Quantum Mechanics

Lecture notes from the third-year undergraduate course *Kvanta Mehanika* (Quantum Mechanics) given by prof. dr. Anton Ramšak at the Faculty of Mathematics and Physics at the University of Ljubljana in the academic year 2020-2021. The course covers the Copenhagen interpretation of quantum mechanics at an upper-undergraduate level. Credit for the material in these notes is due to Professor Ramšak, while the voice, typesetting, and translation to English in this document are my own.

Disclaimer: Mistakes—both simple typos and legitimate errors— are likely. Keep in mind that these are the notes of an undergraduate student in the process of learning the material himself—take what you read with a grain of salt. If you find mistakes and feel like telling me, for example by email, I'll be happy to hear from you, even for the most trivial of errors.

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1 Fundamentals of Wave Quantum Mechanics

1.1 Understanding the Schrödinger Equation

Idea: find the simplest equation the satisfies the following quantum mechanical properties:

- A particle has wave characteristics—a wavelength $\lambda = 2\pi/k$ and frequency $\nu = 2\pi/\omega$

- A particle's energy is proportional to its frequency, i.e. $E = \hbar\omega$ (e.g. photoelectric effect)

- Momentum is related to a wave vector via $\boldsymbol{p} = \hbar\boldsymbol{k}$ (de Broglie)

- A free particle has the classical energy $E = \frac{p^2}{2m}$ and thus the dispersion relation $\omega \propto k^2$

The Schrödinger equation satisfies these requirements

$$i\hbar\frac{\partial\Psi(\boldsymbol{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\boldsymbol{r},t) + V(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)$$

The potential terms accounts for a particle having energy $E = \frac{p^2}{2m} + V$ in a potential. Note that the Schrödinger equation and thus the solution Ψ are complex—we can decompose Ψ into a real and imaginary part via

$$\Psi = \Psi_{\text{Re}} + i\Psi_{\text{Im}}$$

Substituting this decomposition into the Schrödinger equation produces

$$i\hbar(\dot{\Psi}_{\text{Re}} + i\dot{\Psi}_{\text{Im}}) = -\frac{\hbar^2}{2m}(\Psi''_{\text{Re}} + i\Psi''_{\text{Im}}) + V(\Psi_{\text{Re}} + i\Psi_{\text{Im}})$$

Writing the real and imaginary parts separately gives the coupled system of real equations

$$-\hbar\dot{\Psi}_{\text{Im}} = -\frac{\hbar^2}{2m}\Psi''_{\text{Re}} + V\Psi_{\text{Re}}$$

$$-\hbar\dot{\Psi}_{\text{Re}} = -\frac{\hbar^2}{2m}\Psi''_{\text{Im}} + V\Psi_{\text{Im}}$$

Precisely this coupling leads to the desired oscillation and wavelike behavior of the wavefunction Ψ, even though the Schrödinger equation is first degree in time.

On the Diffusion Equation
Note the similarity of the Schrödinger equation to the diffusion equation

$$\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial x^2}$$

Both are first degree in time and second degree in position. The wave-like ansatz $T(x,t) \propto e^{i(kx-\omega t)}$ solves the diffusion equation with a quadratic dispersion relation

$$\omega = -iDk^2,$$

as desired. However, the energy relation requirement $E = \frac{p^2}{2m}$ holds only for $D = \frac{i\hbar}{2m} \in \mathbb{C}$, and a complex diffusion constant is non-physical. We thus reject the diffusion equation.

1.2 Probability Interpretation of the Wavefunction

- The wavefunction encodes the probability of detecting a quantum particle in a region of space. We use the wavefunction to define the probability density

$$\rho(\boldsymbol{r},t) = |\Psi(\boldsymbol{r},t)|^2$$

The probability $\mathrm{d}P$ of finding the particle in the region of space $\mathrm{d}\boldsymbol{r}$ is

$$\mathrm{d}P = \rho(\boldsymbol{r},t)\,\mathrm{d}\boldsymbol{r}$$

Logically, the probability of finding the particle somewhere in all of space V is one:

$$\int_V |\Psi(\boldsymbol{r},t)|^2\,\mathrm{d}^3\boldsymbol{r} \equiv 1.$$

The above relation is called the normalization condition on the wavefunction.

- If a wavefunction is normalized at a given point in time, we would assume it is normalized at all other times, too. We show this "conservation of normalization" by differentiating probability density with the product rule:

$$\frac{\partial \rho(\boldsymbol{r},t)}{\partial t} = \frac{\partial |\Psi(\boldsymbol{r},t)|^2}{\partial t} = \frac{\partial \Psi^*(\boldsymbol{r},t)}{\partial t}\Psi(\boldsymbol{r},t) + \frac{\partial \Psi(\boldsymbol{r},t)}{\partial t}\Psi^*(\boldsymbol{r}t)$$

We substitute in $\dot{\Psi}$ from the Schrödinger equation to get

$$\frac{\partial \rho(\boldsymbol{r},t)}{\partial t} = \left(-\frac{\hbar i}{2m}\nabla^2\Psi^*(\boldsymbol{r},t) + \frac{i}{\hbar}V^*(\boldsymbol{r},t)\Psi^*(\boldsymbol{r},t)\right)\Psi(\boldsymbol{r},t)$$
$$+ \left(\frac{\hbar i}{2m}\nabla^2\Psi(\boldsymbol{r},t) - \frac{i}{\hbar}V(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)\right)\Psi^*(\boldsymbol{r},t)$$

where we have allowed the possibility of complex potential $V(\boldsymbol{r},t) \in \mathbb{C}$ when conjugating the Schrödinger equation. We then use the identity

$$\Psi\nabla^2\Psi^* = \nabla\cdot(\Psi\nabla\Psi^*) - \nabla\Psi\cdot\nabla\Psi^*$$

to write

$$\frac{\partial \rho(\boldsymbol{r},t)}{\partial t} + \nabla\cdot\boldsymbol{j}(\boldsymbol{r},t) = q(\boldsymbol{r},t)$$

where we have defined the probability current

$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{\hbar}{2im}\big[\Psi(\boldsymbol{r},t)\nabla\Psi(\boldsymbol{r},t) - \Psi(\boldsymbol{r},t)\nabla\Psi^*(\boldsymbol{r},t)\big]$$

and the probability source density

$$q(\boldsymbol{r},t) = 2\,\mathrm{Im}\big[V(\boldsymbol{r},t)\rho(\boldsymbol{r},t)\big]$$

- *Important*: Note that probability is conserved when $q(\boldsymbol{r},t) = 0$, resulting in the continuity equation

$$\frac{\partial \rho(\boldsymbol{r},t)}{\partial t} + \nabla\cdot\boldsymbol{j}(\boldsymbol{r},t) = 0$$

The source density q is zero if V is a real function.

Quantum Tomography: Ψ from $|\Psi|^2$

- If you know a system's probability density $|\Psi(\boldsymbol{r}, t)|^2$, it is possible to reconstruct the wavefunction Ψ. This process is called quantum tomography. We consider only the one-dimensional case.

- First, we write the wavefunction in the polar form with complex modulus $|\Psi| = \sqrt{\rho(x, t)}$ and phase $S(x, t)$

$$\Psi(x, t) = \sqrt{\rho(x, t)} e^{\frac{iS(x,t)}{\hbar}}$$

  We substitute this expression for Ψ into the probability current density to get

$$j(x, t) \equiv \frac{\hbar}{2im}\left(\Psi^*(x, t)\frac{\partial}{\partial x}\Psi(x, t) - \Psi(x, t)\frac{\partial}{\partial x}\Psi^*(x, t)\right)$$

$$= \frac{1}{m}\rho(x, t)\frac{\partial S(x, t)}{\partial x}$$

- Substituting the above expression for $j(x, t)$ into the probability continuity equation gives

$$\frac{\partial \rho(x, t)}{\partial t} + \frac{1}{m}\frac{\partial}{\partial x}\left[\rho(x, t)\frac{\partial S(x, t)}{\partial x}\right] = 0$$

  We then integrate the equation with respect to x and rearrange to get

$$\frac{\rho(x, t)}{m}\frac{\partial S(x, t)}{\partial x} = -\int_{-\infty}^{x}\frac{\partial \rho(\chi, t)}{\partial t}\,\mathrm{d}\chi$$

  where we have assumed the boundary condition $\rho(-\infty, t) \to 0$ for the lower limit of integration and χ is a dummy variable for integration. We solve for the wavefunction's phase S to get

$$S(x, t) = S_0 - \int_{-\infty}^{x}\left[\frac{m}{\rho(\xi, t)}\int_{-\infty}^{x}\frac{\partial \rho(\chi, t)}{\partial t}\,\mathrm{d}\chi\right]\mathrm{d}\xi$$

- *Important*: The above expression for $S(x, t)$ shows that, when finding $\boldsymbol{S}(x, t)$ from probability density $\rho(x, t)$, complex phase is determined only up to a constant phase factor e^{iS_0}.

1.3 Stationary States

- "Standing wavefunctions" in the Schrödinger equation, in analogy with standing waves in the wave equation, occur when the wavefunction can be factored into the product of a position-dependent and time-dependent wavefunction in the form

$$\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r})f(t)$$

  Such solutions Ψ are called *stationary states.*

- Derivation of stationary states: assume the potential is independent of time, i.e. $V = V(\boldsymbol{r})$. Substitute the ansatz $\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r})f(t)$ into the Schrödinger equation to get

$$i\hbar\psi(\boldsymbol{r})\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}f(t)\nabla^2\psi(\boldsymbol{r}) + V(\boldsymbol{r})f(t)\psi(\boldsymbol{r})$$

Next, divide by $\psi(\boldsymbol{r})f(t)$ to get

$$\frac{i\hbar}{f(t)}\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\nabla^2\psi(\boldsymbol{r})}{\psi(\boldsymbol{r})} + V(\boldsymbol{r})$$

Since the left-hand side of the equation depends only on time, and the right-hand side only on position, the equality holds for all t and $\boldsymbol{r}$ only if both sides are constant. We make this requirement explicit by writing

$$\frac{i\hbar}{f(t)}\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\nabla^2\psi(\boldsymbol{r})}{\psi(\boldsymbol{r})} + V(\boldsymbol{r}) \equiv E$$

where the constant E represents the stationary state's energy.

- We use the position-dependent portion of the separated equation to form the stationary Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(\boldsymbol{r}) + V(\boldsymbol{r})\psi_n(\boldsymbol{r}) = E_n\psi_n(\boldsymbol{r}), \qquad n \in \mathbb{N}.$$

Note that this is an eigenvalue equation with for the stationary state eigenfunctions ψ_n and energy eigenvalues E_n.

Meanwhile, we solve the time-dependent portion of the separated equation to get

$$f(t) = e^{-i\frac{E_n}{\hbar}t} \equiv e^{-i\omega_n t},$$

which represents oscillation in time with at the frequency ω_n, which satisfies the familiar quantum-mechanical relation $E_n = \hbar\omega_n$.

- The complete set of stationary state eigenfunctions $\{\psi_n(\boldsymbol{r})\}$ form an orthonormal basis of the wavefunction solution space and satisfy the relation

$$\int \psi_n^*(\boldsymbol{r})\psi_m(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} = \delta_{nm},$$

where δ_{nm} is the Kronecker delta.

- It is possible to write any solution $\Psi(\boldsymbol{r}, t)$ Schrödinger equation in terms of the eigenfunction basis. To do this, we first expand the wavefunction Ψ's initial state $\Psi(\boldsymbol{r}, 0)$ in the eigenfunction basis in the form

$$\Psi(\boldsymbol{r}, 0) = \sum_n c_n\psi_n(\boldsymbol{r}), \qquad c_n = \int \psi_n^*\Psi(\boldsymbol{r}, 0)\,\mathrm{d}^3\boldsymbol{r}.$$

We then write the solution $\Psi(\boldsymbol{r}, t)$ at arbitrary time in the form

$$\Psi(\boldsymbol{r}, t) = \sum_n c_n e^{-i\frac{E_n}{\hbar}t}\psi_n(\boldsymbol{r}),$$

where c_n are the coefficients from the expansion of $\Psi(\boldsymbol{r}, 0)$ in the eigenfunction basis and E_n are the eigenfunction' corresponding energy eigenvalues.

1.4 Differentiability of the First and Second Wavefunction Derivatives

- The wavefunction is assumed to be a continuous quantity. What about its derivative? We integrate the stationary Schrödinger equation on the interval $x \in [a, b]$ to get

$$-\frac{\hbar^2}{2m} \int_a^b \psi''(x) \, \mathrm{d}x + \int_a^b V(x)\psi(x) \, \mathrm{d}x = E \int_a^b \psi(x) \, \mathrm{d}x$$

  Evaluating the integral of $\psi''(x)$ and rearranging gives

$$\psi'(b) - \psi'(a) = \frac{2m}{\hbar^2} \int_a^b V(x)\psi(x) \, \mathrm{d}x - \frac{2mE}{\hbar^2} \int_a^b \psi(x) \, \mathrm{d}x$$

- We are interested in the limit behavior $a \to b$. Since ψ is continuous, we have $\int_a^b \psi(x) \, \mathrm{d}x \to 0$ as $a \to b$ (from introductory real analysis). As long as $V(x)$ is continuous, then $V(x)\psi(x)$ is also continuous, implying $\int_a^b V(x)\psi(x) \, \mathrm{d}x \to 0$ as $a \to b$. We then have

$$\lim_{a \to b} \left[\psi'(b) - \psi'(a) \right] = \frac{2m}{\hbar^2} \cdot 0 - \frac{2mE}{\hbar^2} \cdot 0 = 0.$$

  The resulting equality $\lim_{a \to b} \left[\psi'(b) - \psi'(a) \right] = 0$ implies the wavefunction derivative ψ' is also a continuous function.

- If the potential takes the form of a delta function, i.e. $V(x) = \lambda \delta(x)$ where λ is a constant, the wavefunction's first derivative has a discontinuity of the form

$$\lim_{a \to b} \left[\psi'(b) - \psi'(a) \right] = \frac{2m\lambda}{\hbar^2} \psi(a)$$

- To analyze the second derivative, we write the Schrödinger equation in the form

$$\frac{1}{\psi(x)} \frac{\mathrm{d}^2 \psi(x)}{\mathrm{d}x^2} = \frac{2m}{\hbar^2} \left[V(x) - E \right].$$

  By observing the sign of $\psi''(x)$ based on the value of E, we see that ψ is concave where $E > V$ and convex where $E < V$.

- Points of inflection (zeros of ψ'') occur at the classically-expected turning points where $E = V$. The wavefunction must be smooth at the turning points to satisfy the continuity conditions on ψ and ψ'.

1.5 Degeneracy and the Nondegeneracy Theorem

- Consider the one-dimensional stationary Schrödinger equation

$$-\frac{\hbar^2}{2m} \psi_n''(x) + V(x)\psi_n(x) = E_n \psi_n(x).$$

  An energy eigenvalue E is called *degenerate* if there exist multiple linearly independent eigenfunctions, e.g. ψ_1, ψ_2, with the same energy eigenvalue E. The nondegeneracy theorem states that the energy eigenvalue spectrum $\{E_n\}$ of a one-dimensional system is nondegenerate, as long as the wavefunctions ψ_n vanish at $\pm\infty$.

- The stationary Schrödinger equation for the two eigenfunctions reads

$$-\frac{\hbar^2}{2m}\psi_1''(x) + \left[V(x) - E\right]\psi_1(x) = 0$$

$$-\frac{\hbar^2}{2m}\psi_2''(x) + \left[V(x) - E\right]\psi_2(x) = 0$$

We multiply the first equation by ψ_1, the second by ψ_2 and subtract the equations to get

$$\psi_1\frac{\mathrm{d}^2\psi_2}{\mathrm{d}x^2} - \psi_2\frac{\mathrm{d}^2\psi_1}{\mathrm{d}x^2} = 0$$

Mathematical aside: the Wronskian determinant of the wavefunctions ψ_1 and ψ_2 is

$$W_{12} \equiv \det\begin{pmatrix}\psi_1 & \psi_2 \\ \psi_1' & \psi_2'\end{pmatrix} = \psi_1\psi_2' - \psi_2\psi_1'.$$

- In terms of the Wronskian, the above equation relating ψ_1, ψ_2 and their second derivatives reads

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\psi_1\frac{\mathrm{d}\psi_2}{\mathrm{d}x} - \psi_2\frac{\mathrm{d}\psi_1}{\mathrm{d}x}\right) = \frac{\mathrm{d}W_{12}}{\mathrm{d}x} = 0,$$

which implies the Wronskian is constant with respect to x.

- Next, we apply the condition $\psi_{1,2} \to 0$ and $\psi_{1,2}' \to 0$ as $|x| \to \infty$, which implies $W_{12} \to 0$ as $|x| \to \infty$. This implies $W_{12} = 0$ for all x, since W is constant with respect to x. The result $W_{12} = 0$ implies

$$\psi_1\frac{\mathrm{d}\psi_2}{\mathrm{d}x} = \psi_2\frac{\mathrm{d}\psi_1}{\mathrm{d}x} \implies \frac{1}{\psi_1}\frac{\mathrm{d}\psi_1}{\mathrm{d}x} - \frac{1}{\psi_2}\frac{\mathrm{d}\psi_2}{\mathrm{d}x} = \frac{\mathrm{d}}{\mathrm{d}x}(\ln\psi_1 - \ln\psi_2) = 0.$$

Integrating the final equality produces

$$\ln\psi_1 - \ln\psi_2 = \ln\frac{\psi_1}{\psi_2} = C \implies \psi_1(x) = \tilde{C}\psi_2(x).$$

where $\tilde{C}$ is a constant. In other words, ψ_1 and ψ_2 are linearly dependent, implying the one-dimensional energy spectrum $\{E_n\}$ is nondegenerate, as long as $\psi_{1,2}$ vanish at infinity.

1.6 Expectation Value

- Assume we know a particle's wavefunction $\psi(x,t)$ and the associated probability density $\rho(x,t) = |\Psi(x,t)|^2$.

The moments of the probability density are called expectation values. The probability density's n-th moment is defined just like the mathematical definition of a probability distribution's moment, i.e.

$$\langle x^n \rangle = \int_{-\infty}^{\infty} x^n \rho(x,t)\,\mathrm{d}x = \int_{-\infty}^{\infty} \Psi^*(x,t)x^n\Psi(x,t)\,\mathrm{d}x$$

In general, all of the probability density's moments may not exist.

- In quantum mechanics, we generally restrict ourselves to those wavefunctions in the Schwartz space of rapidly falling functions. This space consists of those $\psi \in L^2$ that are infinitely differential and the fall rapidly as $|x| \to \infty$, i.e. those ψ for which there exists finite constant $M \in \mathbb{R}$ such that

$$x^n |\psi(x)|^m < M \qquad \text{for all } n, m \in \mathbb{N} \text{ and all } x \in \mathbb{R}$$

Physical interpretation for why we require wavefunctions fall rapidly: in physical experiments, we expect the majority of the probability for detecting a particle is concentrated in the neighborhood of the experiment and not at infinity.

Example: The Momentum Operator

- We begin by finding the derivative of the position expectation value.

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} \Psi^*(x,t) x \Psi(x,t)\,\mathrm{d}x$$
$$= \int_{-\infty}^{\infty} \left(\frac{\partial \Psi^*(x,t)}{\partial t} x \Psi(x,t) + \Psi^*(x,t) x \frac{\partial \Psi(x,t)}{\partial t} \right) \mathrm{d}x$$

Assuming a real potential $V(x)$, we can express $\frac{\partial \Psi^*}{\partial t}$ and $\frac{\partial \Psi}{\partial t}$ in terms of $\frac{\partial^2 \Psi^*}{\partial x^2}$ and $\frac{\partial^2 \Psi}{\partial x^2}$ using the Schrödinger equation, substitute these expressions in to the above expression for $\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t}$, and simplify like terms to get

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{\hbar}{2im} \int_{-\infty}^{\infty} \left(\frac{\partial^2 \Psi^*(x,t)}{\partial x^2} x \Psi(x,t) - \frac{\partial^2 \Psi(x,t)}{\partial x^2} x \Psi^*(x,t) \right)$$

We then rewrite this expression with a reverse-engineered derivative with respect to x:

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{\hbar}{2im} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left(\frac{\partial \Psi^*}{\partial x} x \Psi - |\Psi|^2 - \Psi^* x \frac{\partial \Psi}{\partial x} \right) \mathrm{d}x$$
$$+ \frac{1}{m} \int_{-\infty}^{\infty} \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \Psi \right) \mathrm{d}x.$$

For rapidly falling wavefunctions in the Schwartz space, the first integral evaluates to zero. We are left with

$$\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \frac{1}{m} \int_{-\infty}^{\infty} \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \Psi \right) \mathrm{d}x$$

- The above result for $\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t}$, written in the momentum-like form

$$m \frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = \langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \Psi \right) \mathrm{d}x,$$

motivates the introduction of the momentum operator

$$\hat{p} \to -\hbar \frac{\partial}{\partial x} \implies \langle p \rangle = \int_{-\infty}^{\infty} \Psi \hat{p} \Psi \, \mathrm{d}x$$

- **Notation:** The hat in $\hat{p}$ explicitly indicates the quantity in question is an operator. By convention, however, we usually write operators without the hat symbol and distinguish between operators and scalar quantities based on context.

- In three dimensions, the momentum operator generalizes to

$$\hat{\boldsymbol{p}} \to i\hbar\nabla \qquad \text{and} \qquad \langle\hat{\boldsymbol{p}}\rangle = m\frac{\mathrm{d}\langle\hat{\boldsymbol{r}}\rangle}{\mathrm{d}t}$$

- The momentum operator (dropping the hat notation) and probability current density are related by

$$\boldsymbol{j}(\boldsymbol{r},t) = \frac{1}{m}\,\mathrm{Re}\left[\Psi^*(\boldsymbol{r},t)\boldsymbol{p}\Psi(\boldsymbol{r},t)\right] \qquad \text{and} \qquad \langle\boldsymbol{p}\rangle = m\int_V \boldsymbol{j}(\boldsymbol{r},t)\,\mathrm{d}^3\boldsymbol{r}$$

We discuss operators formally in the following section.

1.7 Operators

- In quantum mechanics, every measurable quantity—called an *observable*—is assigned a corresponding operator. Some common operators are

$$\hat{x} \to x\mathrm{I} \qquad \hat{\boldsymbol{r}} \to \boldsymbol{r}\mathrm{I} \qquad \hat{V} \to V(\boldsymbol{r},t)\mathrm{I},$$

where $\mathbf{I}$ is the identity operator. We typically leave the identity operator implicit and write e.g. $\hat{x} \to x$.

The momentum operator in various forms reads

$$p_\alpha = -i\hbar\frac{\partial}{\partial\alpha} \qquad p_\alpha = (-i\hbar)^n\frac{\partial^n}{\partial\alpha^n} \qquad \hat{\boldsymbol{p}} = \sum_{\alpha=x,y,z}\hat{p}_\alpha = -i\hbar\nabla \qquad \hat{\boldsymbol{p}}^2 = (-i\hbar)^2\nabla^2.$$

- **Notation:** In this section I will intermittently write operators with a hat, i.e. $\hat{p}$. However, I stress again that by convention we usually write operators without the hat symbol and distinguish between operators and scalar quantities based on context. I will typically denote generic operator quantities by either $\mathcal{O}$ or the capital Latin letters A, B, C, ...

- We can define operators as functions. Consider the analytic complex function $f(x)$ with the power series definition

$$f(z) = \sum_{n=0}^{\infty} c_n z^n$$

As long as the function f is defined as a power series, we can define the function of an operator $\mathcal{O}$, which is itself an operator, as

$$f(\mathcal{O}) = \sum_{n=0}^{\infty} c_n \mathcal{O}^n.$$

For example, the exponential function of an operator $\mathcal{O}$ is defined as via the exponential function's Taylor series as

$$e^{\mathcal{O}} = \mathrm{I} + \mathcal{O} + \frac{\mathcal{O}^2}{2!} + \frac{\mathcal{O}^3}{3!} + \cdots + \frac{\mathcal{O}^n}{n!} + \cdots$$

- A common example of an operator constructed from other operators is the Hamiltonian H, defined as

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

We can use the Hamiltonian to concisely write the Schrödinger equation in operator form:

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

Note that the Hamiltonian operator has the same form as the Hamiltonian function from classical mechanics. If we observe the stationary Schrödinger equation in operator form, i.e.

$$H\psi_n = E_n\psi_n,$$

we see the Hamiltonian's eigenvalues are a quantum system's energy eigenvalues E_n.

- Functions of operators give simple results when applied to eigenvalue relations. Consider for example $\mathcal{O}$ for which we know the eigenvalue relation $\mathcal{O}\psi = \lambda\psi$. In this case the operator function $f(\mathcal{O})$ applied to ψ reads

$$f(\mathcal{O})\psi \equiv \left(\sum_{n=0}^{\infty} c_n\mathcal{O}^n\right)\psi = \sum_{n=0}^{\infty} c_n\left(\mathcal{O}^n\psi\right) = \sum_{n=0}^{\infty} c_n\lambda^n\psi = f(\lambda)\psi.$$

In other words, the operator expression $f(\mathcal{O})\psi$ reduces to the scalar expression $f(\lambda)\psi$.

- Next, we consider the operator $\frac{\partial}{\partial x}$, which forms the basis of the momentum operator p_x. Considering two wavefunctions ϕ and ψ and applying integration by parts, we have

$$\int_{-\infty}^{\infty} \phi^*\frac{\partial \psi}{\partial x}\,\mathrm{d}x = \phi^*\psi\big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \phi^*}{\partial x}\psi\,\mathrm{d}x.$$

If the wavefunctions are well-behaved and vanish at infinity (as is commonly assumed for a wavefunction), the equality reduces to

$$\int_{-\infty}^{\infty} \phi^*\frac{\partial \psi}{\partial x}\,\mathrm{d}x = -\int_{-\infty}^{\infty} \frac{\partial \phi^*}{\partial x}\psi\,\mathrm{d}x.$$

In other words, the action of the operator $\frac{\partial}{\partial x}$ on one wavefunction (e.g. ψ) in the original integrand gives an asymmetric result in which the operator acts on the opposite wavefunction (e.g. ϕ) in the result. Because of the asymmetric minus sign, we say the operator $\frac{\partial}{\partial x}$ is antisymmetric or anti-Hermitian.

Meanwhile, the operator $\frac{\partial^2}{\partial x^2}$ is symmetric (or Hermitian):

$$\int_{-\infty}^{\infty} \phi^*\frac{\partial^2 \psi}{\partial x^2}\,\mathrm{d}x = \cdots = \int_{-\infty}^{\infty} \frac{\partial^2 \phi^*}{\partial x^2}\psi\,\mathrm{d}x.$$

Note that the minus sign does not appear.

- The momentum operator $p \to -i\hbar \frac{\partial}{\partial x}$ is Hermitian—even though it contains the anti-Hermitian operator $\frac{\partial}{\partial x}$, the presence of the imaginary unit i recovers the operator's symmetry. We have

$$\int_{-\infty}^{\infty} \phi^* p\psi \,\mathrm{d}x = \int_{-\infty}^{\infty} \phi^* \left(-i\hbar \frac{\partial \psi}{\partial x}\right) = \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial \phi}{\partial x}\right)^* \psi \,\mathrm{d}x = \int_{-\infty}^{\infty} (p\phi)^* \psi \,\mathrm{d}x$$

Similarly, the operators x, p^2, V and H are all Hermitian[1], i.e.

$$\int_{-\infty}^{\infty} \phi^* \mathcal{O}\psi \,\mathrm{d}x = \int_{-\infty}^{\infty} (\mathcal{O}\phi)^* \psi \,\mathrm{d}x$$

for $\mathcal{O} = x, p^2, V, H$.

1.8 Commutators

- The commutator in quantum mechanics is analogous to the Poisson bracket in classical mechanics. The commutator of two operators A and B is defined as

$$[A, B] = AB - BA$$

If $[A, B] = 0$, the two operators are said to commute, in which case $AB = BA$. If this is not the case, then A and B do not commute.

Note that the commutator of two operators is in general also an operator.

- We calculate the value of a commutator by having the commutator act on an arbitrary wavefunction. As an example, we consider the commutator of position and momentum, which occurs frequently in quantum mechanics. We find $[x, p]$ as follows:

$$[x, p]\psi \equiv (xp - px)\psi = x\left(-i\hbar \frac{\partial}{\partial x}\right)\psi - \left(-i\hbar \frac{\partial}{\partial x}\right)x\psi$$
$$= -i\hbar x\psi' + i\hbar x\psi' + i\hbar\psi = i\hbar\psi$$

The equality $[x, p]\psi = i\hbar\psi$ implies $[x, p] = i\hbar$.

- More generally, the operators $\boldsymbol{r}$ and $\boldsymbol{p}$ obey canonical commutation relations

$$[r_\alpha, r_\beta] = 0$$
$$[p_\alpha, p_\beta] = 0$$
$$[r_\alpha, p_\beta] = i\hbar\delta_{\alpha\beta}$$

for $\alpha, \beta \in \{x, y, z\}$. These are analogous to the canonical Poisson bracket relationships between $\boldsymbol{q}$ and $\boldsymbol{p}$ in classical mechanics.

- Next, we quote some common commutator identities:

$$[\lambda A, B] = \lambda[A, B], \qquad \lambda \in \mathbb{C}$$
$$[A, B] = -[B, A]$$
$$[A + B, C] = [A, C] + [B, C]$$
$$[AB, C] = A[B, C] + [A, C]B$$

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[1]assuming the potential energy V is real

- Finally, we quote three more identities. The Jacobi identity is

$$\big[A, [B, C]\big] + \big[B, [C, A]\big] + \big[C, [A, B]\big] = 0,$$

The Baker-Campbell-Hausdorff formula gives the solution to the equation $e^A e^B = e^C$, which is

$$C = A + B + \frac{1}{2}[A, B] + \frac{1}{12}\big[A - B, [A, B]\big] + \cdots.$$

Finally, the Baker-Hausdorff lemma is

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!}\big[A, [A, B]\big] + \frac{1}{3!}\big[A, [A, [A, B]]\big] + \cdots$$

1.9   Uncertainty Principle

- Recall the for a probability distribution $\rho(x, t) = |\Psi(x, t)|^2$, position expectation values are defined as

$$\langle x^n \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) x^n \Psi(x, t) \, \mathrm{d}x.$$

With reference to this definition of $\langle x^n \rangle$, we define the "width" of a probability distribution ρ as

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}.$$

Note the equivalence of the width Δx to the familiar standard deviation of a statistical distribution.

- More generally, we define the uncertainty of a quantum mechanical operator $\mathcal{O}$ as

$$\Delta \mathcal{O} = \sqrt{\langle \mathcal{O}^2 \rangle - \langle \mathcal{O} \rangle^2},$$

where the expectation values $\langle \mathcal{O}^n \rangle$ are defined as

$$\langle \mathcal{O}^n \rangle = \int_V \Psi^*(\boldsymbol{r}, t) \mathcal{O}^n \Psi(\boldsymbol{r}, t) \, \mathrm{d}^3 \boldsymbol{r}.$$

- We now quote an important result: the product of uncertainties of two operators A and B obeys the inequality

$$\Delta A \Delta B \geq \frac{1}{2}\big|\langle [A, B] \rangle\big|.$$

TODO: consider adding derivation from Exercises.

This inequality, using the commutator $[x, p] = i\hbar$, is responsible for the famous Heisenberg uncertainty principle

$$\Delta x \Delta p \geq \frac{\hbar}{2}.$$

This inequality implicitly assumes two independent measurements of x and p.

1.10 Time-Dependent Expectation Values

- The time-dependent expectation value of an operator $\mathcal{O}$ for a quantum system with the wavefunction $\Psi(\boldsymbol{r}, t)$ is defined as

$$\langle \mathcal{O}, t \rangle = \int_V \Psi^*(\boldsymbol{r}, t) \mathcal{O} \Psi(\boldsymbol{r}, t) \, \mathrm{d}^3 \boldsymbol{r}.$$

- The time derivative of $\langle \mathcal{O}, t \rangle$ is

$$\frac{\mathrm{d} \langle \mathcal{O}, t \rangle}{\mathrm{d}t} = \int_V \left(\frac{\partial \Psi^*}{\partial t} \mathcal{O} \Psi + \Psi^* \frac{\partial \mathcal{O}}{\partial t} \Psi + \Psi^* \mathcal{O} \frac{\partial \Psi}{\partial t} \right) \mathrm{d}^3 \boldsymbol{r}.$$

We then use the Schrödinger equation to express time derivatives of Ψ in terms of position derivatives, i.e.

$$\frac{\partial \Psi}{\partial t} = \frac{1}{i\hbar} H \Psi \qquad \text{and} \qquad \frac{\partial \Psi^*}{\partial t} = -\frac{1}{i\hbar} (H\Psi)^*.$$

Substituting these expressions into the time derivative of $\langle \mathcal{O}, t \rangle$ gives

$$\frac{\mathrm{d} \langle \mathcal{O}, t \rangle}{\mathrm{d}t} = \left\langle \frac{\partial \mathcal{O}}{\partial t} \right\rangle + \frac{1}{i\hbar} \int_V \left[-(H\Psi)^* \mathcal{O} \Psi + \Psi^* \mathcal{O} H \Psi \right] \mathrm{d}^3 \boldsymbol{r}$$

$$= \left\langle \frac{\partial \mathcal{O}}{\partial t} \right\rangle + \frac{1}{i\hbar} \int_V (\Psi^* \mathcal{O} H \Psi - \Psi^* H \mathcal{O} \Psi) \, \mathrm{d}^3 \boldsymbol{r}$$

where we have used $(H\Psi)^* = \Psi^* H^*$ and applied the Hermitian identity $H^* = H$.

Finally, we use a commutator to compactly write the above result for time derivative of $\langle \mathcal{O}, t \rangle$ in the form

$$\frac{\mathrm{d} \langle \mathcal{O}, t \rangle}{\mathrm{d}t} = \left\langle \frac{\partial \mathcal{O}}{\partial t} \right\rangle + \frac{1}{i\hbar} \langle [\mathcal{O}, H] \rangle.$$

Note the similarity to an analogous result from classical mechanics for a function $f(p, q)$ of the canonical coordinates, in terms of Poisson brackets, which reads

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \{f, H\}.$$

1.11 The Ehrenfest Theorem

- The Ehrenfest theorem can be interpreted as an quantum-mechanical analog of Newton's second law. We start the derivation of the Ehrenfest theorem by considering the time-dependent expectation value of the position operator x. Using the above result

$$\frac{\mathrm{d} \langle \mathcal{O}, t \rangle}{\mathrm{d}t} = \left\langle \frac{\partial \mathcal{O}}{\partial t} \right\rangle + \frac{1}{i\hbar} \langle [\mathcal{O}, H] \rangle$$

with $\mathcal{O} = x$ and the identity $\frac{\partial x}{\partial t} = 0$ produces the relationship

$$\frac{\mathrm{d} \langle x, t \rangle}{\mathrm{d}t} = \frac{1}{i\hbar} \langle [x, H] \rangle = \frac{1}{i\hbar} \left\langle \left[x, \frac{p^2}{2m} + V \right] \right\rangle$$

$$= \frac{1}{2i\hbar m} \langle [x, p^2] \rangle + \frac{1}{i\hbar} \langle [x, V] \rangle$$

- We pause for a moment to calculate the two commutators. The first is

$$[x, p^2] = p[x, p] + [x, p]p = p(i\hbar) + (i\hbar)p = 2i\hbar p$$

The second is simply $[x, V] = 0$, since x and V commute.

- Using the just-derived intermediate results $[x, p^2] = 2i\hbar p$ and $[x, V(x,t)] = 0$, the time derivative of $\langle x, t \rangle$ is

$$\frac{\mathrm{d} \langle x, t \rangle}{\mathrm{d}t} = \frac{1}{2i\hbar m} \langle 2i\hbar p \rangle + \frac{1}{i\hbar} \langle 0 \rangle = \frac{1}{m} \langle p, t \rangle,$$

in analogy with the classical result $m\dot{x} = p$.

- Next, we find the time derivative of $\langle p, t \rangle$. Using the general result for the time derivative of an expectation value and implicitly recognizing $\frac{\partial p}{\partial t} = 0$, we have

$$\frac{\mathrm{d} \langle p, t \rangle}{\mathrm{d}t} = \frac{1}{i\hbar} \langle [p, H] \rangle = \frac{1}{i\hbar} \left\langle \left[p, \frac{p^2}{2m} + V \right] \right\rangle$$

$$= \frac{1}{2i\hbar m} \langle [p, p^2] \rangle + \frac{1}{i\hbar} \langle [p, V] \rangle$$

- Again, we pause to calculate the two commutators. The first is simply $[p, p^2] = 0$, which follows from $[p, p] = 0$ and $[A, BC] = B[A, C] + [A, B]C$. We find the second as follows:

$$[p, V]\psi \equiv \left[\left(-i\hbar \frac{\partial}{\partial x} \right) V - V \left(-i\hbar \frac{\partial}{\partial x} \right) \right] \psi = -i\hbar f \frac{\partial V}{\partial x} - i\hbar V \frac{\partial f}{\partial x} + i\hbar V \frac{\partial f}{\partial x}$$

$$= -i\hbar \frac{\partial V}{\partial x} f \implies [p, V] = -i\hbar \frac{\partial V}{\partial x}$$

- Using the just derived intermediate results $[p, p^2] = 0$ and $[p, V] = -i\hbar \frac{\partial V}{\partial x}$, the time derivative of $\langle p, t \rangle$ is

$$\frac{\mathrm{d} \langle p, t \rangle}{\mathrm{d}t} = \frac{1}{2i\hbar m} \langle 0 \rangle + \frac{1}{i\hbar} \left\langle -i\hbar \frac{\partial V}{\partial x} \right\rangle = \left\langle -\frac{\partial V}{\partial x} \right\rangle$$

- *Note*: I must confess that we have been guilty of a minor notational inconsistency—formally, we have been working with the x component of momentum p_x, even though we have been writing just p for conciseness. With unambiguous notation, the above result would read

$$\frac{\mathrm{d} \langle p_x, t \rangle}{\mathrm{d}t} = \left\langle -\frac{\partial V}{\partial x} \right\rangle$$

We could then apply an analogous derivation for the coordinates y and z to get

$$\frac{\mathrm{d} \langle p_y, t \rangle}{\mathrm{d}t} = \left\langle -\frac{\partial V}{\partial y} \right\rangle \qquad \text{and} \qquad \frac{\mathrm{d} \langle p_z, t \rangle}{\mathrm{d}t} = \left\langle -\frac{\partial V}{\partial z} \right\rangle$$

Putting the x, y and z results together and combining the three position derivatives into the single gradient operator gives the Ehrenfest theorem:

$$\frac{\mathrm{d} \langle \boldsymbol{p}, t \rangle}{\mathrm{d}t} = \langle -\nabla V \rangle = \langle \boldsymbol{F} \rangle, \qquad \text{where } \boldsymbol{F}(\boldsymbol{r}) = -\nabla V(\boldsymbol{r}).$$

Note the similarity to Newton's second law $\dot{\boldsymbol{p}} = \boldsymbol{F}$.

- Without proof, we quote a similar result relating angular momentum $\boldsymbol{L}$ and torque $\boldsymbol{M}$:

$$\frac{\mathrm{d}\langle \boldsymbol{L}, t\rangle}{\mathrm{d}t} = \langle \boldsymbol{M}\rangle, \qquad \text{where } \boldsymbol{M}(\boldsymbol{r}) = \boldsymbol{r} \times \boldsymbol{F} = -\boldsymbol{r} \times \nabla V(\boldsymbol{r})$$

The proof analyzes $\boldsymbol{r}$ and ψ in terms of their Cartesian components and rests on the commutator identities

$$[x_\alpha, x_\beta] = 0, \qquad [p_\alpha, p_\beta] = 0, \qquad [x_\alpha, p_\beta] = i\hbar\delta_{\alpha,\beta}.$$

1.12 Virial Theorem

- We derive the virial theorem in quantum mechanics by finding the time derivative of the expectation value $\langle \boldsymbol{r} \cdot \boldsymbol{p}, t\rangle$. Again using the general result for the time derivative of an expectation value and recognizing $\frac{\partial \boldsymbol{r}\cdot\boldsymbol{p}}{\partial t} = 0$, we have

$$\frac{\mathrm{d}\langle \boldsymbol{r}\cdot\boldsymbol{p}\rangle}{\mathrm{d}t} = \frac{1}{i\hbar}\big\langle [\boldsymbol{r}\cdot\boldsymbol{p}, H]\big\rangle$$

- We evaluate the commutator by components, starting with

$$[x_\alpha p_\alpha, H] = \left[x_\alpha p_\alpha, \frac{p_\alpha^2}{2m} + V\right] = \frac{x_\alpha}{2m}[p_\alpha, p_\alpha^2] + [x_\alpha, p_\alpha^2]\frac{p_\alpha}{2m} + x_\alpha[p_\alpha, V] + [x_\alpha, V]p_\alpha$$

We use the results $[p_\alpha, p_\alpha^2] = [x_\alpha, V] = 0$ and expand $[x_\alpha, p_\alpha^2]$ to get

$$[x_\alpha p_\alpha, H] = \frac{p_\alpha}{2m}[x_\alpha, p_\alpha]p_\alpha + [x_\alpha, p_\alpha]\frac{p_\alpha^2}{2m} + x[p_\alpha, V]$$

Reusing the earlier results $[x_\alpha, p_\alpha] = i\hbar$ and $[p_\alpha, V] = -i\hbar\frac{\partial V}{\partial x_\alpha}$ gives

$$[x_\alpha p_\alpha, H] = 2i\hbar\frac{p_\alpha^2}{2m} - i\hbar x_\alpha\frac{\partial V}{\partial x_\alpha}.$$

- If we substitute the above result into the time derivative of $\langle \boldsymbol{r}\cdot\boldsymbol{p}\rangle$, write the components in vector form, and use $\boldsymbol{F} = -\nabla V$, we get the virial theorem

$$\frac{\mathrm{d}\langle \boldsymbol{r}\cdot\boldsymbol{p}\rangle}{\mathrm{d}t} = 2\frac{\langle p^2\rangle}{2m} + \langle \boldsymbol{r}\cdot\boldsymbol{F}\rangle = 2\langle T\rangle + \langle \boldsymbol{r}\cdot\boldsymbol{F}\rangle$$

where we have defined the kinetic energy operator $T = \frac{p^2}{2m}$.

- For a stationary state in which $\frac{\mathrm{d}\langle \boldsymbol{r}\cdot\boldsymbol{p}\rangle}{\mathrm{d}t} = 0$, we recover the familiar classical results

$$2\langle T\rangle = -\langle \boldsymbol{r}\cdot\boldsymbol{F}\rangle.$$

2 The Formalism of Quantum Mechanics

2.1 The Copenhagen Interpretation

1. A quantum system is described by a state vector $|\psi\rangle$ in a function Hilbert space.

2. Every physically observable quantity is associated with a Hermitian operator.

3. The expectation value of an observable with operator A for a system in the state $|\psi\rangle$ is $\langle\psi|A|\psi\rangle$.

4. The time evolution of a state $|\psi\rangle$ is determined by the Schrödinger equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi\rangle = H|\psi\rangle\,,$$

   where H is the Hamiltonian operator.

5. When measuring an observable with operator A, the result of a single measurement is an eigenvalue of A (e.g. the eigenvalue $a \in \mathbb{R}$). The probability of this measurement result is $|\langle a|\psi\rangle|^2$, where $|a\rangle$ is A's eigenstate corresponding to the eigenvalue a. After a measurement, the system's wavefunction "collapses" into the state $|a\rangle$.

2.2 Dirac Notation: Inner Product and Ket

For the remainder of this chapter, L^2 denotes the Hilbert space of all complex functions $\psi : \mathbb{R}^3 \to \mathbb{C}$ for which

$$\|\psi\|_2 \equiv \int_V |\psi|^2\,\mathrm{d}^3\boldsymbol{r} < \infty$$

- The inner product of two vectors $\phi, \psi \in L^2$ is written

$$\langle\phi|\psi\rangle \equiv \int_V \psi^*(\boldsymbol{r})\psi(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r}$$

  Some properties of the inner product include

$$\langle\lambda\psi + \mu\chi|\phi\rangle = \lambda^*\langle\psi|\phi\rangle + \mu^*\langle\chi|\phi\rangle$$
$$\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$$
$$\langle\psi|\psi\rangle \geq 0 \qquad \text{and} \qquad \langle\psi|\psi\rangle = 0 \iff \psi \equiv 0$$
$$|\langle\phi|\psi\rangle|^2 \leq \langle\phi|\phi\rangle\langle\psi|\psi\rangle$$

- In Dirac notation, the wavefunction representing a quantum state is written as a ket, which is interpreted as a vector in the Hilbert space L^2. A generic wavefunction ψ and eigenfunction ψ_n are written

$$\begin{aligned}\psi(\boldsymbol{r}) \in L^2 \quad &\to \quad |\psi\rangle \\ \psi_n(\boldsymbol{r}) \quad &\to \quad |\psi_n\rangle \quad \to \quad |n\rangle\end{aligned}$$

  Note that the eigenfunction is conventionally written just with its index, e.g. ψ_2 is written $|2\rangle$.

- A basis of eigenstates is written $\{|n\rangle\}$, and orthonormal eigenstates obey $\langle m|n\rangle = \delta_{mn}$.

2.3 Linear and Antilinear Operators

- An operator $\mathcal{O}$ is linear if for all vectors $\phi, \psi \in L^2$ and all scalars $\lambda, \mu \in \mathbb{C}$

$$\mathcal{O}(\lambda\phi + \mu\psi) = \lambda\mathcal{O}\phi + \mu\mathcal{O}\psi.$$

  An operator $\mathcal{O}$ is antilinear if

$$\mathcal{O}(\lambda\phi + \mu\psi) = \lambda^*\mathcal{O}\phi + \mu^*\mathcal{O}\psi \qquad \text{or} \qquad \lambda\mathcal{O} = \mathcal{O}\lambda^*.$$

- Because the Hamiltonian (or kinetic energy) operator and potential energy operators are both linear, the Schrödinger equation is linear. The Schrödinger equation thus obeys the superposition principle: any linear combination of solutions to the Schrödinger equation also solves the Schrödinger equation.

2.4 Dirac Notation: Bra

- Linear functionals are linear operators $f : L^2 \to \mathbb{C}$ that map wavefunctions in L^2 to scalars in $\mathbb{C}$.

- Riesz representation theorem: for each linear functional $f : L^2 \to \mathbb{C}$ there exists a vector $|\phi_f\rangle \in L^2$ for which

$$f\,|\psi\rangle = \langle\phi_f|\psi\rangle \equiv \int_V \phi_f^*\psi\,\mathrm{d}^3\boldsymbol{r} \quad \text{for all } \psi \in L^2.$$

- In other words, we can interpret the action of a linear functional f on a wavefunction $|\psi\rangle$ as the expression

$$f\,|\psi\rangle = \int_V \phi_f^*\psi\,\mathrm{d}^3\boldsymbol{r}$$

  In terms of the bra term in braket notation, the above reads

$$f\,|\psi\rangle = \langle\phi_f||\psi\rangle = \langle\phi_f|\psi\rangle$$

  where $\langle\phi_f|$ represents the action of the linear functional f on ψ. A technicality: $\langle\phi_f||\psi\rangle$ represents the action of a linear functional f on the vector in L^2, and the result is the scalar product $\langle\phi_f|\psi\rangle \in \mathbb{C}$.

2.5 Expanding a State in a Basis

Consider an orthonormal basis $\{|\psi_n\rangle\} \equiv \{|n\rangle\}$ consisting of the eigenstates $|n\rangle$ of some operator.

- Every such basis $\{|n\rangle\}$ (of the Hilbert space L^2) has a corresponding basis $\{\langle n|\}$ of the Hilbert space's dual space of linear functionals.

- In Dirac notation, the expansion of a state $|\psi\rangle$ in a basis $\{|n\rangle\}$ takes the general form

$$|\psi\rangle = \sum_n c_n\,|n\rangle$$

We find the coefficients c_n by acting on the basis expansion with $\langle m|$ and applying the basis' orthonormality identity $\langle n|m\rangle = \delta_{nm}$ to get

$$\langle m|n\rangle = \sum_n c_n \langle m|n\rangle = \sum_n c_n \delta_{mn} = c_m,$$

which, switching from m to n, implies

$$c_n = \langle n|\psi\rangle \qquad \text{and} \qquad |\psi\rangle = \sum_n \langle n|\psi\rangle |n\rangle.$$

- Since $\langle n|\psi\rangle$ is a scalar, we can rewrite the above expansion of $|\psi\rangle$ in the basis $\{|n\rangle\}$ and apply $\langle n|\psi\rangle = \langle n|\psi\rangle$ to get

$$|\psi\rangle = \sum_n \langle n|\psi\rangle |n\rangle = \sum_n |n\rangle \langle n|\psi\rangle = \sum_n |n\rangle \langle n||\psi\rangle = \left(\sum_n |n\rangle \langle n|\right)|\psi\rangle$$

Comparing the first and last term gives an important identity:

$$|\psi\rangle = \left(\sum_n |n\rangle \langle n|\right)|\psi\rangle \implies \sum_n |n\rangle \langle n| = I$$

where I is the identity operator. This is an important identity, so I'll write it again:

$$I = \sum_n |n\rangle \langle n|$$

This holds for any orthonormal basis $\{|n\rangle\}$.

2.6   Expanding an Operator in a Basis

Consider an operator $\mathcal{O}$ and an orthonormal basis $\{|n\rangle\}$.

- Using the previous identity for the identity operator, we have

$$\mathcal{O}|\psi\rangle \equiv (I\,\mathcal{O}\,I)|\psi\rangle = \left(\sum_m |m\rangle \langle m|\right)\mathcal{O}\left(\sum_n |n\rangle \langle n|\right)|\psi\rangle$$

$$= \sum_m |m\rangle \langle m|\,\mathcal{O}\sum_n |n\rangle \langle n|\psi\rangle$$

- We introduce the *matrix element* $\mathcal{O}_{mn}$ (more on this later)

$$\mathcal{O}_{mn} = \langle m|\mathcal{O}|n\rangle \in \mathbb{C}$$

In terms of this matrix element, we can then write $\mathcal{O}$ in the basis $\{|n\rangle\}$ as

$$\mathcal{O}|\psi\rangle = \sum_m |m\rangle \langle m|\,\mathcal{O}\sum_n |n\rangle \langle n|\psi\rangle$$

$$= \sum_{mn} |m\rangle\,\mathcal{O}_{mn} \langle n|\psi\rangle$$

Which gives us the desired expression

$$\mathcal{O} = \sum_{mn} |m\rangle\,\mathcal{O}_{mn} \langle n|$$

In other words, an operator $\mathcal{O}$ can be represented in an arbitrary orthonormal basis $\{|n\rangle\}$ in terms of a matrix $\mathcal{O}_{mn}$ with matrix elements

$$\mathcal{O}_{mn} = \langle m|\mathcal{O}|n\rangle \equiv \int_V \psi_m^* \mathcal{O} \psi_n \, \mathrm{d}^3 \boldsymbol{r}$$

- More on writing an operator in an orthonormal basis. Consider the concrete operator equation

$$\mathcal{O}\,|\psi\rangle = |\varphi\rangle\,,$$

where $\mathcal{O}$ acts on the vector $|\psi\rangle$ to produce $|\varphi\rangle$. Additionally, let $|\psi\rangle$ be expanded in the basis $\{|n\rangle\}$ as

$$|\psi\rangle = \sum_n c_n\,|n\rangle = \sum_n \langle n|\psi\rangle\,|n\rangle$$

We write the operator equation $\mathcal{O}\,|\psi\rangle = |\varphi\rangle\,,$ in the basis $\{|n\rangle\}$ as

$$\mathcal{O}\,|\psi\rangle \equiv \sum_{mn} |m\rangle\,\mathcal{O}_{mn}\,\langle n|\psi\rangle = \sum_{mn} |m\rangle\,\mathcal{O}_{mn} c_n$$

$$= \sum_m \left(\sum_n \mathcal{O}_{mn} c_n \right) |m\rangle$$

$$\equiv \sum_m d_m\,|m\rangle$$

$$= |\varphi\rangle$$

In other words, the state $|\varphi\rangle = \mathcal{O}\,|\psi\rangle$ has the basis expansion

$$|\varphi\rangle = \sum_m d_m\,|m\rangle\,,$$

where the the coefficients d_m, operator $\mathcal{O}$, and coefficients c_n of the vector ψ are related by

$$d_m = \sum_n \mathcal{O}_{mn} c_n$$

In vector form, the action of an operator $\mathcal{O}$ in a basis $\{|n\rangle\}$ on a state $|\psi\rangle$ with coefficients c_n to produce a state $|\varphi\rangle$ with coefficients d_m corresponds to the matrix equation

$$\boldsymbol{\mathcal{O}c = d},$$

where the matrix elements $\mathcal{O}_{mn}$ are given by $\mathcal{O}_{mn} = \langle m|\mathcal{O}|n\rangle$.

- An important case occurs when we expand an operator in a basis of its eigenstates. Consider an operator $\mathcal{O}$ with eigenvalues λ_n and eigenstates $|n\rangle$ obeying the eigenvalue relation

$$\mathcal{O}\,|n\rangle = \lambda_n\,|n\rangle\,.$$

In this case, if we expand $\mathcal{O}$ in the basis of the eigenstates $\{|n\rangle\}$, the operator's matrix $\boldsymbol{\mathcal{O}}$ in the basis $\{|n\rangle\}$ is diagonal, and the matrix elements obey

$$\mathcal{O}_{mn} = \langle m|\mathcal{O}|n\rangle = \lambda_n \delta_{mn}.$$

2.7 Hermitian Operators

- An operator $\mathcal{O}$ is symmetric, also called Hermitian, if for all $\phi, \psi \in L^2$ we have

$$\langle \phi | \mathcal{O}\psi \rangle = \langle \mathcal{O}\phi | \psi \rangle .$$

  The operator $\mathcal{O}$ is antisymmetric, or anti-Hermitian, if

$$\langle \phi | \mathcal{O}\psi \rangle = - \langle \mathcal{O}\phi | \psi \rangle .$$

- The expectation values of Hermitian operators are real. We show this by applying $\langle \psi | \mathcal{O}\psi \rangle = \langle \mathcal{O}\psi | \psi \rangle$ (for Hermitian operators), followed by $\langle \psi | \mathcal{O}\psi \rangle = \langle \mathcal{O}\psi | \psi \rangle^*$ (for any operator)

$$\langle \mathcal{O} \rangle \equiv \langle \psi | \mathcal{O}\psi \rangle = \langle \mathcal{O}\psi | \psi \rangle = \langle \psi | \mathcal{O}\psi \rangle^* = \langle \mathcal{O} \rangle^*$$

  The equality $\langle \mathcal{O} \rangle = \langle \mathcal{O} \rangle^*$ implies $\langle \mathcal{O} \rangle \in \mathbb{R}$.

- The expectation value of a squared Hermitian operator is positive, i.e.

$$\left\langle \mathcal{O}^2 \right\rangle = \langle \psi | \mathcal{O}^2 | \psi \rangle = \langle \mathcal{O}\psi | \mathcal{O}\psi \rangle \geq 0$$

  Using the equality $\left\langle \mathcal{O}^2 \right\rangle \geq 0$ to eigenstates of the operator $\mathcal{O}^2$ with the eigenvalue relation $\mathcal{O}^2 | \psi_n \rangle = \lambda_n | \psi_n \rangle$ and applying the identity $\langle \psi_n | \psi_n \rangle \geq 0$ produces

$$\langle \psi_n | \mathcal{O}^2 | \psi_n \rangle = \lambda_n \langle \psi_n | \psi_n \rangle \implies \lambda_n \geq 0$$

  In other words, the square $\mathcal{O}^2$ of a Hermitian operator is positive definite.

- The eigenvalues of a Hermitian operator are real. To show this, we start with a generic Hermitian operator with the eigenvalues relation $\mathcal{O} | \psi_n \rangle = \lambda_n | \psi_n \rangle$. We then act on both sides of the equation with $\langle \psi_n |$ and apply the eigenvalue relation to get

$$\mathcal{O} | \psi_n \rangle = \lambda_n | \psi_n \rangle \implies \langle \psi_n | \mathcal{O} | \psi_n \rangle = \lambda_n \langle \psi_n | \psi_n \rangle$$

  We then apply $\langle \psi_n | \mathcal{O} | \psi_n \rangle \in \mathbb{R}$ (expectation value of a Hermitian operator is real) and $\langle \psi_n | \psi_n \rangle = 1 \in \mathbb{R}$ (the eigenstate normalization condition) to get $\lambda_n \in \mathbb{R}$.

- A Hermitian operator's eigenfunctions corresponding to different eigenvalues are orthogonal.

Derivation: Eigenfunctions with Different Eigenvalues are Orthogonal

- Begin by considering Hermitian operator $\mathcal{O}$ and two eigenfunctions $|a\rangle$ and $|b\rangle$, with corresponding eigenvalues λ_a and λ_b, and eigenvalue equations

$$\mathcal{O} | a \rangle = \lambda_a | a \rangle \qquad \text{and} \qquad \mathcal{O} | b \rangle = \lambda_b | b \rangle .$$

  We act on the two equations with $\langle b |$ and $\langle a |$, respectively, to get

$$\langle b | \mathcal{O} | a \rangle = \lambda_a \langle b | a \rangle \qquad \text{and} \qquad \langle a | \mathcal{O} | b \rangle = \lambda_b \langle a | b \rangle ,$$

  and take the complex conjugate of the second equation and apply $\lambda_n = \lambda_n^*$ for a Hermitian operator to get

$$\lambda_b \langle a | b \rangle^* = \langle a | \mathcal{O} | b \rangle^* .$$

- The rest is just playing around with the inner product identity $\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*$, the Hermitian identity $\langle a|\mathcal{O}b\rangle = \langle\mathcal{O}a|b\rangle$, and the eigenvalue equations for $|a\rangle$ and $|b\rangle$.

$$\lambda_b \langle a|b\rangle^* = \langle a|\mathcal{O}|b\rangle^* \equiv \langle a|\mathcal{O}b\rangle^* = \langle \mathcal{O}b|a\rangle = \langle b|\mathcal{O}a\rangle = \lambda_a \langle b|a\rangle.$$

The first and last term imply $\lambda_b \langle a|b\rangle^* = \lambda_a \langle b|a\rangle$, and applying $\langle a|b\rangle^* = \langle b|a\rangle$ gives

$$\lambda_b \langle b|a\rangle = \lambda_a \langle b|a\rangle \implies (\lambda_b - \lambda_a) \langle b|a\rangle = 0,$$

which implies $\langle b|a\rangle = \langle a|b\rangle = 0$ if $\lambda_a \neq \lambda_b$.

2.8 Adjoint Operators and Their Properties

- Consider an operator $\mathcal{O}$. The operator $\mathcal{O}$'s adjoint, denoted by $\mathcal{O}^\dagger$, is defined by the relationship

$$\langle\phi|\mathcal{O}\psi\rangle = \langle\mathcal{O}^\dagger\phi|\psi\rangle$$

From the general identity $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$, we also have

$$\langle\phi|\mathcal{O}\psi\rangle = \langle\mathcal{O}^\dagger\phi|\psi\rangle = \langle\psi|\mathcal{O}^\dagger\phi\rangle^*$$

- Consider two operators A and B related by $A = \lambda B$ where $\lambda \in \mathbb{C}$ is a constant. The operators' adjoint are then related by

$$A^\dagger = \lambda^* B^\dagger,$$

which follows directly from

$$\langle A^\dagger\phi|\psi\rangle = \langle\phi|A\psi\rangle = \langle\phi|\lambda B\psi\rangle = \langle\lambda^* B^\dagger\phi|\psi\rangle$$

- Any operator $\mathcal{O}$ obeys $\left(\mathcal{O}^\dagger\right)^\dagger = \mathcal{O}$, which implies the operator $\mathcal{O}+\mathcal{O}^\dagger$ is Hermitian and the operator $\mathcal{O} - \mathcal{O}^\dagger$ is anti-Hermitian. More so, if $\mathcal{O}$ is Hermitian, then $i\mathcal{O}$ is anti-Hermitian.

- The expectation values of an operator $\mathcal{O}$ obey the convenient identities

$$
\begin{aligned}
2\operatorname{Re}\langle\mathcal{O}\rangle &\equiv 2\operatorname{Re}\langle\psi|\mathcal{O}|\psi\rangle &= \langle\psi|(\mathcal{O}+\mathcal{O}^\dagger)|\psi\rangle \\
2i\operatorname{Im}\langle\mathcal{O}\rangle &\equiv 2i\operatorname{Im}\langle\psi|\mathcal{O}|\psi\rangle &= \langle\psi|(\mathcal{O}-\mathcal{O}^\dagger)|\psi\rangle
\end{aligned}
$$

- The adjoint of an operator defined by $\mathcal{O} = |m\rangle\langle n|$ is $\mathcal{O}^\dagger = |n\rangle\langle m|$, which follows from

$$\langle\phi|\mathcal{O}\psi\rangle = \langle\phi|m\rangle\langle n|\psi\rangle = \big(\langle\psi|n\rangle\langle m|\phi\rangle\big)^*$$

Similarly, $\big(\langle\psi|\mathcal{O}\big)^\dagger = \mathcal{O}^\dagger|\psi\rangle$

- Two operators A and B obey

$$\left(AB\right)^\dagger = B^\dagger A^\dagger,$$

which follows from

$$\langle\phi|AB\psi\rangle = \langle A^\dagger\phi|B\psi\rangle = \langle B^\dagger A^\dagger\phi|\psi\rangle.$$

The product of two Hermitian operators is Hermitian if the two operators commute.

- The projection operator $P_n \equiv |n\rangle \langle n|$ equals its adjoint, i.e. $P_n = P_n^\dagger$. More so, $P_n = P_n^2$, which follows from

$$P_n^2 = |n\rangle \langle n|n\rangle \langle n| = |n\rangle \langle n| = P_n$$

and the normalization condition $\langle n|n\rangle = 1$.

- Consider an operator $\mathcal{O}$ written in some generic orthonormal basis $\{|n\rangle\}$:

$$\mathcal{O} = \sum_{mn} |m\rangle \, \mathcal{O}_{mn} \, \langle n| \, .$$

The adjoint operator $\mathcal{O}^\dagger$ is then written in the basis as

$$\mathcal{O}^\dagger = \sum_{mn} |n\rangle \, \mathcal{O}_{mn}^* \, \langle m| = \sum_{mn} |m\rangle \, \mathcal{O}_{nm}^* \, \langle n|$$

The matrix elements of an operator and its adjoint are thus related by

$$\left(\mathcal{O}^\dagger\right)_{mn} = \mathcal{O}_{nm}^*$$

2.9 Self-Adjoint Operators

- An operator $\mathcal{O}$ is self-adjoint if:

   1. Both $\mathcal{O}$ and $\mathcal{O}^\dagger$ are Hermitian, i.e.

   $$\langle \phi | \mathcal{O}\psi \rangle = \langle \mathcal{O}\phi | \psi \rangle \qquad \text{and} \qquad \langle \phi | \mathcal{O}^\dagger \psi \rangle = \langle \mathcal{O}^\dagger \phi | \psi \rangle \text{ for all } \phi, \psi \in L^2,$$

   2. $\mathcal{O}$ and $\mathcal{O}^\dagger$ act on the same domain (in our case generally L^2).

   A self-adjoint operator obeys $\mathcal{O} = \mathcal{O}^\dagger$, which makes sense from the name—a self-adjoint operator $\mathcal{O}$ equals its adjoint $\mathcal{O}^\dagger$.

- Every self-adjoint operator is Hermitian, but in general not every Hermitian operator is self-adjoint. However (without proof), in finite N-dimensional vector spaces $\mathbb{C}^N$ and in the Schwartz space of rapidly falling functions, Hermitian and self-adjoint operators are equivalent.

   Since physicists typically work only with quantities in $\mathbb{R}^N$ or functions in the Schwartz space, we tend to incorrectly use the terms Hermitian and self-adjoint interchangeably.

2.10 Unitary Operators

- Unitary operators in quantum mechanics are analogous to orthogonal transformations in classical mechanics. A unitary operator U obeys the relationship

$$UU^\dagger = U^\dagger U = \mathrm{I} \implies U^{-1} = U^\dagger$$

- Unitary operators preserve the inner product. In symbols, for a unitary operator U and any two functions $|\tilde{\phi}\rangle = U |\phi\rangle$ and $|\tilde{\psi}\rangle = U |\psi\rangle$,

$$\langle \phi | \psi \rangle = \langle \tilde{\phi} | \tilde{\psi} \rangle$$

The above follows directly from $\langle \tilde{\phi} | \tilde{\psi} \rangle = \langle U\phi | U\psi \rangle = \langle UU^\dagger \phi | \psi \rangle = \langle \phi | \psi \rangle$.

- For matrix elements, using $U^\dagger = U^{-1}$:

$$\langle\phi|\mathcal{O}|\psi\rangle = \langle U^\dagger\tilde\phi|\mathcal{O}|U^\dagger\tilde\psi\rangle = \langle\tilde\phi|U\mathcal{O}U^\dagger|\tilde\psi\rangle \equiv \langle\tilde\phi|\tilde{\mathcal{O}}|\tilde\psi\rangle$$

where we have defined $\tilde{\mathcal{O}} = U\mathcal{O}U^\dagger$. In other words, the matrix element of $\mathcal{O}$ corresponding to the wavefunctions $|\phi\rangle$ and $|\psi\rangle$ equal the matrix elements of the transformed operator $\tilde{\mathcal{O}} = U\mathcal{O}U^\dagger$ found with the transformed wavefunctions $|\tilde\phi\rangle$ and $|\tilde\psi\rangle$.

- If $|\tilde\psi\rangle = U|\psi\rangle$ then $\langle\tilde\psi| = \langle U\psi| = \langle\psi|U^\dagger$.

- Consider an orthonormal basis $\{|\psi_n\rangle\}$ and the transformed basis $\{|\tilde\psi_n\rangle\} = \{|U\psi_n\rangle\}$ where U is a unitary operator. We then have

$$U = U\,\mathrm{I} = U\sum_n |\psi_n\rangle\langle\psi_n| = \sum_n U|\psi_n\rangle\langle\psi_n| = \sum_n |\tilde\psi_n\rangle\langle\psi_n|$$

We then use $\mathrm{I} = \sum_m |\psi_m\rangle\langle\psi_m|$ and define the matrix elements $U_{mn} = \langle\psi_m|\tilde\psi_n\rangle$ to get

$$U = \sum_n |\tilde\psi_n\rangle\langle\psi_n| = \sum_n \left(\sum_m |\psi_m\rangle\langle\psi_m|\right)|\tilde\psi_n\rangle\langle\psi_n| = \sum_{mn} |\psi_m\rangle U_{mn}\langle\psi_n|$$

- The identity operator takes the same form in the original basis $\{|\psi_n\rangle\}$ and the transformed basis $\{|\tilde\psi_n\rangle\}$:

$$UU^\dagger = \sum_{mn} |\tilde\psi_m\rangle\langle\psi_m|\psi_n\rangle\langle\tilde\psi_n| = \sum_n |\tilde\psi_n\rangle\langle\tilde\psi_n|$$

- In a unitary change of basis $\{|\psi_n\rangle\} \to \{|\tilde\psi_n\rangle\}$, the coefficients transform as

$$|\phi\rangle = \sum_n c_n|\psi_n\rangle = \sum_{mn} |\tilde\psi_m\rangle\langle\tilde\psi_m|c_n|\psi_n\rangle = \sum_n d_n|\tilde\psi_n\rangle$$

where the new coefficients are

$$d_n = \sum_m U^\dagger_{nm}c_m$$

- Unitary transformations preserve eigenvalue equations:

$$\mathcal{O}|\psi_n\rangle = \lambda_n|\psi_n\rangle \implies U\mathcal{O}\,\mathrm{I}|\psi_n\rangle = U\mathcal{O}U^\dagger U|\psi_n\rangle = \lambda_n U|\psi_n\rangle$$
$$\tilde{\mathcal{O}}|U\psi_n\rangle = \lambda_n|U\psi_n\rangle$$
$$\tilde{\mathcal{O}} = |\tilde\psi_n\rangle = \lambda_n|\tilde\psi_n\rangle$$

- If K is Hermitian, then $U = e^{iK}$ is unitary by the Baker-Campbell-Hausdorff formula, i.e. $UU^\dagger = e^{iK}e^{-iK} = \mathrm{I}$.

- Every single-parameter unitary operator $U(s)$, where $s \in \mathbb{R}$ is a real constant, can be written in the form

$$U(s) = e^{isK}$$

where K is a self-adjoint operator called the *generator* of the unitary operator U. Often, for infinitesimal parameters $s \to 0$, we work in the first-order approximation $U(s) \approx \mathrm{I} + isK$.

Derivation:

- To derive the expression $U(s) = e^{isK}$, we first expand an arbitarary unitary operator U in powers of s for vanishingly small $s \to 0$, which gives

$$U(s) = \mathrm{I} + \frac{\mathrm{d}U}{\mathrm{d}s}s + \mathcal{O}(s^2) \qquad \text{and} \qquad U^\dagger(s) = \mathrm{I} + \frac{\mathrm{d}U^\dagger}{\mathrm{d}s} + \mathcal{O}(s^2).$$

  We then write U in terms of the identity operator, i.e.

$$UU^\dagger = \mathrm{I} + \left(\frac{\mathrm{d}U}{\mathrm{d}s} + \frac{\mathrm{d}U^\dagger}{\mathrm{d}s} \right) s + \mathcal{O}(s^2).$$

  To satisfy the unitary identity $UU^\dagger \equiv \mathrm{I}$ to first order in s, the quantity in parentheses must equal zero, i.e.

$$\frac{\mathrm{d}U^\dagger}{\mathrm{d}s} = \left(\frac{\mathrm{d}U}{\mathrm{d}s} \right)^\dagger = -\frac{\mathrm{d}U}{\mathrm{d}s}.$$

  Using the above result, we can write $\frac{\mathrm{d}U}{\mathrm{d}s}$ in the form

$$\frac{\mathrm{d}U}{\mathrm{d}s} = iK,$$

  where K is a Hermitian operator.

- Next, we divide the parameter s into $N \to \infty$ equal subintervals and apply the operator $U(\frac{s}{N})$ N times, which produces the desired result

$$U(s) = \lim_{N \to \infty} U\left(\frac{s}{N} \right) U\left(\frac{s}{N} \right) \cdots U\left(\frac{s}{N} \right) = \lim_{N \to \infty} \left(\mathrm{I} + iK\frac{s}{N} \right)^N = e^{isK}$$

Anti-Unitary Operator:

- An anti-unitary operator U obeys the relationship

$$\langle U\phi | U\psi \rangle = \langle \phi | \psi \rangle^* = \langle \psi | \phi \rangle$$

- Anti-unitary operators are antilinear, i.e.

$$U\big(\lambda \, |\phi\rangle + \mu \, |\psi\rangle \big) = \lambda^* U \, |\phi\rangle + \mu^* U \, |\psi\rangle$$

2.11   Time Evolution

- The time evolution operator for a system with Hamiltonian H is defined as

$$U(t) = e^{-i\frac{H}{\hbar}t}.$$

  The time evolution operator is unitary with generator H. Because U is unitary, it preserves the inner product.

- The time evolution operator gives an alternate way to find the time evolution of an initial state $|\psi(0)\rangle$ via the formula

$$|\psi(t)\rangle = U(t) = |\psi(0)\rangle \,.$$

Derivation: The Time Evolution Operator

- We begin by expanding an arbitrary, time-dependent state $|\psi(t)\rangle$ with the known initial state $|\psi(0)\rangle$ in a basis formed of the energy eigenstates $\{|\varphi_n\rangle\}$, in the form

$$|\psi(t)\rangle = \sum_m \langle\varphi_n|\psi(0)\rangle \, e^{-i\frac{E_n}{\hbar}t} \, |\varphi_n\rangle \, .$$

- We then use the operator function identity $f(\mathcal{O})\varphi_n = f(\lambda_n)\varphi_n$ with $f(x) = e^{-i\frac{x}{\hbar}t}$, to replace the energy eigenvalues E_n with the Hamiltonian operator H, producing

$$|\psi(t)\rangle = \sum_n \langle\varphi_n|\psi(0)\rangle \, e^{-i\frac{E_n}{\hbar}t} |\varphi_n\rangle = \sum_n \langle\varphi_n|\psi(0)\rangle \, e^{-i\frac{H}{\hbar}t} |\varphi_n\rangle \, .$$

Since $e^{-i\frac{H}{\hbar}t}$ is independent of n, we factor it out of the sum to get

$$|\psi(t)\rangle = e^{-i\frac{H}{\hbar}t} \sum_n \langle\varphi_n|\psi(0)|\varphi_n\rangle = e^{-i\frac{H}{\hbar}t} \left(\sum_n |\varphi_n\rangle \langle\varphi| \right) |\psi(0)\rangle$$

$$= e^{-i\frac{H}{\hbar}t} \, \mathrm{I} \, |\psi(0)\rangle$$

$$\equiv U(t) \, |\psi(0)\rangle \, ,$$

where we have defined the time evolution operator $U(t) \equiv e^{-i\frac{H}{\hbar}t}$.

- Applying $U(t)$ to an infinitesimal time step $\mathrm{d}t$ in the evolution of a wavefunction $|\psi\rangle$ gives

$$|\delta\psi\rangle = |\psi(t+\mathrm{d}t)\rangle - |\psi(t)\rangle = -i\frac{H}{\hbar} \, \mathrm{d}t \, |\psi(t)\rangle$$

"Dividing" by $\mathrm{d}t$ and rearranging produces the Schrödinger equation

$$i\hbar \frac{|\psi(t+\mathrm{d}t)\rangle - |\psi(t)\rangle}{\mathrm{d}t} = i\hbar \frac{\mathrm{d}}{\mathrm{d}t} |\psi(t)\rangle = H \, |\psi(t)\rangle$$

2.12   Momentum Eigenfunction Representation

- Review: for rapidly falling functions $f(x)$, the function and its Fourier transform $\widehat{f}$ are related by

$$f(x) = \int_{-\infty}^{\infty} \widehat{f}(k)e^{ikx} \, \mathrm{d}k \qquad \text{and} \qquad \widehat{f}(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(x)e^{-ikx} \, \mathrm{d}x.$$

Next, we note the relationship

$$f(x) = \int_{-\infty}^{\infty} \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} f(x')e^{-ikx'} \, \mathrm{d}x; \right) e^{ikx} \, \mathrm{d}k$$

$$= \int_{-\infty}^{\infty} \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x'-x)} \, \mathrm{d}k \right) f(x') \, \mathrm{d}x'$$

$$= \int_{-\infty}^{\infty} \delta(x' - x)f(x') \, \mathrm{d}x',$$

where we have used the integral definition of the delta function, i.e.

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} \, \mathrm{d}k.$$

Finally, for use later in this section, we quote the following delta function properties:

$$- \ \delta(ax) = \frac{1}{|a|}\delta(x),$$

$$- \ x\delta(x) = 0,$$

$$- \ x\delta(x-y) = y\delta(x-y), \quad \text{and}$$

$$- \ \int_{-\infty}^{\infty} \delta(x-y)\delta(x-z)\,\mathrm{d}x = \delta(y-z).$$

2.12.1 Eigenvalues and Eigenstates of the Momentum Operator

- We begin with the Schrödinger equation for a free particle, which reads

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,|\psi(t)\rangle = \frac{\hat{p}^2}{2m}\,|\psi(t)\rangle\,.$$

  The eigenstates of the momentum operator $\hat{p}$ are plane waves, and the eigenvalue equation reads

$$\hat{p}\,|\varphi_p\rangle = p\,|\varphi_p\rangle\,,$$

  where $p \in \mathbb{R}$ denotes a momentum eigenvalue.

  The momentum eigenstates $|\varphi_p\rangle$ are simultaneously eigenstates of the stationary Schrödinger equation, in which case the eigenvalue equation reads

$$\frac{\hat{p}^2}{2m}\,|\varphi_p\rangle = E\,|\varphi_p\rangle\,, \qquad E = \frac{p^2}{2m}.$$

- Because the momentum eigenstates $|\varphi_p\rangle$ solve the Schrödinger equation, they form a convenient basis in which to find the time evolution of an arbitrary state $|t\rangle$.

- We now consider the wave functions corresponding to an eigenstate $|\varphi_0\rangle$ with eigenvalue p_0. For such a state, the momentum eigenvalue equation $\hat{p}\,|\varphi_p\rangle = p\,|\varphi_p\rangle$ and its simple exponential solution are

$$\hat{p}\,|\varphi_0\rangle \to -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\varphi_{p_0}(x) = p_0\varphi_{p_0}(x) \implies \varphi_{p_0}(x) = Ce^{i\frac{p_0}{\hbar}x}.$$

  Note that a plane wave is not normalizable in the usual sense, i.e. $\int_{-\infty}^{\infty}|\psi|^2\,\mathrm{d}x \equiv 1$, since the integral would diverge. Instead, we normalize plane wave momentum eigenfunctions in the form

$$\int_{-\infty}^{\infty}|\varphi_{p_0}|^2\,\mathrm{d}x = \int_{-\infty}^{\infty}\varphi_{p_0}^*\varphi_{p_0}\,\mathrm{d}x \equiv \delta(p-p_0).$$

  This normalization convention implies a normalization constant of the form $C = \frac{1}{\sqrt{2\pi\hbar}}$ and is derived from the integral definition of the delta function, together with the identity $\delta(ax) = \frac{1}{|a|}\delta(x)$.

- Since the momentum operator has a continuous spectrum of eigenvalues $p \in \mathbb{R}$, the corresponding momentum eigenbasis $\{\varphi_p\}$ is infinite-dimensional. As a result (i.e. because the basis is continuous), we expand an arbitrary function $\psi(x)$ in the momentum eigenbasis using an integral instead of a sum. The expansion in the momentum basis reads

$$\psi(x) = \int_{-\infty}^{\infty}\widehat{\psi}(p)\varphi_p(x)\,\mathrm{d}p, \quad \text{where} \quad \widehat{\psi}(p) = \int_{-\infty}^{\infty}\psi(x)\varphi_p^*\,\mathrm{d}x.$$

Note that $\widehat{\psi}(p)$ is a Fourier transform of the wave function $\psi(x)$ from the position domain to the momentum domain.

The wavefunction ψ may be normalized using the Parseval equality, which reads

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, \mathrm{d}x = \int_{-\infty}^{\infty} \left|\widehat{\psi}(p)\right|^2 \, \mathrm{d}p.$$

- The momentum eigenfunctions φ_p are related to the delta function by the following completeness relation:

$$\int_{-\infty}^{\infty} \varphi_p^*(x')\varphi_p(x) \, \mathrm{d}p = \delta(x' - x),$$

where the integral represents a "sum" over all possible momentum eigenfunctions.

- Finally, note that when a particle occurs in an external potential with $V(x) \neq 0$, the momentum eigenstates $|\varphi_p\rangle$ are no longer stationary states of the stationary Schrödinger equation. However, even for $V(x) \neq 0$, the momentum eigenstates still form a valid basis in which to expand an arbitrary wave function $\psi(x)$.

- To summarize the results so far, it is possible to describe a quantum particle in terms of a position-domain wave function $\psi(x)$ or, equivalently, in terms of the momentum-domain wave function $\widehat{\psi}(p)$, which is a Fourier transform of $\psi(x)$ to the p domain.

The action of the momentum operator $\hat{p}$ on the function $\psi(x)$ in the position domain is equivalent to multiplication of $\widehat{\psi}(p)$ by the eigenvalue p in the momentum domain, i.e.

$$\hat{p}\psi(x) = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\psi(x) = \int_{-\infty}^{\infty} \widehat{\psi}(p)\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}x}\varphi_p(x)\right)\mathrm{d}p = \int_{-\infty}^{\infty} \left(p\widehat{\psi}(p)\right)\varphi_p(x)\,\mathrm{d}p.$$

This relationship generalizes to higher-order derivatives according to

$$(-i\hbar)^n \frac{\mathrm{d}^n}{\mathrm{d}x^n}\psi(x) \iff p^n\widehat{\psi}(p).$$

- Analogously, multiplying the position-domain wave function by x corresponds to differentiation of $\widehat{\psi}(p)$, which we show as follows:

$$\hat{x}\psi(x) = x\psi(x) = \int_{-\infty}^{\infty} \widehat{\psi}(p)x\varphi_p(x)\,\mathrm{d}p = \int_{-\infty}^{\infty} \widehat{\psi}(p)\left(-i\hbar\frac{\mathrm{d}}{\mathrm{d}p}\varphi_p(x)\right)\mathrm{d}p$$
$$= \int_{-\infty}^{\infty} \left(i\hbar\frac{\mathrm{d}}{\mathrm{d}p}\widehat{\psi}(p)\right)\varphi_p(x)\,\mathrm{d}p.$$

The result is

$$x^n\psi(x) \iff (i\hbar)^n\frac{\mathrm{d}^n}{\mathrm{d}p^n}\widehat{\psi}(p).$$

This result also implies the relationship

$$V(x)\psi(x) \iff V\left(i\hbar\frac{\mathrm{d}}{\mathrm{d}p}\right)\widehat{\psi}(p).$$

2.12.2   Eigenvalues and Eigenstates of the Position Operator

- We now consider the position operator $\hat{x}$, for which the eigenvalue relation reads

$$\hat{x}\psi_0(x) = x_0\psi_0(x),$$

where $x_0 \in \mathbb{R}$ is the position eigenvalue. Transferring to momentum space and using the fact that multiplication by x in x space corresponds to applying $i\hbar\frac{\mathrm{d}}{\mathrm{d}p}$ in p space produces

$$\hat{x}\psi_0(x) \to x \int_{-\infty}^{\infty} \widehat{\psi}_0(p)\varphi_p(x)\,\mathrm{d}p = \int_{-\infty}^{\infty} \left(i\hbar\frac{\mathrm{d}}{\mathrm{d}p}\widehat{\psi}_0(p)\right)\varphi_p(x)\,\mathrm{d}p$$

$$= x_0 \int_{-\infty}^{\infty} \widehat{\psi}_0(p)\varphi_p(x)\,\mathrm{d}p$$

The last equality implies the position eigenfunctions ψ_0 obey the relationship

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}p}\widehat{\psi}_0(p) = x_0\widehat{\psi}_0(p) \implies \widehat{\psi}_0(p) = \frac{1}{\sqrt{2\pi\hbar}}e^{-i\frac{p}{\hbar}x_0} = \varphi_p^*(x_0).$$

- Next, we substitute in $\widehat{\psi}_0(p) = \varphi_p^*(x_0)$ to the expanded eigenvalue equation to get

$$\psi_0(x) = \int_{-\infty}^{\infty} \varphi_p^*(x_0)\varphi_p(x)\,\mathrm{d}p = \delta(x - x_0).$$

Interpretation: An eigenfunction of the position operator with eigenvalue x_0 is a delta function centered at x_0, which can be physically interpreted as a localized function centered around the eigenvalue $x = x_0$.

Using $\psi_0(x) = \delta(x - x_0)$, the position eigenvalue equation $\hat{x}\psi_0(x) = x_0\psi_0(x)$ reads

$$\hat{x}\delta(x - x_0) = x_0\delta(x - x_0).$$

2.12.3   Example: Particle in a Gravitational Potential

TODO

2.13   The Probability Amplitudes $\langle p|\psi\rangle$ and $\langle x|\psi\rangle$

- Dirac braket notation allows to represent a system's quantum state $|p\rangle$ as an abstract vector, separate from the coordinate representations $\psi(x)$ or $\widehat{\psi}(p)$ in position and momentum space.

  This is useful—we can denote a system's state with the abstract vector $|\psi\rangle$, and only later decide which representation—x or p—suits the problem better.

- In braket notation, we denote an operator's eigenstates with the eigenvalue, for example we write the momentum eigenstates as $|p\rangle$, where $|p\rangle$ is the momentum eigenstates with eigenvalue p. In this notation, we expand an arbitrary state encoded by the wavefunction ψ in the form

$$|\psi\rangle = \int_{-\infty}^{\infty} \widehat{\psi}(p)\,|p\rangle\,\mathrm{d}p.$$

We say we have written $|\psi\rangle$ in the momentum eigenbasis $\{|p\rangle\}$.

Next, we multiply the equation $|\psi\rangle = \int_{-\infty}^{\infty} \widehat{\psi}(p)\,|p\rangle\,\mathrm{d}p$ by $\langle p'|$ and apply the orthogonal identity $\langle p|p'\rangle = \delta(p - p')$ to get the important result

$$\widehat{\psi}(p) = \langle p|\psi\rangle\,.$$

- Analogously, we can expand an arbitrary state $|\psi\rangle$ in the position eigenbasis via

$$|\psi\rangle = \int_{-\infty}^{\infty} \psi(x)\,|x_0\rangle\,\mathrm{d}x,$$

where $|x_0\rangle$ denotes a position eigenstate with eigenvalue x_0, which corresponds to the function $\delta(x - x_0)$ in the x representation.

- We then multiply the equation through by $\langle x_0|$, which produces

$$\langle x_0|\psi\rangle = \int_{-\infty}^{\infty} \widehat{\psi}(p)\,\langle x_0|p\rangle\,\mathrm{d}p = \int_{-\infty}^{\infty} \widehat{\psi}(p)\varphi_p(x_0)\,\mathrm{d}p = \psi(x_0),$$

where we have substituted in $\langle x_0|p\rangle = \varphi_p(x)$, which follows from

$$\langle x_0|p\rangle = \int_{-\infty}^{\infty} \delta(x - x_0)\varphi_p(x)\,\mathrm{d}x = \varphi_p(x_0).$$

The relationship $\langle x_0|\psi\rangle = \psi(x_0)$ leads us to the general relationship

$$\psi(x) = \langle x|\psi\rangle\,,$$

which corresponds to the above position eigenbasis expansion

$$|\psi\rangle = \int_{-\infty}^{\infty} \psi(x)\,|x_0\rangle\,\mathrm{d}x,$$

- The position eigenstates are orthonormalized in terms of the delta function via $\langle x_0|x\rangle = \delta(x - x_0)$, which implies

$$|x_0\rangle = \int_{-\infty}^{\infty} \delta(x - x_0)\,|x\rangle\,\mathrm{d}x.$$

Next, we multiply the above equation through by $\langle x_1|$, which produces

$$\int_{-\infty}^{\infty} \delta(x - x_0)\delta(x - x_1)\,\mathrm{d}x = \delta(x_0 - x_1).$$

- In terms of the position and momentum eigenstates, the identity operator is written

$$\mathrm{I} = \int_{-\infty}^{\infty} |p\rangle\,\langle p|\,\mathrm{d}p = \int_{-\infty}^{\infty} |x\rangle\,\langle x|\,\mathrm{d}x.$$

2.14   Mutually Commuting Operators

- Consider a one-dimensional plane wave $|p\rangle$ with momentum $p \in \mathbb{R}$. This state is double degenerate, since two linear independent states, $|\pm|p|\rangle$, have the same energy $E = \frac{p^2}{2m}$.

  As a result, the state of a plane wave is not uniquely determined with its energy alone. We have to include a second quantity, such as momentum, to uniquely characterize a plane wave. In this case, the uniquely determined state would be written $|E, p\rangle$. In this case, the energy operator H (the Hamiltonian) and the momentum operator $\hat{p}$ are mutually commuting operators, i.e. $[H, p] = 0$.

- More generally, if the eigenvalue spectrum of some operator A is degenerate (in the above example this was $\hat{p}$), there exists some operator B (H in the above example), such that $[A, B] = 0$. More so, since A and B commute, they have the same basis. The reverse is also true—if two operators have the same basis, then the two operators commute.

- In fact, any number of operators sharing the same basis are mutually commuting, and their eigenvalues serve as quantum numbers that uniquely determine a system's quantum state. For example, we uniquely characterized a plane wave as $|p, E\rangle$, using the eigenvalues of the mutually commuting operators $\hat{p}$ and H. More generally, we could describe a state in terms of the mutually commuting operators A, B, C, ... with eigenvalues a, b and c, ... in the basis $\{|a, b, c, \ldots\rangle\}$.

- We now show that two commuting operators A and B have the same eigenvectors. We begin with the commutation and eigenvalue relations $[A, B] = 0 \implies AB = BA$ and $A|a\rangle = a|a\rangle$. We then multiply the eigenvalue equation by B and apply $AB = BA$ to get
$$BA|a\rangle = A\big(B|a\rangle\big) = a\big(B|a\rangle\big).$$

  In other words, $B|a\rangle$ is an eigenstate of the operator A. This leaves two options:

  1. A non-degenerate case, in which the eigenvalue a corresponds to only one eigenvector $|a\rangle$, which thus differs from $B|a\rangle$ by only a constant factor, implying the eigenvalue equation $B|a\rangle = b|a\rangle$. In other words, $|a\rangle$ is an eigenvector of both A and B, or

  2. A degenerate case—we will consider double degeneracy as a concrete example—in which case there exist two linearly independent vectors $|a_1\rangle$ and $|a_2\rangle$ with the same eigenvalue a. We consider this case in the following section.

The Degenerate Case

- In the degenerate case, every linear combination of the form
$$|\psi\rangle = c_1|a_1\rangle + c_2|a_2\rangle$$

  is an eigenvector of A with eigenvalue a, but not necessarily an eigenvector of B. However, it is possible to create a linear combination of the form
$$B\big(c_1|a_1\rangle + c_2|a_2\rangle\big) = b\big(c_1|a_1\rangle + c_2|a_2\rangle\big)$$

that is an eigenvector of B. Multiplying the above equation through by $|a_1\rangle$ and $|a_2\rangle$ and applying the (assumed, without loss of generality) orthonormality of $|a_1\rangle$ and $|a_2\rangle$ produces the system of equations

$$B_{11}c_1 + B_{12}c_2 = bc_1$$
$$B_{21}c_2 + B_{22}c_2 = bc_2,$$

where $B_{ij} = \langle a_i|B|a_j\rangle$.

- Next, we write the above system of equations in the matrix form

$$\begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = b \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \iff \mathbf{B}\boldsymbol{c} = b\boldsymbol{c}$$

and impose the condition

$$\det \begin{pmatrix} B_{11} - b & B_{12} \\ B_{21} & B_{22} - b \end{pmatrix} = 0,$$

which is equivalent to requiring the system has a nontrivial solution. If the two roots b_1 and b_2 of the above characteristic polynomial are different, their associated eigenvectors are linearly independent, in which case B removes the degeneracy from the operator A.

It is also possible that the polynomial's two roots are equal, i.e. $b_1 = b_2 \equiv b$. In this case, we must continue introducing commuting operators until the system's degeneracy is removed. Intepreted physically, more operators serve as more observable quantities needed to uniquely determine the system's state, just like we needed to introduce the energy operator H in addition to the momentum operator $\hat{p}$ to uniquely determine a plane wave.

A Few More Notes

- If two operators A and B with eigenvalues a_n and b_n share the same basis $\{\varphi_n\}$, then the operators commute. This follows from

$$[A, B]|\varphi_n\rangle = (AB - BA)|\varphi_n\rangle = (a_n b_n - b_n a_n)|\varphi_n\rangle = 0,$$

which implies $[A, B]|\psi\rangle = 0$ for an arbitrary wavefunction $|\psi\rangle$, which in turn implies $[A, B] = 0$.

- Keep in mind that two operators sharing a single eigenvector does not imply the operators commute—they must share an entire eigenbasis. As an example, the angular momentum operators L_x and L_y (discussed further in a future chapter) share the spherical harmonic ground state $Y_0^0(\theta, \phi)$, but the two operators do not commute.

- Consider an operator C of the form $C = A + B$, where C has eigenvalues $\{c_l\}$ and A and B have eigenvalues $\{a_m\}$ and $\{b_n\}$.

  If A and B commute, then C's eigenvalues are the sum of A and B's eigenvalues, i.e.

$$c_l = a_n + b_m.$$

This relationship does not hold if A and B do not commute.

3   Examples of Quantum Systems

3.1   Quantum Harmonic Oscillator

- In one dimension, the quantum harmonic oscillator's Hamiltonian reads

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2, \qquad \omega = \sqrt{\frac{k}{m}}.$$

  This section introduces the standard formalism for analyzing the harmonic oscillator.

- We begin by introducing a characteristic energy $\hbar\omega$ and length $\xi = \sqrt{\frac{\hbar}{m\omega}}$ and write the Hamiltonian as a difference of perfect squares:

$$H = \frac{\hbar\omega}{2}\left(\frac{x^2}{\xi^2} - \xi^2\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right).$$

  Keeping in mind that x and $\frac{\mathrm{d}}{\mathrm{d}x}$ don't commute, we factor the above into

$$H = \frac{\hbar\omega}{4}\left[\left(\frac{x}{\xi} + \xi\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\frac{x}{\xi} - \xi\frac{\mathrm{d}}{\mathrm{d}x}\right) + \left(\frac{x}{\xi} - \xi\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\frac{x}{\xi} + \xi\frac{\mathrm{d}}{\mathrm{d}x}\right)\right].$$

- Next, we introduce the annihilation and creation operators, denoted by a and $a^\dagger$ respectively, and defined by

$$a = \frac{1}{\sqrt{2}}\left(\frac{x}{\xi} + \xi\frac{\mathrm{d}}{\mathrm{d}x}\right) \qquad \text{and} \qquad a^\dagger = \frac{1}{\sqrt{2}}\left(\frac{x}{\xi} - \xi\frac{\mathrm{d}}{\mathrm{d}x}\right).$$

  We recover x and $\frac{\mathrm{d}}{\mathrm{d}x}$ from a and $a^\dagger$ with

$$x = \frac{\xi}{\sqrt{2}}\left(a + a^\dagger\right) \qquad \text{and} \qquad \frac{\mathrm{d}}{\mathrm{d}x} = \frac{1}{\sqrt{2}\xi}\left(a - a^\dagger\right).$$

  In terms of a and $a^\dagger$, the Hamiltonian reads

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

- Next, we quote the commutation relation

$$\left[a, a^\dagger\right] = 1,$$

  which is proven with a direct application of $[x, p] = i\hbar$. The relationship allows use to write the Hamiltonian in the form

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

3.1.1   Eigenvalues and Eigenfunctions

- The next standard step is introducing the counting operator $\hat{n} \equiv a^\dagger a$

$$\hat{n} \, |\phi_n\rangle = n \, |\phi_n\rangle \, ,$$

whose eigenvalues are the index n of the eigenfunction $|\phi_n\rangle$. We search for real n corresponding to normalizable eigenstates. First, we show $n \geq 0$, which follows from

$$\langle \phi_n | \hat{n} | \phi_n \rangle = \langle \phi_n | a^\dagger a | \phi_n \rangle = \langle a\phi_n | a\phi_n \rangle = n \, \langle \phi_n | \phi_n \rangle \geq 0.$$

- Next, we confirm $n = 0$ is a valid solution of counting operator's eigenvalue equation. This comes down to (why only a?) solving the equation

$$a \, |\phi_0\rangle = 0.$$

In the coordinate operator and wavefunction representation, the equation reads

$$\frac{1}{\sqrt{2}} \left(\frac{x}{\xi} + \xi \frac{\mathrm{d}}{\mathrm{d}x} \right) \phi_0(x) = 0 \qquad \text{or} \qquad \xi \frac{\mathrm{d}}{\mathrm{d}x} \phi_0(x) = -\frac{x}{\xi} \phi_0(x)$$

The solution is the Gaussian function

$$\phi_0(x) = \frac{1}{\sqrt{\sqrt{\pi}\xi}} e^{-\frac{1}{2}\frac{x^2}{\xi^2}} \equiv \langle x | \phi_0 \rangle \, .$$

The state $|\phi_0\rangle$ is the oscillator's ground state, with energy $E_0 = \frac{1}{2}\hbar\omega$. We can find all other solutions from the ground state solution.

- First, we derive the commutator relation

$$\left[\hat{n}, a^\dagger \right] = \left[a^\dagger a, a^\dagger \right] = a^\dagger \left[a, a^\dagger \right] + \left[a^\dagger, a^\dagger \right] a = a^\dagger$$

This relationship shows that $a^\dagger$ acts on a state with eigenvalue n to create a state with eigenvalue $n + 1$. We show this with

$$\hat{n} a^\dagger \, |\phi_n\rangle \equiv a^\dagger a a^\dagger \, |\phi_n\rangle = a^\dagger \left(a^\dagger a + 1 \right) |\phi_n\rangle = \left(a^\dagger \hat{n} + a^\dagger \right) |\phi_n\rangle$$
$$= a^\dagger n \, |\phi_n\rangle + a^\dagger \, |\phi_n\rangle = (n+1) a^\dagger \, |\phi_n\rangle \, .$$

Because the counting operator $\hat{n}$ acts on the state $a^\dagger \, |\phi_n\rangle$ to produce an eigenvalue $(n + 1)$, $a^\dagger$ must have the effect of raising $|\phi_n\rangle$'s index by one. In symbols:

$$a^\dagger \, |\phi_n\rangle = c_n \, |\phi_{n+1}\rangle \, .$$

- We find the constant c_n from the assumption that the original state $|\phi_n\rangle$ is normalized, i.e. $\langle \phi_n | \phi_n \rangle = 1$. The relevant calculation reads

$$\langle c_n^* \phi_{n+1} | c_n \phi_{n+1} \rangle = \langle a^\dagger \phi_n | a^\dagger \phi_n \rangle = \langle \phi_n | a a^\dagger \phi_n \rangle = \langle \phi_n | (a^\dagger a + 1) \phi_n \rangle$$
$$= \langle \phi_n | (n+1)\phi_n \rangle \, ,$$

which implies $|c_n|^2 = (n+1)$. Up to a constant phase factor of magnitude one, we define $c_n = \sqrt{n+1}$. The action of $a^\dagger$ is then fully summarized with

$$a^\dagger \, |\phi_n\rangle = \sqrt{n+1} \, |\phi_{n+1}\rangle \qquad \text{or} \qquad |\phi_{n+1}\rangle = \frac{a^\dagger}{\sqrt{n+1}} \, |\phi_n\rangle \, .$$

If we start with $|\phi_n\rangle = |\phi_0\rangle$, the latter expression produces to the recursive relation

$$|\phi_n\rangle = \frac{a^\dagger}{\sqrt{n}} \, |\phi_{n-1}\rangle = \frac{\left(a^\dagger \right)^n}{\sqrt{n!}} \, |\phi_0\rangle \, .$$

- While the creation operator $a^\dagger$ raises the index of a harmonic oscillator's eigenstate, the annihilation operator a lowers a eigenstate's index. The derivation follows the same pattern as above for $a^\dagger$: we use the commutator relation

$$[\hat{n}, a] = a^\dagger[a, a] + [a^\dagger, a]a = -a$$

to show that

$$\hat{n}a\,|\phi_n\rangle = (a\hat{n} - a)\,|\phi_n\rangle = (n-1)a\,|\phi_n\rangle\,.$$

Because the counting operator acts on the state $a\,|\phi_n\rangle$ to produce an eigenvalue $(n-1)$, a must have the effect of lowering $|\phi_n\rangle$'s index by one, i.e.

$$a\,|\phi_n\rangle = d_n\,|\phi_{n-1}\rangle$$

- As for $a^\dagger$, we find the constants d_n under that assumption that the original state $|\phi_n\rangle$ is normalized, i.e. $\langle\phi_n|\phi_n\rangle = 1$. The relevant calculation reads

$$\langle d_n^*\phi_{n-1}|d_n\phi_{n-1}\rangle = \langle a\phi_n|a\phi_n\rangle = \langle\phi_n|a^\dagger a\phi_n\rangle = \langle\phi_n|n\phi_n\rangle = n\langle\phi_n|\phi_n\rangle$$

which implies $|d_n|^2 = n$. Up to a constant phase factor of magnitude one, we define $d_n = \sqrt{n}$. The action of a is then fully summarized with

$$a\,|\phi_n\rangle = \sqrt{n}\,|\phi_{n-1}\rangle \qquad \text{or} \qquad |\phi_{n-1}\rangle = \frac{a}{\sqrt{n}}\,|\phi_n\rangle\,.$$

The latter expression results in the recursion relations

$$|\phi_n\rangle = \frac{a}{\sqrt{n+1}}\,|\phi_{n+1}\rangle \qquad \text{and} \qquad |\phi_0\rangle = \frac{a^n}{\sqrt{n!}}\,|\phi_n\rangle\,.$$

- The recursive relations involving $a^\dagger$ and a solve the harmonic oscillator problem. The results are

$$H\,|n\rangle = E_n\,|n\rangle \qquad E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad \langle m|n\rangle = \delta_{mn}.$$

Some Discussion of the Solution

- In one dimension, the harmonic oscillator's energy eigenvalues E_n are nondegenerate.[2] We prove nondegeneracy by contradiction: assume that in addition to $|\phi_n\rangle$ there exists another linearly independent eigenstates $|\tilde{\phi}_n\rangle$ with the same energy E_n. From the recursion relation

$$|\phi_n\rangle = \frac{a^n}{\sqrt{n!}}\,|\phi_0\rangle\,,$$

the state $|\tilde{\phi}_n\rangle$ must obey $a^n|\tilde{\phi}_n\rangle \propto |\tilde{\phi}_0\rangle$. However, the harmonic oscillator's ground state is non-degenerate, since the earlier ground state equation

$$\xi\frac{\mathrm{d}}{\mathrm{d}x}\phi_0(x) = -\frac{x}{\xi}\phi_0(x)$$

---

[2]This does not hold in higher dimensions

has only one normalized solution:

$$\langle x|\phi_0\rangle = \frac{1}{\sqrt{\sqrt{\pi}\xi}}e^{-\frac{1}{2}\frac{x^2}{\xi^2}}.$$

Because the oscillator's ground state is nondegenerate and all higher states are proportional to the ground state via $a^n|\phi_n\rangle \propto |\phi_0\rangle$, all higher states are also nondegenerate.

- The harmonic oscillator's energy eigenvalues have only integer indexes $n \in \mathbb{N}$. We prove this by contradiction: assume there exists an energy eigenstate $|\phi_\lambda\rangle$ with index $\lambda = n + \nu$ where $\nu \in (0,1)$. Applying the counting operator to $|\phi_\lambda\rangle$ produces

$$\hat{n}|\phi_\lambda\rangle = \lambda|\phi_\lambda\rangle = (n+\nu)|\phi_\lambda\rangle$$

  Repeatedly applying the annihilation operator a to the state $|\phi_\lambda\rangle$ and using the recursion relation $|\phi_n\rangle = \frac{a^n}{\sqrt{n!}}|\phi_0\rangle$ would eventually lead to a state with the index $\lambda \in (-1,0)$, i.e. a negative index. This contradicts the earlier result from the beginning of the "Eigenvalues and Eigenfunctions" section, which showed that harmonic oscillator's indexes are non-negative, i.e. $n \geq 0$.

3.1.2 Eigenfunctions in the Coordinate Representation

- In the coordinate representation, the harmonic oscillators eigenfunctions are found with the generating formula

$$\langle x|\phi_n\rangle = \phi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{x}{\xi} - \xi\frac{\mathrm{d}}{\mathrm{d}x}\right)^n \phi_0(x).$$

  The ground state eigenfunction with $n = 0$ is even, and the excited state eigenfunctions with $n = 1, 2, \ldots$ alternate between even and odd according to the parity of the index n.

- Perhaps more intuitively, the eigenfunctions are just the product of a Hermite polynomial and the fundamental Gaussian solution $\phi_0(x)$. In this form, the eigenfunctions are written

$$\phi_n = C_n H_n\left(\frac{x}{\xi}\right)e^{-\frac{1}{2}\frac{x^2}{\xi^2}},$$

  where H_n is the nth Hermite polynomial and

$$\xi = \sqrt{\frac{\hbar}{m\omega}} \qquad \text{and} \qquad C_n = \frac{1}{\sqrt{2^n n!\xi\sqrt{n}}}$$

- The characteristic width of each eigenfunction increases with the index n; the width σ_x of the nth state obeys

$$\frac{\sigma_{x_n}^2}{\xi^2} = \frac{1}{2}\langle n|(a^\dagger)^2 + a^\dagger a + aa^\dagger + a^2|n\rangle = n + \frac{1}{2}$$

  In the p-space representation, the nth eigenfunction's characteristic width is

$$\xi^2\sigma_{p_n}^2 = -\frac{\hbar^2}{2}\langle n|(a^\dagger)^2 - a^\dagger a - aa^\dagger + a^2|n\rangle = \hbar^2\left(n + \frac{1}{2}\right)$$

The product $\sigma_{x_n}\sigma_{p_n}$ is thus

$$\sigma_{x_n}\sigma_{p_n} = \hbar\left(n + \frac{1}{2}\right)$$

Note that the ground state obeys $\sigma_{x_n}\sigma_{p_n} = \hbar/2$, which brings to mind the Heisenberg uncertainty principle.

3.1.3 The Harmonic Oscillator in Three Dimensions

- We consider the three-dimensional case with an anisotropic potential. The Hamiltonian reads
$$H(\boldsymbol{r}) = \frac{p^2}{2m} + \frac{1}{2}\sum_{ij}\omega_{ij}x_i x_j$$

Just like in classical mechanics in the field of small oscillations modeled by harmonic oscillators, we can transform to normal coordinates and conjugate momenta, in which case the Hamiltonian transforms to the diagonal form

$$H = \frac{p^2}{2m} + \frac{1}{2}\sum_{i=1}^{3} k_i x_i^2, \qquad k_i = m\omega_i^2$$

- As in the one-dimensional case, we introduce annihilation and creation operators, this time for each index i. The Hamiltonian becomes

$$H = \sum_{i=1}^{3} \hbar\omega_i\left(a_i^\dagger a_i + \frac{1}{2}\right), \qquad [a_i, a_j^\dagger] = \delta_{ij}.$$

- Because H is a sum of linearly independent operators H_i, the Hamiltonian's eigenstates can be written in the factored form

$$\Psi_{n_1 n_2 n_3}(\boldsymbol{r}) = \prod_{i=1}^{3}\phi_{n_i}(x_i) \equiv \langle\boldsymbol{r}|n_1 n_2 n_3\rangle$$

The higher states can be constructed from the ground state according to

$$|n_1 n_2 n_3\rangle = \prod_{i=1}^{3}\frac{\left(a_i^\dagger\right)^{n_i}}{\sqrt{n_i!}}|000\rangle$$

3.1.4 Coherent Ground State

- Consider a particle in the ground state of harmonic potential whose initial state at $t = 0$ is displaced by $\langle x\rangle = x_0$ from the equilibrium position. The particle's initial wavefunction is thus $\phi_0(x - x_0)$, where ϕ_0 is the harmonic ground state eigenfunction at the equilibrium position.

- We begin by considering the eigenvalue equation

$$a|\psi_\alpha\rangle = \alpha|\psi_\alpha\rangle$$

where the eigenvalue is the complex number $\alpha = |\alpha|e^{i\delta} \in \mathbb{C}$. We expand the state $|\psi_\alpha\rangle$ in the harmonic oscillator's eigenbasis $\{|n\rangle\}$. Using the recursion relation

$$|n\rangle = \frac{\left(a^\dagger\right)^n}{\sqrt{n!}}|0\rangle,$$

the expansion of $|\psi_\alpha\rangle$ in the basis $\{|n\rangle\}$ reads

$$|\psi_\alpha\rangle = \sum_n \langle n|\psi_\alpha\rangle |n\rangle = \sum_n \frac{1}{\sqrt{n!}}\left\langle \left(a^\dagger\right)^n \phi_0 \middle| \psi_\alpha \right\rangle |n\rangle$$

$$= \langle \phi_0|\psi_\alpha\rangle \sum_n \frac{\alpha^n}{\sqrt{n!}}|n\rangle = \langle \phi_0|\psi_\alpha\rangle \sum_n \frac{\left(\alpha a^\dagger\right)^n}{n!}|0\rangle$$

$$= \langle \phi_0|\psi_\alpha\rangle\, e^{\alpha a^\dagger}|0\rangle$$

where the last line uses the Taylor series definition of the exponential function. We determine the constant $\langle \phi_0|\psi_\alpha\rangle$ from the normalization condition $\langle \psi_\alpha|\psi_\alpha\rangle \equiv 1$; the calculation reads

$$1 \equiv \langle \psi_\alpha|\psi_\alpha\rangle\, |\langle \phi_0|\psi_\alpha\rangle|^2 \sum_n \frac{|\alpha|^{2n}}{n!} \implies \langle \phi_0|\psi_\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2}$$

- The state $|\psi_\alpha\rangle$ at $t = 0$ is called a called a coherent state. Its time evolution reads

$$|\psi_\alpha(t)\rangle = \exp\left(-\frac{1}{2}i\omega t - \frac{1}{2}|\alpha|^2\right) \sum_n \frac{\left(\alpha e^{-i\omega t}a^\dagger\right)^n}{n!}|0\rangle$$

In terms of the eigenfunctions $|\phi_n(t)\rangle$, the above time evolution is written

$$|\psi_\alpha(t)\rangle = \sum_n c_n |\phi_n(t)\rangle \qquad \text{where} \qquad c_n = \frac{\alpha^n}{\sqrt{n!}}e^{-\frac{1}{2}|\alpha|^2}$$

- For the state $|\psi_\alpha(t)\rangle$, the probability P_n for occupation of a state with index n falls exponentially:

$$P_n = |c_n|^2 = \frac{\langle \hat{n}\rangle^2}{n!}e^{-\langle \hat{n}\rangle}$$

where $\langle \hat{n}\rangle = \langle \psi_\alpha|\hat{n}|\psi_\alpha\rangle$.

- The position expectation value of the state $|\psi_\alpha(t)\rangle$ obeys

$$\langle x(t)\rangle = x_0 \cos(\omega t - \delta), \qquad \text{where} \qquad x_0 = \sqrt{2}\xi|\alpha|,$$

which follows from

$$\langle |\psi_\alpha(t)\rangle|x||\psi_\alpha(t)\rangle\rangle = \frac{\xi}{\sqrt{2}}\langle |\psi_\alpha(t)\rangle|\left(a + a^\dagger\right)||\psi_\alpha(t)\rangle\rangle = \frac{\xi}{\sqrt{2}}\left(\alpha e^{-i\omega t} + \alpha^* e^{i\omega t}\right).$$

Note that $\langle x(t)\rangle$ has the time dependence as the analogous classical solution $x(t) = x_0 \cos(\omega t - \delta)$.

The real component of the constant $\alpha = |\alpha|e^{i\delta}$ corresponds to the displacement of the particle (or wavefunction's center) from equilibrium, while the imaginary part of α corresponds to the initial velocity $v_0 = \frac{\langle p\rangle}{m}\big|_{t=0}$.

- Next, we note the energy expectation value is

$$\langle E \rangle = \hbar\omega \left(|\alpha|^2 + \frac{1}{2} \right) = \hbar\omega \left(\frac{m\omega x_0^2}{2\hbar} + \frac{1}{2} \right)$$

In the classical limit $\hbar \to 0$, the energy reduces to the classical value $E = \frac{1}{2}m\omega^2 x_0^2$.

- Finally—characteristic for a coherent state—the probability density $\rho(t)$ oscillates back and forth in the harmonic potential while preserving the shape of the initial Gaussian distribution, i.e.

$$\rho(x, t) = |\psi_\alpha(t)|^2 = \frac{1}{\sqrt{2\pi}\sigma_{x_0}} \exp\left(-\frac{(x - \langle x \rangle)^2}{2\sigma_{x_0}^2} \right)$$

3.1.5 Ladder Operators in Matrix Form

- Finally, as an exercise, we write the operators $a^\dagger$, x and p in the harmonic oscillator eigenbasis $\{|n\rangle\}$.

First, $a^\dagger$. Using the equation $a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle$, the matrix elements are

$$a^\dagger_{mn} = \langle m|a^\dagger|n\rangle = \langle n+1|\sqrt{n+1}|n\rangle \, \delta_{m,n+1}$$

In matrix form $a^\dagger$ reads

$$a^\dagger = \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \cdots \\ \vdots & \vdots & \ddots & \vdots \end{pmatrix}$$

Note that $a^\dagger$ is asymmetric and thus non-Hermitian.

- Similarly, the expressions for x and p are

$$x = \sqrt{\frac{\hbar}{2m\omega}} \begin{pmatrix} 0 & 1 & 0 & \cdots \\ 1 & 0 & \sqrt{2} & \cdots \\ 0 & \sqrt{2} & 0 & \ddots \\ \vdots & \vdots & \ddots & \ddots \end{pmatrix} \quad \text{and} \quad p = \sqrt{\frac{m\hbar\omega}{2}} \begin{pmatrix} 0 & i & 0 & \cdots \\ -i & 0 & i\sqrt{2} & \cdots \\ 0 & -i\sqrt{2} & 0 & \ddots \\ \vdots & \vdots & \ddots & \ddots \end{pmatrix}$$

As expected, both x and p have Hermitian matrices.

3.2 Gaussian Wave Packet

- Consider a free particle with an generic initial wavefunction expanded in the momentum (plane wave) basis, i.e.

$$|\psi(0)\rangle = \int \tilde{\psi}(p) |p\rangle \, \mathrm{d}p.$$

Because of the plane wave dispersion relation $E = \frac{p^2}{2m}$, plane waves have a different phase velocity for each p. This varying phase velocity for different p causes the wavefunction do deform from the initial state in its time evolution $|\psi, (t)\rangle$.

- We analyze this deformation process in the concrete case when the initial state is a Gaussian wave packet. In the momentum representation, the wavefunction is

$$\tilde{\psi}(p) = C \exp\left(-\frac{(p-p_0)^2}{4\sigma_p^2}\right) \qquad \text{where} \qquad C = \frac{1}{\sqrt{\sqrt{2\pi}\sigma_p}}$$

The relevant constants are expectation values:

$$\langle p \rangle = \int p \left|\tilde{\psi}(p)\right|^2 \mathrm{d}p = p_0$$

$$\langle p^2 \rangle = \int p^2 \left|\tilde{\psi}(p)\right|^2 \mathrm{d}p = p_0^2 + \sigma_p^2$$

$$\Delta p^2 \equiv \sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$$

$$\langle E \rangle = \frac{p_0^2 + \sigma_p^2}{2m}$$

- In the x representation, the wavefunction is the characteristic function of the momentum representation $\tilde{\psi}(p)$:

$$\psi(x,0) = \langle x|\psi(0)\rangle = \int \tilde{\psi}(p) \langle x|p\rangle \, \mathrm{d}p = \frac{C}{\sqrt{2\pi\hbar}} \int \exp\left(-\frac{(p-p_0)^2}{4\sigma_p^2} + i\frac{px}{\hbar}\right) \mathrm{d}p$$

$$= \frac{C}{\sqrt{2\pi\hbar}} \int \exp\left\{-\frac{1}{4\sigma_p^2}\left[p - \left(p_0 + 2i\frac{\sigma_p^2}{\hbar}x\right)\right]^2 - \frac{\sigma_p^2 x^2}{\hbar^2} + i\frac{p_0 x}{\hbar}\right\} \mathrm{d}p$$

$$= \frac{1}{\sqrt{\sqrt{2\pi}\sigma_p}} \exp\left(-\frac{x^2}{4\sigma_x^2} + i\frac{p_0 x}{\hbar}\right)$$

where the last line uses $\sigma_x = \frac{\hbar}{2\sigma_p}$ and

$$\int_{-\infty}^{\infty} e^{-zx^2} \, \mathrm{d}x = \sqrt{\frac{\pi}{z}} \quad \text{for } \mathrm{Re}\, z > 0.$$

- Next, the wavefunction's time evolution for $t > 0$ is

$$\psi(x,t) = \frac{C}{\sqrt{2\pi\hbar}} \int \exp\left(-\frac{(p-p_0)^2}{4\sigma_p^2} + i\frac{p^2}{2m\hbar}t\right) \mathrm{d}p$$

$$= \frac{1}{\sqrt{\sqrt{2\pi}\tilde{\sigma}(t)}} \exp\left[-\frac{x^2}{4\sigma_x\tilde{\sigma}(t)} + i\left(\frac{p_0}{\hbar}x - \frac{p_0^2}{2m\hbar}t\right)\right]$$

where

$$\tilde{\sigma}(t) = \sigma_x \left(1 + i\frac{\hbar t}{2m\sigma_x^2}\right)$$

- The corresponding wavefunction (without derivation) is

$$\rho(x,t) = \frac{1}{\sqrt{2\pi}\sigma(t)} \exp\left(-\frac{(x - \langle x \rangle)^2}{2\sigma(t)^2}\right)$$

where

$$\sigma(t) = |\tilde{\sigma}(t)| \qquad \text{and} \qquad \sigma(t)^2 = \sigma_x^2 \left(1 + \frac{\hbar^2 t^2}{4m^2 \sigma_x^4} \right)$$

For reference, this (supposedly) follows from

$$2\,\mathrm{Re}\left[-\frac{x^2}{4\sigma_x \tilde{\sigma}(t)} + i \left(\frac{p_0}{\hbar} x - \frac{p_0^2}{2m\hbar} t \right) \frac{\sigma_x}{\tilde{\sigma}(t)} \right] = -\frac{\left(x - \frac{p_0}{m} t \right)^2}{2|\tilde{\sigma}(t)|^2}$$

Recall that $\tilde{\sigma}(t)$ is complex.

- Summary: the solution to the Schrödinger equation does not preserve the shape of the initial condition (like e.g. the wave equation). The deformation is a consequence of the momentum basis functions $|p\rangle$ having varying phase velocity. The solution remains a Gaussian wave packet, but its width increases with time.

3.3   Phase and Group Velocity

TODO: Optional material, add as time permits.

3.4   Time Evolution of the Dirac Delta Function

TODO: Optional material, add as time permits.

4 Symmetries

4.1 Translational Symmetry

In this section we consider only active translations, which correspond to a translation of a wavefunction, as opposed to a translation of the coordinate system or basis vectors.

- In one dimension, a translation of a wavefunction ψ by s reads

$$\tilde{\psi}(x) = \psi(x - s)$$

  We write the translation in terms of a translation operator $U(s)$ according to

$$U(s)\psi = \psi(x - s)$$

- We find the expression for $U(s)$ with a Taylor series expansion of $\psi(x - s)$:

$$U(s)\psi(x) = \psi(x - s) = \psi(x) - s\frac{\partial x}{\partial \psi(x)} \pm \cdots + \frac{(-s)^n}{n!}\frac{\partial^n \psi(x)}{\partial x^n} + \cdots$$
$$= e^{-s\frac{\partial}{\partial x}}\psi(x)$$
$$= e^{-is\frac{p}{\hbar}}\psi(x)$$

  The translation operator in one dimensions is thus

$$U(s) = e^{-is\frac{p}{\hbar}}$$

- In three dimensions, a translation by a distance s in the direction of the unit vector $\hat{\mathbf{n}}$ reads

$$\tilde{\psi}(\boldsymbol{r}) = \psi(\boldsymbol{r} - s\,\hat{\mathbf{n}})$$

  and the corresponding translation operator is

$$U(s\,\hat{\mathbf{n}}) = e^{-is\frac{\hat{\mathbf{n}}\cdot\boldsymbol{p}}{\hbar}} \qquad \text{or} \qquad U(\boldsymbol{s}) = e^{-i\frac{\boldsymbol{s}\cdot\boldsymbol{p}}{\hbar}}$$

  where we have defined the vector displacement $\boldsymbol{s} = s\,\hat{\mathbf{n}}$. Note that $\hat{\mathbf{n}} \cdot \boldsymbol{p}$, i.e. the projection of momentum in the direction $\hat{\mathbf{n}}$ is the transformation's generator.

- Like in classical mechanics, symmetries in quantum mechanics correspond to a conserved quantity—translational symmetry corresponds to conservation of (translational) momentum.

  In free space (for a globally constant potential), momentum is conserved under the condition $[\boldsymbol{p}, H] = 0$, which occurs when the Hamiltonian is invariant under translation, i.e. when

$$[U(\boldsymbol{s}), H] = 0 \text{ for all } \boldsymbol{s} \in \mathbb{R}^3$$

- In the presence of a periodic potential with period $\boldsymbol{a}$, ie. $V(\boldsymbol{r}) = V(\boldsymbol{r} + n\boldsymbol{a})$ where $n \in \mathbb{Z}$ is an integer, translational invariance holds for translations of the form $\boldsymbol{s}_n = n\boldsymbol{a}$. In this case, the wavefunction takes the form

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u(\boldsymbol{r})$$

  where $u(\boldsymbol{r} + \boldsymbol{a}) = u(\boldsymbol{r})$ is a periodic function.

Example: Position Expectation Value After Translation

- Example: calculating expectation value of position after a one-dimensional translation of the form $\tilde{\psi} = U(s)\psi(x) = \psi(x - s)$.

  First, we define the translated position operator

  $$\tilde{x} = U^\dagger x U = e^{i\frac{sp}{\hbar}} x e^{-i\frac{sp}{\hbar}}$$

  and use the Baker-Hausdorff lemma to write

  $$\tilde{x} = e^{i\frac{sp}{\hbar}} x e^{-i\frac{sp}{\hbar}} = x + \left[i\frac{sp}{\hbar}, x\right] + \frac{1}{2!}\left[i\frac{sp}{\hbar}, \left[i\frac{sp}{\hbar}, x\right]\right] + \cdots$$

  The first commutator evaluates to

  $$\frac{i}{\hbar}[sp, x] = \frac{i}{\hbar}s[p, x] + \frac{i}{\hbar}[s, x]p = \frac{i}{\hbar}(-i\hbar)s + 0 = s$$

  The remaining, higher-order commutators evaluate to zero, leaving

  $$\tilde{x} = x + s + 0 + \cdots$$

- We then find the expectation according to

  $$\begin{aligned}
  \langle \tilde{x} \rangle &= \langle \psi(x - s) | x | \psi(x - s) \rangle \\
  &= \langle U(s)\psi(x) | x | U(s)\psi(x) \rangle \\
  &= \langle \psi(x) | U^\dagger(s) x U(s) | \psi(x) \rangle \\
  &= \langle \psi(x) | \tilde{x} | \psi(x) \rangle \\
  &= \langle \psi(x) | x + s | \psi(x) \rangle \\
  &= \langle x \rangle + s
  \end{aligned}$$

4.2 Rotation

We consider active rotations of a wavefunction ψ about an axis in the direction of the unit vector $\hat{\mathbf{n}}$.

- We first consider rotations by an infinitesimal angle $\mathrm{d}\phi$, for which the rotated wavefunction $\tilde{\psi}$ is

  $$\tilde{\psi}(\boldsymbol{r}) = \psi(\boldsymbol{r} - \mathrm{d}\boldsymbol{r}) \text{ where } \mathrm{d}\boldsymbol{r} = \mathrm{d}\phi(\hat{\mathbf{n}} \times \boldsymbol{r})$$

  We find the expression for the rotation operator with a first-order Taylor expansion

  $$\begin{aligned}
  \tilde{\psi}(\boldsymbol{r}) = \psi(\boldsymbol{r} - \mathrm{d}\boldsymbol{r}) &= \psi(\boldsymbol{r}) - \frac{i}{\hbar}\big[(\hat{\mathbf{n}} \times \boldsymbol{r}) \cdot \boldsymbol{p}\big]\psi(\boldsymbol{r})\,\mathrm{d}\phi + \mathcal{O}(\mathrm{d}\phi^2) \\
  &= \left[\mathbf{I} - \frac{i}{\hbar}\big[\hat{\mathbf{n}} \cdot (\boldsymbol{r} \times \boldsymbol{p})\big]\,\mathrm{d}\phi\right]\psi(\boldsymbol{r}) + \mathcal{O}(\mathrm{d}\phi^2) \\
  &= \left[\mathbf{I} - \frac{i}{\hbar}(\hat{\mathbf{n}} \cdot \boldsymbol{L})\,\mathrm{d}\phi\right]\psi(\boldsymbol{r}) + \mathcal{O}(\mathrm{d}\phi^2)
  \end{aligned}$$

  where $\mathbf{I}$ is the identity operator and $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ is the angular momentum operator.

- We then construct a rotation by the macroscopic angle ϕ from a product of $N \to \infty$ infinitesimal rotations by $\mathrm{d}\phi = \frac{\phi}{N}$ according to

$$\tilde{\psi}(\boldsymbol{r}) = \lim_{N \to \infty} \left(\mathbf{I} - \frac{i}{\hbar} (\hat{\mathbf{n}} \cdot \boldsymbol{L}) \frac{\phi}{N} \right)^N \psi(\boldsymbol{r}) \equiv \exp\left(-\frac{i}{\hbar} (\hat{\mathbf{n}} \cdot \boldsymbol{L}) \phi \right) \psi(\boldsymbol{r})$$

The rotation operator for an angle ϕ about the axis $\hat{\mathbf{n}}$ is thus

$$U(\phi\,\hat{\mathbf{n}}) = U(\boldsymbol{\phi}) = \exp\left(-\frac{i}{\hbar} (\boldsymbol{\phi} \cdot \boldsymbol{L}) \right)$$

where we have defined the "vector angle" $\boldsymbol{\phi} = \phi\,\hat{\mathbf{n}}$. The generator of the rotation operator is $\hat{\mathbf{n}} \cdot \boldsymbol{L}$, the component of angular momentum along the rotation axis $\hat{\mathbf{n}}$.

- Rotational symmetry corresponds to conservation of angular momentum. A system's angular momentum is conserved if the system's Hamiltonian commutes with the angular momentum operator, i.e. $[\boldsymbol{L}, H] = 0$, which occurs when the Hamiltonian is invariant under rotation, i.e.

$$[U(\boldsymbol{\phi}), H] = 0 \text{ for all rotations } \boldsymbol{\phi}$$

This form of conservation occurs for spherically symmetric potentials of the form $V(\boldsymbol{r}) = V(r)$.

4.3   Parity

- Space inversion is encoded by the parity operator $\mathcal{P}$, which maps $\boldsymbol{r}$ to $-\boldsymbol{r}$ in the form $\mathcal{P} : \psi(\boldsymbol{r}) \mapsto \psi(-\boldsymbol{r})$.

- The parity operator is Hermitian, which we prove with

$$\langle \phi(\boldsymbol{r})|\mathcal{P}|\psi(\boldsymbol{r})\rangle = \langle \phi(\boldsymbol{r})|\psi(-\boldsymbol{r})\rangle = \langle \phi(-\boldsymbol{r})|\psi(\boldsymbol{r})\rangle = \langle \mathcal{P}\phi(\boldsymbol{r})|\psi(\boldsymbol{r})\rangle$$

The parity operator is also unitary, i.e. $\mathcal{P}\mathcal{P} = \mathrm{I} \implies \mathcal{P} = \mathcal{P}^{-1}$.

- The parity operator changes the sign of the gradient (or derivative) operator:

$$\mathcal{P}\nabla\psi = -\nabla\mathcal{P}\psi \implies \mathcal{P}\nabla = -\nabla\mathcal{P}$$

The relationship $\mathcal{P}\nabla = -\nabla\mathcal{P}$ implies

$$\mathcal{P}\nabla^n = (-1)^n \nabla^n \mathcal{P} \qquad \text{and} \qquad \mathcal{P}\frac{\mathrm{d}^2}{\mathrm{d}x^2} = \frac{\mathrm{d}^2}{\mathrm{d}x^2}\mathcal{P}$$

The last two identities lead to

$$\mathcal{P}\boldsymbol{p} = -\boldsymbol{p}\mathcal{P} \qquad \text{and} \qquad \mathcal{P}(\boldsymbol{r} \times \boldsymbol{p}) = \mathcal{P}\boldsymbol{L} = \boldsymbol{L}\mathcal{P}$$

- For an even potential $V(\boldsymbol{r}) = V(-\boldsymbol{r})$, the parity operator acts on V as $\mathcal{P}V(\boldsymbol{r}) = V(-\boldsymbol{r})\mathcal{P} = V(\boldsymbol{r})\mathcal{P}$, in which case

$$\mathcal{P}H\psi(\boldsymbol{r}) = H\mathcal{P}\psi(\boldsymbol{r}) \implies [\mathcal{P}, H] = 0$$

In this case, if $|\psi(\boldsymbol{r})\rangle$ is a stationary state of the Hamiltonian and obeys the stationary Schrödinger equation

$$H |\psi(\boldsymbol{r})\rangle = E |\psi(\boldsymbol{r})\rangle$$

then $|\psi(-\boldsymbol{r})\rangle$ is also a stationary state with the same energy E, i.e.

$$H |\psi(-\boldsymbol{r})\rangle = E |\psi(-\boldsymbol{r})\rangle$$

We can then (again, this applies only to an even potential) combine the stationary state solutions $|\psi(\boldsymbol{r})\rangle$ and $|\psi(-\boldsymbol{r})\rangle$ to create the odd and even functions $|\psi_+(\boldsymbol{r})\rangle$ and $|\psi_-(\boldsymbol{r})\rangle$ according to

$$\psi_\pm(\boldsymbol{r}) = \frac{1}{\sqrt{2}} \left(\psi(\boldsymbol{r}) \pm \psi(-\boldsymbol{r}) \right)$$

In other words, for an even potential, we can always create an even or odd stationary state eigenfunction for each energy eigenvalue E (assuming E is nondegenerate).

Note also that both $|\psi_+(\boldsymbol{r})\rangle$ and $|\psi_-(\boldsymbol{r})\rangle$ are eigenfunctions of the parity operator with eigenvalues ± 1, i.e.

$$\mathcal{P}\psi_+(\boldsymbol{r}) = \psi_+(\boldsymbol{r}) \qquad \text{and} \qquad \mathcal{P}\psi_-(\boldsymbol{r}) = -1 \cdot \psi_-(\boldsymbol{r})$$

4.4 Time Reversal

- The time reversal operator T maps time t to $-t$ in the form $T : \Psi(\boldsymbol{r}, t) \mapsto \Psi(\boldsymbol{r}, -t)$.

- Assume $\Psi(\boldsymbol{r}, t)$ solves the Schrödinger equation for some time-independent potential $V = V(\boldsymbol{r})$ and Hamiltonian $H \neq H(t)$. The Schrödinger equation reads

$$i\hbar \frac{\partial \Psi(\boldsymbol{r}, t)}{\partial t} = H\Psi(\boldsymbol{r}, t)$$

We then act on the equation with the time reversal operator to get

$$T\left(i\hbar \frac{\partial \Psi(\boldsymbol{r}, t)}{\partial t} \right) = i\hbar \frac{\partial \Psi(\boldsymbol{r}, -t)}{\partial (-t)} = H\Psi(\boldsymbol{r}, -t)$$

$$\implies i\hbar \frac{\partial \Psi(\boldsymbol{r}, -t)}{\partial t} = -H\Psi(\boldsymbol{r}, -t).$$

In other words, the transformed wavefunction $T\Psi(\boldsymbol{r}, t) = \Psi(\boldsymbol{r}, -t)$ solves the same Schrödinger equation with a transformed Hamiltonian $H \to -H$.

- Alternatively, we can instead define a modified time reversal operator $\mathcal{T} = KT$ where $K : \psi \mapsto \psi^*$ is the complex conjugation operator. The complex conjugation operator obeys $Kz = z^*K$ for all $z \in \mathbb{C}$ and equals its inverse, ie. $K = K^{-1}$.

Again assuming a real Hamiltonian, we return to the Schrödinger equation

$$i\hbar \frac{\partial \Psi(\boldsymbol{r}, t)}{\partial t} = H\Psi(\boldsymbol{r}, t)$$

and act on the equation with the $\mathcal{T}$ to get

$$\mathcal{T}\left(i\hbar\frac{\partial\Psi^*(\boldsymbol{r},t)}{\partial t}\right) = -i\hbar\frac{\partial\Psi^*(\boldsymbol{r},-t)}{\partial(-t)} = H\Psi^*(\boldsymbol{r},-t)$$

$$\implies i\hbar\frac{\partial\Psi^*(\boldsymbol{r},-t)}{\partial t} = H\Psi^*(\boldsymbol{r},-t)$$

In other words, $\Psi^*(\boldsymbol{r},-t)$ also solves the Schrödinger equation for the same Hamiltonian H.

- Next, we consider stationary states of the form

$$\Psi(\boldsymbol{r},t) = \psi(\boldsymbol{r})e^{-i\frac{E}{\hbar}t}$$

The modified time reversal operator $\mathcal{T}$ acts on this state to produce

$$\Psi^*(\boldsymbol{r},-t) = \psi^*(\boldsymbol{r})e^{-(-i)\frac{E}{\hbar}(-t)} = \psi^*(\boldsymbol{r})e^{-i\frac{E}{\hbar}t}$$

In other words, $\mathcal{T}$ affects only the position-dependent term $\psi(\boldsymbol{r})$, which it conjugates. With this in mind, $\mathcal{T}$ acts on the stationary Schrödinger equation $H\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$ to produce

$$H\psi^*(\boldsymbol{r}) = E\psi^*(\boldsymbol{r})$$

In other words, both ψ and ψ^* solve the stationary Schrödinger equation for a given energy eigenvalue E. For a non-degenerate spectrum, the conjugated function can be written $\psi^* = e^{i\phi}\psi(\boldsymbol{r})$. Since ψ and ψ^* differ only by a constant phase term $e^{i\delta}$ of magnitude 1, they correspond to physically identical wavefunction, since phase information is lost in any physically observable quantities, which involve the squared modulus of ψ.

- The time reversal operator $\mathcal{T}$ acts on the momentum operator $\boldsymbol{p}$, angular momentum operator $\boldsymbol{L}$, and Hamiltonian H (assuming H is time-independent and real) as

$$\mathcal{T}\boldsymbol{p} = -\boldsymbol{p}\mathcal{T} \qquad \mathcal{T}\boldsymbol{L} = -\boldsymbol{L}\mathcal{T} \qquad \mathcal{T}H = H\mathcal{T}$$

- Finally, we briefly mention that for particles with spin quantum number $s = 1/2$, we require $\mathcal{T}$ act on the spin operator $\boldsymbol{S}$ according in the same way as for angular momentum, i.e. $\mathcal{T}\boldsymbol{S} = -\boldsymbol{S}\mathcal{T}$. For this too hold, we generalize the definition of $\mathcal{T}$ for spin $s = 1/2$ particles to

$$\mathcal{T} = i\sigma_y KT \quad \text{where } \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

We will discuss spin and time reversal more thoroughly in a dedicated chapter.

- Finally, we note that position doesn't change sign under $\mathcal{T}$ reversal, i.e. $\mathcal{T}x = x\mathcal{T}$, as opposed to momentum, which obeys $\mathcal{T}p = -p\mathcal{T}$. These two identities imply

$$\mathcal{T}[x,p] = -[x,p]\mathcal{T}$$

For the fundamental commutator relationship $[x,p] = i\hbar$ to remain invariant under $\mathcal{T}$ reversal, $\mathcal{T}$ must obey $\mathcal{T}i = i\mathcal{T}$, i.e. $\mathcal{T}$ must be an anti-unitary operator.

4.5 Gauge Transformations

- We have already noted a few times in this text that multiplying a wavefunction by a phase factor $e^{i\delta}$ of magnitude one has no physically observable effect on the wavefunction.

  Multiplying a wavefunction by $e^{i\delta}$ is a case of a so-called global gauge transformation, which is a unitary transformation of the form

  $$U(\delta)\left|\psi\right> = e^{i\delta}\left|\psi\right> \equiv \left|\tilde{\psi}\right>$$

  If we apply the transformation $U(\delta) = e^{i\delta}$ to all basis functions $\{\left|n\right>\}$ spanning the Hilbert space of wavefunctions, then all matrix elements of an arbitrary operator $\mathcal{O}$ remain unchanged, i.e.

  $$\left<U(\delta)\phi\middle|\mathcal{O}\middle|U(\delta)\psi\right> = \left<\tilde{\phi}\middle|\mathcal{O}\middle|\tilde{\psi}\right> = \left<\phi\middle|\mathcal{O}\middle|\psi\right>$$

  Even more, we can multiply each basis vector $\left|n\right>$ by an individual factor $e^{i\delta_n}$, and all physical observable remain unchanged.

- Recall that in classical mechanics potential energy is determined up to an additive constant V_0, i.e we can make the transformation $V(\boldsymbol{r}) \to V(\boldsymbol{r}) + V_0$ without changing a system's equations of motion. This follows from the relationship between force and potential energy $\boldsymbol{F} = -\nabla\big[V(\boldsymbol{r}) + V_0\big] = -\nabla V(\boldsymbol{r})$ is unchanged by V_0.

  Meanwhile, in quantum mechanics, a the transformation $V(\boldsymbol{r}) \to V(\boldsymbol{r}) + V_0$ shifts a system's energy eigenvalues by V_0, i.e. $E_n \to E_n + V_0$. In this case, the time evolution operator changes according to

  $$e^{-i\frac{E}{\hbar}t}\left|\psi\right> \to e^{-i\frac{E+V_0}{\hbar}t}\left|\psi\right> = e^{-i\frac{E}{\hbar}t}e^{-i\frac{V_0}{\hbar}t}\left|\psi\right>$$

  We define the corresponding global gauge transformation as

  $$U(\delta(t)) \equiv e^{-i\frac{V_0}{\hbar}t} \qquad \text{where } \delta(t) = -\frac{V_0}{\hbar}t$$

- We can also define a so-called local gauge transformation

  $$U(\delta(\boldsymbol{r},t))\left|\Psi(\boldsymbol{r},t)\right> = e^{i\delta(\boldsymbol{r},t)}\left|\Psi(\boldsymbol{r},t)\right> \equiv \left|\tilde{\Psi}(\boldsymbol{r},t)\right>$$

  This gauge transformation preserves probability density, i.e.

  $$\left|\tilde{\Psi}(\boldsymbol{r},t)\right|^2 = \left|\Psi(\boldsymbol{r},t)\right|^2$$

  We will return to local gauge transformations when discussing a particle in an electromagnetic field.

5 Angular Momentum

- Angular momentum is associated with the angular momentum operator $\boldsymbol{L}$. The operator $\boldsymbol{L}$ is Hermitian (meaning angular momentum is a physically observable quantity) and obeys

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = -\boldsymbol{p} \times \boldsymbol{r}$$

  This relationship is proven with the help of

$$(\nabla \times \boldsymbol{r})\psi = \nabla \times (\boldsymbol{r}\psi) = (\nabla\psi) \times \boldsymbol{r} + \psi(\nabla \times \boldsymbol{r}) = (\nabla\psi) \times \boldsymbol{r} + 0$$
$$= -\boldsymbol{r} \times (\nabla\psi) = -(\boldsymbol{r} \times \nabla)\psi$$

  We could also prove the relationship by components, e.g.

$$L_z\psi = -i\hbar(yp_x - xp_y)\psi = i\hbar(p_y x - p_x y)\psi$$

  We would proceed analogously for $L_x = yp_z - zp_y$ and $L_y = zp_x - xp_z$.

- As a side note, in quantum mechanics the dot and cross products of non-commutative operators do not commute as in classical mechanics. Consider for example

$$\boldsymbol{r} \cdot \boldsymbol{p} = \boldsymbol{p} \cdot \boldsymbol{r} + 3i\hbar \qquad \boldsymbol{p} \times \boldsymbol{L} = -\boldsymbol{L} \times \boldsymbol{p} + 2i\hbar\boldsymbol{p}$$
$$(\boldsymbol{r} \times \boldsymbol{L}) \cdot (\boldsymbol{r} \times \boldsymbol{L}) = \boldsymbol{r}^2\boldsymbol{p}^2 - (\boldsymbol{r} \cdot \boldsymbol{p})^2 + i\hbar(\boldsymbol{r} \cdot \boldsymbol{p})$$

- The components of angular momentum L_x, L_y and L_z obey analogous commutator relations to the Poisson bracket relations obeyed by angular momentum in classical mechanics, e.g.

$$[L_x, L_y] = i\hbar(xp_y - yp_x) = i\hbar L_z \qquad \text{and} \qquad [L^2, L_\alpha] = 0, \quad \alpha = x, y, z$$

  We can prove the first relationship with

$$[L_x, L_y] = [yp_z - zp_y, zp_x - xp_z]$$
$$= [yp_z, zp_x] - [zp_y, zp_z] - [yp_z, xp_z] + [zp_y, xp_z]$$

  The middle two commutators are zero, since both sides contain identical terms z and p_z, respectively. We expand the remaining commutators using $[AB, C] = A[B, C] + [A, C]B$ and $[A, BC] = B[A, C] + [A, B]C$ and apply the canonical commutator relations $[r_\alpha, r_\beta] = [p_\alpha, p_\beta] = 0$ and $[r_\alpha, p_\beta] = i\hbar\delta_{\alpha\beta}$ to get

$$[L_x, L_y] = yp_x[p_z, z] + xp_y[z, p_z] = i\hbar(yp_x + xp_y) = i\hbar L_z$$

- More generally, angular momentum obeys the commutator relation

$$[L_\alpha, \mathcal{O}_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}\mathcal{O}_\gamma$$

  where the operator $\mathcal{O}$ can be any of $\boldsymbol{r}$, $\boldsymbol{p}$ or $\boldsymbol{L}$.

5.1 Properties of the Angular Momentum Operator

5.1.1 Commutation Relations

- Essentially all properties of the angular momentum operator arise from the commutator relation

$$\left[L_\alpha, L_\beta\right] = i\hbar\epsilon_{\alpha\beta\gamma}L_\gamma \qquad \text{or, in vector form,} \qquad \boldsymbol{L} \times \boldsymbol{L} = i\hbar\boldsymbol{L}$$

- If an operator $\mathcal{O}$ commutes with $\boldsymbol{L}$, then $\boldsymbol{L}$ and $\mathcal{O}$ have mutual eigenvectors, which can be exploited to simplify quantum mechanical problems.

  In general, any operator $\mathcal{O}$ that is invariant under rotation (i.e. for which $U(\boldsymbol{\phi})\mathcal{O} = \mathcal{O}U(\boldsymbol{\phi})$) commutes with the angular momentum operator. In symbols,

$$U(\boldsymbol{\phi})\mathcal{O} = \mathcal{O}U(\boldsymbol{\phi}) \implies [\boldsymbol{L}, \mathcal{O}] = 0$$

  where $U(\phi)$ is the operator encoding rotation about the axis $\hat{\mathbf{n}}$ by the angle ϕ. Applicable operators invariant under rotation include $\boldsymbol{r} \cdot \boldsymbol{p}$, $\boldsymbol{p}^2$, $\boldsymbol{L}^2$ and rotationally invariant potentials $V = V(|\boldsymbol{r}|)$.

- We often work in terms of the squared angular momentum $\boldsymbol{L}^2$, which we can write in any of the equivalent forms[3]

$$\boldsymbol{L}^2 = \boldsymbol{L} \cdot \boldsymbol{L} = L^2 = \sum_\alpha L_\alpha^2$$

  Because $\boldsymbol{L}^2$ is invariant under rotations, we have

$$[L_\alpha, L^2] = 0 \quad \text{for } \alpha \in \{x, y, z\}$$

  which means that squared angular momentum L^2 and its components L_α can share the same eigenvectors and basis.

5.1.2 The Ladder Operators

- We often analyze angular momentum problems in terms of the ladder operators L_+ and L_-, defined by

$$L_+ \equiv L_x + iL_y \qquad \text{and} \qquad L_- \equiv L_x - iL_y$$

  The ladder operators obey $L_\pm = L_\mp^\dagger$, i.e. they are each other's Hermitian conjugates.

- The ladder operators commute with the squared angular momentum operator, i.e.

$$[L^2, L_+] = [L^2, L_-] = 0$$

- Analogy to the quantum harmonic oscillator: the ladder operators L_+ and L_- are analogous to the creation and annihilation operators $a^\dagger$ and a, i.e. they "raise" and "lower" the indexes of angular momentum basis states, just like $a^\dagger$ and a raise and lower the indexes of the harmonic oscillator's Hamiltonian's basis states.

  The operator L_z is analogous to the number operator $\hat{n} = a^\dagger a$, in that it counts the number of angular momentum quanta in an angular momentum basis state.

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[3]Note that we have previously used L^2 in this text to denote the Hilbert space of wavefunctions. The difference between the square of angular momentum and the Hilbert space should be clear from context.

- First, we derive the important commutation relation $[L_z, L_\pm] = \pm\hbar L_\pm$ via

$$[L_z, L_\pm] \equiv [L_z, L_x \pm iL_y] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x)$$
$$= \hbar[\pm L_x + iL_y] = \pm\hbar L_\pm$$

where we have used $[L_\alpha, L_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}L_\gamma$.

- Second, we derive the equally important commutation relation $[L_+, L_-] = 2\hbar L_z$. To show this, we start with

$$L_\pm L_\mp = (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \pm iL_yL_x \mp iL_xL_y$$
$$= L^2 - L_z^2 \pm iL_yL_x \mp iL_xL_y$$

Next, we use $[L_\alpha, L_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}L_\gamma$ to show

$$\pm iL_yL_x \mp iL_xL_y = \pm\hbar L_z,$$

which we substitute into the expresion for $L_\pm L_\mp$ to get

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

which is really two equations of the form

$$L_+L_- = L^2 - L_z^2 + \hbar L_z \qquad \text{and} \qquad L_-L_+ = L^2 - L_z^2 - \hbar L_z.$$

Finally, we subtract the two equations two get the desired identity

$$L_+L_- - L_-+ \equiv [L_+, L_-] = 2\hbar L_z$$

5.2 Eigenvalues and Eigenfunctions of L_z and L^2

We will now use the just-derived relations $[L_z, L_\pm] = \pm\hbar L_\pm$ and $[L_+, L_-] = 2\hbar L_z$ to find the eigenvalues of the operators L_z and L^2.

5.2.1 Eigenvalues of L_z

- Let $|m\rangle$ be an eigenstate of L_z, meaning $|m\rangle$ satisfies the eigenvalue relation

$$L_z |m\rangle = m\hbar |m\rangle$$

Notation: The complete L_z eigenvalue is $m\hbar$, with units of angular momentum. In practice, we often refer to eigenvalues of L_z solely in terms of the dimensionless index m and leave the $\hbar$ implicit.

- Next, using $[L_z, L_\pm] = \pm\hbar L_\pm$ in the form $L_zL_\pm = L_\pm L_z \pm \hbar L_\pm$, the operator $L_zL_\pm$ acts on $|m\rangle$ as

$$L_zL_\pm |m\rangle = (L_\pm L_z \pm \hbar L_\pm) |m\rangle = L_\pm L_z |m\rangle \pm \hbar L_\pm |m\rangle$$
$$= L_\pm m\hbar |m\rangle \pm \hbar L_\pm |m\rangle$$
$$= (m \pm 1)\hbar L_\pm |m\rangle$$

Since L_z acts on the state $L_\pm |m\rangle$, to produce $(m \pm 1)\hbar L_\pm |m\rangle$, i.e. the same state with eigenvalue $(m \pm 1)\hbar$, it follows that L_+ and L_- raise and lower the index m of the state $|m\rangle$ by one, i.e.

$$L_\pm |m\rangle \propto |m + 1\rangle$$

We will determine the exact relationship in the following sections.

- Because L_z and L^2 commute, the eigenstate $|m\rangle$ of L_z is also an eigenstate of $|L^2\rangle$. We now show that the eigenvalues of L^2 cannot be negative:

$$L^2\,|m\rangle = \lambda\,|m\rangle \implies \langle m|L^2|m\rangle = \sum_\alpha \langle L_\alpha m|L_\alpha m\rangle = \lambda\,\langle m|m\rangle$$

  Since the quantities $\langle L_\alpha m|L_\alpha m\rangle$ and $\langle m|m\rangle$ are non-negative, the equality holds only if $\lambda \geq 0$, meaning the eigenvalues of L^2 are non-negative.

- Next, we use the commutator relation $[L^2, L_\pm] = 0 \implies L^2 L_\pm = L_\pm L^2$ and the eigenvalue relation $L^2\,|m\rangle = \lambda\,|m\rangle$ to show

$$L^2 L_\pm\,|m\rangle = L_\pm L^2\,|m\rangle = L_\pm\lambda\,|m\rangle = \lambda L_\pm\,|m\rangle$$

  In other words, the state $L_\pm\,|m\rangle$ is also an eigenstate of L^2 with the eigenvalue λ. Since the state $L_\pm\,|m\rangle$ obeys $L_\pm\,|m\rangle \propto |m+1\rangle$, i.e. has quantum number one higher or one lower than $|m\rangle$, and both $|m\rangle$ and $|m\pm 1\rangle$ have the same eigenvalue λ, it follows that under the action of L^2 states $|m\pm 1\rangle$ have the same eigenvalue as $|m\rangle$.

- Next, we introduce the orbital quantum number[4] $l > 0$, which is related to the L^2 eigenvalue λ by $\lambda = l(l+1)\hbar^2$. The motivation for this apparently strange parameterization of λ will quickly be clear.

  We use $L_\pm L_\mp = L^2 - L_z^2 \pm \hbar L_z$ and $L_\pm = L_\mp^\dagger$ to show

$$\langle L_\pm m|L_\pm m\rangle = \langle m|L_\mp L_\pm|m\rangle = \langle m|(L^2 - L_z^2 \mp \hbar L_z)|m\rangle$$

  Next, we apply the eigenvalue relations for L^2 and L_z to get

$$\langle L_\pm m|L_\pm m\rangle = \langle m|\big[l(l+1) - m(m\pm 1)\big]\hbar^2\big|m\rangle$$
$$\equiv (C_{l,m\pm 1})^2\,\langle m|m\rangle$$

  Where we have defined the constant

$$C_{l,m\pm 1} = \hbar\sqrt{l(l+1) - m(m\pm 1)} \in \mathbb{R}$$

  Since both $\langle L_\pm m|L_\pm m\rangle$ and $\langle m|m\rangle$ are non-negative, it follows that $(C_{l,m\pm 1})^2 \geq 0$, which is why $C_{l,m\pm 1}$ is real.

- The identity $C_{l,m\pm 1} \in \mathbb{R}$ is important—it means that for a state with a given orbital quantum number l, we can raise or lower states with $L_\pm$ only as long as $C_{l,m\pm 1}$ remains real, which implies

$$l(l+1) \geq m(m\pm 1) \implies |m| \leq l$$

5.2.2   Eigenvalues of L^2

- Using $|m| \leq l$, we can now find the possible values of the orbital quantum number l and thus determine L^2's eigenvalues $\lambda = l(l+1)\hbar^2$.

---

[4]Note that l is also called the azimuthal quantum number.

- First, we consider a generic L^2 eigenstate $|lm\rangle$ indexed by both m and l. We start with the maximum permitted value of m, i.e. $m = l$, and act on the state $|ll\rangle$ with L_- until we reach the minimum possible value $m = -l$. This reads

$$
\begin{aligned}
L_- |ll\rangle &= C_{l,l-1} |l, l-1\rangle \\
L_-^2 |ll\rangle &= C_{l,l-2} |l, l-2\rangle \\
&\vdots \\
L_-^k |ll\rangle &= C_{l,l-k} |l, l-k\rangle = C_{l,l-k} |l, -l\rangle
\end{aligned}
$$

Since we reached the state with $m = -l$ after $k \in \mathbb{N}$ integral steps, we have

$$
l - k = -l \implies 2l = k \implies 2l \in \mathbb{N}
$$

The possible values of l, (accounting for $l \geq 0$), are thus

$$
l = \begin{cases} 0, 1, 2, \ldots & k \text{ even} \\ \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots & k \text{ odd} \end{cases}
$$

More so, the unit increments of l mean the general condition $|m| \leq l$ can be written in the form

$$
m \in \{-l, -l+1, \ldots, l-1, l\}
$$

- Since m can take on $2l+1$ values at a given l, the L^2 eigenvalue spectrum has degeneracy $2l+1$, since at a given l there are $2l+1$ linearly independent eigenstates $|lm\rangle$ with the same eigenvalue $\lambda = l(l+1)\hbar^2$.

- The recursive action of L_- on $|lm\rangle$ also reveals the relationship

$$
L_\pm |lm\rangle = C_{l,m\pm1} |l, m \pm 1\rangle = \hbar\sqrt{l(l+1) - m(m \pm 1)} |l, m \pm 1\rangle
$$

Earlier, we had determined this relationship only to $L_\pm |m\rangle \propto |m \pm 1\rangle$.

- **TODO:** Only integer or half-integer values of l are possible because (similar to the harmonic oscillator) non-integer values of l would allow us to repeatedly lower indices with L_- until $C_{l,m-1}$ were a imaginary number, which is prohibited.

5.2.3 Eigenfunctions of L_z

- In spherical coordinates, the coordinate representation of the operator L_z reads

$$
L_z = -i\hbar \frac{\partial}{\partial \phi}
$$

where ϕ is the azimuthal angle. For each m, the eigenvalues equation

$$
L_z \psi_m = \left(-i\hbar \frac{\partial}{\partial \phi}\right) \psi_m = m\hbar \psi_m
$$

has the unique solution

$$
\psi_m = C e^{im\phi}
$$

- We consider only ψ_m solving the Schrödinger equation, which must be continuous. To satisfy continuity, the ψ_m must be periodic over $\phi \in [0, 2\pi]$, i.e.

$$
\psi_m(\phi) = \psi_m(\phi + 2\pi) \iff 1 = e^{2\pi i m} \implies m \in \mathbb{Z}
$$

In other words, only integer values of m satisfy the Schrödinger equation and correspond to physical eigenstates of L_z.

5.2.4   Eigenfunctions of L^2

- Without derivation, the eigenfunctions of the angular momentum operator L^2, in the coordinate representation, are the spherical harmonics, i.e.

$$\langle \boldsymbol{r} | lm \rangle = Y_l^m(\theta, \phi)$$

The spherical harmonics arise in the angular solution of the Laplace equation $\nabla^2 u(\boldsymbol{r}) = 0$, i.e. if we separate $u(\boldsymbol{r})$ into radial and angular component, the solution is

$$\nabla^2 u(\boldsymbol{r}) = f(r) Y_l^m(\theta, \phi) = 0$$

where $Y_l^m(\theta, \phi)$ are the spherical harmonics.

- In quantum mechanics for $m \geq 0$ we often use the definition

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

where P_l^m are the associated Legendre polynomials.

- The spherical harmonics obey

$$Y_l^{-m} = (-1)^m Y_l^{m*}$$

- As a concrete example, the first few spherical harmonics for $l = 0, 1, 2$ are

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$
$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta \qquad\qquad Y_l^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}$$
$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \quad Y_2^{\pm 1} = \mp\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\phi}$$
$$Y_2^{\pm 2} = \sqrt{\frac{5}{32\pi}} \sin^2\theta e^{\pm 2i\phi}$$

5.2.5   Matrix Representation of Angular Momentum

- We write a generic state $|\psi\rangle$ in the basis $\{|lm\rangle\}$ of angular momentum eigenfunctions as

$$|\psi\rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm} |lm\rangle$$

Note that the presence of two quantum numbers l and m introduces a double sum.

- We write a generic operator $\mathcal{O}$ in the $|lm\rangle$ basis as

$$\mathcal{O} = \sum_{l'lm'm} |l'm'\rangle \mathcal{O}_{l'lm'm} \langle lm|$$

- Finally, as a concrete example, for $l = 1$ the matrices for $L_{x,y,z}$ and L^2 read

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad\qquad L_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad\qquad L^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

As would be expected, L^2 and L_z are diagonal in the $|lm\rangle$ basis.

6 Central Potential

- We consider a particle in the time-independent central potential $V = V(r)$ with Hamiltonian

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

The particle's angular momentum $\boldsymbol{L}$ and magnitude of angular momentum L^2 are conserved, i.e.

$$[\boldsymbol{L}, H] = [L^2, H] = 0$$

Second, the we state the relations

$$\boldsymbol{r} \cdot \boldsymbol{L} = 0 \qquad \text{and} \qquad \boldsymbol{p} \cdot \boldsymbol{L} = 0$$

These two equations are the quantum mechanical analog of a particle's motion and velocity lying in a two-dimensional plane in central force motion.

6.1 The Radial Equation

- We analyze rotationally-symmetric central potential problems in spherical coordinates, where the Laplace operator reads

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

Without proof, the Laplace operator's angular component is related to angular momentum L^2 via

$$\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} = -\frac{L^2}{\hbar^2 r^2}$$

The Laplacian can thus be written

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{L^2}{\hbar^2 r^2}$$

where the angular component $\frac{L^2}{\hbar^2 r^2}$ corresponds to rotational kinetic energy.

- We can compose the Hamiltonian into a radial and angular component:

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

Next, to solve the stationary Schrödinger equation

$$H\Psi(\boldsymbol{r}) = E\Psi(\boldsymbol{r}),$$

we use the ansatz

$$\Psi(\boldsymbol{r}) = \psi(r)Y_l^m(\theta, \phi)$$

where we have separated $\Psi(\boldsymbol{r})$ into a radial and angular component. The spherical harmonics $Y_l^m(\theta, \phi)$ are a natural choice for the angular component because they are the eigenfunctions of the angular momentum operator L^2.

- Substituting the ansatz $\Psi(\boldsymbol{r}) = \psi(r)Y_l^m(\theta, \phi)$ into the stationary Schrödinger equation, applying the angular momentum eigenvalue relation

$$L^2 Y_l^m = l(l+1)\hbar^2 Y_l^m$$

and canceling Y_l^m from both sides of the equations produces the purely radial problem

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

Note that all angular dependence is gone—we have completed an important step towards finding the complete eigenfunction $\Psi(\boldsymbol{r})$.

- We solve for the radial eigenfunction $\psi(r)$ with ansatz

$$\psi(r) = \frac{u(r)}{r}$$

We then substitute this ansatz into radial eigenvalue equation. First, as a intermediate step, we calculate

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\left(\frac{u}{r}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\left(\frac{u'}{r} - \frac{u}{r^2}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}(ru' - u) = \frac{u''}{r}$$

Using this intermediate result, the radial eigenvalue equation in terms of u reads

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

- Finally, we define an effective potential

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

which includes the potential $V(r)$ in additional to the "centrifugal" term $\frac{l(l+1)\hbar^2}{2mr^2}$. In terms of V_{eff}, the stationary Schrödinger equation for u reads

$$-\frac{\hbar^2}{2m}u''(r) + V_{\text{eff}}(r)u(r) = Eu(r)$$

Note that we have reduced originally three-dimensional problem, involving the complete position vector $\boldsymbol{r} = (r, \phi, \theta)$ to a one-dimensional problem involving only r.

6.2   General Properties of the Radial Solution

6.2.1   Solutions for $r \to 0$

- We begin by considering solutions near the origin, i.e. for $r \to 0$, and consider potentials of the form

$$\lim_{r \to 0} r^2 V(r) = 0$$

For such potentials, $V(r)$ and energy E in the radial eigenvalue equation for u are negligible in comparison to the centrifugal component of V_{eff}, which scales as

$\sim r^{-2}$ and thus grows rapidly as $r \to 0$. We thus neglect $V(r)$ and E, in which case the eigenvalue equation simplifies to

$$-\frac{\hbar^2}{2m}u''(r) + \frac{l(l+1)\hbar^2}{2mr^2}u(r) = 0 \implies u''(r) = \frac{l(l+1)}{r^2}u(r).$$

We solve the equation with the ansatz $u(r) = Cr^{\lambda}$, which produces

$$\lambda(\lambda-1)Cr^{\lambda-2} = \frac{l(l+1)}{r^2}Cr^{\lambda} \implies \lambda(\lambda-1) = l(l+1).$$

- We solve the equation $\lambda(\lambda-1) = l(l+1)$ with the quadratic formula:

$$\lambda_{\pm} = \frac{1}{2} \pm \frac{1}{2}\sqrt{1+4l(l+1)} = \frac{1}{2} \pm \frac{1}{2}\sqrt{(2l+1)^2} = \frac{1}{2} \pm \left(l+\frac{1}{2}\right).$$

The two possible values of λ are

$$\lambda_+ = l+1 \qquad \text{and} \qquad \lambda_- = -l$$

The general solution to the second-order linear eigenvalue equation is thus the linear combination

$$u(r) = C_+ r^{\lambda_+} + C_- r^{\lambda_-} = C_l r^{l+1} + \frac{D_l}{r^l}$$

- Our next step is to determine the constants C_l and D_l from boundary and normalization conditions. We start all the way back at the normalization condition on $\Psi(\boldsymbol{r})$, which, when integrating in spherical coordinates, reads

$$1 \equiv \langle \Psi | \Psi \rangle = \int_{r=0}^{\infty} |\psi(r)|^2 r^2 \, \mathrm{d}r \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |Y_l^m(\theta,\phi)|^2 \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi$$

From the angular momentum chapter, we know the spherical harmonics are normalized. The integral's angular component thus evaluates to one, which implies

$$\int_0^{\infty} |\psi(r)|^2 r^2 \, \mathrm{d}r = \int_0^{\infty} |u(r)|^2 \, \mathrm{d}r \equiv 1$$

This normalization condition on u requires $D_l = 0$ for $l > 0$, since the integral of $|u(r)|^2$ would otherwise diverge at 0.

- We now separately consider the case $l = 0$, in which case the radial equations for u and $\psi = u/r$ are

$$u(r) = C_0 r + D_0 \qquad \text{and} \qquad \psi(r) = C_0 + \frac{D_0}{r}.$$

It turns out that $D_0 = 0$, leaving us with

$$u(r) = C_0 r \qquad \text{and} \qquad \psi(r) = C_0.$$

We will explain why $D_0 = 0$ using an analogy from electrostatics. We consider the Poisson equation for the electrostatic potential ϕ, which reads

$$\nabla^2 \phi(\boldsymbol{r}) = -\frac{\rho(\boldsymbol{r})}{\epsilon_0}.$$

For a point charge with charge density $\rho(\boldsymbol{r}) = q\delta^3(\boldsymbol{r})$, taking the result from electrostatics and leaving out the derivation, the solution to the Poisson equation is

$$\phi(\boldsymbol{r}) = \frac{q}{4\pi\epsilon_0 r}.$$

$$\phi(\boldsymbol{r}) = \frac{q}{4\pi\epsilon_0 r}.$$

If we substitute in the expressions for ρ and ϕ for a point charge into the Poisson equation and cancel common terms, the result is

$$\nabla^2 \frac{q}{4\pi\epsilon_0 r} = -\frac{q\delta^3(\boldsymbol{r})}{\epsilon_0} \implies \nabla^2 \frac{1}{4\pi r} = -\delta^3(\boldsymbol{r}).$$

We then rewrite the last equality in the more general form

$$\nabla^2 \psi(r) = -4\pi D_0 \delta^3(\boldsymbol{r}),$$

where we have defined $\psi = D_0/r$. In the case of a point charge we have $D_0 = 1$, but we have included D_0 to match the term D_0/r in the $l = 0$ case of the radial equation for $r \to 0$. The conclusion so far is: a wavefunction of the form $\psi(r) = D_0/r$ with $D_0 \neq 0$ corresponds to an equation fo the form

$$\nabla^2 \psi(\boldsymbol{r}) = -4\pi D_0 \delta^3(\boldsymbol{r}),$$

where the key point is that the above equation for ψ contains a delta function at the origin. However, ψ is supposed to solve the Schrödinger equation

$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\psi = E\psi,$$

which certainly does not contain a delta function at the origin. The conclusion is that ψ thus cannot contain terms of the form D_0/r, which requires $D_0 = 0$ for $l = 0$, and in fact $D_l = 0$ for all l. With $D_l = 0$ for all l, the solution to the radial equation in the limit $r \to 0$ simplifies to

$$u(r) = C_l r^{l+1} \qquad \text{and} \qquad \psi(r) = C_l r^l.$$

6.2.2 Solutions for $r \to \infty$

Continuum States with $E > 0$

- We consider potentials $V(r)$ for which

$$\lim_{r \to \infty} V(r) = 0$$

More so, we assume there exists some finite distance $r_0 \in \mathbb{R}$ such that the potential $V(r)$ is negligible for $r > r_0$.

- If we also neglect the centrifugal term, the entire effective potential V_{eff} vanishes for $r > r_0$. The radial eigenvalue equation reduces to

$$-\frac{\hbar^2}{2m}u''(r) = Eu(r)$$

The solution to this problem is

$$u(r) = C_- e^{-ikr} + C_+ e^{ikr}, \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

Note that each energy has degeneracy two, since there exist two linearly independent eigenfunctions $u(r)$ at a given value of k.

- If we neglect $V(r)$ for $r > r_0$ but include the centrifugal term, the radial eigenvalue equation is

$$-\frac{\hbar^2}{2m} u''(r) + \frac{l(l+1)\hbar^2}{2mr^2} u(r) = Eu(r)$$

In this case, without derivation, the solutions for $u(r)$ are the spherical Bessel functions j_l and Neumann functions n_l,

$$u(r) = rj_l(kr) \qquad \text{and} \qquad u(r) = rn_l(kr)$$

In the asymptotic limit $r \to \infty$, the solutions simplify to

$$u(r) \to \sin\left(kr - \tfrac{\pi}{2}l\right) \qquad \text{and} \qquad u(r) \to -\cos\left(kr - \tfrac{\pi}{2}l\right)$$

Bound States with $E < 0$

- We now consider potentials $V(r)$ obeying

$$\lim_{r \to \infty} rV(r) = 0$$

In this case, the asymptotic solution to the radial eigenvalue equation for large r is

$$u(r) \to D_- e^{-\kappa r} + D_+ e^{\kappa r}, \qquad \kappa = \sqrt{\frac{2m|E|}{\hbar^2}}$$

At the energy eigenvalues $E = E_n$ we have $D_+ = 0$, and the corresponding solutions

$$u_n(r) = D_n e^{-\kappa r}$$

is a bound state. Because the problem is one dimensional, the bound energy eigenvalues are nondegenerate by the nondegeneracy theorem.

6.2.3 Discussion of the Solutions for $r \to \infty$

- We now ask more quantitatively how fast the potential $V(r)$ must fall as r approaches infinity to justify the free and bound state ansatzes

$$u_{\text{free}}(r) = C_- e^{-ikr} + C_+ e^{ikr} \qquad \text{and} \qquad u_{\text{bound}}(r) = D_- e^{-\kappa r} + D_+ e^{\kappa r}$$

Bound States with $E < 0$

- We first consider the bound state with $E < 0$ and write the solution as

$$u(r) = v(r)e^{\pm \kappa r}$$

We substitute this expression for $u(r)$ into the radial eigenvalue equation to get

$$-\frac{\hbar^2}{2m}\left[v''(r) \pm 2\kappa v'(r) + \kappa^2 v(r)\right]e^{\pm \kappa r} + V_{\text{eff}}(r)v(r)e^{\pm \kappa r} = Ev(r)e^{\pm \kappa r}$$

We then cancel $e^{\pm i\kappa r}$ from the equation, multiply through by $\frac{2m}{\hbar^2}$, and recognize that $\kappa^2 = \sqrt{\frac{-2mE}{\hbar^2}}$ (recall $E < 0$) cancels with $\frac{2mE}{\hbar^2}$ to get

$$v''(r) \pm \kappa v'(r) - \frac{2m}{\hbar^2} V_{\text{eff}}(r) v(r) = 0$$

- Since $v(r)$ is just a correction to $e^{\pm \kappa r}$, we assume $v(r)$ changes slowly with r and neglect the second derivative $v''(r)$. We're left with

$$\pm \kappa v'(r) = \frac{2m}{\hbar^2} V_{\text{eff}}(r) v(r) \qquad \text{or} \qquad \frac{v'(r)}{v(r)} = \pm \frac{m}{\kappa \hbar^2} V_{\text{eff}}(r)$$

This is a first-order equation with separable variables, which we can integrate, i.e.

$$\int \frac{\mathrm{d}v}{v} = \pm \frac{m}{\kappa \hbar^2} \int V_{\text{eff}}(r) \, \mathrm{d}r$$

to get

$$v(r) = v(r_0) \exp\left(\pm \frac{m}{\kappa \hbar^2} \int_{r_0}^{r} V_{\text{eff}}(\tilde{r}) \, \mathrm{d}\tilde{r} \right)$$

where r_0 is a "large" value of r where V_{eff} decays slowly.

- From the above expression for $v(r)$, we see that the bound state ansatz

$$u_{\text{bound}}(r) = D_- e^{-\kappa r} + D_+ e^{\kappa r} = v(r) e^{\pm \kappa r}$$

is valid as long as $v(r)$ converges to a constant value as r approaches infinity. This holds when the limit

$$\lim_{r \to \infty} \int_{r_0}^{r} V(\tilde{r}) \, \mathrm{d}\tilde{r}$$

converges, which occurs when

$$\lim_{r \to \infty} r V(r) = 0$$

Note that the centrifugal component of V_{eff} falls with r^{-2} and is not problematic. To summarize, the bound state ansatz $u_{\text{bound}}(r) = D_- e^{-\kappa r} + D_+ e^{\kappa r}$ is valid for potentials for which $rV(r)$ vanishes at infinity.

- The limiting case at which the bound state condition

$$\lim_{r \to \infty} r V(r) = 0$$

no long holds is potentials of the form $V(r) = -\lambda/r$, for which we have

$$\lim_{r \to \infty} \int_{r_0}^{r} V(\tilde{r}) \, \mathrm{d}\tilde{r} = \lim_{r \to \infty} \left(-\lambda \ln \frac{r}{r_0} \right) \to \infty.$$

The corresponding solution for $u(r)$ in this limiting case is

$$u(r) \to v(r) e^{\pm \kappa r} = e^{\pm \kappa r} \exp\left(\mp \nu \ln \frac{r}{r_0} \right), \qquad \nu = \frac{m\lambda}{\kappa \hbar^2}$$

Canceling the exponent and logarithm shows the bound state solutions fall as

$$u(r) \sim r^{\nu} e^{-\kappa r}$$

Free Scattering States with $E > 0$

- Finally, we consider the free scattering states with positive energy, for which we assumed the ansatz

$$u_{\text{free}}(r) = C_- e^{-ikr} + C_+ e^{ikr}, \qquad k = \sqrt{\frac{2mE}{\hbar^2}}$$

- Because the free and bound state ansatzes are so similar, differing only by the presence of the imaginary unit i in the exponent and the replacement of κ with k, we would follow an analogous procedure to the above analysis of the bound states. To avoid repeating an analogous procedure, we simply quote the result:

  As before, to justify the exponential free state ansatz, the potential $V(r)$ must obey

  $$\lim_{r \to \infty} r V(r) = 0$$

  The corresponding free state solutions are

  $$u(r) \to e^{\pm ikr} \exp\left(\mp i\nu \ln \frac{r}{r_0}\right), \qquad \nu = \frac{m\lambda}{k\hbar^2}$$

  and decay asymptotically as

  $$u(r) \sim r^\nu e^{-ikr}$$

6.3   The Coulomb Potential

6.3.1   Energy Eigenvalues

- We aim to find energy levels of an electron with charge e_0 and mass m_{e} in a Coulomb potential, for which the radial eigenvalue equation reads

$$-\frac{\hbar^2}{2m_{\mathrm{e}}} u''(r) + \left(\frac{l(l+1)\hbar^2}{2m_{\mathrm{e}}r^2} - \frac{e_0^2}{4\pi\epsilon_0 r}\right) u(r) = E u(r)$$

An electron in a Coulomb potential is the basis for solving the problem of the hydrogen atom.

- We first introduce the dimensionless coordinate $\rho = \kappa r$, where $\kappa = \sqrt{\frac{2m_{\mathrm{e}}E}{\hbar^2}}$. In this case the equation simplifies to

$$\left(-\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} + \frac{l(l+1)}{\rho^2} - \frac{m_{\mathrm{e}}e_0^2}{2\pi\epsilon_0\kappa\hbar^2}\frac{1}{\rho}\right) u(\rho) = -u(\rho)$$

Finally, in terms of ρ_0, we have

$$u'' - \frac{l(l+1)}{\rho^2} u + \frac{\rho_0}{\rho} u - u = 0, \qquad \rho_0 = \frac{m_{\mathrm{e}}e_0^2}{2\pi\epsilon_0\kappa\hbar^2}$$

- We proceed with the ansatz

$$u(\rho) = \rho^{l+1} v(\rho) e^{-\rho},$$

which is intended to model the localized behavior of bound states for large ρ.

- As an intermediate step, the ansatz's first and second derivatives are

$$u' = \rho^l e^{-\rho}\big[(l+1-\rho)v + \rho v'\big]$$

$$u'' = \rho^l e^{-\rho}\left\{\left[-2l - 2 + \rho + \frac{l(l+1)}{\rho}\right]v + 2(l+1-\rho)v' + \rho v''\right\}$$

We substitute then substitute u and u'' into the dimensionless radial eigenvalue equation. After some tedious but straightforward algebra involving combining like terms and dividing through by $\rho^l e^{-\rho}$ we get the equation

$$\rho v'' + 2(l+1-\rho)v' + \big[\rho_0 - 2(l+1)\big]v = 0$$

Note that this equation contains only $v(\rho)$.

- We solve the equation for $v(\rho)$ with the Frobenius method. This involves writing $v(\rho)$ as a power series, i.e.

$$v(\rho) = \sum_{k=0}^{\infty} c_k \rho^k$$

The plan is to find v's first two derivatives, substitute the power series ansatz into the equation for v, cancel like terms, and find a recursion relation for the coefficients. The first two derivatives are

$$v' = \sum_{k=0}^{\infty} k c_k \rho^{k-1} \overset{k \to k+1}{=\!=} \sum_{k=0}^{\infty} (k+1)c_{k+1}\rho^k$$

$$v'' = \sum_{k=0} k(k+1)c_{k+1}\rho^{k-1}$$

Note that we have shifted the index from k to $k+1$, which is shown explicitly for the first derivative v' and left implicit for v''.

We substitute the power series ansatz expressions into the equation for v to get

$$\rho \sum_{k=0}^{\infty} k(k+1)c_k\rho^{k-1} + 2(l+1-\rho)\sum_{k=0}^{\infty}(k+1)c_{k+1}\rho^k$$
$$+ \big[\rho_0 - 2(l+1)\big]\sum_{k}^{\infty} c_k\rho^k = 0$$

We then distribute coefficients and re-index the $2(l+1)$ term from $k+1$ to k to get

$$\sum_{k=0}^{\infty} k(k+1)c_k\rho^k + 2(l+1)\sum_{k=0}^{\infty}(k+1)c_{k+1}\rho^k - 2\sum_{k=1} k c_k\rho^k$$
$$+ \big[\rho_0 - 2(l+1)\big]\sum_{k=0} c_k\rho^k = 0$$

For the equation to hold, the coefficients of ρ^k at a given k must be equal, which implies

$$\big[k(k+1) + 2(l+1)(k+1)\big]c_{k+1} = \big[2k - (\rho_0 - 2(l+1))\big]c_k$$

We then rearrange the above equation to get the recursive relation

$$c_{k+1} = \frac{2(k + l + 1) - \rho_0}{(k+1)(k+2l+2)} c_k$$

For large k, i.e. $k \gg l, \rho_0$, the equation reduces to the relationship for the exponential function, i.e.

$$\frac{c_k}{c_{k-1}} \to \frac{2}{k} \qquad \text{or} \qquad c_k = \frac{2^k}{k!} c_0$$

where we have re-indexed the first term by one. With the coefficients c_k known (at least for large k) we have

$$v(\rho) = \sum_{k=0}^{\infty} c_k \rho^k = c_0 \sum_{k=0}^{\infty} \frac{1}{k!} (2\rho)^k = c_0 e^{2\rho}$$

- In terms of the large k solution $v(\rho) \sim e^{2\rho}$, which corresponds to the asymptotic behavior of $v(\rho)$ for large ρ, the solution for $u(\rho)$ is

$$u(\rho) = \rho^{l+1} v(\rho) e^{-\rho} = \rho^{l+1} e^{2\rho} e^{-\rho} = \rho^{l+1} e^{\rho}$$

The relationship $u(\rho) \sim \rho^{l+1} e^{\rho}$ does not in general converge for large ρ. In fact, $u(\rho)$ is convergent only if the series ansatz for $v(\rho)$, i.e.

$$v(\rho) = \sum_{k=0}^{\infty} c_k \rho^k,$$

truncates at a finite $k_{\max} \geq 0$. Truncating at $k_{\max}$ implies $c_k = 0$ for $k > k_{\max}$. If we return to the recursive coefficient relation

$$c_{k+1} = \frac{2(k + l + 1) - \rho_0}{(k+1)(k+2l+2)} c_k,$$

the condition $c_k = 0$ for $k > k_{\max}$ implies

$$2(k_{\max} + l + 1) - \rho_0 = 0 \implies \rho_0 = 2(k_{\max} + l + 1) \in \mathbb{N}$$

In other words, ρ_0 must be an integer to satisfy the convergence of $v(\rho)$ and thus $u(\rho)$ for large ρ.

- With this integer restriction on ρ_0 in mind, we define the principle quantum number

$$n \equiv k_{\max} + l + 1$$

which implies $\rho_0 = 2n$. In terms of $\rho_0 = 2n$ and the earlier equations

$$\rho_0 = \frac{m_e e_0^2}{2\pi\epsilon_0 \kappa \hbar^2} \qquad \text{and} \qquad \kappa = \sqrt{\frac{2m_e E}{\hbar^2}},$$

the energy eigenvalues of an electron in a Coulomb potential are thus

$$E_n = -\frac{m_e}{2\hbar^2} \left(\frac{e_0^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \equiv -\frac{\text{Ry}}{n^2}, \quad n = 1, 2, 3, \ldots$$

where we have defined the Rydberg energy unit

$$1\,\text{Ry} = \frac{m_e}{2\hbar^2} \left(\frac{e_0^2}{4\pi\epsilon_0} \right)^2 = |E_1| = 13.6\,\text{eV}$$

6.3.2 Eigenfunctions

- First, we consider energy eigenvalue degeneracy. For each value of E_n, which depends only on the principle quantum number n, there exist n values of the orbital quantum number $l = 0, 1, \ldots, n-1$.

  The complete wavefunction

  $$\Psi(\boldsymbol{r}) = \psi(r) Y_l^m(\theta, \phi)$$

  is thus n-times degenerate with respect to the radial component $\psi(r)$, since n values of l correspond to the same energy E_n.

  Additionally, the energy eigenvalues are degenerate with respect to the quantum number m, which corresponds to the projection of angular momentum onto the z axis. Since E_n does not depend on m and m can assume $2l + 1$ values from $-l$ to l, there are $2l + 1$ states proportional to Y_l^m with energy E_n at a given l.

  Considering both the degeneracy with respect to both l and m, the total degeneracy of a given energy level E_n is

  $$\sum_{l=0}^{n-1} (2l + 1) = n^2$$

  In other words, the energy level E_n has degeneracy n^2.

- Next, we return to the series for $v(\rho)$, i.e.

  $$v(\rho) = \sum_{k=0}^{k_{\max}} c_k \rho^k$$

  where we have made the truncation at $k_{\max}$ explicit. Since $k_{\max} = n - l - 1$, the function $v(\rho)$ is a polynomial of order $n - l - 1$.

  Without derivation, it turns out that $v(\rho)$ takes the form of an associated Laguerre polynomial, i.e.

  $$v(\rho) \propto L_{k_{\max}}^{2l+1}(2\rho) = L_{n-l-1}^{2l+1}$$

  Note that $v(\rho)$ is indexed by both l and n.

- The complete wavefunction is thus thus

  $$\Psi_{nlm}(\boldsymbol{r}) = \psi_{nl}(r) Y_l^m(\theta, \phi)$$

  where the radial component is

  $$\psi_{nl} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \cdot \left(\frac{2r}{na_0}\right)^l \cdot L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \cdot e^{-\frac{r}{na_0}}$$

  where we have introduced the Bohr radius

  $$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e_0^2} = 0.053\,\text{nm}$$

- The wavefunctions Ψ_{nlm} are conveniently orthonormal, i.e.

  $$\int \Psi_{n'l'm'}^*(\boldsymbol{r}) \Psi_{nlm}(\boldsymbol{r}) \, \mathrm{d}^3\boldsymbol{r} = \langle n'l'm' | nlm \rangle = \delta_{n'n} \delta_{l'l} \delta_{m'm}$$

6.3.3 Semi-Classical and Classical Limits

- The angular momentum of the electron around the hydrogen nucleus is quantized according to the Wilson-Sommerfeld quantization condition

$$\frac{1}{2\pi} \oint p \, dq = n\hbar, \qquad n \in \mathbb{Z}$$

where p and q are a system's momentum and coordinates.

For an electron on a hypothetical circular orbit of radius r at speed v about the nucleus, the integral reads

$$n\hbar \equiv \frac{1}{2\pi} \oint (m_e v) \, dq = \frac{1}{2\pi} m_e v (2\pi r) = m_e r v = L_z$$

This produces the angular momentum quantization condition $L_z = n\hbar$.

Combining the quantization $n\hbar = L_z = m_e r v$ with Newton's law

$$F = m_e a = \frac{m_e v^2}{r} = \frac{e_0^2}{4\pi\epsilon_0 r^2}$$

Reproduces the Bohr energy formula

$$E_n = -\frac{m_e}{2\hbar^2} \left(\frac{e_0^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \equiv -\frac{\text{Ry}}{n^2}, \quad n = 1, 2, 3, \dots$$

- Next, we consider the eigenfunctions $|nlm\rangle$, which do not in general correspond to a uniform circular orbit of the electron about the nucleus.

Circular orbits correspond to orbits with large angular momentum for which the quantum numbers obey

$$n \gtrsim l \gg 1 \qquad \text{and} \qquad l \gtrsim m \gg 1$$

For maximum possible angular momentum, i.e. $l = n - 1$, the associated Laguerre polynomial is $L_{n-l-1}^{2l+1} = L_0^{2l+1} = 1$ and the corresponding radial eigenfunction is

$$\psi_{n,l}(r) = \psi_{n,n-1}(r) = 2^n \left[n^4 (2n-1)! a_0^3 \right]^{-1/2} \left(\frac{r}{na_0} \right)^{n-1} e^{-\frac{r}{na_0}}$$

The expectation values of r and r^2 for this radial function are

$$\langle r \rangle = \int_0^\infty r \psi_{n,n-1}^2(r) r^2 \, dr = n \left(n + \frac{1}{2} \right) a_0$$

$$\langle r^2 \rangle = \dots = n^2 (n+1) \left(n + \frac{1}{2} \right) a_0^2$$

The corresponding uncertainty in r is

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2} = \frac{n}{2} \sqrt{2n+1} a_0$$

In the limit of large n, the relative uncertainty in radius is

$$\lim_{n \to \infty} \frac{\Delta r}{\langle r \rangle} = \lim_{n \to \infty} \frac{1}{\sqrt{2n+1}} = 0$$

In other words, the orbit approaches a spherical shell with radius $\langle r \rangle$ for large n, in agreement with the classical limit.

6.3.4 The Quantum Laplace-Runge-Lenz Vector

- The n^2-fold degeneracy of the hydrogen atom's energy eigenvalues E_n has a classical analog: in the Kepler problem, multiple elliptical orbits with different orientations in space correspond to the same orbital energy.

  Recall from classical mechanics that the ellipses differ in their orientation of the semi-major axis in space, which corresponds to the orbit's conserved Laplace-Runge-Lenz (LRL) vector.

- We can introduce a quantum LRL vector $\boldsymbol{A}$ of the form

$$\boldsymbol{A} = \frac{1}{2}\big[\boldsymbol{p} \times \boldsymbol{L} + (\boldsymbol{p} \times \boldsymbol{L})^\dagger\big] - \frac{m_\mathrm{e}e_0^2}{4\pi\epsilon_0}\frac{\boldsymbol{r}}{r}$$

  The expression is similar to the classical LRL vector, except that is has been "Hermitized", i.e. we have generalized the classical expression $\boldsymbol{p} \times \boldsymbol{L}$ to

$$\frac{1}{2}\big[\boldsymbol{p} \times \boldsymbol{L} + (\boldsymbol{p} \times \boldsymbol{L})^\dagger\big]$$

  so that $\boldsymbol{A}$ is Hermitian.

- The large degeneracy of E_n in the hydrogen atom indicates the presence of conserved quantity in addition to energy and momentum, and this conserved quantity is precisely the LRL vector $\boldsymbol{A}$.

  Namely, the hydrogen atom obeys the following conservation laws:

$$[\boldsymbol{L}, H] = [L^2, H] = [\boldsymbol{A}, H] = 0 \qquad \text{and} \qquad [\boldsymbol{A}, \boldsymbol{L}] = 0$$

  The relationship $[\boldsymbol{A}, \boldsymbol{L}] = 0$ is analogous to a well-known phenomenon from classical mechanics, namely that the LRL vectors lies in the plane of the elliptical orbit.

7 Charged Particle in a Magnetic Field

- We analyze a particle of charge q and mass m in an electric field in terms of the electric potential ϕ and magnetic potential $\boldsymbol{A}$:

$$\boldsymbol{B} = \nabla \times \boldsymbol{A} \qquad \text{and} \qquad \boldsymbol{E} = -\nabla \phi - \frac{\partial \boldsymbol{A}}{\partial t}$$

  The particle's Hamiltonian is

$$H = \frac{(\boldsymbol{p} - q\boldsymbol{A})^2}{2m} + q\phi$$

- The Schrödinger equation for a particle in an electromagnetic field reads

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{(\boldsymbol{p} - q\boldsymbol{A})^2}{2m} \Psi + q\phi\Psi,$$

  which we multiply out to get

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{1}{2m} \big(- i\hbar\nabla - q\boldsymbol{A} \big)^2 \Psi + q\phi\Psi$$

$$= -\frac{\hbar^2}{2m} \nabla^2 \Psi + \frac{i\hbar q}{2m}(\nabla \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \nabla)\Psi + \frac{q^2}{2m}\boldsymbol{A}^2 \Psi + q\phi\Psi$$

  We then make the intermediate calculation

$$(\nabla \cdot \boldsymbol{A})\Psi + \boldsymbol{A} \cdot \nabla\Psi = \nabla \cdot (\Psi\boldsymbol{A}) + \boldsymbol{A} \cdot \nabla\Psi = \boldsymbol{A} \cdot \nabla\Psi + \Psi\nabla \cdot \boldsymbol{A} + \boldsymbol{A} \cdot \nabla\Psi$$

$$= 2\boldsymbol{A} \cdot \nabla\Psi + \Psi\nabla \cdot \boldsymbol{A},$$

  in terms of which the Schrödinger equation simplifies to

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + i\frac{\hbar q}{m}\boldsymbol{A} \cdot \nabla\Psi + \left(i\frac{\hbar q}{2m}(\nabla \cdot \boldsymbol{A}) + \frac{q^2}{2m}\boldsymbol{A}^2 + q\phi \right) \Psi$$

  In the conventional Coulomb gauge $\nabla \cdot \boldsymbol{A} = 0$, the Schrödinger equation reduces to

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + i\frac{\hbar q}{m}\boldsymbol{A} \cdot \nabla\Psi + \left(\frac{q^2}{2m}\boldsymbol{A}^2 + q\phi \right) \Psi$$

7.1 Zeeman Coupling

- The term $i\frac{\hbar q}{m}\boldsymbol{A} \cdot \nabla\Psi$ in the Schrödinger equation for a particle in a electromagnetic field contains the dominant coupling between the particle and the magnetic field.

  We consider a homogeneous magnetic field $\boldsymbol{B} = (0, 0, B)$, generated by the vector potential

$$\boldsymbol{A} = -\frac{1}{2}\boldsymbol{r} \times \boldsymbol{B},$$

  and continue to use the Coulomb gauge $\nabla \cdot \boldsymbol{A} = 0$.

- For the above choice of vector potential (corresponding to the homogeneous magnetic field $\boldsymbol{B} = (0, 0, B)$), the dominant magnetic coupling term reads

$$i\frac{\hbar q}{m}\boldsymbol{A} \cdot \nabla\Psi = -i\frac{\hbar q}{2m}(\boldsymbol{r} \times \boldsymbol{B}) \cdot \nabla\Psi = i\frac{\hbar q}{2m}(\boldsymbol{r} \times \nabla) \cdot \boldsymbol{B}\Psi$$

$$= \frac{q}{2m}\big[\boldsymbol{r} \times (i\hbar\nabla)\big] \cdot \boldsymbol{B}\Psi = -\frac{q}{2m}(\boldsymbol{r} \times \boldsymbol{p}) \cdot \boldsymbol{B}\Psi$$

$$= -\frac{q}{2m}\boldsymbol{L} \cdot \boldsymbol{B}\Psi$$

- Next, we define the magnetic dipole moment operator $\boldsymbol{\mu}$ and Bohr magnetic μ_B according to
$$\boldsymbol{\mu} = \frac{q}{2m}\boldsymbol{L} \qquad \text{and} \qquad \mu_B = \frac{e_0\hbar}{2m_{\mathrm{e}}}$$
The Bohr magneton is the quantum of magnetic dipole moment.

- In terms of magnetic dipole moment, the above coupling term between a particle and an external magnetic field reads
$$i\frac{\hbar q}{m}\boldsymbol{A}\cdot\nabla = -\frac{q}{2m}\boldsymbol{L}\cdot\boldsymbol{B} = -\boldsymbol{\mu}\cdot\boldsymbol{B}$$
This coupling term is called the normal Zeeman coupling term, defined as
$$H_{\mathrm{Zeeman}} = -\boldsymbol{\mu}\cdot\boldsymbol{B}$$

- The quadratic coupling term $\frac{q^2}{2m}\boldsymbol{A}^2$, again using the vector potential $\boldsymbol{A} = -\frac{1}{2}\boldsymbol{r}\times\boldsymbol{B}$ and homogeneous magnetic field $\boldsymbol{B} = (0,0,B)$, reads
$$\begin{aligned}\frac{q^2}{2m}\boldsymbol{A}\cdot\boldsymbol{A} &= \frac{q^2}{2m}\left[\left(-\frac{1}{2}\boldsymbol{r}\times\boldsymbol{B}\right)\cdot\left(-\frac{1}{2}\boldsymbol{r}\times\boldsymbol{B}\right)\right] = \frac{q^2}{8m}\left[B^2 r^2 - (\boldsymbol{B}\cdot\boldsymbol{r})^2\right] \\ &= \frac{q^2}{8m}\left\{B^2 r^2 - \left[(0,0,B)\cdot(x,y,z)\right]^2\right\} = \frac{q^2}{8m}\left(B^2 r^2 - B^2 z^2\right) \\ &= \frac{q^2 B^2}{8m}(x^2 + y^2)\end{aligned}$$
Note that the value of this quadratic coupling term depends on the choice of the gauge for $\boldsymbol{A}$, and the above result holds only for the Coulomb gauge.

- In terms of the above quadratic coupling term and the linear Zeeman coupling term, the Schrödinger equation for a particle in a homogeneous magnetic field reads
$$H = \frac{p^2}{2m} - \boldsymbol{\mu}\cdot\boldsymbol{B} + \frac{q^2 B^2}{8m}(x^2 + y^2) + q\phi$$
The quadratic coupling term is often negligible; for example, for an electron with magnetic moment $|\boldsymbol{\mu}| = \mu_B$, charge $q = e_0$ and distance scale $x^2 + y^2 \sim a_0$ in a magnetic field $B = 1\,\mathrm{T}$, we have
$$\frac{e_0 B^2}{8m_{\mathrm{e}}}a_0^2 \Big/ (\mu_B B) \sim 10^{-6}$$
In other words, the quadratic coupling term is completely negligible relative to the Zeeman term $\boldsymbol{\mu}\cdot\boldsymbol{B}$.

The Normal Zeeman Effect

- If we neglect the quadratic coupling term, the Hamiltonian for a charged particle in a magnetic field reads
$$H = \frac{p^2}{2m} - \boldsymbol{\mu}\cdot\boldsymbol{B} + q\phi$$
This Hamiltonian is used to analyze the splitting of the electron's energy levels in a hydrogen atom exposed to a weak magnetic field, which is called the normal Zeeman effect.

We can find the wavefunction reusing the results from the central potential chapter, where the general wavefunction reads

$$\Psi_{nlm}(\boldsymbol{r}) = \psi_{nl}(r)Y_l^m(\theta, \varphi)$$

and ψ_{nl} is the radial eigenfunction. Although this eigenfunction was originally derived in the context of angular momentum $\boldsymbol{L}$, since $\boldsymbol{\mu}$ and $\boldsymbol{L}$ commute (recall the relationship $\boldsymbol{\mu} = \frac{q}{2m}\boldsymbol{L}$), eigenfunctions of $\boldsymbol{L}$ are also eigenfunctions of $\boldsymbol{\mu}$.

In the absence of a magnetic field, considering only the electrostatic Coulomb potential $\phi(\boldsymbol{r})$, the hydrogen atom's energy eigenfunctions obey

$$H \ket{nlm} = -\frac{\text{Ry}}{n^2} \ket{nlm}$$

In the presence of a homogeneous magnetic field and the Zeeman coupling term $-\boldsymbol{\mu} \cdot \boldsymbol{B}$, the energy levels split according to

$$H \ket{nlm} = \left(-\frac{\text{Ry}}{n^2} + m\mu_B B\right) \ket{nlm}$$

Note that each energy level now depends on m as well as n, which reduces (but does not fully remove) energy level degeneracy, which still exists with respect to l.

7.2 Landau Levels

7.2.1 The Landau Gauge

- We consider only a particle in the two-dimensional xy plane. The Landau gauge potential is used generate a homogeneous magnetic field of the form $\boldsymbol{B} = B\,\hat{\mathbf{z}}$. Two possible gauge potentials generating this magnetic field are

$$\boldsymbol{A} = xB\,\hat{\mathbf{y}} \qquad \text{and} \qquad \boldsymbol{A} = -yB\,\hat{\mathbf{x}}$$

Both recover $\boldsymbol{B} = B\,\hat{\mathbf{z}}$ via $\boldsymbol{B} = \nabla \times \boldsymbol{A}$; we will work with the latter, i.e. $\boldsymbol{A} = -yB\,\hat{\mathbf{x}}$.

- In terms of the gauge potential $\boldsymbol{A} = -yB\,\hat{\mathbf{x}}$, the stationary Schrödinger equation for a particle in an electromagnetic field reads

$$
\begin{aligned}
H\Psi &= \frac{(\boldsymbol{p} - q\boldsymbol{A})^2}{2m} + q\phi = \frac{1}{2m}\left(-i\hbar\nabla + qyB\right)^2 \Psi + q\phi\Psi \\
&= \frac{1}{2m}\left[\left(-i\hbar\frac{\partial}{\partial x} + qBy\right)^2 - \hbar^2\frac{\partial^2}{\partial y^2} - \hbar^2\frac{\partial^2}{\partial z^2}\right]\Psi + q\phi\Psi = E\Psi
\end{aligned}
$$

Next, we assume the electric potential depends only on the single coordinate y, ie. $\phi(\boldsymbol{r}) = \phi(y)$, and solve the equation with the ansatz

$$\Psi(\boldsymbol{r}) = \exp\left[i\left(\frac{p_x}{\hbar}x + \frac{p_z}{\hbar}z\right)\right]\chi(y)$$

The exponential term contains plane waves in the x and z directions.

- Next, as an intermediate step, we note that applying a function of the operator $\hat{p}_x$ to the operator's plane wave eigenfunction is the same as multiplying the plane wave by the momentum operator's eigenvalue p_x. In equation form, this reads.

$$\hat{f}(\hat{p}_x)e^{i\frac{p_x}{\hbar}x} \equiv \hat{f}\left(-i\hbar\frac{\partial}{\partial x}\right)e^{i\frac{p_x}{\hbar}x} = f(p_x)e^{i\frac{p_x}{\hbar}x}$$

In our case, this identity is used to show

$$\left(-i\hbar\frac{\partial}{\partial x} + qBy\right)^2 \exp\left[i\left(\frac{p_x}{\hbar}x + \frac{p_z}{\hbar}z\right)\right]\chi(y) = (p_x + qBy)^2 \exp\left[i\left(\frac{p_x}{\hbar}x + \frac{p_z}{\hbar}z\right)\right]\chi(y)$$

where p_x on the right hand side is the eigenvalue of the operator $\hat{p}_x \to -i\hbar\frac{\partial}{\partial x}$ on the left hand side, and the corresponding function is $f(x) = x^2$. With this identity in mind, we substitute the ansatz for Ψ into the Schrödinger equation, note that $\phi = \phi(y)$ acts only on the $\chi(y)$ factor of Ψ, evaluate the relevant momentum eigenvalue relations for x and z, and cancel out the common factor $\exp\left[i\left(\frac{p_x}{\hbar}x + \frac{p_z}{\hbar}z\right)\right]$ to get

$$\frac{1}{2m}(p_x + qBy)^2\chi(y) - \frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}y^2}\chi(y) + \frac{p_z^2}{2m}\chi(y) + q\phi(y)\chi(y) = E\chi(y).$$

Note that p_x and p_z are scalar eigenvalues and not operators. We consider only a particle restricted to the xy plane, so $p_z = 0$, and the equation simplifies to

$$\frac{1}{2m}\left[(p_x + qBy)^2 - \hbar\frac{\mathrm{d}^2}{\mathrm{d}y^2}\right]\chi(y) + V(y)\chi(y) = E\chi(y)$$

where we have defined $V(y) = q\phi(y)$ and noted $p_z = 0$. Note than we have reduced the problem to a one-dimensional problem in the coordinate y.

- Next, we define the cyclotron frequency ω and characteristic magnetic length ξ, defined as

$$\omega = \frac{qB}{m} \qquad \text{and} \qquad \xi = \sqrt{\frac{\hbar}{qB}}$$

We introduce a wave vector k, allowing use to write $p_x = \hbar k$, and finally define a k-displacement $y_k = -\xi^2 k$. In terms of these new quantities, we can write the Hamiltonian in the same form as a displaced harmonic oscillator with an additional potential $V(y)$, i.e.

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\chi(y)}{\mathrm{d}y^2} + \frac{m\omega^2}{2}(y - y_k)^2\chi(y) + V(y)\chi(y) = E\chi(y)$$

- In absence of an electric potential, and thus $\phi = V = 0$, the solutions of the above equation are simply the eigenstates of a displaced harmonic oscillator, i.e.

$$\chi_{nk}(y) = \psi_n(y - y_k)$$

The complete solution Ψ, again for a particle in the xy plane with $p_z = 0$, is

$$\Psi_{nk}(x, y) = e^{i\frac{p_x}{\hbar}x}\chi_{nk}(y) = \frac{1}{\sqrt{2\pi}}e^{ikx}\psi_n(y - y_k)$$

where the factor $\sqrt{2\pi}$ is included for normalization. The corresponding energy eigenvalues, i.e.

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega$$

are called Landau levels. These energy eigenvalues are highly degenerate, since a continuum of linearly independent eigenstates Ψ_{nk}, which can exist for any $k \in \mathbb{R}$, will have the same energy eigenvalue E_n.

- Since the energy eigenvalue E_n is independent of k, the time evolution of a wavefunction expanded in the $\{\Psi_{nk}\}$ basis is trivial, since, because of the high degeneracy with respect to k, any linear combination of the stationary states is still a stationary state with the same energy.

  As an example, consider an arbitrary wavefunction ψ initially expanded in the plane wave basis, i.e.

  $$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int \widehat{\psi}(k) e^{ikx} \, \mathrm{d}k$$

  The wavefunction maintains its shape for $t > 0$, since the time evolution reads

  $$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int \widehat{\psi}(k) e^{ikx} e^{-i\frac{E}{\hbar}t} \, \mathrm{d}k = e^{-i\frac{E}{\hbar}t} \frac{1}{\sqrt{2\pi}} \int \widehat{\psi}(k) e^{ikx} \, \mathrm{d}k$$
  $$= e^{-i\frac{E}{\hbar}t} \psi(x, 0)$$

  where we can move the time-dependent factor out of the integral since E does not depend of k. Thus, the wavefunction's probability density $\rho = |\psi|^2$ does not change with time, i.e.

  $$\rho(x, t) = \rho(x, 0)$$

  since the factor $e^{-i\frac{E}{\hbar}t}$ vanishes when taking ψ's squared absolute value.

- Because the Landau energy levels are degenerate with respect to k, which is related to p_x via $p_x = \hbar k$, the particle's eigenstates cannot move in the x direction (if they could move, then E would depend on x and thus k). Similarly eigenstates at a given Landau level cannot move in the y direction, since the states are stationary states.

  The classical analog of this high degeneracy is a particle having fixed energy moving at a given angular speed around a circle with fixed radius, regardless of the position of the circle's center.

7.2.2 Some Generalized Solutions

- We can generalize the solution to a Hamiltonian with the additional y-dependent harmonic potential $V(y) = \frac{1}{2} m\omega_y y^2$. Since the sum of two separate harmonic potentials is still a harmonic potential, the solution in the presence of the additional $V(y)$ term is the same as for $V = 0$, just with renormalized constants

$$\omega \to \omega' = \sqrt{\omega^2 + \omega_y} \qquad \text{and} \qquad y_k \to y_k' = \frac{\omega^2}{\omega^2 + \omega_y^2} y_k$$

- In the presence of a homogeneous electric field $\boldsymbol{\mathcal{E}} = \mathcal{E}\,\hat{\mathbf{y}}$, which corresponds to the linear potential $V(y) = -q\mathcal{E}y$. The corresponding eigenvalue equations is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\chi(y)}{\mathrm{d}y^2} + \frac{m\omega^2}{2}(y - y_k')^2\chi(y) - q\mathcal{E}y\chi(y) = E\chi(y),$$

where the new displacement y_k' is

$$y_k' = -\xi^2 k + \frac{m\mathcal{E}}{qB^2}$$

Next, we define the energy shift

$$\epsilon_k = \frac{\mathcal{E}}{B}\hbar k + \frac{m\mathcal{E}^2}{2B^2},$$

In terms of which the new potential in the presence of the electric field $\boldsymbol{\mathcal{E}} = \mathcal{E}\,\hat{\mathbf{y}}$ reads

$$V'(y) = \frac{m\omega^2}{2}(y - y_k')^2 + \epsilon_k$$

The corresponding energy eigenstates are again shifted harmonic oscillator eigenstates of the form

$$\chi_{nk}(y) = \psi_n(y - y_k') \implies \Psi_{nk}(x,y) = \frac{1}{\sqrt{2\pi}}e^{ikx}\psi_n(y - y_k')$$

while the corresponding eigenvalues are

$$E_{nk} = \left(n + \frac{1}{2}\right)\hbar\omega + \epsilon_k$$

Note that the presence of the ϵ_k term breaks the energy degeneracy with respect to k. Because of the broken degeneracy with respect to k, the corresponding time-dependent wave packets are mobile in the x direction, and propagate with group velocity

$$v_{\mathrm{group}_x} = \frac{\partial E_{nk}}{\partial[\hbar k]} = \frac{\mathcal{E}}{B}$$

In other words, the charged particle moves in the direction $\boldsymbol{\mathcal{E}} \times \boldsymbol{B}$, which is the basis for understanding the quantum Hall effect.

7.2.3   The Cylindrically-Symmetric Gauge Potential

- We write the Hamiltonian operator in the form

$$H = \frac{\boldsymbol{\pi}^2}{2m}$$

where we have defined the kinetic moment operator

$$\boldsymbol{\pi} = \boldsymbol{p} - q\boldsymbol{A}$$

The kinetic moment moment operator is Hermitian, i.e. $\boldsymbol{\pi} = \boldsymbol{\pi}^\dagger$, and depends on the choice of gauge potential $\boldsymbol{A}$.

- The $\boldsymbol{\pi}$ operator obeys the commutation relation $[\pi_x, \pi_y] = i\hbar q B_z$, which we show with

$$[\pi_x, \pi_y] = [p_x - qA_x, p_y - qA_y] = -q[p_x, A_y] - q[A_x, p_y]$$
$$= i\hbar q \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) = i\hbar q B_z$$

where we have used $[p_i, p_j] = 0$ and $\boldsymbol{B} = \nabla \times \boldsymbol{A}$. We can proceed analogously for the other components, which leads to commutation relation

$$[\pi_\alpha, \pi_\beta] = i\hbar q \epsilon_{\alpha\beta\gamma} B_\gamma \qquad \text{or} \qquad \boldsymbol{\pi} \times \boldsymbol{\pi} = i\hbar q \boldsymbol{B}$$

- We now restrict ourselves to a particle confined in the xy plane, and define the raising and lowering operators

$$a = \frac{1}{\sqrt{2\hbar qB}}(\pi_x + i\pi_y) \qquad \text{and} \qquad a^\dagger = \frac{1}{\sqrt{2\hbar qB}}(\pi_x - i\pi_y)$$

These operators obey the commutation relation $\left[a, a^\dagger\right] = 1$, which we show with

$$\left[a, a^\dagger\right] = \frac{1}{2\hbar qB}[\pi_x + i\pi_y, \pi_x - i\pi_y] = \frac{1}{2\hbar qB}\left([\pi_x, i\pi_y] + [i\pi_y, \pi_x]\right)$$
$$= \frac{2}{2\hbar qB}[i\pi_y, \pi_x] = \frac{i}{\hbar qB}(-i\hbar qB) = 1$$

In terms of a and $a^\dagger$, the Hamiltonian reads

$$H = \frac{\boldsymbol{\pi}^2}{2m} = \frac{1}{4m}\left[(\pi_x + i\pi_y)(\pi_x - i\pi_y) + (\pi_x - i\pi_y)(\pi_x + i\pi_y)\right]$$
$$= \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)$$

- We assume a homogeneous magnetic field $\boldsymbol{B} = B\,\hat{\mathbf{z}}$, which we write in terms of the symmetric gauge potential

$$\boldsymbol{A} = \frac{B}{2}(-y\,\hat{\mathbf{x}} + x\,\hat{\mathbf{y}})$$

We continue our analysis in the complex plane (this works well because our particle is restricted to the xy plane) and define the particle's position vector $\boldsymbol{r} = (x, y)$ in terms of the complex number $z = x + iy$.

- *Mathematical aside:* We introduce the Wirtinger derivatives, which read

$$\frac{\partial}{\partial z} = \frac{1}{2}\left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right) \qquad \text{and} \qquad \frac{\partial}{\partial z^*} = \frac{1}{2}\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)$$

The Wirtinger derivatives obey the standard properties of complex differentiation, such as the power rule,

$$\frac{\partial z^m}{\partial z} = mz^{m-1} \qquad \text{and} \qquad \frac{\partial z}{\partial z^*} = 0 = \frac{\partial z^*}{\partial z}$$

- In terms of the Wirtinger derivatives, the lowering operator reads

$$a = \frac{1}{\sqrt{2\hbar qB}} \left(i\hbar \frac{\partial}{\partial x} + \hbar \frac{\partial}{\partial y} - \frac{qB}{2}(-i + ix) \right) = -\frac{i}{\sqrt{2}} \left(2\xi \frac{\partial}{\partial z^*} + \frac{z}{2\xi} \right)$$

where we have defined $\xi = \sqrt{\frac{\hbar}{qB}}$.

- Next, we aim to find the particle's energy eigenfunctions. Similar to our treatment of the harmonic oscillator, we apply the lowering operator a to an as-of-yet unknown ground state:

$$a\psi_0(z, z^*) = 0$$

In the coordinate representation of a, using the Wirtinger derivatives, this reads

$$-\frac{i}{\sqrt{2}} \left(2\xi \frac{\partial}{\partial z^*} + \frac{z}{2\xi} \right) \psi_0(z, z^*) = 0 \implies 2\frac{\partial}{\partial z^*} \psi_0(z, z^*) = -\frac{z}{2\xi^2} \psi_0(z, z^*)$$

Note that we have written the wavefunction ψ_0, which was originally a function of x and y, as a function of the complex variables z and z^*. Since x and y are linearly independent, so are z and z^*.

- We then integrate the above equation with respect to z^*, which results in

$$\psi_0(z, z^*) = C \exp\left(-\frac{zz^*}{4\xi^2} \right) = C \exp\left(-\frac{|z|^2}{4\xi^2} \right)$$

where, because of the integration over z^*, the normalization constant C can also have a dependence on z, i.e. $C = C(z)$. Note that the arbitrary choice of $C(z)$ corresponds to the earlier continuous degeneracy of the Landau levels.

- In general, we can write the analytic function $C(z)$ as a power series, e.g. $C(z) = \sum_m C_m z^m$. Since the choice of $C(z)$ is arbitrary, we will write C as the single term

$$C = C_m z^m \implies \psi_{0_m}(z, z^*) = C_m z^m e^{-\frac{|z|^2}{4\xi^2}}, \qquad m = 0, 1, 2, \ldots$$

To satisfy the normalization condition on ψ_{0_m}, the constant C_m must obey

$$C_m^2 = \pi m! \left(2\xi^2\right)^{m+1}$$

Note that m must be integer-valued to satisfy periodicity of ψ with respect to the azimuthal angle φ on the interval $[0, 2\pi]$; and non-negative to satisfy the normalization condition.

- In terms of both the Cartesian coordinates x and y and the polar coordinates r and φ, the eigenfunctions read

$$\Psi_{0_m}(x, y) \equiv \psi_{0_m}(z, z^*) = C_m(x + iy)^m e^{-\frac{x^2 + y^2}{4\xi}}$$

$$= C_m r^m e^{im\varphi} e^{-\frac{r^2}{4\xi^2}}$$

Meanwhile, the ground state eigenvalue relation reads

$$H\Psi_{0_m} = \frac{\hbar\omega}{2} \Psi_{0_m} \equiv E_{\text{LLL}} \Psi_{0_m}$$

where we have defined the "lowest Landau level" $E_{\text{LLL}} = E_0 = \frac{\hbar\omega}{2}$, which is just the ground state energy eigenvalue.

We generate excited states with the raising operator $a^\dagger$, e.g.

$$\Psi_{1_m} = a^\dagger \Psi_{0_m} \implies \Psi_{n_m} = \left(a^\dagger\right)^n \Psi_{0_m}$$

- Without derivation, the ground state expectation values of r and r^2 are

$$\langle r \rangle = \sqrt{2}\frac{(m+\frac{1}{2})!}{m!}\xi \qquad \text{and} \qquad \langle r^2 \rangle = \langle (x^2 + y^2) \rangle = 2(m+1)\xi^2$$

For $m \gg 1/2$, the expectation value $\langle r \rangle$ approaches $r \to \sqrt{2m}\xi$, and the uncertainty in radius approaches

$$\Delta r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2} \to \sqrt{2(m+1)\xi^2 - 2m\xi^2} = \sqrt{2}\xi$$

7.2.4   Coherent States and the Classical Limit

- In the classical limit, we expect uniform circular motion at the Larmor frequency. We will use the raising and lowering operators, much like when finding the coherent states of a shifted harmonic oscillator. We start with a wave packet shifted to $z \to (z - z_0)$

$$a\psi = -i\frac{z_0}{\xi}\psi \implies \psi = C\exp\left[-\frac{1}{4\xi^2}\left(|z|^2 - 2zz_0 + |z_0|^2\right)\right]$$

- The corresponding probability density is

$$\rho(x,y) = |\psi|^2 = C^2 \exp\left\{-\frac{1}{4\xi^2}\left[(x-x_0)^2 + (y-y_0)^2\right]\right\}$$

and is centered at $\boldsymbol{r}_0 = (x_0, y_0)$. Note that the center $\boldsymbol{r}_0$ moves clockwise in the plane around a circle of radius $|r_0| = x_0^2 + y_0^2$ at the cyclotron frequency $\omega = \frac{qB}{m_{\text{mass}}}$ according to

$$z_0(t) = \left[x_0(0) + iy_0(0)\right]e^{-i\omega t}$$

The wave packet's width is constant is becomes negligible in the classical limit, in which the circular orbit occurs on a macroscopic scale, since $\xi/r \to 0$.

7.3   Local Gauge Transformations

- Recall from the chapter on symmetries that the global gauge transformation $\Psi \to e^{i\delta}\Psi$, in which a wave function is multiplied by a constant phase factor, has no effect on the wavefunction's observable properties, and neither does the general change of basis $\{|n\rangle\} \to \{e^{i\delta_n}\}|n\rangle$.

We now introduce the local gauge transformation, which is time-dependent and reads

$$\Psi'(\boldsymbol{r}, t) = e^{i\delta(\boldsymbol{r},t)}\Psi(\boldsymbol{r}, t)$$

We substitute this transformation into the Schrödinger equation for a particle in an electromagnetic field and get

$$i\hbar\frac{\partial}{\partial t}\Psi' = \frac{1}{2m}(-i\hbar\nabla - q\boldsymbol{A}')^2\Psi' + q\phi'\Psi'$$

- Next, an intermediate mathematical aside which will help us simplify the expression $(-i\hbar\nabla - q\boldsymbol{A}')^2$. For a transformed wavefunction $\Psi' = e^{i\delta(\boldsymbol{r},t)}\Psi$, we have

$$\left(i\frac{\partial}{\partial x} + f\right)e^{i\delta}\Psi = -\frac{\partial\delta}{\partial x}e^{i\delta}\Psi + ie^{i\delta}\frac{\partial\Psi}{\partial x} + fe^{i\delta}\Psi$$

$$= e^{i\delta}\left(i\frac{\partial}{\partial x} + f - \frac{\partial\delta}{\partial x}\right)\Psi$$

Repeating the above procedure recursively leads to

$$\left(i\frac{\partial}{\partial x} + f\right)^2 e^{i\delta}\Psi = e^{i\delta}\left(i\frac{\partial}{\partial x} + f - \frac{\partial\delta}{\partial x}\right)^2\Psi$$

- Next, we choose the gauge potentials

$$\boldsymbol{A}' = \boldsymbol{A} + \nabla\Lambda \qquad \text{and} \qquad \phi' = \phi - \frac{\partial\Lambda}{\partial t}$$

which preserve the magnetic and electric field $\boldsymbol{B}' = \boldsymbol{B}$ and $\boldsymbol{\mathcal{E}}' = \boldsymbol{\mathcal{E}}$.

Finally, we choose the phase term $\delta(\boldsymbol{r},t)$ in the local gauge transform to be

$$\delta(\boldsymbol{r},t) = \frac{q}{\hbar}\Lambda(\boldsymbol{r},t) \implies \Psi'(\boldsymbol{r},t) = e^{i\frac{q}{\hbar}\Lambda(\boldsymbol{r},t)}\Psi(\boldsymbol{r},t)$$

- In terms of the above gauge transforms and the earlier mathematical aside, the Schrödinger equation for the original wavefunction Ψ reads

$$i\hbar\frac{\partial}{\partial t}\Psi = \frac{1}{2m}\sum_\alpha\left(-i\hbar\frac{\partial}{\partial x_\alpha} - qA'_\alpha + \hbar\frac{\partial\delta}{\partial x_\alpha}\right)^2\Psi + \left(q\phi' + \hbar\frac{\partial\delta}{\partial t}\right)\Psi$$

where we have substituted in the identities

$$-qA_\alpha = -qA'_\alpha + \hbar\frac{\partial\delta}{\partial x_\alpha} \qquad \text{and} \qquad q\phi = q\phi' + \hbar\frac{\partial\delta}{\partial t}$$

These follow from our choice of gauge potential and the earlier mathematical aside, but we state them without full derivation.

- Matrix elements of observable quantities, which correspond to Hermitian operators, are gauge-invariant, i.e.

$$\rho'(\boldsymbol{r},t) = \left|e^{i\delta}\Psi(\boldsymbol{r},t)\right|^2 = \rho(\boldsymbol{r},t)$$

As an example, we consider the kinetic moment operator $\boldsymbol{\pi} = \boldsymbol{p} - q\boldsymbol{A}$:

$$\left\langle\Psi'_1\middle|\boldsymbol{\pi}'\middle|\Psi'_2\right\rangle = \left\langle\Psi'_1\middle|\boldsymbol{p} - q\boldsymbol{A}'\middle|\Psi'_2\right\rangle = \left\langle e^{i\frac{q}{\hbar}\Lambda}\Psi_1\middle|\boldsymbol{p} - q(\boldsymbol{A} + \nabla\Lambda)\middle|e^{i\frac{q}{\hbar}\Lambda}\Psi_2\right\rangle$$

$$= \left\langle e^{i\frac{q}{\hbar}\Lambda}\Psi_1\middle|e^{i\frac{q}{\hbar}\Lambda}(\boldsymbol{p} - q\boldsymbol{A})\middle|\Psi_2\right\rangle = \left\langle\Psi_1\middle|(\boldsymbol{p} - q\boldsymbol{A})\middle|\Psi_2\right\rangle$$

$$= \left\langle\Psi_1\middle|\boldsymbol{\pi}\middle|\Psi_2\right\rangle.$$

7.4 Aharonov Bohm Effect

- We continue our study of a particle in a static (time-independent) magnetic field $\boldsymbol{B} = \boldsymbol{B}(\boldsymbol{r})$. Consider a region of space without a magnetic field, which implies

$$\boldsymbol{B} = \nabla \times \boldsymbol{A} = 0$$

Since $\nabla \times \boldsymbol{A} = 0$, we can write $\boldsymbol{A}$ as the gradient of a scalar field $\boldsymbol{A} = \nabla\Lambda$. We then have

$$\Lambda(\boldsymbol{r}) = \Lambda(\boldsymbol{r}_0) + \int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \boldsymbol{A}(\tilde{\boldsymbol{r}}) \cdot \mathrm{d}\tilde{\boldsymbol{r}}$$

Note that this relationship is analogous the work done by the electric force, for which $\nabla \times \boldsymbol{\mathcal{E}} = 0$ allows use to write $\boldsymbol{\mathcal{E}} = -\nabla\phi$ and thus

$$q\phi(\boldsymbol{r}) - q\phi(\boldsymbol{r}_0) = -q\int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \boldsymbol{\mathcal{E}}(\boldsymbol{r}) \cdot \mathrm{d}\tilde{\boldsymbol{r}} \implies \phi(\boldsymbol{r}) = \phi(\boldsymbol{r}_0) - \int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \boldsymbol{\mathcal{E}}(\boldsymbol{r}) \cdot \mathrm{d}\tilde{\boldsymbol{r}}$$

- We choose the origin $\boldsymbol{r}_0$ to occur in the region without magnetic field, i.e. $\boldsymbol{B}(\boldsymbol{r}_0) = 0$. The constant $\Lambda(\boldsymbol{r}_0)$ then represents a global phase shift, which we can freely set to zero. The Schrödinger equation in the region of space with zero magnetic field reads

$$i\hbar\frac{\partial}{\partial t}\Psi = \frac{(\boldsymbol{p} - q\boldsymbol{A})^2}{2m}\Psi + V\Psi$$

However, we can also work with the transformed Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi' = \frac{(\boldsymbol{p} - q\boldsymbol{A}')^2}{2m}\Psi' + V\Psi' = \frac{p^2}{2m}\Psi' + V\Psi'$$

where the vector potential $\boldsymbol{A}'$ (but not necessarily $\boldsymbol{A}$) vanishes in the absence of a magnetic field via

$$\boldsymbol{A}' = \boldsymbol{A} + \nabla(-\Lambda) = \boldsymbol{A} - \boldsymbol{A} = 0$$

- Both wavefunctions Ψ and Ψ' describe the same particle in the absence of a magnetic field, and are related by the local gauge transformation

$$\Psi'(\boldsymbol{r}, t) = e^{-i\frac{q}{\hbar}\Lambda}\Psi(\boldsymbol{r}, t).$$

We then define

$$\Psi_{\mathrm{A}}(\boldsymbol{r}) = \exp\left(i\frac{q}{\hbar}\int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \boldsymbol{A}(\tilde{\boldsymbol{r}}) \cdot \mathrm{d}\tilde{\boldsymbol{r}}\right)\Psi_0(\boldsymbol{r}),$$

where Ψ_{A} denotes the wavefunction evaluated in the presence of a non-zero vector potential and Ψ_0 denotes the wavefunction evaluated in the absence of a vector potential.

Aharonov-Bohm Thought Experiment

- Consider a two-dimensional system in which an electron can move along a straight quantum wire, which briefly splits into two branches, which then join back into a single wire.

- Assume, in the absence of both a magnetic field and vector potential ($\boldsymbol{B} = 0$ and $\boldsymbol{A} = 0$), that an electron wave packet Ψ travels along the wire, splits at the first junction (e.g. Roman numeral I) into two equal parts $\Psi_\mathrm{I} = \Psi_1 + \Psi_2$ where Ψ_1 and Ψ_2 encode the probability for taking either branch 1 and branch 2.

  Both Ψ_1 and Ψ_2 propagate along their respective branches and joint back at the second junction (e.g. Roman numeral II) into the wavefunction Ψ_II.

  The total electric current through the wire after the junction is proportional to $|\Psi_\mathrm{II}|^2$, the probability of finding the particle at the second junction.

- Next, assume the region between the two branches is permeated with a magnetic field $\boldsymbol{B}$, and that $\boldsymbol{B} = 0$ everywhere else, including along the wires carrying the electron wave packet.

  Although $\boldsymbol{B} = 0$ along the wires, the vector potential, defined via $\boldsymbol{B} = \nabla \times \boldsymbol{A}$ "spills out" from the region between the branches, and is non-zero along the wires.

  The corresponding wavefunction encoding the electron at the second junction is then

  $$\Psi_\mathrm{II} = e^{i\delta_1}\Psi_{0_1} + e^{i\delta_2}\Psi_{0_2}$$

  where Ψ_{0_1} and Ψ_{0_2} are wavefunctions in the absence of $\boldsymbol{A}$, while the phases in each branch are defined via

  $$\delta_1 = \frac{q}{\hbar}\int_{\text{branch 1}} \boldsymbol{A}(\boldsymbol{r}) \cdot \mathrm{d}\boldsymbol{r} \qquad \text{and} \qquad \delta_2 = \frac{q}{\hbar}\int_{\text{branch 2}} \boldsymbol{A}(\boldsymbol{r}) \cdot \mathrm{d}\boldsymbol{r}$$

- Assuming the probabilities of taking either branch are equal, we have $\Psi_{0_1} = \Psi_{0_2} \equiv \Psi_0$ and the wavefunction at the second junction is

  $$\Psi_\mathrm{II} = e^{i\delta_2}\left(1 + e^{i(\delta_1 - \delta_2)}\right)\Psi_0$$

  Since the phases δ_1 and δ_2 are defined by path integrals over branches 1 and 2, respectively, the phase difference $\delta_1 - \delta_2$ corresponds to a closed line integral over the loop formed by the two branches:

  $$\delta_1 - \delta_2 = \frac{q}{\hbar}\oint_{\text{loop}} \boldsymbol{A}(\boldsymbol{r}) \cdot \mathrm{d}\boldsymbol{r}.$$

  We then rewrite the closed line integral with Stokes' theorem to get

  $$\delta_1 - \delta_2 = \frac{q}{\hbar}\oiint_S \nabla \times \boldsymbol{A} \cdot \mathrm{d}\boldsymbol{S} = \frac{q}{\hbar}\oiint_S \boldsymbol{B} \cdot \mathrm{d}\boldsymbol{S} = \frac{q}{\hbar}\Phi_\mathrm{M}$$

  where S is the surface bounded by the loop and Φ_M is the magnetic flux through the surface. In other words, the phase difference $\delta_1 - \delta_2$ is proportional to the magnetic flux through the region between the two branches.

  The wavefunction encoding the electron at the second junction is thus

  $$\Psi_\mathrm{II} = e^{i\delta_2}\left(1 + e^{i\frac{q}{\hbar}\Phi_\mathrm{M}}\right)\Psi_0$$

- The ratio of electric currents in the presence of a magnetic field in the intra-branch region, with non-zero Φ_M, and in the absence of a magnetic field, with $\Phi_M = 0$, is thus

$$\frac{I_B}{I_0} = \frac{|\Psi_{II_B}|^2}{|\Psi_{II}|^2} = \frac{\left| e^{i\delta_2} \left(1 + e^{i\frac{q}{\hbar}\Phi_M} \right) \Psi_0 \right|^2}{\left| e^{i\delta_2}(1+1)\Psi_0 \right|^2} = \frac{1}{4}\left| 1 + e^{i\frac{q}{\hbar}\Phi_M} \right|^2 = \cos^2\left(\frac{q}{2\hbar}\Phi_M \right)$$

In other words, the current through the second branch changes with the magnetic field in the region between the two conducting branches, even though the magnetic field is zero along the branches themselves.

Interpretation: the electron current I_B oscillates in an interference pattern as a function of a magnetic field that occurs only in a region the electrons don't travel through!

8   Spin

- We will denote the spin operator by $\boldsymbol{S} = (S_x, S_y, S_z)$. The spin operator, like the angular momentum operator, obeys the fundamental commutation relations

$$[S_\alpha, S_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}S_\gamma \qquad \text{or, in vector form,} \qquad \boldsymbol{S} \times \boldsymbol{S} = i\hbar\boldsymbol{S}$$

- Like for the angular momentum ladder operators, we introduce the spin ladder operators

$$S_+ = S_x + iS_y \qquad \text{and} \qquad S_- = S_x - iS_y$$

The ladder operators are not Hermitian, and instead obey $S_\pm = S_\mp^\dagger$.

When applied to the angular momentum basis states $|sm_s\rangle$, the spin ladder operators produce

$$S_{\pm_s} |sm_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}\,|s, m_s \pm 1\rangle$$

We recover S_x and S_y from the ladder operators via

$$S_x = \frac{1}{2}(S_+ + S_-) \qquad \text{and} \qquad S_y = \frac{1}{2i}(S_+ - S_-)$$

- Spin corresponds to angular momentum with half-integer eigenvalues $s = \frac{1}{2}, \frac{3}{2}, \ldots$, which do not lead to continuous solutions of the Schrödinger equation. As a result, the spin eigenvectors do not have a coordinate representation of the form $\boldsymbol{r}\,|sm_s\rangle$.

Instead, we represent the spin eigenstates with *spinors*, which are $(2s+1)$-tuples in the complex vector space $\mathbb{C}^{2s+1}$.

- The spin states $|sm_s\rangle$ are eigenstates of both the S^2, the squared magnitude of spin, and of S_z, the projection of spin onto the z axis. The relevant eigenvalue relations are

$$S_z |sm_s\rangle = m_s\hbar\,|sm_s\rangle \qquad \text{and} \qquad S^2 |sm_s\rangle = s(s+1)\hbar^2\,|sm_s\rangle$$

As for l and m_l, the spin quantum numbers s and m_s can take on the values

$$s \in \{0, 1, 2, \ldots\} \qquad \text{and} \qquad m_s \in \{-s, -s+1, \ldots, s-1, s\}$$

Of course, states with $s = 0$ have no spin, and we consider only $s \geq 1$ in this chapter.

8.1   Spin 1/2

- Keep in mind that m_l and m_s are different quantum numbers, and correspond to the operators L_z and S_z. When it is clear from context whether we're referring to m_l or m_s, we only write m and drop the subscript, which we will periodically do in the remainder of this section for $m_s \equiv m$.

- We give states with spin $s = 1/2$ special attention. We write these states

$$|sm\rangle = \left|\tfrac{1}{2}m\right\rangle \equiv |\chi_m\rangle$$

When $s = 1/2$, m can be either $-1/2$ or $1/2$, and we often abbreviate the two possible $|sm\rangle$ states with arrows:

$$\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle \equiv |\uparrow\rangle \qquad \text{and} \qquad \left|\tfrac{1}{2} - \tfrac{1}{2}\right\rangle \equiv |\downarrow\rangle$$

to indicate "spin up" or "spin down". These states may also be written as the spinors

$$|\uparrow\rangle \equiv \chi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{and} \qquad |\downarrow\rangle \equiv \chi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The states $|\uparrow\rangle$ and $|\downarrow\rangle$ form an orthonormal basis spanning the space of eigenstates for particles with spin $s = 1/2$.

As a side note, keep in mind that behind the arrow notation is the definition

$$\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle \equiv |\uparrow\rangle \qquad \text{and} \qquad \left|\tfrac{1}{2} - \tfrac{1}{2}\right\rangle \equiv |\downarrow\rangle$$

relating the arrows to the actual values of s and m.

- The spin ladder operators act on the states $|\uparrow\rangle$ and $|\downarrow\rangle$ according to

$$S_+ |\downarrow\rangle = \hbar |\uparrow\rangle \qquad \text{and} \qquad S_- |\uparrow\rangle = \hbar |\downarrow\rangle$$

In matrix form, in the $\{|\uparrow\rangle, |\downarrow\rangle\}$ basis, the ladder operators thus read

$$S_+ = \begin{pmatrix} \langle\uparrow|S_+|\uparrow\rangle & \langle\uparrow|S_+|\downarrow\rangle \\ \langle\downarrow|S_+|\uparrow\rangle & \langle\downarrow|S_+|\downarrow\rangle \end{pmatrix} = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$S_- = \begin{pmatrix} \langle\uparrow|S_-|\uparrow\rangle & \langle\uparrow|S_-|\downarrow\rangle \\ \langle\downarrow|S_-|\uparrow\rangle & \langle\downarrow|S_-|\downarrow\rangle \end{pmatrix} = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Note that the matrices maintain the relationship $S_\pm = S_\mp^\dagger$.

- In matrix form, the spin components S_x and S_y, which we can construct directly from the S_+ and S_- matrices, are

$$S_x = \frac{1}{2}(S_+ + S_-) = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$S_y = \frac{1}{2i}(S_+ - S_-) = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

We find the z component S_z with direct calculation:

$$S_z = \begin{pmatrix} \langle\uparrow|S_z|\uparrow\rangle & \langle\uparrow|S_z|\downarrow\rangle \\ \langle\downarrow|S_z|\uparrow\rangle & \langle\downarrow|S_z|\downarrow\rangle \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} \langle\uparrow|\uparrow\rangle & -\langle\uparrow|\downarrow\rangle \\ \langle\downarrow|\uparrow\rangle & -\langle\downarrow|\downarrow\rangle \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The corresponding eigenvectors (spinors) for S_x, S_y and S_z are

$$\chi_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \qquad \chi_y = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \qquad \chi_z = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- For $\alpha \in \{x, y, z\}$, the squared components S_α^2 read

$$S_\alpha^2 = \frac{\hbar^2}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The squared components obey the commutation relations

$$[S_\alpha, S_\beta^2] = 0 \qquad \text{an} \qquad [S_\alpha^2, S_\beta^2] = 0$$

Finally, the squared spin operator S^2 acts on the states $|\chi_m\rangle \equiv \left|\frac{1}{2}m\right\rangle$ according to

$$S^2 |\chi_m\rangle = \sum_\alpha S_\alpha^2 |\chi_m\rangle = \frac{3}{4}\hbar^2 |\chi_m\rangle$$

- As a final note, for larger spins $s = \frac{3}{2}, \frac{5}{2}, \ldots$, we write the spin wavefunction $|\psi\rangle$ by expanding $|\psi\rangle$ in the $\{|sm\rangle\}$ basis:

$$|\psi\rangle = \sum_{s=1/2}^{\infty} \sum_{m=-s}^{s} c_{sm} |sm\rangle, \qquad c_{sm} = \langle sm|\psi\rangle$$

8.1.1 The Pauli Spin Matrices

- We often analyze states with spin $s = 1/2$ using the Pauli spin matrices σ_x, σ_y and σ_z, which read

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_x = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Together with the 2×2 identity matrix I, the Pauli matrices provide a convenient basis in which to expand an arbitrary 2×2 matrix.

- In terms of the Pauli spin matrices, the spin operator reads

$$\boldsymbol{S} = \frac{\hbar}{2}\boldsymbol{\sigma} \qquad \text{where} \qquad \boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$$

- The Pauli spin matrices are Hermitian, and obey the following properties:

$$\sigma_\alpha = \sigma_\alpha^\dagger \qquad \sigma_\alpha^2 = \text{I} \qquad \det \sigma_\alpha = -1 \qquad \text{tr}\, \sigma_\alpha = 0$$

Each of the spin matrices has eigenvalues $\lambda_\pm = \pm 1$—note that the eigenvalues must be equal and opposite to satisfy $\text{tr}\, \sigma_\alpha = 0$.

- The product of two spin matrices obeys the general formula

$$\sigma_\alpha \sigma_\beta = \delta_{\alpha\beta}\,\text{I} + i\epsilon_{\alpha\beta\gamma}\sigma_\gamma$$

- The commutation relations between the spin matrices are analogous to the spin operator commutation relations, and read

$$[\sigma_\alpha, \sigma_\beta] = 2i\epsilon_{\alpha\beta\gamma}\sigma_\gamma$$

More so, we use matrix multiplication to derive the anti-commutator relation

$$\{\sigma_\alpha, \sigma_\beta\} = \sigma_\alpha \sigma_\beta + \sigma_\beta \sigma_\alpha = 2\delta_{\alpha\beta}\,\text{I}$$

- Finally, in terms of the spin matrices, an arbitrary vector $\boldsymbol{a} \in \mathbb{R}^3$ can be written

$$\boldsymbol{a} \cdot \boldsymbol{\sigma} = \sum_\alpha a_\alpha \sigma_\alpha = (\boldsymbol{a} \cdot \boldsymbol{\sigma})^\dagger$$

Note that σ_α is a 2×2 matrix, while a_α is a scalar. Meanwhile, for two vectors $\boldsymbol{a}, \boldsymbol{b} \in \mathbb{R}^2$ we have

$$(\boldsymbol{a} \cdot \boldsymbol{\sigma})(\boldsymbol{b} \cdot \boldsymbol{\sigma}) = \sum_{\alpha, \beta} a_\alpha \sigma_\alpha b_\beta \sigma_\beta = \boldsymbol{a} \cdot \boldsymbol{b}\, \mathrm{I} + i \sum_{\alpha, \beta} \epsilon_{\alpha\beta\gamma} a_\alpha b_\beta \sigma_\gamma$$
$$= (\boldsymbol{a} \cdot \boldsymbol{b})\, \mathrm{I} + i(\boldsymbol{a} \times \boldsymbol{b}) \cdot \boldsymbol{\sigma}$$

Again, we stress that σ_α and I are 2×2 matrices, while a_α and b_α are scalars.

8.2   Rotation of Spinors

- For particles with spin $s = 1/2$, spinors, which describe general spin states, are determined by $2s + 1 = 2$ coordinates, e.g. $a, b \in \mathbb{C}$, that satisfy the normalization condition $|a|^2 + |b|^2 = 1$. Some notation:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_\uparrow + b\chi_\downarrow \qquad |\chi\rangle = a\,|\uparrow\rangle + b\,|\downarrow\rangle$$

The product of two spinor states reads

$$\langle \chi_1 | \chi_2 \rangle = \begin{pmatrix} a_1^* & b_1^* \end{pmatrix} \cdot \begin{pmatrix} a_2 \\ b_2 \end{pmatrix} = a_1^* a_2 + b_1^* b_2$$

- The expectation values of the Pauli spin matrices in a given spin state $|\chi\rangle$ are

$$\langle \sigma_x \rangle = \langle \chi | \sigma_x | \chi \rangle = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a^* & b^* \end{pmatrix} \cdot \begin{pmatrix} b \\ a \end{pmatrix} = 2\,\mathrm{Re}\left[a^* b\right]$$

$$\langle \sigma_y \rangle = \langle \chi | \sigma_y | \chi \rangle = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a^* & b^* \end{pmatrix} \cdot \begin{pmatrix} -ib \\ ia \end{pmatrix} = 2\,\mathrm{Im}\left[a^* b\right]$$

$$\langle \sigma_z \rangle = \langle \chi | \sigma_z | \chi \rangle = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a^* & b^* \end{pmatrix} \cdot \begin{pmatrix} a \\ -b \end{pmatrix} = |a|^2 - |b|^2$$

- We rotate a spinor by the angle ϕ about the axis $\hat{\mathbf{n}}$ with the unitary rotation operator

$$U(\phi\,\hat{\mathbf{n}})\,|\chi\rangle = \exp\left(-i\phi\frac{\hat{\mathbf{n}} \cdot \boldsymbol{S}}{\hbar}\right) |\chi\rangle$$

We begin by writing the rotation operator as a Taylor series in terms of the spin matrix vector $\boldsymbol{\sigma}$:

$$U(\phi\,\hat{\mathbf{n}}) = \exp\left(-i\phi\frac{\hat{\mathbf{n}} \cdot \boldsymbol{S}}{\hbar}\right) = \exp\left(-\frac{i\phi}{2}\,\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}\right) = \sum_{k=0}^{\infty} \frac{1}{k!}\left(-\frac{i\phi}{2}\,\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}\right)^k$$

We then write $\hat{\mathbf{n}} \cdot \boldsymbol{\sigma}$ in the form

$$(\hat{\mathbf{n}} \cdot \boldsymbol{\sigma})^k = \begin{cases} \mathrm{I} & k \text{ even} \\ \hat{\mathbf{n}} \cdot \boldsymbol{\sigma} & k \text{ odd} \end{cases}$$

The rotation operator then reduces to the linear function

$$U(\phi\,\hat{\mathbf{n}}) = \sum_{k=0}^{\infty} \frac{1}{k!}\left(-\frac{i\phi}{2}\,\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}\right)^k = \left[1 - \frac{1}{2!}\left(\frac{\phi}{2}\right)^2 + \frac{1}{4!}\left(\frac{\phi}{2}\right)^4 \mp \cdots\right]\mathrm{I}$$
$$- i\left[\frac{\phi}{2} - \frac{1}{3!}\left(\frac{\phi}{2}\right)^3 + \frac{1}{5!}\left(\frac{\phi}{2}\right)^5 \mp \cdots\right]\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}$$

Using the power series definitions of the sine and cosine function, this becomes

$$U(\phi\,\hat{\mathbf{n}}) = \cos\left(\frac{\phi}{2}\right)\mathrm{I} - i\sin\left(\frac{\phi}{2}\right)\hat{\mathbf{n}}\cdot\boldsymbol{\sigma}$$

Note that rotating a spinor by an angle $\phi = 2\pi$ corresponds to multiplication by $-\mathrm{I}$, and not simply the identity I. We must rotate a spinor around "twice", by an angle of 4π, to reach its original orientation.

- We can parameterize an arbitrary spinor $|\chi\rangle$ with two angles. We begin by rotating a spin-up state $|\uparrow\rangle$ by an angle θ about the y axis, followed by a rotation by the angle ϕ about the z axis. The result is

$$|\chi\rangle = U(\phi\,\hat{\mathbf{e}}_z)U(\theta\,\hat{\mathbf{e}}_y)|\uparrow\rangle = e^{-i\frac{\phi}{2}\sigma_z}e^{-i\frac{\theta}{2}\sigma_y}|\uparrow\rangle$$
$$= e^{-i\frac{\phi}{2}}\left[\cos\left(\frac{\theta}{2}\right)|\uparrow\rangle + e^{i\phi}\sin\left(\frac{\theta}{2}\right)|\downarrow\rangle\right]$$

Since a wavefunction is determined only up to a constant phase factor, we can neglect the coefficient $e^{-i\frac{\phi}{2}}$ go get

$$|\chi(\theta,\phi)\rangle = \cos\left(\frac{\theta}{2}\right)|\uparrow\rangle + e^{i\phi}\sin\left(\frac{\theta}{2}\right)|\downarrow\rangle$$

- As an example, if we rotate the spinor only about the y axis, we have

$$U(\theta\,\hat{\mathbf{e}}_y) = e^{-i\frac{\theta}{2}\sigma_y} = \begin{pmatrix}\cos\frac{\theta}{2} & -\sin\frac{\theta}{2}\\\sin\frac{\theta}{2} & \cos\frac{\theta}{2}\end{pmatrix}$$

Note that if we rotate $|\uparrow\rangle \equiv |\chi_z\rangle$, which is an eigenstate of S_z, by an angle $\pi/2$ in the x direction, we end up with an eigenstate of the operator S_x:

$$U\left(\frac{\pi}{2}\,\hat{\mathbf{e}}_y\right)\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = \chi_x$$

since $S_x|\chi_x\rangle = \frac{\hbar}{2}|\chi_x\rangle$.

- We then repeat the procedure, rotating the S_z eigenstate $|\uparrow\rangle \equiv |\chi_z\rangle$ by an arbitrary angle θ to get

$$U(\theta\,\hat{\mathbf{e}}_y)\begin{pmatrix}1\\0\end{pmatrix} = \begin{pmatrix}\cos\frac{\theta}{2}\\\sin\frac{\theta}{2}\end{pmatrix} = \chi_z(\theta).$$

The resulting state is an eigenstate of the projection of spin in the direction of the vector $\hat{\mathbf{n}}_0 = \cos\theta\,\hat{\mathbf{e}}_x + \sin\theta\,\hat{\mathbf{e}}_z$, since

$$(\hat{\mathbf{n}}_0\cdot\boldsymbol{S})|\chi_z(\theta)\rangle = (\sin\theta\sigma_x + \cos\theta\sigma_z)|\chi_z(\theta)\rangle = \frac{\hbar}{2}\begin{pmatrix}\cos\theta & \sin\theta\\\sin\theta & -\cos\theta\end{pmatrix}|\chi_z(\theta)\rangle$$
$$= \frac{\hbar}{2}|\chi_z(\theta)\rangle$$

- The above unit vector $\hat{\mathbf{n}}_0$ was constructed with $\phi = 0$. For a more general direction $\hat{\mathbf{n}} = (\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta)$, we have

$$\hat{\mathbf{n}}(\theta, \phi) \cdot \boldsymbol{S}\, |\chi(\theta, \phi)\rangle = \frac{\hbar}{2}\, |\chi(\theta, \phi)\rangle$$

- Finally, we can recover the direction $\hat{\mathbf{n}}$ via

$$\langle\chi(\theta, \phi)|\boldsymbol{\sigma}|\chi(\theta, \phi)\rangle = \hat{\mathbf{n}}(\theta, \phi)$$

We prove this by components. Starting with σ_x, we have

$$\langle\chi(\theta, \phi)|\boldsymbol{\sigma}|\chi(\theta, \phi)\rangle = \begin{pmatrix} \cos\frac{\theta}{2}, & e^{-i\phi}\sin\frac{\theta}{2} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos\frac{\theta}{2} \\ e^{i\phi}\sin\frac{\theta}{2} \end{pmatrix}$$

$$= \begin{pmatrix} \cos\frac{\theta}{2}, & e^{-i\phi}\sin\frac{\theta}{2} \end{pmatrix} \begin{pmatrix} e^{i\phi}\sin\frac{\theta}{2} \\ \cos\frac{\theta}{2} \end{pmatrix}$$

$$= \sin\theta\cos\phi = \hat{\mathbf{n}} \cdot \hat{\mathbf{e}}_x$$

The calculation for σ_y and σ_z is analogous.

8.3 Time Reversal of Spinors

- Recall from the symmetry chapter that the time reversal operator for a particle with spin $s = 1/2$ is

$$\mathcal{T} = i\sigma_y KT \equiv \tau KT, \qquad \tau = i\sigma_y = \begin{pmatrix} 0 & 1 \\ -1 & 1 \end{pmatrix}$$

where K is the complex conjugation operator and T changes the sign of time. We begin by confirming the commutator and anti-commutator relations

$$\{\sigma_x, \tau\} = \{\sigma_z, \tau\} = 0 \qquad \text{and} \qquad [\sigma_y, \tau] = 0$$
$$[\sigma_x, K] = [\sigma_z, K] = 0 \qquad \text{and} \qquad \{\sigma_y, \tau\} = 0$$

From these relations, it follows that $\mathcal{T}$ reverses spin, which we show with the components of $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$:

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} KT\sigma_\alpha = -\sigma_\alpha \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} KT \implies \mathcal{T}\boldsymbol{S} = -\boldsymbol{S}\mathcal{T}$$

- The matrix elements of $\boldsymbol{\sigma}$ obey

$$\langle\mathcal{T}\chi_1|\boldsymbol{\sigma}|\mathcal{T}\chi_2\rangle = \langle i\sigma_y KT\chi_1|\boldsymbol{\sigma} i\sigma_y K|T\chi_2\rangle = -\langle i\sigma_y KT\chi_1|i\sigma_y K\boldsymbol{\sigma}|T\chi_2\rangle$$
$$- \langle KT\chi_1|K\boldsymbol{\sigma}|T\chi_2\rangle = -\langle T\chi_1|\boldsymbol{\sigma}|T\chi_2\rangle^*$$
$$- \langle\chi_1(-t)|\boldsymbol{\sigma}|\chi_2(-t)\rangle^*$$

The above result implies

$$\langle\mathcal{T}\chi|\boldsymbol{\sigma}|\mathcal{T}\chi\rangle = -\langle\chi(-t)|\boldsymbol{\sigma}|\chi(-t)\rangle$$

- Time-dependent spinors $\chi(t)$ transform under time reversal according to

$$\mathcal{T}\chi(t) = \mathcal{T}\begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \begin{pmatrix} b^*(-t) \\ -a^*(-t) \end{pmatrix}$$

- Finally, we write the time-reversed state as

$$\mathcal{T}\left|\chi(\theta,\phi)\right\rangle = \left|\chi(\theta+\pi,\phi)\right\rangle = \left|\tilde{\chi}(\theta,\phi)\right\rangle$$

This state is a second eigenstate of the earlier equation $\hat{\mathbf{n}}(\theta,\phi)\cdot\boldsymbol{S}\left|\chi(\theta,\phi)\right\rangle = \frac{\hbar}{2}\left|\chi(\theta,\phi)\right\rangle$

$$\hat{\mathbf{n}}(\theta,\phi)\cdot\boldsymbol{S}\left|\mathcal{T}\chi(\theta,\phi)\right\rangle = -\frac{\hbar}{2}\left|\mathcal{T}\chi(\theta,\phi)\right\rangle$$

8.4 Changing the Axis of Quantization

- The basis states $\left|\uparrow\right\rangle$ and $\left|\downarrow\right\rangle$ correspond to a choice of the z axis as the axis of quantization.

  More generally, recall that the states $\left|\chi(\theta,\phi)\right\rangle$ and $\left|\mathcal{T}\chi(\theta,\phi)\right\rangle$ are eigenstates of the projection of spin $\boldsymbol{S}$ onto the direction

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

  We can use these states as basis vectors with respect to the new quantization axis $\hat{\mathbf{n}}$. In this cases the basis vectors are

$$\left|\chi_m(\hat{\mathbf{n}})\right\rangle = \begin{cases} \cos\theta\left|\uparrow\right\rangle + e^{i\phi}\sin\theta\left|\downarrow\right\rangle & m = \frac{1}{2} \\ \sin\theta\left|\uparrow\right\rangle - e^{i\phi}\cos\theta\left|\downarrow\right\rangle & m = -\frac{1}{2} \end{cases}$$

- In terms of the basis vectors $\left|\chi_m(\hat{\mathbf{n}})\right\rangle$, we can write an arbitrary spin state $\left|\psi\right\rangle$ as

$$\left|\psi\right\rangle = \sum_m c_m\left|\chi_m(\hat{\mathbf{n}})\right\rangle, \qquad c_m = \left\langle\chi_m(\hat{\mathbf{n}})|\psi\right\rangle$$

8.5 Coupling of Spin and and Electromagnetic Field

- The spin magnetic moment $\boldsymbol{\mu}_S$ of a charged particle with spin $s = 1/2$ is defined as

$$\boldsymbol{\mu}_S = g\frac{q}{2m}\boldsymbol{S}.$$

  The factor g is called the gyromagnetic factor or simply g-factor, and takes on different values for different particles. For an electron, we have $g \approx 2$.

- The spin magnetic moment is used to to define the anomalous Zeeman coupling of a spin $s = 1/2$ particle with a magnetic field:

$$H_{\text{anomalous}} = -\boldsymbol{\mu}_S\cdot\boldsymbol{B}$$

- Next, we consider a semi-classical picture of an electron orbiting a hydrogen nucleus. The electron feels both an electric interaction due to the Coulomb force, and, in its own coordinate system, a magnetic field

$$\boldsymbol{B} = -\frac{1}{c^2}(\boldsymbol{v}\times\boldsymbol{\mathcal{E}})$$

which arises because in the electron's coordinate system, the positively-charged proton orbits the electron at speed $\hat{\mathbf{v}}$, which leads to a magnetic force via the Lorentz interaction.

- In a spherically-symmetric potential $V = V(r)$ we have

$$\boldsymbol{\mathcal{E}} = -\frac{1}{q}\nabla V(r) = \frac{1}{q}\frac{\partial V}{\partial r}\frac{\boldsymbol{r}}{r}$$

The corresponding magnetic field reads

$$\boldsymbol{B} = -\frac{1}{qc^2}\left(\boldsymbol{v}\times\frac{\partial V}{\partial r}\frac{\boldsymbol{r}}{r}\right) = \frac{1}{qmc^2}\frac{1}{r}\frac{\partial V}{\partial r}\boldsymbol{L}$$

- We then apply the quantum-mechanical properties of the angular momentum operator $\boldsymbol{L}$ and use the result in the Zeeman formula with $\boldsymbol{\mu} = \boldsymbol{\mu}_S$. The resulting effective Hamiltonian is

$$H_{\mathrm{LS}} = \frac{1}{m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\boldsymbol{L}\cdot\boldsymbol{S}$$

This heuristically-derived result is too large by a factor of two with respect to the correct result derived from the Dirac equation for relativistic particles, which is beyond the scope of this course.

- Finally, we mention the coupling of spin to angular momentum for a particle moving in a plane that is orthogonal to a homogeneous electric field. As before, we use the Lorentz expression for magnetic field $\boldsymbol{B} = -\frac{1}{c^2}(\boldsymbol{v}\times\boldsymbol{\mathcal{E}})$ and the Zeeman coupling. The result is

$$\boldsymbol{\mu}\cdot(\boldsymbol{v}\times\boldsymbol{\mathcal{E}}) \implies \boldsymbol{\sigma}\cdot(\boldsymbol{p}\times\boldsymbol{\mathcal{E}}) = (\boldsymbol{\sigma}\times\boldsymbol{p})\cdot\boldsymbol{\mathcal{E}}$$

This expression results in the Rashba coupling term

$$H_{\mathrm{Rashba}} = \alpha(\boldsymbol{\sigma}\times\boldsymbol{p})\cdot\hat{\mathbf{e}}_z$$

8.6   More on the Pauli Formalism

- We now consider a spin wavefunction Ψ whose components are both time-dependent spinors:

$$\Psi(\boldsymbol{r},t) = \begin{pmatrix} \psi_\uparrow(\boldsymbol{r},t) \\ \psi_\downarrow(\boldsymbol{r},t) \end{pmatrix}$$

The two components encode the probability amplitudes of detecting the particle with either spin up or spin down near the location $\boldsymbol{r}$ at the time t—the respective amplitudes are

$$\rho_\uparrow(\boldsymbol{r},t) = |\psi_\uparrow(\boldsymbol{r},t)|^2 \qquad \text{and} \qquad \rho_\downarrow(\boldsymbol{r},t) = |\psi_\downarrow(\boldsymbol{r},t)|^2$$

- The total probability density is $\rho = \rho_\uparrow + \rho_\downarrow$ and must satisfy the normalization condition

$$\int \rho(\boldsymbol{r},t)\,\mathrm{d}^3\boldsymbol{r} \equiv 1$$

- We can parameterize the state Ψ at a position $(\boldsymbol{r},t)$ using four dependent real functions ρ, δ, θ and ϕ, in the form

$$\Psi = \psi\begin{pmatrix} \cos\frac{\theta}{2} \\ e^{i\phi}\sin\frac{\theta}{2} \end{pmatrix}, \qquad \psi = e^{i\delta}\sqrt{\rho}$$

We then write the state as the product of the position-dependent state $|\psi\rangle$ and the normalized spin state $|\chi\rangle$:

$$|\Psi\rangle = |\psi(\boldsymbol{r},t)\rangle \otimes |\chi(\theta(\boldsymbol{r},t),\phi(\boldsymbol{r},t))\rangle$$

- In the corresponding Schrödinger equation

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

the Hamiltonian is written as a 2×2 matrix. For example, in the presence of a magnetic field and homogeneous electric field, and taking into account Zeeman and Rashba coupling:

$$H = \left(\frac{p^2}{2m} + V(r) - \frac{q}{2m} \boldsymbol{L} \cdot \boldsymbol{B} \right) \mathrm{I}$$
$$- \frac{qe}{2m} \boldsymbol{S} \cdot \boldsymbol{B} + \frac{1}{m^2 c^2} \frac{1}{r} \frac{\partial V}{\partial r} \boldsymbol{L} \cdot \boldsymbol{S} + \alpha (\boldsymbol{\sigma} \times \boldsymbol{p}) \cdot \hat{\mathbf{e}}_z$$

This corresponds to an expansion of the Hamiltonian operator in the basis of Pauli spin matrices $\{\sigma_x, \sigma_y, \sigma_z, \mathrm{I}\}$:

$$H = E_0 \, \mathrm{I} + \sum_\alpha E_\alpha \sigma_\alpha$$

The first three terms, involving p^2, $V(r)$ and $\boldsymbol{L} \cdot \boldsymbol{B}$, correspond to the energy E_0, while the remaining coupling terms are higher-order corrections.

9   Addition of Angular Momentum

9.1   Particles With Spin $s = 1/2$

- We now consider the possibility of a quantum system consisting of multiple particles, each with their own angular momentum. For the majority of this section we will focus on simple system: a hydrogen atom with an electron in the ground state with angular momentum quantum number $l = 0$. The second particle is of course the proton in the nucleus. Both particles have spin $s_i = 1/2$. The spin operators and basis vectors for each particle are

$$S_i^2 = s_i(s_i + 1)\hbar^2 \ket{s_i m_i} \qquad \text{and} \qquad S_{z_i} \ket{s_i m_i} = m_i \hbar \ket{s_i} \ket{m_i}$$

  where $i = 1$ corresponds to the electron and $i = 2$ to the proton.

- The electron's and proton's angular momentum operators commute with each other, which is summarized in the commutation relation

$$\left[S_{\alpha_i}, S_{\beta_j} \right] = i\hbar \delta_{ij} \epsilon_{\alpha\beta\gamma} S_{\gamma_j}, \qquad \alpha \in \{x, y, z\}$$

  Both sets of spin operators can be written in terms of the Pauli spin matrices as

$$\boldsymbol{S}_i = \frac{\hbar}{2} \boldsymbol{\sigma}, \qquad \boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$$

- We expect the hydrogen atom's total spin $\boldsymbol{S}$ is the sum of the spins of the constituent electron and proton. More generally, for a system of N particles each with spin $\boldsymbol{S}_i$, we expect the total spin $\boldsymbol{S}$ to be

$$\boldsymbol{S} = \sum_i^N \boldsymbol{S}_i$$

  Similarly, we expect the total system's spin expectation value to obey

$$\bra{\Psi} \boldsymbol{S} \ket{\Psi} = \sum_i \bra{\chi_i} \boldsymbol{S}_i \ket{\chi_i}$$

  where Ψ is the system's complete wavefunction and $\ket{\chi_i}$ are the spin states of the constituent particles.

- For these definitions to hold, the operators $\boldsymbol{S}_i$ of each constituent particle act only the spin basis states $\ket{s_i m_i}$ corresponding to that particular particle. With this requirement in mind, we define the total spin of a two particle system as

$$\boldsymbol{S} = \boldsymbol{S}_1 \otimes \mathrm{I}_2 + \mathrm{I}_1 \otimes \boldsymbol{S}_2$$

  where I_i is the identity operator for the spin subspace spanned by the ith particle's spin basis states $\ket{\{s_i m_i\}}$. Similarly, the total spin state $\ket{s_1 s_2 m_1 m_2}$ is written

$$\ket{s_1 s_2 m_1 m_2} = \ket{s_1 m_1} \otimes \ket{s_2 m_2}$$

  Shorthand Notation: Since the spins s_1 and s_2 are both fixed at the constant values $s_{1,2} = 1/2$, we can leave the s_i terms implicit and write the spin state simply as

$$\ket{s_1 s_2 m_1 m_2} \equiv \ket{m_1} \otimes \ket{m_2}$$

- In the $|m_1 m_2\rangle$ notation, the total spin operator S_z acts on the basis state as

$$S_z |m_1 m_2\rangle = (S_{z_1} \otimes I_2 + I_1 \otimes S_{z_2}) |m_1\rangle \otimes |m_2\rangle$$
$$= m_1 \hbar |m_1\rangle \otimes |m_2\rangle + |m_1\rangle \otimes m_2 \hbar |m_2\rangle$$
$$= (m_1 + m_2)\hbar |m_1 m_2\rangle$$

In other words—the total spin operator S_z has the expected property of an angular momentum operator in that it has the eigenvalue $m_1 + m_2$ when acting on the state $|m_1 m_2\rangle$.

- As any angular momentum quantity, the total spin operator $\boldsymbol{S}$ obeys the usual angular momentum commutation relations, which we can derive as follows:

$$[S_\alpha, S_\beta] = \left[S_{\alpha_1} \otimes I_2 + I_1 \otimes S_{\alpha_2}, S_{\beta_1} \otimes I_2 + I_1 \otimes S_{\beta_2} \right]$$
$$= [S_{\alpha_1} \otimes I_2, S_{\beta_1} \otimes I_2] + [I_2 \otimes S_{\alpha_2}, I_1 \otimes S_{\beta_2}]$$
$$= [S_{\alpha_1}, S_{\beta_1}] \otimes I_2 + I_1 \otimes [S_{\alpha_2}, S_{\beta_2}]$$
$$= i\hbar \epsilon_{\alpha\beta\gamma} S_\gamma,$$

where the last equality uses the identities $[S_{\alpha_i}, S_{\beta_i}] = i\hbar \epsilon_{\alpha\beta\gamma} S_{\gamma_i}$. Note also the use of $[S_{\alpha_1} \otimes I_2, I_1 \otimes S_{\beta_2}] = 0$, which follows from $\left[S_{\alpha_i}, S_{\beta_j} \right] = i\hbar \delta_{ij} \epsilon_{\alpha\beta\gamma} S_{\gamma_j}$ (a result of S_i and S_j acting on independent Hilbert spaces).

- The total spin operator $\boldsymbol{S}$ is often analyzed in terms of ladder operators, just like the spin operator for a single particle. The total ladder operators are defined as

$$S_\pm = S_x \pm iS_y = S_{\pm_1} \otimes I_2 + I_1 \otimes S_{\pm_2}.$$

- The basis states $\{|m_1 m_2\rangle\}$ span the system's total spin vector space and are eigenstates of the total angular momentum operator S_z, individual operators S_{z_i} and individual operators S_i^2.

Note, however, that the states $|m_1 m_2\rangle$ are not eigenstates of the total angular momentum operator S^2—only the states $|sm\rangle$ are eigenstates of S^2. The states $|sm\rangle$ obey

$$S^2 |sm\rangle = s(s+1)\hbar^2 |sm\rangle \qquad \text{and} \qquad S_z |sm\rangle = m\hbar |sm\rangle$$

- Although $|m_1 m_2\rangle$ are not directly eigenstates of S^2, we can expand the eigenstates $|sm\rangle$ in the $|m_1 m_2\rangle$ basis in the form

$$|sm\rangle = \sum_{m_1 m_2} c_{m_1 m_2} |m_1 m_2\rangle$$

where we sum over all $m_i = \pm 1/2$ obeying the condition $m = m_1 + m_2$.

- Next, we introduce the earlier arrow notation, which generalizes to a two-particle system with states $|m_1 m_2\rangle$ as follows:

$$\left| \tfrac{1}{2}\tfrac{1}{2} \right\rangle = |\uparrow\rangle \otimes |\uparrow\rangle \equiv |\uparrow\uparrow\rangle$$
$$\left| -\tfrac{1}{2}\tfrac{1}{2} \right\rangle = |\downarrow\rangle \otimes |\uparrow\rangle \equiv |\downarrow\uparrow\rangle$$
$$\left| \tfrac{1}{2} -\tfrac{1}{2} \right\rangle = |\uparrow\rangle \otimes |\downarrow\rangle \equiv |\uparrow\downarrow\rangle$$
$$\left| -\tfrac{1}{2} -\tfrac{1}{2} \right\rangle = |\downarrow\rangle \otimes |\downarrow\rangle \equiv |\downarrow\downarrow\rangle$$

Don't forget that the state $|m_1 m_2\rangle$ is short for the state $|s_1 m_2 s_2 m_2\rangle$—the s_i are left out for conciseness but are still implicitly there. Note also that we have left tensor product $\otimes$ implicit in the last equality of each line. Leaving the tensor product implicit in multi-particle spin systems in conventional, just like leaving the hat on operators implicit. The need for the tensor product is usually clear from context.

- The largest possible value of m for the state $|\uparrow\uparrow\rangle$ is $m = \frac{1}{2} + \frac{1}{2} = 1$. The corresponding $|sm\rangle$ state for $m = 1$, i.e. $|sm\rangle = |11\rangle$ is also an eigenstate of S^2, as shown below:

$$S^2 |sm\rangle = S^2 |11\rangle = 1(1+1)\hbar^2 |11\rangle = 2\hbar^2 |\uparrow\uparrow\rangle .$$

- Next, we apply the ladder operator S_- to the state $|11\rangle$, which gives

$$S_- |11\rangle = \hbar\sqrt{1(1+1) - 1(1-1)} |10\rangle = \sqrt{2}\hbar |10\rangle ,$$

which we can also write in the form

$$\begin{aligned} S_- |11\rangle &= \left(S_{-_1} I_2 + I_1 S_{-_2}\right) |\uparrow\uparrow\rangle = \hbar |\downarrow\uparrow\rangle + \hbar |\uparrow\downarrow\rangle \\ &= \hbar\left(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\right) \end{aligned}$$

In other words, we have derived the identity

$$\sqrt{2}\hbar |10\rangle = \hbar\left(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\right) \implies |10\rangle = \frac{\hbar}{\sqrt{2}}\left(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle\right)$$

Following a similar procedure with $s = 1$ and $m = -1$, we could derive the identity

$$|1, -1\rangle = |\downarrow\downarrow\rangle .$$

The above three states $|sm\rangle = |1m\rangle$ with $m = -1, 0, 1$ are called the *triplet* states for a two-particle spin system with individual spins $s_{1,2} = 1/2$.

- The fourth possible state for the two-particle spin $1/2$ system is the *singlet* state $|sm\rangle = |00\rangle$ with $s = 0$ and $m = 0$. We cannot construct the single state using the ladder operators, since the ladder operators preserve the quantum number s, and we have no way of generating $s = 0$ from a $s = 1$ state.

Instead, we generate the singlet state by expanding the state $|sm\rangle = |00\rangle$ in the $|m_1 m_2\rangle$ basis:

$$|00\rangle = c_{\frac{1}{2}, -\frac{1}{2}} |\uparrow\downarrow\rangle + c_{-\frac{1}{2}, \frac{1}{2}} |\downarrow\uparrow\rangle$$

Because the states $|10\rangle$ and $|00\rangle$ have different values of s, they are orthogonal and obey $\langle 10|00\rangle = 0$, which implies

$$c_{-\frac{1}{2}, \frac{1}{2}} = -c_{\frac{1}{2}, -\frac{1}{2}}$$

The complete set of triplet and singlet states is thus

$$|1m\rangle = \begin{cases} |\uparrow\uparrow\rangle & m = 1 \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) & m = 0 \\ |\downarrow\downarrow\rangle & m = -1 \end{cases}$$

$$|00\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

- *Note on notation*: From here forward, in addition to leaving out the tensor product symbol $\otimes$, we will also leave the identity operator implicit when writing the product of independent operators. Here is an example:

$$S^2 = S_1^2 \otimes I_2 + I_1 \otimes S_2^2 \rightarrow S^2 = S_1^2 + S_2^2$$

  The implicit presence of the tensor product and relevant identity operators are understood from context.

Heisenberg Coupling

- The Heisenberg coupling involves two particles with spin $s_i = 1/2$ and reads

$$H = J_0 \boldsymbol{S}_1 \cdot \boldsymbol{S}_2$$

  where J_0 is called the exchange coupling constant. When $J_0 < 0$, system's spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ are aligned in the ground state (ferromagnetic coupling). When $J_0 > 0$, the spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ are oppositely oriented in the ground state (anti-ferromagnetic coupling).

- Next, we use the identity

$$S^2 = \boldsymbol{S} \cdot \boldsymbol{S} = (\boldsymbol{S}_1 + \boldsymbol{S}_2) \cdot (\boldsymbol{S}_1 + \boldsymbol{S}_2) = S_1^2 + S_2^2 + 2\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$$

  to write the Heisenberg coupling term in the form

$$H = \frac{J_0}{2}\left(S^2 - \frac{3}{2}\hbar^2\right).$$

- Note that the coupling term is rotationally invariant, which implies the commutation relation $[\boldsymbol{S}, H] = 0$. Because of the relation $[\boldsymbol{S}, H] = 0$, the quantities S^2 and S_z are conserved, and the singlet and triplet states are eigenstates of the equation

$$H\left|sm\right\rangle = \frac{J_0\hbar^2}{2}\left(s(s+1) - \frac{3}{2}\right)\left|sm\right\rangle$$

  with corresponding energy eigenvalues

$$E_s = J_0\hbar^2 \begin{cases} \frac{1}{4} & s = 1 \quad \text{(triplet)} \\ -\frac{3}{4} & s = 0 \quad \text{(singlet)} \end{cases}$$

  The ground state (with lowest energy) is thus the singlet state, while the triplet states are triply degenerate with energy $\Delta E = J_0\hbar^2$ above the ground state.

9.2   Addition of Angular Momenta with the Clebsch Gordan Coefficients

- In the previous section, we consider addition of angular momentum operators $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ corresponding to particles with spins $s_1 = s_2 = 1/2$. In this section, we will generalize the addition of angular momenta to arbitrary operators $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$ that obey the usual angular momentum commutation relations

$$\left[J_{\alpha_i}, J_{\beta_j}\right] = i\hbar\delta_{ij}\epsilon_{\alpha\beta\gamma}J_{\gamma_j}$$

- Leaving the tensor product and identity operators implicit, the total angular momentum operator $\boldsymbol{J}$ and corresponding basis states are

$$|j_1 m_1 j_2 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle \qquad \text{and} \qquad \boldsymbol{J} = \boldsymbol{J}_1 + \boldsymbol{J}_2.$$

- By making the substitution $J_{\alpha_i} \to S_{\alpha_i}$ and $(j_i, j) \to (s_i, s)$, we can reuse most of the identities related to addition of angular momentum that were derived in the previous section.

  We begin by expanding the eigenstatates of the operators $\boldsymbol{J}^2$ and J_z in the basis $\left\{ |j_1 m_1 j_2 m_2\rangle \right\}$ in the form

$$|j_1 j_2 j m\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \langle j_1 m_1 j_2 m_2 | j m \rangle |j_1 m_1 j_2 m_2\rangle$$

  The coefficients $\langle j_1 m_1 j_2 m_2 | j m \rangle$ in the expansion are called the Clebsch-Gordon coefficients and encode the transformation between the total angular momentum basis $|jm\rangle$ and the product basis $|m_1 m_2\rangle$.

- Finally, we note that just like in the addition of spins, when adding angular momenta the total quantum number m must obey $m = m_1 + m_2$ and that the values of j must satisfy the corresponding inequality

$$|j_1 + j_2| \le j \le j_1 + j_2$$

9.2.1   Example: Addition of Angular Momenta in the Case $l \times 1/2$

- As an exercise in the addition of angular momentum, we will find the total angular momentum basis representation of an electron in the first excited state of a hydrogen atom. The excited electron has angular momentum $\boldsymbol{J}_1 = \boldsymbol{L}$ and basis states $\{|l m_l\rangle\}$ while the proton in the hydrogen nucleus has angular momentum $\boldsymbol{J}_2 = \boldsymbol{S}$ and basis states $\{|\uparrow\rangle, |\downarrow\rangle\}$.

  The total angular momentum is $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, and the corresponding basis is

$$\{|j_1 j_2 j m\rangle\} \equiv \{|l s j m\rangle\} = \left\{ \left|l \tfrac{1}{2} j m\right\rangle \right\}$$

  where the spin 1/2 proton's angular momentum j_2 is fixed at $j_2 \equiv s = 1/2$. For $l = 0$ and $l = 1$, the electron's basis states are the spherical harmonics

$$Y_{l m_l}(\theta, \phi) = \langle \boldsymbol{r} | l m_l \rangle$$

  Finally, recall that the angular momentum quantum numbers must satisfy

$$|s + l| \le j \le s + l$$

- We begin with the ground state $l = 0$ and $s = 1/2$, in which case the total angular momentum quantum number can be only $j = 1/2$. The corresponding states in the total angular momentum $|lsmj\rangle$ and product $|l m_l s m_s\rangle$ bases are

$$\left|0 \tfrac{1}{2} \tfrac{1}{2} \tfrac{1}{2}\right\rangle = |00\rangle |\uparrow\rangle \qquad \text{and} \qquad \left|0 \tfrac{1}{2} \tfrac{1}{2} - \tfrac{1}{2}\right\rangle = |00\rangle |\downarrow\rangle$$

- We now consider the first excited electron state with $l = 1$, for which we can have both $j = 3/2$ and $j = 1/2$. Here is the plan: We will begin with the state with the largest value of m, which occurs for $j = 3/2$, and generate the $j = 3/2$ states with lower m using the ladder operator J_-. Finally, we find the $j = 1/2$ state using the orthonormality of the basis states.

- The state with the largest possible value of m is $\left|1\frac{1}{2}\frac{3}{2}\frac{3}{2}\right\rangle = \left|11\right\rangle\left|\uparrow\right\rangle$. We then apply the ladder operator $J_- = S_- + L_-$ to determine the state with $\left|jm\right\rangle = \left|\frac{3}{2}\frac{1}{2}\right\rangle$. This reads:

$$J_-\left|1\tfrac{1}{2}\tfrac{3}{2}\tfrac{3}{2}\right\rangle = \hbar\sqrt{3}\left|1\tfrac{1}{2}\tfrac{3}{2}\tfrac{1}{2}\right\rangle$$
$$(L_- + S_-)\left|11\right\rangle\left|\uparrow\right\rangle = \hbar\sqrt{2}\left|10\right\rangle\left|\uparrow\right\rangle + \hbar\left|11\right\rangle\left|\downarrow\right\rangle$$
$$\left|1\tfrac{1}{2}\tfrac{3}{2}\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|10\right\rangle\left|\uparrow\right\rangle + \sqrt{\tfrac{1}{3}}\left|11\right\rangle\left|\downarrow\right\rangle$$

- We then repeat the procedure to generate the state with $\left|jm\right\rangle = \left|\frac{3}{2} - \frac{1}{2}\right\rangle$. This reads

$$J_-\left|1\tfrac{1}{2}\tfrac{3}{2}\tfrac{1}{2}\right\rangle = 2\hbar\left|1\tfrac{1}{2}\tfrac{3}{2} - \tfrac{1}{2}\right\rangle$$
$$(L_- + S_-)\left|10\right\rangle\left|\uparrow\right\rangle = \sqrt{2}\hbar\left|1-1\right\rangle\left|\uparrow\right\rangle + \hbar\left|10\right\rangle\left|\downarrow\right\rangle$$
$$(L_- + S_-)\left|11\right\rangle\left|\downarrow\right\rangle = \sqrt{2}\hbar\left|10\right\rangle\left|\downarrow\right\rangle + 0$$
$$\left|1\tfrac{1}{2}\tfrac{3}{2} - \tfrac{1}{2}\right\rangle = \sqrt{\tfrac{1}{3}}\left|1-1\right\rangle\left|\uparrow\right\rangle + \sqrt{\tfrac{2}{3}}\left|10\right\rangle\left|\downarrow\right\rangle$$

- On more application of the ladder operator leads to the state with $\left|jm\right\rangle = \left|\frac{3}{2} - \frac{3}{2}\right\rangle$, which is

$$\left|1\tfrac{1}{2}\tfrac{3}{2} - \tfrac{3}{2}\right\rangle = \left|1-1\right\rangle\left|\downarrow\right\rangle$$

- Finally, we determine the states with $j = 1/2$ and $\left|jm\right\rangle = \left|\frac{1}{2} \pm \frac{1}{2}\right\rangle$ with the orthogonality condition

$$\left\langle 1\tfrac{1}{2}\tfrac{3}{2} \pm \tfrac{1}{2}\middle|1\tfrac{1}{2}\tfrac{1}{2} \pm \tfrac{1}{2}\right\rangle = 0,$$

since these two states have different values of j. The desired states are then

$$\left|1\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|10\right\rangle\left|\uparrow\right\rangle - \sqrt{\tfrac{1}{3}}\left|11\right\rangle\left|\downarrow\right\rangle$$
$$\left|1\tfrac{1}{2}\tfrac{1}{2} - \tfrac{1}{2}\right\rangle = -\sqrt{\tfrac{2}{3}}\left|1-1\right\rangle\left|\uparrow\right\rangle - \sqrt{\tfrac{1}{3}}\left|10\right\rangle\left|\downarrow\right\rangle$$

10 Perturbation Theory

10.1 The Rayleigh-Schrödinger Method for a Non-Degenerate Spectrum

- We consider quantum system with a Hamiltonian of the form

$$H = H_0 + H',$$

where the term H_0 is a good approximation for the system, while the term H' is a *perturbation* term with a secondary effect on the system. We assume we are able to analytically solve the stationary Schrödinger equation for H_0, which reads

$$H_0 = |n_0\rangle = E_n^{(0)} |n_0\rangle.$$

More so, we assume H_0's eigenstates are orthonormal and obey $\langle m_0 | n_0 \rangle = \delta_{mn}$, and that the energy eigenvalues $E_n^{(0)}$ are non-degenerate.

We write the perturbation term in the form $H' = \lambda V$ where V has units of energy and λ is a dimensional parameter encoding the strength of the perturbation.

- Our goal is to solve the stationary Schrödinger equation for the *total* Hamiltonian $H = H_0 + H'$, which reads

$$H |n\rangle = E_n |n\rangle.$$

Our first step is to expand the desired eigenstates $|n\rangle$ and energy eigenvalues E_n in powers of the perturbation parameter λ in the form

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$
$$|n\rangle = |n_0\rangle + \lambda |n_1\rangle + \lambda^2 |n^2\rangle + \cdots,$$

where $E_n^{(j)}$ and $|n_j\rangle$ are progressively higher-order corrections to the total Hamiltonian H's n-th eigenvalue E_n and eigenstate $|n\rangle$, respectively.

- We proceed by multipliying the equation for $|n\rangle$ by $\langle n_0|$, which gives

$$\langle n_0 | n \rangle = 1 + \lambda \langle n_0 | n_1 \rangle + \lambda^2 \langle n_0 | n_2 \rangle + \cdots$$

We then make an important assumption: we assume the complete solution for $|n\rangle$ is well approximated by the lowest-order approximation $|n_0\rangle$, allowing us to temporarily assume $\langle n_0 | n \rangle = 1$. Under this assumption, the above equation simplifies to

$$\lambda \langle n_0 | n_1 \rangle + \lambda^2 \langle n_0 | n_2 \rangle + \cdots = 0,$$

which is satisfied by all $|n_j\rangle$ only if $\langle n_0 | n_j \rangle = \delta_{0j}$ for all $j \in \mathbb{N}$.

- We then subsitute the expressions for H, $|n\rangle$ and E_n into the stationary Schrödinger equation $H |n\rangle = E_n |n\rangle$ to get

$$(H_0 + \lambda V)\big(|n_0\rangle + \lambda |n_1\rangle + \cdots\big) = \big(E_n^{(0)} + \lambda E_n^{(1)} + \cdots\big)\big(|n_0\rangle + \lambda |n_1\rangle + \cdots\big).$$

We then equate the coefficients of each power of λ. The result up to $\lambda^j = \lambda^3$ is

$$
\begin{array}{r|rcl}
\lambda^0 & H_0 |n_0\rangle & = & E_n^{(0)} |n_0\rangle \\
\lambda^1 & H_0 |n_1\rangle + V |n_0\rangle & = & E_n^{(0)} |n_1\rangle + E_n^{(1)} |n_0\rangle \\
\lambda^2 & H_0 |n_2\rangle + V |n_1\rangle & = & E_n^{(0)} |n_2\rangle + E_n^{(1)} |n_1\rangle + E_n^{(2)} |n_0\rangle \\
\lambda^3 & H_0 |n_3\rangle + V |n_2\rangle & = & E_n^{(0)} |n_3\rangle + E_n^{(1)} |n_2\rangle + E_n^{(2)} |n_1\rangle + E_n^{(3)} |n_1\rangle
\end{array}
$$

The first equation is trivial and represents the known eigenvalue relation for the Hamiltonian H_0.

The second equation with λ^1 is more useful. We first multiply the equation by $\langle n_0 |$ to get

$$E_n^{(0)} \langle n_0 | n_1 \rangle + \langle n_0 | V | n_0 \rangle = E_n^{(0)} \langle n_0 | n_1 \rangle + E_n^{(1)} \langle n_1 | n_1 \rangle .$$

We then apply the orthonormality condition $\langle n_0 | n_j \rangle = \delta_{0j}$ to get

$$E_n^{(1)} = \langle n_0 | V | n_0 \rangle = V_{nn}.$$

- We can perform an analogous procedure with the equations for higher powers λ^j to get expressions for the higher-order corrections $E_n^{(1)}$. For example, using the equation for λ^2 and multiplying by $\langle n_0 |$ as before gives

$$E_n^{(0)} \langle n_0 | n_2 \rangle + \langle n_0 | V | n_1 \rangle = E_n^{(0)} \langle n_0 | n_2 \rangle + E_n^{(1)} \langle n_0 | n_1 \rangle + E_n^{(2)} \langle n_0 | n_0 \rangle ,$$

which produces $E_n^{(2)} = \langle n_0 | V | n_1 \rangle$ after applying $\langle n_0 | n_j \rangle = \delta_{0j}$.

In general, the expression for the j-th correction to the energy E_n is

$$E_n^{(j)} = \langle n_0 | V | n_{j-1} \rangle .$$

- Recall that we have assumed we can solve the stationary Schrödinger equation $H_0 | n \rangle = E_n | n \rangle$, which means we can diagonalize the Hamiltonian H_0. Working in the H_0 basis, we can write the identity operator in the form

$$I = \sum_m | m_0 \rangle \langle m_0 | .$$

We can then expand each higher-order correction $| n_j \rangle$ in the H_0 basis to get

$$| n_j \rangle = \sum_{m \neq n} | m_0 \rangle \langle m_0 | n_j \rangle$$

Note that the term $| n_0 \rangle$ is left out of the sum because of the identity $\langle n_0 | n_j \rangle = 0$.

With this expression for $| n_j \rangle$ in the H_0 basis in mind, we multiply the earlier equation for λ^1 by $| m_0 \rangle$ and then apply $| n_1 \rangle = \sum_{m \neq n} | m_0 \rangle \langle m_0 | n_1 \rangle$ to get

$$\left(E_n^{(0)} - E_m^{(0)} \right) \langle m_0 | n_1 \rangle = \langle m_0 | V | n_0 \rangle = V_{mn}$$

The coefficients in the expansion of $| n_1 \rangle$ are thus

$$\langle m_0 | n_1 \rangle = \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}},$$

which implies the first-order correction $| n_1 \rangle$ to the state $| n \rangle$ is

$$| n_1 \rangle = \sum_{m \neq n} = \frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} | m_0 \rangle .$$

- Using the just-derived result for $|n_1\rangle$, the second-order energy correction $E_n^{(2)}$ is then

$$E_n^{(2)} = \langle n_0|V|n_1\rangle = \sum_{m \neq n} \frac{|V_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}.$$

  Note that in practice, the second-order energy correction $E_n^{(2)}$ and the first-order wavefunction correction $|n_1\rangle$ usually lead to satisfactory approximations of the exact quantities E_n and $|n\rangle$.

- Next, as an exercise in the Rayleigh-Schrödinger method, we will determine the second-order wavefunction correction $|n_2\rangle$, which will also reveal the third-order energy correction $E_n^{(3)}$.

  We begin by multiplying the earlier equation for λ^2 by $\langle m_0|$, which gives

$$\langle m_0|H_0|n_2\rangle + \langle m_0|V|n_1\rangle = E_n^{(0)}\langle m_0|n_2\rangle + E_n^{(1)}\langle m_0|n_1\rangle + E_n^{(2)}\langle m_0|n_0\rangle$$

  This equation, after substituting in the results derived earlier in this section, comes out to, in order,

$$E_m^{(0)}\langle m_0|n_2\rangle + \sum_{l \neq n} \frac{V_{ml}V_{ln}}{E_n^{(0)} - E_l^{(0)}} = E_n^{(0)}\langle m_0|n_2\rangle + E_n^{(1)}\frac{V_{mn}}{E_n^{(0)} - E_m^{(0)}} + E_n^{(2)} \cdot 0.$$

  We then substitute in $E_n^{(1)} = V_{nn}$ and rearrange to get

$$\sum_{l \neq n} \frac{V_{ml}V_{ln}}{E_n^{(0)} - E_l^{(0)}} = \left(E_n^{(0)} - E_m^{(0)}\right)\langle m_0|n_2\rangle + \frac{V_{nn}V_{mn}}{E_n^{(0)} - E_m^{(0)}}$$

  The coefficients $\langle m_0|n_2\rangle$ in the expansion of $E_n^{(3)}$ are thus

$$\langle m_0|n_2\rangle = \sum_{n \neq l} \frac{V_{ml}V_{ln}}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_l^{(0)}\right)} - \frac{V_{mn}v_{nn}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2},$$

  and the second-order wavefunction correction is

$$|n_2\rangle = \sum_{m \neq n} \left[\sum_{n \neq l} \frac{V_{ml}V_{ln}}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_l^{(0)}\right)} - \frac{V_{mn}V_{nn}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2}\right]|m_0\rangle$$

- In terms of the just-derived $|n_2\rangle$, the third-order energy correction $E_n^{(3)}$ is

$$E_n^{(3)} = \sum_{m \neq n} \langle m_0|n_2\rangle V_{nm},$$

  where the expression for $|n_2\rangle$ is left out for conciseness.

- Finally, we consider the normalization of the $|n\rangle$ states. Up to the first-order correction in λ, the $|n\rangle$ are already normalized, since

$$\begin{aligned}
\langle n|n\rangle &= \left(|n_0\rangle + \lambda|n_1\rangle\right)\left(|n_0\rangle + \lambda|n_1\rangle\right) \\
&= \langle n_0|n_0\rangle + \lambda\langle n_0|n_1\rangle + \lambda\langle n_1|n_0\rangle + \mathcal{O}(\lambda^2) \\
&= 1 + \mathcal{O}(\lambda^2)
\end{aligned}$$

However, the $|n\rangle$ are not normalized in the second-order correction, in which case we have

$$\langle n|n\rangle = \langle n_0|n_0\rangle + \lambda^2 \langle n_1|n_1\rangle + \mathcal{O}(\lambda^3)$$

$$= 1 + \lambda^2 \sum_{m\neq n} \frac{|V_{nm}|^2}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} + \mathcal{O}(\lambda^3)$$

If we want the $|n\rangle$ states to be normalized we have two options:

1. Renormalize the entire $|n\rangle$ state into

$$|n\rangle \to \left[\sum_j \langle n_j|n_j\rangle\right]^{-1/2} |n\rangle$$

2. Renormalize only the second-order correction via

$$|n_2\rangle \to |n_2\rangle - \frac{\lambda}{2} \sum_{m\neq n} \frac{|V_{nm}|^2}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} |n_0\rangle\,.$$

In terms of this renormalization, the product $\langle n|n\rangle$ comes out to

$$\langle n|n\rangle = 1 + \mathcal{O}(\lambda^3).$$

Example: The Anharmonic Oscillator: TODO

10.2 Degenerate Perturbation Theory

- As in the Rayleigh-Schrödinger method, we again consider a Hamiltonian of the form
$$H = H_0 + \lambda V.$$

This time, however, we assume the energy eigenvalues of the unperturbed Hamiltonian H_0 are degenerate. As before, our goal is to solve the stationary Schrödinger equation
$$H|n\rangle = E|n\rangle$$

for the Hamiltonian H's eigenstates $|n\rangle$ and eigenvalues E_n.

10.2.1 Example: Doubly Degenerate Energies

- We begin with a concrete example: when H_0's eigenstates are doubly degenerate. The beginning steps of the analysis are the same as for a non-degenerate spectrum. We first expand H's eigenstates and eigenvalues in the form

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$
$$|n\rangle = c_1\big|n_0^{(1)}\big\rangle + c_1\big|n_0^{(2)}\big\rangle + \lambda|n_1\rangle + \cdots.$$

Note that because the unperturbed Hamiltonian H_0's energy levels are doubly degenerate, the zeroth-order energy $E_n^{(0)}$ (which is associated with H_0) corresponds to two linear independent wavefunction corrections, which we have written as the linear combination $c_1\big|n_0^{(1)}\big\rangle + c_1\big|n_0^{(2)}\big\rangle$.

- Next, working only up to first order in λ, we substitute the expansions for $|n\rangle$ and E_n into the stationary Schrödinger equation and equate the coefficients for λ^0 and λ^1 to get the three equations

$$H_0\big|n_0^{(1)}\big\rangle = E_n^{(0)}\big|n_0^{(1)}\big\rangle$$
$$H_0\big|n_0^{(2)}\big\rangle = E_n^{(0)}\big|n_0^{(2)}\big\rangle$$
$$H_0\,|n_1\rangle + c_1 V\big|n_0^{(1)}\big\rangle + c_2 V\big|n_0^{(2)}\big\rangle = E_n^{(0)}\,|n_1\rangle + E_n^{(1)}\big(c_1\big|n_0^{(1)}\big\rangle + c_2\big|n_0^{(2)}\big\rangle\big).$$

- Next, we multiply the last equation through by $\big|n_0^{(1)}\big\rangle$ to get an equation for the coefficients c_1 and c_2:

$$\big\langle n_0^{(1)}\big|H_0\big|n_1\big\rangle + c_1\big\langle n_0^{(1)}\big|V\big|n_0^{(1)}\big\rangle + c_2\big\langle n_0^{(1)}\big|V\big|n_0^{(2)}\big\rangle$$
$$= E_n^{(0)}\big\langle n_0^{(1)}\big|n_1\big\rangle + E_n^{(1)}\big(c_1\big\langle n_0^{(1)}\big|n_0^{(1)}\big\rangle + c_2\big\langle n_0^{(1)}\big|n_0^{(2)}\big\rangle\big).$$

Applying the orthonormality of the $|n_j\rangle$ states simplifies this to

$$0 + c_1 V_{11} + c_2 V_{12} = 0 + E_n^{(1)}(c_1 + 0).$$

We then perform a similar procedure in which we multiply the last equation through by $\big|n_0^{(2)}\big\rangle$ to get a second equation for the coefficients c_1 and c_2. In one place, the first and second equations are

$$c_1 V_{11} + c_2 V_{12} = E_n^{(1)} c_1$$
$$c_1 V_{21} + c_2 V_{22} = E_n^{(1)} c_2.$$

This system of equations is a 2×2 eigenvalues problem of the form

$$\begin{bmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E_n^{(1)} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}.$$

Solving this eigenvalue problem determines the desired first-order perturbation theory correction—the eigenvalues are the two first-order energy corrections $E_{n_1}^{(1)}$ and $E_{n_2}^{(1)}$ and the eigenvectors determine the coefficients c_1 and c_2 of the eigenstate corrections $\big|n_0^{(1)}\big\rangle$ and $\big|n_0^{(2)}\big\rangle$.

10.2.2 The General N-Times Degenerate Case

- The procedure for an N-times degenerate energy level is a generalization of the $N = 2$ case and leads to a corresponding $N \times N$ eigenvalue problem with matrix elements V_{ij} given by

$$V_{ij} = \big\langle n_0^{(i)}\big|V\big|n_0^{(j)}\big\rangle$$

Solving the $N \times N$ eigenvalue problem's corresponding characteristic polynomial

$$\det\big[V_{ij} - E_n^{(1)}\delta_{ij}\big] = 0$$

leads to the energy eigenvalue corrections $E_{n_l}^{(1)}$ where $l = 1, 2, \ldots N$.

Solving the associated eigenvector problem leads to the coefficients c_{i_l} for the eigenstate corrections $\big|n_0^{(i)}\big\rangle$.

- Two final notes: In the above case, the energy corrections $E_{n_l}^{(1)}$ and the diagonal matrix elements V_{ii} obey the relationship

$$\sum_{l=1}^{N} E_{n_l}^{(1)} = \sum_{i=1}^{N} V_{ii}.$$

Second, when the matrix elements $\langle n_0^{(i)} | V | n_0^{(j)} \rangle$ are small (e.g. much less than one), it is also important to consider transitions between excited states with different values of n and m. In this case, we redefine the matrix elements to be

$$V_{ij} \rightarrow V_{ij} + \sum_{m \neq n} \frac{V_{im} V_{mj}}{E_n^{(0)} - E_m^{(0)}},$$

where we leave out the case $m = n$ to avoid a zero in the denominator.

10.3 Time-Dependent Perturbation Theory

- We now consider a quantum system described by a time-dependent Hamiltonian of the form

$$H(t) = H_0 + \lambda V(t),$$

where H_0, as before, is a time-independent, diagonalizable Hamiltonian that reasonably approximates the system, while $V(t)$ is a time-dependent perturbation term of secondary influence and λ parameterizes the perturbation's strength. In time dependent perturbation theory, the goal is to solve for the system's time-dependent wavefunction $|\psi(t)\rangle$ given an initial state $|\psi(0)\rangle$.

- We write the known eigenvalue relation for H_0 in the form

$$H_0 |n\rangle = E_n |n\rangle$$

and assume the orthonormality relation $\langle m|n\rangle = \delta_{mn}$. We then begin our analysis by writing the initial state in the H_0 basis:

$$|\psi(0)\rangle = \sum_n c_n(0) |n\rangle.$$

Similarly, we can write the time-dependent wavefunction in H_0 basis in the general form

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-i \frac{E_n}{\hbar} t} |n\rangle,$$

where the coefficients $c_n(t)$ are time-dependent, since $H(t)$ is time-dependent.

- We then substitute the general expression for $|\psi(t)\rangle$ into the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle,$$

which leads to

$$i\hbar \sum_n \left(\frac{\partial c_n(t)}{\partial t} e^{-i \frac{E_n}{\hbar} t} - i \frac{E_n}{\hbar} c_n(t) e^{-i \frac{E_n}{\hbar} t} \right) |n\rangle = \sum_n \left(E_n + \lambda V(t) \right) c_n(t) e^{-i \frac{E_n}{\hbar} t} |n\rangle.$$

We then multiply the equation by the basis vector $\langle m|$, apply $\langle m|n\rangle = \delta_{mn}$, and cancel like terms to get

$$i\hbar\frac{\partial c_m(t)}{\partial t}e^{-i\frac{E_m}{\hbar}t} = \lambda\sum_n \langle m|V(t)|n\rangle\, e^{-i\frac{E_n}{\hbar}t}c_n(t).$$

This is a system of coupled differential equations for the coefficients $c_n(t)$.

- Alternatively, we can write the above system of equations in the matrix form

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \\ c_m(t) \\ \vdots \end{pmatrix} = \lambda\begin{pmatrix} V_{11}(t) & V_{12}(t) & \cdots & V_{1n}(t) & \cdots \\ V_{21}(t) & V_{22}(t) & \cdots & V_{2n}(t) & \cdots \\ \vdots & \vdots & \ddots & \vdots & \cdots \\ V_{m1}(t) & V_{m2}(t) & \cdots & V_{mn}(t) & \cdots \\ \vdots & \vdots & & \vdots & \ddots \end{pmatrix}\begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \\ c_m(t) \\ \vdots \end{pmatrix},$$

  or the more compact equation

$$i\hbar\frac{\partial}{\partial t}\boldsymbol{c}(t) = \lambda\mathbf{V}(t)\boldsymbol{c}(t).$$

  The time-dependent matrix elements $V_{mn}(t)$ are given by

$$V_{mn}(t) = \langle m|V(t)|n\rangle\, e^{-i\frac{E_n - E_m}{\hbar}t},$$

  where E_n and E_m are H_0's energy eigenvalues. This formalism is called the interaction or Dirac picture, and the system's quantum state is determined by the vector $\boldsymbol{c}(t)$.

  Finally, note that the entire time-dependent theory discussed so far is exact—we will only make perturbation approximations in later sections.

10.3.1   Two-State System and Rabi Oscillations

- As a simple example of the time-dependent formalism, we consider a two-state system corresponding to the two quantum states $|1\rangle$ and $|2\rangle$ and 2×2 Hamiltonian H_0. We take our time-dependent perturbation term to be a harmonic oscillation of the form $V(t) \sim e^{-i\omega t}$. A physical example of such a state would be an atom with two energy levels upon which we shine monochromatic light.

- We begin by writing the two state system's Hamiltonian in the form

$$H = H_0 + V(t),$$

  where H_0 and $V(t)$ are given by

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \qquad \text{and} \qquad V(t) = \hbar\begin{pmatrix} 0 & \Delta e^{i\omega t} \\ \Delta e^{-i\omega t} & 0 \end{pmatrix}.$$

- The system's time-dependent Schrödinger equation reads

$$i\hbar\begin{pmatrix} \dot{c}_1(t) \\ \dot{c}_2(t) \end{pmatrix} = \hbar\begin{pmatrix} 0 & \Delta e^{i(\omega-\tilde\omega)t} \\ \Delta e^{i(\omega-\tilde\omega)t} & 0 \end{pmatrix}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}$$

  where we have defined $\hbar\tilde\omega = E_2 - E_1$.

- We assume the system's initial state is the ground state $|\psi(0)\rangle = |1\rangle$, which implies

$$c_1(0) = 1 \qquad \text{and} \qquad c_2(t) = 0.$$

In this case, the probabilities P_2 and P_1 of the system occupying the states $|2\rangle$ and $|1\rangle$, respectively, oscillate according to

$$P_2(t) = \frac{\Delta^2}{\Omega} \sin^2 \Omega t \qquad \text{and} \qquad P_1 = 1 - P_2,$$

where we have defined the Rabi frequency Ω according to

$$\Omega = \sqrt{\Delta^2 + \tfrac{1}{4}(\omega - \tilde{\omega})^2}.$$

The sinusoidal oscillations of the occupation probabilities P_1 and P_2 are called Rabi oscillations, and have maximum amplitude, exactly equal to one, when $\omega = \tilde{\omega}$.

10.3.2 Time-Dependent Perturbation Approach

- We now consider a perturbation that begins at the time $t = 0$, of the form

$$V(t) = \begin{cases} 0 & t < 0 \\ V(t) & t \geq 0 \end{cases}$$

As before, we work with the Hamiltonian $H = H_0 + \lambda V(t)$, where H_0 is time-independent and diagonalizable.

- We begin by assuming the system occurs in one of the H_0 eigenstates, i.e.

$$|\psi(0)\rangle = |m\rangle, \qquad \text{and thus} \qquad c_k^{(0)}(0) = \delta_{km}.$$

We then substitute this expression into the time-dependent Schrödinger equation to get

$$i\hbar \frac{\partial}{\partial t} c_k^{(1)}(t) = \sum_n V_{kn}(t) c_n^{(0)}(t) = V_{km}(t).$$

The coefficients in the first-order perturbation approximation are then

$$c_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t V_{km}(t') \, \mathrm{d}t'.$$

- Using the just-derived $c_k^{(1)}$, the state $|\psi(t)\rangle$ is given to first-order in λ as

$$|\psi(t)\rangle = \sum_k \left[c_k^{(0)}(t) + \lambda c_k^{(1)}(t) + \mathcal{O}(\lambda^2) \right] e^{-i\frac{E_k}{\hbar}t} |k\rangle.$$

The first-order approximation is valid in the regime $\left| c_k^{(1)}(t) \right| \ll 1$. In practice, the first-order approximation gives an acceptable result for many physical problems.

10.3.3   Fermi's Golden Rule

- We now consider a step-like perturbation of the form

$$V(t) = \begin{cases} 0 & t < 0 \\ V & t \geq 0 \end{cases}.$$

As before, we work with the general Hamiltonian $H = H_0 + \lambda V(t)$ where H_0 is time-independent and diagonalizable with eigenstates $|n\rangle$.

- We assume our system is in the initital state $|\psi(0)\rangle = |m\rangle$ (i.e. in an H_0 eigenstate). We then aim to determine the probability of finding the system in the final state $|k\rangle$ as a function of time.

  Since V is constant, the matrix elements $V_{km} = \langle k|V|m\rangle$ are also constant, and the coefficients in the first-order perturbation approximation are

$$c_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t V_{km} e^{-i\frac{E_m - E_k}{\hbar} t'} \, \mathrm{d}t' = \frac{V_{km}}{i\hbar} \frac{e^{i\omega_{mk}t} - 1}{-i\omega_{mk}},$$

where we have defined $\hbar\omega_{mk} = E_k - E_m$.

- In terms of $c_k^{(1)}(t)$ and ω_{mk}, the probability of a transition from $|m\rangle$ to $|k\rangle$ is

$$P_{km} = \left|c_k^{(1)}\right|^2 = \frac{|V_{km}|^2}{\hbar^2} \frac{\left|e^{-i\omega_{mk}t} - 1\right|^2}{\omega_{mk}^2} = \frac{|V_{km}|^2}{\hbar^2} \frac{\sin^2\left(\frac{1}{2}\omega_{mk}t\right)}{\left(\frac{1}{2}\omega_{mk}\right)^2}$$

$$\equiv \frac{2\pi}{\hbar} |V_{km}|^2 \delta_t(E_k - E_m) t,$$

where we have defined the function

$$\delta_t(x) \equiv \frac{1}{\pi} \frac{\sin^2(xt)}{x^2 t}.$$

- Interpretation: note that δ_t approaches the Dirac delta function in the limit $t \gg \frac{\hbar}{|E_k - E_m|}$. In this regime, there is appreciable likelihood only for transitions to states with energies in a neighborhood of the initial energy E_m.

  Meanwhile, for $t \ll \frac{\hbar}{|E_k - E_m|}$, the function δ_t is very wide, which corresponds to appreciable probability for transitions to states with energies in the range $E_m \pm \frac{\hbar}{t}$.

  In general, the width of the function $\delta_t(E_k - E_m)$ decreases with time according to

$$\Delta E \sim \frac{\hbar}{t}.$$

- Finally, we stress that this analysis of the transition probability P_{km}, which uses the first-order time-dependent perturbation theory, rests on the assumption $P_{km}(t) \ll 1$, which is necessary for the first-order approximation to hold.

- Next, we consider the special case in which our system transitions from the intial H_0 eigenstate $|m\rangle$ to a final state $|k\rangle$ for which there are many states with energies very close to E_k. We describe the densely-spaced states using the concept of a density of states (as in e.g. thermodynamics), which we define as

$$\rho(E_k) = \frac{\mathrm{d}N}{\mathrm{d}E_k},$$

where $\mathrm{d}N$ represents the number of states available in a small energy band $\mathrm{d}E_k$ centered around E_k.

- The total probability for a transition to any state in the neighborhood of E_k is an integral over E_k of the form

$$P(t) = \int P_{km}(t)\rho(E_k)\,\mathrm{d}E_k.$$

For large $t \gg \frac{\hbar}{|E_k - E_m|}$, the transition probability increases with time as

$$P(t) = \frac{2\pi}{\hbar}|V_{km}|^2\rho(E_m)t.$$

The rate of change of probability with respect to time, which we will denote w_{km}, is thus constant and obeys

$$w_{m\to k} \equiv \frac{\mathrm{d}P(t)}{\mathrm{d}t} = \frac{2\pi}{\hbar}|V_{km}|^2\rho(E_m)$$

This important result is called Fermi's golden rule.

Example: The Fermi Golden Rule and Radioactive Decay

- We consider the decay of N radioactive nuclei, where we expect that at a time t after their creation, $\mathrm{d}N$ nuclei decay in the time interval $\mathrm{d}t$, which we write in terms of the transition rate $w(t)$ as

$$-\mathrm{d}N = N\,\mathrm{d}P = Nw(t)\,\mathrm{d}t.$$

In general, a nucleus can decay according to different modes (e.g. α decay, β decay, etc...), which case the total decay rate w is the sum of the decay rate for each individual mode, i.e. $w = \sum_i w_i$, which leads to the familiar radioactive decay law

$$N = N_0 e^{-t/\tau}, \qquad \tau = \frac{1}{w}.$$

- For a quantum system with discretely spaced energy levels, the coefficients $c_k(t)$, for small times in the regime $t \ll \frac{\hbar}{|E_k - E_m|}$, are proportional to t, which corresponds to a decay rate

$$w(t) = \frac{4}{\hbar}|V_{km}|^2 t.$$

The corresponding dependence of the number of nuclei N is

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{4}{\hbar}|V_{km}|^2 tN \implies N(t) = N_0 e^{-\frac{2}{\hbar}|V_{km}|^2 t^2}.$$

10.4   Time Evolution Operator for a Time-Dependent Hamiltonian

- Recall from the section time evolution that for a time-independent Hamiltonian H_0, the time evolution operator reads

$$U(t) = e^{-i\frac{H_0}{\hbar}t}.$$

In this section, we will generalize this result and define a time-evolution operator applicable to the time-dependent Hamiltonian $H = H_0 + V(t)$.

- We begin with the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \boldsymbol{c}(t) = \lambda \mathbf{V}(t)\boldsymbol{c}(t).$$

We then solve the equation iteratively for the coefficients $c_k(t)$ by substituting in the first-order approximation

$$c_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t V_{km}(t')\,\mathrm{d}t'.$$

We write $c_k(t)$ as the power series $c_k(t) = \sum_j \lambda^j c_k^{(j)}(t)$, and use the first order approximation to find the second-order term via

$$i\hbar \frac{\partial}{\partial t} c_k^{(2)}(t) = \sum_n V_{kn}(t) c_n^{(1)}(t) = \frac{1}{i\hbar} \sum_n V_{kn}(t) \int_0^t V_{nm}(t')\,\mathrm{d}t'.$$

We repeat the process iteratively, which leads to the series expression

$$c_k(t) = \delta_{km} + \lambda \frac{1}{i\hbar} \int_0^t V_{km}(t')\,\mathrm{d}t'$$
$$+ \lambda^2 \left(\frac{1}{i\hbar}\right)^2 \sum_n \int_0^t \left[\sum_n V_{kn}(t') \int_0^{t'} V_{nm}(t'')\,\mathrm{d}t''\right]\mathrm{d}t' + \cdots.$$

If we set $\lambda = 1$, this gives an exact, if not particularly practical, solution to the time-dependent wavefunction

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-i\frac{E_n}{\hbar}t} |n\rangle.$$

- We can write the above results more compactly in terms of a generalized time operator in the form

$$\boldsymbol{c}(t) = U(t)\boldsymbol{c}(0),$$

where the time-operator is defined as

$$U(t) = \mathrm{I} + \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_0^t V(t_1) \int_0^{t_1} V(t_2) \cdots \int_0^{t_{n-1}} V(t_n - 1)\,\mathrm{d}t_{n-1} \cdots \mathrm{d}t_2\,\mathrm{d}t_1.$$

The potential energy operators $V(t)$ are applied in the given order for the times $0 \leq t_{n-1} \leq \cdots \leq t_2 \leq t_1 \leq t$, which we can write yet more concisely by defining a time operator T via

$$U(t) = \mathrm{T}\left\{\exp\left[\frac{1}{i\hbar} \int_0^t V(t')\,\mathrm{d}t'\right]\right\}.$$

The thus-defined time-evolution operator $U(t)$ is unitary and an appropriate generalization of the expression

$$U(t) = e^{-i\frac{H_0}{\hbar}t}$$

for a time-dependent Hamiltonian H_0.

10.5 Adiabatic Transistions and Quantum Phases

- We now consider a quantum system described by a time-varying parameter $\lambda(t)$, and thus, implicitly, a time-varying Hamiltonian $H(\lambda(t))$. As a concrete example, consider a particle in the ground state of an infinite potential well with time-varying width $l(t)$, initially equal to l_0 at $t = 0$.

  Adiabatic transitions are those transitions in which the system parameter changes slowly enough that the system remains in the ground state throughout the transition.

- Note that a quantitative analysis of the condition "changes slowly enough" is beyond the scope of this course; we consider only the qualitative condition, that the reate of change of the paratemeter with respect to time is small relative to the energy level between the system's states, i.e.

$$\frac{\mathrm{d}\lambda}{\mathrm{d}t} \ll \frac{|E_m - E_n|}{\hbar}\lambda(t).$$

  This condition ensures that the probability for transitions to excited states is negligible, meaning the particle is likely to stay in its ground state, as required for an adiabatic transition.

- In the more general case, we consider a system described by n time-parameters $\boldsymbol{Q}(t) = (q_1(t), q_2(t), \cdots, q_n(t))$, with a corresponding implicitly time-dependent Hamiltonian $H = H(\boldsymbol{Q}(t))$.

  Let $|\psi_n(\boldsymbol{Q})\rangle$ denote the system's eigenstates for a given value of the parameters $\boldsymbol{Q}$, with corresponding energy eigenvalue relation

$$H(\boldsymbol{Q})|\psi_n(\boldsymbol{Q})\rangle = E_n(\boldsymbol{Q})|\psi_n(\boldsymbol{Q})\rangle.$$

  The parameters, and thus the eigenstate $|\psi_n(\boldsymbol{Q})\rangle$, change with time, so that the exact value of $|\psi_n(\boldsymbol{Q})\rangle$ is different at each value of t. As a result, the wavefunction $\Psi_n^{(0)}(\boldsymbol{r}, t) = \langle \boldsymbol{r}|\psi_n(\boldsymbol{Q})\rangle$ is not in general of the time-dependent Schrödinger equation, i.e.

$$i\hbar\frac{\partial}{\partial t}\left|\Psi_n^{(0)}\right\rangle \neq H(\boldsymbol{Q})\left|\Psi_n^{(0)}(\boldsymbol{r}, t)\right\rangle,$$

  since the stationary states themselves change with time.

- We now assume the parameters change adiabatically, which means the system remains in the n-th eigenstate $|\psi_n(\boldsymbol{Q})\rangle$ of the Hamiltonian $H(\boldsymbol{Q})$ throughout the change. Although the stationary state $|\psi_n(\boldsymbol{Q})\rangle$ is constant, we allow for a potentially-changing global phase $\phi_n(t)$, and thus solve the time-dependent Schrödinger equation with the ansatz

$$|\Psi_n\rangle = e^{i\phi_0(t)}\left|\Psi_n^{(0)}\right\rangle,$$

  which we substitute into the Schrödinger equation $i\hbar\frac{\partial}{\partial t}|\Psi_n\rangle = H|\Psi_n\rangle$ to get

$$i\hbar\left(i\frac{\mathrm{d}\phi_n}{\mathrm{d}t}e^{i\phi_n}\left|\Psi_n^{(0)}\right\rangle + e^{i\phi_n}\frac{\partial}{\partial t}\left|\Psi_n^{(0)}\right\rangle\right) = He^{i\phi_n}\left|\Psi_n^{(0)}\right\rangle = E_ne^{i\phi_n}\left|\Psi_n^{(0)}\right\rangle.$$

  Note that all quantities are dependent on $\boldsymbol{Q}(t)$ and thus implicitly on time, which we have left implicit for conciseness.

- Next, we multiply the equation through by $\left\langle \Psi_n^{(0)} \right|$ to get

$$i\hbar \left(i\frac{\mathrm{d}\phi_n}{\mathrm{d}t} \left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle + \left\langle \Psi_n^{(0)} \middle| \frac{\partial}{\partial t} \middle| \Psi_n^{(0)} \right\rangle \right) = E_n \left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle,$$

  where we assume the state $\Psi_n^{(0)}$ is normalized at every time t.

- Next, we separate the phase ϕ_n into two components $\phi_n = \gamma_n + \theta_n$, chosen such that
$$i\hbar \left(i\frac{\mathrm{d}\gamma_n}{\mathrm{d}t} + \left\langle \Psi_n^{(0)} \middle| \frac{\partial}{\partial t} \middle| \Psi_n^{(0)} \right\rangle \right) = \underbrace{\left(E_N + \hbar\frac{\mathrm{d}\theta_n}{\mathrm{d}t} \right)}_{0},$$

  which implies

$$\theta_n = -\frac{1}{\hbar} \int_0^t E_n(t')\,\mathrm{d}t' \qquad \text{and} \qquad \frac{\mathrm{d}\gamma_n}{\mathrm{d}t} = i \left\langle \Psi_n^{(0)} \middle| \frac{\partial}{\partial t} \middle| \Psi_n^{(0)} \right\rangle.$$

- Next, keeping the $q_i(t)$ parameters' time dependence in mind, we rewrite the wave-function's time derivative as

$$\frac{\partial \Psi_n^{(0)}}{\partial t} = \sum_i \frac{\partial \Psi_n^{(0)}}{\partial q_i}\dot{q}_i \equiv (\nabla_Q \psi_n) \cdot \dot{\boldsymbol{Q}}.$$

  In terms of this notation for $\Psi_n^{(0)}$'s time derivative, the phase term $\gamma_n(t)$ is given by

$$\gamma_n(t) = i \int \left\langle \Psi_n^{(0)} \middle| \frac{\partial}{\partial t} \middle| \Psi_n^{(0)} \right\rangle \mathrm{d}t = i \int_0^t \left\langle \psi_n \middle| \nabla_Q \psi_n \right\rangle \cdot \dot{\boldsymbol{Q}}\,\mathrm{d}t$$
$$= i \int_{\boldsymbol{Q}(0)}^{\boldsymbol{Q}(t)} \left\langle \psi_n \middle| \nabla_Q \psi_n \right\rangle \cdot \mathrm{d}\boldsymbol{Q}.$$

  We have thus separated the phase ϕ_n into two parts:

$$\phi_n(t) = \theta_n + \gamma_n = -\frac{1}{\hbar} \int_0^t E_n(t')\,\mathrm{d}t' + \int_{\boldsymbol{Q}(0)}^{\boldsymbol{Q}(t)} i \left\langle \psi_n \middle| \nabla_Q \psi_n \right\rangle \cdot \mathrm{d}\boldsymbol{Q}.$$

  The first component θ_n is called the dynamic phase and the component γ_n is called the geometric or Berry phase. In the adiabatic limit, the Berry phase does not depend explicitly on time, but instead on the path $\boldsymbol{Q}$ traced out by the system in the parameter space.

  The matrix element $\mathcal{A}_n(\boldsymbol{Q}) = i \left\langle \psi_n \middle| \nabla_Q \psi_n \right\rangle$ is called the Berry connection or Berry potenial. Note that the Berry potential is real-valued, which follows from

$$\nabla_Q \left[\left\langle \psi_n \middle| \psi_n \right\rangle \right] = \nabla_Q [1] = 0 = \left\langle \nabla_Q \psi_n \middle| \psi_n \right\rangle + \left\langle \psi_n \middle| \nabla_Q \psi_n \right\rangle = 2\,\mathrm{Re}\left\langle \psi_n \middle| \nabla_Q \psi_n \right\rangle.$$

  Evidently, $\mathcal{A}_n = 0$ for real functions ψ_n.

- Next, assume the trajectory $\mathcal{C}$ traced out by the parameters $\boldsymbol{Q}$ in parameter space is closed at the time t_0. In this case, the Hamiltonian operator returns to its initial

form: $H(\boldsymbol{Q}(t_0)) = H(\boldsymbol{Q}(0))$, and the corresponding state at time t_0 is multiplied by both the dynamic phase θ, and the Berry phase

$$\gamma_{\text{Berry}}(t_0) = \oint_{\mathcal{C}} \mathcal{A}_n(\boldsymbol{Q}) \cdot \mathrm{d}\boldsymbol{Q}.$$

In a three-dimensional parameter space, in which $\boldsymbol{Q} = (q_1, q_2, q_3)$, the can also define a Berry-curvature

$$\Omega_n(\boldsymbol{Q}) = \nabla_Q \times \mathcal{A}_n(\boldsymbol{Q}).$$

Then, using Stokes' theorem, we can write the Berry phase in terms of an integral over the surface $\mathcal{S}$ defined by the closed curve $\mathcal{C}$, in the form

$$\gamma_n = \iint_{\mathcal{S}} \Omega_n(\boldsymbol{Q}) \cdot \mathrm{d}\boldsymbol{S}.$$

Without derivation, we note that if the surface $\mathcal{S}$ is closed, the Berry phase is a multiple of 2π, and the multiple is called a Chern number.

10.6   The WKB Approximation

In the context of quantum mechanics WKB method is an expansion in terms of $\hbar$, which represents an expansion with respect to the classical limit $\hbar \to 0$.

- We begin by writing the system's wavefunction Ψ with the ansatz

$$\Psi(\boldsymbol{r}, t) = e^{\frac{i}{\hbar} S(\boldsymbol{r}, t)}, \qquad S(\boldsymbol{r}, t) \in \mathbb{C}.$$

We then substitute this ansatz into the Schrödinger equation,

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

which leads to the partial differential equation

$$-\frac{\partial S}{\partial t} \Psi = \left(\frac{1}{2m} (\nabla S)^2 - i \frac{\hbar^2}{2m} \nabla^2 S + V \right) \Psi.$$

Assuming $\Psi \neq 0$, we can then divide through by Ψ to get

$$-\frac{\partial S}{\partial t} = \frac{1}{2m} (\nabla S)^2 + V - i \frac{\hbar^2}{2m} \nabla^2 S.$$

- Next, we note that in the limit $\hbar \to 0$, the above equation reduces to

$$\frac{\partial S}{\partial t} = \frac{1}{2m} (\nabla S)^2 + V,$$

which is a classical Hamilton-Jacobi equation for the principle Hamiltonian function S for a classical particle with velocity $\boldsymbol{v} = \frac{1}{m} \nabla S$. From classical mechanics, we know that Hamilton-Jacobi theory is equivalent to the formalism of Newton's second law, so the limit $\hbar \to 0$ essentially recovers classical mechanics.

- We proceed with the WKB method by expanding S in powers of $\hbar$, in the form

$$S = S_0 + \hbar S_1 + \hbar^2 S_2 + \cdots,$$

where the zero-th order expansion in $\hbar$ produces the aforementioned classical equation

$$\frac{\partial S}{\partial t} = \frac{1}{2m}(\nabla S)^2 + V,$$

while the first order in $\hbar$ corresponds to a first-order quantum correction

$$-\frac{\partial S_1}{\partial t} = \frac{1}{2m}\left(2\nabla S_0 \cdot \nabla S_1 - i\nabla^2 S_0\right).$$

Analysis in the regime of this first-order approximation is called the WKB or semi-classical approximation.

- As an example, we consider the one-dimensional stationary states

$$\Psi(x,t) = e^{-i\frac{E}{\hbar}t}\psi(x).$$

We will write S and ψ as the time-independent functions

$$S(x) = S_0(x) + \hbar S_1(x) + \mathcal{O}(\hbar^2) \qquad \text{and} \qquad \psi(x) = e^{\frac{i}{\hbar}S(x)}.$$

- We begin by solving for $S_0(x)$ using the zero-order classical equation, which gives

$$E = \frac{1}{2m}\left(\frac{\mathrm{d}S_0(x)}{\mathrm{d}x}\right)^2 + V(x)$$

and

$$S_0(x) = \pm \int_{x_0}^{x} \sqrt{2m\left[E - V(x')\right]}\,\mathrm{d}x' \equiv \pm \int_{x_0}^{x} p(x')\,\mathrm{d}x',$$

where we have defined $p(x) = \sqrt{2m[E - V(x)]}$. We then use this expression for $S_0(x)$ to solve for S_1 via

$$2\frac{\mathrm{d}S_0(x)}{\mathrm{d}x}\frac{\mathrm{d}S_1(x)}{\mathrm{d}x} = i\frac{\mathrm{d}^2 S_0(x)}{\mathrm{d}x^2},$$

which leads to

$$S_1(x) = \frac{i}{2}\int_{x_0}^{x} \frac{S_0''(\tilde{x})}{S_0'(\tilde{x})}\,\mathrm{d}\tilde{x} = \frac{i}{2}\ln\frac{p(x)}{p(x_0)}.$$

The approximate solution for the wavefunction in the WKB approximation is thus

$$\psi_{\mathrm{wkb}}(x,t) = \frac{C}{\sqrt{p(x)}}\exp\left[-i\frac{E}{\hbar}t \pm \frac{i}{\hbar}\int_{x}^{x_0} p(x')\,\mathrm{d}x'\right].$$

This solution takes the form of a modulated wave, with a position-dependent wave vector

$$k(x) = \frac{p(x)}{\hbar}.$$

The plus/minus sign in the exponent encodes the wave's direction, just like in a plane wave, and depends on the problem's concrete boundary conditions. The constants C and x_0 are determined by normalization and boundary conditions, respectively.

Finally, we note that the WKB approximation does not hold in the neighborhood of classical turning points where $p(x) = 0$, since this produces a singularity in the denominator. We analyze such turning points using complex-valued connection formulas, but this is beyond the scope of this course.

10.7 The Variational Method

- We consider a Hamiltonian with orthornormalized but otherwise unknown eigenstates and eigenvalues satisfying

$$H \left| n \right\rangle = E_n \left| n \right\rangle, \qquad \left\langle m | n \right\rangle = \delta_{mn}.$$

We then expand an arbitrary wavefunction $\left| \psi \right\rangle$ in the $\left\{ \left| n \right\rangle \right\}$ basis in the form

$$\left| \psi \right\rangle = \sum_n c_n \left| n \right\rangle = \sum_n \left\langle n | \psi \right\rangle \left| n \right\rangle.$$

- The energy expectation value $\left\langle H \right\rangle$ for the state $\left| \psi \right\rangle$ is

$$\begin{aligned}
\left\langle \psi | H | \psi \right\rangle &= \left\langle \sum_m \left\langle m | \psi \right\rangle \left\langle m \right| \middle| H \middle| \sum_n \left\langle n | \psi \right\rangle \left| n \right\rangle \right\rangle \\
&= \left\langle \sum_m \left\langle m | \psi \right\rangle \left\langle m \right| \middle| \sum_n \left\langle n | \psi \right\rangle E_n \left| n \right\rangle \right\rangle \\
&= \sum_n E_n |c_n|^2.
\end{aligned}$$

We can bound this result from above according to

$$E_0 \sum_n |c_n|^2 \leq \sum_n E_n |c_n|^2,$$

where E_0 is the ground state energy, which obeys $E_0 \leq E_1 \leq \cdots \leq E_n \leq \cdots$. This upper bound implies

$$\left\langle \psi | H | \psi \right\rangle \geq E_0 \sum_n |c_n|^2 = E_0 \left\langle \psi | \psi \right\rangle,$$

which we finally rearrange to get the important result

$$E_0 \leq \frac{\left\langle \psi | H | \psi \right\rangle}{\left\langle \psi | \psi \right\rangle}.$$

In other words, the H ground state energy E_0 is smaller than the energy expectation value for any state $\left| \psi \right\rangle$ expanded in the H basis $\left\{ \left| n \right\rangle \right\}$.

- The just-derived inequality forms the basis for a variational method of ground state energy calculation of some Hamiltonian H. The variational method proceeds as follows:

  1. First, we choose $\left| \psi \right\rangle$ to be as good an approximation as possible to the Hamiltonian's ground state, and require that $\left| \psi \right\rangle$ has the same symmetry properties as H.

  2. We then parametrize ψ with n variational parameters α_i in the form $\psi = \psi(\alpha_1, \alpha_2, \ldots, \alpha_n; x)$.
     Using this trial function, we then calculate the expectation value

     $$\left\langle \psi | H | \psi \right\rangle = \mathcal{E}(\alpha_1, \ldots, \alpha_n).$$

3. Next, by varying the parameteris α_i, we determine the minimum energy $\mathcal{E}_{\min}$, which is the best approximation to the ground state within the space of trial functions generated by the parameters $\alpha_1, \ldots, \alpha_n$.

4. Because of the earlier inequality, $\mathcal{E}_{\min}$ must obey

$$E_0 \leq \mathcal{E}_{\min},$$

which theoretically allows us to arbitrarily increase the number of parameters and trial functions, and repeat the process of finding the minimum energy expectation value $\mathcal{E}_{\min}$ until $\mathcal{E}_{\min}$ is an arbitrarily close approximation of E_0. Keep in mind that $E_0 \leq \mathcal{E}_{\min}$ gaurantees we will never drop below E_0 when decreasing $\mathcal{E}_{\min}$, which is why we can be sure we will get an arbitrarily close approximation of E_0 instead.

- As an example of the variational method, we return to Rayleigh-Schrödinger method for solving a Hamiltonian of the form

$$H = H_0 + \lambda V,$$

where λV is a secondary perturbation term and H_0 has the known eigenvalue relation

$$H_0 \left| \varphi_n^{(0)} \right\rangle = E_n^{(0)} \left| \varphi_n^{(0)} \right\rangle.$$

We then calculate the expectation value $\langle H \rangle$ to first order in λ, which reads

$$\langle H \rangle = \langle \psi | H | \psi \rangle = E_0^{(0)} + \lambda \langle \varphi_0^{(0)} | V | \varphi_0^{(0)} \rangle + \mathcal{O}(\lambda^2) = E_0^{(0)} + E_0^{(1)} + \mathcal{O}(\lambda^2)$$

The inequality underlying the variational principle gaurantees $E_0 \leq \langle H \rangle$, which implies

$$E_0 \leq E_0^{(0)} + E_0^{(1)}.$$

In other words, the Hamiltonian H's true ground state energy E_0 is less than the sum of the first two perturbative energy corrections $E_0^{(0)}$ and $E_0^{(1)}$.

11 Scattering

11.1 Scattering in One Dimension

- We first consider one-dimensional scattering problems involving a Hamiltonian of the form

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}2}{\mathrm{d}x^2} + V(x).$$

In the absence of a potential, i.e. for $V(x) = 0$, the Hamiltonian H's stationary states are plane waves with wavefunctions and energies of the form

$$\langle x | \psi \rangle \sim e^{\pm ikx} \qquad \text{with} \qquad E_p = \frac{p^2}{2m} > 0.$$

Each energy eigenvalue E_p is doubly degerate, since the linearly independent states with momenta $\pm p = \pm \hbar k$ have the same energy.

- In scattering problems we have $V(x) \neq 0$; however, we assume the potential is nonzero only in a finite region $x \in [x_a, x_b]$. More so, we assume the potential does not allow for bound states. In such situations, we write stationary scattering states in the form

$$\psi(x) = \begin{cases} A_1 e^{ikx} + B_1 e^{-ikx} & x < x_a \\ \psi_{ab}(x) & x \in [x_a, x_b] \\ A_2 e^{-ikx} + B_2 e^{ikx} & x > x_a. \end{cases}$$

In other words, we assume the wavefunction is a linear superposition of plane waves in the region of zero potential and some wavefunction ψ_{ab} in the region with non-zero potential $V(x), x \in [x_a, x_b]$. The A coefficients denote waves moving toward the potential barrier and the B coefficients denote waves moving away from the barrier.

- Next, we introduce two two-dimensional column vectors, Ψ_{in} and Ψ_{out}, which encode the waves moving toward and away from the potential, respectively. The vectors are:

$$\Psi_{\text{in}} = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} \qquad\qquad \Psi_{\text{out}} = \begin{pmatrix} B_1 \\ B_2 \end{pmatrix}$$

$$\Psi_{\text{in}}^\dagger = \begin{pmatrix} A_1^*, A_2^* \end{pmatrix} \qquad\qquad \Psi_{\text{out}}^\dagger = \begin{pmatrix} B_1^*, B_2^* \end{pmatrix}.$$

- The system's associated probability current density is constant and equal to

$$j_a = \frac{\hbar k}{m}\left(|A_1|^2 - |B_1|^2\right) = j_b = \frac{\hbar k}{m}\left(|B_2|^2 - |A_2|^2\right),$$

from which follows the fundamental relationship between the coefficients A and B, namely:

$$|A_1|^2 + |A_2|^2 = |B_1|^2 + |B_2|^2.$$

In other words, the sum of the currents entering the potential equals the sum of the currents leaving the potential, which may also be written

$$\Psi_{\text{out}}^\dagger \Psi_{\text{out}}^\dagger = \Psi_{\text{in}}^\dagger \Psi_{\text{in}}^\dagger.$$

11.1.1 The Scattering Matrix

- The coefficient vectors Ψ_{in} and Ψ_{out} are related by a scattering matrix $\mathbf{S}$ via

$$\Psi_{\text{out}} = \mathbf{S}\Psi_{\text{in}}.$$

The scattering matrix is unitary, which we can prove via

$$\Psi^{\dagger}_{\text{out}}\Psi_{\text{out}} = \Psi^{\dagger}_{\text{out}}\mathbf{S}\Psi_{\text{in}} = \Psi^{\dagger}_{\text{in}}\mathbf{S}^{\dagger}\mathbf{S}\Psi_{\text{in}}$$

Since $\Psi^{\dagger}_{\text{out}}\Psi^{\dagger}_{\text{out}} = \Psi^{\dagger}_{\text{in}}\Psi^{\dagger}_{\text{in}}$, it follows that $\mathbf{S}^{\dagger}\mathbf{S} = \mathbf{I}$ and thus $\mathbf{S}^{\dagger} = \mathbf{S}^{-1}$, which means $\mathbf{S}$ is indeed unitary.

- We will parameterize the scattering matrix in the form

$$\mathbf{S} = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix} \in \mathbb{C}^{2\times 2},$$

from which follow the relationships

$$\begin{pmatrix} r \\ t \end{pmatrix} = \mathbf{S}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{and} \qquad \begin{pmatrix} t' \\ r' \end{pmatrix} = \mathbf{S}\begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The parameters t and t', which are in general complex numbers, encode the probability for a wave packet to pass through the potential (to transmit, hence the letter t), while the parameters r and r' encode the probability for a wave packet to reflect off the potential barrier.

- The scattering matrix parameters are related according to

$$\mathbf{S}^{\dagger}\mathbf{S} = \mathbf{I} \iff \begin{cases} 1 = |t|^2 + |r|^2 = |t'|^2 + |r'|^2 \\ 0 = r^*t' + t^*r' = (t')^*r + (r')^*t. \end{cases}$$

Additionally, the fact that the scattering matrix is unitary produces the following, perhaps less obvious relationships

$$\mathbf{S}\mathbf{S}^{\dagger} = \mathbf{I} \iff \begin{cases} 1 = |t'|^2 + |r|^2 = |t|^2 + |r'|^2 \\ 0 = r^*t + (t')^*r' = t*r + (r')^*t'. \end{cases}$$

- The scattering matrix is parameterized by four complex numbers, t, t', r and r', which corresponds to eight independent real-valued parameters. However, the condition that $\boldsymbol{S}$ is unitary creates certain restrictions on the parameters, namely:

$$|t| = |t'| \qquad |r| = |r'| \qquad r' = -r^*\frac{t'}{t^*}.$$

These three relationships between the parameters imply that $\mathbf{S}$ is fact described by five real-valued parameters instead of eight. With these relationships in mind, the scattering matrix may be written

$$\mathbf{S} = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix} = \begin{pmatrix} r & t' \\ t & -r^*\frac{t'}{t^*} \end{pmatrix} = \begin{pmatrix} r & e^{i\phi}t^* \\ t & -e^{i\phi}r^* \end{pmatrix},$$

where $\det \mathbf{S} = -e^{i\phi}$.

11.1.2 Time-Reversal Invariance

- We now consider a system invariant under time inversion, using the simple example of a free-particle. In this case, for any ψ solving the stationary Schrödinger equation in the regions $x < x_a$ and $x > x_b$, the time-transformed wavefunction

$$\mathcal{T}\psi(x) = \psi^*(x) = \begin{cases} A_1^* e^{-ikx} + B_1^* e^{ikx} & x < x_a \\ A_2^* e^{ikx} + B_2^* e^{-ikx} & x > x_a \end{cases}$$

also solves the stationary Schrödinger equation. Time invariance thus switches and conjugates the ingoing and outgoing vectors via

$$\mathcal{T}\Psi_{\text{in}} = \begin{pmatrix} B_1^* \\ B_2^* \end{pmatrix} = \Psi_{\text{out}}^* \qquad \text{and} \qquad \mathcal{T}\Psi_{\text{out}} = \begin{pmatrix} A_1^* \\ A_2^* \end{pmatrix} = \Psi_{\text{in}}^*.$$

- Since the time-reversed states also solve the Schrödinger equation, the scattering matrix must be symmetric. To prove this, we begin with the relationship $\Psi_{\text{out}} = \mathbf{S}\Psi_{\text{in}}$. We then replace Ψ with the equivalent solution $\mathcal{T}\Psi$ and apply the above transformation rules of Ψ_{in} and Ψ_{out} under $\mathcal{T}$ to get

$$\mathcal{T}\Psi_{\text{out}} = \mathbf{S}\mathcal{T}\Psi_{\text{in}} \implies \Psi_{\text{in}}^* = \mathbf{S}\Psi_{\text{out}}^*.$$

We then multiply the equation from the left by $\mathbf{S}^\dagger$, apply the unitary identity $\mathbf{S}^\dagger \mathbf{S} = \mathbf{I}$, and take the equation's complex conjugate to get

$$\mathbf{S}^\dagger \Psi_{\text{in}}^* = \mathbf{S}^\dagger \mathbf{S} \Psi_{\text{out}}^* = \Psi_{\text{out}} \implies (\mathbf{S}^\dagger)^* \Psi_{\text{in}} \equiv \mathbf{S}^T \Psi_{\text{in}} = \Psi_{\text{out}}.$$

Comparing this to the original relationship $\mathbf{S}\Psi_{\text{in}} = \Psi_{\text{out}}$ implies $\mathbf{S} = \mathbf{S}^T$, i.e. the scattering matrix is symmetric.

- The symmetry condition $\mathbf{S} = \mathbf{S}^T$ implies $t = t'$, which allows us to write the scattering matrix in the form

$$\mathbf{S} = \begin{pmatrix} r & t \\ t & r' \end{pmatrix} = \begin{pmatrix} r & t \\ t & -r^* \frac{t}{t^*} \end{pmatrix} = \begin{pmatrix} r & |t|e^{i\frac{\phi}{2}} \\ |t|e^{i\frac{\phi}{2}} & -e^{i\phi}r^* \end{pmatrix}, \qquad \det \mathbf{S} = -\frac{t}{t^*}.$$

In passing, we note that in the presence of an external magnetic field, the Hamiltonian for a charged particle is no longer invariant under time reversal, which case the scattering matrix obeys $\mathbf{S}_{-\boldsymbol{B}} = \mathbf{S}_{\boldsymbol{B}}^T$.

11.1.3 Parity Invariance

- We now consider systems that are invariant under parity transformation. Such systems obey $V(-x) = V(x)$ and thus $x_a = -x_b$. In this case, for any ψ solving the stationary Schrödinger equation in the regions $x < x_a$ and $x > x_b$, the parity-transformed wavefunction

$$\mathcal{P}\psi(x) = \psi(-x) = \begin{cases} B_2 e^{-ikx} + A_2 e^{ikx} & x < x_a \\ B_1 e^{ikx} + A_1 e^{-ikx} & x > |x_a| \end{cases}$$

also solves the stationary Schrödinger equation. The parity operator thus transforms the roles of the coefficients in the form $A_{1,2} \longleftrightarrow B_{1,2}$. As a result, the parity operator transforms the ingoing and outgoing vectors in the form

$$\mathcal{P}\Psi_{\text{in}} = \sigma_x \Psi_{\text{in}} \qquad \text{and} \qquad \mathcal{P}\Psi_{\text{out}} = \sigma_x \Psi_{\text{out}},$$

where $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ is the first Pauli spin matrix. As an example, we consider the transformation of Ψ_{in}:

$$\mathcal{P}\Psi_{\text{in}} = \mathcal{P}\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} A_2 \\ A_1 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \sigma_x \Psi_{\text{in}}.$$

- The parity-transformed states are related by the scattering matrix according to

$$\sigma_x \Psi_{\text{out}} = \mathbf{S}\sigma_x \Psi_{\text{in}} \implies \sigma_x^2 \Psi_{\text{out}} \equiv \mathbf{I}\Psi_{\text{out}} = \sigma_x \mathbf{S}\sigma_x \Psi_{\text{in}}.$$

Comparing the last equality to the general relationship $\Psi_{\text{out}} = \mathbf{S}\Psi_{\text{in}}$ implies $\sigma_x \mathbf{S}\sigma_x$, which in turn implies

$$\sigma_x \mathbf{S}\sigma_x = \sigma_x \begin{pmatrix} r & t' \\ t & r' \end{pmatrix} \sigma_x = \begin{pmatrix} r' & t \\ t' & r \end{pmatrix} \mathbf{S} = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix},$$

or, in other words, $r = r'$ and $t = t'$. This condition on r and t implies the scattering matrix for a parity-invariant system is symmetric with respect to both diagonals and can be written in the form

$$\mathbf{S} = \begin{pmatrix} r & t \\ t & r \end{pmatrix} = -e^{i\tau}\begin{pmatrix} i|r| & |t| \\ |t| & i|r| \end{pmatrix}, \qquad t = e^{i\tau}|t|.$$

11.1.4   Multiple Scattering Channels

- We now consider a system with additional degrees of freedom that can change after scattering, for example a particle with spin $s = 1/2$ whose projection can reverse after scattering. In this case, the ingoing and outgoing vectors Ψ_{in} and Ψ_{out} are formed of $2N$ components, while the scattering matrix becomes a $2N \times 2N$ block-diagonal matrix whose block diagonal elements are 2×2 matrices corresponding to the scattering matrix for each individual scattering channel.

- In passing, we mention the possibility of a particle changing effective mass from e.g. m_1 to m_2 when passing through different regions. In this case, the scattering coefficients change according to

$$\begin{Bmatrix} A_1 \\ B_1 \end{Bmatrix} \to \sqrt{\frac{m_1}{p_1}}\begin{Bmatrix} A_1 \\ B_1 \end{Bmatrix} \qquad \text{and} \qquad \begin{Bmatrix} A_2 \\ B_2 \end{Bmatrix} \to \sqrt{\frac{m_2}{p_2}}\begin{Bmatrix} A_2 \\ B_2 \end{Bmatrix}$$

where we have defined $p_{1,2} = \sqrt{2m_{1,2}(E - V_{1,2})}$.

11.1.5   The Transfer Matrix

- In addition to the scattering matrix approach, we often analyze one-dimensional systems in terms of transfer matrices, which we discuss in this section. Scattering matrices relate the waves on one side of a potential barrier to the waves on the other side in the form

$$\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = \mathbf{M}\begin{pmatrix} A_2 \\ B_2 \end{pmatrix} \qquad \text{where} \qquad \mathbf{M} = \begin{pmatrix} \mathrm{M}_{11} & \mathrm{M}_{12} \\ \mathrm{M}_{21} & \mathrm{M}_{22} \end{pmatrix}.$$

- To relate the scattering matrix $\mathbf{S}$ to the transfer matrix $\mathbf{M}$, we begin with

$$\begin{pmatrix} r \\ t \end{pmatrix} = \mathbf{S} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{and} \qquad \begin{pmatrix} t' \\ r' \end{pmatrix} = \mathbf{S} \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Meanwhile, the scattering matrix obeys

$$\begin{pmatrix} 1 \\ r \end{pmatrix} = \mathbf{M} \begin{pmatrix} t \\ 0 \end{pmatrix} \qquad \text{and} \qquad \begin{pmatrix} 0 \\ t' \end{pmatrix} = \mathbf{M} \begin{pmatrix} r' \\ 1 \end{pmatrix},$$

from which follows the relationship

$$\mathbf{M} = \begin{pmatrix} \frac{1}{t} & -\frac{r'}{t} \\ \frac{r}{t} & t' - \frac{rr'}{t} \end{pmatrix} \qquad \text{where} \qquad \det \mathbf{M} = \frac{t'}{t}.$$

Under the condition $t = t'$, the relationship between $\mathbf{S}$ and $\mathbf{M}$ simplifies to

$$\mathbf{M} = \begin{pmatrix} \frac{1}{t} & \frac{r^*}{t^*} \\ \frac{r}{t} & \frac{1}{t^*} \end{pmatrix} \qquad \text{and} \qquad \mathbf{S} = \frac{1}{M_{11}} \begin{pmatrix} M_{21} & 1 \\ 1 & -M_{21}^* \end{pmatrix}.$$

- The transfer matrix approach is well-suited to systems involving a series of multiple (e.g. N) potential barriers, with endpoints at the positions $x_1, x_2, \ldots, x_{2N}$. In this case, we define the wave amplitudes A and B with respect to the shifted plane waves $e^{\pm ik(x-x_i)}$, split the x axis into $2N + 1$ regions, and calculate the $2N - 1$ transfer matrices $\mathbf{M}_{ij} = \mathbf{M}_{12}, \mathbf{M}_{23}, \ldots, \mathbf{M}_{(2N-1)2N}$ connecting the regions. In this case, the transfer matrix for the entire x axis is simply the product

$$\mathbf{M}_{1(2N)} = \mathbf{M}_{12} \mathbf{M}_{23} \cdots \mathbf{M}_{(2N-1)2N}.$$

We can then use the total transfer matrix together with the equations in the previous bullet point to calculate the corresponding total transfer matrix $\mathbf{S}_{1(2N)}$.

11.2 Scattering States

- We now consider plane waves—eigenstates of the momentum operator $\hat{\boldsymbol{p}}$ and also of the stationary Schrödinger equation for a free particle. Such states obey the eigenvalue equations

$$\hat{p}|\psi_p^0\rangle = p|\psi_p^0\rangle \qquad \text{and} \qquad H_0|\psi_p^0\rangle = E_p|\psi_p^0\rangle.$$

Keep in mind that the momentum eigenstates $|\psi_p^0\rangle$ don't directly represent physical states, but instead form a basis for expanding wave packets encoding the system's actual quantum state. The energies E_p are degenerate with respect to the choice of direction of momentum.

The superscript ^{0} is used to denote plane waves—we will use $^+$ and $^-$ superscripts later in this section to denote scattering states.

- We often analyze eigenstates in terms of a Fourier transform to momentum space, using the fact that the momentum operator is self-adjoint. As an example, we consider a one-dimensional system that obeys

$$\langle x|p\rangle = \psi_p^0(x) = Ce^{i\frac{p}{\hbar}x}$$

with the periodic boundary conditions

$$\psi_p(x + L) = \psi_p(x) \implies p_n = \frac{2\pi\hbar}{L}, \quad n = 0, 1, 2, \ldots$$

and orthogonal eigenstates

$$\langle m|n \rangle = \frac{e^{2\pi i(n-m)} - 1}{2\pi i(n - m)} L|C|^2 \quad \text{for } n \neq m.$$

For a choice of normalization constant $C = L^{-1/2}$, the eigenstates are orthonormal and obey $\langle m|n \rangle = \delta_{mn}$. Although the energy spectrum is discrete, in the limit of large L the spacing between energy levels grows arbitrarily small.

- Alternatively, we can normalize states in terms of the Dirac delta function:

$$\langle x|p \rangle = \psi_p^0(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{p}{\hbar}x},$$

where the eigenstates obey $\langle p_1|p_2 \rangle = \delta(p_1 - p_2)$ and the identity operator is written

$$\mathrm{I} = \int_{-\infty}^{\infty} |p\rangle \langle p|\, \mathrm{d}p.$$

This notation allows for orthogonal eigenstates in the case of a continuous spectrum, with momentum eigenvalues $p \in \mathbb{R}$.

- Regardless of the choice of normalization, in the presence of the potential barrier V we define three dimensional scattering states $\left|\psi_{\boldsymbol{p}}^+\right\rangle$ according to

$$(H_0 + V)\left|\psi_{\boldsymbol{p}}^+\right\rangle = E_{\boldsymbol{p}}\left|\psi_{\boldsymbol{p}}^+\right\rangle,$$

where $H_0 = \frac{p^2}{2m}$. This definition ensures that in the limit of a vanishing potential $V(\boldsymbol{r}) \to 0$, the scattering states approach plane waves $|\psi_{\boldsymbol{p}}^0\rangle$, as expected for a free particle with $V(\boldsymbol{r}) = 0$.

- For a one-dimensional system, a scattering state is written in the form

$$\psi_p^+(x) = C \begin{cases} e^{i\frac{p}{\hbar}x} + re^{-i\frac{p}{\hbar}x} & x < x_a \\ \psi_{ab}(x) & x \in [x_a, x_b] \\ te^{i\frac{p}{\hbar}x} & x > x_b, \end{cases}$$

where r and t are parameters from the scattering matrix $\mathbf{S}$ and encode reflection and transmission from the potential barrier, respectively. In the presence of a potential, momentum is in general not conserved, i.e. $[\boldsymbol{p}, H] \neq 0$. However, the energy eigenvalues $E_{\boldsymbol{p}}$ are still degenerate, since each plane wave $\psi_{\boldsymbol{p}}^0(x)$ correponds to a scattering state $\psi_{\boldsymbol{p}}^+(x)$ with equal energy.

- A one dimensional system has two degenerate states, corresponding to the momentum eigenvalues $\pm|p|$. This double denegeracy motives the definition of a quantum number $\eta = \pm 1$ encoding the direction of wave propagation. The corresponding states, i.e.

$$\big||p|, \eta\big\rangle = |p\rangle, \quad \text{with eigenvalues} \quad p = \eta|p|,$$

are eigenstates of the system's Hamiltonian and can thus be described in terms of the eigenvalue E instead of p. As a result, we can write the completeness relation in two equivalent forms:

$$\mathrm{I} = \sum_\eta \int_0^\infty |p, \eta\rangle \langle p, \eta| \, \mathrm{d}p = \sum_\eta \int_0^\infty |E, \eta\rangle \langle E, \eta| \, \mathrm{d}E,$$

where the bases $\{|p, \eta\rangle\}$ and $\{E, \eta\}$ differ only in the normalization of the basis vectors. The state $|E, \eta\rangle$ is normalized according to

$$\langle E_1, \eta_1 | E_2, \eta_2 \rangle = \delta_{\eta_1 \eta_2} \delta(E_1 - E_2).$$

- For momentum eigenvalues $p_i \sqrt{2mE_i} > 0$ we rewrite the Dirac delta function as follows

$$\delta(E_1 - E_2) = \delta\left(\frac{p_1^2}{2m} - \frac{p_2^2}{2m}\right) = 2m\delta\big[(p_1 - p_2)(p_1 + p_2)\big] = \frac{2m}{p_1 + p_2}\delta(p_1 - p_2)$$
$$= \frac{m}{p_1}\delta(p_1 - p_2),$$

where we have used the delta function properties $\delta(ax) = \frac{1}{|a|}\delta(x)$ and $f(x)\delta(x - a) = f(a)\delta(x - a)^3$. In terms of the above expression for the delta function, we have

$$\langle x|E, \eta\rangle = \sqrt{\frac{m}{p}} \langle x|p, \eta\rangle = \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{m}{2E}\right)^{1/4} \exp\left(i\eta\sqrt{\frac{2mE}{\hbar^2}}\right),$$

which is a third way to normalize a plane wave. An analogous normalization relationship holds between the corresponding scattering scates $\psi_{E\eta}^+ = \sqrt{\frac{m}{p}}\psi_{p\eta}^+$.

11.2.1 Formal Scattering Theory and the Møller Operator

- A particle is in the initial asymptotic incident state $\left|\psi_{\boldsymbol{p}_0}^0\right\rangle$, which approaches a plane wave with momentum $\boldsymbol{p}_0$ at $t \to -\infty$.

  At the time $t \sim 0$, the particle (wave packet) occurs in the region of the potential barrier and occurs in the scattering state $\left|\psi_{\boldsymbol{p}_0}^0\right\rangle$, where the scattering state is a superposition of all possible *final* asymptotic states $\left|\psi_{\boldsymbol{p}}^0\right\rangle$.

- We can describe the quantum scattering process in terms of the Møller operator Ω_+. First, the Møller operator applies the time evolution operator $e^{-iH_0 t}$ to the asymptotic incidence state $\left|\psi_{\boldsymbol{p}_0}^0\right\rangle$, which maps the state back in time to $t \to -\infty$. At time $t \to \infty$, the asymptotic state $\left|\psi_{\boldsymbol{p}_0}^0\right\rangle$ equals the the particle's initial state $\left|\psi_{\boldsymbol{p}_0}^+\right\rangle$.

  Then, we apply the time evolution operator e^{iHt}, using the Hamiltonian $H = H_0 + V$, to return the particle to the present:

$$\left|\psi_{\boldsymbol{p}_0}^+\right\rangle = \lim_{t \to -\infty} e^{iHt} e^{-iH_0 t} \left|\psi_{\boldsymbol{p}_0}^0\right\rangle = \Omega_+ \left|\psi_{\boldsymbol{p}_0}^0\right\rangle.$$

  Meanwhile, the operator Ω_- transfers the asymptotic state $\left|\psi_{\boldsymbol{p}}^0\right\rangle$ to the scattering state $\left|\psi_{\boldsymbol{p}_0}^-\right\rangle$, via

$$\left|\psi_{\boldsymbol{p}}^-\right\rangle = \lim_{t \to \infty} e^{iHt} e^{-iH_0 t} \left|\psi_{\boldsymbol{p}}^0\right\rangle = \Omega_- \left|\psi_{\boldsymbol{p}}^0\right\rangle.$$

  The state $\left|\psi_{\boldsymbol{p}}^0\right\rangle$ is a second possible scattering state, which approaches the asymptotic state $\left|\psi_{\boldsymbol{p}}^0\right\rangle$ in the limit $t \to \infty$.

- The asymptotic states are related by the scattering operator S, which is represented by the scattering matrix. The operator's matrix elements

$$S_{\boldsymbol{p}\boldsymbol{p}_0} = \langle \psi_{\boldsymbol{p}}^0 | S | \psi_{\boldsymbol{p}_0}^0 \rangle$$

are the probability amplitudes $P_{\boldsymbol{p}\boldsymbol{p}_0} = |S_{\boldsymbol{p}\boldsymbol{p}_0}|^2$ of detecting a particle in one of the asymptotic states $|\psi_{\boldsymbol{p}}^0\rangle$.

The scattering states, like the asymptotic states, thus form a complete system of basis vectors so that we can expand the state $|\psi_{\boldsymbol{p}_0}^0\rangle$ in the basis $\{|\psi_{\boldsymbol{p}}^0\rangle\}$ to get

$$|\psi_{\boldsymbol{p}_0}^+\rangle = \int |\psi_{\boldsymbol{p}}^-\rangle \langle \psi_{\boldsymbol{p}}^- | \psi_{\boldsymbol{p}_0}^+\rangle \, \mathrm{d}^3\boldsymbol{p} = \Omega_+ |\psi_{\boldsymbol{p}_0}^0\rangle .$$

As time approaches $t \to \infty$, the state $|\psi_{\boldsymbol{p}}^-\rangle$ uniquely evolves into the asymptotic state $|\psi_{\boldsymbol{p}}^0\rangle$. As a result, the probability amplitude $\langle \psi_{\boldsymbol{p}}^- | \psi_{\boldsymbol{p}_0}^+\rangle$ equals $S_{\boldsymbol{p}\boldsymbol{p}_0}$, i.e.

$$S_{\boldsymbol{p}\boldsymbol{p}_0} = \langle \psi_{\boldsymbol{p}}^0 | S | \psi_{\boldsymbol{p}_0}^0 \rangle = \langle \psi_{\boldsymbol{p}}^- | \psi_{\boldsymbol{p}_0}^+\rangle = \langle \psi_{\boldsymbol{p}}^0 | \Omega_-^\dagger \Omega_+ | \psi_{\boldsymbol{p}_0}^0 \rangle .$$

As a result, the scattering operator can be written in terms of the Møller operator as

$$S = \Omega_-^\dagger \Omega_+ .$$

- Finally, we note that the matrix elements $S_{\boldsymbol{p}\boldsymbol{p}_0}$ can be decomposed into a component that preserves the momentum of the asymptotic states and a component that preserves only energy; the decomposition reads

$$S_{\boldsymbol{p}\boldsymbol{p}_0} = \langle \psi_{\boldsymbol{p}}^0 | \psi_{\boldsymbol{p}_0}^0 \rangle - 2\pi i \delta(E_p - E_{p_0}) \langle \psi_{\boldsymbol{p}}^0 | V | \psi_{\boldsymbol{p}_0}^+\rangle ,$$

where we can write the matrix element $\langle \psi_{\boldsymbol{p}}^0 | V | \psi_{\boldsymbol{p}_0}^+\rangle = \langle \psi_{\boldsymbol{p}}^0 | T | \psi_{\boldsymbol{p}_0}^0 \rangle$ in terms of the operator $T = V\Omega_+$.

11.2.2   Example: A Gaussian Wave Packet

- We consider scattering on a narrow, repulsive potential, which we model with a delta function with a positive coefficient:

$$V(x) = \lambda \delta(x), \quad \lambda > 0.$$

The transmission and reflection amplitudes are given by

$$t_\lambda(p) = \frac{p}{p + ip_\lambda} \quad \text{and} \quad r_\lambda(p) = \frac{-ip_\lambda}{p + ip_\lambda},$$

where $p_\lambda = \lambda m$ and m is the scattered particle's mass. Note that because the potential is even, the problem is invariant under parity transformations and thus obeys $t'_\lambda = t_\lambda$ and $r'_\lambda = r_\lambda$.

- We represent the scattered particle with a Gaussian wavepacket moving along the x axis from left to right with group velocity $v_\mathrm{g} = \frac{\langle p \rangle}{m}$ and thus central position value $\langle x \rangle = x_0 + v_\mathrm{g} t$. The corresponding wavefunction is

$$|\psi^+(t)\rangle = \int \widehat{\psi}(p) e^{-i\frac{p^2}{2m\hbar}t} |\psi_p^+\rangle \, \mathrm{d}p,$$

where the scattering basic vector $\left|p_p^+\right\rangle$ is given by

$$\psi_p^+(x) = C \begin{cases} e^{i\frac{p}{\hbar}x} + re^{-i\frac{p}{\hbar}x} & x < x_a \\ \psi_{ab}(x) & x \in [x_a, x_b] \\ te^{i\frac{p}{\hbar}x} & x > x_b. \end{cases}$$

- Without a detailed derivation, we qualitatively consider four regimes:

  1. At early times, the particle is modeled by a standard Gaussian wave packet with a sigmoid shape.

  2. As the particle approaches the potential barrier at $x = 0$ the wave packet begines to deform.

  3. Once the wave packet's center reaches the potential barrier, the reflected and incident waves temporarily interfere to create a typical interference pattern on the left of the barrier.

  4. After the wave packet's center has pass the barrier, both the reflected and transmitted waves are on their way towards the left and right, respectively, and the interference pattern loses its resolution.

  5. At time well after the wave packet's center reached the barrier, the transmitted and reflected waves travel in their respective directions as essentially free wave packets, and begin to approach the asymptotic plane wave states $\psi_{\pm p_0}^0 \propto e^{\pm i\frac{p_0}{\hbar}x}$ as $t \to \infty$.

11.2.3   Example: Alpha Decay

- We now consider the example of radioactive alpha decay. The alpha particle initially occurs in a ground state between two potential barriers, encoded by the potential

$$V(x) = \lambda(t)\delta(x) + \lambda_\infty \delta(x - L),$$

where the two constants λ and λ are very large, i.e. $\lambda, \lambda_\infty \to \infty$, corresponding to a large potential barrier.

- At $t = 0$, the barrier $\lambda(t)$ at $x = 0$ rapidly decreases to its final value $\lambda(t) \to \lambda_0$. The scattering basis vector is zero for $x \geq L$, since any waves reflect off the steep barrier λ_∞ at $x = L$, and thus obeys

$$\psi_p^+(x) = C \begin{cases} e^{i\frac{p}{\hbar}x} + B_1 e^{-i\frac{p}{\hbar}x} & x < 0 \\ \psi_{0_L}(x) & x \in [0, L] \\ 0 & x > L. \end{cases}$$

where we write the wavefunction in the region $x \in [0, L]$ with the ansatz

$$\Psi_{0_L} = A_2 e^{-i\frac{p}{\hbar}x} + B_2 e^{i\frac{p}{\hbar}x}.$$

The coefficients at $x = 0$ are related by the same symmetric scattering matrix from the Gaussian example via

$$\begin{pmatrix} B_1 \\ B_2 \end{pmatrix} = \mathbf{S} \begin{pmatrix} 1 \\ A_2 \end{pmatrix},$$

and can be determined from the equation

$$B_2 e^{i\frac{p}{\hbar}L} = -A_2 e^{-i\frac{p}{\hbar}L},$$

which follows from the continuity condition $\psi_{0_L} = 0$ at the boundary $x = L$.

- We write the initial state at $t = 0$ in the basis of scattering states, where the time evolution proceeds according to the earlier equation

$$\left|\psi^+(t)\right\rangle = \int \widehat{\psi}(p) e^{-i\frac{p^2}{2m\hbar}t} \left|\psi_p^+\right\rangle \mathrm{d}p.$$

When the left barrier $\lambda(t)$ at $x = 0$ decreases to its final value at $t = 0$, a probability current $j_x < 0$ begins to flow to the left, and the probability for finding the particle between the potential barriers begins to decrease.

- We now return to the alpha particle's scattering state ψ_p^+. Because all incident waves are reflected from the right barrier λ_∞ at $x = 0$, the components of the particle's wavepacket reflecting from λ_∞ also scatter off $\lambda_0 x$. The scattering matrix is thus relevant only for the region $x < 0$, to the left of the first barrier, where a scattering state is described by the reflection coefficient B_1 via

$$\psi_p^+(x)\big|_{x<0} = C \left(e^{i\frac{p}{\hbar}x} + B_1 e^{-i\frac{p}{\hbar}x} \right).$$

As a result, the scattering matrix $\mathbf{S}$ reduces to a scalar value S_{11} relating the incident and reflected wave. This relationship reads

$$S_{11} = e^{2i\delta} = 1 + \left(e^{2i\delta} - 1 \right) = 1 + 2i e^{i\delta} sin\delta,$$

which is a scalar analog of the earlier matrix equation

$$S_{\boldsymbol{p}\boldsymbol{p}_0} = \left\langle \psi_{\boldsymbol{p}}^0 \big| \psi_{\boldsymbol{p}_0}^0 \right\rangle - 2\pi i \delta(E_p - E_{p_0}) \left\langle \psi_{\boldsymbol{p}}^0 \big| V \big| \psi_{\boldsymbol{p}_0}^+ \right\rangle.$$

11.3   Scattering in Three Dimensions

- First, we give an overview of the scattering process:

  – An incident quantum particle, described by a wave packet, approaches a scatterer (a target or potential barrier) and scatters from the target in a given spatial direction, where we then detect the particle.

  – The incident wave packet must initially be wide enough that its width does not increase dramatically (with respect to the initial width) over the course of the scattering process. The wavepacket must be large with respect to the target and small with respect to the dimensinos of the laboratory—the second condition ensures the wave packet does not simultaneously cover the scatterer and the detector.
    The wavepacket's width is determed by the cross-sectional width (cross-sectional area) of the beam of incident particles.

  – After the scattering interaction between incident particle and the target, we observe two wave packets: one continues past the target in the original direction of incidence, and one continues at an angle with respect to the direction of incidents and corresponds to the scattered particles.

– The scattering cross section is the fundamental measurable quantity used to analyze scattering processes, and represents the number of particles scattered in a given element of solid angle per unit time per unit incident current.

- We will work with particles expanded in a plane wave basis

$$\psi_k(\boldsymbol{r}) = Ce^{i\boldsymbol{k}\cdot\boldsymbol{r}},$$

where the constant C is independent of the choice of orthonormalization of the basis vectors. The probability current density for these plane waves is given by

$$\boldsymbol{j}_0 = j\frac{\boldsymbol{p}}{p}, \qquad j_0 = \frac{p}{m}|C|^2,$$

where j_0 encodes the probability of a particle being incident on the surface S_0 in the time interval Δt. In this case we can choose the normalization constant

$$|C|^2 = \frac{m}{pS_0\Delta t},$$

which represents a fourth possible means of normalizing plane waves.

- A typical scattering experiment involves a beam of incident particles with cross section S_0 moving along the z axis and described by the probability current density $j_N = \frac{N}{S_0\Delta t} = Nj_0$.

11.3.1   Expansion In Terms of Spherical Waves

- We consider the scattering state $\psi_k^+(\boldsymbol{r})$, which, in the limit of a vanishing scattering potential, approaches the plane wave $\psi_k(\boldsymbol{r}) = Ce^{ikz}$. We begin our analysis by writing the plane wave in a spherical wave basis, i.e.

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{l=}^{\infty}(2l+1)i^l j_l(kr)P_l(\cos\theta),$$

where $j_l(x)$ are the spherical Bessel functions and $P_l(x)$ are the Legendre polynomials.

Next, we expand the spherical wave representation in the limit of large distance of the particle from the target, in which case the the Bessel function approaches the asymptotic limit $j_l(x) \sim \frac{1}{x}\sin\left(x - l\frac{\pi}{2}\right)$. In this limit, the plane wave becomes

$$\psi_k^0 \equiv Ce^{ikz} \to C\sum_{l=0}^{\infty}(2l+1)\frac{i^l}{2ikr}\left[e^{i(kr-l\frac{\pi}{2})} - e^{-i(kr-l\frac{\pi}{2})}\right]P_l(\cos\theta).$$

- We assume the potential is spherically symmetric, in which case the problem's angular momentum is conserved, meaning we can expand the scattering state λ_k^+ in terms of the angular momentum eigenstates analogously to the expansion of the plane wave ψ_k^0. However, when expanding the scattering states in the angular momentum basis, we must also account for the scattering amplitude $S_l(k)$. With the consideration of $S_l(k)$ in mind, the expansion of the scattering states reads

$$\psi_k^+(\boldsymbol{r}) \to C\sum_{l=0}^{\infty}(2l+1)\frac{i^l}{2ikr}\left[S_l(k)e^{i(kr-l\frac{\pi}{2})} - e^{-i(kr-l\frac{\pi}{2})}\right]P_l(\cos\theta).$$

- Expansion in terms of spherical waves is needed in three dimensions because, in three dimensions, a particle can scatter in any spatial direction. Every partial wave has an associated reflection amplitude in the radial direction.

  For a given l, a scattering state has the same structure as a wave reflected from an infinite potential barrier in the previous section, i.e.

  $$\psi_k^+(\boldsymbol{r}) = C \left(e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + B_1 e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \right).$$

  where the origin $r = 0$ corresponds to the infinite potential barrier.

- In elastic scattering, probability is conserved in each scattering channel and the problem's scattering matrix is thus unitary, which allows us to introduce the phase term $\delta_l(k)$ and write the scattering matrix components as

  $$S_l(k) = e^{2i\delta_l(k)} = 1 + 2ie^{i\delta_l(k)} \sin \delta_l(k), \qquad |S_l(k)| = 1.$$

  We then decompose the scattering states into a non-scattered plane wave, which continues in the initial direction of incidence, and a scattered spherical wave. This decomposition reads

  $$\psi_{\boldsymbol{k}}^+(\boldsymbol{r}) \to Ce^{ikz} + C \left[\sum_{l=0}^{\infty} (2l+1) \frac{S_l(k)-1}{2ik} P_l(\cos\theta) \right] \frac{e^{ikr}}{r}$$
  $$= C \left(e^{ikz} + \frac{f(\theta,\phi)}{r} e^{ikr} \right),$$

  where we have defined the scattering amplitude

  $$f(\theta,\phi) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l(k)} \sin \delta_l(k) P_l(\cos\theta).$$

  For a spherically symmetric potential, the scattering amplitude depends only on the polar angle because of rotational invariance about the z axis.

- Finally, we note: the symbol $+$ in the scattering state $\psi_{\boldsymbol{k}}^+$ denotes the outgoing waves $\frac{f}{r} e^{ikr}$, while the scattering state $\psi_{\boldsymbol{k}}^-$ corresponds to the incident wave $\frac{f}{r} e^{-ikr}$. The scattering amplitude f is porportional to the problem's T operator, which we defined in the section on the Møller operator as $T = V\Omega_+$, where Ω_+ is the Møller operator.

11.3.2 Scattering Cross Section

- Consider a beam of incident particles in a scattering experiment, where N particles in the beam pass through the beam's cross section S_0 in the time Δt, of which

  $$N_{\mathrm{s}} = PN$$

  are scattered, where P is the probability of a given particle in the incident beam scattering off the target in any spatial direction.

  The scattering cross section is defined as the ratio between the number of scattered particles per unit time and the number current density of incoming particles,

defined as $j_N = \frac{N}{S_0 \Delta t}$. In equation form, the scattering cross section is denoted by σ and is defined as

$$\sigma = \frac{1}{j_N} \frac{N_s}{\Delta t} = \frac{1}{j_0} \frac{N_s}{N} \frac{1}{\Delta t} = \frac{1}{j_0} \frac{P}{\Delta t},$$

where $j_N = N j_0$. Alternatively, we can write the scattering cross section in the form

$$\sigma = \frac{N_s}{N} S_0 = P S_0,$$

which we interpret as a surface, with surface area σ, through which a particle that has passed through the beam cross section S_0 passes through with probability $P = \frac{N_s}{N} = \frac{\sigma}{S_0}$.

- Next, we define the probability $dP(\mathbf{r})$ of a particle scattering into the element of solid angle $d\Omega$ in the time interval Δt. This probability is defined as

$$dP(\mathbf{r}) = j_{\mathbf{r}} \, dS \Delta t = j_0 |f(\theta, \phi)|^2 \, d\Omega \Delta t,$$

where $j_{\mathbf{r}}$ is the probability current density in the direction $\hat{\mathbf{r}} = \mathbf{r}/r$ and $dS = r^2 \, d\Omega$. We have related the current $j_{\mathbf{r}}$ to the scattering amplitude $f(\theta, \phi)$ via

$$j_{\mathbf{r}}(\theta, \phi) = \mathbf{j}(\mathbf{r}) \cdot \hat{\mathbf{r}} \overset{r \to \infty}{\Longrightarrow} j_0 \frac{|f(\theta, \phi)|^2}{r^2}.$$

- The differential cross section, denoted by $d\sigma$, is defined as

$$d\sigma = \frac{1}{j_N} \frac{dN_s}{\Delta t} = \frac{1}{j_0} \frac{dP}{\Delta t} = |f(\theta, \phi)|^2 \, d\Omega.$$

The differential cross section is independent of the scattering state normalization constant C, and is related to the scattering amplitude via

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2.$$

Note that the expression is not a derivative of σ with respect to Ω—all of $\frac{d\sigma}{d\Omega}$ together is the differential cross section. The total and differential cross section are related by

$$\sigma = \iint \frac{d\sigma}{d\Omega} \, d\Omega,$$

which should be read as an integral of the differential cross section over the entire solid angle.

- The probability P of a particle scattering in any spatial direction in the time interval Δt is determined by the total cross section

$$\frac{1}{j_0} \frac{P}{\Delta t} = \sigma = \iint \frac{d\sigma}{d\Omega} \, d\Omega = \int_0^{2\pi} \int_0^{\pi} |f(\theta, \phi)|^2 \sin \theta \, d\theta \, d\phi$$

$$= \int_0^{2\pi} \int_0^{\pi} \left| \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l(k)} \sin \delta_l(k) P_l(\cos \theta) \right|^2 \sin \theta \, d\theta \, d\phi$$

$$= \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l(k),$$

where we have evaluated the integral using the orthogonality of the Legendre polynomials, i.e.

$$\iint P_l(\cos\theta) P_{l'}(\cos\theta)\,\mathrm{d}\Omega = \frac{4\pi}{2l+1}\delta_{ll'},$$

and the Legendre polynomial identity $P_l(1) = 1$.

- Because the total number of particles is conserved in scattering processes, the number of particles continuing past the scatterer in the original direction of incident is naturally less than the number in the incident beam, which is encoded in the unitary nature of the scattering matrix in the relationship $|S_l(k)| = 1$.

The scattering amplitude for scattering in the forward direction is described by

$$
\begin{aligned}
\mathrm{Im}\left[f(\theta,\phi)\big|_{\theta=0}\right] &= \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\,\mathrm{Im}\left[e^{i\delta_l(k)}\right]\sin\delta_l(k) \\
&= \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l(k) \\
&= \frac{k}{4\pi}\sigma.
\end{aligned}
$$

This result, which is derived using the Legendre polynomial identity $P_l(1) = 1$, is known as the optical theorem.

12 Quantum Measurements (Rough Draft)

12.1 The Quantum Measurement Process

- First, we define a classical measurement: For the purposes of this section, a classical measurement of a physical system is the measurement of some *inherent* property of said system (e.g. mass, length, etc...). They key idea the system has this property whether we perform the measurement or not. In this sense, we are bystanders in the measurement process, because our the process of measurement doesn't affect the outcome.

- Meanwhile, the very process of a quantum measurement[5] actively affects the outcome. We cannot speak of observing a system's inherent property. Instead, a quantum measurement is more properly called an experiment, which concludes with a result that is only one of many possible outcomes for a given quantum state $|\psi\rangle$. The result of any given value is random; we can only accurately predict the expected (average) value of many measurements.

  In fact, the Coopenhagen interpretation of quantum mechanics does not even attempt to answer what is the "inherent" property of a quantum system—it is simply a machinerey for predicting the probability of possible quantum measurement outcomes.

The Quantum Measurement Process

- The following steps are used to experimentally determine the expected value $\langle \mathcal{O} \rangle$ of a physical quantity assigned to the quantum operator $\mathcal{O}$ for a quantum system in the state $|\psi\rangle$.

- The expected value $\langle O \rangle$ is calculated from the average of many quantum measurements of $\mathcal{O}$'s associated quantity. These individual quantum measurements proceed as follows.

  1. We prepare the quantum state $|\psi\rangle$, which much be exactly the same for each measurement.
  2. We perform the quantum measurement. The outcome is one of the operator $\mathcal{O}$'s eigenstates λ_i, and we record the result.
  3. We repeat the process N times to get the outcomes $\lambda_1, \lambda_2, \ldots, \lambda_N$.
  4. We calculate the statistical average of the outcomes:
  $$\bar{\mathcal{O}} = \frac{1}{N} \sum_{i=1}^{N} \lambda_i.$$
  5. The true expectation value $\langle \mathcal{O} \rangle$ is then defined as
  $$\langle O \rangle = \lim_{N \to \infty} \bar{\mathcal{O}}.$$

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[5]There are many interpretations of quantum measurement. For the purposes of this course, we will consider mainly the classical Coopenhagen interpretation of a quantum measurement.

12.2   Stern-Gerlach Experiment

12.2.1   Semi-Classical Analysis

Homogeneous Magnetic Field

- Consider a silver atom of mass m exiting the Stern-Gerlach oven. The silver atom's shells are fully closed up to $4d^{10}$, with a single electron in the 5s shell.

  The electron in the 5s shell has magnetic dipole moment $\boldsymbol{\mu}$.

- The atom flies through a region with a homogeneous magnetic field $\boldsymbol{B}_0 = (0, 0, B_0)$. The electron's magnetic momentum $\boldsymbol{\mu}$ interacts with the magnetic field to produce a torque

$$\boldsymbol{M} = \boldsymbol{\mu} \times \boldsymbol{B}_0.$$

- We assume a simplified model in which the atom moves with uniform speed v_y in the y direction through the Stern-Gerlach apparatus in a precisely defined spin state

$$\chi(0) = \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{pmatrix},$$

  which is determined by the electron in the 5d orbital.

- The angle θ with respect to the z axis determines the spin's orientation in the xz plane. The associated spin orientation, in terms of the spin matrix operator $\boldsymbol{\sigma}$, is

$$\hat{\mathbf{n}}_0 = \langle\chi|\boldsymbol{\sigma}|\chi\rangle = (\sin\theta, 0, \cos\theta).$$

- In the presence of a homogeneous magnetic field $\boldsymbol{B}_0$, the atom would travel in an uninterrupted trajectory straight through the Stern-Gerlach apparatus. However, because of the torque $\boldsymbol{M} = \mu \times \boldsymbol{B}_0$ on the atom's magnetic dipole moment, the orientation of the atom's spin would rotate about the z axis by an angle $\delta\phi$ given by

$$\delta\phi = \omega_0\tau = \omega_0\frac{L}{v_y},$$

  where L is then length of the Stern-Gerlach apparatus, τ is the (short) flight time through the apparatus, and $\omega_0 = \frac{\mu B_0}{\hbar}$ is the Larmor frequency.

  After passing through the Stern-Gerlach apparatus, the silver atom continues along the y axis in the rotated spin state

$$\chi(\tau) = \begin{pmatrix} e^{\frac{i}{2}\delta\phi}\cos\frac{\theta}{2} \\ e^{-\frac{i}{2}\delta\phi}\sin\frac{\theta}{2} \end{pmatrix}.$$

  The new spin orientation is given by

$$\hat{\mathbf{n}}(\tau) = \langle\chi(\tau)|\boldsymbol{\sigma}|\chi(\tau)\rangle = (\sin\theta\cos\delta\phi, -\sin\theta\sin\delta\phi, \cos\theta).$$

Nonhomogeneous Magnetic Field

- The true Stern-Gerlach apparatus contains a magnetic with a nonhomogeneous magnetic field of the form

$$\boldsymbol{B} = (B_x, 0, B_z).$$

In the presence of this magnetic field, a neutral particle with magnetic dipole moment $\boldsymbol{\mu}$ experiences a force

$$\boldsymbol{F} = (\boldsymbol{\mu} \cdot \nabla)\boldsymbol{B}(\boldsymbol{r}) = \nabla(\boldsymbol{\mu} \cdot \boldsymbol{B}(\boldsymbol{r}))$$

The expression for force rests on the assumption that $\boldsymbol{\mu}$ is constant and $\nabla \times \boldsymbol{B} = 0$, and is derived via

$$\nabla(\boldsymbol{\mu} \cdot \boldsymbol{B}) = (\boldsymbol{\mu} \cdot \nabla)\boldsymbol{B} + (\boldsymbol{B} \cdot \nabla)\boldsymbol{\mu} + \boldsymbol{\mu} \times (\nabla \times \boldsymbol{B}) + \boldsymbol{B} \times (\nabla \times \boldsymbol{\mu}) = (\boldsymbol{\mu} \cdot \nabla)\boldsymbol{B}.$$

- Next, we expand the magnetic field to linear order in $\boldsymbol{B}$, which reads

$$\boldsymbol{B}(\boldsymbol{r}) = \boldsymbol{B}_0 + \sum_a \frac{\partial \boldsymbol{B}}{\partial x_\alpha} x_\alpha + \cdots,$$

Along the direction of travel along y axis, where $x \sim 0$ and $z \sim 0$, we can neglect the force in the x direction, and the resulting force on the atom is then

$$\boldsymbol{F} = F_z\, \hat{\mathbf{e}}_z = \mu \frac{\partial B_z}{\partial z}\bigg|_{z=0} \hat{\mathbf{e}}_z.$$

- Assuming the atom's magntic moment $\boldsymbol{\mu}$ is parallel to the magnetic field in the z direction, then after passing through the Stern-Gerlach apparatus in time τ, the atom experiences an impulse $\pm F_z \tau$, and its speed changes according to

$$m v_z = \pm F_z \tau = \pm F_z \frac{L}{v_y},$$

where the sign depends on whether the magnetic moment is parallel or antiparallel to the magnetic field.

The particle is thus incident on the detection screen either above or below the z axis, corresponding to either "up" or "down" states. By measuring the distribution of atoms on the detection screen, we can determine the probabilities $P_\uparrow$ and $P_\downarrow$ for an up or down outcome. In terms of these probabilities, the expected value of spin in the z direction, i.e. $\langle \sigma_z \rangle = \cos \theta$ is found with

$$\langle \sigma_z \rangle = \cos \theta = P_\uparrow - P_\downarrow.$$

- Assume particle enters magnet in quantum state $|\chi\rangle$:

$$\chi = \begin{pmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} \end{pmatrix}$$

Probability for up is

$$P_\uparrow = |\langle \uparrow | \chi \rangle|^2 = \cos^2 \frac{\theta}{2} \qquad \text{and} \qquad P_\downarrow = |\langle \downarrow | \chi \rangle|^2 = \sin^2 \frac{\theta}{2} = 1 - P_\uparrow$$

Expected value of σ_z is thus

$$\langle \sigma_z \rangle = \langle \chi | \sigma_z | \chi \rangle = \left(\cos \frac{\theta}{2}, \sin \frac{\theta}{2} \right) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} \end{pmatrix} = P_\uparrow - P_\downarrow$$

$$= 2 \cos^2 \frac{\theta}{2} - 1 = \cos \theta.$$

12.2.2 Quantum Stern-Gerlach Experiment

- We describe the silver atom of mass m passing through the Stern-Gerlach apparatus with a Hamiltonian of the form

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{q}{m_{\mathrm{e}}}\boldsymbol{S}\cdot\boldsymbol{B} \equiv H_0 - \frac{q}{m_{\mathrm{e}}}\boldsymbol{S}\cdot\boldsymbol{B},$$

where H_0 is the kinetic term and $-\frac{q}{m_{\mathrm{e}}}\boldsymbol{S}\cdot\boldsymbol{B}$ represents the anomolous Zeeman coupling of the 5s electron to the external magnetic field.

- Both energy and force are constants of motion, and we define them as

$$2E_0 \equiv \hbar\omega_0 = \frac{q\hbar}{m_{\mathrm{e}}}B_0 \qquad \text{and} \qquad F = \frac{q\hbar}{2m_{\mathrm{e}}}\frac{\partial B_z}{\partial z}\bigg|_{z=0},$$

where we have assumed the magnetic field has only a z component. In terms of the energy and force terms, the silver atom's Hamiltonian reads

$$H = H_0 - \frac{1}{2}\hbar\omega_0\sigma_z - Fz\sigma_z = H_0 - E_0\sigma_z - Fz\sigma_z,$$

where the force term is constructed so as to satisfy $-\nabla Fz\sigma_z = F\sigma_z$.

- Just before the atom enters the Stern-Gerlach apparatus (before experiencing the magnetic field), which we define to occur at $t = 0$, we describe the atom with the wave packet

$$\Psi(\boldsymbol{r}, 0) = \psi_0(x, y, 0)\phi_0(z)\begin{pmatrix} c_1 \\ c_2 \end{pmatrix},$$

where the initial wavefunction $\phi(z, t = 0) \equiv \phi_0(z)$ is given by

$$\int_{-\infty}^{\infty} \widehat{\phi}(p)e^{i\frac{p}{\hbar}z}\,\mathrm{d}p.$$

The wavefunction ψ_0 corresponds to motion in the xy plane with speed

$$v_y = \frac{1}{m}\langle p_y\rangle.$$

We assume the speed is large, so the initial wave packet doesn't widen significantly in the magnet.

The wavefunction $\phi_0(z)$ encodes motion along the z axis. The coefficients c_1 and c_2 are spinor coefficients encoding the atom's initial spin state.

- At later times, the wavefunction is determined by

$$\Psi(\boldsymbol{r}, t) = \psi_0(z, y, t)\begin{pmatrix} \phi_\uparrow(z, t) \\ \phi_\downarrow(z, t) \end{pmatrix}.$$

- The time evolution of ψ_0, which encodes motion in the xy plane, is simply uniform motion along the y axis and is unrelated to dynamics of spin in the experiment, which is confined to the z axis and represented by the wavefunction ϕ.

- The time evolution of the spin wavefunction is given by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \phi_\uparrow(z,t) \\ \phi_\downarrow(z,t) \end{pmatrix} = -\left(\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \frac{1}{2}\hbar\omega_0\sigma_z + Fz\sigma_z \right) \begin{pmatrix} \sigma_\downarrow(z,t) \\ \sigma_\uparrow(z,t) \end{pmatrix}.$$

  The initial wavefunction ϕ_0 has a unitary time evolution given by

$$e^{-i\frac{H}{\hbar}\tau} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} e^{i\frac{p}{\hbar}z} = \begin{pmatrix} e^{\frac{i}{2}\delta\varphi + i\frac{\delta p}{\hbar}z}c_1 \\ e^{-\frac{i}{2}\delta\varphi - i\frac{\delta p}{\hbar}z}c_2 \end{pmatrix} e^{i\frac{p}{\hbar}z - i\frac{E_p}{\hbar}\tau},$$

  where $e^{i\frac{H}{\hbar}t}$ is the unitary time evolution operator, and we have defined

$$E_p = \frac{p^2}{2m} \qquad \tau \sim \frac{L}{v_y} \qquad \delta\varphi = \omega_0\tau \qquad \delta p = mv = F\tau.$$

- We denote the state immediately after exiting the magnet as

$$\Psi(\boldsymbol{r}, 0^+) \equiv \Psi(\boldsymbol{r}, \tau) = e^{i\frac{H}{\hbar}\tau}\Psi(\boldsymbol{r}, 0).$$

- The solution to the spin Schrödinger equation is

$$\begin{pmatrix} \phi_\uparrow(z, 0^+) \\ \phi_\downarrow(z, 0^+) \end{pmatrix} = \int_{-\infty}^{\infty} \begin{pmatrix} e^{\frac{i}{2}\delta\varphi + i\frac{p+\delta p}{\hbar}z}c_1 \\ e^{-\frac{i}{2}\delta\varphi - i\frac{p-\delta p}{\hbar}z}c_2 \end{pmatrix} \widehat{\phi}(p)\,\mathrm{d}p = \int_{-\infty}^{\infty} \begin{pmatrix} e^{\frac{i}{2}\delta\varphi}\widehat{\phi}(p - \delta p)c_1 \\ e^{-\frac{i}{2}\delta\varphi}\widehat{\phi}(p + \delta p)c_1 \end{pmatrix} e^{i\frac{p}{\hbar}z}\,\mathrm{d}p,$$

  where the spin wave packet has experienced an impulse $\pm\delta p$ and transformed as

$$\phi_0(z) \to \phi(z, 0^+) = e^{\pm i\frac{\delta p}{\hbar}z}\phi_0(z).$$

- Assuming the speed v_y through the Stern-Gerlach apparatus is large and the wavepacket does not appreciably spread out from its initial state, we can write the spin wavefunction at later times as

$$\phi(z, t) = e^{i\frac{(\delta p)^2}{2m\hbar}t}\phi(z - vt, 0^+) = \phi_0(z - vt)e^{i\frac{\delta p}{\hbar}\left(z - \frac{1}{2}vt\right)},$$

  and the solution for the complete wave packet's time evolution is

$$\Psi(\boldsymbol{r}, t) = \psi_0(x, y, t) \begin{pmatrix} e^{\frac{i}{2}\delta\varphi}\phi_0(z - vt)e^{i\frac{\delta p}{\hbar}\left(z - \frac{1}{2}vt\right)}c_1 \\ e^{-\frac{i}{2}\delta\varphi}\phi_0(z + vt)e^{i\frac{\delta p}{\hbar}\left(z + \frac{1}{2}vt\right)}c_2 \end{pmatrix}.$$

Expected Value of Spin

- We assume an initial spin state

$$\chi(0) = \begin{pmatrix} \cos\frac{\theta}{2} \\ \sin\frac{\theta}{2} \end{pmatrix},$$

  and write the time-dependent spin state in the form

$$|\chi(z, t)\rangle = \phi_\uparrow(z, t)\,|\uparrow\rangle + \phi_\downarrow(z, t)\,|\downarrow\rangle,$$

  where the coefficients $\phi_\uparrow$ and $\phi_\downarrow$ are time-dependent.

- The expected value of spin in the z direction is

$$\langle \sigma_z \rangle = \int_{-\infty}^{\infty} \left(|\phi_{ua}(z,t)|^2 - |\phi_{ua}(z,t)|^2 \right) \mathrm{d}z$$

$$= \int_{-\infty}^{\infty} \left(\cos^2 \frac{\theta}{2} |\phi_0(z - vt)|^2 - \sin^2 \frac{\theta}{2} |\phi_0(z + vt)|^2 \right) \mathrm{d}z$$

$$= P_\uparrow - P_\downarrow = \cos \theta,$$

in agreement withthe semi-classical result.

- Next, we calculate spin expectation value in the x direction, which reads

$$\langle \sigma_x \rangle = 2 \, \mathrm{Re} \int_{-\infty}^{\infty} \phi_\uparrow^*(z,t) \phi_\downarrow(z,t) \, \mathrm{d}z$$

We begin by making the auxiliary calculation

$$I \equiv \int_{-\infty}^{\infty} \phi_0 \left(z - \frac{\delta p}{m} t \right) \phi_0 \left(z + \frac{\delta p}{m} t \right) e^{2i \frac{\delta p}{\hbar} z} \, \mathrm{d}z$$

$$= \exp \left[-\frac{(\delta p)^2}{2\sigma_p^2} \left(1 + \frac{4\sigma_p^4 t^2}{m^2 \hbar^2} \right) \right] = \exp \left[- \left(\frac{(\delta p)^2}{2\sigma_p^2} + \frac{2\sigma_p^2 (\delta p)^2}{m^2 \hbar^2} t^2 \right) \right]$$

$$\equiv \exp \left[- \left(\frac{(\delta p)^2}{2\sigma_p^2} + \lambda t^2 \right) \right],$$

where we have defined the constant

$$\lambda \equiv \frac{2\sigma_p^2 (\delta p)^2}{m^2 \hbar^2}.$$

For large times, the exponent and integral approach

$$\frac{(\delta p)^2}{2\sigma_p^2} + \lambda t^2 \to \lambda t^2 \implies I \to e^{-\lambda t^2}.$$

- Next, we combine the result of the integral $I \to e^{-\lambda t^2}$ with the expression for $\langle \sigma_x \rangle$. Without proof, the result is

$$\langle \sigma_x \rangle = e^{-\lambda t^2} \sin \theta \cos \delta\varphi.$$

Again without proof, a similar derivation for $\langle \sigma_y \rangle$ results in

$$\langle \sigma_y \rangle = -e^{-\lambda t^2} \sin \theta \sin \delta\varphi.$$