

## 10.2: Angular Momentum in Hydrogen Atom

In a hydrogen atom, the wavefunction of an electron in a simultaneous eigenstate of  $L^2$  and  $L_z$  has an angular dependence specified by the spherical harmonic  $Y_{l,m}(\theta, \phi)$ . (See Section [sharm].) If the electron is also in an eigenstate of  $S^2$  and  $S_z$  then the quantum numbers  $s$  and  $m_s$  take the values  $1/2$  and  $\pm 1/2$ , respectively, and the internal state of the electron is specified by the spinors  $\chi_{\pm}$ . (See Section [spauli].) Hence, the simultaneous eigenstates of  $L^2$ ,  $S^2$ ,  $L_z$ , and  $S_z$  can be written in the separable form

$$\psi_{l,1/2;m,\pm 1/2}^{(1)} = Y_{l,m} \chi_{\pm}. \quad (10.2.1)$$

Here, it is understood that orbital angular momentum operators act on the spherical harmonic functions,  $Y_{l,m}$ , whereas spin angular momentum operators act on the spinors,  $\chi_{\pm}$ .

Because the eigenstates  $\psi_{l,1/2;m,\pm 1/2}^{(1)}$  are (presumably) orthonormal, and form a complete set, we can express the eigenstates  $\psi_{l,1/2;j,m_j}^{(2)}$  as linear combinations of them. For instance,

$$\psi_{l,1/2;j,m+1/2}^{(2)} = \alpha \psi_{l,1/2;m,1/2}^{(1)} + \beta \psi_{l,1/2;m+1,-1/2}^{(1)} \quad (10.2.2)$$

where  $\alpha$  and  $\beta$  are, as yet, unknown coefficients. Note that the number of  $\psi^{(1)}$  states that can appear on the right-hand side of the previous expression is limited to two by the constraint that  $m_j = m + m_s$  [see Equation ([e11.23])], and the fact that  $m_s$  can only take the values  $\pm 1/2$ . Assuming that the  $\psi^{(2)}$  eigenstates are properly normalized, we have

$$\alpha^2 + \beta^2 = 1. \quad (10.2.3)$$

Now, it follows from Equation ([e11.26]) that

$$J^2 \psi_{l,1/2;j,m+1/2}^{(2)} = j(j+1) \hbar^2 \psi_{l,1/2;j,m+1/2}^{(2)} \quad (10.2.4)$$

where [see Equation ([e11.12])]

$$J^2 = L^2 + S^2 + 2 L_z S_z + L_+ S_- + L_- S_+. \quad (10.2.5)$$

Moreover, according to Equations ([e11.28]) and ([e11.29]), we can write

$$\psi_{l,1/2;j,m+1/2}^{(2)} = \alpha Y_{l,m} \chi_+ + \beta Y_{l,m+1} \chi_-. \quad (10.2.6)$$

Recall, from Equations ([e11.28]) and ([e11.29]), that

$$\begin{aligned} L_+ Y_{l,m} &= [l(l+1) - m(m+1)]^{1/2} \hbar Y_{l,m+1}, \\ L_- Y_{l,m} &= [l(l+1) - m(m-1)]^{1/2} \hbar Y_{l,m-1}. \end{aligned}$$

By analogy, when the spin raising and lowering operators,  $S_{\pm}$ , act on a general spinor,  $\chi_{s,m_s}$ , we obtain

$$\begin{aligned} S_+ \chi_{s,m_s} &= [s(s+1) - m_s(m_s+1)]^{1/2} \hbar \chi_{s,m_s+1}, \\ S_- \chi_{s,m_s} &= [s(s+1) - m_s(m_s-1)]^{1/2} \hbar \chi_{s,m_s-1}. \end{aligned}$$

For the special case of spin one-half spinors (i.e.,  $s = 1/2$ ,  $m_s = \pm 1/2$ ), the previous expressions reduce to

$$S_+ \chi_+ = S_- \chi_- = 0, \quad (10.2.7)$$

and

$$S_{\pm} \chi_{\mp} = \hbar \chi_{\pm}. \quad (10.2.8)$$

It follows from Equations ([e11.32]) and ([e11.34])–([e11.39]) that

$$\begin{aligned} J^2 Y_{l,m} \chi_+ &= [l(l+1) + 3/4 + m] \hbar^2 Y_{l,m} \chi_+ \\ &\quad + [l(l+1) - m(m+1)]^{1/2} \hbar^2 Y_{l,m+1} \chi_-, \end{aligned}$$

and

$$J^2 Y_{l,m+1} \chi_- = [l(l+1) + 3/4 - m - 1] \hbar^2 Y_{l,m+1} \chi_- \\ + [l(l+1) - m(m+1)]^{1/2} \hbar^2 Y_{l,m} \chi_+.$$

Hence, Equations ([e11.31]) and ([e11.33]) yield

$$(x - m) \alpha - [l(l+1) - m(m+1)]^{1/2} \beta = 0, \\ -[l(l+1) - m(m+1)]^{1/2} \alpha + (x + m + 1) \beta = 0,$$

where

$$x = j(j+1) - l(l+1) - 3/4. \quad (10.2.9)$$

Equations ([e11.42]) and ([e11.43]) can be solved to give

$$x(x+1) = l(l+1), \quad (10.2.10)$$

and

$$\frac{\alpha}{\beta} = \frac{[(l-m)(l+m+1)]^{1/2}}{x-m}. \quad (10.2.11)$$

It follows that  $x = l$  or  $x = -l - 1$ , which corresponds to  $j = l + 1/2$  or  $j = l - 1/2$ , respectively. Once  $x$  is specified, Equations ([e11.30]) and ([e11.45]) can be solved for  $\alpha$  and  $\beta$ . We obtain

$$\psi_{l+1/2, m+1/2}^{(2)} = \left( \frac{l+m+1}{2l+1} \right)^{1/2} \psi_{m, 1/2}^{(1)} + \left( \frac{l-m}{2l+1} \right)^{1/2} \psi_{m+1, -1/2}^{(1)}, \quad (10.2.12)$$

and

$$\psi_{l-1/2, m+1/2}^{(2)} = \left( \frac{l-m}{2l+1} \right)^{1/2} \psi_{m, 1/2}^{(1)} - \left( \frac{l+m+1}{2l+1} \right)^{1/2} \psi_{m+1, -1/2}^{(1)}. \quad (10.2.13)$$

Here, we have neglected the common subscripts  $l, 1/2$  for the sake of clarity: that is,  $\psi_{l+1/2, m+1/2}^{(2)} \equiv \psi_{l, 1/2; l+1/2, m+1/2}^{(2)}$ , et cetera. The previous equations can easily be inverted to give the  $\psi^{(1)}$  eigenstates in terms of the  $\psi^{(2)}$  eigenstates:

$$\psi_{m, 1/2}^{(1)} = \left( \frac{l+m+1}{2l+1} \right)^{1/2} \psi_{l+1/2, m+1/2}^{(2)} + \left( \frac{l-m}{2l+1} \right)^{1/2} \psi_{l-1/2, m+1/2}^{(2)}, \\ \psi_{m+1, -1/2}^{(1)} = \left( \frac{l-m}{2l+1} \right)^{1/2} \psi_{l+1/2, m+1/2}^{(2)} - \left( \frac{l+m+1}{2l+1} \right)^{1/2} \psi_{l-1/2, m+1/2}^{(2)}.$$

The information contained in Equations ([e11.47])–([e11.50]) is neatly summarized in Table [t2]. For instance, Equation ([e11.47]) is obtained by reading the first row of this table, whereas Equation ([e11.50]) is obtained by reading the second column. The coefficients in this type of table are generally known as *Clebsch-Gordon coefficients*.

Clebsch-Gordon coefficients for adding spin one-half to spin  $l$ .

	$m, 1/2$	$m+1, -1/2$	$m, m_s$
[0.5ex] $l+1/2, m+1/2$	$\sqrt{(l+m+1)/(2l+1)}$	$\sqrt{(l-m)/(2l+1)}$	
[0.5ex] $l-1/2, m+1/2$	$\sqrt{(l-m)/(2l+1)}$	$-\sqrt{(l+m+1)/(2l+1)}$	
[0.5ex] $j, m_j$			

As an example, let us consider the  $l = 1$  states of a hydrogen atom. The eigenstates of  $L^2$ ,  $S^2$ ,  $L_z$ , and  $S_z$ , are denoted  $\psi_{m, m_s}^{(1)}$ . Because  $m$  can take the values  $-1, 0, 1$ , whereas  $m_s$  can take the values  $\pm 1/2$ , there are clearly six such states: that is,  $\psi_{1, \pm 1/2}^{(1)}$ ,  $\psi_{0, \pm 1/2}^{(1)}$ , and  $\psi_{-1, \pm 1/2}^{(1)}$ . The eigenstates of  $L^2$ ,  $S^2$ ,  $J^2$ , and  $J_z$ , are denoted  $\psi_{j, m_j}^{(2)}$ . Because  $l = 1$  and  $s = 1/2$  can be combined together to form either  $j = 3/2$  or  $j = 1/2$  (see previously), there are also six such states: that is,  $\psi_{3/2, \pm 3/2}^{(2)}$ ,  $\psi_{3/2, \pm 1/2}^{(2)}$ , and  $\psi_{1/2, \pm 1/2}^{(2)}$ . According to Table [t2], the various different eigenstates are interrelated as follows:

$$\begin{aligned}\psi_{3/2,\pm 3/2}^{(2)} &= \psi_{\pm 1,\pm 1/2}^{(1)}, \\ \psi_{3/2,1/2}^{(2)} &= \sqrt{\frac{2}{3}} \psi_{0,1/2}^{(1)} + \sqrt{\frac{1}{3}} \psi_{1,-1/2}^{(1)}, \\ \psi_{1/2,1/2}^{(2)} &= \sqrt{\frac{1}{3}} \psi_{0,1/2}^{(1)} - \sqrt{\frac{2}{3}} \psi_{1,-1/2}^{(1)}, \\ \psi_{1/2,-1/2}^{(2)} &= \sqrt{\frac{2}{3}} \psi_{-1,1/2}^{(1)} - \sqrt{\frac{1}{3}} \psi_{0,-1/2}^{(1)}, \\ \psi_{3/2,-1/2}^{(2)} &= \sqrt{\frac{1}{3}} \psi_{-1,1/2}^{(1)} + \sqrt{\frac{2}{3}} \psi_{0,-1/2}^{(1)},\end{aligned}$$

and

$$\begin{aligned}\psi_{\pm 1,\pm 1/2}^{(1)} &= \psi_{3/2,\pm 3/2}^{(2)}, \\ \psi_{1,-1/2}^{(1)} &= \sqrt{\frac{1}{3}} \psi_{3/2,1/2}^{(2)} - \sqrt{\frac{2}{3}} \psi_{1/2,1/2}^{(2)}, \\ \psi_{0,1/2}^{(1)} &= \sqrt{\frac{2}{3}} \psi_{3/2,1/2}^{(2)} + \sqrt{\frac{1}{3}} \psi_{1/2,1/2}^{(2)}, \\ \psi_{0,-1/2}^{(1)} &= \sqrt{\frac{2}{3}} \psi_{3/2,-1/2}^{(2)} - \sqrt{\frac{1}{3}} \psi_{1/2,-1/2}^{(2)}, \\ \psi_{-1,1/2}^{(1)} &= \sqrt{\frac{1}{3}} \psi_{3/2,-1/2}^{(2)} + \sqrt{\frac{2}{3}} \psi_{1/2,-1/2}^{(2)}.\end{aligned}$$

Thus, if we know that an electron in a hydrogen atom is in an  $l = 1$  state characterized by  $m = 0$  and  $m_s = 1/2$  [i.e., the state represented by  $\psi_{0,1/2}^{(1)}$ ] then, according to Equation ([e11.57]), a measurement of the total angular momentum will yield  $j = 3/2$ ,  $m_j = 1/2$  with probability  $2/3$ , and  $j = 1/2$ ,  $m_j = 1/2$  with probability  $1/3$ . Suppose that we make such a measurement, and obtain the result  $j = 3/2$ ,  $m_j = 1/2$ . As a result of the measurement, the electron is thrown into the corresponding eigenstate,  $\psi_{3/2,1/2}^{(2)}$ . It thus follows from Equation ([e11.52]) that a subsequent measurement of  $L_z$  and  $S_z$  will yield  $m = 0$ ,  $m_s = 1/2$  with probability  $2/3$ , and  $m = 1$ ,  $m_s = -1/2$  with probability  $1/3$ .

Clebsch-Gordon coefficients for adding spin one-half to spin one. Only non-zero coefficients are shown.

	$-1, -1/2$	$-1, 1/2$	$0, -1/2$	$0, 1/2$	$1, -1/2$	$1, 1/2$	$m, m_s$
[0.5ex] $3/2, -3/2$	1						
[0.5ex] $3/2, -1/2$		$\sqrt{1/3}$	$\sqrt{2/3}$				
[0.5ex] $1/2, -1/2$		$\sqrt{2/3}$	$-\sqrt{1/3}$				
[0.5ex] $3/2, 1/2$				$\sqrt{2/3}$	$\sqrt{1/3}$		
[0.5ex] $1/2, 1/2$				$\sqrt{1/3}$	$-\sqrt{2/3}$		
[0.5ex] $3/2, 3/2$						1	
$j, m_j$							

The information contained in Equations ([ecgs])–([ecge]) is neatly summed up in Table [t3]. Note that each row and column of this table has unit norm, and also that the different rows and different columns are mutually orthogonal. Of course, this is because the

$\psi^{(1)}$  and  $\psi^{(2)}$  eigenstates are orthonormal.

### Contributors and Attributions

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