7 Continuous Group

7.4 Clebsch-Gordon Coefficients

Now let's take all the irreps of $SU(2)$ (or all the nonprojective and projective irreps of $SO(3)$) and see how they interact with each other. In particular, we want to know if we take the direct product between two irreps labeled by j and j' (both can be either integer or half integer), how does the composite representation decompose into a direct sum of irreducible blocks? In physics, this is called the 'addition of angular momentum' and it was known that

$$D^{(j_1)} \otimes D^{(j_2)} = \oplus_{j=|j_1-j_2|}^{j_1+j_2} D^{(j)} \tag{1}$$

That is, the addition of angular momentum j_1 with angular momentum j_2 gives rise to angular momentum from $|j_1 - j_2|$ to $j_1 + j_2$.

One comment on terminology. When we talk about addition of angular momentum, we are actually taking the direct product of the corresponding irreps. We say that their angular momentum add, because the angular momentum operator of the direct product representation is the sum of the angular momentum operator of each of the irrep.

$$D_{\vec{n}}^{(j_1)}(\theta) \otimes D_{\vec{n}}^{(j_2)}(\theta) = e^{i\theta J_{\vec{n}}^1} \otimes e^{i\theta J_{\vec{n}}^2} = e^{i\theta(J_{\vec{n}}^1 \otimes I_{j_2(j_2+1)} + I_{j_1(j_1+1)} \otimes J_{\vec{n}}^2)} \tag{2}$$

Therefore, $J_{\vec{n}}^{tot} = J_{\vec{n}}^1 \otimes I_{j_2(j_2+1)} + I_{j_1(j_1+1)} \otimes J_{\vec{n}}^2$, hence the name 'addition'. Note that $J_{\vec{n}}^1 \otimes I_{j_2(j_2+1)}$ and $I_{j_1(j_1+1)} \otimes J_{\vec{n}}^2$ commute, therefore we can simply add them when multiplying their exponential. Usually we just use the short-hand notation $J_{\vec{n}}^1$ for $J_{\vec{n}}^1 \otimes I_{j_2(j_2+1)}$ and $J_{\vec{n}}^2$ for $I_{j_1(j_1+1)} \otimes J_{\vec{n}}^2$. Hence we have the relation

$$J_x^{tot} = J_x^1 + J_x^2, J_y^{tot} = J_y^1 + J_y^2, J_z^{tot} = J_z^1 + J_z^2 \tag{3}$$

Now let's show the relation in Eq. 1 using the character of the irreps. Suppose that $j_1 \geq j_2$. The character of the direct product of $D^{(j_1)}$ and $D^{(j_2)}$ is

$$\chi^{(j_1)}(\theta)\chi^{(j_2)}(\theta) = \frac{\sin(j_1+1/2)\theta}{\sin(\theta/2)} \frac{\sin(j_2+1/2)\theta}{\sin(\theta/2)} \tag{4}$$

Using equivalent expressions for $\chi^{(j_1)}(\theta)$ and $\chi^{(j_2)}(\theta)$, we get

$$\begin{aligned} \chi^{(j_1)}(\theta)\chi^{(j_2)}(\theta) &= \tfrac{e^{i(j_1+1/2)\theta} - e^{-i(j_1+1/2)\theta}}{2i\sin(\theta/2)} \textstyle\sum_{m=-j_2}^{j_2} e^{im\theta} \\ &= \tfrac{1}{2i\sin(\theta/2)} \textstyle\sum_{m=-j_2}^{j_2} e^{i(j_1+m+1/2)\theta} - e^{-i(j_1-m+1/2)\theta} \end{aligned} \tag{5}$$

Because the summation over m is over $-j_2$ to j_2, we can change m to $-m$ in the second term so that j_1 and m always appear as a combination $j = j_1 + m$. Therefore, we can replace the summation as over $j = j_1 - j_2$ to $j = j_1 + j_2$.

$$\begin{aligned} \chi^{(j_1)}(\theta)\chi^{(j_2)}(\theta) &= \tfrac{1}{2i\sin(\theta/2)} \textstyle\sum_{j=j_1-j_2}^{j_1+j_2} e^{i(j+1/2)\theta} - e^{-i(j+1/2)\theta} \\ &= \textstyle\sum_{j=j_1-j_2}^{j_1+j_2} \tfrac{\sin(j+1/2)\theta}{\sin(\theta/2)} = \textstyle\sum_{j=j_1-j_2}^{j_1+j_2} \chi^{(j)}(\theta) \end{aligned} \tag{6}$$

□

In physics, people are not only interested in what $D^{(j)}$ are contained in the direct product of $D^{(j_1)} \otimes D^{(j_2)}$, but also how the basis states of $D^{(j)}$ can be obtained from the basis states of $D^{(j_1)}$ and $D^{(j_2)}$. As we have completely fixed the choice of basis for each of the irrep, there is a concrete process to obtain this relation.

Let's consider the simplest example of the direct product of two $j = 1/2$ irreps $D^{(1/2)} \otimes D^{(1/2)}$. Each $D^{(1/2)}$ is two dimensional and the direct product of two copies of them is four dimensional with basis states

$$\left|\frac{1}{2}\right\rangle \left|\frac{1}{2}\right\rangle, \left|\frac{1}{2}\right\rangle \left|-\frac{1}{2}\right\rangle, \left|-\frac{1}{2}\right\rangle \left|\frac{1}{2}\right\rangle, \left|-\frac{1}{2}\right\rangle \left|-\frac{1}{2}\right\rangle \tag{7}$$

the number in the $|\rangle$ labels the angular momentum m in z direction. In order to make it explicit that these states belong to the $j = 1/2$ irrep, we label the states as $|j_1, m_1; j_2, m_2\rangle$

$$\left|\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\right\rangle, \left|\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\right\rangle, \left|\frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, \frac{1}{2}\right\rangle, \left|\frac{1}{2}, -\frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\right\rangle \tag{8}$$

According to the previous discussion

$$D^{(1/2)} \otimes D^{(1/2)} = D^{(0)} + D^{(1)} \tag{9}$$

$D^{(0)}$ is one dimensional and has one basis state with angular momentum 0. $D^{(1)}$ is three dimensional and has three basis states with z direction angular momentum 1, 0 and -1 respectively. To specify that they comes from the composition of two angular momentum $1/2$ irreps, we label the state as $|(j_1, j_2)j, m\rangle$

$$\left|\left(\frac{1}{2}, \frac{1}{2}\right) 0, 0\right\rangle, \left|\left(\frac{1}{2}, \frac{1}{2}\right) 1, 1\right\rangle, \left|\left(\frac{1}{2}, \frac{1}{2}\right) 1, 0\right\rangle, \left|\left(\frac{1}{2}, \frac{1}{2}\right) 1, -1\right\rangle \tag{10}$$

The basis states listed in Eq. 7 and those listed in Eq. 10 are the basis states of the same four dimensional Hilbert space. Therefore, they are related by a unitary transformation. In particular, each state in Eq. 10 can be decomposed into a linear superposition of the basis states given in Eq. 7 and we want to find out the coefficient of these linear superpositions.

Let's start from the state $\left|\left(\frac{1}{2}, \frac{1}{2}\right) 1, 1\right\rangle$. This state is special in that it has the largest angular momentum $m = 1$ in z direction among the four states in Eq. 10. Because

$$J_z^{tot} = J_z^1 + J_z^2 \tag{11}$$

we have

$$m = m_1 + m_2 \tag{12}$$

Among the four states listed in Eq. 7, only one satisfies $m_1 + m_2 = 1$: $\left|\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\right\rangle$. Therefore, these two states must be the same up to a phase factor. In physics, the convention is to choose the phase factor to be 1. That is

$$\left|\left(\frac{1}{2}, \frac{1}{2}\right) 1, 1\right\rangle = \left|\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\right\rangle \tag{13}$$

Starting from here, we can obtain all other states in $D^{(1)}$ by applying the lowering operator for the total angular momentum

$$J_-^{tot} = J_x^{tot} - iJ_y^{tot} = J_x^1 + J_x^2 - iJ_y^1 - iJ_y^2 = J_-^1 + J_-^2 \tag{14}$$

We find

$$\sqrt{2}\left|\left(\frac{1}{2},\frac{1}{2}\right)1,0\right\rangle = J_-^{tot}\left|\left(\frac{1}{2},\frac{1}{2}\right)1,1\right\rangle = \left(J_-^1+J_-^2\right)\left|\frac{1}{2},\frac{1}{2};\frac{1}{2},\frac{1}{2}\right\rangle = \left|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}\right\rangle + \left|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}\right\rangle \tag{15}$$

That is

$$\left|\left(\frac{1}{2},\frac{1}{2}\right)1,0\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}\right\rangle + \left|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}\right\rangle\right) \tag{16}$$

We can see that this relation is consistent because $m = m_1 + m_2 = 0$.

If we apply the lowering operator again, we get

$$\sqrt{2}\left|\left(\tfrac{1}{2},\tfrac{1}{2}\right)1,-1\right\rangle = J_-^{tot}\left|\left(\tfrac{1}{2},\tfrac{1}{2}\right)1,0\right\rangle = \left(J_-^1+J_-^2\right)\tfrac{1}{\sqrt{2}}\left(\left|\tfrac{1}{2},-\tfrac{1}{2};\tfrac{1}{2},\tfrac{1}{2}\right\rangle + \left|\tfrac{1}{2},\tfrac{1}{2};\tfrac{1}{2},-\tfrac{1}{2}\right\rangle\right) = \sqrt{2}\left|\tfrac{1}{2},-\tfrac{1}{2};\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \tag{17}$$

That is

$$\left|\left(\frac{1}{2},\frac{1}{2}\right)1,-1\right\rangle = \left|\frac{1}{2},-\frac{1}{2};\frac{1}{2},-\frac{1}{2}\right\rangle \tag{18}$$

which can also be obtained by comparing m with $m_1 + m_2$ in the basis states.

Now we have found all the basis states for $D^{(1)}$, we are left with only the basis state for $D^{(0)}$. In order to determine its decomposition in the basis states of Eq. 7, we only need to observe that $\left|\left(\frac{1}{2},\frac{1}{2}\right)0,0\right\rangle$ is a state with $m = 0$, therefore, it has to be equal to some kind of superposition of $\left|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}\right\rangle$ and $\left|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}\right\rangle$ which both have $m_1 + m_2 = 0$. We have already seen one such superposition which gave rise to

$$\left|\left(\frac{1}{2},\frac{1}{2}\right)1,0\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}\right\rangle + \left|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}\right\rangle\right) \tag{19}$$

As $\left|\left(\frac{1}{2},\frac{1}{2}\right)0,0\right\rangle$ is orthogonal to $\left|\left(\frac{1}{2},\frac{1}{2}\right)1,0\right\rangle$, it can only be

$$\left|\left(\frac{1}{2},\frac{1}{2}\right)0,0\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}\right\rangle - \left|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}\right\rangle\right) \tag{20}$$

Now let's put our findings in a table

$j_1 = \frac{1}{2}, j_2 = \frac{1}{2}$	$m_1 = \frac{1}{2}, m_2 = \frac{1}{2}$	$m_1 = -\frac{1}{2}, m_2 = \frac{1}{2}$	$m_1 = \frac{1}{2}, m_2 = -\frac{1}{2}$	$m_1 = -\frac{1}{2}, m_2 = -\frac{1}{2}$
$j = 1, m = 1$	1	0	0	0
$j = 1, m = 0$	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0
$j = 1, m = -1$	0	0	0	1
$j = 0, m = 0$	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0

The numbers in this table is called the Clebsch-Gordon coefficient or CG coefficient for short. It is the coefficient in the decomposition of total angular momentum basis in terms of the tensor product of component angular momentum basis. The CG coefficient of other j_1, j_2 and j can be obtained in a very similar way.

8 Electron orbit in atoms

Now let's see how our understanding of the irreps of $SO(3)$ ($SU(2)$) can help us understand the structure of electron orbits in atoms.

8.1 Central potential

Consider an electron moving around a nucleus. The Hamiltonian of the electron is

$$H = \frac{P^2}{2m} + V(r) \tag{21}$$

$V(r)$ is the Coulomb potential of the electron in the field of the nucleus. The crucial property of this central potential is that it depends only on r, the distance of the electron from the nucleus, and not on the direction of the electron. Therefore, the Hamiltonian is invariant under rotation in full three dimensional space. That is

$$R_{\vec{n}}(\theta) H R_{\vec{n}}(-\theta) = H \tag{22}$$

The wave function of the electron is a (normalized) complex function over space $\psi(x, y, z)$. In spherical coordinates, it is written as $\psi(r, \theta, \phi)$, where r is the radial distance from the origin, θ is the angle between the vector and the positive z direction, ϕ is the angle between the projection on the xy plane and the positive x direction. It lives in an infinite dimensional Hilbert space. In this Hilbert space, the angular momentum operators take the form

$$J_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right),\ J_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right),\ J_z = -i\hbar\frac{\partial}{\partial\phi} \tag{23}$$

Because of this, we can conclude that the the eigenstates of H (the electron orbitals) form irreducible representations of $SO(3)$. That is, the eigenstates can be grouped into subsets labelled by j, $j = 0, 1, 2, ...$. The set labeled by j contains $2j + 1$ states, which can be further labeled by $m = -j, -j + 1, ..., j$. The $2j + 1$ states in the same irrep have the same energy (are degenerate). The irrep labeled by j corresponds to orbits with total angular momentum $J^2 = j(j + 1)$. In atomic physics, the usual notation for angular momentum is l instead of j and the orbits with $l = 0, 1, 2, 3...$ are called $s, p, d, f...$ orbits respectively. The state labeled by m in the l irrep corresponds to orbits with z direction angular momentum m.

l and m are not sufficient to uniquely label different electron orbits in atoms, as they describe only the angular distribution of the electron wave function and does not contain any radial information. We need one more label n which describes roughly how far away the electron is from the nucleus. It turns out for each n, the possible choice of l is limited to be from 0 to $n - 1$. Therefore, we can have orbits $1s$, $2s$, $2p$, $3s$, $3p$, $3d$ etc.

In Hydrogen atom, the energy of the orbits depends solely on n. However, in more general atoms, the energy of the orbits depends both on n and j. Of course, the energy does not depend on m which labels different states of the same irrep, due to the rotation symmetry of the atom. The Hydrogen atom contains a lot of 'accidental' degeneracy if we consider only the $SO(3)$ symmetry. In fact, it was realized that the Hydrogen atom has a higher $SO(4)$ symmetry which guarantees the degeneracy of different orbitals with the same n. Here is an article that explains this http://hep.uchicago.edu/ rosner/p342/projs/weinberg.pdf.

8.2 Spin orbit interaction

If we examine the electron orbits around the Hydrogen atom really carefully, we will find that some electron orbits (e.g. $2p$) spits into two with a small energy difference. How could that happen?

People realized that this is due to the interaction between the orbital and spin degrees of freedom of the electron. That is, the Hamiltonian contains an extra term of the form

$$\Delta H = f(r)\vec{S}\cdot\vec{J} = f(r)\left(S_x J_x + S_y J_y + S_z J_z\right) \tag{24}$$

where $\vec{S}$ denotes the spin angular momentum of the electron and $\vec{J}$ denotes the orbital angular momentum of the electron. Due to this coupling, the Hamiltonian is no longer invariant under rotation on the orbital part or the spin part alone. Instead, it is invariant if the orbital angular momentum and spin angular momentum rotates together so that their dot product remains the same.

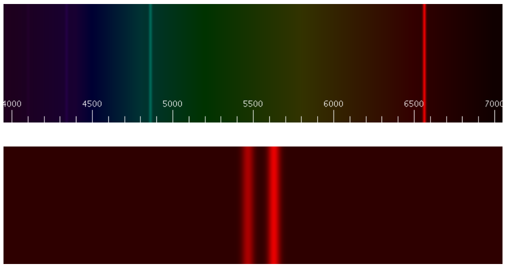
In this case, the spin angular momentum and orbital angular momentum are no longer good labels of the eigenstates of the Hamiltonian. $\vec{S}^2 = s(s+1)$ and $\vec{J}^2 = j(j+1)$ still commute with the Hamiltonian but S_z and J_z do not. Instead, the total angular momentum operator $\vec{L} = \vec{S} + \vec{J}$ commute with the Hamiltonian

$$\vec{L}^2 = \vec{S}^2 + \vec{J}^2 + 2\vec{S}\cdot\vec{J}, L_z = S_z + J_z, [\vec{L}^2, H] = 0, [L_z, H] = 0 \tag{25}$$

and we can use their eigenvalue to label eigenstates of the Hamiltonian. That is, due to spin orbit interaction, the eigenstates of the Hamiltonian are no longer tensor product of eigenstates of spin and orbital angular momentum $|j, m_j; s, m_s\rangle$. Instead they are eigenstates of total angular momentum $|(j,s)\, l, m_l\rangle$, which is the result of adding spin and orbital angular momentum together.

From here we can understand how the atomic spectrum changes with spin orbit interaction. On an s orbital, spin orbital interaction corresponds to the addition of $j = 0$ with $s = 1/2$ which results in a single irrep $l = 1/2$. Therefore, spin orbit interaction does not split the degeneracy of the $j = 0$ orbital. On a p orbital, on the other hand, spin orbital interaction corresponds to the addition of $j = 1$ with $s = 1/2$ which results in two irreps, one with $l = 1/2$ one with $l = 3/2$. These two irreps have different energy (states within each irrep have the same energy). Therefore, spin orbit interaction splits the energy of a p orbital.

If we now look at the spectral line generated by the transition of an electron between a p orbital and an s orbital, a single line will split into a doublet. This is the fine structure of Hydrogen spectrum.



8.3 Transition selection rule

Now imagine we apply an external perturbation to the atom in order to drive transition of the electron from one orbital to another. How does the transition rate depend on the form of the perturbation? Quantum mechanics tells us that the transition amplitude is give by

$$T_{if} = \langle\psi_i|O|\psi_f\rangle \tag{26}$$

where O is the perturbation operator and $|T_{if}|^2$ gives the transition probability.

In the study of atomic spectrum, the most common perturbation is electric dipole operator $\vec{E} \cdot \vec{r}$ (by e.g. shining a laser on the atom). Suppose that we choose the electric field in the laser to point in the z direction, can we drive the transition between two s orbitals? That is, we want to calculate the probability amplitude

$$T_{if} = \langle \psi_i^s | E_z z | \psi_f^s \rangle \tag{27}$$

What we find is that, T_{if} actually has to be zero. To see this, we insert operator $e^{-i\pi J_x} e^{i\pi J_x}$ between the operator and the initial and final states

$$T_{if} = \langle \psi_i^s | e^{-i\pi J_x} e^{i\pi J_x} E_z z e^{-i\pi J_x} e^{i\pi J_x} | \psi_f^s \rangle \tag{28}$$

We combine these operators so that the initial and final state are both acted upon by the operator $e^{i\pi J_x}$ which does a π rotation around the x direction and the dipole operator in the middle gets conjugated by $e^{i\pi J_x}$ which also does the x axis π rotation.

As the initial and final states are both s orbitals, they remain invariant under this rotation

$$e^{i\pi J_x} | \psi_f^s \rangle = | \psi_f^s \rangle, e^{i\pi J_x} | \psi_i^s \rangle = | \psi_i^s \rangle \tag{29}$$

The dipole operator on the other hand, gets a $-$ sign

$$e^{i\pi J_x} E_z z e^{-i\pi J_x} = -E_z z \tag{30}$$

Because of this extra sign

$$T_{if} = -T_{if} \tag{31}$$

and it has to be zero.