# Iteration-Perturbation Theory of Covalent Bonding in Crystals *

## I. General Considerations

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An iteration-perturbation approach is suggested which enables the calculation of the binding energy and equilibrium lattice parameters of non-metallic crystals. Making use of the single-band-gap model, the selfconsistent Schrödinger equation can be solved in terms of the effective matrix elements, $W(g)$'s, which, in general, satisfy the set of nonlinear equations. The latter are solved for those reciprocal lattice vectors $g$ for which the perturbation theory requirements are violated. Since the matrix elements of ion-electron interaction are not small for some $g$'s the screening of all the interactions in the crystal is not linear. The exchange-correlation contributions both in the screening and in the total energy are accounted for by means of the Kohn-Sham density-functional-formalism. A charge transfer is shown to result in excluding part of the electrons from the screening processes. The theory allows also for the possibility of a strongly non-homogeneous electron density distribution in the crystal.

The results of the calculation for magnesium hydride $MgH_2$ are presented in paper II.

## 1. Introduction

The concept of "covalency" comes from chemistry and means first of all directedness of inter-atomic bonds. In a crystal it acquires the negative meaning of "non-metallicity". An illuminating approach to crystal covalency has been developed within the framework of the pseudopotential theory, or, to be more exact, its generalization. From the point of view of this theory "metallicity" means central and pairwise interatomic interaction, additivity of spherical pseudoatoms, etc., that is those features which follow from the perturbation theory in pseudopotentials if restricted to second-order terms. On the other hand, multi-ion interactions (corresponding to higher order perturbation theory) are responsible for the covalency effects. The problem of covalent bonding probably first arose in the pseudopotential theory when attempts were made to describe the electronic and atomic properties of elemental and compound semiconductors. We shall not focus on a discussion of the numerous works concerning crystal covalency. As a whole, the problem has been comprehensively discussed by Heine and Weaire [1]. For more details cf. the review papers and books [2—5].

It is important, that the covalency as a physical phenomenon is connected with a rather strong non-homogeneity of electron density distribution in a crystal. The non-homogeneity is especially strong in a semiconducting or an insulating crystal when the Jones zone (JZ) exists with Fermi surface vanishing on its boundaries. In these cases only the states inside the zone are occupied and the compensation of the contributions of "bonding" and "antibonding" states, characteristic of metallic behaviour, does not happen. The standing waves of electronic density arise as a result of electron Bragg scattering on the JZ faces. From a microscopic point of view, the electron distribution non-homogeneity results as well in nonlinear screening of all the interactions in the crystal. Phillips' "bonding charges" (see, e.g. [4]) are just the manifestations of the latter. On the other hand, the electron non-homogeneity of course originates from the peculiarity of the ion-electron interaction. For example, the charge transfer resulting in the bonding charge formation in Si would be impossible, were not the electrons strongly attracted just into that area between two Si-ions. In the diamond structure the $W(111)$ pseudopotential matrix element is responsible for such an attraction (see, e.g. [1]). The existence of at least one "strong" pseudopotential matrix element is a typical feature of a covalent crystal. From the point of view of the pseudopotential theory the reason is rather clear: covalent crystals have as a rule complex crystal

lattices with more than one atom per primitive cell. The volume of the latter is larger, while on the other hand, the volume of the corresponding Brillouin zone (BZ) is less than those for metallic crystals. As a result, the smallest reciprocal lattice vectors $g$ happen to lie in the wave number region to the left of the first pseudopotential formfactor node (for the simplicity we restrict ourselves to local pseudopotentials only), where the pseudopotential matrix elements $W(g)$ are not small in the sense that

$$W(\tilde{g})/\varepsilon_F \ll 1 \qquad (1)$$

($\varepsilon_F$ is the free electron Fermi energy) does not hold, and the simple second-order perturbation theory breaks down. The same situation arises in alloys, when a crystal undergoes an order-disorder transformation. Below the phase transition temperature an ordered phase appears with the smallest superstructure wave vector being situated just in the region, where (1) does not hold (see, e.g. [6—9]).

Fortunately, sometimes $W(g)$'s (say $W(111)$ in the diamond lattice) happen to be in the second order of perturbation, comparable to the other $W(g)$'s in first order, i.e.

$$\left| \frac{W(\tilde{g})}{\varepsilon_F} \right|^2 \cong \frac{W(g)}{\varepsilon_F} . \qquad (2)$$

The latter means that in order to account for the $W(g)$ contributions one has to go beyond the second order of the perturbation theory and incorporate the corresponding contributions of the third and fourth orders. For the diamond-type lattices the latter results in obtaining the correct values of both the band gaps at point X of the Brillouin zone [10]

$$\text{Gap} = 2W(220) + 2\frac{|W(111)|^2}{\frac{1}{2}(110)^2 - \frac{1}{2}(001)^2} ,$$

and the binding energies and relative structure stability (e.g. [7, 11]). However, the fortunate relation (2) is, perhaps, an accidental one in the sense, that there exist crystals in which it does not hold and the approach of the perturbation theory obviously fails.

An example are, perhaps, metal hydrides. The "bare" potential of a hydrogen ion in a crystal has to be purely coulombic with no "pseudising" and is therefore "strong" from the pseudopotential point of view. The calculations of binding energies of hypothetic metallic hydrogen crystals have

shown the necessity of accounting for higher order perturbation theory contributions. But the incorporating of only the third order ones does not seem to be sufficient in comparing the relative crystal stability (see, e.g. [12]). Hydrogen ions in compounds like metal hydrides also have to contribute appreciably to the total crystal potential (or pseudopotential), resulting in a violation of both the conditions (1) and (2).

In such a situation, the question arises: If one has to apply higher order perturbation theory is perturbation theory still valid at all? This sceptical question is not entirely unreasonable. In principle, the systems with strong electron-ion interaction are already within the realm of tightbinding methods like LCAO. In the present work, however, the attempt is made to develop an approach which may be called an iteration-perturbation one, and which would enable to consider crystals with strong ion-electron interactions (of course, there must not be too many "strong" pseudopotential matrix elements). In paper II the calculation of binding energy and equilibrium lattice parameters of magnesium hydride will be performed within the framework of this approach.

The plan of the present paper is as follows: Section 2 considers a formal solution of the Schrödinger equation for a perfect crystal and presents the basic nonlinear equations for an effective matrix element $W(g)$. In Sect. 3 the single-band-model is introduced and the energy gaps are determined. Section 4 deals with the selfconsistency and nonlinear screening. The expressions for the electron density and its Fourier-transform are obtained and the Hartree screening field is discussed. Section 5 considers the exchange-correlation contribution to the screening field and the total energy using the Kohn-Sham density-functional formalism (DFF). Section 6 describes the procedure of the selfconsistent calculations of the potential matrix elements and the total energy. In Sect. 7 the important functions of the theory are determined. Section 8 — concluding remarks. In App. 1 and 2 a mathematical approximation and the evaluation of some integrals are presented.

## 2. A Formal Solution of the Schrödinger Equation

We shall consider a perfect crystal with a translational periodicity in which an electron at a point

$r$ "feels" the field:

$$W(r) = \sum_{\{R\}} w(r - R). \qquad (3)$$

Here $\{R\}$ is the set of Bravais lattice vectors, but the crystal under consideration may have more than one atom per unit cell, $w(r - R)$ being the potential of the unit cell "belonging" to the Bravais lattice site $R$.

The Schrödinger equation for an electron in the crystal reads:

$$(-\tfrac{1}{2}\Delta + W(r))\,\psi_k(r) = E_k\,\psi_k(r). \qquad (4)$$

Here $\psi_k(r)$ and $E_k$ are respectively the wave (or pseudowave) functions * and energies corresponding to a wave vector quantum number $k$**. We will be using the extended zone scheme; then $k$ may take all the quasicontinuum values allowed by periodic boundary conditions: the "cyclic" crystal has the total volume $\Omega = \Omega_0 N$, where $\Omega_0$ is the volume of the unit cell and $N$ is the number of unit cells in the crystal. At absolute zero temperature, of course, only the lowest energy states are occupied; corresponding $k$'s filling the volume enclosed by a Fermi surface (FS) (which is not supposed to be spherical) or a JZ.

Now, let $W(r)$ be a selfconsistent potential (or pseudopotential). Then

$$W(r) = W^0(r) + W^{\mathrm{scr}}(r), \qquad (5)$$

where $W^0(r)$ is the "bare" potential of the crystal and $W^{\mathrm{scr}}(r)$ is the screening potential including both the direct coulombic and exchange-correlation contribution. According to the Kohn-Sham density-functional formalism (DFF) [13], $W^{\mathrm{scr}}(r)$ is a function of the (selfconsistent) electron density (or pseudo-density) distribution

$$\varrho(r) = \sum_k |\psi_k(r)|^2. \qquad (6)$$

Here, as everywhere throughout the paper $\sum_k$ means the summation over all the occupied electron states within the true FS or JZ, including the spin factor 2.

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* Throughout the paper we will be using the terms "wave function", "electron density", "potential", rather than "pseudowave function", "pseudodensity", "pseudopotential", since the theory is, in principle, applicable also when there is no "pseudizing" of ions.

** We use the atomic units throughout.

It is easy to write the formal solution of the Schrödinger equation (4). It reads (see, e.g. [14])

$$E_k - E_k^0 = \sideset{}{'}\sum_g a_k(g)\,W^*(g), \qquad (7\,\mathrm{a})$$

$$\psi_k(r) = |k\rangle + \sideset{}{'}\sum_g a_k(g)\,|g - k\rangle. \qquad (7\,\mathrm{b})$$

$$(E_k - E_{g-k}^0)\,a_k(g)$$
$$= W(g) + \sideset{}{'}\sum_{g' \neq g} a_k(g')\,W^*(g - g'). \qquad (7\,\mathrm{c})$$

Here $|k\rangle = (1/\Omega^{1/2})\exp(i\,k\,r)$ is the plane wave, $E_k^0 = \tfrac{1}{2}k^2$ is the free electron energy and

$$W(g) \equiv \langle k + g\,|\,W(r)\,|\,k\rangle$$
$$= \int_\Omega \mathrm{d}^3r\, W(r)\,\mathrm{e}^{i g r} \qquad (8)$$

is the matrix element of the potential. Since we restrict ourselves to local potentials, the matrix element is simply the Fourier transform of the potential. The summation is performed over the lattice sites $g$, $g'$ of the reciprocal lattice corresponding to the Bravais lattice $\{R\}$. The zero of energy is chosen to be equal to be $\langle k\,|\,W(r)\,|\,k\rangle = W(g = 0)$. Let us introduce

$$\tilde{W}_k(g) = (E_k - E_{g-k}^0)\,a_k(g).$$

Then (7) take on a more symmetric and, in a sense, more familiar form:

$$E_k - E_k^0 = \sideset{}{'}\sum_g \frac{\tilde{W}_k(g)\,W^*(g)}{E_k - E_{g-k}^0}, \qquad (9\,\mathrm{a})$$

$$\psi_k(r) = |k\rangle + \sideset{}{'}\sum_g \frac{\tilde{W}_k(g)}{E_k - E_{g-k}^0}\,|g - k\rangle, \qquad (9\,\mathrm{b})$$

$$\tilde{W}_k(g) = W(g) + \sideset{}{'}\sum_{g' \neq g} \frac{\tilde{W}_k(g')\,W^*(g - g')}{E_k - E_{g'-k}^0}. \qquad (9\,\mathrm{c})$$

Now both, the energy $E_k$ and the wave function $\psi_k(r)$, are expressed by means of an "effective matrix element" $\tilde{W}_k(g)$, which satisfies (9c). At the same time, the three Eqs. (9) are coupled, since in the denominators the total energy $E_k$ enters, and both $W$ and $\tilde{W}$ depend on electron density distribution, $\varrho(r)$ (see (6)), through the screening potential.

Equations (9) are still precise: no approximation has been introduced until now. (9) could also be obtained within the so-called "Modified Iteration-Perturbation Approach" (see (9.1.89), (9.1.90) [15]). One has only to introduce additionally:

$$\bar{W}_k(g) = W(g) + \sum_{g' \neq g}' \frac{W(g')\,W^*(g-g')}{E_k - E_{g-k}^0} + \sum_{\substack{g' \neq g,\, g'' \\ g'' \neq g,\, g'}} \frac{W(g'')\,W(g''-g')\,W^*(g'-g)}{(E_k - E_{g''-k}^0)(E_k - E_{g'-k}^0)}$$

$$+ \sum_{\substack{g' \neq g,\, g'' \\ g'' \neq g',\, g''' \\ g''' \neq g'',\, g}} \frac{W(g''')\,W(g'''-g'')\,W(g''-g')\,W^*(g'-g)}{(E_k - E_{g'''-k}^0)(E_k - E_{g''-k}^0)(E_k - E_{g'-k}^0)}, \tag{10}$$

and then, by "summing up" the infinite series to obtain (9c). Note, that by substituting (10) into (9a, b) one arrives at the infinite series which differs from the traditional Brillouin-Wigner perturbation series (see, e.g. [16], Chapt. 3), in that now the zero of $E_k$ is taken to be equal to the diagonal matrix element, $W(g=0)$, and all the diagonal matrix elements are excluded from the series.

Now, if one neglects the sum on the right-hand side of eq. (9c) and puts $E_k = E_k^0$ in the denominators, one immediately gets the familiar second-order perturbation theory expression for $E_k$ and the first order one for $\psi_k(r)$.

One can also solve (9c) by iterations. After the first iteration, again putting $E_k = E_k^0$ (which is equivalent to keeping the terms of only second order in $W$), one has

$$\bar{W}_k(g) = W(g) + \sum_{g' \neq g}' \frac{W(g)\,W^*(g-g')}{E_k^0 - E_{g'-k}^0}. $$

This expression was first used by Pryce [17] and is usually obtained by systematically diagonalizing the full Hamiltonian matrix $H(g, g')$. Within such an approach, (10) was used for explaining the band structure in semiconductors [10]; we cited in the Introduction the expression for the energy gap from this work).

If, however, there are some "strong" matrix elements $W$, the simple iteration approach may happen to be unsatisfactory. We wish instead to introduce a different approximation.

First of all we want to get rid of the $k$-dependence in $\bar{W}_k(g)$. In [10] and other works on semiconductors the latter is achieved by just assuming $k$ to be the center of the JZ face, corresponding to the vector $g$. Since we are interested in calculating the total energy, i.e. the contribution of all the $k$-states, it is perhaps more reasonable to average $\bar{W}_k(g)$ over all the occupied states. To be more exact, we want to substitute a $k$-independent $\bar{W}(g)$ for $\bar{W}_k(g)$ with the requirement that

$$\bar{W}(g) = W(g) + \sum_{g' \neq g}' \bar{W}(g')\,W^*(g-g')\,F(g'), \tag{11}$$

where $\tag{12}$

$$F(g') = \left\langle \frac{1}{E_k - E_{g'-k}^0} \right\rangle_{\mathrm{av}} = \frac{1}{ZN} \sum_k \frac{1}{E_k - E_{g'-k}^0}. $$

($Z$ is the total number of electrons per unit cell.)

One sees that the approximation (11) includes not only the averaging of $\bar{W}_k(g)$ but also "decoupling" another average in the sum.

We shall also need the average:

$$\Phi(g'', g') = \left\langle \frac{1}{(E_k - E_{g''-k}^0)(E_k - E_{g'-k}^0)} \right\rangle_{\mathrm{av}} \tag{13}$$

$$= \frac{1}{ZN} \sum_k \frac{1}{(E_k - E_{g''-k}^0)(E_k - E_{g'-k}^0)}. $$

As will be shown in Sect. 7 and App. 2, we can evaluate the averages, (12) (13), and we will be using (13) in calculating the normalization constant and the electron density distribution.

Now, together with (11) for $\bar{W}(g)$ we have

$$E_k - E_k^0 = \sum_g' \frac{\bar{W}(g)\,W^*(g)}{E_k - E_{g-k}^0}, \tag{14}$$

$$\psi_k(r) = |k\rangle + \sum_g' \frac{\bar{W}(g)}{E_k - E_{g-k}^0}\,|g - k\rangle. \tag{15}$$

## 3. Evaluation of Energy

Even if (11) for $\bar{W}(g)$ has been solved, one still faces the nonlinear equations (14) and (15). Let us first consider (14).

In order to determine the energy $E_k$ we shall make use of the so-called "Single Band-Gap Model". Near a Brillouin zone face, corresponding to a reciprocal lattice vector $g$, (14) approximately reads:

$$(E_k - E_k^0)(E_k - E_{g-k}^0) = V^2(g). \tag{16}$$

The solution is very well known:

$$E_k^{\pm} = \tfrac{1}{2}\{E_k^0 + E_{g-k}^0 \tag{17}$$
$$\pm [(E_k^0 - E_{g-k}^0)^2 + 4\,|\,V(g)\,|^2]^{1/2}\},$$

$(+)$ and $(-)$ corresponding to the energy states respectively above and below the Bragg plane, $2\,|\,V(g)\,|$ being the energy gap.

From a first glance at (15a) it may seem that

$$V^2(g) = \tilde{W}(g) W^*(g).$$

However, this would be rather a poor approximation. In semiconductors with diamond-type lattices it would result in wrong values of the energy gaps at X, because the corresponding $W(g)$'s are extremely small.

$$V_k(g)^2 = \tilde{W}_k(g) \left\{ W^*(g) + \sum_{g' \neq g} \frac{W(g') W^*(g-g')}{E_k - E^0_{g'-k}} + \sum_{\substack{g' \neq g'', g \\ g'' \neq g', g}} \frac{W(g'') W^*(g''-g) W^*(g'-g)}{(E_k - E^0_{g''-k})(E_k - E^0_{g'-k})} \right.$$
$$\left. + \sum_{\substack{g' \neq g'', g''', g \\ g'' \neq g', g''', g \\ g''' \neq g', g'', g}} \frac{W(g''') W(g'''-g'') W^*(g''-g') W^*(g'-g)}{(E_k - E^0_{g'''-k})(E_k - E^0_{g''-k})(E_k - E^0_{g'-k})} + \cdots \right\}. \tag{18}$$

Comparing the series (18) with (10), the one that can be generated by iterating (9c), one sees that the terms in the latter may, in principle, have two or more equal energy differences in denominators, e.g., $(E_k - E^0_{g'-k})^2$, while in the former they may not. The first discrepancy arises in the fourth-order term and has the form

$$\sum_{\substack{g' \neq g, g'' \\ g'' \neq g, g'}} \frac{W(g') |W(g'-g)|^2 W(g''-g)}{(E_k - E^0_{g'-k})^2 (E_k - E^0_{g''-k})}.$$

One may hope that contributions of this kind are not likely to be important for the electron spectrum near the $g$-Bragg plane, since the repeating energy differences are not small. Thus, if we add these contributions, we get

$$V_k(g)^2 = \tilde{W}_k(g) \tilde{W}^*_k(g),$$

and, after the averaging,

$$V(g) = \tilde{W}(g). \tag{19}$$

This is again the result familiar from the theory of semiconductors. Within the second order of the perturbation theory it is precise since, as we have seen, the first discrepancy is only of fourth-order.

Now that (16) and (17) are well defined

$$(E_k - E^0_k)(E_k - E^0_{g-k}) = |\tilde{W}_g|^2, \tag{16a}$$

$$E^\pm_k = \tfrac{1}{2}\{E^0_k + E^0_{g-k} \tag{17a}$$
$$\pm [(E^0_k - E^0_{g-k})^2 + 4 |\tilde{W}(g)|^2]^{1/2}\},$$

we may specify the procedure of solving the Schrödinger equation in more detail. Our final goal is the calculation of the total energy, $E$, of the

The origin of this mistake is obvious. If we return to (9a) and (9c) we readily see that, for example, for a given $g = g_0$ there is the denominator $E_k - E_{g-k}$ not only in the $g_0$-term in the right-hand side sum of (9a), but also in all the other terms with $g \neq g^0$ resulting from the sum over $g'$ in (9c). To find the real energy gap, $2V(g)$, one has obviously to sum up all these contributions. The sum is easily seen to be:

crystal. Per unit cell:

$$E = E_0 + E_{xc} + Z W(g=0) + E_c - E_{el} - E_{es}. \tag{20}$$

Here $E_0$ is the "free electron" energy,

$$E_0 = \frac{1}{N} \sum_k E^0_k, \tag{20a}$$

$Z$ is the number of electrons per unit cell, the summation extending on all the occupied states within the true FS or JZ, and not the free electron sphere, as in the pseudopotential theory.

$E_{xc}$ is the exchange-correlation energy; we shall be calculating it within the framework of the Kohn-Sham DFF and discuss it later.

$E_c$ is the "covalent" energy,

$$E_c = \frac{1}{N} \sum_k (E_k - E^0_k) \tag{20b}$$

— the energy of electron states including both the band structure energy of pseudopotential theory and multi-ion interaction contributions, corresponding to higher order perturbation theory terms. The "zero" of the energy, $Z W(g=0)$, is written explicitly in (20).

$E_{el}$ is the energy of electron-electron interaction, which is accounted for twice in $E_c$ and must therefore be subtracted:

$$E_{el} = \tfrac{1}{2}\Omega_0 \sum_g' \frac{4\pi}{g^2} |\varrho(g)|^2, \tag{20c}$$

where $\varrho(g)$ is the Fourier-transform of the electron density distribution (6) (see below, (25)—(27)).

$E_{es}$ is the electrostatic energy of the point charge ion lattice immersed into the uniform medium of negative charge. We shall not be discussing this contribution in the present paper; its evaluation is straightforward if one uses the Ewald-Fuchs method (for the extension of the method to binary alloys, see [18]). Using (9a), the expression for $E_c$ (see (20b)) reads:

$$E_c = \sum_{g}' \tilde{W}(g) W^*(g) \frac{1}{N} \sum_{k} \frac{1}{E_k - E^0_{g-k}}$$
$$= Z \sum_{g}' \tilde{W}(g) W^*(g) F(g), \qquad (21)$$

where $E_k$ is the solution of (16a).

## 4. Selfconsistency: Nonlinear Screening

Until now the wave function, (15), has not been normalized. Introducing a normalization constant $C$, we obtain the electron density, (6):

$$\varrho(r) = C^2 \frac{Z}{\Omega_0} \left\{ 1 + 2 Re \sum_{g}' \tilde{W}(g) F(g) e^{igr} \qquad (22) \right.$$
$$\left. + \sum_{g, g'} \tilde{W}(g) \tilde{W}^*(g') \Phi(g, g') e^{i(g-g') \cdot r} \right\}.$$

(The functions $F(g)$ and $\Phi(g, g')$ were defined by (12) and (13). Note that the second sum in (22) includes the term with $g = g'$.) The normalization constant, $C^2$, is obtained from the condition

$$\int_{\Omega} d^3 r \varrho(r) = ZN.$$

Having integrated (22), one immediately gets:

$$C^2 = \left( 1 + \sum_{g}' |\tilde{W}(g)|^2 \Phi(g, g) \right)^{-1}. \qquad (23)$$

If we would restrict ourselves to the first order contributions in $\psi_k(r)$ (and this is the case in the traditional pseudopotential theory), we would have $C^2 = 1$, $\tilde{W}(g) = W(g)$, and the third term in (22) should be omitted. Then we obtain an electron density distribution typical of simple metals. All the higher order contributions could be looked upon as a "covalent charge".

Now, when $C^2 < 1$, we see that the first constant term in (22) is less than an average electron density in the crystal. The second term is of "fluctuating" nature, its average is 0. As for the third term, the one that gives the main covalent contribution, it represents a charge distribution with non-zero average number of electrons per unit cell. This number, $\Delta Z$, equals:

$$\Delta Z = Z C^2 \sum_{g}' |\tilde{W}(g)|^2 \Phi(g, g) = Z(1 - C^2). \qquad (24)$$

Thus we now have a charge transfer, the one that in the diamond lattice results in the arising of "bonding charges". Of course, the total number of electrons stays unchanged, and it is convenient to unite all the constant contributions to the charge distribution to obtain finally:

$$\varrho(r) = \frac{Z}{\Omega_0} \left\{ 1 + C^2 2 Re \sum_{g}' \tilde{W}(g) F(g) e^{igr} \qquad (22a) \right.$$
$$\left. + C^2 \sum_{\substack{g, g' \\ (g \neq g')}}' \tilde{W}(g) \tilde{W}^*_{(g')} \Phi(g, g') e^{i(g-g') \cdot r} \right\}.$$

The expression for $\varrho(g)$, the Fourier transform of $\varrho(r)$, is also easily obtained from (22a):

$$\varrho(g) = \frac{1}{\Omega} \int_{\Omega} d^3 r \varrho(r) e^{igr}, \qquad (25a)$$

$$\varrho(r) = \sum_{g} \varrho(g) e^{-igr}, \qquad (25b)$$

$$\varrho(g) = \begin{cases} Z/\Omega_0; \ g = 0 & (25c) \\ \frac{Z}{\Omega_0} C^2 \left\{ 2 Re \, \tilde{W}(g) F(g) + \sum_{g' \neq g} \tilde{W}(g - g') \right. \\ \left. \cdot \tilde{W}^*(g') \Phi(g - g', g') \right\}; g \neq 0. \ (25d) \end{cases}$$

Now we shall consider the problem of screening. The screened matrix element, $W(g)$, is obviously (see (5)):

$$W(g) = W^0(g) + W^{scr}(g), \qquad (26)$$

where $W^0(g)$ and $W^{scr}(g)$ are respectively the matrix elements of the bare lattice potential and a screening potential. The latter may be represented as

$$W^{scr}(g) = W^H(g) + W^{xc}(g) \qquad (27)$$

$W^H(g)$, the Hartree potential matrix element, is easily found from the Poisson equation,

$$W^H(g) = 4\pi/g^2 \varrho(g) \qquad (28)$$

$W^{xc}(g)$, the exchange-correlation potential, will be discussed in the next section.

If one restricts oneself for a moment to the Hartree approximation, one sees from (26), (28) and (25c) that $W^H(g)$ does not depend on $W(g)$ linearly. If the matrix elements were small, then all the expressions would reduce to the perturbation theory ones, and one would obtain

$$W(g) = W^0(g)/\varepsilon(g), \qquad (29)$$

$$\varepsilon(g) = 1 + \frac{16\pi}{\Omega_0 g^2} F(g) = 1 - \frac{8\pi}{\Omega_0 g^2} \chi(g), \qquad (29a)$$

$$\chi(g) = -\frac{1}{2} Z \left(\frac{1}{3} k_F^2\right)^{-1} \tag{29b}$$
$$\cdot \left(\frac{1}{2} + \frac{4 k_F^2 - g^2}{8 g k_F} \ln \left|\frac{g + 2 k_F}{g - 2 k_F}\right|\right)$$

$(k_F = (3 \pi^2 Z/\Omega_0)^{1/3}$ is the free electron gas Fermi wavevector).

Equations (29) are the definition of a microscopic dielectric function, $\varepsilon(g)$. In our theory (29) may be introduced only symbolically since $\varepsilon(g)$ would depend functionally on $\tilde{W}(g)$. Such a dielectric function actually does not seem to be helpful either for understanding nor for practical calculations. We shall not be using such a generalized $\varepsilon(g)$, rather solving directly the corresponding nonlinear equations for $\tilde{W}(g)$.

## 5. Exchange-Correlation Contributions

Perhaps the most essential breakthrough towards an adequate description of exchange and correlation was achieved in recent years after the introduction of the DFF by Hohenberg, Kohn and Sham [19, 13]; later the approach was generalized to a spindensity functional [20]. DFF provides a formally exact framework for treating exchange-correlation effects and is particularly exact in the case of slowly varying electron density. In this case the exchange-correlation energy, $E_{xc}$, is a local functional of $\varrho(r)$. If the electron distribution is strongly non-homogeneous some gradient corrections contribute to $E_{xc}$ (see, e.g. [21—23]).

Omitting the latter for the moment, $E_{xc}$, which appears in (20), is (per unit cell):

$$E_{xc} \equiv E_{xc}[\varrho] = \frac{1}{N} \int_\Omega \mathrm{d}^3 r \, \Delta E^{xc}(\varrho(r))$$
$$= \Omega_0 \Delta E^{xc}(g)|_{g=0}, \tag{30a}$$
$$\Delta E^{xc}(\varrho(r))$$
$$= \varrho(r)[E^{xc}(\varrho(r)) - W^{xc}(\varrho(r))]. \tag{30b}$$

Here $E^{xc}(\varrho(r))$ is the density of the exchange-correlation energy; $W^{xc}(\varrho(r))$ is the exchange-correlation potential which an electron "feels", and $\Delta E^{xc}(g)$ is the Fourier transform of $\Delta E^{xc}(\varrho(r))$ (30b).

$W^{xc}(\varrho(r))$ is defined as

$$W^{xc}(\varrho(r)) = \frac{\delta}{\delta \varrho(r)} E_{xc}[\varrho]$$
$$= \frac{\mathrm{d}}{\mathrm{d}\varrho} (\varrho E^{xc}(\varrho))_{\varrho = \varrho(r)}. \tag{31}$$

As for $E^{xc}(\varrho)$:

$$E^{xc}(\varrho) = -\frac{0.458}{r_s(\varrho)} + E^c(\varrho). \tag{32}$$

Here $E^c(\varrho)$ is a correlation energy. We shall consider the forms suggested by Nozieres and Pines [24]:

$$E^c(\varrho) = -0.05750 + 0.01550 \ln(r_s(\varrho)), \tag{33}$$

where

$$r_s(\varrho) = \left(\frac{3}{4\pi}\right)^{1/3} \varrho^{-1/3}. \tag{34}$$

Using (34), one has

$$E^{xc}(\varrho) = -0.73829 \varrho^{1/3} - 0.064901$$
$$- 0.01550 \ln \varrho^{1/3}, \tag{35a}$$
$$W^{xc}(\varrho) = E^{xc}(\varrho) - 0.24610 \varrho^{1/3}$$
$$- 0.005167, \tag{35b}$$
$$\Delta E^{xc}(\varrho) = 0.24610 \varrho^{4/3} + 0.005167 \varrho. \tag{35c}$$

Since in our theory $\varrho(r)$ is expressed through its Fourier-transforms, (25), it would be convenient to Fourier-transform eqs. (35) as well. This happens to be possible if one uses Chebyshev polynomial approximations for the functions (35) *.

Let be

$$\varrho = \bar{\varrho}(1 + \delta),$$
$$\delta = (\varrho - \bar{\varrho})/\bar{\varrho}, \quad \bar{\varrho} = Z/\Omega_0.$$

Then, for $-0.4 \leq \delta \leq 4.0$,

$$W^{xc}(\varrho) = -\frac{4}{3} \frac{0.458}{r_s} (A_0 + A_1 \delta + A_2 \delta^2), \tag{36a}$$
$$\Delta E^{xc}(\varrho) = \frac{Z}{\Omega_0} \frac{1}{3} \frac{0.458}{r_s} (B_0 + B_1 \delta + B_2 \delta^2), \tag{36b}$$

where

$$A_0 = 0.99287 + 0.09040 r_s$$
$$- 0.00938 r_s^2 - 0.00052 r_s^3,$$
$$A_1 = 0.30490 + 0.00751 r_s,$$
$$A_2 = -0.03132 - 0.00100 r_s, \tag{37}$$
$$B_0 = 1.03270 + 0.03385 r_s,$$
$$B_1 = 1.38729 + 0.03385 r_s, \quad B_2 = 0.12496.$$

Here $r_s = r_s(\bar{\varrho})$ of (34) is an average interelectronic distance. The precision of the approximations is the following:

---

* A Chebyshev polynomial approximation for $\varrho(r)^{4/3}$ was recently used by Wendel and Martin [25] for calculating structural properties of covalent semi-conductors.

For $1 \leq r_s \leq 6$ the maximum errors are respectively 2.5% and 1.5% for the functions (36a) and (36b). Fourier-transforming (36a, b) one obtains:

$$
W^{\mathrm{xc}}(\boldsymbol{g}) = -\frac{4}{3} \frac{0.458}{r_s}
\begin{cases}
A_0 + \left(\dfrac{Z}{\Omega_0}\right)^{-2} A_2 \sum_{\boldsymbol{g}'}{}' |\varrho(\boldsymbol{g}')|^2; & \boldsymbol{g} = 0, \\[2mm]
\left(\dfrac{Z}{\Omega_0}\right) A_1 \varrho(\boldsymbol{g}) + \left(\dfrac{Z}{\Omega_0}\right)^{-2} A_2 \sum_{\boldsymbol{g}'}{}' \varrho(\boldsymbol{g}'-\boldsymbol{g}) \varrho^*(\boldsymbol{g}'); & \boldsymbol{g} \neq 0
\end{cases}
\tag{38a}
$$

and, for $\boldsymbol{g}=0$

$$
\Delta E^{\mathrm{xc}}(\boldsymbol{g}=0) = \frac{1}{3} \frac{0.458}{r_s} \left\{ \left(\frac{Z}{\Omega_0}\right) B_0 + \left(\frac{Z}{\Omega_0}\right)^{-1} B_2 \sum_{\boldsymbol{g}'}{}' |\varrho(\boldsymbol{g}')|^2 \right\}.
\tag{38b}
$$

Now, that $W^{\mathrm{xc}}(\boldsymbol{g})$ is known, the total screening matrix element, $W^{\mathrm{scr}}(\boldsymbol{g})$, from (27) and (28) reads:

$$
W^{\mathrm{scr}}(\boldsymbol{g}) = \frac{4\pi}{\boldsymbol{g}^2} \left\{ [1 - f(g)] \varrho(\boldsymbol{g}) + \varphi(g) \frac{\Omega_0}{Z} \sum_{\boldsymbol{g}'}{}' \varrho(\boldsymbol{g}'-\boldsymbol{g}) \varrho^*(\boldsymbol{g}') \right\},
\tag{39}
$$

where

$$
f(g) = 3 A_1 \left(\frac{g}{2 k_F}\right)^2, \quad \varphi(g) = -3 A_2 \left(\frac{g}{2 k_F}\right)^2.
\tag{39a, b}
$$

(39) reminds of the traditional pseudopotential theory. There $\varrho(\boldsymbol{g})$ is linear in $W(\boldsymbol{g})$, therefore the second term in (39) is omitted. Function $f(g)$, which allows for an exchange-correlation contribution to the screening, is in a sense a model one. Various approximate expressions for $f(q)$ have been suggested beginning with the pioneering work by Hubbard [26] (see, e.g. [1], Chapter II). Usually the requirement is imposed that at $q \to 0$ $f(q)$ should satisfy the so-called compressibility sum rule. Being successively used in the pseudo-potential theory, DFF automatically satisfies this requirement [27], the corresponding $f(q)$ being proportional to $(q/2k_F)^2$. At the same time, the DFF expression, (30a), for slowly varying density is actually only the first term in the gradient expansion of an exact exchange-correlation functional. Therefore, in terms of DFF, the numerous attempts of incorporating local field corrections via $f(q)$ are just the attempts of allowing for some higher order terms of the gradient expansion of $E_{\mathrm{xc}}[\varrho]$.

Returning to (39) one sees that now, in the case when $\varrho(\boldsymbol{g})$ is not linear in $W(\boldsymbol{g})$, $f(g)$ is still quadratic in $(g/2k_F)$. The compressibility sum rule is also fulfilled:

$$
3 A_1 = 0.91470 + 0.02253 r_s
$$

which almost coincides with the exact $q \to 0$ limit: $1 + 0.0254 r_s$ (see, e.g. [1]), the deviations resulting from the approximation, eq. (36a). At the same

time, again a $(g/2k_F)^2$-dependence reminds us that we deal only with the first term in the gradient expansion.

It is not quite justified, however, to substitute $f(g)$, (39a), by one of the known expressions, e.g. by the function suggested by Vashishta and Singwi [28]. The reason is that in all the theories of local field correction the "external" field is considered as a weak one. This is not the case in the present theory.

One could, in principle, add gradient-dependent terms to $E^{\mathrm{xc}}$, (30a) [21—23, 29, 30]. Then the first correction to $W^{\mathrm{xc}}(\varrho(\boldsymbol{r}))$ would be:

$$
\Delta W^{\mathrm{xc}}(\varrho) = -\frac{1}{2} \left\{ \frac{\mathrm{d}g^{(2)}(\varrho)}{\mathrm{d}\varrho} |\nabla \varrho|^2 + g^{(2)}(\varrho) \Delta \varrho \right\},
$$

where $g^{(2)}(\varrho) = \beta(r_s) \varrho^{-4/3}$; $\beta(r_s)$ is a coefficient. Inclusion of such a term would drastically complicate the calculations. On the other hand, the coefficient $\beta(r_s)$ is not reliable enough.

Another option would be to use an interpolation procedure of the kind suggested for pseudopotentials by Shaw and Pynn [31]. We shall be considering both $f(g)$ and $\varphi(g)$ of (39a, b) as long-wavelength limits of more general functions:

$$
f(g) = \frac{3 A_1 (g/2 k_F)^2}{1 + 2 \cdot 3 A_1 (g/2 k_F)^2 \exp\{-\alpha/(g/2 k_F)^2\}},
\tag{39c}
$$

$$
\varphi(g) = -\frac{3 A_2 (g/2 k_F)^2}{1 + 4 \cdot 3 |A_2| (g/2 k_F)^2 \exp\{-\alpha/(g/2 k_F)^2\}}.
\tag{39d}
$$

The factor $\alpha$ in the exponentials should keep the functions (39c, d) almost unchanged up to $g/2k_F = 0.75 \div 1$ (see [27]) and then provide for arriving at reasonable short-wave-lengths limits, respectively $1/2$ and $1/4$, due to the factors 2 and 4 in the denominators. This is achieved if $\alpha \simeq 2.5$.

Now the screening field is totally defined.

It is also worth mentioning an important fact. As we see, in general, the screening is not linear. However, for some $g$'s, if $\bar{W}(g) \simeq W(g)$, and the requirement (1) is fulfilled, the nonlinear contributions to the screening are unimportant, and one may introduce a microscopic dielectric function, $\varepsilon^*(g)$:

$$W(g) = W^0(g)/\varepsilon^*(g), \qquad (29c)$$

$$\varepsilon^*(g) = 1 - \frac{8\pi}{\Omega_0 g^2} C^2(1 - f(g))\chi(g) \qquad (29d)$$

($\chi(g)$ is defined by (29b)). The expression for $\varepsilon^*(g)$ is almost the same as the one in the traditional pseudopotential theory. The difference is that now an additional factor $C^2$ enters, which, from the physical point of view, means that $\Delta Z$ transferred electrons, (24), do not participate even in a linear screening. In a sense they are "localized" (c.f. bonding charges in semiconductors with diamond-type lattice).

Let us consider now the direct exchange-correlation contribution $E_{xc}$ to the energy, (30). We should consider it together with the term $ZW(g = 0)$ — formally the first order contribution. Making use of (26), (27) and (38a, b), one obtains:

$$ZW(g = 0) + E_{xc} = E_{nc} + Z \frac{0.458}{r_s}$$
$$\cdot \left[ -\frac{4}{3} A_0 + \frac{1}{3} B_0 + \left( \frac{Z}{\Omega_0} \right)^{-2} \right.$$
$$\left. \cdot \left( -\frac{4}{3} A_2 + \frac{1}{3} B_2 \right) \sum_{g'}' |\varrho(g')|^2 \right]. \qquad (40)$$

Here

$$E_{nc} = Z \lim_{g \to 0} \left[ W^0(g) + \frac{4\pi Z}{\Omega_0 g^2} \right] \qquad (41)$$

is exactly the same term that appears as a first-order contribution in the traditional pseudopotential theory. It is characteristic of a "non-coulombic" pseudopotential interaction with the uniform electron background.

When $\varrho(g)$ is linear in $W(g)$ (nearly free electron gas), the second term in brackets is exactly com-

pensated by the contribution from $W^{xc}(g)$ in the band structure energy [27]. Consequently, the first term

$$-\frac{4}{3} A_0 + \frac{1}{3} B_0$$

is just an approximation of the exchange-correlation energy, $E_{xc}^0$ of a homogeneous electron gas, (32), with $\varrho = Z/\Omega_0$ and $r_s(\varrho) \equiv r_s$.

Now we may introduce a new definition of exchange-correlation energy:

$$E_{xc} = E_{xc}^0 + \Delta E_{xc}, \qquad (42)$$

$$\Delta E_{xc} = \frac{\Omega_0^2}{Z} \frac{0.458}{r_s}$$
$$\cdot \left( -\frac{4}{3} A_2 + \frac{1}{3} B_2 \right) \sum_{g'}' |\varrho(g')|^2. \qquad (43)$$

Finally, the total energy (20), reads:

$$E = E_0 + E_{nc} + E_{xc} + E_c - E_{el} + E_{es}. \qquad (44)$$

## 6. The Procedure of the Selfconsistent Calculations

Now that all the contributions to the total energy have been specified (Eqs. (44), (43), (41), (20a—c), (21)), and the formally closed sets of equations both for $\bar{W}(g)$, Eq. (11), and for $W^{scr}(g)$, Eqs. (27), (38), with the energy spectra, $E_k$, defined within the single-band-gap model, Eqs. (16a), (17a), we may discuss in more detail the procedure of gathering all the components of the theory together.

The analysis begins with calculating "bare" pseudopotential matrix elements, $W^0(g)$. Of course, we have first to chose a potential or pseudopotential. In our case it should be local.

Having calculated $W^0(g)$'s for some, e.g., 20—30 first reciprocal lattice shells we can "sort out" the $g$'s in the sense, that we subdivide them into 3 groups:

1. $W^0(g)$'s are large (the requirement (2) is not fulfilled); we shall denote the set of such wave vectors as $\{\tilde{g}\}$.

2. $W^0(g)$'s are small, and even exactly equal to zero (according to symmetry requirements), but the corresponding $g$'s are such that for some $g' \in \{\tilde{g}\}$ the wave vectors $g - g'$ also belong to $\{\tilde{g}\}$. For such $g$'s the matrix elements are expected to be appreciably changed due to Equations (11). We shall denote this set of wavevectors as $\{\tilde{g}_0\}$.

3. All the other reciprocal lattice vectors, for which the requirement (1) is fulfilled.

The second step is an analysis of the Brillouin zone (BZ) succession in order to state whether the system of interest has JZ with FS vanishing on its faces, or there are some overlapping bands resulting in a "free" FS. Of course, such an analysis may be only tentative. For example, if one finds a set of BZ planes enclosing the area just necessary and sufficient to accomodate all the electrons of the system, then this may possibly be the JZ. If the matrix elements, corresponding to that $g$'s are "strong", then the JZ most probably arises. It can arise even if $W^0(g)$'s are very weak or even equal to zero (the diamond lattice case), but in this case information on $\tilde{W}(g)$ is needed, since these are $\tilde{W}(g)$'s that define the energy gaps. The situation is still more complicated if there exist some "competing" BZ faces with "stronger" matrix elements, intersecting the ones of interest and forming together with some of these faces (or without) another polyhedron but of larger volume. In the latter case some overlapping may arise resulting in a free FS. In any case the situation may be cleared after a few iterations, or even possibly one (see below).

Let the analysis have stated that the JZ exists, $\{g_{JZ}\}$ being the set of the reciprocal lattice vectors, corresponding to the JZ faces. The whole calculation will proceed by iterations. We begin with "0-approximation" and put all the $W(g)$'s equal to their free electron values, (29 c, d), with $C^2 = 1$. Now we can calculate $\tilde{W}(g)$'s. For the set $\{\tilde{g}\}$ we solve the set of simultaneous equations (11). In this set:

Both $\{g'\}$ and $\{g - g'\}$

belong to $\{\tilde{g}\}$. 　　　　　　　　　(45)

The $\tilde{W}(\tilde{g})$'s having been found, we determine $\tilde{W}(\tilde{g}_0)$'s by means of eqs. (11), which now serve as equalities. The wave vectors appearing in the right-hand side sum must also satisfy the requirement (45). For all the other wave vectors $g$, apart from $\{\tilde{g}\}$ and $\{\tilde{g}_0\}$, $\tilde{W}(g) \equiv W(g)$. Function $F(g)$, which depends on $\tilde{W}(g)$, are also calculated for $\tilde{W}(g) = W(g)$ in the first iteration.

Now when $\tilde{W}(g)$'s are known, we calculate the normalization constant $C^2$, (23) (function $\Phi(g, g')$ depends on $\tilde{W}$), the screening matrix elements,

$W^{\text{scr}}(g)$, (38), (35d) (always keeping in mind condition (45)), and finally, the screened matrix elements $W(g)$'s, see (26).

Then the whole iteration process is repeated. After a convergence is achieved (it may be controlled, say, by comparing the successive values of $C^2$), the values of $W(g)$, $\tilde{W}(g)$, $\varrho(g)$ are known and the final calculation of energy, (44), is straightforward.

Before going over to the determination of the functions $F(g)$, $\Phi(g, g')$ and $\Phi(g, g)$ it is worth noting, that in all the integrations over the occupied $k$-states we allow for the energy gaps explicitly. Even for the "weak" matrix elements the computational procedure with the integrals calculated in the sense of principal values is less convenient than allowing for the gaps through the function $F$.

## 7. Determination of the Functions $F(g)$ and $\Phi(g, g')$

In order to determine the functions $F(g)$, Eq. (12), and $\Phi(g, g')$, Eq. (14), one has to be able to evaluate the corresponding integrals with the single-band model function $E_k$, Eq. (17a). The integrations both in (12) and (13) have to be performed within either a true FS or a JZ.

The problem of the integration within the true (non-spherical) FS is a very complicated one. The integral of the type of the one of (12) has been evaluated by Williams and Weaire [32]. As for the more complicated integral (13), it has not been calculated, and the question is still open. Of course, as an approximate procedure, the integration within the Fermi sphere with the contributions of the states in the vicinities of all the Bragg planes included "precisely" might be suggested. Rather we shall focus on the case when a JZ will exist.

In this case the calculation of the integrals may be essentially simplified. For this purpose we introduce the following mathematical approximation:

$$(a^2 + v^2)^{1/2} \cong |a| + \frac{1}{2} \frac{v^2}{|a| + |v|} \tag{46}$$
$$+ \frac{|v|^3}{(|a| + |v|)^2} - \frac{1}{2} \frac{v^4}{(|a| + |v|)^3}.$$

The derivation of this approximation may be found in Appendix 1. Here we only note that for all possible values of $a$ and $v$ the error is less than 1.65% (this is the error at $a = v$). Eq. (46) is also

exact for $a=0$ or $v=0$, and for $v/a \ll 1$ and $a/v \ll 1$ gives the correct second order results.

Making use of Eq. (16a), (17a) and approximation eq. (46), one gets

$$\frac{1}{E_k^\pm - E_{g-k}^0} = \frac{E_k^\pm - E_k^0}{|\bar{W}(g)|^2} \tag{47}$$

$$= \pm \left\{ \frac{1}{|E_k^0 - E_{g-k}^0| + 2|\bar{W}(g)|} \right.$$

$$+ \frac{4|\bar{W}(g)|}{(|E_k^0 - E_{g-k}^0| + 2|\bar{W}(g)|)^2}$$

$$\left. - \frac{4|\bar{W}(g)|^2}{(|E_k^0 - E_{g-k}^0| + 2|\bar{W}(g)|)^3} \right\}.$$

Here again $(+)$ refers to the states above the Bragg plane and $(-)$ to the ones below.

The integrals, defining the functions $F(g)$ and $\Phi(g, g')$ are evaluated in Appendix 2.

First, the integral

$$\frac{\Omega_0}{(2\pi)^3} \int\limits_{JZ} d^3k \, \frac{1}{E_k^\pm - E_{g-k}^0} \tag{12a}$$

is evaluated and a function

$$S(\zeta, \zeta_1, \zeta_2, \beta)$$

is introduced; here $\zeta = 2k_F/g$, $\beta = 4|\bar{W}(g)|/g^2$, and the values of $\zeta_1$ and $\zeta_2$ depend on the area of integration.

There may be three different cases in evaluating the integral (12a). They are shown in Figure A1.

*Case a*: The Bragg plane, corresponding to $g$ lies within the JZ. The integration is performed within the sphere of radius $k_F$, but the states below and above the plane are accounted for separately. Then

$$F(g) \equiv F(\zeta) = -\frac{3}{(2k_F)^2 \zeta} \tag{48a}$$

$$\cdot \{ S(\zeta, -\zeta, 1, \beta) + S(\zeta, 1, \zeta, -\beta) \}.$$

Here the first and second terms correspond to the contributions of the states below and above the plane respectively.

*Case b*: The Bragg plane is one of the JZ faces. As is seen from Fig. A1, the integration is performed within the truncated sphere, the total volume of the integration area being $(4/3)\pi k_F^3$. The radius of the sphere, $r_{ef}$, (in units of $(2k_F)^{-1}$) satiesfies the equation

$$4 r_{ef}^3 \zeta^3 + 3 r_{ef}^2 \zeta^2 - \tfrac{1}{4} = 0. \tag{49}$$

Then, the reciprocal radius, $\zeta_{ef} = 1/r_{ef}$ and

$$F(\zeta) = -\frac{3}{(2k_F)^2 \zeta} S(\zeta, -\zeta_{ef}, 1, \beta). \tag{48b}$$

*Case c*: The Bragg plane lies outside the JZ. The integration is performed within the sphere of radius $k_F$ and

$$F(\zeta) = \frac{3}{(2k_F)^2 \zeta} S(\zeta, -\zeta, \zeta, \beta). \tag{48c}$$

The function $\Phi(g, g)$, appearing in (23) for the normalization constant $C^2$ is expressed by means of the function

$$P(\zeta, \zeta_1, \zeta_2, \beta)$$

in a similar way:

*Case a*:

$$\Phi(g, g) \equiv \Phi(\zeta) = \frac{6\zeta}{(2k_F)^4} \tag{50a}$$

$$\cdot \{ P(\zeta, -\zeta, 1, \beta) + P(\zeta, 1, \zeta, -\beta) \}.$$

*Case b*:

$$\Phi(\zeta) = \frac{6\zeta}{(2k_F)^4} P(\zeta, -\zeta_{ef}, 1, \beta). \tag{50b}$$

*Case c*:

$$\Phi(\zeta) = \frac{6\zeta}{(2k_F)^4} P(\zeta, -\zeta, \zeta, \beta). \tag{50c}$$

In order to determine the function $\Phi(g, g')$, (14), appearing in the definition of the electron density, (22), (25d), the function

$$Q(\zeta, \zeta_1, \zeta_2, \beta, \gamma, \alpha)$$

is introduced, where $\zeta = 2k_F/g'$, $\beta = 4|\bar{W}(g')|/g'^2$, $\gamma = |g|/|g'|$, $\alpha = \cos(\widehat{g, g'})$ and $\zeta_1$ and $\zeta_2$ have the same meaning as above. Now:

*Case a*:

$$\Phi(g - g', g') = -\frac{6\zeta}{(2k_F)^4 \gamma} \tag{51a}$$

$$\cdot \{ Q(\zeta, -\zeta, 1, \beta, \gamma, \alpha) + Q(\zeta, 1, \zeta, -\beta, \gamma, \alpha) \}.$$

*Case b*:

$$\Phi(g - g', g) = -\frac{6\zeta}{(2k_F)^4 \gamma} \tag{51b}$$

$$\cdot Q(\zeta, -\zeta_{ef}, 1, \beta, \gamma, \alpha).$$

*Case c*:

$$\Phi(g - g', g) = -\frac{6\zeta}{(2k_F)^4 \gamma} \tag{51c}$$

$$\cdot Q(\zeta, -\zeta, \zeta, \beta, \gamma, \alpha).$$

## 8. Concluding Remarks

The aim of the present paper has been to develop an approach which allows to calculate the binding energy and electron distribution for non-metallic crystals. Now that the procedure of the calculations is totally described it is worth summarizing the main issues of the approach.

Instead of applying some higher orders of the Schrödinger perturbation theory we solve the non-linear equations for the effective matrix elements $\bar{W}(g)$. The problem is rather simple, unless the number of "strong" matrix elements, which need to be treated "precisely", is too large. Some "weak" matrix elements are also being "renormalized" due to the "indirect" scattering of electrons. The immediate result of the strong electron-ion interaction is the charge transfer: electronic spatial non-homogeneities arise of the type that result in the bonding charge formation in semiconducting crystals. Of course, the screening of the lattice potential is not linear any more, and not all electrons effectively participate in the screening.

In principle, the present theory allows to consider crystals with different types of bonding: purely metallic, covalent, and perhaps even ionic. In the latter case some of the potential (or pseudopotential) matrix elements are complex, but the theory takes this fact into account in a natural way.

Of course, the approach suggested is not free of some shortcomings. These have been pointed out above. Some of the approximations may be controlled only in the course of concrete numerical calculations; for the others, the only criterion is a comparison with experimental data (and this is always the case with a pseudopotential pie: one should taste it first).

The calculations on magnesium hydride, $MgH_2$, to be presented in Part II of the paper, seem to be promising. We believe that the approach may be successfully used in analysing bonding and stability of complex crystal lattices.

## Appendix 1

*The Approximation of the Square Root Function*

By means of an identity transformation one gets

$$(a^2 + v^2)^{1/2} \equiv [(|a| + |v|)^2 - 2|a||v|]^{1/2}. \quad (A.1)$$

Now keeping the terms of the second order in $2|a||v|/(|a|+|v|)^2$ one obtains:

$$(a^2 + v^2)^{1/2} \cong |a| + |v| - \frac{|a||v|}{|a| + |v|}$$
$$- \frac{1}{2} \frac{a^2 v^2}{(|a| + |v|)^3} \quad (A.2a)$$

$$= |a| + \frac{1}{2} \frac{v^2}{|a| + |v|} + \frac{|v|^3}{(|a| + |v|)^2}$$
$$- \frac{1}{2} \frac{v^4}{(|a| + |v|)^3}. \quad (A.2b)$$

(A.2) is seen to be precise in the limiting cases of either $a = 0$ or $v = 0$. The latter is important, since being applied to the single-band-gap model, $a = 0$ means the states right on a Bragg plane. If $v/a \ll 1$, then the correct second order contribution results from (A.2). The same applies to the case $a/v \ll 1$, since $a$ and $v$ enter (A.1) and the series (A.2a) symmetrically.

As for the "intermediate" cases, $a \cong v$, the approximation (A.2) happens to be surprisingly precise: the greatest relative error of 1.65% arises at $a = v$, being less in all other cases.

## Appendix 2

*Evaluation of the Integrals over the Occupied Electron States*

We begin with the integral (12):

$$F(g) = \frac{1}{ZN} \sum_k \frac{1}{E_k - E^0_{g-k}}$$
$$= \frac{2\Omega_0}{Z(2\pi)^3} \int \frac{d^3k}{E_k - E^0_{g-k}}. \quad (A.3)$$

Making use of (47) one sees that three different integrals have to be evaluated:

$$\int d^3k \frac{1}{\frac{1}{2}|g^2 - 2(kg)| + 2|\bar{W}(g)|}, \quad (A.4a)$$

$$\int d^3k \frac{1}{[\frac{1}{2}|g^2 - 2(kg)| + 2|\bar{W}(g)|]^2}, \quad (A.4b)$$

$$\int d^3 k \, \frac{1}{[\frac{1}{2} \, | g^2 - 2(kg) | + 2 \, | \bar{W}(g) |]^3} \, . \quad (A.4c)$$

We are considering the case when the integrations are performed within a JZ, i.e. a polyhedron, which we approximate by a truncated sphere. Then three different situations are possible (see Figure A1).

If one chooses the $k_z$-axis in the direction of the reciprocal lattice vector $g'$, then the integrands (A.4), depend only on $k_z$, and the integrals are easily evaluated.

Let us consider first the integration over the states below the Bragg plane. Then

$$| E_k^0 - E_{g-k}^0 | = \tfrac{1}{2} [g^2 - 2(kg)] \quad (A.5a)$$

and the integral (A.4a) reads:

$$\frac{\pi}{4} \, g \int_{\zeta_1}^{\zeta_2} \frac{dz \, (\zeta^2 - z^2)}{1 - z + \beta} \, . \quad (A.6)$$

Here we introduced the new variable, $z = 2 k_F / g$ and the parameters: $\zeta = 2 k_F / g$ and $\beta = 4 \, | W(g) | / g^2$. The limits of the integration are written in a general form. When integrating below the Bragg plane, $\zeta_1 = -\zeta$ $(k_z = -k_F)$ and $\zeta_2 = 1$ $(k_z = g/2)$. The integral (A.6) is easily evaluated. Now, one sees that the two other integrals, (A.4b) and (A.4c) may be expressed as partial derivatives of (A.6) with respect to $\beta$.

Finally, one may introduce the function, allowing for the contributions to the integral (A.3) due to the states below the Bragg plane:

$$S(\zeta, \zeta_1, \zeta_2, \beta) = J_1 + 2\beta \, J_2 - \beta^2 J_3, \quad (A.7)$$

$$J_1 = \frac{1}{2} \, [\zeta^2 - (1+\beta)^2] \ln \left| \frac{1 + \beta - \zeta_1}{1 + \beta - \zeta_2} \right| + \frac{1}{4} \, (\zeta_2^2 - \zeta_1^2) + \frac{1}{2} \, (1 + \beta)(\zeta_2 - \zeta_1), \quad (A.7a)$$

$$J_2 = (1 + \beta) \ln \left| \frac{1 + \beta - \zeta_1}{1 + \beta - \zeta_2} \right| - \frac{1}{2} \, [\zeta^2 - (1+\beta)^2][(1 + \beta - \zeta_1)^{-1} - (1 + \beta - \zeta_2)^{-1}] + \frac{1}{2} \, (\zeta_1 - \zeta_2), \quad (A.7b)$$

$$J_3 = -\frac{1}{2} \ln \left| \frac{1 + \beta - \zeta_1}{1 + \beta - \zeta_2} \right| - (1 + \beta)[(1 + \beta - \zeta_1)^{-2} - (1 + \beta - \zeta_2)^{-2}]$$

$$- \frac{1}{4} \, [\zeta^2 - (1+\beta)^2][(1 + \beta - \zeta_1)^{-2} - (1 + \beta - \zeta_2)^{-2}] \quad (A.7c)$$

$$\left( \text{here} \quad J_2 = -\frac{\partial}{\partial \beta} \, J_1; \quad J_3 = -\frac{1}{2} \frac{\partial}{\partial \beta} \, J_2 \right).$$

For the integrations over the states above the Bragg plane:

$$| E_k^0 - E_{g-k}^0 | = -\tfrac{1}{2} [g^2 - 2(kg)] \quad (A.5b)$$

and the contribution is expressed by the function

$$- S(\zeta, \zeta_1, \zeta_2, -\beta),$$

where now $\zeta_1 = 1$ $(k_z = g/2)$ and $\zeta_2 = \zeta$ $(k_z = k_F)$. The final results for the three cases a, b and c of Fig. A1 are presented in (48a), (48b) and (48c).

The determination of the function

$$\Phi(g, g) = \frac{1}{ZN} \sum_k \frac{1}{(E_k - E_{k-g}^0)^2}$$

$$= \frac{2 \Omega_0}{Z(2\pi)^3} \int_{JZ} \frac{d^3 k}{(E_k - E_{g-k}^0)^2} \quad (A.8)$$

which enters the expression for the normalization constant (23), is also reduced to the derivatives of the integral (A.6) with respect to $\beta$.

Now the integrand is

$$\left\{ \frac{1}{\frac{1}{2} \, | g^2 - 2(kg) | + 2 \, | \bar{W}(g) |} \right.$$

$$+ \frac{4 \, | \bar{W}(g) |}{[\frac{1}{2} \, | g^2 - 2(kg) | + 2 \, | \bar{W}(g) |]^2}$$

$$\left. - \frac{4 \, | \bar{W}(g) |^2}{[\frac{1}{2} \, | g^2 - 2(kg) | + 2 \, | \bar{W}(g) |]^3} \right\}^2$$
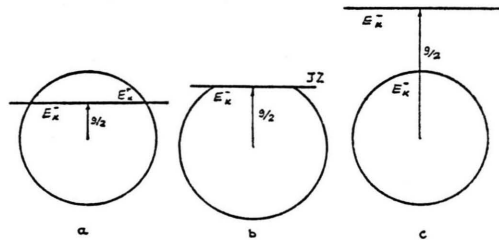


Fig. A1. Three cases of relative situation of the JZ and a Bragg plane. a) The plane intersects the JZ. b) The plane is just a face of a JZ. The truncated sphere has the equivalent volume with the radius satisfying Equation (49). c) The plane is outside the JZ.

and the following function may be introduced:

$$P(\zeta, \zeta_1, \zeta_2, \beta) = J_2 + 4\beta J_3 + 2\beta^2 J_4 - 4\beta^3 J_5 + \beta^4 J_6, \tag{A.9}$$

where $J_2$ and $J_3$ are given by (A.7b) and (A.7c) and

$$J_4 = \tfrac{1}{2}[(1+\beta-\zeta_1)^{-1} - \tfrac{1}{2}(1+\beta-\zeta_2)^{-1}] - \tfrac{1}{2}(1+\beta)[(1+\beta-\zeta_1)^{-2} - (1+\beta-\zeta_2)^{-2}]$$
$$- \tfrac{1}{6}[\zeta^2 - (1+\beta)^2][(1+\beta-\zeta_1)^{-3} - (1+\beta-\zeta_2)^{-3}] \tag{A.9a}$$

$$J_5 = \tfrac{1}{4}[(1+\beta-\zeta_1)^{-2} - (1+\beta-\zeta_2)^{-2}] - \tfrac{1}{3}(1+\beta)[(1+\beta-\zeta_1)^{-3} - (1+\beta-\zeta_2)^{-3}]$$
$$- \tfrac{1}{8}[\zeta^2 - (1+\beta)^2][(1+\beta-\zeta_1)^{-4} - (1+\beta-\zeta_2)^{-4}] \tag{A.9b}$$

$$J_6 = \tfrac{1}{6}[(1+\beta-\zeta_1)^{-3} - (1+\beta-\zeta_2)^{-3}] - \tfrac{1}{4}(1+\beta)[(1+\beta-\zeta_1)^{-4} - (1+\beta-\zeta_2)^{-4}]$$
$$- \tfrac{1}{10}[\zeta^2 - (1+\beta)^2][(1+\beta-\zeta_1)^{-5} - (1+\beta-\zeta_2)^{-5}]. \tag{A.9c}$$

When integrating above the Bragg plane, the function

$$P(\zeta, \zeta_1, \zeta_2, -\beta)$$

enters, with $\zeta_1 = 1$ and $\zeta_2 = \zeta$. The final results for the three cases a, b and c are presented in (50a, b, c). The evaluation of the function $\Phi(g, g')$ which enters the expressions for the electron density (22), (25d) is more sophisticated. The function that is actually used in the calculations is

$$\Phi(g - g', g') = \frac{1}{ZN} \sum_k{}' \frac{1}{(E_k - E^0_{g-g'-k})(E_k - E^0_{g'-k})}$$
$$= \frac{2\Omega_0}{Z(2\pi)^3} \int\limits_{JZ} \frac{\mathrm{d}^3k}{(E_k - E^0_{g-g'-k})(E_k - E^0_{g'-k})}. \tag{A.10}$$

Since this function enters the sum over $g'$ (25d), one may identically write:

$$\Phi(g - g', g') = \frac{4\Omega_0}{Z(2\pi)^3} \int\limits_{JZ} \frac{\mathrm{d}^3k}{(E^0_{g'-k} - E^0_{g-g'-k})(E_k - E^0_{g'-k})}. \tag{A.11}$$

Making use of the approximation (47), one again obtains the integrals of three types. The simplest one reads

$$J_1 = -4\frac{g}{\pi} \int\limits_{JZ} \frac{\mathrm{d}^3k}{[g^2 + 2g(k - g')][|g'^2 - 2kg'| + 4|\tilde{W}(g')|]} \tag{A.12}$$

(for convencience we introduced the factor $g/\pi$).

In the terms of cylindrical coordinates (Fig. A2)

$$J_1 = -4\frac{g}{\pi} \int\limits_{k_1}^{k_2} \mathrm{d}k_z \int\limits_0^{(k_m - k_z^2)^{1/2}} k_\varrho \, \mathrm{d}k_\varrho \int\limits_{-\pi}^{\pi} \mathrm{d}\varphi \frac{1}{g^2 + 2g(k_z \cos\theta + k_\varrho \sin\theta \cos\varphi - g'\cos\theta)}$$
$$\cdot \frac{1}{|g'^2 - 2g'k_z| + 4|\tilde{W}(g')|}$$

(here $k_1$ and $k_2$ are the integration limits in $k_z$ direction and $k_m$ is the radius of the truncated sphere to be integrated over).

Let us first consider the integration over the states below the Bragg plane, corresponding to the reciprocal lattice vector $g'$ ($g'^2 - 2kg' \geqq 0$). Introducing new variables one has:

$$J_1 = \frac{1}{2\pi} \int\limits_{z_1}^{z_2} \frac{\mathrm{d}z}{z} \int\limits_0^{[\zeta^2 - (1+\beta-z)^2]^{1/2}} \varrho \, \mathrm{d}\varrho \int\limits_{-\pi}^{\pi} \mathrm{d}\varphi \frac{1}{\delta + (1+\beta)\cos\theta - z\cos\theta + \varrho\sin\theta\cos\varphi}, \tag{A.13}$$

where

$$\gamma = g/g'; \quad \delta = \gamma - 2\cos\theta; \quad \beta = 4\,|\bar{W}(g')|/g'^2$$
$$\varrho = 2k_\varrho/g'; \quad z = 1 + \beta - 2k_z/g'; \quad \zeta = 2k_m/g';$$
$$z_1 = 1 + \beta - \zeta_1; \quad z_2 = 1 + \beta - \zeta_2$$

(here the limits of integration $\zeta_1$ and $\zeta_2$ are written in a general form; when integrating below the Bragg plane $\zeta_1 = -\zeta$ and $\zeta_2 = 1$).

The integral over $\varphi$ was evaluated in the complex plane and reads:

$$\int_{-\pi}^{\pi} \frac{d\varphi}{A + B\cos\varphi} = \frac{2\pi}{(|A^2 - B^2|)^{1/2}}. \quad (A.14)$$
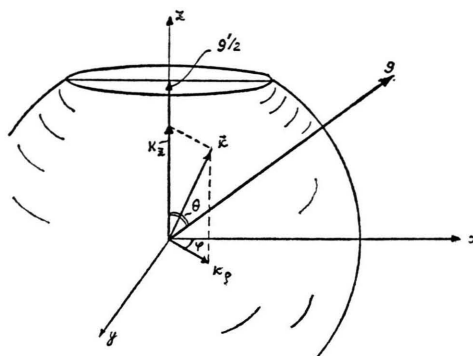
Fig. A2. The coordinate system for evaluating integrals. Explanations in the text.

(Case $A > B$ see, e.g. [33] eq. (2.553.3); in case $A < B$ the principle value of the integral was evaluated.)
After an easy integration over $\varrho$ one obtains:

$$J_1 = \frac{1}{\sin^2\theta} \int_{z_1}^{z_2} \frac{dz}{z} \{\delta + (1 + \beta + z)\cos\theta - [|f(z)|]^{1/2}\}; \quad (A.15)$$

$$f(z) = a + bz + z^2, \quad a = [\delta + (1 + \beta)\cos\theta]^2 - [\zeta^2 - (1 + \beta)^2]\sin^2\theta,$$
$$b = -2[\delta + (1 + \beta)\cos\theta]\cos\theta - 2(1 + \beta)\sin^2\theta.$$

Further integration is straightforward (see [33], Eqs. (2.267.1), (2.266), (2.261)) and one gets

$$J_1 = \frac{1}{\sin^2\theta} \left\{ [\delta + (1 + \beta)\cos\theta]\ln\left|\frac{z_2}{z_1}\right| + \cos\theta(z_1 - z_2) \right.$$
$$\left. - [|f(z_2)|]^{1/2} + [|f(z_1)|]^{1/2} + a[I_1(z_2) - I_1(z_1)] + \frac{b}{2}[I_2(z_2) - I_2(z_1)] \right\} \quad (A.16)$$

$$I_1(z) = -\frac{1}{a^{1/2}}\ln\left|\frac{2a + bz + 2[a|f(z)|]^{1/2}}{z}\right| \quad a > 0$$
$$= \frac{1}{(-a)^{1/2}}\,\text{arc tg}\,\frac{2a + bz}{2[-a|f(z)|]^{1/2}} \quad a < 0$$
$$= -\frac{2[|f(z)|]^{1/2}}{bz}, \quad a = 0 \quad (A.16a)$$

$$I_2(z) = \ln\left|2[|f(z)|]^{1/2} + 2z + b\right|. \quad (A.16b)$$

If $\sin\theta = 0$ ($\cos\theta = \pm 1$),

$$J_1 = \frac{\cos\theta}{[\tilde{\delta} + (1 + \beta)]} \left\{ [\zeta^2 - (1 + \beta)^2]\ln\left|\frac{z_2}{z_1}\right| + [\tilde{\delta} + (1 + \beta)](z_2 - z_1) \right.$$
$$\left. - (\zeta^2 - \delta^2)\ln\left|\frac{\tilde{\delta} + (1 + \beta) - z_2}{\tilde{\delta} + (1 + \beta) - z_1}\right| \right\}, \quad (A.17)$$

where $\tilde{\delta} = \delta\cos\theta$.

The integral of the second type after the steps analogous to (A.14) and (A.15) reads:

$$J_2 = \frac{1}{\sin^2\theta} \int_{z_1}^{z_2} \frac{dz}{z^2} \{\delta + (1 + \beta + z)\cos\theta - [|f(z)|]^{1/2}\} \quad (A.18)$$

and is equal to (see [33], Eqs. (2.267.2), (2.261), (2.266)):

$$J_2 = \frac{1}{\sin^2\theta}\left\{-[\delta + (1+\beta)\cos\theta]\left(\frac{1}{z_2} - \frac{1}{z_1}\right) - \cos\theta\ln\left|\frac{z_2}{z_1}\right|\right.$$
$$\left. + \frac{[|f(z_2)|]^{1/2}}{z_2} - \frac{[|f(z_1)|]^{1/2}}{z_1} + \frac{b}{2}[I_1(z_2) - I_1(z_1)] + I_2(z_2) - I_2(z_1)\right\}. \tag{A.19}$$

If $\sin\theta = 0$,

$$J_2 = \frac{1}{\tilde\delta + (1+\beta)}(J_1 + \tilde{J}_2),$$
$$\tilde{J}_2 = \cos\theta\left\{2(1+\beta)\ln\left|\frac{z_2}{z_1}\right| - [\zeta^2 - (1+\beta)^2]\left(\frac{1}{z_2} - \frac{1}{z_1}\right) - z_2 + z_1\right\}. \tag{A.19a}$$

The integral of the third type:

$$J_3 = \frac{1}{\sin^2\theta}\int_{z_1}^{z_2}\frac{dz}{z^3}\{\delta + (1+\beta+z)\cos\theta - [|f(z)|]^{1/2}\} \tag{A.20}$$

is evaluated in the same manner ([33], Eqs. (2.267.3), (2.266)) and reads:

$$J_3 = \frac{1}{\sin^2\theta}\left\{-\frac{1}{2}[\delta + (1+\beta)\cos\theta]\left(\frac{1}{z_2^2} - \frac{1}{z_1^2}\right) + \cos\theta\left(\frac{1}{z_2} - \frac{1}{z_1}\right)\right.$$
$$\left. + \left(\frac{1}{2z_2^2} + \frac{b}{4az_2}\right)[|f(z_2)|]^{1/2} - \left(\frac{1}{2z_1^2} + \frac{b}{4az_1}\right)[|f(z_1)|]^{1/2}\right.$$
$$\left. - \left(\frac{b^2}{8a} - \frac{1}{2}\right)(I_1(z_2) - I_1(z_1))\right\}. \tag{A.21}$$

For $\sin\theta = 0$:

$$J_3 = \frac{1}{\tilde\delta + 1 + \beta}(J_2 + \tilde{J}_3),$$
$$\tilde{J}_3 = -\cos\theta\left\{\frac{1}{2}\ln\left|\frac{z_2}{z_1}\right| + (1+\beta)\left(\frac{1}{z_2} - \frac{1}{z_1}\right) + \frac{1}{4}[\zeta^2 - (1+\beta)^2]\left(\frac{1}{z_2^2} - \frac{1}{z_1^2}\right)\right\}. \tag{A.21a}$$

Finally, for the integral over the states below the Bragg plane the following function may be introduced $(\alpha = \cos\theta)$

$$Q(\zeta, \zeta_1, \zeta_2, \beta, \gamma, \alpha) = J_1 + 2\beta J_2 - \beta^2 J_3. \tag{A.22}$$

Here, as for the functions $P$ and $S$, $\zeta_1 = -\zeta$ and $\zeta_2 = 1$. For the integration over the states above the plane, the function (A.22) should be substituted for

$$-Q(\zeta, \zeta_1, \zeta_2, -\beta, \gamma, \alpha),$$

where now $\zeta_1 = 1$ and $\zeta_2 = \zeta$. The final results for the three cases a, b and c are presented in Sect. 7, (51 a—c).

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