AUGUST 15, 1937 PHYSICAL REVIEW VOLUME 52

Effect of Time-Reversal Symmetry on Energy Bands of Crystals

CONYERS HERRING
Princeton University, Princeton, New Jersey

(Received June 16, 1937)

In the Hartree and Fock approximations the description of the electronic state of a crystal can be made in terms of one-electron wave functions and one-electron energies, which have a band structure. It is known that in addition to the "sticking together" of these energy bands caused by the spatial symmetry of the crystal, additional "sticking" may be necessitated by the fact that the Hamiltonian of the problem is real. In this paper a criterion is developed to facilitate calculation of when and how such additional degeneracy will occur. The consequences of the reality of the Hamiltonian are tabulated for a number of cases. It is pointed out that the same "sticking together" of bands occurs in the theory of the frequency spectrum of the normal modes of vibration of a crystal.

SINCE much of the work now being done on the electron theory of metals is based on the theory of Brillouin zones, i.e., on the picture of almost free electrons or on the Hartree approximation with or without corrections for exchange, it is desirable that the properties of the wave functions and energy values occurring in this type of approximation be clearly understood. An important one of these properties, namely the "sticking together" of energy bands because of the symmetry of the crystal, has recently been discussed by Bouckaert, Smoluchowski, and Wigner.[1] Additional coincidences in the energies of different wave functions are sometimes necessitated by the fact that the Hamiltonian of the problem is real, as these authors have also noted. It has been shown by Hund[2] that for close-packed hexagonal crystals important coincidences in the energies of wave functions with the same wave vector are necessitated by this reality property. We may class as "accidental" any coincidences in the energies of different wave functions with the same wave vector which are not attributable either to the symmetry or to the reality of the Hamiltonian. In this paper a general theory of coincidences due to the reality of the Hamiltonian will be presented; accidental coincidences will be taken up in the following paper.

In Hartree's equations for a crystal the one-electron wave functions ψ_i satisfy

$$(-\hbar^2/2m\nabla^2+V)\psi_i=E_i\psi_i,$$

where $V(\mathbf{r})$ is the potential of the positive nuclei plus the potential due to the charge distribution of all the electrons. The function $V(\mathbf{r})$ has all the periodicities and symmetries of the lattice. In Fock's equations the ψ_i satisfy

$$(-\hbar^2/2m\nabla^2+V-A)\psi_i=E_i\psi_i,$$

where V is as above and A is the Fock exchange operator. It is not hard to show that solutions of Fock's equations exist for which the operators V and A have all the periodicities and symmetries of the given lattice of nuclei, and for which the operator A as well as V is real, i.e., takes every real wave function into a real wave function. Let us restrict ourselves to the consideration only of those solutions of Fock's equations for which V and A possess the symmetry and reality just mentioned. Now all the considerations to be made below apply to the eigenfunctions and eigenvalues of any real Hamiltonian operator commuting with the space group of the crystal. The results of this paper will therefore apply to the one-electron ψ_i and E_i occurring in the solution of Hartree's or of Fock's equations.

As is well known, the wave functions of an electron moving in the trebly periodic force field of a crystal can be taken to be eigenstates of the three fundamental translations of the crystal lattice, and as such may be written in the form $\psi_k=\exp(i\mathbf{k}\cdot\mathbf{r})u_k$, where u_k is a periodic function of position with the three periodicities of the lattice. This equation leaves $\mathbf{k}$ undetermined by 2π times any translation of the reciprocal lattice; the shortest vector $\mathbf{k}$ with which a given wave function can be written in this form is called the

---

[1] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).

[2] F. Hund, Zeits. f. Physik **99**, 119 (1936).

"reduced wave vector" of the wave function, or in the following simply its "wave vector." The set of all vectors $\mathbf{k}$ having the property that no vector of shorter length can be reached from any of them by adding a vector 2π times a translation of the reciprocal lattice will cover the interior and surface of a polyhedron called the first Brillouin zone, for which the abbreviation B-Z will be used hereafter. Any point $\mathbf{k}$ on the surface of the B-Z is reachable from one or more other points $\mathbf{k}'$ of the surface of the B-Z by 2π times a translation of the reciprocal lattice, and it will be convenient to speak of any function $\exp(i\mathbf{k}\cdot\mathbf{r})u_k$ as possessing the same wave vector as another function of the form $\exp(i\mathbf{k}'\cdot\mathbf{r})u_{k'}$; i.e., two wave functions will be said to possess the same wave vector when they have the same eigenvalues of the operations of the translation group of the crystal.

In the following the terms "linear manifold" and "subspace of Hilbert space" will be used synonymously to denote the set of all linear combinations of any given basic set of wave functions, and the set of all linear combinations of the wave functions of several linear manifolds will be called the "subspace spanned by" these manifolds. The symbol (ψ_1, ψ_2) will be used for the scalar product $\iiint \psi_1^*\psi_2 d\tau$ of any two wave functions ψ_1 and ψ_2.

The coincidences among the energies of the various eigenfunctions which are due to the reality of the Hamiltonian of any problem have been discussed by Wigner.[3] These coincidences, as well as those due to the spatial symmetry of the Hamiltonian, turn out to be connected with the properties of the various representations of the spatial symmetry group of the Hamiltonian, which for the present problem is the space group of the crystal. Some mathematical theorems on the irreducible representations of space groups have been given by Seitz.[4] From references 1, 3, and 4 the following facts may be noted:

The set of all operations of the space group which take every wave function characterized by a particular wave vector $\mathbf{k}$ into the same or another wave function with the same wave vector forms a subgroup G^k of the space group, which may be called the "group of the wave vector." If one forms the subspace of Hilbert space spanned by a manifold σ^k of wave functions with wave vector $\mathbf{k}$ which reduces G^k together with the $(M-1)$ other manifolds into which σ^k is transformed by the operations of the space group, this subspace will be transformed irreducibly into itself by the whole space group. The set of wave vectors occurring in an irreducible representation of the space group may be referred to as the "star" of the representation.

For all wave vectors $\mathbf{k}$ except those lying in certain planes, lines, or isolated points in the B-Z, the group G^k consists only of the translation group, so that for a particular $\mathbf{k}$ all representations of G^k are equivalent and one-dimensional. For wave vectors lying in certain planes but avoiding certain lines and points, G^k may consist of the translation group plus a reflection or glide plane operation. Further symmetry elements, leading to the existence of multidimensional representations of G^k, may be present when $\mathbf{k}$ terminates on certain lines or assumes certain isolated values.

The conclusions of Wigner are based on the fact that whenever the Hamiltonian of a problem is real, the complex conjugate of any eigenfunction is also an eigenfunction with the same energy. The operation of taking the complex conjugate is to be interpreted as an operation which takes a wave function employed by one observer to describe some state of the system into a wave function which could be employed to describe the same physical state by an observer whose space axes coincide with those of the first, but whose time axis is oppositely directed. Wigner shows that if in any linear manifold of eigenfunctions the representation of the spatial symmetry group of the Hamiltonian is irreducible and equivalent to a representation by means of real matrices only, then the wave functions of the manifold will, in general, have an energy different from the energies of all other wave functions; an irreducible manifold the representation in which cannot be made real must however always have the same energy as the complex conjugate manifold, which will be linearly independent of it and in which the representation D^* of the symmetry group may be either equivalent or inequivalent to the original representation D.[5]

It will be convenient to have a criterion by which from a knowledge of the combination laws of the group elements and their characters in any irreducible representation it can be decided whether that representation is inequivalent to its complex conjugate, is equivalent but cannot be made real, or can be made real. Such a criterion can be obtained by using a theorem first proved by Frobenius and Schur.[6] This theorem states that if D is any irreducible representation of a finite group G, of order N, and if $\chi_D(R)$ is the character in D of the group element R, then

---

[3] E. Wigner, Gött. Nachr. (1932), p. 546.

[4] F. Seitz, Ann. of Math. **37**, 17 (1936).

[5] These statements are valid when, as in the present case, the wave function does not contain spin. When spin is included the time-reversal operation takes a more complicated form.

[6] Frobenius and Schur, Berl. Ber. (1906), p. 186.

$$\left.\begin{array}{rl}\sum \chi_D(T^2)=N & \text{if } D \text{ is equivalent to a representation by means of real matrices,}\\ =0 & \text{if } D \text{ and } D^* \text{ are inequivalent,}\\ =-N & \text{if } D \text{ is equivalent to } D^* \text{ but not to any representation consisting entirely of real matrices.}\end{array}\right\}(1)$$

The summation in (1) is to be extended over all elements T of G. The first possibility will from now on be referred to as case (a), the second as case (b), and the third as case (c).

To apply this result to any space group let the space group be replaced by a group containing the same elements with the same combination rules except that the νth power of any translation operation is the identity. This group has only a finite number of elements, so that the summation on T in (1) can be carried out. If, as is usually done, the representation space is made to consist of all wave functions which are unchanged when displaced by ν times any fundamental translation, all representations of the space group will be identical with corresponding representations of the finite group. Any element of the group which belongs to the coset defined by any Q_0 into the translation group is of the form $Q_i=Q_0t_i$ where t_i is some operation of the translation group. So the element $Q_i^2=Q_0^2(Q_0^{-1}t_iQ_0)t_i$ belongs to the coset defined by Q_0^2. The summation over all elements Q_i of the group may be broken up into a summation on t_i and a summation over the different cosets, which may be labeled by the corresponding point group operations Q. If a basis is chosen reducing the translation group,

$$\sum_{Q_i}\chi_D(Q_i^2)=\sum_{\mathbf{k},\,\mu}\sum_{Q}\sum_{\mathbf{t}_i}[\psi_{k\mu},\, Q_0^2 \times\exp\left(-i\mathbf{k}\cdot(Q\mathbf{t}_i+\mathbf{t}_i)\right)\psi_{k\mu}],$$

where the operation t_i replaces the vector $\mathbf{r}$ by $(\mathbf{r}-\mathbf{t}_i)$ and where μ labels the different basis functions when two or more have the same wave vector $\mathbf{k}$. The summation on $\mathbf{k}$ is, of course, over all wave vectors in the star of D. Now

$$\begin{aligned}\sum_{\mathbf{t}_i}\exp\left(-i\mathbf{k}\cdot(Q\mathbf{t}_i+\mathbf{t}_i)\right)=\sum_{\mathbf{t}_i}\exp\left(-i(Q^{-1}\mathbf{k}+\mathbf{k})\cdot\mathbf{t}_i\right)&\\ =0 \quad \text{if } Q^{-1}\mathbf{k}\neq-\mathbf{k}+2\pi\mathbf{g},&\\ =\nu^3 \quad \text{if } Q^{-1}\mathbf{k}=-\mathbf{k}+2\pi\mathbf{g},&\end{aligned}$$

where $\mathbf{g}$ is any translation of the reciprocal lattice. Also, since all the vectors of the star are similar, all terms in the summation on $\mathbf{k}$, which is to be carried out last, are equal. So if h is the order of the macroscopic symmetry group and M the number of distinct wave vectors in the star of D, (1) becomes

$$\sum_{Q}\sum_{\mu}(\psi_{k\mu},\, Q_0^2\psi_{k\mu})=\pm h/M \quad\text{or}\quad 0, \qquad (2)$$

where in the summation on Q only those point group operations Q are to be included which take $\mathbf{k}$ into a vector equivalent to $-\mathbf{k}$, and where Q_0 may be any single space group operation belonging to the coset corresponding to Q. Only one wave vector $\mathbf{k}$ of the star is to be used. The steps in applying (2) are thus:

TABLE I.

Q_0	RELATION D TO D^*
J	(a)
$\underline{C}_2$	(a)
$\bar{C}_2$	(a), (c)
$\underline{C}_2$, J	(a)
$\bar{C}_2$, J	(a), (b)

Determine an irreducible representation of G^k.

Select those operations Q of the point group of the crystal which take $\mathbf{k}$ to a vector equivalent to $-\mathbf{k}$.

To each of the operations Q so chosen, there will correspond a coset in the space group; from each such coset choose an operation Q_0 of the space group arbitrarily.

Evaluate the character of each Q_0^2 in the irreducible representation of G^k, and sum over the different Q_0's. Then, according to whether the result is h/M, 0, or $-h/M$, case (a), (b), or (c) obtains for the irreducible representation D of the space group of which the above irreducible representation of G^k is a part.

When $\mathbf{k}$ is a general point of the B-Z, G^k is the translation group, and if an operation Q is present taking $\mathbf{k}$ to a wave vector equivalent to $-\mathbf{k}$, it can only be the inversion. In such case Q_0^2 is the identity, and the positive sign must occur in (2). So for the general point of the B-Z either D and D^* have different stars or else D can be made real; time-reversal symmetry never causes the energies of two wave functions with the same wave vector $\mathbf{k}$ to coincide when $\mathbf{k}$ is a general point of the B-Z.

Consider next what can happen when $\mathbf{k}$ is a general point of some plane in the B-Z, so that every operation Q which takes $\mathbf{k}$ to a point equivalent to $-\mathbf{k}$ takes any other point $\mathbf{k}'$ of this plane into one equivalent to $-\mathbf{k}'$. The only point operations Q which can take every point of

TABLE II.

Q	RELATION D TO D^*
J, $2S_6$	(a) or (b)
J, $2S_6$, $2S_3$, S_2	(a) or (b)
S_2, $2S_3$	(a) or (b)
$2S_4$	(a) or (c)
J, S_2, $2S_4$	(a) or (b)
$2C_2$, $2S_4$	(a) or (b)

a plane into a point equivalent to its inverse are the inversion J and the rotation C_2 about a twofold axis perpendicular to the plane. If no such operation is present D and D^* must of course be inequivalent with different stars. When D and D^* have the same star their relationship is easily verified to be as given in Table I. The first column contains the coset representatives, one for each point group operation taking **k** to a vector equivalent to $-\mathbf{k}$. All representations of the space group belonging to the star of **k** are of the type denoted by the letter in the second column. In the third and last lines the first letter refers to the case where **k** is in a plane inside the B-Z, the second to the case where **k** is in a boundary plane. The symbols J, C_2 stand, respectively, for an inversion and a pure rotation through π about some axis. The symbol $\bar{C}_2$ is used for a twofold screw axis of such nature that no operation $\bar{C}_2 t$ of the same coset as $\bar{C}_2$ is a pure twofold rotation without an accompanying translation.

Table I shows therefore that: first, if a boundary plane of the B-Z is perpendicular to a twofold screw axis no element of whose coset is a pure twofold rotation, then the energy bands must stick together in pairs at the points of this plane; secondly, under no other circumstances do the symmetry and reality of H require that two eigenfunctions with the same wave vector **k** have the same energy when **k** is a general point of a plane of symmetry.

When **k** is a general point of a line of symmetry there are so many possibilities for the constitution of the group G^k that it is not convenient to list them all. When **k** is an interior point of the B-Z, however, the situation is rather simpler than when the line of which **k** is a general point lies in a boundary plane of the B-Z. For such an interior point it is not difficult to find out whether representations of types (b) or (c) can occur. Consider one of the terms $(\psi_{k\mu}, Q_0{}^2\psi_{k\mu})$ occurring in (2). If this is not to equal $+1$, then either $Q^2 \neq E$, i.e., the square of the point group operation Q is not the identity, or else $Q_0{}^2 = t$, where t is a translation in a direction not perpendicular to **k**. The second possibility is excluded by the fact that Q takes any vector in the direction of **k** into one in the opposite direction (if **k** were a point on the boundary of the B-Z this would not have to be the case). Now it is easily verified that the only operations Q which occur in any of the crystalline point groups and which have the properties, first, that $Q^2 \neq E$, and secondly, that there exists a direction in space taken into the opposite direction by Q, are the following:

$$Q = S_4, \text{ giving } Q^2 = C_2,$$
$$Q = S_6 \text{ or } S_3, \text{ giving } Q^2 = C_3.$$

Here C_2 and C_3 stand for two- and threefold proper rotations, and S_3, S_4, and S_6 for three-, four-, and sixfold rotations followed by reflection in a plane perpendicular to the axis of rotation. It is easily established that when **k** is a general point of a line of symmetry inside the B-Z the positive terms in (2) must always overbalance the complex and negative terms, except in the six cases listed in Table II. This means that if **k** is a point of this type whose star contains $-\mathbf{k}$, all representations of the space group belonging to this star are of type (a) unless the set of point operations Q taking **k** to $-\mathbf{k}$ is exactly one of the sets listed. In all the cases listed some of the representations having the star of **k** are of type (a) and some are of one of the other types; for this reason (a) is always included in the second column.

It can be seen that for all the rows of Table II except the last G^k is cyclic. So we can say that when **k** lies along a three-, four-, or sixfold axis, only case (a) can occur if G^k is not cyclic, i.e., only case (a) can occur if a reflection plane passes through the axis. Further, if the space group contains an inversion, only case (a) can occur if **k** is along a twofold axis.

In conclusion it should be pointed out that the results listed above have consequences not only for the electronic energy spectrum of the crystal, but also for the frequency distribution of its normal modes of vibration. For it can be shown that the normal modes of a crystal correspond to 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 **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.

AUGUST 15, 1937 PHYSICAL REVIEW VOLUME 52

Accidental Degeneracy in the Energy Bands of Crystals

CONYERS HERRING
Princeton University, Princeton, New Jersey

(Received June 16, 1937)

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 **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 **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).