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Crystal Excitation: Survey of Many-Electron Hartree-Fock Calculations of Self-Trapped Excitons in Insulating Crystals

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Crystal excitation: survey of many-electron Hartree–Fock calculations of self-trapped excitons in insulating crystals

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To model successfully the diversity of electronic structure exhibited by excitons in alkali halides and in oxide materials, it is necessary to use a variety or combination of theoretical methods. In this review we restrict our discussion to the results of embedded quantum cluster calculations. By considering the results of such studies, it is possible to recognize the general similarities and differences in detail between the various exciton models in these materials.

1. Introduction

The elementary excitations of some insulating crystals form an interesting bridge between those of molecules, which are necessarily confined by the size of the molecule, and those of semiconductors, in which the electrons, holes and excitons (bound electron-hole pairs) are free to travel through the lattice. In insulating crystals such as alkali-metal halides, alkali-earth fluorides, silica and others, the excitons and holes, or only excitons, may be self-trapped to produce small radius polaron states. This self-trapping into a state which resembles an atom or molecule is accompanied by strong local lattice relaxation, and drastically alters the optical, luminescent and energy transport properties of the crystal.

Some quite basic questions concerning the self-trapped exciton (STE) remain unresolved, even in the alkali halides which are traditionally regarded as prototype insulating materials in which the microscopic features of the self-trapping processes have been studied most extensively. It is known that a self-trapped exciton in insulating crystals is created after the relaxation of a free exciton or the trapping of an electron by a self-trapped hole. Elaborate experimental studies on the STEs have been carried out during the last few decades, using optical absorption, luminescence, ENDOR, dynamics of formation in picosecond and femtosecond ranges, resonant Raman scattering and other techniques, as reviewed by Williams & Song (1990) and Itoh & Tanimura (1990). Nevertheless experimental determination of the model of the STE has not been successful so far. Therefore the model of the STE, i.e. its atomic and electronic structure, is still the main goal of theory.

The general criteria for the localization/delocalization of excitons are developed on the basis of the phenomenological theory of excitons in phonon fields, using the

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Frohlich hamiltonian and more sophisticated methods, as reviewed by Ueta *et al.* (1986). The structure and properties of the self-trapped species, however, may be studied using a static quantum mechanical approach, and it is such calculations which are reviewed in this paper.

2. Calculation techniques

(*a*) *Basic ideas*

The very possibility of this approach is based on the assumption that the exciton is well localized in a small area of the crystal. However, even if it is true, there are apparent distinctions between the ground or excited state of the localized point defect and the STE.

Self-trapped excitons are the short-living luminescent states of excited crystals, which have properties contrasting with those for the crystal ground state. Approximately, the initial states for the luminescence may be treated as stationary and correspond to the minima of the adiabatic potential of the excited crystal. The atomic structure of the excited crystal at these minima are often considered as models for STEs. (We shall not discuss the quenching of the exciton luminescence, although it also provides an insight into the STE structure as was shown by Shluger *et al.* (1991*c*).)

In the alkali-metal halides both singlet and triplet states of the self-trapped exciton have been detected experimentally. In crystalline quartz only the triplet state of the STE has been observed so far, whereas in MgO the multipole state of the exciton is not yet clear. Nevertheless most theoretical studies concern only the triplet excited state of the crystal. This is solely for technical reasons. In wide-gap insulators, as indeed all of these crystals are, the crystal ground triplet state automatically means the excited state. For the lowest multiplicity it may be treated in the single-determinant unrestricted Hartree–Fock approximation. This idea has been used in all the many-electron calculations to date. Conversely, the singlet excited state must be treated using a many-determinant approximation for the wave-function of the crystal. This is much more time-consuming and the first calculations for the singlet state of the STE in several alkali-metal halides have been made only recently using the generalized valence bond (GVB) technique by Song & Baetzold (1992).

The self-trapping of the exciton in many cases is accompanied by its decomposition. The electron and the hole, overlap strongly, but become localized in the lattice for different reasons. According to electron spin resonance (ESR) experimental data, the electron of the STE is much more delocalised than the hole. The former is localized by the crystalline potential and the degree of its localization depends sharply on the relative position of the hole. Special effort is needed in order to take this into account.

(*b*) *Background*

As in the case of experimental studies, most attention has in the past been paid to the STE in alkali halides. The defect here was believed to have D_{2h} symmetry, and the atomic structure of an electron trapped by the Coulomb field of the positively charged self-trapped hole, i.e. a V_k centre (an X_2^- molecular ion occupying two anion sites, where X denotes a halogen atom). This is the $(V_k + e)$ model.

Historically some of the first calculations of the electronic structure of the STE in this model were performed using the many-electron Hartree–Fock method. The idea of the calculations performed by Wood (1966) was to understand the key experimental fact that the luminescence of the STE has a large Stokes shift compared with the exciton excitation energy. These calculations contained all the basic ideas which were used in most further studies: (i) the exciton was treated within the same calculation technique as was developed for the calculations of point defects in insulating crystals; it also accounted for the interaction of the exciton with the polarization of the remaining crystal. (ii) The comparison of the two possible models for the qualitative interpretation of the key experimental facts. It was indeed the first simulation of the STE, which provided strong support for the $(V_k+\mathrm{e})$ model. A similar approach has been applied recently for the studies of the STE models in MgO and SiO_2.

The Hartree–Fock calculations by Stoneham (1974) were performed for a molecular cluster Na_2Cl_2 and treated both singlet and triplet states of the $(V_k+\mathrm{e})$ model of the STE in NaCl. Their aim was to produce results which could be used as a test for the simpler and less sophisticated approaches that will be necessary in more complex situations. This strategy has proved to be very successful and was used in further studies of STE models.

In particular, Song and Leung developed the one-electron approach, in which the STE was treated in an extended ion approximation using the hybrid-potential method. The specific feature of this approach was that it emphasized the role of the electron component of the STE and treated the hole as a frozen quasi-molecule. It has been shown that the X_2^- molecular ion of the STE is displaced along the (110) axis in a wide class of alkali halides and thus the STE has a C_{2v} symmetry and its structure is more like a nearest-neighbour pair: an F centre and an H centre (i.e. an X_2^- molecular ion occupying a single anion site) rather than $(V_k+\mathrm{e})$. The displacement of the X_2^- molecular ion from the $(V_k+\mathrm{e})$ configuration arises from the repulsive character of the non-local pseudo-potential of the X_2^- molecular ion for the STE electron and the attraction of the electron to the anion vacancy formed after the off-centre displacement of the X_2^- molecular ion. A similar structure is characteristic of the STE in alkali-earth halide crystals. A thorough review of this approach has been presented in recent publications by Song (1991) and Williams & Song (1990).

The theory developed by Song *et al.* has given a reasonable account of a large number of the experimental data. It has also shed light on several important questions which remained unsolved. In particular, in the framework of the one-electron approach the interaction between the two unpaired electrons of the STE is not treated explicitly. The exchange and correlation between these two electrons strongly depend on the electronic structure of the hole component of the STE and plays a major role in the process of exciton self-trapping and its decay into the Frenkel pair of the primary defects. Both effects may be treated only by many-electron theory.

(c) *Method of calculation*

Two basic models of the defective lattice were used in the many-electron studies of excitons: the molecular cluster model and the periodic defect model. To present a brief account of the computation techniques we need to give a few details of the methods and computer codes.

ICECAP and CLUSTER codes combine the unrestricted Hartree–Fock (UHF) method of calculating the electronic structure of the molecular cluster with the classical Mott–Littleton approach which accounts for the polarization of the remaining crystal (see Vail 1989; Vail *et al.* 1991 for review). One of the basic ideas of the Mott–Littleton approach is to divide the crystal into two regions: an inner region (I), containing the defect and its immediate surround, and an outer region (II) which responds as a dielectric continuum. The molecular cluster is placed at the centre of region I. There are the following basic differences between the two codes: (i) the ICECAP code uses the *ab initio* UHF method developed by Kunz & Vail (1988), whereas the CLUSTER code is based on the semi-empirical version of the UHF method implementing the approximation of intermediate neglect of differential overlap (INDO) as described by Shluger & Stefanovich (1990); (ii) the lattice ions in region I outside the cluster are treated in the ICECAP code within the shell-model approximation, as described by Vail *et al.* (1984), and in the CLUSTER code using the non-point polarizable ion approximation developed by Kantorovich *et al.* (1988). The ICECAP code was used for the calculation of the STE in alkali-metal halides, whereas the CLUSTER code was used for STE studies in oxides SiO_2, MgO and Li_2O.

The DICAP code uses the same ideas as the ICECAP and CLUSTER codes (see Puchin *et al.* 1992), but does not account for lattice polarization outside the cluster. Therefore it was extensively used to search for the extreme points on the APES in NaCl, and then further calculations using the ICECAP code were made near the extrema for comparison.

In both ICECAP and DICAP codes cations and anions inside the cluster are represented by the semi-local norm-conserving pseudopotentials of Bachelet *et al.* (1982). The same representation was used for the cations outside the cluster; this is essential to prevent unphysical delocalization of the wave-function of the excited electron. Anions may be treated either by the whole-ion pseudopotential approximation or considered as point ions.

A similar but much more simplified approach is used in the *ab initio* CAD-PAC code, which was applied recently to the calculation of the STE in several alkali halides by Song & Baetzold (1992). In this code the quantum-mechanical cluster is embedded within an array of fixed point ions. To prevent the surface atoms of the quantum cluster from undergoing unphysical displacements in the course of geometry optimisation, Born–Mayer repulsive potentials are included between all of the fixed ions adjacent to and interacting with the quantum-mechanical ions.

To follow the changes in the electron distribution, the basis set has to be flexible enough to allow different types of localization. As has been first suggested by Baetzold & Song (1991) this may be achieved by using a set of floating gaussian orbitals (FGOs) centred in different points within the cluster. This method was used in all *ab initio* calculations.

The CLUSTER code combines the possibilities of carrying out calculations of point defects within the embedded cluster and periodic models. The periodic model has an advantage of preserving the equivalence of the perfect lattice. The latter is essential for the simulation of exciton self-trapping. The main limitation of the model is the mutual perturbation of periodically arranged defects. This can be overcome by considering large periodic cells and within simplified semi-empirical techniques. This method has been applied to the study of the STE and the nearest defect pair in SiO_2 by Shluger & Stefanovich (1990).

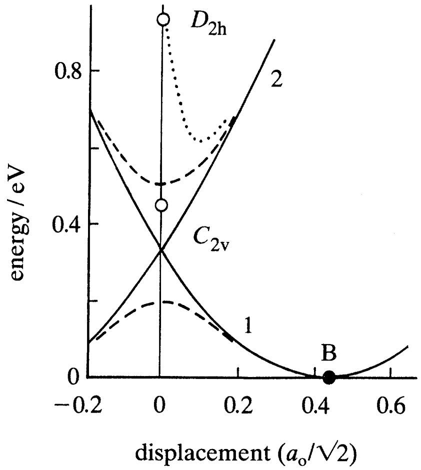

Figure 1. Section of the APES for the lowest triplet state of the STE in NaCl. The energy curves are presented in the coordinates: the displacement of the centre of mass of the Cl_2^- molecular ion along the (110) crystalline axis against the change of the total energy relative to the STE minimum (point B). All other configuration coordinates, which determine the total energy of the system, including the molecular bond length, the displacements of the surrounding ions, the positions and exponents of FGOs (see figure 2) are optimised at each point of the APES. 2 corresponds to the UHF solution with the opposite polarisation of the electron and the hole of the STE to that in 1. Dotted line corresponds to the compact model of the STE in the vicinity of the D_{2h} configuration (see Shluger *et al.* 1991; Puchin *et al.* 1992 for discussion). The D_{2h}, C_{2v} and crossing point at zero displacement of the centre of mass of the Cl_2^- molecule correspond to solutions for which the nuclei and electron wavefunctions have [D_{2h}, D_{2h}], [D_{2h}, C_{2v}] and [C_{2v}, C_{2v}] symmetries respectively.

3. Properties of self-trapped excitons

(*a*) *Atomic and electronic structure*

(i) *Alkali-metal halides*

Since it has been generally assumed that the STEs in alkali halides consist of a diffuse electron bound to a V_k centre, this model was used as a starting point in all theoretical studies. The results of recent *ab initio* calculations of the lowest triplet state of the (V_k+e) model in several alkali halide crystals (LiCl, NaF, NaCl, NaBr, KCl) performed by Baetzold & Song (1991), Shluger *et al.* (1991*b*), Song & Baetzold (1992) and Puchin *et al.* (1992) have indicated that in the framework of the UHF method this configuration is unstable with respect to the displacement of the V_k centre along the (110) crystalline axis from its original position, which had D_{2h} symmetry. However, as has been discussed by Puchin *et al.* (1992), the single-determinant UHF method fails in the vicinity of the point in the configurational space of the (V_k+e) system where the nuclei have D_{2h} symmetry (henceforth we will call it a D_{2h} point). In fact the interaction of several electronic configurations must be taken into account at this point to obtain a correct electronic energy. Nevertheless, we will assume that electron correlation is not vital far from this point and will make a critical analysis of the results obtained for the strongly off-centred configuration of the STE and the F–H pair. Some of these results will allow us to make additional comments regarding the D_{2h} point.

The most complete set of experimental data exists for the STE in NaCl. Therefore it was studied in greatest detail. The section of the APES for the lowest triplet state of NaCl, calculated by Puchin *et al.* (1992) in a wide range of configuration

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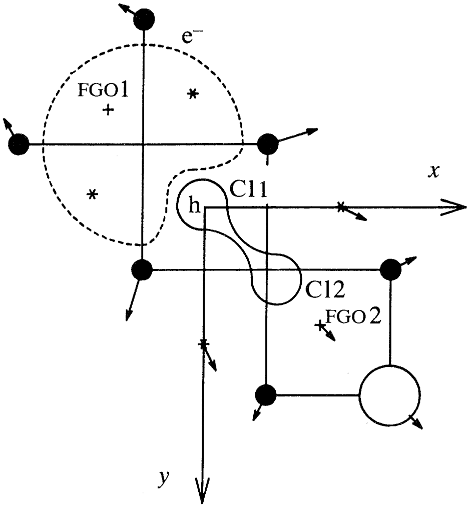

Figure 2. Schematic presentation of the off-centre model of the STE in alkali halide crystals. Arrows show the directions of displacements of ions from their lattice sites, and of floating orbitals from their positions in the D_{2h} configuration. The floating orbitals FGO1 and FGO2 are located in the (110) plane. ○, anions; ●, cations; ✱, pairs of FGOs with coordinates $(x, y, \pm z)$.

Table 1. *The calculated properties of the* STE *in several alkali halide crystals*

	structural properties and the frequencies of stretching vibration of the hole component of STE				optical excitation energy/eV		triplet luminescence energy/eV	
crystal	$R_{\mathrm{Cl1-Cl2}}$/nm	ΔQ_2/nm	δ/nm	$\omega_{\mathrm{str}}/\mathrm{cm}^{-1}$	theor.	exp.[c]	theor.	exp.[c]
LiCl[a]	0.265	0.115	0.163	—	2.8	2.2	4.4	4.18
NaF[b]	—	0.198	—	—	—	—	2.4	2.7
NaCl[a]	0.264	0.087	0.153	218	2.6	1.95	3.8	3.51
NaCl[b]	—	0.099	—	—	—	—	3.8	—
NaBr[b]	—	*ca.* 0.12	—	—	—	—	2.9	4.6
KCl[a]	0.277	0.126	0.208	206	2.0	1.87	3.2	2.31

[a] Results of Shluger *et al.* (1991*b*) and Puchin *et al.* (1992).
[b] Results of Baetzold & Song (1992).
[c] Results of Williams & Song (1990).

coordinates using the DICAP code, is shown in figure 1. The atomic configuration corresponding to the minimum B of the APES is schematically depicted in figure 2. The analysis of the APES indicates that both translational motion and rotation of the hole component of the STE are important for the determination of the positions of extreme points of the adiabatic potential. For LiCl, KCl, NaF and NaBr only the part of the APES near the minimum has been studied; this is usually attributed to the STE (point B in figure 1). Let us first discuss this part of the APES.

Some of the numerical data, characterizing the minima of the APES, are summarized in table 1, which is to be considered together with figure 2. These results were obtained by the DICAP, ICECAP and CADPAC methods. All three methods gave similar results. The electron component of the exciton is localized mainly in the anion vacancy, although about 15% of the spin density is contributed by the s orbitals of the cations surrounding the anion vacancy. More than 80% of the spin density of the hole is localized on Cl1. Thus these minima represent qualitatively the model of the triplet excited state of the crystal, corresponding to preferential localization of the hole on one anion of the X_2^- molecular ion, occupying an intermediate position between the V_k and H-centre configurations (ΔQ_2 corresponds to the displacement of the centre of mass of the Cl_2^- molecule). The excited electron, on the other hand, is attracted to the vacant anion site adjacent to the hole.

The distance between chlorine ions, Cl1 and Cl2 (see figure 2), in the Cl_2^- molecular ion, is slightly different from that in the V_k-centre, but still much larger than in the H-centre. Strong polarization makes the chemical bond in Cl_2^- weaker which results in smaller frequencies of the stretching vibrations as compared with the V_k-centre. We should note that the distances, δ, between the vacant site and the anion Cl1 in LiCl and NaCl are similar and substantially smaller than in KCl (see table 1). The calculated energies of Franck–Condon transitions, corresponding to the π polarized lowest optical excitations of the electron component and triplet luminescence (vertical transition into the ground singlet state), are presented in the last two columns of table 1.

Curve 2 in figure 1 corresponds to the configuration of the STE in which the hole is localized on Cl2 and the electron is near the anion vacancy adjacent to the hole. The points on curves 1 and 2 that have equal total energies represent two physically equivalent configurations of the electron and the hole. The single-determinantal wave-functions of these configurations are not orthogonal. This causes an artificial crossing of the two curves. In the crossing region the substantial interaction between these configurations (or in other words the electron correlation) should lead to a splitting of the two curves (in fact surfaces), which is qualitatively depicted in figure 1 by two broken curves. These may be obtained using the configuration interaction technique developed for non-orthogonal determinantal wave-functions by Broer *et al.* (1991). Therefore the shape of the APES as well as the validity of the adiabatic approximation in this region requires further study.

Since the D_{2h} state of the triplet exciton is apparently unstable, these comments are relevant first of all to the mechanism of diffusion of the STE. Within the many-electron approach this was studied only for the STE in NaCl. As has been pointed out by Chen & Song (1990), in the framework of the off-centre model of the STE, the mechanism for its diffusion in alkali halides may be considered as being comprised of two steps: (i) a joint motion of the electron and the hole along the (110) axis (the barrier for this was just discussed in the previous paragraphs); and (ii) a rotation of the hole component of the STE which changes its direction by 60°, which very much resembles the 60° reorientation of the V_k-centre. The simulation of the diffusion mechanism of the STE in NaCl was performed using the DICAP code. The calculated height of the barrier for the 60° reorientation of the hole component of the STE was equal to 0.44 eV. This is much larger than the activation energy for diffusion of the STE in NaCl (0.13 eV) (observed experimentally by Tanimura & Itoh (1981)) but close to the characteristic values for V_k-centre migration (0.54 eV for KCl). These results show clearly that the exciton relaxation energy and even the shape of its APES can not yet be calculated as accurately as necessary in all cases.

(ii) *Oxides*

Let us now compare the STE model in alkali halide crystals with that in SiO_2 which has a different electronic and crystalline structure. The self-trapping of triplet excitons in crystalline and amorphous SiO_2 has been well established experimentally.

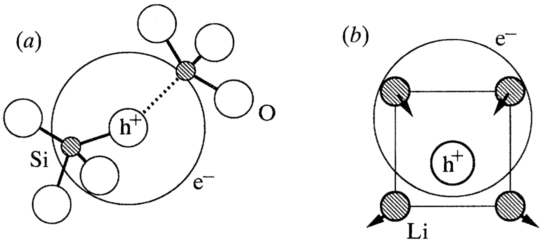

Figure 3. Schematic models for exciton structures in (*a*) SiO_2, (*b*) Li_2O.

The results of recent theoretical calculations by Fisher (1989), Shluger (1988) and Shluger & Stefanovich (1990*b*) are consistent with exciton self-trapping being accompanied by the weakening of one of the two Si–O bonds of an oxygen, in addition to the displacement of the oxygen ion (by 0.03 nm) towards an interstitial position. The electronic and spin density distributions at the minimum of the APES, described in these calculations correspond to almost complete localization of the hole component of the STE on the displaced oxygen. The rather diffuse electron component of the STE is centred at the anion vacancy (see figure 3*a*). The difference in total energy of the ground (singlet) state and the triplet state at the configuration corresponding to the energy minimum of the APES amounts to 2.7 eV. This is the Frank–Condon transition energy from the triplet to the singlet term of the system which compares favourably with the peak position (about 2.8 eV) of the exciton luminescence (see Williams & Song 1990 for a review).

A similar model to that described for SiO_2 has been predicted by Shluger & Itoh (1990) for the STE in Li_2O which has the antifluorite structure and ionic bonding. In this case, exciton self-trapping is accompanied by an almost complete localization of the hole to the oxygen which is displaced slightly along the (110) axis towards the interstitial position. The electron is localized around the lattice site of this displaced oxygen (see figure 3*b*).

In SiO_2 and Li_2O the large lattice relaxation, resulting from the unscreened hole leads to a large (often more than 3 eV) Stokes shift of the excitonic luminescence. The model often used to explain the experimentally observed excitonic-type excitation spectra for MgO is the on-centre oxygen 2p–3s excitation (see, for example, Vail *et al.* 1991). To determine whether the on-centre model of STE can also best explain the experimentally observed relatively small Stokes shift of luminescence (about 0.75 eV), several models of the triplet excitation of MgO were simulated by Shluger *et al.* (1991*a*) using the CLUSTER code. These calculations have shown that the on-centre model of the exciton, in which the hole is screened by the electron, is able to offer a reasonable fit to the available experimental data. Good agreement was found between the calculated (0.65 eV) and experimental Stokes shifts and also between the calculated exciton luminescence energy, 6.95 eV, and the experimental value, 6.9 eV.

(*b*) *Defect formation and recombination*

The creation of primary Frenkel defects, and their separation and recombination constitutes a broad class of problems, which have been studied rather extensively. The main emphasis has been on the kinetic side of the problem, and only a few microscopic calculations have been made so far. The idea of the calculations by Itoh *et al.* (1977, 1980) was to study the role of the electron and hole excited states in the STE decomposition in alkali halides. It is known that F and H centres in alkali halides are formed not only from the ground state of the STE, but also from some of the excited states. Itoh & Saidoh have suggested that there is an almost barrierless downhill potential leading from the hole excited state to the F and H centre pair.

The calculations by Itoh *et al.* (1977, 1980) were performed to check this possibility. Although the significance of the excited states of the STE in the defect formation is still not clear, some of the ideas suggested in these papers are nevertheless important. They used the CNDO semi-empirical calculation scheme and suggested a method of parametrization based on the crystal and defect properties. For the F centre calculation, the basis set of atomic orbitals was extended by a Slater-type orbital centred at the anion vacancy. This idea proved to be very fruitful and has subsequently been used in many other studies. Transfer of excitation energy from the electron to the hole components of the STE was studied quantitatively on the basis of the quantum-chemical calculations of the transition matrix elements.

The possibility of radiative tunnelling transitions (RTT) between close F and H centres was examined by Shluger *et al.* (1992). In these calculations an earlier version of the CLUSTER code was used. The luminescence due to the RTT of an electron between well-separated defects is a well-known effect in both semiconductors and ionic crystals. Its peculiarity is that the RTT occurs directly between ground electronic states of the donor and acceptor as a result of which the emitted energy depends on properties of both partners. The calculations by Shluger *et al.* (1982) predicted a small luminescence energy for the RTT between F and H centres in LiF and KCl. They emphasized the difference in the polarization of the lattice by the F–H pair and the α-I pairs of defects.

A detailed *ab initio* study of the APES for further separation of the electron and the hole components of the STE to form the nearest neighbour and the more distant F–H pair was performed only for NaCl and KCl by Puchin *et al.* (1992). In the KCl case only the adiabatic diffusion of the hole component along the (110) crystal axis was considered. The principal results of this study, which were made using the ICECAP code, may be summarized as follows: (i) the next minimum on the APES along the (110) axis is located at the position corresponding to the next nearest-neighbour F–H pair; (ii) the barrier that the hole needs to overcome to reach this minimum, diffusing straight along the axis, was calculated to be 0.54 eV, which seems too large; (iii) at the next nearest-neighbour configuration the ground singlet state of the crystal, calculated with account of lattice polarization, is located about 0.1 eV lower than the triplet state. This excludes a luminescence from this state.

A more comprehensive study has been made for NaCl, using the DICAP code. These results clearly emphasize the importance of the reorientation of the H-centre. The most compact stable configuration of the nearest F and H centres corresponds to the H-centre located in the site nearest to the F-centre anion and reoriented by 90° with respect to the initial STE orientation along the (110) axis. The H-centre in this configuration is oriented along the (111) axis. The luminescence energy, corresponding to the electron-hole recombination was calculated to be close to zero.

4. Problems and discussion

With respect to the accuracy of the theoretical methods, the single-determinant UHF method and the pseudopotential technique, have made an extensive study of the APES for the STE and the nearest defect pairs possible. However, as is clear from the results, electron correlation and the polarization of the cores of cations (especially for KCl) may play an important role. However, some qualitative conclusions may be made on the basis of the results obtained in the reviewed studies. (i) The reorientation of the hole component of the STE is an important factor which must be taken into account in the construction of the atomistic model of the STE in alkali halides. (ii) The electronic states of the STE which are responsible for the luminescence of the exciton in alkali halides are located within the limits of the configuration coordinates corresponding to the $(V_k+\mathrm{e})$ and the nearest-neighbour F–H pair. (iii) The off-centre model of the STE in alkali halides is valid but the real position of the hole component of the STE and the degree of its polarization cannot be reliably evaluated by the present technique. Despite this, the reasonable agreement between the calculated optical excitation and luminescence energies with the experimental data suggest that the models for the STE in LiCl, NaCl and KCl may not change drastically after the method is improved. The consistency of the results for five crystals also suggests that the present models may provide a good basis for further discussion of the experimental facts. (iv) Self-trapped excitons in wide band insulators are composed of localized electron-hole pairs, whose properties have certain general features. The hole state is mostly localized on one anion displaced from its lattice site. The exciton electron component is localized around the vacant anion site which is adjacent to the hole. The extent of the ion displacements, which can be quite different, depend upon the system in question and influence the degree to which the electron component is localized.

Finally, we should note that the accuracy of the many-electron calculations at the present stage is not high enough to describe fully the electronic and atomic structures of the relaxed configurations of the STEs. It is very important to make clear the elementary processes that play a role in the dynamic properties of the STEs. For instance, the pseudo Jahn–Teller instability of the one-centre and the $(V_k+\mathrm{e})$ models of the STE are not adequately understood in the circumstance where the polarization of the hole plays a role. The most fruitful approach might combine both the many-electron treatment with model hamiltonian methods.

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