namely:

$$V_{ex} = -3e^2 \left(\frac{3}{4\pi} \rho \right)^{\frac{1}{3}}. \tag{4.2}$$

---

[12] J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

[13] F. Herman, J. Callaway, and F. S. Acton, *Phys. Rev.* **95**, 371 (1954); see also V. W. Maslen, *Proc. Phys. Soc.* (*London*) **A69**, 734 (1956), for further discussion.

Here ρ is the density of electrons having the same spin as the state considered and is a function of position. This expression seems to give a reasonably faithful qualitative rendition of the results of (4.1) for many states, but it is inaccurate quantitatively. [It may be noted here that we must include $j = i$ in (4.1).] It seems to over-estimate the effect of exchange by as much as 20 to 30% in some cases.[14] Slater's more involved average[12] does not seem to be appreciably better.[13]

A somewhat better approximation probably can be obtained by assuming that the exchange potential is the same for all states having the same angular momentum.[13] States are not characterized by an angular momentum quantum number in a solid; however, in discussing states at symmetry points of the Brillouin zone in simple metals, it will often be possible to characterize the states by the predominant angular momentum in the expansion of the wave function in terms of spherical harmonics. It is probably better not to average the exchange potential over all the states of the free atom having the angular momentum considered, as proposed in ref. 12, since such states are likely to be more tightly bound than those of interest in the solid. It is more reasonable to construct approximate wave functions and determine an exchange potential from them. One drawback in the procedure of introducing an exchange potential is that V_{ex} will have infinities if the function u_i in (4.1) has nodes. These infinities actually contribute nothing to the energy, but must be removed by some smoothing or averaging process if an exchange potential is to be used like an ordinary potential.

The reader should be aware of the very considerable uncertainty that is involved in a crystal potential. It is likely that this difficulty will not be resolved satisfactorily until such time as it is possible to calculate a self-consistent field for a solid on the basis of Eq. (3.1).

Even in cases in which the questions of the ordinary and exchange potentials within an individual cell are settled, there remains the question of the interactions of the free electrons in different cells with each other. This interaction depends on the wave vector **k** and consequently needs to be included in an energy band calculation. There is, however, no quantitative way of doing this at present.

5. SYMMETRY PROPERTIES

Because uncertainties exist in constructing a crystal potential, it is desirable to employ symmetry considerations whenever possible to aid in determining wave functions and energy levels. The classification of crystal wave functions according to their symmetry properties is, of course, independent of the detailed nature of the crystal potential. Such classification

[14] J. Callaway, *Phys. Rev.* **99**, 500 (1955).

will usually be found to be of considerable value in the calculational process. Often symmetry considerations can be combined with experimental data and simple theoretical inferences to derive quite reasonable ideas of the bands in a particular crystal.

It is assumed that the reader is familiar with the basic ideas concerning the symmetry properties of a crystal, in particular the Brillouin zone, as discussed in standard texts.[15] In this section the principles underlying the symmetry classification of wave functions will be presented, based on the work of Bouckaert, Smoluchowski, and Wigner.[16] A detailed review of these considerations has been given by Koster.[17] In subsequent sections, the behavior of an energy band near a degeneracy will be discussed (6), the application of topological results to the determination of the density of states will be considered (7), and finally a normal form will be proposed for separate bands in simple lattices (8).

In the Hartree-Fock approximation, each one-electron wave function must transform according to some representation of the space group of the crystal. Consider first the invariant subgroup formed by the translations. Since all the translations commute with each other and with the Hamiltonian, the energy eigenfunctions are also eigenfunctions of the translation operators. This statement is equivalent to Bloch's theorem and implies that the functions are characterized by a wave vector $\mathbf{k}$. In addition to the translations, there are other operations which are rotations and reflections in the simplest cases. If such an operation is applied to a wave function for a particular $\mathbf{k}$, the latter will be transformed into a function having a different wave vector $\mathbf{k}'$, which arises from $\mathbf{k}$ by the operation considered. All the $\mathbf{k}'$ formed from a general $\mathbf{k}$, will be different; however, the energy will be the same for each. For some values of $\mathbf{k}$, there will be symmetry operations which carry $\mathbf{k}$ into itself or into vector $\mathbf{k}' = \mathbf{k} + \mathbf{K}$ for which $\mathbf{K}$ is a reciprocal lattice vector. Such operations form a group, which is called the group of the wave vector. The wave function for such a $\mathbf{k}$ will transform, under the group of $\mathbf{k}$, as an irreducible representation of this group, called a small representation.

The small representations and their connections have been worked out for the simple cubic, body-centered cubic, and face-centered cubic lattices in ref. 15. The notation of this paper will be used throughout. The hexagonal lattice and the diamond lattice have been considered by Herring.[18] The zincblende structure has been studied by Parmenter[19] and

---

[15] F. Seitz, "The Modern Theory of Solids." McGraw-Hill, New York, 1940.

[16] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, *Phys. Rev.* **50,** 58 (1936).

[17] G. F. Koster, *Solid State Phys.* **5,** 173 (1957).

[18] C. Herring, *J. Franklin Inst.* **233,** 525 (1940); see also W. Doring and V. Zehler, *Ann. Phys.* **13,** 214 (1953).

[19] R. H. Parmenter, *Phys. Rev.* **100,** 573 (1955).

Dresselhaus.[20] Elliott[21] has discussed the double group (spin included), as have Parmenter and Dresselhaus. The reader is referred to these sources for character tables. A general review of this material is given by Koster.[17]

The utility of classifying the wave functions according to symmetry in a band calculation is that the Hamiltonian has matrix elements only between those functions which belong to the same row of the same irreducible representation. Consequently, use of symmetrized functions is of great value in diagonalizing the Hamiltonian. Modern methods of calculating energy bands employ expansions based on symmetrized functions. The determination of the matrix elements of various operators is also facilitated.

Symmetry considerations also furnish information concerning the form and connections of the various bands in the Brillouin zone. Suppose energy levels have been determined for a particular wave vector $\mathbf{k}_0$ and is desired to obtain the energies at a nearby wave vector $\mathbf{k}_0 + \mathbf{s}$. As is well known, the energies of states at $\mathbf{k}_0 + \mathbf{s}$ can be found from these at $\mathbf{k}_0$ by determining the effect of the perturbation $2i\mathbf{s} \cdot \nabla$ (see Section 7). Symmetry considerations are not particularly helpful if $\mathbf{k}_0$ is a general point in the zone. If $\mathbf{k}_0$ is a symmetry point, and $(\mathbf{k}_0 + \mathbf{s})$ is a general point, all the degeneracy which may have been present at $\mathbf{k}_0$ is removed. If the group of $(\mathbf{k}_0 + \mathbf{s})$ is a subgroup of the group of $\mathbf{k}_0$, but contains more than the identity, as occurs on going away from $\mathbf{k} = 0$ along a symmetry axis, the wave functions at $(\mathbf{k}_0 + \mathbf{s})$ transform according to the subgroup. If the appropriate representation of the group of $\mathbf{k}_0$ is reducible as a representation of the subgroup at $(\mathbf{k}_0 + \mathbf{s})$, the degeneracy at $\mathbf{k}_0$ will be removed at least in part. Of course, if the groups at $\mathbf{k}_0$ and $\mathbf{k}_0 + \mathbf{s}$ are the same, the degeneracy will be the same. The compatibility relations summarize this information and express the way in which levels at symmetry points may connect with the bands along symmetry axes. These relations are obtained from the representations as indicated above, and are given in the references already listed.

A degeneracy, or sticking together of energy bands can be required by symmetry only when the wave vector $\mathbf{k}_0$ is invariant under some symmetry operations. The problem of accidental degeneracy of energy bands (degeneracies not required by symmetry) has been examined by Herring.[22] It is almost impossible for bands having the same symmetry to cross. For example, at a general point, two wave functions having the same wave vector never have the same energy, so that energy bands do not cross at a general point. Similarly, on a symmetry axis, bands of the same sym-

---

[20] G. Dresselhaus, *Phys. Rev.* **100,** 580 (1955).

[21] R. J. Elliott, *Phys. Rev.* **96,** 380 (1954).

[22] C. Herring, *Phys. Rev.* **52,** 365 (1937).

此为试读，需要完整PDF请访问：www.ertongbook.com