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 exci-
tons[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 exci-
ton is determined by the electron-hole inter-
actions. 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 deter-
mined 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 wave-
function 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 indi-
cate that the large hole mass does not lead to
the reduction in splitting. For example,
effective mass theory gives a splitting pro-
portional 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 para-
meters 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:

$\Delta E = 2\ G\ <|\phi(R_o)|^2>$ 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 $<|\phi|^2>$ 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.

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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