basis vectors for a real representation of the space group of the crystal, and that the normal modes belonging to a representation which is irreducible in the field of real numbers, even though reducible in the complex field, must all have the same frequency.[7] Thus mathematically the theory of normal modes and their frequencies is just like the theory of electronic wave functions and their energies: frequency can be plotted as a function of wave vector, and sticking together of two or more of these frequency bands will occur at wave vectors $\mathbf{k}$ where G^k has multidimensional representations or where case (b) or case (c), as defined above, occurs.

It is a pleasure for me to express my thanks to Professor E. Wigner, who suggested this problem.

[7] Cf. E. Wigner, Gött. Nachr. (1930), p. 133.

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Accidental Degeneracy in the Energy Bands of Crystals

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The circumstances are investigated under which two wave functions occurring in the Hartree or Fock solution for a crystal can have the same reduced wave vector and the same energy. It is found that coincidence of the energies of wave functions with the same symmetry properties, as well as those with different symmetries, is often to be expected. Some qualitative features are derived of the way in which energy varies with wave vector near wave vectors for which degeneracy occurs. All these results, like those of the preceding paper, should be applicable also to the frequency spectrum of the normal modes of vibration of a crystal.

IN previous papers, by Bouckaert, Smoluchowski, and Wigner,[1] and by the author,[2] certain properties of the wave functions and energy values of an electron moving in the periodic field of a crystal were derived. These properties were the properties necessitated by the symmetry of the crystal and by the reality of the Hamiltonian. The two questions to be discussed in this paper are:

(1) In the solution of Hartree's or Fock's equations for a crystal to what extent may one expect to encounter accidental coincidences in energy between two one-electron wave functions with the same wave vector? By "accidental" coincidences are to be understood coincidences not necessitated by the symmetry and reality of the Hamiltonian.

(2) If the energies of two or more bands coincide at wave vector $\mathbf{k}$, whether accidentally or for reasons of symmetry and reality, how may the energies of these bands be expected to vary with wave vector in the neighborhood of $\mathbf{k}$?

The analysis necessary to answer these questions is rather tedious. Despite this and the fact that it may not be of practical significance to bother about too fine details in an approximate theory, the discussion to be given below may be of value in forming pictures of the energy band structures of metals, especially of multivalent ones. In particular, it is hoped that the complete determination of energy as a function of wave vector by interpolation from the results of calculations of the Wigner-Seitz-Slater type will be facilitated and made more reliable. The results of this paper also apply, as did those of I, to the frequency spectrum of the normal modes of vibration of a crystal; however numerical calculation of these frequencies has not yet advanced as far as has the calculation of electronic bands.[3]

The notation to be used is the same as in I. In addition, the symbol $[M^1, M^2]$ will be introduced to represent the subspace of Hilbert space spanned together by any two linear manifolds of wave functions M^1 and M^2.

[1] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936), hereafter referred to as BSW.
[2] Preceding paper, hereafter referred to as I.
[3] Calculations for a simple cubic lattice have been made by M. Blackman, Proc. Roy. Soc. **A159**, 416 (1937).

1. Preliminary Definitions

In order to discuss accidental energy coincidences it is first necessary to group together all those eigenfunctions which because of the symmetry and reality of the Hamiltonian necessarily have the same energy. If $\psi_k{}^i$ is any eigenfunction with wave vector $\mathbf{k}$ and energy $E^i(\mathbf{k})$, application to $\psi_k{}^i$ of the operations of the space group and the operation K of taking the complex conjugate will generate a linear manifold of wave functions all eigenfunctions of H with energy $E^i(\mathbf{k})$. Such a linear manifold of eigenfunctions which can be generated from an eigenfunction with wave vector $\mathbf{k}$ will, if it is irreducible under K and the space group, be designated by a symbol $M^i(\mathbf{k})$; of course it will in general contain wave functions with wave vectors different from $\mathbf{k}$. Any $M^i(\mathbf{k})$ will be called equivalent to $M^i(\mathbf{k})$ when the representation of the space group in $M^i(\mathbf{k})$ is equivalent to that in $M^i(\mathbf{k})$. As explained in I, the representation of the space group in $M^i(\mathbf{k})$ may be irreducible (case (a)), reducible into two inequivalent parts (case (b)), or reducible into two equivalent parts (case (c)).

Now the occurrence of an accidental coincidence in energy means simply that for some particular $\mathbf{k}$ two independent manifolds $M^i(\mathbf{k})$ and $M^j(\mathbf{k})$ can be found whose energy values coincide. Such an accidental energy coincidence will be called for brevity a "contact," and $\mathbf{k}$ will be called a "contact point." Two kinds of contacts may occur, according to whether $M^i(\mathbf{k})$ and $M^j(\mathbf{k})$ are inequivalent or equivalent. These will be discussed, respectively, in Sections 2 and 4. In this paper we are not interested in all the types of contacts which are possible with specially chosen forms for the potential energy function occurring in the Hamiltonian, but only in those which may be expected to occur in the Hartree or Fock solution for an actual crystal. For example, it is not hard to find a potential $V=V_0(x, y, z)$ for which the locus of the points of contact between the two lowest energy bands is a two-dimensional surface in $\mathbf{k}$-space. However, almost any infinitesimal change which may be made in the function V will give rise to a new Hamiltonian whose spectrum has no contacts at all.[4] For an actual crystal, the factors determining the potential energy function V are quite unrelated to the conditions V must satisfy in order that there exist a contact region of the type just mentioned; consequently it is safe to assert that no actual crystal will be encountered for which V has the form V_0. In general, it will be legitimate to characterize any property of a contact or a contact region (e.g., the property of the contact region being a two-dimensional surface) as "vanishingly improbable" if it ceases to exist after some infinitesimal change is made in the form of the function V which does not alter the symmetry of V. This concept will be used principally in giving precise formulation to the theorems of Section 4.

2. Contacts of Inequivalent Manifolds

The way in which contacts of wave functions with different symmetry properties come about is most easily seen by considering some particular examples. Consider first the energies of two wave functions whose wave vectors $\mathbf{k}$ lie in a plane of symmetry in the B-Z. Let one of these, say $\psi_k{}^i$, be even with respect to reflection in this plane and the other, $\psi_k{}^j$, be odd. Suppose it is known that at some point $\mathbf{k}_1$ of this plane the even function has higher energy than the odd, and that at another point $\mathbf{k}_2$ the odd has higher energy than the even. Then, since the energy of the odd function and the energy of the even function are both continuous functions of wave vector in this plane, there must be a curve in the plane along which the two energies are equal. It must be impossible to get from $\mathbf{k}_1$ to $\mathbf{k}_2$ without crossing this curve. Therefore this curve must be a closed ring about either $\mathbf{k}_1$ or $\mathbf{k}_2$, or else it must extend to infinity when energy is plotted as a periodic function of wave vector in the infinite reciprocal lattice space. It may happen, of course, that part of this curve coincides with a line of symmetry in the B-Z, along which sticking together of the even band and the odd band is necessitated by symmetry.

For another example consider the band structure of sodium. The graph of energy against k

[4] A simple example occurs when the potential is separable in rectangular coordinates. A two-dimensional contact region will occur when a crossing of energy curves occurs in one of the one-dimensional problems to which the three-dimensional problem is reduced, and it is well known that almost any small perturbation will dissolve such a crossing in one dimension. Cf. v. Neumann and Wigner, Physik. Zeits. **30**, 467 (1929).

when $\mathbf{k}$ lies along a fourfold axis of the B-Z is qualitatively as shown in Fig. 1. It is known[5] that for $\mathbf{k}=0$ the lowest state of the valence electron is the $3s$-like state, which belongs, in the notation of BSW, to the irreducible representation Γ_1 of the full cubic group. The next lowest state at $\mathbf{k}=0$ arises from the atomic $3d$ level; this splits in the crystal field into a triply degenerate level Γ_{25}' and a double degenerate one Γ_{12}. For definiteness it will be assumed here that Γ_{25}' lies lower, although the two are so close together that the usual methods of calculation ignore their separation altogether. At the corner of the B-Z, G^k is again the whole space group. The lowest level is the $3p$-like level Γ_{15}, and the $3s$-like level Γ_1 comes next, a little higher. This information alone suffices to determine the way in which the curves should be drawn between the end points 0 and $2\pi/d$. For we may label the different symmetry types of wave functions at intermediate points by the irreducible representations Δ of the group of their wave vectors. The form of the curves is determined by the fact that the Δ belonging to any curve cannot change suddenly at any place between 0 and $2\pi/d$, and the fact that each Γ contains only certain representations Δ. Note that Γ_{12}, which must connect with Γ_1, lies higher than Γ_{25}', which must connect with something at $2\pi/d$ which is above Γ_1. Therefore the curves of types Δ_2', Δ_1, must cross at some intermediate point.

Considerations of the same sort apply to any path of points in the B-Z whose G^k contains rotations or reflections, provided the path is such that all the representations of the space group vary continuously along the path and bear the same relationships to their complex conjugates. The order in energy of the different types of manifolds $M(\mathbf{k}_1)$, $M(\mathbf{k}_2)$, at the end points may necessitate contacts of inequivalent manifolds at intermediate points. And if either end point, say $\mathbf{k}_1$, has a G^{k_1} of which the G^k of the intermediate points is a subgroup, the types of manifolds at intermediate points which can connect with any $M(\mathbf{k}_1)$ can be determined group-theoretically, with due regard for the consequences of time-reversal symmetry.

[5] Approximate values for the energies of the different eigenfunctions at the center and corner of the B-Z can be obtained from J. C. Slater, Phys. Rev. **45**, 794 (1934), Fig. 1.

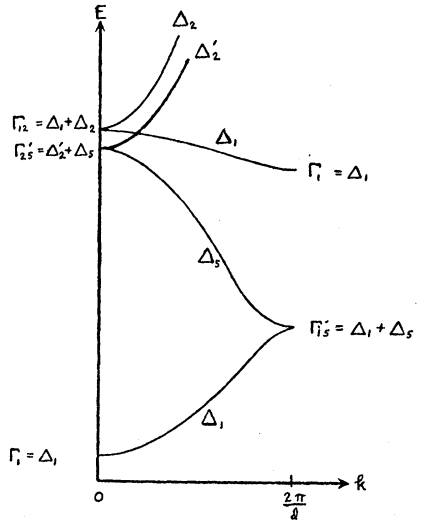

FIG. 1. The representations Δ_1, Δ_2, Δ_2', are one-dimensional, Δ_5 is two-dimensional.

Calculations made for more complicated metals show such contacts of inequivalent manifolds of eigenfunctions along axes of symmetry in the B-Z.[6] Naturally, however, not all such contacts which occur can be predicted from a knowledge of the energies of the different manifolds at the two ends of the axis.

3. Variation of Energy Near Contacts

If all the wave functions which have wave vector $\mathbf{k}$ and a single energy $E^i(\mathbf{k})$ are known, the neighboring energies of the wave functions which have a wave vector $(\mathbf{k}+\boldsymbol{\kappa})$ in the neighborhood of $\mathbf{k}$ can be determined to the first order in κ by perturbation theory. For, since any

$$\psi_k=\exp(i\mathbf{k}\cdot\mathbf{r})u_k$$

where u_k has the periodicities of the lattice,

$$\exp(-i\mathbf{k}\cdot\mathbf{r})H\psi_k=\{-\hbar^2/2m\nabla^2 -i\hbar^2/m\mathbf{k}\cdot\nabla+h^2k^2/2m+V\}u_k=E_ku_k \quad (1)$$

and the term $-i\hbar^2/m\boldsymbol{\kappa}\cdot\nabla$ can be treated as a perturbation. Eq. (1) holds when the Hamiltonian H is of the Hartree type; when we are interested in the solution of Fock's equations we must introduce the exchange operator $-A$

[6] H. M. Krutter, Phys. Rev. **48**, 664 (1935), (copper); Manning and Krutter, Phys. Rev. **51**, 761 (1937), (calcium).

into H, and this means that

$$-A_k = -\exp(-i\mathbf{k}\cdot\mathbf{r})A\exp(i\mathbf{k}\cdot\mathbf{r})$$

must be added to the operator in the brackets. There is then an added perturbation $-\boldsymbol{\kappa}\cdot\partial A_k/\partial\mathbf{k}$.

It will be convenient in the following to use the symbol $m^i(\mathbf{k})$ for the linear manifold spanned by the wave functions u_k which can be obtained by multiplying by $\exp(-i\mathbf{k}\cdot\mathbf{r})$ those wave functions ψ_k of $M^i(\mathbf{k})$ which have wave vector $\mathbf{k}$. If $M^i(\mathbf{k})$ and $M^j(\mathbf{k})$ have the same energy, the neighboring energies at $(\mathbf{k}+\boldsymbol{\kappa})$ are determined to within terms of the order of κ^2 by the solution of a secular equation involving the matrix elements of $i\nabla$ (for the Hartree case) in $[m^i(\mathbf{k}), m^j(\mathbf{k})]$.

When two wave functions $\psi_k{}^i$, $\psi_k{}^j$, and no more, have the same $\mathbf{k}$ and the same energy, the solution of the second order secular equation gives for the energy separation δE at $(\mathbf{k}+\boldsymbol{\kappa})$ of the two bands which come into contact at $\mathbf{k}$

$$\delta E(\mathbf{k}+\boldsymbol{\kappa}) = [(\boldsymbol{\kappa}\cdot\mathbf{f})^2+4|\boldsymbol{\kappa}\cdot\mathbf{g}|^2]^{\frac{1}{2}}+O(\kappa^2), \quad (2)$$

where the vectors $\mathbf{f}$ and $\mathbf{g}$ are defined, for the Hartree case, as

$$\begin{aligned}\mathbf{f} &= -i\hbar^2/m[(u_k{}^i, \nabla u_k{}^i)-(u_k{}^j, \nabla u_k{}^j)],\\ \mathbf{g} &= i\hbar^2/m(u_k{}^i, \nabla u_k{}^j),\end{aligned} \quad (3)$$

and for the Fock case are these quantities plus matrix elements of $\partial A_k/\partial\mathbf{k}$.

When the degeneracy at $\mathbf{k}$ is threefold it is less simple to give an explicit formula for the energies of the three bands at $(\mathbf{k}+\boldsymbol{\kappa})$. It is, however, possible in most cases to derive a criterion which will tell us whether, for a given direction of $\boldsymbol{\kappa}$, the separation of every pair of the bands is of the order of κ as $\kappa\to 0$, as in (A), Fig. 2, whether two of them have a separation of the order κ^2, as in (B), or whether all the separations are of the order κ^2, as in (C). To do this we start from the following fact:[7] if a third order secular equation $\det(H_{\mu\nu}-\lambda\delta_{\mu\nu})=0$ with $H_{\mu\nu}$ real and equal to $H_{\nu\mu}$ possesses two coincident roots $\lambda=\lambda_1$, then the equation obtained by setting to zero the minor of any element in $\det(H_{\mu\nu}-\lambda\delta_{\mu\nu})$ must have λ_1 as a root. Conversely if every minor has λ_1 as a root, the secular equation must have λ_1 as a double root, since in this case the derivative of the secular determinant with respect to λ will have λ_1 as a root. Now the condition that the minors of H_{12}, H_{13}, and H_{23} have the same root turns out to be the same as the condition that for $\mu\neq\nu=1, 2, 3$ the root of the minor of $H_{\mu\nu}$ be also a root of the minor of $(H_{\mu\mu}-\lambda)$. This condition is

$$\begin{aligned}H_{12}H_{13}H_{23}H_{11}-H_{12}{}^2H_{13}{}^2 &= H_{12}H_{13}H_{23}H_{22}\\ -H_{23}{}^2H_{12}{}^2 &= H_{12}H_{13}H_{23}H_{33}-H_{13}{}^2H_{23}{}^2.\end{aligned} \quad (4)$$

So when none of the three quantities H_{12}, H_{13}, H_{23} vanishes, the satisfaction of (4) implies that all minors of the secular determinant have a common root, and thus that the secular equation has a double root. When (4) is satisfied by virtue of the vanishing of two of the three nondiagonal elements, however, two of the nondiagonal minors vanish identically in λ. In this case it cannot be concluded that the principal minors have a root in common, since concerning one of the principal minors nothing more is known than that it has a root in common with a polynomial which vanishes identically. To insure that all the principal minors have a common root it will be sufficient to use the conditions that for μ, ν, σ all different and running from 1 to 3 the minor of $(H_{\mu\mu}-\lambda)$ have a root in common with that of $H_{\nu\sigma}$. These are

$$\left.\begin{aligned}&(H_{22}+H_{33})(H_{23}H_{11}-H_{13}H_{12})H_{23}\\ &\quad -(H_{23}H_{11}-H_{13}H_{12})^2\\ &\quad -H_{23}{}^2(H_{22}H_{33}-H_{23}{}^2)=0,\\ &\quad \text{Permutations of this}=0.\end{aligned}\right\} \quad (5)$$

Thus the satisfaction of (5) as well as (4) insures existence of a double root except in the trivial case where $H_{12}=H_{13}=H_{23}=0$.

In the present case the matrix elements $H_{\mu\nu}$ will be the matrix elements of $-i\hbar^2/m\boldsymbol{\kappa}\cdot\nabla$ or of $-i\hbar^2/m\boldsymbol{\kappa}\cdot\nabla-\boldsymbol{\kappa}\cdot\partial A_k/\partial\mathbf{k}$. The criteria (4), (5), will be applicable if a basis can be found in $[m^i(\boldsymbol{\kappa}), m^j(\mathbf{k})]$ with respect to which all these matrix elements are real.

In order to apply (2), (4) and (5) it is necessary to know what restrictions are placed on the matrix elements of the vector operator $i\nabla$, or of $\partial A_k/\partial\mathbf{k}$, by the fact that all the basis functions ψ_k are eigenfunctions of a real Hamiltonian H which has the symmetry of the crystal. These restrictions can be obtained in a straightforward manner from the fact that the three components

[7] Burnside and Panton, *Theory of Equations*, Vol. II, p. 66.

of the vector operator in question are pure imaginary operators plus the fact that they form a basis for a representation of the space group which is characterized by wave vector zero and which therefore is simply the point group representation for a polar vector. For the various cases which will be needed later on the most general forms consistent with the spatial and time-reversal symmetry restrictions, which the matrix elements of an imaginary Hermitian polar vector operator $\mathbf{F}$ can assume, are listed in Tables I to IV. The basic wave functions to which these matrix elements are referred have been chosen as follows:

All the basis functions have the same wave vector $\mathbf{k}$.

Each basis function is an eigenfunction of some operation in G^k, as is indicated explicitly in connection with each of the tables.

When an inversion J is present in the space group, the phases of the basis functions are so chosen that the operation JK takes each basis function into itself, K being the time-reversal operator which takes every function into its complex conjugate.

When no inversion is present but a twofold rotation C_2 or $\bar{C}_2$ is included among the operations $Q_{(k)0}$ which take $\mathbf{k}$ into a wave vector equivalent to $-\mathbf{k}$, the phases are to be so chosen that C_2K or $\bar{C}_2K$ takes each basis function into itself.

When neither an inversion nor a twofold axis is included among the $Q_{(k)0}$, the phases of the basis functions do not matter.

Table I gives the matrix elements of a vector operator $\mathbf{F}$ of the type described above in the subspace spanned by two wave functions $\psi_k{}^i$ and $\psi_k{}^j$. Each matrix element of $\mathbf{F}$ is a vector. In the first three rows the manifolds $M^i(\mathbf{k})$, $M^j(\mathbf{k})$, to which $\psi_k{}^i$, $\psi_k{}^j$, belong cannot be inequivalent; in the last two, however, the functions $\psi_k{}^i$, $\psi_k{}^j$, may be both even with respect to reflection in the plane of symmetry, both odd, or one even and one odd. The symbol listed first in each of the columns for $\mathbf{F}_{ij}$ refers to the case where both are even or both odd, the second symbol to the the case where one is even and the other odd. The symbol $\perp$ means that the vector in question must be perpendicular to the twofold axis (or perpendicular to the normal to the reflection plane) but is otherwise unrestricted. The symbol $\parallel$ means that the vector must be parallel to this axis. As in I, $\bar{C}_2$ stands for a twofold screw axis, and $\bar{S}_2$ stands for a glide plane. In the column headed "case" $M^i(\mathbf{k})$ and $M^j(\mathbf{k})$ are classified according to their time-reversal properties, as in Table I of I; some of the possibilities are however omitted from the present table.

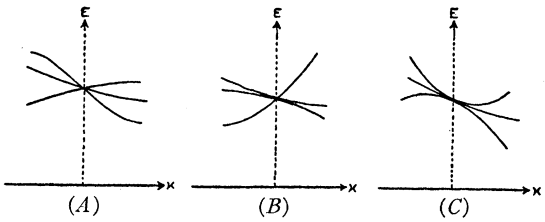

FIG. 2.

Tables II, III, and IV apply along various symmetry axes of the B-Z for simple, body-centered, and face-centered cubic crystals. An inversion is assumed to be present in the space group. Tabulated is the vector $(\psi_k{}^i, \mathbf{F}\psi_k{}^j)$ for the different possible representations of G^k to which $\psi_k{}^i$ and $\psi_k{}^j$ may belong. The notation for these representations is that of BSW. The quantities ρ are arbitrary real numbers, and the ϵ's are unit vectors. Table II is for points $\mathbf{k}$ on a twofold symmetry axis; here ϵ is parallel to the axis of C_2, ϵ_a is perpendicular to the axis of C_2 in the plane taken into itself by $JC_4{}^2$, and ϵ_b is perpendicular to the axis of C_2 and to ϵ_a. Table III is for points $\mathbf{k}$ on a threefold axis. It is supposed that one of the three symmetry planes JC_2 passing through the axis has been singled out; + and − refer, respectively, to eigenfunctions even and odd with respect to reflection in this plane; ϵ is parallel to the axis of C_3, ϵ_a is perpendicular to the axis of C_3 in the plane of the JC_2 selected, and ϵ_b is perpendicular to the axis of C_3 and perpendicular to the plane of the JC_2. Table IV is for points $\mathbf{k}$ on a fourfold axis. It is as before supposed that one of the two symmetry planes JC_2 containing the axis has been chosen; + and − refer to eigenfunctions even and odd with respect to reflection in this plane; ϵ is parallel to the axis of C_4, ϵ_a is perpendicular to the axis of C_4 in the plane of the JC_2 selected, and ϵ_b is perpendicular to the axis of C_4 and to the JC_2.

Table II, given for the representations Σ of the group possessed by points on a twofold axis inside the B-Z may be used also for the representations of the groups belonging to the general points S, Z, G, D, of lines in the boundaries of the B-Z of Figs. 2, 3, and 4 of BSW. The groups of Z and of D do not contain the same operations

as the other two; for these the ϵ's must be oriented relative to the corresponding symmetry planes.

From (2), (3), and the two last lines of Table I we can calculate δE for points in $\mathbf{k}$-space near a curve of contact of even and odd wave functions in a symmetry plane. When no inversion is present in the space group we may expect that as we go out from any point $\mathbf{k}$ of the contact curve the energy separation $\delta E(\mathbf{k}+\boldsymbol{\kappa})$ is of the order κ for any direction of $\boldsymbol{\kappa}$ not in the plane of symmetry. This is because it can safely be assumed that the real and imaginary parts of $\mathbf{g}$ do not vanish simultaneously at any point of the curve. When an inversion is present however the real part of $\mathbf{g}$ always vanishes, and since there will in general be points of the curve at which the imaginary part of $\mathbf{g}$ vanishes, we may expect sometimes to find points on the curve where $\delta E(\mathbf{k}+\boldsymbol{\kappa})$ is of the order κ^2 when $\boldsymbol{\kappa}$ is perpendicular to the plane. Whether an inversion is present or not, $\delta E(\mathbf{k}+\boldsymbol{\kappa})$ may be expected to be of the order κ when $\boldsymbol{\kappa}$ is in the plane and perpendicular to the curve.

For contact points on a symmetry axis where m^i and m^j are each one-dimensional we may expect that $\delta E(\mathbf{k}+\boldsymbol{\kappa})$ is always of the order κ when $\boldsymbol{\kappa}$ is not perpendicular to the axis, and when $\boldsymbol{\kappa}$ is perpendicular to the axis is of order κ^2 or κ according to whether the table requires $\boldsymbol{\kappa}\cdot\mathbf{g}$ to vanish or not. It may be noted too from (2), (3), and Table IV that at points near a fourfold axis the energy separation of two bands which stick together everywhere on the axis (representation Δ_5) is always of the order of the square of the distance from the axis; likewise, from Table III, the separation of two bands which stick together everywhere on a threefold axis (representation Λ_3) is of the order of the distance from the axis, except near points of the axis where $\bar{p}_{33}$ vanishes.

Table I.

$Q_{(k)0}$	Case	$\mathbf{F}_{ii}$ or $\mathbf{F}_{jj}$	Real Part $\mathbf{F}_{ij}$	Imaginary Part $\mathbf{F}_{ij}$
None (G^k the translation group alone)	(*b*)	Unrestricted	Unrestricted	Unrestricted
J	(*a*)	Unrestricted	Unrestricted	0
C_2 or $\bar{C}_2$	(*a*)	$\perp$	$\perp$	$\parallel$
C_2, J or $\bar{C}_2$, J	(*a*)	$\perp$	$\perp$, 0	0, $\parallel$
None (G^k the translation group plus S_2 or $\bar{S}_2$)	(*b*)	$\perp$	$\perp$, $\parallel$	$\perp$, $\parallel$

Consider finally the energy variation near contacts of Λ_3 with one of the other Λ's, or Δ_5 with one of the other Δ's. For a contact of Δ_5 with one of the other Δ's it is easily verified by use of Table IV with (4) and (5), or alternatively by solving the third order secular equation explicitly, that the energy separation of any pair of the three bands may be expected to grow proportionally to κ as we go out from a contact point $\mathbf{k}$ to $(\mathbf{k}+\boldsymbol{\kappa})$ (except when $\boldsymbol{\kappa}$ is in the direction of the axis). In other words, the situation is as in (*A*) of Fig. 2, for every direction of $\boldsymbol{\kappa}$ except along the axis. For a contact of Λ_3 with one of the other Λ's the secular equation obtained from Table III is more complicated, and since it cannot readily be solved explicitly, (4) and (5) must be used. The result is best described with reference to Fig. 3. The plane of the drawing is a plane through the contact point $\mathbf{k}$ and normal to the axis of C_3, and the three lines are the intersections of this plane with the three symmetry planes JC_2. When the projection of $\boldsymbol{\kappa}$ on the plane of the drawing points in one of the three directions shown by the full lines and the angle between $\boldsymbol{\kappa}$ and the axis of C_3 has a certain value θ, we may expect $\delta E(\mathbf{k}+\boldsymbol{\kappa})$ between one pair of the three bands to be of the order κ^2. We may also expect $\delta E(\mathbf{k}+\boldsymbol{\kappa})$ between a pair of the bands to be of the order κ^2 when the projection of $\boldsymbol{\kappa}$ on the plane of the drawing points in the direction of one of the dotted lines and the angle between the axis of C_3 and $\boldsymbol{\kappa}$ is $(\pi-\theta)$. Thus for these directions of $\boldsymbol{\kappa}$ the situation is as in (*B*) of Fig. 2; for all other directions of $\boldsymbol{\kappa}$, except along the axis, $\delta E(\mathbf{k}+\boldsymbol{\kappa})$ is on the order κ, and the situation is as in (*A*) of Fig. 2.

4. Contacts of Equivalent Manifolds

In this section it will be shown that situations exist in which two energy bands touch at general points in $\mathbf{k}$-space and cannot be separated by any perturbation, and some properties of contacts of this sort will be given. More precisely stated, it will be shown that the existence of wave vectors $\mathbf{k}$ for which the energy of some $M^i(\mathbf{k})$ coincides with the energy of some $M^j(\mathbf{k})$

TABLE II.

ψ^i \ ψ^j	Σ_4	Σ_3	Σ_2	Σ_1
Σ_1	$\rho_{14}\epsilon_a$	$\rho_{13}\epsilon_b$	0	$\rho_{11}\epsilon$
Σ_2	$\rho_{34}\epsilon_b$	$\rho_{23}\epsilon_a$	$\rho_{22}\epsilon$	
Σ_3	0	$\rho_{33}\epsilon$		
Σ_4	$\rho_{44}\epsilon$			

TABLE III.

ψ^i \ ψ^j	Λ_3 +	Λ_3 −	Λ_2	Λ_1
Λ_1	$\rho_{13}\epsilon_a$	$\rho_{13}\epsilon_b$	0	$\rho_{11}\epsilon$
Λ_2	$\rho_{23}\epsilon_b$	$\rho_{23}\epsilon_a$	$\rho_{22}\epsilon$	
Λ_3 −	$\bar{\rho}_{33}\epsilon_b$	$\rho_{33}\epsilon-\bar{\rho}_{33}\epsilon_a$		
Λ_3 +	$\rho_{33}\epsilon+\bar{\rho}_{33}\epsilon_a$	$\bar{\rho}_{33}\epsilon_b$		

TABLE IV.

ψ^i \ ψ^j	Δ_5 +	Δ_5 −	Δ_1'	Δ_2'	Δ_2	Δ_1
Δ_1	$\rho_{15}\epsilon_a$	$\rho_{15}\epsilon_b$	0	0	0	$\rho_{11}\epsilon$
Δ_2	$\rho_{25}\epsilon_b$	$-\rho_{25}\epsilon_a$	0	0	$\rho_{22}\epsilon$	
Δ_2'	$\rho_{2'5}\epsilon_a$	$-\rho_{2'5}\epsilon_b$	0	$\rho_{2'2'}\epsilon$		
Δ_1'	$\rho_{1'5}\epsilon_b$	$\rho_{1'5}\epsilon_a$	$\rho_{1'1'}\epsilon$			
Δ_5 −	0	$\rho_{55}\epsilon$				
Δ_5 +	$\rho_{55}\epsilon$	0				

equivalent to it is not a vanishingly improbable phenomenon in the sense of Section 1.

Consider first the case of a crystal without an inversion center. For simplicity the Hartree case only will be considered, as the reasoning proceeds identically in the Fock case. Suppose the potential $V(\mathbf{r})$ of such a crystal to have a form possessing a twofold axis of symmetry, but no other symmetries except its translational periodicities. Suppose further that at some point $\mathbf{k}$ on the axis the energy of the wave function unchanged by the twofold rotation crosses the energy of the wave function which changes sign on rotation. This is a perfectly possible state of affairs. By the same method as was used in constructing Tables I to IV it can be verified that the only restriction placed on the vectors $\mathbf{f}$ and $\mathbf{g}$ defined

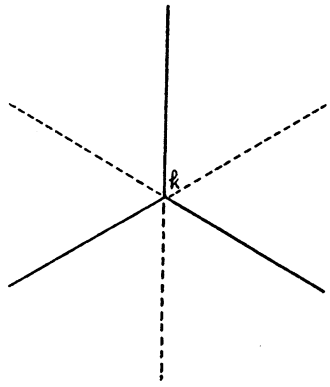

FIG. 3.

in (3) by the symmetry and reality of the Hamiltonian are that $\mathbf{f}$ must lie in the direction of the axis and the real and imaginary parts of $\mathbf{g}$ must be perpendicular to the axis. It will therefore certainly be permissible to assume that the three vectors $\mathbf{f}$, the real part of $\mathbf{g}$, and the imaginary part of $\mathbf{g}$ are not coplanar at the contact point $\mathbf{k}$, i.e., there will certainly exist potential functions $V(\mathbf{r})$ for which a contact occurs at a point on the axis where these vectors are not coplanar. Now let the potential be changed to a form possessing no symmetry at all except the translational periodicity, by addition of a term $vU(\mathbf{r})$. The function $U(\mathbf{r})$ is a fixed unsymmetrical periodic function, and v is an infinitesimal positive number. Treating this term as a perturbation we may calculate its effect on the energies of wave functions whose wave vectors are near to $\mathbf{k}$, by solving a second order secular equation. The result is similar to (2):

$$\delta E=\{[\delta E_0+v(U_{ii}-U_{jj})]^2+4|vU_{ij}|^2\}^{\frac{1}{2}}+R \quad (6)$$

where δE is $(E^i(\mathbf{k}')-E^j(\mathbf{k}'))$ after the perturbation, δE_0 is this quantity before perturbation, and where for sufficiently small v the remainder R satisfies $|R|<2Av^2$ with A independent of $\mathbf{k}'$ in the neighborhood of $\mathbf{k}$. All the quantities on both sides are to be evaluated at the same point $\mathbf{k}'$.

Suppose now that after the potential has been changed to $(V+vU)$ no contact occurs in the neighborhood of the original contact point $\mathbf{k}$. Then the energy separation δE must have a minimum at some point in the neigborhood of $\mathbf{k}$. It can be verified from (6) that the point at

which this minimum occurs must be one at which both the inequalities

$$|\delta E_0+v(U_{ii}-U_{jj})|<4Av^2, \quad |U_{ij}|<2Av \quad (7)$$

were satisfied. At this minimum after the perturbation the gradient of δE must be zero in every direction, i.e., $\mathbf{f}$ must vanish, and so $\mathbf{f}$ must be coplanar with the real and imaginary parts of $\mathbf{g}$. Now a necessary and sufficient condition that these three vectors be coplanar is that the lower bound of the quadratic form $(\boldsymbol{\kappa}\cdot\mathbf{f})^2+4|\boldsymbol{\kappa}\cdot\mathbf{g}|^2$ for all vectors $\boldsymbol{\kappa}$ of unit length and varying direction be zero. This lower bound depends only on the subspace $[u^i, u^j]$ and is independent of the choice of basis functions u^i, u^j within it. Before the perturbation this lower bound was not zero at $\mathbf{k}$, and since the subspace $[u_{k'}{}^i, u_{k'}{}^j]$ must vary in a continuous manner with $\mathbf{k}'$, there must be a finite neighborhood of $\mathbf{k}$ in which this lower bound was $>\epsilon>0$. It will therefore be possible, whatever the form of the function $U(\mathbf{r})$, to find a v small enough to insure that the lower bound of the quadratic form remains >0 after the perturbation at every point at which the inequalities (7) were satisfied. For such a small value of v the supposition that no contact occurs after the perturbation is therefore untenable: after the potential has been changed to the form $(V+vU)$ there is still a contact at some point near $\mathbf{k}$, and since the Hamiltonian no longer possesses any but translational symmetry, this contact is a contact of *equivalent* manifolds $M^i(\mathbf{k})$ and $M^j(\mathbf{k})$.

For a crystal with an inversion center a similar argument can be constructed, which need only be given in outline. Let a potential function possessing an inversion center and a symmetry plane be made into a potential function possessing an inversion center but no symmetry plane by addition of a small unsymmetrical perturbation vU. If a closed curve of contact of the even with the odd wave function in the symmetry plane exists before the perturbation, a closed curve of contact must persist after the perturbation, if the perturbation is sufficiently small. This is because if any portion of the curve disappeared there would have to have to be a whole line of points after the perturbation at which $\mathbf{f}$ practically vanished. It can be seen from the second line of Table I that this means that $\mathbf{f}$ and $\mathbf{g}$ must be practically collinear at these points, and this is impossible if these vectors were not collinear at the corresponding points of the curve of contact before the perturbation.

The preceding paragraphs, although they are not intended as complete proofs and leave unanswered numbers of questions which may come to mind, will, I hope, suffice to make plausible most of the theorems which will now be stated. The proofs of these are too lengthy to be given here;[8] they are based upon the type of perturbation considerations which have been used in this section and in the preceding one. The theorems are:

For crystals without an inversion center, contacts of equivalent manifolds $M^i(\mathbf{k})$, $M^j(\mathbf{k})$ may occur for isolated points $\mathbf{k}$, and such contacts cannot be destroyed by an infinitesimal change in the potential function V. Such contact points $\mathbf{k}$ may lie in a symmetry plane in the B-Z or in a plane perpendicular to a twofold axis, provided the representation of the space group in each of the manifolds $M^i(\mathbf{k})$, $M^j(\mathbf{k})$ is irreducible, i.e., provided case (*a*) occurs; in such case no infinitesimal change in V preserving the symmetry of the crystal can cause the contact point to move out of the plane. Except for this possibility, it is vanishingly improbable for a contact point to lie in a plane or line of symmetry in the B-Z.

For a crystal whose space group consists only of its translation group the total number of distinct points $\mathbf{k}$ of the B-Z at which the energies of two given bands i and j come into contact must be a multiple of four, i.e., any other number is vanishingly improbable. (Time-reversal symmetry requires that $-\mathbf{k}$ be a contact point if $\mathbf{k}$ is a contact point, hence merely that the number of contacts be a multiple of two; the restriction to multiples of four is therefore rather noteworthy.) Since any crystal of higher symmetry can be made into one of such low symmetry by an infinitesimal change in the form of the potential V, this implies a restriction on the number of contact points for any crystal without an inversion center.

[8] They are contained in a dissertation submitted to the faculty of the department of physics at Princeton University, 1937. The proofs are there given for the Hartree case, but may easily be generalized to the Fock case or to the frequency spectrum of normal modes of vibration.

For crystals with an inversion center, contacts of equivalent manifolds $M^i(\mathbf{k})$, $M^j(\mathbf{k})$ may occur at all points $\mathbf{k}$ of an endless curve, or of a number of such curves, in $\mathbf{k}$-space. These contact curves cannot be destroyed or broken by any infinitesimal change in the potential V which preserves the inversional symmetry. It is vanishingly improbable for such curves to lie in planes of symmetry in the B-Z; however a contact curve may pass through a symmetry axis at a point where necessary degeneracy or contact of inequivalent manifolds occurs.

Suppose that for a crystal with an inversion center a contact of inequivalent manifolds $M^i(\mathbf{k})$, $M^j(\mathbf{k})$ occurs at a point $\mathbf{k}$ on a symmetry axis, and suppose that $m^i(\mathbf{k})$ and $m^j(\mathbf{k})$ are each one-dimensional. Then if the vector $\mathbf{g}$ (proportional in the Hartree case to $(\psi_k{}^i, i\nabla\psi_k{}^j)$) does not vanish, a curve of contact must pass through $\mathbf{k}$. This curve may be a curve of contact of equivalent manifolds of the type just described, or it may be a curve of contact of inequivalent manifolds in a plane of symmetry. Naturally if there is no such symmetry plane in the space group, the former alternative must hold.

For a crystal whose space group consists only of its translation group plus an inversion, three types of contact curves may occur, which are most easily described when energy is considered as a trebly periodic function of wave vector in the infinite reciprocal lattice space. The first type is a simple closed circuit which is distinct from the circuit obtained from it by the inversion $\mathbf{k}\rightarrow-\mathbf{k}$. The second type is a simple closed circuit which either coincides with the inverse circuit or can be brought into coincidence with it by 2π times a translation of the reciprocal lattice. The third type is a curve extending periodically to infinity. Now consider any energy band i, and the band j next above it. For each of the eight distinct points $\mathbf{k}_r$ ($r=1$ to 8) of the B-Z whose G^{k_r} contain the inversion let the numbers $N^+(\mathbf{k}_r, i)$, $N^-(\mathbf{k}_r, i)$, of odd and of even eigenfunctions $\psi_{k_r}{}^l$ be counted which have energies $E^l(\mathbf{k}_r) \leqslant E^i(\mathbf{k}_r)$. Now the quantity

$$\tfrac{1}{2}\sum_{r=1}^{8}[N^+(\mathbf{k}_r, i)-N^-(\mathbf{k}_r, i)]$$

is an integer, and according to whether this integer is odd or even the number of circuits of the second type along which contact between the bands i and j occurs must be odd or even. Since any crystal with an inversion center can be made by an infinitesimal change in the form of V into one whose space group is merely its translation group plus the inversion, this implies certain restrictions on the numbers of contact curves which may occur for crystals of higher symmetry. Prediction of the existence of curves of contact of equivalent manifolds may therefore be possible from a knowledge merely of the energies of the different $M^l(\mathbf{k}_r)$ at the eight points $\mathbf{k}_r$.

For a crystal without an inversion center, the energy separation $\delta E(\mathbf{k}+\boldsymbol{\kappa})$ in the neigborhood of a point $\mathbf{k}$ where contact of equivalent manifolds occurs may be expected to be of the order of κ as $\kappa\rightarrow 0$, for all directions of $\boldsymbol{\kappa}$.

For a crystal with an inversion center, the energy separation $\delta E(\mathbf{k}')$ at a point $\mathbf{k}'$ near a curve of contact of equivalent manifolds may be expected to be of the order of the distance of $\mathbf{k}'$ from the curve.

All kinds of contacts of equivalent manifolds except the ones described above are vanishingly improbable. In particular, the occurrence of isolated points of contact of equivalent manifolds for crystals with an inversion center is vanishingly improbable.

I should like to express my gratitude to Professor E. Wigner for his interest in this work, and to Dr. L. P. Bouckaert and Dr. R. Smoluchowski for some interesting discussions.