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ABSTRACT

In this calculation the tight binding method as developed by Slater and Koster, Howland, and Knox is used to investigate the valence bands in NaI. An empirical approach based upon the model of J.C. Phillips is used to obtain the lowest conduction band. Sufficient parameters are used to have a convergent value for the energy of the valence band.

In previous calculations on the various alkali-halides it has not been customary to use trial wave functions which are eigenfunctions of the atomic potentials used to construct the crystal potential. This defect is found in the work of Casella, Shockley, and Howland. In the present calculation, trial wave functions and potentials are obtained by solving the Hartree-Fock-Slater modified equations. In this approximation the crystal potential is simply a sum of the ionic potentials which are centered about their proper sites in the crystal.

The mixing of levels of different quantum numbers is included when allowed by symmetry. It is found that the effects of this are strongly dependent upon lattice parameter. Previously these effects had been included by Howland. Spin-orbit effects are also included and appear for the first time in a tight binding calculation for an alkali halide except for the work on LiCl by the author. In NaI this effect is large. A splitting between $\Gamma_6^- - \Gamma_8^-$ of 1.25 ev is obtained for the 5p band. The band width is seen to vary from 1.75 ev for the lattice parameter of 6.22 Bohr units to 2.45 ev for a lattice parameterof 5.98 Bohr

units. This model is able to predict the spin-orbit splittings at various points in the Brillouin zone which will agree with experiment. Finally the model is able to explain the shift of the band edge with temperature. This model seems able to accurately predict the observed optical properties of NaI.

I.

Chapter I.

INTRODUCTION.

The name "ionic crystal" is given to that class of solids in which the binding is thought of as being due primarily to the electrostatic attractions of the constituent ions. One class of ionic crystals is the alkali-halides. These are crystals formed from the alkali metals: lithium, sodium, potassium, rubidium, cesium, and the halides: fluorine, chlorine, bromine, and iodine. These substances are solid at room temperature. They all exhibit a cubic structure; however, some are face centered cubic, others are body centered cubic and some are simple cubic. The lattice parameter, a, which is the distance separating a given halide from its nearest neighbor alkali, range from 3.79 to 7.46 Bohr units.[1]

Early studies were able to show that many of the properties could be explained using a simple picture of a collection of free ions situated in a lattice. Using a model of point charges representing the individual ions, it was possible to explain most of the observed data about the cohesive energies of the ionic crystals.[2,3] In these studies the detailed structure of the solids was taken into account by including a term $Ae^{-r/\rho}$ in the energy to take into account the repulsion due to the interaction of the electrons located about the various

ions. The constants A and ρ were chosen from consideration of the compressability for the solid. These methods and more refined methods based on quantum mechanics but still considering the solids as being composed of ions were able to yield results for the elastic constants which were in good agreement with the experimentally observed values.[4,5,6]

It is electrical and optical properties of these solids which are of most interest as far as current experiments are concerned. Electrically these solids are insulators,[3] which indicates the presence of filled bands. The absorption spectra lie in the ultra-violet region of the spectrum; i.e. the absorptions lie in the range of five ev and larger. It has been observed that these crystals can be made to conduct by exciting them optically. However, this is only for a short time, as the electrical charges seem to become trapped.[7,8] The conduction properties were considered theoretically by Frohlich[9] and by Frohlich and Mott.[10] The results obtained would be useful regardless of whether the charges were electrons or holes.

From a theoretical point of view, information about the electrical and optical properties may be gained by calculating the energy levels and wave functions for the crystals. In doing this one may hope to predict the optical absorption spectra of the crystals. There have been several calculations of this nature carried out on the alkali-halides. Some of the more interesting of these are NaCl by Shockley[11] and by Casella;[12] KCl by Howland[13] and by DeCicco;[14] LiCl by Kunz and

VanSciver.[15] The valence band, which is the 3p Cl^- band in all of the above cases, was found to vary in width from about 1.2 ev to 4.4 ev.

The experimental evidence is not complete at the present time. Parratt and Jossem[16] investigated the valence band of KCl using X-ray emission studies and found it to be 0.33 ev wide. This disagreed with results predicted by Casella[12] and Howland.[13] Recently however, Phillips[17] has considered the bands in several alkali-halides in a semi-empirical method and obtained results which disagree with Parratt and Jossem[16] but which agree with Howland.[13] Phillips bases his results on a calculation which he made for the zinc blend crystal[18] and the observed optical absorption spectra for the crystals. This study yields information about the structure of the valence band, the conduction band, and the exciton spectra. The excitons may be roughly considered as a hole left in the valence band when an electron is removed, and an electron in the bottom of the conduction band, which are bound together by an electrostatic interaction. The subject of excitons has been the subject of a recent review by Knox.[19]

In addition to the work on the alkali-halides there are other recent calculations of interest. AgCl abd AgBr have been considered by Bassani, Knox, and Fowler.[20] Krypton, a rare gas solid, was considered by Fowler.[21] The above calculations are noteworthy for their completeness.

In the present work sodium iodide is considered. Sodium iodide

is a face-centered cubic crystal (f.c.c.) and has a lattice parameter of 6.15 Bohr units. In the ground state it is in a S-type configuration.[1] The outermost electrons on the iodine ion are in a 5p state, if one considers a single electron picture, and those of the sodium ion are in a 2p state. In the ground state both ions exhibit a closed shell configuration; both are in an S state. Absorption studies have been made for both pure and impure NaI.[22,23] In the present work, the valence band is calculated for axes of high symmetry in the reciprocal lattice and some inferences are made about the conduction band and the exciton spectra from the available absorption data. The effect on the valence band is considered as the lattice parameter is allowed to vary. In addition, the change in valence band is investigated as a stress is applied along the [1 0 0] direction. The results are discussed and compared to recent data. Several interesting experiments which may be performed are discussed.

This calculation shall attempt to improve upon the calculations which have been performed on other alkali halide crystals in several respects. To do this I shall choose a model for the free I^- and Na^+ ions which I can solve self-consistently and which will yield a potential for the various ions which will form the crystal potential as a sum of the potentials of the ions in the crystal in a rigorous way within the context of the model chosen. To this end the chosen model is the Hartree-Fock-Slater modified model. This model along

with the tight binding method used will be discussed in Chapter II. I shall consider second order perturbation corrections to the energy. This correction was previously considered by Howland[13] for KCl and was found to be an important contribution in obtaining the band width in that it altered the band width of KCl by about forty per cent. Bassani, Knox and Fowler[20] found this to have important effects on AgCl which is not an alkali-halide. Fowler[21] investigated this effect in krypton and found it to be less than one per cent.

The final correction to be included is that due to spin-orbit interactions. This had been included previously in the case of LiCl by the author and VanSciver[15] and also in krypton by Fowler[21]. The inclusion of this correction in a tight binding method was first obtained by Fowler for krypton. It is believed that the inclusion of this effect should prove interesting in that J.C.Phillips[17] was unable to account for the size of the spin-orbit splittings which he observed when interpreting the absorption spectrum of NaI.

II.

ENERGY BAND THEORY IN INSULATORS.

A. General Discussion.

One believes that the problem should be solved in terms of a relativistic quantum mechanics. However, since there is no internally self-consistent relativistic quantum theory for a system of many particles, one is forced to hope that the problem is soluble in terms of a non-relativistic quantum theory. Using a non-relativistic quantum theory, one is forced to make simplifying assumptions so that the problem, which may be stated in a completely general way, is computationally manageable. One hopes to obtain a physically meaningful solution despite the assumptions which one is forced to make.

For any non-relativistic system the exact description is given as a solution to the Schrodinger equation for that system:

$$\mathcal{H}\,\Psi_m(\vec{r}) = E_m \Psi_m(\vec{r}) \tag{1}$$

In Eq. (1) $\mathcal{H}$ represents the Hamiltonian of the system; $\Psi_m(\vec{r})$ is the m^{th} eigenfunction of $\mathcal{H}$, and E_m is the corresponding eigenvalue. The space and spin coordinates for the system are represented by $\vec{r}$. One could possibly consider some relativistic corrections to Eq. (1) by use of perturbation theory. One could include the correct form for the spin-orbit interaction in the perturbation.

For a crystal the total Hamiltonian, $\mathcal{H}$, is given as

$$\mathcal{H} = \sum_{i=1}^{n} -\frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_{I=1}^{N} -\frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{i,j}{}' \frac{e^2}{r_{ij}}$$
$$-\sum_{I,i}\frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|} + \frac{1}{2}\sum_{I,J}{}' \frac{Z_I Z_J e^2}{R_{IJ}} + H_{per} + H_{ext} \tag{2}$$

In Eq.(2) i refers to the i^{th} electron, I to the I^{th} nucleus; Z_I is the charge on the I^{th} nucleus, e is the electronic charge; r_{ij} is the separation of the i^{th} from the j^{th} electron and R_{IJ} is the separation of the I^{th} from the J^{th} nucleus; and $|\vec{R}_I - \vec{r}_i|$ is the separation of the i^{th} electron from the I^{th} nucleus. H_{per} takes into account any relativistic effects or spin-orbit effects and is temporarily assumed zero, but may later include as a perturbation. H_{ext} is the interaction between the crystal and any external fields. In the work that follows H_{ext} is always assumed zero. In the above it is assumed that there are n electrons and N nuclei in the crystal. The operators ∇ operate on the spacial parts of the wave functions only. At this point except for H_{per} there is no need to include a spin dependence in the wave functions, however, these shall be assumed present so that the inclusion of spin-orbit effects may proceed smoothly.

Designate $\mathcal{H}$ with H_{rel} and $H_{ext}=0$ as $\mathcal{H}_o$ and then consider the following definition

$$\mathcal{H}_o = T_e + T_N + U(\vec{r},\vec{R}) \tag{3}$$

Here T_e is the total electronic kinetic energy; T_N is the total nuclear kinetic energy; and $U(\vec{r},\vec{R})$ includes all the potential terms of Eq.(2). Using Eq.(1) and Eq.(3), one finds

$$\mathcal{H}_o \Psi_m^{(o)}(\vec{r},\vec{R}) = E_m^{(o)} \Psi_m^{(o)}(\vec{r})$$

In order to keep notation compact, the superscript ^{o} will be omitted in future equations.

B. Born-Oppenheimer Theory.

At this point one is ready to begin making a series of approximations which will yield a computationally manageable model of a crystal. Nuclear motion is still included in the model, and it is this which is eliminated first. To do this one makes the Born-Oppenheimer or adiabatic approximation.[24] Let us assume that the total wave function $\Psi_m(\vec{r},\vec{R})$ may be expressed as

$$\Psi_m(\vec{r},\vec{R}) = \varphi_{n,\vec{R}}(\vec{r})\,\Theta_{n,\vec{r}}(\vec{R}) \tag{4}$$

In Eq. (4) we have $\varphi_{n,\vec{R}}(\vec{r})$ which is a function of the electronic space-spin coordinates and depend parametrically on $\vec{R}$, and $\Theta_{n,\vec{r}}(\vec{R})$ which is a function of the nuclear space-spin coordinate and depends parametrically on the electronic state designated by r. If one requires that the solution be a stationary state, Seitz[1] (Chapter XIV) has shown that one obtains the following two equations:

$$[T_e + U(\vec{r},\vec{R})]\,\varphi_{n,\vec{R}}(\vec{r}) = \epsilon_n(\vec{R})\,\varphi_{n,\vec{R}}(\vec{r}) \tag{5}$$

and

$$[T_N + \epsilon_n(\vec{R})]\,\Theta_{n,\vec{r}}(\vec{R}) = \mathcal{E}_{n,\vec{r}}\,\Theta_{n,\vec{r}}(\vec{R}) \tag{6}$$

Thus one sees that from Eq. (5) one obtains a wave function for the electrons which depends parametrically on the nuclear position $\vec{R}$. and one obtains a wave function for the nuclei in Eq. (6) which depends upon the state of the electron. Thus one obtains a stationary state for the electrons with an eigenvalue $\epsilon_n(\vec{R})$ for each set of

nuclear positions $\vec{R}$. The validity of this rests on the fact that due to the much greater mass of the nuclei compared to electrons, the nuclei move so slowly that the electronic state remains stationary, changing adiabatically with the nuclear motion. At the same time the nuclei are seen to move in a "potential" which is determined by the average electronic positions.

This approximation is satisfactory, to a high degree of accuracy, for most problems in solid state physics and in molecular theory. It is useful in the consideration of electron-nuclear dynamics.[25]

It is not intended in this present work to consider the question of nuclear-electron dynamics. However as the solutions to Eq.(5) will be obtained for several values of lattice parameter, some indications of the form of the solution to Eq.(6) will be obtained.

C. One-Electron Approximation.

The task has been reduced to solving an equation which involves all the coordinates of all the electrons. The equation of interest is Eq.(5) which we write omitting the reference to this equation's dependence on R as

$$[T_e + U(\vec{r}, \vec{R})]\,\varphi_n(\vec{r}) = \epsilon_n\,\varphi_n(\vec{r}) \qquad (5')$$

One notes that the function $\varphi_n(\vec{r})$ is dependent upon the space-spin coordinates of about 10^{23} electrons in the average crystal. If there are four degrees of freedom for each electron, one must obtain

a $\varphi_n(\vec{r})$ which is a function of 4×10^{23} variables. From a computational standpoint, this is a difficult, if not impossible, undertaking. Even if such a general solution were obtained, it might not be of any use.[26]

The mathematics is best understood when one is obtaining a solution to a problem which is the description of a single particle. Thus one wishes to construct an equation describing a single particle which may in some way be equivalent to Eq.(5'). This desire is based upon necessity rather than any desire to be rigorous in the solution. Furthermore, it is common to talk of physical processes which involve single particles rather than collections of them. One must always remember that many-electron processes are important. Thus one may not expect a theory based upon a single-particle approximation to explain all the observed facts about a solid. Mathematically, of course, one recognizes that the solution $\varphi_n(\vec{r})$ may be expanded in a complete set of single particle functions. However in practice such a complete set is often infinite and is thus difficult to handle. Thus one is, of necessity content to use a non-complete set of single-particle wave functions.

In order to solve Eq.(5'), one looks for the best set of single-particle wave functions to serve as a representation for $\varphi_n(\vec{r})$. The set chosen must obey, for electrons, the Pauli principle. That is, the function must be antisymmetric upon the interchange of any two

particles. One may choose orthonormal single-particle wave functions of the form

$$\varphi_i(\vec{r}_j) = \psi_i(\vec{r}_j')\,\chi_i(\xi_j) \tag{7}$$

where r_j is the space coordinates of the j^{th} electron and ξ_j is the spin coordinate of the j^{th} electron. The subscript i refers to the i^{th} state. Thus by $\varphi_i(\vec{r}_j)$ we mean the j^{th} electron is in the i^{th} state. Only one antisymmetric function may be constructed from the $\varphi_i(\vec{r}_j)$ [26]: it is

$$\varphi_i(\vec{r}) = n^{-1/2}\,\det(\varphi_k(\vec{r}_j)) \tag{8}$$

where n is the number of electrons in the system. For n=2, we illustrate

$$\varphi_i(\vec{r}) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r}_1) & \varphi_1(\vec{r}_2) \\ \varphi_2(\vec{r}_1) & \varphi_2(\vec{r}_2) \end{vmatrix}$$

It is obvious from the form of Eq.(8) that the $\varphi_i(\vec{r})$ are antisymmetric upon the interchange of two particles. For the wave function Eq.(8), one must find the best set of $\varphi_k(\vec{r}_j)$ and the equation which they satisfy.

D. Hartree-Fock-Slater Approximation.

Using the function defined in Eq.(8), one may form the matrix elements for $T_e + U(\vec{r},\vec{R})$. This is defined as

$$H_{ii} = \langle i | T_e + U(\vec{r},\vec{R}) | i \rangle = E_{ii} \tag{9}$$

The notation used is the standard Dirac notation from quantum mechanics.[27] By H_{ii} we mean the average or expectation value for the effective

Hamiltonian, $T_e + U(\vec{r},\vec{R})$,over the wave function $\varphi_i(\vec{r})$ This yields the average energy E_i for the system. One applies the variational principle, $\delta E_i = 0$, and requíre as a constraint that the single-electron functions remain orthonormal. The result of this is the Hartree-Fock equation.[26]

$$\frac{-\hbar^2}{2m}\nabla^2\varphi_i(\vec{r}_i) + \left[W(\vec{r}_i,\vec{R}) + \sum_j e^2 \int \frac{|\varphi_j(\vec{r}_j)|^2}{r_{ij}} d\tau_j\right]$$
$$\varphi_i(\vec{r}_i) - \sum_j \left[e^2 \int \frac{\varphi_i(\vec{r}_j)\varphi_j^*(\vec{r}_j)}{r_{ij}} d\tau_j\right] \varphi_j(\vec{r}_i) \qquad (10)$$
$$= \epsilon_i \varphi_i(\vec{r}_i) + \sum_j{}' \lambda_{ij} \varphi_j(\vec{r}_i)$$

In Eq.(10) $\int d\tau_j$ implies integration over the space coordinates and summation over the spin coordinates of electron j. The term $W(r_i, R)$ includes the interaction of the given electron with all the nuclei in the lattice. Eq.(10) is valid only for S-like states. That is, where the total angular momentum of the system is zero. There must be an even number of electrons and they must be half spin up and half spin down. The multiplicity of such a system is zero. In the case which is under consideration, the above restriction is obeyed. However, in many practical cases the equation is used even though the multiplicity is not zero.[28] If the φ_i are orthogonal, the λ_{ij} may be set equal to zero. In the term involving λ_{ij} the summation does not include the term i=j, which is the meaning of the $'$ on the summation.

It is common to call various terms in Eq.(10) by name. Thus one has

$$\sum_j e^2 \int \frac{|\varphi_j(\vec{r}_j)|^2}{r_{ij}} d\tau_j = V(\vec{r}_i)$$

Here $V(r_i)$ is called the potential due to the average positions of the electrons in the system.

$$\frac{\varphi_j(\vec{r}_i)}{\varphi_i(r_i)} \left[-\sum_j e^2 \int \frac{\varphi_i(\vec{r}_j)\,\varphi_i(\vec{r}_j)^*}{r_{ij}} d\tau_j \right] = A_i(\vec{r}_i)$$

The term $A_i(\vec{r}_i)$ is called the "exchange potential." This term arises as a consequence of using an antisymmetric wave function. Using these definitions, Eq.(10) becomes

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + W(\vec{r}_i, \vec{R}) + V(\vec{r}_i) + A(\vec{r}_i) \right] \varphi_i(\vec{r}_i) = \epsilon_i \varphi_i(\vec{r}_i) \qquad (11)$$

In Eq.(11) the first term is just the kinetic energy. The second term is the interaction of electron i with all the nuclei and the mutual interaction of the nuclei which is a constant. This constant we shall set equal to zero. The other terms have been discussed. In what follows we shall omit reference to the parametric dependence upon R in the term $W(r_i,R)$ and call it simply $W(r_i)$. We shall also go over to the atomic system of units.[26] In this system $\hbar = 1.0$. The unit of length is the Bohr radius for the n=1 level of the hydrogen atom and is about 0.529 A. One finds that $e = \sqrt{2}$ and $m = 0.5$. The unit of energy is the Rydberg which is 13.6 ev. Having done this, Eq.(11) becomes

$$\left[-\nabla^2 + W(\vec{r}_i) + V(\vec{r}_i) + A_i(\vec{r}_i) \right] \varphi_i(\vec{r}_i) = \epsilon_i \varphi_i(\vec{r}_i)$$

Another simplification which may be made is to substitute the Slater form for the exchange potential $A_i(\vec{r}_i)$.[29] This defines

$$A_i(\vec{r}_i) \simeq -6\left[\frac{3}{8\pi}\,|\rho(\vec{r})|\right]^{1/3} \tag{12}$$

where $\rho(\vec{r})$ is the radial charge density for the electrons, obtained by squaring and adding the wave functions for all the electrons in the system. One notes that using the Slater exchanges has the advantages that the potential at a point is now a local potential, that is, the potential is independent of the state of the electron which sees the potential. In the Hartree-Fock case the potential was non-local and thus each electron could see a different potential at a given point. This then yields

$$\left[-\nabla^2 + W(\vec{r}_i) + V(\vec{r}_i) - 6\left[\frac{3}{8\pi}\,|\rho(\vec{r})|\right]^{\frac{1}{3}}\right]\varphi_i(\vec{r}_i) = \epsilon_i\,\varphi_i(\vec{r}_i) \tag{13}$$

If one were to consider the case of a single atom or ion in free space, one observes that the Slater form for the exchange potential yields incorrect results for the total potential at large distances. That is, it overestimates the exchange potential. In the case of a free atom, at large distances one would expect an electron on that atom to see a potential of -2/r; however, using the Slater exchange, it sees a potential of zero. Thus at large distance it is customary to modify the Slater form for the exchange so that the potential has the correct form. This is done in the present work at the appropriate places. The question is considered in some detail by Herman and Skillman.[28] Essentially the potential obtained by the Slater potential is plotted and on the same graph the correct asymptotic potential is

plotted, at the point where these potentials are equal one joins the Slater potential from the origin to the point in question onto the correct asymptotic potential from that point out to infinity. This will be discussed again when the specific cases of I and Na are considered. It is noted, however, that the point of changeover usually occurs at a rather short distance from the origin, that is, between one and ten Bohr units. Thus the equation to be used is the Hartree-Fock equation with the Slater form for the exchange which is modified to have the correct asymptotic behavior. This is designated as the Hartree-Fock-Slater modified equation.

E. Group Theory.

1. General Theorems.

The problem to be solved is still a very complex one from both a mathematical and a physical standpoint. It is desirable to develop a scheme of rigorously simplifying the problem without making further assumptions. A resort to group theory will provide some useful theorems. These are general in nature and are of considerable use. In this section, we shall look at proofs for various useful theorems. These theorems are generally available in the literature. However, it is not out of place to include them here, as the inclusion will add to the continuity of the presentation, include the pertinent theorems in one compact setting, and place them in the notation of this thesis.

It is known from quantum mechanics that if two operators commute, they may have the same set of eigenfunctions.[27] That is

$$[A, B] = 0 \tag{14}$$

then

$$A\psi_n = a_n \psi_n$$
$$B\psi_n = b_n \psi_n$$

In Eq.(14) A and B are operators, ψ_n is an eigenfunction of A with eigenvalue a_n and is also an eigenfunction of B with eigenvalue b_n. In our problem we want to obtain eigenvalues and eigenfunctions for the Hamiltonian. It is desired to find a set of operators which commute with the Hamiltonian and which have either known or easily obtained eigenfunctions.

To do this, one considers the group of operators P(R) which are composed of rotations and translations in three dimensions.[30] Thus if f(x) and f(x') are functions of the coordinates

$$P(R)f(x') = P(R)f(Rx) = f(x)$$

By the equality, we mean the function has the same value at the point, but not necessarily the same functional form. There is also an inverse operator, such that

$$P(R)P(R)^{-1} = 1$$

Consider the Schrodinger equation:

$$H(x)\psi_n(x) = E_n \psi_n(x)$$

Now one may have

$$H(x)\psi(x) = P(R)[H(x')\psi(x')]$$
$$= P(R)H(Rx)P(R)^{-1}\psi(x)$$
$$= H(x)\psi(x)$$

thus

$$H(x') = P(R)H(Rx)P(R)^{-1} \tag{15}$$

where $P(R)^{-1}$ denotes the inverse operator. Now if we consider certain operators which we call symmetry operations, these are the ones which leave the Hamiltonian unchanged. Thus

$$H(Rx)=H(x) \tag{16}$$

Then using Eq.(15)

$$H(x)=P(R)H(x)P(R)^{-1}$$

and multiplying from the right by P(R)

$$H(x)P(R)=P(R)H(x)$$

or

$$[H(x),P(R)]=0 \tag{17}$$

Thus one sees that the symmetry operators commute with the Hamiltonian. These symmetry operators form a group.[30]

If one has a set of orthonormal eigenfunctions for the group of symmetry operators P(R), then there exist several theorems which are useful.[31] The method of obtaining these eigenfunctions will be considered shortly. Let $\Gamma^{\alpha}(R)_{ij}$ refer to the α irreducible representation of the group P(R) and the ij matrix element of that representation. Let $\psi_{\alpha j}$ be an eigenfunction of this representation. Then

$$P(R)\psi_{\alpha j} = \sum_{i=1}^{n} \Gamma_{\alpha}(R)_{ij}\,\psi_{\alpha i} \tag{18}$$

The dimensionality of the representation is n.

$$\begin{aligned}
[\psi_i, \psi_j] &= \delta_{ij} \\
&= [P(R)\psi_i, P(R)\psi_j] \\
&= \sum_k \sum_l \Gamma_{\alpha}(R)^{*}_{ki}\,\Gamma_{\alpha}(R)_{lj}\,[\psi_k, \psi_l]\,\delta_{kl} \\
&= \sum_k \Gamma_{\alpha}(R)^{*}_{ki}\,\Gamma_{\alpha}(R)_{kj} \\
&= [\Gamma_{\alpha}(R)^{\dagger}\Gamma_{\alpha}(R)]_{ij} = \delta_{ij}
\end{aligned}$$

thus

$$\Gamma_{\alpha}(R)^{\dagger}\Gamma_{\alpha}(R) = \mathbf{I} \tag{19}$$

where I is the identity. Thus our representation is unitary. Consider matrix elements for the Hamiltonian.

$$\begin{aligned}
\langle n\alpha i \mid H \mid n'\alpha' i' \rangle &= [P(R)\psi_{n\alpha i}, P(R)H\psi_{n'\alpha' i'}] \\
&= [P(R)\psi_{n\alpha i}, HP(R)\psi_{n'\alpha' i'}] \\
&= \sum_j \sum_{j'} \Gamma_{\alpha'}(R)_{j'i'}\,\Gamma^{*}_{\alpha}(R)_{ji}\,[\psi_{n\alpha j}, H\psi_{n'\alpha' j'}]
\end{aligned}$$

By use of the orthogonality condition for unitary irreducible representations,[30,31] and summing over all operators R of the group. To illustrate the idea of summing over the operators of a group, consider the example of a two operator group. Call the operators E and D where E is the identity. Thus one has

E E=E

E D=D

D E=D

D D=E

Thus here there is an irreducible representation which is one dimensional and has matrix elements

$$\Gamma(E)_{11} = 1 \; , \; \Gamma(D)_{11} = 1$$

Thus here the above expression becomes

$$\langle n\alpha i | H | n'\alpha' i' \rangle = [\Gamma(E)_{11} \Gamma^*(E)_{11}] \langle n\alpha i | H | n'\alpha' i' \rangle$$

and when one sums over the operators, one then has

$$\sum(R) \langle n\alpha i | H | n'\alpha i \rangle = \Gamma(E)_{11} \Gamma^*(E)_{11} \langle n\alpha i | H | n'\alpha i \rangle + \Gamma(D)_{11} \Gamma^*(D)_{11} \langle n\alpha i | H | n'\alpha i \rangle$$

Thus for the more general case under consideration, one obtains

$$\sum(R) \langle n\alpha i | H | n'\alpha' i' \rangle = \sum_j \sum_{j'} [\sum(R) \Gamma_{\alpha'}(R)_{j'i'} \Gamma^*_{\alpha}(R)_{ji} [\psi_{n\alpha j} H \psi_{n'\alpha' j'}]]$$

Applying the orthogonality condition

$$\langle n\alpha i | H | n'\alpha' i' \rangle = \delta_{\alpha\alpha'} \delta_{ii'} \left[\frac{1}{n_\alpha} \sum_j \langle n\alpha j | H | n'\alpha j \rangle\right] \qquad (20)$$

The use of Eq.(20) is very important in simplifying the calculation.

Let us now obtain basis functions for our symmetry operators. To do this we define a projection operator,[31,32]

$$O_\alpha^{pq} = \frac{n_\alpha}{g} \sum(R) \Gamma^*_\alpha(R)_{pq} P(R) \qquad (21)$$

Here g is the order of the group. To show that this has the desired properties, consider an arbitrary function F of the coordinates and operate on it with O_α^{pq}.

$$O_\alpha^{iq} F = \frac{n_\alpha}{g} \sum(R) \Gamma^*_\alpha(R)_{iq} P(R) F$$

Operate on this by P(S), an operator of the group.

$$P(S) O_\alpha^{iq} F = \frac{n_\alpha}{g} \sum(R) \Gamma_\alpha(R)^*_{iq} P(S) P(R) F$$

$$= \frac{n_\alpha}{g} \sum(R) \Gamma_\alpha(R)^*_{iq} P(SR) F$$

Now since

$R=S^{-1}T$ for some T in the group

$$P(S)\,O_\alpha^{iq}\,F = \frac{n_\alpha}{g}\sum(T)\,\Gamma_\alpha^{*}(S^{-1}T)_{iq}\,P(T)\,F$$
$$= \frac{n_\alpha}{g}\sum(T)\sum_j \Gamma_\alpha^{*}(S^{-1})_{ij}\,\Gamma_\alpha^{*}(T)_{iq}\,P(T)\,F$$
$$= \sum_j \Gamma_\alpha(S)_{ji}\,O_\alpha^{jq}\,F$$

Thus we see from Eq.(18) that our operator Eq.(21) has the desired property when acting on an arbitrary function.

This operator may be simplified by taking its trace.[31]

$$Tr\,O_\alpha^{ij} = O_\alpha$$

Thus one obtains

$$O_\alpha = \frac{n_\alpha}{g}\sum(R)\chi_\alpha^{*}(R)\,P(R) \qquad (22)$$

In Eq.(22) $\chi_\alpha(R)$ is the trace of the α^{th} irreducible representation of the operator R. The summation here is over all operators R of the group. Thus we have obtained a prescription for obtaining basis functions for our symmetry operators.

2. Periodic Potential.

In the NaI lattice there are symmetry operations which are pure translations. These form a subgroup of the total crystal symmetry group. This implies that we have a crystal symmetry which is infinite or one which has cyclic boundary conditions upon translation. These conditions are called the Born VonKarman boundary conditions.[33] This has the result that if nearest neighbor I^-ions are situated at

$\pm$ [a,a,o], $\pm$ [a,o,a], $\pm$ [o,a,a], $\pm$ [-a,a,o], $\pm$ [-a,o,a], or $\pm$[o,-a,a], then any translation by one of the above vectors or a combination of them or any integer multiple of them will leave the lattice unchanged.

The effects of this have been studied by Bloch.[34] The result of this is the famous Bloch theorem. This says that the wave function $\psi(\vec{r})$ must behave such that if T is a translation operator which displaces things by a vector $\vec{a}$, one must have

$$T\,\psi(\vec{r}) = e^{-i\vec{k}\cdot\vec{a}}\,\psi(\vec{r}) = \psi(\vec{r}-\vec{a}) \qquad (23)$$

In doing this we must define $\vec{k}$. Let the $\vec{a}_i$ be three non-coplanar vectors which can generate the NaI lattice. One defines the unit cell for this lattice as the smallest volume enclosed by the planes which are perpendicular bisectors of the lines joining a given I^- ion to all the other I^- ions in the lattice.[35] Then these three translations can generate the entire lattice. Now if these three vectors are the shortest possible three non-coplanar vectors, one defines[31]

$$b_i\, a_j = \delta_{ij}$$

$$b_i = a_j \times a_k / a_i \cdot (a_j \times a_k) \qquad (i,j,k \text{ are cyclic})$$

and

$$\vec{k} = 2\pi\left(\frac{\nu_1}{N_1} b_1 + \frac{\nu_2}{N_2} b_2 + \frac{\nu_3}{N_3} b_3\right) \qquad (24)$$

N_1 is the number of lattice sites in the crystal in the direction a_1 etc. The ν_i are integers of the range 0 to $N_i - 1$. The vectors b_i determine the reciprocal lattice. Again it is possible to construct a unit cell in the reciprocal lattice. This is done just as for the

direct lattice. In the case of NaI, the direct lattice is face-centered cubic, and the reciprocal lattice is body-centered cubic (bcc). These cells are shown in Figures 1 and 2. It is useful to restrict the range of $\vec{k}$ to have it lie within or on the unit cell for the reciprocal lattice. This restriction does not alter the physics of the situation.[31] This cell is called the first Brillouin zone for the lattice. This is found discussed in virtually every book on solid state physics and we shall not spend more time discussing the consequences of the translational symmetry.

F. Tight Binding Theory.

In the case of ionic crystals such as NaI, considerable success has been obtained in explaining many of the properties in terms of a collection of ions which occupy the necessary places in a regular lattice. In so doing it is assumed that the electronic wave functions are not distorted in any appreciable way by being placed in the lattice.[3] The success of these approaches in explaining the properties of the ionic crystals, leads one to hope that this might be applicable to the problem at hand. The Schrodinger equation for the lattice is, even in terms of the simplifying assumptions which we have made, insoluable using current techniques. This is due to the presence of non-central, non-spherically symmetric potentials in the Hartree-Fock-Slater modified equation. Group theory is some help. The Bloch theorem places

FIGURE 1. Unit cell for a face centered cubic lattice.

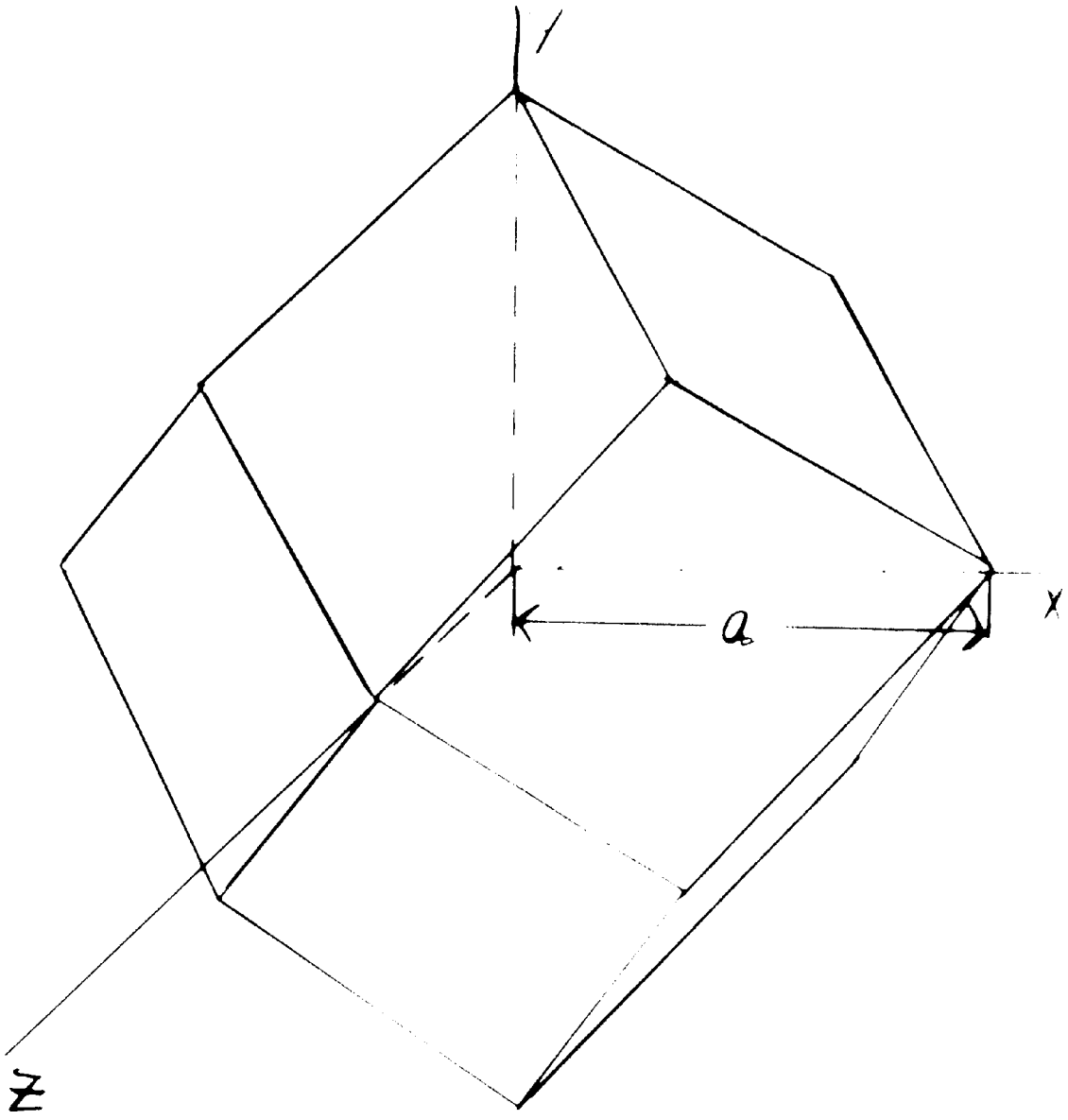
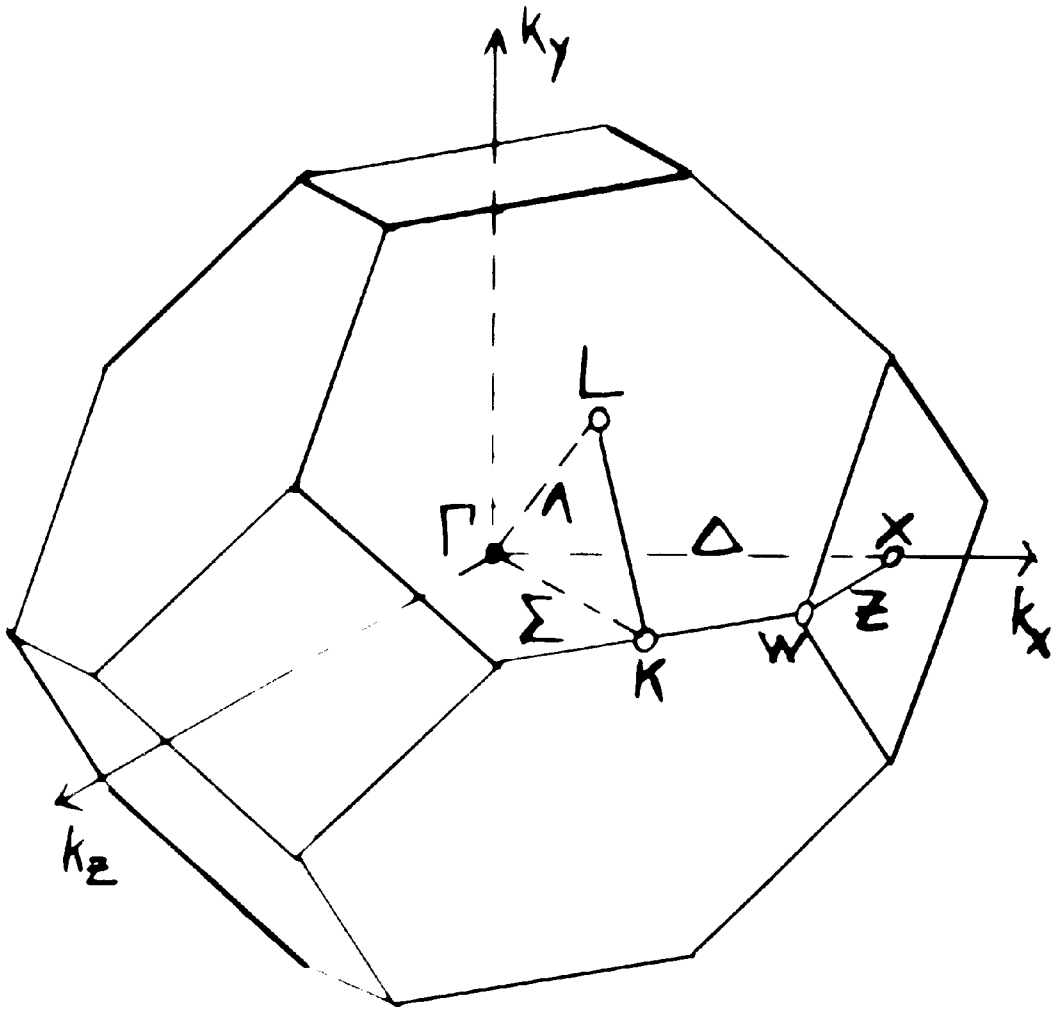


FIGURE 2. First Brillouin zone for a face centered cubic crystal with points and lines of high symmetry shown.



restrictions on the translational properties of the solution. Consideration of the rotation symmetry groups (point groups), which will be done late, obtains the angular dependence of our functions. However, after all the group theory has been carried out, there is still an unknown function of r to be determined subject to the Bloch restriction. This function could be obtained from the H.F.S. equation for the lattice, but it is too difficult to solve.

The answer is to heed the early results and expect the functional dependence upon r to be the same as in the case of the free ion. Thus it is that one solves the H.F.S. equation for the free ion and then uses these functions to form what is hoped to be solutions for the crystal by use of the Bloch condition. This method is called the tight binding approximation. It has been discussed in detail by several authors and used for calculations on ionic crystals[12,13,15,20] and rare gases.[21] Good discussions of this method and comparisons to other methods are given by Callaway[36] amd Ziman.[37]

Assuming one has obtained the solution to the Hartree-Fock-Slater modified equation for a free ion: from this one forms a linear combination which transform as a basis for the α irreducible representation of the point group. Assume the ions are situated in a lattice and the μ ion is at the point $\vec{R}_\mu$. Let the 0^{th} ion be at the origin, $R_0=0$ for simplicity. Then if $\varphi_{n i\alpha}$ is the set which transforms as a basis for the α irreducible representation,

one obtains for $\Psi_{n l \alpha}$, the total crystal wave functions

$$\Psi_{n l \alpha}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\nu=0}^{N-1} \exp(i\vec{k}\cdot\vec{R}_\nu)\, \varphi_{n i \alpha}(\vec{r} - \vec{R}_\nu) \tag{25}$$

Here there are N ions of this type in the lattice. This function, Eq.(25) is easily seen to satisfy the Bloch requirement. Let T be a translation which changes $\vec{r}$ to $\vec{r} - \vec{R}_\nu$. Then operating on Eq.(25) with T, one has

$$\begin{aligned} T\Psi_{n l \alpha}(\vec{r}) &= \frac{1}{\sqrt{N}} \sum_{\nu=0}^{N-1} T \exp(i\vec{k}\cdot\vec{R}_\nu)\, \varphi_{n i \alpha}(\vec{r} - \vec{R}_\nu) \\ &= \frac{1}{\sqrt{N}} \sum_{\nu} e^{-i\vec{k}\cdot\vec{R}_\nu} e^{-i\vec{k}\cdot(\vec{R}_\nu + \vec{R}_\mu)} \varphi_{n i \alpha}(\vec{r} - \vec{R}_\mu - \vec{R}_\nu) \\ &= \frac{1}{\sqrt{N}} e^{-i\vec{k}\cdot\vec{R}_\mu} \sum_{s=0}^{N-1} e^{-i\vec{k}\cdot\vec{R}_s} \varphi_{n i \alpha}(\vec{r} - \vec{R}_s), \quad \vec{R}_s = \vec{R}_\mu + \vec{R}_\nu \\ &= e^{-i\vec{k}\cdot\vec{R}_\mu}\, \Psi_{n l \alpha}(\vec{r}) \end{aligned}$$

Thus we see that the function defined by Eq.(25) does satisfy the Bloch requirement. It is functions of this type with which we shall evaluate our Hamiltonian.

The Hamiltonian H is simply given by

$$H = -\nabla^2 + V(\vec{r}) \tag{26}$$

Here we have included both the coulombic and the exchange terms into a single V(r). The matrix element of this is given as

$$\langle n l \alpha | H | n' l \alpha \rangle = E_{n n' l \alpha} \langle n l \alpha | n l \alpha \rangle^{-1/2} \langle n' l \alpha | n' l \alpha \rangle^{-\frac{1}{2}}$$

or

$$E_{n n' l \alpha} = \frac{\langle n l \alpha | H | n l \alpha \rangle}{\langle n' l \alpha | n' l \alpha \rangle^{1/2} \langle n l \alpha | n l \alpha \rangle^{1/2}} \tag{27}$$

Now each $\psi_{nl\alpha}$ is composed of a sum of $\varphi_{nl\alpha}(\vec{r}-\vec{R}_\nu)$.

Let

$$\varphi_{nl\alpha}(\vec{r}-\vec{R}_\nu) = |nl\alpha\nu\rangle$$

If this is substituted into Eq.(27)

$$E_{nn'l\alpha} = \frac{\sum_{\nu\nu'} \langle e^{-i\vec{k}\cdot\vec{R}_\nu} n l\alpha\nu | H | e^{i\vec{k}\cdot\vec{R}_{\nu'}} n' l\alpha\nu' \rangle}{\sum_{\nu\nu'} \langle e^{i\vec{k}\cdot\vec{R}_\nu} n l\alpha\nu | e^{-ik\cdot R_{\nu'}} n l\alpha\nu' \rangle^{1/2} \langle e^{i\vec{k}\cdot\vec{R}_\nu} n' l\alpha\nu | e^{-i\vec{k}\cdot\vec{R}_{\nu'}} n' l\alpha\nu' \rangle^{1/2}}$$

Now if one factors out a single $|e^{i\vec{k}\cdot\vec{R}_\nu} n' l\alpha\nu'\rangle$ from the right and evaluated the contribution in both numerator and denominator, and if one uses another, one finds that the result is not dependent upon which one is chosen.[36] Thus there is some reduction of labor. Some of the implied summations may be replaced by a multiplicative factor on the entire answer. For the sample term retained we may define for convenience $\vec{R}_\nu = \vec{R}_0 = 0$. Therefore

$$E_{nn'l\alpha} = \frac{\sum_{\nu} \langle e^{i\vec{k}\cdot\vec{R}_\nu} n l\alpha\nu | H | n' l\alpha 0 \rangle}{\sum_{\nu} \langle e^{-i\vec{k}\cdot\vec{R}_\nu} n l\alpha\nu | n l\alpha 0 \rangle^{1/2} \langle e^{-i\vec{k}\cdot\vec{R}_\nu} n' l\alpha\nu | n' l\alpha 0 \rangle^{1/2}}$$

Now define

$$S_{nn\alpha\nu} = \langle nl\alpha\nu | nl\alpha 0 \rangle$$

$$H_{nn'\alpha\nu} = \langle nl\alpha\nu | H | n'l\alpha 0 \rangle$$

or

$$E_{nn'l\alpha} = \frac{\sum_{\nu=0}^{N-1} e^{-i\vec{k}\cdot\vec{R}_\nu} H_{nn'\alpha\nu}}{\sum_{\nu=0}^{N-1} e^{-i\vec{k}\cdot\vec{R}_\nu} S_{nn\alpha l}^{1/2} S_{n'n'\alpha l}^{1/2}}$$

Now if one defines

$$V = V_{ion} + V'$$

here V_{ion} is the Hartree-Fock-Slater potential for the free ion situated at $R_o = 0$. V' is whatever is necessary to make the potential come out all right. Thus

$$H_{nn'\alpha\nu} = \langle n l \alpha \nu | -\nabla^2 + V_{ION} | n' l \alpha 0 \rangle + \langle n l \alpha \nu | V' | n' l \alpha 0 \rangle$$

Now one recognizes that

$$\frac{\sum_{\nu=0}^{N-1} e^{i\vec{k}\cdot\vec{R}_\nu} \langle n l \alpha \nu | -\nabla^2 + V_{ION} | n' l \alpha 0 \rangle}{\sum_{\nu=0}^{N-1} e^{i\vec{k}\cdot\vec{R}_\nu} S_{nn\alpha\nu}^{\vec{k}} S_{n'n'\alpha\nu}^{\vec{k}}}$$

Here ϵ_n is the energy parameter for an electron in the n^{th} state as given by the Hartree-Fock-Slater equation. Using this, one obtains

$$E_{nn'l\alpha} = \epsilon_n \delta_{nn'} + \frac{\sum_{\nu=1}^{N-1} e^{i\vec{k}\cdot\vec{R}_\nu} V_{nn'\alpha\nu}}{\sum_{\nu=1}^{N-1} e^{i\vec{k}\cdot\vec{R}_\nu} S_{nn\alpha\nu}^{\vec{k}} S_{n'n'\alpha\nu}^{\vec{k}}} \qquad (28)$$

where one has defined

$$V_{nn'\alpha\nu} = \langle n l \alpha \nu | V' | n' l \alpha 0 \rangle$$

Eq.(28) is the usual form for the energy band of a tight binding model. In obtaining this, it was not assumed that wave functions were normalized.

G. Solutions to the Hartree-Fock-Slater Equations.

The immediate problem is the solution of the Hartree-Fock-

Slater modified equation for the case of a free I^- or Na^+ ion. Both of these ions have an S-like ground state. Thus the potential which is used will be spherically symmetric.

$$V(\vec{r}) = V(r)$$

Here the potential V(r) includes the coulombic interaction with the nuclei and the electrons, the Slater form of the exchange which is modified to yield correct assymptotic behavior at infinity. This question is discussed in some detail by Herman and Skillman.[28] In the ions in question one proceeds as follows: The I^- ion is negatively charged with a charge of one electronic charge. In this case, an electron on the ion at large distance would see a potential of zero. Using the Slater exchange the potential becomes positive, and to correct things, the potential is set equal to zero in the region where it is positive. In the case of the Na^+ ion, which has a charge of one positive electronic charge, the potential must go as that due to a point charge of two positive electronic charges at infinity or large distance which for Na^+ is 1.25 Bohr units and 4 Bohr units for I^-. One notes that when considering an electron not located on the ion, that one must then remodify the potential so that this electron sees that potential due to all the electrons situated on the ion.

The equation is

$$[-\nabla^2 + V(r)]\,\varphi(\vec{r}) = \epsilon\,\varphi(\vec{r})$$

Here one assumes

$$\varphi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\,\Theta_{\ell m}(\theta)\,\Phi_m(\varphi)$$

Thus one finds that

$$\Theta_{\ell m}(\theta)\,\Phi_m(\varphi) = Y_\ell^m(\theta,\varphi)$$

where the $Y_\ell^m(\theta,\varphi)$ are the normalized spherical harmonics. With this included, the equation for R(r) becomes

$$r R_{n\ell}(r) = P_{n\ell}(r)$$

$$\left[-\frac{d^2}{dr^2} + \ell(\ell+1)/r^2 + V(\vec{r})\right] P_{n\ell}(r) = \epsilon_{n\ell} P_{n\ell}(\vec{r}) \qquad (30)$$

The above equation for $P_{nl}(r)$ must be solved by numerical means. In the present work this was done using the method of Herman and Skillman[28] which was modified by Kunz and Beck[38] using suggestions obtained from Skillman.[39]

The Hartree-Fock-Slater equation had been solved for the case of Cu by Pratt,[40] who obtained results which were in disagreement with those obtained by Hartree[41,42] for the Hartree equation and the Hartree-Fock equation. After this the Hartree-Fock-Slater equation fell into disrepute. However, Herman and Skillman,[28] in using more accurate methods improved the results of Pratt.[40] Also by using the modifies potential, there was a substantial improvement in the results and the energy eigenvalues for Cu were brought into good agreement with the Hartree-Fock results of Hartree.[42]

The method of solving Eq.(30) for the Na^+ and I^- ions is discussed in Appendix A. Numerical results are given there. In Appendix B some numerical results for other alkali and halide ions are given.

In the latter case the results given are not complete even though complete results are in the possession of the author.

H. Crystal Potential

For computational ease, it is desired to be able to write the potential for the entire crystal as a sum of potentials for the individual ions in the crystal. Since the crystal is thought of as a collection of free ions, this might seem to be a reasonable approach to follow. It is noted immediately that this approach is all right as far as the coulombic part of the potential is concerned. However one is in difficulties when the exchange term is included. This term depends upon the cube root of the charge density. This charge density is formed from the squares of the electronic wave functions. Thus an exchange potential formed from a sum of free ionic exchange potentials is seen to be, in general, wrong. That is

$$\sum_{\nu} \left(\rho(\vec{r}-\vec{R}_{\nu})\right)^{1/3} \neq \left(\sum_{\nu} \rho(\vec{r}-\vec{R}_{\nu})\right) \tag{31}$$

where $\rho(\vec{r}-\vec{R}_{\nu})$ is the charge density for the ion centered at the site $\vec{R}_{\nu}$. The only case where there is an equality in Eq. (31) is when there is no overlap of the radial charge densities. When the modified potential is constructed, the exchange term is truncated at large distance, and thus in this case there is little or no overlap in the exchange term for neighboring ions; thus here one uses

$$\sum_{\nu} \left(\rho(\vec{r}-\vec{R}_{\nu})\right)^{1/3} = \left(\sum_{\nu} \rho(\vec{r}-\vec{R}_{\nu})\right)^{1/3} \tag{32}$$

Here again the choice of the modified Slater potential is seen to have yielded a computational advantage.

There are other attempts at constructing crystal potentials. One by Robinson et al.[43] uses a many-body (correlation) corrections to the potential. In this the Slater potential is screened by a linearized Thomas-Fermi dielectric function. Fowler[21] used this type of potential in his work on krypton and discovered that the results obtained were in poor agreement with those using a simple sum of atomic potentials, and probably wrong. This is not necessarily a failing of the potential, but may be due to using the Hartree-Fock eigenfunction for krypton in a potential for which they were not even good approximate eigenfunctions.

In the present work, one uses

$$V(\vec{r}) = \sum_{\nu} \left[V_I(\vec{r} - \vec{R}_\nu) + V_{Na}(\vec{r} - \vec{R}_\nu - \vec{g}) \right] \tag{33}$$

Here one has a=lattice parameter, g=[a,o,o]. Then $V_I(\vec{r} - \vec{R}_\nu)$ is the potential for the I^- ion about the point $\vec{r} - \vec{R}_\nu$, and $V_{Na}(\vec{r} - \vec{R}_\nu - \vec{g})$ is the potential for the Na^+ ion located about the point $\vec{r} - \vec{R}_\nu - \vec{g}$. The summation is over all the I^- ion sites in the crystal.

III

VALENCE BANDS

A. Theory.

The concept of representing the valence states in a crystal as a sum of states associated with the free ions or atoms seems to have originated with Bloch.[34] In actual practice this method seemed to yield poor results. This does not seem to have been due to any error in the theory but rather to the difficulty in applying the theory exactly. These problems are discussed in some detail by Slater and Koster.[46] They conclude that the evaluation of the parameters in the theory by numerical means was too difficult. The suggestion was made that the evaluation of the parameters be fitted using experimental data or the results of more easily performed calculations. However, a calculation by Howland[13] seemed to answer most of the difficulties. Also some almost exact calculations have been made by Fowler[21] and Knox.[20] It would seem reasonable to believe that an accurate tight binding calculation is possible.

It seems that many advanced books on solid state theory either dismiss the tight binding model on the grounds of difficulty of calculations as stated by Slater and Koster or give it a naive treatment. Therefore it seems reasonable to examine the practical application of the theory in some detail here. To this end we shall duplicate to an extent the derivation of the general tight binding formulas as

given in Chapter II,Section F. This is done in that we may then obtain the expressions equivalent to (II-28), but in a form applicable to the case of a face centered cubic crystal, and the case of NaI to be more specific.

One assumes that the single particle wave functions for the crystal are expressable as

$$\Psi_i^{\alpha}(\vec{r}) = \sum(\mu)\, e^{i\vec{k}\cdot\vec{R}_\mu}\, \varphi_j^{\alpha}(\vec{r}-\vec{R}_\mu) \qquad (1)$$

where $\varphi_j^{\alpha}(\vec{r}-\vec{R}_\mu)$ is the j^{th} ionic state centered about the μ^{th} lattice site which transforms according to the i^{th} row of the α^{th} irreducible representation of the symmetry group of the Hamiltonian.

The Hamiltonian is given as

$$\mathcal{H} = -\nabla^2 + \sum(\mu)\left[V_I(\vec{r}-\vec{R}_\mu)+V_{Na}(\vec{r}-\vec{R}_\mu-\vec{g})\right] \qquad (2)$$

We now look for the ii matrix element of $\mathcal{H}$. This is given as

$$\mathcal{H}_{ii} = \frac{\int \Psi_i^{\alpha}(\vec{r})^*\, \mathcal{H}\, \Psi_i^{\alpha}(\vec{r})\, d\tau}{\int \Psi_i^{\alpha}(\vec{r})^*\, \Psi_i^{\alpha}(\vec{r})\, d\tau}$$

Now by using Eq.(1) we obtain

$$\mathcal{H}_{ii} = \frac{\int \Psi_i^{\alpha}(\vec{r})^* \mathcal{H}\left(\sum(\mu) e^{i\vec{k}\cdot\vec{R}_\mu} \varphi_i^{\alpha}(\vec{r}-\vec{R}_\mu)\right) d\tau}{\int \Psi_i^{\alpha}(\vec{r})^* \left(\sum(\mu) e^{i\vec{k}\cdot\vec{R}_\mu} \varphi_i^{\alpha}(\vec{r}-\vec{R}_\mu)\right) d\tau}$$

This is found to equal

$$\mathcal{H}_{ii} = \frac{\int \Psi_i^{\alpha}(\vec{r})\, \mathcal{H}\, \varphi_i^{\alpha}(\vec{r})\, d\tau}{\int \Psi_i^{\alpha}(\vec{r})\, \varphi_i^{\alpha}(\vec{r})\, d\tau}$$

If one substitutes for $\mathcal{H}$ using Eq.(2), one sees that

$$\mathcal{H}_{ii} = \frac{\int \Psi_i^{\alpha}(\vec{r})\left(-\nabla^2 + \sum(\omega)\left[V_I(\vec{r}-\vec{R}_{\omega}) + V_{Na}(\vec{r}-\vec{R}_{\omega}-\vec{g})\right]\right)\varphi_i^{\alpha}(\vec{r})\,d\tau}{\int \Psi_i^{\alpha}(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau}$$

$$\mathcal{H}_{ii} = \frac{\int \Psi_i^{\alpha}(\vec{r})\left(-\nabla^2 + V_I(\vec{r})\right)\varphi_i^{\alpha}(\vec{r})\,d\tau}{\int \Psi_i^{\alpha}(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau}$$

$$+ \frac{\int \Psi_i^{\alpha}(\vec{r})\ \sum(\omega)\left(V_I(\vec{r}-\vec{R}_{\omega}) - V_I(\vec{r}) + V_{Na}(\vec{r}-\vec{R}_{\omega}-\vec{g})\right)\varphi_i^{\alpha}(\vec{r})\,d\tau}{\int \Psi_i^{\alpha}(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau}$$

Now in performing this we have assumed in using tight binding that $\varphi_i^{\alpha}(\vec{r})$ is an eigenfunction of the ionic Hamiltonian $-\nabla^2 + V_I(\vec{r})$. This has eigenvalue ϵ_i^{α}. Thus

$$\mathcal{H}_{ii} = \epsilon_i^{\alpha}\,\frac{\int \Psi_i^{\alpha}(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau}{\int \Psi_i^{\alpha}(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau}$$

$$+ \frac{\int \Psi_i^{\alpha}(\vec{r})\,\sum(\omega)\left(V_I(\vec{r}-\vec{R}_{\omega}) - V_I(\vec{r}) + V_{Na}(\vec{r}-\vec{R}_{\omega}-\vec{g})\right)\varphi_i^{\alpha}(\vec{r})\,d\tau}{\int \Psi_i^{\alpha}(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau}$$

or

$$\mathcal{H}_{ii} = \epsilon_i^{\alpha} + \frac{\int \Psi_i^{\alpha}(\vec{r})\,V'(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau}{\int \Psi_i^{\alpha}(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau} \qquad (3)$$

In using Eq.(3) it has been customary to assume that the denominator is unity if one has

$$\int \varphi_i^{\alpha}(\vec{r})\,\varphi_i^{\alpha}(\vec{r})\,d\tau = 1.0$$

and

$$V'(\vec{r}) = \sum(\omega)\left[V_I(\vec{r}-\vec{R}_{\omega}) - V_I(\vec{r}) + V_{Na}(\vec{r}-\vec{R}_{\omega}-\vec{g})\right]$$

This neglects the fact that the atomic orbitals on different sites

are not orthogonal. Secondly, the numerator is very messy to evaluate. Thus crude approximations were often made. Finally, one observes that in previous calculations, eigenfunctions were used which were not eigenfunctions of the atomic potential used to construct the crystal potential.[12,13,21] This last mentioned defect has been avoided by obtaining wave functions which were eigenfunctions of the potential used to construct the crystal potential in this thesis. It was found that by considering nearest neighbors only in wave functions yielded results which were exact to three significant figures.

Thus one obtains

$$\mathcal{H}_{ii} = \epsilon_i^\alpha + \frac{\sum_{N=1}^{13} e^{-i\vec{k}\cdot\vec{R}_N} \int \varphi_i^{\alpha*}(\vec{r}-\vec{R}_N) V'(\vec{r}) \varphi_i^\alpha(\vec{r})\, d\tau}{\sum_{N=1}^{13} e^{-i\vec{k}\cdot\vec{R}_N} \int \varphi_i^{\alpha*}(\vec{r}-\vec{R}_N) \varphi_i^\alpha(\vec{r})\, d\tau}$$

The sum runs over the lattice site $\vec{R}_N = 0$ and the other twelve sites closest to it. Finally one splits the potentials into two components. These are the long range ionic part and the short range part due to the structure of the ion. Call these parts $V'_{ION}(\vec{r})$ and $V'_{ST}(\vec{r})$ respectively. Thus one obtains

$$\mathcal{H}_{ii} = \epsilon_i^\alpha + \frac{\int \varphi_i^{\alpha*}(\vec{r}) \varphi_i^\alpha(\vec{r}) (V'_{ION}(\vec{r}) + V'_{ST}(\vec{r}))\, d\tau}{1 + \sum_{N=1}^{12} e^{-i\vec{k}\cdot\vec{R}_N} \int \varphi_i^{\alpha*}(\vec{r}-\vec{R}_N) \varphi_i^\alpha(\vec{r})\, d\tau}$$

$$+\frac{\int \sum_{\mu=1}^{12} \varphi_i^{\alpha}(\vec{r})\varphi_i^{\alpha}(\vec{r}-\vec{R}_\mu) e^{-i\vec{k}\cdot\vec{R}_\mu}(U'_{I\alpha}(\vec{r})+V'_{ST}(\vec{r}))\,d\tau}{1+\sum_{\mu=1}^{12} e^{-i\vec{k}\cdot\vec{R}_\mu}\int \varphi_i^{\alpha}(\vec{r}-\vec{R}_\mu)\varphi_i^{\alpha}(\vec{r})\,d\tau}$$

The long range part is handled exactly for s-and p-like states. It is found that this result is simply $V_M(r)$, the Madelung energy of the point ion.[13,20] The short range term is found to be essentially zero after going out more than two lattice sites. Also the short range terms which involve more than two lattice sites are neglected as being small. Thus the final result obtained is

$$\mathcal{H}_{ii} = \epsilon_i^{\alpha} + \frac{\int \varphi_i^{\alpha}(\vec{r})\varphi_i^{\alpha}(\vec{r})\left(\sum_{n=1}^{12} V_{IST}(\vec{r}-\vec{R}_n)+\sum_{n=1}^{6} V_{NaST}(\vec{r}-\vec{R}_n)\right)d\tau}{1+\sum_{\mu=1}^{12} e^{-i\vec{k}\cdot\vec{R}_\mu}\int \varphi_i^{\alpha}(\vec{r}-\vec{R}_\mu)\varphi_i^{\alpha}(\vec{r})\,d\tau}$$

$$+\int \varphi_i^{\alpha}(\vec{r})\varphi_i^{\alpha}(\vec{r})V_M(\vec{r})\,d\tau$$

$$+\sum_{\mu=1}^{12} e^{-i\vec{k}\cdot\vec{R}_\mu}\int \varphi_i^{\alpha}(\vec{r}-\vec{R}_\mu)[V_{IST}(\vec{r})+V_M(\vec{r})]\varphi_i^{\alpha}(\vec{r})\,d\tau \qquad (4)$$

It is this formula, Eq. (4) which is used. In the above, $\vec{R}_n$ refers to the sites occupied by the six sodium ions closest to the iodine ion chosen as the origin. It is noted that for general use one allows several different atomic states to mix in the crystal to form the crystal function. In the present problem the mixing of the iodine 5p and 5s states is sufficient to yield a good answer.

B. Face Centered Cubic Crystal.

The manipulations in the preceeding section yielded results which were applicable for the case of a NaI crystal which is a face

centered cubic. The results are actually more general and with the appropriate change in the limits of summation and changes in the subscripts which refer to specific ions, these results apply to any crystaline solid in which it may be reasonable to consider the electrons as being tightly bound.

In the particular case on hand, it is desired to evaluate the Hamiltonian using Eq.(4). To do this, one must find the proper combination of orbitals such that $\varphi_i^{\alpha}(\vec{r})$ transform according to the α^{th} irreducible representation of the point group appropriate to the vector $\vec{k}$. Figure 2 shows the reciprocal lattice cell for the NaI lattice. For a general point in the cell the only symmetry operation is the identity. This will not simplify the problem. There are, however, lines and points of high symmetry for which the problem simplifies. These are shown in Figure 2. The lines and points of interest here are the line Δ in the [1 0 0] or equivalent directions; the line Λ in the [1 1 0] or equivalent directions, and the line Σ in the [1 1 1] or equivalent direcotions, and the point Γ at the center of the zone. The use of these symmetries to choose wave functions is given in Appendix C. We shall simply consider the results here.

The point Γ has the full cubic symmetry. The group of is O_H. This group contains forty-eight elements in ten classes. If we adopt the notation that C refers to an s-type atomic function,

p_x, p_y, and p_z refer to linear combinations of the $\ell = 1$ spherical harmonics which transform as x,y, and z respectively, then using the standard notation[45]

$$\alpha = \Gamma_1$$
$$\Psi_{\Gamma_1} = C$$
$$\alpha = \Gamma_{15}$$
$$\Psi_{\Gamma_{15}} = p_x, p_y, p_z$$

The line Δ has the same symmetry as a square in two dimensions. This group is C_{4v} and is a subgroup of O_H. If the direction of the line Δ is [1 0 0] one finds

$$\alpha = \Delta_1$$
$$\Psi_{\Delta_1} = C, p_x$$
$$\alpha = \Delta_5$$
$$\Psi_{\Delta_5} = p_y, p_z$$

The line Σ has the symmetry of a line in two dimensions. It is represented by the group C_{2v}, a subgroup of O_H. If the direction of the line Σ is [1 1 0], then

$$\alpha = \Sigma_1$$
$$\Psi_{\Sigma_1} = C, \frac{1}{\sqrt{2}}(p_x + p_y)$$
$$\alpha = \Sigma_3$$
$$\Psi_{\Sigma_3} = p_z$$
$$\alpha = \Sigma_4$$
$$\Psi_{\Sigma_4} = 1/\sqrt{2}(p_x - p_y)$$

The line Λ has the symmetry of the triangle in two dimensions. This has C_{3v} as its group. This is a subgroup of O_H. For Λ in the [1 1 1] direction, one finds

$$\alpha = \Lambda_1$$
$$\Psi_{\Lambda_1} = C_1 \frac{1}{\sqrt{3}}(p_x + p_y + p_z)$$
$$\alpha = \Lambda_3$$
$$\Psi_{\Lambda_3} = \frac{1}{\sqrt{2}}(p_x - p_y), \frac{1}{\sqrt{6}}(p_x + p_y - 2p_z)$$

Thus we have obtained basis vectors for our Hamiltonian.

The next task is to evaluate matrix elements for our Hamiltonian. To do this we adopt the coordinate system shown in Figure 3. Using this system, one defines some terms:

$$V_S = \int \varphi_c^2(\vec{r})\left[V_M(\vec{r}) + \sum_{\nu=1}^{6} V_{NaST}(\vec{r}-\vec{R}_\nu) + \sum_{\mu=1}^{12} V_{IST}(\vec{r}-\vec{R}_\mu)\right] d\tau$$

$$V_p = \int \varphi_{pi}^2(\vec{r})\left[V_M(\vec{r}) + \sum_{\nu=1}^{6} V_{NaST}(\vec{r}-\vec{R}_\nu) + \sum_{\mu=1}^{12} V_{IST}(\vec{r}-\vec{R}_\mu)\right] d\tau$$

$$V_{ss} = \int \varphi_c(\vec{r})\varphi_c(\vec{r}-\vec{R}_\mu)\left[V_M(\vec{r}) + V_{IST}(\vec{r}-\vec{R}_\mu)\right] d\tau$$

$$V_{sp\sigma} = \int \varphi_{3pz}(\vec{r})\varphi_c(\vec{r}-\vec{R}_\mu)\left[V_M(\vec{r}) + V_{IST}(\vec{r}-\vec{R}_\mu)\right] d\tau$$

$$V_{pp\sigma} = \int \varphi_{pz}(\vec{r})\varphi_{pz}(\vec{r}-\vec{R}_\mu)\left[V_M(\vec{r}) + V_{IST}(\vec{r}-\vec{R}_\mu)\right] d\tau$$

$$V_{pp\pi} = \int \varphi_{px}(\vec{r})\varphi_{px}(\vec{r}-\vec{R}_\mu)\left[V_M(\vec{r}) + V_{IST}(\vec{r}-\vec{R}_\mu)\right] d\tau$$

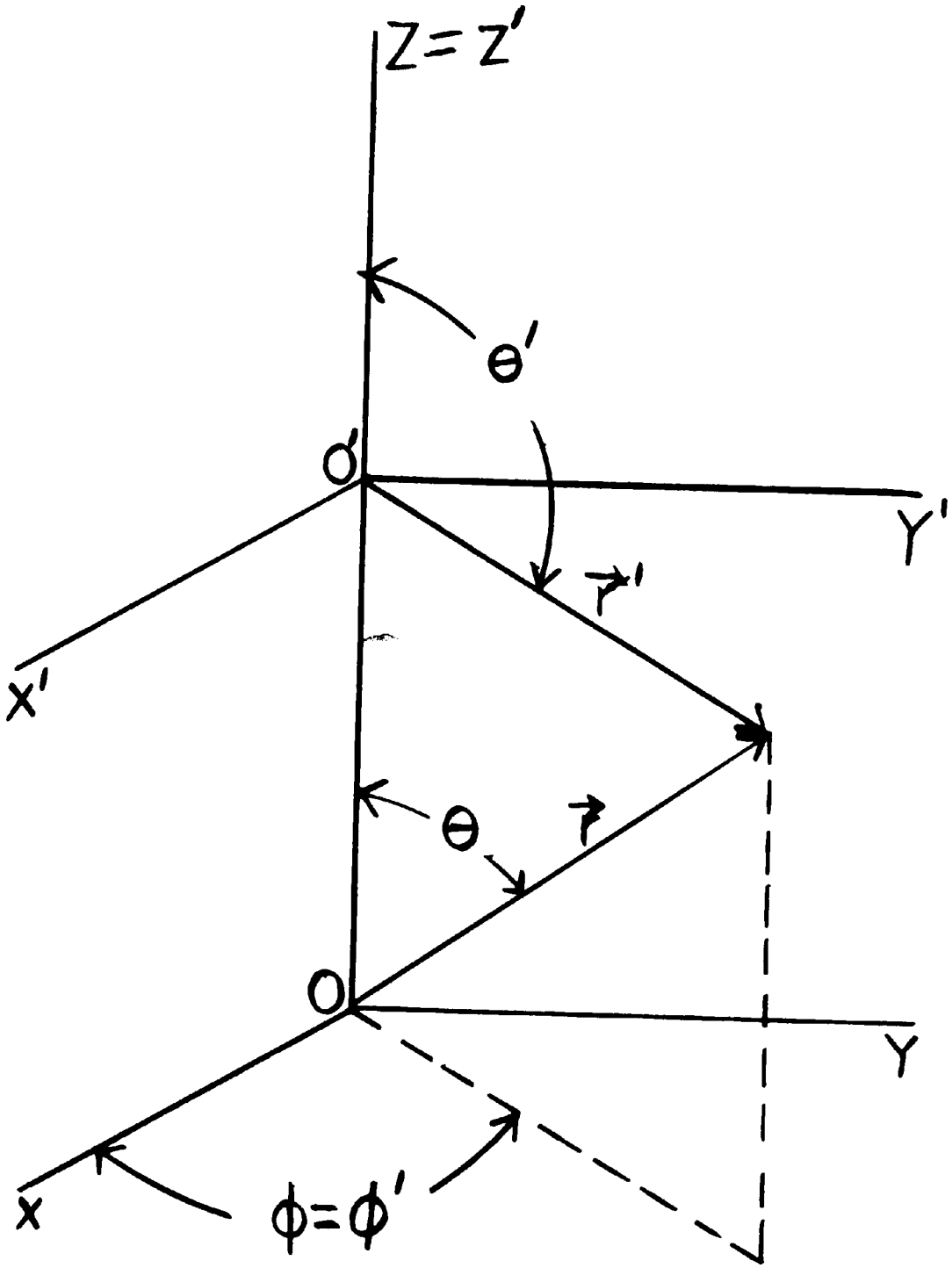
$$S_{ss} = \int \varphi_c(\vec{r})\,\varphi_c(\vec{r}-\vec{R}_\mu)\, d\tau$$

$$S_{sp\sigma} = \int \varphi_{pz}(\vec{r})\varphi_c(\vec{r}-\vec{R}_\mu)\, d\tau$$

$$S_{pp\sigma} = \int \varphi_{pz}(\vec{r})\,\varphi_{pz}(\vec{r}-\vec{R}_\mu)\, d\tau$$

$$S_{pp\pi} = \int \varphi_{px}(\vec{r})\,\varphi_{px}(\vec{r}-\vec{R}_\mu)\, d\tau$$

FIGURE 3. Coordinate system used in the evaluation of two center integrals.



Using the definitions which have been given in Eq.(4), one finds the following expressions for the energy:[46]

At the point $\Gamma\ (\vec{k}=0)$

$$H_{ss}(\Gamma_1) = \epsilon_s + \frac{V_s + 12\,V_{ss}}{1+12\,S_{ss}}$$

$$H_{pp}(\Gamma_{15}) = \epsilon_p + \frac{V_p + 4(V_{pp\sigma} + 2V_{pp\pi})}{1+4(S_{pp\sigma}+2S_{pp\pi})}$$

On the line $\Delta\ (\vec{k} = \frac{\pi}{a}(q,0,0),\ 0<q<1)$

$$H_{ss}(\Delta_1) = \epsilon_s + \frac{V_s + (8\cos\pi q + 4)V_{ss}}{1+(8\cos\pi q+4)S_{ss}}$$

$$H_{pp}(\Delta_1) = \epsilon_p + \frac{V_p + 4[\cos\pi q(V_{pp\pi}+V_{pp\sigma}) + V_{pp\pi}]}{1+4[\cos\pi q(S_{pp\pi}+S_{pp\sigma})+S_{pp\pi}]}$$

$$H_{ps}(\Delta_1) = \frac{i\,4\sqrt{2}\sin\pi q\, V_{sp\sigma}}{[1+(8\cos\pi q+4)S_{ss}]^{\frac{1}{2}}[1+4(\cos\pi q(S_{pp\pi}+S_{pp\sigma})+S_{pp\pi}]^{\frac{1}{2}}}$$

$$H_{pp}(\Delta_5) = \epsilon_p + \frac{V_p + 2[\cos\pi q(V_{pp\sigma}+3V_{pp\pi}) + V_{pp\sigma}+V_{pp\pi}]}{1+2[\cos\pi q(S_{pp\sigma}+3S_{pp\pi})+S_{pp\sigma}+S_{pp\pi}]}$$

Note that $H_{pp}(\Delta_5)$ is two-fold degenerate.

On the line $\Sigma\ (\vec{k} = \frac{3\pi q}{4a}(1,1,0),\ 0<q<1)$

$$H_{ss}(\Sigma_1) = \epsilon_s + \frac{V_s + 2[1+\cos\frac{3\pi}{2}q + 4\cos\frac{3\pi}{4}q]V_{ss}}{1+2[1+\cos\frac{3\pi}{2}q+4\cos\frac{3\pi}{4}q]S_{ss}}$$

$$H_{pp}(\Sigma_1) = \epsilon_p + \frac{V_p + [V_{pp\sigma}(2\cos\frac{3\pi}{2}q + 2\cos\frac{3\pi}{4}q)}{1+[S_{pp\sigma}(2\cos\frac{3\pi}{2}q+2\cos\frac{3\pi}{4}q)}$$

$$\frac{+V_{pp\pi}\left(2+6\cos\frac{3\pi}{4}q\right)]}{+S_{pp\pi}\left(2+6\cos\frac{3\pi}{4}q\right)]}$$

$$H_{sp}(\Sigma_1) = \frac{2i\left(\sin\frac{3\pi}{2}q + 2\sin\frac{3\pi}{4}q\right)V_{sp\sigma}}{\left[1+2\left[1+\cos\frac{3\pi}{2}q+4\cos\frac{3\pi}{4}q\right]S_{ss}\right]^{\frac{1}{2}}}$$

$$\overline{\left[1+\left[S_{pp\sigma}\left(2\cos\frac{3\pi}{2}q+2\cos\frac{3\pi}{4}q\right)+S_{pp\pi}\left(2+6\cos\frac{3\pi}{4}q\right)\right]\right]^{1/2}}$$

$$H_{pp}(\Sigma_3) = \epsilon_p + \frac{V_p + 2\left[V_{pp\pi}\left(1+\cos\frac{3\pi}{2}q\right)+2\left(V_{pp\pi}+V_{pp\sigma}\right)\cos\frac{3\pi}{4}q\right]}{1+2\left[S_{pp\pi}\left(1+\cos\frac{3\pi}{2}q\right)+2\left(S_{pp\pi}+S_{pp\sigma}\right)\cos\frac{3\pi}{4}q\right]}$$

$$H_{pp}(\Sigma_4) = \epsilon_p + \frac{V_p + 2\left[V_{pp\sigma}+V_{pp\pi}\cos\frac{3\pi}{2}q+\cos\frac{3\pi}{4}q\left(V_{pp\sigma}+3V_{pp\pi}\right)\right]}{1+2\left[S_{pp\sigma}+S_{pp\pi}\cos\frac{3\pi}{2}q+\cos\frac{3\pi}{4}q\left(S_{pp\sigma}+3S_{pp\pi}\right)\right]}$$

Finally, we consider the line Λ **which is** $\vec{k} = \frac{\pi}{2a}q(1,1,1)$ $(0<q<1)$

$$H_{ss}(\Lambda_1) = \epsilon_s + \frac{V_s + 6\left(1+\cos\pi q\right)V_{ss}}{1+6\left(1+\cos\pi q\right)S_{ss}}$$

$$H_{pp}(\Lambda_1) = \epsilon_p + \frac{V_p + \left[6V_{pp\pi}+2\left(2V_{pp\sigma}+V_{pp\pi}\right)\cos\pi q\right]}{1+\left[6S_{pp\pi}+2\left(2S_{pp\sigma}+S_{pp\pi}\right)\cos\pi q\right]}$$

$$H_{sp}(\Lambda_1) = \frac{\sqrt{3}\;2i\left(\sqrt{2}\sin\pi q\right)V_{sp\sigma}}{\left[1+6\left(1+\cos\pi q\right)S_{ss}\right]^{1/2}\left[1+6S_{pp\pi}+2\left(2S_{pp\sigma}+S_{pp\pi}\right)\cos\pi q\right]^{1/2}}$$

$$H_{pp}(\Lambda_3) = \epsilon_p + \frac{V_p + \left[V_{pp\sigma}\left(3+\cos\pi q\right)+V_{pp\pi}\left(3+5\cos\pi q\right)\right]}{1+\left[S_{pp\sigma}\left(3+\cos\pi q\right)+S_{pp\pi}\left(3+5\cos\pi q\right)\right]}$$

We note that $H_{pp}(\Lambda_3)$ is two-fold degenerate. We must solve for $H(\Delta_1)$, $H(\Lambda_1)$,and $H(\Sigma_1)$ from the secular equation, since we see that there is a coupling between s and p type functions for these states.

C. Numerical Results for NaI.

The various parameters defining our bands as given in the previous section have been evaluated for several different values of lattice parameter. The value of a=6.15 Bohr units was used as the normal lattice parameter.[1] Also considered were a=6.22, 6.08, and 5.98 Bohr units. A program was written for use on an IBM 7094 or CDC 6600 to evaluate the various two center integrals which occur in the theory. This program uses a double Simpson's rule to perform the computation. It is noted here that it is designed to use the functions and potentials produced by the method of Herman and Skillman.[28] One must also be impressed by the amount of time consumed by a single multiple integration. This program requires about fifty minutes to execute on a 7094 and about three minutes to execute on a 6600. This program is discussed in more detail in Appendix D. For the purposes of comparison a shorter and less accurate program was used. This executed in thirty minutes on the G.E.225 and six seconds on the CDC 6600. This shorter version is not included, as it is good only to two significant figures and was not used in obtaining the final results.

The values of the various band parameters are given in Table 1. Using these parameters and the band form equations given in the previous section, the values of each energy level were obtained for several points in the first Brillouin zone. In the [1 0 0] direction this was evaluated at thirty five equally spaced points along this axis. In the [1 1 0] direction the energy was evaluated at twenty-six equally spaced points, and in the [1 1 1] direction at seventeen equally distant points. The results of doing this for each of the four lattice parameters is given in Figures 4,5,6,and 7. We list the energies of selected points of high symmetry in Table 2. It is noted that these band shapes are in reasonable agreement with those obtained by Howland[13] and Bassani, Knox and Fowler.[20] These bands have widths ranging from about 2.0 ev at a=5.98 to 1.3 ev at a=6.22. For KCl Howland[13] obtained a width of 1.5 ev and Bassani, Knox and Fowler[20] found AgCl to be about 1.7 ev. Thus it is seen that these results are consistent with the results obtained by others for ionic crystals. The above calculations are cited because of their rather complete nature.

Having evaluated the Hamiltonian for the NaI valence bands without spin-orbit effects, but including second order effects due to the electrostatic potentials, we may now apply first order perturbation theory to correct the results of this section. To do this we shall assume $\vec{L} \cdot \vec{S}$ coupling. The method of applying this is con-

sidered in Chapter IV However before considering this, we shall consider the case of an anisotropically strained lattice, since this could have interesting experimental implications in the analysis of data

TABLE I

The Band Parameters for NaI. The atomic system of units is used

ϵ_{ss} = .4344

ϵ_{sp} = .[illegible]

Parameter	a=[illegible]	a=[illegible]	a=[illegible].08	a=5.98
V_s	5705	[illegible]774	.5849	-.5964
V_c	[illegible].3	[illegible].43	6360	- 6456
[illegible]	[illegible].4[illegible]	[illegible]	00302	-.00354
[illegible]	[illegible]	[illegible]	0489	- 0532
[illegible]	[illegible]	[illegible]	[illegible]06920	0.07479
[illegible]	[illegible]	[illegible]	[illegible]1878	-.02066
[illegible]	[illegible]	[illegible]	[illegible]0337	0.00391
[illegible]	[illegible]	[illegible]	[illegible]342	0.0370
[illegible]	[illegible]	[illegible]	08930	- 09454
[illegible]	[illegible]	[illegible]	[illegible]0261	0.02830

TABLE 2.

The Energy of Selected Symmetry Points in the First Brillouin Zone for the Various Lattice Constants. Spin-Orbit Effects not included. (Atomic units.)

Point	a=6.22	a=6.15	a=6.08	a=5.98
Γ_{15}	-.7515	-.7619	-.7720	-.7882
X_4'	-.8227	-.8343	-.8467	-.8662
X_5'	-.7778	-.7890	-.8007	-.8189
L_2'	-.8261	-.8377	-.8500	-.8692
L_3'	-.7517	-.7619	-.7724	-.7887
K_1	-.7984	-.8099	-.8222	-.8412
K_3	-.8132	-.8249	-.8372	-.8567
K_4	-.7685	-.7793	-.7907	-.8083

FIGURE 4. The 5p and 5s valence bands in NaI without spin-orbit interaction. a=5.98 Bohr units. (Note scale change).

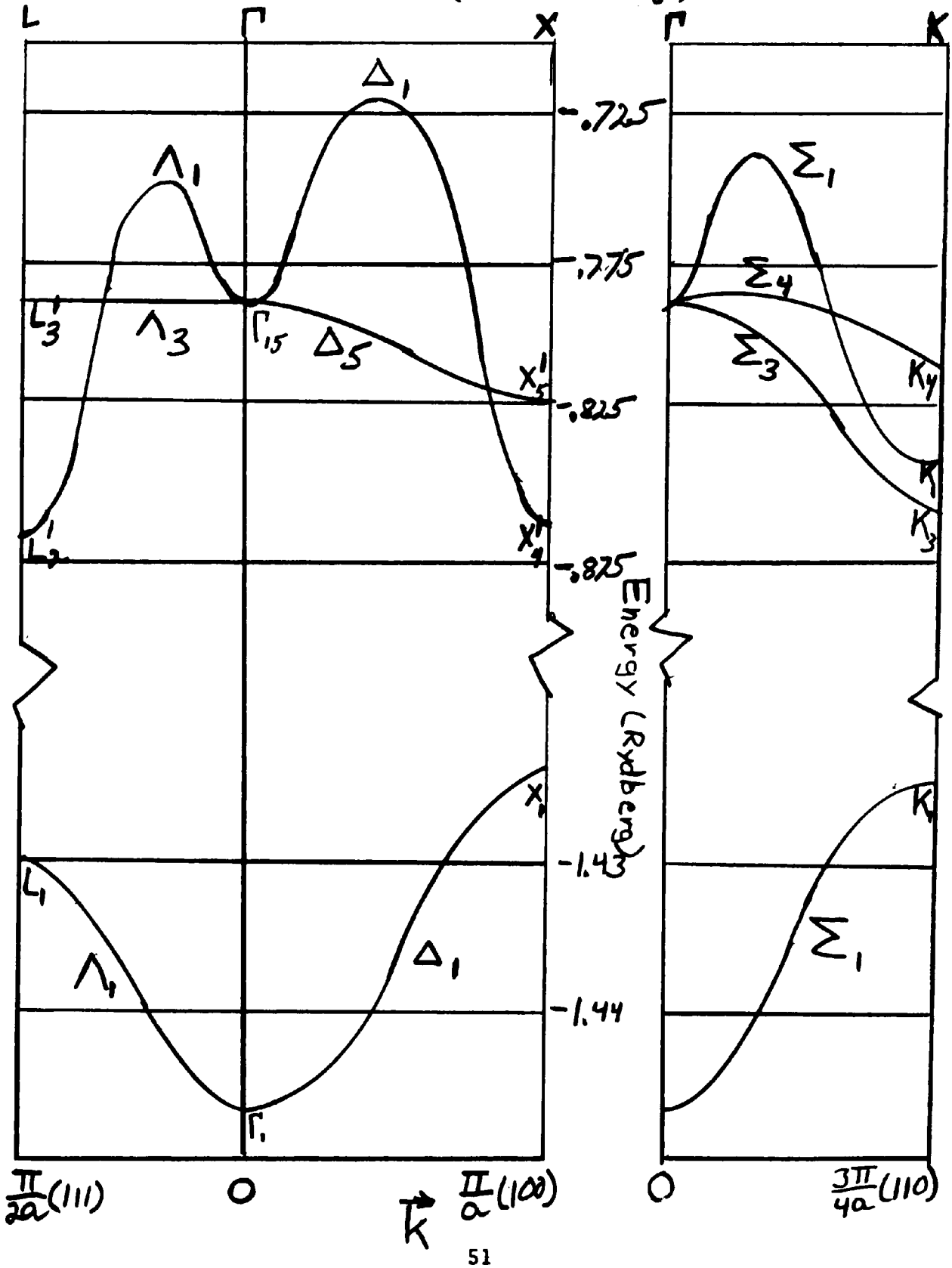


FIGURE 5. The 5p and 5s valence bands in NaI without spin-orbit interaction a=6.08 Bohr units. (Note scale change).

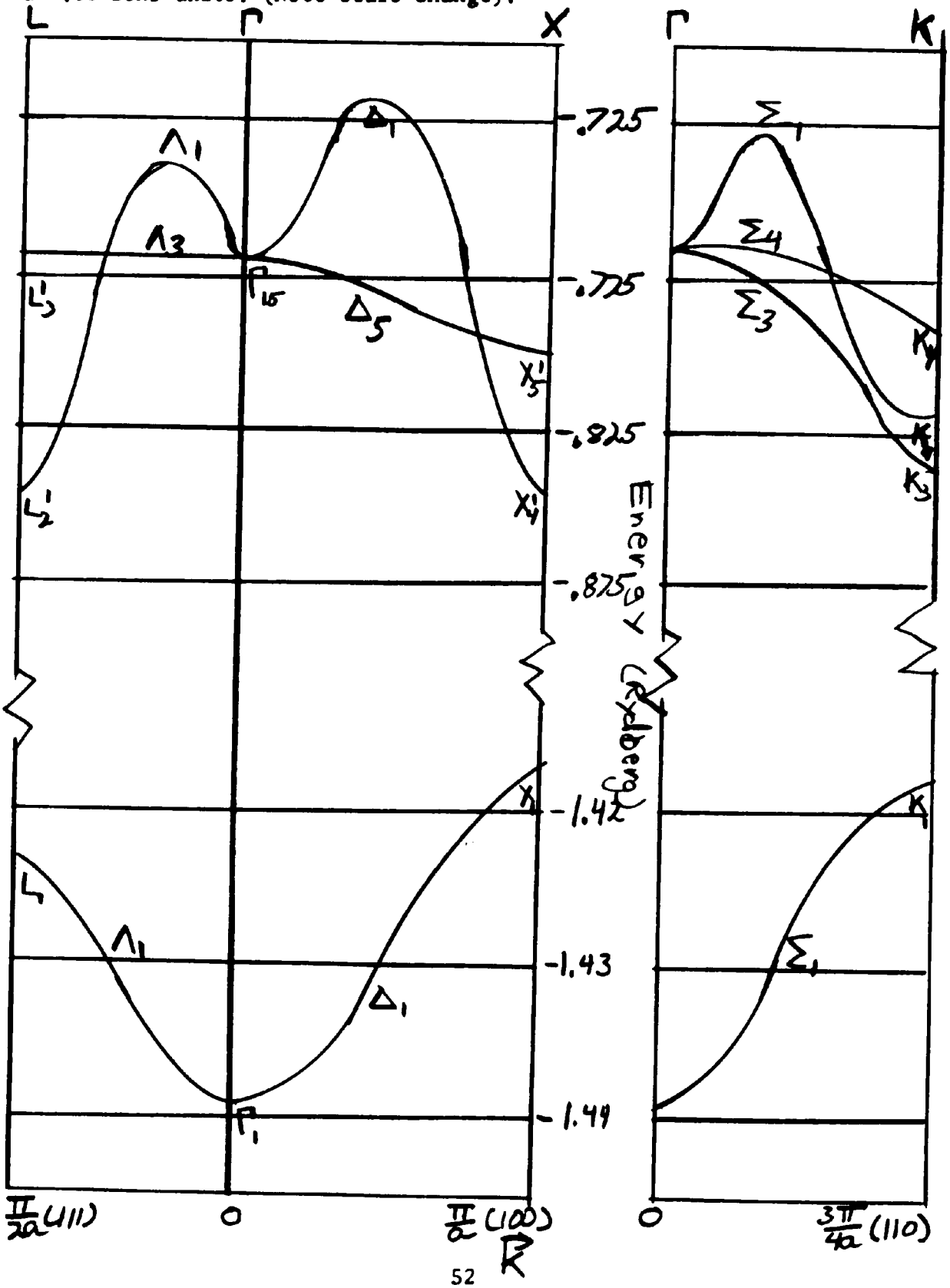


FIGURE 6. The 5p and 5s valence bands in NaI without spin-orbit interaction. a=6.15 Bohr units. (Note scale change).

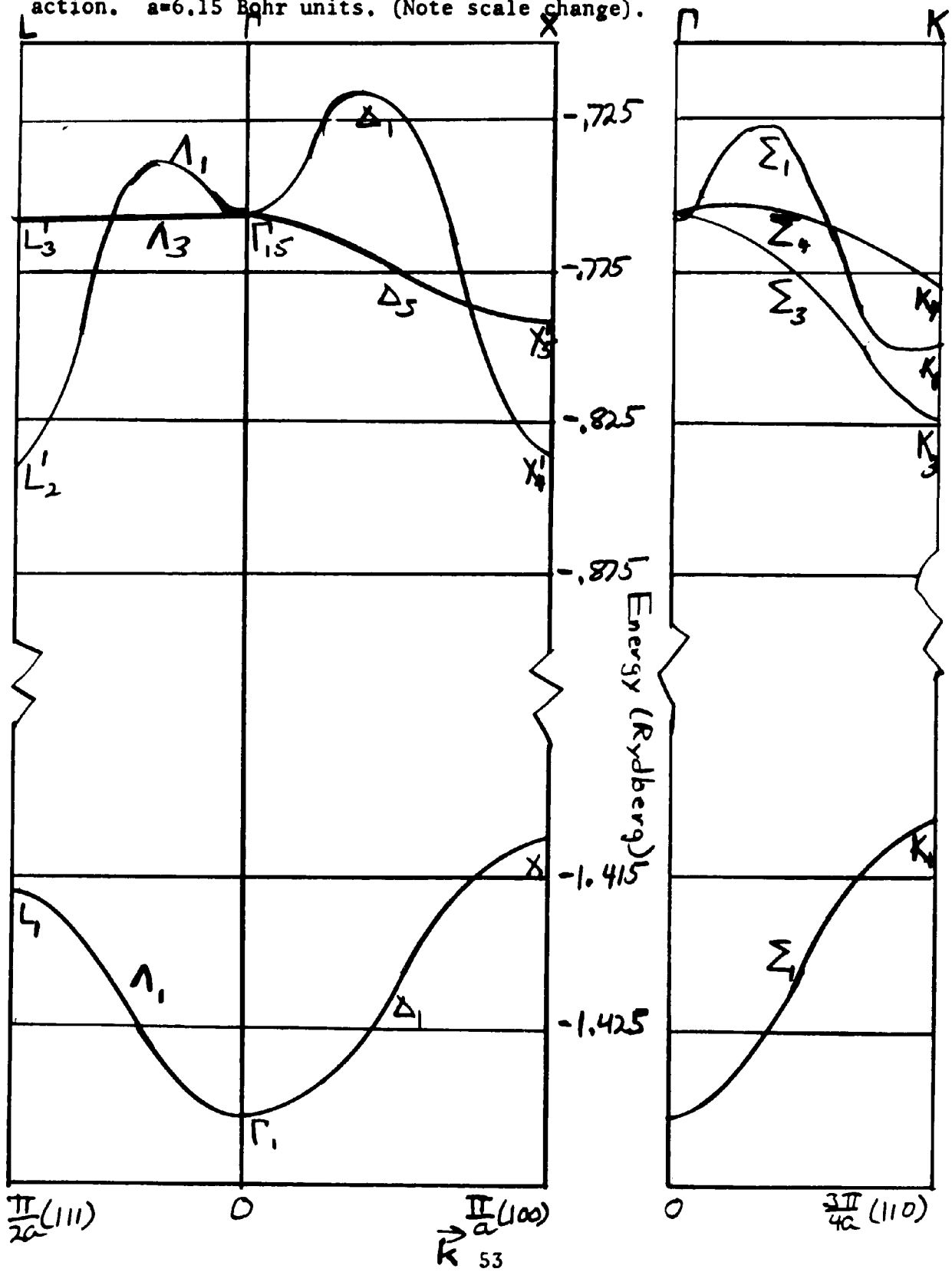
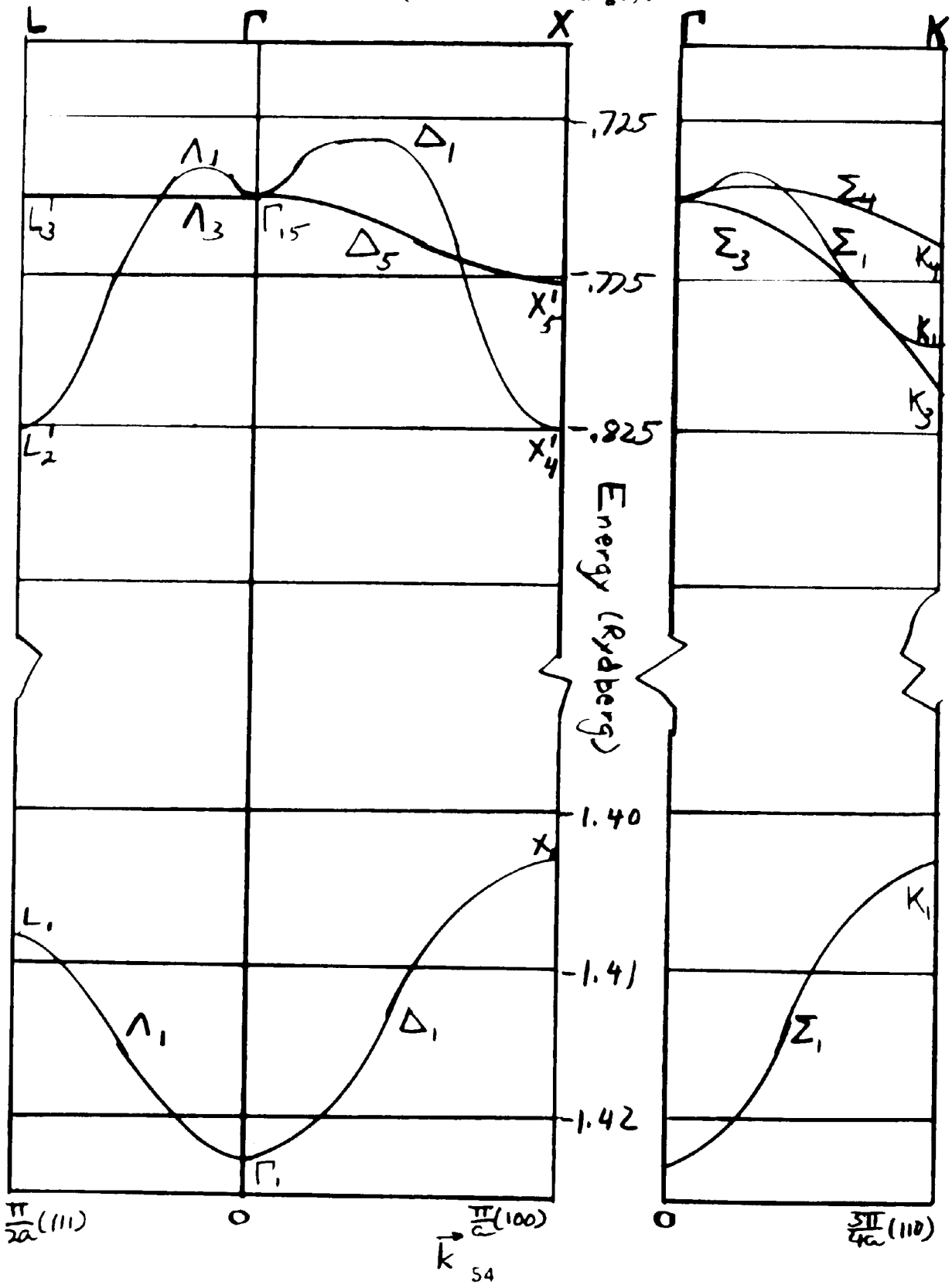


FIGURE 7. The 5p and 5s valence bands in NaI without spin-orbit interaction. a=6.22 Bohr units. (Note scale change).

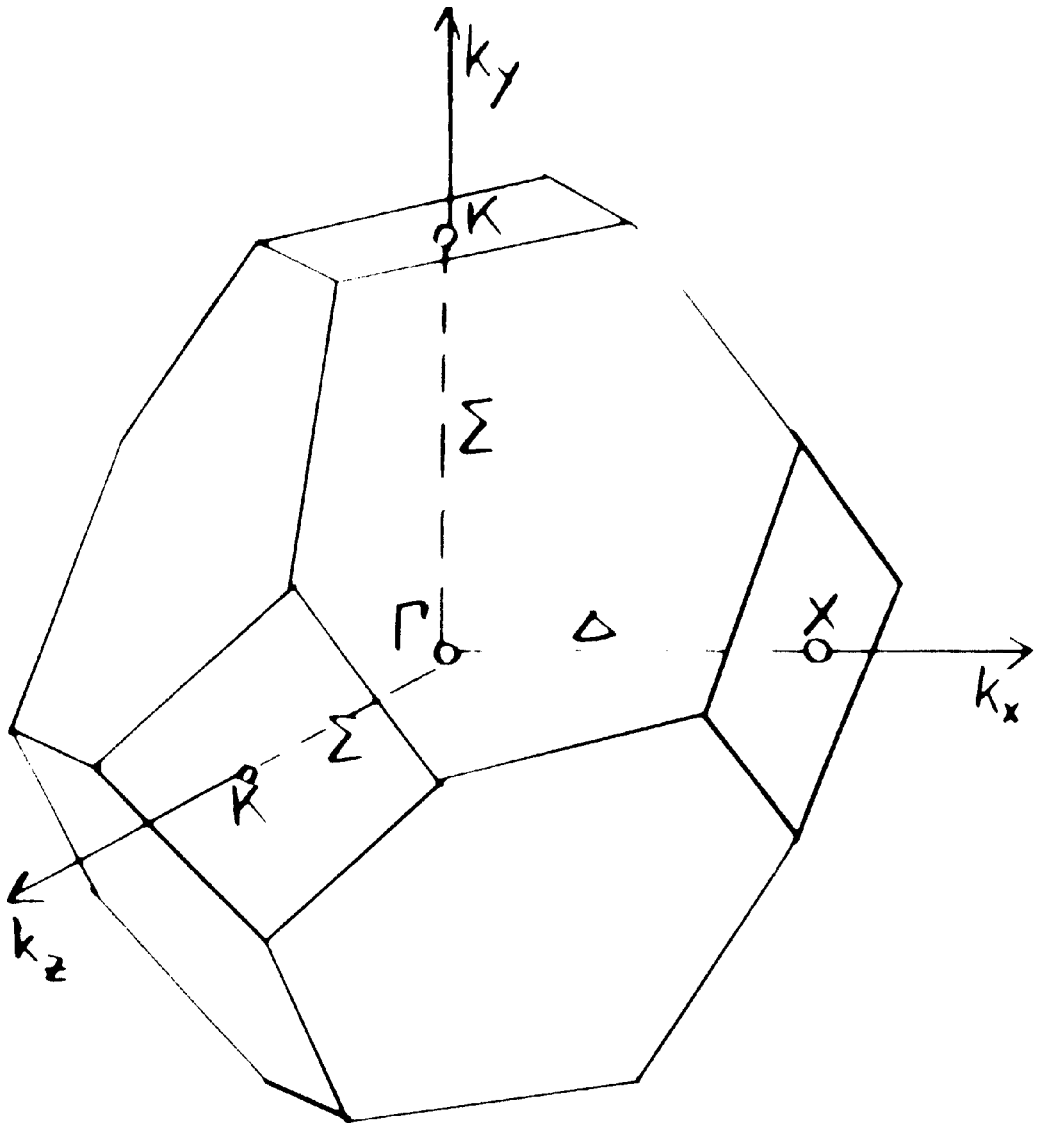


D. Anisotropic Strain in the [1 0 0] Direction

At this point the considerations relating to the valence band are complete except for spin-orbit corrections. However, useful information may be obtained from a simple consideration of a strained lattice. In this section the symmetry and possible energy structure will be considered. No definite results will be included for NaI. The usefulness of this consideration will be seen later, after a discussion of the lowest conduction band and the experimental evidence which is available.

We shall consider only a special case. Assume that one applies a tension along the [1 0 0] axis of the crystal. This will cause the crystal to elongate along the [1 0 0] axis and shorten along the [0 1 0] and [0 0 1] axes. The reciprocal lattice will shorten in the [1 0 0] direction and elongate along the [0 1 0] and [0 0 1] axes. The reciprocal lattice cell for this case is shown in Figure 8. We note that after this stress has been applied the [1 1 0] type directions and the [1 1 1] type directions are no longer axes of high symmetry. The points along the [1 1 1] type direction are just ordinary points in the zone. The four axes, [0 1 1], [0 $\bar{1}$ 1], [0 1 $\bar{1}$], [0 $\bar{1}$ $\bar{1}$], are still symmetry directions with the group C_{2v}. The results for these four axes are essentially the same as those for the [1 1 0] axis in an unstressed crystal, especially if one considers the limit as the strain goes to zero. These axes will not be considered any further

FIGURE 8. First Brillouin zone in a face centered cubic crystal with a strain along the k_x axis. Lines and points of high symmetry marked.



at this point.

Along the three [1 0 0] directions, however, something interesting occurs. The three [1 0 0] axes are no longer equivalent. The symmetry of the [1 0 0] axis is different from the symmetry of the [0 1 0] and [0 0 1] axes. The [0 1 0] and [0 0 1] axes are equivalent. Thus we have two cases to consider. We shall assume the lattice parameter along the [1 0 0] direction is a and along the [0 1 0] and [0 0 1] direction is b.

Let us consider the [1 0 0] direction first. Here one has $\vec{k} = \frac{\pi}{a} q\,(100)$ with $0 < q < 1$. The group of one of these points $\vec{k}$ is the group C_{4v} .[48,49] The properties of this group are given in Appendix C. In order to obtain the eigenfunctions for the irreducible representations of C_{4v} , we apply the projection operator O^{α} . If one uses linear combinations of P_x, P_y, P_z, C as trial functions, then the results are

$\alpha = \Delta_1$

$$\Psi(\vec{r}) = C_1 P_x$$

$\alpha = \Delta_5$

$$\Psi(\vec{r}) = P_{y_1} P_z$$

Δ_5 is two-fold degenerate. Thus one observes that for the [1 0 0] direction, the results obtained are similar to those for the [1 0 0] direction in the strained lattice. In the limit as the strain goes to zero the levels would be identical to those for the unstressed

lattice.

In the direction [0 1 0] or [0 0 1] the symmetry is seen to be that of a line in a plane. To illustrate these results we consider the direction [0 0 1]. The group of this axis is seen to be C_{2v}.[48,49] The properties of this group are given in Appendix C. The basis vectors are obtained using 0 and the trial basis vectors G, P_x, P_y, P_z. One finds that

$$\alpha = \Sigma_1$$
$$\Psi(\bar{P}) = C_j \rho_a$$
$$\alpha = \Sigma_3$$
$$\Psi(\bar{P}) = \rho_y$$
$$\alpha = \Sigma_4$$
$$\Psi(\bar{P}) = \rho_x$$

Thus one sees that along the [0 1 0] or [0 0 1] axes the degeneracy which existed along these axes in an unstrained crystal has been removed. This result and that which predicts the removal of the eight [1 1 1] axes as axes of symmetry are the ones which may be of use in checking the theoretical results and the previously made analysis of the experimental results. The energy structures are obtained to a two center nearest neighbor approximation and are given in Appendix E. The inclusion of an experiment in which a stress is applied along the [1 0 0] direction would remove the singularity in the density of states at the point L and would help check the results

of the analysis presented in Chapter V. Stresses along other axes could remove other singularities and hence check other points of the model presented in Chapter V.

IV.

SPIN-ORBIT EFFECTS.

As stated previously, one should have solved a relativistic Schroedinger equation. However, such an approach seems to be impossible at the present stage of theoretical development. The non-relativistic electrostatic equation was considered ans was solved by approximational techniques. At this point one may consider the validity of that approximation. To do so one obtains approximate corrections to the Hamiltonian and investigates them using perturbation theory.

Basically one starts with the Pauli equation for a one-electron system.[28] This is a two-component equation obtained by removing the two small components from the Dirac equation.[50] From here one requires that the potential be a scalar function of the radius. Rather than solve this equation, we chose to consider the effects of it as a perturbation. One proceeds by considering the terms as an expansion in terms of α. Here one says α is the fine structure constant, ($\alpha = 137^{-1}$). Terms of the order unity and α^2 are retained. To this order the radial part of the Pauli equation is

$$[H_0(\vec{r}) + H_m(\vec{r}) + H_d(\vec{r}) + H_{so}(\vec{r})]\, R(\vec{r}) = E\, R(\vec{r}) \qquad (1)$$

Here R(r) is the two component wave function. $\mathcal{H}_0$ is the non-relativistic Hamiltonian. The other terms are defined as

$$H_m(\vec{r}) = -(\alpha^2/4)[E^0 - V(\vec{r})]^2 \qquad (2)$$

$$H_d(\vec{r}) = -(\alpha^2/4)[dV(r)/dr]\, d/dr \qquad (3)$$

$$H_{so}(\vec{r}) = -(\alpha^2/4)\left[\frac{l}{l+1}\right]\frac{1}{r}\frac{dV(r)}{dr} \qquad (4)$$

In the above the term $H_m(\vec{r})$ is the relativistic variation of mass with velocity. E^o is the zero order energy. $H_d(\vec{r})$ is the Darwin term. This is discussed by Foldy and Woutheusen.[50] The $H_{so}(\vec{r})$ is the spin-orbit correction. The method of evaluating these parameters is given by Herman and Skillman.[28] They include a computer program for evaluating them. For the case of NaI, one will neglect $H_m(\vec{r})$ and $H_d(\vec{r})$ as being small for the states under consideration. However, the term $H_{so}(\vec{r})$ is important because it is large and also because it removes degeneracy from our energy levels. This correction is 0 for the 5s state. However for the 5p state one considers a parameter ξ given as

$$\xi = \int_0^\infty R_{5p}(r) \frac{\alpha^2}{4} \frac{1}{r} \frac{dV(r)}{dr} R_{5p}(r) r^2 dr \qquad (5)$$

One considers here only one center contributions to ξ since the Hamiltonian involves the radial derivative of the potential. This is large in the region of the nucleus and very small or zero at distances far from one. Thus the main contribution is a one center one.[21] The same argument is used to disregard the non-radial derivatives of the potential. For the case considered here one finds that ξ =0.0232 Rydbergs. One hopes that this formalism which is correct for a single electron system will work for a system of many electrons.

One may manipulate this equation to yield

$$H_{so} = \xi \vec{L} \cdot \vec{S} \qquad (6)$$

Here $\vec{L}$ is the orbital angular momentum operator for the electron and

$\vec{s}$ the spin angular momentum operator. From here one proceeds to apply these results to a crystal. To do this one takes the eigenfunctions of the tight binding Hamiltonian and forms linear combinations of them which include spin dependence and transform as irreducible representations of the group of the point in the Brillouin zone.[48,49] The appropriate double groups are given in Appendix F. The correct combinations of wave functions are given by Koster et al.[49] They are given as if $\alpha = |\frac{1}{0}|, \beta = |\frac{0}{1}|$

For the line Δ one finds

Δ_6

$$\Psi(\Delta_6) = \varphi_{5px}\alpha, \frac{1}{\sqrt{2}}[\varphi_{5pz} - i\varphi_{5py}]\beta$$

Δ_7

$$\Psi(\Delta_7) = \frac{1}{\sqrt{2}}(\varphi_{5pz} + i\varphi_{5py})\beta$$

For the line Λ

Λ_6

$$\Psi(\Lambda_6) = \frac{1}{\sqrt{3}}(\varphi_{5px} + \varphi_{5py} + \varphi_{5pz})\left[\frac{\sqrt{2}}{2}e^{i1.098}\alpha + \frac{\sqrt{2}}{2}e^{-i.478}\beta\right],$$
$$\frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(\varphi_x - \varphi_y) + i\frac{1}{\sqrt{6}}(\varphi_x + \varphi_y - 2\varphi_z)\right]\left[-\frac{\sqrt{2}}{2}e^{-i.478}\alpha + \frac{\sqrt{2}}{2}e^{-i1.093}\beta\right]$$

Λ_4, Λ_5

$$\Psi(\Lambda_4) = \pm\left[i\left[\frac{1}{\sqrt{2}}(\varphi_x - \varphi_y) - i\frac{1}{\sqrt{6}}(\varphi_x + \varphi_y - 2\varphi_z)\right]\left[-\frac{\sqrt{2}}{2}e^{i.478}\alpha + \frac{\sqrt{2}}{2}e^{-i1.093}\beta\right] + \left[\frac{1}{\sqrt{2}}(\varphi_x - \varphi_y) + i\frac{1}{\sqrt{6}}(\varphi_x + \varphi_y - 2\varphi_z)\right]\left[\frac{\sqrt{2}}{2}e^{i1.093}\alpha + \frac{\sqrt{2}}{2}e^{-i.478}\beta\right]\right]$$

$\Psi(\Lambda_5)$ = above with α and β interchanged

Here we have Λ_4 and Λ_5 degenerate.

For the line Σ one finds

$$\Sigma_5$$

$$\Psi(\Sigma_5) = \frac{1}{\sqrt{2}}(\varphi_x + \varphi_y)\left[\frac{\sqrt{2}}{2}\alpha + \frac{\sqrt{2}}{2}\beta\right], \quad -\varphi_z\left[-\frac{\sqrt{2}}{2}\alpha + \frac{\sqrt{2}}{2}\beta\right], \quad i\frac{1}{\sqrt{2}}(\varphi_x - \varphi_y)\left[-\frac{\sqrt{2}}{2}\alpha + \frac{\sqrt{2}}{2}\beta\right]$$

To use these functions one uses several identities. These are

$$\varphi_+ = Y_1^1(\theta, \varphi)$$
$$\varphi_- = Y_1^{-1}(\theta, \varphi)$$
$$\varphi_z = Y_1^0(\theta, \varphi)$$
$$\varphi_x = \frac{1}{\sqrt{2}}(\varphi_+ + \varphi_-)$$
$$\varphi_y = -\frac{i}{\sqrt{2}}(\varphi_+ - \varphi_-)$$

Here the $Y_\ell^m(\theta, \varphi)$ are the spherical harmonics.[27]

For the Pauli functions and matrices, one uses the identities

$$L_+ = L_x + iL_y \;, \quad L_- = L_x - iL_y$$

and that

$$L_\pm Y_\ell^m = \left[(\ell \mp m)(\ell \pm m + 1)\right]^{1/2} Y_\ell^{m \pm 1}$$

Now if one uses the relations for f and g which are functions of position, then

$$\vec{L}\cdot\vec{\sigma} = \frac{1}{2}(L_+ + L_-)\sigma_x - \frac{1}{2}(L_+ - L_-)\sigma_y + L_z\sigma_z$$

$$\langle f\alpha | \vec{L}\cdot\vec{\sigma} | g\alpha \rangle = -\langle f\beta | \vec{L}\cdot\vec{\sigma} | g\beta \rangle = \langle f | L_z | g \rangle$$

$$\langle f\alpha | \vec{L}\cdot\vec{\sigma} | g\beta \rangle = \langle f | L_- | g \rangle$$

$$\langle f\beta|\vec{L}\cdot\vec{\sigma}|g\alpha\rangle = \langle f|L_+|g\rangle$$
$$\langle \varphi_+|L_-|\varphi_-\rangle = \sqrt{2} = \langle \varphi_-|L_+|\varphi_+\rangle$$

Using all the above identities and the basis functions of Koster et al,[48] one may evaluate the energy matrix. One identifies the energy levels before spin-orbit interactions as $E(\alpha)$ where α refers to the irreducible representation. One defines

$$O(\alpha) = 1 + \sum_{\mu=1}^{12} e^{i\vec{k}\cdot\vec{R}_\mu} \langle \alpha s_\rho(\vec{r})|\alpha s_\rho(\vec{r}-\vec{R}_\mu)\rangle$$

Thus this is the normalization of the wave function of the α representation as a function of $\vec{k}$. With these definitions one obtains[21]

$\alpha = \Delta$

$$E(\Delta_6) = \tfrac{1}{2}\left[E(\Delta_1) + E(\Delta_5) - \frac{3}{O(\Delta_5)}\right] \pm \tfrac{1}{2}\left[\left(E(\Delta_1) - E(\Delta_5) + \frac{3}{O(\Delta_5)}\right)^2 + \frac{8\xi^2}{O(\Delta_1)O(\Delta_5)}\right]^{1/2}$$

$$E(\Delta_1) = E(\Delta_5) + 3/O(\Delta_5)$$

$\alpha = \Lambda$

$$E(\Lambda_6) = \tfrac{1}{2}\left[E(\Lambda_1) + E(\Lambda_3) - \frac{3}{O(\Lambda_3)}\right] \pm \left[\left(E(\Lambda_1) - E(\Lambda_3) + \frac{3}{O(\Lambda_3)}\right)^2 + \frac{8\xi^2}{O(\Lambda_1)O(\Lambda_3)}\right]^{1/2}$$

$$E(\Lambda_4) = E(\Lambda_5) = E(\Lambda_3) + 3/O(\Lambda_3)$$

$\alpha = \Sigma$

Here one must solve a cubic equation whose matrix elements are

Σ_5

$$E_{11} = E(\Sigma_1) - E$$

$$E_{22} = E(\Sigma_3) - E$$

$$E_{33} = E(\Sigma_4) - E$$

$$E_{12} = E_{21} = -3[O(\Sigma_1)O(\Sigma_3)]^{-1/2}$$

$$E_{23} = E_{32} = 3[O(\Sigma_3)O(\Sigma_4)]^{-1/2}$$

$$E_{13} = E_{31} = 3[O(\Sigma_1)O(\Sigma_4)]^{-1/2}$$

Here one finds $E(\Sigma_5)$ as the roots given by setting the determinant of the above matrix equal to zero.

For NaI one finds that the bands split into two bands at the point $\vec{k}=0$. The separation of these bands is about 1.25 ev. The upper and lower bands no longer overlap. Energy as a function of $\vec{k}$ was evaluated for points on the lines Δ and Λ. Thirty-five points along Δ were used and seventeen points along Λ. The direction Σ was not computed as the results of this would be uninteresting as far as comparison with experiment is concerned. These results along with a plot of the lowest conduction band are shown in Figures 9-12. The method of obtaining the lowest conduction band will be considered in Chapter V. Fowler[21] had predicted that the bands might not overlap for a system with a Sp outer shell, and this prediction is seen to be true for NaI. A table of the energies at

selected symmetry points is given in Table 3.

In Figure 13 the energies of various points as a function of lattice parameter is given. The results thus far obtained seem to be in general agreement with the results of the better previous calculations. The width of the 5p band varies from 2.5 ev at a 5.98 Bohr units to 1.75 ev at a 6.22 Bohr units.

At this point the calculations on the valence bands are complete. However we may obtain more useful information from these results and also from the results of some experiments. We may obtain information about the lowest conduction band using the technique of J.C.Phillips[18] and the experiments of Eby, Teegarden, and Dutton.[22] This is done in the next chapter. We may also obtain values for the effective masses of electrons and holes at selected points in the Brillouin zone. This information is of use to workers in exciton theory and is to be found in Chapter VI.

TABLE 3.

The Energy of Selected Symmetry Points in the First Brillouin Zone for the Various Lattice Constants. Spin-Orbit Effects are included. (Atomic Units)

Point	a=6.22	a=6.15	a=6.08	a=5.98
Γ_8^-	-.7245	-.7348	-.7448	-.7609
X_6^- upper	-.7817	-.7928	-.8035	-.8241
X_7^-	-.7523	-.7632	-.7748	-.7928
L_4^-, L_5^-	-.7223	-.7322	-.7423	-.7580
L_6^- upper	-.7654	-.7761	-.7873	-.8046
Γ_6^-	-.8045	-.8160	-.8263	-.8428
X_6^- lower	-.8444	-.8558	-.8680	-.8871
L_6^- lower	-.8419	-.8532	-.8652	-.8840

FIGURE 9. The 5p valence band and the lowest conduction band of NaI including spin-orbit interaction. a=5.98 Bohr units. (Note scale change).

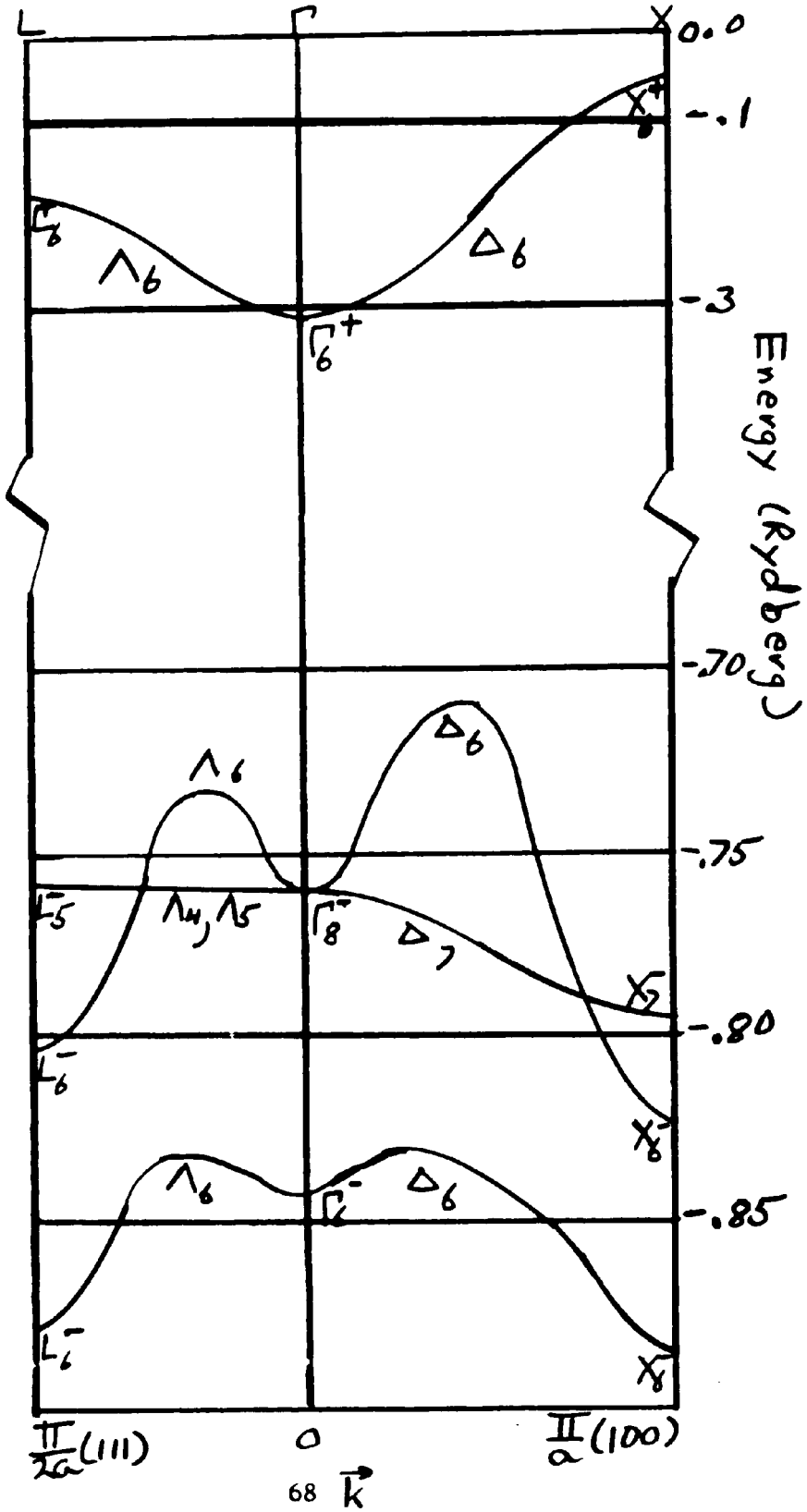


FIGURE 10. The 5p valence band and the lowest conduction band in NaI with spin-orbit interaction. a=6.08 Bohr units. (Note scale change).

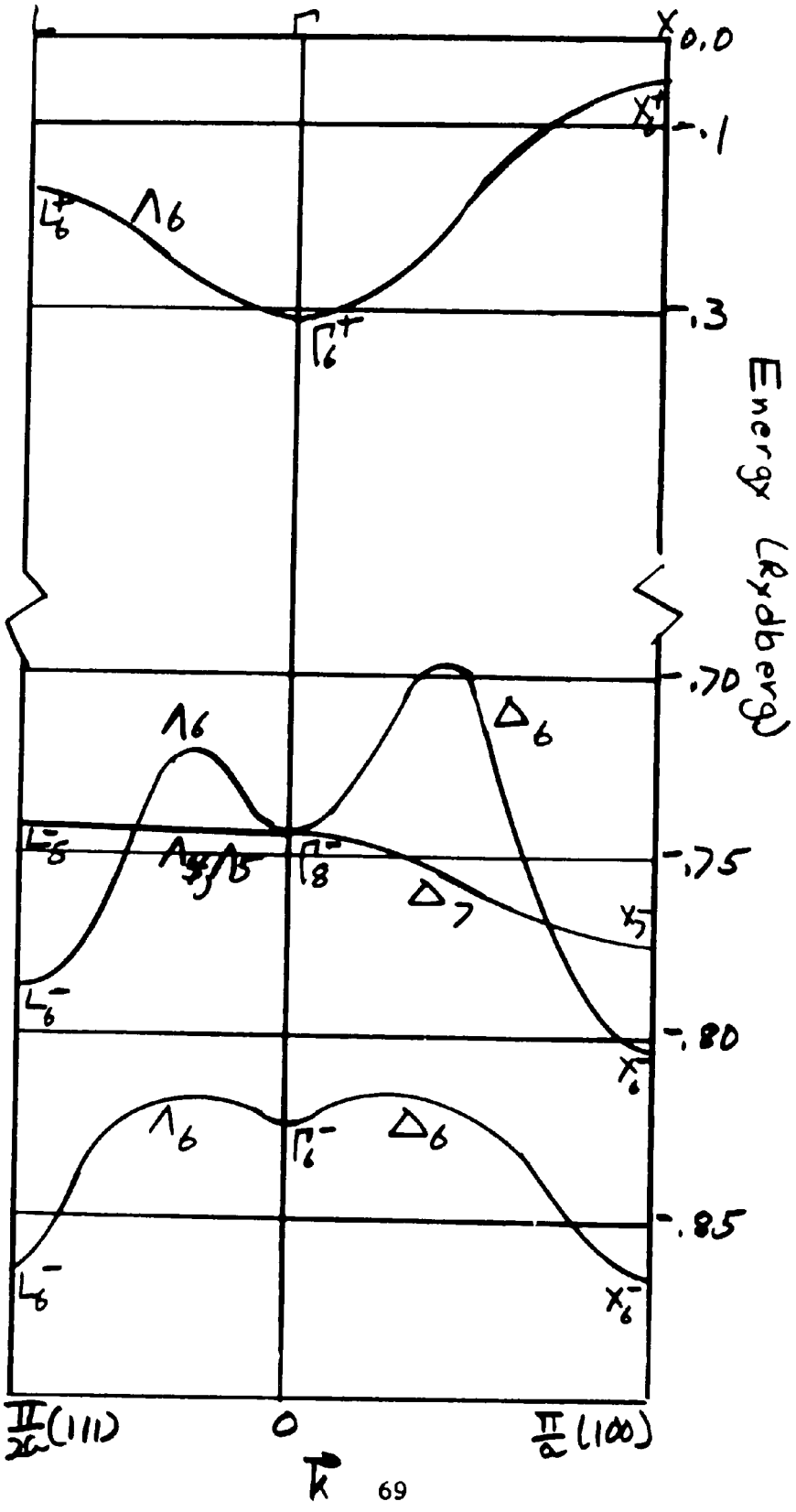


FIGURE 11. The 5p valence band and the lowest conduction band in NaI with spin-orbit interaction. a=6.15 Bohr units. (Note scale change).

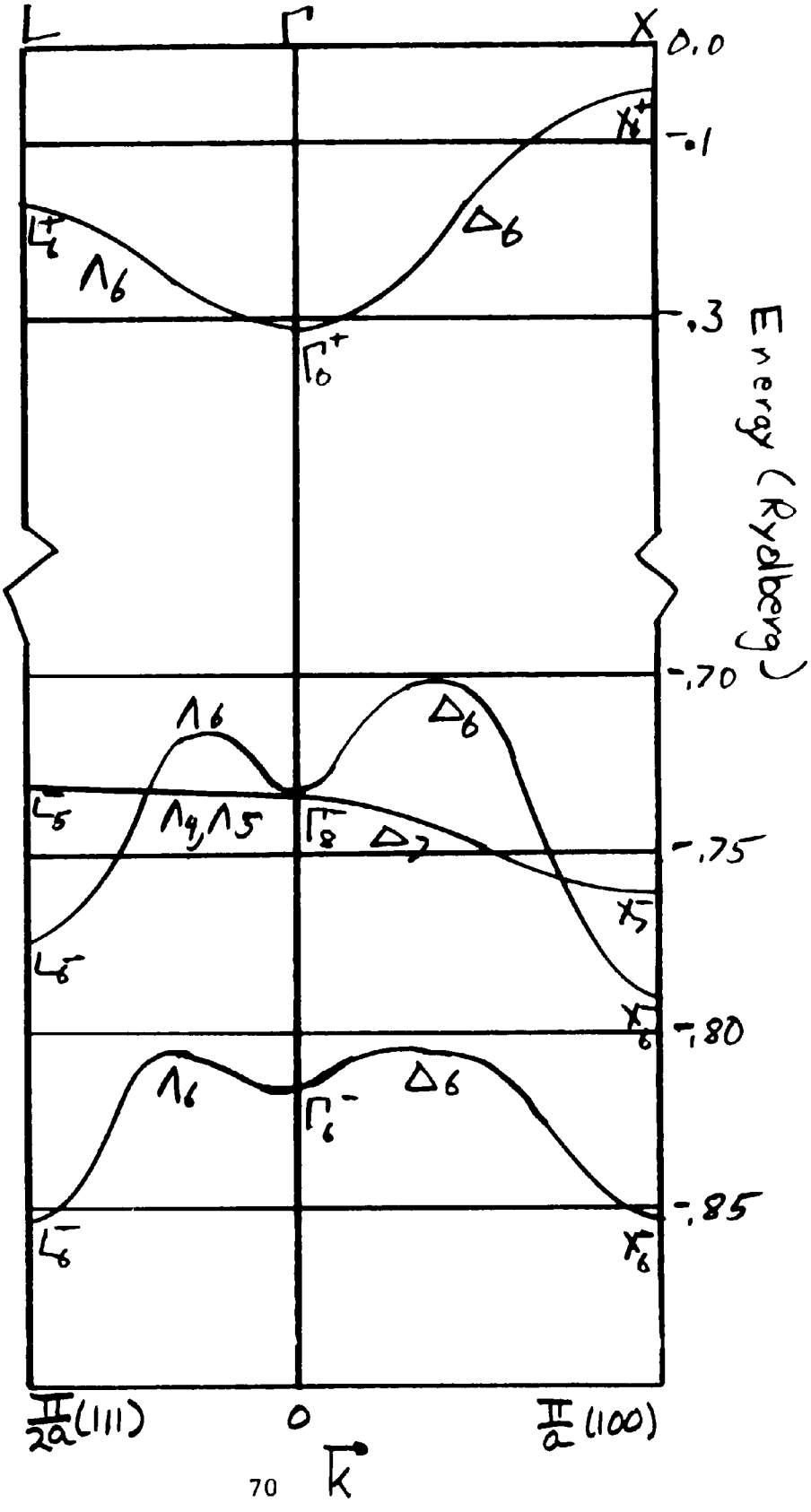


FIGURE 12. The 5p valence band and the lowest conduction band in NaI with spin-orbit interaction. a=6.22 Bohr units. (Note scale change).

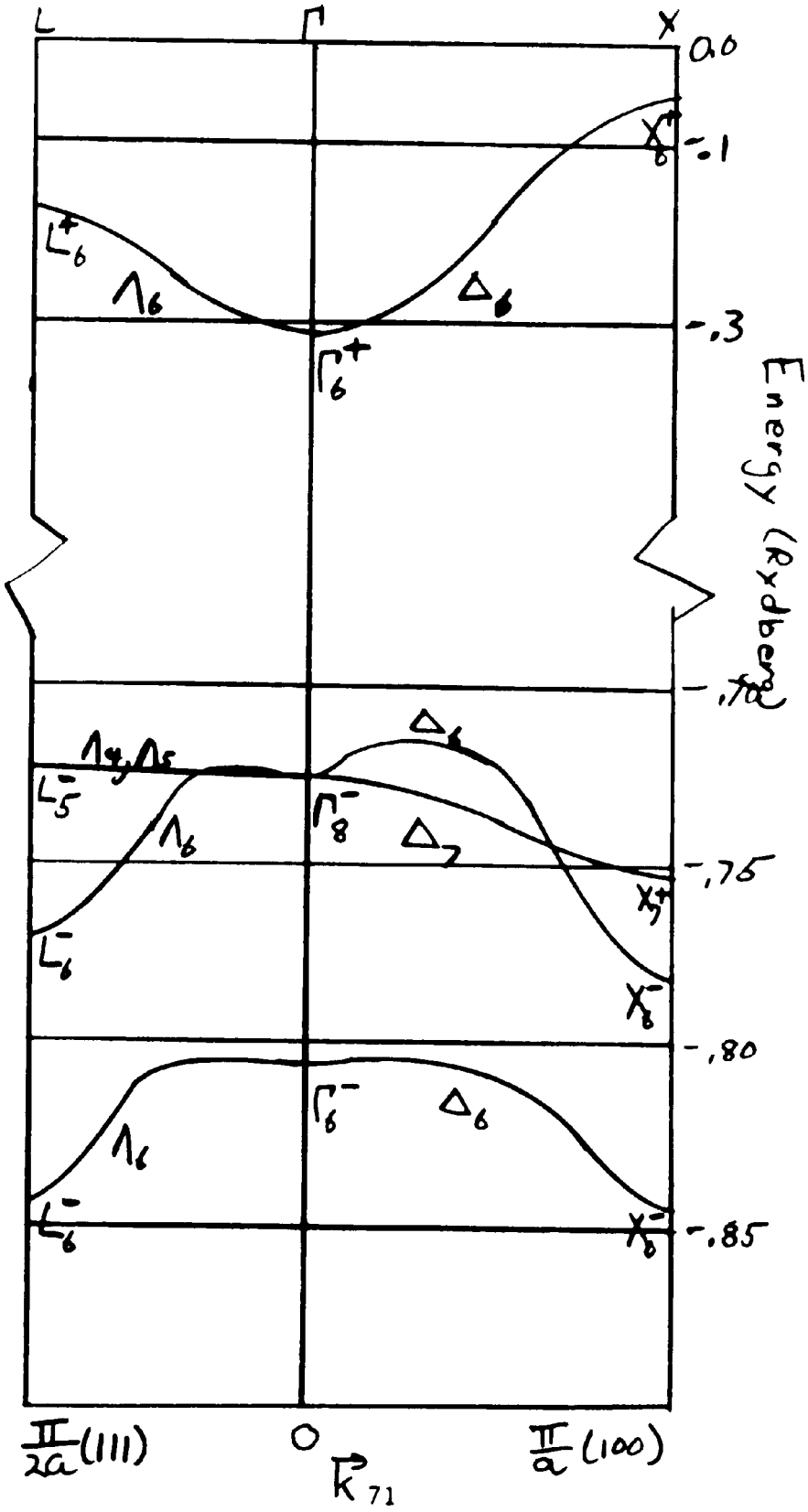
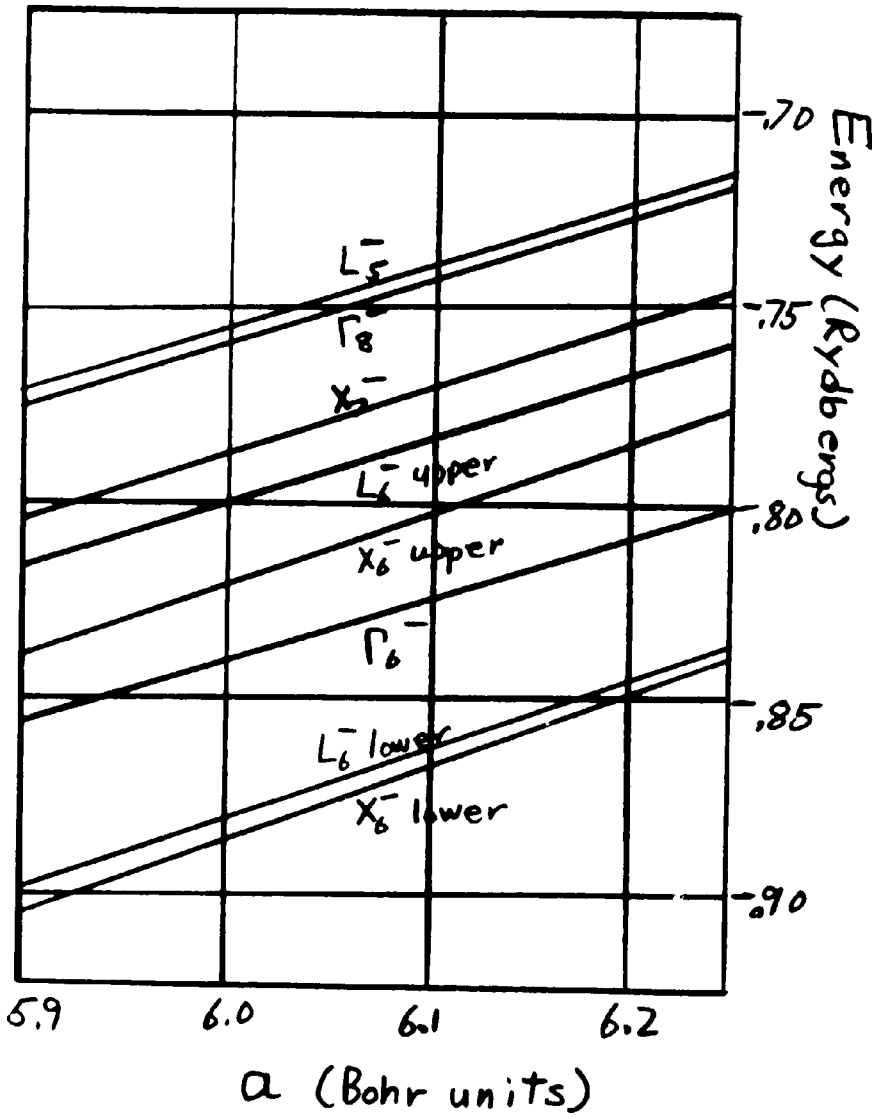


FIGURE 13. Energy as a function of lattice parameter for selected points of symmetry in the first Brillouin zone. (Atomic units). Spin-orbit effects included.



V.

CONDUCTION BAND.

A. Model of J.C.Phillips.

In the previous chapters a model for the valence band has been established, and computations have been performed which have yielded a curve for the valence band as a function of $\vec{k}$ for directions of high symmetry. A model of the excited states of a solid is not easy to come by. The representation of the exciton states by a tight binding method would seem possible; however, to get an adequate representation of the lower conduction bands by this model is difficult. In order to represent the lowest conduction band, one realizes that a large number of atomic states must be considered. Furthermore the ionic configurations are not closed shell and the problems of configuration interaction becomes more acute. This method is not considered further, as at this time it is impractical, from a standpoint of computational difficulty.

The orthogonalized plane wave method seems useful for the conduction states of tightly bound solids.[21] However the convergence of such a scheme usually requires the use of large numbers of plane waves. This is a possible task, however, since the plane waves have desirable analytic properties. There are, however, difficulties with the potential. The potential is a pseudo-potential. It is not always obvious what potential to use. That is, one always must consider

self-consistency when one performs a Hartree-Fock calculation. In the present work, this problem will be avoided by adopting the semi-empirical approach of J.C.Phillips.[17,18]

The model is based upon the part of the imaginary dielectric constant which is due to direct transitions of an electron from one level to the next. This is given as[17]

$$\epsilon_2(\omega) = \frac{e^2\hbar^2}{m} \sum_{ij} \frac{1}{V} \int \frac{f_{ij}(\vec{k})}{(E_j - E_i)} \delta(E_i - E_j - \hbar\omega)\, d\vec{k}$$

Here i and j refer to valence and conduction band states. V is the volume of the Brillouin zone and the integration is over the Brillouin zone. The oscillator strength $f_{ij}(k)$ is defined to be[1,17]

$$f_{ij}(\vec{k}) = \frac{2}{3m} \frac{|\langle i|p|j\rangle|^2}{E_j - E_i}$$

Phillips[51] shows that $f_{ij}(k)$ is a smooth function of $\vec{k}$. Therefore any radical effects noted in ϵ_2 must be due to the δ function. Phillips transforms to an integral over a surface of constant energy to obtain

$$\epsilon_2(\omega) = \frac{e^2\hbar^2}{m} \sum_{ij} \frac{1}{V} \int \frac{f_{ij}(\vec{k})}{E_{ij}\,|\nabla_k E_{ij}|}\, dS_k \qquad (1)$$

In the above $E_{ij}=E_j(k)-E_i(k)$. The density of states having the energy difference E_{ij} is proportional to

$$\frac{dN_{ij}}{dE} \propto \int \frac{1}{|\nabla_k E_{ij}|}\, dS_k \qquad (2)$$

Thus from Eq.(1) and Eq.(2) one recognizes that the singularities in the density of states are also singularities in $\epsilon_2(\omega)$. Thus one expects to see singularities in the absorption spectrum at points for which

$$\nabla_k (E_{ij}) = 0 \tag{3}$$

These points are called critical points in the Brillouin zone.[17] Of importance for this discussion is the identification of the singularities relating to the transition at the points $\vec{k}=0$, $\frac{\pi}{a}$ [1 0 0], $\frac{\pi}{2a}$ [1 1 1]. Phillips[18] has identified the points for most of the face centered cubic alkali-halide crystals. The identification of these points using the spectrum of Eby[22] for NaI is given in Figure 14. The identification of the points is that of Phillips[18] except for the transitions involving $\vec{k} = \frac{\pi}{a}$ [100] which I identify. Phillips only considered the spectra of Eby to 10 ev. The points which I identify lie on or at higher energy than 10 ev and were not considered by Phillips. Using these points and the calculation for the valence band, one may find points on the energy as a function of wave vector graph for the lowest conduction band. I find that $E(\vec{k}=0) = -.303$ Rydbergs, $E(\vec{k}= \frac{\pi}{a}$ [1 0 0]$) = -.051$ Rydbergs, $E(k= \frac{\pi}{2a}$ [1 1 1]$) = -.176$ Rydbergs. This assumes a lattice constant of 6.22 Bohr units. The extension to the other lattice parameters is given in the next section.

B. Results for NaI.

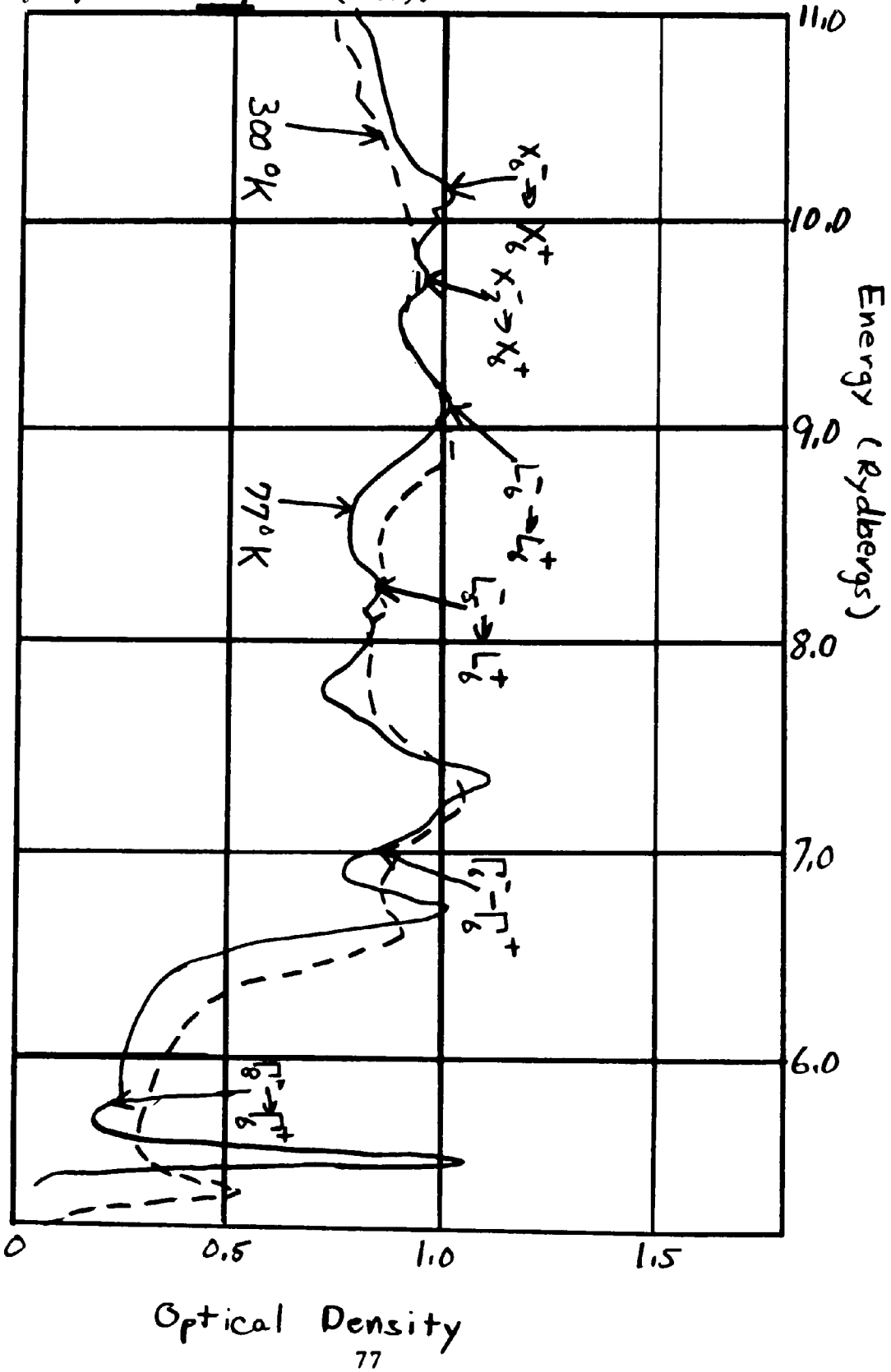
In a recent paper Bassani and Giuliano[52] have considered the band structure of the alkali-halides. Bassami located the position of the valence band by lowering the electron affinity of the halogen ion by the Madelung energy. The $\vec{k}$ dependence of the valence band was deduced from previous tight binding calculations. In doing this the width of the valence band is about 1 ev or less. The conduction band was then constructed by a calculation. Bassani and Giuliano state:[52]

> "The conduction bands are computed by perturbing the free electrons with a model pseudopotential,[53] which is the sum of pseudopotentials of the positive and negative ions. In the pseudopotential of the negative ion a parameter α is included, which cannot be determined from atomic data. The results obtained for the NaCl structure indicate that the minimum of the conduction band is the s-like state at $\vec{k}=0$. This state is insensitive to small changes in the lattice constant, but decreases considerably when the difference between the ionic radii increases."

Bassani observes that his model yields fair agreement with experiment for all alkali-halides. In the context of the above quotation a small change of lattice parameter is of the nature of five to ten per cent.[54]

Slater and Koster[46] have suggested using known energy values and assuming a symmetry type for a band to obtain tight binding type equations for the band. They suggest using general tight binding equations with as many theoretical parameters as there are known things. In the present case one has a s-like band in a face centered

FIGURE 14. Optical absorption spectra of NaI as given by Eby, Teegarden and Dutton, Phys. Rev. 116, 1099 (1959).



cubic lattice. One knows three pieces of data from Section A. The expression involving three parameters for this type of band is given as[46]

$$\alpha = \Delta_1$$

$$E_s(\vec{k}) = \epsilon_s + (8\cos\pi q + 4)V_{ss1} + (2\cos 2\pi q + 4)V_{ss2}$$

$$\alpha = \Lambda_1$$

$$E_s(\vec{k}) = \epsilon_s + 6(1+\cos\pi q)V_{ss1} + 6\cos\pi q\, V_{ss2}$$

Using the available information, one must solve the three equations

$$-.303 = \epsilon_s + 12\,V_{ss1} + 6V_{ss2}$$

$$-.176 = \epsilon_s - 6\,V_{ss2}$$

$$-.051 = \epsilon_s - 4\,V_{ss1} + 6\,V_{ss2}$$

These equations yield the solution

E_s= -.142

V_{ss1}= -.0158

V_{ss2}= 0.0054

Thus one now has obtained an analytic expression for the band forms for the lowest conduction band. It is noted that this work is constructed for a=6.15 Bohr units. However if one uses the results of Bassani and Guiliano,[52] it is seen that these expressions are useful for four lattice parameters chosen. The experimental implications of this assumption will be considered in the last chapter. The lowest conduction band is shown in Figures 9,10,11, and 12.

VI.

EFFECTIVE MASS THEORY.

The concept of an effective mass for electrons or holes has been a useful one in explaining many properties of solids. This concept involves considering an electron or hole as a free particle having an effective mass, m^*, even though the electron is not free and the hole is not a particle but rather the absence of an electron. The problem of an electron being a free particle with an effective mass is useful in the theory of electrical conductivity.[55] It is also useful in considering the properties of Wannier excitons.[19,20] Seitz[57] considers this problem using classical concepts within the framework of a quantum mechanical wave packet idea. For the present we shall not use this method but proceed by a perturbation theory.[21,58]

Bloch's theorem[34] states that the single particle wave function for a periodic lattice may be written as

$$\Psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n\vec{k}}(\vec{r}) \qquad (1)$$

where $u_{n\vec{k}}(\vec{r})$ has the periodicity of the lattice. When the form Eq.(1) is substituted in the Schroedinger for the single particle, one obtains an equation for the $u_{n\vec{k}}(\vec{r})$ which is

$$[-\nabla^2 + k^2 - 2i\vec{k}\cdot\nabla + V(\vec{r})]u_{n\vec{k}}(\vec{r}) = E_{n\vec{k}}\, u_{n\vec{k}}(\vec{r}) \qquad (2)$$

It is on Equation (2) which a perturbation is performed.

One assumes that the solution is known for a point, $\vec{k}$, in the Brillouin zone. Then the solution for a nearby point $\vec{k}'$ is desired.

Here one defines

$\vec{k}' = \vec{k} - \vec{K}$

The Equation (2) becomes

$$\left[-\nabla^2 + k'^2 + K^2 + 2\vec{K}\cdot\vec{k}' - 2i\vec{k}'\cdot\nabla - i\vec{K}\cdot\nabla + V(\vec{r})\right] u_{n\vec{k}}(\vec{r}) = E_{n\vec{K}}\, u_{n\vec{K}}(\vec{r}) \tag{3}$$

The zero order Hamiltonian is the one given in Eq.(2) with $\vec{k}$ replaced by $\vec{K}$. The perturbation is H' where

$$H' = k'^2 + 2\vec{K}\cdot\vec{k}' - i2\vec{k}'\cdot\nabla \tag{4}$$

In evaluating the corrections, one now applies second order perturbation theory.[59] Thus one obtains

$$E_{n\vec{K}} = E_{n\vec{K}} + \langle \vec{K}n | H' | \vec{K}n \rangle + \sum_m{}' \frac{|\langle \vec{K}m | H' | \vec{K}m \rangle|^2}{E_{\vec{K}m} - E_{\vec{K}n}}$$

In the present case assuming normalized $u_{n\vec{K}}$, one obtains

$$E_{n\vec{k}} = E_{n\vec{K}} + k'^2 + 2\vec{K}\cdot\vec{k}' - i2\langle \vec{K}n | \vec{k}'\cdot\nabla | Kn \rangle + 4\sum_m{}' \frac{|\langle \vec{K}m | \vec{k}'\cdot\nabla | \vec{K}n \rangle|^2}{E_{\vec{K}m} - E_{\vec{K}n}} \tag{5}$$

We note that at certain points of high symmetry such as Γ, X, L in the Brillouin zone the term

$$\langle \vec{K}n | \vec{k}'\cdot\nabla | \vec{K}n \rangle = 0$$

If one restricts discussion to these points, one obtains

$$E_{\vec{K}n} = E_{\vec{K}n} + k'^2 + 4\sum_m{}' \frac{|\langle \vec{K}m | \vec{k}'\cdot\nabla | \vec{K}n \rangle|^2}{E_{\vec{K}m} - E_{\vec{K}n}}$$

Thus the E vs. $\vec{K}$ relationships is seen to be quadratic in $\vec{K}$ for these points of high symmetry. By using an analogy to a free electron system, one defines the effective mass to be

$$m^*_{ij} = \pm \frac{1}{2} \left(\frac{\partial^2 E_{\vec{K}n}}{\partial K_i \partial K_j} \right)^{-1} \tag{6}$$

The effective mass as given by Eq.(6) is seen to be in general anisotropic, and hence the effective mass is represented as a tensor. This tensor property is useful in explaining experimental results such as the anamolous Hall effect.[57] The effective masses for the valence band and lowest conduction band have been computed by differentiating twice the energy expressions of Chapter IV and are given in Table 4. The plus sign in Eq.(6) corresponds to electrons and the minus sign to holes.

TABLE 4.

Table of Effective Masses for Electrons in the Lowest Conduction Bands and the Valence Bands. Here m=0.5 (atomic units).

point and direction	m*/m a=6.22	m*/m a=6.15	m*/m a=6.08	m*/m a=5.98
Γ_6^+ isotropic	0.309	0.319	0.325	0.337
X_6^+ along Δ_6	-.152	-.157	-.160	-.166
L_6^+ along Λ_6	-.152	-.157	-.160	-.166
Γ_8^- along Δ_7	-1.71	-1.70	-1.64	-1.63
Γ_8^- along Δ_6	1.23	0.448	0.384	0.310
Γ_8^- along $\Lambda_{4,5}$	26.1	22.4	29.1	21.4
Γ_8^- along Λ_6	4.53	0.615	0.504	0.386
Γ_6^- along Δ_6	2.64	0.923	0.797	0.640
Γ_6^- along Λ_6	2.72	0.934	0.805	0.646
X_7^- along Δ_7	1.91	1.89	1.82	1.78
X_6^- along upper Δ_6	0.554	0.423	0.397	0.367
X_6^- along lower Δ_6	0.387	0.272	0.250	0.221
$L_{4,5}^-$ along $\Lambda_{4,5}$	-22.2	-18.6	-23.9	-17.1
L_6^- along upper Λ_6	0.993	0.718	0.679	0.645
L_6^- along lower Λ_6	0.302	0.213	0.196	0.173

VII.

DISCUSSION OF RESULTS AND COMPARISON WITH EXPERIMENT.

It is concluded that the form of the tight binding method used here yields a convergent set of energy bands for the valence band of NaI. Although the first order perturbation corrections to the energy is large, the use of a second order correction within the framework of a single determinental Slater wave function was seen to produce a small effect on the energies. It is hoped that the higher order corrections will fall off rapidly, and hence be of little consequence. It is believed that the use of self-consistent atomic functions and potentials in forming the corresponding crystal quantities was of considerable value in obtaining a reasonable result.

In previous calculations the use of wave functions which are eigenfunctions of the potential chosen has not always been done.[12,15,21] This has caused a certain amount of problems. Fowler[21] in his work on krypton considered a Robinson,Bassani,Knox, and Schrieffer potential, a Slater potential, and a modified Slater potential. The wave functions used were those for a Hartree-Fock calculation for krypton. Fowler showed that the change in the energy eigenvalue for a single particle in the free atom was small when the Hartree-Fock wave function and the modified Slater potential were used.

This pleasant result was not obtained for the Slater or Robinson, Bassani, Knox, and Schrieffer potential. In general the crystal results

presented were for the modified Slater potential.

This author believes that the use of wave functions for one potential and a different potential in the crystal may introduce a large error in the calculations. We argue this as follows: In the Hartree model, the potential is strictly coulombic. Here the wave functions have a greater spacial extent than in the Hartree-Fock model which contains exchange. Thus one assumes the use of a Hartree potential with Hartree-Fock functions. The corrections to the normalization will be smaller than in the Hartree case. This has the effect of making the bands broader than they should be. If Hartree functions were used with a Hartree-Fock potential the effect would be the opposite and the bands would be narrower than they should be. It is noted that using Hartree functions with a Hartree potential produces both overlaps and energy elements which are larger than in the Hartree-Fock case. However, since the overlaps tend to decrease band width as the energy elements tend to increase band width, there will be cancellation, and hence the Hartree and Hartree-Fock values would tend to converge. One cannot make as strong an argument when using the mixed case.

The success of using a modified Slater potential with Hartree-Fock functions is due to the potential being essentially a Hartree-Fock potential. This is seen since the overlaps calculated for NaI using eigenfunctions of a modified Slater potential agree very well

with the overlaps obtained from eigenfunctions of a Hartree-Fock potential by Hafemeister and Flygare.[60] The present results are found to be less than five per cent smaller than those of Hafemeister and Flygare. Thus confidence in previous calculations[15,21] need not be shaken.

In the work of Casella,[12] a Slater potential was used for Hartree-Fock wave functions. Casella desired to obtain a minimum width for the bands of NaCl and also KCl. This was to cast light on the difference between the calculation due to Schockley[11] and the measurement of Parratt and Jossem.[16] Casella predicted an error in Parratt and Jossem's interpretation. Howland[13] obtained a result for KCl which agreed with the prediction of Casella. The model used by Howland was rather precise but made inclusion of spin-orbit effects difficult due to its complexity.

The present calculation retains essentially all the features of the Howland calculation, but is of a simpler nature due to our choice of crystal. The wave function for Na^+ are smaller and more negatively energetic than those of K^+. Thus in relation to the iodine ion, the interaction of the Na^+ wave functions are negligible. Thus it is possible to include spin-orbit interactions in the present calculation. In this calculation one sees that the band width increases from 1.75 ev when a=6.22 Bohr units to 2.45 ev when a=5.98 Bohr units. The band width is seen to be very sensitive to choice of lattice parameter.

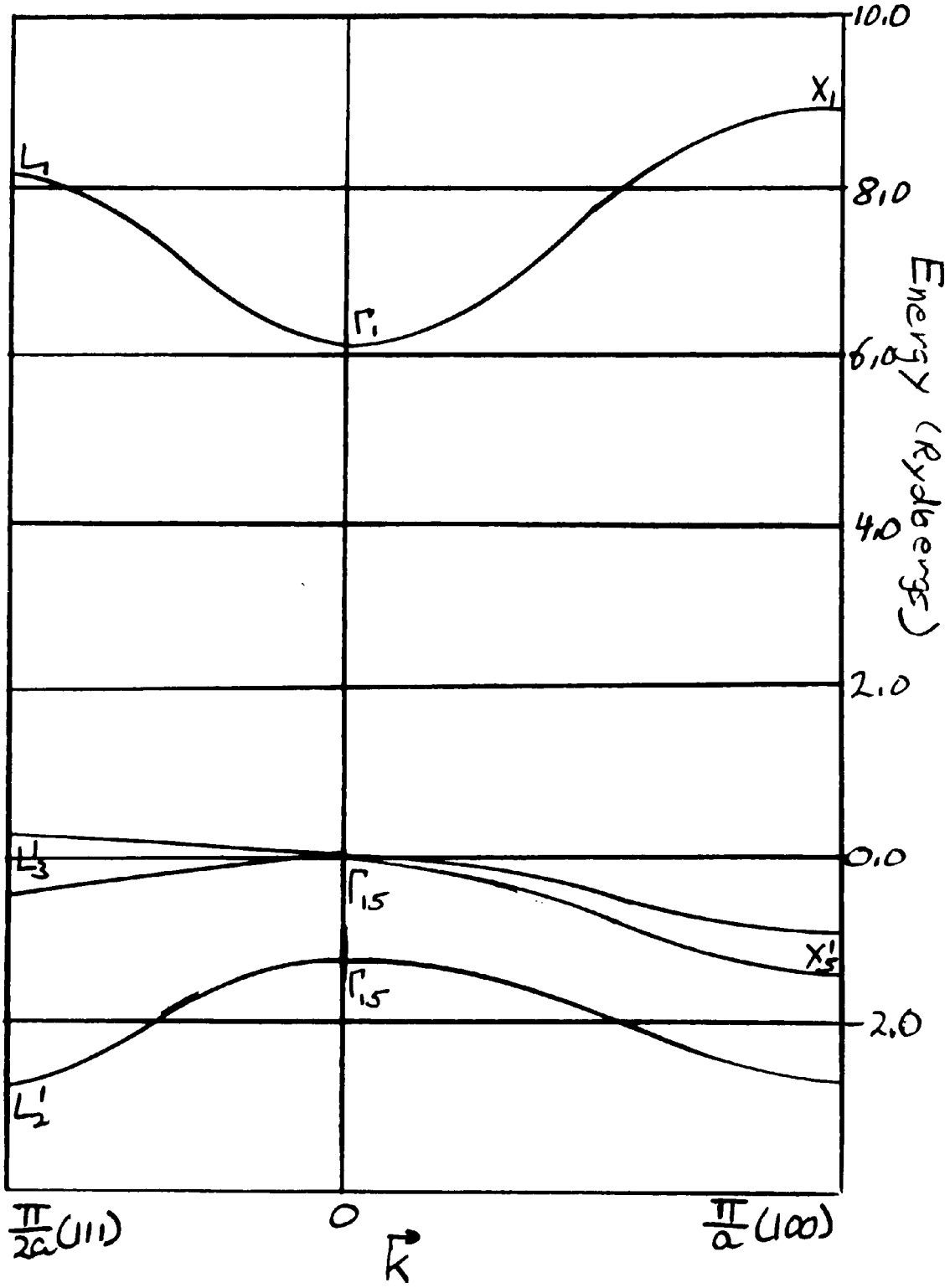
Width increases as lattice parameter decreases. This is partly in contradiction to the argument presented by Casella[12] for the case of NaCl to KCl where he predicts the opposite effect. Using the model of Casella, one also does not obtain Casella's prediction either when calculations are performed for NaCl and KCl.[61] The author suggests that more exact calculations be performed on NaCl and KCl to see if predictions of Casella are actually correct. Furthermore an experiment of the nature of Parratt and Jossem's would be of great value in evaluating the predictions of the present calculation. The large spin-orbit splitting should be of considerable help in isolating the X-ray emissions due to transitions from the 5p valence bands of NaI.

Finally one must consider the meager experimental evidence available which is able to be compared to the results of this calculation. Most of this is due to the measurements of Eby, Teefarden and Dutton.[23] The analysis due to J.C.Phillips[18] is used in identifying the points of interest in the spectrum. This spectrum taken at 70°K is given in Figure 14. Eby also yields a spectrum for about 300°K, but this is not well defined due to thermal broadening. Since the analysis of Phillips was used to construct the conduction band, the only other useful information available is that relating to the spin-orbit splitting for various points in the valence bond. To perform this analysis the results for a=6.15 are used for the temperature of 70°K. At the point Γ Phillips, using experiment, obtains

a split between Γ_6^- and Γ_8^- of 1.25 ev. In the present calculation this split is computed to be 1.25 ev. At this point the agreement is seen to be excellent. The remainder of the splittings given by Phillips are for the upper band only of the two valence bands. Phillips obtains a split between L_5^- and L_6^- of about 0.8 ± 0.2 ev. The present calculation predicts a split of about 0.65 ev. Again there is reasonable agreement of the results. For the points X_6^- and X_7^- the analysis of Phillips would predict a splitting of 0.5 ± 0.1 ev. The calculation predicts that this splitting is 0.4 ev. Thus this calculation is seen to produce results for the spin-orbit splittings which are in agreement with the results of experiment for the few points at which comparison is possible. In Figure 15 we present the results of Phillips for KI so that comparison can be made between our bands for NaI and those of Phillips for KI. We note that our valence band is narrower than Phillips', but the lowest conduction band is broader. This is due to the free electron analysis which Phillips applied to the conduction band. The author believes that the bands of Phillips are useful for qualitative arguments only. The results of this present calculation convince the author that a more accurate analysis than Phillips' is needed to obtain useful quantitative results.

Phillips[18] observes that the spin-orbit splitting for NaI at the Γ point was 1.25 ev which is considerably larger than the 0.9 ev splitting which Phillips has from ionic considerations. Phillips

FIGURE 15. The energy bands of KI as deduced by J.C.Phillips, Phys. Rev. 133, A1705 (1964).



unable to explain what causes this increase in the splitting. We note that this increased splitting is very simple to explain by using the method given in Chapter IV. The error which Phillips makes is assuming the denominator in the perturbation calculation to be unity, whereas the effect of two center corrections to the normalization cause it to be less than unity at the Γ point. Thus even though two center contributions to the H_{so} are small due to the derivative being largest about the origin, the two center effects in the wave functions normalization are not samll. Thus when one uses the theory correctly the enhanced splitting is obtained. The author notes that the splitting is enhanced in the other alkali-halides. This does not show up in the work of Phillips because the splitting is very small and the experimental error in determining them is large enough to hide the error. However, for the iodides this error is quite observable and hence lead to an apparent anomaly in Phillips' paper. For example, in LiCl the crystal splitting at Γ is calculated to be 0.13 ev while the ionic splitting is about 0.1 ev.[15]

There is one other possible experimental check which can be made at the present. This concerns the shift in energy due to the crystal being at two different temperatures. Eby, Teegarden, and Dutton[22] measured the absorption spectrum of NaI at both 70°K and 300°K. As the temperature increases the absorption energy for a given transition generally decreases. In the present model any

change in absorption energy is due to change in the location of the valence band. Hence we make reference to Table 4 and Figure 13. In Figure 13 we see that the shift in the energy of Γ_6^- and Γ_8^- with lattice parameter is essentially linear. We shall restrict our analysis to the points Γ_6^- and Γ_8^-. It should be possible to explain the energy shift in terms of changing lattice parameter.

Recently Meincke and Graham[62] measured the thermal expansion of several alkali-halides including NaI in the range from 4°K to 300°K. Since the change of energy for Γ_6^- and Γ_8^- is linear with lattice parameter, it does not matter which point one chooses for the lattice parameter for 70°K. As previously assumed the value of 6.15 Bohr units is used. Using this and the results of Meincke and Graham one finds that at 300°K the lattice parameter is about 6.20 Bohr units. Thus the shift in energy due to lattice expansion at the point Γ_6^- is 0.11 ev and at Γ_8^- is also 0.11 ev as a result of the calculation.

The experimental determination of these shifts is not very simple. The edges at 300°K are smeared out due to thermal effects, and hence an accurate determination of its precise position is not possible. In order to avoid this problem the change in position of the exciton peaks which predeed the band edges is considered. These peaks remain reasonably sharp at 300°K. The change at Γ_8^- is found to be

about 0.12 $\pm$ .025 ev and the change at Γ_6^- is about 0.10 $\pm$ .025 ev. Thus the current model is able to explain the shift in absorption energy as the temperature is raised from 70°K to 300°K. I also believe that if one were to examine the absorption spectrum of NaI at low temperature, for good resolution, and apply a strain along a [1 0 0] direction, then as noted in Chapter III, Section D, the point L should no longer be a symmetry point in the sense used in the conduction band theory as given in Chapter V, and hence one would expect the density of states at L to be nonsingular. Thus the peak associated with the point L in the spectrum should vanish. An experiment of this type would be of use in checking on the assignments of peaks with transitions as done by Phillips.[18] The use of strains along other axes than the [1 0 0] would be of use in checking on points other than L. This experiment would also be of use in checking the interpretations used in this thesis to check the results of the calculation.

In sum it is seen that the current model is able to explain such effects as the spin-orbit splitting for various band points and the temperature dependence of the band edges to the degree of accuracy of the current experiments. The author believes that the tight binding method in the present form, including second order corrections due to mixing of wave functions of different n and l and spin-orbit effects, is capable of yielding reasonable results for the valence

and lower bands of the various ionic crystals. However a procedure is needed to compute the exciton levels and perhaps also the conduction bands in order to yield a complete model of the crystal electronic structure. Perhaps an OPW or APW method would be useful for the conduction bands, however, care should be taken to produce a self-consistent result in this case. The author believes that the correct treatment of the exciton levels lies somewhere between the Frenkel and the Wannier picture for this solid. It is suggested that the exciton levels and the conduction bands should be subjected to a rigorous type of calculation.

Experimentally there is work to be done. A measurement of the type of Parratt and Jossem is needed.[16] If the absorption spectrum could be measured at liquid helium temperatures in the region from about 5 ev to 20 ev, the results would be of interest, as the thermal effects should be so small that very accurate determination of the spin-orbit splitting would be possible. Furthermore, in the region of from 4°K to about 100°K the shift of band points with temperature would be measurable with considerably more accuracy than is possible with the present data. Measurements of the suggested type would be of considerable value as they would either tend to confirm or to contradict the results of the present work.

Appendix A.

Solutions of the Hartree-Fock-Slater Equation for Na^+ and I^-.

The assumptions regarding the free ion Hartree-Fock-Slater equations have been considered in Chapter II and in several references.[26,28] In this section we shall present the changes necessary to obtain our result from the program given by Herman and Skillman.[28] In what follows we adopt the convention that if a card is given the number of a card in the program, the given card replaces that card in the program. The symbols B,C,D,etc. after the numbers on the cards are to establish sequence. If no letter appears the letter is assumed to be A.

Modifications to the Hartree-Fock-Slater Self-Consistent Atomic Field Main Program.

Remove card 58

```
                IF(KEY-1) 1203, 208, 1203                          082
1212            DO 1213 I 2, M                                     154
```

Remove card 94

Remove card 188

Remove card 380

```
                WRITE OUTPUT TAPE 6, 2003, Z, NCORES,              383
                NVALES, ION, IZ, IC
                WRITE OUTPUT TAPE 6, 2010,(RUINL2(M),              394
                M=MIN, MAX), IZ, NC
```

Remove card 397

```
      WRITE OUTPUT TAPE 6, 2002, NLZ, XL                    412
      EE(M), WWNL(M), KKK, A(1,5),IZ, NC
      WRITE OUTPUT TAPE 6, 2010, (SNL(M,I),                 417
      I=MIN, MAX), IZ, NC
```

Remove card 420

Remove cards 422-432

```
      GO TO 3000                                            433
```

Remove cards 435-442

```
      NSTOP=98                                              435
      GO TO 3002                                            336
3003  NSTOP= 98                                             337
      GO TO 3002                                            338
3002  WRITE OUTPUT TAPE 6,7, NSTOP                          339
```

Corrections to Schroedinger equation subroutine.

```
      EG=E                                                  25B
      QQ(1)=0.                                              25C
      QQ(2)=0.                                              25D
      QQ(3)=0.                                              25E
      P(2)=P(3)                                             126B
      Q(2)=Q(3)                                             126C
```

P(2)=P(3)	135B
Q(2)=Q(3)	135C
T(2)=T(3)	135D
D(3)=D(4)	135E
D(2)=D(3)	135F

Modifications to Relativistic Corrections Main Program.

Remove cards 48-68

With the changes made as given above the results used in this work may be obtained. In Tables 5 and 6 some of the results for Na^+ and I^- are given. In Table 5 the energy eigenvalues for each level in Na^+ and I^- are given. In Table 6 we present r(V(r)) for Na^+ and I^- and also $r\psi 5p(r)$ and $r\psi 5s(r)$ for I^- as a function of r. In the calculations more points were used than are given in Table 6. These functions are given graphically in Figures 16 and 17. It is noted that the potential given is that seen by an electron on the ion in question. In performing calculations one often is concerned with the potential seen by an electron not on the ion. Thus one also constructs from this data the potential seen by an electron not on the ion. If this were not the case, then the inclusion of the Madelung term in the potential would be incorrect. This point is adequately discussed in the literature.[13,20]

TABLE 5.

The Energy Eigenvalues Given for the Various Levels in I^- and Na^+. (Atomic Units).

Substance	Level	Energy
Na^+	1s	-7.88x10
Na^+	2s	-5.38
Na^+	2p	-3.34
I^-	1s	$-2.34x10^3$
I^-	2s	$-3.55x10^2$
I^-	2p	$-3.34x10^2$
I^-	3s	-7.19x10
I^-	3p	-6.31x10
I^-	3d	-4.67x10
I^-	4s	-1.23x10
I^-	4p	-9.27
I^-	4d	-3.85
I^-	5s	-0.838
I^-	5p	-0.174

TABLE 6.

The Values of r(V(r)) and r(ψ(r)) are Given as a Function of r for Na^+ and I^-.

Na^+		I^-			
r	-rV(r)	r	-rV(r)	rψ(r)5s	rψ(r)5p
.0099	21.55	.0058	103.1	8.002×10^{-2}	6.729×10^{-3}
.0199	21.08	.0117	100.1	1.11×10^{-1}	2.297×10^{-2}
.0298	20.60	.0170	97.33	1.089×10^{-1}	4.403×10^{-2}
.0398	20.13	.0235	95.99	8.585×10^{-2}	5.655×10^{-2}
.0597	19.22	.0353	92.19	9.577×10^{-3}	1.073×10^{-1}
.0796	18.36	.0471	87.59	-7.196×10^{-2}	1.346×10^{-1}
.0995	17.56	.0589	83.47	-1.364×10^{-1}	1.451×10^{-1}
.1094	16.81	.0707	79.73	-1.754×10^{-1}	1.396×10^{-1}
.1394	15.45	.0942	74.64	-1.767×10^{-1}	9.111×10^{-2}
.1792	14.25	.1178	68.66	-1.042×10^{-1}	1.522×10^{-2}
.2189	13.19	.1414	63.44	1.0420×10^{-3}	-6.487×10^{-2}
.2587	12.28	.1649	58.85	1.078×10^{-1}	-1.336×10^{-1}
.3184	10.70	.2121	52.99	2.516×10^{-1}	-2.093×10^{-1}
.3980	9.497	.2592	46.68	2.712×10^{-1}	-1.997×10^{-1}
.4777	8.447	.3064	41.40	1.908×10^{-1}	-1.286×10^{-1}
.5573	7.990	.3535	37.09	5.601×10^{-2}	-2.659×10^{-2}
.6767	7.573	.4478	31.75	-2.254×10^{-1}	1.773×10^{-1}
.8359	6.254	.5421	26.31	-3.922×10^{-1}	3.035×10^{-1}
.9952	5.355	.6363	22.17	-4.118×10^{-1}	3.310×10^{-1}

1.154	4.728	.7306	18.84	-3.179×10^{-1}	2.800×10^{-1}
1.234	4.272	.9.92	14.91	2.685×10^{-2}	5.371×10^{-2}
1.314	4.00	1.107	11.18	3.743×10^{-1}	-2.038×10^{-1}
1.394	4.00	1.296	8.582	6.228×10^{-1}	$-4,144\times10^{-1}$
etc.	etc.	1.484	6.732	7.626×10^{-1}	-5.610×10^{-1}
		1.861	4.861	8.081×10^{-1}	-6.900×10^{-1}
		2.239	3.249	6.973×10^{-1}	-6.810×10^{-1}
		2.616	2.151	4.740×10^{-1}	-6.110×10^{-1}
		2.993	1.367	2.945×10^{-1}	-5.214×10^{-1}
		3.747	.5571	1.485×10^{-1}	-3.577×10^{-1}
		4.501	0.0	7.448×10^{-2}	-2.441×10^{-1}
		5.256	0.0	3.733×10^{-2}	-1.693×10^{-1}
		6.010	etc.	1.325×10^{-2}	-1.182×10^{-1}
		7.518		3.329×10^{-3}	-5.965×10^{-2}
		10.027		8.366×10^{-4}	-3.050×10^{-2}
		10.53		2.103×10^{-4}	-1.567×10^{-2}
		12.04		2.64×10^{-5}	-8.20×10^{-3}
		15.06		1.67×10^{-6}	-2.25×10^{-3}
		18.07		1.05×10^{-7}	-6.24×10^{-4}
		21.09		6.66×10^{-9}	-1.74×10^{-4}

FIGURE 16. rV(r) is shown as a function of r for Na^+ and I^- ions. The potential is that seen by an electron on that ion.

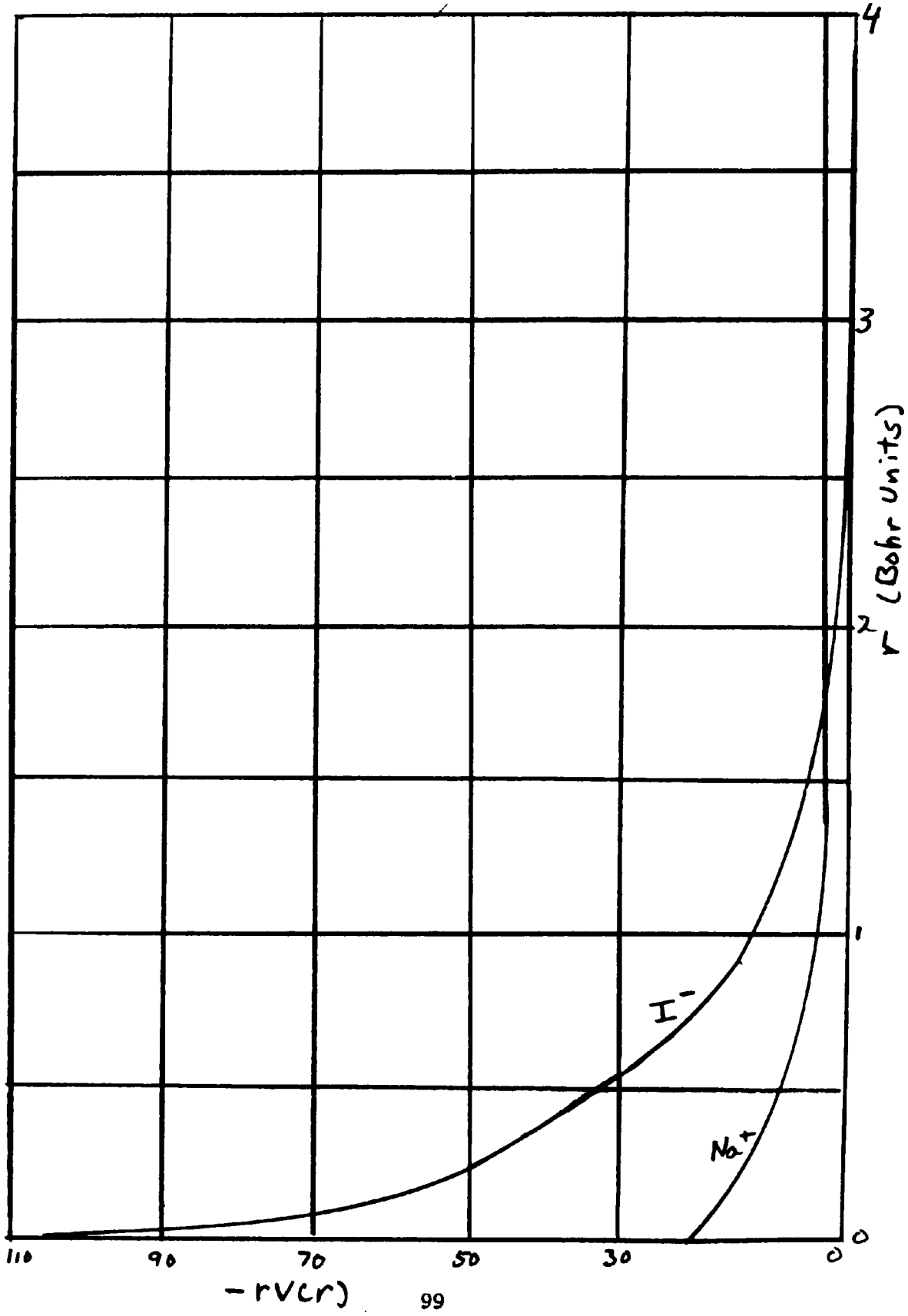
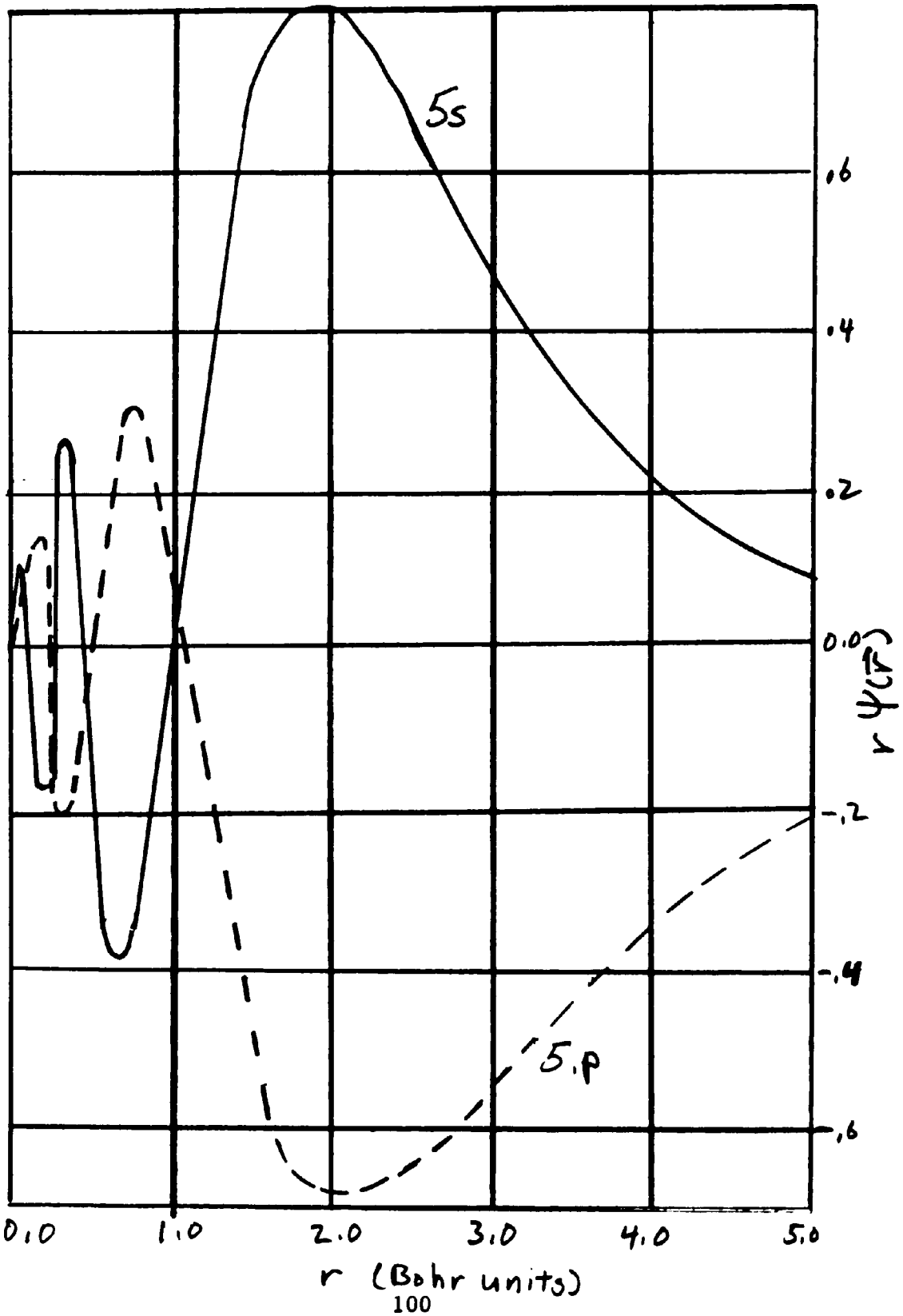


FIGURE 17. $r\psi(r)$ is given as a function of r for the 5s and 5p levels in I^-. Atomic units.



APPENDIX B.

Some Numerical Results for Other Alkali and Halide Ions.

In the process of obtaining the wave functions and the potentials for the I^- and Na^+ ions, the author and Donald Beck obtained numerical results for other alkali and halide ions in their ground state. The wave functions, potentials, and energy eigenvalues were obtained for the F^-, Cl^-, Br^-, Li^+, K^+, Rb^+, and Cs^+ ions. Due to limitations of space these results cannot be presented at this point. However in Table 7 the energy eigenvalues are presented for the levels in the above-mentioned ions. These results are for the modified Hartree-Fock-Slater potential.

TABLE 7.

The Energy Eigenvalues for the Ground State of the F^-, Cl^-, Br^-, Li^+, K^+, Rb^+, and Cs^+ ions. (Atomic units).

Ion and Level	Energy	Ion and Level	Energy
F^-1s	-49.30	K^+3s	-3.448
F^-2s	-1.548	K^+3p	-2.231
F^-2p	-0.1879	Rb^+1s	-1093
Cl^-1s	-204.5	Rb^+2s	-14[illegible]
Cl^-2s	-18.74	Rb^+2p	-133.4
Cl^-2p	-14.47	Rb^+3s	-[illegible]
Cl^-3s	-1.062	Rb^+3p	-[illegible]
Cl^-3p	-0.1909	Rb^+3d	-[illegible]
Br^-1s	-969.9	Rb^+4s	-[illegible]
Br^-2s	-125.5	Rb^+4p	-[illegible]
Br^-2p	-113.7	Cs^+1s	-[illegible]
Br^-3s	-17.12	Cs^+2s	-[illegible]
Br^-3p	-12.87	Cs^+2p	-[illegible]
Br^-3d	-5.189	Cs^+3s	-[illegible]
Br^-4s	-1.038	Cs^+3p	-[illegible]
Br^-4p	-0.1818	Cs^+3d	-[illegible]
Li^+1s	-5.389	Cs^+4s	-[illegible]
K^+1s	-262.6	Cs^+4p	-[illegible]
K^+2s	-27.58	Cs^+4d	-[illegible]
K^+2p	-22.53	Cs^+5s	-[illegible]
		Cs^+5p	-[illegible]

APPENDIX C.

Selection of Basis Vectors for a Face Centered Cubic Lattice.

In this appendix the selection of the basis functions for the lines Λ , Σ , and Δ is considered. Here we assume that there are no spin-orbit considerations. That is, the transformation properties of the Pauli spinors α and β are neglected. Here we are interested in the groups C_{2v} , C_{3v} ,and C_{4v} . This has been a topic for many authors.[32,45,48,49]

First one consideres the group of the line Δ . This line has the symmetry of a square in a plane and is represented by the group C_{4v}. C_{4v} has eight operations in five classes. If one assumes that the square lies in the plane defined as X=0, then one defines the eight operations of the group by their action on an arbitrary function of the coordinates, (x,y,z).

$E\ (x,y,z) \longrightarrow (x,y,z)$

$C_4\ (x,y,z) \longrightarrow (x,z,-y)$

$C_4^3\ (x,y,z) \longrightarrow (x,-z,y)$

$C_2\ (x,y,z) \longrightarrow (x,-y,-z)$

$\sigma_v\ (x,y,z) \longrightarrow (x,y,-z)$

$\sigma_v'\ (x,y,z) \longrightarrow (x,-y,z)$

$\sigma_d\ (x,y,z) \longrightarrow (x,y,z)$

$\sigma_d'\ (x,y,z) \longrightarrow (x,-z,-y)$

The operators C_4, C_4^3 are in a class as are σ_v and σ_v' .

and σ_d and σ_d' . The character table for the irreducible representations of this group is[48]

Representation	E	$2C_1$	C_2	$2\sigma_v$	$2\sigma_d$
Δ_1	1	1	1	1	1
Δ_1'	1	1	1	-1	-1
Δ_2	1	-1	1	1	-1
Δ_2'	1	-1	1	-1	1
Δ_5	2	0	-2	0	0

If one uses the projection operator O^{α} as discusses in Section E of Chapter II, then one finds that the basis vectors are (the line is along the [1 0 0] direction)

Δ_1 $\psi = C_1 x$

Δ_5 $\psi = y, z$.

The group of the line $\sum$ is C_{2v} . This line has the symmetry of a line in a plane. C_{2v} contains four operations in four classes. If one considers the line to be the z axis, then one defines the following operations:

$E\ (x,y,z) \rightarrow (x,y,z)$

$C_2(x,y,z) \rightarrow (x,-y,-z)$

$\sigma_v(x,y,z) \rightarrow (x,y,-z)$

$\sigma_v'(x,y,z) \quad (x,-y,z)$

The character table for C_{2v} is[48]

Representation	E	C	σ_v	σ_v'
Σ_1	1	1	1	1
Σ_2	1	1	-1	-1
Σ_3	1	-1	1	-1
Σ_4	1	-1	-1	1

By use of the operator O^{α}, one finds the basis vectors to be (when the line Σ is in the [1 1 0] direction)

Σ_1 $\psi = C_1 \psi_z (x+y)$

Σ_3 $\psi = z$

Σ_4 $\psi = \psi_z (x-y)$

The group of the line Λ is C_{3v}. This is the group of an equilateral triangel in a plane. Let us assume the triangle has an apex on the z axis and lies in the plane x=0. This group has six operations in three classes. The operations are defined as

$E\ (x,y,z) \rightarrow (x,y,z)$

$C_3(x,y,z) \rightarrow (x, z\cos 30° - y \sin 30°, y \cos 30° z \sin 30°)$

$C_3'(x,y,z) \rightarrow (x, -z \cos 30° y \sin 30°, y - os 30° - z \sin 30°)$

$\sigma_v(x,y,z) \rightarrow (x,-y,z)$

$\sigma_v'(x,y,z) \rightarrow (x,-z,-y)$

$\sigma_v''(x,y,z) \rightarrow (x,y,z)$

Here C_3 and C_3^1 are in a class and σ_v, σ_v', and σ_v'' are in a class. The character table is[48]

Representation	E	$2C_3$	$3\sigma_v$
Λ_1	1	1	1
Λ_2	1	1	-1
Λ_3	2	-1	0

By use of the projector O^{α}, one finds basis vectors to be (Here one has Λ in the [1 1 1] direction)

Λ_1

$\psi = C, \frac{1}{\sqrt{3}}(x+y+z)$

Λ_3

$\psi = \frac{1}{\sqrt{2}}(x-y), \frac{1}{\sqrt{6}}(x+y-2z)$

APPENDIX D.

Evaluation of Two Center Matrix Elements.

In the problem under consideration it was necessary to evaluate two dimensional integrals for functions centered about two origins. One has two functions of r and Θ centered about one origin and a function of r' and Θ' centered about a second origin. The coordinate system used is shown in Figure 3. Any φ dependence of the functions was eliminated by direct integration. A program was written in Fortran II to perform these integrations using a double Simpson's Rule.[47] This program is designed to be used with the wave functions and potentials generated by our Hartree-Fock-Slater program. The program is included in this appendix and is given below.

```
C       TWO CENTER INTEGRALS ARE EVALUATED FOR CERTAIN SOLID STATE
        CASES
C       BY A COUBLE APPLICATION OF SIMPSON RULE THE FUNCTIONS ARE S OR
C       P FUNCTIONS ENDINGS I OR J REFER TO CENTER ONE AND K REFERS TO
C       CENTER TWO     A IS THE SEPARATION   L  S  ARE ANGULAR
        QUANTUM NUMBERS
C       -1 IS S STATE 0 IS PX STATE   1 IS PZ STATE  XL IS RANGE
C       OF INTEGRATION    I   J   K   DESIGNATES THE FUNCTION TO BE
C       INTEGRATED WRITTEN IN FORTRAN TWO FOR IBM 7094 OR CDC 6600 OR
C       GE 225 WITH DIMENSION MODIFICATION IN THE SPRING 1965 AT
C       LEHIGH UNIVERSITY BY A BARRY KUNZ
        DIMENSION X(441), FI(441),  RK(441),SNLO(10,441), Z(IC),
        IXFUN(441), THFUN(501), TH(3,501)
   10   FORMAT (212)
   20   FORMAT (10F6.1)
   30   FORMAT (1X,5F12.6)
   40   FORMAT (612,F8.4)
   50   FORMAT (1H, 5F12.6)
   60   FORMAT (1HO,9HINTEGRAL=.F12.8,16)
   70   FORMAT(1HO, 50HTHIS PROGRAM HAS RUN TO COMPLETION AND CALLED
        EXIT)
   80   FORMAT (1H, F8.4)
        XFUN(1) = 0.0
        DTHETA =.015708
        THETA = 0.0
```

```
      DO  18  J=1,201
      SNLO (J,I)=0.0
    2 CONTINUE
    1 CONTINUE
C     GENERATE X MESH
      DELTA=.00250
      I=1
      X(1)=0.0
      DO  11  J=1,11
      DO  12  K=1,40
      I=I+1
   12 X(I)=X(I-L)+ DELTA
   11 DELTA=DELTA+DELTA
      DO  101  KLM=1,NOINT
C     DETERMINE WHICH FUNCTIONS ARE TO BE INTEGRATED
      READ INPUT TAPE 5, 40, IFI, IFJ,IFK,LI,LJ,LK,A
C     DETERMINE F BY INTEGRATION OVER THETA
      CI=.88534/Z(IFI)**(1./3.)
      CK=.88534/Z(IFK)**(1./3.)
      DO  13  I=I,441
      RI(I)=CI*X(I)
   13 RK(I)=CK*X(I)
      DO  14  M=2,401
```

```
      XFUN(M)=0.0
      THETA=0.0
      XFU=SNLO(IFI,M)*SNLO(IFJ,M)
      RR= RI(M)
18    TH(1,J)=1.0
      DO  19  J=1,201
      TH(2,J)=(3./4.)**(1./2.)*SINF(THETA)
19    THETA=THETA+DTHETA
      THETA=0.0
      DO  21  J=1,201
      TH(3,J)=(3./2.)**(1./2.)*COSF(THETA)
21    THETA=THETA+DTHETA
      READ INPUT TAPE 5, 10, NOFN,NOINT
      READ INPUT TAPE5, 20,(Z(I),I=I,NOFN)
      DO  1  J=1, NOFN
      READ INPUT TAPE 5, 30. (SNLO(J,I), I=I, 441)
      READ INPUT TAPE 5, 10, KEY, KSN
      IF (KEY) 2,2,3
3     DELTA= .00250
      I=1
      X(I)=0.0
      C=.88534/Z(J)**(1./3.)
      DO  6  JJ=1,11
```

```
      DO  7  KK=1,40
      I=I+1
    7 X(I)=X(I-1)+DELTA*C
    6 DELTA=DELTA+DELTA
      DO  8  I=2,441
    8 SNLO(J,1)=SNLO (J,I)?X(I)
      KZ=1
      DO   15  N=1,201
      YI=RR*SINF(THETA)
      ZI=RR*COSF(THETA)
      YK=YI
      ZJ=ZI-A
      R=SQRTF(YK**2 ZK**2)
      SIK=YK/R
      COK=ZK/R
C     GET ANGULAR DEPENDENCE
      THI=TH(LJ,N)
      THJ=TH(LJ,N)
      IF  (LK)  26,27,28
   26 THK=1.0
      GO TO 29
   27 THK=(3./4.)**(1./2.)*SIK
      GO TO 29
```

```
   28   THK=(3./2.)**(1./2.)*COK
   29   CONTINUE
        DO  31  I=KZ,401
        J=I
        IF  (RK(I)-R) 32,33,34
   32   CONTINUE
   31   CONTINUE
   33   RAD=SNLO(IFK,J)
        GO TO 35
   34   RAD=SNLO(IFK,J-1)+(R-RK(J-1))*(SNLO(IFK,J)-SNLO(IFK,J-1))/
        1(RK(J)-RK(J-1))
   35   KZ=J
        THFUN(N)=XFU*RAD*THI*THK*SINF(THETA)
   15   THETA=THETA+DTHETA
        DO 36  N=1,199.2
        XFUN(M)+(DTHETA/3.)+(THFUN(N)+4.*THFUN(N+1)+THFUN(N+2))
   36   CONTINUE
   14   CONTINUE
        DO  37 I=2,401
   37   XFUN(I)=XFUN(I)*(RI(I)**2)
        WRITE OUTPUT TAPE 6,50,(XFUN(I),I=I,301)
C       INTEGRATE OVER RI
        ANS=0.0
```

```
      DO  38  I=1, 399,2
38    ANS=ANS+((RI(I I)-RI(I))/3.)*(XFUN(I)+4.*XFUN(I+I)+XFUN(I+2))
      WRITE OUTPUT TAPE 6,60,ANS, KLM
      PRINT 60, ANS, KLM
101   CONTINUE
      WRITE OUTPUT TAPE 6,70
      CALL EXIT
      END
```

APPENDIX E.

Matrix Elements for the Strained Lattice.

In Section D of Chapter III the case of a face centered cubic lattice with an elongation along the [1 0 0] direction was considered. Basis functions were obtained for the [1 0 0] and [0 1 0] direction in reciprocal space. One may obtain the expressions for the energy of this system. They are found to be

[1 0 0] direction

$$\alpha = \Delta_1, \vec{k} = \frac{\pi}{a} q(100), \quad 0 < q < 1$$

$$E_{xx}(\Delta_1) = \epsilon_n + [V_p + 8\cos ka [\cos^2\theta, \langle z|V(c)|z(c)\rangle + \sin^2\theta, \langle x|V(c)|x(c)\rangle] + \sin^2\theta, \langle x|V(d)|x(d)\rangle]$$
$$[1 + 8\cos ka [\cos^2\theta, \langle z|z(c)\rangle + \sin^2\theta, \langle x|x(c)\rangle] + 4\langle x|x(d)\rangle]^{-1}$$

$$\alpha = \Delta_5$$

$$E_{yy}(\Delta_5) = \epsilon_n + [V_p + 4\cos ka [\sin^2\theta, \langle z|V(c)|z(c)\rangle + (1+\cos^2\theta,)\langle x|V(c)|x(c)\rangle] + 2[\langle z|V(d)|z(d)\rangle + \langle x|V(d)|x(d)\rangle]][1 + 4\cos ka [\sin^2\theta, \langle z|z(c)\rangle + (1+\cos^2\theta,)\langle x|x(c)\rangle] + 2[\langle z|z(d)\rangle + \langle x|x(d)\rangle]]^{-1}$$

[0 0 1] direction

$$\alpha = \Sigma_1, \quad \vec{k} = \frac{\pi}{b} q\,(001), \quad 0 < q < 1$$

$$E_{zz}(\Sigma_1) = \epsilon_n + \Big[V_0 + 4\langle x|V(c)|x(c)\rangle + 4\cos kb\,[\sin^2\theta_1 \langle z|V(c)|z(c)\rangle + \cos^2\theta_1 \langle x|V(c)|x(c)\rangle] + 2\cos kb\,[\langle z|V(d)|z(d)\rangle + \langle x|V(d)|x(d)\rangle]\Big]$$

$$\Big[1 + 4\langle x|x(c)\rangle + 4\cos kb\,[\sin^2\theta_1 \langle z|z(c)\rangle + \cos^2\theta_1 \langle x|x(c)\rangle] + 2\cos kb\,[\langle z|z(d)\rangle + \langle x|x(d)\rangle]\Big]^{-1}$$

$$\alpha = \Sigma_3$$

$$E_{yy}(\Sigma_3) = \epsilon_n + \Big[V_0 + 4\,[\sin^2\theta_1 \langle z|V(c)|z(c)\rangle + \cos^2\theta_1 \langle x|V(c)|x(c)\rangle] + 4\cos kb\,[\langle x|V(c)|x(c)\rangle] + 2\cos kb\,[\langle z|V(d)|z(d)\rangle + \langle x|V(d)|x(d)\rangle]\Big]$$

$$\Big[1 + 4\,[\sin^2\theta_1 \langle z|z(c)\rangle + \cos^2\theta_1 \langle x|x(c)\rangle] + 4\cos kb\,[\langle x|x(c)\rangle] + 2\cos kb\,[\langle z|z(d)\rangle + \langle x|x(d)\rangle]\Big]^{-1}$$

$$\alpha = \Sigma_4$$

$$E_{xx}(\Sigma_4) = \epsilon_n + \Big[V_p + 4\big[\cos^2\theta_1 \langle z|V(c)|z(c)\rangle + \sin^2\theta_1 \langle x|V(c)|x(c)\rangle\big] + 4\cos kb\big[\cos^2\theta_1 \langle z|V(c)|z(c)\rangle + \sin^2\theta_1 \langle x|V(c)|x(c)\rangle\big] + 4\cos kb \langle x|V(d)|x(d)\rangle\Big]\Big[1 + 4\big[\cos^2\theta_1 \langle z|z(c)\rangle + \sin^2\theta_1 \langle x|x(c)\rangle\big] + 4\cos kb\big[\cos^2\theta_1 \langle z|z(c)\rangle + \sin^2\theta_1 \langle x|x(c)\rangle\big] + 4\cos kb \langle x|x(d)\rangle\Big]^{-1}$$

In the above formulas a is the lattice parameter in the [1 0 0] direction, b is the lattice parameter in the [0 1 0] direction. One also defines

$$\vec{c} = (a\ b\ 0) \text{ or } (a\ 0\ b), \text{ etc.}$$

$$|c| = (a^2 + b^2)^{1/2}$$

$$\vec{d} = (0\ a\ a), \text{ etc.}$$

$$|d| = \sqrt{2}\, a$$

$$\theta_1 = \arctan(a/b)$$

Thus one has expressions for the energy of a p type band in a strained face centered cubic lattice assuming no spin-orbit interaction and a strain in the [1 0 0] direction.

APPENDIX F.

Double Groups, Extra Irreducible Representations

When one wishes to consider spin-orbit interactions, the theory is somewhat complicated by the transformation properties of the Pauli spinors. The groups of interest, C_{4v}, C_{3v}, C_{2v}, have additional operations, classes, and irreducible representations.

Consider the Euler angles θ, φ, and ψ, then the two matrices corresponding to this rotation on the Pauli spinors are defined by

$$u_{11} = u_{22}^{*} = \cos\theta/2 \exp[-i(\varphi+\psi)/2]$$

$$u_{12} = -u_{21} = \sin\theta/2 \exp[i(\varphi-\psi)/2]$$

Thus here the identity rotation is one of 4π. The identity rotation for simple vectors of 2π is the improper rotation for spinors. Thus for each previous operator we have a new operator which is the same rotation as before plus 2π. The new operators are designated by the same symbols as used previously, and the old operators use their same symbols with a bar over them. For example

$$E(\theta,\varphi,\psi) = (\theta+4\pi, \varphi+4\pi, \psi+4\pi),$$

$$\bar{E}(\theta,\varphi,\psi) = (\theta+2\pi, \varphi+2\pi, \psi+2\pi),$$

For the present not all irreducible representations need be considered. For the direction C_4, one needs the representations C_4 and C_2. Here the group C_{4v} has sixteen operators in seven classes. The character table is

BIBLIOGRAPHY.

1. F.Seitz, Modern Theory of Solids, (McGraw-Hill, New York,1940), chapters 1,2,8,14.

2. M.Born and M.Goppert-Mayer, Handb. d. Phys.,24/2,623 (1933).

3. N.F.Mott and R.W.Gurney, Electronic Processes in Ionic Crystals, (Oxford at the Clarendon Press, Oxford, England, 1948 second edition), chapters 1,3.

4. H.B.Huntington, The Elastic Constants of Crystals, (Academic Press, Solid State Reprints, New York, 1958), chapters 1,3,10.

5. R.S.Krishman and S.K.Roy, Proc. Roy.Soc. (London) 210,481 (1952).

6. P.O.Lowdin, Advances in Physics, 5, 1 (1956).

7. C.Tubandt and S.Eggert, Zeits. f. Anorg. Chem. 110, 196 (1920).

8. A.Smekal, Handb. d. Phys. 24/2, 881 (1933).

9. H.Frohlich, Proc.Roy.Soc. (London) 160, 230 (1937).

10. H.Frohlich and N.F.Mott, Proc. Roy.Soc. (London) 171, 496 (1939).

11. W.Shockley, Phys. Rev. 50, 754 (1936).

12. R.C.Casella, Phys. Rev. 104, 1260 (1956).

13. L.P.Howland, Phys. Rev. 109, 1927 (1958).

14. P.D.DeCicco, "Validity of the'Muffin Tin Approximation to the KCl Crystal Potential'" Quarterly Progress Report No.54 October 15, 1964, Solid State and Molecular Theory Group, M.I.T. (unpublished); "Self-Consistent Energy Bands for Potassium Chloride," Quarterly Progress Report No.56 April 15,1965, Solid State and Molecular Theory Group, M.I.T. (unpublished).

15. A.B.Kunz and W.J.VanSciver,"3p Energy Band in Lithium Chloride," Lehigh University 1965 (to be published).

16. L.G.Parratt and E.L.Jossem, Phys. Rev. 97, 916 (1955).

17. J.C.Phillips, Phys. Rev. 133 A, 1705 (1964).

18. J.C.Phillips, Phys.Rev. 133 A, 452 (1964).

19. R.S.Knox, Theory of Excitons, (Academic Press, New York, 1963) from Solid State Physics, Supplement 5, Seitz and Turnbull editors.

20. F.Bassani, R.S.Knox and W.Beall Fowler, Phys. Rev. 137 A, 1217 (1965).

21. W.Beall Fowler, Energy Bands in Solid Krypton, thesis, University of Rochester, 1963 (unpublished); Phys. Rev. 132, 1591 (1963).

22. J.E.Eby, K.J.Teegarden and D.B.Dutton, Phys. Rev. 116, 1099 (1959).

23. W.J.VanSciver, Phys. Rev. 120. 1193 (1960).

24. M.Born and J.R.Oppenheimer, Ann. Physik. 84, 457 (1927).

25. M.Lax, J. Chem. Phys. 20, 1752 (1952).

26. D.R.Hartree, The Calculation of Atomic Structures, (John Wiley, New York, 1957), chapters 1,2,3.

27. A.Messiah, Quantum Mechanics, Vols. I,II. (John Wiley,New York,1962).

28. F.Herman and S.Skillman, Atomic Structure Calculations, (Prentice-Hall, Englewood Cliffs, New Jersey, 1963).

29. J.C.Slater, Phys. Rev. 81, 385 (1951).

30. M.Hammermesh, Group Theory, (Addison Wesley, Reading, Massachusetts, 1962).

31. R.S.Knox and A.Gold, Symmetry in the Solid State, (Benjamin, New York, 1964).

32. J.C.Slater, Rev. Mod. Phys. 37, 68 (1965).

33. M.Born and K.Huang, Dynamical Theory of Crystal Lattices, (Oxford Press, Oxford, England, 1954).

34. F.Bloch, Z. Physik. 52, 555 (1928).

35. E.Wigner and F.Seitz, Phys. REv. 43, 804 (1933); 46, 509, (1934).

36. J.Callaway, Energy Band Theory, (Academic Press, New York, 1964), chapter 2.

37. J.Ziman, Electrons and Phonons, (Oxford at the Clarendon Press, Oxford, England, 1963), chapter 2.

38. The basic program was obtained form I.B.M. and modified to a more convenient form by Kunz and Beck. Several Fortran errors were corrected which did not alter the accuracy of the program, but which may have made it more efficient.

39. S.Skillman, private communication.

40. G.W.Pratt, Jr., Phys. Rev. 88, 1217 (1952); Phys. Rev. 102, 1303 (1956).

41. D.R.Hartree, Proc. Roy. Soc. (London) A141, 282 (1933).

42. D.R. and W.Hartree, Proc. Roy. Soc. (London) A157, 490, (1930).

43. J.E.Robinson, F.Bassani, R.S.Knox, J.R.Schrieffer, Phys. Rev. Letters, 9, 521 (1962).

44. T.Koopmans, Physica, 1, 104 (1933).

45. L.P.Bouckaert, R.Smoluchowski, and E.W.Wigner, Phys. Rev. 50,58 (1938).

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

47. J.B.Scarborough, Numerical Mathematical Analyses 5th Edition (The Johns Hopkins Press, Baltimore, 1962), chapter 8.

48. G.F.Koster, Space Groups and Their Representations, (Academic Press, New York, 1957).

49. G.F.Koster,J.O.Dimmock, R.G.Wheeler, Hermann Statz, Properties of the Thirty Two Point Groups, (The M.I.T.Press, Cambridge, Mass., 1963).

50. L.T.Foldy and S.A.Wouthuysen, Phys. Rev. 78, 29 (1950).

51. J.C.Phillips, J.Phys. Chem. Solids, 12, 208 (1960).

52. F.Bassani, S.Giuliano, Proc. of International Symposium on Color Centers in Alkali Halides, 9 (1965).

53. F.Bassani and V.Celli, J.Phys. Chem. Solids, 20, 64 (1961); M.L.Cohen and V.Heine, Phys. Rev. 122. 1821 (1961).

54. R.S.Knox, private communications.

55. W.Heinenberg, Ann. Physik, 10, 888 (1931).

56. J.M.Luttiger and W.Kohn, Phys. Rev. 97, 869 (1955).

57. See Reference 1, pages 314 through 319.

58. See Reference 36, pages 80 through 86.

59. See Reference 27, Vol.II, pages 686 through 698.

60. D.W.Hafemeister and W.H.Flygare, J.Chem. Phys. 43, 795 (1965).

61. A.B.Kunz and W.J.VanSciver, 3p Energy Bands in KCl, NaCl, and LiCl, Lehigh University (unpublished).

62. P.P.M.Meincke and G.M.Graham, Canadian Journal of Physics, 43, 1853 (1965).

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