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SINGLET-TRIPLET SPLITTINGS IN FREE AND SELF-TRAPPED EXCITONS

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We discuss the available experimental data for the singlet-triplet splitting of free and self-trapped excitons in alkali halides. These data are analysed quantitatively using the pseudopotential method of Bartram, Stoneham and Gash. The predictions confirm the trend emerging from the observed data, namely that the splittings are systematically lower for the self-trapped systems. This difference comes principally from the spread of the self-trapped hole onto two ions, and would not be expected, for example, if the hole were localised on a single site.

The various experimental data on excitons in alkali halides suggest that the singlet-triplet splittings are systematically smaller in the self-trapped exciton than in the free exciton. These splittings are, however, not measured directly as such. Rather, they are deduced from analyses of optical absorption for free excitons[1,2,3], and of emission or spin resonance for self-trapped excitons[4,5]. Further the data are not so complete as to make trends obvious. Nevertheless, it appears that the splitting is definitely lower for the self-trapped exciton than for the free exciton. This difference is the main subject we discuss in the present note, and we shall verify the mechanism we propose by the agreement between observed values and those predicted using a pseudopotential method.

The singlet-triplet splitting of the exciton is determined by the electron-hole interactions. This, in turn, depends on the correlated motions of the particles. A full discussion is given by Knox[6]. For present purposes, the singlet-triplet splitting is determined to sufficient accuracy by a factor S which describes the probability that the electron and hole are in the same unit cell. A similar factor enters in the oscillator strength too, so there should be a parallel in the behaviour of radiative lifetime and singlet-triplet splitting. Some of the relevant expressions are given by Stoneham[7]. Using an explicit expression of the electron-hole relative motion wave function ψ, S can be written as $S = \Omega_{cell}|\psi\ (R_{eh} = 0|^2$. The exchange splitting is simply 2JS, with J the exchange integral involving the conduction and valence Wannier functions in the same cell. Implicit in the last expression are a number of small corrections, detailed by Knox, and the assumption that the envelope function does not vary rapidly over the unit cell. We shall use the parallel idea of pseudopotential theory with the same assumption of slow varying pseudo wavefunction over a core[8].

Before presenting specific results, we will discuss the principal mechanisms which lead to the reduction of the splitting for the two-site self-trapped excitons. Simple arguments indicate that the large hole mass does not lead to the reduction in splitting. For example, effective mass theory gives a splitting proportional to $(1 + m_e^*/m_h^*)^{-3}$, which has the opposite trend. Indeed, the major factor is the two-centre nature of the self-trapped exciton. This can be seen from calculations on H_2[9], which show a pronounced decrease in the exchange splitting as the interatomic distance increases. A simple system closer to the self-trapped exciton might be the excited state of a helium molecule He_2^*. Indeed, one can simulate the situation in such a system by using very simple molecular orbitals, and finds that the exchange energy is reduced by a factor between 1 and 10 in going from He_2^* to $2He^*$.

The pseudopotential method of Bartram, Stoneham and Gash[8] is employed to evaluate the exchange splittings for the free and self-trapped excitons in alkali halides. The method is the same as that successfully employed in studies of F centres and self-trapped excitons. As in earlier work on the self-trapped excitons[10], the hole is assumed to be localised on anion sites. The necessary ion-size parameters for the anion atom have been determined earlier[10]. The exchange splitting requires calculations using two different pseudopotential coefficients for each ion, namely ${}^1A$ and ${}^3A$, depending on whether the electron and hole spins are anti parallel or parallel. The term in the hamiltonian leading to the exchange splitting is proportional to $({}^1A - {}^3A)$. Values are given in Table 1. In order to be able to compare the results for two different systems (free and self-trapped excitons), the simplest version of

TABLE 1

Values of ion-size parameters. The values quoted are of ${}^1A - {}^3A$ in Ry/a_o^3.

F^o	1.14
Cl^o	3.94
Br^o	8.24
I^o	10.30

pseudopotential method is used. The wave function is determined variationally using a single Slater-type orbital centred on the defect centre, with the ion-size corrections on the sites of the localized hole only. Ion-size terms of the square-well type are used, with the appropriate atomic radii taken from previous work by Song and Lewis[11]. As in many other papers on similar systems[11, 12], we find a 2s-like Slater orbital gives systematically lower energy than a 1s-like basis function. The results reported in the present paper are those obtained with 2s-like basis. Once the energy is minimized variationally, we evaluate the splittings using the expression:

$\Delta E = 2\ G\ \langle|\phi(R_o)|^2\rangle$ where $G = {}^1A - {}^3A$, the difference of the ion-size parameter A for the singlet and triplet states. Evaluating the probability of the electron and the hole being in the same atomic volume is slightly more realistic than taking the point contact value, so we have taken $\langle|\phi|^2\rangle$ as the average charge density taken over one atomic volume around the site where the hole is localized. This introduces very little change for the self-trapped exciton. For the free exciton, however, the point contact form gives about twice as large a value. In Table 2 we assemble the results obtained for the self-trapped excitons and the free excitons in most alkali halides. Where available, we have also included the experimental data of the exchange splittings.

In general, the observed exchange splitting for the self-trapped exciton is smaller than that for the free exciton by a factor of 5 to 10. Our present analysis, despite its limited choice of basic functions, and the simple form in which ion-size terms are represented, consistently predicts reductions of similar magnitude. On comparing with the experimental data available so far, we find a reasonable general agreement. Indeed, better agreement would have been fortuitous both in view of the complexity of the problem, and because the experimental data for the self-trapped excitons were derived in a rather indirect way from theoretical analyses. Our work suggests that, for any system where the self-trapped hole is spread over more than one site, the singlet-triplet splitting for the self-trapped exciton should be systematically smaller than for the corresponding free exciton.

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Table 2 Singlet-Triplet Splittings (in eV)

Host	Free exciton		Self-trapped exciton	
	Theory	Experiment	Theory	Experiment
NaCl	0.104	0.048	0.009	
KCl	0.095	0.052	0.014	0.015
RbCl	0.091	0.058	0.014	
NaBr	0.183	0.37	0.013	
KBr	0.167	0.26	0.020	0.0075
RbBr	0.167	0.16	0.020	
NaI	0.169		0.010	
KI	0.161	0.044	0.017	
RbI	0.161		0.017	
CsBr	-		-	0.018
CsI	-		-	0.035

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