of strontium atoms at the temperature of the crystal was then computed using the ideal gas law. The density of color centers was calculated using Dexter's formula relating the color-center density to the area under the absorption curve.[10] The F' band was assumed to have the shape depicted by curve 6 in Fig. 3. Only the leading edges of the experimental curves were used in fitting the data to avoid contributions due to the F band and any aggregate centers present. The index of refraction used was 1.89,[11] and the oscillator strength was arbitrarily chosen to be 0.8. Since some of the actual temperatures differed by as much as 25°C from the average used, the large points represent the data corrected to the indicated temperature using Eq. (1) developed below. Where significantly different, the uncorrected data are shown by the small points connected to the large points. Straight lines of slope 1 have been fitted to the data for each of these temperatures.

For thermal equilibrium, the density of color centers $N_{F'}$ in the crystal should be related to the density of atoms in the vapor N_{Sr} by the equation[12]

$$N_{F'}/N_{\mathrm{Sr}}=Ce^{-\phi/kT}, \qquad (1)$$

where C is a slowly varying function of the temperature which will be treated as a constant, k is Boltzmann's constant, and ϕ is the energy of formation of the color centers. In Fig. 5, the ratio of the densities $N_{F'}/N_{\mathrm{Sr}}$ has been plotted as a function of the reciprocal of the temperature on a semilog graph. The three closed points represent the ratios depicted by the straight lines in Fig. 4. The straight line in Fig. 5 represents a least-squares fit of the data. From its slope an estimate of the activation energy ϕ for F'-center creation is found to be -1.1 eV. The negative sign indicates that energy is released when a strontium atom is taken from the vapor to the crystal.

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Combined Plane-Wave Tight-Binding Method for Energy-Band Calculations with Application to Sodium Iodide and Lithium Iodide*

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A method of calculating energy bands, which we name the mixed-basis method, is developed. This method uses a wave-function expansion which includes free-atom or ion wave functions and plane waves, and it may incorporate relativistic effects. It is, in general, not equivalent to the orthogonalized-plane-wave (OPW) method, although the cases for which the two methods are equivalent are developed. A sample calculation is made for LiI and NaI, for which x-ray, valence, and conduction states are calculated. The agreement between theory and x-ray and optical-absorption data is excellent. The importance of relativistic effects is explored, and comparisons are made with conventional OPW results, which include relativity by first-order perturbation theory.

I. INTRODUCTION

A METHOD of computing energy bands in solids is developed. This method involves expanding an electronic wave function in terms of plane waves and tight-binding Bloch functions, hence, it is named the mixed basis method (MB).

The MB method may be developed in such a way that it offers several advantages over other current approaches, such as the OPW or the Green's-function method.[1–6] These advantages, and certain disadvantages, are explored in an extensive comparison with other approaches. In particular, it is shown that convergence difficulties encountered when the OPW method is used to compute the valence states of insulating solids can be avoided. It is also shown how relativistic effects may be included in a nonperturbative way; this distinguishes the MB technique from one introduced some time ago by Brown.[7]

The results of relativistic calculations on LiI and NaI using the MB method are presented and compared with OPW results. Agreement with recent experimental results is shown to be excellent.

II. MATHEMATICAL DEVELOPMENT

In the MB method, as in many other approaches, one desires to find eigenfunctions and eigenvalues of an

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effective one-electron Hamiltonian of the form

$$H=T+V(\mathbf{r})+H_{\mathrm{rel}}. \tag{1}$$

In the above equation T is the kinetic-energy operator and $V(\mathbf{r})$ is the effective lattice potential; H_{rel} includes relativistic effects. In many cases, the potential may be given as a superposition of potentials for the free atoms or ions which constitute that lattice. For the MB method, this need not be the case. In any event, one starts by solving a Hartree-Fock, Hartree-Fock-Slater, Hartree, Dirac, or some other equation for the free atoms or ions which constitute the lattice.[8] These solutions comprise part of the basis. The potentials obtained from this may be used to form the lattice potential, if desired. The remainder of the basis is formed from linear combinations of plane waves.

It is customary and also useful to symmetrize the basis set so that the labor of computation is reduced to a minimum.[9,10] Thus, one forms a wave function to transform as the γth row of the αth irreducible representation of the group of the wave vector $\mathbf{k}$ for which a solution is desired. In terms of the mixed basis, this wave function is of the form

$$\psi_n{}^{\alpha\gamma}(\mathbf{k},\mathbf{r})=\sum_{j,l} A_{njl}{}^{\alpha\gamma} \sum_m C_{lm}{}^{\alpha\gamma}(\mathbf{k},\mathbf{r})\varphi_{jlm}(\mathbf{k},\mathbf{r}) +\sum_{q=1}^{N} d_{nq}{}^{\alpha\gamma} \sum_t b_{qt}{}^{\alpha\gamma}e^{i(\mathbf{k}+\mathbf{h}_t)_q\cdot\mathbf{r}}. \tag{2}$$

Here, the functions $\varphi_{jlm}(\mathbf{k},\mathbf{r})$ are Bloch functions formed from the solutions of the free-atom or ion problem or possibly some other convenient set of functions. There are M such functions and the $C_{lm}{}^{\alpha\gamma}$ are chosen so that the Bloch functions have the desired symmetry. The wave vector in the first Brillouin zone is $\mathbf{k}$, and $\mathbf{h}_t$ is a reciprocal-lattice vector. It is required that $|(\mathbf{k}+\mathbf{h}_t)_q|$ be constant for all t. One chooses $b_{qt}{}^{\alpha\gamma}$ such that the plane-wave part also has the desired symmetry. N such combinations of symmetrized plane waves are used. The coefficients $A_{njl}{}^{\alpha\gamma}$ and $d_{nq}{}^{\alpha\gamma}$ are chosen such that $\psi_n{}^{\alpha\gamma}(\mathbf{k},\mathbf{r})$ is a solution to Eq. (1). The quantities l and m refer to the angular momentum and its Z component for the atomic states from which the Bloch sums are formed.

It is observed that the wave function ψ is being expanded in an over-complete set of functions since both the solutions to the atomic problem and the plane waves form complete sets. As a practical matter, one uses only a finite number of atomic functions and plane waves and the solution to Eq. (1) is obtained by the variational method. Thus, one finds the solution given by

$$\text{Determinant } [H_{ij}-ED_{ij}]=0. \tag{3}$$

In Eq. (3), H_{ij} is the Hamiltonian matrix and D_{ij} is the overlap matrix. These matrices are $(M+N)\times(M+N)$ in size. The first M members of the basis from which H_{ij} and D_{ij} are formed are given by

$$\Phi_{njl}{}^{\alpha\gamma}=\sum_{m=-l}^{l} C_{njlm}{}^{\alpha\gamma}\varphi_{jlm}(\mathbf{k},\mathbf{r}). \tag{4}$$

The final N members of the basis are given by

$$S_{nq}{}^{\alpha\gamma}=\sum_t b_{qt}{}^{\alpha\gamma}e^{i(\mathbf{k}+\mathbf{h}_t)_q\cdot\mathbf{r}}. \tag{5}$$

Thus, one has three types of integrals to evaluate in forming an H or D matrix. These are

$$\begin{aligned} A&=\int \varphi_{njl}{}^{\alpha\gamma*}O_p\varphi_{n'j'l'}{}^{\alpha\gamma}d\tau\,,\\ B&=\int \varphi_{njl}{}^{\alpha\gamma*}O_pS_{n'q}{}^{\alpha\gamma}d\tau\,,\\ C&=\int S_{nq}{}^{\alpha\gamma*}O_pS_{n'q'}{}^{\alpha\gamma}d\tau\,. \end{aligned} \tag{6}$$

In Eq. (6) the integrals extend over the volume of the crystal. When $O_p=H$ the Hamiltonian matrix is obtained, and when $O_p=1$, the overlap matrix is obtained. The methods of evaluating the nonrelativistic parts of the matrix elements are similar to those employed in the OPW method[1] or the tight-binding method.[5]

III. INCLUSION OF RELATIVISTIC EFFECTS

With the advent of large synchrotrons, soft x-rays are available of sufficient intensity so that experimental studies of x-ray absorptions by crystalline solids are possible.[11] Thus, it is useful to compute the x-ray levels of solids as well as the valence and conduction states. Using the MB method, it is possible to compute the x-ray terms directly along with the valence and conduction levels. For crystals containing nuclei of large atomic number, it is important to include relativistic effects in the calculation of the x-ray levels. Several formalisms exist for including relativistic effects for valence and conduction states. Soven has given a relativistic generalization of the OPW method[12] and Onodera and Okazaki have developed a relativistic Green's-function method.[6] The method to be presented here differs from either of the previous methods in that, by using the MB method, it is unnecessary to solve a free-ion Dirac equation for the constituent ions. In fact, a Dirac equation need not be used at all.

It is possible to start with the Dirac equation, or a Foldy-Wouthuysen transformation on the Dirac equation,[13] or with the Pauli approximation to the Breit

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operator for the interaction of two electrons.[14] However, if one includes only the principal effects, the results are similar. Thus, one may approximate

$$H=p^2/2m+V(\mathbf{r})+H_{\text{rel}}. \tag{7}$$

In Eq. (7), m is the electronic mass, $V(\mathbf{r})$ is the classical lattice potential, and H_{rel} is the relativistic correction to the Hamiltonian. To the first order of accuracy one has

$$H_{\text{rel}}=H_m+H_{\text{D}}+H_{\text{so}}. \tag{8}$$

Here H_m is the relativistic variation of mass with velocity, H_{D} is the Darwin or nonphysical operator, and H_{so} is the spin-orbit interaction.[15] One may represent these operators in rydberg units as

$$\begin{aligned} H_m&=-\tfrac{1}{4}\alpha^2\nabla^2\nabla^2, \\ H_{\text{D}}&=\tfrac{1}{8}\alpha^2\nabla\cdot[\nabla V(\mathbf{r})], \\ H_{\text{so}}&=\tfrac{1}{4}\alpha^2\boldsymbol{\sigma}\cdot[\nabla V(\mathbf{r})\times(-i\nabla)], \end{aligned} \tag{9}$$

where $\boldsymbol{\sigma}$ represents the Pauli-spin matrices, α is the fine-structure constant ($\alpha=1/137.037$), and ∇ is the gradient operator. Since the matrix elements of the classical part of the Hamiltonian are well defined in numerous papers on OPW or tight-binding calculations, we may restrict out attention to the matrix elements of H_{rel}. To do this, one uses the results of Liu, Chow and Liu, and Reilly.[16] That is, to a high degree of accuracy, one may assume that

$$\begin{aligned} &\int \varphi_{njl}{}^{\alpha\gamma *}H_{\text{rel}}S_{nq}{}^{\alpha\gamma}d\tau=0, \\ &\int S_{nq}{}^{\alpha\gamma *}H_{\text{rel}}S_{nq'}{}^{\alpha\gamma}d\tau=0. \end{aligned} \tag{10}$$

Thus, one must evaluate

$$A_{\text{rel}}=\int \varphi_{njl}{}^{\alpha\gamma *}H_{\text{rel}}\varphi_{n'j'l'}{}^{\alpha\gamma}d\tau. \tag{11}$$

In evaluating A_{rel} it is necessary to include only one center term.[16] Thus, if about a given lattice site the potential is given essentially as $\bar{V}(r)$, and if $R_{jl}(r)$ is the radial part of $\varphi_{njl}{}^{\alpha\gamma}$ at that same lattice site, one finds that

$$\begin{aligned} (H_m)_{jl,j'l'}&=-\frac{\alpha^2}{4}\delta_{ll'}\int R_{jl}{}^*R_{j'l'}[\epsilon_{jl}-\bar{V}(r)] \\ &\qquad\times[\epsilon_{j'l'}-\bar{V}(r)]r^2dr, \\ (H_{\text{D}})_{jl,j'l'}&=\frac{1}{8}\alpha^2\delta_{ll'}\int R_{jl}{}^*R_{j'l'}\frac{d}{dr}\left[r^2\frac{d\bar{V}(r)}{dr}\right]dr, \\ (H_{\text{so}})_{jl,j'l'}&=-\tfrac{1}{4}\alpha^2\xi_{jl,j'l'}\delta_{ll'}\langle\mathbf{L}\cdot\boldsymbol{\sigma}\rangle, \end{aligned} \tag{12}$$

and

$$\xi_{jl,j'l}=\int R_{jl}{}^*R_{j'l}\frac{1}{r}\frac{d\bar{V}(r)}{dr}r^2dr.$$

In the above equations, ϵ_{jl} is the classical energy of the jl electronic state, $\langle\mathbf{L}\cdot\boldsymbol{\sigma}\rangle$ is the expectation value of $\mathbf{L}\cdot\boldsymbol{\sigma}$ for the states jl and $j'l$, and $\mathbf{L}$ is the orbital angular-momentum operator, and $\boldsymbol{\sigma}$ is the spin angular-momentum operator. Using the results of Eq. (12) and the formulas from OPW or tight-binding theory one may then form the matrix for H and D and solve Eq. (3). Thus, this method obtains the x-ray levels directly as well as other levels of the crystal. One notes that it is not possible to avoid obtaining the x-ray levels since core solutions are not assumed and no orthogonalization is performed.

It is noted that Rössler has included relativistic effects in the augmented-plane-wave (APW) method and Treusch has included relativistic effects in the Green's-function method, using a technique similar to that employed in this paper.[17] It should be mentioned that there is an indirect relativistic effect which is ignored in this presentation. This has been discussed by Boyd *et al.*[18] and is best understood in terms of a self-consistent field model. States of low angular momentum (s states) are very compact in relativistic formalism and hence in a self-consistent calculation and states of higher angular momentum become less well bound because the s states shield the nuclear charge more completely in relativistic calculations than in nonrelativistic calculations. Since in this work the crystal problem is not considered self-consistently, this effect is neglected. The author believes that this effect is very small in the alkali iodides because as is seen in Sec. VI, the relativistic shifts encountered here agree in size and sign with those of Onodera *et al.*,[6] who use a crystal potential for KI formed from self-consistent solutions to the free-ion Dirac equation for the K^+ and I^- ions.

IV. DISCUSSION OF THE METHOD

In this section, the advantages and disadvantages of the MB method are discussed. (The MB method is seen to be equivalent to the OPW approach in certain circumstances.) For most applications, it is necessary to obtain solutions for both the valence bands and the conduction bands. Tight-binding theory is often used for valence bands but to use it accurately is extremely difficult.[5] Thus, if one wishes to compute the valence bands accurately, it is necessary in many cases to use OPW, APW, or Green's-function techniques. The Green's-function technique is limited to the use of a muffin-tin potential,[6] which may be unreasonable in

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some cases.[4,19] In many cases the APW method also uses this potential; however, this is not an essential limitation of this method.[4] Nonetheless, some of the restrictions of the muffin-tin potential can be removed only by perturbation theory.

The MB method is not limited in its choice of potential. This is an advantage which this method shares with the OPW method. However, unlike the OPW method, it is not required that one be able to solve the pertinent free-ion or atom problems. Thus, the core states used in this method need not be even approximate eigenfunctions to the core states of the crystal. Hence one's choice of Hamiltonian need not be limited to one for which the equivalent atomic problem is soluble.

In the OPW method it is assumed that

$$\int \varphi_{njl}{}^{\alpha\gamma*} H S_{nq}{}^{\alpha\gamma} d\tau = \epsilon_{njl}{}^{\alpha\gamma} \int \varphi_{njl}{}^{\alpha\gamma*} S_q{}^{\alpha\gamma} d\tau. \quad (13)$$

In the above equation, $\epsilon_{njl}{}^{\alpha\gamma}$ is the energy eigenvalue in the crystal of the Hamiltonian H. If this equation is valid and if

$$\int \varphi_{njl}{}^{\alpha\gamma*} H \varphi_{nj'l'}{}^{\alpha\gamma} = \epsilon_{njl}{}^{\alpha\gamma} \delta_{jj'} \delta_{ll'}, \quad (14)$$

the MB method is equivalent to the OPW method. In other words, if the core states are very good eigenstates of the crystal Hamiltonian, the two methods are equivalent.

There are additional advantages of the MB method over the OPW method. For insulating solids, it is not always possible to compute the conduction bands by OPW and the valence states by tight-binding methods. This is because the tight-binding valence states may be poor eigenstates of the crystal Hamiltonian; this in turn may lead to the lowest OPW energy value converging to the valence band.[20] Thus, it is necessary to evaluate the valence bands by OPW also. Unfortunately, this requires that a large number of plane waves be used (400–600). This also means that one may evaluate the energy levels for only a few points of high symmetry in the Brillouin zone.[2] When it is possible to represent the valence states by tight-binding functions, fewer than 100 plane waves are needed to represent the conduction states.[21] Using the MB method and including core states for the valence band, we shall see that it is possible to obtain reasonable results for both core and valence states with very few plane waves. With this improvement, it is possible to compute the energy levels for even general points in the Brillouin zone using modern digital computers.

A formalism to facilitate OPW calculations using pseudocore orbitals has been developed by Deegan and Twose.[22] These pseudo-orbitals are chosen to be nonoverlapping between the various ion sites. This is also a form of mixed basis technique. In general, the method of Deegan and Twose is not equivalent to that given in this paper; however, it could be of considerable practical advantage to incorporate the nonoverlapping pseudocore orbitals into the mixed basis formalism as developed here.

V. APPLICATION

In order to test the MB formalism, the band structures of LiI and NaI were computed at points of high symmetry in the first Brillouin zone. In this particular case the MB formalism is not equivalent to the OPW formalism. Solutions are obtained in three different ways. Firstly, the conventional nonrelativistic OPW equations were solved[2]; second, relativistic effects were added by first-order perturbation theory[16–18]; third, the relativistic MB equations were solved for these systems. Spin-orbit effects were neglected initially and were later added using degenerate perturbation theory for those states for which they were important. This use of perturbation theory seems totally adequate for the alkali halides.[16,23] The potential used is that which the author has used in recent OPW calculations on the alkali halides.[20] A discussion of this potential is given in Ref. 20, along with a discussion of the results obtained by changing the form of the potential.

In the case of the MB problem the Hamiltonian is

$$H = p^2/2m + V(\mathbf{r}) + H_m + H_{\mathrm{D}}. \quad (13')$$

The core states used for the calculation were those nonoverlapping core orbitals which were solutions to the equation

$$[p^2/2m + V(\mathbf{r})]\varphi_{jlm}(\mathbf{k},\mathbf{r}) = \epsilon_{jlm}(\mathbf{k})\varphi_{jlm}(\mathbf{k},\mathbf{r}). \quad (14')$$

Thus, the core orbitals chosen were eigenfunctions of the nonrelativistic Hamiltonian. Therefore, in setting up the MB Hamiltonian matrix defined by Eqs. (6) there are nondiagonal matrix elements between the core orbitals due to the presence of H_m and H_{D} in the Hamiltonian. Thus, in the context of the variational method one is obtaining exact eigenvalues to the Hamiltonian given by Eq. (13).

In Tables I and II, we present the results for the valence and conduction bands of LiI and NaI. The notation is that of Bouckaert *et al.*[24] An iodine ion site is used as the origin of the coordinate system. Because of their small size, spin-orbit effects are neglected in presenting the conduction-band effects.[25] The x-ray levels and the probable atomic state of origin are given

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TABLE I. The energies of selected symmetry points in the first Brillouin zone of NaI are given. Column I gives the symmetry of the state, column II is the nonrelativistic OPW energy, column III is the OPW result, including relativistic effects by first-order perturbation theory, and column IV contains the MB energies including relativistic corrections. Rydberg units are used and the notation is that of Bouchaert *et al.*[a] $\xi=0.0277$ Ry and $a=12.3$ Bohr units.

I	II	III	IV
s-type valence state (5*s* I^- mostly)			
Γ_1	−1.428	−1.600	−1.576
X_1	−1.401	−1.586	−1.557
L_1	−1.407	−1.590	−1.562
Δ_1	−1.415	−1.593	−1.567
p-type valence state (5*p* I^- mostly)			
Γ_8^-	−0.657	−0.726	−0.721
X_7^-	−0.696	−0.757	−0.752
X_6^-	−0.728	−0.783	−0.782
L_4^-	−0.674	−0.740	−0.735
L_6^-	−0.712	−0.770	−0.771
Γ_6^-	−0.740	−0.809	−0.804
X_6^-	−0.817	−0.872	−0.866
L_6^-	−0.820	−0.878	−0.869
conduction states			
Γ_1	−0.240	−0.302	−0.287
Γ_{25}'	0.037	0.035	0.035
Γ_{12}	0.144	0.139	0.139
Γ_2'	0.150	0.150	0.150
Γ_{15}	0.422	0.420	0.421
Γ_1	0.868	0.867	0.867
X_1	−0.125	−0.138	−0.136
X_1	0.482	0.408	0.424
X_4'	0.099	0.059	0.064
X_4'	0.841	0.832	0.833
X_5'	0.315	0.291	0.294
X_5'	0.831	0.830	0.830
X_3	−0.177	−0.179	−0.179
X_3	0.864	0.862	0.862
X_2	0.266	0.258	0.258
X_5	0.310	0.309	0.309
X_5	0.840	0.840	0.840
L_1	−0.234	−0.254	−0.250
L_1	0.361	0.306	0.317
L_1	0.708	0.701	0.701
L_2'	0.092	0.052	0.056
L_2'	0.290	0.284	0.286
L_2'	0.830	0.827	0.827
L_3'	0.387	0.377	0.378
L_3'	0.859	0.849	0.850
L_3	−0.133	−0.133	−0.133
L_3	0.116	0.115	0.116
L_3	0.856	0.855	0.856
Δ_1	−0.125	−0.179	−0.169
Δ_1	0.020	0.008	0.011
Δ_1	0.579	0.573	0.574
Δ_1	0.746	0.692	0.700

[a] Reference 24.

in Tables III and IV. These results are discussed in Sec. VI.

There are several comments which may be made at this time about the MB technique. The first comment is that the plane-wave part of the basis makes nonnegligible contributions to the core states. This may be seen from the following results. It is assumed for the sake of argument that a given core state is only a linear combination of other nonrelativistic core states. Thus one diagonalizes the Hamiltonian equation (13′) using only the core states as a basis. One then computes the eigenstates of this problem. These eigenstates are then used as the core eigenstates of Eq. (13′), and one then attempts to compute the valence and conduction states of the Hamiltonian by the OPW method. This technique was attempted for NaI and the lowest-energy eigenvalues were found to lie in the core region when about 400 plane waves were used. Thus, one concludes that the linear combination of nonrelativistic core states is not an adequate representation of the eigenfunction of the Hamiltonian and that the plane waves form a nonnegligible part of the core eigenfunctions.

TABLE II. The energies of selected symmetry points in the first Brillouin zone of LiI are given. Column I gives the symmetry type, column II is the nonrelativistic OPW energy, column III is the MB relativistic result. Rydberg units are used and the notation is that of Bouchaert *et al.*[a] $\xi=0.03015$ Ry and $a=11.3$ Bohr units.

I	II	III
s-like valence state		
Γ_1	−1.490	−1.635
X_1	−1.440	−1.599
L_1	−1.454	−1.609
Δ_1	−1.467	−1.618
p-like valence state (I^- 5*p* mostly)		
$\Gamma_8-(\Gamma_{15})$	−0.701	−0.739
$X_7-(X_5')$	−0.857	−0.827
$X_6-(X_4')$	−0.917	−0.857
$L_4-(L_3')$	−0.789	−0.759
$L_6-(L_2')$	−0.921	−0.804
Γ_6^-		−0.830
X_6^-		−0.947
L_6^-		−0.937
conduction states		
Γ_1	−0.189	−0.253
Γ_{25}'	0.049	0.046
Γ_{12}	0.168	0.161
Γ_2'	0.183	0.183
Γ_{15}	0.350	0.347
Γ_1	0.969	0.988
X_3	−0.201	−0.203
X_1	−0.147	−0.159
X_4'	0.192	0.145
X_2	0.313	0.302
X_5	0.319	0.318
X_5'	0.336	0.311
X_1	0.659	0.587
X_4'	0.825	0.820
X_5'	0.858	0.857
X_5	0.998	0.998
L_1	−0.270	−0.291
L_3	−0.255	−0.256
L_2'	0.189	0.155
L_2'	0.326	0.318
L_1	0.423	0.373
L_3'	0.464	0.455
L_3	0.585	0.585
L_3	0.752	0.751
L_1	0.821	0.815
L_2'	0.937	0.933
L_3'	0.988	0.981
Δ_1	...	−0.122
Δ_1	...	−0.027
Δ_1	0.658	0.652
Δ_1	0.930	0.884

[a] Reference 24.

Another comment which must be made is that the Hamiltonian and overlap matrices are generally complex. The author does not have in his possession a program which evaluates the eigenfunctions of a complex matrix and hence is not able to provide any information on the eigenfunctions of the Hamiltonian.

This method is rather fast in terms of computer time used. The calculations presented here for LiI and NaI were performed using less than 14 min of time on a CDC 6600. The OPW calculations including relativistic effects by first-order perturbation theory required less than 20 min of CDC 6600 time for both NaI and LiI.

It is possible to reduce the computer time by including overlapping valence orbitals in the basis. This has been done for LiI and it was found that one can obtain reasonable convergence with about 150 plane waves when overlapping valence orbitals are included in the basis. If these are neglected, it is necessary to use about 400 plane waves. By including the overlapping valence orbitals in the basis, one reduces the computer time to about one-half of that used when only nonoverlapping core orbitals are included in the basis. This is discussed in the Appendix.

It should be mentioned that the core states as computed were found to be totally independent of **K**. This result is expected since the core states are nonoverlapping. The author estimates that the core states are convergent to one part in 10^{-4} and the valence and conduction levels are convergent to about 10^{-3} Ry. This claim is based upon studying the change in energy as the number of plane waves are increased and also upon second-order perturbation theory. This use of second-order perturbation theory to study the convergence has been the subject of recent discussion.[20]

TABLE III. The x-ray levels of NaI are given. In each case, the atomic state of origin is indicated. The free-ion nonrelativistic and relativistic energies are also given. Spin-orbit splittings are included and rydberg units used. The results are valid in the entire Brillouin zone.

Free-ion state	Energy in crystal	Nonrelativistic free-ion energy	Relativistic free-ion energy
$\mathrm{I}^- 1s$	−2430	−2340	−2430
$\mathrm{I}^- 2s$	−379	−355	−379.0
$\mathrm{I}^- 2p,\ j=\frac{1}{2}$	−359	−334	−360
$\mathrm{I}^- 2p,\ j=\frac{3}{2}$	−339	−334	−339
$\mathrm{Na}^+ 1s$	−78.2	−78.8	−78.9
$\mathrm{I}^- 3s$	−77.6	−71.9	−77.0
$\mathrm{I}^- 3p,\ j=\frac{1}{2}$	−69.0	−63.1	−68.5
$\mathrm{I}^- 3p,\ j=\frac{3}{2}$	−65.2	−63.1	−64.6
$\mathrm{I}^- 3d,\ j=\frac{3}{2}$	−48.5	−46.7	−48.0
$\mathrm{I}^- 3d,\ j=\frac{5}{2}$	−47.6	−46.7	−47.0
$\mathrm{I}^- 4s$	−14.0	−12.2	−13.46
$\mathrm{I}^- 4p,\ j=\frac{1}{2}$	−10.9	−9.27	−10.34
$\mathrm{I}^- 4p,\ j=\frac{3}{2}$	−10.1	−9.27	−9.59
$\mathrm{Na}^+ 2s$	−4.80	−5.38	−5.65
$\mathrm{I}^- 4d,\ j=\frac{3}{2}$	−4.68	−3.85	−4.09
$\mathrm{I}^- 4d,\ j=\frac{5}{2}$	−4.54	−3.85	−3.97
$\mathrm{Na}^+ 2p,\ j=\frac{1}{2}$	−2.77	−3.34	−3.34
$\mathrm{Na}^+ 2p,\ j=\frac{3}{2}$	−2.75	−3.34	−3.34

TABLE IV. The x-ray levels of LiI are given. In each case, the atomic state of origin is indicated. The free-ion nonrelativistic energies are also given. The results are valid for all points in the Brillouin zone. Rydberg units are used and spin-orbit effects are included.

State of origin	Relativistic energies on the crystal	Free-ion energy
$\mathrm{I}^- 1s$	−2430	−2340
$\mathrm{I}^- 2s$	−379	−355
$\mathrm{I}^- 2p,\ j=\frac{1}{2}$	−359	−334
$\mathrm{I}^- 2p,\ j=\frac{3}{2}$	−339	−334
$\mathrm{I}^- 3s$	−77.6	−71.9
$\mathrm{I}^- 3p,\ j=\frac{1}{2}$	−69.1	−63.1
$\mathrm{I}^- 3p,\ j=\frac{3}{2}$	−65.2	−63.1
$\mathrm{I}^- 3d,\ j=\frac{3}{2}$	−48.5	−46.7
$\mathrm{I}^- 3d,\ j=\frac{5}{2}$	−47.6	−46.7
$\mathrm{I}^- 4s$	−14.1	−12.3
$\mathrm{I}^- 4p,\ j=\frac{1}{2}$	−10.9	−9.27
$\mathrm{I}^- 4p,\ j=\frac{3}{2}$	−10.2	−9.27
$\mathrm{I}^- 4d,\ j=\frac{3}{2}$	−4.85	−3.85
$\mathrm{I}^- 4d,\ j=\frac{5}{2}$	−4.71	−3.85
$\mathrm{Li}^+ 1s$	−4.64	−5.38

If one uses only nonoverlapping core orbitals in both MB and OPW formalism, one must use about the same number of plane waves in each case. Thus, in order to fully utilize the advantages of the MB method, it is necessary to include overlapping valence orbitals in the basis. The increase in the number of rows and columns in the mixed-basis secular determinant due to the presence of the core orbitals seems to have a negligible effect on the time of calculation if one compares this time to that required for the equivalent OPW calculation. In the case of NaI and LiI, the advantage of the MB method lies in its ability to solve the relativistic problem in the solid while one need only solve a much simpler nonrelativistic equation for the free members of the lattice.

VI. DISCUSSION OF RESULTS

The author finds the valence band of sodium iodide to be 0.101 Ry wide if spin-orbit effects are neglected. By the tight-binding method, the width was found to be about 0.103 Ry. This agreement is excellent. The inclusion of spin-orbit effects splits the valence band into two nonoverlapping bands. At the point Γ, the splitting is 0.092 Ry, a result which agrees well with experiment.[22] The band gap is found to be 0.43 Ry. Experimentally, the band gap is 0.44 Ry.[26] This agreement is excellent. Using soft x-ray absorption, Haensel *et al.* have found the onset of absorption from the Na^+ $2p$ state to the lowest conduction band to lie to about 2.42 Ry.[27] This energy is predicted by the MB method to be 2.48 Ry. Again the agreement is good.

Relativity is important in the band structure of NaI. Because of relativistic effects, the Γ_{15} point of the valence band is shifted downward by about 0.059 Ry,

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[26] K. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967).

[27] R. Haensel, C. Kunz, T. Sasaki, and B. Sonntag, Phys. Rev. Letters **20**, 1436 (1968).

and the lowest conduction Γ_1 state is shifted downward by about 0.052 Ry; however, the $\Gamma_{25'}$ conduction state is shifted by only about 0.005 Ry. Thus, the structure of the conduction band is seen to be rather sensitive to the inclusion of relativistic effects even though the effect on the band gap is small. The size of the relativistic contributions is essentially the same as that found for KI by Onodera, Okazaki, and Inui,[6] who solve a Dirac equation for the lattice.

At the point X, the lowest level is X_3. This level lies about 0.044 Ry below the next state which is of X_1 type. Thus, it is reasonable to expect that an exciton might be associated with X_3 in NaI as it is in KI.[25] Based on the present calculation, this should lie at about 0.125 Ry above the Γ exciton. There is a sharp spike in the NaI absorption at about 0.54 Ry,[26] which is, in fact, about 0.125 Ry above the first Γ exciton. It is suggested that this peak is due to an exciton associated with X.

The valence band of LiI is found to be about 0.16 Ry wide if spin-orbit effects are neglected. The inclusion of spin-orbit effects increases the band width to about 0.26 Ry. The band gap is found to be 0.485 Ry at Γ and is 0.467 Ry at L. Hence, the direct edge is predicted to be at the point L rather than at Γ. There should be an indirect transition from Γ_8^- to L_1 at about 0.022 Ry before the onset of the fundamental absorption. In the x-ray spectrum, it is predicted that the onset of absorption should be at about 4.38 Ry for transitions from the Li^+ 1*s* level to the conduction band. This is in excellent agreement with the results of Haensel *et al.*,[11] who predict the onset of absorption to be at about 4.40 Ry. It is found that there is an I^- *d*-like level just below the Li^+ 1*s* level and this is in keeping with the conjecture given by Haensel *et al.*; however, the present work finds the order of the levels to be the reverse of the order which Haensel *et al.* suggest. At present, it is not possible to say which assignment is correct.

The optical data for LiI is sparse. Fischer and Hilsch measured the optical-absorption spectrum of LiI in its fcc phase at 78°K, but very little structure is visible in their data.[28] The first exciton peak occurs at 0.44 Ry and is not as great as the exciton peak found in the other alkali halides. They are unable to resolve any well-defined structure at energies higher than the first exciton peak. Recently, Bachrach has measured the absorption of thin films of LiI in the exciton region at 4.7, 78, and 295°K.[29] These measurements were made using strain-reduced thin-film techniques. The first exciton peak is found to occur at 0.41 Ry at 4.7°K, 0.43 Ry at 78°K, and 0.44 Ry at 295°K. Bachrach observes a rather broad indirect edge preceding the first exciton peak. There is a second exciton peak about 0.025 Ry above the first exciton peak which is nearly as strong as the first peak. This splitting is in good agreement with the computed splitting for the L and Γ band edges. It appears that this data is in good agreement with the predictions of this present calculation. Unfortunately, because of instrument limitations, Bachrach was unable to measure the spectrum of LiI above 0.47 Ry and no more comparison with experiment is presently possible.

The band structure of LiI is quite different from that obtained for the other alkali halides. This is not believed to be function of the model potential chosen since essentially the same band structure has been obtained using several different model potentials.

There is one important point to be made at this time. A true Hartree-Fock type of calculation has not been performed, and hence, Koopman's theorem is not satisfied.[30] Therefore, the calculation must be regarded as using a type of model potential and is not a first-principles calculation. In this sense, the good agreement between theory and experiment is fortuitous. This does not imply that the calculation is of no value, but that it must be used as a qualitative tool for understanding the optical properties of NaI and LiI. Thus one must await more and better experimental data before the validity of these calculations can be either accepted or rejected.

VII. CONCLUSIONS

The MB method is seen to produce reasonable results for LiI and NaI for the model potential which was chosen. The OPW results which include relativistic effects by first-order perturbation theory are in excellent agreement with the MB results, where these effects are treated in an essentially exact manner. It is also noted that the size and direction of the relativistic effects are the same as those for KI which were obtained by Onodera using a Dirac equation.[6] Therefore, it is felt that the MB method presented here provides an excellent method for the inclusion of relativistic effects into band-structure calculations.

It has been seen that by including overlapping valence orbitals in the basis one may achieve a considerable saving in computer time. The author believes that this method would work as well for metals or semiconductors as it does for NaI and LiI.

Continuing development of the MB method is being undertaken and more calculations are being performed. At the present time, calculations on LiF and KI are being completed. It is also expected that true Hartree-Fock calculations will be performed using this method and that one will overcome the theoretical limitations inherent to the use of model potentials.

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[28] F. Fischer and R. Hilsch, Z. Physik **158**, 553 (1960).

[29] R. Bachrach (private communication, 1969).

[30] J. Lindgren, Arkiv Fysik **31**, 59 (1965).

tivistic effects. The hospitality extended the author by the staff of the Courant Institute, where these calculations were made, is deeply appreciated. The author wishes to thank Dr. R. Haensel of the Physikalisches Staatsinstitut der Universitat, Hamburg, for providing the author with results of his unpublished experiments on the x-ray spectra of LiI and NaI, and for a very stimulating discussion. Finally, he expresses his deepest appreciation to Robert Bachrach for providing him with the results of his recent optical-absorption measurements on LiI prior to publication.

APPENDIX

In this appendix, explicit forms are developed for the integrals in Eqs. (6). These forms are first developed for the specific example given in this paper and then for a more general case. Insofar as most of these expressions can be found in either the OPW literature[1] or the tight-binding literature,[22,24] little detail will be given.

In the present application to NaI, the core functions used were those for states for which $E(\mathbf{k})=\text{const}$, that is, the Na^+ $1s$, $2s$, and $2p$ and the I^- $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, $4s$, $4p$, and $4d$ states. These states were solutions to the Hartree-Fock-Slater equation for the free sodium and iodine ions. Therefore, one finds that

$$\int \varphi_{njl}{}^{\alpha\gamma*}\varphi_{nj'l'}{}^{\alpha\gamma}d\tau=\delta_{jj'}\delta_{ll'}\,,$$

$$\int S_{nq}{}^{\alpha\gamma*}S_{nq'}{}^{\alpha\gamma}d\tau=\delta_{qq'}\,,$$

$$\int \varphi_{njl}{}^{\alpha\gamma*}S_{nq}{}^{\alpha\gamma}d\tau=\Omega^{-1/2}4\pi i^l\sum_t\sum_m b_{qt}{}^{\alpha\gamma}\,, \qquad \text{(A1)}$$

$$C_{lm}{}^{\alpha\gamma*}Y_l{}^m(\theta_{\mathbf{k}+\mathbf{h}_t},\varphi_{\mathbf{k}+\mathbf{h}_t})\,,$$

$$\int_0^\infty r^2 j_l[(|\mathbf{k}+\mathbf{h}_t|)r]R_{jl}(r)dr\,.$$

In Eqs. (A1), Ω is the volume of the unit cell, and $Y_l{}^m(\theta_{\mathbf{k}+\mathbf{h}_t},\varphi_{\mathbf{k}+\mathbf{h}_t})$ is the usual spherical harmonic where the angles are between a fixed set of axes and the line joining $\mathbf{k}+\mathbf{h}_t$ and the origin. R_{jl} is the jl radial solution of the free-ion problem and j_l is the spherical Bessel function of order 1. When the origin is on a halogen ion and the function in question is an alkali ion, one must multiply each term in the third of Eqs. (A1) by $e^{(i\mathbf{g}\cdot\mathbf{h}_t)}$, with $\mathbf{g}$ being the vector from a halogen-ion site to an alkali-ion site.

In the case of the Hamiltonian matrix, the relativistic part has been defined in Eqs. (10)–(12); therefore, only the classical terms need be considered here. One finds that

$$\int \varphi_{njl}{}^{\alpha\gamma*}H_{cl}\varphi_{nj'l'}{}^{\alpha\gamma}=\epsilon_{njl}\delta_{jj'}\delta_{ll'}\,,$$

$$\int \varphi_{njl}{}^{\alpha\gamma*}H_{cl}S_{nq}{}^{\alpha\gamma}d\tau=\epsilon_{njl}\int \varphi_{njl}{}^{\alpha\gamma*}S_{nq}{}^{\alpha\gamma}d\tau\,, \qquad \text{(A2)}$$

$$\int S_{nq}{}^{\alpha\gamma*}H_{cl}S_{nq'}{}^{\alpha\gamma}d\tau=(\mathbf{k}+\mathbf{h}_t)_q{}^2\delta_{qq'}+\int S_{nq}{}^{\alpha\gamma}V_a(\mathbf{r})S_{nq'}{}^{\alpha\gamma}d\tau\,.$$

In Eq. (A2), ϵ_{njl} contains the energy of the jl free-ion orbital plus the Madelung potential which is negative if an halogen orbital is being used and positive if an alkali orbital is being used. The integral of the plane waves and the crystal potential is well known from OPW theory and need not be given here.

For other substances, one needs to make changes in Eqs. (A1) and (A2). However, it is noted that the second of Eqs. (A1) and the third of Eqs. (A2) are always valid. If one were to include tight-binding valence-band orbitals, thereby reducing the size of the basis greatly, one makes the following modification:

$$\int \varphi_{njl}{}^{\alpha\gamma*}\varphi_{nj'l'}{}^{\alpha\gamma}d\tau\neq\delta_{jj'}\delta_{ll'}\,.$$

This expression must be evaluated explicitly,

$$\int \varphi_{njl}{}^{\alpha\gamma*}\varphi_{nj'l'}{}^{\alpha\gamma}d\tau=O_{njl,j'l'}{}^{\alpha\gamma}\,. \qquad \text{(A3)}$$

Then one finds that the third of Eqs. (A1) is correct if one divides the right-hand side of this equation by $(O_{njl,njl}{}^{\alpha\gamma})^{1/2}$.

In general, one must also explicitly evaluate the first of Eqs. (A2) using tight-binding theory[5] and one may define

$$\int \varphi_{njl}{}^{\alpha\gamma*}H_{cl}\varphi_{nj'l'}{}^{\alpha\gamma}d\tau=\epsilon_{njl,j'l'}{}^{\alpha\gamma}\,. \qquad \text{(A4)}$$

The second of Eqs. (A2) is, in general, difficult to evaluate; however, as is usual in OPW theory, if the tight-binding function is almost an eigenfunction of H_{cl} one may approximate

$$\int \varphi_{njl}{}^{\alpha\gamma*}H_{cl}S_{nq}{}^{\alpha\gamma}d\tau=\epsilon_{njl,jl}{}^{\alpha\gamma}(O_{njl,jl}{}^{\alpha\gamma})^{-1/2}\int \varphi_{njl}{}^{\alpha\gamma*}S_{nq}{}^{\alpha\gamma}d\tau\,. \qquad \text{(A5)}$$