of the iterative calculation.

[14] Compare, for instance, the existence of self-consistent solutions of Hartree-Fock equations that do not correspond to any physically significant solution of the exact Schrödinger equation. S. I. Pekar, Zh. Eksperim. i Teor. Fiz. 18, 525 (1948).

[15] For this to be true, it is of course essential to calculate *F* using equations valid for any distribution [such as Eq. (14) of Ref. 11] , rather than equations valid only for self-consistent distributions [such as Eq. (13) of Ref. 11] .

[16] Corresponding data for other temperatures are available on request to the author.

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Self-Consistent Local Orbitals for Lithium Halide Crystals[†]

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Using the Adams-Gilbert local-orbital theory, it has been possible to obtain approximate self-consistent local orbitals for the fcc lithium halide crystals. In this formalism, terms to first order in interatomic overlap are included. Nearest neighbors are considered exactly in this formalism, and more distant neighbors in a point-ion model. The method of Roothaan is used to obtain the solutions. All relativistic effects are neglected in this calculation

I. INTRODUCTION

Because of the introduction of localized-orbital theories by Adams,[1] Gilbert,[2] and Anderson,[3] self-consistent Hartree-Fock solutions for ground-state wave functions of polyatomic systems have become possible. The author has taken the theory of Gilbert, expanded the environment in powers of interatomic overlap, and retained terms to first order in interatomic overlap.[4] This seems justified for most ionic or insulating solids, since the overlaps are typically of the order 0.1 or less.[5] In the original paper by the author, self-consistent orbitals for the LiH crystal were reported. In the present paper orbitals are obtained for LiF, LiCl, LiBr, and LiI using the analytic Hartree-Fock technique of Roothann[6] in a somewhat modified form.

These localized orbitals, which the author obtains for the ground state of the lithium halide crystal, should prove very useful for band-structure calculations. The preliminary results for LiCl crystal have been used with great success by the author in computing a band structure.[7] The author

TABLE I. The values of $A_{\ell j}$ and $Z_{\ell j}$ are given for the *s* levels of the Li^+, F^-, Cl^-, Br^-, and I^- ions.

	Li^+		F^-		Cl^-		Br^-		I^-	
J	A_{oj}	Z_{oj}	A_{oj}	Z_{oj}	A_{oj}	Z_{oj}	A_{oj}	Z_{oj}	A_{oj}	Z_{oj}
1	0	2.69	0	10.040	0	18.9832	0	37.3527	0	56.5239
2	0	4.00	0	8.3691	0	14.7941	1	33.1430	1	26.1681
3	0	2.00	0	5.5505	1	14.7181	2	17.2808	2	24.7445
4			1	4.9546	1	9.6220	2	16.3407	2	12.7500
5			1	3.3675	1	6.7665	2	8.4198	3	10.0218
6			1	1.9804	2	6.2190	2	6.6235	3	5.2591
7			1	1.1869	2	3.2450	3	6.6182	3	3.3269
8					2	2.1679	3	3.4730	4	3.0142
9					2	1.3550	3	2.1970	4	2.2501
10							3	1.4859	4	1.4859
11									4	1.1889

TABLE II. The values of $A_{\ell j}$ and $Z_{\ell j}$ are given for the p levels of F^-, Cl^-, Br^-, and I^-.

	F^-		Cl^-		Br^-		I^-	
J	A_{1j}	Z_{1j}	A_{1j}	Z_{1j}	A_{1j}	Z_{1j}	A_{1j}	Z_{1j}
1	0	7.1171	0	13.7900	0	23.3102	0	26.0738
2	0	3.5586	0	8.8355	0	15.6532	1	19.6079
3	0	2.4367	0	5.3987	1	14.8256	1	9.2975
4	0	1.0219	1	4.0186	1	9.5909	2	8.0386
5	0	0.5003	1	2.4367	1	6.1399	2	4.2627
6			1	1.6382	2	5.3085	2	2.4794
7			1	0.8219	2	2.8150	3	2.4546
8			1	0.4120	2	1.6374	3	1.6713
9					2	1.1277	3	1.0150
10							3	0.5075

has also completed a detailed study of the band structure of LiCl using the final LiCl local orbitals.[8]

These local orbitals should also prove useful for computing lattice constants, binding energies, and the elastic properties of the pure solids. In addition, these orbitals should provide an excellent starting point for studies of color centers in these solids.

Computer codes were developed, for this calculation by the author, for the IBM 360-75 computer. Sufficient accuracy has been maintained in the codes and in self-consistency requirements so that the one-electron energy parameters appear to be accurate to about ±2 in the fourth significant figure in virtually all cases. In Sec. II the local-orbital method is discussed as are the techniques of solution. In Sec. III numerical results are presented for the Li⁺, F⁻, Cl⁻, Br⁻, and I⁻ ions as well as for the crystals. The free-ion results are compared to the other calculations on these systems and conclusions are drawn from this comparison.

II. LOCAL-ORBITAL TECHNIQUES

A. Local-Orbital Equation

In the case of solids with closed-shell ground states one may write the Hartree-Fock operation for the solid in the form

$$F_i = -\nabla_i^2 - 2\sum_A \frac{Z_A}{|\vec{R}_{Ai}|} + 4\int |\vec{r}_i - \vec{r}_j|^{-1}\rho(\vec{r}_j, \vec{r}_j)d\vec{r}_j - \frac{2\rho(\vec{r}_i, \vec{r}_j)}{|\vec{r}_i - \vec{r}_j| I(i,j)} \quad . \tag{1}$$

The operator $I(i,j)$ interchanges coordinates i and j. In Eq. (1), the Fock operator for the ith electron is in Ry, Z_A is the charge on the Ath nucleus, $\vec{R}_{Ai}$ is the radial vector from the Ath nucleus to the ith electron. The summation is over all nuclei in the polyatomic system. $\rho(\vec{r}, \vec{r}')$ is the spin-independent part of the kernel of the density operator and is seen to be

TABLE III. The values of $A_{\ell j}$ and $Z_{\ell j}$ are given for the d levels of Br^- and I^-.

	Br^-		I^-	
j	A_{2j}	Z_{2j}	A_{2j}	Z_{2j}
1	0	16.0578	0	19.7943
2	0	10.0855	0	11.0375
3	0	7.2889	0	7.1802
4	0	4.7416	1	6.9183
5	0	2.9679	1	4.4943
6			1	3.0332
7			1	2.2939

$$\rho(\vec{r}, \vec{r}') = \sum_{Ai, Bj} |Ai(\vec{r})\rangle S^{-1}_{Ai,Bj}\langle Bj(\vec{r}')| \quad . \tag{2}$$

The quantity $S^{-1}_{Ai,Bj}$ is the Ai, Bjth element of the inverse of the overlap matrix for the solid and may be evaluated using the familiar Löwdin expansion:

$$S^{-1}_{Ai,Bj} = \delta_{Ai,Bj} - (S_{Ai,Bj} - \delta_{Ai,Bj}) + \sum_{CK}(1 - \delta_{CA})(1 - \delta_{CB})S_{Ai,CK}S_{CK,Bj} + \cdots \quad , \tag{3}$$

with

$$S_{Ai,Bj} = \langle Ai | Bj \rangle \quad .$$

In the above we allow for the case in which the Hartree-Fock orbitals are not orthogonal. As has been demonstrated by Gilbert,[2] if one removes the restriction on orthogonality in the Hartree-Fock case, one is able to add in an additional constraint such that the Hartree-Fock equation is of the form

$$(F_i - \rho U_A' \rho)\phi_{Ai} = \epsilon_{Ai}\phi_{Ai} \quad . \tag{4}$$

In Eq. (4) U_A' is an arbitrary function, chosen to maintain localization. It is convenient to break the Fock operator into two parts such that

$$F_i = F_A + U_A \quad , \tag{5}$$

$$F_A = -\nabla_i^2 - \frac{2Z_A}{|\vec{R}_{Ai}|} + 4\int |\vec{r}_i - \vec{r}_j|^{-1}\sum_k |Ak(\vec{r}_j)\rangle^2 d\vec{r}_j - 2\sum_{k,l}\frac{|Ak(\vec{r}_i)\rangle\langle Al(\vec{r}_j)| S^{-1}_{Ak,Al}}{|\vec{r}_i - \vec{r}_j| I(i,j)} \quad . \tag{6}$$

TABLE IV. The lithium orbitals for the free ion and in the crystals. The normalization chosen is such that $\sum_j C_{10j}^2 = 1$.

C_{10j}					
j	Free ion	LiF	LiCl	LiBr	LiI
1	0.587 107	0.532 146	0.565 27	0.563 807	0.576 913
2	0.387 533	0.401 144	0.393 11	0.393 430	0.390 119
3	0.710 720	0.745 590	0.725 21	0.726 178	0.717 620

The expression for U_A is found by subtracting Eq. (6) from Eq. (1).

If one has $U_A = U_A'$ and if one expands the expression for U_A and $\rho U_A \rho$ in powers of the interatomic overlaps and retains terms linear in overlap one finds[4]

$$\left(-\nabla_1^2 - \frac{2Z_A}{|\vec{R}_{A1}|} + 4\sum_j \int \phi_{Aj}^2(\vec{r}_2)|\vec{r}_{12}|^{-1}\,d\vec{r}_2 - \sum_B{}' \frac{2Z_B}{|\vec{R}_{B1}|} + 4\sum_{B,j}{}' \int \phi_{Bj}^2(\vec{r}_2)|\vec{r}_{12}|^{-1}\,d\vec{r}_2 - \epsilon_{Ai}\right)\phi_{Ai}(\vec{r}_1)$$
$$-2\sum_j \phi_{Aj}(\vec{r}_1)\int \phi_{Aj}^*(\vec{r}_2)\phi_{Ai}(\vec{r}_2)|\vec{r}_{12}|^{-1}\,d\vec{r}_2 = \sum_k{}' \phi_{Ak}(\vec{r}_1)\iint\Big[\phi_{Ak}^*(\vec{r}_1)\phi_{Ai}(\vec{r}_1)$$
$$\times\left(-\sum_B{}' \frac{2Z_B}{|\vec{R}_{B1}|} + 4\sum_{Bj}{}'\int \phi_{Bj}^2(\vec{r}_2)|\vec{r}_{12}|^{-1}\right)d\vec{r}_2\; d\vec{r}_1\Big] . \tag{7}$$

It is this equation which we will solve iteratively for the lithium halide crystals. Invoking the lattice symmetry, it is necessary to solve Eq. (7) for both a Li$^+$ and an X^- lattice site.

B. Method of Solution

Equation (7) is to be solved using the analytic expansion techniques of Roothaan.[6] This method has been used previously to obtain solutions for the free Cl$^-$ ion,[9,10] the Br$^-$ ion,[11] and the F$^-$ ion.[9] In this method, one assumes the one-electron solution (dropping the subscript referring to the lattice site) to be of the form

$$\phi_n(\vec{r}) = R_{nl}(r)Y_l^m(\theta,\phi)X(s) . \tag{8}$$

In Eq. (8) the Y_l^m's are the usual spherical harmonics and the X's are the spin functions. Then one assumes

$$rR_{nl}(r) = \sum_j C_{jnl}P_{jl}(r) ,$$
$$P_{jl}(r) = N_{lj}r^{l+1+A_{lj}}\exp(-Z_{lj}r) , \tag{9}$$
$$N_{lj} = [(2Z_{lj})^{2+2A_{lj}+3}/(2l+2A_{lj}+2)!]^{1/2} .$$

The quantities A_{lj} and Z_{lj} are either set by variational techniques or otherwise determined. The C_{jnl} are determined by the variational technique.

In this method of solution the local-orbital equation [Eq. (7)] is used in integral form. If one uses the notation of Hartree,[12] one has for the $1s$ shell in Li$^+$

$$\epsilon_{1s} = K_{1s} + 2F^0(1s,1s) - G^0(1s,1s) + V_{1s} , \tag{10}$$

and for the np shell of Cl$^-$

TABLE V. The fluorine orbitals are given for both the free ion and the LiF crystal. The normalization chosen is $\sum_j C_{nlj}^2 = 1$.

	j	C_{10j}	C_{20j}	C_{21j}
Free ion	1	0.778 122	0.082 182	0.068 222
	2	0.124 024	0.059 816	0.343 162
	3	0.591 516	0.240 537	0.676 917
	4	−0.168 621	0.026 460	0.643 332
	5	0.027 204	−0.787 052	−0.074 111
	6	0.007 684	−0.553 971	
	7	−0.004 222	−0.069100	
Crystal	1	0.778 075	0.081 802	0.066 004
	2	0.123 480	0.059 759	0.342 894
	3	0.591 661	0.242 616	0.647 003
	4	−0.168 725	0.021 947	0.665 854
	5	0.027 306	−0.780 186	−0.126 857
	6	0.007 639	−0.563 129	
	7	−0.004 208	−0.067 734	

TABLE VI. The chlorine ion orbitals are given in free space and in the LiCl crystal. The normalization chosen is $\sum_j C_{nlj}^2 = 1$.

	j	C_{10j}	C_{20j}	C_{30j}	C_{21j}	C_{31j}
Free ion	1	0.838 748	0.274 404	0.085 654	0.035 792	0.016 475
	2	0.016 207	0.002 254	−0.000 169	0.341 779	0.054640
	3	0.322 883	0.282 570	0.097 782	0.938 861	0.338 205
	4	−0.313 642	−0.250 04	−0.120 651	−0.001 885	−0.145 742
	5	0.282 767	−0.796 700	−0.205 331	0.019 121	−0.544 533
	6	−0.112 708	−0.384 156	−0.276 684	−0.008 634	−0.694 377
	7	0.026 265	−0.002 011	0.508 816	0.001 600	−0.287 094
	8	−0.015 685	−0.006 020	0.740 437		
	9	0.004 186	0.001 676	0.206 614		
Crystal	1	0.838 394	0.274 574	0.085 598	0.035 844	0.017 550
	2	0.014 900	0.001 976	−0.000 147	0.341 382	0.047 003
	3	0.232 146	0.282 659	0.097 129	0.938 959	0.342 845
	4	−0.313 982	−0.249 998	−0.116 000	−0.002 573	−0.163 889
	5	0.283 122	−0.796 624	−0.211 443	0.020 415	−0.488 331
	6	−0.112 875	−0.384 132	−0.271 583	−0.009 943	−0.730 251
	7	0.026 320	−0.002 035	0.502 281	0.002 570	−0.276 374
	8	−0.015 722	−0.006 065	0.744 897	0.000 757	0.070 455
	9	0.004 197	0.001 693	0.209 809		

$$\epsilon_{np} = K_{np} + 2F^0(np, 1s) + 2F^0(np, 2s) + 2F^0(np, 3s) + 6F^0(np, 2p) + 6F^0(np, 3p) - \tfrac{1}{3}G^1(np, 1s)$$
$$- \tfrac{1}{3}G^1(np, 2s) - \tfrac{1}{3}G^1(np, 3s) - G^0(np, 2p) - G^0(np, 3p) - 0.4G^2(np, 2p) - 0.4G^2(np, 3p) + V_{np} \quad . \qquad (11)$$

TABLE VII. The bromine ion orbitals are given in free space and in the LiBr crystal. The normalization chosen is $\sum_j C_{nlj}^2 = 1$.

	j	C_{10j}	C_{20j}	C_{30j}	C_{40j}	C_{21j}	C_{31j}	C_{41j}	C_{32j}
Free ion	1	0.988 316	0.318 424	0.129 509	0.041 520	0.155 636	0.055 366	0.013738	0.051 836
	2	0.144 863	0.192 586	0.076 024	0.023 708	0.963 736	0.315 855	0.096 578	0.308 338
	3	−0.015 697	−0.729 571	−0.292 020	−0.091 232	0.211 547	0.181 161	0.047 802	0.542 486
	4	0.012 837	−0.554 566	−0.430 410	−0.153 770	0.046 484	−0.345 795	−0.094 146	0.766 566
	5	−0.023 362	−0.110 747	−0.462 644	0.204 422	−0.008 121	−0.858 684	−0.323 529	0.142 568
	6	0.023 799	0.092 369	0.663 131	0.215 529	0.003 206	−0.083 781	0.041 937	
	7	−0.014 589	−0.030 025	0.228 283	0.127 586	−0.000 493	−0.018 095	0.725 964	
	8	0.001 036	−0.000 439	0.209 722	−0.680 340	0.000 260	0.008 697	0.526 995	
	9	−0.000 573	0.005 83	−0.012 192	−0.615 244	−0.000 109	−0.003 821	0.261 093	
	0	0.000 200	−0.000 239	0.004 455	−0.140 848				
Crystal	1	0.988 347	0.318 304	0.129 256	0.041 466	0.155 643	0.055 239	0.011 531	0.051 846
	2	0.144 849	0.192 578	0.075 962	0.023 818	0.963 733	0.316 026	0.100 718	0.308 304
	3	−0.015 646	−0.729 481	−0.291 735	−0.091 608	0.211 546	0.180 742	0.039 172	0.542 661
	4	0.012 764	−0.554 119	−0.429 080	−0.152 570	0.046 515	−0.345 198	−0.078 004	0.766 409
	5	−0.023 037	−0.111 981	0.457 433	0.191 645	−0.008 166	−0.858 995	−0.343 122	0.142 816
	6	0.032 296	0.094 364	0.661 74	0.237 821	0.003 237	−0.083 368	0.063 582	
	7	−0.014 347	−0.031 014	0.223 973	0.114 294	−0.000 505	−0.018 240	0.689 343	
	8	0.001 012	−0.000 326	0.030 226	−0.674 324	0.000 269	0.008 768	0.587 966	
	9	−0.000 558	0.000 511	−0.012 527	−0.620 659	−0.000 118	−0.003 840	0.198 569	
	0	0.000 194	−0.000 213	0.004 587	−0.140 578				

TABLE VIII. The iodine ion orbitals are given in free space and in the LiI crystal. $\sum_j C_{nej}^2 = 1$.

	j	C_{10j}	C_{20j}	C_{30j}	C_{40j}	C_{50j}	C_{21j}	C_{31j}	C_{41j}	C_{51j}	C_{32j}	C_{42j}
Free space	1	0.908 751	0.256 507	0.095 829	0.025 364	0.013 466	0.976 380	0.210 702	0.107 499	0.050 609	0.196 383	0.098 725
	2	0.218 448	−0.232 535	−0.076 394	−0.015 542	−0.007 873	0.200 409	−0.018 519	0.011 767	0.007 853	0.912 755	0.485 891
	3	−0.205 193	−0.703 736	−0.469 050	−0.157 342	−0.086 688	−0.043 688	−0.723 071	−0.599 550	−0.305 746	−0.259 236	−0.182 102
	4	0.109 253	0.196 784	0.848 575	0.338 725	0.191 636	0.033 438	0.341 377	0.658 317	0.366 594	0.229 501	−0.407 046
	5	−0.085 398	−0.171 069	0.044 201	−0.083 019	−0.052 020	−0.022 569	−0.211 386	0.364 924	0.243 941	−0.077 976	−0.739 719
	6	0.091 798	0.197 648	0.602 650	−0.602 483	−0.476 065	0.040 734	0.386 915	−0.200 261	−0.700 172	0.045 486	−0.080 518
	7	−0.151 448	−0.332 446	−0.065 349	0.465 561	0.633 786	−0.035 343	−0.338 382	0.147 047	0.027 082	−0.017 004	−0.040 596
	8	0.156 525	0.347 255	0.130 496	−0.449 535	−0.210 177	0.008 267	0.808 771	−0.203 278	−0.450 019		
	9	−0.085 195	−0.191 027	−0.075 110	0.235 682	0.522 269	−0.002 157	0.021 385	0.004 889	−0.128 305		
	10	0.041 026	0.092 834	0.037 911	−0.114 011	−0.052 250	0.000 458	0.004 578	−0.000 928	−0.004 053		
	11	−0.017 712	−0.040 211	−0.016 649	0.049 655	0.069 422						
Crystal	1	0.908 752	0.256 505	0.095 823	0.025 367	0.013 703	0.976 382	0.210 746	0.107 519	0.048 190	0.196 937	0.098 880
	2	0.218 451	−0.232 528	−0.076 387	−0.015 545	−0.008 002	0.200 405	−0.018 532	0.011 769	0.007 241	0.913 723	0.485 504
	3	−0.205 195	−0.703 738	−0.469 029	−0.157 345	−0.088 250	−0.043 684	−0.723 186	−0.599 672	−0.289 873	−0.257 433	−0.180 381
	4	0.109 252	0.196 789	0.848 546	0.338 752	0.195 118	0.033 434	0.341 406	0.685 463	0.346 285	0.227 737	−0.409 255
	5	−0.085 398	−0.171 073	0.044 158	−0.083 010	−0.053 235	−0.022 565	−0.211 356	0.346 893	0.242 377	−0.076 910	−0.739 059
	6	0.091 796	0.197 654	0.065 702	−0.602 602	−0.482 551	0.040 726	0.386801	−0.199 844	−0.707 385	0.044 681	−0.081 473
	7	−0.151 445	−0.332451	−0.119 456	0.465 565	0.638 540	−0.035 335	−0.338 247	0.146 564	0.081 461	−0.016 668	−0.040 443
	8	0.156 521	0.347 255	0.130 618	−0.449 496	−0.201 321	0.008 265	0.080 701	−0.203 059	−0.466 758		
	9	−0.085 192	−0.191 020	−0.075 176	0.235 452	0.515 780	−0.002 156	−0.021 346	0.004 794	−0.099 269		
	10	0.041 024	0.092 821	0.037 929	−0.113 618	−0.029 810	0.004 57	0.004 570	−0.000 909	0.013 855		
	11	−0.017 711	−0.040 202	−0.016 649	0.049 372	0.054 941						

In this notation the term V_{nx} is to specify the term

$$V_{nx} = \langle nx | U_A | nx \rangle \ ,$$

$$U_A = -\sum_B{}' \frac{2Z_B}{|\vec{R}_{B1}|} + 4 \sum_{B,j}{}' \int \phi_{Bj}^2(\vec{r}_2) |\vec{r}_{12}|^{-1} \, d\vec{r}_2 \ . \qquad (12)$$

III. RESULTS

Although the one-center integrals which occur in this theory could be evaluated analytically, the author has evaluated these integrals by numerical techniques using previously developed and tested computer codes. The multicenter integrals would need to be computed numerically in any event. Sufficient accuracy was maintained so that the one-electron eigenvalues agreed with previously obtained values of 1 part in 1000 or better. In all cases the final one-electron orbitals agreed with previously obtained results within the self-consistency tolerance of 1 part in 1000 established for this calculation. This self-consistency requirement on the wave functions produced one-electron eigenvalues which were consistent to at least 1 part in 10 000. In testing these results one curious fact emerged: In the case of Cl^- using the values of Z's and A's given by Watson and Freeman,[10] the resulting C's for the s levels obtained by the

TABLE IX. The free-ion one-electron energy parameters are given for the Li^+, F^-, Cl^-, Br^-, and I^- ions. The parameters for Cl^- according to Refs. 9, 10, and 13 are also given. Ry are used.

Parameter	Li^+	F^-	Br^-	I^-	Cl^-	Cl^- (Ref. 9)	Cl^- (Ref. 10)	Cl^- (Ref. 13)
ϵ_{1s}	−5.597	−51.73	−980.1	−2354	−209.2	−209.0	−209.0	−209.0
ϵ_{2s}		−2.159	−129.8	−359.1	−20.48	−20.46	−20.46	−20.46
ϵ_{3s}			−19.07	−75.06	−1.473	−1.466	−1.471	−1.454
ϵ_{4s}			−1.370	−13.84				
ϵ_{5s}				−1.110				
ϵ_{2p}		−0.3712	−116.4	−330.7	−15.39	−15.39	−15.40	−15.39
ϵ_{3p}			−14.27	−65.42	−0.3035	−0.3004	−0.3036	−0.2970
ϵ_{4p}			−0.2767	−10.35				
ϵ_{5p}				−0.2619				
ϵ_{3d}			−5.761	−48.29				
ϵ_{4d}				−4.249				

TABLE X. The one-electron energy parameters are given for the LiF, LiBr, and LiI crystals. Ry are used and the definition of the parameters is given in the text.

Crystal parameter	LiF	LiCl	LiBr	LiI
Li^+ ϵ_{1s1s}	-4.762	-4.910	-4.957	-5.079
X^- ϵ_{1s1s}	-52.62	-210.0	-980.8	$-2354.$
ϵ_{2s2s}	-3.059	-21.16	-130.4	-539.6
ϵ_{3s3s}		-2.162	-19.72	-75.59
ϵ_{4s4s}			-2.024	-14.36
ϵ_{4s5s}				-1.636
ϵ_{1s2s}	36×10^{-7}	11×10^{-7}	6×10^{-7}	24×10^{-7}
ϵ_{1s3s}		18×10^{-7}	1×10^{-7}	10×10^{-7}
ϵ_{1s4s}			0.0	-43×10^{-7}
ϵ_{1s5s}				-92×10^{-7}
ϵ_{2s3s}		17×10^{-7}	5×10^{-7}	31×10^{-7}
ϵ_{2s4s}			2×10^{-7}	-120×10^{-7}
ϵ_{2s5s}				-254×10^{-7}
ϵ_{3s4s}			-5×10^{-7}	-55×10^{-7}
ϵ_{3s5s}				-127×10^{-7}
ϵ_{4s5s}				623×10^{-7}
ϵ_{2p2p}	-1.274	-16.07	-117.1	-340.2
ϵ_{3p3p}		-0.9965	-14.92	-65.96
ϵ_{4p4p}			-0.9325	-10.87
ϵ_{5p5p}				-0.7896
ϵ_{2p3p}		-155×10^{-7}	4×10^{-7}	15×10^{-7}
ϵ_{2p4p}			-4×10^{-7}	-1×10^{-7}
ϵ_{2p5p}				69×10^{-7}
ϵ_{3p4p}			-201×10^{-7}	-37×10^{-7}
ϵ_{3p5p}				1608×10^{-7}
ϵ_{4p5p}				268×10^{-7}
ϵ_{3d3d}			-6.408	-48.81
ϵ_{4d4d}				-4.769
ϵ_{3d4d}				4×10^{-7}

author were in poor agreement with those of Watson and Freeman, even though the resulting orbitals and one-electron eigenvalues were in good agreement. Since the physical quantities were in good agreement, no serious effort was expended in understanding the disagreement of the C's. It is obvious that this difference is due to computer coding differences and/or different computer operating systems. In fact, using our current codes, the values of the C's are somewhat dependent upon the compiler used.

In the case of Cl^- and Br^- the values of the A's and Z's given by Watson and Freeman were used.[10,11] In the case of Li^+, F^-, and I^- the author determined the A's and Z's by a combination of scaling the Z's from one system to another and the variational theorem. No great effort was expended in minimizing the total system energy. It was considered sufficient to obtain good values for the one-electron eigenvalues and eigenvectors. Calculations were perfomed for the free ion as well as for the solids. A common set of A's and Z's was used for solid-state and free-ionic calculations. The values of the A's and Z's used are given in Tables I–III.

In the solid-state calculation, the detailed part of U_A was only constructed for the nearest neighbors; however, the point-ion part of the potential was considered exactly out to about four lattice constants. This degree of accuracy seems to be consistent with the use of an expansion linear in interatomic overlap.

In Table IV the values of the C's for the Li^+ ion in free space and the several crystals are given. In Tables V–VIII the C's for the free ion and the Li X crystals are given for the F^-, Cl^-, Br^-, and I^- ions. The normalization chosen is that

$$\sum_{j=1}^{m} C_{nlj}^2 = 1 \quad . \qquad (13)$$

In Table IX the one-electron eigenvalues are given for the various free ions. In the case of Cl^- we also present the free-ion one-electron eigenvalues given by other authors.[10,11,13] It is seen that a good degree of agreement is achieved among the several calculations.

Finally, in Table X the one-electron energy parameters are presented for the several crystals. These are not the eigenvalues of Eq. (7), the local-orbital equation, but the expectation values of the Fock operator, Eq. (1), for the solutions to Eq. (7) accurate to first order in interatomic overlap; thus one defines

$$\epsilon_{nl,n'l'} = \delta_{ll'}\langle nl|F|n'l'\rangle \quad . \qquad (14)$$

It is noted that except for the inner orbitals these one-electron expectation values have no direct physical meaning since the translational symmetry of the lattice is neglected here, and hence all band effects are neglected. Thus if one requires energy bands, it is necessary to use these wave functions in a proper energy-band calculation. Such a calculation has been performed with considerable success by the author for LiCl[7,8] and a calculation is currently under way for LiBr.[14]

In conclusion, it has been possible to obtain self-consistent solutions to the local-orbital Hartree-Fock equations for the lithium halides. These solutions are useful for energy-band calculations and defect calculations.[15] The amount of computer time required to complete such a calculation varies from about 10 min of IBM 360-75 time for LiF to 3 h for LiI. It is also seen from Tables IV–VIII that the principal effect of the lattice is to cause distortions of the outer-shell orbitals. The inner shells are essentially stable.

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Thermal Expansion and Phonon Frequency Shifts in Nonprimitive Lattices

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Expressions have been derived in the quasiharmonic approximation for the change in normal-mode frequencies associated with thermal expansion in a nonprimitive lattice. The work is formulated in terms of coupling parameters for an undistorted lattice with cubic anharmonicity. Symmetric finite-strain parameters and appropriate internal strains are introduced in such a manner that the formulation exhibits explicitly the invariance of the crystal potential energy and normal-mode frequencies under rigid-body rotations. As a numerical application, the coefficient of linear expansion and the phonon frequency distributions at 300 and 800 °K have been calculated for zirconium hydride with a short-range central-force model including third-nearest-neighbor forces.

I. INTRODUCTION

The temperature dependence of phonon frequencies in a crystal can be conveniently divided into two parts: (1) a quasiharmonic part associated with thermal expansion, which results in a change of interatomic distances and a corresponding change in the harmonic force constants, and (2) a part arising directly from terms in the potential-energy expansion of higher order than quadratic in powers of displacements of the atoms from their mean positions. We shall refer to the latter contribution, which is present even if the crystal is held at constant volume, as a pure anharmonic effect. In this paper we are concerned with the effects of thermal expansion on phonon frequencies. This problem was considered in a plausible but nonrigorous manner by Maradudin and Fein[1] as part of a study of anharmonic effects on neutron scattering by Bravais crystals. Further justification for their result was later provided by Maradudin[2] in a separate study also limited to Bravais crystals, in which explicit expressions for thermal deformations and frequency shifts in terms of force constants were given. Neutron scattering and thermal expansion in more general anharmonic crystals have been studied by Cowley.[3] However, in these treatments the introduction of finite-strain parameters[4] was carried out in an approximate manner and internal strains (relative displacement of sublattices) were not included. It turns out that it is possible to introduce finite-strain parameters rigorously, so that at all stages of the calculation the phonon frequencies are manifestly invariant under rigid-body rotation of the crystal (in the absence of external forces or fields). Constructing the formalism in this manner is not only desirable from the standpoint of elegance but is also essential in the event that an extension to higher orders of approximation becomes necessary – for example, over wide temperature ranges for a strongly anharmonic crystal.

It is the purpose of the present paper to study thermal expansion and related phonon frequency shifts in nonprimitive lattices, employing a rigorous introduction of finite-strain parameters and appropriate internal strains. The calculation fol-