Chapter 16. Addition of Angular Momenta

§1 *Introduction.* In classical mechanics the total angular momentum of a swarm of interacting particles is conserved if no torque acts on it. This is one of the main reasons why the total angular momentum is an important quantity. In the case of a system with two particles the total angular momentum is

$$\vec{L} = \vec{L}(1) + \vec{L}(2) \tag{1}$$

By now you are used to the idea that the dynamic equations of classical mechanics are valid in quantum mechanics if observables are replaced with the appropriate operators. This is true in the case of angular momentum, and

$$\hat{\vec{L}} = \hat{\vec{L}}(1) + \hat{\vec{L}}(2) \tag{2}$$

is the quantum total angular momentum. Here $\hat{\vec{L}}(1)$ and $\hat{\vec{L}}(2)$ are the angular momentum operators of particle 1 and particle 2, respectively. We also write

$$\hat{L}_\alpha(i),\ i = 1, 2 \text{ and } \alpha = 1, 2, 3 \tag{3}$$

for the components α of the angular momentum of particle i, in a Cartesian coordinate system. For example, $\hat{L}_1(1)$ is the x-component of the angular momentum of particle 1.

In the case of orbital angular momentum, we have

$$\hat{\vec{L}}(1) \equiv \hat{\vec{r}}(1)\times\hat{\vec{p}}(1) \tag{4}$$

and

$$\hat{\vec{L}}(2) \equiv \hat{\vec{r}}(2)\times\hat{\vec{p}}(2) \tag{5}$$

We know that the commutators of $\hat{\vec{r}}(1)$ with $\hat{\vec{r}}(2)$, $\hat{\vec{p}}(1)$ with $\hat{\vec{p}}(2)$, $\hat{\vec{r}}(1)$ with $\hat{\vec{p}}(2)$ and $\hat{\vec{p}}(2)$ with $\hat{\vec{r}}(1)$ are all equal to zero. Therefore each component of $\hat{\vec{L}}(1)$ commutes with each component of $\hat{\vec{L}}(2)$. This means that

$$[\hat{L}_\alpha(1), \hat{L}_\beta(2)] = 0 \text{ for } \alpha, \beta = 1, 2, 3 \tag{6}$$

For the components of the angular momentum of the same particle, we have the usual commutation relations:

$$[\hat{L}_\alpha(1),\ \hat{L}_\beta(1)] = i\hbar \sum_k \varepsilon_{\alpha\beta k}\ \hat{L}_k(1) \tag{7}$$

$$[\hat{L}_\alpha(2),\ \hat{L}_\beta(2)] = i\hbar \sum_k \varepsilon_{\alpha\beta k}\ \hat{L}_k(2) \tag{8}$$

The relations (6-8) are summarized in the formula

$$[\hat{L}_\alpha(i),\ \hat{L}_\beta(j)] = \delta_{ij}\ i\hbar \sum_k \varepsilon_{\alpha\beta k}\ \hat{L}_k(i) \tag{9}$$

So far we have relied only on the definitions, Eqs. 4 and 5, and the known commutation properties of position with momentum. This line of argument is correct for orbital angular momentum. We will postulate that the same equations (Eqs. 6-8) are valid for the total spin of two particles and all we need to do to extend these relations to spin is to replace $\hat{L}_\alpha(1)$ with $\hat{S}_\alpha(1)$ and $\hat{L}_\alpha(2)$ with $\hat{S}_\alpha(2)$.

In some cases we are concerned with one particle which moves in the central field of force and has a spin. An example is the *electron* in the hydrogen atom. In this case the total angular momentum $\hat{\vec{J}}$ is

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}} \tag{10}$$

where $\hat{\vec{L}}$ is the orbital angular momentum, and $\hat{\vec{S}}$ is the spin of the particle. Obviously $\hat{\vec{L}}$ and $\hat{\vec{S}}$ commute. If we want the total angular momentum of the hydrogen *atom*, we add to $\hat{\vec{J}}$ the spin of the nucleus. As in many other examples we have encountered the dynamic equations of classical mechanics are preserved in quantum mechanics: all we have to do is convert the classical observables into the appropriate operators.

§2 *The space on which the total angular momentum acts.* So far, so good. Life becomes more interesting when we think about kinematics. Here the key question is: what basis set do we use to describe the total angular momentum of two particles?

First let us look at the case of two particles in one dimension. The wave function is $\psi(x,y)$ with x the position of particle 1 and y the position of particle 2. For now, consider x to be variable and of y as having a fixed numerical value. Let $\{\ \phi_\alpha(x)\ \}$ be an orthonormal basis set that is capable of describing the state of particle one. This means that I can expand $\psi(x,y)$ as

$$\psi(x,y) = \sum_{\alpha} c_{\alpha}(y)\, \phi_{\alpha}(x) \qquad ((11)$$

The notation $c_{\alpha}(y)$ reminds me of the obvious fact that this coefficient depend on y. In fact, because

$$\int dx\, \phi_{\alpha}(x)^* \phi_{\beta}(x) = \delta_{\alpha\beta}, \qquad (12)$$

we have and explicit formula for this dependence:

$$c_{\alpha}(y) = \int dx\, \phi_{\alpha}(x)^* \psi(x,y) \qquad (13)$$

Since $c_{\alpha}(y)$ is a function of y, I can also expand it by using a basis set appropriate for describing the states of the 2 (remember: y is the position of particle 2 and x is the position of particle 1). Let that orthornormal basis set be $\{ \chi_{\beta}(y) \}$. Then

$$c_{\alpha}(y) = \sum_{\beta} a_{\alpha\beta}\, \chi_{\beta}(y) \qquad (14)$$

The coefficient a has two subscripts since I am expanding $c_1(y)$, $c_2(y)$, ... Now insert Eq. 14 in Eq. 11:

$$\psi(x,y) = \sum_{\alpha} \sum_{\beta} a_{\alpha\beta}\, \phi_{\alpha}(x)\, \chi_{\beta}(y) \qquad (15)$$

It is very important to remember that x and ϕ_{α} refer to particle 1 and that y and χ_{β} refer to particle 2.

Now let us rewrite Eq. 15 using kets and bras:

$$\begin{aligned} \langle\, x, y \mid \psi \,\rangle &= \sum_{\alpha} \sum_{\beta} a_{\alpha\beta} \langle\, x \mid \phi_{\alpha} \,\rangle \langle\, y \mid \chi_{\beta} \,\rangle \\ &= \langle\, x, y \mid \sum_{\alpha} \sum_{\beta} a_{\alpha\beta} |\phi_{\alpha}\rangle\, |\chi_{\beta}\rangle \end{aligned} \qquad (16)$$

Here

$$\langle\, x, y \mid \equiv \langle x|\, \langle y| \qquad (17)$$

Eq. 16 is the coordinate representation of the ket

$$|\psi\rangle = \sum_{\alpha} \sum_{\beta} a_{\alpha\beta} |\phi_{\alpha}\rangle\, |\chi_{\beta}\rangle \qquad (18)$$

This notation has a shortcoming. We need to specify that in $|\phi_{\alpha}\rangle\, |\chi_{\beta}\rangle$, the first ket describes particle 1 and the second describes particle 2, so a better notation is

$$|\psi\rangle = \sum_{\alpha} \sum_{\beta} a_{\alpha\beta} |1;\phi_{\alpha}\rangle\, |2;\chi_{\beta}\rangle \qquad (19)$$

The indices 1 and 2 indicate that $|1;\phi_{\alpha}\rangle$ refers to particle 1 and $|2;\chi_{\beta}\rangle$, to particle 2.

This procedure is very general and it is widely used in quantum mechanics. Note that we did not have to specify the nature of particles 1 or 2 nor did we give any particulars regarding what the basis sets are.

Let us apply this ideas to the case in which we want to add the angular momenta of two particles. The joint basis set will be

$$\{ |1;j,m\rangle|2;j',m'\rangle \}, \qquad m = -j, -j+1, \ldots, j-1, j;\ \ m' = -j', -j'+1, \ldots, j'-1, j' \tag{20}$$

We will have

$$\hat{L}_z(1)|1;j,m\rangle|2;j',m'\rangle = (\hat{L}_z(1)|1;j,m\rangle)|2;j',m'\rangle = \hbar\, m\, |1;j,m\rangle|2;j',m'\rangle \tag{21}$$

$$\hat{L}_z(2)|1;j,m\rangle|2;j',m'\rangle = \hbar\, m'\, |1;j,m\rangle|2;j',m'\rangle \tag{22}$$

$$\hat{L}^2(1)|1;j,m\rangle|2;j',m'\rangle = \hbar^2\, j(j+1)\, |1;j,m\rangle|2;j',m'\rangle \tag{23}$$

and so on. Any angular momentum operator of the particle 1 acts on the kets $|1;j,m\rangle$ and any angular momentum operator of particle 2 acts on the ket $|2;j,m\rangle$.

It is easy to see how one defines the scalar product in the joint space

$$\begin{aligned}&(\langle 1;j,m|\langle 2;j',m'|)\,(|1;j'',m''\rangle|2;j''',m'''\rangle)\\ &\qquad = (\langle 1;j,m \mid 1;j'',m''\rangle)\,(\langle 2;j',m' \mid 2;j''',m'''\rangle)\\ &\qquad = (\delta_{jj''}\,\delta_{mm''})\,(\delta_{j'j'''}\,\delta_{m'm'''})\end{aligned}$$

The last line is obtained from the known properties of the set kets $|j,m\rangle$. The rule is the same as one for operators: the bra for particle 1 acts only on kets of particle one and the same goes for a bra for particle 2.

One can now calculate matrix elements. Let us look, for example, at a matrix element of $\hat{L}_z(1)$:

$$\begin{aligned}&\langle 1;j,m|\langle 2;j',m'|\ \hat{L}_z(1)\ |1;j'',m''\rangle|2;j''',m'''\rangle\\ &\qquad = \langle 1;j,m|\ \hat{L}_z(1)\ |1;j'',m''\rangle\ \langle 2;j',m' \mid 2;j''',m'''\rangle\end{aligned}$$

We know that (see Eq. 13.32)

$$\langle 1;j,m|\ \hat{L}_z(1)\ |1;j'',m''\rangle = \delta_{j\,j''}\delta_{m\,m''}\ \hbar\, m$$

and

$$\langle 2;j',m' \mid 2;j''',m'''\rangle = \delta_{j'\,j'''}\ \delta_{m'\,m'''}$$

Therefore we have

$$\langle 1;j,m|\langle 2;j',m'|\, \hat{L}_z(1)\, |1;j'',m''\rangle|2;j''',m'''\rangle = \delta_{j'j'''}\,\delta_{m'm'''}\,\delta_{jj''}\,\delta_{m\,m''}\,\hbar\, m$$

The matrix elements in this two-particle space reduce to products of matrix elements in the one-particle spaces, and we know how to calculate the latter.

We can do this for any operator acting on particle 1 or on particle 2, and even for operators such as $\hat{L}_z(1)\ \hat{L}_x(2)$ and $\hat{L}_x(1)\hat{L}^2(2)$. You can calculate the matrix of any two-particle combination of angular momenta.

If you want to add $\hat{\vec{L}}+\hat{\vec{S}}$ where $\hat{\vec{L}}$ is an orbital angular momentum, you make a basis set from products of orbital angular momentum states $|j,m\rangle$ and spin states $|s,m_s\rangle$. Orbital angular momentum operators act on $|j,m\rangle$ and spin operators on $|s,m_s\rangle$. You can thus calculate any matrix element you need and solve any eigenvalue problem you are interested in.

In my opinion, this is all you need to know about addition of angular momenta. Older books have a lot of material regarding various choices of basis for the two particle space, the connection between these different choices, the connection between states expressed in these different basis sets and the connection between the matrices of the same operator expressed in different basis sets, etc., etc. All of this is an application of representation theory and transformation theory for different basis sets. All this material is interesting and sometimes amusing, especially if you like manipulating quantities with many subscripts. It was important when we did not have computers but it is now obsolete. Moreover, angular momentum was very important at a time when many physicists and chemists applied quantum mechanics to calculate the properties of atoms. There is little interest in doing such calculations today. However, if you want to learn more about the addition of angular moments, you should consult the books given in the references to this chapter.

The addition of spins remains a major concern in the calculation of the electronic energy of molecules. For most problems one can neglect the terms in the Hamiltonian that depend on spin since they are small. Such a Hamiltonian commutes with the total electron-spin squared $\hat{S}^2$ and its projection $\hat{S}_z$ on the z-axis. This means that the wave function of the electrons must be an eigenstate of $\hat{S}^2$ and of $\hat{S}_z$. Enforcing the first requirement is difficult. You can learn how this is done from specialized books. One of them is *Spin Eigenfunctions, Construction and Use* by Ruben Pauncz (Plenum Press, New York, 1979), which was mercifully supplemented with an exercise book *The Construction of Spin Eigen-Functions: An Exercise Book*, also by Ruben Pauncz (Kluwer Academic/Plenum Publishers, New York, 2000).

§3 *References.* People of my generation learned about angular momentum from

- D. M. Brink and G. R. Satchler, *Angular Momentum*, Clarendon Press, Oxford, 1968
- A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, Princeton University Press, Princeton, 1960 (third printing 1974)
- M. E. Rose, *Elementary Theory of Angular Momentum*, John Wiley & Sons, New York, 1957 (also Courier Dover Publications 1995)

An excellent book for physical chemists is

- R. N. Zare, *Angular Momentum*, John Wiley & Sons, New York, 1988 (2nd edition 2014)

A very enjoyable book, which explains advanced material in a simple way is

- W. J. Thomson, *Angular Momentum*, John Wiley & Sons, New York, 1994