Continuous Groups and their Representations

for some of the matrix elements by (a) using equation (7.53) with the
Clebsch–Gordan coefficients from question 7.8, and (b) carrying out the explicit
integrals using the scalar product of subsection 3.2.A, i.e. an integral over the unit
sphere.

7.13 Show that \( \langle j | J | j' \rangle = (j(j+1))^{1/2} \sum L \langle j' | J' | j' \rangle \) by introducing a sum over 'intermediate states'
\( \sum \langle j | J | j' \rangle \langle j' | J' | j' \rangle \) and using equation (7.53) together with the
normalisation sum over the coupling coefficients.

7.14 Show that the Clebsch–Gordan coefficients \( C(l|l, m-m0) \) have the simple form
\[
C(l|l, m-m0) = (-1)^{l-m}/(2l+1)^{1/2}
\]
(Use the method of question 7.8 by (a) writing \( \Psi^{(2)}_m = \sum_n C(l|l, m-m0) \phi^{(0)}_n \psi^{(0)}_m \).

(b) making use of \( J \), \( \Psi^{(0)}_m = 0 \) to relate successive coefficients, and (c) using
normalisation and the convention that \( C(l|l, l-m0) > 0 \) Hence construct an
invariant under \( \mathbb{R}_3 \) from the five spherical harmonics \( Y^{(1)}_{l,m} \).

7.15 Show that, in the case of the group \( \mathbb{R}_3 \), the general definition (7.61) of the Casimir
operator leads to \( G = -\frac{1}{4} J^2 \).
Angular Momentum and the Group $R_3$ with Illustrations from Atomic Structure

The properties of the group $R_3$ were investigated in the previous chapter and the relation between the infinitesimal operators and the angular momentum operators was noted. In the present chapter we explore this relation in more detail by studying first one particle and then several particles and by introducing the concept of intrinsic spin. We then move to the realistic problem of atomic structure in which there are many examples of the effects of $R_3$ symmetry. We consider not only the hydrogen atom but also many-electron atoms.

8.1 Rotational invariance and its consequences

If a Hamiltonian is spherically symmetric, in other words if it has no preferred direction in space, then it has $R_3$ as its symmetry group. We shall therefore have the various consequences listed generally in chapter 5. Having studied the
8.1 Angular Momentum and the Group $\mathcal{S}_3$

In the first place, each eigenvalue will carry one of the labels $j = 0, \frac{1}{2}, 1 \ldots$ of the irreducible representations $D^{(j)}$ of $\mathcal{S}_3$. For an energy level $E$ there will be a $(2j + 1)$-fold degeneracy with the eigenfunctions forming the basis of the representation $D^{(j)}$. These eigenfunctions may be distinguished from each other by their behaviour with respect to rotations about some chosen axis which we call the $z$-axis. This corresponds to the reduction (7.38)

$$D^{(j)} = \sum_{m=-j}^{j} T^{(m)}$$

of $D^{(j)}$ into irreducible representations $T^{(m)}$ of the subgroup $\mathcal{S}_3$. Thus we may denote the energies by $E(\gamma j)$ and the wave functions by $\psi(\gamma jm)$, where $\gamma$ denotes all other quantum numbers which have nothing to do with rotational invariance.

As we have seen in the preceding chapter the wave function $\psi(\gamma jm)$ is therefore an eigenfunction both of $J_z$, the infinitesimal operator for rotations about the $z$-axis, and of the Casimir operator $J^2$. From equations (7.39) and (7.36)

$$J_z \psi(\gamma jm) = m \psi(\gamma jm)$$
$$J^2 \psi(\gamma jm) = (j(j + 1)) \psi(\gamma jm)$$

At this stage we have not specified anything about our physical system other than its spherical symmetry so that the explicit form of the operators $J_z$ and their physical significance cannot yet be discussed. Nevertheless, the results (8.2) can be stated.

Because the Hamiltonian is invariant the operators $J_x$, $J_y$, $J_z$ and also the Casimir operator $J^2$ all commute with the Hamiltonian and are therefore conserved in the usual sense, discussed in section 5.5.

If we classify any transition operators according to their behaviour under rotations, then selection rules in $j$ follow immediately from the discussion of section 5.4 using the rule (7.44) for the reduction of product representations in $\mathcal{S}_3$. Thus, for example, if $j$ and $j'$ denote the $\mathcal{S}_3$ labels for initial and final states and if the relevant transition operator transforms like $D^{(k)}$, then given $j$, the final state $j'$ is restricted by the condition

$$j' = (j + k), (j + k - 1), \ldots, |j - k|$$

We note from subsection 7.4.5 that a spherical harmonic $Y^m_l$ transforms like $D^{(l)}$. In particular, the dipole operators described in section 5.4, which transform like the vector representation of $\mathcal{S}_3$, correspond to $k = 1$. The expansion (7.49) of an arbitrary function into spherical harmonics is often called a multipole expansion with the term $Y^m_l$ being a $2^m$ pole. (It may be shown that $2^m$ is the minimum number of point charges needed to produce a potential field which is proportional to a single spherical harmonic $Y^m_l$ with fixed $k$.) A transition governed by an operator transforming like $D^{(l)}$ is said to
have multipolarity \(2^k\), i.e. dipole \((k = 1)\), quadrupole \((k = 2)\), octupole \((k = 3)\), etc.

If the group is enlarged from \(\mathcal{A}_3\) to \(O_3\) by including the inversion then, since \(O_3 = \mathcal{A}_3 \times S_2\), a product group, it follows that the system acquires the properties described above for \(\mathcal{A}_3\) together with those of \(S_2\) described in section 5.6. In other words, the states are labelled by \(jm\) and the parity \(\pm\). In particular, from their manner of construction in subsection 7.4.5, one sees that the spherical harmonics \(Y_{l}^{m}\) have parity \((-1)^m\).

### 8.2 Orbital angular momentum of a system of particles

In quantum mechanics the orbital angular momentum of a single particle is obtained from the classical expression \(r \times p\) by the substitution \(p \to -i\hbar \nabla\). Thus, in units of \(\hbar\),

\[
l_z = -i (r \times \nabla)_z = -i \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i \frac{\partial}{\partial \phi} \tag{8.4}\]

where \(\phi\) is the polar coordinate with respect to the \(z\)-axis. But we have seen that the explicit form for the infinitesimal rotation operator in the space of functions of a single particle is, from equation (7.20),

\[
J_z = -i \frac{\partial}{\partial \phi} = l_z \tag{8.5}
\]

Thus for a single particle the infinitesimal operators are identical with the angular-momentum operators in units of \(\hbar\) (Since the \(z\)-axis has no real significance this identification is equally valid for all three components.)

For the reasons discussed in subsection 7.3.1, namely that they are not continuous functions of angle over the range \(2\pi\), the wave functions with half-integer angular momentum are not acceptable solutions.

On a question of notation, we have previously denoted the angular momentum operators by \(J\) and the eigenvalues by the small letters \(jm\). Since we are now about to consider a system of particles it will be convenient to use small letters consistently for a single particle, i.e. for both operators and eigenvalues, and to use capitals for systems of more than one particle. In addition we use \(L\) (or \(l\)) for the orbital angular momentum and \(S\) (or \(s\)) for the intrinsic spin, to be described in section 8.4. The symbols \(J\) (or \(j\)) are reserved for the total angular momentum, orbital plus spin.

Consider now a system of \(n\) particles. The total orbital angular momentum of the system, denoted by \(L\) is given by

\[
L = \sum_{i=1}^{n} l(i) = \sum_{i} \left[ r(i) \times p(i) \right] / \hbar
\]
8.3 Angular Momentum and the Group $\mathfrak{S}_3$

so that in particular

$$L_i = -i \sum \frac{\partial}{\partial \phi_i}$$  \hspace{1cm} (8.6)

as in equation (8.4), where \(\phi_i\) is the usual polar angle of the \(i\)th particle. To connect this operator with rotations we follow the same argument which led to equation (7.20). Denoting any wave function for the system by \(\Psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2, \ldots, r_n, \theta_n, \phi_n)\) the immediate generalisation of equation (7.17) is that a rotation of the entire system through an angle \(a\) about the \(z\)-axis leaves all \(r_i\) and \(\theta_i\) unchanged and replaces \(\phi_i\) by \(\phi_i - a\). Thus, omitting the labels \(r_i\) and \(\theta_i\) for brevity,

$$T(R_z(a)) \Psi(\phi_1, \phi_2, \ldots, \phi_n) = \Psi(\phi_1 - a, \phi_2 - a, \ldots, \phi_n - a)$$

For small \(a\) we expand the right-hand side of this equation using the Taylor series for a function of \(n\) variables. Keeping only the first two terms

$$T(R_z(a)) \Psi(\phi_1, \phi_2, \ldots, \phi_n)$$

$$\approx \Psi(\phi_1, \phi_2, \ldots, \phi_n) - \sum a \frac{\partial}{\partial \phi_i} \Psi(\phi_1, \phi_2, \ldots, \phi_n)$$

so that we may write

$$R_z(a) \approx 1 - a \sum \frac{\partial}{\partial \phi_i}$$  \hspace{1cm} (8.7)

Thus the explicit form of the infinitesimal rotation operator for a system of particles is

$$J_z = -i \sum \frac{\partial}{\partial \phi_i} = L_z$$

Comparing with equation (8.6) shows that for a system of particles the total angular momentum operator, in units of \(\hbar\), is identical with the infinitesimal rotation operator for the system. This is exactly the same conclusion that we reached for a single particle.

8.3 Coupling of angular momenta

Now consider a two-particle wave function which is the product of two single-particle wave functions,

$$\Psi'(r_1, r_2) = \psi_{1m_1}(r_1) \psi_{2m_2}(r_2)$$  \hspace{1cm} (8.8)

where the suffices denote the single-particle angular momenta and their \(z\)-
components. Under rotation $R(a)$, the induced transformation is

$$\Psi' = T(R(a))\Psi = \psi'_{l_1 m_1} \psi'_{l_2 m_2} = \sum_{m'_1, m'_2} D_{m'_1 m'_2}^{(l_1)}(a) D_{m'_1 m'_2}^{(l_2)}(a) \psi_{l_1 m_1} \psi_{l_2 m_2},$$

showing that the set of $(2l_1 + 1)(2l_2 + 1)$ product functions (8.8) with fixed $l_1$ and $l_2$ span the product representation $D^{(l_1)} \times D^{(l_2)}$ of the group $\mathcal{S}_3$. The reduction

$$D^{(l_1)} \times D^{(l_2)} = \sum_{|l_1 - l_2|} D^{(L)}$$

(8.9)

of the product representation into its irreducible constituents was deduced in subsection 7.4.4. But since the total angular momentum of the pair is associated with overall rotations of the pair it follows that the total angular momentum of the pair may take the values

$$L = (l_1 + l_2), (l_1 + l_2 - 1) \ldots |l_1 - l_2|$$

(8.10)

which is known as the vector-coupling rule for angular momenta. Classically, an angular momentum is a vector and the sum of two angular momenta $l_1$ and $l_2$ is given by the usual vector addition $L = l_1 + l_2$ so that, depending on the angle between $l_1$ and $l_2$, the magnitude of $L$ lies between the sum $|l_1| + |l_2|$ and the difference $||l_1| - |l_2||$ of the magnitudes of $l_1$ and $l_2$. This is the origin of the name 'vector coupling rule' for equation (8.10) which would approach the classical result in the limit of large angular momenta and small $\hbar$.

For rotations about the $z$-axis the simple additive property of the representations of $\mathcal{S}_2$ (see subsection 7.3.3)

$$T^{(m_1)} \times T^{(m_2)} = T^{(m_1 + m_2)}$$

means that the $z$-component of total angular momentum is just the sum of the $z$-components for the two particles. The eigenfunctions of total angular momentum will be those combinations of the product functions (8.8) which achieve the reduction (8.9) and the Clebsch–Gordan coefficients were defined (see subsection 7.4.4) to do just this. We write the eigenfunctions as

$$\Psi_{LM}(r_1, r_2) = \sum_{m_1} C_{m_1 m_2, M}^{|m_1, m_2} \psi_{l_1 m_1}(r_1) \psi_{l_2 m_2}(r_2)$$

(8.11)

with the properties

$$L_z \Psi_{LM} = M \Psi_{LM}$$

$$L_z \Psi_{LM} = L(L + 1) \Psi_{LM}$$
8.4 Angular Momentum and the Group $\mathbb{R}_3$

By adding the angular momentum of one particle at a time, the rule (8.10) may be used to deduce the total angular momentum of any number of particles. Because of the Pauli principle some of the states of total angular momentum may not be physically acceptable but this point will be discussed in subsection 8.6.4 after the concept of spin has been introduced.

8.4 Intrinsic spin

Physical systems are generally regarded as being built from particles, like electrons, protons, neutrons, etc. We assign to each point particle a finite mass and a finite charge. Experimentally one finds that such a picture is incomplete and in particular it would fail to explain the behaviour of the energy levels of the hydrogen atom in the presence of a weak magnetic field. One is led to the conclusion, as we shall see below, that the point particles should be assigned an intrinsic angular momentum (or spin) and consequently an intrinsic magnetic moment. It is supposed that the intrinsic spin and moment are fundamental properties of the particles like their mass and charge. Even at rest, a particle will still have a spin and moment. Furthermore, a particle, like the neutron, with no charge may (and does) have a magnetic moment which may be imagined to arise from charge currents within the particle which have a net moment but no net charge. Most 'elementary' particles like the electron, proton and neutron are found experimentally to have a spin of $\frac{1}{2} \hbar$ but in contrast to this the $\rho$-meson has a spin of $\hbar$ and the $\Omega^-$ particle has a spin of $\frac{3}{2} \hbar$.

The appearance of an angular momentum in half-integer units is something which we did not encounter in describing the orbital motion of particles but it is not completely unexpected. Remember the link established in section 8.2 between the angular momentum and the rotation operators and remember that in section 7.4 we found that the irreducible representations $D^{(J)}$ of the rotation group were labelled by integer or half-integer values of $J$. The reason for rejecting the half-integer functions in the description of the orbital motion of a particle does not apply to the spin variable. The orbital motion was described by the Schrodinger differential equation, whose solution must be a continuous function. A half-integer wave function would change by a factor $-1$ as the angle goes through a full revolution of $2\pi$ and so lack continuity. The spin degree of freedom is not described by the Schrodinger equation but, as we shall see in chapter 15 of volume 2, arises naturally from a relativistic treatment. In the solution of these equations the occurrence of half-integer spin brings no conflict. A change of sign in the wave function does not affect the probability $|\Psi|^2$.

To clarify the need, from the point of view of the observed data, for introducing spin let us first consider the effect of an external uniform magnetic field on the energy levels of an electron moving in a spherically symmetric potential. In particular, consider the $(2l + 1)$-fold degenerate level $E_l$ with angular momentum $l$ and a set of wave functions $\psi(lm)$ with
Angular Momentum and the Group $\mathfrak{S}_3$ 8.4

$m = l, l-1, \ldots, -l$. The additional term in the Hamiltonian due to a constant magnetic field of strength $B$ is

$$\frac{eB l_z}{2M_e c} \quad (8.12)$$

where the $z$-axis has been chosen in the direction of the magnetic field, $-e$ and $M_e$ are the charge and mass of the electron and $c$ is the velocity of light. The operator $eB l_z/2M_e c$ is called the 'magnetic moment' operator, while the coefficient of $B l_z$ is called the Bohr magneton and is denoted by

$$\mu_B = \frac{eB}{2M_e c} \quad (8.13)$$

Notice that the contribution (8.12) to the Hamiltonian is proportional to the angular momentum of the particle and the strength of the field. The term (8.12) commutes with the original Hamiltonian $T + V(r)$ and its effect on the spectrum is simply to split the degeneracy. The $\psi(lm)$ will be eigenfunctions of the final Hamiltonian with energies $E_n = \mu_B B m$. This splitting of the levels by a magnetic field is called the Zeeman effect. Group theoretically, the symmetry of the Hamiltonian has been reduced from $\mathfrak{S}_3$ to $\mathfrak{S}_2$ so that the $(2l+1)$-fold degeneracy splits into $(2l+1)$ levels labelled by the irreducible representations $T^{(m)}$ of $\mathfrak{S}_2$.

The ground state of the hydrogen atom and of almost any attractive spherically symmetric potential has $l=0$ and is therefore non-degenerate and cannot be split. However it is found experimentally to split into two levels. This immediately suggests that there is another degree of freedom in addition to the position coordinates and that, at least for the ground state, this extra degree of freedom only allows two possible states. Furthermore the interaction with the magnetic field suggests that the splitting is due to an additional source of angular momentum. The fact that the $l=0$ state splits into two levels suggests a spin of $\frac{1}{2} \hbar$ since $(2J+1) = 2$ for $J = \frac{1}{2}$. It is usual to denote the spin angular momentum of a particle by the symbol $s$. One soon verifies that the splitting of the excited states with $l \neq 0$ is also consistent with this hypothesis of $s = \frac{1}{2} \hbar$ for the electron. Let us now see how to express these ideas precisely in mathematical form.

To any particle of a given type, e.g. electrons, we assign a spin $s$ and suppose that the possible spin states of the particle are spanned by a set of $(2s+1)$ basis states $\chi_{m_s}^{(s)}$ with $m_s = s, s-1, \ldots, -s$. Under rotations we suppose that the states transform according to the irreducible representation $D^{(s)}$ of $\mathfrak{S}_3$:

$$(\chi_{m_s}^{(s)})^\prime = T(R(a)) \chi_{m_s}^{(s)} = \sum_{m_{s'}} D^{(s)}_{m_{s'}m_s}(a) \chi_{m_{s'}}^{(s)} \quad (8.14)$$

where $s$ may be an integer or a half-integer. In other words we suppose that they behave like angular momentum eigenfunctions. Since the space of the spin states is of finite dimension $(2s+1)$, the explicit form for the infinitesimal operators for rotations of the spin states are just the matrices of the infinitesimal operators deduced generally in subsection 7.4.2. Denoting these
operators by \( s_x, s_y, \) and \( s_z \) we have from equation (7.40) for particular values of \( s \),

\[
\begin{align*}
\text{s} = \frac{1}{2} & \quad s_x = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad s_y = \frac{1}{2}i \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \quad s_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\
\text{s} = 1 & \quad s_x = \frac{1}{2} \begin{pmatrix} 0 & \sqrt{2} \\ \sqrt{2} & 0 \end{pmatrix}, \quad s_y = \frac{1}{2}i \begin{pmatrix} \sqrt{2} & 0 \\ 0 & -\sqrt{2} \end{pmatrix}, \quad s_z = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \\
& \quad s_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}
\end{align*}
\] (8.15)

For \( s = \frac{1}{2} \), it is common practice to define \( \sigma = 2s \) and to refer to the three operators \( \sigma \) as the Pauli spin matrices. From equations (7.36) and (7.39) the basis states are eigenstates of \( s_z \) and \( s^2 \),

\[
s_z \chi_m^{(s)} = m \chi_m^{(s)} \quad s^2 \chi_m^{(s)} = s(s+1) \chi_m^{(s)}
\]

We speak of \( s_z \) as the \( z \)-component of the spin and \( s^2 \) as the square of the total spin. As with angular momentum generally, one may take linear combinations of the basis \( \chi_m^{(s)} \) to form a new basis in which any other chosen component of the spin is diagonal.

For a system of particles, the total spin operators \( \Sigma \chi_m^{(s)} \) may be defined in a way precisely parallel to the introduction of the total orbital angular momentum \( L_z \) in section 8.2. The coupling of spins similarly follows the development in section 8.3.

The complete wave function for a particle with spin \( s \) will need to describe both the orbital state and the spin state and may generally be written as

\[
\Psi = \sum_{m=-s}^{s} \phi_m(r) \chi_m^{(s)}
\] (8.16)

where the coefficients \( \phi_m(r) \) are arbitrary functions of position. At every point \( r \), the wave function \( \Psi \) does not simply have a numerical value; it has a prescribed spin state. The spin state of a particle may be represented as a column vector with \( (2s+1) \) components. If we write

\[
\chi^{(s)} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}, \quad \chi^{(s-1)} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}, \text{ etc.}
\]
then the general wave function (8.16) may be written

$$\Psi = \begin{pmatrix} \phi_+ (r) \\ \phi_{-1} (r) \\ \vdots \end{pmatrix} \tag{8.17}$$

The spin states \( \chi_{m_s}^{(s)} \) are taken to be an orthonormal set of basis vectors in the \((2s + 1)\)-dimensional vector space describing the spin state of the particle. Thus we imagine a scalar product with the property

\[
(\chi_{m_s}^{(s)}; \chi_{m_s'}^{(s)}) = \delta_{m_s, m_s'};
\]

For two complete wave functions \( \Psi \) and \( \Psi' \), as defined by equation (8.16), the scalar product is to be imagined in two parts—an integral over position space \( r \) and the scalar product in spin space. Thus

\[
(\Psi, \Psi') = \sum_{m, m'} \int \phi_{m_s}^*(r) \phi_{m_s'}(r) dr (\chi_{m_s}^{(s)}; \chi_{m_s'}^{(s)})
\]

\[= \sum_{m_s} \int \phi_{m_s}^*(r) \phi_{m_s}(r) dr \]

The effect of a rotation on \( \Psi \) is given by a rotation of both \( \phi \) and \( \chi \),

\[T(R) \Psi = \sum_{m_s} \phi_{m_s} (R^{-1} r) (\chi_{m_s}^{(s)})' \]

using equations (3.37) and (8.14). For a small rotation about the \( z \)-axis through an angle \( \alpha \) we have from the definition (7.4) with the introduction of factors \( i \), as explained just before equation (7.26),

\[T(R) \Psi \approx \sum_{m_s} (1 - i \alpha l_z) \phi_{m_s} (r) (1 - i \alpha s_z) \chi_{m_s}^{(s)}
\]

\[\approx \sum_{m_s} \left[ 1 - i \alpha (l_z + s_z) \right] \phi_{m_s} (r) \chi_{m_s}^{(s)}
\]

\[\approx \left[ 1 - i \alpha (l_z + s_z) \right] \Psi \tag{8.18}\]

Thus the infinitesimal operator for the complete wave function \( \Psi \) is the sum \((l_z + s_z)\) of orbital and spin angular momenta. We write \( j_s = l_z + s_z \) and refer to \( j \) as the total angular momentum of the particle, in units of \( \hbar \).

The effect of a finite rotation \( R(a) \) on \( \Psi \) is given by

\[T(R) \Psi = \sum_{m_s} \phi_{m_s} (R^{-1} r) (\chi_{m_s}^{(s)})'
\]

\[= \sum_{m_s} \phi_{m_s} (R^{-1} r) \sum_{m} D_{m m_s}^{(j_s)}(a) \chi_{m_s}^{(s)}
\]

\[= \sum_{m_s} \left\{ \sum_{m} D_{m m_s}^{(j_s)}(a) \phi_{m_s} (R^{-1} r) \right\} \chi_{m_s}^{(s)} \tag{8.19}\]