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Evaluation of the zero-field splitting of the triplet self-trapped exciton in CaF_2 , SrF_2 and BaF_2

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Abstract. A general and analytical method of evaluating the zero-field splitting parameter D originating from the spin–spin interaction is presented. Application of this method to the self-trapped excitons (STE) in alkaline earth fluorides identifies the geometry of the STE in an unambiguous way and gives values of the zero-field splitting parameter D in good agreement with experiment. A recently proposed model of the STE in alkali halide crystals involving rotations is briefly discussed on the basis of the zero-field splitting.

1. Introduction

In an earlier paper [1], we performed a semi-quantitative analysis of the zero-field splitting (ZFS) parameter D for the self-trapped excitons (STE) in alkali fluorides and alkaline earth fluorides. In these materials, the spin–orbit coupling is weak and as a result D is almost entirely due to the magnetic dipole–dipole interaction between the electron and hole: $D = D_{ss}$. The expression for D_{ss} employed was approximate, involving the use of a scaling factor and the neglect of the exchange-like term. Among other things, we were able to explain the STE's sign reversal of D between the NaCl and CaF_2 lattices and to identify the geometry of the STE in the fluorite structure among the several possible configurations previously suggested [2].

In this paper, we present a more exact analysis of the parameter D_{ss} , specifically by the development of a general and analytic expression of the integrals which are required in evaluating D_{ss} based on the use of floating 1s Gaussian orbitals. Analytic results for D_{ss} have been obtained by several authors. Most of these employed Slater orbitals and the final form is rather complex [3, 4]. Moreover, in many cases the interest was on the spin–spin interaction between electrons of the same orbital belonging to a molecule [5]. In contrast, we are interested in the spin–spin interaction between an excited electron and a hole occupying different orbitals. Following our earlier works on floating 1s Gaussians, we represent the electron and hole wavefunctions of the STE as linear combinations of floating Gaussians, and show in section 2 that D_{ss} has a simple analytic form expressed in terms of the $F_m(r)$ functions defined by Shavitt [6].

In section 3, we apply the analytic formulae derived to the evaluation of D_{ss} of the STE in fluorides. For the alkaline earth fluorides, we find that configuration 2 of [2] is the only geometry which is compatible with the optically detected magnetic resonance (ODMR) data. In addition, we obtain a very reasonable agreement of D_{ss} with experiment.

For the alkali fluorides of NaCl structure, we deduce the separation between the two spins which is close to the values obtained in the classical limit of D_{ss} . A recent proposal made by Itoh [7] regarding the possible involvement of rotation of the F_2^- in the off-centre STE is examined for the fluorides of NaCl structure.

2. Derivation of an analytic expression for D_{ss}

The zero-field splitting (zfs) parameter D contains two components: $D = D_{ss} + D_{so}$, where D_{ss} describes the magnetic dipole-dipole interaction and D_{so} is due to the spin-orbit coupling. We are only concerned here with the fluorides where the spin-orbit coupling is weak so that we can neglect D_{so} . The spin triplet state of the STE has a wavefunction of the form:

$$\Psi_{12} = (1/\sqrt{N_{12}})[\psi_e(r_1)\psi_h(r_2) - \psi_h(r_1)\psi_e(r_2)]\alpha_1\alpha_2 \quad (1)$$

where ψ_e and ψ_h are the orbital wavefunctions of the electron and the hole respectively, and $\alpha_1\alpha_2$ is the spin wavefunction. The zfs parameter D_{ss} is given by

$$D_{ss} = \frac{3}{4}(g\beta)^2 \langle \psi_{12} | (r_{12}^2 - 3z_{12}^2) / r_{12}^5 | \psi_{12} \rangle \quad (2)$$

(D in tesla is obtained by multiplying the above equation by $4\pi \times 10^{-7}/g\beta$).

On substituting equation (1) in equation (2), there appear two groups of integrals. The first is Coulomb-like, for example $\langle \psi_e(r_1)\psi_h(r_2) | H_{ss} | \psi_e(r_1)\psi_h(r_2) \rangle$, and decreases as R^{-3} as a function of the distance R between the two spins. The second is exchange-like, for example $\langle \psi_e(r_1)\psi_h(r_2) | H_{ss} | \psi_h(r_1)\psi_e(r_2) \rangle$, and in general decays exponentially with R . H_{ss} is the spin-spin interaction operator of equation (2).

We assume that ψ_e and ψ_h can each be expressed as linear combinations of floating 1s Gaussians:

$$\psi_e(r) = \sum_i C_i^e N_i^e \exp[-\alpha_i^e |r - R_i^e|^2] \quad \psi_h(r) = \sum_j C_j^h N_j^h \exp[-\alpha_j^h |r - R_j^h|^2]. \quad (3)$$

Here, the α and N are respectively the Gaussian exponents and the normalization constants for the single Gaussians, the R are the centres of the 1s Gaussians and the C are the expansion coefficients. Substituting equation (3) into equation (1) and using equation (2), it is straightforward to see that D_{ss} can be written as a linear combination of two-electron four-centre integrals of the form

$$d_{ss} = \int \frac{(r_{12}^2 - 3z_{12}^2)}{r_{12}^5} \exp(-ar_{1A}^2 - br_{1B}^2 - cr_{2C}^2 - dr_{2D}^2) dr_1 dr_2 \quad (4)$$

where $r_{1A} = |r_{1A}| = |r_1 - A|$, $r_{2C} = |r_2 - C|$ and so on. We note that the form d_{ss} in equation (4) is quite general. It includes as special cases Coulomb-like integral for which $a = b$, $A = B$, $c = d$ and $C = D$, as well as exchange-like integrals for which $a = c$, $A = C$, $b = d$ and $B = D$.

The problem now is to evaluate d_{ss} . This can be done by generalizing the method of Shavitt [6] for the evaluation of the two-electron four-centre exchange integral. We first introduce

$$\lambda_{12} = [\xi(x_1 - x_2)^2 + \eta(y_1 - y_2)^2 + \zeta(z_1 - z_2)^2]^{1/2} \tag{5}$$

so that we can write

$$d_{ss} = \langle 1/\lambda_{12}^3 \rangle_{\xi=\eta=\zeta=1} + [(\partial/\partial \xi) < 1/\lambda_{12}^3 \rangle]_{\xi=\eta=\zeta=1} \tag{6}$$

with

$$\left\langle \frac{1}{\lambda_{12}^3} \right\rangle = \int \frac{1}{\lambda_{12}^3} \exp(-ar_{1A}^2 - br_{1B}^2 - cr_{2C}^2 - dr_{2D}^2) \, d\mathbf{r}_1 \, d\mathbf{r}_2. \tag{7}$$

If we now make use of the identity

$$\frac{1}{\lambda_{12}^3} = \frac{2}{\sqrt{\pi}} \int_0^\infty \sqrt{S} \exp(-S\lambda_{12}^2) \, dS \tag{8}$$

and follow closely the method of Sharitt ([6], equation (51) and pp 31–33), we obtain, after some tedious manipulation,

$$d_{ss} = \frac{2\pi^{5/2}}{(pq)^{3/2}} \exp \left[-\frac{ab}{a+b} |A - B|^2 - \frac{cd}{c+d} |C - D|^2 \right] \int_0^\infty (1+fS)^{-3/2} S \times \exp \left[-\frac{S}{1+fS} |P - Q|^2 \right] \left\{ 1 + \frac{1}{1+fS} \left[-\frac{fS}{2} - SZ^2 + \frac{fS^2 Z^2}{1-fS} \right] \right\} \, dS. \tag{9}$$

Here,

$$P = \frac{aA + bB}{a + b} \qquad Q = \frac{cC + dD}{c + d} \tag{10}$$

$$p = a + b \qquad q = c + d \qquad f = \frac{p + q}{pq} \qquad Z = P_z - Q_z.$$

The integral in equation (9) can be simplified by a change of variable

$$1 + fS = 1/(1 - t^2) \tag{11}$$

and the final expression for d_{ss} is

$$d_{ss} = \frac{4\pi^{5/2}}{(p + q)^{3/2}} \exp \left[-\frac{ab}{a+b} |A - B|^2 - \frac{cd}{c+d} |C - D|^2 \right] \int_0^1 t^2 (1 - 2ft^2 Z^2) \times \exp[-f|P - Q|^2 t^2] \, dt. \tag{12}$$

We note that the last integral in equation (12) belongs to the class of integrals

$$F_m(x) = \int_0^1 t^{2m} \exp[-xt^2] \, dt \qquad x > 0; m = 0, 1, 2, \dots \tag{13}$$

defined on p 7 of [6].

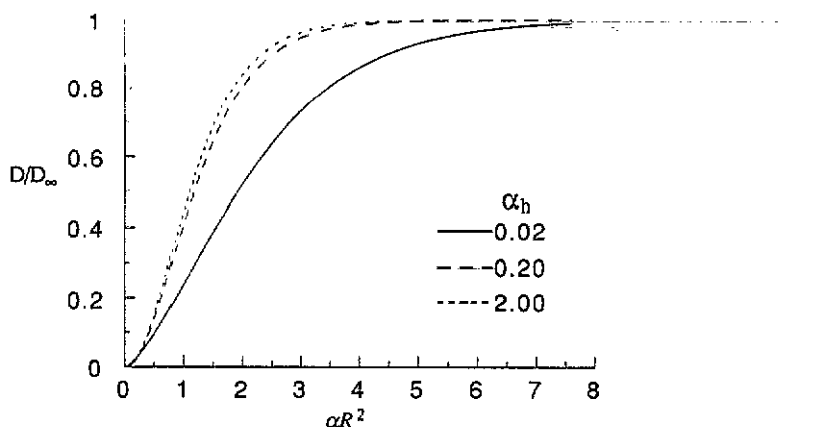


Figure 1. Dependence of the zero-field splitting parameter D_{ss} on the distance R separating the two spins. D_{ss} scaled by the classical limit D_s is plotted against $\alpha_c R^2$, where α is the Gaussian exponent of the electron wavefunction α_e . Three different values of α_h are used to examine the influence of the hole wavefunction.

3. Applications

A computer program for the ZFS parameter D_{ss} , based on the above method, has been implemented. Owing to the exclusive use of 1s Gaussians, the program is much simpler than the use of Slater-type orbitals. As an example, we consider a simple case of an electron-hole pair separated by a distance R , where the electron and hole wavefunctions are represented by single 1s Gaussians of exponent α_e and α_h respectively. In figure 1 we plot $D_{ss}(R)/D_{ss}(R \rightarrow \infty)$ against $\alpha_e R^2$ for various values of α_h (α_e was fixed at 0.02 au). The solid curve for $\alpha_h = 0.02$ au can be compared with the one in [8] for Slater orbitals. These two curves are qualitatively quite similar, except that the curve in figure 1 here includes the contribution from the exchange-like terms. We have found that in general the Coulomb-like term dominates except when $\alpha_e R^2$ is small (e.g. the contribution of the exchange-like term is less than about 10% for $\alpha_e R^2 > 2.6$). In the following, we consider the ZFS of the STE in the fluorides of NaCl and CaF_2 structures. As noted above, in these materials the parameter D is almost entirely due to the magnetic dipole-dipole interaction and the other term originating from the spin-orbit coupling is negligible.

3.1. STE in CaF_2 structure

Optically detected magnetic resonance (ODMR) experiments have shown that the STE in the fluorites is oriented approximately along the (111) axis. Several possible configurations of the electron and hole core have been proposed between which the experimental data could not discriminate [2]. These are the configurations 1, 2 and 3 as shown in figure 2. For comparison, a fourth configuration, 4, with a higher symmetry is also examined here, although this corresponds to a further separation of the electron and hole. In our earlier work [1] we have shown by means of a semi-quantitative analysis of the ZFS parameters that configuration 2 is the most likely geometry. We evaluate now the numerical values of D_{ss} for the four possible configurations of the STE using the method of section 2 and realistic wavefunctions for the hole and electron.

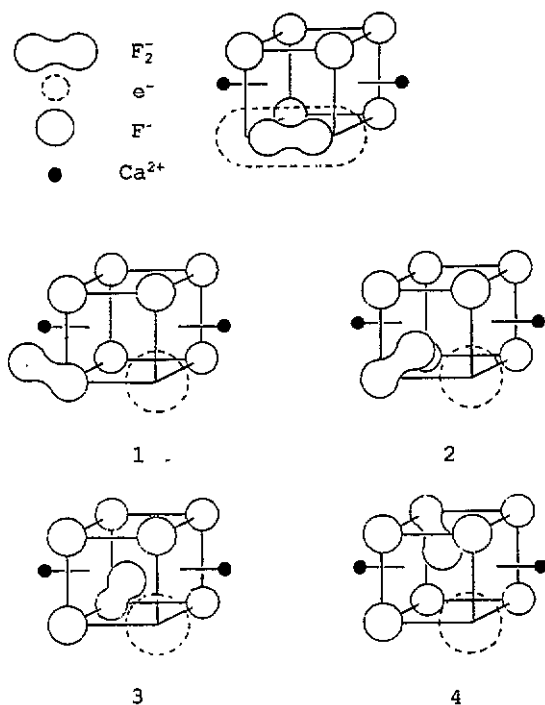


Figure 2. Geometry of four possible structures of the STE in the fluorites. Configurations 1, 2 and 3 are as proposed in [2]. Configuration 4 is added for comparison. The top of the figure represents the on-centre STE which occupies the same symmetry as the self-trapped hole F_2^- .

For the STE in the CaF_2 structure, the hole is localized on a pair of F ions along the (111) axis, with 30% of the hole charge on the substitutional F ion and 70% on the interstitial F ion [9]. Following equation (3), the hole wavefunction is represented as

$$\psi_h(\mathbf{r}) = c_1 N \exp(-\alpha_h |\mathbf{r} - \mathbf{R}_1|^2) - c_2 N \exp(-\alpha_h |\mathbf{r} - \mathbf{R}_2|^2) \quad (14)$$

where \mathbf{R}_1 and \mathbf{R}_2 are the positions of the substitutional and interstitial F ions respectively, c_1 and c_2 are the respective weights $\sqrt{0.3}$ and $\sqrt{0.7}$. The bond length of F_2^- , $|\mathbf{R}_1 - \mathbf{R}_2|$, is taken as 3.6 au for all three fluorides CaF_2 , SrF_2 and BaF_2 . Based on an earlier approximate calculation [10], we have placed the ion $\text{F}^{-0.7}$ on the normal F ion site and the ion $\text{F}^{-0.3}$ on the axis (111) at a distance of 3.6 au from the anion site. To reflect the compact nature of the hole wavefunction, α_h is chosen to be 0.5 au. We note that the results presented in figure 1 show that D_{ss} is quite insensitive to α_h for $\alpha_h > 0.2$ au. For the excited electron of the STE, the wavefunction is taken as a single 1s Gaussian of exponent α_e varying between 0.03 and 0.06 au. Using these data, D_{ss} is calculated for the four configurations of figure 2. The best set of results with $\alpha_e = 0.04$ au is presented in table 1, together with the experimental data of D and some other parameters. For comparison, the Coulomb-like and exchange-like contributions to D_{ss} have been presented also. The results show unambiguously that only configuration 2 is consistent with experiment. Furthermore, the calculated values of D_{ss} are in very reasonable agreement with experiment [11]. Table 1 also shows that the short-range exchange-like contribution is as important as the Coulomb-like term in the present case.

3.2. STE in the NaCl structure

The same method is used to study the STE in LiF, NaF and KF. The hole is again represented by equation (14) with $c_1 = c_2$ and $\alpha_h = 0.5$ au. We consider only the off-centre model of the STE, in which the STE is equivalent to a close F-H pair along the (110)

Table 1. D_{ss} of the STE in four possible F-H pair configurations in CaF_2 , SrF_2 and BaF_2 . Beside the calculated values, the terms arising from Coulomb-like and exchange-like terms are also shown in parentheses. Experimental values are also given. All values in G.

CaF_2	D_{ss} (calc)	(Coulomb/exchange)	D_{ss} (expt)
CaF_2			
1	-1953	(-892/-1061)	1552
2	1362	(6778/-5416)	
3	-240	(2527/-2766)	
4	-6413	(-4840/-1572)	
SrF_2			
1	-1695	(-897/-797)	1588
2	1707	(6253/-4547)	
3	-321	(1658/-1980)	
4	-5832	(-4896/-936)	
BaF_2			
1	-1434	(-880/-555)	1397
2	1991	(5620/-3629)	
3	-425	(853/-1278)	
4	-5063	(-4605/-459)	

axis. By representing the electron as a single Gaussian of exponent α_e , the separation R between the electron and the F ion nearest to the electron is adjusted to fit the experimental value of D [12]. It is found that the results are not sensitive to α_e in the range $0.04 \text{ au} < \alpha_e < 0.06 \text{ au}$ (the typical Gaussian basis used in earlier extended-ion works [13, 14]). Values of R obtained are 11.3, 12.8 and 14.3 au for LiF, NaF and KF respectively. These are very close to those obtained earlier using the classical limit of D_{ss} . The values of R obtained from electronic structure calculations are somewhat smaller (7.2 au for NaF and 8.8 au for KF [13]). Recent works based on *ab initio* approaches confirmed the off-centre structure of the STE in alkali halides [15, 16]. Earlier works based on the extended-ion approach as well as detailed studies undertaken with the *ab initio* code (CADPAC code) indicate that the potential energy surface of the STE is remarkably flat after the initial energy drop from the on-centre geometry [17]. In this condition it is not simple to determine the position of the energy minimum from calculation. Instead, the value of R deduced from D values, for example, should be given more significance.

The triplet STE has been classified according to the magnitude of the off-centre shift in three groups [14]. Kan'no *et al* [18] have proposed an empirical classification based on the relative Stokes shift of the π emission bands. The schemes agree with each other. In group I belong NaBr and NaI, with small Stokes shift and fast triplet lifetime. Group III comprises NaF, KF, RbF, KCl, RbCl, KBr and RbBr, and is characterized by large Stokes shift and slow lifetime. Group II is made up of NaCl, KI and RbI and is considered the intermediate group. The reason why the off-centre axial shift ΔQ_2 is bunched in three fairly distinct groups rather than being distributed continuously is an interesting question. It is possible that there are only a small number of possible geometries with local minima on the potential energy surface, such as the 'on-centre', nearest neighbour F-H and next nearest F-H pairs and so on.

N. Itoh [7] has recently made an interesting proposition in this regard. He argued that groups II and III may involve rotations which follow the off-centre shift of the

molecular ion (group II and group III with rotations of 60° and 90° relative to the original axis). This model was partly motivated by recent results of resonant Raman scattering work on the STE in NaCl [19]. According to this work, the hole component of the STE in NaCl interacts with a lattice vibration whose frequency is equal to that of the H centre (297 cm^{-1}), which is about 30% larger than that of the V_k centre. We have therefore examined the D_{ss} value of the STE with the molecular ion rotated by 90° . As we have pointed out previously [1] the sign of D_{ss} at large distance R is determined by the orientation of the molecular ion relative to the electron. In the present case with the electron on the bisecting axis of the molecular ion, we find $D_{ss} > 0$ for $R > 3.5$ au. The sign of D_{ss} reverts to negative for short distances: $R < 2.5$ au. Its magnitude is in the range of -3500 to -7000 G for $R < 2.5$ au, however. This is much too large compared with the experimental value of around -1000 G. Owing to the cancellation between the Coulomb-like term ($D_{ss} > 0$) and the exchange-like term ($D_{ss} < 0$) near $R = 3.5$ au, the value of R fitting $D_{ss} = -1000$ G is limited to a narrow range of about 3.5 au. These findings seem to be incompatible with both the experimental data and the theoretical values of R . We must conclude that the off-centre STE studied by ODMR at low temperatures remains on the original axis.

In conclusion, we have presented an exact and analytic way of evaluating the ZFS parameter D_{ss} of the STE represented by Gaussian-type functions. Application of the method to the STE of the CaF_2 structure gives good agreement with experiment. For the NaCl structure, the present calculation confirms that the classical limit of D_{ss} employed earlier is sufficiently accurate.

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