Baby Quantum Mechanics

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Contents

1 The Very Basics

1.1 The Schrödinger Equation

Our journey begins with the ubiquitous Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = \hat{\mathcal{H}}\left|\psi\right\rangle. \tag{1}$$

We've already acquiesced the existence of these seeming anomalies in the above equation as we coursed through the river of quantum mechanics. However, as beginners, we shall reclaim our attention to the two anomalies:

- The ket vector $|\psi\rangle$;
- The operator $\hat{\mathcal{H}}$.

1.2 Everything about Ket Vectors

1.2.1 Wavefunctions & States: Definition

The state of systems in quantum mechanics can be expressed as a ket vector $|\psi\rangle$ in the **Hilbert space** $\mathcal{H}$. There are different bases in the Hilbert space to describe the state vector. The following five sentences mean the same thing:

- The system has wavefunction ψ at time t;
- The wavefunction of the system is ψ at time t;
- The system has state ψ at time t;
- The system is in state ψ at time t;
- The state of the system is ψ at time t.

The algebra of ket vectors are analogous to the common vectors.

1.2.2 Bras

The bra space is a vector space **dual** to the ket space.

Dual Space

The dual space of V, denoted by V', is the vector space of all linear functionals on V:

$$V' = \mathcal{L}(V, \mathbb{F}). \tag{2}$$

There is a one-to-one correspondence between a ket space and a bra space:

$$a\,|\alpha\rangle + b\,|\beta\rangle \overset{\text{DC}}{\rightleftharpoons} a^*\,\langle\alpha| + b^*\,\langle\beta|\,, \tag{3}$$

where DC stands for **dual correspondence**.

1.2.3 Inner Product

We can now define the inner product of a bra and a ket. The product is written as a bra standing on the left $\langle u|$ and a ket standing on the right $|v\rangle$: $\langle u|v\rangle \in \mathbb{F}$

- Positivity:

$$\langle v|v\rangle \geq 0, \qquad \forall v \in V. \tag{4}$$

- Definiteness;

$$\langle v|v\rangle = 0 \quad \Leftrightarrow \quad v = 0. \tag{5}$$

- Additivity;

$$\langle u|v+w\rangle = \langle u|v\rangle + \langle u|w\rangle\,, \qquad \langle u+v|w\rangle = \langle u|w\rangle + \langle v|w\rangle\,. \tag{6}$$

- Homogeneity (only in the second slot);

$$\langle u|\lambda v\rangle = \lambda\,\langle u|v\rangle\,, \qquad \langle \lambda u|v\rangle = \lambda^*\,\langle u|v\rangle\,. \tag{7}$$

- Conjugate symmetry;

$$\langle v|u\rangle = \langle u|v\rangle^*\,. \tag{8}$$

Let us also meet the outer product $|\beta\rangle\langle\alpha|$, which should be understood as an operator of projection: $|\beta\rangle\langle\alpha|$ rotates $|\gamma\rangle$ into the direction of $|\beta\rangle$.

1.2.4 The Hilbert Space

The Hilbert space $\mathcal{H}$ is a complete inner product space (vector space + definition of inner product).

Vector Space (V)

A vector space on a set V along with an addition and a scalar multiplication on V such that the following properties hold:

- Commutativity;
- Associativity (addition and scalar multiplication);
- Identity (addition and scalar multiplication);
- Additive inverse (unique);
- Distributive properties.

Another property of the Hilbert space is that it is complete. By this "complete", we mean Cauchy complete.

Complete Vector Space

A **complete vector space** V is a normed linear space for which every Cauchy sequence of vectors in V has a limit vector in V. In other words, if

$$\{|a_i\rangle\}_{i=1}^{\infty}$$

is a Cauchy sequence, then there exists a vector $|\alpha\rangle \in V$ such that

$$\lim_{i\to\infty} \|a_i - \alpha\| = 0. \tag{9}$$

Actually, every Cauchy sequence in a finite-dimensional inner product space over $\mathbb{F}$ is convergent. In other words, every finite-dimensional complex (or real) inner product space is complete with respect to the norm induced by its inner product.

With the above investigations, we come to our final result:

All finite-dimensional real or complex inner product spaces are Hilbert spaces.

1.3 Operators

1.3.1 Definition

Operator

A linear map from a vector space to itself is called an operator. In other words, every $T \in \mathcal{L}(V)$ is an operator.

In quantum mechanics, every observable (dynamical variable) O corresponds to a **self-adjoint** (Hermitian) operator $\hat{O}$. The outcome of a measurement of the observable O is an eigenvalue of the corresponding operator $\hat{O}$. This is why operators are omnipresent in quantum mechanics.

An operator acts on a ket from the left and a bra from the right.

Eigenstates with Eigenkets and Eigenvalues

Like what we do in linear algebra, if an operator $\hat{A}$ satisfies the equation

$$\hat{A}\left|u\right\rangle = \lambda\left|u\right\rangle, \tag{10}$$

then we call λ the **eigenvalue** and $|u\rangle$ the **eigenket** of the operator $\hat{A}$ (which corresponds to the physical observable A). The physical state corresponding to an eigenket is an **eigenstate**.

1.3.2 Hermitian Adjoint

In general, $\hat{X}\left|\alpha\right\rangle$ is not dual to $\left\langle\alpha\right|\hat{X}$. We define

$$\hat{X}\left|\alpha\right\rangle \overset{\text{DC}}{\rightleftharpoons} \left\langle\alpha\right|\hat{X}^{\dagger} \quad \text{or} \quad \left\langle\beta\middle|\hat{X}\middle|\alpha\right\rangle = \left\langle\alpha\middle|\hat{X}^{\dagger}\middle|\beta\right\rangle^{*}, \tag{11}$$

where $\hat{X}^{\dagger}$ is called the **Hermitian adjoint** (adjoint) of $\hat{X}$. An operator $\hat{X}$ is said to be **Hermitian** if

$$\hat{X} = \hat{X}^{\dagger}. \tag{12}$$

If $\hat{X}$ is Hermitian, then we say

$$\left\langle\alpha\middle|\hat{X}\beta\right\rangle = \left\langle\hat{X}\alpha\middle|\beta\right\rangle. \tag{13}$$

Theorem

A Hermitian operator has **real eigenvalues** and **orthogonal eigenkets**.

Proof. Firstly, we assume that the operator $\hat{A}$ has eigenvalues and associated eigenkets:

$$\hat{A}\left|n\right\rangle = \lambda_n \left|n\right\rangle .$$

By the definition of Hermitian operators,

$$\left\langle n\middle|\hat{A}m\right\rangle = \left\langle \hat{A}n\middle|m\right\rangle .$$

Therefore,

$$(\lambda_m - \lambda_n^*)\left\langle n|m\right\rangle = 0.$$

- $n = m$: by the positive definiteness of inner product, λ must be real.
- $n \neq m$: $\langle n|m\rangle = 0$ shows orthogonality.

□

Theorem

For any self-adjoint operator $\hat{A}$, there is an orthonormal set of eigenfunctions $\{|n\rangle\}$

$$\hat{A}\left|n\right\rangle = \lambda_n \left|n\right\rangle \quad \text{where} \quad \left\langle n|m\right\rangle = \delta_{mn} \tag{14}$$

such that any arbitrary ket $|\alpha\rangle$ can be written as

$$\left|\alpha\right\rangle = \sum_n^N c_n \left|n\right\rangle , \tag{15}$$

with complex coefficients c_n.

By the completeness of the set of eigenkets (intrinsic to our initial construction of ket space), we can write

$$\left|\alpha\right\rangle = \sum_n^N c_n \left|n\right\rangle .$$

By the orthonormality of the eigenkets,

$$\langle m|\alpha\rangle = \sum_n^N c_n \langle m|n\rangle = c_m.$$

Therefore,

$$|\alpha\rangle = \sum_n |n\rangle \langle n|\alpha\rangle .$$

This leads us to the **completeness relation** (closure):

$$\mathbb{1} = \sum_n |n\rangle\langle n| . \tag{16}$$

For normalized $|\alpha\rangle$,

$$\langle\alpha|\alpha\rangle = \langle\alpha| \left(\sum_n |n\rangle\langle n|\right) |\alpha\rangle = \sum_n \|\langle n|\alpha\rangle\|^2 = \sum_n \|c_n\|^2 = 1. \tag{17}$$

We shall identify $|n\rangle\langle n|$ as the projection operator $\hat{\lambda}_n$:

$$\sum_n \hat{\lambda}_n = \mathbb{1}. \tag{18}$$

1.3.3 Linearity

We would only consider linear operators in this course; by this linearity, we mean

$$\begin{aligned} \hat{X}\left(a|\alpha\rangle + b|\beta\rangle\right) &= a\hat{X}|\alpha\rangle + b\hat{X}|\beta\rangle \\ \left(a\langle\alpha| + b\langle\beta|\right)\hat{X} &= a\langle\alpha|\hat{X} + b\langle\beta|\hat{X}. \end{aligned} \tag{19}$$

1.3.4 Operator Algebra

- Commutator:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}, \tag{20}$$

  The commutator is a measure of commutativity of two operators $\hat{A}$ and $\hat{B}$. If $\left[\hat{A}, \hat{B}\right] = 0$, then we say that operators $\hat{A}$ and $\hat{B}$ are compatible ($\hat{A}$ commutes with $\hat{B}$). The important thing about commutativity is that, if two observables commute, then they share simultaneous eigenkets and can be measured at the same time.

For any operators $\hat{A}$, $\hat{B}$, and $\hat{C}$,

$$\begin{aligned}\left[\hat{A},\hat{B}\hat{C}\right] &= \hat{B}\left[\hat{A},\hat{C}\right] + \left[\hat{A},\hat{B}\right]\hat{C} \\ \left[\hat{A}\hat{B},\hat{C}\right] &= \hat{A}\left[\hat{B},\hat{C}\right] + \left[\hat{A},\hat{C}\right]\hat{B}.\end{aligned} \tag{21}$$

The commutator is also linear in both slots (unlike inner product with antilinearity in left slot). The most important commutation relations we should pay attention to is:

$$\begin{aligned}[\hat{x}_i,\hat{p}_j] &= i\hbar\delta_{ij} \\ \left[\hat{L}_i,\hat{L}_j\right] &= i\hbar\epsilon_{ijk}\hat{L}_k \\ \left[\hat{S}_i,\hat{S}_j\right] &= i\hbar\epsilon_{ijk}\hat{S}_k.\end{aligned} \tag{22}$$

- Simultaneous eigenkets:

Theorem

If $\left[\hat{A},\hat{B}\right] = 0$, $\{|n\rangle\}$ are eigenkets of $\hat{A}$ with nondegenerate eigenvalues, then $\left\langle n\middle|\hat{B}\middle|m\right\rangle$ is diagonal.

Proof. The fact that $\left[\hat{A},\hat{B}\right] = 0$ implies

$$\left\langle i\middle|\left[\hat{A},\hat{B}\right]\middle|j\right\rangle = 0.$$

Therefore,

$$\begin{aligned}\left\langle i\middle|\left[\hat{A},\hat{B}\right]\middle|j\right\rangle &= \left\langle i\middle|\hat{A}\hat{B}-\hat{B}\hat{A}\middle|j\right\rangle \\ &= \left\langle i\middle|\hat{A}\hat{B}\middle|j\right\rangle - \left\langle i\middle|\hat{B}\hat{A}\middle|j\right\rangle \\ &= (\lambda_i-\lambda_j)\left\langle i\middle|\hat{B}\middle|j\right\rangle.\end{aligned}$$

With nondegenerate eigenvalues, $\left\langle i\middle|\hat{B}\middle|j\right\rangle$ must be diagonal.

□

- Anticommutator:

$$\left\{\hat{A},\hat{B}\right\} = \hat{A}\hat{B}+\hat{B}\hat{A}. \tag{23}$$

- Adjoint of two operators:

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger. \tag{24}$$

Proof.

$$\left\langle f \middle| (\hat{A}\hat{B})^\dagger g \right\rangle = \left\langle g \middle| (\hat{A}\hat{B}) f \right\rangle^* = \left\langle \hat{B} f \middle| \hat{A}^\dagger g \right\rangle = \left\langle \hat{A}^\dagger g \middle| \hat{B} f \right\rangle^* = \left\langle f \middle| \hat{B}^\dagger \hat{A}^\dagger g \right\rangle.$$

□

I have only one line of comment here: don't you love this proof....

1.4 Matrix Representations

To obtain the matrix representation of an operator $\hat{X}$, we can apply the completeness relation twice:

$$\hat{X} = \left(\sum_n |n\rangle\langle n| \right) \hat{X} \left(\sum_m |m\rangle\langle m| \right) = \sum_{n,m} |n\rangle \, \langle n|\hat{X}|m\rangle \, \langle m| \,. \tag{25}$$

If eigenkets are base kets, then the operator matrix is diagonal:

$$\hat{X} = \sum_{n,m} |n\rangle \, \langle n|\hat{X}|m\rangle \, \langle m| = \sum_{n,m} \lambda_m \delta_{mn} \, |n\rangle\langle m| = \sum_n \lambda_n \hat{\Lambda}_n. \tag{26}$$

The same thing can be done to a composition of operators, a bra relation, a ket relation, and even inner and outer products.

1.5 Measurements and Observables

Suppose we want to measure an observable A in the state $|\alpha\rangle$. We define the **expectation value** as

$$\langle A \rangle \equiv \langle \alpha | \hat{A} | \alpha \rangle \,. \tag{27}$$

To see it more clearly, let us use the completeness relations:

$$\langle A \rangle \equiv \langle \alpha | \hat{A} | \alpha \rangle = \sum_{n,m} \langle \alpha | n \rangle \, \langle n | \hat{A} | m \rangle \, \langle m | \alpha \rangle = \sum_n \lambda_n \| \langle n | \alpha \rangle \|^2.$$

This agrees with our classical expectations:

$$\langle A \rangle = \sum_n \lambda_n \| \langle n | \alpha \rangle \|^2, \tag{28}$$

where λ_n is the measured value, and $\|\langle n|\alpha\rangle\|^2$ is the corresponding **probability** of obtaining it.

1.6 Continuous Spectra

	Discrete	Continuous
Orthonormality	$\langle n\|m\rangle = \delta_{mn}$	$\langle \xi\|\xi'\rangle = \delta(\xi - \xi')$
Completeness	$\mathbb{1} = \sum_n \|n\rangle\langle n\|$	$\mathbb{1} = \int \mathrm{d}\xi \, \|\xi\rangle\langle\xi\|$
Normalization	$\sum_n \|\langle n\|\alpha\rangle\|^2 = 1$	$\int \mathrm{d}\xi \, \|\langle \xi\|\alpha\rangle\|^2 = 1$
Unique expansion	$\|\alpha\rangle = \sum_n \|n\rangle \langle n\|\alpha\rangle$	$\|\alpha\rangle = \int \mathrm{d}\xi \, \|\xi\rangle \langle\xi\|\alpha\rangle$
Inner product	$\langle\beta\|\alpha\rangle = \sum_n \langle\beta\|n\rangle \langle n\|\alpha\rangle$	$\langle\beta\|\alpha\rangle = \int \mathrm{d}\xi \, \langle\beta\|\xi\rangle \langle\xi\|\alpha\rangle$

1.7 Wavefunctions in Position and Momentum Space

In position basis, we shall write

$$\psi_\alpha(x) = \langle x|\alpha\rangle \,. \tag{29}$$

There's another interpretation of inner product, which is the probability amplitude for one state to be found in the other:

$$\langle\beta|\alpha\rangle = \int \mathrm{d}x \, \langle\beta|x\rangle \, \langle x|\alpha\rangle = \int \mathrm{d}x \, \psi^*_\beta(x)\psi_\alpha(x). \tag{30}$$

To expand $\left\langle \beta \middle| \hat{A} \middle| \alpha \right\rangle$, we need to employ the completeness relation twice:

$$\left\langle \beta \middle| \hat{A} \middle| \alpha \right\rangle = \int \mathrm{d}x \int \mathrm{d}x' \, \langle\beta|x\rangle \left\langle x \middle| \hat{A} \middle| x' \right\rangle \langle x'|\alpha\rangle \,. \tag{31}$$

If $\hat{A}$ is a function of position, this expression can be simplified:

$$\langle\beta|A(\hat{x})|\alpha\rangle = \int \mathrm{d}x \, \psi^*_\beta(x)A(x)\psi_\alpha(x). \tag{32}$$

The momentum operator in position basis needs some tedious derivation:

$$\hat{p} = \int \mathrm{d}x \, |x\rangle \left(-i\hbar \frac{\partial}{\partial x} \langle x| \right). \tag{33}$$

To work out the wavefunction in momentum basis ($\phi_\alpha(p) = \langle p|\alpha\rangle$), it is natural to think of a completeness relation. Nevertheless, we still have no information about the eigenkets of $\hat{x}$ and $\hat{p}$.

- Position eigenket:

  The equation

  $$\hat{x}\,|a\rangle = a\,|a\rangle \tag{34}$$

  is only satisfied if $|a\rangle = \delta(x-a)$.

- Momentum eigenket:

  The equation

  $$\langle x|\hat{p}|p\rangle = -i\hbar\frac{\partial}{\partial x}\langle x|p\rangle = p\,\langle x|p\rangle \tag{35}$$

  is a differential equation and has the solution

  $$\langle x|p\rangle = A\exp\left(\frac{ipx}{\hbar}\right). \tag{36}$$

However, we can see that these two eigenfunctions cannot be properly normalized. To solve this issue, we turn to the **delta-function normalization condition**. As an example, the orthonormality condition in position eigenfunctions is

$$\langle a|b\rangle = \delta(a-b). \tag{37}$$

To normalize $|p\rangle$, consider acting $\langle p'|$ on $|p\rangle$:

$$\langle p'|p\rangle = A^2\int \mathrm{d}x\exp\left[\frac{ix}{\hbar}(p'-p)\right] = 2\pi\hbar A^2\delta(p'-p).$$

Therefore, we know that

$$A = \frac{1}{\sqrt{2\pi\hbar}}. \tag{38}$$

Therefore,

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}\exp\left(\frac{ipx}{\hbar}\right). \tag{39}$$

So, the wavefunction in momentum basis is:

$$\langle p|\psi\rangle = \int \mathrm{d}x\,\langle p|x\rangle\,\langle x|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int \mathrm{d}x\exp\left(-\frac{ipx}{\hbar}\right)\psi(x), \tag{40}$$

redolent of the Fourier transforms. Similarly,

$$\langle x|\psi\rangle = \int \mathrm{d}p\, \langle x|p\rangle\, \langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int \mathrm{d}p \exp\left(\frac{ipx}{\hbar}\right)\psi(p). \tag{41}$$

1.8 Separable Solutions to Schrödinger Equation: Stationary States

As what we've learned in homogeneous partial differential equations, the first solutions to the Schrödinger equation that pop into our mind should be separable solutions:

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{x},t) = \hat{\mathcal{H}}\psi(\mathbf{x},t) \quad \Rightarrow \quad \psi(\mathbf{x},t) = X(\mathbf{x})T(t).$$

While we may not know the exact form of the Hamiltonian, but we can safely assume that it doesn't involve time. A little manipulation leads us to:

$$\frac{i\hbar}{T}\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{X}\hat{\mathcal{H}}X = \text{const.}$$

If we identify the RHS as the definition of the eigenfunction of $\hat{\mathcal{H}}$ (with energy eigenvalues E), then we are left with

$$T = A\exp\left(\frac{-iEt}{\hbar}\right). \tag{42}$$

The separable solutions of the Schrödinger equation implies that the states have time dependence of $\exp(-iEt/\hbar)$, where E is the energy eigenvalue of the Hamiltonian operator. In fact, these separable solutions have far more implications than we may have expected. They are referred to as "stationary states". To appreciate this, let us consider, generally, the time dependence of an expectation value:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle &= \frac{\mathrm{d}}{\mathrm{d}t}\left\langle\psi\middle|\hat{A}\middle|\psi\right\rangle \\
&= \left\langle\frac{\hat{\mathcal{H}}\psi}{i\hbar}\middle|\hat{A}\middle|\psi\right\rangle + \left\langle\psi\middle|\hat{A}\middle|\frac{\hat{\mathcal{H}}\psi}{i\hbar}\right\rangle \\
&= \frac{i}{\hbar}\left(\left\langle\hat{\mathcal{H}}\psi\middle|\hat{A}\middle|\psi\right\rangle - \left\langle\psi\middle|\hat{A}\middle|\hat{\mathcal{H}}\psi\right\rangle\right) \\
&= \frac{i}{\hbar}\left\langle\left[\hat{\mathcal{H}},\hat{A}\right]\right\rangle.
\end{aligned}$$

Note that in the above derivation, we are complicit in using the Schrödinger picture, where only state vectors evolve in time.

This expression is completely general:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A\rangle = \frac{i}{\hbar}\left\langle\left[\hat{\mathcal{H}},\hat{A}\right]\right\rangle. \tag{43}$$

The above equation leads us the way to the famous **Ehrenfest's theorem**: the equations of motion for the expectation values of observables are the same as the equations of motion for their classical counterparts.

Now let's consider the separable solutions. From the time dependence and the antilinearity of the braket notation, we shall see that the expectation values of observables in a stationary state is really "stationary"; this is where it got its name.

Theorem

If one knows a basis of energy eigenstates and one knows the initial quantum state, then one knows what the quantum state is for all time. In other words, one has solved the Schrödinger equation.

Proof. We know the initial state and can expand it in terms of energy eigenstates:

$$|\psi\rangle = \int \mathrm{d}E\, |E\rangle \langle E|\psi\rangle\,. \tag{44}$$

As we know the way each energy eigenstate depends on time, we shall write:

$$|\psi\rangle_t = \int \mathrm{d}E\, |E\rangle \langle E|\psi\rangle \exp\left(-\frac{iEt}{\hbar}\right). \tag{45}$$

□

This theorem manifests the importance of stationary states (and also separable solutions) in quantum mechanics.

Note that the summation of two stationary states is no longer stationary.

1.9 Uncertainty Principle & Other Quantum Effects

We shall define the variance as

$$\sigma^2(\hat{A}) = \left\langle \left(\hat{A} - \langle A \rangle\right)^2 \right\rangle. \tag{46}$$

This leads us to the **Heisenberg uncertainty principle**:

$$\sigma_x \sigma_p \geq \frac{1}{2}\hbar. \tag{47}$$

Other quantum effects include superposition, interference, nonlocality, entanglement, and the collapse of wavefunctions:

- Interference:

  The interference is responsible for the remarkable results of the double slit experiment.

- Nonlocality:

  "Quantum mechanics predicts that if Andreas finds the particle in A, then Bai does not find the particle in B." This provably cannot have a locally caisal explanation.

- Collapse of wavefunctions:

  As an example, if the particle is found between $x = a$ and $x = b$ (and no more accurate value is measured), then immediately the wavefunction for the particle collapses to reflect the measurement outcome:

$$\psi(x) \quad \Rightarrow \quad \tilde{\psi}(x) = \begin{cases} N\psi(x), & \text{if } a \leq x \leq b \\ 0, & \text{otherwise.} \end{cases} \tag{48}$$

  In a discrete case, if we measure the value r,

$$\psi(x) = \sum_n \langle x|n\rangle \langle n|\psi\rangle \quad \Rightarrow \quad \tilde{\psi}(x) = N \sum_{\lambda_n = r} \langle x|n\rangle \langle n|\psi\rangle, \tag{49}$$

  where N is the normalization factor.

  The principle is: immediately after the measurement, if the same observable is measured again, then the same outcome must occur with certainty.

2 The Harmonic Oscillator

2.1 Introduction

The potential of the harmonic oscillator is proportional to x^2:

$$V(x) = \frac{1}{2}m\omega^2 x^2. \tag{50}$$

This scenario of harmonic oscillators is actually more prevalent than one would have expected. In fact, for any system with potential minimum at $x = x_0$, the potential, by Taylor expansion, has the form

$$V(\hat{x}_0 + \delta x) = V(x_0) + \frac{1}{2}\left.\frac{\mathrm{d}^2 V}{\mathrm{d}x^2}\right|_{x_0} (\delta x)^2 + \dots, \tag{51}$$

as the potential minimum suggests $\left.\mathrm{d}V/\mathrm{d}x\right|_{x_0} = 0$ (force $= 0$).

2.2 Energy Eigenstates & Eigenvalues

As before, we seek for separable solutions to the Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2\right) u(x) = Eu(x), \qquad u(x \to \pm\infty) \to 0, \tag{52}$$

where $u(x)$ is an energy eigenstate.

Considering the variable substitution $\xi = x\sqrt{\dfrac{m\omega}{\hbar}}$ and $k = \dfrac{2E}{\hbar\omega}$, we see

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\xi^2} + (k - \xi^2)u = 0. \tag{53}$$

After the atrocity of the differential equations course, one would think of series solutions, where we shall identify $x = 0$ as an ordinary point. This leads us to

$$y = \sum_{n=0} c_n x^n \quad \Rightarrow \quad c_{n+2} = \frac{c_{n-2} - kc_n}{(n+1)(n+2)}. \tag{54}$$

As not all the terms begin at $n = 0$, we can find

$$c_2 = -\frac{k}{2}c_0, \qquad c_3 = -\frac{k}{6}c_1. \tag{55}$$

This seems to solve the original ODE, but the problem is that the powers of x extends to infinity: it's

hard to satisfy the BC's and check the convergence.

In order to solve this equation, some ingenious people began by first finding the asymptotic solutions at infinity and then applying the variation of parameters method.

- Asymptotic solutions:

  As we can expect, when $\xi \to \infty$, $(u - \xi^2)$ approximates to $(-\xi^2)$. Therefore, the asymptotic equation reads

  $$\frac{\mathrm{d}^2 u}{\mathrm{d}\xi^2} = \xi^2 u. \tag{56}$$

  Again, the series solutions yield some complicated formulas that turns out to be unfathomable to physicists. The "correct" way to do this is by noting that

  $$u = \exp\left(-\frac{\xi^2}{2}\right) \quad \Rightarrow \quad u'' = (\xi^2 - 1)u \approx \xi^2 u, \quad \xi \to \infty. \tag{57}$$

  Therefore, we say the solution is $u = \exp\left(-\frac{\xi^2}{2}\right)$. Also, don't you dare to ask about the second linearly independent solution.

- Variation of parameters:

  Given the asymptotic solution, we can attempt the full solution through variation of parameters:

  $$u = f(\xi)\exp\left(-\frac{\xi^2}{2}\right). \tag{58}$$

  Plugging this into the original equation, we get the **Hermite differential equation**:

  $$\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}f}{\mathrm{d}\xi} + (k-1)f = 0. \tag{59}$$

  Finally, we're comfortable to use the series solution. A little manipulation gives

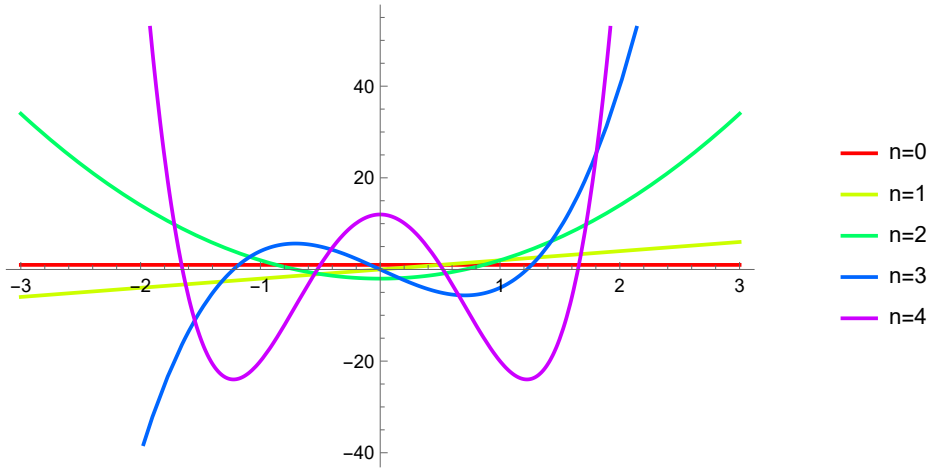
  $$c_{n+2} = \frac{2n+1-k}{(n+2)(n+1)}c_n. \tag{60}$$

  Clearly, the polynomial ends when

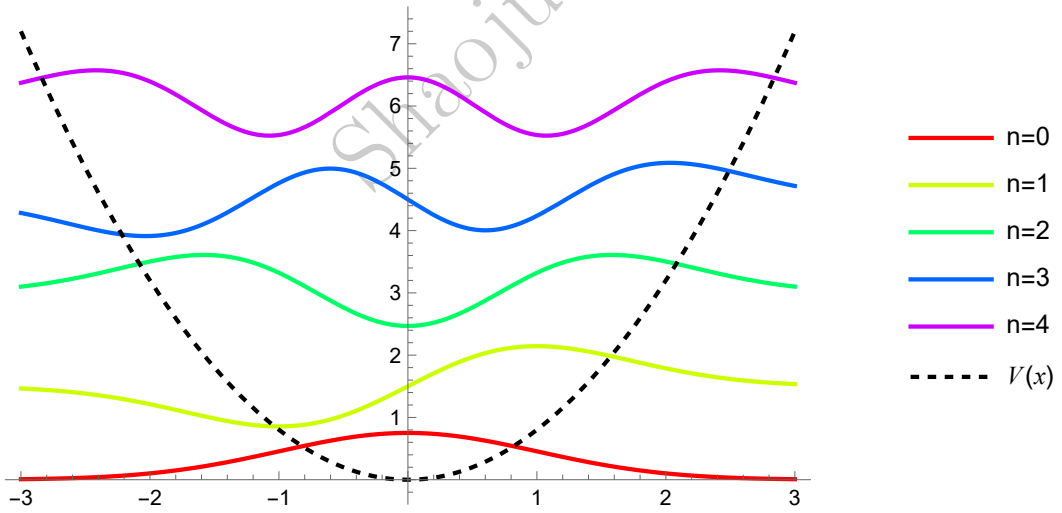
  $$k = 2n + 1, \tag{61}$$

  which is also an indication of convergence.

By collecting the truncated terms we get the Hermite polynomials:



After multiplying by $\exp\left(-\frac{\xi^2}{2}\right)$ and a normalization constant, we get the energy eigenstates:



To get the energy eigenvalues, just simply look at k:

$$\frac{2E}{\hbar\omega} = k = 2n + 1 \quad \Rightarrow \quad E_n = \frac{1}{2}\hbar\omega\left(n + \frac{1}{2}\right). \tag{62}$$

2.3 Raising and Lowering Operators

By defining

$$\begin{aligned} a &= \frac{1}{\sqrt{2m\hbar\omega}}\left(m\omega\hat{x} + i\hat{p}\right) \\ a^\dagger &= \frac{1}{\sqrt{2m\hbar\omega}}\left(m\omega\hat{x} - i\hat{p}\right) \end{aligned} \tag{63}$$

we can see

$$\hat{\mathcal{H}} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right). \tag{64}$$

This leads us further to the definition of the operator

$$\mathcal{N} = a^\dagger a. \tag{65}$$

Clearly, the eigenfunctions of $\hat{\mathcal{H}}$ are the eigenfunctions of $\mathcal{N}$, and the eigenvalues of $\hat{\mathcal{H}}$ are $\hbar\omega(\nu + 1/2)$ for each eigenvalue ν of $\mathcal{N}$.

In addition, we should meet the commutation relations:

$$\begin{aligned} \left[a, a^\dagger\right] &= \mathbb{1} \\ \left[\mathcal{N}, a\right] &= -a \\ \left[\mathcal{N}, a^\dagger\right] &= a^\dagger. \end{aligned} \tag{66}$$

Lemma

If f is an eigenfunction of $\mathcal{N}$ with eigenvalue ν, then:

- af is an eigenfunction of $\mathcal{N}$ with eigenvalue $\nu - 1$ (annihilation / lowering operator);
- $a^\dagger f$ is an eigenfunction of $\mathcal{N}$ with eigenvalue $\nu + 1$ (creation / raising operator).

The proofs are easy with the aid of the commutation relations above.

We shall reclaim the fact that ν is an integer. Firstly we see that ν is actually n that arises in series solution, so it should be an integer. Another way to appreciate this fact is that if ν is not an integer, then we can keep lowering the eigenvalue by 1 without end. Eventually, we will reach negative eigenvalues, which is not physical.

Therefore, ν must be non-negative integers and the process of lowering must come to an end when the eigenvalue reaches $\nu = 0$.

Let us denote the $\nu = 0$ state as $u_0(x)$ and call it the **ground state**. This means we have

$$\mathcal{N} u_0 = 0, \quad \Rightarrow \quad a u_0 = 0. \tag{67}$$

The above implies that we can get the ground state through solving a much simpler differential equation:

$$a u_0 = \left(m\omega x + \hbar \frac{\mathrm{d}}{\mathrm{d}x} \right) u_0(x) = 0. \tag{68}$$

The solution, after a normal normalization, is

$$u_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar} x^2 \right). \tag{69}$$

To get the other states, just act $a^\dagger$ on the $u_0(x)$. We call the these states with higher energies the **excited states**. They are related to u_0 by

$$u_n(x) \propto \left(a^\dagger \right)^n u_0(x) \tag{70}$$

up to a constant. To find this constant, note that

$$\begin{aligned} \left(\langle n | \, a^\dagger \right) a \, |n\rangle &= \langle n | \mathcal{N} | n \rangle = n \\ \left(\langle n | \, a \right) a^\dagger \, |n\rangle &= \langle n | \left[a, a^\dagger \right] + \mathcal{N} \big| n \rangle = n + 1. \end{aligned}$$

Therefore,

$$\begin{aligned} a \, |n\rangle &= \sqrt{n} \, |n-1\rangle \\ a^\dagger &= \sqrt{n+1} \, |n+1\rangle \, . \end{aligned} \tag{71}$$

3 Angular Momentum & Spin

3.1 Introduction to Angular Momentum

The definition of angular momentum in quantum mechanics follows the legacy of classical mechanics:

$$\hat{\mathbf{L}} = \hat{\mathbf{x}} \times \hat{\mathbf{p}}, \qquad \hat{L}_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k. \tag{72}$$

The commutation relation here is

$$\begin{aligned} \left[\hat{L}_i, \hat{L}_j\right] &= i\hbar\epsilon_{ijk}\hat{L}_k \\ \left[\hat{L}^2, \hat{L}_i\right] &= 0. \end{aligned} \tag{73}$$

Central Potential

Remarkably, if we have a central potential $V(r)$, then the Hamiltonian commutes with $\hat{L}_i$:

$$\left[\hat{\mathcal{H}}, \hat{L}_i\right] = \frac{1}{2m}\left[\hat{\mathbf{p}}^2, \hat{L}_i\right] + \left[\hat{\mathbf{x}}^2, \hat{L}_i\right] = 0.$$

Since each component of angular momentum commutes with $\hat{\mathcal{H}}$, $\hat{L}^2$ also commutes with $\hat{\mathcal{H}}$.

Note that there is **no transitivity** in the commutation relations.

3.2 Complete Sets of Compatible Observables

Before delving into the vertiginous derivation, we should meet an important theorem.

Theorem

For any quantum system, there is a complete set of compatible observables. Compatible means the operators all mutually commute, and complete means that the basis of eigenstates is non-degenerate: the basis states differ in the eigenvalue of at least one of the operators.

- For a 1D harmonic oscillator, $\hat{\mathcal{H}}$ by itself is a complete set.
- For a 2D harmonic oscillator, $\hat{\mathcal{H}}$ and $\hat{L}_3$ form a complete set.
- For a 3D particle in central potential, the corresponding complete set is $\left\{\hat{\mathcal{H}}, \hat{L}^2, \hat{L}_3\right\}$.

Later we shall see the spin degree of freedom; as a separate property of particles with no classical counterpart, it adds to each set of compatible operators.

3.3 Abstract Angular Momentum Algebra

Unfathomably, we can derive numerous properties of the angular momentum through the commutation relations alone. The algebra of spin is analogous to that of angular momentum, which made this even more remarkable. Let us begin with three self-adjoint operators J_i:

$$[J_l, J_m] = i\hbar\epsilon_{lmn}J_n. \tag{74}$$

We can also see

$$\left[J^2, J_l\right] = 0, \tag{75}$$

as this is derived through the commutation relations alone. Now, we define the ladder operators:

$$J_\pm = J_1 \pm iJ_2. \tag{76}$$

The commutation relations with these two new operators are as follows:

$$\begin{aligned} \left[J^2, J_\pm\right] &= 0 \\ [J_3, J_\pm] &= \pm\hbar J_\pm. \end{aligned} \tag{77}$$

We should also notice that

$$\begin{aligned} J^2 &= J_+J_- + J_3^2 - \hbar J_3 \\ J^2 &= J_-J_+ + J_3^2 + \hbar J_3. \end{aligned} \tag{78}$$

Now let's observe magic. Firstly, J^2 and J_3 share simultaneous eigenstates, which we denote as $|\alpha\beta\rangle$:

$$J^2 |\alpha\beta\rangle = \alpha |\alpha\beta\rangle, \qquad J_3 |\alpha\beta\rangle = \beta |\alpha\beta\rangle. \tag{79}$$

Lemma

- If $J_\pm |\alpha\beta\rangle$ is nonzero, then it is an eigenstate of J_3 with eigenvalue $(\beta \pm \hbar)$;
- If $J_\pm |\alpha\beta\rangle$ is nonzero, then it is an eigenstate of J^2 with (unchanged) eigenvalue α.

Proof.

$$J_3 (J_\pm |\alpha\beta\rangle) = ([J_3, J_\pm] + J_\pm J_3) |\alpha\beta\rangle = (\beta \pm \hbar) J_\pm |\alpha\beta\rangle,$$

$$J^2 (J_\pm |\alpha\beta\rangle) = \left(\left[J^2, J_\pm\right] + J_\pm J^2\right) |\alpha\beta\rangle = \alpha J_\pm |\alpha\beta\rangle.$$

□

Lemma

If simultaneous eigenstate $|\alpha\beta\rangle$ has J^2 eigenvalue α and J_3 eigenvalue β, then

$$\beta^2 \leq \alpha. \tag{80}$$

Proof. By self-adjointness of J_l,

$$\langle\psi|J_l^2\psi\rangle = \langle J_l\psi|J_l\psi\rangle \geq 0.$$

Then,

$$\langle\psi|(J^2 - J_3^2)\psi\rangle = \langle\psi|J_1^2\psi\rangle + \langle\psi|J_2^2\psi\rangle \geq 0.$$

If we set $|\psi\rangle = |\alpha\beta\rangle$, then we get

$$\langle\psi|J^2\psi\rangle \geq \langle\psi|J_3^2\psi\rangle \quad \Rightarrow \quad \alpha \geq \beta^2.$$

□

This indicates that β cannot be increasing or decreasing without end. Therefore, we can see $\beta_{\max}$ and $\beta_{\min}$ where

$$\begin{aligned} J_+ |\alpha\beta_{\max}\rangle &= 0 \\ J_- |\alpha\beta_{\min}\rangle &= 0. \end{aligned} \tag{81}$$

Also, these values are separated by an integer multiple of $\hbar$:

$$\beta_{\max} - \beta_{\min} = 2j\hbar, \qquad 2j \in \mathbb{N}. \tag{82}$$

We can even work out the values of α and β:

$$\begin{aligned} J_- \left(J_+ |\alpha\beta_{\max}\rangle\right) &= \left(J^2 - J_3^2 - \hbar J_3\right) |\alpha\beta_{\max}\rangle \\ &= \left(\alpha - \beta_{\max}^2 - \hbar\beta_{\max}\right) |\alpha\beta_{\max}\rangle \\ &= 0. \end{aligned} \tag{83}$$

Similarly,

$$\begin{aligned} J_+ \left(J_- |\alpha\beta_{\min}\rangle\right) &= \left(J^2 - J_3^2 + \hbar J_3\right) |\alpha\beta_{\min}\rangle \\ &= \left(\alpha - \beta_{\min}^2 + \hbar\beta_{\min}\right) |\alpha\beta_{\min}\rangle \\ &= 0. \end{aligned} \tag{84}$$

Combining these two equations, we get

$$(\beta_{\max} + \beta_{\min})(\beta_{\max} - \beta_{\min} + \hbar) = 0. \tag{85}$$

As we require $\beta_{\max} > \beta_{\min}$, we get

$$\beta_{\max} + \beta_{\min} = 0. \tag{86}$$

Therefore, we finally get

$$\beta_{\max} = j\hbar, \qquad \alpha = j(j+1)\hbar^2, \tag{87}$$

where j is a half integer.

3.4 Energy Eigenstates of 3D Particles in a Central Potential

The energy eigenstate satisfies

$$-\frac{\hbar^2}{2m}\nabla^2 u + V(r)u = Eu. \tag{88}$$

Let us begin by seeking separable solutions. In spherical coordinates,

$$\nabla^2 \equiv \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}. \tag{89}$$

Plugging the trial solution $u(r,\theta,\phi) = R(r)T(\theta)F(\phi)$ while multiplying r^2/u, we get

$$\frac{1}{R}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R}{\mathrm{d}r}\right) + \frac{1}{T}\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}T}{\mathrm{d}\theta}\right) + \frac{1}{F\sin^2\theta}\frac{\mathrm{d}^2F}{\mathrm{d}\phi^2} = -\frac{2m(E-V)}{\hbar^2}r^2.$$

3.4.1 Spherical Harmonics

This indicates two separation constants. If we claim

$$\frac{1}{F}\frac{\mathrm{d}^2F}{\mathrm{d}\phi^2} = -m^2 \tag{90}$$

and change $x = \cos\theta$, we get the **associated Legendre's equation**:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[(1-x^2)\frac{\mathrm{d}T}{\mathrm{d}x}\right] + \left[l(l+1) - \frac{m^2}{1-x^2}\right]T = 0, \tag{91}$$

where $k = l(l+1)$ comes from the separation in r and the eigenvalue of standard Legendre's equation.

We've already known the standard Legendre's equation, where $m = 0$. Actually, the associated Legendre

polynomials relate to the Legendre polynomials by

$$P_{lm}(x) \equiv (1-x^2)^{m/2} P_l^{(m)}(x), \qquad m < l. \tag{92}$$

To check the above, simply differentiate Legendre's equation by m times and plug in the expression.

The azimuthal angle has $r = \pm m$ as roots of the characteristic equation. By identifying that m can be any real number, the general solution is

$$F(\phi) = \mathrm{e}^{im\phi} \tag{93}$$

up to an arbitrary constant.

As m is involved in both angular solutions, we shall denote the total angular solutions as Y_{lm} and call them as **spherical harmonics**:

$$Y_{lm}(\theta, \phi) = N_{lm} P_{lm}(\cos\theta) \mathrm{e}^{im\phi}, \tag{94}$$

where N_{lm} is the normalization constant, and

$$P_{lm}(\cos\theta) = (\sin\theta)^{|m|} \left[\frac{\mathrm{d}}{\mathrm{d}(\cos\theta)}\right]^{|m|} P_l(\cos\theta). \tag{95}$$

The functions Y_{lm} form a complete orthonormal basis:

$$\int \mathrm{d}\phi \int \sin\theta \, \mathrm{d}\theta \, Y_{lm}^* Y_{l'm'} = \delta_{ll'}\delta_{mm'}. \tag{96}$$

The final steps are to reclaim l and m as something we are familiar with. The spherical polar coordinates are defined as

$$\begin{aligned} r &= \sqrt{x_i x_i} \\ \theta &= \sin^{-1}\left(\frac{\sqrt{x_1^2 + x_2^2}}{r}\right) \\ \phi &= \tan^{-1}\frac{x_2}{x_1} \end{aligned} \tag{97}$$

Although tedious, it is still possible to show that

$$\begin{aligned} \hat{L}_1 &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right) \\ \hat{L}_2 &= i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right) \\ \hat{L}_3 &= -i\hbar\frac{\partial}{\partial\phi}. \end{aligned} \tag{98}$$

Also, the $\hat{L}^2$ operator:

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]. \tag{99}$$

Guess what? While $\hat{L}_3$ is so conspicuous in terms of its eigenvalues, $\hat{L}^2$ also happens to coincide with the angular parts of the Laplacian.

More explicitly,

$$\nabla^2 = D_r - \frac{1}{r^2\hbar^2}\hat{L}^2. \tag{100}$$

Back to the time when we separate the constants, we used

$$\begin{aligned} \nabla^2 u &= D_r u - \frac{1}{r^2\hbar^2}\hat{L}^2 u \\ &= TF \cdot D_r R - \frac{R}{r^2\hbar^2}\hat{L}^2(TF) \\ \Rightarrow \frac{r^2}{u}\nabla^2 u &= \frac{r^2}{R} D_r R - \frac{1}{TF\cdot\hbar^2}\hat{L}^2(TF). \end{aligned}$$

With the constant of separation $k = l(l+1)$ and identifying $TF = Y_{lm}$, we get

$$\frac{r^2}{R} D_r R = l(l+1) = \frac{1}{\hbar^2 Y_{lm}}\hat{L}^2 Y_{lm} \quad \Rightarrow \quad \hat{L}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}. \tag{101}$$

Also, as Y_{lm} has $\mathrm{e}^{im\phi}$ azimuthal dependence, we get

$$\hat{L}_3 Y_{lm} = m\hbar Y_{lm}. \tag{102}$$

Like what we did in statistical physics, the choice of separation constants (or constants of Lagrange multipliers) seems arbitrary, but later we shall find out their profound implications.

3.4.2 Radial Solutions

From the above discussion, our solution has the form

$$u = R(r) Y_{lm}(\theta, \phi). \tag{103}$$

Therefore,

$$-\frac{\hbar^2}{2m}\left(D_r - \frac{1}{r^2\hbar^2}\hat{L}^2 \right) u + V(r) u = E u.$$

With the angular operator $\hat{L}^2$ spitting out a value of $\hbar^2 l(l+1)$, we are left with

$$-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}R}{\mathrm{d}r} \right) + \left[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] R = ER. \tag{104}$$

The evil substitution $\chi(r) = rR(r)$ brings us to

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2} + \left[\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right]\chi = E\chi. \tag{105}$$

The above just looks like a 1D energy eigenstate equation with an **effective potential**:

$$\tilde{V}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}, \tag{106}$$

where the second term is referred to as the angular momentum barrier. For a bound system, we know the energy eigenvalues are discrete, labeled by E_n. However, the eigenfunction is also influenced by the parameter l, and this leads us to

$$u_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi). \tag{107}$$

3.5 Spin

Most of the contents in angular momentum applies to the spin ($\hat{\mathbf{S}}$). However, spin is another degree of freedom that doesn't have a classical counterpart. This means

- $\hat{\mathbf{S}}$ commutes with all $\hat{x}_i$ and p_i. This means that it also commutes with $\hat{\mathcal{H}}(\hat{x}_i, \hat{p}_j)$ and $\hat{L}_i$. We say that spin operators act on spin space.
- $\hat{\mathbf{S}}$ cannot be built from $\hat{x}_i$ and p_i.

We shall, in particular, explore spin 1/2 particles, like electrons and protons. By this, we mean

$$\hat{S}^2 |\psi\rangle = \hbar^2 \frac{1}{2}\left(\frac{1}{2} + 1\right)|\psi\rangle = \frac{3\hbar^2}{4}|\psi\rangle, \tag{108}$$

and the possible eigenvalues of $\hat{S}_3$ are $\pm\hbar/2$.

In spin 1/2 space, spin operators are 2×2 matrices that act on 2×1 column vectors. The adjoint of the operator is just the Hermitian conjugate of the matrix.

Therefore, in this world of spin, the three spin operators are three 2×2 Hermitian matrices that satisfy

$$\left[\hat{S}_i, \hat{S}_j\right] = i\hbar\epsilon_{ijk}\hat{S}_k. \tag{109}$$

Let's begin by choosing the eigenvectors of $\hat{S}_3$ as $|\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ and $|\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix}$:

$$\hat{S}_3\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{2}\hbar\begin{pmatrix}1\\0\end{pmatrix}, \qquad \hat{S}_3\begin{pmatrix}0\\1\end{pmatrix} = -\frac{1}{2}\hbar\begin{pmatrix}0\\1\end{pmatrix}. \tag{110}$$

The above equations imply that

$$\hat{S}_3 = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{111}$$

The other two matrices that satisfy the commutation relations with $\hat{S}_3$ are

$$\hat{S}_1 = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \hat{S}_2 = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{112}$$

To see them, think of the raising and lowering operators. One thing to notice is that the raising operator acts on the $|\downarrow\rangle$ state and generates $\hbar\,|\uparrow\rangle$ instead of $(\hbar/2)\,|\uparrow\rangle$.

It's convenient to define the **Pauli matrices** (σ_i) by dropping the $\hbar/2$ term:

$$[\sigma_i, \sigma_j] = 2i\sigma_k, \qquad \sigma_i^2 = \mathbb{1}. \tag{113}$$

We cannot prove the above formula by cyclic permutation, because the Pauli matrices show no obvious cyclic symmetry.

Also, as expected, the raising and lowering operators are $\hat{S}_\pm = \hat{S}_1 \pm i\hat{S}_2$, where $\hat{S}_+$ kills the top state and $\hat{S}_-$ kills the bottom state.

3.6 Spin in Magnetic Fields

Analogous to the energy of a magnetic dipole in magnetic fields, we define the quantum Hamiltonian for an electron with spin in a magnetic field:

$$\hat{\mathcal{H}}_s = g_e \frac{\mu_B}{\hbar} \hat{\mathbf{S}} \cdot \mathbf{B}, \tag{114}$$

where $g_e \approx 2$ and μ_B is the Bohr magneton,

$$\mu_B = \frac{e\hbar}{2m_e}. \tag{115}$$

Therefore, by defining the spin magnetic dipole moment,

$$\hat{\underline{\mu}}_s = -g_e \frac{\mu_B}{\hbar} \hat{\mathbf{S}} \quad \Rightarrow \quad \hat{\mathcal{H}}_s = -\hat{\underline{\mu}}_s \cdot \mathbf{B}. \tag{116}$$

If we define a 3-vector of matrices $\underline{\sigma}$, a little manipulation gives

$$\hat{\mathcal{H}}_s \approx \mu_B \underline{\sigma} \cdot \mathbf{B}. \tag{117}$$

In a uniform magnetic field $\mathbf{B} = B\hat{\mathbf{e}}_3$, we can show

$$\begin{aligned} \hat{\mathcal{H}}_s \left|\uparrow\right\rangle &= \mu_B B \left|\uparrow\right\rangle \\ \hat{\mathcal{H}}_s \left|\downarrow\right\rangle &= -\mu_B B \left|\downarrow\right\rangle . \end{aligned} \tag{118}$$

3.7 Larmor Precession

Let us consider a product state

$$\left|\Psi\right\rangle = \psi_t(x) \left|\chi(t)\right\rangle = \psi_t(x) \left[\chi_1(t) \left|\uparrow\right\rangle + \chi_2(t) \left|\downarrow\right\rangle\right]. \tag{119}$$

The normalization condition in spin space reads

$$\left|\chi_1(t)\right|^2 + \left|\chi_2(t)\right|^2 = 1. \tag{120}$$

Also, as we know

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \left|\chi(t)\right\rangle = \hat{\mathcal{H}}_s \left|\chi(t)\right\rangle , \tag{121}$$

if the initial state is $\left|\chi(0)\right\rangle = \chi_1 \left|\uparrow\right\rangle + \chi_2 \left|\downarrow\right\rangle$, then we know

$$\left|\chi(t)\right\rangle = \chi_1 \left|\uparrow\right\rangle \exp\left(-i\frac{\mu_B B}{\hbar} t\right) + \chi_2 \left|\downarrow\right\rangle \exp\left(i\frac{\mu_B B}{\hbar} t\right). \tag{122}$$

Therefore,

$$\left\langle \mathbf{S} \right\rangle = \left(\left\langle S_1 \right\rangle, \left\langle S_2 \right\rangle, \left\langle S_3 \right\rangle\right) = \hbar \left[\chi_1 \chi_2 \cos\left(\frac{2\mu_B B t}{\hbar}\right), \chi_1 \chi_2 \sin\left(\frac{2\mu_B B t}{\hbar}\right), 2\left(\left|\chi_1\right|^2 + \left|\chi_2\right|^2\right)\right]. \tag{123}$$

This vector of expectation values precesses around the magnetic field direction with an angular frequency $\dfrac{2\mu_B B}{\hbar} = \dfrac{eB}{m_e}$. This is called "Larmor precession".

4 Time Independent Perturbation Theory

The Hamiltonian of interest is $\hat{\mathcal{H}}'$:

$$\hat{\mathcal{H}}' = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1, \tag{124}$$

where the normalized eigenstates and eigenvalues of $\hat{\mathcal{H}}_0$ are known. The perturbation $\hat{\mathcal{H}}_1$ is small:

$$\hat{\mathcal{H}}_1 = \epsilon \hat{K} \tag{125}$$

for some small real number $\epsilon > 0$ and self-adjoint operator $\hat{K}$.

4.1 Non-degenerate Case

Given

$$\hat{\mathcal{H}}_0 |n\rangle = E_n |n\rangle , \tag{126}$$

we want to solve

$$\hat{\mathcal{H}}' |n'\rangle = E'_n |n'\rangle . \tag{127}$$

By Taylor expansion, we see

$$\begin{aligned} |n'\rangle &= |n\rangle + |\delta n\rangle + \mathcal{O}(\epsilon^2) \\ E'_n &= E_n + \delta E_n + \mathcal{O}(\epsilon^2). \end{aligned} \tag{128}$$

Plugging the above equations back to the Hamiltonian of interest,

$$\left(\hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1\right) \left[|n\rangle + |\delta n\rangle + \mathcal{O}(\epsilon^2)\right] = \left[E_n + \delta E_n + \mathcal{O}(\epsilon^2)\right] \left[|n\rangle + |\delta n\rangle + \mathcal{O}(\epsilon^2)\right] .$$

Therefore,

$$\begin{cases} \text{Zeroth order:} & \hat{\mathcal{H}}_0 |n\rangle = E_n |n\rangle \\ \text{First Order:} & \hat{\mathcal{H}}_1 |n\rangle + \hat{\mathcal{H}}_0 |\delta n\rangle = E_n |\delta n\rangle + \delta E_n |n\rangle . \end{cases} \tag{129}$$

In order to find δE_n and $|\delta n\rangle$, assume

$$|n\rangle + |\delta n\rangle = \sum_k a_{nk} |k\rangle . \tag{130}$$

If we choose $a_{nn} = 1$, then we are left with

$$|\delta n\rangle = \sum_{k \neq n} a_{nk} |k\rangle . \tag{131}$$

- Finding δE_n: left multiply $\langle n|$

$$\langle n|\hat{\mathcal{H}}_1|n\rangle + \langle n|\hat{\mathcal{H}}_0|\delta n\rangle = \langle n|E_n|\delta n\rangle + \langle n|\delta E_n|n\rangle$$
$$\langle n|\hat{\mathcal{H}}_1|n\rangle + \langle n|\,\hat{\mathcal{H}}_0\left(\sum_{k\neq n} a_{nk}\,|k\rangle\right) = \langle n|\,E_n\left(\sum_{k\neq n} a_{nk}\,|k\rangle\right) + \langle n|\delta E_n|n\rangle\,.$$

By the orthonormality of the energy eigenstates, we get

$$\delta E_n = \langle n|\hat{\mathcal{H}}_1|n\rangle\,. \tag{132}$$

- Finding $|\delta n\rangle$: left multiply $\langle l|$, $l \neq n$

$$\langle l|\hat{\mathcal{H}}_1|n\rangle + \langle l|\hat{\mathcal{H}}_0|\delta n\rangle = \langle l|E_n|\delta n\rangle + \langle l|\delta E_n|n\rangle$$
$$\langle l|\hat{\mathcal{H}}_1|n\rangle + \langle l|\,\hat{\mathcal{H}}_0\left(\sum_{k\neq n} a_{nk}\,|k\rangle\right) = \langle l|\,E_n\left(\sum_{k\neq n} a_{nk}\,|k\rangle\right) + \langle l|\delta E_n|n\rangle$$
$$\langle l|\hat{\mathcal{H}}_1|n\rangle + a_{nl}E_l = a_{nl}E_n.$$

This gives us

$$a_{nl} = \frac{\langle l|\hat{\mathcal{H}}_1|n\rangle}{E_n - E_l}. \tag{133}$$

The above derivations showcase the first order approximation in the perturbation theory:

$$\begin{aligned} |n'\rangle &= |n\rangle + \sum_{k\neq n} \frac{\langle k|\hat{\mathcal{H}}_1|n\rangle}{E_n - E_k}\,|k\rangle + \mathcal{O}\big(\epsilon^2\big) \\ E'_n &= E_n + \langle n|\hat{\mathcal{H}}_1|n\rangle + \mathcal{O}\big(\epsilon^2\big). \end{aligned} \tag{134}$$

The problem is that when E_n and E_l are very close, the term of perturbation blows up. Hence, a different approach is needed in the degenerate case.

4.2 Degenerate Case

When there are degeneracies, we first label the list of energy eigenvalues like

$$E_1 = E_2 = \ldots = E_s < E_{s+1} = E_{s+2} = \ldots = E_{s+r} < E_{s+r+1} = \ldots.$$

The corresponding orthonormal energy eigenvectors can be grouped in the same manner:

$$\{u_1, \ldots, u_s\}, \{u_{s+1}, u_{s+2}, \ldots, u_{s+r}\}, \{u_{s+r+1}, \ldots\}, \ldots.$$

Each of these sets of states is a basis for a subspace of the full Hilbert space; we call that subspace the **eigenspace** of the corresponding eigenvalue that all the states in the set share.

Eigenspace

Suppose $T \in \mathcal{L}(V)$ and $\lambda \in \mathbb{F}$. The eigenspace of T corresponding to λ is the subspace $E(\lambda, T)$ of V defined by

$$E(\lambda, T) = \text{null}(T - \lambda I) = \{v \in V : Tv = \lambda v\}. \tag{135}$$

Hence $E(\lambda, T)$ is the set of all eigenvectors of T corresponding to λ, along with the 0 vector.

The point is, in the degenerate case, the set of perturbed energy eigenstates must be eigenstates of the perturbation $\hat{\mathcal{H}}_1$ within the eigenspace.

For example, consider the eigenspace $V_{\mathcal{E}}$ spanned by $E_1 = E_2 = \ldots = E_s = \mathcal{E}$. The first order equation is the same as before,

$$\hat{\mathcal{H}}_1 |n\rangle + \hat{\mathcal{H}}_0 \left(\sum_{k \neq n} a_{nk} |k\rangle \right) = \mathcal{E} \left(\sum_{k \neq n} a_{nk} |k\rangle \right) + \delta E_n |n\rangle,$$

but then we will split the sum over all other eigenstates into a sum over eigenstates in $V_{\mathcal{E}}$ and the others:

$$\hat{\mathcal{H}}_1 |n\rangle + \hat{\mathcal{H}}_0 \left[\left(\sum_{k \neq n}^{s} + \sum_{k=s+1}^{\infty} \right) a_{nk} |k\rangle \right] = \mathcal{E} \left[\left(\sum_{k \neq n}^{s} + \sum_{k=s+1}^{\infty} \right) a_{nk} |k\rangle \right] + \delta E_n |n\rangle.$$

By the fact that $|k\rangle$ is the eigenstate of $\hat{\mathcal{H}}_0$ and the terms in the first sum all have energy eigenvalue $\mathcal{E}$,

$$\hat{\mathcal{H}}_1 |n\rangle + \sum_{k=s+1}^{\infty} a_{nk} E_k |k\rangle = \mathcal{E} \sum_{k=s+1}^{\infty} a_{nk} |k\rangle + \delta E_n |n\rangle.$$

Rearranging gives us

$$\hat{\mathcal{H}}_1 |n\rangle = \delta E_n |n\rangle + \sum_{k=s+1}^{\infty} (\mathcal{E} - E_k) a_{nk} |k\rangle. \tag{136}$$

This means that when $\hat{\mathcal{H}}_1$ acts on $|n\rangle$, it gives a multiple of $|n\rangle$ plus a bit that lies out $V_{\mathcal{E}}$.

To summarize, in order for perturbation theory to work here, the original eigenstates of $\hat{\mathcal{H}}_0$ must be "eigenstates of the perturbation $\hat{\mathcal{H}}_1$ within the eigenspace".