SHORT COMMUNICATIONS

CRYSTAL FIELD THEORY AND MAGNETIC GROUPS: SPIN–ORBIT COUPLING*

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Some initial work has recently been done (Cracknell 1966*a*) on the application of the theory of the corepresentations of non-unitary groups to the consideration of the splitting of atomic energy levels in a crystalline field possessing the symmetry of one of the magnetic point groups, or Shubnikov point groups. In that work only the situation of a strong crystalline field in the complete absence of spin–orbit coupling was considered; at that time it was not possible to include any consideration of the effect of spin–orbit coupling on the theory because detailed tables of the irreducible corepresentations ("coreps") of the double point groups were not available, neither was there available any work on the Krönecker products of corepresentations. This situation has now been remedied (Bradley and Davies, personal communication 1966; Cracknell and Wong 1967), so that it now seems appropriate to give some consideration to the inclusion of spin–orbit coupling in a crystalline field with the symmetry of one of the magnetic point groups.

Conventional crystal field theory (see, for example, Tinkham 1964) studies various different situations and the relations between them; they are

(1) free atom, neglecting spin–orbit coupling;
(2) free atom with spin–orbit coupling;
(3) strong spin–orbit coupling and weak crystal field;
(4) weak spin–orbit coupling and strong crystal field;
(5) crystal field with no spin–orbit coupling.

The procedure for determining the splitting of any given term for these various situations is well known and can be divided into four stages, as follows:

A: (1) → (5) Subduction of the rep $\mathscr{D}^L$ of the three-dimensional rotation group $O(3)$ onto the point group **G** of the crystal.

B: (5) → (4) The reduction of the inner Krönecker product of the rep $\mathscr{D}^S$ and the reps of **G** obtained in A.

C: (1) → (2) The reduction of the inner Krönecker product of the reps $\mathscr{D}^L$ and $\mathscr{D}^S$ of $O(3)$, corresponding to the orbital and spin angular momenta to give the reps $\mathscr{D}^J$ of $O(3)$.

* Manuscript received November 28, 1966.

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D: (2) → (3) The subduction of the rep $\mathscr{D}^J$ of $O(3)$ onto the point group **G** (these reps will be single-valued or double-valued depending on the value of J).

It should be fairly clear how this scheme is to be modified when one includes the operation of time inversion and allows the crystalline field to have the symmetry of one of the type II or type III magnetic point groups (Cracknell 1966*b*). The group of the symmetry operations of the atom is then no longer simply $O(3)$, the three-dimensional rotation group, but is $RO(3)$, where $RO(3)$ is the direct product of the group $O(3)$ with the group $(E+R)$, where R is the operation of time inversion. The symbol $\mathrm{D}\mathscr{D}^L$ is used to denote the corepresentation of $RO(3)$ derived from the rep $\mathscr{D}^L$ of $O(3)$. The steps that we have called A, B, C, and D above therefore become, for the case of the magnetic groups,

A: (1) → (5) The subduction of the single-valued coreps $\mathrm{D}\mathscr{D}^L$ of $RO(3)$ onto the magnetic point group **M**.

B: (5) → (4) The reduction of the inner Krönecker product of the corep $\mathrm{D}\mathscr{D}^S$ with the coreps of **M** that were obtained in A ($\mathrm{D}\mathscr{D}^S$ may be single-valued or double-valued depending on the value of S).

C: (1) → (2) The reduction of the inner Krönecker product of the coreps $\mathrm{D}\mathscr{D}^L$ and $\mathrm{D}\mathscr{D}^S$ of $RO(3)$ corresponding to the orbital and spin angular momenta.

D: (2) → (3) The subduction of the corep $\mathrm{D}\mathscr{D}^J$ of $RO(3)$ onto the magnetic group **M** (these coreps will be single-valued or double-valued depending on the value of J).

The stage A was considered, in outline at least, by Cracknell (1966*a*).

The stages B and C have been made possible by the work of Bradley and Davies (personal communication 1966), who show that it is possible to obtain very easily the reduction of the inner Krönecker product of two irreducible corepresentations; this is done by first considering the reduction of the inner Krönecker product of the irreducible representations of the unitary subgroup of the magnetic group in question, and then applying a simple rule to obtain the Clebsch–Gordan coefficients in the reduction of the product of the coreps. Further consideration of this must wait until their work has been published.

The stage D has now been made possible by the work of Cracknell and Wong (1967). This process, the subduction of the coreps $\mathrm{D}\mathscr{D}^J$ of $RO(3)$ onto the coreps of the magnetic point group **M**, proceeds as follows. If J takes the value of zero or of an integer then the corep $\mathrm{D}\mathscr{D}^J$ of $RO(3)$ is single-valued and the analysis proceeds exactly as for the stage A (Cracknell 1966*a*). If J takes a value of half an odd integer then the corep $\mathrm{D}\mathscr{D}^J$ is double-valued and the subduction of $\mathrm{D}\mathscr{D}^J$ onto **M** proceeds in a similar way, except that we are dealing with double-valued coreps rather than single-valued coreps. The character of a rotation through $(2\pi/n)$ in the representation $\mathscr{D}^J$ of $O(3)$, where n is 2, 3, 4, or 6, is assumed to be given by the same formula for

both integer and half-odd-integer values of the angular momentum (Bethe 1929), so that for a half-odd-integer value of J we have

$$\chi^J(2\pi/n) = \frac{\sin\{(J+\frac{1}{2})(2\pi/n)\}}{\sin(\pi/n)}. \tag{1}$$

Using this equation and the method of inspection of the character table of **H**, the unitary subgroup of **M**, or else equation (3.1) given by Cracknell (1966*a*), it is possible to determine which double-valued reps of **H** appear on restricting $\mathscr{D}^J$ of $O(3)$ to **H**. The determination of the coreps of **M** that are obtained from these double-valued reps of **H** can then be performed by following the work of Cracknell and Wong (1967).

We illustrate this process with just one example. If we consider an atomic ^2F term, that is $L = 3$ and $S = \frac{1}{2}$, then it is well known that the introduction of spin–orbit coupling, in the absence of any crystalline field, splits this term into two levels with $J = \frac{5}{2}$ and $J = \frac{7}{2}$. These two levels therefore belong to the two reps $\mathscr{D}^{5/2}$ and $\mathscr{D}^{7/2}$ of $O(3)$. If we consider the introduction of a weak crystalline field with the symmetry of the magnetic point group $m'3$ then the first step is to consider the subduction of $\mathscr{D}^{5/2}$ and $\mathscr{D}^{7/2}$ onto the unitary subgroup of $m'3$, that is onto the point group 23 (T). Using equation (1) the characters of the elements of 23 (T) in the reps $\mathscr{D}^{5/2}$ and $\mathscr{D}^{7/2}$ are

	E	C_{31}^-, etc.	C_{2x}, etc.
$\mathscr{D}^{5/2}$	6	0	0
$\mathscr{D}^{7/2}$	8	1	0

and we can easily see from inspection of Table 1 of Cracknell and Wong (1967) that these two representations can be reduced to give

$$\mathscr{D}^{5/2} = \bar{E} + {}^1\bar{F} + {}^2\bar{F} \tag{2}$$

and

$$\mathscr{D}^{7/2} = 2\bar{E} + {}^1\bar{F} + {}^2\bar{F}. \tag{3}$$

From Table 7 of the same work (Cracknell and Wong 1967) we see that the corep of $m'3$ derived from the double-valued rep $\bar{E}$ of the unitary subgroup of **M** belongs to case 1; this corep may be denoted by $\mathrm{D}\bar{E}$, and it is clearly two-dimensional. From the same work we can also see that the two two-dimensional reps ${}^1\bar{F}$ and ${}^2\bar{F}$ of 23 (T) stick together to form a four-dimensional (case 3) corep of $m'3$; we may denote this corep by $\mathrm{D}\bar{F}$. We can therefore say that the coreps $\mathrm{D}\mathscr{D}^{5/2}$ and $\mathrm{D}\mathscr{D}^{7/2}$ of $RO(3)$, which are derived from $\mathscr{D}^{5/2}$ and $\mathscr{D}^{7/2}$, split in a crystalline field with the symmetry of $m'3$ according to

$$\underset{1(2)}{\mathrm{D}\mathscr{D}^{5/2}} = \underset{1(2)}{\mathrm{D}\bar{E}} + \underset{1(4)}{\mathrm{D}\bar{F}} \tag{4}$$

and

$$\underset{2(2)}{\mathrm{D}\mathscr{D}^{7/2}} = \underset{2(2)}{2\mathrm{D}\bar{E}} + \underset{1(4)}{\mathrm{D}\bar{F}}. \tag{5}$$

The numbers in brackets indicate the degeneracy, that is, $p(q)$ signifies that there are p levels each of which is q-fold degenerate. It will be noted that the $J = \frac{5}{2}$ and

$J = \frac{7}{2}$ levels have split into a number of levels containing a total of 6 states and 8 states respectively, as might have been expected. The splitting in this example is illustrated in Figure 1.

In conclusion, we would like to clarify one point arising out of the earlier work on this subject (Cracknell 1966*a*). That work really ignores spin altogether; the

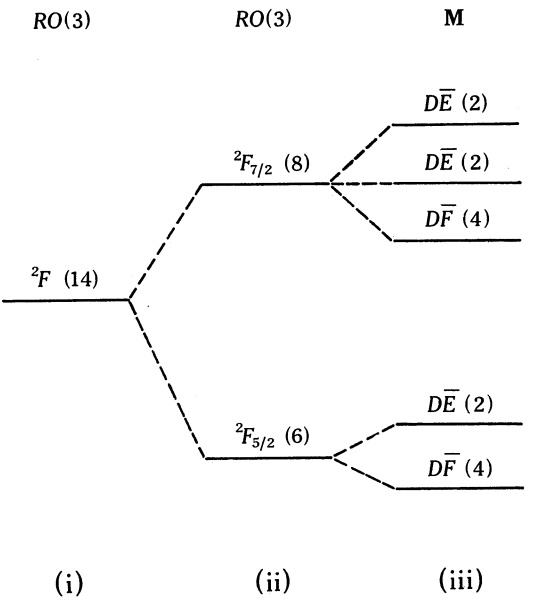

Fig. 1.—Splitting of an atomic ^2F term in $m'3$. (i) free atom; (ii) spin–orbit coupling, no crystal field; (iii) strong spin–orbit coupling, weak crystal field. The degeneracy of each level is shown in brackets.

scheme whereby the coreps are derived and which is said to be relevant to particles of zero or integral spin is in fact also applicable to particles with half-odd-integer spin in the approximation of completely disregarding spin. This is because what decides whether $\Delta(R^2) = +\mathbf{1}$ or $\Delta(R^2) = -\mathbf{1}$ (Wigner 1959) is not the intrinsic nature of the particles themselves but the properties of the basis functions of the representations that we are using. Since there we were using single-valued representations $\Delta(R^2) = +\mathbf{1}$ always, even though the particles that we are describing may be fermions. The consequence of this is that it is only the first half of the last column of Tables 1 and 2 of that work (Cracknell 1966*a*) that is actually meaningful and it applies to all kinds of particles, e.g. to both phonons and electrons.

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