$$\therefore \sqrt{2}\hbar\,|\frac{1}{2},\frac{1}{2},1,0> = \hbar\,|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}> + \hbar\,|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}>$$

$$\Rightarrow |\frac{1}{2},\frac{1}{2},1,0> = \frac{1}{\sqrt{2}}\,|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}> + \frac{1}{\sqrt{2}}\,|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}>$$

$$\Rightarrow \boxed{C_{-\frac{1}{2},\frac{1}{2}} = \frac{1}{\sqrt{2}}} \qquad \boxed{C_{\frac{1}{2},-\frac{1}{2}} = \frac{1}{\sqrt{2}}}$$

For the **singlet state**

Let $|\frac{1}{2},\frac{1}{2},0,0> = a_1\,|\frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2}> + a_2\,|\frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2}>$ and require

$\left\langle \frac{1}{2},\frac{1}{2},0,0 \middle| \frac{1}{2},\frac{1}{2},0,0 \right\rangle = 1$ and $\left\langle \frac{1}{2},\frac{1}{2},0,0 \middle| \frac{1}{2},\frac{1}{2},1,0 \right\rangle = 0$

$$\left\langle \frac{1}{2},\frac{1}{2},0,0 \middle| \frac{1}{2},\frac{1}{2},0,0 \right\rangle = a_1^2 \underbrace{\left\langle \frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2} \middle| \frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2} \right\rangle}_{=1} + a_2^2 \underbrace{\left\langle \frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2} \middle| \frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2} \right\rangle}_{=1}$$

$$+ a_1^* a_2 \underbrace{\left\langle \frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2} \middle| \frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2} \right\rangle}_{=0} + a_1 a_2^* \underbrace{\left\langle \frac{1}{2},\frac{1}{2};\frac{1}{2},-\frac{1}{2} \middle| \frac{1}{2},-\frac{1}{2};\frac{1}{2},\frac{1}{2} \right\rangle}_{=0}$$

$$= a_1^2 + a_2^2$$

Next: $$\left\langle \frac{1}{2},\frac{1}{2},0,0 \middle| \frac{1}{2},\frac{1}{2},1,0 \right\rangle \underset{\text{same idea}}{=} \frac{a_1}{\sqrt{2}} + \frac{a_2}{\sqrt{2}} = 0 \Rightarrow a_2 = -a_1$$

= two equations in two unknowns: a_1 and a_2

Solve to find:

$$a_1 = \boxed{\frac{1}{\sqrt{2}} = C_{-\frac{1}{2},\frac{1}{2}}} \qquad a_2 = \boxed{-\frac{1}{\sqrt{2}} = C_{\frac{1}{2},-\frac{1}{2}}}$$

Summary

$$|\frac{1}{2},\frac{1}{2},0,0> = \frac{1}{\sqrt{2}}(\beta_1\alpha_2 - \alpha_1\beta_2)$$

$$|\frac{1}{2},\frac{1}{2},1,1> = \alpha_1\alpha_2$$

$$|\frac{1}{2},\frac{1}{2},1,0> = \frac{1}{\sqrt{2}}(\beta_1\alpha_2 + \alpha_1\beta_2)$$

$$|\frac{1}{2},\frac{1}{2},1,-1> = \beta_1\beta_2$$

Note: there is not always a direct one-to-one correspondence between the coupled and uncoupled wave functions, but the number of states (for obvious physical reasons) remains the same regardless of which representation you use.

35. CLEBSCH-GORDAN COEFFICIENTS, SPHERICAL HARMONICS, AND d FUNCTIONS

Note: A square-root sign is to be understood over *every* coefficient, *e.g.*, for −8/15 read $-\sqrt{8/15}$.

Notation:

	J	J	...
	M	M	...
m_1 m_2			
m_1 m_2	Coefficients		
. .			

1/2×1/2

m_1 m_2	J=1, M=+1
+1/2 +1/2	1

m_1 m_2	J=1, M=0	J=0, M=0
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

m_1 m_2	J=1, M=−1
−1/2 −1/2	1

1×1/2

m_1 m_2	J=3/2, M=+3/2
+1 +1/2	1

m_1 m_2	J=3/2, M=+1/2	J=1/2, M=+1/2
+1 −1/2	1/3	2/3
0 +1/2	2/3	−1/3

m_1 m_2	J=3/2, M=−1/2	J=1/2, M=−1/2
0 −1/2	2/3	1/3
−1 +1/2	1/3	−2/3

m_1 m_2	J=3/2, M=−3/2
−1 −1/2	1

2×1

m_1 m_2	J=3, M=+3
+2 +1	1

m_1 m_2	J=3, M=+2	J=2, M=+2
+2 0	1/3	2/3
+1 +1	2/3	−1/3

m_1 m_2	J=3, M=+1	J=2, M=+1	J=1, M=+1
+2 −1	1/15	1/3	3/5
+1 0	8/15	1/6	−3/10
0 +1	2/5	−1/2	1/10

m_1 m_2	J=3, M=0	J=2, M=0	J=1, M=0
+1 −1	1/5	1/2	3/10
0 0	3/5	0	−2/5
−1 +1	1/5	−1/2	3/10

m_1 m_2	J=3, M=−1	J=2, M=−1	J=1, M=−1
0 −1	2/5	1/2	1/10
−1 0	8/15	−1/6	−3/10
−2 +1	1/15	−1/3	3/5

m_1 m_2	J=3, M=−2	J=2, M=−2
−1 −1	2/3	1/3
−2 0	1/3	−2/3

m_1 m_2	J=3, M=−3
−2 −1	1

1×1

m_1 m_2	J=2, M=+2
+1 +1	1

m_1 m_2	J=2, M=+1	J=1, M=+1
+1 0	1/2	1/2
0 +1	1/2	−1/2

m_1 m_2	J=2, M=0	J=1, M=0	J=0, M=0
+1 −1	1/6	1/2	1/3
0 0	2/3	0	−1/3
−1 +1	1/6	−1/2	1/3

m_1 m_2	J=2, M=−1	J=1, M=−1
0 −1	1/2	1/2
−1 0	1/2	−1/2

m_1 m_2	J=2, M=−2
−1 −1	1

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{4\pi}}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}$$

$$Y_2^2 = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{2i\phi}$$

$$Y_\ell^{-m} = (-1)^m Y_\ell^{m*}$$

$$d^{\,\ell}_{m,0} = \sqrt{\frac{4\pi}{2\ell+1}}\, Y_\ell^m\, e^{-im\phi}$$

2×1/2

m_1 m_2	J=5/2, M=+5/2
+2 +1/2	1

m_1 m_2	J=5/2, M=+3/2	J=3/2, M=+3/2
+2 −1/2	1/5	4/5
+1 +1/2	4/5	−1/5

m_1 m_2	J=5/2, M=+1/2	J=3/2, M=+1/2
+1 −1/2	2/5	3/5
0 +1/2	3/5	−2/5

m_1 m_2	J=5/2, M=−1/2	J=3/2, M=−1/2
0 −1/2	3/5	2/5
−1 +1/2	2/5	−3/5

m_1 m_2	J=5/2, M=−3/2	J=3/2, M=−3/2
−1 −1/2	4/5	1/5
−2 +1/2	1/5	−4/5

m_1 m_2	J=5/2, M=−5/2
−2 −1/2	1

3/2×1/2

m_1 m_2	J=2, M=+2
+3/2 +1/2	1

m_1 m_2	J=2, M=+1	J=1, M=+1
+3/2 −1/2	1/4	3/4
+1/2 +1/2	3/4	−1/4

m_1 m_2	J=2, M=0	J=1, M=0
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

m_1 m_2	J=2, M=−1	J=1, M=−1
−1/2 −1/2	3/4	1/4
−3/2 +1/2	1/4	−3/4

m_1 m_2	J=2, M=−2
−3/2 −1/2	1

3/2×1

m_1 m_2	J=5/2, M=+5/2
+3/2 +1	1

m_1 m_2	J=5/2, M=+3/2	J=3/2, M=+3/2
+3/2 0	2/5	3/5
+1/2 +1	3/5	−2/5

m_1 m_2	J=5/2, M=+1/2	J=3/2, M=+1/2	J=1/2, M=+1/2
+3/2 −1	1/10	2/5	1/2
+1/2 0	3/5	1/15	−1/3
−1/2 +1	3/10	−8/15	1/6

m_1 m_2	J=5/2, M=−1/2	J=3/2, M=−1/2	J=1/2, M=−1/2
+1/2 −1	3/10	8/15	1/6
−1/2 0	3/5	−1/15	−1/3
−3/2 +1	1/10	−2/5	1/2

m_1 m_2	J=5/2, M=−3/2	J=3/2, M=−3/2
−1/2 −1	3/5	2/5
−3/2 0	2/5	−3/5

m_1 m_2	J=5/2, M=−5/2
−3/2 −1	1

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 J M\rangle = (-1)^{J-j_1-j_2}\langle j_2 j_1 m_2 m_1 | j_2 j_1 J M\rangle$$

$$d^{\,j}_{m',m} = (-1)^{m-m'} d^{\,j}_{m,m'} = d^{\,j}_{-m,-m'}$$

3/2×3/2

m_1 m_2	J=3, M=+3
+3/2 +3/2	1

m_1 m_2	J=3, M=+2	J=2, M=+2
+3/2 +1/2	1/2	1/2
+1/2 +3/2	1/2	−1/2

m_1 m_2	J=3, M=+1	J=2, M=+1	J=1, M=+1
+3/2 −1/2	1/5	1/2	3/10
+1/2 +1/2	3/5	0	−2/5
−1/2 +3/2	1/5	−1/2	3/10

m_1 m_2	J=3, M=0	J=2, M=0	J=1, M=0	J=0, M=0
+3/2 −3/2	1/20	1/4	9/20	1/4
+1/2 −1/2	9/20	1/4	−1/20	−1/4
−1/2 +1/2	9/20	−1/4	−1/20	1/4
−3/2 +3/2	1/20	−1/4	9/20	−1/4

m_1 m_2	J=3, M=−1	J=2, M=−1	J=1, M=−1
+1/2 −3/2	1/5	1/2	3/10
−1/2 −1/2	3/5	0	−2/5
−3/2 +1/2	1/5	−1/2	3/10

m_1 m_2	J=3, M=−2	J=2, M=−2
−1/2 −3/2	1/2	1/2
−3/2 −1/2	1/2	−1/2

m_1 m_2	J=3, M=−3
−3/2 −3/2	1

$$d^{\,1}_{0,0} = \cos\theta \qquad d^{\,1/2}_{1/2,1/2} = \cos\frac{\theta}{2} \qquad d^{\,1/2}_{1/2,-1/2} = -\sin\frac{\theta}{2}$$

$$d^{\,1}_{1,1} = \frac{1+\cos\theta}{2} \qquad d^{\,1}_{1,0} = -\frac{\sin\theta}{\sqrt{2}} \qquad d^{\,1}_{1,-1} = \frac{1-\cos\theta}{2}$$

2×3/2

m_1 m_2	J=7/2, M=+7/2
+2 +3/2	1

m_1 m_2	J=7/2, M=+5/2	J=5/2, M=+5/2
+2 +1/2	3/7	4/7
+1 +3/2	4/7	−3/7

m_1 m_2	J=7/2, M=+3/2	J=5/2, M=+3/2	J=3/2, M=+3/2
+2 −1/2	1/7	16/35	2/5
+1 +1/2	4/7	1/35	−2/5
0 +3/2	2/7	−18/35	1/5

m_1 m_2	J=7/2, M=+1/2	J=5/2, M=+1/2	J=3/2, M=+1/2	J=1/2, M=+1/2
+2 −3/2	1/35	6/35	2/5	2/5
+1 −1/2	12/35	5/14	0	−3/10
0 +1/2	18/35	−3/35	−1/5	1/5
−1 +3/2	4/35	−27/70	2/5	−1/10

m_1 m_2	J=7/2, M=−1/2	J=5/2, M=−1/2	J=3/2, M=−1/2	J=1/2, M=−1/2
+1 −3/2	4/35	27/70	2/5	1/10
0 −1/2	18/35	3/35	−1/5	−1/5
−1 +1/2	12/35	−5/14	0	3/10
−2 +3/2	1/35	−6/35	2/5	−2/5

m_1 m_2	J=7/2, M=−3/2	J=5/2, M=−3/2	J=3/2, M=−3/2
0 −3/2	2/7	18/35	1/5
−1 −1/2	4/7	−1/35	−2/5
−2 +1/2	1/7	−16/35	2/5

m_1 m_2	J=7/2, M=−5/2	J=5/2, M=−5/2
−1 −3/2	4/7	3/7
−2 −1/2	3/7	−4/7

m_1 m_2	J=7/2, M=−7/2
−2 −3/2	1

2×2

m_1 m_2	J=4, M=+4
+2 +2	1

m_1 m_2	J=4, M=+3	J=3, M=+3
+2 +1	1/2	1/2
+1 +2	1/2	−1/2

m_1 m_2	J=4, M=+2	J=3, M=+2	J=2, M=+2
+2 0	3/14	1/2	2/7
+1 +1	4/7	0	−3/7
0 +2	3/14	−1/2	2/7

m_1 m_2	J=4, M=+1	J=3, M=+1	J=2, M=+1	J=1, M=+1
+2 −1	1/14	3/10	3/7	1/5
+1 0	3/7	1/5	−1/14	−3/10
0 +1	3/7	−1/5	−1/14	3/10
−1 +2	1/14	−3/10	3/7	−1/5

m_1 m_2	J=4, M=0	J=3, M=0	J=2, M=0	J=1, M=0	J=0, M=0
+2 −2	1/70	1/10	2/7	2/5	1/5
+1 −1	8/35	2/5	1/14	−1/10	−1/5
0 0	18/35	0	−2/7	0	1/5
−1 +1	8/35	−2/5	1/14	1/10	−1/5
−2 +2	1/70	−1/10	2/7	−2/5	1/5

m_1 m_2	J=4, M=−1	J=3, M=−1	J=2, M=−1	J=1, M=−1
+1 −2	1/14	3/10	3/7	1/5
0 −1	3/7	1/5	−1/14	−3/10
−1 0	3/7	−1/5	−1/14	3/10
−2 +1	1/14	−3/10	3/7	−1/5

m_1 m_2	J=4, M=−2	J=3, M=−2	J=2, M=−2
0 −2	3/14	1/2	2/7
−1 −1	4/7	0	−3/7
−2 0	3/14	−1/2	2/7

m_1 m_2	J=4, M=−3	J=3, M=−3
−1 −2	1/2	1/2
−2 −1	1/2	−1/2

m_1 m_2	J=4, M=−4
−2 −2	1

$$d^{\,3/2}_{3/2,3/2} = \frac{1+\cos\theta}{2}\cos\frac{\theta}{2}$$

$$d^{\,3/2}_{3/2,1/2} = -\sqrt{3}\frac{1+\cos\theta}{2}\sin\frac{\theta}{2}$$

$$d^{\,3/2}_{3/2,-1/2} = \sqrt{3}\frac{1-\cos\theta}{2}\cos\frac{\theta}{2}$$

$$d^{\,3/2}_{3/2,-3/2} = -\frac{1-\cos\theta}{2}\sin\frac{\theta}{2}$$

$$d^{\,3/2}_{1/2,1/2} = \frac{3\cos\theta-1}{2}\cos\frac{\theta}{2}$$

$$d^{\,3/2}_{1/2,-1/2} = -\frac{3\cos\theta+1}{2}\sin\frac{\theta}{2}$$

$$d^{\,2}_{2,2} = \left(\frac{1+\cos\theta}{2}\right)^2$$

$$d^{\,2}_{2,1} = -\frac{1+\cos\theta}{2}\sin\theta$$

$$d^{\,2}_{2,0} = \frac{\sqrt{6}}{4}\sin^2\theta$$

$$d^{\,2}_{2,-1} = -\frac{1-\cos\theta}{2}\sin\theta$$

$$d^{\,2}_{2,-2} = \left(\frac{1-\cos\theta}{2}\right)^2$$

$$d^{\,2}_{1,1} = \frac{1+\cos\theta}{2}(2\cos\theta-1)$$

$$d^{\,2}_{1,0} = -\sqrt{\frac{3}{2}}\sin\theta\cos\theta$$

$$d^{\,2}_{1,-1} = \frac{1-\cos\theta}{2}(2\cos\theta+1)$$

$$d^{\,2}_{0,0} = \left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$

Figure 35.1: The sign convention is that of Wigner (*Group Theory*, Academic Press, New York, 1959), also used by Condon and Shortley (*The Theory of Atomic Spectra*, Cambridge Univ. Press, New York, 1953), Rose (*Elementary Theory of Angular Momentum*, Wiley, New York, 1957), and Cohen (*Tables of the Clebsch-Gordan Coefficients*, North American Rockwell Science Center, Thousand Oaks, Calif., 1974). The coefficients here have been calculated using computer programs written independently by Cohen and at LBNL.

6. Spin-Orbit Coupling Constants (for H-atom-like (1 e^-) systems)

Argued at the beginning that the movement of the electron couples with its spin such that the energy of spin-orbit coupling is proportional to:

$$\vec{\mu}_S \cdot \vec{B}' \propto \vec{\mu}_S \cdot \vec{\mu}_L \propto \vec{L} \cdot \vec{S}$$

Thus, we can expect a have a Hamiltonian term $\mathbf{H}_{SO}$ which goes as:

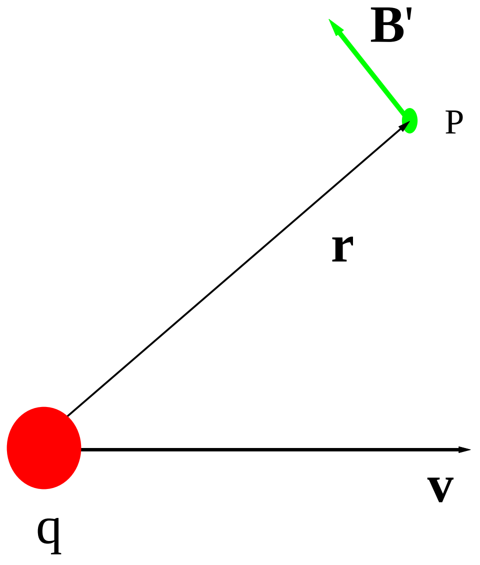
$$\hat{H}_{SO} = \xi(r)\hat{L} \cdot \hat{S}$$

Now, we want a measure of $\xi(r)$ = a spin-orbit coupling constant (units of energy).

i) Classically, a charge q moving a a velocity, **v**, gives rise to a magnetic field **B**' at a point P such that:

$$\vec{B}' = \frac{\mu_o q}{4\pi}\frac{\vec{v}\times\vec{r}}{r^3}$$

μ_o = magnetic permeability in vacuum = $4\pi \times 10^{-7}$ $NC^{-2}s^2$
q = charge in Coulomb, C
B' in Tesla, T (1 T = 1 $NC^{-1}m^{-1}s$)



From the electron's point of view, the nucleus is moving at a velocity $\mathbf{v_n} = -\mathbf{v_e} = -\mathbf{v}$

Therefore at the electron (charge of the nucleus = Ze)

$$\vec{B}' = \frac{\mu_o Ze}{4\pi r^3}\left(\vec{v}_n \times r\right) = \frac{\mu_o Ze}{4\pi r^3}\left(r \times \vec{v}\right)$$

On the other hand, the electric field at the electron is given by:

$$\vec{E} = \frac{\vec{r}}{r}\frac{d\phi(r)}{dr}$$ where Φ is the electric potential.

$$\phi(r) = \frac{Ze}{4\pi\varepsilon_o r} \Rightarrow V(r) = -e\phi(r) = -\frac{Ze^2}{4\pi\varepsilon_o r}$$

This is in SI units, and ε_o is the electrical permittivity in vacuum.

$$\therefore \vec{E} = \frac{Ze\vec{r}}{4\pi\varepsilon_o r}\frac{d}{dr}\left(\frac{1}{r}\right) = \frac{Ze\vec{r}}{4\pi\varepsilon_o r^3}$$

Now:

$$\vec{B}' = \left(\frac{\mu_o Ze\,\vec{r}}{4\pi r^3}\right)\times\vec{v} = \mu_o\varepsilon_o\left(\frac{Ze\,\vec{r}}{4\pi\varepsilon_o r^3}\right)\times\vec{v}$$

Comparing the two equation shows that

$$\vec{B}' = \mu_o\varepsilon_o\left(\vec{E}\times\vec{v}\right) = \frac{1}{c^2}\left(\vec{E}\times\vec{v}\right) \because c^2 = \left(\mu_o\varepsilon_o\right)^{-1}$$

Again

$$\vec{E} = -\frac{\vec{r}}{er}\frac{dV(r)}{dr}$$

6.1 Spin-orbit coupling

1. Qualitative Description

Orbital motion of the electron generates a field **B** which is felt by the electron spin; that is, **B** acts as an external field.

This should lead to a term: $$\hat{H}_{SO} = -\vec{\mu}_s \cdot \vec{B} \propto \vec{\mu}_s \cdot \vec{\mu}_L \propto \vec{S} \cdot \vec{L}$$