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Spectroscopic Selection Rules: The Role of Photon States

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Selection rules are vital in the interpretation of atomic and molecular spectra. The usual starting point for a derivation of selection rules is the transition moment which, in introductory spectroscopy courses, is normally taken on trust. However, many students find the transition moment to be a somewhat obscure quantity that does little to reveal the underlying physics. Furthermore, the journey from the transition moment to a particular selection rule is not always easy. This is especially troublesome when all one wishes to achieve is a *justification* of certain selection rules, rather than to give a full-blown account.

An easier way of justifying selection rules is to apply conservation arguments to individual photon–atom (or photon–molecule) interactions. One quantity that must be conserved is angular momentum. To invoke this argument, the angular momentum of the photon must first be known. A transition that satisfies angular momentum conservation must cause a change in angular momentum state of the absorbing or emitting atom (or molecule) that compensates for the loss or gain of photon angular momentum.

It is commonly assumed that a photon possesses an angular momentum of $\pm\hbar$ where $\hbar = h/2\pi$. In other words, it has a unit quantum of angular momentum and therefore unit changes in the angular momentum quantum number are expected for an absorbing or emitting atom or molecule. Foss presented this argument in an article in this *Journal* some years ago (*1*) to rationalize selection rules such as $\Delta l = \pm 1$ and $\Delta J = \pm 1$, and it has also appeared in several textbooks (e.g., see refs *2–5*). While it is a useful starting point, this model fails to account properly for selection rules when subjected to closer examination. In this article a more comprehensive, but nevertheless straightforward, justification of angular momentum selection rules is presented. I begin with a very brief review of some key results from the quantum theory of angular momentum. I then show some of the flaws in the model used by Foss and others. Finally, I explain how these flaws disappear when a more complete quantum electrodynamic model of a photon is employed.

Review of the Basic Elements of the Quantum Theory of Angular Momentum

Most undergraduate courses on quantum mechanics include a description of the angular momentum of a single rotating or orbiting body. Many also include an elementary account of the coupling of angular momenta. Some key facts from both topics are summarized below without proof.

Single Body

Angular momentum is a vector quantity. An example is the orbital angular momentum of an individual electron in an atom (the possibility of coupling is dealt with in the next section). In quantum mechanics, all three Cartesian components of this vector cannot be known simultaneously (for a proof see ref *2*). Instead, there are only two simultaneously observable quantities, the total angular momentum and any *one* of its Cartesian components. Which component is chosen is arbitrary in the absence of some external constraint but it is conventional to select the *z*-component. As a result there are two quantum numbers that define the orbital angular momentum of an electron, the total quantum number l and its corresponding projection onto the *z*-axis, quantum number m_l.

Figure 1 summarizes the findings in a vector diagram. Similar diagrams are commonplace in textbooks dealing with the quantum theory of angular momentum. The total angular momentum, represented by the length of the vector, has the magnitude

$$\sqrt{l(l+1)}\,\hbar$$

The quantum number l may have any integer value including zero. Although only one is indicated in the figure, there are $2l + 1$ possible values of m_l ranging from $-l$ to $+l$ in unit steps. The values of the projection of the orbital angular momentum on the *z*-axis are $m_l\hbar$.

Strictly speaking, l and m_l are not the only important angular momentum quantum numbers. Angular momentum states also possess *parity*. Parity refers to the effect of an inversion of all spatial coordinates on the sign of the angular momentum wave function. If there is no change in sign the parity is said to be even; a change in sign corresponds to a state of odd parity. For orbital angular momentum the parity is $(-1)^l$. This is easily seen by considering the well-known shapes of s, p, d, and f orbitals. An inversion of coordinates about the atomic nucleus does not change the sign of s and d orbitals, and so they possess even parity; but it does change the sign of p and f orbitals, so they must have odd parity. Parity places restrictions on spectroscopic transitions, as will be seen later.

Coupling of Two Angular Momenta

The coupling of two angular momenta, l_1 and l_2, yields a resultant L, which is the vector sum of the two individual

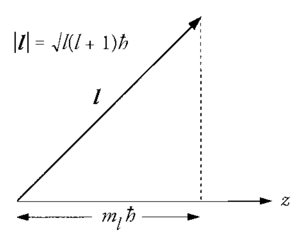

Figure 1. Vector model of quantized angular momentum. The magnitude of the angular momentum, represented by the length of the vector, is

$$\sqrt{l(l+1)}\,\hbar$$

The vector precesses (not shown) about the *z* axis, producing indeterminate components in the *x* and *y* directions but a well-defined component along the *z* axis.

angular momentum vectors,

$$L = l_1 + l_2 \quad (1)$$

In quantum mechanics, the total orbital angular momentum is quantized and has a quantum number L, which is restricted to the values

$$|l_1 + l_2| \geq L \geq |l_1 - l_2| \quad (2)$$

This important result is central to the arguments about conservation of angular momentum presented later.

Transitions between Angular Momentum States: The Failure of the Simple Model

Photons possess quantized angular momentum. As discussed by Foss (*1*), experiments have shown that all photons have an angular momentum of $\pm\hbar$ along the axis of propagation. This is known as the *helicity* of a photon. The two possible signs refer to the two possible states of circularly polarized light, left and right circular polarization. Linearly polarized light can be thought of as an equal mixture of left and right circularly polarized light, while any other state of polarization (e.g., elliptical polarization) will contain unequal proportions of photons with opposite helicities.

Now consider a transition in which an electron moves from one atomic orbital to another by photon absorption or emission. According to the Laporte selection rule, only transitions for which $\Delta l = \pm 1$ are allowed. This selection rule can be justified on the grounds of parity conservation, as will be shown later. But it should also be possible to show that it is consistent with angular momentum conservation. The argument that is normally employed, as mentioned earlier, is that since a photon possesses unit angular momentum, $\pm\hbar$, only a compensating unit change in the electron orbital angular momentum is compatible with the conservation of overall angular momentum.

However, a trivial example will show that this explanation is flawed. Consider the transition $l = 1 \leftrightarrow l = 0$. The conservation of angular momentum requires that the vector sum of all angular momenta is zero. For $l = 0$ the orbital angular momentum is zero and so in a transition to $l = 1$ the magnitude of the angular momentum gained by the electron must exactly equal that of the photon that is being absorbed. However, it will be clear from the previous section that the magnitude of the electron orbital angular momentum for $l = 1$ is $\sqrt{2}\hbar$ and not $\hbar$!

The Foss model also fails to account for other processes, such as electric quadrupole transitions. The selection rules for electric quadrupole transitions are $\Delta l = 0, \pm 2$, but if a photon can only possess an angular momentum of $\pm\hbar$, then one cannot explain how $\Delta l = \pm 2$ transitions can occur.

Photon States

Quantum electrodynamics is concerned with the application of quantum mechanics to the motion of charged particles and electromagnetic fields. When applied to the latter, the radiation field is found to be quantized, giving rise to the familiar concept of photons. Further, these light quanta, like atoms and molecules, can exist only in certain *quantum states*.

Also as for atoms and molecules, several parameters may be required to specify a particular photon state. These parameters are as follows.

Photon energy. This is familiar from elementary physics—it depends linearly on the frequency ν; that is, $E = h\nu$.

Angular momentum. The quantum mechanics of photon angular momentum has much in common with any other type of angular momentum. A photon can be ascribed a total angular momentum quantum number, j, and a projection quantum number m_j. The magnitude of this momentum is given by

$$\sqrt{j(j+1)}\,\hbar$$

and the projection along the z axis is $m_j\hbar$. Photons may possess any positive integer j, but $j = 0$ is impossible; that is, photons cannot have zero angular momentum.

Parity. An angular momentum state of a photon must have parity. For a given j both odd and even parities are possible.

Proof of the above statements are rather involved and can be found in books on quantum electrodynamics (see, for example, refs *6*, *7*). However, the take-home message is very simple. *The different possible angular momentum states and parities can be identified with different types of photons.* Notice that, in contrast to the electron orbital angular momentum, both even and odd parities are possible for each value of the photon angular momentum quantum number j. Taking $j = 1$ and $j = 2$ as examples, the following types of photon occur:

$j = 1$, parity = odd	electric dipole photon
$j = 1$, parity = even	magnetic dipole photon
$j = 2$, parity = even	electric quadrupole photon
$j = 2$, parity = odd	magnetic quadrupole photon

In a classical electromagnetic field, the electric and magnetic parts contain various multipole components: dipole, quadrupole, and onwards to higher multipoles. In quantum electrodynamics, we can think of these parts as arising from different types of photon, and the names of the photon states given above reflects this.

It can be shown (*6*, *7*) that all photons, regardless of j or parity, must possess an angular momentum along their direction of propagation of $\pm\hbar$, thus concurring with experiment (*1*, *8*); this is the helicity referred to earlier. However, it is important to recognize that the direction of propagation is not the same as the axis (z) along which the projection quantum number m_j is defined (m_j may take any integer value in the range $-j \leq m_j \leq j$). It is the vector coupling of j with the initial and final state angular momenta of an atom or molecule, not the helicity, that determines the total angular momentum selection rules.[1]

To close this section a word of caution is appropriate. Although it is convenient to subdivide a collection of photons into electric dipole, magnetic dipole, etc. photons, this model should not be taken too literally. Strictly speaking, these photon states manifest themselves only when the radiation interacts with an atom or molecule. Fortunately, since the aim of this article is to deal with precisely these interactions, this subtlety need not concern us further.

Conservation of Angular Momentum in Spectroscopic Transitions: A Vector Model

To conserve angular momentum in a transition, the vector sum of the initial angular momenta must equal the vector sum of the final angular momenta. For an absorption transition, the initial state consists of the orbital angular momentum

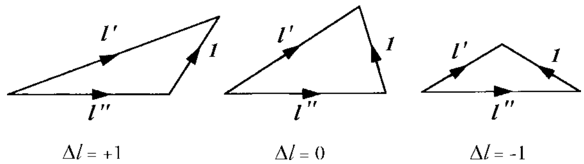

Figure 2. Vector model of the possible angular momentum changes for an electric dipole transition. The length of each vector represents the magnitude of the angular momentum and these are scale drawings for l'' = 2. The label **1** refers to the angular momentum vector of a photon with j = 1. Although $\Delta l = 0$ satisfies angular momentum conservation, this transition is parity forbidden.

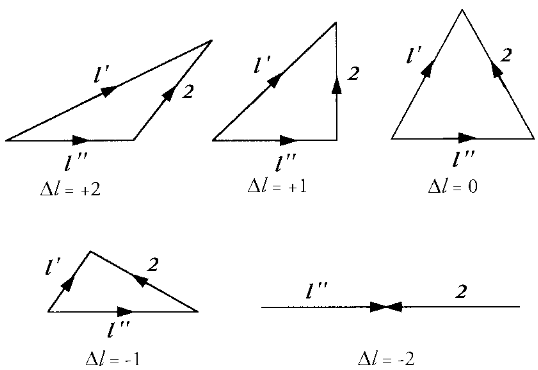

Figure 3. Vector model of the orbital angular momentum changes for an electric quadrupole transition. These are scale drawings assuming l'' = 2. The vector labeled **2** represents the angular momentum of the photon (j = 2). Although $\Delta l = \pm 1$ transitions satisfy angular momentum conservation, these transitions are parity forbidden.

vector l'' and the photon angular momentum j. In the final state there is only one angular momentum vector, the upper state orbital angular momentum vector l', which is given by

$$l' = l'' + j \tag{3}$$

The rules for coupling two angular momenta were given earlier (*2*), and so we deduce that the corresponding quantum numbers must satisfy $|l'' + j| \geq l' \geq |l'' - j|$.

For an electric dipole photon, for which j = 1, it is seen that $l' - l'' = \Delta l = 0, \pm 1$. A convenient way of illustrating this is by a vector diagram, as shown in Figure 2. Notice that the angular momentum "deficit" discussed earlier no longer occurs when the total photon angular momentum is properly accounted for. If conservation of angular momentum were the only requirement, then the $\Delta l = 0$ transition, shown in the center of Figure 2, would be allowed in addition to $\Delta l = \pm 1$. However, the parities of the photon and the initial and final electron orbital angular momentum states must also be taken into account. The role of parity in determining selection rules has been discussed in detail in a recent article by Chowdhury in this *Journal* (*9*). Since parity must be conserved in any process[2] and since an electric dipole photon has odd parity, the parities of the upper and lower orbitals must be opposite. This does not occur for $\Delta l = 0$, and so this is a strictly forbidden transition. However, it is satisfied by $\Delta l = \pm 1$, thus yielding the Laporte selection rule.

These arguments are easily extended to other types of transitions. It is well known that electric dipole selection rules can be violated by electric quadrupole or magnetic dipole transitions. The interaction of electric quadrupole and magnetic dipole photons with atoms or molecules is normally several orders of magnitude weaker than with electric dipole photons. Nevertheless, it is an interesting and easy exercise to determine the allowed transitions.

For a magnetic dipole transition, the angular momentum restriction is the same as for electric dipole transitions, since j = 1; but the even parity of the photon now allows $\Delta l = 0$ but forbids $\Delta l = \pm 1$. Notice, however, that $l' = 0 \leftrightarrow l'' = 0$ is not allowed because a photon cannot possess zero angular momentum. In fact, this is a general result: whenever both the initial and final states of an atom or molecule have a zero total angular momentum, then no transition between them is possible by single photon absorption (or emission) because there is no way of compensating for the nonzero photon angular momentum.

For electric quadrupole transitions, the angular momentum restriction alone dictates that $\Delta l = 0, \pm 1, \pm 2$ (see Fig. 3), but the even parity of an electric quadrupole photon forbids $\Delta l = \pm 1$.

Conclusions

A knowledge of the angular momenta and parities of photons provides a simple and yet powerful justification of total angular momentum selection rules in spectroscopy. This model is accessible to any student who has encountered angular momentum coupling in an elementary quantum mechanics course. In the undergraduate spectroscopy lecture course that I deliver, the material contained in this paper is easily covered in a single one-hour lecture.

The focus in this article has been on selection rules for the orbital angular momentum of a single electron in an atom, this system being chosen because of its familiarity to all chemists and physicists. However, these arguments are easily generalized to include other types of angular momentum, such as the total angular momentum of an atom or molecule (derived from the coupling of angular momenta of individual electrons) and the rotational angular momentum of a molecule. They can also be successfully applied to multiphoton transitions.

Notes

1. Although it has a somewhat uncertain physical meaning, the angular momentum of a photon can be subdivided into orbital and spin contributions. The helicity can be associated with the spin part; that is, a photon has a spin quantum number of unity and its projection along the direction of photon propagation takes on the two values $\pm\hbar$. A zero projection of the spin along the propagation direction is impossible. The helicity is important in determining selection rules involving magnetic (projection) quantum numbers, but it does not account for changes in the total angular momentum.

2. Parity violations, caused by nuclear forces, are well known in high-energy nuclear spectroscopy. However, for atomic and molecular spectroscopy, parity conservation can be regarded as absolute.

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