

PLANE WAVE METHOD WITH A MODIFIED POTENTIAL FIELD

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A new method is developed for the determination of the energy band spectrum of metal electrons. An essential advantage of the method is that it applies plane waves. This is made possible by the introduction of a "repulsive" potential, which takes care of the high kinetic energy of the eigenfunction oscillating in the neighbourhood of the nuclei. Thus the valence electrons can be treated as if they filled the Brillouin zones gradually from the lowest Brillouin zone. This also means that in this model the eigenfunctions of the metal electrons can be well approximated by the linear combination of a few plane waves. The number of the rows and columns of the secular equations arising at the degenerate points in the neighbourhood of the boundaries of the Brillouin zones is low. The problems associated with the repulsive potential in the matrix components of the secular equation are investigated in detail. It is shown that these matrix components are such that they do not alter the qualitative structure of the secular equation. The value of the matrix components of the Hamiltonian varies in the Brillouin zone from place to place. This fact considerably increases the numerical work as compared to the older free-electron model. As compared to the newer methods, however, this disadvantage, is not peculiar to the method presented here as they, although for other reasons, also involve tedious numerical work.

Introduction

In the electronic theory of solids the quantitative determination of the energy spectrum presents a very important problem, a satisfactory solution of which has up to now been obtained only for a few metals. The method of WIGNER and SEITZ [1] is simple and yields good results for the lower edge of the energy band of metal electrons. However, the generalization of this method given by SLATER [2] can be applied to alkali metals only, because, as was shown by SHOCKLEY [3], the method involves an error, which makes the qualitative results doubtful already for the upper edge of the highest filled band. Although the recent extension of the method by LACE and BETHE [4] increased the accuracy it also involved a considerable increase in work. Another method by SLATER [5] is easier to apply to higher energies, but it is very tiresome. The method described in the present paper is a generalization of GOMBÁS's [6] method and is based partly on the statistical theory. Thus it can be well used, particularly for the treatment of heavier metals and can be regarded as a natural supplement to HERRING's method [7] which is mainly applicable to lighter metals. The chief advantage of the method to be described is that it proceeds on a mathematically well prepared way and is thus easy to apply.

1. Electronic structure of solids and the valence electrons

If we want to draw a comparison between the electrons of free atoms and those of solids (excluding solids, which contain transition elements) we have to classify them into two main groups, namely 1. the core electrons, which form a noble gas like $(ns)^2 (np)^6$ or a $(nd)^{10}$ shell and exhibit to good approximation, an identical distribution in the free atom and in the solid. 2. the valence electrons, the possible energy values of which in the stationary states of the free atom show the characteristic distribution of a discrete spectrum. In the solids the energy of the same electrons have a band spectrum. A further essential difference between the two groups is that whereas in solids for the core electrons the grouping according to the orbital quantum number can be regarded as a good approximation just as for the core electrons in the free atom, no definite orbital quantum number can be assigned in solids (in good approximation) to the valence electrons apart from some exceptional cases. The physical reason for this is the following. In solids it is a common property of the electrons that in principle none of them belongs to a definite atom, they wander from atom to atom. The essential difference between the core electrons bound in the inner shell and the valence electrons is that the density maximum of the former is in the neighbourhood of the nucleus and thus the probability for these electrons to approach a "foreign" atom is small. For the valence electrons the outer density maximum is in the region midway between the atoms and thus they cannot be localized around an atom not even for a short period. One of the consequences of the properties mentioned here is that the electrons in the inner shells keep the quantum numbers assigned to them in the atom in the solid too and these play an essential role in the description of their eigenfunctions, while for valence electrons these quantum numbers may have but symbolic significance if any. The classification of the core electrons according to the orbital quantum number plays an important role in the statistical theory of metallic bond and thus it is absolutely necessary to investigate how the theoretical determination of the energy band spectrum of valence electrons can be carried out with regard to this fact.

In most solids, owing to the high constancy of the potential field, the eigenfunctions of valence electrons can be described by few plane waves in the $7/8$ th of the elementary cell. In the $1/8$ th of the cell around the nucleus the eigenfunctions of valence electrons have nodal surfaces and oscillate intensely, which is due to their orthogonality to the eigenfunctions of the electrons of the ionic core. This intense oscillation increases the kinetic energy and thus the total energy (the sum of the kinetic and potential energies) is comparatively great ensuring that the valence electrons remain in the very high-lying valence band. Thus it can be seen that the region around the ionic core, which is at equilibrium nuclear distance about $1/8$ th of the elementary cell is very signi-

ficant. If the energetical conditions of the valence electrons of solids are to be treated the above mentioned increase of the kinetic energy must be taken into account. Here we restrict ourselves to the cases where the initial eigenfunctions are plane waves. This condition ensures namely that the eigenfunction with any arbitrary wave number vector can be set up readily and besides in 7/8 th of the elementary cell already the zeroth approximation yields excellent values. In this connection we may refer to two methods, that of orthogonalized plane waves developed by HERRING and the one to be developed here, which is not orthogonalized, i. e. it works with simple plane waves, but investigates the motion of electrons in a modified potential field. As in the construction of the modified potential field the classification of electrons according to their orbital quantum numbers plays an important role, we shall investigate the behaviour of an electron represented by a plane wave from the point of view of classification according to the orbital quantum number.

Be the eigenfunction of the electronic state in a space of volume Ω

$$\psi_{\mathbf{k}} = \frac{1}{\Omega^{1/2}} e^{i(\mathbf{k} \cdot \mathbf{r})} \quad (1)$$

with the wave number vector \mathbf{k} , and the kinetic energy of this electron

$$E = \frac{1}{2} |\mathbf{k}|^2, \quad (2)$$

where \mathbf{r} is the radius vector. There exists a close relation between the plane wave (1) and the spherical harmonics occurring in the classification of electrons in the centrally symmetrical potential field of the free atom. The plane wave can thus be expanded in a series

$$\psi_{\mathbf{k}} = \frac{e^{i(\mathbf{k} \cdot \mathbf{r}_n)}}{\Omega^{1/2}} \sum_{l=0}^{\infty} (2l+1) i^l j_l(kr) P_l(\cos \vartheta) \quad (3)$$

[8]; $r = |\mathbf{r} - \mathbf{r}_n|$, ϑ and φ are polar coordinates around the n -th nucleus as centre and have an axis parallel to the direction of \mathbf{k} . $k = |\mathbf{k}|$, \mathbf{r}_n is the radius vector drawn to the n -th nucleus, $P_l(x)$ is a Legendre polynomial and

$$j_l(x) = \left(\frac{\pi}{2x} \right)^{1/2} J_{l+\frac{1}{2}}(x); \quad (4)$$

$J_{l+\frac{1}{2}}(x)$ is a Bessel polynomial. From (3) we obtain after multiplication by the conjugate complex and averaging over all possible values of the ϑ

and φ the weight of the electrons of orbital quantum number l at a distance r from the nucleus

$$a_l = \frac{4\pi}{\Omega} (2l + 1) j_l^2(kr). \quad (5)$$

Or, by introducing the normalized probability a'_l corresponding to the assumption $\sum_l a'_l = 1$ we obtain

$$a'_l = (2l + 1) j_l^2(kr). \quad (5')$$

Fig. 1 shows the probabilities a'_l plotted as functions of kr . It is clear that a

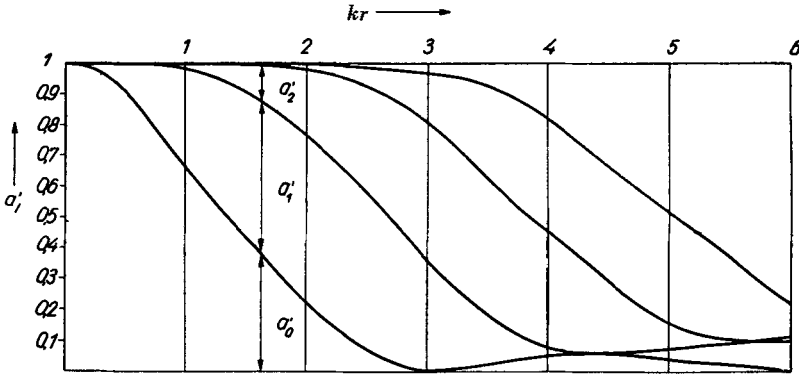


Fig. 1. The quantities a'_l occurring in the expansion of the plane wave in terms of spherical harmonics. The quantities in the figure are given in atomic units

small values of kr the s states prevail, whereas at places near the edge of the elementary cell, especially at higher values of the wave number vector, the states of higher orbital quantum numbers predominate.

2. General characteristics of the matrix elements of operators in the valence electron states in solids

The most important problem of the electronic theory of solids is the determination of the energy spectrum. With the aid of the latter the other data can be obtained by direct methods. To determine the energy spectrum the average values and matrix elements, respectively, of the operators must be evaluated. We now want to discuss the problems associated with these.

The situation is the simplest in the cases where the operator to be averaged over is spherically symmetrical around each of the nuclei, i. e. it depends on r only (the potential energies are mostly of this kind, e. g. the Coulomb interaction with the nucleus, the average field of the other electrons etc.). In such

a case averaging over the angles can be carried out immediately and the matrix elements can be obtained by a single integration over r [9].

A more difficult case is where the operator also depends on the angles and contains just the differential operators with respect to these angles. An operator of such a type is e. g. that of the kinetic energy and that of the square of the total angular momentum. Consider a prototype of such operators in detail. Be our operator, which we denote for brevity by κ , defined by the equation

$$\kappa = \begin{cases} M^2, & \text{if } r \leq R, \\ 0, & \text{if } r > R, \end{cases} \quad (6)$$

where

$$M^2 = \hbar^2 \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right]$$

is the operator of the square of the total angular momentum. Thus the operator essentially is one of the square of the total angular momentum within a sphere of radius R , whereas outside this sphere it is the operator of the multiplication by the constant 0. Let us form the average value of the operator κ over a sphere of radius r_0 ($R < r_0$). [In the theory of solids this sphere is as a rule the so-called elementary sphere (see later)]. With (6) and (3) we obtain

$$\bar{\kappa} = \sum_l A_l \hbar^2 l(l+1), \quad (7)$$

where

$$A_l = \frac{3\pi}{4} \frac{2l+1}{kr_0} \left(\frac{R}{r_0} \right)^2 \left\{ J_{l+\frac{1}{2}}^2(kR) - J_{l-\frac{1}{2}}(kR) J_{l+\frac{3}{2}}(kR) \right\}. \quad (8)$$

In the detailed examination of the weight factors A_l we take into account the dependence of the wave number factor on r_0 . As the wave number vectors are defined in the reciprocal lattice, we may write

$$k = \frac{b}{r_0}, \quad (9)$$

where b under the normal conditions is a number of the order of 1. With the aid of (9) (8) may be written in the form

$$A_l = \frac{3\pi}{4} \frac{2l+1}{b} \left(\frac{R}{r_0} \right)^2 \left\{ J_{l+\frac{1}{2}}^2\left(b \frac{R}{r_0}\right) - J_{l-\frac{1}{2}}\left(b \frac{R}{r_0}\right) J_{l+\frac{3}{2}}\left(b \frac{R}{r_0}\right) \right\}. \quad (10)$$

It is obvious that (10) can be regarded as a function of the quantities $b \frac{R}{r_0} = y$ and b , where b solely depends on the type of lattice and the place

occupied by the valence electrons in the band but does not depend on the lattice constant. The dependence of A_l on the lattice constant as well as on the radius R in the definition of the operator κ is involved in y . In Fig. 2 the so-called normalized A'_l 's are exhibited in accordance with the representation of Fig. 1. The normalization was carried out in such a way that

$$\sum_l A'_l(y) = 1.$$

Thus we only want to know how the ratios of the s, p, d, f, g, \dots -states vary,

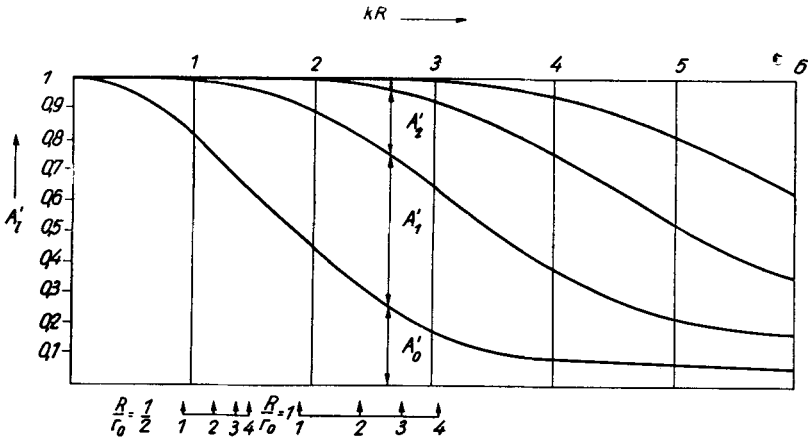


Fig. 2. The auxiliary quantities A'_l necessary for the determination of the matrix element for the operator κ . The quantities in the figure are given in atomic units

for the time being the variation of the absolute value of the weight factors not investigated. Accordingly

$$A'_l = \frac{3\pi}{4} \frac{2l+1}{y} \left\{ J_{l+\frac{1}{2}}^2(y) - J_{l-\frac{1}{2}}(y) J_{l+\frac{3}{2}}(y) \right\}, \quad (11)$$

which is already a function of y only.

Under the Figure there are several scales with arrows showing the places corresponding to various values of b at various values of R/r_0 . The arrows marked 1, 2, 3 etc. indicate the radii of the Fermi sphere at 1, 2, 3 etc. electrons per atom. It is clear that at lower values of R/r_0 the weight of the states of lower orbital quantum numbers (mainly that of the s -state) are great. This is very important from the point of view of the repulsive potentials because (see later) these take values different from zero only within the ionic core, which is a region of small radius near the nucleus. R , which can be defined in connection with the repulsive potentials, is smaller than $r_0/2$, which

makes it plausible that the weight of these states greatly increases. This was confirmed in the case of the Al metal [10] that carrying out the calculation associated with the metallic bond, even with the aid of an s type repulsive potential, results not very different from the experimental data were obtained.

3. The free electron method and the difficulties involved

In principle the theory of the electronic structure of solids [11] can be developed simplest by building up the total eigenfunctions of metal electrons of plane waves of the form

$$\psi = e^{i(\mathbf{k}\mathbf{r})}, \quad (12)$$

where \mathbf{k} is the wave number vector of a free electron. In the periodic potential field

$$V = \sum_{\substack{h_1, h_2, h_3 \\ =-\infty \\ +\infty}} V_{\mathfrak{h}} e^{2\pi i(\mathfrak{h}, \mathbf{r})} \quad (13)$$

the eigenfunction of an electron can be written in the form

$$\psi = \sum_{\substack{h_1, h_2, h_3 \\ =-\infty \\ +\infty}} a_{\mathfrak{h}} e^{i[(\mathbf{k} + 2\pi\mathfrak{h}), \mathbf{r}]}. \quad (14)$$

In (13) and (14)

$$\mathfrak{h} = h_1 \mathfrak{b}_1 + h_2 \mathfrak{b}_2 + h_3 \mathfrak{b}_3 \quad (15)$$

is the lattice vector of the reciprocal lattice and $\mathfrak{b}_1, \mathfrak{b}_2, \mathfrak{b}_3$ are the basic vectors determining the axes of this lattice. The eigenfunction ψ satisfies the Schrödinger equation

$$\Delta\psi + \frac{2m}{\hbar^2} (E - V) \psi = 0, \quad (16)$$

if the $a_{\mathfrak{g}}$ -coefficients satisfy the homogeneous linear equations

$$\left[E - V_{000} - \frac{\hbar^2}{2m} |\mathbf{k} + 2\pi\mathfrak{g}|^2 \right] a_{\mathfrak{g}} = \sum_{\mathfrak{h}} a_{\mathfrak{g}-\mathfrak{h}} V_{\mathfrak{h}}. \quad (17)$$

(17) has a solution only if the determinant which can be formed from the coefficients vanishes. The determinantal equation thus provides a defining equation for E which so far is unknown; the solution of this equation thus immediately gives the energy of the electron belonging to the wave number vector \mathbf{k} . Inserting the value of E into (17) and solving this equation for the $a_{\mathfrak{h}}$ coefficients we obtain the unknown coefficients of the eigenfunction. In

the course of the actual determination of the energy eigenvalue we cannot of course take all Fourier coefficients V_g into account but have to select those the order of magnitude of which is relevant for the secular equation. According to (17) those Fourier coefficients for which the condition

$$E_{2\pi g} - E_0 \gg |V_g| \quad (18)$$

is fulfilled can be neglected. In (18)

$$E_{2\pi g} = \frac{\hbar^2}{2m} |2\pi g|^2 + V_{000}. \quad (19)$$

For metals occurring in nature $E_{2\pi g} - E_0 \sim 20eV$, when for g its smallest possible value is taken into account. If the potential is the potential of the ionic core and that of the valence electrons without any repulsive potential then there are many Fourier coefficients V_g the order of magnitude of which agrees with that of $E_{2\pi g} - E_0$ and thus the free electron method in this form is not suitable for the determination of either the energy or the eigenfunction.

Let us consider the real reason for the inapplicability of the method in some more detail. Retaining in the system of equations (17) but a few coefficients, (the largest of them), the smallest root of the secular equation gives a rough approximate value for the energy of the valence electrons. Taking more and more coefficients into account the lowest root of the secular equation does not approximate the energy of a valence electron but that of a core electron of smaller energy, while the energy of valence electrons is approximated by a larger root of the secular equation. Thus the above formulation of the problem is too general, demanding, that the method yield the energy and eigenfunctions of the core electrons too. This is, however, not necessary at all, since we already know these to an accuracy satisfactory for our purpose. The excessive generality of the method becomes still more obvious if the situation is examined from the standpoint of eigenfunctions. The assumption of the eigenfunction in the form (14) is based on the assumption that the approximate eigenfunction can be well approximated at least partly by plane waves. This is the case for electrons in the valence band and in the conduction bands. For the core electrons, however, the case is essentially different. The eigenfunction of the core electron keeps its atomic character and is no plane wave, it is exponential far from the nucleus and oscillates inside near him. To approximate such an eigenfunction by plane waves is of course very difficult and most of the difficulties associated with the method treated above are due to this fact. The solution is obvious: the method has to be modified so as to be applicable to valence electrons and conduction electrons only, which are interesting for us in any case.

Let us now proceed to investigate the eigenfunctions of valence and conduction electrons in some more detail. As has been mentioned above the eigenfunction of these electrons can be well approximated by a plane wave in the greater part (about 85%) of the elementary cell, as there the potential is constant. Significant deviation from the plane wave eigenfunction can only be experienced in the immediate neighbourhood of the nucleus where the eigenfunction begins to oscillate just like the atomic eigenfunctions. What is the immediate reason for this? In this region the potential changes very rapidly and near the nucleus tends to infinity as Ze/r . Owing to the smallness of the average value taken over this region the potential energy of the electron is very small (its absolute value is very large). The valence electron is in a state of higher energy; this is made possible by the average value of the operator of the kinetic energy taken in the inner region for the oscillating part of the eigenfunction. The situation can be described in this way if the energy relations are considered only in a formal manner.

It is due to the Pauli principle that the electrons in the atom occupy states of higher and higher energies. It has to be considered in detail how the difficulties associated with the eigenfunction can be overcome, if the kinetic energy increase due to the Pauli principle is taken explicitly into account.

4. Reduction of the problem to the treatment of valence and conduction electrons

As has been shown above the most obvious solution of the problems would be to eliminate the core electrons from our treatment and to simplify our method to such an extent that it becomes suitable but for the treatment of valence and conduction electrons only. As the eigenfunctions of the core electrons are practically the same for the free atom and the solid, these could, if necessary, be used for the above simplification.

For this simplification several methods present themselves. Among these we mention those which aim at the correction of the plane wave. HERRING orthogonalized the plane waves to the eigenfunctions of the core electrons and achieved thus the appropriate behaviour of the eigenfunctions in the neighbourhood of the nucleus; further the orthogonality secures the necessary smallness of the matrix components of the potential energy. The second possible method was suggested by SLATER [13]. The essence of the method is to retain the plane wave far from the ionic core and to replace it inside a sphere of radius R around the nucleus by the linear combination of core electron solutions having the energy of the plane wave. Whereas HERRING's method has already been tried out in the theoretical treatment of several metal and semiconductor SLATER's method has not been applied yet.

Both these methods require an essential modification of the plane wave eigenfunction in order that the matrix components satisfy relation (18). This results in the loss of the most desirable property of the older methods, their comparatively simple structure and easiness to handle. We shall attempt to modify the free electron method in such a manner which makes possible to start from the plane wave eigenfunctions of the free electrons when treating the valence and conduction electrons.

The solution of the problem is made possible by the fact that for the valence and conduction electrons a modified potential field can be given

$$V' = V + \Phi, \quad (20)$$

which possesses several important properties.

1. The operator Φ in (20) is such that if the density and the wave function of the core electrons of the free atom are given, the operator can immediately be determined with their aid.

2. The average value of the potential field taken over not too small regions does not, in the regions near the nucleus, significantly decrease below the average value over the regions far from the nucleus. In this connection we may refer to our investigations into the binding and electronic structure of the K metal [9].

3. Consequently, the eigenfunctions of the valence and conduction electrons can be well approximated by plane waves all over the sphere (including the 1/8 th part of the volume around the nucleus).

5. Introduction of the repulsive potential and the total potential

For the calculation of atomic term values and for the treatment of monovalent metals a certain form of the repulsive potential has been used for a long time, the kinetic energy increase due to the Pauli principle having been taken into account in the form of a potential energy [6]. The potential of this energy is

$$\Phi_l = -\gamma_0 (\varrho^{2/3} - \varrho_l^{2/3}) \quad (21)$$

In (21) ϱ is the total electron density of the ionic core and ϱ_l the density of the electrons which occupy states of energy lower than that of the lowest possible energy of the electron to be treated, l is the orbital quantum number of this electron and $\gamma_0 = \frac{1}{2} (3\pi^2)^{2/3} e a_0$ is a constant. As has been shown by some recent investigations [14] the modified potential field obtained with the aid of (21) yields good approximation only if the outermost closed shell of

the ionic core is an $(ns)^2 (np)^6$, a so-called noble gas like shell. According to GOMBÁS the repulsive potential

$$\Phi_l' = - \frac{\pi^2 e a_0}{8 (2l + 1)^2} D_l^2 - \frac{1}{4} \frac{e a_0}{r^2} \quad (22)$$

is correct not only for noble gas like ionic cores, but it is correct for other ones, e. g. for a closed $(nd)^{10}$ core. In (22) D_l is the radial density of the electrons with the orbital quantum number l of the ion and e is the charge of the proton. a_0 is the first Bohr hydrogen radius.

The above repulsive potentials (21) and (22) were introduced with the aid of statistical methods. Several authors have dealt with their wave-mechanical foundations [15].

To a good approximation the atomic electrons move in a central symmetrical potential field and as a result the states of these electrons can be characterized by the magnitude of the total angular momentum and one of its components, i. e. by the orbital and magnetic quantum numbers. Accordingly the repulsive potentials vary with these quantum numbers of the electrons. In solids the central field remains for the electrons of the ionic cores a good approximation i. e. it remains practically the same as in the free atom and thus the form of the repulsive potentials remains as given by the expressions (21) and (22). However, we want to characterize the metal electrons by plane waves and for these the momentum and not the angular momentum is well defined. It is thus necessary to replace the repulsive potential by an operator which can be applied to an arbitrary eigenfunction and leads in the special case of atoms to the former well proved form. Be the operator Φ diagonal in the system of spherical harmonics and its eigenvalues the repulsive potentials (21) and (22) respectively, i. e.

$$\Phi Y_l^m = \Phi_l(r) Y_l^m, \quad (23)$$

where Y_l^m is the spherical harmonic with indices l and m . It is certain that operator Φ is hermitic as its eigenvalues are real. Assuming that it is linear too, it can be written in the form

$$\Phi(r, \vartheta, \varphi) = \frac{1}{c_l^2} \Phi_l(r) M^2, \quad (24)$$

where M^2 is the operator of the square of the total angular momentum and $c_l^2 = \hbar^2 l(l + 1)$ is its eigenvalue. Thus in the case of atoms operator Φ leads to the same repulsive potentials as the selection according to orbital quantum numbers. For a valence electron, as will be shown later, it can be well applied

too. The author has already used the operator Φ for investigations on the binding of the Al metal [10] and the results obtained were in good agreement with experiment.

To set up the total potential is a very delicate task, as the first term of expression (20) is composed of several parts

$$V = V_c^{\text{ion}} + V_{\text{ex}}^{\text{ion}} + V_{\text{korr}}^{\text{ion}} + V_c^{\text{electron}} + V_{\text{ex}}^{\text{electron}} + V_{\text{k,rr}}^{\text{electron}} \quad (25)$$

The first three terms of (25) are the Coulomb, the exchange and correlation potentials due to the ion with closed shell. The second three terms denote the corresponding terms due to the valence electrons except the one in question. Here we do not deal with the individual terms in detail, but will refer to them in connection with their practical application further below. In any case it is evident that the modified potential which is the sum of (25) and (24) is a very intricate function consisting of many terms and thus we will describe a simpler semi-empirical method by which it is easier to determine the potential of the ionic core.

For the treatment of alkali metals HELLMANN [16] succeeded in applying a semi-empirical method which essentially consists of the following: The part due to the ions of the periodic potential can also be determined by using the term values of the atom or ion (ionic core and one electron). Hellmann's method will be generalized for the determination of the resultant of the ionic potentials.

In the investigation of the structure of solids ions of its atoms with closed electron shells play a great role. Supplementing each shell with one valence electron it forms an atom or ion the term values of which are known from the study of arc and spark spectra. Knowing the term values we can always construct a potential function with the aid of which, in the case of an adequate form of the eigenfunction we can reproduce the term values. In practice, however, the method set up in this way is too general, because the few term values do not uniquely determine the potential function owing to the great variety of possible forms of the eigenfunction. Taking however, the experience gained from the calculations of atomic and ionic eigenfunctions into account, in the region far from the nucleus the form of the eigenfunction can qualitatively be well given as an exponentially decreasing function, provided however, that the eigenfunctions of the electrons of the ionic core are known. Then the requirement that the eigenfunction of the valence electron should be orthogonal to those of the same orbital quantum number of the ionic core, determines the form of the eigenfunction comparatively well. Naturally, the eigenfunctions of the electrons of the ionic core are generally not available. Then we may proceed in such a manner that we neglect the internal oscillation of the eigenfunction of the valence electron and take the kinetic energy thus neglected in

the form of a potential energy into account. From all this follows that the potential set up in this way for states of various orbital quantum numbers will differ from state to state. Again be r the distance from the nucleus and ze the charge of the ion, then the simplest form of the potential is

$$V_l = \frac{ze}{r} - A_l r^{n_l} e^{-\alpha_l r} \quad (n_l \geq -1). \quad (26)$$

The first term of (26) represents the Coulomb-like potential outside the ionic core, and the second term, the deviation from the former inside the ionic core, the non-Coulomb-like part. A_l and α_l are constants the values of which must be determined with the aid of the experimental atomic terms of the orbital quantum number $l \cdot n_l$ is an integer, which will be determined in advance in concrete cases on the basis of trivial considerations. The second term in (26) actually involves all the non-Coulomb-like electrostatic terms as well as the repulsive potentials taking account of the missing kinetic energy. Writing (24) in the form

$$V_l = V_{\text{coulomb}} + \omega_l. \quad (27)$$

the formalism of the theory set up on the basis of the former repulsive potentials can be applied with the difference that the role of the Φ_l -s in it is formally played by the ω_l -s. Of course, we want to emphasize that the Φ_l -s and the ω_l -s differ greatly from each other. The Φ_l -s occur but in the operator representing the repulsive potential while the ω_l -s include the non-Coulomb-like interaction with the ionic core, the exchange interaction with the core electrons, the correlation interaction due to the electrostatic forces and still other possible interactions which would otherwise be very difficult to take into account.

6. The matrix elements of the Hamiltonian

The one-electron Hamiltonian occurring in the determination of the energy of the electrons is now

$$H = -\frac{\hbar^2}{2m} \Delta - Ve - \Phi_e \quad (28)$$

and its matrix element which can be most generally defined is

$$\begin{aligned} H_{\eta\eta'}^{\dagger} &= \frac{1}{\Omega} \int e^{-i[(\xi+2\pi\eta)r]} H e^{i[(\xi+2\pi\eta')r]} d\tau \\ &= \Delta_{\eta\eta'}^{\dagger} - e V_{\eta\eta'} - e \Phi_{\eta\eta'}^{\dagger}, \end{aligned} \quad (29)$$

where the integration is to be carried out over the total volume Ω . In the following we assume that Ω is a so-called basic region of the solid i. e. Ω represents the period of the wave function occurring in the averaging and the possible values of \mathfrak{k} form a quasi-continuous discrete set. Taking this into account the matrix element of the operator of the kinetic energy is

$$A_{\mathfrak{h}\mathfrak{h}'}, = \frac{\hbar^2}{2m} |\mathfrak{k} + 2\pi\mathfrak{h}|^2 \delta_{\mathfrak{h}\mathfrak{h}'}, \quad (30)$$

where $\delta_{\mathfrak{h}\mathfrak{h}'}$ is the Weierstrass symbol. The matrix element of the electrostatic type potentials can be very easily determined

$$V_{\mathfrak{h}\mathfrak{h}'} = \frac{1}{\Omega} \int V e^{2\pi i [(\mathfrak{h}' - \mathfrak{h}) \cdot \mathfrak{r}]} d\mathfrak{r} = V_{\mathfrak{g}}, \quad (31)$$

as $\mathfrak{h}' - \mathfrak{h} = \mathfrak{g}$ is a lattice vector of the reciprocal lattice and thus (31) is a coefficient of the Fourier expansion of the potential V . (31) is in general independent of \mathfrak{k} and thus it need be determined only once, regardless of the value of \mathfrak{k} .

The matrix element of the operator of the repulsive potential is

$$\Phi_{\mathfrak{h}\mathfrak{h}'}^{\mathfrak{k}} = \frac{1}{\Omega} \int e^{-i[(\mathfrak{k} + 2\pi\mathfrak{h}) \cdot \mathfrak{r}]} \Phi e^{i[(\mathfrak{k} + 2\pi\mathfrak{h}') \cdot \mathfrak{r}]} d\mathfrak{r}. \quad (32)$$

Taking (23) and (24) into account and using relations

$$\frac{2n+1}{2} P_n(\cos \omega) = \sum_{m=-n}^{+n} \bar{P}_n^m(\cos \vartheta) \bar{P}_n^m(\cos \vartheta_0) e^{im(\varphi - \varphi_0)} \quad (33)$$

and

$$\bar{P}_n^m = \sqrt{\frac{2n+1}{2} \frac{(n-m)!}{(n+m)!}} P_n^m(x) \quad (34)$$

and by integrating over the angles we obtain

$$\Phi_{\mathfrak{h}\mathfrak{h}'}^{\mathfrak{k}} = \frac{4\pi}{\Omega} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \omega) \int_0^{r_0} \Phi_l(r) j_l(kr) j_l(k'r) r^2 dr \quad (35)$$

In (35) $k = |\mathfrak{k} + 2\pi\mathfrak{h}|$, $k' = |\mathfrak{k} + 2\pi\mathfrak{h}'|$ and ω is the angle formed by the vectors $\mathfrak{k} + 2\pi\mathfrak{h}$ and $\mathfrak{k} + 2\pi\mathfrak{h}'$. For sake of clearness the quantities in integral (32) are shown in Fig. 3.

On the boundary surfaces of the Brillouin zones the eigenvalues obtained in the free electron approximation are degenerate. The degeneracy vanishes under the influence of the periodic potential field (at least partly). The complete solution of the corresponding approximation of the perturbation theory requires the solution of a secular equation. The matrix elements of the secular equation are just those of the Hamiltonian. As is immediately evident from

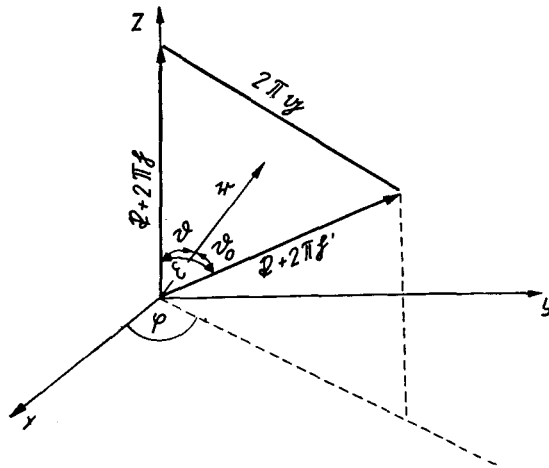


Fig. 3. Quantities and coordinate system for the calculation of the matrix element $\Phi_{\hbar\hbar'}^{\mathfrak{f}}$.

expressions (31) and (32) g is also a lattice vector if in the relation $\hbar' - \hbar = g$ \hbar' and \hbar are lattice vectors, thus apart from the diagonal terms the secular equation only involves the Fourier coefficients of index g of the potential. In addition to these the diagonal elements contain only the unknown energy and the average value of the operator of the kinetic energy.

If the one-electron Hamiltonian also contains a repulsive potential the above assertion is not true as $\Phi_{\hbar\hbar'}^{\mathfrak{f}}$ is not only a function of g but also of other reciprocal lattice vectors and of \mathfrak{f} . It can be proved, however, that the structure of the secular equation will be such as if $\Phi_{\hbar\hbar'}^{\mathfrak{f}}$ were a function of the reciprocal lattice vector g only. It is very important to prove this fact as it is only this way that it can be ascertained that our theory provides the same results in its qualitative aspects as the other theories.

The general condition of degeneracy can be written in the form

$$|\mathfrak{f} + 2\pi \hbar|^2 = |\mathfrak{f} + 2\pi \hbar'|^2 = \dots = |\mathfrak{f} + 2\pi \hbar^{(n)}|^2 \tag{36}$$

and with our notations

$$k = k' = \dots = k^{(n)}. \tag{37}$$

With regard to (36) it is evident that the integrals in (35) are the same for all the $\Phi_{\eta\eta'}^{\xi}$ matrix elements in the secular equation. Thus the $\Phi_{\eta\eta'}^{\xi}$ matrix elements differ from each other only owing to the different values of ω . The value of ω , however, as is shown in Fig. 3, depends on the g only as the sides of the angles are, owing to (37) all equal and the third side of the triangle is $2\pi g$. Thus we have proved that $\Phi_{\eta\eta'}^{\xi}$, owing to (36) and (37) as well as to the relation $(k + 2\pi \eta') - (\xi + 2\pi \eta) = 2\pi (\eta' - \eta) = 2\pi g$, does not change the structure of the secular equation although it is a function of the three quantities indicated by the indices.

Discussion

In the preceding sections it was shown how to determine the eigenfunctions and energy eigenvalues of the valence and conduction electrons by our method. Of course, the practical applicability of the method depends on whether the simplification introduced decreases the number of rows and columns of the secular equations by a sufficient order of magnitude.

In this respect valence electrons can be classified into two groups: *a*) Valence electrons for which the overlap of atomic eigenfunctions on neighbouring atoms is great, such as the *s* and *p* electrons of the outermost shell. The eigenfunction of these can be well approximated in the whole elementary cell by a plane wave, if the end point of the wave number vector is not in the neighbourhood of any of the boundary surfaces of the Brillouin zone. However, even in the latter case the linear combination of a few plane waves will yield a satisfactory result, as even in the most intricate case, when the planes bounding the zone cut each other, there are at most four Brillouin zones and not many more reciprocal lattice vectors determining the former. *b*) As belonging to the second group we may classify the *d* and *f* electrons of transition metals. In our approximation these can of course also be described by an eigenfunction which is free of internal nodal surfaces and here our method also provides for a significant simplification. In the case of these electrons a greater difficulty lies in that the eigenfunctions of *d* and *f* electrons keep their atomic character and form, rather than do those of the other electrons. This is due to the fact that the spatial dimensions of the *d* and *f* atomic eigenfunctions are smaller than that of the outermost *s* and *p* electrons. The difficulty here lies in the fact that for the description of these states such a linear combination of plane waves must be selected, which is similar to the eigenfunctions of the atomic *d* electrons in the greater part of the elementary cell (particularly in most part of the neighbourhood of the nuclei). To this end, of course, several plane waves must be superimposed. Further investigations would be necessary to decide whether the difficulties encountered here are significant.

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ОПРЕДЕЛЕНИЕ ЗОННОГО ЭНЕРГЕТИЧЕСКОГО СПЕКТРА ЭЛЕКТРОНОВ В МЕТАЛЛАХ

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Резюме

В работе выработан новый метод для определения зонного спектра электронов в металлах. Существенное преимущество метода, что он пользуется чистыми плоскими волнами. Это достигается тем, что в случае плоских волн вводится дополнительный потенциал для возмещения большой кинетической энергии собственных функций, осциллирующих в близости атомных ядер. Таким образом электроны проводимости можно трактовать так, как будто бы они заполняли зоны Бриллюэна постепенно, начиная от низшей. Это значит, что собственные функции металлических электронов хорошо аппроксимируются комбинацией нескольких плоских волн. Степень секулярных уравнений на вырожденных местах вблизи границы зон Бриллюэна является низкой. Детально исследованы в работе проблемы секулярного уравнения в связи с дополнительным потенциалом. Показано, что матричные элементы дополнительного потенциала таковы, что они не изменяют качественную структуру секулярного уравнения. Значение матричных элементов гамилтониана меняется в зоне Бриллюэна с места на место. Этот факт значительно увеличивает объем исчислительной работы по отношению к старшей модели со свободными электронами. По отношению к более новым методам, это не является недостатком, так как — хотя по этой причине — там встречается подобное же положение.