Effective Hamiltonian parameters for *ab initio* energy-level calculations of $\text{SrCl}_2:\text{Yb}^{2+}$ and $\text{CsCaBr}_3:\text{Yb}^{2+}$

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Abstract

Calculated energy levels from recent *ab initio* studies of the electronic structure of $\text{SrCl}_2:\text{Yb}^{2+}$ and $\text{CsCaBr}_3:\text{Yb}^{2+}$ are fitted with a semi-empirical ‘crystal-field’ Hamiltonian, which acts within the model space $4f^{14} + 4f^{13}5d + 4f^{13}6s$. Parameters are obtained for the minima of the potential energy curves for each energy level and also for a range of anion–cation separations. The parameters are compared with published parameters fitted to experimental data and to atomic calculations. The states with significant $4f^{13}6s$ character give a good approximation to the impurity-trapped exciton states that appear in the *ab initio* calculations.

(Some figures may appear in colour only in the online journal)

1. Introduction

The energy levels of lanthanide ions in solids, which give rise to transitions from the UV to the IR regions of the electromagnetic spectrum, have important applications, such as lighting, lasers and scintillators. The vast majority of energy-level calculations for these materials make use of a ‘crystal-field’ Hamiltonian, though there have been some *ab initio* calculations [1]. The Hamiltonian was originally developed for the $4f^N$ configuration of lanthanide ions [2, 3]. It has also been applied to actinides and extended to include the $4f^{N-1}5d$ configuration of both divalent [4–7], and trivalent [8–10] lanthanide ions. Spectra involving the $4f^{N-1}5d$ configuration are generally in the UV and VUV region. Due to changes in bonding, and hence bond length, between $4f^N$ and $4f^{N-1}5d$, transitions between configurations generally involve broad vibronic bands, though in materials with heavy ligands it is possible to observe vibronic progressions, particularly for divalent ions [4–7].

In addition to the $4f^{N-1}5d$ configuration, other excited configurations play a role in high-energy spectra. The $4f^{N-1}6s$ configuration generally overlaps the $4f^{N-1}5d$ configuration [7, 11], and there are also states involving charge transfer between the lanthanide and the other ions in the material. Charge can be transferred from a ligand to the lanthanide, giving broad charge-transfer absorption bands [8]. On the other hand, charge from the lanthanide may become delocalized, leading to an impurity-trapped exciton state (ITE). The delocalization gives a very large change in bond length relative to the $4f^N$ configuration and so these states may sometimes be directly observed by their broad, red-shifted, ‘anomalous’ emission bands [12–16], and are also thought to play a crucial role in non-radiative relaxation from states in the $4f^{N-1}5d$ configuration [17, 18].
There is little direct knowledge of the electronic and geometrical structure of ITEs in lanthanide materials. We have recently reported the use of two-color (UV–IR) excitation to probe the energy-level structure of ITEs in the CaF$_2$:Yb$^{2+}$ system [19]. The energy levels of the ITE were modeled using a simple crystal-field model where the localized 4f$^{13}$ electrons were coupled to an s electron, since the delocalized electron would be expected to be hybridized Yb$^{2+}$ 6s and Ca$^{2+}$ 4s orbitals.

ITE states have also been a subject of ab initio calculations in various materials [20–22]. Relevant to this paper, these calculations determine potential energy curves of the electronic states of the materials involved. The most comprehensive calculation is for the SrCl$_2$:Yb$^{2+}$ system [21, 22]. This model does not exhibit excitonic emission [7], but the absorption bands vary considerably in width [4], indicating that the excited states do not all have the same equilibrium bond length. In the calculations of Sánchez-Sanz et al [21] there is a double-well energy curve for some states, as shown in figure 1. At long anion–cation separations these states have predominantly 6s character, but at shorter distances they become $a_{1g}$ symmetry combinations composed of 5s orbitals on the next-nearest-neighbor Sr$^{2+}$ ions, with a contribution from interstitial charge density. The combined 4f$^{13}a_{1g}$ configuration has $A_{1u}$ symmetry. It was demonstrated by Sánchez-Sanz et al [22] that all of the states were crucial in explaining the different band-widths observed in the absorption spectrum [4]. In this calculation the $A_{1u}$ potential curve minima have higher energies than the minima of the 6s or 5d states, but could be described as a ‘precursor’ to the exciton states that occurs in SrF$_2$:Yb$^{2+}$ and CaF$_2$:Yb$^{2+}$ at lower energy than the 4f$^{13}5d$ configuration [12, 16].

The calculations of Sánchez-Sanz et al [21] were directly compared with absorption [4] and emission [7] spectra. While this gives a good match to the data, it does not provide information directly about the magnitudes of the physical interactions involved, and hence this calculation cannot be compared to the crystal-field calculation of Pan et al [7]. The advantage of determining the crystal-field parameters of the system is that the corresponding interactions have predictable behavior across the lanthanide series, allowing for the parameters determined for this system to be extrapolated to other lanthanide systems. In simple systems with high symmetry and one valence electron, such as the BaF$_2$:Ce$^{3+}$ system [23] it is relatively easy to relate the energy levels to crystal-field parameters. However, for a many-electron system such as SrCl$_2$:Yb$^{2+}$ the relationship is much more complicated because there are many more parameters in the effective Hamiltonian.

Recent work has shown that it is possible to construct an effective Hamiltonian matrix from ab initio calculations, and hence determine crystal-field and other parameters by a straightforward projection technique [24–26]. There the relevant parameters were extracted directly from the ab initio Hamiltonian. However, those works were on systems with a single valence electron. In systems with more than one valence electron the labeling of the states in terms of the states used in the effective Hamiltonian approach is not straightforward. Therefore, in this work we use the approach of fitting the effective Hamiltonian parameters to calculated energy levels, as in Duan et al [27].

The focus of this paper is to describe the behavior of exciton energy levels using the eigenvalues of a semi-empirical effective Hamiltonian operator acting on a model space of the SrCl$_2$:Yb$^{2+}$ system. The energy-level structure calculated by Sánchez-Sanz et al [21] is used as model data to test whether the chosen effective Hamiltonian operator can reproduce the ‘precursor’ exciton results, and to find values for the physical parameters describing the effective Hamiltonian in this case. Ab initio calculations of a second crystal, CsCaBr$_3$:Yb$^{2+}$, are also examined. The crystal CsCaBr$_3$:Yb$^{2+}$ is not excitonic and does not exhibit precursor exciton behavior, so it is of interest to study the similarities and differences between the excitonic and non-excitonic cases. The motivations to determine the parameters for these systems are two-fold; as a supplement they reinforce the ab initio calculations, allowing comparison to the expected magnitudes of electron interactions. Secondly, the parameters should be comparable in other lanthanide ions, and the ‘free ion’ parameters transferable between materials. Therefore, the analysis will be of interest beyond the systems considered here.

2. Effective Hamiltonian

For a Hamiltonian $H$, with eigenstates $\psi_i$ and eigenvalues $E_i$, an effective Hamiltonian $H_{\text{eff}}$ is defined so that within a subspace of the full Hamiltonian it has eigenstates $\phi_i$ with the same eigenvalues as $H$:

$$H\psi_i = E_i\psi_i, \quad (1)$$

$$H_{\text{eff}}\phi_i = E_i\phi_i. \quad (2)$$

General discussions of effective Hamiltonians may be found in the literature [28–30]. In many cases the effective Hamiltonian, $H_{\text{eff}}$, is the effective Hamiltonian of a Hamiltonian matrix, a matrix whose entries are the effective Hamiltonian.

**Figure 1.** Calculated energy levels as a function of anion–cation separation ($R_{\text{Cl}}$) for the SrCl$_2$:Yb$^{2+}$ system of Sánchez-Sanz et al [21]. The double-well potential curves occur on states with predominantly 6s character. The 4f$^{13}$ curve, which has a minimum at 2.954 Å, is omitted.
Hamiltonian is expressed in terms of parameters that are understood to represent various physical interactions. This is the case for a ‘crystal-field’ Hamiltonian applied to lanthanide ions where operators represent atomic interactions such as the Coulomb and spin–orbit interactions, and also ‘crystal-field’ interactions with the surroundings. The analysis of lanthanide energy levels in solids has, since the 1960s, made use of such a ‘crystal-field’ effective Hamiltonian (e.g. [2]) for the 4f energy levels in solids has, since the 1960s, made use of such interactions with the surroundings. The analysis of lanthanide ions where operators represent atomic interactions such as the case for a ‘crystal-field’ Hamiltonian applied to lanthanide understand to represent various physical interactions. This is J. Phys.: Condens. Matter 25

in (3). Finally, an operator accounting for the interaction between 5d and 6s orbitals is added:

\[ H_{4f^{11}5d} = E_{\text{avg}}(f) + \Delta_E(f_d) + \zeta(f)A_{5d}(f) + \sum_{k=4,6} B_{q}^{k}(f)C_{q}^{k}(f) + \sum_{j=1,3,5} G_{q}(f)G_{q}(fd) + \sum_{k=4} B_{q}^{k}(d)C_{q}^{k}(d). \] (3)

Here \( \Delta_E(f_d) \) is the average energy of the 4f13 5d configuration relative to 4f14. The \( \zeta(f) \) and \( \zeta(d) \) parameters, and corresponding \( A_{5d} \) operators, comprise the spin–orbit effects on the 4f electrons and 5d electron respectively. The \( F^k(fd) \) and \( G^k(fd) \) parameters are the direct and exchange Slater parameters for the Coulomb interaction between electrons in different shells. \( B_{q}^{k} \) parameters describe the crystal-field effects for the appropriate electrons.

Impurity sites in SrCl2:Yb2+ and CsCaBr3:Yb2+ have eight- and six-coordinate cubic symmetry respectively. Cubic symmetry at the impurity site reduces the number of crystal-field parameters to two non-zero parameters for the 4f crystal-field, and to one non-zero 5d crystal-field parameter [10, 31]. Due to the different coordinations, the values of these parameters should differ by a sign between SrCl2:Yb2+ and CsCaBr3:Yb2+.

In order to extend the model space to include states involving 6s orbitals of the Yb2+ ion, the 4f13 6s effective Hamiltonian,

\[ H_{4f^{11}6s} = E_{\text{avg}}(f) + \Delta_E(fs) + \zeta(f)A_{5d}(f) + \sum_{k=4,6} B_{q}^{k}(f)C_{q}^{k}(f) + G^k(fs)g^{k}(fs), \] (4)

is added to the 4f13 5d effective Hamiltonian. Here the \( \Delta_E(fs) \) term is the average energy of the 4f13 6s configuration relative to 4f14. The \( g^{k}(fs) \) parameter is the only non-zero Coulomb interaction term acting between 4f and 6s electrons. Duplicate parameters \( \zeta(f) \) and \( B_{q}^{k}(f) \) are set equal to their counterparts in (3). Finally, an operator accounting for the interaction between 5d and 6s orbitals is added:

\[ H_{ds} = \sum_{k=2,3} R^k(ds)r_1(ds), \] (5)

where the \( R^k \) parameters measure the mixing of states that occurs due to coulomb interactions.

3. Calculations

This section is divided into two parts. Firstly, the parameters of the effective Hamiltonian operator, (equations (3)–(5)), are fitted to the energy eigenvalues at the minima of the potential curves of Sánchez-Sanz et al [21, 32]. These are the predicted positions of the zero-phonon lines, so, this calculation is directly comparable to the crystal-field calculation of Pan et al [7] (for SrCl2). Secondly, the same effective Hamiltonian operator is fitted to the energy eigenvalues calculated at fixed anion–cation separation. This allows for the investigation of the variation in parameter values with anion–cation separation.

3.1. Fit to potential curve minima

Initial values for the effective Hamiltonian parameters were chosen from values determined by Pan et al [7] for the 4f and 5d parameters. Values for the \( G^k(fd) \), \( R^k(ds) \) and \( R^k(ds) \) parameters were calculated from their integral definitions [33, 29], using Hartree–Fock wavefunctions as estimates of electron radial distribution [29].

Non-linear least-squares regression was used to optimize the parameters by fitting the energy eigenvalues of the effective Hamiltonian to the minima of the potential energy curves calculated by Sánchez-Sanz et al [21, 32]. A fit was performed for each level of the calculations presented in these references. For the states with double-well potential curves, the longer anion–cation separation (6s character) minima were used. The ratios of direct and exchange Coulomb parameter values were not constrained in any way.

The standard deviation of the fits are calculated via

\[ \sigma = \sqrt{\frac{\sum_{i} N_{\text{fit}} (E_i - x_i)^2}{N_{\text{fit}} - N_{\text{vars}}}}, \] (6)

where \( N_{\text{fit}} \) is the number of energies fitted, and \( N_{\text{vars}} \) is the number of free parameters.

Additionally, for the spin–orbit inclusive calculation of SrCl2:Yb2+, (labeled SO-CI), the convergence of the fit was tested. To test the convergence of the fit, we took a large number of starting positions in the 15-dimensional parameter space to provide varying initial values. A number of solutions converging to local minima in the parameter space were identified. Several local minima occur around the best standard deviation, \( \sigma \approx 190 \text{ cm}^{-1} \), varying mostly in \( R^2(ds) \) and \( R^3(ds) \) parameter values. This is similar to the fit to SrCl2:Yb2+ spectra [7] where \( \sigma \approx 174 \text{ cm}^{-1} \) (fitted to \( T_{1u} \) states). The averaged parameter values from these solutions are presented in table 1.

3.2. Fit by ligand separation

The effective Hamiltonian operator was also used to fit to the energies at a fixed anion–cation separation for each separation
Table 1. Parameter values for the effective Hamiltonian of SrCl$_2$:Yb$^{2+}$ fitted to experimental observations [7]; calculated for a free Yb$^{2+}$ ion [33]; and fitted to ab initio calculations of Sánchez-Sanz et al [21]. The labels CASSCF, MS-CASPT2 and SO-CI refer to the level of the reference calculation. At CASSCF level, only basic interactions are considered. MS-CASPT2 includes dynamic correlation of electrons, and SO-CI includes spin–orbit interactions. All parameter values and uncertainties ($\sigma$) are in cm$^{-1}$. The standard deviation for the SO-CI SrCl$_2$ fit is $\sigma \approx 190$ cm$^{-1}$.

| Parameter | CASSCF | CASPT2 | SO-CI |
|-----------|--------|--------|-------|
|           | CsCaBr$_3$ | SrCl$_2$ | CsCaBr$_3$ | SrCl$_2$ | CsCaBr$_3$ | SrCl$_2$ | Expt [7] | Atomic [33] |
| $\Delta_\sigma$(fd) | 13 905 $\pm$ 275 | 12 099 $\pm$ 202 | 39 847 $\pm$ 390 | 41 873 $\pm$ 351 | 39 793 $\pm$ 365 | 41 802 $\pm$ 42 | 38 382 |
| $\zeta$(f) | 21 390 $\pm$ 703 | 23 665 $\pm$ 487 | 15 946 $\pm$ 1013 | 17 815 $\pm$ 880 | 16 795 $\pm$ 2841 | 18 393 $\pm$ 169 | 14 355 | 23 210 |
| $F^2$(fd) | 9 837 $\pm$ 1287 | 10 649 $\pm$ 922 | 11 403 $\pm$ 1871 | 13 475 $\pm$ 1700 | 9 489 $\pm$ 8174 | 13 099 $\pm$ 449 | 7 222 | 10 646 |
| $G^1$(fd) | 8 761 $\pm$ 221 | 9 202 $\pm$ 139 | 2 916 $\pm$ 437 | 4 864 $\pm$ 358 | 4 331 $\pm$ 2412 | 5 408 $\pm$ 93 | 4 693 | 10 059 |
| $G^1$(fd) | 7 155 $\pm$ 701 | 9 062 $\pm$ 560 | 7 436 $\pm$ 1022 | 9 403 $\pm$ 946 | 6 947 $\pm$ 6126 | 8 901 $\pm$ 454 | 5 382 | 8 046 |
| $G^3$(fd) | 6 199 $\pm$ 960 | 6 351 $\pm$ 653 | 5 655 $\pm$ 1518 | 5 459 $\pm$ 1251 | 7 511 $\pm$ 9474 | 7 165 $\pm$ 544 | 4 349 | 6 085 |
| $\Delta_\sigma$(fs) | 21 280 $\pm$ 159 | 9 221 $\pm$ 119 | 21 357 $\pm$ 228 | 23 665 $\pm$ 487 | 21 605 $\pm$ 562 | 11 093 $\pm$ 45 | 3 168 |
| $G^1$(fs) | 2 733 $\pm$ 882 | 1 724 $\pm$ 675 | 1 498 $\pm$ 1270 | 2 484 $\pm$ 1138 | 2 543 $\pm$ 4324 | 2 604 $\pm$ 505 |
| $R^2$(ds) | 9 22 $\pm$ 2462 | 3 474 $\pm$ 898 | 7 934 $\pm$ 2406 | 1 038 $\pm$ 2066 | 8 839 $\pm$ 6185 | 2 449 $\pm$ 900 | 1 468 |
| $B^1$ (f)$^a$ | 595 $\pm$ 334 | 533 $\pm$ 256 | 1 721 $\pm$ 476 | 473 $\pm$ 326 | 1 381 $\pm$ 1702 | 2 194 $\pm$ 24 | 725 |
| $B^1$ (f)$^b$ | 89 $\pm$ 173 | 41 $\pm$ 123 | 108 $\pm$ 258 | 73 $\pm$ 422 | 187 $\pm$ 1113 | 592 $\pm$ 28 | 292 |
| $B^1$ (d)$^a$ | 35 199 $\pm$ 245 | 18 966 $\pm$ 199 | 39 763 $\pm$ 328 | 20 221 $\pm$ 232 | 39 639 $\pm$ 853 | 20 100 $\pm$ 79 | 20 442 |

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$a$ $B^1_0 = B^1$, $B^1_{\pm 1} = \sqrt{2} B^1$.

$b$ $B^1_0 = B^1$, $B^1_{\pm 1} = -\sqrt{2} B^1$.
Figure 2. Parameters for the 4f¹⁴ + 4f¹³5d + 4f¹³6s effective Hamiltonian, optimized by fitting to energies of SrCl₂:Yb²⁺ using the spin–orbit level calculation (SO-CI) of Sánchez-Sanz et al [21]. The plots are split into groups of comparable parameters: (a) average configuration energy parameters; (b) fd Coulomb parameters; (c) fs Coulomb parameters; (d) spin–orbit parameters; (e) 4f crystal-field parameters; (f) 5d crystal-field parameter.

calculated by Sánchez-Sanz et al [21, 32]. The separation of 2.9514 Å was chosen first, as the minima of most states occur around this ion separation. Thus, the best fit parameters in table 1 could be used as suitable initial parameter values. The best fit for each anion–cation separation was subsequently determined using the best fit parameters for an adjacent separation as initial parameter estimates.

The fitted parameters are plotted against ligand separation for the SrCl₂:Yb²⁺ SO-CI fits in figure 2. Several clear trends are visible in the parameters as they vary with length, holding even at the point of discontinuity between the 6s-electron and a₁g ITE regimes. These trends are also visible in the fits to other calculation levels, and for the calculations of CsCaBr₃:Yb²⁺ (not shown).

For SrCl₂:Yb²⁺, the best fits were obtained at ion separations that correspond to either minimum of the double-well potential curves. For the longer ion separation potential well, the fits ranged in standard deviation from
130 cm$^{-1}$ to 190 cm$^{-1}$, with the best parameter fit to the energy levels occurring at a separation of 3.1164 Å. The shorter separation well, corresponding to $a_{1g}$ exciton-like behavior, has a minimum standard deviation of $\sigma = 156$ cm$^{-1}$ at a separation of 2.7498 Å. However, the accuracy of the fit decreases rapidly as the ion separation decreases, with the standard deviation climbing to $\sigma \approx 500$ cm$^{-1}$. Fits for anion–cation separations shorter than 2.7 Å have not been shown on the plots, since the parameter values fluctuated wildly. At the point of discontinuity between the 6s-electron and $a_{1g}$ exciton regimes (separation of 2.8414 Å) there is a reasonable fit to the energies, with a standard deviation of $\sigma = 190$ cm$^{-1}$.

Similarly, the fixed ion separation fits were performed for the calculations of CsCaBr$_3$:Yb$^{2+}$ [32]. These had fewer data points, which had a more consistent accuracy of fit, with a standard deviation of 140–200 cm$^{-1}$.

4. Discussion

For all calculations, the $4f^{13}5d$ parameters converge to a small range of values for each parameter. The largest variation arises in the $R^2$(ds) and $R^3$(ds) parameters. The matrix representations of the $r_2$ and $r_3$ operators have no diagonal elements, hence there is only a weak mixing of some 5d and 6s states. The energies are insensitive to variations in $R^2$(ds) and $R^3$(ds) parameters, hence the fit uncertainties of these are correspondingly large, as shown in table 1. In the SrCl$_2$:Yb$^{2+}$ system, the $R^2$(ds) and $R^3$(ds) parameters tend to converge to positive and negative values, of similar magnitude. These values are more stable for the CsCaBr$_3$:Yb$^{2+}$ fits.

4.1. Fit to potential curve minima

In table 1 the parameters from experimental fits [7], atomic calculations [33], and fits to the $ab\ initio$ potential minima [21] are shown. The experimental fit is to a subset of the energy levels, since only $T_{1u}$ states are accessible by absorption from the ground state [4]. However, experimental fits to the SrF$_2$:Sm$^{2+}$ spectrum [6] and the SrF$_2$:Eu$^{2+}$ spectrum [5] are also available, and these are in broad agreement with the parameters for SrF$_2$:Yb$^{2+}$ of Pan et al [7].

We begin by considering the parameters relevant to the $4f^{13}5d$ configuration. The experimental, atomic, and $ab\ initio$ spin–orbit parameters $\zeta (f)$ and $\zeta (d)$ of SrCl$_2$ and $\zeta (f)$ of CsCaBr$_3$ are very similar. The atomic calculations and all of the $ab\ initio$ calculations overestimate the fd Coulomb parameters $F^6(fd)$ and $G^6(fd)$. This is consistent with many studies of trivalent lanthanide ions [2, 3], and is an indication that electron correlation effects are not fully accounted for by the $ab\ initio$ calculations. Since the atomic calculations are at the Hartree–Fock level, it is expected that they would overestimate these parameters [34, 27].

There is excellent agreement between $ab\ initio$ and experimental values for the 5d crystal-field parameter $B^4(d)$. However, the 4f crystal-field parameters show poor agreement, with the $B^8(f)$ parameter disagreeing in sign. This may be simply a problem of insensitivity, and it is notable that in the experimental fits to SrF$_2$:Eu$^{2+}$ the $B^8(f)$ parameter was also negative. A key aspect is that the 4f crystal-field parameters are up to two orders of magnitude weaker than the other electronic interactions. Thus, the individual contributions from these crystal-field operators are easily lost in the noise of the fit to the other parameters.

Now we turn to the $4f^{13}6s$ configuration of SrCl$_2$:Yb$^{2+}$. As discussed above, the $R^2$(ds) and $R^3$(ds) parameters are not well determined. However, the $G^3$(ls) parameter is well determined, and the $ab\ initio$ value is similar to the atomic value. This is to be expected since at the minima fitted the $ab\ initio$ calculation predicts predominantly 6s character for the excited electron [21].

4.2. Fit by ligand separation

Parameters as a function of anion–cation separation for the SrCl$_2$:Yb$^{2+}$ SO-CI calculation are shown in figure 2. Similar analyses were performed on all levels of the calculations presented by Sánchez-Sanz et al [21, 32]. The $E_{avg}(f)$ parameter reflects the potential well for the system. The $4f^{13}6d$ configuration average follows almost the same curve, so $\Delta_E(fd)$ is approximately constant. The $4f^{13}6s$ average has a discontinuity at 2.85 Å, as seen in $\Delta_E(fs)$, reflecting an avoided crossing between localized and delocalized states of the excited electron. At longer distances these states are predominantly $4f^{13}6s$, but at shorter distances they have significant delocalization, and can be considered an ITE state [21].

The $4f^{13}6d$ spin–orbit parameters show little variation with anion–cation separation. However, the $F^6(fd)$ and $G^6(fd)$ parameters show a general decline with decreasing ion separation which is consistent with a nephelauxetic-effect interpretation, where increased bonding delocalizes the electrons, and reduces the Coulomb interactions [35]. This pattern is observed in the Coulomb parameters for all calculation levels of both crystals.

The SrCl$_2$ 4f crystal-field parameters $B^4(f)$ and $B^6(f)$ show wide fluctuations. As noted above, they appear to be poorly determined. However, between 2.8 and 3.0 Å, a marked increase in magnitude with decreasing anion–cation separation is apparent. The fits to the other calculation levels have less fluctuation in the 4f crystal-field parameters.

The 5d crystal-field parameter $B^4(d)$ shows a smooth increase in magnitude. This may be approximated by a power-law dependence of $R_\text{Cl}^{-2.7}$. As would be expected, this dependence is steeper than a simple point-charge crystal-field model [36]. Correspondingly, CsCaBr$_3$:Yb$^{2+}$ shows a smooth decrease in magnitude of 5d crystal-field parameter, due to the ligand configuration. This has an approximate dependence of $R_\text{Cl}^{-2.7}$.

We have already noted the discontinuity in $\Delta_E(fs)$ at 2.85 Å for SrCl$_2$, as the excited electron switches between 6s character at long anion–cation separations, and delocalized character at short separations. The $R^2$(ds) and $R^3$(ds) parameters are too uncertain to draw any conclusions. However, the $G^3$(ls) parameter does appear to exhibit a
discontinuity, dropping in value by a factor of 3 at the discontinuity. If the excited electron becomes delocalized, as in the case of ITEs, it would be expected that the magnitude of the Coulombic interaction between the excited electron and the 4f$^{13}$ core would decrease, which indicates that this occurrence is a good description of excitonic behavior. The $R^2$ and $R^3$ parameters are more stable for the CsCaBr$_3$ system, but this may be due to the limited range of ion separations spanned by those calculations.

4.3. Possible extensions

Since the fits obtained are not exact, we investigated a number of possible extensions, such as considering any electron correlation effects that could modify the crystal-field, or allowing the 4f crystal-field parameters for the 4f$^{13}$d and 4f$^{13}$6s configurations to vary independently. None of these had a significant impact on the fits.

4.4. Comparison of fits

The fits to experimental data, minima of the calculated curves for SrCl$_2$ and energies at particular anion–cation separations (>2.7 Å) give comparable deviations, with the particular ion separation fit always slightly lower. It is notable that the fit at 3.116 Å gave a significantly lower deviation than the fit to the minima or the fit to experimental energies. Both the minima and the fit to experimental energies are intended to be the zero-phonon line positions, which are, in principle, determined from the absorption spectrum. However, it is clear from the avoided crossings in figure 1 that the eigenstates will be very different for different ion separations, which may be why the fit to the minima is not as good as some of the constant separation fits.

5. Conclusions

A ‘crystal-field’ effective Hamiltonian has been constructed to model the energy levels of SrCl$_2$:Yb$^{2+}$ and CsCaBr$_3$:Yb$^{2+}$, extending upon a 4f$^{14}$ + 4f$^{13}$d effective Hamiltonian to incorporate model states with 6s character. The parameters were optimized by fitting to energy levels determined by ab initio calculations of Sánchez-Sanz et al., for SrCl$_2$:Yb$^{2+}$ [21] and CsCaBr$_3$:Yb$^{2+}$ [32] respectively. A good approximation can be achieved to both the minima of the energy curves, and most of the energies at set anion–cation separations at each level of calculation presented in these references. The accuracy of the fits improved considerably at the positions of local minima of the energy curves determined in the ab initio calculations.

The 4f$^{13}$d effective Hamiltonian parameters are comparable to those determined from measured energy levels of SrCl$_2$:Yb$^{2+}$ with good agreement for the spin–orbit and 5d crystal-field parameters; and a reasonable fit for the Coulomb parameters, particularly the $G^2$ exchange parameters. The 4f crystal-field parameters determined are of similar magnitude to the values determined by Pan et al. [7], but differ in relative sign. The 5d crystal-field parameter increases in magnitude under contraction of the ion separation. For the SrCl$_2$ system, this can be approximated by a power-law dependence of $R^{-5.5}$. The 6s and A$_{1g}$ ITE potential wells can both be described by the constructed effective Hamiltonian, with a different G$^3$ exchange parameter in each regime. This corresponds well with the excited electron being in a localized or delocalized state respectively.

Most of the parameters determined here should be transferable to other divalent ions (such as Tm$^{2+}$) and other crystals, (such as CaF$_2$). Of particular interest are the excitonic states of CaF$_2$:Yb$^{2+}$ and SrF$_2$:Yb$^{2+}$ [12, 19], which will be the subjects of future study.

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