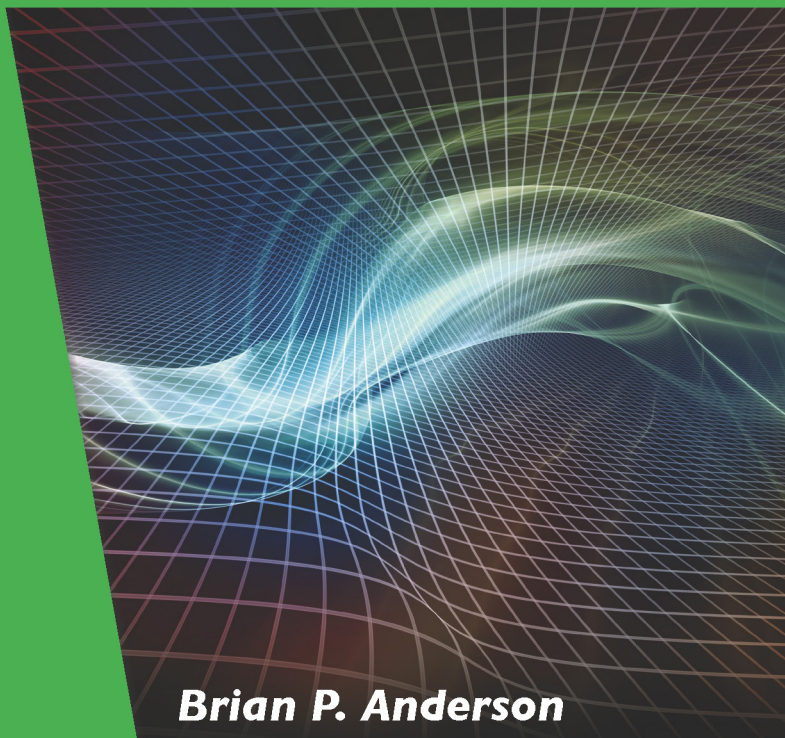
SPIE. FIELD GUIDE

Field Guide to

Quantum Mechanics



Brian P. Anderson

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In 2004, SPIE launched a new book series, the SPIE *Field Guides*, focused on SPIE's core areas of Optics and Photonics. The idea of these *Field Guides* is to give concise presentations of the key subtopics of a subject area or discipline, typically covering each subtopic on a single page, using the figures, equations, and brief explanations that summarize the key concepts. The aim is to give readers a handy desk or portable reference that provides basic, essential information about principles, techniques, or phenomena, including definitions and descriptions, important equations, illustrations, application examples, design considerations, and additional resources.

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We are interested in your suggestions for new *Field Guide* topics as well as what could be added to an individual volume to make these *Field Guides* more useful to you. Please contact us at **fieldguides@SPIE.org**.

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Field Guide to Quantum Mechanics

This *Field Guide* is a condensed reference to the concepts, definitions, formalism, equations, and problems of quantum mechanics. Many topics covered in quantum mechanics courses are included, while numerous details and derivations are necessarily omitted. This *Field Guide* is envisioned to appeal to undergraduate and graduate students engaged in quantum mechanics research or courses; to professors, as an aid in teaching and research; and to professional physicists and engineers pursuing cutting-edge applications of quantum mechanics. The mathematical formalism used here involves Dirac notation, with which the reader should be (or become) familiar to make the most of this *Field Guide*. Nevertheless, readers who are not yet familiar with this formalism should be able to utilize various aspects of this *Field Guide*, especially with extra attention directed to the basic concepts addressed in the first few sections.

I owe sincere thanks to mentors, professors, colleagues, collaborators, and friends too numerous to single out by name who have taught, motivated, and encouraged me throughout more than three decades of studying quantum physics. Since joining the University of Arizona faculty, the unwavering support and partnership of local and international colleagues and collaborators has been indispensable in learning and appreciating many of the numerous facets of this fascinating subject.

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This *Field Guide* is dedicated to Jeff and Al, and to the students who have worked in my labs, sat through my courses, and made my career as a mentor and educator profoundly fulfilling.

Brian P. Anderson
University of Arizona
June 2019

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Glossary of Symbols

Assorted symbols

$\mathbf{B}$	Magnetic field vector
$\mathcal{E}$	A quantum-mechanical state space
g_J	g-Factor for an angular momentum J
g_n	Degree of degeneracy for a quantum state with quantum number n
i	(i) $i \equiv \sqrt{-1}$; (ii) a discrete index
J, $\mathbf{J}$	Probability current (scalar and vector). For angular momentum symbols, see page 101.
m	(i) Mass of a particle; (ii) with subscript J, a magnetic quantum number associated with an angular momentum quantum number J
$\mathcal{P}$	Probability
$\mathcal{P}_{a\to b}(t)$	Time-dependent transition probability from state $\|a\rangle$ to state $\|b\rangle$
$\mathcal{R}_{n,l}(r)$	(i) Radial part of energy eigenfunction for a central potential; (ii) hydrogen radial wavefunction
t	Time
$Y_l^m(\theta, \phi)$	Spherical harmonic

Position and momentum coordinates

$d^n\mathbf{p}$	Differential volume element in n-dimensional momentum space
$d^n\mathbf{r}$	Differential volume element in n-dimensional position space
$\mathbf{p}$	(i) 3D momentum vector: $\mathbf{p} = (p_x, p_y, p_z)$; (ii) n-dimensional momentum vector
p	(i) Momentum variable in a 1D coordinate system; (ii) magnitude of n-dimensional momentum vector $\mathbf{p}$: $p = \|\mathbf{p}\|$
p_x, p_y, p_z	Orthogonal momentum coordinates
$\mathbf{r}$	(i) 3D position vector: $\mathbf{r} = (x, y, z)$; (ii) n-dimensional position vector
r	Magnitude of n-dimensional position vector $\mathbf{r}$: $r = \|\mathbf{r}\|$
x, y, z	Orthogonal spatial coordinates

Glossary of Symbols

Greek letters

α	(i) Phase-space displacement coordinate; (ii) an eigenvalue of the harmonic oscillator annihilation operator $\hat{a}$; (iii) fine-structure constant
γ_J	Gyromagnetic ratio for an angular momentum $\boldsymbol{J}$
δ_{jk}	Kronecker delta for discrete indices j, k
$\delta(x)$	Dirac delta function over a continuous variable x
Δ	Detuning, a difference of angular frequencies
θ	(i) An arbitrary angle; (ii) the polar angle in a spherical coordinate system
λ	(i) Perturbation scale parameter; (ii) deBroglie wavelength; (iii) general scalar quantity, such as an eigenvalue
μ	Reduced mass: for masses m_1 and m_2, $\mu \equiv \frac{m_1 m_2}{m_1+m_2}$; for $\hat{\boldsymbol{\mu}}$, see page xvi
σ	(i) Harmonic oscillator length: $\sigma_j \equiv \sqrt{\hbar/(m\omega_j)}$; (ii) a Pauli spin matrix; (iii) for $\hat{\boldsymbol{\sigma}}$, see page xvii
ϕ	(i) An arbitrary angle; (ii) the azimuthal angle in a spherical coordinate system (to be distinguished from φ)
φ	(i) Within a ket, denotes a quantum state vector; (ii) a wavefunction of a continuous parameter, such as $\varphi(x)$ (to be distinguished from ϕ)
ψ	(i) Within a ket, denotes a quantum state vector; (ii) a wavefunction of a continuous parameter, such as $\psi(x)$
Ψ	(i) Within a ket, denotes a time-dependent quantum state vector; (ii) a time-dependent wavefunction of a continuous parameter, such as $\Psi(x,t)$
ω	An angular frequency
ω_L	Larmor frequency: $\omega_L \equiv -\gamma\lvert\mathbf{B}\rvert$
Ω	Rabi frequency: $\Omega \equiv \sqrt{\Delta^2 + \lvert\Omega_0\rvert^2}$
Ω_0	Bare or resonant Rabi frequency

Glossary of Symbols

Acronyms

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AM	Angular momentum
CG	Clebsch–Gordan (coefficient)
CSCO	Complete set of commuting observables
OAM	Orbital angular momentum
SI	International System of Units
SPT	Stationary perturbation theory
TAM	Total angular momentum (basis)
TDPT	Time-dependent perturbation theory
TP	Tensor product (basis)

Mathematical operations and symbols

$\|\mathbf{v}\|$	Norm of vector $\mathbf{v}$: $\|\mathbf{v}\| = \sqrt{\mathbf{v}^\dagger \mathbf{v}}$
$\mathcal{F}\{\cdots\}$	Fourier transform
$\mathcal{F}^{-1}\{\cdots\}$	Inverse Fourier transform
$\otimes$	Denotes a tensor product
∇	3D vector differential operator ("del"). In Cartesian coordinates: $\nabla = \hat{\mathbf{x}}\frac{\partial}{\partial x} + \hat{\mathbf{y}}\frac{\partial}{\partial y} + \hat{\mathbf{z}}\frac{\partial}{\partial z}$
∇^2	Laplacian operator: $\nabla^2 = \nabla \cdot \nabla$
$\mathrm{Re}\{\alpha\}$	Real part of a complex scalar α
$\mathrm{Im}\{\alpha\}$	Imaginary part of a complex scalar α
$\mathbb{1}$	Identity matrix
$\sum_k$	Sum over all values of discrete index k

Glossary of Symbols

Quantum mechanics symbols

$\lvert\cdots\rangle$	Ket vector (ket)
$\langle\cdots\rvert$	Bra vector (bra)
$\langle\varphi\vert\psi\rangle$	Scalar or inner product of the ordered pair of kets $(\lvert\varphi\rangle, \lvert\psi\rangle)$
$\hat{A}$	The "hat" or caret (i) denotes an operator; (ii) a directional unit vector when used over a coordinate (in bold), as in $\hat{\mathbf{x}}$; (iii) $\hat{A}$ is used throughout this *Field Guide* as an arbitrary operator
$\hat{A}^\dagger$	The "dagger" superscript denotes the Hermitian conjugate of operator $\hat{A}$
$\hat{A}^{-1}$	The superscript denotes the inverse of operator $\hat{A}$
$\langle\cdots\lvert\hat{A}\rvert\cdots\rangle$	A matrix element of operator $\hat{A}$
A_{jk}	Matrix element of operator $\hat{A}$ associated with matrix row j and column k in a discrete representation
$\langle\hat{A}\rangle$	An expectation value of operator $\hat{A}$
$\Delta\hat{A}$	Uncertainty or standard deviation of operator $\hat{A}$: $\Delta\hat{A} \equiv \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}$
$[\hat{A}, \hat{B}]$	Commutator of operators $\hat{A}$ and $\hat{B}$: $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$
$\langle\hat{\boldsymbol{\sigma}}\rangle$	Bloch vector: $\langle\hat{\boldsymbol{\sigma}}\rangle = (\langle\hat{\sigma}_x\rangle, \langle\hat{\sigma}_y\rangle, \langle\hat{\sigma}_z\rangle)$
$\lVert\lvert\psi\rangle\rVert$	Norm of ket $\lvert\psi\rangle$: $\lVert\lvert\psi\rangle\rVert = \sqrt{\langle\psi\vert\psi\rangle}$
$\lvert\psi\rangle_{\{v\}}$	A ket $\lvert\psi\rangle$ expressed as a column vector in the representation labeled by $\{v\}$
$\langle\psi\rvert_{\{v\}}$	A bra $\langle\psi\rvert$ expressed as a row vector in the representation labeled by $\{v\}$
$A_{\{v\}}$	An operator $\hat{A}$ expressed as a matrix in the representation labeled by $\{v\}$
$\tilde{\psi}(\mathbf{p})$	Momentum-space wavefunction associated (by Fourier transform) with position-space wavefunction $\psi(\mathbf{r})$

See page 101 for angular momentum quantum numbers.

Glossary of Operators

$\hat{H}$	Hamiltonian
$\hat{\mathbf{P}} = (\hat{P}_x, \hat{P}_y, \hat{P}_z)$	Vector momentum operator
$\hat{P}_x, \hat{P}_y, \hat{P}_z$	Scalar momentum operators
$\hat{\mathbf{R}} = (\hat{X}, \hat{Y}, \hat{Z}) = (\hat{R}_x, \hat{R}_y, \hat{R}_z)$	Vector position operator
$\hat{X}, \hat{Y}, \hat{Z}$ or $\hat{R}_x, \hat{R}_y, \hat{R}_z$	Scalar position operators
$\hat{W}$ or $\lambda\hat{W}$	A perturbation Hamiltonian
$\hat{\boldsymbol{\mu}}$	Magnetic dipole moment

Angular momentum (AM): Various vector, magnitude-squared, and $\hat{\mathbf{u}}$-component AM operators

$\hat{\mathbf{F}}, \hat{\mathbf{F}}^2, \hat{F}_u$	Total atomic AM
$\hat{\mathbf{I}}, \hat{\mathbf{I}}^2, \hat{I}_u$	Nuclear spin AM
$\hat{\mathbf{J}}, \hat{\mathbf{J}}^2, \hat{J}_u$	(i) Any generalized AM; (ii) sum of electron spin AM and orbital AM
$\hat{\mathbf{L}}, \hat{\mathbf{L}}^2, \hat{L}_u$	Orbital AM
$\hat{\mathbf{S}}, \hat{\mathbf{S}}^2, \hat{S}_u$	Spin AM

Harmonic oscillator: where $j \in \{x, y, z\}$ and $\sigma_j \equiv \sqrt{\hbar/(m\omega_j)}$

$\hat{a}_j = \frac{1}{\sqrt{2}}(\frac{1}{\sigma_j}\hat{R}_j + i\frac{\sigma_j}{\hbar}\hat{P}_j)$	Lowering operator
$\hat{a}_j^\dagger = \frac{1}{\sqrt{2}}(\frac{1}{\sigma_j}\hat{R}_j - i\frac{\sigma_j}{\hbar}\hat{P}_j)$	Raising operator
$\hat{N}_j = \hat{a}_j^\dagger \hat{a}_j$	Number operator

Projectors

$\hat{\mathbb{P}}_\psi = \lvert\psi\rangle\langle\psi\rvert$	Projector onto $\lvert\psi\rangle$
$\hat{\mathbb{P}}_q = \sum_{k=1}^{q} \lvert v_k\rangle\langle v_k\rvert$	Projector onto the subspace $\mathcal{E}_q$ spanned by $\{\lvert v_k\rangle\}$, $k \in \{1, \ldots, q\}$

Glossary of Operators

Unitary time evolution from t_0 to t

$\hat{\mathbb{U}}(t,t_0) = e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}$ For time-independent $\hat{H}$

$\hat{\mathbb{U}}(t,t_0) = e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' \hat{H}(t')}$ If and only if $[\hat{H}(t), \hat{H}(t')] = 0$ for arbitrary t and t'

Other unitary operators

$\hat{\mathbb{I}}$ Identity operator

$\hat{\mathbb{S}}(x') = e^{-ix'\hat{P}_x/\hbar}$ Spatial translation by x' in the $\hat{\mathbf{x}}$ direction

$\hat{\mathbb{T}}(p') = e^{ip'\hat{X}/\hbar}$ Translation by p' of the x component of momentum

$\hat{\mathbb{D}}(\alpha) = e^{\alpha\,\hat{a}_x^\dagger - \alpha^*\hat{a}_x}$ Phase-space displacement (translation) in $\hat{\mathbf{x}}$-direction position and momentum by $\alpha \equiv \frac{1}{\sqrt{2}}(x'/\sigma + i\sigma p'/\hbar)$, where $\sigma \equiv \sqrt{\hbar/(m\omega)}$, $\phi_0 = x'p'/(2\hbar)$

$= e^{i(p'\hat{X} - x'\hat{P}_x)/\hbar}$

$= e^{i\phi_0}\hat{\mathbb{T}}(p')\hat{\mathbb{S}}(x')$

$\hat{\mathbb{R}}_u(\theta) = e^{-i\theta\hat{J}_u/\hbar}$ Rotation through angle θ about a unit vector $\hat{\mathbf{u}}$

$\hat{\sigma}_u$ Pauli spin operator associated with the $\hat{\mathbf{u}}$ direction

$\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$ Vector of Pauli spin operators

Commutation relations

$[\hat{R}_j, \hat{P}_k] = i\hbar\delta_{jk}$ $j,k \in \{x,y,z\}$

$[\hat{a}_j, \hat{a}_k^\dagger] = \delta_{jk}$

Vector Operators	
Angular momentum: $\hat{\mathbf{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$	Pauli spin operators: $\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$
$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z$	$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z$
$[\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x$	$[\hat{\sigma}_y, \hat{\sigma}_z] = 2i\hat{\sigma}_x$
$[\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y$	$[\hat{\sigma}_z, \hat{\sigma}_x] = 2i\hat{\sigma}_y$

Quantum States, Kets, and State Space

The formalism of quantum mechanics involves symbols and methods for denoting and determining the time-dependent **state** of a physical system, and a mathematical structure for evaluating the possible outcomes and associated probabilities of measurements that can be made on the system. Here, "state" implies everything knowable about the dynamical aspects of a system at a certain time.

In **classical mechanics**, the state at time t of a particle of mass m is given by the particle's position $\mathbf{r}(t)$ and momentum $\mathbf{p}(t)$, which are determined by initial conditions and the laws of classical mechanics. Neither m nor t are state variables: m is assumed to be an immutable property of the particle, and t is a parameter used in specifying the dynamics of state variables.

In **quantum mechanics**, the state of a physical system at time t is associated with a symbol such as ψ placed within half-right-angled brackets: $|\psi\rangle$. This symbol is called a **ket vector** or a **ket**. A symbol within a ket may represent a physical quantity. For instance, if E_1 is a possible energy of a particle, then $|E_1\rangle$ indicates that the particle is in a state with an energy of precisely E_1. Kets may contain multiple symbols that represent multiple physical quantities.

> A ket is the quantum mechanical symbol that encodes the state of a system. The symbols within a ket explicitly indicate or serve as an abstract placeholder for precisely known information about the system.

The mathematical structure of quantum mechanics formalism mirrors that of **linear algebra** (see pages 113–114) and encapsulates rules regarding the manipulation of kets to determine the time dependence of a system's state and how statistical information (such as measurement outcome predictions) about a system may be determined from its state. The **state space** $\mathcal{E}$ for a given physical system is the set of all of the possible states in which it can exist. The statement $|\psi\rangle \in \mathcal{E}$ indicates that $|\psi\rangle$ encodes a state in which the given system can exist.

Elements of Dirac Notation

Dirac notation is a standard system of notation used in quantum mechanics that efficiently keeps track of information about states. Expressions given in Dirac notation can often be replaced by expressions involving the elements and operations of calculus or linear algebra. However, the system of Dirac notation is compact, adaptable to any quantum mechanics problem, and can be related to other mathematical and notational systems as needed. Dirac notation involves four categories of elements: kets (page 1), complex scalars, operators, and bras.

Operators: In this *Field Guide*, operators are denoted in Dirac notation with a "hat" or caret placed over a letter or symbol, as in $\hat{X}$. Outside of Dirac notation, operators may be represented by matrices, or by operations such as multiplication or differentiation; in these cases the caret is not used in this *Field Guide*. Most operators in this *Field Guide* are denoted with capital letters, with a few exceptions (see the Glossary of Operators, pages xvi–xvii). Formally, an operator is a quantity that associates every ket in a given state space $\mathcal{E}$ with the same or another ket. For an arbitrary operator $\hat{A}$ and an arbitrary ket $|\psi\rangle \in \mathcal{E}$, this association is denoted $\hat{A}|\psi\rangle = |\psi'\rangle$. Operators are therefore said to "act to the right" on kets to produce new kets.

Many operators are associated with measurable physical quantities. Most operators of mathematical utility that do not correspond to physical quantities are written in this *Field Guide* in a "hollow" typeface, such as $\hat{\mathbb{U}}$ and $\hat{\mathbb{P}}$. All projection operators and unitary operators (except the Pauli spin operators) are written in this typeface throughout this *Field Guide*.

Bras: A bra or **bra vector** is a symbol placed within a half-left-angled bracket, such as $\langle\varphi|$. A bra is a **functional**: it associates a complex scalar with each ket in a given state space, whereas operators associate a ket with another ket. A bra placed immediately to the left of a ket creates a bra–ket compound symbol such as $\langle\varphi|\psi\rangle$ that is equivalent to a complex scalar. As with kets, the symbol(s) inside a bra designates information about the properties of the bra. Operators may "act to the left" on bras to produce new bras, as indicated by the expression $\langle\varphi|\hat{A} = \langle\varphi'|$.

Vector Spaces and Scalar Products

The state space $\mathcal{E}$ of an arbitrary quantum-mechanical system has the properties of a **vector space**. The dimensionless elements of $\mathcal{E}$ symbolized by kets are called the **state vectors** of $\mathcal{E}$. The principle of **superposition** enables the mathematical construction of new elements of $\mathcal{E}$ from other elements of $\mathcal{E}$; e.g., if $|\varphi_1\rangle$ and $|\varphi_2\rangle$ are elements of $\mathcal{E}$, then

$$c_1|\varphi_1\rangle + c_2|\varphi_2\rangle \equiv |\varphi'\rangle \in \mathcal{E}$$

where c_1 and c_2 are complex scalars.

The **scalar** or **inner product** of two elements of $\mathcal{E}$ is denoted by a bra–ket pair. The scalar product associated with the ordered pair $(|\varphi\rangle, |\psi\rangle)$ is written with the second ket preceded by a bra containing the symbol(s) within the first ket; i.e., $\langle\varphi|\psi\rangle$. The bra $\langle\varphi|$ is called the **adjoint** (or **Hermitian conjugate**) of $|\varphi\rangle$, and symbolizes the concept that for every ket, there is a corresponding bra. State vectors and their scalar products have the following properties:

1. Scalar products are generally complex. Reversing the order of the kets in the ordered pair $(|\varphi\rangle, |\psi\rangle)$ is equivalent to complex conjugation. This property is written in bra–ket notation as $\langle\psi|\varphi\rangle = \langle\varphi|\psi\rangle^*$

2. **Anti-linearity** in the 1st term: if $|\varphi'\rangle \equiv c_1|\varphi_1\rangle + c_2|\varphi_2\rangle$, then

$$\langle\varphi'|\psi\rangle = c_1^*\langle\varphi_1|\psi\rangle + c_2^*\langle\varphi_2|\psi\rangle$$

3. **Linearity** in the 2nd term: if $|\psi'\rangle \equiv d_1|\psi_1\rangle + d_2|\psi_2\rangle$, then

$$\langle\varphi|\psi'\rangle = d_1\langle\varphi|\psi_1\rangle + d_2\langle\varphi|\psi_2\rangle$$

4. Any ket $|\psi\rangle$ that corresponds to a physically realizable quantum state must be **normalizable**, meaning that the **norm**

$$\||\psi\rangle\| \equiv \sqrt{\langle\psi|\psi\rangle}$$

is real, finite, and positive. $|\psi\rangle$ is normalized if $\||\psi\rangle\| = 1$. If $\||\psi\rangle\| \neq 1$, then dividing $|\psi\rangle$ by $\sqrt{\langle\psi|\psi\rangle}$ normalizes $|\psi\rangle$.

5. If the scalar product of two normalizable state vectors is zero, then the state vectors are said to be **orthogonal**.

Linear Operators and Commutators

The formalism of quantum mechanics involves **linear** operators. Consider two operators $\hat{A}$ and $\hat{B}$ that act on elements of an arbitrary state space $\mathcal{E}$. Also suppose the following: (i) $|\psi\rangle, |\varphi\rangle \in \mathcal{E}$; (ii) $\hat{A}|\psi\rangle = |\psi'\rangle \in \mathcal{E}$; (iii) $\hat{B}|\psi\rangle = |\psi''\rangle \in \mathcal{E}$; (iv) c_1 and c_2 are complex scalars. **Linearity** implies the following:

1. $\hat{A}(c_1|\psi\rangle + c_2|\varphi\rangle) = c_1\hat{A}|\psi\rangle + c_2\hat{A}|\varphi\rangle$
2. $\hat{B}\hat{A}\,|\psi\rangle = \hat{B}(\hat{A}|\psi\rangle) = \hat{B}|\psi'\rangle$
3. $\hat{A}\hat{B}\,|\psi\rangle = \hat{A}(\hat{B}|\psi\rangle) = \hat{A}|\psi''\rangle$

The outcomes of the sequential operations $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ are generally different. When products of operators act on a ket, a standard **order of operations** is used: the rightmost operator acts first on the ket, then the next operator to the left acts on the new ket that is the outcome of the first operator's action, and so on.

Commutators: The commutator of operators $\hat{A}$ and $\hat{B}$ is denoted and defined as

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

Commutators have the following properties:

1. A commutator is itself an operator. If $\hat{C} \equiv [\hat{A}, \hat{B}]$, then

$$\hat{C}|\psi\rangle = \hat{A}\hat{B}\,|\psi\rangle - \hat{B}\hat{A}\,|\psi\rangle = \hat{A}|\psi''\rangle - \hat{B}|\psi'\rangle$$

2. If $[\hat{A}, \hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ **commute**: the order in which they act on any ket does not matter, and $\hat{A}|\psi''\rangle = \hat{B}|\psi'\rangle$.

3. If $[\hat{A}, \hat{B}] \neq 0$, then the order of operations of $\hat{A}$ and $\hat{B}$ is **noncommutative**: the order of operations does matter. For arbitrary $|\psi\rangle$, if $[\hat{A}, \hat{B}] \neq 0$, then

$$\hat{A}\hat{B}\,|\psi\rangle \neq \hat{B}\hat{A}\,|\psi\rangle$$

4. A **commutation relation** for operators $\hat{A}$ and $\hat{B}$ identifies the specific operator that is equivalent to $[\hat{A}, \hat{B}]$, which may be identical to zero, or to a scalar multiple of the identity operator $\hat{\mathbb{I}}$ (in which case $\hat{\mathbb{I}}$ is often omitted from the commutation relation).

Hermitian Conjugation

Hermitian conjugation involves symbolic manipulation of mathematical expressions. Consider elements $|\psi\rangle$ and $|\varphi\rangle$ of a state space $\mathcal{E}$, and a bra $\langle\chi|$ and operator $\hat{A}$ defined to "act on" elements of $\mathcal{E}$. Let $\hat{A}|\psi\rangle = |\psi'\rangle$. Hermitian conjugation involves the following concepts and rules:

1. **Bra–ket correspondence:** for every ket $|\psi\rangle$, there is a corresponding bra $\langle\psi|$. For every bra $\langle\chi|$, there is a corresponding ket $|\chi\rangle$ that is not necessarily an element of $\mathcal{E}$. $|\psi\rangle$ and $\langle\psi|$ are Hermitian conjugates of one another, as are $|\chi\rangle$ and $\langle\chi|$.

2. The **Hermitian conjugate**, or **adjoint**, of $\hat{A}$ is denoted $\hat{A}^\dagger$. If $\hat{A} = \hat{A}^\dagger$, then $\hat{A}$ is said to be **Hermitian**.

3. An operator can act "to the right" on a ket, or "to the left" on a bra. The quantity $\langle\varphi|\hat{A}|\psi\rangle$ is called a **matrix element** of $\hat{A}$ and can be evaluated as $\langle\varphi|\hat{A}|\psi\rangle = \langle\varphi|(\hat{A}|\psi\rangle) = \langle\varphi|\psi'\rangle$, or equivalently as $\langle\varphi|\hat{A}|\psi\rangle = (\langle\varphi|\hat{A})|\psi\rangle = \langle\varphi'|\psi\rangle$, where $\langle\varphi'|$ is the adjoint of $|\varphi'\rangle = \hat{A}^\dagger|\varphi\rangle$ (see item 6 below).

4. $\hat{A}$ acting (to the left) on $\langle\xi| = \lambda_1\langle\psi| + \lambda_2\langle\varphi|$ is linear:

$$\langle\xi|\hat{A} = \lambda_1\langle\psi|\hat{A} + \lambda_2\langle\varphi|\hat{A}$$

where λ_1 and λ_2 are complex scalars.

5. Hermitian conjugation of operators and operator sequences adheres to the following rules, where $\hat{A}$, $\hat{B}$, and the ket–bra pairs $|\varphi\rangle\langle\psi|$ and $|\psi\rangle\langle\varphi|$ are operators, and λ is a scalar:

$$(\hat{A}^\dagger)^\dagger = \hat{A}, \qquad (\lambda\hat{A})^\dagger = \lambda^*\hat{A}^\dagger$$

$$(|\varphi\rangle\langle\psi|)^\dagger = |\psi\rangle\langle\varphi|, \qquad (\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$$

$$(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger = \hat{B}^\dagger + \hat{A}^\dagger = (\hat{B} + \hat{A})^\dagger$$

6. To obtain the Hermitian conjugate of an expression, first take the complex conjugates of all scalars, replace kets with their corresponding bras, replace bras with their corresponding kets, and replace operators with their adjoints; then reverse the order of all elements, noting that scalars commute with all elements. For example, the Hermitian conjugate of the expression $\hat{A}|\psi\rangle = \lambda|\psi'\rangle$ is $\langle\psi'|\lambda^* = \langle\psi|\hat{A}^\dagger$.

Bases

A **basis** for $\mathcal{E}$ is a set of kets that are often (but not necessarily) elements of $\mathcal{E}$, and which can be used to construct any element of $\mathcal{E}$ via **superposition**. The elements of a basis may be **discretely** or **continuously** indexed, depending on the basis. For the arbitrary **discrete basis** $\{|v_k\rangle\}$, the **index** k numbers the elements of the basis; e.g., $\{|E_1\rangle, |E_2\rangle, \dots\}$ might be the notation used for a basis where the labels indicate possible energies of a particle in a potential well. For a **continuous basis** $\{|w_\beta\rangle\}$, the subscript β is a continuously varying index, such as real numbers that might correspond to positions along a coordinate axis. The bases used in this *Field Guide* have the following properties:

1. For every $|\psi\rangle \in \mathcal{E}$, there is one and only one way to expand $|\psi\rangle$ as a superposition of the elements of any particular basis, up to a **global phase** factor (page 36). The superposition is written

$$|\psi\rangle = \sum_k c_k |v_k\rangle \quad \text{(for a discrete basis)}$$

$$|\psi\rangle = \int_{\text{all } \beta} d\beta\, c(\beta) |w_\beta\rangle \quad \text{(for a continuous basis)}$$

There is therefore one unique set of **expansion coefficients** $\{c_k\}$ (discrete basis) or $\{c(\beta)\}$ (continuous basis) for any state vector's expansion into any given basis, where $c_k = \langle v_k|\psi\rangle$ for any k, and $c(\beta) = \langle w_\beta|\psi\rangle$ for any β. The sets $\{|v_k\rangle\}$ and $\{|w_\beta\rangle\}$ are said to **span** the state space $\mathcal{E}$ if they are bases for $\mathcal{E}$.

2. Every discrete basis used in this *Field Guide* is **orthonormal** (all elements are normalized and mutually orthogonal). This means that for a basis $\{|v_k\rangle\}$, $\langle v_j|v_k\rangle = \delta_{jk}$, where δ_{jk} is the **Kronecker delta** (page 112).

3. The continuous basis $\{|w_\beta\rangle\}$ is conventionally said to be orthonormal if $\langle w_{\beta'}|w_\beta\rangle = \delta(\beta' - \beta)$, where $\delta(\beta' - \beta)$ is the **Dirac delta function** (page 112). Although this condition is not normalization in the strictest sense, the elements of a continuous basis are not physically realizable quantum states and do not belong to the state space $\mathcal{E}$, despite forming a basis for $\mathcal{E}$.

Eigenvalue Equations

An **eigenvalue equation** for an arbitrary operator $\hat{A}$ is similar to that of a matrix (page 114), and takes the form

$$\hat{A}|\varphi_\mu\rangle = \lambda_\mu|\varphi_\mu\rangle$$

where μ is a discretely or continuously varying index. For a given operator $\hat{A}$, the equation is satisfied for a particular set of kets $\{|\varphi_\mu\rangle\}$, where each ket $|\varphi_\mu\rangle$ is associated with a scalar λ_μ (generally complex). The kets of the set $\{|\varphi_\mu\rangle\}$ are the **eigenkets** or **eigenstates** of $\hat{A}$. The scalars of the set $\{\lambda_\mu\}$ are the **eigenvalues** of $\hat{A}$. The set $\{\lambda_\mu\}$ is the eigenvalue **spectrum** of $\hat{A}$. Eigenvalue equations have the following characteristics:

1. The eigenkets are indexed, as indicated above by μ. Often the symbol that labels an eigenket is the associated eigenvalue or the index. The eigenvalue equation above and the two below show three equivalent ways of labeling the eigenkets of $\hat{A}$:

$$\hat{A}|\lambda_\mu\rangle = \lambda_\mu|\lambda_\mu\rangle \quad \text{and} \quad \hat{A}|\mu\rangle = \lambda_\mu|\mu\rangle$$

2. Quantum mechanics problems often involve finding the eigenkets and the eigenvalues of operators. It is possible that an operator does not have solutions to its eigenvalue equation.

3. If a basis for a state space $\mathcal{E}$ has n orthonormal elements, then $\mathcal{E}$ is said to have a **state-space dimension** of n, to be distinguished from a coordinate-space dimension. For any Hermitian operator that acts on elements of an n-dimensional state space $\mathcal{E}$, a set of n distinct mutually orthonormal eigenkets of that operator can be found; this set is a basis that spans $\mathcal{E}$.

4. **Degeneracy** means that $g_\mu > 1$ different orthogonal eigenkets of an operator are associated with the same eigenvalue λ_μ; g_μ is the **degree of degeneracy**. An additional index may label these degenerate eigenkets; e.g., for a given eigenvalue λ_μ,

$$\hat{A}|\varphi_\mu^i\rangle = \lambda_\mu|\varphi_\mu^i\rangle; \quad i \in \{1, 2, \cdots g_\mu\}$$

The superscript i is omitted from $|\varphi_\mu^i\rangle$ if $g_\mu = 1$ for a given λ_μ. If $g_\mu > 1$ for one or more values of λ_μ, then various sets of mutually orthogonal eigenkets can be specified. If no degeneracies exist, then there is one unique set of orthonormal eigenkets (up to global phase factors; see page 36).

Projectors

A **projector** or **projection operator** onto $|\psi\rangle$ is defined as $\hat{\mathbb{P}}_\psi \equiv |\psi\rangle\langle\psi|$. Projectors are operators, as seen in the following:

$$\hat{\mathbb{P}}_\psi |\varphi\rangle = (|\psi\rangle\langle\psi|)\,|\varphi\rangle = |\psi\rangle\,\langle\psi|\varphi\rangle = \lambda\,|\psi\rangle$$

where $\lambda = \langle\psi|\varphi\rangle$ is a complex scalar, so that $\hat{\mathbb{P}}_\psi$ produces a new (and generally unnormalized) ket proportional to $|\psi\rangle$.

If the scalar product $\lambda = \langle\psi|\varphi\rangle$ is non-zero, then $|\varphi\rangle$ and $|\psi\rangle$ are said to **overlap**: $\langle\psi|\varphi\rangle$ quantifies how much the state $|\psi\rangle$ and $|\varphi\rangle$ have in common (and thus "overlap") in terms of their expansions into the same basis. If the states have non-zero overlap, then there are basis elements that appear with nonzero coefficients in the expansions of both $|\psi\rangle$ and $|\varphi\rangle$. $\hat{\mathbb{P}}_\psi|\varphi\rangle$ "projects $|\varphi\rangle$ onto $|\psi\rangle$" and can be thought of as picking out the portion of $|\varphi\rangle$ that overlaps with $|\psi\rangle$. If $|\varphi\rangle$ and $|\psi\rangle$ have no overlap, then $\langle\psi|\varphi\rangle = 0$, and $\hat{\mathbb{P}}_\psi|\varphi\rangle = 0$.

Projectors have the following properties:

1. Projectors have the property of **idempotency**, meaning that $\hat{\mathbb{P}}_\psi^2 = \hat{\mathbb{P}}_\psi$. Since $\hat{\mathbb{P}}_\psi^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi|$, the idempotency condition is only met if $\langle\psi|\psi\rangle = 1$, so $|\psi\rangle$ must be properly normalized for $|\psi\rangle\langle\psi|$ to be a projector onto $|\psi\rangle$.

2. If two kets $|\varphi\rangle$ and $|\psi\rangle$ are orthogonal (and therefore have no overlap), then $\langle\psi|\varphi\rangle = 0$ and the projectors onto these states are also said to be orthogonal, implying that

$$\hat{\mathbb{P}}_\psi\hat{\mathbb{P}}_\varphi = |\psi\rangle\langle\psi|\varphi\rangle\langle\varphi| = 0$$

3. A sum of orthogonal projectors is a projector onto a **subspace**. Consider a discrete basis $\{|v_k\rangle\}$ that **spans** a state space $\mathcal{E}$, where $k \in \{1, \ldots, k_{\max}\}$. For $q < k_{\max}$, the **subspace projector**

$$\hat{\mathbb{P}}_q \equiv \sum_{k=1}^{q} |v_k\rangle\langle v_k|$$

projects onto the subspace $\mathcal{E}_q$ of $\mathcal{E}$, where $\mathcal{E}_q$ is spanned by $\{|v_1\rangle, |v_2\rangle, \ldots, |v_q\rangle\}$.

Closure Relations

Every basis is associated with a **closure relation**, which is formally a projector onto the entire state space rather than onto a subspace. Every ket in the state space remains unchanged when acted upon by this projector. Consider an arbitrary state space $\mathcal{E}$. Let $\hat{\mathbb{I}}$ be the **identity operator**, such that $\hat{\mathbb{I}}|\psi\rangle = |\psi\rangle$ for any $|\psi\rangle \in \mathcal{E}$. Closure relations are expressed as follows:

Closure Relation (Discrete Basis)

For a discrete orthonormal basis $\{|v_k^i\rangle\}$, with $i \in \{1, 2, \ldots g_k\}$ and where g_k is the degree of degeneracy for index k, the closure relation is

$$\sum_k \sum_{i=1}^{g_k} |v_k^i\rangle\langle v_k^i| = \hat{\mathbb{I}}$$

Closure Relation (Continuous Basis)

For a continuous non-degenerate orthonormal basis $\{|w_\beta\rangle\}$, where β labels the (infinitely many) orthogonal elements of the basis, the closure relation is

$$\int_{\text{all}\,\beta} d\beta\, |w_\beta\rangle\langle w_\beta| = \hat{\mathbb{I}}$$

Because a closure relation's sum or integral is equivalent to the identity operator, it can be inserted into an expression immediately before a ket or after a bra, or next to an operator (i.e., making a product with that operator), without changing the meaning of the expression. In this manner, closure relations aid in problem solving and manipulation of expressions.

Formally, a closure relation is a mathematical statement that a basis exists and is complete; i.e, there are neither missing nor extraneous elements in the construction of the basis. The expression of a closure relation can be given as a definition of the symbols used to specify the elements of a basis.

Functions of Operators

A **function of an operator** can be defined by a **Taylor series expansion** of the same function of a continuous variable, with the operator replacing the variable. For a variable x, a function $F(x)$ has a Taylor series expansion about $x = a$ given by

$$F(x) = \sum_{n=0}^{\infty} \frac{(x-a)^n}{n!} \cdot \left. \frac{d^n F(x)}{dx^n} \right|_{x=a} = \sum_{n=0}^{\infty} b_n \cdot (x-a)^n$$

where b_n is the coefficient of the n^{th}-power term. Most commonly, expansions are taken about $a = 0$. The same function of an operator $\hat{A}$ is constructed by replacing x with $\hat{A}$:

$$F(\hat{A}) = \sum_{n=0}^{\infty} b_n \cdot (\hat{A} - a)^n$$

For example, expanding e^x about $x = 0$ gives $e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n$, so that $e^{\hat{A}} = 1 + \hat{A} + \frac{1}{2!}\hat{A}^2 + \ldots = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n$. Note that $\hat{A}^0 = \hat{\mathbb{I}}$. The identity operator $\hat{\mathbb{I}}$ is often omitted from operator expansions when it is multiplied by a scalar quantity (1 in this case).

Functions of operators are themselves operators. Consider an operator $\hat{A}$ that has a non-degenerate discrete spectrum $\{\lambda_k\}$ and eigenkets $\{|v_k\rangle\}$. Two special cases for simplifying the actions of functions of operators are given below.

1. If $|v_k\rangle$ is an eigenket of $\hat{A}$ with eigenvalue λ_k, then $|v_k\rangle$ is an eigenket of $F(\hat{A})$ with eigenvalue $F(\lambda_k)$. This statement can be demonstrated by expanding $F(\hat{A})$ about 0:

$$F(\hat{A})|v_k\rangle = \sum_{n=0}^{\infty} b_n \hat{A}^n |v_k\rangle = \sum_{n=0}^{\infty} b_n \lambda_k^n |v_k\rangle = F(\lambda_k)|v_k\rangle$$

2. $F(\hat{A})$ acting on an arbitrary ket $|\psi\rangle$ can be calculated by first expanding $|\psi\rangle$ in the $\{|v_k\rangle\}$ basis: $|\psi\rangle = \sum_k c_k |v_k\rangle$, where $c_k = \langle v_k|\psi\rangle$. $F(\hat{A})|\psi\rangle$ is then evaluated using the closure relation $\hat{\mathbb{I}} = \sum_k |v_k\rangle\langle v_k|$ as follows:

$$F(\hat{A})|\psi\rangle = F(\hat{A})\hat{\mathbb{I}}|\psi\rangle = \sum_k F(\hat{A})|v_k\rangle\langle v_k|\psi\rangle = \sum_k c_k F(\lambda_k)|v_k\rangle$$

Postulates of Quantum Mechanics

The **postulates** of quantum mechanics are the assumptions upon which the mathematics and interpretations of quantum mechanics are based. There are six basic postulates; three are expressed below, with the remaining three on pages 12 and 13.

1. State postulate

The state of a system (or particle), denoted at a time t as $|\Psi(t)\rangle$, is an element of a vector space consisting of all physically realizable states of the system.

Postulate 1 implies the existence of a superposition principle, and defined scalar products (page 3). The linear vector space is called the system's state space (or **Hilbert space**). Every given physical system has an associated state space.

2. Observable postulate

Every measurable, dynamical physical quantity corresponds to a **linear Hermitian** operator, called an **observable**.

An observable is defined to act on all elements of a specified state space. The word "observable" may also refer to the physical quantity with which the Hermitian operator is associated.

3. Evolution postulate

As a quantum system evolves over time t, the corresponding dynamics of the physical state are governed by the **Schrödinger equation**

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle$$

where $\hat{H}(t)$ is the observable associated with the total energy of the system, and is called the **Hamiltonian**; $\hat{H}$ may or may not depend on time.

Eigenvalue and Collapse Postulates

The remaining three postulates involve outcomes and predictions of measurements. The specific outcome of any single measurement in an actual experiment is generally not predictable with certainty, even in principle. Measurement predictions in quantum mechanics are inherently statistical.

4. Eigenvalue postulate

The only possible results of a measurement of a physical quantity are the eigenvalues of the Hermitian operator associated with that quantity.

The eigenvalues of Hermitian operators are always real, and only real quantities can be obtained in measurements. If the eigenvalues of an operator form a discretely indexed (rather than continuously varying) **spectrum**, the associated physical quantity is said to be **quantized**.

5. Collapse postulate

If a measurement is made on a system in state $|\Psi(t_0)\rangle$ at time t_0, then immediately after the measurement the system is left in the eigenstate associated with the measured eigenvalue of the corresponding observable. The measurement is said to **collapse** the system into that eigenstate. If the measured eigenvalue is degenerate, the system is left in a superposition of the associated eigenstates.

Suppose that $\hat{A}$ is the observable for the quantity measured, λ_q is the eigenvalue of $\hat{A}$ that is the measurement result, and $\{|v_q^i\rangle\}$ is the set of g_q associated degenerate eigenkets, with q a specific index, and $i \in \{1, 2, \ldots, g_q\}$. Immediately after the measurement, the system is left in the normalized state

$$\frac{\hat{\mathbb{P}}_q|\Psi(t_0)\rangle}{\sqrt{\langle\Psi(t_0)|\hat{\mathbb{P}}_q|\Psi(t_0)\rangle}}$$

where $\hat{\mathbb{P}}_q$ projects onto the subspace $\mathcal{E}_q$ spanned by $\{|v_q^i\rangle\}$.

Probability Postulate

6. Probability postulate

If a measurement of a quantity corresponding to an observable $\hat{A}$ is to be made on a system in the normalized state $|\Psi(t)\rangle$, then the probability (discrete spectrum) or **probability density** (continuous spectrum) of obtaining the result λ is the scalar product of $|\Psi(t)\rangle$ with the projection of $|\Psi(t)\rangle$ onto the state space spanned by the eigenstates corresponding to eigenvalue λ of $\hat{A}$.

Consider an observable $\hat{A}$ with a discrete spectrum and eigenvalue equation $\hat{A}|v_k^i\rangle = \lambda_k|v_k^i\rangle$. Let λ_q be one possible measurement outcome (a specific eigenvalue of $\hat{A}$), and $\{|v_q^i\rangle\}$ the g_q degenerate eigenstates associated with λ_q, where $i \in \{1, 2, \ldots, g_q\}$. The **probability** of obtaining λ_q in a measurement is

$$\mathcal{P}(\lambda_q) = \langle\Psi(t)|\hat{\mathbb{P}}_q|\Psi(t)\rangle = \sum_{i=1}^{g_q} |\langle v_q^i|\Psi(t)\rangle|^2$$

where $\hat{\mathbb{P}}_q$ projects onto the subspace $\mathcal{E}_q$ (of the full state space) spanned by the g_q kets $\{|v_q^i\rangle\}$. If $g_q = 1$ for that value of q, then λ_q is non-degenerate and the index (and summation over) i is omitted. The probability of obtaining λ_q in a measurement of the physical quantity associated with $\hat{A}$ is then

$$\mathcal{P}(\lambda_q) = \langle\Psi(t)|\hat{\mathbb{P}}_q|\Psi(t)\rangle = |\langle v_q|\Psi(t)\rangle|^2 = |c_q|^2$$

where $c_q = \langle v_q|\Psi(t)\rangle$ is the $|v_q\rangle$ term's expansion coefficient when $|\Psi(t)\rangle$ is expanded into the $\{|v_k^i\rangle\}$ basis.

If $\hat{A}$ has a continuous spectrum, where $\hat{A}|w_\beta\rangle = \lambda_\beta|w_\beta\rangle$ is the eigenvalue equation and $\hat{\mathbb{P}}_{\beta'} = |w_{\beta'}\rangle\langle w_{\beta'}|$ is a projector onto $|w_{\beta'}\rangle$, then the probability density of $|\Psi(t)\rangle$ at $\lambda_{\beta'}$ is

$$\langle\Psi(t)|\hat{\mathbb{P}}_{\beta'}|\Psi(t)\rangle = |\langle w_{\beta'}|\Psi(t)\rangle|^2$$

For a probability density that is approximately constant over the sufficiently narrow range $\lambda_{\beta'}$ to $\lambda_{\beta'} + d\lambda$, the probability that the result will lie within this range is given by

$$d\mathcal{P}(\lambda_{\beta'}) = d\lambda|\langle w_{\beta'}|\Psi(t)\rangle|^2$$

Note that $\int_{\text{all }\lambda_{\beta'}} d\mathcal{P}(\lambda_{\beta'}) = \int_{\text{all }\lambda_{\beta'}} d\lambda|\langle w_{\beta'}|\Psi(t)\rangle|^2 = 1$.

Examples of Observables: $\hat{H}$, $\hat{X}$, and $\hat{P}_x$

Hamiltonian: $\hat{H}$ is the conventional symbol for the Hamiltonian, the operator corresponding to the total energy of a given system (postulate 3, page 11). Since energy is a dynamical, measurable quantity, $\hat{H}$ is an observable and is Hermitian. Consider a 1D potential well (such as a **harmonic oscillator**, page 54) for which $\hat{H}$ has a non-degenerate discrete spectrum and an eigenvalue equation expressed as

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$$

where E_n is a real eigenvalue with dimensional units of energy, the index n varies discretely and each eigenket $|\varphi_n\rangle$ is associated with one specific eigenvalue E_n. The full set of eigenvalues $\{E_n\}$ is the **energy spectrum** of the system. Since $\hat{H}$ is Hermitian, the set of eigenkets $\{|\varphi_n\rangle\}$ is a basis for $\mathcal{E}$ (see page 7) called the **energy eigenstate basis**, which has the orthonormality condition

$$\langle\varphi_j|\varphi_k\rangle = \delta_{jk}$$

Position and momentum operators: Consider a state space $\mathcal{E}_x$ that corresponds to a particle whose positions and motion are constrained to the x axis. In $\mathcal{E}_x$, position and momentum are measurable quantities. Let $\hat{X}$ and $\hat{P}_x$ denote the associated position and momentum operators, which are observables. Let the following eigenvalue equations define the symbols for the eigenvalues and eigenkets of $\hat{X}$ and $\hat{P}_x$:

$$\hat{X}|x\rangle = x|x\rangle$$

$$\hat{P}_x|p\rangle = p|p\rangle$$

Note that the eigenvalues x and p (and $\hat{X}$ and $\hat{P}_x$) are quantities with dimensional units. In correspondence with the **eigenvalue postulate** (page 12), the eigenvalues denoted by x must be all real numbers with dimensional units of position. The eigenvalues p are all real numbers with dimensional units of momentum. Since both x and p are continuously distributed (any real value is allowed), the associated bases $\{|x\rangle\}$ and $\{|p\rangle\}$ are continuous and have the orthonormality conditions

$$\langle x|x'\rangle = \delta(x - x') \quad \text{and} \quad \langle p|p'\rangle = \delta(p - p')$$

Calculating Quantities in Quantum Mechanics

Calculations of expressions that are given in Dirac notation often involve three steps: (i) expanding the elements of Dirac notation into known bases; (ii) representing these elements by vectors and matrices, or functions and continuous operations (e.g., multiplication and differentiation); and (iii) performing the operations indicated. Step (i) involves the use of closure relations to re-express kets, bras, and operators, as indicated below for a discrete basis $\{|v_k\rangle\}$ and a continuous basis $\{|w_\beta\rangle\}$.

Quantity	Discrete Basis (Sum Over All j, k)
$\hat{\mathbb{I}}$	$= \sum \lvert v_k\rangle\langle v_k\rvert$
$\lvert\psi\rangle = \hat{\mathbb{I}}\lvert\psi\rangle$	$= \sum \lvert v_k\rangle\langle v_k\rvert\psi\rangle$
$\langle\varphi\rvert = \langle\varphi\rvert\hat{\mathbb{I}}$	$= \sum \langle\varphi\rvert v_k\rangle\langle v_k\rvert$
$\hat{A} = \hat{\mathbb{I}}\hat{A}\hat{\mathbb{I}}$	$= \sum\sum \lvert v_j\rangle\langle v_j\rvert\hat{A}\rvert v_k\rangle\langle v_k\rvert$

Quantity	Continuous Basis (Integrate Over All β, β')
$\hat{\mathbb{I}}$	$= \int d\beta \lvert w_\beta\rangle\langle w_\beta\rvert$
$\lvert\psi\rangle = \hat{\mathbb{I}}\lvert\psi\rangle$	$= \int d\beta \lvert w_\beta\rangle\langle w_\beta\rvert\psi\rangle$
$\langle\varphi\rvert = \langle\varphi\rvert\hat{\mathbb{I}}$	$= \int d\beta \langle\varphi\rvert w_\beta\rangle\langle w_\beta\rvert$
$\hat{A} = \hat{\mathbb{I}}\hat{A}\hat{\mathbb{I}}$	$= \int\int d\beta d\beta' \lvert w_\beta\rangle\langle w_\beta\rvert\hat{A}\rvert w_{\beta'}\rangle\langle w_{\beta'}\rvert$

Manipulation of expressions in Dirac notation further involves the use of the following relationships:

- Discrete-basis orthonormality: $\langle v_j|v_k\rangle = \delta_{jk}$
- Continuous-basis orthonormality: $\langle w_\beta|w_{\beta'}\rangle = \delta(\beta - \beta')$
- Scalars such as $\langle v_j|\hat{A}|v_k\rangle$ and $\langle w_\beta|\psi\rangle$ commute with operators, bras, and kets
- $\langle\varphi|v_k\rangle = \langle v_k|\varphi\rangle^*$ and $\langle\varphi|w_\beta\rangle = \langle w_\beta|\varphi\rangle^*$

For cases in which multiple physical quantities define a single basis element, a single index (such as k, above) may serve as a **compound index** that represents multiple quantities, including different degenerate states.

Calculating Quantities Using a Discrete Basis

When a discrete basis is known, the relationships given in the upper table on page 15 can be used to manipulate expressions that involve elements of Dirac notation. Calculations may then proceed by re-writing the discrete sums in terms of vectors and matrices, and performing calculations according to the methods of linear algebra. As an example, calculation of the quantity $\langle\varphi|\hat{A}|\psi\rangle$ is shown below using the arbitrary discrete basis $\{|v_k\rangle\}$, where k may serve as a compound index. Assume the following expansions for the kets $|\psi\rangle$ and $|\varphi\rangle$ into this basis:

$$|\psi\rangle = \sum_k |v_k\rangle\langle v_k|\psi\rangle = \sum_k c_k|v_k\rangle \qquad \text{where } c_k = \langle v_k|\psi\rangle$$

$$|\varphi\rangle = \sum_j |v_j\rangle\langle v_j|\varphi\rangle = \sum_j d_j|v_j\rangle \qquad \text{where } d_j = \langle v_j|\varphi\rangle$$

By defining the **matrix element** $A_{jk} \equiv \langle v_j|\hat{A}|v_k\rangle$ and using the expansions given above and the upper table on page 15, $\langle\varphi|\hat{A}|\psi\rangle$ is expressed as

$$\begin{aligned}\langle\varphi|\hat{A}|\psi\rangle &= \sum_j \sum_k \langle\varphi|v_j\rangle\langle v_j|\hat{A}|v_k\rangle\langle v_k|\psi\rangle \\ &= \sum_j \sum_k d_j^* A_{jk}\, c_k\end{aligned}$$

Making use of vector and matrix notation, and the standard rules of vector and matrix multiplication that are implied by the notation, the double-summation above is equivalent to

$$\langle\varphi|\hat{A}|\psi\rangle = \begin{bmatrix} d_1^* & d_2^* & \cdots \end{bmatrix} \begin{bmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix}$$

Kets and bras can be replaced by vectors of the coefficients of expansion into a discrete basis, and operators can be replaced by matrices of discretely indexed elements in that basis. Calculations then proceed by performing the implied vector and matrix multiplication, demonstrating the utility of working with a **discrete representation**, defined on page 17.

Discrete Representations

A **representation** is a specific basis selected to aid in the expression of information about kets and bras, and the actions of operators. In a discrete representation, a discrete basis is selected. A ket is then represented by a column vector of expansion coefficients for that basis, and the corresponding bra is represented as the adjoint of that column vector (page 113).

The example given on page 16 illustrates the utility of a discrete representation, and is expanded upon below. In the example, the expansion of $|\psi\rangle$ into the $\{|v_k\rangle\}$ basis is given by

$$|\psi\rangle = \sum_k \langle v_k|\psi\rangle |v_k\rangle = \sum_k c_k |v_k\rangle$$

Let $|\psi\rangle_{\{v\}}$ denote the column vector of expansion coefficients:

$$|\psi\rangle_{\{v\}} \equiv \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix} = \begin{bmatrix} \langle v_1|\psi\rangle \\ \langle v_2|\psi\rangle \\ \vdots \end{bmatrix}$$

The vector $|\psi\rangle_{\{v\}}$ is not identical to the ket $|\psi\rangle$; a different choice of basis will have a different set of expansion coefficients for the same ket. The corresponding bra $\langle\psi|$ is represented by

$$\langle\psi|_{\{v\}} \equiv \begin{bmatrix} c_1^* & c_2^* & \cdots \end{bmatrix} = \begin{bmatrix} \langle v_1|\psi\rangle^* & \langle v_2|\psi\rangle^* & \cdots \end{bmatrix}$$

The representation is named by the basis chosen; the example above defines the "$\{|v_k\rangle\}$ representation." If the chosen basis kets are eigenkets of some operator, then the operator or its associated physical quantity may be used to name the representation [e.g., the "$\hat{X}$ (or position) representation" on page 19].

In a **discrete representation**, operators are represented by matrices. In the example on page 16, $\hat{A}$ is represented by the matrix $A_{\{v\}}$ of discretely indexed elements $A_{jk} = \langle v_j|\hat{A}|v_k\rangle$:

$$A_{\{v\}} \equiv \begin{bmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

For the matrix element subscripts, the row index (j) is listed first, followed by the column index (k).

Transformation of Discrete Representation

In a **discrete representation**, a ket is represented by a column vector of scalars that are the coefficients of the expansion of the ket into a specified basis. To construct the representation of the same ket by a column vector of coefficients of expansion into a different basis, the initial column vector can be acted upon by a **transformation matrix** $\mathbb{M}$.

Let $|\psi\rangle_{\{u\}}$ and $|\psi\rangle_{\{v\}}$ denote the representations of $|\psi\rangle$ obtained by expanding $|\psi\rangle$ into the $\{|u_j\rangle\}$ and $\{|v_k\rangle\}$ bases, respectively. The bases span the same n-dimensional state space, so $\{|u_j\rangle\}$ and $\{|v_k\rangle\}$ each have n elements. $|\psi\rangle_{\{u\}}$ and $|\psi\rangle_{\{v\}}$ are related by

$$|\psi\rangle_{\{u\}} = \mathbb{M}|\psi\rangle_{\{v\}} \quad \text{and} \quad |\psi\rangle_{\{v\}} = \mathbb{M}^\dagger|\psi\rangle_{\{u\}}$$

where the elements of the square matrix $\mathbb{M}$ are given by

$$\mathbb{M}_{jk} = \langle u_j|v_k\rangle$$

Matrices representing operators are also transformed using $\mathbb{M}$. Let $A_{\{u\}}$ and $A_{\{v\}}$ be the matrices representing $\hat{A}$ in the $\{|u_j\rangle\}$ and $\{|v_k\rangle\}$ bases, respectively. Then

$$A_{\{u\}} = \mathbb{M}A_{\{v\}}\mathbb{M}^\dagger \quad \text{and} \quad A_{\{v\}} = \mathbb{M}^\dagger A_{\{u\}}\mathbb{M}$$

Example: Consider a 2D state space that is spanned by two bases, $\{|u_1\rangle, |u_2\rangle\}$ and $\{|v_1\rangle, |v_2\rangle\}$, where

$$|v_1\rangle = \frac{1}{\sqrt{2}}|u_1\rangle + \frac{i}{\sqrt{2}}|u_2\rangle \quad \text{and} \quad |v_2\rangle = \frac{1}{\sqrt{2}}|u_1\rangle - \frac{i}{\sqrt{2}}|u_2\rangle$$

Suppose that there is an operator $\hat{A}$ that is expressed as the following matrix in the $\{|u_j\rangle\}$ representation:

$$A_{\{u\}} = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

To express $A_{\{u\}}$ in the $\{|v_k\rangle\}$ representation, the matrix $\mathbb{M}$ is

$$\mathbb{M} = \begin{bmatrix} \mathbb{M}_{11} & \mathbb{M}_{12} \\ \mathbb{M}_{21} & \mathbb{M}_{22} \end{bmatrix} = \begin{bmatrix} \langle u_1|v_1\rangle & \langle u_1|v_2\rangle \\ \langle u_2|v_1\rangle & \langle u_2|v_2\rangle \end{bmatrix} = \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ i/\sqrt{2} & -i/\sqrt{2} \end{bmatrix}$$

which is then used to calculate $A_{\{v\}}$:

$$A_{\{v\}} = \begin{bmatrix} 1/\sqrt{2} & -i/\sqrt{2} \\ 1/\sqrt{2} & i/\sqrt{2} \end{bmatrix} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ i/\sqrt{2} & -i/\sqrt{2} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Continuous Representations: $\hat{X}$, $\hat{P}_x$

In a **continuous representation**, a ket is expressed as a continuous superposition of the orthonormal kets of a continuous basis. The expansion coefficients are continuously indexed, and the ket is represented by this continuous set of numbers, which is called a **wavefunction** (page 20).

Examples of continuous representations are the **position** and **momentum representations**, defined on page 20 and based on the closure relations below. In one spatial dimension, eigenkets of the position and momentum operators $\hat{X}$ and $\hat{P}_x$ define bases $\{|x\rangle\}$ and $\{|p\rangle\}$ (page 14). In this notation, the general parameter β previously used as a continuous index or eigenvalue (pages 9 and 15) is replaced by the eigenvalues x and p themselves, and these eigenvalues are used to label the corresponding kets of the bases, consistent with item 1 on page 7.

The bases $\{|x\rangle\}$ and $\{|p\rangle\}$ have the associated closure relations

$$\int_{-\infty}^{\infty} dx|x\rangle\langle x| = \hat{\mathbb{I}} \quad \text{and} \quad \int_{-\infty}^{\infty} dp|p\rangle\langle p| = \hat{\mathbb{I}}$$

Since x and p carry dimensional units of length and momentum, respectively, dx and dp also carry those same dimensional units. In order for the identity operator to be dimensionless, each bra and ket in the expressions above may be thought of as carrying the inverse-square-root of the dimensional units of the associated eigenvalue. Since the SI dimensional units of dx are meters ([m]), $|x\rangle$ and $\langle x|$ may be considered as carrying the dimensional units $[\text{m}^{-1/2}]$. The dimensional units of $|p\rangle$ and $\langle p|$ may be considered to be $[(\text{kg}\cdot\text{m/s})^{-1/2}]$. However, while $\{|x\rangle\}$ and $\{|p\rangle\}$ serve as bases, the elements of these bases are not physically realizable states and these kets (and bras) are not quantities with a physical dimension. Treating the elements of $\{|x\rangle\}$ and $\{|p\rangle\}$ (and the associated bras) as having dimensional units is a convenience that is consistent with (i) the construction of wavefunctions and the interpretation of the dimensional units of wavefunctions (page 20); and (ii) scalar products involving these kets, such as the quantities on pages 14 and 23, noting that a Dirac delta function (page 112) carries dimensional units that are the inverse of those of its argument.

Continuous Representations: Wavefunctions

Let $\mathcal{E}_x$ be the state space associated with 1D motion along x. The position and momentum representations that are used to describe a state vector $|\psi\rangle \in \mathcal{E}_x$ are based on the closure relations given on page 19 as follows:

$$|\psi\rangle = \hat{\mathbb{I}}|\psi\rangle = \int_{-\infty}^{\infty} dx|x\rangle\langle x|\psi\rangle = \int_{-\infty}^{\infty} dx\,\psi(x)|x\rangle$$

$$|\psi\rangle = \hat{\mathbb{I}}|\psi\rangle = \int_{-\infty}^{\infty} dp|p\rangle\langle p|\psi\rangle = \int_{-\infty}^{\infty} dp\,\tilde{\psi}(p)|p\rangle$$

where $\psi(x) \equiv \langle x|\psi\rangle$ is the expansion coefficient associated with the $\hat{X}$ eigenket $|x\rangle$, and $\tilde{\psi}(p) \equiv \langle p|\psi\rangle$ is the expansion coefficient associated with the $\hat{P}_x$ eigenket $|p\rangle$. In this sense, the expansion coefficient corresponding to a specific value of x or p is the continuous-representation equivalent of one element of a column vector representing a ket in a discrete representation (page 17). When $\psi(x)$ and $\tilde{\psi}(p)$ are considered as functions over all possible values of x or p, then these functions are the continuous-representation equivalents of the entire column vector representing a state in a discrete representation. These functions are called wavefunctions and are defined as follows:

- The 1D **position-space wavefunction** $\psi(x)$ is the continuous distribution of expansion coefficients obtained when expanding $|\psi\rangle$ into the basis of position-operator ($\hat{X}$) eigenkets $\{|x\rangle\}$.
- The 1D **momentum-space wavefunction** $\tilde{\psi}(p)$ is the continuous distribution of expansion coefficients obtained when expanding $|\psi\rangle$ into the basis of momentum-operator ($\hat{P}_x$) eigenkets $\{|p\rangle\}$.

The **SI** dimensional units of $\psi(x)$ are $[\mathrm{m}^{-1/2}]$, and those of $\tilde{\psi}(p)$ are $[(\mathrm{kg}\cdot\mathrm{m/s})^{-1/2}]$, consistent with the discussion of dimensional units on page 19. In higher spatial dimensions, the dimensional units of wavefunctions are similarly determined by the closure relations involved. The characteristics of physically realizable wavefunctions are given on page 32.

Calculating Quantities Using a Continuous Basis

In a continuous representation, a bra is represented by the complex conjugate of the wavefunction representing the associated ket, and operators are represented by actions on functions (e.g., multiplication and differentiation). Calculations involve replacing bras, kets, and operators with functions and continuous operators, then performing the operations. To illustrate these steps, let the state space $\mathcal{E}_x$ correspond to the states available to a particle with 1D motion along x. The eigenkets $\{|x\rangle\}$ of the position operator $\hat{X}$ span $\mathcal{E}_x$ and define the position representation, also called here the "$\hat{X}$ representation" since the associated basis is formed of the eigenkets of $\hat{X}$. Let $\psi(x)$ and $\varphi(x)$ be wavefunctions representing the state vectors $|\psi\rangle, |\varphi\rangle \in \mathcal{E}_x$. Using the closure relation $\hat{\mathbb{I}} = \int_{-\infty}^{\infty} dx|x\rangle\langle x|$, the scalar product $\langle\varphi|\psi\rangle$ is evaluated as

$$\langle\varphi|\psi\rangle = \langle\varphi|\hat{\mathbb{I}}|\psi\rangle = \int_{-\infty}^{\infty} dx\langle\varphi|x\rangle\langle x|\psi\rangle = \int_{-\infty}^{\infty} dx\, \varphi^*(x)\psi(x)$$

This calculation shows that in the position representation, the scalar product $\langle\varphi|\psi\rangle$ is calculated by integrating the product of the associated functions $\varphi^*(x)$ and $\psi(x)$ over all space. This integral is called an **overlap integral** since it evaluates the overlap $\langle\varphi|\psi\rangle$. Similarly, the scalar product can be calculated in the momentum representation (or the "$\hat{P}_x$ representation"): $\langle\varphi|\psi\rangle = \int_{-\infty}^{\infty} dp\, \tilde{\varphi}^*(p)\tilde{\psi}(p)$ (also see page 24).

In a continuous representation, operators are not represented by matrices of discretely indexed elements. The term **generalized matrix element** refers to quantities that have the formal bra–operator–ket structure of a matrix element but that involve the elements of a continuous basis. For example, an operator $\hat{A}$ that acts on elements of $\mathcal{E}_x$ has generalized matrix elements in the $\hat{X}$ representation given by $A(x, x') \equiv \langle x|\hat{A}|x'\rangle$ for any positions x, x'. Using the closure relation for the $\{|x\rangle\}$ basis (twice, see page 15), the quantity $\langle\varphi|\hat{A}|\psi\rangle$ is evaluated as

$$\begin{aligned}\langle\varphi|\hat{A}|\psi\rangle &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \langle\varphi|x\rangle\langle x|\hat{A}|x'\rangle\langle x'|\psi\rangle \\ &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \varphi^*(x)A(x, x')\psi(x')\end{aligned}$$

Operators in the $\hat{X}$ Representation

The examples below illustrate the use of the $\hat{X}$ representation in performing calculations involving the state space $\mathcal{E}_x$ and arbitrary state vectors $|\psi\rangle, |\varphi\rangle \in \mathcal{E}_x$. These examples also involve the 1D momentum operator $\hat{P}_x$. As stated on page 23, the momentum operator $\hat{P}_x$ has the continuously indexed generalized matrix elements

$$P_x(x, x') = \langle x|\hat{P}_x|x'\rangle = -i\hbar \frac{\partial}{\partial x}\delta(x - x')$$

Example 1: The ket $|\xi\rangle$ defined by $|\xi\rangle \equiv \hat{P}_x|\psi\rangle$ can be expanded into the $\{|x\rangle\}$ basis by the following steps. First, using closure relations, $\hat{P}_x$ can be written as $\hat{P}_x = \int dx\, dx'\, |x\rangle\langle x|\hat{P}_x|x'\rangle\langle x'|$ (see pages 15 and 21), integrating over all space. Next,

$$\begin{aligned}
|\xi\rangle = \hat{P}_x|\psi\rangle &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' |x\rangle\langle x|\hat{P}_x|x'\rangle\langle x'|\psi\rangle \\
&= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' |x\rangle P_x(x, x')\psi(x') \\
&= -i\hbar \int_{-\infty}^{\infty} dx\, |x\rangle \frac{\partial}{\partial x} \int_{-\infty}^{\infty} dx' \delta(x - x')\psi(x') \\
&= \int_{-\infty}^{\infty} dx \left(-i\hbar \frac{\partial \psi(x)}{\partial x}\right)|x\rangle
\end{aligned}$$

The last line above shows that $|\xi\rangle$ is a continuous superposition of elements of the $\{|x\rangle\}$ basis. The expansion coefficients are given by $-i\hbar \frac{\partial \psi(x)}{\partial x}$ for all x so that $|\xi\rangle = \hat{P}_x|\psi\rangle$ is a ket represented by the position-space wavefunction

$$\xi(x) = -i\hbar \frac{\partial \psi(x)}{\partial x}$$

In the position representation, $\hat{P}_x$ is represented by the differential operator $-i\hbar \frac{\partial}{\partial x}$, which acts on position-space wavefunctions.

Example 2: The quantity $\langle \varphi|\hat{P}_x|\psi\rangle$, which is the scalar product $\langle \varphi|\xi\rangle$, is calculated as follows:

$$\langle \varphi|\hat{P}_x|\psi\rangle = -i\hbar \int_{-\infty}^{\infty} dx\, \varphi^*(x) \frac{\partial \psi(x)}{\partial x}$$

$\hat{X}$ and $\hat{P}_x$ Representations: Eigenkets and Operators

The multiplication and differentiation operations of $\hat{X}$ and $\hat{P}_x$ in the position and momentum representations are given in the table below. To obtain the expressions, the following generalized matrix elements are used, where $\delta(x-x')$ is the Dirac delta function centered at position x', and $\delta(p-p')$ is the Dirac delta function centered at momentum p':

$$\langle x|\hat{X}|x'\rangle = x'\delta(x-x') \qquad \langle x|\hat{P}_x|x'\rangle = -i\hbar\frac{\partial}{\partial x}\delta(x-x')$$

$$\langle p|\hat{P}_x|p'\rangle = p'\delta(p-p') \qquad \langle p|\hat{X}|p'\rangle = i\hbar\frac{\partial}{\partial p}\delta(p-p')$$

Position and momentum representations of $\hat{X}$ and $\hat{P}_x$ and their eigenkets $|x'\rangle$ and $|p'\rangle$ are given below.

Quantity	$\hat{X}$ Representation	$\hat{P}_x$ Representation
$\hat{X}$	x	$i\hbar\frac{\partial}{\partial p}$
$\hat{P}_x$	$-i\hbar\frac{\partial}{\partial x}$	p
$\|x'\rangle$	$\langle x\|x'\rangle = \delta(x-x')$	$\langle p\|x'\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-ix'p/\hbar}$
$\|p'\rangle$	$\langle x\|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ixp'/\hbar}$	$\langle p\|p'\rangle = \delta(p-p')$

Interpretation:

- $\langle p|x'\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-ix'p/\hbar}$ shows that an eigenket of $\hat{X}$ is a plane wave in the $\hat{P}_x$ representation.
- $\langle x|p'\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ixp'/\hbar}$ shows that an eigenket of $\hat{P}_x$ is a plane wave in the $\hat{X}$ representation.
- $\langle x|x'\rangle = \delta(x-x')$ shows that an eigenket of $\hat{X}$ is a Dirac delta function in the $\hat{X}$ representation.
- $\langle p|p'\rangle = \delta(p-p')$ shows that an eigenket of $\hat{P}_x$ is a Dirac delta function in the $\hat{P}_x$ representation.

Note that none of the functions above are normalizable or physically realizable wavefunctions.

$\hat{X}$ and $\hat{P}_x$ Representations: Fourier Transforms

Transformations between discrete representations are covered on page 18. Transformations between continuous representations such as the $\hat{X}$ and $\hat{P}_x$ representations are also possible. The expressions on pages 19–23 can be used to show that the wavefunctions $\psi(x)$ and $\tilde{\psi}(p)$ are a **Fourier-transform** pair. Using closure relations, this relationship between $\psi(x)$ and $\tilde{\psi}(p)$ is constructed as follows:

$$\begin{aligned}\tilde{\psi}(p) = \langle p|\psi\rangle &= \langle p|\hat{\mathbb{I}}|\psi\rangle \\ &= \langle p|\left(\int_{-\infty}^{\infty} dx|x\rangle\langle x|\right)|\psi\rangle \\ &= \int_{-\infty}^{\infty} dx\langle p|x\rangle\langle x|\psi\rangle \\ &= \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} dx\, e^{-ixp/\hbar}\,\psi(x)\end{aligned}$$

The last line above is a Fourier transform. The Fourier and inverse Fourier transforms for 1D wavefunctions are defined as follows, where $\mathcal{F}\{\psi(x)\}$ denotes the Fourier transform of $\psi(x)$, and $\mathcal{F}^{-1}\{\tilde{\psi}(p)\}$ denotes the inverse Fourier transform of $\tilde{\psi}(p)$.

Fourier Transforms for 1D Wavefunctions
$\tilde{\psi}(p) = \mathcal{F}\{\psi(x)\} = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} dx\, e^{-ixp/\hbar}\,\psi(x)$
$\psi(x) = \mathcal{F}^{-1}\{\tilde{\psi}(p)\} = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty} dp\, e^{ixp/\hbar}\,\tilde{\psi}(p)$

In three spatial dimensions with 3D position and momentum vectors $\mathbf{r}$ and $\mathbf{p}$, the transforms are as follows:

Fourier Transforms for 3D Wavefunctions
$\tilde{\psi}(\mathbf{p}) = \mathcal{F}\{\psi(\mathbf{r})\} = \left(\frac{1}{2\pi\hbar}\right)^{3/2}\int_{-\infty}^{\infty} d^3\mathbf{r}\, e^{-i\mathbf{r}\cdot\mathbf{p}/\hbar}\,\psi(\mathbf{r})$
$\psi(\mathbf{r}) = \mathcal{F}^{-1}\{\tilde{\psi}(\mathbf{p})\} = \left(\frac{1}{2\pi\hbar}\right)^{3/2}\int_{-\infty}^{\infty} d^3\mathbf{p}\, e^{i\mathbf{r}\cdot\mathbf{p}/\hbar}\,\tilde{\psi}(\mathbf{p})$

Tensor Products: Merging State Spaces

$\mathcal{E}' = \mathcal{E}_1 \otimes \mathcal{E}_2$ indicates that the state space $\mathcal{E}'$ is the **tensor product** of independent state spaces $\mathcal{E}_1$ and $\mathcal{E}_2$ with properties described below. Consider the following assumptions:

- Let $\{|u_j\rangle\}$ and $\{|v_k\rangle\}$ be bases for $\mathcal{E}_1$ and $\mathcal{E}_2$, respectively. No elements of $\mathcal{E}_1$ or the basis $\{|u_j\rangle\}$ are elements of $\mathcal{E}_2$, and no elements of $\mathcal{E}_2$ or basis $\{|v_k\rangle\}$ are elements of $\mathcal{E}_1$.
- Let D_1 and D_2 be the state-space dimensions of $\mathcal{E}_1$ and $\mathcal{E}_2$. The state-space dimension is the number of elements in a basis, which may be infinite.
- Let $\hat{A}_1$ be any operator acting on elements of $\mathcal{E}_1$, but not on elements of $\mathcal{E}_2$. Let $\hat{A}_2$ be any operator acting on elements of $\mathcal{E}_2$ but not on elements of $\mathcal{E}_1$.
- $\hat{\mathbb{I}}_1$ and $\hat{\mathbb{I}}_2$ are identity operators for $\mathcal{E}_1$ and $\mathcal{E}_2$, respectively.

$\mathcal{E}'$ has the following properties:

- One basis for $\mathcal{E}'$ is the **tensor-product basis** denoted as $\{|u_j\rangle|v_k\rangle\}$ or $\{|u_j, v_k\rangle\}$ or $\{|j,k\rangle\}$. Thus the tensor product basis consists of every possible pairing of one element of $\{|u_j\rangle\}$ with an element of $\{|v_k\rangle\}$. The basis has $D_1 \cdot D_2$ elements.
- The dimension of $\mathcal{E}'$ is $D_1 \cdot D_2$.
- $\hat{A}_1\hat{A}_2|u_j, v_k\rangle$ is interpreted as $(\hat{A}_1|u_j\rangle)(\hat{A}_2|v_k\rangle)$.
- $\hat{A}_1|u_j, v_k\rangle$ is interpreted as $(\hat{A}_1|u_j\rangle)(\hat{\mathbb{I}}_2|v_k\rangle)$.
- $\hat{A}_2|u_j, v_k\rangle$ is interpreted as $(\hat{\mathbb{I}}_1|u_j\rangle)(\hat{A}_2|v_k\rangle)$.

Tensor products formalize the incorporation of additional physical properties into a given system. An example involves increasing the spatial dimension of a system: $\mathcal{E}_\mathbf{r} = \mathcal{E}_x \otimes \mathcal{E}_y \otimes \mathcal{E}_z$ is the tensor-product state space corresponding to 3D coordinate space (the state-space dimension of $\mathcal{E}_\mathbf{r}$ is infinite), and $\mathcal{E}_x$, $\mathcal{E}_y$, and $\mathcal{E}_z$ correspond to independent state spaces of a particle with motion constrained to the x, y, and z spatial dimensions, respectively. $\mathcal{E}_\mathbf{r}$ has a tensor-product basis denoted as $\{|x\rangle|y\rangle|z\rangle\}$, $\{|x, y, z\rangle\}$, or $\{|\mathbf{r}\rangle\}$, although bases other than this tensor product basis also exist for $\mathcal{E}_\mathbf{r}$.

Operator Definitions and Operator Manipulation

Inverse: The inverse of an operator $\hat{A}$ is designated $\hat{A}^{-1}$ and is defined by the property $\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{\mathbb{I}}$.

Hermitian conjugate: The Hermitian conjugate or adjoint of an operator $\hat{A}$ is designated $\hat{A}^{\dagger}$. $\hat{A}$ is called Hermitian if $\hat{A}^{\dagger} = \hat{A}$. If $\hat{A}^{\dagger} = -\hat{A}$, then $\hat{A}$ is called **anti-Hermitian.** In a discrete representation defined by a basis $\{|v_k\rangle\}$, the matrix representing $\hat{A}^{\dagger}$ is the complex conjugate of (all elements of) the transpose of the matrix representing $\hat{A}$:

$$A^{\dagger}_{\{v\}} = \left(A^{T}_{\{v\}}\right)^{*}$$

Unitary operators: An operator $\hat{\mathbb{Q}}$ is **unitary** if its inverse equals its adjoint, $\hat{\mathbb{Q}}^{-1} = \hat{\mathbb{Q}}^{\dagger}$, so that

$$\hat{\mathbb{Q}}^{\dagger}\hat{\mathbb{Q}} = \hat{\mathbb{Q}}\hat{\mathbb{Q}}^{\dagger} = \hat{\mathbb{I}}$$

Unitary transformations and common unitary operators are discussed on pages 38 and 39.

Commutators of Hermitian operators: The commutator of two non-commuting Hermitian operators is anti-Hermitian. If $\hat{A}$ and $\hat{B}$ are Hermitian operators, then $[\hat{A},\hat{B}]^{\dagger} = -[\hat{A},\hat{B}]$.

Commutators involving functions of operators: For any two operators $\hat{A}$ and $\hat{B}$ that each commute with their commutator (i.e., $[\hat{A},[\hat{A},\hat{B}]] = [\hat{B},[\hat{A},\hat{B}]] = 0$), the commutator of $\hat{A}$ and a function $F(\hat{B})$ is

$$[\hat{A},F(\hat{B})] = [\hat{A},\hat{B}]\frac{dF(\hat{B})}{d\hat{B}}$$

The **Baker-Campbell-Hausdorff (BCH) formula** (or **Glauber formula)** involves exponentials of two operators. The formula is expressed for arbitrary operators $\hat{A}$ and $\hat{B}$ as follows:

$$e^{\hat{A}}e^{\hat{B}} = e^{\hat{A}+\hat{B}}e^{\frac{1}{2}[\hat{A},\hat{B}]} \quad \text{and} \quad e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-\frac{1}{2}[\hat{A},\hat{B}]}$$

Expectation Values

The **expectation value** of an operator $\hat{A}$ for a ket $|\psi\rangle$ is denoted $\langle\hat{A}\rangle$ and defined as

$$\langle\hat{A}\rangle \equiv \langle\psi|\hat{A}|\psi\rangle$$

An expectation value of an observable is a real scalar that carries the dimensional units of the corresponding physical quantity and corresponds to the mean outcome of a large number of identical measurements of that physical quantity made on identically prepared systems. An expectation value does not necessarily correspond to a possible outcome of a single measurement; i.e., $\langle\hat{A}\rangle$ does not have to be an eigenvalue of $\hat{A}$, and despite the terminology it is not generally interpreted as an "expected" outcome of a single measurement.

Expectation values may be calculated and further interpreted as follows:

- If for any discrete basis $\{|v_k\rangle\}$ the expansion of a state $|\psi\rangle$ is given as $|\psi\rangle = \sum_k \langle v_k|\psi\rangle|v_k\rangle = \sum_k c_k|v_k\rangle$, then

  $$\langle\hat{A}\rangle = \sum_j\sum_k c_j^* c_k \langle v_j|\hat{A}|v_k\rangle$$

  If it is also the case that $\hat{A}|v_k\rangle = \lambda_k|v_k\rangle$, then $\langle\hat{A}\rangle = \sum_k |c_k|^2\lambda_k$.

  In this latter case, the expectation value of $\hat{A}$ is a weighted sum of eigenvalues of $\hat{A}$, where the weighting for each eigenvalue is the probability (page 13) of obtaining that particular eigenvalue in a measurement.
- If, for any continuous basis $\{|w_\beta\rangle\}$, $\hat{A}$ has the generalized matrix elements $A(\beta,\beta') \equiv \langle w_\beta|\hat{A}|w_{\beta'}\rangle$, and $|\psi\rangle$ is represented by $\psi(\beta) = \langle w_\beta|\psi\rangle$, then

  $$\langle\hat{A}\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\beta\, d\beta'\, \psi^*(\beta)A(\beta,\beta')\psi(\beta')$$

  If it is also the case that $\hat{A}|w_\beta\rangle = \beta|w_\beta\rangle$, then $\langle\hat{A}\rangle = \int_{-\infty}^{\infty} d\beta\, \beta\, |\psi(\beta)|^2$.

Commutation Relations

Two operators $\hat{A}$ and $\hat{B}$ that are defined to act on elements of a state space $\mathcal{E}$ are said to commute if $[\hat{A}, \hat{B}] = 0$. This **commutation relation** implies the following:

- $\hat{A}$ and $\hat{B}$ have a common set of eigenkets, which may be discretely or continuously indexed.
- If there are degeneracies in the spectrum of $\hat{A}$ (or $\hat{B}$), then not every eigenket of $\hat{A}$ (or $\hat{B}$) is necessarily also an eigenket of $\hat{B}$ (or $\hat{A}$). $[\hat{A}, \hat{B}] = 0$ indicates that only particular superpositions of degenerate and orthogonal eigenkets of one operator are also eigenkets of the other operator. This property also holds for matrices and can be illustrated using the following two matrices, which commute with each other:

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

  While any two-element column vector is an eigenvector of the first matrix (the identity matrix), only

$$\begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix}$$

  are the (normalized) eigenvectors of the second matrix (up to a global phase factor). These two column vectors form the unique set of eigenvectors common to both matrices.
- If $[\hat{A}, \hat{B}] = 0$, the order of operation of $\hat{A}$ and $\hat{B}$ on a ket is irrelevant, since $\hat{A}\hat{B}|\psi\rangle = \hat{B}\hat{A}|\psi\rangle$. Physically, this implies that the order of measurement also does not matter if these operators correspond to observable quantities. A measurement of both quantities in sequence or simultaneously will leave the system in the common eigenstate (or subspace) of $\hat{A}$ and $\hat{B}$ associated with the two eigenvalues that are the outcomes of the measurements. Observables for which the measurement order plays no role in determining the final state are said to be **compatible**.

Non-Commuting Operators, Uncertainty Relations

For two operators $\hat{A}$ and $\hat{B}$ that act on elements of a state space $\mathcal{E}$, if $[\hat{A}, \hat{B}] \neq 0$, then $\hat{A}\hat{B}|\psi\rangle \neq \hat{B}\hat{A}|\psi\rangle$ for arbitrary $|\psi\rangle \in \mathcal{E}$. Consequently, if $\hat{A}$ and $\hat{B}$ are observables, the measurement order matters for the possibilities and probabilities of measurement outcomes: measurement of the quantity corresponding to $\hat{A}$ collapses the system into an eigenstate of $\hat{A}$, but subsequent measurement of the quantity corresponding to $\hat{B}$ collapses the system into an eigenstate of $\hat{B}$. If the state resulting from this second measurement is not also an eigenstate of $\hat{A}$, then information obtained in the first measurement (of $\hat{A}$) is lost. The observables are **incompatible.**

With incompatible observables there is a fundamental limit on how well the corresponding physical quantities can be simultaneously specified or predicted. This limit is independent of measurement apparatus performance and is expressed by the **generalized uncertainty relation**

$$(\Delta\hat{A})(\Delta\hat{B}) \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle|$$

where the **standard deviation** or **uncertainty** of an operator $\hat{Q}$ for a given quantum state is defined as

$$\Delta\hat{Q} = \sqrt{\langle\hat{Q}^2\rangle - \langle\hat{Q}\rangle^2}$$

The uncertainty indicates how precisely the associated physical quantity can be predicted or specified about a mean value for the state in question.

The **Heisenberg uncertainty principle** is obtained for conjugate position and momentum operators $\hat{R}_j$ and $\hat{P}_j$, where $j \in \{x, y, z\}$, for which $[\hat{R}_j, \hat{P}_j] = i\hbar$, indicating the fundamental quantum-mechanical limits of precision in simultaneously specifying or predicting a particle's position and momentum:

$$(\Delta\hat{R}_j)(\Delta\hat{P}_j) \geq \hbar/2$$

Complete Sets of Commuting Observables

A **complete set of commuting observables (CSCO)** for a state space $\mathcal{E}$ is a set of observables $\{\hat{A}, \hat{B}, \hat{C}, \dots\}$ for which

- All observables in the set are mutually compatible
- All observables in the set share a single, unique set of eigenstates. In the notation below, the ket $|a, b, c, \dots\rangle$ is one element of this set and is labeled with a full set of eigenvalues of the different observables such that

$$\hat{A}|a, b, c, \dots\rangle = a|a, b, c, \dots\rangle$$
$$\hat{B}|a, b, c, \dots\rangle = b|a, b, c, \dots\rangle$$
$$\text{etc.}$$

  Discrete or continuous indices may be used to label the full sets of eigenvalues of the operators.
- While there may be degeneracy in a particular observable's eigenvalue spectrum, any specified complete set of eigenvalues corresponds to one and only one of the mutual eigenstates of the CSCO, with no ambiguity.
- Multiple CSCOs may be specified for a given state space
- A CSCO may consist of a single observable if that observable has no degeneracies in its eigenvalue spectrum. For the 1D infinite square well (page 49) and harmonic oscillator problems (page 54), $\{\hat{H}\}$, $\{\hat{X}\}$, and $\{\hat{P}_x\}$ are each single-observable CSCOs.
- A CSCO has no extra elements once the above conditions are satisfied; additional compatible observables may exist, but they are not included in that CSCO

Identification of CSCOs is necessary in order to construct physically meaningful bases for $\mathcal{E}$. Identifying a CSCO is experimentally helpful when determining how to make a set of sequential measurements on an unknown initial state such that the system is left in a final state with as many knowable properties as possible completely determined by measurement. Knowing the CSCOs that are available tells the experimenter the possible sets of measurements that can be made to achieve this goal.

CSCOs for Specific Problems

The table below lists CSCOs for specific problems; see the specific problem for definitions of the observables given (also see page xvi). Only the most experimentally relevant, conventional, or common CSCOs are included in the table. The specification (e.g., through measurement) of one eigenvalue for each observable in a CSCO determines a state vector that is a unique common eigenstate of the CSCO.

Problem	**CSCO(s)**
Particle subject to arbitrary 1D potential $V(x)$	$\{\hat{X}\}$, $\{\hat{P}_x\}$
Particle subject to arbitrary 3D potential $V(\mathbf{r})$	$\{\hat{X}, \hat{Y}, \hat{Z}\}$, $\{\hat{P}_x, \hat{P}_y, \hat{P}_z\}$
Free particle, 1D (in x) (p. 48)	$\{\hat{P}_x\}$, $\{\hat{X}\}$
1D infinite square well (p. 49)	$\{\hat{H}\}$
1D harmonic oscillator (p. 54)	$\{\hat{H}\}$
2D harmonic oscillator in (x, y)	$\{\hat{H}_x, \hat{H}_y\}$
If isotropic, then also:	$\{\hat{H}, \hat{L}_z\}$ $(\hat{L}_z = \hat{X}\hat{P}_y - \hat{Y}\hat{P}_x)$
3D harmonic oscillator in (x, y, z) (p. 62)	$\{\hat{H}_x, \hat{H}_y, \hat{H}_z\}$
If isotropic, then also:	$\{\hat{H}, \hat{\mathbf{L}}^2, \hat{L}_z\}$
An angular momentum j (p. 64)	$\{\hat{\mathbf{J}}^2, \hat{J}_z\}$
Two-level systems (p. 75)	$\{\hat{\sigma}_z\}$
If spin 1/2 (p. 68), then also:	$\{\hat{S}_z\}$
Two angular momenta, j_1 and j_2 (p. 82)	$\{\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}_2^2, \hat{J}_{1z}, \hat{J}_{2z}\}$, $\{\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}_2^2, \hat{\mathbf{J}}^2, \hat{J}_z\}$
"Spinless" hydrogen (p. 97)	$\{\hat{H}, \hat{\mathbf{L}}^2, \hat{L}_z\}$
Hydrogen fine-structure problem (p. 102)	$\{\hat{H}, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2, \hat{L}_z, \hat{S}_z\}$, $\{\hat{H}, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2, \hat{\mathbf{J}}^2, \hat{J}_z\}$
Hydrogen hyperfine-structure problem (p. 104)	$\{\hat{H}, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2, \hat{\mathbf{I}}^2, \hat{L}_z, \hat{S}_z, \hat{I}_z\}$, $\{\hat{H}, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2, \hat{\mathbf{I}}^2, \hat{\mathbf{J}}^2, \hat{J}_z, \hat{I}_z\}$, $\{\hat{H}, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2, \hat{\mathbf{I}}^2, \hat{\mathbf{J}}^2, \hat{\mathbf{F}}^2, \hat{F}_z\}$

Properties of Wavefunctions

Let $|\Psi(t)\rangle$ denote the dynamical state of a particle in an n-dimensional (nD) coordinate space at time t. $\Psi(\mathbf{r},t) = \langle \mathbf{r}|\Psi(t)\rangle$ is the nD position representation of $|\Psi(t)\rangle$, where $\mathbf{r}$ is the nD position vector. $\Psi(\mathbf{r},t)$ has dimensional units of $[\mathrm{m}^{-n/2}]$. In the conventional interpretation of quantum theory, the wavefunction $\Psi(\mathbf{r},t)$ is also called a **probability amplitude** and is used to determine the probability of finding the particle near position $\mathbf{r}$ at time t (see page 13).

The probability density at $\mathbf{r}$ is $|\Psi(\mathbf{r},t)|^2$, with dimensional units of $[\mathrm{m}^{-n}]$. The probability (see page 13) of finding the particle at time t within a sufficiently small nD volume $d^n\mathbf{r}$ centered at $\mathbf{r}$ is

$$d\mathcal{P}(\mathbf{r}) = |\langle \mathbf{r}|\Psi(t)\rangle|^2\, d^n\mathbf{r} = |\Psi(\mathbf{r},t)|^2\, d^n\mathbf{r}$$

This shows the application of the **probability postulate** (page 13) in a continuous representation using wavefunction notation. The normalization condition for $\Psi(\mathbf{r},t)$ is an integrated probability distribution,

$$1 = \int_{\text{all space}} d^n\mathbf{r}|\Psi(\mathbf{r},t)|^2$$

which is interpreted as indicating that "the particle must be found somewhere in space." Properties analogous to those above also exist for momentum-space wavefunctions.

For $\Psi(\mathbf{r},t)$ to be **physically realizable** and represent the state of a particle at time t, it must have the following characteristics:

- $\Psi(\mathbf{r},t)$ is defined and single-valued everywhere in space
- $\Psi(\mathbf{r},t)$ is continuous everywhere in space
- The spatial gradient of $\Psi(\mathbf{r},t)$ is continuous everywhere, except where the potential energy of the particle goes to positive or negative infinity
- $\Psi(\mathbf{r},t)$ is **square-integrable**, i.e., $\int_{\text{all space}} d^n\mathbf{r}|\Psi(\mathbf{r},t)|^2$ is finite, implying that $|\Psi(\mathbf{r},t)| \to 0$ as $|\mathbf{r}| \to \infty$

Wave-Like Properties of Matter

The wavefunction for a particle of mass m characterizes the particle's wave-like properties. For a **free particle** (i.e., there are no external forces on the particle) with a precise momentum of magnitude p, the **deBroglie wavelength** is $\lambda_{dB} \equiv h/p$.

The energy eigenstates of a particle in a 1D time-independent potential well $V(x)$ have wave-like characteristics that may be graphically represented to gain understanding about a problem. For a particle subject to the Hamiltonian $\hat{H} = \frac{1}{2m}\hat{P}_x^2 + V(\hat{X})$, with eigenstates and eigenvalues defined by the eigenvalue equation $\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$, an **energy eigenfunction** $\varphi_n(x) \equiv \langle x|\varphi_n\rangle$ has the following properties.

Energy: The local **potential energy** at any position x is $V(x)$, and the local **kinetic energy** is $K(x) = E_n - V(x)$.

Wavefunction curvature: The wavefunction curvature of $\varphi_n(x)$ is defined as $C_n(x) \equiv \frac{\partial^2}{\partial x^2}\varphi_n(x)$. The energy eigenvalue equation implies that

$$C_n(x) = -\frac{2mK(x)}{\hbar^2}\varphi_n(x)$$

and that the local kinetic energy is $K(x) = -\frac{\hbar^2}{2m}\frac{1}{\varphi_n(x)}C_n(x)$.

Classically allowed region: A classically allowed region of a potential $V(x)$ is a region in which $K(x) > 0$. For an energy eigenfunction $\varphi_n(x)$, $C_n(x)$ and $\varphi_n(x)$ have opposite signs for $K(x) > 0$, so that $\varphi_n(x)$ is concave towards the x axis and $C_n(x)$ changes sign when $\varphi_n(x)$ crosses the x axis.

Classically forbidden region: A classically forbidden region is one in which $K(x) < 0$. For an energy eigenfunction $\varphi_n(x)$, $C_n(x)$ and $\varphi_n(x)$ have the same sign if $K(x) < 0$, so that $\varphi_n(x)$ curves away from and does not cross the x axis.

Classical turning points separate the classically allowed and forbidden regions. For $\varphi_n(x)$, they occur at points x for which $V(x) = E_n$.

Graphical Interpretation of the Schrödinger Equation

Qualitative graphical sketches of energy eigenfunctions in the position representation can be made when the energy eigenvalue equation is not readily solvable. In addition to indicating wavefunction curvature and continuity in classically allowed and classically forbidden regions (page 33), the following characteristics can be graphically illustrated:

1. A **potential well** is a region in the vicinity of a local or global minimum of potential energy, and for which there may be a finite or infinite number of discretely indexed energy eigenstates. The shape of a potential well is often sketched as an aid in building intuition about a problem and about the shape of energy eigenfunctions.

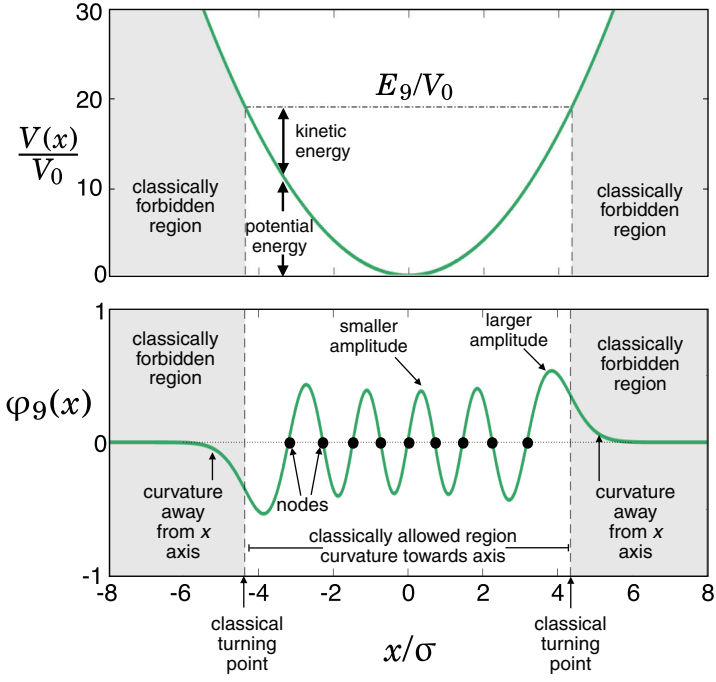
2. **Nodes** of a wavefunction are locations where the wavefunction magnitude is zero, so the probability density at those locations is zero. The **ground-state wavefunction** solution of a 1D potential well is the energy eigenfunction associated with the lowest energy eigenvalue, and has no nodes; i.e., the ground-state wavefunction does not cross the x axis. The first excited-state wavefunction has one node and therefore crosses the axis once. The n^{th} excited state has n nodes.

3. **Parity.** A 1D potential $V(x)$ is **symmetric** about $x = 0$ if $V(-x) = V(x)$. For a 1D potential well $V(x)$ that is symmetric about $x = 0$, the ground-state wavefunction is **even**, such that $\varphi_{\text{ground}}(-x) = \varphi_{\text{ground}}(x)$. The first excited-state wavefunction is **odd**, such that $\varphi_{\text{first}}(-x) = -\varphi_{\text{first}}(x)$. As energy increases, the discretely indexed energy eigenfunctions are alternately even and odd.

4. In regions where there is less kinetic energy and greater potential energy, a particle would be found to move more slowly, leading to a higher probability density of finding the particle in such a region. Because the wavefunction amplitude determines the probability density, the wavefunction amplitude is therefore larger in classically allowed regions with greater potential energy.

Graphical Interpretation: Example

The upper illustration shows classically forbidden regions (in gray) and classically allowed regions for an example potential well and energy eigenfunction. In this example, the **harmonic oscillator** (page 54) potential well $V(x) = V_0 \frac{x^2}{\sigma^2}$ is plotted (green line, upper plot), where V_0 is an energy constant, and σ is a length constant. The 9th excited-state wavefunction $\varphi_9(x)$ (arbitrary units in this example) is shown in green in the lower plot; the associated energy eigenvalue E_9 is indicated in the upper plot. Black dots in the lower plot indicate the 9 nodes of $\varphi_9(x)$. In the lower plot, note that the wavefunction curvature is always towards the x axis in the classically allowed region, and away from the x axis in the classically forbidden region. Also note the larger wavefunction amplitude in classically allowed regions of larger potential energy and smaller kinetic energy.



Superpositions, Relative and Global Phases

Suppose that $|\psi\rangle$ and $|\psi'\rangle$ are normalized elements of the state space $\mathcal{E}$, and let $\{|v_k\rangle\}$ be a discrete basis for $\mathcal{E}$, such that

$$|\psi\rangle = \sum_k c_k |v_k\rangle$$

$$|\psi'\rangle = e^{i\theta}|\psi\rangle = \sum_k e^{i\theta} c_k |v_k\rangle = \sum_k c'_k |v_k\rangle$$

where $c'_k = e^{i\theta} c_k$, and θ is a real scalar. Here, θ is a global phase; it is global in the sense that $e^{i\theta}$ multiplies every element in the superposition of basis states used to construct $|\psi\rangle$ in order to define $|\psi'\rangle$. Global phase factors such as this can be neglected or conveniently chosen when defining kets (such as the eigenstates of an operator, or the elements of a basis) because there are no measurable consequences of the global phase factor. The expectation value of any observable is the same for both $|\psi\rangle$ and $|\psi'\rangle$, and no measurement can differentiate between the kets $|\psi\rangle$ and $|\psi'\rangle$. The kets $|\psi\rangle$ and $|\psi'\rangle$ are therefore two ways of writing or encoding the same physical state.

A **relative phase** is the phase angle between two superposition coefficients in the expansion of $|\psi\rangle$ into the $\{|v_k\rangle\}$ basis and is physically significant. For any two non-zero superposition coefficients $c_j = |c_j| e^{i\phi_j}$ and $c_k = |c_k| e^{i\phi_k}$, the relative phase between the components $|v_j\rangle$ and $|v_k\rangle$ is $\phi_{kj} \equiv \phi_k - \phi_j$. In the superposition $|\psi\rangle = \frac{1}{\sqrt{2}} e^{i\theta}(e^{i\phi_1}|v_1\rangle + e^{i\phi_2}|v_2\rangle)$, the term $e^{i\theta}$ is a global phase factor, and $\phi_{21} \equiv \phi_2 - \phi_1$ is the relative phase between components $|v_2\rangle$ and $|v_1\rangle$.

In superpositions involving a continuous basis, relative phase factors are expressed as continuous functions. If $|\psi\rangle$ is an element of the state space corresponding to 1D motion along x, with the basis $\{|x\rangle\}$ defining the position representation, then $|\psi\rangle$ can be expanded as follows:

$$|\psi\rangle = \int_{-\infty}^{\infty} dx\, |x\rangle\langle x|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi(x)|x\rangle$$

The expansion coefficients are given by $\psi(x) = |\psi(x)| e^{i\phi(x)}$, where the relative phases between the continuously distributed elements of the basis $\{|x\rangle\}$ are determined by $\phi(x)$.

Probability Currents

A particle of mass m that is associated with the wavefunction $\Psi(\mathbf{r},t)$ has a **probability current**

$$\begin{aligned}\mathbf{J}(\mathbf{r},t) &= \frac{\hbar}{2mi}[\Psi^*\nabla\Psi - \Psi\nabla\Psi^*] \\ &= \frac{\hbar}{m}\mathrm{Im}[\Psi^*(\nabla\Psi)]\end{aligned}$$

$\mathbf{J}(\mathbf{r},t)$ describes the rate of change—or flow—of probability through regions in space and satisfies a **continuity equation**

$$\frac{\partial}{\partial t}|\Psi(\mathbf{r},t)|^2 + \nabla\cdot\mathbf{J}(\mathbf{r},t) = 0$$

A 1D wavefunction can be written as $\Psi(x,t) = |\Psi(x,t)|e^{i\phi(x,t)}$, where the phase distribution $\phi(x,t)$ is a real function. This gives a probability current

$$J(x,t) = \frac{\hbar}{m}\mathrm{Im}\left[\Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\right] = |\Psi(x,t)|^2\frac{\hbar}{m}\frac{\partial\phi(x,t)}{\partial x}$$

which has dimensional units of [1/s]. Consider the wavefunction

$$\Psi(x,t) = |\Psi(x,t)|e^{ixp'/\hbar}$$

where p' is a scalar with units of momentum. For this case, $\frac{\hbar}{m}\frac{\partial\phi(x,t)}{\partial x} = p'/m = v'$, where v' is a scalar with units of velocity. This example shows that the spatial gradient of the phase of the wavefunction is associated with the velocity of probability flow. For this example,

$$J(x,t) = v'|\Psi(x,t)|^2$$

A 3D wavefunction can be written as $\Psi(\mathbf{r},t) = |\Psi(\mathbf{r},t)|e^{i\phi(\mathbf{r},t)}$. By defining a velocity distribution for the flow of probability as

$$\mathbf{v}(\mathbf{r},t) = \frac{\hbar}{m}\nabla\phi(\mathbf{r},t)$$

the probability current can be written as the velocity distribution $\mathbf{v}$ weighted by the probability density distribution:

$$\mathbf{J}(\mathbf{r},t) = \mathbf{v}(\mathbf{r},t)|\Psi(\mathbf{r},t)|^2$$

Unitary Transformations

Unitary transformations involve transforming kets, bras, and operators by acting upon them or multiplying them with unitary operators (see page 26). Consider an arbitrary unitary operator $\hat{\mathbb{Q}}$ and an arbitrary operator $\hat{A}$, both of which are defined to act on all elements of a state space $\mathcal{E}$ and the elements of any basis that spans $\mathcal{E}$. The following actions define a unitary transformation.

- **Unitary transformation of state vectors:** For every $|\psi\rangle \in \mathcal{E}$, a unitary transformation is defined by $|\psi'\rangle = \hat{\mathbb{Q}}|\psi\rangle$, where $|\psi'\rangle$ is the transformed ket.
- **Unitary transformation of operators:** The transform of $\hat{A}$ is defined by $\hat{A}' = \hat{\mathbb{Q}}\hat{A}\hat{\mathbb{Q}}^\dagger$.

Unitary transformations as defined above have the following properties:

1. Scalar products and orthonormality are preserved when the same unitary operation is applied to all elements and basis kets of a state space. If $|\psi'\rangle \equiv \hat{\mathbb{Q}}|\psi\rangle$ and $|\varphi'\rangle \equiv \hat{\mathbb{Q}}|\varphi\rangle$, then

$$\langle\varphi'|\psi'\rangle = \langle\varphi|\hat{\mathbb{Q}}^\dagger\hat{\mathbb{Q}}|\psi\rangle = \langle\varphi|\hat{\mathbb{I}}|\psi\rangle = \langle\varphi|\psi\rangle$$

2. Due to property 1, a unitary transformation of all elements of an orthonormal basis produces a new orthonormal basis.

3. If $\hat{A}$ has eigenvalues and eigenkets given by $\hat{A}|v_k\rangle = \lambda_k|v_k\rangle$, then the eigenvalues of $\hat{A}'$ are the same as those of $\hat{A}$. The eigenkets of $\hat{A}'$ are the transforms of those of $\hat{A}$. If a transformed eigenket of $\hat{A}$ is defined as $|v'_k\rangle \equiv \hat{\mathbb{Q}}|v_k\rangle$, then

$$\hat{A}'|v'_k\rangle = (\hat{\mathbb{Q}}\hat{A}\hat{\mathbb{Q}}^\dagger)\hat{\mathbb{Q}}|v_k\rangle = \hat{\mathbb{Q}}\hat{A}|v_k\rangle = \hat{\mathbb{Q}}\lambda_k|v_k\rangle = \lambda_k|v'_k\rangle$$

Any unitary operator $\hat{\mathbb{Q}}$ can be written as $\hat{\mathbb{Q}} = e^{i\hat{\mathcal{A}}}$, where $\hat{\mathcal{A}}$ is some Hermitian operator. Also, for any Hermitian operator $\hat{\mathcal{A}}$, the operator $e^{i\hat{\mathcal{A}}}$ is unitary; e.g., for a time-independent Hamiltonian $\hat{H}$, the unitary time evolution operator (page 39) is $\hat{\mathbb{U}}(t, t_0) = e^{-i(t-t_0)\hat{H}/\hbar}$.

Common Unitary Operators

The time evolution operator $\hat{\mathbb{U}}(t,t_0)$ evolves a state vector from time t_0 to time t under a specified Hamiltonian $\hat{H}(t)$:

$$\hat{\mathbb{U}}(t,t_0)|\Psi(t_0)\rangle = |\Psi(t)\rangle$$

- For time-independent $\hat{H}$: $\hat{\mathbb{U}}(t,t_0) = e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}$
- If $[\hat{H}(t_1),\hat{H}(t_2)] = 0$ for arbitrary times t_1 and t_2, then

$$\hat{\mathbb{U}}(t,t_0) = e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'\hat{H}(t')}$$

- Otherwise, for small enough δt so that $\hat{H}(t') \approx \hat{H}(t'+\delta t)$ for times $t_0 \le t' < t$, with $t = t_0 + N\delta t$ for some integer $N > 0$:

$$\hat{\mathbb{U}}(t,t_0) \approx \prod_{n=0}^{N-1} \exp\left\{-\frac{i}{\hbar}\delta t\hat{H}(t_0+n\delta t)\right\}$$

  The product is constructed with $n = 0$ to $n = N-1$ terms ordered from right to left.

Position and **momentum translation operators** $\hat{\mathbb{S}}$ and $\hat{\mathbb{T}}$ enable unitary operations that correspond to position and momentum translations of a system, or of a ket's position or momentum expectation values. These operators and their basic properties are defined below for the $\hat{\mathbf{x}}$-direction position and momentum operators $\hat{X}$ and $\hat{P}_x$, and translations x' and p'.

x' Position Translation	p' Momentum Translation
$\hat{\mathbb{S}}(x') = e^{-ix'\hat{P}_x/\hbar}$	$\hat{\mathbb{T}}(p') = e^{ip'\hat{X}/\hbar}$
$\hat{\mathbb{S}}(x')\|x\rangle = \|x+x'\rangle$	$\hat{\mathbb{T}}(p')\|p\rangle = \|p+p'\rangle$
$\langle x\|\hat{\mathbb{S}}(x') = \langle x-x'\|$	$\langle p\|\hat{\mathbb{T}}(p') = \langle p-p'\|$
$\hat{\mathbb{S}}^\dagger(x')\hat{X}\,\hat{\mathbb{S}}(x') = \hat{X}+x'$	$\hat{\mathbb{T}}^\dagger(p')\hat{P}_x\hat{\mathbb{T}}(p') = \hat{P}_x+p'$
$\hat{\mathbb{S}}^\dagger(x')\hat{X}^2\hat{\mathbb{S}}(x') = (\hat{X}+x')^2$	$\hat{\mathbb{T}}^\dagger(p')\hat{P}_x^2\hat{\mathbb{T}}(p') = (\hat{P}_x+p')^2$

Example: For $|\psi'\rangle = \hat{\mathbb{S}}(x')|\psi\rangle$, the mean position of the wavefunction $\psi'(x) = \langle x|\psi'\rangle$ (i.e., the position expectation value $\langle\psi'|\hat{X}|\psi'\rangle$) is larger than that of $\psi(x) = \langle x|\psi\rangle$ by x':

$$\langle\psi'|\hat{X}|\psi'\rangle = \langle\psi|\hat{\mathbb{S}}^\dagger(x')\hat{X}\,\hat{\mathbb{S}}(x')|\psi\rangle = \langle\psi|(\hat{X}+x')|\psi\rangle = \langle\psi|\hat{X}|\psi\rangle + x'$$

Conservative Systems

A **conservative system** is one for which the Hamiltonian does not depend on time. The mean energy for such a system is constant in time; it is conserved. To illustrate this concept, consider a particle of mass m in one spatial dimension (x) within a time-independent potential well $V(x)$, and a corresponding time-independent Hamiltonian $\hat{H}$ with no degeneracies in its eigenvalue spectrum. Solving the energy eigenvalue equation

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle$$

often called the **time-independent Schrödinger equation**, permits the construction of a basis $\{|\varphi_n\rangle\}$ composed of energy eigenstates.

Any initial arbitrary state of the system at time t_0 can be expanded as a superposition of the energy eigenstates:

$$|\Psi(t_0)\rangle = \sum_n c_n|\varphi_n\rangle$$

where the coefficients c_n are time-independent complex scalars that satisfy $\sum_n |c_n|^2 = 1$ in order for $|\Psi(t_0)\rangle$ to be properly normalized.

After evolving to time t, the system is in the state

$$\begin{aligned}|\Psi(t)\rangle = \hat{\mathbb{U}}(t,t_0)|\Psi(t_0)\rangle &= \sum_n c_n\, e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}|\varphi_n\rangle \\ &= \sum_n c_n\, e^{-\frac{i}{\hbar}(t-t_0)E_n}|\varphi_n\rangle\end{aligned}$$

where $\hat{\mathbb{U}}(t,t_0)$ is the **time evolution operator** (page 39). Property 1 on page 10 was used to produce the last line above.

The energy expectation value for $|\Psi(t)\rangle$ is

$$\langle\hat{H}\rangle = \sum_n |c_n|^2 E_n$$

which shows that the mean energy of a conservative system is constant in time, an expression of the **conservation of energy** within quantum mechanics.

Stationary States

For a conservative system that at some initial time t_0 is in an energy eigenstate $|\varphi_n\rangle$ associated with eigenvalue E_n, time evolution only introduces a time-dependent global phase factor. Consider a state vector at time $t_0 = 0$ given by $|\Psi(0)\rangle = |\varphi_n\rangle$. At a later time t, the state vector is

$$|\Psi(t)\rangle = \hat{\mathbb{U}}(t,0)|\Psi(t_0)\rangle = e^{-i\phi_n(t)}|\varphi_n\rangle$$

where $\phi_n(t) = E_n t/\hbar$, and $\hat{\mathbb{U}}(t,0)$ is the time evolution operator (page 39). For this state vector, the only time-dependent factor is the global phase $\phi_n(t)$, implying that the expectation values of any observable are constant in time, as are the probabilities of measurement outcomes. The energy eigenstates of a conservative system are therefore called **stationary states**.

If $|\Psi(t)\rangle = e^{-i\phi_n(t)}|\varphi_n\rangle$ can be represented by the wavefunction $\Psi(\mathbf{r},t) = e^{-i\phi_n(t)}\varphi_n(\mathbf{r})$, where $\varphi_n(\mathbf{r}) = \langle\mathbf{r}|\varphi_n\rangle$ is an energy eigenfunction, then $|\Psi(\mathbf{r},t)|^2 = |\varphi_n(\mathbf{r})|^2$ is the probability density and is independent of time.

If $|\Psi(t)\rangle$ is a superposition of different energy eigenstates, each component of the superposition has a phase factor that evolves in time at a rate that depends on that component's energy eigenvalue. In such a superposition, relative phase factors evolve in time, leading to system **dynamics**: time-dependent changes in the properties of the system.

Example: Consider a superposition of two non-degenerate energy eigenstates $|\varphi_1\rangle$ and $|\varphi_2\rangle$. At time $t = 0$, the superposition has the wavefunction $\Psi(\mathbf{r},0) = \frac{1}{\sqrt{2}}[\varphi_1(\mathbf{r}) + \varphi_2(\mathbf{r})]$. At a later time t, the wavefunction and probability density are

$$\Psi(\mathbf{r},t) = \frac{1}{\sqrt{2}}[e^{-iE_1 t/\hbar}\varphi_1(\mathbf{r}) + e^{-iE_2 t/\hbar}\varphi_2(\mathbf{r})]$$

$$|\Psi(\mathbf{r},t)|^2 = \frac{1}{2}|\varphi_1(\mathbf{r})|^2 + \frac{1}{2}|\varphi_2(\mathbf{r})|^2 + \frac{1}{2}e^{i(E_2-E_1)t/\hbar}\varphi_1(\mathbf{r})\varphi_2^*(\mathbf{r}) + \frac{1}{2}e^{-i(E_2-E_1)t/\hbar}\varphi_1^*(\mathbf{r})\varphi_2(\mathbf{r})$$

Since $|\Psi(\mathbf{r},t)|^2$ depends on time, this superposition of energy eigenstates is not a stationary state.

Time-Dependent Reference Frames

The state of a system can be evaluated in various **reference frames** that evolve in time, such as rotating frames or frames moving at a constant velocity relative to one another. Let $|\Psi(t)\rangle$ be the evolving state vector of a system in a given reference frame, where $|\Psi(t_0)\rangle$ is the initial state vector at time t_0. $|\Psi(t)\rangle$ satisfies the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle$$

To reformulate the problem for a second reference frame that may evolve in time relative to the initial one, assume the existence of a time-dependent unitary transformation operator $\hat{\mathbb{F}}(t)$ defined such that

$$|\Psi_E(t)\rangle = \hat{\mathbb{F}}(t)|\Psi(t)\rangle$$

$|\Psi_E(t)\rangle$ is the transformed state vector (see page 38), also called the **effective state** that characterizes the state vector in the second frame. The two frames are assumed to coincide at t_0 such that $\hat{\mathbb{F}}(t_0) = \hat{\mathbb{I}}$. In the second frame $|\Psi_E(t)\rangle$ obeys an **effective Schrödinger equation** that is obtained by inserting $|\Psi(t)\rangle = \hat{\mathbb{F}}^\dagger(t)|\Psi_E(t)\rangle$ into the Schrödinger equation of the initial frame. The effective Schrödinger equation and the **effective Hamiltonian** for the second frame are

$$i\hbar\frac{\partial}{\partial t}|\Psi_E(t)\rangle = \hat{H}_E(t)|\Psi_E(t)\rangle$$

$$\hat{H}_E(t) = \hat{\mathbb{F}}(t)\hat{H}(t)\hat{\mathbb{F}}^\dagger(t) - i\hbar\hat{\mathbb{F}}(t)\frac{\partial}{\partial t}\hat{\mathbb{F}}^\dagger(t)$$

Frame transformations are generally used to simplify calculations and the time dependence of the Schrödinger equation.

Although $\hat{\mathbb{F}}(t)$ is unitary, $\hat{H}_E$ is not the transformed Hamiltonian $\hat{\mathbb{F}}(t)\hat{H}(t)\hat{\mathbb{F}}^\dagger(t)$ that results from a unitary transformation under $\hat{\mathbb{F}}(t)$, as defined on page 38. The effective Hamiltonian $\hat{H}_E$ equals $\hat{\mathbb{F}}(t)\hat{H}(t)\hat{\mathbb{F}}^\dagger(t)$ plus an additional term whose form is an outcome of the structure of the Schrödinger equation.

Schrödinger, Heisenberg, and Interaction Pictures

The terms **Schrödinger picture**, **Heisenberg picture**, and **interaction picture** are given to three particular frames of reference. The pictures are distinguished from one another by the specific time-dependent unitary transformations involved in defining the different reference frames.

In the Schrödinger picture, state vectors evolve in time under the action of the Hamiltonian according to the Schrödinger equation and postulate 3 on page 11. If a time evolution operator $\hat{\mathbb{U}}(t, t_0)$ and an initial state vector $|\Psi_S(t_0)\rangle$ are known for a given system, then the state vector dynamics in the Schrödinger picture are found via $|\Psi_S(t)\rangle = \hat{\mathbb{U}}(t, t_0)|\Psi_S(t_0)\rangle$. The state vectors are labeled with the subscript S here to identify that the state vectors correspond to the Schrödinger picture. Also in the Schrödinger picture, position and momentum operators have no time dependence. If not explicitly stated otherwise, the state vectors and operators of this *Field Guide* are given in the Schrödinger picture. The Schrödinger picture is the frame of reference on which the transformations to the other two pictures are based.

The Heisenberg picture (page 45) is defined by a unitary transformation operator $\hat{\mathbb{F}}(t) = \hat{\mathbb{U}}^\dagger(t, t_0)$ (see page 42) that is the adjoint of the time evolution operator of the Schrödinger picture. When this unitary transformation is applied to a Schrödinger-picture state vector $|\Psi_S(t)\rangle$, time dependence vanishes: $|\Psi_H\rangle \equiv \hat{\mathbb{U}}^\dagger(t, t_0)|\Psi_S(t)\rangle = |\Psi_S(t_0)\rangle$, where $|\Psi_H\rangle$ is the transformed ket of the Heisenberg picture. The Heisenberg picture is therefore the specific time-dependent reference frame in which the transformed state vectors are constant in time, while operators (such as the position and momentum operators) that have no time dependence in the Schrödinger picture may depend on time in the Heisenberg picture.

The interaction picture (page 46) is used when the Schrödinger-picture Hamiltonian is time dependent. In this picture, operators and state vectors generally evolve in time.

Schrödinger Picture: Expectation Value Dynamics

Position and momentum operators have no explicit time dependence in the Schrödinger picture. Nevertheless, other operators that do have explicit time dependence can be constructed. Let $\hat{A}_S(t)$ be an arbitrary operator in the Schrödinger picture that may have explicit time dependence.

For a given Schrödinger-picture state vector $|\Psi_S(t)\rangle$ evolving under a Hamiltonian $\hat{H}_S(t)$, the expectation value of $\hat{A}_S(t)$ will generally have time dependence that results from both the time dependence of $|\Psi_S(t)\rangle$ and any time dependence in $\hat{A}_S(t)$. This time-dependent expectation value may be calculated as

$$\langle \hat{A}_S(t) \rangle(t) = \langle \Psi_S(t) | \hat{A}_S(t) | \Psi_S(t) \rangle$$

Differentiating the equation above with respect to time produces the following differential equation for the dynamics of expectation values in the Schrödinger picture, noting that $\hat{A}_S$, $\hat{H}_S$ and the expectation values are generally time dependent.

Schrödinger-picture expectation values:

$$\frac{d}{dt}\langle \hat{A}_S \rangle = \frac{1}{i\hbar}\left\langle [\hat{A}_S, \hat{H}_S] \right\rangle + \left\langle \frac{\partial \hat{A}_S}{\partial t} \right\rangle$$

Ehrenfest's equations (or Ehrenfest's theorem) are obtained by replacing $\hat{A}_S(t)$ in the equation above with the position operator $\hat{\mathbf{R}} = (\hat{X}, \hat{Y}, \hat{Z})$, and also with the momentum operator $\hat{\mathbf{P}} = (\hat{P}_x, \hat{P}_y, \hat{P}_z)$. Noting that $\frac{\partial \hat{\mathbf{R}}}{\partial t} = 0$ and $\frac{\partial \hat{\mathbf{P}}}{\partial t} = 0$, and that the expectation value of the gradient of the potential energy operator $V(\hat{\mathbf{R}})$ is $\langle \nabla V(\hat{\mathbf{R}}) \rangle \equiv \left(\left\langle \frac{\partial V(\hat{\mathbf{R}})}{\partial \hat{X}} \right\rangle, \left\langle \frac{\partial V(\hat{\mathbf{R}})}{\partial \hat{Y}} \right\rangle, \left\langle \frac{\partial V(\hat{\mathbf{R}})}{\partial \hat{Z}} \right\rangle \right)$, the pair of Ehrenfest's equations can be solved to determine how expectation values of position and momentum evolve for any state of a system.

Ehrenfest's equations (Ehrenfest's theorem):

$$\frac{d}{dt}\langle \hat{\mathbf{R}} \rangle = \frac{1}{m}\langle \hat{\mathbf{P}} \rangle$$

$$\frac{d}{dt}\langle \hat{\mathbf{P}} \rangle = -\langle \nabla V(\hat{\mathbf{R}}) \rangle$$

Heisenberg Picture: Operators and Dynamics

The adjoint $\hat{\mathbb{U}}^\dagger(t,t_0)$ of the time evolution operator $\hat{\mathbb{U}}(t,t_0)$ defines a unitary transformation that transforms state vectors of the Schrödinger picture into time-independent state vectors within the Heisenberg picture. An arbitrary operator $\hat{A}_S(t)$ in the Schrödinger picture is transformed into the Heisenberg operator

$$\hat{A}_H(t) = \hat{\mathbb{U}}^\dagger(t,t_0)\hat{A}_S(t)\hat{\mathbb{U}}(t,t_0)$$

The expectation value of an observable is a physically meaningful quantity and must be the same in any picture, since transforming between pictures is only of mathematical utility for performing calculations. As shown below, the time-dependent expectation value of $\hat{A}_H(t)$ calculated in the Heisenberg picture is equivalent to that of $\hat{A}_S(t)$. In the table, $\hat{H}_S$ and $|\Psi_S(t)\rangle$ are the Schrödinger-picture Hamiltonian and state vector.

Heisenberg Picture Quantities and Dynamics

$\lvert\Psi_H\rangle$	$\equiv \hat{\mathbb{U}}^\dagger(t,t_0)\lvert\Psi_S(t)\rangle = \lvert\Psi_S(t_0)\rangle$
$\hat{A}_H(t)$	$\equiv \hat{\mathbb{U}}^\dagger(t,t_0)\hat{A}_S(t)\hat{\mathbb{U}}(t,t_0)$
$\hat{H}_H$	$= \hat{H}_S$, for time-independent H_S
$\hat{H}_H(t)$	$= \hat{H}_S(t)$, for $[\hat{H}_S(t),\hat{H}_S(t')] = 0$
$\langle\hat{A}_H(t)\rangle(t)$	$= \langle\Psi_H\lvert\hat{A}_H(t)\rvert\Psi_H\rangle$
	$= \langle\Psi_S(t_0)\lvert\hat{\mathbb{U}}^\dagger(t,t_0)\hat{A}_S(t)\hat{\mathbb{U}}(t,t_0)\rvert\Psi_S(t_0)\rangle$
	$= \langle\Psi_S(t)\lvert\hat{A}_S(t)\rvert\Psi_S(t)\rangle = \langle\hat{A}_S(t)\rangle(t)$
$i\hbar\frac{d}{dt}\hat{A}_H(t)$	$= [\hat{A}_H(t),\hat{H}_H(t)]$
	$\quad + i\hbar\hat{\mathbb{U}}^\dagger(t,t_0)\left(\frac{d}{dt}\hat{A}_S(t)\right)\hat{\mathbb{U}}(t,t_0)$

The effective Hamiltonian of the Heisenberg picture is $\hat{H}_E = 0$, which is not identical to the transformed Hamiltonian $\hat{H}_H(t)$ (see page 42). Since $\hat{H}_E = 0$ in the Heisenberg picture, the effective Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\Psi_H\rangle = 0$ is solved by $|\Psi_H\rangle = |\Psi_S(t_0)\rangle$. In the Heisenberg picture, only operators evolve in time, satisfying the differential equation in the last line of the table above. These operators are then used with $|\Psi_H\rangle$ in calculations of physically meaningful quantities.

Interaction Picture

The interaction picture is obtained with a unitary transformation of the state vectors and operators of the Schrödinger picture. This transformation removes some of the time dependence of the Schrödinger-picture state vectors, while also altering the time dependence of operators. The interaction picture is typically used with a time-dependent Schrödinger-picture Hamiltonian $\hat{H}_S(t) = \hat{H}_0 + \hat{W}(t)$, where the eigenstates of the time-independent term $\hat{H}_0$ are known, and $\hat{W}(t)$ is a time-dependent **perturbation**. $\hat{W}(t)$ can induce time-dependent dynamics and **transitions** between the eigenstates of $\hat{H}_0$, which are not stationary states of the system. These dynamics are often of primary interest when the interaction picture is used.

To transform into the interaction picture, an evolution operator $\hat{\mathbb{U}}_0(t, t_0) \equiv e^{-\frac{i}{\hbar}(t-t_0)\hat{H}_0}$ is associated with $\hat{H}_0$. Note that $\hat{\mathbb{U}}_0$ is not the time evolution operator associated with $\hat{H}_S(t)$. If $|\Psi_S(t)\rangle$ is a state vector and $\hat{A}_S(t)$ is an arbitrary operator, both specified in the Schrödinger picture, then the transformed state vector and arbitrary operator expressed in the interaction picture are

$$|\Psi_I(t)\rangle \equiv \hat{\mathbb{U}}_0^\dagger(t, t_0)|\Psi_S(t)\rangle$$
$$\hat{A}_I(t) \equiv \hat{\mathbb{U}}_0^\dagger(t, t_0)\hat{A}_S(t)\hat{\mathbb{U}}_0(t, t_0)$$

The effective Schrödinger equation in the interaction picture is

$$i\hbar\frac{\partial}{\partial t}|\Psi_I(t)\rangle = \hat{H}_E(t)|\Psi_I(t)\rangle$$

where $\hat{H}_E(t)$ is an effective Hamiltonian given by

$$\hat{H}_E(t) = \hat{\mathbb{U}}_0^\dagger(t, t_0)\hat{W}(t)\hat{\mathbb{U}}_0(t, t_0)$$

and is not identical to the transformed Hamiltonian $\hat{H}_I(t) \equiv \hat{\mathbb{U}}_0^\dagger(t, t_0)\hat{H}_S(t)\hat{\mathbb{U}}_0(t, t_0)$ (see the boxes at the bottom of pages 42 and 45). In the interaction picture, calculation of state vector dynamics that are due entirely to $\hat{W}(t)$ are emphasized, since the dynamics due to $\hat{H}_0$ are removed in the transformation. If $\hat{W}(t) = 0$, then the interaction picture reduces to the Heisenberg picture; in that case, $\hat{H}_E(t) = 0$ and $|\Psi_I(t)\rangle = |\Psi_S(t_0)\rangle$.

Exactly Solvable Problems in One Dimension

There are a few common **exactly solvable problems** consisting of a particle of mass m in a 1D time-independent potential well $V(x)$. A "problem" in this context means the identification of a specific state space and a Hamiltonian. A "solution" usually involves determining the energy eigenvalues and energy eigenstates, the relationships between these quantities, and the expression of energy eigenstates in representations that are meaningful for the given problem. Exactly solvable problems are ones for which solutions can be found analytically and without approximation methods.

For each of the exactly solvable 1D problems described on the following pages, the Hamiltonian has the form

$$\hat{H} = \frac{1}{2m}\hat{P}_x^2 + V(\hat{X})$$

In the 1D position representation, $\hat{H}$ takes the form

$$H_{\{x\}} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$$

If a constant energy term is added to $\hat{H}$, all energy eigenvalues will be shifted by that amount. However, the physical dynamics of the system depend only on differences between energy eigenvalues, so the dynamics remain unchanged. Energy is therefore measured and specified with respect to some implicit or specified reference value for every problem.

The examples on the following pages utilize the position representation. The problems and solutions include

- The potential $V(x)$, which defines the problem
- The energy eigenvalue equation, which defines the notation used to specify energy eigenvalues, quantum numbers, and the energy eigenkets and eigenfunctions
- Solutions to the energy eigenvalue equation
- Explanatory or illustrative notes, plots, and special features about the specific problem

Free Particle and Delta Function Potential Well

Free particle:

$$V(x) = 0$$

$$H_{\{x\}}\,\varphi_{p'}(x) = E_{p'}\,\varphi_{p'}(x)$$

Solutions:

$$E_{p'} = \frac{p'^2}{2m}; \quad \left\{ p' \in \mathbb{R} \,|\, p' : \left[\frac{\text{kg}\cdot\text{m}}{\text{s}}\right] \right\}$$

$$\varphi_{p'}(x) = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ixp'/\hbar}$$

The functions $\varphi_{p'}(x)$ are **plane waves**, each indexed by a precise particle momentum p'. These solutions are non-degenerate eigenkets of the momentum operator, expressed in the position representation; they are non-normalizable and are not physically realizable wavefunctions. In the momentum representation, $\varphi_{p'}(x)$ transforms (page 24) into a Dirac delta function $\tilde{\varphi}_{p'}(p) = \delta(p - p')$.

For any $p' \neq 0$, $\varphi_{p'}(x)$ and $\varphi_{-p'}(x)$ have the same energy eigenvalue $E_{p'}$, so that for scalars c_+ and c_-, the superposition

$$\psi(x) = c_+\varphi_{p'}(x) + c_-\varphi_{-p'}(x)$$

is also an energy eigenfunction with eigenvalue $E_{p'}$.

Dirac delta function potential well:

$$V(x) = -\alpha\delta(x); \qquad \{\alpha \in \mathbb{R}^+ \,|\, \alpha : [\text{J}\cdot\text{m}]\}$$

$$H_{\{x\}}\,\varphi_\alpha(x) = E_\alpha\,\varphi_\alpha(x)$$

Solutions:

$$E_\alpha = -\frac{m\alpha^2}{2\hbar^2}$$

$$\varphi_\alpha(x) = \sqrt{m\alpha/\hbar^2}\, e^{-m\alpha|x|/\hbar^2}$$

$\varphi_\alpha(x)$ is the wavefunction for the ground state, which is also the system's only bound state (i.e., localized about $x = 0$).

Infinite Square Well

Infinite square well:

$$V(x) = \begin{cases} 0 & 0 \le x \le L \\ \infty & \text{otherwise} \end{cases}$$

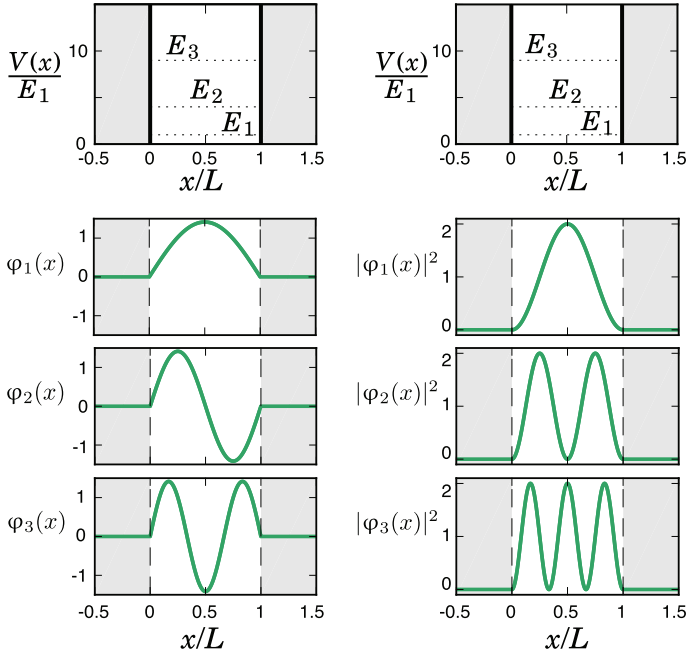
$$H_{\{x\}}\,\varphi_n(x) = E_n\,\varphi_n(x)$$

Solutions:

$$E_n = \frac{\pi^2\hbar^2 n^2}{2mL^2}; \qquad \{n \in \mathbb{N}^+\}$$

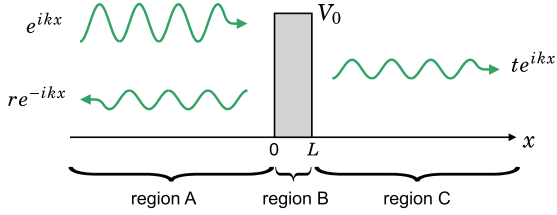
$$\varphi_n(x) = \begin{cases} \sqrt{2/L}\sin(n\pi x/L) & 0 \le x \le L \\ 0 & \text{otherwise} \end{cases}$$

$V(x)$ and the energy eigenvalues, eigenfunctions (in units of $L^{-1/2}$), and probability density distributions (in units of L^{-1}) for the first three energy eigenstates are illustrated below. Shading indicates classically forbidden regions.



Potential Barrier: Transmission and Reflection

In this problem, a free particle traveling in the $+\hat{\mathbf{x}}$ direction with total kinetic energy E (and no potential energy) encounters a region $0 < x < L$ in which there is a sudden change in potential energy of V_0. For $V_0 > 0$, this region is a localized barrier, and for $V_0 < 0$, it is a localized potential well. The particle has a probability R of being reflected by the barrier or well, and a probability T of transmission beyond the region. The position representation is used to analyze this problem. The potential barrier is illustrated below in gray for $V_0 > 0$.



Using the definitions $k \equiv \sqrt{\frac{2mE}{\hbar^2}}$ and $k' \equiv \sqrt{\frac{2m|E-V_0|}{\hbar^2}}$, the components of the (non-normalizable) wavefunctions in regions A and C are illustrated above in green; these wavefunctions have the functional forms

$$\psi_A(x) = e^{ikx} + r\,e^{-ikx}$$
$$\psi_C(x) = t\,e^{ikx}$$

where r and t are reflection and transmission amplitudes. The wavefunction in region B is initially written as

$$\psi_B(x) = \begin{cases} B_+ e^{ik'x} + B_- e^{-ik'x} & \text{for } E > V_0 \\ B_1 + B_2 x & \text{for } E = V_0 \\ B_+ e^{k'x} + B_- e^{-k'x} & \text{for } E < V_0 \end{cases}$$

The equations are solved for $T = |t|^2$ and $R = 1 - T = |r|^2$ by applying the criteria for physically realizable wavefunctions (page 32) at the boundaries of the barrier:

$$\psi_A(0) = \psi_B(0) \qquad \psi_B(L) = \psi_C(L)$$
$$\left(\tfrac{\partial}{\partial x}\psi_A\right)(0) = \left(\tfrac{\partial}{\partial x}\psi_B\right)(0) \qquad \left(\tfrac{\partial}{\partial x}\psi_B\right)(L) = \left(\tfrac{\partial}{\partial x}\psi_C\right)(L)$$

Potential Barrier: Energy above Barrier

Solutions to the potential barrier problem on page 50 are given below for $E > V_0$ (**above-barrier transmission**) and on page 52 for the cases $E = V_0$ and $E < V_0$ (**tunneling**). The solutions involve a dimensionless real parameter defined as

$$\kappa \equiv \frac{k^2 - k'^2}{2kk'}$$

Transmission amplitude t and reflection amplitude r are given in terms of a parameter D, defined separately for each case. Transmission probability T is given; in all cases, $R = 1 - T$. The wavefunction $\psi_B(x)$ in the region of the barrier is also given.

Case 1: $E > V_0$. The solution to this case holds for both $V_0 > 0$ (potential barrier) and $V_0 < 0$ (potential well):

$$\begin{aligned}
t &= \frac{1}{D} e^{-ikL} \\
r &= -\frac{i\kappa}{D} \sin(k'L) \\
D &= \cos(k'L) - i\sqrt{1+\kappa^2}\,\sin(k'L) \\
T &= [1 + \kappa^2 \sin^2(k'L)]^{-1} \\
&= \left[1 + \frac{\pi^2 V_0^2}{4E\epsilon_1} \operatorname{sinc}^2\left(\pi\sqrt{\frac{E-V_0}{\epsilon_1}}\right)\right]^{-1} \\
\psi_B(x) &= (1+r)\cos(k'x) + i\frac{k}{k'}(1-r)\sin(k'x) \\
&= (1+r)\cos(k'x) + ikx(1-r)\operatorname{sinc}(k'x)
\end{aligned}$$

The energy $\epsilon_1 = \frac{\pi^2\hbar^2}{2mL^2}$ is the ground-state energy of an infinite square well of width L (page 49). The second expression for T shows that when the kinetic energy $E - V_0$ in the barrier region equals the energy of the n^{th} excited state of an infinite square well of width L ($\epsilon_n = n^2\epsilon_1$), there is a resonance that gives a transmission probability of 1. This resonance is due to constructive interference of the wave in the barrier region, similar to resonant transmission of a monochromatic laser beam through a **Fabry–Perot resonator**. Note that if $k' = 0$, $\psi_B(x)$ matches the solution for the $E = V_0$ case (page 52).

Potential Barrier: Tunneling

Case 2: $0 < E < V_0$. For this case, the potential barrier problem has the following solution:

$$
\begin{aligned}
t &= \frac{1}{D} e^{-ikL} \\
r &= -\frac{i\sqrt{1+\kappa^2}}{D} \sinh(k'L) \\
D &= \cosh(k'L) - i\kappa \sinh(k'L) \\
T &= [1 + (1+\kappa^2)\sinh^2(k'L)]^{-1} \\
\psi_B(x) &= (1+r)\cosh(k'x) + i\frac{k}{k'}(1-r)\sinh(k'x)
\end{aligned}
$$

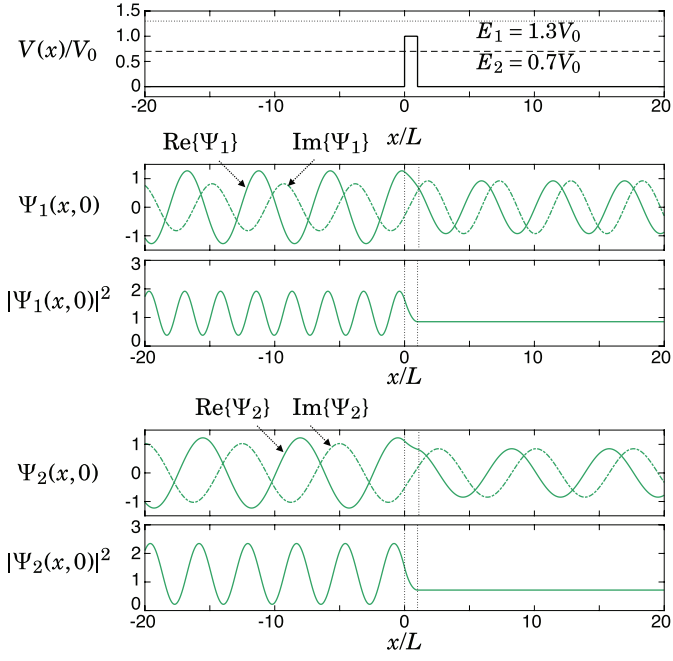
The results above show that there is a non-zero probability of transmission through the barrier when the kinetic energy of the particle is formally negative, a condition that is forbidden in classical mechanics. For this case, transmission through the barrier is called **tunneling**. Tunneling of material particles is due to the wave nature of matter, and is a phenomenon similar to the **evanescent coupling** of light between closely spaced materials.

Case 3: $E = V_0$. For this case, the potential barrier problem has the following solution:

$$
\begin{aligned}
t &= \frac{1}{D} e^{-ikL} \\
r &= -\frac{ikL}{2D} \\
D &= 1 - \frac{ikL}{2} \\
T &= \left[1 + \frac{k^2L^2}{4}\right]^{-1} \\
&= \left[1 + \frac{mL^2V_0}{2\hbar^2}\right]^{-1} \\
\psi_B(x) &= (1+r) + ikx(1-r)
\end{aligned}
$$

Potential Barrier: Examples

Above-barrier transmission and reflection, and below-barrier tunneling, are graphically illustrated below, corresponding to cases 1 and 2, respectively, from pages 51 and 52. In the examples, a plane wave is incident on a potential barrier from the left and undergoes partial reflection from the barrier and partial transmission through the barrier. The first plot shows a barrier of width L and height $V_0 = \hbar^2/(2mL^2)$ (solid line), a dotted line representing an incident plane-wave energy above that of the barrier height ($E_1 = 1.3V_0$), and a dashed line representing an incident plane-wave energy below that of the barrier height ($E_2 = 0.7V_0$). For a single instant in time $t = 0$, the second plot shows the real (solid line) and imaginary (dot-dashed line) parts of $\Psi_1(x, 0)$ (the wave of energy E_1), and the third plot shows the probability density $|\Psi_1(x, 0)|^2$ with a transmission probability $T \approx 0.85$. The fourth and fifth plots are the same as plots two and three but for incident plane-wave energy E_2, with a transmission probability $T \approx 0.72$.



1D Quantum Harmonic Oscillator

1D harmonic oscillator:

$$V(x) = \frac{1}{2} m\omega^2 x^2 = \frac{1}{2}\hbar\omega\left(\frac{x}{\sigma}\right)^2$$

$$H_{\{x\}}\,\varphi_n(x) = E_n\,\varphi_n(x)$$

Definitions:

ω oscillator frequency $\left[\frac{\text{rad}}{\text{s}}\right]$

$\sigma \equiv \sqrt{\frac{\hbar}{m\omega}}$ oscillator length [m]

Solutions:

$$E_n = \hbar\omega(n + 1/2) \quad \{n \in \mathbb{N}^0\}$$

$$\varphi_0(x) = \left(\tfrac{1}{\pi\sigma^2}\right)^{\frac{1}{4}} e^{-\frac{x^2}{2\sigma^2}} \qquad \text{ground state}$$

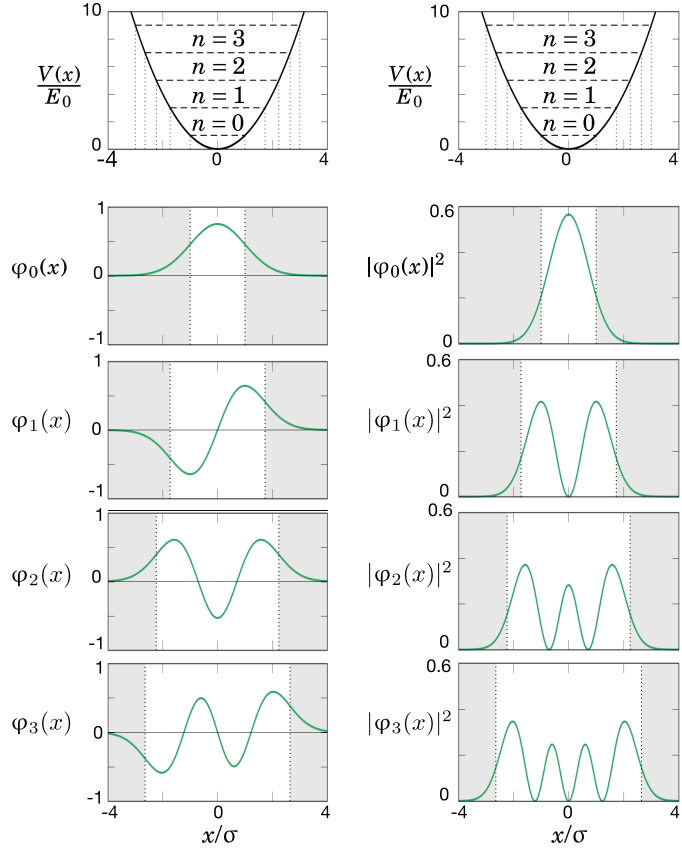
$$\varphi_n(x) = \tfrac{1}{\sqrt{2^n n!}}\varphi_0(x)\mathcal{H}_n\left(\tfrac{x}{\sigma}\right) \qquad n^{\text{th}} \text{ excited state}$$

The orthonormal set of energy eigenfunctions $\{\varphi_n(x)\}$ are the **Hermite–Gaussian** functions. $\mathcal{H}_n(\xi)$ is the **Hermite polynomial** of order n.

Hermite Polynomials up to $n = 9$
$\mathcal{H}_0(\xi) = 1$
$\mathcal{H}_1(\xi) = 2\xi$
$\mathcal{H}_2(\xi) = 4\xi^2 - 2$
$\mathcal{H}_3(\xi) = 8\xi^3 - 12\xi$
$\mathcal{H}_4(\xi) = 16\xi^4 - 48\xi^2 + 12$
$\mathcal{H}_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$
$\mathcal{H}_6(\xi) = 64\xi^6 - 480\xi^4 + 720\xi^2 - 120$
$\mathcal{H}_7(\xi) = 128\xi^7 - 1344\xi^5 + 3360\xi^3 - 1680\xi$
$\mathcal{H}_8(\xi) = 256\xi^8 - 3584\xi^6 + 13440\xi^4 - 13440\xi^2 + 1680$
$\mathcal{H}_9(\xi) = 512\xi^9 - 9216\xi^7 + 48384\xi^5 - 80640\xi^3 + 30240\xi$

Harmonic Oscillator: Energy Eigenfunctions

The plots below (green lines) show the normalized harmonic oscillator (page 54) energy eigenfunctions $\varphi_n(x)$ (left column, in units of $\sigma^{-1/2}$) for $n = 0$ through $n = 3$ and the associated probability density distributions $|\varphi_n(x)|^2$ (right column, in units of σ^{-1}). The curves shown below are for the potential energy $V(x)/E_0$ (solid-line curve in top-row plots). Vertical dashed lines indicate the classical turning points at $\pm\sigma\sqrt{2n+1}$ for each state. Horizontal dashed lines on the potential energy plots indicate the quantum numbers n for the first few energy eigenvalues.



Harmonic Oscillator: Ladder Operators

The 1D harmonic oscillator problem can be expressed in terms of a **lowering operator** $\hat{a}$ and a **raising operator** $\hat{a}^\dagger$ (the adjoint of $\hat{a}$). These operators $\hat{a}$ and $\hat{a}^\dagger$ are alternatively called the **annihilation** and **creation operators** (respectively); $\hat{a}$ and $\hat{a}^\dagger$ together are the harmonic oscillator **ladder operators**.

The ladder operators $\hat{a}$ and $\hat{a}^\dagger$ are defined in terms of the position and momentum operators $\hat{X}$ and $\hat{P}_x$. $\hat{X}$ and $\hat{P}_x$ can then be written in terms of $\hat{a}$ and $\hat{a}^\dagger$. These relationships are given as follows:

$$\hat{a} \equiv \tfrac{1}{\sqrt{2}}(\hat{X}/\sigma + i\hat{P}_x\sigma/\hbar) \qquad \hat{X} = \tfrac{\sigma}{\sqrt{2}}(\hat{a}^\dagger + \hat{a})$$
$$\hat{a}^\dagger \equiv \tfrac{1}{\sqrt{2}}(\hat{X}/\sigma - i\hat{P}_x\sigma/\hbar) \qquad \hat{P}_x = \tfrac{i\hbar}{\sigma\sqrt{2}}(\hat{a}^\dagger - \hat{a})$$

The 1D harmonic oscillator Hamiltonian is written as

$$\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)$$

where $\hat{N} \equiv \hat{a}^\dagger\hat{a}$ is called the **number operator**.

The ladder operators have the following properties and actions on the harmonic oscillator energy eigenstates $\{|\varphi_n\rangle\}$:

Ladder Operator Properties and Actions
$[\hat{a}, \hat{a}^\dagger] = 1$
$\hat{a}^\dagger\|\varphi_n\rangle = \sqrt{n+1}\|\varphi_{n+1}\rangle$ for any $n \in \mathbb{N}^0$
$\|\varphi_n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\|\varphi_0\rangle$
$\hat{a}\|\varphi_n\rangle = \sqrt{n}\|\varphi_{n-1}\rangle$ for $n \in \mathbb{N}^+$
$\hat{a}\|\varphi_0\rangle = 0$ or $\hat{a}\|\varphi_0\rangle = 0\|\varphi_0\rangle$

Both expressions in the last line above are found in quantum mechanics textbooks. The first shows that $|\varphi_0\rangle$ is the ground state; i.e., there are no kets $|\varphi_n\rangle$ for which n is negative. The second expression is found in the context of **coherent states** (also called **quasi-classical states**), described on page 59, and it emphasizes that $|\varphi_0\rangle$ is an eigenstate of $\hat{a}$ with eigenvalue 0.

Harmonic Oscillator: Properties and Dynamics

Position and momentum: An energy eigenstate $|\varphi_n\rangle$ of a 1D harmonic oscillator centered at position $x = 0$ has the following position and momentum properties:

$$\langle \hat{X} \rangle = 0 \qquad \langle \hat{P}_x \rangle = 0$$
$$\langle \hat{X}^2 \rangle = \sigma^2 (n + 1/2) \qquad \langle \hat{P}_x^2 \rangle = \tfrac{\hbar^2}{\sigma^2} (n + 1/2)$$
$$\Delta \hat{X} = \sigma \sqrt{n + 1/2} \qquad \Delta \hat{P}_x = \tfrac{\hbar}{\sigma} \sqrt{n + 1/2}$$
$$(\Delta \hat{X})(\Delta \hat{P}_x) = \hbar (n + 1/2)$$

Ehrenfest's equations: For a 1D harmonic oscillator, Ehrenfest's equations (page 44) are

$$\frac{d}{dt} \langle \hat{X} \rangle = \frac{1}{m} \langle \hat{P}_x \rangle \quad \text{and} \quad \frac{d}{dt} \langle \hat{P}_x \rangle = -m\omega^2 \langle \hat{X} \rangle$$

These equations have the time-dependent solutions shown below, which hold for any state of the harmonic oscillator with known initial conditions $\langle \hat{X} \rangle(t_0)$ and $\langle \hat{P}_x \rangle(t_0)$ at time t_0.

Harmonic Oscillator: Schrödinger Picture
$\langle \hat{X} \rangle(t) = \langle \hat{X} \rangle(t_0) \cos[\omega(t - t_0)] + \frac{1}{m\omega} \langle \hat{P}_x \rangle(t_0) \sin[\omega(t - t_0)]$
$\langle \hat{P}_x \rangle(t) = \langle \hat{P}_x \rangle(t_0) \cos[\omega(t - t_0)] - m\omega \langle \hat{X} \rangle(t_0) \sin[\omega(t - t_0)]$

The expectation values $\langle \hat{X} \rangle(t)$ and $\langle \hat{P}_x \rangle(t)$ are periodic in time. The period $\tau = 2\pi/\omega$ defines the temporal periodicity of the physical dynamics and characteristics of oscillator states.

Relative to the time-independent Schrödinger-picture (page 43) position ($\hat{X}$), momentum ($\hat{P}_x$), and ladder ($\hat{a}$ and $\hat{a}^\dagger$) operators, the corresponding Heisenberg-picture operators (page 45) are listed below and denoted with a subscript H.

Harmonic Oscillator: Heisenberg Picture
$\hat{X}_H(t) = \hat{X} \cos[\omega(t - t_0)] + \frac{1}{m\omega} \hat{P}_x \sin[\omega(t - t_0)]$
$(\hat{P}_x)_H(t) = \hat{P}_x \cos[\omega(t - t_0)] - m\omega \hat{X} \sin[\omega(t - t_0)]$
$\hat{a}_H(t) = \hat{a}\, e^{-i\omega(t - t_0)}$
$\hat{a}_H^\dagger(t) = \hat{a}^\dagger\, e^{i\omega(t - t_0)}$

Harmonic Oscillator: Fourier Transforms

For any state $|\Psi(t=0)\rangle$ of the harmonic oscillator, the position representation of the state after a subsequent quarter-period of evolution—that is, $\Psi(x, \frac{\pi}{2\omega}) = \langle x|\Psi(t=\frac{\pi}{2\omega})\rangle$—is a scaled and normalized Fourier transform of $\Psi(x,0) = \langle x|\Psi(t=0)\rangle$. Specifically,

$$\Psi\left(x,\ \frac{\pi}{2\omega}\right) = e^{-i\pi/4}\sqrt{\hbar/\sigma^2}\,\mathcal{F}\{\Psi(x,0)\}_{p=\hbar x/\sigma^2}$$

where $\mathcal{F}$ denotes the Fourier transform (page 24), and the subscript indicates that after taking the Fourier transform of $\Psi(x,0)$, all instances of p are to be replaced by $\hbar x/\sigma^2$. The coefficient $\sqrt{\hbar/\sigma^2}$ ensures proper normalization and dimensional units, and $e^{-i\pi/4}$ is a phase factor relative to the phase of the wavefunction at time $t=0$. Similarly, for the momentum distribution, where $\mathcal{F}^{-1}$ is an inverse Fourier transform,

$$\tilde{\Psi}\left(p,\ \frac{\pi}{2\omega}\right) = e^{-i\pi/4}\sqrt{\sigma^2/\hbar}\,\mathcal{F}^{-1}\{\tilde{\Psi}(p,0)\}_{x=-\sigma^2 p/\hbar}$$

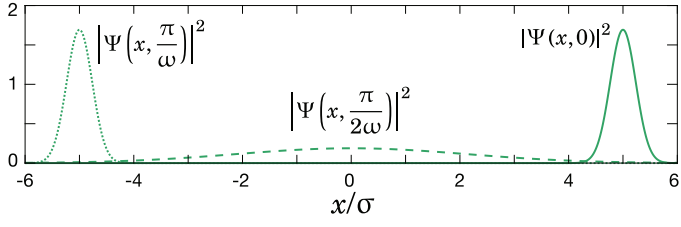
Example: Let $|\Psi(x,0)|^2$ be a **Gaussian wavefunction** of $1/e$ radius w (not necessarily equal to σ), centered at $x = x_0$, and having zero mean momentum at time $t=0$. For this case,

$$\Psi(x,0) = \left(\frac{1}{\pi w^2}\right)^{1/4} e^{-\frac{(x-x_0)^2}{2w^2}}$$

$$\Psi\left(x,\frac{\pi}{2\omega}\right) = e^{-i\pi/4}\left(\frac{w^2}{\pi\sigma^4}\right)^{1/4} e^{-\frac{ixx_0}{\sigma^2}} e^{-\frac{x^2w^2}{2\sigma^4}}$$

$$\Psi\left(x,\frac{\pi}{\omega}\right) = -i\left(\frac{1}{\pi w^2}\right)^{1/4} e^{-\frac{(x+x_0)^2}{2w^2}}$$

The probability density distributions for these three wavefunctions are shown below, in units of $1/\sigma$, for $w = \sigma/3$ and $x_0 = 5\sigma$.



Coherent States (Quasi-Classical States)

The raising operator $\hat{a}^\dagger$ does not have solutions to its eigenvalue equation. The lowering operator $\hat{a}$, however, does have solutions to its eigenvalue equation $\hat{a}|\alpha\rangle = \alpha|\alpha\rangle$ given by

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |\varphi_n\rangle; \qquad \{\alpha \in \mathbb{C}\}$$

These solutions to the eigenvalue equation for $\hat{a}$ are called **coherent states** or **quasi-classical states**. The scalar product of two coherent states $|\alpha'\rangle$ and $|\alpha''\rangle$ is

$$\langle\alpha'|\alpha''\rangle = e^{-\frac{1}{2}|\alpha'|^2} e^{-\frac{1}{2}|\alpha''|^2} \sum_{n=0}^{\infty} \frac{(\alpha'^* \alpha'')^n}{n!}$$

Because $|\langle\alpha'|\alpha''\rangle|^2 = e^{-|\alpha' - \alpha''|^2}$, coherent states are properly normalized but not orthogonal to one another. A coherent state's probability density distribution in the position or momentum representation has the same shape as that of the ground state; however, a coherent state can have non-zero real values of $\langle\hat{X}\rangle$ and $\langle\hat{P}_x\rangle$ at some instant. A coherent state is formally constructed from the ground state as follows:

1. Associate the **displacements** $\langle\hat{X}\rangle$ and $\langle\hat{P}_x\rangle$ at some instant with the complex number $\alpha = \frac{1}{\sqrt{2}}(\langle\hat{X}\rangle/\sigma + i\sigma\langle\hat{P}_x\rangle/\hbar)$.

2. Construct the unitary **displacement operator** $\hat{\mathbb{D}}(\alpha)$:

$$\hat{\mathbb{D}}(\alpha) \equiv e^{\alpha\hat{a}^\dagger - \alpha^*\hat{a}} = e^{\frac{i}{\hbar}(\langle\hat{P}_x\rangle\hat{X} - \langle\hat{X}\rangle\hat{P}_x)} = e^{i\phi_0}\hat{\mathbb{T}}(\langle\hat{P}_x\rangle)\hat{\mathbb{S}}(\langle\hat{X}\rangle)$$

where $\phi_0 = \frac{\langle\hat{P}_x\rangle\langle\hat{X}\rangle}{2\hbar}$. $\hat{\mathbb{S}}(x') = e^{-ix'\hat{P}_x/\hbar}$ and $\hat{\mathbb{T}}(p') = e^{ip'\hat{X}/\hbar}$ are position and momentum translation operators, respectively.

3. Finally, $\hat{\mathbb{D}}(\alpha)|\varphi_0\rangle = |\alpha\rangle$. Through $\hat{\mathbb{S}}(x')$ and $\hat{\mathbb{T}}(p')$, $\hat{\mathbb{D}}(\alpha)$ shifts a ground-state wavefunction in position and momentum by x' and p'. The wavefunction for the displaced state $|\alpha\rangle$ has the same shape as that of the ground state but has expectation values $\langle\hat{X}\rangle = \sqrt{2}\sigma\mathrm{Re}\{\alpha\}$ and $\langle\hat{P}_x\rangle = \sqrt{2}\frac{\hbar}{\sigma}\mathrm{Im}\{\alpha\}$.

The value of α associated with a coherent state evolves in time: for an initial ($t = 0$) **displacement** coordinate α_0, the coherent state $|\Psi(0)\rangle = |\alpha_0\rangle$ evolves as $|\Psi(t)\rangle = |\alpha_0 e^{-i\omega t}\rangle$, corresponding to the harmonic motion described on page 57.

Phase-Space Diagrams

The properties and dynamics of 1D harmonic oscillator states may be visualized with 2D **phase-space diagrams** or plots, which show position scaled by $\sqrt{2}\sigma$ on the horizontal axis, and momentum scaled by $\sqrt{2}\hbar/\sigma$ on the vertical axis, where $\sigma = \sqrt{\hbar/(m\omega)}$. The coordinates in a phase-space diagram therefore correspond to the dimensionless **displacement coordinate**

$$\alpha = \frac{1}{\sqrt{2}}\left(\frac{x}{\sigma} + i\frac{p\,\sigma}{\hbar}\right)$$

where $\mathrm{Re}\{\alpha\}$ and $\mathrm{Im}\{\alpha\}$ are the coordinates for the horizontal and vertical axes, respectively. A phase-space diagram indicates the mean values of position and momentum ($\langle\hat{X}\rangle$ and $\langle\hat{P}_x\rangle$) for any harmonic oscillator state by placing an oval centered at the corresponding point $(\mathrm{Re}\{\langle\hat{a}\rangle\}, \mathrm{Im}\{\langle\hat{a}\rangle\}) = \left(\frac{\langle\hat{X}\rangle}{\sqrt{2}\sigma}, \frac{\langle\hat{P}_x\rangle\sigma}{\sqrt{2}\hbar}\right)$, where $\hat{a}$ is the lowering operator (page 56).

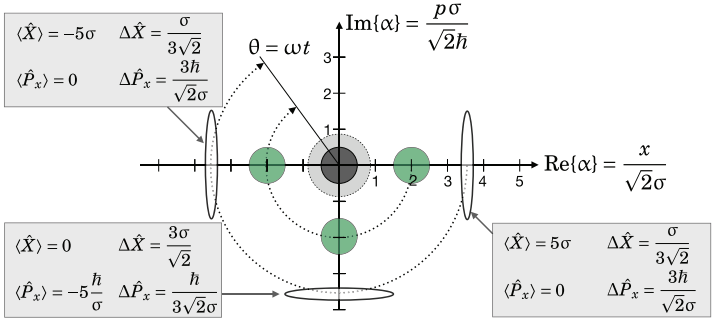
By letting the horizontal and vertical radii of the oval correspond to $\frac{\Delta\hat{X}}{\sqrt{2}\sigma}$ and $\frac{\Delta\hat{P}_x\sigma}{\sqrt{2}\hbar}$, respectively, the area of the oval is proportional to the uncertainty product $(\Delta\hat{X})(\Delta\hat{P}_x)$. This oval, which may be called an **uncertainty patch**, aids in visualizing uncertainties in both $\hat{X}$ and $\hat{P}_x$ for any state.

Because $\langle\hat{X}\rangle(t)$ and $\langle\hat{P}_x\rangle(t)$ are harmonic and out of phase (page 57), an uncertainty patch that is initially displaced from the origin will subsequently orbit the origin. By plotting the trajectory $\mathrm{Im}\{\langle\hat{a}(t)\rangle\}$ versus $\mathrm{Re}\{\langle\hat{a}(t)\rangle\}$ of the center of an uncertainty patch, the dynamics of any state of the oscillator correspond to circular trajectories or **orbits** of the uncertainty patch. All orbits are clockwise, and the center of the uncertainty patch moves through an angle $\theta = \omega t$ in the time t.

The shape of the uncertainty patch for a given state remains constant in time. However, as it orbits around the origin the uncertainty patch also rotates clockwise at the angular frequency ω. Because of this rotation, for every quarter-period of harmonic motion, the scaled position and momentum uncertainties are exchanged; this is due to the Fourier transformation property of the harmonic oscillator described on page 58.

Phase-Space Diagrams: Examples

The following phase-space diagram illustrates the dynamics of four harmonic oscillator states and their uncertainty patches.



Ground state: The dark gray circle at the coordinate system origin corresponds to the ground state $|\varphi_0\rangle$. The uncertainty patch is circular, with a position and shape that are constant in time since this is a stationary state. Its area is $\pi/4$ in the scaled units of the plot, the smallest area possible since $|\varphi_0\rangle$ satisfies the minimum uncertainty product $(\Delta\hat{X})(\Delta\hat{P}_x) = \hbar/2$.

First excited state: The light gray circle at the origin corresponds to the first excited state $|\varphi_1\rangle$. The associated uncertainty patch is stationary, but its area is three times that of $|\varphi_0\rangle$.

Squeezed state: The elongated white ovals show the uncertainty patches associated with the example given at the bottom of page 58, at the same points in time ($t = 0, t = \frac{\pi}{2\omega}$, $t = \frac{\pi}{\omega}$); time evolution corresponds to clockwise motion starting from the right-most oval at $t = 0$. For this state $(\Delta\hat{X})(\Delta\hat{P}_x) = \hbar/2$, but the uncertainties in $\hat{X}$ and $\hat{P}_x$ are alternately "squeezed" below their ground-state values, hence the name.

Coherent state: The three green circles correspond to a coherent state $|\alpha(t) = 2e^{-i\omega t}\rangle$, at the same points in time as those of the squeezed-state example. The uncertainty patch has the same shape and area as that of the ground state.

3D Quantum Harmonic Oscillator

The 3D harmonic oscillator involves three independent 1D harmonic oscillators. The 3D harmonic oscillator is defined by the Hamiltonian

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

where

$$\hat{H}_j = \frac{1}{2m}\hat{P}_j^2 + \frac{1}{2}m\omega_j^2\hat{R}_j^2$$

and $j \in \{x, y, z\}$ runs over the three orthogonal components of position. The energy eigenvalues are

$$E_{n_x,n_y,n_z} = \hbar\omega_x(n_x + 1/2) + \hbar\omega_y(n_y + 1/2) + \hbar\omega_z(n_z + 1/2)$$
$$\{n_x, n_y, n_z \in \mathbb{N}^0\}$$

In Dirac notation, the energy eigenstates are often expressed in various equivalent ways as **tensor-product states**

$$\{|\varphi_{n_x}\rangle|\varphi_{n_y}\rangle|\varphi_{n_z}\rangle\} \quad \text{or} \quad \{|n_x, n_y, n_z\rangle\} \quad \text{or} \quad \{|n_x\rangle|n_y\rangle|n_z\rangle\}$$

An energy eigenfunction has the position representation

$$\varphi_{n_x,n_y,n_z}(x, y, z) = \varphi_{n_x}(x) \cdot \varphi_{n_y}(y) \cdot \varphi_{n_z}(z)$$

where $\varphi_{n_j}(r_j) = \langle r_j|\varphi_{n_j}\rangle = \langle r_j|n_j\rangle$ is the n_j^{th} energy eigenfunction (a Hermite–Gaussian function) of a 1D harmonic oscillator in the coordinate r_j (page 54).

Each spatial dimension is associated with a lowering operator

$$\hat{a}_j = \frac{1}{\sqrt{2}}(\hat{R}_j/\sigma_j + i\hat{P}_j\sigma_j/\hbar)$$

(and its adjoint), where $\sigma_j = \sqrt{\hbar/(m\omega_j)}$. Each lowering (or raising) operator acts only on the elements of the state space $\mathcal{E}_j$ of the corresponding spatial dimension.

The 3D **isotropic harmonic oscillator** is defined by a single oscillator frequency $\omega = \omega_x = \omega_y = \omega_z$ and has energy eigenvalues given by $E_n = \hbar\omega(n + \frac{3}{2})$, where $n = n_x + n_y + n_z$, and $\{n \in \mathbb{N}^0\}$. For an energy eigenvalue E_n, the degree of degeneracy is $g_n = \frac{1}{2}(n + 1)(n + 2)$. Because of this degeneracy, the $\{|n_x, n_y, n_z\rangle\}$ set of energy eigenstates is not the only energy-eigenstate basis, although it is commonly used.

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 $\hat{\mathbf{J}}$:

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

$\hat{\mathbf{J}}^2$ 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):

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

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

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.

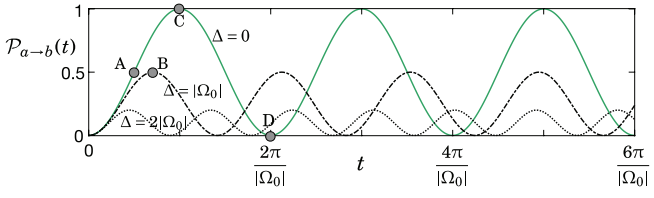
The typical case is one in which the system is known to be in state $|a\rangle$ (or $|b\rangle$) at time $t = 0$ and to then determine the **transition probability** $\mathcal{P}_{a\to b}$ (or $\mathcal{P}_{b\to a}$) that the system would be found in state $|b\rangle$ (or $|a\rangle$) at a later time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

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

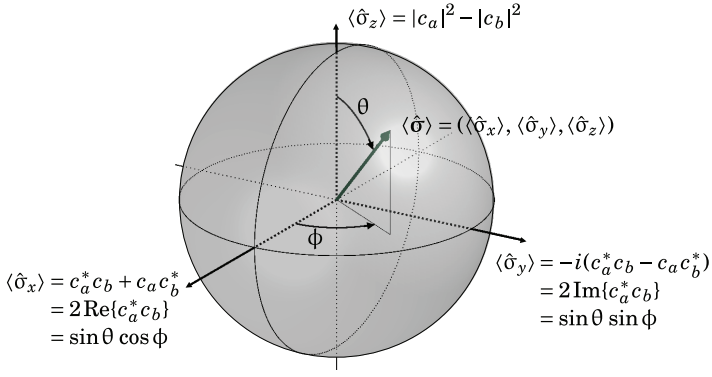
From this it is straightforward to determine that the Bloch vector associated with any state vector has unit magnitude:

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

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

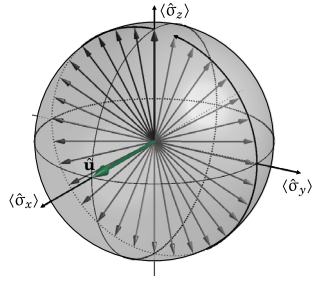
$$\langle\hat{\sigma}_x\rangle(t) = \sin\theta\{\cos\theta\cos\phi[1 - \cos(\Omega t)] + \sin\phi\sin(\Omega t)\}$$
$$\langle\hat{\sigma}_y\rangle(t) = \sin\theta\{\cos\theta\sin\phi[1 - \cos(\Omega t)] - \cos\phi\sin(\Omega t)\}$$
$$\langle\hat{\sigma}_z\rangle(t) = 1 - \sin^2\theta[1 - \cos(\Omega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

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).

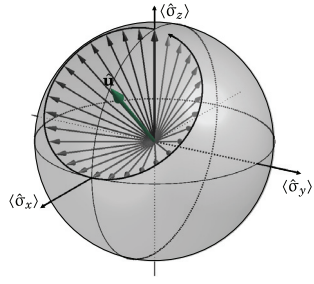
The figures on page 81 illustrate trajectories of $\langle\hat{\boldsymbol{\sigma}}\rangle(t)$ for a spin-1/2 particle's spin state for three cases. $B_\perp$ is assumed to be the same in each case, with $\mathbf{B}_\perp$ pointing in the $\hat{\mathbf{x}}$ direction so that $\phi = 0$. The spin state 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

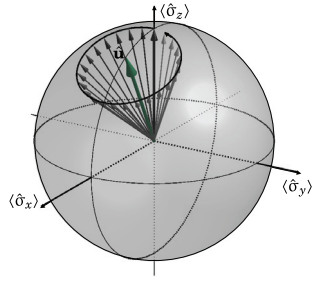
The three Bloch sphere figures below illustrate the precession of a Bloch vector $\langle\hat{\boldsymbol{\sigma}}\rangle$ (darker arrows represent earlier times) about a unit vector $\hat{\mathbf{u}}$ (in green) that corresponds to the direction of an applied constant magnetic field. The figures correspond 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:

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

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 $|m_1 = -3/2, m_2 = -1/2\rangle = |S = 2, m_S = -2\rangle$).

TP Basis	**TAM Basis**
$\|m_1 = 3/2, m_2 = 1/2\rangle$	$\|S = 2, m_S = 2\rangle$
$\|m_1 = 3/2, m_2 = -1/2\rangle$	$\|S = 2, m_S = 1\rangle$
$\|m_1 = 1/2, m_2 = 1/2\rangle$	$\|S = 1, m_S = 1\rangle$
$\|m_1 = 1/2, m_2 = -1/2\rangle$	$\|S = 2, m_S = 0\rangle$
$\|m_1 = -1/2, m_2 = 1/2\rangle$	$\|S = 1, m_S = 0\rangle$
$\|m_1 = -1/2, m_2 = -1/2\rangle$	$\|S = 2, m_S = -1\rangle$
$\|m_1 = -3/2, m_2 = 1/2\rangle$	$\|S = 1, m_S = -1\rangle$
$\|m_1 = -3/2, m_2 = -1/2\rangle$	$\|S = 2, m_S = -2\rangle$
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: $m_J = m_1 + m_2$.

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.

Ritz Variational Method

The **Ritz variational method** is useful for estimating or placing an upper bound on the ground-state energy eigenvalue in problems that are difficult or impossible to solve analytically. The primary concept involved is the following: for any "trial" normalized quantum state $|\psi\rangle$, the true ground-state energy E_g of a system can be no larger than $\langle\hat{H}\rangle = \langle\psi|\hat{H}|\psi\rangle$; i.e,

$$E_g \leq \langle\psi|\hat{H}|\psi\rangle$$

for any physically acceptable $|\psi\rangle$. This principle implies that a guess can be made for a trial solution $|\psi\rangle$ in order to find the energy expectation value for that guess, and the actual ground-state energy must be less than or equal to that value.

Example: Using the 1D position representation, a potential well $V(x)$ may be given for which the ground-state wavefunction and energy are not analytically obtainable. A guess can be made for a ground-state wave function $\psi_{\text{guess}}(x,\lambda)$ that includes an adjustable **variational parameter** λ. By minimizing the energy expectation value $\langle\hat{H}\rangle$ for $\psi_{\text{guess}}(x,\lambda)$ with respect to λ, an upper bound on the ground-state energy is obtained.

To demonstrate this procedure, let a 1D potential well be defined as $V(x) = \frac{1}{2}\hbar\omega(x/\sigma)^4$, where $\sigma = \sqrt{\hbar/(m\omega)}$. Consider a normalized trial wavefunction

$$\psi_{\text{guess}}(x,\lambda) = \left(\frac{1}{\pi\lambda^2\sigma^2}\right)^{1/4} e^{-\frac{x^2}{2\lambda^2\sigma^2}}$$

Calculating $\langle\hat{H}\rangle$ and then minimizing the result with respect to λ determines that $\langle\hat{H}\rangle$ is minimized for $\lambda \approx 0.833$. The minimum value of $\langle\hat{H}\rangle$ for this trial wavefunction is $0.54\hbar\omega$. This result shows that the true ground-state energy E_g of the given potential $V(x)$ must be less than or equal to $0.54\hbar\omega$. Other trial wavefunctions closer to the true ground-state wavefunction may help set even lower limits to the true ground-state energy.

Stationary Perturbation Theory

Stationary perturbation theory (SPT) constructs approximate energy eigenvalues and eigenstates of a time-independent Hamiltonian $\hat{H} = \hat{H}_0 + \lambda\hat{W}$, for which

- $\hat{H}_0|\varphi_n^i\rangle = E_n^0|\varphi_n^i\rangle$, where all E_n^0 and $|\varphi_n^i\rangle$ are known. For each eigenvalue E_n^0, the superscript i accounts for degeneracy, $i \in \{1, 2, \ldots, g_n\}$.
- λ is a positive or negative real scalar, $|\lambda| \ll 1$
- $\lambda\hat{W}$ is a small perturbation, meaning that the matrix elements of $\lambda\hat{W}$ are much smaller in magnitude than the differences between the eigenvalues of $\hat{H}_0$.
- The eigenvalues and eigenstates of $\hat{H}$ are defined by $\hat{H}|\psi_{nj}\rangle = E_{nj}|\psi_{nj}\rangle$. For a given n, the eigenvalues $\{E_{nj}\}$ and eigenstates $\{|\psi_{nj}\rangle\}$ may be different than the associated unperturbed quantities E_n^0 and $\{|\varphi_n^i\rangle\}$, where $i, j \in \{1, 2, \ldots, g_n\}$. The index j labels the different solutions to the eigenvalue equation for $\hat{H}$ in cases where $g_n > 1$. The indices i and j associated with a given n may be omitted if $g_n = 1$.

Non-degenerate SPT is used to find approximate solutions to the eigenvalue equation for $\hat{H}$ for a given n when there is no degeneracy in the $\hat{H}_0$ eigenvalue E_n^0 (i.e., $g_n = 1$). $\hat{H}_0$ may have degeneracies associated with other eigenvalues E_p^0, where $p \neq n$. Solutions are expanded as power series in λ.

The non-degenerate SPT solutions to second order in λ for E_n and to first order in λ for $|\psi_n\rangle$ are

$$E_n \approx E_n^0 + \lambda\langle\varphi_n|\hat{W}|\varphi_n\rangle + \lambda^2\sum_{p\neq n}\sum_{i=1}^{g_p}\frac{|\langle\varphi_p^i|\hat{W}|\varphi_n\rangle|^2}{E_n^0 - E_p^0}$$

$$|\psi_n\rangle \approx |\varphi_n\rangle + \lambda\sum_{p\neq n}\sum_{i=1}^{g_p}\frac{\langle\varphi_p^i|\hat{W}|\varphi_n\rangle}{E_n^0 - E_p^0}|\varphi_p^i\rangle$$

The approximate $|\psi_n\rangle$ must be then be normalized. Expansions to first order in λ for E_n and to zeroth order in λ for $|\psi_n\rangle$ are obtained by omitting the double-summation terms in the two expressions above.

Degenerate Stationary Perturbation Theory

Degenerate SPT applies SPT (page 90) to treat a g_n-fold degeneracy ($g_n > 1$) in an unperturbed eigenvalue E_n^0 of $\hat{H}_0$. As with the non-degenerate case, solutions to the eigenvalue equation for $\hat{H}$ are expressed as power series in λ. Solutions to first order in λ for the eigenvalues of $\hat{H}$ and to zeroth order in λ for the eigenstates are described below. In this limit, the g_n eigenstates $\{|\psi_{n,j}\rangle\}$ of $\hat{H}$ that are associated with eigenvalues $\{E_{n,j}\}$ are found to be superpositions of the g_n degenerate eigenstates $\{|\varphi_n^i\rangle\}$ of $\hat{H}_0$, with $i, j \in \{1, 2, \ldots, g_n\}$. Some or all of these degeneracies may be removed when the perturbation is present. Given specific values of n and g_n, solutions to first order in λ for the set $\{E_{n,j}\}$ and to zeroth order in λ for the set $\{|\psi_{n,j}\rangle\}$ are obtained by the following steps:

1. Given a state space $\mathcal{E}$, identify the subspace $\mathcal{E}_n$ that is spanned by the degenerate state vectors $\{|\varphi_n^i\rangle\}$, with $i \in \{1, 2, \ldots, g_n\}$.

2. Define $\hat{H}_0^{(n)}$ and $\lambda\hat{W}^{(n)}$ as the unperturbed Hamiltonian and the perturbation that act within subspace $\mathcal{E}_n$. The Hamiltonian acting within this subspace is then $\hat{H}^{(n)} = \hat{H}_0^{(n)} + \lambda\hat{W}^{(n)}$.

3. Find the g_n eigenstates and eigenvalues of $\hat{W}^{(n)}$; that is, solve the eigenvalue equation

$$\hat{W}^{(n)}|v_{n,j}\rangle = \epsilon_{n,j}|v_{n,j}\rangle$$

This step is performed by first constructing the $g_n \times g_n$ matrix that represents $\hat{W}^{(n)}$ in the representation defined by the basis $\{|\varphi_n^1\rangle, |\varphi_n^2\rangle, \ldots, |\varphi_n^{g_n}\rangle\}$ that spans the subspace $\mathcal{E}_n$. The matrix elements are given by $W_{pq}^{(n)} = \langle\varphi_n^p|\hat{W}^{(n)}|\varphi_n^q\rangle$ $(p, q \in \{1, 2, \ldots, g_n\})$.

Results: The eigenvalues (to first order in λ) and eigenstates (to zeroth order in λ) of $\hat{H}$ that are associated with the unperturbed energy eigenvalue E_n^0 are

$$E_{n,j} \approx E_n^0 + \lambda\epsilon_{n,j}$$

$$|\psi_{n,j}\rangle \approx |v_{n,j}\rangle$$

Time-Dependent Perturbation Theory

Time-dependent perturbation theory (TDPT) is used to find an approximate time-dependent expansion of a quantum state $|\Psi(t)\rangle$ into a known basis; the basis states are the eigenstates of a time-independent Hamiltonian $\hat{H}_0$ but not eigenstates of the full time-dependent system Hamiltonian $\hat{H}(t)$. TDPT is commonly used to find the approximate time-dependent probability $\mathcal{P}(t)$ of measuring that a transition has occurred from some known initial state to some specified final state. The system Hamiltonian is given by $\hat{H}(t) = \hat{H}_0 + \lambda\hat{W}(t)$ for which

- $\hat{H}_0|\varphi_n\rangle = E_n|\varphi_n\rangle$, where all E_n and $|\varphi_n\rangle$ are known. The index n may be a compound index representing a set of quantum numbers, including indices that indicate energy degeneracy.
- λ is a positive or negative real scalar, $|\lambda| \ll 1$
- $\lambda\hat{W}(t)$ is a weak perturbation, or timescales of interest are short enough, so that $\mathcal{P}(t) \ll 1$
- $|\Psi(t)\rangle$ is expanded into the $\{|\varphi_n\rangle\}$ basis as follows:

$$|\Psi(t)\rangle = \sum_n c_n(t)|\varphi_n\rangle = \sum_n b_n(t)e^{-iE_n(t-t_0)/\hbar}|\varphi_n\rangle$$

  where the terms $b_n(t) = c_n(t)e^{iE_n(t-t_0)/\hbar}$ are the expansion coefficients in the interaction picture (page 46)
- Each interaction-picture coefficient $b_n(t)$ is expanded in powers of λ: $b_n(t) = b_n^{(0)} + \lambda b_n^{(1)}(t) + \cdots + \lambda^r b_n^{(r)}(t) + \cdots$, where $b_n^{(r)}(t)$ is the r^{th}-order coefficient in the expansion of $|\varphi_n\rangle$, $b_n^{(0)} = b_n(t_0)$ is the expansion coefficient of $|\varphi_n\rangle$ for the initial initial state $|\Psi(t_0)\rangle$, and $b_n^{(r)}(t_0) = 0$ for $r > 0$ for every n

The TDPT solution for the r^{th}-order term ($r > 0$) is

$$\lambda^r b_n^{(r)}(t) = \frac{\lambda^r}{i\hbar}\int_{t_0}^{t}\sum_k dt'\, e^{i\omega_{nk}t'}W_{nk}(t')b_k^{(r-1)}(t')$$

where $\omega_{nk} \equiv \frac{E_n - E_k}{\hbar}$ and $W_{nk}(t') = \langle\varphi_n|\hat{W}(t')|\varphi_k\rangle$.

TDPT: First-Order Solution

The **first-order transition probability** $\mathcal{P}_{if}^{(1)}$ from a known initial eigenstate $|\varphi_i\rangle$ of $\hat{H}_0$ to a final eigenstate $|\varphi_f\rangle$ of $\hat{H}_0$ is determined by first specifying the initial condition at time t_0: $|\Psi(t_0)\rangle = |\varphi_i\rangle$, so that $b_n^{(0)} = \delta_{ni}$ (Kronecker delta) for each n.

The first-order term in the expansion of $b_n(t)$ $(n \neq i)$ is

$$\lambda b_n^{(1)}(t) = \frac{\lambda}{i\hbar}\int_{t_0}^{t} dt'\, e^{i\omega_{ni}t'} W_{ni}(t')$$

The time-dependent transition probability $\mathcal{P}_{if}(t)$ from the initial state $|\Psi(t_0)\rangle = |\varphi_i\rangle$ to $|\Psi(t)\rangle = |\varphi_f\rangle$ $(f \neq i)$ is then approximated as $\mathcal{P}_{if}^{(1)}$, where the superscript indicates that the probability is associated with expansion of $b_f(t)$ to first order:

$$\mathcal{P}_{if}^{(1)}(t) = \left|\lambda b_f^{(1)}(t)\right|^2 = \frac{\lambda^2}{\hbar^2}\left|\int_{t_0}^{t} dt'\, e^{i\omega_{fi}t'} W_{fi}(t')\right|^2$$

Pulse perturbations are perturbations for which $\lambda\hat{W} = 0$ when the system is known to be in the initial state $|\varphi_i\rangle$. The perturbation then turns on and off again, after which the probability $\mathcal{P}_{if}$ of finding the system in state $|\varphi_f\rangle$ is determined. In such cases, the temporal limits in the $\lambda b_n^{(1)}(t)$ integral can formally be extended to $-\infty$ and ∞. The integral for $\lambda b_n^{(1)}(t)$ is then

$$\lambda b_f^{(1)} = \frac{\lambda}{i\hbar}\mathcal{F}\{W_{fi}(t')\}_{\omega=-\omega_{fi}}$$

where $\mathcal{F}\{W_{fi}(t')\}_{\omega=-\omega_{fi}} = \int_{-\infty}^{\infty} dt'\, e^{i\omega_{fi}t'} W_{fi}(t')$ is the **time-domain Fourier transform** (page 94) of $W_{fi}(t')$ evaluated at frequency $\omega = -\omega_{fi}$.

For a pulse perturbation, the first-order transition probability from an initial state $|\varphi_i\rangle$ to a final state $|\varphi_f\rangle$ is

$$\mathcal{P}_{if}^{(1)} = \frac{\lambda^2}{\hbar^2}\left|\mathcal{F}\{W_{fi}(t')\}_{\omega=-\omega_{fi}}\right|^2$$

Fourier Transform Pairs for Pulse Perturbations

A time-domain function $f(t)$ has a corresponding frequency-domain function $F(\omega)$ that is the Fourier transform of $f(t)$.

The Fourier and inverse Fourier transform relationships between $f(t)$ and $F(\omega)$ are

$$F(\omega) = \mathcal{F}\{f(t)\} = \int_{-\infty}^{\infty} dt\, e^{-i\omega t} f(t)$$

$$f(t) = \mathcal{F}^{-1}\{F(\omega)\} = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{i\omega t} F(\omega)$$

Note that these transforms are defined differently than the transforms between the position and momentum representations of a wavefunction (page 24).

Each row of the following table gives a **Fourier transform pair** of functions $f(t)$ and $F(\omega)$ that can be associated with pulse perturbations. Note that for all examples given, $f(t)$ is free of dimensional units and has a peak value of 1.

Fourier Transform Pairs	
$f(t)$	$F(w)$
$e^{-t^2/(2\tau^2)}$	$\tau\sqrt{2\pi}e^{-\omega^2\tau^2/2}$
$e^{-\lvert t\rvert/\tau}$	$\frac{2\tau}{1+\omega^2\tau^2}$
$\frac{1}{1+t^2/\tau^2}$	$\pi\tau e^{-\lvert\omega\rvert\tau/(2\pi)}$
$\mathrm{rect}(t/\tau)$	$\tau\,\mathrm{sinc}(\omega\tau/2)$
$\mathrm{rect}(t/\tau - 1/2)$	$\tau\, e^{-i\omega\tau/2}\mathrm{sinc}(\omega\tau/2)$
$\mathrm{sinc}(\pi t/\tau)$	$\tau\,\mathrm{rect}[\omega\tau/(2\pi)]$
$\Lambda(t/\tau) = \begin{cases} 1-\lvert t\rvert/\tau & \lvert t\rvert/\tau \le 1 \\ 0 & \text{otherwise} \end{cases}$	$\frac{\tau}{2}\mathrm{sinc}^2(\omega\tau/4)$

The special functions **rect** and **sinc** are defined as follows:

$$\mathrm{rect}(\xi) = \begin{cases} 1 & -\frac{1}{2} \le \xi \le \frac{1}{2} \\ 0 & \text{otherwise} \end{cases}$$

$$\mathrm{sinc}(\xi) = \frac{1}{\xi}\sin(\xi)$$

TDPT: Harmonic Perturbations

The special case of harmonic perturbations involves time-dependent perturbations $\lambda\hat{W}(t) = \lambda\hat{\mathcal{W}}\sin(\omega t)$ with matrix elements $W_{fi}(t) = \mathcal{W}_{fi}\sin(\omega t)$, where $\hat{\mathcal{W}}$ is time independent. The $t = 0$ initial state is assumed to be $|\Psi(0)\rangle = |\varphi_i\rangle$, and the time and frequency-dependent transition probability $\mathcal{P}_{if}(t,\omega)$ to a final state $|\varphi_f\rangle$ is to be approximately determined.

To reach the solutions given below, the following assumptions are made:

- $|\omega|$ is sufficiently near $|\omega_{fi}|$ such that the conditions $\big||\omega_{fi}| - |\omega|\big| \ll |\omega_{fi}|$ and $\big||\omega_{fi}| - |\omega|\big| \ll |\omega|$ are satisfied. These conditions allow for a simplification in the calculation of $\mathcal{P}_{if}(t,\omega)$ that is called the **resonant approximation** or the **rotating wave approximation**.
- The duration of the perturbation is long enough that ω is well defined (i.e., there are many cycles of the harmonic perturbation during the interaction time).
- The transition probability remains small: $\mathcal{P}_{if}(t,\omega) \ll 1$ for all t and ω considered.

The last two assumptions above are together expressed as the double inequality (for $t > 0$)

$$\frac{1}{|\omega|} \ll t \ll \frac{\hbar}{|\lambda\mathcal{W}_{fi}|}$$

Within these limits and approximations, the first-order transition probability as a function of t and ω is given by

$$\mathcal{P}_{if}^{(1)}(t,\omega) = \frac{|\lambda\mathcal{W}_{fi}|^2}{4\hbar^2}\left\{\frac{\sin(t\Delta/2)}{\Delta/2}\right\}^2 = \left|\frac{\Omega_{fi}}{\Delta}\right|^2 \sin^2\left(\frac{t\Delta}{2}\right)$$

where $\Delta \equiv \omega - \omega_{fi}$, and $\Omega_{fi} \equiv \lambda\mathcal{W}_{fi}/\hbar$. When $\lambda\hat{W}(t)$ primarily couples $|\varphi_i\rangle$ to $|\varphi_f\rangle$ and no other states, this result is approximately equal to the results for Rabi oscillations of a two-level system (page 76) in the limit that Δ is much larger than the resonant Rabi frequency.

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: $\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}}$

Fine Structure of Hydrogen: Perturbation Terms

The spinless hydrogen model (page 97) neglects physical effects arising from the electron's spin, relativistic motion, and small-scale rapid position oscillations (called **zitterbewegung**) that require the evaluation of the Coulomb potential over a spatial volume. When the dominant terms associated with these corrections are included in the hydrogen problem, the energy levels from the spinless hydrogen model are found to shift and to split; this energy-level structure is called the **fine structure** of hydrogen. When the nuclear spin is also considered, an even finer splitting of the energy levels is found; this is the **hyperfine structure** of hydrogen.

The fine-structure problem is exactly solvable using the **Dirac equation**, which is beyond the scope of this *Field Guide*, or approximately solved using stationary perturbation theory. In the latter approach, discussed below, the small expansion parameter is α^2, where α is the dimensionless **fine-structure constant**:

$$\alpha \equiv \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c} = \frac{\hbar}{m_e c a_0} \sim 1/137$$

where the constants are defined on page 125. The unperturbed Hamiltonian is given by the spinless hydrogen Hamiltonian $\hat{H}_0$ (page 97) with the eigenvalues $E_n = -E_I/n^2$ and eigenstates $\{|n, l, m_l\rangle\}$. The electron spin states $\{|s = 1/2, m_s = \pm 1/2\rangle\}$ are incorporated using a tensor-product basis often denoted as either $\{|n, l, m_l\rangle|s, m_s\rangle\}$ or $\{|n, l, s; m_l, m_s\rangle\}$.

The fine-structure Hamiltonian is $\hat{H}_{FS} = \hat{H}_0 + \hat{W}_{FS}$. The components of the perturbation $\hat{W}_{FS} = \alpha^2\hat{W}_{SO} + \alpha^2\hat{W}_R + \alpha^2\hat{W}_D$ are defined as

- **Spin–orbit coupling:** $\alpha^2\hat{W}_{SO} = \alpha^2 \cdot \frac{a_0^2}{2\hbar^2\hat{R}}\frac{dV(\hat{R})}{d\hat{R}}\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$
- **Relativistic term:** $\alpha^2\hat{W}_R = -\alpha^2 \cdot \frac{a_0^2}{8m_e\hbar^2}\hat{\mathbf{P}}^4$
- **"Darwin" term:** $\alpha^2\hat{W}_D = \alpha^2 \cdot \frac{1}{8}a_0^2\nabla^2 V(\hat{R}) = \alpha^2 \cdot \frac{a_0^2 e^2}{8\epsilon_0}\delta(\hat{\mathbf{R}})$

where $\hat{\mathbf{P}}^4 = (\hat{\mathbf{P}}\cdot\hat{\mathbf{P}})^2$, $\hat{R} \equiv |\hat{\mathbf{R}}|$, $V(\hat{R})$ is the Coulomb interaction energy, $\hat{\mathbf{L}}$ is the electron OAM operator, and $\hat{\mathbf{S}}$ is the $s = 1/2$ electron spin operator.

Fine Structure of Hydrogen: Solutions

The fine-structure perturbations break some of the degeneracies of the $\{|n,l,s;m_l,m_s\rangle\}$ states. Under the perturbation, the eigenstates of $\hat{H}_{FS}$ remain eigenstates of $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{S}}^2$. They are also eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ where $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, so they are therefore not eigenstates of $\hat{L}_z$ and $\hat{S}_z$. Due to this, the eigenstates of $\hat{H}_{FS}$ involve new quantum numbers J and m_J (associated with $\hat{\mathbf{J}}^2$ and $\hat{J}_z$, respectively) instead of m_l and m_s.

The notation used below involves the standard symbols for atomic angular momentum quantum numbers (page 101). Note that it is common to use capital letters L and S as the quantum numbers for the total orbital angular momentum and the total spin of all electrons in an atom, respectively. In hydrogen, with one electron, L is equivalent to l, and S is equivalent to s. The eigenstates of $\hat{H}_{FS}$ can therefore be labeled $|n,L,S;J,m_J\rangle$. Transformations between the $\{|n,L,S;J,m_J\rangle\}$ basis and the $\{|n,L,S;m_L,m_S\rangle\}$ basis are accomplished through the use of Clebsch–Gordan coefficients.

The quantum numbers J and m_J are defined through the eigenvalue equations

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

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

For arbitrary L and S, J can be any value in the range $\{|L-S|, |L-S|+1, \ldots, L+S-1, L+S\}$. Since $S = 1/2$ for hydrogen, J can be either $L + 1/2$ or $L - 1/2$ for $L > 0$. If $L = 0$, then $J = 1/2$. For each J: $m_J \in \{-J, -J+1, \ldots, J-1, J\}$.

Stationary perturbation theory to first order in α^2 gives the following approximate energy eigenvalues for the hydrogen fine-structure problem:

$$E_{n,J} = E_n\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{J+1/2} - \frac{3}{4}\right)\right]$$

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

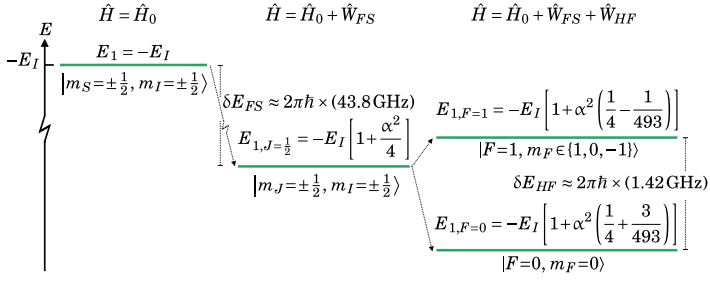
$$\hat{\mathbf{F}}^2|n, L, S, J, I; F, m_F\rangle = F(F+1)\hbar^2|n, L, S, J, I; F, m_F\rangle$$

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

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

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

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 $m_L = 0$.



Zeeman Effect in Hydrogen: $n = 1$

In the presence of a uniform magnetic field $\mathbf{B}$, the energy eigenvalue for the state $|n, L, S, J, I; F, m_F\rangle$ is shifted by an amount that depends on the angular momentum quantum numbers; this energy shift is the **Zeeman effect**. Let the direction of the magnetic field define the $\hat{\mathbf{z}}$ direction, so that $\mathbf{B} = B_0\hat{\mathbf{z}}$ leads to a perturbation Hamiltonian

$$\hat{W}_Z = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}$$

with

$$\hat{\boldsymbol{\mu}} = \frac{\mu_B}{\hbar}\left(-g_L\hat{\mathbf{L}} + g_e\hat{\mathbf{S}} + g_p\frac{m_e}{m_p}\hat{\mathbf{I}}\right)$$

where $g_L \approx 1$, $g_e \approx -2.002$, and $g_p \approx 5.586$ (see page 72).

For $n = 1$, the electron has no orbital angular momentum, so the $\hat{\mathbf{L}}$ term can be neglected, and $\hat{\mathbf{S}} = \hat{\mathbf{J}}$ for this case. Since $m_e \ll m_p$, the atomic magnetic moment is approximately

$$\hat{\boldsymbol{\mu}} \approx \frac{2\mu_B}{\hbar}\hat{\mathbf{S}} = \frac{2\mu_B}{\hbar}\hat{\mathbf{J}}$$

Defining $\omega_0 \equiv \mu_B B_0/\hbar$, the Zeeman perturbation (for $n = 1$) is

$$\hat{W}_Z \approx 2\omega_0\hat{J}_z$$

The hydrogen Hamiltonian is then

$$\hat{H} = \hat{H}_0 + \hat{W}_{FS} + \hat{W}_{HF} + \hat{W}_Z$$

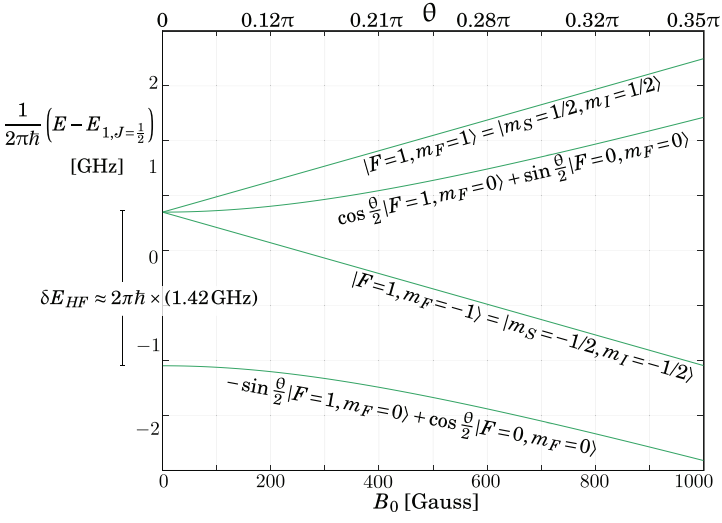
For weak magnetic fields, $\hat{W}_Z \ll \hat{W}_{HF}$, and the Zeeman effect is treated as a small perturbation to the hyperfine structure of hydrogen. This leads to the **weak-field Zeeman effect**. For larger magnetic fields, with $\hat{W}_{HF} \ll \hat{W}_Z \ll \hat{W}_{FS}$, the Zeeman effect shifts the fine-structure energy levels according to the value of m_J; the hyperfine term $\hat{W}_{HF}$ is then treated as a small perturbation on the levels $|n, L, S, J, I; m_J, m_I\rangle$ that are shifted in energy by the magnetic field. This is the **strong-field Zeeman effect**. The energy eigenvalues within both limits, as well as the **intermediate-field Zeeman effect**, can be found using stationary perturbation theory; results for the $n = 1$ level are given and illustrated on page 106.

Zeeman Effect in Hydrogen: $n = 1$ Solutions

The approximate energy eigenvalues and eigenstates for the $n = 1$ level of hydrogen in the presence of a uniform magnetic field $\mathbf{B} = B_0\hat{\mathbf{z}}$ are given and plotted below in terms of the $n = 1$ level's hyperfine splitting δE_{HF} (defined in the figure on page 104), $\omega_0 \equiv \mu_B B_0/\hbar$, and $\theta \equiv \tan^{-1}(2\hbar\omega_0/\delta E_{HF})$.

For all of the $n = 1$ states, $L = 0$, $S = 1/2$, $J = 1/2$, and $I = 1/2$; these labels are omitted from the kets given below. Furthermore, m_s is used instead of m_J since $m_L = 0$ for this case.

Energy Eigenvalues	Energy Eigenstates
$\frac{\delta E_{HF}}{4} + \hbar\omega_0$	$\lvert F = 1, m_F = 1\rangle$
$-\frac{\delta E_{HF}}{4} + \sqrt{\left(\frac{\delta E_{HF}}{2}\right)^2 + (\hbar\omega_0)^2}$	$\cos\frac{\theta}{2}\lvert F = 1, m_F = 0\rangle$ $+ \sin\frac{\theta}{2}\lvert F = 0, m_F = 0\rangle$
$\frac{\delta E_{HF}}{4} - \hbar\omega_0$	$\lvert F = 1, m_F = -1\rangle$
$-\frac{\delta E_{HF}}{4} - \sqrt{\left(\frac{\delta E_{HF}}{2}\right)^2 + (\hbar\omega_0)^2}$	$-\sin\frac{\theta}{2}\lvert F = 1, m_F = 0\rangle$ $+ \cos\frac{\theta}{2}\lvert F = 0, m_F = 0\rangle$



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 $|4, 1, -1\rangle$.

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.

Identical Particles: Two Particles

A spin quantum number is associated with every quantum-mechanical particle, whether the particle is elementary (such as an electron), composite (such as an atom), or force-mediating (such as a photon). The **many-body states** available to a system of **identical particles** each having spin s may be tentatively described as if each particle could be separately labeled and assigned an individual single-particle state. The actual quantum states physically available to a system of identical particles are then constructed, as shown below.

Consider two identical particles in states $|\psi_A\rangle$ and $|\psi_B\rangle$. At first consideration, a two-particle state might be labeled $|\psi_A\rangle|\psi_B\rangle$, where the first ket is the state of (nominal) "particle 1," and the second is that of (nominal) "particle 2." However, since the particles are identical, no measurement can distinguish this state from $|\psi_B\rangle|\psi_A\rangle$ (i.e., "particle 1" in state $|\psi_B\rangle$ and "particle 2" in state $|\psi_A\rangle$), so these two tensor product kets cannot be different elements of the state space of the two-particle system. The physically available two-particle states are rather

$$|\Psi\rangle = \frac{\beta}{\sqrt{2}}(|\psi_A\rangle|\psi_B\rangle \pm |\psi_B\rangle|\psi_A\rangle)$$

The plus sign is used if the particles have integer (including 0) spin; these particles are called **bosons**. The minus sign is used if the particles have half-integer spin (1/2, 3/2, etc.); these particles are called **fermions**. The normalization coefficient β depends on states $|\psi_A\rangle$ and $|\psi_B\rangle$: $\beta = 1$ if $\langle\psi_A|\psi_B\rangle = 0$, but $\beta \neq 1$ otherwise and must be found after constructing the superposition so that $\langle\Psi|\Psi\rangle = 1$.

If $|\psi_A\rangle = |\psi_B\rangle$, then (after normalizing the boson case)

$$|\Psi\rangle = \begin{cases} |\psi_A\rangle|\psi_A\rangle & \text{(bosons)} \\ 0 & \text{(fermions)} \end{cases}$$

The boson state above is an element of the two-particle state space; the fermion case is not ($|\Psi\rangle = 0$ is not a physical state). The conclusion from this result is that two identical fermions cannot occupy the same single-particle quantum state; this is the **Pauli exclusion principle**.

Identical Particles: Three or More Particles

Three-particle case: The physical state of three identical fermions in orthogonal single-particle quantum states $|\psi_A\rangle$, $|\psi_B\rangle$, and $|\psi_C\rangle$ is given by

$$|\Psi\rangle = \frac{1}{\sqrt{6}} \begin{vmatrix} |\psi_A\rangle & |\psi_B\rangle & |\psi_C\rangle \\ |\psi_A\rangle & |\psi_B\rangle & |\psi_C\rangle \\ |\psi_A\rangle & |\psi_B\rangle & |\psi_C\rangle \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}} (|\psi_A\rangle|\psi_B\rangle|\psi_C\rangle - |\psi_A\rangle|\psi_C\rangle|\psi_B\rangle + |\psi_B\rangle|\psi_C\rangle|\psi_A\rangle$$
$$- |\psi_B\rangle|\psi_A\rangle|\psi_C\rangle + |\psi_C\rangle|\psi_A\rangle|\psi_B\rangle - |\psi_C\rangle|\psi_B\rangle|\psi_A\rangle)$$

The right side of the first expression is a **Slater determinant**. It is evaluated as a matrix determinant, although a proper order must be kept when constructing each tensor product of three kets. The first row is associated with (nominal) particle 1; the elements of this row appear first in each tensor product. The second row is associated with particle 2; these kets appear second, etc. The second expression above is the evaluated determinant. Again, these expressions show that two identical fermions cannot occupy the same single-particle state.

The three-particle quantum state (prior to finding the normalization coefficient β) of identical bosons is

$$|\Psi\rangle = \frac{\beta}{\sqrt{6}} (|\psi_A\rangle|\psi_B\rangle|\psi_C\rangle + |\psi_A\rangle|\psi_C\rangle|\psi_B\rangle + |\psi_B\rangle|\psi_C\rangle|\psi_A\rangle$$
$$+ |\psi_B\rangle|\psi_A\rangle|\psi_C\rangle + |\psi_C\rangle|\psi_A\rangle|\psi_B\rangle + |\psi_C\rangle|\psi_B\rangle|\psi_A\rangle)$$

***N*-particle case:** For N identical fermions in states $|\psi_1\rangle$ to $|\psi_N\rangle$, the N-particle state is given by the Slater determinant

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\psi_1\rangle & |\psi_2\rangle & \cdots & |\psi_N\rangle \\ |\psi_1\rangle & |\psi_2\rangle & \cdots & |\psi_N\rangle \\ \vdots & \vdots & \ddots & \vdots \\ |\psi_1\rangle & |\psi_2\rangle & \cdots & |\psi_N\rangle \end{vmatrix}$$

For N identical bosons in states $|\psi_1\rangle$ to $|\psi_N\rangle$, the same sequence of tensor-product states as above is constructed, except all of the minus signs from the Slater determinant are replaced by plus signs (this is a matrix **permanent** rather than a determinant). $|\Psi\rangle$ is then normalized.

Identical Particles: Occupation Number Basis

For a system of N identical particles, the formalism given on pages 108–109 describes the physical states that are elements of the state space $\mathcal{E}_N$ of the entire many-body system. A basis for $\mathcal{E}_N$ can be constructed using a simplified notation that enables the specification of the number of particles n_k that can be found in each single-particle state of a discrete basis $\{|\psi_k\rangle\}$ that spans the state space for a single particle; n_k is called the **occupation number** for state $|\psi_k\rangle$.

For example, if N identical particles are confined in a 1D potential well, and if $|\psi_1\rangle$ is the single-particle ground state of the well, then $n_1 = 3$ indicates that there are three particles in the ground state (necessarily implying that the particles are bosons). Correspondingly, $N - 3$ particles must occupy excited states. The occupation-number formalism avoids the need to invoke language and terminology that artificially label the particles.

The many-particle **occupation number basis** for $\mathcal{E}_N$ is specified by $\{|n_1, n_2, \cdots, n_k, \cdots\rangle\}$, where n_k is the occupation number for the k^{th} single-particle state and is found in the k^{th} position within the many-body ket, and $N = \sum_k n_k$.

For example, the state $|0, 1, 0, 1, 0, \cdots\rangle$ (with all other occupation numbers being zero) indicates that there is one particle in the single-particle state $|\psi_2\rangle$ and one particle in the single-particle state $|\psi_4\rangle$. This is a physical state available to a system of two identical particles, either bosons or fermions. However, the superpositions of tensor-product states are different for the boson and fermion cases. For idential bosons, the occupation-number state $|0, 1, 0, 1, 0, \cdots\rangle$ coincides with the two-particle state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\psi_2\rangle|\psi_4\rangle + |\psi_4\rangle|\psi_2\rangle)$$

whereas for fermions it coincides with the two-particle state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\psi_2\rangle|\psi_4\rangle - |\psi_4\rangle|\psi_2\rangle)$$

Identical Particles: Occupation Number Basis States

The occupation number basis states $\{|n_1, n_2, \cdots, n_k, \cdots\rangle\}$ defined on page 110 have the following properties:

- The basis is orthonormal:

$$\langle n'_1, n'_2, \cdots, n'_k, \cdots | n_1, n_2, \cdots, n_k, \cdots \rangle = (\delta_{n_1,n'_1})(\delta_{n_2,n'_2}) \cdots (\delta_{n_k,n'_k}) \cdots$$

- For a system of N fermions, the Pauli exclusion principle constrains each occupation number to be either 0 or 1, along with the constraint $N = \sum_k n_k$
- For a system of bosons, each occupation number may be any non-negative integer, limited only by $N = \sum_k n_k$
- For the occupation number n_k, the index k may be a compound index that represents or is replaced by a set of single-particle indices. For example, consider a 3D isotropic harmonic oscillator potential of frequency ω. The energy eigenvalues for the single-particle Hamiltonian are

$$E_{n_x,n_y,n_z} = \hbar\omega(n_x + n_y + n_z + 3/2)$$

$$\{n_x, n_y, n_z \in \mathbb{N}^0\}$$

following the notation defined on page 62. The occupation-number basis states for three identical particles (bosons or fermions) in this potential may be written as

$$\{|n_{0,0,0}, n_{1,0,0}, n_{0,1,0}, n_{0,0,1}, \cdots\rangle\}$$

where the subscripts indicate the degree of excitation of each of the three orthogonal dimensions of the oscillator. If there is no energy of interaction between the three particles, then the energy of the occupation-number state $|0, 1, 1, 1, 0, \cdots\rangle$ is $3 \cdot \frac{5}{2}\hbar\omega$.

- The occupation number basis is used in problems that involve quantifying the states and dynamics of systems of **interacting particles**, and in the formalism of **second quantization**.

Miscellaneous Symbols and Notation

Notation for Sets of Numbers	
$\mathbb{Z}$	the set of all integers
$\mathbb{N}^0$	the set of all integers greater than or equal to 0
$\mathbb{N}^+$	the set of all integers greater than or equal to 1
$\mathbb{R}$	the set of all real numbers
$\mathbb{R}^+$	the set of all real numbers greater than 0
$\mathbb{C}$	the set of all complex numbers

Dimensional units: Square brackets indicate the dimensional units of a quantity. For example, $\{x \in \mathbb{R} | x : [\mathrm{m}]\}$ is interpreted as "x belongs to the set of real numbers such that x has dimensional units of meters."

Vectors and **unit vectors** (directional vectors with a norm of 1 and no dimensional units) are written in bold. For example, if x_0, y_0, and z_0 are real numbers, $\mathbf{r}_0 = (x_0, y_0, z_0)$ is a 3D vector pointing from the coordinate-system origin to the point (x_0, y_0, z_0). $\hat{\mathbf{y}} = (0, 1, 0)$ is a unit vector.

Complex conjugation is indicated with an asterisk superscript. For example, $(2 + 4i)^* = 2 - 4i$.

The **Kronecker delta** is indicated by the Greek letter δ with two subscripts, δ_{jk}, for example. $\delta_{jk} = 1$ if $j = k$, and $\delta_{jk} = 0$ if $j \neq k$. The indices are usually integers.

The **Dirac delta function** of a continuous parameter x is denoted $\delta(x)$, where $\delta(0) = \infty$ and $\delta(x) = 0$ for $x \neq 0$. For a general function $f(x)$,

$$\int_{-\infty}^{\infty} dx f(x)\delta(x - x') = f(x')$$

The dimensional units of $\delta(x)$ are the inverse of those of x; if x is a scalar and dx has units of meters, for example, then $\delta(x)$ has units of inverse meters.

Linear Algebra Basics

Quantum mechanics utilizes the structure and terminology of **linear algebra**. Especially common are operations of the form $A\mathbf{v} = \mathbf{v}'$, where

- A is an N-dimensional (N rows by N columns) **matrix** of scalars that are generally complex
- $\mathbf{v}$ and $\mathbf{v}'$ are column **vectors** (N rows, 1 column) of scalars that are generally complex; A is said to "act to the right" on $\mathbf{v}$ to produce a new column vector $\mathbf{v}'$

The following terms and symbols associated with matrices are also found in the formalism of quantum mechanics:

- A^T, the **transpose** of A, is obtained by exchanging the rows and columns of A: the n^{th} row of A is the n^{th} column of A^T, and the n^{th} column of A is the n^{th} row of A^T, where the order of the elements is maintained
- A^{-1}, the **inverse** of A, is defined by $AA^{-1} = A^{-1}A = \mathbb{1}$, where $\mathbb{1}$ is the identity matrix
- $A^\dagger$, the **adjoint** of A, is the complex conjugate of (all elements of) A^T
- If $A = A^\dagger$, then A is said to be **Hermitian**
- If $A^{-1} = A^\dagger$, then A is said to be **unitary**

The following terms and symbols associated with vectors are found in the formalism of quantum mechanics:

- $\mathbf{v}^T$, the transpose of $\mathbf{v}$, is a row vector created by placing the elements of $\mathbf{v}$ in a row with N columns, maintaining the order of all elements
- The adjoint operation applies to vectors as well as matrices. Let $\mathbf{v}^\dagger$ be the adjoint of $\mathbf{v}$. The row vector $\mathbf{v}^\dagger$ is the complex conjugate of (all elements of) $\mathbf{v}^T$.
- The **scalar product** associated with the ordered vector pair ($\mathbf{u}$, $\mathbf{v}$) is the complex scalar result of the vector multiplication $\mathbf{u}^\dagger\mathbf{v}$
- The **norm** of $\mathbf{v}$ is defined as $\|\mathbf{v}\| \equiv \sqrt{\mathbf{v}^\dagger\mathbf{v}}$ and is real and positive (unless all elements of $\mathbf{v}$ equal zero, in which case $\|\mathbf{v}\| = 0$). The norm is a generalized magnitude of $\mathbf{v}$ for complex vectors of arbitrary dimension.

Eigenvalue Equations in Linear Algebra

Eigenvalue equations for matrices and vectors are of the form $A\mathbf{v}_k = \lambda_k \mathbf{v}_k$, where

- A is an N-dimensional square matrix; its elements may be complex
- $\mathbf{v}_k$ is one element of a set of particular column vectors, indexed by $k \in \{1, 2, \ldots, N\}$. Each element of the set $\{\mathbf{v}_k\}$ solves the eigenvalue equation in conjunction with a specific associated scalar λ_k. $\mathbf{v}_k$ is an **eigenvector** of A.
- λ_k is an element of a set of particular scalars and may be complex. λ_k is an **eigenvalue** of A. The set of eigenvalues of A, denoted $\{\lambda_k\}$, is the eigenvalue **spectrum** of A.
- Multiple eigenvectors may be associated with the same eigenvalue; e.g., $\lambda_j = \lambda_k$ for $j \neq k$. In this case there is **degeneracy** in the spectrum of A. The **degree of degeneracy** for a given eigenvalue is the number of eigenvectors that solves the eigenvalue equation for that eigenvalue.
- If A is **Hermitian**, then a set of N eigenvectors of A can be found such that $\mathbf{v}_j^\dagger \mathbf{v}_k = 0$ for any two different eigenvectors $\mathbf{v}_j$ and $\mathbf{v}_k$. The eigenvectors $\mathbf{v}_j$ and $\mathbf{v}_k$ are then said to be **orthogonal**, and $\{\mathbf{v}_k\}$ denotes the full set of mutually orthogonal eigenvectors. If the spectrum of A has degeneracies, a set $\{\mathbf{v}_k\}$ is not unique (i.e, there are multiple ways to construct sets of orthogonal eigenvectors).

If $\mathbf{v}_k$ is an eigenvector of A associated with eigenvalue λ_k, then for any two real scalars c and ϕ, $\mathbf{w}_k \equiv ce^{i\phi}\mathbf{v}_k$ also solves the eigenvalue equation and is associated with the eigenvalue λ_k. To remove this ambiguity in specifying eigenvectors, this *Field Guide* uses the following **eigenvector conventions**:

- Every eigenvector $\mathbf{v}_k$ of a matrix A is **normalized** to 1, meaning that its norm $\|\mathbf{v}_k\|$ is 1: $\|\mathbf{v}_k\| \equiv \sqrt{\mathbf{v}_k^\dagger \mathbf{v}_k} = 1$.
- When the eigenvectors of the set $\{\mathbf{v}_k\}$ are found and defined independently of each other, the first non-zero element of each vector $\mathbf{v}_k$ is chosen to be real and positive.

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., $\hat{\mathbf{x}} = (1, 0, 0)$.

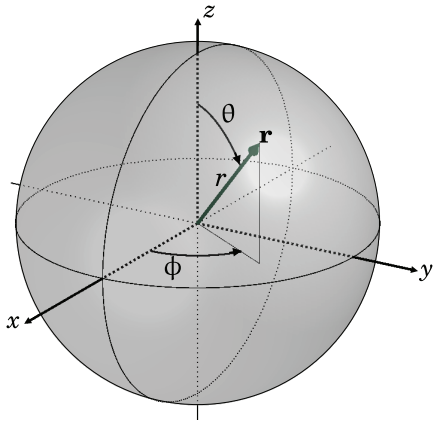
Coordinate Conversion	
$r = \lvert\mathbf{r}\rvert = \sqrt{x^2 + y^2 + z^2}$	Magnitude of $\mathbf{r}$
$\theta = \tan^{-1}\left(\frac{1}{z}\sqrt{x^2 + y^2}\right)$	Polar angle
$\phi = \tan^{-1}\left(\frac{y}{x}\right)$	Azimuthal angle
$x = r\sin\theta\cos\phi$ $y = r\sin\theta\sin\phi$ $z = r\cos\theta$	

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 $f(r, \theta, \phi)$.

Properties of 1D Gaussian Wavefunctions

A normalized 1D Gaussian wavefunction over the position coordinate x has the form

$$\psi(x) = \left(\frac{1}{\pi w^2}\right)^{1/4} e^{-\frac{x^2}{2w^2}}$$

First and second derivatives:

$$\frac{\partial\psi(x)}{\partial x} = -\frac{x}{w^2}\psi(x) \qquad \frac{\partial^2\psi(x)}{\partial x^2} = \frac{1}{w^2}\left(\frac{x^2}{w^2} - 1\right)\psi(x)$$

Probability density distribution:

$$|\psi(x)|^2 = \frac{1}{\sqrt{\pi}w} e^{-x^2/w^2}$$

Standard deviation in the coordinate x:

$$\Delta x = \left[\int_{-\infty}^{\infty} dx\, x^2 |\psi(x)|^2 - \left(\int_{-\infty}^{\infty} dx\, x|\psi(x)|^2\right)^2\right]^{1/2} = \frac{w}{\sqrt{2}}$$

For a particle whose wavefunction is given by $\psi(x)$, the net probability of finding the particle within the range $-a < x < a$ is the probability density distribution $|\psi(x)|^2$ integrated over this range:

$$\mathcal{P}(|x| < a) = \int_{-a}^{a} dx |\psi(x)|^2 = \text{erf}\left(\frac{a}{w}\right)$$

where $\text{erf}(\frac{a}{w})$ is the error function (page 122). Probabilities associated with various ranges are given below:

$$\mathcal{P}\left(|x| < \frac{\Delta x}{2}\right) \approx 0.38$$

$$\mathcal{P}\left(|x| < \frac{2}{3}\Delta x\right) \approx 0.50$$

$$\mathcal{P}(|x| < \Delta x) \approx 0.68$$

$$\mathcal{P}(|x| < 2\Delta x) \approx 0.95$$

The Fourier transform of $\psi(x)$ is a Gaussian over the momentum coordinate p (see pages 24 and 57):

$$\tilde{\psi}(p) = \mathcal{F}\{\psi(x)\} = \left(\frac{w^2}{\pi\hbar^2}\right)^{1/4} e^{-\frac{w^2p^2}{2\hbar^2}}$$

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.

Notation Guide

$J_1 \times J_2$	J	J	⋯
	m_J	m_J	⋯
m_1 m_2	Coefficients		
m_1 m_2			
⋮ ⋮			

1/2 × 1/2

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

	1	0
	0	0
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

	1
	−1
−1/2 −1/2	1

1 × 1/2

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

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

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

	3/2
	−3/2
−1 −1/2	1

3/2 × 1/2

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

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

	2	1
	0	0
+1/2 −1/2	1/2	1/2
−1/2 +1/2	1/2	−1/2

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

	2
	−2
−3/2 −1/2	1

2 × 1/2

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

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

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

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

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

	5/2
	−5/2
−2 −1/2	1

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

1 × 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 × 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 × 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

Integrals of Exponential Forms

[1] $\int x e^{bx}\,dx = e^{bx}(bx-1)/b^2$

[2] $\int x^n e^{bx} dx = x^n e^{bx}/b - (n/b)\int x^{n-1} e^{bx} dx \qquad \text{for } \{n \in \mathbb{N}^+\}$

[3] $\int_0^\infty x^n e^{-bx} dx = n!/b^{n+1} \qquad \text{for } \mathrm{Re}\{b\} > 0, \{n \in \mathbb{N}^0\}$

[4] $\int_0^\infty x^{1/2} e^{-x} dx = \sqrt{\pi}/2$

[5] $\int_0^\infty x^{3/2} e^{-x} dx = 3\sqrt{\pi}/4$

[6] $\int_0^\infty e^{-x^2} dx = \sqrt{\pi}/2$

[7] $\int_0^\infty x e^{-x^2} dx = 1/2$

[8] $\int_0^\infty x^2 e^{-x^2} dx = \sqrt{\pi}/4$

[9] $\int_0^\infty x^3 e^{-x^2} dx = 1/2$

[10] $\int_0^\infty x^4 e^{-x^2} dx = 3\sqrt{\pi}/8$

[11] $\int_0^\infty x^5 e^{-x^2} dx = 1$

[12] $\int_0^\infty x^6 e^{-x^2} dx = 15\sqrt{\pi}/16$

[13] $\int_0^\infty x^{2n} e^{-x^2} dx = [1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2n-1)]\sqrt{\pi}/2^{n+1} \quad \text{for } \{n \in \mathbb{N}^+\}$

[14] $\int_{-\infty}^\infty e^{-x^2/2a^2} e^{bx} dx = \sqrt{2\pi} \cdot a\, e^{a^2 b^2/2} \quad \text{for } \{a \in \mathbb{R} | a \geq 0\}$

[15] $\int_0^\infty x e^{-x^2/2a^2} e^{bx} dx = a^2 + \sqrt{\tfrac{\pi}{2}} a^3 b\, e^{a^2 b^2/2} \left[1 + \mathrm{erf}\left(\tfrac{ab}{\sqrt{2}}\right)\right]$

The **error function** is defined as

$$\mathrm{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y dx\, e^{-x^2}$$

with $\mathrm{erf}(\infty) = 1$. The value of $\mathrm{erf}(y)$ for a real number y can be numerically computed or found in tables.

Identities and Series Expansions

Trigonometry Identities with sin and cos	
[1]	$e^{i\theta} = \cos\theta + i\sin\theta$
[2]	$\cos^2\theta + \sin^2\theta = 1$
[3]	$\cos\theta = \frac{1}{2}[e^{i\theta} + e^{-i\theta}]$
[4]	$\sin\theta = \frac{1}{2i}[e^{i\theta} - e^{-i\theta}]$
[5]	$\cos(2\theta) = \cos^2\theta - \sin^2\theta = 2\cos^2\theta - 1 = 1 - 2\sin^2\theta$
[6]	$\sin(2\theta) = 2\sin\theta\cos\theta$
[7]	$\cos^2\theta = \frac{1}{2}[1 + \cos(2\theta)]$
[8]	$\sin^2\theta = \frac{1}{2}[1 - \cos(2\theta)]$
[9]	$\operatorname{sinc}\theta = \frac{1}{\theta}\sin\theta \quad [\text{where } \operatorname{sinc}(0) = 1]$

Hyperbolic sin and cos (sinh and cosh)	
[1]	$e^{\theta} = \cosh\theta + \sinh\theta$
[2]	$\cosh^2\theta - \sinh^2\theta = 1$
[3]	$\cosh\theta = \cos(i\theta) = \frac{1}{2}[e^{\theta} + e^{-\theta}]$
[4]	$\sinh\theta = i\sin(-i\theta) = \frac{1}{2}[e^{\theta} - e^{-\theta}]$

Power Series Expansions of $F(x)$ about $x = 0$	
[1]	$F(x) = \sum_{n=0}^{\infty} \frac{x^n}{n!} \frac{d^n F(x)}{dx^n}\Big\|_{x=0}$
[2]	$e^x = 1 + x + x^2/2! + x^3/3! + \ldots = \sum_{n=0}^{\infty} \frac{1}{n!} x^n$
[3]	$\cos(x) = 1 - x^2/2! + x^4/4! - \ldots = \sum_{n=0 \mid n \text{ even}}^{\infty} \frac{(-1)^{n/2}}{n!} x^n$
[4]	$\sin(x) = x - x^3/3! + x^5/5! - \ldots = \sum_{n=1 \mid n \text{ odd}}^{\infty} -\frac{(-1)^{n/2}}{n!} x^n$

Dimensional Units (SI)

Base Units		
Unit	**Name**	**Dimension**
s	second	time interval
m	meter	length, distance
kg	kilogram	mass
K	kelvin	temperature
A	ampere	electric current
c	candela	luminous intensity
mol	mole	amount of substance

Derived Units		
Unit	**Name**	**Measures**
m/s		velocity
$kg \cdot m/s$		momentum
m/s^2		acceleration
$Hz = 1/s$	hertz	cycle frequency
radians/s (rad/s)		angular frequency
$N = kg \cdot m/s^2$	newton	force
$J = kg \cdot m^2/s^2$	joule	energy
$W = J/s$	watt	power
$Pa = N/m^2$	pascal	pressure
$C = A \cdot s$	coulomb	electric charge
$V = J/C = W/A$	volt	voltage
$Wb = V \cdot s = J/A$	weber	magnetic flux
$T = Wb/m^2$	tesla	magnetic flux density
$H = J/A^2 = Wb/A$	henry	magnetic inductance

Dimensional Unit Conversions		
Unit	**Name**	**Equivalent SI value**
eV	electron-volt	$\approx 1.602 \times 10^{-19}$ J
G	gauss	10^{-4} T

Common Physical Constants (to Four Significant Digits)

c	$= 2.998 \times 10^{8}$ m/s	speed of light in vacuum
h	$= 6.626 \times 10^{-34}$ J · s	Planck's constant
	$= 4.136 \times 10^{-15}$eV · s	
$\hbar$	$= 1.055 \times 10^{-34}$ J · s	reduced Planck's constant;
	$= 6.582 \times 10^{-16}$ eV · s	$\hbar = h/2\pi$
k_B	$= 1.381 \times 10^{-23}$ J/K	Boltzmann's constant
μ_B	$= 9.274 \times 10^{-24}$ J/T	Bohr magneton
μ_N	$= 5.051 \times 10^{-27}$ J/T	nuclear magneton
m_e	$= 9.109 \times 10^{-31}$ kg	electron rest mass
m_p	$= 1.673 \times 10^{-27}$ kg	proton rest mass
e	$= 1.602 \times 10^{-19}$ C	elementary charge; electron charge is $-e$
ϵ_0	$= 8.854 \times 10^{-12}$ C^2/(J · m)	permittivity of free space
μ_0	$= 4\pi \times 10^{-7}$ T · m/A	magnetic constant (permeability of free space)

Hydrogen atom	
$\alpha = \dfrac{e^2}{4\pi\epsilon_0\hbar c}$ $= 7.297 \times 10^{-3}$ $\approx 1/137$	fine-structure constant
$a_0 = \dfrac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \dfrac{\hbar}{\alpha m_e c}$ $= 5.292 \times 10^{-11}$ m	Bohr radius
$E_I = \dfrac{1}{2}\alpha^2 m_e c^2 = \dfrac{\hbar^2}{2a_0^2 m_e}$ $= 2.180 \times 10^{-18}$J $= 13.61$ eV $= h \cdot (3.290 \times 10^{15}\text{Hz})$ $= hc \cdot (91.13 \times 10^{-9}\text{m})^{-1}$	ionization energy
$R_\infty = \dfrac{E_I}{hc}$ $= 1.097 \times 10^{7}\text{m}^{-1}$ $= (91.13 \times 10^{-9}\text{m})^{-1}$	Rydberg constant

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