Angular Momentum: Definitions

An **angular momentum** in quantum mechanics is a vector operator $\hat{\mathbf{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$ whose properties are defined by the commutation relations

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z \qquad [\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x \qquad [\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y$$

The commutation relations show that $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are not compatible observables. Therefore, $\hat{\mathbf{J}}$ does not have eigenstates, and a physical angular momentum vector cannot be precisely specified or determined for any quantum-mechanical system.

However, the operator $\hat{\mathbf{J}}^2 \equiv \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ is an observable that corresponds to the square of the magnitude of the physical angular momentum. $\hat{\mathbf{J}}^2$ commutes with each component of $\hat{\mathbf{J}}$:

$$[\hat{\mathbf{J}}^2, \hat{J}_x] = [\hat{\mathbf{J}}^2, \hat{J}_y] = [\hat{\mathbf{J}}^2, \hat{J}_z] = 0$$

important

$\hat{\mathbf{J}}^2$ and one of the components of $\hat{\mathbf{J}}$ can be chosen as a pair of commuting observables for simultaneously specifying the (square) magnitude of an angular momentum vector, and one of the components of the angular momentum vector. Typically, $\{\hat{\mathbf{J}}, \hat{J}_z\}$ is chosen as the CSCO for angular momentum problems; the z axis is then called the **quantization axis**. Other angular momentum operators used in calculations are

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y \qquad \hat{J}_x = \tfrac{1}{2}(\hat{J}_+ + \hat{J}_-)$$
$$\hat{J}_- = \hat{J}_x - i\hat{J}_y \qquad \hat{J}_y = -\tfrac{i}{2}(\hat{J}_+ - \hat{J}_-)$$

where $\hat{J}_+$ and $\hat{J}_-$ are non-Hermitian **angular momentum ladder operators** that have the following relations:

$$[\hat{J}_z, \hat{J}_+] = \hbar\hat{J}_+$$
$$[\hat{J}_z, \hat{J}_-] = -\hbar\hat{J}_-$$
$$[\hat{\mathbf{J}}^2, \hat{J}_+] = [\hat{\mathbf{J}}^2, \hat{J}_-] = 0$$
$$\hat{J}_+\hat{J}_- = \hat{\mathbf{J}}^2 - \hat{J}_z^2 + \hbar\hat{J}_z$$
$$\hat{J}_-\hat{J}_+ = \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar\hat{J}_z$$

Angular Momentum: Eigenvalues and Eigenstates

The eigenvalue equations for $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ are

$$\hat{\mathbf{J}}^2|j,m_j\rangle = j(j+1)\hbar^2|j,m_j\rangle$$

$$\hat{J}_z|j,m_j\rangle = m_j\hbar|j,m_j\rangle$$

$\{j \in \mathbb{N}^0\}$ or $\{j \in \mathbb{N}^0 + 1/2\}$ (a "half-integer")

For any specific j : $m_j \in \{-j, -j+1, \ldots, j-1, j\}$

In the eigenvalue equations, j can be an integer or **half-integer** (i.e., half of an odd integer) greater than or equal to zero. For any given j, there are $2j+1$ possible values of m_j. The state $|j,m_j\rangle$ is interpreted as having a magnitude of angular momentum that is precisely $\hbar\sqrt{j(j+1)}$, and a z-component of angular momentum of precisely $m_j\hbar$.

When a particle with physical angular momentum is placed in an external magnetic field that points in the $\hat{\mathbf{z}}$ direction, the total energy of the particle depends on the magnitude of the field and on m_j, as described on page 71. For this reason, m_j is called the **magnetic quantum number**. Note that unless explicitly stated otherwise, the magnetic quantum numbers in this *Field Guide* are always associated with the z-component of angular momentum, although magnetic quantum numbers can be associated with any spatial direction.

Angular momentum ladder operators act on $|j,m_j\rangle$ as follows:

$$\hat{J}_+|j,m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j+1)}\,|j,m_j+1\rangle$$

$$\text{for } -j \le m_j \le j-1 \quad (\hat{J}_+|j,m_j=j\rangle = 0)$$

$$\hat{J}_-|j,m_j\rangle = \hbar\sqrt{j(j+1) - m_j(m_j-1)}\,|j,m_j-1\rangle$$

$$\text{for } -j+1 \le m_j \le j \quad (\hat{J}_-|j,m_j=-j\rangle = 0)$$

For a given j, the discretely indexed orthonormal basis $\{|j,m_j\rangle\}$ spans the $(2j+1)$-dimensional state space $\mathcal{E}_j$.

Orbital Angular Momentum: Operators

Orbital angular momentum (OAM) is one type of angular momentum in quantum mechanics for which

- The angular momentum quantum number j is necessarily a positive integer
- The angular momentum eigenstates $\{|j, m_j\rangle\}$ can be expressed in the position representation as functions of position coordinates; these functions are the spherical harmonics (page 100)

Instead of the generic quantum-number letters j and m_j, and the operator $\hat{\mathbf{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$, the letters l and m_l are usually used for OAM quantum numbers, and $\hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$ usually specifies an OAM vector operator.

The OAM eigenstates and eigenvalues are defined by the eigenvalue equations

$$\hat{\mathbf{L}}^2|l, m_l\rangle = l(l+1)\hbar^2|l, m_l\rangle$$

$$\hat{L}_z|l, m_l\rangle = m_l\hbar|l, m_l\rangle$$

$$\{l \in \mathbb{N}^0\}$$

For any specific l: $m_l \in \{-l, -l+1, \ldots, l-1, l\}$

Physically, OAM corresponds to the motion of a particle or the flow of a probability current through positions in space that periodically or momentarily orbit about some coordinate system's origin. For this reason, the OAM eigenstates $\{|l, m_l\rangle\}$ may be expressed in the position representation. OAM is involved when characterizing (for example):

- Angular momentum of an electron about an atomic nucleus
- The motion of particle about the center of a 2D or 3D harmonic oscillator potential well
- Rotation of a molecule

Orbital Angular Momentum: Position Representation

For a particle with position and momentum vector operators $\hat{\mathbf{R}}$ and $\hat{\mathbf{P}}$, the vector operator associated with OAM about the coordinate system origin is

$$\hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z) = \hat{\mathbf{R}} \times \hat{\mathbf{P}}$$

In Cartesian coordinates and with $\mathbf{r} = (x, y, z)$, the position representation of $\hat{\mathbf{L}}$ is obtained by substituting the position-representation operations of $\hat{\mathbf{R}}$ and $\hat{\mathbf{P}}$ (i.e., $\mathbf{r}$ and $-i\hbar\nabla$, respectively) into the expression above, giving

$$\begin{aligned}\mathbf{L}_{\{\mathbf{r}\}} &= -i\hbar(\mathbf{r} \times \nabla) \\ &= -i\hbar\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right]\end{aligned}$$

In spherical coordinates (page 115), ∇ is given by

$$\nabla = \hat{\mathbf{r}}\frac{\partial}{\partial r} + \hat{\boldsymbol{\theta}}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

and the x, y, and z components of $\hat{\mathbf{L}}$ are written in the position representation as

$$(L_x)_{\{\mathbf{r}\}} = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$(L_y)_{\{\mathbf{r}\}} = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$(L_z)_{\{\mathbf{r}\}} = -i\hbar\frac{\partial}{\partial\phi}$$

In spherical coordinates, $\mathbf{L}_{\{\mathbf{r}\}}$ and $\mathbf{L}^2_{\{\mathbf{r}\}}$ are

$$\mathbf{L}_{\{\mathbf{r}\}} = -i\hbar\left(\hat{\boldsymbol{\phi}}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right)$$

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

which have an orthonormal set of eigenfunctions called the **spherical harmonics**, described on page 100. These functions are the position-representation wavefunctions corresponding to the state vectors $\{|l, m_l\rangle\}$. Also see page 116.

Spin Angular Momentum

Spin angular momentum, or **spin**, is the second type of angular momentum in quantum mechanics. While the magnitude and one component of a spin vector can be specified, in the absence of orbital angular momentum neither a particle with spin nor any portion of the particle's mass density can be said to "orbit" around that axis as if it were a spinning object. Spin states and spin operators do not have position representations.

Instead of a general angular momentum operator $\hat{\mathbf{J}}$ and the quantum numbers j and m_j (pages 63–64), spin is often denoted by the operator $\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ and quantum numbers s and m_s.

The spin eigenstates and eigenvalues are defined by the eigenvalue equations

$$\hat{\mathbf{S}}^2|s, m_s\rangle = s(s+1)\hbar^2|s, m_s\rangle$$

$$\hat{S}_z|s, m_s\rangle = m_s\hbar|s, m_s\rangle$$

$$\{s \in \mathbb{N}^0\} \quad \text{or} \quad \{s \in \mathbb{N}^0 + 1/2\} \text{ (a half-integer)}$$

$$\text{For any given } s\text{: } m_s \in \{-s, -s+1, \ldots, s-1, s\}$$

The spin quantum number s can be an integer or half-integer. An elementary particle's spin s is an immutable property of the particle, like its mass and electric charge. Composite particles formed from elementary particles also have an associated spin. For example, every electron, quark, proton, and neutron has a spin quantum number $s = 1/2$.

The equations given on pages 63–64 hold for any angular momentum: a single particle's orbital or spin angular momentum, or the total angular momentum of a system (page 82). Therefore, it is common to use symbols other than $\hat{\mathbf{J}}$, $\hat{\mathbf{L}}$, and $\hat{\mathbf{S}}$ (and their associated quantum numbers) to differentiate various angular momentum quantities. Symbols used to express the various angular momenta of atoms are given on page 101.

Spin Angular Momentum: $s = 1/2$

The $s = 1/2$ problem has a 2D state space $\mathcal{E}_{s=1/2}$, meaning that any orthonormal basis that spans $\mathcal{E}_{s=1/2}$ has exactly two elements. The basis elements can be denoted $|+\rangle_u$ and $|-\rangle_u$, which are respectively read as "spin up and spin down along the $\hat{\mathbf{u}}$ direction." The x, y, and z components of the unit vector $\hat{\mathbf{u}}$ are written using spherical coordinates (page 115) as

$$\hat{\mathbf{u}} = (\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)$$

For example, the pair of angles $\theta = \pi/2$ and $\phi = 0$ indicates the unit vector $\hat{\mathbf{u}} = (1, 0, 0)$, which is the $\hat{\mathbf{x}}$ direction.

$|+\rangle_u$ and $|-\rangle_u$ are the common eigenstates of $\hat{\mathbf{S}}^2$ and $\hat{S}_u$, where

$$\hat{S}_u = \hat{\mathbf{S}} \cdot \hat{\mathbf{u}} = \hat{S}_x \sin\theta\cos\phi + \hat{S}_y \sin\theta\sin\phi + \hat{S}_z \cos\theta$$

$$|\pm\rangle_u = |s = 1/2, m_u = \pm 1/2\rangle$$

In the case above, the magnetic quantum number m_u is associated with the component of spin about $\hat{\mathbf{u}}$, which does not necessarily equal $\hat{\mathbf{z}}$. The eigenvalues of $\hat{S}_u$ are $\pm\hbar/2$: $|+\rangle_u$ is associated with the eigenvalue $\hbar/2$, and $|-\rangle_u$ is associated with the eigenvalue $-\hbar/2$:

$$\hat{S}_u|\pm\rangle_u = \pm\frac{\hbar}{2}|\pm\rangle_u$$

The eigenstates of $\hat{S}_u$ can be expanded into the $\{|\pm\rangle_z\}$ basis where $|+\rangle_z \equiv |s = 1/2, m_s = 1/2\rangle$ is the ket for "spin up along $\hat{\mathbf{z}}$," and $|-\rangle_z \equiv |s = 1/2, m_s = -1/2\rangle$ is the ket for "spin down along $\hat{\mathbf{z}}$" (see page 67). The following normalized state vectors follow the global phase **conventions** specified on page 114 (i.e., the first non-zero expansion coefficient—associated with $|+\rangle_z$ in this case—is real and positive):

$$|+\rangle_u = \cos(\theta/2)|+\rangle_z + \sin(\theta/2)e^{i\phi}|-\rangle_z \qquad \text{L18}$$

$$|-\rangle_u = \sin(\theta/2)|+\rangle_z - \cos(\theta/2)e^{i\phi}|-\rangle_z$$

Expressing the eigenstates of $\hat{S}_x$ (for which $\theta = \pi/2$ and $\phi = 0$) and $\hat{S}_y$ (for which $\theta = \pi/2$ and $\phi = \pi/2$) in terms of the $\{|\pm\rangle_z\}$ basis is then straightforward:

	Spin along x	**Spin along y**
Spin up	$\|+\rangle_x = \frac{1}{\sqrt{2}}\|+\rangle_z + \frac{1}{\sqrt{2}}\|-\rangle_z$	$\|+\rangle_y = \frac{1}{\sqrt{2}}\|+\rangle_z + \frac{i}{\sqrt{2}}\|-\rangle_z$
Spin down	$\|-\rangle_x = \frac{1}{\sqrt{2}}\|+\rangle_z - \frac{1}{\sqrt{2}}\|-\rangle_z$	$\|-\rangle_y = \frac{1}{\sqrt{2}}\|+\rangle_z - \frac{i}{\sqrt{2}}\|-\rangle_z$

Pauli Spin Operators

The $s = 1/2$ spin operators $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ can be written in terms of the **Pauli spin operators** $\hat{\sigma}_x$, $\hat{\sigma}_y$, and $\hat{\sigma}_z$:

$$\hat{S}_x = \tfrac{\hbar}{2}\hat{\sigma}_x \qquad \hat{S}_y = \tfrac{\hbar}{2}\hat{\sigma}_y \qquad \hat{S}_z = \tfrac{\hbar}{2}\hat{\sigma}_z$$

These three relations are compactly expressed together as $\hat{\mathbf{S}} = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}$, where $\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$. Each Pauli spin operator $\hat{\sigma}_u$ (where $u \in \{x, y, z\}$) has the eigenvalues ± 1, with the same eigenstates as those of $\hat{\mathbf{S}}^2$ and $\hat{S}_u$ for a system with $s = 1/2$.

Using the $\{|\pm\rangle_z\}$ representation, the Pauli spin operators are expressed as 2×2 **Pauli spin matrices**. Following standard notation conventions, these are defined as

$$\sigma_x \equiv \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \sigma_y \equiv \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \sigma_z \equiv \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

The eigenvectors of the Pauli spin matrices are given below (each eigenvector is listed below its associated eigenvalue).

	Eigenvectors of Pauli Spin Matrices					
Matrix	σ_x		σ_y		σ_z	
Eigenvalues	1	-1	1	-1	1	-1
Eigenvectors	$\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{-1}{\sqrt{2}} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{-i}{\sqrt{2}} \end{bmatrix}$	$\begin{bmatrix} 1 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 0 \\ 1 \end{bmatrix}$

The Pauli spin operators have the commutation relations

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z \qquad [\hat{\sigma}_y, \hat{\sigma}_z] = 2i\hat{\sigma}_x \qquad [\hat{\sigma}_z, \hat{\sigma}_x] = 2i\hat{\sigma}_y$$

The Pauli spin operators, matrices, and their eigenvalues and eigenvectors are also commonly used in **two-level problems** that do not necessarily involve a physical spin angular momentum (page 75).

Angular Momentum $j = 1$

For a system with the generalized angular momentum quantum number $j = 1$, the eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ form the three-element basis

$$\{|j = 1, m_j = 1\rangle, |j = 1, m_j = 0\rangle, |j = 1, m_j = -1\rangle\}$$

that spans the state space $\mathcal{E}_{j=1}$. In a representation defined by this basis, the three components of the $j = 1$ angular momentum operator $\hat{\mathbf{J}}$, and their eigenvalues and orthonormal eigenvectors, are given in the following table. For each operator, the associated matrix is given below the operator. For each matrix, the eigenvectors are listed immediately below their associated eigenvalues $\hbar$, 0, and $-\hbar$.

$j = 1$ Angular Momentum Matrices, Eigenvectors

$\hat{J}_x$			$\hat{J}_y$			$\hat{J}_z$		
$\frac{\hbar}{\sqrt{2}}\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$			$\frac{\hbar}{\sqrt{2}}\begin{bmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{bmatrix}$			$\hbar\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$		
$\hbar$	0	$-\hbar$	$\hbar$	0	$-\hbar$	$\hbar$	0	$-\hbar$
$\begin{bmatrix} \frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{-1}{\sqrt{2}} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} \\ \frac{-1}{\sqrt{2}} \\ \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} \\ \frac{i}{\sqrt{2}} \\ \frac{-1}{2} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} \\ \frac{-i}{\sqrt{2}} \\ \frac{-1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$

The $j = 1$ case can apply to various systems, including spin and orbital angular momentum problems. For example, the electron of hydrogen (page 97) can exist in an excited state with orbital angular momentum quantum number $l = 1$. In this case, there are three possible outcomes of a measurement of the electron's component of orbital angular momentum about any direction: $\hbar$, 0, and $-\hbar$. As another example, two spin-1/2 particles might together form a system with a net spin quantum number $s = 1$ (see the rules for addition of angular momenta, page 82). In this case, also, $\hbar$, 0, and $-\hbar$ are the possible outcomes of a measurement of the component of the system's net spin about any spatial direction.

Magnetic Dipole Moments and Magnetic Fields

When placed in an external vector **magnetic field** $\mathbf{B}$, a classical **magnetic dipole moment** $\boldsymbol{\mu}$ has a potential energy due to its interaction with the field that is given by

$$W_B = -\boldsymbol{\mu} \cdot \mathbf{B}$$

In quantum mechanics, magnetic dipole moments may correspond to a particle or system's spin, orbital, or net angular momentum. For a system with a generalized angular momentum operator $\hat{\mathbf{J}}$, the magnetic dipole moment operator is

$$\hat{\boldsymbol{\mu}} = \gamma \hat{\mathbf{J}}$$

where γ is the **gyromagnetic ratio**, a constant of proportionality between $\hat{\boldsymbol{\mu}}$ and $\hat{\mathbf{J}}$ that has a numerical value that depends the specific particle or system. As is the case with angular momentum, the direction of a particle's magnetic moment cannot be precisely specified, and the operator $\hat{\boldsymbol{\mu}}$ is therefore not an observable (although its magnitude $|\hat{\boldsymbol{\mu}}|$ can be precisely specified and is proportional to the magnitude of angular momentum).

In atomic and nuclear physics, the magnitudes of magnetic dipole moments are commonly specified in terms of either μ_B or μ_N. The **Bohr magneton** μ_B is used to quantify the magnetic dipole moments of electrons with spin or orbital angular momenta, or of atoms with net angular momenta arising from a sum of the net spin and orbital angular momenta of all electrons and the nuclear spin. The **nuclear magneton** μ_N is used to express magnetic dipole moments arising from the spin of neutrons, protons, and atomic nuclei. The Bohr and nuclear magnetons are

$$\mu_B = \frac{e\hbar}{2m_e} \approx 9.274 \times 10^{-24}\,\text{J/T}$$

$$\mu_N = \frac{e\hbar}{2m_p} \approx 5.051 \times 10^{-27}\,\text{J/T}$$

where e is the fundamental unit of electric charge, and m_e and m_p are the masses of the electron and proton, respectively.

Gyromagnetic Ratios and *g*-Factors

Gyromagnetic ratios in nuclear- and atomic-physics problems are commonly expressed in terms of either the Bohr magneton μ_B or the nuclear magneton μ_N and a dimensionless number called the ***g*-factor**, denoted as g. The table below lists the relationships between angular momenta, magnetic dipole moments, gyromagnetic ratios, and g-factors for the angular momenta associated with an atom.

In the table, $\hat{\mathbf{S}}$ is the vector spin operator for the particle in question (the spin quantum number $s = 1/2$ applies to a single electron, proton, and neutron) or for the net spin angular momentum of all electrons in an atom. $\hat{\mathbf{I}}$ is the operator for nuclear spin, and $\hat{\mathbf{L}}$ is an OAM operator for a single electron or the net OAM of all electrons in an atom.

Angular Momentum	Magnetic Dipole Moment	Gyromagnetic Ratio	*g*-Factor
Electron spin	$\hat{\boldsymbol{\mu}}_e = \gamma_e \hat{\mathbf{S}}$	$\gamma_e = g_e \mu_B / \hbar$	$g_e \approx -2.002$
Proton spin	$\hat{\boldsymbol{\mu}}_p = \gamma_p \hat{\mathbf{S}}$	$\gamma_p = g_p \mu_N / \hbar$	$g_p \approx -5.586$
Neutron spin	$\hat{\boldsymbol{\mu}}_n = \gamma_n \hat{\mathbf{S}}$	$\gamma_n = g_n \mu_N / \hbar$	$g_n \approx -3.826$
Nuclear spin	$\hat{\boldsymbol{\mu}}_I = \gamma_I \hat{\mathbf{I}}$	$\gamma_I = g_I \mu_N / \hbar$	$\lvert g_I \rvert$ varies (on the order of 1)
Electron OAM	$\hat{\boldsymbol{\mu}}_L = \gamma_L \hat{\mathbf{L}}$	$\gamma_L = -g_L \mu_B / \hbar$	$g_L = 1 - \frac{m_e}{M_N}$ (for nuclear mass M_N)
			$g_L = 1$ (in the limit $M_N \approx \infty$)

An alternative expression for the nuclear gyromagnetic ratio is $\gamma_I = g_I \mu_B / \hbar$, in which case $|g_I| \ll 1$.

Magnetic Moment Dynamics: Uniform Fields

For problems in which the only energy involved is the energy of a magnetic moment $\hat{\boldsymbol{\mu}}$ interacting with an external magnetic field $\mathbf{B}$, the Hamiltonian is (see page 71)

$$\hat{H} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = -\gamma \hat{\mathbf{J}} \cdot \mathbf{B}$$

where γ is the gyromagnetic ratio (pages 71–72), and $\hat{\mathbf{J}}$ is a generalized angular momentum (spin, orbital, or net angular momentum) associated with an angular momentum quantum number j.

Uniform magnetic field: For this case, $\mathbf{B}$ is constant in time and is spatially homogeneous, with a magnitude B_0. Here it is assumed that $\mathbf{B}$ points in the $\hat{\mathbf{z}}$ direction. For these conditions,

$$\hat{H} = -\gamma B_0 \hat{J}_z$$

The energy eigenstates are therefore the $\{|j, m_j\rangle\}$ eigenstates of $\hat{J}_z$. The energy eigenvalues are

$$E_m = -\gamma B_0 \hbar m_j = \hbar \omega_L m_j$$

where $\omega_L \equiv -\gamma B_0$ is called the **Larmor frequency**. Note that the determination of whether a given state has a higher or lower energy eigenvalue than another state depends on the sign of γ.

Spin precession: Consider a particle with spin quantum number $s = 1/2$ in a uniform magnetic field of magnitude B_0 that points in the $\hat{\mathbf{z}}$ direction. The energy eigenvalues are given by $\pm\frac{1}{2}\hbar\omega_L = \mp\frac{1}{2}\gamma B_0 \hbar$. Suppose also that the particle has a spin expectation value at time $t = 0$ that points in the $\hat{\mathbf{u}}$ direction: $\langle\hat{\mathbf{S}}\rangle(t=0) = \frac{\hbar}{2}\hat{\mathbf{u}}$. For $t > 0$, the vector $\langle\hat{\mathbf{S}}\rangle(t)$ precesses about $\hat{\mathbf{z}}$ with angular frequency ω_L. This precession of $\langle\hat{\mathbf{S}}\rangle(t)$ is called spin precession or **Larmor precession**. Note that it is $\langle\hat{\mathbf{S}}\rangle$ that precesses, not a physical angular momentum vector itself, since the latter quantity cannot be precisely specified in quantum mechanics. Spin precession is illustrated on pages 80–81 for a spin-1/2 system.

Magnetic Moment Dynamics: Gradient Fields

A particle associated with a magnetic-dipole-moment operator $\hat{\boldsymbol{\mu}} = \gamma\hat{\mathbf{J}}$ will experience a state-dependent force when the particle moves through an inhomogeneous magnetic field $\mathbf{B}(x, y, z)$. For simplicity, a magnetic field that points along the $\hat{\mathbf{z}}$ direction is considered, with a magnitude that varies linearly with z: $\mathbf{B}(x, y, z) = (0, 0, zB')$, where B' is a constant value that is the spatial **gradient** of the magnetic field.

Neglecting kinetic energy and considering only the magnetic dipole interaction energy, the Hamiltonian in the region of the field gradient is

$$\hat{H} = -\gamma z B' \hat{J}_z$$

The energy eigenstates in the field gradient are the $\{|j, m_j\rangle\}$ eigenstates of $\hat{J}_z$. However, the energy eigenvalues are spatially dependent; they are given by $E_m(z) = -\gamma z B' \hbar m_j$. Due to the gradient B', there is an m_j-dependent force in the $\hat{\mathbf{z}}$ direction:

$$\mathbf{F}_m = -\nabla E_m(z) = \gamma B' \hbar m_j \hat{\mathbf{z}}$$

If a particle in the state $|j, m_j\rangle$ has a trajectory (along $\hat{\mathbf{x}}$, say) that passes through a region with the field gradient given above, the particle will experience a positive or negative force and therefore receive a positive or negative momentum kick along the $\hat{\mathbf{z}}$ direction; the direction and magnitude of the momentum kick depend on m_j.

If the particle is in a superposition of $|j, m_j\rangle$ states, each superposition component will be associated with a different momentum kick, therefore correlating or **entangling** the different superposition components with different propagation directions. This is the **Stern–Gerlach effect**. The deflections are quantized, with the deflection for each component of the superposition depending on that component's magnetic quantum number, which is then correlated with a final measured position of the particle. With various orientiations of the magnetic field gradient, the Stern–Gerlach effect can be used to measure the possible values of m_j for a sample or beam of identical particles, the fraction of particles with each m_j value, and the angular momentum quantum number j for the particles.

Two-Level Systems

Two-level systems are systems that have a state-space dimension of two. Any basis for the system consists of exactly two elements; a spin-1/2 system is an example. A simple generalized two-level problem begins with a time-independent Hamiltonian $\hat{H}_0$ with eigenstates and eigenvalues defined by

$$\hat{H}_0|a\rangle = E_a|a\rangle \qquad \text{and} \qquad \hat{H}_0|b\rangle = E_b|b\rangle$$

Now consider the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{W}$, where $\hat{W}$ is time-independent and has off-diagonal matrix elements in the $\{|a\rangle, |b\rangle\}$ representation, so that $|a\rangle$ and $|b\rangle$ are not stationary states of the full Hamiltonian $\hat{H}$. $\hat{W}$ may be called a **coupling** or **perturbation Hamiltonian**. In the $\{|a\rangle, |b\rangle\}$ representation $\hat{W}$ can be expressed in terms of its matrix elements as

$$W_{\{ab\}} = \begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix} = \begin{bmatrix} W_{aa} & 0 \\ 0 & W_{bb} \end{bmatrix} + \frac{\hbar}{2}\begin{bmatrix} 0 & \Omega_0^* \\ \Omega_0 & 0 \end{bmatrix}$$

where $\Omega_0 = 2W_{ba}/\hbar = 2\langle b|\hat{W}|a\rangle/\hbar$ is a complex number, and $|\Omega_0|$ quantifies the strength of coupling between $|a\rangle$ and $|b\rangle$. $\hat{H}$ can then be represented by

$$H_{\{ab\}} = E_c\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{\hbar}{2}\begin{bmatrix} \Delta & \Omega_0^* \\ \Omega_0 & -\Delta \end{bmatrix}$$

where

$$E_c \equiv (E_a + E_b)/2 + (W_{aa} + W_{bb})/2$$
$$\Delta \equiv (E_a - E_b)/\hbar + (W_{aa} - W_{bb})/\hbar$$

The parameter Δ is an angular frequency called the **detuning**. The eigenvalue equation for $\hat{H}$ is written as $\hat{H}|\pm\rangle = E_\pm|\pm\rangle$, where $E_+ \geq E_-$, and is solved by

$$E_\pm = E_c \pm \frac{\hbar\Omega}{2}$$
$$|+\rangle = \cos(\theta/2)|a\rangle + \sin(\theta/2)e^{i\phi}|b\rangle$$
$$|-\rangle = \sin(\theta/2)|a\rangle - \cos(\theta/2)e^{i\phi}|b\rangle$$

where Ω, θ, and ϕ are defined by

$$\tan(\theta) = |\Omega_0|/\Delta \qquad \Omega_0 = |\Omega_0|e^{i\phi} \qquad \Omega = \sqrt{\Delta^2 + |\Omega_0|^2}$$

Rabi Oscillations

When the eigenstates $|a\rangle$ and $|b\rangle$ of a two-level Hamiltonian $\hat{H}_0$ are coupled by $\hat{W}$, as in the two-level system defined on page 75, the probabilities of finding the system in either state $|a\rangle$ or $|b\rangle$ become time dependent.

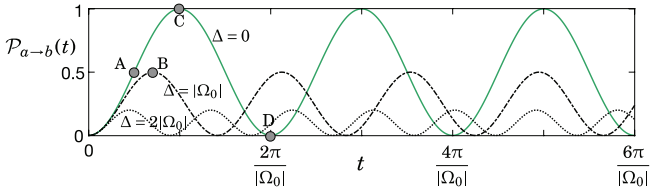
The typical case is one in which the system is known to be in state $|a\rangle$ (or $|b\rangle$) at time $t = 0$ and to then determine the **transition probability** $\mathcal{P}_{a\to b}$ (or $\mathcal{P}_{b\to a}$) that the system would be found in state $|b\rangle$ (or $|a\rangle$) at a later time t. Consider the case that the system is in state $|a\rangle$ at time $t = 0$:

$$|\psi(t=0)\rangle = |a\rangle$$

Using the symbols defined on page 75, the transition probability $\mathcal{P}_{a\to b}(t)$ from state $|a\rangle$ to $|b\rangle$ is sinusoidal in time with a frequency Ω, called the **Rabi frequency**. Ω_0 is called the **resonant** or **bare Rabi frequency**. The probability oscillations are called **Rabi oscillations**. For $|\psi(t=0)\rangle = |a\rangle$, the probability that the system would be found in state $|b\rangle$ is given by

$$\mathcal{P}_{a\to b}(t) = \frac{|\Omega_0|^2}{\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right)$$

The plot below illustrates Rabi oscillations for three values of the detuning Δ.



In the plot, points A and B, for which $\mathcal{P}_{a\to b} = 0.5$, indicate times when the system is in an equal-probability superposition of states $|a\rangle$ and $|b\rangle$; point A is for $\Delta = 0$ (green line), and point B is for $\Delta = |\Omega_0|$ (dot-dashed line). For the $\Delta = 0$ curve, point C indicates the total time $t = \pi/|\Omega_0|$ (a "**π pulse**") at which there is a transition probability $\mathcal{P}_{a\to b} = 1$. Also for $\Delta = 0$, point D indicates the total time $t = 2\pi/|\Omega_0|$ (a "**2π pulse**") at which the transition probability is $\mathcal{P}_{a\to b} = 0$.

The Bloch Vector

In a two-level system with a 2D state space $\mathcal{E}_2$ spanned by a basis $\{|a\rangle, |b\rangle\}$, any arbitrary state vector $|\psi\rangle \in \mathcal{E}_2$ can be written as $|\psi\rangle = c_a|a\rangle + c_b|b\rangle$. The Pauli spin operators (page 69) are used to construct the **Bloch vector** for state $|\psi\rangle$, defined as

$$\langle\hat{\boldsymbol{\sigma}}\rangle = \langle\psi|\hat{\boldsymbol{\sigma}}|\psi\rangle = (\langle\psi|\hat{\sigma}_x|\psi\rangle, \langle\psi|\hat{\sigma}_y|\psi\rangle, \langle\psi|\hat{\sigma}_z|\psi\rangle)$$

The Bloch vector is used in generalized two-level problems even when the problem does not have a physical spin. The components of the Bloch vector for state $|\psi\rangle$ are

$$\langle\hat{\sigma}_x\rangle = c_a^* c_b + c_a c_b^* = 2\mathrm{Re}\{c_a^* c_b\}$$
$$\langle\hat{\sigma}_y\rangle = -i(c_a^* c_b - c_a c_b^*) = 2\mathrm{Im}\{c_a^* c_b\}$$
$$\langle\hat{\sigma}_z\rangle = |c_a|^2 - |c_b|^2$$

By defining θ and ϕ via the relations

$$\cos\theta = |c_a|^2 - |c_b|^2 \quad \text{and} \quad e^{i\phi} = \frac{c_a^*}{|c_a|} \cdot \frac{c_b}{|c_b|}$$

so that ϕ is the phase of c_b with respect to c_a (unless $|c_a|$ or $|c_b|$ equals 0 or 1, for which ϕ is undefined), the state vector $|\psi\rangle$ can be expressed as

$$|\psi\rangle = \cos(\theta/2)|a\rangle + \sin(\theta/2)e^{i\phi}|b\rangle$$

up to a negligible global phase factor. The Bloch vector can then be written as

$$\langle\hat{\boldsymbol{\sigma}}\rangle = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$$

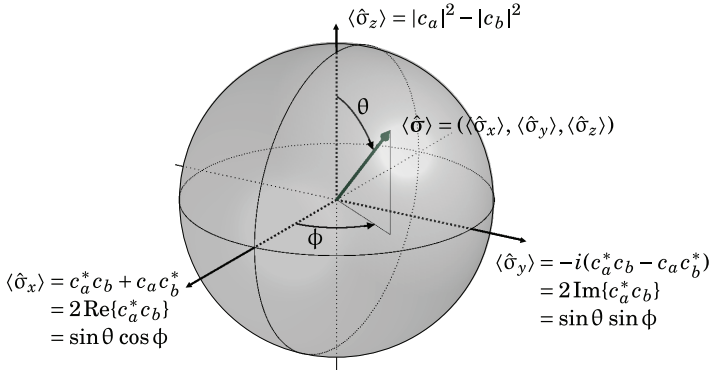
From this it is straightforward to determine that the Bloch vector associated with any state vector has unit magnitude:

$$||\langle\hat{\boldsymbol{\sigma}}\rangle|| = \sqrt{|\langle\hat{\sigma}_x\rangle|^2 + |\langle\hat{\sigma}_y\rangle|^2 + |\langle\hat{\sigma}_z\rangle|^2} = 1$$

The results above show that there is a one-to-one correspondence between any given state vector $|\psi\rangle$ of a 2D state space and a Bloch vector $\langle\hat{\boldsymbol{\sigma}}\rangle$ that has unit magnitude and points in a direction (in an abstract 3D coordinate space) that is completely determined by $|\psi\rangle$. This correspondence results from the fact that both $|\psi\rangle$ and $\langle\hat{\boldsymbol{\sigma}}\rangle$ are uniquely determined by the same pair of angles θ and ϕ, where $0 \le \theta \le \pi$, and $0 \le \phi < 2\pi$.

The Bloch Sphere

Due to the one-to-one correspondence between all unit-magnitude Bloch vectors (page 77) and the state vectors of a two-level system, the dynamics of quantum states in a two-level system can be characterized by the dynamics of a 3D Bloch vector. Since the Bloch vector corresponding to a state vector $|\psi\rangle$ has unit magnitude, the associated Bloch vector dynamics correspond to the motion of a point on the surface of a unit sphere. This abstract sphere is called the **Bloch sphere**, below, and exists in the same abstract 3D coordinate system as that of the Bloch vector (in green). The Bloch vector that corresponds to the state $|\psi\rangle$ is defined by the angles θ and ϕ.



The Bloch sphere provides a powerful means of visualizing the dynamics of the state of a two-level system under the influence of a Hamiltonian that couples the two elements of the chosen basis, which are visually represented by the north and south poles of the sphere. If the Hamiltonian $\hat{H}$ is time independent, then there is an abstract stationary vector in the Bloch sphere diagram about which the time-dependent Bloch vector $\langle\hat{\boldsymbol{\sigma}}\rangle(t)$ precesses. Plotting Bloch vector dynamics on the Bloch sphere is a graphical visualization alternative to Rabi oscillation plots, as shown on page 76. The example presented on pages 79–81 illustrates Bloch vector precession for a spin-1/2 particle in a uniform magnetic field.

Spin 1/2 in a Uniform Magnetic Field

The problem of a spin-1/2 particle in a uniform magnetic field ties together the concepts of spin precession, Rabi oscillations, and Bloch vector dynamics. The following example assumes that a spin-1/2 particle is initially in the $|+\rangle_z$ (spin-up along $\hat{\mathbf{z}}$) eigenstate of a Hamiltonian

$$\hat{H}_0 = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}_z = \frac{1}{2}\hbar\omega_z\hat{\sigma}_z$$

where $\mathbf{B}_z = B_z(0, 0, 1)$ is a uniform magnetic field of magnitude B_z that points in the $\hat{\mathbf{z}}$ direction, and $\omega_z \equiv -\gamma B_z$, where γ is the gyromagnetic ratio. At time $t = 0$, a second magnetic field $\mathbf{B}_\perp = B_\perp(\cos\phi, \sin\phi, 0)$ is instantaneously applied, and is associated with a second Hamiltonian term

$$\hat{W} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}_\perp = \frac{1}{2}\hbar\omega_\perp(\hat{\sigma}_x\cos\phi + \hat{\sigma}_y\sin\phi)$$

where $\omega_\perp = -\gamma B_\perp$. The problem now is to determine the dynamics of the particle's spin state under the influence of the full Hamiltonian $\hat{H} = \hat{H}_0 + \hat{W}$.

The eigenstates and eigenvalues of $\hat{H}$ are first found using the solutions given on pages 68 and 75. In the $\{|+\rangle_z, |-\rangle_z\}$ representation (labeled below as $\{m_s\}$ due to the fact that $|+\rangle_z$ and $|-\rangle_z$ correspond to the quantum numbers $m_s = 1/2$ and $m_s = -1/2$), the Hamiltonian $\hat{H}$ is expressed as

$$H_{\{m_s\}} = \frac{\hbar}{2}\begin{bmatrix} \omega_z & \omega_\perp e^{-i\phi} \\ \omega_\perp e^{i\phi} & -\omega_z \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} \Delta & \Omega_0^* \\ \Omega_0 & -\Delta \end{bmatrix}$$

where $\Delta = \omega_z$ and $\Omega_0 = \omega_\perp e^{i\phi}$ following the definitions introduced on page 75. The total field $\mathbf{B}_z + \mathbf{B}_\perp$ points in the direction

$$\hat{\mathbf{u}} = \left(\frac{\omega_\perp}{\Omega}\cos\phi,\ \frac{\omega_\perp}{\Omega}\sin\phi,\ \frac{\omega_z}{\Omega}\right)$$

where $\Omega = \sqrt{\omega_z^2 + \omega_\perp^2}$. Defining θ by $\tan\theta = \omega_\perp/\omega_z = B_\perp/B_z$, the spin-up and spin-down eigenstates of $\hat{H}$ along $\hat{\mathbf{u}}$ are

$$|+\rangle_u = \cos(\theta/2)|+\rangle_z + \sin(\theta/2)e^{i\phi}|-\rangle_z$$
$$|-\rangle_u = \sin(\theta/2)|+\rangle_z - \cos(\theta/2)e^{i\phi}|-\rangle_z$$

The respective energy eigenvalues are $E_\pm = \pm\frac{1}{2}\hbar\Omega$.

Spin 1/2 in a Uniform Magnetic Field: Dynamics

For the Hamiltonian $\hat{H}$ given on page 79, and an initial state at time $t = 0$ of $|\psi(0)\rangle = |+\rangle_z$, the state at time t is given by

$$|\psi(t)\rangle = \hat{\mathbb{U}}(t, 0)|+\rangle_z$$

where $\hat{\mathbb{U}}$ is the time evolution operator for $\hat{H}$. In the representation labeled as $\{m_s\}$ (see page 79), $\hat{\mathbb{U}}(t, 0)$ is expressed as

$$\mathbb{U}_{\{m_s\}}(t, 0) = \begin{bmatrix} e^{-i\Omega t/2} & 0 \\ 0 & e^{i\Omega t/2} \end{bmatrix} + i \sin(\Omega t/2) \begin{bmatrix} 1 - \cos\theta & -\sin\theta\, e^{-i\phi} \\ -\sin\theta\, e^{i\phi} & \cos\theta - 1 \end{bmatrix}$$

The time-dependent spin state is then

$$|\psi(t)\rangle = \left(\cos\frac{\Omega t}{2} - i\cos\theta\sin\frac{\Omega t}{2}\right)|+\rangle_z - i\sin\theta\sin\frac{\Omega t}{2}e^{i\phi}|-\rangle_z$$

with a Bloch vector that has the time-dependent components

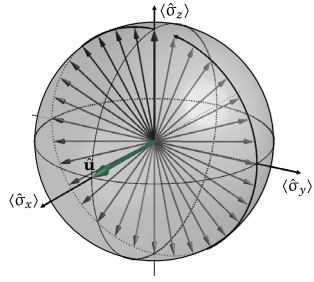
$$\langle\hat{\sigma}_x\rangle(t) = \sin\theta\{\cos\theta\cos\phi[1 - \cos(\Omega t)] + \sin\phi\sin(\Omega t)\}$$
$$\langle\hat{\sigma}_y\rangle(t) = \sin\theta\{\cos\theta\sin\phi[1 - \cos(\Omega t)] - \cos\phi\sin(\Omega t)\}$$
$$\langle\hat{\sigma}_z\rangle(t) = 1 - \sin^2\theta[1 - \cos(\Omega t)]$$

These components define a unit vector $\langle\hat{\boldsymbol{\sigma}}\rangle(t)$ precessing at an angular frequency Ω about $\hat{\mathbf{u}} = (\frac{\omega_\perp}{\Omega}\cos\phi,\ \frac{\omega_\perp}{\Omega}\sin\phi,\ \frac{\omega_z}{\Omega})$; that is, the Bloch vector precesses about a vector corresponding to the magnetic field direction, demonstrating spin precession (page 73).

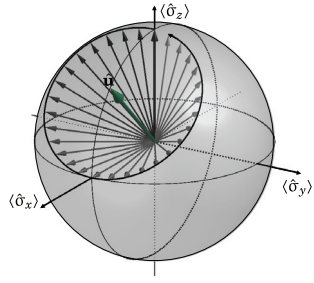
The figures on page 81 illustrate trajectories of $\langle\hat{\boldsymbol{\sigma}}\rangle(t)$ for a spin-1/2 particle's spin state for three cases. $B_\perp$ is assumed to be the same in each case, with $\mathbf{B}_\perp$ pointing in the $\hat{\mathbf{x}}$ direction so that $\phi = 0$. The spin state at time $t = 0$ is $|\psi(0)\rangle = |+\rangle_z$ (the vertical black arrow represents the initial Bloch vector). The trajectories are shown at periodic times throughout nearly one full orbit of the Bloch vector. The vector $\hat{\mathbf{u}}$ corresponding to the direction of the total magnetic field (green arrow) is shown for each case; the Bloch vector precesses about $\hat{\mathbf{u}}$ in a direction that assumes a positive value for the angular frequencies ω_z and $\omega_\perp$.

Bloch Vector Dynamics: Examples

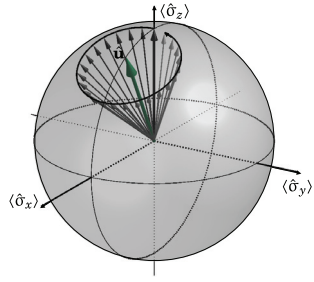
The three Bloch sphere figures below illustrate the precession of a Bloch vector $\langle\hat{\boldsymbol{\sigma}}\rangle$ (darker arrows represent earlier times) about a unit vector $\hat{\mathbf{u}}$ (in green) that corresponds to the direction of an applied constant magnetic field. The figures correspond to the problem defined on pages 79 and 80. These three cases also correspond to the three Rabi oscillation plots on page 76. For this example problem, $\Omega_0 = \omega_\perp = -\gamma B_\perp$ (assumed the same for all figures below), $\Delta = \omega_z = \frac{B_z}{B_\perp}\Omega_0$, and $\Omega = \Omega_0\sqrt{1 + B_z^2/B_\perp^2}$. Values of B_z, Δ, Ω, and θ (where $\tan\theta = |\Omega_0|/\Delta = B_\perp/B_z$) are given for each figure.



- $B_z = 0$
- $\theta = \pi/2$
- $\Delta = 0$
- $\Omega = \Omega_0$



- $B_z = B_\perp$
- $\theta = \pi/4$
- $\Delta = \Omega_0$
- $\Omega = \sqrt{2}\Omega_0$



- $B_z = 2B_\perp$
- $\theta = 0.15\pi$
- $\Delta = 2\Omega_0$
- $\Omega = \sqrt{5}\Omega_0$

Addition of Two Angular Momenta

The total angular momentum of a system may consist of individual angular momenta combined together. The addition of two generalized angular momenta is considered here. The two individual angular momentum vector operators $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ (with z components $\hat{J}_{1z}$ and $\hat{J}_{2z}$, respectively) are associated with the following eigenvalue equations:

$$\hat{\mathbf{J}}_1^2|j_1,m_1\rangle = j_1(j_1+1)\hbar^2|j_1,m_1\rangle$$

$$\hat{\mathbf{J}}_2^2|j_2,m_2\rangle = j_2(j_2+1)\hbar^2|j_2,m_2\rangle$$

$$\hat{J}_{1z}|j_1,m_1\rangle = m_1\hbar|j_1,m_1\rangle$$

$$\hat{J}_{2z}|j_2,m_2\rangle = m_2\hbar|j_2,m_2\rangle$$

The two pairs of individual quantum numbers (j_1,m_1) and (j_2,m_2) separately follow the constraints given on page 64.

The eigenvalues and eigenstates related to the system's total angular momentum are determined by first constructing the vector operator for the **total angular momentum:**

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 = (\hat{J}_x,\hat{J}_y,\hat{J}_z) = (\hat{J}_{1x}+\hat{J}_{2x},\hat{J}_{1y}+\hat{J}_{2y},\hat{J}_{1z}+\hat{J}_{2z})$$

from which is obtained $\hat{\mathbf{J}}^2 = \hat{\mathbf{J}}\cdot\hat{\mathbf{J}} = \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + 2\hat{\mathbf{J}}_1\cdot\hat{\mathbf{J}}_2$.

Tensor-product (TP) basis: When the state spaces associated with j_1 and j_2 are merged, one basis that spans the merged state space is the TP basis expressed as

$$\{|j_1,m_1\rangle|j_2,m_2\rangle\} \quad \text{or} \quad \{|j_1,j_2,m_1,m_2\rangle\}$$

These **tensor-product states** are eigenstates of the CSCO $\{\hat{\mathbf{J}}_1^2,\hat{\mathbf{J}}_2^2,\hat{J}_{1z},\hat{J}_{2z}\}$. The individual angular momentum quantum numbers that appear in these kets may be simultaneously specified or measured to uniquely identify one of the states of the tensor-product basis. However, neither $\hat{J}_{1z}$ nor $\hat{J}_{2z}$ commute with $\hat{\mathbf{J}}^2$, so the states of the TP basis are generally not eigenstates of $\hat{\mathbf{J}}^2$. This means that if the magnitude of the system's total angular momentum is measured, the system would subsequently be found in an eigenstate of $\hat{\mathbf{J}}^2$, as described on page 83, and not in one of the TP basis states.

Total Angular Momentum Basis

When the state spaces associated with individual angular momenta are merged, one basis for the merged state space is the tensor-product basis (page 82). Another basis is the **total angular momentum (TAM) basis**, written as

$$\{|j_1, j_2, J, m_J\rangle\}$$

where j_1 and j_2 are the individual angular momentum quantum numbers. This basis consists of eigenstates of $\hat{\mathbf{J}}_1^2$ and $\hat{\mathbf{J}}_2^2$ (as does the TP basis) and of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ (instead of $\hat{J}_{1z}$ and $\hat{J}_{2z}$). The CSCO $\{\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}_2^2, \hat{\mathbf{J}}^2, \hat{J}_z\}$ is associated with the set of eigenvalue equations

$$\hat{\mathbf{J}}_1^2|j_1, j_2, J, m_J\rangle = j_1(j_1+1)\hbar^2|j_1, j_2, J, m_J\rangle$$

$$\hat{\mathbf{J}}_2^2|j_1, j_2, J, m_J\rangle = j_2(j_2+1)\hbar^2|j_1, j_2, J, m_J\rangle$$

$$\hat{\mathbf{J}}^2|j_1, j_2, J, m_J\rangle = J(J+1)\hbar^2|j_1, j_2, J, m_J\rangle$$

$$\hat{J}_z|j_1, j_2, J, m_J\rangle = m_J\hbar|j_1, j_2, J, m_J\rangle$$

Note that J is a quantum number, whereas $\hat{J}_z$, $\hat{\mathbf{J}}^2$, and $\hat{\mathbf{J}}$ are explicitly labeled as operators. The new quantum numbers J and m_J follow the quantization rules on page 64: J must be an integer or half-integer, and m_J can only take values from $-J$ to J in integer steps. J is restricted further: given two values j_1 and j_2, J can only take any value from $|j_1-j_2|$ to $|j_1+j_2|$ in integer steps: important

$$J \in \{|j_1-j_2|, |j_1-j_2|+1, \ldots, j_1+j_2-1, j_1+j_2\}$$

For each possible J, there is a range of possible m_J values:

$$m_j \in \{-J, -J+1, \ldots, J-1, J\}$$

If j_1 and j_2 are both integers ($j_1, j_2 \in \mathbb{N}^0$) or half-integers ($j_1, j_2 \in \{\mathbb{N}^0 + 1/2\}$), then J and hence m_J must be integers. Otherwise: J, $m_J \in \{\mathbb{N}^0 + 1/2\}$.

By letting J vary over all allowed values, and by letting m_J vary over all allowed values for each J, it is seen that the TAM basis has the same number of elements as the TP basis, and either basis can be used in problems involving the addition of two angular momenta.

Addition of Angular Momentum: Example

The example below illustrates the addition of two angular momenta and the construction of two different bases. Suppose that two particles with spin quantum numbers $s_1=3/2$ and $s_2=1/2$ form a composite particle that has a total spin quantum number S. Each of these quantum numbers has an associated magnetic quantum number; they are m_1, m_2, and m_S, respectively. In this example, the quantum number S is used in place of the generic angular momentum quantum number J of pages 82–83.

The possible values of S for the composite particle are given by the general formula (see page 83)

$$S \in \{|s_1-s_2|,\ |s_1-s_2|+1,\ \ldots,\ s_1+s_2-1,\ s_1+s_2\}$$

which means that S can have the values $S=1$ (for which $m_S \in \{-1,0,1\}$) and $S=2$ (for which $m_S \in \{-2,-1,0,1,2\}$).

The elements of the TP basis and the TAM basis are given below. Each basis has eight orthogonal elements. The quantum numbers s_1 and s_2 are omitted from all kets because they are common to all kets of both bases in the merged state space. Generally, any element of one basis is a superposition of multiple elements of the other basis, with the exception of the first and last items in each list (for which $|m_1=3/2, m_2=1/2\rangle = |S=2, m_S=2\rangle$ and $|m_1=-3/2, m_2=-1/2\rangle = |S=2, m_S=-2\rangle$). important

TP Basis		TAM Basis
$\lvert m_1=3/2, m_2=1/2\rangle$	=	$\lvert S=2, m_S=2\rangle$
$\lvert m_1=3/2, m_2=-1/2\rangle$		$\lvert S=2, m_S=1\rangle$
$\lvert m_1=1/2, m_2=1/2\rangle$		$\lvert S=1, m_S=1\rangle$
$\lvert m_1=1/2, m_2=-1/2\rangle$		$\lvert S=2, m_S=0\rangle$
$\lvert m_1=-1/2, m_2=1/2\rangle$		$\lvert S=1, m_S=0\rangle$
$\lvert m_1=-1/2, m_2=-1/2\rangle$		$\lvert S=2, m_S=-1\rangle$
$\lvert m_1=-3/2, m_2=1/2\rangle$		$\lvert S=1, m_S=-1\rangle$
$\lvert m_1=-3/2, m_2=-1/2\rangle$	=	$\lvert S=2, m_S=-2\rangle$
CSCO: $\hat{\mathbf{S}}_1^2, \hat{\mathbf{S}}_2^2, \hat{S}_{1z}, \hat{S}_{2z}$		CSCO: $\hat{\mathbf{S}}_1^2, \hat{\mathbf{S}}_2^2, \hat{\mathbf{S}}^2, \hat{S}_z$

Addition of Angular Momentum: Comments

Standard ordering: When constructing TAM and TP bases for angular momentum problems, as on page 84, the following convention is used to order the elements in each basis:

- Choose indices 1 and 2 for j_1, j_2, m_1, and m_2 such that $j_1 \geq j_2$ and m_1 appears before m_2 in the TP basis kets; i.e., if the magnitude of one angular momentum is larger than the other, the larger one is assigned the index 1
- For two angular momentum quantum numbers j_1 and j_2, basis elements are arranged in order of decreasing $m_1 + m_2$ (TP basis) or decreasing m_J (TAM basis)
- The elements of the TP basis that have identical values of $m_1 + m_2$ are arranged in order of decreasing m_1
- The elements of the TAM basis that have identical values of m_J are arranged in order of decreasing J

Conservation of angular momentum: When two individual angular momenta with quantum number pairs (j_1, m_1) and (j_2, m_2) are added together, the system's TAM quantum number J can take a range values as described on page 83. When expressing an element of the TP basis as a superposition of elements of the TAM basis, the superposition will generally include elements of the TAM basis that have different values of J. However, every one of these elements in the superposition must have a total magnetic quantum number that equals the sum of the individual magnetic quantum numbers; i.e., $m_J = m_1 + m_2$. This statement expresses the conservation of angular momentum about the $\hat{\mathbf{z}}$ direction.

Similarly, if angular momentum quantum numbers j_1 and j_2 are given and the TAM basis element $|J, m_J\rangle$ is expressed as a superposition of TP basis elements, there may be multiple combinations of m_1 and m_2 in the superposition of TP states. In all cases, however, the sum $m_1 + m_2$ for any TP basis state in the superposition must match the value of m_J of the TAM state: $m_J = m_1 + m_2$.

either way, we must have m_J=m_1+m_1

Clebsch–Gordan Coefficients

When a system has a total angular momentum that arises from the addition of two individual angular momenta, the system's angular momentum quantum states can be expanded into the TAM basis (page 83) or the TP basis (page 82). **Clebsch-Gordan (CG) coefficients**, described below, are the superposition coefficients of the expansion of an element of one of these bases into the other basis. The CG coefficient tables on pages 118–121 provide these coefficients for angular momentum quantum numbers $1/2 \leq j_1 \leq 2$ and $1/2 \leq j_2 \leq j_1$ where $j_1 \geq j_2$.

The notation below follows that of pages 82–83 and assumes the convention $j_1 \geq j_2$ usually adopted for the tabulation of CG coefficients. For brevity, the quantum numbers j_1 and j_2 are often omitted from the TAM kets and bras.

For two individual angular momenta with quantum numbers j_1 and j_2, the expansion of a TP basis element into the TAM basis is written (using a closure relation) as

$$|j_1, j_2, m_1, m_2\rangle = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{m_J=-J}^{J} \langle J, m_J | j_1, j_2, m_1, m_2\rangle |J, m_J\rangle$$

where $\langle J, m_J \,|j_1, j_2, m_1, m_2\rangle$ is a CG coefficient. The expansion of a TAM basis element into the TP basis is written as

$$|J, m_J\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \langle j_1, j_2, m_1, m_2 \,|J, m_J\rangle \,|j_1, j_2, m_1, m_2\rangle$$

By convention, the CG coefficients are defined to be real, so that $\langle j_1, j_2, m_1, m_2 \,|J, m_J\rangle = \langle J, m_J \,|j_1, j_2, m_1, m_2\rangle$.

Note the following:

- For the case $J = j_1 + j_2$:
  $\langle J, m_J = J | j_1, j_2, m_1 = j_1, m_2 = j_2\rangle = 1$
- Also for $J = j_1 + j_2$:
  $\langle J, m_J = -J | j_1, j_2, m_1 = -j_1, m_2 = -j_2\rangle = 1$
- If $m_1 + m_2 \neq m_J$, then $\langle J, m_J | j_1, j_2, m_1, m_2\rangle = 0$

Clebsch–Gordan Coefficients: Usage

When merging the state spaces of two systems characterized by angular momentum quantum numbers j_1 and j_2, the steps below are used to determine the associated CG coefficients using the tables given on pages 118–121. As is done on pages 84–86, the quantum numbers j_1 and j_2 are omitted from the row and column labels (explained below) in a given CG table because they are associated with every ket in the given table. CG coefficient tables are used as follows:

1. Identify the relevant tabular group. The two numbers in the upper-left corner of each grouping of tables are j_1 and j_2, with j_1 assumed to be the larger of the two values if they are not equal.

2. Within a table, the column labels are J and m_J (J is above m_J). The row labels are m_1 and m_2 (m_1 is to the left of m_2). Note the order of m_1 and m_2: m_1 is associated with j_1, the larger of the two angular momenta.

3. Every number (on a white background) in the tables is associated with a pair of values (J, m_J) given by the column label above that number and a pair of values (m_1, m_2) given by the row label to the left of that number. The CG coefficient is the square root of that number within the table, with any minus sign (if present) placed outside of the radical.

4. Using the steps described above, the expansion of a TAM basis element $|J, m_J\rangle$ into the TP basis involves reading a column of numbers in the column headed by J and m_J. Each CG coefficient is the coefficient for the associated TP basis element $|m_1, m_2\rangle$ in the superposition. All coefficients are zero for which there is not a corresponding pair of m_1 and m_2 row labels within that section of the table; such is the case if $m_J \neq m_1 + m_2$. Similarly, the expansion of a TP basis element into the TAM basis involves reading a row of numbers to the right of the relevant m_1 and m_2 labels.

Clebsch–Gordan Coefficients: Examples

The following examples incorporate the rules for addition of angular momentum given on pages 83–87 and the usage of the CG coefficient tables on pages 118–121. The examples are based on the addition of two spins $s_1 = 3/2$ and $s_2 = 1/2$, following the example and table given on page 84.

Example 1: The ket $|s_1 = 3/2, s_2 = 1/2, m_1 = -3/2, m_2 = 1/2\rangle$ is compactly written $|m_1 = -3/2, m_2 = 1/2\rangle$ by omitting the quantum numbers s_1 and s_2 from all kets and bras below. To expand this TP basis state into the TAM basis $\{|S, m_S\rangle\}$, the $\frac{3}{2} \times \frac{1}{2}$ CG coefficient table on page 118 is used. Since $m_S = m_1 + m_2 = -1$ (for this case), the only elements of the superposition with non-zero coefficients are $|S = 2, m_s = -1\rangle$ and $|S = 1, m_s = -1\rangle$.

The coefficients are determined by the numbers to the right of the row labels $-3/2$ (left) and $+1/2$ (right). The number 1/4 is found in the column headed by 2 (above) and -1 (below). This column corresponds to the TAM state $|S = 2, m_S = -1\rangle$, and the corresponding CG coefficient is $\sqrt{1/4}$. The number $-3/4$ is found in the column headed by 1 (above) and -1 (below). This column corresponds to the TAM state $|S = 1, m_S = -1\rangle$, and the corresponding CG coefficient is $-\sqrt{3/4}$. The expansion of $|m_1 = -3/2, m_2 = 1/2\rangle$ into the TAM basis is then written as

$$|m_1 = -\frac{3}{2}, m_2 = \frac{1}{2}\rangle = \sqrt{\frac{1}{4}}|S = 2, m_S = -1\rangle - \sqrt{\frac{3}{4}}|S = 1, m_S = -1\rangle$$

Example 2: Expanding a TAM basis state into the TP basis is similar to the above example, but the numbers in a column (rather than a row) of a section of the table determine the expansion coefficients. For $s_1 = 3/2$ and $s_2 = 1/2$, the TAM state $|S = 1, m_S = 1\rangle$ is written in the TP basis as

$$|S = 1, m_S = 1\rangle = \sqrt{\frac{3}{4}}|m_1 = \frac{3}{2}, m_2 = -\frac{1}{2}\rangle - \sqrt{\frac{1}{4}}|m_1 = \frac{1}{2}, m_2 = \frac{1}{2}\rangle$$

Note that the sum of the squares of the CG coefficients in the expansion of any state into another basis must equal 1.

normalization

Central Potential Problems

A 3D **central potential** problem consists of a particle of mass m in a spherically symmetric potential well $V(r)$, where $r = |\mathbf{r}|$, and $\mathbf{r} = (x, y, z)$. For a time-independent potential, a general central-potential Hamiltonian is written in the position representation as

$$H_{\{\mathbf{r}\}} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

Because $[\hat{H}, \hat{\mathbf{L}}^2] = [\hat{H}, \hat{L}_z] = 0$ for a central potential, there exists a set of quantum states that are common eigenstates of the CSCO $\{\hat{H}, \hat{\mathbf{L}}^2, \hat{L}_z\}$. These eigenstates are often labeled with the quantum numbers n, l, and m_l, defined by the set of eigenvalue equations

$$\hat{H}|n, l, m_l\rangle = E_{n,l}|n, l, m_l\rangle$$

$$\hat{\mathbf{L}}^2|n, l, m_l\rangle = l(l+1)\hbar^2|n, l, m_l\rangle$$

$$\hat{L}_z|n, l, m_l\rangle = m_l\hbar|n, l, m_l\rangle$$

where the energy eigenvalues $E_{n,l}$ depend on a **principal quantum number** n and the OAM quantum number l, and can only be determined once $V(r)$ is specified. For any central potential, the energy eigenvalues do not depend on m_l, and l and m_l are limited to the ranges

$$\{l \in \mathbb{N}^0\}; \quad m_l \in \{-l, -l+1, \ldots, l-1, l\} \quad \text{for any } l$$

The quantum number l is further constrained by n. In the position representation, the $\{|n, l, m_l\rangle\}$ state vectors are expressed in spherical coordinates as

$$\psi_{n,l,m_l}(r, \theta, \phi) = \langle \mathbf{r}|n, l, m_l\rangle = \mathcal{R}_{n,l}(r)\, Y_l^{m_l}(\theta, \phi)$$

where the angular functions $Y_l^{m_l}(\theta, \phi)$ are spherical harmonics, and the radial functions $\mathcal{R}_{n,l}(r)$ can only be determined once $V(r)$ is specified. The "spinless" hydrogen problem (pages 97–98) and the 3D isotropic harmonic oscillator (page 62) are examples of central potential problems, although the energy eigenfunctions of the latter problem are usually expressed as products of Hermite–Gaussian functions (page 54) rather than as products of radial functions and spherical harmonics.

"Spinless" Hydrogen: Energy Eigenvalues

A **hydrogen** atom consists of an **electron** and **proton** bound together by the **Coulomb interaction**, given in SI units as

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

where $-e$ is the charge of an electron, ϵ_0 is the permittivity of free space (values of physical constants are given on page 125), and $r = |\mathbf{r}|$ is the coordinate for the distance between the electron and proton.

The **"spinless" hydrogen** atom problem assumes non-relativistic electron motion and that the electron and proton have zero spin. This model is an exactly solvable central potential problem and provides a good approximation to the energy eigenvalues of the "real" hydrogen atom. Once the solutions are known, better approximations can be obtained using stationary perturbation theory. In the center-of-mass frame of the atom, the spinless hydrogen problem is defined by the Hamiltonian

$$\hat{H}_0 = \frac{1}{2\mu}\hat{\mathbf{P}}^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\hat{\mathbf{R}}|}$$

The **reduced mass** μ is defined as

$$\mu = \frac{m_e\, m_p}{m_e + m_p} \approx m_e$$

where m_e and m_p are electron and proton masses (not angular momentum quantum numbers). In the position representation, where division by $|\hat{\mathbf{R}}|$ acts as division by r, the Hamiltonian is

$$H_{0_{\{\mathbf{r}\}}} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

The eigenvalues of $\hat{H}_0$ are given by

$$E_n = -E_I/n^2; \qquad \{n \in \mathbb{N}^+\}$$

where $E_I \approx 13.6$ eV is the ground-state **ionization energy** of hydrogen, and n is the principal quantum number.

Spinless Hydrogen: Energy Eigenfunctions

The spinless hydrogen energy-eigenvalue problem is solved in the position representation using spherical coordinates. Since this is a central potential problem, the angular parts of the energy eigenfunctions are spherical harmonics $Y_l^{m_l}(\theta,\phi)$ (see page 100). The full expression for the hydrogen energy eigenfunctions (in the position representation) is

$$\psi_{n,l,m_l}(r,\theta,\phi) = \mathcal{R}_{n,l}(r)\,Y_l^{m_l}(\theta,\phi)$$

$$\{n\in\mathbb{N}^+;\quad l\in\mathbb{N}^0\,|\,0\le l<n;\quad m_l\in\mathbb{Z}\,|\,-l\le m_l\le l\}$$

where $\mathcal{R}_{n,l}(r)$ are the **radial wavefunctions** for hydrogen (see page 99). The radial wavefunctions are expressed in terms of the **Bohr radius** $a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.5\times10^{-10}$ m, a length constant used in atomic physics that defines an approximate radius of a ground-state hydrogen atom. The spherical harmonics and the radial wavefunctions are separately normalized, and while the spherical harmonics form an orthonormal basis for functions of θ and ϕ, the radial wavefunctions do not separately constitute an orthogonal basis set for functions of r.

The energy eigenfunctions give the wavefunction for the electron, with the proton's position defining the coordinate system origin. Each energy eigenfunction ψ_{n,l,m_l} is the position representation of the energy eigenstate $|n,l,m_l\rangle$. The energy eigenstates form an orthonormal basis $\{|n,l,m_l\rangle\}$:

$$\begin{aligned}
&\langle n',l',m_{l'}|n,l,m_l\rangle \\
&\quad= \int_0^\infty dr\,r^2 \int_0^\pi d\theta\sin\theta \int_0^{2\pi} d\phi\,(\psi_{n',l',m_{l'}})^*\psi_{n,l,m_l} \\
&\quad= \left(\int_0^\infty dr\,r^2\mathcal{R}_{n',l'}\mathcal{R}_{n,l}\right)\left(\int_0^\pi d\theta\sin\theta\int_0^{2\pi}d\phi\,[Y_{l'}^{m_{l'}}]^*[Y_l^{m_l}]\right) \\
&\quad= (\delta_{n,n'})(\delta_{l,l'})(\delta_{m_l,m_{l'}})
\end{aligned}$$

The ground state of "spinless" hydrogen is denoted $|n=1,l=0,m_l=0\rangle$, or $|1,0,0\rangle$, with energy eigenvalue $E_1 = -E_I$ and a spherically symmetric wavefunction:

$$\psi_{1,0,0}(r) = \mathcal{R}_{1,0}(r)\,Y_0^0(\theta,\phi) = (\pi a_0^3)^{-1/2}\,e^{-r/a_0}$$

Because $l=0$, the electron in the hydrogen ground state has no orbital angular momentum and therefore should not be described as "orbiting" the proton.

Hydrogen Radial Wavefunctions

The radial wavefunctions $\mathcal{R}_{n,l}(r)$ of hydrogen are given by

$$\mathcal{R}_{n,l}(r) = \left(\frac{2}{na_0}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}} \left(\frac{2r}{na_0}\right)^l e^{-\frac{r}{na_0}} \mathcal{L}^{2l+1}_{n-l-1}\left(\frac{2r}{na_0}\right)$$

where a_0 is the Bohr radius;

$$\mathcal{L}^p_{q-p}(u) \equiv (-1)^p \left(\frac{d}{du}\right)^p L_q(u)$$

is an **associated Laguerre polynomial**; and

$$L_q(u) \equiv e^u \left(\frac{d}{du}\right)^q (e^{-u}u^q)$$

is the q^{th} **Laguerre polynomial**. The radial wavefunctions are not all mutually orthogonal. However, radial wavefunctions with the same quantum number l are orthogonal (note that the radial wavefunctions are all real):

$$\int_0^\infty dr\, r^2 \mathcal{R}_{n',l}\mathcal{R}_{n,l} = \delta_{n,n'}$$

Radial Wavefunctions of Hydrogen through $n = 4$
$\mathcal{R}_{1,0} = 2a_0^{-3/2}\, e^{-r/a_0}$
$\mathcal{R}_{2,0} = \frac{1}{\sqrt{2}} a_0^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a_0}\right)e^{-r/2a_0}$
$\mathcal{R}_{2,1} = \frac{1}{\sqrt{24}} a_0^{-3/2}\left(\frac{r}{a_0}\right)e^{-r/2a_0}$
$\mathcal{R}_{3,0} = \frac{2}{\sqrt{27}} a_0^{-3/2}\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2\right)e^{-r/3a_0}$
$\mathcal{R}_{3,1} = \frac{8}{27\sqrt{6}} a_0^{-3/2}\left(1 - \frac{1}{6}\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)e^{-r/3a_0}$
$\mathcal{R}_{3,2} = \frac{4}{81\sqrt{30}} a_0^{-3/2}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$
$\mathcal{R}_{4,0} = \frac{1}{4} a_0^{-3/2}\left(1 - \frac{3}{4}\frac{r}{a_0} + \frac{1}{8}\left(\frac{r}{a_0}\right)^2 - \frac{1}{192}\left(\frac{r}{a_0}\right)^3\right)e^{-r/4a_0}$
$\mathcal{R}_{4,1} = \frac{\sqrt{5}}{16\sqrt{3}} a_0^{-3/2}\left(1 - \frac{1}{4}\frac{r}{a_0} + \frac{1}{80}\left(\frac{r}{a_0}\right)^2\right)\left(\frac{r}{a_0}\right)e^{-r/4a_0}$
$\mathcal{R}_{4,2} = \frac{1}{65\sqrt{5}} a_0^{-3/2}\left(1 - \frac{1}{12}\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)^2 e^{-r/4a_0}$
$\mathcal{R}_{4,3} = \frac{1}{768\sqrt{35}} a_0^{-3/2}\left(\frac{r}{a_0}\right)^3 e^{-r/4a_0}$

Spherical Harmonics

The spherical harmonics are special functions defined on the surface of a sphere of arbitrary radius. They are denoted $Y_l^m(\theta,\phi)$ with $\{l, m \in \mathbb{N}^0 \mid -l \le m \le l\}$. Following the usual conventions of quantum physics, the spherical harmonics are given by

$$Y_l^m(\theta,\phi) = i^{\{m+|m|\}}\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}e^{im\phi}P_l^m(\cos\theta)$$

where

$$P_l^m(\xi) = (1-\xi^2)^{\frac{|m|}{2}}\left(\frac{d}{d\xi}\right)^{|m|}\left\{\frac{1}{2^l l!}\left(\frac{d}{d\xi}\right)^l(\xi^2-1)^l\right\}$$

is an **associated Legendre polynomial**. The quantity in curly brackets is the **Legendre polynomial** $P_l(\xi)$. The spherical harmonics form a basis for functions of θ and ϕ. Their orthonormality is expressed as

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

Spherical Harmonics through $l = 3$
$Y_0^0 = \sqrt{\frac{1}{4\pi}}$
$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$
$Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$
$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
$Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
$Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
$Y_3^0 = \sqrt{\frac{7}{16\pi}}(5\cos^3\theta - 3\cos\theta)$
$Y_3^{\pm1} = \mp\sqrt{\frac{21}{64\pi}}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_3^{\pm2} = \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
$Y_3^{\pm3} = \mp\sqrt{\frac{35}{64\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

Atomic Angular Momentum Quantum Numbers

Various types of angular momenta associated with atoms are listed in the table below, represented by a letter that is conventionally used as the quantum number associated with the magnitude of the angular momentum. The symbol for the associated z-component magnetic quantum number in all cases is m with the given angular momentum quantum number as a subscript. For example, since I is the quantum number for the magnitude of nuclear spin, m_I is the z-component magnetic quantum number for the nuclear spin.

The standard symbol for an angular momentum quantum number is often the same as the standard symbol for the angular momentum operator, so the meaning of a symbol must often be determined by the context in which it is used. In this *Field Guide*, operators are always indicated with carets (or "hats") over the symbols to aid in the interpretation of expressions. Vector notation and subscripts further help identify the meaning of a symbol. Note that operators are not necessarily denoted with carets in other books and resources.

Quantum Number	Angular Momentum (AM) Type
l	orbital AM of a single electron
s	spin AM of a single electron
L	net orbital AM of all electrons in an atom
S	net spin AM of all electrons in an atom
J	net orbital + spin AM of all electrons in an atom; vector AM operator: $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$
I	spin AM of an atomic nucleus
F	total atomic AM; vector AM operator: $\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}}$

Hyperfine Structure of Hydrogen

The hydrogen nucleus is a single proton, so the nucleus has a spin quantum number $I = 1/2$. The nuclear spin and electronic state spaces are merged to give a tensor-product basis $\{|n, L, S; J, m_J\rangle|I, m_I\rangle\}$. These are not eigenstates of the full atomic Hamiltonian due to coupling of the magnetic dipole moment of the proton with the electron's magnetic dipole moment. This coupling leads to the hyperfine structure of hydrogen and associated shifts in the energy eigenvalues of hydrogen that are even smaller than the fine-structure energy shifts.

Hydrogen's hyperfine structure is calculated using a perturbation Hamiltonian $\hat{W}_{HF}$ (not given here) that is much weaker than $\hat{W}_{FS}$; the approximate energy eigenstates of the perturbed Hamiltonian are $\{|n, L, S, J, I; F, m_F\rangle\}$. Quantum numbers F and m_F are associated with the observables $\hat{\mathbf{F}}^2$ and $\hat{F}_z$ where $\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}}$ is the vector operator for the total angular momentum of the atom. $\hat{\mathbf{F}}^2$ and $\hat{F}_z$ have the eigenvalue equations

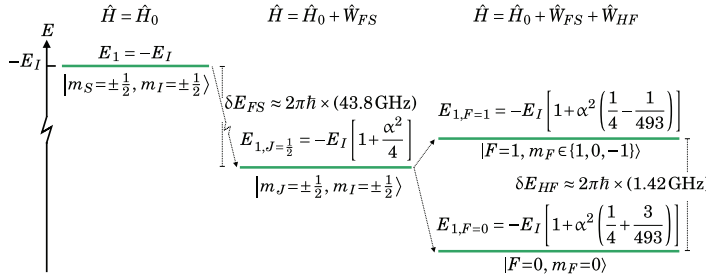
$$\hat{\mathbf{F}}^2|n, L, S, J, I; F, m_F\rangle = F(F+1)\hbar^2|n, L, S, J, I; F, m_F\rangle$$

$$\hat{F}_z|n, L, S, J, I; F, m_F\rangle = m_F\hbar|n, L, S, J, I; F, m_F\rangle$$

$$F \in \{|J-I|, |J-I|+1, \ldots, J+I-1, J+I\}$$

$$m_F \in \{-F, -F+1, \ldots, F-1, F\} \text{ for each } F$$

Since $I = 1/2$ for hydrogen, F has the values $J+1/2$ and $J-1/2$ for each J. The unperturbed, fine-structure, and hyperfine-structure energy levels, shifts, and eigenstates are shown below for the $n = 1$ level. The kets omit the quantum numbers $n = 1$, $L = 0$, $S = 1/2$, $J = 1/2$, $I = 1/2$, and $m_L = 0$.



Spectroscopic Notation and Term Symbols

Spectroscopic notation is used to indicate the value of the OAM quantum number of a single electron within an atom. The lowest few values of l are assigned the following letters:

$$\begin{aligned} l = 0 &\leftrightarrow s \\ l = 1 &\leftrightarrow p \\ l = 2 &\leftrightarrow d \\ l = 3 &\leftrightarrow f \\ l = 4 &\leftrightarrow g \end{aligned}$$

These letters are used immediately following the principal quantum number n to identify an energy level. For example, the $4p$ level of hydrogen denotes $n = 4$ and $l = 1$. The $4p$ level consists of the set of three $|n, l, m_l\rangle$ states $|4, 1, 1\rangle$, $|4, 1, 0\rangle$, and $|4, 1, -1\rangle$. given the l, m evolves: -1,0,1

important notation

When OAM quantum numbers are associated with the net OAM of all electrons in an atom (i.e., L instead of l), the same spectroscopic notation is used but the letters are capitalized. In either case, symbols must be interpreted in context, as various meanings are assigned to these letters throughout quantum and atomic physics.

The angular momentum quantum numbers S, L, and J for all electrons of an atom can also be incorporated into an atomic **term symbol**, following the notation

$$^{2S+1}L_J$$

where the superscript $2S+1$ is the **spin multiplicity** (the number of orthogonal spin states for total electron spin quantum number S), L is the total electron OAM quantum number and is replaced by the equivalent (capitalized) letter given by the spectroscopic notation convention, and J is the quantum number associated with the sum of the net electron spin and OAM for a given level. For example, all states of hydrogen have $S = 1/2$, so the spin multiplicity is 2. For a hydrogen atom in a state that has $L = 1$ and $J = 3/2$, the term symbol is $^2P_{3/2}$, and the possible values of m_J associated with this level are 3/2, 1/2, $-1/2$, and $-3/2$.

Spherical Coordinates

Spherical coordinates and expressions for the conversion between rectilinear and spherical coordinate systems are defined below.

Conventionally, x, y, and z indicate orthogonal spatial coordinates in a 3D rectilinear coordinate system, where

$$\mathbf{r} = (x, y, z) = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$$

is a position vector. Vectors are denoted in bold. Unit (directional) vectors have a norm of 1 and are denoted with a hat or caret over a coordinate symbol, e.g., $\hat{\mathbf{x}} = (1, 0, 0)$.

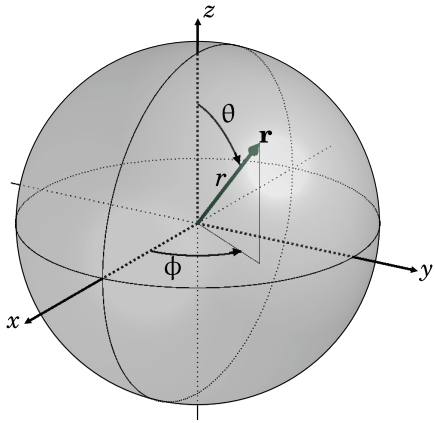
Coordinate Conversion	
$r = \lvert\mathbf{r}\rvert = \sqrt{x^2 + y^2 + z^2}$	Magnitude of $\mathbf{r}$
$\theta = \tan^{-1}\left(\frac{1}{z}\sqrt{x^2 + y^2}\right)$	Polar angle
$\phi = \tan^{-1}\left(\frac{y}{x}\right)$	Azimuthal angle
$x = r\sin\theta\cos\phi$ $y = r\sin\theta\sin\phi$ $z = r\cos\theta$	

Unit (Directional) Vector Conversion
$\hat{\mathbf{r}} = \sin\theta\cos\phi\,\hat{\mathbf{x}} + \sin\theta\sin\phi\,\hat{\mathbf{y}} + \cos\theta\,\hat{\mathbf{z}}$ $\hat{\boldsymbol{\theta}} = \cos\theta\cos\phi\,\hat{\mathbf{x}} + \cos\theta\sin\phi\,\hat{\mathbf{y}} - \sin\theta\,\hat{\mathbf{z}}$ $\hat{\boldsymbol{\phi}} = -\sin\phi\,\hat{\mathbf{x}} + \cos\phi\,\hat{\mathbf{y}}$
$\hat{\mathbf{x}} = \sin\theta\cos\phi\,\hat{\mathbf{r}} + \cos\theta\cos\phi\,\hat{\boldsymbol{\theta}} - \sin\phi\,\hat{\boldsymbol{\phi}}$ $\hat{\mathbf{y}} = \sin\theta\sin\phi\,\hat{\mathbf{r}} + \cos\theta\sin\phi\,\hat{\boldsymbol{\theta}} + \cos\phi\,\hat{\boldsymbol{\phi}}$ $\hat{\mathbf{z}} = \cos\theta\,\hat{\mathbf{r}} - \sin\theta\,\hat{\boldsymbol{\theta}}$

Spherical coordinates are illustrated on page 116.

Operators in Spherical Coordinates

The spherical coordinates defined on page 115 are illustrated below.



The vector differential operator ∇ is given by

$$\nabla = \hat{\mathbf{r}}\frac{\partial}{\partial r} + \hat{\boldsymbol{\theta}}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\boldsymbol{\phi}}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}$$

The **Laplacian** ∇^2 is given by

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

The 3D differential volume element $d^3\mathbf{r}$, given in Cartesian coordinates as $d^3\mathbf{r} = dx\,dy\,dz$, is expressed in spherical coordinates as

$$d^3\mathbf{r} = r^2\sin\theta\,dr\,d\theta\,d\phi$$

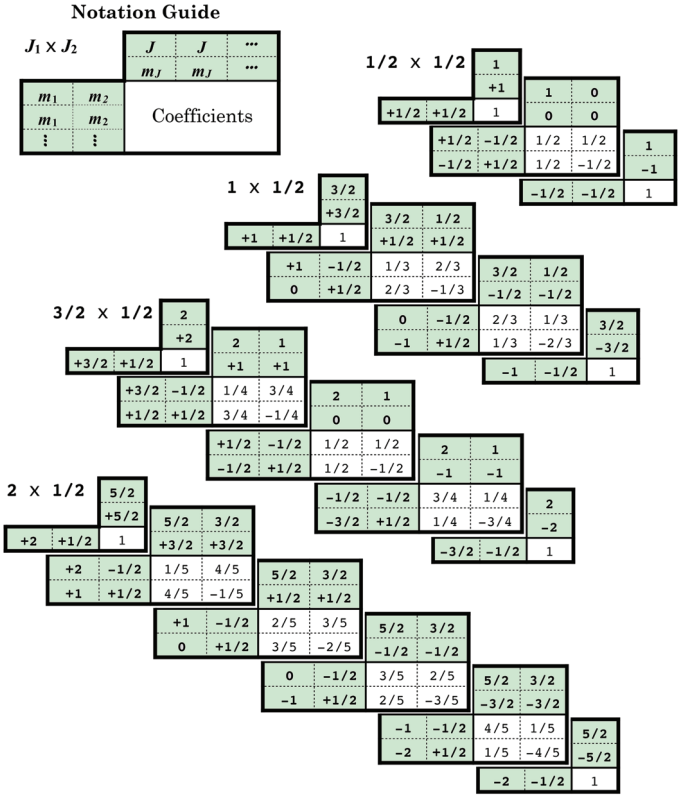
so that

$$\int d\phi \int d\theta \sin\theta \int dr\, r^2 f(r,\theta,\phi)$$

is an indefinite volume integral of function $f(r, \theta, \phi)$.

Clebsch–Gordan Coefficient Tables: $J_1 \times 1/2$

Tables of Clebsch–Gordan coefficients are given below and on pages 119–121. Two individual angular momentum quantum numbers are denoted J_1 and J_2, with $J_1 \geq J_2$. The corresponding z-component magnetic quantum numbers are m_1 and m_2. The columns are labeled by the total-angular-momentum quantum numbers J (magnitude) and m_J (z-component magnetic quantum number) on a green background, with J above m_J. The rows are labeled by m_1 (left) and m_2 (right) on a green background. The square-root is to be taken of every number in a table, and any minus sign (if present) is placed outside of the radical. For example, a table entry of $-4/5$ is interpreted as $-\sqrt{4/5}$. See page 88 for an example that uses Clebsch–Gordan-coefficient tables.



Clebsch–Gordan Coefficient Tables: $J_1 \times 1$

1 x 1

		2
		+2
+1	+1	1

2	1
+1	+1
+1	0	1/2	1/2
0	+1	1/2	−1/2

2	1	0
0	0	0
+1	−1	1/6	1/2	1/3
0	0	2/3	0	−1/3
−1	+1	1/6	−1/2	1/3

2	1
−1	−1
0	−1	1/2	1/2
−1	0	1/2	−1/2

2
−2
−1	−1	1

3/2 x 1

		5/2
		+5/2
+3/2	+1	1

5/2	3/2
+3/2	+3/2
+3/2	0	2/5	3/5
+1/2	+1	3/5	−2/5

5/2	3/2	1/2
+1/2	+1/2	+1/2
+3/2	−1	1/10	2/5	1/2
+1/2	0	3/5	1/15	−1/3
−1/2	+1	3/10	−8/15	1/6

5/2	3/2	1/2
−1/2	−1/2	−1/2
+1/2	−1	3/10	8/15	1/6
−1/2	0	3/5	−1/15	−1/3
−3/2	+1	1/10	−2/5	1/2

5/2	3/2
−3/2	−3/2
−1/2	−1	3/5	2/5
−3/2	0	2/5	−3/5

5/2
−5/2
−3/2	−1	1

2 x 1

		3
		+3
+2	+1	1

3	2
+2	+2
+2	0	1/3	2/3
+1	+1	2/3	−1/3

3	2	1
+1	+1	+1
+2	−1	1/15	1/3	3/5
+1	0	8/15	1/6	−3/10
0	+1	2/5	−1/2	1/10

3	2	1
0	0	0
+1	−1	1/5	1/2	3/10
0	0	3/5	0	−2/5
−1	+1	1/5	−1/2	3/10

3	2	1
−1	−1	−1
0	−1	2/5	1/2	1/10
−1	0	8/15	−1/6	−3/10
−2	+1	1/15	−1/3	3/5

3	2
−2	−2
−1	−1	2/3	1/3
−2	0	1/3	−2/3

3
−3
−2	−1	1

Clebsch–Gordan Coefficient Tables: $J_1 \times 3/2$

3/2 × 3/2

		3
		+3
+3/2	+3/2	1

		3	2
		+2	+2
+3/2	+1/2	1/2	1/2
+1/2	+3/2	1/2	−1/2

		3	2	1
		+1	+1	+1
+3/2	−1/2	1/5	1/2	3/10
+1/2	+1/2	3/5	0	−2/5
−1/2	+3/2	1/5	−1/2	3/10

		3	2	1	0
		0	0	0	0
+3/2	−3/2	1/20	1/4	9/20	1/4
+1/2	−1/2	9/20	1/4	−1/20	−1/4
−1/2	+1/2	9/20	−1/4	−1/20	1/4
−3/2	+3/2	1/20	−1/4	9/20	−1/4

		3	2	1
		−1	−1	−1
+1/2	−3/2	1/5	1/2	3/10
−1/2	−1/2	3/5	0	−2/5
−3/2	+1/2	1/5	−1/2	3/10

		3	2
		−2	−2
−1/2	−3/2	1/2	1/2
−3/2	−1/2	1/2	−1/2

		3
		−3
−3/2	−3/2	1

2 × 3/2

		7/2
		+7/2
+2	+3/2	1

		7/2	5/2
		+5/2	+5/2
+2	+1/2	3/7	4/7
+1	+3/2	4/7	−3/7

		7/2	5/2	3/2
		+3/2	+3/2	+3/2
+2	−1/2	1/7	16/35	2/5
+1	+1/2	4/7	1/35	−2/5
0	+3/2	2/7	−18/35	1/5

		7/2	5/2	3/2	1/2
		+1/2	+1/2	+1/2	+1/2
+2	−3/2	1/35	6/35	2/5	2/5
+1	−1/2	12/35	5/14	0	−3/10
0	+1/2	18/35	−3/35	−1/5	1/5
−1	+3/2	4/35	−27/70	2/5	−1/10

		7/2	5/2	3/2	1/2
		−1/2	−1/2	−1/2	−1/2
+1	−3/2	4/35	27/70	2/5	1/10
0	−1/2	18/35	3/35	−1/5	−1/5
−1	+1/2	12/35	−5/14	0	3/10
−2	+3/2	1/35	−6/35	2/5	−2/5

		7/2	5/2	3/2
		−3/2	−3/2	−3/2
0	−3/2	2/7	18/35	1/5
−1	−1/2	4/7	−1/35	−2/5
−2	+1/2	1/7	−16/35	2/5

		7/2	5/2
		−5/2	−5/2
−1	−3/2	4/7	3/7
−2	−1/2	3/7	−4/7

		7/2
		−7/2
−2	−3/2	1

Clebsch–Gordan Coefficient Tables: 2×2

2 × 2

		4
		4
+2	+2	1

		4	3
		+3	+3
+2	+1	1/2	1/2
+1	+2	1/2	−1/2

		4	3	2
		+2	+2	+2
+2	0	3/14	1/2	2/7
+1	+1	4/7	0	−3/7
0	+2	3/14	−1/2	2/7

		4	3	2	1
		+1	+1	+1	+1
+2	−1	1/14	3/10	3/7	1/5
+1	0	3/7	1/5	−1/14	−3/10
0	+1	3/7	−1/5	−1/14	3/10
−2	+2	1/14	−3/10	3/7	−1/5

		4	3	2	1	0
		0	0	0	0	0
+2	−2	1/70	1/10	2/7	2/5	1/5
+1	−1	8/35	2/5	1/14	−1/10	−1/5
0	0	18/35	0	−2/7	0	1/5
−1	+1	8/35	−2/5	1/14	1/10	−1/5
−2	+2	1/70	−1/10	2/7	−2/5	1/5

		4	3	2	1
		−1	−1	−1	−1
+1	−2	1/14	3/10	3/7	1/5
0	−1	3/7	1/5	−1/14	−3/10
−1	0	3/7	−1/5	−1/14	3/10
−2	+1	1/14	−3/10	3/7	−1/5

		4	3	2
		−2	−2	−2
0	−2	3/14	1/2	2/7
−1	−1	4/7	0	−3/7
−2	0	3/14	−1/2	2/7

		4	3
		−3	−3
−1	−2	1/2	1/2
−2	−1	1/2	−1/2

		4
		−4
−2	−2	1