This is to certify that the

thesis entitled

BAND STRUCTURE AND REFRACTIVE
INDEX CALCULATIONS FOR SEMICONDUCTORS

presented by

Mark Douglas Ewbank

has been accepted towards fulfillment
of the requirements for

Master degree in Physics

Major professor

Date 4/4/79

O-7639

BAND STRUCTURE AND REFRACTIVE INDEX CALCULATIONS FOR SEMICONDUCTORS

By

Mark Douglas Ewbank

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

Department of Physics

1979

ABSTRACT

BAND STRUCTURE AND REFRACTIVE
INDEX CALCULATIONS FOR SEMICONDUCTORS

By

Mark Douglas Ewbank

A "chemical bond" approach was employed to provide a means of theoretically predicting material properties of semiconductors which can be used to delimit the performance characteristics in specific device applications. First, a set of empirical parameters used to represent the interaction between atomic orbitals was investigated by performing numerical band structure computations following the LCAO or tight binding method and utilizing the Slater-Koster 2-center integral approximation. Band structures were acquired for zinc-blendes (Si, Ge, GaAs, ZnSe), chalcopyrites ($ZnSiAs_2$, $CdGeAs_2$ and $CdGeP_2$) and a sulfosalt (Tl_3AsSe_3). Then Harrison's bond-orbital model (BOM) was engaged to predict the principal refractive indices of the chalcopyrites through a similar parameterization. Both numerical calculations were implemented with "generalized" Fortran computer programs (listings included).

To

Laurian,

Shawn,

and

Cathy

ACKNOWLEDGMENTS

The author would like to express his appreciation to E.A. Kraut and W.A. Harrison for the vast amounts of consultation they offered. Also, P.R. Newman deserves recognition for many fruitful suggestions concerning the subject matter of the work. Finally, the author wishes to thank J. Tracy and P.A. Schroeder for making this effort possible.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

LIST OF FIGURES (Cont'd)

LIST OF FIGURES (Cont'd)

LIST OF TABLES

INTRODUCTION

Sophisticated space surveillance requires a "solid state" electronically tunable filter which functions in the infrared region of the electromagnetic spectrum. In other words, the optical filter should exhibit, for example, a spectral passband of approximately ten nanometers about a central wavelength that is remotely tunable from three to five or eight to twelve microns. Two possible devices which can fulfill these types of requirements are Acousto-Optical Tunable Filters (AOTF) and Electro-Optic Tunable Filters (EOTF). Also, future applications may arise in the visible and even ultraviolet portions of the spectrum which could be satisfied by similar devices.

There is a variety of physical problems to resolve in the development of such devices--crystal growth, material properties characterizations, acoustic wave propagation, infrared imaging through an optically anisotropic medium, etc. The primary purpose of this work is to initiate the evolution of working theoretical models that are capable of predicting some pertinent material properties which are necessary for tunable filter design. In particular, by qualitatively ranking ternary crystalline semiconductors with respect to a specific physical property (e.g., birefringence, elasto-optical coefficients or electro-optical coefficients), the numerous candidates can be screened in an attempt at optimizing crystal selection for tunable filter development. More generally, the underlying intention of this

endeavor is to furnish theories that can benefit the needs of eventual, yet unforeseen, device applications.

The emphasis of the present work involves predicting the principle refractive indices using a "chemical bond" approach. The empirical parameters used to characterize a "bond interaction" are initially investigated, in detail, with energy band structure calculations. And then, subsequently, the principal indices of refraction are computed by employing an equivalent set of parameters. Both numerical calculations are implemented on a computer, incorporating the concept of general applicability to any semiconductor which helps to fulfill the criterion of providing a theoretical foundation for future requirements.

ENERGY BAND CALCULATIONS

To test the numerical accuracies of the parameters used to describe the interaction of electronic orbitals between two atoms (transfer integral), energy band calculations have been performed and compared with similar band structures that can be found in the literature ad infinitum.[1] The approach taken here utilizes the LCAO (Linear Combination of Atomic Orbitals) or tight binding method to determine the quantized energy states of electrons at various points in the Brillouin zone.[2,3]

FORMULISM

First, define and specify the notation, following that of Zunger.[4] Atomic orbitals (see Appendix A) are symbolized by $\phi_\mu(\vec{r}-\vec{R}_n^\alpha)$, where μ denotes the type of valence orbital (s, p_x, p_y, p_z, etc.) and $\vec{R}_n^\alpha$ is the vector distance to the αth atom in the nth unit cell. Bloch functions are formed by taking linear combinations of "equivalent" atomic orbitals in each unit cell where the expansion coefficients are determined by the periodicity of the lattice,

$$\Phi_\mu^\alpha(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{i\vec{k}\cdot\vec{R}_n^\alpha} \phi_\mu(\vec{r}-\vec{R}_n^\alpha) \qquad (1)$$

The summation is over unit cells and approaches an infinite sum for real crystals. "Equivalent" atomic orbitals imply one type of atomic orbital on the same atom in each unit cell. Crystal wave functions or eigenfunctions are linear combinations of the above Bloch

functions:

$$\psi_j(\vec{k},\vec{r}) = \sum_{\mu=1}^{\sigma} \sum_{\alpha=1}^{\eta} C_{\mu j}^{\alpha}(\vec{k})\, \Phi_{\mu}^{\alpha}(\vec{k},\vec{r}) \tag{2}$$

where j specifies which band (j = 1,2...., M and M = $\sigma\eta$ = number of bands). The summation over μ is a sum over all valence atomic orbitals and the summation over α is a sum over all atoms in the unit cell.

Each wavefunction $|\psi_j\rangle$, is a solution to the time independent Schrodinger equation,

$$H|\psi_j\rangle = E_j|\psi_j\rangle \tag{3}$$

To determine the coefficients, $C_{\mu j}^{\alpha}(\vec{k})$, minimize the energy eigenvalues, E_j, with respect to each coefficient. In other words,

$$\frac{\partial E_j}{\partial C_{\mu j}^{\alpha}} = 0 \tag{4}$$

for each μ and α, where

$$E_j = \frac{\langle\psi_j|H|\psi_j\rangle}{\langle\psi_j|\psi_j\rangle} \tag{5}$$

This results in a set of M = $\sigma\eta$ "Secular Equations" (see Equations 47 through 64 for an example)

$$\sum_{\mu=1}^{\sigma} \sum_{\alpha=1}^{\eta} C^{\alpha}_{\mu j}(\vec{k}) \langle \Phi^{\beta}_{\nu}(\vec{k},\vec{r}) | H | \Phi^{\alpha}_{\mu}(\vec{k},\vec{r}) \rangle - C^{\beta}_{\nu j}(\vec{k}) E_j = 0 \quad , \tag{6}$$

one for each $\nu = 1,\ldots,\sigma$ and $\beta = 1,\ldots,\eta$. These M equations contain M unknowns -- the coefficients, $C^{\alpha}_{\mu j}(\vec{k})$. If a nontrivial solution exists for a system of M linear, homogeneous equations in M unknowns, then the determinant of the coefficient of those M unknowns must be zero.[5] For the sake of illustration, let the double indices μ and α be represented by a single index. Then the Bloch function $\Phi^{\alpha}_{\mu}(\vec{k},\vec{r})$ goes to $\Phi_i(\vec{k},\vec{r})$ and the "Secular Determinant" can be written as

$$\begin{vmatrix} [\langle\Phi_1|H|\Phi_1\rangle - E_j] & \langle\Phi_1|H|\Phi_2\rangle & \langle\Phi_1|H|\Phi_3\rangle & \cdots & \langle\Phi_1|H|\Phi_M\rangle \\ \langle\Phi_2|H|\Phi_1\rangle & [\langle\Phi_2|H|\Phi_2\rangle - E_j] & \langle\Phi_2|H|\Phi_3\rangle & \cdots & \langle\Phi_2|H|\Phi_M\rangle \\ \langle\Phi_3|H|\Phi_1\rangle & \langle\Phi_3|H|\Phi_2\rangle & [\langle\Phi_3|H|\Phi_3\rangle - E_j] & \cdots & \langle\Phi_3|H|\Phi_M\rangle \\ \vdots & \vdots & \vdots & & \vdots \\ \langle\Phi_M|H|\Phi_1\rangle & \langle\Phi_M|H|\Phi_2\rangle & \langle\Phi_M|H|\Phi_3\rangle & \cdots & [\langle\Phi_M|H|\Phi_M\rangle - E_j] \end{vmatrix} = 0 \quad . \tag{7}$$

The solution of this secular determinant, which results in M energy eigenvalues, E_j, that correspond to each of the eigenfunctions, $\psi_j (j = 1,2,\ldots,M)$, is obtained by "diagonalizing" the matrix of the Hamiltonian, H. That is, perform a unitary transformation, $H' = U^{-1}HU$, which puts the Hamiltonian, H', into diagonal form. In other words,

$$\begin{vmatrix} [\langle\Phi'_1|H|\Phi'_1\rangle - E_j] & 0 & 0 & \cdots & 0 \\ 0 & [\langle\Phi'_2|H|\Phi'_2\rangle E_j] & 0 & \cdots & 0 \\ 0 & 0 & [\langle\Phi'_3|H|\Phi'_3\rangle - E_j] & & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & 0 & 0 & \cdots & [\langle\Phi'_M|H|\Phi'_M\rangle - E_j] \end{vmatrix} = 0 \quad . \tag{8}$$

The roots of this new secular determinant are

$$E_j = \langle\Phi'_j|H'|\Phi'_j\rangle \quad . \tag{9}$$

Also, the new eigenfunctions associated with these eigenvalues, E_j, are $\psi_j = \Phi'_j$. Since the eigenvalues are invariant under unitary transformation, the secular determinant of H and the diagonalized secular determinant of H' yield the same eigenvalues. (This diagonalization is done numerically on a computer by a Fortran subroutine, provided by the International Mathematical and Statistical Libraries (IMSL), which requires each of the matrix elements, $\langle\Phi_i|H|\Phi_j\rangle$, as input and returns the energy eigenvalues, E_j, and optionally the eigenfunctions, ψ_j.)

Consequently, to determine the eigenvalue energies at a given wave-vector, $\vec{k}$, in the Brillouin zone, the matrix elements, $\langle\Phi^\alpha_\mu(\vec{k},\vec{r})|H|\Phi^\beta_\nu(\vec{k},\vec{r})\rangle$ must be evaluated -- that is, the matrix element of the Hamiltonian between two Bloch functions of atomic orbitals. Writing out each Bloch function as an expansion of atomic orbitals from Equation 1,

$$\langle\Phi_\mu^\alpha|H|\Phi_\nu^\beta\rangle = \frac{1}{N}\langle[\sum_{n=1}^{N} e^{i\vec{k}\cdot\vec{R}_n^\alpha}\phi_\mu(\vec{r}-\vec{R}_n^\alpha)]|H|[\sum_{n'=1}^{N} e^{i\vec{k}\cdot\vec{R}_{n'}^\beta}$$

$$\phi_\nu(\vec{r}-\vec{R}_{n'}^\beta)]\rangle \ . \tag{10}$$

Since the Hamiltonian only operates on functions of $\vec{r}$,

$$\langle\Phi_\mu^\alpha|H|\Phi_\nu^\beta\rangle = \frac{1}{N}\sum_{n=1}^{N}\sum_{n'=1}^{N} e^{i\vec{k}\cdot(\vec{R}_{n'}^\beta-\vec{R}_n^\alpha)}\langle\phi_\mu(\vec{r}-\vec{R}_n^\alpha)|H|\phi_\nu(\vec{r}-\vec{R}_{n'}^\beta)\rangle. \tag{11}$$

This double sum can be reduced to N times a single sum, as illustrated in the following example. Consider the interaction between atomic orbitals ϕ_{A_5} and ϕ_{B_1} in the two-dimensional lattice with nine unit cells, as shown in Figure 1. This interaction corresponds to only one term in Equation 11. But an identical interaction occurs between the pairs of atoms (A_6, B_2), (A_8, B_4), and (A_9, B_5). In general, for N unit cells, there are N such identical interactions, neglecting edge effects.

Therefore, Equation 11 becomes

$$\langle\Phi_\mu^\alpha|H|\Phi_\nu^\beta\rangle = \sum_{n=1}^{N} e^{-i\vec{k}\cdot(\vec{R}_n^\alpha-\vec{R}_1^\beta)}\langle\phi_\mu(\vec{r}-\vec{R}_n^\alpha)|H|\phi_\nu(\vec{r}-\vec{R}_1^\beta)\rangle \tag{12}$$

where $\vec{R}_1^\beta$ is arbitrarily taken to imply the unit cell "at" the origin.

Now recall that the sum over N unit cells is essentially an infinite sum. To reduce this to a finite sum, consider only "near neighbors". In other words, assume that the matrix element, $\langle\phi_\mu(\vec{r}-\vec{R}_n^\alpha)|H|\phi_\nu(\vec{r}-\vec{R}_1^\beta)\rangle$, is negligible when the overlap is small. A

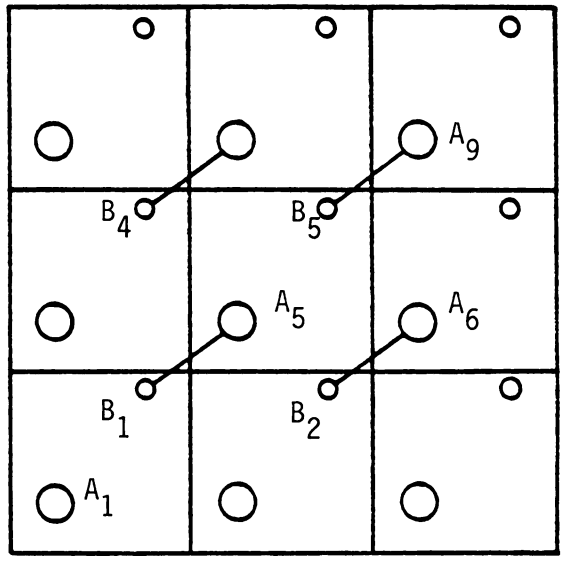


Figure 1 Identical interaction between pairs of atomic orbitals from 2-D lattice periodicity

small overlap between the two atomic orbital occurs when $(\vec{r}-\vec{R}_n^\alpha)-(\vec{r}-\vec{R}_1^\beta) = \vec{R}_n^\alpha-\vec{R}_1^\beta$ is large. To insure that all interactions are weighted equally by distance, choose the cutoff such that only atoms (specified by n and α) inside a spherical shell of radius, D_{max}, about the central atom (specified by $\vec{R}_1^\beta$) are included. That is, the matrix element, $\langle\phi_\mu(\vec{r}-\vec{R}_n^\alpha)|H|\phi_\nu(\vec{r}-\vec{R}_1^\beta)\rangle$, contributes to the sum in Equation 12 only when the two atoms involved are "near neighbors" or

$$|\vec{R}_n^\alpha - \vec{R}_1^\beta| < D_{max} \quad . \tag{13}$$

Then,

$$\langle\Phi_\mu^\alpha|H|\Phi_\nu^\beta\rangle = \sum_{\substack{\text{near}\\ \text{neighbors}\\ n}} e^{-i\vec{k}\cdot(\vec{R}_n^\alpha-\vec{R}_1^\beta)}\langle\phi_\mu(\vec{r}-\vec{R}_n^\alpha)|H|\phi_\nu(\vec{r}-\vec{R}_1^\beta)\rangle \quad . \tag{14}$$

IMPLEMENTATION

In view of Equation 14, the energy band structure can be obtained by specifying the crystal structure (i.e., knowing the position, $\vec{R}_1^\beta$) of each atom in the unit cell along with the positions, $\vec{R}_n^\alpha$, of all "near neighbor" atoms in real coordinate space) and numerically evaluating the matrix element of the Hamiltonian between pairs of atomic orbitals. It is these same matrix elements that enter into calculations of index of refraction, birefringence, elastic constants, etc., and whose validity we wish to investigate via the band structure calculations.

The implementation of Equations 7 and 14 to determine the energy eigenvalues as a function of wave-vector has been accomplished by

writing a Fortran program, which is flowcharted and listed in Appendix C. (Note: the listings are commented in detail for readability without an indepth Fortran background.) The problem of obtaining the crystal structure was handled separately -- i.e., communicate the crystal geometry via a "list" of atoms with vector coordinates generated by a separate computer program (see, for example, Appendix F). The evaluation of matrix elements of the Hamiltonian between two atomic orbitals was done by using the Slater and Koster "two-center integral" approximation[2] (see Appendix B). One generalized method of numerically specifying the parameters in this approximation was suggested by Harrison.[6,7]

For two s orbitals, an s and p orbital, and two p orbitals, respectively, Harrison's "Solid State Interatomic Matrix Elements" are given below.

$$\langle s_2|H|s_1\rangle = V_{ss} \tag{15}$$

$$\langle s_2|H|p_1\rangle = V_{sp}\ (\hat{p}_1 \cdot \hat{d}) \tag{16}$$

$$\langle p_2|H|p_1\rangle = V_{pp\pi}\ (\hat{p}_1 \cdot \hat{p}_2) - [V_{pp\sigma} + V_{pp\pi}](\hat{p}_1 \cdot \hat{d})(\hat{p}_2 \cdot \hat{d}) \tag{17}$$

$$V_{ss} = -1.40\ \frac{\hbar^2}{md^2} \tag{18}$$

$$V_{sp} = -1.84\ \frac{\hbar^2}{md^2} \tag{19}$$

$$V_{pp\sigma} = -3.24 \quad \frac{\hbar^2}{md^2} \tag{20}$$

$$V_{pp\pi} = -0.81 \quad \frac{\hbar^2}{md^2} \tag{21}$$

$$\frac{\hbar^2}{m} = 7.62 \text{ eV} - \text{Å}^2 \tag{22}$$

$\vec{d}$ is the vector distance from atom #1 to atom #2 and $\hat{p}_1$ and $\hat{p}_2$ are unit vectors describing the orientations of the positive lobes of the p orbitals. Note that the geometrical factors of the matrix elements involving s and p orbitals are compatible with those of Slater and Koster as shown in Appendix B. For matrix elements involving two atomic orbitals on the same atom, it is convenient to use the Herman and Skillman atomic term values for non-orthogonal orbitals.[6,8] For the sake of simplicity, d orbitals were neglected in this work since, for most semiconductors of interest, the d shell is completely filled.

RESULTS

Zincblendes

The first step in performing numerical calculations with a computer is to show that the computer program being used generates valid results. This was accomplished by reproducing the energy bands for GaAs and ZnSe from Chadi and Cohen,[1] using their first nearest neighbor parameters (Table 5) for the matrix elements of the Hamiltonian between two atomic orbitals. A special subroutine, incorporating these parameters, was written to evaluate the matrix elements and is

listed in Appendix H. Energy eigenvalues of GaAs and ZnSe, at symmetry points Γ, L and X in the Brillouin zone, are compared in Tables 1 and 2, respectively. Note that Γ implies $\vec{k} = (0,0,0)$, L implies $\vec{k} = \pi/a\ (1,1,1)$, and X implies $\vec{k} = 2\pi/a\ (1,0,0)$ where "a" is the lattice constant. The calculated band structures for GaAs from Γ to L and from Γ to X are shown in Figure 2. These can be compared with Figure 7 of Chadi and Cohen,[1] which is mislabeled as Ge instead of GaAs. Similarly, the energy bands for ZnSe from Γ to L and Γ to X, plotted in Figure 3, are equivalent to portions of Figure 9 in Chadi and Cohen.[1] For the sake of completeness, the energy bands of Si and Ge, using Chadi and Cohen's first nearest neighbor parameters, are given in Tables 3 and 4, and in Figures 4 and 5, respectively.

Since Harrison's formulas in Equations 15 through 21, in conjunction with the Herman-Skillman atomic term values, provide a more general way of numerically evaluating matrix elements of the Hamiltonian between two atomic orbitals, a comparison of the energy band structures for the zincblendes using these parameters was made against the calculations with the Chadi and Cohen parameters. The results for GaAs, ZnSe, Si and Ge, assuming only first neighbor interactions, are given in Tables 1, 2, 3 and 4, and in Figures 6, 7, 8 and 9, respectively. The qualitative shape of the energy bands from Harrison's parameters agree very well with the bands of Chadi and Cohen, but the quantitative properties such as the band gap for GaAs are not as accurately predicted.

To investigate Harrison's formulas further, the inclusion of higher order near neighbors was attempted. One would expect the band

Table 1

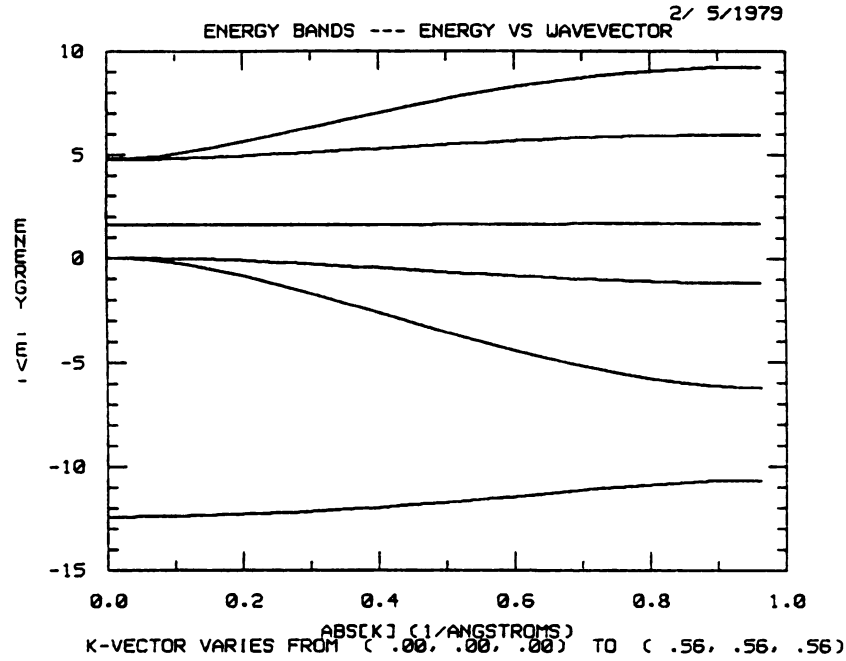
Selected Energy Eigenvalues for GaAs Using First Nearest Neighbors

Symmetry Point	Chadi & Cohen Results[1]	Calculated Chadi & Cohen/Harrison Parameters		Degeneracy
Γ	-12.4 eV	-12.43 eV	-22.07 eV	1
Γ	0.0	0.00	-9.54	3
Γ	1.6	1.63	-6.63	1
Γ	4.8	4.78	-3.27	3
L	-10.7	-10.69	-20.20	1
L	-6.2	-6.24	-15.58	1
L	-1.2	-1.19	-11.44	2
L	1.7	1.70	-6.19	1
L	6.0	5.97	-1.37	2
L		9.21	0.47	1
X	-9.7	-9.71	-19.35	1
X	-6.8	-6.76	-15.31	1
X	-2.8	-2.82	-13.43	2
X	2.2	2.16	-3.97	1
X		7.60	-2.88	2/1
X		8.29	0.62	1/2

Table 2

Selected Energy Eigenvalues for ZnSe Using First Nearest Neighbors

Symmetry Point	Chadi & Cohen Results[1]	Calculated Chadi & Cohen/Harrison Parameters		Degeneracy
Γ	-12.1 eV	-12.11 eV	-23.62 eV	1
Γ	0.0	0.00	-10.57	3
Γ	2.9	2.91	-5.10	1
Γ	7.5	7.54	-2.34	3
L	-11.0	-11.02	-22.36	1
L	-4.7	-4.71	-15.22	1
L	-0.75	-0.75	-12.14	2
L	3.9	3.88	-4.96	1
L	8.3	8.29	-0.77	2
L		10.19	0.91	1
X	-10.6	-10.58	-21.88	1
X	-4.8	-4.81	-14.37	1
X	-1.9	-1.93	-13.94	2
X	4.7	4.65	-3.56	1
X		9.08	-1.82	1
X		9.47	1.03	2



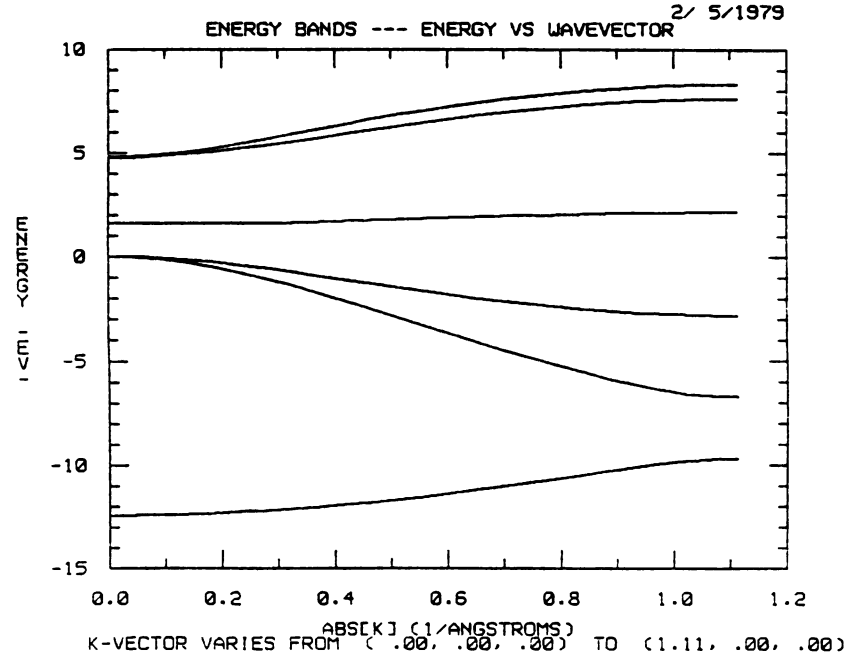


Figure 2. Energy bands of GaAs using Chadi and Cohen's first nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X

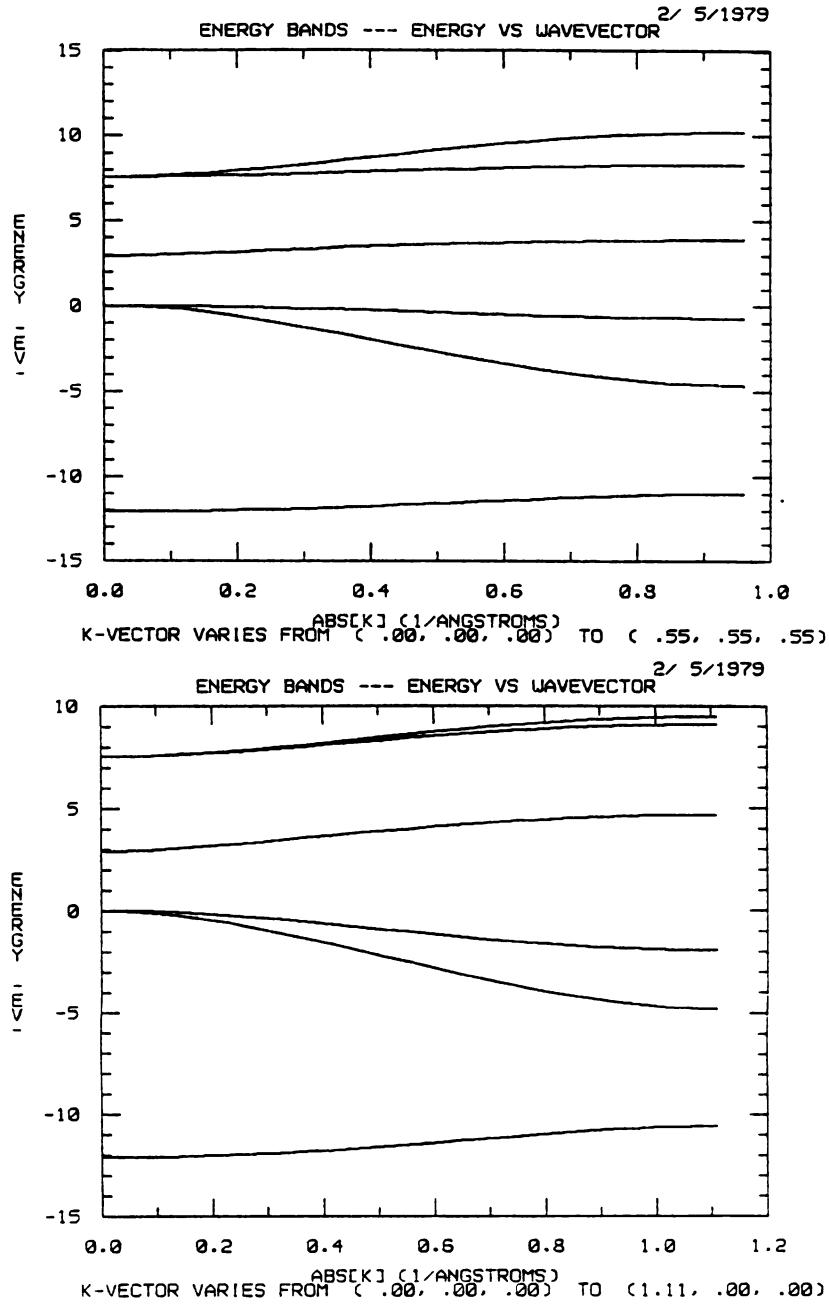


Figure 3. Energy bands of ZnSe using Chadi andCohen's first nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X

Table 3

Selected Energy Eigenvalues for Si

Symmetry Point	Chadi & Cohen* Results[1]	Calculated** Chadi & Cohen/Harrison Parameters		Degeneracy
Γ	-12.16 eV	-12.16 eV	-21.27 eV	1
Γ	0.00	0.00	-9.50	3
Γ	3.42	4.10	-5.83	1
Γ	4.10	6.34	-3.54	3
L	-9.44	-9.49	-18.82	1
L	-7.11	-6.64	-16.34	1
L	-1.44	-2.17	-11.73	2
L		3.92	-5.82	1
L		8.51	-1.31	2
L		10.49	0.84	1
X	-7.70	-7.32	-16.86	2
X	-2.85	-4.34	-13.96	2
X		6.46	-3.21	2
X		10.68	0.92	2

Notes: * for first and second nearest neighbor parameters
** for first nearest neighbor parameters only.

Table 4

Selected Energy Eigenvalues for Ge

Symmetry Point	Chadi & Cohen* Results[1]	Calculated** Chadi & Cohen/Harrison Parameters		Degeneracy
Γ	-12.57 eV	-12.57 eV	-21.49 eV	1
Γ	0.00	0.00	-9.10	3
Γ	0.99	.99	-7.27	1
Γ	3.24	-5.24	-3.62	3
L	-10.30	-10.33	-19.13	1
L	-7.52	-7.25	-16.03	1
L	-1.60	-2.10	-11.16	2
L		1.96	-6.64	1
L		7.34	-1.56	2
L		9.28	0.32	1
X	-8.60	-8.36	-17.09	2
X	-3.30	-4.20	-13.22	2
X		5.19	-3.65	2
X		9.44	0.50	2

Notes: * for first and second nearest neighbor parameters
** for first nearest neighbor parameters only.

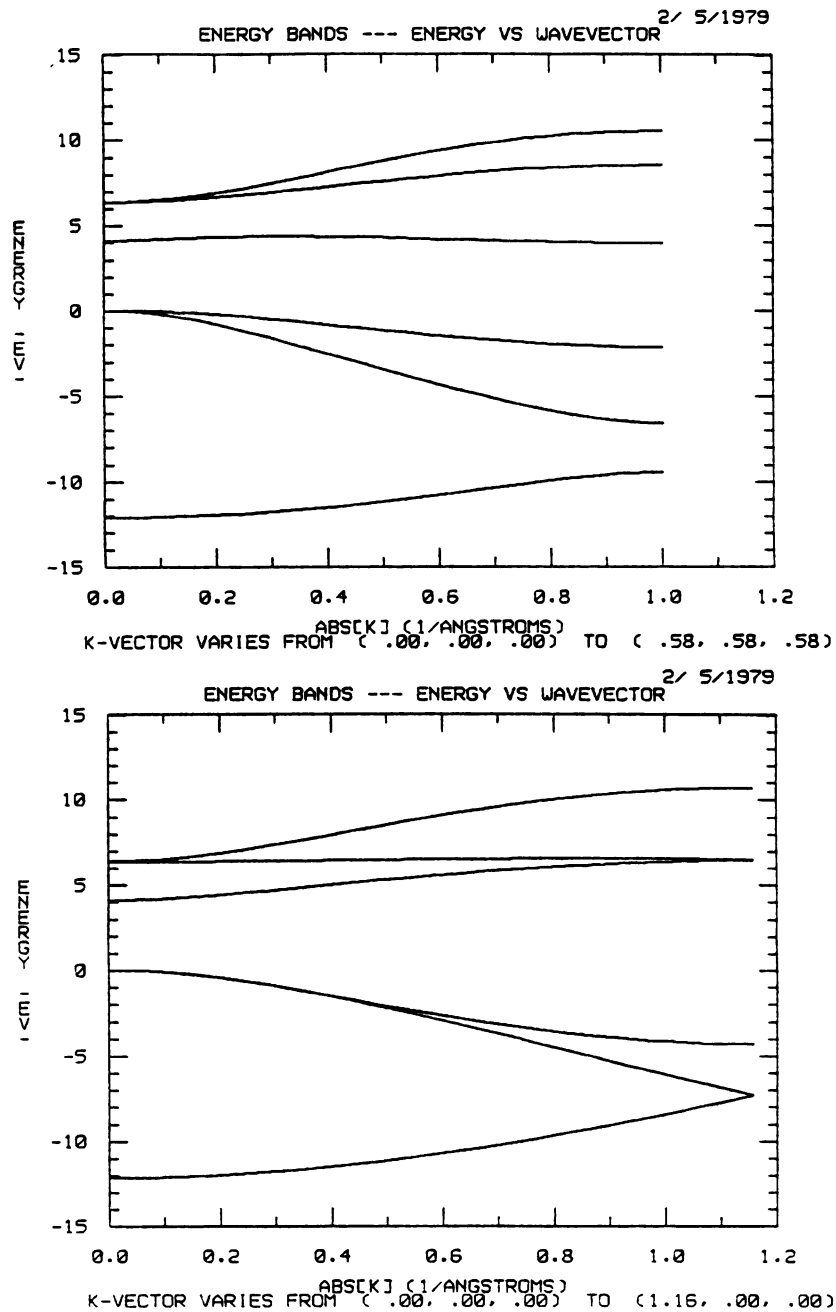


Figure 4. Energy bands of Si using Chadi and Cohen's first nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X

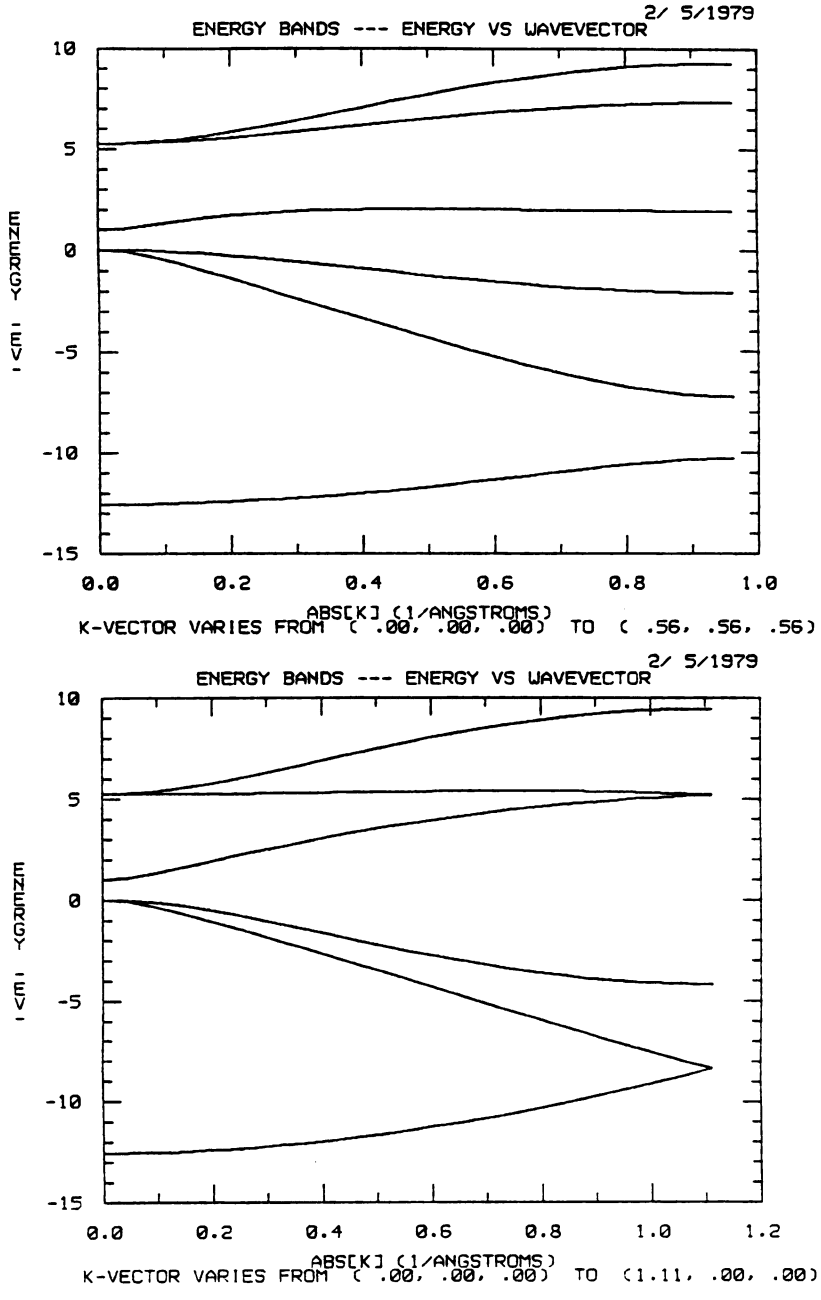
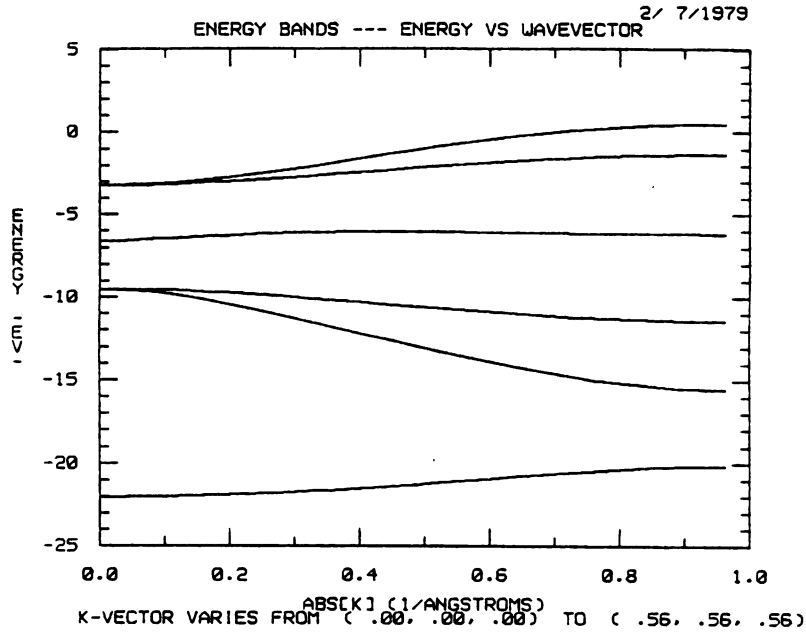


Figure 5. Energy bands of Ge using Chadi and Cohen's first nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X



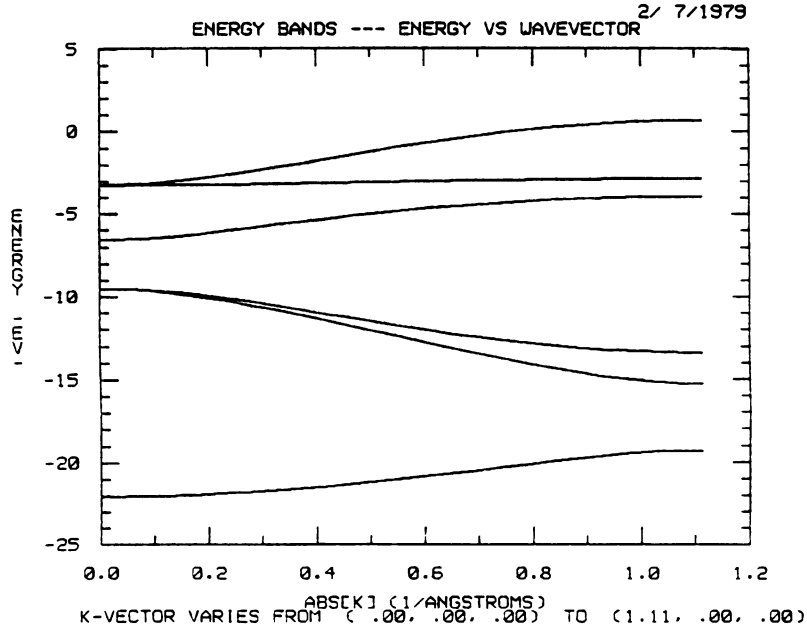
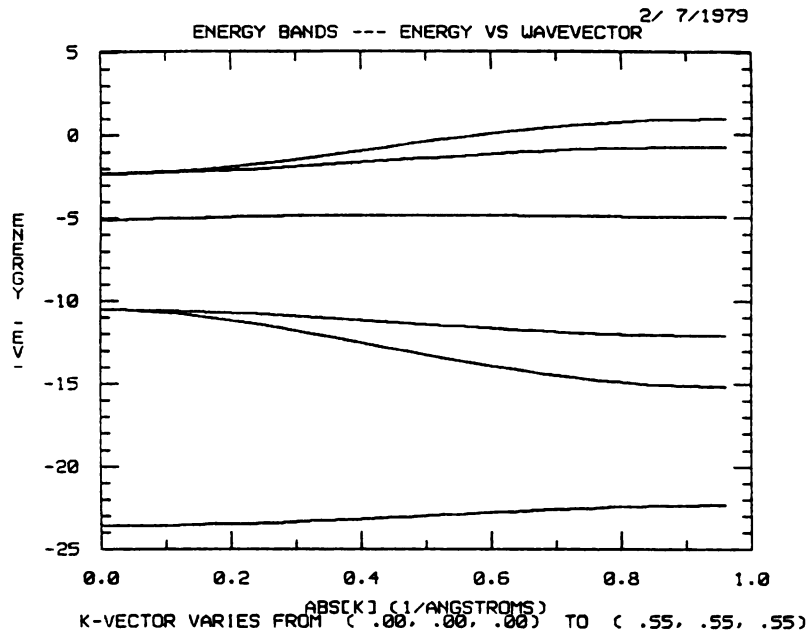


Figure 6. Energy bands of GaAs using Harrison's parameters for first nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X



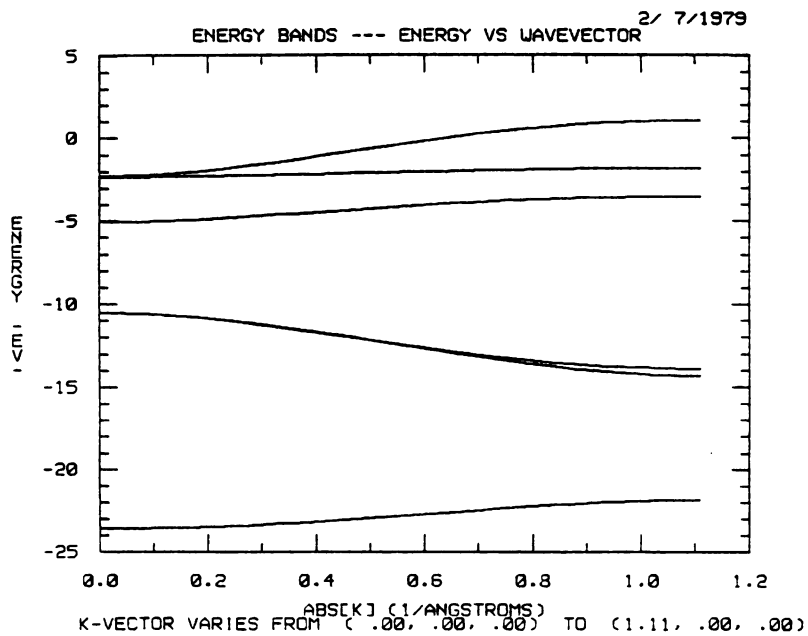


Figure 7. Energy bands of ZnSe using Harrison's parameters for first nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X

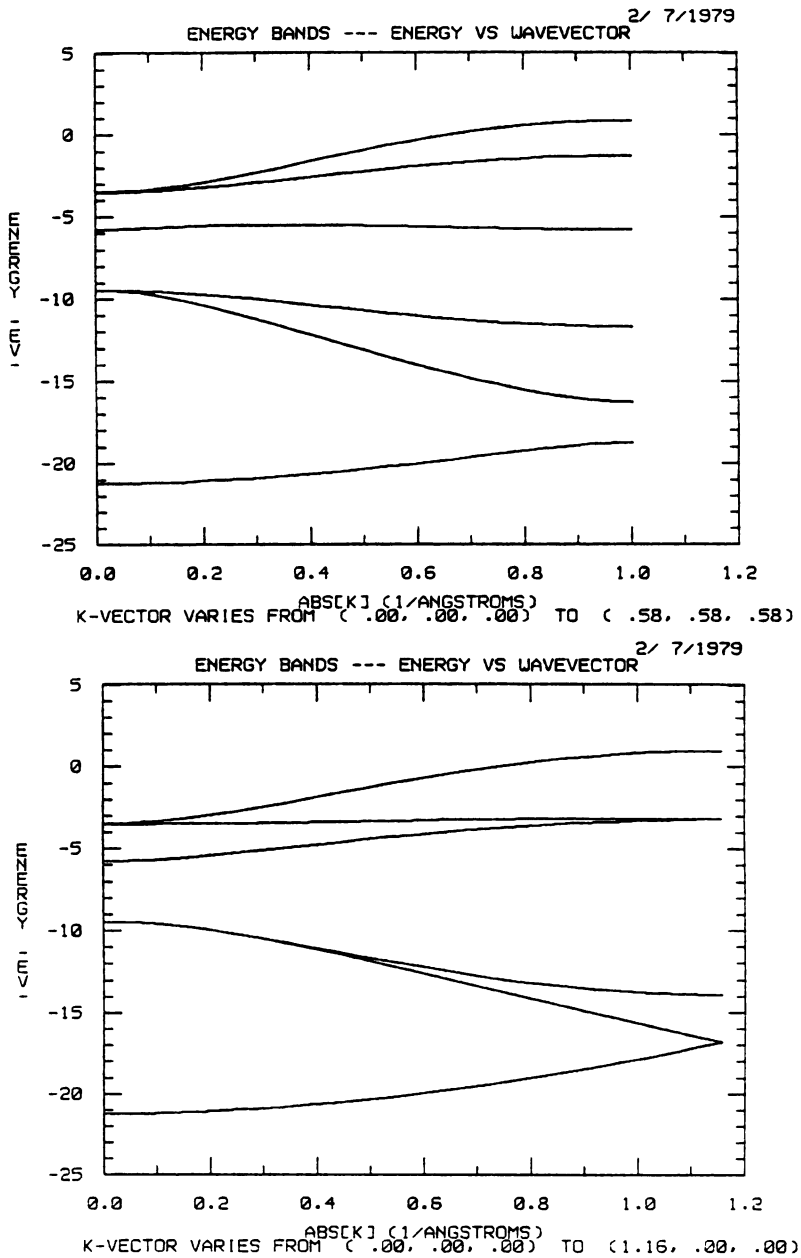
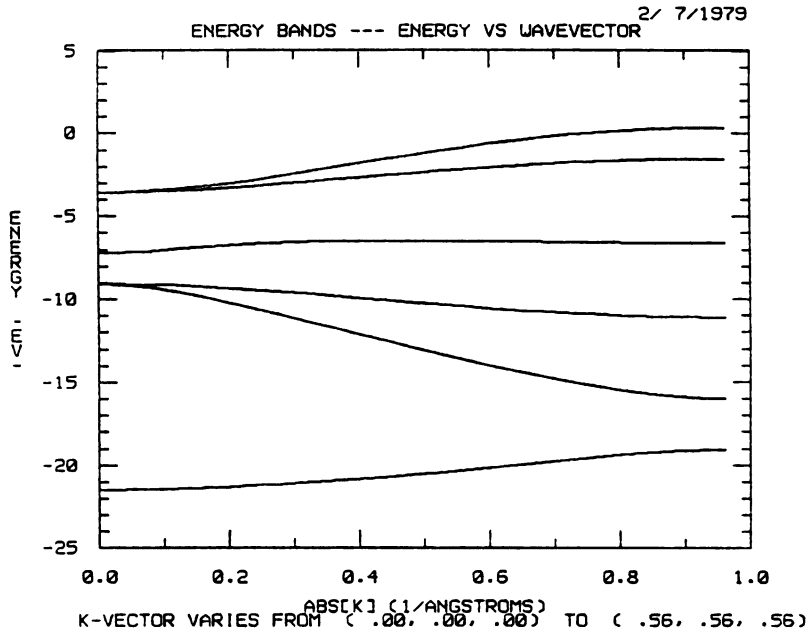


Figure 8. Energy bands of Si using Harrison's parameters for first nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X



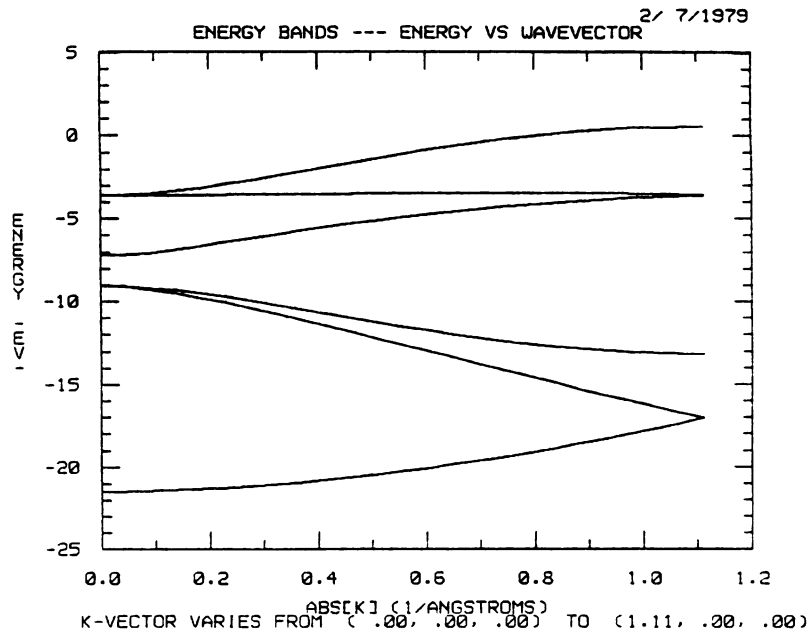
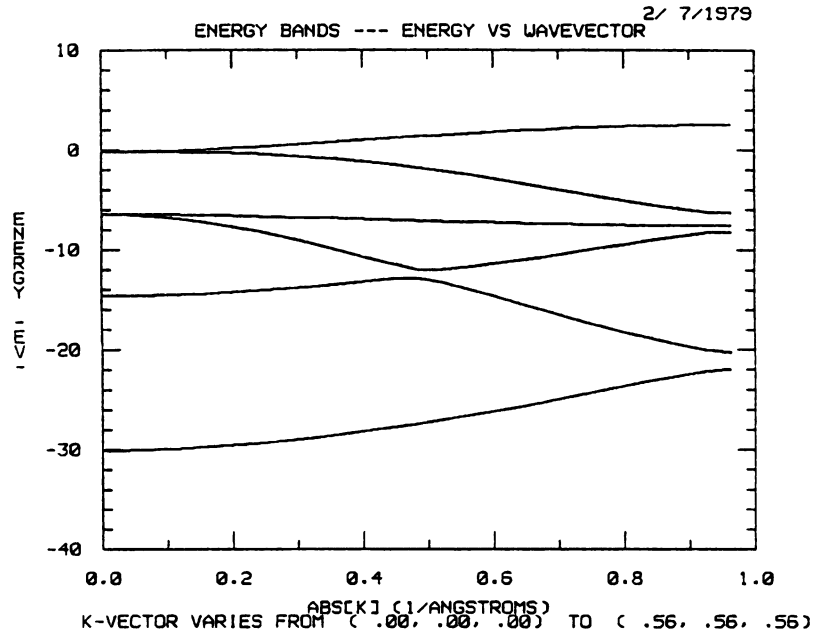


Figure 9. Energy bands of Ge using Harrison's parameters for first nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X

structure to asymtotically approach some stable structure by considering higher and higher order neighbors. Figures 10 and 11 show the energy bands of GaAs from including second and third nearest neighbors, respectively. From these two calculations, it is apparent that Harrison's formulas are valid only for nearest neighbors; that is, they overestimate the interaction between atomic orbitals to compensate for the neglecting of higher order neighbors. To obtain the desired asymtotic behavior mentioned above, the dependence of the interaction on distance needs to fall off more rapidly than d^{-2} (in fact, since volume or number of neighbors varies as d^3, really need faster than d^{-3}). It has been suggested[9] that perhaps an exponential dependence, $e^{-\lambda d}$, be tried to accomplish this.

Chalcopyrites

In view of the above limitations when using Harrison's parameters, these parameters were then utilized in determining the energy band structures of more complicated semiconductors. One class of compounds, the chalcopyrites (see Appendix F), is closely related to the zincblendes. The 16 atoms per unit cell in the chalcopyrites imply that the matrix to diagonalize in Equation 7 has dimensionality 64x64 when considering only the valence s and p orbitals. This is no problem on a "big" computer (CDC, IBM, etc.) except for cost. However, on a 16-bit minicomputer with only 32K integer words of addressable memory, the maximum number of atoms per unit cell is approximately ten, assuming that each matrix element is "double precision complex" and that swapping submatrices to and from magnetic



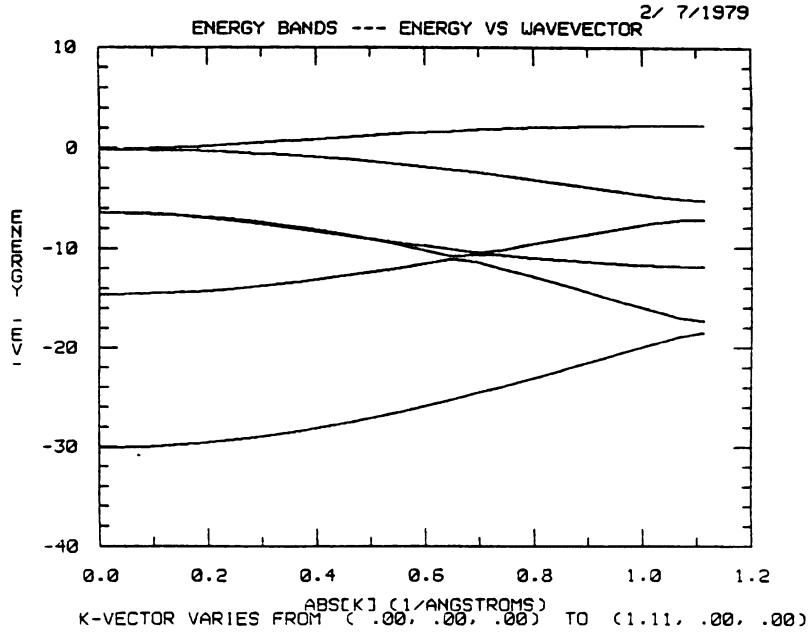
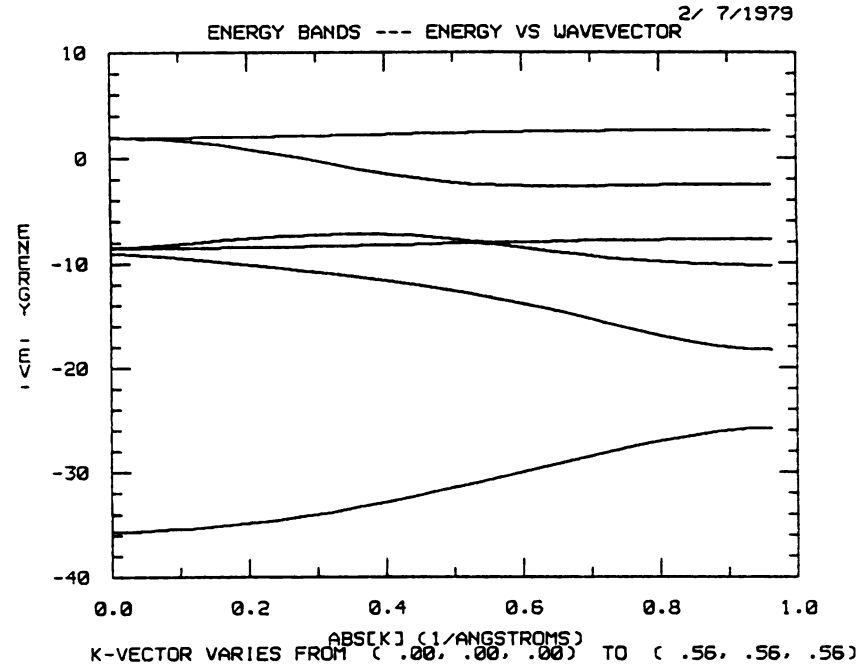


Figure 10. Energy bands of GaAs using Harrison's parameters for second nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X



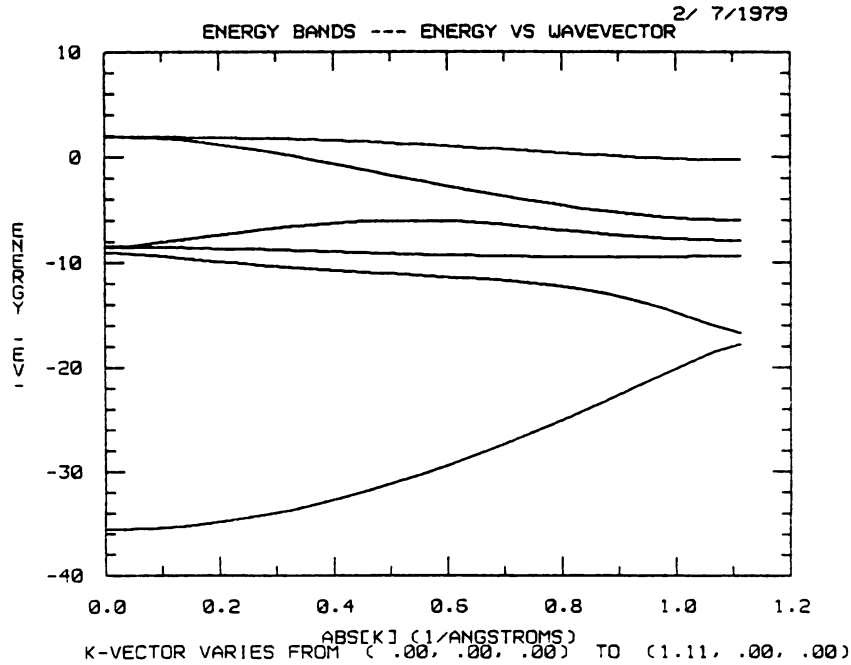


Figure 11. Energy bands of GaAs using Harrison's parameters for third nearest neighbor parameters; (Top) from Γ to L, (Bottom) from Γ to X

disk during diagonalization is to be avoided. Therefore, in order to perform a chalcopyrite band structure calculation on the minicomputer, symmetry arguments must be invoked to reduce the number of atoms per "unit cell" for a given direction in k-space. From Equation F8, it can be seen that only eight atoms per "unit cell" are necessary to specify the crystal structure by using the twofold screw axis symmetry. Consequently, the energy bands of the chalcopyrites along the c-axis can then be calculated on a minicomputer. Three examples are shown in Figures 12, 13, and 14 which correspond to $ZnSiAs_2$, $CdGeAs_2$, and $CdGeP_2$, respectively. Again, due to limitations on Harrison's parameters, only first nearest neighbor interactions were included.

Tl_3AsSe_3

The band structure of one other semiconductor, Tl_3AsSe_3 or TAS, which is a sulfosalt, has been investigated. Once more, the 21 atoms per unit cell (see Appendix G) mean diagonalizing an 84x84 matrix, for s and p valence orbitals. By identifying the c-axis as a threefold screw axis (Equation G4), the number of atoms per effective "unit cell" was reduced to seven, thereby allowing the band calculation to be done on the 16-bit minicomputer. The result, for first nearest neighbors along the c-axis, is shown in Figure 15.

Tl_3AsSe_3 with Group Theory

As a precursor towards doing the above calculation on TAS, group theory was employed to analytically simplify the problem. In par-

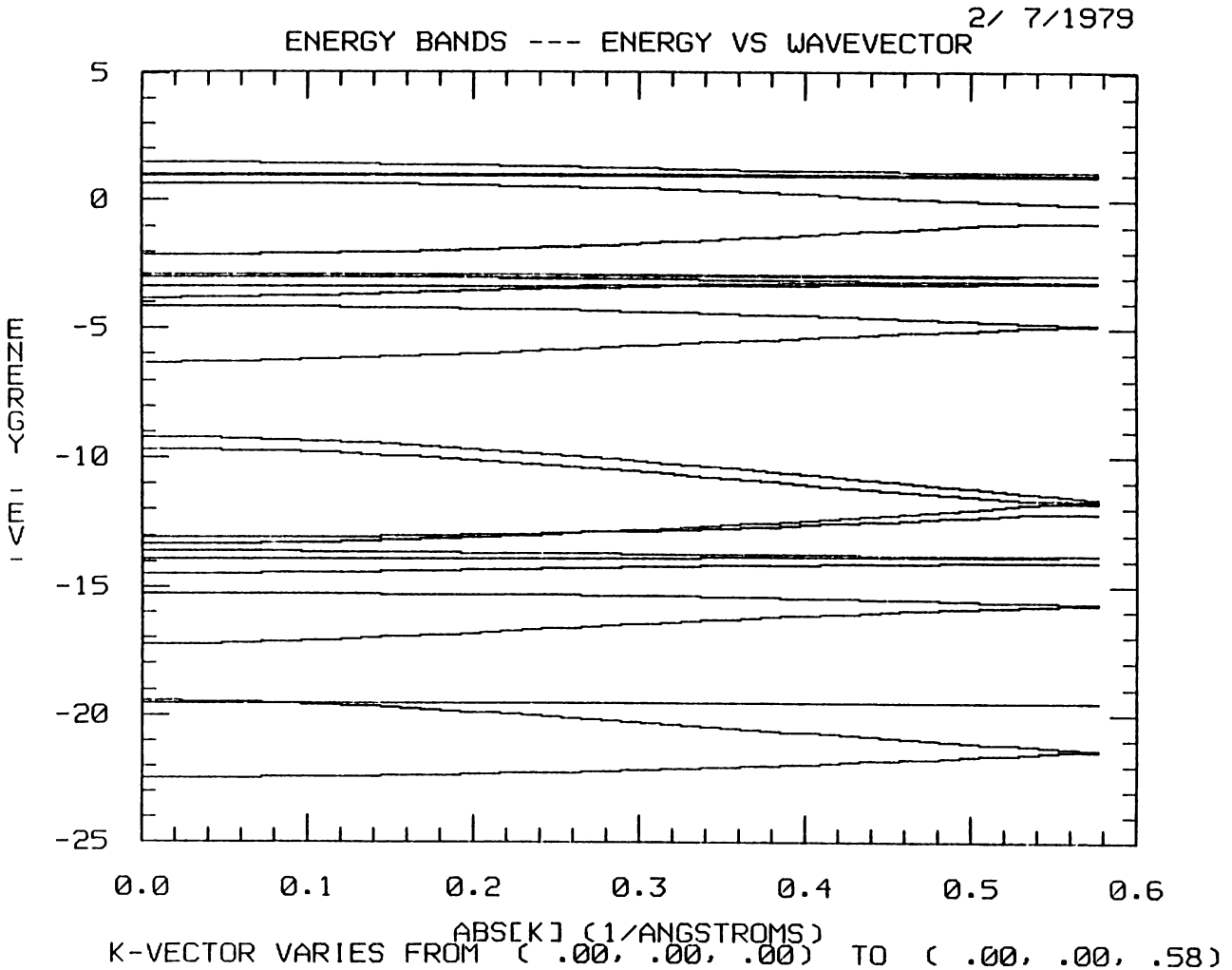
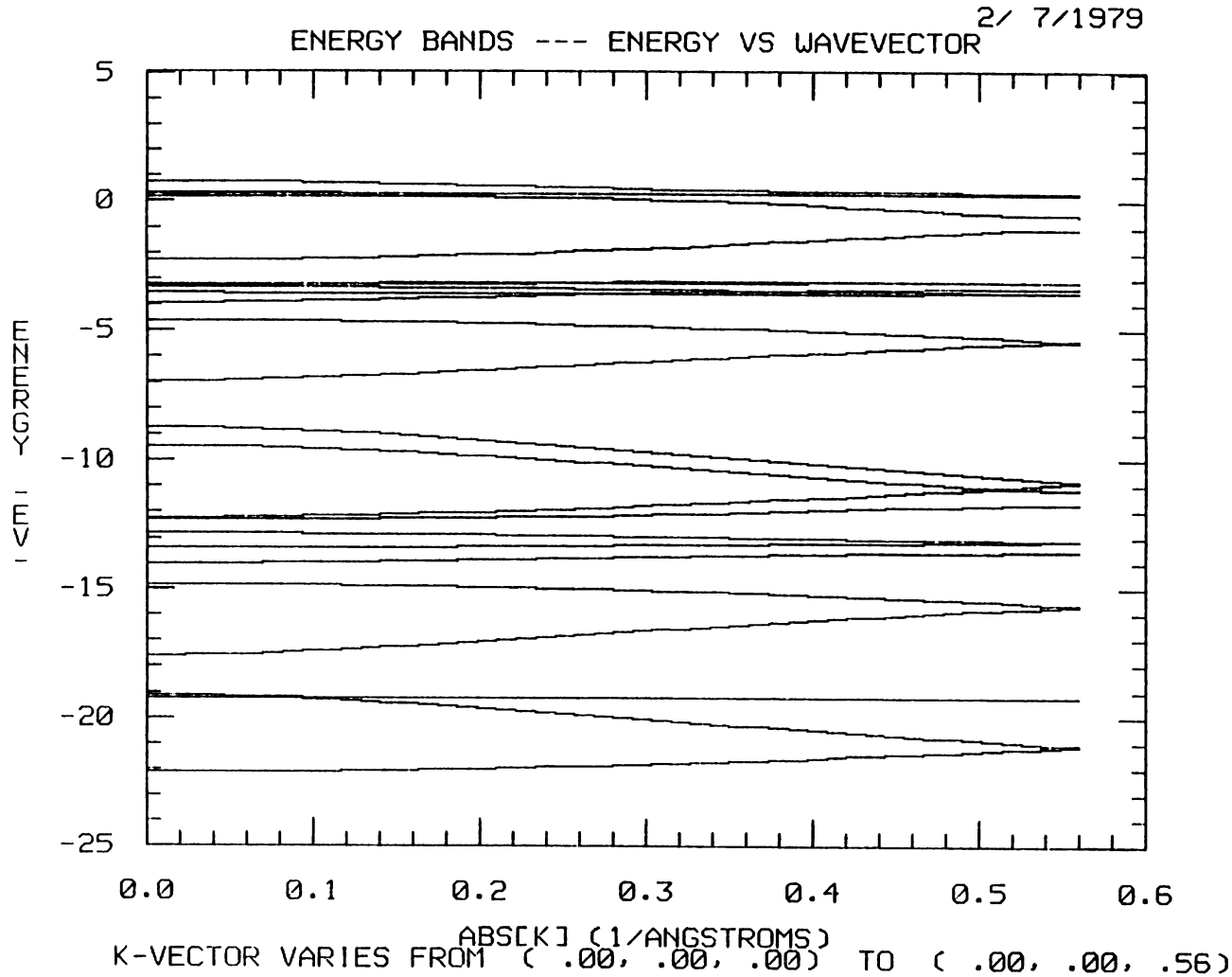


Figure 12. Energy bands of $ZnSiAs_2$ using Harrison's parameters for first nearest neighbors



K-VECTOR VARIES FROM (.00, .00, .00) TO (.00, .00, .56)

Figure 13. Energy bands of $CdGeAs_2$ using Harrison's parameters for first nearest neighbors.

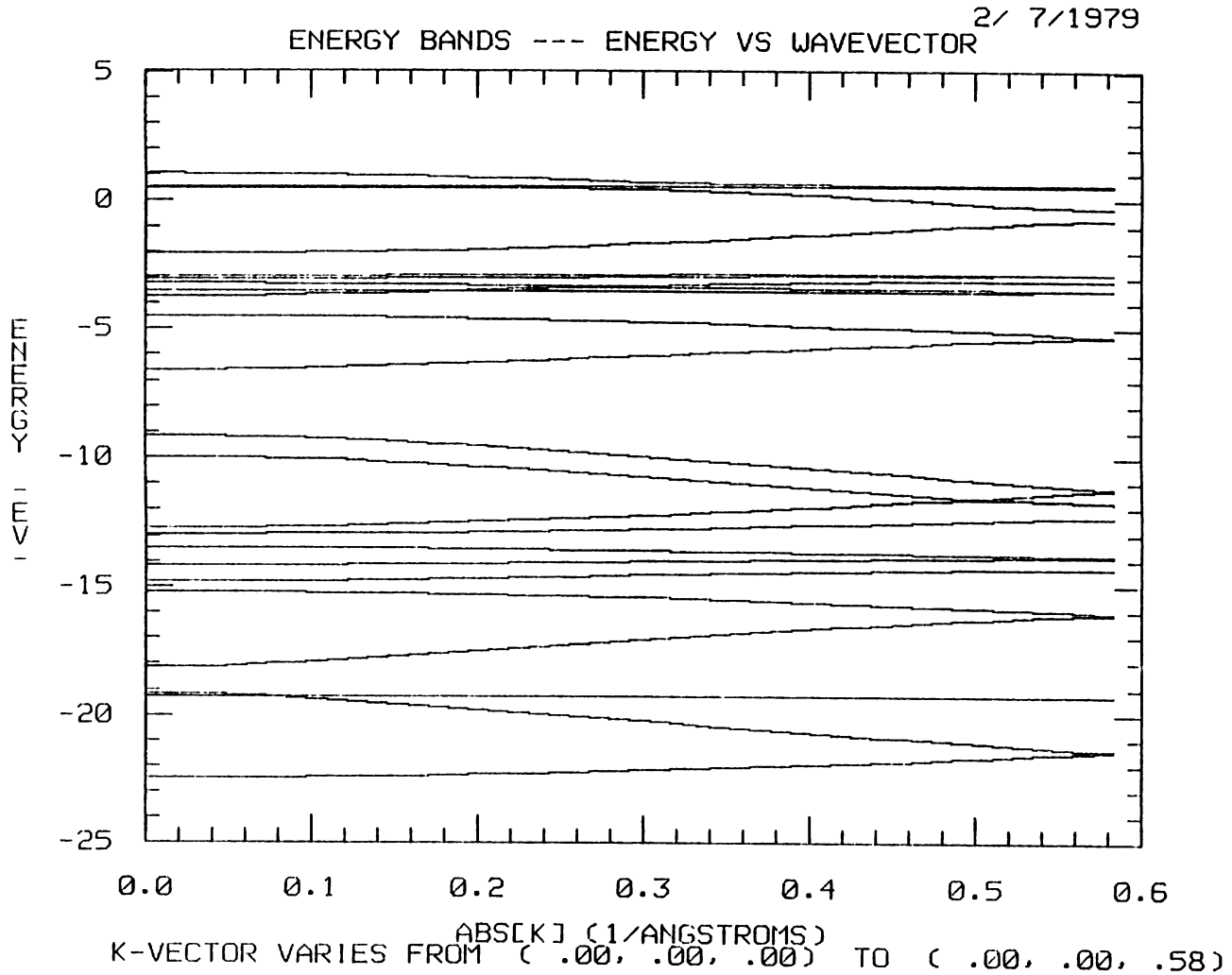


Figure 14. Energy bands of $CdGeP_2$ using Harrisons parameters for first nearest neighbors

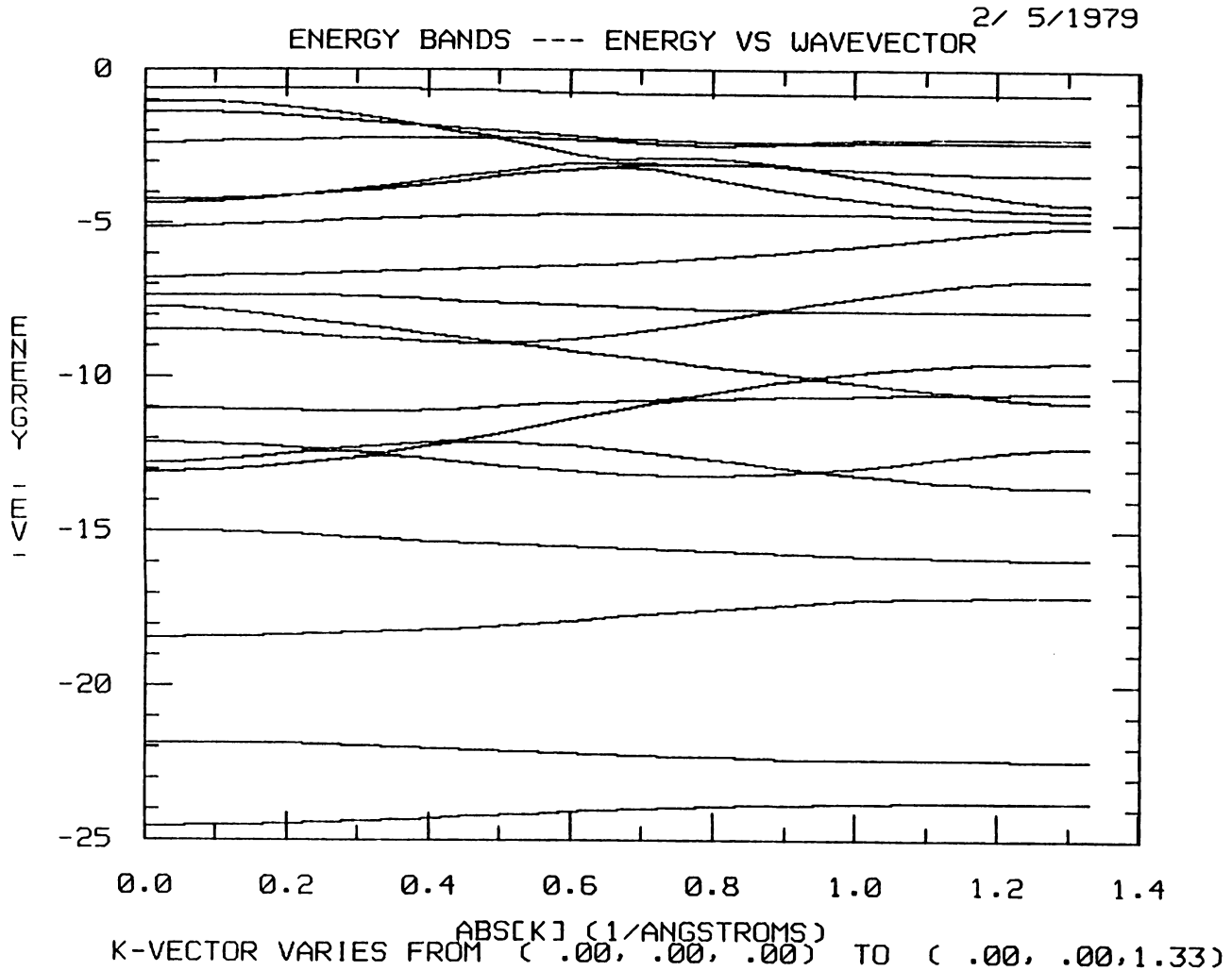


Figure 15. Energy bands of Tl_3AsSe_3 using Harrison's parameters for first nearest neighbors

ticular, the threefold screw axis symmetry was used to reduce the 84 states to 28, or to seven atoms, as above. But in addition, these seven atoms (one formula unit, Tl_3AsSe_3) exhibit triangular symmetry;[7] i.e., three reflections and two rotations. The irreducible representation for the group C_{3v} are given below.[10]

	E	3σ	3σ	3σ	2C	2C
Λ_1	1	1	1	1	1	1
Λ_2	1	-1	-1	-1	1	1
Λ_3	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{-\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{-1}{2} & \frac{\sqrt{3}}{2} \\ \frac{-\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{-1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{-1}{2} \end{pmatrix}$

(23)

The character table for the irreducible representations of C_{3v} is written as follows

	E	3σ	2C
Λ_1	1	1	1
Λ_2	1	-1	1
Λ_3	2	0	-1

(24)

By considering a linear combination of atomic orbitals that is compatible with the triangular symmetry (see Figure 16) and examining how these states transform under symmetry operations, the following character table for TAS was obtained.

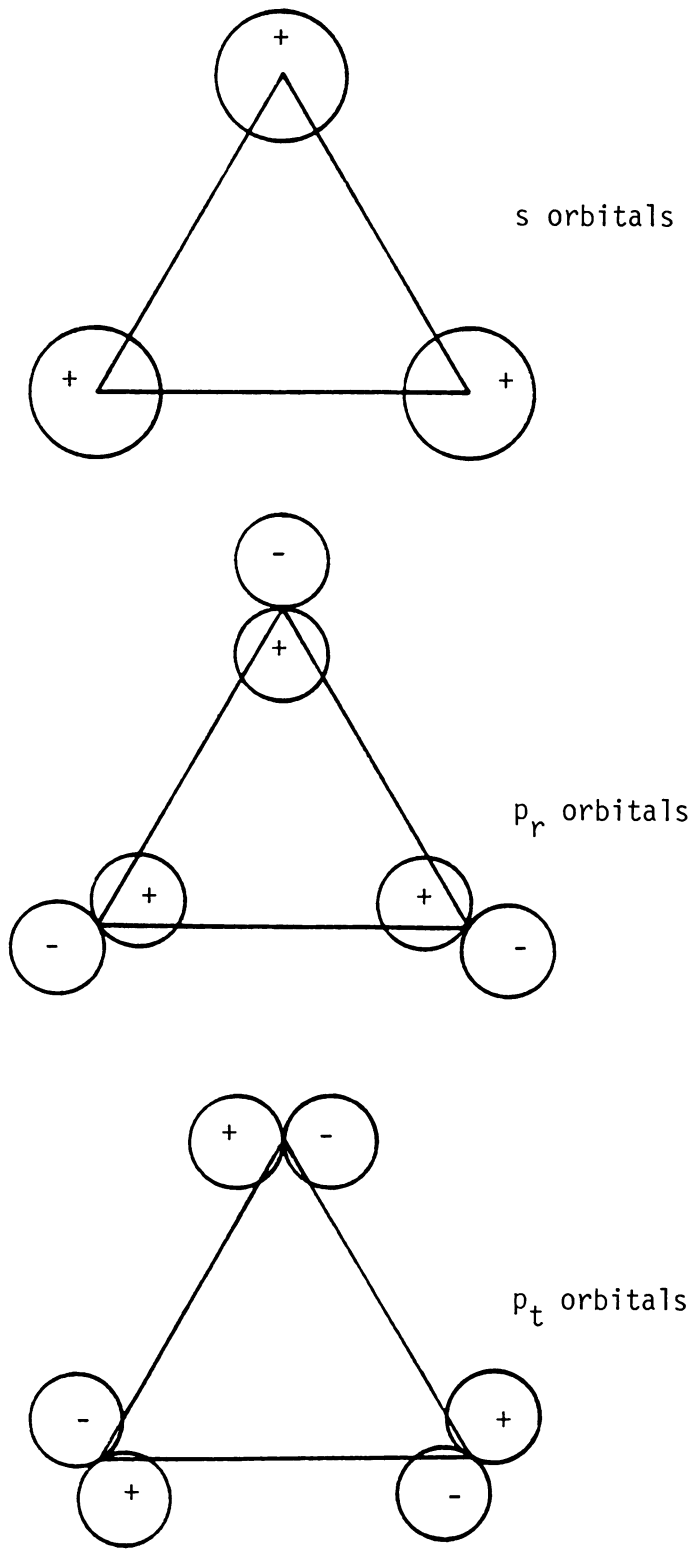


Figure 16. Atomic orbitals with triangular symmetry

	E	3σ	2C
Λ	28	6	1

(25)

Therefore,

$$\Lambda = 8\Lambda_1 + 2\Lambda_2 + 9\Lambda_3, \tag{26}$$

which implies that in the three irreducible representations Λ_1, Λ_2 and Λ_3, there are eight, two and nine basis states, respectively. These basis states are[7]

Λ_1:

$$|1\rangle = s(As) \tag{27}$$

$$|2\rangle = p_z\ (As) \tag{28}$$

$$|3\rangle = \frac{1}{\sqrt{3}}\,[s(Se)_a + s(Se)_b + s(Se)_c] \tag{29}$$

$$|4\rangle = \frac{1}{\sqrt{3}}\,[p_r(Se)_a + p_r(Se)_b + p_r(Se)_c] \tag{30}$$

$$|5\rangle = \frac{1}{\sqrt{3}}\,[p_z(Se)_a + p_z(Se)_b + p_z(Se)_c] \tag{31}$$

$$|6\rangle = \frac{1}{\sqrt{3}}\,[s(T|)_a + s(T|)_b + s(T|)_c] \tag{32}$$

$$|7\rangle = \frac{1}{\sqrt{3}}\,[p_r(T|)_a + p_r(T|)_b + p_r(T|)_c] \tag{33}$$

$$|8\rangle = \frac{1}{\sqrt{3}}\,[p_t(T|)_a + p_z(T|)_b + p_z(T|)_c] \tag{34}$$

Λ_2:

$$|1\rangle = \frac{1}{\sqrt{3}}\,[p_t(Se)_a + p_t(Se)_b + p_t(Se)_c] \tag{35}$$

$$|2\rangle = \frac{1}{\sqrt{3}}\,[p_t(T|)_a + p_t(T|)_b + p_t(T|)_c] \tag{36}$$

Λ_3:

$$|1\rangle = \frac{1}{\sqrt{2}}[p_x(As) + ip_y(As)] \tag{37}$$

$$|2\rangle = \frac{1}{\sqrt{3}}[s(Se)_a + \Phi s(Se)_b + \Phi^* s(Se)_c] \tag{38}$$

$$|3\rangle = \frac{1}{\sqrt{3}}[p_z(Se)_a + \Phi p_z(Se)_b + \Phi^* p_z(Se)_c] \tag{39}$$

$$|4\rangle = \frac{1}{\sqrt{3}}[p_r(Se)_a + \Phi p_r(Se)_b + \Phi^* p_r(Se)_c] \tag{40}$$

$$|5\rangle = \frac{1}{\sqrt{3}}[p_t(Se)_a + \Phi p_t(Se)_b + \Phi^* p_t(Se)_c] \tag{41}$$

$$|6\rangle = \frac{1}{\sqrt{3}}[s(T|)_a + \Phi s(T|)_b + \Phi^* s(T|)_c] \tag{42}$$

$$|7\rangle = \frac{1}{\sqrt{3}}[p_z(T|)_a + \Phi p_z(T|)_b + \Phi^* p_z(T|)_c] \tag{43}$$

$$|8\rangle = \frac{1}{\sqrt{3}}[p_r(T|)_a + \Phi p_r(T|)_b + \Phi^* p_r(T|)_c] \tag{44}$$

$$|9\rangle = \frac{1}{\sqrt{3}}[p_t(T|)_a + \Phi p_t(T|)_b + \Phi^* p_t(T|)_c] \tag{45}$$

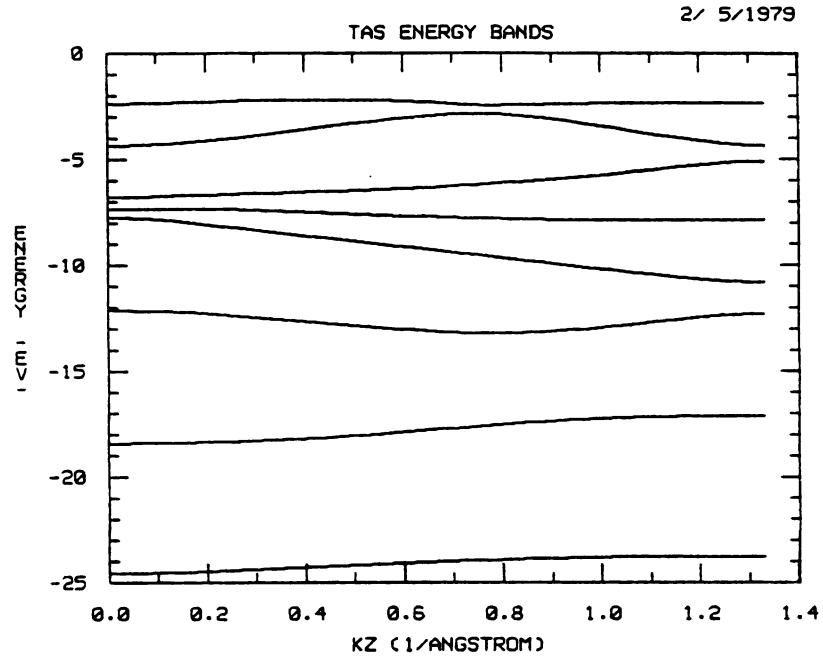
where $\Phi = \exp(2\pi i/3)$. Nine additional basis states are obtained by complex conjugation of the Λ_3 states, thus giving the desired 28 states.

Now, by following the formularization set forth in Equations 1 through 7, one only needs to replace the atomic orbitals in the Bloch function (Equation 1) by the above basis states. Since these basis states are in the irreducible representations, Equation 7 turns out to be in "block-diagonal" form. Therefore, the diagonalization of the 28x28 matrix is reduced to four independent diagonalizations: an 8x8 for Λ_1, a 2x2 for Λ_2, and two 9x9's for Λ_3. This analytical

"simplification" was considerably more cumbersome to code as a Fortran program when compared with the program listed in Appendix C. Nonetheless, the resultant energy band structures for Λ_1 and Λ_2, using Harrison's formulas in Equations 15 through 21 and the Herman-Skillman atomic term values to numerically evaluate the matrix elements for first nearest neighbors, are shown in Figure 17. Upon close comparison of this figure with Figure 15, it is obvious that the diagonalization of the 28x28 matrix yields identical eigenvalues to the method utilizing the basis states in the irreducible representations, provided that the interaction parameters and number of nearest neighbors are the same.

Symmetry Considerations

The above examples of energy band structure calculated for TAS indicate that the symmetry or group theory portion of the energy bond problem can be set aside by the programmer and handled solely by having the computer diagonalize a larger matrix (at correspondingly longer computer execution times). In particular, a graph similar to Figure 15 for TAS would be generated, in a reduced Brillouin zone, by a diagonalization of the 84x84 along the c-axis. To make this point more explicit, silicon was treated as a chalcopyrite -- that is, eight atoms per "unit cell" with a twofold screw axis symmetry. The resultant band structure along the c-axis is shown in Figure 18 and, for direct comparison, the bands for the two atoms per unit cell are also plotted. The existence of an additional symmetry can be



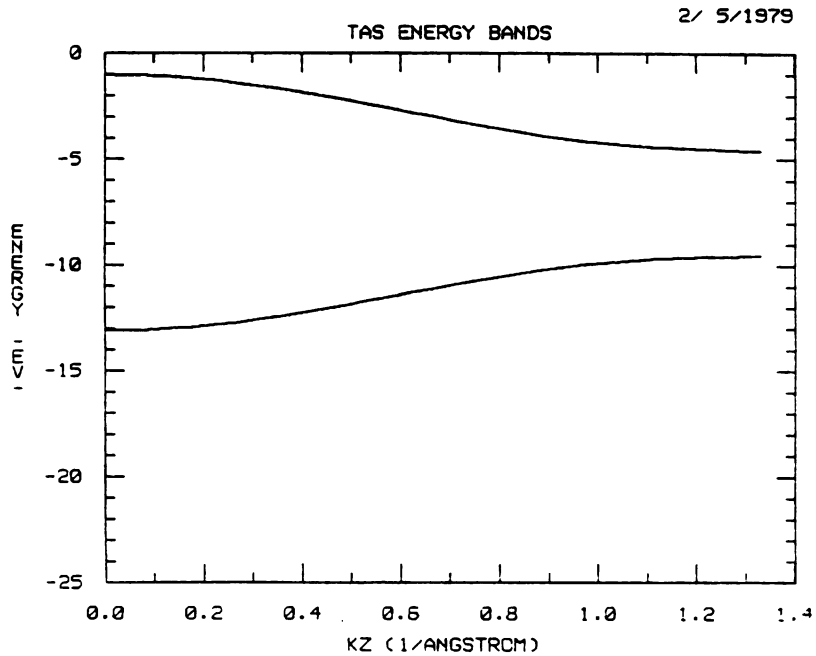
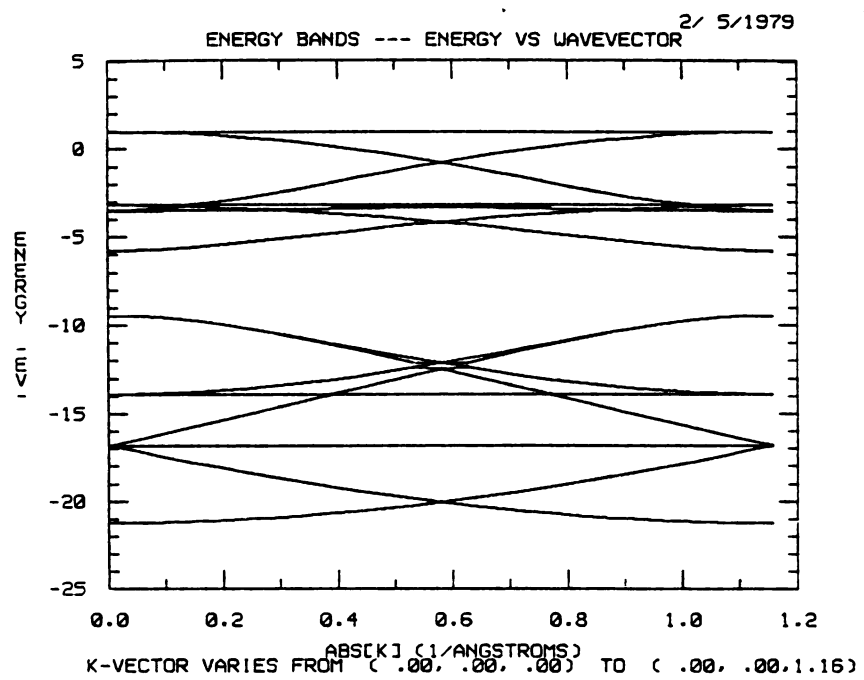


Figure 17. Energy bands of two irreducible representations of Tl_3AsSe_3 using Harrison's parameters for first nearest neighbors; (Top) Λ_1, (Bottom) Λ_2



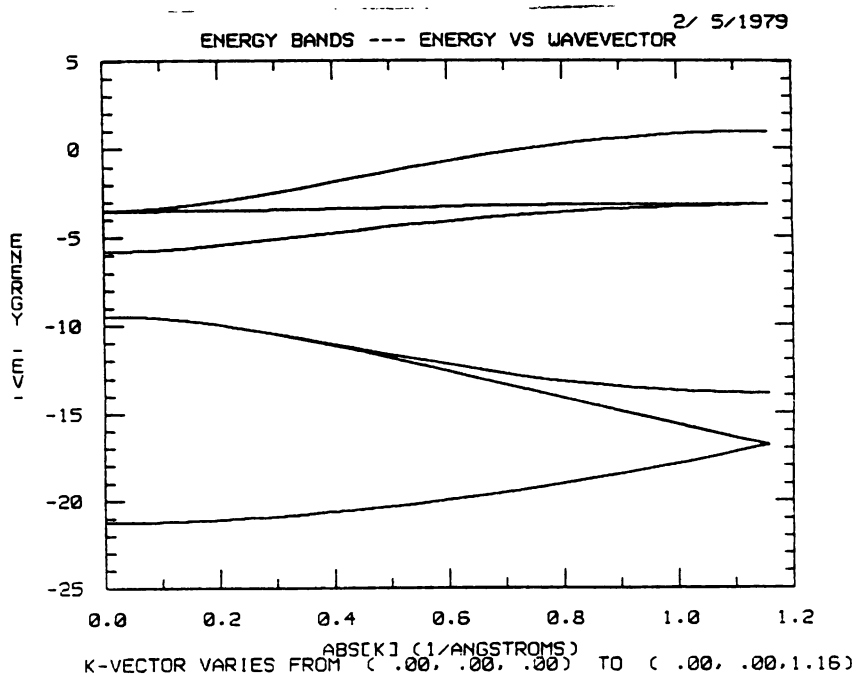


Figure 18. Energy bands of Si along c-axis; (Top) one degree of symmetry omitted, (Bottom) all symmetry included

recognized from the mirror reflection symmetry about the reduced Brillouin zone edge at $k_z = \pi/(c/2)$ in the energy bands.

More importantly, by using the larger matrices, the diagonalization is not restricted to wave-vectors that lie on symmetry axes, but can be done for any wave-vector in the Brillouin zone.

CONCLUSION

To summarize the section on energy bands, a computer program has been written and tested to perform energy band structure calculations on <u>any</u> crystal. The foundation of the approach lies in the LCAO model and the Slater and Koster two-center integral approximation. The only input requirements are the crystal geometry and a set of parameters which characterize the interactions between pairs of atomic orbitals.

DENSITY OF STATES CALCULATIONS

Since it is now possible to calculate the energy eigenvalues for any crystal at an arbitrary wave-vector in the Brillouin zone as shown above, the corresponding energy density of states may be obtained by performing an integration over a constant energy surface in the Brillouin zone:[11]

$$g(E) \sim \int \frac{dS}{\nabla_{\vec{k}} E} \quad . \tag{46}$$

Considerable effort has been put forth to increase the computational efficiency of algorithms evaluating this type of integral.[12-14] But if the calculation is done on a minicomputer, which is idle more than 50% of the time, simplification in programming is traded for maximum efficiency of execution. Therefore, the statistical histogram or root sampling method[15] can be used to greatly simplify the density of states calculation. This method involves generating the energy eigenvalues at a large number of random wave-vectors in the Brillouin zone and then sorting these eigenvalues into "buckets" that subdivide the energy range. This procedure suggests that the shape of the Brillouin zone must be known. Because different crystals possess Brillouin zones of various shapes, the sought after generality of applicability to all crystals, as exhibited by the energy band program, would be lost. In order to retain this generality feature, the following fact was recognized and employed: choosing a random wave-

vector in a single Brillouin zone is equivalent to choosing a random wave-vector in any random Brillouin zone.

Consequently, in order to simplify the geometry, a wave-vector that falls within an "arbitrarily large sphere" was selected. This "sphere" must be large enough that the edge effects do not interfere with randomizing. The edge effect problem can be readily understood with an example. Consider a cubic Brillouin zone and let the "sphere" circumscribe the cube. A wave-vector, $\vec{k}$, that falls outside the cube is equivalent to the wave-vector, $\vec{k}'$, shown in Figure 19, where $\vec{k}' = \vec{k} + \vec{G}$ and $\vec{G}$ is a reciprocal lattice vector. Therefore, for a random wave-vector inside the sphere, the probability that this wave-vector (or its equivalent) falls between the dotted circular arcs of Figure 19 and the Brillouin zone edge is enhanced by a factor of two, due to the portion of the sphere outside the cube which is folded back into the Brillouin zone. By choosing a sphere of sufficiently large radius, the perturbation on the randomizing process, from fractional Brillouin zones at the edge of the sphere is small because: i) the probability that a random wave-vector falls within a partial Brillouin zone is given by the ratio of the volume of all fractional Brillouin zones to the volume of the sphere; and ii) the fractional Brillouin zones, when combined, will form a number of "complete" Brillouin zones which do not contribute to the edge effect.

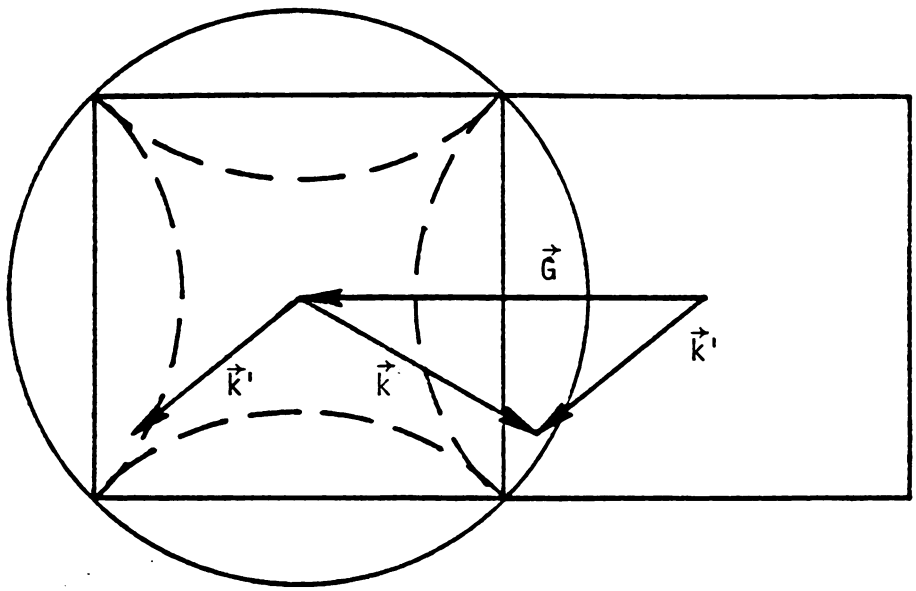


Figure 19. Wave-vector, $\vec{k}$, which falls outside a cubic Brillouin zone is related to wave-vector, $\vec{k}'$, within the Brillouin zone by reciprocal lattice vector, $\vec{G}$

RESULTS

The flowchart and listing for a Fortran program to compute the density of states, using the above method, are given in Appendix D. The density of states of various zincblende compounds -- Si, Ge, GaAs and ZnSe -- are shown in Figures 20, 21, 22 and 23, respectively, for first nearest neighbors and both Chadi-Cohen[1] and Harrison's parameters (Equations 15 through 21). The plots for Ge, GaAs, and ZnSe can be compared with Figures 4, 7 (mislabeled), and 9 of Chadi-Cohen,[1] respectively. To carry out the density of states calculations on the chalcopyrites on Tl_3AsSe_3, the symmetries along the c-axes are no longer useful. That is, the diagonalization of the full 64x64 or 84x84 matrix for each random wave-vector is required. These calculations will be performed when the program is transferred onto a CDC computer.

SUMMARY

In summary of the density of states calculation, a computer program is available to determine the density of states for any crystal, requiring only the specification of atomic numbers and atomic coordinates of the atoms in the crystal, along with a set of parameters which characterize the interactions between pairs of atomic orbitals.

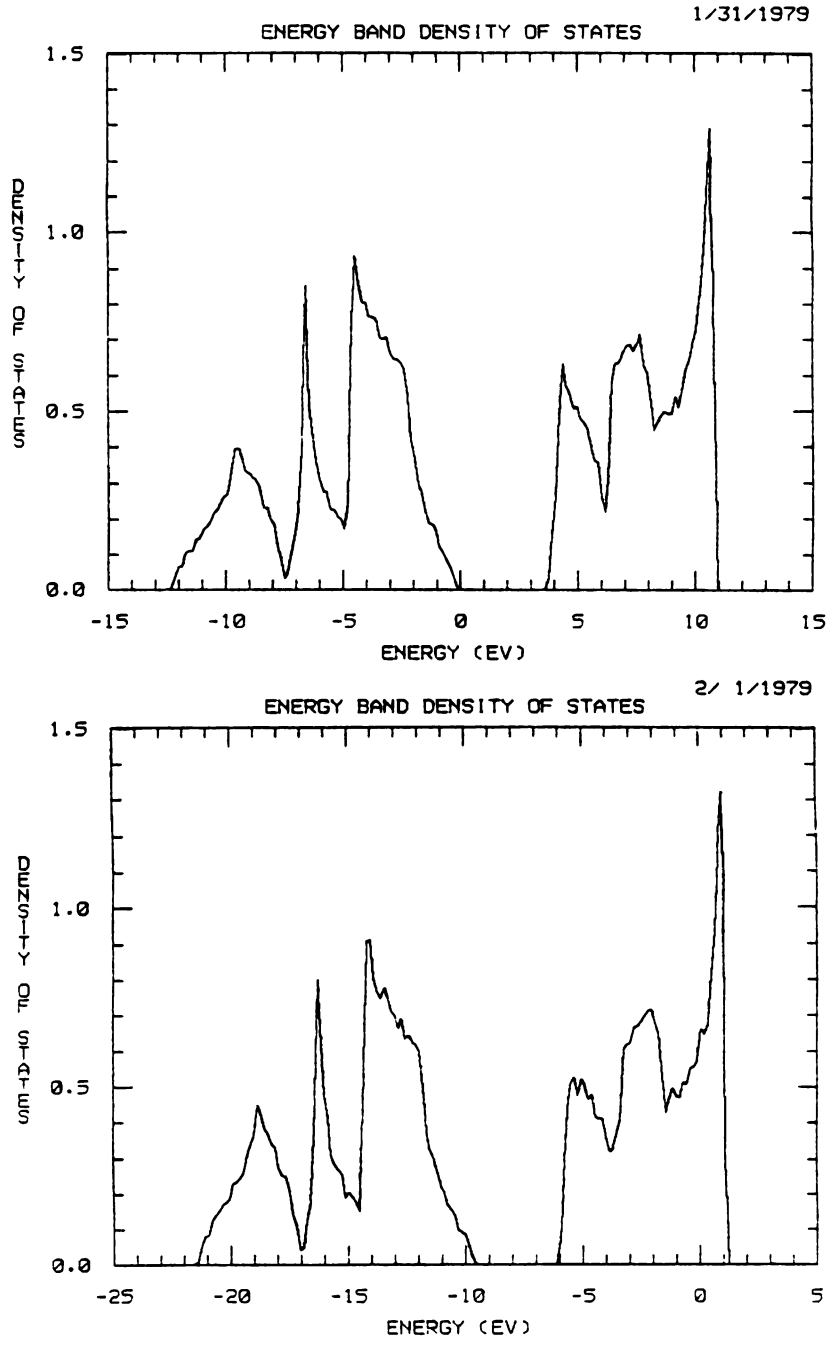


Figure 20. Density of states of Si for first nearest neighbors; (Top) Chadi and Cohen parameters, (Bottom) Harrison's parameters

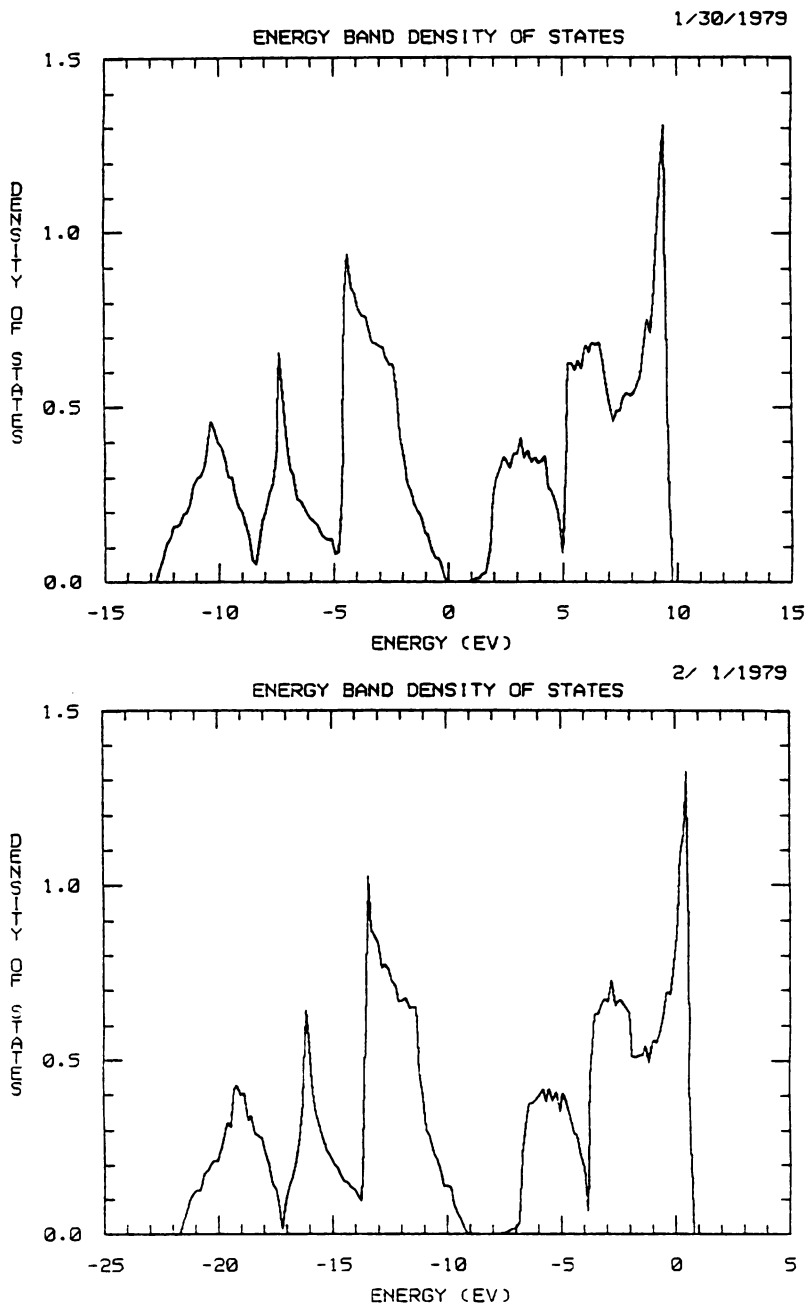


Figure 21. Density of states of Ge for first nearest neighbors; (Top) Chadi and Cohen parameters, (Bottom) Harrison's parameters

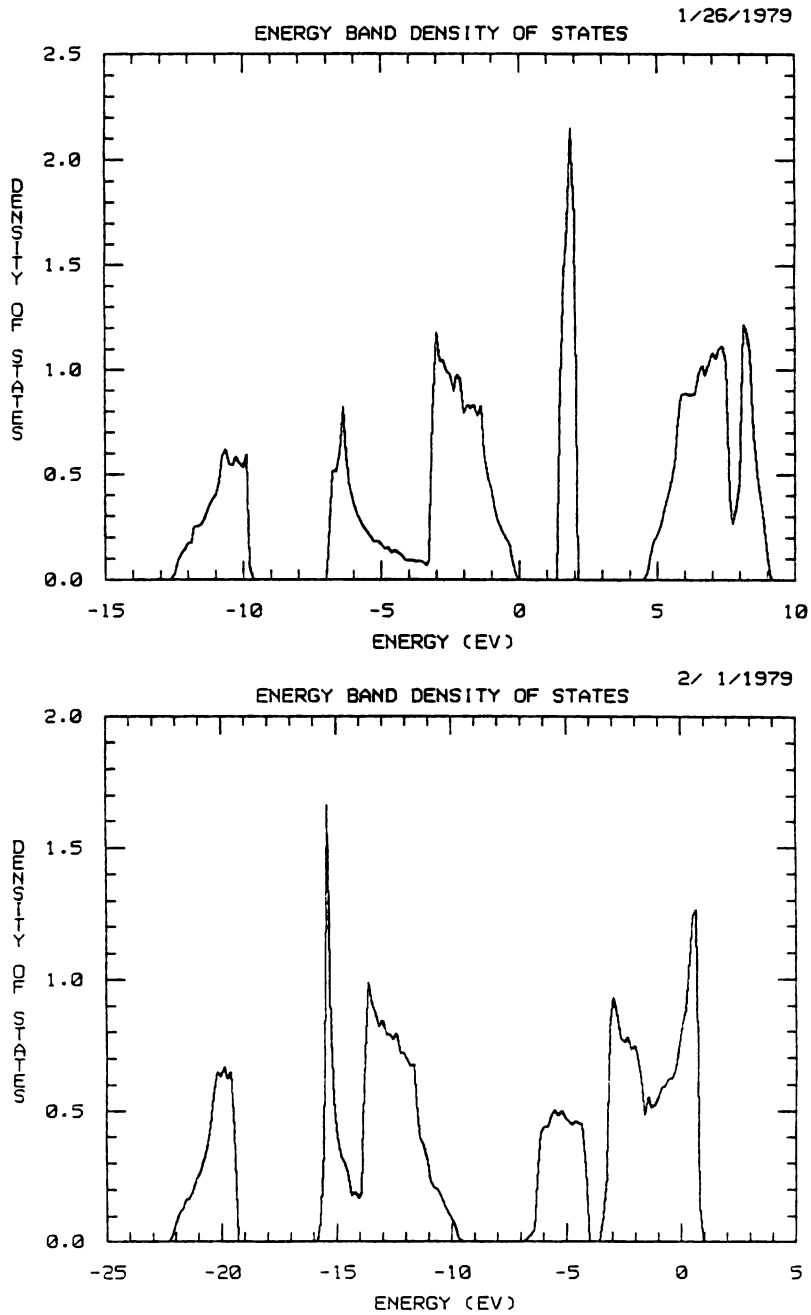


Figure 22. Density of states of GaAs for first nearest neighbors; (Top) Chadi and Cohen parameters, (Bottom) Harrison's parameters

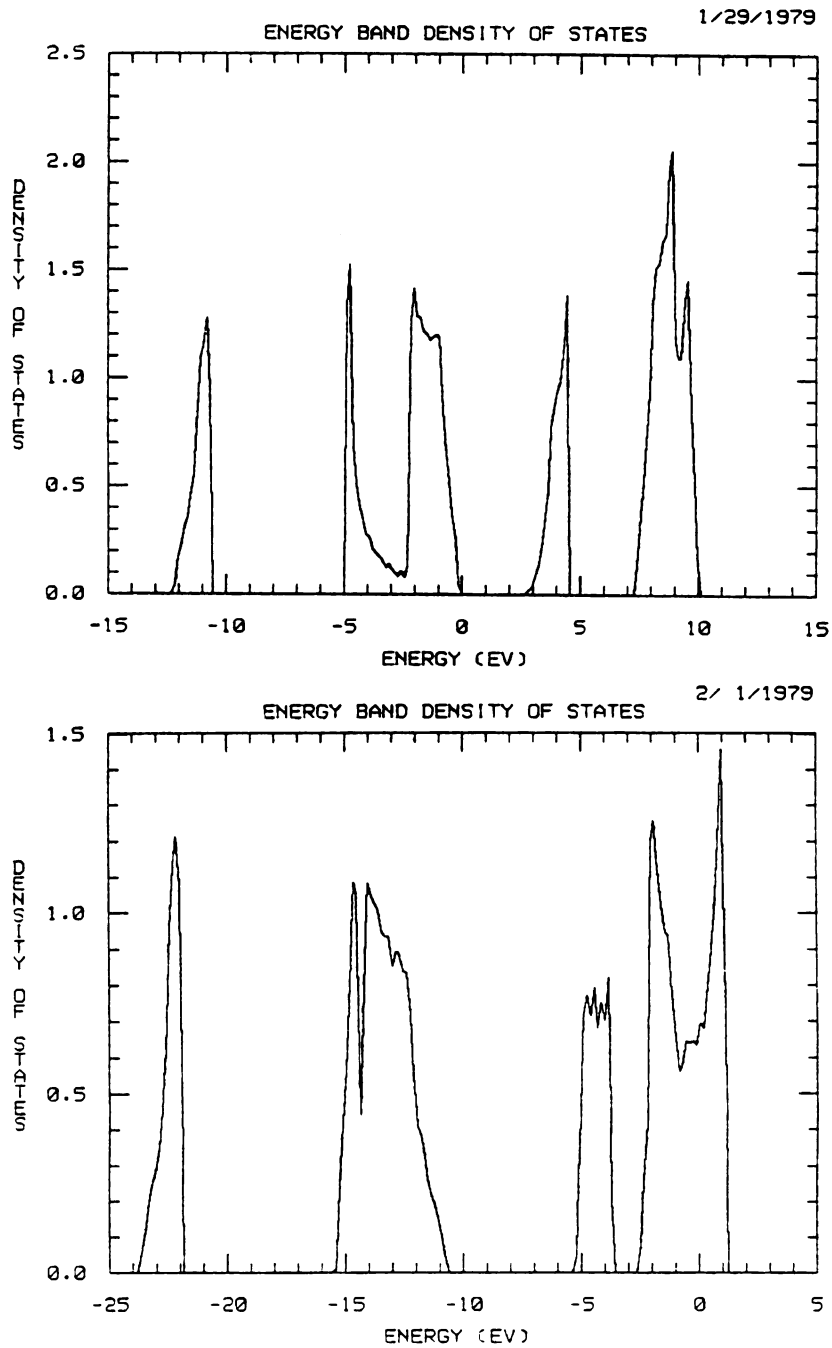


Figure 23. Density of states of ZnSe for first nearest neighbors; (Top) Chadi and Cohen parameters, (Bottom) Harrison's parameters

INDEX OF REFRACTION AND BIREFRINGENCE CALCULATIONS

A systematic method for numerically describing the interaction between two atomic orbitals has been presented in the preceding sections and appendices. Now this "chemical bond" approach will be applied to the prediction of the electronic susceptibility in semiconductors. An equivalent set of interaction parameters, as was utilized in the band structure calculations, will enter into the formularization. Harrison's Bond-Orbital Model (BOM),[16,17] which provides the theoretical foundation, is reviewed below as an introduction to the concepts and notation.

FORMULISM

Consider a linear combination of an anion sp^3 hybrid orbital and a cation sp^3 hybrid orbital,

$$|\psi\rangle = u_a|h_a\rangle + u_c|h_c\rangle \tag{47}$$

where

$$u_a^2 + u_c^2 = 1 \tag{48}$$

for normalization. The coefficients, u_a and u_c, are determined by minimizing the energy, E, of the hybrid orbital with respect to these coefficients. That is,

$$\frac{\partial E}{\partial u_a} = 0 \qquad \text{and} \qquad \frac{\partial E}{\partial u_c} = 0 \tag{49}$$

where

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \quad . \tag{50}$$

By defining the following parameters:

$$V_2 = -\langle h_a|H|h_c\rangle = -\langle h_c|H|h_a\rangle \tag{51}$$

$$\varepsilon_a = \langle h_a|H|h_a\rangle \tag{52}$$

$$\varepsilon_c = \langle h_c|H|h_c\rangle \ , \tag{53}$$

the energy can be written as

$$E = \frac{u_a^{\,2}\varepsilon_a + u_c^{\,2}\varepsilon_c - 2u_a u_c V_2}{u_a^{\,2} + u_c^{\,2}} \quad . \tag{54}$$

Then, from Equations 49,

$$\frac{\partial E}{\partial u_a} = \frac{2u_a\varepsilon_a - 2u_c V_2}{u_a^{\,2} + u_c^{\,2}} - \frac{E(2u_a)}{u_a^{\,2} + u_c^{\,2}} = 0$$

or

$$u_a(\varepsilon_a - E) - u_c V_2 = 0 \quad . \tag{55}$$

Similarly, from $(\partial E/\partial u_c) = 0$,

$$u_c(\varepsilon_c - E) - u_a V_2 = 0 \quad . \tag{56}$$

If a nontrivial solution for u_a and u_c, in Equations 55 and 56, is to exist, then the determinant of the coefficients must be zero. That is,

$$\begin{vmatrix} (\varepsilon_a - E) & -V_2 \\ -V_2 & (\varepsilon_c - E) \end{vmatrix} = 0 \tag{57}$$

or

$$\varepsilon_a \varepsilon_c + E^2 - E(\varepsilon_a + \varepsilon_c) - V_2^{\,2} = 0. \tag{58}$$

The energy solution to this quadratic equation in E is

$$E = \frac{\varepsilon_a + \varepsilon_c}{2} \pm \frac{1}{2} \sqrt{(\varepsilon_a + \varepsilon_c)^2 - 4\varepsilon_a \varepsilon_c + 4V_2^{\,2}} \quad . \tag{59}$$

Now, defining

$$V_3 = \frac{1}{2}(\varepsilon_c - \varepsilon_a) \tag{60}$$

and

$$\bar{\varepsilon} = \frac{1}{2}(\varepsilon_c + \varepsilon_a) \tag{61}$$

yields

$$E = \bar{\varepsilon} \pm \sqrt{V_2^{\,2} + V_3^{\,2}} \quad . \tag{62}$$

The "minus" sign corresponds to the bonding state and "plus" sign gives the antibonding state. By substituting the bonding energy back into Equations 48 and (55 or 56), solutions to u_a and u_c are obtained for the bonding orbital:

$$u_a = \sqrt{\frac{1 + \alpha_p}{2}} \quad \text{and} \quad u_c = \sqrt{\frac{1-\alpha_p}{2}} \tag{63}$$

where

$$\alpha_p = \frac{V_3}{\sqrt{(V_2^2 + V_3^2)}} = \frac{u_a^2 - u_c^2}{u_a^2 + u_c^2} \quad . \tag{64}$$

Note that V_2, V_3 and α_p are called the covalent energy, the polar energy, and the polarity, respectively. Now, since the probability of a bonding electron being "on" the anion or cation is u_a^2 or u_c^2, the charge per bond (two electrons for each bond) associated with the anion is

$$-2e\ u_a^2 = -e(1 + \alpha_p) \tag{65}$$

and with the cation is

$$-2e\ u_c^2 = -e(1 - \alpha_p) \quad . \tag{66}$$

The electronic dipole moment of the bond is therefore

$$\vec{p} = \sum_i q_i \vec{x}_i = -e(1 + \alpha_p) \langle\vec{x}_a\rangle - e(1 - \alpha_p) \langle\vec{x}_c\rangle \tag{67}$$

where $\langle\vec{x}_a\rangle$ and $\langle\vec{x}_c\rangle$ represent the average vector positions of the bonding electron distributions about the anion and cation, respectively. If the origin is chosen to be at the center of the bond and if $\vec{d}$ is the internuclear vector distance from the cation to anion, then

$$\langle\vec{x}_a\rangle = +\gamma\ \vec{d}/2 \tag{68}$$

and

$$\langle\vec{x}_c\rangle = -\gamma\ \vec{d}/2 \tag{69}$$

where γ scales the "center of gravity" of the electron charge distribution in both anion and cation hybrid orbitals. Therefore, the dipole moment per bond can be written

$$\vec{p} = -e(1+\alpha_\rho)\gamma\vec{d}/2 + e(1-\alpha_p)\gamma\vec{d}/2$$

which reduces to

$$\vec{p} = -\gamma e\ \alpha_p\ \vec{d}. \tag{70}$$

A change in this dipole moment occurs in response to an external electric field, $\vec{\xi}$. Upon application of this external electric field, there is an interaction energy of

$$-\vec{p}\cdot\vec{\xi} = -\gamma e\alpha_p\ \vec{d}\cdot\vec{\xi} \tag{71}$$

which corresponds to a change in polar energy, V_3,[16] given by

$$V_3 \rightarrow V_3 - \gamma e \vec{d} \cdot \vec{\xi}/2. \tag{72}$$

The polarization per bond, when an external electric field is present, is derivable from Equations 64, 70 and 72 as follows:

$$\vec{p} = -\gamma e \frac{\vec{d} V_3 - \gamma e \vec{d} \cdot \vec{\xi}/2}{\sqrt{\left(V_2^{\,2} + (V_3 - \gamma e \vec{d} \cdot \vec{\xi}/2)^2\right)}} \tag{73}$$

Using a binomial expansion,[19]

$$(1+x)^n = 1 + nx + n(n-1)\frac{x^2}{2!} + \ldots\ldots, \tag{74}$$

on the denominator for small electric field, and collecting terms with similar powers of $\vec{\xi}$ yields

$$\vec{p} = -\gamma e \alpha_p \vec{d} + \frac{\gamma^2 e^2 V_2^{\,2}}{2(V_2^{\,2} + V_3^{\,2})^{3/2}} \vec{d}(\vec{d} \cdot \vec{\xi}) + \frac{3\gamma^3 e^3 V_2^{\,2} V_3}{8(V_2^{\,2} + V_3^{\,2})^{5/2}} \vec{d}(\vec{d} \cdot \vec{\xi})^2 + \ldots. \tag{75}$$

As an alternative, the first and second order terms of the polarization per bond can also be separately obtained from

$$\frac{\partial \vec{p}}{\partial \xi} = \left(\frac{\partial \vec{p}}{\partial V_3}\right)\left(\frac{\partial V_3}{\partial \xi}\right) = -\gamma e \vec{d} \left(\frac{\partial \alpha_p}{\partial V_3}\right)\left(\frac{\partial V_3}{\partial \xi}\right) \tag{76}$$

and

$$\frac{\partial^2 \vec{p}}{\partial \xi} = \frac{\partial}{\partial \xi}\left[\left(\frac{\partial \vec{p}}{\partial V_3}\right)\left(\frac{\partial V_3}{\partial \xi}\right)\right] = \left(\frac{\partial^2 \vec{p}}{\partial V_3^2}\right)\left(\frac{\partial V_3}{\partial \xi}\right)^2 \quad , \tag{77}$$

respectively.

In order to compute the overall polarization, the contributions from each bond in a unit cell are added together and normalized to volume. That is,

$$\vec{P} = \frac{1}{V} \sum_{\text{bonds}} (\vec{p}_0 + \vec{p}_1 + \vec{p}_2 + \ldots.) \tag{78}$$

where $\vec{p}_0$, $\vec{p}_1$ and $\vec{p}_2$ are the zeroth, first and second order dipole moments per bond as given in Equation 75 and V is the volume of the unit cell. For non-ferroelectric materials, the zeroth order term averages to zero. (This makes a nice consistency check to verify that the appropriate bonds are all included in the sum.) And for zincblende crystals, with a regular tetrahedral structure, the first order geometric factor, $\vec{d}(\vec{d}\cdot\vec{\xi})$, averages to $d^2\xi\cos^2\theta = d^2\xi/3$ (see Appendix I), as is found in the literature.[16,18]

By evaluating Equation 78 for each of the three orthogonal electric fields, ξ_x, ξ_y and ξ_z, the nine components of the susceptibility tensor are obtained since

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & \chi_{22} & \chi_{23} \\ \chi_{31} & \chi_{32} & \chi_{33} \end{pmatrix} \begin{pmatrix} \xi_x \\ 0 \\ 0 \end{pmatrix} \text{ or } \begin{pmatrix} 0 \\ \xi_y \\ 0 \end{pmatrix} \text{ or } \begin{pmatrix} 0 \\ 0 \\ \xi_z \end{pmatrix}. \tag{79}$$

Diagonalization of this 3x3 susceptibility matrix results in the three principal susceptibilities which are denoted by χ_1, χ_2 and

χ_3. Consequently, the principal indices of refraction can be calculated from

$$n_i = \sqrt{1 + 4\pi\chi_i} \quad \text{for } i = 1,2,3. \tag{80}$$

For all three principal indices of refraction equal, the crystal is optically isotropic.[20] If only two of the principal indices of refraction are equal (e.g., $n_o = n_1 = n_2 \neq n_3 = n_e$), then the crystal is uniaxial with the birefringence given by

$$\Delta n = n_e - n_o \tag{81}$$

where subscripts "e" and "o" denote extraordinary and ordinary. Finally, when all three principal indices of refraction are unequal, the crystal is biaxial.

IMPLEMENTATION

Therefore, the principal indices of refraction can be numerically predicted by incorporating Equations 75, 78, 79 and 80 into a computer program. The only requirements to perform this calculation are the crystal geometry, a procedure for summing over bonds, and the set of parameters V_2, V_3 and γ, which describe the interaction between each pair of sp^3 hybrid orbitals. A Fortran program (flowcharted and listed in Appendix E) was written utilizing the above formularization, specifically for the tetrahedrally coordinated chalcopyrites (see Appendix F). The geometry was again handled separately by the generation of a list of atoms and their coordinate positions. (In

fact, both this calculation and the band structure calculations utilized the same geometry file list.)

Two different sets of parameters describing each hybrid bond were tried. The first is a set of empirical parameters based on experimental dielectric constants of the III-V and II-VI binary semiconductors.[17] V_2 and γ were found to correspond to the row of the periodic table to which each atom involved belongs. And the set of V_3 was directly related to a set of hybrid energies via Equation 60. A second set of parameters, based on atomic orbitals rather than sp^3 hybrids, were also used. Since sp^3 hybrid orbitals can be decomposed into a linear combination of atomic orbitals, it is possible to express V_2 and V_3 in terms of Harrison's "Solid State Interatomic Matrix Elements" (Equations 15 through 21) and the Herman-Skillman atomic term values.[6,8] To be more explicit, the hybrid orbitals for the anion and the cation are written

$$|h_a\rangle = \frac{1}{2}|s_a\rangle + \frac{\sqrt{3}}{2d}(d_x|p_{ax}\rangle + d_y|p_{ay}\rangle + d_z|p_{az}\rangle) \tag{82}$$

and

$$|h_c\rangle = \frac{1}{2}|s_c\rangle - \frac{\sqrt{3}}{2d}(d_x|p_{cx}\rangle + d_y|p_{cy}\rangle + d_z|p_{cz}\rangle) \tag{83}$$

where $\vec{d} = d_x\hat{x}$ and $d_y\hat{y} + d_z\hat{z}$ is the vector distance from cation to anion. [Notes: i) the minus sign in Equation 83 makes the cation hybrid orbital point in the opposite direction of the anion orbital; ii) the factors d_i/d permit the directions of the hybrid orbitals to deviate from the (±1, ±1, ±1) directions of a "regular" tetrahedron -- that is, these hybrid orbitals can reflect the distorted tetrahedral angles of the chalcopyrites; iii) the orthogonality of the

hybrid orbitals is lost except, for the "regular" tetrahedron, when $d_x = d_y = d_z = d/\sqrt{3}$]. Then, from Equation 51,

$$V_2 = \frac{3}{4d^2} \sum_{i=1}^{4} \sum_{j=1}^{4} d_i d_j \langle a_{ci} | H | a_{aj} \rangle \tag{84}$$

where a_{ci} and a_{aj} are the cation and anion atomic orbitals (i and j = 1,2,3,4 denotes s, p_x, p_y, p_z), d_i and d_j equal $-d/\sqrt{3}$ and $+d/\sqrt{3}$, d_x, d_y, d_z for i and j = 1,2,3,4 and $\langle a_{ci} | H | a_{aj} \rangle$ is a "Solid State Interatomic Matrix Element". Also, from Equations 52, 53, and 60,

$$V_3 = \frac{1}{8} [(\varepsilon_s^c + 3\varepsilon_p^c) - (\varepsilon_s^a + 3\varepsilon_p^a)] \tag{85}$$

where ε_s, ε_p, ε_s and ε_p are "atomic term values" for the cation and anion.

RESULTS FOR CHALCOPYRITES

The calculations were performed on the chalcopyrites because: i) the lattice parameters and optical properties have been experimentally established and ii) the chalcopyrites, being closely related to the zincblende semiconductors, can be treated by simply extending some well-developed empirical theories for zincblendes. The indices of refraction as a function of wavelength for many chalcopyrites were measured by Boyd et. al.[21-25] The predicted static (long wavelength limit) indices of refraction and birefringence, using the above BOM theory with parameters from the binary semiconductors and only the first order polarization, are compared to experiment in Table 5. Also listed in Table 5 are the results of

TABLE 5

INDICES OF REFRACTION AND BIREFRINGENCE FOR VARIOUS CHALCOPYRITES--A COMPARISON OF THEORY AND EXPERIMENT

Compound	Experimental* (Boyd et. al.)		Theoretical Lines & Waszczak	Theoretical 1st Order Binary BOM Parameters		
	n_o	Δn	n	n_o	n_e	Δn
$CuGaS_2$	2.4275	-.0154	2.51	2.525	2.484	-.0414
$AgGaS_2$	2.3266	-.0550	2.45	2.524	2.305	-.2186
$CuInS_2$	2.5166	-.0179	2.53	2.519	2.522	+.0032
$ZnGeP_2$	3.0552	+.0397	3.10	3.114	3.084	-.0302
$CdGeAs_2$	3.5004	+.0868	3.36	3.414	3.277	-.1368
$CdGeP_2$	3.1165	+.0167	3.08	3.123	2.990	-.1330
$ZnSiAs_2$	3.1685	+.0268	3.22	3.248	3.178	-.0704
$CuAlSe_2$	2.4659	-.0126	2.64	2.667	2.605	-.0615
$AgGaSe_2$	2.5731	-.0327	2.61	2.684	2.485	-.1985
$CuGaSe_2$	2.6872	+.0026	2.69	2.698	2.655	-.0430
$AgInSe_2$	2.6167	+.0017	2.63	2.655	2.573	-.0822

* at longest measured wavelength (generally ~12μm)

Lines and Waszczak,[18] who used an equivalent BOM theory, but treated only the average index of refraction and did not attempt to include the birefringence. As is evident from Table 5, the computer program of Appendix E is capable of reproducing the number of Lines and Waszczak for the average index of refraction which shows reasonable agreement with the experimental values. However, the predicted birefringence appears to have no correlation if compared to the corresponding measured quantity. More particularly, even the sign of the birefringence differs when contrasting theory and experiment for all of the II-IV-V compounds and some of the I-III-VI compounds.

As an attempt to resolve the above conflict with regard to birefringence, the same calculation was repeated using a different set of parameters (Harrison's "Solid State Interatomic Matrix Elements" and Herman-Skillman's atomic term values). The resultant first order ordinary index of refraction and birefringence are given in Table 6. For comparison, the first order predictions with the binary compound BOM parameters and calculations including the second order polarization term are also presented in Table 6. It is evident from Table 6 that the relative qualitative arrangement of birefringence from compound to compound is, in general, unchanged by using a different set of BOM parameters or including the second order polarization.

In addition, slight variations in the assumed chalcopyrite geometry were tried in order to account for the discrepency in birefringence between experiment and theory. Specifically, the calculated birefringence is plotted as a function of lattice constant, x,

TABLE 6

THEORETICAL ORDINARY INDEX OF REFRACTION AND BIREFRINGENCE FOR VARIOUS CHALCOPYRITES

Compound	1st Order Polarization Decomposed sp^3 Parameters		1st Order Polarization Binary BOM Parameters		1st & 2nd Order Polarization Binary BOM Parameters	
	n_o	Δn	n_o	Δn	n_o	Δn
$CuGaS_2$	1.620	-.0181	2.525	-.0414	3.307	-.0587
$AgGaS_2$	1.603	-.0928	2.524	-.2186	3.374	-.3308
$CuInS_2$	1.590	+.0014	2.519	+.0032	3.384	+.0045
$ZnGeP_2$	1.823	-.0176	3.114	-.0302	3.862	-.0449
$CdGeAs_2$	1.844	-.0666	3.414	-.1368	4.405	-.2271
$CdGeP_2$	1.827	-.0736	3.123	-.1330	3.988	-.2125
$ZnSiAs_2$	1.839	-.0349	3.248	-.0704	4.071	-.1077
$CuAlSe_2$	1.630	-.0245	2.667	-.0615	3.533	-.0902
$AgGaSe_2$	1.621	-.0780	2.684	-.1985	3.682	-.3075
$CuGaSe_2$	1.640	-.0173	2.698	-.0430	3.623	-.0622
$AgInSe_2$	1.591	-.0330	2.655	-.0822	3.721	-.1242

in Figure 24, using the first order polarization with binary semiconductor BOM parameters for $CdGeAs_2$. As illustrated in this figure, the dependence on lattice constant is not strong enough to accomodate a change in sign of the birefringence.

Synopsis

The simplistic "chemical bond" approach to calculating the refractive indices and birefringence is very attractive when contrasted with the more common "oscillator strength" method. Consequently, a computer program employing the former scheme has been written in which, again, the crystal geometry and a set of parameters that describe the interactions between orbitals are supplied. Upon application to the chalcopyrites, the indices of refraction are predicted quite well (for the appropriate set of BOM parameters) but the birefringence is not. In trying to infer a qualitative aspect of the birefringence calculation, it appears that the geometric factors $\vec{d}(\vec{d}\cdot\vec{\xi})^n$ in Equation 75 are the dominant contributions to the sign of the birefringence as calculated using the theory presented above. The fact that the calculations do not agree with experiment implies that something in the theory is missing. Speculation as to possible origins is currently in progress and has led to reformulation and generalization of the BOM in terms of coupled states between valence and conduction bands which yields a susceptibility related to, in part, the energy difference between the states.[7]

In addition to not being able to account for the birefringence, the Bond-Orbital Model theory, as it now stands, assumes a static

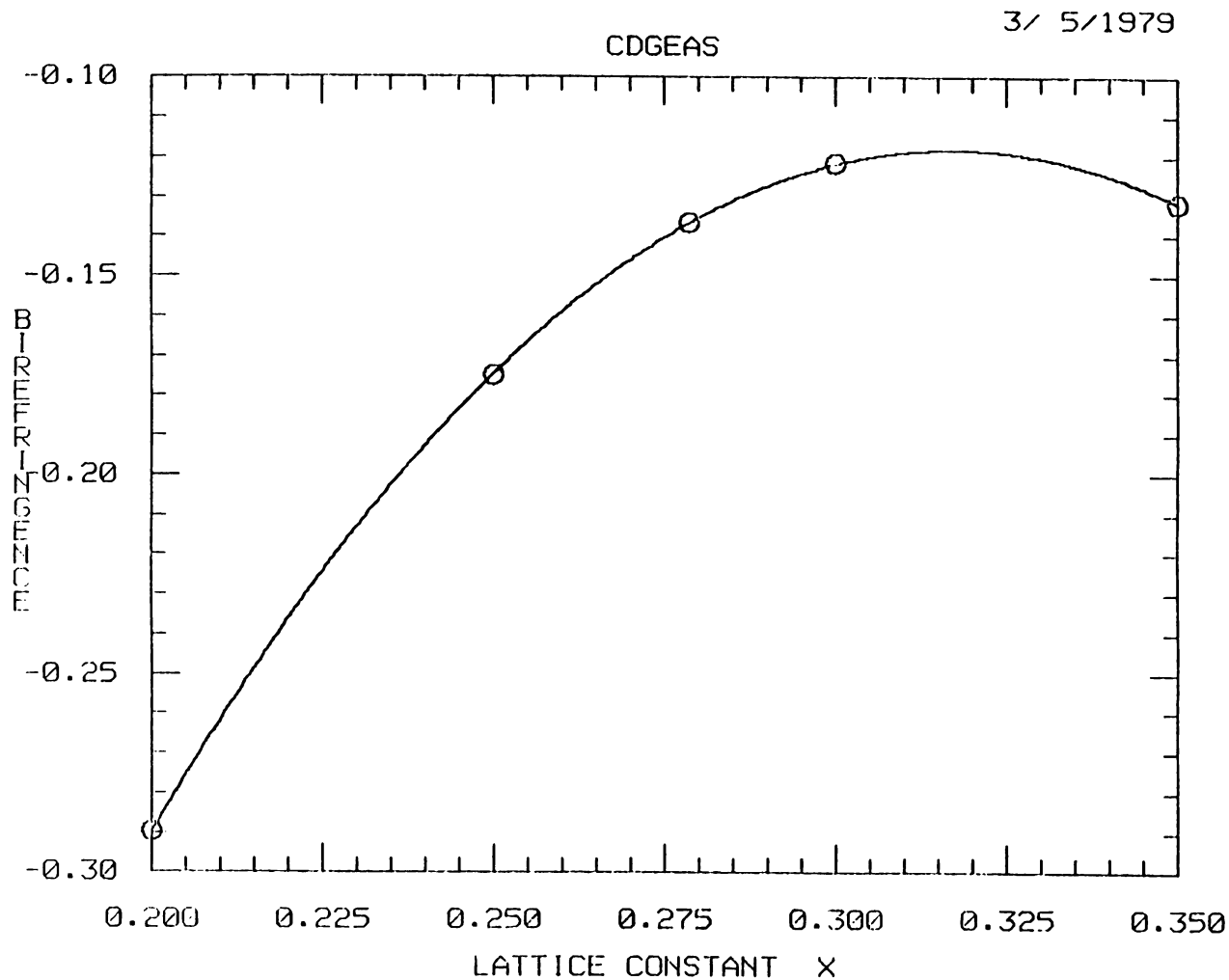


Figure 24. Theoretical birefringence of $CdGeAs_2$ as a function of lattice constant, x

electric field. Since the interest is actually in the optical properties of semiconductors, a more applicable theory should yield the frequency dependencies of the indices of refraction. Also Equations 75, 78 and 79 yield a susceptibility tensor with real components, but in optically active materials, for example, some components of the susceptibility tensor are complex[20] and therefore these materials cannot be correctly characterized within the framework of the present theory.

CONCLUSION

As a continuation of the band structure calculations performed in this work, similar calculations will be carried out on the more complex, ternary semiconductors once the energy band and density of states programs have been successfully transferred to a CDC computer. Specifically, the density of states for the chalcopyrites and Tl_3AsSe_3 are scheduled for completion. In addition, the band structures for such ternary compounds as $Hg_xCd_{1-x}Te$ and $In_xAs_{1-x}Sb$ are of interest since these materials are being utilized as intrinsic semiconducting quantum detectors of infrared radiation.

A second area of activity relating to band structure calculations is apparent--the determination of a more realistic set of parameters which quantify the interaction between pairs of atomic orbitals. These parameters need to be consistent with the formulism of including higher order neighbors into the calculation as indicated above. To this end, the incorporation of a "least squares" fitting routine or a "self-consistent" LCAO method[9] (or equivalent) into the band calculation may be necessary to resolve a "best" set of parameters for each crystal.

Except for changing crystal structures and modifying the interaction parameters, the energy band structure problem has been solved in general. The only remaining step is the execution of the computer program for each material of interest.

With regard to the principal indices of refraction calculation, the conflict between theoretical and experimental birefringence

demands resolution. This may be accomplished with a refinement of the BOM theory as indicated above, or it might require the implementation of another formulation (e.g., Lindhard's or "Oscillator Strength").

If a reasonable solution to the birefringence problem (one that depends on crystal geometry) can be found, then a handle on two additional material properties might be procured. The stress induced birefringence gives information about the elasto-optic or piezo-optic tensors.[26] Stressing the crystal results in a strain or change in the geometric positions of atoms (quantified by the elastic stiffness tensor). The application of a large electric field also results in a variation in the refractive indices which is characterized by the electro-optic tensor. Generally, the electric field will cause a strain in the crystal (given by the piezoelectric tensor) in addition to the "primary" effect of the electric field interacting directly with the bonding electronic orbitals. Consequently, by simply considering a change in crystal geometry due to either an applied stress or electric field, the corresponding change in the principal indices of refraction should relate to the elasto-optical or electro-optical coefficients.

APPENDICES

APPENDIX A

ATOMIC ORBITALS

The time dependent Schrodinger's equation is

$$H|\psi\rangle = E|\psi\rangle \tag{A1}$$

or

$$\frac{-\hbar^2}{2m} \nabla^2\psi + V\psi = E\psi \tag{A2}$$

where ψ is the wavefunction for a single electron in the crystal. In spherical coordinates, with vector components written as

$$\begin{aligned} x &= r\cos\phi\sin\theta \\ y &= r\sin\phi\sin\theta \\ z &= r\cos\theta \ , \end{aligned} \tag{A3}$$

Equation A2 becomes

$$\frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\theta^2}\right]\psi$$

$$+ V\psi = E\psi \quad . \tag{A4}$$

Assume that all interactions between the electron and the rest of the crystal are described by the potential, $V(\vec{r})$ and, furthermore, assume that this potential is a central potential; i.e.,

$$V(r,\theta,\phi) = V(r) \quad . \tag{A5}$$

Then, in order to solve the differential equation, Equation A4,[27] separate angular and radial coordinates,

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \ . \tag{A6}$$

Consider only the resultant angular differential equation, where β is a separation constant,

$$\left[\frac{1}{\sin\theta}\ \frac{\partial}{\partial\theta}\ \left(\sin\theta\ \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\ \frac{\partial^2}{\partial\phi^2}\right] Y = -\beta Y \tag{A7}$$

and perform another separation of variables, θ and ϕ,

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi) \tag{A8}$$

which yields

$$\frac{d^2\Phi}{d\phi^2} = -\alpha^2\Phi \tag{A9}$$

and

$$\left[\sin\theta\ \frac{d}{d\theta}\left(\sin\theta\ \frac{d}{d\theta}\right) + \beta\sin^2\theta\right]\ \Theta = \alpha^2\Theta \tag{A10}$$

where α^2 is the second separation constant.

The normalized solutions to this last pair of differential equations are the set of spherical harmonics,

$$Y_l^m(\theta,\phi) = (-1)^{(\ m+|m|)/2}\ \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}}\ P_l^m(\cos\theta)\ e^{im\phi} \tag{A11}$$

where $\beta = l(l+1)$ for $l = 0,1,2,\ldots$, $\alpha = m$ for $m = 0, \pm1,\pm2,\ldots$, and $P_l(\cos\theta) = P_l\ (\cos\theta)$ are the associated Legendre functions given by[28]

$$P_n^m(x) = (1-x^2)^{m/2}\ \frac{d^m}{dx^m} P_n(x) \qquad \text{(A12)}$$

for $m \geq 0$ and

$$P_n(x) = \frac{1}{2^n n!}\ \frac{d^n(x^2-1)^n}{dx^n} \quad . \qquad \text{(A13)}$$

A few of these angular solutions are written out in Table A1.[3] By taking the appropriate linear combinations of these solutions, the "standard" atomic orbitals, which are real, of elementary chemistry are obtained, as shown in Table A2. Note that the subscript notation in Table A2 utilizes the spherical to rectangular coordinate conversion of Equations A3. The directional characteristics of some of the atomic orbitals, as shown in Figure A1, are determined by making three dimensional polar plots of each orbital in Table A2 against the angular direction specified by θ and ϕ. The sign associated with each "lobe" of an atomic orbital is also indicated.

The primary purpose of this appendix was to present a review of atomic orbitals while specifying the notation. In addition, the assumption of a central potential seen by any electron in an atomic orbital is again explicitly emphasized.

Table A1

Spherical Harmonics

l	m	Symbol	$Y_l^m(\theta,\phi)$
0	0	s	$\sqrt{\frac{1}{4\pi}}$
1	1	p_{+1}	$-\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}$
1	0	p_o	$\sqrt{\frac{3}{4\pi}}\cos\theta$
1	-1	p_{-1}	$\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi}$
2	2	d_{+2}	$\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{2i\phi}$
2	1	d_{+1}	$-\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}$
2	0	d_o	$\sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
2	-1	d_{-1}	$\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{-i\phi}$
2	-2	d_{-2}	$\sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{-2i\phi}$

Table A2

Atomic Orbital Functions

$$s = \frac{1}{\sqrt{4\pi}}$$

$$p_x = \frac{1}{2}[p_{-1}-p_{+1}] = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$$

$$p_y = i\,\frac{1}{2}[p_{-1}+p_{+1}] = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$$

$$p_z = p_o = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$d_{x^2-y^2} = \frac{1}{2}[d_{-2} + d_{+2}] = \sqrt{\frac{15}{16\pi}}\sin^2\theta(\cos^2\phi-\sin^2\phi)$$

$$d_{xy} = i\,\frac{1}{2}[d_{-2} - d_{+2}] = \sqrt{\frac{15}{4\pi}}\sin^2\theta\cos\phi\sin\phi$$

$$d_{yz} = i\,\frac{1}{2}[d_{-1} + d_{+1}] = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin\phi$$

$$d_{xz} = \frac{1}{2}[d_{-1} - d_{+1}] = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin\phi$$

$$d_{z^2} = d_o = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$$

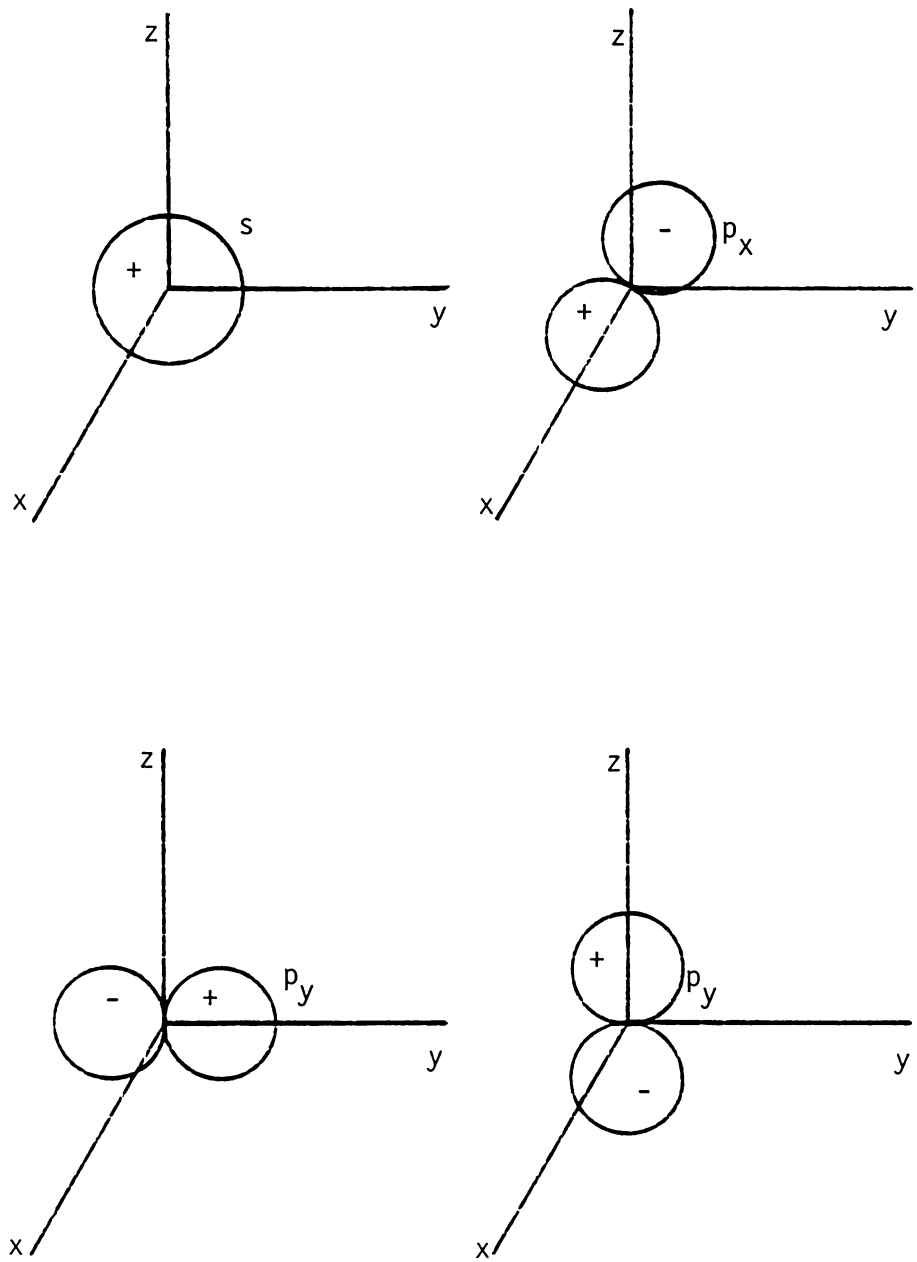


Figure A1. Directional nature of atomic orbitals

APPENDIX B

SLATER AND KOSTER 2-CENTER INTEGRALS OF ATOMIC ORBITALS

Slater and Koster[2] have provided a reasonable approach toward handling the geometrical considerations of a tight-binding calculation; that is, a convenient and concise way of separating the "interaction parameters" from the orientation or geometry of the atomic orbitals involved in a "chemical bond".

MEANING OF 2-CENTER INTEGRALS

From Equation 14, the matrix element of the Hamiltonian between two atomic orbitals is written

$$\langle \phi_\mu(\vec{r}-\vec{R}_n^\alpha)|H|\phi_\nu(\vec{r}-\vec{R}_1^\beta)\rangle = \int \phi_\mu(\vec{r}-\vec{R}_n^\alpha) H \phi_\nu(\vec{r}-\vec{R}_1^\beta)\, dV \qquad \text{(B1)}$$

where the Hamiltonian, H, is

$$H = \frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r}-\vec{R}_n^\alpha) + V(\vec{r}-\vec{R}_1^\beta) + \sum_{(m,\gamma) \neq (n,\alpha) \text{ or } (1,\beta)} V(\vec{r}-\vec{R}_m^\gamma). \qquad \text{(B2)}$$

and the summation over (m,γ) includes all atoms in the crystal except the two at $\vec{R}_n^\alpha$ and $\vec{R}_1^\beta$. Therefore, the matrix element in Equation B1 can be broken up into separate terms. The "Three-Center Integrals" are

$$\int \phi_\mu^* (\vec{r}-\vec{R}_n^\alpha)\ V(\vec{r}-\vec{R}_m^\gamma)\phi_\nu(\vec{r}-\vec{R}_1^\beta)dV \tag{B3}$$

where $(m,\gamma) \neq (n,\alpha)$ or $(1,\beta)$; that is, the matrix element involves two atomic orbitals on two distinct atoms interacting via a potential on yet a third atom. These are assumed to be negligible. The "Two-Center Integral", on the other hand, is a matrix element of atomic orbitals and potentials on only two atoms.

COMPONENT NATURE OF ATOMIC ORBITALS

Before proceeding with the discussion of the interaction (transfer integral) between two atomic orbitals, the transformation properties of an atomic orbital will be explored. First consider a two-dimensional transformation of coordinates for a p orbital, as illustrated in Figure B1. The p orbital is written in primed coordinates (see Table A2) as,

$$p_x' = c\ \sin\theta'\cos\phi' = \frac{c}{r'}\ x'\ . \tag{B4}$$

A transformation from the unprimed to the primed coordinates, corresponding to a rotation of angle θ_r about the z-axis, is represented in matrix notation by

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\theta_r & \sin\theta_r & 0 \\ -\sin\theta_r & \cos\theta_r & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{B5}$$

By expressing p_x' in terms of the unprimed coordinates,

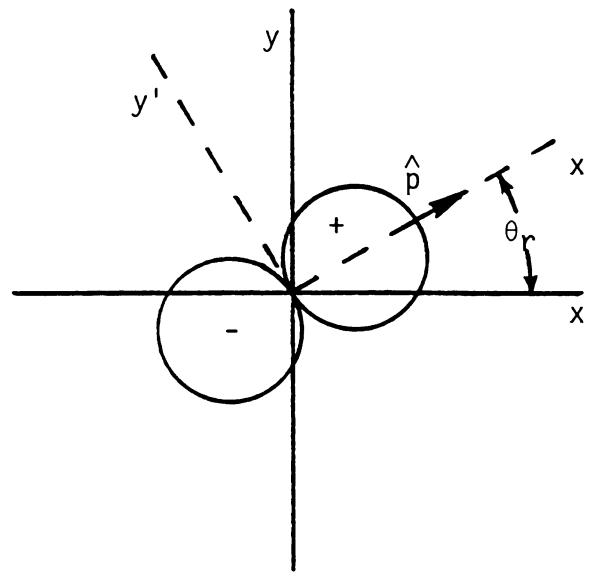


Figure B1. Two dimensional transformation of a p orbital.

$$p_x' = \frac{c}{r'} (x\cos\theta_r + y\sin\theta_r). \tag{B6}$$

And since r' is equal to r for a pure rotation,

$$p_x' = p_x \cos\theta_r + p_y \sin\theta_r . \tag{B7}$$

In other words, a p orbital oriented in some arbitrary direction in the x-y plane can be written as a linear combination of p_x and p_y orbitals.

Now generalize the above result to three dimensions; that is, consider the transformation of coordinates for a p orbital in three dimensions, shown in Figure B2. Writing the p orbital in primed coordinates (again see Table A2),

$$p_z' = c \cos\theta' = \frac{c}{r'} z'. \tag{B8}$$

Also, by transforming coordinates with a rotation or ϕ_r about the z-axis followed by a rotation of θ_r about the y'-axis,

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\theta_r & 0 & -\sin\theta_r \\ 0 & 1 & 0 \\ \sin\theta_r & 0 & \cos\theta_r \end{pmatrix} \begin{pmatrix} \cos\phi_r & \sin\phi_r & 0 \\ -\sin\phi_r & \cos\phi_r & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{B9}$$

or

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\phi_r \cos\theta_r & \sin\phi_r \cos\theta_r & -\sin\theta_r \\ -\sin\phi_r & \cos\phi_r & 0 \\ \cos\phi_r \sin\theta_r & \sin\phi_r \sin\theta_r & \cos\theta_r \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{B10}$$

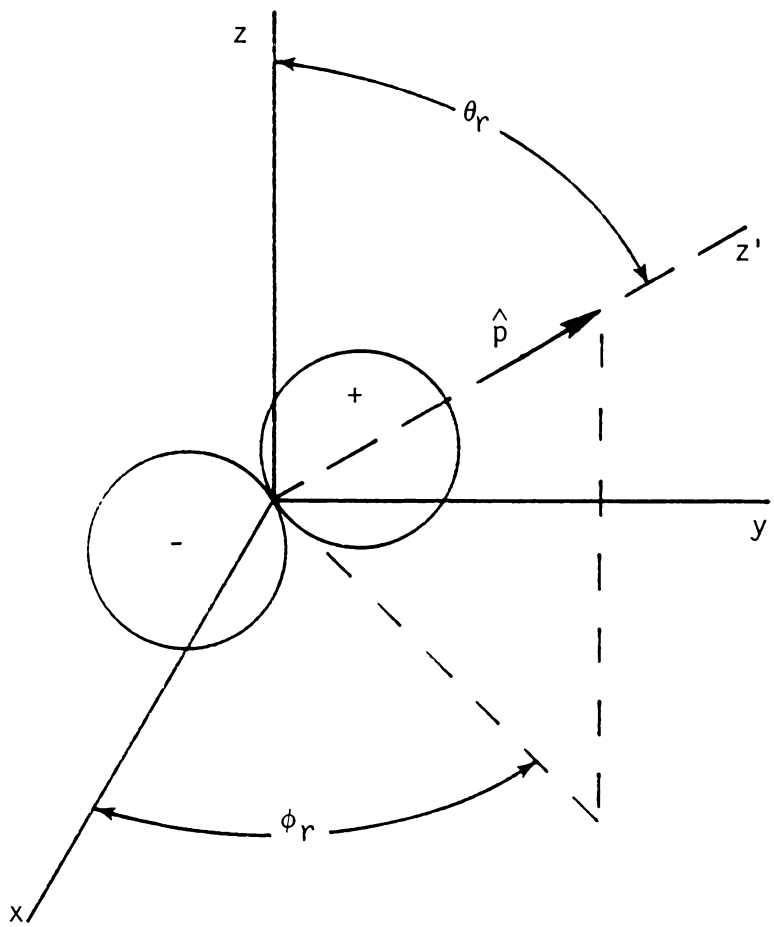


Figure B2. Three dimensional transformation of a p orbital

Finally, as was done in the two-dimensional case, expressing p_z' in terms of the unprimed coordinates with r'=r yields,

$$p_z' = \frac{c}{r} \left(x\cos\phi_r\sin\theta_r + y\sin\phi_r\sin\theta_r + z\cos\theta_r\right) \tag{B11}$$

or

$$p'_z = p_x \cos\phi_r\sin\theta_r + p_y\sin\phi_r\sin\theta_r + p_z\cos\theta_r \ . \tag{B12}$$

Consequently, any randomly oriented p orbital can be written as a linear combination of three mutually orthogonal p orbitals, as in Equation B12. Furthermore, the coefficients of this linear combination are seen to be identical to the spherical coordinate components of a unit vector (see Figure B2) oriented in the direction of the positive lobe of the p orbital:

$$\hat{p} = \hat{x} \cos\phi_r\sin\theta_r + \hat{y} \sin\phi_r\sin\theta_r + \hat{z} \cos\theta_r \ . \tag{B13}$$

INTERACTION BETWEEN TWO ATOMIC ORBITALS

Define the Slater and Koster symbols[2] ($ss\sigma$), ($sp\sigma$), ($ps\sigma$) and ($pp\pi$) as indicated in Figure B3. For certain orientations of s and p orbitals, the matrix element of the Hamiltonian is zero, as shown in Figure B4. Now specify the interaction between two atomic orbitals, oriented in arbitrary directions, in terms of these symbols. In other words, express the two arbitrary atomic orbitals as a linear combination of atomic orbitals, where the coefficients of each linear

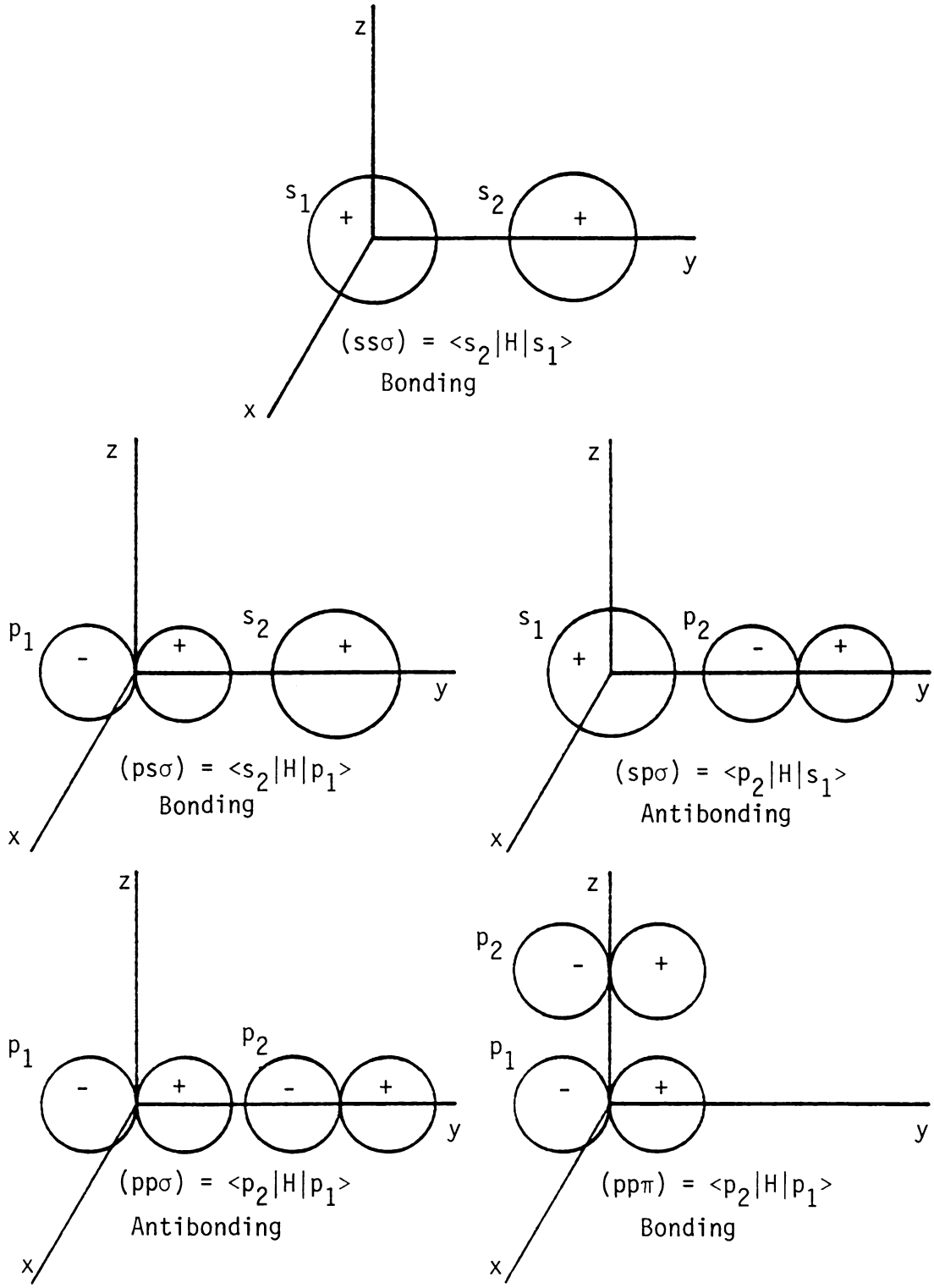


Figure B3. Slater and Koster's matrix element symbols

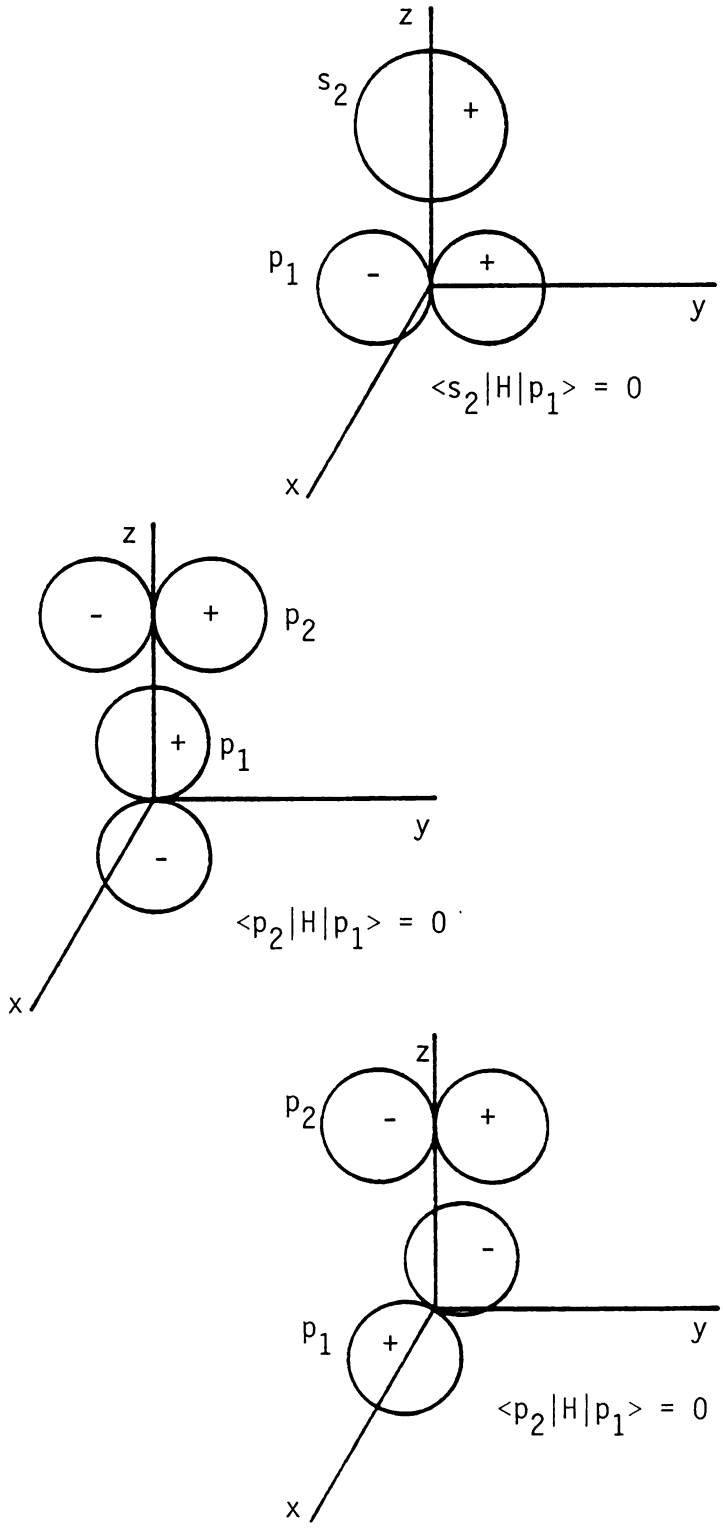


Figure B4. Transfer integrals between atomic orbitals which are zero

combination is determined by a rotation into a coordinate system with the orbitals oriented as in Figures B3 and B4.

Consider first a p orbital interacting with an s orbital, a shown in Figure B5a. By expressing the p orbital as a linear combination of p_x, p_y and p_z, as done in Equation B12,

$$\begin{aligned}\langle s_2|H|p_1\rangle = {} & \langle s_2|H|p_{1x}\rangle\cos\phi_r\sin\theta_r + \\ & \langle s_2|H|p_{1y}\rangle\sin\phi_r\sin\theta_r + \\ & \langle s_2|H|p_{1z}\rangle\cos\theta_r.\end{aligned} \tag{B14}$$

This is illustrated in Figures B5b, c, and d. Comparing Figures 3, 4 and 5 suggests that only the last term of Equation B14 is nonzero and consequently Equation B14 becomes

$$\langle s_2|H|p_1\rangle = (ps\sigma)\cos\theta_r\ . \tag{B15}$$

Next, consider the interaction of two randomly oriented p orbitals, shown in Figure B6a. As before, both p orbitals can be written as linear combinations of p_x, p_y and p_z in the same manner as Equation B12. Therefore,

$$\begin{aligned}\langle p_2|H|p_1\rangle = {} & \langle(p_{2x}\cos\phi_2\sin\theta_2 + p_{2y}\sin\phi_2\sin\theta_2 + p_{2z}\cos\theta_2)| \\ & H|(p_{1x}\cos\phi_1\sin\theta_1 + p_{1y}\sin\phi_1\sin\theta_1 + p_{1z}\cos\theta_1)\rangle.\end{aligned} \tag{B16}$$

Upon comparison of Figures 3, 4 and 6, it is evident that only three matrix elements are nonzero, as illustrated in Figures 6b, c and d.

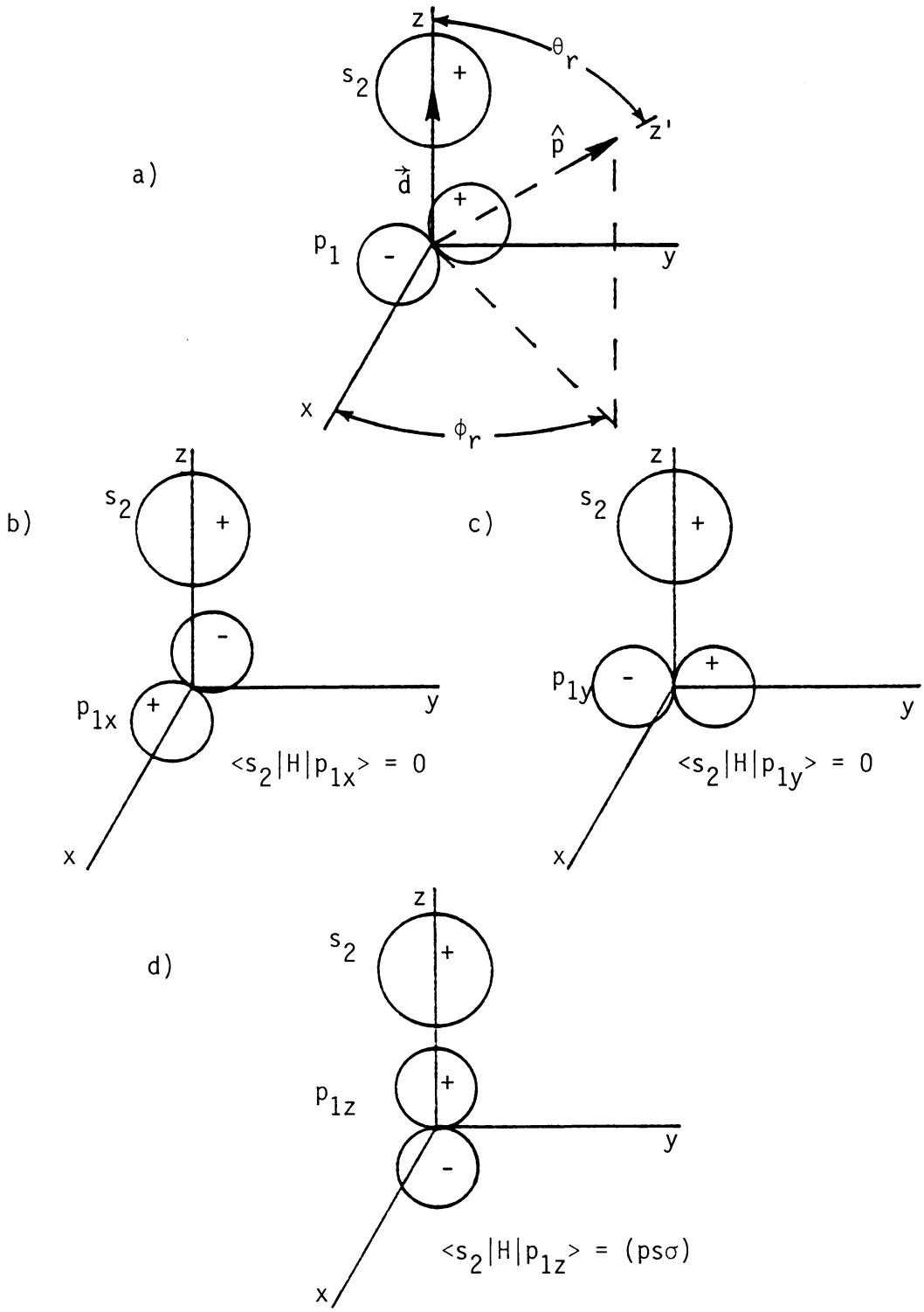


Figure B5. Interaction between an s orbital and a randomly oriented p orbital

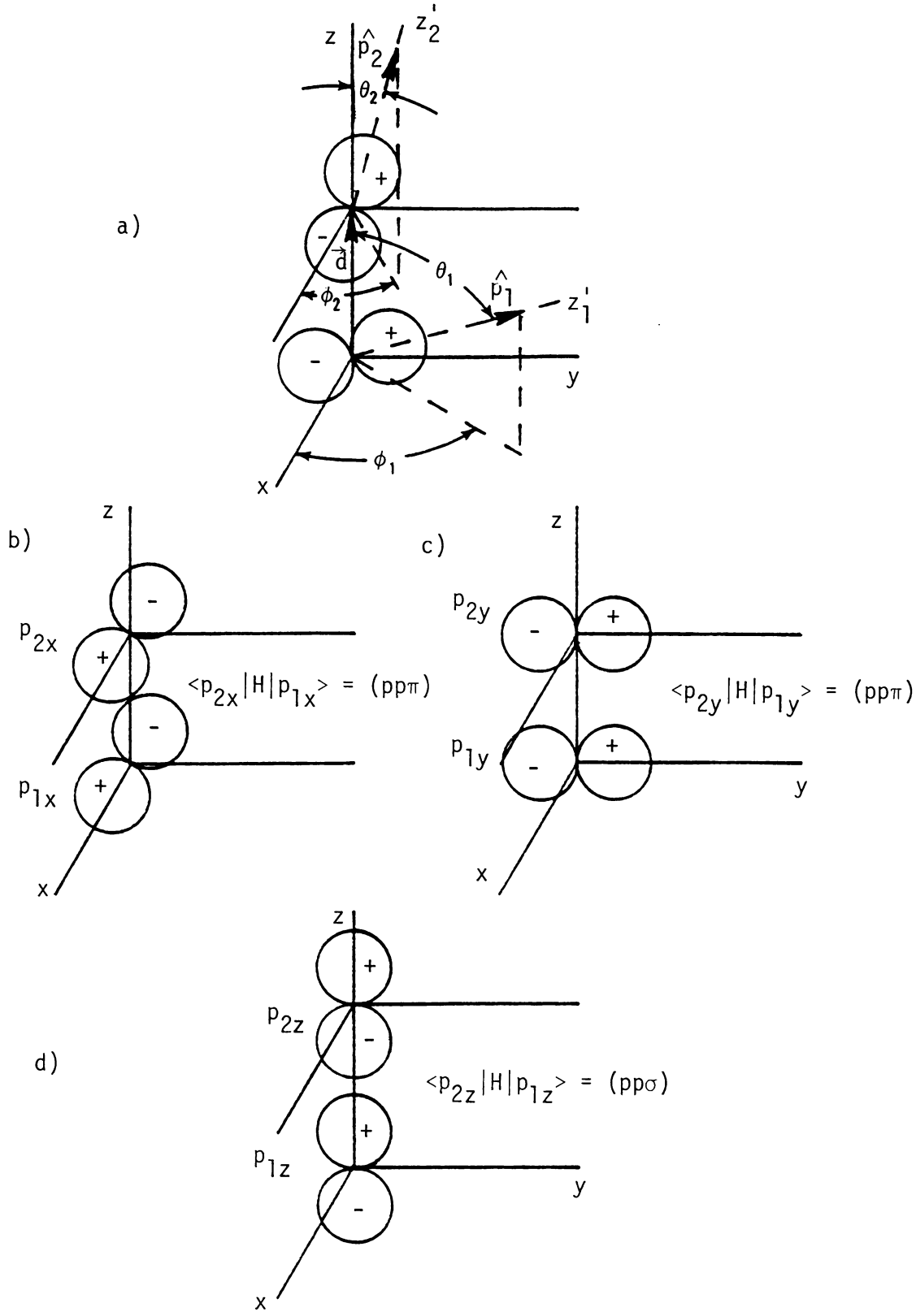


Figure B6. Interaction between two randomly oriented p orbitals

In terms of the Slater and Koster symbols, Equation B16 can be written

$$\begin{aligned} \langle p_2|H|p_1\rangle = \quad & (pp\pi)\cos\phi_2\sin\theta_2\cos\phi_1\sin\theta_1 + \\ & (pp\pi)\sin\phi_2\sin\theta_2\sin\phi_1\sin\theta_1 + \\ & (pp\sigma)\cos\theta_2\cos\theta_1 \quad . \end{aligned} \tag{B17}$$

Now introduce the "direction cosines" to put Equations B15 and B17 in the notation of Slater and Koster. Note that Slater and Koster required that the z_1 and z_2 axes of Figure B6a be parallel or perpendicular. The parallel case implies $\phi_1 = \phi_2$ and $\theta_1 = \theta_2$. Then the direction cosines can be defined as

$$\begin{aligned} l &= \cos\alpha = \cos\phi_1\sin\theta_1 \\ m &= \cos\beta = \sin\phi_1\sin\theta_1 \\ n &= \cos\gamma = \cos\theta_1 \quad . \end{aligned} \tag{B18}$$

Hence, Equation B15 becomes

$$\langle s_2|H|p_1\rangle = n(ps\sigma) \tag{B19}$$

and Equation B17 becomes (using $l^2 + m^2 + n^2 = 1$)

$$\langle p_2|H|p_1\rangle = n^2\,(pp\sigma) + (1-n^2)\,(pp\pi). \tag{B20}$$

Both Equations B19 and B20 appear in Table 1 of Slater and Koster.[2]

It is also possible to express the interaction between two atomic orbitals in vector notation.[7] Define $\hat{d}$ as the unit vector from orbital #1 to orbital #2. In addition, for a p orbital, define $\hat{p}$ as the unit vector in the direction of the positive lobe of the orbital. These vectors are indicated in Figures B5a and B6a. From Equations B15 and B17, it is evident that

$$\langle s_2|H|p_1\rangle = (\hat{p}_1 \cdot \hat{d})\ (ps\sigma) \tag{B21}$$

and

$$\begin{aligned}\langle p_2|H|p_1\rangle = {} & [\hat{p}_1 \cdot \hat{p}_2 - (\hat{p}_1 \cdot \hat{d})\ (\hat{p}_2 \cdot \hat{d})]\ (pp\pi) \\ & + (\hat{p}_1 \cdot \hat{d})\ (\hat{p}_2 \cdot \hat{d})\ (pp\sigma)\end{aligned} \tag{B22}$$

since $\hat{p}_1 \cdot \hat{d} = \cos\theta_1$, $\hat{p}_2 \cdot \hat{d} = \cos\theta_2$, and $\hat{p}_1 \cdot \hat{p}_2 = \cos\phi_1 \sin\theta_1 \cos\phi_2 \sin\theta_2 + \sin\phi_1 \sin\theta_1 \sin\phi_2 \sin\theta_2 + \cos\theta_1 \cos\theta_2$. Equations B21 and B22 are similar to those of Harrison's listed in Equations 16 and 17. The correlation between Harrison's parameters (Equations 18 through 21) and Slater and Koster's symbols (Figure B3) is given in Table B1.

To conclude this appendix, the Slater and Koster method permits the numerical evaluation of the matrix element of the Hamiltonian between two atomic orbitals with the specification of a set of well-defined parameters.

Table B1

Correlation of Harrison and Slater-Koster Notation

Harrison	Slater and Koster
V_{ss}	$+(ss\sigma)$
V_{sp}	$+(ps\sigma) = -(sp\sigma)$
$V_{pp\sigma}$	$-(pp\sigma)$
$V_{pp\pi}$	$+(pp\pi)$

APPENDIX C

ENERGY BAND COMPUTER PROGRAM

An overall flowchart for the energy band program is shown in Figure C1. The three software functions performed in this energy band computer program -- interactive input, calculation, and graphic output -- are handled by separate, stand-alone routines. The listings for these three programs, including non-library subroutines, are given in Figure C2. This division was made in an attempt to minimize the memory requirements of the calculation portion. The program is designed to run both on 16-bit minicomputers (e.g., DEC, DG, etc.) and the large number crunchers (e.g., IBM, CDC, etc.). The subroutines listed here which evaluate the matrix elements of the Hamiltonian between two atomic orbitals utilize Harrison's formulas (Equations 15-21) and Herman-Skillman's atomic term values. Replacing these subroutines with the subroutine in Appendix H yields the Chadi and Cohen calculations.

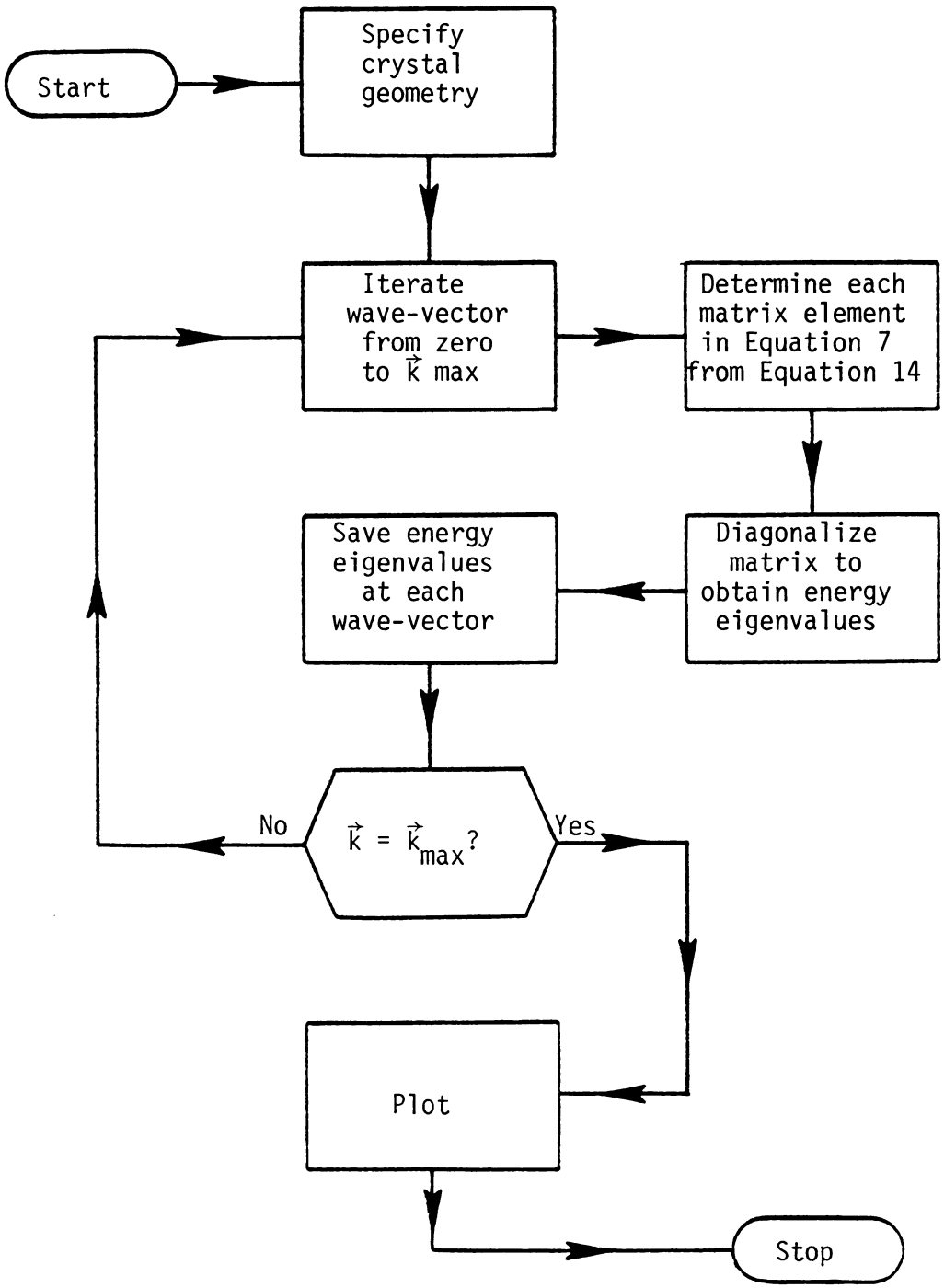


Figure C1. Flowchart for energy band program

```
:UDD:EWBANK:EBAND.DIR:EBINPUT.FR

C                                EBINPUT.FR
C.
C       ROUTINE TO ALLOW INPUTTING OF CONTROL PARAMETERS USED BY
C       PROGRAM 'EBAND.FR' FROM CONSOLE AND GENERATES THE
C       CONTROL PARAMETER FILE.
C.
C       INPUT PARAMETERS:
C               FROM CONSOLE
C       OUTPUT PARAMETERS:
C               I) CONTROL PARAMETER FILE --- CONTAINING:
C                       A) NAPUC --- # ATOMS PER 'UNIT CELL'
C                       B) NATMNUM --- ATOMIC NUMBER OF EACH ATOM IN
C                                      'UNIT CELL'.  (ORDERED ACCORDING
C                                      TO 'ENUMERATION' (SEE BELOW))
C                       C) WVKMAX --- 3D K-VECTOR (KX,KY,KZ) REPRESENTING
C                                     MAXIMUM K-VECTOR
C                       D) KPTS --- # PTS IN K-SPACE AT WHICH TO
C                                   CALCULATE THE ENERGY BANDS
C                       E) DMAX2 --- MAXIMUM 'NEAR NEIGHBOR' DISTANCE
C                                    SQUARED FOR ATOMS TO BE INCLUDED
C                                    IN BLOCH FCN
C                       F) IFILE --- FILENAME OF INPUT DATA FILE (BELOW)
C                     FORMAT --- BINARY
C       EXTERNAL REFERENCES:  NONE
C.
        PARAMETER IN=11,IOUT=10,NPAGE=27*400K+12
        PARAMETER  KKPTS=100            ;MAXIMUM # KPTS ALLOWED
        PARAMETER  MAXAPUC=10           ;MAXIMUM # ATOMS PER UNIT CELL
        DIMENSION NATMNUM(MAXAPUC),WVKMAX(3),KXYZ(3),IFILE(31)
        DATA KXYZ/'KX','KY','KZ'/
C.
C               ENTER # ATOMS PER 'UNIT CELL'
C.
        WRITE (IOUT) NPAGE
150     WRITE (IOUT,160)
160     FORMAT (/," ENTER # ATOMS PER UNIT CELL: ",Z)
        READ FREE (IN,ERR=150) NAPUC
        IF (NAPUC.LT.1 .OR. NAPUC.GT.MAXAPUC) GOTO 150
C.
C               ENTER ATOMIC NUMBERS ASSOCIATED WITH EACH ATOM IN
C               UNIT CELL.  (ORDER MUST REFLECT 'ENUMERATION' OF
C               DATA FILE TO BE INPUT)
C.
        WRITE (IOUT,210)
210     FORMAT (/," ENTER ATOMIC NUMBER OF EACH ATOM IN UNIT CELL",
     &    /,"   (ORDER MUST CORRESPOND TO ",1H',"ENUMERATION",2H'))
        DO 220 I=1,NAPUC
230     WRITE (IOUT,240) I
240     FORMAT (8X,"ATOM #",I2,4X,Z)
        READ FREE (IN,ERR=230) NATMNUM(I)
220     IF (NATMNUM(I).LT.1 .OR. NATMNUM(I).GT.89) GOTO 230
```

Figure C2. Computer listings for energy band program

```
:UDD:EWBANK:EBAND.DIR:EBINPUT.FR

C.
C                ENTER 3D K-VECTOR
C.
250      WRITE.(IOUT,260)
260      FORMAT (/," ENTER MAXIMUM K-VECTOR : ")
         DO 270 I=1,3
280      WRITE (IOUT,290) KXYZ(I)
290      FORMAT (8X,A2," = ",Z)
         READ FREE (IN,ERR=280) WVKMAX(I)
270      IF (WVKMAX(I).LT.0.0 .OR. WVKMAX(I).GT.10.0) GOTO 280
C.
C                ENTER # KPTS
C.
50       WRITE.(IOUT,60)
60       FORMAT (/," ENTER # PTS IN K-SPACE AT WHICH TO CALC E-BANDS: ",Z)
         READ FREE (IN,ERR=50) KPTS
         IF (KPTS.LT.2 .OR. KPTS.GT.KKPTS) GOTO 50
C.
C                ENTER 'NEAR NEIGHBOR' MAXIMUM DISTANCE FOR INCLUSION
C                IN BLOCH FUNCTION SUM
C.
100      WRITE.(IOUT,110)
110      FORMAT(/," ENTER ",1H',"NEAR NEIGHBOR",1H',"  MAXIMUM DISTANCE ",
     &     /," (ANGSTROMS) FOR INCLUSION IN BLOCH FCN:  ",Z)
         READ FREE (IN,ERR=100) DMAX
         IF (DMAX.LT.0.9 .OR. DMAX.GT.40.0) GOTO 100
         DMAX2=DMAX*DMAX                  ;DISTANCE SQUARED
C.
C                ENTER FILENAME OF INPUT DATA FILE
C.
350      WRITE.(IOUT,360)
360      FORMAT(/," ENTER FILENAME OF FILE CONTAINING ATOM POSITIONS: ",Z)
         READ (IN,370,ERR=350) IFILE(1)
370      FORMAT (S60)
         OPEN 6,IFILE,ERR=350
         CLOSE.6
C.
C                WRITE INPUT CONTROL PARAMETERS TO FILE.
C                (TO SAVE CORE, READ IN CONTROL PARAMETERS FROM
C                CONSOLE IN THIS STAND-ALONE PROGRAM, THEREBY AVOIDING
C                ASSOCIATED FORMAT STATEMENTS IN EBAND.FR)
C.
         OPEN 6,"?EB←INPUT"
         WRITE BINARY (6) KPTS,DMAX2,NAPUC,(NATMNUM(I),I=1,NAPUC),
     &     (WVKMAX(I),I=1,3),(IFILE(I),I=1,31)
         CLOSE.6
C.
C                NOW CHAIN TO EBAND --- CALCULATE BANDS
C.
         CALL FCHAN("EBAND.PR")
         END
```

Figure C2. (Continued)

```
:UDD:EWBANK:EBAND.DIR:EBAND.FR

C                        EBAND.FR
C.
C       PROGRAM DOES THE FOLLOWING:
C               I) GENERATES A SLATER-KOSTER MATRIX CONTAINING ELEMENTS
C                  BETWEEN BLOCH FUNCTIONS & ATOMIC ORBITALS
C               II) DIAGONALIZES EACH MATRIX TO OBTAIN THE ENERGY
C                   EIGENVALUES AT A GIVEN WAVEVECTOR, (KX,KY,KZ)
C               III) PLOTS THE ENERGIES VS WAVEVECTOR TO CONSTRUCT THE
C                    THE ENERGY BANDS.
C.
C       INPUT PARAMETERS:
C               I) CONTROL PARAMETER FILE --- CONTAINING:
C                       A) NAPUC --- # ATOMS PER 'UNIT CELL'
C                       B) NATMNUM --- ATOMIC NUMBER OF EACH ATOM IN
C                                      'UNIT CELL'.  (ORDERED ACCORDING
C                                      TO 'ENUMERATION' (SEE BELOW))
C                       C) WVKMAX --- 3D K-VECTOR (KX,KY,KZ) REPRESENTING
C                                     MAXIMUM K-VECTOR
C                       D) KPTS --- # PTS IN K-SPACE AT WHICH TO
C                                   CALCULATE THE ENERGY BANDS
C                       E) DMAX2 --- MAXIMUM 'NEAR NEIGHBOR' DISTANCE
C                                    SQUARED FOR ATOMS TO BE INCLUDED
C                                    IN BLOCH FCN
C                       F) IFILE --- FILENAME OF INPUT DATA FILE (BELOW)
C                     FORMAT --- BINARY
C               II) DATA FILE ('IFILE') --- EACH RECORD OF FILE CONTAINS:
C                         A) ATOMIC NUMBER
C                         B) ATOM ENUMERATION IN 'UNIT CELL'
C                              'ENUMERATION' IMPLIES THAT EACH
C                              ATOM IN 'UNIT CELL' IS ASSIGN A
C                              UNIQUE NUMBER, 1 TO NAPUC (WHERE NAPUC
C                              IS THE # ATOMS PER 'UNIT CELL')
C                         C) ATOM POSITION (X,Y,Z) IN RECTANGULAR
C                            COORDINATES
C                  FORMATTED AS FOLLOWS:  (12X,I2,3X,I2,3(3X,E14.7))
C.
C       OUTPUT PARAMETERS:
C               I) DATA FILE --- "?EB←DATA" --- CONTAINING CALCULATED
C                       EIGENVALUES, ETC BEING PASSED TO PLOTTING PROGRAM
C.
C       EXTERNAL REFERENCES:
C               I) INPUT CONTROL PARAMETER FILE --- "?EB←INPUT"
C                       GENERATED BY STAND-ALONE PROGRAM "EBINPUT.FR"
C               II) INPUT DATA FILE --- ATOM POSITIONS & TYPES
C                       A)SUBROUTINE ATOMIN
C                               1) COMMON/ATMPOS/....
C               III) GENERATE MATRIX ELEMENTS
C                       A) SUBROUTINE BLOCH
C                               1) SUBROUTINE SSIAME
C                                       A) SUBR SSIME
C                                               1) FCN ATTMV
```

Figure C2. (Continued)

```
:UDD:EWBANK:EBAND.DIR:EBAND.FR

C                                                   2) SUBR UVECT
C                                                   3) FCN DOTPD
C                                   2) COMMON/ATMPOS/....
C                 IV) DIAGONALIZE
C                         A) SUBROUTINE EIGCH  (IMSL LIBRARY)
C.                                  1) EHBKH
C.                                  2) EHOUHS..
C.                                  3) EQRT2S.
C.                                  4) UERTST
C                 V) PLOT ENERGY BANDS --- STAND-ALONE PROGRAM --- EBPLOT
C                         A) SUBROUTINE GRIDR
C                         B) SUBROUTINE CURVE
C                         C) SUBROUTINE TPOT
C                         D) SUBOUTINE QPLOT
C                         E) PLOT10 LIBRARY (TEKTRONIX)
C                         F) AGII LIBRARY (TEKTRONIX)
C..
C..
        PARAMETER  MAXAPUC=10            ;MAXIMUM # ATOMS PER UNIT CELLS
        PARAMETER  NOPA=4                         ;# ORBITALS PER ATOM
        PARAMETER  NDIM=NOPA*MAXAPUC              ;MAXIMUM # BANDS
        PARAMETER  NNDIM=NDIM*(NDIM+1)/2, NNNDIM=3*NDIM
C..
        DOUBLE PRECISION COMPLEX  HA(NNDIM), VALUE
        DOUBLE PRECISION  WORKSP(NNNDIM), E(NDIM)
        DIMENSION  EE(NDIM),WVK(3),WVKMAX(3),IFILE(31),NATMNUM(MAXAPUC)
        EQUIVALENCE (EE(1),E(1))
C..
C               READ INPUT CONTROL PARAMETER FILE.
C               (TO SAVE CORE, READ IN CONTROL PARAMETERS FROM
C               CONSOLE IN STAND-ALONE PROGRAM,THEREBY AVOIDING
C               ASSOCIATED FORMAT STATEMENTS HERE)
C..
        OPEN 6,"?EB←INPUT"
        READ BINARY (6) KPTS,DMAX2,NAPUC,(NATMNUM(I),I=1,NAPUC),
     &    (WVKMAX(I),I=1,3),(IFILE(I),I=1,31)
        CLOSE 6
C..
C               READ ATOMIC POSITIONS FROM DATA FILE
C..
        CALL ATOMIN(IFILE,DMAX2,NAPUC,NATMNUM)
C..
C               TO SAVE CORE, DO PLOTTING IN SEPARATE STAND-ALONE
C               PROGRAM.  THEREFORE, NEED TO WRITE EIGENVALUES TO A
C..             DISK FILE,
C..
        CALL FDELETE ("?EB←DATA")
        OPEN 6, "?EB←DATA"
        NBANDS = NAPUC * NOPA
        WRITE BINARY (6) NBANDS,KPTS,(WVKMAX(I),I=1,3)
C..
```

Figure C2. (Continued)

```
:UDD:EWBANK:EBAND.DIR:EBAND.FR

C               ITERATE WAVENUMBER
C..
        DO 300 KINCR=1,KPTS
C                       VARY K-VECTOR FROM (0,0,0) TO (KXMAX,KYMAX,KZMAX)
                DO 350 I=1,3
350             WVK(I)=WVKMAX(I)*(KINCR-1)/(KPTS-1)
X       WRITE (12,370) (WVK(I),I=1,3)
X370    FORMAT(/,10X,'(KX,KY,KZ)=(',2(F5.3,1H,),F5.3,1H))
C..
C               FIND EACH MATRIX ELEMENT A(I,J) --- ON & BELOW DIAGONAL
C..
        DO 400 IALPHA=1,NAPUC                   ;WHICH ATOM (COL)
        DO 400 IMU=1,NOPA                       ;WHICH ORBITAL (COL)
        DO 400 JBETA=IALPHA,NAPUC               ;WHICH ATOM (ROW)
                JNUMIN=1
                IF (JBETA.EQ.IALPHA) JNUMIN=IMU
        DO 400 JNU=JNUMIN,NOPA                  ;WHICH ORBITAL (ROW)
                IATOM=NATMNUM(IALPHA)           ;ASSIGN ATOMIC NUMBER
                JATOM=NATMNUM(JBETA)            ;ASSIGN ATOMIC NUMBER
        CALL BLOCH (IALPHA,IMU,IATOM,JBETA,JNU,JATOM,WVK,VALUE)
                I=(IALPHA-1)*NOPA+IMU           ;I & J TAKE ON VALUES
                J=(JBETA-1)*NOPA+JNU            ;FROM 1-NBANDS (I.LE.J)
C               A(I,J)=VALUE
C                       CONVERT 2-D ARRAY INTO 1-D ARRAY USED BY EIGCH
C                       (REFERENCE PAGE INTRO-10 OF IMSL MANUAL)
                L=(J*(J-1)/2) + I
C               HA(L)=A(I,J)
X       WRITE (12,390) I,J,L,VALUE
X390    FORMAT(3H A(,I2,1H,,I2,5H)=HA(,I2,2H)=,2(D14.7,4X))
400     HA(L)=VALUE
C..
C               NOW DIAGONALIZE
C..
        CALL EIGCH (HA,NBANDS,0,E,DUMMY,DUMMY,WORKSP,IER)
C..
C               CONVERT DOUBLE PRECISION REAL TO SINGLE PRECISION REAL
C..
        DO 500 I=1,NBANDS
X       WRITE (12,450) I,E(I)
X450    FORMAT(5X,2HE(,I2,2H)=,D14.7)
500     EE(I)=E(I)
C..
C               WRITE EIGEN VALUES TO DISK FILE
C..
300     WRITE BINARY (6) (EE(I),I=1,NBANDS)
        CLOSE 6
C..
C               NOW PLOT
C..
        CALL FCHAN("EBPLOT.PR")         ;TO SAVE CORE,CHAIN
        END
```

Figure C2. (Continued)

```
:UDD:EWBANK:EBAND.DIR:EBPLOT.FR

C.                                EBPLOT.FR
C.
C       ROUTINE TO MAKE THE GRAPHICS CALLS FOR EBAND.FR
C       IE, PLOT ENERGY BANDS VS WAVENUMBER (K-VECTOR)
C.
C       INPUT PARAMETERS:
C               DATA FILE --- CONTAINING THE FOLLOWING:
C                       1) RECORD 1 --- #BANDS,#PTS/BAND,MAX K-VECTOR(3D)
C                       2) RECORDS 2 THRU N --- EIGENVALUES FOR EACH BAND
C                                               AT PARTICULAR K-VECTOR.
C                                               (N = # PTS/BAND + 1)
C                                 FORMAT --- BINARY
C       OUTPUT PARAMETERS:
C.              PLOTFILE."?EB←PLOT"
C       EXTERNAL REFERENCES:
C               FCN DOTPD
C               SUBR GRIDR
C               SUBR CURVE
C.              SUBR TPOT
C.              SUBR QPLOT.
C               AGII LIBRARY
C               PLOT10 LIBRARY
C.
        PARAMETER IOUT=10, NPAGE=27*400K+12
        PARAMETER NDIM=50,KKPTS=100
        DIMENSION WVK(KKPTS),WVKMAX(3),WVKXYZ(3),EE(KKPTS,NDIM)
C.
C.
C               READ IN DATA FOR BANDS FROM FILE
C.
        OPEN 6, "?EB←DATA"
        READ BINARY (6) NBANDS,KPTS,(WVKMAX(I),I=1,3)
C.
C               GENERATE WAVENUMBERS AND INPUT ENERGY EIGENVALUES
C.
        DO 300 KINCR=1,KPTS
        READ BINARY (6) (EE(KINCR,J),J=1,NBANDS)
C                       VARY K FROM (0,0,0) TO (KXMAX,KYMAX,KZMAX)
                DO 350 I=1,3
350             WVKXYZ(I)=WVKMAX(I)*(KINCR-1)/(KPTS-1)
C                       NOW FIND MAGNITUDE OF WAVEVECTOR K
        WVK(KINCR)=SQRT(DOTPD(WVKXYZ,WVKXYZ,3))
300     CONTINUE
        CLOSE 6
C.
C               CONSTRUCT GRID
C.
        CALL AMNMX (KPTS,WVK,XMIN,IDUMMY,XMAX,IDUMMY)
        YMIN=+1E12
        YMAX=-1E12
        DO 400 J=1,NBANDS
```

Figure C2. (Continued)

```
:UDD:EWBANK:EBAND.DIR:EBPLOT.FR

      CALL AMNMX (KPTS,EE(1,J),EMIN,IDUMMY,EMAX,IDUMMY)
      IF (EMIN.LT.YMIN) YMIN=EMIN
400   IF (EMAX.GT.YMAX) YMAX=EMAX
      CALL GRIDR ($999,XMIN,XMAX,YMIN,YMAX,"?EB←PLOT",37,
     &  "ENERGY BANDS --- ENERGY VS WAVEVECTOR",20,
     &  "ABS[K] (1/ANGSTROMS)",11,"ENERGY -EV-",
     &  XMN,XMX,YMN,YMX,0)
      OPEN 7,"?EB←PLOT",ATT="AO"
      WRITE (7        ,450) (WVKMAX(I),I=1,3)
450   FORMAT(33(/),9X,'K-VECTOR VARIES FROM  ( .00, .00, .00)  TO  (',
     &  2(F4.2,','),F4.2,')')
      CLOSE 7
C.
C             NOW PLOT BANDS
C.
      DO 500 J=1,NBANDS
500   CALL CURVE ($999,KPTS,WVK,EE(1,J),"?EB←PLOT",XMN,XMX,
     &  YMN,YMX,0,0,0,0)
C.
      WRITE BINARY (IOUT) NPAGE                ;CLEAR CONSOLE SCREEN
      CALL TPOT (6,"?EB←PLOT",IOUT)            ;COPY TO CONSOLE
      CALL QPLOT ("?EB←PLOT",IER)              ;COPY TO VERSATEC
      IF (IER.NE.1) GOTO 999
C.
      STOP..
C.
C.
999   WRITE (10,998)
998   FORMAT (" PLOTTING ERROR")
      STOP..
C.
      END
```

Figure C2. (Continued)

```
:UDD:EWBANK:EBAND.DIR:ATOMIN.FR

      SUBROUTINE ATOMIN(FILENAME,DMAX2,NAUC,NATMNUM)
C..
C     ROUTINE TO INPUT ATOM POSITIONS, ATOMIC NUMBER, AND
C     ENUMERATION OF ATOMS IN UNIT CELL FOR BLOCH FCN SUM.  ALSO,
C     ASSIGN 'NEAR NEIGHBOR' ATOMS TO EACH ATOM IN 'UNIT CELL'.
C..
C     INPUT PARAMETERS:
C             1) FILENAME --- DATA FILE CONTAINING ATOM POSITIONS,ETC
C                      EACH RECORD OF FILE CONTAINS:
C                        A) ATOMIC NUMBER
C                        B) ATOM ENUMERATION IN 'UNIT CELL'
C                        C) ATOM POSITION (X,Y,Z) IN RECTANGULAR
C                           COORDINATES
C                        FORMATTED AS --- (12X,I2,3X,I2,3(3X,E14.7))
C                    NATOM --- ATOMIC NUMBER OF EACH ATOM
C                    NENUM --- ENUMERATION OF EACH ATOM IN
C                              'UNIT CELL' FOR BLOCH FCN SUM.
C                              IE, ASSIGN EACH ATOM IN 'UNIT CELL'
C                              A UNIQUE NUMBER, 1 THRU N, WHERE
C                              THERE ARE N ATOMS IN 'UNIT CELL'
C                    R --- 3-D ARRAY FOR ATOM POSITION (X,Y,Z)
C                    ASSUMPTIONS MADE ABOUT INPUT DATA FILE:
C                     1) NEED TO INCLUDE AT LEAST AS MANY UNIT
C                        CELLS AS BLOCH SUM 'NEAR NEIGHBOR'
C                        DISTANCE NECESSITATES
C                     2) ALL ATOMS IN THE UNIT CELL AT THE 'ORIGIN'
C                        MUST BE LISTED FIRST.
C             2) DMAX2 --- DISTANCE SQUARED WITHIN WHICH 'NEAR
C                          NEIGHBORS' WILL BE INCLUDED IN BLOCH FCN
C             3) NAUC --- NUMBER OF ATOMS PER 'UNIT CELL'
C             4) NATMNUM --- ARRAY OF ATOMIC NUMBERS CORRESPONDING TO
C                          EACH ATOM IN 'UNIT CELL'
C                            (ORDER GIVEN BY ENUMERATION)
C     OUTPUT PARAMETERS:
C             COMMON/ATMPOS/AR(..),JENUM(..),NMAX(..)
C               AR(IXYZ,J,K) --- GIVES ATOMIC COORDINATES (IXYZ=1,2,3)
C                    OF JTH ATOM IN 'UNIT CELL' (ENUMERATION=J & K=1)
C                    ALONG WITH POSITIONS OF ALL ITS 'NEAR NEIGHBORS'
C                    (K=2,...,NMAX(J))
C               JENUM(J,K) --- GIVES ENUMERATION ASSOCIATED WITH
C                          EACH ATOM ABOVE
C               NMAX(J) --- NUMBER OF 'NEAR NEIGHBORS' + 1 AROUND THE
C                          JTH ATOM IN THE 'UNIT CELL'
C     EXTERNAL REFERENCES:
C             FUNCTION DOTPD
C..
      DIMENSION FILENAME(1),R(3),D(3),NATMNUM(1)
      PARAMETER IOUT=10
      PARAMETER  MAXAUC=10            ;MAXIMUM # ATOMS/UNIT CELL
      PARAMETER  NNMAX=40             ;MAXIMUM # NEAR NEIGHBORS
      COMMON/ATMPOS/AR(3,MAXAUC,NNMAX),JENUM(MAXAUC,NNMAX),NMAX(MAXAUC)
```

Figure C2. (Continued)

```
:UDD:EWS[illegible]:EDAND.DIR:ATOMIN.FR

C..
        DO 1 I=1,NAUC
1       NMAX(I)=0
C..
        OPEN 6, FILENAME,ATT="I",ERR=900
        DO 5 IENUM=1,NAUC
        NFLAG=1
10      READ (6,20,END=30) NATOM,NENUM,(R(I),I=1,3)
20      FORMAT (12X,I2,3X,I2,3(3X,E14.7))
        GOTO (40,50) NFLAG
40      IF (IENUM.NE.NENUM) GOTO 10
        REWIND 6
        NFLAG=2
        GOTO 60
C..
50      DO 55 I=1,3
55      D(I)=R(I)-AR(I,IENUM,1)
        D2=DOTPD(D,D,3)
        IF (D2.GT.DMAX2 .OR. D2.LT.0.01) GOTO 10
60      IF (NATOM.NE.NATMNUM(NENUM)) GOTO 920
        NMAX(IENUM)=NMAX(IENUM)+1
        DO 65 I=1,3
65      AR(I,IENUM,NMAX(IENUM))=R(I)
        JENUM(IENUM,NMAX(IENUM))=NENUM
        GOTO 10
30      IF (NMAX(IENUM).EQ.0) GOTO 940
        IF (NMAX(IENUM).GT.NNMAX) GOTO 960
        REWIND 6
5       CONTINUE
        CLOSE 6
C..
        RETURN
C..
C.              ERRORS
C..
900     WRITE (IOUT,910)
910     FORMAT (" ERROR ON GEOMETRY FILE OPEN",Z)
        GOTO 999
920     WRITE (IOUT,930)
930     FORMAT (" ERROR ON ATOMIC NUMBER",Z)
        GOTO 999
940     WRITE (IOUT,950)
950     FORMAT (" ERROR ON ENUMERATION",Z)
        GOTO 999
960     WRITE (IOUT,970)
970     FORMAT (" ERROR --- TOO MANY NEAR NEIGHBORS",Z)
999     WRITE (IOUT,1000)
1000    FORMAT (" --- SUBR ATOMIN")
        STOP...
        END
```

Figure C2. (Continued)

```
:UDD:EWBANK:EBAND.DIR:BLOCH.FR

      SUBROUTINE BLOCH (IALPHA,IMU,IATOM,JBETA,JNU,JATOM,WVK,VALUE)
C..
C     ROUTINE TO EVALUATE A MATRIX ELEMENT OF THE HAMILTONIAN
C     BETWEEN 2 BLOCH FUNCTIONS OR (WITH NORMALIZATION) BETWEEN
C     A BLOCH FUNCTION ORBITAL (LCAO) AND A SINGLE ATOMIC
C     ORBITAL --- IE,  EVALUATE
C          <BLOCH FCN (STATES 2) [H] BLOCH FCN (STATES 1)>
C        N*<BLOCH FCN (STATES 2) [H] ATOMIC ORB (STATE 1)>
C       N*<BLOCH FCN (JBETA,JNU) [H] ATOMIC ORB (IALPHA,IMU)>
C..
C     INPUT PARAMETERS:
C             IALPHA --- ENUMERATION FOR ATOM # 1  --- IE, WHICH
C                        ATOM IN 'UNIT CELL' TO USE FOR STATE 1
C             IMU --- ENUMERATION FOR ATOMIC ORBITAL # 1 --- IE,
C                     WHICH ATOMIC ORBITAL ON ATOM # 1 TO USE AS
C                     STATE 1     (S,PX,PY,PZ) --> (1,2,3,4)
C                  NOTE:  IALPHA & IMU TOGETHER SPECIFY WHICH ATOMIC
C                         ORBITAL IN 'UNIT CELL' IS STATE 1
C             IATOM --- ATOMIC NUMBER FOR ATOM # 1
C             JBETA --- ENUMERATION FOR ATOM # 2  --- IE, WHICH
C                        ATOM IN 'UNIT CELL' TO USE FOR STATE 2
C             JNU --- ENUMERATION FOR ATOMIC ORBITAL # 2 --- IE,
C                     WHICH ATOMIC ORBITAL ON ATOM # 2 TO USE AS
C                     STATE 2     (S,PX,PY,PZ) --> (1,2,3,4)
C                  NOTE:  JBETA & JNU TOGETHER SPECIFY WHICH ATOMIC
C                         ORBITAL IN 'UNIT CELL' IS STATE 2
C             JATOM --- ATOMIC NUMBER FOR ATOM # 2
C             WVK --- WAVEVECTOR AT WHICH TO EVALUATE THE BLOCH FCN
C                     (3-D ARRAY)
C     OUTPUT PARAMETERS:
C             VALUE --- EVALUATED BLOCH FUNCTION MATRIX ELEMENTS
C     EXTERNAL REFERENCES:
C             I) SUBROUTINE SSIAME
C                     A) SUBR SSIME
C                             1) SUBR ATTMV
C                             2) SUBR UVECT
C                             3) FCN DOTPD
C             II) FUNCTION DOTPD
C             III) COMMON/ATMPOS/....
C..
      PARAMETER  MAXAUC=10            ;MAXIMUM # ATOMS/UNIT CELL
      PARAMETER  NNMAX=40             ;MAXIMUM # NEAR NEIGHBORS
      COMMON/ATMPOS/AR(3,MAXAUC,NNMAX),JENUN(MAXAUC,NNMAX),NMAX(MAXAUC)
      DIMENSION DD(3),WVK(3)
      COMPLEX CEXP,BLHEXP
      DOUBLE PRECISION COMPLEX   VALUE
C..
      VALUE = (0.0,0.0)
C..
C             SUM OVER 'NEAR NEIGHBOR' ATOMS
C..
```

Figure C2. (Continued)

```
:UDD:EWBANK:EBAND.DIR:BLOCH.FR

      DO 10 J=1,NMAX(IALPHA)
C..
C             INCLUDE ONLY ATOMS WITH CORRECT ENUMERATION
C..
      IF (JENUM(IALPHA,J).NE.JBETA) GOTO 10
C..
C             FIND 'SOLID STATE MATRIX ELEMENT' OR 'ATOMIC TERM VALUE'
C..
      CALL SSIAME(AR(1,IALPHA,1),AR(1,IALPHA,J),IMU,JNU,IATOM,JATOM,SSME)
C..
C             VECTOR DISTANCE BETWEEN ATOMS
C..
      DO 20 I=1,3
20    DD(I)=AR(I,IALPHA,J)-AR(I,IALPHA,1)
C..
C             CALCULATE ARGUMENT OF EXPONENTIAL IN BLOCH FCN
C..
      BLHEXP = (0.0,1.0) * DOTPD(WVK,DD,3)          ;DOT PRODUCT
C..
C             DETERMINE ONE TERM OF BLOCH FCN & ACCUMULATE TERMS
C..
      VALUE = VALUE + SSME*CEXP(BLHEXP)             ;COMPLEX EXPONENT
10    CONTINUE
C..
      RETURN
      END
```

Figure C2. (Continued)

```
:UDD:EWBANK:UTILITY.DIR:SSIAME.FR

      SUBROUTINE SSIAME(R1,R2,NOR1,NOR2,NATOM1,NATOM2,SSME)
C.
C     ROUTINE TO EVALUATE A 'SOLID STATE INTERATOMIC MATRIX ELEMENT' OF
C     THE HAMILTONIAN BETWEEN TWO ATOMIC ORBITALS OF 'STANDARD'
C     ORIENTATION---IE, S,PX,PY, OR PZ.
C     IF ATOMIC ORBITALS ARE ON DIFFERENT ATOMS, USE THE
C     SLATER-KOSTER 2-CENTER INTEGRAL APPROXIMATION ALONG WITH
C     HARRISON'S PARAMETERS.
C     IF ATOMIC ORBITALS ARE ON SAME ATOM, THEN MATRIX ELEMENT IS:
C             1) ZERO FOR DIFFERENT (ORTHOGONAL) ORBITALS
C             2) HERMAN-SKILLMAN ATOMIC TERM VALUE FOR SAME ORBITAL
C.
C     INPUT PARAMETERS:
C             R1--VECTOR POSITION IN RECTANGULAR COORDINATES OF
C                     ATOM #1 (ANGSTROMS)  (3 ELEMENT ARRAY)
C             R2--VECTOR POSITION IN RECTANGULAR COORDINATES OF
C                     ATOM #2 (ANGSTROMS)  (3 ELEMENT ARRAY)
C             NOR1---SPECIFIES ATOMIC ORBITAL #1
C                     =1 IMPLIES S ORBITAL
C                     =2 IMPLIES PX ORBITAL
C                     =3 IMPLIES PY ORBITAL
C                     =4 IMPLIES PZ ORBITAL
C             NOR2---SPECIFIES ATOMIC ORBITAL #2
C                     =1 IMPLIES S ORBITAL
C                     =2 IMPLIES PX ORBITAL
C                     =3 IMPLIES PY ORBITAL
C                     =4 IMPLIES PZ ORBITAL
C             NATOM1---ATOMIC NUMBER OF ATOM # 1
C             NATOM2---ATOMIC NUMBER OF ATOM # 2
C.
C     OUTPUT PARAMETERS:
C             SSME--EVALUATED SOLID STATE MATRIX ELEMENT
C.
C     EXTERNAL REFERENCES:
C             SUBROUTINE SSIME
C.
C.
      DIMENSION R1(3),R2(3),OR1(4),OR2(4)
C.
C             CHECK INPUTTED ORBITALS
      IF (NOR1.LT.1 .OR. NOR1.GT.4) GOTO 20
      IF (NOR2.LT.1 .OR. NOR2.GT.4) GOTO 20
C.
C             GENERATE 4-D ORBITAL VECTORS REQUIRED BY SSIME
      DO 10 I=1,4
      OR1(I)=0.0
 10   OR2(I)=0.0
C.
      OR1(NOR1)=1.0
      OR2(NOR2)=1.0
C.
```

Figure C2. (Continued)

```
:UDD:EWBANK:UTILITY.DIR:SSIAME.FR

C                EVALUATE SOLID STATE MATRIX ELEMENT
        CALL SSIME (R1,R2,OR1,OR2,NATOM1,NATOM2,SSME)
C.
        RETURN
C.
C.
C.               ERROR
20      WRITE (10,30) NOR1,NOR2
30      FORMAT (" ERROR---ILLEGAL ORBITAL SPECIFICATION---",
     &     "SUBROUTINE SSIAME",/,10X,"NOR1=",I3,5X,"NOR2=",I3)
        PAUSE
        STOP..
        END
```

Figure C2. (Continued)

```
:UDD:EWBANK:UTILITY.DIR:SSIME.FR

      SUBROUTINE SSIME(R1,R2,OR1,OR2,NATOM1,NATOM2,SSME)
C.
C     ROUTINE TO EVALUATE A 'SOLID STATE INTERATOMIC MATRIX ELEMENT' OF
C     THE HAMILTONIAN BETWEEN TWO ATOMIC ORBITALS OF ANY ORIENTATION.
C     IF ATOMIC ORBITALS ARE ON DIFFERENT ATOMS, USE THE
C     SLATER-KOSTER 2-CENTER INTEGRAL APPROXIMATION ALONG WITH
C     HARRISON'S PARAMETERS.
C     IF ATOMIC ORBITALS ARE ON SAME ATOM, THEN MATRIX ELEMENT IS:
C             1) ZERO FOR DIFFERENT (ORTHOGONAL) ORBITALS
C             2) HERMAN-SKILLMAN ATOMIC TERM VALUE FOR SAME ORBITAL
C.
C     INPUT PARAMETERS:
C             R1--VECTOR POSITION IN RECTANGULAR COORDINATES OF
C                     ATOM #1 (ANGSTROMS)  (3 ELEMENT ARRAY)
C             R2--VECTOR POSITION IN RECTANGULAR COORDINATES OF
C                     ATOM #2 (ANGSTROMS)  (3 ELEMENT ARRAY)
C             OR1--4 ELEMENT ARRAY TO SPECIFY ATOMIC ORBITAL #1 AND
C                     ITS DIRECTION (S1,PX1,PY1,PZ1)
C                     (DON'T WORRY ABOUT NORMALIZATION)
C                     EG, 'S' ORBITAL ==> (1,0,0,0)
C                     EG, 'P' ORBITAL DIRECTED IN X-Y PLANE, 30
C                         DEGREES ABOVE X-AXIS ==> (0,COS30,SIN30,0)
C             OR2--4 ELEMENT ARRAY TO SPECIFY ATOMIC ORBITAL #2 AND
C                     ITS DIRECTION (S2,PX2,PY2,PZ2)
C                     (DON'T WORRY ABOUT NORMALIZATION)
C             NATOM1--ATOMIC NUMBER OF ATOM #1
C             NATOM2--ATOMIC NUMBER OF ATOM #2
C     OUTPUT PARAMETERS:
C             SSME--EVALUATED SOLID STATE MATRIX ELEMENT
C                     OR ATOMIC TERM VALUE
C     EXTERNAL REFERENCES:
C             SUBROUTINE UVECT
C             FUNCTION DOTPD
C             FUNCTION ATTMV
C.
C.
      DIMENSION R1(3),R2(3),OR1(4),OR2(4)
      DIMENSION D(3),P1(3),P2(3)
      DIMENSION UD(3),UP1(3),UP2(3)
      PARAMETER H2M=7.62, C1=-1.40, C2=-1.84, C3=-0.81, C4=+4.05
C.
C             SEPARATE 'S' AND 'P' ORBITALS
      S1=OR1(1)
      S2=OR2(1)
      DO 1 I=1,3
      P1(I)=OR1(I+1)
1     P2(I)=OR2(I+1)
C.
C             CHECK INPUT PARAMETERS OR1 & OR2 TO VERIFY THAT ONLY
C             AN 'S' OR 'P' TYPE ORBITAL IS SPECIFIED (NOT BOTH!!!)
      NS1=0
```

Figure C2. (Continued)

```
:UDD:EWBANK:UTILITY.DIR:SSIME.FR

        NS2=0
        NP1=0
        NP2=0
        IF (S1.NE.0.0) NS1=1
        IF (S2.NE.0.0) NS2=1
        DO 5 I=1,3
        IF (P1(I).NE.0.0) NP1=1
5       IF (P2(I).NE.0.0) NP2=1
        IF ( (NS1+NP1).NE.1 .OR. (NS2+NP2).NE.1 ) GOTO 20
C.
C               CALCULATE VECTOR D
        DO 10 I=1,3
10      D(I)=R2(I)-R1(I)
C.
C               CALCULATE MAGNITUDE OF VECTOR D SQUARED (=VECTOR DOT
C.                 RRODUCT OF D WITH ITSELF)
        D2=DOTPD(D,D,3)
C.
C               FIND UNIT VECTORS CORRESPONDING TO D,P1,P2,S1,& S2
C               UNIT VECTOR OF A 'NULL' VECTOR IS DEFINED TO BE A
C               NULL VECTOR.
        CALL UVECT(D,3,UD)
        CALL UVECT(P1,3,UP1)
        CALL UVECT(P2,3,UP2)
        CALL UVECT(S1,1,US1)
        CALL UVECT(S2,1,US2)
C.
C               DO R1 & R2 SPECIFY 2 DIFFERENT ATOMS (IE, D>.1 ANGSTROM)?
C               IF 2 DIFFERENT ATOMS, CALCULATE "SOLID STATE MATRIX ELEM"
C               IF SAME ATOM, ASSIGN "ATOMIC TERM VALUE"
        IF (D2.GT.(.01)) GOTO 18
C.
C               FOR D<.1 ANGSTROM, MAKE SURE ATOMIC NUMBERS SAME
        IF (NATOM1.NE.NATOM2) GOTO 40
C.
C               ARE ORBITALS ORTHOGONAL?  IF SO, RETURN ZERO.
C               IF NOT, CHOOSE TYPE OF ORBITAL ('S' OR 'P')
        SSME=0.0
        SCALE=1.0
        NORB=0
        IF (NS1.EQ.1 .AND. NS2.EQ.1) NORB=1             ;S ORBITAL
        IF (NP1.EQ.1 .AND. NP2.EQ.1) NORB=2             ;P ORBITAL
        GOTO (19,12,11) (NORB+1)
C               FOR P-ORBITALS, INCLUDE POSSIBILITY THAT ORB1 & ORB2
C               ARE NOT STRICTLY ORTHONORMAL.
11      SCALE=DOTPD(UP1,UP2,3)
C.
C               ASSIGN ATOMIC TERM VALUE
12      SSME=SCALE*ATTMV(NATOM1,NORB)
        GOTO 19
C.
```

Figure C2. (Continued)

```
:UDD:EWBANK:UTILITY.DIR:SSIME.FR

C.
C                CALCULATE SOLID STATE MATRIX ELEMENT
18       SSME=(H2M/D2)*( C1*US1*US2 +
     &     C2*(US2*DOTPD(UP1,UD,3)-US1*DOTPD(UP2,UD,3)) +
     &     C3*DOTPD(UP1,UP2,3) +
     &     C4*DOTPD(UP1,UD,3)*DOTPD(UP2,UD,3) )
C.
19       RETURN
C.
C                ERROR ON INPUT PARAMETERS
20       WRITE (10,30) (OR1(I),I=1,4),(OR2(I),I=1,4)
30       FORMAT (/,/," ONE AND ONLY ONE TYPE OF ATOMIC ORBITAL MUST BE",
     *     " NON-ZERO",/," S1=",F7.3,"   PX1=",F7.3,"   PY1=",
     *     F7.3,"   PZ1=",F7.3,/,
     *     " S2=",F7.3,"   PX2=",F7.3,"   PY2=",F7.3,"   PZ2=",F7.3)
         GOTO 60
40       WRITE (10,50)
50       FORMAT (/,/," FOR ATOM POSITIONS IDENTICAL, ATOMIC NUMBERS ",
     &    "MUST BE SAME",/," ATOM 1  :",Z)
         WRITE (10,54) NATOM1,(R1(I),I=1,3)
54       FORMAT (" ATOMIC NUMBER=",I3,"   X=",F7.3,"   Y=",F7.3,"   Z=",
     &    F7.3)
         WRITE (10,56)
56       FORMAT (" ATOM 2:  ",Z)
         WRITE (10,54) NATOM2,(R2(I),I=1,3)
60       PAUSE " *** ERROR ON INPUT PARAMETERS *** SUBROUTINE SSIME ***"
         STOP..
         END
```

Figure C2. (Continued)

```
:UDD:EWBANK:UTILITY.DIR:ATTMV.FR

      FUNCTION ATTMV(NATOM,NORB)
C.
C     ROUTINE TO ASSIGN AN ENERGY FOR THE DIAGONAL MATRIX ELEMENTS
C     OF THE HAMILTONIAN (ATOMIC TERM VALUES) FROM F. HERMAN &
C     S. SKILLMAN, "ATOMIC STRUCTURE CALCULATIONS" (1963) USING THE
C     HARTREE-FOCH-SLATER SELF-CONSISTENT ATOMIC FIELD APPROXIMATION.
C.
C     INPUT PARAMETERS:
C             NATOM --- ATOMIC NUMBER OF ATOM UNDER CONSIDERATION
C             NORB --- 1==>S ORBITAL;2==>P ORBITAL
C     OUTPUT PARAMETERS:
C             ATTMV --- ATOMIC TERM VALUE
C     EXTERNAL REFERENCES:
C             NONE
C.
      DIMENSION ATV(2,89)
C             DOUBLE DIMENSIONED ARRAY STORED BY INCREMENTING LEFT
C             MOST INDEX FASTER
      DATA ATV/13.60,.0,.0,.0,5.48,.0,8.17,4.14,12.54,6.64,
     &17.52,8.97,23.04,11.47,29.14,14.13,35.80,16.99,.0,.0,
     &5.13,.0,6.86,2.99,10.11,4.86,13.55,6.52,17.10,8.33,20.80,10.27,
     &24.63,12.31,2*.0,4.19,.0,5.41,.0,5.85,.0,14*.0,6.92,1.83,8.4,3.38,
     &11.37,4.90,14.38,6.36,17.33,7.91,20.32,9.53,23.35,11.20,.0,.0,
     &3.94,.0,5.00,.0,5.53,.0,14*.0,6.41,2.05,7.70,3.38,10.12,4.69,
     &12.50,5.94,14.80,7.24,17.11,8.59,19.42,9.97,.0,.0,3.56,.0,4.45,.0,
     &4.86,.0,42*.0,6.48,2.38,7.68,3.48,9.92,4.61,12.07,5.77,14.15,6.97,
     &16.21,8.19,18.24,9.44,.0,.0,3.40,.0,4.24,.0,4.63,.0/
C.
      IF (NORB.LT.1.OR.NORB.GT.2) GOTO 5
      IF (NATOM.LT.0.OR.NATOM.GT.89) GOTO 10
      IF (ATV(NORB,NATOM).EQ.0.0) GOTO 10
      ATTMV=-ATV(NORB,NATOM)
      RETURN
C.
5     WRITE (10,6) NORB
6     FORMAT (/,/," ONLY S ORBITAL (NORB=1) OR P ORBITAL (NORB=2)",
     &  "ALLOWED --- NORB=",I1)
      GOTO 50
10    WRITE (10,20) NATOM
20    FORMAT (/,/," ATOMIC TERM VALUE NOT AVAILABLE FOR:",
     &    "  ATOMIC NUMBER=",I3,5X,Z)
      GOTO (30,40) NORB
30    WRITE (10,35)
35    FORMAT ("S ORBITAL")
      GOTO 50
40    WRITE (10,45)
45    FORMAT ("P ORBITAL")
50    PAUSE " *** ERROR ON INPUT PARAMETERS *** FUNCTION ATTMV ***"
      STOP..
      END
```

Figure C2. (Continued)

:UDD:EWBANK:UTILITY.DIR:UVECT.FR

```
      SUBROUTINE UVECT(X,N,XUNIT)
C.
C     ROUTINE TO GENERATE A N-DIMENSIONAL 'UNIT' VECTOR FROM
C     A GIVEN VECTOR.  IF INPUT VECTOR IS A 'NULL' VECTOR, THEN
C     THE 'UNIT' VECTOR IS ALSO NULLED.
C.
C     INPUT PARAMETERS:
C             X--VECTOR TO BE 'NORMALIZED'; A N-DIMENSIONAL ARRAY
C             N--DIMENSIONALITY OF VECTOR
C     OUTPUT PARAMETERS:
C             XUNIT--UNIT VECTOR; A N-DIMENSIONAL ARRAY
C     EXTERNAL REFERNCES:
C             FUNCTION DOTPD
C.
      DIMENSION X(1),XUNIT(1)
C.
      DO 10 I=1,N
10    XUNIT(I)=0.0
C.
C     MAGNITUDE OF VECTOR SQUARED IS EQUAL TO THE DOT PRODUCT OF
C     VECTOR WITH ITSELF
      D=SQRT(DOTPD(X,X,N))
C.
C     NULL VECTOR FOR D=0
      IF (D.EQ.0.0) GOTO 30
C.
      DO 20 I=1,N
20    XUNIT(I)=X(I)/D
C.
30    RETURN
      END
```

:UDD:EWBANK:UTILITY.DIR:DOTPD.FR

```
      FUNCTION DOTPD(X1,X2,N)
C.
C     ROUTINE TO EVALUATE A N-DIMENSIONAL VECTOR DOT PRODUCT
C     BETWEEN 2 VECTORS
C.
C     INPUT PARAMETERS:
C             X1--VECTOR #1; A N-DIMENSIONAL ARRAY
C             X2--VECTOR #2; A N-DIMENSIONAL ARRAY
C             N--DIMENSIONALITY OF VECTORS X1 & X2
C     OUTPUT PARAMETERS:
C             DOTPD--EVALUATED DOT PRODUCT
C     EXTERNAL REFERENCES:  NONE
C.
      DIMENSION X1(1),X2(1)
C.
      DOTPD=0.0
      DO 10 I=1,N
10    DOTPD=DOTPD+X1(I)*X2(I)
C.
      RETURN
      END
```

Figure C2. (Continued)

APPENDIX D

DENSITY OF STATES COMPUTER PROGRAM

An overall flowchart for the density of states program is shown in Figure D1. The basic structure of this density of states computer program is identical to the energy band program in Appendix C. The listings for this program, excluding subroutines which appear in Appendix C, are given in Figure D2.

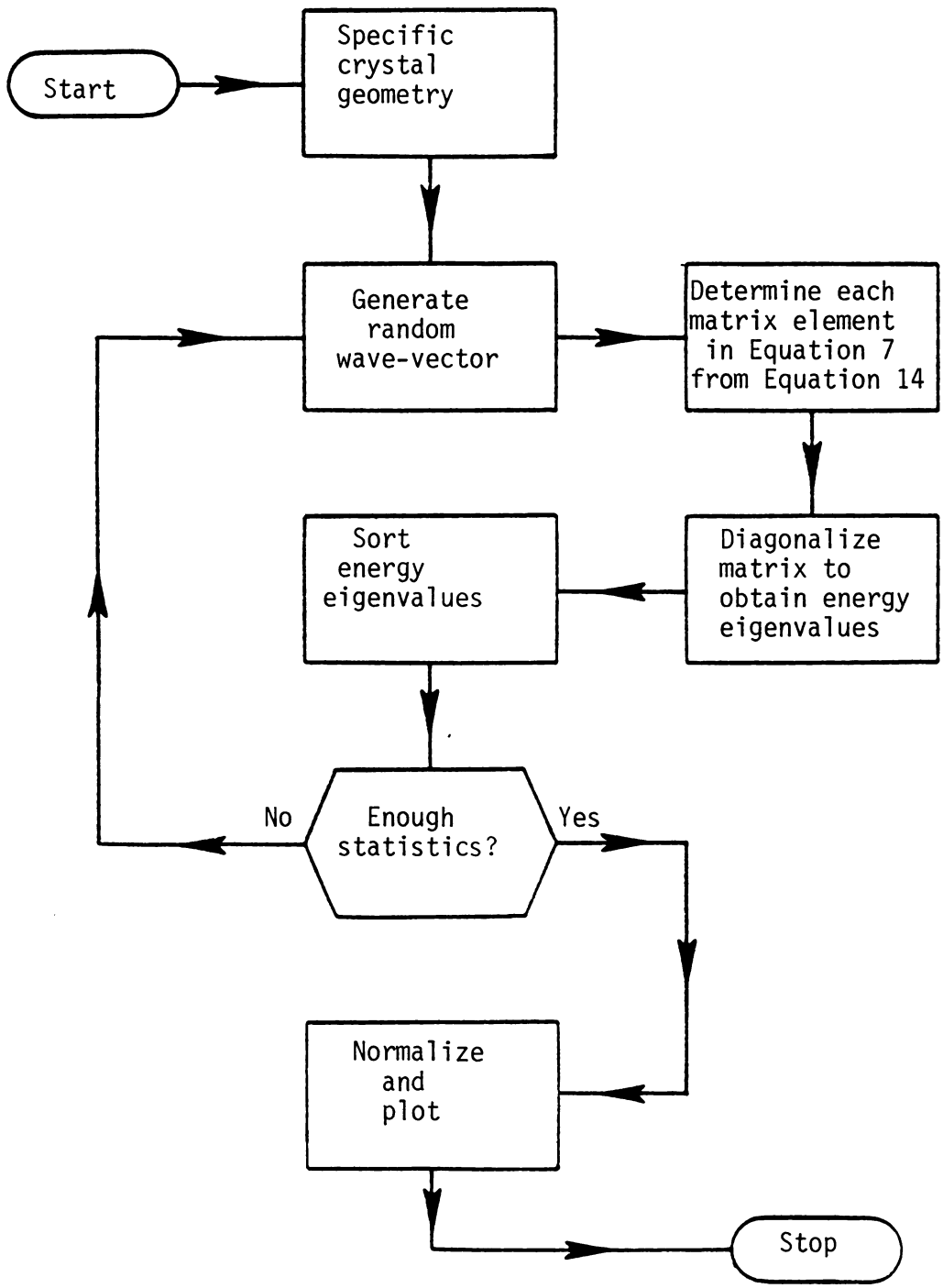


Figure D1. Flowchart for density of states program

```
:UDD:EWBANK:DSTATE.DIR:DSINPUT.FR

C                       DSINPUT.FR --- DENSITY OF STATES
C.
C       ROUTINE TO ALLOW INPUTTING OF CONTROL PARAMETERS USED BY
C       PROGRAM 'DSTATE.FR' FROM CONSOLE AND GENERATES THE
C       CONTROL PARAMETER FILE.
C.
C       INPUT PARAMETERS:
C               FROM CONSOLE
C       OUTPUT PARAMETERS:
C               I) CONTROL PARAMETER FILE --- CONTAINING:
C                       A) NAPUC --- # ATOMS PER 'UNIT CELL'
C                       B) NATMNUM --- ATOMIC NUMBER OF EACH ATOM IN
C                                      'UNIT CELL'.  (ORDERED ACCORDING
C                                      TO 'ENUMERATION' (SEE BELOW))
C                       C) EMIN & EMAX --- ENERGY MIN & MAX FOR 'WINDOW'
C                                          OF HISTOGRAM
C                       D) KPTS --- # PTS IN K-SPACE AT WHICH TO
C                                  CALCULATE THE ENERGY EIGENVALUES
C                       E) DMAX2 --- MAXIMUM 'NEAR NEIGHBOR' DISTANCE
C                                    SQUARED FOR ATOMS TO BE INCLUDED
C                                    IN BLOCH FCN
C                       F) IFILE --- FILENAME OF INPUT DATA FILE (BELOW)
C                     FORMAT --- BINARY
C       EXTERNAL REFERENCES:
C               NONE
C.
C.
        PARAMETER IN=11,IOUT=10,NPAGE=27*400K+12
        PARAMETER  KKPTS=1E5              ;MAXIMUM # KPTS ALLOWED
        PARAMETER  MAXAPUC=10             ;MAXIMUM # ATOMS PER UNIT CELL
        DIMENSION NATMNUM(MAXAPUC),IFILE(31)
C.
        WRITE (IOUT) NPAGE
C.
C               ENTER # ATOMS PER 'UNIT CELL'
C.
150     WRITE (IOUT,160)
160     FORMAT (/," ENTER # ATOMS PER UNIT CELL: ",Z)
        READ FREE (IN,ERR=150) NAPUC
        IF (NAPUC.LT.1 .OR. NAPUC.GT.MAXAPUC) GOTO 150
C.
C               ENTER ATOMIC NUMBERS ASSOCIATED WITH EACH ATOM IN
C               UNIT CELL.  (ORDER MUST REFLECT 'ENUMERATION' OF
C               DATA FILE TO BE INPUT)
C.
        WRITE (IOUT,210)
210     FORMAT (/," ENTER ATOMIC NUMBER OF EACH ATOM IN UNIT CELL",
     &    /,"   (ORDER MUST CORRESPOND TO ",1H',"ENUMERATION",2H'))
        DO 220 I=1,NAPUC
230     WRITE (IOUT,240) I
240     FORMAT (8X,"ATOM #",I2,4X,Z)
```

Figure D2. Computer listings for density of states program

```
:UDD:EWBANK:DSTATE.DIR:DSINPUT.FR

        READ FREE (IN,ERR=230) NATMNUM(I)
        IF (NATMNUM(I).LT.1 .OR. NATMNUM(I).GT.89) GOTO 230
220     CONTINUE
C.
C               ENTER ENERGY MIN & MAX
C.
250     WRITE (IOUT,260)
260     FORMAT (/," ENTER ENERGY MINIMUM: ",Z)
        READ FREE (IN,ERR=250) EMIN
270     WRITE (IOUT,280)
280     FORMAT (" ENTER ENERGY MAXIMUM: ",Z)
        READ FREE (IN,ERR=270) EMAX
        IF (EMIN.GE.EMAX) GOTO 250
C.
C               ENTER # KPTS
C.
50      WRITE (IOUT,60)
60      FORMAT (/," ENTER # PTS IN K-SPACE AT WHICH TO CALCULATE",/,
     &    "  THE ENERGY EIGENVALUES: ",Z)
        READ FREE (IN,ERR=50) KPTS
        IF (KPTS.LT.2 .OR. KPTS.GT.KKPTS) GOTO 50
C.
C               ENTER 'NEAR NEIGHBOR' MAXIMUM DISTANCE FOR INCLUSION
C               IN BLOCH FUNCTION SUM
C.
100     WRITE (IOUT,110)
110     FORMAT(/," ENTER ",1H',"NEAR NEIGHBOR",1H',"  MAXIMUM DISTANCE ",
     &    /," (ANGSTROMS) FOR INCLUSION IN BLOCH FCN:  ",Z)
        READ FREE (IN,ERR=100) DMAX
        IF (DMAX.LT.0.9 .OR. DMAX.GT.40.0) GOTO 100
        DMAX2=DMAX*DMAX                  ;DISTANCE SQUARED
C.
C               ENTER FILENAME OF INPUT DATA FILE
C.
350     WRITE (IOUT,360)
360     FORMAT(/," ENTER FILENAME OF FILE CONTAINING ATOM POSITIONS: ",Z)
        READ (IN,370,ERR=350) IFILE(1)
370     FORMAT (S60)
        OPEN 6,IFILE,ERR=350
        CLOSE 6
C.
C.
C               WRITE INPUT CONTROL PARAMETERS TO FILE.
C               (TO SAVE CORE, READ IN CONTROL PARAMETERS FROM
C               CONSOLE IN THIS STAND-ALONE PROGRAM, THEREBY AVOIDING
C               ASSOCIATED FORMAT STATEMENTS IN EBAND.FR)
C.
        OPEN 6,"?DS←INPUT"
        WRITE BINARY (6) KPTS,DMAX2,NAPUC,(NATMNUM(I),I=1,NAPUC),
     &    EMIN,EMAX,(IFILE(I),I=1,31)
        CLOSE 6
```

Figure D2. (Continued)

```
:UDD:EWBANK:DSTATE.DIR:DSINPUT.FR

C.
C.
C                NOW CHAIN TO DSTATE --- CALCULATE DENSITY OF STATES
C                TO ALLOW FOR THE OPTION OF EXECUTING DSTATE.PR IN
C                BATCH AT OFF-HOURS, MAKE CHAINING OPTIONAL.
C.
400      WRITE (IOUT,410)
410      FORMAT (/," CHAIN?  (YES/NO): ",Z)
         READ (IN,420,ERR=400) NANS
420      FORMAT (A2)
         IF (NANS.EQ.'NO') STOP
         IF (NANS.NE.'YE') GOTO 400
         CALL FCHAN("DSTATE.PR")
C.
         END
```

Figure D2. (Continued)

```
:UDD:EWBANK:DSTATE.DIR:DSTATE.FR

C                       DSTATE.FR --- DENSITY OF STATES
C.
C       PROGRAM DOES THE FOLLOWING:
C               I) SELECTS RANDOM K-VECTORS
C               II) GENERATES A SLATER-KOSTER MATRIX CONTAINING ELEMENTS
C                   BETWEEN BLOCH FUNCTIONS & ATOMIC ORBITALS FOR EACH
C                   K-VECTOR
C               III) DIAGONALIZES EACH MATRIX TO OBTAIN THE ENERGY
C                    EIGENVALUES AT A GIVEN WAVEVECTOR, (KX,KY,KZ)
C               IV) SORTS EIGENVALUES INTO ENERGY RANGE BUCKETS
C               V) NORMALIZE DENSITY OF STATES
C               VI) PLOTS THE DENSITY OF STATES VS ENERGY
C.
C.
C       INPUT PARAMETERS:
C               I) CONTROL PARAMETER FILE --- CONTAINING:
C                       A) NAPUC --- # ATOMS PER 'UNIT CELL'
C                       B) NATMNUM --- ATOMIC NUMBER OF EACH ATOM IN
C                                      'UNIT CELL'.  (ORDERED ACCORDING
C                                      TO 'ENUMERATION' (SEE BELOW))
C                       C) EMIN & EMAX --- ENERGY MIN & MAX FOR 'WINDOW'
C                                          OF HISTOGRAM
C                       D) KPTS --- # PTS IN K-SPACE AT WHICH TO
C                                  CALCULATE THE ENERGY EIGENVALUES
C                       E) DMAX2 --- MAXIMUM 'NEAR NEIGHBOR' DISTANCE
C                                    SQUARED FOR ATOMS TO BE INCLUDED
C                                    IN BLOCH FCN
C                       F) IFILE --- FILENAME OF INPUT DATA FILE (BELOW)
C                     FORMAT --- BINARY
C               II) DATA FILE ('IFILE') --- EACH RECORD OF FILE CONTAINS:
C                         A) ATOMIC NUMBER
C                         B) ATOM ENUMERATION IN 'UNIT CELL'
C                              'ENUMERATION' IMPLIES THAT EACH
C                              ATOM IN 'UNIT CELL' IS ASSIGN A
C                              UNIQUE NUMBER, 1 TO NAPUC (WHERE NAPUC
C                              IS THE # ATOMS PER 'UNIT CELL')
C                         C) ATOM POSITION (X,Y,Z) IN RECTANGULAR
C                            COORDINATES
C                   FORMATTED AS FOLLOWS:  (12X,I2,3X,I2,3(3X,E14.7))
C.
C       OUTPUT PARAMETERS:
C               I) DATA FILE --- "?DS←DATA" --- CONTAINING CALCULATED
C                         DENSITY OF STATES, ETC BEING PASSED TO
C                         PLOTTING PROGRAM
C.
C       EXTERNAL REFERENCES:
C               I) INPUT CONTROL PARAMETER FILE --- "?EB←INPUT"
C                       GENERATED BY STAND-ALONE PROGRAM "EBINPUT.FR"
C               II) INPUT DATA FILE --- ATOM POSITIONS & TYPES
C                       A)SUBROUTINE ATOMIN
C                               1) COMMON/ATMPOS/....
```

Figure D2. (Continued)

```
:UDD:EWBANK:DSTATE.DIR:DSTATE.FR

C               III) GENERATE RANDOM K-VECTOR
C                       A) SUBR TIME (SYSTEM ROUTINE)
C                       B) SUBR IRANDOM (SYSTEM ROUTINE)
C                       C) SUBR RANDOM (SYSTEM ROUTINE)
C               IV) GENERATE MATRIX ELEMENTS
C                       A) SUBROUTINE BLOCH
C                               1) SUBROUTINE SSIAME
C                                       A) SUBR SSIME
C                                               1) FCN ATTMV
C                                               2) SUBR UVECT
C                                               3) FCN DOTPD
C                               2) COMMON/ATMPOS/....
C               V) DIAGONALIZE
C                       A) SUBROUTINE EIGCH  (IMSL LIBRARY)
C.                              1) EHBKH
C.                              2) EHOUHS.
C.                              3) EQRT2S
C.                              4) UERTST
C               VI) NORMALIZE --- INTEGRATED DENSITY OF STATES = # BANDS
C                       A) SUBROUTINE TRAPINT --- TRAPEZOIDAL INTEGRATION
C               VII) PLOT DENSITY OF STATES VS ENERGY ---
C                   STAND-ALONE PROGRAM --- DSPLOT
C                       A) SUBROUTINE GRIDR
C                       B) SUBROUTINE CURVE
C                       C) SUBROUTINE TPOT
C                       D) SUBOUTINE QPLOT
C                       E) PLOT10 LIBRARY (TEKTRONIX)
C                       F) AGII LIBRARY (TEKTRONIX)
C.
C.
        PARAMETER  MAXAPUC=10           ;MAXIMUM # ATOMS PER UNIT CELLS
        PARAMETER  NOPA=4                       ;# ORBITALS PER ATOM
        PARAMETER  NDIM=NOPA*MAXAPUC            ;MAXIMUM # BANDS
        PARAMETER  NNDIM=NDIM*(NDIM+1)/2, NNNDIM=3*NDIM
        PARAMETER  NEPTS=200            ; # BUCKETS FOR HISTOGRAM
        PARAMETER  CONV=1000            ;CONVERT RANDOM K-VECTOR FROM
C                                       ;0 THRU 1 TO 0 THRU 1000 (1/ANGST)
C.
        DIMENSION  IFILE(31)
        DIMENSION  NATMNUM(MAXAPUC)
        DOUBLE PRECISION COMPLEX  HA(NNDIM)
        DOUBLE PRECISION COMPLEX   VALUE
        DOUBLE PRECISION  WORKSP(NNNDIM), E(NDIM)
        DIMENSION  G(NEPTS),WVK(3),KSEED(3),IHMS(3)
C.
C.
C               READ INPUT CONTROL PARAMETER FILE.
C               (TO SAVE CORE, READ IN CONTROL PARAMETERS FROM
C               CONSOLE IN STAND-ALONE PROGRAM,THEREBY AVOIDING
C               ASSOCIATED FORMAT STATEMENTS HERE)
C.
```

Figure D2. (Continued)

```
:UDD:EWBANK:DSTATE.DIR:DSTATE.FR

        OPEN 6,"?DS←INPUT"
        READ BINARY (6) KPTS,DMAX2,NAPUC,(NATMNUM(I),I=1,NAPUC),
     &    EMIN,EMAX,(IFILE(I),I=1,31)
        CLOSE 6
C..
C..
C               READ ATOMIC POSITIONS FROM DATA FILE
C..
        CALL ATOMIN(IFILE,DMAX2,NAPUC,NATMNUM)
C..
C               INITIALIZE DENSITY OF STATES ARRAY
C..
        DO 100 J=1,NEPTS
100     G(J)=0.0
C..
C..
C                       GENERATE RANDOM 'SEEDS' FOR K-VECTOR
C..
                CALL TIME (IHMS,IER)
                DO 200 I=1,3
200             CALL IRANDOM(KSEED(I),IHMS(I))
C..
C                       GENERATE RANDOM WAVENUMBERS (KPTS) TIMES
C..
        DO 300 KINCR=1,KPTS
                DO 350 I=1,3
                CALL RANDOM(WVK(I),KSEED(I))
                KSIGN=KSEED(I)/3+WVK(I)*CONV            ;IFIX
                CALL RANDOM(SIGN,KSIGN)
                IF (SIGN.GT.0.5) SIGN=+1.0
                IF (SIGN.LE.0.5) SIGN=-1.0
350             WVK(I)=SIGN*CONV*WVK(I)
C..
C..
C               FIND EACH MATRIX ELEMENT A(I,J) --- ON & BELOW DIAGONAL
C..
        DO 400 IALPHA=1,NAPUC                   ;WHICH ATOM (COL)
        DO 400 IMU=1,NOPA                       ;WHICH ORBITAL (COL)
        DO 400 JBETA=IALPHA,NAPUC               ;WHICH ATOM (ROW)
                JNUMIN=1
                IF (JBETA.EQ.IALPHA) JNUMIN=IMU
        DO 400 JNU=JNUMIN,NOPA                  ;WHICH ORBITAL (ROW)
                IATOM=NATMNUM(IALPHA)           ;ASSIGN ATOMIC NUMBER
                JATOM=NATMNUM(JBETA)            ;ASSIGN ATOMIC NUMBER
        CALL BLOCH (IALPHA,IMU,IATOM,JBETA,JNU,JATOM,WVK,VALUE)
                I=(IALPHA-1)*NOPA+IMU           ;I & J TAKE ON VALUES
                J=(JBETA-1)*NOPA+JNU            ;FROM 1-NBANDS (I.LE.J)
C               A(I,J)=VALUE
C                       CONVERT 2-D ARRAY INTO 1-D ARRAY USED BY EIGCH
C                       (REFERENCE PAGE INTRO-10 OF IMSL MANUAL)
                L=(J*(J-1)/2) + I
```

Figure D2. (Continued)

```
:UDD:EWBANK:DSTATE.DIR:DSTATE.FR

C               HA(L)=A(I,J)
400     HA(L)=VALUE
C.
C.
C               NOW DIAGONALIZE
C.
        NBANDS = NAPUC * NOPA
        CALL EIGCH (HA,NBANDS,0,E,DUMMY,DUMMY,WORKSP,IER)
C.
C.
C               ACCUMULATE EACH EIGENVALUE IN APPROPRIATE BUCKET
C.
        DO 500 I=1,NBANDS
        IF (E(I).GT.EMAX .OR. E(I).LT.EMIN) GOTO 500
        J=IFIX( (E(I)-EMIN)*(NEPTS-1)/(EMAX-EMIN) + 1 )
        G(J) = G(J) + 1
500     CONTINUE
300     CONTINUE
C.
C.
C               NORMALIZE
C.
        CALL TRAPINT (G,NEPTS,EMIN,EMAX,GI)
        DO 600 J=1,NEPTS
600     G(J)=G(J)*NBANDS/GI
C.
C.
C               TO SAVE CORE, DO PLOTTING IN SEPARATE STAND-ALONE
C               PROGRAM.  THEREFORE, NEED TO WRITE DENSITY OF STATES
C               TO A DISK FILE.
C.
        CALL FDELETE ("?DS←DATA")
        OPEN 6, "?DS←DATA"
        WRITE BINARY (6) NEPTS,EMIN,EMAX,(G(J),J=1,NEPTS)
        CLOSE 6
C.
C.
C               NOW PLOT
C.
        CALL FCHAN("DSPLOT.PR")         ;TO SAVE CORE,CHAIN
        END
```

Figure D2. (Continued)

```
:UDD:EWBANK:DSTATE.DIR:DSPLOT.FR

C                       DSPLOT.FR --- DENSITY OF STATES
C.
C       ROUTINE TO MAKE THE GRAPHICS CALLS FOR DSTATE.FR
C       IE, PLOT DENSITY OF STATES VS ENERGY
C.
C       INPUT PARAMETERS:
C               DATA FILE --- CONTAINING THE FOLLOWING:
C                       # ENERGY PTS, ENERGY MIN & MAX, DENSITY OF STATES
C                       ARRAY
C                               FORMAT --- BINARY
C       OUTPUT PARAMETERS:
C.              PLOTFILE."?DS←PLOT"
C       EXTERNAL REFERENCES:
C               FCN DOTPD
C               SUBR AMNMX
C               SUBR GRIDR
C               SUBR CURVE
C.              SUBR TPOT
C.              SUBR QPLOT.
C               AGII LIBRARY
C               PLOT10 LIBRARY
C.
        PARAMETER IOUT=10, NPAGE=27*400K+12
        PARAMETER NNEPTS=200
        DIMENSION E(NNEPTS),G(NNEPTS)
C.
C.
C               READ IN DATA FOR DENSITY OF STATES FROM FILE
C.
        OPEN 6, "?DS←DATA"
        READ BINARY (6) NEPTS,EMIN,EMAX,(G(J),J=1,NEPTS)
        CLOSE 6
C.
C               GENERATE ENERGY DATA ARRAY
C.
        DO 100 J=1,NEPTS
100     E(J)=((J-1)/FLOAT(NEPTS))*(EMAX-EMIN)+EMIN
C.
C               CONSTRUCT GRID
C.
        CALL AMNMX (NEPTS,G,GMIN,IDUMMY,GMAX,IDUMMY)
        CALL GRIDR ($999,EMIN,EMAX,GMIN,GMAX,"?DS←PLOT",30,
     &    "ENERGY BAND DENSITY OF STATES",11,"ENERGY (EV)",
     &    17,"DENSITY OF STATES",XMN,XMX,YMN,YMX,0)
C.
C               NOW PLOT BANDS
C.
        CALL CURVE ($999,NEPTS,E,G,"?DS←PLOT",XMN,XMX,
     &    YMN,YMX,0,0,0,0)
C.
X       WRITE BINARY (IOUT) NPAGE                ;CLEAR CONSOLE SCREEN
```

Figure D2. (Continued)

```
:UDD:EWBANK:DSTATE.DIR:DSPLOT.FR

X       CALL TPOT (6,"?DS←PLOT",IOUT)           ;COPY TO CONSOLE
        CALL QPLOT ("?DS←PLOT",IER)             ;COPY TO VERSATEC
        IF (IER.NE.1) GOTO 999
C.
        STOP..
C.
C.
999     WRITE (10,998)
998     FORMAT (" PLOTTING ERROR")
        STOP..
C.
        END
```

```
:UDD:EWBANK:DSTATE.DIR:TRAPINT.FR

        SUBROUTINE TRAPINT (FX,NPTS,XMIN,XMAX,FXINT)
C.
C       ROUTINE TO DO TRAPIZOIDAL RULE INTEGRATION OF FUNCTION FX
C       BETWEEN XMIN & XMAX GIVEN FX AT NPTS EQUALLY SPACED (IN X) POINTS
C.
C       INPUT PARAMETERS:
C               FX --- ARRAY OF DEPENDENT VARIABLE VALUES AT EQUALLY
C                       SPACED INTERVALS OF INDEPENDENT VARIABLE VALUES
C               NPTS --- NUMBER OF POINTS IN ARRAY FX
C               XMIN & XMAX --- DEFINITE INTEGRAL ==> EVALUATE BETWEEN
C                               XMIN AND XMAX
C       OUTPUT PARAMETERS:
C               FXINT --- EVALUATED INTEGRAL
C       EXTERNAL REFERENCES:
C               NONE
C.
        DIMENSION FX(1)
C.
        FXINT=(FX(1)+FX(NPTS))/2
        DO 10 I=2,(NPTS-1)
10      FXINT=FXINT+FX(I)
        XDELTA=(XMAX-XMIN)/(NPTS-1)
        FXINT=XDELTA*FXINT
C.
        RETURN
        END
```

Figure D2. (Continued)

APPENDIX E

PRINCIPAL INDICES OF REFRACTION COMPUTER PROGRAM

The flowchart for the principal indices of refraction computer program is shown in Figure E1, and the listings are given in Figure E2. Unlike the general applicability to any crystal exhibited by the energy band and density of states programs, portions of this program were specifically written for the chalcopyrite crystals. In particular, the summation of polarization over each bond in the unit cell assumed a chalcopyrite structure. However, only two routines reflect this assumption. The first is the subroutine to input the crystal geometry (CPATMIN) and the second is the subroutine that computes the net polarization (POLARIZ). Also listed are two different routines (HBOMHYB and HBOMATM) for calculating Bond Orbital Model parameters V_2, V_3 and γ. Some lower level subroutines, which were also used by the band structure programs, are not listed here but appear in Appendix C.

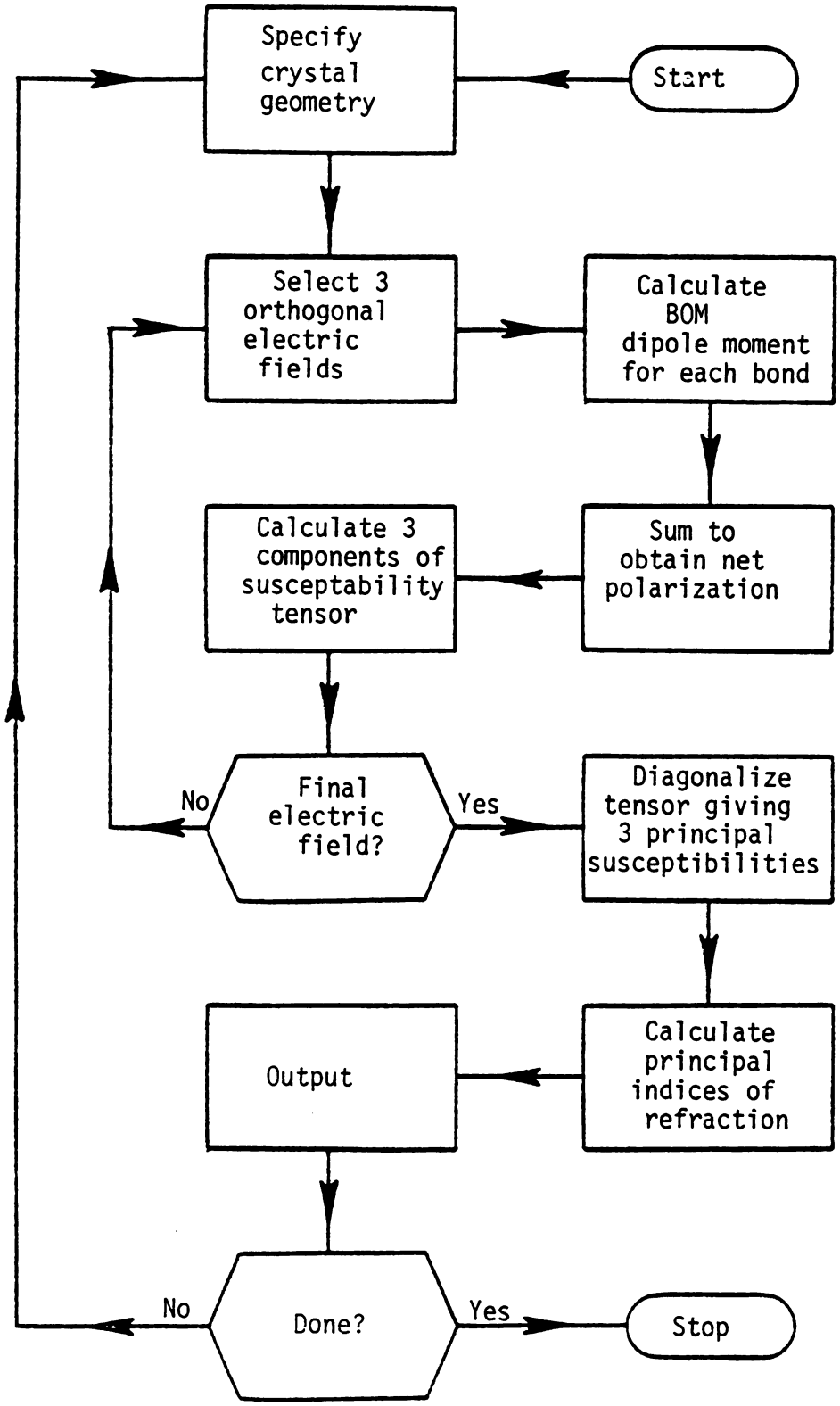


Figure E1. Flowchart for principal indices of refraction program

```
:UDD:EWBANK:DIELECTRIC.DIR:PRINDEX.FR

C                                   FRINDEX.FR
C..
C                 MAIN PROGRAM TO DETERMINE THE PRINCIPAL INDICES OF
C                 REFRACTION FOR A CRYSTAL USING HARRISON'S BOND ORBITAL
C                 MODEL (BOM) APPROACH.  THIS METHOD INVOLVES CALCULATING
C                 THE POLARIZATION FOR EACH BOND AND SUMMING UP THE
C                 CONTRIBUTIONS FROM ALL BONDS.  BY CALCULATING THE NET
C                 POLARIZATION AT 3 ORTHOGONAL ORIENTATIONS OF THE
C                 EXTERNAL ELECTRIC FIELD, THE NINE COMPONENTS OF THE
C                 SUSCEPTABILITY TENSOR ARE OBTAINED.  DIAGONALIZATION
C                 OF THIS 3X3 MATRIX YIELDS THE PRINCIPAL SUSCEPTABILITIES
C                 AND, CONSEQUENTLY, THE PRINCIPAL INDICES OF REFRACTION.
C..
C        INPUT PARAMETERS (FROM CONSOLE):
C                 IFILE --- FILENAME OF FILE CONTAINING ATOM POSITIONS
C                                   AND ATOMIC NUMBERS DESCRIBING CRYSTAL
C                 A,C --- LATTICE PARAMETERS
C        OUTPUT PARAMETERS (TO CONSOLE):
C                 PRINCIPAL INDICES OF REFRACTION
C        EXTERNAL REFERENCES:
C                 SUBROUTINE PIINPUT
C                 SUBROUTINE PIOUTPUT
C                 SUBROUTINE CPATMIN
C                         COMMON/ATMPOS/....
C                 SUBROUTINE POLARIZ
C                         SUBR HBOMHYB OR HBOMATM
C.                        SUBR DOTPD
C                         COMMON/ATMPOS/....
C                 SUBROUTINE EIGRF  (IMSL LIBRARY)
C                         SUBR EBALAF
C.                        SUBR EHESSF
C.                        SUBR EQRH3F
C.                        SUBR EHSCKF
C.                        SUBR EBBCKF
C..
         PARAMETER  PI=3.1415927, N3=3
         DIMENSION JATOM(3),IFILE(10)
         DIMENSION E(N3),POL(N3),CHIBAV(N3,N3),PIR(N3)
         DOUBLE PRECISION CHI(N3,N3),WK(N3)
         DOUBLE PRECISION COMPLEX PRCHI(N3)
C..
C                 INPUT CONTROL INFORMATION FROM CONSOLE
C..
         NFLAG=-1
1        CALL PIINPUT(NFLAG,IFILE,A,C,JATOM)
C..
C                 INPUT ATOM POSITION FROM DATA FILE
C..
         IF (NFLAG.EQ.1) CALL CPATMIN(IFILE,A,C,JATOM,S1)
C..
C                 SPECIFY 3 ORTHOGONAL ELECTRIC FIELDS
```

Figure E2. Computer listings for principal indices of refraction program

```
:UDD:EWBANK:DIELECTRIC.DIR:PRINDEX.FR

C..
        DO 10 I=1,N3
        DO 20 J=1,N3
20      E(J)=0.0
        E(I)=1.0
C..
C               CALCULATE POLARIZATION FOR EACH ELECTRIC FIELD VECTOR
C..
        CALL POLARIZ(A,C,E,JATOM,POL)
C..
C               CALCULATE SUSCEPTABILITY TENSOR COMPONENTS
C..
        DO 10 J=1,3
        CHISAV(J,I)=POL(J)
10      CHI(J,I)=POL(J)
C..
C               DIAGONALIZE SUSCEPTABILITY MATRIX TO GET
C               PRINCIPAL SUSCEPTABILITIES
C..
        CALL EIGRF(CHI,N3,N3,0,PRCHI,DUMMY,DUMMY,WK,IER)
C..
C               CALCULATE PRINCIPAL INDICES OF REFRACTION
C..
        DO 30 I=1,N3
        PRC=PRCHI(I)
30      PIR(I)=SQRT(1.0+4*PI*PRC)
C..
C..             OUTPUT..
C..
        CALL PIOUTPUT(CHISAV,PRCHI,PIR,IFILE(4))
C..
        GOTO 1
C..
        END
```

Figure E2. (Continued)

```
:UDD:EWBANK:DIELECTRIC.DIR:PIINPUT.FR

      SUBROUTINE PIINPUT(NFLAG,IFILE,A,C,JATOM)
C..
C     ROUTINE TO INPUT PARAMETERS FROM CONSOLE FOR PRINDEX.FR
C..
C     INPUT PARAMETERS:
C             NFLAG --- .EQ.-1 ==> FIRST TIME THRU
C     OUTPUT PARAMETERS:
C             NFLAG ---  .EQ.0 => DON'T NEED TO READ ATOM POSITION FILE
C                        .EQ.1 => NEED TO READ ATOM POSITION FILE
C             IFILE --- FILENAME OF FILE CONTAINING ATOM POSITIONS
C             A & C --- LATTICE CONSTANTS
C             JATOM --- ARRAY OF ATOMIC NUMBERS FOR EACH OF THE 3
C                       TYPES OF ATOMS IN UNIT CELL OF CHALCOPYRITE
C     EXTERNAL REFERENCES:
C             NONE
C..
      DIMENSION IFILE(16),JATOM(3)
      PARAMETER  IN=11, IOUT=10, NPAGE=27*400K+12
C..
      IF (NFLAG.NE.-1) GOTO 2
      WRITE (IOUT) NPAGE
      WRITE (IOUT,1)
1     FORMAT (/,25X,"CHALCOPYRITE INDEX OF REFRACTION")
      GOTO 99
2     WRITE (IOUT,3)
3     FORMAT (/," DONE? (YES/NO): ",Z)
      READ (IN,4,ERR=2) IANS
4     FORMAT (A2)
      IF (IANS.EQ.'YE') STOP
      IF (IANS.NE.'NO') GOTO 2
C..
      NFLAG=0
10    WRITE (IOUT) NPAGE
      WRITE (IOUT,20)
20    FORMAT (/,/,/," CHANGE CRYSTAL GEOMETRY? (YES/NO):  ",Z)
      READ (IN,30,ERR=10) IANS
30    FORMAT (A2)
      IF (IANS.EQ.'NO') GOTO 250
      IF (IANS.NE.'YE') GOTO 10
C..
C             INPUT LATTICE CONSTANTS
C..
99    NFLAG=1
100   WRITE (IOUT,110)
110   FORMAT (/," ENTER LATTICE CONSTANTS: ",/,5X,"A = ",Z)
      READ FREE (IN,ERR=100) A
      IF (A.LT.4.0 .OR. A.GT.7.0) GOTO 100
      WRITE (IOUT,130)
130   FORMAT (5X,"C = ",Z)
      READ FREE (IN,ERR=100) C
      IF (C.LT.9.0 .OR. C.GT.13.0) GOTO 100
```

Figure E2. (Continued)

```
:UDD:EWBANK:DIELECTRIC.DIR:PIINPUT.FR

C..
C                INPUT ATOMIC NUMBERS
C..
150     WRITE (IOUT,160)
160     FORMAT (/," SPECIFY 3 TYPES OF ATOMS IN UNIT CELL IN ORDER")
        DO 170 I=1,3
190     WRITE (IOUT,195) I
195     FORMAT (" ENTER ATOMIC NUMBER FOR ATOM #",I1,":  ",Z)
        READ FREE (IN,ERR=190) JATOM(I)
        IF (JATOM(I).LT.5 .OR. JATOM(I).GT.89) GOTO 190
170     CONTINUE
C..
C                ENTER FILENAME OF INPUT DATA FILE
C..
350     WRITE (IOUT,360)
360     FORMAT(/," ENTER FILENAME OF FILE CONTAINING ATOM POSITIONS: ",Z)
        READ (IN,370,ERR=350) IFILE(1)
370     FORMAT (S60)
C..
250     RETURN
        END
```

Figure E2. (Continued)

```
:UDD:EWBANK:DIELECTRIC.DIR:CPATMIN.FR

      SUBROUTINE CPATMIN(IFILE,A,C,JATOM,$)
C..
C     ROUTINE TO INPUT ATOM POSITIONS AND  ATOMIC NUMBERS
C..
C     INPUT PARAMETERS:
C             1) IFILE --- DATA FILE CONTAINING ATOM POSITIONS,ETC
C                      EACH RECORD OF FILE CONTAINS:
C                        A) ATOMIC NUMBER
C                        B) ATOM POSITION (X,Y,Z) IN RECTANGULAR
C                           COORDINATES
C                        FORMATTED AS --- (12X,I2,5X,3(3X,E14.7))
C                    NATOM --- ATOMIC NUMBER OF EACH ATOM
C                    R --- 3-D ARRAY FOR ATOM POSITION (X,Y,Z)
C             2) A & C --- LATTICE CONSTANTS
C             3) JATOM --- 3D ARRAY OF ATOMIC NUMBERS
C     OUTPUT PARAMETERS:
C             ERROR RETURN
C     EXTERNAL REFERENCES:
C             COMMON/ATMPOS/R,NATOM
C..
      PARAMETER GTONE=1.01
      COMMON/ATMPOS/R(3,NAUC),NATOM(NAUC)
      DIMENSION IFILE(1),RR(3),JATOM(3)
      PARAMETER NAUC=31                 ;# ATOMS IN UNIT CELL (INCLUDE
C                                       ;FULL ATOM AT EDGES)
      J=0
      OPEN 6, IFILE,ATT="I",ERR=900
10    READ (6,20,END=40) IATOM,(RR(I),I=1,3)
20    FORMAT (12X,I2,5X,3(3X,E14.7))
      IF (ABS(RR(1)).GT.(A/2*GTONE)) GOTO 10
      IF (ABS(RR(2)).GT.(A/2*GTONE)) GOTO 10
      IF (ABS(RR(3)).GT.(C/2*GTONE)) GOTO 10
      DO 25 I=1,3
25    IF (IATOM.EQ.JATOM(I)) GOTO 27
      GOTO 900
27    J=J+1
      IF (J.GT.NAUC) GOTO 900
      NATOM(J)=IATOM
      DO 30 I=1,3
30    R(I,J)=RR(I)
      GOTO 10
40    CLOSE 6
C..
      RETURN
C..
C.            ERRORS.
C..
900   RETURN 5
      END
```

Figure E2. (Continued)

```
:UDD:EWBANK:DIELECTRIC.DIR:POLARIZ.FR

        SUBROUTINE POLARIZ(A,C,E,JATOM,POL)
C..
C       PROGRAM TO CALCULATE THE POLARIZATION FOR A GIVEN
C       ELECTRIC FIELD DIRECTION FOR A CHALCOPYRITE CRYSTAL USING
C       HARRISON'S BOND ORBITAL MODEL (BOM)
C..
C       INPUT PARAMETERS:
C               A & C --- LATTICE CONSTANTS
C               E --- 3D ARRAY FOR THE ELECTRIC FIELD VECTOR
C               JATOM --- ARRAY OF ATOMIC NUMBERS FOR EACH OF THE 3
C                                 TYPES OF ATOMS IN UNIT CELL
C       OUTPUT PARAMETERS:
C               POL --- 3D ARRAY FOR THE POLARIZATION VECTOR
C       EXTERNAL REFERENCES:
C               FCN DOTPD
C               SUBR HBOMHYB OR HBOMATM
C               COMMON/ATMPOS/...
C..
C..
        PARAMETER  EE=3.7949, N3=3
        DIMENSION  P0(N3),P1(N3),P2(N3)
        DIMENSION  JATOM(1),E(1),D(N3),POL(1)
        PARAMETER NAUC=31                ;# ATOMS IN UNIT CELL (INCLUDE
C                                        ;FULL ATOM AT EDGES)
        COMMON/ATMPOS/R(3,NAUC),NATOM(NAUC)
C..
C               ANION DISPLACED FROM CENTER OF TETRAHEDRAL BY DELX
        DELX=(.25-SQRT(C*C/32/A/A-1./16.))*A
C               NEAREST NEIGHBOR DISTANCE SQUARED
        DNN2=(A*A/8+C*C/64+DELX*DELX+A*DELX/2)*1.3
C               INITIALIZE POLARIZATION VECTOR
        DO 5 K=1,N3
        P0(K)=0.0
        P1(K)=0.0
5       P2(K)=0.0
C..
C               CHOOSE ANION --- 8 PER UNIT CELL
C..
        IANEXT=1
        DO 10 IIA=1,8
        DO 20 I=IANEXT,NAUC
        IA=I
20      IF (NATOM(IA).EQ.JATOM(N3)) GOTO 30
        PAUSE " CANNOT FIND ANION"
        STOP...
30      IANEXT=IA+1
C..
C               CHOOSE CATION --- 4 PER EACH ANION
C..
        ICNEXT=1
        DO 40 IIC=1,4
```

Figure E2. (Continued)

```
:UDD:EWBANK:DIELECTRIC.DIR:POLARIZ.FR

        DO 50 I=ICNEXT,NAUC
        IC=I
        DO 45 K=1,N3
45      D(K)=R(K,IC)-R(K,IA)
        D2=DOTPD(D,D,N3)
50      IF ((D2.LT.DNN2) .AND. (D2.GT.0.01)) GOTO 60
        PAUSE " CANNOT FIND CATION"
        STOP....
60      ICNEXT=IC+1
C..
C               CALCULATE BOM PARAMETERS V2,V3 & GAMMA FOR BOND BETWEEN
C               ANION SP3 HYBRID AND CATION SP3 HYBRID
C..
C               USE DECOMPOSED SP3 HYBRIDS AND HARRISON'S SOLID STATE
C               MATRIX ELEMENTS FOR ATOMIC ORBITALS ALONG WITH HERMAN-
C               SKILLMAN'S ATOMIC TERM VALUES
        CALL HBOMATM(R(1,IA),R(1,IC),NATOM(IA),NATOM(IC),V2,V3,GAMMA)
C..
C               USE HARRISON'S EMPIRICAL BOM PARAMETERS FOR BINARY CMPDS
C       CALL HBOMHYB(NATOM(IC),NATOM(IA),V2,V3,GAMMA)
C..
C               VECTOR SUM OF POLARIZATION FROM EACH BOND IN UNITCELL
        SV23=SQRT(V2*V2+V3*V3)
        DO 70 K=1,N3
        P0(K)=P0(K)*(-GAMMA*EE*V3)*D(K)/SV23
        P1(K)=P1(K)+((GAMMA*EE*V2)**2)*DOTPD(E,D,N3)*D(K)/2/(SV23**3)
70      P2(K)=P2(K)+3*(GAMMA*EE)**3*V2*V2*V3*D(K)*DOTPD(E,D,N3)/8/(SV23**5)
40      CONTINUE
10      CONTINUE
C..
C               CALCULATE & NORMALIZE POLARIZATION
C..
        DO 80 K=1,N3
        IF (ABS(P0(K)).GT.1E-6) WRITE FREE (12) " FERROELECTRIC? <NL>"
C80     POL(K)=(P0(K)+P1(K)+P2(K))/(A*A*C)       ;INCLUDE 2ND ORDER TERM
80      POL(K)=(P0(K)+P1(K))/(A*A*C)             ;FIRST ORDER ONLY
X       WRITE FREE (12) " P0 = ",(P0(I),I=1,N3)
X       WRITE FREE (12) " P1 = ",(P1(I),I=1,N3)
X       WRITE FREE (12) " P2 = ",(P2(I),I=1,N3)
X       WRITE FREE (12) " POLARIZATION VECTOR = ",(POL(I),I=1,N3)
C..
        RETURN
        END
```

Figure E2. (Continued)

```
:UDD:EWBANK:DIELECTRIC.DIR:HBOMATM.FR

      SUBROUTINE HBOMATM(R1,R2,NATOM1,NATOM2,V2,V3,GAMMA)
C..
C     ROUTINE TO CALCULATE HARRISON'S BOND ORBITAL MODEL (BOM)
C     PARAMETERS FOR THE DIELECTRIC FUNCTION FROM ATOMIC ORBITALS USING
C     HIS 'SOLID STATE INTERATOMIC MATRIX ELEMENTS' AND HERMAN-SKILLMAN'S
C     ATOMIC TERM VALUES.
C..
C     INPUT PARAMETERS:
C             R1--VECTOR POSITION IN RECTANGULAR COORDINATES OF
C                     ANION (ANGSTROMS)  (3 ELEMENT ARRAY)
C             R2--VECTOR POSITION IN RECTANGULAR COORDINATES OF
C                     CATION (ANGSTROMS)  (3 ELEMENT ARRAY)
C             NATOM1---ATOMIC NUMBER OF ANION
C             NATOM2---ATOMIC NUMBER OF CATION
C..
C     OUTPUT PARAMETERS:
C             V2,V3,GAMMA --- BOM PARAMETERS NEEDED FOR DIELECTRIC FCN
C..
C     EXTERNAL REFERENCES:
C             SUBROUTINE SSIAME
C                     SUBROUTINE SSIME
C                             SUBROUTINE ATTMV
C                             SUBROUTINE UVECT
C                             SUBROUTINE DOTPD
C..
C     NOTES:
C             NORB1---SPECIFIES ATOMIC ORBITAL OF ANION
C                     =1 IMPLIES S ORBITAL
C                     =2 IMPLIES PX ORBITAL
C                     =3 IMPLIES PY ORBITAL
C                     =4 IMPLIES PZ ORBITAL
C             NORB2---SPECIFIES ATOMIC ORBITAL OF CATION
C                     =1 IMPLIES S ORBITAL
C                     =2 IMPLIES PX ORBITAL
C                     =3 IMPLIES PY ORBITAL
C                     =4 IMPLIES PZ ORBITAL
C..
      PARAMETER  SQR3=1.732051
      DIMENSION R1(3),R2(3),D(3),SA(4),SC(4)
C..
      GAMMA=1.0
C..
C             DETERMINE V2 FROM HARRISON'S "SOLID STATE INTERATOMIC
C                     MATRIX ELEMENTS" FOR ATOMIC ORBITALS.
C             DECOMPOSE SP3 HYBRID ORBITALS OF ANION & CATION INTO
C             RESPECTIVE LINEAR COMBINATIONS OF ATOMIC ORBITALS
C..
C             DISTANCE BETWEEN ANION & CATION
      DO 10 I=1,3
10    D(I)=R2(I)-R1(I)
      DD=SQRT(DOTPD(D,D,3))
```

Figure E2. (Continued)

:UDD:EWBANK:DIELECTRIC.DIR:HBOMATM.FR

```
C..
C                SET SCALE FACTORS & SIGNS OF ANION & CATION ATOMIC
C                 ORBITAL TERMS THAT MAKE UP HYBRID
C..
        SA(1)=DD/SQR3
        SC(1)=-DD/SQR3
        DO 20 I=2,4
        SA(I)=D(I-1)
20      SC(I)=SA(I)
C..
C                ITERATE OVER ANION & CATION ATOMIC ORBITALS
C                AND ACCUMULATE MATRIX ELEMENTS
C..
        V2=0.0
        DO 40 NORB1=1,4
        DO 40 NORB2=1,4
        CALL SSIAME(R1,R2,NORB1,NORB2,NATOM1,NATOM2,SSME)
        V2=V2+SA(NORB1)*SC(NORB2)*SSME
40      CONTINUE
        V2=3*V2/4/DD/DD
C..
C                CALCULATE V3 FROM ATOMIC TERM VALUES FOR ATOMIC ORBITALS.
C                DECOMPOSE SP3 HYBRIDS INTO ATOMIC ORBITALS
C..
C                ATOMIC TERM VALUE FOR ANION S-ORBITAL
        CALL SSIAME(R1,R1,1,1,NATOM1,NATOM1,EAS)
C                ATOMIC TERM VALUE FOR ANION P-ORBITAL
        CALL SSIAME(R1,R1,2,2,NATOM1,NATOM1,EAP)
C                ATOMIC TERM VALUE FOR CATION S-ORBITAL
        CALL SSIAME(R2,R2,1,1,NATOM2,NATOM2,ECS)
C                ATOMIC TERM VALUE FOR CATION P-ORBITAL
        CALL SSIAME(R2,R2,2,2,NATOM2,NATOM2,ECP)
C..
        V3=(ECS+3*ECP-EAS-3*EAP)/8
C..
        RETURN
        END
```

Figure E2. (Continued)

```
:UDD:EWBANK:DIELECTRIC.DIR:HBOMHYB.FR

      SUBROUTINE HBOMHYB (NATOMC,NATOMA,V2,V3,GAMMA)
C..
C     ROUTINE TO OBTAIN HARRISON'S BOND ORBITAL MODEL (BOM) PARAMETERS
C     FOR A GIVEN CATION AND ANION FROM BINARY CMPDS EMPIRICAL NUMBERS
C..
C     INPUT PARAMETERS:
C             NATOMC --- ATOMIC NUMBER OF CATION
C             NATOMA --- ATOMIC NUMBER OF ANION
C     OUTPUT PARAMETERS:
C             V2 --- COVALENT ENERGY
C             V3 --- POLAR ENERGY
C             GAMMA --- OVERLAP INTEGRAL,INTERNAL FIELD, ETC
C     EXTERNAL REFERENCES:
C             NONE
C..
      DIMENSION EH(42)
      DATA EH/3.88,4.74,5.70,7.10,8.12,8.70,11*0.0,
     &  3.76,3.48,4.44,5.80,6.86,8.00,9.30,11*0.0,
     &  3.34,3.30,4.28,5.30,6.47,7.46,8.64/
C..
      IF (NATOMC.LT.12 .OR. NATOMC.GT.52) GOTO 999
      IF (NATOMA.LT.12 .OR. NATOMA.GT.52) GOTO 999
C..
C             DETERMINE V2
C..
      V2C=V2A=2.2                                  ;ROW 3
      IF (NATOMC.GE.19) V2C=2.15                   ;ROW 4
      IF (NATOMA.GE.19) V2A=2.15
      IF (NATOMC.GE.37) V2C=1.76                   ;ROW 5
      IF (NATOMA.GE.37) V2A=1.76
      V2=SQRT(V2C*V2A)
C..
C             DETERMINE GAMMA
C..
      GC=GA=1.2                                    ;ROW 3
      IF (NATOMC.GE.19) GC=1.42                    ;ROW 4
      IF (NATOMA.GE.19) GA=1.42
      IF (NATOMC.GE.37) GC=1.69                    ;ROW 5
      IF (NATOMA.GE.37) GA=1.69
      GAMMA=SQRT(GC*GA)
C..
C             DETERMINE V3
C..
      V3=-(EH(NATOMC-11)-EH(NATOMA-11))/2
      RETURN
C..
C.            ERRORS.
C..
999   PAUSE " ERROR --- SUBROUTINE HBOMP ...."
      STOP....
      END
```

Figure E2. (Continued)

```
:UDD:EWBANK:DIELECTRIC.DIR:PIOUTPUT.FR

      SUBROUTINE PIOUTPUT(CHI,PRCHI,PIR,IXSTAL)
C..
C     ROUTINE TO OUTPUT THE PRINCIPAL INDICES OF REFRACTION.
C     ALSO, SPECIFIES ISOTROPIC,UNIAXIAL, OR BIAXIAL AND OPTIONALLY
C     CAN OUTPUT THE COMPLETE SUSCEPTABILITY TENSOR AND THE
C     PRINCIPAL SUSCEPTABILITIES.
C..
C     INPUT PARAMETERS:
C             CHI --- 3X3 MATRIX FOR THE SUSCEPTABILITY TENSOR
C             PRCHI --- 3D ARRAY FOR THE PRINCIPAL SUSCEPTABILITIES
C             PIR --- 3D ARRAY FOR THE PRINCIPAL INDICES OF REFRACTION
C             IXSTAL --- ASCII CHARACTER STRING DESCRIBING CRYSTAL
C     OUTPUT PARAMETERS:
C             ANY OR ALL OF THE INPUT PARAMETERS
C     EXTERNAL REFERENCES:
C             NONE
C..
      PARAMETER  N3=3, SN=1E-3, IOUT=12
      DOUBLE PRECISION COMPLEX  PRCHI(N3)
      DIMENSION  CHI(N3,N3), PIR(N3), IXSTAL(1)
C..
C             OUTPUT SUSCEPTABILITY TENSOR
C..
X     WRITE (IOUT,4) ((CHI(I,J),J=1,N3),I=1,N3)
X4    FORMAT (/,/,18X,"SUSCEPTABILITY TENSOR",
X   &   3(/,5X,1H(,3(E12.5,3X),1H)),/)
C..
C             OUTPUT PRINCIPAL SUSCEPTABILITIES
C..
X     WRITE (IOUT,6) (I,PRCHI(I),I=1,N3)
X6    FORMAT (/,/,18X,"PRINCIPAL SUSCEPTABILITIES",
X   &   3(/,11X,"CHI#",I1,5X,E12.5," + I*",E12.5))
C..
C             OUTPUT PRINCIPAL INDICES OF REFRACTION
C..
      X21=ABS(PIR(2)-PIR(1))
      X31=ABS(PIR(3)-PIR(1))
      X32=ABS(PIR(3)-PIR(2))
      NTYPE=5                                   ;BIAXIAL
      IF (X21.LT.SN) NTYPE=2                    ;UNIAXIAL
      IF (X31.LT.SN) NTYPE=3                    ;UNIAXIAL
      IF (X32.LT.SN) NTYPE=4                    ;UNIAXIAL
      IF ((X21.LT.SN) .AND. (X31.LT.SN) .AND. (X32.LT.SN))
     &   NTYPE=1                                ;ISOTROPIC
      WRITE (IOUT,8) IXSTAL(1)
8     FORMAT (/,/,22X,S24,/)
      GOTO (10,20,22,24,30) NTYPE
C..
10    WRITE (IOUT,15) PIR(1)
15    FORMAT (20X,"ISOTROPIC CRYSTAL",/,15X,"INDEX OF REFRAC",
     &   "TION = ",F6.3,/)
```

Figure E2. (Continued)

:UDD:EWBANK:DIELECTRIC.DIR:PIOUTPUT.FR

```
      GOTO 40
C..
20    NO=1
      NE=3
      GOTO 26
22    NO=1
      NE=2
      GOTO 26
24    NO=2
      NE=1
26    BIREF=PIR(NE)-PIR(NO)
      WRITE (IOUT,28) PIR(NO),PIR(NE),BIREF
28    FORMAT (20X,"UNIAXIAL CRYSTAL",/,12X,"ORDINARY INDEX OF REF",
     &  "RACTION = ",F6.3,/,12X,"EXTRAORDINARY INDEX OF REFRACTION = ",
     &  F6.3,/,17X,"BIREFRINGENCE = ",F6.4,/)
      GOTO 40
C..
30    WRITE (IOUT,35) (I,PIR(I),I=1,N3)
35    FORMAT (20X,"BIAXIAL CRYSTAL",/,15X,"THE THREE PRINCIPAL ",
     &  "INDICES OF REFRACTION ARE:",3(/,18X,"#",I1,5X,F6.3),/)
C..
40    RETURN
      END
```

Figure E2. (Continued)

APPENDIX F

CHALCOPYRITE CRYSTAL STRUCTURE

The tetragonal structure of the chalcopyrites closely resembles the cubic zincblende structure. For example, by replacing the Ga atoms in the binary compound, GaAs, with Cd and Ge atoms, the ternary chalcopyrite, $CdGeAs_2$, is obtained (see Figure 1 of Lines and Waszazak[18]). The space group is $I\bar{4}2d$ and the point group is $\bar{4}2m$.[29]

The lattice parameters a and c determine the distortion of the tetrahedron; that is, c = 2a implies a "regular" tetrahedron and c>2a means that the tetrahedron is stretched along the z axis or compressed along the x and y axes. Lattice parameter x describes the displacement in the x-y plane of an anion from the center of a tetrahedron, formed by four cations, one at each corner. Specifically, the anion is displaced by an amount, $a|x-.25|$, towards the smaller of the cations; for example, in $CdGeAs_2$, the As anion is closer to the two Ge cations. The lattice constants for many of the chalcopyrites have been measured and/or predicted by Abrahams and Bernstein.[29,30,31] Also, they obtained an empirical equation for lattice parameter x which is given by,

$$x = \frac{1}{2} - \sqrt{\frac{c^2}{32a^2} - \frac{1}{16}} \qquad \text{(F1)}$$

To generate the crystal structure in crystal coordinates (which are also rectangular), the following formulas[32] could be used (with $CdGeAs_2$ again as the example):

$$\text{Cd:}\quad [(0,0,0;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) + (0,0,0;0,\tfrac{1}{2},\tfrac{1}{4})]\cdot(a,a,c) + (la,ma,nc) \qquad \text{(F2)}$$

$$\text{Ge:}\quad [(0,0,0;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) + (0,0,\tfrac{1}{2};0,\tfrac{1}{2},\tfrac{3}{4})]\cdot(a,a,c) + (la,ma,nc) \qquad \text{(F3)}$$

$$\text{As:}\quad [(0,0,0;\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) + (x,\tfrac{1}{4},\tfrac{1}{8};\bar{x},\tfrac{3}{4},\tfrac{1}{8};\tfrac{3}{4},x,\tfrac{7}{8};\tfrac{1}{4},\bar{x},\tfrac{7}{8})]\cdot(a,a,c) + (la,ma,nc) \qquad \text{(F4)}$$

where $\bar{x} = 1-x$ and l,m and n are integers. These formulas result in four Cd atoms, four Ge atoms, and eight As atoms per unit cell; in other words, there are four formula units of $CdGeAs_2$ per unit cell. However, an equivalent structure can be generated by considering only two formula units. The corresponding relations are

$$\text{Cd:}\quad (0,0,0;0,\tfrac{1}{2},\tfrac{1}{4})\cdot(a,a,c) + ([2l-n]a/2,[2m+n]a/2,nc/2) \qquad \text{(F5)}$$

$$\text{Ge:}\quad (\tfrac{-1}{2},\tfrac{1}{2},0;\tfrac{-1}{2},0,\tfrac{1}{4})\cdot(a,a,c) + ([2l-n]a/2,[2m+n]a/2,nc/2) \qquad \text{(F6)}$$

$$\text{As:}\quad (-x,\tfrac{1}{4},\tfrac{1}{8};\tfrac{-1}{4},[\tfrac{1}{2}+x],\tfrac{3}{8};\bar{x},\tfrac{3}{4},\tfrac{1}{8};\tfrac{-3}{4},[\tfrac{1}{2}-x],\tfrac{3}{8})\cdot(a,a,c) + ([2l-n]a/2,[2m+n]a/2,nc/2)\ . \qquad \text{(F7)}$$

This translation vector between 'unit cells',

$$a(l\hat{x} + m\hat{y}) + n(\tfrac{-a}{2}\hat{x} + \tfrac{a}{2}\hat{y} + \tfrac{c}{2}\hat{z}) \qquad \text{(F8)}$$

corresponds to a twofold screw axis.

A Fortran program was written (listed in Figure F1) to generate a list of atom positions, compatible with the list required by the energy band program, by using Equations F1, F5, F6, and F7. As an example, a portion of the list of atoms for $CdGeAs_2$ is given in Table F1 for a = 5.94Å and c = 11.22Å. From this list, it is easy to verify the interatomic distances of 2.629Å for Cd-As and 2.429Å for Ge-As.

```
:UDD:EWBANK:GEOMETRY.DIR:CPGEOM.FR

C                                   CPGEOM.FR
C.
C       ROUTINE TO GENERATE CHALCOPYRITE ATOM POSITIONS,ATOMIC NUMBERS,
C       ENUMERATION OF ATOMS IN UNIT CELL, ETC  IN DATA FILE
C       TO BE INPUT FOR EBAND.FR
C.
C       CHALCOPYRITES HAVE A TETRAHEDRAL STRUCTURE:
C               A(II)B(IV)C2(V)     [LIKE A III-V COMPOUND]
C               OR  A(I)B(III)C2(VI)   [LIKE A II-VI COMPOUND]
C       USE THE FOLLOWING TO GENERATE THE CRYSTAL STRUCTURE:
C       CONSIDER 2 FORMULA UNITS (AN 'A' ATOM AT THE ORIGIN,
C       1 COMPLETE TETRAHEDRAL ABOUT A 'C' ATOM, AND 3 OTHER
C       ADJACENT 'C' ATOMS) AND THE TRANSLATION VECTOR:
C               ((L*A+N*A/2),(M*A-N*A/2),(N*C/2))
C       WHERE L,M,N ARE INTEGERS AND A & C ARE THE LATTICE CONSTANTS
C       NOTE: THE 'C' ATOM IS DISPLACED FROM CENTER OF TETRAHEDRAL
C       BY DISTANCE DELX TOWARD THE SMALLER TWO 'B' ATOMS
C       X=FCN(A,C) FORMULA FROM ABRAHAMS & BERNSTEIN,J CHEM PHYS,
C       VOL 55,NO 2,(7/15/71),P796
C.
C       INPUT PARAMETERS:   (FROM CONSOLE)
C               1) LATTICE CONSTANTS (A & C)
C               2) ATOMIC SYMBOL & ATOMIC NUMBER FOR 3 TYPES OF ATOMS
C                  IN UNIT CELL
C               3) NCELL --- DETERMINES NUMBER OF UNIT CELLS TO CONSTRUCT
C               4) DMAX --- MAXIMUM DISTANCE FOR ATOMS TO BE STORED ON FILE
C       OUTPUT PARAMETERS:
C               DATA FILE --- "?GEOM←GAAS" --- CONTAINS THE FOLLOWING
C                       INFORMATION ON EACH RECORD:
C                       1) RUNNING INDEX OF NUMBER OF ATOMS IN FILE
C                       2) ATOMIC SYMBOL
C                       3) ATOMIC NUMBER
C                       4) ENUMERATION
C                       5) ATOMIC POSITION IN RECTANGULAR COORDINATES
C                       6) DISTANCE FROM ORIGIN
C                   FORMAT IS (1X,I3,3X,A2,2(3X,I2),3(3X,E14.7),6X,E14.7)
C       EXTERNAL REFERENCES:
C               SUBROUTINE CPUC
C                       FUNCTION DOTPD
C               SUBROUTINE CPSORT
C.
C.
        COMMON/ATMPOS/NENUM(800),RR(4,800),INDEX
        DIMENSION  IATOM(3),JATOM(3)
        PARAMETER IN=11,IOUT=10,NPAGE=27*400K+12
C..
        WRITE (IOUT) NPAGE
        WRITE (IOUT,1)
1       FORMAT (25X," CHALCOPYRITE GEOMETRY")
100     WRITE (IOUT,110)
110     FORMAT (/," ENTER LATTICE CONSTANTS: ",/,5X,"A = ",Z)
```

Figure F1. Computer listings for chalcopyrite crystal structure program

```
:UDD:EWBANK:GEOMETRY.DIR:CPGEOM.FR

        READ FREE (IN,ERR=100) A
        IF (A.LT.4.0 .OR. A.GT.7.0) GOTO 100
        WRITE (IOUT,130)
130     FORMAT (5X,"C = ",Z)
        READ FREE (IN,ERR=100) C
        IF (C.LT.9.0 .OR. C.GT.13.0) GOTO 100
140     WRITE (IOUT,145)
145     FORMAT (5X,"X (ENTER 0 IF UNKNOWN) = ",Z)
        READ FREE (IN,ERR=140) X
        IF (X.NE.0.0 .AND. (X.LT.0.15 .OR. X.GT.0.35)) GOTO 140
        IF (X.EQ.0.0) X=.5-SQRT(C*C/A/A/32-1./16)
        DELX=(X-.25)*A
C.
150     WRITE (IOUT,160)
160     FORMAT (/," SPECIFY 3 TYPES OF ATOMS IN UNIT CELL IN ORDER")
        DO 170 I=1,3
180     WRITE (IOUT,185) I
185     FORMAT (" ENTER ATOMIC SYMBOL FOR ATOM #",I1,":  ",Z)
        READ (IN,187,ERR=180) IATOM(I)
187     FORMAT (A2)
190     WRITE (IOUT,195) I
195     FORMAT (" ENTER ATOMIC NUMBER FOR ATOM #",I1,":  ",Z)
        READ FREE (IN,ERR=190) JATOM(I)
        IF (JATOM(I).LT.5 .OR. JATOM(I).GT.89) GOTO 190
170     CONTINUE
C.
10      WRITE (IOUT,15)
15      FORMAT (/," ENTER NCELL: ",Z)
        READ FREE (IN,ERR=10) NCELL
        IF (NCELL.LT.0 .OR. NCELL.GT.10) GOTO 10
20      WRITE (IOUT,25)
25      FORMAT (/," ENTER MAXIMUM DISTANCE FOR INCLUDING ATOMS: ",Z)
        READ FREE (IN,ERR=20) DMAX
        IF (DMAX.LE.0.0 .OR. DMAX.GT.100.0) GOTO 20
C..
        INDEX=0
        DO 30 L=-NCELL,+NCELL
        DO 30 M=-NCELL,+NCELL
        DO 30 N=-NCELL,+NCELL
C..
C               FIND COORDINATES OF EACH ATOM IN UNIT CELL SPECIFIED
C               BY L,M, & N
        CALL CPUC(L,M,N,DMAX,A,C,DELX)
30      CONTINUE
C..
C.              SORT & WRITE TO FILE
C..
        CALL CPSORT(IATOM,JATOM)
C.
        STOP...
        END
```

Figure F1. (Continued)

```
:UDD:EWBANK:GEOMETRY.DIR:CPSORT.FR

        SUBROUTINE CPSORT(IATOM,JATOM)
C.
C       ROUTINE TO SORT ATOM POSITIONS
C       ACCORDING TO DISTANCE FROM ORIGIN
C.
C       INPUT PARAMETERS:
C               IATOM --- ATOMIC SYMBOL FOR EACH OF 3 TYPES OF
C                         ATOMS IN UNIT CELL
C               JATOM --- ATOMIC NUMBER FOR EACH OF 3 TYPES OF
C                         ATOMS IN UNIT CELL
C       OUTPUT PARAMETERS:
C               DATA FILE---EG.---"?GEOM←CDGEAS"---SORTED ATOM POSITIONS
C       EXTERNAL REFERENCES:
C               COMMON/ATMPOS/....
C.
        COMMON/ATMPOS/NENUM(800),RD(4,800),JMAX
        DIMENSION IATOM(3),R(4),JATOM(3),IFILE(7)
        DATA IFILE/'?G','EO','M←',3*'XX',0/
        PARAMETER IN=11,IOUT=10
C.
C               SORT IN INCREASING DISTANCE FROM ORIGIN
        DO 110 J=2,JMAX
        IF (RD(4,J).GE.RD(4,(J-1))) GO TO 110
        DO 50 K=1,J
50      IF (RD(4,J).LE.RD(4,K)) GO TO 60
60      NE=NENUM(J)
        DO 70 I=1,4
70      R(I)=RD(I,J)
        M=J
        DO 90 L=K,J
        NENUM(M)=NENUM(M-1)
        DO 80 I=1,4
80      RD(I,M)=RD(I,(M-1))
90      M=M-1
        NENUM(K)=NE
        DO 100 I=1,4
100     RD(I,K)=R(I)
110     CONTINUE
C.
C               NOW WRITE OUT SORTED ATOM POSITIONS
        DO 115 I=1,3
        J=I+3
115     IFILE(J)=IATOM(I)
        CALL FDELETE (IFILE)
        OPEN 7, IFILE
        J=1
120             K=2
                IF (NENUM(J).LT.3) K=1
                IF (NENUM(J).GT.4) K=3
        WRITE (7,130) J,IATOM(K),JATOM(K),NENUM(J),(RD(I,J),I=1,4)
130     FORMAT (1X,I3,3X,A2,2(3X,I2),3(3X,E14.7),6X,E14.7)
```

Figure F1. (Continued)

:UDD:EWBANK:GEOMETRY.DIR:CPSORT.FR

```
      J=J+1
      IF (J.LE.JMAX) GO TO 120
      CLOSE 7
C.
      RETURN
      END
```

:UDD:EWBANK:GEOMETRY.DIR:CPUC.FR

```
      SUBROUTINE CPUC(L,M,N,DMAX,A,C,DELX)
C..
C     ROUTINE TO GENERATE COORDINATES OF ALL 8 ATOMS IN 'UNIT CELL'
C      SPECIFIED BY L,M, & N FOR CHALCOPYRITE COMPOUND.
C.
C     INPUT PARAMETERS:
C             L,M,N --- DETERMINES WHICH 'UNIT CELL'
C             DMAX --- MAXIMUM DISTANCE FOR ATOM TO BE FROM ORIGIN
C                              AND STILL GET STORED IN COMMON BLOCK
C             A,C,DELX --- LATTICE PARAMETERS
C     OUTPUT PARAMETERS:
C             NONE
C     EXTERNAL REFERENCES:
C             FUCNCTION DOTPD
C             COMMON/ATMPOS/....
      DIMENSION R(3),X(4),Y(4),Z(4)
      DATA X,Y,Z/.0,.0,-.5,-.5,.0,+.5,+.5,.0,.0,+.5,.0,+.5/
      COMMON/ATMPOS/NENUM(800),RR(4,800),INDEX
C.
      DO 60 J=1,2
             K=0
50           K=K+1
             R(1)=L*A-N*A/2-(J-1)*A/4+X(K)*A
             IF (J.EQ.2 .AND. (K.EQ.1 .OR. K.EQ.3))
     &               R(1)=R(1)-((-1.)**(K/2))*DELX
             R(2)=M*A+N*A/2+(J-1)*A/4+Y(K)*A
             IF (J.EQ.2 .AND. (K.EQ.2 .OR. K.EQ.4))
     &               R(2)=R(2)+((-1.)**((K-1)/2))*DELX
             R(3)=N*C/2+(J-1)*C/8+Z(K)*C/2
             D=SQRT(DOTPD(R,R,3))
             IF (D.GT.DMAX) GOTO 30
             INDEX=INDEX+1
      DO 55 I=1,3
55    RR(I,INDEX)=R(I)
      RR(4,INDEX)=D
      NENUM(INDEX)=(J-1)*4+K
      IF (K.LT.4) GOTO 50
60    CONTINUE
C.
30    RETURN
      END
```

Figure F1. (Continued)

Table F1. List of Atom Positions for the Chalcopyrite, $CdGeAs_2$. [Listed from left to right: Index, Atomic Symbol, Atomic Number, Enumeration, Coordinates (x,y,z), Distance (Å)]

:UDD:EWBANK:GEOMETRY.DIR:?GEOM←CDGEAS

1	CD	48	1	.0000000E 00	.0000000E 00	.0000000E 00	.0000000E 00
2	AS	33	7	.1655168E 01	-.1485001E 01	.1402499E 01	.2629030E 01
3	AS	33	5	-.1655167E 01	.1485000E 01	.1402499E 01	.2629030E 01
4	AS	33	8	-.1485000E 01	-.1655167E 01	-.1402501E 01	.2629030E 01
5	AS	33	6	.1485000E 01	.1655167E 01	-.1402501E 01	.2629030E 01
6	GE	32	4	-.2969999E 01	.0000000E 00	.2804999E 01	.4085205E 01
7	CD	48	2	.0000000E 00	.2969999E 01	.2804999E 01	.4085205E 01
8	GE	32	4	.2970000E 01	.0000000E 00	.2804999E 01	.4085207E 01
9	GE	32	4	.0000000E 00	.2970000E 01	-.2805000E 01	.4085207E 01
10	GE	32	4	.0000000E 00	-.2969999E 01	-.2805000E 01	.4085207E 01
11	CD	48	2	.2969999E 01	.0000000E 00	-.2805000E 01	.4085207E 01
12	CD	48	2	.0000000E 00	-.2970000E 01	.2804999E 01	.4085207E 01
13	CD	48	2	-.2970000E 01	.0000000E 00	-.2805000E 01	.4085207E 01
14	GE	32	3	.2970000E 01	.2969999E 01	.0000000E 00	.4200212E 01
15	GE	32	3	-.2969999E 01	.2969999E 01	.0000000E 00	.4200212E 01
16	GE	32	3	-.2969999E 01	-.2970000E 01	.0000000E 00	.4200212E 01
17	GE	32	3	.2970000E 01	-.2970000E 01	.0000000E 00	.4200213E 01
18	AS	33	8	.1485001E 01	.1314832E 01	.4207499E 01	.4651563E 01
19	AS	33	7	-.1314832E 01	.1485000E 01	-.4207500E 01	.4651563E 01
20	AS	33	5	.1314832E 01	-.1485000E 01	-.4207500E 01	.4651563E 01
21	AS	33	6	-.1485000E 01	-.1314833E 01	.4207499E 01	.4651563E 01
22	AS	33	5	.4204832E 01	.1485000E 01	.1402499E 01	.4746786E 01
23	AS	33	8	-.1485000E 01	.4204832E 01	-.1402501E 01	.4746786E 01
24	AS	33	7	-.4204831E 01	-.1485001E 01	.1402499E 01	.4746786E 01
25	AS	33	6	.1485000E 01	-.4204832E 01	-.1402501E 01	.4746786E 01
26	AS	33	8	.4455000E 01	-.1655167E 01	-.1402501E 01	.4955155E 01
27	AS	33	5	-.1655167E 01	-.4455000E 01	.1402499E 01	.4955155E 01
28	AS	33	6	-.4455000E 01	.1655167E 01	-.1402501E 01	.4955155E 01
29	AS	33	7	.1655168E 01	.4454999E 01	.1402499E 01	.4955157E 01
30	GE	32	3	.9536743E-06	-.9536743E-06	.5610000E 01	.5609999E 01
31	GE	32	3	.0000000E 00	.0000000E 00	-.5610000E 01	.5609999E 01
32	CD	48	1	.5940000E 01	.0000000E 00	.0000000E 00	.5939999E 01
33	CD	48	1	.0000000E 00	.5940000E 01	.0000000E 00	.5939999E 01
34	CD	48	1	.0000000E 00	-.5940000E 01	.0000000E 00	.5939999E 01
35	CD	48	1	-.5940000E 01	.0000000E 00	.0000000E 00	.5939999E 01

APPENDIX G

Tl_3AsSe_3 CRYSTAL STRUCTURE

The trigonal sulfosalt, Tl_3AsSe_3 or TAS, has a point group of 3m and a space group of R3m. The lattice parameters, a, c, x and z, which are needed to specify the atomic positions, are given in Table G1.[33] The generation of the structure in hexagonal crystal coordinates was accomplished with the following formulas:[34]

$$\text{Tl \& Se: } [(0,0,0;\tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3}) + (x,\bar{x},z;x,2x,z;2\bar{x},\bar{x},z)]\cdot(a,a,c) + (la,ma,nc) \qquad \text{(G1)}$$

$$\text{As: } [(0,0,0;\tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3}) + (0,0,z)]\cdot(a,a,c) + (la,ma,nc) \qquad \text{(G2)}$$

where $\bar{x} = 1-x$ and l, m and n are integers. Also implicit in the above formulas are the number of each kind of atom in a unit cell. There are nine Tl and Se atoms along with three As atoms per unit cell. In other words, the unit cell is composed of three formula units of Tl_3AsSe_3. To obtain the atom positions in rectangular coordinates (x_r, y_r, z_r), a transformation from the hexagonal crystal coordinates (x_c, y_c, z_c), was also necessary;

$$\begin{aligned} x_r &= x_c + y_c\cos\theta \\ y_r &= y_c\sin\theta \\ z_r &= z_c \end{aligned} \qquad \text{(G3)}$$

where $\theta = 2\pi/3$.

Table G1

Lattice Parameters for Tl_3AsSe_3

a = 9.897Å
c = 7.094Å

	Tl	Se	As
x	.2052	.2052	0
z	0	.4480	.745

The above formulas and lattice parameters were incorporated into a Fortran program to generate a list of atom positions representing the crystal geometry. A portion of this list is shown in Table G2. The interatomic distances associated with this list are 2.206Å for As-Se, 3.178Å and 3.439Å for Se-Tl, and 3.651Å for As-Tl. The resulting crystal structure is shown in Figure G1, where a slight projection of the z-axis into the x-y plane has been used. Each formula unit consists of an equilateral triangle of three Se atoms in the x-y plane with an As atom approximately in the center of this triangle, only slightly displaced in the z direction toward an equilateral triangle of Tl atoms. The two triangles, Se and Tl, are parallel and have the same orientation, lying one on top of the other as illustrated. The unit cell is comprised of three such formula units arranged in a helix whose axis runs parallel to the z axis, which is a threefold screw axis described by the translation vector,

$$a(l\hat{x} + m\hat{y}) + n(\frac{1}{2\sqrt{3}}\hat{x} - \frac{a}{2}\hat{y} + \frac{c}{3}\hat{z}). \qquad \text{(G4)}$$

Figure G2. List of Atom Positions for the Sulfosalt, Tl_3AsSe_3. [Listed from left to right: Index, Atomic Symbol, Atomic Number, Enumeration, Coordinates (x,y,z,) Distance (Å)]

:UDD:EWBANK:GEOMETRY.DIR:?TAS←GEOM

1	AS	33	1	.4768369E-06	.8259063E-06	.0000000E 00	.9536742E-06
2	SE	34	4	.2190899E 01	.3516674E-05	.2577486E 00	.2206007E 01
3	SE	34	3	-.1095450E 01	-.1897377E 01	.2577406E 00	.2206013E 01
4	SE	34	2	-.1095454E 01	.1897380E 01	.2577406E 00	.2206015E 01
5	TL	81	7	.2190899E 01	.3516674E-05	-.2920363E 01	.3650829E 01
6	TL	81	6	-.1095450E 01	-.1897377E 01	-.2920363E 01	.3650831E 01
7	TL	81	5	-.1095454E 01	.1897380E 01	-.2920363E 01	.3650833E 01
8	TL	81	5	.1753767E 01	-.3037606E 01	.1808970E 01	.3946533E 01
9	TL	81	6	.1753763E 01	.3037621E 01	.1808970E 01	.3946545E 01
10	TL	81	7	-.3507541E 01	.8583069E-05	.1808970E 01	.3946545E 01
11	SE	34	2	.1753767E 01	-.3037606E 01	-.2106917E 01	.4091601E 01
12	SE	34	3	.1753763E 01	.3037621E 01	-.2106917E 01	.4091690E 01
13	SE	34	4	-.3507541E 01	.8583069E-05	-.2106917E 01	.4091692E 01
14	TL	81	7	.2190899E 01	.3516674E-05	.4173635E 01	.4713730E 01
15	TL	81	6	-.1095450E 01	-.1897377E 01	.4173635E 01	.4713731E 01
16	TL	81	5	-.1095454E 01	.1897380E 01	.4173635E 01	.4713733E 01
17	TL	81	7	-.6583157E 00	-.4934980E 01	-.5556965E 00	.5009617E 01
18	TL	81	5	-.3944674E 01	-.3037609E 01	-.5556965E 00	.5009622E 01
19	TL	81	6	.4602985E 01	-.1897382E 01	-.5556965E 00	.5009624E 01
20	TL	81	5	.4602983E 01	.1897390E 01	-.5556965E 00	.5009624E 01
21	TL	81	6	-.3944677E 01	.3037610E 01	-.5556965E 00	.5009624E 01
22	TL	81	7	-.6583214E 00	.4935004E 01	-.5556965E 00	.5009635E 01
23	SE	34	4	-.6583157E 00	-.4934980E 01	.2622411E 01	.5627122E 01
24	SE	34	2	-.3944674E 01	-.3037609E 01	.2622411E 01	.5627126E 01
25	SE	34	3	.4602985E 01	-.1897382E 01	.2622411E 01	.5627127E 01
26	SE	34	2	.4602983E 01	.1897390E 01	.2622411E 01	.5627129E 01
27	SE	34	3	-.3944677E 01	.3037610E 01	.2622411E 01	.5627129E 01
28	SE	34	4	-.6583214E 00	.4935004E 01	.2622411E 01	.5627138E 01
29	SE	34	2	.1753767E 01	-.3037606E 01	.4987081E 01	.6097025E 01
30	SE	34	3	.1753763E 01	.3037621E 01	.4987081E 01	.6097032E 01
31	SE	34	4	-.3507541E 01	.8583069E-05	.4987081E 01	.6097033E 01
32	AS	33	1	.5698430E 01	.6675720E-05	.2364663E 01	.6169500E 01
33	AS	33	1	.2849217E 01	.4934982E 01	-.2364667E 01	.6169501E 01
34	AS	33	1	-.2849217E 01	-.4934992E 01	.2364663E 01	.6169580E 01
35	AS	33	1	.2849225E 01	-.4934991E 01	-.2364667E 01	.6169591E 01
36	AS	33	1	-.2849226E 01	.4934995E 01	.2364663E 01	.6169594E 01
37	AS	33	1	-.5698443E 01	.4768372E-05	-.2364667E 01	.6169594E 01

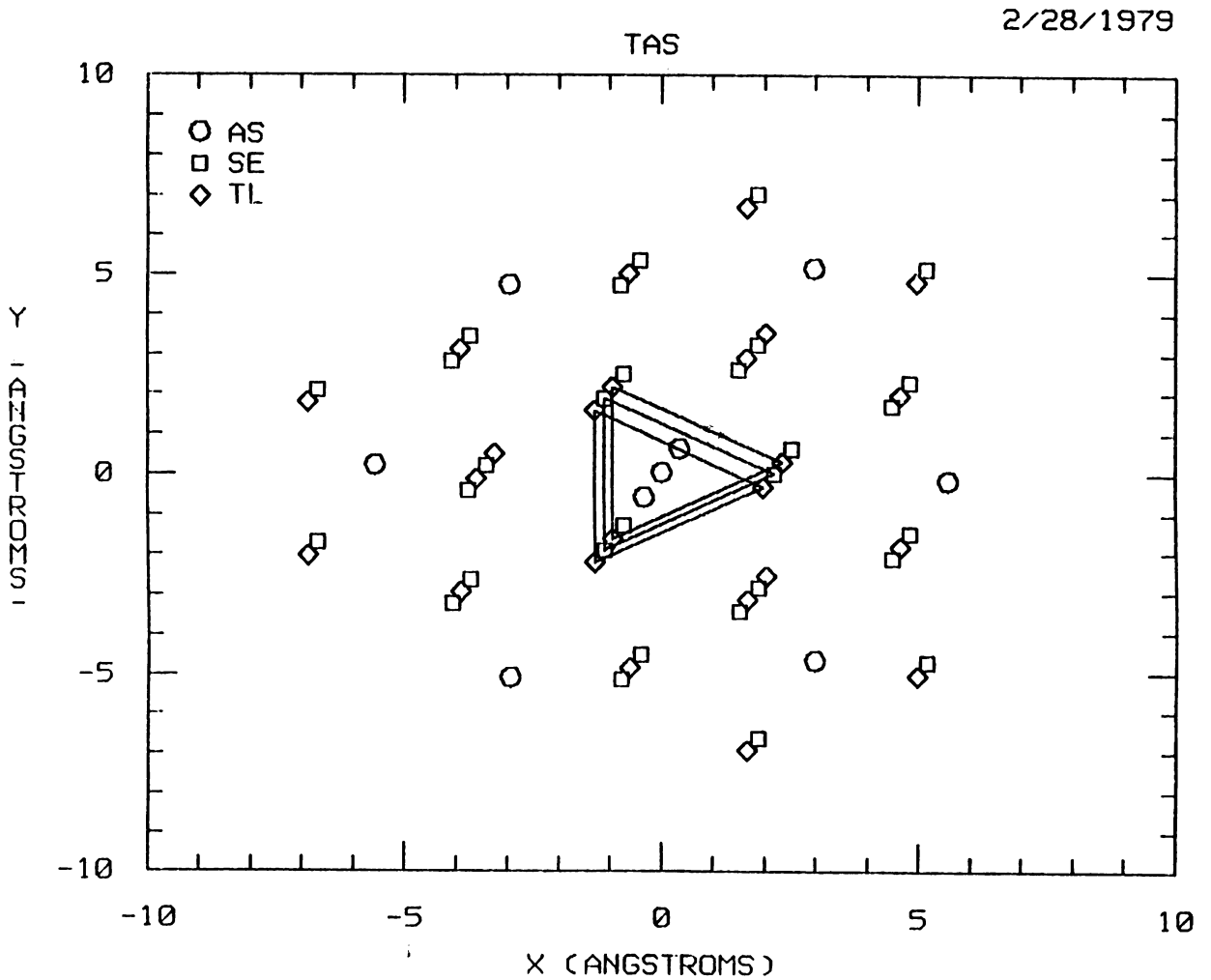


Figure G1. Crystal structure of Tl_3AsSe_3

APPENDIX H

SUBROUTINE FOR CHADI AND COHEN'S FIRST NEAREST NEIGHBOR PARAMETERS

Listed in Figure H1 is the subroutine used to assign numerical values to the various Slater-Koster type matrix elements of the Hamiltonian between pairs of atomic orbitals for Si, Ge, GaAs and ZnSe. The first nearest neighbor parameters were obtained from Tables 3 and 5 of Chadi and Cohen.[1] Recall that a set of these parameters and the crystal geometry are the only inputs required to solve the band structure (energy bands and density of states) problem.

```
:UDD:EWBANK:EBAND.DIR:CCSSME.FR

      SUBROUTINE SSIAME(R1,R0,JNU,IMU,JATOM,IATOM,SSME)
C.
C     ROUTINE TO EVALUATE THE SOLID STATE MATRIX ELEMENTS FOR NEAREST
C     NEIGHBOR SI,GE,GAAS OR ZNSE USING THE CHADI-COHEN PARAMETERS.
C     CHOOSE SI,GE,,GAAS OR ZNSE BY ATOMIC NUMBER.
C     REFERENCE:  CHADI & COHEN, PHYS.STAT.SOL.(B),68,P405,(1975).
C.
      DIMENSION R1(3),R0(3),D(3)
C.
      IF (IATOM.EQ.30 .OR. IATOM.EQ.34) GOTO 1
      IF (IATOM.EQ.14) GOTO 2
      IF (IATOM.EQ.32) GOTO 3
C.
C             GAAS (TABLE 5)
       NATOM0=33
       NATOM1=31
       ES0=-6.01
      ES1=-4.79
      EP0=+0.19
      EP1=+4.59
       VXY=+4.72
      VXX=+0.93
      VSS=-7.00
      VS0P=+7.28
      VS1P=+3.70
      GOTO 4
C             ZNSE (TABLE 5)
1      NATOM0=34
       NATOM1=30
       ES0=-8.92
      ES1=-0.28
      EP0=+0.12
      EP1=+7.42
       VXY=+4.38
      VXX=+0.96
      VSS=-6.14
      VS0P=+5.47
      VS1P=+4.73
      GOTO 4
C             SI (TABLE 3)
2     NATOM0=NATOM1=14
      ES0=ES1=-4.03
      EP0=EP1=+7.20+ES0
      VXY=+7.51
      VXX=+3.17
      VSS=-8.13
      VS0P=VS1P=+5.88
      GOTO 4
C             GE (TABLE 3)
3     NATOM0=NATOM1=32
      ES0=ES1=-5.79
```

Figure H1. Computer listings of subroutine for Chadi and Cohen's first nearest neighbor parameters

```
:UDD:EWBANK:EBAND.DIR:CCSSME.FR

        EP0=EP1=+8.41+ES0
        VXY=+6.82
        VXX=+2.62
        VSS=-6.78
        VS0P=VS1P=+5.31
C.
4       IF (IATOM.NE.NATOM1 .AND. IATOM.NE.NATOM0) GOTO 100
        IF (JATOM.NE.NATOM1 .AND. JATOM.NE.NATOM0) GOTO 100
C.
        SSME=0.0
        SIGN=1.0
        DO 25 I=1,3
25      D(I)=R0(I)-R1(I)
        IF (DOTPD(D,D,3).GT.0.1) GOTO 10          ;SAME ATOM?
        IF (IMU.NE.JNU) GOTO 200                  ;ORTHOGONAL
        IF (IATOM.EQ.NATOM0 .AND. IMU.EQ.1) SSME=ES0     ;ES0
        IF (IATOM.EQ.NATOM1 .AND. IMU.EQ.1) SSME=ES1     ;ES1
        IF (IATOM.EQ.NATOM0 .AND. IMU.GE.2) SSME=EP0     ;EP0
        IF (IATOM.EQ.NATOM1 .AND. IMU.GE.2) SSME=EP1     ;EP1
        GOTO 20
C.
10      IF (IMU.GE.2 .AND. JNU.GE.2) SSME=VXY/4          ;VXY
        IF (IMU.EQ.JNU) SSME=VXX/4                       ;VXX
        IF (IMU.EQ.1 .AND. JNU.EQ.1) SSME=VSS/4          ;VSS
        IF (SSME.NE.0.0 .AND. SSME.NE.(VXY/4)) GOTO 200
C.
C               NEED TO DETERMINE SIGN FOR VXY,VS0P & VS1P
        IF ((D(IMU-1)*D(JNU-1)).LT.0.0) SIGN=-1.0        ;SIGN FOR VXY
        IF (SSME.NE.0.0) GOTO 200
        SIGN=1.
        IF (IMU.EQ.1) SSME=VS1P/4                        ;VS1P
        IF (IMU.NE.1) GOTO 30
        IF (D(JNU-1).LT.0.0) SIGN=-1.                    ;SIGN FOR VS1P
30      IF (JNU.EQ.1) SSME=VS0P/4                        ;VS0P
        IF (JNU.NE.1) GOTO 20
        IF (D(IMU-1).GT.0.0) SIGN=-1.                    ;SIGN FOR VS0P
C.
20      IF (SSME.NE.0.0) GOTO 200
100     PAUSE " ERROR --- CHADI-COHEN PARAMETERS"
        STOP..
C.
200     SSME=SIGN*SSME
        RETURN
        END
```

Figure H1. (Continued)

APPENDIX I

SIMPLIFICATION OF THE 1ST ORDER BOND POLARIZATION FORMULA

Equation 75 implies that the first order polarization per sp^3 hybrid bond is

$$\vec{p} = \frac{\gamma^2 e^2 V_2^{\,2}}{2(V_2^{\,2} + V_3^{\,2})^{3/2}} \vec{d}(\vec{d}\cdot\vec{\xi}) = A\vec{d}(\vec{d}\cdot\vec{\xi}) \qquad \text{(I1)}$$

where $\vec{\xi}$ is the electric field vector and $\vec{d}$ is the vector distance from cation to anion. By evaluating the geometric factor when summed over all bonds in the unit cell for one specific direction of electric field (choose $\vec{\xi} = \xi_z \hat{z}$) which gives a principal susceptability,

$$\sum_{\text{bonds}} \vec{d}(\vec{d}\cdot\vec{\xi}) = \xi_z \sum_{\text{bonds}} (d_x d_z \hat{x} + d_y d_z \hat{y} + d_z^{\,2} \hat{z}) \qquad \text{(I2)}$$

Now, when considering tetrahedrally coordinated crystals, for each term of the form $(+|d_x|d_z\ \hat{x})$ or $(+|d_y|d_z\ \hat{y})$, there will be corresponding terms of $(-|d_x|d_z\ \hat{x})$ and $(-|d_y|d_z\ \hat{y})$ which cancel the former terms. However, similar pairs of the z component terms do not cancel; that is,

$$(+|d_z|)^2\ \hat{z} + (-|d_z|)^2\ \hat{z} = 2d_z^{\,2}\ \hat{z}. \qquad \text{(I3)}$$

Therefore, the summation in Equation I2 can neglect components perpendicular to the electric field or

$$\sum_{\text{bonds}} \vec{d}(\vec{d}\cdot\vec{\xi}) = \xi_z \sum_{\text{bonds}} d_z^{\,2}\,\hat{z} \tag{I4}$$

which can be written as

$$\sum_{\text{bonds}} |\vec{d}|(\vec{d}\cdot\vec{\xi}) = \sum_{\text{bonds}} d^2\xi\,\cos^2\theta \tag{I5}$$

where θ is the angle between $\vec{\xi}$ and $\vec{d}$. It is this form that appears in the literature,[16,18] but the result is used <u>before</u> the summation over bonds is performed.

Further simplification is realized by considering a "regular" tetrahedral structure. Then $\hat{d} = (\pm\,\hat{x} \pm \hat{y} \pm \hat{z})/\sqrt{3}$ and, again letting $\vec{\xi} = \xi_z\,\hat{z}$, the geometric factor from Equation I4 reduces to

$$\sum_{\text{bonds}} \hat{d}(\hat{d}\cdot\hat{\xi}) = \sum_{\text{bonds}} \left(\pm\,\frac{1}{\sqrt{3}}\right)^2 \hat{z}. \tag{I6}$$

Consequently, there is a geometric factor of one-third associated with each bond in a "regular" tetrahedron.

LIST OF REFERENCES

LIST OF REFERENCES

1. D.J. Chadi and M.L. Cohen, Phys. Stat. Sol. 68, 405 (1975).

2. J.C. Slater and G.F. Koster, Phys. Rev. 94, 1498 (1954).

3. A. Nussbaum, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1965), Vol. 18, p. 165.

4. A. Zunger, Phys. Rev. B 17, 626 (1978).

5. G. Arfken, Mathematical Methods for Physicists, (Academic Press, New York, 1970), p. 159.

6. W.A. Harrison, Festkorperprobleme XVII, 135 (1977).

7. W.A. Harrison, private communication.

8. F. Herman and S. Skillman, Atomic Structure Calculations, (Prentice-Hall, Englewood Cliffs, N.J., 1963).

9. E.A. Kraut, private communication.

10. W.A. Harrison, Solid State Theory (McGraw-Hill, New York, 1970), pp. 25-40.

11. C. Kittel, Introduction to Solid State Physics (John Wiley and Sons, Inc., New York, 1971), p. 211.

12. G. Gilat and L.J. Raubenheimer, Phys. Rev. 144, 390 (1966).

13. J. Rath and A.J. Freeman, Phys. Rev. B 11, 2109 (1975).

14. An-Ban Chen, Phys. Rev. B 16, 3291 (1977).

15. M. Buchkeit and P.D. Loly, Amer. J. Phys. 40, 289 (1972).

16. W.A. Harrison, Phys. Rev. B 8, 4487 (1973).

17. W.A. Harrison and S. Ciraci, Phys. Rev. B 10, 1516 (1974).

18. M.E. Lines and J.V. Waszczak, J. Appl. Phys. 48, 1395 (1977).

19. G. Arfken, op. cit. p. 262.

20. G.R. Fowles, Introduction to Modern Optics (Holt, Rinehart, and Winston, New York, 1968), pp. 168-190.

21. G.D. Boyd, E. Buehler and F.G. Storz, Appl. Phys. Lett. 18, 301 (1971).

22. G.D. Boyd, H. Kasper and J.H. McFee, IEEE J. Quantum Electron. QE-7, 563 (1971).

23. G.D. Boyd, E. Buehler, F.G. Storz and J.H. Wernick, IEEE J. Quantum Electron. QE-8, 419 (1972).

24. G.D. Boyd, H. Kasper, J.H. McFee and F.G. Storz, IEEE J. Quantum Electron. QE-8, 900 (1972).

25. S.H. Wemple, J.D. Gabbe and G.D. Boyd, J. Appl. Phys. 46, 3597 (1975).

26. J.F. Nye, Physical Properties of Crystals (Oxford, London, 1975), pp. 235-259.

27. D.S. Saxon, Elementary Quantum Mechanics (Holden-Day, San Francisco, 1968), pp. 268-275.

28. G. Arfken, op. cit., pp. 554-558.

29. S.C. Abrahams and J.L. Bernstein, J. Chem. Phys. 55, 796 (1971).

30. S.C. Abrahams and J.L. Bernstein, J. Chem. Phys. 52, 5607 (1970).

31. S.C. Abrahams and J.L. Bernstein, J. Chem. Phys. 59, 5415 (1973).

32. International Tables for X-Ray Crystallography, Vol. 1, edited by N. Henry and K. Loundale (Kynoch Press, Birmingham, England, 1965), p. 212.

33. H. Y-P Hong, J.C. Mikkelsen and G.W. Roland, Mat. Res. Bull. 9, 365 (1974).

34. International Tables for X-Ray Crystallography, op. cit., p. 266.