SOLID STATE PHYSICS

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Advances in
Research and Applications

Editors

FREDERICK SEITZ
Department of Physics
University of Illinois
Urbana, Illinois

DAVID TURNBULL
General Electric
Research Laboratory
Schenectady, New York

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Contributors to Volume 1

H. Y. FAN, *Department of Physics, Purdue University, Lafayette, Indiana*

FRANK S. HAM,* *Department of Physics, University of Illinois, Urbana, Illinois*

TOSHINOSUKE MUTO, *Institute of Science and Technology, University of Tokyo, Tokyo, Japan*

DAVID PINES, *Palmer Physical Laboratory, Princeton University, Princeton, New Jersey*

JOHN R. REITZ, *Case Institute of Technology, Cleveland, Ohio*

FREDERICK SEITZ, *Department of Physics, University of Illinois, Urbana, Illinois*

YUTAKA TAKAGI, *Tokyo Institute of Technology, Tokyo, Japan*

EUGENE P. WIGNER, *Department of Physics, Princeton University, Princeton, New Jersey*

* *Present address:* Research Laboratory, General Electric Company, Schenectady, New York.

Articles Planned for Future Volumes

Preface

The knowledge of solid state physics has grown tremendously since 1940. This growth has occurred on an international scale and perhaps has been more rapid, in relation to the 1940 effort, than that in most other major fields of physics. Although this growth of solid state physics has not been characterized by radical changes in basic physical theory, it has greatly extended the theory and the understanding of its implications. Also, the viewpoints and activities in certain closely allied fields, particularly in electronics, metallurgy, crystallography, and chemistry of solids, have been influenced markedly by developments in solid state science.

As a result of this expansion in knowledge solid state physicists are finding that, in order to make significant contributions, it is necessary to concentrate their efforts in narrower fields than formerly. Because of this specialization it is desirable that a mechanism exist whereby investigators and students can readily obtain a balanced view of the whole field. Also, it would be very helpful to workers in allied fields if the results of solid state science, pertinent to their activity, were readily available. However, the descriptions of solid state developments are widely dispersed in many journals so that it is difficult to obtain a broad and unified picture of the field. Although excellent short texts have appeared recently, many scientists have come to recognize the need for an up-to-date treatise on solid state science that reviews comprehensively all of the important facets of the subject. The purpose of the present series is to fulfill this need, at least in part, by publication of compact and authoritative reviews of the important areas of the field.

The editors and publishers hope that it will be possible to publish most of the basic reviews in about a dozen volumes. The plan of publication selected is similar to that used in the "Advances" series covering various other scientific fields. Well qualified scientists, many of whom are in the early years of professional life, will prepare articles on parts of the field that seem ripe for presentation. Three general types of articles are solicited: (1) broad elementary surveys that have particular value in orienting the advanced graduate student or an investigator having little previous knowledge of the subject; (2) broad surveys of fields of advanced research that serve to inform and stimulate the more experienced investigators; (3) more specialized articles describing important new techniques, both experimental and theoretical. It is planned that the authorship be international even though the articles will be written in English.

It would be desirable to publish the articles in a more highly organized sequence than that which actually will be followed. However, it appeared that an ideally organized presentation sequence could not be adhered to without serious delays in publication. Therefore, the actual selection of articles for a given volume results from compromise between considerations such as timeliness of the subjects, availability of authors, and interrelation of subject matter.

The volumes will be published semiannually for a period of time. It is hoped that this publication rate will be sufficient to fulfill, in a reasonable period, the pressing need for a survey and to insure that individual articles will not be subjected to long publication delays. After a few years it is expected that the volumes will be published annually.

A list of articles in prospect for future volumes is given on page vii. It will be noted that the concentration of theoretical articles is much greater in the first than it is planned to be in later volumes. Actually it proved easier to initiate the series by directing requests primarily to theoretical physicists since their work is usually more amenable to general presentation at any given time. It is intended that the over-all content of the series will stress the experimental as well as the theoretical aspects of the field.

The editors are deeply indebted to many colleagues for valuable advice during the period of formulation of the series. We owe particular thanks to Dr. Conyers Herring.

August 1, 1955   Frederick Seitz
                                                 David Turnbull

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Methods of the One-Electron
Theory of Solids

John R. Reitz

Case Institute of Technology, Cleveland, Ohio

I. Introduction

This chapter has been written in an attempt to consolidate the methods developed during the past fifteen years for calculating electron wave functions and electronic structures in solids. For the sake of completeness, much of the early (pre-1940) work that is basic to the new developments is also presented, although not always in as much detail as its importance merits.[1] Except for Part III, which gives a brief historical survey of the one-electron formulation, no attempt has been made to preserve the chronological sequence of developments in this field; instead, each technique is discussed independently and as a unit. The emphasis here is on method, the brief applications to actual solids serving for the purpose of illustration.

We are concerned here with an approximate method for solving the Schrödinger equation for a system which contains a large number of interacting particles, such as is encountered in a crystalline solid. We restrict the investigation to the case of a perfect crystal, and further, we neglect effects that arise from the motion of atomic nuclei, that is, it is assumed that the nuclei are at rest at fixed positions in the crystal lattice. Thus, the nuclear coordinates enter the problem only as parameters. Having defined the problem as a purely electronic one, we are still left with a many-electron problem which cannot be solved explicitly, and thus we must resort to some approximate treatment for handling the Schrödinger equation.

One of the most fruitful methods devised for the solution of many-electron problems is the *one-electron formulation*, in which the total wave

[1] For a review of the early work on this subject, the reader is referred to F. Seitz, "Modern Theory of Solids." McGraw-Hill, New York, 1940.

function for the system of electrons is chosen to be a combination of functions, each of which involves the coordinates of only one electron. It is this approximation which forms the basic framework for calculating electronic wave functions in solids. Equivalently, the method may be described by saying that each electron sees, in addition to the potential of the fixed charges, only some average potential due to the charge distribution of the other electrons, and moves essentially independently throughout the system.

By means of this approximation, then, the solution of the many-electron problem is reduced to (1) finding the equations to be satisfied by the one-particle wave functions, and (2) finding accurate solutions to these equations for the electronic system under consideration. Part II of this chapter will deal with the first of these problems, and the rest of the chapter will be devoted to methods for solving one-electron equations in crystals.

The one-electron scheme has been applied to atoms, molecules, and crystalline solids. In the case of solids, with which we are primarily interested here, this scheme is the only one which has successfully related electronic structure of the solid to crystal structure; since it is essentially the only method available to us at the present time, it is important to know what errors, if any, are inherent in its use. This is particularly important because the one-electron equations cannot, in general, be solved precisely, and one would like to know whether the difference between the calculated and experimental values of the energy of the system is due to inadequate solution of the one-electron equations, or actually arises from the fundamental approximation which is used. Unfortunately this is a problem which cannot be resolved completely at present, and we must rely, for a test of the approximation, upon the detailed comparison of various one-electron results with experiment. It should be mentioned, however, that there are other considerations which support the one-electron point of view. This general problem will be discussed in Section 4; for the present, suffice it to say that the validity of the one-electron scheme is assumed. We shall see how far we can go toward explaining the properties of perfect crystals.

II. The Fock Equation

Let us consider a system of N interacting electrons which we may assume represents a crystal. The system is completely specified if we know the total electronic wave function of the system,

$$\Psi(\mathbf{q}_1, \mathbf{q}_2, \cdots \mathbf{q}_N),$$

where $\mathbf{q}_i$ represents the coordinates of the ith electron including its spin coordinate. We shall assume that Ψ is normalized. If we let $\mathcal{H}$ represent

the Hamiltonian operator for the system, the energy of one of the stationary states is given by the integral

$$E = \int \Psi^* \mathcal{H} \Psi d\tau_1 d\tau_2 \cdots d\tau_N,$$

where $\int d\tau_i$ represents an integration over the space coordinates and a summation over the spins of the ith electron. Now the energy integral is stationary with respect to arbitrary variations of Ψ which leave the normalization of Ψ unchanged; if we perform the variation using the method of undetermined multipliers, we obtain in the usual way the Schrödinger equation,

$$\mathcal{H}\Psi = E\Psi.$$

We are not concerned with the most general variation in Ψ, however; but restrict ourselves to the case where Ψ can be represented by a combination of one-electron functions, $\varphi_i(\mathbf{q}_1)$. Let us replace Ψ in the energy integral by a suitable combination of the φ_i; we may then make independent variations in Ψ by varying each of the φ_i individually. If we vary one of the one-electron φ's, e.g. φ_j, we obtain the Schrödinger equation to be satisfied by φ_j. Thus, the condition that the energy integral be stationary, with respect to arbitrary variations in the φ_i, is that each φ_j satisfy a certain Schrödinger equation; if we have chosen the proper antisymmetrical combination of φ_i, this equation will be the Hartree-Fock or Fock equation for the orbital φ_j.

1. DERIVATION OF THE FOCK EQUATION

We have thus far merely outlined the variational procedure to be used in finding the Schrödinger equations to be satisfied by the one-electron wave functions. In order to carry it out, we must specify Ψ as a function of the φ_i, and, further, must specify the Hamiltonian for the system. The simplest combination of φ_i's which might be used is the product function

$$\Psi = \varphi_1(\mathbf{q}_1)\varphi_2(\mathbf{q}_2) \cdots \varphi_N(\mathbf{q}_N); \tag{1.1}$$

this function, unfortunately, does not satisfy the Pauli exclusion principle, for it is not antisymmetric in the interchange of electrons. The antisymmetric function which may be constructed from the φ_i was shown by Slater[2] to be the determinantal function,

$$\Psi = \begin{vmatrix} \varphi_1(\mathbf{q}_1) & \varphi_1(\mathbf{q}_2) & \cdots & \varphi_1(\mathbf{q}_N) \\ \varphi_2(\mathbf{q}_1) & \varphi_2(\mathbf{q}_2) & \cdots & \varphi_2(\mathbf{q}_N) \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \varphi_N(\mathbf{q}_1) & \varphi_N(\mathbf{q}_2) & \cdots & \varphi_N(\mathbf{q}_N) \end{vmatrix}, \tag{1.2}$$

[2] J. C. Slater, *Phys. Rev.* **34,** 1293 (1929).

in which the individual φ_i are elements. The correct symmetry properties of Ψ are evident from the properties of determinants, since the process of interchanging two columns, which reverses the sign of Ψ, corresponds to the interchange of two electrons. In addition, the determinant vanishes when any two φ_i are identical. Hence, the Pauli principle is automatically satisfied by (1.2). It may be shown from the principles of group theory[3] that (1.2) is the only antisymmetrical combination of the φ_i.

The function (1.2) is not normalized when the φ_i are normalized, and, thus, (1.2) must be multiplied by a constant. The normalization constant usually depends upon the choice of the φ_i, but it is particularly simple in the case where they are orthogonal to each other, namely, $(N!)^{-\frac{1}{2}}$. Since a substantial simplification in the energy integral,

$$E = \int \Psi^* \mathcal{H} \Psi d\tau_1 d\tau_2 \cdots d\tau_N, \tag{1.3}$$

results when the one-electron wave functions are orthogonal, we shall impose this condition. This does not place any important restriction on the φ_i, because, even if we start with a nonorthogonal set of one-electron functions, we may convert them to an orthogonal set before proceeding. This problem will be discussed in more detail later; for the present, we assume the φ_i orthonormal.

It is convenient to consider each φ_i as constructed from a space function $\psi_i(\mathbf{r}_1)$ and a spin function $\eta_i(\boldsymbol{\zeta}_1)$, namely,

$$\varphi_i(\mathbf{q}_1) = \psi_i(\mathbf{r}_1)\eta_i(\boldsymbol{\zeta}_1), \tag{1.4}$$

where $\mathbf{r}_1$ represents the space coordinates of particle one and $\boldsymbol{\zeta}_1$ its spin coordinate. We shall assume in the following discussion that the η_i are normalized eigenfunctions of the z component of the spin; they may be labeled as "spin-up" or "spin-down," the two functions being mutually orthogonal. Hence, the ψ_i are themselves orthogonal and normalized.

The requirement that the φ_i form an orthonormal set may be written

$$\int \varphi_i^*(\mathbf{q}_1)\varphi_j(\mathbf{q}_1)d\tau_1 = \delta_{ij} \tag{1.5}$$

where the integration implies a summation over the two values of spin variable as well as a space integration. The total wave function Ψ may then be written symbolically

$$\Psi = (N!)^{-\frac{1}{2}} \det |\varphi_i(\mathbf{q}_j)| \tag{1.6}$$

where, by this expression, we mean the normalized determinant in (1.2).

In setting up the Hamiltonian $\mathcal{H}$ for our crystal problem, it is expedient to make certain simplifications from the start. We assume that all

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[3] E. P. Wigner, "Gruppentheorie." Vieweg, Braunschweig, Germany, 1931.

the electrons may be divided into two classes: (1) the inner electrons which belong to closed shells and may be regarded as rigidly attached to the nuclei, and (2) the outer electrons whose wave functions are appreciably affected by changes in interatomic distances, and which, therefore, contribute to the binding energy of the solid. The latter class certainly includes the valence electrons and may, in some cases, include the outermost closed shell of electrons in each atom as well. Where we draw the line between inner and outer electrons depends upon the solid under consideration; certainly the more electrons per atom included in the second group, the higher the ultimate precision which can be expected from the calculation.

It will be assumed that the effect of the rigidly bound electrons on the outer electrons can be expressed in terms of a potential function; thus, each nucleus and its rigidly attached unit of electrons produces an ion-core potential for the rest of the system. The system of electrons representing our crystal is now defined, more explicitly than it was at the beginning of this section, as an assembly of N outer electrons interacting with each other and with a group of M fixed rigid ion cores.

The Hamiltonian operator for the system just described may be written

$$\mathcal{H} = \sum_i^N \left(-\frac{\hbar^2}{2m}\Delta_i + V_i \right) + \frac{1}{2}\sum_{i,j}^N{}' \frac{e^2}{r_{ij}} + I, \tag{1.7}$$

where the indices i and j are to be summed over all N electrons, Δ_i is presumed to operate on the coordinates of the ith electron, and V_i is the potential energy of the ith electron in the field of all M ion cores. Since e^2/r_{ij} is the Coulomb interaction of the ith and jth electron, the terms $i = j$ are excluded from the second summation in (1.7); this is indicated in the usual way by a prime on the summation. Finally, I is a constant which represents the interaction of the rigid ion cores with each other. We need not, at this time, specify an explicit form for I, but if the division into inner and outer electrons has been carried out properly, the ion cores overlap to a negligible amount, and since, in addition, they consist of spherically symmetric charge distributions,

$$I = \frac{1}{2}\sum_{\alpha,\beta}^M{}' \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}}, \tag{1.8}$$

where $Z_\alpha e$ is the asymptotic charge of ion α. The self-energy of the ion cores need not be included in (1.7) since it is essentially the same in the solid and in free atoms, and, thus, drops out of the cohesive energy. It

should be noted that both V_i and I depend upon the crystal structure of the solid, in that they contain the internuclear distances parametrically.

We are now in a position to reduce the energy integral (1.3) which, in terms of the determinantal function discussed in the preceding section, has become:

$$E = (N!)^{-1}\int \det |\varphi_{k'}*(\mathbf{q}_m)|\mathfrak{K} \det |\varphi_k(\mathbf{q}_n)|d\tau_1 \cdots d\tau_N. \qquad (1.9)$$

Since the Hamiltonian (1.7) is a linear operator, the contribution to E from each term in $\mathfrak{K}$ may be considered separately. It is convenient to define

$$\mathfrak{K}_i \equiv -(\hbar^2/2m)\Delta_i + V_i. \qquad (1.10)$$

Let us first consider the contribution from one of the $\mathfrak{K}_i$, e.g. from $\mathfrak{K}_j$. The integral,

$$(N!)^{-1}\int \det |\varphi_{k'}*(\mathbf{q}_m)|\mathfrak{K}_j \det |\varphi_k(\mathbf{q}_n)|d\tau_1 \cdots d\tau_N, \qquad (1.11)$$

can easily be evaluated if we recall the basic properties of determinants. Each of our determinants has $N!$ terms and each term is a product of N factors. Furthermore, no two factors in a given term come from the same row, nor do they come from the same column of the determinant. Thus, $\mathfrak{K}_j$ operates on one $\varphi_k(\mathbf{q}_j)$ in each term. Because of the orthogonality relationship between the φ_k, the contribution to (1.11) will vanish unless all the factors in a term from $\det |\varphi_{k'}*|$ are identical (except for complex conjugate signs) to the factors in a given term from $\det |\varphi_k|$; this will be true for only one term in $\det |\varphi_{k'}*|$ for each term in $\det |\varphi_k|$. A term from the determinant is either positive or negative, but the product of identical terms from each determinant is always positive. Using the fact that the φ_k are normalized, we can perform all of the one-particle integrals except those involving particle $\mathbf{q}_j$; then, (1.11) is reduced to a sum of $N!$ one-particle integrals which have the form $\int\varphi_k*(\mathbf{q}_j)\mathfrak{K}_j\varphi_k(\mathbf{q}_j)d\tau_j$. Since the φ_k enter the determinant symmetrically, we expect the same contribution from each φ_k, and may thus write the $N!$ terms making up (1.11) as

$$(N!)^{-1}(N-1)! \sum_k^N \int \varphi_k*(\mathbf{q}_j)\mathfrak{K}_j\varphi_k(\mathbf{q}_j)d\tau_j. \qquad (1.12)$$

All of the $\mathfrak{K}_i$ are identical, except that they operate on different particle coordinates, $\mathbf{q}_i$. The integrals in (1.12) do not depend on $\mathbf{q}_j$ because this is merely an integration variable. Thus, each $\mathfrak{K}_i$ gives the same contribution to the energy, namely, (1.12), and the total contribution from $\Sigma\mathfrak{K}_i$ may be written as

$$\sum_k^N \int \varphi_k*(\mathbf{q}_1)\mathfrak{K}_1\varphi_k(\mathbf{q}_1)d\tau_1. \qquad (1.13)$$

The second summation in the Hamiltonian (1.7) may be handled in a similar fashion. Again we consider the contribution to the energy integral term by term, but where $\mathfrak{IC}_i$ operated on the coordinates of one particle only, we now have $(\frac{1}{2})e^2/|\mathbf{r}_i - \mathbf{r}_j|$, which involves the coordinates of two electrons. Thus, for each term in the summation, there are *two* terms in det $|\varphi_{k'}{}^*|$ for *each* term in det $|\varphi_k|$ which give nonvanishing contributions. For the sake of brevity, we shall skip over the detailed arguments here, and merely state the result; the total contribution from $(\frac{1}{2})\Sigma e^2/r_{ij}$ to the energy integral is

$$\frac{1}{2}\sum_{k,k'}^{N}{}' \left[\int |\varphi_k(\mathbf{q}_1)|^2 (e^2/r_{12}) |\varphi_{k'}(\mathbf{q}_2)|^2 d\tau_1 d\tau_2 \right.$$
$$\left. - \int \varphi_k{}^*(\mathbf{q}_1)\varphi_{k'}{}^*(\mathbf{q}_2)(e^2/r_{12})\varphi_k(\mathbf{q}_2)\varphi_{k'}(\mathbf{q}_1)d\tau_1 d\tau_2 \right]. \quad (1.14)$$

The first term in the brackets has an obvious interpretation. Since $|\varphi_k(\mathbf{q}_1)|^2$ is the probability density that particle 1 will be found at the coordinate $\mathbf{q}_1$, this term is the Coulomb interaction of two electrons having one-electron wave functions, φ_k and $\varphi_{k'}$. This interaction energy is then summed over all electron pairs. The summation arising from the second term in brackets in (1.14) has a less obvious interpretation; it is called the *exchange energy* of the electron system and is a direct result of having used the determinantal wave function. It is readily seen from (1.14) that only electron pairs with parallel spin contribute to the exchange term

The energy integral (1.3) has now been reduced to a summation of one- and two-particle integrals which involve orthonormal one-electron wave functions:

$$E = \sum_{k}^{N} \int \varphi_k{}^* \mathfrak{IC}_1 \varphi_k d\tau_1 + \frac{1}{2}\sum_{k,k'}^{N}{}' \int |\varphi_k(\mathbf{q}_1)|^2 (e^2/r_{12}) |\varphi_{k'}(\mathbf{q}_2)|^2 d\tau_1 d\tau_2$$
$$- \frac{1}{2}\sum_{k,k'}^{N}{}' \int \varphi_k{}^*(\mathbf{q}_1)\varphi_{k'}{}^*(\mathbf{q}_2)(e^2/r_{12})\varphi_k(\mathbf{q}_2)\varphi_{k'}(\mathbf{q}_1)d\tau_1 d\tau_2 + I. \quad (1.15)$$

It is to be noted that the primes may be dropped from the last two summations in this equation without affecting E, since the two additional terms (for which $k = k'$) are just equal and opposite. Equation (1.15) may be used to calculate the total energy of a solid (within the approximation discussed above) in terms of the one-electron solutions, φ_k. The summations are over the occupied electronic states. Of more interest to us at the present time, however, is the fact that the one-electron equations to be satisfied by the φ_k may, themselves, be derived from (1.15) by means of the variational principle.