<u>Lecture 15</u> Title: Evaluation of coupled wavefunction

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In this lecture we will the procedure for evaluating the coupled wavefunctions in terms of the uncoupled states.

Initially, we will start with coupling of two generalized angular momenta.

Since the total wavefunction for the electron is the product of the space and spin wavefunction, we will learn how to make the total wavefunction antisymmetric.

As mentioned in the previous lectures that for three angular momenta coupling, the final wavefunctions depend on the detailed coupling scheme, we will find the proof.

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In previous lecture we learnt that when non-spherical part of the electron-electron repulsion $\sum \frac{e^2}{r_{ij}}$ is included in the Hamiltonian , these single electron quantum numbers are no more the good quantum numbers since they do not commute with the Hamiltonian

$$H = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z\,e^2}{r_1} - \frac{Z\,e^2}{r_2} + \frac{e^2}{r_{12}}$$

In this case $\left[H, L\right] = 0 \qquad \left[H, S\right] = 0$

And also $\left[H, L^2\right] = 0 \qquad \left[H, S^2\right] = 0$

Where $L = l_1 + l_2 + l_3 + ... = \sum l_i$, similarly $S = s_1 + s_2 + s_3 + ... = \sum s_i$

So, *L* and *S* are the good quantum numbers to characterize the total wavefunction of the system. In this regard we have discussed in the last lecture about procedure and rules of the coupling of angular momenta.

The energy levels will be in terms of *L* and *S* and are thus named as Terms. The notataion for these terms are ${}^{2S+1}L$ and coupled wavefunctions are $\left|L, S, M_L, M_S\right\rangle$

We can evaluate the coupled wavefunction $\left|L, S, M_L, M_S\right\rangle$ in terms of uncoupled basis sets $\left|l_1\, m_{l_1}\right\rangle \left|l_2\, m_{l_2}\right\rangle$ and $\left|s_1\, m_{s_1}\right\rangle \left|s_2\, m_{s_2}\right\rangle$

Here we will learn this method.

We have understood in lecture-13 about the coupling of angular momenta. The uncoupled wavefunctions are $\left| j_1\ m_1 \right\rangle$ and $\left| j_2\ m_2 \right\rangle$. The $J_1^2,\ J_2^2$ and $J_{1z},\ J_{2z}$ when operate on these eigenfunctions provide

$$\left.\begin{aligned}
J_1^{\ 2} \mid j_1\, m_1\rangle &= j_1\left(j_1+1\right) \mid j_1\, m_1\rangle \\
J_{1z} \mid j_1\, m_1\rangle &= m_1 \mid j_1\, m_1\rangle \\
J_2^{\ 2} \mid j_2\, m_2\rangle &= j_2\left(j_2+1\right) \mid j_2\, m_2\rangle \\
J_{2z} \mid j_2\, m_2\rangle &= m_2 \mid j_2\, m_2\rangle
\end{aligned}\right\}$$

Also we know that

$$J_-\left|J,m\right\rangle = \sqrt{\frac{1}{2}\left[J(J+1)-m(m-1)\right]}\ \left|J,m-1\right\rangle$$

The coupled wavefunction $\left|J,m\right\rangle$ is related to uncoupled wavefunctions $\left| j_1\ m_1 \right\rangle$ and $\left| j_2\ m_2 \right\rangle$ as

$$\underbrace{\mid j_1\ j_2\ J\ m\rangle}_{\substack{Eigen\ function\ of \\ J^2\ and\ J_z}} = \sum_{m_1, m_2} \underbrace{\langle j_1\ j_2\ m_1\ m_2 \mid j_1\ j_2\ J\ m\rangle}_{\substack{Numeric\ value\ known\ as \\ Vector\ Addition\ Coefficients \\ or, \\ Clebsch-Gordon\ Coefficients}} \underbrace{\mid j_1\ j_2\ m_1\ m_2\rangle}_{\substack{Eigen\ function\ of \\ J_1\ and\ J_2}}$$

$$= (-1)^{j_2-j_1-m} \sum_{m_1,m_2} \sqrt{2J+1}\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -m \end{pmatrix} \left| j_1\ j_2\ m_1\ m_2 \right\rangle$$

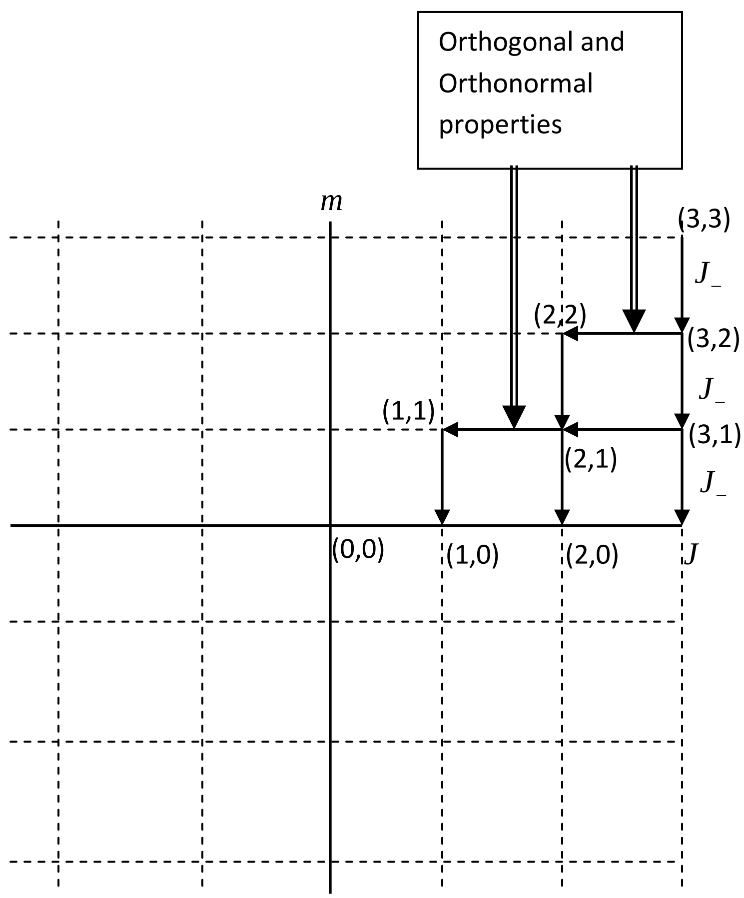
With restriction $m = m_1 + m_2$. Here $\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -m \end{pmatrix}$ is known as 3j symbol. Using this relation, one can calculate the coupled wavefunction by knowing the value of 3j.

However, there is a simple method to calculate the coupled wavefunction. In the following we discuss this method.

The method is

1. First find out the maximum J from j_1 and j_2.
2. Write down the wavefunction $\left|J_{\max}, m_{\max}\right\rangle = \left|j_{1_{\max}}, m_{1_{\max}}\right\rangle\left|j_{2_{\max}}, m_{2_{\max}}\right\rangle$. The coefficient will be one because there will be only one term ($m = m_1 + m_2$) and the uncoupled wavefunctions are normalized.
3. Then operate J_- on $\left|J_{\max}, m_{\max}\right\rangle$ to obtain $\left|J_{\max}, m_{\max} - 1\right\rangle$
4. Then write $\left|J_{\max} - 1, m_{\max} - 1\right\rangle$ in terms of $\left|j_1\ m_1\right\rangle$ and $\left|j_2\ m_2\right\rangle$ using all possible combination keeping in mind $m = m_1 + m_2$.
5. Use orthogonal and orthonormal properties to find out the coefficients of these.

The figure below illustrates this method.



Let us work out some examples.

$$j_1 = \frac{1}{2} \;\; ; \;\; j_2 = \frac{1}{2} \qquad m_1 = \frac{1}{2}\,,\,-\frac{1}{2} \;\; ; \;\; m_2 = \frac{1}{2}\,,\,-\frac{1}{2}$$

$$\begin{aligned} \left| j_1\, j_2\, m_1\, m_2 \right\rangle &= \left| j_1\, m_1 \right\rangle \left| j_2\, m_2 \right\rangle \\ &= \left| \frac{1}{2}\;\frac{1}{2} \right\rangle \left| \frac{1}{2}\;\frac{1}{2} \right\rangle \end{aligned}$$

$$\begin{aligned} J &= \left| j_1 + j_2 \right| \quad \textit{to} \quad \left| j_1 - j_2 \right| \\ &= 1 \;\; , \;\; 0 \end{aligned}$$

$$\left.\begin{aligned} &J = 1\,; \quad m = 1, 0, -1 \quad ; \quad && \left| J\, m \right\rangle \Rightarrow \left| 1\, 1 \right\rangle \\ & && \left| 1\, 0 \right\rangle \\ & && \left| 1\, -1 \right\rangle \\ &J = 0\,; \quad m = 0 \quad ; \quad && \left| J\, m \right\rangle \Rightarrow \left| 0\;\, 0 \right\rangle \end{aligned}\right]$$

$$m = m_1 + m_2$$

$$\overbrace{\left| 1\, 1 \right\rangle}^{J,m} = \overbrace{\left| \frac{1}{2}\;\frac{1}{2} \right\rangle}^{j_1, m_1} \overbrace{\left| \frac{1}{2}\;\frac{1}{2} \right\rangle}^{j_2, m_2}$$

Operate both sides J_- to get $\left| 1, 0 \right\rangle$

$$\begin{aligned} J_- \left| 1\, 1 \right\rangle &= \sqrt{1(1+1) - 1(1-1)}\; \left| 1\; 0 \right\rangle \\ &= \sqrt{2}\; \left| 1\; 0 \right\rangle \end{aligned}$$

$$\begin{aligned} J_- \left| \frac{1}{2}\;\frac{1}{2} \right\rangle \left| \frac{1}{2}\;\frac{1}{2} \right\rangle &= J_{1-} \left| \frac{1}{2}\;\frac{1}{2} \right\rangle \left| \frac{1}{2}\;\frac{1}{2} \right\rangle + J_{2-} \left| \frac{1}{2}\;\frac{1}{2} \right\rangle \left| \frac{1}{2}\;\frac{1}{2} \right\rangle \\ &= \sqrt{\frac{1}{2}\left(\frac{1}{2} + \frac{1}{2}\right) - \frac{1}{2}\left(\frac{1}{2} - \frac{1}{2}\right)}\; \left| \frac{1}{2}\; -\frac{1}{2} \right\rangle \left| \frac{1}{2}\;\frac{1}{2} \right\rangle + \sqrt{\frac{1}{2}\left(\frac{1}{2} + \frac{1}{2}\right) - \frac{1}{2}\left(\frac{1}{2} - \frac{1}{2}\right)}\; \left| \frac{1}{2}\;\frac{1}{2} \right\rangle \left| \frac{1}{2}\; -\frac{1}{2} \right\rangle \end{aligned}$$

$$\left| 1\; 0 \right\rangle = \frac{1}{\sqrt{2}} \left| \frac{1}{2}\; -\frac{1}{2} \right\rangle \left| \frac{1}{2}\;\frac{1}{2} \right\rangle + \frac{1}{\sqrt{2}} \left| \frac{1}{2}\;\frac{1}{2} \right\rangle \left| \frac{1}{2}\; -\frac{1}{2} \right\rangle$$

Then write $|0\ 0\rangle$ as

$$|0\ 0\rangle = a\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + b\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

To evaluate these constants *a* and *b*, use orthogonal and orthonomal properties

$$\frac{a}{\sqrt{2}} + \frac{b}{\sqrt{2}} = 0 \ \ ; \ \ a^2 + b^2 = 1 \ \ ; \ \ a = -b$$

$$a^2 + a^2 = 1 \ \Rightarrow 2a^2 = 1 \ \Rightarrow a = \frac{1}{\sqrt{2}} \ ; \ b = -\frac{1}{\sqrt{2}}$$

So $|0\ 0\rangle = \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$

Again, the wavefuntion $|1\ -1\rangle = \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$

If we consider $j_1 = s_1 = \frac{1}{2}$; $j_2 = s_2 = \frac{1}{2}$ the spin orbitals then

The three symmetric wavfunctions χ_S are

$$\overbrace{|1\ 1\rangle}^{J,m} = \overbrace{\left|\frac{1}{2}\ \frac{1}{2}\right\rangle}^{j_1,m_1}\overbrace{\left|\frac{1}{2}\ \frac{1}{2}\right\rangle}^{j_2,m_2} = \alpha(1)\alpha(2)$$

$$|1\ 0\rangle = \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right]$$

$$|1\ -1\rangle = \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle = \beta(1)\beta(2)$$

And the antisymmetric wavefunction χ_A is

$$|0\ 0\rangle = \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

To construct the total wavefunction of the atom,

1. we need to construct the coupled wavefunction for the spin orbital $\left| S\, M_S \right\rangle$
2. we need to construct the coupled wavefuntion for the space orbital $\left| L\, M_L \right\rangle$
3. Construct an antisymmetric wavefunction from the result of 1 and 2

Example (1) : For $1s^2$ we have terms ${}^1S$

$$\ell_1 = 0 \;\; ; \;\; m_{l_1} = 0 \qquad \ell_2 = 0 \;\; ; \;\; m_{l_1} = 0$$
$$L = 0, \quad M_L = 0$$

$$\left| L\, M_L \right\rangle = \left| 0\, 0 \right\rangle = 1s(1)1s(2)$$

This is the only possibility because the wavefunction will be same even we interchange the electrons.

This is symmetric, so we have to multiply with the antisymmetric wavefunction of spin orbital to get the wavefunction of the term ${}^1S$

$$\left| {}^1S\, 00 \right\rangle = \left| L\, M_L S\, M_s \right\rangle = \left| L\, M_L \right\rangle_S \left| S\, M_s \right\rangle_A = 1s(1)1s(2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$
$$= \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} \equiv \left| 1s^+\, 1s^- \right\rangle \equiv \left| 0^+\, 0^- \right\rangle$$

Example (2) : For $1s2s$, we have terms ^1S and ^3S

$$\ell_1 = 0 \;\; ; \;\; m_{l_1} = 0 \qquad \ell_2 = 0 \;\; ; \;\; m_{l_1} = 0$$

$$L = 0, \quad M_L = 0$$

$$\left| L\, M_L \right\rangle = \left| 0\, 0 \right\rangle = 1s(1)2s(2)$$

Now it is possible to make symmetric and antisymmetric wavefunctions by interchanging the electrons.

$$\left| L\, M_L \right\rangle_S = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) + 1s(2)2s(1)\right] \text{ and } \left| L\, M_L \right\rangle_A = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 1s(2)2s(1)\right]$$

$$\begin{aligned}
\left| {}^1S\, 00 \right\rangle &= \left| L\, M_L S\, M_s \right\rangle = \left| L\, M_L \right\rangle_S \left| S\, M_s \right\rangle_A \\
&= \frac{1}{\sqrt{2}}\left[1s(1)2s(2) + 1s(2)2s(1)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right] \\
&= \frac{1}{\sqrt{2}}\left\{\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix}\right\} - \frac{1}{\sqrt{2}}\left\{\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}\right\} \\
&= \frac{1}{\sqrt{2}}\left[\left|1s^+\, 2s^-\right\rangle - \left|1s^-\, 2s^+\right\rangle\right] = \frac{1}{\sqrt{2}}\left[\left|0^+\, 0^-\right\rangle - \left|0^-\, 0^+\right\rangle\right]
\end{aligned}$$

Similarly we get

$$\begin{aligned}
\left| {}^3S\, 01 \right\rangle &= \left| L\, M_L S\, M_s \right\rangle = \left| L\, M_L \right\rangle_A \left| S\, M_s \right\rangle_S \\
&= \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 1s(2)2s(1)\right]\alpha(1)\alpha(2) \\
&= \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix} \equiv \left|1s^+\, 2s^+\right\rangle \equiv \left|0^+\, 0^+\right\rangle
\end{aligned}$$

$$\begin{aligned}
\left| {}^3S\, 00 \right\rangle &= \left| L\, M_L S\, M_s \right\rangle = \left| L\, M_L \right\rangle_A \left| S\, M_s \right\rangle_S \\
&= \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 1s(2)2s(1)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right] \\
&= \frac{1}{\sqrt{2}}\left\{\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix}\right\} + \frac{1}{\sqrt{2}}\left\{\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}\right\} \\
&= \frac{1}{\sqrt{2}}\left[\left|1s^+\, 2s^-\right\rangle + \left|1s^-\, 2s^+\right\rangle\right] = \frac{1}{\sqrt{2}}\left[\left|0^+\, 0^-\right\rangle + \left|0^-\, 0^+\right\rangle\right]
\end{aligned}$$

And

$$\left|{}^{3}S\,0\,-1\right\rangle = \left|L\,M_{L}S\,M_{s}\right\rangle = \left|L\,M_{L}\right\rangle_{A}\left|S\,M_{s}\right\rangle_{S}$$

$$= \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 1s(2)2s(1)\right]\beta(1)\beta(2)$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix} \equiv \left|1s^{-}\ 2s^{-}\right\rangle \equiv \left|0^{-}\ 0^{-}\right\rangle$$

Property of C.G. Coefficient,

$$\langle j_1\ j_2\ m_1\ m_2 \mid j_1\ j_2\ J\ m\rangle = (-1)^{J_1+J_2-J}\langle J_2\ J_1\ m_2\ m_1 \mid J_2\ J_1\ J\ m\rangle$$

$$\langle J_1\ J_2\ m_1\ m_2 \mid J_1\ J_2\ J\ m\rangle = \delta(m, m_1+m_2)$$
$$\sqrt{\frac{(J_1+J_2-J)!\,(J+J_1-J_2)!\,(J+J_2-J_1)!\,(2J+1)}{(J+J_1+J_2+1)!}}$$
$$\times\sum_k \frac{(-1)^k\sqrt{(J_1+m_1)!\,(J_1-m_1)!\,(J_2+m_2)!\,(J_2-m_2)!\,(J+m)!\,(J-m)!}}{k!\,(J_1+J_2-J-k)!\,(J_1-m_1-k)!\,(J_2-m_2-k)!\,(J-J_2+m_1+k)!\,(J-J_1-m_2+k)!}$$

For two electrons

$\ell_1\ ;\ \ell_2$

$|\ell_1(1)\ \ell_2(1)\ L\ M_L\rangle$

$$|L\ M_L\rangle_A^S = \frac{1}{\sqrt{2}}\left[|\ell_1(1)\ \ell_2(1)\ L\ M_L\rangle \pm |\ell_1(2)\ \ell_2(1)\ L\ M_L\rangle\right]$$
$$= \frac{1}{\sqrt{2}}\left[|\ell_1(1)\ \ell_2(1)\ L\ M_L\rangle \pm (-1)^{\ell_1+\ell_2-L}|\ell_2(1)\ \ell_1(2)\ L\ M_L\rangle\right]$$

$$|{}^1\ L\ M_L\ M_S\rangle = \frac{1}{\sqrt{2}}\left[|\ell_1(1)\ \ell_2(2)\ L\ M_L\rangle + (-1)^{\ell_1+\ell_2-L}|\ell_2(1)\ \ell_1(2)\ L\ M_L\rangle\right]{}^1\chi$$

$$|{}^3 L\ M_L\ M_S\rangle = \frac{1}{\sqrt{2}}\left[|\ell_1(1)\ \ell_2(1)\ L\ M_L\rangle - (-1)^{\ell_1+\ell_2-L}|\ell_2(1)\ \ell_1(2)\ L\ M_L\rangle\right]{}^3\chi$$

For equivalent electrons we have $l_1 = l_2$. The singlet function (S = 0) will vanish unless L is even. The triplet function (S = 1) will vanish unless L is odd. Thus the wavefunction for the equivalent electrons will vanish unless $L + S$ = even.

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THREE ANGULAR MOMENTA

Here we will evaluate the coupled wavefunction arising from coupling of three angular momenta. The points to be noted here that,

When three angular momentum operators are J_1 , J_2, J_3 are coupled to form J, the possible values of J are independent of the coupling scheme.

However, the eigenfunctions are dependent of the detailed of the coupling scheme.

In the following we will see it.

$$J = J_1 + J_2 + J_3$$

Let us take $j_1 = 1 \;\; ; \;\; j_2 = \frac{1}{2} \;\; ; \;\; j_3 = \frac{1}{2}$

Case 1: Scheme-1

$$j_{12} = j_1 + j_2$$
$$j = j_{12} + j_3$$

$$j_1 j_2 \left(j_{12} \right) \quad 1\,\frac{1}{2}\left(\frac{3}{2}\right) \quad \left\{ \begin{matrix} \left|\frac{3}{2},\frac{3}{2}\right\rangle \left|\frac{3}{2}\; -\frac{1}{2}\right\rangle \\ \left|\frac{3}{2},\frac{1}{2}\right\rangle \left|\frac{3}{2}\; -\frac{1}{2}\right\rangle \end{matrix} \right. \quad \text{wavefunctions}$$

$$j_1 j_2 \left(j_{12} \right) \quad 1\,\frac{1}{2}\left(\frac{1}{2}\right) \quad \left\{ \begin{matrix} \left|\frac{1}{2}\; -\frac{1}{2}\right\rangle \\ \left|\frac{1}{2}\; -\frac{1}{2}\right\rangle \end{matrix} \right. \quad \text{wavefunctions}$$

$$\left| j_1 \;\; j_2 \;\; j_{12} \;\; m_{12} \right\rangle \equiv \left| 1\; \frac{1}{2}\; \frac{3}{2}\; \frac{3}{2} \right\rangle = \left| 1\, 1 \right\rangle \left| \frac{1}{2}\; \frac{1}{2} \right\rangle$$

…..Eqn. (1)

Applying J_- on both sides

$$J_-\left|1\ \frac{1}{2}\ \frac{3}{2}\ \frac{3}{2}\right\rangle=\sqrt{\frac{1}{2}\left[\frac{3}{2}\left(\frac{3}{2}+1\right)-\frac{3}{2}\left(\frac{3}{2}-1\right)\right]}\left|1\ \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}\right\rangle$$

$$=\sqrt{\frac{1}{2}[3]}\left|1\ \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}\right\rangle=\sqrt{\frac{3}{2}}\left|1\ \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}\right\rangle$$

$$J_-\left|1\,1\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle=J_{1-}\left|1\,1\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle+J_{2-}\left|1\,1\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

$$=\sqrt{\frac{1}{2}\left[1(1+1)-1(1-1)\right]}\left|1\,0\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle+\sqrt{\frac{1}{2}\left[\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)\right]}\left|1\,1\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

$$=\left|1\,0\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle+\frac{1}{2}\left|1\,1\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

So,

$$\left|1\ \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}\right\rangle=\frac{\sqrt{2}}{\sqrt{3}}\left|1\,0\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle+\frac{1}{\sqrt{3}}\left|1\,1\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle \qquad \text{.....}$$

Eqn. (2)

Similarly,

$$\left|1\ \frac{1}{2}\ \frac{3}{2}\ -\frac{3}{2}\right\rangle=\left|1\ -1\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle \qquad \text{.....}$$

Eqn. (3)

Applying J_+ on both sides

$$J_+\left|1\ \frac{1}{2}\ \frac{3}{2}\ -\frac{3}{2}\right\rangle = -\sqrt{\frac{1}{2}\left[\frac{3}{2}\left(\frac{3}{2}+1\right)-\left(-\frac{3}{2}\right)\left(-\frac{3}{2}+1\right)\right]}\left|1\ \frac{1}{2}\ \frac{3}{2}\ -\frac{1}{2}\right\rangle$$

$$=\sqrt{\frac{1}{2}\left[\frac{1}{4}\frac{5}{}-\frac{3}{4}\right]}\left|1\ \frac{1}{2}\ \frac{3}{2}\ -\frac{1}{2}\right\rangle = -\sqrt{\frac{3}{2}}\left|1\ \frac{1}{2}\ \frac{3}{2}\ -\frac{1}{2}\right\rangle$$

$$J_+\left|1\ -1\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle = J_{1+}\left|1\ -1\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle + J_{2+}\left|1\ -1\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

$$= -\sqrt{\frac{1}{2}\left[1(1+1)-(-1)(-1+1)\right]}\left|1\ 0\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

$$-\sqrt{\frac{1}{2}\left[\frac{1}{2}\left(\frac{1}{2}+1\right)-\left(-\frac{1}{2}\right)\left(-\frac{1}{2}+1\right)\right]}\left|1\ -1\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

$$=\left|1\ 0\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle - \frac{1}{\sqrt{2}}\left|1\ -1\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

So,

$$\left|1\ \frac{1}{2}\ \frac{3}{2}\ -\frac{1}{2}\right\rangle = \frac{\sqrt{2}}{\sqrt{3}}\left|1\ 0\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle + \frac{1}{\sqrt{3}}\left|1\ -1\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle \qquad \text{.....}$$

Eqn. (4)

Now we can write

$$\left|1\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\right\rangle = a\left|1\ 0\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + b\left|1\ 1\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

Using orthonormal & orthogonal properties:

$$a^2+b^2=1$$
$$\Rightarrow \frac{b^2}{2}+b^2=1$$
$$\Rightarrow \frac{3b^2}{2}=1$$
$$\Rightarrow b=-\frac{\sqrt{2}}{\sqrt{3}}$$

$$\frac{a\sqrt{2}}{\sqrt{3}}+\frac{b}{\sqrt{3}}=0$$
$$\Rightarrow a\sqrt{2}=-b$$
$$\Rightarrow a=-\frac{b}{\sqrt{2}}$$

$$a=+\frac{1}{\sqrt{2}}\cdot\frac{\sqrt{2}}{\sqrt{3}}=\frac{1}{\sqrt{3}}$$

So,

$$\left|1\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left|1\ 0\right\rangle \left|\frac{1}{2}\ \frac{1}{2}\right\rangle - \frac{\sqrt{2}}{\sqrt{3}}\left|1\ 1\right\rangle \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$ .....

Eqn. (5)

Now we can write

$$\left|1\ \frac{1}{2}\ \frac{1}{2}\ -\frac{1}{2}\right\rangle = a_1\left|1\ 0\right\rangle \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle - b_1\left|1\ -1\right\rangle \left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

$$\frac{a_1\sqrt{2}}{\sqrt{3}} + \frac{b_1}{\sqrt{3}} = 0 \qquad a_1^2 + b_1^2 = 1$$

$$\Rightarrow a_1 = -\frac{b_1}{\sqrt{2}}$$

$$b_1 = -\frac{\sqrt{2}}{\sqrt{3}} \qquad a_1 = \frac{1}{\sqrt{3}}$$

$$\left|1\ \frac{1}{2}\ \frac{1}{2}\ -\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}\left|1\ 0\right\rangle \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle - \frac{\sqrt{2}}{\sqrt{3}}\left|1\ -1\right\rangle \left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$ .....

Eqn. (6)

Next we will find

$$1\ \frac{1}{2}\left(\frac{3}{2}\right)\frac{1}{2}\qquad 2$$

$$1\ \frac{1}{2}\left(\frac{3}{2}\right)\frac{1}{2}\qquad 1$$

$$1\ \frac{1}{2}\left(\frac{1}{2}\right)\frac{1}{2}\qquad 1$$

$$1\ \frac{1}{2}\left(\frac{1}{2}\right)\frac{1}{2}\qquad 0$$

$\left|\frac{3}{2}\ \frac{1}{2}\ 1\ 1\right\rangle$ Calculate

$$\left|\frac{3}{2}\ \frac{1}{2}\ 2\ 2\right\rangle = \left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle = |1\,1\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

$$J_-\left|\frac{3}{2}\ \frac{1}{2}\ 2\ 2\right\rangle = \sqrt{\frac{1}{2}\left[2(2+1)-2(2-1)\right]}\left|\frac{3}{2}\ \frac{1}{2}\ 2\ 1\right\rangle$$

$$= \sqrt{2}\left|\frac{3}{2}\ \frac{1}{2}\ 2\ 2\right\rangle$$

$$J_-\left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle = J_{1-}\left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + J_{2-}\left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

$$= \sqrt{\frac{1}{2}\left[\frac{3}{2}\left(\frac{3}{2}+1\right)-\frac{3}{2}\left(\frac{3}{2}-1\right)\right]}\left|\frac{3}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

$$+\sqrt{\frac{1}{2}\left[\frac{1}{2}\left(\frac{1}{2}+1\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)\right]}\left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

$$= \sqrt{\frac{3}{2}}\left|\frac{3}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}}\left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

$$\Rightarrow \left|\frac{3}{2}\ \frac{1}{2}\ 2\ 1\right\rangle = \frac{\sqrt{3}}{2}\left|\frac{3}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + \frac{1}{2}\left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

$$\left|\frac{3}{2}\ \frac{1}{2}\ 1\ 1\right\rangle = a\left|\frac{3}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + b\left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

$$\frac{a\sqrt{3}}{2}+\frac{b}{2}=0$$

$$\Rightarrow a\sqrt{3}=-b$$

$$\Rightarrow a=-\frac{b}{\sqrt{3}}$$

$$a^2+b^2=1$$

$$\Rightarrow \frac{b^2}{3}+b^2=1$$

$$\Rightarrow \frac{4}{3}b^2=1$$

$$\Rightarrow b=-\frac{\sqrt{3}}{2} \qquad , \qquad a=\frac{\sqrt{3}}{2}\cdot\frac{1}{\sqrt{3}}=\frac{1}{2}$$

$$\left|\frac{3}{2}\ \frac{1}{2}\ 1\ 1\right\rangle=\frac{1}{2}\left|\frac{3}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle-\frac{\sqrt{3}}{2}\left|\frac{3}{2}\ \frac{3}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

Now will calculate the final wavefunction

$$\left| j_1\ \ j_2\ (j_{12})\ j_3\ ;\ J\ \ m \right\rangle = \left| 1\ \frac{1}{2}\left(\frac{3}{2}\right)\frac{1}{2}\ ;\ 1\,1 \right\rangle$$

$$= \frac{1}{2}\left|\frac{3}{2}\,\frac{1}{2}\right\rangle_{12}\left|\frac{1}{2}\,\frac{1}{2}\right\rangle - \frac{\sqrt{3}}{2}\left|\frac{3}{2}\,\frac{3}{2}\right\rangle_{12}\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle$$

$$\left| j_1\ \ j_2\ (j_{12})\ j_3\ ;\ J\ \ m \right\rangle =$$

$$\left| 1\ \frac{1}{2}\left(\frac{3}{2}\right)\frac{1}{2}\ ;\ 1\,1 \right\rangle = \frac{1}{2}\left[\frac{\sqrt{2}}{\sqrt{3}}|1\,0\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + \frac{1}{\sqrt{3}}|1\,1\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\right]\left|\frac{1}{2}\ \frac{1}{2}\right\rangle - \frac{\sqrt{3}}{2}\left[|1\,1\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\right]\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

$$= \frac{\sqrt{2}}{2\sqrt{3}}|1\,0\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle + \frac{1}{2\sqrt{3}}|1\,1\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle - \frac{\sqrt{3}}{2}|1\,1\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle$$

.....

<u>Check:</u> $\frac{2}{4\times 3} + \frac{1}{4\times 3} + \frac{3}{4} = \frac{2+1+9}{12} = \frac{1}{12}\overset{2}{=}1$

<u>The other one</u>

$$\left| j_1\ \ j_2\ (j_{12})\ j_3\ ;\ J\ \ m \right\rangle = \left| 1\ \frac{1}{2}\left(\frac{1}{2}\right)\frac{1}{2}\ ;\ 1\,1 \right\rangle = \left|\frac{1}{2}\ \frac{1}{2}\right\rangle_{12}\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

$$= \frac{1}{\sqrt{3}}|1\,0\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle - \frac{\sqrt{2}}{\sqrt{3}}|1\,1\rangle\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$$

Case 2:

$$J_{23} = J_2 + J_3 \qquad \frac{1}{2}\ \frac{1}{2}\ 1 \begin{cases} 1 \\ 0 \\ -1 \end{cases}$$
$$J = J_1 + J_{23} \qquad \frac{1}{2}\ \frac{1}{2}\ 0 \ \{0$$

$$\left|\frac{1}{2}\ \frac{1}{2}\ 1\ 1\right\rangle = \left|\frac{1}{2}\ \frac{1}{2}\right\rangle \left|\frac{1}{2}\ \frac{1}{2}\right\rangle \qquad \ldots..$$
Eqn. (1)

$$\left|\frac{1}{2}\ \frac{1}{2}\ 1\ 0\right\rangle = \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle \left|\frac{1}{2}\ \frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ \frac{1}{2}\right\rangle \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle \qquad \ldots..$$
Eqn. (2)

$$\left|\frac{1}{2}\ \frac{1}{2}\ 1\ -1\right\rangle = \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle \qquad \ldots..$$
Eqn. (3)

$$\left|\frac{1}{2}\ \frac{1}{2}\ 0\ 0\right\rangle = \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ -\frac{1}{2}\right\rangle \left|\frac{1}{2}\ \frac{1}{2}\right\rangle - \frac{1}{\sqrt{2}}\left|\frac{1}{2}\ \frac{1}{2}\right\rangle \left|\frac{1}{2}\ -\frac{1}{2}\right\rangle \qquad \ldots..$$
Eqn. (4)

Now the coupled wavefunctions

$$\left| j_1\ j_2\ j_3\left(j_{23}\right);\ j\ m\right\rangle$$

$$1\,,\ \frac{1}{2}\ \frac{1}{2}\,(1) \qquad 2$$
$$1\ \ \frac{1}{2}\ \frac{1}{2}\,(1) \qquad 1\,,\,1$$
$$1\ \ \frac{1}{2}\ \frac{1}{2}\,(1) \qquad 0$$
$$1\ \ \frac{1}{2}\ \frac{1}{2}\,(0) \qquad 1\,,\,1$$

$$\left|1\,1\,2\;2\right\rangle = \left|1\,1\right\rangle \left|1\,1\right\rangle$$

$$J_- \left|1\,1\,2\;2\right\rangle = \sqrt{\frac{1}{2}\left[2(2+1)-2(2-1)\right]}\left|1\,1\,2\,1\right\rangle$$
$$= \sqrt{\frac{1}{2}[4]}\left|1\,1\,2\,1\right\rangle = \sqrt{2}\left|1\,1\,2\,1\right\rangle$$

$$J_- \left|1\,1\right\rangle \left|1\,1\right\rangle = J_{1-}\left|1\,1\right\rangle \left|1\,1\right\rangle + J_{2-}\left|1\,1\right\rangle \left|1\,1\right\rangle$$
$$= \sqrt{\frac{1}{2}\left[1(1+1)-1(1-1)\right]}\left|1\,0\right\rangle \left|1\,1\right\rangle + \sqrt{\frac{1}{2}\left[1(1+1)-1(1-1)\right]}\left|1\,1\right\rangle \left|1\,0\right\rangle$$
$$= \left|1\,0\right\rangle \left|1\,1\right\rangle + \left|1\,1\right\rangle \left|1\,0\right\rangle$$

$$\left|1\,1\,2\,1\right\rangle = \frac{1}{\sqrt{2}}\left|1\,1\right\rangle \left|1\,0\right\rangle + \frac{1}{\sqrt{2}}\left|1\,1\right\rangle \left|1\,0\right\rangle$$

$$\left|1\,1\,1\,1\right\rangle = a\left|1\,0\right\rangle \left|1\,1\right\rangle_{23} + b\left|1\,1\right\rangle \left|1\,0\right\rangle_{23}$$

$$\frac{a}{\sqrt{2}} + \frac{b}{\sqrt{2}} = 0$$
$$\Rightarrow a = -b$$

$$a^2 + b^2 = 1$$
$$\Rightarrow 2b^2 = 1 \;\; \Rightarrow b = -\frac{1}{\sqrt{2}}$$
$$a = \frac{1}{\sqrt{2}}$$

$$\left|1\,1\,1\,1\right\rangle = \frac{1}{\sqrt{2}}\left|1\,0\right\rangle \left|1\,1\right\rangle_{23} - \frac{1}{\sqrt{2}}\left|1\,1\right\rangle \left|1\,0\right\rangle_{23}$$
$$= \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left|\frac{1}{2}\;-\frac{1}{2}\right\rangle \left|\frac{1}{2}\;\frac{1}{2}\right\rangle + \frac{1}{\sqrt{2}}\left|\frac{1}{2}\;\frac{1}{2}\right\rangle \left|\frac{1}{2}\;-\frac{1}{2}\right\rangle\right]\left|1\,1\right\rangle - \frac{1}{\sqrt{2}}\left|\frac{1}{2}\;\frac{1}{2}\right\rangle \left|\frac{1}{2}\;\frac{1}{2}\right\rangle \left|1\,0\right\rangle$$

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

$$\left|1\,0\,1\,1\right\rangle = \left|1\,1\right\rangle \left|0\;0\right\rangle_{23}$$
$$= \left|1\,1\right\rangle \frac{1}{\sqrt{2}}\left[\left|\frac{1}{2}\;-\frac{1}{2}\right\rangle \left|\frac{1}{2}\;\frac{1}{2}\right\rangle - \left|\frac{1}{2}\;\frac{1}{2}\right\rangle \left|\frac{1}{2}\;-\frac{1}{2}\right\rangle\right]$$
$$= \frac{1}{\sqrt{2}}\left|1\,1\right\rangle \left|\frac{1}{2}\;-\frac{1}{2}\right\rangle \left|\frac{1}{2}\;\frac{1}{2}\right\rangle - \frac{1}{\sqrt{2}}\left|1\,1\right\rangle \left|\frac{1}{2}\;\frac{1}{2}\right\rangle \left|\frac{1}{2}\;-\frac{1}{2}\right\rangle$$

…..

So all the wavefunctions $\left|J=1\, m=1\right\rangle$ are not same, it depends on the coupling scheme.

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In this lecture we came to know the procedure of evaluating the coupled wavefunctions.

Then we made the total wavefunction antisymmetric by multiplying symmetric $\left|L\, M_L\right\rangle$ with antisymmetric $\left|S\, M_S\right\rangle$ and vice versa.

Then we prove that for three angular coupling, the final wavefunctions depend on the detailed coupling scheme. It should be noted that, under a coupling scheme, the wavefunctions are orthogonal. But the wavefunctions should not be orthogonal for different coupling scheme.