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A non-Euclidean crystal field for f electrons

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Abstract

To honor the memory of Clyde A. Morrison, some aspects are discussed of the two-electron crystal field that exhibits the symmetry of a regular didodecahedron, a non-Euclidean figure in which 24 regular heptagons meet in threes at 56 vertices. The group D, which comprises the 168 elements representing the rotations that send the didodecahedron into itself, is a subgroup of the group G_2 that Racah used for f electrons, but it is not a subgroup of $SO(3)$. Reflections extend D to D_h. The matrix elements of four two-electron operators scalar with respect to D_h, which have been previously evaluated in f^2 and f^3 within an $SO(3)$ basis, are studied to find some isoscalar factors involving the irreducible representations of G_2 and D_h. Selection rules and reciprocity relations are examined, and two unexpectedly null matrix elements of an operator scalar with respect to D but odd under reflection are accounted for. The effect of a perturbation possessing didodecahedral symmetry on the energy levels of a free ion is shown in a correlation diagram for the singlet terms of f^2. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Crystal fields, for both transition-metal ions and lanthanides, were a subject of lifelong interest to Clyde Arthur Morrison [1,2], whose memory we honor at the Fourth International Conference of f Elements. Although he might have regarded the present topic of non-Euclidean crystal fields as being too exotic for his taste, there is a long history of the usefulness of extensions to physical models. One of the most remarkable is the discovery of Coulomb degeneracies in the d shell that occur when the Slater integrals are assigned physically impossible ratios [3]. With hindsight, we can interpret these degeneracies in terms of the Lie group $SO(5)$, a precursor to the $SO(7)$ that was put to good use by Racah [4] in his analysis of the f shell just a few years later. More complicated degeneracies (involving the unitary groups) have been used to check the accuracy of the energy matrices for configurations involving inequivalent electrons [5]. Similar checks can be carried out for crystal-field Hamiltonians that convert to more symmetrical forms when special values are selected for the crystal-field parameters.

The symmetry to be studied here is a natural extension of that of the regular dodecahedron. Instead of 12 regular pentagons meeting in threes at 20 vertices, we have 24 regular heptagons meeting in threes at 56 vertices. We call this figure a didodecahedron. Since the internal angle of a regular heptagon is $5\pi/7$, and $3\times5\pi/7=15\pi/7>2\pi$, the space must be hyperbolic, that is, non-Euclidean, for three heptagons to fit together at a vertex. From Euler's formula relating edges, faces and vertices, it can be shown that the genus of the didodecahedron is 3, the same as that of a three-holed torus. The symmetries of the didodecahedron are most easily studied through a plane tessellation, the classical form of which was given more than a century ago by Felix Klein [6]. Since that date the topic has been of considerable interest to mathematicians, and a historical survey has been assembled by Levy [7]. Our own interest in the didodecahedron stems from a desire to extend to f electrons the fact that the five orbital components of a d electron form a basis for the single irreducible representation (IR) h of the icosahedral group I. We have been able to show [8] that the seven components of an f orbital form a basis for the seven-dimensional IR of the didodecahedral group D, which, coincidentally, is also called h by King et al. [9]. Unlike I, the group D is not a subgroup of $SO(3)$,

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Table 1
Characters of the group D_h. The classes are distinguished by their cycles, their order (the number of elements they contain) and by their type, following the traditional crystallographic notation

Cycles	1^8	2^4	$1^2 3^2$	4^2	17	$1^2 2^3$	$1^2 6$	8	8
Order	1	21	56	42	48	28	56	42	42
Type	E	C_2	C_3	C_4	C_7	σ	S_6	S_8	S_8'
a_1	1	1	1	1	1	1	1	1	1
a_2	1	1	1	1	1	-1	-1	-1	-1
t	6	-2	0	2	-1	0	0	0	0
b_1	6	2	0	0	-1	0	0	$\sqrt{2}$	$-\sqrt{2}$
b_2	6	2	0	0	-1	0	0	$-\sqrt{2}$	$\sqrt{2}$
h_1	7	-1	1	-1	0	1	1	-1	-1
h_2	7	-1	1	-1	0	-1	-1	1	1
j_1	8	0	-1	0	1	2	-1	0	0
j_2	8	0	-1	0	1	-2	1	0	0

the group of rotations in ordinary space, but it is a subgroup of G_2, which Racah used to great effect as a subgroup of *SO*(7) [4]. If we restrict our attention to rotations, D comprises 168 elements. When reflections are included, the number of elements is doubled and we refer to this enlarged group as D_h. Its character table turns out to be the same as one included by Littlewood in the Appendix of his book [10]; it is given here as Table 1 in the slightly rearranged form that we have found useful [8].

A difficulty of working with the IRs of D is that nothing is known of the analogues of the 3-*j* and 6-*j* symbols. In our earlier work [8] we took advantage of the extensive literature on G_2 and used its subgroup *SO*(3) as a basis for our calculations. This allowed us to find the matrix elements in f^2 and f^3 of what could be described as the simplest non-trivial didodecahedral crystal-field Hamiltonian H. Because a single f electron is not split by a didodecahedral crystal field, the simplest H involves two-electron operators scalar with respect to both D and the spin S. However, D is not a subgroup of *SO*(3), and this leads to algebraic complexities which nevertheless largely disappear in the final stages of evaluating the matrix elements. In the present article we aim to construct some of the didodecahedral isoscalar factors which, had they been known before, would have simplified our analysis. The need for consistency provides many checks on our earlier work, and, as is shown below, allows an explanation to be given of some unexpected null matrix elements that had surprised us earlier.

2. Crystal-field matrix elements

Our basic equation is a generalization of Eq. (1) of Racah [4], which expresses a matrix element in f^N of an operator scalar with respect to *SO*(3) as a sum over matrix elements of the same operator in f^{N-1}. For us the group is D_h rather than *SO*(3), and we limit our attention to $N = 3$. In terms of the IR's Γ of D_h, we write

$$\begin{aligned}\langle \mathrm{f}^3\ \Psi\, \Gamma \,|\, H \,|\, \mathrm{f}^3\ \Psi' \Gamma\rangle &= 3\sum(\mathrm{f}^3\ \Psi\, \Gamma \,|\, \mathrm{f}^2\ \overline{\Psi}\, \overline{\Gamma} + \mathrm{f}\ h_1)\\ &\times \langle \mathrm{f}^2\ \overline{\Psi}\, \overline{\Gamma} \,|\, H \,|\, \mathrm{f}^2\ \overline{\Psi}' \overline{\Gamma}\rangle(\mathrm{f}^2\ \overline{\Psi}' \overline{\Gamma} + \mathrm{f}\ h_1 \,|\, \mathrm{f}^3\ \Psi' \Gamma)\,, \qquad (1)\end{aligned}$$

where the sum runs over the parent states $\overline{\Psi}\, \overline{\Gamma}$ and $\overline{\Psi}' \overline{\Gamma}$ of f^2. In detail, each Ψ specifies the spin S, the IR U of G_2, and the IR W^+ (for f^2) or W^- (for f^3) of $O(7)$. The labels W to which the signs are attached are identical to Racah's labels for *SO*(7). As we have indicated, we have already found by other means the matrix elements of the various operators that can contribute to H, and so Eq. (1) provides a source of information for the coefficients of fractional parentage (cfp) appearing there. The operators that are G_2 scalars as well as D_h scalars are not useful and are dropped. There remain four Hermitian two-electron operators scalar with respect to D_h; they are listed with their matrix elements in f^2 in Table 2. The entries are taken from Table 10 of our earlier article [8], but we have taken the opportunity to interchange the state labels b_1 and b_2. Their assignment in f^2 is arbitrary, but they need to be switched for consistency with the assignments in f^3.

In the absence of any multiplicity difficulties, the cfp of Eq. (1) can be immediately factorized by the lemma of Racah [4], and we get

$$\begin{aligned}&(\mathrm{f}^3\ SW^- U\, \Gamma \,|\, \mathrm{f}^2\ SW^+ \overline{U}\, \overline{\Gamma} + \mathrm{f}\ h_1)\\ &\quad= (\mathrm{f}^3 SWU \,|\, \mathrm{f}^2\, \overline{S}\, \overline{W}\, \overline{U} + \mathrm{f})(U^-\, \Gamma \,|\, \overline{U}^+ \overline{\Gamma} + (10)^- h_1) \qquad (2)\end{aligned}$$

in which the signs on the W's have been transferred forward to the U's. This is done because D_h is a subgroup of $O(7)$ but not of G_2, so the information that the signs convey needs to be represented in the isoscalar on the far right of Eq. (2), in which the Γ's appear. The preceding isoscalar is independent of didodecahedral quantities and can be rapidly found by dividing the entries of the tables of Nielson and Koster [11] by the isoscalars $(UL|\overline{U}\, \overline{L} + \mathrm{f})$ given by Racah [4] in his Table IVa. The results are listed in Table 3.

Once the matrix elements of the various D_h scalars are fed into both sides of Eq. (1), an overdetermined set of equations is obtained for the isoscalars $(U^-\Gamma|\overline{U}^+\overline{\Gamma} + (10)^- h_1)$. Because the equations are quadratic, it is impossible to find the phases of the isoscalars unambiguous-

Table 2
Matrix elements of the two-electron operators e^{Ua} in f^2. They are all scalar with respect to S and D_h

f^2	$e_1^{(22)a}$	$e_2^{(22)a}$	$e_1^{(40)a}$	$e_2^{(40)a}$
$^3(11)^+ t$	-2	2	0	0
$^3(10)^+ h_2$	0	0	0	0
$^3(11)^+ j_2$	$\frac{3}{2}$	$-\frac{3}{2}$	0	0
$^1(00)^+ a_1$	0	0	0	0
$^1(20)^+ b_1$	$-1-2\sqrt{2}$	$-1-2\sqrt{2}$	$\frac{7}{3}$	$8-5\sqrt{2}$
$^1(20)^+ b_2$	$-1+2\sqrt{2}$	$-1+2\sqrt{2}$	$\frac{7}{3}$	$8+5\sqrt{2}$
$^1(20)^+ h_1$	0	0	$-\frac{20}{3}$	0
$^1(20)^+ j_1$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{7}{3}$	-12

Table 3
The isoscalars ($f^3\ SWU|\ f^2\ \bar{S}\,\bar{W}\,\bar{U}+f$)

	$^{[\bar{S}]}\bar{W}\,\bar{U}$			
$^{[S]}WU$	$^3(110)(10)$	$^3(110)(11)$	$^1(000)(00)$	$^1(200)(20)$
$^4(111)(00)$	-1	0	0	0
$^4(111)(10)$	$-\frac{\sqrt{2}}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	0	0
$^4(111)(20)$	$-\frac{\sqrt{2}}{3}$	$\frac{\sqrt{7}}{3}$	0	0
$^2(100)(10)$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{3}}$	$\frac{\sqrt{2}}{\sqrt{7}}$	$\frac{\sqrt{3}}{\sqrt{14}}$
$^2(210)(11)$	$-\frac{1}{\sqrt{2}}$	0	0	$\frac{1}{\sqrt{2}}$
$^2(210)(20)$	$-\frac{\sqrt{7}}{3\sqrt{2}}$	$-\frac{1}{3}$	0	$\frac{1}{\sqrt{2}}$
$^2(210)(21)$	0	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{\sqrt{2}}$

ly. However, we have made choices that are consistent with both the diagonal and the off-diagonal matrix elements of the e^{Ua} operators. The results are given in Tables 4 and 5. These results are made complete for the daughters of f^2 by including the trivial sets

$$((10)^-h_1\,|\,(00)^+a_1+(10)^-h_1)=1 \tag{3}$$

and

$$(U^-\Gamma\,|\,(10)^+h_2+(10)^-h_1)=1\ , \tag{4}$$

Table 4
The isoscalars ($U^-\Gamma|(11)^+\bar{\Gamma}+(10)^-h_1$)

	$(11)^+\bar{\Gamma}$	
$U^-\Gamma$	$(11)^+t$	$(11)^+j_2$
$(10)^-h_1$	$\frac{\sqrt{3}}{\sqrt{7}}$	$\frac{2}{\sqrt{7}}$
$(20)^-b_1$	$\frac{\sqrt{3}(1-2\sqrt{2})}{7}$	$\frac{(2+3\sqrt{2})}{7}$
$(20)^-b_2$	$\frac{\sqrt{3}(1+2\sqrt{2})}{7}$	$\frac{(-2+3\sqrt{2})}{7}$
$(20)^-h_2$	$\frac{\sqrt{3}}{\sqrt{7}}$	$\frac{2}{\sqrt{7}}$
$(20)^-j_2$	$\frac{2\sqrt{3}}{7}$	$(\frac{1}{7},\ \frac{-6}{7})$
$(21)^-t$	0	1
$(21)^-b_1$	$\frac{3\sqrt{2}+2}{7}$	$\frac{-\sqrt{3}(1-2\sqrt{2})}{7}$
$(21)^-b_2$	$\frac{3\sqrt{2}-2}{7}$	$\frac{-\sqrt{3}(1+2\sqrt{2})}{7}$
$(21)^-h_1$	$\frac{2}{\sqrt{7}}$	$\frac{-\sqrt{3}}{\sqrt{7}}$
$(21)^-h_2$	$\frac{2}{\sqrt{7}}$	$\frac{-\sqrt{3}}{\sqrt{7}}$
$(21)^-j_1$	0	1
$(21)^-j_1'$	1	0
$(21)^-j_2$	$\frac{-2\sqrt{3}}{7}$	$(\frac{6}{7},\ \frac{-1}{7})$
$(21)^-j_2'$	$\frac{5}{7}$	$\left(\frac{2\sqrt{3}}{7},\ \frac{2\sqrt{3}}{7}\right)$

Table 5
The isoscalars ($U^-\Gamma|(20)^+\bar{\Gamma}+(10)^-h_1$)

	$(20)^+\bar{\Gamma}$			
$U^-\Gamma$	$(20)^+b_1$	$(20)^+b_2$	$(20)^+h_1$	$(20)^+j_1$
$(10)^-h_1$	$\frac{\sqrt{2}}{3}$	$\frac{\sqrt{2}}{3}$	$\frac{\sqrt{7}}{3\sqrt{3}}$	$\frac{2\sqrt{2}}{3\sqrt{3}}$
$(11)^-t$	$\frac{\sqrt{2}+4}{\sqrt{63}}$	$\frac{\sqrt{2}-4}{\sqrt{63}}$	$\frac{\sqrt{7}}{3\sqrt{3}}$	$\frac{4\sqrt{2}}{3\sqrt{21}}$
$(11)^-j_1$	$\frac{3-\sqrt{2}}{3\sqrt{7}}$	$\frac{3+\sqrt{2}}{3\sqrt{7}}$	$\frac{\sqrt{7}}{3\sqrt{3}}$	$\left(\frac{-\sqrt{2}}{3\sqrt{21}},\frac{2\sqrt{2}}{\sqrt{21}}\right)$
$(20)^-b_1$	0	$\frac{4-\sqrt{2}}{7}$	$\frac{1}{\sqrt{3}}$	$\frac{6+2\sqrt{2}}{7\sqrt{3}}$
$(20)^-b_2$	$\frac{-4-\sqrt{2}}{7}$	0	$\frac{-1}{\sqrt{3}}$	$\frac{-6+2\sqrt{2}}{7\sqrt{3}}$
$(20)^-h_2$	$\frac{\sqrt{2}}{\sqrt{7}}$	$\frac{\sqrt{2}}{\sqrt{7}}$	$\frac{1}{\sqrt{21}}$	$\frac{\sqrt{8}}{\sqrt{21}}$
$(20)^-j_2$	$\frac{3-\sqrt{2}}{7}$	$\frac{3+\sqrt{2}}{7}$	$\frac{1}{\sqrt{3}}$	$\frac{4\sqrt{2}}{7\sqrt{3}}$
$(21)^-t$	$\frac{-1+\sqrt{2}}{3}$	$\frac{-1-\sqrt{2}}{3}$	$\frac{-2\sqrt{2}}{3\sqrt{3}}$	$\frac{-1}{3\sqrt{3}}$
$(21)^-b_1$	0	$\frac{-6-2\sqrt{2}}{7\sqrt{3}}$	$\frac{2}{3}$	$\frac{-9+4\sqrt{2}}{21}$
$(21)^-b_2$	$\frac{6-2\sqrt{2}}{7\sqrt{3}}$	0	$\frac{-2}{3}$	$\frac{9+4\sqrt{2}}{21}$
$(21)^-h_1$	$\frac{-1-2\sqrt{2}}{\sqrt{21}}$	$\frac{-1+2\sqrt{2}}{\sqrt{21}}$	0	$\frac{1}{\sqrt{7}}$
$(21)^-h_2$	$\frac{-1}{\sqrt{21}}$	$\frac{-1}{\sqrt{21}}$	$\frac{-4\sqrt{2}}{3\sqrt{7}}$	$\frac{5}{3\sqrt{7}}$
$(21)^-j_1$	$\frac{-1}{3}$	$\frac{1}{3}$	$\frac{2\sqrt{2}}{3\sqrt{3}}$	$\left(\frac{2}{3\sqrt{3}},\ \frac{-1}{\sqrt{3}}\right)$
$(21)^-j_1'$	$\frac{-1}{\sqrt{6}}$	$\frac{-1}{\sqrt{6}}$	$\frac{\sqrt{2}}{3}$	$(\frac{-2}{3},\ 0)$
$(21)^-j_2$	$\frac{3-\sqrt{2}}{7}$	$\frac{-3-\sqrt{2}}{7}$	0	$\frac{3\sqrt{3}}{7}$
$(21)^-j_2'$	$\frac{-9-4\sqrt{2}}{7\sqrt{6}}$	$\frac{-9+4\sqrt{2}}{7\sqrt{6}}$	$\frac{\sqrt{2}}{3}$	$\frac{2}{21}$

where

$$U\Gamma=(00)a_2;(10)h_1;(11)t,j_1;(20)b_1,b_2,h_2,j_2\ . \tag{5}$$

3. Isoscalars

Our assumption that multiplicities can be ignored in writing down Eq. (2) does not always hold. The IR j_i occurs twice in the reduction of the Kronecker product $j_i\times h_1$, for $i=1$ or 2. This means that in these cases the group labels are inadequate to define the daughter states. In our tabulation of matrix elements [8], we made an arbitrary separation and denoted the states by j_i and j_i'. Each column headed j_i in Tables 4 and 5 breaks up into two entries for the rows j_i and j_i', and these two entries (set within large parentheses) correspond to the two values of an index α which needs to be added as a subscript to the isoscalar. It is identical to the multiplicity index γ appearing in Eq. (11) of Racah [4], and would appear again in the Clebsch–Gordan coefficient $(\alpha j_i p|j_i q,h_1 r)$, where p, q and r specify the particular components of the IR's standing to their left. The need for two entries in the j_1 rows of the j_1 column of Table 5 can be understood by recognizing that the G_2 Kronecker product $(20)\times(10)$ contains the IR (30), which, although not required within the physical configuration f^3, contains two IR's j_1 of D_h. These would provide two additional j_1 rows to the extended isoscalar table; and, for orthogonality to the three rows already listed, each must possess five entries.

From Table 5, we see that

$$((21)^- h_1|(20)^+ h_1 + (10)^- h_1) = 0\,. \tag{6}$$

At first sight this is difficult to understand because $h_1 \times h_1$ contains h_1 and $(20)^+ \times (10)^-$ contains $(21)^-$. However, the group sequence $O(7) \supset S_8 \supset D_h$ serves as an alternative to $SO(7) \supset G_2 \supset D$ [8], where S_8 is the group of permutations that interchange the eight affinity groups of the didodecahedron. When the relevant IR's of $O(7)$, S_8, and D_h are included in the isoscalar above, we get

$$((210)^-[521]h_1|(200)^+[62]h_1 + (100)^-[71]h_1)\,, \tag{7}$$

and this is obviously zero because [521] does not appear in the reduction of $[62]\times[71]$ (see Table B-2 of Wybourne [12]).

Many entries in Tables 4 and 5 are related by a generalization of the reciprocity relation given in Eq. (46) of Racah [4]. An example is provided by

$$((20)^- b_1\,|\,(11)^+ j_2 + (10)^- h_1)$$

$$= \sqrt{\frac{18}{7}}((11)^- j_1\,|\,(20)^+ b_2 + (10)^- h_1) \tag{8}$$

$$= \frac{2+3\sqrt{2}}{7}\,. \tag{9}$$

The factor 18/7 comes from

$$\frac{(\mathrm{Dim}\ j_2)(\mathrm{Dim}\ (20))}{(\mathrm{Dim}\ b_1)(\mathrm{Dim}\ (11))} = \frac{8\times 27}{6\times 14} = \frac{18}{7} \tag{10}$$

and would be equal to 1 if we had generalized the isoscalars to 3-U symbols (the analogues for G_2 of 3-j symbols for $SO(3)$), since the manoeuvre of Eq. (8) would then correspond to the interchange of two columns of the symbol. It is to be noticed, however, that the subscripts 1 and 2 defining the IR's of D_h are switched in step with the sign changes to (20) and (11). This is a consequence of our choice of labels for the IR's of D_h (see Tables 7 and 8 of Ref. [8]).

4. Unexpected vanishings

In addition to the four D_h scalars, there are two other two-electron operators that are D scalars, but they belong to the IR a_2 of D_h rather than a_1. They are also scalar with respect to the spin S, but change sign under reflection of the didodecahedron. In our earlier work [8] we called them $e_i^{(30)a}$, where $i=1$ and 2. The first belongs to $(211)^+$ of $O(7)$, and its only non-vanishing matrix elements in f^2 are within the states $(11)t$. The second belongs to $(310)^+$ of $O(7)$, and its only non-vanishing matrix elements in f^2 connect ${}^1(20)b_1$ to ${}^1(20)b_2$. One of our most surprising results concerns the separation of $(21)j_1$ and $(21)j_1'$ in f^3. This can be done in an infinity of ways, but by choosing j_1 to satisfy

$$\langle f^3\ \Psi\,|\,e_1^{(30)a}\,|\,f^3\ {}^2(21)j_1\rangle = 0 \tag{11}$$

for $\Psi = {}^2(20)j_2$, we found that Eq. (11) is also valid for $\Psi = {}^2(21)j_2$ and ${}^2(21)j_2'$. That is, our choice of one zero in our tables unexpectedly produced two other zeros.

To understand this result, we turn to Eq. (1). It cannot immediately be used because $e_1^{(30)a}$ belongs to a_2 of D_h, and is not a D_h scalar. However, Racah's original equation can be readily generalized to cope with operators that are not $SO(3)$ scalars, and an analogous procedure can be adopted here. Following Eq. (9) of Trees [13], we work with reduced matrix elements and introduce a 6-Γ symbol. The only relevant parent states of f^2 belongs to the IR t of D_h, and we get, ignoring possible phase factors,

$$\begin{aligned}(f^3\ \Psi\,\|\,e_1^{(30)a}\,\|\,f^3\ {}^2(21)j_1) &= 24(f^3\ \Psi|\,f^2\ t + f\ h_1)(f^2\ t\|\,e_1^{(30)a}\,\|\,f^2\ t)\\ &\quad\times(f^2\ t + f\ h_1\,|\,f^3\ {}^2(21)j_1)\begin{Bmatrix} j_2 & a_2 & j_1\\ t & h_1 & t\end{Bmatrix},\end{aligned} \tag{12}$$

the factor 24 coming from $3\sqrt{(\mathrm{Dim}j_1)(\mathrm{Dim}j_2)}$. To be technically correct, the 6-Γ symbol should have two multiplicity labels attached to it. The first is needed to indicate that the j_1 appearing therein refers to j_1 rather than j_1'; the second that the j_2 refers to the particular IR j_2 implied by Ψ. However, it is not necessary to go to these details because we see from Table 4 that our choice that

$$(f^2\ t + f\ h_1\,|\,f^3\ {}^2(21)j_1) = 0 \tag{13}$$

forces the right-hand side of Eq. (12) to be zero for any Ψ. The 6-Γ symbol in Eq. (12) plays no role. This means that Eq. (11) is valid for all Ψ, and our isoscalars can thus be used to explain an apparently mysterious coincidence.

5. Concluding remarks

Table 2 defines four two-electron operators e_i^{Ua} through their matrix elements in f^2. It is natural to wonder if they can be realized physically without having to suppose that space is non-Euclidean. Neither the Coulomb interaction between the electrons nor the spin–orbit interaction is a D_h scalar, so the IR's of D_h would be lost as good quantum labels if the energy levels of the free ion Pr^{3+} were subjected to a didodecahedral crystal field. The largest group that is a subgroup of both D and $SO(3)$ (the symmetry group of the free ion) is the octahedral group O. Klein discussed how the didodecahedral tessellation can be made to exhibit the rotations that send an octahedron into itself [6]. King et al. [9] point out that the sequence $G_2 \supset D \supset O$ is an alternative to $G_2 \supset SO(3) \supset O$, and this raises the question whether the addition of a didodecahedral field to the terms ^1D, ^1G and ^1I of the free Pr^{3+} ion might be indistinguishable from a two-electron octahedral field. However, this is not so. A correlation diagram connecting the spectroscopic terms (the $SO(3)$ levels) to the didodecahedral levels (the D levels) makes this clear. The energy levels in the intermediate region are produced by a Hamiltonian that is the sum of a D scalar and an $SO(3)$ scalar, and so must necessarily belong to the scalar IR A_1 of O, if a unique O is involved; but, as can be seen from Fig. 1, the levels do not exhibit the characteristic degeneracies of the IR combination $2A_1 + A_2 + 3E + 2T_1 + 4T_2$ of O that the branching rules would demand.

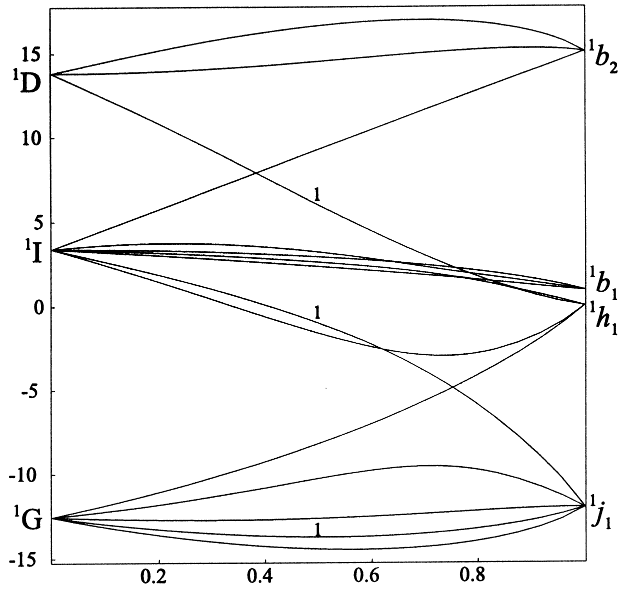

Fig. 1. A correlation diagram for the configuration f^2 in a Hamiltonian that is a sum of the $SO(3)$ scalar e_2 of Racah [4] and the D scalar $e_2^{(40)a}$. All the lines are two-fold degenerate except for the non-degenerate ones labelled ‘1’. The coordinates are chosen according to the traditional scheme for preserving the ratios of energies in a correlation diagram [14]. Thus the overall separations of the energies in both limits are the same, and intermediate positions are determined by a coordinate that runs from 0 to 1.

A referee has raised the question of the symmetry descent from D. Since $SO(3)$ is not a subgroup of D, we cannot presume that a particular crystal point group is a subgroup of D. Each must be examined separately. We should add that generalizations of D are possible. For example, the finite group of order 660, which corresponds to the non-Euclidean figure in which 60 regular undecagons meet in threes at 220 vertices, contains the icosahedral group as a subgroup and has been examined for possible applications to C_{60} by Kostant [15].

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