The foundations of quantum mechanics were established during the first half of the twentieth century by Niels Bohr, Werner Heisenberg, Max Planck, Louis de Broglie, Albert Einstein, Erwin Schrödinger, Max Born, John von Neumann, Paul Dirac, Wolfgang Pauli, David Hilbert,....

Erwin Schrödinger

In January 1926, Schrödinger published in *Annalen der Physik* the paper "*Quantisierung als Eigenwertproblem*" [*tr.* Quantization as an Eigenvalue Problem] on wave mechanics and what is now known as the Schrödinger equation. .... This paper has been universally celebrated as one of the most important achievements of the twentieth century, and created a revolution in quantum mechanics, and indeed of all physics and chemistry.

Important steps in the development of our atomic models

400 B.C.	Democritus	Empty space and indivisible particles
330 B.C.	Aristotle's	Continuous matter made up of the 4 elements
1810	Dalton	Hard sphere, kinetic theory of gases
1888	Rydberg	Systematic studies of experimental spectra
1900	Thomson	"Plum pudding", negative electrons imbedded in a positive nucleus
1910	Rutherford	Classically impossible planetary atom
1913	Bohr	Postulated stable "Rutherford atom". Introduced quantization
1922	Stern-Gerlach	Experimental determination of magnetic moments - spin
1926	Schrödinger	Non relativistic quantum mechanics. Stable orbits follow from general postulates. Probability interpretation of wavefunctions
1928	Dirac	Relativistic quantum mechanics. Explains spin and antiparticles
1950	Feynman et al.	Quantum electrodynamics (QED). Quantized EM field that exists even in vacuum. Explains spontaneous emission.
1960	Weinberg/Salam	Electroweak interaction. QED + weak interaction
1970	Many	"Standard model"; Electroweak + strong interaction. Higgs boson (2012)
20??	??	Quantized gravity, TOE (Theory of everything) String theory? Time-dependent fundamental constants....

Some quantum mechanical results.

See e.g. McMurry Ch. 1 - 4 and G. Ohlén Ch. 5

Some postulates:

The state of a particle at time t is fully described by a continuous, complex wavefunction $u(z,y,z,t)$ which can be normalized so that $|u|^2$ gives the probability density for the results of a position measurement. This means that:

$$\int |u|^2 \, dV = 1$$

Every measurable quantity, A, in physics is represented by a Hermitian operator, $\hat{A}$.

If $\hat{A}$ has a discrete, non-degenerate spectrum i.e.

$$\hat{A} u_n = \lambda_n u_n, \; n = 1,2,\ldots N,$$

a measurement of A can only give as a result an eigenvalue λ_n of $\hat{A}$. After the measurement the system is described by the corresponding eigenfunction u_n.

An important special case is when $\hat{A} = \hat{H}$ = total energy. Then we get the famous (time independent) Schrödinger equation:

$$\hat{H} u_n = E_n u_n$$

Hermitian operators:

An operator is Hermitian if

$$\langle u | \hat{A} v \rangle = \langle \hat{A} u | v \rangle \Leftrightarrow \int u^* \hat{A} v \, dV = \int (\hat{A} u)^* v \, dV$$

A Hermitian operator has real eigenvalues and orthogonal eigenfunctions

If a Hermitian operator has a discrete eigenvalue spectrum the set of all eigenfunctions is complete, i.e. arbitrary function, f, in the same coordinate space, can be written as:

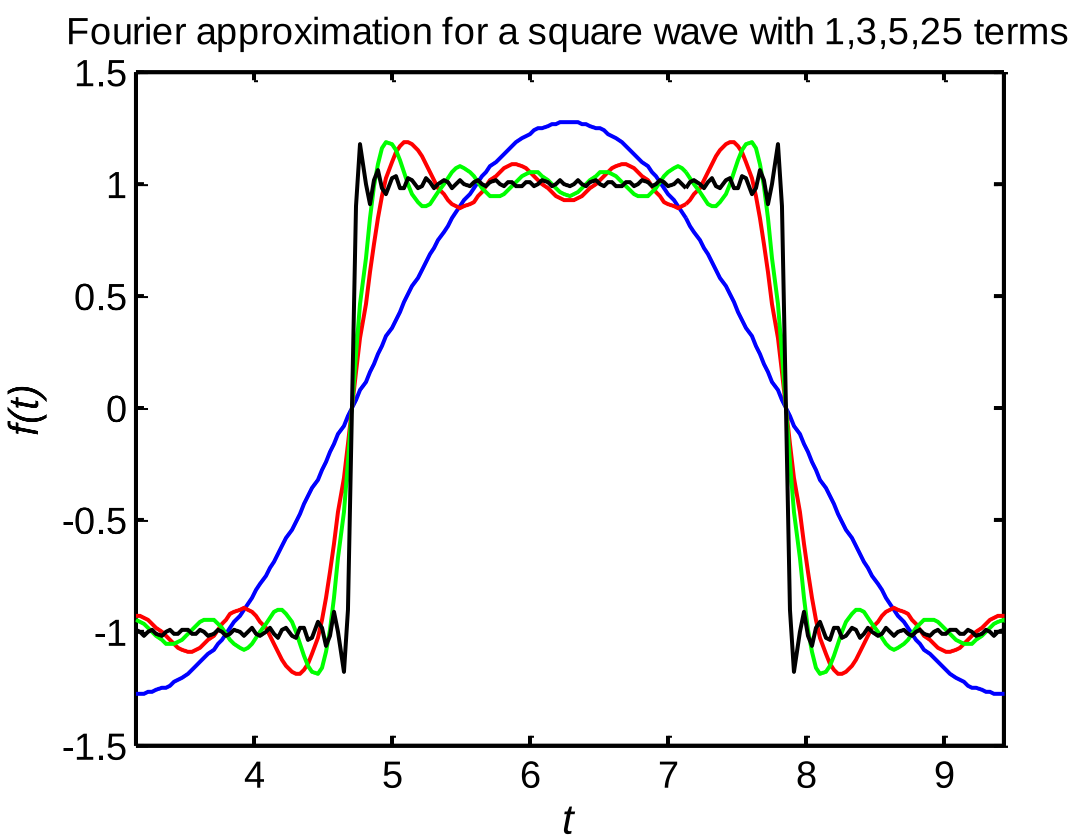
$$f = \sum_n c_n u_n$$

Completeness of sin(*t*) and cos(t) Fourier analysis.

An arbitrary function *f*(*t*) with a period of *T* can always be written as:

$$f(t) = \frac{1}{2}a_0 + \sum_{m=1}^{\infty}\left(a_m \cos(m\omega t) + b_m \sin(m\omega t)\right)$$

$$\omega = \frac{2\pi}{T}$$



Commutator:

The commutator of two operators is defined as:

$$\left[\hat{A},\hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

Some relations:

$$\left[\hat{A},\hat{B}\right] = -\left[\hat{B},\hat{A}\right], \quad \left[\hat{A},\hat{B}+\hat{C}\right] = \left[\hat{A},\hat{B}\right] + \left[\hat{A},\hat{C}\right]$$

$$\left[\hat{A}\hat{B},\hat{C}\right] = \hat{A}\left[\hat{B},\hat{C}\right] + \left[\hat{A},\hat{C}\right]\hat{B}$$

$i \cdot \left[\hat{A},\hat{B}\right]$ is Hermitian if $\hat{A}$ and $\hat{B}$ are.

If $\hat{A}$ and $\hat{B}$ are Hermitian and $\left[\hat{A},\hat{B}\right] = 0$ there exists a set of common eigenfunctions, u_n, i.e. $\hat{A}u_n = a_n u_n$ and $\hat{B}u_n = b_n u_n$.

If $\hat{A}$ and $\hat{B}$ commute they can simultaneously be measured with arbitrary accuracy.

Expectation value:

The expectation (mean) value of an operator in a state described by the wavefunction u is defined as:

$$<\hat{A}> \equiv \left\langle u \middle| \hat{A}u \right\rangle$$

The variance of the operator is defined as:

$$(\Delta\hat{A})^2 \equiv <\hat{A}^2> - <\hat{A}>^2$$

General statement of the uncertainty principle:

Let $\hat{A}$ and $\hat{B}$ be Hermitian and $\hat{C} = i \cdot \left[\hat{A},\hat{B}\right]$ then

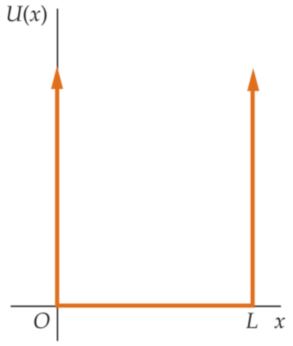
$$\Delta\hat{A} \cdot \Delta\hat{B} \geq \frac{1}{2}\left|<\hat{C}>\right|$$

Constant of the motion:

$\frac{d}{dt} <\hat{A}> = \frac{i}{\hbar} <\left[\hat{H},\hat{A}\right]>$, where $\hat{H}$ is the Hamilton operator.

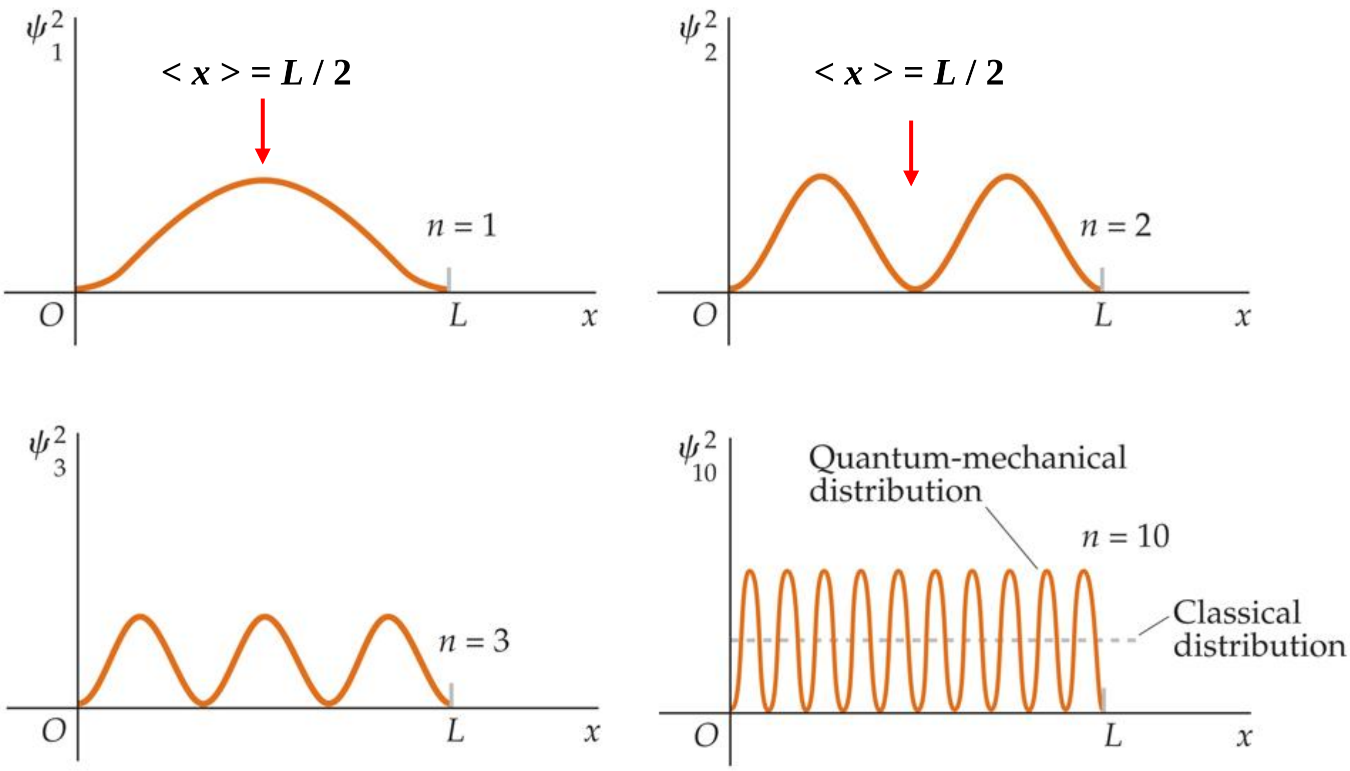
$\left[\hat{H},\hat{A}\right] = 0 \Rightarrow \hat{A}$ is a constant of the motion

1-dim infinite box of length *L*.



$$E_n = \frac{h^2}{8mL^2} \cdot n^2,\ n = 1, 2, 3...$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin(n\pi \frac{x}{L}),\ n = 1, 2, 3....$$



Quantum mechanical treatment of angular momentum.

McMurry Ch. 4 and 6. (G. Ohlén Ch. 5 and 7.) Exercises: 7 - 9 (H2)

Recapitulation of basic quantum mechanical concepts. Ch 2-4.

Orbital angular momentum operators and commutator relations. Ch 4.

$$\left[\hat{L}_x,\hat{L}_y\right]=i\hbar\hat{L}_z,\left[\hat{L}_y,\hat{L}_z\right]=i\hbar\hat{L}_x,\left[\hat{L}_z,\hat{L}_x\right]=i\hbar\hat{L}_y$$

$$\left[\hat{L}^2,\hat{L}_z\right]=0$$

General (orbital and spin) angular momentum operators ($\hat{J}^2$, $\hat{J}_z$) and commutator relations. Ch 6.1, 6.2.

$$\hat{J}^2\chi_{j,m}=\hbar^2 j(j+1)\cdot\chi_{j,m}$$

$$\hat{J}_z\chi_{j,m}=m\cdot\hbar\cdot\chi_{j,m}.$$

j integer or half integer and $m=-j,-j+1,\ldots..j-1,j$

Orbital angular momentum eigenfunctions $Y_{\ell,m}(\theta,\varphi)$, ℓ integer. Ch 4.5, 4.6

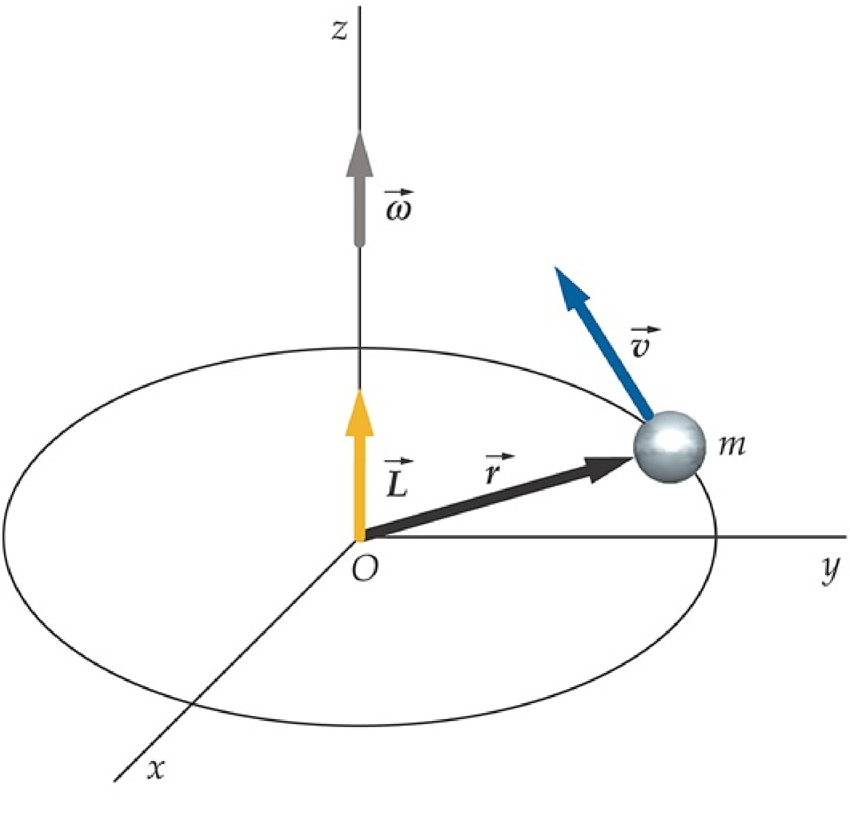
Parity $\prod(Y_{\ell,m})=(-1)^{\ell}$

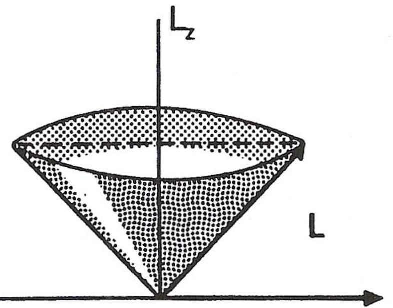
Angular distributions $\left|Y_{\ell,m}(\theta,\varphi)\right|^2$

Orbital Angular Momentum

McMurry Ch. 4

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$




L_z
L

General Angular Momentum Operators.

Orbital, spin, nuclear, sums of momenta....
Defined from the commutator relations derived for the orbital case.

$$\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z, \quad \left[\hat{J}_y, \hat{J}_z\right] = i\hbar\hat{J}_x, \quad \left[\hat{J}_z, \hat{J}_x\right] = i\hbar\hat{J}_y.$$

$$\left[\hat{J}^2, \hat{J}_z\right] = 0$$

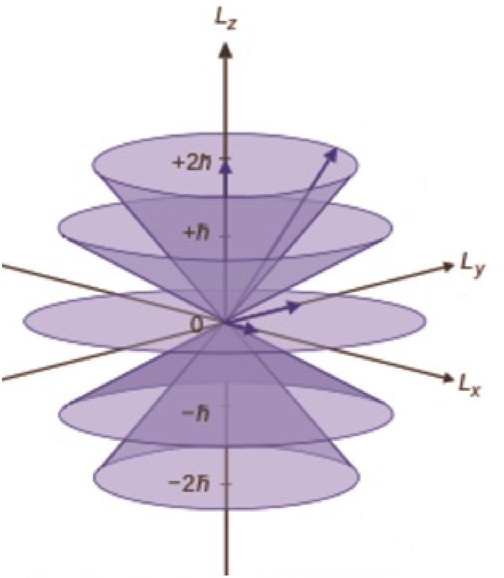
McMurry Ch 6 solves the general eigenvalue problem using step operators $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$ and obtains the following eigenvalue relations:

$$\hat{J}^2 \chi_{j,m} = \hbar^2 j(j+1) \cdot \chi_{j,m}$$

$$\hat{J}_z \chi_{j,m} = m \cdot \hbar \cdot \chi_{j,m}.$$

j integer or half integer

$$m = -j, -j+1, \ldots..j-1, j$$



j = 2, m = -2, -1, 0, 1, 2

Notation for angular momentum operators and eigenfunctions

General:

$\hat{J}^2, \hat{J}_z, \chi_{j,m}$ **(Orbital-, spin-, nuclear- or sums of momenta)**

quantum numbers: j **and** m

Orbital angular momentum:

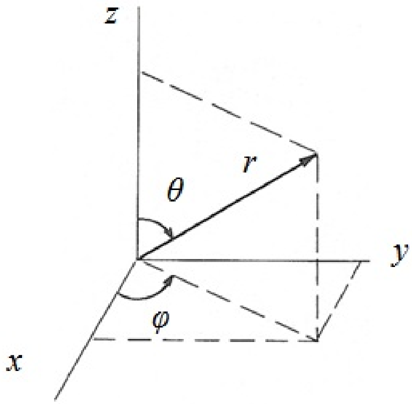
$\hat{L}^2, \hat{L}_z, Y_{\ell,m}$. $Y_{\ell,m}$ is called a spherical harmonics

quantum numbers: ℓ **and** m

Show that m**, and hence also** ℓ**, must be an integer. Determine** $Y_{\ell,m}$

Orbital angular momentum in spherical coordinates.

McMurry Ch. 4. GO Ch. 7



$$\begin{cases} x = r\sin\theta\cos\varphi \\ y = r\sin\theta\sin\varphi \\ z = r\cos\theta \end{cases} \qquad dV = dxdydz = r^2\sin\theta \cdot drd\theta d\varphi$$

$$\mathbf{L}_x = i\hbar(\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}),$$

$$\mathbf{L}_y = i\hbar(-\cos\varphi\frac{\partial}{\partial\theta} + \frac{\sin\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}),$$

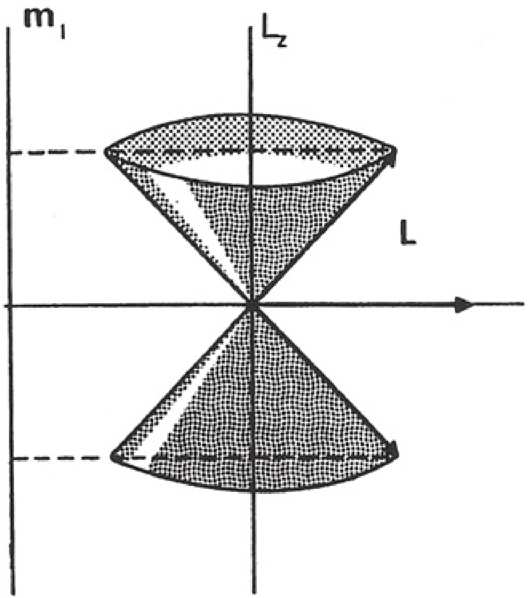
$$\mathbf{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

Note, independent of r!

$$\mathbf{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

Examples of orbital angular momentum with ℓ = 1 and 2.

$$L = \hbar \cdot \sqrt{\ell(\ell+1)}$$
$$L_z = \hbar \cdot m_\ell$$



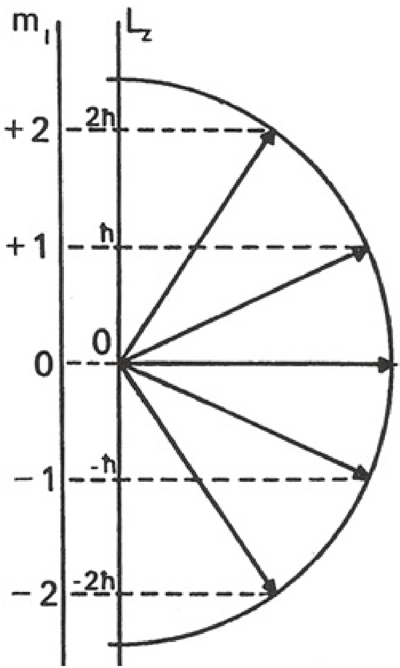


Table 4.1 Legendre polynomials and associated Legendre functions.

Legendre polynomials

$$P_0(\cos\theta) = 1$$
$$P_1(\cos\theta) = \cos\theta$$
$$P_2(\cos\theta) = \tfrac{1}{2}(3\cos^2\theta - 1)$$
$$P_3(\cos\theta) = \tfrac{1}{2}(5\cos^3\theta - 3\cos\theta)$$
$$P_4(\cos\theta) = \tfrac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$$

Associated Legendre functions

$$P_l^0(\cos\theta) \equiv P_l(\cos\theta)$$
$$P_1^1(\cos\theta) = \sin\theta$$
$$P_2^1(\cos\theta) = 3\sin\theta\cos\theta$$
$$P_2^2(\cos\theta) = 3\sin^2\theta$$
$$P_3^1(\cos\theta) = \tfrac{3}{2}\sin\theta\,(5\cos^2\theta - 1)$$
$$P_3^2(\cos\theta) = 15\sin^2\theta\cos\theta$$
$$P_3^3(\cos\theta) = 15\sin^3\theta$$

TABLE 2.1 SPHERICAL HARMONICS

$l = 0$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$l = 1$

$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$l = 2$

$$Y_{2,\pm 2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta \, e^{\pm 2i\phi}$$

$$Y_{2,\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \, e^{\pm i\phi}$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}} (2\cos^2\theta - \sin^2\theta)$$

$l = 3$

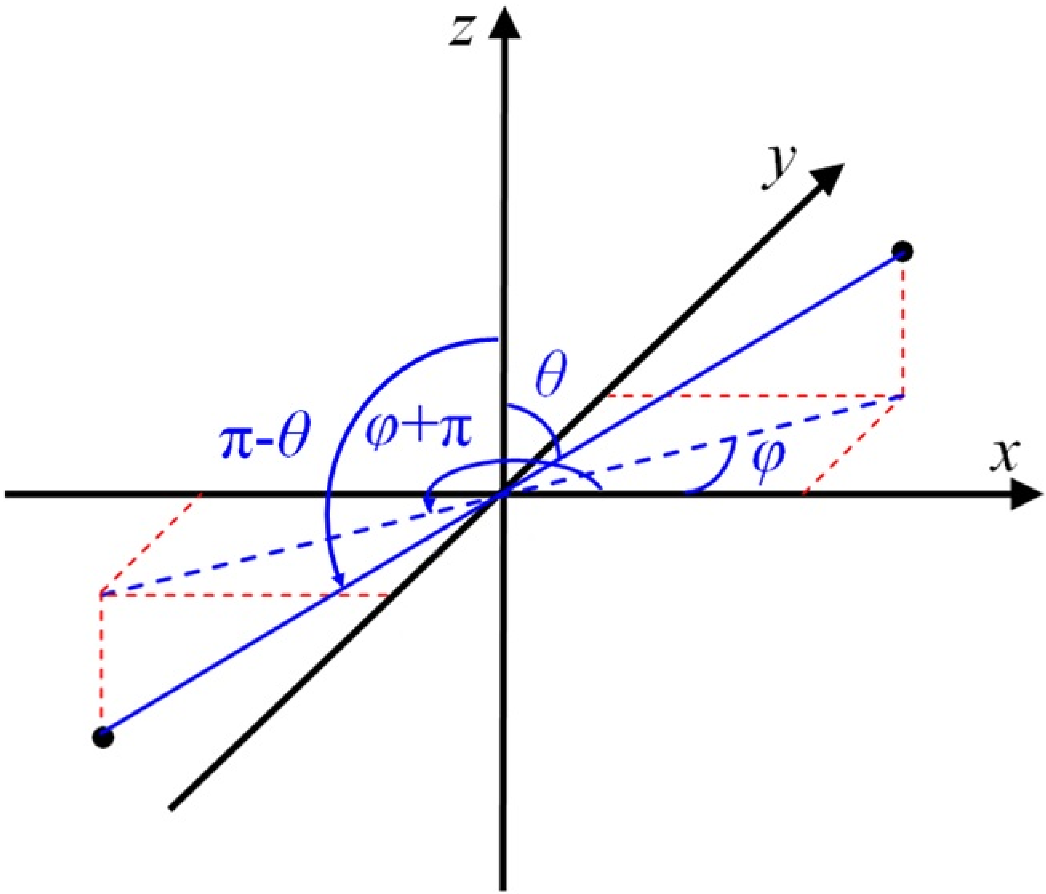
$$Y_{3,\pm 3} = \mp \sqrt{\frac{35}{64\pi}} \sin^3\theta \, e^{\pm 3i\phi}$$

$$Y_{3,\pm 2} = \sqrt{\frac{105}{32\pi}} \sin^2\theta \cos\theta \, e^{\pm 2i\phi}$$

$$Y_{3,\pm 1} = \mp \sqrt{\frac{21}{64\pi}} (4\cos^2\theta \sin\theta - \sin^3\theta) \, e^{\pm i\phi}$$

$$Y_{30} = \sqrt{\frac{7}{16\pi}} (2\cos^3\theta - 3\cos\theta \sin^2\theta)$$

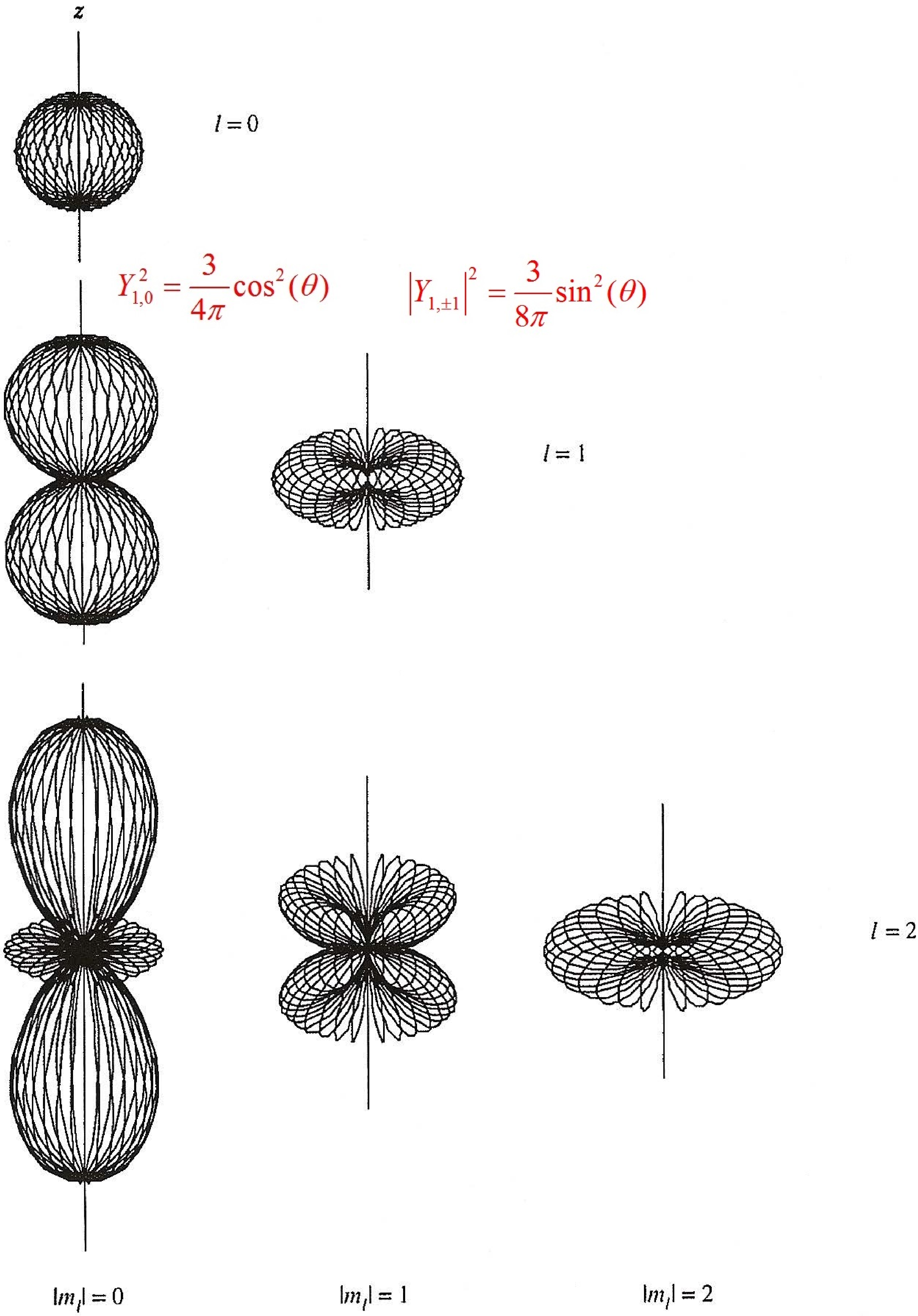
Parity.



Cartesian: $(x, y, z) \rightarrow (-x, -y, -z)$

Polar coordinates: $r \rightarrow r, \theta \rightarrow \pi - \theta, \varphi \rightarrow \varphi + \pi$

Spherical harmonics $Y_{\ell,m}(\pi - \theta, \varphi + \pi) = (-1)^{\ell} \cdot Y_{\ell,m}(\theta, \varphi)$



$$Y_{1,0}^2 = \frac{3}{4\pi}\cos^2(\theta) \qquad \left|Y_{1,\pm 1}\right|^2 = \frac{3}{8\pi}\sin^2(\theta)$$

Spin angular momentum, S

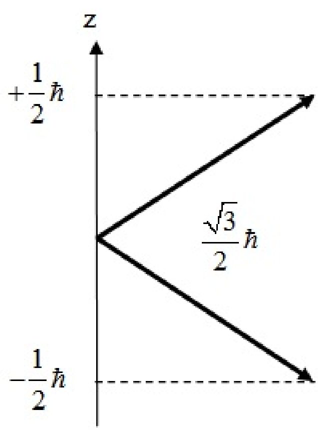
McMurry Ch 6.2

Magnitude quantum number $s = 1/2$

$$\mathbf{S} = \hbar\sqrt{s(s+1)} \Rightarrow S = |\mathbf{S}| = \frac{\sqrt{3}}{2}\hbar$$

Projection quantum number $m_s = \pm 1/2$

$$S_z = m_s\hbar = \pm\frac{1}{2}\hbar$$



$$\chi_{1/2,m_s}(sz) = \delta_{m_s,sz} \Leftrightarrow \begin{cases} \chi_{1/2,\pm1/2}(\pm 1/2) = 1 \\ \chi_{1/2,\pm1/2}(\mp 1/2) = 0 \end{cases}$$