Angular Momentum and Central Potentials: Part II

We use index and vector notation to streamline our work on angular momentum and to define scalar and vector operators. Using the algebra of angular momentum operators, we show that multiplets are labeled by j, with 2j a nonnegative integer, and contain 2j + 1 states with different values of the z-component of angular momentum. We list the complete set of commuting observables for a Hamiltonian with a three-dimensional central potential. We discuss the free particle solutions, which are used to solve classes of radial problems and to derive Rayleigh's formula: a representation of a plane wave in terms of an infinite sum of spherical waves. We examine the three-dimensional isotropic harmonic oscillator, describing the spectrum in terms of multiplets of angular momentum. Finally, focusing on the hydrogen atom, we discuss the conservation of the classical Runge-Lenz vector and that of its quantum analogue.

19.1 Angular Momentum and Quantum Vector Identities

We had our first exposure to angular momentum in chapter 10. There we learned how to build orbital angular momentum operators using position and momentum operators. Here, we revisit this construction using vector notation and index manipulation. This enables us to streamline computations involving angular momentum as well as position and momentum operators. Moreover, it allows us to define operators that are scalars under rotations and operators that are vectors under rotations.

In order to use index notation, we must call the x-, y-, and z-components of vectors the first, second, and third components. We use indices $i, j, k, \ldots = 1, 2, 3$ that run over three values (context will distinguish between an index i and the imaginary complex number i). Therefore, for position, momentum, and angular momentum operators we have $(\hat{x}_1, \hat{x}_2, \hat{x}_3)$ instead of $(\hat{x}, \hat{y}, \hat{z})$, $(\hat{p}_1, \hat{p}_2, \hat{p}_3)$ instead of $(\hat{p}_x, \hat{p}_y, \hat{p}_z)$, and $(\hat{L}_1, \hat{L}$

$_2$, $\hat{L}_3$) instead of ($\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$). The triplets of position and momentum operators satisfy commutation relations that are fully summarized by

$$[\hat{x}_i, \hat{p}_j] = i\hbar\,\delta_{ij}, \quad [\hat{x}_i, \hat{x}_j] = 0, \quad [\hat{p}_i, \hat{p}_j] = 0. \tag{19.1.1}$$

The angular momentum operators, inspired by their classical analogues, were defined by

$$\hat{L}_1 \equiv \hat{x}_2\,\hat{p}_3 - \hat{x}_3\,\hat{p}_2, \quad \hat{L}_2 \equiv \hat{x}_3\,\hat{p}_1 - \hat{x}_1\,\hat{p}_3, \quad \hat{L}_3 \equiv \hat{x}_1\,\hat{p}_2 - \hat{x}_2\,\hat{p}_1. \tag{19.1.2}$$

The angular momentum operators are Hermitian since $\hat{x}_i$ and $\hat{p}_i$ are Hermitian, and the products can be reordered without cost:

$$\hat{L}_i^\dagger = \hat{L}_i. \tag{19.1.3}$$

We will write triplets of operators as boldface vectors so that

$$\hat{\mathbf{r}} \equiv (\hat{x}_1, \hat{x}_2, \hat{x}_3), \quad \hat{\mathbf{p}} \equiv (\hat{p}_1, \hat{p}_2, \hat{p}_3), \quad \hat{\mathbf{L}} \equiv (\hat{L}_1, \hat{L}_2, \hat{L}_3). \tag{19.1.4}$$

These are not familiar vectors, as their components are operators. We therefore call them **operator-valued vectors**. Operator-valued vectors are useful whenever we want to use the dot and cross products of three-dimensional space. The identities of vector analysis have analogues for operator-valued vectors. We will develop these identities now. Let us therefore consider operator-valued vectors $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$:

$$\hat{\mathbf{a}} = (\hat{a}_1, \hat{a}_2, \hat{a}_3), \quad \hat{\mathbf{b}} = (\hat{b}_1, \hat{b}_2, \hat{b}_3), \tag{19.1.5}$$

and we will assume that the components $\hat{a}_i$ and $\hat{b}_i$ are operators that, in general, fail to commute. The following are our definitions of dot and cross products for our operator-valued vectors:

$$\begin{aligned} \hat{\mathbf{a}} \cdot \hat{\mathbf{b}} &\equiv \hat{a}_i\,\hat{b}_i, \\ (\hat{\mathbf{a}} \times \hat{\mathbf{b}})_i &\equiv \epsilon_{ijk}\,\hat{a}_j\,\hat{b}_k. \end{aligned} \tag{19.1.6}$$

In the second equation, the left-hand side is the ith component of the cross product. Repeated indices are summed over the three possible values 1,2, and 3. The order of the operators on the above right-hand sides cannot be changed; it was chosen to be the same as the order of the operators on the left-hand sides. We also define

$$\hat{\mathbf{a}}^2 \equiv \hat{\mathbf{a}} \cdot \hat{\mathbf{a}}. \tag{19.1.7}$$

Since the operators do not commute, familiar properties of vector analysis do not hold. For example, $\hat{\mathbf{a}} \cdot \hat{b}$ is not equal to $\hat{b} \cdot \hat{\mathbf{a}}$. Indeed,

$$\hat{\mathbf{a}} \cdot \hat{\mathbf{b}} = \hat{a}_i \hat{b}_i = [\hat{a}_i, \hat{b}_i] + \hat{b}_i \hat{a}_i \tag{19.1.8}$$

so that

$$\boxed{\hat{\mathbf{a}} \cdot \hat{\mathbf{b}} = \hat{\mathbf{b}} \cdot \hat{\mathbf{a}} + [\hat{a}_i, \hat{b}_i].} \tag{19.1.9}$$

As an application we have

$$\hat{\mathbf{r}} \cdot \hat{\mathbf{p}} = \hat{\mathbf{p}} \cdot \hat{\mathbf{r}} + [\hat{x}_i, \hat{p}_i]. \tag{19.1.10}$$

The rightmost commutator gives $i\hbar\, \delta_{ii} = 3i\hbar$ so that we have the amusing three-dimensional identity

$$\boxed{\hat{\mathbf{r}} \cdot \hat{\mathbf{p}} = \hat{\mathbf{p}} \cdot \hat{\mathbf{r}} + 3\, i\hbar.} \tag{19.1.11}$$

For cross products we typically have $\hat{\mathbf{a}} \times \hat{\mathbf{b}} \neq -\hat{\mathbf{b}} \times \hat{\mathbf{a}}$. Indeed,

$$\begin{aligned} (\hat{\mathbf{a}} \times \hat{\mathbf{b}})_i &= \epsilon_{ijk}\, \hat{a}_j \hat{b}_k = \epsilon_{ijk} \left([\hat{a}_j, \hat{b}_k] + \hat{b}_k \hat{a}_j \right) \\ &= -\epsilon_{ikj}\, \hat{b}_k \hat{a}_j + \epsilon_{ijk} [\hat{a}_j, \hat{b}_k], \end{aligned} \tag{19.1.12}$$

where we flipped the k, j indices in one of the epsilon tensors in order to identify a cross product. Indeed, we now have

$$\boxed{(\hat{\mathbf{a}} \times \hat{\mathbf{b}})_i = -(\hat{\mathbf{b}} \times \hat{\mathbf{a}})_i + \epsilon_{ijk} [\hat{a}_j, \hat{b}_k].} \tag{19.1.13}$$

The simplest example of the use of this identity is one where we use $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$. Certainly,

$$\hat{\mathbf{r}} \times \hat{\mathbf{r}} = 0, \quad \text{and} \quad \hat{\mathbf{p}} \times \hat{\mathbf{p}} = 0, \tag{19.1.14}$$

but more nontrivially,

$$(\hat{\mathbf{r}} \times \hat{\mathbf{p}})_i = -(\hat{\mathbf{p}} \times \hat{\mathbf{r}})_i + \epsilon_{ijk} [\hat{x}_j, \hat{p}_k]. \tag{19.1.15}$$

The last term vanishes, for it is equal to $i\hbar\, \epsilon_{ijk}\delta_{jk} = 0$: the epsilon symbol is antisymmetric in j, k, while the delta is symmetric in j, k, resulting in a zero result. We therefore have, quantum mechanically,

$$\boxed{\hat{\mathbf{r}} \times \hat{\mathbf{p}} = -\hat{\mathbf{p}} \times \hat{\mathbf{r}}.} \tag{19.1.16}$$

Thus, $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ can be moved across in the cross product but not in the dot product.

Exercise 19.1. *Prove the following identities for Hermitian conjugation:*

$$\begin{aligned} (\hat{\mathbf{a}} \cdot \hat{\mathbf{b}})^\dagger &= \hat{\mathbf{b}}^\dagger \cdot \hat{\mathbf{a}}^\dagger, \\ (\hat{\mathbf{a}} \times \hat{\mathbf{b}})^\dagger &= -\,\hat{\mathbf{b}}^\dagger \times \hat{\mathbf{a}}^\dagger. \end{aligned} \tag{19.1.17}$$

The angular momentum operators are in fact given by the cross product of the operator-valued vectors $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$:

$$\boxed{\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -\hat{\mathbf{p}} \times \hat{\mathbf{r}}.} \tag{19.1.18}$$

Given the definition of the product, we have

$$\boxed{\hat{L}_i = \epsilon_{ijk}\, \hat{x}_j\, \hat{p}_k.} \tag{19.1.19}$$

If you evaluate the right-hand side for $i = 1, 2, 3$, you will recover the expressions in (19.1.2). The Hermiticity of the angular momentum operator is verified using (19.1.17), and recalling that $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ are Hermitian,

$$\hat{\mathbf{L}}^\dagger = (\hat{\mathbf{r}} \times \hat{\mathbf{p}})^\dagger = -\hat{\mathbf{p}}^\dagger \times \hat{\mathbf{r}}^\dagger = -\hat{\mathbf{p}} \times \hat{\mathbf{r}} = \hat{\mathbf{L}}. \tag{19.1.20}$$

The use of vector notation implies that, for example,

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \hat{L}_1\hat{L}_1 + \hat{L}_2\hat{L}_2 + \hat{L}_3\hat{L}_3 = \hat{L}_i\hat{L}_i. \tag{19.1.21}$$

The classical angular momentum $\vec{L}$ is orthogonal to both $\vec{r}$ and $\vec{p}$, as it is built from the cross product of these two vectors. Happily, these properties also hold for the quantum analogues. Take, for example, the dot product of $\hat{\mathbf{r}}$ with $\hat{\mathbf{L}}$:

$$\hat{\mathbf{r}} \cdot \hat{\mathbf{L}} = \hat{x}_i \hat{L}_i = \hat{x}_i \epsilon_{ijk} \hat{x}_j \hat{p}_k = \epsilon_{ijk} \hat{x}_i \hat{x}_j \hat{p}_k = 0. \tag{19.1.22}$$

The last expression is zero because the $\hat{x}$'s commute and thus form an object symmetric in i, j, while the epsilon symbol is antisymmetric in i, j. Similarly,

$$\hat{\mathbf{p}} \cdot \hat{\mathbf{L}} = \hat{p}_i \hat{L}_i = -\hat{p}_i (\hat{\mathbf{p}} \times \hat{\mathbf{r}})_i = -\hat{p}_i \epsilon_{ijk} \hat{p}_j \hat{x}_k = -\epsilon_{ijk} \hat{p}_i \hat{p}_j \hat{x}_k = 0. \tag{19.1.23}$$

In summary,

$$\boxed{\hat{\mathbf{r}} \cdot \hat{\mathbf{L}} = \hat{\mathbf{p}} \cdot \hat{\mathbf{L}} = 0.} \tag{19.1.24}$$

In manipulating multiple cross products, the following identities are quite useful:

$$\epsilon_{ijk} \epsilon_{ipq} = \delta_{jp} \delta_{kq} - \delta_{jq} \delta_{kp} \quad \Rightarrow \quad \epsilon_{ijk} \epsilon_{ijq} = 2\delta_{kq}. \tag{19.1.25}$$

The most familiar application involves triple products, which we consider now for the operator case. Taking care not to move operators across each other, we find that

$$\begin{aligned}
[\hat{\mathbf{a}} \times (\hat{\mathbf{b}} \times \hat{\mathbf{c}})]_k &= \epsilon_{kji} \hat{a}_j (\hat{\mathbf{b}} \times \hat{\mathbf{c}})_i \\
&= \epsilon_{kji} \epsilon_{ipq} \hat{a}_j \hat{b}_p \hat{c}_q \\
&= -\epsilon_{ijk} \epsilon_{ipq} \hat{a}_j \hat{b}_p \hat{c}_q \\
&= -\left(\delta_{jp} \delta_{kq} - \delta_{jq} \delta_{kp}\right) \hat{a}_j \hat{b}_p \hat{c}_q \\
&= \hat{a}_j \hat{b}_k \hat{c}_j - \hat{a}_j \hat{b}_j \hat{c}_k.
\end{aligned} \tag{19.1.26}$$

At this point, there is a dot product in the second term. In the first term, the components of $\hat{\mathbf{a}}$ and $\hat{\mathbf{c}}$ are contracted, but there is an operator $\hat{b}_k$ in between. To have a dot product, the components of $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ must be next to each other. Commuting $\hat{a}_j$ and $\hat{b}_k$, we get

$$
\begin{aligned}
[\hat{\mathbf{a}}\times(\hat{\mathbf{b}}\times\hat{\mathbf{c}})]_k &= [\,\hat{a}_j,\, \hat{b}_k\,]\,\hat{c}_j \,+\, \hat{b}_k\,\hat{a}_j\,\hat{c}_j \,-\, \hat{a}_j\,\hat{b}_j\,\hat{c}_k \\
&= [\,\hat{a}_j,\, \hat{b}_k\,]\,\hat{c}_j \,+\, \hat{b}_k\,(\hat{\mathbf{a}}\cdot\hat{\mathbf{c}}) \,-\, (\hat{\mathbf{a}}\cdot\hat{\mathbf{b}})\,\hat{c}_k.
\end{aligned} \tag{19.1.27}
$$

We can write this as

$$
\hat{\mathbf{a}}\times(\hat{\mathbf{b}}\times\hat{\mathbf{c}}) = \hat{\mathbf{b}}\,(\hat{\mathbf{a}}\cdot\hat{\mathbf{c}}) \,-\, (\hat{\mathbf{a}}\cdot\hat{\mathbf{b}})\,\hat{\mathbf{c}} \,+\, [\,\hat{a}_j,\, \hat{\mathbf{b}}\,]\,\hat{c}_j. \tag{19.1.28}
$$

The first two terms are all there is in the familiar classical identity; the last term is quantum mechanical. Another familiar relation from classical vector analysis is

$$
(\vec{a}\times\vec{b}\,)^2 \equiv (\vec{a}\times\vec{b}\,)\cdot(\vec{a}\times\vec{b}\,) = \vec{a}^{\,2}\,\vec{b}^{\,2} \,-\, (\vec{a}\cdot\vec{b}\,)^2. \tag{19.1.29}
$$

In deriving this equation, the vector components are assumed to be commuting numbers. If we have operator-valued vectors, additional terms arise.

Exercise 19.2. *Show that*

$$
\begin{aligned}
(\hat{\mathbf{a}}\times\hat{\mathbf{b}})^2 = \;& \hat{\mathbf{a}}^2\,\hat{\mathbf{b}}^2 - (\hat{\mathbf{a}}\cdot\hat{\mathbf{b}})^2 \\
& - \hat{a}_j\,[\hat{a}_j, \hat{b}_k]\,\hat{b}_k + \hat{a}_j\,[\hat{a}_k, \hat{b}_k]\,\hat{b}_j - \hat{a}_j\,[\hat{a}_k, \hat{b}_j]\,\hat{b}_k \,-\, \hat{a}_j\hat{a}_k\,[\hat{b}_k, \hat{b}_j],
\end{aligned} \tag{19.1.30}
$$

and verify that this yields

$$
(\hat{\mathbf{a}}\times\hat{\mathbf{b}})^2 = \hat{\mathbf{a}}^2\,\hat{\mathbf{b}}^2 - (\hat{\mathbf{a}}\cdot\hat{\mathbf{b}})^2 + \gamma\,\hat{\mathbf{a}}\cdot\hat{\mathbf{b}}, \quad \textit{if} \;\; [\hat{a}_i, \hat{b}_j] = \gamma\,\delta_{ij}, \;\; \gamma\in\mathbb{C}, \;\; [\hat{b}_i, \hat{b}_j] = 0. \tag{19.1.31}
$$

As an application we calculate $\hat{\mathbf{L}}^2 = (\hat{\mathbf{r}}\times\hat{\mathbf{p}})^2$. Equation (19.1.31) can be applied with $\hat{\mathbf{a}} = \hat{\mathbf{r}}$ and $\hat{\mathbf{b}} = \hat{\mathbf{p}}$. Since $[\hat{a}_i, \hat{b}_j] = [\hat{x}_i, \hat{p}_j] = i\hbar\,\delta_{ij}$, we identify $\gamma = i\hbar$ so that

$$
\boxed{\hat{\mathbf{L}}^2 = \hat{\mathbf{r}}^2\,\hat{\mathbf{p}}^2 - (\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})^2 + i\hbar\,\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}.} \tag{19.1.32}
$$

Another useful and simple identity is the following:

$$
\hat{\mathbf{a}}\cdot(\hat{\mathbf{b}}\times\hat{\mathbf{c}}) = (\hat{\mathbf{a}}\times\hat{\mathbf{b}})\cdot\hat{\mathbf{c}}, \tag{19.1.33}
$$

as you should confirm in a one-line computation. In commuting vector analysis, this triple product is known to be cyclically symmetric. Note that in the above, no operator has been moved across another—that's why it holds.

$\hat{x}$ $\hat{p}$