Angular Momentum in Quantum Mechanics:
Spin-Orbit Interaction, Zeeman Effect and all that

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It is simple to convince oneself that rotations in 3D do not commute. For example, rotations by 90^o in the positive sense about the x and y axes are clearly represented (as regards their effect on vectors) by,

$$R_x\left(90^o\right)=\begin{pmatrix}1 & 0 & 0\\ 0 & 0 & -1\\ 0 & 1 & 0\end{pmatrix} \quad \text{and} \quad R_y\left(90^o\right)=\begin{pmatrix}0 & 0 & 1\\ 0 & 1 & 0\\ -1 & 0 & 0\end{pmatrix} \qquad (1)$$

This can be checked for the three unit vectors, and hence must hold for an arbitrary vector. The x-rotation matrix gives $\hat{x}\to\hat{x}$, $\hat{y}\to\hat{z}$ and $\hat{z}\to-\hat{y}$ as it should. Similarly, the y-rotation gives $\hat{x}\to-\hat{z}$, $\hat{y}\to\hat{y}$ and $\hat{z}\to\hat{x}$ as it should. Consequently,

$$R_x\left(90^o\right)R_y\left(90^o\right)\hat{z}=\hat{x} \quad \text{but} \quad R_y\left(90^o\right)R_x\left(90^o\right)\hat{z}=-\hat{y} \qquad (2)$$

So, in general, two rotations do not commute, i.e., $\left[R_x,R_y\right]\neq 0$. (3)

Rotations by angle θ about either the x, y or z axes are given by, (4)

$$R_x(\theta)=\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\theta & -\sin\theta\\ 0 & \sin\theta & \cos\theta\end{pmatrix} \quad R_y(\theta)=\begin{pmatrix}\cos\theta & 0 & \sin\theta\\ 0 & 1 & 0\\ -\sin\theta & 0 & \cos\theta\end{pmatrix} \quad R_z(\theta)=\begin{pmatrix}\cos\theta & -\sin\theta & 0\\ \sin\theta & \cos\theta & 0\\ 0 & 0 & 1\end{pmatrix}$$

It is simply shown, by expanding in a power series, that these can be written,

$$R_x(\theta)=\exp\left\{-\theta\Omega_x\right\}, \quad R_y(\theta)=\exp\left\{-\theta\Omega_y\right\}, \quad R_z(\theta)=\exp\left\{-\theta\Omega_z\right\} \qquad (5)$$

where,

$$\overline{\Omega}=\left\{\begin{pmatrix}0 & 0 & 0\\ 0 & 0 & 1\\ 0 & -1 & 0\end{pmatrix},\begin{pmatrix}0 & 0 & -1\\ 0 & 0 & 0\\ 1 & 0 & 0\end{pmatrix},\begin{pmatrix}0 & 1 & 0\\ -1 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}\right\} \qquad (6)$$

Equivalently, defining $\overline{L}=-i\hbar\overline{\Omega}$ these can be written $R_i(\theta)=\exp\left\{-i\frac{\theta L_i}{\hbar}\right\}$. (7)

It is easily shown that $\left[\Omega_x,\Omega_y\right]=-\Omega_z$, etc., so that, (8)

$$\left[L_x,L_y\right]=i\hbar L_z \qquad \left[L_y,L_z\right]=i\hbar L_x \qquad \left[L_z,L_x\right]=i\hbar L_y \qquad (9)$$

We note that the same commutation relations follow from the definition of the angular momentum operators as $\overline{L}=\overline{r}\times\overline{p}$, where $\overline{p}=-i\hbar\overline{\nabla}$. For example, (10)

$$\left[L_x,L_y\right]=(-i\hbar)^2\left[y\partial_z-z\partial_y,z\partial_x-x\partial_z\right]=(-i\hbar)^2\left\{\left[y\partial_z,z\partial_x\right]+\left[z\partial_y,x\partial_z\right]\right\}=(-i\hbar)^2\left\{y\partial_x-x\partial_y\right\}=i\hbar L_z \qquad (11)$$

For spin ½ a representation of the same algebra as (9) is given by the Pauli matrices,

$$\overline{S}=\frac{\hbar}{2}\overline{\sigma} \quad \text{where,} \quad \overline{\sigma}=\left\{\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix},\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right\} \qquad (12)$$

giving, $\left[S_x,S_y\right]=i\hbar S_z \qquad \left[S_y,S_z\right]=i\hbar S_x \qquad \left[S_z,S_x\right]=i\hbar S_y$ (13)

i.e., the same algebra as (9). This algebra is the Lie algebra of the group SO(3), of which SU(2) is the universal covering group. The lowest dimensional representations of these groups are given by (6) and (12) respectively (vectors and spin ½ spinors).

What are the eigenvalues of L_z and $L^2 = L_x^2 + L_y^2 + L_z^2$?

This can be answered from the Lie algebra, (9) or (13), alone. Hence, what follows applies equally for S_z and S^2. Note that L_z and $L^2 = L_x^2 + L_y^2 + L_z^2$ commute,

$$\begin{aligned}\left[L_z, L^2\right] &= \left[L_z, L_x^2 + L_y^2\right] = L_z L_x^2 - L_x^2 L_z + L_z L_y^2 - L_y^2 L_z \\ &= \left(L_x L_z + i\hbar L_y\right)L_x - L_x\left(L_z L_x - i\hbar L_y\right) + \left(L_y L_z - i\hbar L_x\right)L_y - L_y\left(L_z L_y + i\hbar L_x\right) = 0\end{aligned} \tag{14}$$

Consequently there are states which are eigenstates simultaneously of both L_z and L^2. Suppose $|a,b\rangle$ is such as state, where,

$$L^2|a,b\rangle = a|a,b\rangle \qquad\qquad L_z|a,b\rangle = b|a,b\rangle \tag{15}$$

Define
$$L_\pm = L_x \pm iL_y \tag{16}$$

Then,
$$\left[L_z, L_\pm\right] = \left[L_z, L_x\right] \pm i\left[L_z, L_y\right] = i\hbar L_y \pm i(-i\hbar L_x) = \pm\hbar L_x + i\hbar L_y = \pm\hbar\left(L_x \pm iL_y\right) = \pm\hbar L_\pm \tag{17}$$

These operators $L_\pm$ act as “ladder operators” which change one eigenstate into another. This can be seen using (15,17) as follows,

$$L_z L_+|a,b\rangle = \left(L_+ L_z + \hbar L_+\right)|a,b\rangle = \left(bL_+ + \hbar L_+\right)|a,b\rangle = (b+\hbar)L_+|a,b\rangle \tag{18}$$

So, given an eigenstate $|a,b\rangle$ of L_z with eigenvalue *b*, we can find another eigenstate of L_z namely $L_+|a,b\rangle$ with eigenvalue $(b+\hbar)$. In the same way the operator L_- forms a new eigenstate with eigenvalue $b-\hbar$. A sequence of eigenstates with eigenvalues spaced by $\hbar$ is therefore constructed by repeating these operations,

$$L_+{}^n|a,b\rangle \text{ has eigenvalue } (b+n\hbar); \quad L_-{}^n|a,b\rangle \text{ has eigenvalue } (b-n\hbar) \tag{19}$$

It follows from $L^2 = L_x^2 + L_y^2 + L_z^2$ that $\left\langle L^2\right\rangle = a \geq \left\langle L_z^2\right\rangle = b^2$. Hence, for a given value of *a* there is an upper bound for *b* such that $b^2 \leq a$. It follows that the process defined by (19) cannot go on for ever because eventually we get to the largest possible value for the eigenvalue. So where does the reasoning leading to 919) break down? The only possibility is that, for some largest possible *b* we get $L_+|a,b_{\max}\rangle = 0$ and the process terminates. Now consider,

$$L_- L_+ = \left(L_x - iL_y\right)\left(L_x + iL_y\right) = L_x^2 + L_y^2 + i\left[L_x, L_y\right] = L^2 - L_z^2 - \hbar L_z \tag{20}$$

Hence,
$$L_- L_+|a,b\rangle = \left(L^2 - L_z^2 - \hbar L_z\right)|a,b\rangle = \left(a - b^2 - \hbar b\right)|a,b\rangle \tag{21}$$

So, if we choose $b = b_{\max}$ in (21), we must have $a - b_{\max}^2 - \hbar b_{\max} = 0$, i.e.,

$$a = b_{\max}\left(b_{\max} + \hbar\right) \tag{22}$$

By the same reasoning there is a minimum *b* so that $L_-|a,b_{\min}\rangle = 0$ and so consider,

$$L_+L_- = (L_x + iL_y)(L_x - iL_y) = L_x^2 + L_y^2 - i[L_x, L_y] = L^2 - L_z^2 + \hbar L_z \tag{23}$$

This gives, $$a = b_{\min}(b_{\min} - \hbar) \tag{24}$$

But we also know that the eigenvalues are spaced apart by $\hbar$, so that the maximum and minimum values for *b* must differ by an integral multiple of $\hbar$, i.e., there must be a positive integer *n* such that $b_{\max} - b_{\min} = n\hbar$. Equating (22) and (24) and using this relation between $b_{\max}$ and $b_{\min}$ gives,

$$a = b_{\max}(b_{\max} + \hbar) = (b_{\max} - n\hbar)(b_{\max} - n\hbar - \hbar) \tag{25}$$

Re-arranging and simplifying this gives simply,

$$b_{\max} = \frac{n}{2}\hbar \qquad \text{and} \qquad b_{\min} = -\frac{n}{2}\hbar \tag{26}$$

Substitution in (22) gives $$a = \frac{n}{2}\left(\frac{n}{2} + 1\right)\hbar^2 \tag{27}$$

Hence, we find that any system of operators obeying the commutator algebra given by (9) or (13) has total angular momentum given by $L^2 \to l(l+1)\hbar^2$, where *l* = *n*/2 can only take half-integral values, 0, ½ , 1, $^3/_2$, 2,…etc.

The possible azimuthal quantum numbers are $m = b_{\max}/\hbar = -l, -l+1, \ldots .0, \ldots .(l-1), +l$ **Hence, there are** $(2l+1)$ **azimuthal states for a given *l*.** For example, for *l* = 2 there are 5 states.

Spin states can take any of these possible values, i.e., *l* = 0, ½ , 1, $^3/_2$, 2,…etc.

Orbital angular momentum states can only take integral values, *l* = 0, 1, 2,…etc.

Note that this eigenvalue structure for L_z and L^2 follows from the commutator algebra, (9) or (13), alone. It does not require any particular representation of this algebra such as that provided by the matrices (6) or (12) or by the differential operator representation, (10).

Application to Many Electron Atoms

We can define an orbital angular momentum operator for every electron separatrely, i.e., for the i$^{\text{th}}$ electron at position $\overline{r}_i$ put $\overline{L}_i = \overline{r}_i \times \overline{p}_i$, where $\overline{p}_i = -i\hbar\overline{\nabla}_i$ and $\overline{\nabla}_i = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i}\right)$. The total orbit angular momentum is just the sum over the N electrons, $\overline{L} = \sum_{i=1}^{N} \overline{L}_i$. The same applies to the total spin, $\overline{S} = \sum_{i=1}^{N} \overline{S}_i$. The operators for one electron commute with the operators for a different electron. Consequently, the total operators obey the same commutator algebra as (19) and (13). Consequently we know that the total orbital angular momentum must be given by an integer quantum number *l* and the total spin by a half-integral quantum number *s*, just as if it were one electron.

How many states? Given *l* and *s* there are a total of $(2l+1)(2s+1)$ azimuthal states. These states can be labelled by the four angular momentum quantum numbers l, m, s, m_s. (NB: There is also the principle quantum number, *n*, which we are not addressing here).

Fr some purposes it is better to label the states using the total angular momentum. This is defined by $\bar{J} = \bar{L} + \bar{S}$. Since $\bar{L}$ and $\bar{S}$ commute, $\bar{J}$ also has commutator algebra like (9) and (13). Hence J^2 has eigenvalues $j(j+1)\hbar^2$ for half-integral *j*, and azimuthal quantum numbers m_j which take values from $-j$ to $+j$ at integer spacings. Now it can be shown that both J^2 and J_z commute with both of L^2 and S^2, and with each other, so that there are states which are simultaneously eigenstates of all four of J^2, J_z, L^2 and S^2. Hence, instead of labelling states using l, m, s, m_s we can label using j, l, s, m_j. Note that it must be the total azimuthal number, m_j, here when *j* is included.

The allowed values of *j* follow from the definition $\bar{J} = \bar{L} + \bar{S}$. When the orbital angular momentum is aligned with the total spin, then the maximum *j* is $l + s$. Similar, anti-alignment gives the minimum *j* of $|l - s|$.

Example: $l = 2$, $s = 3/2$. The possible values of j are ½ , $3/2$, $5/2$, $7/2$. The total number of states for these fixed values of *l* and *s* calculated in the l, m, s, m_s basis is $(2 \times 2 + 1)\left(2 \times \frac{3}{2} + 1\right) = 20$. Using the j, l, s, m_j basis we get:-

$j = \frac{1}{2}$ 2 states; $j = \frac{3}{2}$ 4 states; $j = \frac{5}{2}$ 6 states; $j = \frac{7}{2}$ 8 states; **total = 20** - OK.

Singlet and Triplet States & Anti-Symmetric Fermion Wavefunctions

A special case is just two electrons. The possible total spin states are then S = 0 and S = 1. The former has just one state, since the only possible m_s is 0. This is the singlet state. However, S = 1 can have m_s = -1, 0 or +1, and hence has 3 possible states. This is the triplet state.

It is important to realise that the singlet state is an anti-symmetric spin state, given explicitly by,

Singlet State: $\frac{1}{\sqrt{2}}\left[|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\right]$ S = 0; m_s = 0

The first ‘bra’ represents the first electron, and the second ‘bra’ the second electron. If the states of the first and second electrons are swapped in each term, the overall wavefunction changes sign. The three triplet states are given explicitly by,

Triplet State: $|\uparrow\rangle|\uparrow\rangle$ S = 1; m_s = 1

Triplet State: $\frac{1}{\sqrt{2}}\left[|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle\right]$ S = 1; m_s = 0

Triplet State: $|\downarrow\rangle|\downarrow\rangle$ S = 1; m_s = -1

Note that all three states are ***symmetric*** under interchange of the first and second electrons.

The ***Pauli Exclusion Principle*** (or, rather, its generalisation) says that the wavefunction of a system of fermions, such as electrons, must be ***anti-symmetric*** with respect to interchange of any pair of the particles. So how can the triplet state be allowed? The answer is that it is the overall state which must be anti-symmetric, and this includes the spatial (or orbital) part of the wavefunction. So the requirement for a two electron system is that ***the singlet spin state must be combined with a symmetric spatial state, whilst the triplet spin state must be combined with an anti-symmetric spatial state***.

Implications

Helium atom

The ground state has both electrons in an l = 0 state, and hence must be spatially symmetric. It therefore must be a singlet spin state with anti-aligned spins (net spin zero).

A spatial state which is anti-symmetric means that the two electrons cannot be in the same place. If the electrons could be in the same place, their mutual repulsion would create a positive potential energy. Hence, the spatial symmetric excited states, and thus the singlet states, will have higher energy than the corresponding triplet states.

The generalisation of this is ***exchange energy***. This is the energy difference between singlet and triplet states due to the symmetry condition imposed on the spatial states. In this way the spin affects the energy levels of an atom even when there are no explicit spin dependent terms n the Hamiltonian. This is a purely quantum effect.

Hydrogen Molecule

The lowest energy will occur when both the electrons are close to both protons. But this means that both electrons must be predominantly midway between the protons, and hence in the same place. This can only happen for a symmetric spatial state, and hence a singlet spin state. The ground state of the hydrogen molecule is thus a spin singlet.

Magnetic Moments

A magnetic dipole is just like a little bar magnet. It has a north and a south pole and creates a magnetic field around it. Two closely spaced magnetic dipoles will want to anti-align. The dipole strength is represented by a vector $\overline{\mu}$, where the direction of the vector points along the 'bar magnet'. The way in which dipoles arise is due to current loops. The magnitude of a dipole equals the current times the area of the loop, $\mu = IA$. The direction is perpendicular to the plane of the loop. In practice the current is due to a charge which is moving. Consider a charge q moving in a circle of radius r at speed v. The time taken to complete an orbit is $t = \frac{2\pi r}{v}$, so the current is $I = \frac{q}{t} = \frac{qv}{2\pi r}$. This gives the dipole moment to be $\mu = I\pi r^2 = \frac{qvr}{2}$. But the orbital angular momentum is $L = mvr$, where m is the mass of the orbiting particle. Hence we get, $\mu = \frac{q}{2m}L$. If the orbiting particle is an electron, the q and m are the charge and mass of the electron. This is often written $\mu = g\mu_B \frac{L}{\hbar}$, where $g = 1$ and $\mu_B = \frac{e\hbar}{2m_e}$ is the Bohr magneton which converts the orbital quantum number $l = \frac{L}{\hbar}$ into a magnetic dipole moment. The g-factor is 1 for orbital angular momentum.

The spin of a particle also causes a dipole moment. For reasons which lie deeply buried in relativity theory, the g-factor for spin is ~2 (to be more accurate g_s = 2.0023). The dipole due to the total spin is thus just $\mu_S = g_s \mu_B S$, where S is the spin quantum number.

NMR

The same applies to the proton spins in a nucleus, for which $\mu_S = g_s \mu_N S$, but the difference is that the "nuclear magneton" involves the charge and mass of the proton $\mu_N = \frac{e\hbar}{2m_p}$. Since $m_p = 1836 m_e$, the nuclear dipole moment is tiny compared with that of the atomic electrons. This is why NMR machines require huge magnets, whereas the atomic Zeeman effect (see below) requires only a simple bench-top magnetic field source.

Spin-Orbit Coupling

The simplest Hamiltonian for a multi-electron atom does not include the effect of electron (or nuclear) spins. However, because both the orbital and spin motions generate dipole moments, there is an energy of interaction between them given by $V = \frac{\bar{\mu} \cdot \bar{\mu}_S}{R^3} = g g_s \left(\frac{\mu_B}{\hbar} \right)^2 \frac{\bar{L} \cdot \bar{S}}{R^3}$ where *R* is some average orbital radius. The value of the dot product of the orbital and spin angular momenta can be found as follows,

Since
$$J^2 = \left| \bar{L} + \bar{S} \right|^2 = L^2 + S^2 + 2\bar{L} \cdot \bar{S} \tag{28}$$

we have
$$\left\langle \bar{L} \cdot \bar{S} \right\rangle = \frac{1}{2} \left[j(j+1) - l(l+1) - s(s+1) \right] \tag{29}$$

We have already noted that the requirement for an anti-symmetric electron state causes a spin state, *s*, dependence of the energy. We see from (29) that spin-orbit coupling means that there is an *l* and *j* dependence also.

So, of the four quantum numbers, j, l, s, m_j , the only one which the energy does *not* depend upon is m_j. For an isolated atoms this is inevitable since it is a result of symmetry. Dependence upon m_j would imply a preferred direction in space.

The Zeeman Effect

A preferred direction in space can be defined by imposing a magnetic field on the atom. This will cause an m_j dependence of the energy states, and hence the last degeneracy of the energy levels is broken. All electron states will now have distinct spectral lines. The weak field Zeeman effect can be quantified as follows. Provided that the field is weak, the orbital and spin momenta will precess around the total momentum vector, so that their average values are given by,

$$\left\langle \bar{L} \right\rangle = \frac{\vec{L} \cdot \bar{J}}{J^2} \bar{J} \quad \text{and} \quad \left\langle \bar{S} \right\rangle = \frac{\bar{S} \cdot \bar{J}}{J^2} \bar{J} \tag{30}$$

The total dipole moment is $\bar{\mu} = \mu_B \left(g\bar{L} + g_s \bar{S} \right)$ and the energy due to the magnetic external field, $\bar{B}$, is $\bar{\mu} \cdot \bar{B} = \mu_B B \left(g \frac{\bar{L} \cdot \bar{J}}{J^2} m_j + g_s \frac{\bar{S} \cdot \bar{J}}{J^2} m_j \right)$. Using g =1, gs = 2 together two relations derived in a similar manner to (29),

$$\left\langle \bar{L} \cdot \bar{J} \right\rangle = \frac{1}{2}\left[j(j+1) + l(l+1) - s(s+1) \right] \tag{31}$$

$$\left\langle \bar{S} \cdot \bar{J} \right\rangle = \frac{1}{2}\left[j(j+1) - l(l+1) + s(s+1) \right] \tag{32}$$

the interaction energy becomes,

$$\bar{\mu} \cdot \bar{B} = \frac{\mu_B B m_j}{2j(j+1)}\left[3j(j+1) - l(l+1) + s(s+1) \right] \tag{33}$$

which displays explicitly the dependence upon m_j (being proportional to it).