

ENERGY-BAND STRUCTURE OF SOLIDS FROM A PERTURBATION ON THE “EMPTY LATTICE”^{*†}

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Abstract—A simple perturbation approach is developed to obtain the energy-band structure of solids. The unperturbed Hamiltonian consists of the kinetic part and of a uniform potential; the perturbing operator is the crystal potential plus a term which originates from the requirement that valence and conduction states be orthogonal to the inner states. This amounts to an approximation to the O.P.W. method.

Reasons are given for the validity of such a simple scheme and applications are made to the case of the diamond lattice and of the zincblende lattice.

It is shown how features of the energy-band structure depend on the symmetry of the lattice, on the lattice parameter and on the “core states” of the atomic components. Numerical results obtained for diamond, silicon and BN are in fair agreement with recent calculations.

An energy-band structure consistent with experimental information is obtained for Ge and GaAs by fixing the values of a few parameters.

1. INTRODUCTION

IN THE past few years a number of calculations of the energy-band structure of solids have been published⁽¹⁾ and in the case of many monatomic solids the energies of a number of valence and conduction states have been computed with a remarkable amount of labor.

An examination of the results obtained on different elements having the same lattice symmetry and a comparison with results of calculations on fictitious crystals^(2,3,4) seem to indicate that the relative positions of the energy levels at symmetry points of the Brillouin zone and the general energy-band structure are quite independent of the lattice potential. The important regularities characteristic of the monovalent

metals in the body centered cubic structure have been discussed by COHEN and HEINE⁽⁵⁾ on the basis of a simplified model derived from the Wigner-Seitz method.

It is recognized that similar regularities exist for every crystal symmetry. We want to point out that they can be most easily explained in the framework of the Orthogonalized Plane Wave (O.P.W.) method. The reason why this can be done is the same one which is responsible for the good convergence of the O.P.W. method itself, namely the approximate cancellation of the Fourier coefficients of the crystal potential against the terms arising from the procedure of orthogonalization of the trial wave functions to the core states. As recognized by PHILLIPS and KLEINMAN⁽⁶⁾, the effect of orthogonalization is formally equivalent to the addition of a repulsive term in an effective Hamiltonian acting on the non-orthogonalized trial wave functions. Though this extra term does not have in general the simple form of a

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potential function of coordinates $V_r(\mathbf{r})$, PHILLIPS and KLEINMAN found that an approximate "effective potential" $V_r(\mathbf{r})$ can be simply constructed from the O.P.W. method. ANTONCIK⁽⁷⁾ makes use of the same idea, but approximates the repulsive potential by a formula derived from the statistical theory of the atom. The calculations performed using these simplifications give good results in the case of diamond,⁽⁸⁾ where only s core states are present, but are not so accurate in the case of silicon.⁽⁹⁾ The idea of a repulsive potential has been mainly successful in the formulation of an interpolation scheme,⁽¹⁰⁾ in which the high Fourier coefficients of $V_r(\mathbf{r})$ are assumed to cancel exactly the high Fourier components of the crystal potential and the low Fourier components are chosen to fit a few calculated or experimental values.

The justification of these procedures first suggested by COHEN⁽¹¹⁾ will be used here to show that the combined effect of the crystal potential and the repulsive term can be treated as a perturbation on the eigenstates of a uniform potential. In this scheme the first and second order corrections to the energy of a level can be visualized as arising from the core states of the atoms composing the crystal and from the first few Fourier coefficients of the crystal potential and thus a criterion is given for predicting the positions of energy levels belonging to different irreducible representations of the group of the wave vector \mathbf{k} .

This simple approach will be shown to give qualitative information on the energy-band structure of crystals with diamond and zincblende type structure. A quantitative application of the method to the case of diamond, silicon and boron nitride gives results in good agreement with previous calculations. A simplified interpolation scheme has been set up in this framework, which is shown to reproduce the band structure obtained by PHILLIPS for Ge⁽¹⁰⁾ and is further applied to the case of gallium arsenide.

2. PERTURBATION APPROACH TO THE O.P.W. METHOD

Let $H = H_0 + V(\mathbf{r})$ be the one-electron Hamiltonian of the crystal and let ψ_c be the wave functions of the core states, which satisfy the equations $H\psi_c = E_c\psi_c$, where E_c is the atomic eigenvalue for the core state c . The unperturbed Hamiltonian

H_0 is the sum of the kinetic energy and the Fourier coefficient $V(0)$ of the potential, so that the space average of $V(\mathbf{r})$ can be taken to be zero.

The eigenfunction $\psi^\alpha(\mathbf{k}, \mathbf{r})$ of a valence or conduction state associated with the irreducible representation α of the group of \mathbf{k} is determined in the O.P.W. method by putting

$$\begin{aligned} \psi^\alpha(\mathbf{k}, \mathbf{r}) &= \phi^\alpha(\mathbf{k}, \mathbf{r}) \\ &- \sum_c (\psi_c, \phi^\alpha) \psi_c(\mathbf{k}, \mathbf{r}) \end{aligned}$$

and expanding ϕ in the appropriate set of symmetrized linear combinations of plane waves. The Schrödinger equation can be transformed into:

$$(H + R)\phi = E\phi \quad (1)$$

where the operator R is defined by:

$$R\phi = \sum_c (E - E_c) (\psi_c, \phi) \psi_c. \quad (1')$$

It is clear that the function ϕ is not uniquely defined. In fact, adding to ϕ any arbitrary combination of core wave-functions we obtain a wave function ϕ' which satisfies equations (1) and (1') and gives the same results for $\psi^\alpha(\mathbf{k}, \mathbf{r})$ and E . It is possible in principle to remove this indeterminacy from ϕ by substituting R in equation (1) with an operator R' defined by:

$$R'\phi = \sum_c (\psi_c, A\phi) \psi_c \quad (1'')$$

where A is any chosen operator. Then the solutions of the equation:

$$(H + R')\phi = E\phi \quad (2)$$

also satisfy equation (1) because by multiplying equation (2) on the left by ψ_c and integrating we obtain, for every value of the index c :

$$(\psi_c, A\phi) = (E - E_c) (\psi_c, \phi). \quad (3)$$

However, now the function ϕ belonging to a given eigenvalue E is uniquely defined because of equation (3).

Several choices of A are possible: (a) for $A = 0$, ϕ reduces to the eigenfunction ψ ; (b) for $A = E - H$ equation (3) becomes an identity and gives back the equations (1) and (1'); (c) for $A = -V$, equation (1) becomes:

$$H_0\phi + V\phi - \sum_c (\psi_c, V\phi) \psi_c = E\phi \quad (4)$$

and this shows that the orthogonalization has the effect of subtracting from $V\phi$ that part which can be expanded over the core states, that is a large fraction of the potential V near the nuclei is cancelled. The most convenient choice depends on the method used to solve equation (2).

In the present paper $V+R'$ will be treated as a perturbation and R' will be defined by choosing the operator A in such a way that $\phi^\alpha(\mathbf{k}, \mathbf{r})$ be as close as possible to a combination of a few plane waves of the appropriate symmetry. Rules have been given in detail by HERMAN⁽¹²⁾ and others to construct such combinations. In short the "empty lattice" analysis is first performed, grouping into a set all the plane waves of the form $\exp[i(\mathbf{k} + \mathbf{h}_i)\mathbf{r}]$ belonging to the same eigenvalue of H_0 ,

$$W_i^0 = V(0) + \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{h}_i|^2.$$

As usual, \mathbf{k} indicates the reduced wave vector and \mathbf{h}_i a reciprocal lattice vector. Out of every set one then forms linear combinations $S_i^\alpha(\mathbf{k}, \mathbf{r})$ which transform according to a given irreducible representation α of the group of the \mathbf{k} vector. Matrix elements of $V+R'$ between S_i^α and S_j^β will vanish for $\alpha \neq \beta$, so that the correct zero order linear combinations are directly obtained by symmetry arguments, unless the same irreducible representation appears more than once in a given set or it appears in two sets which lie close in energy in the empty lattice.

To obtain general formulae let us consider the case of two quasi-degenerate or degenerate states $S_1^\alpha(\mathbf{k}, \mathbf{r})$ and $S_2^\alpha(\mathbf{k}, \mathbf{r})$ having energies W_1^0 and W_2^0 with $W_1^0 \leq W_2^0$. The perturbed wave functions of these states are expanded as follows:

$$\phi = c_1 S_1 + c_2 S_2 + \sum_j' a_j S_j$$

where S_1 and S_2 appear only in the zero-order combination $S_1^0 = c_1 S_1 + c_2 S_2$ which is normalized to unity. For the lower energy level we set $E_1 = W_1^0 + W_1' + W_1''$. Substituting into (2) and considering zero and first-order terms together we obtain:

$$\begin{aligned} c_1(S_1, (H+R')S_1) + c_2(S_1, (V+R')S_2) \\ = (W_1^0 + W_1')c_1 \\ c_1(S_2, (V+R')S_1) + c_2(S_2, (H+R')S_2) \\ = (W_1^0 + W_1')c_2 \end{aligned} \quad (5)$$

Solving equation (5) one obtains the first-order correction to the energy and the zero-order correct wave function S_1^0 . For the coefficients a_j we obtain:

$$a_j = \frac{(S_j, (V+R')S_1^0)}{W_1^0 - W_j^0}$$

The energy to second order is then formally given by the same expression as for a non-degenerate level; but now S_1^0 needs not to be an eigenfunction of the unperturbed Hamiltonian.

$$\begin{aligned} E_1 = (S_1^0, (H+R')S_1^0) \\ + \sum_j' \frac{(S_1^0, (V+R')S_j) (S_j, (V+R')S_1^0)}{W_1^0 - W_j^0} \end{aligned} \quad (6)$$

The question arises at this point as to which is the most convenient form of the operator R' to be inserted into equations (5) and (6). In the Appendix we show that the requirement that ϕ be as close as possible to S_1^0 is consistent with considering $R'\phi$ as the sum of a first order term.

$$R_1'\phi = \sum_c (W_1^0 - E_c) (\psi_c, \phi) \psi_c$$

and a second order correction

$$R_2'\phi = \sum_c W_1' (\psi_c, \phi) \psi_c$$

The first order term is the one used in obtaining W_1' and S_1^0 from equation (5). When both terms are substituted into equation (6) the second order correction to the energy becomes:

$$\begin{aligned} W_1'' = W_1' \sum_c |(\psi_c, S_1^0)|^2 \\ + \sum_j' \frac{|(S_1^0, V S_j) + \sum_c (W_1^0 - E_c) (S_1^0, \psi_c) (\psi_c, S_j)|^2}{W_1^0 - W_j^0} \end{aligned} \quad (7)$$

The perturbation formulae so obtained reduce to the ones previously derived in the appendix of Ref. (2) in the case of well separated unperturbed eigenvalues.

The problem of checking the convergence of the method cannot be treated without considering higher order terms in the perturbation expansion,

which is extremely unpractical. The confidence that the present method gives a reliable picture and can be used in practice lies mainly in the cancellation between the attractive potential and the repulsive term, which makes the matrix elements of the perturbation very small. As in the case of the O.P.W. method^(6,7) a great simplification is introduced if the repulsive operator R' is substituted by a repulsive potential appropriate to the core state and independent of ϕ since then the present approach does not differ from the usual free electron perturbation theory except for the fact that the perturbation is now the total potential $V+R'$ instead of the crystal potential V . The perturbation method in this simplified form has been presented in 1954 by ANTONCIK⁽⁷⁾, who applied it to some metals of the b.c.c. structure. The accuracy of the results obtained in this way depends on the choice of the repulsive potential and is poorer in general than in our more consistent approach; in the case of Si for instance, the error introduced into the first order perturbation term by choosing the repulsive effective potential suggested by KLEINMAN and PHILLIPS⁽⁹⁾ or the one used by ANTONCIK⁽⁷⁾ would not be negligible. This simplification however can be probably accepted when the method is used as an interpolation scheme, where the values of the Fourier coefficients of the total potential are chosen *a posteriori*; it becomes then very similar to the interpolation scheme used by PHILLIPS⁽¹⁰⁾ on Si and Ge and by HARRISON⁽¹³⁾ on some polyvalent metals.

The present formulation allows one to draw up some qualitative rules for the sequence of the energy levels at a given symmetry point of the Brillouin zone. From formulae (5) and (6) one sees that the lowest energy levels in the empty lattice will be the lowest levels in the perturbed crystal too. The first order correction is generally positive, its magnitude depends on the structure of the matrix element determined from the irreducible representation considered and on the core eigenstates which belong to the same irreducible representation. *s*-Like states will have a larger term than *p*-like states and *d*-like states because the orthogonality coefficients are larger. In the second order correction the interaction with higher unperturbed states decreases the energy and the interaction with lower unperturbed states increases the energy, the correction decreasing as

the states are farther apart. The preceding arguments are mostly valid at symmetry points, where the group theoretical classification of the plane waves is of great advantage.

In proximity of a symmetry point the number of levels to be treated as quasi-degenerate becomes larger. It is then convenient to resort to the perturbation approach discussed by KANE⁽¹⁴⁾. In the following applications to the study of the energy-band structure of solids in the diamond and zincblende structure we shall be concerned only with energy levels at special points. In a more detailed study of experimental data the effect of spin-orbit interaction should also be considered.

3. THE DIAMOND LATTICE STRUCTURE: NUMERICAL RESULTS FOR Si AND DIAMOND

The perturbation approach described in Section (2) will now be tested for crystals with the diamond structure.

We will consider unperturbed energy values up to the energy

$$8 \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2$$

where a is the lattice constant. The value of $V(0)$ can be estimated in the same way as by HERMAN and WOODRUFF⁽¹⁵⁾ or can be directly inferred from experimental data.⁽⁹⁾ The effect of the perturbation on the various energy levels is obtained from formulae (5), (6) and (7). The symmetry analysis given in Table 1, Ref. (2), in Table 2 of HERMAN's paper⁽¹²⁾ and in Table 5 of CASELLA's paper⁽⁴⁾ enables one to obtain explicit expressions for the energy levels at the symmetry points Γ ($\mathbf{k} = 0$),

$$X \left(\mathbf{k} = \frac{2\pi}{a} (1,0,0) \right) \text{ and } L \left(\mathbf{k} = \frac{2\pi}{a} \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) \right)$$

as functions of the Fourier coefficients of the crystal potential $V(\mathbf{h}_i)$, of the orthogonality coefficients

$$(\psi_c, S_i^{\alpha}(\mathbf{k}))$$

and of the core energies E_c .

Qualitative considerations can be immediately drawn in the way indicated in Section (2). At the point $\mathbf{k} = 0$ the lowest lying valence level is expected to be Γ_1 . There will be a splitting of the levels Γ_2' , $\Gamma_1(2)$, Γ_{25}' , and Γ_{15} which come next in

the empty lattice. The first order perturbation increases the energy of $\Gamma_1(2)$ and $\Gamma_{2'}$ more than that of Γ_{15} and $\Gamma_{25'}$ for light elements because the repulsion from s -states is larger than that from p -states and $\Gamma_1(2)$ is further raised at second order by the positive interaction with $\Gamma_1(1)$. The second order correction lowers $\Gamma_{25'}$ with respect to Γ_{15} because of the interaction with the set $\langle 200 \rangle$ in the former case. The sequence of the energy levels at the Γ point in the diamond structure is then:

$$\Gamma_1 < \Gamma_{25'} < \Gamma_{15} \sim \Gamma_{2'} < \Gamma_1(2)$$

This is verified in calculations on C, Si and pseudocrystals. However, HERMAN's calculations for Ge⁽¹⁶⁾ give $\Gamma_{2'}$ lower than Γ_{15} ; we think that this can be attributed to the presence of d -core states which raise Γ_{15} with respect to $\Gamma_{2'}$ which is an s -like state.

in lattice constant and consequently an increase in the energy gap as experimentally observed.⁽¹⁷⁾

Quantitative results can also be obtained from formulae (5), (6), and (7) with a small amount of labor. We have carried out the calculations for silicon using the same core states and crystal potential as KLEINMAN and PHILLIPS^{(9)*} rather than the expressions given by WOODRUFF⁽¹⁵⁾, which one of us used in a previous O.P.W. calculation.⁽¹⁸⁾ In Table 1 we give our numerical results and for comparison the results obtained by KLEINMAN and PHILLIPS, who used their "effective potential method" but introduced corrections to make it equivalent to a complete O.P.W. method. The difference in the results due to our use of the perturbation approach is seen to be not significantly large with a maximum difference of about 0.1 Ry for the level L_3 . The agreement can still

Table 1. Energy levels at points Γ , X , L in Si (in Ry)

Irr. rep.	Γ_1	$L_{2'}$	X_1	L_1	X_4	L_3	$\Gamma_{25'}$	$X_1(2)$	Γ_{15}	L_3	$L_1(2)$
Present calculations	-2.35	-2.15	-2.08	-2.00	-1.73	-1.60	-1.57	-1.32	-1.32	-1.22	-1.19
KLEINMAN and PHILLIPS ⁽⁹⁾	-2.32	-2.11	-2.01	-1.96	-1.77	-1.70	-1.56	-1.38	-1.35	-1.28	-1.18

At the other symmetry points of the Brillouin zone also, the sequence of the energy levels at each point can be inferred in the same way and is in agreement with the calculations performed and with the experimental evidence available. However, very little can be said in this qualitative way about the relative position of energy levels at different symmetry points.

It is to be expected from the present approach that an increase in the lattice constant will contract the energy scale of the empty lattice eigenvalues and consequently will make the separation between final energy levels smaller. This is in agreement with the experimental observation that the energy gap and the valence band width decrease going from diamond to silicon to germanium. On this basis one can also explain qualitatively the effect of pressure on the energy gap; an increase in pressure will cause a decrease

be improved by including more plane waves in the perturbation expansion since this will lower our energies for the states $L_{3'}$ and L_3 by a few hundredths of a Rydberg and have a much smaller effect on the other states. However, the main interest of this calculation is that of showing that perturbation corrections of order higher than second are small enough to have a negligible effect on the general energy-band structure. The quantitative application of this procedure to the case of diamond has also been made but in this case we felt justified to use for the operator R' in equations (5) and (6) the effective repulsive potential evaluated by KLEINMAN and PHILLIPS⁽⁸⁾. The results for s -like states are quite good but, as expected,

* We are very grateful to Dr. KLEINMAN for giving us the new values of the "orthogonality coefficients" which were not reproduced in the paper of Ref. (9).

the p -like states Γ_{15} , $\Gamma_{25'}$, X_4 , L_3 and L_3' do not show the same good convergence because of the absence of the repulsive terms in this case. However, the relative position of these states is obtained correctly and, by adding a constant value (-0.3 Ry) to compensate for the neglect of plane waves of higher energy, we can still reproduce the correct energy-band structure. In Table 2 our results are

are reviewed by CALLAWAY⁽¹⁾ and by WELKER and WEISS⁽²³⁾. An O.P.W. calculation has been done by KOBAYASHI on SiC.⁽²⁴⁾

The application to this structure of the perturbation procedure described in Section (2) has been carried out in detail. The Crystal Symmetry Combinations of Plane Waves (C.S.C.P.W.) are chosen to be the same as in the diamond structure

Table 2. Energy levels at points Γ , X , L in diamond (in Ry)

	Γ_1	L_2'	X_1	L_1	X_4	L_3'	$\Gamma_{25'}$	Γ_{15}	$X_1(2)$	L_3	$L_1(2)$
Present results	-2.44	-1.98	-1.66	-1.48	-1.30	-1.02	-0.79	-0.36	-0.23	-0.04	-0.03
HERMAN's results	-2.41	-1.97	-1.64	-1.55	-1.29	-1.14	-0.80	-0.35	-0.28	-0.14	-0.14

given together with the results reported by KLEINMAN and PHILLIPS⁽⁸⁾, which are extrapolations of HERMAN's previous results.⁽¹⁵⁾ The general energy band structure is the same but the states L_3' , L_3 , $L_1(2)$ are about 0.1 Ry higher in our calculations. We feel that this is not an essential disagreement and can be sensibly reduced just by including a larger number of plane waves in the perturbation approach.

We have not performed numerical calculations of this kind on Ge but we might expect that the effect of orthogonalizing to the d -core states will be to raise the energies of the states Γ_{15} and L_3 with respect to that of the predominantly s -like states Γ_2' and $L_1(2)$.

4. THE ZINCBLLENDE STRUCTURE: NUMERICAL RESULTS FOR BN

This structure consists of two f.c.c. lattices made of different atoms, one of the lattices being obtained from the other by a translation $a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, a being the lattice constant. The symmetry analysis of the Brillouin zone has been given by PARMENTER⁽¹⁹⁾ and we will use his notations. HERMAN⁽²⁰⁾ and CALLAWAY⁽²¹⁾ have made qualitative considerations on the energy bands by considering the crystal potential as a perturbation on the diamond lattice potential; along the same line KLEINMAN and PHILLIPS⁽²²⁾ have given results for BN; other calculations and experimental data

at the points Γ and L . At these points the number of irreducible representations for the zincblende structure is half as much as for diamond, because the group of the k vector for the diamond structure is the direct product of that of the zincblende structure times the group composed by identity and inversion. The situation is different at the point X , where the two-dimensional irreducible representation X_1 in diamond splits into X_1 and X_3 (one dimensional) in zincblende, and similarly X_2 splits into X_2 and X_4 . The other irreducible representations of diamond X_3 and X_4 coalesce into X_5 . In order to get real matrix elements we found it convenient to use for X_1 and X_3 new C.S.C.P.W.'s obtained by taking the origin at a lattice point. The irreducible representations which appear in the lowest empty-lattice levels are given in Table 3. The C.S.C.P.W.'s can be taken from previous papers on the diamond structure⁽¹²⁾ except those belonging to the irreducible representations X_1 and X_3 which are given in Table 4. A connection between the matrix elements of the zincblende and the diamond lattice can be established by dividing the crystal potential and the repulsive terms in two parts, which are symmetric and antisymmetric about the middle point of the two nearest atoms. The method of Section (2) enables one to derive explicit expressions for the energy values of all irreducible representations listed in Table 3. We do not think it necessary to give tables for them, but rather we will discuss

Table 3. Symmetry analysis of the "Empty Lattice" in the zincblende structure

Number of plane waves	Empty lattice eigenvalues		Irreducible representations
	in units	$\frac{\hbar^2}{2m} \times \frac{4\pi^2}{a^2}$	
Point Γ $\mathbf{k} = 0$	1	$(0, 0, 0)^2$	$\Gamma_1(s)$
	8	$(1, 1, 1)^2$	$2\Gamma_1, 2\Gamma_{15}(p, d)$
	6	$(2, 0, 0)^2$	$\Gamma_{15}, \Gamma_1, \Gamma_{12}(d)$
	12	$(2, 2, 0)^2$	$\Gamma_1, 2\Gamma_{15}, \Gamma_{25}, \Gamma_{12}$
Point X $\frac{2\pi}{a}(1, 0, 0)$	2	$(1, 0, 0)^2$	$X_1(s, p, d), X_3(s, p, d)$
	4	$(0, 1, 1)^2$	$X_1, X_3, X_5(p, d)$
	8	$(1, 2, 0)^2$	$X_1, X_3, 2X_5, X_2(p, d), X_4(p, d)$
	8	$(2, 1, 1)^2$	$2X_1, 2X_3, 2X_5$
Point L $\frac{2\pi}{a}(1/2, 1/2, 1/2)$	2	$(1/2, 1/2, 1/2)^2$	$2L_1(s, p, d)$
	6	$(3/2, 1/2, 1/2)^2$	$2L_1, 2L_3(p, d)$
	6	$(1/2, 3/2, 3/2)^2$	$2L_1, 2L_3$
	6	$(5/2, 1/2, 1/2)^2$	$2L_1, 2L_3$
	2	$(3/2, 3/2, 3/2)^2$	$2L_1$

N.B.—The core states which belong to a given irreducible representation are indicated in parentheses every time the irreducible representation appears first.

the qualitative features as done for the diamond structure.

At the point Γ the lowest eigenvalue will be Γ_1 . The first order correction to the energy of this state contains only the symmetric part of the potential and is very close to that for the diamond structure. The second order correction is expected to be larger than in the diamond structure because of terms from the antisymmetric part of the potential. The second eigenvalue of Γ_1 is degenerate in zero order and as a result of the splitting in first order due to the antisymmetric perturbation this level will be lowered with respect to the

corresponding Γ_2' of the diamond structure. The next irreducible representation Γ_{15} is also degenerate in zero order and the effect of the antisymmetric potential to first order will be to lower $\Gamma_{15}(1)$ with respect to Γ_{25}' of the diamond structure and to raise $\Gamma_{15}(2)$ with respect to Γ_{15} of the diamond structure. The expected order of the energy levels will then be:

$$\Gamma_1 \ll \Gamma_{15}(1) < \Gamma_1(2) \sim \Gamma_{15}(2).$$

The relative positions of $\Gamma_1(2)$ and $\Gamma_{15}(2)$ depend on the core states which are present; if there are

Table 4. Crystal symmetry combinations of plane waves in the zincblende structure with the origin at a lattice point for the wave vector $\mathbf{k} = 2\pi/a(100)$ (point X)

Set of plane waves	C.S.C.P.W. for X_1 and X_3
$\langle 100 \rangle$	$1/\sqrt{2}[(100) \pm (\bar{1}00)]$
$\langle 011 \rangle$	$1/2 [(011) + (0\bar{1}\bar{1}) \pm (0\bar{1}1) \pm (01\bar{1})]$
$\langle 120 \rangle$	$1/\sqrt{8} [(120) + (\bar{1}20) + (102) + (\bar{1}02) \pm (\bar{1}20) \pm (\bar{1}\bar{2}0) \pm (\bar{1}02) \pm (\bar{1}0\bar{2})]$
$\langle 211 \rangle$	$1/\sqrt{8} [211) + (2\bar{1}\bar{1}) + (2\bar{1}1) + (2\bar{1}\bar{1}) \pm (2\bar{1}\bar{1}) \pm (2\bar{1}1) \pm (2\bar{1}\bar{1}) \pm (21\bar{1})]$
	$1/\sqrt{8} [(211) + (2\bar{1}\bar{1}) - (2\bar{1}1) - (2\bar{1}\bar{1}) \pm (2\bar{1}\bar{1}) \pm (2\bar{1}1) \mp (2\bar{1}\bar{1}) \mp (21\bar{1})]$

N.B.—In any of the combinations of plane waves the first choice of signs gives a combination belonging to X_1 , and the second choice the combination belonging to X_3 .

other core states besides (1s) we may expect $\Gamma_1(2)$ to lie lower than $\Gamma_{15}(2)$.

A similar analysis at the point L , also with the help of the Table 3, gives the sequence:

$$L_1(1) < L_1(2) \ll L_3(1) \ll L_1(3) \approx L_3(2).$$

If p or d core states are present, we expect $L_1(3)$ to be lower than $L_3(2)$.

At the point X the levels X_1 and X_3 correspond to the twice degenerate level X_1 of diamond. They differ by a consistent change in sign of the anti-symmetric terms in all matrix elements. The levels X_5 correspond to the levels X_4 of the diamond structure. The sequence of levels that we expect will be:

$$X_1(1) < X_3(1) < X_5(1) < X_1(2) < X_3(2) < X_5(2).$$

An energy gap exists and the material is an insulator when $\Gamma_{15}(1)$, $L_3(1)$ and $X_5(1)$ are all lower than the levels appearing next in the sequences. This appears always to be the case for the compounds which are known to crystallize in this structure.

We have made numerical computations for BN using the parameters reported by KLEINMAN and PHILLIPS⁽²²⁾ and their repulsive potential approximation to the operator R' , as we have done for diamond, because only the core state 1s is present. As in the case of diamond the convergence of p -like states is rather poor and the same correction -0.3 Ry has been added to the states Γ_{15} , X_5 , and L_3 . The results so obtained from our usual perturbation on the "empty lattice" are shown in Table 5 together with the results of KLEINMAN and PHILLIPS⁽²²⁾ obtained from a perturbation on the diamond lattice. While the general energy-band structure in both approximations displays the same physical features, increase in the energy gap with respect to diamond and splitting of the

valence band into two separated bands, the quantitative results do not show the same good agreement as in the cases of Si and diamond. A complete O.P.W. calculation on BN is in progress.

It is a rather difficult task to predict the relative positions of levels of the same band at different points of the Brillouin zone because the difference is very small and is rather sensitive to the particular elements which form the structure. In the case of BN the minimum of the lowest conduction band was found at the point X (see Table 5), but for the elements with p and d core states as GaAs, InSb, CdS ... we may expect the minimum to be at the center of the zone and to be the state $\Gamma_1(2)$ since the effect of p and d core states is to increase the energies of X_1 , X_3 , L_1 and Γ_{15} with respect to that of $\Gamma_1(2)$ as can be seen from Table 3 and more clearly from the matrix elements of the perturbation. These considerations are in agreement with the results obtained by SHAKIN and BIRMAN⁽²⁵⁾ in ZnS with the Wigner-Seitz method.

5. ENERGY BAND STRUCTURE OF Ge AND GaAs

It seems of interest to use the present method as an interpolation scheme for the case of Ge and GaAs, where the large number of electrons would make the calculation of the parameters quite laborious. These two crystals are very similar having the same kind of core states and lattice constants nearly equal, $a = 5.647$ Å in Ge and $a = 5.635$ Å in GaAs. For both of them we approximate the repulsive operator R' of Section (2) with an effective potential depending on the core states. The quantity $V+R'$ which appears as a perturbation on the "empty lattice" is called the total potential and we consider its Fourier coefficients as disposable parameters as PHILLIPS has done with the O.P.W. method.⁽¹⁰⁾ We assume

Table 5. Energy values at the symmetry points Γ , X and L in BN (in Ry)

	Γ_1	L_1	X_1	$L_1(2)$	X_5	X_3	L_3	Γ_{15}	$X_1(2)$	$\Gamma_{15}(2)$	$X_3(2)$	$\Gamma_1(2)$	$L_1(3)$
Present calculations	-2.52	-2.24	-2.17	-1.45	-1.34	-1.33	-1.06	-0.95	-0.45	-0.32	-0.17	-0.14	-0.13
KLEINMAN and PHILLIPS	-2.48	-2.16	-2.07	-1.42	-1.21	-1.37	-1.26	-1.16	-0.39	-0.11	-0.29	-0.31	-0.20

that the effect of the perturbation on the "empty lattice" can be represented by giving appropriate values to a few Fourier coefficients of the total potential and that the other Fourier coefficients are zero because of the cancellation between the crystal potential and the repulsive term near the nucleus. The constant part of the crystal potential does not have any effect on the relative positions

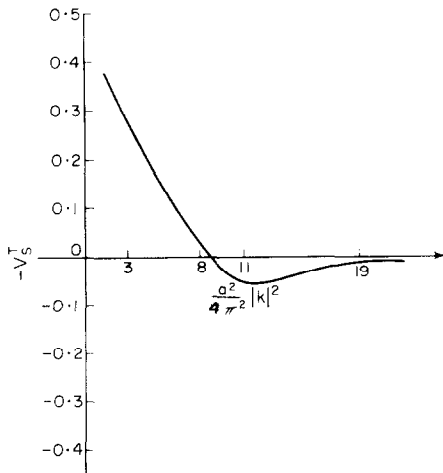


FIG. 1. Fourier coefficients of the total effective potential assumed for Ge (in Ry).

of the energy bands in our approximation, but the first order correction contains a term arising from the core states, which has the effect of raising the energy of s -like states more than that of other states. Unlike PHILLIPS⁽¹⁰⁾ we take this effect into account by allowing for two Fourier coefficients with wave vector 0, one $V_s(0)$ for s -like states and the other $V_p(0)$ for non s -like states. Their difference is taken as one of the parameters and can be fitted to give the experimental energy gap of Ge. The other values of the parameters are chosen according to estimates of their order of magnitude and to the requirement of reproducing the experimental energy levels. The experience with Si, diamond and BN suggests that the Fourier coefficients of the total potential can be represented as functions of $|K|^2$ in the way indicated in Fig. 1 for the symmetric part to be considered in the case of Ge (see Fig. 2 of Ref. (3) for comparison with the case of Si). For the Fourier coefficients of the antisymmetric part of the potential we

assume a behavior as indicated in Fig. 2. In this way the energy-band structure of Ge is made to depend on the values of the parameters $V_s(0) - V_p(0)$, $V_s(3)$ and $V_s(11)$, the other Fourier coefficients of the potential being considered negligible; the energy-band structure of GaAs is made to depend on the same quantities plus the additional parameter $V_A(3) = V_A(4)$. Using

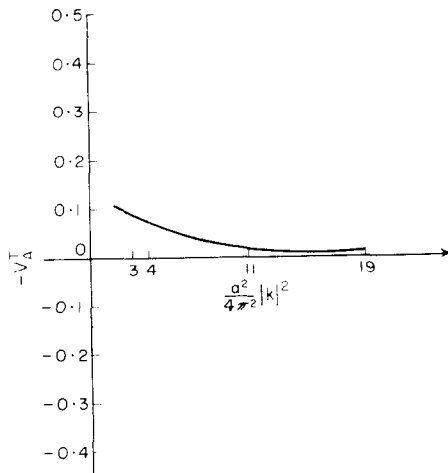


FIG. 2. Antisymmetric Fourier coefficients of the total effective potential assumed for GaAs (in Ry).

this scheme the calculation of the energy levels becomes very simple. For the lowest valence state Γ_1 for instance the formula is:

$$E_{\Gamma_1} = V_s(0) - \frac{4|V_s(3)|^2}{3\left(\frac{2\pi}{a}\right)^2} - \frac{4|V_A|^2}{3\left(\frac{2\pi}{a}\right)^2} - \frac{6|V_A|^2}{4\left(\frac{2\pi}{a}\right)^2}.$$

In other cases the method of Section (2) has been used to split the degeneracies and the quasi-degeneracies. The sets of plane waves $\langle 300 \rangle$ and $\langle 221 \rangle$ at the point X and $\langle \frac{5}{2}, \frac{3}{2}, \frac{1}{2} \rangle$ at the point L have also been considered in addition to those reported in Table 3; their effect is that of lowering the higher states at the points L and X by about 0.02 Ry. We have performed calculations with slightly different sets of values for the parameters and in all cases we have obtained basically the same energy-band structure with differences of the order of 0.01 Ry; since this is the order of magnitude of the energy separation of the various

Table 6. Energy values at the points Γ , X , L in Ge and in GaAs (in Ry)

Irr. rep.	Energy in Ge	Irr. rep.	Energy in GaAs
Γ_1	-0.80	Γ_1	-0.84
L_2'	-0.69	L_1	-0.81
X_1	-0.51	X_1	-0.78
		X_3	-0.34
L_1	-0.36	L_1	-0.34
X_4	-0.12	X_5	-0.14
L_3'	-0.01	L_3	-0.03
Γ_{25}'	+0.09 (0.09)	Γ_{15}	+0.04 (0.03)
Γ_2'	+0.15 (0.15)	Γ_1	+0.14 (0.14)
L_1	+0.14 (0.14)	L_1	+0.15 (≥ 0.16)
X_1	+0.20 (~ 0.17)	X_1	+0.19 (≥ 0.18)
		X_3	+0.29
Γ_{15}	+0.34	Γ_{15}	+0.32
L_3	+0.39	L_3	+0.40

N.B.—The values in brackets are the experimental values. The scale is adjusted to Γ_{25}' in Ge and $\Gamma_1(2)$ in GaAs. The experimental values for $L_1(3)$ and $X_1(2)$ in GaAs are the lowest limit since they are appropriate to minima in the direction $[111]$ and $[100]$.⁽²⁶⁾

minima of the conduction band the choice of the parameters is rather critical if the correct order has to be obtained for energy levels at different points of the reduced zone. With $V_S(3) = -0.230$ Ry and $V_S(11) = +0.055$ Ry the minimum of the conduction band in Ge turns out to be the state $L_1(2)$ as experimentally observed. The values of $V_s(0)$ and $V_p(0)$ which adjust the scale for s -like and p -like states respectively are $V_s(0) = -0.60$ Ry and $V_p(0) = -0.64$ Ry. The results obtained for Ge are reported in Table 6 together with the experimental values as given by PHILLIPS⁽¹⁰⁾. Our results as well as the values of the parameters are very close to those of PHILLIPS⁽¹⁰⁾ because of the similar interpolation schemes, however our choice of the parameters allows a better agreement with the experimental results. In Table 6 are also given the results for GaAs obtained with $V_A = -0.075$ Ry together with the values of a few energy levels which can be inferred from the band structure assumed by EHRENREICH⁽²⁵⁾ to interpret transport properties in GaAs. The main effect of the heteropolar term V_A is seen to be that of lowering the energy of $\Gamma_{15}(1)$ in GaAs with respect to that of Γ_{25}' in Ge with the result of increasing the energy gap by an amount in reasonable agreement with experiment; the energy of $\Gamma_1(2)$ is also slightly lowered with respect

to that of Γ_2' in Ge so that the minimum of the conduction band is now at the centre of the zone. While the first effect is probably a general result

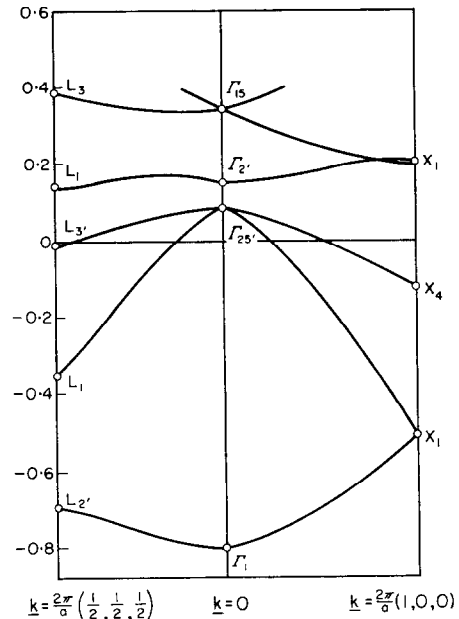


FIG. 3. Energy-band structure of Ge (energies in Ry).

of the method, the change in position of the minimum of the conduction band is strongly dependent on the choice of the parameters and on the number of plane waves considered so that little significance can be attached to it. The energy band structures of Ge and GaAs obtained by joining the points of Table 6 are sketched in Fig. 3 and Fig. 4 respectively. We have not interpolated explicitly along the two symmetry lines Λ and Δ but we feel confident that the results of such

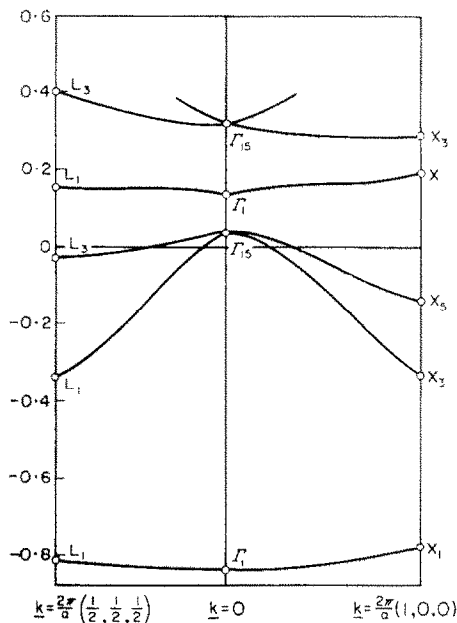


FIG. 4. Energy-band structure of GaAs (energies in Ry).

a detailed interpolation would be essentially the same as those found by PHILLIPS⁽¹⁰⁾. The predictions on some energy levels proposed by CALLAWAY for GaAs⁽²¹⁾ are confirmed, except for the level $L_3(1)$ which is not sensibly changed from Ge. The valence band is separated into two subbands, the lowest of which appears to be very narrow; this result could be experimentally detected by soft X-ray emission as already pointed out by KLEINMAN and PHILLIPS⁽²²⁾.

6. CONCLUSIONS

The simplified approach we have given to derive qualitative features and quantitative results for

the energy-band structure does not rule out the necessity for more precise calculations, but it is justified in view of the present uncertainty related to such calculations. Its main advantage is that of exhibiting explicitly the role of the lattice symmetry, core states and lattice parameter on the energy-band structure of different compounds. The critical role played by the few lowest Fourier coefficients of the potential with the corresponding terms from the core states explains the good results obtained in spite of the poor knowledge of the crystal potential. This also points to the conclusion that the energy-band structure is not strongly dependent on the potential and on the degree of ionicity of the crystal. We feel that our method, or the more complete O.P.W. method, could be also applied to obtain the conduction bands of ionic crystals though it may not be appropriate for the energy levels of the valence states.

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APPENDIX

As an additional condition on the operator A and the function ϕ , we require that the contribution to ϕ from combinations of plane waves other than S_1 and S_2 be as small as possible. This can be simply achieved by minimizing the quantity:

$$\begin{aligned} & \sum_j |a_j(W_1^0 - W_j^0)|^2 \\ &= \sum_j |(S_j, VS_1^0) + \sum_c (S_j, \psi_c)(\psi_c, AS_1^0)|^2 \end{aligned} \quad (\text{A1})$$

with respect to the parameters (ψ_c, AS_1^0) . We obtain the condition:

$$\sum_j (\psi_c, S_j) \{ (S_j, VS_1^0) + \sum_{c'} (S_j, \psi_{c'}) (\psi_{c'}, AS_1^0) \} = 0. \quad (\text{A2})$$

Using the completeness of the set $\langle S_j \rangle$ equation (A2)

can be written:

$$\begin{aligned} & (\psi_c, VS_1^0) - (\psi_c, S_1^0)(S_1^0, VS_1^0) \\ &+ (\psi_c, AS_1^0) - \sum_{c'} (\psi_c, S_1^0)(S_1^0, \psi_{c'}) (\psi_{c'}, AS_1^0) = 0. \end{aligned}$$

From the definition of ψ_c and E_c and the orthogonality between S_1^0 and S_j , we finally obtain:

$$\begin{aligned} & (\psi_c, S_1^0) \{ E_c - W_1^0 + (S_1^0, VS_1^0) \} \\ &+ (\psi_c, AS_1^0) - \sum_{c'} (\psi_{c'}, AS_1^0) (\psi_c, S_1^0) (S_1^0, \psi_{c'}) = 0. \end{aligned} \quad (\text{A3})$$

The first order solution of (A3) is:

$$(\psi_c, AS_1) = (W_1^0 - E_c) (\psi_c, S_1^0). \quad (\text{A4})$$

In this way the repulsive term which appears in equations (5) is defined and this allows us to obtain W_1' , S_1^0 and the coefficients a_j . By iteration the solution of (A3) to second order is found to be:

$$(\psi_c, AS_1) = (W_1^0 + W_1' - E_c) (\psi_c, S_1^0). \quad (\text{A5})$$

This is the same result we would obtain from equation (3) by using for ϕ the zero order wave function. Since we have established it independently, we can use equation (A5), together with equation (3) to obtain to first order the following set of linear equations between the coefficients a_j :

$$\sum_j a_j (\psi_c, AS_j) = (W_1^0 - E_c) \sum_j a_j (\psi_c, S_j). \quad (\text{A6})$$

Expressions (A5) and (A6) give equation (7) for the second order correction to the energy when substituted into equation (6).