

## Electronic structure of the self-trapped exciton in alkali fluorides and chlorides

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**Abstract.** We report pseudopotential calculations for the relaxed exciton in alkali fluorides and chlorides, with emphasis on NaCl. These calculations supplement earlier Hartree-Fock calculations by permitting investigation of a number of specific features. We have studied the more extended and higher energy excitations of the electron associated with the exciton, and we have considered a wider range of host lattices and crystal geometries.

The most important result is that the origin of the  $\sigma$  (singlet) and  $\pi$  (triplet) luminescence bands can be understood: the two bands derive from different orbital states, contrary to previous assumptions. Estimates of hyperfine constants, the  $\sigma$ - $\pi$  splitting and oscillator strengths are also given and agree well with experiment. The results suggest that there should be an additional  $\sigma$ -polarized absorption band of the self-trapped exciton in the infrared.

### 1. Introduction

The creation of an exciton in alkali halides is followed by substantial lattice distortion. The resulting centre, the self-trapped exciton, can be regarded for many purposes as an electron bound to an  $X_2^-$  ion, for the hole is strongly localized on two of the  $X^-$  anions. The self-trapped exciton has been the subject of much spectroscopic work, both in emission and absorption, and its nonradiative transitions play an important rôle in the radiation damage of ionic crystals.

The properties of most interest in the present paper concern the spin triplet state of the exciton, notably its spin resonance and optical absorption, and the relation between the singlet and triplet emissions associated with the self-trapped exciton. Experimentally, two luminescent bands are seen: a spin-allowed  $\sigma$  band, polarized parallel to the axis of the exciton, and a spin-forbidden  $\pi$  band with electric field vector normal to the axis. In some systems the  $\sigma$  band is not seen, and only the  $\pi$  band associated with spin triplet states is found. Qualitatively, the transitions can be understood in terms of the excitations of two halogens,  $(X^-)_2$ . The  $\sigma$  and  $\pi$  bands are usually assumed to derive from the same orbital states, differing only in spin; the different polarizations occur because the spin-orbit coupling is necessary to render allowed transitions from the triplet state. Quantitatively, this description fails miserably. Hartree-Fock calculations on NaCl (Stoneham 1974) show that the energy difference predicted is almost two orders of magnitude

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smaller than the 2 eV or so observed in practice. This discrepancy is far too large to result from a theoretical approximation, especially since the same calculations give very good predictions of other transition energies. The conclusions drawn by Stoneham, which we confirm in this paper, were these. Firstly, the singlet and triplet states derive from different orbital configurations, and not from different spin states associated with the same one-electron orbitals. Secondly, since one must explain now why there is no conspicuous emission from the spin singlet state which corresponds to the ground state of the triplet exciton, it was concluded that kinetics are important too. In essence, the excitons formed in singlet states must decay radiatively or nonradiatively before reaching the lowest singlet state.

In the earlier paper, these conclusions could not be made very precise, for the orbital basis used (whilst large) was not sufficient to identify the state from which the singlet luminescence derived. In the present calculations we use a simpler approach, based on the pseudopotential method of Bartram *et al* (1968). The method can only treat the electronic (as opposed to hole) excitations of the exciton, but is very convenient for looking at the more extended and weakly-bound excited states. It calculates the properties of the electron component of the exciton moving in a potential determined by the lattice and the self-trapped hole. We have been able to identify the states from which the two emission bands derive, and we have been able to discuss a number of other factors, including oscillator strengths and spin resonance parameters. Whilst there are still a number of questions unresolved in detail, it is possible now to give a good qualitative and reasonable quantitative description of the energy levels of the self-trapped exciton. Further, the methods used here are readily extended to discuss excitons involving impurity ions.

## 2. The model

In this section we discuss three basic aspects of the model: the geometry, the choice of Hamiltonian, and the form of trial functions used.

### 2.1. Geometry

The particular model we use allows us to treat all crystal ions in a point-charge approximation, and a finite number (typically the first ten shells) in a way which includes ion-size corrections. Thus the most important aspect of the geometry concerns the self-trapping distortion assumed.

Most of the calculations displace only the two halogens on which the hole is self-trapped. The separation of these ions in LiF, NaF and NaCl was estimated by Stoneham (1974) by fitting optical and spin-resonance observations to predictions of  $F_2^-$  and  $Cl_2^-$  properties. Other estimates are available from entirely different data (Legendijk and Schoemaker 1975, Adrian and Jette 1974, Daly and Mieher 1969, Kabler private communication) and all give very similar values. Thus, unless otherwise stated, we should assume the halogen separations to be these:

Fluorides:  $F_2^-$  separation 3.75 au

Chlorides:  $Cl_2^-$  separation 5.0 au.

No dependence of this separation on the cation species is assumed, for such a dependence is believed to be small.

Some of our calculations also displace the two cations closest to the self-trapped

exciton. Such displacements were typically 10%, an amount chosen arbitrarily so that the effects of these ion motions could be discerned.

Certain of the predictions are not sensitive to the precise displacements. The order of the electronic excited states of the self-trapped exciton is hardly altered, for example. But the luminescence energies for the  $\sigma$  and  $\pi$  emissions appear to be very sensitive. The reason seems to be this. When the exciton recombines, the electron makes a transition from a relatively diffuse state to one which is strongly localized on two halogen ions. Thus, in the final state small movements of the ions can change the Madelung potential appreciably, so the energy of this final state varies greatly with detailed geometry. By contrast, the relatively extended states of the electron are much less sensitive to distortion. In passing, we comment that the energies of  $\sigma$  and  $\pi$  luminescence will not be calculated specifically in this paper, for pseudopotential methods are not suitable for calculations of the hole state; one could, of course, use two separate methods, but this introduces addition problems. However, we shall calculate the energy difference of the  $\sigma$  and  $\pi$  bands.

## 2.2. The Hamiltonian

The pseudopotential calculations follow the approach of Bartram *et al* (1968). In this method, the defect electron (here the excited electron of the exciton) moves in a potential which is the sum of the point-ion potential and an 'ion-size' correction of the form:

$$V_{\text{IS}} = \sum_i \{A_i + B_i(\bar{v} - U_i)\} \delta(r - \mathbf{R}_i). \quad (2.1)$$

This term is a sum over ions  $i$ .  $\bar{v}$  is the expectation value of the potential energy and  $U_i$  the point-ion potential at site  $\mathbf{R}_i$ . The coefficients  $A_i$  and  $B_i$  depend only on the species of ion.

The values of the coefficients for the alkali ions  $M^+$  and halogens  $X^-$  were given in the original paper by Bartram *et al*. In their work on the F centre, it was found necessary to reduce the terms  $A_i$  by a factor  $\alpha$ , essentially independent of host and species. This factor, usually taken to be 0.53, is an empirical correction for the variation of the pseudo-wavefunction over the ion cores (Gash 1970). In the present work we have usually made the same correction for the ions surrounding the self-trapped exciton.

The parameters  $A_i$  and  $B_i$  present more problems for the two  $X^{-\frac{1}{2}}$  ions on which the hole is localized. We have estimated these as the mean of the  $A_i$  or  $B_i$  for the two charge states  $X^0$  and  $X^-$  of the halogen. In general terms, the results are that the  $B_i$  are insensitive to the charge state, and that the  $A_i$  are roughly the same in magnitude but opposite in sign for  $X^0$  and  $X^-$ . Thus  $A(X^{-\frac{1}{2}})$  is small, and it makes little difference whether any factor  $\alpha$  is included or not. Values of the parameters are listed in table 1, based on the wavefunctions of Clementi (1965). Since the  $X_2^-$  molecular ion is an open-shell system, questions arise about the spin state. We found that the difference between the exchange contributions to  $A_x$  for the singlet and triplet cases of  $X^0$  differed very little. This is consistent with the small singlet-triplet splittings given by the Hartree-Fock calculations. So in most calculations the values of  $A$  used were  $-10.10 \text{ Ryd } a_0^3$  for  $F^{-\frac{1}{2}}$  and  $-36.20 \text{ Ryd } a_0^3$  for  $\text{Cl}^{-\frac{1}{2}}$ , prior to any correction by a factor  $\alpha$ .

## 2.3. Wavefunction basis

The calculations used a general computer code, PRISM, developed at Harwell by A H Harker. This code allows one to use linear combinations of Slater functions centred on the geometric centre of the exciton. One may choose to optimize the exponents in these

Table 1. Ion-size parameters for the halogens. The results are based on Clementi's (1965) wavefunctions. For the neutral halogen,  $X^0$ , the singlet and triplet exchange terms are given separately.  $A$  is in units Rydbergs (atomic units)<sup>3</sup> and  $B$  is in units (atomic units)<sup>3</sup>.

Ion	$A_H$	$^1A_X$	$^3A_X$	$^1A$	$^3A$	$B$
$F^0$	22.236	7.324	6.186	29.560	28.422	42.68
$F^{-\frac{1}{2}}$	-10.79	0.97	0.41	-9.82	-10.38	46.77
$F^{-1}$	-43.81				-49.20	50.84
$Cl^0$	38.234	5.712	1.770	43.946	40.004	123.856
$Cl^{-\frac{1}{2}}$	-28.32	-6.92	-8.88	-35.24	-37.20	134.34
$Cl^{-1}$	-94.87		-19.54		-114.41	144.82
$Br^0$	44.374	2.335	-5.905	-46.71	-38.47	161.91
$Br^{-\frac{1}{2}}$	-36.35	-10.84	-14.97	-47.19	-51.32	176.21
$Br^{-1}$	-117.82		-24.02		-141.84	190.50

functions or the relative weights of the components of the linear combination. As a general rule we have tried two possibilities for each state:

- we have first taken a single Slater function and optimized the orbital exponent. The results make trends in behaviour particularly clear, and give guidance as to suitable exponents to take in the second method. The energies given tend to be rather high, and the convergence in the minimization is very slow.
- we have then taken a large number of Slater functions (typically 15) of s, p and d symmetry, and minimized the energy by adjusting the weights of the different terms. This method gives better energies and converges faster.

We shall usually be interested in the results of the second approach.

Since this is a one-electron calculation, we shall define the states by the one-electron orbital of the electron component of the exciton. The remaining electrons are in the same electronic configuration as in the ground state of the self-trapped hole. The symmetries of the one-electron states of the electron component will be given using the same notation as Stoneham (1974). Thus the totally symmetric states are  $A_{1g}$ , and the states which transform in the same way as p-states are  $B_{3u}$  (parallel to the  $[110]$  axis of the exciton, say) and  $B_{1u}$  ( $[\bar{1}\bar{1}0]$ ) and  $B_{2u}$  ( $[\bar{0}01]$ ) normal to the axis. We have also calculated some of the higher excited states, notably  $A_{1g}^*$  and  $B_{3u}^*$ .

### 3. Energy levels for the self-trapped exciton

We shall discuss the results in stages, so that the effects of various modifications can be determined. The effects of interest involve the trends from crystal to crystal, the flexibility of the wavefunction, the ion-size correction and the effects of lattice distortion. Results are listed in tables 2-5.

#### 3.1. The point-ion model

In the point-ion model, there are two characteristic lengths: the  $X_2^-$  separation, assumed constant for a particular halogen  $X$ , and the host lattice parameter. Thus we expect a systematic trend from one fluoride to another, and an analogous trend in the chlorides.

**Table 2.** Results for all alkali fluorides and chlorides in the point-ion approximation. The energies are in eV. In each case the bracketed energies are for trial functions consisting of a single Slater function whose exponent was varied; the other results use many Slater functions.

System	$A_{1g}$	$B_{3u}$	$B_{2u}$	$B_{1u}$	$A_{1g}^*$
LiF	-5.228 (-4.687)	-4.064 (-3.785)	-3.038 (-2.655)	-2.521 (-2.496)	-1.517
NaF	-4.726 (-4.039)	-3.948 (-3.641)	-2.940 (-2.559)	-2.352 (-2.329)	-2.351
KF	-4.431 (-3.460)	13.757 (-3.445)	-2.850 (-2.440)	-2.177 (-2.150)	-2.846
RbF	-4.225 (-3.271)	-3.675 (-3.368)	-2.831 (-2.393)	-2.115 (-2.086)	-2.623
LiCl	-4.325 (-4.016)	-3.678 (-3.354)	-2.952 (-2.578)	-2.309 (-2.291)	-1.908
NaCl	-4.304 (-3.565)	-3.568 (-3.239)	-2.865 (-2.463)	-2.178 (-2.155)	-2.469
KCl	-4.014 (-3.132)	-3.409 (-3.089)	-2.791 (-2.337)	-2.037 (-2.008)	-2.677
RbCl	-3.610 (-2.973)	-3.334 (-3.022)	-2.765 (-2.285)	-1.981 (-1.950)	-3.115

**Table 3.** Results for NaCl.

Case	Specification				State					
	$\alpha_V$	$N_S$	$N_B$	$D$	$A_{1g}$	$B_{3u}$	$B_{2u}$	$B_{1u}$	$B_{3u}^*$	$A_{1g}^*$
1	PI	0	1	0	-3.565	-3.239	-2.463	-2.155		
2	0.7	3	1	0	-1.49	-1.99	-1.31	-1.40		
3	PI	0	M	0	-4.304	-3.568	-2.865	-2.178		-2.469
4	1.32	3	M	0	-3.52	-2.73	-1.39	-1.45	-1.26	-1.34
5	1.32	3	M	10	-3.28	-2.61	-1.38	-1.44	-1.27	-1.34
6	1.32	10	M	10	-3.26	-2.50	-0.80	-0.82	-0.80	-0.53
7	1.32	10	M'	10	-3.15	-2.04	-0.84	-0.84	-0.81	-0.66
8	1.0	10	M''	10	-3.132	-2.019	-0.842	-0.841	-0.814	-0.654
9	1.0	10	M'''	10	-3.181	-2.439	-0.817	-0.818	-0.767	-0.432
10	1.0	10	M''''	10	-2.434			-0.827		-0.814
11	0.53	10	M''	10	-3.121	-1.995	-0.842	-0.841	-0.813	-0.651
12	0.53	10	M'''	10	-3.154	-2.391	-0.817	-0.818	-0.764	-0.426
13	0.53	10	M''''	10	-2.390			-0.827		-0.814
14	0.53	10	M <sup>v</sup>	10	-2.992			-0.787		-0.847

$\alpha_H = \alpha$  for ions other than  $V_K$  ions = 0.53 in all cases.  $\alpha_V = \alpha$  for the two  $X^{-1/2}$  ions; PI means point-ion approximation.  $N_S$  = number of shells with ion-size correction.  $N_B = 1$  when only one Slater function, and = M when many functions. Here M, M', M'' indicate different choices in detail. The exponents are in ratios  $K(M''') : K(M'') : K(M') = 1.3 : 0.7 : 1.0$ .  $D = \%$  outward displacement of the two nearest cations.

This is what is found, and is seen most clearly from the results using a single Slater function with variable exponent. As the lattice parameter increases, the energy levels rise, so that the energies for transitions between excited states of the exciton fall. At the same time, the wavefunctions become more extended. The trend is very similar to that for F centres in the same hosts. To give a rough order-of-magnitude, for the lowest  $A_{1g}$

Table 4. Results for NaF.

Case	Specification				State					
	$\alpha_V$	$N_S$	$N_B$	$D$	$A_{1g}$	$B_{3u}$	$B_{2u}$	$B_{1u}$	$B_{3u}$	$A_{1g}^*$
1	PI	0	1	0	-4.039	-3.641	-2.559	-2.329		
2	PI	0	M	0	-4.726	-3.948	-2.940	-2.352		-2.351
3	1.0	10	M	14	-3.113	-2.296	-0.919	-1.020	-0.894	-0.326
4	1.0	10	M'	14	-3.289			-1.033		+0.497
5	0.53	10	M	14	-3.086	-2.251	-0.919	-1.020	-0.888	-0.324
6	0.53	10	M'	14	-3.271			-0.928		+1.168
7	0.53	10	M''	k4	-2.328			-0.951		-1.006

The notation is as in table 3, except that here  $K(M)$ :  $K(M) = 0.7:1.0$ .

Table 5. Spectroscopy of the relaxed exciton in NaCl.

Transition	Hartree-Fock theory (Stoneham 1974)	Experiment (Williams and Kabler 1974)	Pseudopotential (present paper)
Ionization	3.16	2.8	Not calculated
M-like:			
$A_{1g} \leftrightarrow B_{2u}$	Not calculated		2.3-2.4 [0.24]
$A_{1g} \leftrightarrow B_{1u}$	1.49	2.1	2.3-2.4 [0.26]
$A_{1g} \leftrightarrow B_{3u}^*$	Not found		2.3-2.5 [0.02]
Other:			
$A_{1g} \leftrightarrow B_{3u}$	Not found	Not seen	0.7-1.1 [0.50]

The transition energies are in eV. The oscillator strengths for the pseudopotential case are given in square brackets [ ]; for  $A_{1g} \leftrightarrow B_{3u}$ ,  $B_{3u}^*$  the results are sensitive to factors like choice of basis. The range of values indicates the model-dependence.

Table 6. Spectroscopy of the relaxed exciton in NaF.

Transition	Hartree-Fock theory (Stoneham 1975)	Experiment	Pseudopotential (present paper)
Ionization	3.63	Not seen	Not calculated
M-like:			
$A_{1g} \leftrightarrow B_{2u}$		Not seen; M band at 2.47 eV	2.2
$A_{1g} \leftrightarrow B_{1u}$	Not calculated		2.1-2.2
$A_{1g} \leftrightarrow B_{3u}$			2.2-2.25
Other:			
$A_{1g} \leftrightarrow B_{3u}$	0.35	Not seen	0.82

state, the mean radius  $\langle r \rangle$  and lattice parameter are roughly proportional:

$$\langle r \rangle \simeq 1.23 a \quad (\text{fluorides})$$

$$\langle r \rangle \simeq 1.13 a \quad (\text{chlorides}).$$

When a large number of radial functions is used (typically 15 for the  $A_{1g}$  states and 6 for the others), the conclusions are qualitatively similar, although the energies are significantly lower. The  $A_{1g}$  state is lowest, as expected. A  $B_{3u}$  state lies a mere 0.6-0.8 eV higher

in energy, with  $B_{2u}$  and  $B_{1u}$  states lying around 2 eV above the  $A_{1g}$  state. Even at this stage, there is fair agreement with experiment, for the  $A_{1g}$ - $B_{1u}$  and  $A_{1g}$ - $B_{2u}$  transitions are the  $\pi$ -polarized M-like transitions seen by Williams and Kabler (1974). Further, the point-ion model correctly predicts the trend with lattice parameter seen by these workers. We shall argue later that the  $A_{1g}$ - $B_{3u}$  transition has not been found yet although it should be observable; it is not the M-like transition reported by Williams and Kabler, which is  $A_{1g}$ - $B_{3u}^*$  in our notation. We also argue that the  $A_{1g}^*$  state, located about 2 eV above  $A_{1g}$  in most cases, is the source of the  $\sigma$  emission.

Problems can arise in the point-ion model because the cations are so very attractive, favouring too-anisotropic functions. An example can be seen for RbF and RbCl, where the one-Slater  $A_{1g}$  state lies above the corresponding  $B_{3u}$  state. Even the simplest ion-size corrections eliminate these anomalies.

### 3.2. Effects of finite ion-size, extended basis and distortion

We need to study two separate ion-size corrections: those concerned with the two  $X^{-\frac{1}{2}}$  ions, and those concerned with the anions and cations of the 'perfect' host lattice outside. Since many of the wavefunctions we shall consider are comparable in extent with an F centre, it is reasonable to follow Bartram *et al* (1968) in reducing the  $A$  for the host ions by the empirical factor  $\alpha = 0.53$ . Various possibilities are open for the  $X^{-\frac{1}{2}}$  ions, for the rate of change of the wavefunction over their cores is different from that for the  $X^-$ , leading to other values of  $\alpha$ . We denote by  $\alpha_H$  and  $\alpha_V$  the values of  $\alpha$  for the host and  $V_K$  ions respectively.

**3.2.1. Effects of ion size.** The effects can be seen both from the single-Slater data for NaCl and from the NaF and NaCl calculations with more extended basis.

Qualitatively, all results show that the energies with ion-size corrections are less negative and the orbits somewhat more extended than the results for the point-ion model. This occurs because the ion-size corrections are repulsive on the attractive cations. The order of the energy levels is as for the point-ion case ( $A_{1g} < B_{3u} < B_{2u} < B_{1u} \leq B_{3u}^* \leq A_{1g}^*$ ) except for the single-Slater case, where the  $A_{1g}$  state is represented badly, and lies above  $B_{3u}$ .

The extent of the cancellation between the  $A$  and  $B$  terms in equation (2.1) is sensitive to  $\alpha_V$ , the values of  $\alpha_V \sim 1.3$  being closest to the point-ion results. However, the results for the energy splittings are much less sensitive to  $\alpha_V$ . We discuss later the splittings and their comparison with experiment and earlier Hartree-Fock values.

The highly-excited states prove relatively extended, and it is necessary to include ion-size corrections for at least ten shells; the lowest  $A_{1g}$  and  $B_{3u}$  states are fairly compact and the differences between three and ten shells are not important.

**3.2.2. Effects of choice of basis.** As mentioned earlier, the lowest  $A_{1g}$  state is represented badly by a single Slater function. But even with 15 Slater functions, the absolute energy levels are sensitive to the precise basis chosen. This sensitivity is most important for the lowest  $A_{1g}$  state, the higher-energy  $B_{2u}$ ,  $B_{1u}$ ,  $B_{3u}^*$  and  $A_{1g}^*$  states being roughly independent of basis. Unfortunately, the  $A_{1g}$ - $A_{1g}^*$  separation varies markedly with basis, ranging from 1.47 eV to 2.74 eV for NaCl. Since these two states have the same symmetry, one cannot merely select the lowest energy for each state separately. There is also a technical problem concerning orthogonality. In the point-ion model,  $A_{1g}$  and  $A_{1g}^*$  are orthogonal. But, with the ion-size corrections, the Hamiltonian depends on the state through  $\bar{v}$  in equation

(2.1), and strict orthogonality is not guaranteed. Fortunately, the ion-size corrections are small for NaCl and NaF, and the problem has no consequences of real significance. But care is necessary in other systems involving larger ions. Most of the sets of results for NaCl give  $A_{1g}-A_{1g}^*$  separations in the range 2.15–2.75 eV, centring on 2.45 eV, and we shall assume this is a good value. The corresponding value for NaF is around 2.75 eV.

*3.2.3. Effects of lattice distortion.* It is likely that the cations nearest to the two  $X^{-\frac{1}{2}}$  ions are displaced outwards as the two halogens are drawn together. This follows from both theoretical (Jette *et al* 1969) and experimental (Daly and Mieher 1969) work on the  $V_K$  centre. We have usually assumed a 14% outward displacement for NaF and a 10% displacement for NaCl.

The distortion has very little effect. The lowest electron levels ( $A_{1g}$  and  $B_{3u}$ ) are raised by about 0.1 eV as the attractive cations move away; the higher states are unaffected. However, as mentioned in §2.1, the energy of the state to which recombination occurs does vary with geometry. As a result, the energy of the recombination luminescence is very sensitive to distortion.

### 3.3. Summary of results

It is useful to summarize the results of these calculations to point out the common features. The notable points are these, irrespective of model, distortion, or basis:

(a) the order of the

$$A_{1g} < B_{3u} < B_{2u} < B_{1u} \leq B_{3u}^* < A_{1g}^*$$

and this order is only violated in rare special cases not of immediate concern here.

(b) the  $A_{1g}$  and  $B_{3u}$  levels are relatively compact, roughly similar in extent to an F centre. In consequence their properties are sensitive to the choice of basis, distortion and  $\alpha_V$ , but not to the number of shells for which the ion-size correction is applied.

(c) the higher states ( $B_{2u}$ ,  $B_{1u}$ ,  $B_{3u}^*$  and  $A_{1g}^*$ ) are relatively diffuse, with  $\langle r \rangle$  three or four times larger than for the lower states. The choices of local lattice distortion and  $\alpha_V$  are not important, nor is the choice of basis critical except possibly for  $A_{1g}^*$ . On the other hand, one must include ion-size corrections out to at least ten shells.

These features hold for NaCl, NaF and for the less-detailed calculations on other systems.

## 4. Discussion: spectroscopy of the self-trapped exciton

We now relate the results of §3 to experiment and with earlier theory. For simplicity, in defining the exciton states formed from the hole in its lowest state and the electron in an orbital of symmetry  $\Gamma$ , we shall write  ${}^T\Gamma$  for the triplet exciton and  ${}^S\Gamma$  for the corresponding singlet. The essential clue in understanding the observations is this: the long-lived state which gives rise to the  $\pi$ -luminescence is  ${}^T A_{1g}$ , and the short-lived state giving  $\sigma$ -luminescence is  ${}^S A_{1g}^*$ . The recombination occurs from a different orbital state in each case. This is a new feature, for the standard assumption has always been that recombination has been from a single orbital state, for example, that the  $\pi$ - and  $\sigma$ -luminescence derive from  ${}^T A_{1g}$  and  ${}^S A_{1g}$  respectively.

#### 4.1. Spectroscopy of the triplet exciton

We begin by discussing the allowed electronic transitions of the  ${}^1A_{1g}$  state, since this allows a check of our work by comparison with theory and experiment. The results for NaCl are summarized in table 5. It can be seen that there are four allowed transitions. Three (to the  $B_{2u}$ ,  $B_{1u}$  and  $B_{3u}^*$  states) correspond closely in energy to the M-like transitions of Kabler and Williams. There is also an *extra* transition to  $B_{3u}$ , with much lower energy but with a significant oscillator strength. This extra transition has not been seen yet. Its energy is somewhat model-dependent.

For NaF, similar results are found, with M-like transitions predicted at about 2.2 eV plus a  $\sigma$ -polarized transition at about 0.8 eV. The oscillator strength for this lower-energy transition is around 0.23, similar to the value for the  $\pi$ -polarized M-like transitions. Hartree-Fock calculations also show a low-energy  $\sigma$  excitation (A M Stoneham unpublished). No experimental data are available for NaF.

The results for NaCl show very satisfying consistency. The agreement of experiment and theory is at least as good as one would expect for such complicated systems. The differences between the Hartree-Fock and pseudopotential results have several obvious sources. One is the lattice distortion, since the nearest cations were moved in the present calculations. A second difference is the number of point-ions included: the present work takes an infinite crystal, whereas Stoneham (1974) treated only 48 sites. The differences in degree of self-consistency and in basis are other factors. Given so many differences, the results are acceptably close.

#### 4.2. The $\sigma$ -luminescence

We now turn to the evidence that the singlet  $\sigma$ -luminescence involves recombination from  ${}^S A_{1g}^*$  rather than  ${}^S A_{1g}$ . The arguments are these. Firstly, the  ${}^T A_{1g}$  and  ${}^S A_{1g}$  states differ in energy by a few hundredths of an eV. This is almost two orders of magnitude less than that observed, and the difference cannot be resolved by changes in geometry or basis. But  ${}^S A_{1g}^*$  and  ${}^T A_{1g}$  differ in energy by about the right amount (1.6 to 2.7 eV in NaCl, depending on the model, cf 2.0 eV observed) and both states have the correct spin and symmetry. Secondly, as Blair *et al* (1972) have argued, the dipole matrix elements for the  $\sigma$  and  $\pi$  transitions appear to be inconsistent if one assumes they both refer to the same orbital state. Finally, Kabler (1974) has argued that this work with Williams on inter-system crossing also favours an interpretation in terms of two distinct orbital states.

One obvious question follows: if the  $\sigma$  luminescence derives from  ${}^S A_{1g}^*$ , why is no luminescence seen from  ${}^S A_{1g}$ , the lower singlet state? The answer (see eg Stoneham 1974 §3.2) presumably lies in kinetics, rather than energetics. When an exciton is formed in a singlet state, as it evolves there must be a high probability of recombination (either radiative or nonradiative) before the  ${}^S A_{1g}$  state is reached. But when the exciton is formed as a spin triplet, radiative recombination is spin-forbidden in the absence of spin-orbit coupling, so that the exciton is able to reach the lowest orbital state,  ${}^T A_{1g}$ , prior to luminescing.

Two deductions can be made if this is the explanation. First, there will be a variation from system to system of the nonradiative and other processes which lead to luminescence from  ${}^S A_{1g}^*$  rather than  ${}^S A_{1g}$ . It would not be surprising if, in some systems, nonradiative processes prevent  ${}^S A_{1g}^*$ , as well as  ${}^S A_{1g}$ , being populated. Thus one might expect to find  $\pi$ -luminescence in all cases, but  $\sigma$ -luminescence only in some. This is observed: neither KCl or RbCl appear to show  $\sigma$ -luminescence, for example. Secondly, if one could popu-

late the  ${}^5A_{1g}$  state, it should luminesce. Since  ${}^1A_{1g}$  has a long lifetime, it might be possible to populate  ${}^5A_{1g}$  thermally. This would lead to a temperature-dependence of the degree of polarization and of the lifetime. Pooley and Runciman (1970 §3.4) observe a different temperature-dependence of lifetime and luminescent intensity in KCl which may be relevant; the same phenomenon may occur in KBr. There have also been some recent measurements on KCl (Purdy and Murray 1974) which indicate a state at about the right position above  ${}^1A_{1g}$ , although the observed behaviour is more complicated than suggested above. But the result is sufficiently encouraging that the effect should be sought in other systems.

#### 4.3. Spin resonance and transition probabilities

So far we have been concerned primarily with the energies of the states. We now verify that the wavefunction predictions are also satisfactory.

*4.3.1. Dipole matrix elements.* Blair *et al* (1972) have estimated that the dipole matrix element for the  $\sigma$  transition is about 0.61 Å. This is strictly  $(E_{\text{eff}}/E_0) |\langle i | r | f \rangle|$ , where  $(E_{\text{eff}}/E_0)$  is the effective-field correction, and  $|i\rangle$  and  $|f\rangle$  are the initial and final states. We have estimated  $|\langle A_{1g}^* | r | B_{3u}^0 \rangle|$ , where  $B_{3u}^0$  is an LCAO approximation to the hole state to which recombination occurs. The result is sensitive to the detailed assumptions, for there can be cancellation between the various components of the  $A_{1g}^*$  wavefunction. For the case we believe most plausible (case 8 of table 3) we find

$$|\langle A_{1g}^* | r | B_{3u}^0 \rangle| = 0.32 \text{ Å}.$$

Even without an effective-field correction, this is satisfactorily close to observation. With an effective-field correction of about a factor 2 (typical of many effective-mass and compact systems: see the surveys by Smith and Dexter 1973, Stoneham 1975) the result would be still more satisfactory.

*4.3.2. The isotropic hyperfine constants.* Spin resonance has been observed for triplet self-trapped excitons in NaF (Call 1974) and NaCl (Wasiela *et al* 1973). The zero-field splitting has been obtained in both cases, although hyperfine constants have been obtained only for NaF. Call has measured the axial hyperfine constant on the central fluorines as 395 gauss, and finds a linewidth (presumably due to hyperfine interactions with other fluorines) of 160 gauss. The hyperfine constant on the central ions is dominated by the hole wavefunction, and is not really a test of the present work. However, the electron part of the wavefunction dominates in the linewidth, where the standard formulae (eg Kittel 1954 or equation (5.8) of Stoneham 1969) are applicable.

We have calculated the isotropic hyperfine constants by orthogonalizing the electron pseudowavefunction to the ion cores using the SOPHC program developed by A H Harker. The ion cores were symmetrically-orthogonalized to each other (cf Harker 1974). The linewidths predicted (omitting contributions from the central ions) are 126 gauss for NaF and 80 gauss for NaCl. The electron contribution to the isotropic constants for the central ions is 72 gauss for NaF and 20 gauss for NaCl, assuming  ${}^{35}\text{Cl}$ . The predictions are of the isotropic constants, whereas the measurements also involve the anisotropic constants. However, it is clear that the results agree well with experiment.

## 5. Conclusions

The model proposed here is in qualitative and quantitative agreement with all available experimental data on the self-trapped excitons in alkali halides. Successful predictions include nine different energy splittings (including results from our earlier Hartree-Fock work), electric-dipole matrix elements and hyperfine constants.

The main new feature of our model is the recognition that different electronic configurations are responsible for the singlet and triplet luminescence bands. This assumption appears to remove all the significant problems of earlier models, and suggests that the main aspects of the self-trapped exciton are now satisfactorily understood.

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