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Electronic charge distribution and the degree of ionicity in crystalline NaF, NaCl, SrF_2, and $SrCl_2$ as found by the local-orbitals Hartree-Fock method*

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We present the local orbitals for NaF, SrF_2, and $SrCl_2$. We use these results, along with previously reported local orbitals for NaCl, to calculate the electron density. We find that NaF has 65% more electron density at the density minimum located along the nearest-neighbor axis than NaCl. In addition, SrF_2 has 79% more density at the minimum than $SrCl_2$. The latter result is in agreement with recently reported experimental evidence indicating more dynamical charge overlap in SrF_2 than $SrCl_2$. We find the NaCl electron density agrees extremely well with experimental results obtained from x-ray scattering measurements. The implications of the above result are discussed in terms of relative ionicity. Dividing the charge density into ions along the surfaces of density minima (i.e., along the ionic radii) yields a net charge per ion which is inconsistent with the actual Coulomb potential in the solids. The reasons for this are discussed.

I. INTRODUCTION

Experimental evidence has recently come to our attention which suggests that the degree of ionic charge overlap of SrF_2 and $SrCl_2$ may be opposite to that which one might naively assume based on ionicity theories, as those of Pauling[1] and Phillips.[2] Indeed, the experimental work of Man and Bron[3] (see previous article) definitely indicates that there exists more dynamic charge overlap in SrF_2 than in $SrCl_2$. This paper represents an attempt to determine if such results are in disagreement with a static electron density found from a nonparametrized theoretical approach. We find no disagreement.

The local-orbitals method of restricted Hartree-Fock[4] has long been known to provide accurate results for ionic materials.[5] Recently, it has also been successfully used to treat a metallic solid[6] (Ca) and a transition-metal carbide[7] (TiC). In all cases the accuracy achieved has been quantitatively satisfactory, provided that correlation effects are added to the Hartree-Fock bands.[8] Physical properties which depend only on the first-order density matrix, however, are expected to be predicted well by local-orbitals theory alone. Such properties are the electron density and the Compton profile.

The concept of ionicity is basically a conceptual aid. As such it is only useful if it directly relates to physical observables which may be unambiguously measured and calculated. Of the many physical observables which are related to ionicity, the one which lends itself most strongly to conceptualizing the nature of bonding is that of the electron density. The latter permits us to think in terms of ionic charges, radii, polarizations, and overlaps. We wish to find if there is a simple relationship between the electron density and the degree of ionicity.

In Sec. II we recall the Adams-Gilbert equation upon which local-orbital theory is based and discuss the calculation of the electron density. In Sec. III we discuss a theoretical basis relating electron density and the degree of ionicity. In Sec. IV we present the local orbitals and the electron densities for the solids in question. In Sec. V we discuss the comparison with experiment, and we conclude in Sec. VI.

II. LOCAL-ORBITALS THEORY

The Adams-Gilbert equation,[9]

$$(\hat{F} - \hat{\rho}\hat{A}\hat{\rho})\,\phi_{ai} = \epsilon_{ai}\,\phi_{ai} \tag{1}$$

provides a means to solve the restricted Hartree-Fock problem within a nonorthogonal set of functions localized on the atomic sites of a solid. This method of solution provides computational simplicity with no loss of accuracy. The localized nature of the functions means that intersite Coulomb and exchange forces may be expanded in a rapidly converging series which may be terminated at any point when the desired accuracy is obtained. One of us (A.B.K.) has shown that sufficient accuracy is provided upon taking the series to first order in overlap.[10] Here $\hat{F}$ is the Fock operator, ϕ_{ai} is the ith local orbital about site a, ϵ_{ai} is the eigenvalue, $\hat{A}$ is the localizing potential (which we take for simplicity as a square well[11]), and $\hat{\rho}$ is the first-order density matrix. The latter is written in terms of the local orbitals and the inverse of the local-orbital overlap matrix $(S^{-1}_{ai,bj})$ as

$$\rho(\vec{r},\vec{r}\,') = \sum_{ai,bj} \phi_{ai}(\vec{r})\, S^{-1}_{ai,bj}\, \phi^{\dagger}_{bj}(\vec{r}\,'). \tag{2}$$

We express the local orbitals in terms of Slater-

TABLE I. Basis functions and local orbitals for NaF.

A_{0j}	Z_{0j}	C_{10j}	C_{20j}	A_{1j}	Z_{1j}	C_{21j}
Na$^+$ ion						
0	15.949	0.133 98	0.005 75	0	12.048	0.007 81
0	9.439	0.918 05	−0.308 67	0	5.703	0.230 34
2	11.624	−0.058 14	−0.024 05	0	3.336	0.455 02
1	4.384	0.001 48	0.491 69	0	2.146	0.384 63
1	2.811	0.000 65	0.612 26			
F^- ion						
0	14.090	0.087 84	0.004 70	0	7.798	0.022 96
0	7.921	0.952 02	−0.272 94	0	3.789	0.333 19
2	9.939	−0.042 78	−0.024 66	0	1.946	0.522 31
1	3.230	0.002 73	0.637 07	0	0.968	0.261 83
1	1.834	0.000 08	0.467 48			

type basis functions. These are obtained from Huzinaga's optimized atomic bases,[12] which we use in the form

$$\chi_{lmj}(\vec{r}) = N_{lj} r^{A_{lj}+l-1} e^{-Z_{lj} r} Y_{lm}, \tag{3}$$

so that,

$$\phi_{ai} \equiv \phi_{anlm} = \sum_j C_{nlj} \chi_{lmj}. \tag{4}$$

The electron density at a point $\vec{r}$ is then

$$\rho(\vec{r}) = \sum_{ai,bj} \phi_{ai}(\vec{r}) S^{-1}_{ai,bj} \phi^{\dagger}_{bj}(\vec{r}), \tag{5}$$

where we compute the inverse of the overlap matrix using Löwdin's formula to the quadratic term:

$$S^{-1}_{ai,bj} = 2\delta_{ai,bj} - S_{ai,bj} + \sum_{ck} (1-\delta_{ac})(1-\delta_{bc}) S_{ai,ck} S_{bj,ck}. \tag{6}$$

TABLE II. Basis functions and local orbitals for SrF_2.

Sr^{++}ion

A_{0j}	Z_{0j}	C_{10j}	C_{20j}	C_{30j}	C_{40j}
0	40.65	0.891 96	0.281 49	0.115 29	0.040 87
1	36.19	0.137 44	0.171 45	0.067 82	0.023 77
1	18.91	−0.020 37	−0.636 99	−0.255 20	−0.089 38
2	17.89	0.018 40	−0.499 31	−0.393 37	−0.154 38
2	9.39	−0.044 77	−0.045 97	0.359 05	0.201 05
2	7.38	0.066 89	0.001 06	0.672 72	0.195 93
3	7.47	−0.031 40	0.012 14	0.143 69	0.177 85
3	4.24	0.001 83	−0.003 31	0.016 73	−0.647 77
3	2.67	−0.000 50	0.001 13	−0.001 79	−0.536 54

A_{1j}	Z_{1j}	C_{21j}	C_{31j}	C_{41j}	A_{2j}	Z_{2j}	C_{32j}
0	25.19	0.120 91	0.046 13	0.028 58	0	11.25	0.326 55
0	17.35	0.706 18	0.305 62	0.060 70	0	8.26	0.144 21
1	16.50	0.181 71	0.154 96	0.098 07	0	5.59	0.597 75
1	10.72	0.033 10	−0.259 38	−0.153 30	0	3.61	0.014 86
1	6.91	−0.002 48	−0.884 09	−0.265 46			
2	3.47	0.000 42	−0.029 25	0.654 55			
2	2.10	−0.000 18	0.009 14	0.458 07			

F$^-$ion

A_{0j}	Z_{0j}	C_{10j}	C_{20j}	A_{1j}	Z_{1j}	C_{21j}
0	14.090	0.087 83	0.004 73	0	7.798	0.021 90
0	7.921	0.952 06	−0.273 32	0	3.789	0.338 67
2	9.939	−0.042 79	−0.024 81	0	1.946	0.507 55
1	3.230	0.002 69	0.639 42	0	0.968	0.275 33
1	1.834	0.000 09	0.465 29			

TABLE III. Basis functions and local orbitals for $SrCl_2$.

Sr^{++}ion

A_{0j}	Z_{0j}	C_{10j}	C_{20j}	C_{30j}	C_{40j}
0	40.65	0.891 96	0.281 48	0.115 25	0.041 02
1	36.19	0.137 44	0.171 46	0.067 81	0.022 92
1	18.91	−0.020 36	−0.637 00	−0.255 16	−0.086 30
2	17.89	0.018 40	−0.499 18	−0.393 08	−0.162 72
2	9.39	−0.044 79	−0.047 04	0.357 43	0.327 83
2	7.38	0.066 92	0.002 72	0.674 74	−0.041 72
3	7.47	−0.031 42	0.011 31	0.142 44	0.322 63
3	4.24	0.001 84	−0.003 23	0.017 82	−0.684 85
3	2.67	−0.000 50	0.001 11	−0.002 00	−0.515 96

A_{1j}	Z_{1j}	C_{21j}	C_{31j}	C_{41j}	A_{2j}	Z_{2j}	C_{32j}
0	25.19	0.120 92	0.046 04	0.020 47	0	11.25	0.325 81
0	17.35	0.706 10	0.305 68	0.085 70	0	8.26	0.144 87
1	16.50	0.181 77	0.154 68	0.073 77	0	5.59	0.595 18
1	10.72	0.033 11	−0.258 89	−0.124 83	0	3.61	0.018 27
1	6.91	−0.002 48	−0.884 06	−0.310 53			
2	3.47	0.000 42	−0.030 04	0.749 39			
2	2.10	−0.000 18	0.009 25	0.368 82			

Cl^-ion

A_{0j}	Z_{0j}	C_{10j}	C_{20j}	C_{30j}	A_{1j}	Z_{1j}	C_{21j}	C_{31j}
0	18.9832	0.456 92	0.111 58	0.047 15	0	13.7900	0.026 73	0.010 46
0	14.7941	0.534 45	0.173 63	0.030 91	0	8.8355	0.269 62	0.040 64
1	14.7181	0.028 08	0.137 55	0.060 49	0	5.3987	0.750 07	0.235 85
1	9.6220	−0.031 02	−0.098 62	−0.077 70	1	4.0186	−0.025 36	−0.113 81
1	6.7665	0.028 01	−0.776 89	−0.181 60	1	2.4367	0.025 59	−0.402 71
2	6.2190	−0.009 89	−0.279 62	−0.217 07	1	1.6382	−0.013 20	−0.425 36
2	3.2450	0.001 80	−0.016 04	0.407 22	1	0.8219	0.003 44	−0.277 08
2	2.1679	−0.001 03	0.004 28	0.597 36	1	0.4120	−0.001 02	0.024 05
2	1.3550	0.000 26	−0.001 33	0.159 77				

We surround the point $\vec{r}$ with atoms sufficient in number to characterize the electron density there completely.

III. ELECTRON DENSITY AND DEGREE OF IONICITY

Although the concept of an ionic solid is an idealization, many solids approach this limit in that there is great charge separation and only minor overlap of the electron densities which may be unambiguously associated with one ion or another. Thus, the electron density along the nearest-neighbor axis displays a deep minimum, the position of which determines the ionic radii of the solid.

Although it is simple to describe the ionic and covalent extremes in terms of electron density, no simple prescription exists to our knowledge for de-

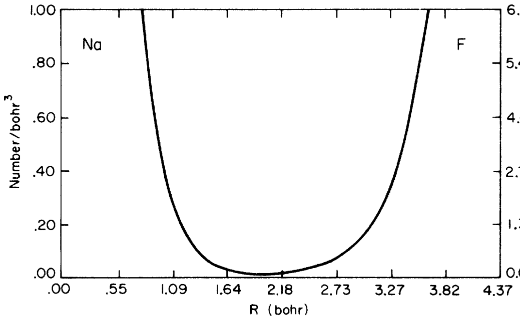

FIG. 1. NaF electron density along [100].

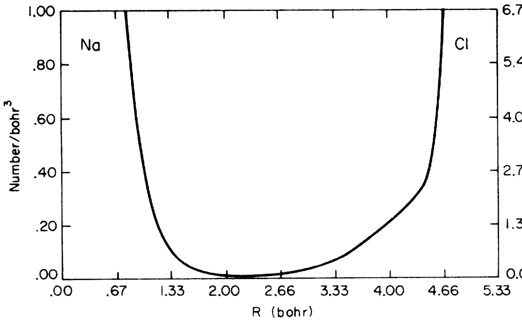

FIG. 2. NaCl electron density along [100].

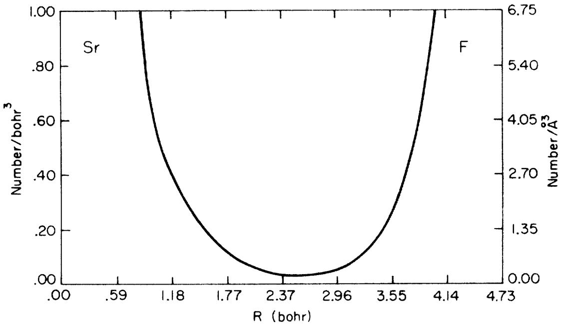

FIG. 3. SrF_2 electron density along [111] .

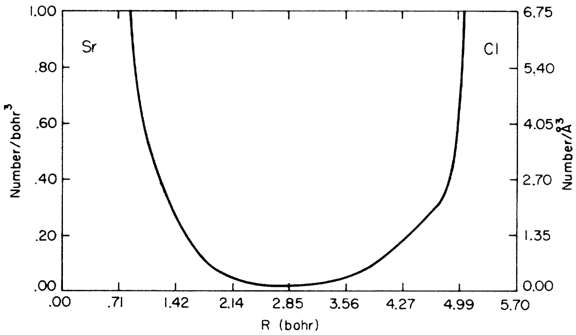

FIG. 4. $SrCl_2$ electron density along [111] .

fining a "degree of ionicity" directly from the electron distribution. One might suspect that, as we mentally travel from the ionic to the covalent extreme, the charge clouds associated with each ion (or atom) would progressively overlap, that charge would be shifted from one site to the other, and that the electron density at the midpoint between nearest neighbors would increase. However, there exist purely covalent solids with little charge overlap (e.g., inert gas solids) and solids with much overlap but some ionic character (e.g., boron nitride). So investigating the ionic charge overlap in highly ionic solids does not yield the degree of ionicity directly. Other effects (relative ion sizes, the nature of the Coulomb potential, the net ionic charge, etc.) must be taken into account.

One unambiguous, quantitative method does exist for directly relating charge density and a degree of ionicity. We may compare the actual electrostatic potential in a solid to that produced by an ideal ionic solid of the same interatomic spacing, composed of nonoverlapping ions with the proper closed-shell configuration. An alternate quantitative definition would be to compare the ionic part of the cohesive energy to the total cohesive energy; however, a difficulty exists in that the ionic contribution cannot be isolated and defined. While a long range potential may be found, overlapping charge distributions make the effect of such a potential on a specific ion a quantity without meaning. Hence, if one insists on defining a fractional ionicity for a solid, it is least ambiguous to define the ionicity in terms of the electrostatic potential.

We may make a thought experiment to realize the effect on the electrostatic potential of a continuous progression from an ionic to a covalent solid. We begin with a purely ionic solid and expand the total intersite Coulomb potential in a spherical harmonic expansion (i.e., a Löwdin α-function expansion) about the center of each ion. The result is the Madelung potential for each ion site. In an A^+B^- solid, one (on B) would be positive, and the other (on A) equally negative. As the ions overlap and/or charge is transferred between the ion types, the above potentials shift unequally. As a completely covalent solid is reached, both potentials are the same and both are positive. Evidently, there must be a more rapid change to the potential at A than the one at B. At any step, we may take as twice the "effective Madelung potential" the difference between the two potentials (or appropriately averaged potentials in more complex solids). Using the usual formula, we may then ascribe to each atom an effective net charge. We may take the ratio of the effective Madelung potential to the ideal one as a relative ionicity f.

It is certain that our definition of fractional ionicity would lead to differences with the values of f given by other authors. Any difference would obviously be due to differences in the definition of fractional ionicity. For qualitative purposes, relative ionicites rather than absolute ionicities are

TABLE IV. Ionic radii (Å).

Ion	NaF	NaCl	SrF_2	$SrCl_2$
Na	1.06	1.15	···	···
Sr	···	···	1.34	1.46
F	1.25	···	1.17	···
Cl	···	1.67	···	1.56

TABLE V. Density minima ($e^-/\text{Å}^3$) along nearest-neighbor axis.

NaF	0.116
NaCl	0.070
SrF_2	0.195
$SrCl_2$	0.109

TABLE VI. Comparison of NaCl to experiment.

	Expt.	Theory
Radii (% a_0)		
Na	21	20.4
Cl	29	29.6
Minimum ($e^-/\text{Å}^3$)		
	0.069 ± 0.007	0.070

sufficient.

IV. RESULTS

The local orbitals for NaF, SrF_2, and $SrCl_2$ are presented in Tables I–III (here we use the normalization convention $\int \phi_{a i}^2 d\vec{r} = 1$). They are typical of those for ionic solids, being similar to free-ion orbitals. The largest overlap integrals between any local orbitals range from 0.05 for NaF to 0.13 for $SrCl_2$. These low values are also typical of ionic solids. In Figs. 1–4 the electron density along the nearest-neighbor axis has been plotted for the solids NaF, NaCl, SrF_2, and $SrCl_2$, where we have used the previously reported local orbitals for NaCl.[13] The plots have the same vertical scale, and the horizontal ranges are set to the nearest-neighbor distance. One may note the well defined ionic radii. These are listed in Table IV. The electron densities at the minima are listed in Table V. It is seen that NaCl has 65% less electron density at the minimum than NaF. It is also noted that the comparison of $SrCl_2$ and SrF_2 yields the same result with the fluoride having 79% more electron density at the minimum.

We compare the actual intersite Coulomb potentials at the position of the nuclei with the ideal Madelung potentials in Table VII. It is seen that, even though there is more overlap in the fluorides, they deviate less from ideal ionicity, at least by the definition of Sec. III. The shifts from ideal ionicity are indeed different for the two sites, as was predicted in Sec. III.

We compare our ionicities with those of Phillips[2] for NaF and NaCl and Levine[14] (based on the Phillips[2] and Van Vechten[15] theory) for SrF_2 and $SrCl_2$. As can be seen in Table VII, our definition yields results in relative agreement with theirs.

An instructive exercise was to integrate the electron densities on each ion. We divided the ions along the surface of the density minimum. This was done for NaCl and NaF and net positive ion charges of 0.769 for NaCl and 0.771 for NaF were obtained. Thus we conclude that one cannot obtain the "net ionic charge" from simply integrating the electron density over ionic volumes defined by this procedure. The above method yields values inconsistent with the actual Coulomb potential which is almost perfectly Madelung like as is evident in Table VII. If one defines the net or effective ionic charge from $q = RV/\alpha$, where V is the actual potential at the nucleus, R is the nearest-neighbor spacing, and α is the Madelung constant, these solids all have $q > 0.99$.

V. DISCUSSION

Unfortunately, the only relevant experimental electron density we can find is on NaCl. We compare Schoknecht's[16] detailed description of the density along (100) to our calculated values in Table VI. We note that there is outstanding agreement as to both the position and magnitude of the minimum.

We call the attention of the reader to the narrow nature of the core electron density on the chloride ion in Figs. 2 and 4. This feature is also seen in a contour plot of Ref. 16 and thus appears to be a real feature of the chloride ion.

The low net ionic charge found by integrating the charge density was at first puzzling, and seemed out of order with the calculated electrostatic potential. Our volume integral routine, when integrated over all space, gave only a 0.1% error in the total charge per unit cell. This also provided a check on the charge density program, and indicates that the net charges are not in significant error. The

TABLE VII. Potentials and fractional ionicities for NaF, NaCl, SrF_2, and $SrCl_2$. V is actual Coulomb potential, V_M is the ideal Madelung potential. The shifts (δ) yield a fractional ionicity (f) as discussed in Sec. III. Results of Phillips and Levine (f_P) are indicated below ours with reference numbers. Relative ionicities are seen to agree.

Solid	NaF		NaCl		SrF_2		$SrCl_2$	
ion	Na	F	Na	Cl	Sr	F	Sr	Cl
V_M	−0.8006	0.8006	−0.6558	0.6558	−4.2584	2.1292	−3.5187	1.7593
V	−0.7984	0.8007	−0.6521	0.6562	−4.2571	2.1297	−3.5155	1.7603
δ	0.0022	0.0001	0.0037	0.0004	0.0013	0.0005	0.0032	0.0010
f	0.9987		0.9975		0.9997		0.9992	
f_P	0.946 (Ref. 2)		0.935 (Ref. 2)		0.971 (Ref. 14)		0.968 (Ref. 14)	

problem lies with dividing the solid along the surface of minimum density. Charge on the far side of the surface from, say, ion A, if possessing a spherically symmetric component about A, will by elementary electrostatics produce a long-range potential as though the spherically symmetric component were concentrated at the center of A. Thus we find a strong long-range potential of much higher strength in these solids than would be estimated on the basis of the volume integration of the charge. The result simply indicates the considerable interpenetration of the ions, and that the ions may interpenetrate without weakening the Madelung potential significantly.

VI. CONCLUSIONS

We find that local-orbitals Hartree-Fock is useful for finding the electron densities of NaF, NaCl, SrF_2, and $SrCl_2$. In both types of compounds, we find the chloride to have less static ionic charge overlap. This agrees with the results on dynamical charge overlap found in the recent experimental work of Man and Bron[3] on SrF_2 and $SrCl_2$. We find excellent agreement with the experimental electron density results of Schoknecht[16] on NaCl.

Our results indicate that, even in highly ionic solids, appreciable interpenetration exists, and the solid cannot be viewed electrostatically as separate ions even though the Coulomb potential is nearly perfectly ionic. This fact causes one to question any quantitative use for concepts as ionic radii and net charge.

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