Two types of self-trapped excitons in alkali halide crystals

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We have carried out *ab initio* many-electron variational calculations of the adiabatic potential-energy surface (APES) for the lowest triplet state of the self-trapped exciton (STE) in KCl and LiCl. For KCl, it is found that at the APES minimum, the Cl_2^- molecular ion comprising the STE hole is displaced along the $\langle 110 \rangle$ axis by about 0.90 Å from its symmetrical position. The STE electron and hole are shifted in the direction opposite to that of the Cl_2^- displacement. The calculated optical-transition energies due to electron and hole excitations of the STE at the APES minimum, and the luminescence energy due to the transition to the crystal ground state agree well with the experimental results. It is found that the $\langle 110 \rangle$ displacement of the Cl_2^- molecular ion at the APES minimum from its symmetrical position for LiCl is 0.07 Å, much smaller than that in KCl, and that the direction of the shift of the electron and hole is opposite to that for KCl; the electron and hole are localized near one of the Cl_2^- ions located closer to the lattice site. It is shown that, for a small shift of the Cl_2^- molecular ion from its symmetrical position, the states in which electron and hole are shifted to opposite directions appear in both LiCl and KCl crystals within energy intervals less than 0.8 eV. It is pointed out that the configuration interaction between the two states with the electron and hole shifted in opposite directions should be included for more precise APES calculations at small off-center displacements, and that the electron-hole correlation is important to determine the electronic structure of the STE.

I. INTRODUCTION

Mechanisms of self-trapping of excitons and the electronic and atomic structures of self-trapped excitons (STE's) have attracted the interest of scientists, in particular since it was made clear that the primary processes of photolysis of the crystal are initiated by self-trapping of excitons.[1,2] Presently a great deal of information on spectroscopic properties of the STE has accumulated and been reviewed by several authors.[3–5] Despite many current investigations utilizing sophisticated experimental techniques, the microscopic structure of the self-trapped excitons is not yet clear. The structure of the self-trapped holes (V_K centers) in alkali halides has been well established: it consists of an X_2^- molecular ion (X denotes a halogen atom) occupying two halogen lattice sites and has a local symmetry corresponding to the D_{2h} point group.[6,7] It is known that a self-trapped exciton is created after relaxation of a free exciton or trapping of an electron by a V_K center.[3–5,8]

It has been believed for a long time that the self-trapped exciton has a D_{2h} symmetry, having the atomic structure of an electron trapped by the Coulomb field of a positively charged V_K center ($V_K + e$ model) (Refs. 3 and 9) as shown in Fig. 1(a). Electron-nuclear double-resonance (ENDOR) studies[10,11] of the STE in KCl have shown that the two chlorine atoms of the Cl_2^- molecular ion are not equivalent. Furthermore, the isotropic hyperfine interaction of the STE electron with surrounding cations is more likely that of the F center (an electron

trapped by an anion vacancy) rather than that which one can expect from the ($V_K + e$) model. These experimental results have been explained by theoretical calculation using the one-electron model on the basis of the pseudo-Jahn-Teller effects.[12] Further development of this theory has been carried out by Song and Leung (SL theory) using the one-electron approach, where the STE electron has been treated in an extended ion approximation using the hybrid-potential method.[5,13–16] It has been shown that the X_2^- molecular ion of the STE is displaced along the $\langle 110 \rangle$ axis in a wide class of alkali halides, and thus the STE has a C_{2v} symmetry and its structure is more likely the nearest pair of an F center and an H center (X_2^- molecular ion occupying a single anion site) rather than ($V_K + e$) [see Fig. 1(c)]. The configuration of the STE in which the halogen molecular ion is displaced is referred to as an off-center configuration and the ($V_K + e$) configuration as an on-center configuration. According to the SL theory, the displacement of the X_2^- molecular ion from the ($V_K + e$) configuration arises from the repulsive character of the nonlocal pseudopotential of the X_2^- molecular ion for the STE electron and the attraction of the electron to the anion vacancy formed after off-center displacement of the X_2^- molecular ion.

The SL theory has given reasonable accounts of a large number of the experimental data[5,16] but leaves several substantial questions unsolved. According to the theory, the X_2^- molecular ion of the STE occupies an intermediate position between the ($V_K + e$) and nearest F-H pair configurations and hence their two halogen ions are not

necessarily located at equivalent positions of the crystalline lattice. Thus the gradient of the crystalline field between the nonequivalent positions may produce a large polarization of the X_2^- molecular ion, which has to be taken into account in the calculation. Such polarization has been indeed observed for the H center in CaF_2.[17] Moreover, although the SL theory deals with the triplet STE state, the interaction between the two unpaired electrons is not treated explicitly. The exchange and correlation between these two electrons may play a major role in the process of exciton self-trapping and its decay to the Frenkel pair. Both effects can be treated only in the many-electron theory.

Recently, many-electron *ab initio* theory has been applied to the study of the structure of the self-trapped excitons in LiCl by Shluger, Grimes and Catlow[18] and in several alkali halides by Baetzold and Song.[19] The results of the calculation have confirmed the off-center character of the STE. The former authors have calculated the adia-

batic potential-energy surface (APES) and according to their results the shift of the X_2^- molecular ion in LiCl from the on-center position is very small, the X_2^- molecular ion is strongly polarized, and both the electron and hole are located near one of the anions of the X_2^- molecular ion situated closer to the anion site, as shown in Fig. 1(b). We refer to this type of STE as the *compact* type, since the electron and hole are localized in a potential well having small extent. These results are the consequence of the many-electron approach which treats correctly the polarization of the hole component of the exciton and considers the interaction between the unpaired electrons on the background of unrestricted Hartree-Fock theory. Further analysis of this STE model may bring deeper understanding of the nature of self-trapping in alkali halide crystals. Moreover, it was concluded that the new type of electronic structure of the STE is due to a large anion- to cation-radius ratio of LiCl. The results of the calculation by Baezold and Song for other alkali halides have given the noncompact-type configuration, as shown in Fig. 1(c), although their calculation has been carried out only for a fixed amount of displacement. It is of interest to carry out calculation of the APES for an alkali halide having a smaller anion- to cation-radius ratio, for instance for KCl, for which a large number of experimental data are available.

The self-trapped excitons in KCl emit only the so-called π luminescence due to radiative transition from the triplet state. The transition energy for creation of the 1s free exciton is 7.77 eV, while the photon energy of the π luminescence is 2.31 eV.[3-5] The absorption energies due to electron transitions of the STE are known to be 1.87, 2.10, and 2.19 eV (Ref. 20) and that due to the hole transition is 3.7 eV.[21] The quenching of π luminescence occurs at very low temperature.[22] The magnetic-resonance parameters of the STE in KCl have been studied[10,11] and it has been shown that the hyperfine interactions of the unpaired electrons with the two halogen nuclei consisting of the X_2^- molecular ion are not substantially different.

The purpose of the present paper is to study the APES for the lowest triplet excited state and the structure of the self-trapped exciton in KCl and LiCl on the basis of a many-electron *ab initio* approach. The atomic and electronic structures of the V_K center in KCl have also been studied using the same method. The results of calculation for KCl show that, at the configuration of the APES minimum, the X_2^- molecular ion of the STE is off centered and the STE is polarized strongly in such a way that both the electron and hole are shifted towards the direction of the vacancy, as shown in Fig. 1(c). We obtained the optical-absorption energies and vibrational frequencies of the STE and V_K center and the π luminescence energy of the STE; all of these values agree with experimental results. The nature of the instability of the on-center configuration and of the strong shift of the electron and hole of the STE is discussed on the basis of quantum-chemical and pseudo-Jahn-Teller analysis. It is shown that, for a small shift from the on-center position both in KCl and LiCl crystals, two states of the STE, compact and noncompact [see Figs. 1(b) and 1(c)], can
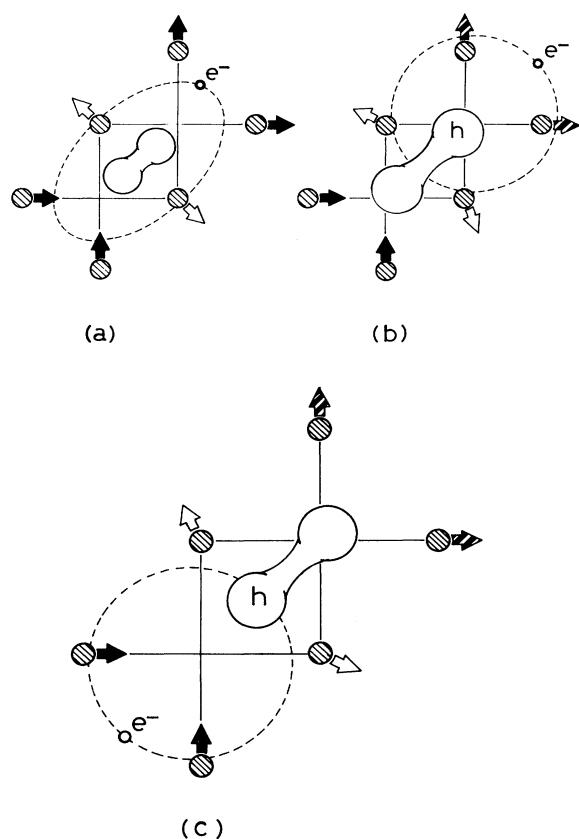

FIG. 1. Schematic diagram of on-center and off-center positions of the self-trapped exciton: (a) the on-center configuration (D_{2h} symmetry), in which each halogen of the X_2^- molecular ion possesses a half positive hole, (b) the off-center configuration of compact type, in which both the electron and hole are shifted toward the halogen ion usually by a small amount, and (c) the off-center configuration of the noncompact type in which both the electron and hole are shifted toward the halogen ion by relatively a large amount.

appear with only a small difference in energy. It is concluded that the configuration interaction between these two states should be taken into consideration for precise APES calculation at small off-center displacements, and that the correlation of the two unpaired electrons is important in determining the electronic structure of the STE.

II. METHOD OF CALCULATION

In the present study of the STE structure of LiCl and KCl, we used the ICECAP (an acronym for ionic crystal with electronic cluster: automated program) method and computer code. Several papers have been devoted to the description of the basis of the method and its applications to simple defects in several ionic crystals (see Ref. 23 for a review). Thus we restrict ourselves only to brief explanation and discussions of calculation necessary for understanding the physical implication and accuracy of the obtained results.

In the ICECAP method an infinite crystal including a point defect is treated on the basis of the embedded-molecular-cluster model. Generally in this model the wave function of a crystal with a defect is considered to be an antisymmetrized product of many-electronic wave functions of a small quasimolecular cluster (referred to as a quantum cluster) and the rest of the crystal.[24,25] In this approximation, two separate problems, the electronic structure of the quantum cluster in the field of the rest of the crystal and the distortion of the structure of the rest of the crystal (the polarization) as a result of the perturbation produced by the defect, have to be solved self-consistently. The same theory has been employed in the cluster methods,[26−28] which have been used successfully for investigations of defects in ionic crystals.

As has been shown by several authors, the crystal can be divided most precisely into two regions, the quantum cluster and the rest of the crystal, in the case when the electron density of the perfect crystal may be represented by a combination of the localized electronic groups.[27−31] This representation is not unique generally. However, separation of the electron density of an ionic crystal into a combination of densities of ions is usually a good approximation. This explains the success of the application of the cluster model to defects in ionic crystals. However, the quantum theory of polarization of a crystal by a point defect is rather complicated and is far from completion.[27,32] In particular, it has been shown recently that the correct account of the exchange and correlation effects between localized electronic groups outside of the cluster and the cluster electrons requires further development of the general theory of many-electron systems.[33,34]

Presently, for practical applications simplified approaches have been used in treating the polarization of a crystal by a point defect. One of the best known methods for calculation of the polarization is to use the Mott-Littleton procedure based upon a description of a lattice in terms of effective potentials and the shell model of ions.[35] The known computer codes, HADES and CASCADE, are based on this approach, which is described in several reviews.[36]

The ICECAP code is a combination of the two well-known programs, namely unrestricted Hartree-Fock (UHF) and HADES.[23] The UHF code allows one to carry out *ab initio* calculation of the electronic structure of a quantum cluster embedded in the Coulomb field of the rest of the crystal using the unrestricted Hartree-Fock-Roothaan method. The HADES code calculates the response of the lattice around the quantum cluster due to the presence of a defect on the basis of the shell model.

In the present calculation, in order to consider the transformation of the STE from the D_{2h} to C_{2v} symmetry, we used mainly $K_{10}Cl_2$ and $K_{10}Cl_4$ quantum clusters (see Fig. 2). To make the calculation of the electronic structure of the quantum cluster not so time-consuming, we employed semilocal norm-conserving pseudopotentials, developed by Bachelet, Hamann, and Schlüter[37] (BHS). In exciton calculations, the basis set of the quantum cluster was extended by including several $1s$ floating atomic orbitals (FO's). The total energy of the crystal with an exciton is a function of several parameters, namely, the coordinate of the cores of the ions of the quantum cluster and of the centers of the FO's, the exponents of the atomic orbitals including the FO's, and the coordinates of the cores and shells of ions of the rest of the crystal. In principle all the parameters described above can be varied so that the total energy of the crystal with a STE is minimized at each point on the APES. In the present calculation the basis sets of atomic orbitals of the ions in the quantum cluster were fixed.

The energy of each point on the APES for the STE and V_K center contains the following contributions: (i) the HADES energy of all the ions of the rest of the crystal,
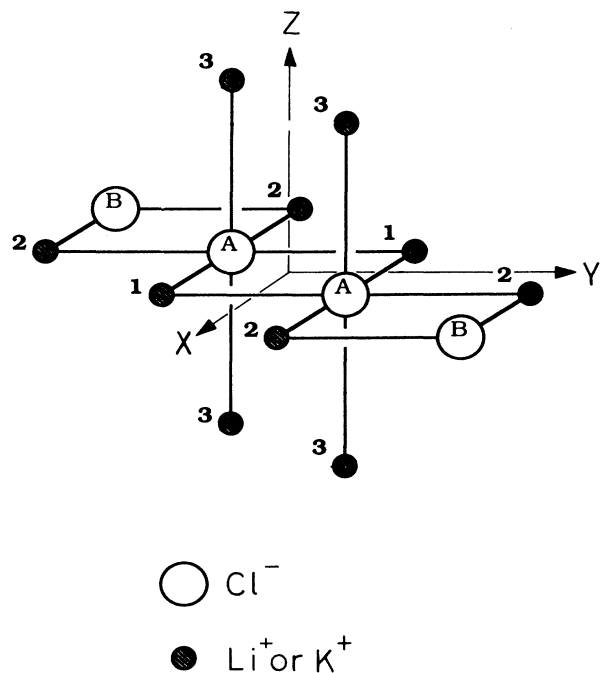

FIG. 2. The $K_{10}Cl_4$ cluster treated quantum mechanically in ICECAP calculations of triplet self-trapped excitons.

TABLE I. The parameters of $7sp$-511 basis set optimized for $3s$ and $3p$ atomic orbitals of the Cl^- ion in KCl treated with the BHS pseudopotential.

Exponents	Coefficients for s orbitals	Coefficients for p orbitals
4.153 59	0.151 216	0.004 189 34
2.239 26	−0.625 767	−0.080 448 6
1.072 13	0.259 945	0.299 490
0.477 264	0.623 183	0.546 637
0.256 532	0.459 593	0.274 116
0.133 158	1.0	1.0
0.062 397 4	1.0	1.0

represented by the shell model, for a given defect configuration; (ii) the interaction energy in the HADES calculation among all shell-model ions in region I outside the quantum cluster and of these ions with the rest of the crystal, including Coulomb, short-range, and shell-core energies; and (iii) the UHF energy of the quantum cluster, which includes the Coulomb interaction with the embedding lattice.

After each successive step of the UHF calculation of the electronic structure, the dipole and quadrupole moments were calculated and compared with those produced by the charges of the shell-model ions representing the cluster. The difference in the multipole moments was compensated by generating the additional charges which were situated near the origin of the cluster.[23] By this way the multipole consistency between the quantum-mechanical and HADES-type representations of the charge distribution in the cluster area can be achieved with a certain accuracy. The total energy of the crystal in each APES point was obtained for given positions of the nuclei of ions in the quantum cluster and of the centers of the floating functions, with the rest of the crystal relaxed according to the electron-density distribution in the quan-

tum cluster. After minimization of the total energy of the system relative to the FO's positions and their exponents, the coordinates of the ions in the quantum cluster were changed in order to find the global minimum of the total energy.

As mentioned above we did not vary the parameters of the basis sets of the atomic orbitals of the ions in the quantum cluster during APES calculation. Thus the initial choice of these parameters is crucial. In the present calculations we tried several basis sets for chlorine ions. Finally we have found that the best basis set for chlorine ions, which still allows one to make calculation of the STE in reasonable computation time, is the $7sp$-511 basis set shown in Table I. It was contracted from the $7sp$-1111111 basis set optimized to that the total energy of the K_6Cl_1 quantum cluster simulating the perfect lattice takes the minimum. Two split orbitals are necessary to reproduce the polarization of the Cl_2^- molecular ion when it is displaced from the on-center position in the lattice. For potassium ions we have used the valence portion of the (4333/43) Huzinaga contracted basis set.[38] Other comments on the basis sets will be described together with the results of calculations later.

It is known that the interaction between cores of the ions represented by the pseudopotentials is not correct for heavy ions including chlorine and potassium.[39] To avoid this problem, we introduced the exponential repulsive potential $A \exp(-BR)$ in calculating the Cl-K core-core interactions, where R is the intercore distance. The parameters A and B were obtained by fitting the adiabatic potential curve for a KCl molecule[40] to be $A = 62.958\,740\,2$ and $B = 1.479\,353\,1$.

The Buckingham pair-potential parameters for the interaction between the shell-model ions were taken from Ref. 41 and were not changed in the calculation. The value of the cation-anion separation in the lattice was taken to be 3.116 Å in all calculations, the same as that obtained in a HADES calculation of the perfect lattice using these parameters.

TABLE II. The coordinates of the quantum-mechanical cluster ions for perfect lattice, V_K center, and on- and off-center STE. The results for the V_K center obtained using several basis sets and those for the STE's obtained using basis III are shown. + superscript denotes the ions situated towards the direction of the displacement of the X_2^- molecular ion and − superscript denotes those situated in the opposite direction. The coordinates of $Cl^-(B)$ for STE indicate those of cores of the shell-model ions obtained by HADES calculation.

Ion	Perfect lattice	V_K center (basis I)	V_K center (basis II)	V_K center (basis III)	on center STE	off center STE
$Cl^-(A)$ $Cl^+(A)$	0.5;0.5;0.0	0.315;0.315;0.0	0.298;0.298;0.0	0.313;0.313;0.0	0.313;0.313;0.0	−0.023;−0.023;0.0 0.603;0.603;0.0
$Cl^-(B)$ $Cl^+(B)$	1.51;1.51;0.0	1.48;1.48;0.0	1.49;1.49;0.0	1.477;1.477;0.0		−1.49;−1.49;0.0 1.54;1.54;0.0
$K^+(1)$	−0.53;0.53;0.0	−0.66;0.66;0.0	−0.64;0.64;0.0	−0.64;0.64;0.0	−0.64;0.64;0.0	−0.65;0.69;0.0
$K^-(2)$ $K^+(2)$	1.52;0.52;00	1.56;0.48;0.0	1.56;0.48;0.0	1.56;0.48;0.0	1.55;0.48;0.0	−1.52;−0.48;0.0 1.58;0.52;0.0
$K^-(3)$ $K^+(3)$	0.5;0.5;1.03	0.497;0.497;1.06	0.496;0.496;1.06	0.497;0.497;1.06	0.493;0.493;1.05	0.49;−0.49;1.04 0.50;0.50;1.06

In order to find lattice distortion due to the presence of a defect and the defect formation energy, it is necessary to find the equilibrium positions of the ions in the cluster simulating the perfect lattice. These ions may be displaced from the ideal lattice site because of the difference in the way of treating the interactions between ions in the quantum cluster and those of the ions in the cluster with the rest of the crystal. In Table II, the first column shows the equilibrium positions of the ions in the cluster $K_{10}Cl_4$ for the basis set of Cl^- shown in Table I. One can see that the ions on the border of the cluster are displaced outwards but their displacements do not exceed 0.03 of the cation-anion distance. We can argue from the smallness of the displacements that the parameters for the interaction between ions used in the calculation are appropriate.

III. BRIEF DISCUSSION ON THE STE STRUCTURE IN LiCl

In order to compare the STE structure in LiCl with that in KCl, we give a brief discussion of results on the STE in LiCl obtained since the relevant paper[18] was submitted. As described in Ref. 18, the previous ICECAP calculation of the STE structure for LiCl gave the exciton model (compact-type STE) shown in Fig. 1(b). Three natural questions arise: (i) How may this model be influenced by changing the parameters of calculation, particularly the basis sets? (ii) Can one obtain the noncompact-type STE in LiCl [Fig. 1(c)]? (iii) How are the F-H Frenkel pairs evolved from the compact-type STE? In order to answer these questions, we made additional studies on the compact STE in LiCl.

In the previous work, ions of the quantum cluster were described using the BHS pseudopotentials and the valence portions of the Huzinaga contracted (43) and (533/53) standard atomic basis sets for Li and Cl, respectively. In addition, the basis set was extended by adding 10 or 14 1s floating atomic orbitals for STE simulation. In both D_{2h} and C_{2v} STE configurations these floating orbitals were strongly occupied by the STE electron. This result may be due to the limited basis sets, which did not include the polarization atomic orbitals.

In the present calculation we tried more extended basis sets for cluster ions and included only ten additional FO's. We used (31)-type valence basis sets for both cations and anions with exponents of the polarization functions from Ref. 38, and also optimized for usage with the BHS pseudopotential 7sp-511 basis set for Cl^- shown in Table I. In both cases we obtained qualitatively the same results as previously: the APES took a minimum for a compact-type STE with a very small displacement (0.2 Å) of the Cl_2^- molecular ion from the on-center position. These results show that the compact exciton configuration arises irrespective of the choice of the basis sets. The analysis of the population of the atomic orbitals for the extended basis sets showed that in the previous calculations floating atomic orbitals partly played a role of polarization functions of anions and cations.

We tried to obtain the noncompact-type STE in LiCl by taking the variation for the positions of the ions in the quantum cluster and also for the centers of the floating orbitals and their exponents. We indeed found the noncompact-type STE for some particular values of these parameters, but in all cases the total energy of the system was higher by not more than 0.8 eV comparing with that for the compact-type STE. All our efforts to obtain the APES for the noncompact STE in LiCl failed; the noncompact-type solution could not be obtained when the coordinates and parameters were changed only by small values. From this point of view we found that the noncompact-type UHF solution is unstable in LiCl, but its energetical closeness to the compact one indicates that the configuration interaction between these two types of Hartree-Fock solutions should be considered. We cannot justify this assumption directly by calculating the interaction of these configurations because of the computation time, but we can do so indirectly by showing that one-electron excitation does not change the STE type. We calculated the several excited states by exciting the electron and hole of the STE of the compact configuration and found that one-electron excitation indeed did not change the STE type. This result shows that the one-electron excitation is not sufficient to produce the change in the STE type and that the correlation between the unpaired two electrons is important.

One can expect that a large displacement of the X_2^- molecular ion from the on-center position would result in the noncompact-type STE or even the F-H pair, because of the Coulombic attraction of the anion vacancy to the STE electron. Thus we tried to extend the calculation of the APES for larger displacements of the X_2^- molecular ion, using the same basis set as in the previous work.[18] We found that the total energy continues to increase when the displacement is increased from the APES minimum to 0.6 Å. We did not make a calculation for larger displacement for two reasons. First, one can expect that the interaction between the two configurations mentioned above is larger at the intermediates between the compact-type STE and F-H pair; and second, as shown in the previous paper the pair-potential parameters are not accurate for a large displacement of the X_2^- molecular ion from the on-center position. Experimentally thermal conversion from the STE to the F-H pair has been observed in alkali halides having large anion- to cation-radius ratio, including LiCl.[42] Thus we expect that the compact-type STE may be converted adiabatically to the F-H pair, the wave function of which will be dominantly of the noncompact type.

IV. RESULTS OF CALCULATION FOR THE V_k CENTER AND STE IN KCl

In order to answer the question whether the on-center or off-center STE configuration is more stable, we took the following procedures: first we calculated the electronic and atomic structures of the V_K center, calculated the triplet STE of the ($V_K + e$) configuration, by adding an electron and keeping the same D_{2h} symmetry, and finally we displaced the X_2^- molecular ion along the $\langle 110 \rangle$ axis and investigated the stability of the on-center

configuration and the adiabatic potential-energy surface of the lowest triplet state of the STE.

A. V_K center

In our V_K center study we used a $K_{10}Cl_4$ (see Fig. 2) quantum cluster and several basis sets of the chlorine ions. The first basis set (basis I) consists of the valence portions of Huzinaga's standard contracted basis sets (533/53) for chlorine atoms and (4333/43) for potassium atoms. The second basis set (basis II) was the same as basis I for potassium but included the d polarization functions for a chlorine atom with exponents from Ref. 38. Finally the third basis set (basis III) was the same as basis I and II for potassium atoms and the optimized basis set shown in Table I for chlorine ions.

The HADES pair potentials suggested in Ref. 41 were fitted to reproduce the characteristics of perfect KCl with ion charges of $\pm0.994e$. In order to reproduce the polarization of the lattice by the positively charged V_K center, generally the parameters for the pair potentials between chlorine ions constructing the X_2^- molecular ion and between each of these ions and other lattice ions should be different from those between ions in the perfect lattice. As has been shown in HADES studies of the V_K center[7] and in our previous ICECAP calculation for the V_K center in LiCl,[18] alternation of the charge keeping the parameters of the short-range potential the same is sufficient to obtain a reasonable geometry of the V_K center. Therefore in the present study we also did not change the parameters of the short-range potentials.

The coordinates of the ions of the quantum cluster including a V_K obtained using the three basis sets mentioned above are shown in Table II. One can see that there is no substantial difference between the geometries of the V_K center obtained for the different basis sets. Only for basis II the equilibrium distance between the Cl ions of the Cl_2^- molecular ion is slightly smaller than those for the others. We have calculated also the optical-transition energies and the Cl-Cl stretching vibrational wave number for the V_K center using basis III. The σ- and π-transition energies were obtained to be 3.4 and 1.85 eV, in good agreement with experimental values. The stretching vibration wave number was 241 cm^{-1}, to be compared with the experimental value of 242 cm^{-1}.[43] The good agreement with experimental results shows that the pair-potential parameters and the basis sets for ions are sufficiently good for reproducing the hole component of the exciton.

B. STE of the on-center configuration

For studies of the STE we first added an electron to the V_K center and calculated the electronic structures of the lowest triplet state of the crystal using different basis sets. If the same basis sets as those used for the V_K center were used for the calculation, we found that the additional electron is spread over all cation atomic orbitals but localized mostly on K_1 and K_2 (see Fig. 2). As has been suggested by Song and co-workers[13-15] and also confirmed by Shluger, Grimes, and Catlow[18] in the STE

calculation for LiCl, one needs to extend the basis set by including the floating atomic orbitals to obtain more appropriate STE electron wave functions.

In practice, use of the floating orbitals is the simplest way to improve the quality of the basis sets. As described above in discussing the STE in LiCl, the role of the floating orbitals to extend the basis set of the type of basis I is twofold: they extend the basis set of the ions and give flexibility to the wave function of the STE electron. Such an approach gave reasonable results for LiCl, but for KCl a mere addition of the floating orbitals to basis I did not change the character of the density distribution of the STE electron; the electron wave function is still spread over the cations. It turned out that optimization of the positions and exponents of the FO's is necessary only to reproduce the distortion of the wave functions of the Cl_2^- molecular ion in the crystalline field. This shows that one needs a more complete basis set for reproducing the electron distribution of the STE correctly.

Basis III gave qualitatively most satisfactory results: wave functions of the STE electron were to be a linear combination of the atomic orbitals of cations and FO's and FO's did not participate substantially in the wave functions of the hole component of the exciton. We did not extend the basis set of the cations by including the polarization atomic orbitals because of the necessity of keeping the cluster size as large as possible in view of limited computational time. In the following calculations of the STE in KCl we used cluster $K_{10}Cl_2$ and basis III extended by 10 1s FO's, the positions and exponents of which were optimized for each point of the APES so that the total energy of the crystal took a minimum.

Similarly to the case of the V_K-center calculation, we used the same HADES parameters for the pair potentials between Cl ions in the quantum cluster and other ions in the crystal as in the perfect lattice but took the charges of the ions constituting the Cl_2^- molecular ion to be $-0.5e$. Due to the neutrality of the exciton, the distribution of the density of the exciton electron has to be reproduced also in the HADES calculation. It means that one has to keep the electron ionized from the Cl_2^{2-} molecular ion in the cluster area. There are several ways to simulate the diffuse electron-density distribution in the ICECAP method.[23] In our calculation we found it most appropriate to introduce charges on the FO's. It indeed appears that such a procedure allows one to reach rather good multipole consistency necessary for accurate calculation of the response of the lattice to the perturbation produced by the STE. Almost all the calculations were done with the same charges set equal to $-0.1e$ for all floating functions. As will be shown later, the results of the calculations did not depend substantially on the way in which the charge distribution of the exciton electron is simulated.

First we calculated the electronic structures of the ground singlet and lowest triplet states of the cluster simulating the perfect lattice. We found that the presence of the floating orbitals does not change the geometry of the singlet state, and we obtained a singlet- to triplet-exciton transition energy of 9.2 eV. The energy is larger than the experimental value by 1.4 eV, probably because

TABLE III. The relation between off-center displacement and the total energy ΔE of the crystal relative to the ground singlet state, the position, exponent and population of the floating orbital FO_1 and Mulliken populations of the two halogen ions in the quantum cluster. $Cl^+(A)$ denotes the halogen ion situated toward the directions of the displacement of the X_2^- molecular ion and $Cl^-(A)$ denotes the other halogen ion.

Δ (Å)	ΔE (eV)	Coordinates of FO_1	Exponent of FO_1	Population of $Cl^-(A)$	Population of $Cl^+(A)$	Population of FO_1
0.000	7.56	0.95;0.95;0.0	0.125	7.53	7.53	0.007
0.312	7.156	0.90;0.90;0.0	0.105	7.31	7.95	0.208
0.499	7.062	0.86;0.86;0.0	0.102	7.27	7.95	0.274
0.686	6.975	0.82;0.82;0.0	0.100	7.25	7.93	0.332
0.841	6.888	0.78;0.78;0.0	0.096	7.24	7.91	0.417
0.904	6.852	0.765;0.765;0.0	0.094	7.24	7.90	0.438
0.975	6.888	0.75;0.75;0.0	0.092	7.23	7.89	0.466
1.109	6.921	0.72;0.72;0.0	0.088	7.22	7.87	0.521
1.202	7.094	0.69;0.69;0.0	0.085	7.18	7.87	0.525
1.483	7.476	0.60;0.60;0.0	0.076	7.13	7.86	0.667

we did not optimize and extend the basis set of the cation atomic orbitals. We minimized the total energy of the triplet state by following the procedure described in Sec. II keeping the D_{2h} symmetry. The coordinates of the quantum cluster ions at the APES minimum are close to that for the V_K center and are shown in Table II. The optimized positions of the FO's were $(\pm 0.95, \pm 0.95, 0.0)$ for two orbitals situated on the $\langle 110 \rangle$ axis and $(\pm 1, 0.0, \pm 0.5)$ and $(0.0, \pm 1, \pm 0.5)$ for the other eight orbitals. The exponents of all floating functions were found to be 0.125 a.u. The populations of the Cl ions and the FO's located on the $\langle 110 \rangle$ axis (FO_1 and FO_2) are shown in Table III. The gain of the energy due to the exciton localization on the D_{2h} configuration was found to be 1.7 eV.

C. Off-center STE

In the ICECAP code the Hartree-Fock-Roothaan equations can be solved under a restriction for the point symmetry. In order to analyze the stability of the on-center STE, we lowered the prescribed symmetry from D_{2h} to C_{2v}, keeping the coordinates the same as those for the APES minimum in the D_{2h} configuration. We found a solution in which the Cl_2^- molecular ion and the STE electron-density distribution are strongly polarized in such a way that the electron and hole are localized mostly in the vicinity of one of the anions. The energy of this solution was about 0.6 eV higher than that for the D_{2h} symmetry. This polarized configuration cannot be stable in the D_{2h} symmetry and its closeness to the D_{2h} configuration energetically may indicate that the STE is unstable with respect to the off-center displacement of the Cl_2^- molecular ion.

Direct calculation of the APES has indeed shown that the global minimum of the total energy appears at the off-center displacement by 0.9 Å, as seen in Table III. In this table, which contains the results for several off-center displacements of the Cl_2^- molecular ion, ΔE indicates the energy difference between the singlet state of the perfect cluster and the triplet state at each off-center displacement, minimized with respect to all other variational parameters (see Sec. II). $Cl^+(A)$ denotes the anion which becomes closer to the lattice site [see Fig. 1(c)] and $Cl^-(A)$ denotes the other anion, while FO_1 denotes the floating orbital situated on the $\langle 110 \rangle$ axis on the side of $Cl^-(A)$. According to Table III, it is clear that the STE in the off-center position is of noncompact type; both the electron and hole are strongly displaced to the vacancy side [see Fig. 1(c)]. The configuration of the ions at the minimum of the APES is shown in Table II. The gain of the energy by the off-center displacement is about 0.7 eV.

Table III indicates also that the coordinates and exponents of FO_1 depend strongly on the off-center displacement. In particular, its population becomes closer and closer to the F-center type as the displacement increases. The change in the exponent is also substantial. Although not shown in the table, we found that the exponents and positions of other FO's change from the values for the D_{2h} configuration. It is evident from Table III that the APES in a wide region near the minimum is very soft with respect to the off-center displacement of the Cl_2^- molecular ion. On the other hand, we estimated the wave number for the Cl-Cl stretching vibration to be about 355 cm^{-1}, which is much larger than that for the V_K center.

The energy of the vertical transition from the minimum of the APES of the triplet state to the singlet APES (π luminescence) is found to be 3.8 eV. If we take into account that the exciton transition energy is larger than the experimental value by 1.4 eV and assume that the real APES should be shifted down by this value, the difference 2.4 eV shows a good agreement with the experimental value 2.31 eV. The vertical excitation energy corresponding to the electron transitions to the lowest π- and σ-excited states were calculated to be about 2.0 and 2.2 eV, in good agreement with experimental values 1.87 and 2.10 eV for the π-polarized absorption and 2.19 eV for the σ-polarized absorption.[20] The hole transition energy was obtained to be 3.4 eV, the same as for the V_K center, in good agreement with experimental results.[21]

As for the LiCl case, we found two UHF solutions qualitatively corresponding to the compact- and non-

compact-type STE for off-center displacements smaller than 0.3 Å, although it was difficult to study the solution of the two types at this amount of displacement due to self-consistent-field (SCF) convergence reasons. In all cases when the solution was found, the energy of the compact-type solution was higher than that of the noncompact-type solution. The difference in the energy was always within 0.5 eV. Which solution was obtained depended very much on the initial wave functions for SCF iteration procedures, indicating a mixture of the compact and noncompact types of STE. These results may suggest that near the on-center configuration the real wave functions should be treated as a linear combination of the wave functions corresponding to the two types by taking the configuration interaction into account directly.

V. DISCUSSION

First let us discuss the problems existing in the approach employed in the present investigation, in order to examine the accuracy of the results of calculation. The most fundamental one is the use of the single-determinantal approximation for constructing the many electronic wave functions of the system. Partly it was discussed in Secs. III and IV and will be discussed later in conjunction with the nature of self-trapping.

There are several problems of a technical nature, besides those discussed already. One of them is the way of representing the charge-density distribution of the STE electron in the HADES part calculation. It can influence the results of calculations because the multipole consistency discussed in Sec. II may be attained only in a limited extent. In the HADES calculation the STE is represented by a charge of $e/2$ located on each of the halogen ions of the X_2^- molecular ion (hole) and a charge of $-0.1e$ on the positions where the floating orbitals are placed (electron). This presentation was kept the same in all on-center and off-center STE calculations. In order to examine how the choice of the classical representation of the charge-density distribution of the STE affects its electronic structure, we have tried several assignments of point charges to the quantum cluster ions and to the floating orbitals. In particular, we used charge-density distribution where floating function charges were taken to be $-0.05e$ or $-0.02e$ and the other part of the STE electron was distributed over all cations and calculated several points of the APES. We did not find any qualitative difference in the electronic structure of the exciton and the shape of the APES including the position of the minima obtained using different sets of charge-density distributions. The difference in the total energy in each particular point of the APES calculated with different charge distributions did not exceed 0.2 eV.

Another technical problem is the dependence of the short-range pair potential between the ions in the quantum cluster and surrounding lattice on the electron population on quantum cluster ions, which may affect the shape of the APES. This problem, which is common for the pair-potential method, has been discussed in several papers (see, for example, Ref. 44).

Using the many-electron approach, we showed that, at

the minimum of the APES of the STE in KCl, the Cl_2^- molecular ion is displaced along the $\langle 110 \rangle$ axis about 0.9 Å from the on-center position and the electron and hole are shifted strongly opposite to the direction of the displacement. The calculated energies of the optical absorption due to the electron and hole transitions and of luminescence agree with experimental results. Analysis of the spin-density distribution in the quantum cluster indicates that spin densities of both unpaired electrons should be taken into account in calculating the hyperfine interaction for both ions of the Cl_2^- molecular ion. Detailed calculation of the hyperfine interaction cannot be carried out in the present investigation, but we expect that the contribution of the exciton electron may cancel the asymmetrical spin distribution due to the polarization of the hole component of the Cl_2^- molecular ion.

Although the direction of the shift of the STE electron in the present calculation for KCl is the same as that obtained by the one-electron approach by Song and Leung, additional information has been provided by the present calculation. The most important point is that the hole as well as the electron are strongly shifted. Similar shift of the electron and hole has been obtained also be a recent many-electron calculation by Baetzold and Song.[19] The results imply that STE does not consist of simply a nonpolarized X_2^- molecular ion and an electron, as generally believed. Another important point is the small amount of the off-center displacement of the halogen molecular ion and also the small energy gain by the displacement, comparing with the results of the SL theory. According to the present result, the STE configuration is far from the nearest pair (F-H pair) of an F center and H center, and it appears that there is a relatively high potential barrier between the STE and the nearest F-H pair. The model of the Frenkel pair (F-H pair) formation, suggested by Williams et al.,[45] that the energy gain by the relaxation from the on-center to the off-center configuration leads to further separation of the vacancy (F center) and interstitial (H center), should be reconsidered. On the other hand, the configuration interaction between the electron- and hole-excited states of the STE is shown to play important roles in the construction of the APES, and consequently it may play a role in the dynamics of the Frenkel-pair formation process.

Now we discuss the nature of the compact- and noncompact-type STE configurations. Our results for both LiCl and KCl show that the polarization of the Cl_2^- molecular ion and the displacement of the molecule are strongly connected. Even in the on-center position the molecule can be polarized by odd-parity cation vibration, which is shown in Fig. 1(a). From this point of view, one can expect the pseudo-Jahn-Teller effect due to the interaction of the STE electron and hole with this vibration and consequently the mixing between the ground and excited odd-parity exciton many-electron states. Indeed the first unoccupied one-electron state in the on-center configuration has the symmetry of this vibration, and the exciton-electron transition energy to this state was evaluated to be 0.3 eV. The direct calculation of the APES confirms the instability of the on-center configuration. For a small displacement of the Cl_2^- molecular ion, both
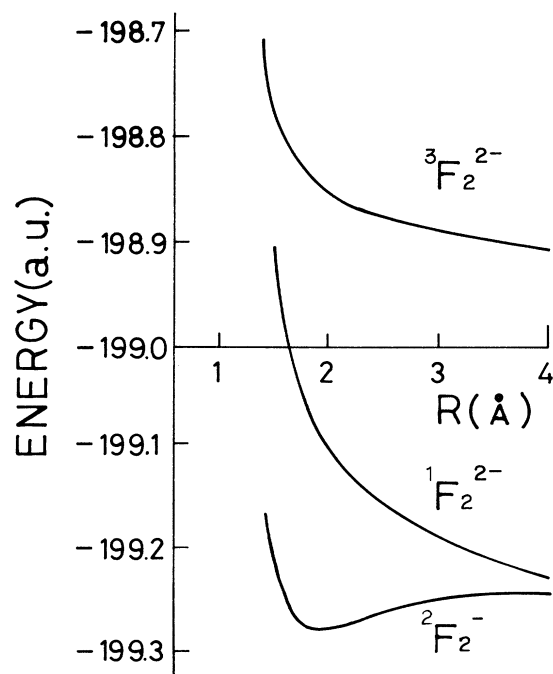
FIG. 3. The energy of an F_2 molecular ion at the ground state and an F_2^{2-} molecular ion at the ground and singlet states as a function of the F-F distance R.

the compact- and noncompact-type STE may coexist, being energetically close to each other as shown in our calculation (see Secs. III and IV). The final stable configuration is the matter of correlation between the unpaired electrons. Although the ICECAP code can take into account the electron correlation on the basis of the Moller-Plesset perturbation theory, we did not use this possibility in the present calculation due to the limitation of the computation time.

In order to confirm the importance of the electron correlation, we studied this effect for the triplet state of the free F_2^{2-} molecular ion. The calculation was carried out using the GAUSSIAN-80 ab initio molecular calculation computer code[46] using the unrestricted Hartree-Fock method. The correlation was taken into account on the basis of the second- and third-order perturbation theories.[47] As the basis set we have used the standard set of the Gaussian atomic orbitals 6-311G*+.[48] The exponent for the polarization atomic orbital was taken to be 1.750 and that for the diffuse atomic orbital which is necessary for description of the Rydberg-type excited states was taken to be 0.1076.

We have calculated the adiabatic potential energies for the F_2^- molecular ion and the singlet and the triplet states of the F_2^{2-} molecular ion as a function of the F-F

distance. The adiabatic potential-energy curves are shown in Fig. 3. The adiabatic potential-energy curve for the triplet state is much less repulsive than that for the singlet state. In the region of the F-F distance larger than 2.0 Å, the electronic configuration of the triplet state was found to be asymmetric; both the electron and hole are located on one of the anions. For smaller F-F distances the symmetric and asymmetric UHF solutions are found to coexist. The symmetry of the wave function of the triplet state of the F_2^{2-} molecular ion for distances close to the F-F equilibrium distance (1.0 Å) in the F_2^- molecular ion indicates a substantial role of the interaction of at least two electronic configurations with the same symmetry. In the first configuration the excited electron occupies the symmetrical (a_{1g}) molecular orbital and the hole an asymmetrical (b_{3u}) one. In the second configuration, in opposition to the first one, the symmetry of the molecular orbital of the excited electron is b_{3u} and that of the hole is a_{1g}. Using the perturbation theory of the third order, it was shown that, at F-F distances smaller than 2.0 Å, the coefficient of the doubly excited determinant wave function in the configuration-interaction expansion, corresponding to the double excitation mentioned above, was about 0.15. In its turn the total wave function was normalized in such a way that the coefficient of the ground-state determinant wave function was equal to 1. The coefficients of the wave functions of the other doubly excited states are much smaller.

The result shown above indicates that the asymmetry of the wave function or the polarization of the F_2^- molecular ion exists even in its free state. We expect that qualitatively the same symmetry-breaking instability occurs in other free X_2^- molecular ions and that this instability is closely related to the instability of the STE at the on-center configuration and also to the presence of the compact and noncompact types of STE. Our results indicate that the direction of the shift of the STE electron and hole depends strongly on the anion- to cation-radius ratio: for alkali halides with larger ratio the compact-type STE emerges and vice versa. One may expect that both types of STE appear in intermediate cases.

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