Physics 731 Lecture Notes 6

Summary: Angular Momentum and Rotations

These notes summarize the basics of angular momentum and rotations, including rotation operators, angular momentum operators and eigenstates, orbital angular momentum, and rotational invariance. References include **S1r**, **S2**, **S3**, Ch 3, Shankar 12-15, Gottfried 10-11, 25, 32-36, and Schiff 7, among many others.

Rotations. Consider the classical rotations of a system in three dimensions, in which $R_{\hat{n}}(\phi)$ represents the rotation by an angle ϕ about the axis $\hat{n}$. Here we consider active transformations rather than passive transformations. Upon a rotation, vector $\mathbf{v}$ transforms as

$$\mathbf{v} \to \mathbf{v}' = R_{\hat{n}}(\phi)\mathbf{v}. \tag{1}$$

The preservation of the length of $\mathbf{v}$ implies that $R_{\hat{n}}(\phi)$ is orthogonal:

$$\mathbf{v}^T \cdot \mathbf{v}' = \mathbf{v}^T R^T R \mathbf{v} = \mathbf{v}^T \mathbf{v}. \tag{2}$$

The properties of $R_{\hat{n}}(\phi)$ are as follows:

- $R^T R = R R^T = \mathbb{1}$ (orthogonality).
- $R_{\hat{n}}(0) = \mathbb{1}$ (identity).
- $R_{\hat{n}}(\phi_1) R_{\hat{n}}(\phi_2) = R_{\hat{n}}(\phi_1 + \phi_2) = R_{\hat{n}}(\phi_2) R_{\hat{n}}(\phi_1)$ (rotations about the same axis commute).
- $R_{\hat{n}_1}(\phi_1) R_{\hat{n}_2}(\phi_2) = R_{\hat{n}_3}(\phi_3)$ (closure).

In general, rotations about different axes do not commute:

$$[R_{\hat{n}_1}(\phi_1), R_{\hat{n}_2}(\phi_2)] \neq 0. \tag{3}$$

The set of rotations form a group. A group G is a set of objects $\{g_1, g_2, \ldots\}$ (the number of elements can be finite, countably infinite or continuous) and an operation (multiplication) such that

- $g_1 g_2 = g_3 \in G$ (closure)
- There exists a unique identity ($\mathbb{1}$) such that $\mathbb{1} g = g \mathbb{1} = g$ for all $g \in G$.
- For all $g \in G$, there exists a unique inverse g^{-1} such that $g g^{-1} = g^{-1} g = \mathbb{1}$.
- Multiplication is associative: $g_1(g_2 g_3) = (g_1 g_2) g_3$.

The rotation group in three dimensions is $SO(3)$ (special orthogonal 3×3 matrices; "special" means that $\det R = 1$). The rotation group is non-Abelian, as group elements do not generally commute. The axial rotation group is the set of rotations about a single fixed axis, which do commute; this is an Abelian group that is a subset of the full rotation group. Another example of a group, which will be of interest for describing rotations in quantum mechanics, is the $SU(2)$ group (special unitary 2×2 matrices).
Consider now the effects of rotations on a state ket $|\alpha\rangle$:

$$|\alpha\rangle \to |R\alpha\rangle = |\alpha\rangle_R = D(R_{\hat{n}}(\phi))|\alpha\rangle. \tag{4}$$

$D(R_{\hat{n}}(\phi))$ is a unitary operator defined as follows:

$$D(R_{\hat{n}}(\phi)) = e^{-i\mathbf{J}\cdot\hat{n}\phi/\hbar}, \tag{5}$$

in which $\mathbf{J}$, the generator of rotations, is defined to be the angular momentum operator. The J_i are Hermitan operators. Considering infinitesimal rotations and requiring that the rotation group law is satisfied, we arrive at the commutation relations satisfied by the angular momentum operators:

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k. \tag{6}$$

The operator $J^2 = J_x^2 + J_y^2 + J_z^2$ commutes with each of the components of the angular momentum operator: $[J^2, J_i] = 0$. Therefore, we can find simultaneous eigenstates of J^2 and one of the J_i (it is conventional to choose J_z). In doing so, it is useful to define the (non-Hermitian) ladder operators $J_\pm = J_x \pm iJ_y$. In terms of these operators, $J^2 = \frac{1}{2}(J_+J_- + J_-J_+) + J_z^2$.

Solving the eigenvalue problem leads to the familiar results:

$$J^2|jm\rangle = \hbar^2 j(j+1)|jm\rangle; \quad J_z|jm\rangle = m\hbar|jm\rangle; \quad J_\pm|jm\rangle = \hbar\sqrt{j(j+1) - m(m\pm 1)}|jm\pm 1\rangle, \tag{7}$$

where j is restricted to be either integers or half integers, and $-j \leq m \leq j$.
Let us now construct the $D(R)$ operators, starting with the case of $j = 1/2$ (spin $1/2$). In this case,

$$D(R_{\hat{n}}(\phi)) = e^{-i\mathbf{S}\cdot\hat{n}\phi/\hbar} = e^{-i\boldsymbol{\sigma}\cdot\hat{n}\phi/2}, \tag{8}$$

where σ_i are the Pauli matrices. This implies that for $j = 1/2$, a rotation by 2π gives an overall minus sign:

$$D(R_{\hat{n}}(2\pi))|\alpha\rangle = -|\alpha\rangle. \tag{9}$$

This turns out to be true for any half-integer j, whereas for integer j a rotation by 2π does not result in an overall minus sign. This indicates that the half-integer j representations are not true one-to-one representations of $SO(3)$. They in fact are one-to-one representations of $SU(2)$, which is locally isomorphic to $SO(3)$ but has different global properties.

To compute the D matrices for the $j = 1/2$ case, the following property of the Pauli matrices is useful:

$$(\boldsymbol{\sigma}\cdot\mathbf{a})(\boldsymbol{\sigma}\cdot\mathbf{b}) = \mathbf{a}\cdot\mathbf{b} + i\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b}). \tag{10}$$

Applying this formula to Eq. (8), we obtain

$$D^{(1/2)}(R_{\hat{n}}(\phi)) = e^{-i\boldsymbol{\sigma}\cdot\hat{n}\phi/2} = \begin{pmatrix} \cos\frac{\phi}{2} - in_z\sin\frac{\phi}{2} & (-in_x - n_y)\sin\frac{\phi}{2} \\ (-in_x + n_y)\sin\frac{\phi}{2} & \cos\frac{\phi}{2} + in_z\sin\frac{\phi}{2} \end{pmatrix}, \tag{11}$$

in which $\hat{n} = (n_x, n_y, n_z)$.

For general j, instead of parametrizing rotations by $\hat{n}$ and the rotation angle ϕ (three parameters), it is useful to introduce the three Euler angles α, β, γ, as follows:

$$R(\alpha,\beta,\gamma) = R_{\hat{z}}(\alpha)R_{\hat{y}}(\beta)R_{\hat{z}}(\gamma), \tag{12}$$

and hence

$$D(R(\alpha,\beta,\gamma)) = e^{-iJ_z\alpha/\hbar}e^{-iJ_y\beta/\hbar}e^{-iJ_z\gamma/\hbar}. \tag{13}$$

We wish to consider matrix elements of this operator with respect to the $|jm\rangle$ states: $\langle jm'|D(R)|jm\rangle$. These matrix elements vanish unless $j' = j$, since J^2 commutes with each of the J_i. Therefore, we can consider the following functions (known as Wigner functions):

$$D^{(j)}_{m'm}(\alpha,\beta,\gamma) \equiv \langle jm'|e^{-iJ_z\alpha/\hbar}e^{-iJ_y\beta/\hbar}e^{-iJ_z\gamma/\hbar}|jm\rangle. \tag{14}$$

With these functions, any rotation can be described:

$$|jm\rangle_R = D(R)|jm\rangle = \sum_{m'} |jm'\rangle\langle jm'|D(R)|jm\rangle = \sum_{m'} |jm'\rangle D^{(j)}_{m'm}(\alpha,\beta,\gamma). \tag{15}$$

The $D^{(j)}_{m'm}(\alpha,\beta,\gamma)$ functions can be simplified as follows:

$$D^{(j)}_{m'm}(\alpha,\beta,\gamma) = e^{-i(m'\alpha+m\gamma)}\langle jm'|e^{-iJ_y\beta/\hbar}|jm\rangle = e^{-i(m'\alpha+m\gamma)}d^{(j)}_{m'm}(\beta). \tag{16}$$

We can compute the $D^{(j)}_{m'm}$ functions, or equivalently the $d^{(j)}_{m'm}$ by brute force. For example, in the $j = 1/2$ case, we have

$$d^{(1/2)}(\alpha,\beta,\gamma) = \begin{pmatrix} \cos\frac{\beta}{2} & -\sin\frac{\beta}{2} \\ \sin\frac{\beta}{2} & \cos\frac{\beta}{2} \end{pmatrix}, \tag{17}$$

and thus

$$D^{(1/2)}(\alpha,\beta,\gamma) = \begin{pmatrix} e^{-i(\alpha+\gamma)/2}\cos\frac{\beta}{2} & -e^{-i(\alpha-\gamma)/2}\sin\frac{\beta}{2} \\ e^{i(\alpha-\gamma)/2}\sin\frac{\beta}{2} & e^{i(\alpha+\gamma)/2}\cos\frac{\beta}{2} \end{pmatrix}, \tag{18}$$

The brute force method is clearly impractical for large values of j. A closed form expression for arbitrary j is available (thanks to Wigner and Schwinger); there are a number of ways to derive it. We will return to this issue later when discussing the addition of angular momenta.

Orbital Angular Momentum. Let us now consider the case in which we project the $|jm\rangle$ states into position space. As we will see, this can only be done consistently for the case in which $j = \ell$, in which ℓ is an integer. The angular momentum operators $\mathbf{J}$ are then given by $\mathbf{L}$, where

$$\mathbf{L} = \mathbf{x} \times \mathbf{p} \tag{19}$$

is the orbital angular momentum. Recall that here $\mathbf{x}$ and $\mathbf{p}$ are operators (and operator ordering is important, as position and momentum operators satisfy the canonical commutation relations). Let us begin by considering a rotation about the z axis by an infinitesimal angle ϵ:

$$D_{\hat{z}}(\epsilon) = e^{-iL_z\epsilon/\hbar} = \mathbb{1} - i\epsilon L_z/\hbar + \ldots = 1 - \frac{i\epsilon}{\hbar}(xp_y - yp_x) + \ldots \tag{20}$$

From now on, we will now drop all terms of $O(\epsilon^2)$ and higher. Acting this operator on the position space eigenket $|\mathbf{x}\rangle = |x,y,z\rangle$, we have

$$D_{\hat{z}}(\epsilon)|\mathbf{x}\rangle = \left(1 - \frac{i\epsilon}{\hbar}(xp_y - yp_x)\right)|\mathbf{x}\rangle = |x - \epsilon y, y + \epsilon x, z\rangle \equiv |x',y',z'\rangle = |\mathbf{x}'\rangle, \tag{21}$$

in which we have noted that the terms proportional to p_x and p_y correspond to infinitesimal translations in the x and y directions, respectively. We see that $\mathbf{x}'$ is related to $\mathbf{x}$ by the appropriate rotation, as follows:

$$\mathbf{x}' = R_{\hat{z}}(\epsilon)\mathbf{x}, \tag{22}$$

such that up to terms of $O(\epsilon^2)$ and higher, we have

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & -\epsilon & 0 \\ \epsilon & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x - \epsilon y \\ y + \epsilon x \\ z \end{pmatrix}, \tag{23}$$

as expected. More generally, we have

$$D(R)|\mathbf{x}\rangle = |\mathbf{x}'\rangle = |R\mathbf{x}\rangle. \tag{24}$$

Acting on an arbitrary state $|\alpha\rangle$, this implies that for $\langle\mathbf{x}|\alpha\rangle = \psi_\alpha(\mathbf{x})$, the position space wavefunction of the rotated state $|\alpha\rangle_R = D(R)|\alpha\rangle$ is given by

$$\psi_{R_\alpha}(\mathbf{x}) = \langle\mathbf{x}|D(R)|\alpha\rangle = \langle D(R)^\dagger\mathbf{x}|\alpha\rangle = \langle D(R)^{-1}\mathbf{x}|\alpha\rangle = \langle R^{-1}\mathbf{x}|\alpha\rangle = \psi_\alpha(R^{-1}\mathbf{x}). \tag{25}$$

Let us now pass to spherical coordinates, $|\mathbf{x}\rangle = |r\theta\phi\rangle$, such that the rotation about the z axis by the infinitesimal angle ϵ of an arbitrary state $|\alpha\rangle$ then takes the form

$$\langle r\theta\phi|D(R_{\hat{z}}(\epsilon))|\alpha\rangle = \langle r\theta\phi - \epsilon|\alpha\rangle, \tag{26}$$

in which we have used Eq. (25). This expression can then be Taylor expanded to yield

$$\langle r\theta\phi|D(R_{\hat{z}}(\epsilon))|\alpha\rangle = \langle r\theta\phi|\alpha\rangle - \epsilon\frac{\partial}{\partial\phi}\langle r\theta\phi|\alpha\rangle, \tag{27}$$

again dropping terms of $O(\epsilon^2)$ or higher. Hence, L_z takes the form

$$\langle r\theta\phi|D(R_{\hat{z}}(\epsilon))|\alpha\rangle = \langle r\theta\phi|\mathbb{1} - \frac{i\epsilon}{\hbar}L_z|\alpha\rangle = \langle r\theta\phi|\alpha\rangle - \epsilon\frac{\partial}{\partial\phi}\langle r\theta\phi|\alpha\rangle, \tag{28}$$

such that we can identify

$$L_z = -i\hbar\frac{\partial}{\partial\phi}. \tag{29}$$

Similar considerations result in the identifications of L_x and L_y:

$$L_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right), \qquad L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right), \tag{30}$$

as well as $L_\pm = L_x \pm iL_y$:

$$L_\pm = -i\hbar\, e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right). \tag{31}$$

$L^2 = L_x^2 + L_y^2 + L_z^2 = L_z^2 + \{L_+, L_-\}$ thus takes the form

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \tag{32}$$

This is just the expression for the angular piece of the kinetic energy term:

$$\langle\mathbf{x}|\frac{p^2}{2m}|\alpha\rangle = -\frac{\hbar^2}{2m}\nabla^2\langle\mathbf{x}|\alpha\rangle = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2}\right]\langle\mathbf{x}|\alpha\rangle. \tag{33}$$

Let us now consider the situation in which the potential is independent of (θ, ϕ). In this case, the angular piece of the eigenstates of the system are the states $|\ell\, m\rangle$ projected into position space. Defining $|\hat{n}\rangle = |\theta\,\phi\rangle$, which corresponds to the position space eigenkets in spherical coordinates, restricted to the surface of a sphere, the spherical harmonics $Y_{\ell m}$ are defined by

$$\langle\hat{n}|\ell\, m\rangle = Y_{\ell m}(\hat{n}), \tag{34}$$

or equivalently

$$\langle \theta\phi|\ell\, m\rangle = Y_{\ell m}(\theta,\phi). \tag{35}$$

To determine the $Y_{\ell m}$ functions, the first step is to solve the eigenvalue equation for L_z explicitly:

$$\langle \theta\phi|L_z|\ell\, m\rangle = \hbar m\langle \theta\phi|\ell\, m\rangle, \tag{36}$$

or equivalently

$$-i\hbar\frac{\partial}{\partial\phi}Y_{\ell m}(\theta,\phi) = \hbar m Y_{\ell m}(\theta,\phi), \tag{37}$$

which shows that the ϕ-dependence of $Y_{\ell m}$ is $e^{im\phi}$. To obtain the θ-dependence, one method is to solve the corresponding eigenvalue equation for L^2 projected into position space:

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_{\ell m} = \hbar^2\ell(\ell+1)Y_{\ell m} \tag{38}$$

The solutions are the associated Legendre polynomials $P_{\ell m}(\cos\theta)$, which are given for $m>0$ by

$$P_{\ell m}(x) = (-1)^m(1-x^2)^{m/2}\frac{d^m}{dx^m}P_\ell(x) = \frac{(-1)^m}{2^\ell\ell!}(1-x^2)^{m/2}\frac{d^{\ell+m}}{dx^{\ell+m}}(x^2-1)^\ell. \tag{39}$$

Upon ensuring proper normalization, $Y_{\ell m}$ for $m>0$ takes the form:

$$Y_{\ell m} = \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}}P_{\ell m}(\cos\theta)e^{im\phi}. \tag{40}$$

The $m<0$ states can be obtained from the $m>0$ states using

$$Y_{\ell -m} = (-1)^m Y^*_{\ell m}. \tag{41}$$

Rather than solving this second-order differential equation, a simpler method is to use ladder operators. Using the fact that L_+ annihilates the state $|\ell\ell\rangle$ yields

$$\left(\frac{\partial}{\partial\theta}-\ell\cot\theta\right)Y_{\ell\ell} = 0. \tag{42}$$

This can be integrated to yield

$$Y_{\ell\ell}(\theta,\phi) = c_{\ell\ell}\sin^\ell\theta e^{i\ell\phi}. \tag{43}$$

The normalization coefficient takes the form (the phase choice is the standard convention):

$$c_{\ell\ell} = \frac{(-1)^\ell}{2^\ell\ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}}. \tag{44}$$

Acting on $|\ell\ell\rangle$ with L_- repeatedly yields the rest of the $Y_{\ell m}$, which take the form (again, for $m>0$):

$$Y_{\ell m}(\theta,\phi) = \frac{(-1)^\ell}{2^\ell\ell!}\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell+m)!}{(\ell-m)!}}e^{im\phi}(\sin\theta)^{-m}\left(\frac{d}{d\cos\theta}\right)^{\ell-m}\sin^{2\ell}\theta. \tag{45}$$

This form can be shown to be equivalent to Eq. (40) above, and as in that case, we use $Y_{\ell -m} = (-1)^m Y^*_{\ell m}$ to get the $m<0$ solutions. Note that we could instead have started with $L_-|\ell\ -\ell\rangle = 0$ and used L_+ to generate the rest. It is also worth noting that

$$Y_{\ell 0}(\theta,\phi) = \delta_{m0}P_\ell(\cos\theta)\sqrt{\frac{2\ell+1}{4\pi}}. \tag{46}$$

The $|\ell m\rangle$ states are orthonormal:

$$\langle \ell' m' | \ell m \rangle = \delta_{\ell\ell'}\delta_{mm'}, \tag{47}$$

such that

$$\int d\Omega \, \langle \ell' m' | \theta \, \phi \rangle \langle \theta \, \phi | \ell m \rangle = \int d\Omega \, Y^*_{\ell' m'} Y_{\ell m} = \delta_{\ell\ell'}\delta_{mm'}. \tag{48}$$

They also are complete:

$$\sum_{\ell m} |\ell m\rangle\langle \ell m| = \mathbb{1}, \tag{49}$$

or equivalently,

$$\sum_{\ell m} Y^*_{\ell m}(\theta', \phi') Y_{\ell m}(\theta, \phi) = \delta(\cos\theta - \cos\theta')\delta(\phi - \phi') = \frac{\delta(\theta - \theta')\delta(\phi - \phi')}{\sin\theta}. \tag{50}$$

The $Y_{\ell m}$'s are only defined for integer ℓ. Recall that the $|\ell m\rangle$ states, like any $|jm\rangle$ states, have the following properties under rotations:

$$|\ell m\rangle_R = \sum_{m'} |\ell m'\rangle D^{(\ell)}_{m'm}(R). \tag{51}$$

For half integer ℓ, attempts to define $Y_{\ell m}$ functions lead to results that do not have the correct properties with respect to rotations. Thus, to account for half-integer values of the angular momentum, we need spinors. Finally, the $Y_{\ell m}$'s can be related to the $D^{(\ell)}(R)$ functions as follows:

$$Y^*_{\ell m}(\theta, \phi) = \sqrt{\frac{2\ell + 1}{4\pi}} D^{(\ell)}_{m0}(\phi, \theta, \gamma = \text{arbitrary}). \tag{52}$$

Using this fact, one can also derive the famous relation

$$P_\ell(\cos\theta') = \frac{4\pi}{2\ell + 1} \sum_m Y_{\ell m}(\theta, \phi) Y^*_{\ell m}(\beta, \alpha), \tag{53}$$

where α, β relate (θ, ϕ) to (θ', ϕ').

Rotational Invariance. The Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}) \tag{54}$$

is rotationally invariant if $V(\mathbf{x}) = V(r)$. In this case,

$$[H, L_i] = 0, \tag{55}$$

and therefore the energy eigenstates are also eigenstates of orbital angular momentum:

$$H|E\ell m\rangle = E|E\ell m\rangle, \quad L^2|E\ell m\rangle = \hbar^2 \ell(\ell + 1)|E\ell m\rangle, \quad L_z|E\ell m\rangle = \hbar m|E\ell m\rangle. \tag{56}$$

A consequence of rotational invariance is that the energy E is independent of m. This can be seen by noticing that since $[H, L_i] = 0$, the ladder operators $L_\pm$ also commute with the Hamiltonian. Therefore,

$$L_\pm H|E\ell m\rangle = H(L_\pm|E\ell m\rangle) = E(L_\pm|E\ell m\rangle), \tag{57}$$

and hence the fact that $|E\ell m\rangle$ is an eigenstate of the Hamiltonian with the energy eigenvalue E means that the state $L_\pm|E\ell m\rangle \sim |E\ell m \pm 1\rangle$ is also an energy eigenstate of the Hamiltonian with the same energy

eigenvalue E (or it is zero). The energy eigenvalue can and in general will depend on ℓ. Therefore, we can write the wavefunction as $\psi(r,\theta,\phi) = R_{E\ell}(r)Y_{\ell m}(\theta,\phi)$. The Schrödinger equation then takes the form

$$\left\{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\ell(\ell+1)}{r^2}\right] + V(r)\right\} R_{E\ell}(r) = ER_{E\ell}(r). \tag{58}$$

Writing $u(r) = R(r)r$ (and dropping subscripts),

$$\left[\frac{d^2}{dr^2} + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right)\right] u(r) = 0, \tag{59}$$

which is similar to the 1-dimensional Schrödinger equation except that $0 \le r \le \infty$, and $V_{\text{eff}}(r) = V(r) + \ell(\ell+1)\hbar^2/(2mr^2)$; this additional contribution to the potential is the centrifugal barrier term. The boundary conditions on $u(r)$ are the following:

- As $r \to \infty$, $u(r)$ either tends toward 0 (bound states), or e^{ikr} (scattering states).
- As $r \to 0$, the condition that the wavefunction is normalizable says that $u(r)$ must be less singular than $1/\sqrt{r}$. A stronger condition results from the Hermiticity of H, which is that $u(r) \to c$ (c is a constant) as $r \to 0$. Finally, unless $V(r)$ contains a delta function, $c = 0$ (recall $\nabla^2(1/r) = -4\pi\delta(\mathbf{x})$).

Consider the radial equation in the $r \to 0$ limit, and consider the case in which the potential can be neglected in favor of the centrifugal term. In this case, $u(r) \sim r^{\ell+1}$, and hence $R(r) \sim r^\ell$. (This argument holds for nonvanishing ℓ; often this behavior also holds for $\ell = 0$.) In the $r \to \infty$ limit, the centrifugal term is irrelevant, and the solution depends on the form of the potential. There are three cases of interest:

- $rV(r) \to 0$ as $r \to \infty$. In this case, the Schrödinger equation for $u(r)$ looks like that of a free particle in 1 dimension. For $E > 0$, one has scattering states:

  $$u(r) = Ae^{ikr} + Be^{-ikr}, \tag{60}$$

  where $k = \sqrt{2mE/\hbar^2}$, while for $E < 0$,

  $$u(r) = Ae^{-\kappa r} + Be^{\kappa r}, \tag{61}$$

  with $\kappa = \sqrt{-2mE/\hbar^2}$. For discrete values of E, the growing exponential term can be consistently discarded, as is the usual case for bound state problems.

- $rV(r) \to$ constant as $r \to \infty$. This is the case of the Coulomb potential. In this case, the effects of the potential are never negligible. To see this, take a trial solution for the $E > 0$ states of the form $u(r) \sim f(r)e^{\pm ikr}$, in which $f(r)$ satisfies the condition

  $$f'' \pm 2ikf' - \frac{2mV(r)f}{\hbar^2} = 0. \tag{62}$$

  Anticipating that $f(r)$ should go like a power law, f'' will be negligible compared to the other terms. Dropping this term, Eq. (62) can be solved explicitly to yield

  $$f(r) = f(r_0)e^{\mp\frac{im}{\hbar^2 k}\int_{r_0}^{r} V(r)dr}. \tag{63}$$

  For the Coulomb potential, $V(r) = -e^2/r$,

  $$f(r) = f(r_0)\left(\frac{r}{r_0}\right)^{\pm ime^2/(\hbar^2 k)}. \tag{64}$$

  Therefore, $u(r) \sim r^{\pm ime^2/(\hbar^2 k)}e^{\pm ikr}$. Similarly, for $E < 0$, $u(r) \sim r^{\pm me^2/(\hbar^2\kappa)}e^{\mp\kappa r}$. The moral of this story is that one can never escape the effects of the Coulomb potential, even at $r \to \infty$.

- $rV(r) \to \infty$ as $r \to \infty$. This case depends on the details of the potential.

Free particle. For the free particle in spherical coordinates ($E > 0$), upon changing variables to $\rho = kr$, where $k = \sqrt{2mE/\hbar^2}$, the radial equation for $R(r)$ is just the spherical Bessel equation. The solutions are thus

$$R_{E\ell}(r) = Aj_\ell(kr) + Bn_\ell(kr), \tag{65}$$

where $j_\ell(kr)$ and $n_\ell(kr)$ are the spherical Bessel and spherical Neumann functions. These functions obey the following relations:

$$j_\ell(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\sin x}{x}, \qquad n_\ell(x) = -(-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \frac{\cos x}{x}. \tag{66}$$

As $x \to 0$,

$$j_\ell(x) = \frac{x^\ell}{(2\ell+1)!!}, \quad n_\ell(x) = -\frac{(2\ell-1)!!}{x^{\ell+1}}. \tag{67}$$

Thus, if the region of interest contains the origin, the $n_\ell(kr)$ term must be discarded. The free particle wavefunction is then given by $\psi_{E\ell m} = c_k j_\ell(kr) Y_{\ell m}(\theta, \phi)$, with the normalization constant obtained from the relation

$$\int_0^\infty dr\, r^2 j_\ell(kr) j_\ell(k'r) = \frac{\pi}{2k^2}\delta(k - k'). \tag{68}$$

Instead of dealing with $R_{E\ell}(r)$, it is of course also possible to consider the Schrödinger equation for $u_{E\ell}(r)$, as given in Eq. (59). This is especially useful for considering the case of $\ell = 0$, since in this case the centrifugal barrier term also vanishes. In any case, upon changing variables once again to $\rho = kr$, the Schrödinger equation can be rewritten in terms of the functions $u_\ell(\rho)$ as

$$\left(-\frac{d^2}{d\rho^2} + \frac{\ell(\ell+1)}{\rho^2}\right) u_\ell(\rho) = u_\ell(\rho), \tag{69}$$

which in turn can be factorized as

$$\left(\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right)\left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right) u_\ell(\rho) = u_\ell(\rho). \tag{70}$$

It can be shown that the operator $(-d/d\rho + (\ell+1)/\rho)$ effectively is a "raising" operator for u_ℓ, *i.e.*

$$\left(-\frac{d}{d\rho} + \frac{\ell+1}{\rho}\right) u_\ell(\rho) = c_\ell u_{\ell+1}(\rho). \tag{71}$$

Thus, the solutions for $\ell = 0$ can then be used as a starting point for obtaining all higher ℓ values. This is particularly useful because for the case of $\ell = 0$, it is clear from Eq. (59) that the solutions for u_0 are elementary sine and cosine functions, *i.e.*, $u_0(\rho) = A\cos\rho + B\sin\rho$, such that

$$u_{E0}(r) = A\cos(kr) + B\sin(kr). \tag{72}$$

Expressing the result for the $\ell \neq 0$ case in terms of the $R_\ell(\rho)$ functions, after some work we can obtain

$$R_\ell(\rho) = (-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell R_0(\rho), \tag{73}$$

in which $R_0(\rho) = u_0(\rho)/\rho$. Therefore, we see upon comparison with Eq. (66) that if we take $R_0 = \sin\rho/\rho$, this generates all of the j_ℓ functions, while for $R_0 = -\cos\rho/\rho$, the n_ℓ functions are obtained.

Comparing this to the known form of the wavefunction in rectangular coordinates, for example with $\mathbf{k} = k\hat{z}$, leads to the useful relation

$$e^{ikz} = \sum_{\ell} i^{\ell}(2\ell+1) j_{\ell}(kr) P_{\ell}(\cos\theta). \tag{74}$$

Hydrogen Atom. The time-independent Schrödinger equation for the hydrogen atom is

$$\left[-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{e^2}{|\mathbf{x}_e - \mathbf{x}_p|}\right]\psi_E(\mathbf{x}_e, \mathbf{x}_p) = E\psi_E(\mathbf{x}_e, \mathbf{x}_p). \tag{75}$$

Separating the center of mass motion, $\mathbf{x}_{\rm cm} = (m\mathbf{x}_e + M\mathbf{x}_p)/(m+M)$, and the relative motion, $\mathbf{x} = \mathbf{x}_e - \mathbf{x}_p$, results in

$$H = \frac{p_{\rm cm}^2}{2M} + \frac{p^2}{2\mu} + V(r), \tag{76}$$

in which $V(r) = -e^2/r$, $M = m_e + m_p$, and $\mu = m_e m_p/M \approx m_e$ since $m_e \ll m_p$. Therefore,

$$\psi_E(\mathbf{x}_e, \mathbf{x}_p) = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{p}_{\rm cm}\cdot\mathbf{x}_{\rm cm}} \psi_E(\mathbf{x}). \tag{77}$$

From now on, we will consider the bound state ($E < 0$) problem for the relative motion. Using rotational invariance, we know that $\psi_E(\mathbf{x}) = R_{E\ell}(r) Y_{\ell m}(\theta, \phi)$. To solve for the radial eigenfunctions, we can either solve the radial equation for the functions $R(r)$, or the functions $u(r) = rR(r)$ (we will drop the $E \ll$ subscript for notational simplicity).

Here we will focus on the $u(r)$ functions. From the general discussion, we know from Eq. (59) the radial equation for $u(r)$ takes the form

$$\left[\frac{d^2}{dr^2} - \kappa^2 + \frac{2\mu}{\hbar^2}\frac{e^2}{r} - \frac{\ell(\ell+1)}{r^2}\right] u(r) = 0, \tag{78}$$

in which $\kappa^2 = -2\mu E/\hbar^2$, and $u(r) \to 0$ as $r \to 0$ and $r \to \infty$. Changing variables to $\rho = \kappa r$, Eq. (78) takes the form

$$\frac{d^2u}{d\rho^2} + \left(-1 + \frac{e^2\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) u = 0, \tag{79}$$

in which

$$\lambda = \frac{2\mu}{\hbar^2\kappa} = \sqrt{-\frac{2\mu}{\hbar^2 E}}. \tag{80}$$

From the general discussion, we also anticipate that $u_{E\ell}(\rho) = e^{-\rho} v_{E\ell}(\rho)$, in which $v_{E\ell}$ is of power law form. Substituting this form yields the equation

$$\frac{d^2v}{d\rho^2} - 2\frac{dv}{d\rho} + \left(\frac{e^2\lambda}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right) v = 0. \tag{81}$$

Inserting a power series of the form $v_{E\ell}(\rho) = \rho^{\ell+1}\sum_{k=0}^{\infty} c_k \rho^k$ (again recalling the general discussion), one obtains the recursion relation

$$\frac{c_{k+1}}{c_k} = \frac{-e^2\lambda + 2(\ell+k+1)}{(k+\ell+2)(k+\ell+1) - \ell(\ell+1)}. \tag{82}$$

To avoid reintroducing divergent solutions in the large r limit, this series must terminate, such that $e^2\lambda = 2(\ell + k + 1)$. Recalling Eq. (80), this yields the following expression for the bound state energies:

$$E = -\frac{\mu e^4}{2\hbar^2(\ell + k + 1)^2} \equiv -\frac{\mu e^4}{2\hbar^2 n^2}, \tag{83}$$

in which $n = \ell + k + 1 = 1, 2, 3, \ldots$ is known as the *principal quantum number*. For a given value of n, ℓ then runs from $\ell = 0, \ldots n - 1$. The degeneracy of the levels is

$$d = \sum_{\ell=0}^{n-1}(2\ell + 1) = n^2. \tag{84}$$

To get the states, we can further substitute $v_{E\ell} = \rho^{\ell+1}\tilde{v}$, which yields

$$\rho\tilde{v}'' + (2(\ell + 1) - 2\rho)\tilde{v}' + 2k\tilde{v} = 0, \tag{85}$$

in which the primes denote differentiation by ρ. With a further substitution of $\tilde{\rho} = 2\rho$, we obtain

$$\tilde{\rho}\tilde{v}'' + (2(\ell + 1) - \tilde{\rho})\tilde{v}' + k\tilde{v} = 0, \tag{86}$$

in which the primes now denote differentiation by $\tilde{\rho}$. This takes the form of the Laguerre equation,

$$\tilde{\rho}\tilde{v}'' + (\alpha + 1 - \tilde{\rho})\tilde{v}' + \tilde{n}\tilde{v} = 0, \tag{87}$$

with solutions of $\tilde{v}(\tilde{\rho} = L_{\tilde{n}}^{\alpha}(x) = L_{n-\ell-1}^{2\ell+1}(2\rho)$. Note that Eq. (87) is not the only form of the Laguerre equation that one sees in texts; an alternate form is

$$\tilde{\rho}L_q^{p\prime\prime} + (p + 1 - \rho)L_q^{p\prime} + (q - p)L_q^P = 0, \tag{88}$$

which then leads to the labeling of solutions in our case as $L_{n+\ell}^{2\ell+1}(2\rho)$. This is the notation we will use here.

If instead we work with the radial wavefunctions $R(r)$, the starting point is the following differential equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2} - \frac{e^2}{r}\right]R(r) = ER(r). \tag{89}$$

Changing variables from r to $\tilde{\rho} = \alpha r$, and choosing the quantities α and $\tilde{\lambda}$ such that

$$\alpha = \sqrt{-\frac{8\mu E}{\hbar^2}}, \qquad \tilde{\lambda} = \frac{e^2 2\mu}{\hbar^2\alpha} = \frac{e^2}{\hbar}\sqrt{-\frac{\mu}{2E}}, \tag{90}$$

the radial equation can be rewritten as

$$\frac{1}{\tilde{\rho}^2}\frac{d}{d\tilde{\rho}}\left(\tilde{\rho}^2\frac{dR}{d\tilde{\rho}}\right) + \left(\frac{\tilde{\lambda}}{\tilde{\rho}} - \frac{1}{4} - \frac{\ell(\ell+1)}{\tilde{\rho}^2}\right)R = 0. \tag{91}$$

From here, we can follow a similar procedure as we did for the $u(r)$ case, taking $R(r)$ to be of the form

$$R(r) \sim \tilde{\rho}^{\ell}e^{-\tilde{\rho}/2}L(\tilde{\rho}), \qquad L(\tilde{\rho}) = \sum_{k=0}^{\infty} a_k\tilde{\rho}^k. \tag{92}$$

Using the power series method, and requiring acceptable asymptotic behavior via the truncation of the series, it is straightforward to obtain

$$E_n = -\frac{\mu e^4}{2\hbar^2 n^2}, \qquad n = 1, 2, 3, \ldots \tag{93}$$

where $n = k + \ell + 1$ is the principal quantum number (as before).

Taking $\mu = m_e$ (a very good approximation, since $m_p \sim 1000 m_e \gg m_e$), the bound state energies can be rewritten as follows:

$$E_n = -\frac{\mathrm{R_y}}{n^2} = -\frac{e^2}{2a_0}\frac{1}{n^2}, \qquad n = 1, 2, 3, \ldots, \tag{94}$$

where $\mathrm{R_y}$ is the Rydberg constant,

$$\mathrm{R_y} = \frac{m_e e^4}{2\hbar^2} = 13.6 \text{ eV}, \tag{95}$$

and a_0 is the Bohr radius:

$$a_0 = \frac{\hbar^2}{m e^2} \sim 0.053 \,\mathrm{nm}. \tag{96}$$

Here we note that the "hydrogen-like" potential $V(r) = -Ze^2/r$ can be accounted for by taking $e^2 \to Ze^2$, and thus $a_0 \to a_0/Z$. The energies are then given by

$$E_n = -\frac{Z^2 \mathrm{R_y}}{n^2} = -\frac{Z^2 e^2}{2a_0}\frac{1}{n^2}, \qquad n = 1, 2, 3, \ldots \tag{97}$$

as obtained before in Eq. (83). The resulting $L(\tilde{\rho})$ functions are the associated Laguerre polynomials $L_{n+\ell}^{2\ell+1}(\tilde{\rho})$, as expected. Explicitly, the normalized radial wavefunctions take the form

$$R_{nl}(r) = \left(\frac{2Zr}{na_0}\right)^{\ell} e^{-Zr/(na_0)} L_{n+\ell}^{2\ell+1}(2Zr/(na_0)) \left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n((n+\ell)!)^3}\right]^{1/2}, \tag{98}$$

in which here $\rho = \alpha r = 2Zr/(na_0)$.

The first few hydrogen atom bound state wavefunctions $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$ are given as follows:

- $n = 1$, $\ell = m = 0$

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} 2\, e^{-Zr/a_0}, \qquad \psi_{100} = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0}. \tag{99}$$

- $n = 2$, $\ell = m = 0$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/(2a_0)}, \qquad \psi_{200} = \left(\frac{Z^3}{32\pi a_0^3}\right)^{1/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/(2a_0)} \tag{100}$$

- $n = 2$, $\ell = 1, m = 0$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{\sqrt{3}a_0} e^{-Zr/(2a_0)}, \qquad \psi_{210} = \left(\frac{Z^3}{32\pi a_0^3}\right)^{1/2} \frac{Zr}{a_0} \cos\theta e^{-Zr/(2a_0)}. \tag{101}$$

- $n = 2$, $\ell = 1, m = \pm 1$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{\sqrt{3}a_0} e^{-Zr/(2a_0)}, \qquad \psi_{21\pm 1} = \mp \left(\frac{Z^3}{64\pi a_0^3}\right)^{1/2} \frac{Zr}{a_0} \sin\theta e^{\pm i\phi} e^{-Zr/(2a_0)}. \tag{102}$$

For $r \to \infty$, $R_{n\ell}(r) \to e^{-Zr/(na_0)} r^\ell$, which agrees with the general discussion. Note also that

$$\langle r \rangle_{nlm} = \frac{a_0}{2Z}(3n^2 - \ell(\ell+1)), \tag{103}$$

which is $O(n^2 a_0/Z)$; thus, the typical size grows like n^2 and varies inversely with Z.

The energies here only depend on n, and not ℓ. Rotational invariance only dictates that the energies do not depend on m, and hence the lack of dependence on ℓ is due to the presence of an additional symmetry (often called a "hidden" or "dynamical" symmetry). In practice, these additional symmetries are consequences of the fact that there are additional constants of the motion, which also allow for the separation of variables in more than one coordinate system. For example, for the free particle, there is both translational invariance $[H, \mathbf{p}] = 0$, and rotational invariance $[H, \mathbf{L}] = 0$, so that the energies only depend on $p = |\mathbf{p}|$, and the Hamiltonian operator can be separated in many coordinate systems (Cartesian, spherical, cylindrical, and so on).

For the hydrogen atom, there is indeed an additional symmetry, and indeed the Hamiltonian operator can be separated both in spherical coordinates and in parabolic coordinates. (More details on the parabolic coordinate separation of variables can be found in Schiff's text.) The additional symmetry is a consequence of the conservation of the (rescaled) Runge-Lenz vector $\mathbf{M}$, which classically is given by

$$\mathbf{M} = \frac{1}{\mu}\mathbf{p} \times \mathbf{L} - e^2 \hat{\mathbf{r}}. \tag{104}$$

This vector quantity is in the plane of the orbit. It satisfies $\mathbf{L} \cdot \mathbf{M} = 0$, and

$$M^2 = \frac{2H}{\mu} L^2 + (e^2)^2. \tag{105}$$

In quantum mechanics, $\mathbf{M}$ is promoted to an operator, as follows:

$$\mathbf{M} = \frac{1}{2\mu}(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}) - e^2 \hat{\mathbf{r}}, \tag{106}$$

with

$$\mathbf{L} \cdot \mathbf{M} = 0, \qquad M^2 = \frac{2H}{\mu}(L^2 + \hbar^2) + (e^2)^2. \tag{107}$$

It can be shown that this operator commutes with the Hamiltonian: $[H, \mathbf{M}] = 0$. (Note the symmetrization is needed since $\mathbf{p}$ and $\mathbf{L}$ do not commute with each other). If one restricts to the subspace of a particular energy eigenvalue E, it can be shown for the bound state problem ($E < 0$) that the angular momentum operators L_i and $M_i' = \sqrt{-\mu/2E} M_i$ together form a closed $SO(4)$ algebra, *i.e.* a rotation in 4-d space. The condition that $\mathbf{L} \cdot \mathbf{M}$ further forces an identification of the quantum numbers $\hbar^2 i(i+1)$ and $\hbar^2 k(k+1)$ associated with the quantities $I^2 = \frac{1}{4}(\mathbf{L} + \mathbf{M}')^2$ and $K^2 = \frac{1}{4}(\mathbf{L} - \mathbf{M}')^2$. From this identification, we have

$$I^2 + K^2 = 2k(k+1)\hbar^2 = \frac{1}{2}\left(L^2 - \frac{\mu}{2E} M^2\right) = -\frac{\mu(e^2)^2}{4E} - \frac{\hbar^2}{2}, \tag{108}$$

which can be solved for E to obtain

$$E = -\frac{\mu(e^2)^2}{2\hbar^2(2k+1)^2}, \qquad 2k+1 = n = 1, 2, \ldots, \tag{109}$$

where we have made the identification of the principal quantum number n with the quantity $(2k+1)$.

Isotropic 3-d oscillator. The Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2 = \sum_{i=x,y,z}\left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 r_i^2\right). \tag{110}$$

We've already solved the problem in rectangular coordinates: the energy eigenvalues are $E = (n_x + n_y + n_z + 3/2)\hbar\omega = (n + 3/2)\hbar\omega$, where we have set $n = n_x + n_y + n_z$. The eigenfunctions are $\psi(\mathbf{x}) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$ in which the ψ_{n_i} are the usual 1-d SHO wavefunctions, and the degree of degeneracy for the level n is $(n+1)(n+2)/2$.

This system can also be analyzed using spherical coordinates. We start with

$$\psi_{E\ell m} = \frac{u_{E\ell m}(r)}{r}Y_{\ell m}(\theta, \phi), \tag{111}$$

and solve the radial equation given the potential $V(r) = (1/2)m\omega^2 r^2$. Solving this system in the usual way (identify asymptotic behavior, write the solution in terms of a power series that must be truncated to avoid divergent behavior as $r \to \infty$) leads to the expected result:

$$E = (n + 3/2)\hbar\omega.$$

The degeneracy factor for an energy level with a given value of n, can be understood as follows: when n is even ℓ must be even, and when n is odd, ℓ must be odd. The degeneracy of states is again $(n+1)(n+2)/2$ (this can most easily be evaluated treating the even and odd n cases separately).

Here once again we see that the energies only depend on n, and not ℓ. The additional symmetry is a $SU(3)$ symmetry that stems from the fact that we can define the vector quantities $\mathbf{a}$ and $\mathbf{a}^\dagger$, as follows:

$$\mathbf{a} = \sqrt{\frac{m\omega}{2\hbar}}\left[\mathbf{x} + \frac{i\mathbf{p}}{m\omega}\right], \qquad \mathbf{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left[\mathbf{x} - \frac{i\mathbf{p}}{m\omega}\right], \tag{112}$$

and rewrite the Hamiltonian as

$$H = \hbar\omega\left(\mathbf{a}^\dagger \cdot \mathbf{a} + \frac{3}{2}\right). \tag{113}$$

For more details on these symmetries and the corresponding operators for both the hydrogen atom and the isotropic 3-d simple harmonic oscillator, see Shankar 15.4, and Schiff 30.