

# A New Method for Calculating the Energy Levels of Electrons in Solids.\*)

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*The described method starts from the assumption that each valency electron in a crystal is subject to the following potential: inside the atomic sphere surrounding each atom this potential is spherically symmetrical while outside this sphere it is constant. The corresponding Schrödinger equation is solved by means of the perturbation theory with the help of certain approximate wave functions. The parameters determining the spherically symmetrical potential inside the sphere are determined from the values of energy for the lowest energy level, calculated by statistical methods.*

## Introduction.

The determination of the energies of valency electrons in the periodic field of a crystal lattice is the fundamental problem in the theory of solids, up till now not solved in a satisfactory manner. Once we know the energy spectrum of valency electrons in some solid, we can at once interpret a number of its physical properties or even foretell other at the time unknown physical phenomena. The method of calculation elaborated by WIGNER, SEITZ and SLATER [1, 2] is comparatively simple and gives quite good results for electronic levels of lower states in the energy bands. SHOCKLEY [3] however showed that for higher energy states this method fails and that the energy levels of electrons thus determined do not correspond at all to real values. C. von der LAGE and BETHE [4] recently showed on a concrete example (metallic sodium), that the method of Wigner, Seitz and Slater gives in fact wrong results for the excited states and showed how to modify this method so as to reproduce correctly the physical conditions accompanying these higher energy levels.

A number of improvements [5, 4] on the Wigner, Seitz, Slater method have been proposed, but only two of them, i. e. the Herring-Hill and C. von der Lage-Bethe methods were used for the solution of practical problems. The main disadvantage of all existing methods lies in the fact that they are associated with considerable numerical calculations. Even in the simplest of cases it is often only possible to accomplish the necessary numerical

integrations of the differential equations by means of modern calculating machines.

The method described in this paper, although in essence only an approximate method, has certain advantages in that it can be used in cases where the older methods fail. The numerical calculations connected with it are neither complicated nor tiring. The method was used by the author and his collaborators for calculating a number of concrete examples (metallic sodium, magnesium and aluminium) and it always showed results, which, as far as it is possible to judge by comparison with experiment, seem to be correct.

## I. The Principle of the Method.

Our method takes as a starting point an idea which was once suggested by J. C. SLATER [5]. Valency electrons in the crystal move in a field which we idealise in the following way.

The positive ions in the crystal we surround by spheres of radius  $R$  and assume that inside these spheres the potential in which each valency electron is moving is spherically symmetrical:  $V(|\mathbf{r} - \mathbf{r}_n|)$ , where  $\mathbf{r}$  is the position vector of an arbitrary point of the lattice and  $\mathbf{r}_n$  the position vector of the  $n$ -th positive ion at a lattice point. Outside these spheres we assume the potential constant. To obtain a continuous potential we require the potential  $V(|\mathbf{r} - \mathbf{r}_n|)$  to attain this constant value on the surface of the sphere of radius  $R$ .

It is clear that this idealised potential is really some average potential caused by the action of forces of the positive ions and the rest of the va-

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lency electrons so that in fact we are solving the task as a "single electron" problem.

The wave function corresponding to this potential can be expressed as the product of spherical harmonics with the radial solution of the wave equation inside each sphere of radius  $R$  and as strictly plane waves outside these spheres.

In the first part of this paper we give an approximate solution of the Schrödinger equation, which enables us to express the wave functions inside the above-mentioned spheres in a suitable analytic form. From these functions we now construct the "unperturbed" solution of our problem which consists of plane waves outside the spheres of radius  $R$  and of certain spherical harmonics inside these spheres. The sought for function  $\psi$  we then express as a linear combination of the "unperturbed" wave functions and determine the corresponding coefficients in this linear combination by perturbation methods. Some of these coefficients can in certain cases be directly determined from group considerations.

At the same time we can see that no special assumptions regarding the spherically symmetric potential inside the spheres have to be made. A certain number of parameters related to this part of the potential of the valency electron can be determined from the known energy of the lowest level of the energy spectrum, which can be determined with sufficient accuracy by statistical considerations.

## II. The Wave Function in a Spherically Symmetrical Field.

Our task then is to determine the solution of the Schrödinger equation inside the spheres where the potential  $V(r)$  in which the electron moves is spherically symmetrical;  $r$  is the distance of an arbitrary point from the centre of the sphere. Schrödinger's equation can be separated in polar coordinates with the origin at the positive ion in question. If we denote the coordinates by  $r, \vartheta, \varphi$  we can write the wave function in the well-known form.

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} A_{lm} P_l^{|m|}(\cos\vartheta) \exp\{im\varphi\} u_l(r). \quad (1)$$

Here  $u_l(r)$  denotes the radial function which is determined by the equation

$$u_l'' + \frac{2}{r} u_l' + \left( E - \frac{l(l+1)}{r^2} + V(r) \right) u_l = 0. \quad (2)^*$$

For further calculating it will be convenient to normalise our potential  $V(r)$  so that on the surface of the sphere of radius  $R$  it should be equal to zero; the constant potential on the outside of the sphere, mentioned in I is also equal to zero everywhere.

When substituting this potential in equation (2) we have to replace  $V(r)$  by the expression

$$\bar{V}(r) = V(r) - V(R) = V(r) - \beta, \quad (3)$$

$$\beta = V(R).$$

and the energy  $E$  by the parameter  $E'$  where

$$E' = E + \beta. \quad (4)$$

Equation (2) for the radial function now becomes

$$u_l'' + \frac{2}{r} u_l' + \left( E' - \frac{l(l+1)}{r^2} + \bar{V}(r) \right) u_l = 0. \quad (5)$$

Let us now assume that we know the function  $\psi_0$ , which satisfies the following equation

$$\psi_0'' + \frac{2}{r} \psi_0' + (E'_0(r_0) + \bar{V}(r)) \psi_0 = 0. \quad (6)$$

at the same time satisfying the following boundary conditions:

$$\left. \frac{d\psi_0}{dr} \right|_{r=r_0} = 0, \quad \left. \frac{d^2\psi_0}{dr^2} \right|_{r=r_0} = 0. \quad (7)$$

It is quite clear that the proper value  $E'_0(r_0)$  is a function of the radius  $r_0$  for which the boundary conditions (7) are fulfilled. From equation (6) there follows that

$$\left. \begin{aligned} E'_0(r_0) &= -\bar{V}(r_0) \\ E_0(r_0) &= -V(r_0). \end{aligned} \right\} \quad \text{or} \quad (8)$$

Let us now try the solution of equation (5) in the form  $u_l = \psi_0 \cdot f_l$ ; after substituting into equation (5) we obtain the following condition:

$$\left[ \psi_0'' + \frac{2}{r} \psi_0' + (E'_0(r_0) + \bar{V}(r)) \psi_0 \right] f_l + \left[ f_l'' + 2f_l' \left( \frac{1}{r} + \frac{\psi_0'}{\psi_0} \right) + \left( \alpha^2 - \frac{l(l+1)}{r^2} \right) f_l \right] \psi_0 = 0,$$

where we expressed  $E'$  in the form

$$E' = E'_0(r_0) + \alpha^2. \quad (9)$$

\*) The following units are used in this paper: Rydberg units  $= \frac{2\pi^2 m e^4}{h^2}$  are used consistently for energy and the Bohr radius  $\frac{h^2}{4\pi^2 m e^2}$  for length.

The first square bracket in the above expression vanishes as it satisfies equation (6). For the second bracketed expression to vanish, the function  $f_l$  must satisfy the following equation:

$$f_l'' + 2 \cdot f_l' \left( \frac{1}{r} + \frac{\psi_0'}{\psi_0} \right) + \left( \alpha^2 - \frac{l(l+1)}{r^2} \right) f_l = 0. \quad (10)$$

As we see later we shall always be interested in a solution in the neighbourhood of the point  $r = r_0$  and here considering conditions (7),  $\psi_0$  is practically constant. The term  $\frac{\psi_0'}{\psi_0}$  in equation (10) can therefore be neglected; the equation for  $f_l$  now takes the form

$$f_l'' + \frac{2}{r} f_l' + \left( \alpha^2 - \frac{l(l+1)}{r^2} \right) f_l = 0. \quad (11)$$

We can immediately write down the solution of this equation which is regular at the origin of the coordinate system:

$$f_l = \sqrt{\frac{\pi}{2\alpha r}} J_{l+\frac{1}{2}}(\alpha r) = j_{l+\frac{1}{2}}(\alpha r), \quad (12)$$

where  $J_{l+\frac{1}{2}}(\alpha r)$  is the Bessel function of half order. The approximate solution of equation (5) can now be written in the form:

$$u_i = \psi_0 \cdot j_{l+\frac{1}{2}}(\alpha r). \quad (13)$$

### III. The Wave Function in a Crystal.

Outside our spheres, where the potential is constant, the solution of the Schrödinger equation is the known plane wave  $\exp\{i(\mathbf{k}_i \cdot \mathbf{r})\}$ , where  $\mathbf{k}_i$  denotes the wave vector. This solution must now continuously change into that solution inside the sphere which is due to the same energy. This problem has already been solved by SLATER [5]. He showed that the wave function inside the sphere of radius  $R$  with its centre at  $\mathbf{r}_n$ , which on its surface changes continuously into a plane wave  $\exp\{i(\mathbf{k}_i \cdot \mathbf{r}_n)\}$ , is of the form

$$\begin{aligned} \psi_{\mathbf{k}_i} = \exp\{i(\mathbf{k}_i \cdot \mathbf{r}_n)\} & \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} (2l+1) i^l \frac{j_{l+\frac{1}{2}}(k_i R)}{u_l(R)} \cdot \\ & \cdot u_l(|\mathbf{r} - \mathbf{r}_n|) \frac{(l-|m|)!}{(l+|m|)!} P_l^{|m|}(\cos\vartheta) P_l^{|m|}(\cos\vartheta_i) \cdot \\ & \cdot \exp\{im(\varphi - \varphi_i)\}, \end{aligned} \quad (14)$$

where  $u_l(|\mathbf{r} - \mathbf{r}_n|)$  is a radial function determined from equation (5) and  $\vartheta_i, \varphi_i$  determined the direction of  $\mathbf{k}_i$  in polar coordinates.

The above value (14) inside each sphere together with the expression  $\exp\{i(\mathbf{k}_i \cdot \mathbf{r})\}$  outside each

sphere completely determines the wave function  $\psi_{\mathbf{k}_i}$  which is our unperturbed function. These wave functions are continuous; their gradient, however, on the surface of the spheres of radius  $R$ , is not.

It is natural to expect that the complete solution of the Schrödinger equation in a crystal will also have a continuous gradient at every point. This means that the correct wave function must be equal to the linear combination of the above "unperturbed" wave functions. The coefficients in this linear combination have to be determined in such a way as to make the gradient of the resultant wave function everywhere continuous. To solve this problem this way would be very difficult. It is, however, possible to attain the end more readily, if perturbational methods are used suitably.

We shall therefore assume that the exact wave function can be expressed by the series:

$$\sum_i c_i \psi_{\mathbf{k}_i} \quad (15)$$

where  $c_i$  are constants to be determined. Then according to the general methods of quantum mechanics (15) will be a solution of the problem if the following equations are satisfied

$$\sum_j (H - E)_{ij} c_j = 0 \quad (16)$$

for all  $i$ . Here  $H$  denotes the energy operator,  $E$  the proper value of energy and

$$(H - E)_{ij} = \int \psi_{\mathbf{k}_i}^* (H - E) \psi_{\mathbf{k}_j} d\tau \quad (17)$$

the well known perturbational matrix element. Equation (16) will be satisfied if the determinant of the coefficients  $(H - E)_{ij}$  is equal to zero. Let us now examine what  $\mathbf{k}$ -vectors have to be used in expression (15) for constructing the exact wave function. Let us choose in  $\mathbf{k}$ -space a fixed vector  $\mathbf{k}_0$  which we shall identify with  $\mathbf{k}_1$  in (15). The complete wave function (15) can then be written

$$\psi(\mathbf{k}_0) = c_0 \psi_{\mathbf{k}_0} + c_2 \psi_{\mathbf{k}_2} + c_3 \psi_{\mathbf{k}_3} + \dots \quad (18)$$

If  $\psi(\mathbf{k}_0)$  is to be the exact wave function for the crystal, then it necessarily has to show those symmetric properties which are prescribed by the symmetry group appertaining to the crystal lattice in question. One of these is the behaviour of the wave function towards the translation crystal group expressed by the well-known Bloch theorem. According to this theorem the application of an arbitrary translation from the translation crystal group to the wave function reproduces the latter except for a constant factor. Let us now rewrite the analytical expression for the wave function  $\psi_{\mathbf{k}_i}$

inside the sphere in a more concise form. In equation (14) we can use the well-known relation from the theory of spherical harmonics and carry out the summation over  $m$ ; we then get:

$$\psi_{\mathbf{r}_i} = e^{i(\mathbf{k}_i \cdot \mathbf{r}_n)} \sum_{l=0}^{\infty} (2l+1) \cdot i^l \cdot \frac{j_{l+\frac{1}{2}}(k_j R)}{u_l(\alpha R)} u_l(|\mathbf{r} - \mathbf{r}_n|) P_l \left( \frac{(\mathbf{k}_i(\mathbf{r} - \mathbf{r}_n))}{|\mathbf{k}_i||\mathbf{r} - \mathbf{r}_n|} \right).$$

If we now transform  $\psi_{\mathbf{r}_i}$  so that to every position vector  $\mathbf{r}$ ,  $\mathbf{r}_n$  we add a certain vector  $\mathbf{t}$ ,  $\psi_{\mathbf{r}_i}$  is multiplied only by the factor  $e^{i(\mathbf{k}_i \cdot \mathbf{t})}$ . The wave function is transformed equally on the outside of the sphere. From the above follows at once that Bloch's theorem is fulfilled for functions of the type (18) if the wave vector  $\mathbf{k}_n$  is written

$$\mathbf{k}_n = \mathbf{k}_0 + \mathbf{k}_n$$

where  $\mathbf{k}_n$  is the vector of the reciprocal lattice to given translation crystal lattice. The exact function (18) can therefore be written

$$\psi(\mathbf{k}_0) = \sum_n c_n \psi_{\mathbf{r}_0 + \mathbf{r}_n}. \quad (19)$$

To every vector of  $\mathbf{k}$ -space one can therefore construct a wave function of type (19) and the corresponding proper value of energy can be calculated by equating the perturbation determinant, the elements of which are given by expressions (17), to zero. In many cases it is quite sufficient to use in expression (19) for the wave function only those functions the wave vectors of which are equal in magnitude to the magnitude of vector  $\mathbf{k}$ . The addition of further terms to expansion (19) affects the proper value of energy only negligibly. Other symmetric properties of wave functions in crystals may also be used and with the help of the theory of crystal group representation it is easily possible to determine the relative ratio of whole groups of coefficients in expansion (19), which makes it unusually simple to write down the explicit form of the vanishing perturbation determinant.

M. TRLIČAJ and E. ANTONČÍK undertook the above task and so introduced an unusually clear system into the whole energy spectrum of electrons in solids.

#### IV. Matrix Elements.

We shall now explicitly express the matrix element (17). Using function (14) we can write this element according to SLATER [5] in the following form:

$$(H - E')_{ij} = [(\mathbf{k}_i \mathbf{k}_j) - E'] \delta_{ij} + \frac{1}{\Omega} \sum_n \exp [i((\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}_n)] \cdot F_{ij}, \quad (20)$$

where

$$F_{ij} = 4\pi R^2 \left\{ -((\mathbf{k}_i \mathbf{k}_j) - E') \frac{j_{\frac{1}{2}}(|\mathbf{k}_j - \mathbf{k}_i| R)}{|\mathbf{k}_j - \mathbf{k}_i|} + \sum_{l=0}^{\infty} (2l+1) P_l(\cos \vartheta_{ij}) j_{l+\frac{1}{2}}(k_i R) j_{l+\frac{1}{2}}(k_j R) \frac{u'_l(R)}{u_l(R)} \right\}.$$

Here  $\Omega$  is the volume of the elementary cell, the sum  $\sum_n$  is to be summed over the positions of the atoms in the cell and  $\vartheta_{ij}$  is the angle between vectors  $\mathbf{k}_i$  and  $\mathbf{k}_j$ .

For the function  $u_l(R)$  we can use the approximate expressions (13), because, as will follow from more detailed numerical calculations,  $R$  does not differ much from  $r_0$ . If we substitute from equation (13) into expression (20) and use the well-known addition theorems for Bessel functions

$$\frac{\sin \omega}{\omega} = \sum_{l=0}^{\infty} (2l+1) P_l(\cos \vartheta_{ij}) j_{l+\frac{1}{2}}(k_i R) j_{l+\frac{1}{2}}(k_j R),$$

$$\omega = R \sqrt{|k_i^2 + k_j^2 - 2k_i k_j \cos \vartheta_{ij}|},$$

we obtain the following formulas

$$i \neq j;$$

$$\frac{(H - E')_{ij}}{4\pi R \sum \exp} = \left[ \frac{\psi'_0(R)}{\psi_0(R)} R - \frac{1}{2} \right] \frac{\sin \omega}{\omega} + \frac{j_{\frac{1}{2}}(\omega)}{\omega} R^2 [\alpha^2 + E_0(r_0) + \beta - (\mathbf{k}_i \mathbf{k}_j)] + \frac{R\alpha}{2} \sum_{l=0}^{\infty} (2l+1) P_l(\cos \vartheta_{ij}) j_{l+\frac{1}{2}}(k_i R) j_{l+\frac{1}{2}}(k_j R) \cdot \frac{j_{l-\frac{1}{2}}(\alpha R) - j_{l+\frac{3}{2}}(\alpha R)}{j_{l+\frac{1}{2}}(\alpha R)}, \quad (21a)$$

$$i = j;$$

$$\frac{(H - E')_{ii}}{4\pi R \sum \exp} = \left[ \frac{\Omega}{4\pi R \sum \exp} - \frac{R^2}{3} \right] \cdot [k_i^2 - E_0(r_0) - \beta - \alpha^2] - \frac{1}{2} + \frac{\psi'_0(R)}{\psi_0(R)} R + \frac{R\alpha}{2} \sum_{l=0}^{\infty} (2l+1) j_{l+\frac{1}{2}}^2(k_i R) \frac{j_{l-\frac{1}{2}}(\alpha R) - j_{l+\frac{3}{2}}(\alpha R)}{j_{l+\frac{1}{2}}(\alpha R)}, \quad (21b)$$

where  $\sum \exp$  is a symbol standing for

$$\sum_n \exp \{i((\mathbf{k}_j - \mathbf{k}_i) \cdot \mathbf{r}_n)\}.$$

In order to be able to start evaluating these expressions we have to determine the constants  $R$ ,  $\beta$ , and  $\psi'_0(R)/\psi_0(R)$ . Let us first find the radius of the sphere  $R$ . This constant  $R$  determines the distance from the positive ion at which the spheric-

ally symmetric potential changes into the constant value. It is clear that this change comes about at the boundary surfaces of the well-known Wigner-Seitz polyhedrons, which for symmetric lattices can well be replaced by atomic spheres. We therefore identify our radius  $R$  with the radius of atomic spheres defined thus: if we designate with  $n$  the number of atoms in the elementary cell of volume  $\Omega$  then

$$\frac{4\pi}{3} R^3 = \frac{\Omega}{n} \quad (22)$$

defines the radius  $R$ .

As a result of the above definition expressions

$$\left[ \frac{\Omega}{4\pi R \sum \exp} - \frac{R^2}{3} \right]$$

in the matrix element (21b) vanish identically as in this case  $\sum \exp = n$ .

In order to determine  $\psi'_0(R)/\psi_0(R)$  let us recall how the lowest energy levels in the Wigner-Seitz method are determined. Here it is necessary to point out that the value of energy determined in this way is very precise as the boundary conditions which have to be fulfilled for the determination of the individual levels are fulfilled in this case with great precision. We feel, therefore, justified in expecting that our method on determining the lowest levels must give in essence the same results as the classical method. According to Wigner and Seitz we calculate the lowest energy value of the valency electron by determining the  $s$ -function  $u_{l=0}$  satisfying an equation which is identical with our equation (5) and subject it to the boundary condition  $\left\{ \frac{du_0}{dr} \right\}_{r=R} = 0$  where  $R$  again stands for the radius of the atomic sphere. In our case, when  $u_0(\alpha_0 r)$  is given by the following expression (see equation 13)

$$u_0(\alpha_0 r) = \psi_0(r) \frac{\sin \alpha_0 r}{\alpha_0 r}$$

the condition

$$0 = \frac{\psi'_0(R)}{\psi_0(R)} R - 1 + \alpha_0 R \cot \alpha_0 R \quad (23)$$

has to be fulfilled.

Knowing  $\psi'_0(R) : \psi_0(R)$ , enables us to determine  $\alpha_0$  easily from the above condition and also from equation (9) the corresponding proper value of energy:

$$E'_0(R) = E'_0(r_0) + \alpha_0^2, \quad (24a)$$

$$E_0(R) = E_0(r_0) + \alpha_0^2. \quad (24b)$$

In our method the lowest proper value of energy is easily determined by means of the single function  $\psi_{t=0}$  to which corresponds a zero wave vector. The corresponding matrix element is of the form:

$$\frac{(H - E')_{00}}{\frac{4\pi}{\Omega} R \sum \exp} = \frac{\psi'_0(R)}{\psi_0(R)} R - 1 + \alpha_0 R \cot \alpha_0 R.$$

Setting the lefthand side of the above equal to zero we get the same condition for  $\alpha_0$  as before.

Later we shall show how it is possible by a statistical method to determine the lowest levels as a function of the radius of the atomic sphere. Let us now assume that we already know that function. Then from relation (24b) follows at once that for  $R = r_0$  the value of the lowest energy attains its minimum  $E$  and that this minimum is equal to  $E_0(r_0)$ . We can therefore easily determine the constants  $E_0(r_0)$  and  $r_0$  from the condition  $\left\{ \frac{\partial E_0}{\partial R} \right\}_{R=r_0} = 0$ .

If we determine the above two constants we can equally easily find  $\alpha_0$  which follows from equation (24b) from which

$$\alpha_0^2 = E_0(R) - E_0(r_0).$$

If we substitute in the condition for the lower level (equation 23) we obtain  $\frac{\psi'_0(R)}{\psi_0(R)}$ .

There remains the determination of the constant  $\beta = V(R)$ . We shall make a very acceptable assumption regarding the potential  $V(r)$  valid for distances in the neighbourhood of  $r_0$  and greater than the radius of the ions, i. e.  $r$  is in the interval  $r_0 \leq r \leq R$ . We assume that in this case it is possible to express the potential  $V(r)$  simply by:

$V(r) = \frac{2Z_{ef}}{r}$ . From equation (8) we get at once

$$2Z_{ef} = -E_0(r_0) \cdot r_0$$

so that

$$\beta = -E_0(r_0) \frac{r_0}{R}. \quad (26)$$

## V. Calculation of the Energy of the Lowest Level.

We shall first try to calculate the total energy per atom of all valency electrons of a solid. For this purpose we use statistical methods. In this paper we shall only indicate the fundamental idea and the results of our calculations; more detailed considerations will be published in a later paper. We are

proceeding in a similar manner as GOMBÁS [7] in his work on the statistical theory of solids. We again replace the Wigner-Seitz polyhedrons by atomic spheres, assuming that the valency electrons are on the average uniformly distributed throughout the whole crystal. The charge inside each sphere is equal to  $N$  electron charges, where  $N$  is the number of valency electrons in the atom of which the solid under consideration is made up. The total energy  $E_t$  per atom, i. e. the energy of the uniformly distributed electron gas inside the atomic sphere is equal to the sum of the following energies. First we have to take into account the electrostatic energy of repulsion of the electron gas  $E_c$  inside the sphere. This energy is equal to

$$E_c = \frac{6N^2}{5R}.$$

Further,  $E_A$  and  $E_{kor}$  denote the exchange and correlation energies of such a gas.

In our case these energies can easily be enumerated. They are

$$E_A = -\frac{0,9164N^{\frac{4}{3}}}{R},$$

$$E_{kor} = -\frac{0,576N}{5,1 + R \cdot N^{-\frac{1}{3}}}.$$

Further it is necessary to calculate the so-called kinetic energy  $E_{kin}$  of the electron gas, which is the consequence of the validity of Pauli's principle. This energy is also easily obtained and its value is given by

$$E_{kin} = \frac{2,21N^{\frac{5}{3}}}{R^2}.$$

Finally it is necessary to add the energy which has its origin in the interaction of the electron gas with the positive ion of the atomic sphere under consideration. If we denote by  $h(r)$  the potential of the positive ion at the distance  $r$ , then this energy is given by

$$E_i = \nu \cdot 4\pi \int_0^R h(r) r^2 dr,$$

where  $\nu = -\frac{3N}{4\pi R^3}$  denotes the charge density of the valency electrons. The potential  $h(r)$  can be determined in various ways. According to Gombás  $h(r)$  is given for example by the following expression:

$$h(r) = -\left[\chi(r) - \frac{2N}{r}\right] - 2\gamma_0\{[\varrho(r)]^{\frac{2}{3}} - k[\varrho_i(r)]^{\frac{2}{3}}\} + \frac{2N}{r},$$

where  $\chi(r)$  stands for the Hartree potential of the positive ion bared of all valency electrons, the second term is the non-classic repulsion potential which is a consequence of the Pauli principle and which essentially corresponds to the resistance to intrusion of valency electrons into the electron shells of the positive ion.  $\varrho(r)$ ,  $\varrho_i(r)$  are the total charge densities of the positive ion and density of  $s$ -electrons respectively, in case part of the electrons in the free atom are in the  $p$ -state also. The constant  $k$  for bivalent elements is equal to zero, for trivalent or quadrivalent it takes up the value  $\frac{1}{3}$  and  $\frac{1}{2}$  respectively.  $\gamma_0$  is given by the expression  $\frac{1}{2}(3\pi^2)^{\frac{2}{3}}|e_0|a_0$ , where  $|e|$  is the charge of the electron and  $a_0$  is the Bohr radius.

The total energy of the valency electrons is therefore

$$E_t = E_c + E_A + E_{kor} + E_{kin} + E_i. \quad (27)$$

Let us now try to express the total energy by means of the energy of the lowest level in the band spectrum. The energy  $E$  of the individual valency electrons we normalise with regard to the lowest level and write

$$E = E_0 + \eta.$$

Let  $N(\eta)$  denote the density of energy states the energies of which lie between  $\eta$  and  $\eta + d\eta$ . Then clearly

$$N = 2 \int_0^{\eta_{\max}} N(\eta) d\eta,$$

where  $\eta_{\max}$  denotes the Fermi limit. The total energy  $E_t$  of the valency electrons per atom is therefore given by

$$E_t = 2 \int_{E_0}^{E_{\max}} N(E) E dE = 2 \int_0^{\eta_{\max}} N(\eta) (E_0 + \eta) d\eta =$$

$$= N(E_0) + 2 \int_0^{\eta_{\max}} N(\eta) \eta d\eta.$$

The last integral, however, stands for the total kinetic energy per atom. We can therefore write the last relation in a simple form

$$E_t = NE_0 + E_{kin}.$$

Comparing both expressions for the total energy  $E_t$  we at once obtain for  $E_0$  the following expression:

$$E_0 = \frac{1}{N} (E_c + E_A + E_{kor} + E_i). \quad (28)$$

If we approximate the Hartree potential  $\left[\chi(r) - \frac{2N}{r}\right]$ ,  $\varrho(r)$  and  $\varrho_i(r)$  by suitable analytic

functions from the Hartree tables and for the rest of the terms in (28) we substitute the expressions introduced above we obtain  $E_0$  as a function of the radius  $R$  of the atomic spheres.

## VI. Concluding Remarks.

To some of the approximations carried out on the preceding pages, I should like to make the following remarks.

First of all in equation (10) we neglected the term  $2f'_i \frac{\psi'_0}{\psi_0}$ . This step is certainly permissible in those cases when  $r$  is in the neighbourhood of  $r_0$ , because  $\psi'_0$  is then a very small quantity, ( $\psi_0(r)$  is nearly constant in the neighbourhood of  $r_0$ ). For larger differences ( $r - r_0$ ) we of course introduce certain errors.

When calculating the energy of the lowest level in  $V$ , some doubts can arise as to the justification of the uniformly distributed electron gas. The decisive terms in expression (28) for  $E_0$  however are

$\frac{1}{N} (E_c + E_i)$ . These expressions represent the quantum mechanical average of the type  $\int \psi_0^* V \psi_0 d\tau$  taken over the electrostatic repulsion of  $(N - 1)$  valency electrons and the interaction of the valency electron in the lowest state with the positive ion. The wave function  $\psi_0$  is at the same time taken as a constant and is normalised to the volume of the atomic sphere. It is, however, well known [8] and it follows from our calculations as well that the wave function of the valency electron in the lowest state is practically constant over the whole space of the atomic spheres. Besides, the results thus obtained are in good agreement with the corresponding numerically integrated Schrödinger equation.

The described method was applied to a number of solids, i. e. metallic sodium [9], magnesium [10] and aluminium [11]. Summarily we can say that the results seem to be in good agreement either with measured values or with the calculated values of energies in the Brillouin zones as, for example, with the results obtained by Von der Lage and Bethe for metallic sodium.

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