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APPLICATION OF QUANTUM THEORY OF ELECTRONS TO THE  
MECHANICAL AND THERMAL PROPERTIES OF METALS

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## INTRODUCTION

Previous works  
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The first successful application of quantum mechanics to the problem of metallic cohesion was made by Wigner and Seitz(1933). They approximated sodium metal by a number of isolated spheres of equal atomic volume and integrated, for various values of the radius of the sphere, the Schrödinger wave equation for the valence electron with the boundary condition that the derivative of the wave function should vanish at the surface of the sphere. To obtain the energy per atom of the metal, they further corrected the energy of the sphere by the mean Fermi energy of free electrons. From the resultant dependence of the energy on the radius of the sphere, they derived the lattice constant, the heat of sublimation per atom, and also roughly the compressibility.

Wigner and Seitz(1934) later considered their first attempt as an indirect approach to the solution of Fock's equations for the whole collection of the valence electrons in the metal. The Fermi energy was now calculated by perturbation methods, which verified their previous assumption of free electrons.

Other corrections to the energy introduced by the approximation of the lattice by isolated spheres were investigated; the "exchange" interaction among the electrons with parallel spins (a special feature of the Fock method,) was also included. But the agreement with experimental values (cf. Table below) became considerably poorer. They were able, however, to improve greatly the calculated values of the lattice constant and the heat of sublimation per atom by an extension of Fock's method to take into account the correlation between electrons with antiparallel spins, the theory of this correlation being given in more details by Wigner(1934) in a separate paper.

The following table indicates the adequacy of the various approximations used by Wigner and Seitz for sodium.

Summary of Wigner and Seitz' results for sodium.

|   | Lattice constant<br>in A. | Heat of<br>sublimation in Cal./mol. |
|---|---------------------------|-------------------------------------|
| value calc. to the<br>isolated spheres appro. | 4.2                       | 25.6                                |
| value calc. to the<br>Fock approximation      | 4.86                      | 9.0                                 |
| value calc. to the<br>Wigner approximation    | 4.62                      | 26.1                                |
| Extrapolated experi-<br>mental value          | 4.23                      | 26.9                                |

The above method was then applied by Seitz(1935)

to lithium, by Fuchs(1935) to copper, and by Gorin(1936) to potassium, with success.

On the other hand, analytical calculations by Feinberg(1935) and numerical calculations by Slater and Krutter(1935) with the Thomas-Fermi method failed to obtain a minimum in the energy with respect to various values of lattice constant. When the exchange interaction among the electrons was neglected, both calculations agreed in that the energy of the metal would continuously decrease with increasing lattice constant. Feinberg further pointed out that this would also be the case if the exchange interaction among the electrons were neglected in Wigner and Seitz's calculations. Slater and Krutter showed that considerable improvement could be made by adopting Dirac's(1930) modification of the Thomas-Fermi method to take into account the exchange effect. This depressed the energy, but it was not enough to produce a minimum of the binding energy.

Based on the results of the investigations of Wigner and Seitz and Seitz and his own result, Fuchs(1936) made certain simplifying assumptions and calculated the elastic constants at constant volume. Based on the analytical attempt made by Fröhlich<sup>(1936) (1937/1938)</sup> for the calculation of the energy of the sphere introduced above by Wigner and Seitz, Fuchs(1936a) made further

calculation of the compressibility. Since Fröhlich's "perturbation of the boundary condition" gave the change of the energy of the sphere to the first order in the fractional change of the radius of the sphere, in applying Fröhlich's formula to the calculation of the compressibility, Fuchs had to introduce certain simplifying assumptions.

Recently Fuchs(1940)\*developed an operator calculus particularly designed for electron theory of metals and emphasized that Fröhlich's perturbation of the boundary condition could not meet the general demand for the calculation of the elastic constants and the normal frequencies of the thermal oscillations of metals. He further pointed out that it should be possible to develop a consistent perturbation theory for the calculation of these quantities. The aim of the present investigation is to develop such a perturbation theory.

Present investigation  
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In what follows I shall deal with a dynamical system which consists of a finite lattice of ions of a certain metallic element and a number of electrons. As a whole, the system is electrically neutral, carries

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\* I wish to thank Dr. Fuchs for allowing me to see the manuscript.

no electric current, and is magnetically unpolarised by itself or external fields; but it may be elastically deformed by a constant external stress.

My task is to simplify the above dynamical system to a form accessible to approximate treatment by statistical mechanics. The following three approximations are introduced for this purpose.

The first concern the motion of the electrons as compared with that of the ions. It is allowable to assume that the motion of the ions is very much slower than that of the electrons. This enables the motion of the electrons and that of the ions to be treated separately; in considering the rapid motion of the electrons, the slow motion of the ions may be neglected, and they may be assumed to be at rest in arbitrary positions. In treating the slow motion of the ions, the averaged total energy of the rapid motion of the electrons, which still depends on the configuration of the ions, may then be considered as a contribution to the potential energy of the ions.

The second approximation introduced concerns the motion of the electrons. This must, of course, be treated according to quantum mechanics, but a rigorous treatment involves serious mathematical difficulties. In view of the high precision needed in the present problem I shall use the Fock-Dirac method of approximation. Wigner's extension of the Fock-Dirac method is

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mathematically too involved and will not be attempted here. The correction to elastic constants to the Wigner approximation is estimated, in order to see whether improvement upon the Fock-Dirac method is necessary or not.

The third and last approximation needed concerns the motion of the lattice of ions. This may be treated by classical mechanics, and I shall follow the method developed by Born. I therefore assume that there exists a unique configuration of the ions for which the potential energy of the lattice is a minimum, and that the actual configuration of the ions does not deviate very much from this. Then it follows from the general theory of small motions in classical mechanics that the motions of the ions are harmonic. By a transformation to normal coordinates in terms of which the potential energy of the actual lattice exceeds its minimum value by a sum of squares, the lattice is reducible to a collection of independent simple harmonic oscillators which can easily be treated by statistical mechanics.

With the help of these three approximations, the original dynamical system is reducible to a collection of simple harmonic oscillators. The chief calculation involved is the development, up to the quadratic terms in the small displacements of the ions,

of the potential energy of the lattice. Part of this potential energy is contributed by the electrons; the development of this part with respect to the displacements of the ions depends on the solution of the electronic motion by perturbation methods.

The displacements of the ions cause the electrons to move not only in a different field of force but also in a different domain of space when surface effects are neglected. By applying a contact transformation, I have succeeded to bring the problem over to such a form that the ordinary perturbation method becomes applicable. The perturbation theory is developed in Chapter I and is applied in Chapter II to the calculation of elastic constants, and in Chapter III to the calculation of normal frequencies of the thermal oscillations of metallic lattices.

In the calculation of elastic constants, special attention is paid to examine the simplifying approximations introduced in the various previous works reviewed above. Among the results achieved I may mention the derivation of Fröhlich's formula and its extension, and the justification of Fuchs' calculation of the elastic constants at constant volume for sodium only. But most important of all is that more accurate calculations can be made with the present method provided that the unperturbed eigenfunctions

needed are known.

In the case of thermal oscillations, general considerations are given to show that the thermal waves are independent, and that the normal frequencies for metals of simple lattice structure (one particle per cell) vanish with vanishingly small wave vectors. Accurate calculations of the normal frequencies for not too small wave vectors are possible provided that the unperturbed eigenfunctions needed are known. Rough calculations for small wave vectors could be made at present, but this is not included in the following thesis.

## MOTION OF ELECTRONS AND IONS IN METALS

## 1. Notation

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The following notation will be used throughout this chapter.

Vectors will be distinguished by a bar below the symbol.

Matrices will be distinguished by two bars below the symbol.

Operators and functions will usually be distinguished by writing out the arguments.

1.1. Spatial coordinates. These will be denoted by  $\underline{r}_\alpha$  ( $\alpha = 1, 2, 3$ ) and are the components of the vector  $\underline{r}$ . The  $r_\alpha$  take real values in a domain  $\mathcal{R}$ .

Transformed spatial coordinates will be distinguished by a bar above the letter. The components  $\bar{r}_\alpha$  of the vector  $\bar{\underline{r}}$  take real values in the transformed domain  $\bar{\mathcal{R}}$ .

1.2. Symbols relating to the electrons.

The total number of electrons is  $N$ ; the electronic mass is  $m$ .

The configuration of the electrons is specified by vectors  $\underline{r}, \underline{r}', \underline{r}'', \dots, \underline{r}^{(N-1)}$  or in general  $\underline{r}^{(i)}$ .

The spin coordinate of an electron is  $s$ , which

takes either of the two values 1 and 2. The spin configuration of the electrons is specified by

$$s, s', s'', \dots, s^{(N-1)} \quad \text{or in general } s^{(i)}.$$

$\psi_i(\underline{r}, s)$  ( $i = 1, 2, \dots, N$ ) denotes the Fock functions of the electrons including spin.

$\psi_j(\underline{r})$  ( $j = 1, 2, \dots, N/2$ ) denotes the Fock functions of the electrons excluding spin.

$\underline{p}(\underline{r})$  denotes the momentum operator of an electron at  $\underline{r}$ .

$T(\underline{r})$  denotes the kinetic energy operator of an electron at  $\underline{r}$ .

$V_+(\underline{r})$  denotes the potential energy of an electron at  $\underline{r}$  due to the lattice of ions only.

$V_-(\underline{r}; \underline{r}')$  denotes the electrostatic interaction of two electrons at  $\underline{r}$  and  $\underline{r}'$ .

1.3. Symbols relating to the ions.

The total number of ions is  $N_+$ ; the ionic mass is  $M$ . The configuration of the ions is specified by the vectors  $\underline{r}^l$ , where the superscript  $l$  actually represents three indices  $l_1, l_2, l_3$ , each of which takes all integral values from  $-L$  to  $+L$ .

Thus  $N_+ = (2L+1)^3$ .

$\underline{p}(\underline{r}^l)$  denotes the momentum operator of an ion at  $\underline{r}^l$ ;  $\underline{p}^l$  denotes the momentum of an ion at  $\underline{r}^l$ .

$V_{++}(\underline{r}^l; \underline{r}^{l'})$  denotes the interaction of two ions at  $\underline{r}^l$  and  $\underline{r}^{l'}$ .  $V_{+-}(\underline{r}^l; \underline{r})$  denotes the interaction of

an ion at  $\underline{r}'$  and an electron at  $\underline{r}$ .

1.4. Symbols relating to the crystal lattice.

The lattice vectors of the homogeneously deformed lattice are denoted by  $\underline{a}_1, \underline{a}_2, \underline{a}_3$ . The reciprocal lattice vectors are denoted by  $\underline{b}_1, \underline{b}_2, \underline{b}_3$ . The reduced wave vectors are denoted by  $\underline{q}^n$ , which stands for  $\underline{q}^n = n_1 \left( \frac{2\pi}{2L+1} \underline{b}_1 \right) + n_2 \left( \frac{2\pi}{2L+1} \underline{b}_2 \right) + n_3 \left( \frac{2\pi}{2L+1} \underline{b}_3 \right)$  where  $n_1, n_2, n_3$  take all integral values between  $-L$  and  $+L$ .

Quantities referring to the undeformed lattice will be distinguished by a zero above the letter, as  $\underline{a}^0$ .

Note that in symbols relating to the lattice a superscript is always to be taken as representing three indices.

1.5. Summation and integrations. When the range of a summation depends on the number of particles considered in the problem, I use the summation sign  $\mathcal{S}$ , otherwise I use the summation sign  $\sum$ . The range of the summation is implied in the summation index; any sum is to be taken over the complete range of values which this index may take. For double summations, only one summation sign is written.

In the accented summation sign  $\mathcal{S}'_l$ , the single term  $l=000$  is excluded. In the accented

summation sign  $\mathcal{S}'_{ll'}$  the terms for which  $l_1 = l'_1$ ,  $l_2 = l'_2$ , and  $l_3 = l'_3$  simultaneously are excluded.

For integrations, the domain is implied in the integration volume element or surface element; the domain of the integration is always complete. This also applies to double integrations.

1.6. Scalar products. The scalar product of two spatial vectors is denoted by a dot between the vectors without any brackets enclosing the whole product. The scalar product of two functions  $g_i(r, s)$  and  $g_j(r, s)$  is defined as  $\sum_r \int dr g_i^*(r, s) g_j(r, s)$  and is denoted by  $(g_i(r, s) \cdot g_j(r, s))$  with brackets enclosing the product. The domain of the volume integration (or summation) in the scalar product is implied in the argument of the functions. In particular, the scalar product  $(\psi_j(r') \cdot \nabla_{r'} \psi_i(r'))$  represents a volume integration over the argument  $r'$  and yields a function of the argument  $r$ . The double scalar product  $(\psi_j(r) \cdot (\psi_i(r') \cdot \nabla_{r'} \psi_k(r'))) \psi_l(r')$  is then a constant.

Other symbols not listed above will be explained when they first occur.

2. The motion of the electrons in metals

In dealing with the rapid motion of the electrons, the ions may be assumed to be at rest in arbitrary positions. The electrons then form a conservative dynamical system described by the Hamiltonian

$$(2.1) \quad H_{\text{electrons}}(\underline{r}^{(i)}, \underline{s}^{(i)}) = \sum_{(i)} T(\underline{r}^{(i)}) + \sum_{(i)} V_+(r^{(i)}) + \frac{1}{2} \sum_{(i)(i')} V_{--}(r^{(i)}; r^{(i')})$$

where the terms on the right represent respectively the kinetic energy of the electrons, the potential energy of the electrons due to the ions, and the electrostatic energy of the pairs of electrons properly counted. It will be shown in the next section that the state of motion of this system is stationary.

According to quantum mechanics, the stationary state of motion of a conservative dynamical system is characterised by the variational principle that the energy, i.e. the expectation value of the Hamiltonian, of the system is a minimum.

$$(2.2) \quad \left( \int_{\text{electrons}} \psi(\underline{r}^{(i)}, s^{(i)}) \cdot H_{\text{electrons}}(\underline{r}^{(i)}) \psi(\underline{r}^{(i)}, s^{(i)}) \right) = \text{minimum}$$

The exact variational equations obtained from this for determining the wave function  $\psi_{\text{electrons}}(\underline{r}^{(i)}, s^{(i)})$  which describes the precise state of motion of the

numerous electrons need not be written down here, and there is no way of attacking the problem in this form. For an approximate treatment, I shall adopt the method of Fock and Dirac.

2.1. The method of Fock(1930) and Dirac(1930). In this method the assumption is made that the wave function of the electrons is of the form of a determinant

$$(2.3) \quad \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x, s) & \psi_2(x, s) & \dots & \psi_{N-1}(x, s) \\ \psi_1(x', s') & \psi_2(x', s') & \dots & \psi_{N-1}(x', s') \\ \dots & \dots & \dots & \dots \\ \psi_1(x^{(N-1)}, s^{(N-1)}) & \dots & \dots & \psi_{N-1}(x^{(N-1)}, s^{(N-1)}) \end{vmatrix}$$

In this way the original single function of  $4N$  variables is decomposed into  $N$  functions of four variables each, denoted by  $\psi_i$  ( $i = 1, 2, \dots, N$ ), without violating the Pauli principle, which demands that the wave function of a number of electrons should be antisymmetric with respect to an interchange of the coordinates of any two electrons. These functions are to be determined according to the variational principle (2.2). The system of variational equations thus obtained may be abbreviated as follows

$$(2.4) \quad (T(x) + V(x) + P(x, s) - A(x, s) - W_i) \psi_i(x, s) = 0$$

$$(i = 1, 2, \dots, N)$$

in which the superscripts of the arguments have been dropped. The parameters  $W_i$  ( $i = 1, 2, \dots, N$ ) are just defined by the above system of equations. The operators  $P(r, s)$  and  $A(r, s)$  are defined in terms of the following quantities

$$(2.5) \quad \rho(r, s; r', s') = \sum_i \varphi_i(r, s) \varphi_i^*(r', s')$$

$$(2.6) \quad P(r, s) = P(r, s; r, s)$$

$$(2.7) \quad A(r, s; r', s') = V_-(r; r') \rho(r, s; r', s')$$

as follows

$$(2.8) \quad P(r, s) = \sum_{s'} \int dr' V_-(r; r') \rho(r', s')$$

$$(2.9) \quad A(r, s) \varphi_i(r, s) = \sum_{s'} \int dr' A(r, s; r', s') \varphi_i(r', s')$$

By the definition (2.9), the operator  $A(r, s)$  is self-adjoint, i.e.

$$(2.10) \quad (\varphi_i(r, s) \cdot A(r, s) \varphi_j(r, s)) = (\varphi_j(r, s) \cdot A(r, s) \varphi_i(r, s))^*$$

The other operators appearing in the Fock-Dirac system of equations are also self-adjoint. Hence the functions  $\varphi_i$  ( $i = 1, 2, \dots, N$ ) are mutually orthogonal.

Substituting (2.3) into (2.2), and making use of the orthogonality of the functions  $\varphi_i$ , we find for the total energy of the electrons

$$(2.11) \quad \sum_i \left( \varphi_i(r,s) \cdot (\nabla_r^2 + \nabla_s^2) + \frac{P(r,s) - A(r,s)}{2} \right) \varphi_i(r,s)$$

or, in terms of the parameters defined by (2.5),

$$(2.12) \quad \sum_i W_i = \sum_i \left( \varphi_i(r,s) \frac{P(r,s) - A(r,s)}{2} \varphi_i(r,s) \right)$$

By multiplying the wave functions(2.3) by its complex conjugate, and summing and integrating over all the spin and the spatial coordinates with the exception of  $r, s$  and  $r', s'$ , it is seen that the determinant

$$(2.13) \quad \begin{vmatrix} \rho(r,s) & \rho(r,s; r',s') \\ \rho(r',s'; r,s) & \rho(r',s') \end{vmatrix}$$

gives the total probability of finding a pair of electrons at  $r, s$  and  $r', s'$  (Dirac(1931)).

Similarly the quantity

$$(2.14) \quad \rho(r,s)$$

gives the total probability of finding a single electron at  $r, s$ .

The total electrostatic energy of the pairs of electrons is, by (2.14),

$$(2.15) \quad \frac{1}{2} \sum_{ss'} \iint d\underline{r} d\underline{r}' V_{--}(\underline{r}; \underline{r}') \begin{vmatrix} \rho(\underline{r}, s) & \rho(\underline{r}, s; \underline{r}', s') \\ \rho(\underline{r}', s'; \underline{r}, s) & \rho(\underline{r}', s') \end{vmatrix}$$

where the factor one-half is necessary in order to avoid counting every interaction twice. By making use of (2.5) - (2.9), (2.15) can also be written in the form

$$(2.16) \quad \sum_i \left( \mathcal{G}_i(\underline{r}, s) \cdot \frac{\mathcal{P}(\underline{r}, s) - A(\underline{r}, s)}{2} \mathcal{G}_i(\underline{r}, s) \right)$$

## 2.2. Separation of the spin (Brillouin (1934)).

For metals which are magnetically unpolarised, the total spin of the electrons must cancel. In this case, the  $\mathcal{N}_-$  functions can be grouped, by a proper arrangement, into  $\frac{\mathcal{N}_-}{2}$  pairs, so that the functions belonging to the same pair do not differ in their dependence on the spatial coördinates. Furthermore, both of them belong to the same parameter.

If we agree to denote the functions of the  $j$ -th pair by  $\mathcal{G}_{j,\sigma}$  ( $\sigma = 1, 2$ ) and to replace the single index  $i$  used above by the double indices  $j, \sigma$ , then we may write

$$(2.17) \quad W_i = W_{j,\sigma} = W_j$$

$$(2.18) \quad \varphi_i(\underline{r}, s) = \varphi_{j, \sigma}(\underline{r}, s) = \psi_j(\underline{r}) \delta_{\sigma}^s$$

where the spin-dependent part is simply Kronecker's delta.

By substituting (2.17) and (2.18) into (2.4), it is readily verified that, <sup>(2.17) and (2.18)</sup> form a self-consistent solution of (2.4) provided that the  $\psi_j(\underline{r})$ 's satisfy the following system of equations

$$(2.19) \quad \left( T(\underline{r}) + V_{\pm}(\underline{r}) + P(\underline{r}) - \frac{A(\underline{r})}{\lambda} - W_j \right) \psi_j(\underline{r}) = 0$$

The operators  $P(\underline{r})$  and  $A(\underline{r})$  are defined by dropping the spin coordinates everywhere in (2.5)-(2.9), and by substituting  $\psi_j$  for  $\varphi_i$  and  $\lambda S_j$  for  $S_i$ . E.g., (2.5) becomes

$$(2.20) \quad \rho(\underline{r}, \underline{r}') = \lambda S_j \psi_j(\underline{r}) \psi_j^*(\underline{r}')$$

The connection of  $\rho(\underline{r}, \underline{r}')$  with  $\rho(\underline{r}, s; \underline{r}', s')$  is

$$(2.21) \quad \rho(\underline{r}, s; \underline{r}', s') = \frac{1}{\lambda} \rho(\underline{r}, \underline{r}') \delta(s, s')$$

where the spin-dependent part is simply Kronecker's delta.

From (2.21) and from (2.13), it follows that the total probability of finding a pair of electrons at  $\underline{r}$

and  $r'$  with their spins parallel or antiparallel is

$$(2.22) \quad \left| \begin{matrix} \rho(r,1) & \rho(r,1;r',1) \\ \rho(r',1;r,1) & \rho(r',1) \end{matrix} \right| + \left| \begin{matrix} \rho(r,2) & \rho(r,2;r',2) \\ \rho(r',2;r,2) & \rho(r',2) \end{matrix} \right| = \frac{1}{2} \left| \begin{matrix} \rho(r) & \rho(r;r') \\ \rho(r';r) & \rho(r') \end{matrix} \right|$$

(spins parallel)

or

$$(2.23) \quad \left| \begin{matrix} \rho(r,1) & \rho(r,1;r',2) \\ \rho(r',2;r,1) & \rho(r',2) \end{matrix} \right| + \left| \begin{matrix} \rho(r,2) & \rho(r,2;r',1) \\ \rho(r',1;r,2) & \rho(r',1) \end{matrix} \right| = \frac{1}{2} \rho(r) \rho(r')$$

(spins antiparallel).

From (2.21) and (2.14), it follows that the total probability of finding an electron at  $r$  of a specified or an unspecified spin is

$$(2.24) \quad \rho(r,1) = \rho(r,2) = \frac{1}{2} \rho(r)$$

(specified spin)

or

$$(2.25) \quad \rho(r,1) + \rho(r,2) = \rho(r)$$

(unspecified spin).

The fact that the the expression (2.25) is the product of (2.24) and (2.25) shows that, in this approximation, there is no statistical correlation between the positions of two electrons with their spins anti-parallel.

By (2.17) and (2.18), the total energy of the electrons can be reduced to

$$(2.26) \quad 2 \sum_j W_j - 2 \sum_j \left( \psi_j(r) \cdot \frac{P(r) - \frac{A(r)}{2}}{2} \psi_j(r) \right)$$

2.3. Wigner's extension of the above method. Wigner(1934) has made an improvement upon the above method to allow for a statistical correlation between the positions of electrons with antiparallel spins, by generalising one half of the  $\psi_j$  functions of (2.3) to become functions involving the relative coordinates also. The method is designed as an extension of the method of Fock and Dirac, and is to be applied only after the functions  $\psi_j$  of (2.19) have been found.

In the simple case when the  $\psi_j$  are plane wave functions, Wigner's calculations show that the probability (2.25) of finding a pair of electrons with their spins antiparallel should be corrected by a factor depending on their relative distance. The total energy of the electrons is to be depressed by an amount depending on the volume of the metal. This "correlation energy" (Fig.7, Wigner, loc.cit. p.1010.) contributes much to the binding energy of metals, but it may not affect the elastic and thermic properties of metals so seriously. This will be discussed later.

3. The motion of the ions in metals

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In dealing with the motion of the ions in metals, I assume that the motion of the electrons reaches its stationary state instantaneously. The instantaneous stationary state of the motion of the electrons can be determined by the methods given in the preceding section. This point of view is a good approximation, for owing to the enormous difference in the rapidity of the respective motions, an "instant" to the ions is an "era" to the electrons, the transient motion of the electrons in the earlier period of which can therefore be neglected on the average. The quantitative justification of this assumption will be given later.

As the configuration of the ions changes, the stationary motion of the electrons changes with it. The adaptation of the stationary motion of the electrons to the slowly changing configuration of the ions gives rise to a kind of potential energy which partly determines the motion of the ions. The above consideration therefore shows that the original dynamical system of ions and electrons may be somehow reduced to a system in which only the coordinates of the ions appear. This may be done as follows.

### 3.1. Reduction of the total Hamiltonian of

the metal. The total Hamiltonian of the metal is

$$(3.1) \quad H_{\text{metal}} = \sum_l \frac{p(r^l) \cdot p(r^l)}{2M} + \frac{1}{2} \sum_{ll'} V_{++}(r_-^l; r_-^{l'}) \\ + \sum_l \sum_{ij} V_{+-}(r_-^l; r_-^{(ij)}) \\ + \sum_{ij} T(r_-^{(ij)}) + \frac{1}{2} \sum_{ijij'} V_{--}(r_-^{(ij)}; r_-^{(ij')})$$

The terms of this expression represent the kinetic energy of the ions and of the electrons and the interaction energy of the various sorts of pairs of particles. As the term  $V_+(r_-^{(ij)})$  used in (2.1) stands just for the lattice sum

$$(3.2) \quad V_+(r_-^{(ij)}) = \sum_l V_{+-}(r_-^l; r_-^{(ij)})$$

the equation (3.1) may also, by (2.1), be written in the form

$$(3.3) \quad H_{\text{metal}}(r_-^l; r_-^{(ij)}) = \sum_l \frac{p(r^l) \cdot p(r^l)}{2M} + \frac{1}{2} \sum_{ll'} V_{++}(r_-^l; r_-^{l'}) \\ + H_{\text{electrons}}$$

The state of motion of this complicated system may be assumed to be stationary, as time does not appear explicitly in (3.1). The stationary state of motion is again characterised by the variational principle of the total energy, i.e.

$$(3.4) \quad (\varphi_{\text{metal}}(r_-^l; r_-^{(ij)}; s^{(ij)}) \cdot H_{\text{metal}} \varphi_{\text{metal}}) = \text{minimum} = E_{\text{metal}}$$

If the  $r^l$ 's are regarded as given constants, (3.4) reduces to (2.2), which therefore describes the instantaneous stationary motion of the electrons.

I now assume that the wave function of the metal is approximately

$$(3.5) \quad \psi_{metal}(r^l; r^{(i)}, s^{(i)}) = \psi_{ions}(r^l) \psi_{electrons}(r^{(i)}, s^{(i)})$$

where  $\psi_{electrons}(r^{(i)}, s^{(i)})$  satisfies (2.2) and therefore involves the  $r^l$ 's only as parameters.

Substituting (3.2) and (3.5) into (3.4), commuting  $\int \frac{p(r^l) \cdot p(r^l)}{2M}$  and  $\psi_{electrons}(r^{(i)}, s^{(i)})$ , and making use of the normalisation condition of the wave function of the electrons, we obtain

$$(3.6) \quad \left( \psi_{ions}(r^l) \cdot \left\{ \int \frac{p(r^l) \cdot p(r^l)}{2M} + \frac{1}{2} \sum_{ll'} V_{++}(r^l, r^{l'}) + E_{electrons} \right\} \psi_{ions}(r^l) \right) = \text{minimum} = E_{metal}$$

in which terms arising from commuting  $\int \frac{p(r^l) \cdot p(r^l)}{2M}$  and  $\psi_{electrons}(r^{(i)}, s^{(i)})$  have been dropped in view of that I shall treat the motion of the ions by classical mechanics.

As classical mechanics is the limiting case of quantum mechanics and is sufficiently accurate for treating the motion of heavy particles if they are not too close to each other, I may pass from quantum mechanics to classical mechanics by replacing the

variational principle (3.6) by its analogue, namely the Hamiltonian equations derived from the Hamiltonian

$$(3.7) \quad H_{\text{ions}} = \sum_l \frac{p_l \cdot p_l}{2M} + \frac{1}{2} \sum_{ll'} S'_{ll'} V_{++}(r_l^l; r_{-}^{l'}) + E_{\text{electrons}}$$

This is the Hamiltonian describing the slow motion of the ions in metals, when the motion of the electrons is regarded as subordinate. The potential energy in (3.7) is partly contributed by the electrons, and is equal, when the method of Fock and Dirac is used for approximating the motion of the electrons, (cf. (2.26)), to

$$(3.8) \quad 2 \sum_j W_j - 2 \sum_j (\psi_j(r_j) \cdot \frac{p(r_j) - \frac{A(r_j)}{2}}{2} \psi_j(r_j)) + \frac{1}{2} \sum_{ll'} S'_{ll'} V_{++}(r_l^l; r_{-}^{l'})$$

Although (3.7) is very much simpler than (3.1), it still involves a large number of coordinates. An exact solution of a many-body problem is impracticable in classical mechanics as well as in quantum mechanics. Turning to approximate methods, I shall adopt Born's theory of crystals.

3.2. Born's theory of crystals (1923, 1939). For simplicity, only cubic crystals will be considered. Surface effects will be neglected.

At zero temperature and stresses, the ions are at rest in a unique configuration, specified by the lattice points  $\underline{a}^l$ ,

$$(3.9) \quad \underline{\dot{a}}^l = l_1 \underline{\dot{a}}_1 + l_2 \underline{\dot{a}}_2 + l_3 \underline{\dot{a}}_3 \quad (l_1, l_2, l_3 = -L, -L+1, \dots, +L)$$

Under an external stress, the crystal is homogeneously deformed, that is to say, that the positions of the ions are  $\underline{a}^l$ , related to  $\underline{\dot{a}}^l$  as follows:

$$(3.10) \quad \underline{a}_\alpha^l = \underline{\dot{a}}_\alpha^l + \sum_{\alpha\beta} S_{\alpha\beta} \underline{\dot{a}}_\beta^l \quad \begin{matrix} (\alpha, \beta = 1, 2, 3) \\ (l_1, l_2, l_3 = -L \dots +L) \end{matrix}$$

The positions  $\underline{a}^l$  may also be specified by

$$(3.11) \quad \underline{a}^l = l_1 \underline{a}_1 + l_2 \underline{a}_2 + l_3 \underline{a}_3 \quad (l_1, l_2, l_3 = -L \dots +L)$$

Where the lattice vectors  $\underline{a}_1, \underline{a}_2, \underline{a}_3$  are related to  $\underline{\dot{a}}_1, \underline{\dot{a}}_2, \underline{\dot{a}}_3$  by relations similar to (3.10).

At finite temperatures, according to Born, the motion of the ions are small, and therefore harmonic. The harmonic oscillations of the ions may be analysed, by a Fourier series, into a superposition of <sup>the</sup> so-called thermal waves: -

$$(3.12) \quad r_\alpha^l = \underline{a}_\alpha^l + \sum_n U_\alpha^n e^{i \underline{q}^n \cdot \underline{a}^l} \quad \begin{matrix} (n_1, n_2, n_3 = -L \dots +L) \\ (l_1, l_2, l_3 = -L \dots +L) \end{matrix}$$

in which the wave vectors  $\underline{q}^n$  form a lattice

$$(3.13) \quad \underline{q}^n = n_1 \underline{q}_1 + n_2 \underline{q}_2 + n_3 \underline{q}_3 \quad (n_1, n_2, n_3 = -L \dots +L)$$

with lattice vectors

$$(3.14) \quad \underline{q}_1 = \frac{2\pi}{2L+1} \underline{b}_1, \quad \underline{q}_2 = \frac{2\pi}{2L+1} \underline{b}_2, \quad \underline{q}_3 = \frac{2\pi}{2L+1} \underline{b}_3$$

The vectors  $\underline{b}_1, \underline{b}_2, \underline{b}_3$  of (3.14) are the vectors reciprocal to  $\underline{a}_1, \underline{a}_2, \underline{a}_3$ , defined by

$$(3.15) \quad \begin{aligned} \underline{a}_1 \cdot \underline{b}_1 &= \underline{a}_2 \cdot \underline{b}_2 = \underline{a}_3 \cdot \underline{b}_3 = 1 \\ \underline{a}_1 \cdot \underline{b}_2 &= \underline{a}_2 \cdot \underline{b}_1 = \underline{a}_1 \cdot \underline{b}_3 = \underline{a}_3 \cdot \underline{b}_1 = \underline{a}_2 \cdot \underline{b}_3 = \underline{a}_3 \cdot \underline{b}_2 = 0 \end{aligned}$$

It is easily verified, by (3.11), (3.13), (3.14) and (3.15), that the following identities

$$(3.16) \quad \int_{\underline{a}'} e^{i\mathbf{g}^n \cdot \underline{a}'} e^{-i\mathbf{g}^{n'} \cdot \underline{a}'} = N_+ \delta^{nn'}$$

$$(3.17) \quad \int_{\underline{a}'} e^{i\mathbf{g}^n \cdot \underline{a}'} e^{-i\mathbf{g}^{n'} \cdot \underline{a}'} = N_+ \delta^{ll'}$$

hold, where the delta with superscripts represent the product of three Kronecker's deltas. These identities show that the  $\underline{U}^n$  of (3.12) represent the Fourier amplitudes of the small oscillations of the ions.

The amplitudes  $\underline{U}^n$  are generally complex, satisfy

$$(3.18) \quad \underline{U}^{n*} = \underline{U}^{-n}$$

and can be used, instead of the positions  $\underline{r}^l$  of the ions, to specify the dynamical state of the crystal.

Now substitute (3.12) in the expression (3.8) for the potential energy of the metal and expand the result with respect to the  $\underline{U}_\alpha^n$  as far as the quadratic terms, neglecting the terms of higher order, the normal

frequencies for small oscillations of the ions are then to be determined by transforming the quadratic form thus obtained to its principal axes. These frequencies depend on the external stresses (Born(1939)). A statistical treatment of these normal oscillations gives the thermal properties of the crystal.

The elastic properties of the crystal at zero temperature may be simply obtained by expanding the potential energy (3.8) with respect to the strain parameters  $\epsilon_{\alpha\beta}$  introduced by the homogeneous deformation (3.10).

Because a part of the potential (3.8) of the metal is contributed by the electrons, the explicit expansion must be postponed until later, after a study of the motion of the electrons in a "lattice" of ions specified by their actual positions. The word "lattice" used here deviates from its usual meaning and will be explained below.

3.3. Generalisation of the word "lattice".

The usual meaning of the word "lattice" used in the theory of crystals is best seen from the equations (3.9), (3.11), and (3.13). The word conveys the idea of a set of points possessing three translational periods, namely, the lattice vectors. In what follows, I shall use for this idea the word "periodic lattice" and reserve the word "lattice" for the vague

idea of a set of points arbitrarily arranged.

Thus the instantaneous positions of the ions form a lattice in the above sense. This lattice is not

periodic, but it possesses the following property.

If we extend the domain of  $l_1, l_2, l_3$  to all positive and negative integral values, (the  $l_1, l_2, l_3$  were limited to the integral values from  $-L$  to  $+L$ ,

cf. (3.9),) the resultant infinite lattice formed by

the  $\underline{x}^l$  of (3.12) is nothing but an assemblage of smaller lattices congruent to the original lattice formed by the instantaneous positions of the ions.

Lattices possessing this property will, in general,

be called "cyclic lattices". Note that periodic

lattices, (i.e. lattices in the usual sense,) are a

particular kind of cyclic lattices.

After this literary digression, I must return to the physical problem. The problem at hand is to

expand the potential energy of the metal (3.8) with

respect to the parameters  $S_{\alpha\beta}$  of (3.10) and

the parameters  $U_\alpha^2$  of (3.12). This will

be done in the next section.

4. The motion of the electrons perturbed by the  
 displacements of the ions

In this section a general method will be developed for the expansion of the total energy of the electrons in solids with respect to the displacements of the ions. The displacements of the ions may be due to either thermal oscillations (cf. (3.12)) or a homogeneous deformation (cf. (3.10)). The law of displacement of the ion, say, the  $l$ -th, may be written in the form

$$(4.1) \quad \underline{r}_\alpha^l = \underline{r}_\alpha^{o l} + u_\alpha(\underline{r}_\alpha^{o l})$$

where  $\underline{r}_\alpha^l$  and  $\underline{r}_\alpha^{o l}$  represent respectively the displaced and the undisplaced positions of the  $l$ -th ion. The functions  $u_\alpha$  are either superpositions of plane wave functions or simply linear functions.

4.1. The motion of the electrons in cyclic lattices. As shown in §3.3, the positions of the ions  $\underline{r}_\alpha^l$  form a cyclic lattice. It follows from the property of the cyclic lattice given in the paragraph already quoted, that the domain of space in which the electrons move must possess parallel, opposite faces, separated by the dimensions of the crystal. Apart from this, the choice of the

boundary is arbitrary; - we can always deform the parallel, opposite face in the same arbitrary way.

This arbitrariness in the choice of the boundary of the domain gives rise to the following boundary condition on the functions  $\psi_j(\mathbf{r})$  of (2.19). The functions  $\psi_j(\mathbf{r})$ , when extended across one face of the boundary of the domain, should reproduce the values they assumed at the corresponding points by the parallel, opposite face. If this process is continued indefinitely, the extended functions are then continuous functions with the periodicity of the dimensions of the crystal. Functions which will be called "cyclic functions", so that the boundary conditions on the  $\psi_j(\mathbf{r})$  become simply that they are cyclic.

It is satisfactory that the normalisation of the  $\psi_j(\mathbf{r})$  are independent of the particular domain chosen for the range of integration. As a matter of fact, it will be seen that all physical quantities are independent of the choice of the domain.

To show this, it is only necessary to verify that the operators appearing in (2.19) are all "cyclic operators", i.e. operators which can be applied to cyclic functions to yield cyclic functions. For then the expectation values of these operators will be independent of the choice of the domain of integration.

That the kinetic energy operator  $T(\underline{r})$  of (2.19) is cyclic follows directly from the fact that the derivatives of cyclic functions are cyclic functions. The potential energy of the electron due to the ions, the term  $V_+(\underline{r})$  of (2.19), is naturally cyclic for a cyclic lattice. The other two operators  $P(\underline{r})$  and  $A(\underline{r})$  are defined by (cf. (2.8), (2.9), and (2.20))

$$(4.2) \quad P(\underline{r}) = \int d\underline{r}' V_-(\underline{r}; \underline{r}') \sum_j S_j \psi_j(\underline{r}') \psi_j^*(\underline{r}')$$

$$(4.3) \quad A(\underline{r}) \psi_j(\underline{r}) = \int d\underline{r}' V_-(\underline{r}; \underline{r}') \sum_j S_j \psi_j(\underline{r}') \psi_j^*(\underline{r}') \psi_j(\underline{r}')$$

where  $V_-(\underline{r}; \underline{r}')$  denotes the coulomb interaction of two electrons. As  $V_-(\underline{r}; \underline{r}')$  is a function of the relative coordinates, and as the rest of the integrands of (4.2) and (4.3) are cyclic functions, the results of the integrations are cyclic functions in the argument  $\underline{r}$ . Hence the operators  $P(\underline{r})$  and  $A(\underline{r})$  are also cyclic operators.

In the above consideration, emphasis has been given to the arbitrariness in the choice of the boundary of the domain of a cyclic lattice. There is, however, the trivial condition that the domain must contain the ions. It follows from this that, if the ions are displaced, the domain in which the electrons move must be displaced also. By a homogeneous deformation,

some ions will be displaced, in fact, to outside the original domain. This difference of the domains makes it impossible to apply directly the ordinary perturbation method for dealing with the motion of the electrons in a displaced lattice.

I shall avoid this difficulty by applying a contact transformation by means of which the whole effect of the displacements of the ions may be represented as a change of potential only, so that the ordinary perturbation theory becomes applicable.

#### 4.2. Transformation to the image-space.

The law of the displacements (4.1) of the ions suggests the introduction of the coordinate transformation

$$(4.4) \quad \tilde{r}_\alpha = \bar{r}_\alpha + u_\alpha(\bar{r})$$

which, being a one-to-one continuous transformation, may be conveniently conceived as mapping real space where the coordinates are  $\tilde{r}_\alpha$  on an image space where the coordinates are  $\bar{r}_\alpha$ . The "bar" over a quantity will always denote this transformation.

From (4.1) and (4.4), we see that the "images" of the ions are given by

$$(4.5) \quad \bar{r}_\alpha^l = \bar{r}_\alpha^o$$

and form an undisplaced lattice. Hence it is convenient to choose the domain  $R$  of the displaced

lattice so that its image  $\bar{R}$  coincides with the domain  $\overset{\circ}{R}$  of the undisplaced lattice. This is, of course, allowable, for so long as  $\overset{\circ}{R}$  fulfills the necessary conditions given in §4.1 of being a domain of the cyclic lattice formed by the undisplaced ions, the  $R$ , as chosen above, fulfills these conditions for the displaced lattice. The advantage of this choice of  $R$  will be seen immediately; the domain  $\overset{\circ}{R}$  of the undisplaced lattice may be assumed as given.

I shall now transform the equations of motion of the electrons (2.19) to the image-space by applying the following contact transformation "associated" with the coordinate transformation (4.1): -

$$(4.6) \quad \bar{\psi}(\bar{r}) = w(\bar{r}) \psi(r(\bar{r})) \quad (\text{for all the } \psi\text{-functions})$$

$$(4.7) \quad \bar{Q}(\bar{r}) = w(\bar{r}) Q(r(\bar{r})) \{w(\bar{r})\}^{-1} \quad (\text{for all operators}).$$

The weight function

$$(4.8) \quad w(\bar{r}) = \sqrt{\frac{\partial(r_1, r_2, r_3)}{\partial(\bar{r}_1, \bar{r}_2, \bar{r}_3)}}$$

is purposely included in (4.6) in order to simplify the normalisation of  $\bar{\psi}(\bar{r})$  so that

$$\begin{aligned}
 (4.9) \quad (\bar{\psi}_j(\bar{r}) \cdot \bar{\psi}_{j'}(\bar{r})) &= \int_R d\bar{r} \bar{\psi}_j^*(\bar{r}) \bar{\psi}_{j'}(\bar{r}) \\
 &= \int_R d\bar{r} \frac{\partial(r_1, r_2, r_3)}{\partial(\bar{r}_1, \bar{r}_2, \bar{r}_3)} \bar{\psi}_{j'}^*(r(\bar{r})) \psi_{j'}(r(\bar{r})) = \int_R d\bar{r} \bar{\psi}_j^*(\bar{r}) \bar{\psi}_{j'}(\bar{r}) = (\bar{\psi}_j(\bar{r}) \cdot \bar{\psi}_{j'}(\bar{r}))
 \end{aligned}$$

and in (4.7) in order to simplify the calculation of the expectation values of the operators, so that,

$$(4.10) \quad (\bar{\psi}_j(\bar{r}) \cdot \bar{Q}(\bar{r}) \bar{\psi}_{j'}(\bar{r})) = (\psi_j(r) \cdot Q(r) \psi_{j'}(r))$$

By substituting (4.4) into (2.19), pre-multiplying it by  $\mathcal{W}(r)$ , and making use of the definitions (4.6) and (4.7), it is readily verified that the transformed equations of (2.19) can be written in the form similar to (2.19),

$$\begin{aligned}
 (4.11) \quad \left( \bar{\mathcal{T}}(\bar{r}) + \bar{V}_+(\bar{r}) + \bar{\rho}(\bar{r}) - \frac{\bar{A}(\bar{r})}{2} - \bar{W}_j \right) \bar{\psi}_j(\bar{r}) &= 0 \\
 (j = 1, 2, \dots, n/2)
 \end{aligned}$$

with the following similar definitions

$$(4.12) \quad \bar{\rho}(\bar{r}; \bar{r}') = 2 \sum_j \bar{\psi}_j(\bar{r}) \bar{\psi}_j^*(\bar{r}')$$

$$(4.13) \quad \bar{\rho}(\bar{r}) = \bar{\rho}(\bar{r}; \bar{r})$$

$$(4.14) \quad \bar{A}(\bar{r}; \bar{r}') = \bar{V}_-(\bar{r}; \bar{r}') \bar{\rho}(\bar{r}; \bar{r}')$$

$$(4.15) \quad \bar{\rho}(\bar{r}) = \int d\bar{r}' \bar{V}_-(\bar{r}; \bar{r}') \bar{\rho}(\bar{r}')$$

$$(4.16) \quad \bar{A}(\bar{r}) \bar{\psi}_j(\bar{r}) = \int d\bar{r}' \bar{A}(\bar{r}; \bar{r}') \bar{\psi}_j(\bar{r}')$$

The equations (4.9) - (4.16) confirm that the

transformation defined by (4.6), (4.7) is a contact transformation.

From the boundary conditions that the  $\psi_j(r)$  are cyclic functions in the domain  $R$ , it follows that their continuous transform  $\bar{\psi}_j(r(\bar{r}))$  are cyclic functions in the transformed domain  $\bar{R}$ .

Furthermore, it is easily verified, by (4.4) and (4.8), that the weight functions  $w(\bar{r})$  is a cyclic function in the domain  $\bar{R}$ , - it is a constant or a superposition of plane wave functions according to whether the displacements of the ions are due to the homogeneous deformation or due to thermal oscillations.

Hence, by (4.6), the boundary conditions of the  $\bar{\psi}_j(\bar{r})$  are that they are cyclic in the domain  $\bar{R}$ .

Similarly all operators appearing in (4.11) are cyclic. For vanishing displacements of the ions, in which

case the transformation to the image space reduces to the identity transformation of replacing  $r_\alpha$  by  $\bar{r}_\alpha$ , the equations (4.11) becomes therefore the equations of motion of the electrons in the undisplaced lattice, only written in the coordinates  $\bar{r}_\alpha$ . As the domain  $\bar{R}$  can be chosen to coincide with the domain of the undisplaced lattice and the boundary conditions of the  $\bar{\psi}_j(\bar{r})$  are the same as the boundary conditions of the  $\psi$ -functions in the undisplaced lattice, the equations (4.11) may therefore be solved by the ordinary perturbation method.

4.3. Perturbation theory of the Fock-Dirac system of equations. All quantities in the equations (4.11) - (4.16) will be expanded with respect to the displacements of the ions.

Successive order terms of the expansions will be denoted by the numerals above the letters, e.g.

$$(4.17) \quad \bar{\psi}_j(\bar{r}) = \overset{0}{\psi}_j(\bar{r}) + \overset{1}{\psi}_j(\bar{r}) + \overset{2}{\psi}_j(\bar{r}) + \dots$$

In the expansions of (4.14), (4.15), (4.16), it is convenient to add another numeral, enclosed in a bracket, to indicate the order of the factor  $\rho$  involved. E.g., the second-order term of (4.16) is

$$(4.18) \quad \overset{2}{A}(\bar{r}) = \overset{2(0)}{A}(\bar{r}) + \overset{2(1)}{A}(\bar{r}) + \overset{2(2)}{A}(\bar{r})$$

where

$$(4.19) \quad \overset{2(\mu)}{A}(\bar{r}) \overset{0}{\psi}_j(\bar{r}) = \int d\bar{r}' V_{-}^{2-\mu}(\bar{r}; \bar{r}') \rho(\bar{r}; \bar{r}') \overset{0}{\psi}_j(\bar{r}')$$

According to the above notation, the zero-order equation of (4.11) assumes the form

$$(4.20) \quad \overset{0}{H}(\bar{r}) + \overset{0}{V}_+(\bar{r}) + \overset{0(0)}{P}(\bar{r}) - \frac{\overset{0(0)}{A}(\bar{r})}{2} - \overset{0}{W}_j \overset{0}{\psi}_j(\bar{r}) = 0$$

(  $j = 1, 2, \dots, N/2$  )

As clearly indicated by the bracketed numeral affixed

to the operators  $\overset{\circ}{P}(\bar{x})$  and  $\overset{\circ}{A}(\bar{x})$ , this system of equations are non-linear, for  $\overset{\circ}{P}$  involves the  $\overset{\circ}{\psi}_J$ . In the perturbation theory, however, this unperturbed problem is assumed as having been previously solved.

This being so, the operators  $\overset{\circ(0)}{P}(\bar{x})$  and  $\overset{\circ(0)}{A}(\bar{x})$  are known operators. The multiplication operator  $\overset{\circ(0)}{P}(\bar{x})$  is linear, and the integral operator  $\overset{\circ(0)}{A}(\bar{x})$  is also linear, i.e.

$$(4.21) \quad \overset{\circ(0)}{A}(\bar{x}) \psi(\bar{x}) = \int d\bar{x}' V_{-}(\bar{x}; \bar{x}') \overset{\circ}{P}(\bar{x}; \bar{x}') \psi(\bar{x}')$$

where  $\psi(\bar{x})$  stands for an arbitrary cyclic function.

Let us consider then the linear equation, the eigenvalue problem,

$$(4.22) \quad (\overset{\circ}{H}(\bar{x}) - W_J) \overset{\circ}{\psi}_J(\bar{x}) = 0$$

where

$$(4.23) \quad \overset{\circ}{H}(\bar{x}) = \overset{\circ}{T}(\bar{x}) + \overset{\circ}{V}_+(\bar{x}) + \overset{\circ(0)}{P}(\bar{x}) - \frac{\overset{\circ(0)}{A}(\bar{x})}{\mathcal{L}}$$

with the boundary condition that the  $\overset{\circ}{\psi}_J$  are cyclic. This boundary condition is consistent with the requirement that the momentum operator  $\overset{\circ}{p}(\bar{x})$  and consequently the kinetic energy operator  $\overset{\circ}{T}(\bar{x})$  ought to be self-adjoint. For the difference of the scalar product

$$(\psi_J^0(\bar{x}) \cdot \underline{r}(\bar{x}) \psi_{J'}^0(\bar{x}))$$

and

$$(\psi_{J'}^0(\bar{x}) \cdot \underline{r}(\bar{x}) \psi_J^0(\bar{x}))^*$$

being reducible, by Green's theorem, to the surface integral

$$-i\hbar \int_{\underline{v}} \psi_J^0(\bar{x}) \psi_{J'}^0(\bar{x}) dS$$

(where  $\underline{v}$  denotes the outward normal and  $2\pi\hbar$ , the Planck constant), vanishes identically. The contribution due to one face of the domain is just cancelled by that due to the opposite, parallel face, on which the outward normal reverses its sign.

And similarly the difference of the scalar products

$$(\psi_J^0(\bar{x}) \cdot \underline{r}(\bar{x}) \psi_{J'}^0(\bar{x})) \text{ and } (\psi_{J'}^0(\bar{x}) \cdot \underline{r}(\bar{x}) \psi_J^0(\bar{x}))^*$$

vanishes identically.

Hence the operator  $\hat{H}(\bar{x})$  is a linear self-adjoint operator. According to the theory of such operators, (4.22) admits and defines a complete set of orthogonal eigenfunctions to which set the original functions  $\psi_J^0(\bar{x})$  naturally belong, in virtue of (4.20).

This set of eigenfunctions can be used as a basis for the expansion of any cyclic function defined in the same

domain as the eigenfunctions  $\psi_j^0(\bar{r})$ .

The original  $\psi_j^0$ -functions will be specially called Fock's functions.

The perturbed Fock's functions  $\bar{\psi}_j(\bar{r})$ , being cyclic, may be expanded in the set  $\psi_J^0(\bar{r})$ ,

$$(4.24) \quad \bar{\psi}_j(\bar{r}) = \sum_J \psi_J^0(\bar{r}) U_{Jj}$$

where  $U_{Jj}$  are constant coefficients. After the perturbed Fock's functions are obtained, a perturbed eigenvalue problem similar to (4.22), (4.23) may be introduced to construct the complete set of perturbed eigenfunctions. Although for the calculation of the energy of the electrons, no perturbed eigenfunctions other than the perturbed Fock's functions are needed, it is convenient, however, to expand the complete set  $\bar{\psi}_j(\bar{r})$  of the perturbed eigenvalue problem

$$(4.25) \quad \{ \bar{H}(\bar{r}) - W_J \} \bar{\psi}_j(\bar{r}) = 0$$

in the set  $\psi_J^0(\bar{r})$ ,

$$(4.26) \quad \bar{\psi}_j(\bar{r}) = \sum_{J'} \psi_{J'}^0(\bar{r}) U_{J'j}$$

in order to use the abstract perturbation theory of Born and Jordan (1930).

In the abstract notation, <sup>the</sup> equation (4.26) can be written simply

$$(4.27) \quad \bar{\psi}_J(\bar{x}) = U(\bar{x}) \psi_J^0(\bar{x})$$

where  $U(\bar{x})$  is to be regarded as an operator, in fact a cyclic operator, for both the  $\bar{\psi}_J$  and the  $\psi_J^0$  are cyclic functions. With every cyclic operator

$Q(\bar{x})$ , a matrix  $\underline{Q}$  of elements  $Q_{J'J}$  defined by

$$(4.28) \quad Q(\bar{x}) \psi_J^0(\bar{x}) = \sum_{J'} \psi_{J'}^0(\bar{x}) Q_{J'J}$$

may be associated, so that the matrix elements associated with the product of two cyclic operators

$Q'(\bar{x})$  and  $Q(\bar{x})$  can be calculated according to matrix calculus, i.e.

$$(4.29) \quad (Q'Q)_{J''J} = \sum_{J'} Q'_{J''J'} Q_{J'J}$$

This follows by a consistent application of the definition (4.28), namely on the one hand one writes

$$(4.30) \quad (Q'(\bar{x})Q(\bar{x})) \psi_J^0(\bar{x}) = \sum_{J''} \psi_{J''}^0(\bar{x}) (Q'Q)_{J''J}$$

while on the other hand, using (4.28) twice in

succession, one writes

$$(4.31) \quad Q'(\bar{E}) Q(\bar{E}) \psi_J^0(\bar{E}) = \sum_{J'} Q'(\bar{E}) \psi_{J'}^0(\bar{E}) Q_{J'J} = \sum_{J''} \sum_{J'''} \psi_{J''}^0(\bar{E}) Q'_{J''J'''} Q_{J''J}$$

A comparison of these ways of writing gives (4.29), for the functions  $\psi_{J'}^0$  are mutually orthogonal.

The practical way of calculating the matrix element  $Q_{J'J}$  of a known cyclic operator  $Q(\bar{E})$  is, by (4.28), to calculate the scalar product

$$(4.32) \quad (\psi_{J'}^0(\bar{E}) \cdot Q(\bar{E}) \psi_J^0(\bar{E}))$$

4.4. Perturbation equations. As shown above all the operators appearing in the perturbed and the unperturbed eigenvalue problems are cyclic operators, and for cyclic operators, matrix representations are defined, I can therefore apply the perturbation theory of Born and Jordan(1930, Kap.5), using matrix representations for all operators. In particular, the determination of the perturbed functions  $\bar{\psi}_J$  is equivalent to the determination of the matrix  $\underline{U}$ , cf.(4.26).

In the matrix representations, the determination of the eigenfunctions of an operator  $Q(\bar{E})$  is equivalent to the transformation of the matrix  $\underline{Q}$  to diagonal form. As the unperturbed eigenvalue problem is

assumed as having been previously solved, the matrix

$\underline{\underline{\overset{\circ}{H}}}$  is in diagonal form

$$(4.33) \quad \underline{\underline{\overset{\circ}{H}}} = \underline{\underline{\overset{\circ}{W}}} \quad (\underline{\underline{\overset{\circ}{W}}} \text{ being a diagonal matrix}).$$

Solution of (4.25) by the expansion (4.26) of the

$\bar{\psi}_J$  is equivalent to transformation of the matrix  $\underline{\underline{\bar{H}}}$  to diagonal form by the change of basis defined by (4.26), i.e.

$$(4.34) \quad \underline{\underline{U}}^{-1} \underline{\underline{\bar{H}}} \underline{\underline{U}} = \underline{\underline{W}} \quad (\underline{\underline{W}} \text{ being a diagonal matrix}).$$

Pre-multiplying this equation by the matrix  $\underline{\underline{U}}$ , the equation for the determination of  $\underline{\underline{U}}$  may be taken as

$$(4.35) \quad \underline{\underline{\bar{H}}} \underline{\underline{U}} - \underline{\underline{U}} \underline{\underline{W}} = 0$$

This is equivalent to the equations of motion of the electrons in the displaced lattice.

From the normalisation conditions imposed on the

$\bar{\psi}_J(\vec{r})$  and the  $\psi_J^0(\vec{r})$ , it follows that the matrix is unitary

$$(4.36) \quad \underline{\underline{U}}^\dagger \underline{\underline{U}} = \underline{\underline{I}},$$

$\underline{\underline{U}}^\dagger$  denoting the matrix adjoint to  $\underline{\underline{U}}$ , defined by

$$(4.37) \quad U_{JJ}^{\dagger} = U_{JJ}^*$$

This is equivalent to the normalisation condition of the perturbed functions  $\bar{\psi}_J(\bar{r})$ .

Expansion of the operators in the manner described by (4.17), (4.18) corresponds to expansion of the corresponding matrices. The expansion of the matrix matrices will be denoted by  $\underline{A}^a$  similar notation, e.g.

$$(4.38) \quad \underline{U} = \underline{U}^0 + \underline{U}^1 + \underline{U}^2 + \dots$$

$$(4.39) \quad \underline{A}^2 = \underline{A}^{2(0)} + \underline{A}^{2(1)} + \underline{A}^{2(2)}$$

where the bracketed numeral now signifies the total order of the factor  $U_{J_j}$  involved in the  $\underline{A}^{2(a)}$ .

The matrix equations (4.35), (4.36) for the determination of  $\underline{U}$  may therefore be expanded into equations for the determination of  $\underline{U}^1, \underline{U}^2$  etc., the zero-order equation gives simply (4.33) and the trivial solution

$$(4.40) \quad \underline{U}^0 = \underline{I}$$

By (4.33) and (4.40), the perturbation equations of the first order and of the second order are respectively

$$(4.41) \quad \underline{\underline{W}}^0 \underline{\underline{U}}^1 - \underline{\underline{U}}^1 \underline{\underline{W}}^0 + \underline{\underline{H}}^1 - \underline{\underline{W}}^1 = 0$$

$$(4.42) \quad \underline{\underline{U}}^{1\dagger} + \underline{\underline{U}}^1 = 0$$

and

$$(4.43) \quad \underline{\underline{W}}^0 \underline{\underline{U}}^2 - \underline{\underline{U}}^2 \underline{\underline{W}}^0 + \underline{\underline{H}}^1 \underline{\underline{U}}^1 - \underline{\underline{U}}^1 \underline{\underline{W}}^1 + \underline{\underline{H}}^2 - \underline{\underline{W}}^2 = 0$$

$$(4.44) \quad \underline{\underline{U}}^{2\dagger} + \underline{\underline{U}}^2 + \underline{\underline{U}}^{1\dagger} \underline{\underline{U}}^1 = 0$$

The special feature of the Fock-Dirac [may be seen from

equations?  
methods?

$$(4.45) \quad \underline{\underline{H}}^1 = \underline{\underline{T}}^1 + \underline{\underline{V}}_+^1 + \underline{\underline{P}}^{1(0)} - \frac{1}{2} \underline{\underline{A}}^{1(0)} + \underline{\underline{P}}^{1(1)} - \frac{1}{2} \underline{\underline{A}}^{1(1)}$$

and

$$(4.46) \quad \underline{\underline{H}}^2 = \underline{\underline{T}}^2 + \underline{\underline{V}}_+^2 + \underline{\underline{P}}^{2(0)} - \frac{1}{2} \underline{\underline{A}}^{2(0)} + \underline{\underline{P}}^{2(1)} - \frac{1}{2} \underline{\underline{A}}^{2(1)} + \underline{\underline{P}}^{2(2)} - \frac{1}{2} \underline{\underline{A}}^{2(2)}$$

where the bracketed numerals show that  $\underline{\underline{H}}^1, \underline{\underline{H}}^2$  actually depend on the matrix elements  $\underline{\underline{U}}^1_{ji}, \underline{\underline{U}}^2_{ji}$ . Thus

by taking the diagonal elements of (4.41) and (4.42), we obtain

$$(4.47) \quad \underline{\underline{W}}^1_{jj} = \underline{\underline{T}}^1_{jj} + \underline{\underline{V}}^1_{jj} + \underline{\underline{P}}^{1(0)}_{jj} - \frac{1}{2} \underline{\underline{A}}^{1(0)}_{jj} + \underline{\underline{P}}^{1(1)}_{jj} - \frac{1}{2} \underline{\underline{A}}^{1(1)}_{jj}$$

and in the explicit form

$$(4.48) \quad \overset{2}{W}_{ji} = \overset{2}{H}_{ji} + (\overset{1}{H}\overset{1}{U} - \overset{1}{U}\overset{1}{W})_{ji}$$

which can only be evaluated after  $\overset{1}{U}_{Jj}$  and  $\overset{2}{U}_{Jj}$  are known. It will be shown later, however, that in the calculation of the perturbation energy of the electrons,  $\overset{1}{U}_{Jj}$  will not be needed for the first-order energy, and similarly  $\overset{2}{U}_{Jj}$  will not be needed for the second-order energy.

By taking the non-diagonal element of (4.41), we obtain

$$(4.49) \quad (\overset{0}{W}_J - \overset{0}{W}_j) \overset{1}{U}_{Jj} + \overset{1}{P}_{Jj} - \frac{1}{2} \overset{1(1)}{A}_{Jj} = -\overset{1}{T}_{Jj} - \overset{1}{V}_{+Jj} - \overset{1(0)}{P}_{Jj} + \frac{1}{2} \overset{1(0)}{A}_{Jj}$$

The matrix element  $\overset{1(1)}{A}_{Jj}$  may be calculated from the operator  $\overset{1(1)}{A}(\vec{E})$  (4.19) by forming the scalar product

$$(4.50) \quad (\overset{0}{\Psi}_J(\vec{E}) \cdot \overset{1(1)}{A}(\vec{E}) \overset{0}{\Psi}_j(\vec{E})) = \overset{1(1)}{A}_{Jj}$$

From the definition of  $\overset{1}{\rho}(\vec{E}; \vec{E}')$  (cf(4.12)) and from the expansion (4.26) or (4.27), (4.50) may be written in the explicit form

$$(4.51) \quad \overset{1(1)}{A}_{Jj} = 2S_j \sum_{J'} (\overset{0}{\Psi}_J(\vec{E}) \cdot (\overset{0}{\Psi}_{J'}(\vec{E}') \cdot \overset{1}{V}(\vec{E}; \vec{E}') \overset{0}{\Psi}_{J'}(\vec{E}')) \overset{0}{\Psi}_{J'}(\vec{E})) \overset{1}{U}_{Jj}^* + 2S_j \sum_{J'} (\overset{0}{\Psi}_J(\vec{E}) \cdot (\overset{0}{\Psi}_{J'}(\vec{E}') \cdot \overset{1}{V}(\vec{E}; \vec{E}') \overset{0}{\Psi}_{J'}(\vec{E}')) \overset{0}{\Psi}_{J'}(\vec{E})) \overset{1}{U}_{Jj}$$

or in the abstract form

$$(4.52) \quad A_{J_j}^{(1)} = 2S_{j'} \sum_{J_j'} \{ \dot{V}_{-J_j'; J_j'} \dot{U}_{J_j'}^* + \dot{V}_{-J_j'; J_j} \dot{U}_{J_j'} \}$$

The expression

where

where

$$(4.53) \quad \dot{V}_{-J_j'; J_j'} = (\dot{\psi}_J(\vec{r}) \cdot \dot{\psi}_{J'}(\vec{r}') \cdot \dot{V}(\vec{r}; \vec{r}') \dot{\psi}_{J'}^*(\vec{r}') \dot{\psi}_J^*(\vec{r}))$$

Since  $\dot{V}(\vec{r}; \vec{r}')$  is symmetric in the two arguments  $\vec{r}$  and  $\vec{r}'$ , we have

$$(4.54) \quad \dot{V}_{-J_j'; J_j'} = \dot{V}_{-J_j'; J_j}$$

Similarly the matrix element  $P_{J_j}^{(1)}$  may be written in the form

$$(4.55) \quad \begin{aligned} P_{J_j}^{(1)} &= 2S_{j'} \sum_{J_j'} (\dot{\psi}_J(\vec{r}) \cdot \dot{\psi}_{J'}(\vec{r}') \cdot \dot{V}(\vec{r}; \vec{r}') \dot{\psi}_{J'}^*(\vec{r}') \dot{\psi}_J^*(\vec{r})) \dot{U}_{J_j'}^* \\ &+ 2S_{j'} \sum_{J_j'} (\dot{\psi}_J(\vec{r}) \cdot \dot{\psi}_{J'}(\vec{r}') \cdot \dot{V}(\vec{r}; \vec{r}') \dot{\psi}_{J'}^*(\vec{r}') \dot{\psi}_J^*(\vec{r})) \dot{U}_{J_j'} \\ &= 2S_{j'} \sum_{J_j'} \{ \dot{V}_{-J_j'; J_j} \dot{U}_{J_j'}^* + \dot{V}_{-J_j'; J_j} \dot{U}_{J_j'} \} \end{aligned}$$

Substituting (4.55) and (4.52) into (4.49), we obtain a system of equations in  $\dot{U}_{J_j}$  ( $j=1, 2, \dots, N/2$ ) which is equivalent to the perturbed Fock-Dirac system of equations to the first-order perturbation, namely

$$(4.56) \quad \begin{aligned} &(\dot{W}_J - \dot{W}_J) \dot{U}_{J_j} + 2S_{j'} \sum_{J_j'} (\dot{V}_{-J_j'; J_j} - \frac{1}{2} \dot{V}_{-J_j'; J_j'}) \dot{U}_{J_j'}^* \\ &+ 2S_{j'} \sum_{J_j'} (\dot{V}_{-J_j'; J_j} - \frac{1}{2} \dot{V}_{-J_j'; J_j}) \dot{U}_{J_j'} \\ &= -\dot{V}_{-J_j'; J_j} - \dot{V}_{+J_j'; J_j} - \dot{P}_{J_j}^{(1)} + \frac{1}{2} A_{J_j}^{(1)} \end{aligned}$$

Solution of this system of equations is needed for the calculation of the second-order perturbation energy of the electrons.

4.5. Perturbation energy of the electrons.

The expression (2.26) for the total energy of the electrons, when transformed to the image space, becomes

$$(4.57) \quad E_{electrons} = 2 \sum_j W_j - 2 \sum_j (\bar{\psi}_j(\bar{r}) \cdot \frac{\bar{p}(\bar{r}) - \frac{\bar{A}(\bar{r})}{c}}{2} \bar{\psi}_j(\bar{r}))$$

If this expression is expanded with respect to the displacements of the ions in accordance with the notation used above, we obtain for the perturbation energy of the first order and of the second order

$$(4.58) \quad E_{electrons}^1 = 2 \sum_j W_j^1 - 2 \sum_j (\bar{\psi}_j^0(\bar{r}) \cdot \frac{\bar{p}^1(\bar{r}) - \frac{\bar{A}^1(\bar{r})}{c}}{2} \bar{\psi}_j^0(\bar{r})) - 2 \sum_j [(\bar{\psi}_j^1(\bar{r}) \cdot \frac{\bar{p}^0(\bar{r}) - \frac{\bar{A}^0(\bar{r})}{c}}{2} \bar{\psi}_j^0(\bar{r})) + (\bar{\psi}_j^0(\bar{r}) \cdot \frac{\bar{p}^1(\bar{r}) - \frac{\bar{A}^1(\bar{r})}{c}}{2} \bar{\psi}_j^1(\bar{r}))]$$

and

$$(4.59) \quad E_{electrons}^2 = 2 \sum_j W_j^2 - 2 \sum_j (\bar{\psi}_j^0(\bar{r}) \cdot \frac{\bar{p}^2(\bar{r}) - \frac{\bar{A}^2(\bar{r})}{c}}{2} \bar{\psi}_j^0(\bar{r})) - 2 \sum_j [(\bar{\psi}_j^1(\bar{r}) \cdot \frac{\bar{p}^1(\bar{r}) - \frac{\bar{A}^1(\bar{r})}{c}}{2} \bar{\psi}_j^1(\bar{r})) + (\bar{\psi}_j^1(\bar{r}) \cdot \frac{\bar{p}^0(\bar{r}) - \frac{\bar{A}^0(\bar{r})}{c}}{2} \bar{\psi}_j^0(\bar{r})) + (\bar{\psi}_j^0(\bar{r}) \cdot \frac{\bar{p}^2(\bar{r}) - \frac{\bar{A}^2(\bar{r})}{c}}{2} \bar{\psi}_j^0(\bar{r})) + (\bar{\psi}_j^0(\bar{r}) \cdot \frac{\bar{p}^1(\bar{r}) - \frac{\bar{A}^1(\bar{r})}{c}}{2} \bar{\psi}_j^1(\bar{r})) + (\bar{\psi}_j^1(\bar{r}) \cdot \frac{\bar{p}^2(\bar{r}) - \frac{\bar{A}^2(\bar{r})}{c}}{2} \bar{\psi}_j^1(\bar{r}))]$$

respectively. These expressions will be transformed to convenient forms as follows.

Substituting for  $W_j^1$  the expression (4.47) into (4.58), and making use of the equivalence of the matrix element  $\bar{p}_{jj}^1 - \frac{1}{2} \bar{A}_{jj}^1$  and the scalar product

$(\psi_j^0(\vec{r}) \cdot (\hat{p}(\vec{r}) - \frac{1}{2} \hat{A}(\vec{r}))) \psi_j^0(\vec{r})$ , we obtain

$$(4.60) \quad \begin{aligned} \hat{E}_{\text{electrons}} = & 2 S_j (\hat{T}_{jj}^1 + \hat{V}_{jj}^1) + 2 S_j (\psi_j^0(\vec{r}) \cdot \frac{\hat{p}(\vec{r}) - \frac{1}{2} \hat{A}(\vec{r})}{2} \psi_j^0(\vec{r})) \\ & - 2 S_j \left[ (\psi_j^0(\vec{r}) \cdot \frac{\hat{p}(\vec{r}) - \frac{1}{2} \hat{A}(\vec{r})}{2} \psi_j^0(\vec{r})) + (\psi_j^0(\vec{r}) \cdot \frac{\hat{p}(\vec{r}) - \frac{1}{2} \hat{A}(\vec{r})}{2} \psi_j^0(\vec{r})) \right] \end{aligned}$$

With the help of the first-order equation of (4.12),  
i.e.

$$(4.61) \quad \hat{p}(\vec{r}, \vec{r}') = 2 S_j \left[ \psi_j^0(\vec{r}) \psi_j^{0*}(\vec{r}') + \psi_j^0(\vec{r}') \psi_j^{0*}(\vec{r}) \right]$$

and the zero-order equations of (4.12) - (4.16), it is readily verified that

$$(4.62) \quad \begin{aligned} & 2 S_j \left[ (\psi_j^0(\vec{r}) \cdot \frac{\hat{p}(\vec{r}) - \frac{1}{2} \hat{A}(\vec{r})}{2} \psi_j^0(\vec{r})) + (\psi_j^0(\vec{r}') \cdot \frac{\hat{p}(\vec{r}') - \frac{1}{2} \hat{A}(\vec{r}')}{2} \psi_j^0(\vec{r}')) \right] \\ = & 2 S_j \iint d\vec{r} d\vec{r}' \psi_j^{0*}(\vec{r}) \frac{\hat{V}_{-}(\vec{r}, \vec{r}')}{2} [\hat{p}(\vec{r}') \psi_j^0(\vec{r}) - \frac{1}{2} \hat{p}(\vec{r}, \vec{r}') \psi_j^0(\vec{r}')] \\ & + 2 S_j \iint d\vec{r} d\vec{r}' \psi_j^{0*}(\vec{r}') \frac{\hat{V}_{-}(\vec{r}, \vec{r}')}{2} [\hat{p}(\vec{r}) \psi_j^0(\vec{r}') - \frac{1}{2} \hat{p}(\vec{r}, \vec{r}') \psi_j^0(\vec{r}')] \\ = & \iint d\vec{r} d\vec{r}' \frac{\hat{V}_{-}(\vec{r}, \vec{r}')}{2} [\hat{p}(\vec{r}') \hat{p}(\vec{r}) - \frac{1}{2} \hat{p}(\vec{r}, \vec{r}') \hat{p}(\vec{r}', \vec{r})] \\ = & \iint d\vec{r}' d\vec{r} \frac{\hat{V}_{-}(\vec{r}, \vec{r}')}{2} [\hat{p}(\vec{r}) \hat{p}(\vec{r}') - \frac{1}{2} \hat{p}(\vec{r}', \vec{r}) \hat{p}(\vec{r}, \vec{r}')] \\ = & 2 S_j \iint d\vec{r} d\vec{r}' \psi_j^{0*}(\vec{r}') \frac{\hat{V}_{-}(\vec{r}, \vec{r}')}{2} [\hat{p}(\vec{r}') \psi_j^0(\vec{r}) - \frac{1}{2} \hat{p}(\vec{r}, \vec{r}') \psi_j^0(\vec{r}')] \\ = & 2 S_j (\psi_j^0(\vec{r}) \cdot \frac{\hat{p}(\vec{r}) - \frac{1}{2} \hat{A}(\vec{r})}{2} \psi_j^0(\vec{r})) \end{aligned}$$

the last step being a consequence of the notation explained above in (4.18), (4.19).

Hence, by substituting (4.62) into (4.60), we obtain finally for the first-order perturbation energy of the electrons

$$(4.63) \quad \overset{1}{E}_{\text{electrons}} = 2S_j (\overset{1}{T}_{jj} + \overset{1}{V}_{jj}) + 2 \int_j (\overset{0}{\psi}_j(\bar{r}) \cdot \frac{\overset{1(0)}{P}(\bar{r}) - \frac{1}{2} \overset{1(0)}{A}(\bar{r})}{\lambda} \overset{1}{\psi}_j(\bar{r}))$$

or, (cf. (4.62)),

$$(4.64) \quad \overset{1}{E}_{\text{electrons}} = 2S_j (\overset{1}{T}_{jj} + \overset{1}{V}_{jj}) + \iint d\bar{r} d\bar{r}' \frac{\overset{1}{V}(\bar{r}; \bar{r}')}{\lambda} [\overset{0}{\rho}(\bar{r}; \bar{r}') \overset{0}{\rho}(\bar{r}) - \frac{1}{2} \overset{0}{\rho}(\bar{r}; \bar{r}') \overset{0}{\rho}(\bar{r}; \bar{r}')]$$

It is satisfactory to see that for the calculation of the first-order perturbation energy, the first-order perturbed eigenfunctions need not be known.

In order to transform the second-order energy (4.59), in a way similar to the above, the following preliminary step is necessary. Since the

perturbation operators are self-adjoint and consequently  $\overset{1}{W}_j$ ,  $\overset{2}{W}_j$  are real, the expression (4.48) for  $\overset{2}{W}_j$  may be replaced by the mean of (4.48) and its adjoint, i.e.

$$(4.65) \quad \overset{2}{W}_j = \frac{(\overset{2}{H} + \overset{1}{H}\overset{1}{U} - \overset{1}{U}\overset{1}{W})_{jj} + (\overset{2}{H} + \overset{1}{H}\overset{1}{U} - \overset{1}{U}\overset{1}{W})_{jj}^\dagger}{2}$$

By (4.42), and that  $\overset{1}{W}$  is diagonal and real, we have

$$(4.66) \quad \begin{aligned} \{ -\overset{1}{U}\overset{1}{W} - (\overset{1}{U}\overset{1}{W})^\dagger \}_{jj} &= \{ -\overset{1}{U}\overset{1}{W} - \overset{1}{W}\overset{1}{U}^\dagger \}_{jj} \\ &= \{ -\overset{1}{U}\overset{1}{W} + \overset{1}{W}\overset{1}{U} \}_{jj} = 0 \end{aligned}$$

Hence (4.65) becomes simply

$$(4.67) \quad \overset{2}{W}_j = \frac{(\overset{2}{H} + \overset{2}{H}\overset{1}{U})_{ji}}{2} + \frac{(\overset{2}{H} + \overset{2}{H}\overset{1}{U})_{ji}^\dagger}{2}$$

or, explicitly,

$$(4.68) \quad \overset{2}{W}_j = \frac{(\overset{2}{T} + \overset{2}{V} + (\overset{2}{T} + \overset{2}{V})\overset{1}{U})_{ji} + (\overset{2}{T} + \overset{2}{V} + (\overset{2}{T} + \overset{2}{V})\overset{1}{U})_{ji}^\dagger}{2} + (\overset{2}{P} - \frac{\overset{2}{A}}{2})_{ji} + \frac{((\overset{2}{P} - \frac{\overset{2}{A}}{2})\overset{1}{U} + \overset{1}{U}^\dagger(\overset{2}{P} - \frac{\overset{2}{A}}{2}))_{ji}}{2}$$

Now with the help of the first-order equation of (4.27), i.e.

$$(4.69) \quad \overset{1}{\psi}_j(\bar{x}) = \overset{1}{U}(\bar{x}) \overset{0}{\psi}_j(\bar{x})$$

the terms of (4.68) depending on the  $\overset{2}{P}$  and the  $\overset{2}{A}$  can be transformed as follows

$$(4.70) \quad \begin{aligned} & \frac{((\overset{2}{P} - \frac{\overset{2}{A}}{2})\overset{1}{U} + \overset{1}{U}^\dagger(\overset{2}{P} - \frac{\overset{2}{A}}{2}))_{ji}}{2} \\ &= (\overset{0}{\psi}_j(\bar{x}) \cdot \frac{\overset{2}{P}(\bar{x}) - \frac{\overset{2}{A}(\bar{x})}{2}}{2} \overset{1}{U}(\bar{x}) \overset{0}{\psi}_j(\bar{x})) \\ &+ (\overset{1}{U}(\bar{x}) \overset{0}{\psi}_j(\bar{x}) \cdot \frac{\overset{2}{P}(\bar{x}) - \frac{\overset{2}{A}(\bar{x})}{2}}{2} \overset{0}{\psi}_j(\bar{x})) \\ &= (\overset{0}{\psi}_j(\bar{x}) \cdot \frac{\overset{2}{P}(\bar{x}) - \frac{1}{2}\overset{2}{A}(\bar{x})}{2} \overset{1}{\psi}_j(\bar{x})) \\ &+ (\overset{1}{\psi}_j(\bar{x}) \cdot \frac{\overset{2}{P}(\bar{x}) - \frac{1}{2}\overset{2}{A}(\bar{x})}{2} \overset{0}{\psi}_j(\bar{x})) \end{aligned}$$

Hence substituting (4.68) into (4.57), and making use of (4.70) for cancelling terms, we find

$$(4.71) \quad \begin{aligned} \bar{E}_{\text{electrons}}^2 &= 2S_j \frac{(\vec{p} + \vec{v}_+ + (\vec{p} + \vec{v}_+) \dot{U})_{jj} + (\vec{p} + \vec{v}_+ + (\vec{p} + \vec{v}_+) \dot{U})_{jj}^\dagger}{2} \\ &\quad + 2S_j (\psi_j^0(\vec{r})) \cdot \frac{\beta(\vec{r}) - \frac{1}{2} \dot{A}(\vec{r})}{2} \psi_j^0(\vec{r}) \\ &\quad - 2S_j \left[ (\psi_j^2(\vec{r})) \cdot \frac{\beta(\vec{r}) - \frac{1}{2} \dot{A}(\vec{r})}{2} \psi_j^0(\vec{r}) + (\psi_j^1(\vec{r})) \cdot \frac{\beta(\vec{r}) - \frac{1}{2} \dot{A}(\vec{r})}{2} \psi_j^1(\vec{r}) + (\psi_j^0(\vec{r})) \cdot \frac{\beta(\vec{r}) - \frac{1}{2} \dot{A}(\vec{r})}{2} \psi_j^2(\vec{r}) \right] \end{aligned}$$

which may be compared with (4.60). The rest of the transformation is similar. With the help of the identity (cf. (4.62),)

$$(4.72) \quad \begin{aligned} &2S_j \left[ (\psi_j^2(\vec{r})) \cdot \frac{\beta(\vec{r}) - \frac{1}{2} \dot{A}(\vec{r})}{2} \psi_j^0(\vec{r}) + (\psi_j^1(\vec{r})) \cdot \frac{\beta(\vec{r}) - \frac{1}{2} \dot{A}(\vec{r})}{2} \psi_j^1(\vec{r}) + (\psi_j^0(\vec{r})) \cdot \frac{\beta(\vec{r}) - \frac{1}{2} \dot{A}(\vec{r})}{2} \psi_j^2(\vec{r}) \right] \\ &= 2S_j (\psi_j^0(\vec{r})) \cdot \frac{\beta^{(2)}(\vec{r}) - \frac{1}{2} \dot{A}^{(2)}(\vec{r})}{2} \psi_j^0(\vec{r}) \end{aligned}$$

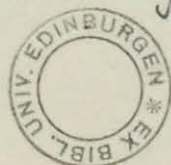
we obtain finally for the second-order perturbation energy of the electrons (cf. (4.63),)

$$(4.73) \quad \begin{aligned} \bar{E}_{\text{electrons}}^2 &= 2S_j \frac{(\vec{p} + \vec{v}_+ + (\vec{p} + \vec{v}_+) \dot{U})_{jj} + (\vec{p} + \vec{v}_+ + (\vec{p} + \vec{v}_+) \dot{U})_{jj}^\dagger}{2} \\ &\quad + 2S_j (\psi_j^0(\vec{r})) \cdot \frac{\beta^{(2)}(\vec{r}) - \frac{1}{2} \dot{A}^{(2)}(\vec{r})}{2} \psi_j^0(\vec{r}) \end{aligned}$$

or (cf. (4.64),) the equivalent form

$$(4.74) \quad \begin{aligned} \bar{E}_{\text{electrons}}^2 &= 2S_j \frac{(\vec{p} + \vec{v}_+ + (\vec{p} + \vec{v}_+) \dot{U})_{jj} + (\vec{p} + \vec{v}_+ + (\vec{p} + \vec{v}_+) \dot{U})_{jj}^\dagger}{2} \\ &\quad + \iint d\vec{r} d\vec{r}' \frac{V_{-}(\vec{r}; \vec{r}')}{2} [\beta(\vec{r}') \beta(\vec{r}) - \frac{1}{2} \beta(\vec{r}; \vec{r}') \beta(\vec{r}; \vec{r}')] \\ &\quad + \iint d\vec{r} d\vec{r}' \frac{V_{-}(\vec{r}; \vec{r}')}{2} [\beta(\vec{r}) \beta(\vec{r}') - \frac{1}{2} \beta(\vec{r}; \vec{r}') \beta(\vec{r}'; \vec{r})] \end{aligned}$$

Here the matrix elements  $U_{Jj}^1$  are involved.



NOTE ADDED IN PROOF: - The last line of (4.74)

can be transformed, by a procedure similar to (4.62), into

$$(4.75) \quad 2S_j \frac{((P^{1(0)} - \frac{1}{2}A^{1(0)})U)_{ij} + ((P^{1(0)} - \frac{1}{2}A^{1(0)})U)_{ij}^*}{2}$$

The second line of (4.74) is originally (cf. (4.73))

$$2S_j \frac{(P^{2(0)} - \frac{1}{2}A^{2(0)})_{ij}}{2}$$

Hence (4.74) may be written in the form

$$(4.76) \quad \begin{aligned} \sum_{\text{electrons}}^2 E &= 2S_j \frac{((V_+^1 + P^{1(0)} - \frac{1}{2}A^{1(0)})U)_{ij} + ((V_+^1 + P^{1(0)} - \frac{1}{2}A^{1(0)})U)_{ij}^*}{2} \\ &+ 2S_j \frac{(V_+^2 + P^{2(0)} - \frac{1}{2}A^{2(0)})_{ij}}{2} \end{aligned}$$

The combination  $V_+^1 + P^{1(0)}$  represents the change of the potential of the ions and the unperturbed electron cloud, and is finite. When the energy of the ions

is added to the combination  $2S_j (V_+^2 + \frac{P^{2(0)} - \frac{1}{2}A^{2(0)}}{2})_{ij}$  the resultant energy will be finite for finite crystal, or, the energy per atom will be finite.

4.6. Concluding remarks. To solve the perturbation equations (4.41) - (4.44) and to evaluate the perturbation energy (4.64), (4.74) in the two case of the homogeneous deformation and the thermal displacements forms the task of the next two chapters. There is considerable difference in the two cases which may be noted here.

It will be shown that the perturbation operators in the two cases obey different selection rules with the consequence that, for thermal displacements of the ions, the unperturbed system behaves as a degenerate system in the sense of perturbation theory, while for homogeneous deformation, the unperturbed system behaves, at least for monovalent metals, as a non-degenerate system. For this reason, the homogeneous deformation is treated prior to the thermal displacements.

It will be shown, furthermore, that the system of perturbations (4.56) behave differently in the two cases. In the case of homogeneous deformation, the coefficient  $\dot{w}_j \sim \dot{w}_j$  in (4.56) will always be large in comparison with the other coefficients. By dividing the equations by this large coefficient, the method of successive approximations can be applied for the solution of (4.56). In the case of thermal displacements,

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this will not always be the case. For small thermal wave vectors, it will be seen that, when the coefficient  $\overset{\circ}{W}_j - \overset{\circ}{W}_j$  fails to be large, some other coefficient in (4.56) originated in the operator  $\overset{1(1)}{P}(\xi)$  will be large. Since the operator  $\overset{1(1)}{P}(\xi)$  represents the potential produced by the change of the electronic density, i.e.  $\overset{1}{\rho}(\xi')$ , (cf. (4.15)), this shows that in the case of thermal displacements, it is necessary to treat the motion of electrons by non-linear equations. Further discussion will be given later.

## ELASTIC PROPERTIES OF METALS

5. Notation  
=====

In this chapter only periodic lattices (cf. §3.3) are dealt with and a slight modification of the notation is convenient.

## 5.1. Eigenfunctions of periodic lattices.

These will be enumerated by two indices  $K$  and  $B$  in place of the single index  $J$  used in the last chapter. The index  $K$  is put as a superscript and it represents three indices  $K_1, K_2, K_3$  each of which takes all integral values from  $-L$  to  $+L$ .

The original Fock's functions are denoted by  $\psi_b^k$ .

## 5.2. Spatial coördinates. A periodic lattice

may be divided up into congruent atomic polyhedra.

When the domain of the spatial coördinates is not specially restricted to the basic polyhedron, which is that atomic polyhedron containing the origin of coördinates, the coördinates will be denoted by  $r_\alpha$  as in the last chapter. But when the domain of the

coördinates is specially restricted to the basic polyhedron the coördinates will be denoted by  $w_\alpha$ .

The domain of the basic polyhedron will be denoted by  $\Omega$ , and the surface element of the  $\Omega$ , by  $d\sigma$ .

A similar notation is used for the transformed

coordinates and domains, which are still distinguished by a bar above the symbol.

5.3. Spatial indices and the summation convention. The symbols  $\alpha, \beta, \gamma, \delta$  are all used for the spatial indices and summation over repeated Greek indices ranging from 1 to 3 is understood.

Other symbols used in the last chapter will have their original meaning.

The ionic charge is  $e_+$ , the electronic charge is  $e_-$ , the square of the electronic charge is  $e^2$ .

In the case of monovalent metals, the number of ions  $N_+$  and the number of electrons  $N_-$  are both simply  $N$ .

The periodic potential of the lattice will be denoted by  $V(\mathbf{r})$ . The wave function  $\psi(\mathbf{r})$  will be applied to periodic functions of the periodic function will be called periodic functions. The motion of the electrons in periodic lattices. The motion of electrons in a periodic field has been studied by Bloch (1929). According to Bloch's theorem, the eigenfunctions of the electron are of the form

(5.1) 
$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

## 6. Homogeneous deformation as a perturbation

The perturbation theory developed in the last chapter will now be applied to calculate the elastic constants of metals at zero temperature. For this purpose, it is only <sup>necessary</sup> to consider the homogeneous deformation(3.10) as a perturbation.

Since both the deformed and the undeformed lattices are periodic in the sense possessing three translational periods, a general consideration of the motion of the electrons in periodic lattices will be given with the view to derive certain selection rules for the perturbation operators.

For convenience, functions possessing the three translational periods of the lattice will be simply called periodic functions, and operators that can be applied to periodic functions to yield periodic functions will be called periodic operators.

6.1. The motion of the electrons in periodic lattices. The motion of electrons in a periodic field has been studied by Bloch(1928). According to Bloch's theorem, the eigenfunctions of the electrons are of the form

$$(6.1) \quad \psi_B^K(r) = \frac{e^{i\mathbf{K} \cdot \mathbf{r}}}{\sqrt{N_+}} u_B^K(r)$$

in which the  $\frac{1}{f} K$  are reduced wave vectors and the  $u_B^K$  are periodic functions. In our case where the field is represented by the operator  $V_+(r) + P(r) - \frac{A(r)}{2}$ , it is easily verified that Bloch's theorem gives a self-consistent solution. For, if we assume that the Fock functions are of the form (6.1), i.e.,

$$(6.2) \quad \psi_b^k(r) = \frac{e^{i g^k \cdot r}}{\sqrt{N_+}} u_b^k(r)$$

we have, for the quantity  $\rho(r; r')$  (4.12),

$$(6.3) \quad \rho(r; r') = 2 S_b^k \frac{e^{i g^k \cdot r - r'}}{N_+} u_b^k(r) u_b^{k*}(r')$$

From this and from the definitions of the operators  $P(r)$  and  $A(r)$  (4.13) - (4.16), we see that the latter operators are really periodic. The field due to the ions is also periodic.

The above theorem can be applied to both the deformed and the undeformed lattices. By exactly the same argument used in connection with the cyclic operators, (4.2.), it follows that, when the equations of motion of the electrons in a deformed lattice are transformed to the image-space and expanded with respect to the displacements of the ions, the resultant perturbation operators are periodic in the undeformed

lattice. The eigenfunctions of the undeformed lattice will be denoted by  $\psi_B^{\circ K}(\bar{r})$ ,

$$(6.4) \quad \psi_B^{\circ K}(\bar{r}) = \frac{e^{i\bar{k} \cdot \bar{r}}}{\sqrt{N_+}} u_B^{\circ K}(\bar{r})$$

where the  $\bar{k}^{\circ K}$  are reduced wave vectors in the reciprocal lattice of the undeformed lattice,  $\underline{a}^L$ .

It is readily seen that for any periodic operator  $Q(\bar{r})$ , the following scalar product

$$(6.5) \quad (\psi_B^{\circ K'}(\bar{r}) \cdot Q(\bar{r}) \psi_B^{\circ K}(\bar{r})) = \frac{1}{N_+} (u_B^{\circ K'}(\bar{r}) \cdot e^{i\bar{k}' \cdot \bar{r}} Q(\bar{r}) e^{i\bar{k} \cdot \bar{r}} u_B^{\circ K}(\bar{r}))$$

vanishes in general except when  $K' = K$ . This follows from the fact that for a periodic operator  $Q(\bar{r})$ , the following operator

$$(6.6) \quad e^{-i\bar{k}' \cdot \bar{r}} Q(\bar{r}) e^{i\bar{k} \cdot \bar{r}} = Q(\bar{r})$$

is also periodic, and the fact that functions of the form of (6.4) with different values of  $K$  are orthogonal.

Since the perturbation operator are periodic, we have the selection rule that the unperturbed eigenfunctions (6.4) with different  $K$  do not combine under the perturbation of homogeneous deformation.

When the condition  $K' = K$  is satisfied, (6.5)

can be reduced to the volume integral over the domain of a single atomic polyhedron (cf. Mott and Jones (1936), p. 76), say for definiteness, the basic polyhedron  $\bar{\Omega}$  containing the origin of coordinates. When it is desired to emphasize the limitation of the domain of the spatial coordinates to  $\bar{\Omega}$ , the corresponding coordinates will be denoted by  $\bar{u}_\alpha$ . By this notation, (6.5) can be simply written in the form

$$(6.7) \quad \left( \psi_{\beta}^{K'}(\bar{r}) \cdot Q(\bar{r}) \psi_{\beta}^{K}(\bar{r}) \right) = \int^{K'K} \left( u_{\beta}^{K}(\bar{\omega}) \cdot Q(\bar{\omega}) u_{\beta}^{K}(\bar{\omega}) \right)$$

A special selection rule which holds only for the unperturbed eigenfunctions  $u_{\beta}^{K}$  ( $K=000$ ) may be obtained by symmetry consideration given below.

Since these functions  $u_{\beta}^{K}$  ( $K=000$ ) satisfy the unperturbed eigenvalue problem

$$(6.8) \quad \left( \hat{H}(\bar{r}) - W_{\beta}^{K} \right) u_{\beta}^{K} = 0 \quad (K=000)$$

and since the operator  $\hat{H}(\bar{r})$  is invariant with respect to the group of reflexions admitted by the crystal, it follows that these eigenfunctions may be classified into odd or even functions with respect to the three reflexions in mutually perpendicular planes. E.g. it is known that the Fock function  $u_{\beta}^k$  ( $k=000$ ) for alkali metals is an even-even-even function.

In the present consideration, we need only to classify

these functions into odd or even functions with respect to the central reflexion. Now the deformed lattice admits the central reflexion and therefore the perturbation operator must be even. Hence we have the selection rule that the eigenfunctions  $\dot{u}_B^K$  ( $K=000$ ) of different parity with respect to the central reflexion do not combine under the perturbation of homogeneous deformation.

There is no such selection rule for arbitrary values of  $K$  for then the functions  $\dot{u}_B^K$  cannot be classified into odd and even functions. If we substitute (6.4) into the unperturbed eigenvalue problem (cf. (4.22), (4.23)), we obtain the following equations for the

$$(6.9) \quad (\dot{H}^K(\bar{r}) - \dot{W}_B^K) \dot{u}_B^K(\bar{r}) = 0$$

where  $\dot{H}^K(\bar{r})$  is derived from  $\dot{H}(\bar{r})$  according to (6.6).

By a central reflexion,  $\dot{H}^K$  will go to  $\dot{H}^{-K}$  which is in general different from  $\dot{H}^K$ .

6.2. Perturbation operators. The law of the displacements of the ions for homogeneous deformation is given by (5.10) where the strain components  $S_{\alpha\beta}$  may be taken as constants satisfying

$$(6.10) \quad S_{\alpha\beta} = S_{\beta\alpha}$$

The coordinate transformation to the image-space is homogeneous therefore a linear transformation with constant coefficients

$$(6.11) \quad \bar{r}_\alpha = r_\alpha(\bar{r}) \equiv \bar{r}_\alpha + S_{\alpha\beta} \bar{r}_\beta$$

The Jacobian of this transformation is constant, hence the transformation of the operators reduces to a substitution of variables. The transformation of the eigenfunctions consists of a substitution of variables together with a constant normalisation factor.

The transformed operators are then expanded with respect to the strain components. Successive terms of the expansions will be denoted by symbol  $0, 1, 2$  above the letters, following entirely the notation used in the last chapter. The various terms of  $\overset{1}{H}(\bar{r}), \overset{2}{H}(\bar{r})$  will be given below.

For the expansion of  $\bar{T}(\bar{r})$ , it is only necessary to note that the momentum operator is transformed contragrediently to the coordinates. By inverting (6.11) and substituting  $\bar{p}_\alpha(\underline{r})$  for  $\bar{r}_\alpha$  and  $\bar{p}_\alpha(\bar{r})$  for  $r_\alpha$  we obtain the expansion

$$(6.12) \quad \bar{p}_\alpha(\underline{r}(\bar{r})) = \bar{p}_\alpha(\bar{r}) - \delta_{\alpha\beta} \bar{p}_\beta(\bar{r}) + \delta_{\alpha\beta} \delta_{\beta\gamma} \bar{p}_\gamma(\bar{r}) - \dots$$

Hence the expansion of  $\bar{T}(\bar{r})$  is

$$(6.13) \quad \bar{T}(\bar{r}) = \overset{0}{T}(\bar{r}) + \overset{1}{T}(\bar{r}) + \overset{2}{T}(\bar{r}) + \dots$$

$$(6.14) \quad \overset{1}{T}(\bar{r}) = \frac{1}{2m} (-2 \delta_{\alpha\beta} \bar{p}_\alpha(\bar{r}) \bar{p}_\beta(\bar{r}))$$

$$(6.15) \quad \overset{2}{T}(\bar{r}) = \frac{1}{2m} (+3 \delta_{\alpha\beta} \delta_{\beta\gamma} \bar{p}_\alpha(\bar{r}) \bar{p}_\gamma(\bar{r}))$$

For the expansion of  $\bar{V}_+(\bar{r})$ , it is convenient to approximate  $V_+(\underline{r})$  by a lattice sum of the contribution due to the individual ions

$$(6.16) \quad V_+(\underline{r}) = \sum_p V_{+-}(\underline{r} - \underline{r}^p)$$

the interaction  $V_{+-}(\underline{r} - \underline{r}^p)$  of an electron at  $\underline{r}$  with an ion at  $\underline{r}^p$  being taken as depending only on the relative coordinates of these particles. This neglects the change of the interaction between an ion and an electron due to the relative displacements of the ions which cause a change in the core electrons of the ions - the polarisation effect. Assume further that  $V_{+-}(\underline{r} - \underline{r}^p)$  can be expanded by Taylor's series, then the terms in the expansion of  $\bar{V}_+(\bar{r})$  are

$$(6.17) \quad \bar{V}_+(\bar{r}) = \sum_p \bar{V}_{+-}(\bar{r} - \bar{r}^p)$$

$$(6.18) \quad \bar{V}_+(\bar{r}) = \sum_p \bar{V}_{+-}(\bar{r} - \bar{r}^p)$$

where  $\bar{V}_{+-}(\bar{r} - \bar{r}^p)$  and  $\bar{V}_{+-}(\bar{r} - \bar{r}^p)$  are given below

$$(6.19) \quad \bar{V}_{+-}(\bar{r} - \bar{r}^p) = \sum_{\alpha} \delta_{\alpha p}(\bar{r} - \bar{r}^p)_{\alpha} \frac{\partial V_{+-}(\bar{r} - \bar{r}^p)}{\partial (r - r^p)_{\alpha}}$$

$$(6.20) \quad \bar{V}_{+-}(\bar{r} - \bar{r}^p) = \sum_{\alpha} \delta_{\alpha p} \sum_{\beta} \delta_{\beta p}(\bar{r} - \bar{r}^p)_{\alpha} (\bar{r} - \bar{r}^p)_{\beta} \frac{\partial^2 V_{+-}(\bar{r} - \bar{r}^p)}{\partial (r - r^p)_{\alpha} \partial (r - r^p)_{\beta}}$$

The expansion of the operators  $\bar{P}(\bar{r})$  and  $\bar{A}(\bar{r})$

are double series like

$$(6.21) \quad \bar{P}(\bar{z}) = \overset{0(0)}{P}(\bar{z}) + \overset{1(0)}{P}(\bar{z}) + \overset{1(1)}{P}(\bar{z}) + \overset{2(0)}{P}(\bar{z}) + \overset{2(1)}{P}(\bar{z}) + \overset{2(2)}{P}(\bar{z}) + \dots$$

with

$$(6.22) \quad \overset{\lambda(\mu)}{P}(\bar{z}) = \int d\bar{r}' \overset{\lambda-\mu}{V_{--}}(\bar{z}-\bar{z}') \overset{\mu}{\rho}(\bar{z}')$$

$$(6.23) \quad \overset{\lambda(\mu)}{A}(\bar{z}; \bar{z}') = \overset{\lambda-\mu}{V_{--}}(\bar{z}-\bar{z}') \overset{\mu}{\rho}(\bar{z}; \bar{z}')$$

$$(6.24) \quad \overset{\lambda(\mu)}{A}(\bar{z}) \overset{0K}{\psi}_B(\bar{z}) = \int d\bar{r}' \overset{\lambda(\mu)}{A}(\bar{z}; \bar{z}') \overset{0K}{\psi}_B(\bar{z}')$$

The  $\overset{\mu}{\rho}(\bar{z}; \bar{z}')$  can be directly expressed in terms of the  $\overset{0k}{\psi}_b(\bar{z})$  as follows,

$$(6.25) \quad \begin{aligned} \overset{\mu}{\rho}(\bar{z}; \bar{z}') &= 2 \int_b^k \left\{ \overset{0k}{\psi}_b(\bar{z}) \left( \overset{1}{U}(\bar{z}) \overset{0k}{\psi}_b(\bar{z}') \right)^* + \right. \\ &\quad \left. \left( \overset{1}{U}(\bar{z}) \overset{0k}{\psi}_b(\bar{z}) \right) \overset{0k*}{\psi}_b(\bar{z}') \right\} \\ &= 2 \int_b^k \frac{1}{N_+} e^{i\frac{0k}{4} \cdot \bar{z} - \bar{z}'} \left\{ \overset{0k}{u}_b(\bar{z}) \left( \overset{1k}{U}(\bar{z}) \overset{0k}{u}_b(\bar{z}') \right)^* + \right. \\ &\quad \left. \left( \overset{1k}{U}(\bar{z}) \overset{0k}{u}_b(\bar{z}) \right) \overset{0k*}{u}_b(\bar{z}') \right\} \end{aligned}$$

where  $\overset{1k}{U}(\bar{z})$  is derived from  $\overset{1}{U}(\bar{z})$  according to (6.6), which is still to be determined.

In the actual calculation of the matrix elements of the above operators with respect to the  $\overset{0K}{\psi}_B$ 's, we need according to (6.7) the operators  $\overset{\lambda}{\pi}^K$ ,  $\overset{\lambda(\mu)}{A}^K$ , etc. derived from the corresponding operators according to (6.6). For the multiplication operators, e.g.  $\overset{\lambda}{V}_+$ , the superscript  $K$  is entirely immaterial and hence will not be written. For the differential operators,

the operators with the superscript  $K$  can simply be obtained from the corresponding operators without the superscript by replacing  $f_\alpha(\bar{r})$  by  $f_\alpha^K(\bar{r})$

$$(6.26) \quad f_\alpha^K(\bar{r}) = f_\alpha(\bar{r}) + \hbar g_\alpha^{0K}$$

Thus (6.14) gives

$$(6.27) \quad \frac{1}{\hbar} \mathcal{T}^K(\bar{r}) = -\frac{2}{2m} \gamma_3 (f_\alpha(\bar{r}) + \hbar g_\alpha^{0K}) (f_\beta(\bar{r}) + \hbar g_\beta^{0K})$$

For the integral operators  $A^{(N)}(\bar{r})$  (cf. (6.24)),  $A^{(N)K}(\bar{r})$  can be obtained from  $A^{(N)}(\bar{r}; \bar{r}')$  by replacing  $A^{(N)}(\bar{r}; \bar{r}')$  by

$$(6.28) \quad A^{(N)K}(\bar{r}; \bar{r}') = A^{(N)}(\bar{r}; \bar{r}') e^{-i g_\alpha^{0K} \cdot \bar{r} - \bar{r}'}$$

6.3. Perturbation equation and energy. The

first-order perturbation energy of the electrons is given by (4.64), which, on replacing the index  $j$  by the double indices  $k, b$  and evaluating the matrix elements according to (6.7), becomes in the present case,

$$(6.29) \quad E_{\text{electrons}}^1 = 2S_b^k (u_b^{0k}(\bar{\omega})) \cdot (\mathcal{T}_{\bar{\omega}}^k + \mathcal{V}_{\bar{\omega}}^k) u_b^{0k}(\bar{\omega}) + \iint d\bar{r} d\bar{r}' \frac{\mathcal{V}_{\bar{r}-\bar{r}'}}{2} [\hat{\rho}_{\bar{r}}(\bar{r}) \hat{\rho}_{\bar{r}'}(\bar{r}') - \frac{1}{2} \hat{\rho}_{\bar{r}; \bar{r}'}(\bar{r}; \bar{r}')]$$

The first-order perturbation equation (4.49) gives, apart from

$$(6.30) \quad \bigcup_{B b}^1 \frac{K k}{B b} = 0 \quad (K \neq k)$$

which is a consequence of the selection rule, and

$$(6.31) \quad \sum_b^1 k = 0$$

which is a consequence of the normalisation condition, the following equation for the determination of  $\sum_b^1 k$

$$(6.32) \quad \begin{aligned} & (W_B^0 - W_b^0) \sum_b^1 k + P_{Bb}^{(1)} - \frac{1}{2} A_{Bb}^{(1)k} = \\ & - T_{Bb}^1 - V_{+Bb} - P_{Bb}^{(0)} + \frac{1}{2} A_{Bb}^{(0)k} \end{aligned} \quad (B \neq b)$$

In these equations,  $\sum_b^1 k$ ,  $A_{Bb}^{(1)k}$ , etc. are written instead of  $\sum_{Bb}^{1kk}$ ,  $A_{Bb}^{(1)kk}$ , etc. for they are all diagonal in the superscript  $k$  according to (6.7), which also shows that

$$(6.33) \quad A_{Bb}^{(1)k} = \langle \psi_B^0 | A^{(1)k} | \psi_b^0 \rangle$$

and similarly for the others.

The second order perturbation energy of the electrons given by (4.73) or (4.74) becomes similarly

$$(6.34) \quad \begin{aligned} \tilde{E}_{\text{electrons}}^2 &= 2 S_b^k \frac{(\tilde{T}^2 + \tilde{V}_+^2 + (\tilde{T}^1 + \tilde{V}_+^1) \tilde{U})_{bb}^k + (\tilde{T}^2 + \tilde{V}_+^2 + (\tilde{T}^1 + \tilde{V}_+^1) \tilde{U})_{bb}^{1k}}{\lambda} \\ &+ 2 S_b^k \langle \psi_b^0 | \frac{P^{(2)k} - \frac{1}{2} A^{(2)k}}{\lambda} + \frac{P^{(1)k} - \frac{1}{2} A^{(1)k}}{\lambda} | \psi_b^0 \rangle \end{aligned}$$

or

$$(6.35) \quad \begin{aligned} \tilde{E}_{\text{electrons}}^2 &= 2 S_b^k \frac{(\tilde{T}^2 + \tilde{V}_+^2 + (\tilde{T}^1 + \tilde{V}_+^1) \tilde{U})_{bb}^k + (\tilde{T}^2 + \tilde{V}_+^2 + (\tilde{T}^1 + \tilde{V}_+^1) \tilde{U})_{bb}^{1k}}{\lambda} \\ &+ \iint d\tilde{z} d\tilde{z}' \frac{\tilde{V}_- (\tilde{z} - \tilde{z}')}{2} [ \tilde{\rho}(\tilde{z}') \tilde{\rho}(\tilde{z}) - \frac{1}{2} \tilde{\rho}(\tilde{z}; \tilde{z}') \tilde{\rho}(\tilde{z}'; \tilde{z}) ] \\ &+ \iint d\tilde{z} d\tilde{z}' \frac{\tilde{V}_- (\tilde{z} - \tilde{z}')}{2} [ \tilde{\rho}(\tilde{z}') \tilde{\rho}(\tilde{z}) - \frac{1}{2} \tilde{\rho}(\tilde{z}; \tilde{z}') \tilde{\rho}(\tilde{z}'; \tilde{z}) ] \end{aligned}$$

The first form shows the origin of the integrands occurring in the double integrals of the second form, which is preferred in actual calculation.

The above equations are sufficient for the calculation of the elastic constants, provided that the eigenfunctions of the electrons in the undeformed lattice are known.

The eigenfunctions of the electrons in the undeformed lattice are given by  $\psi_{\mathbf{k}} = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{\mathbf{r}}$ , where  $\psi_{\mathbf{r}}$  are the atomic orbitals. The eigenvalues are given by  $\epsilon_{\mathbf{k}} = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \epsilon_{\mathbf{r}}$ , where  $\epsilon_{\mathbf{r}}$  are the atomic energy levels. The eigenfunctions of the electrons in the deformed lattice are given by  $\psi_{\mathbf{k}} = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{\mathbf{r}}$ , where  $\psi_{\mathbf{r}}$  are the atomic orbitals. The eigenvalues are given by  $\epsilon_{\mathbf{k}} = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \epsilon_{\mathbf{r}}$ , where  $\epsilon_{\mathbf{r}}$  are the atomic energy levels.

To obtain the perturbation  $\delta\epsilon_{\mathbf{k}}$  of the energy levels  $\epsilon_{\mathbf{k}}$  due to the deformation, we use the perturbation theory. The unperturbed energy levels are  $\epsilon_{\mathbf{k}}^0 = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \epsilon_{\mathbf{r}}^0$ , where  $\epsilon_{\mathbf{r}}^0$  are the atomic energy levels in the undeformed lattice. The perturbation  $\delta\epsilon_{\mathbf{k}}$  is given by  $\delta\epsilon_{\mathbf{k}} = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \delta\epsilon_{\mathbf{r}}$ , where  $\delta\epsilon_{\mathbf{r}}$  are the atomic energy level shifts due to the deformation. The perturbation  $\delta\epsilon_{\mathbf{k}}$  is given by  $\delta\epsilon_{\mathbf{k}} = \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \delta\epsilon_{\mathbf{r}}$ , where  $\delta\epsilon_{\mathbf{r}}$  are the atomic energy level shifts due to the deformation.

$$(1.1) \quad \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} \delta\epsilon_{\mathbf{r}} = 0$$

A knowledge of the unperturbed eigenfunctions is necessary in solving the perturbation equation and evaluating the perturbation energy given in the last section. This is only available for some monovalent metals, for which the method of Wigner and Seitz works.

7.1. Eigenfunctions of electrons in the undeformed lattice. For monovalent metals, we have

$$N_+ = N_- = N. \quad \text{For a fixed } B \text{ there are } N$$

eigenfunctions corresponding to the  $N_+$  values which

$K$  in general can assume. The  $\frac{N_+}{2} = \frac{N}{2}$  Fock's

functions differ only in the index  $k$ , but not in  $b$ .

The parameter  $\overset{\circ}{W}_b^k$  assumes a minimum for  $k=000$ ,

when the corresponding Fock's function  $\overset{\circ}{u}_b^k$  ( $k=000$ )

possesses all the symmetry of the lattice.

To avoid the parenthesis ( $k=000$ ) which would so often occur below,  $\overset{\circ}{u}_B^K$  ( $K=000$ ) will be denoted

by  $\overset{\circ}{u}_B$  and  $\overset{\circ}{W}_b^k$  ( $k=000$ ) will be denoted by  $\overset{\circ}{W}_b$ .

That is to say, whenever the superscript is missing, it

assumes the particular value  $000$ . For operators

this is automatically true according to the definition

(6.6). Thus  $\overset{\circ}{u}_b$  satisfies

$$(7.1) \quad (H(\vec{r}) - \overset{\circ}{W}_b) \overset{\circ}{u}_b(\vec{r}) = 0$$

Since  $\dot{u}_j(\vec{r})$  is periodic, it is sufficient to solve (7.1) in the basic polyhedron. By symmetry,  $\dot{u}_j(\vec{r})$  satisfies the boundary condition that its normal derivative vanishes on the surface of the polyhedron. Within the polyhedron, it is convenient to divide  $\dot{H}(\vec{r})$  into two parts, the first consisting of the kinetic energy of the electron and the potential energy due to the basic ion. Thus, we have

$$(7.2) \quad \dot{H}(\vec{r}) = \dot{T}(\vec{r}) + \dot{V}_+^0(\vec{r}) + \dot{H}'(\vec{r})$$

with

$$(7.3) \quad \dot{H}'(\vec{r}) = \dot{V}_+^{\prime 0}(\vec{r}) + \dot{P}(\vec{r}) - \frac{1}{2} \dot{A}(\vec{r})$$

where the dash affixed to  $\dot{V}_+^{\prime 0}$  serves to indicate that it represents the restricted lattice sum of the potential due to all the other ions outside the basic polyhedron.

In the method of Wigner and Seitz,  $\dot{H}'(\vec{r})$  is treated as a constant,  $\dot{u}_j(\vec{r})$  and  $\dot{V}_+^0(\vec{r})$  are approximated by functions of *the radial* distance only, and the boundary condition of  $\dot{u}_j(\vec{r})$  is approximated by replacing the atomic polyhedron by a sphere of equal volume. These approximations are introduced to reduce the equation to an ordinary differential equation so that numerical integration is applicable. The other Fock functions  $\dot{u}_j^k(\vec{r})$  are calculated by the perturbation methods.

When this method is successful the function  $\dot{u}_j(\vec{r})$

is practically constant, deviating from the constant value only in a very small neighbourhood of the ion - the region of this neighbourhood can be neglected in volume integration. This is true for sodium (Wigner and Seitz(1933)(1934)), lithium(Seitz(1935)), and copper(Fuchs(1935)). And when the function  $u_b^0(\vec{r})$  does not possess the above simple feature, the method of Wigner and Seitz is not very accurate, as shown in the case of potassium by Gorin(1936). The reason for this will be given in the next paragraph.

For eigenfunctions other than the Fock functions, a much less exact knowledge is sufficient for the calculation of the perturbation energy of the electrons in the deformed lattice. When the parameter  $\frac{W^0 K}{B}$  ( $B \neq b$ ) is algebraically less than  $\frac{W^0}{b}$ , the corresponding eigenfunction may be approximated by a Fock's function of a core electron. For alkali metals the Fock functions of the core electrons practically vanish at the boundary of the atomic polyhedron.

The eigenfunctions  $u_b^0$  having parameters immediately larger than  $\frac{W^0}{b}$  are of the type even-even-odd with respect to the three reflexions in mutually perpendicular planes and will not enter into later calculations, because of the selection rule given in §6.1. Only eigenfunctions of the symmetry character even-even-even

or even-odd-odd are needed later; the parameters for such eigenfunctions may be considered as rather high above those of the Fock functions. For sodium, the difference is at least thirteen electron-volts. (Fig. 9b, Slater(1934)p.240).

For sodium, there is another simplification of the Fock functions. The difference of  $u_b^{ok}$  and  $u_b^o$  is entirely negligible for all  $k$ . For lithium, the difference is small but appreciable.

7.2. Simplification of the perturbation energy for monovalent metals. By making use of the knowledge given in the last paragraph, it is intended to simplify the perturbation equation and the perturbation energy to a form comparable to previous works on the elastic constants of simple monovalent metals. Discussion of the errors will be given later.

The unperturbed Fock functions will be taken as

$$(7.4) \quad u_b^{ok}(\bar{\omega}) = u_b^o(\bar{\omega}) + i g^{ok} \cdot \underline{v}_b^o(\bar{\omega})$$

to the first order of  $f^{ok}$ . It is known that  $u_b^o, \underline{v}_b^o$  may be taken as real(cf.Bardeen(1938)) and that  $u_b^o$  is even while  $\underline{v}_b^o$  is odd with respect to the central reflexion. The quantity  $i g^{ok} \underline{v}_b^o$  will be treated as a small quantity of the first order, the second-order terms will be neglected. The  $u_b^o$  will be treated

as constant in volume integration.

To this accuracy, it is easily verified (cf. (6.3)) that  $\rho^0(\vec{r}; \vec{r}')$  is a function of the relative coordinates only

$$(7.5) \quad \rho^0(\vec{r} - \vec{r}') = \frac{2}{N} \sum^k e^{i \frac{2\pi}{f} \cdot \vec{r} - \vec{r}'} u_b^{0,2}$$

and that  $\rho^0(\vec{r})$  is constant

$$(7.6) \quad \rho^0(\vec{r}) = u_b^{0,2}$$

It then follows from (6.23) and (7.5) that the  $A^{\lambda(0)k}(\vec{r}; \vec{r}')$  depend only on the relative coordinates, and hence the operators  $A^{\lambda(0)k}(\vec{r})$  may be treated as constants. For no matter whatever function they are applied to operate, we always get constants. Similarly from (6.22)

and (7.6), it follows that  $\rho^{\lambda(0)}(\vec{r})$  are constants. we have

Consequently, the following simplification of the perturbation energy (6.35). Let us consider the term

$$(7.7) \quad \iint d\vec{r} d\vec{r}' \frac{V_{-}(\vec{r} - \vec{r}')}{2} \rho^1(\vec{r}') \rho^0(\vec{r})$$

of the last line of (6.35). Since  $\rho^0(\vec{r})$  is constant, the integration over  $\vec{r}$  gives a constant. The final integration over  $\vec{r}'$  vanishes by the normalisation of  $\rho^1(\vec{r}')$ . Similarly the term of (6.35) containing  $\rho^1(\vec{r}; \vec{r}')$  may be neglected.

Since the contribution of  $\rho^1$  to the energy is

thus negligible, the term  $\frac{1^{(1)}}{P_{Bb}} - \frac{1^{(2)}}{2} A_{Bb}^k$  of the perturbation equation (6.52) which describes the effect of  $\rho$  on the eigenfunction may also be considered as small. This is further supported by the fact that, in virtue of the selection rule of the central symmetry, the coefficient  $\overset{0}{W}_B^k - \overset{0}{W}_b^k$  of  $\overset{1}{U}_{Bb}^k$  is large, being 13 e.v. for sodium. While if  $\overset{1^{(1)}}{P}_{Bb}$  is expressed in a series of  $\overset{1}{U}_{B'b'}^k$  (cf. (4.56)), the coefficients cannot be so large.

The above also shows why the method of Wigner and Seitz gives a fair accurate Fock function for simple monovalent metals. For  $\overset{0}{P}^{(0)}$ ,  $\overset{0}{A}^{(0)k}$  are constants. And if we assume further that  $\overset{0}{V}_+^{(0)}(\bar{r})$  (cf. (7.3)) may be treated as constant when the polyhedron is replaced by a sphere, we arrive at the method of Wigner and Seitz.

Strictly speaking, both the  $\overset{0}{V}_+^{(0)}(\bar{r})$  and the shape of the atomic polyhedron depends on the structure of the lattice. It seems to me that if the polyhedron could be approximated by a sphere, the ions outside the polyhedron could be approximated by concentric spherical shells, and hence  $\overset{0}{V}_+^{(0)}$  would be constant by electrostatics.

In our present case, the basic polyhedron  $\bar{r}$  is in the image space. Later it will be approximated by a sphere. Then the images of the ions would be distributed on concentric spherical shells, i.e. the

ions in the real space would be distributed on concentric ellipsoidal shells. However, it is easily verified by electrostatics that the potential of such shells is constant at points surrounded by them.

Hence, when the basic polyhedron  $\bar{\Omega}$  is replaced by a sphere, the  $\bar{V}'_+(\bar{\omega})$ , where the dash omits the contribution due to the basic ion, may be approximated by a constant. The contribution  $\bar{V}'_+ \bar{U}_{bb}^k + \bar{V}'_+ \bar{U}_{bb}^{+k}$  (cf. (6.35)) to the energy  $\bar{\mathcal{E}}_{\text{electrons}}$  vanishes by the normalisation condition.

In the contribution of  $\bar{V}'_+(\bar{\omega})$  to  $\bar{\mathcal{E}}_{\text{electrons}}$ , and that of  $\bar{V}'_+(\bar{\omega})$  to  $\bar{\mathcal{E}}_{\text{electrons}}$ , the lattice structure will be taken into account.

7.3. First-order perturbation. Keeping the possible simplification given in the last paragraph in mind, I now proceed to solve the first-order perturbation equation (6.32); which for convenience will now be written, by (6.35), in the form

$$(7.8) \quad (\bar{W}_B^k - \bar{W}_b^k) \bar{U}_{Bb}^k = -(\bar{u}_B^{ok}(\bar{\omega}) \cdot (\bar{T}^k(\bar{\omega}) + \bar{V}'_+(\bar{\omega}) \bar{u}_b^{ok}(\bar{\omega}))) \\ - (\bar{u}_B^{ok}(\bar{\omega}) \cdot \bar{H}'^{(0)k}(\bar{\omega}) \bar{u}_b^{ok}(\bar{\omega})) - (\bar{u}_B^{ok}(\bar{\omega}) \cdot (\bar{P}^{(0)}(\bar{\omega}) - \frac{\bar{A}^{(0)k}(\bar{\omega})}{2}) \bar{u}_b^{ok}(\bar{\omega})) \\ (B \neq b)$$

where  $\bar{H}'^{(0)k}(\bar{\omega})$  stands for

$$(7.9) \quad \bar{H}'^{(0)k}(\bar{\omega}) = \bar{V}'_+(\bar{\omega}) + \bar{P}^{(0)}(\bar{\omega}) - \frac{1}{2} \bar{A}^{(0)k}(\bar{\omega})$$

and will be approximated by  $\frac{a}{\lambda}$  constant later.

It will now be shown that the scalar product

$$(7.10) \quad \langle u_B^{0k}(\bar{\omega}) | (T^{1k}(\bar{\omega}) + V_{+-}^1(\bar{\omega})) | u_B^{0k}(\bar{\omega}) \rangle$$

may be evaluated with the help of the unperturbed eigenvalue problem

$$(7.11) \quad (H(\bar{\omega}) - W_B^{0k}) u_B^{0k}(\bar{\omega}) = 0; \quad H(\bar{\omega}) = T^{0k}(\bar{\omega}) + V_{+-}^{0k}(\bar{\omega}) + H^{0'k}(\bar{\omega}).$$

Here  $H^{0'k}(\bar{\omega})$  stands for

$$(7.12) \quad H^{0'k}(\bar{\omega}) = V_{+-}^{0'k}(\bar{\omega}) + P^{0\omega}(\bar{\omega}) - \frac{1}{2} A^{0\omega k}(\bar{\omega})$$

and will be approximated by a constant in the method of Wigner and Seitz.

The explicit expression of  $T^{1k}(\bar{\omega}) + V_{+-}^1(\bar{\omega})$  is, by (6.19) and (6.27),

$$(7.13) \quad \sum_{\alpha\beta} \bar{u}_\alpha \frac{\partial V_{+-}^1(\bar{\omega})}{\partial \bar{u}_\beta} - \frac{1}{2m} \sum_{\alpha\beta} (p_\alpha(\bar{\omega}) + \hbar \nabla_\alpha^{0k}) (p_\beta(\bar{\omega}) + \hbar \nabla_\beta^{0k})$$

It is easily verified that this can be expressed in terms of  $H^{0k}(\bar{\omega})$  of (7.11) as follows

$$(7.14) \quad T^{1k}(\bar{\omega}) + V_{+-}^1(\bar{\omega}) = \{ J(\bar{\omega}) H^{0k}(\bar{\omega}) - H^{0k}(\bar{\omega}) J(\bar{\omega}) \} - \frac{1}{2m} \sum_{\alpha\beta} (p_\alpha(\bar{\omega}) + \hbar \nabla_\alpha^{0k}) \hbar \nabla_\beta^{0k} - \{ J(\bar{\omega}) H^{0'k}(\bar{\omega}) - H^{0'k}(\bar{\omega}) J(\bar{\omega}) \}$$

with

$$(7.14a) \quad J(\bar{\omega}) = \sum_{\alpha\beta} \bar{u}_\alpha \frac{\partial}{\partial \bar{u}_\beta}$$

Here the last bracket would disappear when  $H^{0k}(\bar{\omega})$  is approximated by a constant. The scalar product of

the first bracket can be evaluated with the help of

(7.11) and with the help of Green's theorem as follows,

$$\begin{aligned}
 (7.15) \quad & (u_B^k(\bar{\omega}) \cdot \{J(\bar{\omega}) H^k(\bar{\omega}) - H^k(\bar{\omega}) J(\bar{\omega})\} u_b^k(\bar{\omega})) \\
 & = (W_b^k - W_B^k) (u_B^k(\bar{\omega}) \cdot J(\bar{\omega}) u_b^k(\bar{\omega})) \\
 & \quad + (H^k(\bar{\omega}) u_B^k(\bar{\omega}) \cdot J(\bar{\omega}) u_b^k(\bar{\omega})) - (u_B^k(\bar{\omega}) \cdot H^k(\bar{\omega}) J(\bar{\omega}) u_b^k(\bar{\omega})) \\
 & = (W_b^k - W_B^k) (u_B^k(\bar{\omega}) \cdot J(\bar{\omega}) u_b^k(\bar{\omega})) \\
 & \quad + \frac{\hbar^2}{2m} \int d\bar{\sigma} u_B^{k*}(\bar{\omega}) \bar{J}_\alpha \left( \frac{\partial}{\partial x_\alpha} + i g_\alpha^k \right) J(\bar{\omega}) u_b^k(\bar{\omega}) \\
 & \quad - \frac{\hbar^2}{2m} \int d\bar{\sigma} J(\bar{\omega}) u_b^k(\bar{\omega}) \bar{J}_\alpha \left( \frac{\partial}{\partial x_\alpha} + i g_\alpha^k \right)^* u_B^{k*}(\bar{\omega}) \\
 & \quad - \frac{1}{2} \left[ (A(\bar{\omega}) u_B^k(\bar{\omega}) \cdot J(\bar{\omega}) u_b^k(\bar{\omega})) - (u_B^k(\bar{\omega}) \cdot A(\bar{\omega}) J(\bar{\omega}) u_b^k(\bar{\omega})) \right]
 \end{aligned}$$

where the last line would disappear to the approximation that  $\rho(\bar{\omega}) = \text{constant}$ . The surface integrals thus originated will play the most important rôle in the evaluation of the perturbation energy, and may be evaluated by replacing the polyhedron by a sphere. This will be done later.

Substituting (7.15) and (7.14) into (7.10), then substituting (7.10) into (7.8), and then dividing (7.3) by  $W_b^k - W_B^k$ , we obtain

$$\begin{aligned}
 (7.16) \quad U_{Bb}^k & = \frac{(u_B^k(\bar{\omega}) \cdot \{P(\bar{\omega}) - \frac{1}{2} A(\bar{\omega})\} u_b^k(\bar{\omega}))}{W_b^k - W_B^k} + \frac{(u_B^k(\bar{\omega}) \cdot H^k(\bar{\omega}) u_b^k(\bar{\omega}))}{W_b^k - W_B^k} \\
 & \quad - \frac{1}{2m} \frac{2 \int d\bar{\sigma} u_B^{k*}(\bar{\omega}) \bar{J}_\alpha \left( \frac{\partial}{\partial x_\alpha} + i g_\alpha^k \right) J(\bar{\omega}) u_b^k(\bar{\omega})}{W_b^k - W_B^k} \\
 & \quad - \frac{(u_B^k(\bar{\omega}) \cdot \{J(\bar{\omega}) H^k(\bar{\omega}) - H^k(\bar{\omega}) J(\bar{\omega})\} u_b^k(\bar{\omega}))}{W_b^k - W_B^k} + \frac{1}{2} \frac{[(A(\bar{\omega}) u_B^k(\bar{\omega}) \cdot J(\bar{\omega}) u_b^k(\bar{\omega})) - (u_B^k(\bar{\omega}) \cdot A(\bar{\omega}) J(\bar{\omega}) u_b^k(\bar{\omega}))]}{W_b^k - W_B^k} \\
 & \quad + \frac{(u_B^k(\bar{\omega}) \cdot J(\bar{\omega}) u_b^k(\bar{\omega}))}{W_b^k - W_B^k} + \frac{\hbar^2}{2m} \frac{\int d\bar{\sigma} u_B^{k*}(\bar{\omega}) \bar{J}_\alpha \left( \frac{\partial}{\partial x_\alpha} + i g_\alpha^k \right) J(\bar{\omega}) u_b^k(\bar{\omega}) - \int d\bar{\sigma} J(\bar{\omega}) u_b^k(\bar{\omega}) \bar{J}_\alpha \left( \frac{\partial}{\partial x_\alpha} + i g_\alpha^k \right)^* u_B^{k*}(\bar{\omega})}{W_b^k - W_B^k}
 \end{aligned}$$

(B ≠ b)

where the second term and the third line disappear when  $H_{\alpha\beta}^{(0)k}$ ,  $H_{\beta\alpha}^{(0)k}$ , and  $A_{\alpha\beta}^{(0)k}$  are approximated by constants. The only term without the determinant is also small since  $u_{\beta}^{(0)k}(\bar{\omega})$  is approximately constant (the operator  $J(\bar{\omega})$  is  $\mathcal{O}_{\alpha\beta} \frac{\partial}{\partial \omega_{\beta}}$ ). Hence, (7.16) can be solved by the

method of successive approximations, the first approximation gives, by dropping the terms  $P_{\alpha\beta}^{(1)k}, \frac{1}{2} A_{\alpha\beta}^{(1)k}, \dots$

$$(7.17) \quad U_{Bb}^{1k} \Rightarrow -\frac{1}{2m} 2 \mathcal{O}_{\alpha\beta} \frac{\partial}{\partial \omega_{\beta}} \frac{\partial}{\partial \omega_{\alpha}} \frac{(u_{B\alpha}^{(0)k} \cdot p_{\alpha}(\bar{\omega}) u_{\beta}^{(0)k}(\bar{\omega}))}{\dot{\omega}_{\beta}^k - \dot{\omega}_{\alpha}^k} + \frac{\hbar^2}{2m} \frac{\int d\bar{\omega} u_{B\alpha}^{(0)k*} \bar{\mathcal{V}}_{\alpha} (\frac{\partial}{\partial \omega_{\alpha}} + i \frac{\partial}{\partial \omega_{\alpha}}) J(\bar{\omega}) u_{\beta}^{(0)k}(\bar{\omega}) - \int d\bar{\omega} J(\bar{\omega}) u_{\beta}^{(0)k}(\bar{\omega}) \bar{\mathcal{V}}_{\alpha} (\frac{\partial}{\partial \omega_{\alpha}} + i \frac{\partial}{\partial \omega_{\alpha}}) u_{B\alpha}^{(0)k*}(\bar{\omega})}{\dot{\omega}_{\beta}^k - \dot{\omega}_{\alpha}^k}$$

From (7.14) and (7.15) we have for the contribution to the first-order perturbation energy, approximately

$$(7.18) \quad (u_{\beta}^{(0)k}(\bar{\omega}) \cdot (T_{\alpha\beta}^{(1)k} + \bar{V}_{\alpha}(\bar{\omega})) u_{\beta}^{(0)k}(\bar{\omega})) = -\frac{1}{2m} 2 \mathcal{O}_{\alpha\beta} \frac{\partial}{\partial \omega_{\beta}} \frac{\partial}{\partial \omega_{\alpha}} (u_{\beta}^{(0)k}(\bar{\omega}) \cdot p_{\alpha}(\bar{\omega}) u_{\beta}^{(0)k}(\bar{\omega})) - \frac{1}{2m} 2 \mathcal{O}_{\alpha\beta} \frac{\partial}{\partial \omega_{\beta}} \frac{\partial}{\partial \omega_{\alpha}} (u_{\beta}^{(0)k}(\bar{\omega}) \cdot p_{\alpha}(\bar{\omega}) u_{\beta}^{(0)k}(\bar{\omega})) + \frac{\hbar^2}{2m} \int d\bar{\omega} u_{\beta}^{(0)k*}(\bar{\omega}) \bar{\mathcal{V}}_{\alpha} (\frac{\partial}{\partial \omega_{\alpha}} + i \frac{\partial}{\partial \omega_{\alpha}}) J(\bar{\omega}) u_{\beta}^{(0)k}(\bar{\omega}) - \frac{\hbar^2}{2m} \int d\bar{\omega} J(\bar{\omega}) u_{\beta}^{(0)k}(\bar{\omega}) \bar{\mathcal{V}}_{\alpha} (\frac{\partial}{\partial \omega_{\alpha}} + i \frac{\partial}{\partial \omega_{\alpha}}) u_{\beta}^{(0)k*}(\bar{\omega})$$

The total perturbation energy of the electrons of the first order is, by (6.29),

$$(7.19) \quad \bar{E}_{\text{electrons}} = 2 \int d\bar{\omega} (u_{\beta}^{(0)k}(\bar{\omega}) \cdot (T_{\alpha\beta}^{(1)k} + \bar{V}_{\alpha}(\bar{\omega})) u_{\beta}^{(0)k}(\bar{\omega})) + N \int d\bar{\omega} \bar{V}_{+}'(\bar{\omega}) \rho(\bar{\omega}) + \int d\bar{r} d\bar{r}' \frac{V_{-}(\bar{r}-\bar{r}')}{2} [\rho(\bar{r}') \rho(\bar{r}) - \frac{1}{2} \rho(\bar{r}, \bar{r}') \rho(\bar{r}, \bar{r}')]$$

where  $(u_{\beta}^{(0)k}(\bar{\omega}) \cdot (T_{\alpha\beta}^{(1)k} + \bar{V}_{\alpha}(\bar{\omega})) u_{\beta}^{(0)k}(\bar{\omega}))$  is given by (7.18).

order perturbation energy is given by (6.35). The

term  $((T+V_+)U)_{bb}^k$  may be evaluated, according to the matrix calculus and (6.7), from

$$(7.20) \quad ((T+V_+)U)_{bb}^k = \sum_B (u_B^{ok}(\omega) \cdot (T+V_+(\omega)) u_B^{ok}(\omega)) U_{Bb}^k$$

Substituting (6.31) for  $U_{bb}^k$  and (7.17) for  $U_{Bb}^k$  ( $B \neq b$ ) into (7.20), we obtain

$$(7.21) \quad ((T+V_+)U)_{bb}^k = \sum_{B \neq b} (u_B^{ok}(\omega) \cdot (T(\omega) + V_+(\omega)) u_B^{ok}(\omega)) (u_B^{ok}(\omega) \cdot J(\omega) u_B^{ok}(\omega)) \\ + \sum_{B \neq b} \frac{(u_B^{ok}(\omega) \cdot (T(\omega) + V_+(\omega)) u_B^{ok}(\omega))}{\omega_b^k - \omega_B^k} \left\{ -\frac{1}{2m} \sum_{\alpha\beta} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} (u_B^{ok}(\omega) \cdot J(\omega) u_B^{ok}(\omega)) \right. \\ \left. + \frac{\hbar^2}{2m} \int d\sigma u_B^{ok}(\omega) \bar{u}_\alpha \left( \frac{\partial}{\partial x_\alpha} + i\gamma_\alpha^k \right) J(\omega) u_B^{ok}(\omega) \right. \\ \left. - \frac{\hbar^2}{2m} \int d\sigma J(\omega) u_B^{ok}(\omega) \bar{u}_\alpha \left( \frac{\partial}{\partial x_\alpha} + i\gamma_\alpha^k \right) u_B^{ok}(\omega) \right\}$$

The terms having the denominators  $\omega_b^k - \omega_B^k$  will be estimated later. The sum of the products of the scalar products will be summed now.

The sum will be completed by adding and subtracting the missing term. Since the operator  $T^k + V_+$

is self-adjoint and cyclic in the domain  $\bar{\Omega}$ , the sum can be evaluated by the completeness relation of the functions  $u_B^{ok}$ , thus

$$(7.22) \quad \sum_B (u_B^{ok}(\omega) \cdot (T(\omega) + V_+(\omega)) u_B^{ok}(\omega)) (u_B^{ok}(\omega) \cdot J(\omega) u_B^{ok}(\omega)) \\ = \sum_B ((T(\omega) + V_+(\omega)) u_B^{ok}(\omega) \cdot u_B^{ok}(\omega)) (u_B^{ok}(\omega) \cdot J(\omega) u_B^{ok}(\omega)) \\ = ((T(\omega) + V_+(\omega)) u_b^{ok}(\omega) \cdot J(\omega) u_b^{ok}(\omega))$$

By a partial integration, (7.22) becomes

$$(7.23) \quad (u_b^{ok}(\omega) \cdot \{T(\omega) + V_+(\omega)\} J(\omega) u_b^{ok}(\omega)) - \frac{2\mathcal{D}_{\alpha\beta}}{2m} \int d\bar{\sigma} \left\{ \bar{u}_\beta^{ok*}(\omega) (\mathcal{D}_\alpha(\omega) + \mathcal{H}_\alpha^{ok}) J(\omega) u_b^{ok}(\omega) + \bar{u}_\alpha \left[ (\mathcal{D}_\beta(\omega) + \mathcal{H}_\beta^{ok}) u_b^{ok}(\omega) \right]^* J(\omega) u_b^{ok}(\omega) \right\}$$

The incomplete sum required in (7.21) may be obtained from this by subtracting the single term

$$(7.24) \quad (u_b^{ok}(\omega) \cdot \{T(\omega) + V_+(\omega)\} u_b^{ok}(\omega)) (u_b^{ok}(\omega) \cdot J(\omega) u_b^{ok}(\omega))$$

On dividing  $V_+(\omega)$  into  $V_{+-}(\omega)$  and  $V_+'(\omega)$ , and approximating the latter by a constant, so that

$(u_b^{ok} \cdot V_+'(\omega) u_b^{ok}) (u_b^{ok} \cdot J(\omega) u_b^{ok})$  of (7.24) and  $(u_b^{ok} \cdot V_+'(\omega) J(\omega) u_b^{ok})$  of (7.23) cancel off, we obtain for the first sum of (7.21),

$$(7.25) \quad \begin{aligned} & \sum_{B \neq b} (u_b^{ok} \cdot \{T(\omega) + V_+(\omega)\} u_B^{ok}(\omega)) (u_B^{ok}(\omega) \cdot J(\omega) u_b^{ok}(\omega)) \\ &= (u_b^{ok}(\omega) \cdot \{T(\omega) + V_+(\omega)\} J(\omega) u_b^{ok}(\omega)) \\ & \quad - (u_b^{ok}(\omega) \cdot \{T(\omega) + V_+(\omega)\} u_b^{ok}(\omega)) (u_b^{ok}(\omega) \cdot J(\omega) u_b^{ok}(\omega)) \\ & - 2\mathcal{D}_{\alpha\beta} \frac{ik}{2m} \int d\bar{\sigma} \left\{ \bar{u}_\beta^{ok*}(\omega) (\mathcal{D}_\alpha(\omega) + \mathcal{H}_\alpha^{ok}) J(\omega) u_b^{ok}(\omega) + \right. \\ & \quad \left. + \bar{u}_\alpha \left[ (\mathcal{D}_\beta(\omega) + \mathcal{H}_\beta^{ok}) u_b^{ok}(\omega) \right]^* J(\omega) u_b^{ok}(\omega) \right\} \end{aligned}$$

Substituting (7.25) into (7.21), and then substituting (7.21) into the expression (6.35) for the second-order perturbation energy, we have, after dividing  $V_+(\omega)$  into  $V_{+-}(\omega)$  and  $V_+'(\omega)$ ,

$$\begin{aligned}
 E_{\text{electrons}}^2 &= N \int d\bar{\omega} \left[ V_+^{\circ k}(\bar{\omega}) \rho(\bar{\omega}) + \int d\bar{\omega}' \frac{V_+(\bar{\omega}-\bar{\omega}')}{2} \left[ \rho(\bar{\omega}) \rho(\bar{\omega}') - \frac{1}{2} (\rho(\bar{\omega}+\bar{\omega}') \rho(\bar{\omega}')) \right] \right. \\
 (7.26) \quad &- 2 \int \frac{1}{2} \left[ (u_{\beta}^{\circ k}(\bar{\omega}) \cdot \nabla_{\beta}^{\circ k}(\bar{\omega}) + \nabla_{\beta}^{\circ k}(\bar{\omega}) \cdot u_{\beta}^{\circ k}(\bar{\omega})) (u_{\alpha}^{\circ k}(\bar{\omega}) \cdot \nabla_{\alpha}^{\circ k}(\bar{\omega}) u_{\beta}^{\circ k}(\bar{\omega})) + \text{conj.} \right] \\
 &- 2 \int \frac{1}{2} \left[ 2 \mathcal{A}_{\beta\gamma} \frac{1}{2m} \int d\bar{\omega}' \left\{ \frac{1}{\rho} u_{\beta}^{\circ k}(\bar{\omega}) (k_{\alpha}(\bar{\omega}) + k_{\alpha}(\bar{\omega}')) \nabla_{\alpha}^{\circ k}(\bar{\omega}) u_{\beta}^{\circ k}(\bar{\omega}) + \right. \right. \\
 &\quad \left. \left. + \frac{1}{\rho} (k_{\alpha}(\bar{\omega}) + k_{\alpha}(\bar{\omega}')) u_{\beta}^{\circ k}(\bar{\omega}) \nabla_{\alpha}^{\circ k}(\bar{\omega}) u_{\beta}^{\circ k}(\bar{\omega}) \right\} \right. \\
 &\quad \left. + \text{conj.} \right] \\
 &+ 2 \int \frac{1}{2} \left[ \sum_{B \neq b} \frac{(7.21)}{W_b^{\circ k} - W_B^{\circ k}} + \text{conj.} \right] \\
 &+ 2 \int \frac{1}{2} \left[ (u_{\beta}^{\circ k}(\bar{\omega}) \cdot \nabla_{\beta}^{\circ k}(\bar{\omega}) + \nabla_{\beta}^{\circ k}(\bar{\omega}) \cdot u_{\beta}^{\circ k}(\bar{\omega})) + (\nabla_{\alpha}^{\circ k}(\bar{\omega}) + \nabla_{\alpha}^{\circ k}(\bar{\omega}')) \nabla_{\alpha}^{\circ k}(\bar{\omega}) \cdot u_{\beta}^{\circ k}(\bar{\omega}) \right] + \text{conj.} \Big]
 \end{aligned}$$

where  $\sum_{B \neq b} \frac{(7.21)}{W_b^{\circ k} - W_B^{\circ k}}$  stands for the sum given in (7.21).

It will now <sup>be</sup> shown that the <sup>last</sup> scalar product of (7.26) can be evaluated in the same way used in the evaluation of the scalar product (7.10). With the explicit expressions for  $\nabla^{\circ k}(\bar{\omega})$  (cf. (6.27)(6.15)),  $V_+(\bar{\omega})$  (cf. (6.19)(6.20)), and  $J(\bar{\omega})$  (7.14a) and the abbreviation

$$(7.27) \quad \tilde{J}(\bar{\omega}) = \mathcal{A}_{\alpha\beta} \mathcal{A}_{\gamma\delta} \bar{\omega}_{\alpha} \bar{\omega}_{\gamma} \frac{1}{2!} \frac{\partial^2}{\partial \bar{\omega}_{\beta} \partial \bar{\omega}_{\delta}}$$

it is easily verified that

$$\begin{aligned}
 (7.28) \quad & \nabla^{\circ k}(\bar{\omega}) + \nabla_{+}^{\circ k}(\bar{\omega}) + [\nabla^{\circ k}(\bar{\omega}) + \nabla_{+}^{\circ k}(\bar{\omega})] \tilde{J}(\bar{\omega}) \\
 &= \left\{ \tilde{J}(\bar{\omega}) \dot{H}^{\circ k}(\bar{\omega}) - \dot{H}^{\circ k}(\bar{\omega}) \tilde{J}(\bar{\omega}) \right\} \\
 &- 2 \mathcal{A}_{\alpha\beta} \mathcal{A}_{\gamma\delta} \frac{1}{2m} \frac{(k_{\alpha}(\bar{\omega}) + k_{\alpha}(\bar{\omega}'))}{2m} \tilde{J}(\bar{\omega}) \\
 &+ \mathcal{A}_{\alpha\beta} \mathcal{A}_{\gamma\delta} \frac{1}{2m} \left\{ 4 \mathcal{A}_{\alpha}^{\circ k} \mathcal{A}_{\beta}^{\circ k} \tilde{J}(\bar{\omega}) + 3 \mathcal{A}_{\alpha}^{\circ k} \mathcal{A}_{\beta}^{\circ k} \right\} \\
 &- \left\{ \tilde{J}(\bar{\omega}) \dot{H}^{\circ k}(\bar{\omega}) - \dot{H}^{\circ k}(\bar{\omega}) \tilde{J}(\bar{\omega}) \right\}
 \end{aligned}$$

which may be compared with (7.14). The first bracket of (7.28) contributes surface integrals (cf. (7.15)), and the second bracket of (7.28) may be neglected in accordance with the method of Wigner and Seitz. Thus we have,

$$\begin{aligned}
 (7.29) \quad & (u_b^{ok}(\bar{\omega}) \cdot \{ \nabla_{\bar{\omega}}^k + V_+(\bar{\omega}) + [\nabla_{\bar{\omega}}^k + V_+(\bar{\omega})] J(\bar{\omega}) \} u_b^{ok}(\bar{\omega})) \\
 & = \delta_{\alpha\beta} \delta_{\beta\gamma} \left\{ \frac{3k^{\alpha k} k^{\beta k}}{2m} + \frac{4k^{\alpha k}}{2m} (u_b^{ok}(\bar{\omega}) \cdot \nabla_{\bar{\omega}}^k u_b^{ok}(\bar{\omega})) \right\} \\
 & - 2\delta_{\alpha\beta} \frac{k^{\alpha k} k^{\beta k}}{2m} (u_b^{ok}(\bar{\omega}) \cdot J(\bar{\omega}) u_b^{ok}(\bar{\omega})) - 2\delta_{\alpha\beta} \frac{k^{\alpha k}}{\beta 2m} (u_b^{ok}(\bar{\omega}) \cdot \nabla_{\bar{\omega}}^k J(\bar{\omega}) u_b^{ok}(\bar{\omega})) \\
 & + \frac{k^2}{2m} \int d\bar{\omega} u_b^{ok*}(\bar{\omega}) \nabla_{\bar{\omega}} \left( \frac{\partial}{\partial \bar{\omega}_\alpha} + i\nabla_{\bar{\omega}}^k \right) J(\bar{\omega}) u_b^{ok}(\bar{\omega}) \\
 & - \frac{k^2}{2m} \int d\bar{\omega} J(\bar{\omega}) u_b^{ok}(\bar{\omega}) \nabla_{\bar{\omega}} \left( \frac{\partial}{\partial \bar{\omega}_\alpha} + i\nabla_{\bar{\omega}}^k \right)^* u_b^{ok*}(\bar{\omega})
 \end{aligned}$$

The sum containing the denominator  $W_B^{ok} - W_B^{ok}$  cannot be transformed to a form that does not contain eigenfunctions other than the Fock functions. In the curl bracket of (7.21), it is easily shown by symmetry consideration that the first term depends quadratically on  $k^{\alpha k}$ , and vanishes if the difference of  $u_b^{ok}$  and  $u_b^o$  is neglected. The second surface integral vanishes by the approximate boundary condition of Wigner and Seitz. And since the Fock functions of the core electrons contribute little to the surface integral, the parameters  $W_B^{ok}$  may be restricted to those which are larger than

$W_b^{0k}$ . By replacing  $W_B^{0k}$  by a certain average value, which is certainly not less than the smallest parameter among those larger than  $W_b^{0k}$  and having the right symmetry character (i.e. the corresponding  $k=000$  eigenfunction is an even function with respect to the central reflexion), the sum may be <sup>evaluated</sup> summed up. It is estimated for sodium that this sum, when  $k=000$ , is less than ten percent of the surface integrals occurring in (7.26).

7.5. Sodium. The above calculation is accurate enough for all monovalent metals for which the method of Wigner and Seitz works. It is correct to the first order of the difference of  $u_b^{0k}$  and  $\bar{u}_b$ , and may therefore be applied as well to lithium (cf. (7.4)). For simplicity, the difference of  $u_b^{0k}$  and  $\bar{u}_b$  will be neglected from now on, so that the result applies only to sodium.

As consequences of this; the term  $(\bar{u}_b(\bar{\omega}) \cdot h_2(\bar{\omega}) \bar{u}_b(\bar{\omega}))$  of (7.18) vanishes by symmetry; the term having a factor  $i\gamma_\alpha^{0k}$  in the first surface integral and the whole of the second surface integral of (7.18) vanish by the boundary condition of Wigner and Seitz. Hence

(7.18) reduces to

$$(7.30) \quad (\bar{u}_b(\bar{\omega}) \cdot \{T_1^k(\bar{\omega}) + V_4^k(\bar{\omega})\} \bar{u}_b(\bar{\omega})) = -\frac{1}{2m} 2\delta_{\alpha\beta} k\gamma_\alpha^{0k} k\gamma_\beta^{0k} + \frac{k^2}{2m} \int d\bar{\omega} \bar{u}_b(\bar{\omega}) \cdot \bar{r}_\alpha \frac{\partial}{\partial \bar{\omega}_\alpha} \bar{J}(\bar{\omega}) \bar{u}_b(\bar{\omega})$$

Similarly (7.29) reduces to

$$(7.31) \quad (u_b^0(\omega) \cdot \{T^k(\omega) + V_+^k(\omega) + [T^k(\omega) + V_+^k(\omega)] J^k(\omega)\} u_b^0(\omega)) = \mathcal{S}_{\alpha\beta} \mathcal{S}_{\gamma\delta} \frac{3\hbar^2 g_\alpha^k g_\beta^k g_\gamma^k g_\delta^k}{2m} \\ - 2\mathcal{S}_{\alpha\beta} \frac{\hbar^2 g_\alpha^k g_\beta^k}{2m} (u_b^0(\omega) \cdot J^k(\omega) u_b^0(\omega)) + \frac{\hbar^2}{2m} \int d\sigma u_b^0(\omega) \bar{V}_\alpha \frac{\partial}{\partial \omega_\alpha} J^k(\omega) u_b^0(\omega) + 2i g_\alpha^k J^k(\omega) u_b^0(\omega)$$

where the pure imaginary term may be neglected when we substitute (7.31) into (7.26). The complete expression of (7.26) becomes -

$$(7.32) \quad \bar{E}_{electrons}^k = N \int d\omega \bar{V}_+^k(\omega) \rho(\omega) + \iint d\omega_1 d\omega_2 \frac{V_+(\omega_1 - \omega_2)}{2} [\rho(\omega_1)\rho(\omega_2) - \frac{1}{2}\rho(\omega_1)\rho(\omega_2)] \\ + 2S^k \bar{E}_b^k$$

with

$$(7.33) \quad \bar{E}_b^k = \mathcal{S}_{\alpha\beta} \mathcal{S}_{\gamma\delta} \frac{3\hbar^2 g_\alpha^k g_\beta^k g_\gamma^k g_\delta^k}{2m} + \frac{\hbar^2}{2m} \int d\sigma u_b^0(\omega) \bar{V}_\alpha \frac{\partial}{\partial \omega_\alpha} J^k(\omega) u_b^0(\omega) \\ + \frac{\hbar^2}{2m} \int d\sigma u_b^0(\omega) \bar{V}_\alpha \frac{\partial}{\partial \omega_\alpha} J^k(\omega) u_b^0(\omega) \times (u_b^0(\omega) \cdot J^k(\omega) u_b^0(\omega)) \\ - 2\mathcal{S}_{\alpha\beta} \frac{\hbar^2}{2m} \int d\sigma \bar{V}_\alpha u_b^0(\omega) \frac{\partial}{\partial \omega_\alpha} J^k(\omega) u_b^0(\omega) \\ + \sum_{B \neq b} \frac{(u_b^0(\omega) \cdot \{T^k(\omega) + V_+^k(\omega)\} u_B^0(\omega))}{\omega_b^k - \omega_B^k} \frac{\hbar^2}{2m} \int d\sigma u_B^0(\omega) \bar{V}_\alpha \frac{\partial}{\partial \omega_\alpha} J^k(\omega) u_b^0(\omega)$$

In conformity with the above notation, (7.19) may be written in the form

$$(7.34) \quad \bar{E}_{electrons}^k = N \int d\omega \bar{V}_+^k(\omega) \rho(\omega) + \iint d\omega_1 d\omega_2 \frac{V_+(\omega_1 - \omega_2)}{2} [\rho(\omega_1)\rho(\omega_2) - \frac{1}{2}\rho(\omega_1)\rho(\omega_2)] \\ + 2S^k \bar{E}_b^k$$

with

$$(7.35) \quad \bar{E}_b^k = -2\mathcal{S}_{\alpha\beta} \frac{\hbar^2 g_\alpha^k g_\beta^k}{2m} + \frac{\hbar^2}{2m} \int d\sigma u_b^0(\omega) \bar{V}_\alpha \frac{\partial}{\partial \omega_\alpha} J^k(\omega) u_b^0(\omega)$$

If the parameters of the equation of Wigner and Seitz for the undeformed polyhedron be denoted by  $\bar{E}_b^k$ , i.e.

$$(7.36) \quad (T^k(\omega) + V_+^k(\omega) - \bar{E}_b^k) u_b^k(\omega) = 0$$

then the parameters  $w_b^{0k}$  of the Fock equations are given, on comparing (7.36) and (7.2), by

$$(7.37) \quad w_b^{0k} = \tilde{z}_b^{0k} + (u_b^{0k}(\bar{\omega}) \cdot [V_+^{0k}(\bar{\omega}) + P(\bar{\omega}) - \frac{1}{2} A(\bar{\omega})] u_b^{0k}(\bar{\omega}))$$

The total energy of the electrons in the undeformed lattice (cf. (2.26)) may therefore be calculated from the parameters  $\tilde{z}_b^{0k}$  according to

$$(7.38) \quad \tilde{E}_{\text{electrons}}^0 = N \int d\bar{\omega} V_+^{0k}(\bar{\omega}) \rho(\bar{\omega}) + 2 \int d\bar{\omega} (u_b^{0k}(\bar{\omega}) \cdot [P(\bar{\omega}) - \frac{1}{2} A(\bar{\omega})] u_b^{0k}(\bar{\omega})) + 2 \int d\bar{\omega} \tilde{z}_b^{0k} E_b^{0k}$$

or, by the definitions of the  $P^{0k}$  and  $A^{0k}$ ,

$$(7.39) \quad \tilde{E}_{\text{electrons}}^0 = N \int d\bar{\omega} V_+^{0k}(\bar{\omega}) \rho(\bar{\omega}) + \int d\bar{\omega} d\bar{r} \frac{1}{2} \frac{V_+^{0k}(\bar{r}-\bar{r}')}{2} [\rho(\bar{r}) \rho(\bar{r}') - \frac{1}{2} \rho(\bar{r}) \rho(\bar{r}')] + 2 \int d\bar{\omega} \tilde{z}_b^{0k} E_b^{0k}$$

On comparing (7.32), (7.34) with (7.39), we see that  $\tilde{z}_b^{0k}$  and  $\tilde{E}_b^{0k}$  may be considered as the perturbation of the parameters of Wigner and Seitz. This is of course to be expected, for the approximations made above (i.e. treating  $V_+^{0k}(\bar{\omega})$  as constant and regarding  $\frac{1}{2} P_{Bb}^{0k} - \frac{1}{2} A_{Bb}^{0k}$  as small in solving the perturbation equation) is equivalent to replacing the perturbed equations of Fock and Dirac by the perturbed equations of Wigner and Seitz.

In (7.39), since the difference of  $\tilde{z}_b^{0k}$  and  $\tilde{z}_b^{0k}$

may be neglected for sodium, we take, by (7.36), simply

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$$(7.40) \quad \overset{0}{E}_b^k = \overset{0}{E}_b + \frac{1}{2m} \sum_{\alpha} \sum_{\beta} \overset{0}{k}_{\alpha}^k \overset{0}{k}_{\beta}^k$$

Similarly (7.33) and (7.35) may be written in the forms

$$(7.41) \quad \overset{2}{E}_b^k = \overset{2}{E}_b + \frac{1}{2m} 3 \sum_{\alpha\beta\gamma} \overset{2}{k}_{\alpha}^k \overset{2}{k}_{\beta}^k \overset{2}{k}_{\gamma}^k$$

$$(7.42) \quad \overset{1}{E}_b^k = \overset{1}{E}_b - \frac{1}{2m} 2 \sum_{\alpha\beta} \overset{1}{k}_{\alpha}^k \overset{1}{k}_{\beta}^k$$

where  $\overset{2}{E}_b$  and  $\overset{1}{E}_b$  stands for  $\overset{2}{E}_b^k$  ( $k=000$ ) and  $\overset{1}{E}_b^k$  ( $k=000$ ).

It is to be noted that when we add together (7.40), (7.41) and (7.42), the terms depending on  $\overset{0}{k}_{\alpha}^k$  may be summed up according to the expansion (cf. (6.12)) of the wave vectors in the real space, thus

$$(7.43) \quad \overset{0}{k}_{\alpha}^k \overset{0}{k}_{\beta}^k = \overset{0}{k}_{\alpha}^k \overset{0}{k}_{\beta}^k - 2 \sum_{\alpha\beta\gamma} \overset{0}{k}_{\alpha}^k \overset{0}{k}_{\beta}^k \overset{0}{k}_{\gamma}^k + 3 \sum_{\alpha\beta\gamma\delta} \overset{0}{k}_{\alpha}^k \overset{0}{k}_{\beta}^k \overset{0}{k}_{\gamma}^k \overset{0}{k}_{\delta}^k - \dots$$

Similarly when we add together (7.32), (7.34) and (7.39), the various order terms of the  $\overset{0}{V}_r(\vec{r})$  and the  $\overset{1}{V}_r(\vec{r}-\vec{r}')$  may be summed according to, e.g.

$$(7.44) \quad \overset{0}{V}_r(\vec{r}-\vec{r}') + \overset{1}{V}_r(\vec{r}-\vec{r}') + \overset{2}{V}_r(\vec{r}-\vec{r}') + \dots = \overset{0}{V}_r(\vec{r}-\vec{r}') = \overset{0}{V}_r(\vec{r}-\vec{r}')$$

where the last expression denotes the potential function in the real space. If we abbreviate the sum of the

various order terms of  $\overset{0}{E}_b^k$  by  $\overset{0}{E}_b^k$ , though  $\overset{2}{E}_b^k$  and

$\overset{1}{E}_b^k$  are to be calculated from (7.33) and (7.35),

the total energy of the electrons in a deformed lattice

of sodium becomes

$$(7.45) \quad E_{\text{electrons}} = N \int d\vec{r} V_+(\vec{r}) \rho(\vec{r}) + 2S \sum_{\alpha} \frac{k_{\alpha}^2}{2m} \hbar^2 \rho_{\alpha}^k \rho_{\alpha}^k$$

$$+ \iint d\vec{r} d\vec{r}' \frac{V_-(\vec{r}-\vec{r}')}{2} (\rho(\vec{r})\rho(\vec{r}') - \frac{1}{2} \rho(\vec{r},\vec{r}')\rho(\vec{r}',\vec{r})) + NE_b$$

which is similar to (7.39), the total energy of the electrons in the undeformed lattice of sodium.

The actual evaluation of this expression (7.45) will be given in the next section. All the surface integrals can be evaluated with the help of the equation (7.36) of Wigner and Seitz. The other terms of (7.45), when combined with the energy due to the interaction between the ions, will be transformed in the same way as Wigner and Seitz did in the case of the undeformed lattice of sodium, and then evaluated.

In the case of lithium, a similar expression like (7.45) may be obtained, only with the difference that there are additional terms quadratically in the  $k_{\alpha}^2$  arising from the difference of  $u_b^{\alpha k}$  and  $u_b^0$ .

It is convenient to evaluate this into several terms as follows, in which the case where the energy of the undeformed lattice has been divided up by Wigner

## 8. Elastic constants at zero temperature

For the calculation of the elastic constants at zero temperature, we need only to expand the potential energy of the lattice with respect to the elastic deformations. The expansion will be postponed to § 8.2. after the potential energy of the lattice has been transformed to a convenient form for actual calculation.

8.1. Analysis of the potential energy of the lattice. It has shown above (3.7) that the potential energy of the lattice consists of the total energy of the electrons plus the interaction between the ions. Denoting the potential energy of the deformed lattice by  $\Phi$ , the interaction between ions at their deformed positions by  $V_{++}(\underline{a}^l - \underline{a}^{l'})$ , and using the approximate expression (7.45) for the total energy of the electrons in the deformed lattice of sodium, we have

$$\begin{aligned}
 \Phi = & NE_b + 2S^k \frac{\hbar^2 g^k}{2m} + \frac{1}{2} \sum_{ll'} V_{++}(\underline{a}^l - \underline{a}^{l'}) \\
 (8.1) \quad & + N \int d\bar{\omega} V_+(\bar{\omega}) \rho^0(\bar{\omega}) + \frac{1}{2} \int d\bar{r} d\bar{r}' V_-(\underline{r} - \underline{r}') \left[ \rho^0(\bar{r}) \rho^0(\bar{r}') - \frac{1}{2} \rho^0(\bar{r} - \bar{r}') \rho^0(\bar{r} + \bar{r}') \right]
 \end{aligned}$$

It is convenient to divide up this into several items as follows, in much the same manner that the energy of the undeformed lattice has been divided up by Wigner

and Seitz (cf. Mott and Jones (1936) pp. 136-140).

The first and the second terms of (8.1) will be regarded as two items of the energy, the first will be referred as the Wigner-Seitz energy, while the second, as the Fermi energy. The energy arising from the fact that the probability of finding a pair of electrons deviates from the product of the probabilities of finding them independently will, <sup>be</sup> in general, referred to as the correlation energy; in the Fock-Dirac approximation only correlation between electrons with parallel spins has been taken into account. The last term of (8.1) will therefore be referred <sup>to</sup> as the correlation energy for parallel spins, <sup>and</sup> denoted by  $\Gamma_{\text{parallel spins}}$ ; i.e.

$$(8.2) \quad \Gamma_{\text{parallel spins}} = -\frac{1}{4} \iint d\vec{r} d\vec{r}' V_{--}(\vec{r}-\vec{r}') \rho(\vec{r}-\vec{r}') \rho(\vec{r}'-\vec{r})$$

or, by (7.5),

$$(8.3) \quad \Gamma_{\text{parallel spins}} = -\frac{1}{4} \iint d\vec{r} d\vec{r}' V_{--}(\vec{r}-\vec{r}') \left| \frac{25k}{4} e^{i\vec{q} \cdot (\vec{r}-\vec{r}')} \right|^2 \left( \frac{e_+}{u_b} \right)^2$$

The energy arising from the interaction of the core electrons of the ions will also <sup>be</sup> considered as an item,

$$(8.4) \quad I = \frac{1}{2} \sum_{ll'} \left\{ V_{++}(\underline{a}_l, \underline{a}_{l'}) - \frac{e_+ e_+}{|\underline{a}_l \underline{a}_{l'}|} \right\}$$

though this may again be separated into the van der Waals energy and the overlap energy. The rest of (8.1) then consists solely of Coulomb interactions, for

the interaction of an electron inside the basic polyhedron  $\Omega$  with the ions outside the polyhedron may be approximated by such, i.e. (cf. (8.1.)),

$$(8.5) \quad V'_+(\omega) = S'_l \frac{e_+ e_-}{|a^l - \omega|}$$

These Coulomb interactions may be expressed as the difference of the energy  $L$  of positive point charges embedded in a negative charge distribution and the interaction  $S$  of the point charges with the charge distributions within their polyhedra, and will be abbreviated by

Collecting the above, we have altogether six items

$$(8.6) \quad \Phi = E + F + I + T_{\text{parallel spins}} + L - S$$

where  $I$ ,  $T_{\text{parallel spins}}$  are given by (8.4), (8.3), and  $E$ ,  $F$ ,  $L$ ,  $S$  are given by

$$(8.7) \quad E = NE_b$$

$$(8.8) \quad F = 2S^k \frac{k^k k^k}{2m}$$

$$(8.9) \quad L = \frac{1}{2} S'_l \frac{e_+ e_-}{|a^l - a^{l'}|} + \frac{1}{2} \int \rho(\vec{r}) \rho(\vec{r}') \frac{e_+ e_-}{|\vec{r} - \vec{r}'|} \rho(\vec{r}) \rho(\vec{r}') + \int d\vec{r} \rho(\vec{r}) S'_l \frac{e_+ e_-}{|\vec{r} - a^l|}$$

$$(8.10) \quad S = N \int d\omega \rho(\omega) \frac{e_+ e_-}{|\omega|}$$

8.2. Three independent elastic constants of cubic lattices. The general expression of the

expansion of  $\Phi$  is, to the second order in  $d_{\alpha\beta}$ ,

$$(8.11) \quad \Phi = \Phi^0 + d_{\alpha\beta} \Phi^{\alpha\beta} + d_{\alpha\beta} d_{\gamma\delta} \Phi^{\alpha\beta\gamma\delta}$$

For cubic lattices the above must reduce to

$$(8.12) \quad \Phi = \Phi^0 + \Phi_1 (d_{11}^2 + d_{22}^2 + d_{33}^2) + \frac{\Phi_2}{2} (d_{11}^2 + d_{22}^2 + d_{33}^2) + \Phi_{12} (d_{11}d_{22} + d_{11}d_{33} + d_{22}d_{33}) + 2\Phi_{44} (d_{12}^2 + d_{23}^2 + d_{31}^2)$$

with

$$(8.13) \quad \Phi_1 = \Phi''; \quad \frac{\Phi_2}{2} = \Phi'''; \quad \Phi_{12} = \Phi''^{12} + \Phi''^{21};$$

$$2\Phi_{44} = \Phi''^{122} + \Phi''^{212} + \Phi''^{121} + \Phi''^{211}$$

where  $\Phi''$ ,  $\Phi''$  and  $\Phi_{44}$  are connected with the three usual elastic constants  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  of cubic lattices by

$$(8.14) \quad \Phi'' : c_{11} = \Phi'' : c_{12} = \Phi_{44} : c_{44} = N\bar{\Omega},$$

$N\bar{\Omega}$  being the volume of the undeformed lattice.

In an earlier attempt of calculating the elastic constants of metals, Fuchs(1956) introduced the following three independent elastic deformations: (A) compression and expansion in two directions parallel to two of the cube edges, keeping the volume unchanged, (B) shear in one plane parallel to one face of the cube, and (C) uniform compression. Each of these deformations depend on one parameter. The parameter of the deformation (A) is the fractional increase of the length

of one edge, that of the deformation (B) is the angle of shear and that of the deformation (C) is the fractional increase of the volume. If these parameters are denoted respectively by  $\epsilon_A, \epsilon_B, \epsilon_C$  and if  $\Phi_A, \Phi_B, \Phi_C$  are defined by

$$(8.15) \quad \Phi_A = \frac{1}{2!} \frac{d^2 \Phi}{d \epsilon_A^2}, \text{ etc.}$$

then it may be verified that  $\Phi_A, \Phi_B, \Phi_C$  are connected with  $\Phi_I, \Phi_{II}, \Phi_{II}, \Phi_{44}$  as follows:

$$(8.16) \quad \begin{aligned} \Phi_A &= \Phi_I + \Phi_{II} - \Phi_{II} ; & 2\Phi_B &= \frac{\Phi_I}{2} + \Phi_{44} ; \\ 2\Phi_C &= \frac{\Phi_{II} + 2\Phi_{II} - 2\Phi_I}{3} \end{aligned}$$

Deviding both sides of the above equations by the volume of the undeformed lattice, we obtain

$$(8.17) \quad \begin{aligned} c_A &= c_I + c_{II} - c_{II} , & 2c_B &= \frac{c_I}{2} + c_{44} \\ 2c_C &= \frac{c_{II} + 2c_{II} - 2c_I}{3} \end{aligned}$$

where  $c_A, c_B, c_C$  are defined similar to (8.14).

For ordinary pressures  $c_I$  is negligible, and  $c_A, 2c_B, 2c_C$ , serve as another set of three independent elastic constants for cubic lattices.

The above expansion of  $\Phi$  may be applied to each item(cf.(8.6)) of  $\Phi$  with similar notation as that introduced in (8.11)(8.12)(8.13) and (8.15),(8.16).

For an isotropic body it is well-known that the elastic constants satisfy the condition

$$(8.18) \quad \frac{c_{11} - c_{12}}{2} \approx c_{44} \quad \text{or, by (8.17), } \frac{c_A}{2} = 2c_B$$

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In the present case some terms of  $\Phi$  will satisfy the isotropic condition when the atomic polyhedron is replaced by a sphere.

### 8.3. Fermi energy and the correlation energy.

It will be shown in this paragraph that for sodium the Fermi energy and the correlation energy depend only on the volume of the metal. The reason for this, it will be seen immediately, lies in the fact that for sodium, the electrons in the metal are practically free.

The expression for the Fermi energy  $F$  of the electrons in the deformed lattice of sodium is given by (8.3) in which the range of the summation  $\sum \delta^k$  is determined, for practically all temperatures up to the melting point of the metal, by that  $F$  is minimum. As this expression is the same as that for free electrons with momenta  $\hbar \gamma_\alpha^k$ , the result is given by Sommerfeld's formula (1928)

$$(8.19) \quad F = N \frac{3}{5} \frac{\hbar^2}{2m} \left( \frac{3\pi^2}{\Omega} \right)^{2/3}$$

where  $\Omega$  is the <sup>atomic</sup> volume of the deformed lattice.

It is convenient to introduce a length  $r_0$ , the atomic radius, to measure the atomic volume, defined by

$$(8.20) \quad \Omega = \frac{4\pi}{3} r_0^3$$

If we measure  $r_0$  in the Bohr unit ( $\hbar^2/m_e^2 = 0.5284A.$ ) and measure the Fermi energy  $F$  in the Rydberg unit ( $me^4/2\hbar^2 = 13.53$  electron volts), Sommerfeld's formula assumes the numerical form (Fröhlich (1936) p. 277)

$$(8.21) \quad F = N \frac{2.21}{r_0^2}$$

where  $r_0$  measures the deformed atomic volume.

In the expression (8.3) for the correlation energy of the electrons with parallel spins,  $u_i^{0,2}$  may be replaced by the constant  $1/\bar{\Omega}$ . The integral may then be transformed to the real space, and the transformed expression

$$(8.22) \quad \Gamma_{\text{parallel spins}} = -\frac{1}{4} \iint \frac{dr}{\Omega} \frac{dr'}{\Omega} V_{-}(r-r') \left| \frac{2}{N} \sum_k e^{i\mathbf{k} \cdot (r-r')} \right|^2$$

is identical with that for free electrons. This has been evaluated by Wigner and Seitz ((1934) p. 512.) with the result

$$(8.23) \quad \Gamma_{\text{parallel spins}} = -N \cdot 0.458 \frac{e^2}{r_0}$$

of (8.22) Since the integrand depends only on the volume of the metal, the energy (8.23) depends only on the volume.

The above results that the Fermi energy and the correlation energy for electrons with parallel spins depend only on the volume hold only for sodium.

In the Fermi energy for lithium, there are additional

terms arising from the difference of  $u_b^{pk}$  and  $u_b^0$  which may not be expressible in terms of the volume alone.

A change in the expression for Fermi energy will cause a change in the range of summation  $2s^k$  of (8.22) and consequently a change in the resultant correlation energy(8.23) for electrons with parallel spins.

8.4. The Wigner-Seitz energy. The first and the second-order energy of Wigner and Seitz are given by (7.35) and(7.33) where the terms depending on  $u_{\alpha}^{pk}$  are to be dropped. All the surface integrals can be evaluated with the help of the equation of Wigner and Seitz

$$(8.24) \quad \left\{ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + V_{+-}(r) - \epsilon_b \right\} u_b^0(r) = 0$$

and the boundary condition

$$(8.24a) \quad \left( \frac{du_b^0(r)}{dr} \right)_{r=r_0} = 0$$

by replacing the basic polyhedron  $\bar{\Omega}$  in the image-space by a sphere of equal volume,

$$(8.24b) \quad \frac{4\pi}{3} r_0^3 = \bar{\Omega} \quad ;$$

except the last term of (7.35) which needs the knowledge of other eigenfunctions.

In evaluating the surface integrals,  $\nabla$  substitute for the derivatives at the boundary of the sphere their values calculated from the equation(8.24) and average

over the angles. Since  $u_b^0(r)$  is a function of the radial distance only, all the derivatives needed can be expressed in terms of the following ones :

(8.24c)  $\frac{\hbar^2}{2m} \left( \frac{d^2 u_b^0(r)}{dr^2} \right)_{r=r_0} = (V_+^0(r_0) - \epsilon_b^0) u_b^0(r_0)$

(8.24d)  $\frac{\hbar^2}{2m} \left( \frac{d^3 u_b^0(r)}{dr^3} \right)_{r=r_0} = \left[ \left( \frac{dV_+(r)}{dr} \right)_{r=r_0} - \frac{2}{r_0} (V_+^0(r_0) - \epsilon_b^0) \right] u_b^0(r_0)$

which are consequences of (8.24), (8.24a) There will be always a factor

(8.24e)  $4\pi r_0^3 u_b^0{}^2(r_0) = 3\gamma$

which is denoted by  $3\gamma$  so that  $\gamma$  represents the ratio of the density of electron at the boundary of the atomic polyhedron to the mean density  $\frac{3}{4\pi r_0^3}$ . Since  $u_b^0(\bar{r})$  is practically constant over the whole domain of the atomic sphere,  $\gamma$  is approximately one. The numerical value of  $\gamma$  is 1.005 for the actual lattice distance of sodium and decreases slowly when the metal expands (cf. Bardeen(1958)).

In the second-order energy (7.35) we have also the term proportional to  $(u_b^0(\bar{r}) \cdot \int(\bar{r}) u_b^0(\bar{r}))$ . This scalar product can be easily evaluated by a partial integration. with the result expressible again in  $\gamma$ ,

(8.24f)  $(u_b^0(\bar{r}) \cdot \int(\bar{r}) u_b^0(\bar{r})) = \frac{1}{2} \delta_{\alpha\beta} (\gamma - 1) \delta_{\gamma\beta}$

and is small.

The results are given below: (cf. (8.11))

$$(8.25) \quad \bar{E}_b^{\alpha\beta} = 3\gamma \mu_{\alpha\beta} \{V_+(\bar{r}_0) - \bar{E}_b\}$$

$$(8.26) \quad \bar{E}_b^{\alpha\beta\gamma\delta} = 3\gamma \left\{ \frac{1}{2} \mu_{\alpha\beta\gamma\delta} \left[ \bar{r}_0 \left( \frac{dV_+(\bar{r})}{d\bar{r}} \right)_{\bar{r}=\bar{r}_0} - 5(V_+(\bar{r}_0) - \bar{E}_b) \right] \right. \\ \left. + \frac{1}{2} \mu_{\alpha\beta} \delta_{\alpha\gamma} (V_+(\bar{r}_0) - \bar{E}_b) - \frac{\mu_{\alpha\beta} \delta_{\alpha\gamma} (\gamma-1)(V_+(\bar{r}_0) - \bar{E}_b)}{2} \right\} \\ + (V_+(\bar{r}_0) - \bar{E}_b) \sum_{B \neq b} \frac{(\dot{u}_B(\bar{q})) \cdot (-\frac{2\mu_{\alpha\beta} + \dot{\omega}_B}{2\dot{\omega}_B} \frac{\partial V_+(\bar{q})}{\partial \bar{q}_\beta} \dot{u}_B(\bar{q}))}{\dot{\omega}_b - \dot{\omega}_B} \int d\bar{q} \frac{\dot{u}_B(\bar{q})}{\dot{\omega}_B} \bar{q}_\alpha \bar{q}_\gamma \dot{u}_B(\bar{q})$$

where  $\mu_{\alpha\beta}$  and  $\mu_{\alpha\beta\gamma\delta}$  denote respectively the average of the products of two direction cosines and four direction cosines. These averages vanish except the following

$$(8.27) \quad \mu_{11} = \frac{1}{3}; \quad \mu_{1111} = \frac{1}{5}; \quad \mu_{1122} = \mu_{2211} = \frac{1}{15}.$$

Hence the expansion of  $\bar{E}$  is of the form (8.19) with

$$(8.28) \quad \bar{E}_1/N = \gamma (V_+(\bar{r}_0) - \bar{E}_b)$$

$$(8.29) \quad \frac{\bar{E}_{11}}{2}/N = \frac{\gamma}{2} \left\{ \frac{3}{5} \bar{r}_0 \left( \frac{dV_+(\bar{r})}{d\bar{r}} \right)_{\bar{r}_0} - 2(V_+(\bar{r}_0) - \bar{E}_b) \right\} - \frac{\gamma}{2} (\gamma-1)(V_+(\bar{r}_0) - \bar{E}_b)$$

$$(8.30) \quad \bar{E}_{12}/N = \gamma \left\{ \frac{1}{5} \bar{r}_0 \left( \frac{dV_+(\bar{r})}{d\bar{r}} \right)_{\bar{r}_0} - (V_+(\bar{r}_0) - \bar{E}_b) \right\} - \gamma(\gamma-1)(V_+(\bar{r}_0) - \bar{E}_b)$$

$$(8.31) \quad 2\bar{E}_{44}/N = \gamma \left\{ \frac{2}{5} \bar{r}_0 \left( \frac{dV_+(\bar{r})}{d\bar{r}} \right)_{\bar{r}_0} - (V_+(\bar{r}_0) - \bar{E}_b) \right\}$$

The last term of (8.26) has been neglected.

The combinations  $\bar{E}_A$ ,  $2\bar{E}_B$  are particularly simple,

$$(8.32) \quad \bar{E}_A/N = \gamma \frac{2}{5} \bar{r}_0 \left( \frac{dV_+(\bar{r})}{d\bar{r}} \right)_{\bar{r}_0} = -\frac{2}{5} \gamma \frac{e_+ e_-}{\bar{r}_0} \\ 2\bar{E}_B/N = \gamma \frac{1}{5} \bar{r}_0 \left( \frac{dV_+(\bar{r})}{d\bar{r}} \right)_{\bar{r}_0} = -\frac{1}{5} \gamma \frac{e_+ e_-}{\bar{r}_0}$$

It is easily verified that  $\epsilon_{11}$ ,  $\epsilon_{22}$ , and  $\epsilon_{44}$  satisfy the isotropic condition, or more directly seen from  $\epsilon_A$ ,  $2\epsilon_B$ .

In the particular case of uniform dilatation, when we have

$$(8.33) \quad \delta_{\alpha\beta} = \delta_{\alpha\beta} \frac{d\bar{r}_0}{\bar{r}_0}$$

it then follows from Taylor's theorem that (cf. (8.12))

$$(8.34) \quad \begin{aligned} 3E_1 &= \delta_{\alpha\beta} \epsilon^{\alpha\beta} = \bar{r}_0 \frac{d\bar{\epsilon}}{d\bar{r}_0} \\ 3\left(\frac{E_4}{2} + \epsilon_{22}\right) &= \delta_{\alpha\beta} \delta_{\gamma\delta} \epsilon^{\alpha\beta\gamma\delta} = \frac{1}{2} \bar{r}_0^2 \frac{d^2\bar{\epsilon}}{d\bar{r}_0^2} \end{aligned}$$

With the expansion coefficients calculated by the perturbation method, given in (8.28) + (8.31), we have therefore the differential equations

$$(8.35) \quad \bar{r}_0 \frac{d\bar{\epsilon}_b}{d\bar{r}_0} = 3\gamma (V_{+}(\bar{r}_0) - \bar{\epsilon}_b)$$

$$(8.36) \quad \begin{aligned} \frac{1}{2} \bar{r}_0^2 \frac{d^2\bar{\epsilon}_b}{d\bar{r}_0^2} &= 3\gamma \left\{ \frac{1}{2} \bar{r}_0 \left( \frac{dV_{+}(\bar{r})}{d\bar{r}} \right)_{\bar{r}_0} - 2(V_{+}(\bar{r}_0) - \bar{\epsilon}_b) - \frac{3}{2}(\gamma-1)(V_{+}(\bar{r}_0) - \bar{\epsilon}_b) \right\} \\ &+ (V_{+}(\bar{r}_0) - \bar{\epsilon}_b) \sum_{B \neq b} \frac{(u_b^{(0)}(\bar{\omega})) \left( -\frac{2\hbar k_\alpha}{2m} + \bar{\omega}_\alpha \frac{\partial V_{+}(\bar{\omega})}{\partial \bar{\omega}_\alpha} \right) u_B^{(0)}(\bar{\omega})}{\bar{\omega}_b - \bar{\omega}_B} \int d\bar{\sigma} u_B^{*}(\bar{\omega}) \bar{r}_0 u_b(\bar{\omega}) \end{aligned}$$

It is easily verified by (8.35), (8.36) that the terms with the denominators  $\bar{\omega}_b - \bar{\omega}_B$  represent the change of the factor  $\gamma$  introduced by (8.28), i.e.

$$(8.37) \quad \frac{3}{2} \bar{r}_0 \frac{d\gamma}{d\bar{r}_0} = \sum_{B \neq b} \frac{(u_b^{(0)}(\bar{\omega})) \left( -\frac{2\hbar k_\alpha}{2m} + \bar{\omega}_\alpha \frac{\partial V_{+}(\bar{\omega})}{\partial \bar{\omega}_\alpha} \right) u_B^{(0)}(\bar{\omega})}{\bar{\omega}_b - \bar{\omega}_B} \int d\bar{\sigma} u_B^{*}(\bar{\omega}) \bar{r}_0 u_b(\bar{\omega})$$

The first differential equation (8.35) has been derived by Fröhlich (1937)(1938) by the method of the perturbation of the boundary condition. It has been applied to the calculation of compressibility(Fuchs(1936a)) assuming the factor  $\gamma$  to be constant. In the present perturbation method, the change of the boundary condition has been compensated by the coordinate transformation to the image-space, so that  $E_{11}$ ,  $E_{22}$ ,  $E_{44}$  can be calculated separately.

8.5. The term  $S$ . In this paragraph, I intend to show that the combination  $E - S$  depends only on the volume for most monovalent metals. Since  $E_A$  and  $2E_B$  have been calculated in the preceding paragraph, we need only consider the term  $S$ .

Expanding the  $\frac{1}{|\underline{\omega}|}$  of (8.10) in the image-space, we have, according to the notation of (8.11), the following integrals over the domain of a sphere in the image-space,

$$(8.38) \quad S^0/N = \int d\bar{\omega} \rho^0(\bar{\omega}) \frac{e_+ e_-}{|\bar{\omega}|}$$

$$(8.39) \quad S^{\alpha\beta}/N = \int d\bar{\omega} \rho^{\alpha\beta}(\bar{\omega}) \bar{\omega}_\alpha \frac{\partial}{\partial \bar{\omega}_\beta} \frac{e_+ e_-}{|\bar{\omega}|}$$

$$(8.40) \quad S^{\alpha\beta\gamma\delta}/N = \int d\bar{\omega} \rho^{\alpha\beta\gamma\delta}(\bar{\omega}) \frac{1}{2!} \bar{\omega}_\alpha \bar{\omega}_\beta \frac{\partial^2}{\partial \bar{\omega}_\gamma \partial \bar{\omega}_\delta} \frac{e_+ e_-}{|\bar{\omega}|}$$

There is really no need to integrate all of them, for there are algebraic relations among them, e.g. the

isotropic condition,

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$$(8.41) \quad \frac{1}{2} (\mathcal{S}_{11} - \mathcal{S}_{22}) = \mathcal{S}_{44}$$

Three other algebraic relations may be derived as follows, which will enable us to express  $\mathcal{S}_i$ ,  $\mathcal{S}_{11}$ ,  $\mathcal{S}_{12}$  and  $\mathcal{S}_{44}$  in terms of  $\mathcal{S}_0$ , which may be directly integrated.

It follows from (8.39) and Euler's theorem on homogeneous functions, that

$$(8.42) \quad \mathcal{S}^{\alpha\alpha} = -\mathcal{S}^0$$

Similarly, applying Euler's theorem to (8.40), we have

$$(8.43) \quad \mathcal{S}^{\alpha\alpha\gamma\gamma} = \mathcal{S}^{\alpha\beta\beta\alpha} = \frac{(-1)(-1-1)}{2} \mathcal{S}^0 = \mathcal{S}^0$$

While applying Poisson's equation

$$(8.44) \quad \frac{\partial^2}{\partial \bar{x}_3 \partial \bar{x}_3} \frac{1}{|\bar{\omega}|} = -4\pi \delta(\bar{\omega})$$

where  $\delta(\bar{\omega})$  denotes Dirac's delta function, we get another relation from (8.40),

$$(8.45) \quad \mathcal{S}^{\alpha\beta\alpha\beta} = 0$$

Adding (8.43) and (8.45), I shall replace (8.45) by

$$(8.46) \quad \mathcal{S}^{\alpha\beta\alpha\beta} + \mathcal{S}^{\alpha\beta\beta\alpha} = \mathcal{S}^0$$

According to the notation of (8.13); (8.42), (8.43), and (8.46) may be expressed in terms of  $\mathcal{S}_i$ ,  $\mathcal{S}_{11}$ ,  $\mathcal{S}_{12}$ ,  $\mathcal{S}_{44}$  and  $\mathcal{S}^0$ , algebraically as follows:

(8.47)  $3 S_1 = - S^0$

(8.48)  $3 ( \frac{S_{11}}{2} + S_{12} ) = S^0$

(8.49)  $6 ( \frac{S_{11}}{2} + S_{44} ) = S^0$

which together with (8.41) can be solved for  $S_1$ ,  $S_{11}$ ,  $S_{12}$  and  $S_{44}$  in terms of  $S^0$  which may be integrated directly. The results are

(8.50)  $\frac{S^0}{N} = \frac{3}{2} \gamma \frac{e_+ e_-}{r_0} ; S_1/N = -\frac{1}{3} \frac{S^0}{N} = -\frac{1}{2} \gamma \frac{e_+ e_-}{r_0}$

(8.51)  $\frac{S_{11}}{2} / N = \frac{2}{15} \frac{S^0}{N} = \frac{1}{5} \gamma \frac{e_+ e_-}{r_0}$

(8.52)  $S_{12} / N = \frac{1}{5} \frac{S^0}{N} = \frac{3}{10} \gamma \frac{e_+ e_-}{r_0}$

(8.53)  $2 S_{44} / N = \frac{1}{15} \frac{S^0}{N} = \frac{1}{10} \gamma \frac{e_+ e_-}{r_0}$

with the combinations

(8.54)  $S_A / N = -\frac{4}{15} \frac{S^0}{N} = -\frac{2}{5} \gamma \frac{e_+ e_-}{r_0}$

(8.54)  $2 S_B / N = -\frac{2}{15} \frac{S^0}{N} = -\frac{1}{5} \gamma \frac{e_+ e_-}{r_0}$

The factor  $\gamma$  arises from the fact that in the division of the Coulomb interaction of the lattice into  $L - S$ , only the electron density at the boundary of the polyhedron plays important rôle. The term  $L$  is also to be multiplied by the factor  $\gamma$  .(cf.Fuchs(1936)p.629).

On comparing (8.54) with (8.32), we see that the combination  $E - S$  depends only on the volume. The reason for this is that the kinetic energy of the electron (this is contained in  $E_b$ , by (8.23)) is practically not affected by the distortions keeping the volume unchanged, while that the change of the potential energy due to distortions in  $E_b$  and in

$S/V$  practically cancel. It may be added here that Wigner and Seitz have shown that the error in the kinetic energy introduced by replacing the atomic polyhedron by the atomic sphere is extremely small (Wigner and Seitz(1934)Appendix I)\*\*

The consideration of this paragraph applies also to lithium, but probably not to copper.

3.6. Elastic constants at constant volume.

Fuchs(1936) has calculated the elastic constants at constant volume of monovalent metals based on the assumption that

$$(8.55) \quad \Phi_A = I_A + L_A \quad 2\Phi_B = 2I_B + 2L_B$$

From the result of §8.5 that the difference  $E - S$  depends only on the volume and from the approximate result of §8.3 that the Fermi energy and the correlation energy between electrons with parallel spins depend, for sodium, only on the volume, we see that Fuchs' assumption is completely justified in the case of sodium. For lithium, some correction is necessary for the Fermi energy of the deformed lattice arising from the difference of  $u_b^{ok}$  and  $u_b^o$  may not be expressible in terms of the volume alone.

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\*\* It is further estimated that the neglected term, the last one of (8.26), does not affect this conclusion.

bulk moduli can be calculated if the binding energy as a function of the volume is known. In order to avoid numerical calculations of the binding energy for various lattice distances, Fröhlich (1937)(1938) developed a method of "perturbation of the boundary condition" and derived the first order differential equation (8.35). Fuchs(1936a) then applied this formula, assuming the factor  $\gamma$  to be constant and equal to one. He took, as the total energy of the lattice, simply

$$\bar{E} = E + F + I \quad (8.56)$$

and calculated the bulk moduli of monovalent metals by differentiations, assuming that the Fermi energy is given by Sommerfeld's formula for free electrons.

The corrections to Fröhlich's formula for  $E$  and Sommerfeld's formula for  $F$  will not be considered here, though the perturbation method given above is sufficient for this. It is only intended to examine the corrections due to the other items of (8.6), i.e.  $L - S + \Gamma_{\text{parallel spins}}$ , which must be added to (8.56) in the Fock-Dirac approximation; and furthermore the correction due to the correlation energy for electrons with antiparallel spins, which has not been taken into account in the Fock-Dirac approximation but

has been shown to be very important in the heat of sublimation of metals. This additional energy due to the correlation of electrons with antiparallel spins has been investigated by Wigner (1934) and will be denoted by  $\Gamma_{\text{antiparallel spins}}$ .

Fuchs' original calculation of the bulk modulus may be repeated here. From the equation of state we have, at zero pressure,

$$(8.57) \quad \frac{d\Phi}{dr_0} = 0 \quad \text{i.e.} \quad \frac{dE}{dr_0} + \frac{dF}{dr_0} + \frac{dI}{dr_0} = 0$$

With the help of Fröhlich's formula and Sommerfeld's formula, this becomes

$$(8.58) \quad \frac{d\Phi/N}{dr_0} = \frac{3(V_+(r_0) - \dot{E}_b)}{r_0} - \frac{2 \times 2.21}{r_0^3} + \frac{dI/N}{dr_0} = 0$$

The bulk modulus  $\frac{1}{\kappa}$  is then calculated by another differentiation,

$$(8.59) \quad \frac{1}{\kappa} = \frac{1}{9\Omega} r_0^{-2} \frac{d^2\Phi/N}{dr_0^2} \\ = \frac{1}{4\pi r_0^3} \left[ r_0 \left( \frac{dV_+(r_0)}{dr_0} \right) - 4(V_+(r_0) - \dot{E}_b) + \frac{2 \times 2.21}{r_0^2} + \frac{1}{3} r_0^2 \frac{d^2I/N}{dr_0^2} \right]$$

where  $V_+(r_0) - \dot{E}_b$  may be eliminated by the equation of state (8.58). The final expression for  $\frac{1}{\kappa}$  is therefore

$$(8.60) \quad \frac{1}{\kappa} = \frac{1}{4\pi r_0^3} \left[ r_0 \frac{dV_+(r_0)}{dr_0} - \frac{2}{3} \frac{2.21}{r_0^2} + \frac{4}{3} \frac{r_0}{dr_0} \frac{dI/N}{dr_0} + \frac{1}{3} r_0^2 \frac{d^2I/N}{dr_0^2} \right]$$

If we interpret the  $I$  in (8.56) differently by including the additional terms  $L-S+P$  the final expression for  $\frac{1}{K}$  will be still of the form (8.60). Hence the correction to the bulk modulus due to  $L-S+P$  is

$$(8.61) \quad \frac{1}{4\pi r_0^3} \left[ \frac{4}{3} \frac{d}{r_0} + \frac{1}{3} \frac{d^2}{r_0^2} \right] \frac{L-S+P_{\text{parallel spins}}+P_{\text{antiparallel spins}}}{N}$$

or

$$(8.62) \quad \frac{1}{4\pi r_0^3} \left[ \frac{4}{3} \frac{d}{r_0} + \frac{1}{3} \frac{d^2}{r_0^2} \right] \frac{L-S+P_{\text{parallel spins}}}{N}$$

According to whether the correlation energy for electrons with antiparallel spins is taken into account or not. The numerical value originally calculated by Fuchs and the values corrected according to (8.61) and (8.62) are summarized in the table below where the experimental value extrapolated by Bardeen (1938) to zero temperature and pressure is also included for comparison.

| Bulk modulus of sodium in c.g.s. units $\times 10^{11}$ |  |       |
|---|--|-------|
| Value calc. from  | $\bar{\Phi} = E + F + I$   | 0.878 |
| Value calc. from  | $\bar{\Phi} = E + F + I + L - S + P_{\text{parallel spins}}$                                 | 0.781 |
| Value calc. from  | $\bar{\Phi} = E + F + I + L - S + P_{\text{parallel spins}} + P_{\text{antiparallel spins}}$ | 0.825 |
| Extrapolated experimental value                         |  | 0.813 |

The numerical value of  $L$  is taken from Wigner and Seitz(1934)Appendix II, namely

$$(8.63) \quad L/N = -0.89593 \frac{e^2}{\bar{r}_0}$$

The dependence of the correlation energy for electrons with antiparallel spins, is given by Fig.7 (Wigner(1934)) which may be represented by the interpolation formula

$$(8.64) \quad T_{\text{antiparallel spins}}/N = -\frac{e^2}{\bar{r}_0} (0.0170 + 0.0295\bar{r}_0 - 0.0015\bar{r}_0^2)$$

within the range  $\bar{r}_0 = 1$  to  $\bar{r}_0 = 8$ . The actual value of  $\bar{r}_0$  is taken as 3.94 Bohr units.

The numerical expressions for  $J$  and  $T_{\text{parallel spins}}$  are given in (8.23) and (8.50), in which  $e^2$  takes the numerical value 2 in the atomic units used above.

## THERMAL OSCILLATIONS OF METALLIC LATTICES

## 9. Notation

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In this chapter the unperturbed lattice is periodic in the sense of possessing three translational periods. All periodic quantities refer to these periods.

The unperturbed eigenfunctions are enumerated either by two indices  $K$  and  $B$ , or by three indices  $\varepsilon$ ,  $(K)$  and  $B$ , or by another set of three indices  $(K)$ ,  $e$  and  $B$ . The indices  $\varepsilon$  and  $e$  assume two values each, while  $(K)$  assumes one half of the values which  $K$  assume.

The Fock functions are distinguished by small letters  $k$ ,  $b$  or  $\varepsilon$ ,  $(k)$ ,  $b$  or  $(k)$ ,  $e$ ,  $b$  replacing the capital letters in the indices. The index  $k$  does not assume all the values which  $K$  assume.

The summation sign  $S_b^k$  covers all the Fock functions. The summation sign  $\sum_B^K$  covers all the eigenfunctions.

The perturbed lattice formed by the displaced positions of the ions is not periodic, but it is cyclic. The displacements of the ions are analyzed into thermal waves. The summation sign  $S_n$  covers all modes of thermal waves.

The perturbed eigenfunctions are only enumerated by  $(K)$ ,  $e$ ,  $B$ , and the perturbed Fock functions, by  $(k)$ ,  $e$ ,  $b$ .

10. Thermal displacements as a perturbation

The general procedure of treating the displacements of the ions as a perturbation to the motion of the electrons has been described in §4. This will now be applied to the case of thermal displacements of the ions described by

$$(10.1) \quad r_{\alpha}^l = a_{\alpha}^l + \sum_n U_{\alpha}^n e^{i g^{\alpha} \cdot a^l}$$

where the wave amplitudes  $\underline{U}^{\lambda}$  satisfy

$$(10.2) \quad \underline{U}^{-\lambda} = \underline{U}^{\lambda *}$$

$$(10.3) \quad \underline{U}^{\lambda} = 0 \quad \text{for} \quad \lambda = 000$$

The equation (10.2) expresses the condition that the displacements of the ions are real while (10.3) eliminates the translation of the crystal as a whole.

The first step of the perturbation method is the contact transformation to the image-space. This transformation is determined by the law of the displacements of the ions. In the present case, the coordinate transformation to the image-space is

$$(10.4) \quad r_{\alpha} = \bar{r}_{\alpha} + \sum_{\lambda} U_{\alpha}^{\lambda} e^{i g^{\lambda} \cdot \bar{r}}$$

from which the transformation of the operators and the eigenfunctions may be derived according to (4.6), (4.7).

The transformed quantities in the image-space, distinguished by the bars above the letters and in the arguments, are then to be expanded with respect to the parameters  $U_\alpha^n$ .

10.1. Perturbation operators. The expansion of the various operators contained in the perturbed eigenvalue problem (4.25) will now be given, term by term. The general form of the expansion is written as

$$(10.5) \quad \bar{H}(\bar{z}) = \overset{0}{H}(\bar{z}) + \overset{1}{H}(\bar{z}) + \overset{2}{H}(\bar{z}) + \dots$$

or, in details,

$$(10.6) \quad \bar{H}(\bar{z}) = \overset{0}{H}(\bar{z}) + \sum_n U_\alpha^n \overset{n}{H}(\bar{z}) + \sum_{n\lambda} U_\alpha^n U_{\alpha'}^{\lambda'} \overset{n\lambda}{H}(\bar{z}) + \dots$$

where the summation over repeated Greek indices is understood. The indices  $n, \alpha$  have been written on the left corners of the operators  $\overset{n}{H}(\bar{z})$  etc. in order to avoid any confusion with the notation of matrix elements. The quantities  $\overset{0}{H}(\bar{z}), \overset{2}{H}(\bar{z}), \overset{\lambda'n}{\alpha'\alpha} H(\bar{z})$  etc. will be referred to as the expansion coefficients of  $\bar{H}(\bar{z})$ .

To begin with, the potential energy  $V_+(\bar{z})$  in the real space will be assumed to be of the form of a lattice sum,

$$(10.7) \quad V_+(\bar{z}) = \sum_l V_{+l}(\bar{z} - \bar{z}^l)$$

By substituting (10.1), (10.4) into (10.7) and expanding the result by Taylor's series, we obtain the following

expansion coefficients of  $\bar{V}_+(\bar{r})$ ,

$$(10.8) \quad \overset{\circ}{V}_+(\bar{r}) = \sum_l V_+(\bar{r} - \underline{a}^l)$$

$$(10.9) \quad \frac{\hbar}{\alpha} \nabla_+^2 V_+(\bar{r}) = \sum_l (e^{i\frac{\hbar}{\alpha} \cdot \bar{r}} - e^{i\frac{\hbar}{\alpha} \cdot \underline{a}^l}) \frac{\partial^2 V_+(\bar{r} - \underline{a}^l)}{\partial(\bar{r} - \underline{a}^l)_\alpha^2}$$

$$(10.10) \quad \frac{\hbar^2}{\alpha^2} \nabla_+^4 V_+(\bar{r}) = \sum_l (e^{i\frac{\hbar}{\alpha} \cdot \bar{r}} - e^{i\frac{\hbar}{\alpha} \cdot \underline{a}^l}) (e^{i\frac{\hbar}{\alpha} \cdot \bar{r}} - e^{i\frac{\hbar}{\alpha} \cdot \underline{a}^l}) \frac{\partial^4 V_+(\bar{r} - \underline{a}^l)}{\partial(\bar{r} - \underline{a}^l)_\alpha^4}$$

It is seen from (10.9) that  $\frac{\hbar}{\alpha} \nabla_+^2 V_+(\bar{r})$  is the product of  $e^{i\frac{\hbar}{\alpha} \cdot \bar{r}}$  and a periodic function of  $\bar{r}$ , the periods being the lattice vectors of the undisplaced lattice. For convenience, such functions will be called "cyclic functions of the class  $n$ ".

Similarly it is seen from (10.10) that  $\frac{\hbar^2}{\alpha^2} \nabla_+^4 V_+(\bar{r})$  are cyclic functions of the class  $n'+n$ . The zero-order term  $\overset{\circ}{V}_+(\bar{r})$  is of course a periodic function, or a cyclic function of the class  $\infty$ .

Next, the transformed kinetic energy  $\bar{T}(\bar{r})$  is to be calculated from

$$(10.11) \quad \bar{T}(\bar{r}) = \omega(\bar{r}) \mathcal{T}(\underline{r}(\bar{r})) \{v(\bar{r})\}^{-1}$$

where  $\mathcal{T}(\underline{r}(\bar{r}))$  denotes the operator obtained from  $\mathcal{T}(\underline{r})$  by the substitution of variables (10.4), and  $v(\bar{r})$ , the square root of the Jacobian of the substitution. By a substitution of variables, we

have,

$$(10.12) \quad \frac{\partial}{\partial r_\beta} = \frac{\partial \bar{r}_\alpha}{\partial r_\beta} \frac{\partial}{\partial \bar{r}_\alpha} ; \quad \omega(\bar{r}) = \sqrt{\left| \frac{\partial \underline{r}_\alpha}{\partial \bar{r}_\beta} \right|}$$

from which  $\bar{T}(\bar{x})$  can be calculated. It is easily seen from (10.12) that  ${}^n T(\bar{x})$  (cf. (10.6) for the notation) is the product of  $e^{i\eta \cdot \bar{x}}$  and a homogeneous quadratic form of  $f_\beta(\bar{x})$ , and that  ${}^h T(\bar{x})$  is the product of  $e^{i\eta' \cdot \bar{x}}$  and a constant. Hence  ${}^h T(\bar{x})$  is the product of  $e^{i\eta' \cdot \bar{x}}$  and an inhomogeneous quadratic form of  $f_\beta(\bar{x})$  and similarly  ${}^{h'n} T(\bar{x})$  is the product of  $e^{i\eta' \cdot \bar{x}} e^{i\eta \cdot \bar{x}}$  and an inhomogeneous quadratic form of  $f_\beta(\bar{x})$ .

The explicit expressions of some of the expansion coefficients of  $\bar{T}(\bar{x})$  are given below which are sufficient for the later calculations:

$$(10.13) \quad {}^n T(\bar{x}) = -\frac{1}{2h} e^{i\eta \cdot \bar{x}} \left[ 2i \eta_\beta^\alpha (f_\beta(\bar{x}) + h g_\beta^\alpha) (f_\alpha(\bar{x}) + h g_\alpha^\beta) \right]$$

$$(10.14) \quad {}^{h'n} T(\bar{x}) = -\frac{1}{2h} \left\{ i\eta^\alpha i\eta^\beta f_\alpha(\bar{x}) f_\beta(\bar{x}) + 2i\eta^\alpha f_\alpha(\bar{x}) i\eta^\beta f_\beta(\bar{x}) \right. \\ \left. + \frac{1}{4} i\eta^\alpha i\eta^\beta h g_\alpha^\gamma h g_\gamma^\beta \right\}$$

Since  $f_\alpha(\bar{x})$  may be considered as a periodic operator, i.e. an operator which can be applied to periodic functions to yield periodic functions, it follows from (10.13) that  ${}^n T(\bar{x})$  is the product of  $e^{i\eta \cdot \bar{x}}$  and a periodic operator. For convenience, such operators will be called "cyclic operators of the class  $n$ ". It follows from (10.12), by direct calculation, that the  ${}^{h'n} T(\bar{x})$  are cyclic functions of the class  $h' + n$ , etc. In particular,  ${}^{h'n} T(\bar{x})$

is a cyclic operator of the class  $000$ , i.e. a periodic operator.

The general form of the expansion coefficients of  $\bar{V}_+(\bar{r})$  and  $\bar{T}(\bar{r})$  naturally suggests that the expansion coefficients of  $\bar{P}(\bar{r})$  and  $\bar{A}(\bar{r})$  may be of the same form, i.e. the  ${}^n_\alpha P(\bar{r})$ ,  ${}^{n'}_\alpha P(\bar{r})$ , etc. may be cyclic functions of the class  $n$ ,  $n'+n$ , etc. and the  ${}^n_\alpha A(\bar{r})$ ,  ${}^{n'}_\alpha A(\bar{r})$ , etc. may be cyclic operators of the class  $n$ ,  $n'+n$ , etc. It is readily seen, from the definitions of the  $\bar{P}(\bar{r})$  and the  $\bar{A}(\bar{r})$

((4.14)-(4.16)) and with the help of the expansion of

$$\begin{aligned}
 \bar{V}_-(\bar{r}; \bar{r}'), & \\
 (10.15) \quad \bar{V}_-(\bar{r}; \bar{r}') &= V_-(\bar{r}-\bar{r}') + \int_n U_\alpha^{\lambda} (e^{i\frac{\lambda}{\alpha}\bar{r}} - e^{i\frac{\lambda}{\alpha}\bar{r}'} ) \frac{\partial V_-(\bar{r}-\bar{r}')}{\partial(\bar{r}-\bar{r}')_\alpha} \\
 &+ \int_{n\lambda} U_\alpha^{\lambda} U_{\alpha'}^{\lambda'} (e^{i\frac{\lambda}{\alpha}\bar{r}} - e^{i\frac{\lambda}{\alpha}\bar{r}'} ) e^{i\frac{\lambda'}{\alpha'}\bar{r}'} \frac{\partial^2 V_-(\bar{r}-\bar{r}')}{\partial(\bar{r}-\bar{r}')_\alpha \partial(\bar{r}-\bar{r}')_{\alpha'}} \\
 &= V_-(\bar{r}-\bar{r}') + \int_n U_\alpha^{\lambda} {}^n_\alpha V_-(\bar{r}; \bar{r}') + \int_{n\lambda} U_\alpha^{\lambda} U_{\alpha'}^{\lambda'} {}^{n'}_\alpha V_-(\bar{r}; \bar{r}'),
 \end{aligned}$$

that the expansion coefficients of the  $\bar{P}(\bar{r})$  and the  $\bar{A}(\bar{r})$  will be of the suggested form provided that the expansion coefficients of the quantity  $\bar{\rho}(\bar{r}; \bar{r}')$  are of the following forms

$$(10.16) \quad {}^n_\alpha \rho(\bar{r}; \bar{r}') = e^{i\frac{\lambda}{\alpha}\bar{r}} f(\bar{r}-\bar{r}') g(\bar{r}) h(\bar{r}')$$

$$(10.17) \quad {}^{n'}_\alpha \rho(\bar{r}; \bar{r}') = e^{i\frac{\lambda}{\alpha}\bar{r}} e^{i\frac{\lambda'}{\alpha'}\bar{r}'} f(\bar{r}-\bar{r}') g(\bar{r}) h(\bar{r}')$$

where  $f$  denotes an arbitrary function and  $g, h$  denote arbitrary periodic functions.

Conversely, however, if we assume that the expansion coefficients  ${}^n_\alpha A(\bar{r})$  and  ${}^n_\alpha P(\bar{r})$ ,  ${}^{n'}_\alpha A(\bar{r})$

and  $\frac{\alpha'}{\alpha} \rho(\bar{z})$ , etc. are cyclic operators and cyclic functions of the class  $n$ ,  $n'+n$ , etc., it can be shown by perturbation calculations, which will be done below, that the expansion coefficients of  $\bar{\rho}(\bar{z}; \bar{z}')$  are really of the form anticipated above (10.16), (10.17).

Hence the above particular forms of  $\frac{\alpha'}{\alpha} \rho(\bar{z}; \bar{z}')$  etc. and  $\frac{\alpha'}{\alpha} \rho(\bar{z})$  etc. give a self-consistent general solution for the motion of electrons in displaced lattices.

It follows from (10.16), (10.17), by putting  $\bar{z} = \bar{z}'$  that the expansion coefficients  $\frac{\alpha'}{\alpha} \rho(\bar{z}')$ ,  $\frac{\alpha'}{\alpha} \rho(\bar{z})$ , etc. are cyclic functions of the class  $n$ ,  $n'+n$ , etc. Hence we have the theorem that both the potential and the density of the electrons in the displaced lattice are superpositions of periodic quantities modulated by the various thermal waves.

10.2. Selection rules. Since the undisplaced lattice is periodic in the sense possessing three translational periods, the unperturbed eigenfunctions are given by Bloch's theorem,

$$(10.18) \quad \psi_B^{0K} = \frac{e^{i\mathbf{g}^K \cdot \bar{r}}}{\sqrt{N_+}} u_B^K(\bar{z})$$

where the  $\mathbf{g}^K$  are the reduced wave vectors and the  $u_B^K$  are periodic functions, all referring to the undisplaced lattice. When the metal carries no

current, it is known that, corresponding to every Fock's function  $\psi_b^{0k}(\vec{r})$  there is another Fock's function  $\psi_b^{0-k}(\vec{r})$  belonging to the same parameter  $W_b^{0-k} = W_b^{0k}$ .

In fact, it follows from (10.18) and the fact that  $H(\vec{r})$  is real, that we may put  $\psi_b^{0-k} = \psi_b^{0k}^*$ , or, in general,

$$(10.19) \quad \psi_B^{0-K} = \psi_B^{0K}^* ; \quad W_B^{0K} = W_B^{0-K}$$

This will be referred to as the degeneration of the sense of the wave vectors  $\vec{K}$ .

Let us now consider the first-order perturbation operator due to the thermal displacements of the ions,

$$(10.20) \quad H(\vec{r}) = \sum_n U_n^{\vec{r}} H(\vec{r})$$

where, as shown above, the  $U_n^{\vec{r}} H(\vec{r})$  are cyclic operators of the classes  $u$ . It follows directly from the definitions of the classes of the cyclic operators and the cyclic functions that, e.g.  $U_n^{\vec{r}} H(\vec{r}) \psi_B^{0K}$  is a cyclic function of the class  $u+K$ . As cyclic

functions of different classes are orthogonal, the matrix element  $H_{B'B}^{1K'K}$  reduces to a single term contributed by that particular  $U_n^{\vec{r}} H(\vec{r})$  for which the equation

$$(10.21) \quad u_\alpha + K_\alpha - K'_\alpha = h_\alpha (2L+1) \quad (\alpha=1,2,3)$$

can be satisfied by some integral values of  $h_\alpha$ . Since all the three integers  $u_\alpha, K_\alpha, K'_\alpha$  are limited to



We have also the case (B) when  $\beta' = \beta$ . It follows from (10.21) that in general  $H_{\beta\beta}^{K'K}$  by no

means vanishes. The difference of the parameters  $\omega_{\beta}^K$  and  $\omega_{\beta}^{K'}$  becomes very small for small difference of  $\pm K$  and  $\pm K'$ , but the corresponding eigenfunctions  $\psi_{\beta}^K, \psi_{\beta}^{K'}$  do still combine. In

particular, when  $K' = -K$ , the degenerate eigenfunctions  $\psi_{\beta}^K$  and  $\psi_{\beta}^{-K}$  always combine under the first order perturbation for there exists always such an  $n$ , responsible for this, satisfying

$$(10.24) \quad n_{\alpha} + 2K_{\alpha} = h_{\alpha} (2L+1) \quad (\alpha=1,2,3)$$

It is to be noted that for a given  $n$ , (10.24) gives a unique  $K$ , and vice versa, - a one-to-one correspondence between the reduced thermal wave vectors  $g^n$  and the reduced wave vectors  $g^K$  of the eigenfunctions.

For the second-order perturbation operator,

$$(10.25) \quad H^{(2)}(\alpha) = \int_{\alpha\alpha'} U_{\alpha}^{(2)} U_{\alpha'}^{(2)} \frac{\alpha\alpha'}{\alpha\alpha} H(\alpha)$$

the general selection rule for the matrix elements  $H_{\beta'\beta}^{2K'K}$  is similar to (10.21) with  $n'+n$  replacing  $n$ . Limited to the second-order perturbation

energy, only the diagonal elements  $H_{\beta\beta}^{2kk}$  of the second-order perturbation operator need to be considered.

The selection rule for the diagonal elements  $H_{\beta\beta}^{2kk}$

is, by replacing  $n$  of (10.21) by  $n'+n$ , and by putting  $K=K'$  in (10.21), simply

$$(10.26) \quad n_\alpha + n'_\alpha = h_\alpha (2L+1) \quad (\alpha=1,2,3)$$

Since both  $n_\alpha$  and  $n'_\alpha$  are limited to the range  $-L \dots +L$ , this equation can only be satisfied by

$$(10.27) \quad n_\alpha + n'_\alpha = 0 \quad \text{i.e.} \quad n'_\alpha = -n_\alpha \quad (\alpha=1,2,3)$$

Hence, we have for the diagonal element  $H_{bb}^{kk}$ , the simple summation

$$(10.28) \quad H_{bb}^{kk} = \int_n U_\alpha^n U_\alpha^{-n} \frac{-n^2}{\alpha^2} H_{bb}^{kk}$$

It is for this reason that the expansion coefficients of the second order of  $\bar{T}(\epsilon)$  other than  $\frac{-n^2}{\alpha^2} T(\epsilon)$  have not been given in connexion with (10.14).

By (10.2), (10.1), the wave amplitudes  $u^k$  and  $u^{-k}$  refer to the same thermal wave, only running in opposite senses. Owing to the selection rules given above, (cf. (10.22) and (10.25)) these thermal waves are independent to the second order terms in the wave amplitudes  $u^k$ .

10.3. Preparation of the unperturbed eigenfunctions. It has <sup>been</sup> shown above that the degenerate eigenfunctions  $\psi_B^{\alpha K}$  and  $\psi_B^{\alpha -K}$  do combine under the first-order perturbation. It is known, then, the perturbed eigenfunctions will approach neither of

these eigenfunctions when the perturbation parameters  $U_n$  approach zero, but they will approach certain linear combinations of the  $\psi_B^{0K}$  and the  $\psi_B^{0-K}$ .

Since all normalised eigenfunctions are only determined to within arbitrary constant factors of moduli unity, the "phase factors", the required linear combinations of the  $\psi_B^{0K}$  and the  $\psi_B^{0-K}$  cannot be specified definitely without specifying the choice of these phase factors. By (10.19), we may regard the phase factors of the  $\psi_B^{0K}$  as fixed provided the phase factors of the  $\psi_B^{0-K}$  are fixed. The phase factors of the  $\psi_B^{0K}$  will now be fixed in the following way.

It has <sup>been</sup> shown above that for a given  $n$ , there exists a unique  $K$ , such that (10.24) is satisfied. We then have,

$$(10.29) \quad H_{BB}^{-KK} = U_n^\alpha H_{BB}^{-KK}$$

If the right hand side of this is written out in the form of a volume integral, it will be seen, by (10.19), that it contains only the eigenfunction  $\psi_B^{0K}$ , namely,

$$(10.30) \quad H_{BB}^{-KK} = \int \psi_B^{0K}(\bar{r}) U_n^\alpha H(\bar{r}) \psi_B^{0K}(\bar{r}) d\bar{r}$$

Since the phase factors of the  $U_n^\alpha$  are given and since the correspondence (10.24) between the  $n$  and the  $K$  is one-to-one, we may fix the phase factors

of the  $\psi_B^0$  such that the  $H_{BB}^{-K, K}$  are real for all  $K, B$ . It is possible to do so, for corresponding to a given  $K$  we have, by (10.24), a particular  $n$  and since the phase factors of the various  $\psi_n^A$  are entirely independent, the conditions that the  $H_{BB}^{-K, K}$  are real for the various  $K, B$  can be fulfilled independently.

It follows from (10.19) and the fact that the perturbation operator  $H^{(1)}$  is real, that, once the  $H_{BB}^{-K, K}$  are real, the  $H_{BB}^{K, -K}$  are also real. In general, they are conjugate complex to each other.

Now let us divide the domain of the reduced wave vectors  $K$  into two equal parts by a plane passing the origin  $K=000$ . Let the left half be denoted by  $-(K)$ , and the right half, by  $+(K)$ , the domain of  $(K)$  being only one-half of that of  $K$ . The unperturbed eigenfunctions  $\psi_B^0$  will be divided according to the wave vectors, and denoted by  $\psi_B^0 \epsilon(K)$  ( $\epsilon = +, -$ ). The preparation of the unperturbed eigenfunctions then consists of the transformation of the following matrix of two rows and two columns to diagonal form:

$$(10.51) \quad \begin{pmatrix} H_{BB}^{-K, -K} & H_{BB}^{-K, +K} \\ H_{BB}^{-K, +K} & H_{BB}^{-K, -K} \end{pmatrix} = \begin{pmatrix} H_{BB}^{\epsilon(K), \epsilon'(K)} \\ B & B \end{pmatrix} \quad \epsilon, \epsilon' = +, -$$

Since the matrix (10.51) is, by the above choice of the phase factors and by the selection rule (10.23),

$$(10.32) \quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} H_B^{(K)}$$

with

$$(10.33) \quad H_B^{(K)} = H_{BB}^{(K)} = H_B^{(K)} H_B^{(K)}$$

being real, the transformation to diagonal form may be accomplished by the following change of basis,

$$(10.34) \quad \psi_B^{(K)e} = \frac{1}{\sqrt{2}} \left\{ \psi_B^{(K)-} + (-)^e \psi_B^{(K)+} \right\}; \quad (e=1,2)$$

We then have

$$(10.35) \quad H_B^{(K)} e' (K) e = \left( \psi_B^{(K)e'} \cdot H \psi_B^{(K)e} \right) = \frac{(-)^e + (-)^{e'}}{2} H_B^{(K)} = (-)^e \delta_{ee'} H_B^{(K)}$$

or, in matrix form,

$$(10.36) \quad \begin{pmatrix} H_B^{(K)1(K)1} & H_B^{(K)1(K)2} \\ H_B^{(K)2(K)1} & H_B^{(K)2(K)2} \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} H_B^{(K)}$$

The equation (10.34) gives, therefore, the prepared unperturbed eigenfunctions which are to be used in the subsequent perturbation calculations. It expresses

a unitary transformation from the  $\psi_B^{\varepsilon(K)}$  ( $\varepsilon = +, -$ ) to the  $\psi_B^{(K)e}$  ( $e = 1, 2$ ), and may be inverted to give the transformation from the  $\psi_B^{(K)e}$  ( $e = 1, 2$ ) to the  $\psi_B^{\varepsilon(K)}$  ( $\varepsilon = +, -$ ) with the result,

$$(10.37) \quad \psi_B^{\varepsilon(K)} = \frac{1}{\sqrt{2}} \left\{ -\varepsilon \psi_B^{(K)1} + \psi_B^{(K)2} \right\} \quad (\varepsilon = +, -)$$

It is hoped that the indices  $\varepsilon$  and  $e$  will not be mixed up.

10.4. Perturbation equation and perturbation energy. Substituting (4.62) into (4.58) and then replacing the single index  $j$  by the triple indices  $(k)$ ,  $e$ ,  $b$ , we have for the first-order perturbation energy of the electrons

$$(10.38) \quad \begin{aligned} \bar{E}_{\text{electrons}} &= 2 S_b^{(k)} \sum_e W^{(k)e} \\ &- 2 S_b^{(k)} \sum_e (\psi_b^{(k)e}(\bar{r})) \cdot \frac{\bar{p}(\bar{r}) - \frac{1}{2} \frac{\partial}{\partial \bar{r}} + \frac{1}{2} \frac{\partial}{\partial \bar{r}} - \frac{1}{2} \frac{\partial}{\partial \bar{r}}}{2} \psi_b^{(k)e}(\bar{r}) \end{aligned}$$

The summation over  $e$  is complete, since we have originally Fock's functions  $\psi_b^{(k)}$  and  $\psi_b^{(k)}$ . (cf. (10.2)).

The first-order perturbation equation will be written in the matrix form, (cf. (4.41), (4.42))

$$(10.39) \quad \underline{\underline{W}} \underline{\underline{U}} - \underline{\underline{U}} \underline{\underline{W}} + \underline{\underline{H}} - \underline{\underline{W}} = 0$$

or, (cf. (4.45)),

$$(10.40) \quad \underline{\underline{W}} \underline{\underline{U}} - \underline{\underline{U}} \underline{\underline{W}} + \underline{\underline{P}} - \frac{1}{2} \underline{\underline{A}} = - \underline{\underline{T}} + \underline{\underline{V}} - \underline{\underline{P}} + \frac{1}{2} \underline{\underline{A}}$$

Because of the degeneracy of the sense of the wave vectors  $\underline{k}$ , the matrix elements  $\int_B^{(k)e} (\delta) e'$  cannot be determined by the first-order perturbation equation. They are to be determined by the second-order perturbation equation. (cf. Born and Jordan (1930) p. 208.). It will be shown in the next section that for the calculation of the perturbation energy of the second order, these matrix elements will not be needed.

The second-order perturbation energy is given, by replacing the index  $j$  of (4.74) by the triple indices

(k), e, b; by

$$(10.41) \quad \bar{E}_{\text{electrons}} = 2 S_b^{(k)} \sum_e \frac{(\bar{V}_+ \bar{V}_+ + (\bar{V}_+ \bar{V}_+) U) \left( \frac{d^2 \rho_e}{d \bar{z}^2} + (\bar{V}_+ \bar{V}_+) \right) + \frac{d^2 \rho_e}{d \bar{z}^2}}{2} \\ + \iint d\bar{z} d\bar{z}' \frac{\bar{V}_-(\bar{z}, \bar{z}')}{2} [\rho(\bar{z}) \rho(\bar{z}') - \frac{1}{2} \rho(\bar{z}, \bar{z}') \rho(\bar{z}', \bar{z})] \\ + \iint d\bar{z} d\bar{z}' \frac{\bar{V}_-(\bar{z}, \bar{z}')}{2} [\rho(\bar{z}') \rho(\bar{z}) - \frac{1}{2} \rho(\bar{z}, \bar{z}') \rho(\bar{z}', \bar{z})]$$

The expansion of  $\bar{V}_-(\bar{z}, \bar{z}')$  has been given above (10.15).

To obtain the potential energy of the lattice, we must add to the above energy of the electrons the energy of the pairs of the ions. The latter is represented by a lattice sum,

$$(10.42) \quad \frac{1}{2} \sum_{ll'} V_{++}(\underline{r}^l - \underline{r}^{l'})$$

where the interaction between an ion at  $\underline{r}^l$  and an ion at  $\underline{r}^{l'}$  depends only on the relative coordinates. Substituting (10.1) into (10.42) and expanding the result by Taylor's series, we obtain the following expansion coefficients of (eq. (10.3)) for

the potential

$$(10.43) \quad \frac{1}{2} S'_{ll'} V_{++}(\underline{r}^l - \underline{r}^{l'}) = \frac{1}{2} S'_{ll'} V_{++}(\underline{a}^l - \underline{a}^{l'}) \\ + S_{\alpha\alpha'} U_{\alpha}^{\alpha} \frac{1}{2} S'_{ll'} (e^{i q_{\alpha}^l \underline{a}^l} - e^{i q_{\alpha}^{l'} \underline{a}^{l'}}) \frac{\partial V_{++}(\underline{a}^l - \underline{a}^{l'})}{\partial (\underline{a}^l - \underline{a}^{l'})_{\alpha}} \\ (10.44) \quad + S_{\alpha\alpha'} U_{\alpha}^{\alpha} U_{\alpha'}^{\alpha'} \frac{1}{2} S'_{ll'} (e^{i q_{\alpha}^l \underline{a}^l} - e^{i q_{\alpha}^{l'} \underline{a}^{l'}}) \frac{\partial^2 V_{++}(\underline{a}^l - \underline{a}^{l'})}{\partial (\underline{a}^l - \underline{a}^{l'})_{\alpha} \partial (\underline{a}^l - \underline{a}^{l'})_{\alpha'}}$$

It will be shown in the next section that the first-order potential energy of the lattice vanishes identically, The second-order potential energy of the lattice then gives the normal frequencies of the metal.

11.1. First-order potential energy of the lattice. It will be shown in this paragraph that the first-order potential energy of the lattice vanishes identically.

The first-order perturbation energy of the electrons is given by (10.38). The first term of (10.38) vanishes by (10.36), for  $\sum_b \langle k|e|b\rangle$  is, by (10.39), simply  $\sum_b \langle k|e|b\rangle \langle b|e|k\rangle$ . The rest of (10.38) vanishes by the selection rule (10.23), for, by hypothesis, the expansion coefficients  $\sum_b A(b)$  and  $\sum_b \rho(b)$  are cyclic quantities of the class  $\eta$ .

The first-order energy of the ions (cf. (10.43)) vanishes as usual. If one of the double summation is evaluated, then the second summation vanishes by (3.16).

11.2. Elimination of the matrix element  $\sum_b \langle k|e'|b\rangle \langle b|e|k\rangle$ . It will be shown in this paragraph that for the calculation of the second-order perturbation energy of the electrons, the matrix element  $\sum_b \langle k|e'|b\rangle \langle b|e|k\rangle$  is not needed. For this, cf. (10.41), we have to show that the matrix element  $\sum_b \langle k|e'|b\rangle \langle b|e|k\rangle$  really disappears in both the quantity  $\sum_b \rho(\vec{k}; \vec{k})$  and the quantity

$$2 \sum_b \langle k|e'|b\rangle \langle b|e|k\rangle + \frac{\sum_b \langle k|e'|b\rangle \langle b|e|k\rangle}{2}$$

Let a matrix  $\underline{U}'$  be defined by the following matrix elements:

$$(11.1) \quad \underline{U}'_{b'}^{(k')e'} \quad \underline{U}_{b'}^{(k)e} = 0$$

$$(11.2) \quad \underline{U}'_{B'}^{(K')e'} \quad \underline{U}_B^{(K)e} = \underline{U}'_{B'}^{(K')e'} \quad \underline{U}_B^{(K)e}$$

where the second part of the definition covers all cases for which the first part of the definition cannot be applied. Then the combination

$$(11.3) \quad \int_b^{(k)} \sum_e \{ (\hat{T} + \hat{V}_+) \underline{U}' + [(\hat{T} + \hat{V}_+) \underline{U}]^\dagger \} \quad \underline{U}_{b'}^{(k)e} \quad \underline{U}_{b'}^{(k)e}$$

can be written in the form

$$(11.4) \quad \int_b^{(k)} \sum_e \{ (\hat{T} + \hat{V}_+) \underline{U}' + [(\hat{T} + \hat{V}_+) \underline{U}]^\dagger \} \quad \underline{U}_{b'}^{(k)e} \quad \underline{U}_{b'}^{(k)e} \\ + \int_b^{(k)} \sum_e \int_{e'}^{(k')} \sum_{e'} \{ (\hat{T} + \hat{V}_+) \quad \underline{U}_{b'}^{(k)e} \quad \underline{U}_{b'}^{(k')e'} \quad \underline{U}_{b'}^{(k')e'} \quad \underline{U}_{b'}^{(k)e} + \underline{U}_{b'}^{(k)e} \quad \underline{U}_{b'}^{(k')e'} \quad \underline{U}_{b'}^{(k')e'} \quad \underline{U}_{b'}^{(k)e} \}$$

Since the summations over  $(k)e$  and  $(k')e'$  are both complete, the indices  $(k)e$  and  $(k')e'$  may be interchanged in the last term of the second line of (11.4). The second line

of (11.4) then vanishes by the normalisation condition

$$\underline{U} + \underline{U}^\dagger = 0, \text{ cf. (4.42).}$$

Similarly, let  $\underline{U}'(\bar{E})$  represent the operator associated with the matrix  $\underline{U}'$ , the quantity  $\beta(\bar{E}; \bar{E}')$  may be written in the form, (cf. (4.61) and (4.69)),

$$(11.5) \quad \beta(\bar{E}; \bar{E}') = 2 \int_b^{(k)} \sum_e \{ \underline{U}'_{b'}^{(k)e} \} \underline{U}'_{b'}^{(k)e} \{ \underline{U}'_{b'}^{(k)e} \}^* + \underline{U}'_{b'}^{(k)e} \underline{U}'_{b'}^{(k)e} \} \\ + 2 \int_b^{(k)} \sum_e \int_{e'}^{(k')} \sum_{e'} \{ \underline{U}'_{b'}^{(k)e} \quad \underline{U}'_{b'}^{(k')e'} \quad \underline{U}'_{b'}^{(k')e'} \quad \underline{U}'_{b'}^{(k)e} + \underline{U}'_{b'}^{(k)e} \quad \underline{U}'_{b'}^{(k')e'} \quad \underline{U}'_{b'}^{(k')e'} \quad \underline{U}'_{b'}^{(k)e} \}$$

Here the last line disappears exactly as above.

## 11.3. First order perturbation equation.

The matrix  $\underline{\underline{U}}'$  introduced above (11.1)(11.2) can be completely determined by the first order perturbation equation

$$(11.6) \quad \underline{\underline{W}}^0 \underline{\underline{U}}' - \underline{\underline{U}}' \underline{\underline{W}}^0 + \underline{\underline{P}}^{(1')} - \frac{1}{2} \underline{\underline{A}}^{(1')} = -\frac{1}{2} \underline{\underline{V}}_+ - \underline{\underline{P}}^{(10)} + \frac{1}{2} \underline{\underline{A}}^{(10)} + \underline{\underline{W}}^1$$

where the dash affixed to the bracketed numeral

emphasize the fact that only the matrix elements of

$\underline{\underline{U}}'$  are contained in the operators  $\underline{\underline{P}}^{(1')}(\bar{\epsilon})$  and  $\underline{\underline{A}}^{(1')}(\bar{\epsilon})$ .

The latter operators involve the quantity  $\underline{\underline{\rho}}^1(\bar{\epsilon}; \bar{\epsilon}')$ ,

but in  $\underline{\underline{\rho}}^1(\bar{\epsilon}; \bar{\epsilon}')$  the matrix element  $\underline{\underline{U}}^{(k)l}(\bar{\epsilon}; \bar{\epsilon}')$  does not appear.

It is convenient to solve the matrix equation

$$(11.6) \text{ with the eigenfunctions } \underline{\underline{\psi}}^0_{\mathcal{B}}(\mathcal{K}) \text{ as the basis.}$$

The index  $\mathcal{L}$  may again be included in the wave vector

$\mathcal{K}$  without the bracket.

Thus, taking the element

of (11.6) with respect to the eigenfunctions

$\underline{\underline{\psi}}^0_{\mathcal{B}}(\mathcal{K})$

and  $\underline{\underline{\psi}}^0_{\mathcal{B}}(\mathcal{K}')$ , we have

$$(11.7) \quad (\underline{\underline{W}}^0_{\mathcal{B}}(\mathcal{K}) - \underline{\underline{W}}^0_{\mathcal{B}}(\mathcal{K}')) \underline{\underline{U}}'_{\mathcal{B}\mathcal{B}}(\mathcal{K}, \mathcal{K}') = -\mathcal{K}'_{\alpha} \mathcal{K}_{\alpha} H_{\mathcal{B}\mathcal{B}}(\mathcal{K}, \mathcal{K}') \quad (\mathcal{K}' \neq \mathcal{K})$$

which shows that the expansion coefficient  $\underline{\underline{U}}'(\bar{\epsilon})$  of the

operator  $\underline{\underline{U}}'(\bar{\epsilon})$  is a cyclic operator of the class

$\mathcal{N}$ .

This result justifies the assumption (10.16).

According to (11.5), (the last line of (11.5) being identically zero), by a change of basis (10.34) we

have for the expansion coefficient  $\rho(\bar{z}, \bar{z}')$ ,

$$(11.8) \quad 2 \int_b^k \left\{ \left[ \int U'(\bar{z}) \psi_b^k(\bar{z}) \right] \psi_b^{k*}(\bar{z}') + \psi_b^k(\bar{z}) \left[ \int U'(\bar{z}') \psi_b^k(\bar{z}') \right]^* \right\}$$

Since  $\int U'(\bar{z})$  is a cyclic operator of the class  $k$ , the function  $\int U'(\bar{z}) \psi_b^k(\bar{z})$  is a cyclic function of the class  $n+k$ . The product  $\int U'(\bar{z}) \psi_b^k(\bar{z}) \psi_b^{k*}(\bar{z}')$  is therefore of the form (10.16). And similarly the second term of (11.8) is also of the form (10.16).

It will be shown later that explicit solution of (11.7) demands much knowledge of the unperturbed eigenfunctions. Nevertheless, some general theorems about the thermal oscillation of the ions can be derived without solving (11.7) in details. I therefore proceed <sup>now</sup> to the second-order potential energy of the lattice.

11.4. Second-order potential energy of the lattice. It has <sup>been</sup> shown above that the matrix element  $\int \psi_b^{k'e'} \psi_b^k$  does not really appear in the expression (10.41) for the second-order perturbation energy of the electrons. Since the summation over the index

$e$  is complete in the first term of (10.41), by a change of basis from the  $\psi_b^{k'e}$  to the  $\psi_b^{ek}$  (cf. (10.34)), we have,

$$(11.9) \quad \begin{aligned} \sum_{\text{electrons}} &= 2 \int_b^k \frac{(\bar{z}_1 \bar{z}_2 + (\bar{z}'_1 \bar{z}'_2) \int U')_{bb}^{kk} + (\bar{z}_1 \bar{z}_2 + (\bar{z}'_1 \bar{z}'_2) \int U')_{bb}^{kk}}{2} \\ &+ \iint d\bar{z} d\bar{z}' \frac{V_{-}(\bar{z}, \bar{z}')}{2} [\rho(\bar{z}) \rho(\bar{z}') - \frac{1}{2} \rho(\bar{z}, \bar{z}') \rho(\bar{z}, \bar{z}')] \\ &+ \iint d\bar{z} d\bar{z}' \frac{V_{+}(\bar{z}, \bar{z}')}{2} [\rho(\bar{z}) \rho(\bar{z}') - \frac{1}{2} \rho(\bar{z}, \bar{z}') \rho(\bar{z}, \bar{z}')] \end{aligned}$$

where the index  $\epsilon$  has been reabsorbed in the wave vector  $k$  without the bracket. Because of the

selection rule (10.28) and because of the fact that  $\nabla U(\vec{r})$  is a cyclic operator of the class  $n$ , the first term of (11.9) becomes a simple sum <sup>over  $n$</sup>  as follows,

$$(11.10) \quad \int_n U_\alpha^n U_{\alpha'}^{-n} 2S_b^k \frac{-\frac{n}{2} \frac{\nabla^2 k k}{\alpha \alpha} + \frac{-n}{2} \frac{V_{+bb} k k}{\alpha \alpha} + \sum_B \frac{\nabla^2 k k}{\alpha \alpha} \frac{-\frac{n}{2} \frac{\nabla^2 k k}{\alpha \alpha} - \frac{n}{2} \frac{V_{+bb} k k}{\alpha \alpha}}{2} U_{bb}^k + \text{conj.}$$

Similarly the rest of (11.9) gives only

$$(11.11) \quad \int_n U_\alpha^n U_{\alpha'}^{-n} \left\{ \iint d\vec{r} d\vec{r}' \frac{-\frac{n}{2} \frac{V_{-}(\vec{E}; \vec{E}')}{\alpha \alpha}}{2} [\rho(\vec{r}) \rho(\vec{r}') - \frac{1}{2} \rho(\vec{r}; \vec{r}') \rho(\vec{r}'; \vec{E})] \right. \\ \left. + \iint d\vec{r} d\vec{r}' \frac{-\frac{n}{2} \frac{V_{-}(\vec{E}; \vec{E}')}{\alpha \alpha}}{2} [\rho(\vec{r}) \rho(\vec{r}') - \frac{1}{2} \rho(\vec{r}; \vec{r}') \rho(\vec{r}'; \vec{E})] \right.$$

by direct integration, with the help of (10.16), (10.17). A simpler procedure is to transform the rest of (11.9) into the following form, (cf. (4.74) - (4.76)),

$$(11.12) \quad 2S_b^{(k)e} \frac{(\overset{2(0)}{P} - \frac{1}{2} \overset{2(0)}{A}) (k)e (k)e}{2} \\ + 2S_b^{(k)e} \left\{ \frac{(\overset{1(0)}{P} - \frac{1}{2} \overset{1(0)}{A}) (k)e (k)e}{2} + \frac{(\overset{1(0)}{P} - \frac{1}{2} \overset{1(0)}{A}) (k)e (k)e}{2} \right.$$

which becomes, exactly as above,

$$(11.13) \quad \int_n U_\alpha^n U_{\alpha'}^{-n} \left\{ 2S_b^k \frac{-\frac{n}{2} \frac{\overset{(0)}{P} k k}{\alpha \alpha} - \frac{1}{2} \frac{-\frac{n}{2} \overset{(0)}{A} k k}{\alpha \alpha}}{2} \right. \\ \left. + 2S_b^k \sum_B \frac{(-\frac{n}{2} \frac{\overset{(0)}{P} k k}{\alpha \alpha} - \frac{1}{2} \frac{-\frac{n}{2} \overset{(0)}{A} k k}{\alpha \alpha}) \nabla U_{bb}^k}{2} + \text{conj.} \right.$$

with  $\overset{(0)}{P}(\vec{r})$  denoting the expansion coefficient of  $\overset{1(0)}{P}(\vec{r})$ , etc.

The results (11.11) and (11.13) are equivalent.

It can be easily verified, furthermore, that the second-order energy of the ions (cf. (10.43)) is also of the form of a simple summation over the thermal waves  $\alpha$ . For, if one summation of the double summation over  $l, l'$  has been evaluated, the second summation may then be evaluated by (3.16). The result is,

$$(11.14) \quad \sum_{\alpha} U_{\alpha}^2 U_{\alpha'}^{-2} = \frac{1}{2} \sum_{ll'} e^{-i\omega^{\alpha} a^l - a^{l'}} - 1 / e^{i\omega^{\alpha} a^l - a^{l'}} - 1 / 2! \frac{\partial^2 V_{ll'}(a^l, a^{l'})}{\partial a^l \partial a^{l'}}_{\alpha}$$

Collecting (11.10), (11.13) and (11.14), we have for the second order potential energy of the lattice

$$(11.15) \quad \Phi^{(2)} = \sum_{\alpha} U_{\alpha}^2 U_{\alpha'}^{-2} \frac{-\hbar^2}{2\alpha} \Phi$$

with

$$(11.16) \quad \frac{-\hbar^2}{2\alpha} \Phi = 2 \sum_b^k \frac{\sum_B (-\hbar^2 T_{bB}^{kB} + \hbar^2 V_{+bB}^{kB} + \hbar^2 P_{bB}^{(0)kB} - \frac{1}{2} \hbar^2 A_{bB}^{(0)kB})}{2} U_B^k + \text{adj.}$$

$$+ 2 \sum_b^k \left\{ \frac{-\hbar^2 T_{bb}^{kk} + \hbar^2 V_{+bb}^{kk}}{2\alpha} + \frac{-\hbar^2 P_{bb}^{(0)kk} - \frac{1}{2} \hbar^2 A_{bb}^{(0)kk}}{2\alpha} \right\} + \frac{1}{2} \sum_{ll'} \frac{-\hbar^2}{2\alpha} V_{ll'}(a^l, a^{l'})$$

where

$$\frac{-\hbar^2}{2\alpha} V_{ll'}(a^l, a^{l'}) = \frac{1}{2!} \frac{\partial^2 V_{ll'}(a^l, a^{l'})}{\partial a^l \partial a^{l'}}_{\alpha}$$

The connection of the expansion coefficients (11.16) of the potential energy of the lattice with the normal frequencies of the metal will be given immediately.

Hamiltonian describing the motion of the ions is, by (3.7), the sum of the kinetic energy of the ions and the potential energy of the lattice. The kinetic energy of the ions is given by

$$(11.17) \quad \sum_l \frac{p_\alpha^l p_\alpha^l}{2M}$$

where the momentum  $p_\alpha^l$  of the  $l$ -th ion is

$$(11.18) \quad p_\alpha^l = M \frac{dr_\alpha^l}{dt}$$

Substituting (3.12) for  $r_\alpha^l$  and evaluating the summation over  $l$  by (3.16), we have for the kinetic energy of the ions,

$$(11.19) \quad \frac{M}{2} N_+ \sum_n \frac{dU_\alpha^n}{dt} \frac{dU_\alpha^n}{dt}$$

The Hamiltonian describing the small motion of the ions is therefore

$$(11.20) \quad \frac{M}{2} N_+ \sum_n \frac{dU_\alpha^n}{dt} \frac{dU_\alpha^n}{dt} + \bar{\Phi} + \sum_n U_\alpha^n U_{\alpha'}^{n'} \frac{-\hbar^2}{\alpha \alpha'} \bar{\Phi}$$

where  $\bar{\Phi}$  denotes the potential energy of the non-vibrating lattice  $\underline{a}^l$ .

Now it is easily verified that the transformation (3.12) may be interpreted as a contact transformation from the "generalised coördinates"  $r_\alpha^l$  to the generalised coördinates  $U_\alpha^n$ , -the generalised momenta

canonically conjugate to the  $U_\alpha^n$  are

$$(11.21) \quad P_\alpha^n = N_+ M \frac{dU_\alpha^{-n}}{dt},$$

being determined from the following condition

$$(11.22) \quad \int_{\mathcal{L}} P_\alpha^n dx_\alpha^n = \int_{\mathcal{L}} P_\alpha^n dU_\alpha^n.$$

The transformed Hamiltonian equations are then,

$$(11.23) \quad \frac{dU_\alpha^n}{dt} = \frac{\partial H}{\partial P_\alpha^n} = \frac{P_\alpha^{-n}}{N_+ M}$$

which is the same as (11.21), and

$$(11.24) \quad -\frac{dP_\alpha^n}{dt} = \frac{\partial H}{\partial U_\alpha^n} = U_{\alpha'}^{-n} \left( \frac{-n}{\alpha \alpha'} \Phi + \frac{n}{\alpha \alpha'} \Phi \right)$$

which gives the equation of motion of the  $U_\alpha^{-n}$ ,

$$(11.25) \quad -N_+ M \frac{d^2 U_\alpha^{-n}}{dt^2} = U_{\alpha'}^{-n} \left( \frac{-n}{\alpha \alpha'} \Phi + \frac{n}{\alpha \alpha'} \Phi \right)$$

Putting

$$(11.26) \quad U_\alpha^{-n} = \hat{U}_\alpha^{-n} e^{i\omega^{-n}t}$$

where  $\hat{U}_\alpha^{-n}$  denotes the amplitude, i.e. the peak value of  $U_\alpha^{-n}$ , and  $\omega^{-n}$ , the normal frequencies, we have, from (11.25), the following secular equation for the determination of the normal frequencies  $\omega^{-n}$ ,

$$(11.27) \quad \begin{vmatrix} \frac{-n}{11} \Phi + \frac{n}{11} \Phi & -(\omega^{-n})^2 & \frac{-n}{12} \Phi + \frac{n}{12} \Phi & \frac{-n}{13} \Phi + \frac{n}{13} \Phi \\ \frac{-n}{21} \Phi + \frac{n}{21} \Phi & & \frac{-n}{22} \Phi + \frac{n}{22} \Phi & \frac{-n}{23} \Phi + \frac{n}{23} \Phi \\ \frac{-n}{31} \Phi + \frac{n}{31} \Phi & & \frac{-n}{32} \Phi + \frac{n}{32} \Phi & \frac{-n}{33} \Phi + \frac{n}{33} \Phi \end{vmatrix} = 0$$

11.6. Small wave vectors. In this paragraph the it is intended to verify the theorem that, three normal frequencies  $\omega^n$  should vanish with vanishingly small wave vectors. The wave vector  $q^n$  will be treated as a small quantity of the first order. If the leading term of a quantity is of the first order in  $q^n$ , the quantity will be referred as to be of the first order and will be denoted by  $\sim O(q^n)$ . Similarly quantities of the second order will be denoted by  $\sim O(q^n q^n)$ .

It follows from (11.16) and (11.27) that the theorem would be verified if the following relations can be verified:

$$(11.28) \quad 2 \int_b^k \frac{-\alpha \alpha' \gamma_{bb} k k + -\alpha \alpha' \gamma_{+bb} k k + \frac{-\alpha \alpha' P_{bb}^{(0)} k k - \frac{1-\alpha \alpha'}{2} A_{bb}^{(0)} k k}{\alpha \alpha'}}{\frac{1}{2} \int_{ll'} (c_{ll'}^2 - \alpha \alpha' d_{ll'}^2) = 1 \chi e^{i g l a_{ll'} - 1} \frac{1}{2} \frac{\partial^2 V_{+}(a_{ll'})}{\partial (a_{ll'}^2) \partial (a_{ll'}^2)_{\alpha}} \sim O(q^n q^n)$$

$$(11.29) \quad \frac{-\alpha \alpha' \gamma_{bb} k K + -\alpha \alpha' \gamma_{+bb} k K + \frac{-\alpha \alpha' P_{bb}^{(0)} k K - \frac{1}{2} \alpha \alpha' A_{bb}^{(0)} k K}{\alpha \alpha'}}{\alpha \alpha'} \sim O(q^n)$$

$$(11.30) \quad \alpha \alpha' \gamma_{bb} k K \sim O(q^n)$$

The proof of (11.29) and (11.28) are similar.

Let us consider (11.29). The left hand side does not vanish only when the superscripts  $\alpha, k, K$  satisfy the selection rule similar to (10.21), and when the selection rule is satisfied, it can be reduced to a volume integral over the domain of the basic polyhedron. The domain of the basic polyhedron

will be denoted by  $\Omega$ , When it is desired to emphasize the limitation of the domain of the spatial coordinates to  $\Omega$ , the corresponding coordinates will be denoted by  $\omega$ . Hence it is to show

$$(11.31) \quad \frac{-\hbar}{\alpha} T(\omega) + \frac{-\hbar}{\alpha} V_+(\omega) + \frac{-\hbar}{\alpha} \overset{(0)}{P}(\omega) - \frac{-\hbar}{\alpha} \overset{(0)}{A}(\omega) \sim O(\eta^2)$$

The operator  $\frac{-\hbar}{\alpha} T(\omega)$  contains, by (10.13), a factor  $\int_{\omega}^{\eta}$ . The operator  $\frac{-\hbar}{\alpha} \overset{(0)}{A}(\omega)$  is defined by

$$(11.32) \quad \begin{aligned} \frac{-\hbar}{\alpha} \overset{(0)}{A}(\omega) u(\bar{r}) &= \int \frac{-\hbar}{\alpha} V_+(\bar{r}, \bar{r}') \rho(\bar{r}, \bar{r}') u(\bar{r}') d\bar{r}' \\ &= \int d\bar{r}' (e^{i\mathbf{q} \cdot \bar{r}} - e^{-i\mathbf{q} \cdot \bar{r}}) \frac{\partial V_-(\bar{r}-\bar{r}')}{\partial(\bar{r}-\bar{r}')_{\alpha}} \rho(\bar{r}, \bar{r}') u(\bar{r}') \end{aligned}$$

The integral converges because the function  $\rho(\bar{r}, \bar{r}')$  decreases very rapidly for increasing  $|\bar{r} - \bar{r}'|$ . For free electrons, for example, we have

$$(11.33) \quad \rho(\bar{r}, \bar{r}') = \frac{2}{N\Omega} \int^k e^{i\mathbf{q} \cdot \bar{r} - \bar{r}'}$$

Where the plane wave functions  $e^{i\mathbf{q} \cdot \bar{r} - \bar{r}'}$  interfere for large  $|\bar{r} - \bar{r}'|$ . (cf. Fig. 13, Brillouin (1934) p. 27.)

Since the integrand of (11.32) vanishes for vanishing  $\int_{\omega}^{\eta}$ , the matrix element  $\frac{-\hbar}{\alpha} \overset{(0)}{A} \frac{k}{B}$  is of the first order in  $\eta^2$ .

The combination  $\frac{-\hbar}{\alpha} V_+(\omega) + \frac{-\hbar}{\alpha} \overset{(0)}{P}(\omega)$  gives a lattice sum and a volume integral,

$$(11.34) \quad \begin{aligned} &\frac{-\hbar}{\alpha} V_+(\omega) + \frac{-\hbar}{\alpha} \overset{(0)}{P}(\omega) \\ &= e^{-i\mathbf{q} \cdot \omega} \left\{ \int_{\omega} (1 - e^{i\mathbf{q} \cdot \omega - \omega'}) \frac{\partial V_+(\omega - \omega')}{\partial(\omega - \omega')_{\alpha}} \right. \\ &\quad \left. + \int d\bar{r}' (1 - e^{i\mathbf{q} \cdot \omega - \bar{r}'}) \frac{\partial V_-(\omega - \bar{r}')}{\partial(\omega - \bar{r}')_{\alpha}} \right\} \end{aligned}$$

The potential  $V_+ (\omega - a^l)$  ( $l \neq 000$ ) due to ions outside the basic polyhedron may be replaced by Coulomb potential, so that (11.35) becomes,

$$(11.36) \quad e^{-ig^4 \omega} \left[ (1 - e^{ig^4 \omega}) \frac{\partial V_+ (\omega)}{\partial \omega} - (1 - e^{ig^4 \omega}) \frac{\partial}{\partial \omega} \frac{e_+ e_-}{|\omega|} \right] \\ + e^{-ig^4 \omega} \left[ \int_{\mathcal{L}} (1 - e^{ig^4 \omega - a^l}) \frac{\partial}{\partial \omega} \frac{e_+ e_-}{|\omega - a^l|} \right. \\ \left. + \int d\vec{r}' (1 - e^{ig^4 \omega - \vec{r}'}) \frac{\partial}{\partial \omega} \left( \frac{e_+ e_-}{|\omega - \vec{r}'|} \right) \cdot \rho(\vec{r}') \right]$$

The last bracket converges for small  $g^4$  because the total charge is neutral, and therefore vanishes with  $g^4$  because of the factor  $(1 - e^{ig^4 \omega - a^l})$  or  $(1 - e^{ig^4 \omega - \vec{r}'})$ . The first line of (11.36) vanishes for vanishing  $g^4$ . Hence (11.29) is proved.

Similarly (11.28) may be proved, for the Coulomb interaction contained in the combination

$$(11.39) \quad 2 S_b^k \left( \frac{-\gamma \gamma}{\alpha \alpha} V_{+ \frac{kk}{bb}} + \frac{-\gamma \gamma}{\alpha \alpha} \frac{\rho_{kk}}{bb} \right) + \frac{1}{2} S_{ll'} \frac{-\gamma \gamma}{\alpha \alpha} V_{++} (a^l; a^{l'}) \\ = \int \frac{-\gamma \gamma}{\alpha \alpha} V_+ (\vec{r}) \rho(\vec{r}) d\vec{r} + \frac{1}{2} \iint \frac{-\gamma \gamma}{\alpha \alpha} V_{++} (\vec{r}; \vec{r}') \rho(\vec{r}) \rho(\vec{r}') d\vec{r} d\vec{r}' \\ + \frac{1}{2} S_{ll'} \frac{-\gamma \gamma}{\alpha \alpha} V_{++} (a^l; a^{l'})$$

converges, and  $\frac{-\gamma \gamma}{\alpha \alpha} V_+ (\vec{r})$ ,  $\frac{-\gamma \gamma}{\alpha \alpha} V_{++} (\vec{r}; \vec{r}')$ , and  $\frac{-\gamma \gamma}{\alpha \alpha} V_{++} (a^l; a^{l'})$  all contain factors of the second order of  $g^4$ .

In proving (11.30), two cases may be distinguished according to whether  $B = b$  or not. When  $B \neq b$ , the first-order perturbation equation

$$(11.40) \quad \left( \frac{0K}{W_B} - \frac{0k}{W_b} \right) \frac{1}{\alpha} \frac{1}{2} U' \frac{Kk}{Bb} + \frac{1}{\alpha} \frac{1}{2} P \frac{Kk}{Bb} - \frac{1}{2} \frac{1}{\alpha} \frac{1}{2} A \frac{Kk}{Bb} \\ = - \frac{1}{\alpha} \frac{1}{2} T \frac{Kk}{Bb} - \frac{1}{\alpha} \frac{1}{2} V \frac{Kk}{Bb} - \frac{1}{\alpha} \frac{1}{2} P \frac{Kk}{Bb} + \frac{1}{2} \frac{1}{\alpha} \frac{1}{2} A \frac{Kk}{Bb}$$

can be used to show (11.30). Since the right hand side of (11.40) has been shown to be of the first order in  $g^{\frac{1}{2}}$ , and the coefficient  $\frac{0K}{W_B} - \frac{0k}{W_b}$  ( $K = k + \alpha$ ) is finite for vanishing  $g^{\frac{1}{2}}$ , it follows that

$$(11.41) \quad \frac{1}{\alpha} \frac{1}{2} U' \frac{Kk}{Bb} \sim O(g^{\frac{1}{2}})$$

provided that

$$(11.42) \quad \frac{1}{\alpha} \frac{1}{2} P \frac{Kk}{Bb} - \frac{1}{2} \frac{1}{\alpha} \frac{1}{2} A \frac{Kk}{Bb} \sim O(g^{\frac{1}{2}})$$

The quantity  $\frac{1}{\alpha} \frac{1}{2} P^{(1)}(\bar{z})$ , being the coefficient of  $U^{\frac{1}{2}}$  in  $P^{(1)}(\bar{z})$ , is

$$(11.43) \quad \frac{1}{\alpha} \frac{1}{2} P^{(1)}(\bar{z}) = \int d\bar{z}' \frac{V_-(\bar{z}-\bar{z}')}{\alpha} \frac{1}{2} p(\bar{z}')$$

where  $\frac{1}{2} p(\bar{z}')$  is a cyclic function of the class  $u$ .

Let  $\frac{1}{2} p(\bar{z}')$  be expanded into the Fourier series

$$(11.44) \quad \frac{1}{2} p(\bar{z}') = e^{i g^{\frac{1}{2}} \bar{z}'} \sum_h \frac{1}{\alpha} p^h e^{2\pi i b^h \bar{z}'} \\ (b^h = b_1 + h_2 b_2 + h_3 b_3)$$

then, by the formula\*

$$(11.45) \quad \int \frac{e^{i g^{\frac{1}{2}} \bar{z}'}}{|\bar{z}-\bar{z}'|} d\bar{z}' = \frac{4\pi}{(g^{\frac{1}{2}})^2} e^{i g^{\frac{1}{2}} \bar{z}}$$

(11.43) becomes

$$(11.46) \quad \frac{1}{\alpha} \frac{1}{2} P^{(1)}(\bar{z}) = e^{i g^{\frac{1}{2}} \bar{z}} \sum_h \frac{\frac{1}{\alpha} p^h \cdot 4\pi e^2}{12\pi b^h g^{\frac{1}{2}} |^2} e^{2\pi i b^h \bar{z}}$$

\* Cf. Mott and Massey (1935), Atomic Collisions, p.161

Hence, in order that  $\alpha^2 P^{(1)}(z)$  may be of the first order in  $g^\alpha$ , it is necessary that

(11.47) for  $h=000$ ,  $\alpha^2 \rho^h \sim (g^\alpha)^2 O(g^\alpha)$  and that

(11.48) for  $h \neq 000$ ,  $\alpha^2 \rho^h \sim O(g^\alpha)$ .

The latter is satisfied as a consequence of (11.41).

The former may be shown as follows.

Consider the first-order perturbation equation (11.40) with  $B = b$ . The coefficient of  $\alpha U'_{bb} K^k$ , namely the difference of  $\dot{W}^k_B$  and  $\dot{W}^k_b$  is, in general, of the first order in  $g^\alpha$ . The right hand side of (11.40) is also of the first order. It does not follow, however, that  $\alpha U'_{bb} K^k$  is of the zeroth-order in  $g^\alpha$ , which is in fact wrong.

Using (11.46) for  $\alpha^2 P^{(1)}(z)$ , and (10.13) for  $\mathcal{P}^k_b(z)$ , we have

(11.49) 
$$\alpha^2 P^{(1)}_{bb} K^k = \frac{1}{N_+} \int u_b^{R^*}(\bar{z}) \sum_h \frac{\alpha^2 \rho^h \cdot 4\pi e^2}{(2\pi b^h + g^\alpha)^2} e^{2\pi i b^h \bar{z}} u_b^k(\bar{z}) d\bar{z}$$

The term ( $h=000$ )

(11.50) 
$$\frac{1}{N_+} \int u_b^{R^*}(\bar{z}) u_b^k(\bar{z}) d\bar{z} \frac{\alpha^2 \rho^h \cdot 4\pi e^2}{(g^\alpha)^2} \quad (h=000)$$

approaches  $\frac{\alpha^2 \rho^h \cdot 4\pi e^2}{(g^\alpha)^2}$  ( $h=000$ ) for small  $g^\alpha$  for the integral  $\frac{1}{N_+} \int u_b^{R^*}(\bar{z}) u_b^k(\bar{z}) d\bar{z}$  approaches unity by normalisation, noting that  $K = k + n$ .

This shows that the first-order perturbation equation (11.40) cannot be used to solve for  $\alpha^2 U'_{bb} K^k$ , but it can be used to solve for  $\alpha^2 \rho^h (h=000)$ . Dividing

the whole equation (11.40) in the case  $B=b$  by the large coefficient of  ${}^2\rho^k(k=000)$ , we have

$$(11.51) \quad {}^2\rho^k(k=000) = \frac{1}{N_+} \frac{1}{\int dr u_b^{k*}(r) u_b^k(r)} \frac{1}{4\pi c^2} \left[ -2T_{bb}^k - 2V_{bb}^k - 2P_{bb}^{(0)k} + \frac{1}{2} 2A_{bb}^k - (W_B^k - W_b^k) {}^2U_{bb}^k + \frac{1}{2} {}^2A_{bb}^k - \sum_{k \neq 000} \frac{{}^2\rho^k 4\pi c^2}{4\pi r^2} \frac{dr u_b^{k*}(r) e^{2i\omega t} u_b^k(r)}{N_+} \right]$$

which proves (11.47). This completes the proof for (11.30) with the exception of  ${}^2U_{bb}^k$ .

The element  ${}^2U_{bb}^k$  cannot be determined from the first-order perturbation equation, but it is probably of the second order in the  $\gamma_\alpha^k$ , by the following consideration.

From the definition of  ${}^2\rho^k(z)$ , the coefficient of  $z^k$  in  $\tilde{f}(z)$ , we have

$$(11.52) \quad \begin{aligned} {}^2\rho^k(z) &= 2S_b^k \psi_b^{k*}(z) \left\{ {}^2U_{bb}^k \psi_b^k(z) \right\} + \text{conjugate} \\ &= 2S_b^k \left\{ \psi_b^{k*}(z) \psi_b^k(z) {}^2U_{bb}^k + \text{conj.} \right\} \\ &+ 2S_b^k \sum_{B \neq b} \left\{ \psi_b^{k*}(z) \psi_B^k(z) {}^2U_{Bb}^k + \text{conj.} \right\} \end{aligned}$$

From this, and from (11.44), we obtain for  ${}^2\rho^k(k=000)$ ,

$$(11.53) \quad \begin{aligned} {}^2\rho^k(k=000) &= 2S_b^k \frac{1}{N_+ \Omega} \int dr \psi_b^{k*}(z) \psi_b^k(z) e^{-i\omega t} {}^2U_{bb}^k \\ &+ \text{conj.} \\ &+ 2S_b^k \sum_{B \neq b} \frac{1}{N_+ \Omega} \int dr \psi_b^{k*}(z) \psi_B^k(z) e^{-i\omega t} {}^2U_{Bb}^k \\ &+ \text{conj.} \end{aligned}$$

For small  $\gamma_\alpha^k$ , the leading term of the right hand side of (11.53) is

$$(11.54) \quad \frac{2}{N+2} \int_b^k \sum_{\alpha} U'_{bb}{}^k + \text{conj.}$$

while the left hand side of (11.53) has been shown to be of the third order in  $\delta_{\alpha}^k$ . Since, by definition (11.1),  $\sum_{\alpha} U'_{bb}{}^k$  vanishes if  $K = k + \alpha$  is in the domain of  $k$ , the range of summation  $\int_b^k$  of (11.54) is of the first order in  $\delta_{\alpha}^k$ . Hence  $\sum_{\alpha} U'_{bb}{}^k$  is of the second order in  $\delta_{\alpha}^k$ .

That the element  $\sum_{\alpha} U'_{bb}{}^k$  is of higher order in  $\delta_{\alpha}^k$  shows that in the limiting case of homogeneous deformation,  $U_{bb}^k$  vanishes while  $U_{Bb}^k$  ( $B \neq b$ ) remains to be finite.

By using the symmetry character of the functions  $u_B^K$  ( $K = 000$ ) with respect to the central reflexion (cf. §6.1.), it can be shown that  $\sum_{\alpha} U'_{Bb}{}^k$  for small  $\delta_{\alpha}^k$  and with  $k = 000$  is of the first or second order in  $\delta_{\alpha}^k$  according to whether  $u_B$  and  $u_b$  are of the same or opposite symmetry character. In the limiting case of homogeneous deformation, this becomes the selection rule for central symmetry of §6.1.

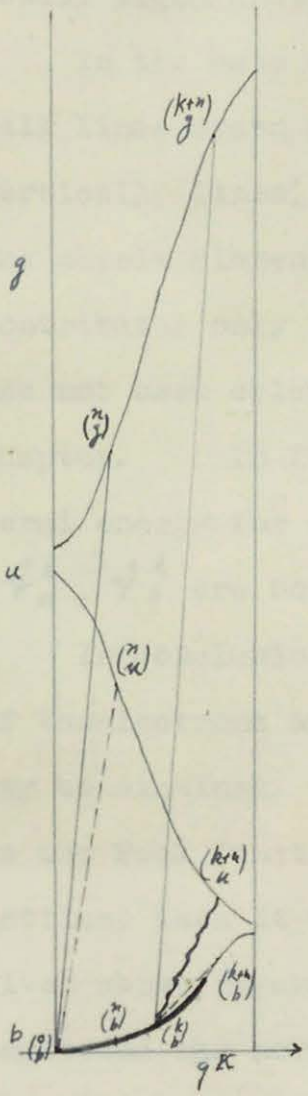
11.7. Concluding remarks. I have not carried out the actual calculation of the normal frequencies for any metal. An indication of what eigenfunctions of the unperturbed eigenvalue problem are needed for this calculation for alkali metals together with a comparison with the calculation of the elastic constants given in the last chapter will conclude this thesis.

It is convenient to plot the unperturbed eigenvalues  $\frac{W^0}{B}$  with respect to the wave vector  $f^K$ , the direction of which may be assumed as given. Since the number of atoms in a crystal is large, the wave vector  $f^K$  assumes almost continuous values. For a given  $B$ , the eigenvalues for various  $K$  may be represented by a smooth curve. For different  $B$ , we have different branches or "bands". Three bands are drawn in the diagram on the next page.

For alkali metals, the parameters  $\frac{W^0}{B}$  of the Fock functions occupy the lower half of the "valence band", the heavy portion of the lowest curve drawn on the next page. The bands having eigenvalues lower than the Fock parameters for the metallic electron are not drawn; -- the corresponding eigenfunctions and eigenvalues correspond to the Fock functions and the Fock parameters for the core electrons of an isolated atom. As shown in the calculation of the elastic constants, the final result of the perturbation energy may be expressed by surface integrals, to which the eigenfunctions of these lower bands contribute little. A similar transformation to surface integrals can be made in the calculation of the perturbation energy due to the thermal displacements of the ions, and therefore these lower bands need not be considered.

Based on the free electron approximation, three

bands,  $b, u, g$  are drawn in the accompanying diagram. For  $k = 000$ , the eigenfunctions  $\psi_b^0$  and  $\psi_g^0$  are even with respect to the central reflexion, while  $\psi_u^0$  is odd. The full line drawn from the point  $(b^0)$  to the



point  $(g^n)$  indicates that the corresponding matrix element  ${}^n U_{g^0 b}^n$  is of the first order in  $g^n$ . The dash-line drawn from the point  $(b^0)$  to the point  $(u^n)$  indicates that  ${}^n U_{u^0 b}^n$  is of the second order in  $g^n$ . No line is drawn from the point  $(b^0)$  to the point  $(b^n)$ , for  ${}^n U_{b^0 b}^n$  vanishes by (11.1), if the point  $(b^n)$  belongs to the heavy portion of the curve  $b$ .

Similar lines are drawn from the point  $(b^k)$ . The full line to the point  $(g^{k+n})$  still represents that  ${}^n U_{g^k b^k}^n$  is of the first order in  $g^n$ , but the undulating line from  $(b^k)$  to  $(u^{k+n})$  indicates that special investigation on  ${}^n U_{u^k b^k}^n$  is needed in view of the small difference  $W_{u^k}^{k+n} - W_{b^k}^k$ ,

as may be seen from the diagram. The dash-line from the point  $(b^k)$  to the point  $(b^{k+n})$ , which is not on the heavy portion of the curve, indicates that  ${}^n U_{b^k b^k}^n$  is of the second order in  $g^n$ .

For an actual calculation of the perturbation energy for not too small wave vectors, it seems that the quantities  $\frac{\partial U}{\partial u}^0$ ,  $\frac{\partial U}{\partial b}^k$  cannot be neglected. Since the difference of  $W_u^0$  and  $W_b^0$  is not very large, the actual eigenfunctions  $\psi_u^0$ ,  $\psi_b^0$  are needed.

In the case of homogeneous deformation, all the full lines drawn on the last page are to be replaced by vertical lines; the dash-lines are to be rubbed out. The matrix element  $U_{ab}^k$  (cf. the undulating line), contributes only to the Fermi energy, which, however, has not been calculated accurately enough in the last chapter. In fact, for an accurate calculation of the Fermi energy for a deformed lattice, the eigenfunctions  $\psi_a^k$ ,  $\psi_b^k$  are both desirable.

In conclusion, the assumption of treating the motion of the electrons and the motion of the ions separately may be examined. If the time factors  $e^{-\frac{i}{\hbar} W_b^k t}$  are added to the Fock functions of the electrons in the non-vibrating lattice, then it is easily seen that in the treatment given above regarding the  $U_\alpha^k$  as constants, I have neglected the normal frequencies  $\omega^k$  of the thermal oscillation of the ions in comparison with the  $W_b^k / \hbar$ . The  $W_b^k$  are of the order of a few electron volts while the  $\hbar \omega^k$  are of the order of a few hundreds of an electron volt. The error thus introduced may be neglected.

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