# Lecture 16 & 17

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## 1 Orbital angular momentum

Our discussion of angular momentum so far has focused on the perspective that angular momentum is a fundamental quantity not derived from other quantities. This is indeed the case for spin which is an intrinsic property of the quantum system that cannot be derived from other properties. However, the notion of angular momentum we know from classical physics is the orbital angular momentum. This is not fundamental and is derived from the position and momentum variables via

$$\boldsymbol{L} = \boldsymbol{x} \times \boldsymbol{p} \tag{1}$$

However, since orbital angular momentum is also an angular momentum, it should satisfy the commutation relations (**??**). We can verify that the definition (1) together with the position-momentum commutation relations indeed yield the correct commutation relations for orbital angular momentum. We can verify this explicitly for $L_x$ and $L_y$ by writing

$$[L_x, L_y] = [yp_z - zp_y, zp_x - xp_z] = [yp_z, zp_x] + [zp_y, xp_z] = i\hbar(-yp_x + xp_y) = i\hbar L_z \tag{2}$$

The relation for other components can be derived in a similar fashion. It is instructive to compare the discussion here to the discussion of the creation and annihilation operators in the harmonic oscillator. The way we introduce the operators was by building them out of $x$ and $p$ and showing that they satisfy the harmonic oscillator algebra. Alternatively, we could have introduced them as fundamental objects defined by the commutation relations $[a, a^\dagger] = 1$.

Drawing further parallels with the harmonic oscillator, recall that we have presented an algebraic construction of the harmonic oscillator spectrum that only used the commutation relations to construct the spectrum and the wavefunctions. This is similar to the construction of the eigenfunctions $|j, m\rangle$ for the angular momentum operators. However, we have also shown that we can solve the harmonic oscillator in the position basis using the representation of the creation/annihilation operators in terms of $x$ and $p$.

Using the position representation of the momentum operator $p_i = -i\hbar\frac{\partial}{\partial x_i}$, we see that $L_z$ acts on the wavefunction as

$$L_z\psi(x, y, z) = -i\hbar[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}]\psi(x, y, z) \tag{3}$$

This action is a lot simpler in spherical coordinates, where rotation by around the $z$ axis just shifts the azimuthal angle $\varphi$ leading to

$$L_z\psi(r, \theta, \varphi) = -i\hbar\frac{\partial}{\partial\varphi}\psi(r, \theta, \varphi) \tag{4}$$

Similarly, we can construct the action of $L_x$ and $L_y$ as

$$L_x\psi(x, y, z) = -i\hbar[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}]\psi(x, y, z), \quad L_x\psi(r, \theta, \varphi) = -i\hbar(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi})\psi(r, \theta, \varphi) \tag{5}$$

$$L_y\psi(x, y, z) = -i\hbar[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}]\psi(x, y, z), \quad L_y\psi(r, \theta, \varphi) = -i\hbar(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi})\psi(r, \theta, \varphi) \tag{6}$$

This leads to the slightly simpler expression for $L_\pm$ as

$$L_\pm \psi(x,y,z) = -i\hbar e^{\pm i\varphi}[\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}]\psi(x,y,z) \tag{7}$$

Finally, the expression for $\boldsymbol{L}^2$ is

$$\boldsymbol{L}^2\psi(x,y,z) = -\hbar^2[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}]\psi(x,y,z) \tag{8}$$

This coincides with the angular part of the Laplacian in spherical coordinates.

Our goal now is to construct the wavefunctions $\langle r,\theta,\varphi|l,m\rangle$. These are usually called spherical harmonics and denoted by $Y_l^m(\theta,\varphi)$. Note that the spherical harmonics do not depend on the radial coordinate since the orbital angular momentum operators $L_i$ do not depend on $r$. We can also use the notation $Y_l^m(\hat{n})$ where $\hat{n}$ is a unit vector. Spherical harmonics satisfy

$$L_z Y_l^m(\theta,\varphi) = m\hbar Y_l^m(\theta,\varphi), \qquad \boldsymbol{L}^2 Y_l^m(\theta,\varphi) = \hbar^2 l(l+1)Y_l^m(\theta,\varphi) \tag{9}$$

with $L_z$ and $\boldsymbol{L}^2$ given by (4) and (8). The first equation is easily solved by $e^{im\varphi}$ which means we can write $Y_m^l(\theta,\varphi) = e^{im\varphi}\tilde{Y}_m^l(\theta)$. To solve for $\tilde{Y}$, we note that $L_+Y_l^l = 0$ which implies

$$0 = [+i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}]Y_l^l(\theta,\varphi) = [\frac{\partial}{\partial\theta} - l\cot\theta]\tilde{Y}_l^l(\theta) \tag{10}$$

whose solution is $\tilde{Y}_m^l(\theta) = \sin^l\theta$ up to some normalization factor. To construct the other spherical harmonics, we simply apply the lowering operator to $Y_l^l$. The unnormalized spherical harmonics wavefunctions are thus given by

$$Y_m^l(\theta,\varphi) \propto J_-^{l-m}Y_l^l(\theta,\varphi) \propto e^{-i(l-m)\varphi}[-i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}]^{l-m}e^{il\varphi}\sin^l\theta = (-i)^{l-m}e^{im\varphi}[\frac{\partial}{\partial\theta} + l\cot\theta]^{l-m}\sin^l\theta \tag{11}$$

The normalization of the spherical functions is given by

$$\int d\varphi d\theta \sin\theta Y_m^l(\theta,\varphi)Y_{m'}^{l'}(\theta,\varphi) = \delta_{ll'}\delta_{mm'} \tag{12}$$

The spherical harmonics at $m = 0$ are given by Legendre polynomials

$$Y_0^l(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}}P_l(\cos\theta) \tag{13}$$

An important property of the spherical harmonics is that they correspond to angular momentum which is quantized to integers not half-integers. We can see this from the angular dependence of the wavefunction which has the form $e^{im\varphi}$ which is only single-valued for integer $m$.

We are now going to apply these results to the solution of the Schrödinger wave equation for spherically symmetric potentials.

## 2 Schrödinger equation for central potential

A spherically symmetric or central potential is a potential that only depends on the radial distance from the origin $r = \sqrt{x^2+y^2+z^2}$. The Hamiltonian for a central potential has the form

$$\mathcal{H} = -\frac{\hbar^2\nabla^2}{2m} + V(r) \tag{14}$$

Recall the form of the Laplacian in spherical coordinates:

$$\nabla^2\psi(r,\theta,\varphi) = \frac{1}{r}\frac{\partial^2}{\partial r^2}r\psi(r,\theta,\varphi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\psi(r,\theta,\varphi) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\psi(r,\theta,\varphi)$$
$$= [\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{r^2\hbar^2}\boldsymbol{L}^2]\psi(r,\theta,\varphi) \quad (15)$$

Substituting in the Hamiltonian, we get

$$\mathcal{H} = -\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}r + \frac{1}{2mr^2}\boldsymbol{L}^2 + V(r) = \mathcal{H}(r) + \frac{1}{2mr^2}\boldsymbol{L}^2 \quad (16)$$

Notice several things about this equation. First, it is clear that the Hamiltonian commutes with $\boldsymbol{L}^2$ and $L_z$ since both only depend on $\theta$ and $\varphi$ while ?$\mathcal{H}(r)$ only depends on $r$. Second notice the appearance of the term proportional to $\boldsymbol{L}^2$ which represents an effective repulsive "centrifugal" potential. This can be made more transparent by separating the radial and angular dependence of the eigenfunctions of the Hamiltonian. Since the Hamiltonian commutes with both $L_z$ and $\boldsymbol{L}^2$, we can simultaneoulsy diagonalize $H$, $L_z$ and $\boldsymbol{L}^2$. As a result, we can label the wavefunction with the eigenvalues of the three operators as follows

$$H|E,l,m\rangle = E|E,l,m\rangle, \qquad \boldsymbol{L}^2|E,l,m\rangle = \hbar^2 l(l+1)|E,l,m\rangle, \qquad L_z|E,l,m\rangle = \hbar m|E,l,m\rangle \quad (17)$$

Since we have already constructed the eigenfunctions of $L_z$ and $\boldsymbol{L}^2$ given by the spherical harmonics in Eq. 11, we can write the wavefunctions in spherical coordinates as

$$\psi_{E,l,m}(r,\theta,\varphi) = \langle r,\theta,\varphi|E,l,m\rangle = Y^l_m(\theta,\varphi)R_{E,l}(r) \quad (18)$$

with $R_{E,l}(r)$ satisfying the equation

$$\mathcal{H}R_{R,l}(r) = [-\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)]R_{E,l}(r) = ER_{E,l}(r) \quad (19)$$

We see the appearance of an extra repulsive potential that is non-vanishing for $l > 0$ and is singular at $r = 0$. This implies that for $l > 0$, the electrons face an infinite potential barrier to be at the origin. The normalization of the wavefunction is given by

$$1 = \int_0^\infty dr r^2 \int_0^\pi d\theta\sin\theta \int_0^{2\pi} d\varphi|\psi_{E,l,m}(r,\theta,\varphi)|^2 = \int_0^\infty dr r^2|R_{E,l}(r)|^2 \int_0^\pi d\theta\sin\theta \int_0^{2\pi} d\varphi|Y^l_m(\theta,\varphi)|^2 \quad (20)$$

Since the spherical harmonics are assumed to be normalized on the unit sphere ($r = 1$), this means that the normalization for $R_{E,l}(r)$ is

$$\int_0^\infty dr r^2|R_{E,l}(r)|^2 = 1 \quad (21)$$

This suggests defining the function $u_{E,l}(r) = rR_{E,l}(r)$ such that

$$\int_0^\infty dr|u_{E,l}(r)|^2 = 1 \quad (22)$$

which is a normalized wavefunction describing an electron living on the one-dimensional semi-infinite line $r > 0$. Substituting $R_{E,l}(r) = \frac{u_{E,l}(r)}{r}$ in the Schrödinger equation (19), we get

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_{E,l}(r) + [\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)]u_{E,l}(r) = Eu_{E,l}(r) \quad (23)$$

This describes a 1D particle living in the region $r > 0$ and experiencing the potential $V_l(r) = \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)$.

To understand the general structure of this equation, let us first consider the limit $r \to 0$. Let us also assume that the potential is not very singular at $r = 0$, i.e. $\lim_{r\to 0} r^2 V(r) = 0$. Since the wavefunction itself cannot be singular in the limit $r \to 0$ (otherwise it will not be normalizable) then in the limit $r \to 0$ and for $l > 0$, we have

$$\frac{d^2}{dr^2} u_{E,l}(r) = \frac{l(l+1)}{r^2} u_{E,l}(r) \tag{24}$$

The general solution to this equation is

$$u_{E,l}(r) = A r^{l+1} + B \frac{1}{r^l} \tag{25}$$

Normalizability of the wavefunctions implies $B = 0$. Thus $u_{E,l}(r) \sim r^{l+1}$ for $r \to 0$. This result makes sense since the centrifugal potential barrier at $r = 0$ for $l > 0$ implies the vanishing of the wavefunction at $r = 0$. As the strength of this barrier is increased, the power by which the function vanishes also increases.

For $l = 0$, we can consider a general expansion

$$u_{E,0}(r) = \sum_{n=0}^{\infty} a_n r^n \tag{26}$$

at small $r$. Let us assume that the constant term is non-vanishing. Then $u_{E,0}(r) \sim 1$ for small $r$ which implies $R_{E,0}(r) \sim \frac{1}{r}$ and $\psi_{E,0,0}(r, \theta, \varphi) \sim \frac{1}{r}$. However, since $\nabla^2 \frac{1}{r} = -4\pi\delta(\boldsymbol{r})$, we can only get this result for a fine-tuned delta potential. For any other potential, the expansion (26) generically starts at $u_{E,0} \sim r$.

## 2.1 Isotropic harmonic oscillator

Consider the isotropic harmonic oscillator where $V(r) = \frac{1}{2} m\omega^2 r^2$. Substituting in Eq. 23, we get

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u_{E,l}(r) + [\frac{\hbar^2 l(l+1)}{2mr^2} + \frac{1}{2} m\omega^2 r^2] u_{E,l}(r) = E u_{E,l}(r) \tag{27}$$

This equation can be simplified by introducing the dimensionless variables $\lambda$ and $\rho$ via

$$E = \frac{1}{2}\hbar\omega\lambda, \qquad r = \sqrt{\frac{\hbar}{m\omega}}\rho \tag{28}$$

Substituting in (27), we get

$$u''(\rho) - \frac{l(l+1)}{\rho^2} u(\rho) + (\lambda - \rho^2) u(\rho) = 0 \tag{29}$$

We have already seen from our earlier discussion that for $\rho \to 0$, $u(\rho) \sim \rho^{l+1}$. We would also like to extract the asymptotics at $\rho \mapsto \infty$ where the above equation reduces to

$$u''(\rho) - \rho^2 u(\rho) = 0 \tag{30}$$

whose solution is $u(\rho) \sim e^{-\frac{\rho^2}{2}}$. Similar to what we did when we solved the harmonic oscillator, it is usually convenient to extract the asymptotic dependence of the wavefunction. In this case, we can extract the asymptotics both at small and large $\rho$, leading to

$$u(\rho) = \rho^{l+1} e^{-\frac{\rho^2}{2}} f(\rho) \tag{31}$$

Substituting in (29), we get the differential equation for $f(\rho)$

$$\rho f''(\rho) + 2[(l+1) - \rho^2] f'(\rho) + [\lambda - (2l+3)]\rho f(\rho) = 0 \tag{32}$$

We can solve this equation by assuming the series expansion

$$f(\rho) = \sum_{n=0}^{\infty} a_n \rho^n \tag{33}$$

Substituting in (32), we get

$$\begin{aligned} 0 &= \sum_{n=0}^{\infty} a_n \left\{ n(n-1)\rho^{n-1} + 2(l+1)n\rho^{n-1} - 2n\rho^{n+1} + [\lambda - (2l+3)]\rho^{n+1} \right\} \\ &= \sum_{n=0}^{\infty} \rho^n \left\{ n(n+1)a_{n+1} + 2(l+1)(n+1)a_{n+1} - 2(n-1)a_{n-1} + [\lambda - (2l+3)]a_{n-1} \right\} \end{aligned} \tag{34}$$

For $n = 0$, the only surviving term is $2(l+1)a_1 = 0$ which implies $a_1 = 0$. Otherwise, we have the relation

$$a_{n+2} = \frac{2n + 2l + 3 - \lambda}{(n+2)(n+2l+3)} a_n \tag{35}$$

since $a_1 = 0$, this equation implies $a_{2r+1} = 0$ for any $r$, i.e. only even terms contribute to the series. Similar to our discussion for the harmonic oscillator, we can find the asymptotic value of $a_{n+2}/a_n$ for large $n$

$$\frac{a_{n+2}}{a_n} \to \frac{2}{n}, \qquad n \to \infty \tag{36}$$

Thus, $a_{2r}$ behaves asymptotically as $a_{2r} \sim \frac{1}{r!}$ giving $f(\rho) \sim \sum_r \frac{1}{r!}(\rho^2)^r \sim e^{\rho^2}$. This yields a non-normalizable function unless the series terminates which is realized if

$$\lambda = 2n + 2l + 3 = 4r + 2l + 3 \tag{37}$$

This gives the energy eigenvalues

$$E = \hbar\omega(2r + l + \frac{3}{2}) = \hbar\omega(N + \frac{3}{2}), \qquad N = 2r + l \tag{38}$$

where $r$ and $l$ are non-negative integers. The factor of $3/2$ is what we expect since we have three independent harmonic oscillator. The degeneracy of the energy level labelled by integer $N$ is given by

$$g_N = \sum_{l \leq N, l = N \mod 2} (2l+1) \tag{39}$$

For $N = 0$, the sum only contains $l = 0$ which gives $g_0 = 1$, for $N = 1$, the sum only contains $l = 1$ which gives $g_1 = 3$. The first few degeneracies are $\{1, 3, 6, 10, 15, 21, \ldots,\}$.

## 2.2 Hydrogen atom

One of the most famous and iconic example for the success of quantum mechanics was the explanation of the spectral lines of the hydrogen atom by Schrödinger in 1926. With our developed formalism, we can finally discuss the hydrogen atom which is given by the central potential $V(r) = -\frac{e^2}{r}$. We note that since the potential is produced by the proton, the proper quantum mechanical treatment of the problem involves writing a wavefunciton describing the coordinates of both the electron and the proton. However, since the proton mass is almost 2000 times larger than the electron mass, we can assume that the proton is not really affected by the potential of the electron and just provides a static potential [1]. A more principled way of doing

[1] this is similar to the case when we consider the effect of earth's gravity on a small everyday object. Although the object and the earth affect each other with the same force, the earth moves very little as a result of this force and it is a very good approximation to think of the earth as being fixed

this is to introduce the relative and center of mass coordinates. In the center of mass frame, the Schrodinger equation reduces to that of a particle with reduced mass $\mu = \frac{m_e m_p}{m_e+m_p}$. Since $m_e \ll m_p$, this reduces to $\mu \approx m_e$ and the relative coordinates basically becomes the electron coordinates. Thus, we can think of the electron moving in a central potential generated by the proton.

The analysis of the Coulomb potential is very similar to the isotropic 3D harmonic oscillator. The first step is to identify the asymptotic behavior of the wavefunction at large $r$. Unlike the harmonic oscillator potential which grows at infinity, the Coulomb potential decays at infinity. This means that we can have both bound and propagating states like the square well potential. We will now focus on the bound states with $E < 0$. At large $r$, the radial Schrödinger equation (23) becomes

$$u''(r) = \kappa^2 u(r), \qquad \kappa^2 = -\frac{2mE}{\hbar^2} > 0 \tag{40}$$

The only normalizable solution is $u(r) \propto e^{-\kappa r}$. Defining $\rho = \kappa r$, we can separate the asymptotic behavior at small and large $\rho$ by writing

$$u_{E,l}(\rho) = \rho^{l+1} e^{-\rho} f(\rho) \tag{41}$$

We further define

$$\rho_0 = \sqrt{\frac{2m}{-E}}\frac{e^2}{\hbar} \tag{42}$$

$f(\rho)$ satisfies the equation

$$\rho f''(\rho) + 2(l+1-\rho)f'(\rho) + [\rho_0 - 2(l+1)]f(\rho) = 0 \tag{43}$$

Substituting a series solution of the form (33), we get

$$\begin{aligned} 0 &= \sum_{r=0}^{\infty} a_n \left\{ n(n-1)\rho^{n-1} + 2(l+1)n\rho^{n-1} - 2n\rho^n + [\rho_0 - 2(l+1)]\rho^n \right\} \\ &= \sum_{n=0}^{\infty} \rho^n \left\{ n(n+1)a_{n+1} + 2(l+1)(n+1)a_{n+1} - 2na_n + [\rho_0 - 2(l+1)]a_n \right\} \end{aligned} \tag{44}$$

which gives

$$a_{r+1} = \frac{-\rho_0 + 2(r+l+1)}{(r+1)(r+2(l+1))} a_r \tag{45}$$

For large $r$, we have $\frac{a_{r+1}}{a_r} \to \frac{2}{r}$ which implies $a_r \sim \frac{2^r}{r!}$. This gives $f(\rho) \sim e^{2\rho}$ which is unnormalizable. Thus, we require the series to terminate which implies

$$\rho_0 = 2(r+l+1) = 2n \tag{46}$$

where we defined the principal quantum number $n = r + l + 1 = 1, 2, 3, \ldots$. The energy is

$$E = -\frac{me^4}{2\hbar^2 n^2} = -\frac{1}{2}mc^2\frac{\alpha^2}{n^2} \tag{47}$$

where $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant. The energy scale $\frac{1}{2}mc^2\alpha^2 \approx 13.6$ eV is called a Rydberg. For a nucleas with atomic number $Z$, it is straightforward to see that $E$ will be modified as

$$E_Z = E_{Z=1} Z^2 \tag{48}$$

We see that the energy eigenvalues only depend on the principle quantum number $n$. For $n = 1$, we have $r = l = 0$. For $n = 2$, we have $r = 0, l = 1$ or $r = 1, l = 0$. In general, the degeneracy of the $n$-the level is

$$g_n = \sum_{l=0}^{n-1}(2l+1) = n^2 \tag{49}$$

Notice that this degeneracy is larger than what we would have expected on symmetry ground only. Symmetry will tell us that for a given $l$, all $2l + 1$ states with different values of $m = -l, \ldots, l$ are degenerate but there is no reason for different values of $l$ to give rise to degenerate energy eigenvalues. It turns out that the Coulomb potential has an extra symmetry that explains this accidental degeneracy. We will discuss this symmetry later.

We note that in realistic systems, there are corrections beyond the $1/r$ correction, e.g. relativistic corrections that split this degeneracy. Furthermore, in crystals, even the degeneracy associated with different values of $m$ is lifted since the crystal breaks continuous rotation symmetry.

We also note that the Coulomb problem has a build-in length scale

$$\frac{1}{\kappa} = a_0 \frac{n}{Z} \tag{50}$$

where $a_0$ is called the Bohr radius

$$a_0 = \frac{\hbar^2}{me^2} \tag{51}$$

The bohr radius gives the characteristic size of the bound state. In the energy level labelled by the principle quantum number $n$, the size of the bound state is roughly given by $n^2 a_0$.