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UNIVERSITÉ D'OTTAWA
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A DEVELOPMENT OF THE
LCAO METHOD OF ENERGY BAND THEORY:
APPLICATION TO THE DIAMOND STRUCTURE

by

A.R. Briggs

A thesis submitted to the School of Graduate Studies of the University of Ottawa in partial fulfillment of the requirements for the degree of Master of Science in the Department of Physics.

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(iii)

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Date

Chairman

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Table of Contents

Abstract	1
Résumé	2
Chapter 1 THE DEVELOPMENT OF THE LCAO METHOD	
1.1 A Review of the Energy Band Theory	3
1.2 A Development of the Method of LCAO	6
1.3 The Matrix Elements and the Crystal Potential	8
Chapter 2 THE ANALYSIS OF THE LCAO METHOD	
2.1 The Lattice Symmetry and the Reduced Wavevector	13
2.2 The Direct Variational Method	16
2.3 The Factorisation of the Secular Determinant	18
2.4 The Matrix Elements and the Crystal Potential	22
Chapter 3 THE ENERGY BAND CALCULATION	
3.1 The Numerical Analysis	32
3.2 The Effective Atomic Potential	35
3.3 The Crystal Lattice	38
3.4 The Representation of the Crystal Potential	39
3.5 The Matrix Elements and the Multi-Center Integrals	41
Chapter 4 THE RESULT OF THE ENERGY BAND CALCULATION	
4.1 The Numerical Analysis	43
4.2 The Effective Atomic Potential	45
4.3 The Crystal Lattice	45

4.4	The Representation of the Crystal Potential	49
4.5	The Matrix Elements and the Multi-Center Integrals	55
Chapter 5 A DISCUSSION OF THE LCAO METHOD		
5.1	The Application of the Method of LCAO	62
5.2	The Development of the Method of LCAO	65
5.3	The Comparison of the Results	70
5.4	An Interpretation of the Results	71
5.5	The Possibilities of Any Further Developments	74
Appendix 1	THE BLOCH WAVE FUNCTION BASIS	76
Appendix 2	THE FACTORISATION OF THE SECULAR DETERMINANT	84
Appendix 3	THE EXPANSION OF THE LATTICE POTENTIAL	90
Appendix 4	THE TRANSFORMATION OF THE MATRIX ELEMENTS	97
Appendix 5	THE CALCULATION OF THE MATRIX ELEMENTS	101
References		105

List of Tables

Table 1	The Basis Functions of the Unitary Irreducible Representations at the Special-Symmetry Points	23
Table 2	The Independent Matrix Elements of the Symmetrised Basis Functions	24
Table 3	The Transformations for the Cubic Harmonics	26
Table 4	The Independent Matrix Element of the Bloch Wave Function Basis	28
Table 5	The Transformation of the Simplest Two-Center Integrals	30
Table 6	The Lagrange Interpolation Coefficients	34
Table 7	The Effective Atomic Potential	46
Table 8	Analysis of Neighbouring Points in Finite Diamond Lattice	48
Table 9	The Multi-Center Integrals for the Nearer Neighbours	56
Table 10	The Overlap and Energy Elements Summed Over the Individual Shells	59
Table 11	The Energy Eigenvalues at the Symmetry Points	61
Table 12	The Parameters of Four Crystal Structures	63

List of Figures

Figure 1	The Zero-Order Expansion Coefficients	50
Figure 2	The Third-Order Expansion Coefficients	51
Figure 3	The Fourth-Order Expansion Coefficients	52
Figure 4	The Sixth-Order Expansion Coefficients	53
Figure 5	The Seventh-Order Expansion Coefficients	54

Abstract

The LCAO method of energy band theory is equivalent to a linear variational method where atomic orbitals are utilised in defining a competitive Bloch wave function basis. The LCAO method is developed as a general method of calculation in contrast to the qualitative scheme of the traditional tight-binding approximation. The practical limitations imposed by the efficiency of the computational techniques applied are analysed with regard to the critical convergence in such a calculation. The crystal potential of the non-relativistic one-electron Hamiltonian is carefully defined in the absence of a self-consistent calculation. An effective atomic potential is employed in an overlapping atomic potential model incorporating a free-electron exchange treatment appropriate to the crystal lattice. The matrix elements of the basis functions are reduced to a series of three-center integrals in this potential representation. The matrix elements are further reduced to a series of two-center integrals on expanding the lattice potential in a series of cubic harmonics to seventh order. The relation of these integrals through the symmetry of the lattice group decreases the number of individual integrals required. The calculation of the multi-center integrals presents a formidable computational problem which requires extensive optimisation. The diamond structure is tightly bound such that many orders of neighbouring atoms interact. This provides a demanding case study requiring an accurate potential representation and convergence over a substantial number of multi-center integrals. The results of these calculations are analysed for diamond and a comparison is made with recent alternatives for a systematic band calculation.

Résumé

La méthode LCAO de la théorie des bandes est comparable à la méthode linéaire variationnelle où les orbitales atomiques définissent une base compétitive de fonctions de Bloch. La méthode LCAO est utilisée comme méthode générale pour les calculs plutôt que l'approximation qualitative des liaisons fortes dans son cadre général. Les limitations pratiques imposées par les techniques de calcul qui ont été choisies sont analysées ainsi que la convergence critique. Le potentiel cristallin de l'hamiltonien non relativiste est soigneusement défini en l'absence de calcul self consistent. Un potentiel atomique effectif est utilisé dans un modèle de potentiel atomique recouvrement tenant compte de l'échange dû aux électrons libres qui est approprié au réseau. Les éléments de matrices des fonctions de la base sont réduits en une série d'intégrales à trois centres dans ce potentiel. Ensuite, les éléments de matrices sont réduits en une série d'intégrales à deux centres en développant le potentiel cristallin en série d'harmoniques critiques poussée au septième ordre. Les relations de symétrie imposée par la structure de groupe de réseau réduit le nombre d'éléments de matrices nécessaires. Le calcul des intégrales à plusieurs centres présente de grands difficultés et nécessite d'optimiser au maximum. La structure de diamant est fortement liée ce qui nécessite l'utilisation des atomes voisins à plusieurs ordres, par contraste avec l'approximation traditionnelle qui ne tient compte que des proches voisins. On doit donc introduire une représentation du potentiel qui est très détaillée et on doit s'assurer de la convergence en introduisant un grand nombre d'intégrales à plusieurs centres. Les résultats sont particulièrement analysés pour le cas du diamant et des comparaisons sont faites avec d'autres méthodes récentes.

Chapter 1

THE DEVELOPMENT OF THE LCAO METHOD

1.1 A Review of Energy Band Theory.

The energy band theory of electrons in solids is a form of a general many-body problem of periodic structures which is far older than the quantum theory of solids. Although a great amount of work has been done on this general problem, the quantum mechanical formulation of the structure of solids represents a particularly difficult system for solution. The separation of the electronic state and the lattice state of the system allowed by the adiabatic principle reduces the complex problem of a solid to that of a more general class of problems.^(1,2) Although solutions for the three-dimensional wave equation with periodic coefficients have wide application, the practical limitations of the methods so far available are well realized in energy band theory.⁽³⁻⁵⁾ Except for certain solutions available in idealized cases, ⁽⁶⁻⁸⁾ the general progress made has arisen largely from the analysis of the symmetry of the problem where the earlier work concerning the translational symmetry and the later work concerning the point symmetry are now combined in the application of the theory of space groups.⁽⁹⁾

These remarks serve to indicate the sources of severe limitation in the methods available which are present in all level of attempts to formulate the problem. The specialized field of energy band theory is normally concerned with physically interesting solutions; the consequent simplification possible is generally insufficient to overcome the inherent complexity of any adequate model retaining the significant features of the system. (10,11)

The large number and variety of the methods of solution developed for energy band problems reflects the nature of the difficulty involved and the form of the approach amenable to progress. It is not unusual to find good basis for the belief that results may be fortuitous, even in the case of the more successful methods of band theory. In view of this, the success of any development should be judged wherever possible from a direct understanding of the extent to which the method applies. It is therefore necessary never to lose sight of the fundamental problem in any development of an energy band problem in order to be able to appreciate the physical significance of any solution. These elementary observations have influence on the study undertaken here, and no further review of energy band theory will be given unless of direct relevance or for particular illustration.

The central development of energy band theory has been the application of the direct variational method based on the concept of minimizing sequences; in the practical formulation of physical solutions many specialized approaches are available which are directly equivalent to this basic method. The Rayleigh-Ritz method, dominating the modern approach, is comprised of a sequence of a finite linear subspace of a complete normed linear space of functions, and the variety of formulations available reflect the necessary optimization of the rate of convergence in a practical method. Although the problem of convergence is critical, the existence follows for a physical solution while achievement and assessment of convergence is a general problem normally tackled in a direct calculation and where great care is necessary to ensure the validity of the solution. The associated computational problems and limitations are strictly defined and the advent of the modern digital computer has effectively increased the range of calculations possible.⁽¹²⁾ The rate of convergence depends critically on the choice of trial or competitive functions appropriate to the problem under solution. The linear combinations of atomic orbitals or LCAO method employs competitive functions appropriate to the so-called tight-binding approximation, where originally an electron was considered strongly bound by the localized atomic

potentials within the structure.⁽¹³⁾ A principal aim of the present work is to explore the LCAO method as a general quantitative scheme; that is to consider the practical application and the corresponding limitations of linear combinations of atomic orbitals as competitive basis functions in an extensive sense. In order to make any progress in such a study a method allowing solution of the demanding calculation implicit in the LCAO method is necessary. The employment of a set of atomic orbitals as competitive functions has been liable to consideration as generally unsatisfactory, particularly in view of the success of the methods incorporating a set of plane waves in the minimizing sequence; while suggesting a convergence problem this does not preclude the development of the quantitative LCAO method.

1.2 A Development of the Method of LCAO.

On application of the standard adiabatic and Hartree-Fock approximations the non-relativistic Schroedinger equation for a crystal system is reduced to the form of a one-electron problem for the electronic states.^(1,14) The complex structure of a crystal will not allow direct solution of the resulting formulation as is possible in the case of an atomic structure. The concept of a single particle Hamiltonian H may be applied where the one-

electron crystal potential V is no longer considered to be defined by the original formulation and is developed alongside a satisfactory physical model. The Hamiltonian is expressed in a system of units which is closely related to atomic units (a.u.); the unit of length is the Bohr radius ($\hbar^2/me^2$) and the unit of energy is the Rydberg ($me^4/2\hbar^2$).

$$H = -\nabla^2 + V(r) \quad [1.1]$$

In an attempt to interpret the simple LCAO scheme directly in the development, the overlapping atomic potential or OAP is taken as the natural basis for the crystal potential. The corresponding potential $V(r)$ for an elemental solid formed from the atomic potential $v(r)$ at the lattice position vectors R_i is uniquely defined in a manner which ensures the appropriate symmetry of the structure. (15)

$$V(r) = \sum (R_i) v(r-R_i) \quad [1.2]$$

The expression for the potential represents a general form of reduction in the sense that an effective atomic potential $v(r)$ may be considered for a general lattice potential. The choice of an effective atomic potential is therefore equivalent to the crystal potential model; since a self-consistent calculation is unfeasible here the form of this potential is a critical factor. The coulomb and exchange interactions considered here are incorporated in the electrostatic central field and average free electron

exchange terms employed in the construction of the potential. It is reasonable to neglect further effects apart from the inherent simplification in the crystal potential defined, as the treatment of the exchange problem is already inadequate in the normal application.

1.3 The Matrix Elements and the Crystal Potential.

The computational problem is the calculation of the matrix elements of atomic orbitals and the effective atomic potentials distributed over the lattice points in the LCAO and OAP formulations. A rigorous calculation is carried out over the finite range of the lattice defined by the most extensive orbital applied in which all the distinct elements are found. Although in practice a reduced range may contain all the significant elements, in contrast to the first and second nearest neighbours approximation in the quantitative LCAO treatment for the present case of diamond a valence electron will interact with 19 orders of neighbours or 356 nearby atoms in an orbital range of 15 a.u. The free atomic potential in the $(1s)^2(2s)^2(2p)^2$ configuration will be applied with a simple modification employed in other calculations in order to facilitate comparison. The exchange potential applied can dominate the calculation for the tail region of an atomic potential and this largely determines the mean or core-level potential in the OAP.

model.⁽¹⁶⁾ The mean value of the crystal potential with the free atomic potential is approximately -9 Rydbergs and, in calculating the atomic potential, the application of an exchange potential appropriate to the crystal potential required increases this mean level to a realistic value close to -3 Rydbergs. The approximate ranges of the pure and modified atomic potentials are 12 a.u. and 7 a.u. respectively, and their typical spheres of influence enclose 275 and 35 atomic sites in the lattice; these numbers indicate the atomic potentials contributing to the crystal potential at any point. The problem remains to calculate the multicenter integrals defined by the matrix elements of the single particle Hamiltonian with respect to the electron wavefunctions. The evaluation of the matrix elements formed from two LCAO wave functions and an OAP potential is equivalent to that of a set of three-center integrals in a finite range of the lattice; the general form of function for triple integration is the product of an atomic orbital, an effective atomic potential and an atomic orbital centered on distinct lattice positions. The three-center integrals require an elaborate computation which is generally less effective as the separation of the centers increase and the number is prohibitive to a direct calculation. The diamond structure has been selected as a decisive case in view of these problems as the extent of

the atomic orbitals are large with respect to the primitive cell of the lattice and the group of the lattice is non-symmorphic representing the general symmetry form of a crystal potential. The recent attempts to overcome the problems outlined have emphasized methods to evaluate the multicenter integrals efficiently as necessary for severe cases such as diamond.

The development of the calculation concentrates on an optimum representation of the crystal potential in the computation. While the number of effective atomic potentials in the region of integration illustrates the problem it also suggests a simple representation of the crystal potential may have significance. The direct calculation is tackled for reference with the generation of the OAP function defined and although this method allows solution it is an extremely arduous form of the computation. An alternative line of development considers an expansion of the crystal potential $V(r, \theta, \phi)$ in the complete sequence of spherical harmonics $Y_{lm}(\theta, \phi)$ and the corresponding general radial function $a_{lm}(r)$:

$$V(r, \theta, \phi) = \sum_{l,m} a_{lm}(r) \cdot Y_{lm}(\theta, \phi)$$

$$a_{lm} = \int_{\Omega} V(r, \theta, \phi) \cdot Y_{lm}(\theta, \phi) \cdot d\Omega \quad [1.3]$$

The number of terms defining an OAP is therefore reduced in a finite expansion providing a general representation

of the crystal potential; the expansion is related to elementary physical descriptions capable of limited application. The approximate number of free and modified atomic potentials defining the OAP function in the range of finite integration are 3000 and 1200 respectively in the case of diamond. On application of the lattice symmetry, the general expansion in spherical harmonics may be expressed in a reduced sequence of kubic harmonics defined as linear combinations of the elements of the complete sequence. The general form of the matrix elements is reduced to a two-center integral when the crystal potential is expanded about the center of the atomic orbitals in the lattice. A separable analytical form exists relative to the axis defined by the two centers in this class of integrals, allowing analytical integration over the respective azimuthal coordinate. The choice of diamond may also have significance in developing the method as, for example, the traditional choice of lithium with relatively extended orbitals has a body-centered cubic structure of higher symmetry more amenable to a kubic harmonic expansion. The application of the representation outlined reduces the computation by more than an order of magnitude in a simple direct calculation whereas the alternative methods currently being exploited have a tendency to greater complexity and specialization.

In the outline given a simplicity in the general approach has been preserved where the intention is for progress to follow through the optimization of the computational methods. Such ab initio calculations have advanced rapidly lately in requiring specialized and complex treatments; these methods normally employ an analytical development of the atomic structure functions allowing varying simplifications of the computational problem. As an alternative, the method undertaken here employs the atomic structure functions directly and attempts simplification in a satisfactory representation of the physical model. An aim of the thesis is to examine the feasibility of this development in comparison to the recent alternatives. (17)

Chapter 2

THE ANALYSIS OF THE LCAO METHOD

2.1 The Lattice Symmetry and the Reduced Wavevector.

The consideration of the crystal symmetry allows simplification in the calculation of the matrix elements and the representation of the overlapping atomic potential as well as the classification of the electronic wave functions. The diamond structure consists of two face-centered cubic lattices displaced by a quarter of the body diagonal. The primitive lattice is generated by the fundamental translation vectors $\{a_1, a_2, a_3\}$ which are normally defined with respect to the axes of the cube of the associated Bravais lattice of dimensions a ; there are two identical atoms per unit cell separated by a basis vector τ .

$$a_1 = \frac{a}{2}(1, 1, 0) \quad a_2 = \frac{a}{2}(0, 1, 1) \quad a_3 = \frac{a}{2}(1, 0, 1)$$

$$\tau = \frac{a}{4}(1, 1, 1)$$

The reciprocal lattice is body-centered cubic with basis vectors $\{b_1, b_2, b_3\}$ and the first Brillouin zone is in the form of a truncated octahedron.

$$b_1 = \frac{2\pi}{a}(-1, 1, 1) \quad b_2 = \frac{2\pi}{a}(1, -1, 1) \quad b_3 = \frac{2\pi}{a}(1, 1, -1)$$

In the case of diamond the space group O_h^F (Fd3m) is non-symmorphic. In general the group of primitive translations

Γ is an invariant subgroup of the space group S .

Symbolically

$$S = (\Gamma) \cdot (S/\Gamma) = (S/\Gamma) \cdot (\Gamma) \quad [2.1]$$

where the normal divisor (S/Γ) corresponds to the factor

group of the space group with respect to the translation group. The complex of symmetry operations (SIR) form a factor group in which I corresponds to the identity operation. The complex of non-translational symmetry operations

G will not in general form a group. When the basis functions considered contain the translational symmetry of I the functions forming the basis of the factor group will be generated. The representation of the complex G will then correspond to a group. Therefore the complex G may be regarded as a group with respect to any basis invariant under the group I . The factor group O_h^+ has 24 simple and 24 complex operators and is isomorphic to the complete cubic symmetry group. (18, 19)

On applying the Born-von Karman boundary conditions the translational symmetry group I may be expressed as the direct product of the three cyclic abelian groups generated by the fundamental translation vectors. An abelian group of order N necessarily has N one-dimensional representations $I^{(w)}$; since each element forms a class by itself the number of irreducible representations equals the order of the group. The elements of the translation group I all commute with the crystal Hamiltonian and form a group of the Schroedinger equation. Therefore the set of basic functions of the group I is comprised of N orthogonal non-degenerate functions corresponding to distinct

one-dimensional irreducible representations. (20)

Adopting the notation of Jones⁽²¹⁾ the form of the Bloch wave functions $\psi_K(r)$ is defined by the basis functions of the translation group.

$$\Gamma^{(A)}(A_i) = \exp(i \frac{2\pi}{N} A_i) = \exp 2\pi i \left(\frac{a_1}{N_1} s_1 + \frac{a_2}{N_2} s_2 + \frac{a_3}{N_3} s_3 \right)$$

$$\tilde{K} = \frac{1}{N} B \quad \Gamma(A_i) \psi_K(r) = e^{i K \cdot A_i} \psi_K(r) \quad [2.2]$$

A Bloch wave function $\psi_K(r)$ may be constructed from a linear combination of the atomic wave function $\phi_j(r)$ located over the primitive lattice r_j in a single periodicity region R ;

$$r_j = r + \epsilon_j \quad \epsilon_j = \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \end{pmatrix} \quad 0 \leq \epsilon_1, \epsilon_2, \epsilon_3 \leq 1$$

where ϵ_j corresponds to the basis vector of the orbital with respect to a general lattice indexed by n .

$$\psi_K(r) = \sum_R (a_n) e^{i K \cdot A_n} \phi_j(r - A_n) \quad [2.3]$$

The infinite crystal approximation is valid along with the periodic boundary conditions on considering the typical number of atoms in a solid. The symmetry required of a Bloch wave function is given directly within this approximation.

$$\Gamma(A_n) \psi_K(r) = e^{i K \cdot A_n} \psi_K(r) \quad [2.4]$$

The generality of the reduced wave vector representation which simplifies the analysis throughout derives from the form of the LCAO wave function where K is a reciprocal lattice vector.

$$\tilde{K} = \frac{1}{N} B \quad \psi_{K+K'}(r) = \sum_R (a_n) e^{i K \cdot A_n} e^{i K' \cdot A_n} \phi(r - A_n) = \psi_K(r) \quad [2.5]$$

It is convenient to define the LCAO wave functions in terms of an independent lattice.

$$\begin{aligned}\psi_{\underline{k}}^{\sigma}(\underline{r}) &= \sum_{\underline{R}} (\underline{r}) e^{i\underline{k} \cdot \underline{A}\underline{R}} \phi_{\sigma}(\underline{r} - \underline{A}(\underline{r} + \underline{E})) \\ \phi_{\sigma}(\underline{r}) &= e^{i\underline{k} \cdot \underline{A}\underline{E}} \psi_{\sigma}(\underline{r})\end{aligned}\quad [2.6]$$

2.2 The Direct Variational Method.

A Bloch wave function basis allows construction of an approximate solution of Schrodinger's equation which is uniquely defined on application of the linear variational method.

$$(\underline{\Psi}_{\underline{k}}^{\sigma}(\underline{r})) = (\alpha_{\sigma}); (\psi_{\underline{k}}^{\sigma}(\underline{r})) \quad [2.7]$$

The energy eigenvalues $E_{\underline{k}}^{\sigma}$ are calculated directly from the matrix elements of the crystal Hamiltonian and of unity with respect to the basis wave functions. On applying the translational symmetry, the matrix elements take on the following form where H denotes the crystal Hamiltonian and I denotes the identity operator.

$$H_{\underline{k}'\underline{k}}^{\sigma\sigma'} = \langle \underline{k}', \sigma' | H | \underline{k}, \sigma \rangle = \int_{\underline{R}} \psi_{\underline{k}'}^{\sigma'}(\underline{r}') \cdot H(\underline{r}') \cdot \psi_{\underline{k}}^{\sigma}(\underline{r}') d^3r'$$

$$I_{\underline{k}'\underline{k}}^{\sigma\sigma'} = \langle \underline{k}', \sigma' | I | \underline{k}, \sigma \rangle = \int_{\underline{R}} \psi_{\underline{k}'}^{\sigma'}(\underline{r}') \cdot I(\underline{r}') \cdot \psi_{\underline{k}}^{\sigma}(\underline{r}') d^3r'$$

$$H_{\underline{k}'\underline{k}}^{\sigma\sigma'} = N \sum_{\underline{R}} e^{i\underline{k} \cdot \underline{A}\underline{R}} \cdot H_{\underline{k}'\underline{k}}^{\sigma\sigma'} \cdot \delta_{\underline{k}'\underline{k}}$$

$$H_{\underline{k}'\underline{k}}^{\sigma\sigma'} = \int_{\underline{R}} \phi_{\sigma'}^{\sigma'}(\underline{r}' - \underline{A}\underline{E}') \cdot H(\underline{r}') \cdot \phi_{\sigma}(\underline{r}' - \underline{A}\underline{E} - \underline{A}\underline{E}) \cdot d^3r'$$

$$I_{\mathbf{k}\mathbf{k}'} = N \sum_{\mathbf{n}} \exp(i\mathbf{k} \cdot \mathbf{A}_{\mathbf{n}}) \int_{\mathbf{r}} \delta_{\mathbf{k}\mathbf{k}'} \cdot \delta_{\mathbf{k}\mathbf{k}'}$$

$$g_{\mathbf{n}}^{\mathbf{k}\mathbf{k}'} = \int_R \phi_{\mathbf{k}'}^*(\mathbf{r}' - \mathbf{A}_{\mathbf{k}j}) \cdot I(\mathbf{r}') \cdot \phi_{\mathbf{k}}(\mathbf{r}' - \mathbf{A}_{\mathbf{k}j} - \mathbf{A}_{\mathbf{n}}) \cdot d\mathbf{r}'$$

$$\begin{aligned} \delta_{\mathbf{k}\mathbf{k}'} &= 1 & - & \mathbf{k}' - \mathbf{k} = \mathbf{k} \\ &= 0 & - & \mathbf{k}' - \mathbf{k} \neq \mathbf{k} \end{aligned} \quad [2.8]$$

The delta function is defined essentially for the case of the reduced wavevector and it expresses the irreducible representation of the translation group with respect to the LCAO basis functions.

On applying the one-electron crystal Hamiltonian to the general formulation given a separation is possible into a kinetic energy and local potential operator and a remaining crystal potential operator. If the atomic eigenvalue $E_0^{\mathbf{k}}$ of an orbital $\phi_{\mathbf{k}}$ is known, a further simplification follows where $v(\mathbf{r})$ denotes the atomic potential function.

$$H = -\nabla^2 + V(\mathbf{r}) = H_0 + H' \quad H_0 = -\nabla^2 + v(\mathbf{r} - \mathbf{A}_{\mathbf{k}j}) \quad [2.9]$$

The independence of the wave functions associated with different wavevectors has been given and in the following analysis the wavevector under consideration need no longer be specified explicitly. The appearance of N in the expressions has no significance; the normalisation is arbitrary and this common factor may be omitted throughout. The revised expressions are given for reference.

$$H_{ij} = E_0 \sum_n \exp(i\mathbf{k} \cdot \mathbf{A}_0) \cdot g_n^{ij} + \sum_n \exp(i\mathbf{k} \cdot \mathbf{A}_n) \cdot H_n^{ij} \rightarrow$$

$$H_n^{ij} = \int_R \phi_i^*(\mathbf{r} - \mathbf{A}_j) \cdot H(\mathbf{r}) \cdot \phi_j(\mathbf{r} - \mathbf{A}_i - \mathbf{A}_n) \cdot d^3\mathbf{r}$$

$$I_{ij} = \sum_n \exp(i\mathbf{k} \cdot \mathbf{A}_n) \cdot g_n^{ij}$$

$$H_{ij} = \sum_n \exp(i\mathbf{k} \cdot \mathbf{A}_n) \cdot H_n^{ij}$$

$$H_{ij} = E_0 I_{ij} + H_{ij} \quad [2.10]$$

The atomic potential $v(\mathbf{r})$ and associated eigenvalue E_0 can be consistently applied for either orbital center.

The results of this section are developed in appendix 1.

2.3 The Factorization of the Secular Determinant.

The Rayleigh-Ritz direct variational method is employed where the functional J is the quantum mechanical expectation value and the finite minimizing sequence the set of linear combinations of the LCAO wave functions considered. (22)

$$J[\Psi_i] = \frac{\int_R \Psi_i^* H \Psi_i d\tau}{\int_R \Psi_i^* \Psi_i d\tau} \quad [2.11]$$

The solution for the minimal values E_i of the extremum reduces to a system of linear homogeneous equations; the necessary and sufficient conditions for a non-trivial wave function solution corresponds to the characteristic equation of the system. (23)

$$(\bar{\Psi}_i) = (a_{ij}) \cdot (\Psi_j) \quad | H_{ij} - E I_{ij} | = 0 \quad [2.12]$$

The critical rate of convergence depends on the choice of the finite minimizing sequence M_m of order m and determines the practical limitation of the method. The LCAO wave function is of a general form for the basis of the irreducible representation of the translation group when the component function ϕ_j is no longer restricted to an atomic orbital. The variational formulation can therefore in principle represent the wave function of appropriate symmetry to any degree of accuracy through the choice of the minimizing sequence which is defined by the set of functions ϕ_j . The translational symmetry alone has been considered and further restrictions on the minimizing sequence arise from the symmetry of the entire space group.

Adopting the convention of Slater, (19) the operations of the complex G may be expressed directly in terms of an orthogonal transformation matrix R and a non-primitive translation vector τ .

$$G(R, \tau) \psi_k(r) = \psi_k(Rr + \tau) \quad [2.13]$$

On application of the alternative formulation of a Bloch wave function and the invariance of a scalar product under an orthogonal transformation it follows that the form of the Bloch wave function is preserved under the operations of the associated factor group.

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

$$\Gamma(A_0) u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})$$

$$\mathbf{k} \cdot \mathbf{R}_{\mathbf{r}} = \mathbf{R}^{-1} \mathbf{k} \cdot \mathbf{R}^{-1} \mathbf{R}_{\mathbf{r}} = \mathbf{R}^{-1} \mathbf{k} \cdot \mathbf{r}$$

$$G(\mathbf{R}, \mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{r}}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{R}_{\mathbf{r}} + \mathbf{r}) = e^{i\mathbf{R}^{-1} \mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}'(\mathbf{r})$$

$$u_{\mathbf{k}}'(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{R}_{\mathbf{r}} + \mathbf{r})$$

$$\Gamma(A_0) u_{\mathbf{k}}'(\mathbf{r}) = u_{\mathbf{k}}'(\mathbf{r}) \quad [2.14]$$

The symmetry of the last expression is a natural consequence of the lattice invariance under the space group. The operations of the complex G generate the star of the wavevector such that at a symmetry point in the zone there exists a subgroup of operations leaving the wavevector invariant. This subgroup is the group of the wavevector and the eigenfunctions of the Schroedinger equation correspond to the basis functions of the irreducible representation of the little group. An irreducible representation of the entire group is determined by the irreducible representation of the little group. (24)

The analysis of symmetry in the LCAO method allows the factorization of the secular determinant on application of the group theoretical matrix element theorem. At a general point in the zone the number of wavevectors in the star equals the order of the complex and the little group consists of the identity element; there are no further symmetry requirements for the eigenfunctions and no possible

factorization for the secular determinant. At a symmetry point in the zone the little group is no longer trivial and the eigenfunctions form a basis of irreducible representations of the group of the wavevector. The symmetrized eigenfunctions are found directly on applying the elementary theory of group representations; the decomposition theorems and the basis function generating machinery are sufficient. (25)

The three non-equivalent symmetry points Γ , X , L in the notation of Bouckaert, Smoluchowski and Wigner (BSW) will be considered. (26) The s and p (x,y,z) orbitals centered on the two face-centered cubic lattices are employed in the competitive Bloch wavefunctions. The eight trial functions are indexed with respect to the first or second sublattices; the corresponding basis vectors are conveniently chosen as $\underline{e}_1$ and $\underline{e}_2$.

$$M_8 = \sum_{\lambda=1,2} \{ |s_{\lambda}\rangle, |x_{\lambda}\rangle, |y_{\lambda}\rangle, |z_{\lambda}\rangle \}$$

$$\underline{e}_1 = (0, 0, 0) \quad \underline{e}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \quad [2.15]$$

The group of the wavevector at the Γ point contains the entire complex of 48 operations. The general representation decomposes into two one-dimensional and two three-dimensional representations. At the X point the group of the wavevector is of order 32 and the representation factors into four two-dimensional irreducible representations. There are only 12 elements in the wavevector group at the

L point; there are four one-dimensional and two two-dimensional irreducible representations in the general representation. The simplified secular determinant factorizes into linear and quadratic terms and the corresponding symmetrized eigenvectors and the associated matrix elements are listed in table 1 and table 2 respectively; the symmetrical relations between the matrix elements of the LCAO wave functions will be given later. (27-30)

The results of this section are considered in appendix 2.

2.4 The Matrix Elements and the Crystal Potential.

A convenient representation of the crystal potential in the calculation is given by a cubic harmonic expansion. The cubic harmonics are the basis functions of the representations of the cubic symmetry groups. (31,32). It is sufficient to consider the set of cubic harmonics $K_n(\theta, \phi)$ which are invariant under the diamond group; these are the basis functions of the trivial one-dimensional representation. (33-35)

$$V(r, \theta, \phi) = \sum_{l,m} a_{lm}(r) Y_{lm}(\theta, \phi) = \sum_n V_n(r) K_n(\theta, \phi)$$

$$V_n(r) = \int_{\Omega} K_n(\theta, \phi) \cdot V(r, \theta, \phi) \cdot d\Omega = \sum_{\mathbf{R}_0} \int_{\Omega} K_n(\theta, \phi) \cdot v(\mathbf{r} - \mathbf{R}_0) d\Omega \quad [2.16]$$

The integrals in the lattice summation are reduced by a transformation which is developed in appendix 3. The

Table 1
The Basis Functions of
the Unitary Irreducible Representations
at the Special Symmetry Points.

Point	B.S. & W.	Basis Functions
$\Gamma: \frac{2\pi}{a}(0,0,0)$	Γ_1	$ 5_1\rangle + 5_2\rangle.$
	Γ'_2	$ 5_1\rangle - 5_2\rangle.$
	Γ_{15}	$ x_1\rangle + x_2\rangle, y_1\rangle + y_2\rangle, z_1\rangle + z_2\rangle.$
	Γ'_{15}	$ x_1\rangle - x_2\rangle, y_1\rangle - y_2\rangle, z_1\rangle - z_2\rangle.$
$X: \frac{2\pi}{a}(1,0,0)$	X_1	$ 5_1\rangle + 5_2\rangle, x_1\rangle - x_2\rangle.$
	X_2	$ x_1\rangle + x_2\rangle, 5_1\rangle - 5_2\rangle.$
	X_3	$(y_1\rangle + y_2\rangle) + (y_1\rangle + y_2\rangle), (y_1\rangle - y_2\rangle) + (y_1\rangle - y_2\rangle).$
	X_4	$(y_1\rangle + y_2\rangle) - (y_1\rangle + y_2\rangle), (y_1\rangle - y_2\rangle) - (y_1\rangle - y_2\rangle).$
$L: \frac{2\pi}{a}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	L_1	$ 5_1\rangle + e^{-ik \cdot T} 5_2\rangle.$
	L_2	$(x_1\rangle + y_1\rangle + z_1\rangle) - e^{-ik \cdot T} (x_2\rangle + y_2\rangle + z_2\rangle).$
	L'_2	$ 5_1\rangle - e^{-ik \cdot T} 5_2\rangle.$
	L'_2	$(x_1\rangle + y_1\rangle + z_1\rangle) + e^{-ik \cdot T} (x_2\rangle + y_2\rangle + z_2\rangle).$
	L_3	$(x_1\rangle + y_1\rangle) + e^{-ik \cdot T} (x_2\rangle - y_2\rangle),$ $(x_1\rangle + y_1\rangle - 2 z_1\rangle) + e^{-ik \cdot T} (x_2\rangle + y_2\rangle - 2 z_2\rangle).$
	L'_3	$(x_1\rangle - y_1\rangle) - e^{-ik \cdot T} (x_2\rangle - y_2\rangle),$ $(x_1\rangle + y_1\rangle - 2 z_1\rangle) - e^{-ik \cdot T} (x_2\rangle + y_2\rangle - 2 z_2\rangle).$

Table 2

The Independent Matrix Elements of
the Symmetrised Basis Functions

B.S.&W.	Independent Matrix Elements
σ, σ	$H_{11} = 2 (\langle s, 1s \rangle \pm R \langle s, 1s \rangle)$
π, π	$H_{11} = 2 (\langle x, 1x \rangle \pm R \langle x, 1x \rangle)$
$2, x_1$	$H_{11} = 2 (\langle s, 1s \rangle + R \langle s, 1s \rangle)$ $H_{12} = 2g (\langle s, 1x_1 \rangle + \langle s, 1x_2 \rangle)$ $H_{22} = 2 (\langle x, 1x_1 \rangle + R \langle x, 1x_2 \rangle)$
x_1, x_2	$H_{11} = 4 (\langle y, 1y_1 \rangle + R \langle y, 1y_2 \rangle \pm R \langle y, 1y_2 \rangle \pm R \langle y, 1y_2 \rangle)$
$2s, 2s$	$H_{11} = 2 \langle s, 1s \rangle \pm \frac{2}{\sqrt{2}} (-R \langle s, 1s \rangle + g \langle s, 1s \rangle)$ $H_{12} = 3 (2R \langle s, 1x \rangle \pm \frac{2}{\sqrt{2}} (-R \langle s, 1x \rangle + g \langle s, 1x \rangle))$ $H_{22} = 3 (2 \langle x, 1x \rangle \pm \frac{2}{\sqrt{2}} (-R \langle x, 1x \rangle + g \langle x, 1x \rangle))$ $+ 6 (2R \langle x, 1y \rangle \pm \frac{2}{\sqrt{2}} (-R \langle x, 1y \rangle + g \langle x, 1y \rangle))$
L_3, L_3	$H_{11} = 4 (\langle s, 1x \rangle - R \langle x, 1y \rangle - -$ $- \pm \frac{1}{\sqrt{2}} (-R \langle x, 1x \rangle + g \langle x, 1x \rangle) - -$ $- \pm \frac{1}{\sqrt{2}} (-R \langle x, 1y \rangle + g \langle x, 1y \rangle))$

simplified form requires a single one-dimensional integration for each lattice shell and the summation may be expressed in terms of the indices j and k referring to the order of the lattice shell and the members of that shell respectively.

$$V_n(r) = \sum_{j,k} K_n(\theta_{jk}, \phi_{jk}) \cdot S_{n,j}(r) = \sum_j S_{n,j}(r) \sum_k K_n(\theta_{jk}, \phi_{jk})$$

$$S_{n,j}(r) = 2\pi \int_0^1 \sqrt{(r^2 + R_j^2 - 2rR_j t)^{1/2}} \cdot P_n(t) dt \quad [2.17]$$

In the computation an equivalent transformation of the original kubic harmonic form was employed in an integration with respect to θ in the plane $y=0$ for practical reasons. The kubic harmonics, Legendre polynomials and the equivalent transformations are given in table 3.

The matrix elements for evaluation in equation [2.10] may be reduced to the following form where R_j is the difference of the position vectors of the atomic orbitals involved.

$$R_j = A(\xi + \eta - \xi\mu)$$

$$\langle \mu | H | \nu \rangle = \sum_R (R_j) \exp(iK \cdot R_j) \cdot E_{\mu\nu}(R_j)$$

$$E_{\mu\nu}(R_j) = \int_R \varphi_\mu^*(r) \cdot H(r) \cdot \varphi_\nu(r - R_j) \cdot d^3r \quad [2.18]$$

It remains to deduce that all the independent matrix elements are given through the restriction $\xi\mu = 0$ in which case R_j ranges over the lattice position vectors; the two basis vectors have been defined as 0 and 1 . It is convenient

Table 3

The Transformations for the Kubic Harmonics.

Order	Kubic Harmonic	Legendre Form	Alternative Form
0	$\frac{1}{\sqrt{N}} \cdot 1$ $\frac{1}{N} = \frac{1}{4\pi}$	1	$\frac{1}{1}$
3	$\frac{1}{\sqrt{N}} \cdot \frac{1}{r^3} (xy z)$ $\frac{1}{N} = \frac{(3 \cdot 5 \cdot 7)}{4\pi}$	$\frac{1}{2} (5t^3 - 3t)$	$\frac{1}{r^3} (z^3 - 3zx^2)$ $\hat{r}$
4	$\frac{1}{\sqrt{N}} \cdot \frac{1}{r^4} (x^4 + y^4 + z^4 - \frac{3}{2}r^4)$ $\frac{1}{N} = \frac{5^2 \cdot 3 \cdot 7}{4 \cdot 4\pi}$	$\frac{1}{8} (35t^4 - 30t^2 + 3)$	$\frac{1}{r^4} (z^4 + x^4 - 6z^2x^2)$
6	$\frac{1}{\sqrt{N}} \cdot \frac{1}{r^6} (x^2y^2z^2 - \frac{1}{105}r^6 - \frac{1}{22}(x^4 + y^4 + z^4 - \frac{3}{2}r^4)r^2)$ $\frac{1}{N} = \frac{5^2 \cdot 13^2 \cdot 3 \cdot 11 \cdot 17}{4^2 \cdot 4\pi}$	$\frac{1}{16} (231t^6 - 315t^4 - 105t^2 - 5)$	$\frac{1}{r^6} (z^6 - 15z^4x^2 + 15z^2x^4 - x^6)$
7	$\frac{1}{\sqrt{N}} \cdot \frac{1}{r^7} (xyx(x^4 + y^4 + z^4 - \frac{3}{2}r^4))$ $\frac{1}{N} = \frac{11^2 \cdot 3 \cdot 5 \cdot 7 \cdot 13}{4^2 \cdot 4\pi}$	$\frac{1}{16} (429t^7 - 693t^5 + 315t^3 - 35t)$	$\frac{1}{r^7} (z^7 - 21z^5x^2 + 35z^3x^4 - 7zx^6)$

to index the vectors $\underline{R}_i^{\lambda}$ by the respective sublattices and that the LCAO wavefunctions are easily expressed in terms of the lattice position vectors.

$$\{\underline{R}_i\} = \{\underline{R}_i^{\lambda}; \lambda = 1, 2\} \quad \underline{R}_i^2 = \underline{R}_i^1 + \underline{1}$$

$$|1i\rangle = \sum (\underline{R}_i^1) e^{i\mathbf{k} \cdot \underline{R}_i^1} \varphi_1(\underline{r} - \underline{R}_i^1); |2i\rangle = \sum (\underline{R}_i^2) e^{i\mathbf{k} \cdot \underline{R}_i^2} \varphi_2(\underline{r} - \underline{R}_i^2); \dots \quad [2.19]$$

The relations between the various matrix elements are found on applying the symmetrical equivalence of the two displaced sublattices and are listed in table 4; the $|1i\rangle$, $|1j\rangle$ and $|2i\rangle$ eigenfunctions are symmetrically equivalent and therefore interchangeable in the analysis. In a previous section the matrix elements were required for the OAP with a potential omitted at one of the atomic sites now chosen at the lattice origin. The elements $E_{\mu\nu}(\underline{R}_i)$ then reduce to a series of three-center integrals.

$$H^1(\underline{r}) = V^1(\underline{r}, \theta, \phi) = \sum (\underline{R}_i \neq 0) V(\underline{r} - \underline{R}_i) = \sum^1 (\underline{R}_i) V(\underline{r} - \underline{R}_i)$$

$$E_{\mu\nu}^1(\underline{R}_i) = \sum^1 (\underline{R}_i) \int_R \varphi_{\mu}^*(\underline{r}) \cdot V(\underline{r} - \underline{R}_i) \cdot \varphi_{\nu}(\underline{r} - \underline{R}_i) \cdot d^3r \quad [2.20]$$

There are symmetry relations between the components $E_{\mu\nu}(\underline{R}_i)$ in a given shell arising from the simple elements of the complex G ; these are given by considering the symmetry operations directly. An efficient development will allow direct computation of the matrix elements in an energy band calculation and will also serve as a reference for comparison with alternative formulations. The notation of this

Table 4

The Independent Matrix Elements of
the Bloch Wave Function Basis

Independent Elements	Equivalent Elements	Definition of Elements
$\langle s_1 H s_1 \rangle$	$\langle s_2 H s_2 \rangle$	$\sum (\underline{R}_j^1) e^{i\mathbf{k} \cdot \underline{R}_j^1} \cdot E_{ss}(\underline{R}_j^1)$
$\langle s_1 H s_2 \rangle$	$\langle s_2 H s_1 \rangle^*$	$\sum (\underline{R}_j^2) e^{i\mathbf{k} \cdot \underline{R}_j^2} \cdot E_{ss}(\underline{R}_j^2)$
$\langle s_1 H x_1 \rangle$	$-\langle s_2 H x_2 \rangle^*$	$\sum (\underline{R}_j^1) e^{i\mathbf{k} \cdot \underline{R}_j^1} \cdot E_{sx}(\underline{R}_j^1)$
$\langle s_1 H x_2 \rangle$	$-\langle s_2 H x_1 \rangle^*$	$\sum (\underline{R}_j^2) e^{i\mathbf{k} \cdot \underline{R}_j^2} \cdot E_{sx}(\underline{R}_j^2)$
$\langle x_1 H x_1 \rangle$	$\langle x_2 H x_2 \rangle$	$\sum (\underline{R}_j^1) e^{i\mathbf{k} \cdot \underline{R}_j^1} \cdot E_{xx}(\underline{R}_j^1)$
$\langle x_1 H x_2 \rangle$	$\langle x_2 H x_1 \rangle^*$	$\sum (\underline{R}_j^2) e^{i\mathbf{k} \cdot \underline{R}_j^2} \cdot E_{xx}(\underline{R}_j^2)$
$\langle x_1 H y_1 \rangle$	$\langle x_2 H y_2 \rangle^*$	$\sum (\underline{R}_j^1) e^{i\mathbf{k} \cdot \underline{R}_j^1} \cdot E_{xy}(\underline{R}_j^1)$
$\langle x_1 H y_2 \rangle$	$\langle x_2 H y_1 \rangle^*$	$\sum (\underline{R}_j^2) e^{i\mathbf{k} \cdot \underline{R}_j^2} \cdot E_{xy}(\underline{R}_j^2)$

section is based on the treatment of Slater and Koster.⁽³⁶⁾

The application of the cubic harmonic expansion of the OAP $V'(r, \theta, \phi)$ reduces the elements $E_{\mu\nu}(\underline{R}_i)$ to a series of two-center integrals.

$$V'(r, \theta, \phi) = \sum_n V'_n(r) \cdot K_n(\theta, \phi)$$

$$E_{\mu\nu}(\underline{R}_i) = \sum_n \int_A \varphi_\mu^*(\underline{r}) \cdot V'_n(r) \cdot K_n(\theta, \phi) \cdot \varphi_\nu(\underline{r} - \underline{R}_i) \cdot d^3r \quad (2.21)$$

A separable analytical form exists relative to the axis along $\underline{R}_i$ allowing analytical integration over the corresponding azimuthal coordinate.⁽³⁷⁾ The transformations of the cubic and spherical harmonics in a general frame of reference are required.⁽³⁸⁾ The transformation analysis generates the form of the independent two-center integrals in any lattice shell and the component $E_{\mu\nu}$ may be expressed in terms of the reduced integrals and the direction cosine $(\ell_{jk}, m_{jk}, n_{jk})$ of the vector $\underline{R}_{jk}$. The transformation of the function and the analytical reduction of the integration are outlined in appendix 4. A basic set of the transformation for the first cubic harmonic is summarized in table 5; the notation is borrowed from chemical physics,⁽³⁹⁾ where the symbols $\sigma, \pi, \delta \dots$ refer to the azimuthal component of angular momentum and the symbols $s, p, d \dots$ refer to the orbitals contributing. This class of simpler integrals corresponds to the traditional two-center tight-binding approximation where the reduction may

Table 5
The Transformation of the Simplest
Two-Center Integrals.

Component	Transformation
$E'_{ss}(R_{jk})$	$1.55\sigma_j$
$E'_{sx}(R_{jk})$	$l_{jk}(s p \sigma)_j$
$E'_{xx}(R_{jk})$	$l_{jk}^2 \cdot (p p \sigma)_j + (1 - l_{jk}^2) \cdot (p p \pi)_j$
$E'_{xy}(R_{jk})$	$l_{jk} \cdot m_{jk} \cdot (p p \sigma)_j - l_{jk} \cdot m_{jk} \cdot (p p \pi)_j$
$E'_{xz}(R_{jk})$	$l_{jk} \cdot n_{jk} \cdot (p p \sigma)_j - l_{jk} \cdot n_{jk} \cdot (p p \pi)_j$

be applied to evaluate the more significant components of the lattice series for the matrix elements exactly.

$$\int_R \varphi_m^*(\underline{r}) \cdot v(\underline{r} - \underline{R}_j) \cdot \varphi_n(\underline{r} - \underline{R}_j) \cdot d^3r \quad [2.22]$$

The integration is then divided into two components corresponding to the atomic potential $v(\underline{R}_j)$ at the second center $\underline{R}_j$ and the cubic harmonic expansion $V_m''(\underline{r}, \underline{R}_j)$ omitting the contribution from the atomic potential included exactly. The expansion coefficient for an incomplete lattice may be defined rigorously in a general expansion; however, in the present application the original crystal cubic harmonic representation for the complete lattice is extended to the incomplete lattice of lower symmetry.

$$V''(\underline{r}, \theta, \phi; \underline{R}_j) = \sum (\underline{R}_\ell \neq 0, \underline{R}_j) v(\underline{r} - \underline{R}_\ell) = \sum'' (\underline{R}_\ell) v(\underline{r} - \underline{R}_\ell)$$

$$V''(\underline{r}, \theta, \phi; \underline{R}_j) = \sum (m) V_m''(\underline{r}, \underline{R}_j) \cdot k_m(\theta, \phi) \quad [2.23]$$

An analogous method applies when the significant potential terms are omitted in the OAP expansion and evaluated directly. The three-dimensional three-center integrals have therefore been replaced by two-dimensional two-center integrals in the final analysis. If such a potential expansion converges in a reasonable number of terms it will represent a significant efficiency in the calculation.

Chapter 3

THE ENERGY BAND CALCULATION

3.1 The Numerical Analysis.

The basic computational problem in the scheme outlined is the evaluation of the matrix elements. The extensive calculations necessary generate an endless variety of formulations which reflect the degree of optimization necessary in any practical method. The numerical representation of the atomic structure functions and the direct numerical integration which are developed here represent a relatively simple approach in comparison to recent alternatives. In such an attempt an emphasis will be placed on the effectiveness of the numerical techniques necessary to reduce the problem overall and allow progress. The form of the effective atomic potential and the lattice parameter employed were taken to facilitate comparison with an orthogonalized plane-wave method ⁽⁴⁰⁾ and a tight-binding method ⁽⁴¹⁾ available.

A typical three-dimensional integration may require the order of a million increments to achieve the accuracy necessary where an integration mesh with approximately one hundred points per dimension represents a reasonable sampling of the space. An efficient computation requires the simplest representation of the function consistent with the minimum number of increments necessary.

A second-order interpolation was found to represent the atomic structure functions adequately. The Lagrange interpolation formula applies defining the unique polynomial $f(x)$ of second order through the three reference points x_1 , x_2 and x_3 .

$$f(x) = f(x_1) \frac{(x-x_2)(x-x_3)}{(x_1-x_2)(x_1-x_3)} + f(x_2) \frac{(x-x_3)(x-x_1)}{(x_2-x_3)(x_2-x_1)} + f(x_3) \frac{(x-x_1)(x-x_2)}{(x_3-x_1)(x_3-x_2)}$$

$$f(x) = ax^2 + bx + c \quad [3.1]$$

At a general point x the value of an atomic structure function is given by the computation of the quadratic function $f(x)$ with the interpolation coefficients determined by the three neighbouring reference points of x . The interpolation coefficients given in table 6 are required throughout the range of the atomic functions. The method requires an efficient determination of the neighbouring reference points for the general point x . The functions $f(x)$ are generally evaluated at a sequence of points on the integration mesh. In this application this suggests a simple search by working away from the previous reference points for the sequence. This technique was found to be as efficient as any of the more general complex methods developed. The numerical integration of the functions required is carried out by the Simpson quadrature formula.

$$x_{+1} - x_0 = x_0 - x_{-1} = h$$

$$\int_{x_{-1}}^{x_{+1}} f(x) dx = \frac{h}{3} (f(x_{-1}) + 4f(x_0) + f(x_{+1})) \quad [3.2]$$

Table 6

The Lagrange Interpolation Coefficients.

$a(x_1, x_2, x_3)$	$\frac{f(x_1)}{(x_2-x_1)(x_3-x_1)} + \frac{f(x_2)}{(x_1-x_3)(x_2-x_1)} + \frac{f(x_3)}{(x_3-x_1)(x_3-x_2)}$
$b(x_1, x_2, x_3)$	$\frac{-f(x_1)(x_2+x_3)}{(x_2-x_1)(x_3-x_1)} + \frac{-f(x_2)(x_3+x_1)}{(x_2-x_3)(x_2-x_1)} + \frac{-f(x_3)(x_1+x_2)}{(x_3-x_1)(x_3-x_2)}$
$c(x_1, x_2, x_3)$	$\frac{f(x_1) \cdot x_2 \cdot x_3}{(x_2-x_1)(x_3-x_1)} + \frac{f(x_2) \cdot x_3 \cdot x_1}{(x_2-x_3)(x_2-x_1)} + \frac{f(x_3) \cdot x_1 \cdot x_2}{(x_3-x_1)(x_3-x_2)}$

The quadrature is equivalent to an analytical integration of the second-order polynomial passing through the points x_1 , x_0 and x_{-1} . The consistent degree of approximation in the interpolation and quadrature reflects the efficiency of the method.⁽⁴²⁾ This method was found superior to several alternative attempts; the simplicity is a factor determining an efficient computation.

3.2 The Effective Atomic Potential.

The atomic wave functions and energy levels were employed from a Hartree self-consistent field calculation for the ground state (3P) of carbon by Jucy.⁽⁴³⁾ The atomic wave functions are applied in the calculation of an effective atomic potential function following a prescription first suggested by Woodruff.^(44,45) The construction of the effective atomic potential in this manner involves various approximations that have been analysed by several authors.^(40,46,47) The concept of an effective atomic potential is valid where the potential may be determined in principle by a full self-consistent calculation. The alternative forms of effective atomic potential available may generate significant variations in the calculation. In the present application the effective atomic potential selected can be justified very simply. In the outer region of the atomic potential the exchange interaction in the Slater approximation dominates the coulomb interaction

extending the range of the potential. An effective atomic potential given by the truncation of the original atomic potential at the range where the exchange correction dominates is similar to that proposed by Woodruff. The Woodruff formulation considers a range for the exchange potential defined by the radius of the sphere whose volume equals that of the unit cell. The exchange contribution for the valence electrons in the treatment of Woodruff corresponds to that of a uniform charge distribution over the truncated range. The effective atomic potential defines a reasonable mean crystal potential or core level with a considerable shift from that corresponding to the atomic potential, calculated with the Slater exchange. The range of the effective atomic potential developed will reduce the potential overlap within the crystal and the associated error in the treatment of the Slater exchange approximation.

The expressions defining the atomic potential are well known and are given in this section in the notation of Herman and Skillman or Slater. (48,49) There is no significant difference between the absolute atomic units and the practical atomic units defined by the reduced mass in such calculations.

$$(-\nabla^2 + v(r)) R_{nl}(r) Y_{lm}(\theta) \Phi_m(\phi) = E_{nl} R_{nl}(r) Y_{lm}(\theta) \Phi_m(\phi) \quad (3.3)$$

The atomic potential function $v(r)$ is defined by the nuclear coulomb, inner electron shielding, outer electron shielding

and free-electron exchange terms respectively, (50-52)

$$V(r) = -\frac{Z}{r} - \frac{2}{r} \int_0^r \sigma(r') dr' - 2 \int_r^\infty \frac{\sigma(r')}{r'} dr' - 6 \left[\frac{3}{8\pi} \rho(r) \right]^{1/3} \quad [3.4]$$

$$\sigma(r) = 4\pi r^2 \rho(r) = \sum_{n,l} (n,l) \omega_{nl} [r R_{nl}(r)]^2 = \sum_{n,l} (n,l) \omega_{nl} [P_{nl}(r)]^2$$

where the summation extends over all the occupied states with occupation numbers ω_{nl} which are considered to be spherically averaged in the central field approximation. The atomic structure functions $u(r)$ and $P_{nl}(r)$ are conveniently defined following Herman and Skillman employing the Thomas-Fermi parameter for tabulation.

$$\mu = \frac{1}{2} \cdot \left(\frac{3\pi}{4} \right)^{2/3} \cdot 2^{-1/3} = 0.85534138 \cdot 2^{-1/3} \quad r = \mu x \quad [3.5]$$

$$u(r) = -\frac{\pi}{2r} V(r) \quad P_{nl}(r) = r R_{nl}(r)$$

In the present formulation the free-electron exchange potential is given by the modified charge distribution defined in terms of the volume Ω of the unit cell.

$$\Omega = \frac{4}{3} \pi r_3^3: \quad \rho_e(r) = \frac{1}{4\pi r^2} \sum_{(l,m)} 2(2l+1) P_{nl}(r) + \frac{2}{\Omega} \sum_{(l,m)} \omega_{nl} \quad r \leq r_3 \\ = \frac{1}{4\pi r^2} \sum_{(l,m)} 2(2l+1) P_{nl}(r) \quad r > r_3 \quad [3.6]$$

The mean value of the crystal potential $\bar{V}$ is defined by the effective atomic potential and the volume of the unit cell.

$$\bar{V} = \frac{4\pi}{\Omega} \int_0^\infty V(r) \cdot r^2 \cdot dr \quad [3.7]$$

The computations necessary are not demanding and the functions of the charge densities may be interpolated and integrated by the methods outlined in the previous section. The lattice parameter $a=6.728a.u.$ was employed throughout.

3.3 The Crystal Lattice.

A nearest neighbour analysis of the diamond lattice is required in several calculations; the lattice position vectors $\underline{R}_{jk}$ may be ordered with respect to the lattice shell radius $\underline{R}_j$. A simple generation of the diamond lattice in terms of the primitive face-centered cubic lattice is sufficient for the present application.⁽⁵³⁾ The reference frame is defined by the axes of the conventional cubic unit cell having dimensions of four arbitrary units.

$$\underline{a}_1 = \begin{pmatrix} 2 \\ 2 \\ 0 \end{pmatrix}, \quad \underline{a}_2 = \begin{pmatrix} 0 \\ 2 \\ 2 \end{pmatrix}, \quad \underline{a}_3 = \begin{pmatrix} 2 \\ 0 \\ 2 \end{pmatrix}; \quad \underline{t} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad [3.8]$$

$$\underline{R}_{jk} = \underline{A}\underline{n} + \underline{t} = \begin{pmatrix} 2 & 0 & 2 \\ 2 & 2 & 0 \\ 0 & 2 & 2 \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} + \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix} = \begin{pmatrix} 2(n_1 + n_3) + t_1 \\ 2(n_1 + n_2) + t_2 \\ 2(n_2 + n_3) + t_3 \end{pmatrix}$$

The lattice vectors generated in this manner are organised into sets of nearest neighbours. The final data set contains the magnitude, the number and the coordinates of the position vectors for every shell analysed. The main consideration is the efficient flexible retrieval of the information in the data set and the system developed gave reference to any shell distance or to any number of sets of nearest neighbours. The first 150 orders of neighbours with 8165 members within a shell radius of 25 arbitrary units were generated.

3.4 The Representation of the Crystal Potential.

The crystal potential defined by the OAP function is required in the evaluation of the three-center integrals.

$$V(\underline{r}) = \sum (\underline{R}_i) v(\underline{r} - \underline{R}_i) \quad [3.9]$$

The computation requires the determination of the function over the set of points taken in the numerical integration. There are approximately 2×10^5 points over an adequate integration mesh and this is necessarily fixed for all the calculations. The construction of the crystal function represents a massive computation requiring consideration of all the effective atomic potentials within a certain range for every point on the integration mesh. The process of calculation is complex and is undertaken in stages. A neighbouring lattice site $\underline{R}_i$ to the point $\underline{r}$ is determined. The neighbouring effective atomic potentials contributing to the crystal potential at any point $\underline{r}$ can then be systematically considered. There is a significant number of effective atomic potentials contributing to the crystal potential at any point; a minimum number of 35 potentials with a range of 7 a.u. has been given as an example. In the formulation developed it was necessary to consider approximately 150 effective atomic potentials for every point on the integration mesh. A data set containing the neighbouring lattice point for all the points on the integration mesh is generated for reference. The nearest

neighbour in the first face-centered cubic sublattice to a general point $\underline{r}$ was considered for simplicity; the lattice generation with respect to any point of a primitive lattice is trivial. The rhombohedral primitive cell, in which the general point $\underline{r}$ is located, is given directly on factoring the primitive translation vectors,

$$\underline{r} = x\underline{a}_1 + y\underline{a}_2 + z\underline{a}_3 \quad \underline{R}_i = \ell\underline{a}_1 + m\underline{a}_2 + n\underline{a}_3$$

$$\underline{r} = (\ell+r)\underline{a}_1 + (m+s)\underline{a}_2 + (n+t)\underline{a}_3 \quad (0 \leq r, s, t \leq 1)$$

$(\ell+r) = \frac{1}{4}(x+y-z)$, $(m+s) = \frac{1}{4}(y+z-x)$, $(n+t) = \frac{1}{4}(z+x-y)$ [3.10]
 The nearest of the eight neighbours bounding this primitive cell may be found directly. The crystal potential may now be calculated with contributions from the various orders of neighbouring shells corresponding to degrees of approximation in the computation. A flexible form of computation was developed for the construction of the crystal potential function. The main consideration is the efficient retrieval of the crystal function required in the optimized computation of the three-center integrals.

The calculation of the cubic harmonic expansion coefficients is defined by the reduced formulation of equation (2.4). The expansion coefficients are required for the radial coordinates of the integration mesh. The transformations generated may be employed directly in the calculation of the expansion coefficients and also in the representation of the crystal potential. The computation

can be reduced by careful analysis of the calculation; in the case of diamond with the effective atomic potential there are over 40 shells with over 1000 members in the OAP expansion region. A highly efficient computation has been developed to determine the feasibility of generating the coefficients in higher order expansions.

3.5 The Matrix Elements and the Multi-Center Integrals.

The two-center and three-center integrals have the same form and differ only in the number of dimensions for numerical integration. A general computational scheme has been developed for such integrals on a given integration mesh. After some experimentation, an integration mesh was selected with $200 \times 30 \times 30$ increments for the variables r , θ and ϕ respectively; the range of r was limited to 15 a.u. A two-dimensional integration may be taken over any plane on the integration mesh defined by a constant value of ϕ . The restriction to a fixed integration mesh arises for the calculations involving the crystal potential defined over the mesh. A flexible and efficient computational scheme was developed allowing various combinations of the functions available to be integrated; the radial wave functions, the spherical harmonic functions, the cubic harmonic expansion functions and the crystal lattice functions are interchangeable in the computational scheme. The problem of optimization of the three-center integrals was considered

and after intensive development it was found that a limit had been reached. It was concluded that it was not possible to increase the efficiency of calculation of the three-center integrals significantly without adopting a fundamentally different method.

The remaining calculations of the matrix elements and the eigenvalues are straightforward. The details of the programs developed to perform the computations are outlined in appendix 5.

Chapter 4

THE RESULT OF THE ENERGY BAND CALCULATION

4.1 The Numerical Analysis.

In the development of the computational scheme an accuracy corresponding to three significant figures was attained at every stage of the computation. This was determined partly by the accuracy of the atomic structure functions employed; although the atomic wave functions defined the general basis functions, the representation in the computation is only accurate to three significant figures. The number of computations involved in a typical calculation is so great that it is difficult to assess directly the overall accuracy in any computation. An indirect assessment involving considerable experimentation was developed in order to optimise the efficiency of the calculation. The principal result employed in this development is the normalisation of the atomic structure functions; the normalisation integrals were computed in order to test the accuracy of the calculation.

$$\int_R \varphi_{\mu}^*(\mathbf{r} - \mathbf{R}_j) \cdot \varphi_{\mu}(\mathbf{r} - \mathbf{R}_j) \cdot d^3\mathbf{r} = 1 \quad [4.1]$$

The simplest normalisation integration corresponding to two atomic wave functions at the origin of the integration mesh where $\mathbf{R}_j = \mathbf{0}$ does not give a very critical test; it represents an extremely symmetric integral concentrated heavily around the origin. The normalisation integration

corresponding to two atomic wave functions at the center of the lattice cube where $R_j = \frac{1}{2} A_1$ gives a more severe test; the lattice origin is at the origin of the integration mesh. The computed values of these normalisation integrals for the 2s and the 2p orbitals in diamond were 0.985 and 1.033 respectively, suggesting an accuracy to within approximately 3%. It was found by this technique that an integration mesh as fine as 500x50x100 increments gave no significant increase in accuracy. The contributions to the integrals from the extreme inner and outer ranges of the atomic structure functions were investigated. The representation of the atomic structure functions for these special regions was found to be sufficient and no further considerations were necessary.

An analysis of the symmetrically equivalent matrix elements indicates that the precision of the triple numerical integration is of the order of 0.001 Rydbergs; a comparison of the three-dimensional integrations employing the crystal potential function is necessary. The results of the calculations required for such numerical comparisons are found later in the chapter. The degree of accuracy indicated in this analysis is consistently within the theoretical and experimental estimates for the computations involved in a three-dimensional numerical integration.

4.2 The Effective Atomic Potential.

The effective atomic potential function $U(r)$ was calculated directly as outlined and is given in table 7; the X tabulation refers to the method of Herman and Skillman ⁽⁴⁸⁾ of defining a tabulation net employing the Thomas-Fermi scaling parameter μ . The first potential function is calculated with the Slater exchange treatment following Herman and Skillman. The second potential function is calculated in the present treatment with the modified exchange potential outlined; an irregular effect arising from the artificial exchange prescription may be easily detected in the tabulation. The mean values for the crystal potential with the Slater and the present exchange potentials are -9.09 Rydbergs and -3.12 Rydbergs respectively.

The electron energies of the atomic ground state of carbon for the 2s-orbitals and 2p-orbitals are 1.4126 Rydbergs and 0.8632 Rydbergs respectively; the energy band levels will be conveniently considered relative to the 2s-orbital energy as any determination of the absolute energy levels is difficult to justify.

4.3 The Crystal Lattice.

The results of the nearest neighbour analysis for the diamond lattice are summarised in table 8 for the first twenty orders of neighbours. The table illustrates the rapid rate of increase of the total number of

Table 7
The Effective Atomic Potential

X Tabulation	Slater Exchange	Present Exchange
0.00	1.0000	1.0000
0.01	0.9954	0.9953
0.02	0.9887	0.9886
0.03	0.9818	0.9816
0.04	0.9749	0.9746
0.05	0.9680	0.9676
0.06	0.9612	0.9608
0.07	0.9545	0.9540
0.08	0.9479	0.9473
0.09	0.9412	0.9406
0.10	0.9344	0.9337
0.12	0.9206	0.9198
0.14	0.9070	0.9061
0.16	0.8936	0.8926
0.18	0.8804	0.8793
0.20	0.8674	0.8663
0.22	0.8547	0.8535
0.24	0.8422	0.8411
0.26	0.8301	0.8290
0.28	0.8183	0.8172
0.30	0.8069	0.8057
0.34	0.7847	0.7836
0.38	0.7638	0.7627
0.42	0.7438	0.7428
0.46	0.7247	0.7238
0.50	0.7067	0.7059
0.54	0.6895	0.6888
0.58	0.6728	0.6723
0.62	0.6565	0.6561
0.66	0.6409	0.6406
0.70	0.6259	0.6256
0.78	0.5973	0.5969
0.86	0.5705	0.5696
0.94	0.5455	0.5436
1.02	0.5225	0.5190
1.10	0.5017	0.4960
1.18	0.4829	0.4743
1.26	0.4660	0.4545
1.34	0.4506	0.4362
1.42	0.4367	0.4195

Table 7: continued

1.50	0.4239	0.4044
1.66	0.4005	0.3779
1.82	0.3791	0.3557
1.98	0.3592	0.3368
2.14	0.3408	0.3209
2.30	0.3234	0.3074
2.46	0.3071	0.2962
2.62	0.2919	0.2870
2.78	0.2777	0.2797
2.94	0.2644	0.2742
3.10	0.2522	0.2703
3.42	0.2300	0.2668
3.74	0.2108	0.2680
4.06	0.1940	0.2730
4.38	0.1792	0.1476
4.70	0.1660	0.0253
5.02	0.1543	0.0194
5.34	0.1436	0.0148
5.66	0.1339	0.0114
5.98	0.1249	0.0088
6.30	0.1165	0.0068
6.94	0.1018	0.0041
7.58	0.0888	0.0026
8.22	0.0775	0.0018
8.86	0.0688	0.0013
9.50	0.0573	0.0011
10.14	0.0376	0.0010
10.78	0.0374	0.0009
11.42	0.0396	0.0008
12.06	0.0356	0.0008
12.70	0.0287	0.0008
13.98	0.0210	0.0008
15.26	0.0160	0.0000
16.54	0.0123	0.0000
17.82	0.0095	0.0000
19.10	0.0062	0.0000
20.38	0.0049	0.0000
21.66	0.0045	0.0000
22.94	0.0034	0.0000
24.22	0.0018	0.0000
25.50	0.0000	0.0000
28.06	0.0000	0.0000
30.62	0.0000	0.0000
33.18	0.0000	0.0000
35.74	0.0000	0.0000

Table 8

ANALYSIS OF NEIGHBOURING POINTS
IN FINITE DIAMOND LATTICE

Order	Number	Distance	Total Number
0	1	0.000000	1
1	4	1.732051	5
2	12	2.828427	17
3	12	3.316625	29
4	6	4.000000	35
5	12	4.358899	47
6	24	4.898979	71
7	16	5.196152	87
8	12	5.656854	99
9	24	5.916080	123
10	24	6.324555	147
11	12	6.557439	159
12	8	6.928203	167
13	24	7.141428	191
14	48	7.483315	239
15	36	7.681146	275
16	6	8.000000	281
17	12	8.185353	293
18	36	8.485281	329
19	28	8.660254	357

The reference frame is defined by the axes of the conventional cubic unit cell having dimensions of four arbitrary units.

neighbours enclosed within the distance considered. The distance covered by the table corresponds to the range of atomic wave functions in the calculation; this defines the limiting distance of interaction for the two wave functions in the multicenter integrals.

4.4 The Representation of the Crystal Potential.

The OAP crystal potential function was calculated where a data set was generated for the points on the integration mesh. The information available is sufficient to determine the potential at any point in the crystal directly.

The kubic harmonic expansion coefficients $V_n(r)$ were calculated for the radial coordinates of the integration mesh; the representation of the crystal potential is retrieved from a data set containing the expansion coefficients. The modified expansion coefficients $\overline{V_n(r)}$ for $n = 0, 3, 4, 6, 7$ are sketched in figure 1 to figure 5 respectively. The particular functions $\overline{V_n(r)}$ considered are normalised in order to facilitate comparison of the contributions from different orders of the kubic harmonic expansion defined in table 3:

$$\overline{V_n(r)} = \frac{1}{\sqrt{N_n}} V_n(r) \quad [4.2]$$

The higher order expansion coefficients are rapidly oscillating functions of the radial coordinate. The kubic harmonic expansion coefficients were considered for

Figure 1
THE ZERO-ORDER EXPANSION COEFFICIENTS

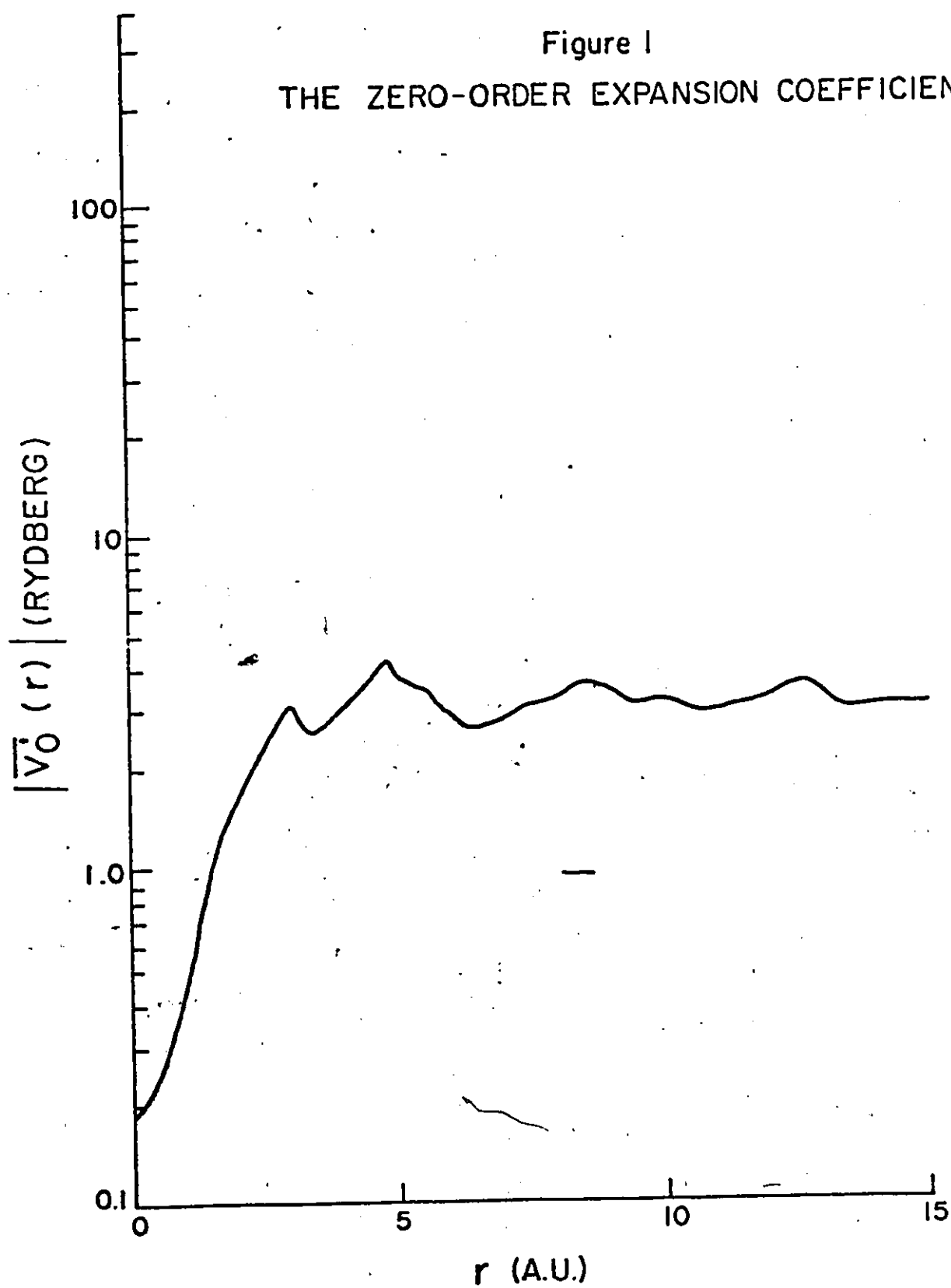


Figure 2
THE THIRD-ORDER EXPANSION COEFFICIENTS

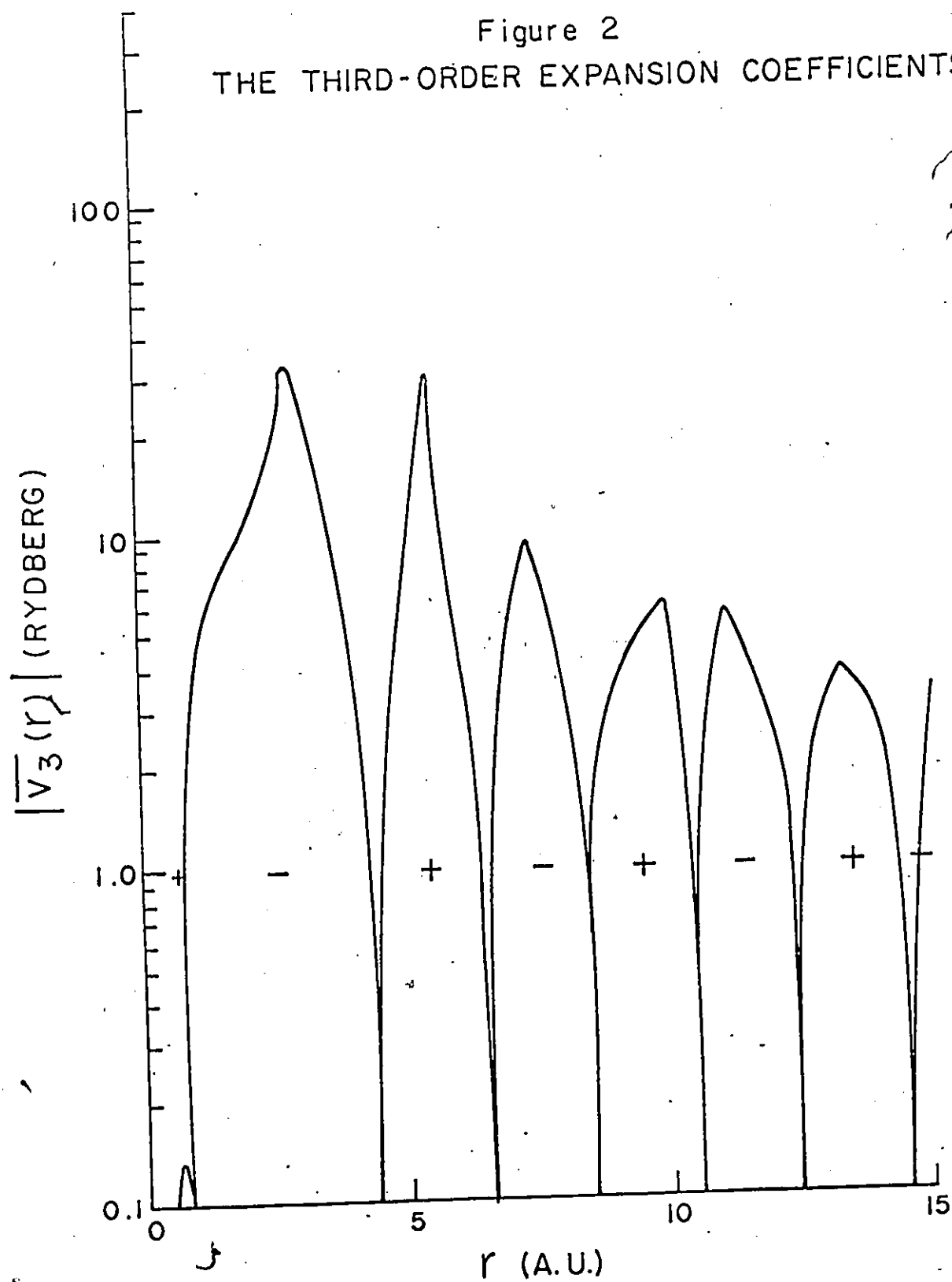


Figure 3
THE FOURTH-ORDER EXPANSION COEFFICIENTS

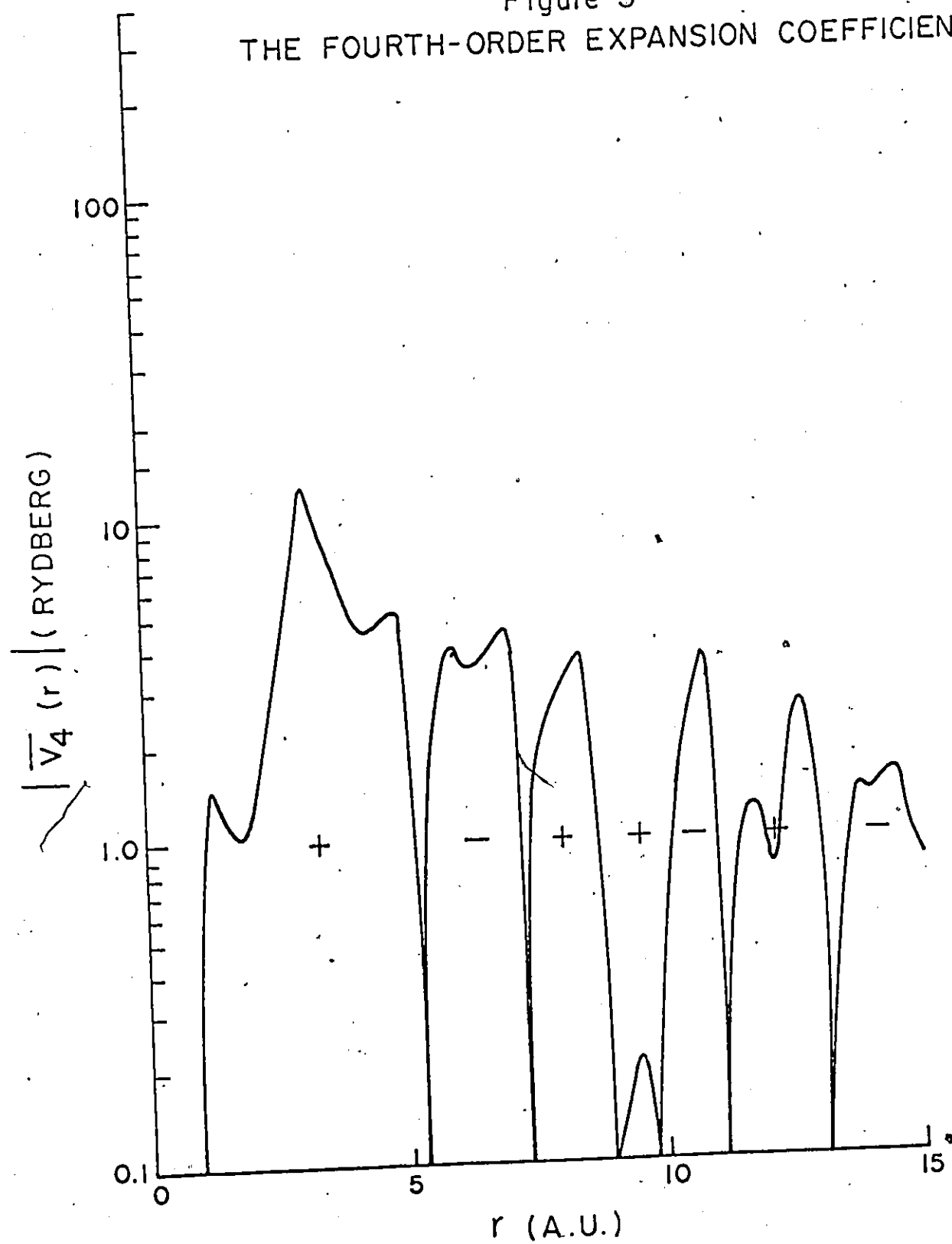


Figure 4

THE SIXTH-ORDER EXPANSION COEFFICIENTS.

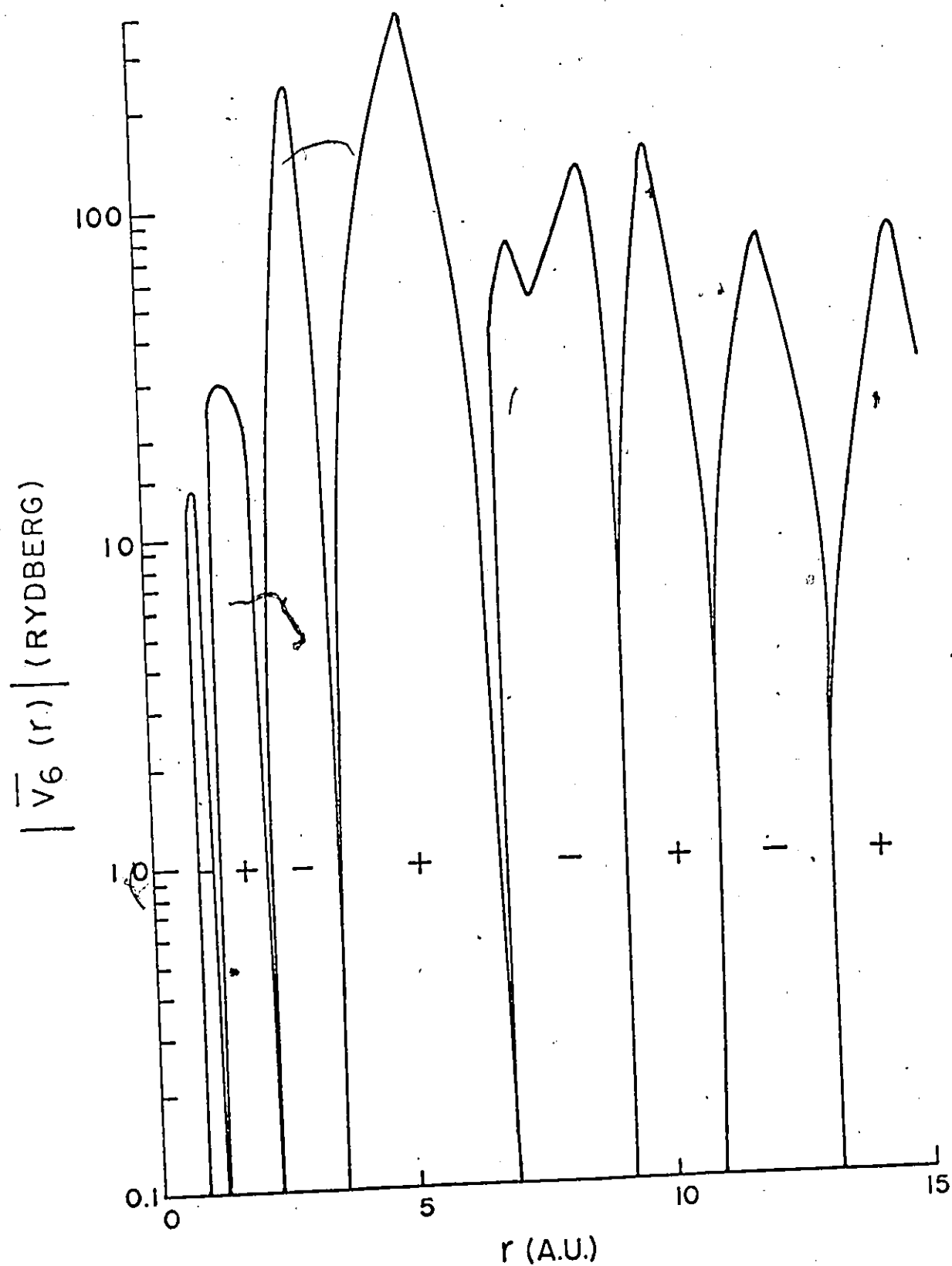
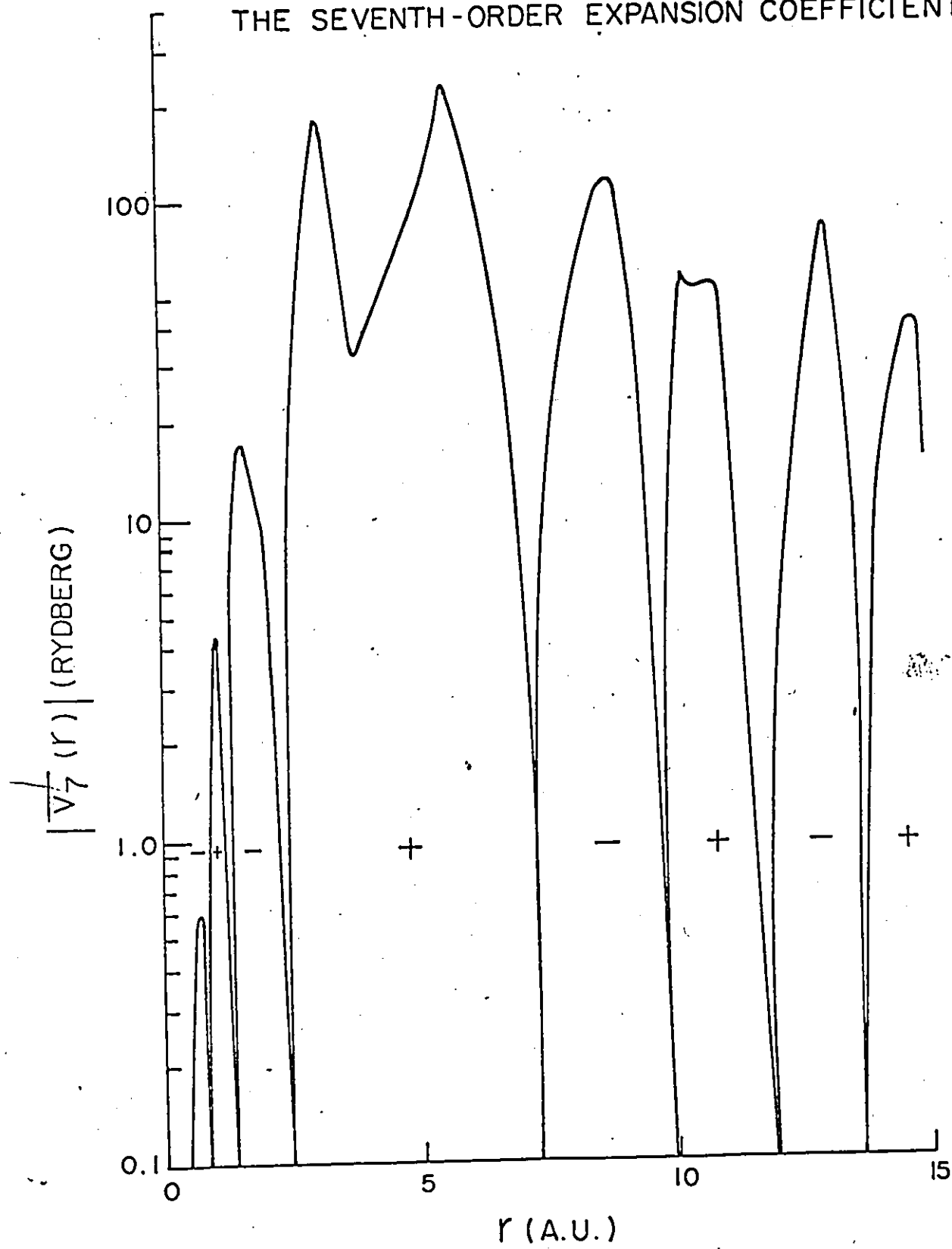


Figure 5

THE SEVENTH-ORDER EXPANSION COEFFICIENTS



differing atomic potentials in order to assess the significance of the choice of the effective atomic potential. The difference between the coefficients with the Slater exchange potential and the present exchange potential was in the shift of the zeroth-order component; the higher order components did not vary significantly. This suggests that the higher-order expansion coefficients are determined largely by the inner region of the effective atomic potential as expected.

4.5 The Matrix Elements and the Multicenter Integrals.

The independent forms of the three-center integrals for the first few orders of nearest neighbours were calculated employing the crystal potential function $V'(r, \theta, \phi)$; they are given in table 9 along with the corresponding two-center integrals for comparison employing the zeroth-order harmonic potential representation $V_0(r)$. A number of integrals listed in the table are equivalent and are calculated for comparison. The three-center integrals for the s-orbitals were evaluated for all the neighbours employing the crystal potential function. In the two-center integral formulation the matrix elements for the s-orbitals were calculated with the cubic harmonic expansion of the crystal potential. The matrix elements were also calculated in the zeroth-order potential representation for all orbitals;

Table 9

The Multi-center Integrals for the Nearer Neighbours

Multi-center Integration	Three-center Representation	Two-center Representation
$E'_{sx}(1,1,1)$	-0.3709	-0.3355
$E'_{xx}(1,1,1)$	-0.1912	-0.2562
$E'_{xy}(1,1,1)$	0.3415	0.3049
$E'_{sx}(2,2,0)$	-0.2254	-0.2155
$E'_{xx}(2,2,0)$	0.1575	0.1258
$E'_{xy}(2,2,0)$	0.2927	0.2914
$E'_{sx}(0,2,2)$	0.0469	0.0
$E'_{xx}(0,2,2)$	-0.1807	-0.1655
$E'_{xy}(0,2,2)$	0.0564	0.0
$E'_{sx}(2,0,2)$	-0.2254	-0.2155
$E'_{xx}(2,0,2)$	0.1598	0.1258
$E'_{xy}(2,0,2)$	-0.0564	0.0
$E'_{sx}(3,1,1)$	0.1539	0.1740
$E'_{xx}(3,1,1)$	0.1805	0.2222
$E'_{xy}(3,1,1)$	0.0775	0.1035
$E'_{sx}(1,3,1)$	0.0522	0.0580
$E'_{xx}(1,3,1)$	-0.0561	-0.0549
$E'_{xy}(1,3,1)$	0.0814	0.1035
$E'_{sx}(1,1,3)$	0.0490	0.0580
$E'_{xx}(1,1,3)$	-0.0612	-0.0549
$E'_{xy}(1,1,3)$	0.0434	0.0345

Table 9: continued

$E_{sx}^1(4,0,0)$	-0.0782	-0.0894
$E_{xx}^1(4,0,0)$	0.1310	0.1560
$E_{xy}^1(4,0,0)$	0.0	0.0
$E_{sx}^1(0,4,0)$	0.0010	0.0
$E_{xx}^1(0,4,0)$	-0.0404	-0.0370
$E_{xy}^1(0,4,0)$	-0.0006	-0.0
$E_{sx}^1(0,0,4)$	-0.0004	0.0
$E_{xx}^1(0,0,4)$	-0.0380	-0.0370
$E_{xy}^1(0,0,4)$	-0.0003	0.0
$E_{sx}^1(1,3,3)$	-0.0150	-0.0131
$E_{xx}^1(1,3,3)$	-0.0141	-0.0157
$E_{xy}^1(1,3,3)$	0.0233	0.0205
$E_{sx}^1(3,1,3)$	-0.0416	-0.0393
$E_{xx}^1(3,1,3)$	0.0441	0.0389
$E_{xy}^1(3,1,3)$	0.0254	0.0205
$E_{sx}^1(3,3,1)$	-0.0413	-0.0393
$E_{xx}^1(3,3,1)$	0.0442	0.0389
$E_{xy}^1(3,3,1)$	0.0629	0.0615

The components of the lattice vector defining the multi-center integration are expressed in the arbitrary units defined in table 8.

this involves the evaluation of the $(ss\sigma)$, $(sp\sigma)$, $(pp\sigma)$ and $(pp\pi)$ types of integrals. The complete set of two-center integrals was calculated with the simplest harmonic representation $V_0'(r)$, and with the atomic potential $v(r_j)$ at the second center included exactly and a zero-order potential representation $V_0''(r; r_j)$ omitting the contribution from that center. The corresponding overlap and energy integral summations over each lattice shell are summarised in table 10 for the elements of the s-orbitals; the results for the more significant orders are given in the table although the calculation was carried out for the entire twenty orders of interacting shells.

The final energy eigenvalues computed are given in table 11; the crystal potential representations employed in the calculation are indicated by the corresponding symbols. In the second part of the table the energy eigenvalues are shifted by 1.4713 Rydbergs to facilitate comparison with the results of other studies (41,54) given there; the valence (V) and conduction (C) bands are indicated. The values for the atomic energy levels employed in the calculation have considerable influence on the relative levels of the eigenvalues corresponding to different symmetry types.

Table 10

The Overlap and Energy Elements
Summed Over the Individual Shells

Shell Order	I	V'	V_o'	V_o''	$\sim$
0	1.0000	-1.2758	-1.2758	-1.2758	0.0
1	1.4266	-2.4300	-2.6116	-2.1213	-1.9320
2	1.1031	-2.1628	-2.6007	-2.5299	-0.8378
3	0.5513	-1.1881	-1.4031	-1.3833	-0.3350
4	0.0983	-0.2425	-0.2658	-0.2640	-0.0428
5	0.1121	-0.2926	-0.3084	-0.3069	-0.0302
6	0.0945	-0.2585	-0.2655	-0.2647	-0.0119
7	0.0389	-0.1071	-0.1103	-0.1101	-0.0036
8	0.0136	-0.0376	-0.0391	-0.0390	-0.0010
9	0.0174	-0.0486	-0.0506	-0.0505	-0.0002
10	0.0083	-0.0236	-0.0247	-0.0247	-0.0000
11	0.0027	-0.0077	-0.0081	-0.0081	
12	0.0009	-0.0025	-0.0027	-0.0027	
13	0.0017	-0.0049	-0.0053	-0.0053	
14	0.0017	-0.0049	-0.0054	-0.0054	
15	0.0009	-0.0025	-0.0027	-0.0027	

Table 10: continued

Shell Order	v_0'	v_3'	v_4'	v_6'	v_7'
0	-1.2758	0.0	0.0	0.0	0.0
1	-2.6116	-0.5355	-0.1016	0.0508	0.0490
2	-2.6007	0.0	-0.0935	-0.1079	0.0
3	-1.4031	0.0765	0.0350	0.0092	-0.0593
4	-0.2658	0.0	0.0142	0.0127	0.0
5	-0.3084	-0.0077	-0.0037	-0.0058	-0.0003
6	-0.2655	0.0	-0.0017	0.0025	0.0
7	-0.1103	0.0005	0.0010	0.0009	0.0020
8	-0.0391	0.0	-0.0003	-0.0003	0.0
9	-0.0506	0.0002	-0.0001	-0.0002	0.0000
10	-0.0247	0.0	0.0002	0.0000	
11	-0.0081	-0.0002	-0.0001	0.0001	
12	-0.0027	0.0	0.0001	0.0000	
13	-0.0053	-0.0000	-0.0001		
14	-0.0054		0.0000		
15	-0.0027				

Table 11

The Energy Eigenvalues at the Symmetry Points

1. Γ_1 and Γ_2 Symmetry Eigenvalues.

Symmetry	V'	V_0'	$V_0' + V_3'$	$V_0' + \dots + V_4'$	$V_0' + \dots + V_6'$	$V_0' + \dots + V_7'$
Γ_1	-1.809	-2.008	-2.112	-2.146	-2.154	-2.156
Γ_2	0.427	0.119	2.873	2.804	1.930	1.980

2. Γ , X and L Point Eigenvalues.

Symmetry	Type	Chaney et al	Painter et al	V_0'
Γ_1	V	-1.480	-1.441	-1.949
Γ_2'	V	0.000	0.000	0.000
Γ_3'	C	0.460	0.441	-0.003
Γ_4'	C	0.988	0.794	0.178
X_1	V	-0.870	-0.853	-1.054
X_2	V	-0.408	-0.390	-0.520
X_3	C	0.622	0.463	-0.264
X_4	C	1.190	1.051	0.409
L_1	V	-1.098	-1.066	-1.217
L_2	V	-0.848	-0.860	-1.318
L_3	V	-0.190	-0.176	-0.202
L_4	C	0.742	0.603	-0.072
L_5	C	0.742	0.654	0.160
L_6	C	1.316	-	0.151

Chapter 5

A DISCUSSION OF THE LCAO METHOD

5.1 The Application of the Method of LCAO.

The method of LCAO was applied in the early development of quantitative energy band calculations within the limits of the traditional tight-binding approximation. Such a calculation may be valid for the simple ionic crystals exemplified by the alkali halides; in particular, there are several calculations for NaCl and an accurate calculation for KCl has been available for some time (55). An insight into the validity of the LCAO method is given by analysis of the atomic and crystal structure parameters for the different crystal types listed in table 12. The quantities in the table are considered following Slater (19); the outer shell radius is defined as the maximum radial charge density for the appropriate atomic or ionic orbital and the bond distance is defined as the separation of the nearest neighbours in the crystal lattice. There is a simple relationship between the elementary crystal bonding types and the amenability of the corresponding crystal wave functions to a representation as a linear combination of atomic orbitals. It is interesting to realise that, in such a qualitative analysis, sodium lies somewhere between lithium and diamond in terms of the degree of atomic overlap and the associated free-electron-like behaviour. This is in contrast to the accepted nature

Table 12

The Parameters of Four Crystal Structures

Crystal Parameters in a.u.			Atomic/Ionic Parameters in a.u.	
Lattice Structure	Lattice Size	Bond Distance	Empirical Radius	Outer-Shell Radius and Orbital
Li; bcc (Metallic)	6.63	5.74	2.74	3.00 Li(2s)
Na; bcc (Metallic)	8.09	7.00	3.40	3.38 Na(3s)
C; dmd (Covalent)	6.73	2.91	1.32	1.17 C(2s)
NaCl; fcc (Ionic)	10.66	5.33	1.79 3.42	0.60 Na ⁺ (2s) 1.38 Cl ⁻ (3p)

of energy levels which place sodium as the extreme case of a free-electron-like structure. The extension of the atomic orbitals of lithium through the crystal lattice represents an extreme degree of atomic overlap in the crystal. The variation in this effect may be appreciated by considering the typical number of atoms within the range of an outer atomic orbital within the crystal; the 30 orders of nearest neighbours with 645 members for lithium compare to the 19 orders of nearest neighbours with 357 members in diamond. The analysis of the localisation of electrons in solids has gained significance in recent years (56) and supports the simple claim that the variation of the electron localisation between metallic and covalent systems does not require alternative representations for the different crystal types. Further, if the crystal wave functions may be expressed in terms of the wave functions of the constituent atoms, it should be possible to make a more direct correlation between the properties of crystals and those of free atoms on both the qualitative and quantitative level.

It has been established in the theory of band structure that a given LCAO representation of the one-electron wave functions is adequate in an accurate calculation of the energy levels of lithium (57), sodium (41), and diamond (41). There are several factors in the problem of an accurate calculation apart from the representation of the electron wave functions. The representation of the crystal

potential is equally important and this is a more critical problem for covalent structures than for metallic structures; this has been referred to already in terms of the lower symmetry of the non-symmorphic diamond lattice.

These remarks serve to indicate the range of validity of the LCAO representation in view of the recent developments of the general theory of solids.

5.2 The Development of the Method of LCAO.

An earlier calculation of the energy band structure of diamond by Bassani and Yoshimine⁽⁴⁰⁾ employing the orthogonalised-plane-wave (OPW) method, has several features in common with the present calculation and provides a useful comparison. The lattice constant and atomic wave functions are identical and an analysis following Woodruff of the core-level shift problem reduces the potential space average to a free parameter in the Fourier expansion of the crystal potential. The energy band structure is found to be independent of the space average potential over the range of values in any practical calculation. The convergence of the calculation is inferred from other calculations and the plane-wave function basis, which is thoroughly discussed, therefore remains a questionable representation. The Slater exchange treatment is claimed as a major source of error in this calculation; this statement is justified by the incorrect application of the free-electron exchange potential to the individual atomic charge densities rather than to the total

crystal charge density. The effect of taking the atomic wave functions as an initial approximation to the crystal problem is considered and it is claimed that a more accurate representation of the crystal potential and the associated core wave functions is necessary in such an CPW calculation.

A further attempt at an accurate calculation of the energy band structure of diamond was made by Neown (58) applying the augmented-plane-wave (APW) method. Although this calculation has been considered as an accurate reference, it should be realised that the general validity of the method may be limited by the restrictive form of the muffin-tin representation of the crystal potential.

The alternative development of the LCAO method by Lafon, Lin and Chaney, referred to previously, represents a complex development in which the atomic wave functions are expressed in simple analytical forms (Slater-type orbitals) and the lattice potential represented by a Fourier series. The matrix elements are then computed following an analytical reduction involving the Laplace transformation of the exponential components of the analytical wave functions. The accurate calculation of the matrix elements remains the principle problem of the tight-binding method and a further development is applied in which the atomic wave functions are represented in an alternative analytical form (Gaussian-type orbital). The variational nature of the calculation is emphasized and the optimum form of the finite minimising

sequence is considered. It is established that there is no particular advantage in taking free-atomic orbitals as basis functions while the 1s, 2s and 2p orbitals provide a satisfactory representation for an accurate calculation; the results for this simple basis set were given in table 11. The alternative crystal potential models employed correspond to an CAP and a muffin-tin formulation following Bassani and Yoshimine and Keown respectively. The analytical atomic wave functions are a representation of the valence state of carbon computed by Jucy (59) whereas the lattice potential is constructed from the ground state wave functions employed in the present calculation.

An analysis of the effect of introducing intermediate and extended orbitals as further basis functions illustrates that the critical degrees of freedom correspond to variations of the basis functions within a region with dimensions of the atomic spacing of the crystal. In view of these results, the advantages of Gaussian-type orbitals far outweigh their unfamiliar appearance in this application. The results of the computation compare well with the earlier calculations they are related to, having an estimated error of approximately 0.02 Rydbergs. The discrepancy with the OPW method is attributed to the incomplete convergence in that calculation; this is verified in the case of silicon. Apart from the good agreement with the APW method, particularly as the number of basis functions is increased, the

significant superiority in the representation of the CAP model over the muffin-tin model is established. Although there are no considerations of self-consistency, there is close agreement with a self-consistent field calculation by Herman (60,61) which is adjusted to agree with experimental values.

A review of the work of Lafon, Lin and Chaney is given because of the significance in understanding the general validity of the so-called tight-binding method; that is the linear variational method employing orbital basis functions. The tendency to standardise the crystal potential in ab initio calculations allows the direct comparison of results where the lowest eigenvalues attained in any variational formulation are necessarily the closest approximation to the solution of that problem.

An alternative development of the LCAO method by Painter, Ellis and Lubinsky (54,62,63) called the discrete variational method (DVM) verifies the results and conclusions of Lafon, Lin and Chaney. The matrix elements, associated with the Bloch wave function basis, are calculated directly without the usual decomposition into the multi-center component elements which characterises the tight-binding method. The lattice symmetry may be applied to reduce the necessary computation significantly; the drawback to this formulation is that an independent calculation is required at every point in the Brillouin zone. The inadequacy of the muffin-

tin potential is verified by calculation and the CAP potential employed differs in the lattice parameter, the atomic wave functions and the exchange treatment from that of the present calculation. The exact form of the free-electron exchange treatment is applied with the exchange scaling parameter adjusted to an intermediate value (0.76) between the Kohn-Sham (0.66) and Slater (1.00) exchange parameters. The results of the calculation with a basis formed from 26 components of Slater-type orbitals are summarised in table 11. The close agreement with a calculation by Chaney employing 20 similar basis functions, omitting the compact components of the 3s and 3p orbitals, is in contrast to the significance of the outer orbitals in the convergence of the DVM calculation. The superior form of the components of the Slater-type orbitals over the complete atomic orbitals is explained by the greater freedom given to the positions of the nodes in the crystal wave functions; this corresponds to the expansion and contraction of the atomic orbitals while undergoing crystal formation. The accuracy claimed compares favourably with that of Chaney's tight-binding calculation. An extensive analysis of the CAP crystal potential illustrates that the calculation is already close to a self-consistent solution.

The developments outlined define the present limits of the LCAO method although a full self-consistent treatment now seems feasible in a first-principles calculation. A

fundamental understanding of the problem has not developed alongside the recent progress in computational methods in which the statistical exchange treatment appears satisfactory and indicates that the correlation effects are cancelling out in the one-electron model (17,64).

5.3 The Comparison of the Results.

There remains little doubt that the form of the present calculation is sufficient for an accurate calculation of the energy levels of diamond. This is a definite conclusion of the analysis given in the previous section and the discrepancy in the comparison, summarised in table 11, therefore arises from the computational method. The principle sources of error are detected directly in the calculation and are evident from a simple analysis of the conclusions of Chaney and Painter. The representation of the crystal potential as a spherical harmonic expansion is inadequate in the calculation; the expression is slowly convergent and many higher order terms are clearly required. A cubic harmonic expansion of low orders provides an approximate representation where an accurate crystal potential representation is necessary in an energy band calculation. The problem of numerical error dominates the entire calculation. The calculation of the three-center integrals is insufficiently accurate and requires extensive optimisation; this problem is compounded by the number of three-center integrals involved in the calculation of a simple matrix element of a crystal wave function.

The accuracy of a three-dimensional integration in the DVM calculation is comparable while the number of such calculations required is relatively small. A calculation with the lattice potential function is capable of good results for the valence bands but the accuracy is reduced for the conduction bands which are associated with the antibonding wave functions (39). The problem of a reduced symmetry arises when the more significant effective atomic potentials are considered individually and the remaining lattice potential is represented by a harmonic expansion; this is discussed in section 2.4. The inadequacy of the cubic harmonic expansion for an incomplete lattice is critical in the present calculation; the results of table 10 verify the consistent overestimation of the lattice potential introduced by such a treatment. This hybrid formulation reverts to a three-center calculation before sufficient accuracy is achieved. The improvement of the results is not stressed as the present development is clearly inadequate for an exact calculation.

5.4 An Interpretation of the Results.

The convergence over the successive neighbours commences around the 15th order while the convergence with respect to the cubic harmonic expansion is rapid for all but the first few shells. The contribution from the first shell is critical to the convergence of the cubic harmonic expansion; the seventh-order expansion is therefore inadequate for

the calculation of the conduction levels. The approximation to the energy levels in the calculation employing the lowest order potential representation $V_0'(r)$ was analysed in terms of the average effect of the crystal potential over a range of the lattice. It is found that the ratio of the energy elements and associated overlap elements, listed in table 10, is fairly constant and approaches the average value of the crystal potential after the first few shells; this is particularly valid for the matrix elements defined by the representation involving $V_0''(r; R_j)$ and $v(R_j)$. After the first few shells, the energy elements defined by the different potential representations approach each other rapidly; in particular, the component of $v(R_j)$ becomes negligible indicating that the principle contribution comes from the intermediate region between the two atoms defining the energy integral. At the other extreme, the contribution to the energy element is dominated by the component of $v(R_j)$ at the first shell and the incomplete convergence of the expansion is evident on comparison with the exact integral employing $V_0'(r)$. The problem encountered in the calculation of the conduction levels arises from the antibonding nature of the associated wave functions. The calculation of the final matrix elements involves a summation of the energy elements over the different lattice shells. These contributions generally add for the valence states while they alternate in sign for the conduction states; this process generates a significantly larger fractional error

in the matrix elements defining the conduction levels. The error introduced by the two-center reduction of an energy integral is of the order of 0.02 Rydbergs while the estimated error for a three-center integration is 0.004 Rydbergs; a more accurate computation is necessary for a reliable calculation of the conduction levels.

A simple analytical development may be considered for a qualitative analysis of the convergence of the cubic harmonic expansion and the associated energy elements. The atomic structure functions are represented as square well functions of characteristic radii and severe approximations are introduced to facilitate the evaluation of the expansion coefficients and the energy integrals. These involve the assumptions that the spherical harmonic expansion is dominated by the nearest neighbour shells and that the expansion coefficients are constant over the range of atomic overlap. An analysis over a range of the crystal parameters illustrates the extreme nature of diamond in the present calculation. The general conclusions of the numerical calculation are verified while the awkward behaviour of the expansion arising from the first shell is well predicted. Although the validity of the approximations breaks down as the range of the atomic structure functions increases, the analysis provides considerable insight into the problems of any calculation. A more reliable analysis is given from a study of figures 1-5. (65)

5.5 The Possibilities of Any Further Developments.

The limit of the present calculation is defined by the accuracy and efficiency of the numerical methods involved. A considerable degree of improvement is required in the numerical analysis although the potential of the various methods available is by no means clear. It was felt that the main alternative lies between an analytical or a computational development and that any such formulations would be closely related to those of Chaney and Painter respectively. The present calculation represents a distinct formulation of the LCAO method which remains to be developed to the level of these recent alternatives.

A novel method has been considered for computing the three-dimensional integrals which appears promising and requires further development. The atomic and crystal wave functions are first tabulated at the points of a simple cubic lattice which includes the crystal lattice points. An integration is then defined by the relative displacement of the three lattices which represent the functions involved. The principle advantage of this method is that the functions required are calculated once in a single cartesian coordinate system for all the matrix elements.

The problem arising from the error of numerical integration may be reduced by employing a spline quadrature which has been recently developed (66). The method employs a spline interpolation which generates a superior representation.

tion without the traditional restriction to analytical functions. A cubical spline quadrature, where the spline is defined by the set of twice-differentiable functions C^2 , is closely related to the Simpson quadrature which is based on a polynomial interpolation. The performance of the spline is far more accurate than a comparable Simpson quadrature. An improvement of an order of magnitude in the basic quadrature would provide a significant reduction in the problem of computing a two-dimensional integration.

A general analysis for an analytical reduction of the various energy elements considered has not been given. The transformation of the integral elements has been carried out with explicit reference to the lattice structure in order to illustrate the nature of the symmetry in the problem. A general integral form corresponds to a product of three spherical harmonic functions which may be reduced in terms of a standard representation employing the Clebsch-Gordan coefficients and the generalised spherical functions or Wigner D-functions (67-69).

Finally, although the absolute accuracy of the present calculation has been stressed throughout, it should be realised that the development has a considerable range of application. In particular, it extends directly to the analysis of the band structure of complicated compounds.

Appendix 1

THE BLOCH WAVE FUNCTION BASIS

The form of the Bloch wave function may be derived from that of the basis functions forming a representation of the translational symmetry group. (70) The derivation outlined in section 2.1 is developed here to determine the structure of the basis functions. The elements of the abelian translation group Γ all commute with the crystal Hamiltonian H ; they form a cyclic abelian group of the Schroedinger equation whose representation decomposes into

N one-dimensional irreducible representations. The lattice translation vectors may be indexed by the vector $\underline{n} = (n_1)$ within the range of the periodic boundary conditions and where $N = N_1 N_2 N_3$; that is, $\{\underline{n} = (n_1); 1 \leq n_1 \leq N_1\}$. The lattice translation operators are then defined as follows in the notation given. (21)

$$\Gamma(\underline{A}_n) = \Gamma(n_1, \underline{a}_1) \cdot \Gamma(n_2, \underline{a}_2) \cdot \Gamma(n_3, \underline{a}_3) = \prod_{\lambda=1}^3 [\Gamma(n_\lambda, \underline{a}_\lambda)]^{n_\lambda} \quad [A1.1]$$

Similarly, the N irreducible representations Γ^k may be referenced by the vector $\underline{k} = (k_1)$ and the associated elements $\Gamma^k(\underline{A}_n)$ are defined by considering the periodic boundary conditions which correspond to the periods of the component cyclic groups.

$$\Gamma^k(\underline{A}_n) = \prod_{\lambda=1}^3 [\Gamma^{k_\lambda}(n_\lambda, \underline{a}_\lambda)]^{n_\lambda}$$

$$[\Gamma^E(a_\lambda)]^{N_\lambda} = 1 \Rightarrow$$

$$\Gamma^E(a_\lambda) = \exp\left(2\pi i \frac{\ell_\lambda}{N_\lambda}\right) = \exp(2\pi i h_\lambda)$$

$$0 \leq \ell_\lambda \leq (N_\lambda - 1)$$

$$h_\lambda = \frac{\ell_\lambda}{N_\lambda}$$

[A1.2]

Therefore, the N irreducible representations are indexed by the row vector $\underline{h} = (h_i)$ and it remains to express $\underline{k}$ in terms of $\underline{h}$. The conventional choice of the reduced wave vector $\underline{k}$ is defined in terms of the reciprocal lattice vectors $\{\underline{b}_1, \underline{b}_2, \underline{b}_3\}$.

$$\underline{a}_i \cdot \underline{b}_j = 2\pi \delta_{ij}$$

$$\underline{B} \underline{A} = 2\pi \underline{1}$$

$$\underline{A} = (\underline{a}_1, \underline{a}_2, \underline{a}_3)$$

$$\underline{B} = \begin{pmatrix} \underline{\tilde{b}}_1 \\ \underline{\tilde{b}}_2 \\ \underline{\tilde{b}}_3 \end{pmatrix}$$

$$\underline{k}_\lambda = \frac{\ell_\lambda}{N_\lambda} \underline{\tilde{b}}_\lambda = h_\lambda \underline{\tilde{b}}_\lambda$$

$$\underline{k} = \underline{k}_1 + \underline{k}_2 + \underline{k}_3 \Leftrightarrow \underline{\tilde{k}} = \underline{h} \underline{B} \quad [A1.3]$$

The elements of the representation are easily defined in the notation given.

$$\Gamma^E(\underline{A}_n) = \prod_{\lambda=1}^3 [\exp(i \underline{k}_\lambda \cdot \underline{a}_\lambda)]^{n_\lambda} = \exp\left(2\pi i \sum_{\lambda=1}^3 n_\lambda \frac{\ell_\lambda}{N_\lambda}\right)$$

$$\Gamma^E(\underline{A}_n) = \exp(i \underline{h} \underline{B} \underline{A}_n) = \exp(i \underline{k} \cdot \underline{A}_n)$$

[A1.4]

A result of group theory states that the eigenfunctions $\psi_E(r)$ of the Hamiltonian H will form basis functions of the irreducible representations of any group Γ of the Schrodinger equation, and that such basis functions $\psi_E(r)$ of the distinct irreducible representations Γ^E are orthogonal. The representations $\psi_E(r)$ generate a particular representation Γ^E of the group of Schrodinger equation corresponding to each eigenvalue E of the Hamiltonian.

$$\Gamma(A_n) \psi_E(r) = \psi_E(r + A_n) = \Gamma^E(A_n) \psi_E(r) = e^{ik \cdot A_n} \psi_E(r) \quad [A1.5]$$

The eigenfunctions $\psi_E(r)$ of the Hamiltonian are therefore orthogonal non-degenerate basis functions $\psi_k(r)$ of the translation group.

$$\int \psi_{E'k'}^*(r) \psi_{Ek}(r) d^3r = \delta_{E'E} \delta_{k'k} \quad [A1.6]$$

A degeneracy may arise on consideration of any further symmetry the Hamiltonian may contain. These statements are a direct consequence of the symmetry of the Hamiltonian and are related to the theorems on the representations of commuting operators. However, although the operators Γ and H commute, Γ is clearly not Hermitian since the eigenvalue spectrum $\{e^{ik \cdot A_n}\}$ is complex.

The result of the analysis given may be expressed in the following equivalent form and is generally known as Bloch's theorem.

$$\Gamma(A_n) \psi_k(r) = e^{ik \cdot A_n} \psi_k(r)$$

$$\Leftrightarrow \psi_k(r) = e^{ik \cdot r} u_k(r), \quad \Gamma(A_n) u_k(r) = u_k(r).$$

[A1.7]

The theorem may be derived in a number of ways which range from a variety of intuitive physical formulations to the classical proof of Floquet's theorem^(6,7,16). The proof given here develops the exact result in an elegant manner. It remains to verify that the LCAO wave functions $\psi_k^p(r)$ are Bloch wave functions.

$$\psi_k^p(r) = \sum_R (c_j) e^{ik \cdot A_j} \phi_j(r - A_j)$$

$$\psi_k^p(r + A_m) = \Gamma(A_m) \psi_k^p(r)$$

$$= \sum_R (c_j) e^{ik \cdot A_j} \phi_j(r - A_j - A_m)$$

$$= e^{ik \cdot A_m} \sum_R (c_j) e^{ik \cdot A_j} \phi_j(r - A_j)$$

$$(l_j = j - m)$$

$$\psi_k^p(r + A_m) = e^{ik \cdot A_m} \psi_k^p(r)$$

[A1.8]

The Bloch wave functions $\psi_k^p(r)$ are chosen as a minimising sequence in a variational calculation since they are formed from the linear combination of an atomic wave function of each lattice site. Incidentally, if the atomic orbitals $\phi_j(r - A_j)$ at each lattice site are chosen as a minimising

sequence, the Bloch wave function $\psi_{\mathbf{k}}^{\sigma}(\mathbf{r})$ will be derived as the extremising function in a variational calculation. In a general calculation, the functions $\phi_j(\mathbf{r})$ may be freely chosen and this is illustrated by the fact that it is immaterial how a minimising sequence is constructed.

$$\bar{\psi}_{\mathbf{k}}^{\sigma}(\mathbf{r}) = (a_{\mathbf{j}}) \cdot (\psi_{\mathbf{k}}^{\sigma}(\mathbf{r}))$$

$$\bar{\psi}_{\mathbf{k}}^{\sigma}(\mathbf{r}) = \sum_{\mathbf{j}} a_{\mathbf{j}} \sum_{\mathbf{R}} (\mathbf{r}_{\mathbf{j}}) e^{i\mathbf{k} \cdot \mathbf{A}\mathbf{R}_{\mathbf{j}}} \phi_{\mathbf{j}}(\mathbf{r} - \mathbf{A}\mathbf{R}_{\mathbf{j}})$$

$$= \sum_{\mathbf{R}} (\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{A}\mathbf{R}} \cdot \sum_{\mathbf{j}} a_{\mathbf{j}} \phi_{\mathbf{j}}(\mathbf{r} - \mathbf{A}(\mathbf{R} + \mathbf{R}_{\mathbf{j}}))$$

$$(\phi_{\mathbf{j}}(\mathbf{r} - \mathbf{A}(\mathbf{R} + \mathbf{R}_{\mathbf{j}})) = e^{i\mathbf{k} \cdot \mathbf{A}\mathbf{R}_{\mathbf{j}}} \phi_{\mathbf{j}}(\mathbf{r} - \mathbf{A}(\mathbf{R} + \mathbf{R}_{\mathbf{j}}))$$

$$\bar{\psi}_{\mathbf{k}}^{\sigma}(\mathbf{r}) = \sum_{\mathbf{R}} (\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{A}\mathbf{R}} \bar{\phi}_{\mathbf{k}}^{\sigma}(\mathbf{r})$$

$$\bar{\phi}_{\mathbf{k}}^{\sigma}(\mathbf{r}) = \sum_{\mathbf{j}} a_{\mathbf{j}} \cdot \phi_{\mathbf{j}}(\mathbf{r} - \mathbf{A}(\mathbf{R} + \mathbf{R}_{\mathbf{j}}))$$

[A1.9]

The functions $\{\bar{\psi}(\mathbf{r})\}$ may be estimated to any degree of accuracy by considering a complete set of functions $\{\phi(\mathbf{r})\}$ defining a minimising sequence for all orders of calculation.

The matrix elements of the Bloch wave functions are reduced in section 2.2 on consideration of the translational symmetry of the lattice.

$$H_{\mathbf{k}'\mathbf{k}}^{\sigma\sigma} = \langle \mathbf{k}' | H | \mathbf{k} \rangle = \int_{\mathbf{R}} \bar{\psi}_{\mathbf{k}'}^{\sigma}(\mathbf{r}) \cdot H(\mathbf{r}) \cdot \psi_{\mathbf{k}}^{\sigma}(\mathbf{r}) d^3r$$

$$H_{\mathbf{k}'\mathbf{k}}^{\sigma\sigma} = \sum_{\mathbf{R}'} \sum_{\mathbf{R}} a_{\mathbf{R}'} e^{i\mathbf{k}' \cdot \mathbf{A}\mathbf{R}'} \cdot a_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{A}\mathbf{R}} \cdot \int_{\mathbf{R}} \phi_{\mathbf{j}'}(\mathbf{r} - \mathbf{A}\mathbf{R}' - \mathbf{A}\mathbf{R}_{\mathbf{j}'}) \cdot H(\mathbf{r}) \cdot \phi_{\mathbf{j}}(\mathbf{r} - \mathbf{A}\mathbf{R} - \mathbf{A}\mathbf{R}_{\mathbf{j}}) \cdot d^3r$$

[A1.10]

A transformation of the lattice origin where $r' = (r - A_n')$ may be applied and the difference vector $m = (n - n')$ then generates the entire lattice with respect to the origin considered at A_m .

$$H_{\underline{m}} = \sum_{\underline{n}} \exp(i(\underline{k} - \underline{k}'). A_n) \sum_{\underline{m}} \exp(i\underline{k}'. A_m) H_{\underline{m}}$$

$$H_{\underline{m}} = \int_R \phi_j^*(r' - A_{\underline{k}'}') \cdot H(r) \cdot \phi_j(r - A_{\underline{k}'} - A_m) \cdot d^3r$$

$$(\phi_j^*(r - A_n - A_{\underline{k}'})) = \phi_j^*(r' - A_{\underline{k}'}'), H(r) = H(r'), \phi_j(r - A_n - A_{\underline{k}'}') = \phi_j(r' - A_{\underline{k}'} - A_m)$$

[A1.11]

The infinite crystal approximation is valid here since the selection of the atomic wave functions $\phi_j(r)$ reduces the range of overlap defining $H_{\underline{m}}$ to the order of the lattice parameter. The translational symmetry allows a further reduction.

$$\begin{aligned} \sum_{\underline{n}} \exp(i(\underline{k} - \underline{k}'). A_n) &= \frac{3}{\pi} \sum_{\substack{\lambda=1 \\ n \neq 0}}^{(N_\lambda-1)} \exp(2\pi i \cdot (\underline{\ell}_\lambda - \underline{\ell}_\lambda') \cdot \frac{\underline{n}_\lambda}{N_\lambda}) \\ &= \frac{3}{\pi} \cdot \frac{1 - \exp(2\pi i \cdot (\underline{\ell}_\lambda - \underline{\ell}_\lambda') \cdot \frac{N_\lambda}{N_\lambda})}{1 - \exp(2\pi i \cdot \frac{(\underline{\ell}_\lambda - \underline{\ell}_\lambda')}{N_\lambda})} \\ &= 0 \quad (\underline{\ell}_\lambda - \underline{\ell}_\lambda') \neq m_\lambda N_\lambda \end{aligned}$$

[A1.12]

The remaining case corresponds to an indeterminate form where m_λ is any integer: this may be evaluated by the method of L'Hospital.

$$\begin{aligned}
 \lim_{(x_i - x_i') \rightarrow 0, N_i} \prod_{i=1}^3 \frac{1 - \exp(2\pi i (x_i - x_i'))}{1 - \exp(2\pi i \frac{(x_i - x_i')}{N_i})} \\
 = \lim_{(x_i - x_i') \rightarrow 0, N_i} \prod_{i=1}^3 N_i \cdot \frac{\exp(2\pi i (x_i - x_i'))}{\exp(2\pi i \frac{(x_i - x_i')}{N_i})} = N_1 N_2 N_3 = N
 \end{aligned}
 \quad [A1.13]$$

The limiting condition is related to the fact that the wave vector $\underline{k}$ for any Bloch wave function is undefined to within a reciprocal lattice vector $\underline{K}$. The final result may be expressed in terms of a delta function $\delta_{\underline{k}'\underline{k}}$ where $\delta_{\underline{k}'\underline{k}} = 1$ if $\underline{k}' - \underline{k} = \underline{K}$, and, $\delta_{\underline{k}'\underline{k}} = 0$ otherwise.

$$H_{\underline{k}'\underline{k}} = N \sum_{\underline{m}} \exp(i \underline{k} \cdot \underline{A}_{\underline{m}}) \cdot \Phi_{\underline{m}}^{\underline{k}'} \cdot \delta_{\underline{k}'\underline{k}}
 \quad [A1.14]$$

The delta function given may also be derived from a result of group theory which states that the matrix elements vanish between functions belonging to different irreducible representations. The unity operator may be substituted within the expressions developed as it contains the symmetry of the Hamiltonian.

The notation of section 2.2 defines H^1 as a Hamiltonian where the contribution of a single atomic potential function $v(r)$ is omitted; the missing potential function may be conveniently chosen at either orbital center defining a matrix element.

$$H_{\underline{j}\underline{j}'} = E_0^{\underline{j}} I_{\underline{j}\underline{j}'} + H_{\underline{j}\underline{j}'}^1, \quad H_{\underline{j}\underline{j}'}^1 = H - v(\underline{r} - \underline{A}_{\underline{j}})
 \quad [A1.15]$$

The analogous expression for the alternative orbital center

is given by transforming $\psi_{\underline{m}}^{\prime\prime}$ through application of the translational symmetry.

$$\psi_{\underline{m}}^{\prime\prime} = \int_R \psi_{\underline{m}}^{\prime}(\underline{r} - A\underline{e}_j + A\underline{m}) \cdot H(\underline{r}') \cdot \varphi_j(\underline{r}' - A\underline{e}_j) \cdot d^3r'$$

$$H_{jj} = E_j I_{jj} + H'_{jj}, \quad H'_{jj} = H - v(r - A\underline{e}_j)$$

[A1.16]

Appendix 2

THE FACTORISATION OF THE SECULAR DETERMINANT

The Bloch wave function basis may be employed as a minimising sequence in a linear variational method. The variational coefficients a_j are complex in the general case.

$$\bar{\Psi}_{(k)}(\tau) = (a_{kj}) \cdot (\psi_{(k)}^j(\tau))$$

$$E[\bar{\Psi}] = \frac{\int_R \bar{\Psi}^* H \bar{\Psi} d\tau}{\int_R \bar{\Psi}^* \bar{\Psi} d\tau} \quad [A2.1]$$

The Hamiltonian H defines a real expectation value E which may be extremised in a variational analysis.

$$I_{jj} = \int_R \psi_j^* \psi_j d\tau, \quad H_{jj} = \int_R \psi_j^* H \psi_j d\tau$$

$$E = \sum_{j,j} a_{kj}^* a_{kj} \cdot I_{jj} = \sum_{j,j} a_{kj}^* a_{kj} \cdot H_{jj} \quad [A2.2]$$

The complex variational coefficients a_j contain two independent variational parameters. Although the complex function $E(a_{kj}, a_{kj}^*)$ is not analytic, a requirement for an extremum may be derived directly from the condition that the differential vanish.

$$E(z, z^*), \quad z = x + iy \Rightarrow E(x, y)$$

$$dE = \frac{\partial E}{\partial z} dz + \frac{\partial E}{\partial z^*} dz^* = \left(\frac{\partial E}{\partial z} + \frac{\partial E}{\partial z^*} \right) dx + \left(\frac{\partial E}{\partial z} - \frac{\partial E}{\partial z^*} \right) i dy$$

$$dE = 0 \Rightarrow \frac{\partial E}{\partial z} = \frac{\partial E}{\partial z^*} = 0$$

[A2.3]

The standard result follows immediately on differentiating the expression defining E with respect to a_{ij} .

$$\frac{\partial E}{\partial a_{ij}} \sum_j a_{ij}^* a_{ij} I_{jj} + E \sum_j a_{ij}^* I_{jj} = \sum_j a_{ij}^* H_{jj}$$

$$\frac{\partial E}{\partial a_{ij}} = 0 \Rightarrow \sum_j (H_{jj} - E I_{jj}) a_{ij} = 0 \quad [A1.4]$$

The system of linear homogeneous equations defining a_{ij} have a non-trivial solution if and only if the secular determinant vanishes.

$$| H_{jj} - E I_{jj} | = 0 \quad [A1.5]$$

It follows from the variational principle that the lowest root of the polynomial in E will exceed the ground state eigenvalue of the system. In order to estimate any higher eigenvalue the variational theorems require that the minimising sequence is orthogonal to the lower eigenstates of the system. The exact eigenstates may not be derived in a variational calculation and consequently the variational results are frequently employed as a valid approximation to the eigenstates in this case. It is generally accepted that the remaining roots of the secular determinant are generally less good approximations to the higher energy levels of the system. This approximation would be justified if the minimising sequence covered an adequate range of functions. This can be understood by considering a limiting case of an orthogonal sequence which generates the related secular equation arising in either the corresponding perturbation

theory or the diagonalisation which defines the energy representation. Clearly, the variational principle may be applied to any set of functions which is orthogonal to the remaining functions of the minimising sequence; in the present application, the minimising sequence may be divided into such orthogonal sets of functions.

The little group corresponding to the group of the wave vector is introduced in section 2.3. The little group is developed as a subgroup of the factor group defining a ray representation within the Bloch wave function basis. A ray representation may be defined as a representation where the basis functions are considered equivalent although they differ by a phase factor. The general significance of this extended concept is immediately apparent for the state vectors of a Hilbert space. The operations of the complex $G(R, \tau)$ on any Bloch wave function will generate alternative Bloch wave functions; the wave vector k of the original wave function is related to the wave vector of the transformed function by the rotation transformation R employed. These results are expressed in equation 2.14 and may be restated as follows; the prime notation allows a distinction in the case where

$$k \equiv R^{-1}k' \quad \text{and} \quad \psi_k \neq \psi_{k'}$$

$$G(R, \tau) \psi_k(\mathbf{r}) = \psi_{k'}(\mathbf{r})$$

$$\psi_{k'}(\mathbf{r}) = e^{iR^{-1}k' \cdot \mathbf{r}} u_{R^{-1}k'}(\mathbf{r}), \quad u_{R^{-1}k'}(\mathbf{r}) = e^{i k' \cdot \mathbf{r}} u_k(R\mathbf{r} + \mathbf{T})$$

[A2.6]

The wave vector $\mathbf{k}$ indexing the irreducible representations of the translation group is defined to within a reciprocal lattice vector as explained in appendix 1. The group of a wave vector is defined as the collection of operations which leave the wave vector invariant. These operations form a subgroup of the factor group as they include the elements of identity and inversion and closure is clearly required. The wave functions $\{\psi_{\mathbf{k}}; \mathbf{k} = \mathbf{R}\mathbf{k}\}$ form an invariant subspace under the group of the wave vector $\mathbf{k}$ and therefore define a set of basis functions for a representation of the group. Consequently, a set of wave functions $\{\psi_{\mathbf{k}}\}$ may be uniquely defined as the basis functions of the unitary irreducible representation of the group of the wave vector $\mathbf{k}$. These Bloch wave functions are therefore defined as the basis functions of irreducible representations where the functions belonging to different representations or different rows of the same unitary representations (partners) are orthogonal. The group of the wave vector at a symmetry point in the Brillouin zone may contain several irreducible representations which will allow considerable factorisation of the secular determinant in a variational calculation.

An arbitrary function ψ may be symmetrised to form a basis function $\psi^{(\mu)}$ of the irreducible representation μ through the application of a projection operator $P^{(\mu)}$.

$$P^{(\mu)} \psi = \psi^{(\mu)}$$

[A 7.7]

The orthogonality relations of representation theory allow

the definition of $\rho^{(\mu)}$ in terms of the characters $\chi^{(\mu)}(g)$ of the representation. The irreducible representation has order n_μ and the group has order g .

$$\rho^{(\mu)} = \frac{n_\mu}{g} \sum_G \chi^{(\mu)}(g) \cdot g \quad [A2.8]$$

The relationship between the order of a group and the order of the irreducible representations is given as follows:

$$g = \sum_\mu n_\mu^2 \quad [A2.9]$$

The elements of any given class have a common character and the number of classes equals the number of irreducible representations. The symmetrised basis functions required in the present calculation are given in the literature and are not derived here. (18,21,36) The multiplication and character tables of the irreducible representations required are given elsewhere. (71-73)

The dimensions of the irreducible representations of the group of the wave vector may be easily derived from the previous statements. The group of the wave vector of the point Γ is of order 48 and contains 10 classes. The group therefore contains 10 irreducible representations and the dimensions are given from the solution of equation A2.9. The corresponding results for the three symmetry points Γ , X and L are summarised in the following identities; the groups of the wave vector contain 10, 14 and 6 classes respectively.

$$g(r) = 48 = 4 \cdot 1^2 + 2 \cdot 2^2 + 4 \cdot 3^2$$

$$g(x) = 32 = 8 \cdot 1^2 + 6 \cdot 2^2$$

$$g(L) = 12 = 4 \cdot 1^2 + 2 \cdot 2^2 \quad [A2.10]$$

The basis functions of the irreducible representations employed in the calculation are given in table 1. The orthogonality relations for the basis functions may be derived directly on consideration of the lattice inversion symmetry; for example, consider the two basis functions ψ_1 and ψ_2 from alternative rows of the X_1 representation.

$$\psi_1 = |s_1\rangle + |s_2\rangle, \psi_2 = |s_1\rangle - |s_2\rangle, \langle s_1|x_1\rangle = -\langle s_2|x_1\rangle, \langle s_1|x_2\rangle = -\langle s_2|x_2\rangle;$$

$$\langle \psi_1 | \psi_2 \rangle = \langle s_1|x_1\rangle + \langle s_2|x_2\rangle - \langle s_1|x_2\rangle - \langle s_2|x_1\rangle = 0 \quad [A2.11]$$

The matrix elements of the Hamiltonian are derived analogously and the group-theoretical matrix-element theorem may be verified directly; for example, consider the diagonal matrix element of the basis function ψ of the L_1 representation.

$$\psi = |s_1\rangle + e^{-ik \cdot T} |s_2\rangle, \langle s_1|s_1\rangle = \langle s_2|s_2\rangle, \langle s_1|s_2\rangle = \langle s_2|s_1\rangle^*;$$

$$E = \frac{2\pi}{a} (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), T = a (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), e^{-ik \cdot T} = -\frac{1}{\sqrt{2}} (1+i)$$

$$H_{11} = \langle \psi | H | \psi \rangle = \langle s_1|s_1\rangle + \langle s_2|s_2\rangle + e^{-ik \cdot T} \langle s_1|s_1\rangle + e^{ik \cdot T} \langle s_2|s_1\rangle$$

$$H_{11} = 2 \langle s_1|s_1\rangle + \frac{2}{\sqrt{2}} (-R \langle s_1|s_2\rangle + J \langle s_1|s_2\rangle) \quad [A2.12]$$

The non-vanishing matrix elements are given in table 2. The symmetry relations of the matrix elements are defined in appendix 4 and specified in table 4.

Appendix 3

THE EXPANSION OF THE LATTICE POTENTIAL

The kubic harmonics were introduced in section 2.4 as the basis functions of the irreducible representations of the lattice point group.⁽⁷⁴⁾ The 24 simple operations outlined in section 2.1 define the point group of the diamond lattice;⁽¹⁴⁾ the operations of a point group involve rotation and inversion at a lattice point. The basis functions may be generated as outlined in appendix 2 and the required results are available in the literature.⁽³¹⁾ The spherical harmonics $Y_l^m(\theta, \phi)$ correspond to the basis functions for the $(2l+1)$ -dimensional irreducible representations of the three-dimensional rotation group.^(24,75) A general point group is a finite subgroup of the group formed by the product of the full rotation group and the inversion group of order 2. The spherical harmonics $Y_l^m(\theta, \phi)$ are defined with a definite parity $(-1)^l$ such that they form the basis functions for the representation of this product group; consequently the functions of a given representation form an invariant subspace with respect to any lattice point group. The kubic harmonics of lower order may therefore be found directly by inspection. The relation between a third-order kubic harmonic and the associated spherical harmonic basis is given in the following example; the normalisation is verified directly.

$$K_3(\theta, \phi) = \frac{1}{\sqrt{2}} (Y_3^2 - Y_3^{-2}) = \sqrt{\frac{15}{4\pi}} \cdot \frac{x y z}{r^3}$$

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta$$

$$\begin{aligned} \int k_3^2 d\Omega &= \frac{105}{4\pi} \int_0^{2\pi} \sin^2 \phi \cos^2 \phi d\phi \int_0^\pi \sin^5 \theta \cos^2 \theta d\theta \\ &= \frac{105}{4\pi} \int_0^{2\pi} \frac{1}{6}(1 - \cos 4\phi) d\phi \int_0^\pi (y^5 - 2y^3 + y) dy = \frac{105}{4\pi} \cdot \frac{\pi}{4} \cdot \frac{16}{105} = 1 \end{aligned} \quad [A3.1]$$

This cubic harmonic forms a basis function for the trivial one-dimensional representation of the point group of the diamond lattice. The representation is trivial in the sense that the operations are all equivalent to the identity operation within this representation. The basis functions of all such representations will form the complete set of orthonormal functions defining a general expansion of the lattice potential function.

$$V(r, \theta, \phi) = \sum_n V_n(r) \cdot k_n(\theta, \phi) \quad [A3.2]$$

The cubic harmonics defining the lower order terms of this expansion are given in table 3. The cubic harmonics were first derived by von der Lage and Bethe⁽³⁴⁾ for the full cubic symmetry group of order 48; the behaviour of the basis functions under the 10 distinct classes of operations is summarised in this reference. The diamond symmetry group is a subgroup of this cubic symmetry group. The diamond point group has five classes and irreducible representations; the orders of the representations may be derived from equation A2.9.

$$g = 24 = 2 \cdot 1^2 + 1 \cdot 2^2 + 2 \cdot 3^2 \quad [A3.3]$$

The irreducible representations of the diamond point group are therefore contained in the irreducible representations of the cubic symmetry group and may be derived within such representations.

The cubic harmonic expansion coefficients $V_n(r)$ are defined in equation 2.16 ..

$$V(r, \theta, \phi) = \sum (R_i) v(r - R_i)$$

$$V_n(r) = \sum (R_i) \int K_n(\theta, \phi) \cdot v(r - R_i) d\Omega \quad [A3.4]$$

The integrals defined in the previous expression are not independent since they are related through the transformations which connect the lattice points R_i where the spherically-symmetric atomic potential functions $v(r - R_i)$ are located. These integrals are invariant under the operations of the lattice point group; the lattice vectors R_i which are equivalent under the operations of the point group will clearly define an identical integration. However, there are other cases where the required integrals are related; for example, the lattice points related by the inversion operation will generate integrals which differ only in sign depending on the parity of the cubic harmonic involved. The study of these symmetry relations is facilitated by considering the individual integrals in a coordinate system which is defined relative to the position of the associated potential function. A general coordinate transformation may be defined which allows the systematic evaluation of the integrals required. The transformation may be expressed in terms of the conventional Euler angles (ϕ, θ, ψ) .⁽⁷⁶⁾ A unique transformation S which aligns the z axis along the position vector R_i of an atomic potential function is defined by the following equation; the

position vector R_i may be expressed in spherical polar coordinates (R_i, θ_i, ϕ_i) .

$$R_i = R_i (\underline{e}_x + m_i \underline{e}_y + n_i \underline{e}_z)$$

$$R_i = |R_i|$$

$$R_i' = R_i \underline{e}_i$$

$$\phi = -(\pi/2 - \phi_i)$$

$$\cos \phi = \frac{m}{(l^2 + m^2)^{1/2}}, \quad \sin \phi = \frac{-l}{(l^2 + m^2)^{1/2}}$$

$$\theta = -\theta_i$$

$$\cos \theta = n$$

$$\sin \theta = -(l^2 + m^2)^{1/2}$$

$$\psi = 0$$

$$\cos \psi = 1$$

$$\sin \psi = 0$$

$$\underline{e}' = S \underline{e}$$

$$\underline{e} = \underline{S} \underline{e}'$$

$$S = (s_{ij}) = \begin{bmatrix} \frac{m}{(l^2 + m^2)^{1/2}} & \frac{-l}{(l^2 + m^2)^{1/2}} & 0 \\ \frac{2n}{(l^2 + m^2)^{1/2}} & \frac{mn}{(l^2 + m^2)^{1/2}} & -(l^2 + m^2)^{1/2} \\ l & m & n \end{bmatrix}$$

[A3.5]

The relation between the integrals in any lattice shell may therefore be evaluated directly; $\{R_i; |R_i| = R\}$ defines the members of the shell of radius R .

$$\int k_n(\theta, \phi) r(\underline{e} - R_i) d\Omega = \int_{-1}^{+1} \left[\int_0^{2\pi} k_n'(\theta', \phi') d\phi' \right] r((r^2 + R^2 - 2rR_i t)^{1/2}) dt \quad [A3.6]$$

The corresponding results are easily derived for the case of the third kubic harmonic expansion coefficients.

$$k_3'(\theta', \phi') = \sqrt{\frac{105}{4\pi}} \frac{x y z}{r^3}$$

$$\int_0^{2\pi} k_3'(\theta', \phi') d\phi' =$$

$$\sqrt{\frac{105}{4\pi}} \cdot \frac{1}{r^3} \left[2mn \int_0^{2\pi} z'^3 d\phi' - \frac{2mn}{(l^2 + m^2)^{1/2}} \int_0^{2\pi} x'^2 z' d\phi' + \left(\frac{2mn}{(l^2 + m^2)^{1/2}} - 3lmn \right) \int_0^{2\pi} y'^2 z' d\phi' \right] \quad [A3.7]$$

While there are ten distinct terms in the transformed harmonic $k_3'(\theta', \phi')$, the three terms given in the previous equation are the remaining terms which contribute to the integral required. This number may be further reduced on integration of

the remaining terms defined in equation A3.7 .

$$\int_0^{2\pi} \frac{z'^3}{r^3} d\phi' = 2\pi \cos^3 \theta' \quad \int_0^{2\pi} \frac{x'^2 z'}{r^3} d\phi' = \int_0^{2\pi} \frac{y'^2 z'}{r^3} d\phi' = \pi \sin^2 \theta' \cos \theta'$$

$$\int k_3(\theta, \phi) v(r-R_2) d\Omega = \sqrt{\frac{105}{4\pi}} \cdot 2\pi \sin \theta \int_{-1}^1 \int_0^{2\pi} \frac{1}{r^3} (z'^3 - 3x'z'x') \cdot v((r^2 + R_2^2 - 2rR_2\cos\theta')^{1/2}) \cdot d\phi' d\cos\theta' \quad [A3.8]$$

The general case may be expressed in terms of an alternative form of the kubic harmonic $\bar{k}_n(\theta, \phi)$; the alternative forms for the lower order kubic harmonics are defined in table 3.

$$\int k_n(\theta, \phi) v(r-R_2) d\Omega = k_n(\theta_2, \phi_2) \int \bar{k}_n(\theta', \phi') v(r-R_1) d\Omega' \quad [A3.9]$$

The final result requires a single integration within each lattice shell of radius R where $R_2 = R_1 \cos \theta_2 / R \cos \theta_1$.

$$V_n(r) = \sum (A_n) k_n(\theta_2, \phi_2) \int \bar{k}_n(\theta', \phi') \cdot v(r-R_1) d\Omega' \quad [A3.10]$$

Although the development of this transformation is quite general, a manual calculation of the alternative form of the kubic harmonics become prohibitive at higher orders.

A similar reduction for the expansion of the lattice potential may be developed directly in terms of harmonic functions defined on the sphere. The kubic harmonic functions $Z_2^m(\theta, \phi)$ correspond to a complete set of orthonormal real-valued functions over the sphere; they may be defined as the unitary transformation of the spherical harmonic functions $Y_l^m(\theta, \phi)$ within their individual irreducible representations.

$$Z_2^m(\theta, \phi) = \sum_{m'=-2}^2 A_{2m'} Y_2^{m'}(\theta, \phi)$$

$$\int Z_2^{m'}(\theta, \phi) Z_2^m(\theta, \phi) d\Omega = \left(\sum_{m''=-2}^2 A_{2m''} A_{2m} \right) \delta_{2'2} \delta_{m'm} = \delta_{2'2} \delta_{m'm} \quad [A3.11]$$

The atomic potential function $v(\underline{r}-\underline{R}_i)$ may be expanded about the lattice origin in a series of Legendre polynomials $P_\ell(\cos \gamma_i)$ which are functions of the angle γ_i between the vectors $\underline{r}$ and $\underline{R}_i$.

$$v(\underline{r}-\underline{R}_i) = \sum_{\ell=0}^{\infty} \frac{(2\ell+1)}{2} S_{\ell,i} P_\ell(\cos \gamma_i).$$

$$\cos \gamma_i = \hat{\underline{r}} \cdot \hat{\underline{R}}_i = \cos \theta \cos \theta_i + \sin \theta \sin \theta_i \cos(\phi - \phi_i)$$

$$S_{\ell,i} = \int_{-1}^{+1} v(\underline{r}-\underline{R}_i) P_\ell(\cos \gamma_i) d(\cos \gamma_i) \quad [A3.12]$$

The Legendre polynomial $P_\ell(\cos \gamma_i)$ may be expanded in the lattice frame in a series of kubic harmonics, $Z_\ell^m(\theta, \phi)$. The expansion required corresponds to the addition theorem for kubic harmonics which may be derived in the manner of the analogous theorem for spherical harmonics. (77)

$$P_\ell(\cos \gamma_i) = \sum_{\ell'=0}^{\infty} \sum_{m=-\ell'}^{\ell'} A_{\ell',m}(\theta_i, \phi_i) Z_{\ell'}^m(\theta, \phi)$$

$$A_{\ell',m}(\theta_i, \phi_i) = \frac{4\pi}{(2\ell'+1)} Z_{\ell'}^{m*}(\theta_i, \phi_i) \delta_{\ell',\ell}$$

$$P_\ell(\cos \gamma_i) = \frac{4\pi}{(2\ell+1)} \sum_{m=-\ell}^{\ell} Z_{\ell}^{m*}(\theta_i, \phi_i) Z_{\ell}^m(\theta, \phi) \quad [A3.13]$$

The lattice potential function may therefore be expanded in terms of the complete set of kubic harmonic functions.

$$V(\underline{r}, \theta, \phi) = \sum_i (\underline{R}_i) v(\underline{r}-\underline{R}_i) = \sum_{\ell=0}^{\infty} V_{\ell}(\underline{r}) K_{\ell}(\theta, \phi)$$

$$V(\underline{r}, \theta, \phi) = 2\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left(\sum_i (\underline{R}_i) S_{\ell,i} Z_{\ell}^{m*}(\theta_i, \phi_i) \right) Z_{\ell}^m(\theta, \phi) \quad [A3.14]$$

The expansion coefficients $V_{\ell}(\underline{r})$ are defined by equating the two equivalent expansions in the kubic harmonic functions.

The coefficients are necessarily zero for the harmonics which do not correspond to an identity representation of the cubic group.

$$V_n(r) = 2\pi \sum_i S_{n,i} \cdot k_n(\theta_i, \phi_i) \quad [A3.15]$$

The coefficient $S_{n,i}$ is invariant for the members $\{\underline{R}_i; |\underline{R}_i| = R\}$ of a lattice shell of radius R ; this may be derived by considering the transformation developed in the previous section. The final result defined in equation 2.17 follows immediately from these observations. The Legendre functions $P_n(t)$ of order n are readily derived and the forms of the lower order polynomials are defined in table 3.

The two forms of the expansion developed are clearly equivalent and may be directly related in the following sense; for example, consider the expansion coefficient of the third cubic harmonic function $k_3(\theta, \phi)$.

$$\begin{aligned} V_3(r) &= \sum_i (\underline{R}_i) k_3(\theta_i, \phi_i) \int \bar{F}_n(\theta', \phi') \cdot r(r - \underline{R}_i') d\Omega' \\ &= 2\pi \sum_i (\underline{R}_i) k_3(\theta_i, \phi_i) \int_{-1}^1 \frac{1}{2} (5t^2 - 3t) r(r^2 + R_i^2 - 2rR_i t)^{1/2} dt \\ &= 2\pi \sum_i (\underline{R}_i) k_3(\theta_i, \phi_i) \int_{-1}^1 r(r - R_i) \cdot P_3(\cos \theta_i) \cdot d(\cos \theta_i) \\ &= 2\pi \sum_i (\underline{R}_i) S_{3,i} \cdot k_3(\theta_i, \phi_i) \quad [A3.16] \end{aligned}$$

Consequently, the alternative form of a cubic harmonic $k_n(\theta, \phi)$ may be derived from the Legendre form of the polynomial $P_n(t)$ and vice versa.

Appendix 4

THE TRANSFORMATION OF THE MATRIX ELEMENTS

The matrix elements $\langle \mu | H | \mu \rangle$ of the crystal Hamiltonian H and the Bloch wave function basis $|\mu\rangle$ were reduced in section 2.4 to a series of three-center integrals defined in equation 2.20. The reduction is defined in equation 2.18 and the corresponding results are summarised in table 4. The derivation of equation 2.18 is developed here from the analysis of section 2.2; a result of equation 2.8 may be redefined in the following form.

$$\langle \mu | H | \mu \rangle = \exp(-ik \cdot T_i) \cdot \exp(ik \cdot T_j) \sum (R) \exp(ik \cdot R) \cdot E_{\mu, \mu_j}(R)$$

$$E_{\mu, \mu_j}(R) = \int \psi_{\mu}^*(r - T_i) H(r) \psi_{\mu}(r - T_j - R) d^3r$$

$$(R = A_1, T_i = A_{T_1}, T_j = A_{T_2})$$

[A4.1]

The translation and inversion symmetry of the diamond lattice are defined by the following expressions; the center of inversion symmetry is given by the position vector $T/2$.

$$H(r) = H(r + R) = H(-r + T)$$

[A4.2]

The identity of inversion symmetry may be derived by translating and inverting the lattice frame at a symmetry center.

$$H(r) = H(r + T/2) = H(r') = H(r' + T/2) = H(-r' + T) \quad [A4.3]$$

The atomic wave functions $\psi_{\mu}(r)$ defining the Bloch wave function basis $|\mu\rangle$ have a definite parity γ_{μ} under inversion.

$$\psi_{\mu}(-r) = \gamma_{\mu} \cdot \psi_{\mu}(r), \quad \gamma_{\mu} = \pm 1$$

[A4.4]

The components $E_{\mu, \mu_j}(R)$ of the matrix elements are interrelated through the symmetry of the Hamiltonian; a simple relation

follows from consideration of the translational symmetry.

$$E_{\mu\nu}(\mathbf{R}) = \int \varphi_{\mu}^*(\mathbf{r}-\mathbf{T}) H(\mathbf{r}) \varphi_{\nu}(\mathbf{r}-\mathbf{T}+\mathbf{R}) d^3r = \left(\int \varphi_{\mu}^*(\mathbf{r}-\mathbf{T}) H(\mathbf{r}) \varphi_{\nu}(\mathbf{r}-\mathbf{T}+\mathbf{R}) d^3r \right)^*$$

$$E_{\mu\nu}(\mathbf{R}) = E_{\nu\mu}^*(-\mathbf{R}) \quad [A4.5]$$

A further relation may be derived on applying the inversion symmetry of the lattice.

$$E_{\mu\nu}(\mathbf{R}) = \int \varphi_{\mu}^*(\mathbf{r}-\mathbf{T}) H(\mathbf{r}) \varphi_{\nu}(\mathbf{r}-\mathbf{T}+\mathbf{R}) d^3r = \int \varphi_{\mu}^*(\mathbf{r}+\mathbf{T}-\mathbf{T}) H(\mathbf{r}) \varphi_{\nu}(-\mathbf{r}+\mathbf{T}-\mathbf{T}+\mathbf{R}) d^3r$$

$$= \gamma_{\mu} \gamma_{\nu} \int \varphi_{\mu}^*(\mathbf{r}-\mathbf{T}) H(\mathbf{r}) \varphi_{\nu}(\mathbf{r}-\mathbf{T}+\mathbf{R}) d^3r, \quad \mathbf{T}' = \mathbf{T} - \mathbf{T}$$

$$E_{\mu\nu}(\mathbf{R}) = \gamma_{\mu} \gamma_{\nu} E_{\mu\nu}(-\mathbf{R}) \quad [A4.6]$$

The results of equations A4.5 and A4.6 are easily visualised although the notation may appear confusing. The expressions defined in table 4 may be derived directly on application of the relations given; the Hamiltonian nature of H may also be verified explicitly.

$$\begin{aligned} \langle s_1 | H | s_2 \rangle^* &= \left(e^{-i\mathbf{k} \cdot \mathbf{T}} \sum(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} E_{s_1 s_2}(\mathbf{R}) \right)^* = e^{i\mathbf{k} \cdot \mathbf{T}} \sum(\mathbf{R}) e^{-i\mathbf{k} \cdot \mathbf{R}} E_{s_1 s_2}^*(\mathbf{R}) \\ &= e^{i\mathbf{k} \cdot \mathbf{T}} \sum(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} E_{s_1 s_2}^*(-\mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{T}} \sum(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} E_{s_1 s_2}(\mathbf{R}) = \langle s_1 | H | s_2 \rangle \end{aligned} \quad [A4.7]$$

A further relation for the matrix element $\langle s_1 | H | s_2 \rangle$ may be determined.

$$\langle s_1 | H | s_2 \rangle = e^{i\mathbf{k} \cdot \mathbf{T}} \sum(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} E_{s_1 s_2}(\mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{T}} \sum(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} E_{s_2 s_1}(-\mathbf{R})$$

$$\langle s_1 | H | s_2 \rangle = -e^{i\mathbf{k} \cdot \mathbf{T}} \sum(\mathbf{R}) e^{i\mathbf{k} \cdot \mathbf{R}} E_{s_2 s_1}^*(\mathbf{R}) \quad [A4.8]$$

The final expressions are particularly simple in the case where the atomic wave functions are chosen as real-valued functions.

$$\varphi_{\mu}^*(\mathbf{r}) = \varphi_{\mu}(\mathbf{r}), \quad \varphi_{\nu}^*(\mathbf{r}) = \varphi_{\nu}(\mathbf{r}) \Rightarrow E_{s_1 s_2}(\mathbf{R}) = E_{s_2 s_1}(\mathbf{R})$$

$$\langle s_1 | H | s_2 \rangle = -\langle s_1 | H | s_2 \rangle = -\langle s_2 | H | s_1 \rangle \quad [A4.9]$$

The independent matrix elements of table 4 are derived in this manner; the present notation may be reduced to the form

employed in section 2.4 .

$$E_{\mu, \nu_1}(\underline{R}) = E_{\mu\nu}(\underline{R}_1^2) \quad E_{\mu, \nu_2}(\underline{R}) = E_{\mu\nu}(\underline{R}_1^2) \quad [A4.10]$$

The application of the lattice potential expansion reduces the components $E_{\mu\nu}(\underline{R})$ to a series of two-center integrals in equation 2.21 . A simple calculation may be developed by considering the lowest order potential expansion which involves only the zero-order cubic harmonic term $K_0(\theta, \phi)$.

$$K_0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

$$E_{\mu\nu}^{(0)}(\underline{R}_1) = \int \frac{V_0(r)}{\sqrt{4\pi}} \int \varphi_\mu^*(\underline{r}) \varphi_\nu(\underline{r} - \underline{R}_1) d\Omega dr \quad [A4.11]$$

The integral may be reduced through application of the transformation defined in equation A3.5 .

$$E_{\mu\nu}^{(0)}(\underline{R}_1) = \int \frac{V_0(r')}{\sqrt{4\pi}} \int \varphi_\mu^*(\underline{r}') \varphi_\nu(\underline{r}' - \underline{R}_1) d\Omega' dr' \quad [A4.12]$$

A reduction follows from an analytical integration over the azimuthal coordinate as outlined in appendix 3. The transformations of the components $E_{\mu\nu}^{(0)}(\underline{R})$ may be considered individually; for example, the component $E_{xy}^{(0)}(\underline{R}_1)$ may be reduced as follows.

$$\varphi_x(r') = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cdot \varphi_p(r') \frac{x}{r'} \quad , \quad \varphi_y(r' - \underline{R}_1) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cdot \varphi_p(r'') \cdot \frac{y - y_1}{r''}$$

$$\underline{r}'' = \underline{r}' - \underline{R}_1 \quad , \quad \underline{R}_1 = R_1 \underline{e}_1 \quad (x_1' = y_1' = 0, \quad z_1' = R_1 = y_1/w)$$

$$\int_0^{2\pi} \varphi_x^*(\underline{r}') \varphi_y(\underline{r}' - \underline{R}_1) d\phi' =$$

$$\frac{3}{4\pi} \cdot \frac{\varphi_p^*(r')}{r'} \cdot \frac{\varphi_p(r'')}{r''} \left[\frac{-8w}{(4^2 + w^2)} \int_0^{2\pi} x'^2 d\phi' + \frac{8w^2}{(4^2 + w^2)} \int_0^{2\pi} y'^2 d\phi' + 8w \int_0^{2\pi} z'(z' - z_1) d\phi' \right] \quad [A4.13]$$

There are three terms which contribute to the integral and two of these remaining terms are equivalent under integration.

$$\int_0^{2\pi} r'^2 d\phi' = \int_0^{2\pi} r'^2 d\phi' = \pi r'^2 \sin^2 \theta' \quad \int_0^{2\pi} z' (z' - z) d\phi' = 2\pi r' \cos \theta' (r' \cos \theta' - z) \quad [A4.14]$$

The final transformation may be expressed in the notation of section 2.4 .

$$(pp\sigma)_i = \int \frac{V_\sigma(r)}{\sqrt{4\pi}} \int \varphi_\sigma^*(r) \varphi_\sigma(r - R_i) d\Omega' dr' \quad (pp\pi)_i = \int \frac{V_\pi(r)}{\sqrt{4\pi}} \int \varphi_\pi^*(r) \varphi_\pi(r - R_i) d\Omega' dr' \\ E_{xy}^{(0)}(R_i) = \lim (pp\sigma)_i - \lim (pp\pi)_i \quad [A4.15]$$

The two-center integrals $(pp\sigma)$ and $(pp\pi)$ may be reduced to two-dimensional integrals as outlined and are invariant in any lattice shell $\{R_i; |R_i|=R\}$ of radius R . The components $E_{MN}^{(0)}(R_i)$ defined in table 5 may be transformed in this manner.

A general analysis is required for the higher-order components $E_{MN}^{(n)}(R_i)$ and this may be developed through the methods introduced in appendix 3.

The application of the symmetry relations of the matrix elements may be illustrated by calculating the eigenvalues of the Γ_1 and Γ_2 representations; these eigenvalues are denoted E_+ and E_- respectively.

$$E_{\pm} = \frac{\langle s_1 | H | s_1 \rangle \pm \langle s_1 | H | s_2 \rangle}{\langle s_1 | s_1 \rangle \pm \langle s_1 | s_2 \rangle} \quad [A4.16]$$

It is emphasised that the symmetry relations are defined in this appendix for the crystal Hamiltonian H . Alternatively, the result may be expressed in terms of the reduced Hamiltonian H' .

$$H = H_0 + H' \quad E_{\pm} = E_0 + \frac{\langle s_1 | H' | s_1 \rangle \pm \langle s_1 | H' | s_2 \rangle}{\langle s_1 | s_1 \rangle \pm \langle s_1 | s_2 \rangle} \quad [A4.17]$$

The last expression incorporates the result developed in equation 2.10 .

Appendix 5

THE CALCULATION OF THE MATRIX ELEMENTS

This appendix describes the structure and characteristics of the computer programs developed to perform the calculations. The computations were carried out by Fortran programs using an IBM System 360 model 65 computer. Although great emphasis was placed on optimisation during program development, the programs generated are comprised of practical general purpose routines offering maximum utility and convenience. A general programming system was designed for maximum flexibility by adapting a structure closely related to the mathematical expressions under evaluation; this assists development considerably by facilitating adaption to the variety of computations required. The programs were generally run in source form as the computational scheme was under continuous development and the estimates given exclude the associated Fortran H compilation offering maximum optimisation. The programs generally required less than 200K bytes of core storage including compilation. The larger storage requirements of the data generated were handled by sequential access records on magnetic disc and tape devices. The program estimates are approximate and are given as general information for guidance and should not be interpreted as significant lower limits.

The calculation of the effective atomic potential function presents little difficulty and is carried out accu-

ately in 5 seconds of computing time. The contribution of the Coulomb terms is calculated efficiently by the subroutine APFC. The inner and outer electron shielding terms are evaluated by a systematic outward and inward integration over the range of the atomic structure. The contribution of the exchange term was computed separately by the subroutine APFE in order to facilitate comparison of the various exchange treatments. The calculation of the mean value of the crystal potential is carried out by the program NISQ1 and corresponds to an efficient Simpson quadrature. The atomic wave functions are evaluated in these calculations by the general optimised subprograms developed for the calculation of the multi-center integrals. The Lagrange interpolation coefficients are computed over the range of the tabulated atomic structure functions by the subroutine LAIC2. The atomic wave functions are then defined in the computation by the associated subprograms designated ASFL.

The nearest neighbour analysis of the finite diamond lattice is carried out directly by the subroutines FCCPCM, FDSORT, SGROUP and FCCCVN. The program is simple and emphasis is placed on developing the subroutines FCCREF and FCCDIS which store, retrieve and display any data set required. A single generation of the data set NNADMD for 150 orders of neighbours requires several minutes of computing time, while the corresponding data may be retrieved from disc in an insignificant amount of time.

The calculation of the lattice potential function at every point of the integration mesh requires a lengthy computation which is divided into several convenient program steps. The data set NLVXYZ containing the neighbouring lattice point for every point on the integration mesh is generated by subroutines NLVXYZ, NLVFCC and NLVDIS. The data set is stored on magnetic tape. The lattice potential is evaluated at any point of the mesh by summing the contributions of every atomic potential overlapping that point. The subroutines LPFS, LPFNNA and LPFDIS trace the nearest lattice point in the data set NLVXYZ and sum the contributions from all the neighbouring lattice points. The programs available require more than an hour of computer time for the generation of the associated data set CLFPTR although this may be reduced considerably by further development. In the present application, the emphasis is placed on the efficient retrieval of the sequential data set CLFPTR from disc by the subroutine APFLPF. The cubic harmonic expansion coefficients for the lattice potential are calculated by the subroutines SHEKHA and RITFMN which employ the function subroutines FN and CHANOP for the Nth order term. The program is well structured and optimised and requires 150 seconds of computing time to calculate each set of coefficients for the 201 points on the integration mesh. The potential representation in a cubic harmonic expansion is defined for any order in a series of subroutines APFSHE.

The calculation of the multi-center integrals is carried out by the subroutines NISRT and NISPTR for the two-dimensional and three-dimensional cases respectively. The various functions required are calculated by the individual subroutines ASFL, APFLPF and APFSHE already outlined and by the subroutines SHM which define the angular variation of the atomic wave functions. The functions for a particular integral are combined in the subroutines INTE which characterise the general classes of calculation. The two-center and three-center integrals require 5 seconds and 120 seconds of computing time respectively.

Finally, the matrix and overlap elements are calculated for the different wavevectors by the elementary subroutines ASUMOP, SPHASE and SUMMEC.

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