19.4 CentralPotentialsandRadialEquation

Angular momentum plays a crucial role in the study of Hamiltonians for a particle that moves in a three-dimensional *central potential*, a potential V that depends only on the distance r from the particle to the origin. The Hamiltonian $\hat{H}$ takes the form:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(r). \tag{19.4.1}$$

Although technically r is an operator, for convenience we leave the hat off of r while using a hat for the vector position $\hat{\mathbf{r}}$. The angular momentum operator $\hat{L}^2$ turns out to be the angular part of the Laplacian operator. This result was obtained in chapter 10 by a long calculation. We can do better now and directly find how $\hat{L}^2$ enters the Hamiltonian using the vector identities of section 19.1. We related $\hat{L}^2$ to $\hat{\mathbf{p}}^2$ in (19.1.32). From this equation we can solve for $\hat{\mathbf{p}}^2$ and write

$$\frac{\hat{\mathbf{p}}^2}{2m} = \frac{1}{2m}\frac{1}{r^2}\left[(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})^2 - i\hbar\,\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}\right] + \frac{1}{2mr^2}\hat{L}^2, \tag{19.4.2}$$

where we use $r^2 = \hat{\mathbf{r}}^2$, a useful notation in coordinate space. The first term on the above right-hand side is purely radial. While the gradient has components along all spherical unit vectors, the radial component is quite simple: $\hat{\mathbf{r}}\cdot\hat{\mathbf{p}} = \frac{\hbar}{i}r\frac{\partial}{\partial r}$. Therefore,

$$(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})^2 - i\hbar\,\hat{\mathbf{r}}\cdot\hat{\mathbf{p}} = -\hbar^2\left(r\frac{\partial}{\partial r}r\frac{\partial}{\partial r} + r\frac{\partial}{\partial r}\right) = -\hbar^2\left(r^2\frac{\partial^2}{\partial r^2} + 2r\frac{\partial}{\partial r}\right). \tag{19.4.3}$$

It then follows that

$$\frac{1}{r^2}\left[(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})^2 - i\hbar\,\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}\right] = -\hbar^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) = -\hbar^2\frac{1}{r}\frac{\partial^2}{\partial r^2}r, \tag{19.4.4}$$

where the last step is readily checked by explicit expansion. Back to the kinetic term (19.4.2), we can now rewrite the three-dimensional Hamiltonian as

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2mr^2}\hat{L}^2 + V(r). \tag{19.4.5}$$

This is a useful result because the eigenfunctions and eigenvalues of $\hat{L}^2$ are well understood.

Possibly the most important property of central potential problems is that the angular momentum operators commute with the Hamiltonian:

$$\boxed{\text{Central potential Hamiltonians:}\quad [\hat{L}_i, \hat{H}] = 0.} \tag{19.4.6}$$

We have seen that $\hat{L}_i$ commutes with $\hat{p}^2$, so it is only needed to show that any $\hat{L}_i$ commutes with $V(r)$. But we have also seen that $\hat{L}_i$ commutes with $\hat{r}^2 = \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}$, and therefore it commutes with any function of $\mathbf{r}^2$. Since $\mathbf{r}^2 = r^2$, it is clear that $r = \sqrt{\mathbf{r}^2}$ is a function of $\mathbf{r}^2$ and so is any $V(r)$. Thus, $\hat{L}_i$ commutes with $V(r)$ and, as a result, commutes with the central potential Hamiltonian. This is true for all i. This vanishing commutator implies that the $\hat{L}_i$ operators are conserved in central potentials:

$$i\hbar \frac{d}{dt} \langle \hat{L}_i \rangle = \langle [\hat{L}_i, \hat{H}] \rangle = 0. \tag{19.4.7}$$

Since $[\hat{L}_i, \hat{H}] = 0$, if $|\psi\rangle$ is an energy eigenstate with some energy E, $\hat{L}_i|\psi\rangle$ if nonzero is also an energy eigenstate with energy E. We learned in the previous section that states can be organized into angular momentum multiplets characterized by the value of ℓ. All states in a multiplet are connected by the action of the angular momentum operators $\hat{L}_\pm$. It follows that each angular momentum multiplet corresponds to a set of degenerate states! The whole energy spectrum can be organized as multiplets of angular momentum. To summarize:

Claim: The energy spectrum of a central potential Hamiltonian can be described as a collection of angular momentum multiplets. Each multiplet is a set of degenerate eigenstates.

The above statement is consistent with the insight provided by the set of commuting observables of a central potential Hamiltonian. Consider the following list of operators always available in a central potential problem:

$$\hat{H}, \ \hat{x}_1, \hat{x}_2, \hat{x}_3, \ \hat{p}_1, \hat{p}_2, \hat{p}_3, \ \hat{L}_1, \hat{L}_2, \hat{L}_3, \ \hat{\mathbf{r}}^2, \ \hat{\mathbf{p}}^2, \ \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}, \ \hat{\mathbf{L}}^2,$$
$$\hat{x}_i \hat{x}_j, \ \hat{p}_i \hat{p}_j, \ \hat{x}_i \hat{p}_j, \ \hat{x}_i \hat{L}_j, \ \hat{p}_i \hat{L}_j, \ \hat{L}_i \hat{L}_j, \ldots, \ (i, j = 1, 2, 3). \tag{19.4.8}$$

For the time being, we explicitly include all operators up to squares of coordinates, momenta, and angular momenta. There is a bit of redundancy here; some combinations of the $\hat{x}_i \hat{p}_j$ products appear in the angular momentum operators. Commuting observables are required to label states uniquely with their eigenvalues. Since we want to understand the spectrum of the Hamiltonian, one of the labels of states will be the energy, and $\hat{H}$ must be in the list of commuting observables. Because $\hat{H}$ contains the potential $V(r)$, none of the $\hat{p}_i$ operators commutes with the Hamiltonian.

Because it contains a $\hat{\mathbf{p}}^2$, none of the $\hat{x}_i$ commutes with the Hamiltonian. Nor will $\hat{\mathbf{r}}^2, \hat{\mathbf{p}}^2, \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}, \hat{x}_i, \hat{x}_j, \hat{p}_i \hat{p}_j$. Moreover, the only combinations of $\hat{x}_i \hat{p}_j$ that commute with $\hat{H}$ are the angular momentum operators. The list, reduced to $\hat{H}$ and the operators that commute with $\hat{H}$, reads

$$\hat{H}, \quad \hat{L}_1, \hat{L}_2, \hat{L}_3, \quad \hat{\mathbf{L}}^2, \hat{L}_i \hat{L}_j \ldots . \tag{19.4.9}$$

But all these operators do not commute with each other. From the $\hat{L}_i$ we can only pick at most one, for then the other two necessarily do not commute with the chosen one. Happily, we can also keep $\hat{\mathbf{L}}^2$ because of its Casimir property (19.2.14). Conventionally, everybody chooses $\hat{L}_3 = \hat{L}_z$ as the angular momentum component in the set of commuting observables. Thus, we have the following:

$$\boxed{\text{Central potential commuting observables: } \hat{H}, \hat{\mathbf{L}}^2, \hat{L}_z.} \tag{19.4.10}$$

Remarks:

1. The labels associated to $\hat{H}$, $\hat{\mathbf{L}}^2$, and $\hat{L}_z$ are E, ℓ, and m, respectively. The eigenvalues of $\hat{H}$, $\hat{\mathbf{L}}^2$, and $\hat{L}_z$ are E, $\hbar^2 \ell(\ell + 1)$, and $\hbar m$, respectively.

2. One can clearly add to the list (19.4.10) any product of operators in the list, like $\hat{L}_z \hat{L}_z$. But this would not help labeling states since on any simultaneous eigenstate of the original operators the eigenvalue of any such product operator is redundant information.

3. Although we did not give a complete proof, we claim that there is no extra operator built from the $\hat{x}_i$ and $\hat{p}_i$ that can be added to the list (19.4.10) with an eigenvalue that is not determined by the eigenvalues of the original operators on the list.

4. Since we claimed above that the central potential spectrum can be organized in terms of angular momentum multiplets, given an energy E for which there is a single multiplet of angular momentum ℓ, the $2\ell + 1$ states are indeed uniquely specified by the energy and the eigenvalues of $\hat{\mathbf{L}}^2$ and $\hat{L}_z$.

5. We can ask if the above set is complete. More explicitly, are the energy eigenstates of a central potential uniquely labeled by the eigenvalues of

the operators in the list? The way this could fail is apparent from the previous remark. If at some fixed energy E there are two or more multiplets with the *same* angular momentum ℓ, our labels do not suffice to identify the states uniquely because they cannot distinguish the multiplets. We will explicitly see that this *cannot happen* for the bound state spectrum of a central potential. If the particle has spin or other degrees of freedom, however, the complete set of commuting observables will include additional operators.

The radial equation   This equation was derived in section 10.6. The energy eigenstates $\psi_{E\ell m}$, appropriately labeled by quantities encoding the eigenvalues of the set of commuting observables, take the form

$$\psi_{E\ell m}(r,\theta,\phi) = \frac{u_{E\ell}(r)}{r} Y_{\ell m}(\theta,\phi). \tag{19.4.11}$$

You can look back at the derivation of the radial equation satisfied by $u_{E\,\ell}(r)$, or better, just redo it using the rewriting of the Hamiltonian in (19.4.5) and starting from $H\psi_{E\ell m} = E\psi_{E\ell m}$. The result is

$$-\frac{\hbar^2}{2m}\frac{d^2 u_{E\ell}}{dr^2} + V_{\text{eff}}(r)u_{E\ell} = Eu_{E\ell}, \tag{19.4.12}$$

where the effective potential V_{eff} is the potential $V(r)$ supplemented by a contribution from the angular momentum, a centrifugal barrier preventing the particle from reaching the origin:

$$V_{\text{eff}}(r) \equiv V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}. \tag{19.4.13}$$

The range of motion is $r \in [0, \infty)$. The state $\psi_{E\ell m}$ is normalized if

$$\int_0^\infty dr\,|u_{E\ell}(r)|^2 \; = \; 1, \tag{19.4.14}$$

a rather natural constraint for a function $u_{E\,\ell}(r)$ that obeys a one-dimensional Schrödinger equation.

When the centrifugal barrier dominates the potential as $r \to 0$, the behavior of the radial solution at the origin is known. In that case we showed that

$$u_{E\ell} \sim c\,r^{\ell+1}, \quad \text{as } r \to 0. \tag{19.4.15}$$

This allows for a constant nonzero wave function at the origin only for $\ell = 0$.

Definite statements about the $r \to \infty$ behavior of the wave function are possible when the potential $V(r)$ vanishes beyond some radius or, at least, decays fast enough as the radius grows without bound:

$$V(r) = 0, \text{ for } r > r_0, \quad \text{or} \quad \lim_{r\to\infty} rV(r) = 0. \tag{19.4.16}$$

The above assumptions are violated for the $1/r$ potential of the hydrogen atom, so our conclusions below require some modification in that case (see problem 19.4 for details). Under the above assumptions, as $r \to \infty$ we can ignore the effective potential completely, and the radial equation becomes

$$\frac{d^2 u_{E\ell}}{dr^2} = -\frac{2mE}{\hbar^2} u_{E\ell}. \tag{19.4.17}$$

The resulting $r \to \infty$ behavior follows immediately:

$$\begin{aligned} E < 0, \quad & u_{E\ell} \sim \exp\left(-\sqrt{\frac{2m|E|}{\hbar^2}}\,r\right), \\ E > 0, \quad & u_{E\ell} \sim \exp(\pm ikr), \quad k = \sqrt{\frac{2mE}{\hbar^2}}. \end{aligned} \tag{19.4.18}$$

The first behavior for $E < 0$ is typical of bound states. For $E > 0$ we have a continuous spectrum with degenerate solutions (hence the $\pm$). Having understood the behavior of solutions near $r = 0$ and for $r \to \infty$, this allows for qualitative plots of radial solutions.

The discrete spectrum of a central potential is organized as follows. We have energy eigenstates for all values of ℓ. For each value of ℓ, the potential V_{eff} in the radial equation is different. The radial equation must therefore be solved for $\ell = 0, 1, \dots$. For each *fixed* ℓ, we have a one-dimensional problem. Recalling that one-dimensional potentials have no degeneracies in the bound state spectrum, we conclude that we have no degeneracies in each fixed-ℓ bound state spectrum. We have a set of allowed values of energies that depend on ℓ and are numbered using an

integer $n = 1, 2\ldots$. For each allowed energy $E_{n\ell}$, we have a single radial solution $u_{n\ell}$.

Of course, each solution $u_{n\,\ell}$ of the radial equation represents $2\ell + 1$ degenerate solutions to the Schrödinger equation, corresponding to the possible values of the $\hat{L}_z/\hbar$ eigenvalue m in the range $(-\ell, \ell)$. Note that n has replaced the label E in the radial solution, and the energies have now been labeled. This is illustrated in figure 19.5, where each solution of the radial equation is shown as a short line atop an ℓ label on the horizontal axis. This is the spectral diagram for the central potential Hamiltonian. Each line of a given ℓ represents an angular momentum multiplet, the $(2\ell + 1)$ degenerate basis states obtained with $m = -\ell, \ldots, \ell$. As explained above, the radial equation can't have any degeneracies for any fixed ℓ: for a fixed ℓ, all solutions have different energies. Thus, all the lines on the diagram are single lines, representing single multiplets. Of course, other types of degeneracies of the spectrum can exist: multiplets with different values of ℓ may have the same energy. In other words, the states may match across columns on the figure. This happens, for example, in the hydrogen atom spectrum. Since the effective potential of a general central potential becomes more positive as ℓ is increased, the lowest-energy bound state occurs for $\ell = 0$. The energy $E_{1,\ell}$ of the lowest-ℓ multiplet increases as we increase ℓ. These facts are consequences of the variational argument discussed in problem 7.15.
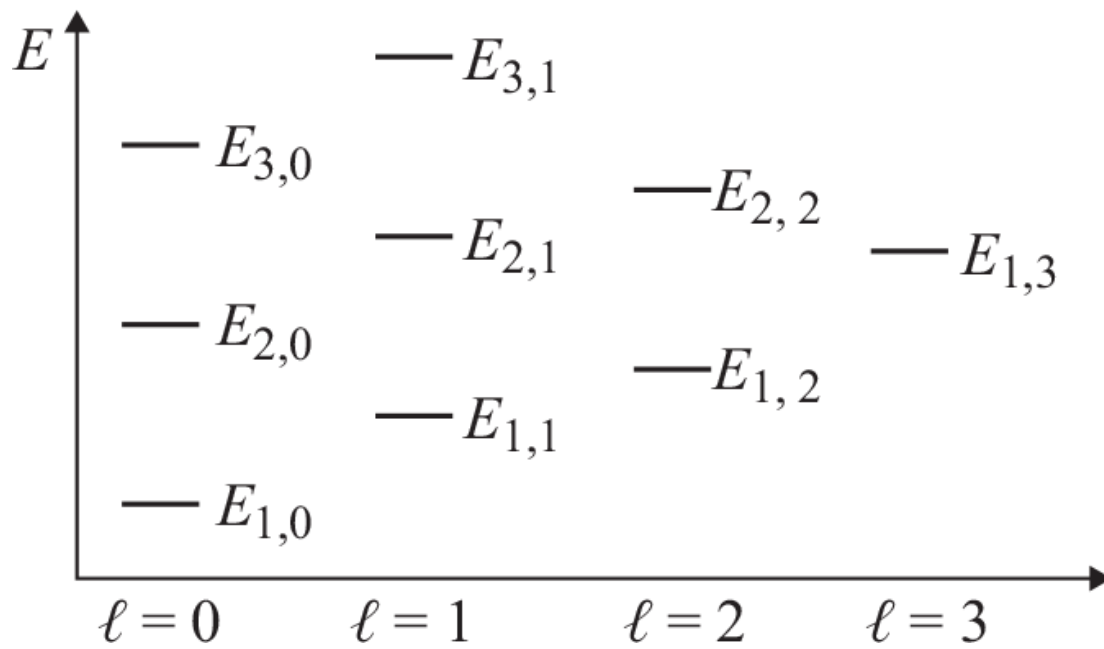
Figure19.5
The generic discrete spectrum of a central potential Hamiltonian, showing the angular momentum ℓ multiplets and their energies $E_{n\ell}$.