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An *Ab Initio* Molecular Orbital Approach to Electronic Structures of the F Center in NaCl.[†] Effects of Basis Set and Cluster Size

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NaCl clusters with a Cl^- ion vacancy, $Na_6{}^{6+}$, $Na_6Cl_{12}{}^{6-}$, $Na_{14}Cl_{12}{}^{2+}$, and $Na_{14}Cl_{18}{}^{4-}$, are calculated by *ab initio* molecular orbital calculations to investigate electronic states of F centers in alkali halides. The model clusters are embedded in a point charge field. Description of "1s" ground and "2s" and "2p" excited states of an electron trapped by the vacancy is discussed concerning to basis set and cluster size. The 1s and 2p wave functions of the F-center electron are efficiently described by one s Gaussian-type function placed on the vacancy center and one p Gaussian-type functions placed on the nearest neighbor Na ions when Na 3s is of double ζ quality. The 1s–2p excitation energy is in good agreement with the experimental data. As regards the electron binding energies and the orbital size the 1s wave function almost converges in the cluster $Na_6Cl_{12}{}^{6-}$ but the 2p wave function does not converge even in the largest cluster $Na_{14}Cl_{18}{}^{4-}$.

The alkali halides are transparent to the visible light and are insulators. These properties are well explained by the results of the band theory; that is, the energy gaps between the valence and conduction bands are of the order of 10 eV. However, when the alkali halide crystals are exposed to X-rays, new photoabsorption bands appear in the visible range, and are not simply understood within the band theory. It is well known that these absorption bands come from electrons or holes trapped by defects in the crystal. The defects with trapped electrons or holes are called color centers. Of the color centers the F center has been most widely studied. The F center is regarded as an electron trapped by a vacancy at one of the halide ion sites (negative ion vacancy). The trapped electron is bound by an O_h-symmetry electrostatic field created with the surrounding ions. The visible absorption would correspond to transitions from a 1s state to np states (n=2,3,$\cdots$) if a negative ion vacancy in an electronically neutral lattice were approximated as a localized positive charge and an F-center electron behaved hydrogenic in a spherical potential field.

Several groups have applied the Hartree–Fock (HF) theory, or molecular orbital (MO) theory, to investigate electronic structures of the F center.[1—12] In 1950's and 1960's one-electron model calculations based on HF-like methods were performed.[1—7] Inui and Uemura[1] obtained one-electron wave functions of an F-center electron by multi-center expansion with an s-type function on each nearest neighbor alkali ion and by hydrogenic functions at the vacancy center. They treated other ions as point charges and evaluated the Madelung energies by using Evjen's method[13] and the dielectric polarization by locating dipoles at the lattice points. Gourary and Adrian[2] improved one-center wave functions of an F-center electron by using several trial functions so as to avoid the violation of the boundary condition at the vacancy center. They regarded all ions as point charges and summed up Coulomb potentials with series of spherical harmonics. Kojima[3] improved the one-electron wave functions by combining one-center and multi-center expansions, by adding a p-type function on each nearest neighbor Li^+ ion, and by orthogonalization up to the fifth neighbor ion cores in LiF.

In 1961 Wood and Korringa[4] compared the one-center and multi-center wave functions and concluded that the properties of the F center could be described quite well with simple hydrogenic functions if they were orthogonalized to the functions of neighboring ion cores. Martino[5] and Opik and Wood[6] tried describing the one-electron wave functions by linear combinations of Slater-type functions and orthogonalized them up to sixth and third neighbor ion cores, respectively. Martino[5] reported that exchange effects with at least first and second neighbors should be considered. Leung and Song[7] described the wave functions with Gaussian-type functions orthogonalized to the ion cores up to the fifth neighbors in LiF, and found that the results were quite sensitive to the choice of core orbitals. In those approaches exchange interaction of the F-center electron with the ion cores was included through the orthogonalization but polarization of the ion cores was not allowed.

In 1976 Chaney and Lin[8] obtained many-electron wave functions with an F-center electron in LiF based on an approximated (not self-consistent) Hartree–Fock–Slater method. They placed Li 1s and F 1s, 2s, and 2p minimal CGTF's (contracted Gaussian-type functions) up to the sixth neighbor ions and added several sp (s and p) primitive functions at the first neighbor Li^+ ions and a few sp primitive functions at the second neighbor F^- ions. They placed four s primitive functions at the vacancy center for the 1s state and no functions for the 2p state. However, their primitive functions

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[†] This paper is dedicated to the late Professor Hiroshi Kato.

were rather tight and were not specifically optimized. In 1980 Murrell and Tennyson[9] performed for the first time *ab initio* SCF-MO calculations including the third neighbor ions in LiF. They added Li 2s and 2p minimal CGTF's at the first neighbors and placed F double ζ (DZ) CGTF's with addition of some optimized sp functions at the vacancy center. Kung, Kunz, and Vail[10] applied the spin-unrestricted HF (UHF) method and found that the spin polarization is important in predicting spin density of F-center electrons, but included no higher shells of neighbors than the first one. In LiF they placed several primitive s functions at the vacancy center and Li 1s quadruple ζ CGTF's with addition of a few p functions at the first neighbors.

To avoid difficulties in the lattice sum some approaches were proposed.[11,12] Yu, De Siqueira, and Connolly[11] included only first neighbor ions in model clusters and wrapped them in the Watson sphere[14] carrying charges equal and opposite to those of the clusters. Pandey, Seel, and Kunz[12] calculated isolated alkali halide cation clusters such as $(\mathrm{Na}_n\mathrm{Cl}_{n-1})^+$, without Coulomb fields created by surrounding ions, and discussed excitation energies of an excess electron by relating to electron affinities. Unfortunately their cluster models were too small to simulate negative ion vacancies embedded in crystals (the maximum number of n was 6).

Even with large amount of work, there is no apparent consensus on the basis set and cluster size and on the method to evaluate exchange interaction and polarization correctly. In the present work, the wave functions of ground "1s" and excited "2p" states of the F-center electron are investigated in the NaCl crystal by including up to the fourth neighbors based on the *ab initio* SCF-MO method. The cluster size dependence and the basis set dependence are discussed as regards the shape of one-electron wave functions and the excitation energies.

Method

Primitive basis functions for Na and Cl were taken from (533/5) and (533/53) contracted Gaussian-type functions of Huzinaga et al.[15] The contraction schemes used are (5321/5) and (5321/521) for Na and Cl, respectively. The cluster models examined are $\mathrm{Na}_6{}^{6+}$ (the first neighbors), $\mathrm{Na}_6\mathrm{Cl}_{12}{}^{6-}$ (the first and second neighbors), $\mathrm{Na}_{14}\mathrm{Cl}_{12}{}^{2+}$ (up to the third neighbors), $\mathrm{Na}_{14}\mathrm{Cl}_{18}{}^{4-}$ (up to the fourth neighbors). The bond length between Na and Cl was taken from the crystal data. The distances between the vacancy center and the first and third neighbor Na ions are 2.810 and 4.867 Å, and the distances between the vacancy center and the second and fourth neighbor Cl ions are 3.974 and 5.620 Å. The largest cluster $\mathrm{Na}_{14}\mathrm{Cl}_{18}{}^{4-}$ is shown in Fig. 1. The geometry was kept unchanged around a vacancy. Relaxation in the local structure will be discussed elsewhere. Vertical excitation energies are discussed on the basis of the Franck–Condon principle.

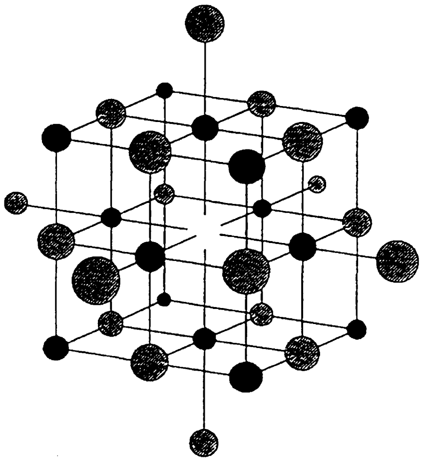

Fig. 1. $\mathrm{Na}_{14}\mathrm{Cl}_{18}{}^{4-}$ model cluster including the fourth neighbor ions around a Cl^- vacancy in NaCl.

The surrounding ions were treated as point charges ($q=\pm1$) within a radius of ca. 22 Å based on Evjen's method.[13] The total number of ions included is 1373. The resulting Madelung constant is 1.747531 and is in good agreement with the converged value 1.747565. Only 342 point charges within a radius of ca. 14 Å are enough to evaluate the Madelung constant (1.7470). The 1373 point charges are at least necessary to evaluate the Medelung constant on every ion in model clusters as accurately as possible. Similar discussion on the point charges was reported by Murrell and Tennyson.[9] All the model clusters calculated have closed shell structures and the total charges are +1 when the point charges are included. The F-center electron occupies the lowest unoccupied molecular orbital, and is excited to other unoccupied orbitals. The unoccupied orbitals are optimized for the 2N+1 system in the Hartree–Fock solution of the 2N electron (closed shell) system. Therefore, the orbital energies were optimized, and the binding energies and excitation energies were evaluated by using them based on the frozen orbital approximation. The present optimization method is different from usual methods to minimize corresponding state energies (2N+1 electron systems in the present case). The reason is to avoid the possibilities that functions to be optimized may be used to improve insufficient description of surrounding ions (so-called basis set superposition error[15]). The wave function of the F-center electron was expanded by s and p primitive Gaussian-type functions placed on the vacancy center and the nearest neighbors. The calculations were carried out using the GSCF3 code[16,17] recently adapted to a MIPS RS3230 UNIX workstation.

Results and Discussion

Basis Set Dependence. The wave functions of the "1s" and "2p" states of the F-center electron were described by the following five models.

Model A: no functions are added.

Model B: one s function at each nearest neighbor Na ion.

Model C: one p function at each nearest neighbor Na ion.

Model D: one s function at the vacancy center.

Model E: one p function at the vacancy center.

Table 1. Optimized Primitive Gaussian-Type Functions, Average Orbital Radii $<r^2>^{1/2}$ (Å), Orbital Energies (a.u.) for the F-Center Electron in a Model Cluster $Na_6Cl_{12}{}^{6-}$ Embedded in a Point Charge Field

Model		A	B	C	D	E
Orbital exponent	s		0.075		0.063	
	p			0.024		0.085
Orbital size	1s	4.23	4.25	2.92	2.12	4.27
	2p	5.71	5.70	5.36	5.71	5.38
Orbital energy	1s	−0.1131	−0.1193	−0.1434	−0.1625	−0.1112
	2p	−0.0522	−0.0539	−0.0659	−0.0521	−0.0557

Table 2. Average Orbital Raii $<r^2>^{1/2}$ (Å), Orbital Energies (a.u.), and Excitation Energies (eV) for the F-Center Electron in Some Model Clusters Embedded in Point Charge Fields

		$Na_6{}^{6+}$	$Na_6Cl_{12}{}^{6-}$	$Na_{14}Cl_{12}{}^{2+}$	$Na_{14}Cl_{18}{}^{4-}$
Orbital size	1s	1.90	2.15	2.12	2.14
	2s	5.66	5.49	6.50	6.38
	2p	4.02	5.27	5.69	6.14
Orbital energy	1s	−0.1847	−0.1601	−0.1570	−0.1545
	2s	−0.0641	−0.0746	−0.0493	−0.0603
	2p	−0.0769	−0.0671	−0.0487	−0.0535
Excit. energy	1s–2p[a)]	2.93	2.53	2.95	2.75

a) The experimental excitation energy is in the range of 2.63—2.73 eV.[18)]

The cluster $Na_6Cl_{12}{}^{6-}$ were used for all the cases. The exponents were optimized to minimize the corresponding orbital energies. The electron binding energies and the 1s–2p excitation energies obtained by direct comparison between 2N and 2N+1 electron systems (the ΔSCF method) agreed with those evaluated using the orbital energies within 0.01 a.u. and 0.004 a.u., respectively. Similar results were obtained by Murrell and Tennyson.[9)] The spin-unrestricted HF (UHF) energies are in good agreement with the spin-restricted HF (RHF) energies within 0.0004 a.u. and the spin polarization is very weak. These indicate that the frozen orbital approximation used is very effective in the present systems.

The results are shown in Table 1. Even when no functions are added (Model A), description of the 2p state is not so bad. It is probably because the 2p state is described in some degree by use of the double ζ (DZ) functions of Na 3s. The result of Model B is not so different from that of Model A. This indicates that additional s-type functions are no longer needed on the nearest neighbor Na ions because two functions with $\zeta_s \approx 0.055$ and 0.021 are placed on Na in Model A. In Model A and Model B, description of the 1s state is very bad, but in Model C the description is improved. Contribution of diffuse p functions centered on the nearest neighbors is important for the 1s state as well as the 2p state. The diffuse p function corresponds to a Na 3p orbital. This is consistent with Kojima's result that on each nearest neighbor the Li 2p function was much more important than the Li 2s function in LiF.[3)]

In Model D, the 1s state is better described than that in Model C. One s-type function placed on the vacancy center is much more effective than p-type functions placed on the six nearest neighbor Na ions in Model C. Additional s-type functions little changed the result. This is consistent with the result by Leung and Song[7)] who found that an optimized single Gaussian-type function gave energies very close to those obtained with seven unoptimized functions. In Model E, the 2p state is not so much improved. The p-type functions placed on the vacancy center are less contributive than placed on the nearest neighbors. Murrell and Tennyson[9)] also found no significant improvement in using three diffuse p functions over a single p function of exponent 0.0166 on the vacancy center in LiF.

The present results indicate that the 1s and 2p wave functions of the F-center electron are efficiently described by one s Gaussian-type function placed on the vacancy center and one p Gaussian-type functions placed on the nearest neighbor ions when the basis function of Na 3s is of DZ quality (5321/5). This result is not inconsistent with the result by Murrell and Tennyson[9)] who reported that minimal 2s and 2p functions at the first neighbor Li^+ ions and F^- DZ plus diffuse sp functions at the vacancy center appeared to be nearly saturated in the F center of LiF. The present results did not significantly change when Cl^- DZ basis functions were added on the vacancy center (without a nuclear charge $Z=17$).

Cluster Size Dependence. Through the clusters $Na_6{}^{6+}$, $Na_6Cl_{12}{}^{6-}$, $Na_{14}Cl_{12}{}^{2+}$, and $Na_{14}Cl_{18}{}^{4-}$, two functions ($\zeta_s=0.063$, $\zeta_p=0.085$) are placed on the vacancy center and one p function ($\zeta_p=0.024$) is placed on

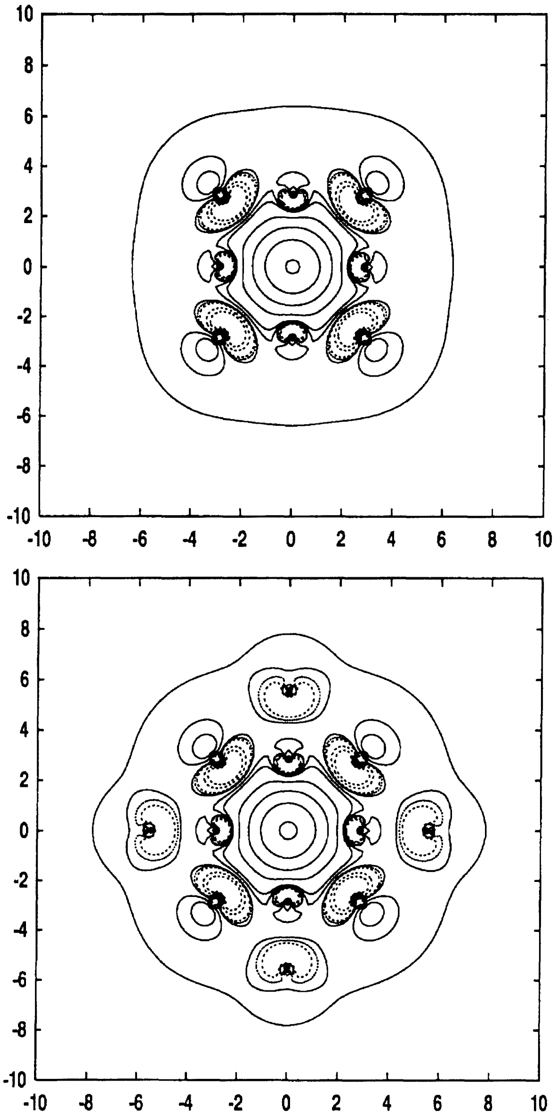

Fig. 2. Contour maps of the 1s orbitals in the model clusters, $Na_6Cl_{12}{}^{6-}$ and $Na_{14}Cl_{18}{}^{4-}$.

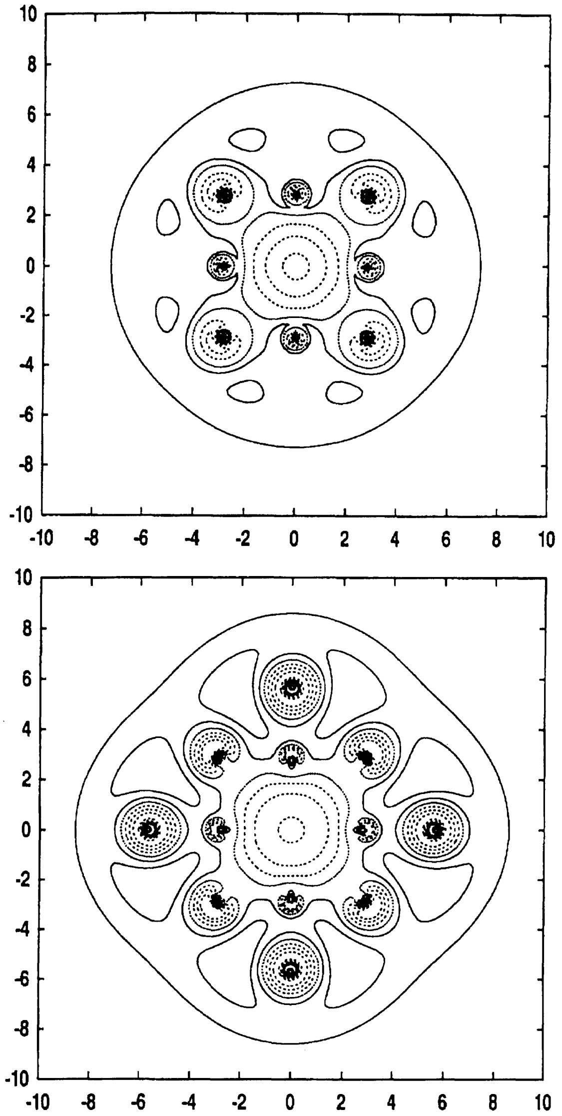

Fig. 3. Contour maps of the 2s orbitals in the model clusters, $Na_6Cl_{12}{}^{6-}$ and $Na_{14}Cl_{18}{}^{4-}$.

the nearest neighbor Na ions. The basis functions for Na and Cl are (5321/5) and (5321/521). When exponents were optimized for each model cluster of $Na_6{}^{6+}$, $Na_{14}Cl_{12}{}^{2+}$, and $Na_{14}Cl_{18}{}^{4-}$, change in the results was very small. Even when several additional functions were placed between the vacancy center and the first or second neighbors in $Na_6Cl_{12}{}^{6-}$, the results were not improved. Therefore, only the results by use of the common basis functions are shown in Table 2. The excitation energies are in agreement with the experimental values[18] within ±0.2 eV, though the lattice relaxation (distortion) around the F center is not taken into account in the present calculations.

The 1s–2p excitation energies are almost in the range of the experimental values.[18] As regards the electron binding energies and the orbital size, the 1s wave function almost converges in the cluster $Na_6Cl_{12}{}^{6-}$, but the 2p wave function does not seem to converge even in the largest cluster $Na_{14}Cl_{18}{}^{4-}$ in the present work. The 1s orbital size corresponds to the inside of the first shell; therefore, the 1s wave function has only a little effect from outer shells. On the other hand, the 2p orbital size corresponds to the outside of the maximum shell in each model, and the effects of the second and fourth neighbor Cl^- ions are large. This indicates that diffuse orbitals of surrounding Cl^- ions are used to describe the 2p state and the orthogonality with surrounding Na^+ ion cores raises the energy of 2p electron. The 2s state is found in the lower energy region than the 2p state, though the basis functions are optimized for the 1s and 2p states of $Na_6Cl_{12}{}^{6-}$. The 2s orbital is converging to nearly the same size as the 2p orbital. Similarly to the 2p state, the 2s state is stabilized by the surrounding Cl^- ions and destabilized by the surrounding Na^+ ions.

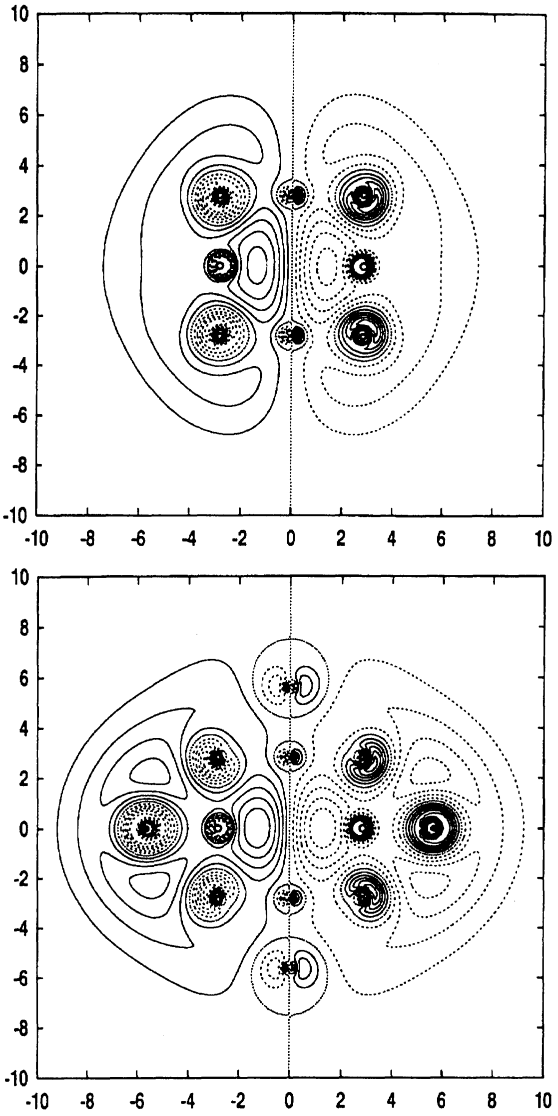

Fig. 4. Contour maps of the 2p orbitals in the model clusters, $Na_6Cl_{12}^{6-}$ and $Na_{14}Cl_{18}^{4-}$.

Figures 2, 3, and 4 show contour maps of the 1s, 2s, and 2p orbitals in the clusters $Na_6Cl_{12}^{6-}$ and $Na_{14}Cl_{18}^{4-}$. Figure 2 clearly shows that in the 1s state most part of the wave function lies inside the vacancy. This is consistent with the orbital size. To describe the 1s state the cluster $Na_6Cl_{12}^{6-}$ is a good model when s-type basis functions are placed on the vacancy center. Furthermore, the first and second neighbor ions are polarized towards the vacancy center. This is the reason why diffuse p functions like Na 3p are important on the first neighbors. In the 2s state the nodal plane lies near the first neighbors and most part of the wave function lies outside the vacancy. The inside part is well described by the basis function used to describe the 1s state and the outside part is described by diffuse functions on the surrounding Cl^- ions. To more satisfactorily describe the 2s state additional basis functions may be needed outside the second neighbors as well as inside. In the 2p state the wave function lies both inside the vacancy and around the third and fifth neighbor Cl^- ions. This is the reason why diffuse p functions placed on the first neighbors are more important than p functions placed on the vacancy center.

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