Quantum Mechanics Lecture Notes

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2020-21 Winter Semester

About These Notes

These are my lecture notes from the course *Kvanta Mehanika* (Quantum Mechanics), a mandatory course for third-year physics students at the Faculty of Math and Physics in Ljubljana, Slovenia. The exact material herein is specific to the physics program at the University of Ljubljana, but the content is fairly standard for an late-undergraduate course in quantum mechanics. I am making the notes publicly available in the hope that they might help others learning the same material.

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On Content: The material herein is far from original—it comes almost exclusively from Professor Anton Ramšak's lecture notes on quantum mechanics at the University of Ljubljana. I take credit for nothing beyond translating the notes to English and typesetting.

Disclaimer: Mistakes—both trivial 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, by GitHub pull request, email or some other means, I'll be happy to hear from you, even for the most trivial of errors.

Contents

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

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

Substituting this decomposition into the Schrödinger equation produces

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

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

$$\begin{aligned} -\hbar\dot{\Psi}_{\mathrm{Im}} &= -\frac{\hbar^2}{2m}\Psi''_{\mathrm{Re}} + V\Psi_{\mathrm{Re}} \\ -\hbar\dot{\Psi}_{\mathrm{Re}} &= -\frac{\hbar^2}{2m}\Psi''_{\mathrm{Im}} + V\Psi_{\mathrm{Im}} \end{aligned}$$

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 finding 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:

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

  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

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

  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

$$\begin{aligned} j(x,t) &\equiv \frac{\hbar}{2im}\left(\Psi^*(x,t)\frac{\partial}{\partial x}\Psi(x,t) - \Psi(x,t)\frac{\partial}{\partial x}\Psi^*(x,t)\right) \\ &= \frac{1}{m}\rho(x,t)\frac{\partial S(x,t)}{\partial x} \end{aligned}$$

- 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 $\S(x,t)$ 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

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

The resulting equality $\lim_{a\to b}\big[\psi'(b) - \psi'(a)\big] = 0$ 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

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

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

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

We see 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 condition's 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 their 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 read

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\psi_1''(x) + \big[V(x) - E\big]\psi_1(x) &= 0 \\
-\frac{\hbar^2}{2m}\psi_2''(x) + \big[V(x) - E\big]\psi_2(x) &= 0
\end{aligned}
$$

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 $W_{12} = 0$ 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.

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

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:

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

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 form 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

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

  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

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

  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 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] assuming the potential energy V is real

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:

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

  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

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

  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:

$$\begin{aligned}&[\lambda A, B] = \lambda[A, B], \qquad \lambda \in \mathbb{C} \\ &[A, B] = -[B, A] \\ &[A + B, C] = [A, C] + [B, C] \\ &[AB, C] = A[B, C] + [A, C]B.\end{aligned}$$

- 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
$$\Delta A \Delta B \geq \frac{1}{2}\big|\big\langle [A,B] \big\rangle\big|.$$
TODO: consider adding proof 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
$$\frac{\mathrm{d}\left\langle O, t \right\rangle}{\mathrm{d}t} = \int_V \left(\frac{\partial \Psi^*}{\partial t} \mathcal{O} \Psi + \Psi^* \frac{\partial \mathcal{O}}{\partial t} \Psi + \Psi^* \mathcal{O} \frac{\partial \Psi}{\partial t} \right) \mathrm{d}^3\boldsymbol{r}.$$
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

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

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

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

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

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

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

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

- 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

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

- 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:

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

- 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

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

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

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

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

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

- 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

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

- 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

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

  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 $\lambda, \mu \in \mathbb{C}$

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

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

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

- 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 that 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:
$$|\psi\rangle = \left(\sum_n |n\rangle\,\langle n|\right)|\psi\rangle \implies \sum_n |n\rangle\,\langle n| = \mathrm{I}$$
where I is the identity operator. This is an important identity, so I'll write it again:
$$\mathrm{I} = \sum_n |n\rangle\,\langle n|$$
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

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

- 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

$$\begin{aligned}\mathcal{O}\,|\psi\rangle &= \sum_m |m\rangle\,\langle m|\,\mathcal{O}\sum_n |n\rangle\,\langle n|\psi\rangle \\ &= \sum_{mn} |m\rangle\,\mathcal{O}_{mn}\,\langle n|\,|\psi\rangle\end{aligned}$$

  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

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

  i.e. $\mathcal{O}$ 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

$$\begin{aligned}\mathcal{O}\,|\psi\rangle \equiv \sum_{mn} |m\rangle\,\mathcal{O}_{mn}\,\langle n|\,|\psi\rangle &= \sum_{mn} |m\rangle\,\mathcal{O}_{mn}c_n \\ &= \sum_m \left(\sum_n \mathcal{O}_{mn}c_n\right)|m\rangle \\ &\equiv \sum_m d_m\,|m\rangle \\ &= |\phi\rangle\end{aligned}$$

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

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

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 $\mathcal{O}\left|\psi_n\right\rangle = \lambda_n \left|\psi_n\right\rangle$. We then act on both sides of the equation with $\left\langle\psi_n\right|$ and apply the eigenvalue relation to get

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

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

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

$$\mathcal{O}\left|1\right\rangle = \lambda_1 \left|1\right\rangle \qquad \text{and} \qquad \mathcal{O}\left|2\right\rangle = \lambda_2 \left|2\right\rangle,$$

and act on each equation with $\left\langle 2\right|$ and $\left\langle 1\right|$, respectively, to get

$$\left\langle 2\middle|\mathcal{O}\middle|1\right\rangle = \lambda_1 \left\langle 2\middle|1\right\rangle \qquad \text{and} \qquad \left\langle 1\middle|\mathcal{O}\middle|2\right\rangle = \lambda_2 \left\langle 1\middle|2\right\rangle$$

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

$$\left\langle 1\middle|\mathcal{O}\middle|2\right\rangle^* = \lambda_2 \left\langle 1\middle|2\right\rangle^*$$

The rest is just playing around with the general identity $\left\langle\psi\middle|\phi\right\rangle = \left\langle\phi\middle|\psi\right\rangle^*$, the Hermitian identity $\left\langle 1\middle|\mathcal{O}2\right\rangle = \left\langle\mathcal{O}1\middle|2\right\rangle$, and the eigenvalue relation to get

$$\lambda_2 \left\langle 1\middle|2\right\rangle^* = \left\langle 1\middle|\mathcal{O}\middle|2\right\rangle^* \equiv \left\langle 1\middle|\mathcal{O}2\right\rangle^* = \left\langle O2\middle|1\right\rangle = \left\langle 2\middle|O1\right\rangle = \lambda_1 \left\langle 2\middle|1\right\rangle$$

We end up with

$$\lambda_2 \left\langle 1\middle|2\right\rangle^* = \lambda_1 \left\langle 2\middle|1\right\rangle \implies \lambda_2 \left\langle 2\middle|1\right\rangle = \lambda_1 \left\langle 2\middle|1\right\rangle$$

And end up with

$$(\lambda_2 - \lambda_1)\left\langle 2\middle|1\right\rangle = 0$$

Goodness gracious I made that way more convoluted than it needed to be.

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

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

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

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

- 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

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

- Any operator $\mathcal{O}$ obeys $\big(\mathcal{O}^\dagger\big)^\dagger = \mathcal{O}$, 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

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

- 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

$$\big(AB\big)^\dagger = B^\dagger A^\dagger,$$

which follows from

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

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

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

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.

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

  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 $\left|\tilde{\phi}\right\rangle = U\left|\phi\right\rangle$ and $\left|\tilde{\psi}\right\rangle = U\left|\psi\right\rangle$,

$$\langle\phi|\psi\rangle = \left\langle\tilde{\phi}\middle|\tilde{\psi}\right\rangle$$

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

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

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

  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 $\left|\phi\right\rangle$ and $\left|\psi\right\rangle$ equal the matrix elements of the transformed operator $\tilde{\mathcal{O}} = U\mathcal{O}U^\dagger$ found with the transformed wavefunctions $\left|\tilde{\phi}\right\rangle$ and $\left|\tilde{\psi}\right\rangle$.

- If $\left|\tilde{\psi}\right\rangle = U\left|\psi\right\rangle$ then $\left\langle\tilde{p}\right| = \left\langle U\psi\right| = \left\langle\psi\right| U^\dagger$.

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

$$U = U\,\mathrm{I} = U\sum_n \left|\psi_n\right\rangle\left\langle\psi_n\right| = \sum_n U\left|\psi_n\right\rangle\left\langle\psi_n\right| = \sum_n \left|\tilde{\psi}_n\right\rangle\left\langle\psi_n\right|$$

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

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

- **TODO** The identity operator takes the same form in the original basis $\{\left|\psi_n\right\rangle\}$ and the transformed basis $\{\left|\tilde{\psi}_n\right\rangle\}$:

$$UU^\dagger = \sum_{mn}\left|\tilde{\psi}_m\right\rangle\left\langle\psi_m\middle|\psi_n\right\rangle\left\langle\tilde{\psi}_n\right| = \sum_n \left|\tilde{\psi}_n\right\rangle\!\left\langle\tilde{\psi}_n\right|$$

- In a unitary change of basis $\{|\psi_n\rangle\} \to \{|\tilde{\psi}_n\rangle\}$, the coefficients transform according to
$$|\phi\rangle = \sum_n c_n |\psi_n\rangle = \sum_{mn} |\tilde{\psi}_m\rangle\langle\tilde{\psi}_m|c_n|\psi_n\rangle = \sum_n d_n|\tilde{\psi}_n\rangle$$
where the new coefficients are
$$d_n = \sum_m U_{nm}^\dagger c_m$$

- Unitary transformations preserve eigenvalue equations:
$$\begin{aligned}
&\mathcal{O}|\psi_n\rangle = \lambda_n |\psi_n\rangle \implies U\mathcal{O}\,\mathrm{I}\,|\psi_n\rangle = U\mathcal{O}U^\dagger U|\psi_n\rangle = \lambda_n U|\psi_n\rangle \\
&\tilde{\mathcal{O}}|U\psi_n\rangle = \lambda_n |U\psi_n\rangle \\
&\tilde{\mathcal{O}} = |\tilde{\psi}_n\rangle = \lambda_n|\tilde{\psi}_n\rangle
\end{aligned}$$

- 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.

  TODO derivation on page 35 of KvaMeh notes.

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

- Expanding in basis formed of the energy eigenstates $\{|\phi_n\rangle\}$ of the Hamiltonian operator H reads
$$|\psi(t)\rangle = \sum_m \langle\phi_n|\psi(0)\rangle\, e^{-i\frac{E_n}{\hbar}t}|\phi_n\rangle$$
Using the operator function identity $f(\mathcal{O})\psi_n = f(\lambda_n)\psi_n$, we can replace the energy eigenvalues E_n in the last line with the Hamiltonian operator H to get
$$|\psi(t)\rangle = \sum_m \langle\phi_n|\psi(0)\rangle\, e^{-i\frac{E_n}{\hbar}t}|\phi_n\rangle = \sum_m \langle\phi_n|\psi(0)\rangle\, e^{-i\frac{H}{\hbar}t}|\phi_n\rangle$$
Factoring $e^{-i\frac{H}{\hbar}t}$ out of the sum gives
$$|\psi(t)\rangle = e^{-i\frac{H}{\hbar}t}\langle\phi_n|\psi(0)|\phi(n)\rangle \equiv U(t)|\psi(0)\rangle$$
where we have defined the time evolution operator $U(t) \equiv e^{-i\frac{H}{\hbar}t}$.

- As the notation $U(t)$ suggests, the time evolution operator is unitary with generator H. Because U is unitary, it preserves the inner product.

- 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

3 Examples of Quantum Systems

3.1 Quantum Harmonic Oscillator

- In one dimension, the quantum harmonic oscillator's Hamiltonian reads
$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 = - - \frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2, \qquad \omega = \sqrt{\frac{k}{m}}.$$
The standard formalism for analyzing the harmonic oscillator follows.

- We introduce 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
$$x = \frac{\xi}{\sqrt{2}}\left(a + a^\dagger\right) \qquad \text{and} \qquad \frac{\mathrm{d}}{\mathrm{d}x} = \frac{1}{\sqrt{2}\xi}\left(a - a^\dagger\right).$$
Additionally, we can write the Hamiltonian as
$$H = \frac{\hbar\omega}{2}\left(aa^\dagger + a^\dagger a\right)$$

- Next, we quote to 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 $\hat{n} \equiv a^\dagger a$

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

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

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

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

$$a \left| \phi_0 \right\rangle = 0.$$

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

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

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:

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

- 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

$$\begin{aligned} \left\langle c_n^* \phi_{n+1} \middle| c_n \phi_{n+1} \right\rangle &= \left\langle a^\dagger \phi_n \middle| a^\dagger \phi_n \right\rangle = \left\langle \phi_n \middle| a a^\dagger \phi_n \right\rangle = \left\langle \phi_n \middle| (a^\dagger a + 1) \phi_n \right\rangle \\ &= \langle \phi_n | (n+1) \phi_n \rangle , \end{aligned}$$

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

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

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

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

- 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

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

  to show that

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

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

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

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

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

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

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

  The latter expression results in the recursion relations

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

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

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

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 in addition to $\left|\phi_n\right\rangle$ there exists another linearly independent eigenstates $\big|\tilde{\phi}_n\big\rangle$ with the same energy E_n. From the recursion relation

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

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

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

  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 $a^n\big|\phi_n\big\rangle \propto \big|\phi_0\big\rangle$, all higher states are also nondegenerate.

[2] This does not hold in higher dimensions

- 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

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

In the p-space representation, the nth eigenfunctions characteristic width is

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

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 in the ground state $\sigma_{x_n}\sigma_{p_n} = \hbar/2$, in agreement with 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

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

- 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 initially 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

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

  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

$$\begin{aligned}
|\psi_\alpha\rangle &= \sum_n \langle n|\psi_\alpha\rangle\,|n\rangle = \sum_n \frac{1}{\sqrt{n!}}\left\langle \left(a^\dagger\right)^n\phi_0 \middle| \psi_\alpha\right\rangle |n\rangle \\
&= \langle\phi_0|\psi_\alpha\rangle \sum_n \frac{\alpha^n}{\sqrt{n!}}\,|n\rangle = \langle\phi_0|\psi_\alpha\rangle \sum_n \frac{\left(\alpha a^\dagger\right)^n}{n!}\,|0\rangle \\
&= \langle\phi_0|\psi_\alpha\rangle\, e^{\alpha a^\dagger}\,|0\rangle
\end{aligned}$$

where we 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

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

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.

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

3.2 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

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

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

- Similarly, the expressions for x and p are

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

  As expected, both x and p have Hermitian matrices.

3.3 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:

$$\begin{aligned} \langle p\rangle &= \int p\left|\tilde{\psi}(p)\right|^2 \mathrm{d}p = p_0 \\ \langle p^2\rangle &= \int p^2\left|\tilde{\psi}(p)\right|^2 \mathrm{d}p = p_0^2 + \sigma_p^2 \\ \Delta p^2 \equiv \sigma_p^2 &= \langle p^2\rangle - \langle p\rangle^2 \\ \langle E\rangle &= \frac{p_0^2+\sigma_p^2}{2m} \end{aligned}$$

- 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

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

- 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

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

  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.

3.4 Phase and Group Velocity

TODO: Optional material, add as time permits.

3.5 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 $\psi(x - s)$:

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

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 $\hat{\boldsymbol{n}}$ reads

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

and the corresponding translation operator is

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

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

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

4.2 Rotation

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

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

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

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

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

  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

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

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

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

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

- 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 $V(\boldsymbol{r}) = V(r)$ where $r = |r|$.

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 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

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

  In other words, $T\Psi(\boldsymbol{r}, t) = \Psi(\boldsymbol{r}, -t)$ solves the same Schrödinger for $H \to -H$.
- Alternatively, we can define a modified time reversal operator $\mathcal{T} = KT$ where $K : \psi \mapsto \psi^*$ is the complex conjugation operator. The complex conjugation 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

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

  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, but ψ and ψ^* solve the stationary Schrödinger equation for a given energy eigenvalue E. For a non-degenerate spectrum, the conjugate 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 to 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

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

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

$$\langle U(\delta)\phi|\mathcal{O}|U(\delta)\psi\rangle = \langle\tilde{\phi}|\mathcal{O}|\tilde{\psi}\rangle = \langle\phi|\mathcal{O}|\psi\rangle$$

Even more, we can multiply each basis vector $|n\rangle$ 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 $V(\boldsymbol{r}) \to\to V(\boldsymbol{r}) + V_0$ 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

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

  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

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

  This gauge transformation preserves probability density, i.e.

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

  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 (so 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

$$\begin{aligned}(\nabla\times\boldsymbol{r})\psi = \nabla\times(\boldsymbol{r}\psi) &= (\nabla\psi)\times\boldsymbol{r} + \psi(\nabla\times\boldsymbol{r}) = (\nabla\psi)\times\boldsymbol{r} + 0\\ &= -\boldsymbol{r}\times(\nabla\psi) = -(\boldsymbol{r}\times\nabla)\psi\end{aligned}$$

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

$$L_z\psi = -i\hbar(yp_x - xp_y)\psi = i\hbar(p_yx - p_xy)\psi$$

  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

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

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 $\hat{\boldsymbol{n}}$ 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 $V = V(|\boldsymbol{r}|)$.

- **TODO** we proof the above commutation relation with the series definition of $U(\boldsymbol{\phi})$.

- 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 basis state.

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

$$\begin{aligned}[L_z, L_\pm] &\equiv [L_z, L_x \pm iL_y] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm i(-i\hbar L_x) \\ &= \hbar[\pm L_x + iL_y] = \pm\hbar L_\pm\end{aligned}$$

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

$$\begin{aligned}L_\pm L_\mp &= (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \pm iL_yL_x \mp iL_xL_y \\ &= L^2 - L_z^2 \pm iL_yL_x \mp iL_xL_y\end{aligned}$$

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 leaves the two equations (two because of the $\pm$ terms)

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

Finally we subtract the equations with plus and minus to get

$$L_+L_- - L_- + \equiv [L_+, L_-] = 2\hbar L_z$$

[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.

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

$$L_z |m\rangle = m\hbar |m\rangle$$

  Note: although the complete corresponding eigenvalue is $m\hbar$ with units of angular momentum; 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 $L_z L_\pm = L_\pm L_z \pm \hbar L_z$, the operator $L_z L_\pm$ acts on $|m\rangle$ as

$$\begin{aligned} L_z L_\pm |m\rangle &= (L_\pm L_z \pm \hbar L_z) |m\rangle = L_\pm L_z |m\rangle \pm \hbar L_z |m\rangle \\ &= L_\pm \hbar |m\rangle \pm \hbar L_z |m\rangle \\ &= (m \pm 1)\hbar L_\pm |m\rangle \end{aligned}$$

  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 $\boldsymbol{L}_+$ 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 $\left|L^2\right\rangle$. 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 eigenvalue of L^2 with the same eigenvalue λ. But we know from the previous bullet that $L_\pm$ raises or lowers the index of $|m\rangle$ by one, i.e. $L_\pm |m\rangle \propto |m \pm 1\rangle$, which means 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.

[4]Note that l is also called the azimuthal quantum number.

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

$$\begin{aligned}\langle L_\pm m | L_\pm m\rangle &= \big\langle m \big| \big[l(l+1) - m(m\pm 1)\big]\hbar^2 \big| m\big\rangle \\ &\equiv (C_{l,m\pm 1})^2 \langle m|m\rangle\end{aligned}$$

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 both 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 $\lambda = l(l+1)\hbar^2$.

- 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

$$m \in \big\{-l, -l+1, \ldots, l-1, l\big\}$$

- Since m can take on $2l+1$ values at a given l, L^2's 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

$$L_\pm |lm\rangle = C_{l,m\pm 1} |l, m\pm 1\rangle = \hbar\sqrt{l(l+1) - m(m\pm 1)}\, |l, m\pm 1\rangle$$

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

$$\psi_m = Ce^{im\phi}$$

- 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.

$$\psi_m(\phi) = \psi_m(\phi + 2\pi) \iff 1 = e^{2\pi im} \implies m \in \mathbb{Z}$$

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 for $l = 0, 1, 2$ are

$$\begin{aligned}
&Y_0^0 = \tfrac{1}{\sqrt{4\pi}} && \\
&Y_1^0 = \sqrt{\tfrac{3}{4\pi}}\cos\theta && Y_l^{\pm1} = \mp\sqrt{\tfrac{3}{8\pi}}\sin\theta e^{\pm i\phi} \\
&Y_2^0 = \sqrt{\tfrac{5}{16\pi}}(3\cos^2\theta - 1) && Y_2^{\pm1} = \mp\sqrt{\tfrac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\phi} \\
&Y_2^{\pm2} = \sqrt{\tfrac{5}{32\pi}}\sin^2\theta e^{\pm 2i\phi} &&
\end{aligned}$$

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
$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad L_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$
$$L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad L^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
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:

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

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

$$\psi(\boldsymbol{r}) = \frac{u(r)}{r}$$

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_{veff}, 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 $\boldsymbol{r} = (r, \phi, \theta)$ to a one-dimensional problem.

6.2 General Properties of the Radial Solution

6.2.1 Solutions for $r \to 0$

- We consider potentials of the form

$$\lim_{r\to 0} r^2 V(r) = 0$$

For such potentials, the potential $V(r)$ and energy E in the radial eigenvalue equation for u are negligible in comparison to the centrifugal component of V_{eff}, and 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

$$u(r) = C_+ r^{\lambda_+} + C_- r^{\lambda_-} = C_l r^{l+1} + \frac{D_l}{r^l}$$

- We 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.

- **TODO:** resolve what's going on here.

  For $l = 0$, we turn to the solution of the Poisson equation for electrostatic potential ϕ, which reads

$$\nabla^2\phi(\boldsymbol{r}) = -\frac{\rho(\boldsymbol{r})}{\epsilon_0}$$

For a point charge, with charge density $\rho(\boldsymbol{r}) = q\delta^3(\boldsymbol{r})$, the solution is

$$\phi(\boldsymbol{r}) = \frac{q}{4\pi\epsilon_0 r}$$

If we cancel like terms, the Poisson equation reads

$$\nabla^2 \frac{1}{4\pi\epsilon_0 r} = \delta^3(\boldsymbol{r})$$

TODO: so this step here I'm not sure about. The above implies that $\psi(\boldsymbol{r})$ solves the equation

$$\nabla^2\psi(\boldsymbol{r}) = -4\pi D_0\delta^3(\boldsymbol{r})$$

But a solution $\psi \sim r^{-1}$ does not solve the Schrödinger equation, because the potential does not agree with $\delta^3(\boldsymbol{r})$ at the origin.

This means that, to satisfy the Schrödinger equation, we must have $D_l = 0$ for all l (to remove proportionality of ψ to $\delta^3(\boldsymbol{r})$ at the origin). With $D_l = 0$ we're left with

$$u(r) = C_l r^{l+1} \qquad \text{and} \qquad \psi(r) = C_l r^l$$

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 their 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

$$-\frac{\hbar^2}{2m}\Big[v''(r) \pm 2\kappa v'(r) + \kappa^2 v(r)\Big] e^{\pm\kappa r} + V_{\text{eff}}(r) v(r) e^{\pm \kappa r} = E v(r) e^{\pm\kappa r}$$

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

$$v(r) = v(r_0) \exp\bigg(\pm \frac{m}{\kappa\hbar^2} \int_{r_0}^{r} V_{\text{eff}}(\tilde{r})\, \mathrm{d}\tilde{r}\bigg)$$

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

$$\lim_{r\to\infty} rV(r) = 0$$

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

$$\lim_{r\to\infty} rV(r) = 0$$

no long holds is potentials of the form $V(r) = -\lambda/r$, for which we have

$$\lim_{r\to\infty} \int_{r_0}^{r} V(\tilde{r})\, \mathrm{d}\tilde{r} = \lim_{r\to\infty} \left(-\lambda \ln \frac{r}{r_0}\right) \to \infty$$

To correspond solutions 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

$$\lim_{r\to\infty} rV(r) = 0$$

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

$$-\frac{\hbar^2}{2m_\mathrm{e}}u''(r) + \left(\frac{l(l+1)\hbar^2}{2m_\mathrm{e}r^2} - \frac{e_0^2}{4\pi\epsilon_0 r}\right)u(r) = Eu(r)$$

  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, as before, $\kappa = \sqrt{\frac{2mE}{\hbar^2}}$. 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 are

$$\begin{aligned} u' &= \rho^l e^{-\rho}\big[(l+1-\rho)v + \rho v'\big] \\ u'' &= \rho^l e^{-\rho}\left\{\left[-2l - 2 + \rho + \frac{l(l+1)}{\rho}\right]v + 2(l+1-\rho)v' + \rho v''\right\} \end{aligned}$$

  We substitute then substitute u and u'' into the dimensionless radial eigenvalue equation. After some tedious but simple 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

$$\begin{aligned} v' &= \sum_{k=0}^{\infty} kc_k\rho^{k-1} \overset{k\to k+1}{=} \sum_{k=0}^{\infty}(k+1)c_{k+1}\rho^k \\ v'' &= \sum_{k=0} k(k+1)c_{k+1}\rho^{k-1} \end{aligned}$$

Note the shifting of the index, which is shown explicitly for the 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 un 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, their 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

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_{\mathrm{e}} e_0^2} = 0.053\,\mathrm{nm}$$

- 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

$$\frac{1}{2\pi}\oint p\, \mathrm{d}q = n\hbar, \qquad n \in \mathbb{Z}$$

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

$$n\hbar \equiv \frac{1}{2\pi}\oint (m_{\mathrm{e}} v)\, \mathrm{d}q = \frac{1}{2\pi} m_{\mathrm{e}} v (2\pi r) = m_{\mathrm{e}} r v = L_z$$

This produces the angular momentum quantization condition $L_z = n\hbar$.

Combining the quantization $n\hbar = L_z = m_{\mathrm{e}} r v$ with Newton's law

$$F = m_{\mathrm{e}} a = \frac{m_{\mathrm{e}} v^2}{r} = \frac{e_0^2}{4\pi\epsilon_0 r^2}$$

Reproduces the Bohr energy formula

$$E_n = -\frac{m_{\mathrm{e}}}{2\hbar^2}\left(\frac{e_0^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2} \equiv -\frac{\mathrm{Ry}}{n^2}, \quad n = 1, 2, 3, \ldots$$

- 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

$$\begin{aligned} \langle r \rangle &= \int_0^\infty r \psi_{n,n-1}^2(r) r^2 \, \mathrm{d}r = n \left(n + \frac{1}{2}\right) a_0 \\ \langle r^2 \rangle &= \cdots = n^2 (n+1) \left(n + \frac{1}{2}\right) a_0^2 \end{aligned}$$

  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

$$\boldsymbol{A} = \frac{1}{2}\left[\boldsymbol{p} \times \boldsymbol{L} + (\boldsymbol{p} \times \boldsymbol{L})^\dagger\right] - \frac{m_\mathrm{e} e_0^2}{4\pi\epsilon_0} \frac{\boldsymbol{r}}{r}$$

  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

$$\frac{1}{2}\left[\boldsymbol{p} \times \boldsymbol{L} + (\boldsymbol{p} \times \boldsymbol{L})^\dagger\right]$$

  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.