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Comparison between correlation crystal field calculations using extended basis sets and two-electron operators

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Abstract

There are two established methods for extending the crystal-field model for $4f^N$ configurations. One is to add two-electron correlation crystal-field operators, the other is to extend the basis set to include more configurations. We consider the case of Pr^{3+} ions in $LiYF_4$ and show, by projecting the configuration-interaction Hamiltonian into the $4f^2$ configuration, that in this case the two approaches give very similar results. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The crystal-field model for calculating the energy levels of the states of the $4f^N$ configurations of lanthanide ions in a crystal has been widely used [1]. In this approach an *effective Hamiltonian* is defined that acts within the $4f^N$ basis. In addition to atomic interactions the *crystal-field* interaction with the lattice is parametrized by

$$H_{\mathrm{CF}} = \sum_{kq} B^k_q C^{(k)}_q, \tag{1}$$

where the $C^{(k)}_q$ are spherical tensor operators and the B^k_q are crystal field parameters. Experimental energy levels are used to fit the atomic and crystal field parameters, which may subsequently be compared with ab initio calculations. It should be noted that when fits are made to experimental energy levels the parameters values may reflect effects that were not envisaged in the original formulation of the theory. For example, the crystal-field parameters represent not only the electrostatic interaction with the lattice, but also complex quantum–mechanical effects from the mixing of ligand and 4f orbitals (e.g. Ref. [2]).

The crystal-field Hamiltonian defined in Eq. (1) contains only *one-electron* operators. That analyses using Eq. (1) within a $4f^N$ basis give good fits to most of the observed crystal field splitting in lanthanide spectra can be taken as evidence that two-electron crystal-field effects are relatively small. However, though most levels of the $4f^N$ configuration may be well explained by the crystal-field model a few anomalous multiplets have stood out [3–6].

In response to these observed discrepancies, extensions have been made to the crystal field model [7]. There are two main approaches. One involves adding two-electron correlation crystal field (CCF) operators to the Hamiltonian. A general parameterization may be written in the form [3,8]

$$H_{\mathrm{CCF}} = \sum_{kqi} G^k_{i\,q} g^{(k)}_{i\,q}, \tag{2}$$

where the $g^{(k)}_{i\,q}$ are orthogonal correlation crystal field operators and the $G^k_{i\,q}$ are CCF parameters. The i that distinguish the operators are shorthand for irreducible representations of the parentage groups, Sp_{14}, SO_7, and G_2. Unfortunately, the number of CCF parameters is so large that it is not possible to fit all of them to experimental data. However, it appears that a subset of the parameters are particularly effective at removing the discrepancies [4]. Recently Burdick and Richardson [9] have used a 'delta-function' model based on a suggestion of Judd [10]. In this model a restricted CCF Hamiltonian

$$H_{\mathrm{CCF}(\delta)} = \sum_{kq} D^k_q \delta^{(k)}_q \tag{3}$$

is defined, where the $\delta^{(k)}_q$ operators are sums of the $g^{(k)}_{i\,q}$

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operators [9–11]. The delta function operator definitions for the cases $k=2$ and $k=4$ are

$$\delta_q^{(2)} \equiv \frac{35\sqrt{7}}{3\sqrt{2}} g_{2\,q}^{(2)} - \frac{35\sqrt{7}}{\sqrt{22}} g_{3\,q}^{(2)} - \frac{28\sqrt{105}}{\sqrt{143}} g_{10\,q}^{(2)}, \tag{4}$$

$$\delta_q^{(4)} \equiv -\frac{21\sqrt{105}}{2\sqrt{11}} g_{2\,q}^{(4)} + \frac{63\sqrt{105}}{22} g_{3\,q}^{(4)} + \frac{84\sqrt{42}}{\sqrt{715}} g_{10A\,q}^{(4)} + \frac{8232\sqrt{3}}{11\sqrt{1105}} g_{10B\,q}^{(4)}. \tag{5}$$

Only the $k=2$ and $k=4$ operators were found by Burdick and Richardson [9] to be effective in improving the fit.

The other approach to the breakdown of the one-electron $4f^N$ crystal-field model is to perform configuration-interaction (CI) crystal-field calculations in which the basis set is extended by explicitly including excited configurations (e.g. $4f^{N-1}6p$) [12,13].

Both CCF and CI approaches lead to similar fits to experimental data [9,13]. However, it is not clear from merely comparing the energy levels whether the calculations are equivalent. Since the two calculations use different basis sets, the parameters and Hamiltonian matrices cannot be directly compared. The aim of the work reported here is to demonstrate that the two calculations are, in fact, very similar. We do this by projecting the CI Hamiltonian into the $4f^N$ space and fitting the resulting *matrix* using the CCF Hamiltonian.

2. Matrix reduction and model spaces

The projection of a Hamiltonian into a ‘model space’ is a well-established procedure [14,15]. Given a Hamiltonian in a ‘complete’ space H, with eigenstates $|a\rangle$

$$H|a\rangle = E_a|a\rangle \tag{6}$$

an effective Hamiltonian for a smaller ‘model’ space may be constructed, with an effective Hamiltonian H_{eff} whose eigenstates $|a_0\rangle$ give identical eigenvalues, i.e.

$$H_{\mathrm{eff}}|a_0\rangle = E_a|a_0\rangle. \tag{7}$$

It is possible to define a *canonical* projection from the full space to the model space [14]

$$|a_0\rangle = \hat{k}|a\rangle. \tag{8}$$

For this canonical projection the effective Hamiltonian

$$H_{\mathrm{eff}} = \hat{k}H\hat{k}^{\dagger}, \tag{9}$$

is Hermitian. The construction of the transformation $\hat{k}$ is a relatively simple matter of linear algebra [14].

3. Application to the crystal field

In our application we are interested in the states of Pr^{3+} in $LiYF_4$ that are commonly referred to as $4f^2$, though the true states contain admixtures of other Pr^{3+} and ligand orbitals. In the calculation presented here the ‘full’ space is the CI space of $4f^2+4f6p$ used by Faucher and Moune [13]. The ‘model’ space is the $4f^2$ configuration used in the crystal field and correlation crystal field fits of Burdick and Richardson [9], who performed CCF fits using the delta-function model. For this work the fit of Ref. [13] was repeated using exactly the same set of measurements as in Ref. [9]. Though configurations other than $4f^2+4f6p$ undoubtedly make important contributions to correlation crystal field effects (see, for example, Ref. [2]) the relatively small basis set used in this work is convenient to illustrate the relationship between the CI and CCF approaches.

Table 1 displays fitting results for Pr^{3+} in $LiYF_4$.

The column labeled CF is a conventional crystal field fit. This gives a good fit to most of the observed energy levels, but a poor fit to the $^1D_2$ multiplet.

The CCF column is the result of a CCF calculation using the delta-function model. This gives an improved fit, particularly for the $^1D_2$ multiplet. Only two parameters, D_0^2 and D_0^4 are added. The D_4^4 parameter is constrained to have the same ratio to D_0^4 as B_4^4 to B_0^4 [9].

The CI column is the calculation using the extended basis set [13]. The $4f^2$ free-ion and the crystal field operators used within $4f^2$ are the same as in the CF and CCF calculations. For the excited configuration, the ratio $B_4^4(fp)/B_0^4(fp)$ is constrained to be equal to $B_4^4(ff)/B_0^4(ff)$. The interconfigurational atomic parameters are calculated using standard atomic codes [16]. However two variable multipliers, X^2 and X^4 are applied to the two-electron R^2 and R^4 integrals, so the CI fit has two more free parameters than the CCF fit and gives a better overall fit to the experimental energies.

The $4f^2$ parameters fitted in the CCF and CI fits look very different, particularly the one-electron crystal-field parameters. This is not surprising because the two calculations use very different basis sets. It only makes sense to compare the parameters after we project the CI Hamiltonian into the $4f^2$ basis.

Column PCI gives the result of projecting the CI Hamiltonian into the $4f^2$ basis and then fitting the parameters shown to the resulting *matrix*. Only the $g_{iq}^{(K)}$ operators that contribute to the δ_q^2 and δ_q^4 operators are included, but their ratios are not constrained by Eqs. (4) and (5).

Several features are apparent from comparing the PCI and CCF columns. The one-electron crystal-field parameters, B_q^K are very similar, emphasizing that the CI parameters cannot be directly compared to parameters derived within the $4f^N$ basis until the projection into the smaller space is carried out. The G_{iq}^K parameters in the PCI and CCF columns are also quite similar, even though we have

Table 1
Parameter fits for $LiYF_4$:Pr^{3+}. Parameter units are cm^{-1}. CF and CCF are fits within the $4f^2$ configuration excluding and including the two-electron crystal-field operators. CI is the configuration-interaction $4f^2+4f6p$ fit. The PCI parameters are obtained by projecting the CI Hamiltonian into the $4f^2$ configuration and fitting the resulting matrix with the indicated operators. Parameters in square brackets were held fixed in the fits. The G^K_{i0} parameters (shown in parentheses) are calculated from the D^K_0 parameters (Eqs. (4) and (5)). N is the number of energy levels in the fit. σ is the standard deviation for the fit and $\sigma(^1D_2)$ is the RMS deviation for the $^1D_2$ multiplet

Parameter	CF	CI	PCI	CCF
F^2	68979	69209	69145	69025
F^4	50619	50765	50634	50580
F^6	33276	33586	33456	33326
α	[23.0]	[23.0]	23.8	[23.0]
β	−637	−670	−680	−649
γ	[1371]	[1371]	1340	[1371]
$\zeta(f)$	750	751	749	750
M^0 [a]	[2.00]	[2.00]	1.99	[2.00]
P^2 [b]	220	206	210	215
$B^2_0(ff)$	433	178	524	542
$B^4_0(ff)$	−1068	−783	−1174	−1093
$B^4_4(ff)$	1319	990	1423	1327
$B^6_0(ff)$	−67	−327	−60	−45
$B^6_4(ff)$	1187	1534	1128	1165
$G^2_{2\,0}$			−161	(−347)
$G^2_{3\,0}$			141	(314)
$G^2_{10\,0}$			345	(381)
$G^4_{2\,0}$			−274	(−285)
$G^4_{3\,0}$			204	(258)
$G^4_{10\,A0}$			628	(179)
$G^4_{10\,B0}$			626	(343)
D^2_0				−15.9
D^4_0				8.8
X^2		1.297		
X^4		1.899		
$B^2_0(fp)$		4377		
$B^4_0(fp)$		−11411		
$B^4_4(fp)$		[14428]		
$\zeta(p)$		[3800]		
$R^2(ff,pp)$		[15014]		
$R^2(fp,fp)$		[4214]		
$R^4(fp,fp)$		[5646]		
$R^2(ff,fp)$		[−6337]		
$R^4(ff,fp)$		[−5636]		
N	46	46		46
σ	22.6	10.6		15.5
$\sigma(^1D_2)$	40.6	10.7		10.8

[a] $M^2=0.56M^0$, $M^4=0.38M^0$.

[b] $P^4=0.75P^2$, $P^6=0.50P^2$.

not restricted the ratios of these parameters in the PCI calculation.

In addition to the results shown here we also performed reductions that took into account more operators. Including all the g^K_{iq} operators gives a better fit to the matrix, but the operators shown in the calculation of column PCI gave the dominant effect. Calculations using spin-dependent operators were also carried out, but these operators only had a small effect.

Comparisons were also made for fits to Pr^{3+} energy levels in other hosts, including $LaCl_3$ and $CsCdBr_3$. The results obtained were similar to those reported here [17].

The PCI calculation gives contributions to the two-electron crystal-field parameters G^K_{iq} by the explicit inclusion of (one-electron) crystal-field and (two-electron) Coulomb interactions between the $4f^2$ and 4f6p states. This calculation is equivalent to carrying out a perturbation calculation (such as in Ref. [2]) to infinite order for a specific excited configuration. Perturbation-theory calculations [2,4] suggest that excitations involving p electrons are important, though in the latter work excitations from core 5p orbitals were calculated to have the largest effect.

4. Conclusions

By performing a projection from the extended configuration interaction basis $4f^2+4f6p$ we have shown that the configuration interaction approach gives very similar results to the correlation crystal field approach of adding two-electron crystal-field parameters to the Hamiltonian. The two approaches give very similar results not only for the energy levels, but also for the Hamiltonian matrix. The success of the configuration interaction calculations is evidence that excitations involving p electrons give important correlation effects, as has been discussed in other work using a perturbation-theory approach [4]. However, we point out that the CCF approach of adding two-electron operators is more general and is capable of taking into account excitations involving other lanthanide or ligand orbitals.

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