4.1 Schrödinger Equation in Spherical Coordinates

$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$, where $H = \frac{p^2}{2m} + V$

$\mathbf{p} \to (\hbar/i)\nabla$ implies $i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$

normalization: $\int d^3\mathbf{r} \ |\Psi|^2 = 1$

If V is independent of t, $\exists$ a complete set of stationary states $\ni \ \Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_nt/\hbar}$, where the spatial wavefunction satisfies the time-independent Schrödinger equation:
$-\frac{\hbar^2}{2m}\nabla^2\psi_n + V\psi_n = E_n\psi_n$.

An arbitrary state can then be written as a sum over these $\Psi_n(\mathbf{r}, t)$.

Spherical symmetry

If the potential energy and the boundary
conditions are spherically symmetric, it is
useful to transform H into spherical
coordinates and seek solutions to
Schrödinger's equation which can be written
as the product of a radial portion and an
angular portion: $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, or
even $R(r)\Theta(\theta)\Phi(\phi)$.

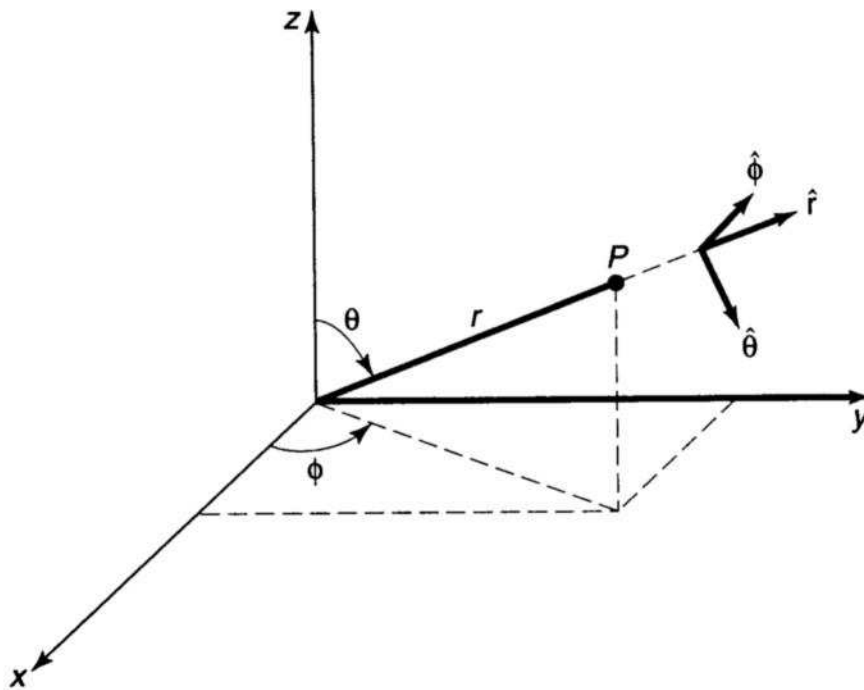This type of solution is known as 'separation of
variables'.

Figure 4.1 - Spherical coordinates.

In spherical coordinates, the Laplacian takes
the form:

$$\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)$$

$$+\frac{1}{r^2 \sin^2\theta}\left(\frac{\partial^2 f}{\partial\phi^2}\right).$$

After some manipulation, the equations for the
factors become:

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi,$$

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)\sin^2\theta\,\Theta = m^2\Theta,\text{ and}$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = l(l+1)R,$$

where m^2 and $l(l+1)$ are constants of
separation.

The solutions to the angular equations with spherically symmetric boundary conditions are: $\Phi_m = (2\pi)^{-1/2} e^{im\phi}$
and $\Theta_l^m \propto P_l^m(\cos\theta)$,
where m is restricted to the range $-l, ..., l$,
$P_l^m(x) \equiv (1 - x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_l(x)$ is the 'associated Legendre function,' and $P_l(x)$ is the lth Legendre polynomial.

The product of Θ and Φ occurs so frequently in quantum mechanics that it is known as a spherical harmonic:

$$Y_l^m(\theta, \phi) = \epsilon \left[\frac{(2l+1)}{4\pi}\frac{(l - |m|)!}{(l + |m|)!}\right]^{1/2} e^{im\phi} P_l^m(\cos\theta),$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$, and the spherical harmonics are orthonormal:

$$\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \, [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] = \delta_{ll'}\delta_{mm'}.$$

While the angular part of the wavefunction is $Y_l^m(\theta, \phi)$ for all spherically symmetric situations, the radial part varies.

The equation for R can be simplified in form by substituting $u(r) = rR(r)$:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu,$$

with normalization $\int dr\, |u|^2 = 1$.

This is now referred to as the radial wave equation, and would be identical to the one-dimensional Schrödinger equation were it not for the term $\propto r^{-2}$ added to V, which pushes the particle away from the origin and is therefore often called 'the centrifugal potential.'

Let's consider some specific examples.

Infinite spherical well

$$V(r) = \begin{cases} 0, & r < a \\ \infty, & r > a. \end{cases}$$

The wavefunction $= 0$ for $r > a$;
for $r < a$, the differential equation is

$$\frac{d^2 u}{dr^2} = \left[\frac{l(l+1)}{r^2} - k^2 \right] u, \text{ where } k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

The 'stationary' eigenfunctions of this potential are all bound states, confined to the region $r < a$.

The solutions to this equation are Bessel functions, specifically the *spherical Bessel* and *spherical Neumann functions* of order l:

$$u(r) = Ar j_l(kr) + Br n_l(kr),$$

$$\text{where } j_l(x) \equiv (-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\sin x}{x},$$

$$\text{and } n_l(x) \equiv -(-x)^l \left(\frac{1}{x} \frac{d}{dx} \right)^l \frac{\cos x}{x}.$$

The requirement that the wavefunctions be 'regular' at the origin eliminates the Neumann function from any region including the origin. The Bessel function is similarly eliminated from any region including ∞.
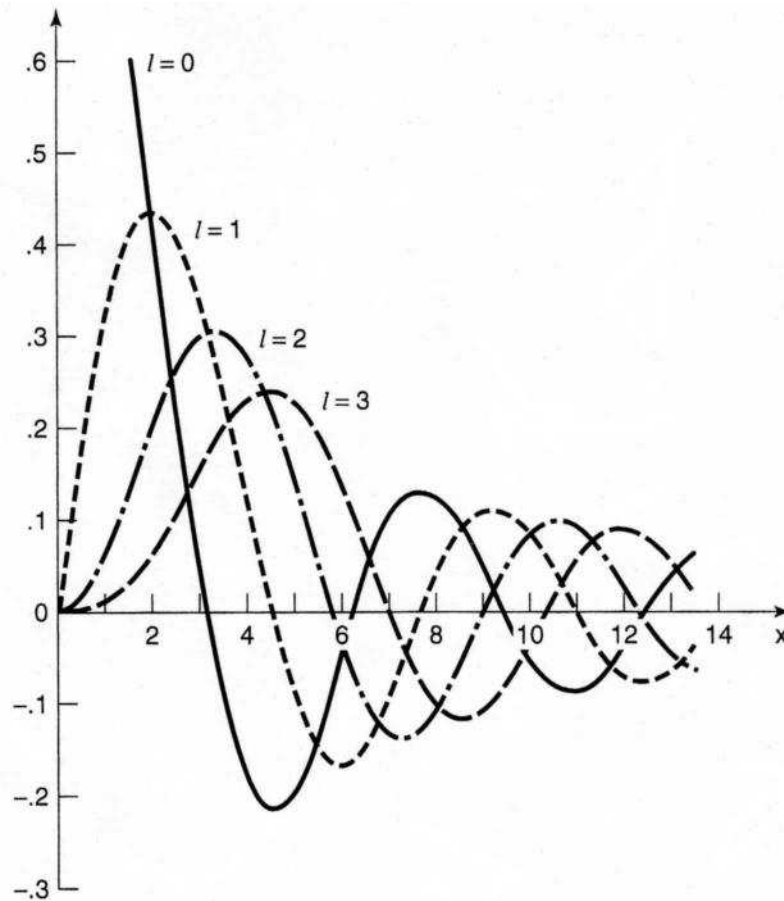

Figure 4.2 - First four spherical Bessel functions.

The remaining constants, k (substituting for E) and A, are satisfied by requiring that the solution vanish at $r = a$ and normalizing, respectively: $j_l(ka) = 0 \Rightarrow ka = \beta_{nl}$, where β_{nl} is the nth zero of the lth spherical Bessel function.

Adding the angular portion, the complete time-independent wavefunctions are

$$\psi_{nlm}(r, \theta, \phi) = A_{nl} j_l(\beta_{nl} r / a) Y_l^m(\theta, \phi),$$

$$\text{where } E_{nl} = \frac{\hbar^2}{2ma^2} \beta_{nl}^2.$$

4.2 Hydrogen Atom

The hydrogen atom consists of an electron orbiting a proton, bound together by the Coulomb force. While the correct dynamics would involve both particles orbiting about a center of mass position, the mass differential is such that it is a very good approximation to treat the proton as fixed at the origin.

The Coulomb potential, $V \propto \frac{1}{r}$, results in a Schrödinger equation which has both continuum states $(E > 0)$ and bound states $(E < 0)$, both of which are well-studied sets of functions. We shall neglect the former, the confluent hypergeometric functions, for now, and concentrate on the latter.

Including constants, the potential is
$V = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$, leading to the following
differential equation for u:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu.$$

This equation can be simplified with two
substitutions: since $E < 0$, both $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$
and $\rho \equiv \kappa r$ are non-negative real variables;
furthermore, ρ is dimensionless.

With these substitutions, $u(\rho)$ satisfies:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u; \;\; \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}.$$

Having simplified this equation more or less as
much as possible, let us now look at the
asymptotic behavior:

As $\rho \to \infty$, the constant term in brackets
dominates, or $\frac{d^2u}{d\rho^2} \to u$, which is satisfied by
$u = Ae^{-\rho} + Be^{\rho}$. The second term is irregular
as $\rho \to \infty$, so $B = 0 \Rightarrow u \to Ae^{-\rho}$ as $\rho \to \infty$.

Similarly, as $\rho \to 0$, the term in brackets $\propto \rho^{-2}$ dominates, leading to $\frac{d^2 u}{d\rho^2} \to \frac{l(l+1)}{\rho^2} u$, which is satisfied by $u = C\rho^{l+1} + D\rho^{-l}$. The second term is irregular at $\rho \to 0$, so $D = 0 \Rightarrow u \to C\rho^{l+1}$ as $\rho \to 0$.

We might hope that we can now solve the differential equation by assuming a new functional form for u which explicitly includes both kinds of asymptotic behavior: let $u(\rho) \equiv \rho^{l+1} e^{-\rho} v(\rho)$. The resulting differential equation for v is

$$\rho \frac{d^2 v}{d\rho^2} + 2(l + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(l + 1)]v = 0.$$

Furthermore, let us assume that $v(\rho)$ can be expressed as a power series in ρ:

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j.$$

The problem then becomes one of solving for $\{a_j\}$.

If we had expanded in a series of orthonormal functions, it would now be possible to substitute that series into the differential equation and set the coefficients of each term equal to zero.

Powers of ρ are not orthonormal, however, so we must use a more difficult argument based on the equation holding for all values of ρ to group separately the coefficients for each power of ρ:

$$a_{j+1} = \left[\frac{2(j + l + 1) - \rho_0}{(j + 1)(j + 2l + 2)} \right] a_j.$$

Let's examine the implications of this recursion relation for the solutions to the Schrödinger equation.

As $j \to \infty$, $a_{j+1} \to \frac{2}{j+1}a_j$, which is the same term-to-term ratio as $e^{2\rho}$. Thus, $u \to A\rho^{l+1}e^{\rho}$, a solution we rejected. The only way to continue to reject this solution is for the infinite series implied by the recursion relation to terminate due to a zero factor: *i.e.*, $2(j_{\text{max}} + l + 1) = \rho_0$. If $n \equiv j_{\text{max}} + l + 1$, then n is the familiar *principal quantum number*.

$$\rho_0 = 2n \Rightarrow E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2} \equiv \frac{-13.6 \text{ eV}}{n^2}.$$

Also, $\kappa = \dfrac{1}{an} \Rightarrow a \equiv \dfrac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}\text{m}.$

The truncated series formed in this way is, apart from normalization, the 'well-known' associated Laguerre polynomials:
$v(\rho) \propto L_{n-l-1}^{2l+1}(2\rho)$, where
$L_{q-p}^{p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$ and
$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q (e^{-x}x^q)$ is the qth Laguerre polynomial.

With these definitions, the orthonormalized solutions to the Schrödinger equation for hydrogen can now be written as

$$\psi_{nlm} = A_{nl}e^{-r/na}\left(\frac{2r}{na}\right)^{l}L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)Y_{l}^{m}(\theta,\phi),$$

where $A_{nl} \equiv \sqrt{\left(\frac{2}{na}\right)^{3}\frac{(n-l-1)!}{2n[(n+l)!]^{3}}}$

and $\int dr\,d\theta\,d\phi\,r^{2}\sin\theta\,\psi_{nlm}^{*}\psi_{n'l'm'} = \delta_{nn'}\delta_{ll'}\delta_{mm'}.$
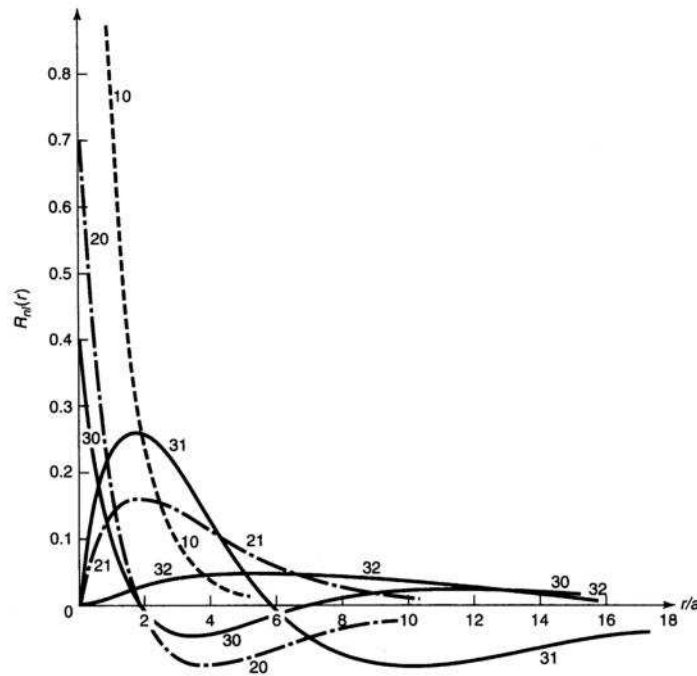

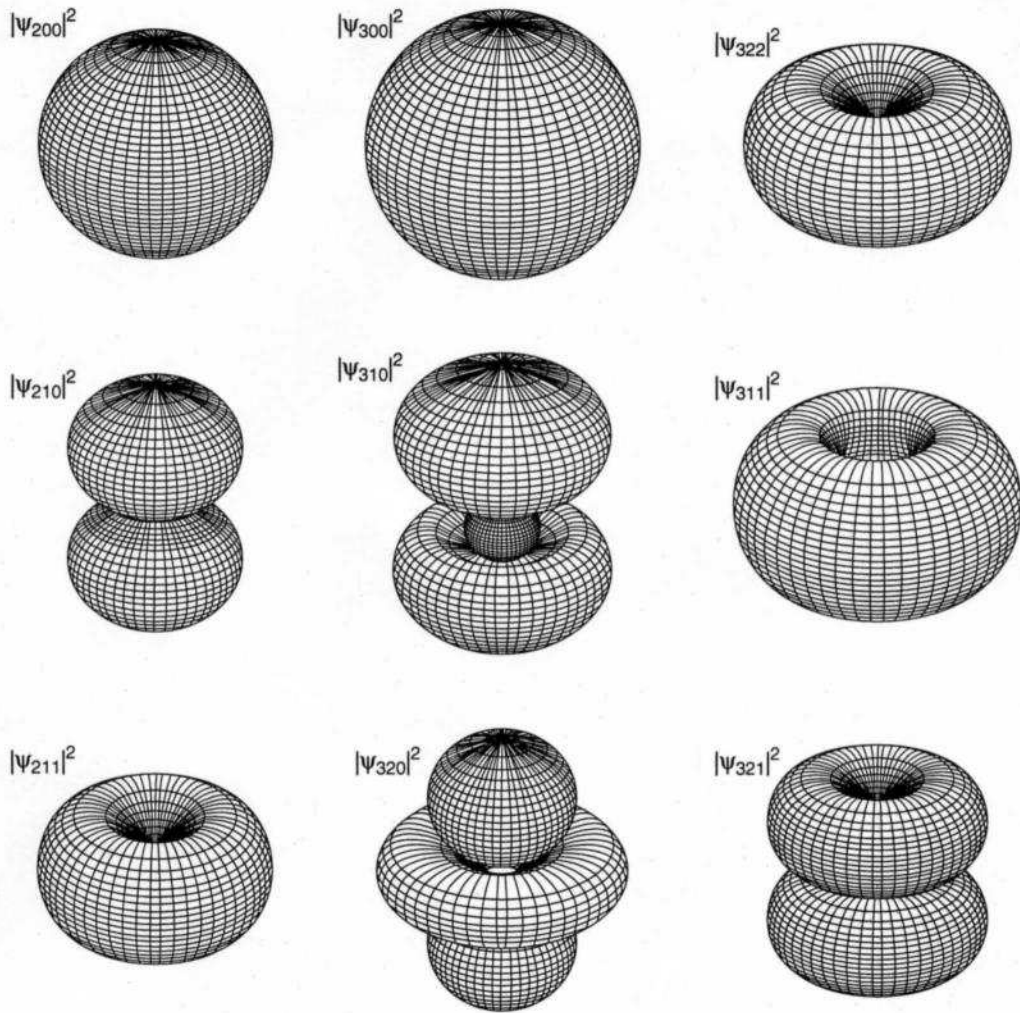Figure 4.4 - First few hydrogen radial wave functions, $R_{nl}(r)$.

Figure 4.6 - Surfaces of constant $|\psi|^2$ for the first few hydrogen wave functions.

The eigenvalues of these states are
$E_n = -\dfrac{me^4}{32\pi^2\epsilon_0^2\hbar^2 n^2}$, which correspond very
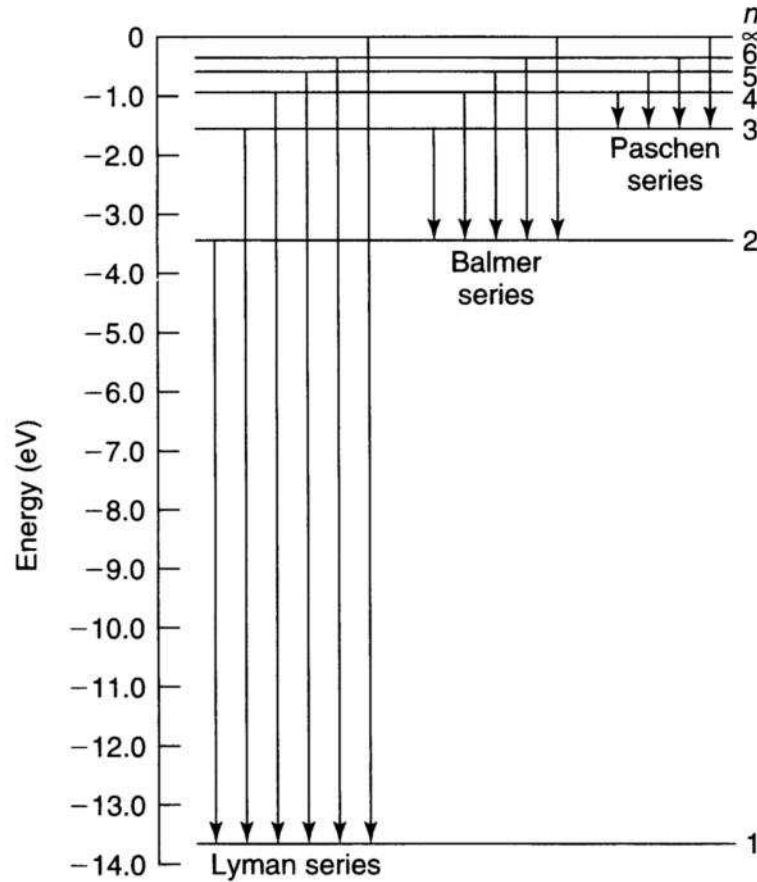closely to the measured absorption and
emission spectra of hydrogen.

Figure 4.7 - Energy levels and transitions in the
spectrum of hydrogen.

4.3 Angular Momentum

The classical mechanics quantity $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ becomes the quantum mechanical operator $\mathbf{L} = \mathbf{r} \times (\hbar/i)\nabla$. Interestingly, L_x and L_y do not commute: $[L_x, L_y] = i\hbar L_z, \ldots$. On the other hand, $[L^2, \mathbf{L}] = 0$. Thus, it is sensible to look for states which are simultaneously eigenfunctions of both L^2 and one component of $\mathbf{L}$.

Choosing L_z as that component, let's define a 'ladder operator' such as is used for the harmonic oscillator problem: $L_\pm \equiv L_x \pm iL_y$. With this definition, $[L^2, L_\pm] = 0$ and $[L_z, L_\pm] = \pm\hbar L_\pm$.

If f is an eigenfunction of both L^2 and L_z, it can be shown that $L_\pm f$ is also an eigenfunction of those same operators. Furthermore, its eigenvalue of L^2 is unchanged, while its eigenvalue of L_z is raised (lowered) by $\hbar$.

But it cannot be that the eigenvalue of L_z exceeds the magnitude of $\mathbf{L}$. Therefore, there must exist a 'top rung' of the 'ladder' f_t such that $L_+ f_t = 0$. For this state, let the eigenvalues of L_z and L^2 be $\hbar l$ and λ, respectively. Since $L_\pm L_\mp = L^2 - L_z^2 \pm \hbar L_z$, it can be shown that $\lambda = \hbar^2 l(l+1)$.

Similarly, there must exist a bottom rung f_b such that $L_- f_b = 0$. For this state, let the eigenvalue of L_z be $\hbar \bar{l}$. It can be shown that $\lambda = \hbar^2 \bar{l}(\bar{l}-1)$, so $\bar{l} = -l$.

There must be some number of integer steps between l and $-l$, so l must be either an integer or a half-integer. It is sometimes called the *azimuthal quantum number*.

The joint eigenstates of L^2 and L_z are characterized by eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$, respectively, where $l = 0, 1/2, 1, 3/2, ...$ and $m = -l, -l+1, ..., l-1, l$.

The eigenfunctions of L^2 and L_z can be identified by expressing all of the above operators (L_x, L_y, L_z, $L_\pm$, L^2) in spherical coordinates. These are just the operators of which the $Y_l^m(\theta, \phi)$ are the eigenfunctions. Thus, when we solved for the eigenfunctions of the hydrogen atom, we inadvertently found those functions which are simultaneously eigenfunctions of H, L^2, and L_z.

Note also that we have discovered that the azimuthal quantum number, l, in addition to taking on integer values, may also take on half-integer values, leading to a discussion of the property of 'spin'.

4.4 Spin

In classical systems, two different words are used to describe two rather similar types of rigid body rotation: 'spin' for rotation about its center of mass; 'orbital' for rotation of its center of mass about another axis.

The same two words are used in quantum mechanical systems, but they *do not* refer to similar types of motion. Experiments have shown that the behavior of electrons in magnetic fields, for example, *cannot* be explained without invoking the existence of a constant of motion in addition to the energy and momentum. It apparently must be characterized by an *intrinsic* angular momentum $\mathbf{S}$, or spin, in addition to whatever *extrinsic* angular momentum $\mathbf{L}$ it might carry.

Spin quantities are defined in analogy to comparable orbital angular momentum quantities: $[S_x, S_y] = i\hbar S_z, ...$; $S_\pm \equiv S_x \pm i S_y$; $S_\pm |s\,m\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)}\,|s\,(m \pm 1)\rangle$; $S^2|s\,m\rangle = \hbar^2 s(s+1)|s\,m\rangle$; $S_z|s\,m\rangle = \hbar m|s\,m\rangle$, where $s = 0, 1/2, 1, 3/2, ...$ and $m = -s, -s+1, ..., s-1, s$.

This time, however, the eigenfunctions are not expressible as a function of any spatial coordinates.

Every elementary particle has a specific and immutable value of s, which we call its spin: *e.g.*, π mesons have spin 0; electrons have spin 1/2; photons have spin 1; deltas have spin 3/2; and so on.

In contrast, the orbital angular momentum l for each particle can take on any integer value, and can change whenever the system is perturbed.

An electron has spin $s = 1/2$, leading to two eigenstates which we can call *spin up* ($\uparrow$) and *spin down* ($\downarrow$) referring to the 'projection of the spin on the z axis'. We will express the eigenfunction as a two-element column matrix, or *spinor*: $\chi_+ \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}$; $\chi_- \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}$.

In the same notation, the operators are 2×2 matrices which we will express in terms of the *Pauli spin matrices*:
$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$
Therefore, $\mathbf{S} = (\hbar/2)\sigma$.

The σ_z matrix is already diagonal, so the eigenspinors of S_z are simply χ_+ and χ_- with eigenvalues $+\hbar/2$ and $-\hbar/2$, respectively.

Since these eigenstates span the space, we can express any general spinor as a sum of these:
$\chi = a\chi_+ + b\chi_-$.

If you measure S_z on a particle in this state χ, you will measure $+\hbar/2$ with probability $|a|^2$ and $-\hbar/2$ with probability $|b|^2$.

Suppose now that you want to measure S_x on this same state. The e.f. of S_x are $\chi_\pm^{(x)} = \frac{1}{\sqrt{2}}(\chi_+ \pm \chi_-)$ expressed in the basis of the e.f. of S_z, with e.v. $\pm\hbar/2$. Thus $\langle S_x \rangle = (1/2)|a+b|^2(+\hbar/2) + (1/2)|a-b|^2(-\hbar/2)$.

NB, even if the particle is in a pure 'up' state relative to the z axis (*i.e.*, $a, b = 1, 0$), it can be in either of two different states when projected on the x axis. This uncertainty is an expected result since $[S_z, S_x] \neq 0$ (*i.e.*, *incompatible* observables).

Experiments on electrons imply that the electrons possess a magnetic moment unrelated to any orbital motion, as though the electron were a macroscopic charged body 'spinning' on an axis through its center of mass. This magnetic moment is related to this presumed 'spin' through $\mu = \gamma \mathbf{S}$, leading to a Hamiltonian $H = -\mu \cdot \mathbf{B} = -\gamma \mathbf{B} \cdot \mathbf{S}$.

This term in the Hamiltonian can be used to explain on a purely quantum mechanical basis the observation of Larmor precession and the Stern-Gerlach experiment.

Larmor precession

Consider a particle of spin $\frac{1}{2}$ at rest in a uniform magnetic field: $\mathbf{B} = B_0 \widehat{k}$, so that $H = -\gamma B_0 S_z$. The eigenstates of H are the same as those of S_z, χ_+ and χ_- with eigenvalues $\mp \frac{\gamma B_0 \hbar}{2}$, respectively.

Since H is time independent, the general solution to the time-independent Schrödinger equation, $i\hbar \frac{\partial \chi}{\partial t} = H\chi$, can be expressed in terms of the stationary states:
$\chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar}$.

Since χ is normalized, we can substitute $a = \cos\frac{\alpha}{2}$ and $b = \sin\frac{\alpha}{2}$. Calculating $\langle \mathbf{S} \rangle$:

$\langle S_x \rangle = \frac{\hbar}{2} \sin\alpha \cos(\gamma B_0 t/2)$,

$\langle S_y \rangle = -\frac{\hbar}{2} \sin\alpha \sin(\gamma B_0 t/2)$,

and $\langle S_z \rangle = \frac{\hbar}{2}\cos\alpha$.

These equations describe a spin vector which has a constant component in the field direction, but which precesses in the xy-plane with frequency $\omega = \gamma B_0$.
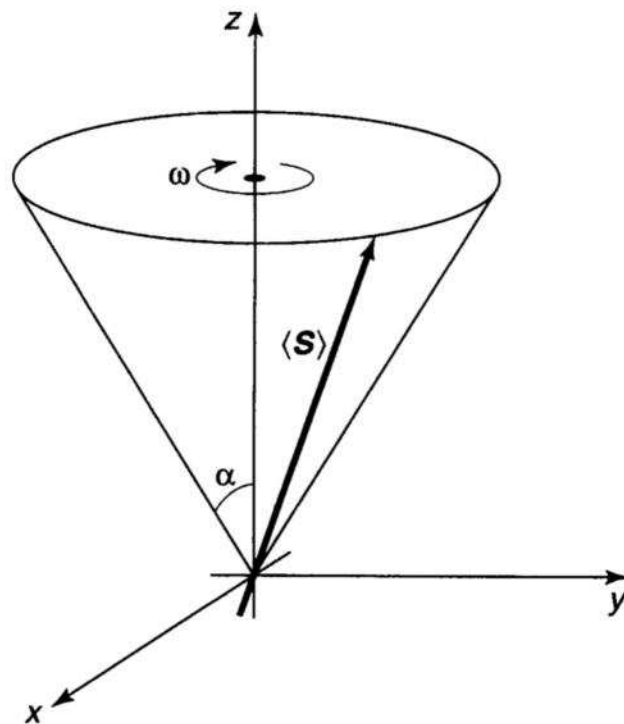

Figure 4.7 - Precession of $\langle \mathbf{S} \rangle$ in a magnetic field.

Stern-Gerlach experiment

Suppose a beam of spin-$\frac{1}{2}$ particles moving in the y direction passes through a region of inhomogeneous $\mathbf{B} = (B_0 + \alpha z)\widehat{k}$, where the constant α denotes a small deviation from homogeneity.
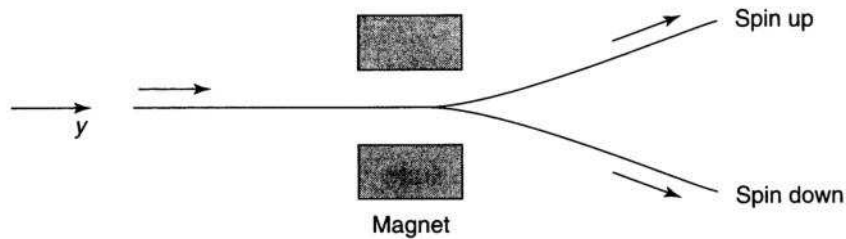

Figure 4.11 - The Stern-Gerlach configuration.

In addition to the effect of the Lorentz force, the inhomogeneity gives rise to a spatially dependent energy which affects the wavefunctions as follows:

$$\chi(t) = a\chi_+ e^{-iE_+T/\hbar} + b\chi_- e^{-iE_-T/\hbar}$$
$$= (ae^{i\gamma B_0 T/2}\chi_+)e^{i(\alpha\gamma T/2)z}$$
$$+ (be^{-i\gamma B_0 T/2}\chi_-)e^{-i(\alpha\gamma T/2)z},$$

where T is the amount of time spent in the inhomogeneous field.

The z-dependent portion of the wavefunction is equivalent to $p_z = \pm\frac{\alpha\gamma T\hbar}{2}$, and leads to the splitting of the beam into $2s + 1$ individual beams, demonstrating the quantization of S_z.

Addition of angular momenta

Suppose we have a system with two spin-1/2
particles. Since each can be 'up' or 'down',
there are four possible combinations:
$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$.

Define the total angular momentum:
$\mathbf{S} \equiv \mathbf{S}^{(1)} + \mathbf{S}^{(2)}$.
Then $S_z \chi_1 \chi_2 = (S_z^{(1)} + S_z^{(2)})\chi_1 \chi_2$
$= (S_z^{(1)}\chi_1)\chi_2 + \chi_1(S_z^{(2)}\chi_2) = \hbar(m_1 + m_2)\chi_1\chi_2$.

$\therefore m_{\uparrow\uparrow} = 1; m_{\uparrow\downarrow} = 0; m_{\downarrow\uparrow} = 0; m_{\downarrow\downarrow} = -1$.

There are two e.s. degenerate in S_z, but not in
S^2. Sort them out by applying S_- to the $\uparrow\uparrow$
state: $S_-(\uparrow\uparrow) = (S_-^{(1)} \uparrow)\uparrow + \uparrow(S_-^{(2)} \uparrow)$
$= (\hbar \downarrow)\uparrow + \uparrow(\hbar \downarrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow)$.

Thus, there are three e.s. in one group and one in another: $|sm\rangle = |1\,1\rangle$ ($\uparrow\uparrow$);
$|1\,0\rangle$ $[\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)]$; $|1\,-1\rangle$ ($\downarrow\downarrow$);
$|0\,0\rangle$ $[\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)]$.

The first three e.s. constitute a *triplet* set, and the last a *singlet*. You can show that they are all e.s. of S^2 with e.v. $= \hbar^2 s(s+1)$, as anticipated.

Finally, to generalize, if you combine s_1 with s_2, the possible resulting total spin of the system ranges over every value between $(s_1 + s_2)$ and $|s_1 - s_2|$ in integer steps. This relationship is summarized in the following equation involving the Clebsch-Gordan coefficients:

$$|s_1 m_1\rangle\,|s_2 m_2\rangle = \sum_s C^{s_1 s_2 s}_{m_1 m_2 m}\,|sm\rangle$$

and the reciprocal relation, where $m = m_1 + m_2$ and s ranges as noted above.

These relationships hold for both orbital and spin angular momentum, and mixtures, and can be used to express products of spherical harmonics as a sum of spherical harmonics.