carried out.

Figures 1 and 2 show that there is reasonably satisfactory agreement between theoretical and experimental data, except for the longitudinal branches in the $[00\zeta]$ and $[\zeta\zeta\zeta]$ directions near the zone boundary. The deviations are attributable to the assumption of short-range interionic interaction in the secular equation.

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Energy Bands for KCl[†]

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Two *ab initio* calculations for KCl are reported. The first is a self-consistent Hartree-Fock calculation (accurate to first order in interatomic overlap) and the second includes correlation effects due to electron-electron interaction. The results are in excellent agreement with previous *ab initio* calculations and with experiment.

In the last two years a great deal of effort has been made by the authors, individually[1,2] and jointly,[3] in calculating the energy bands of insulating crystals from a first-principles point of view. These calculations have proved that (a) A Hartree-Fock calculation gives results which do not compare well with experiments; (b) correlation effects are very important and, after they are properly included, the agreement with experiment is very good. In this short paper we show that this is also true in the case of KCl.

Since the various techniques used in the present calculations are extensively described elsewhere[1-3] we refer the reader to those papers for details.

We proceed as follows: (a) We first perform a Hartree-Fock calculation using local orbitals[4] for the K^+ and Cl^- ion accurate to first order in interatomic overlap[5]; (b) we then include electronic correlation effects using the same procedure as in our previous works.[1,3] The method used for calculations is the mixed-basis (MB) method.[6] All the calculations were performed on the IBM 360-75 computer at the University of Illinois. The local orbital core states included in the MB method were the $1s$, $2s$, $2p$ states for both the Cl^- and K^+ states. The dielectric function $\epsilon(q)$ needed in treating correlation effects is that given in Ref. 7. The results at Γ, X, L, and Δ[8] are shown in Table I. From the Hartree-Fock results we obtain a band gap $(\Gamma_{15} \rightarrow \Gamma_1)$ of 11.76 eV; the electronic affinity is -1.69 eV; the photoemission threshold is 10.07 eV; the $3p(Cl^-)$ valence bandwidth is 3.63 eV and the $3s$ (Cl^-) band is 0.50 eV wide. When correlation effects are included, we get the values

TABLE I. Energy bands for KCl at the points Γ, X, L, and $\Delta \equiv \{(2\pi/a)(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})\}$ of the first Brillouin zone. The notation is that of Ref. 8. Results are in eV.

Point	Irr. rep.	Hartree–Fock			With correlation		
	Γ_1	−29.04	1.69	21.95	−26.67	−0.30	19.59
	Γ_{15}	−10.07	17.82		−9.00	15.50	
Γ	Γ_{25}'	7.44			5.25		
	Γ_{12}	8.81			6.65		
	Γ_2'	9.59			7.24		
	X_1	−28.54	5.94	10.87	−26.41	3.85	8.65
	X_4'	−11.52	7.68		−9.98	5.42	19.77
X	X_5'	−10.53	12.76		−9.32	10.45	
	X_3	3.64	19.74		1.57	17.38	
	X_2	10.76			8.59		
	X_5	14.34			12.06		
	L_1	−29.04	4.68	13.71	−26.71	2.63	11.42
	L_2'	−13.69	6.52	11.71	−11.58	4.30	9.43
L	L_3'	−10.50	14.52		−9.79	8.23	12.28
	L_3	9.61	14.35		7.45	12.17	
		−29.02	−11.99	3.74	−26.67	−10.44	1.66
	Δ_1			9.62			7.46
Δ	Δ_5	−10.25	8.68	15.07	−9.15	6.49	12.81
	Δ_2	10.32			8.13		
	Δ_2'	4.71	13.47		2.60	11.12	

8.70, 0.30, 9.01, 2.58, and 0.30 eV for the same quantities, respectively. The experimental value of the KCl band gap is[9] 8.69 ±0.07 eV, in excellent agreement with our predicted value. We also find a relative conduction-band minimum at X_3, which is in good agreement with current exciton theories for KCl.

It is interesting to compare this result with a previous approximate Hartree-Fock effort for KCl by Howland.[10] Howland computed the valence bands by linear-combination-of-atomic-orbitals (LCAO) tight-binding theory. We find excellent agreement in absolute terms for our points L_2' and L_3' in the Cl⁻ $3p$ band with the nonhybridized L_2' and L_3' Cl⁻ $3p$ band of Howland, suggesting that hybridization

between the $3p$ Cl⁻ and $3s$ K⁺ bands for L_2' might have been overestimated by Howland. We believe our valence bandwidths are experimentally justified in that Krolikowski and Spicer[11] find the outer p band in KI to be about 3.25 eV wide, and in recent work Thomas[12] has found our previous results for NaCl to be in good agreement with his electron-spectroscopy-for-chemical-analysis (ESCA) data. The KI band should be somewhat broader than the KCl band owing to spin-orbit effects. If these are neglected, past experience has shown that the outer bands of the potassium halides have similar widths.

In conclusion, the present work confirms the validity of *ab initio* calculations when effects of electronic correlation are properly taken into account.

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