PHYS 304

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Preliminaries

Spherical coordinates

$$\begin{cases} x = r\sin(\theta)\cos(\phi) \\ y = r\sin(\theta)\sin(\phi) \\ z = r\cos(\theta) \end{cases} \qquad \begin{cases} r = \sqrt{x^2+y^2+z^2} \\ \theta = \arctan\left(\sqrt{x^2+y^2}/z\right) \\ \phi = \arctan(y/x) \end{cases}$$

θ is the polar angle, measured from $+z$ axis. ϕ is the azimuthal angle, measured from the $+x$ axis. Cartesian basis $\underline{e}_i$ are dependent on $\underline{s}_j(r,\theta,\phi)$

$$\begin{cases} \underline{e}_1 = \sin(\theta)\cos(\phi)\underline{s}_1 + \cos(\theta)\cos(\phi)\underline{s}_2 - \sin(\phi)\underline{s}_3 \\ \underline{e}_2 = \sin(\theta)\sin(\phi)\underline{s}_1 + \cos(\theta)\sin(\phi)\underline{s}_2 + \cos(\phi)\underline{s}_3 \\ \underline{e}_3 = \cos(\theta)\underline{s}_1 - \sin(\theta)\underline{s}_2 \end{cases}$$

Spherical basis in terms of Cartesian basis

$$\begin{cases} \underline{s}_1 = \sin(\theta)\cos(\phi)\underline{e}_1 + \sin(\theta)\sin(\phi)\underline{e}_2 + \cos(\theta)\underline{e}_3 \\ \underline{s}_2 = \cos(\theta)\cos(\phi)\underline{e}_1 + \cos(\theta)\sin(\phi)\underline{e}_2 - \sin(\theta)\underline{e}_3 \\ \underline{s}_3 = -\sin(\phi)\underline{e}_1 + \cos(\phi)\underline{e}_2 \end{cases}$$

$\underline{s}_i$ are dependent on r, θ, ϕ themselves.

$$dV = dx\,dy\,dz \mapsto r^2\sin(\theta)\,dr\,d\theta\,d\phi$$

Gradient

$$\underline{\nabla}u = \frac{\partial u}{\partial r}\underline{s}_1 + \frac{1}{r}\frac{\partial u}{\partial\theta}\underline{s}_2 + \frac{1}{r\sin(\theta)}\frac{\partial u}{\partial\phi}\underline{s}_3$$

Divergence

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

Curl

$$\begin{aligned}\underline{\nabla}\times\underline{u} = {} & \frac{1}{r\sin(\theta)}\left[\frac{\partial}{\partial\theta}\left(\sin(\theta)u_\phi\right) - \frac{\partial u_\theta}{\partial\phi}\right]\underline{s}_1 \\ & + \frac{1}{r}\left[\frac{1}{\sin(\theta)}\frac{\partial u_r}{\partial\phi} - \frac{\partial}{\partial r}\left(ru_\phi\right)\right]\underline{s}_2 + \frac{1}{r}\left[\frac{\partial}{\partial r}\left(ru_\theta\right) - \frac{\partial u_r}{\partial\theta}\right]\underline{s}_3\end{aligned}$$

Laplacian

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

Alternatively, we can replace

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) \mapsto \frac{1}{r}\frac{\partial^2}{\partial r^2}r$$

Cylindrical coordinates

$$\begin{cases} x = r\cos(\phi) \\ y = r\sin(\phi) \\ z = z \end{cases} \qquad \begin{cases} r = \sqrt{x^2+y^2} \\ \phi = \arctan(y/x) \\ z = z \end{cases}$$

r is the distance to the closest point on the z axis (different from spherical coordinates). ϕ is the azimuthal angle, measured from the $+x$ axis.

$$\begin{cases} \underline{e}_1 = \cos(\phi)\underline{s}_1 - \sin(\phi)\underline{s}_2 \\ \underline{e}_2 = \sin(\phi)\underline{s}_1 + \cos(\phi)\underline{s}_2 \\ \underline{e}_3 = \underline{s}_3 \end{cases} \qquad \begin{cases} \underline{s}_1 = \cos(\phi)\underline{e}_1 + \sin(\phi)\underline{e}_2 \\ \underline{s}_2 = -\sin(\phi)\underline{e}_1 + \cos(\phi)\underline{e}_2 \\ \underline{s}_3 = \underline{e}_3 \end{cases}$$

$$dx\,dy\,dz \mapsto r\,dr\,d\phi\,dz$$

Gradient

$$\underline{\nabla}u = \frac{\partial u}{\partial r}\underline{s}_1 + \frac{1}{r}\frac{\partial u}{\partial\phi} + \frac{\partial u}{\partial z}\underline{s}_3$$

Divergence

$$\underline{\nabla}\cdot\underline{u} = \frac{1}{r}\frac{\partial}{\partial r}(ru_1) + \frac{1}{r}\frac{\partial u_2}{\partial\phi} + \frac{\partial u_3}{\partial z}$$

Curl

$$\begin{aligned}\underline{\nabla}\times\underline{u} = {} & \left[\frac{1}{r}\frac{\partial u_3}{\partial\phi} - \frac{\partial u_2}{\partial z}\right]\underline{s}_1 + \left[\frac{\partial u_1}{\partial z} - \frac{\partial u_3}{\partial r}\right]\underline{s}_2 \\ & + \frac{1}{r}\left[\frac{\partial}{\partial r}(ru_2) - \frac{\partial u_1}{\partial\phi}\right]\underline{s}_3\end{aligned}$$

Laplacian

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

Vectors

A vector space is a set of vectors, $(|\alpha\rangle, |\beta\rangle, \dots)$ a set of scalars, $(a, b, \cdots)$, that is closed under vector addition and scalar multiplication.

- α, β are labels for some vector. We can equally label vectors by numbers, such as $|1\rangle$

The set $|\alpha\rangle, |\beta\rangle, \dots$ is **linearly independent** if the only combination that gives the zero vector

$$a|\alpha\rangle + b|\beta\rangle + \cdots = \underline{0}$$

is for all $a, b, \cdots = 0$.

Given a n dimension basis,

$$|e_1\rangle, |e_2\rangle, \dots, |e_n\rangle$$

we can always expand vectors in a linear combination of the basis vectors:

$$|\alpha\rangle = \sum_{i=1}^{n} a_i|e_i\rangle$$

The coefficients a_i for $n = 1, 2, \dots, n$ are the components of $|\alpha\rangle$ under a particular basis.

Inner Products

A vector space endowed with an inner product is also an **inner product space**.We denote the inner product of $|\alpha\rangle$ and $|\beta\rangle$ as $\langle\alpha|\beta\rangle$.

- Noncommutative: $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*$
- Distributive: $\langle\alpha|(b|\beta\rangle + c|\gamma\rangle)\rangle = b\langle\alpha|\beta\rangle + c\langle\alpha|\gamma\rangle$
- $\langle\alpha|\alpha\rangle \geq 0$
- $\langle\alpha|\alpha\rangle = 0$ iff $|\alpha\rangle = 0$
- $\|\alpha\|^2 = \langle\alpha|\alpha\rangle$

A set of vectors is orthonormal when

$$\langle\alpha_i|\alpha_j\rangle = \delta_{ij}$$

Its always possible to choose an orthonormal basis to express our vectors in. With an orthonormal basis,

$$\langle\alpha|\beta\rangle = \sum_{i=1}^{n} a_i^*\beta_i$$

Under the inner product:

- Multiplication by a constant:

$$\langle c\,\alpha|\beta\rangle = c^*\langle\alpha|\beta\rangle$$
$$\langle\alpha|c\beta\rangle = c\langle\alpha|\beta\rangle$$

- For a linear transformation $\hat{T}$:

$$\langle\hat{T}\,\alpha|\beta\rangle = \left\langle\alpha\middle|\hat{T}^\dagger\beta\right\rangle$$
$$\left\langle\hat{T}^\dagger\alpha\middle|\beta\right\rangle = \langle\alpha|\hat{T}\beta\rangle$$

We are abusing the notation here: $\left\langle\hat{T}\,\alpha\middle|\beta\right\rangle$. Since α, β are labels, not vectors. $\hat{T}$ acting on a label has no meaning. $\hat{T}\beta$ means $\hat{T}|\beta\rangle$.The following are unproven:

Schwarz inequality:

$$|\langle\alpha|\beta\rangle|^2 \leq \langle\alpha|\alpha\rangle\langle\beta|\beta\rangle$$

Matrices

A transformation is linear when

$$\hat{T}\left(a\left|\alpha\right\rangle + b\left|\beta\right\rangle\right) = a\hat{T}\left|\alpha\right\rangle + b\hat{T}\left|\beta\right\rangle$$

If we know how $\hat{T}$ transforms a basis, we can find out how it will transform any vectors expressible by that basis

$$\hat{T}\left|e_j\right\rangle = \sum_{i=1}^{n} T_{ij}\left|e_i\right\rangle \qquad\qquad j = 1, 2, \ldots$$

Consider a vector $\left|\alpha\right\rangle$.

$$\hat{T}\left|\alpha\right\rangle = \hat{T}\sum_{j=1}^{n} a_j\left|e_j\right\rangle$$
$$= \sum_{j=1}^{n}\sum_{i=1}^{n} a_j T_{ij}\left|e_i\right\rangle$$

we can exchange the summations, and make it look more suggestive:

$$\sum_{i=1}^{n}\left(\sum_{j=1}^{n} a_j T_{ij}\right)\left|e_i\right\rangle$$

So $\hat{T}$ transforms a vector with components $a_1, a_2, \ldots$ into a vector with components

$$a_i' = \sum_{j=1}^{n} a_j T_{ij}$$

- With an orthonormal basis,
$$T_{ij} = \left\langle e_i\right|\hat{T}\left|e_j\right\rangle$$
- A transformation is hermitian iff $\hat{T}^\dagger = \hat{T}$ if it is invariant under hermitian conjugation (conjugate transpose)
- Assuming an orthonormal basis, $\langle\alpha|\beta\rangle = \underline{a}^\dagger\underline{b}$, where $\underline{a}$ and $\underline{b}$ are column vectors
- Anti-hermitian/skew-hermitian operator: $\hat{T}^\dagger = -\hat{T}$
- $\left(\hat{A}\hat{B}\ldots\hat{Z}\right)^\dagger = \hat{Z}^\dagger\ldots\hat{B}^\dagger\hat{A}^\dagger$
- Matrix transpose: $\underline{T} \mapsto \widetilde{\underline{T}}$

Unitary matrix: If $\underline{A}$ is an unitary, then
- $\underline{A}\underline{A}^\dagger = \underline{A}^\dagger\underline{A} = I \implies \underline{A}^\dagger = \underline{A}^{-1}$
- Columns of $\underline{A}$ are orthonormal
- Rows of $\underline{A}$ are orthonormal
- $\|\underline{A}\|_2 = 1$

Existence of inverse: The inverse of $\underline{A}$ only exists if $\det(\underline{A}) \neq 0$.

Determinant: The determinant of any diagonal square matrix is the product of its diagonal entires.

Changing basis

A change of basis can be represented by a linear transformation. We can expand old basis vectors in terms of new ones:

$$\left|e_j\right\rangle = \sum_{i=1}^{n} S_{ij}\left|f_i\right\rangle$$

Eigenvectors and eigenvalues

The collection of all eigenvalues of a matrix is its **spectrum**.

The spectrum is degenerate when two ore more linearly independent eigenvectors share the smae eigenvalue.

Diagonalizability

$\underline{A}$ is **diagonalizable** if there exists an invertible matrix $\underline{P}$ and a diagonal matrix $\underline{D}$ such that $\underline{A} = \underline{P}\underline{D}\underline{P}^{-1}$.

Diagonalizable check #1: $\underline{A}$ is **diagonalizable** if the columns of $\underline{P}$ are eigenvectors and the diagonal entries of $\underline{D}$ are the corresponding eigenvalues of $\underline{A}$, where $\underline{A} = \underline{P}\underline{D}\underline{P}^{-1}$.

The multiplicity of an eigenvalue is the number of times it appears as a root to the characteristic polynomial.

Diagonalizability check #2: If a square matrix $\underline{A}$ has distinct eigenvalues (all eigenvalues have multiplicity 1), then $\underline{A}$ is diagonalizable.

Diagonalizability check #3: A square matrix $\underline{A}$ is diagonalizable iff every eigenvalue λ of multiplicity m yields m basic eigenvectors. (Every eigenvalue of algebraic multiplicity of m also has m geometric multiplicity. So some matrices with repeated eigenvalues are also diagonalizable.)

Normal matrix: All **normal** matrices are diagonalizable. A matrix is normal when it commutes with its hermitian conjugate:

$$\left[\underline{A}^\dagger, \underline{A}\right] = 0$$

Diagonalizability check #4: All **normal** matrices are diagonalizable. A matrix is normal when it commutes with its hermitian conjugate:

$$\left[\underline{A}^\dagger, \underline{A}\right] = 0$$

Always diagonalizable:

- Matrices with a basis of eigenvectors
- Matrices with distinct eigenvalues
- Hermitian matrices
- Non-zero orthogonal projection matrices

Sometimes diagonalizable:

- Matrices with repeated eigenvalues

Applications of diagonalization

Suppose $\underline{A} = \underline{P}\underline{D}\underline{P}^{-1}$.

1. Recall two properties of the determinant:
$$\det(\underline{B}\underline{C}) = \det(\underline{B})\det(\underline{C})$$
$$\det\left(\underline{B}^{-1}\right) = 1/\det(\underline{B})$$
Then,
$$\det(\underline{A}) = \det(\underline{P})\det(\underline{D})\det\left(\underline{P}^{-1}\right) = \det(\underline{D})$$
so the determinant of a diagonalizable matrix is the product of its eigenvalues
2. The trace of a square matrix is the sum of its entries on the main diagonal. We have the following property
$$\mathrm{tr}(\underline{A}\underline{B}) = \mathrm{tr}(\underline{B}\underline{A})$$
Therefore,
$$\mathrm{tr}(\underline{A}) = \mathrm{tr}(\underline{P}\underline{D}\underline{P}^{-1}) = \mathrm{tr}(\underline{P}\underline{P}^{-1}\underline{D}) = \mathrm{tr}(\underline{D})$$
So the trace of a diagonalizable matrix is the sum of its eigenvalues
3. The k^{th} power of a diagonalizable matrix, for $k \leq 0$, can be computed by
$$\underline{A}^k = \underline{P}\underline{D}^k\underline{P}^{-1}$$
If all eigenvalues of $\underline{A}$ are non-zero, then
$$\underline{D}^k = \begin{bmatrix} \lambda_1^k & 0 & & 0 \\ 0 & \lambda_2^k & & 0 \\ & & \ddots & \\ 0 & 0 & & \lambda_n^k \end{bmatrix}$$
$\forall\, k \in \mathbb{Z}$.

Trace and determinant: In general, even for non-diagonalizable matrices,

$$\det(\underline{A}) = \lambda\ldots\lambda_n$$
$$\mathrm{tr}(\underline{A}) = \lambda_1 + \cdots + \lambda_n$$

Hermitian transformations

Properties:

1. Eigenvalues of a hermitian transformation are real
2. Eigenvectors a hermitian transformation belonging to distinct eigenvalues are orthogonal
3. Eigenvectors of a hermitian transformation form an eigenbasis

Spectral theorem: Let $\underline{A}$ be a Hermitian matrix. There exists an unitary matrix $\underline{P}$ and diagonal matrix $\underline{D}$ such that

$$\underline{A} = \underline{P}\underline{D}\underline{P}^{\dagger}$$

and $\underline{A}$ is diagonalizable ("orthogonally diagonalizable").
The columns of $\underline{P}$ are a set of orthonormal eigenvectors, and the diagonal entries of $\underline{D}$ are the eigenvalues.

Leibniz's rule

Recall, for $a, b \in \mathbb{R}$, and $f(x) = dF(x)/dx$, the fundamental theorem of calculus

$$I = \int_a^b f(t)\,dt = F(a) - f(b)$$

Clearly,

$$\frac{d}{dx} I = 0$$

since we are differentiating a number.

Consider now

$$I = \int_a^x f(t)\,dt = F(x) - F(a)$$

If we differentiate w.r.t. x, we get

$$\frac{d}{dx} I = \underbrace{\frac{d}{dx} F(x)}_{=f(x)} - 0$$

Similarly,

$$\frac{d}{dx} \int_x^b f(t)\,dt = -f(x)$$

Let's now go to a more general case. Consider integration of f over functions v and u of x.

$$I(u, v) = \int_{u(x)}^{v(x)} f(t)\,dt$$

I should have no terms that "explicitly" depend on x alone.

By the chain rule,

$$\frac{dI}{dx} = \frac{\partial I}{\partial u}\frac{du}{dx} + \frac{\partial I}{\partial v}\frac{dv}{dx}$$

This gets us to

$$\frac{d}{dx} \int_{u(x)}^{v(x)} f(t)\,dt = f(v)\frac{dv}{dx} - f(u)\frac{du}{dx}$$

Consider the following equality:

$$\frac{d}{dx} \int_a^b f(x,t)\,dt = \int_a^b \frac{\partial f(x,t)}{\partial x}\,dt$$

the equality holds when both integrals exists.

Leibniz's rule: Consider functions $f(x,t), v(x), u(x)$. **Leibniz's rule** gives a formula to the total derivative of an definite integral:

$$\frac{d}{dx} \int_{u(x)}^{v(x)} f(x,t)\,dt = f(x,v)\frac{dv}{dx} - f(x,u)\frac{du}{dx} + \int_u^v \frac{\partial f}{\partial x}\,dt$$

The rule holds when both integrals in the relation exist.

The Leibniz rule give us a nice way to evaluate some integrals. We know

$$I(b) = \int_0^\infty e^{-bx}\,dx = \frac{1}{b}$$

Repeated differentiation by b gives:

$$\int_0^\infty x^n e^{-bx}\,dx = \frac{n!}{b^{n+1}}$$

We know

$$I = \int_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}}$$

Differentiating both sides by a.

The wave function

The Schrödinger equation

In classical mechanics, given approprate initial and boundary conditions, we can completely determine the behaviour of a conservative system using Newton's laws.

Given initial conditions ($\Psi(x,0)$) the Schrödinger equations determines the wave function $\Psi(x,t)$ for all future times

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi,$$

where $\hbar = h/2\pi = 1.054 \times 10^{-34}$ Joule-seconds.

Fundamental laws in physics are postulated. Newton nor Schrödinger derived their equations.

- $\hbar$ is also called a coupling constant.

The statistical interpretation

The wave function is a complex object that spreads out through all of space.

Born's statistical interpretation:

$$\int_a^b |\Psi(x,t)|^2\,dx$$

is the probability of finding the particle between a and b at time t

Quantum mechanics offers statistical information about the possible results. It does not predict with certainty.

If we make a measurement, and finds the particle at a point C, where was the particle just before the measurement was made?

Realist: particles do not have an indeterminant position. And quantum mechanics is an incomplete theory. There is some additional information missing.

Orthodox (Copenhagen): the act of measurement compels the particle to take on a definite position. We do not ask why it does so (this is the measurement problem).

Agnostic: refuse to answer. It does not make sense to worry about what happens before the measurement was made, since this cannot be tested.

The current agreed upon interpretation is the orthodox position.

Making a measurement **collapses** the wave function to a sharp peak about a point. It then relaxes again. Fast repeated measurements yield similar results since it some time for the wave function to spread out.

Probability

Discrete Variables

Given outcomes j, a discrete variable, $N : \mathbb{Z} \to \mathbb{Z}$, gives $N(j)$, a measure of likelihood for each possible j.

- The probability of outcome j is $P(j) = N(j)/N$.

The probability for all outcome must sum to 1:

$$\sum_j P(j) = 1$$

- **Median** outcome, i, is the outcome for which $P(j > i) = P(j < i)$
- Most probable outcome is $\max_j P(j)$

The average outcome (or expectation value), is

$$\langle j \rangle = \frac{1}{N(j)} \sum_j jN(j) = \sum_j jP(j)$$

Average/Expectation value: The average value of some function of j is

$$\langle f(j) \rangle = \sum_j f(j)P(j)$$

Since the average of the deviation is zero, we define average of the square of the deviation to be the measure of spread - the **variance**:

$$\sigma^2 = \left\langle (\Delta j)^2 \right\rangle,$$

where $\Delta j = j - \langle j \rangle$ is the **deviation**.

The square root of variance is the standard deviation.

Variance identity: $\sigma^2 = \langle j^2 \rangle - \langle j \rangle^2 \geq 0$

The average of the squares is greater than the square of the average. They are equal only when $\sigma = 0$, the case where the data do not spread at all.

Continuous Variables

It only makes sense speak about the probability that an outcome x lies in some interval.

Probability density function: The probability that a outcome lies between x and $x + dx$ is $\rho(x)\,dx$.

The probability that an outcome lies between $[a, b]$ is

$$P_{ab} = \int_a^b \rho(x)\,dx$$

We require

$$\int_{-\infty}^{\infty} \rho(x)\,dx = 1$$

The average is

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

The average of a function of x is

$$\langle f(j) \rangle = \int_{-\infty}^{\infty} f(x)\rho(x)\,dx$$

And the standard deviation:

$$\sigma^2 = \left\langle (\Delta x)^2 \right\rangle = \left\langle x^2 \right\rangle - \langle x \rangle^2$$

Normalization

We require

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = \int_{-\infty}^{\infty} \Psi^*\Psi\,dx = 1,$$

where Ψ^* denotes the complex conjugate of Ψ.

Physical solutions: are square-integrable, and are normalizable.

Conservation of probability: The Schrödinger equation preserves the normalization of the wave function. This is true when the integral has no time dependence.

$$\frac{d}{dt}\int_{-\infty}^{\infty} |\Psi(x,t)|^2\,dx = 0$$

We can derive this result by noting $|\Psi|^2 = \Psi^*\Psi$, using product rule on $\Psi^*\Psi$, substituting the Schrödinger equation.
On the assumptions that

$$\lim_{x\to\pm\infty} \Psi(x,t) = 0, \text{ and } \mathrm{Im}\{V(x)\} = 0$$

Probability current

Recall the "continuity equation" in electrodynamics.

$$-\underline{\nabla} \cdot \underline{J} = \frac{\partial \rho}{\partial t}$$

This is the statement of the conservation of charge. If we volume integrate both sides and invoke Stoke's theorem, we get that the negative current flux is equal to the rate of change in charge.

A similar parallel can be drawn in quantum mechanics by defining a "probability current".

Probability current: is the rate at which probability is flowing past the point x (units 1/s):

$$J = \frac{i\hbar}{2m}\left(\Psi\frac{\partial \Psi^*}{\partial x} - \Psi^*\frac{\partial \Psi}{\partial x}\right)$$

We can show that

$$\frac{d}{dt}\int_a^b |\Psi|^2\,dx = J(a,t) - J(b,t)$$

The conservation of probability in 1-D quantum mechanics is that statement:

$$\frac{\partial J}{\partial x} + \frac{\partial |\Psi|^2}{\partial t} = 0$$

We will see that in higher dimensions, the "continuity equation" takes on an identical form as the one we encountered in electrodynamics.

In scattering, where we have left and right plane waves on both sides of some potential,

$$\psi_{\text{left}} = Ae^{ikx} + Be^{-ikx}$$
$$\psi_{\text{right}} = Ce^{ikx} + Be^{-ikx}$$

we have $J_{\text{left}} = J_{\text{right}}$.

Momentum

The expectation value of x is

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi(x,t)|^2\,dx$$

interpreted as the average of measurements performed using **identical particles** all described by the same Ψ.

It is not the average of repeated measurements on the same particle, as the wave function collapses after initial measurement.

Momentum expectation value: We postulate that $\langle v \rangle$ is equal to $d\langle x \rangle/dt$. Since $p = mv$, the expectation value of momentum, $\langle p \rangle$ is

$$\langle p \rangle = m\langle v \rangle = -i\hbar\int \Psi^*\frac{\partial \Psi}{\partial x}\,dx$$

This correspondance of $md\langle x \rangle/dt = \langle p \rangle$, along with $d\langle p \rangle/dt = -\langle dV/dt \rangle$ is also known as Ehrenfest theorem.
The expectation values appear to obey Newton's classical equations. This is only partially true. (See wiki article on why this is not the case).

Our derivation of expectation value of momentum relied on the Schrödinger equation. We can arrive at the same result using the notion of operators.

Without the notion of operators, let's compute $d\langle x \rangle/dt$.

$$\begin{aligned}\frac{d\langle x \rangle}{dt} &= \int x\frac{\partial}{\partial t}|\Psi|^2\,dx \\ &= \int x\left(\frac{\partial \Psi^*}{dt}\Psi - \Psi^*\frac{\partial \Psi}{\partial t}\right)dx\end{aligned}$$

Using the Schrödinger equation, we can convert the time derivatives into spatial derivatives:

$$= \frac{i\hbar}{2m}\int x\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial \Psi}{dx} + \Psi\frac{\partial \Psi^*}{\partial x}\right)dx$$

Applying integration by parts, and the assumption that $\Psi \to 0$ for $x \to \pm\infty$, we recover the expectation value for the momentum of a particle in 1-D.

Operators

Operators map functions to functions. We denote operators with a hat:

$\hat{x} = x$	position operator
$\hat{p} = -i\hbar\frac{\partial}{\partial x}$	momentum operator
$\hat{T} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$	kinetic energy operator

Operators do not depend on time. This is why we do not differentiate x with respect to time when computing $d\langle x \rangle/dt$.

The expectation values can be found by sandwiching operators between Ψ^* and Ψ:

$$\langle x \rangle = \int \Psi^*[x]\Psi\,dx$$

and

$$\langle p \rangle = \int \Psi^*\left[-i\hbar\frac{\partial}{\partial x}\right]\Psi\,dx$$

Sandwiching: The expectation value of any dynamical quantity $Q(x,p)$ can be found sandwiching an operator between Ψ^* and Ψ:

$$\langle Q(x,p)\rangle = \int \Psi^* \left[Q\left(x, -i\hbar\frac{\partial}{\partial x}\right)\right]\Psi\, dx$$

Properties of operators:

- Like matrices, operators can act to the left or to the right
- Operators, $\hat{a}$, $\hat{b}$, commute when $\hat{a}\hat{b} = \hat{b}\hat{a}$

A Hermitian (self-adjoint) operator is an operator whose expectation value is real.

$$\langle \hat{p}\rangle^* = \langle \hat{p}\rangle$$

- Powers of Hermitian operators are also Hermitian operators

Position and momentum are Hermitian: Such that

$$\hat{x}^\dagger = \hat{x}$$
$$\hat{p}^\dagger = \hat{p}$$

sup dagger represent complex conjugation.

When $\Psi = \Psi^*$ (Ψ is real), $\langle p\rangle = 0$.

$$\langle p\rangle = \int \Psi^* \hat{p}\Psi\, dx = -i\hbar\int \Psi^*\frac{\partial\Psi}{\partial x}\, dx$$
$$= 0$$

The right will have imaginary components. But since $\hat{p}$ is self-adjoint, its expectation value cannot be imaginary, so the right must be zero.

When manipulating operators, its a good practice to assign a test function for the operators to act on. We can throw the test function away afterwards.

Uncertainty principle

Waves can have a well-defined wavelength, but an ill-defined position, since it is spread out.

Waves can also have a well-defined position (a single bump), but an ill-defined wavelength, since there is little periodicity.

The wavelength of Ψ is related to the momentum of particle, by the de Broglie wavelength:

$$p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}$$

Uncertainty principle: The more precise the position measurement of a particle is, the less precise is its momentum measurement.

$$\sigma_x\sigma_p \geq \hbar/2$$

Measurements on systems with Ψ that is a single localized spike will produce widely scattered momentum measurements.

Measurements on systems with Ψ that is a long sine wave will produce widely scattered position measurements.

When considering only one of σ_x or σ_p, there is no limit on how big or small it can be.

Time-independent Schrödinger equation

Stationary states

A time-independent potential, V, allows us to use separation of variables.

We write $\Psi(x,t) = \psi(x)\phi(t)$ and substitute into the Schrödinger equation.

$$i\hbar\psi\frac{d\phi}{dt} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\phi + V\psi\phi$$
$$i\hbar\frac{1}{\phi}\frac{d\phi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V$$

Setting the both sides to equal a constant E, we get two ODES:

$$\frac{d\phi}{dt} = -\frac{iE}{\hbar}\phi$$

and

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V = E$$

A single solution to the 1-D Schrödinger equation has the form $\Psi(x,t) = \psi(x)\phi(t)$, where

$$\phi(t) = \exp(-iEt/\hbar)$$

and ψ solves the time independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

Bound states (normalizable states): All normalizable solutions satisfy $E > V_{\min}$

Stationary states: Solutions of the form $\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$ are stationary states since their probability density functions are time independent

$$\Psi^*\Psi = \psi^* e^{iEt/\hbar}\psi e^{-iEt/\hbar} = \psi^*\psi$$

The Hamiltonian operator

The Hamiltonian operator is a linear operator.

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

we can write the write the time-independent Schrödinger equation as

$$\hat{H}\psi = E\psi$$

The total energy of a particle is the Hamiltonian (kinetic plus potential energy):

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

The Hamiltonian operator is obtained by substituting p for the momentum operator:

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

- ψ, an eigenstate of $\hat{H}$
- E is the corresponding eigenvalue

Time independence: Any expectation value for a single eigenstate (stationary state) cannot depend on time.

If $\hat{H}\Psi_1 = E_1\Psi_1$, and $\hat{H}\Psi_2 = E_2\Psi_2$, and $E_1 \neq E_2$, (the Hamiltonian is not "degenerate"), so both Ψ_1 and Ψ_2 are eigenstates of the Hamiltonian.

But $\Psi_1 + \Psi_2$ cannot be an eigenstate.

$$\begin{aligned}\hat{H}(\Psi_1+\Psi_2) &= \hat{H}\Psi_1 + \hat{H}\Psi_2\\ &= E_1\Psi_1 + E_2\Psi_2\\ &\neq \lambda(\Psi_1+\Psi_2)\end{aligned}$$

The expectation value of the Hamiltonian:

$$\langle H\rangle = E\underbrace{\int \psi^*\psi\, dx}_{=1} = E$$

The expecation value of the square of the Hamiltonian:

$$\left\langle H^2\right\rangle = \int \psi^*\hat{H}^2\psi\, dx = E^2$$

Every eigenstate has definite energy:

$$\sigma_H^2 = \left\langle H^2\right\rangle - \langle H\rangle^2 = 0$$

$\hat{H}$ is a linear operator implies: for $c_n \in \mathbb{C}$.

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n e^{-iE_nt/\hbar}$$

is the most general solution to the 1-D Schrödinger equation.

Recall the linear differential operators we defined in the study of PDEs. Their solutions took a similar form.

The time-independent Schrödinger equation yields an infinite set of solutions, each with an associated energy. By taking a linear combination of Ψ_n, we can find a solution that matches the initial condition and boundary conditions.Each eigenstate Ψ_n is a stationary state, but a superposition of eigenstates do not have to be a stationary state.

Statistical interpretation: Each $c_n^* c_n$ is the probability that a measurement of the energy would return E_n. So the sum of all $|c_n|^2$ must equal 1.

Time independence: The expectation value of a time-independent Hamiltonian for a superposition of eigenstate is time-independent

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

The infinite square well

Is characterized by the potential:

$$V(x) = \begin{cases} 0 & x \in [0, a] \\ \infty & \text{otherwise} \end{cases}$$

We require

- ψ is continuous: $\psi(0) = \psi(a) = 0$ (boundary condition)
- ψ is normalized

Let $k = \sqrt{2mE}/\hbar$. Inside the well,

$$\frac{d^2\psi}{dx^2} = -k^2\psi,$$

Has solution

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

Applying the boudary condition, We will find that $B = 0$, and that

$$ka = n\pi \qquad\qquad n \in [1, 2, \dots]$$

We neglected $n = 0$, since this would immediately imply that $ka = 0$, and so $\psi(x) = 0$. This is a trivial solution.

We neglected $n < 0$ since $\sin(-\theta) = -\sin(\theta)$, and we can absorb the negative sign into A.

Quantization: arises from applying boundary conditions.

Each ψ (normalized) inside the well has the form

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

We could have considered A to be a complex number. But it has no significance when computing probability density functions.

- From $n = 1$, each ψ_n alternate between symmetric (even) and anti-symmetric (odd) functions.

  $\psi_{1,3,5,\dots}(a - x) = \psi_{1,3,5,\dots}(x)$ symmetric

  $\psi_{2,4,6,\dots}(a - x) = -\psi_{2,4,6,\dots}(x)$ anti-symmetric

  We can define a **symmetry operator**:

  $$\mathbb{P} : x \to (a - x)$$

  So that,

  $$\mathbb{P}\psi_n = (-1)^{n+1}\psi_n$$

Symmetry: The symmetry of the potential determines the parity of eigenstates.

- Energy eigenstates are orthonormal over $[0, a]$:

  $$\int_0^a \psi_m^* \psi_n(x)\, dx = \delta_{mn}$$

- For $m \neq n$, and ψ_m, ψ_n are both symmetric/anti-symmetric,

  $$\int_{a/2}^a \psi_m^* \psi_n(x)\, dx = 0$$

- The n^{th} eigenstate has $n - 1$ nodes, for $n = 1, 2, \dots$

The energy eigenvalues (the **spectrum**) are

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{a}\right)^2 = \frac{\hbar^2}{2m}k_n^2,$$

for $n = 1, 2, \dots$.

Complete eigenbasis: The eigenstates form a complete basis. Any function, $f(x)$ can be expressured as a linear combination of $\psi(x)$, even if $f(0), f(a) \neq 0$.

$$f(x) = \sum_n c_n \psi_x(x)$$

Time independence: $\langle \hat{H} \rangle$ does not depend on time for any superposition of states, $f(x, t)$,

$$f(x, t) = \sum_n c_n \psi_n e^{-iE_n t/\hbar}$$

and

$$\langle \hat{H} \rangle = \int f^* \hat{H} f\, dx = \sum_n |c_n|^2 E_n$$

We can show that this is true by similarly proving

$$\langle \hat{H} \rangle = \int f^*(x, 0)\hat{H} f(x, 0)\, dx = \sum_n |c_n|^2 E_n$$

Since the Hamiltonian is a time independent operator, it is sufficient to consider the case at time $t = 0$.

In general, orthogonality of sines:

$$\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right) dx = \begin{cases} 0 & n \neq m \\ L/2 & n = m \end{cases}$$

And cosines:

$$\int_0^L \cos\left(\frac{n\pi x}{L}\right)\cos\left(\frac{m\pi x}{L}\right) dx = \begin{cases} 0 & n \neq m \\ L/2 & n = m \neq 0 \\ L & n = m = 0 \end{cases}$$

We can compute the integrals explicitly by expanding them using complex exponentials.

A set of functions $f_n(y)$ is complete over an interval if any other function over the interval can be expanded in terms of a linear combination of them:

$$f(y) = \sum_{n=1}^{\infty} C_n f_n(y)$$

A set of functions is orthogonal over Ω if the integral of the product of any two different members of the set is zero:

$$\langle f_i, f_j \rangle := \int_\Omega f_i(y) f_j(y)\, dy = 0 \qquad \text{when } i \neq j$$

The harmonic oscillator

Has the characteristic potential:

$$V(x) = \frac{1}{2}m\omega^2 x^2$$

Recall that in classical mechanics, the elastic potential of a spring is given by

$$U(\ell) = \frac{k}{2}(\ell - \ell_0)^2$$

where k is the spring constant, with units [kg/s^2]. The angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{k}{m}}$$

which arises naturally from the solution to the Netwon's second law.

- $k = m\omega^2$ is analogous the classical spring constant [kg/s^2]

The time independent equation is then

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi$$

Algebraic Method

The Hamiltonian operator for our equation is

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2$$

This can be written using $\hat{p}$ and $\hat{x}$:

$$\hat{H} = \frac{1}{2m}\left(\hat{p}^2 + (m\omega\hat{x})^2\right)$$

We wish to factor $\hat{H}$. If $\hat{H}$ were a polynomial equation, then

$$u^2 + v^2 = (iu + v)(-iu + v)$$

Let's introduce the ladder operators:

$$\hat{a}_\pm = \frac{1}{\sqrt{2\hbar m\omega}}\left(\mp i\hat{p} + m\omega\hat{x}\right)$$

Equivalently:

$$\hat{a} = \hat{a}_- = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{\hat{p}}{\sqrt{2m\hbar\omega}}$$

and

$$\hat{a}^\dagger = \hat{a}_+ = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{\hat{p}}{\sqrt{2m\hbar\omega}}$$

$\hat{a}$ and $\hat{a}^\dagger$ are hermitian conjugates of each other.

Simplified ladder operators: Let $x_0^2 = \hbar/m\omega$ (units of length squared), and $\xi = x/x_0$, the ladder operators become

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\frac{\hat{x}}{x_0} + i\frac{x_0\hat{p}}{\hbar}\right) = \frac{1}{\sqrt{2}}\left(\hat{\xi} + \frac{\partial}{\partial\xi}\right)$$
$$\hat{a}^\dagger = \frac{1}{\sqrt{2}}\left(\hat{\xi} - \frac{\partial}{\partial\xi}\right)$$

We can see that

$$\hat{a}_-\hat{a}_+ = \frac{1}{2\hbar m\omega}\left(i\hat{p} + m\omega\hat{x}\right)\left(-i\hat{p} + m\omega\hat{x}\right)$$
$$= \frac{1}{2\hbar m\omega}\left(\hat{p}^2 + (m\omega\hat{x})^2 - im\omega\left(\hat{x}\hat{p} - \hat{p}\hat{x}\right)\right)$$

The additional term, $\hat{x}\hat{p} - \hat{p}\hat{x}$ is the **commutator** of $\hat{x}$ and $\hat{p}$.

The ordering of $\hat{a}_-$ and $\hat{a}_+$ also matters, as they do not commute.

Commutator: is an operator that measures of how well two operators commute. In general the commutator of $\hat{A}$ and $\hat{B}$ is denoted

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

Properties of commutators:

- Antisymmetry: $\left[\hat{A}, \hat{B}\right] = -\left[\hat{B}, \hat{A}\right]$
- Hermitian conjugation: $\left[\hat{A}, \hat{B}\right]^\dagger = \left[\hat{B}^\dagger, \hat{A}^\dagger\right]$
- Operators and constants always commute $\left[c, \hat{A}\right] = 0$
- Linearity: $\left[\hat{A}, \hat{B} + \hat{C} + \dots\right] = \left[\hat{A}, \hat{B}\right] + \left[\hat{A}, \hat{C}\right] + \dots$
- Distributivity:
$$\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right]$$
$$\left[\hat{A}\hat{B}, \hat{C}\right] = \hat{A}\left[\hat{B}, \hat{C}\right] + \left[\hat{A}, \hat{C}\right]\hat{B}$$
- We can always factor coefficients in operators out of the commutator:
$$\left[a\hat{A}/b, c\hat{B}/d\right] = \frac{ac}{bd}\left[\hat{A}, \hat{B}\right]$$
- Jacobi identity:
$$\left[\hat{A}, \left[\hat{B}, \hat{C}\right]\right] + \left[\hat{B}, \left[\hat{C}, \hat{A}\right]\right] + \left[\hat{C}, \left[\hat{A}, \hat{B}\right]\right] = 0$$

The canonical commutation relation is

$$[\hat{x}, \hat{p}] = i\hbar$$

Let's compute the commutator of the position and momentum operator.

First, let $f(x)$ be a test function.

$$\hat{x}\hat{p}f - \hat{p}\hat{x}f = x(-i\hbar)\frac{\partial}{\partial x}f(x) - (-i\hbar)\frac{\partial}{\partial x}(xf)$$
$$= i\hbar f$$

Throwing f away, we find that that $[\hat{x}, \hat{p}]$ is $i\hbar$.

Mysterys of quantum mechanics can be traced back to this relation. Its sometimes taken to be an axiom of the theory.

We have:

$$\hat{a}_\pm\hat{a}_\mp = \frac{1}{\hbar\omega}\hat{H} \mp \frac{1}{2}$$

- $\hat{a}_-\hat{a}_+ = (\hat{a}_+\hat{a}_- + 1)$
- $\left[\hat{a}, \hat{a}^\dagger\right] = 1$
- $\left[\hat{a}^\dagger, \hat{a}\right] = -1$
- $\left[\hat{H}, \hat{a}\right] = -\hbar\omega\hat{a}$

  First, we use
  $$\left[\hat{A} + \hat{B}, \hat{C} + \hat{D}\right] = \left[\hat{A}, \hat{C}\right] + \left[\hat{B}, \hat{C}\right] + \left[\hat{A}, \hat{D}\right] + \left[\hat{B}, \hat{D}\right]$$
  to write
  $$\left[\hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right), \hat{a}\right] = \hbar\omega\left[\hat{a}^\dagger\hat{a}, \hat{a}\right] + \hbar\omega\left[\frac{1}{2}, a\right]$$
  Then, we can apply
  $$\left[\hat{A}\hat{B}, \hat{C}\right] = \left[\hat{A}, \hat{C}\right]\hat{B} + \hat{A}\left[\hat{B}, \hat{C}\right]$$
  To the first term:
  $$\hbar\omega\left(\left[\hat{a}^\dagger, \hat{a}\right]\hat{a} + \hat{a}^\dagger\left[\hat{a}, \hat{a}\right]\right)$$
  Which simplifies to our desired result.
- $\left[\hat{H}, \hat{a}^\dagger\right] = \hbar\omega\hat{a}^\dagger$

Using a_- and a_+, we factor the Hamiltonian:

$$\hat{H} = \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)$$

Equivalently:

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

Rewriting the time independent equation:

$$\hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\psi = E\psi$$

Action of ladder operators: Let ψ is an normalized eigenstate of the Hamiltonian,

$$\hat{H}\psi = E\psi \quad \text{then} \quad \hat{H}\hat{a}_\pm\psi = (E \pm \hbar\omega)\psi$$

We introduced this result as a postulate. But here is the derivation. Consider

$$\left(\left[\hat{H}, \hat{a}^\dagger\right] - \hbar\omega\hat{a}^\dagger\right)\psi_n = 0$$

We can verify that this equality holds. Assuming we have solved the Schrödinger equation, (we have $\hat{H}\psi = E\psi$ as a relation at our disposal) we can manipulate this equation to arrive at our desired result.

We can explicitly show that $\hat{a}_\pm\psi$ is also an eigenstate of $\hat{H}$ with eigenvalue $E \pm \hbar\omega$.

$$\hat{H}a_\pm\psi = \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)a_\pm\psi = \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp a_\pm \pm \frac{1}{2}a_\pm\right)\psi$$
$$= \hat{a}_\pm\hbar\omega\left(\hat{a}_\mp a_\pm \pm \frac{1}{2}\right)\psi = \hat{a}_\pm\hbar\omega\left(\hat{a}_\pm a_\mp \pm 1 \pm \frac{1}{2}\right)\psi$$
$$= \hat{a}_\pm\left(\hat{H} \pm \hbar\omega\right)\psi = \hat{a}_\pm E\psi \pm \hat{a}_\pm\hbar\omega\psi$$
$$= \hat{a}_\pm\left(E \pm \hbar\omega\right)\psi$$
$$= \left(E \pm \hbar\omega\right)\hat{a}_\pm\psi$$

Operators $\hat{a}_+, \hat{a}_-$ are **raising and lowering ladder operators**.

- Given an eigenstate ψ, we can find all other eigenstates by applying $\hat{a}_\pm$
- $\hat{a}_-^n\psi$ need not be normalizable, since $(E - n\hbar\omega)$ will eventually be less than $V_{\min}$

The lowest energy state of the harmonic oscillator potential is found by setting

$$\hat{a}_- \psi_0 = 0$$

This is the **ONLY** consistent solution.

While we have started our numbering from 1 in the past, ground state starts from 0 from the harmonic oscillator.

This is a first order ODE with the solution

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(\frac{-m\omega}{2\hbar}x^2\right)$$

In terms of ξ:

$$\psi_0(\xi) = \frac{1}{x_0^{1/2}\pi^{1/4}} e^{-\xi^2/2}$$

We see that

$$\int \psi_n^\dagger \psi_n \, dx = \int \psi_n^\dagger \psi_n x_0 \, d\xi = 1$$

Thus:

$$\int \psi_n^\dagger \psi_n \, d\xi = \frac{1}{x_0}$$

To change the differentiation variable from x to ξ, we do the following:

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

which means that

$$\frac{\partial}{\partial x} \mapsto \frac{\partial \xi}{\partial x}\frac{\partial}{\partial \xi}$$

For the second partial, we need to apply the product rule:

$$\begin{aligned}\frac{\partial^2 \psi}{\partial x^2} &= \frac{\partial \xi}{\partial x}\frac{\partial}{\partial \xi}\left(\frac{\partial \psi}{\partial \xi}\frac{\partial \xi}{\partial x}\right) \\ &= \left(\frac{d\xi}{dx}\right)^2 \frac{d^2\psi}{d\xi^2} + \frac{d\psi}{d\xi}\frac{d^2\xi}{dx^2}\end{aligned}$$

Thus:

$$\frac{\partial^2}{\partial x^2} \mapsto \left(\frac{\partial \xi}{\partial x}\right)^2 \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2 \xi}{\partial x^2}\frac{\partial}{\partial \xi}$$

The ground state energy is $E_0 = \hbar\omega/2$. We can find this by substituting it into the time independent equation written using the Hamiltonian in terms of the ladder operators.

Harmonic oscillator potential: The n^{th} excited eigenstate can be found by

$$\psi_n = A_n \hat{a}_+^n \psi_0 \qquad E_n = \hbar\omega\left(\frac{1}{2} + n\right)$$

where A_n is the n^{th} normalization constant, given by

$$A_n = \frac{1}{\sqrt{n!}}$$

We can derive the normalization constant for all eigenstates algebraically. First, let's consider

$$\hat{a}\psi_n = c_n \psi_{n-1},$$

where c_n is the normalization constant for ψ_{n-1}, and we assume that ψ_n is already nromalized.

1. Take the hermitian conjugate of both sides:
$$\psi_n^\dagger \hat{a}^\dagger = c_n^* \psi_{n-1}^\dagger$$
the hermitian conjugate of numbers is simply the complex conjugate.
2. Multiply conjugated expression by the original
$$\begin{aligned}\psi_n^\dagger \hat{a}^\dagger \hat{a} \psi_n &= c_n^* \psi_{n-1}^\dagger c_n \psi_{n-1} \\ &= |c_n|^2 \psi_{n-1}^\dagger \psi_{n-1}\end{aligned}$$
3. Write $\hat{a}^\dagger\hat{a}$ in terms of the Hamiltonian:
$$\hat{a}^\dagger\hat{a} = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2}$$
4. Substitute into our expression:
$$\psi_n^\dagger\left(\frac{\hat{H}}{\hbar\omega} - \frac{1}{2}\right)\psi_n = |c_n|^2 \psi_{n-1}^\dagger \psi_{n-1}$$
5. Integrate both sides. Consider the integral on the right:
$$|c_n|^2 \int \psi_{n-1}^\dagger \psi_{n-1} \, dx = |c_n|^2$$
This is due to our normalization condition. Consider now the integral on the left:
$$\begin{aligned}\int \psi_n^\dagger\left(\frac{\hat{H}}{\hbar\omega} - \frac{1}{2}\right)\psi_n \, dx &= \int \psi_n^\dagger \frac{\hat{H}}{\hbar\omega}\psi_n \, dx - \frac{1}{2}\int \psi_n^\dagger \psi_n \, dx \\ &= \left(n + \frac{1}{2}\right) - \frac{1}{2} \\ &= n\end{aligned}$$
6. Equate the left and right integrals:
$$c_n = \sqrt{n} \iff \hat{a}\psi_n = \sqrt{n}\psi_{n-1}$$

In a similar fashion, we can find that

$$\hat{a}^\dagger \psi_n = \sqrt{n+1}\psi_{n+1}$$

Action of ladder operators: Assuming ψ_n is normalized:

$$\begin{aligned}\hat{a}\psi_n &= \sqrt{n}\psi_{n-1} \\ \hat{a}^\dagger\psi_n &= \sqrt{n+1}\psi_{n+1}\end{aligned}$$

Different stationary states of the same Hamiltonian are orthogonal.

$$\int \psi_m^\dagger \psi_n \, dx = \delta_{mn}$$

We can use an operators approach to when integrating ψ_m and ψ_n. The key is to utilize the identity:

$$\hat{a}\psi_0 = 0$$

and its hermitian conjugate:

$$\psi_0^\dagger \hat{a}^\dagger = 0$$

and the fact that any excited state can be found be repeated applying the raising operator to the ground state.

In position space, we can express the position and momentum operator in terms of $\hat{a}, \hat{a}^\dagger$.

$$\begin{aligned}\hat{x} &= \frac{x_0}{\sqrt{2}}\left(\hat{a}^\dagger + \hat{a}\right) \\ \hat{p} &= \frac{i\hbar}{x_0\sqrt{2}}\left(\hat{a}^\dagger - \hat{a}\right)\end{aligned}$$

Instead of directly computing $\langle\psi_n|\,\hat{x}\,|\psi_m\rangle$, we can leverage orthogoality by writing $\hat{x}, \hat{p}$ using $\hat{a}, \hat{a}^\dagger$.

For two eigenstates $|n\rangle$, $|m\rangle$ of the harmonic oscillator in position space, while

$$\langle n|\,x\,|m\rangle = \langle m|\,x\,|n\rangle$$

in general,

$$\langle n|\,\hat{p}\,|m\rangle = \langle m|\,\hat{p}\,|m\rangle^*$$

First three eigenstates:

$$\begin{aligned}\psi_0 &= \alpha e^{-\xi^2/2} \\ \psi_1 &= \sqrt{2}\alpha\xi e^{-\xi^2/2} \\ \psi_2 &= \frac{\alpha}{\sqrt{2}}\left(2\xi^2 - 1\right)e^{-\xi^2/2}\end{aligned}$$

where $\alpha = 1/(x_0^{1/2}\pi^{1/4})$, $x_0^2 = \hbar/m\omega$, $\xi = x/x_0$.

The free particle

The free particle is characterized by

$$V(x) = 0 \qquad \forall x \in \Omega$$

Recall that the time-independent equation can be put into the form

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

where $k = \sqrt{2mE}/\hbar$.

The solution has the form

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

which can be converted in terms of sines and cosines.

The general solution to the time-dependent equation is

$$\Psi(x,t) = Ae^{ik\left(x-\frac{\hbar k}{2m}t\right)} + Be^{-ik\left(x+\frac{\hbar k}{2m}t\right)}$$

Functions of the form $f(x \pm vt)$ are waves travelling to the $\mp x$ direction with speed v.

Every point in the wave travels with the same speed v, and the shape of wave remains the same as it travels.

Letting $k = \pm\sqrt{2mE}/\hbar$, we can write

$$\Psi_k = Ae^{ik\left(x-\frac{\hbar k}{2m}t\right)} = Ae^{i\left(kx-\frac{\hbar k^2}{2m}t\right)}$$

and $\pm k$ corresponds to waves traveling in $\pm x$ direction (called **plane wave solutions**).

We can expand

$$e^{ik\left(x-\frac{\hbar k}{2m}t\right)} = e^{ikx}e^{-ik\frac{\hbar k}{2m}t}$$

Recall that

$$e^{i\theta} = e^{i\theta+i2\pi n} = e^{i\theta}e^{i2\pi n} = e^{i\theta}$$

Thus

$$e^{ikx} = e^{ikx+i2\pi n} = e^{ikx}e^{i2\pi n}$$

this means for every multiple of $2\pi/k$, the wave repeats it self. This means that Ψ has wave length

$$\lambda = 2\pi/|k|$$

This is analogous to the classical mechanical wave equation:

$$y(x,t) = A\sin(kx - \omega t + \phi)$$

where k is the wave number, such that $k = 2\pi/\lambda$, $\omega = 2\pi/T$, and ϕ is the phase.

- k plays same the role of the wave number in a classical plane wave
- $\hbar k^2/2m$ plays the role of angular frequency, $\hbar k^2/2m = 2\pi f$

De Broglie wavelength: The plane wave solutions have a well-defined momentum,

$$p = \frac{2\pi\hbar}{\lambda} = \hbar k$$

The waves also have well-defined energies. But as we will see, our solutions are not normalizable.

Eigenstates of the momentum operator: are wave functions with a definite momentum:

$$\hat{p}\Psi_k = \hbar k\Psi_k$$

A superposition of states are not necessarily eigenstates.

Since $v = \lambda f$,

$$v_{\text{quantum}} = \frac{2\pi}{k}\frac{\hbar k^2}{4\pi m} = \frac{\hbar|k|}{2m} = \sqrt{\frac{E}{2m}}$$

Recall that classical kinetic energy is

$$E = \frac{1}{2}mv^2 \implies v = \sqrt{\frac{2E}{m}}$$

The wave function travels half as fast as the particle it represents.

The separable solution (plane wave solution) to the Schrödinger equation is not normalizable.

$$\int_{-\infty}^{\infty}\Psi_k^*\Psi_k\,dx = |A|^2\int_{-\infty}^{\infty}dx = |A|^2(\infty)$$

- A free particle cannot exist in a stationary state
- Plane waves cannot represent free particles, they have both definite momentum and energy, which violates the uncertainty principle

Instead of summing over and index, we integrate over k (hence a range of energies and speeds), to find a general solution to the time-dependent equation. This is the wave packet solution:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i\left(kx-\frac{\hbar k^2}{2m}t\right)}\,dk$$

The wave packet solution is a superposition of sinusoidal functions with amplitude modulated by $\phi(k)$. ($\phi(k)/\sqrt{2\pi}\,dk$ plays the role of c_n.)

To find $\phi(k)$, we use the initial condition. The equation must satisfy our initial condition:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{ikx}\,dk$$

We recognize that this is the INVCTFT of $\phi(k)$. To find $\phi(k)$, we find the CTFT of $\Psi(x,0)$:

$$\phi(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\Psi(x,0)e^{-ikx}\,dx$$

Parseval's Theorem: the normalized wave function in real space remain normalized in momentum space

$$\int_{-\infty}^{\infty}|\Psi(x,0)|^2\,dx = \int_{-\infty}^{\infty}|g(k)|^2\,dk$$

We are transforming between position and k-space. Since $p = \hbar k$, we can also say that we can transforming between momentum and position space.

Also, this definition of CTFT has a different normalization constant than what we encountered in other courses.

There is another interpretation to this normalization. We are normalizing to the delta function:

$$\int\Psi_p^*(x)\Psi_{p'}(x)\,dx = \delta(p-p')$$

Interpretation of momentum wave function: $\phi(k)\,dk$ is the probability to find a particle with momentum between $\hbar k$ and $\hbar(k+dk)$.

Instead of transforming into k-space, we can transform into momentum-space instead.

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\phi(p)e^{ipx/\hbar}\,dp$$

and

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\phi(x)e^{-ipx/\hbar}\,dx$$

Since if

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\delta(x)e^{-ipx/\hbar}\,dx = \frac{1}{\sqrt{2\pi\hbar}}$$

we have

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}\,dp = \delta(x)$$

A wave packet is made of many individual ripples, each with its own **phase velocity**, but altogether contributes to the **group velocity** of the wave packet.

Consider the wave packet solution where $\phi(k)$ is sharply peaked about some value k_0. About k_0, we can write

$$\omega(k) \approx \omega(k_0) + \omega'(k_0)(k-k_0) + O(k^2)$$

Substitution into the solution, and let $k - k_0 = s$,

$$\begin{aligned}\Psi(x,t) &\approx \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k_0+s)e^{i\left((k_0+s)x-(\omega_0+\omega_0's)t\right)}\,ds \\ &= \frac{1}{\sqrt{2\pi}}e^{i(k_0x-\omega_0t)}\int_{-\infty}^{\infty}\phi(k_0+s)e^{is\left(x-\omega_0't\right)}\,dk\end{aligned}$$

The factor infront of the integral represents a single moving wave at speed ω_0/k_0, where as the integral is a collection of waves all moving at ω_0'.

About some value k_0, the group velocity is

$$v_{\text{group}} = \frac{d}{dk}\omega$$

In our case, the **dispersion relation** is $\hbar k^2/2m$, so the group velocity is $\hbar k/m$, which is the velocity of the classical particle.

There is nothing wrong with a broad composition of k values in the wave packet, but group velocity loses its meaning since the wave packet changes it's shape rapidly.

$\omega(k)$ is called a dispersion relation since the frequency of the wave depends on the wave number, or momentum of the wave. This causes means that waves at different frequencies do not travel at same speeds, and the wave "disperses".

The delta function potential

Bound and scattering states

We have seen two types of general solutions to the Schrödinger equation.

1. Sum of eigenstates over an index: infinite well
2. Integral of eigenstates over wave number k: free particle

In classical mechanics, we have the distinction of bound and scattering states.

We have a bound state when the energy of the particle is less than that of the potential, and the particle cannot escape.

In a scattering state, the particle energy is more than that of the potential.

Scattering and bound states:

$$\begin{cases} E < V(-\infty) \wedge V(+\infty) & \text{bound} \\ E > V(-\infty) \wedge V(+\infty) & \text{scattering} \end{cases}$$

The delta function potential support both bound and scattering states.

- Bound states are differentiated by an discrete index
- Scattering states are differentiated by a continuous variable

If V goes to zero for $x \to \infty$, then E alone determines whether we have a bound or scattering state.

So the free particle potential ($V = 0$ every where) result in only scattering states, and the square well result in only bound states.

Recall the general rule, that we require $E > V_{\min}$, but this does not apply as the scattering states are not normalizable in the way we do for bound states.

The delta-function well

The characteristic potential is:

$$V(x) = -\alpha\delta(x),$$

where $\alpha \in \mathbb{R}$, and

$$\delta(x) = \begin{cases} 0 & x \neq 0 \\ \infty & x = 0 \end{cases}$$

- The delta function has units [1/Length]
- α has units [Energy/Length]

Bound states ($E < 0$): When $x \neq 0$, the time independent Schrödinger equation reads

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$$

If we divide both sides by $-\hbar^2/2m$.Since $E < 0$, κ be real and positive:

$$\kappa = \frac{\sqrt{-2mE}}{\hbar}$$

Our time independent eqution becomes:

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

The general solution to

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

is

$$\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}$$

Boundary conditions: To determine the constants, we require the following conditions:

1. ψ is symmetric
2. ψ is continuous
3. $d\psi/dx$ is continuous except where V is infinite
4. $\psi \to 0$ when $x \to \pm\infty$

The general solution to the time independent equation is

$$\psi(x) = \begin{cases} Be^{-\kappa x} & x \geq 0 \\ Be^{\kappa x} & x \leq 0 \end{cases}$$

Discontinuity: The delta function adds a discontinuity to $d\psi/dx$. It modifies the boundary condition at $x = 0$ from $\Delta(d\psi/dx) = 0$ to :

$$\lim_{\epsilon\to 0}\left(\frac{d\psi}{dx}(\epsilon) - \frac{d\psi}{dx}(-\epsilon)\right) = \frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon} V\psi\, dx$$

If we integrate the time independent equation over $[-\epsilon, \epsilon]$,

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon}\frac{d^2\psi}{dx^2}\,dx + \int_{-\epsilon}^{\epsilon} V\psi\, dx = E\int_{-\epsilon}^{\epsilon}\psi\, dx$$

In the limit as $\epsilon \to 0$, the leftmost term becomes

$$-\frac{\hbar^2}{2m}\left(\frac{d\psi}{dx}(\epsilon) - \frac{d\psi}{dx}(-\epsilon)\right)$$

The rightmost term must be zero. Rearranging,

$$\left(\frac{d\psi}{dx}(\epsilon) - \frac{d\psi}{dx}(-\epsilon)\right) = \frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon} V\psi\, dx$$

When V is finite, the right hand side is zero. Since the difference between the derivative of ψ at two infinitely close neighbouring points is zero, we conclude that ψ is continuous.

For $V = -\alpha\delta(x)$, we have

$$\Delta\left(\frac{d\psi}{dx}\right) = \frac{-2m\alpha}{\hbar^2}\psi(0)$$

This leads to

$$\kappa = \frac{m\alpha}{\hbar^2}$$

which result in

$$E = \frac{-\hbar^2\kappa^2}{2m}$$

Fact: The delta function potential only admits a single energy level

Normalizing ψ gives $B = \sqrt{\kappa}$, and the general solution becomes

$$\psi(x) = \frac{\sqrt{m\alpha}}{\hbar}\exp\left(\frac{-m\alpha|x|}{\hbar^2}\right)$$

Scattering states ($E > 0$): Since $E < 0$, we define k

$$k = \frac{\sqrt{2mE}}{\hbar}$$

and the time independent equation is

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

The general solution are is similar to what we found for the free particle.

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Fe^{ikx} + Ge^{ikx} & x > 0 \end{cases}$$

Applying

1. Continuity at 0 gives:

$$A + B = F + G$$

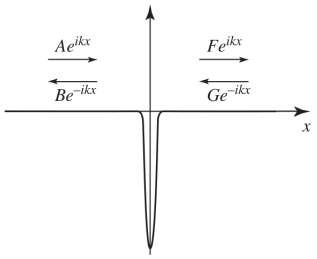
2. Discontinuity condition at $x = 0$:

$$ik(F - G - A + B) = \frac{-2m\alpha}{\hbar^2}(A + B)$$

defining $\beta = \frac{m\alpha}{\hbar^2 k}$, we can write

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta)$$

When we consider the time dependent term, from the free particle case we know that our solution resemble plane waves.



Interpreting A, B, G, F as amplitudes:

- A: wave coming from the left
- G: wave coming from the right
- B: wave return to the left
- F wave travelling off to the right

we can set any one of A, B, G, F to zero, and interpret the remain coefficients as terms describing an incident wave, reflected wave, and trasmitted wave across the delta potential.

$$G = 0$$

let's us say that

- A: incident wave
- F: transmitted wave
- B: reflected wave

We can arrange

$$A + B = F + G$$

and

$$F - G = A(1 + 2i\beta) - B(1 - 2i\beta)$$

to write B and F in terms of A.

$$B = \frac{i\beta}{1 - i\beta} A$$

and

$$F = \frac{1}{1 - i\beta} A$$

Reflection coefficient: The relative probability that an incident particle will be reflected back:

$$R = \left| \frac{J_{\text{reflected}}}{J_{\text{incident}}} \right|$$

Transmission coefficient: The relative probability that a particle will travel through the potential:

$$T = \left| \frac{J_{\text{transmitted}}}{J_{\text{incident}}} \right|$$

In our case:

$$R = \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2} \qquad \beta = \frac{m\alpha}{\hbar^2 k}$$

$$T = \frac{|F|^2}{|A|^2} = \frac{1}{1 + \beta^2}$$

- $R + T = 1$
- R and T are independent of α (sign of V), so a quantum particle is just as likely to pass through a barrier as to cross over a well

We could have written the out-going amplitudes, B and F, as a function of the in-going amplitudes, A and G:

$$B = S_{11}A + S_{12}G$$
$$F = S_{21}A + S_{22}G$$

We define the **S-matrix**, or **Scattering matrix** as the matrix that relates B, F to A, G:

$$\begin{bmatrix} B \\ F \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} A \\ G \end{bmatrix}$$

In our case,

$$\underline{S} = \frac{1}{1 - i\beta} \begin{bmatrix} i\beta & 1 \\ 1 & i\beta \end{bmatrix}$$

$\underline{S}$ is unitary (but not hermitian):

$$\underline{S}^\dagger \underline{S} = \underline{I}$$

Notice that each term in ψ, if we interpret it as a superposition of left and right travelling waves, is not normalizable.

We know how to deal with it, but integrating over k, and thereby a range of energies, as we did for the free particle.

Only when we get a wave packet is our solution normalizable.

"R and T should be interpreted as the approximate relfection and transmission probabilities for particles with energies in the vicinity of E"

The fact that T is non zero, even for an infinitely deep/tall delta well/barrier, is the phenomenon of quantum tunnelling.

Triple delta potential

Has the characteristic potential

$$V(x) = -\alpha\delta(x - a) - \alpha\delta(x) - \alpha\delta(x + a)$$

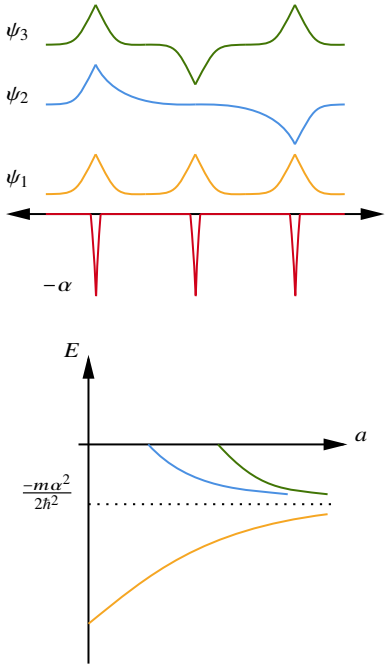
- V is symmetric, so the eigenstate be even, odd, even,...
- For small a, $V(x, a = 0) = -3\alpha\delta(x)$; single bound state with energy

$$E = \frac{-m(3\alpha)^2}{2\hbar^2}$$

- For large a, there will be three degenerate bound states, with the same energy

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

- Starting from 0, as $a \to \infty$, the number of bound states goes from 1 to 3 distinct bound states, to 3 degenerate bound states



Dirac Delta

We can define it in two ways:

1. $\delta(x)$ as a limit of a sequence fo functions peaked at $x = 0$. In the limit, the peak rises and the width shrinks in such a way that the area under the curve remains 1.

   $$\delta(x) = \lim_{\epsilon \to 0} \delta_\epsilon(x)$$

   where

   $$\delta_e(x) = \begin{cases} \frac{1}{\epsilon} & -\epsilon/2 < x < \epsilon/2 \\ 0 & \text{otherwise} \end{cases}$$

   Similarly,

   $$\delta(x) = \lim_{\epsilon \to 0} \frac{1}{\pi} \frac{\epsilon}{\epsilon^2 + x^2}$$

   (In the limit as ϵ goes to zero, but never zero.)
2. For some $\epsilon > 0$, $\epsilon \in \mathbb{R}$,

   $$\int_{a-\epsilon}^{a+\epsilon} f(x)\,\delta(x - a)\,dx = f(a)$$

Equivalence

Expressions $D_1(x), D_2(x)$ involving the delta function are equal if

$$\int_{-\infty}^{\infty} f(x) D_1(x)\, dx = \int_{-\infty}^{\infty} f(x) D_2(x)\, dx,$$

for all $f(x)$.

Scaling

$$\delta(kx) = \delta(x)/|k|$$

So $\delta(-x) = \delta(x)$.

Three dimensions

$$\delta^3(\underline{r}) = \prod_{i=1}^{3} \delta(x_i)$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(\underline{r})\,\delta^3(\underline{r}-\underline{a})\, dV = f(\underline{a})$$

Differentiation

By repeated applications of integration by parts, we can show that

$$\int_{-\infty}^{\infty} f(x)\frac{d^n}{dx^n}\delta(x-a)\, dx = (-1)^n \frac{d^n f}{dx^n}(a)$$

We can also think of $\delta(x)$ as

$$\delta(x) = \frac{d}{dx}\theta(x)$$

where $\theta(x)$ is the step function.

Formalism

Hilbert Space

Quantum theory is based on wave functions and operator.

Wave functions: represent the state of a system

Operators: represent observables.

Operators act on wave functions as linear transformations.

The space of all square integrable functions defined over a domain Ω, is an instance of a more general abstract vector space, called a **Hilbert space**. L^2 is only an example of a Hilbert space.

$$f \in L^2(\Omega) \iff \int_\Omega |f|^2\, dx < 0$$

Fact: All wave functions live in L^2.

The inner product of two functions, $f(x), g(x) \in L^2(a,b)$ is given by:

$$\langle f|g\rangle = \int_a^b f^*(x) g(x)\, dx$$

When $f, g \in L^2$, their inner product must exist. This comes from the integral Schwarz inequality:

$$\left|\int_a^b f^*(x) g(x)\, dx\right| \le \sqrt{\int_a^b |f(x)|^2\, dx \int_a^b |g(x)|^2\, dx}$$

L^2 inner product:

- Non-commutative: $\langle g|f\rangle = \langle f|g\rangle^*$
- $\langle f|f\rangle \ge 0$; $\langle f|f\rangle = 0 \iff f = 0$

Schwarz inequality: $|\langle f|g\rangle|^2 \le \langle f|f\rangle\langle g|g\rangle$

In linear algebra, we are more familiar with the following statement:

$$|\underline{v}\cdot\underline{w}| \le \|\underline{v}\|\|\underline{w}\|$$

A set of functions, V, is:

- orthonormal when any $f_m, f_n \in V$:
$$\langle f_m|f_n\rangle = \delta_{mn}$$
- complete when any other L^2 function $g(x)$ can be expanded in terms of functions of V:
$$g(x) = \sum_{n=1}^{\infty} c_n f_n(x)$$
- When V is an orthonormal set,
$$c_n = \langle f_n|g\rangle$$

Observables

Observables: Hermitian operators represent observables, since the expectation value of hermitian operators is real.

The expectation value of an observables is can be written as

$$\langle Q\rangle = \langle\Psi|\hat{Q}\Psi\rangle = \langle Q\rangle^*$$

The expectation value is real, so it is equal to its complex conjugate.

Recall the adjoint of $\hat{Q}$, $\hat{Q}^\dagger$ has the property that

$$\langle f|\hat{Q}g\rangle = \left\langle \hat{Q}^\dagger f\middle| g\right\rangle$$

All hermitian (self-adjoint) operators satisfy:

- $\langle f|\hat{Q}g\rangle = \langle \hat{Q}f|g\rangle$
- $\hat{Q} = \hat{Q}^\dagger$

In Dirac notation:

$$\langle f|\hat{Q}|g\rangle = \langle \hat{Q}f|g\rangle = \langle f|\hat{Q}^\dagger|g\rangle$$

An operator that is hermitian on the real line may not be hermitian on a finite interval.

If we know $\hat{Q}|\psi\rangle$, then

$$\langle\psi|\hat{Q}^2|\psi\rangle = \left(\hat{Q}|\psi\rangle\right)^\dagger \hat{Q}|\psi\rangle$$

Determinate states

Determinate state: A determinate state, Ψ, of an observable, Q, is such that every measurement of Q on Ψ returns the same value. Ψ is an eigenstate of Q

For example, a single eigenstate of the Hamiltonian is a determinate state of energy. Every measurement of energy on a system of that eigenstate will return a single energy value.

Since σ_Q^2 must be zero for determinate states:

$$\sigma_Q^2 = \left\langle (Q - \langle Q\rangle)^2\right\rangle = 0$$

This is the expectation value of the deviation squared:

$$\left\langle \Psi\middle|(\hat{Q} - \langle Q\rangle)^2\Psi\right\rangle$$

Since $\hat{Q}$ is hermitian, so too is $\hat{Q} - \langle Q\rangle$. This lets us move a factor of deviation over:

$$\left\langle (\hat{Q} - \langle Q\rangle)\Psi\middle|(\hat{Q} - \langle Q\rangle)\Psi\right\rangle = 0$$

The only vector whose inner product with it self vanishes is $|0\rangle$. We can conclude:

- The set of all eigenvalues of a operator is the **spectrum** of the operator
- The spectrum is degenerate when two linearly independen eigenfunctions share the same eigenvalue

Eigenfunctions of a hermitian operator

When the spectrum is discrete:

- Eigenfunctions are in Hilbert space (thus normalizable)
- They are physically realizable states

Whent the spectrum is continuous:

- Eigenfunctions are not normalizable
- A superposition of eigenfunctions may be normalizable
- On their own, they are not physically realizable

Discrete spectra

Fact: Eigenvalues of normalizable eigenfunctions of a Hermitian operator are real.

Fact: Eigenfunctions of distinct eigenvalues are orthogonal.

Its possible to use Gram-Schmidt to construct a orthonormal basis of eigenfunctions.

In a finite dimensional vector space, eigenvectors of a Hermitian matrix form an eigenbasis.

Complete eigenbasis: Eigenfunctions of an observable operator are complete: Any function (in Hilbert space) can be expressed as a linear combination of them.

Continuous Spectra

Eigenvalues of the hermitian operators are labeled by a continuous variable.

- Eigenfunctions are not normalizable, ($\notin H(\Omega)$)
- Eigenfunctions with real eigenvalues are **Dirac orthonormalizable** and complete

Momentum operator: Consider the eigenvalue problem involving the 1-D momentum operator.

$$-i\hbar\frac{d}{dx}f_p(x) = pf_p(x)$$

This is a 1-D separable ODE we can solve:

$$f_p(x) = Ae^{ipx/\hbar}$$

$f_p(x) \notin H(\Omega)$, but if we only consider eigenvalues $p \in \mathbb{R}$, then

$$\langle f_{p'}|f_p\rangle = |A|^2\int_{-\infty}^{\infty} e^{i(p-p')x/\hbar}\,dx$$

By a fourier transform identity, and letting $A = 1/\sqrt{2\pi\hbar}$ we arrive at

$$\langle f_{p'}|f_p\rangle = \delta(p-p')$$

The eigenfunctions of the momentum operator

$$f_p = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}$$

are sinusoidal, with wavelength equal to the de Broglie wavelength, $2\pi\hbar/p$.

Position operator: The eigenvalue problem:

$$\hat{x}g_y(x) = xg_y(x) = yg_y(x)$$

The only function such that multiplying by a variable is the same as multiplication a constant y is the Dirac delta function. When $g_{y'} = A\delta(x-y')$, $A = 1$, we can check that

$$\langle g_{y'}|g_y\rangle = \delta(y-y')$$

Generalized statistical interpretation

Generalized statiscal interpretation: Consider a particle in a general state $\Psi(x,t)$. A measurement of an observable $Q(x,p)$ will return an eigenvalue of the hermitian operator

$$\hat{Q}(\hat{x},\hat{p})$$

Recall that when the spectrum is discrete, then the probability of getting eigenvalue q_n associated with the orthonormal eigenfunction $f_n(x)$ is

$$|c_n|^2 \qquad c_n = \langle f_n|\Psi\rangle$$

When the spectrum is continuous, the probility of getting $q(z)$ associated with the Dirac-orthonormal eigenfunction $f_z(x)$, within dz, is

$$|c(z)|^2\,dz \qquad c(z) = \langle f_z|\Psi\rangle$$

Collapse: The wave function collapses into the eigenstate upon measurement.

The uncertainty principle

Proof of the generalized uncertainty principle

Consider two hermitian operators, $\hat{A}$ and $\hat{B}$. Let us define the variances:

$$\Delta\hat{A} = \hat{A} - \langle A\rangle \qquad \Delta\hat{B} = \hat{B} - \langle B\rangle$$

and

$$f = \Delta\hat{A}\Psi \qquad g = \Delta\hat{B}\Psi$$

Since $\hat{A}$ and $\hat{B}$ are hermitian, we have

$$\sigma_A^2 = \langle f|f\rangle \qquad \sigma_B^2 = \langle g|g\rangle$$

The product of σ_A^2 and σ_B^2 is the upper bound of $|\langle f|g\rangle|^2$, by the Schwarz inequality.:

$$\langle f|f\rangle\langle g|g\rangle \geq |\langle f|g\rangle|^2$$

Since $|z|^2 \geq \mathrm{Im}(z)^2$ for all $z \in \mathbb{C}$, and invoking

$$\mathrm{Im}(z) = \frac{1}{2i}(z-z^*)$$

we have

$$|\langle f|g\rangle|^2 \geq \left(\frac{\langle f|g\rangle - \langle g|f\rangle}{2i}\right)^2$$

Let's consider the terms $\langle f|g\rangle$ and $\langle g|f\rangle$. Since $\Delta\hat{A}$ and $\hat{B}$ are hermitian, we can write

$$\langle f|g\rangle = \langle\Psi|\Delta\hat{A}\Delta\hat{B}\Psi\rangle$$

We can expand $\Delta\hat{A}\Delta\hat{B}$:

$$\hat{A}\hat{B} - \hat{A}\langle B\rangle - \langle A\rangle\hat{B} + \langle A\rangle\langle A\rangle$$

This lets us break up $\langle\Psi|\Delta\hat{A}\Delta\hat{B}\Psi\rangle$ into a sum of inner products.

$$\langle\Psi|\Delta\hat{A}\Delta\hat{B}\Psi\rangle = \langle\Psi|\hat{A}\hat{B}\Psi\rangle - \langle B\rangle\langle\Psi|\hat{A}\Psi\rangle - \langle A\rangle\langle\Psi|\hat{B}\Psi\rangle + \langle A\rangle\langle B\rangle\langle\Psi|\Psi\rangle$$

We can show that

$$\langle f|g\rangle = \langle\hat{A}\hat{B}\rangle - \langle A\rangle\langle B\rangle$$
$$\langle g|f\rangle = \langle\hat{B}\hat{A}\rangle - \langle A\rangle\langle B\rangle$$

Then,

$$\langle f|g\rangle - \langle g|f\rangle = \langle\hat{A}\hat{B}\rangle - \langle\hat{B}\hat{A}\rangle = \langle[\hat{A},\hat{B}]\rangle$$

Generalized uncertainty principle: Given two hermitian operators, $\hat{A}$ and $\hat{B}$, we have

$$\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle\right)^2$$

When the operators commute, $\sigma_A\sigma_B \geq 0$

The commutator of two hermitian operators is **anti-hermitian**. And operator is anti-hermitian when

$$\hat{Q}^\dagger = -\hat{Q}$$

Compatible: two commuting hermitian operators are **compatible**. Compatible observables:

- share a complete set of eigenfunctions
- we can measure both observables at the same time

Incompatible: two non-commuting hermitian operators are **incompatible**. Incompatible observables:

- do not share a complete set of eigenfunctions
- measuring one observable will render the measurement of other observable obsolete

For example, measuring the position of the particle collapses the wave function to an eigenstate of the position operator (a delta function). The Fourier transform into momentum space will be a complex exponential.

Measuring the momentum of the particle collapses the wave function into an eigenstate of the momentum operator (a complex exponential). And its position will be undefined.

The energy-time uncertainty principle

In non-relativistic quantum theory, time is considered to be an independent variable, of which dynamic quantities are functions. Consider the time derivative of the expectation value some observable, $Q(x,p,t)$.

$$\frac{d}{dt}\langle\hat{Q}\rangle = \left(\frac{\partial}{\partial t}\langle\Psi|\right)\hat{Q}|\Psi\rangle + \langle\Psi|\left(\frac{\partial}{\partial t}\hat{Q}\right)|\Psi\rangle + \langle\Psi|\hat{Q}\left(\frac{\partial}{\partial t}|\Psi\rangle\right)$$

Invoking the time dependent equation:

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

We can substitute time derivatives of the wave function for the Hamiltonian acting on the wave function.

$$\frac{d}{dt}\langle\hat{Q}\rangle = \frac{-1}{i\hbar}\hat{H}\langle\Psi|\hat{Q}|\Psi\rangle + \langle\Psi|\left(\frac{\partial}{\partial t}\hat{Q}\right)|\Psi\rangle + \frac{1}{i\hbar}\langle\Psi|\hat{Q}\hat{H}|\Psi\rangle$$

Since

$$\hat{H}\langle\Psi| = \langle\Psi|\hat{H}^\dagger = \langle\Psi|\hat{H}$$

we arrive at

Generalized Ehrenfest theorem: For a hermitian operator $\hat{Q}$,

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

- When $\hat{Q}$ has no explicit time dependence, $\langle \partial \hat{Q}/\partial t \rangle = 0$
- If $\langle \partial \hat{Q}/\partial t \rangle = 0$, and $\hat{Q}$ commutes with the Hamiltonian, its expectation value does not change with time
- An observable whose expectation value is time-independent is said to be **conserved**

Consider the generalized uncertainty principle applied to the Hamiltonian, and a hermitian operator with no explicit time-dependence.

$$\sigma_H^2 \sigma_Q^2 \geq \frac{1}{4} \langle [\hat{H}, \hat{Q}] \rangle^2 = \frac{1}{4}\hbar^2 \left(\frac{d}{dt} \langle \hat{Q} \rangle \right)^2$$

Energy-time uncertainty principle:

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

where $\Delta E = \sigma_H$, is the standard deviation of Hamiltonian, and let's define

$$\Delta t = \frac{\sigma_Q}{|d\langle \hat{Q} \rangle / dt|}$$

Δt is the time required for $\langle \hat{Q} \rangle$ to change by one standard deviation.

- Δt is the amount of time needed for the system to change substantially
- Δt depends on the operator $\hat{Q}$
- If $\Delta E \ll \hbar/(2\Delta t)$, then Δt will be large
- If expectation value of the observable changes quickly, then there will be a large uncertainty in the energy

Virial theorem: For a stationary state:

$$2\langle T \rangle = \langle \underline{r} \cdot \underline{\nabla} V \rangle$$

Expectation value of operators that have no explicit time dependence for a stationary state is time independent. We prove the general case by using the generalized Ehrenfest theorem. We show that

$$\frac{d}{dt} \left\langle \underline{r} \cdot \underline{p} \right\rangle = 2\langle T \rangle - \langle \underline{r} \cdot \underline{\nabla} V \rangle = 0$$

We first compute $\left[\hat{H}, \underline{r} \cdot \underline{p}\right]$.

$$\begin{aligned} \left[\hat{H}, \underline{r} \cdot \underline{p}\right] &= \sum_{i=1}^{3} \left[\hat{H}, r_i p_i\right] \\ &= \sum_{i=1}^{3} \left(\left[\hat{H}, r_i\right] p_i + x \left[\hat{H}, p_i\right] \right) \end{aligned}$$

Where

$$\begin{aligned} \left[\hat{H}, r_i\right] &= \frac{1}{2m} \left[p^2, r_i\right] \\ &= \frac{1}{2m} \sum_{j=1}^{3} \left[p_j^2, r_i\right] \\ &= \frac{1}{2m} \sum_{j=1}^{3} \left(p_j \left[p_j, r_i\right] + \left[p_j, r_i\right] p_j \right) \\ &= \frac{-i\hbar p_i}{m} \end{aligned}$$

and

$$\left[\hat{H}, p_i\right] = [V, p_i] = i\hbar \frac{\partial V}{\partial r_i}$$

Vectors and operators

Bases in Hilbert space

- The physical state of a system is represented by a state vector that lives in Hilbert space
- We can choose the basis we want to represent them in
- Operators are transformations on Hilbert space - they transform once vector into another
- While $\Psi(x,t)$ represents a quantum state in the **position basis**, $\Phi(x,t)$ is an equal representatopm in **momentum basis**

Let $|x\rangle$ denote eigenfunctions of $\hat{x}$ with eigenvalue x, $|p\rangle$ be eigenfunctions of $\hat{p}$ with eigenvalue p, and $|S(t)\rangle$ be a general quantum state. Then

$$\Psi(x,t) = \langle x | S(t) \rangle$$
$$\Phi(p,t) = \langle p | S(t) \rangle$$

We do not specify the form of $\hat{x}$ or $\hat{p}$. Since their representations also depend on what basis we express them in.

A vector can be expanded in terms of an orthonormal basis:

$$|\alpha\rangle = \sum_n a_n |e_n\rangle \iff a_n = \langle e_n | \alpha \rangle$$

An operator in a particular basis are represented by their **matrix element** (often an infinite number of them),

$$\langle e_m | \hat{Q} | e_n \rangle = Q_{mn}$$

Consider the following transformation:

$$|\beta\rangle = \hat{Q} |\alpha\rangle$$

In a particular basis, we have

$$\sum_n b_n |e_n\rangle = \sum_n a_n \hat{Q} |e_n\rangle$$

Taking the inner product with $|e_m\rangle$ with both sides:

$$\sum_n b_n \langle e_m | e_n \rangle = \sum_n a_n \langle e_m | \hat{Q} | e_n \rangle$$

Since we have an orthonormal basis,

$$b_m = \sum_n a_n Q_{mn}$$

Operators have different representations in different bases:

$$\hat{x} \to \begin{cases} x & \text{position space} \\ i\hbar \partial/\partial p & \text{momentum space} \end{cases}$$

$$\hat{p} \to \begin{cases} -i\hbar \partial/\partial x & \text{position space} \\ p & \text{momentum space} \end{cases}$$

Dirac notation

Ket: are elements of a Hilbert vector space H, denoted by $|a\rangle$; a is merely a label.

A **ket** analogous to a column vector:

$$|\alpha\rangle = \begin{bmatrix} a_1 \\ a_2 \\ \dots \\ a_n \end{bmatrix}$$

Bra: belongs to the dual Hilbert vector space, denoted by $\langle a|$; a is merely a label.

Riesz representation theorem: For every ket vector there exists a unique bra, and vice versa

$$|a\rangle \leftrightarrow \langle a|$$
$$\alpha |a\rangle + \beta |b\rangle \leftrightarrow \alpha^* \langle a| + \beta^* \langle b|$$

A **bra** is

- returns a complex number, given a vector
- an instruction to integrate (in coordinate notation)

$$\langle f | = \int f^* (\dots)\, dx$$

- analogous to row vectors:

$$\langle \beta | = \begin{bmatrix} b_1^* & b_2^* & \dots & b_n^* \end{bmatrix}$$

Bra-ket: is the Dirac notation for the inner product. Between two kets $|a\rangle$, $|b\rangle$, the braket is $\langle a|b\rangle$. The antisymmetry property implies that, for a hermitian operator, $\hat{Q}$,

$$\langle f | \hat{Q} | g \rangle = \left(\langle g | \hat{Q} | f \rangle \right)^\dagger = \langle f | \hat{Q}^\dagger | g \rangle$$

Schwarz inequality: For any two states $|a\rangle, |b\rangle$ of the Hilbert space, we can show

$$|\langle a|b\rangle|^2 \leq \langle a|a\rangle \langle b|b\rangle$$

If $|a\rangle = \alpha |b\rangle$ for some scalar, then

$$|\langle a|b\rangle|^2 = \langle a|a\rangle \langle b|b\rangle$$

Triangle inequality: For any two states $|a\rangle, |b\rangle$,

$$\sqrt{\langle a+b|a+b\rangle} \leq \sqrt{\langle a|a\rangle} + \sqrt{\langle b|b\rangle}$$

Adjoint

For every ket, there is a corresponding bra; for some coefficient a:

$$\langle aV| = \langle V|\, a^* \leftrightarrow a\,|V\rangle = |aV\rangle$$

In the same manner, for an operator Ω:

$$\langle \Omega V| = \langle V|\,\Omega^\dagger \leftrightarrow |\Omega V\rangle = \Omega\,|V\rangle$$

Recall the matrix that projects a vector $\underline{x}$ onto a vector $\underline{u}$ is given by

$$\underline{\underline{P}} = \frac{\underline{u}\cdot\underline{u}^\intercal}{\|\underline{u}\|^2}$$

where $\underline{u}\cdot\underline{u}^\intercal$ returns a matrix, and is called an **outer product**.

Projection operator: for a normalized ket-vector: $|\alpha\rangle$, the operator

$$\hat{P} = |\alpha\rangle\langle\alpha|$$

projects another ket-vector onto the 1-D subspace spanned by $|\alpha\rangle$.

Two states $|a\rangle, |b\rangle$ are orthogonal if

$$\langle a|b\rangle = 0$$

Completeness is possible only if the eigenfunctions for a complete basis that spans the space. This basis can always be orthonormalized. So an alternative statement of completeness is that

$$\sum |e_n\rangle\langle e_n| = \mathbb{I}$$

or when the functions are Dirac-orthonormal,

$$\int |e_z\rangle\langle e_z|\, dz = \mathbb{I}$$

- $\mathbb{I} \neq 1$. They are the result of different operations.

Forbidden quantities: if $|a\rangle, |b\rangle$ belong to the same Hilbert space, then products of the type: $|a\rangle\,|b\rangle$, or $\langle a|\,\langle b|$ are forbidden. They have no meaning **in general**.

Changing bases in Dirac notation

Let $|x\rangle$, $|p\rangle$, $|n\rangle$ be eigenstates of the position, momentum, and energy (discrete) operator.

The eigenstates are orthonormal, which means that

$$\begin{aligned}\mathbb{I} &= \int dx\, |x\rangle\langle x| \\ &= \int dp\, |p\rangle\langle p| \\ &= \sum |n\rangle\langle n|\end{aligned}$$

If we act on a general quantum state: $|\mathcal{S}(t)\rangle$

$$\begin{aligned}|\mathcal{S}(t)\rangle &= \mathbb{I}\,|\mathcal{S}(t)\rangle \\ &= \int dx\,|x\rangle\,\langle x|\mathcal{S}(t)\rangle & &= \int dx\,|x\rangle\,\Psi(x,t) \\ &= \int dp\,|p\rangle\,\langle p|\mathcal{S}(t)\rangle & &= \int dp\,|p\rangle\,\Phi(p,t) \\ &= \sum_n |n\rangle\,\langle n|\mathcal{S}(t)\rangle & &= \sum |n\rangle\, c_n(t)\end{aligned}$$

We see the components of $|\mathcal{S}(t)\rangle$ are expressed as the position-space, momentum-space, and "energy-space" wave functions, in their corresponding basis.

Quantum mechanics in three dimensions

The Schrödinger equation

In three dimensions, the classical Hamiltonian for a single particle is

$$H = \frac{p^2}{2m} + V$$

by substituting

$$p_i \to -i\hbar\frac{\partial}{\partial x_i}$$

we get

$$\hat{H} = \frac{-\hbar^2}{2m}\underline{\nabla}^2 + V$$

Schrödinger's equation:

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

- V and Ψ are now functions of $\underline{r} = (x, y, z)$

Position probability in 3D: the probability of finding the particle in the volume $d^3\underline{r}$ is:

$$|\Psi(\underline{r}, t)|^2 d^3\underline{r}$$

Normalization:

$$\int |\Psi|^2\, d^3\underline{r} = 1$$

As before, when V is time independent, we can apply separation of variables to find

$$\phi_n(t) = e^{iE_n t/\hbar}$$

and the time-independent equation:

$$\frac{-\hbar^2}{2m}\underline{\nabla}^2\psi + V\psi = E\psi$$

whose's solution are eigenstates of the Hamiltonian. The general solution to the time-dependent equation is a superposition of eigenstates:

$$\Psi(\underline{r}, t) = \sum c_n \psi_n(\underline{r}) e^{-iE_n t/\hbar}$$

Canonical commutation relations in 3-D: For $i, j = 1, 2, 3$:

$$\begin{aligned}[x_i, p_j] &= i\hbar\delta_{ij} \\ [x_i, x_j] &= 0 \\ [p_i, p_j] &= 0\end{aligned}$$

The fact that $[x_i, p_j]$ commutes only when $i \neq j$ is obvious. In 1-D, we already $[x, p] = i\hbar$. Nonetheless,

$$\begin{aligned}[x_i, p_j]\, f(x_1, x_3, x_2) &= -i\hbar x_i\frac{\partial}{\partial x_j}f + i\hbar\frac{\partial}{\partial x_j}(x_i f) \\ &= i\hbar f\,\frac{\partial x_i}{\partial x_j} \\ &= i\hbar f\,\delta_{ij}\end{aligned}$$

$[p_i, p_j]$ commutes come from the fact that partial derivatives commute for nice functions.

The 3D free particle

Is characterized by a zero potential everywhere. So there will only be scattering states. We look for solutions of the form:

$$\psi(x, y, z) = X(x)Y(x)Z(z)$$

The time-independent equation is

$$\frac{-\hbar^2}{2m}\underline{\nabla}^2 XYZ = EXYZ$$

Let's expand the Laplacian:

$$\underline{\nabla}^2\psi(x, y, z) = YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2}$$

We divide this result by XYZ, and substitute it back into our equation:

$$\frac{-\hbar^2}{2m}\left(\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right) = E$$

We have three terms that only depend on X, Y, Z respectively. This only makes sense if each term is a constant. So we arrive three equations:

$$\begin{aligned}\frac{-\hbar^2}{2m}\frac{\partial^2 X}{\partial x^2} &= E_x X \\ \frac{-\hbar^2}{2m}\frac{\partial^2 Y}{\partial y^2} &= E_y Y \\ \frac{-\hbar^2}{2m}\frac{\partial^2 Z}{\partial z^2} &= E_z Z\end{aligned}$$

where

$$E_x + E_y + E_z = E$$

Separation of variable leads to three 1D free particle equations. The general solution is given by the product of three plane wave solutions

$$\psi(x,y,z) = \frac{1}{(2\pi)^{3/2}} e^{ik_x x} e^{ik_y y} e^{ik_y y}$$
$$= \frac{1}{(2\pi)^{3/2}} e^{i\underline{k}\cdot\underline{r}}$$

where the components of the **wave vector** are given by

$$k_i^2 = \frac{2mE_i}{\hbar^2}$$

The energy of the particle is given by

$$E = \frac{\hbar^2}{2m} \|\underline{k}\|$$

The time evolution is

$$\Psi(\underline{r},t) = \frac{1}{(2\pi)^{3/2}} e^{i\underline{k}\cdot\underline{r}-\omega t}$$

where $\omega = E/\hbar$. Dirac orthonormality of free particle wave functions tells us

$$\left\langle \Psi_{\underline{k}'}(t) \middle| \Psi_{\underline{k}}(t) \right\rangle = \left\langle \psi_{\underline{k}'} \middle| \psi_{\underline{k}} \right\rangle = \delta(\underline{k} - \underline{k}')$$

The free particle can be represented by a wave superposition of plane waves with different wave vectors

$$\Psi(\underline{r},t) = \int \phi(\underline{k},t)\Psi_{\underline{k}}(\underline{r},t)\, d^3k$$

where $\phi(\underline{k},t)$ is the CTFT of $\Psi(\underline{r},t)$.

Spherical coordinates

Using the spherical Laplacian, we can write Schrödinger's equation using spherical coordinates.

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

Spherical separation of variables:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

$R(r)$ is the solution to the radial equation:

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

and $Y(\theta,\phi)$, **the angular wave function**, is the solution to the angular equation:

$$\frac{1}{Y}\left(\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}\right) = -\ell(\ell+1)$$

where $\ell(\ell+1)$ is the separation constant.

The angular equation

- The angular equation is independent of the central field.

We solve the angular equation by separation of variables:

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

Multiply both sides by $Y\sin^2(\theta)$, to find that

$$\sin(\theta)\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -\ell(\ell+1)\sin^2(\theta)Y$$

Substituting:

$$\sin(\theta)\frac{\partial}{\partial\theta}\left(\sin(\theta)\Phi\frac{\partial\Theta}{\partial\theta}\right) + \Theta\frac{\partial^2\Phi}{\partial\phi^2} = -\ell(\ell+1)\sin^2(\theta)\Phi\Theta$$

Divide both sides by $\Theta\Phi$:

$$\frac{1}{\Theta}\sin(\theta)\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -\ell(\ell+1)\sin^2(\theta)$$

Let the separation constant be m^2 (m is any complex number, not mass):

$$\frac{1}{\Theta}\sin(\theta)\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) + \ell(\ell+1)\sin^2(\theta) = m^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

The ϕ equation has solution:

$$\Phi(\phi) = e^{im\phi}$$

- Let m run from $(-\infty,\infty)$
- Absorb constant into $\Theta(\theta)$
- Require $\Phi(\phi+2\pi) = \Phi(\phi)$, this implies $m = 0, \pm1, \pm2, \ldots$

Fact: The Θ equation as solution

$$\Theta(\theta) = AP_\ell^m(\cos(\theta))$$

Where $P_\ell^m(x)$ is the **associated Legendre function**

The associated Legendre function:

$$P_\ell^m(x) = (-1)^m\left(1-x^2\right)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x)$$

The Legendre polynomials are given by the **Rodrigues formula**:

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell\left(x^2-1\right)^\ell \qquad \ell \geq 0$$

The first couple of Legendre polynomials are given by

$$P_1(x) = x$$
$$P_2(x) = \left(3x^2-1\right)/2$$
$$P_3(x) = \left(5x^3-3x\right)/2$$
$$P_4(x) = \left(35x^4-30x^2+3\right)/8$$
$$P_5(x) = \left(63x^5-70x^3+15x\right)/8$$

Properties of Legendre polynomials:

- $P_l(1) = 1$
- P_ℓ is a polynomial of degree ℓ

Properties of associated Legendre function:

- $P_\ell^m(x)$ is not a polynomial in general; when m is odd, $(1-x^2)^{m/2}$ results in a term with a square root
- $P_\ell^m(x)$ is a polynomial in $\cos(\theta)$, or in $\sin(\theta)$ when m is odd
- When $m > \ell$, $P_\ell^m = 0$
- For some ℓ, there exists $2\ell+1$ values of m such that $P_\ell^m \neq 0$

To normalize $\psi = R(r)Y(\theta,\phi)$:

$$1 = \int |R|^2|Y|^2 r^2\sin(\theta)\, dr\, d\theta\, d\phi$$

Implies

$$1 = \int_0^\infty |R|^2 r^2\, dr$$

and

$$1 = \int_0^{2\pi}\int_0^\pi |Y|^2\sin(\theta)\, d\theta\, d\phi$$
$$= \int_0^{2\pi}\int_0^\pi |Y|^2 d\Omega$$

$d\Omega \mapsto \sin(\theta)\, d\theta\, d\phi$ is an element of "solid angle".

Spherical harmonics: are the normalized angular wave functions:

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

Spherical harmonics are orthogonal:

$$\int \left(Y_\ell^m\right)^* Y_{\ell'}^{m'}\, d\Omega = \delta_{\ell\ell'}\delta_{mm'}$$

Instead of performing this analysis using Legendre polynomials, we will come to recognize that the angular part of the Schrödinger equation is the L^2 operator, in spherical coordinate representation.

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

Since $\hat{H}$ and $\hat{L}^2$ commute, we can replace these differential operators by eigenvalue of L^2, which greatly simplifies our Schrödinger equation.

$$\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{L^2}{2mr^2}\psi + V(r)\psi = E\psi$$

The radial equation

The central field, $V(r)$ only effects the radial equation.

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

Multiply both sides by R:

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

We introduce subscripts $E\ell$ to the solution, since the radial equation depends on both the total energy, and the value of ℓ.

Let $u_{E\ell}(r) = rR_{E\ell}(r)$, we will find that the angular equation reduces to

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dr^2} + V_{\text{eff}}\right)u_{E\ell} = Eu$$

where

$$V_{\text{eff}} = V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}$$

is the **effective potential**.

Since the additional term is also called the **centrifugal term**, because it can be interpreted as a repulsive potential (positive sign) and proportional to the square of the angular momentum.

Recall the relative motion Lagrangian. We refered to the following as the centrifugal term,

$$\frac{\ell^2}{2\mu r^2}$$

where ℓ is the classical angular momentum, r is the relative positive vector.

Normalizing $R_{E\ell}$ implies normalizing $u_{E\ell}$:

$$1 = \int_0^\infty |u_{E\ell}|^2\,dr = \int_0^\infty r^2|R_{E\ell}|^2\,dr$$

Behaviour near the origin

As $r \to 0$, the centifugal term of V_{eff} dominates. To leading order, we can say

$$\frac{-\hbar^2}{2m}\frac{d^2u_{E\ell}}{dr^2} + \frac{\hbar^2\ell(\ell+1)}{2mr^2}u_{E\ell} = 0 \qquad \text{as } r \to 0$$

Rearranging,

$$r^2\frac{d^2u_{E\ell}}{dr^2} - \ell(\ell+1)u_{E\ell} = 0$$

is a Cauchy-Euler equation. We guess $u_{E\ell} = r^s$, and substitute to find

$$s(s-1) = \ell(\ell+1) \implies s = \ell+1, -\ell$$

So near $r = 0$, the equation can be either

$$u_{E\ell} \approx r^{\ell+1} \qquad u_{E\ell} \approx \frac{1}{r^\ell}$$

1. If $\ell > 0$, $u_{E\ell} \approx r^{-\ell}$ diverges
2. If $\ell = 0$, $u_{E\ell} \approx 1$, and $R = 1/r$ is not a solution to the Schrödinger equation

Radial solution near the origin: for all $\ell \geq 0$, $u_{E\ell} \approx r^{\ell+1}$ leads to a radial solution that is

$$R_{E\ell} \approx r^\ell$$

- Only if $\ell = 0$ can $R_{E\ell}(0) \neq 0$
- Otherwise, the angular momentum barrier prevents the particle from reaching the origin

Angular momentum

In classical mechanics, energy and momentum is conserved for motion in a central field.

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

By substituting $\underline{p}$ for the operator $\hat{\underline{p}} = -i\hbar\underline{\nabla}$, and $\underline{r}$ for the position operator, we find the quantum mechanical angular momentum operator

$$\hat{\underline{L}} = -i\hbar\left(\underline{r} \times \underline{\nabla}\right) \to \begin{cases} \hat{L}_x &= yp_z - zp_y \\ \hat{L}_y &= zp_x - xp_z \\ \hat{L}_z &= xp_y - yp_x \end{cases}$$

Remembering $\hat{L}_x = yp_z - zp_y$, we can always cyclically permute $(x \to y \to z \to x)$ each subscript and position operator to get the other components.

For example, we can change $x \to y$, $y \to z$, $z \to x$ in L_x to find that $\hat{L}_y = zp_x - xp_z$.

We can define $\hat{L}^2$ as

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

L, L^2 are hermitian: they both are observables

Eigenvalues

Consider the commutator

$$\begin{aligned}\left[L_x, L_y\right] &= \left[yp_z - zp_y, zp_x - xp_z\right] \\ &= \left[yp_z, zp_x\right] - \left[yp_z, xp_z\right] - \left[zp_y, zp_x\right] + \left[zp_y, xp_z\right]\end{aligned}$$

The first and last term is nonzero, since p_z do not commute with z. Then,

$$\left[L_x, L_y\right] = \left[yp_z, zp_x\right] + \left[zp_y, xp_z\right]$$

using distributive identities, we will find that

$$\left[L_x, L_y\right] = i\hbar L_z$$

Components of angular momentum are incompatible: Different components of angular momentum in Cartesian coordinates do not commute:

$$\left[L_i, L_j\right] = i\hbar\epsilon_{ijk}L_k$$

Levi-Civita symbol:

$$\epsilon_{ijk} = \begin{cases} 1 & ijk \text{ is a cyclic permutation of 123} \\ -1 & ijk \text{ is a anticyclic permutation of 123} \\ 0 & \text{if } i = j, \text{ or } j = k, \text{ or } k = i \end{cases}$$

This is an equivalent statement to

$$\begin{aligned}\left[L_x, L_y\right] &= i\hbar L_z \\ \left[L_y, L_z\right] &= i\hbar L_x \\ \left[L_z, L_x\right] &= i\hbar L_y\end{aligned}$$

So L_i, L_j, for $i \neq j$, are incompatible. They do not share a complete set of eigenfunctions.

$$\begin{aligned}\left[L_z, x\right] &= i\hbar y & \left[L_z, p_x\right] &= i\hbar p_y \\ \left[L_z, y\right] &= -i\hbar x & \left[L_z, p_y\right] &= -i\hbar p_x \\ \left[L_z, z\right] &= 0 & \left[L_z, p_z\right] &= 0\end{aligned}$$

L^2 is compatible with each component of L:

$$\left[L^2, L_i\right] = 0 \qquad i = 1, 2, 3$$

L commutes with all rotationally invariant observables:

$$\left[\underline{L}, r^2\right] = \left[\underline{L}, p^2\right] = \left[\underline{L}, V(r)\right] = \left[\underline{L}, L^2\right] = 0$$

A "central potential", $V(r)$, only depends on the radial distance $r = \|r\|_2$ from some reference point.

L, L^2, H are compatible:

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

provided that the H has a central potential

We can define ladder operators for angular momentum:

$$L_\pm = L_x \pm iL_y$$

We can verify that

Commutation relations involving $L_\pm$

$$\begin{aligned}\left[L_z, L_\pm\right] &= \pm\hbar L_\pm \\ \left[L^2, L_\pm\right] &= 0\end{aligned}$$

- $L_\pm$ are not hermitian, they are not observables
- We can write $L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$
- $L_x = (L_+ + L_-)/2$

- $L_y = (L_+ - L_-)/(2i)$

We can derive the last fact:

$$\begin{aligned} L_\pm L_\mp &= (L_x \pm iL_y)(L_x \mp iL_y) \\ &= L_x^2 \mp iL_xL_y \pm iL_yL_x + L_y^2 \\ &= L_x^2 + L_y^2 \mp i(L_xL_y - L_yL_x) \\ &= L_x^2 + L_y^2 \mp i[L_x, L_y] \\ &= L_x^2 + L_y^2 \pm \hbar L_z \end{aligned}$$

Rearraning, we have $L_x^2 + L_y^2 = L^2 - L_z^2$. Substituting:

$$L_\pm L_\mp = L^2 - L_z^2 \pm \hbar L_z$$

If f is an eigenfunction of L^2 and L_z, then

- $L_\pm f$ is an eigenfunction of L^2 with same eigenvalue λ
- $L_\pm f$ is an eigenfunction of L_z with a different eigenvalue $\mu \pm \hbar$

The property of $L_\pm$ to increment/decrement the eigenvalues of L_z parallels with $\hat{a}, \hat{a}^\dagger$ in the harmonic oscillator.

First show that $L_\pm f$ is an eigenfunction of L^2, with the same eigenvalue λ:

$$L^2(L_\pm f) = L_\pm\left(L^2 f\right) = L_\pm(\lambda f) = \lambda(L_\pm f)$$

Then we show that $L_\pm f$ is an eigenfunction of L_z, with new eigenvalue $\mu \pm \hbar$

$$\begin{aligned} L_z(L_\pm f) &= [L_z, L_\pm] f + L_\pm L_z f \\ &= \pm\hbar L_\pm f + L_\pm(\mu f) \\ &= (\mu \pm \hbar) L_\pm f \end{aligned}$$

Repeatedly applying L_+ to an eigenstate would increase the associated eigenvalue of L_z by a factor of $\hbar$. "We will reach a state for which the z-component exceeds the total." So there must a state such that

$$L_+ f_t = 0$$

Mathematically, we require

$$L^2|\ell, m\rangle \geq L_z^2|\ell, m\rangle \iff \ell(\ell+1) \geq m^2$$

Let $\hbar\ell$ be the eigenvalue associated with f_t for L_z. Then

$$\begin{aligned} L_z f_t &= \hbar\ell f_t \\ L^2 f_t &= \lambda f_t \end{aligned}$$

Substituting L^2 for $L_-L_+ + L_z^2 + \hbar L_z$, we will find that

$$L^2 f_t = \hbar^2\ell(\ell+1) f_t \iff \lambda = \hbar^2\ell(\ell+1)$$

There must exists also a bottom eigenstate, such that

$$L_- f_b = 0$$

Let $\hbar\overline{\ell}$ be the eigenvalue of L_z at the bottom eigenstate:

$$\begin{aligned} L_z f_b &= \hbar\overline{\ell} f_t \\ L^2 f_b &= \lambda f_t \end{aligned}$$

Substituting L^2 for $L_+L_- + L_z^2 - \hbar L_z$, we will find that

$$\lambda = \hbar^2\overline{\ell}(\overline{\ell} - 1)$$

And we have

$$\overline{\ell}(\overline{\ell} - 1) = \ell(\ell+1)$$

This implies that $\overline{\ell} = -\ell$. To go from f_b to f_t, or from eigenvalue equal to $-\ell$ to ℓ, we will need to take N steps. So $\ell = -\ell + N$, and $\ell = N/2$.

Let's define a new index m, which goes from $-\ell$ to ℓ in N steps.

Simultaneous eigenfunctions of L^2 and L_z:

$$\begin{aligned} L^2 f_\ell^m &= \hbar^2\ell(\ell+1) f_\ell^m \\ L_z f_\ell^m &= \hbar m f_\ell^m \end{aligned}$$

for $\ell = 0, (1/2), 1, \ldots$ and $m = -\ell, (-\ell+1), \ldots, (\ell-1), \ell$. And f_ℓ^m is eigenstate of L_z and L^2.

We will come to find that ℓ cannot take on half integer values.

Action of ladder operators:

$$L_\pm f_\ell^m = \hbar\sqrt{\ell(\ell+1) - m(m\pm1)}\, f_\ell^{m\pm1}$$

When $m = \pm\ell$, the normalization constant is 0. So there must be a top and bottom rung of the ladder.

Angular momentum cannot completely point along a given direction. If it is well defined in one direction, say along the z-axis, the x and y components will have non-zero uncertainty, as different components do not commute.

Normalization: If we apply $L_\pm$ to a superposition of eigenstates, $|\psi\rangle$, the resulting state still requires normalization!

Unitless angular momentum operators

An alternate formulation involves dividing each component of angular momentum by $\hbar$, such that $L_i = \hbar\ell_i$.

Eigenfunctions

Our goal is to construct eigenstates of L_z and L^2, which we denote by $|\ell, m\rangle$, that are orthonormal

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

- $|\ell, m\rangle$ states are $2\ell + 1$ degenerate
- For every ℓ, there are $2\ell + 1$ values of m

If we can find the states f_ℓ^ℓ. By repeated application of $L_\pm$, we can construct all possible states of f_ℓ^m.

Recall the spherical gradient operator:

$$\underline{\nabla} = \hat{\underline{r}}\frac{\partial}{\partial r} + \hat{\underline{\theta}}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{\underline{\phi}}\frac{1}{r\sin(\theta)}\frac{\partial}{\partial\phi}$$

Substitute the spherical gradient into the angular momentum operator. Remeber that the cross product is distributive:

$$\underline{L} = -i\hbar\left(r(\hat{\underline{r}}\times\hat{\underline{r}})\frac{\partial}{\partial r} + (\hat{\underline{r}}\times\hat{\underline{\theta}})\frac{\partial}{\partial\theta} + (\hat{\underline{r}}\times\hat{\underline{\phi}})\frac{1}{\sin(\theta)}\frac{\partial}{\partial\phi}\right)$$

By the relations

$$\begin{aligned} \hat{\underline{r}}\times\hat{\underline{r}} &= 0 \\ \hat{\underline{r}}\times\hat{\underline{\theta}} &= \hat{\underline{\phi}} \\ \hat{\underline{r}}\times\hat{\underline{\phi}} &= -\hat{\underline{\theta}} \end{aligned}$$

Simplifying:

$$\underline{L} = -i\hbar\left(\hat{\underline{\phi}}\frac{\partial}{\partial\theta} - \hat{\underline{\theta}}\frac{\partial}{\partial\phi}\right)$$

With components

L_z in spherical coordinates:

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

$$\begin{aligned} L_x &= -i\hbar\left(-\sin(\phi)\frac{\partial}{\partial\theta} - \cos(\phi)\cot(\theta)\frac{\partial}{\partial\phi}\right) \\ L_y &= -i\hbar\left(+\cos(\phi)\frac{\partial}{\partial\theta} - \sin(\phi)\cot(\theta)\frac{\partial}{\partial\phi}\right) \end{aligned}$$

The raising and lower operator become

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

Using the fact that $L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$, and

$$L_+L_- = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot(\theta)\frac{\partial}{\partial\theta} + \cot^2(\theta)\frac{\partial^2}{\partial\phi^2} + i\frac{\partial}{\partial\phi}\right)$$

we can show that

L^2 operator in spherical coordinates:

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

Let's call the eigenfunctions $Y_\ell^m(\theta, \phi)$. Consider

$$\hat{\ell}_z|\ell, m = \ell\rangle = (m = \ell)|\ell, m = \ell\rangle$$

Substituting the spherical representation

$$-i\frac{\partial}{\partial\phi}Y_\ell^{m=\ell} = \ell Y_\ell^{m=\ell}$$

This is a first order ODE, with the solution

$$Y_\ell^{m=\ell} = f(\theta)e^{i(m=\ell)\phi}$$

No half-integers for orbital angular momentum: If ℓ can take on half-integer values, so too can m. But we require

$$e^{im\phi} = e^{im(\phi+2\pi)} = e^{im\phi}e^{im2\pi} \iff e^{im2\pi} = 1$$

which is not possible if when m can be a half-integer.

We also know that

$$\ell_+ Y_\ell^\ell = 0$$

Substituting the spherical representation for ℓ_+:

$$0 = e^{i\phi}\left(\frac{\partial}{\partial\theta} \pm i\cot(\theta)\frac{\partial}{\partial\phi}\right) f(\theta)e^{i\ell\phi}$$

We can find that Y_ℓ^ℓ is of the form

$$Y_\ell^\ell = A\sin^\ell(\theta)e^{i\ell\phi}$$

Computing the normalization:

$$\begin{aligned}\langle \ell, \ell | \ell, \ell\rangle &= |A|^2 \int \sin^{2\ell}(\theta)\, d\Omega \\ &= |A|^2 \int_0^{2\pi}\int_0^{\pi} \sin^{2\ell}(\theta)\sin(\theta)\, d\theta\, d\phi \\ &= 1\end{aligned}$$

Maximum projection state:

$$|\ell, \ell\rangle = Y_\ell^\ell(\theta,\phi) = \sqrt{\frac{(2\ell+1)!!}{2\pi(2\ell)!!}}\sin^\ell(\theta)e^{i\ell\phi}$$

The **double factorial** is defined to be

$$\ell!! = \begin{cases}(\ell)(\ell-2)\ldots 5\cdot 3\cdot 1 & n>0 \text{ odd}\\ (\ell)(\ell-2)\ldots 6\cdot 4\cdot 2 & n>0 \text{ even}\\ 1 & n=-1,0\end{cases}$$

Table of spherical harmonics:

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2} \qquad Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{\pm 2i\phi}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta \qquad Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$$

$$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\phi} \qquad Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1) \qquad Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta e^{\pm 2i\phi}$$

$$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{\pm i\phi} \qquad Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta e^{\pm 3i\phi}$$

Symmetry

In one dimension, we discussed the $x \to -x$ symmetry.

Mirror symmetry: Spherical coordinates obey **mirror symmetry** about the origin.

$$\underline{r} \to -\underline{r}$$

under the transformations

$$\theta \to \pi - \theta$$
$$\phi \to \phi + \pi$$

In spherical coordinates,

$$x = r\sin(\theta)\cos(\phi)$$
$$y = r\sin(\theta)\sin(\phi)$$
$$z = r\cos(\theta)$$

We see that

$$\sin(\pi-\theta) = \sin(\theta)$$
$$\cos(\pi-\theta) = -\cos(\theta)$$
$$\sin(\phi+\pi) = -\sin(\phi)$$
$$\cos(\phi+\pi) = -\cos(\phi)$$

So applying θ and ϕ transformations, we get

$$x \to -x$$
$$y \to -y$$
$$z \to -z$$

which is precisely $\underline{r} \to -\underline{r}$

Under the transformations, we define spherical harmonics to be

$$Y_\ell^m \to \begin{cases}Y_\ell^m & \ell = 2n;\ \text{symmetric}\\ -Y_\ell^m & \ell = 2n+1;\ \text{anti-symmetric}\end{cases}$$

for some $n \in \mathbb{Z}$. This can be used to reason why

$$\int Y_a^{b^*} Y_c^d\, d\Omega = 0$$

when a is even and c is odd.

Consider $\langle \ell, m | z | \ell, m\rangle$. Since z changes sign under the transformations, while sign changes of $|\ell, m\rangle$ will cancel, so we expect this to be 0. In coordinate representation, we have a product of symmetric and anti-symmetric functions, which is anti-symmetric.

We cannot expect that $\langle \ell, m | z^2 | \ell, m\rangle$ to vanish. z^2 does not change sign under the transformations.

Since both $\underline{r}$ and $\underline{p}$ change sign under the transformations, $\underline{L}$ does not change sign. So $\underline{L}$ is symmetric under the transformations. We call $\underline{L}$ a **pseudo-** or **axial** vector.

Spin

Elementary particles carry **intrinsic** angular momentum ($\underline{S}$) in addition to their extrinsic angular momentum ($\underline{L}$).

In classical mechanics, we had two forms of angular momentum. Obital, and spin angular momentum. But this is not the case in quantum mechanics.

In quantum mechanics, we cannot imagine particles as small spinning balls. Spin has no coordinate-space representation.

Spin operators: We postulate that Spin obeys the same algebra as angular momentum.

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k$$

And there exists an operator S^2, such that

$$S^2|s,m\rangle = \hbar^2 s(s+1)|s,m\rangle$$
$$S_z|s,m\rangle = \hbar m|s,m\rangle$$

The parallel to angular momentum can be seen by switching from $s \to \ell$.

Fact: Spin does not have a coordinate representation. So $|s,m\rangle$ are strictly eigenstates, not eigenfunctions.

And we can similarly define ladder operators, $S_\pm = S_x + iS_y$, such that:

$$S_\pm|s,m\rangle = \hbar\sqrt{s(s+1)-m(m\pm 1)}\,|s,m\pm 1\rangle$$

- for a given particle, the spin quantum number, s, can only take on a specific integer/half-integer number

Recall that for any particle, ℓ is allowed to be any integer, and it changes whenever the system is pertubed.

Different elementary particle species take on different values of spin.

Spin 1/2

Protons, electrons, neutrons have $s = 1/2$. When $s = 1/2$, we have two eigenstates of S_z. They are spin up, and spin down states:

$$|\uparrow\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle \qquad |\downarrow\rangle = \left|\frac{1}{2},-\frac{1}{2}\right\rangle$$

This is a "two level system". We can treat this problem by using a matrix basis. In this basis, we represent the states as

$$|\uparrow\rangle \to \chi_+ = \begin{bmatrix}1\\0\end{bmatrix} \qquad |\downarrow\rangle \to \chi_- = \begin{bmatrix}0\\1\end{bmatrix}$$

Spinor: The "spin state" of a stationary particle is described by two element column matrix called a spinor

$$\chi = \begin{bmatrix}a\\b\end{bmatrix} = a\chi_+ + b\chi_-$$

We require χ to be normalized.

The most general spinor has the form

$$\chi = \begin{bmatrix}e^{i\alpha}\cos(\gamma)\\ e^{i\beta}\sin(\gamma)\end{bmatrix} = e^{i\alpha}\begin{bmatrix}\cos(\gamma)\\ e^{i(\beta-\alpha)}\sin(\gamma)\end{bmatrix}$$

But only the phase difference $\beta - \alpha$ is observable. Since $e^{i\alpha}$ will cancel in all computations of probability (and so in all computations of expectation values as well).

In our choice of a matrix basis, we can verify that

$$\underline{S}^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\underline{S}_+ = \hbar \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \qquad \underline{S}_- = \hbar \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

If we define the **Pauli spin matrices**,

$$\underline{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \underline{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \underline{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

We can write

$$\underline{S}_x = \frac{\hbar}{2}\underline{\sigma}_x \qquad \underline{S}_y = \frac{\hbar}{2}\underline{\sigma}_y \qquad \underline{S}_z = \frac{\hbar}{2}\underline{\sigma}_z$$

- χ_+, χ_- are "eigenspinors" of $\underline{S}_z$
- Under this basis, S_x, S_y may have eigenspinors of a different form. We denote them $\chi_\pm^{(x)}, \chi_\pm^{(y)}$.
- The Pauli matrices are unitary. This implies that $S_i^2 = \hbar^2/4$
- We can prove that

$$\sigma_j \sigma_k = \delta_{jk} + i\epsilon_{jkl}\sigma_l$$

- $S_+\chi_+ = S_-\chi_- = 0$
- $S_\pm \chi_\mp = \hbar\chi_\pm$

At least for spin 1/2, we have

$$\underline{S}_x^2 = \underline{S}_y^2 = \underline{S}_z^2 = \frac{\hbar^2}{4}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

The eigenvalue, eigenvector pairs of $\underline{S}_x$:

$$\left\{\frac{\hbar}{2}, \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}\right\}, \left\{\frac{-\hbar}{2}, \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}\right\}$$

The eigenvalue, eigenvector pairs of $\underline{S}_y$:

$$\left\{\frac{\hbar}{2}, \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \end{bmatrix}\right\}, \left\{\frac{-\hbar}{2}, \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -i \end{bmatrix}\right\}$$

Electron in a magnetic field

Recall the gyromagnetic ratio, the ratio of the magnetic dipolment to the angular momentum of some configuration. Classically,

$$\underline{\mu} = \gamma \underline{S}$$

- μ is the magnetic dipole moment
- $\underline{S}$ is the spin angular momentum of a particle

A current loop placed in a uniform magnetic field experiences a torque that aligns the magnetic dipole moment of the loop to the direction of the field.

Assumming the particle is stationary. This potential energy associated with this torque is

$$\hat{H} = -\underline{\mu} \cdot \underline{B} = -\gamma \underline{B} \cdot \underline{S}$$

- No magnetic field quantization
- Quantize spin: $\underline{S}$ becomes a spin matrix

Uniform magnetic field: let $\underline{B} = B_0\hat{\underline{k}}$. The Hamiltonian

$$\underline{H} = -\gamma B_0 \underline{S}_z = -\frac{\gamma B_0 \hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Hamiltonian share the same eigenvectors as $\underline{S}_z$, which means that $[\underline{H}, \underline{S}_z] = 0$:

$$\underline{H}\chi_+ = -\frac{\gamma B_0 \hbar}{2}\chi_+ \qquad \underline{H}\chi_- = +\frac{\gamma B_0 \hbar}{2}\chi_-$$

- E_+ associated with χ_+ is less than E_-: energy is lowest when the magnetic dipole moment is parallel to the field

The general solution can be found by appending our time dependent wiggle factors

$$\chi(t) = a\chi_+ e^{-iE_+ t/\hbar} + b\chi_- e^{-iE_- t/\hbar}$$

The coefficients, a and b are determined by initial conditions at $\chi(0)$. Since we require $\chi(t)$ to be normalized, we can substitute

$$a = \cos(\alpha/2)$$
$$b = \sin(\alpha/2)$$

to replace two cofficients by a single angle α. Recognize that

$$\omega = \gamma B_0$$

is the classical Larmor frequency, so the eigenenergies can be written as

$$E_\pm = \mp\omega\hbar/2$$

Direct computation of $\langle S_x\rangle, \langle S_y\rangle, \langle S_z\rangle$ gives

$$\langle S_x\rangle = \frac{\hbar}{2}\sin(\alpha)\cos(\omega t)$$
$$\langle S_y\rangle = \frac{\hbar}{2}\sin(\alpha)\sin(\omega t)$$
$$\langle S_z\rangle = \frac{\hbar}{2}\cos(\alpha)$$

which tells us that the expectation value, $\langle \underline{S}\rangle$ precesses about the magnetic field at a frequency ω.

- $\langle S_z\rangle$ is time-independent, since χ is a superposition of eigenstates of S_z, who shares the same eigenstates as our time independent Hamiltonian
- The expectation value of a time independent $\hat{H}$ is time independent, even for a superposition of eigenstates
- The probability to get $\hbar/2$ or $-\hbar/2$ for S_z is time independent This is the same as asking the probability to find a particular eigenstate of S_z. As S_z commutes with $\hat{H}$, and $\hat{H}$ is time independent, the probabilities are time independent.

For example,

$$\begin{aligned}
\langle S_x\rangle &= \chi^\dagger \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\chi \\
&= \frac{\hbar}{2}\begin{bmatrix} \cos\left(\frac{\alpha}{2}\right)e^{-i\omega t/2} & \sin\left(\frac{\alpha}{2}\right)e^{i\omega t/2} \end{bmatrix}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\chi \\
&= \frac{\hbar}{2}\begin{bmatrix} \sin\left(\frac{\alpha}{2}\right)e^{i\omega t/2} & \cos\left(\frac{\alpha}{2}\right)e^{-i\omega t/2} \end{bmatrix}\begin{bmatrix} \cos\left(\frac{\alpha}{2}\right)e^{i\omega t/2} \\ \sin\left(\frac{\alpha}{2}\right)e^{-i\omega t/2} \end{bmatrix} \\
&= \frac{\hbar}{2}\left(\sin\left(\frac{\alpha}{2}\right)\cos\left(\frac{\alpha}{2}\right)e^{i\omega t} + \sin\left(\frac{\alpha}{2}\right)\cos\left(\frac{\alpha}{2}\right)e^{-i\omega t}\right) \\
&= \frac{\hbar}{2}2\cos(\omega t)\sin\left(\frac{\alpha}{2}\right)\cos\left(\frac{\alpha}{2}\right) \\
&= \frac{\hbar}{2}\cos(\omega t)\sin(\alpha)
\end{aligned}$$

And

$$\begin{aligned}
\langle S_z\rangle &= \chi^\dagger \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\chi \\
&= \frac{\hbar}{2}\begin{bmatrix} \cos\left(\frac{\alpha}{2}\right)e^{-i\omega t/2} & \sin\left(\frac{\alpha}{2}\right)e^{i\omega t/2} \end{bmatrix}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\chi \\
&= \frac{\hbar}{2}\begin{bmatrix} \cos\left(\frac{\alpha}{2}\right)e^{-i\omega t/2} & -\sin\left(\frac{\alpha}{2}\right)e^{i\omega t/2} \end{bmatrix}\begin{bmatrix} \cos\left(\frac{\alpha}{2}\right)e^{i\omega t/2} \\ \sin\left(\frac{\alpha}{2}\right)e^{-i\omega t/2} \end{bmatrix} \\
&= \frac{\hbar}{2}\left(\cos^2\left(\frac{\alpha}{2}\right) - \sin^2\left(\frac{\alpha}{2}\right)\right) \\
&= \frac{\hbar}{2}\cos(\alpha)
\end{aligned}$$

Stern-Gerlach experiement: demonstrated the quantization of spin for spin 1/2 particles. It involved

- beam of silver atoms (neutral, so we avoid talking about the Lorentz force)
- an inhomogenous magnetic field:

$$\underline{B} = -\alpha x\hat{\underline{x}} + (B_0 + \alpha z)\hat{\underline{k}}$$

Recall that the force exerted on a magnetic dipole is given by the gradient of the potential energy

$$\underline{F} = \underline{\nabla}(\underline{\mu} \cdot \underline{B})$$

If the field were homogeneous, then there be no deflection force on the atoms since the gradient would be zero. Particles passing through the field was deflected into 2 separate streams, depending on the spin of the particle. While we expected a smear of particles instead.

Direction of spin polarization

Along an arbitrary direction, $\hat{\underline{r}}$,

$$\hat{\underline{r}} = \sin(\theta)\cos(\phi)\hat{\underline{x}} + \sin(\theta)\sin(\phi)\hat{\underline{y}} + \cos(\theta)\hat{\underline{z}}$$

The matrix representing the componenet of spin along $\hat{\underline{r}}$ is

$$\begin{aligned}
S_r &= S_x\sin(\theta)\cos(\phi)\hat{\underline{x}} + S_y\sin(\theta)\sin(\phi)\hat{\underline{y}} + S_z\cos(\theta)\hat{\underline{z}} \\
&= \frac{\hbar}{2}\begin{bmatrix} \cos(\theta) & e^{-i\phi}\sin(\theta) \\ e^{-\phi}\sin(\theta) & -\cos(\theta) \end{bmatrix}
\end{aligned}$$

The eigenvalues and eigenvector pairs are

$$\left\{\frac{\hbar}{2}, \begin{bmatrix}\cos(\theta/2)\\ e^{i\phi}\sin(\theta/2)\end{bmatrix}\right\}, \left\{\frac{-\hbar}{2}, \begin{bmatrix}e^{-\phi}\sin(\theta/2)\\ -\cos(\theta/2)\end{bmatrix}\right\}$$

Given an arbitrary spinor, the direction of polarization is parallel to

$$\langle\chi|S_x|\chi\rangle\,\underline{\hat{x}} + \langle\chi|S_y|\chi\rangle\,\underline{\hat{y}} + \langle\chi|S_z|\chi\rangle\,\underline{\hat{z}}$$

up to normalization.

Spin 1

There are three eigenspinors of S_z:

$$|1,-1\rangle \to \begin{bmatrix}0\\0\\1\end{bmatrix} \qquad |1,0\rangle \to \begin{bmatrix}0\\1\\0\end{bmatrix} \qquad |1,1\rangle \to \begin{bmatrix}1\\0\\0\end{bmatrix}$$

The spin matrices are

$$\underline{S}^2 = 2\hbar^2\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}$$

$$\underline{S}_+ = \hbar\sqrt{2}\begin{bmatrix}0&1&0\\0&0&1\\0&0&0\end{bmatrix} \qquad \underline{S}_- = \hbar\sqrt{2}\begin{bmatrix}0&0&0\\1&0&0\\0&1&0\end{bmatrix}$$

$$\underline{S}_x = \frac{\hbar}{\sqrt{2}}\begin{bmatrix}0&1&0\\1&0&1\\0&1&0\end{bmatrix} \qquad \underline{S}_x = \frac{i\hbar}{\sqrt{2}}\begin{bmatrix}0&-1&0\\1&0&-1\\0&1&0\end{bmatrix}$$

$$\underline{S}_z = \hbar\begin{bmatrix}1&0&0\\0&0&0\\0&0&-1\end{bmatrix}$$

The hydrogen atom

Classically, The hydrogen atom is a **two-body problem**, involving: a proton of mass m_p, charge $+e$; an electron of mass m_e, charge $-e$.

If we say that $m_p \gg m_e$, then the proton can be taken to be at the origin, and the potential is a central potential:

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

where Z is a free parameter ($Z = 1$ for hydrogen). This is not the electric potential of a positive point charge. The reason for an extra factor of $-e$ comes from how we account for electromagnetic fields in the Hamiltonian (the **minimum coupling rule**).

Reasonably, the proton and electron's position and momentum are specified by two pairs of **independent canonical variables**, subscript p for proton, and e for electron.

$$\left[(\hat{x}_p)_i, (\hat{p}_p)_j\right] = i\hbar\delta_{ij}$$
$$\left[(\hat{x}_e)_i, (\hat{p}_e)_j\right] = i\hbar\delta_{ij}$$

- One would also expect the proton variables to commute with electron variables
- We can measure the momentum of both the proton and electron simultaneously (to arbitrary precision)

The Hamiltonian of system is given by

$$\hat{H} = \frac{\hat{p}_p^2}{2m_p} + \frac{\hat{p}_e^2}{2m_e} + V(|\underline{\hat{x}}_e - \underline{\hat{x}}_p|)$$

Instead of deriving the center of mass and relative Hamiltonians through the following change of variables, if we know the classical center of mass and relative Lagrangians from the two body problem, we can simply Legendre transform them into the Hamiltonians.

We introduce two new pairs of canonical variables. The first pair includes

- the total momentum operator

$$\underline{\hat{P}} = \underline{\hat{p}}_p + \underline{\hat{p}}_e$$

- the center of mass position operator

$$\underline{\hat{X}} = \frac{m_e\underline{\hat{x}}_e + m_p\underline{\hat{x}}_p}{m_e + m_p}$$

Their commutator is

$$\left[(\hat{X})_i, (\hat{P})_j\right] = i\hbar\delta_{ij}$$

Let's verify this. Using the distributivity of commutators, and setting all commutators involving only both electron and proton variables to zero:

$$\begin{aligned}\left[\frac{m_e(\hat{x}_e)_i + m_p(\hat{x}_p)_i}{m_e+m_p}, (\hat{p}_p)_j + (\hat{p}_e)_j\right] &= \frac{m_e}{m_e+m_p}\left[(\hat{x}_e)_i, (\hat{p}_e)_j\right]\\ &+ \frac{m_p}{m_e+m_p}\left[(\hat{x}_p)_i, (\hat{p}_p)_j\right]\\ &= i\hbar\delta_{ij}\end{aligned}$$

For convenience, we introduce the total mass and the reduced mass,

$$M = m_e + m_p$$
$$\mu = \frac{m_e m_p}{m_e + m_p}$$

The second pair of variables we introduce are

- the relative position operator

$$\underline{\hat{x}} = \underline{\hat{x}}_e - \underline{\hat{x}}_p$$

- the relative momentum operator

$$\underline{\hat{p}} = \mu\left(\frac{\underline{\hat{p}}_e}{m_e} - \frac{\underline{\hat{p}}_p}{m_p}\right) = \frac{m_p}{M}\underline{\hat{p}}_e - \frac{m_e}{M}\underline{\hat{p}}_p$$

Since our original pairs of canonical variables commutes with each other, we also require that $\underline{\hat{x}}$, and $\underline{\hat{p}}$ commutes with $\underline{\hat{X}}$ and $\underline{\hat{P}}$, and that

$$\left[(\hat{x})_i, (\hat{p})_j\right] = i\hbar\delta_{ij}$$

$\underline{\hat{x}}$ and $\underline{\hat{X}}$ definitely commute. And $\underline{\hat{x}}$ and $\underline{\hat{P}}$:

$$\begin{aligned}\left[(\hat{x}_e)_i - (\hat{x}_p)_i, (\hat{p}_p)_{ji} + (\hat{p}_e)_j\right] &= \left[(\hat{x}_e)_i, (\hat{p}_e)_j\right] - \left[(\hat{x}_p)_i, (\hat{p}_p)_j\right]\\ &= 0\end{aligned}$$

also commute.

To derived the coefficients in the $\underline{\hat{p}}$ operator, we first let

$$\underline{\hat{p}} = \alpha\underline{\hat{p}}_e - \beta\underline{\hat{p}}_p$$

α, β can be derived from requiring

$$\begin{aligned}\left[(\hat{x})_i, (\hat{p})_j\right] &= i\hbar\delta_{ij}\\ &= \left[(\hat{x}_e)_i - (\hat{x}_p)_i, \alpha(\hat{p}_e)_j - \beta(\hat{p}_p)_j\right]\\ &= \alpha i\hbar\delta_{ij} + \beta i\hbar\delta_{ij}\\ &\implies \alpha + \beta = 1\end{aligned}$$

and similarly

$$\left[(\hat{X})_i, (\hat{p})_i\right] = 0$$

In terms of the new momentum variables,

$$\underline{\hat{p}}_p = \frac{m_p}{M}\underline{\hat{P}} - \underline{\hat{p}} \qquad \underline{\hat{p}}_e = \frac{m_e}{M}\underline{\hat{P}} + \underline{\hat{p}}$$

We can write the Hamiltonian as

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2\mu} + V(r)$$

First compute the squares of $\underline{\hat{p}}_p$ and $\underline{\hat{p}}_e$:

$$\underline{\hat{p}}_p^2 = \left(\frac{m_p}{M}\underline{\hat{P}}\right)^2 - 2\left(\frac{m_p}{M}\underline{\hat{P}}\underline{\hat{p}}\right) + \underline{\hat{p}}^2$$
$$\underline{\hat{p}}_e^2 = \left(\frac{m_e}{M}\underline{\hat{P}}\right)^2 + 2\left(\frac{m_e}{M}\underline{\hat{P}}\underline{\hat{p}}\right) + \underline{\hat{p}}^2$$

Substituting into the kinetic energy portion of the Hamiltonian:

$$\begin{aligned}\frac{\underline{\hat{p}}_p^2}{2m_p} + \frac{\underline{\hat{p}}_e^2}{2m_e} &= \frac{1}{2m_p}\left(\left(\frac{m_p}{M}\underline{\hat{P}}\right)^2 - 2\left(\frac{m_p}{M}\underline{\hat{P}}\underline{\hat{p}}\right) + \underline{\hat{p}}^2\right)\\ &+ \frac{1}{2m_e}\left(\left(\frac{m_e}{M}\underline{\hat{P}}\right)^2 + 2\left(\frac{m_e}{M}\underline{\hat{P}}\underline{\hat{p}}\right) + \underline{\hat{p}}^2\right)\\ &= \frac{m_p}{2M^2}\underline{\hat{P}}^2 - \frac{1}{M}\underline{\hat{P}}\underline{\hat{p}} + \frac{1}{2m_p}\underline{\hat{p}}^2\\ &+ \frac{m_e}{2M^2}\underline{\hat{P}}^2 + \frac{1}{M}\underline{\hat{P}}\underline{\hat{p}} + \frac{1}{2m_e}\underline{\hat{p}}^2\\ &= \frac{\underline{\hat{P}}^2}{2M^2}(m_p + m_e) + \frac{\underline{\hat{p}}^2}{2}\left(\frac{1}{m_p} + \frac{1}{m_e}\right)\\ &= \frac{\underline{\hat{P}}^2}{2M} + \frac{\underline{\hat{p}}^2}{2\mu}\end{aligned}$$

In position space, we can write the new momentum operators as gradients with respect to the center of mass coordinates

$$\underline{\hat{P}} \to -i\hbar\underline{\nabla}_{\underline{X}}$$

and the relative position coordinates

$$\underline{\hat{p}} \to -i\hbar\underline{\nabla}_{\underline{x}}$$

Our wave function is now a function of $\underline{x}, \underline{X}$. We solve the equation by considering the separation of variables

$$\psi(\underline{x}, \underline{X}) = \psi_{\text{cm}}(\underline{X})\psi_{\text{rel}}(\underline{x})$$

The Schrödinger equation

$$\hat{H}\psi_{\text{cm}}(\underline{X})\psi_{\text{rel}}(\underline{x}) = E\psi_{\text{cm}}(\underline{X})\psi_{\text{rel}}(\underline{x})$$

is reduced to solving the center of mass equation

$$\frac{\hat{P}^2}{2M}\psi_{\text{cm}}(\underline{X}) = E_{\text{cm}}\psi_{\text{cm}}(\underline{X})$$

and the relative position equation

$$\left(\frac{\hat{p}^2}{2\mu} + V(|\underline{x}|)\right)\psi_{\text{rel}}(\underline{x}) = E_{\text{rel}}\psi_{\text{rel}}(\underline{x})$$

where

$$E = E_{\text{cm}} + E_{\text{rel}}$$

- The center of mass equation appears like the equation for a free particle of mass M, so energy is not quantized
- The relative position equation is the equation for a particle in a central field
- The total energy is the sum of the energies of the relative and center of mass motion

Center of mass equation

Resembles the equation for the free particle in three dimensions. And has solution

$$\psi_R = (2\pi\hbar)^{-3/2}e^{i\underline{\mathbb{P}}\cdot\underline{R}/\hbar}$$

Relative distance equation

Resembles the equation for a single particle in a central potential. We can show that the relative distance Hamiltonian reduces to

$$H_{\text{rel}} = \frac{-\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{L^2}{2\mu r^2} + V(r)$$

We showed that L^2 commutes with the Hamiltonian with a central potential. This allows us to replace the operator, L^2, by its eigenvalue. The relative distance equation becomes

$$\frac{-\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi_{\text{rel}}) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\psi_{\text{rel}} + V(r)\psi_{\text{rel}} = E_{\text{rel}}\psi_{\text{rel}}$$

We can multiply by r on both sides, and define a new variable, $u = r\psi_{\text{rel}}$:

$$\left(\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right)u = E_{\text{rel}}u$$

Subsitute the characteristic potential,

$$\frac{-\hbar^2}{2\mu}\frac{\partial^2 u}{\partial r^2} + \left(\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{e^2Z}{4\pi\epsilon_0 r}\right)u = E_{\text{rel}}u$$

Our equation in the form of a **radial equation**.

Bound states of the radial equation

Since we are considering bound states, E_{rel} is taken to be < 0.

When $m_p \gg m_e$,

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

To simplify our notation, we interchange μ with m, and E_{rel} with E.

We can get rid of the cofficients infront of the second derivative.

$$\frac{\partial^2 u}{\partial r^2} - \frac{2m}{\hbar^2}\left(\frac{\hbar^2\ell(\ell+1)}{2mr^2} - \frac{e^2Z}{4\pi\epsilon_0 r}\right)u = \frac{-2mE}{\hbar^2}u$$

Define

$$\kappa^2 = \frac{-2mE}{\hbar^2} \qquad [\text{length}]^{-2}$$

we have

$$\frac{\partial^2 u}{\partial r^2} - \left(\frac{\ell(\ell+1)}{r^2} - \frac{me^2Z}{2\pi\epsilon_0\hbar^2 r}\right)u = \kappa^2 u$$

Dividing both sides by κ^2,

$$\frac{1}{\kappa^2}\frac{\partial^2 u}{\partial r^2} + \left(\frac{me^2Z}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{r\kappa} - \frac{\ell(\ell+1)}{(\kappa r)^2}\right) = u$$

Nondimensionalization: We introduce the dimensionless variables

$$\rho = \kappa r \qquad \rho_0 = \frac{me^2Z}{2\pi\epsilon_0\hbar^2\kappa} = \frac{e^2Z}{4\pi\epsilon_0}\frac{2m}{\hbar^2\kappa}$$

- ρ_0 will be important when we discuss the hydrogen spectrum
- ρ_0 contains the factor $2m/\hbar^2\kappa$, which resembles energy:

$$E = \frac{-\hbar^2\kappa^2}{2m}$$

In the original ODE, the second derivative has units $1/u$. This implies that the righthand side must have units $1/u$ as well. This tells us that κ has units of $1/u$.

$$\frac{du}{dr} = \frac{du}{d\rho}\frac{d\rho}{dr} = \frac{du}{d\rho}\kappa$$

and

$$\frac{d^2u}{dr^2} = \frac{d}{dr}\left(\frac{du}{d\rho}\kappa\right) = \kappa\frac{d}{d\rho}\frac{du}{dr} = \kappa\frac{d}{d\rho}\frac{du}{d\rho}\kappa = \kappa^2\frac{d^2u}{d\rho^2}$$

We can write

$$\frac{d^2u}{d\rho^2} = \left(1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right)u$$

This equation isn't yet ready for a series solution as it would require a three term recurrence relation. To make progress, we need to look at the asymotic behaviour.

For large ρ, the 1 dominates in the brackets.

$$\frac{d^2u}{d\rho^2} \approx u$$

This has general solutions involving exponentials. For the solution to normalizable, the term involving positive powers of ρ is must be discarded. So

$$u(\rho) \approx e^{-\rho} \qquad \text{large } \rho$$

For small ρ, $1/\rho^2$ is the most singular.

$$\frac{d^2u}{d\rho^2} \approx \frac{\ell(\ell+1)}{\rho^2}u$$

This is a Cauchy Euler equation. Normalizability requires that we discard the term being raised to a negative power. So

$$u(\rho) \approx \rho^{\ell+1} \qquad \text{small } \rho$$

Radial equation ansatz:

$$u(\rho) = \rho^{\ell+1}e^{-\rho}v(\rho)$$

where $v(\rho)$ is to be determined.

The first derivative

$$\begin{aligned}\frac{du}{d\rho} &= (\ell+1)\rho^\ell e^{-\rho}v(\rho) - \rho^{\ell+1}e^{-\rho}v(\rho) + \rho^{\ell+1}e^{-\rho}\frac{dv}{d\rho}\\ &= \rho^\ell e^{-\rho}\left((\ell+1)v(\rho) - \rho v(\rho) + \rho\frac{dv}{d\rho}\right)\\ &= \rho^\ell e^{-\rho}\left((\ell+1-\rho)v(\rho) + \rho\frac{dv}{d\rho}\right)\end{aligned}$$

We can show that in terms of $v(\rho)$, the radial equation becomes

$$\rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + (\rho_0 - 2(\ell+1))v = 0$$

For $\rho \to \infty$, $v(\rho)$ cannot be increasing at a faster rate than $e^{-\rho}$ decays. So a series solution is possible:

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

The derivatives

$$\begin{aligned}\frac{dv}{d\rho} &= \sum_{j=1}^{\infty} c_j j\rho^{j-1} = \sum_{j=0}^{\infty} c_{j+1}(j+1)\rho^j\\ \frac{d^2v}{d\rho^2} &= \sum_{j=2}^{\infty} c_j j(j-1)\rho^{j-2} = \sum_{j=1}^{\infty} c_{j+1}(j+1)j\rho^{j-1}\end{aligned}$$

At $j = 0$, $j(j+1) = 0$, so we may as well start indexing at $j = 0$.

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} c_{j+1}(j+1)j\rho^{j-1}$$

We can subsitute into our ODE to find the recurrence relation:

$$c_{j+1} = \frac{2(j+\ell+1)-\rho_0}{(j+1)(j+2\ell+2)}c_j$$

To analyse the convergence, we look at the coefficents at large ρ, where large j dominates.

$$c_{j+1} \approx \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j$$

Writing c_j in terms of c_0 and j:

$$c_j \approx \frac{2^j}{j!}c_0$$

Then,

$$v(\rho) \approx c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!}\rho^j = c_0 e^{2\rho}$$

But,

$$u(\rho) = c_0 \rho^{\ell+1} e^{-\rho} e^{2\rho}$$

blows up at large ρ.Since the series diverge for large values of ρ, the series must terminate. There must be some integer N such that

$$c_{j_{\max}} \neq 0 \wedge c_{j>j_{\max}} = 0$$

This leads us to require that

$$c_{j_{\max}+1} = \frac{2(j_{\max}+\ell+1)-\rho_0}{(j_{\max}+1)(j_{\max}+2\ell+2)}c_{j_{\max}} = 0$$

which holds given

$$0 = 2(j_{\max}+\ell+1)-\rho_0$$

$j_{\max}$ is called the **Radial quantum number**.

- $v(\rho)$ is a polynomial of order $j_{\max}$, so it has $j_{\max}$ roots
- The radial wave function has $j_{\max}$ nodes

Imposing that the series must terminate (to satisfy a vanishing boundary condition) leads to quantization of ρ_0, which represents the energy of the system.

Recall the definition of ρ_0:

$$2n = \frac{e^2 Z}{4\pi\epsilon_0}\frac{2m}{\hbar^2\kappa}$$

we can isolate κ:

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} = \frac{e^2 Z}{4\pi\epsilon_0}\frac{m}{\hbar^2 n}$$

from which we can solve for E. The quantity

$$\frac{me^2 Z}{4\pi\epsilon_0\hbar^2} = \frac{1}{a} \implies \kappa = \frac{1}{an}$$

is inverse of the **Bohr radius** of the system. When $Z = 1$, in the case of hydrogen,

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \text{ Angstroms} = 53 \text{ pm}$$

- If we increase the proton's electric charge by factor of Z, the Bohr radius decrease by a factor of Z due to stronger attraction
- This is the maximum of the radial probability density function of ground state hydrogen

Energy quantization: Let $n = j_{\max} + \ell + 1$

$$E_n = \frac{-m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{Z^2}{n^2} = \frac{-\hbar^2}{2ma}\frac{Z^2}{n^2} \approx (-13.6 \text{ eV})\frac{Z^2}{n^2}$$

The quantity

$$\frac{-m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = \frac{-\hbar^2}{2ma} = -13.6 \text{ eV}$$

is the amount of energy we need to ionize a hydrogen atom with the electron in its ground state, called the **binding energy**

- Increasing the charge of proton by a factor Z increases the binding energy of the electron by a factor Z^2
- One power of Z comes from increased columb attraction
- One power comes from decreased Bohr radius

Construction of wave functions

Solutions of the radial equation depends on both ℓ and E. But since E is described by n, we denote the solution to the relative position (or radial) equation by $R_{n\ell}$, instead of $R_{E\ell}$.

Quantum numbers of hydrogen atom: The complete solution,

$$|n,\ell,m\rangle \mapsto \psi_{n\ell m}(r,\theta,\phi) \propto R_{n\ell}(r)Y_\ell^m(\theta,\phi)$$

is described by

- Principal quantum number: $n = j_{\max} + \ell + 1, n \in [1,\infty)$
- Angular momentum quantum number: $\ell \in [0, n-1]$
- Magnetic quantum number: $m \in [-\ell, \ell]$

- Commonly, $\ell = 0, 1, 2, 3$ are also refered to as the s,p,d,f states.

For the ground state, $v(\rho)$ terminates after $j_{\max} = 0$, so $n = 1$. Since $n = 1 = 0 + \ell + 1$, ℓ can only be 0. The radial wave function

$$R_{10} = \frac{u}{r} = e^{-\kappa r}\kappa c_0 = \frac{c_0}{a}e^{-r/a}$$

Normalization:

$$\int_0^\infty r^2|R_{10}|^2\,dr = \frac{c_0}{a}\int_0^\infty r^2 e^{-2r/a}\,dr$$

Using the Leibniz rule, we can find the normalization constant for R_{10}. We already computed the all spherical harmonics with their normalizations. So

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$$

For any combination of $n\ell m$ quantum numbers, we can find $R_{n\ell}$ up to its normalization constant, by

$$R_{n\ell} \propto \frac{1}{r}e^{-\kappa r}(\kappa r)^{\ell+1}\sum_{j=0}^{j_{\max}} c_j(\kappa r)^j$$

where by setting $\rho_0 = 2n$,

$$c_{j+1} = \frac{2(j+\ell+1-n)}{(j+1)(j+2\ell+2)}c_j$$

Orthogonality: The orthogonality of wave functions:

$$\langle n,\ell,m|n',\ell',m'\rangle = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}$$

- Orthogonality stems from the orthogoality of spherical harmonics

Orthogonality of radial wave functions: When $\ell = \ell'$, and $n \neq n'$, we can conclude

$$\int_0^\infty R_{n\ell}^* R_{n'\ell} r^2\,dr = 0$$

If $\ell \neq \ell'$ and $n \neq n'$, we cannot draw such conclusions.

Behaviour at infinity

For large r, $R_{n\ell}$ behaves like

$$R_{n\ell} \approx e^{-r/an}$$

The electron is well localized within a distance a from the proton for $n = 1$, and spreads out for larger values of n.

The spectrum of hydrogen

Degeneracy: For every n, there are $n-1$ possible values of ℓ. For Every ℓ, there are $2\ell+1$ possible values of m. The electron can have spin quantum $\pm(1/2)$. So the degeneracy at E_n is

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

If we also accounted for the spin of the proton, then $d(n) = 4n^2$.

When perturbed, the hydrogen atom can absorb energy and become excited, or release energy and transition to closer to the ground state.

Such perturbations always present, and are called **quantum jumps**.

The energy of the photon released from the electron transitioning from n_i to n_f is

$$E_\gamma = E_i - E_f = -13.6 \text{ eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Complete classification

Up to this point, our complete classification of an eigenstate is

$$\left|n, \ell, m, s = \frac{1}{2}, s_z\right\rangle \propto R_{n\ell} Y_\ell^m \underline{\chi}$$

where $s = 1/2$ is the spin of the electron. They correspond to the operators

$$\hat{H}, \hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$$

which are all compatible with each other.

Spin-orbit inteaction is the interaction between the "orbital and spin magnetic moments"

$$\begin{aligned}\hat{H}_{\text{so}} &\propto -\frac{\underline{\mu}_L \cdot \underline{\mu}_s}{r^3} \propto -\text{const}\ \underline{S} \cdot \underline{L} \\ &\propto -\text{const}\ \left(S_x L_x + S_y L_y + S_z L_z\right)\end{aligned}$$

Total Hamiltonian: Accounting for spin-orbit interactions results in the total Hamiltonian,

$$\hat{H}_{\text{tot}} = \frac{\hat{p}^2}{2m} + V_{\text{eff}}(r) + \hat{H}_{\text{so}}$$

where $\hat{p}$ is relative momentum operator, and m is the reduced mass (effectively, the electron mass).

A quantum number is "good" when their associated operators commute with the total Hamiltonian:

- n is a good quantum number; The original Hamiltonian commute with both S and L
- ℓ is a good quantum number
- m is not a good quantum number; L_z does not commute with H_{so}
- s is a good quantum number
- s_z is not a good quantum number

m is not a good quantum number:

$$\begin{aligned}\left[L_z, H_{\text{total}}\right] &\propto \left[L_z, H_{\text{so}}\right] \\ &\propto \left[L_z, S_x L_x + S_y L_y + S_z L_z\right] \\ &\propto S_x i\hbar L_y - S_y i\hbar L_x + 0 \\ &= i\hbar\left(S_x L_y - S_y L_x\right)\end{aligned}$$

s_z is not a good quantum number:

$$\begin{aligned}\left[S_z, H_{\text{total}}\right] &\propto \left[S_z, H_{\text{so}}\right] \\ &\propto \left[S_z, S_x L_x + S_y L_y + S_z L_z\right] \\ &\propto L_x i\hbar S_y - L_y i\hbar S_x + 0 \\ &= i\hbar\left(L_x S_y - L_y S_x\right)\end{aligned}$$

Total angular momentum operators:

$$\begin{aligned}\hat{\underline{J}} &= \hat{\underline{L}} + \hat{\underline{S}} \\ \hat{J}^2 &= \hat{\underline{L}}^2 + \hat{\underline{S}}^2 + 2\underline{L} \cdot \underline{S}\end{aligned}$$

- $\left[J_i, J_j\right] = i\hbar\epsilon_{ijk} J_k$
- And

$$\left[J^2, J_z\right] = \left[H_{\text{so}}, J_z\right] = \left[H_{\text{tot}}, J^2\right] = \left[J^2, L^2\right] = \left[J^2, S^2\right] = 0$$

Consider

$$\begin{aligned}\left[J_x + J_y\right] &= \left[L_x + S_x, L_y + S_y\right] \\ &= \left[L_x, L_y\right] + \left[S_x, S_y\right] \\ &= i\hbar L_z + i\hbar S_z \\ &= i\hbar J_z\end{aligned}$$

$$\left[J^2, J_z\right] = \left[\hat{\underline{L}}^2 + \hat{\underline{S}}^2 + 2\underline{L} \cdot \underline{S}, L_z + S_z\right]$$

Certainly, L^2 and S^2 commute with L_z and S_z. The only term to check is

$$\begin{aligned}\left[\underline{L} \cdot \underline{S}, L_z\right] + \left[\underline{L} \cdot \underline{S}, S_z\right] &= \left[L_x S_x + L_y S_y + L_z S_z, L_z\right] \\ &+ \left[L_x S_x + L_y S_y + L_z S_z, S_z\right] \\ &= -S_x i\hbar L_y + S_y i\hbar L_x - L_x i\hbar S_y + L_y i\hbar S_x \\ &= i\hbar\left(-S_x L_y + S_y L_x - L_x S_y + L_y S_x\right) \\ &= i\hbar\left(\left[S_y, L_x\right] + \left[L_y, S_x\right]\right) \\ &= 0\end{aligned}$$

Which implies that

$$\left[\underline{L} \cdot \underline{S}, L_z\right] + \left[\underline{L} \cdot \underline{S}, S_z\right] \propto \left[H_{\text{so}}, J_z\right] = 0$$

The new classification, accounting for spin-orbit interaction, is

$$|n, \ell, s, J, J_z\rangle$$

Total degeneracy at each n is unchanged under this new classification.

Addition of angular momenta

Two spin 1/2 particles at rest: We say that all spin operators of particle 1 commute with particle 2.

$$\left[S_i^{(1)}, S_j^{(2)}\right] = \left[\left(S^{(1)}\right)^2, \left(S^{(2)}\right)^2\right] = 0$$

Total spin operators:

$$\begin{aligned}\underline{S}^{\text{tot}} &= \underline{S}^{(1)} + \underline{S}^{(2)} \\ \left(S^{\text{tot}}\right)^2 &= \left(\underline{S}^{(1)}\right)^2 + \left(\underline{S}^{(2)}\right)^2 + 2\underline{S}^{(1)} \cdot \underline{S}^{(2)} \\ S_\pm^{\text{tot}} &= S_\pm^{(1)} + S_\pm^{(2)}\end{aligned}$$

The total spin operators follow the same algebra as the conventional spin operators.

$$\begin{aligned}\left[S_i^{\text{tot}}, S_j^{\text{tot}}\right] &= i\hbar\epsilon_{ijk} S_k^{\text{tot}} \\ \left[\left(S^{\text{tot}}\right)^2, S_i^{\text{tot}}\right] &= 0\end{aligned}$$

We can verify that

$$2\underline{S}^{(1)} \cdot \underline{S}^{(2)} = 2S_z^{(1)} S_z^{(2)} + S_+^{(1)} S_-^{(2)} + S_-^{(1)} S_+^{(2)}$$

Each particle can either be spin $\uparrow$ or $\downarrow$. We define the composed state of the two particles by

$$|\uparrow;\uparrow\rangle = |\uparrow\rangle^{(1)} \otimes |\uparrow\rangle^{(2)}$$

where $\otimes$ denotes the **direct product**.

- All operators are either applied to particle 1 or particle 2

There are 4 possible combinations s_z for the two spin 1/2 particles

$$\begin{aligned}|\uparrow;\uparrow\rangle &= \left|\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\right\rangle && s_z^{(1)} + s_z^{(2)} = 1 \\ |\uparrow;\downarrow\rangle &= \left|\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{-1}{2}\right\rangle && s_z^{(1)} + s_z^{(2)} = 0 \\ |\downarrow;\uparrow\rangle &= \left|\frac{1}{2}, \frac{-1}{2}; \frac{1}{2}, \frac{1}{2}\right\rangle && s_z^{(1)} + s_z^{(2)} = 0 \\ |\downarrow;\downarrow\rangle &= \left|\frac{1}{2}, \frac{-1}{2}; \frac{1}{2}, \frac{-1}{2}\right\rangle && s_z^{(1)} + s_z^{(2)} = -1\end{aligned}$$

The action of $S_z^{\text{tot}} = S_z^{(1)} + S_z^{(2)}$ on $\left|s_z^{(1)}; s_z^{(2)}\right\rangle$ is as the there were only a single particle with $s_z = s_z^{(1)} + s_z^{(}2)$

$$S_z^{\text{tot}}\left|s_z^{(1)}; s_z^{(2)}\right\rangle = \hbar\left(s_z^{(1)} + s_z^{(2)}\right)|\uparrow,\uparrow\rangle$$

For example,

$$\begin{aligned}S_z^{\text{tot}} &= S_z^{(1)} + S_z^{(2)} \\ &= S_z^{(1)} \otimes \mathbb{I}^{(2)} + S_z^{(2)} \otimes \mathbb{I}^{(1)}\end{aligned}$$

acting on the state $|\uparrow,\uparrow\rangle$ is

$$\begin{aligned}S_z^{\text{tot}}|\uparrow;\uparrow\rangle &= \left(S_z^{(1)} + S_z^{(2)}\right)|\uparrow\rangle^{(1)} \otimes |\uparrow\rangle^{(2)} \\ &= \left(S_z^{(1)} \otimes \mathbb{I}^{(2)} + S_z^{(2)} \otimes \mathbb{I}^{(1)}\right)|\uparrow\rangle^{(1)} \otimes |\uparrow\rangle^{(2)} \\ &= \frac{\hbar}{2}|\uparrow\rangle^{(1)} \otimes |\uparrow\rangle^{(2)} + \frac{\hbar}{2}|\uparrow\rangle^{(2)} \otimes |\uparrow\rangle^{(1)} \\ &= \hbar\,|\uparrow\rangle^{(1)} \otimes |\uparrow\rangle^{(2)}\end{aligned}$$

If we are to treat the two particle system together, it appears as if we have a single spin 1 particle, but we have an additional $s_z = 0$ state which is not represent in a regular spin 1 particle.

If we apply

$$S_-^{\text{tot}} = S_-^{(1)} + S_-^{(2)}$$

to the state $|\uparrow;\uparrow\rangle$.

$$\begin{aligned}S_-^{\text{tot}}|\uparrow;\uparrow\rangle &= S_-^{(1)}|\uparrow;\uparrow\rangle + S_-^{(2)}|\uparrow;\uparrow\rangle \\ &= \hbar\left(|\downarrow;\uparrow\rangle + |\uparrow;\downarrow\rangle\right)\end{aligned}$$

This allows us to interpret the states:

$$|1,1\rangle = |\uparrow;\uparrow\rangle$$
$$|1,0\rangle = \frac{1}{\sqrt{2}}\left(|\downarrow;\uparrow\rangle + |\uparrow;\downarrow\rangle\right)$$
$$|1,-1\rangle = |\downarrow;\downarrow\rangle$$

as if we have a single particle of spin quantum number $s = 1$. These are call the **triplet states**.

There were 4 possible combinations of $\uparrow, \downarrow$ among the two particles. There is a missing state. Since

Different quantum numbers: states with different quantum numbers must be orthogonal

The last state, call the **singlet state**, $|0,0\rangle$, must be orthogonal to all the triplet states.

$$\langle s=0, s_z=0 | s=1, s=\pm 1, 0\rangle = 0$$

We say that

$$|0,0\rangle = a\,|\uparrow;\downarrow\rangle + b\,|\downarrow;\uparrow\rangle$$

We can find the relationships between a and b by

$$\langle 1,0|0,0\rangle = \frac{a}{\sqrt{2}}\langle\uparrow;\downarrow|\uparrow;\downarrow\rangle + \frac{b}{\sqrt{2}}\langle\uparrow;\downarrow|\uparrow;\downarrow\rangle = 0$$

implying

$$a + b = 0$$

Accounting also for normalization

$$|0,0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow;\downarrow\rangle - |\downarrow;\uparrow\rangle\right)$$

Maximum and minimum total spins: The total spin cannot be greater than the sum of the individual spins. The minimum spin cannot be less than the difference between the two spins.

$$S_{\max} = \left|S^{(1)} + S^{(2)}\right|$$
$$S_{\min} = \left|S^{(1)} - S^{(2)}\right|$$

Clebsch–Gordan coefficients: For two particles of arbitrary spins s_1, s_2 and m_1, m_2, the combined state is given by

$$|S, M\rangle = \sum_{m_1+m_2=M} C^{s_1 s_2 s}_{m_1 m_2 m}\,|s_1, m_2\rangle \otimes |s_2, m_2\rangle$$

Electromagnetic interactions

Recall the magnetic vector potential, $\underline{A}$, such that

$$\underline{B} = \underline{\nabla} \times \underline{A}$$

and we define a new scalar potential φ, such that

$$\underline{E} = -\underline{\nabla}\varphi - \frac{\partial \underline{A}}{\partial t}$$

EM-Field Hamiltonian Operator: A particle of charge q and momentum $\underline{p}$ is

$$\hat{H} = \frac{1}{2m}\left(-i\hbar\underline{\nabla} - q\underline{A}\right)^2 - q\varphi$$

We substituted $\underline{p}$ for the quantum momentum operator, $-i\hbar\underline{\nabla}$ results in the quantum Hamiltonian. This is called the **minimal coupling rule** since the fields themselves are not quantized.

Landau Levels

Consider:

$$\underline{A} = \frac{B_0}{2}\begin{bmatrix}-y & x & 0\end{bmatrix} \qquad \varphi = Kz^2$$

Where B_0 has units of Tesla, and K has units of V/m^2.

We can verify that

$$\underline{E} = -2Kz\hat{\underline{k}} \qquad [\text{V/m; N/C}]$$

and

$$\underline{B} = B_0\hat{\underline{k}} \qquad [\text{T; N/(A·m)}]$$

The time independent equation is

$$\frac{1}{2m}\left(-\hbar\underline{\nabla} - q\underline{A}\right)^2\psi + q\varphi\psi = E\psi$$

Expanding:

$$\frac{-\hbar^2}{2m}\nabla^2\psi + \frac{iq\hbar}{2m}\left(\underline{\nabla}\cdot(\underline{A}\psi) + \underline{A}\cdot(\underline{\nabla}\psi)\right) + \frac{q^2}{2m}A^2\psi + q\varphi\psi = E\psi$$

To simplify the equation, we consider the vector identity:

$$\underline{\nabla}\cdot(\underline{A}\psi) = (\underline{\nabla}\cdot\underline{A})\,\psi + \underline{A}\cdot(\underline{\nabla}\psi)$$

Explicit computation of $\underline{\nabla}\cdot\underline{A}$, $\underline{A}\cdot(\underline{\nabla}\psi)$, A^2, gives

$$\frac{-\hbar^2}{2m}\nabla^2\psi + \frac{iq\hbar}{2m}B_0\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\psi + \frac{(qB_0)^2}{8m}\left(x^2+y^2\right) + qKz^2 = E\psi$$

Recall that the z-orbital angular momentum operator

$$\hat{L}_z = xp_y - yp_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

One can verify that L_z commutes with H. This allows us to replace the operator with its eigenvalue $\hbar\overline{m}$. Rearraning,

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + \frac{(qB_0)^2}{8m}\left(x^2+y^2\right) + qKz^2\right)\psi = \left(E + \frac{qB_0\hbar}{2m}\overline{m}\right)\psi$$

We define two frequencies:

$$\omega_1 = \frac{qB_0}{m}$$
$$\omega_2 = \sqrt{\frac{2Kq}{m}}$$

Since B_0 has units N/(A · s) which is equal to kg/(C· s), when we multiply B_0 by q/m the units become $1/s$. ω_1 is also the classical cyclotron orbit frequency.

Since 1 V is equivalent to 1 (N·m)/C, Kq/m has units of $1/s^2$.and substitute for the cylindrical Laplacian.

$$\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\phi^2} + \frac{\partial^2\psi}{\partial z^2}\right) + \left(\frac{1}{8}m\omega_1^2\left(x^2+y^2\right) + \frac{1}{2}m\omega_2^2z^2\right)\psi = \left(E + \frac{qB_0\hbar}{2m}\overline{m}\right)\psi$$

In cylindrical coordinates, L_z has representation $-i\hbar\partial/\partial\phi$. So

$$\frac{\partial^2}{\partial\phi^2}\psi = -\frac{1}{\hbar^2}L_z^2\psi = -\overline{m}^2\psi$$

To solve the equation, we used the method of separation of variables, $\psi = R(r)\Phi(\phi)Z(z)$. This gives two equations as the $\Phi(\phi)$ factor vanishes.

$$\frac{-\hbar^2}{2m}\left(\frac{1}{r}\frac{d}{dr}\left(r\frac{dR}{dr}\right) - \frac{\overline{m}^2}{r^2}R\right) + \frac{1}{8}m\omega_1^2r^2R = E_rR$$
$$\frac{-\hbar^2}{2m}\frac{d^2Z}{dz^2} + \frac{1}{2}m\omega_2^2z^2Z = E_zZ$$

where

$$E = E_r + E_z - \frac{1}{2}\overline{m}\hbar\omega_1$$

The z-equation is a 1D harmonic oscillator. The R equation turns out to be a 2D harmonic oscillator.

The result is that the total energy is

$$E = \left(n_1 + \frac{1}{2}\right)\hbar\omega_1 + \left(n_2 + \frac{1}{2}\right)\hbar\omega_2$$

Landau Levels: An electron moving the xy-plane, with a uniform magnetic field pointing in the z-direction undergoes cyclotron motion. The electron's energy is discretized into Landau levels:

$$E_{n_1} = \hbar\frac{qB_0}{m}\left(n_1 + \frac{1}{2}\right)$$

where qB_0/m is the classical cyclotron frequency.

Identical particles

Two-particle systems

The wave function depends on both the position of particle one and particle two:

$$\Psi(\underline{r}_1, \underline{r}_2, t)$$

The potential energy of the particles are encoded by

$$V(\underline{r}_1, \underline{r}_2, t)$$

The Hamiltonian is

$$\hat{H} = \frac{-\hbar^2}{2m_1}\underline{\nabla}_1^2 - \frac{-\hbar^2}{2m_2}\underline{\nabla}_2^2 + V(\underline{r}_1, \underline{r}_2, t)$$

The probability to find particle one in volume $d^3\underline{r}_1$ and particle two in volume $d^3\underline{r}_2$ is given by

$$|\Psi(\underline{r}_1, \underline{r}_2, t))|\, d^3\underline{r}_1\, d^3\underline{r}_2$$

Non-interacting: the potential energy can be written as a sum of two potential energies.

$$V(\underline{r}_1, \underline{r}_2, t) = V_1(\underline{r}_1) + V_2(\underline{r}_2)$$

The time-independent equation can be separated into two one-particle equations.

$$\psi(\underline{r}_1, \underline{r}_2) = \psi_a(\underline{r}_1)\psi_b(\underline{r}_2)$$

The total energy $E = E_1 + E_2$. A superposition of non-interacting, two particle wave-functions is an example of entanglement.

$$\Psi(\underline{r}_1, \underline{r}_2, t) = \frac{3}{5}\Psi_a(\underline{r}_1, t)\Psi_b(\underline{r}_2, t) + \frac{4}{5}\Psi_c(\underline{r}_1, t)\Psi_d(\underline{r}_2, t)$$

For particle one, if an energy measurement returns E_a, we know that the energy of particle two must be E_b. If an energy measurement returns E_c, we know that the energy of particle two must be E_d.

Central potential: If the potential energy depends only on the distance between the two particle, arrive at the classical two-body problem.

Bosons and Fermions

Two non-interacting particles that belong to the same "class" (i.e. two electrons, two protons. . .) cannot be distinguished.

Boson: particle with integer spins, including 0 (photon, higgs boson)

Fermion: particle with half-integer spins (electron)

Since there is no way to tell between identical particles, the most general way to construct a single state possible state of the two particles is

$$\psi_\pm(\underline{r}_1, \underline{r}_2) = A\left(\psi_a(\underline{r}_1)\psi_b(\underline{r}_2) \pm \psi_b(\underline{r}_2)\psi_a(\underline{r}_1)\right)$$

- No commitment to which particle is in which state (a or b)
- Choose ψ_+ when both particles are Bosons. This is **symmetric** under interchange

$$\psi_+(\underline{r}_1, \underline{r}_2) = \psi_+(\underline{r}_2, \underline{r}_1)$$

- Choose ψ_- when both particles are fermions. This is **anti-symmetric** under interchange

$$\psi_-(\underline{r}_1, \underline{r}_2) = -\psi_-(\underline{r}_2, \underline{r}_1)$$

Pauli exclusion principle: Two identical fermions cannot occupy the same quantum state.

When $\psi_a = \psi_b$, then $\psi_- = 0$. But if we also account for spin, then the story can be different.

Exchange forces

Consider two distinguishable particles. Suppose particle one is in state ψ_a, and particle two is in state ψ_b. The two states are normalized and orthogonal. The combined wave function is

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2)$$

But if they are identical particles, then

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\psi_a(x_1)\psi_b(x_2) \pm \psi_b(x_1)\psi_a(x_2)\right)$$

Depending on whether the particles are distinguishable, consider

$$\left\langle (x_1 - x_2)^2 \right\rangle = \left\langle x_1^2 \right\rangle + \left\langle x_2^2 \right\rangle - 2\left\langle x_1 x_2 \right\rangle$$

If the particles are distinguishable, then

$$\left\langle (x_1 - x_2)^2 \right\rangle = \left\langle x^2 \right\rangle_a + \left\langle x^2 \right\rangle_b - 2\left\langle x \right\rangle_a \left\langle x \right\rangle_b$$

Our result holds even if particle one were in state b, and particle two were in state a.

If the particles are identical, then

$$\begin{aligned}\left\langle x_1^2 \right\rangle &= \frac{1}{2}\left(\langle ab|\, x_1^2\, |ab\rangle + \langle ba|\, x_1^2\, |ba\rangle\right) \\ &\pm \frac{1}{2}\left(\langle ba|\, x_1^2\, |ab\rangle + \langle ab|\, x_1^2\, |ba\rangle\right) \\ &= \frac{1}{2}\left(\langle x_1^2\rangle_a + \langle x_1^2\rangle_b\right) = \frac{1}{2}\left(\langle x^2\rangle_a + \langle x^2\rangle_b\right)\end{aligned}$$

The terms $\langle ba|\, x_1^2\, |ab\rangle + \langle ab|\, x_1^2\, |ba\rangle$ vanish since $\psi_a(x)$ and $\psi_b(x)$ are orthogonal. Similarly, we must have

$$\left\langle x_2^2 \right\rangle = \frac{1}{2}\left(\langle x_2^2\rangle_a + \langle x_2^2\rangle_b\right) = \frac{1}{2}\left(\langle x^2\rangle_a + \langle x^2\rangle_b\right)$$

And

$$\begin{aligned}\langle x_1 x_2\rangle &= \frac{1}{2}\left(\langle ab|\, x_1 x_2\, |ab\rangle + \langle ba|\, x_1 x_2\, |ba\rangle\right) \\ &\pm \frac{1}{2}\left(\langle ba|\, x_1 x_2\, |ab\rangle + \langle ab|\, x_1 x_2\, |ba\rangle\right) \\ &= \frac{1}{2}\left(\langle x_1\rangle_a \langle x_2\rangle_b + \langle x_1\rangle_b \langle x_2\rangle_a\right) \\ &\pm \frac{1}{2}\left(\langle x_1\rangle_{ba} \langle x_2\rangle_{ab} + \langle x_1\rangle_{ab} \langle x_2\rangle_{ba}\right) \\ &= \langle x\rangle_a \langle x\rangle_b \pm |\langle x\rangle_{ba}|^2\end{aligned}$$

Thus,

$$\begin{aligned}\left\langle (x_1 - x_2)^2 \right\rangle_\pm &= \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a \langle x\rangle_b \mp |\langle x\rangle_{ba}|^2 \\ &= \left\langle (x_1 - x_2)^2 \right\rangle \mp |\langle x\rangle_{ba}|^2\end{aligned}$$

Exchange force: purely quantum mechanical phenomena that occurs when the wave functions of two identical, non-interacting fermions/bosons overlap. Due to $\langle x\rangle_{ba} \neq 0$.
Bosons tend to be attracted towards each other, and fermions tend pushed apart.

Slater determinant: used construct non-interacting fermion wave functions, which are anti-symmetric under pairwise exchange of coordinates. For N particles:

$$\psi_-\left(\underline{r}_1, \ldots, \underline{r}_N\right) = \frac{1}{\sqrt{N!}}\det\begin{bmatrix}\psi_1(\underline{r}_1) & \cdots & \psi_N(\underline{r}_1) \\ \vdots & \ddots & \vdots \\ \psi_N(\underline{r}_1) & b & \psi_N(\underline{r}_N)\end{bmatrix}$$

Permanent: used construct non-interacting boson wave functions, which are symmetric under pairwise exchange of coordinates. The Permanent is evaluated like the determinant, but without the negative signs.

Spin

A more accurate description of particles also account for their spins. Assuming **no spin-position coupling**.

The condition for boson and fermion wave functions of non-interacting identical particles must also account for the spins of the particles.

- If the particles bosons,

$$\psi\left(\underline{r}_1, \underline{r}_2\right)\chi(1, 2) = \psi\left(\underline{r}_2, \underline{r}_1\right)\chi(2, 1)$$

- If the particles fermions,

$$\psi\left(\underline{r}_1, \underline{r}_2\right)\chi(1, 2) = -\psi\left(\underline{r}_2, \underline{r}_1\right)\chi(2, 1)$$

For two Fermions of spin $1/2$, recall the singlet wave function:

$$|0, 0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow;\downarrow\rangle - |\downarrow;\uparrow\rangle\right)$$

But $|0, 0\rangle$ is anti-symmetric under interchange. So we require the tensor product wave function to be symmetric, so that the total wave function is anti-symmetric.

As long as the particle are in different spin states, the particles are allowed to be in the same position state, without violating Pauli's exclusion principle.

Generalized symmetrization principle

We define the **exchange operator**, $\hat{P}$ with the property that it interchanges two, **identical, non-interacting, spin-position decoupled** particles.

- It is unitary, in that $\hat{P}^2 = 1$
- It has eigenvalues ± 1
- It commutes with the Hamiltonian

Since it commutes with the Hamiltonian, and has no explicit time dependence, the Generalized Ehrenfest theorem tells us that

$$\frac{d}{dt}\langle \hat{P} \rangle = 0$$

This means that the symmetry/anti-symmetry of the eigenstate is preserved.

Atoms

A neurtral atom of atomic number Z has Z electrons, Z protons, and Z neutrons. Assuming a stationary nucleus, the Hamiltonian is

$$\hat{H} = \sum_{j=1}^{Z}\left(\frac{-\hbar^2}{2m}\underline{\nabla}_j^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_j}\right) + \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{j\neq k}^{Z}\frac{e^2}{\|\underline{r}_j - \underline{r}_k\|}$$

- The first sum is the total Hamiltonian of Z non-interacting electrons in the electric field of the nucleus
- The second sum accounts for mutual repulsion of the electrons

Solids

In a solid, valence electrons become free to roam and are subjected to the combined potential of the entire crystal lattice. We consider two models

1. Sommerfeld's free electron gas model: ignore all forces, except at the boundary of the crystal - free electrons in a 3D box
2. Bloch's theory: ignores electron-electron repulsion; but introduces a periodic potential to account for electron-nucleus attraction

The free electron gas/Fermi gas

The characteristic potential:

$$V(\underline{r}) = \begin{cases} 0 & x \in \Omega \\ \infty & x \notin \Omega \end{cases}$$

where Ω is the space taken up by a perfect crystal with dimensions l_x, l_y, l_z.

The time-independent equation is

$$\frac{-\hbar^2}{2m}\underline{\nabla}^2\psi = E\psi$$

Similar to the free particle, we get one sinusoidal solutions for each x, y, z. The only difference is that we also require

$$X(0) = X(l_x) = 0$$
$$Y(0) = Y(l_y) = 0$$
$$Z(0) = Z(l_z) = 0$$

which leads to

$$X(x) = A_x \sin(k_x x)$$
$$Y(y) = A_y \sin(k_y y)$$
$$Z(z) = A_z \sin(k_z z)$$

where

$$k_j = \frac{\sqrt{2mE_j}}{\hbar} \qquad j = 1, 2, 3$$

and

$$k_j l_j = n_j \pi \qquad n_j \in [1, 2, \dots]$$

$X(0) = Y(0) = Z(0) = 0$ made the cosine term vanish. The restrictions on k_j comes from $X(l_x) = Y(l_y) = Z(l_z) = 0$. Like the 1D problem, we neglect when $n_j \leq 0$.

Requiring that X, Y, Z are individually normalized, the general solution becomes

$$|n_x, n_y, n_z\rangle = \sqrt{\frac{8}{l_x l_y l_z}}\sin\left(\frac{n_x \pi x}{l_x}\right)\sin\left(\frac{n_y \pi y}{l_y}\right)\sin\left(\frac{n_z \pi z}{l_z}\right)$$

And the energy is

$$\begin{aligned} E &= E_x + E_y + E_z \\ &= \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right) \\ &= \frac{\hbar^2\|\underline{k}\|^2}{2m} \end{aligned}$$

The existence of boundary conditions led to the quantization of the wave vector, and so the energy, too.

When we generalize our system to involve N atoms (on the order of 10^{23}), and each atom contributes d electrons, its useful to think of **k-space**. In k-space, three orthogonal axes respectively represent k_x, k_y, k_z.

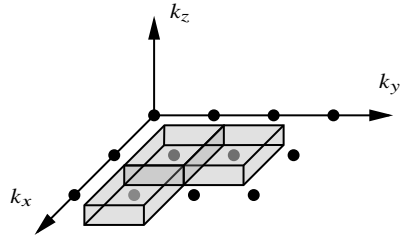
Pauli's exclusion principle tells us that no two fermions can be in the same quantum state. Considering spin, this means that at most two electrons can have same position wave function.

Since $\underline{k}$ is quantized, k-space is a discrete set of points. Each point defines a unique position wave function.

Each pair of electrons with the same $|n_x, n_y, n_z\rangle$ takes up a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$$

in k-space. (This way, k-space is filled.)



If electrons were bosons, or are distinguishable, they would all be in ground state, assuming little thermal excitation or disturbances.

But since electrons are fermions, the Nd electrons will start in ground state, and fill up increasing excited states until the electrons are exhausted.

In k-space, the electrons would take up an eighth of a sphere in octant I.

The total volume in k-space taken up by Nd electrons is

$$\frac{Nd}{2}\frac{\pi^2}{V} = \frac{1}{8}\left(\frac{4}{3}\pi k_F^3\right)$$

Solving for k_F,

$$k_F = \left(3\rho\pi^2\right)^{1/3}$$

and where ρ is the **free electron density**

$$\rho = \frac{Nd}{V}$$

the number of electrons per unit volume.

The surface which separates the occupied and unoccupied states in k-space is called the **Fermi surface**. When $k = k_F$, the associated energy is the **Fermi energy**

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

To find the total energy of the electrons, we first consider the volume of $1/8$ of a spherical shell of thickness dk.

$$\frac{1}{8}\int_k^{k+dk}\int_0^{\pi}\int_0^{2\pi} r^2\sin(\theta)\,d\phi\,d\theta\,dr$$

which gives

$$\begin{aligned} &= \frac{4\pi}{3\cdot 8}\left((k+dk)^3 - k^3\right) \\ &= \frac{4\pi}{3\cdot 8}\left(3k^2\,dk + 3k\,(dk)^2 + (dk)^3\right) \end{aligned}$$

The volume of a thin shell can be found by keeping only the term linear in dk.The volume of the shell in k-space is

$$\frac{4\pi}{8}k^2\,dk = \frac{\pi k^2\,dk}{2}$$

Since each pair of electrons occupy a volume of π^3/V, the number of electrons in the thin shell is given by

$$2\frac{\pi k^2\,dk}{2}\frac{V}{\pi^3} = \frac{Vk^2\,dk}{\pi^2}$$

The factor of 2 in front comes from the fact that two electrons can have the same position wave function, as long as they have different spins.

The total energy in the shell is

$$dE = \frac{\hbar^2 k^2}{2m}\frac{Vk^2\,dk}{\pi^2}$$

Integrating from $k = 0$ up to the Fermi surface gives the total energy of the free electrons.

$$\begin{aligned} E_{\text{tot}} &= \frac{\hbar^2 V}{2m\pi^2}\int_0^{k_F} k^4\,dk \\ &= \frac{\hbar^2 V}{2m\pi^2}\frac{k_F^5}{5} \\ &= \frac{\hbar^2 V}{10m\pi^2}\left(\frac{3Nd\pi^2}{V}\right)^{5/3} \\ &= \frac{\hbar^2\left(3\pi^2 Nd\right)^{5/3}}{10m\pi^2}V^{-2/3} \end{aligned}$$

The total energy is inversely proportional to the volume of the crystal.

$$\frac{dE_{\text{tot}}}{dV} = \frac{-2}{3}\frac{E_{\text{tot}}}{V}$$

The energy of the free electrons decrease when the volume of the crystal increases, while keeping the number of atoms and free electrons constant. But work must be done to cause the crystal volume to increase. This must be equal to the decrease in energy of the electron gas.

We can interpret

$$-\frac{dE_{\text{tot}}}{dV} = P = \frac{2E_{\text{tot}}}{3V}$$

The electrons applies a pressure to the boundary of the infinite potential box, results in the expansion of the crystal.

Degeneracy pressure: Pauli's exclusion principle explains why Fermi gases fill up 1/8 of a sphere in k-space. The total energy of the gas decreases with increasing crystal volume, since the gas exerts a pressure on the boundaries of the crystal.

Cold solids do not simply collapse onto itself. There is a self-stablizing internal pressure that arises purely from quantum mechanics.

The free electron gas model gives no explanation to why there is a great range of conductivity seen in metals.

Its more natural to use **periodic boundary conditions** when describing electrical current as traveling plane waves (as opposed to standing waves). We require

$$\begin{aligned} \psi(x,y,z) &= \psi(x+l_x,y,z) \\ &= \psi(x,y+l_y,z) \\ &= \psi(x,y,z+l_z) \end{aligned}$$

Recall the general free particle solution.

$$\begin{aligned} \psi(\underline{r}) &= Ae^{i\underline{k}\cdot\underline{r}} \\ &= Ae^{i\left(k_x x+k_y y+k_z z\right)} \end{aligned}$$

where

$$k_j = \frac{\sqrt{2mE_j}}{\hbar}$$

Normalization

$$\int_0^{l_x}\int_0^{l_y}\int_0^{l_z}|A|^2\,dx\,dy\,dz = 1$$

Implying that $A = 1/\sqrt{l_x l_y l_z}$.

For $j = 1, 2, 3$, representing x, y, z, imposing periodicity means

$$\frac{1}{\sqrt{l_j}}e^{ik_j x_j} = \frac{1}{\sqrt{l_j}}e^{ik_j(x_j+l_j)}$$

This means that $e^{ik_j l_j} = 1$. So

$$k_j l_j = 2\pi n_j \qquad n_j \in [\ldots,-1,0,1,\ldots]$$

The solution is now

$$\psi(\underline{r}) = \frac{1}{\sqrt{l_x l_y l_z}}e^{i\underline{k}\cdot\underline{r}} = \frac{1}{\sqrt{\mathcal{V}}}e^{i\underline{k}\cdot\underline{r}}$$

where $\underline{k}$ is quantized for integers n_x, n_y, n_z, which is allowed to run negative

$$\underline{k} = \left[\frac{2\pi n_x}{l_x} \quad \frac{2\pi n_y}{l_y} \quad \frac{2\pi n_z}{l_z}\right]$$

Periodic boundary conditions result in traveling waves. When we considered the infinite well case, we could afford to neglect the negative integers since the solutions were standing waves.

In k-space, each pair of electrons now take up

$$\frac{(2\pi)^2}{l_x l_y l_z} = \frac{(2\pi)^3}{\mathcal{V}}$$

It turns out that the Fermi energy, total energy, that we found still applies. Each state occupies 8-times larger volume in k-space, k-space is also 8 times larger (all 8 octants filled). With negative integers of n allowed, the Fermi surface is a sphere as opposed to 1/8 of a sphere.

Band structure

It takes band theory of explain why there is a wide variability in the conductance of metals.

Improving on the particles in a box model, we introduce a periodic potential. All periodic potential satisify

$$V(x+a) = V(x)$$

Bloch's theorem: Solutions to the time-independent equation with a periodic potential, $V(x) = V(x+a)$, must satisfy

$$\psi(x+a) = e^{iqa}\psi(x)$$

for $q, a \in \mathbb{R}$, and both q and a are independent of x.

- $\psi(x)$ itself is not periodic
- But $|\psi(x+a)|^2 = e^{-iqa}e^{iqa}|\psi(x)|^2$, so the probability is periodic

Crystals are not infinite, but since the number atoms in a crystal is on the order of 10^{23}, we reason that edge effects are negligible when we consider electrons in the center of the crystal.

We impose the boundary condition

$$\psi(x+Na) = \psi(x)$$

so by Bloch's theorem,

$$e^{iNqa}\psi(x) = \psi(x)$$

and $e^{iNqa} = 1$ requires

$$Nqa = 2\pi n \qquad n \in \mathbb{Z}$$

By solving the equation in a single interval, say from $[0, a)$, we can use Bloch's theorem to generate solutions elsewhere.

We introduce the periodic potential:

$$V(x) = \alpha\sum_{j=0}^{N-1}\delta(x-ja)$$

We imagine the x-axis wrapping around itself, such that when $j = N-1$, the N^{th} delta function, is located at $x = -a$.

Further, the delta functions have a positive amplitude, which would suggest represent a repulsive potential.

In $0 < x < a$, $V(x) = 0$, and we find sinusoidal solutions.

$$\psi_{(0,a)}(x) = A\sin(kx) + B\cos(kx) \qquad x \in (0,a)$$

By Bloch's theorem, the wave function satisfy

$$\psi(x+a) = e^{iqa}\psi(x)$$

Rearranging,

$$\psi(x) = e^{-iqa}\psi(x+a) \qquad -a < x < 0$$

Continuity at $x = 0$ requires

$$B = e^{-iqa}\psi(a) = e^{-iqa}\left(A\sin(ka) + B\cos(ka)\right)$$

The delta function introduces a discontinuity to $d\psi/dx$. Recall that the discontinuity is equal to

$$\frac{2m}{\hbar^2}\lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}\alpha\delta(x)\psi(x)\,dx = \frac{2m\psi(0)}{\hbar^2} = \frac{2m\alpha}{\hbar^2}B$$

When $0 < x < a$:

$$\left(\frac{d\psi}{dx}\right)_{x=0} = Ak$$

When $-a < x < 0$:

$$\left(\frac{d\psi}{dx}\right)_{x=0} = e^{-iqa}k\left(A\cos(ka) - B\sin(ka)\right) + \frac{2m\alpha}{\hbar^2}B$$

So

$$Ak - e^{-iqa}k\left(A\cos(ka) - B\sin(ka)\right) = \frac{2m\alpha}{\hbar^2}B$$

and we have two equations and two unknowns A, B. From continuity,

$$\frac{B\left(e^{iqa} - \cos(ka)\right)}{\sin(ka)} = A$$

From the first derivative equation,

$$\begin{aligned} \frac{2m\alpha}{\hbar^2}B = &\frac{B\left(e^{iqa} - \cos(ka)\right)}{\sin(ka)}k \\ &- e^{-iqa}k\left(\frac{B\left(e^{iqa} - \cos(ka)\right)}{\sin(ka)}\cos(ka) - B\sin(ka)\right) \end{aligned}$$

Multiply both sides by

$$\frac{\sin(ka)}{kB}$$

Rearranging,

$$\begin{aligned}\frac{2m\alpha}{\hbar^2 k}\sin(ka) &= \left(e^{iqa} - \cos(ka)\right) \\ &- e^{-iqa}\left(\left(e^{iqa} - \cos(ka)\right)\cos(ka) - \sin^2(ka)\right) \\ &= \left(e^{iqa} - \cos(ka)\right) \\ &- e^{-iqa}\left(e^{iqa} - \cos(ka)\right)\cos(ka) + e^{-iqa}\sin^2(ka) \\ &= \left(e^{iqa} - \cos(ka)\right)\left(1 - e^{-iqa}\cos(ka)\right) \\ &+ e^{-iqa}\sin^2(ka)\end{aligned}$$

We can show that by first eliminating A, B will cancel. The resulting equation gives the possible values of k.

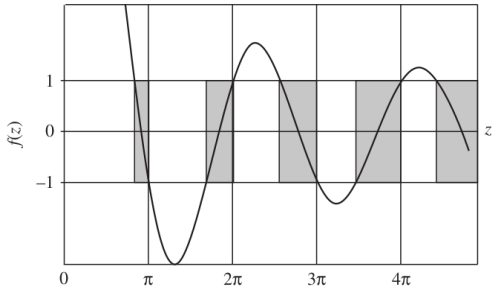
$$\cos(qa) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)$$

Let $z = ka, \beta = m\alpha a/\hbar^2$.

$$\cos\left(\frac{2\pi n}{N}\right) = f(z) = \cos(z) + \beta\frac{\sin(z)}{z}$$

- Valid values of z determines valid values of k
- β is proportional to α - the strength of the potential

Since $-1 \leq \cos(qa) \leq 1$, $f(z)$ can only take on values between -1 and 1. For a given β, we can plot $f(z)$ to see the allowed regions of z



- At large z, $f(z) \to \cos(z)$ so gaps gets thinner
- Width of gaps for the first few bands increase for larger β

The intervals of allowed values of z form **bands**, and the disallowed values are the **gaps**.

Within each band, since the argument of

$$\cos(qa) = \cos\left(\frac{2\pi n}{N}\right)$$

is quantized, this means that between the minimum and maximum values of a single band, the energies are discretized into N possible values (but N is very big, so we may as well neglect the quantization).

In practice, there are Nd free electrons. In pairs, electrons and start to fill bands, until all Nd electrons have been exhausted.

The property the material depends on how many free-electrons it can contribute. If d is

- Odd, then the top-most band that is partially filled. The material will be a **conductor** since it takes little energy to excite an electron to a higher energy level
- Even, this means that the top-most band is completely filled. The material will be a **insulator**, since it takes more energy to excite an electron to the next energy state, since it must jump over a gap

At room temperature, If $d = 1$, then the first band will be half-filled, since the first band can accommodate $2N$ electrons.

If $d = 2$, then the first band will be completely filled.

If $d = 3$, then the second band will be half-filled.

Band structure: the separation of the energy spectrum into bands and gaps when a periodic potential is present. Bands represent a group of allowed energy values. Gaps represent regions of forbidden energy values.

In three dimensions, and with more complex periodic potentials, the band structure is more complex. Such as the square comb potential used in the Kronig–Penney model.