Spin–orbit coupling in low-symmetry systems

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Abstract. Some of the complications which arise in labelling angular-momentum states in low-symmetry systems are discussed. In particular the assignment of irreducible representation labels for spin–orbit coupled states can be quite tricky because of the existence of automorphisms of the symmetry group of the system which affect the labelling of the representations if the definitions of the symmetry elements are changed. A detailed study is made for molecules of C₄ symmetry as the automorphism group structure is particularly rich especially when the number of electrons is odd.

1. Introduction

In high-symmetry cases quantum numbers can be correlated with labels of irreducible representations. In the ideal case this correlation derives from the eigenvalues of one or more operators. When two states correspond to the same irreducible representation, however, an additional quantum number is used which indicates the position of the state in the energetical sequence. Such subsidiary quantum numbers are well-known and sometimes useful. A notable example occurs in atomic systems in the presence of a linear magnetic field since component operators can be defined which have eigenvalues which can be used to define subsidiary quantum numbers. In the presence of an electric, molecular or crystal field, however, the situation becomes more interesting.

Low symmetries have been thought by some to be of little interest because of the small number of irreducible representations of the corresponding symmetry groups. However, in some cases this leads to interesting consequences for the definition of the states (as defined by irreducible representations) in terms of quantum numbers. To illustrate the problem the well-known case of spin–orbit coupling in atomic [1,2] and molecular systems [3] will be examined.

In the high-symmetry case of atoms, orbital states and even-electron spin states are described by irreducible representations of O(3)⁺ while odd-electron spin states are described by irreducible representations of SU(2). Spin–orbit coupled states derive from weighted sums of products of spin states and orbital states and are constructed in the context of O(3)⁺ for even-electron atoms and SU(2) for odd-electron atoms.

For atoms an orbital quantum number, L, is defined by the dimensionality of the orbital representation, 2L+1, while the spin quantum number, S, is defined by the dimensionality, 2S+1, of the spin representation. Multiplication of the spin and orbital irreducible representations leads in general to a reducible representation. When this is reduced to a sum of irreducible representations one obtains the spin–orbit quantum number, J, from the dimensionality, 2J+1, of each component irreducible representation. J turns out to be quantised (since consecutive values differ by 1 unit) and bounded by the limits L+S ≥ J ≥ |L−S|. In low-symmetry systems, however, the (2J+1)-fold degeneracy is lifted...
and it is the purpose of this contribution to assess the extent to which this lifting of the degeneracy has any effect on the physical properties of the states.

2. Orbital states

One well-known example which illustrates the effect of the lifting of the degeneracy is that of the use of magnetic quantum numbers. These are really only relevant to the properties of orbital and spin angular momenta in a linear magnetic field which can be internal or external. In such a scenario there is a unique direction, $z$, related to the field and the orbital magnetic quantum numbers, $L_z$, are related to the characters for the smallest rotation about that direction. In the case of an atom, $L \geq L_z \geq -L$, and, by analogy, $S \geq S_z \geq -S$, while for a linear molecule $L_z = \pm L$ and $S_z = \pm S$.

The point group $C_4$ will be chosen as a suitable example of a low-symmetry system. The character table for this group may be written

$$
\begin{array}{c|cccc}
  & E & A^2 & A & A^3 \\
\hline
\Gamma_1 & 1 & 1 & 1 & 1 \\
\Gamma_2 & 1 & 1 & -1 & -1 \\
\Gamma_3 & 1 & -1 & i & -i \\
\Gamma_3^* & 1 & -1 & -i & i \\
\end{array}
$$

where the symmetry elements are written at the tops of the columns and the representation labels at the left-hand side of the rows of characters. The generator $A$ is a rotation operator such that $A\phi = \phi + \pi/2$ where $\phi$ is an angle expressed in radians. The effect of $A$ on the wave function $\psi = \exp(iL_z\phi) \psi$ is to produce $A\psi = \exp(i\pi L_z/2) \psi$. This can be factorised as $A\psi = \exp(i\pi L_z/2) \psi$ so that the eigenvalue, $\exp(i\pi L_z/2)$, which is the imaginary $i$ raised to the power $L_z$, defines the character for the single generating element $A$ and hence the irreducible representation spanned by $\psi$ is identified. The result is that when $|L_z| \mod 4 = 0$ or 2 the representation is $\Gamma_1$ or $\Gamma_2$ respectively. When $|L_z| \mod 4 = 1$ or 3 the representation is $\Gamma_3$ or $\Gamma_3^*$ respectively if $L_z > 0$ and $\Gamma_3$ or $\Gamma_3^*$ respectively if $L_z < 0$.

3. Spin states

The discussion of the effect of a molecular field on spin states differs from the above only when the number of electrons is odd. Then the double group, which is a subgroup of SU(2) must be used. In the case of $C_4$ the double group is isomorphic to the cyclic group $C_8$ for which the character table is:

$$
\begin{array}{c|cccccccc}
  & E & A^4 & A^2 & A^6 & A & A^5 & A^3 & A^7 \\
\hline
\Gamma_1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\Gamma_2 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\
\Gamma_3 & 1 & 1 & -1 & -1 & i & i & -i & -i \\
\Gamma_3^* & 1 & 1 & -1 & -1 & -i & -i & i & i \\
\Gamma_4 & 1 & -1 & i & -i & -i & i & -i & i \\
\Gamma_4^* & 1 & -1 & -i & i & i & -i & -i & -i \\
\Gamma_5 & 1 & -1 & i & i & i & -i & -i & -i \\
\Gamma_5^* & 1 & -1 & -i & -i & -i & i & i & i \\
\end{array}
$$

In the top line of this table the generator $A$ is now of order 8 and the correlation of elements with those of the single group $C_4$ discussed in the preceding section is effected by arranging the columns so that the single group is effectively embedded in the double group.

For odd-electron spin states the only relevant irreducible representations are the lower four in the table, i.e. $\Gamma_4$, $\Gamma_4^*$, $\Gamma_5$ and $\Gamma_5^*$, which in this context are often referred to as double-valued representations. They can be characterised by their characters under the generating element $A$ of $C_8$.
which are respectively the first, seventh, fifth and third powers of $\sqrt{i}$ which is $(i + 1)/\sqrt{2} = \exp(i\pi/2)$. When $2|S_z| \mod 8 = 1$ or 7 the representation is $\Gamma_3$ or $\Gamma_5^*$ respectively if $S_z > 0$ and respectively $\Gamma_3^*$ or $\Gamma_3$ respectively if $S_z < 0$. When $2|S_z| \mod 8 = 3$ or 5 the representation is $\Gamma_5^*$ or $\Gamma_3$ respectively if $S_z > 0$ and $\Gamma_3$ or $\Gamma_5^*$ respectively if $S_z < 0$. For even-electron spin states the results are identical to those for $L_z$ states of the same numerical value as $S_z$.

4. Spin–orbit coupled states
The spin–orbit coupled states are characterised by a quantum number $J_z$ which is the sum of $L_z$ and $S_z$. The rules for assigning irreducible representation labels to $J_z$ should parallel those for the corresponding determination for $S_z$.

In the model case of atomic symmetry the spacing pattern of the spin–orbit coupled states is obtained by assuming that the spin–orbit coupling term in the Hamiltonian operator is $\zeta L \cdot S$ where $\zeta$ is a spin–orbit coupling constant and $L \cdot S$ is the scalar product of the axial-vector angular-momentum operators $L$ and $S$. To evaluate this contribution to the energy one expands $L \cdot S$ as $\frac{1}{2}(J^2 - L^2 - S^2)$ and then by assuming that the eigenvalues of $J^2$, $L^2$ and $S^2$ are respectively $J(J+1)$, $L(L+1)$ and $S(S+1)$ the contribution of the term $\zeta L \cdot S$ to the energy of the atomic state is $\frac{1}{2}\zeta(J(J+1) - L(L+1) - S(S+1))$. Since the energy of a set of states is usually largely dependent on $L$ and $S$, the spacing pattern is determined by the $J$-values of the states. The number of levels in the pattern will be $2L+1$ if $L < S$ or $2S+1$ if $S < L$. The spacings between energetically-adjacent states will form an arithmetic progression from which information can be deduced leading to the identification of $L$, $S$ and $J$ for each state. Identification of a $J_z$-value requires the states to be split using a small external linear magnetic field.

In linear molecules the external field is essentially present as an internal field and two types of field need to be distinguished. A purely electric field retains the degeneracy of complex-conjugate pairs of states. These would be states characterised by $\pm$ pairs of $J_z$-values. Such degeneracies would be lifted by magnetic fields.

In the low-symmetry case of molecules of point-group symmetry $C_4$ the physical effect of spin–orbit coupling is such that states with values of $J$ differing by an integral multiple of 4 have the same symmetry and so can interact. The evidence for this interaction is derived from spectroscopy. This interaction of states with the same symmetry is known as quenching since the mixing of states of lower $J_z$-value with the states of higher $J_z$-value reduces the interaction with the magnetic field.

5. The effect of automorphisms
In all cases where representation labels are being assigned to physical states one must examine the automorphism group of the symmetry group to see what additional information needs to be specified to fix a label [4]. In the case of the cyclic group $C_4$ discussed in the preceding section, the only automorphism is that which interchanges the rotation $A$ with its inverse $A^{-1} = A^3$. The choice of the sense of direction of the angle $\phi$ is purely one of convention and is difficult to relate to the macroscopic choice of the north or south pole of a magnet. Inevitably this means that different authors have used different conventions and so the labelling of a state as $\Gamma_3$ or $\Gamma_3^*$ needs to be interpreted with caution and consistency.

The double group of $C_4$ is particularly interesting from the point of view of its automorphisms.

| $A$ | $A^7$ | $A^5$ | $A^3$ |
|-----|-------|-------|-------|
| $\Gamma_3$ | $\Gamma_3^*$ | $\Gamma_3$ | $\Gamma_3^*$ |
| $\Gamma_3^*$ | $\Gamma_3$ | $\Gamma_3^*$ | $\Gamma_3$ |
| $\Gamma_4$ | $\Gamma_4^*$ | $\Gamma_5$ | $\Gamma_5^*$ |
| $\Gamma_4^*$ | $\Gamma_4$ | $\Gamma_5^*$ | $\Gamma_5$ |
| $\Gamma_5$ | $\Gamma_5^*$ | $\Gamma_4$ | $\Gamma_4^*$ |
| $\Gamma_5^*$ | $\Gamma_5$ | $\Gamma_4^*$ | $\Gamma_4$ |
These only affect the single-valued representations $\Gamma_3$ and $\Gamma_3^*$ and the four double-valued representations. The columns of the table above show the four possible cases. These are characterised by the power of the generating element $A$ to which $A$ is transformed by the automorphism. The first column gives the irreducible representation which will be changed and the subsequent columns give the transformed sets. The automorphism $A \rightarrow A^2$ produces complex conjugation while the automorphism $A \rightarrow A^3$ only affects the double-valued representations and can be regarded as the second generator of the automorphism group which is isomorphic to Klein’s Vierergruppe.

The effect on the $J_z$ quantum numbers is non-trivial. Replacing $A$ by $A^3$, for instance, would relabel a $\Gamma_4$ ($J_z = \frac{1}{2}$ or $-\frac{1}{2}$) state as a $\Gamma_3^*$ ($J_z = \frac{3}{2}$ or $-\frac{3}{2}$). In fact the four possible values, ($\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, $-\frac{3}{2}$) of $J_z$ for a $J = \frac{3}{2}$ state, which would be degenerate in the parent atomic symmetry, would all have separate symmetry labels and the relationship between the label to be chosen by convention and the explicit form of an electronic wave function for each would depend on the model chosen to describe the Hamiltonian operator and its eigenfunctions for the system.

6. Conclusion

The aim of this contribution is to indicate how the study of the automorphisms of a group in certain systems of low symmetry is important for establishing conventions for the labelling of electronic states. Due to the existence of automorphisms which have no effect on the labelling of states in symmetries which can be regarded as supergroups of the low-symmetry groups discussed, these problems have not been explicitly addressed hitherto.

Spin–orbit coupling was chosen as one well-known example which would illustrate the relevant points. Couplings involving rotational or vibrational angular momenta would also serve as interesting examples for future work.

References

[1] Herzberg G 1936 Atomspektren und Atomstruktur: eine Einführung für Chemiker, Physiker und Physikochemiker (Dresden: Theodor Steinkopff)
[2] Wybourne B G 1965 Spectroscopic Properties of the Rare Earths (New York: Interscience)
[3] Herzberg G 1966 Electronic Spectra and Electronic Structure of Polyatomic Molecules (New York: Van Nostrand Reinhold)
[4] Boyle L L 2014 J. Phys.: Conf. Ser. 512 012019