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Electric dipole moment due to overlapping charges in ionic crystals

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The electric dipole moments arising from the overlap between the atomic Hartree-Fock functions of the nearest-neighbor cation and anion in several ionic crystals are calculated by using a type of integral $\int \Phi_\mu r \cos\theta \Phi_\nu dv$. The dependence of dipole moments on the nearest-neighbor distance is also obtained which is useful for computation of three-center integrals appearing in our calculations of the lattice-relaxation parameters in the impurity-doped ionic crystals. Many single- and two-center integrals involving the overlap integrals are computed and their dependences upon the internuclear distance are used in the coming paper referred to as RIII.

I. INTRODUCTION

The exchange charge polarization due to the overlap between the electron orbitals of the nearest-neighbor ions in alkali halide crystals was calculated and applied to the theory of the dielectric constants in these crystals by Dick and Overhauser.[1] It was ascertained by them that this polarization and the short-range interaction polarization mechanisms are responsible for part of the deviations of e^*/e in the second Szigeti relation from unity, and these mechanisms also give an explanation of the deviations of the so-called crystal polarizabilities from the free-ion polarizabilities. Dick has also explained the failure of the Cauchy relations[2,3] between the elastic constants of alkali halide crystals by using this exchange charge polarization model.[4]

On the other hand, the dipole moment due to overlap charges and its internuclear-distance dependence are utilized for calculation of the three-body potential[2,3] as follows. In the coming paper, referred to as RIII hereafter,[5] the lattice-relaxation parameters (ion displacements) and the electric field gradients in impurity-doped alkali halides are calculated including the three-body potentials. Some point-charge approximations for the overlap-charge distribution will be necessary for calculation of these potentials.

In one of these approximations total overlap charges between the nearest-neighbor ions are divided into two point charges by the dividing parameters, and each of these divided charges is put on the overlap cation or anion site so that the dipole moment originating in the point charges should coincide with that due to the actual overlap-charge distribution.[3] Accordingly, in order to obtain the dividing parameters, it will be necessary to calculate the dipole moment due to the overlap charges.

Another approximation[6,7] does not divide the overlap charges but puts them on the electric center of gravity (ECG) of the overlap-charge distribution, as shown in the RIII. Therefore, in this case the ECG and the Madelung potential at the ECG are calculated to obtain the three-body potentials.

For the case of atomic Hartree-Fock functions given numerically in the form of a table, Löwdin has calculated[2,3] the overlap integrals $S_{\mu\nu}$ by using the α-function technique and compared them with the same integrals tabulated by Mulliken *et al.*[8] through the elliptic coordinate transformation.

The overlap integrals among the *s*- and *p*-electron orbitals in the outer shells of the ions were computed for many combinations of ion pairs in the alkali halide pure crystals by using the radial and lateral double-integral method by Hafemeister and Flygare.[9] The nearest-neighbor and next-nearest-neighbor overlap integrals were computed at several internuclear distances and were found to follow the exponential form,

$$S_{ab} = A \exp(-r_{ab}/\rho) \quad .$$

In calculation of the two-center integrals which appear in the expression of the electric dipole moment, we have used the exponential forms for the radial parts of Hartree-Fock (HF) functions which are obtainable from a table of atomic HF functions made by Clementi,[10] and calculated the integrals by using α functions. Similarly we have computed the overlap integrals in the same equation by the α-function technique and compared them with Hafemeister and Flygare's results. Hereafter Refs. 2 and 3 will be called TI and TII, respectively.

In Sec. II we describe the electric dipole moment originating in overlap charges of ionic crystals by using the atomic HF functions. The two-center integrals I and overlap integrals S in the expression of the dipole moments are calculated in Sec. III. The dependences of the dipole moments in various ionic crystals on the nearest-neighbor distance are computed by using dependence of the I and S integrals in Sec. IV. In Sec. V, the overlap integrals S and integrals I between outer-shell electron orbitals of the nearest-neighbor ions, and also those involving the inner-shell electrons are tabulated and will be used in the RIII. Finally in Sec. VI, the ECG's of the overlapping-charge distribution and the Madelung potentials at the ECG's are calculated, besides, internuclear-distance dependence of the position of the ECG is computed, and all of them will be utilized in the RIII.

II. ELECTRIC DIPOLE MOMENT DUE TO OVERLAPPING CHARGE

In Fig. 1, the line μ-ν will be designated as z axis, where μ and ν are the atomic orbitals (AO) of the nearest-neighbor anion h and cation g, respectively. Here O′ represents the middle point of the separation "a" between the g and h ion in atomic units, and 1 expresses the position of the charge density due to overlapping electrons whose spherical coordinates are (R,Θ,Φ) relative to O″ as the origin, (R',Θ',Φ') relative to O′, and (r,θ,ϕ) relative to O. Here we choose the azimuthal angles as $\Phi=\Phi'=\phi$.

Let $\Phi_\mu(\vec{R})$ be the AO with the atomic quantum numbers N, L, and M having coordinates (R,Θ,Φ), so that[3]

$$\Phi_\mu(\vec{R})=\Phi(NLM/R\,\Theta\Phi)$$

$$=k_{LM}\frac{f_{NL}(R)}{R}P_L^M(\cos\Theta)\times\begin{cases}\cos M\Phi\\ \sin M\Phi\end{cases}, \quad (1)$$

where k_{LM} is the normalization constant

$$k_{LM}=\left[\frac{\epsilon_M(2L+1)(L-M)!}{4\pi(L+M)!}\right]^{1/2}, \quad (2)$$

$$\epsilon_0=1,\ \epsilon_\nu=2\ (\nu\geqslant 1)\ ,$$

and $P_L^M(\cos\Theta)$ represents the associated Legendre function. We have a similar expression with respect to $\Phi_\nu(\vec{r}\,)=\Phi(nlm/r\,\theta\phi)$. Then the total electric dipole moment along the z axis relative to O′ as the origin, due to the overlaps in atomic units will be

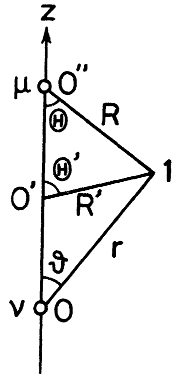

FIG. 1. Overlapping charge density, 1 between μ and ν atomic orbitals whose spherical coordinates are (R,Θ,Φ) with respect to O″, (R',Θ',Φ') to O′, and (r,θ,ϕ) to O, where $\Phi=\Phi'=\phi$. The O′ is the middle point of $\overline{\mathrm{OO}''}$.

$$\mu_z=-\sum_{\mu,\nu}\left[\int\Phi_\mu(\vec{R})R'\cos\Theta'\Phi_\nu(\,\vec{r}\,)\,dv_1\right]R_{\nu\mu}$$

$$=-\sum_{\mu,\nu}\left[\int\Phi_\mu(\vec{R})r\cos\theta\Phi_\nu(\,\vec{r}\,)\,dv_1\right]R_{\nu\mu}$$

$$+\tfrac{1}{2}a\sum_{\mu,\nu}\left[\int\Phi_\mu(\vec{R})\Phi_\nu(\,\vec{r}\,)\,dv_1\right]R_{\nu\mu}\ , \quad (3)$$

where $R_{\nu\mu}$ is a multiplier due to the orthogonalization between ν- and μ-AO and summation goes over all overlapping orbitals.

III. TWO-CENTER INTEGRALS $I_i(i=1,\ldots,5)$

We consider, for simplicity, the case when the concerned ions have valence electrons of $l=0$ or 1. The integrals in the first term of Eq. (3) are a kind of two-center integral and will be designated as $I_i(i=1,\ldots,5)$, in which $I_1=I(n's\,|\,ns)$, $I_2=I(n's\,|\,np0)$, $I_3=I(n'p0\,|\,ns)$, $I_4=I(n'p0\,|\,np0)$, and $I_5=I(n'p1\,|\,np1)$, where n' and n represent the principal quantum number of the anion and cation, respectively. The last one, I_5 is doubly contained in summation of Eq. (3) compared with the others. The integrals in the second term of Eq. (3) are the ordinary overlap integrals called $S_{\mu\nu}$. When the α-function technique developed by Löwdin is applied to the first integrals, we obtain

$$I_i=\int\int\int\Phi_\mu(NLM\,|\,R\,\Theta\Phi)\,r\cos\theta\Phi_\nu(nlm\,|\,r\,\theta\phi)\,r^2\sin\theta\,dr\,d\theta\,d\phi$$

$$=k_{LM}k_{lm}^{-1}\left[\frac{l+1}{2l+3}\int_0^\infty\alpha_{l+1}(NLM\,|\,ar)f_{nl}(r)r^2\,dr+\frac{l}{2l-1}\int_0^\infty\alpha_{l-1}(NLM\,|\,ar)f_{nl}(r)r^2\,dr\right], \quad (4)$$

where we have used a relation of the Legendre functions

$$(2l+1)\cos\theta P_l(\cos\theta) = (l+1)P_{l+1}(\cos\theta) + lP_{l-1}(\cos\theta) \ . \tag{5}$$

The α functions with $l+1$ or $l-1$ are obtained from TI and TII:

$$\alpha_{l+1}(NLM|ar) = \frac{2l+3}{(2a)^L(2ar)^{l+2}} \sum_{s=0}^{L+l+1} Q_{l+1,s}(NLM|ar) \int_{|a-r|}^{a+r} f_{NL}(R) R^{2s-L}\,dR \ , \tag{6}$$

$$\alpha_{l-1}(NLM|ar) = \frac{2l-1}{(2a)^L(2ar)^{l}} \sum_{s=0}^{L+l-1} Q_{l-1,s}(NLM|ar) \int_{|a-r|}^{a+r} f_{NL}(R) R^{2s-L}\,dR \ , \tag{7}$$

where $Q_{ls}(NLM|ar)$ is a homogeneous polynomial in a^2 and r^2 of degree $2(L+l-s)$, obtainable from TII. Substituting Eqs. (6) and (7) into Eq. (4), the general formulas of I_i are derived as follows:

$$I_i = \delta_{Mm} k_{LM} k_{lm}^{-1} \left[\frac{l+1+m}{(2a)^{L+l+2}} \sum_{s=0}^{L+l+1} \int_0^\infty f_{nl}(r) r^{-l} Q_{l+1,s}(NLM|ar)\,dr \int_{|a-r|}^{a+r} f_{NL}(R) R^{2s-L}\,dR \right.$$
$$\left. + \frac{l-m}{(2a)^{L+l}} \sum_{s=0}^{L+l-1} \int_0^\infty f_{nl}(r) r^{-l+2} Q_{l-1,s}(NLM|ar)\,dr \int_{|a-r|}^{a+r} f_{NL}(R) R^{2s-L}\,dR \right] \ , \tag{8}$$

$$i = 1, \ldots, 5 \ ,$$

where $i=1$, 2, 3, 4, and 5 correspond to $L=l=M=m=0$; $L=M=m=0$, $l=1$; $L=1$, $l=M=m=0$; $L=l=1$, $M=m=0$; and $L=l=M=m=1$, respectively. The equations for the overlap integrals between the nearest-neighbor ions, $S_i(i=1,\ldots,5)$, are taken from the similar equations in TII.

Then we are able to calculate I_i and S_i by using a computer. We have computed[11] these double integrals in increments of 0.05 atomic units (a.u.) for a total distance of 12.17 a.u., where accuracy of calculation was comparable with Hafemeister and Flygare's (H-F) one. The results of computation of S_i in the pure ionic crystals were very near to H-F's values; however, for a large change in the internuclear distance, "a," the exponential dependences of I_i and S_i upon "a" were not so good as expected. Therefore it was necessary to perform a number of calculations in these cases.

IV. DEPENDENCE OF DIPOLE MOMENT UPON NEAREST-NEIGHBOR DISTANCE

When we utilize $-S_{\nu\mu}$ as the orthogonalization constant in Eq. (3) as shown in TII, then we have

$$\mu_z = 4\left[\sum_{i=1} I_i S_i - \tfrac{1}{2}a \sum_{i=1} S_i^2\right] \ . \tag{9}$$

The dependences of $\sum I_i S_i$ and $\sum S_i^2$ on a change of the internuclear distance will be

$$\sum_{i=1} I_i S_i = X_{IS} + Y_{IS}\epsilon + Z_{IS}\epsilon^2 \ , \tag{10}$$

$$\sum_{i=1} S_i^2 = X + Y\epsilon + Z\epsilon^2 \ , \tag{11}$$

where ϵ is the variation of the nearest-neighbor distance (for instance, due to substitution of the monovalent impurity ions), and is taken to the extent of the second order and

$$a = a_0(1+\epsilon) \ , \tag{12}$$

where a_0 represents the internuclear distance in the pure crystals. Then the dependence of the dipole moment on the internuclear distance will be

$$\begin{aligned}\mu_z &= \xi + \eta\epsilon + \zeta\epsilon^2 \\ &= 4(X_{IS} - \tfrac{1}{2}a_0 X) + 4[Y_{IS} - \tfrac{1}{2}a_0(X+Y)]\epsilon \\ &\quad + 4[Z_{IS} - \tfrac{1}{2}a_0(Y+Z)]\epsilon^2 \ .\end{aligned} \tag{13}$$

The ξ, η, and ζ values for the overlap ion pairs in various impurity-doped alkali halide crystals are shown in Table I where the a.u. is used and the middle point of the nearest-neighbor distance is taken as the origin. As shown on the table, the ion pairs containing K^+ ions have a remarkably large μ_z, and especially K-F in NaF and K-Cl in NaCl crystal correspond to this case. This fact will be discussed in connection with covalency in RIII.[5]

TABLE I. Dependence of the electric dipole moment due to overlapping charges upon the nearest-neighbor distance in atomic units [Eq. (13)] where the middle point of this distance is taken as the origin.

Ion pair in crystal	ξ (10^{-2})	η (10^{-1})	ζ (10^{-1})
Li-F in NaF	−1.083	0.669	−2.007
Na-F in NaF	−2.082	1.246	−3.454
K-F in NaF	−6.992	4.711	−2.133
Na-F in KF	−0.834	0.565	−1.812
K-F in KF	−2.853	1.925	−4.968
Li-Cl in NaCl	−1.306	0.896	−3.019
Na-Cl in NaCl	−2.512	1.617	−4.985
Na-Br in NaCl	−3.832	2.383	−7.105
K-Cl in NaCl	−7.204	3.618	−7.138
Na-I in NaCl	−6.686	3.967	−11.38
Na-Cl in NaBr	−1.726	1.188	−3.940
Na-Br in NaBr	−2.666	1.770	−5.660
Na-I in NaBr	−4.728	2.997	−9.201
K-Cl in KCl	−3.937	2.390	−6.338
Na-Cl in NaI	−0.989	0.747	−2.739
Na-Br in NaI	−1.560	1.132	−3.980
Na-I in NaI	−2.837	1.953	−6.530
Na-Br in KBr	−1.309	0.976	−3.532
K-Cl in KBr	−2.901	1.907	−5.635
K-Br in KBr	−4.620	2.981	−8.811

V. TABULATION OF THE OVERLAP INTEGRALS S AND THE INTEGRALS I

In order to study the lattice-relaxation parameters (the displacements of the ions around the substitutional impurity ion) and the electric field gradients on these displaced ions, it is necessary to calculate the three-body potentials, the point-charge approximation of which contains many overlap integrals between the impurity and host ion and also between the host cation and anion, as shown in RIII.

First, the single-center integrals appearing in RIII,

$$J=\int \Phi_{Ans}\Phi_{An'p}\, r\cos\theta\, dv_1 \tag{14}$$

are listed in Table II, where Φ_{Ans} and $\Phi_{An'p}$ are the AO's with atomic quantum numbers n, 0 and n', 1, respectively, for A ion, one of the nearest-neighbor overlap-pair ions. The integrals are extended over whole space with respect to the electron 1 of A ion whose coordinates are r, θ, and ϕ.

The outer-shell overlap integrals, S, the integrals, I, and those involving inner-shell electrons between nearest-neighbor ions are shown in Tables III, IV, and V, respectively, where S and I are given by the equations (the primes on S and I in Table V denote the including of inner-shell electrons, and we neglect these primes in the next equations),

$$S_i=A_i\exp(-R/\rho_i)\ , \tag{15}$$

$$I_i=B_i\exp(-R/\sigma_i)\ , \tag{16}$$

$$i=1,\ldots,5\ ,$$

where R represents a distance between the nearest-

TABLE II. Single-center integrals. The r, θ, and ϕ represent the spherical coordinates of electron 1 with respect to the concerned ion.

Electron	Ion A	n	n'	$\int \Phi_{Ans}\Phi_{An'p}\, r\cos\theta\, dv_1$
Outer-shell electrons	Na^+	2	2	−0.4456
	K^+	3	3	−0.7671
	F^-	2	2	−0.6178
	Cl^-	3	3	−0.9812
	Br^-	4	4	−1.0957
	I^-	5	5	−1.3142
Including inner-shell electrons	Na^+	1	2	+0.0491
	K^+	2	2	−0.2075
	K^+	1	3	+0.0086
	K^+	2	3	+0.0589
	K^+	3	2	+0.0532

TABLE III. Outer-shell overlap integrals between nearest-neighbor ions. Abbreviations for overlap integrals, $S_1=S(n's|ns)$, $S_2=S(n's|np0)$, $S_3=S(n'p0|ns)$, $S_4=S(n'p0|np0)$, and $S_5=S(n'p1|np1)$ were used, where n' and n represent the principal quantum number of the anion and cation, respectively. Equation (15) gives the overlap integrals for any internuclear distance by means of the A and ρ (in angstroms).

Pair in crystal		S_1	S_2	S_3	S_4	S_5
Li-F in NaF	A	−4.527 703		−1.595 361		
	ρ	0.354 361		0.623 613		
Li-Cl in NaCl	A	4.685 452		2.039 091		
	ρ	0.429 449		0.703 876		
Na-F in NaF	A	6.000 367	−5.504 392	2.015830	−1.190 444	1.016 138
	ρ	0.352 479	0.400 964	0.621 951	0.699 854	0.520 667
Na-F in KF	A	7.093 762	−6.784 675	1.874 374	−1.358 425	0.924 001
	ρ	0.344 228	0.387 760	0.633 623	0.674 129	0.531 322
K-F in KF	A	−10.842 98	11.229 64	−2.862 734	1.331 057	−1.672 503
	ρ	0.384 845	0.447 524	0.679 033	0.891 687	0.588 661
K-F in NaF	A	−8.262 688	8.525 854	−2.475 064	0.518 620	−1.371 884
	ρ	0.401 928	0.471 078	0.707 791	1.362 168	0.618 292
Na-Cl in NaCl	A	−5.986 703	4.906 694	−2.534 055	1.721 513	−1.249 204
	ρ	0.428 877	0.476 754	0.704 050	0.744 383	0.578 122
Na-Cl in NaBr	A	−6.508 814	5.476 110	−2.523 781	1.749 559	−1.200 005
	ρ	0.423 587	0.468 212	0.704 762	0.741 253	0.582 844
Na-Br in NaBr	A	4.420 545	−4.405 857	2.651 335	−1.735 447	1.239 207
	ρ	0.475 908	0.504 345	0.734 253	0.774 891	0.604 012
Na-Br in NaCl	A	4.441 766	−4.168 436	2.665 010	−1.646 633	1.286 722
	ρ	0.475 536	0.509 321	0.733 295	0.786 073	0.599 269
Na-Br in KBr	A	4.361 996	−4.732 199	2.611 429	−1.841 665	1.145 600
	ρ	0.476 887	0.498 523	0.736 889	0.763 479	0.613 379
K-Cl in KCl	A	11.313 16	−10.886 88	4.212 365	−3.404 422	2.769 711
	ρ	0.452 989	0.515 618	0.735 674	0.813 968	0.615 269
K-Cl in NaCl	A	8.977 798	−8.161 626	3.942 590	−2.855 523	2.783 894
	ρ	0.469 685	0.543 006	0.748 073	0.855 722	0.614 626
K-Cl in KBr	A	12.608 66	−12.444 77	4.333 005	−3.641 213	2.763 531
	ρ	0.446 115	0.504 698	0.730 911	0.800 206	0.615 535
K-Br in KBr	A	−8.665 355	9.792 614	−4.376 632	3.459 982	−2.750 031
	ρ	0.496 388	0.544 360	0.767 455	0.844 197	0.642 023
Na-I in NaI	A	−4.220 051	4.572 103	−2.677 244	1.857 350	−1.177 410
	ρ	0.528 012	0.540 490	0.786 672	0.804 220	0.646 006
Na-Br in NaI	A	4.373 399	−4.665 236	2.621 651	−1.821 660	1.167 951
	ρ	0.476 702	0.499 625	0.736 232	0.765 465	0.611 134
Na-Cl in NaI	A	−7.401 862	6.432 318	−2.535 215	1.777 936	−1.142 225
	ρ	0.416 205	0.456 990	0.704 059	0.738 370	0.588 378
Na-I in NaCl	A	−4.423 940	3.389 206	−2.776 269	1.504 849	−1.312 572
	ρ	0.523 935	0.571 663	0.779 454	0.853 177	0.631 292
Na-I in NaBr	A	−4.457 787	3.883 783	−2.763 432	1.674 455	−1.266 509
	ρ	0.523 170	0.556 540	0.780 397	0.826 837	0.636 271

neighbor ions in Å units and the quantized axes of these pair ions are taken toward the opposite directions of each other, which procedure is the same as Löwdin's[2,3] while the reverse of Hafemeister and Flygare's method.[9] The calculations of S and I have been performed[11] by using the α-function technique as shown in Sec. III and the accuracy of calculation was also the same as in that section.

Secondly, the internuclear-distance dependences, λ, μ, and ν of total overlap charges, $4(\sum S_i^2+\sum S_i'^2)$ are listed in Table VI, and satisfy the following equations:

$$\frac{e^2}{R_0}W_{gh}(g,h)=\lambda+\mu\epsilon+\nu\epsilon^2\ , \tag{17}$$

$$W_{gh}(g,h)=4(\textstyle\sum S_i^2+\sum S_i'^2)\ , \tag{18}$$

TABLE IV. Outer-shell integrals between nearest-neighbor ions, $I_i = \int \Phi_\mu r \cos\theta \Phi_\nu dv_1$. Abbreviations for $I_i (i = 1, \ldots, 5)$ are similar to those of S_i in Table III. The $I_i (i = 1, \ldots, 5)$ for any internuclear distance are given by Eq. (16) with B and σ (in Å).

Pair in crystal		I_1	I_2	I_3	I_4	I_5
Li-F in NaF	B	−2.985 649		−0.678 677		
	σ	0.392 824		0.670 327		
Li-Cl in NaCl	B	2.568 131		0.876 172		
	σ	0.470 020		0.735 389		
Na-F in NaF	B	4.721 597	−6.778 685	1.112 436	−0.819 256	0.456 218
	σ	0.379 932	0.450 698	0.641 736	0.982 014	0.633 617
Na-F in KF	B	6.137 561	−8.750 430	1.151 026	−1.546 535	0.644 992
	σ	0.365 126	0.430 594	0.635 703	0.781 664	0.581 096
K-F in KF	B	−13.191 79	18.094 31	−1.883 077	a	−0.650 714
	σ	0.426 172	0.509 092	0.794 548	a	0.836 711
K-F in NaF	B	−9.057 538	13.418 55	−0.872 657	a	a
	σ	0.455 844	0.542 495	1.061 116	a	a
Na-Cl in NaCl	B	−3.910 926	6.447 765	−1.269 586	2.903 234	−1.059 300
	σ	0.458 244	0.520 793	0.722 257	0.788 985	0.599 647
Na-Cl in NaBr	B	−4.368 787	7.359 968	−1.276 520	3.099 851	−1.047 640
	σ	0.450 281	0.508 573	0.721 242	0.774 975	0.601 017
Na-Br in NaBr	B	3.452 094	−6.251 216	1.278 974	−2.880 924	0.992 596
	σ	0.486 014	0.544 094	0.752 134	0.827 294	0.627 937
Na-Br in NaCl	B	3.283 217	−5.586 736	1.227 771	−2.606 608	0.966 505
	σ	0.490 202	0.555 958	0.760 322	0.851 889	0.631 625
Na-Br in KBr	B	3.599 540	−7.481 473	1.323 173	−3.304 736	1.000 172
	σ	0.482 798	0.527 442	0.745 890	0.798 014	0.626 928
K-Cl in KCl	B	12.161 25	−16.999 43	3.464 077	−6.261 272	3.320 304
	σ	0.496 021	0.578 412	0.791 817	0.891 333	0.656 415
K-Cl in NaCl	B	8.722 063	−12.117 06	2.868 222	−4.694 203	3.027 065
	σ	0.525 453	0.619 601	0.834 381	0.976 778	0.670 322
K-Cl in KBr	B	14.108 27	−19.932 41	3.696 969	−7.039 430	3.436 814
	σ	0.484 814	0.562 174	0.779 193	0.863 024	0.651 774
K-Br in KBr	B	−10.785 15	16.713 33	−3.555 819	6.046 792	−3.126 362
	σ	0.524 627	0.600 066	0.819 471	0.938 370	0.685 693
Na-I in NaI	B	−3.486 013	5.742 702	−1.351 007	3.010 309	−0.972 494
	σ	0.523 959	0.594 959	0.783 365	0.871 000	0.658 828
Na-Br in NaI	B	3.581 061	−7.188 918	1.317 679	−3.207 610	1.000 995
	σ	0.483 174	0.530 907	0.746 616	0.803 955	0.626 833
Na-Cl in NaI	B	−5.119 883	8.893 719	−1.270 353	3.360 849	−1.024 508
	σ	0.440 036	0.493 096	0.722 048	0.759 417	0.603 638
Na-I in NaCl	B	−2.577 688	4.173 236	−1.111 194	2.309 388	−0.867 923
	σ	0.553 488	0.635 607	0.826 341	0.944 629	0.676 082
Na-I in NaBr	B	−2.964 152	4.815 150	−1.231 339	2.617 100	−0.923 415
	σ	0.538 941	0.616 058	0.802 523	0.907 186	0.666 310

[a] Values of these I_i are extremely large and they cannot be expressed by exponential forms since their dependence upon internuclear distances shows a tendency towards saturation. However, they have the definite first- and second-order terms in the distance dependence.

TABLE V. Overlap integrals S_i' and two-center integrals I_i' between nearest-neighbor ions involving inner-shell electrons. Abbreviations for overlap integrals, $S_i'(i=1,\ldots,4)$, and those for two-center integrals, $I_i'(i=1,\ldots,4)$, including inner-shell electrons are similar to those for outer-shell integrals, $S_i(i=1,\ldots,4)$, and for $I_i(i=1,\ldots,4)$ in Tables III and IV, respectively. The S_i' and I_i' for any internuclear distance are given by Eqs. (15) and (16) with A, ρ (in Å) and B, σ (in Å), respectively.

Overlap pair in crystal		S_1'	S_3'		I_1'	I_3'
Na $1s$-F $2s, 2p$ in NaF	A	−0.557 566	−0.204 386	B	−0.092 183	−0.011 532
	ρ	0.324 204	0.603 286	σ	0.270 023	0.529 781
Na $1s$-F $2s, 2p$ in KF	A	−0.616 306	−0.181 459	B	−0.152 975	−0.007 255
	ρ	0.319 994	0.621 604	σ	0.255 958	0.588 939
Na $1s$-Cl $3s, 3p$ in NaCl	A	0.606 718	0.260 437	B	0.035 172	0.009 128
	ρ	0.403 303	0.685 367	σ	0.384 811	0.655 972
Na $1s$-Cl $3s, 3p$ in NaBr	A	0.655 241	0.256 686	B	0.038 124	0.008 182
	ρ	0.398 993	0.687 776	σ	0.380 713	0.672 835
Na $1s$-Br $4s, 4p$ in NaBr	A	−0.355 289	−0.276 494	B	−0.018 914	−0.009 769
	ρ	0.468 206	0.713 200	σ	0.441 775	0.676 162
Na $1s$-Br $4s, 4p$ in NaCl	A	−0.369 210	−0.284 844	B	−0.022 532	−0.010 574
	ρ	0.465 277	0.707 961	σ	0.430 174	0.663 772
Na $1s$-Br $4s, 4p$ in KBr	A	−0.343 353	−0.262 971	B	−0.014 381	−0.008 531
	ρ	0.470 681	0.721 532	σ	0.459 787	0.696 754
Na $1s$-I $5s, 5p$ in NaI	A	0.355 162	0.273 509	B	0.032 637	0.011 351
	ρ	0.519 436	0.768 762	σ	0.448 169	0.691 528
Na $1s$-Br $4s, 4p$ in NaI	A	−0.344 414	−0.265 919	B	−0.015 205	−0.008 806
	ρ	0.470 465	0.719 735	σ	0.456 157	0.692 016
Na $1s$-Cl $3s, 3p$ in NaI	A	0.738 097	0.256 860	B	0.044 747	0.007 355
	ρ	0.392 913	0.687 716	σ	0.373 319	0.689 060
Na $1s$-I $5s, 5p$ in NaCl	A	0.462 581	0.315 463	B	0.029 305	0.012 690
	ρ	0.496 990	0.741 677	σ	0.455 779	0.674 455
Na $1s$-I $5s, 5p$ in NaBr	A	0.432 398	0.300 081	B	0.031 498	0.012 361
	ρ	0.502 813	0.751 353	σ	0.450 598	0.678 602
K $1s$-F $2s, 2p$ in KF	A	−0.260 666	−0.076 457			
	ρ	0.318 548	0.621 018			
K $1s$-F $2s, 2p$ in NaF	A	−0.234 995	−0.086 033			
	ρ	0.322 870	0.602 879			
K $1s$-Cl $3s, 3p$ in KCl	A	0.300 051	0.108 069			
	ρ	0.393 665	0.687 431			
K $1s$-Cl $3s, 3p$ in NaCl	A	0.256 511	0.109 833			
	ρ	0.402 073	0.684 744			
K $1s$-Cl $3s, 3p$ in KBr	A	0.324 532	0.108 996			
	ρ	0.389 890	0.686 185			
K $1s$-Br $4s, 4p$ in KBr	A	−0.143 602	−0.110 855			
	ρ	0.470 254	0.720 962			

Overlap pair in crystal		S_1'	S_2'	S_3'	S_4'
K $2s, 2p$-F $2s, 2p$ in KF	A	2.109 600	−2.116 958	0.608 267	−0.243 988
	ρ	0.324 933	0.299 033	0.623 542	0.588 408
K $2s, 2p$-F $2s, 2p$ in NaF	A	1.898 883	−1.487 046	0.685 752	−0.332 457
	ρ	0.329 495	0.312 349	0.604 990	0.547 758
K $2s, 2p$-Cl $3s, 3p$ in KCl	A	−2.356 098	1.185 200	−0.849 307	0.240 822
	ρ	0.399 624	0.393 509	0.691 176	0.687 736
K $2s, 2p$-Cl $3s, 3p$ in NaCl	A	−2.012 655	0.960 785	−0.864 493	0.274 688
	ρ	0.408 331	0.404 817	0.688 221	0.667 133
K $2s, 2p$-Cl $3s, 3p$ in KBr	A	−2.553 073	1.331 462	−0.855 382	0.231 487
	ρ	0.395 643	0.387 942	0.690 128	0.693 684
K $2s, 2p$-Br $4s, 4p$ in KBr	A	1.197 181	−0.563 683	0.874 549	−0.263 921
	ρ	0.471 855	0.458 048	0.724 114	0.703 689

TABLE V (*Continued*).

Overlap pair in crystal		I_1'	I_2'	I_3'	I_4'
K 2*s*, 2*p* -F 2*s*, 2*p* in KF	*B*	0.475 400	−357885.2	0.097 781	−0.441 149
	σ	0.340 984	0.115 454	0.614 219	0.554 063
K 2*s*, 2*p* -F 2*s*, 2*p* in NaF	*B*	0.436 181	−28.547 89	0.123 637	−0.551 515
	σ	0.345 065	0.208 813	0.580 080	0.527 612
K 2*s*, 2*p* -Cl 3*s*, 3*p* in KCl	*B*	−0.414 137	8.737 907	−0.107 663	0.413 368
	σ	0.419 369	0.299 140	0.702 515	0.658 182
K 2*s*, 2*p* -Cl 3*s*, 3*p* in NaCl	*B*	−0.351 941	3.008 504	−0.119 123	0.437 339
	σ	0.429 278	0.335 098	0.685 867	0.649 931
K 2*s*, 2*p* -Cl 3*s*, 3*p* in KBr	*B*	−0.452 327	20.726 73	−0.104 737	0.407 295
	σ	0.414 562	0.276 815	0.706 836	0.660 217
K 2*s*, 2*p* -Br 4*s*, 4*p* in KBr	*B*	0.238 844	−1.383 095	0.116 672	−0.425 294
	σ	0.475 932	0.394 761	0.720 133	0.689 667

where the charges are multiplied by e^2/R_0. The dependences of divided charges, ξ_1, η_1, and ζ_1 at the overlap anion site are also represented in the same table (the way of division of total charges is shown in RIII), and are given as follows:

$$\frac{e^2}{R_0}Q_{h0}=\xi_1+\eta_1\epsilon+\zeta_1\epsilon^2\ , \tag{19}$$

$$\frac{e^2}{R_0}Q_{g0}=\xi_2+\eta_2\epsilon+\zeta_2\epsilon^2\ , \tag{20}$$

$$\xi_2=-\xi_1,\quad \eta_2=-\eta_1,\quad \zeta_2=-\zeta_1\ , \tag{21}$$

$$Q_{h0}=4\sum_{i=1}(\lambda_1^{(i)}-\tfrac{1}{2})S_i^2,\quad Q_{g0}=4\sum_{i=1}(\lambda_2^{(i)}-\tfrac{1}{2})S_i^2\ . \tag{22}$$

Here $\lambda_1^{(i)}$ and $\lambda_2^{(i)}$ are the dividing parameters as shown in RIII, and ξ_2, η_2, and ζ_2 express the internuclear-distance dependences of divided charges at the overlap cation site, and all charges are multiplied by e^2/R_0.

For the charges related to the second-order terms in expansion of the potentials about the concerned ion, we obtain similar equations:

$$\frac{e^2a_H^2}{R_0^3}Q_{i1}=\alpha_i+\beta_i\epsilon+\gamma_i\epsilon^2,\quad i=1,2, \tag{23}$$

$Q_{i1}\equiv Q_{h1}$ and $Q_{i1}\equiv Q_{g1}$ for $i=1$ and $i=2$, respective-

TABLE VI. Internuclear-distance dependences of total charges $4(\sum_i S_i^2+\sum_i S_i'^2)$ due to overlap, λ, μ, ν and those of divided charges of them at the overlap anion site, ξ_1, η_1, ζ_1, all charges of which are multiplied by e^2/R_0. The ξ_1, η_1, ζ_1 and λ, μ, ν (in units of 10^{-12} esu^2/cm) satisfy Eqs. (19) and (17), and are used in the Löwdin-Satoh-Taki (LST) and Ra-Abarenkov-Antonova (RAA) models in paper RIII, respectively. Internuclear-distance dependences of divided charges at the overlap cation site, ξ_2, η_2, ζ_2 are given by Eq. (21).

Pair in crystal	ξ_1	η_1	ζ_1	λ	μ	ν
Li-F in NaF	−0.0257	0.1869	−0.6832	0.0685	−0.5146	1.9617
Li-Cl in NaCl	−0.0208	0.1647	−0.6580	0.0511	−0.4135	1.6937
Na-F in NaF	−0.0692	0.5181	−1.9494	0.2168	−1.6201	6.2550
Na-F in KF	−0.0194	0.1593	−0.6580	0.0597	−0.5032	2.1625
K-F in KF	−0.0970	0.7982	−3.1152	0.3474	−2.5891	10.273
K-F in NaF	−0.3352	2.5104	−6.3690	1.0706	−6.5824	23.358
Na-Cl in NaCl	−0.0515	0.4053	−1.6141	0.1472	−1.1938	4.9336
Na-Cl in NaBr	−0.0309	0.2553	−1.0669	0.0870	−0.7419	3.2149
Na-Br in NaBr	−0.0475	0.3801	−1.5352	0.1302	−1.0664	4.4362
Na-Br in NaCl	−0.0780	0.5942	−2.2884	0.2161	−1.6793	6.6467
Na-Br in KBr	−0.0184	0.1613	−0.7108	0.0494	−0.4441	2.0171
K-Cl in KCl	−0.0881	0.7217	−2.9867	0.3201	−2.7016	11.669
K-Cl in NaCl	−0.2294	1.6849	−6.2798	0.8518	−6.3796	24.625
K-Cl in KBr	−0.0560	0.4815	−2.0874	0.2007	−1.7837	8.0880
K-Br in KBr	−0.0875	0.7283	−3.0589	0.2955	−2.5072	10.850
Na-I in NaI	−0.0422	0.3466	−1.4382	0.1102	−0.9232	3.9238
Na-Br in NaI	−0.0232	0.1988	−0.8581	0.0626	−0.5501	2.4474
Na-Cl in NaI	−0.0147	0.1309	−0.5860	0.0408	−0.3726	1.7256
Na-I in NaCl	−0.1361	0.9924	−3.6762	0.3611	−2.6578	9.9870
Na-I in NaBr	−0.0842	0.6479	−2.5241	0.2224	−1.7346	6.8857

TABLE VII. Internuclear-distance dependence of the charges connected with the small correction terms of potentials, all charges of which are multiplied by $e^2a_H^2/R_0^3$. The a_H represents the first Bohr radius. The α_i, β_i, γ_i and ρ_i, σ_i π_i ($i=1,2$) (in units of 10^{-12} esu^2/cm) satisfy Eqs. (23) and (26), and are used in the LST and RAA models of the paper RIII, respectively. Charges with suffix 1 and 2 represent those on the anion and cation sites of the overlap pair, respectively.

Pair in crystal	α_1 (10^{-2})	β_1 (10^{-2})	γ_1 (10^{-2})	α_2 (10^{-2})	β_2 (10^{-2})	γ_2 (10^{-2})
Li-F in NaF	−0.06	0.42	−1.49	0	0	0
Li-Cl in NaCl	−0.07	0.57	−2.21	0	0	0
Na-F in NaF	−0.14	1.02	−3.66	0.01	−0.10	0.38
Na-F in KF	−0.03	0.25	−0.98	0	−0.02	0.09
K-F in KF	−0.15	1.23	−4.70	0.06	−0.56	2.05
K-F in NaF	−0.68	5.05	−12.0	0.31	−2.50	2.03
Na-Cl in NaCl	−0.16	1.24	−4.65	0.01	−0.05	0.16
Na-Cl in NaBr	−0.09	0.72	−2.84	0	−0.03	0.10
Na-Br in NaBr	−0.17	1.32	−5.07	0	−0.04	0.14
Na-Br in NaCl	−0.31	2.26	−8.17	0.01	−0.06	0.22
Na-Br in KBr	−0.06	0.48	−2.02	0	−0.01	0.06
K-Cl in KCl	−0.22	1.72	−6.71	0.04	−0.27	0.96
K-Cl in NaCl	−0.68	4.74	−16.4	0.11	−0.70	2.24
K-Cl in KBr	−0.13	1.07	−4.38	0.02	−0.17	0.64
K-Br in KBr	−0.25	1.99	−7.92	0.03	−0.26	0.97
Na-I in NaI	−0.17	1.38	−5.40	0	−0.03	0.12
Na-Br in NaI	−0.07	0.61	−2.53	0	−0.02	0.07
Na-Cl in NaI	−0.04	0.32	−1.39	0	−0.01	0.05
Na-I in NaCl	−0.70	4.82	−16.5	0.02	−0.10	0.36
Na-I in NaBr	−0.40	2.89	−10.5	0.01	−0.06	0.24

Pair in crystal	ρ_1 (10^{-2})	σ_1 (10^{-2})	π_1 (10^{-2})	ρ_2 (10^{-2})	σ_2 (10^{-2})	π_2 (10^{-2})
Li-F in NaF	−0.08	0.59	−2.16	0	0	0
Li-Cl in NaCl	−0.09	0.72	−2.85	0	0	0
Na-F in NaF	−0.21	1.47	−5.11	−0.04	0.28	−1.04
Na-F in KF	−0.05	0.38	−1.52	−0.01	0.07	−0.29
K-F in KF	−0.24	1.58	−5.29	−0.18	1.21	−4.51
K-F in NaF	−0.84	4.01	−10.5	−0.65	3.40	−11.8
Na-Cl in NaCl	−0.23	1.80	−6.91	−0.02	0.13	−0.53
Na-Cl in NaBr	−0.13	1.03	−4.19	−0.01	0.07	−0.32
Na-Br in NaBr	−0.23	1.83	−7.17	−0.01	0.10	−0.41
Na-Br in NaCl	−0.43	3.13	−11.5	−0.02	0.17	−0.66
Na-Br in KBr	−0.07	0.65	−2.84	0	0.03	−0.16
K-Cl in KCl	−0.39	3.09	−12.2	−0.12	0.98	−4.03
K-Cl in NaCl	−1.21	8.28	−28.3	−0.38	2.69	−9.73
K-Cl in KBr	−0.23	1.92	−8.05	−0.07	0.60	−2.61
K-Br in KBr	−0.42	3.32	−13.3	−0.10	0.79	−3.28
Na-I in NaI	−0.23	1.82	−7.27	−0.01	0.07	−0.30
Na-Br in NaI	−0.10	0.84	−3.56	0	0.05	−0.20
Na-Cl in NaI	−0.05	0.46	−2.03	0	0.03	−0.15
Na-I in NaCl	−0.92	6.33	−21.8	−0.04	0.25	−0.89
Na-I in NaBr	−0.52	3.82	−14.1	−0.02	0.15	−0.58

ly,

$$Q_{h1}=\tfrac{4}{5}[\,(\lambda_1^{(3)}-\tfrac{1}{2})S_3^2+(\lambda_1^{(4)}-\tfrac{1}{2})S_4^2-(\lambda_1^{(5)}-\tfrac{1}{2})S_5^2\,]\int_0^\infty P_{n'hp}^2(r)\,r^2\,dr\ , \quad (24)$$

$$Q_{g1}=\tfrac{4}{5}[\,(\lambda_2^{(2)}-\tfrac{1}{2})S_2^2+(\lambda_2^{(4)}-\tfrac{1}{2})S_4^2-(\lambda_2^{(5)}-\tfrac{1}{2})S_5^2\,]\int_0^\infty P_{ngp}^2(r)\,r^2\,dr\ , \quad (25)$$

and

$$\frac{e^2a_H^2}{R_0^3}W_i=\rho_i+\sigma_i\epsilon+\pi_i\epsilon^2,\quad i=1,2, \qquad (26)$$

$W_i\equiv W_h$ and $W_i\equiv W_g$ for $i=1$ and $i=2$, respectively,

$$W_h=-\tfrac{2}{5}(S_3^2+S_4^2-S_5^2)\int_0^\infty P_{n'hp}^2(r)\,r^2\,dr\ , \quad (27)$$

$$W_g=-\tfrac{2}{5}(S_2^2+S_4^2-S_5^2)\int_0^\infty P_{ngp}^2(r)\,r^2\,dr\ , \quad (28)$$

where a_H is the first Bohr radius and $P_{n'hp}$, P_{ngp} are the normalized radial wave functions as shown in RIII. The α_i, β_i, γ_i and ρ_i, σ_i, π_i $(i=1,2)$ are shown in Table VII. Of these values, α_2, β_2, and γ_2 of the K-F overlap pair in the NaF crystal give a partial saturation, namely, they do not show the usual exponential dependence on the internuclear distance.

VI. ELECTRIC CENTER OF GRAVITY OF OVERLAP-CHARGE DISTRIBUTION

In the Ra-Abarenkov-Antonova (RAA) model of RIII,[5] the overlap-charge distributions are replaced by a point charge on the ECG of these distributions.[6,7] Therefore, in order to compute the three-body potentials it is necessary to calculate the Madelung potential at this ECG due to the point charges on the normal lattice sites including the substitutional impurity charge. We have calculated this potential at the ECG of the overlap-charge distribution between the nearest-neighbor ions, and also those between the next-nearest-neighbor ions involving the contributions from 120^3 ions as shown in Table VIII.

TABLE VIII. Madelung potentials at the electric center of gravity of overlap-charge distributions. Madelung potentials except the contribution from overlap-pair ions are shown on the table, in order to exclude the two-body potential. The positions of ECG are described in the paper RIII.

Overlap pair	ECG	Potential
Nearest neighbor	0.6338	−0.2280
	0.6806	−0.3074
	0.7448	−0.4110
	0.7882	−0.4766
	0.8104	−0.5087
	0.8683	−0.5874
Next-nearest neighbor (anion-anion)	0.4319	2.8027
	0.4445	2.8074
	0.4500	2.8092
	0.5613	2.8054
	0.5732	2.8005

All values on Tables II–VIII in this study are utilized in calculation of the three-body potentials in RIII.

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