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Electronic Structure of NaBr[†]

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In this paper, *ab initio* energy bands for NaBr are obtained by means of the nonrelativistic mixed-basis (MB) method. The calculation is performed self-consistently in the Hartree-Fock limit, accurate to first order in interatomic overlap. We assume the core states to be non-overlapping. Koopman's theorem is assumed here. Correlation effects are then included and are found to be important in that they reduce substantially the band gap, and also the widths of the valence bands. The resultant bands are fitted with a pseudopotential and the density of states of the valence and conduction bands are obtained as are the joint density of states for both valence and core excitations. These results are compared to recent optical and soft-x-ray absorption studies of NaBr, and the valence results are compared to x-ray emission studies. The experimental comparisons favor the more distinctive results of this calculation such as the wide (4 eV) $4p$ valence bands and the structured state density of the conduction bands.

I. INTRODUCTION

Despite the great deal of effort expended in recent years on calculating the energy bands of insulating crystals, agreement between the results of different calculations for the same material is generally not obtained.[1] This discrepancy between the different calculations is due in part to the differing assumptions made in forming the crystal potential.[2] Therefore, it seems useful to obtain energy bands *ab initio* whenever possible. This means that for insulating solids, one should use the correct Fock operator, self-consistently if possible, and should correct for correlation effects.[3] There were some early attempts to produce

such *ab initio* calculations[4] but these were by tight-binding techniques and limited to the valence and the lowest conduction band.

Recently the authors, individually and jointly, have made considerable progress in obtaining *ab initio* energy bands for these materials.[5] It has been seen from these calculations for LiCl, LiBr, NaCl, Ar, and Kr that the *ab initio* energy bands differ substantially from those obtained using approximate exchange potentials.

One of us (A. B. K.) has developed a local-orbitals theory[6] which allows us to obtain accurate self-consistent charge densities for alkali halide crystals in their ground state in the Hartree-Fock limit. These orbitals are accurate to first order

in interatomic overlap. These charge densities allow us to compute the Hartree-Fock energy bands for these solids using Koopman's theorem and assuming the core states to be nonoverlapping.

In this previous work,[5] it was seen that polarization corrections, clearly neglected in the Hartree-Fock limit used above, are important and should be included before a comparison with experiment is made. These effects substantially reduce the optical band gap and substantially narrow the valence bands. These effects may be roughly included using the method of Fowler[3] or more accurately by the method of Hedin[7] as used for semiconductors by Brinkman and Goodman.[8] Previously, we have investigated both methods[5] and find them to be qualitatively the same for conduction states.

In the present paper, we investigate the electronic structure and optical properties of the NaBr crystal using the same techniques used previously,[5] except that a more accurate expression for the dielectric function is used in computing the polarization corrections. New results for NaCl using this function are also given by means of comparison. First we obtain the self-consistent charge density using local-orbital theory accurate to the first order in interatomic overlap. Then the energy bands in our Hartree-Fock approximation are obtained. Finally correlation effects are included. The method used for the band calculation is the MB method.[9] Actual calculations are only performed for Γ, X, and L in the first Brillouin zone. The resultant bands are in good agreement with those previously found for NaCl,[5] and the NaCl pseudopotential is scaled to allow us to generate the complete energy-band structure for NaBr. Using this pseudopotential the densities of states for the valence and conduction bands and several useful joint densities of states are obtained at 505 nonequivalent points in $\frac{1}{48}$ of the first Brillouin zone.

In Sec. II, we briefly review the main features of the calculation. In Sec. III, the results are presented and compared with available experiment. Finally, the chief results are summarized and suggestions for future work are made.

II. METHOD OF CALCULATION

Since the various techniques used in the present calculations are described elsewhere,[5] we will give here only a brief outline of them in order to better appreciate the results obtained. As mentioned before, Kunz[6] has been able to obtain local orbitals correct to first order in the interatomic overlap. These orbitals satisfy the following equations:

$$(F_A + U_A - \epsilon_{Ai})\phi_{Ai} = \sum_k{}' \phi_{Ak}\langle\phi_{Ak}|U_A|\phi_{Ai}\rangle, \quad (1)$$

where A denotes nuclear coordinates, i refers to electronic coordinates; the $\sum_k'$ means sum over all

occupied electron states except $|Ai\rangle$. F_A is the usual Fock operator (in Rydberg units)

$$F_A = -\nabla_1^2 + 2Z_A/|\vec{r}_{A1}| + 4\sum_i \int |\vec{r}_{12}|^{-1}\phi_{Ai}{}^2(r_2)$$
$$-2\sum_i |\phi_{Ai}\rangle\langle\phi_{Ai}||r_{12}|^{-1} \quad (2)$$

and

$$U_A = -\sum_B{}' \frac{2Z_B}{r_{B1}} + 4\sum_{B,i}{}' \int |\vec{r}_{12}|^{-1}\phi_{Bi}{}^2(r_2). \quad (3)$$

In all the above summations we include only one member of a spin-up spin-down pair of orbitals.

Solving self-consistently Eq. (1), we get the local orbitals ϕ_{Ai} and the energies ϵ_{Ai}. These quantities are needed when one uses the mixed-basis method.[9] In this method, one writes the one-electron wave functions $\Psi_{n,\vec{k}}^{\alpha,i}(\vec{r})$ as

$$\Psi_{n,\vec{k}}^{\alpha,i}(\vec{r}) = \sum_{j,l} b_{njl}^{\alpha,i} \sum_m c_{l,m}^{\alpha,i}(\vec{k})\,\phi_{jlm\vec{k}}(\vec{r})$$
$$+ \sum_q d_{n,q}^{\alpha,i} \sum_l A_{q,l}^{\alpha,i} e^{i(\vec{k}+\vec{h}_l)_q\cdot\vec{r}}, \quad (4)$$

where the quantities $C_{l,m}^{\alpha,i}$ and $A_{q,l}^{i,i}$ are chosen so that the Bloch function $\phi_{jlm\vec{k}}(\vec{r})$ and the plane wave $e^{i(\vec{k}+\vec{h}_l)_q\cdot\vec{r}}$, respectively, transform accounting to the ith row of the αth irreducible representation of the group of the wave vector $\vec{k}$; $\vec{h}_l$ denotes reciprocal-lattice vectors and $b_{njl}^{\alpha,i}$ and $d_{np}^{\alpha,i}$ are variational parameters. In the Hartree-Fock approximation, the functions $\psi_{n,k}^{\alpha,i}$ are solutions of the equations

$$(F - \epsilon_k^{\alpha,i})\psi_{n,\vec{k}}^{\alpha,i} = 0 \quad (5a)$$

or

$$(T + V_N + V_c + V_{ex} - \epsilon_k^{\alpha,i})\psi_{n,\vec{k}}^{\alpha,i} = 0. \quad (5b)$$

In (5b), the total Fock operator has been divided into a Coulomb, an exchange, a nuclear, and kinetic-energy part. In order to solve (5a) one has to evaluate the matrix elements of the Fock operator and the overlap matrix. The techniques used for the computation of the matrix elements are extensively described elsewhere[5] so that we will not discuss them here.

We have mentioned that no correlation effects, except that coming from the assumption of a total antisymmetric wave function, are included in the Hartree-Fock approximation. The problem of treating these effects is extensively discussed in the literature.[3] It is possible to show[8] that one can write equations, similar to (5b), which include these effects, i.e.,

$$(T + V_N + V_c + M - \epsilon_k^{\alpha,i})\psi_{n,k}^{\alpha,i} = 0, \quad (6)$$

where M is the so-called self-energy operator. All correlation is included in it. It is obviously impossible to treat M exactly, however one can

approximate it. In accord with the previous calculations,[5] we shall treat M in the random-phase approximation. In this case, M can be written as a sum of a screened exchange potential and a self-energy term[5]:

$$M(\vec{p}, \vec{p} + \vec{K}) = V_{ex}^c(\vec{p}, \vec{p} + \vec{K}) + V^{sch}(\vec{p}, \vec{p} + \vec{K})$$

$$+ E_{ch}(\delta_0, \vec{\kappa} - \langle \vec{p} | \overline{P_c} | \vec{p} + \vec{K} \rangle) , \quad (7)$$

where all quantities are defined as in Ref. 5.

Another way of treating polarization effects has been proposed by Fowler,[3] whose method is an extension of the theories of Haken and Schottky[10] and Toyozawa.[11] Essentially, Fowler shows that these theories reduce, for most insulators, to a static limit which he evaluates using the Mott and Littleton[12] approach. The effect of electronic correlation, when treated this way, is only a rigid shift of the conduction and valence bands, with a consequent reduction of the energy gap.

Before actually computing the energy bands of NaBr, it is worthwhile to say that in principle Eqs. (5) and (6) could be solved for any point in the first Brillouin zone. However, the amount of work involved is in general large. The amount of work gets larger and larger as one goes from points of high symmetry to points of low symmetry because, in doing so, group theory gives less and less help. It is therefore economically inconvenient to consider many points and we have computed the energy bands only at Γ, X, L. The resultant bands are similar to those found for NaCl. However, in order to facilitate comparison between theory and experimental data, we have fitted the valence bands with tight-binding expressions[13] and the conduction bands with a pseudo-Hamiltonian of the following form[14]:

$$\mathcal{K}_{ps} = \alpha p^2/2m + \sum_k v(\vec{k}) e^{i\vec{k}\cdot\vec{r}} . \quad (8)$$

Here α and $v(\vec{k})$ are adjustable parameters.

III. RESULTS AND EXPERIMENTAL COMPARISON

These calculations were performed on the IBM 360-75 computer at the University of Illinois. In Tables I and II, we present the local-orbital solutions to Eq. (1) for the Na^+ and Br^- lattice sites. The local-orbital core states included in the MB calculation included the $1s$, $2s$, $2p$ orbitals about a Na^+ site and the $1s$, $2s$, $2p$, $3s$, $3p$, $3d$ orbitals at Br^- site. The lattice constant used is 11.20 Bohr radii. In presenting results, the BSW notation is to be used.[15] Our calculations included all plane waves of $p^2 \le 32$. In Table III, we present the Hartree-Fock energy levels. The probable Hartree-Fock bands are shown in Fig. 1 and are modeled on our previous bands for NaCl. The computed band gap ($\Gamma_{15} \rightarrow \Gamma_1$) is found to be 11.03 eV,

TABLE I. Atomic parameters for Na^+ ion in NaBr. The notation is that of Ref. 6.

Energy parameters, defined as $\epsilon_{nn^1} = \langle n | F_A + V_A | n^1 \rangle$, Ry.

$\epsilon_{1s,1s} = -81.06$	$\epsilon_{1s,2s} = 1197 \times 10^{-7}$
$\epsilon_{2s,2s} = -5.539$	$\epsilon_{2p,2p} = -2.997$

Basis members A_{lj} and Z_{lj}

	$l=0$			$l=1$	
j	A_{0j}	Z_{0j}	j	A_{1j}	Z_{1j}
1	0	15.949	1	0	12.048
2	0	9.439	2	0	5.703
3	2	11.624	3	0	3.336
4	1	4.384	4	0	2.146
5	1	2.811			

Expansion coefficients C_{nlj}

j	C_{10j}	C_{20j}	c_{21j}
1	0.213930	0.014886	0.012045
2	0.976289	0.334190	0.362503
3	-0.011272	0.054260	0.708541
4	-0.027057	-0.601092	0.605322
5	0.015342	-0.723768	

the electron affinity is found to be -1.01 eV and the photoemission threshold is 10.02 eV. The $4d$ band is 5.66 eV wide and the $4s$ band is 1.51 eV wide.

The experimental value for the band gap in this substance lies between 7.1 and 7.4 eV.[16,17] The value of 7.1 eV given by Fröhlich and Staginus[16] is probably most reliable. The computed Hartree-Fock gap exceeds this by 3.93 eV. According to Fowler, polarization corrections would reduce the computed band gap by a value E_c which is $3.22 \le E_c \le 4.21$ eV.[3] Thus the Hartree-Fock value seems quantitatively reasonable.

In order to investigate this aspect more closely, we shall treat correlation explicitly using the second approach as outlined in Sec. II. In order to treat the screened exchange, a knowledge of the dielectric function is required. Different models have been proposed,[18] and the agreement for these models is generally satisfactory. Here we use the dielectric function $\epsilon(q)$, which is obtained using the Fry model[19] as described in Ref. 18. This function is shown in Fig. 2. This is a more accurate dielectric function than that obtained from Fowler, which we used in our previous work on NaCl. The NaCl calculation is repeated using the Fry dielectric function for comparison purposes. In Table IV, we give the correlated bands for NaBr and also for NaCl using both the Fowler and Fry dielectric functions. It is seen in NaCl that the principal effect of this is an upward shift of the upper valence bands and a downward shift of the conduction bands. The shapes of the bands are relatively undistorted. By means of comparison, the

TABLE II. Atomic parameters for Br⁻ in NaBr. Energy parameters, defined as $\epsilon_{nnl} = \langle n l \, | \, F_A + U_A \, | \, n l \rangle$, Ry. The notation of Ref. 6 is used.

$\epsilon_{1s,1s} = -980.8$	$\epsilon_{1s,3s} = 10^{-7}$	$\epsilon_{2p,2p} = -117.0$
$\epsilon_{2s,2s} = -130.4$	$\epsilon_{1s,4s} = 2 \times 10^{-7}$	$\epsilon_{3p,3p} = -14.92$
$\epsilon_{3s,3s} = -19.71$	$\epsilon_{2s,3s} = -10^{-7}$	$\epsilon_{4p,4p} = -0.9112$
$\epsilon_{4s,4s} = -2.005$	$\epsilon_{2s,4s} = -3 \times 10^{-7}$	$\epsilon_{2p,3p} = -10^{-7}$
$\epsilon_{1s,2s} = 6 \times 10^{-7}$	$\epsilon_{3s,4s} = 48 \times 10^{-7}$	$\epsilon_{2p,4p} = -10^{-7}$
	$\epsilon_{3d,3d} = -6.403$	$\epsilon_{3p,4p} = -27 \times 10^{-7}$

Basis members A_{lj} and Z_{lj}

	$l=0$		$l=1$		$l=2$	
j	A_{0j}	Z_{0j}	A_{1j}	Z_{1j}	A_{2j}	Z_{2j}
1	0	37.3527	0	23.3102	0	16.0578
2	1	33.1430	0	15.6532	0	10.0855
3	1	17.2808	1	14.8256	0	7.2889
4	2	16.3407	1	9.5909	0	4.7416
5	2	8.4198	1	6.1399	0	2.9679
6	2	6.6235	2	5.3085		
7	3	6.6182	2	2.8150		
8	3	3.4730	2	1.6374		
9	3	2.1970	2	1.1277		
10	3	1.4859				

Expansion coefficients c_{nlj}

$l=0$

j	c_{10j}	c_{20j}	c_{30j}	c_{40j}
1	0.988320	0.318673	0.129551	0.041564
2	0.144865	0.192659	0.076029	0.023638
3	-0.015696	-0.729875	-0.292041	-0.090983
4	0.012828	-0.555448	-0.430691	-0.145691
5	-0.023306	-0.107880	0.463690	0.215380
6	0.032710	0.087670	0.661950	0.196048
7	-0.14545	-0.027669	0.228957	0.139643
8	0.001031	-0.000723	0.029638	-0.687148
9	-0.000570	0.000767	-0.012168	-0.606511
10	0.000199	-0.000308	0.004452	-0.145448

$l=1,2$

j	c_{21j}	c_{31j}	c_{41j}	c_{32j}
1	0.155471	0.055336	0.014064	0.051797
2	0.963835	0.315906	0.095743	0.308490
3	0.211122	0.181064	0.049119	0.542042
4	0.046856	-0.345677	-0.096732	0.766897
5	-0.008472	-0.858743	-0.319643	0.142165
6	0.003400	-0.083717	0.037767	
7	-0.000555	-0.018078	0.733829	
8	0.000302	0.008686	0.503758	
9	-0.000128	-0.003813	0.288080	

model potential bands previously obtained by one of us (A. B. K.) for NaBr are also given in Table IV.[20] It is seen that the more correct theory employed here yields substantial changes in the band structure. The NaBr bands are shown in Fig. 3.

If we correct for spin-orbit coupling in the valence band of NaBr,[21] we compute a band gap of 7.50 eV which is in error with experiment by 0.1–0.4 eV, a very acceptable amount. In the case of NaCl, the band gap using the Fry dielectric function is 8.61 eV. The experimental value for NaCl

is 8.75 eV.[22] Previously, we found the NaCl band gap to be 9.96 eV.[5] Using the Fry model for the dielectric function, we seem to obtain satisfactory values for optical band gaps.

Using the correlated results the $4p$ band in NaBr is found to be 3.76 eV wide if spin-orbit effects are neglected and the $4s$ band is 0.79 eV wide. The photoemission threshold is found to be 8.66 eV and the electron affinity is 0.96 eV.

In order to facilitate comparison with experiment we fitted the valence bands with tight-binding ex-

TABLE III. Hartree-Fock valence and conduction energies are given at Γ, X, and L. Results are in eV.

Point	Irr. rep.	1st	2nd	3rd
Γ	Γ_1	-28.22	1.01	19.07
	Γ_{15}	-9.80	12.94	25.49
	Γ_{25}'	7.88		
	Γ_{12}	10.03	28.68	
	Γ_2'	10.25		
X	X_1	-26.73	3.08	14.63
	X_4'	-14.89	8.72	20.54
	X_5'	-11.67	11.68	21.47
	X_3	3.66	21.95	27.59
	X_2	12.65	32.85	
	X_5	16.18		
L	L_1	-27.08	2.98	14.74
	L_2'	-15.68	8.07	10.62
	L_3'	-10.60	13.54	20.62
	L_3	6.04	11.28	20.93

FIG. 2. NaBr and NaCl dielectric function is shown using the Fry model (Refs. 18 and 19) in the text as is the Fowler dielectric function for NaCl.

pressions using Slater and Koster theory.[13] The conduction bands were fitted by scaling the pseudo-parameters for NaCl[5] to obtain the proper Γ_1-Γ_{25} conduction gaps. The density of states for the $4s$, $4p$ and conduction bands are shown in Figs. 4–6.

In comparing the NaBr results to experiment we concentrated on three experiments, the near-ultra-violet absorption data of Teegarden and Baldini,[23] the soft-x-ray data of Brown and Scheifley,[24] and the x-ray emission data of O'Brian and Skinner.[25] In this discussion we ignore the 30-eV region soft-x-ray data.[26] This is due to the near degeneracy of the broad $4s$ level on Br⁻ and the Na⁺ $2p$ shell and it is doubted that an unambiguous interpretation is possible.

In Fig. 7, we show the imaginary part of the dielectric constant which we compute using a constant transition matrix element for excitation from the $4p$ Br⁻ band. Also shown are the optical-absorption data of Teegarden and Baldini.[23] It is seen that except for the excitons which our calculations omit, the agreement is quite good.

In Fig. 8, the joint density of states for excitation for the Na⁺ $2s$ state and the Br⁻ $3d$ states to the conduction band is given along with the soft-x-ray absorption data of Brown and Scheifley.[24] In constructing this figure the experimental value of the spin-orbit splitting of the Br⁻ $3d$ levels is used as is the experimental value of separation of the Na⁺ $2s$ state from the Br⁻ $3d$ states.[27] This is necessary since we ignored relativistic effects in our calculation and also since polarization effects in the computation of core states is neglected. As is seen from Fig. 8, this provides a reasonable interpretation for this region of the spectrum.

FIG. 1. Hartree-Fock energy bands for NaBr are shown. Only Γ, X, and L were actually computed and the resultant structure is based upon a prior similar calculation for NaCl.

FIG. 3. Energy bands with correlation are shown for NaBr. Only the points Γ, X, and L were actually computed and the structure shown is based upon a previous similar calculation for NaCl.

TABLE IV. The energy bands for NaBr and NaCl are shown. In column I, the irreducible representation is given; in II, the correlated results for NaBr using the Fry dielectric function are given; in II, the results for NaBr using a modified Slater exchange are given (Ref. 20). In columns IV and V, results for NaCl are given. Those in IV are obtained using the Fry dielectric function and those in V using a Fowler dielectric function and are from Ref. 5. Results in eV.

I	II	III	IV	V
Outer occupied s band				
Γ_1	-24.17	$\bullet\bullet\circ$	-26.25	-27.94
X_1	-23.38	$\bullet\bullet\bullet$	-25.45	-26.90
L_1	-23.58	$\bullet\bullet\circ$	-25.65	-27.58
Outer occupied p band				
Γ_{15}	-8.66	-10.01	-9.32	-9.94
$X_{4'}$	-12.02	-11.48	-12.82	-13.78
$X_{5'}$	-9.88	-10.52	-10.57	-11.23
$L_{2'}$	-12.42	-11.70	-13.30	-14.32
$L_{3'}$	-9.14	-10.30	-9.85	-10.50
Conduction bands				
Γ_1	-0.96	-3.72	-0.71	0.02
Γ_1	16.35	15.63	19.63	20.66
Γ_{15}	10.27	8.69	12.64	13.59
Γ_{15}	22.54	17.00	24.28	25.34
$\Gamma_{25'}$	5.15	2.00	6.69	7.62
Γ_{12}	7.34	4.15	9.17	10.04
$\Gamma_{2'}$	7.28	3.66	8.85	9.89
X_1	0.89	-0.55	2.14	2.91
X_1	12.09	7.75	13.41	14.37
X_1	20.62	17.81	23.59	24.63
$X_{4'}$	6.16	1.58	6.46	7.39
$X_{4'}$	17.83	15.50	20.96	21.97
$X_{5'}$	9.08	5.71	10.37	11.32
$X_{5'}$	18.63	15.92	22.03	23.08
X_3	1.13	-1.37	2.12	3.01
X_3	18.95	15.22	21.63	22.79
X_2	9.95	6.11	11.99	12.97
X_5	13.27	8.17	15.56	16.63
L_1	0.69	-2.46	1.42	2.21
L_1	12.19	7.29	13.90	14.86
L_1	18.72	13.28	21.14	22.23
$L_{2'}$	5.59	1.40	5.90	6.81
$L_{2'}$	7.78	6.29	9.75	10.80
$L_{2'}$	19.45	15.74	22.57	23.69
$L_{3'}$	10.59	7.36	12.24	13.33
$L_{3'}$	17.71	15.33	19.92	21.02
L_3	3.57	1.72	$\bullet\bullet\bullet$	6.84
L_3	8.62	6.78	$\bullet\bullet\bullet$	13.74
L_3	18.17	17.53	$\bullet\bullet\bullet$	24.17

It is not necessary to invoke excitons to explain this soft-x-ray structure. This is in good agreement with our previous work.[5,27,28]

Finally we turn to the x-ray emission data of O'Brian and Skinner.[25] This data yields some quantitative information on the widths of the outer valence bands for a number of alkali halides. The emission data generally consist of a multipeaked
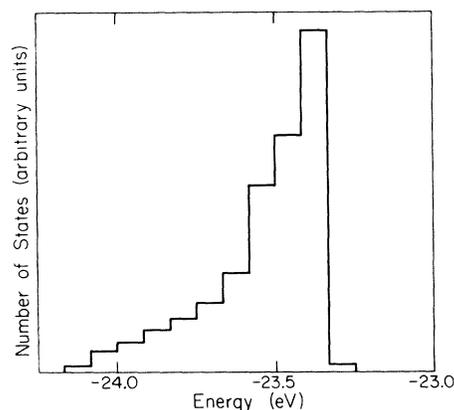
FIG. 4. Density of states for the NaBr $4s$ valence band is given.

spectrum. It is not always possible to unambiguously assign a bandwidth to such bands. Therefore one obtains several measures of the bandwidth. These are the width at half the height of the principal emission peak, a width of the total structure observed, and possibly a width obtained by omitting possible satellite bands from the total width. In Table V we give the values obtained by O'Brian and Skinner for several insulators including NaBr. We see that the experimental values for the width of the $4p$ band range from 4.3 to 6.5 eV. Thus these calculations agree well with the results of O'Brian and Skinner. It is also seen that the general trend in these materials is to quite broad valence bands. This is in contrast to the calculated results for these substances using approximate potentials where band widths of 0.5–1.5 eV are obtained.[1]

Finally, we have computed by numerical differentiation the effective mass for the lowest Γ_1
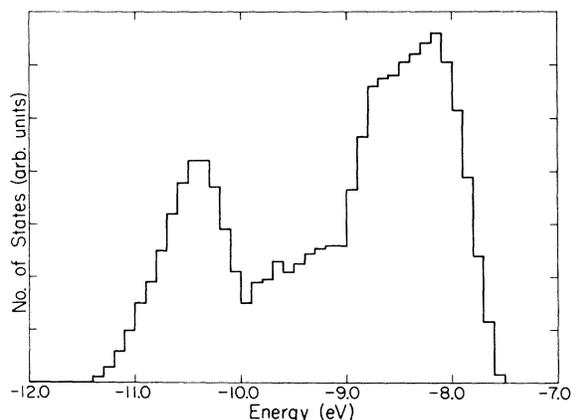
FIG. 5. Density of states for the NaBr $4p$ valence band is given. Spin-orbit effects have been ignored here.
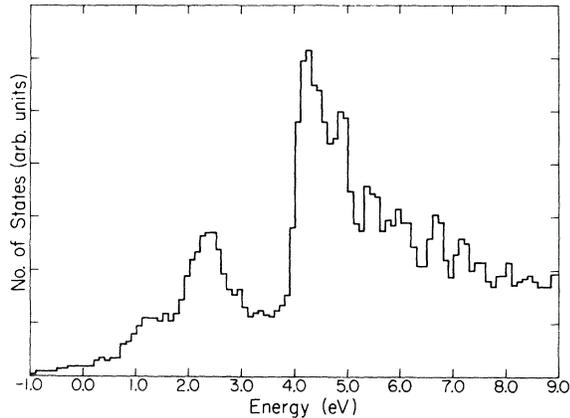
FIG. 6. Density of states for the NaBr conduction bands are shown. All spin-orbit effects have been ignored here.

conduction state and find it to be 0.3 electron masses. The mass of a hole at Γ_{15} along Δ_5 is found to be 0.74 electron masses.

We note that the valence bands are severely narrowed when we correlate. This is contrary to the simple static model of Fowler[3] which indicates a rigid shift of these bands only. However the model used by Fowler assumes the valence electron to be a point charge situated on a halogen nuclear site. The model we employ is rather more general than that of Fowler and takes into account the band nature of the valence electron. Our conduction bands shift rigidly when correlated however and in this case we find no differences with the simple Fowler correlation model. We not do fully understand why the conduction bands undergo a rigid shift.

FIG. 8. Joint density of states for absorption from the Na^+L_1 and $Br^-M_{4,5}$ edges to the conduction band is shown. Experimental values for the spin-orbit splitting of the $M_{4,5}$ edge is used as is the experimental splitting of the L_1 to M_4 edge since these quantities were not accurately computed. Comparison is made to the experimental optical density for these transitions of Ref. 24.

IV. CONCLUSIONS

An *ab initio* calculation of the energy bands and optical properties of NaBr has been performed. The results obtained from such a calculation are seen to be in agreement with experiment in both the near and far ultraviolet and consistent with the results of x-ray emission spectroscopy. Correlation effects have been included and are quite important.

It is believed that calculations of this type, if extended to covalent insulators, semiconductors and metals, would be quite useful provided that the

FIG. 7. Imaginary part of the dielectric response function ϵ_2 is given for NaBr. Comparison is made to the experimental optical density of Ref. 23. The theoretical band gap has been corrected for spin-orbit coupling although the actual splittings are ignored (Ref. 21).

TABLE V. Experimental estimates of the widths of several alkali halide valence bands are given. W is the width at half-height of the principal emission band for x-ray emission from these substances, E_{max} is the maximum width of the emission structure, and E_{min} is an alternate width of the emission line after possible satellites are removed. The data is from Ref. 25. Results are in eV.

Substance	Band	W	E_{max}	E_{min}
LiF	F^-2p	2.7	18	9
NaF	F^-2p	2.0	16	8
KF	F^-2p	1.7	15	7.5
LiBr	Br^-4p	1.2	> 7	•••
NaBr	Br^-4p	0.75	6.5	4.3
KBr	Br^-4p	0.55	6.1	4.1
RbBr	Br^-4p	0.45	5.6	3.8
CsI	I^-5p	0.7	6.5	3.7
LiCl	Cl^-3s	1.3	•••	•••
KCl	Cl^-3s	0.65	•••	•••
RbCl	Cl^-3s	0.65	•••	•••
CsCl	Cl^-3s	0.75	•••	•••

assumptions of nonoverlapping core states can be eliminated. In particular, better understanding of the correlation effects could be obtained here. It is also believed some effort should be extended in improving the local-orbitals methods, either to minimize overlap of these functions or to include higher-order overlap terms in obtaining the local orbitals.

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