7310 Quantum Mechanics I

University of Colorado, Boulder (Fall 2019)

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This is the first in a series of 3 graduate level classes on quantum mechanics taught at the University of Colorado Boulder. The textbook we will be using for most of this class is *Modern Quantum Mechanics* by J. J. Sakurai, with other relevant texts being *Quantum Mechanics* by E. Merzbacher, *Principles of Quantum Mechanics* by R. Shankar and *The Feynman Lectures on Physics (Vol. III)* by R. P. Feynman. As an overview, the topics we will be aiming to cover this semester are listed below.

1. Formalism of Quantum Mechanics.
2. The Schrödinger Equation and Quantum Dynamics.
3. Symmetries and Conservation Laws.
4. Spin and Angular Momentum.
5. The Hydrogen Atom Fine and Hyperfine Structure.
6. Perturbation Theory.
7. ~~Identical Particles~~.

All notes were taken real-time in the class (i.e. there are bound to be typos) taught by Professor Ethan Neil. For all useful information on this class, visit this link. [1]

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[1] For CU graduate students, we will be using the https://canvas.colorado.edu/ website for grading and administrative purposes.

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Chapter 1

Introduction

What evidence is there for a quantum mechanical world? There have been many things that point to the need for a quantum theory. Things such as the ultraviolet catastrphe, the electron double slit experiment, wave-particle duality, the Stern-Gerlach experiment, the uncertainty principles, energy quantization, entanglement and of course, the loss of determinism. This course aims to provide some of the experimental evidence that points to the need for a quantum theory and develops the formalisms and tools required to model such phenomena. For starters, we will be looking at several of the aforementioned experiments starting with the double-slit experiment. This should get our intuitions right off the classical track once more.

§1.1 Double-Slit Experiment

In 1927, Clinton Davisson and Lester Germer performed the double slit experiment with a beam of electrons. At that time, it was believed that electrons were simply point particles with (*semi*)classical behaviour (following the *Bohr model*). This essentially meant that electrons were pretty much believed to be little charged hard spheres, so shooting a bunch of them through slits would have the equivalent result as throwing bullets/billiard balls through holes.

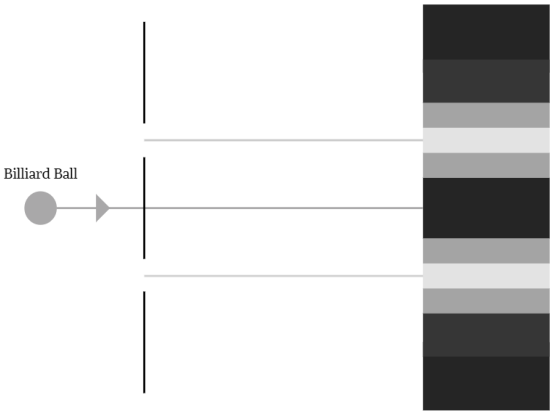


Figure 1.1: Billiard Ball Double Slit Experiment

The classical expectation of throwing billiard balls through 2 slits would produce a distribution shown in figure 1.1. In words, these are basically 2 approximately *Gaussian* peaks centered along the slit axes. **But** electrons, as it turns out, are not just your everyday classical objects. What was seen by Davisson and Germer was in fact an interference pattern on the screen (figure 1.2), exactly as what Young did for light (or what one would see with any perturbed classical wave medium). Not just that, but they also observed that if a measurement of the electrons was made **at** the slits, the electrons would behave just as the billiard balls would. This led to the notion of *wave-particle duality*.

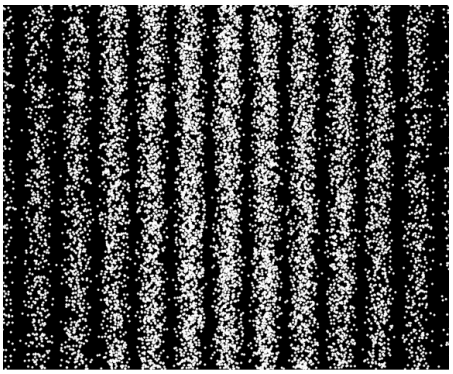


Figure 1.2: Electron Double Slit Experiment

§1.2 Lifetime of Excited Atoms

Consider the following set-up. We shine a laser on a material (which we prepare to be in the ground state) such that we excite the material's atoms to an excited state (higher energy state). We then have an emitter that collects the photons emitted from the material when the atom spontaneously falls back to its initial unexcited state. We then measure the spontaneous emission lifetime (time it takes to spontaneously emit a photon). It turns out that the lifetimes follow a distribution (**not** due to experimental errors) which we call the "*natural linewidth*". This tells us that there is some **inherent** randomness in physical systems and the uncertainty in the decay lifetime is a **fundamental** property of the atomic state.

Additionally, if we were to measure the energy E along with these spontaneous emission lifetimes τ, we see we will always retrieve the relation:

$$\Delta E \Delta \tau \geq \frac{\hbar}{2} \tag{1.1}$$

That is these quantities are correlated in their uncertainties. An application of this would be for Z-Bosons (neutral force carrier particles of the weak force) which particle physicists exploit all the time. This relation allows us to estimate the decay lifetimes of these particles which would be practically impossible to experimentally measure. However, with the relation, what physicist do is measure the distribution of energies associated to the Z boson and calculate its uncertainty to retrieve an estimate of its decay lifetime. To give an idea on how insurmountable the task of measuring decay lifetimes would be, the measured energy uncertainty is ~ 2.5 GeV, which means the decay would be $\sim 2.6 \times 10^{-13}$ ps!

§1.3 Stern-Gerlach Experiment

The Stern-Gerlach experiment is one where we fire silver atoms (which can be effectively thought of as heavy electrons) through a uniform magnetic field (in the $\hat{z}$ direction) and measure their resultant positions on a detector screen. From classical electrodynamics, we know that these "heavy electrons" will experience a Lorentz force which goes like:

$$F_z = \frac{\partial}{\partial z}(\vec{\mu} \cdot \vec{B}) \approx \mu_z \frac{\partial B_z}{\partial z} \tag{1.2}$$

where z is the axis that points upward, orthogonal to the beam axis. What we would classically expect is a smearing (continuous distribution) of the silver atoms which land on the screen. However of course, our world is indeed quantum mechanical and what we see is instead 2 concentrated regions of silver atoms on the screen with spin values $\pm\hbar/2$. This finite "binning" is known as the *quantization* of spin. If we now think of the Stern-Gerlach experiment as a black box such that when we send in spin 1-half particles, they emerge as either their '*up*' or '*down*' states, then we can have an abstracted visualization as follows.

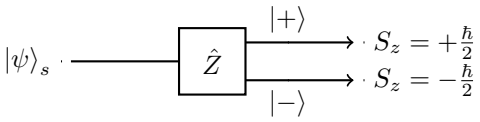


Figure 1.3: Spin-Z Black Box

Stern and Gerlach continued to perform experiments by placing these black boxes in a chain, and the results are as follows.

1. The first experimental set-up as shown in figure 1.4 showed that we can have 2 orthogonal states for the electron. These states are with respect to the $\hat{z}$ orientation and we will label them as $\{|z;+\rangle, |z;-\rangle\}$.

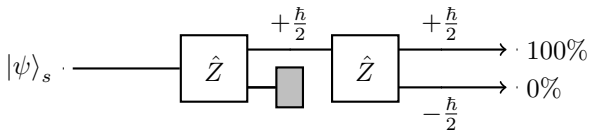


Figure 1.4: 2 $\hat{z}$-oriented Black Boxes with Blockage

2. A second experiment set up as shown in figure 1.5. These results show that basis states of one orientation of the Stern-Gerlach experiment have overlap with the basis states of another orientation $\Rightarrow \langle x;\pm|z;\pm\rangle \neq 0$.

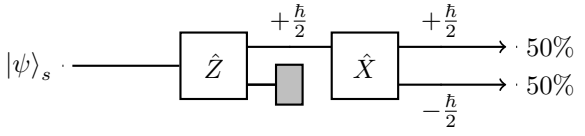


Figure 1.5: $\hat{z}/\hat{x}$-oriented Black Boxes with Blockage

3. The third experimental set up shown in figure 1.6 shows that any 'memory' of a having passed through previous filters is **not** retained.

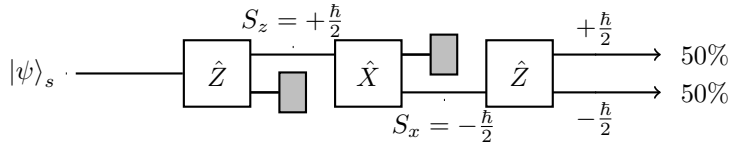


Figure 1.6: $\hat{z}/\hat{x}/\hat{z}$-oriented Black Boxes with Blockages

However, these results thus far are **not** sufficient to dismiss classical theory, because our machinery could be noisy and induce some sort of precession to the silver atoms to produce such an output. Thus the final we require the final experiment as demonstrtated below.

4. The last experimental set up shown in figure 1.7 finally dictates that we need a theory beyond classical mechanics.

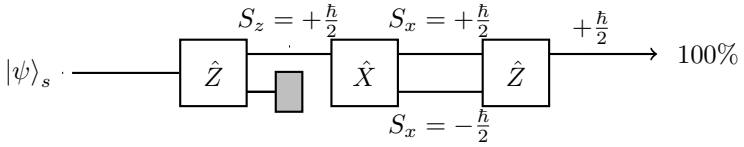


Figure 1.7: $\hat{z}/\hat{x}/\hat{z}$-oriented Black Boxes with Blockage

How this allows us to question classical physics is that given the assumption of classical laws, the rules of probability tell us that the outcome of the fourth experiment should be:

$$\begin{aligned} &p(S_z = -|S_x = + \text{ or } S_x = -) \\ =&p(S_z = -|S_x = +)p(S_x = +) + p(S_z = -|S_x = -)p(S_x = -) \end{aligned} \tag{1.3}$$

Every term on the right-hand side of equation 1.3 should be 50%, yet the left-hand side is experimentally zero! How can this be? The only way to resolve this is by working with probability amplitudes. That is:

$$p_{\text{Quantum}}(A \text{ or } B) = |\psi(A) + \psi(B)|^2 \tag{1.4}$$

$$= p(A) + p(B) + 2\,\text{Re}\{\psi^*(A)\psi(B)\} \tag{1.5}$$

where the ψ terms are probability amplitudes (complex variables) rather than probability distributions. We require to take the absolute square of the probability amplitudes to retrieve the probabilities. This third term is what is known as an interference effect and would not be present in standard classical theories of a spinning charge. It turns out that this system can be modelled as a 2-dimensional complex vector space with an orthonormal basis consisting of these up and

down states $\{|+\rangle, |-\rangle\}$:

$$|\hat{z};+\rangle = \begin{bmatrix}1\\0\end{bmatrix}, \quad |\hat{z};-\rangle = \begin{bmatrix}0\\1\end{bmatrix} \tag{1.6}$$

$$|\hat{x};+\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix}, \quad |\hat{x};-\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\-1\end{bmatrix} \tag{1.7}$$

where passing through the different black boxes along each axes would just be a projection of these vectors onto the other basis. However, if we try to extend this experiment into the y-direction, we find that we **must** introduce complex numbers where the y-basis is written as:

$$|\hat{y};+\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\i\end{bmatrix}, \quad |\hat{y};-\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix}1\\-i\end{bmatrix} \tag{1.8}$$

Chapter 2

Hilbert Spaces

We're gonna stop being hand-wavey now and get into the meat of things. This section will be laying out a bunch of mathematics so get ready. However if you want more math, the lecture notes by Landsman and "Analysis" by Lieb and Loss should satiate that desire. Vector spaces (or more specifically Hilbert spaces) are the universal language of quantum mechanics. Whether you are working with wave mechanics or in matrix mechanics, vector spaces are the embedded in both of these methods. Why working with vector spaces is useful in quantum mechanics is because most of the time, we will be working with finite dimensional spaces and operators. To start, let's begin with a definition.

Definition 2.0.1. Hilbert Spaces: *A Hilbert space is a complex vector space that is complete (all Cauchy sequences converge) with an inner product*:

$$(\ ,\ ) : \mathcal{H} \times \mathcal{H} \quad \to \quad \mathbb{C} \tag{2.1}$$

where $\mathcal{H}$ is the Hilbert space.

§2.1 Dirac Notation

The particular construction of quantum mechanics is nicely described when adopting what is known as Dirac's notation. In this notation, we have *kets* being the elements of the Hilbert space, and hence are sometimes also referred to as vectors. These are written as:

$$|\psi\rangle \in \mathcal{H} \tag{2.2}$$

where $\mathcal{H}$ is the Hilbert space. Some properties of kets are listed below.

1. $|\alpha\rangle + |\beta\rangle = |\beta\rangle + |\alpha\rangle$
2. $|\alpha\rangle + (|\beta\rangle + |\gamma\rangle) = (|\beta\rangle + |\alpha\rangle) + |\gamma\rangle$
3. $(c_1 + c_2)\,|\alpha\rangle = c_1\,|\alpha\rangle + c_2\,|\alpha\rangle$
4. $c_1(c_2\,|\alpha\rangle) = (c_1 c_2)\,|\alpha\rangle$
5. $\exists \mathbb{I}$ s.t. $\mathbb{I}\,|\alpha\rangle = |\alpha\rangle$

6. $\exists\,|\rangle$ s.t. $|\alpha\rangle + |\rangle = |\alpha\rangle$ and $0\,|\alpha\rangle = |\rangle$
7. $\exists\,|-\alpha\rangle$ for all $|\alpha\rangle$ s.t. $|\alpha\rangle + |-\alpha\rangle = |\rangle$

§2.2 Relevant Linear Algebra Concepts

It would prove useful now to first refresh our memory on some concepts from linear algebra.

Definition 2.2.1. Linear Independence: *A set of vectors $\{|\lambda_j\rangle\}$ are linearly independent iff $\sum_j c_j\lambda_j = 0$ has **no** solutions except for the trivial one $c_j = 0 \quad \forall j$.*

Definition 2.2.2. Dual Correspondence: *Every element of the Hilbert space has a dual, which is its bra that lives in the dual Hilbert space. This correspondence map is non-linear because*:

$$\sum_j c_j\,|\alpha_j\rangle <\!\!\rightarrow \sum_j c_j^*\,\langle\alpha_j| \tag{2.3}$$

is a non-linear isomorphic map.

Note: Dual Hilbert spaces are not really necessary for us physicists to know but is the mathematically rigorous way of keeping track of spaces. However, we will always just defer to using one all-encompassing Hilbert space in this class.

We also want to list some bra-ket inner product properties.

1. $(c\,\langle\alpha|)\,|\beta\rangle = c\,\langle\alpha|\beta\rangle$
2. $(\langle\alpha_1| + \langle\alpha_2|)\,|\beta\rangle = \langle\alpha_1|\beta\rangle + \langle\alpha_2|\beta\rangle$
3. $\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle^*$
4. $\langle\alpha|\alpha\rangle = \langle\alpha|\alpha\rangle^* \geq 0$

As per the standard notion of orthogonality in linear algebra, we can express this in bra-ket notation as well.

Definition 2.2.3. Orthogonality: *2 vectors (kets) are orthogonal iff*:

$$\langle\beta|\alpha\rangle = \langle\alpha|\beta\rangle = 0 \tag{2.4}$$

We denote a vector (ket) as normalized if it satisfies the relation:

$$|\psi\rangle = \frac{|\psi\rangle}{\||\psi\rangle\|} \tag{2.5}$$

In infinite dimesional Hilbert spaces, we define the inner product as follows.

Definition 2.2.4. *The infinite dimensional Hilbert space inner product between 2 elements $|f\rangle$ and $|g\rangle$ is given by:*

$$\langle f|g\rangle = \int f^*(x) \cdot g(x) d^n x \tag{2.6}$$

where the integral is over all space defined by the system and n is the coordinate-space dimensionality.

An important relation is the Cauchy-Schwarz inequality which reads:

$$\boxed{\langle\alpha|\alpha\rangle \langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2} \tag{2.7}$$

where we call equality "*saturation*". The proof is as follows:

Proof. Consider the portion of $|\alpha\rangle$ that is orthogonal to $|\beta\rangle$. This would be:

$$|\alpha_\perp\rangle = |\alpha\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\beta|\beta\rangle} |\beta\rangle \tag{2.8}$$

Then consider the inner product of this ket with itself:

$$\langle\alpha_\perp|\alpha_\perp\rangle = \left(\langle\alpha| - \frac{\langle\beta|\alpha\rangle}{\langle\beta|\beta\rangle} \langle\beta|\right)\left(|\alpha\rangle - \frac{\langle\alpha|\beta\rangle}{\langle\beta|\beta\rangle} |\beta\rangle\right) \tag{2.9}$$

$$= \langle\alpha|\alpha\rangle + \frac{\langle\alpha|\alpha\rangle \langle\alpha|\beta\rangle}{\langle\beta|\beta\rangle} - 2\frac{\langle\alpha|\alpha\rangle \langle\alpha|\beta\rangle}{\langle\beta|\beta\rangle} \tag{2.10}$$

$$\Rightarrow \quad \langle\alpha|\alpha\rangle \langle\beta|\beta\rangle = |\langle\alpha|\beta\rangle|^2 + \langle\alpha_\perp|\alpha_\perp\rangle \langle\beta|\beta\rangle \tag{2.11}$$

and since we know that $\langle\alpha_\perp|\alpha_\perp\rangle \langle\beta|\beta\rangle \geq 0$, the inequality is proven. □

§2.3 Operators

This section is just going to be a bunch of definitions and properties to catch us up to speed on some of the tools necessary for doing quantum mechanics in any practical sense.

Definition 2.3.1. Operators: *An operator is a map from a Hilbert space to itself.*

$$\hat{O} : \mathcal{H} \quad \rightarrow \quad \mathcal{H} \tag{2.12}$$

where $\mathcal{H}$ is the Hilbert space.

Some properties that these satisfy are as follows.

1. $\hat{A} = \hat{B}$ if $\hat{A}|\psi\rangle = \hat{B}|\psi\rangle$ for all $|\psi\rangle$.

2. $\exists$ such that $\hat{}|\psi\rangle = |\rangle$
3. $\exists\hat{\mathbb{I}}$ such that $\hat{\mathbb{I}}\,|\psi\rangle = |\psi\rangle$
4. $\hat{A} + \hat{B} = \hat{B} + \hat{A}$
5. $\hat{A} + (\hat{B} + \hat{C}) = (\hat{A} + \hat{B}) + \hat{C}$
6. $(c + d)\hat{A} = c\hat{A} + d\hat{A}$ for $c, d \in \mathbb{C}$

Definition 2.3.2. Linear Operators: *A special kind of operator whereby it satisfies the property:*

$$\hat{A}\left(c_\alpha\,|\alpha\rangle + c_\beta\,|\beta\rangle\right) = c_\alpha\hat{A}\,|\alpha\rangle + c_\beta\hat{A}\,|\beta\rangle \tag{2.13}$$

Definition 2.3.3. Commutator: *The commutator between 2 operators $\hat{A}$ and hat$B$ is defined as*:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{2.14}$$

A list of commutator properties are listed below.

1. $\left[\hat{A}, \hat{A}\right] = 0$
2. $\left[\hat{A}, \hat{B}\right] = -\left[\hat{B}, \hat{A}\right]$
3. $\left[\hat{A} + \hat{B}, \hat{C}\right] = \left[\hat{A}, \hat{C}\right] + \left[\hat{B}, \hat{C}\right]$
4. $\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right]$
5. $\left[\hat{A}\hat{B}, \hat{C}\right] = \hat{A}\left[\hat{B}, \hat{C}\right] + \left[\hat{A}, \hat{C}\right]\hat{B}$
6. Jacobi Identity: $\left[\hat{A}, \left[\hat{B}, \hat{C}\right]\right] + \left[\hat{B}, \left[\hat{C}, \hat{A}\right]\right] + \left[\hat{C}, \left[\hat{A}, \hat{B}\right]\right] = 0$

Definition 2.3.4. Operator Inverses: *Most operators $\hat{A}$ have an inverse $\hat{A}^{-1}$ such that*:

$$\hat{A}\hat{A}^{-1}\,|\psi\rangle = \hat{A}^{-1}\hat{A}\,|\psi\rangle = \mathbb{I}\,|\psi\rangle \tag{2.15}$$

when $\hat{A}$ exists, it is unique.

Definition 2.3.5. Adjoint Operator: *Given an operator $\hat{A}$, the adjoint of $\hat{A}$ is denoted $\hat{A}^\dagger$ as satisfies:*

$$\left(|\alpha\rangle\,, \hat{A}\,|\beta\rangle\right) = \left(\hat{A}^\dagger\,|\alpha\rangle\,, |\beta\rangle\right) \tag{2.16}$$

If we exist in $\mathbb{C}^n$, then $\hat{A}$ can have a matrix representation $[A]_{ij}$. It is convenient to note that the adjoint of the this matrix would be $[A^\dagger]_{ij} = [A]^*_{ji}$. Some properties of the adjoint operator are listed below.

1. $(c\hat{A})^\dagger = c^*\hat{A}^\dagger$
2. $(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$
3. $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$

Some special operators largely used in quantum mechanics are *Hermitian* and *Unitary* operators. These satisfy the properties:

1. **Hermitian Operators**: $\hat{A} = \hat{A}^\dagger$
2. **Unitary Operators**: $\hat{U}^\dagger = \hat{U}^{-1}$

Definition 2.3.6. Eigen-Kets: *An eigen-ket $|a\rangle$ of $\hat{A}$ is a ket that is left invariant up to a scalar when acted on by operator $\hat{A}$:*

$$\hat{A}\,|a\rangle = a\,|a\rangle \tag{2.17}$$

where a is the eigenvalue of $\hat{A}$ associated to $|a\rangle$.

A special property of Hermitian operators and their eigen-kets are that their eigen-kets with distinct eigenvalues are **all** orthogonal.

Proof. Let $\hat{A}$ be a Hermitian operator with 2 of its eigen-kets being $|a_1\rangle$ and $|a_2\rangle$. Then we know that:

$$\begin{aligned} & \langle a_1|\,\hat{A}\,|a_2\rangle = \langle a_2|\,\hat{A}\,|a_1\rangle^* \\ \Rightarrow\quad & a_2\,\langle a_1|a_2\rangle = a_1^*\,\langle a_1|a_2\rangle \\ \Rightarrow\quad & (a_2 - a_1^*)\,\langle a_1|a_2\rangle = 0 \end{aligned} \tag{2.18}$$

Now we have 2 cases:

1. If $a_1 \neq a_1$: $a_1 - a_1^* = 0$, which means that the eigenvalues of Hermitian operators **must** be real.
2. If $a_1 \neq a_2$: $\langle a_1|a_2\rangle = 0$, which concludes the proof.

□

The 2 results in the proof constitute what is known as the *spectral theorem.*

Definition 2.3.7. Basis: *A set of vectors (kets) $\{|e_j\rangle\}$ which span the Hilbert space and also has the same dimension as the Hilbert space.*

An orthonormal basis is a special kind of basis whereby every one of its elements satisfies:

$$\langle e_i|e_j\rangle = \delta_{ij} \tag{2.19}$$

Orthonormal bases allow us to express the coefficients of some arbitrary ket in the Hilbert space

with projectors:

$$|\psi\rangle = \sum_n (|e_n\rangle \langle e_n|) |\psi\rangle \tag{2.20}$$

where we denote the $|\ldots\rangle \langle \ldots|$ operation as an *outer product*.

Note: Notice the relation:

$$\sum_n |e_n\rangle \langle e_n| = \mathbb{I} \tag{2.21}$$

known as the *completeness relation* or"inserting a complete set of states".

Chapter 3

Two-Level Systems

Also known as the qubit system, these have many applications that go beyond just the commonly talked about quantum computing. An exapmle of such a system that we have already seen is the spin system discovered by Stern and Gerlach's experiment. 2-state systems are extremely important in physics and have applications in lasers, atomic transitions, neutrinos, quantum computing and many more. To set these systems up, we're first going to need to know the postulates of quantum mechanics.

§3.1 Postulates of Quantum Mechanics

1. **Postulate 1**: The state of a physical system is a normalized ket in a Hilbert space $\mathcal{H}$.
2. **Postulate 2**: Any physical observable is a Hermitian operator (with real eigenvalues as proven last time) acting on a Hilbert space $\mathcal{H}$.
3. **Postulate 3**: Taking a measurement of an operator $\hat{A}$, we will measure some eigenvalue a of $\hat{A}$ and the state collapses to the corresponding eigenvector.
4. **Postulate 4 (Born's Rule)**: If the system is in the state $|\psi\rangle$, then the probability of getting an outcome a from measuring $\hat{A}$ is given as:
$$\mathbb{P}(a) = |\langle a|\psi\rangle|^2 \tag{3.1}$$
5. **Postulate 5**: The states of a quantum system evolve in time according to:
$$\begin{aligned} & i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \\ \Rightarrow \quad & -i\hbar\frac{\partial}{\partial t}\langle\psi(t)| = \hat{H}\langle\psi(t)| \end{aligned} \tag{3.2}$$
(will be further elaborated on in the chapter on quantum dynamics).

Note: Postulate 4 is the reason why we need our states to be unit normalized.

Note: Postulate 5 is phrased in the *Schrödinger picture* which is where states evolve in time instead of the operators (which is called the *Heisenberg picture*).

Example:

Consider the Stern-Gerlach experiment, for which we want to the measure the spin in the z axis/basis. The corresponding observable would be the Hermitian operator $\hat{S}_z$ with the matrix representation:

$$\hat{S}_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{3.3}$$

where we got this by taking the some of the outer products of the eigenstates scaled by their corresponding eigenvalues. Equivalently, the entries of this matrix could have been computed by the relation:

$$\left[\hat{S}_z\right]_{ij} = \langle i|\, \hat{S}_z\, |j\rangle \tag{3.4}$$

where $|i\rangle, |j\rangle$ are eigenstates $\in \{|S_z;+\rangle, |S_z;-\rangle\}$.

§3.1.1 Repeated Measurements

In experiment, we can't talk about probability unless we repeat the experiment and attain some statistics on the results. As such, we need to know some relevant statistics.

1. **Expectation**:

$$\begin{aligned} \langle \hat{A} \rangle &= \sum_j a_j \mathbb{P}(a_j) \\ &= \sum_j a_j |\langle a_j|\psi\rangle|^2 \\ &= \sum_j \langle \psi|a_j\rangle\, a_j\, \langle a_j|\psi\rangle \\ &= \sum_j \langle \psi|\, \hat{A}\, |a_j\rangle\, \langle a_j|\psi\rangle \\ &= \langle \psi|\, \hat{A} \left(\sum_j |a_j\rangle\, \langle a_j| \right) |\psi\rangle = \langle \psi|\, \hat{A}\, |\psi\rangle \end{aligned} \tag{3.5}$$

2. **Variance**:

$$\begin{aligned} \Delta \hat{A}^2 &= \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2 \\ &= \langle \psi|\, \hat{A}^2\, |\psi\rangle - \langle \psi|\, \hat{A}\, |\psi\rangle^2 \end{aligned} \tag{3.6}$$

§3.1.2 More on 2-Level Systems

Going back to the 2-state system, even though we are working in a complex field which would give 2 real numbers per coefficient, of which there are 2 to describe a general state, the normalization condition and Born's rule eliminate 2 of these:

$$\begin{aligned} |\psi\rangle &= \alpha\,|+\rangle + \beta\,|-\rangle \\ &= \cos\left(\frac{\theta}{2}\right)|+\rangle + \sin\left(\frac{\theta}{2}\right)e^{i\phi}\,|-\rangle \end{aligned} \tag{3.7}$$

where a global phase $e^{i\zeta}$ does **not** affect the physics since the wavefunction (kets) are useful only when we square them to get the probabilities. In general, the number of free real parameters required to describe a quantum system of N states is $N-2$. The reason why we choose to parameterize the state with angular coordinates is so that we can have a geometric picture of the state with what is called a *Bloch sphere* (figure 3.1 below).

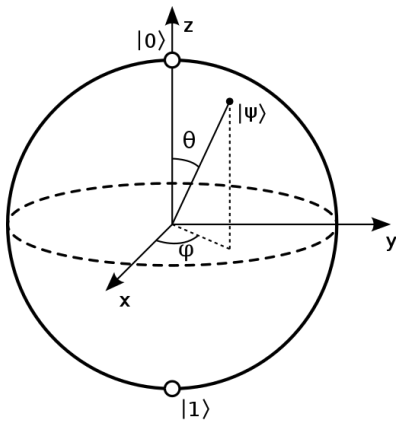


Figure 3.1: Bloch Sphere

where in the figure above, the eigenstates are written as $|0\rangle$ and $|1\rangle$ because that is the convention that quantum information theorists use. In this geometric representation, quantum states live on the surface of the Block sphere due to the normalization condition, and they move around via unitary operators.

The results from the Stern-Gerlach experiment are sufficient to dictate the need for complex numbers, so that we have the eigenstates of spin observable along each axis is given by:

$$\hat{S}_x: \quad |x;+\rangle = \frac{\hbar}{2}\begin{bmatrix}1\\1\end{bmatrix}, \quad |x;-\rangle = \frac{\hbar}{2}\begin{bmatrix}1\\-1\end{bmatrix} \tag{3.8}$$

$$\hat{S}_y: \quad |y;+\rangle = \frac{\hbar}{2}\begin{bmatrix}1\\i\end{bmatrix}, \quad |y;-\rangle = \frac{\hbar}{2}\begin{bmatrix}1\\-i\end{bmatrix} \tag{3.9}$$

$$\hat{S}_z: \quad |z;+\rangle = \frac{\hbar}{2}\begin{bmatrix}1\\0\end{bmatrix}, \quad |z;-\rangle = \frac{\hbar}{2}\begin{bmatrix}0\\1\end{bmatrix} \tag{3.10}$$

for which their matrix representations are:

$$\hat{S}_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}, \quad \hat{S}_y = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}, \quad \hat{S}_z = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} \tag{3.11}$$

The *Pauli matrices* are then defined as the spin operators but with a factor $2/\hbar$. Some properties of the Pauli matrices are listed below.

1. $\hat{\sigma}_j^2 = \mathbb{I}$
2. $[\hat{\sigma}_i, \hat{\sigma}_j] = 2i\epsilon_{ijk}\hat{\sigma}_k$
3. $\{\hat{\sigma}_i, \hat{\sigma}_j\} = 2\delta_{ij}\mathbb{I}$

§3.1.3 Compatible Observables and Uncertainty

In general, we have that observables do **not** commute. That is:

$$\hat{A}\hat{B} \neq \hat{B}\hat{A} \tag{3.12}$$

So the order of measurement matters! However, there is an exception to this. That is when:

$$\begin{aligned} &\hat{A}\left|\chi\right\rangle = a\left|\chi\right\rangle \quad \text{and} \quad \hat{B}\left|\chi\right\rangle = b\left|\chi\right\rangle \\ \Rightarrow \quad &\hat{A}\hat{B}\left|\chi\right\rangle = \hat{B}\hat{A}\left|\chi\right\rangle = ab\left|\chi\right\rangle \end{aligned} \tag{3.13}$$

In fact if the observables commute, they are said to be *simultaneously diagonalizable*, and share the same set of eigenstates.

Theorem 3.1.1. *If $\hat{A}$ has non-degenerate eigenvalues, then we have a compatible $\hat{B}$ that is diagonale in the basis of eigenstates of $\hat{A}$.*

Proof. First consider:

$$\begin{aligned} \left\langle a_j\right|\left[\hat{A},\hat{B}\right]\left|a_i\right\rangle &= \left\langle a_j\right|\hat{A}\hat{B} - \hat{B}\hat{A}\left|a_j\right\rangle \\ &= \sum_k \left[\left\langle a_j\right|\hat{A}\left|a_k\right\rangle\left\langle a_k\right|\hat{B}\left|a_i\right\rangle\right] - a_j\left\langle a_j\right|\hat{B}\left|a_i\right\rangle \\ &= \sum_k a_k\delta_{jk}\left\langle a_k\right|\hat{B} - a_j\left\langle a_j\right|\hat{B}\left|a_i\right\rangle \\ &= (a_j - a_i)\left\langle a_j\right|\hat{B}\left|a_i\right\rangle = 0 \end{aligned} \tag{3.14}$$

This tells us that $\left[\hat{A},\hat{B}\right] = 0$ iff there exists a basis where **both** $\hat{A}$ and $\hat{B}$ are diagonal (simultaneously diagonalizable). □

An application of this would be for the spin observables along with the total spin operators $\hat{S}^2$ which is defined as:

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3}{4}\hbar^2\mathbb{I} \tag{3.15}$$

which turns out that $\left[\hat{S}_j, \hat{S}^2\right] = 0$ (check this as an exercise).

§3.1.4 Incompatible Observables

Now we think about the converse scenario. Consider 3 observables $\hat{A}, \hat{B}$ and $\hat{C}$ that are incompatible. We send an input state into the respective operators in sequence, that is $\hat{A} \to \hat{B} \to \hat{C}$. At each step, we block all the outgoing states except the top eigenstate with the exception of $\hat{C}$ outputs. Then to compute the probability of obtaining the first eigenstate of $\hat{C}$, $|c_1\rangle$ given that we came from the eigenstate $|b_1\rangle$ of $\hat{B}$ and also from the eigenstate $|a_1\rangle$ before that:

$$\mathbb{P}(c_1|b_1, a_1) = |\langle c_1|b_1\rangle|^2 |\langle b_1|a_1\rangle|^2 \tag{3.16}$$

And if we repeat this over all the eigenstates of $\hat{B}$, we get:

$$\boxed{\mathbb{P}(c_1|\hat{B}, a_1) = \sum_b |\langle c_1|b\rangle|^2 |\langle b|a_1\rangle|^2} \tag{3.17}$$

But now if we completely remove $\hat{B}$, we have instead:

$$\boxed{\mathbb{P}(c_1|\text{no } \hat{B}, a_1) = |\langle c_1|a_1\rangle|^2 = \left|\sum_b \langle c_1|b\rangle \langle b|b\rangle\right|^2} \tag{3.18}$$

The 2 boxed equations are **not** equal in general, **unless** $\hat{A}$ and $\hat{B}$ commute! Otherwise, they are known as *incompatible* observables. Now we will show that 2 incompatible observables satisfy an *uncertainty relation*. An uncertainty relation means that we cannot know both a and b simultaneously if $\left[\hat{A}, \hat{B}\right] =\neq 0$. We however can know the expectation of the observables but **not** arbitrarily precisely. The uncertainty is quantified by the variance (a.k.a *dispersion*), which corresponds to the width of the statistical distribution of the observable measurements.

Note: The variance can be zero if we measure eigenstates of the observable.

Theorem 3.1.2. *There exists an uncertainty relation between 2 non-commuting (incompatible) observables written as:*

$$\Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2}\left|\langle\left[\hat{A}, \hat{B}\right]\rangle\right| \tag{3.19}$$

Proof. First let:

$$|\alpha\rangle = \Delta\hat{A}\,|\psi\rangle \tag{3.20}$$

$$|\beta\rangle = \Delta\hat{B}\,|\psi\rangle \tag{3.21}$$

for some arbitrary state $|\psi\rangle$, then we know from the Cauchy-Schwarz inequality that:

$$\begin{aligned} & \langle\alpha|\alpha\rangle \langle\beta|\beta\rangle \geq |\langle\alpha|\beta\rangle|^2 \\ \Rightarrow \quad & \langle\psi| \Delta\hat{A} |\psi\rangle \langle\psi| \Delta\hat{B} |\psi\rangle \geq \left|\langle\psi| \Delta\hat{A}\Delta\hat{B} |\psi\rangle\right|^2 \end{aligned} \tag{3.22}$$

Now we use the identity:

$$\begin{aligned} & \Delta\hat{A}\Delta\hat{B} = \frac{1}{2}\left[\Delta\hat{A}, \Delta\hat{B}\right] + \frac{1}{2}\left\{\Delta\hat{A}, \Delta\hat{B}\right\} \\ \text{where} \quad & \left[\Delta\hat{A}, \Delta\hat{B}\right] = \left[\hat{A}, \hat{B}\right] \end{aligned} \tag{3.23}$$

Also notice that $\left[\hat{A}, \hat{B}\right]$ is anti-Hermitian (purely imaginary eigenvalues) while $\left\{\Delta\hat{A}, \Delta\hat{B}\right\}$ is Hermitian (purely real eigenvalues). So this gives us:

$$\left|\langle\psi| \Delta\hat{A}\Delta\hat{B} |\psi\rangle\right|^2 = \frac{1}{4}\left|\left[\hat{A}, \hat{B}\right]\right|^2 + \frac{1}{4}\left|\left\{\Delta\hat{A}, \Delta\hat{B}\right\}\right|^2 \geq \frac{1}{4}\left|\left[\hat{A}, \hat{B}\right]\right|^2 \tag{3.24}$$

□

§3.2 Change of Basis

What we wanted to move from one basis to another, we would then need to construct an operator such that:

$$\hat{U}_{B_1 \to B_2} = \sum_k |k; B_1\rangle \langle k; B_2| \tag{3.25}$$

This operator turn out to be unitary and satisfies;

$$\hat{U}^\dagger_{B_1 \to B_2} \hat{U}_{B_1 \to B_2} = \hat{U}_{B_2 \to B_1} \hat{U}_{B_1 \to B_2} = \mathbb{I} \tag{3.26}$$

If we write our state in the eigenstate expansion of bases, we have:

$$\begin{aligned} |\psi\rangle &= \sum_j |a_j\rangle \langle a_j|\psi\rangle \\ &= \sum_j |b_j\rangle \langle b_j|\psi\rangle \end{aligned} \tag{3.27}$$

where we see that:

$$\begin{aligned} \langle b_j|\psi\rangle &= \sum_j \langle b_j|a_j\rangle \langle a_j|\psi\rangle \\ &= \sum_j \langle a_j| \hat{U}^\dagger |a_j\rangle \langle a_j|\psi\rangle \end{aligned} \tag{3.28}$$

As such, state and operator transformations from one basis to another is written as:

$$\begin{aligned} \psi &\to \hat{U}^\dagger \left|\psi\right\rangle \\ \hat{A} &\to \hat{U}^\dagger \hat{A} \hat{U} \end{aligned} \tag{3.29}$$

Note: The norm of a state and trace of an operator are preserved under change of basis transformations, where the trace is defined as:

$$\mathrm{Tr}\Big\{\hat{A}\Big\} = \sum_j \left\langle j\right| \hat{A} \left|j\right\rangle \tag{3.30}$$

Traces satisfy the properties below.

1. Cyclic triplet permutation.
2. $\mathrm{Tr}\{\left|a_i\right\rangle \left\langle a_j\right|\} = \delta_{ij}$
3. $\mathrm{Tr}\{\left|a\right\rangle \left\langle b\right|\} = \left\langle b|a\right\rangle$

We will see later that unitary operators are related to symmetries in our real physical system.

Chapter 4

Infinite Dimensional Systems

Thus far, we have been dealing with finite dimensional Hilbert spaces due to the fact that the systems we have seen only need a finite number of states to completely describe it. On the other hand, for measurements where we have observables having a continuous spectrum (e.g. position), then our Hilbert space for these system would be an infinite dimensional Hilbert space. In general, a lot of the treatment of such systems remains analogous. For instance, the eigenvalue equation for these observables remain the same. However, the completeness and orthonormality relations become:

$$\int d\xi \, |\xi\rangle \langle\xi| = \mathbb{I} \tag{4.1}$$

$$\langle\xi|\xi'\rangle = \delta(\xi - \xi') \tag{4.2}$$

Let's take a deeper look into how we extend our intuition from finite dimensional systems into infinite dimensional ones.

§4.1 Continuous Operators

In finite dimensional systems, we can no longer explicitly write out the matrix and vector representations of the operators and states, however we can still think of them following the same rules (e.g. eigendecompositions, linear combinations, etc...). To express a state in terms of some basis then, we can write:

$$|\psi\rangle = \int d\xi \, |\xi\rangle \langle\xi|\psi\rangle \tag{4.3}$$

And the eigenstate relations of for instance the position operators is still:

$$\begin{aligned} & \hat{x} \, |x\rangle = x \, |x\rangle \\ \Rightarrow \quad & \langle x'|x\rangle = \delta(x - x') \\ \Rightarrow \quad & \langle x'| \, \hat{x} \, |x\rangle = x\delta(x - x') \end{aligned} \tag{4.4}$$

Now, we can construct a projection operator that asserts some form of uncertainty in position during measurement which reads:

$$\begin{aligned}\hat{M}(x,\Delta_x) &= \int_{x-\Delta_x}^{x+\Delta_x} dx' \left|x'\right\rangle \left\langle x'\right| \\ &= \int_{-infty}^{\infty} dx' \left|x'\right\rangle \left\langle x'\right| \left[\Theta(x'-x+\Delta_x) - \Theta(x'-x+\Delta_x)\right]\end{aligned} \tag{4.5}$$

With this, we then have:

$$\begin{aligned}\left\langle\psi\right| \hat{M}(x,\Delta_x) \left|\psi\right\rangle &= \int_{x-\Delta_x}^{x+\Delta_x} dx' \left\langle\psi|x'\right\rangle \left\langle x'|\psi\right\rangle \\ &= \int_{x-\Delta_x}^{x+\Delta_x} dx' |\psi(x')|^2\end{aligned} \tag{4.6}$$

So this allows us to retrieve the probability of attaining the particle within the region $x \in [x-\Delta_x, x+\Delta_x]$ (where $|\psi(x')|^2$ is the probability density function). To get expectation values, we perform it as follows:

$$\begin{aligned}\left\langle\hat{x}\right\rangle &= \left\langle\psi\right| \hat{x} \left|\psi\right\rangle \\ &= \int dx \int dx' \left\langle\psi|x'\right\rangle \left\langle x'\right| \hat{x} \left|x\right\rangle \left\langle x\right| \left\langle\psi\right| \\ &= \int dx \int dx' \psi^*(x')\psi(x) x \delta(x-x') \\ &= \int dx |\psi(x)|^2 x\end{aligned} \tag{4.7}$$

More generally, for any operator that is a function of $\hat{x}$, we have:

$$\boxed{\left\langle A(\hat{x})\right\rangle = \int dx |\psi(x)|^2 A(x)} \tag{4.8}$$

We have been working with position, but what about momentum? We, we can take it as a definition that the *momentum operator* must satisfy the commutator relationship:

$$\boxed{[\hat{x},\hat{p}] = i\hbar} \tag{4.9}$$

To get the explicit form of the $\hat{p}$ operator, we compare 2 equations:

$$\begin{cases}\left\langle\phi\right| [\hat{x},\hat{p}] \left|\psi\right\rangle & = \int dx \int dx' \left\langle\phi|x'\right\rangle \left\langle x'\right| \hat{x}\hat{p} - \hat{p}\hat{x} \left|x\right\rangle \left\langle x\right| \left\langle\psi\right| \\ & = \int dx \int dx' \phi^*(x') \left[x' \left\langle x'\right| \hat{p} \left|x\right\rangle - x \left\langle x'\right| \hat{p} \left|x\right\rangle\right] \psi(x)\end{cases} \tag{4.10}$$

and

$$\begin{cases}\left\langle\phi\right| [\hat{x},\hat{p}] \left|\psi\right\rangle & = i\hbar \left\langle\phi|\psi\right\rangle \\ & = i\hbar \int dx \phi^*(x)\psi(x)\end{cases} \tag{4.11}$$

$$\Rightarrow \quad \left\langle x'\right| \hat{p} \left|x\right\rangle = \delta(x-x') \frac{\hbar}{i} \frac{\partial}{\partial x} \tag{4.12}$$

Now, if we wanted to change from the position to the momentum basis, we project the position eigenstates onto the momentum eigenstates using the momentum operator and solve the associated differential equation:

$$\begin{aligned} \langle x|\,\hat{p}\,|p\rangle &= p\,\langle x|p\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x}\,\langle x|p\rangle \\ \Rightarrow \quad \langle x|p\rangle &= \frac{1}{\sqrt{2\pi\hbar}}\exp\left\{\frac{ipx}{\hbar}\right\} \end{aligned} \tag{4.13}$$

which shows that the momentum eigenstate written in the x-basis is a planewave and is **not** normalizable. In the same way, we can express the position operator in the momentum basis as follows:

$$\langle p|\,\hat{x}\,|p'\rangle = \delta(p-p')i\hbar\frac{\partial}{\partial p} \tag{4.14}$$

It then works out that the position and momentum basis states are simply Fourier transforms of one another:

$$\boxed{\psi(x) = \frac{1}{\sqrt{2\pi\hbar}}\int dp\exp\left(\frac{ipx}{\hbar}\right)\tilde{\psi}(p)} \tag{4.15}$$

In higher dimensions, we have the commutation relations:

$$\begin{cases} [\hat{x}_i,\hat{p}_j] = i\hbar\delta_{ij} \\ [\hat{x}_i,\hat{x}_j] = [\hat{p}_i,\hat{p}_j] = 0 \end{cases} \tag{4.16}$$

And we generalize the differential operators with gradients.

§4.2 Wave Packets

Previously when we looked at these "measurement operators" $M(x,\Delta_x)$, it was not a very precise object and was constructed mainly to invoke some notion of localization. In real systems, we can have actual wavefunctions that a localized to a region in space (unlike planewave solutions). These are known as *wave packets* and are objects which are normalizable. We will have these take the shape of Gaussians:

$$\langle x|\psi\rangle = \psi(x) = \frac{1}{\pi^{1/4}\sqrt{d}}\exp\left\{ikx - \frac{x^2}{2d^2}\right\} \tag{4.17}$$

Let's try to compute several statistics with this function.

1. **Expectation of x**:

$$\langle\hat{x}\rangle = \langle\psi|\,\hat{x}\,|\psi\rangle = \frac{1}{\sqrt{\pi}d}\int dx x\exp\left(-\frac{x^2}{d^2}\right) = 0 \tag{4.18}$$

2. **Expectation of x^2**:

$$\langle \hat{x}^2 \rangle = \frac{1}{\sqrt{\pi} d} \int dx x^2 \exp\left(-\frac{x^2}{d^2}\right) = \frac{d^2}{2} \tag{4.19}$$

3. **Expectation of p**:

$$\begin{aligned} \langle \hat{p} \rangle &= \int dx \int dx' \, \langle \psi | x \rangle \, \langle x | \, \hat{p}\hat{x} \, | x \rangle \, \langle x | \psi \rangle \\ &= \int dx \int dx' \psi^*(x) \left[\frac{\hbar}{i} \delta(x - x') \frac{\partial}{\partial x} \right] \psi(x') \\ &= \frac{\hbar}{i\sqrt{\pi} d} \int dx e^{-ikx + \frac{x^2}{2d^2}} \left(ik - \frac{x}{d^2} \right) \exp\left\{ ikx - \frac{x^2}{2d^2} \right\} \\ &= \hbar k \end{aligned} \tag{4.20}$$

4. **Expectation of p^2**:

$$\langle \hat{p}^2 \rangle = \frac{\hbar^2}{2d^2} + \hbar^2 k^2 \tag{4.21}$$

From these, we can also compute the uncertainty relation of position and momentum for the Gaussian wave packet:

$$\Delta x = \sqrt{\langle \hat{x}^2 \rangle} = \frac{d}{\sqrt{2}} \quad \text{and} \quad \Delta p = \sqrt{\langle \hat{p} \rangle^2 - \langle \hat{p}^2 \rangle} = \frac{\hbar}{d\sqrt{2}} \tag{4.22}$$

$$\Rightarrow \quad \Delta x \Delta p = \frac{\hbar}{2} \tag{4.23}$$

So we see that this actually saturates the uncertainty principle! We thus call this state a *minimum uncertainty state*. Now, if we want to find the wavefunction of a wave packet in momentum space, we can use the Fourier transform (change of basis) as follow:

$$\begin{aligned} \tilde{\psi}(p) &= \langle p | \psi \rangle \\ &= \int dx \, \langle p | x \rangle \, \langle x | \psi \rangle \\ &= \frac{1}{\pi^{1/4} \sqrt{\hbar / d}} \exp\left\{ -\frac{(p - \hbar k)^2}{2(\hbar/d)^2} \right\} \end{aligned} \tag{4.24}$$

which we see that we could have actually just written these down knowing the expectation value and uncertainty in p, given that we knew it is also a Gaussian.

§4.3 Hamiltonians

In quantum mechanics, we define the Hamiltonian as a Hermitian operator where its eigenstates are energy eigenstates. We can extend the definition from the classical Hamiltonian by just "putting hats on everything":

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) \tag{4.25}$$

In the position basis, we get the explicit form of the Hamiltonian as:

$$\begin{aligned}\langle x|\,\hat{H}\,|\psi\rangle &= \int dx'\,\langle x|\,\hat{H}\,|x'\rangle\,\langle x'|\psi\rangle \\ &= \int dx'\delta(x-x')\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x'^2}+V(x')\right]\psi(x') \\ &= \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\psi(x)\end{aligned} \tag{4.26}$$

If $|\psi\rangle$ is an energy eigenstate $|E\rangle$, then we retrieve the *time-independent Schrödinger's equation*:

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\psi_E(x) = E\psi_E(x) \tag{4.27}$$

Note: For a free particles, since there is no potential energy term, the Hamiltonian commutes with the momentum operators and thus, energy eigenstates are also momentum eigenstates.

§4.3.1 Quantum Harmonic Oscillators

Consider the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m}+\frac{1}{2}m\omega^2x^2 \tag{4.28}$$

This is arguably the most relevant Hamiltonian since it would be the leading order term in the Taylor expansion of any attractive potential (potential well) around the equilibrium position. To solve this, we will be using the operator (algebraic) approach. First, notice that if the operators were simply numbers:

$$H = \frac{1}{2}m\omega^2\left(x+i\frac{p}{m\omega}\right)\left(x-i\frac{p}{m\omega}\right) \tag{4.29}$$

However, operators do not commute and the above expression is not exactly true. But we construct the following operators anyway:

$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x}+i\frac{\hat{p}}{m\omega}\right) \tag{4.30}$$

$$\Rightarrow \quad \hat{a}^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x}-i\frac{\hat{p}}{m\omega}\right) \tag{4.31}$$

Notice that these are **not** Hermitian operators so they are **not** observables. Writing their product, this grants us:

$$\begin{aligned}\hat{a}^\dagger\hat{a} &= \frac{m\omega}{2\hbar}\left(\hat{x}^2+\frac{\hat{p}^2}{m^2\omega^2}+\frac{i}{m\omega}[\hat{x},\hat{p}]\right) \\ &= \frac{1}{\hbar\omega}\hat{H}-\frac{1}{2}\mathbb{I}\end{aligned} \tag{4.32}$$

This operator is important enough that we give it a name, the *number operator*, where we write its definition as:

$$\boxed{\hat{N} \equiv \hat{a}^\dagger \hat{a}} \tag{4.33}$$

for which its name will become apparent soon. Not that the number operator and the Hamiltonian commute, so they share the same eigenstates which allow us to retrieve:

$$\begin{aligned} & \left[\hat{N}, \hat{H}\right] = 0 \\ \Rightarrow \quad & \hat{N} |n\rangle = n |n\rangle \\ \Rightarrow \quad & \boxed{\hat{H} |n\rangle = \hbar\omega \left(n + \frac{1}{2}\right) |n\rangle} \end{aligned} \tag{4.34}$$

Some other useful commutations with these a operators we've constructed are listed below.

1. $\left[\hat{N}, \hat{a}\right] = -\hat{a}$
2. $\left[\hat{N}, \hat{a}^\dagger\right] = \hat{a}^\dagger$

Now consider:

$$\begin{aligned} \left[\hat{N}, \hat{a}\right] |n\rangle &= \hat{N}\hat{a} |n\rangle - \hat{a}\hat{N} |n\rangle \\ &= \hat{a} |n\rangle \end{aligned} \tag{4.35}$$

$$\Rightarrow \quad \hat{N} \left(\hat{a} |n\rangle\right) = (n-1)\hat{a} |n\rangle \tag{4.36}$$

And we can also similarly show that:

$$\hat{N} \left(\hat{a}^\dagger |n\rangle\right) = (n)\hat{a} |n+1\rangle \tag{4.37}$$

These results give us that:

$$\boxed{\hat{a} |n\rangle = \sqrt{n} |n-1\rangle \quad \text{and} \quad \hat{a}^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle} \tag{4.38}$$

So they are given the names the *raising/creation* and *lowering/annihilation* operators, also known as the *ladder operators* collectively. The way we've defined these operators, we also have:

$$\hat{a} |0\rangle = 0, \quad \text{and} \quad n \in \mathbb{N} \tag{4.39}$$

From these ladder operators, we can construct any eigenstate state from the groundstate via the relation:

$$\boxed{|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}} |0\rangle} \tag{4.40}$$

Let's now look for the explicit form of the ground state in the x basis. We can do this by creating a differential equation as follows:

$$\begin{aligned} & \langle x|\,\hat{a}\,|0\rangle = 0 \\ \Rightarrow \quad & \sqrt{\frac{m\omega}{2\hbar}}\,\langle x|\left[\hat{x} + i\frac{\hat{p}}{m\omega}\right]|0\rangle = 0 \\ \Rightarrow \quad & \left[\hat{x} + \frac{\hbar}{m\omega}\frac{\partial}{\partial x}\right]\langle x|0\rangle = 0 \\ \Rightarrow \quad & \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\exp\!\left\{-\frac{m\omega}{2\hbar}x^2\right\} \end{aligned} \tag{4.41}$$

Then if we want to find any of the excited states, we can simply just apply the raising operator and close the bracket with a $\langle x|$ to get these:

$$\boxed{\psi_n(x) = \langle x|\,\frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\,|0\rangle} \tag{4.42}$$

"*Now that I have told you how to derive these wavefunctions, I'm going to tell you you won't need it!*"

– E. Neil (2019)

We will see in a bit a general form for the wavefunctions of a quantum harmonic oscillator in the x basis. First we note the relations:

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}^\dagger + \hat{a}) \tag{4.43}$$

$$\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}}(\hat{a}^\dagger - \hat{a}) \tag{4.44}$$

If we now consider the $\hat{X}$ operator in the number (energy) eigen-basis, this gives us the nice relation:

$$\begin{aligned} \langle n'|\,\hat{x}\,|n\rangle &= \sqrt{\frac{\hbar}{2m\omega}}\,\langle n'|\,(\hat{a}^\dagger + \hat{a})\,|n\rangle \\ &= \sqrt{\frac{\hbar}{2m\omega}}\left[\delta_{n',n+1}\sqrt{n+1} + \delta_{n',n-1}\sqrt{n}\right] \end{aligned} \tag{4.45}$$

which allows us to think of these as having a matrix representation with entries specified by the values $\langle n'|\,\hat{x}\,|n\rangle$.

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\begin{bmatrix} 0 & 1 & & \cdots & \\ 1 & 0 & \sqrt{2} & & \\ & \sqrt{2} & 0 & \sqrt{3} & \\ \vdots & & \sqrt{3} & 0 & \sqrt{4} \\ & & & \ddots & \end{bmatrix} \tag{4.46}$$

It turns out that if we try to write the eigenket $|x\rangle$ as a vector, then apply the $\hat{x}$ matrix on it in the eigenvalue equation, we find a recurrence relation that dictates the form of the coefficients in the number basis (energy basis):

$$\begin{aligned} c_n &= \langle n|x\rangle \\ &= \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left\{-\frac{m\omega}{2\hbar}x^2\right\} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \end{aligned} \tag{4.47}$$

where these H_n functions are known as *Hermite polynomials*.

Chapter 5

Quantum Dynamics

Thus far, we have looked into the time-independent states of a system and gone through formalisms of working with kets and wavefunction objects in quantum mechanics. We are now going to look at what is known as time-evolution, which will allow us to study the dynamics of a quantum system.

§5.1 Unitary Time-Evolution

Looking back at postulate 5 of quantum mechanics, we recall that it states:

$$i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{H}\left|\psi(t)\right\rangle \tag{5.1}$$

The solution to this differential equation is given as:

$$\boxed{\left|\psi(t)\right\rangle = \exp\left\{-\frac{i}{\hbar}\hat{H}(t-t_0)\right\}\left|\psi(t)\right\rangle} \tag{5.2}$$

The exponential operator is in fact unitary, which leads to *conservation of probability.* In practice, there are several ways to define the exponential of an operator.

1. **Taylor Expansion**:

$$\exp\left\{-\frac{i}{\hbar}\hat{H}(t-t_0)\right\} = \mathbb{I} - \frac{i}{\hbar}(t-t_0)\hat{H} - \frac{\hbar^2}{2}(t-t_0)^2\hat{H}^2 + \dots \tag{5.3}$$

   This is useful in situation where the series terminates ($\hat{H} \propto 1$ or 0) or the higher order terms are effectively very small (negligible), allowing us to truncate the series.

2. **Energy Eigenstates**:

$$\begin{aligned} |\psi(t)\rangle &= \sum_E \exp\left\{-\frac{i}{\hbar}\hat{H}(t-t_0)\right\} |E\rangle \langle E|\psi(t)\rangle \\ &= \sum_E \exp\left\{-\frac{i(t-t_0)E}{\hbar}\right\} |E\rangle \langle E|\psi(t)\rangle \end{aligned} \tag{5.4}$$

So we see that the energy eigenstates evolve with just a pure phase (this is also true for eigenstates of any observable that commutes with the Hamiltonian).

§5.1.1 General 2-State Systems

Because of Hermiticity of the Hamiltonian, we find that we can actually write the most general Hamiltonian of a 2-state system as:

$$\hat{H} = \begin{bmatrix} \epsilon_1 & \delta \\ \delta^* & \epsilon_2 \end{bmatrix} \tag{5.5}$$

where $\epsilon_j \in \mathbb{R}$ and $\delta \in \mathbb{C}$. Diagonalizing this, we get the eigen-energies are:

$$\boxed{E_\pm = \frac{\epsilon_1 + \epsilon_2}{2} \pm \sqrt{\left(\frac{\epsilon_1 - \epsilon_2}{2}\right)^2 + |\delta|^2}} \tag{5.6}$$

As for the eigenstates:

$$|+\rangle = \begin{bmatrix} \cos\theta \\ e^{i\phi}\sin\theta \end{bmatrix}, \quad |-\rangle = \begin{bmatrix} -e^{-i\phi}\sin\theta \\ \cos\theta \end{bmatrix} \tag{5.7}$$

where θ and ϕ are real parameters. Plugging this and the matrix into the eigenvalue equation, we get that:

$$e^{i\phi} = \delta^*/|\delta| \tag{5.8}$$

$$\tan\theta = \frac{\epsilon_1 - \epsilon_2}{2|\delta|} - \sqrt{1 + \left(\frac{\epsilon_1 - \epsilon_2}{2|\delta|}\right)^2} \tag{5.9}$$

This tells us that we can actually generically write the Hamiltonian in the energy basis as:

$$\hat{H} = \frac{1}{2}(\epsilon_1 + \epsilon_2)\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + \begin{bmatrix} \epsilon & \delta \\ \delta^* & -\epsilon \end{bmatrix} \tag{5.10}$$

where $\epsilon \equiv (\epsilon_1 - \epsilon_2)/2$. Now if we define:

$$\lambda = \frac{|\delta|}{\epsilon} \tag{5.11}$$

$$\Rightarrow \quad \tan(2\theta) = \lambda \tag{5.12}$$

From here if we consider the following limits.

1. $|\delta|/\epsilon \ll 1$:

$$\begin{aligned} E_+ &= \epsilon_1 + \frac{|\delta|^2}{\epsilon_1 - \epsilon_2} \\ E_- &= \epsilon_2 - \frac{|\delta|^2}{\epsilon_1 - \epsilon_2} \end{aligned} \tag{5.13}$$

2. $|\delta|/\epsilon \gg 1$:

$$E_\pm = \frac{\epsilon_1 + \epsilon_2}{2} \pm |\delta| \tag{5.14}$$

So if we plot this, we see the energies behave with asymptotic behaviour as shown in figure 5.1 below.

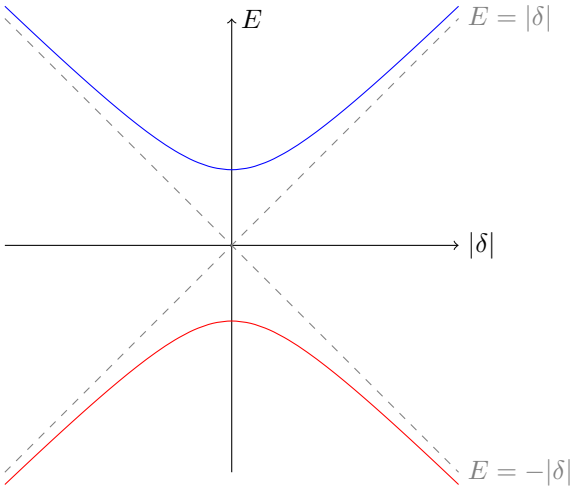


Figure 5.1: Energy profiles against $|\delta|$

This gives rise to the *no-crossing theorem* of the energies.

Example 1 (Larmor Precession):

Consider a 2 state system where we have an electron in an external magnetic field $\vec{B}$. The Hamiltonian of this system is then given by:

$$\begin{aligned} \hat{H} &= -\vec{\mu} \cdot \vec{B} \\ &= \frac{e}{m_e c} \hat{\vec{S}} \cdot \vec{B} \\ &= \frac{e}{m_e c} \frac{\hbar}{2} \hat{\vec{\sigma}} \cdot \vec{B} \\ &= \frac{e\hbar}{m_e c} \begin{bmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{bmatrix} \end{aligned} \tag{5.15}$$

We can also define an angular frequecy for this problem:

$$\omega = \frac{e|B|}{m_e c} \tag{5.16}$$

From here, we can always choose a convenient coordinate system such that $\vec{B} = B_z \hat{z}$, which gives us that:

$$\hat{H} = \frac{\hbar\omega}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{5.17}$$

which give us that the eigenvalues are:

$$E_\pm = \pm\frac{\hbar}{2} \tag{5.18}$$

$$\Rightarrow \quad |\psi(t)\rangle = \alpha e^{-i\omega t/2}|+\rangle + \beta e^{i\omega t/2}|-\rangle \tag{5.19}$$

This grants us that if we start at anyone one of the z eigenstates, we will remain in that eigenstate for all time (check this for yourself!). Now consider if we start instead with $|\psi(0)\rangle = (|+\rangle + |-\rangle)/\sqrt{2}$. So we check the probability of obtaining this state in time as follows:

$$\begin{aligned} \mathbb{P}\left(S_x = +\frac{\hbar}{2}\right) &= |\langle\psi(0)|\psi(t)\rangle|^2 \\ &= \frac{1}{4}\left|(\langle+| + |-\rangle)\left(e^{-i\omega t/2}|+\rangle + e^{i\omega t/2}|-\rangle\right)\right|^2 \\ &= \cos^2\left(\frac{\omega t}{2}\right) \end{aligned} \tag{5.20}$$

and similarly if we start with $|\psi(0)\rangle = (|+\rangle - |-\rangle)/\sqrt{2}$, we will get the probability:

$$\mathbb{P}\left(S_x = +\frac{\hbar}{2}\right) = \sin^2\left(\frac{\omega t}{2}\right) \tag{5.21}$$

where the expectation value of $\langle\hat{S}_x(t)\rangle$ is given as $\hbar\cos(\omega t)/2$, and for the other 2 axes, $\langle\hat{S}_y(t)\rangle = \hbar\sin(\omega t)/2$ and $\langle\hat{S}_z(t)\rangle = 0$. So we see that the spin in fact precesses with the defined frequency ω. It turns out that there is a general precession frequency in quantum mechanics called the *Larmor frequency* given by:

$$\omega = \frac{eg|B|}{2m_e c} \tag{5.22}$$

where g is called the *g-factor*, for which it is 1 for classical objects and ≈ 2 for electrons (g is **not** exactly two for the electron. Quantum electrodynamics predicts small corrections as a power series in the fine-structure constant $\alpha \approx 1/137$.). The previously defined frequency is actually known as the *cyclotron frequency* (without the factor $g/2$, where a classical charge of magnitude e will undergo circular motion in a transverse magnetic field with that angular frequency).

Example 2:

Now consider the experiment where we inject a beam of muons into a storage ring which accelerates the muons around at the cyclotron frequency. Since muons are ustable, we use this to measure $\langle \hat{S}_x \rangle$ in the muons by looking for the decay $\mu^- \to e^- + 2\nu$ and measuring the direction of emitted electrons (which will allow us to then compute the muon spin). If $g = 2$, we in fact see no time-dependence in the electron direction at all. However, the experimental results produced a modulated signal with:

$$\omega_a = \frac{(g-2)e|B|}{2m_e c} \tag{5.23}$$

This experiment was done at Brookhaven, for which the period of this modulated oscillations was measured to be $\sim 5\mu s$, where the value stated in the paper was:

$$\frac{g_\mu - 2}{2} = 0.0011659208(5)(3) \tag{5.24}$$

The Standard Model of particle physics predicts a value of the muon $g-2$ which is very close to the number given above, but actually around 4 standard deviations away from it based on the best estimates of the theoretical uncertainty, leading us to believe in new physics to be discovered.

§5.2 General 2-State Time-Evolution

Now, we go into a generalized treatment of 2-state systems and its time-evolution which will eventually lead us into the Heisenberg picture of quantum mechanics. We start with the Hamiltonian:

$$\hat{H} = \frac{\hbar\omega}{2}\hat{\vec{\sigma}} \cdot \hat{n} \tag{5.25}$$

Plugging this into the unitary time-evolution operator, we get:

$$\hat{U}(t) = \exp\Big\{-i\frac{\omega}{2}\hat{\vec{\sigma}} \cdot \hat{n}t\Big\} \tag{5.26}$$

To work this out, we first need the identity:

$$\boxed{\hat{\sigma}_i\hat{\sigma}_j = i\varepsilon_{ijk}\hat{\sigma}_k + \mathbb{I}\delta_{ij}} \tag{5.27}$$

where *Einstein-summation* convention is used above (you should prove this as an exercise). Using this identity, we obtain:

$$\begin{aligned} \hat{\vec{\sigma}} \cdot \hat{n} &= \hat{\sigma}_i\hat{\sigma}_j n_i n_j \\ &= \left(i\varepsilon_{ijk}\hat{\sigma}_k + \mathbb{I}\delta_{ij}\right) n_i n_j \\ &= \mathbb{I} \end{aligned} \tag{5.28}$$

where we used the fact that $\varepsilon_{ijk}n_in_j = 0$ (since ε_{ijk} is anti-symmetric and n_in_j is symmetric) and $n_in_j = 1$. As such, our unitary operator simplifies to:

$$\begin{aligned}\exp\Big\{-i\frac{\omega}{2}\hat{\vec{\sigma}}\cdot\hat{n}t\Big\} &= \sum_{k=0}^{\infty}\frac{1}{k!}\left[\frac{i\omega t}{2}\hat{\vec{\sigma}}\cdot\hat{n}\right]^k \\ &= \sum_{k=0}^{\infty}\left[\frac{1}{(2k)!}(i\omega t)^{2k}\mathbb{I} + \frac{1}{(2k+1)!}(i\omega t)^{2k+1}\left(\hat{\vec{\sigma}}\cdot\hat{n}\right)\right] \\ \Rightarrow\quad \hat{U}(t) &= \mathbb{I}\cos\frac{\omega t}{2} - i\left(\hat{\vec{\sigma}}\cdot\hat{n}\right)\sin\frac{\omega t}{2}\end{aligned} \tag{5.29}$$

Example (Magnetic Resonance):

Here, we will have explicit time-variation in the Hamiltonian. First, we consider a spin-particle in an external magnetic field which goes as:

$$\vec{B} = [b\cos(\nu t), b\sin(\nu t), B]^T \tag{5.30}$$

We choose the coordinate frame such that the Hamiltonian is:

$$\hat{H} = \frac{\hbar\omega}{2}\hat{\sigma}_z + \frac{\hbar\Omega_0}{2}\left(\hat{\sigma}_x\cos(\nu t) + \hat{\sigma}_y\sin(\nu t)\right) \tag{5.31}$$

$$= \frac{\hbar}{2}\begin{bmatrix}\omega & \Omega_0 e^{-i\omega t}\\ \Omega_0 e^{i\omega t} & -\omega\end{bmatrix} \tag{5.32}$$

where again, ω is the Larmor frequency and $\Omega_0 = e|b|/mc$. Now we consider some state $|\psi(t)\rangle = [a_+, a_-]^T$, we plug this into the Schrödinger's equation, we have:

$$2i\frac{da_+}{dt} = \omega a_+ + \Omega_0\exp\{-i\omega t\}a_- \tag{5.33}$$

$$2i\frac{da_-}{dt} = \Omega_0\exp\{i\omega t\}a_+ - \omega a_- \tag{5.34}$$

We try the ansatz:

$$a_\pm(t) = A_\pm\exp\{-i\lambda_\pm t\} \tag{5.35}$$

This grants us:

$$\begin{bmatrix}2\lambda_+ - \omega & -\Omega_0\exp\{-i(\nu - \lambda_+ + \lambda_-)t\}\\ -\Omega_0\exp\{i(\nu - \lambda_+ + \lambda_-)t\} & 2\lambda_- + \omega\end{bmatrix}\begin{bmatrix}A_+\\ A_-\end{bmatrix} = \vec{0} \tag{5.36}$$

Notice that if we set $\lambda_+ = \lambda_- + \nu$, the equation above is no longer time-dependent:

$$\begin{bmatrix}2(\lambda_- + \nu) - \omega & -\Omega_0\\ -\Omega_0 & 2\lambda_- + \omega\end{bmatrix}\begin{bmatrix}A_+\\ A_-\end{bmatrix} = \vec{0} \tag{5.37}$$

We now assert for the existence of a solution by taking the determinant and setting it to 0:

$$\Rightarrow\quad \lambda_- = -\frac{\nu}{2} \pm \sqrt{\Omega_0^2 + (\nu - \omega)^2} \tag{5.38}$$

Now defining $\Omega \equiv \sqrt{\Omega_0^2 + (\nu - \omega)^2}$, we finally get:

$$a_-(t) = A_-^{(1)} \exp\left\{-i\left(\Omega - \frac{\nu}{2}\right)t\right\} + A_-^{(2)} \exp\left\{-i\left(-\Omega - \frac{\nu}{2}\right)t\right\} \tag{5.39}$$

To get these coefficients, we need initial conditions, so we choose that the initial state be $|\psi(0)\rangle = |+\rangle$. This gives us:

$$a_-(t) = A \exp\left\{\frac{i\omega t}{2}\right\} \sin(\Omega t) \tag{5.40}$$

Then plugging this again into the Schrödinger's equation and evaluating the ansatz at $t = 0$, we get:

$$\begin{aligned} & A\Omega = \Omega_0 \\ \Rightarrow \quad & a_-(t) = \frac{\Omega_0}{\Omega} \exp\left\{\frac{i\omega t}{2}\right\} \sin(\Omega t) \\ \Rightarrow \quad & \boxed{\mathbb{P}(-) = \frac{\Omega_0^2}{\Omega_0^2 + (\omega - \nu)^2} \sin^2(\Omega t)} \end{aligned} \tag{5.41}$$

which shows a resonance for obtaining the $|-\rangle$ state that occurs when $\omega \approx \nu$ and Ω_0 is small. The probability will be more sharply peaked as the strength of the rotating field b becomes small.

So far we have solved problems in quantum mechanics with 3 different techniques.

1. Operator Methods.
2. Eigenvalue Decomposition.
3. Differential Equations.

Often, there are more than one way to solve a quantum mechanical problem but there is often a better way to approach solving problems.

§5.3 The Heisenberg Picture

Thus far we have been using the SChrödinger picture where this is governed by:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}\psi(t) \tag{5.42}$$

So only the state-vectors evolve in time and not the operators. We have also seen that if we solve this equation, we get:

$$\psi(t) = e^{-i\hat{H}t/\hbar}\psi(0) \tag{5.43}$$

However, now we ask the question, "*what if the Hamiltonian is time-dependent*?". We know that time-evolution operators must always be unitary, so we know even in the time-dependent case,

we must have an expression like:

$$\psi(t) = \hat{H}(t)\psi(0) \tag{5.44}$$

It turns out that this unitary can be explicitly expressed as:

$$\hat{U}(t) = \exp\left\{-\frac{i}{\hbar}\int_0^t \hat{H}(t)dt\right\} \tag{5.45}$$

given that the Hamiltonian at any 2 given times commute. Now if they don't commute at different times, we have to use a *Dyson series*:

$$\hat{U}(t) = \mathbb{I} + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n \hat{H}(t_1)\hat{H}(t_2)\ldots\hat{H}(t_n) \tag{5.46}$$

The inner product of 2 states can be written equivalently as:

$$\begin{aligned}\langle\alpha(t)|\beta(t)\rangle &= \langle\alpha(t)|\,\hat{U}^\dagger(t)\hat{U}(t)\,|\beta(t)\rangle \\ &= \langle\alpha(0)|\beta(0)\rangle\end{aligned} \tag{5.47}$$

This grants us:

$$\begin{aligned}\langle\alpha(t)|\,\hat{A}\,|\beta(t)\rangle &= \langle\alpha(t)|\,\hat{U}^\dagger(t)\hat{A}\hat{U}(t)\,|\beta(t)\rangle \\ &\neq \langle\alpha(0)|\beta(0)\rangle \quad \text{unless} \quad \left[\hat{A},\hat{H}\right] = 0\end{aligned} \tag{5.48}$$

We can then write that the operator is what is time-dependent instead of the state-vectors:

$$\begin{aligned}&\langle\alpha(t)|\,\hat{A}\,|\beta(t)\rangle = \langle\alpha(0)|\,\hat{A}(t)\,|\alpha(0)\rangle \\ \Rightarrow\quad &\boxed{\hat{A}^H(t) = \hat{U}^\dagger(t)\hat{A}^S\hat{U}(t)}\end{aligned} \tag{5.49}$$

This formalism is known as the *Heisenberg picture* of quantum mechanics, where the H and S superscripts stand for Heisenberg and Schrödinger respectively. This picture allows us to better connect to classical mechanics because there is not really a corresponding quantity to the state-vector, but there are time-dependent observables in classical mechanics. Now consider the time derivative of a Heisenberg operator:

$$\begin{aligned}\frac{d}{dt}\hat{A}^H(t) &= \frac{d}{dt}\hat{U}^\dagger(t)\hat{A}^S\hat{U}(t) \\ &= \frac{d\hat{U}^\dagger(t)}{dt}\hat{A}^S\hat{U}(t) + \hat{U}^\dagger(t)\hat{A}^S\frac{d\hat{U}(t)}{dt} \\ &= -\frac{1}{i\hbar}\hat{H}\frac{d}{dt}\hat{U}^\dagger(t)\hat{A}^S\hat{U}(t) + \frac{1}{i\hbar}\frac{d}{dt}\hat{U}^\dagger(t)\hat{A}^S\hat{U}(t)\hat{H} \\ &= i\hbar\left[\hat{A}^H,\hat{H}\right]\end{aligned} \tag{5.50}$$

More generally, if we observable $\hat{A}$ already had explicit time-dependence (which does not vary according to the Hamiltonian) in the Schrödinger picture, we have:

$$\boxed{\frac{d}{dt}\hat{A}^H(t) = i\hbar\Big[\hat{A}^H, \hat{H}\Big] + \hat{U}^\dagger(t)\frac{\partial \hat{A}^S}{\partial t}\hat{U}(t)} \tag{5.51}$$

Recall that in Hamiltonian mechanics:

$$\frac{dA}{dt} = \{A, H\}_{pq} + \frac{\partial A}{\partial t} \tag{5.52}$$

where $\{\ ,\ \}$ is the Poisson bracket defined as:

$$\{f, g\}_{qp} = \sum_j \left[\frac{\partial f}{\partial q_j}\frac{\partial g}{\partial p_j} - \frac{\partial f}{\partial p_j}\frac{\partial g}{\partial q_j}\right] \tag{5.53}$$

So in the early days, the procedure to *quantize* system was to let:

$$\{\ ,\ \} \quad \to \quad \frac{1}{i\hbar}[\ ,\ ] \tag{5.54}$$

which was called *Dirac's quantization*. However, this often fails when there really is no classical corresponding system such as spin. It is now a good time to look at some useful commutator identities.

1. $[\hat{x}, \hat{p}^n] = ni\hbar\hat{p}^{n-1}$
2. $\Big[\hat{x}_j, f(\hat{\vec{p}})\Big] = i\hbar\frac{\partial f}{\partial \hat{p}_j}$
3. $[\hat{p}, \hat{x}^n] = -ni\hbar\hat{x}^{n-1}$
4. $\Big[\hat{p}_j, g(\hat{\vec{x}})\Big] = -i\hbar\frac{\partial g}{\partial \hat{x}_j}$

Note: In the Heisenberg picture, we have:

$$|a; t\rangle = \hat{U}^\dagger(t)\,|a; 0\rangle \tag{5.55}$$

which is the opposite of how time-evolution occurs in the Schrödinger picture (analogous to active and passive transformations).

Example 1:

Consider the single free-particle Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} \tag{5.56}$$

In the Heisenberg picture (dropping all the superscripts), we have:

$$\frac{d\hat{p}}{dt} = \frac{1}{i\hbar}\Big[\hat{p}, \hat{H}\Big] = 0 \tag{5.57}$$

$$\frac{d\hat{x}}{dt} = \frac{1}{i\hbar}\Big[\hat{x}, \hat{H}\Big] = \frac{1}{2mi\hbar}\left(i\hbar\frac{\partial \hat{H}_0}{\partial \hat{p}}\right) = \frac{\hat{p}}{m} \tag{5.58}$$

These results grant us that:

$$\hat{x}(t) = \hat{x}(0) + \frac{\hat{p}(0)}{m}t \tag{5.59}$$

which is the classical result for a free-particle! However, note now that:

$$\begin{aligned} [\hat{x}(t), \hat{x}(0)] &= -\frac{i\hbar t}{m} \\ \Rightarrow \quad \Delta x(t)\Delta x(0) &\geq \frac{\hbar t}{2m} \end{aligned} \tag{5.60}$$

which tells us that the uncertainty relation in the initial and current positions increase in time.

Example 2:

Now if we don't have a free-particle, that is a particle subject to some potential energy. We get:

$$\frac{d\hat{p}}{dt} = \frac{1}{i\hbar}[\hat{p}, V(\hat{x})] = -\frac{\partial V}{\partial \hat{x}} \tag{5.61}$$

which looks very much like Newton's second law. But to get something that is actually physical, we need to take expectation values which gives:

$$\frac{d^2\langle \hat{x}\rangle}{dt^2} = -\langle \frac{\partial V}{\partial \hat{x}}\rangle \tag{5.62}$$

This can be generalized to 3D to give:

$$\boxed{\frac{d^2\langle \hat{x}\rangle}{dt^2} = -\langle \boldsymbol{\nabla}_x V(\hat{x})\rangle} \tag{5.63}$$

which is known as the *Ehrenfest's theorem*.

Now, we list some properties of Heisenberg operators.

1. Time evolution does **not** change the spectrum of the operator:

$$\begin{aligned} \hat{A}^S \left|a\right\rangle &= a \left|a\right\rangle \\ \Rightarrow \quad \hat{A}^H(t) \left|a; t\right\rangle &= a \left|a; t\right\rangle \end{aligned} \tag{5.64}$$

2. If we use the set $\{\hat{a}\}$ as a basis, then in the Heisenberg picture, we have:

$$|\psi\rangle^{(H)} = \sum_a c_a^{(H)}(t)\,|a(t)\rangle \tag{5.65}$$

where the way the coefficients and basis vectors evolve in time has to exactly cancel since we state-vector in the Heisenberg picture remains time-independent (analogous to passive transformations).

§5.3.1 Heisenberg Picture Time-Evolution of the QHO

Recall the Hamiltonian for the quantum harmonic oscillator:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 \tag{5.66}$$

In the Heisenberg picture (again dropping all the H superscripts), we have:

$$\begin{aligned} \frac{d\hat{p}}{dt} &= \frac{1}{i\hbar}\Big[\hat{p},\hat{H}\Big] = -m\omega^2\hat{x}^2 \\ \frac{d\hat{x}}{dt} &= \frac{1}{i\hbar}\Big[\hat{x},\hat{H}\Big] = \frac{1}{2mi\hbar}\left(i\hbar\frac{\partial\hat{H}_0}{\partial\hat{p}}\right) = \frac{\hat{p}}{m} \end{aligned} \tag{5.67}$$

$$\begin{aligned} \Rightarrow\quad \hat{x}(t) &= \hat{x}(0)\cos(\omega t) + \frac{\hat{p}(0)}{m\omega}\sin(\omega t) \\ \hat{p}(t) &= -m\omega\hat{x}(0)\sin(\omega t) + \hat{p}(0)\cos(\omega t) \end{aligned} \tag{5.68}$$

With the commutation relations above, we also have that:

$$\begin{aligned} \frac{d\hat{a}}{dt} &= \sqrt{\frac{m\omega}{2\hbar}}\left[\frac{\hat{p}}{m} - \frac{im\omega^2\hat{x}}{m\omega}\right] = -i\omega\hat{a}^\dagger \\ \Rightarrow\quad \hat{a}(t) &= e^{-i\omega t}\hat{a}(0) \\ \hat{a}^\dagger(t) &= e^{i\omega t}\hat{a}^\dagger(0) \end{aligned} \tag{5.69}$$

And if we apply a theorem known as the Baker-Hausdorff formula, we get:

$$\Big[\hat{H},\hat{x}(0)\Big] = -\frac{i\hbar}{m}\hat{p}(0) \tag{5.70}$$

$$\Big[\hat{H},\hat{p}(0)\Big] = i\hbar m\omega^2\hat{x}(0) \tag{5.71}$$

Theorem 5.3.1. Baker-Hausdorff Theorem: *For any 2 Hermitian operators $\hat{A}$ and $\hat{G}$, then:*

$$e^{i\lambda\hat{G}}\hat{A}e^{-i\lambda\hat{G}} = \hat{A} + i\lambda\Big[\hat{G},\hat{A}\Big] - \frac{\lambda^2}{2}\Big[\hat{G},\Big[\hat{G},\hat{A}\Big]\Big] + \ldots + \left(\frac{(i\lambda)^n}{n!}\right)\Big[\hat{G},\Big[\hat{G},\Big[\ldots,\Big[\hat{G},\hat{A}\Big]\Big]\Big]\Big] \tag{5.72}$$

§5.4 The Interaction Picture

There are actually other ways of looking at the states and operators of quantum mechanics that have usefulness in certain circumstances. The one we will be looking at is called the *interaction picture*. In this picture, we split the Hamiltonian into 2 parts:

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{5.73}$$

where $\hat{H}_0$ is either time-independent, relatively simple, much smaller than $\hat{V}$ or all of the above. The interaction picture states are then written as:

$$|\psi(t)\rangle^{(I)} = e^{i\hat{H}_0 t/\hbar} |\psi(t)\rangle^{(s)} \tag{5.74}$$

$$\Rightarrow \quad \hat{O}^{(I)}(t) = e^{i\hat{H}_0 t/\hbar} \hat{O} e^{-i\hat{H}_0 t/\hbar} \tag{5.75}$$

$$\Rightarrow \quad i\hbar \frac{\partial}{\partial} |\psi(t)\rangle^{(I)} = \hat{V}^{(I)} |\psi(t)\rangle^{(I)} \tag{5.76}$$

Chapter 6

Wave Mechanics

We are going to take a step back now and solve the Schrödinger's equation using the method of ordinary differential equations to get continuous function solutions. This will lead to some very interesting insights that can be generalized to more complex systems. We will also begin discussions on scattering theory and using the formalism developed here to guide us through working through scattering problems.

§6.1 Probability Flux

We can think of the $|\psi(x)|^2$ as a probability density $\rho(x)$. Then given a general time-dependent wavefunction, we can define a notion of probability flux. First looking that the Schrödinger equation:

$$\begin{aligned} i\hbar\frac{\partial\rho(x,t)}{\partial t} &= i\hbar\frac{\partial}{\partial t}(\Psi^*\Psi) \\ &= i\hbar\frac{\partial\Psi^*}{\partial t}\Psi + i\hbar\frac{\partial\Psi}{\partial t}\Psi^* \\ &= \Psi^*\hat{H}\Psi + \Psi\hat{H}\Psi^* \\ &= -\frac{\hbar^2}{2m}\boldsymbol{\nabla}\cdot[\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*] \end{aligned} \tag{6.1}$$

where capital Ψ denotes the **time-dependent** wavefunction. Now defining a probability current $\vec{J}$ as:

$$\begin{aligned} &\vec{J} \equiv \frac{\hbar}{2im}\left[\Psi^*\boldsymbol{\nabla}\Psi - \Psi\boldsymbol{\nabla}\Psi^*\right] = \frac{\hbar}{m}\,\mathrm{Im}\{\Psi^*\boldsymbol{\nabla}\Psi\} \\ \Rightarrow\quad &\boxed{\frac{\partial\rho(x,t)}{\partial t} + \boldsymbol{\nabla}\cdot\vec{J} = 0} \end{aligned} \tag{6.2}$$

which is the *continuity equation*. In general, we can write the wavefunction in terms of its

probability density along with a phase:

$$\begin{aligned} & \psi = \sqrt{\rho} e^{iS/\hbar} \\ \Rightarrow \quad & \mathrm{Im}\{\Psi^* \boldsymbol{\nabla} \Psi\} = \mathrm{Im}\left\{ \sqrt{\rho} \boldsymbol{\nabla} \sqrt{\rho} + \frac{i}{\hbar} \rho \boldsymbol{\nabla} S \right\} \\ \Rightarrow \quad & \boxed{\vec{J} = \frac{\rho \boldsymbol{\nabla} S}{m}} \end{aligned} \tag{6.3}$$

So we see that the probability current is governed by the phase of the wavefunction.

§6.2 1D Potentials

We are now going to solve the time-independent Schrödinger's equation by means of methods in ordinary differential equations. To do so, we will start by looking at several specific forms for $V(x)$ and exploring where this intuition takes us. Specifically, we start our analysis in regimes where $E < 0$ which will give rise to *bound-states*.

§6.2.1 Delta-Function Potentials

To start, will study a potential that will illuminate facts about the continuity of the wavefunction. This is the (attractive) Dirac delta-function potential:

$$V(x) = -a\delta(x - x_0) \tag{6.4}$$

Checking continuity at the center of the delta-function:

$$\psi'(x_0 + \varepsilon) - \psi'(x_0 - \varepsilon) = \int_{x_0 - \varepsilon}^{x_0 + \varepsilon} \frac{2m}{\hbar^2} \left[a\delta(x - x_0) - E \right] \psi(x) = -\frac{2ma}{\hbar^2} \psi(x_0) \tag{6.5}$$

Which actually gives us a finite value and a very specific boundary condition for $\psi'(x)$. Fortunately, this still grants us that $\psi(x)$ is continuous. Below is a table (6.1) of general facts on continuity of the wavefunction and its derivative.

$V(x)$	Finite	$a\delta(x - x_0)$	∞
Continuity of $\psi(x)$	Yes	Yes	$\psi = 0$
Continuity of $\psi'(x)$	Yes	No	$\psi' = 0$

Table 6.1: Table of Wavefunction Continuity Conditions

Additionally, we have $\psi''(x)$ is continuous is $V(x)$ is, $\psi'''(x)$ is continuous if $V'(x)$ is and so on. In general, we have that (smooth $V(x) \iff$ smooth $\psi(x)$).

§6.2.2 Square-Well

Now we look to solving for bound-state ansatz with a model 1-d potential. This is the finite square-well potential. Solving this parity symmetric (symmetric about $x \to -x$) potential will also illuminate facts about parity operators which we will be using further down the road as well.

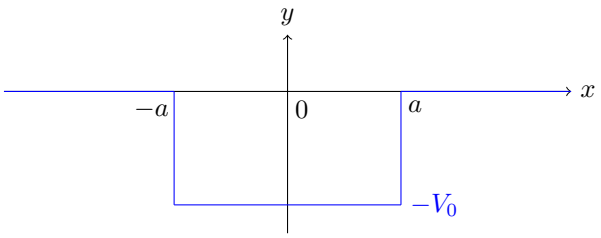


Figure 6.1: Square-well potential.

Consider the potential illustrated in figure 6.1 above:

$$V(x) = \begin{cases} -V_0, & |x| < a \\ 0, & |x| > a \end{cases} \tag{6.6}$$

Let us look at the case where $-V_0 < E < 0$. We define a term $\epsilon \equiv V_0 - |E|$. We know roughly what the wave-vectors of the solution would be like even before we solve it, which are:

$$k = \frac{\sqrt{2m\epsilon}}{\hbar}, \quad |x| < a \tag{6.7}$$

$$\kappa = \frac{\sqrt{2m|E|}}{\hbar}, \quad |x| > a \tag{6.8}$$

In this problem, we are going to exploit a symmetry known as *mirror reflection*, which is the symmetry of parity swaps in the coordinate variable ($x \to -x$). we can define this parity transformation as an operator $\hat{P}$, which has property:

$$\hat{P}^\dagger \hat{x} \hat{P} = -\hat{x} \tag{6.9}$$

It also works out that the parity operator is unitary. we note also that $\hat{P}^2 = \mathbb{I}$, so the symmetry group associated to $\hat{P}$ is $\mathbb{Z}^2$. To act on kets, these transform as:

$$\hat{P}^\dagger |\vec{x}\rangle = |-\vec{x}\rangle \tag{6.10}$$

It can be proven that if the Hamiltonian is invariant under the parity operator ($\hat{H} = \hat{P}^\dagger \hat{H} \hat{P}$), then it commutes with it. Because of this, we can find simultaneous eigenstates of the Hamiltonian and the parity operator. To diagonalize the parity operator:

$$\begin{aligned} & \hat{P} |P\rangle = P |P\rangle \\ \Rightarrow \quad & \hat{P}^2 |P\rangle = P^2 |P\rangle = |P\rangle \\ \Rightarrow \quad & \boxed{P = \pm 1} \end{aligned} \tag{6.11}$$

where $P = +1$ is known as positive-parity (even), and $P = -1$ is known as negative-parity (odd). So eigenstates associated to these even and odd parities would satisfy:

$$\psi_e(x) = \psi_e(-x) \tag{6.12}$$
$$\psi_o(x) = -\psi_o(-x) \tag{6.13}$$

So going back to our problem, we can have the even and odd wavefunction solutions to this parity symmetric potential to be:

$$\psi_e(x) = \begin{cases} A\cos(kx), & |x| < a \\ Be^{-\kappa|x|}, & |x| > a \end{cases} \tag{6.14}$$

$$\psi_o(x) = \begin{cases} A'\sin(kx), & |x| < a \\ B'e^{-\kappa|x|}, & |x| > a \end{cases} \tag{6.15}$$

Working through all these parity was useful because we now see that we have reduced our number of coefficients to just 4, as opposed to 6 previously. Working with the continuity conditions on ψ and ψ' we get:

$$\begin{aligned} \textbf{Even} \text{ parity}: &\quad (ka)\tan(ka) = \kappa a \\ \textbf{Odd} \text{ parity}: &\quad (ka)\cot(ka) = -\kappa a \end{aligned} \tag{6.16}$$

We are now going to define to variables that are functions of k, κ and a:

$$\xi \equiv ka, \quad \eta \equiv \kappa a \tag{6.17}$$

With this we get the transcendental relations:

$$\boxed{\xi\tan\xi = \eta, \quad \xi\cot\xi = -\eta} \tag{6.18}$$

Furthermore, by rearranging terms in the definitions, we arrive at:

$$\xi^2 + \eta^2 = \frac{2ma^2}{\hbar^2}V_0 \tag{6.19}$$

We can plot the transcendental relations and the circle equation in ξ and η above as follows (figures 6.2, 6.3).

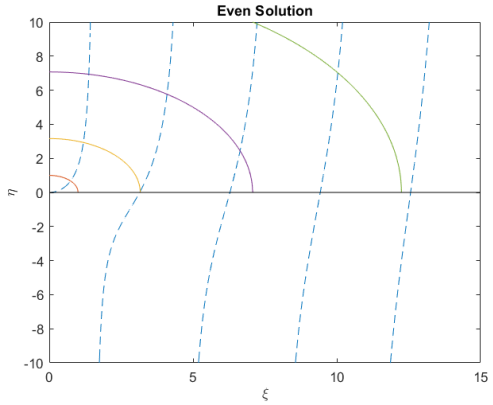


Figure 6.2: Blue dotted curves: $\xi \tan \xi = \eta$. Solid curves: $\xi^2 + \eta^2 = \frac{2ma^2}{\hbar^2} V_0$

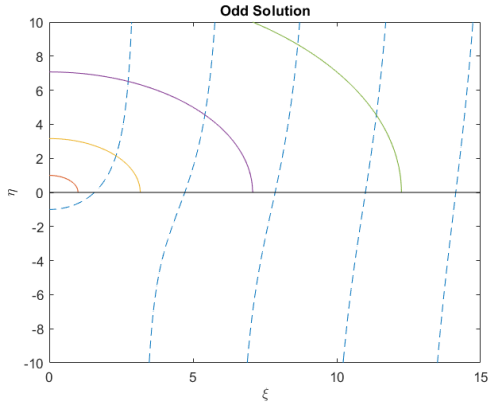


Figure 6.3: Blue dotted curves: $\xi \cot \xi = -\eta$. Solid curves: $\xi^2 + \eta^2 = \frac{2ma^2}{\hbar^2} V_0$

We can then check that if $V_0 \to 0$, we always find at least one even parity bound state, whereas if $V_0 \to \infty$, we get infinite square-well potential solutions. Also we see that there will never be an odd parity solution if:

$$\boxed{\sqrt{\frac{2mV_0a^2}{\hbar^2}} < \frac{\pi}{2}, \quad \Rightarrow \quad \textbf{no odd solutions.}} \tag{6.20}$$

Scattering Off the Well

Strangely enough in quantum mechanics, scattering can occur off potential wells even when the energy is larger than the depth of the well. Consider the case where $E > 0$, which would result in transmitted and reflected portions in the rectangular symmetric potential well. It works out

that the tranmission coefficient (probability of transmission) here works out to be:

$$\boxed{T = \left[1 + \frac{\sin^2(2k'a)}{4(E/V_0)(e/v_0 - 1)}\right]^{-1}} \tag{6.21}$$

where here, $k' = \sqrt{2m(E+V_0)}/\hbar$. We see that a transmission resonance occurs here when $2k'a = n\pi$ where $n \in \mathbb{N}$. Why this resonance occurs is because it is the case where the wavelength is exactly such that the reflected waves are exactly in phase with the transmitted waves, leading to constructive interference of the transmitted wave. We will be studying more on scattering theory in the next chapter. and how we derive transmission and reflection coefficients.

§6.2.3 Bound States and Zero-Point Energies

In quantum mechanics, we always have that bound states occur only when $E > V_0$, where $V_0 = \min\{V(x)\}$. This is known as the zero-point energy.

Proof. Consider some energy eigenstate $|E\rangle$ and $\psi(x) = \langle x|E\rangle$. We know that:

$$\begin{aligned}
\langle \hat{T} \rangle &= \frac{1}{2m}\langle \hat{p}^2 \rangle \\
&= -\frac{\hbar^2}{2m}\int dx \psi^*(x)\frac{d^2}{dx^2}\psi(x) \qquad (6.22)\\
&= \frac{\hbar^2}{2m}\int dx \left|\frac{d\psi(x)}{dx}\right|^2 \\
\langle \hat{V} \rangle &= \int dx V(x)|\psi(x)|^2 \\
&\geq \int dx V_{\min}|\psi(x)|^2 \qquad (6.23)\\
\Rightarrow \quad E &= \langle \hat{T} \rangle + \langle \hat{V} \rangle > V_{\min} \qquad (6.24)
\end{aligned}$$

□

Why this is true is because of the uncertainty principle, because only way to saturate the potential inequality is to have $|\psi(x)|^2 = \delta(x - x_0)$ where at x_0, we have $V(x_0) = V_{\min}$. However, dictating this creates an enormous uncertainty in momentum. Knowing that $\langle \hat{p}^2 \rangle \geq (\Delta p)^2$, this means the kinetic energy is going to be very large so the inequality still holds.

§6.3 The Ammonia Maser

To get an application of wave mechanics and parity in a real physical system, we will now look at the Ammonia (NH_3, figure 6.4) maser.

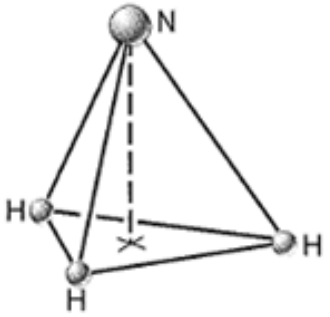


Figure 6.4: Ammonia molecule.

Here, we want to probe excited state of this molecule via emission lines and look at the spectral lines (types of excitations, i.e. what kinds of motions). There are several types of motion this molecule can undergo.

Excitation	**Frequency**
Inversion	Microwave
Rotation	Far-IR
Vibration	IR
Electronic	Visible/UV
Nuclear	Gamma

Table 6.2: Modes of Ammonia

The one we are going to study is the inversion motion, which corresponds to the molecule inverting it's structure. Inversion is **not** the same as vibration because it jumps discontinuously across some potential barrier unlike in vibration (perturbations about some equilibrium). The effective potential energy for this inversion mode is a 1D double-well potential (each well with the same minimum potential energy). Here, we use the reduced mass:

$$\mu = \frac{3m_H m_N}{3m_H + m_N} \tag{6.25}$$

We will make the approximation that the potential is effectively 2 square wells of widths a, each centered at $-b$ and b, while the height of the middle barrier is b:

$$V(x) = \begin{cases} V_0, & |x| < b - \frac{a}{2} \\ 0, & b - \frac{a}{2} \leq |x| \leq b + \frac{a}{2} \\ V_0, & |x| > b + \frac{a}{2} \end{cases} \tag{6.26}$$

we note that when $E < V_0$, inversion corresponds to tunneling between the 2 wells. First consider 2 infinite-square wells ($V_0 \to \infty$). This gives us the spectrum:

$$E_n = \frac{\hbar^2 k^2}{2m}, \quad k_n = \frac{n\pi}{a} \tag{6.27}$$

with solutions:

$$\psi_n^{(L)}(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left[k_n(b+\frac{a}{2}+x)\right], & b-\frac{a}{2} < -x < b+\frac{a}{2} \\ 0, & \text{otherwise} \end{cases} \tag{6.28}$$

$$\psi_n^{(R)}(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left[k_n(b+\frac{a}{2}+x)\right], & b-\frac{a}{2} < x < b+\frac{a}{2} \\ 0, & \text{otherwise} \end{cases} \tag{6.29}$$

where the L and R superscript corresponds to the solutions where the wavefunction is localized in either one of the left or right wells (since tunneling is impossible in this case). We now make a defintion:

$$\psi_n^{(e)}(x) = \frac{\psi_n^{(L)}(x) + \psi_n^{(R)}(x)}{\sqrt{2}}, \quad \psi_n^{(o)}(x) = \frac{\psi_n^{(L)}(x) - \psi_n^{(R)}(x)}{\sqrt{2}} \tag{6.30}$$

where these are even and odd parity functions. Now, let us lower this infinite potential barrier to a finite one (i.e. V_0 is finite). The most general form of the wave function outside the barrir in this case would be:

$$\psi(x) \begin{cases} A\sin(k(b+a/2-x)), & b-\frac{a}{2} < x < b+\frac{a}{2} \\ A'\sin(k(b+a/2+x)), & b-\frac{a}{2} < -x < b+\frac{a}{2} \end{cases} \tag{6.31}$$

Symmetry still helps us here as it asserts that for even parity, we have:

$$\textbf{even}\text{-parity}: \quad A_e = A'_e \tag{6.32}$$

$$\textbf{odd}\text{-parity}: \quad A_o = -A'_o \tag{6.33}$$

Then inside the barrier, we have:

$$\psi_e(x) = B_e\cosh(\kappa_e x), \quad \psi_o(x) = B_o\sinh(\kappa_o x) \tag{6.34}$$

where $\kappa = \sqrt{2m(V_0-E)/\hbar^2}$. To match these boundary conditions, we have for the even solution:

$$\begin{aligned} A_e\sin(k_e a) &= B_e\cosh(\kappa_e(b-a/2)) \\ -k_e A_e\cos(k_e a) &= B_e\kappa_e\sinh(\kappa_e(b-a/2)) \end{aligned} \tag{6.35}$$

$$\Rightarrow \quad \tan(k_e a) = \frac{k_e}{\kappa_e}\coth\kappa_e(b-a/2) \tag{6.36}$$

Doing the same for the odd solution, we have:

$$\tan(k_o a) = \frac{k_o}{\kappa_o}\tanh\kappa_o(b-a/2) \tag{6.37}$$

So we indeed see that as a direct result of this, we have $E_o \neq E_e$! More specifically, we have that $E_e < E_o$ (validated numerically). So this gives us an energy splitting away from the energy

value obtained from 2 separate infinite square-wells where $E_e < E_{isw}$ and $E_o > E_{isw}$. We also observe that:

$$E_o^{(1)} - E_e^{(1)} \ll E_2^{(2)} - E_o^{(1)} \tag{6.38}$$

where the superscripts denote the excitation of the state, 1 being the ground state. This allows us to study the inversion energy splitting as an effective 2-level system and look at it's time-dependence.

Note: In the limit where $V_0 \to 0$ for the problem above, we indeed retrieve the result for a single infinite-square well of width $2(a+b)$.

Consider the case where at $t = 0$, the state is majority localized in the right well:

$$|\psi(t=0)\rangle = \frac{\left|\psi_e^{(1)}\right\rangle + \left|\psi_o^{(1)}\right\rangle}{\sqrt{2}} \tag{6.39}$$

Time-evolution would be rather straight forward here since these are energy eigenstates:

$$\begin{aligned} |\psi(t=0)\rangle &= \frac{e^{-iE_e^{(1)}t/\hbar}\left|\psi_e^{(1)}\right\rangle + e^{-iE_o^{(1)}t/\hbar}\left|\psi_o^{(1)}\right\rangle}{\sqrt{2}} \\ &= e^{-i(E_e^{(1)}+E_o^{(1)})t/\hbar}\left[\frac{e^{-i\Omega^{(1)}t/2}\left|\psi_e^{(1)}\right\rangle + e^{-i\Omega^{(1)}t/2}\left|\psi_o^{(1)}\right\rangle}{\sqrt{2}}\right] \end{aligned} \tag{6.40}$$

where we define $\Omega^{(1)} = (E_o^{(1)} - E_e^{(1)})/\hbar$. So this would give us the probability density:

$$|\psi(x)|^2 = \frac{(\psi_e^{(1)})^2 + (\psi_o^{(1)})^2}{2} + \cos\Big(\Omega^{(1)}t\Big)\psi_e^{(1)}\psi_o^{(1)} \tag{6.41}$$

This grants us that at $t = 0$, we get $(\psi_e^{(1)} + \psi_o^{(1)})^2$ and at $t = \pi/\Omega^{(1)}$, we get $(\psi_e^{(1)} - \psi_o^{(1)})^2$. So we see that we have oscillation between the wells at a frequency:

$$\boxed{f = \frac{\Omega^{(1)}}{2\pi}} \tag{6.42}$$

This is not a unique case where we have a ground-state superposition has an energy lower than each ground-state by themselves. Another example of this is a Benzene ring. This implies that the superposition state is more stable then having only consider one of the 2 parity states (Read lecture 10 in the *Feynman lectures on quantum mechanics* for an explanation on this).

Now if were to do a 2-state system treatment of the Ammonia molecule, we can write its basis states as $\{|\psi_L'\rangle, |\psi_R'\rangle\}$. For $V_0 \to \infty$, the Hamiltonian can be written as:

$$\hat{H}_0 = \begin{bmatrix} E^{(1)} & 0 \\ 0 & E^{(1)} \end{bmatrix} \tag{6.43}$$

where $E^{(1)}$ is the ground-state energy of the infinite square-well. If we have a finite V_0 (but still large), then there must be off-diagonal terms, which would be the interaction terms between the 2-wells:

$$\hat{H}_0 = \begin{bmatrix} E^{(1)} & -A \\ -A & E^{(1)} \end{bmatrix} \tag{6.44}$$

where $A \in \mathbb{R}$ due to parity (proof is left to the reader, and $A > 0$ since we are working with a system where the even state has a lower energy than the odd state. We have solved this 2-state system before in general, and using those results, we get:

$$\begin{aligned} E_\pm &= E^{(1)} \pm A \\ \theta &= \frac{\pi}{4} \end{aligned} \tag{6.45}$$

$$\Rightarrow \quad |+\rangle = \frac{\left|\psi_L^{(1)}\right\rangle - \left|\psi_R^{(1)}\right\rangle}{\sqrt{2}}, \quad |-\rangle = \frac{\left|\psi_L^{(1)}\right\rangle + \left|\psi_R^{(1)}\right\rangle}{\sqrt{2}} \tag{6.46}$$

where A is a number associated to the height of the potential barrier. Indeed retrieving that the even parity eigenstate is of lower energy. Note that this is still an approximate solution since we are working with $V_0 \gg 1$. What if we now turn on an external electric field of magnitude ε along the axis of Nitrogen inversion? The molecule has a dipole moment:

$$\vec{D} = \sum_j q_j \vec{x}_j \tag{6.47}$$

This can be written as an operator:

$$\begin{aligned} \hat{D} &= \begin{bmatrix} -\mu & 0 \\ 0 & \mu \end{bmatrix} \\ \Rightarrow \quad \hat{H} &= \begin{bmatrix} E^{(1)} - \mu\varepsilon & 0 \\ 0 & E^{(1)} + \mu\varepsilon \end{bmatrix} \end{aligned} \tag{6.48}$$

Diagonalizing this, we get:

$$\begin{aligned} &E_\pm = E^{(1)} \pm \sqrt{\mu^2\varepsilon^2 + A^2} \\ &|\psi_-\rangle = \cos\theta\,|\psi_L\rangle + \sin\theta\,|\psi_R\rangle\,, \quad |\psi_-\rangle = -\sin\theta\,|\psi_L\rangle + \cos\theta\,|\psi_R\rangle \end{aligned} \tag{6.49}$$

So thie grants us:

$$\tan(2\theta) = \frac{A}{\mu\varepsilon} \tag{6.50}$$

Now consider the limit where $\mu\varepsilon \gg A$. That is, the energy eigenstates become localized in each well. Physically, we have a polarization such that one of the states become aligned and the other anti-aligned to the external field. We can show that:

$$\begin{aligned} \langle\psi_-|\,\hat{D}\,|\psi_-\rangle &= -\langle\psi_+|\,\hat{D}\,|\psi_+\rangle \\ &= \mu\cos(2\theta) = -\frac{\mu^2\varepsilon}{\sqrt{A^2 + \mu^2\varepsilon^2}} \end{aligned} \tag{6.51}$$

So we have induced a dipole moment in the molecule where it goes away as we turn off the electric field ($D \to 0$ as $\varepsilon \to 0$). Consider again the parity operator introduced earlier. Recall that this operator can only have eigenvalues ± 1 by construction. Now consider eigenstates of the parity operator $|\alpha\rangle$ and $|\beta\rangle$:

$$\begin{aligned} \langle\beta|\,\hat{x}\,|\alpha\rangle &= \langle\beta|\,\hat{P}^\dagger \hat{x} \hat{P}^\dagger \hat{P}\,|\alpha\rangle \\ &= -\varepsilon_\alpha \varepsilon_\beta \langle\beta|\,\hat{x}\,|\alpha\rangle \end{aligned} \tag{6.52}$$

where $\varepsilon_\alpha, \varepsilon_\beta = \pm 1$. From above, we get that:

$$\langle\beta|\,\hat{x}\,|\alpha\rangle = 0 \quad \text{if} \quad -\varepsilon_\alpha \varepsilon_\beta = -1, \varepsilon_\alpha = \varepsilon_\beta \tag{6.53}$$

$$\langle\beta|\,\hat{x}\,|\alpha\rangle \neq 0 \quad \text{if} \quad \varepsilon_\alpha \neq \varepsilon_\beta \tag{6.54}$$

This is known as a *selection rule*. Going back to the Ammonia molecule, we have that:

$$\begin{aligned} E_+ &\approx E_o^{(1)} + A + \frac{\mu^2 \varepsilon^2}{2A} \\ E_- &\approx E_e^{(1)} - A - \frac{\mu^2 \varepsilon^2}{2A} \end{aligned} \tag{6.55}$$

in the limit of $\mu\varepsilon \ll A$. So we have that the permanent dipole energy is proportional to ε, where we call the $\mu^2/2A$ term the *polarizability*. It turns out that Ammonia has a relatively small value of A, so we can indeed leverage this to make a beam of effectively pure $|\psi_+\rangle$ ammonia that would mimic the Stern-Gerlach experiment with silver atoms. The force on the Ammonia molecule would then be:

$$\vec{F} = \frac{\mu^2}{2A} \boldsymbol{\nabla}\left(\varepsilon^2\right) \tag{6.56}$$

An application of this is an Ammonia maser (microwave laser), by passing a beam of higher excited state Ammonia molecules $|\psi_+\rangle$ through a cavity with EM fields. This would produce stimulated emission of probability 1 as the Ammonia traverses the cavity, resulting in a laser.

Chapter 7

1D Quantum Scattering Theory

At this point, we move away from the study of bound-states in the wave mechanics formalism and instead, go into the regime of scattering. Quantum scattering for single particles is a process where the particle enters from a region of no potential, interacts with a localized potential, and then exits the effective range of this potential off into infinity. Scattering is an important concept and comes into play in many areas of physics (e.g. high energy physics, quantum field theories, AMO physics, condensed matter physics, etc...).

§7.1 1-d Scattering Potentials

§7.1.1 Step-Function Potential

To start our discussions of scattering, consider the potential as shown in figure 7.1 below.

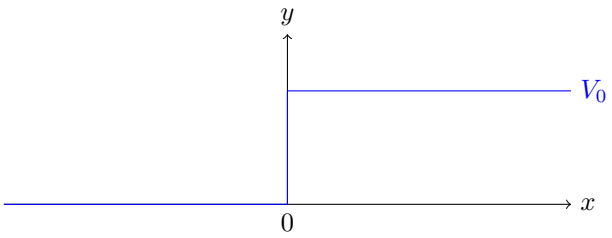


Figure 7.1: Step-function potential.

Formally, this can be written as:

$$V(x) = \begin{cases} V_0, & x \geq 0 \\ 0, & x < 0 \end{cases} \tag{7.1}$$

Since in everyone region, the potential is a constant, we get that the time-independent Schrödinger

equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + (V(x) - E)\psi(x) = 0 \tag{7.2}$$

$$\Rightarrow \quad \psi(x) = Ae^{ikx} + Be^{-ikx} \tag{7.3}$$

where $k = \sqrt{2m(E - V(x))/\hbar}$. There are several regimes we can look at the problem here.

1. $\underline{E < 0}$:

   In this regime (classically forbidden), we have that k would be imaginary and we get that the solutions blow up for $|x| \gg 1$. So there are no solutions here. In fact in general, there does **not** exist any solution for E being less than the global minimum of the potential $V_{\min}(x)$.

2. $\underline{0 < E \leq V_0}$:

   This grants the solution:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < 0 \quad (k = \sqrt{2mE/\hbar}) \\ Ce^{-\kappa x}, & x \geq 0 \quad (\kappa = \sqrt{2m(V_0 - E)/\hbar}) \end{cases} \tag{7.4}$$

   Now in order to find the coefficients A and B we need to look at the boundary conditions, where having a second-order differential equation, we must have 2 of these. These are that $\psi(x)$ and $\psi'(x)$ must be continuous at the boundary $x = 0$. Why this continuity must hold comes directly from the Schrödinger equation when we integrate it:

$$\psi'(x_0 + \varepsilon) - \psi'(x_0 - \varepsilon) = \int_{x_0-\varepsilon}^{x_0+\varepsilon} \frac{2m}{\hbar^2}\left[V(x) - E\right]\psi(x) \tag{7.5}$$

   where the right-hand side vanishes as $\varepsilon \to 0$. So this dictates that $\psi'(x)$ is continuous which also implies that $\psi(x)$ is continuous. Using these boundary conditions, we get that:

$$\begin{cases} A + B = C \\ ik(A - B) = -\kappa C \end{cases} \tag{7.6}$$

$$\Rightarrow \quad \begin{cases} \frac{B}{A} = \frac{ik+\kappa}{ik-\kappa} \\ \frac{C}{A} = \frac{2ik}{ik-\kappa} = 1 + \frac{B}{A} \end{cases} \tag{7.7}$$

$$\Rightarrow \quad \left|\frac{B}{A}\right| = 1 \quad \Rightarrow \quad \frac{B}{A} = e^{i\alpha} \tag{7.8}$$

   Plugging this back into the solution, we have:

$$\psi(x) = \begin{cases} 2Ae^{i\alpha}\cos\left(kx - \frac{\alpha}{2}\right), & x < 0 \quad (k = \sqrt{2mE/\hbar}) \\ 2Ae^{i\alpha/2}\cos\left(\frac{\alpha}{2}\right)e^{\kappa x}, & x \geq 0 \quad (\kappa = \sqrt{2m(V_0 - E)/\hbar}) \end{cases} \tag{7.9}$$

   Notice that $|A|^2 = |B|^2$, which corresponds to total reflection of the wave off the step occurs for the plane-wave solution ($\vec{J} = \vec{0}$).

3. $\underline{E > V_0}$:

For this case, the wavefunction would all be classically allowable solutions (plane-waves), which would give us:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < 0 \quad (k = \sqrt{2mE/\hbar}) \\ Ce^{ik'x} + De^{-ik'x}, & x \geq 0 \quad (k' = \sqrt{2m(E - V_0)/\hbar}) \end{cases} \tag{7.10}$$

We now assume that $D = 0$ because we would assume no left-moving wave from $x = +\infty$. Applying again the boundary conditions to solve for the coefficients, we get:

$$\begin{aligned} & \begin{cases} A + B = C \\ k(A - B) = k'C \end{cases} \\ \Rightarrow \quad & \begin{cases} \frac{B}{A} = \frac{k-k'}{k+k'} \\ \frac{C}{A} = \frac{2k}{k+k'} \end{cases} \\ \Rightarrow \quad & \left|\frac{B}{A}\right|^2 \neq 1 \end{aligned} \tag{7.11}$$

Computing the probability flux, we get:

$$\vec{J} = \begin{cases} \frac{\hbar k}{m}\left(|A|^2 - |B|^2\right), & x < 0 \\ \frac{\hbar k}{m}|C|^2, & x > 0 \end{cases} \tag{7.12}$$

Noting that $\partial\rho/\partial t = 0$ (since we are solving for energy eigenstates), implying $\boldsymbol{\nabla} \cdot \vec{J} = 0$, which means that $\vec{J}$ must be the same at $x = 0$, granting us:

$$\left|\frac{B}{A}\right|^2 + \frac{k'}{k}\left|\frac{C}{A}\right|^2 = 1 \tag{7.13}$$

where the first term on the left is the *reflected amplitude* and the second term on the left id the *transmitted amplitude*. So we can define:

$$\boxed{R \equiv \left|\frac{B}{A}\right|^2 = \frac{(k - k')^2}{(k + k')^2}, \quad T \equiv \frac{k'}{k}\left|\frac{C}{A}\right|^2 = \frac{4kk'}{(k + k')^2}} \tag{7.14}$$

which we call the *reflection* and *transmission coefficients* respectively (as alluded to in the previous chapter).

§7.1.2 Rectangular Barrier Potential

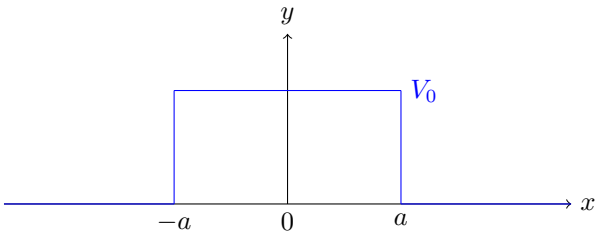


Figure 7.2: Rectangular barrier potential.

Consider the potential illustrated in figure 7.2 above:

$$V(x) = \begin{cases} V_0, & |x| < a \\ 0, & |x| > a \end{cases} \tag{7.15}$$

For this, we will only be looking at the case where $E < V_0$. So setting this up, we know that the solutions will be plane-waves outside the barrier, and decaying exponentials in side it:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < -a \quad (k = \sqrt{2mE/\hbar}) \\ Ce^{-\kappa x} + De^{\kappa x} & |x| \leq a \quad (\kappa = \sqrt{2m(V_0 - E)/\hbar}) \\ Fe^{ikx} + Ge^{-ikx}, & x > a \quad (k = \sqrt{2mE/\hbar}) \end{cases} \tag{7.16}$$

Applying all the continuity boundary conditions at $x = -a$ and solving for the coefficients, we get:

$$\begin{aligned} Ae^{-ika} + Be^{ika} &= Ce^{\kappa a} + De^{-\kappa a} \\ Ae^{-ika} + Be^{ika} &= \frac{i\kappa}{k}\left[Ce^{\kappa a} + De^{-\kappa a}\right] \end{aligned} \tag{7.17}$$

We can write this in matrix form instead to get:

$$\begin{bmatrix} A \\ B \end{bmatrix} = \frac{1}{2}\begin{bmatrix} ze^{\kappa a + ika} & z^\star e^{-\kappa a + ika} \\ z^\star e^{\kappa a - ika} & ze^{-\kappa a - ika} \end{bmatrix}\begin{bmatrix} C \\ D \end{bmatrix} \tag{7.18}$$

$$\begin{bmatrix} C \\ D \end{bmatrix} = \frac{1}{2}\begin{bmatrix} z^\star e^{\kappa a + ika} & ze^{\kappa a - ika} \\ ze^{-\kappa a + ika} & z^\star e^{-\kappa a - ika} \end{bmatrix}\begin{bmatrix} F \\ G \end{bmatrix} \tag{7.19}$$

$$\begin{aligned} \Rightarrow \quad \begin{bmatrix} A \\ B \end{bmatrix} &= \frac{1}{4}\begin{bmatrix} ze^{\kappa a + ika} & z^\star e^{-\kappa a + ika} \\ z^\star e^{\kappa a - ika} & ze^{-\kappa a - ika} \end{bmatrix}\begin{bmatrix} z^\star e^{\kappa a + ika} & ze^{\kappa a - ika} \\ ze^{-\kappa a + ika} & z^\star e^{-\kappa a - ika} \end{bmatrix}\begin{bmatrix} F \\ G \end{bmatrix} \\ &\equiv \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix}\begin{bmatrix} F \\ G \end{bmatrix} \end{aligned} \tag{7.20}$$

where the matrix entries are not explicitly computed because they are not particularly illuminating. Furthermore, this convention is awkward because this relates outgoing to incoming

coefficients, when we generally want things the other way round. As such, could have instead written:

$$\begin{bmatrix} F \\ B \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} A \\ G \end{bmatrix} \tag{7.21}$$

where this relation matrix is known as the *S-matrix*. Now looking at the probability fluxes, it works out that for $x < -a$, we have:

$$\begin{aligned} \vec{J} &= \mathrm{Im}\Big\{ ik \left(|A|^2 - |B|^2 \right) + k \,\mathrm{Im}\big\{ A^* B e^{-2ikx} \big\} \Big\} \\ &= k \left(|A|^2 - |B|^2 \right) \end{aligned} \tag{7.22}$$

Similarly on the right, we also end up with something similar:

$$\vec{J} = k \left(|F|^2 - |G|^2 \right) \tag{7.23}$$

By conservation of probability, we get:

$$\begin{aligned} & |A|^2 + |G|^2 = |F|^2 + |B|^2 \\ \Rightarrow \quad & \begin{bmatrix} A^* & G^* \end{bmatrix} \begin{bmatrix} A \\ G \end{bmatrix} = \begin{bmatrix} F^* & B^* \end{bmatrix} \begin{bmatrix} F \\ B \end{bmatrix} = \begin{bmatrix} A^* & G^* \end{bmatrix} S^\dagger S \begin{bmatrix} A \\ G \end{bmatrix} \end{aligned} \tag{7.24}$$

which tells us that the ***S*-matrix is unitary**! We now note that:

$$\frac{F}{A} = \frac{e^{-2ika}}{\cosh(2\kappa a) + i\frac{\varepsilon}{2}\sinh(2\kappa a)}, \qquad \text{where} \quad \varepsilon \equiv \frac{\kappa}{k} - \frac{k}{\kappa} = \frac{1 - 2E/V_0}{\sqrt{E/V_0(1 - E/V_0)}} \tag{7.25}$$

This allows us to compute the tranmission coefficient as:

$$\boxed{T = \left| \frac{F}{A} \right|^2 = \frac{1}{\cosh^2(2\kappa a) + \frac{\varepsilon^2}{4}\sinh^2(2\kappa a)}} \tag{7.26}$$

which gives us 2 parameters V/E_0 that tells us about the height of the barrier, and κa which tells us about the width of it. Consider the following regimes.

1. $\underline{\kappa a \gg 1}$:

   In this regime, we have:

   $$\begin{aligned} & \cosh(2\kappa a) \approx \sinh(2\kappa a) \approx e^{2\kappa a}/2 \\ \Rightarrow \quad & T \approx 16 e^{-4\kappa a} \left(\frac{V/E_0 - 1}{(V/E_0 - 1)^2 + 1} \right)^2 \end{aligned} \tag{7.27}$$

   which shows exponential sensitivity to a! An application of this approximation would be in scanning tunneling microscopes, where the air gap between the scanning tip and the surface is the potential barrier.

2. $V_0 \gg E$, $\kappa a \ll 1$:

   In this regime, we have:

$$\begin{aligned} \kappa \approx k \quad &\Rightarrow \quad \varepsilon \approx \frac{\kappa}{k} \\ \Rightarrow \quad T \approx \frac{k^2}{k^2 + \kappa^4 a^2} &= \frac{1}{1 + \frac{2mV_0}{\hbar^2} a^2 (V_0/E)} \end{aligned} \tag{7.28}$$

   Notice that the transmission rate now goes to 1 in the limit of an infinitely narrow barrier, but goes to 0 as the barrier height tends to infinity.

3. $a \to 0$ and $V_0 \to \infty$:

   In this regime, we get:

$$T = \frac{E}{E + \frac{mg^2}{2\hbar^2}}, \quad g = \lim_{V_0 \to \infty} \lim_{a \to 0} 2aV_0 \tag{7.29}$$

   where the limit on g is taken for $a \to 0$ and $V_0 \to \infty$. This is exactly what you would get for a delta function potential $g\delta(x)$.

To briefly just mention the $E > V_0$ regime, we don't have to redo the math but just redefine $\kappa \to k' = i\kappa$. This will grant us the transmission coefficient:

$$T = \frac{1}{\cos^2(2k'a) - \frac{1}{4}\sin^2(2k'a)} = \left[1 + \frac{\sin^2(2k'a)}{4E/V_0(E/V_0 - 1)}\right]^{-1} \tag{7.30}$$

so we see there are cases where $T = 1$ in this regime, which is when the $\sin^2(2k'a) \Rightarrow 2k'a = n\pi$ term vanishes. These scenarios are known as *transmission resonances* (will be touched on in more detail when we get deeper into S-matrices).

§7.2 General 1-d Quantum Scattering

Now consider the most general case, where we have a potential that is a blackbox in the region $|x| < a$, and zero everywhere else (illustrated in figure 7.3 below).

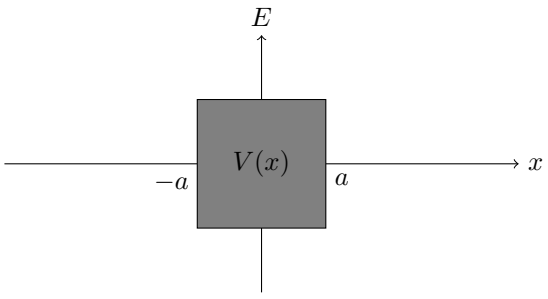


Figure 7.3: Blackbox potential.

This would give us the wavefunction:

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, & x < -a \quad (k = \sqrt{2mE/\hbar}) \\ \text{something} & |x| \leq a \quad (\kappa = \sqrt{2m(V_0 - E)/\hbar}) \\ Fe^{ikx} + Ge^{-ikx}, & x > a \quad (k = \sqrt{2mE/\hbar}) \end{cases} \tag{7.31}$$

We saw earlier that we can write the S-matrix just knowing A, B, F and G:

$$\begin{bmatrix} F \\ B \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} A \\ G \end{bmatrix} \tag{7.32}$$

If $G = 0$, we get $F = S_{11}A \equiv t$, where $T = |t|^2$ is the transmission coefficient, and also if $A = 0$, we have $r' \equiv S_{12}G = F$, where $R = |r'|^2$ is the reflection coefficients. Doing this same procedure also for $B = 0$ and $G = 0$, it turns out that:

$$\begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} = \begin{bmatrix} t & r' \\ r & t' \end{bmatrix} \tag{7.33}$$

Note: Every entry in the S-matrix is a function of k (i.e. momentum).

We see that if $E > 0$, k is real which means that $0 \leq T,\ R \leq 1$ and so on (conservation of probability). However if $E > 0$, the free-particle Schrödinger equation does not actually dictate if k is real of imaginary. This is the case wher $k \to i\kappa$, which gives us the asymptotic solutions:

$$\psi(x) = \begin{cases} Ae^{-\kappa x} + (rA + t'G)e^{-\kappa x}, & x \to +\infty \\ (tA + r'G)e^{-\kappa x} + Ge^{\kappa x}, & x \to -\infty \end{cases} \tag{7.34}$$

In order to normalize these states, the only interesting way to do so is to let t and r to diverge when A and $G \to 0$. So we see that the bound state energies correspond to poles of $S(k)$ on the imaginary axis. To write this out succinctly:

$$\boxed{\text{Bound-State Energies} \iff \text{Poles of } S(k) \text{ are on the Imaginary Axis}} \tag{7.35}$$

Note: $T + R \neq 1$ for the $E < 0$ case since this is no longer a scattering experiment.

Now assume that $S(k)$ has a pole at $k = k_0 - i\gamma$ where $\gamma > 0$. So plugging this into the energy, we get:

$$\begin{aligned} E &= \frac{\hbar^2 k^2}{2m} \\ &= \frac{\hbar^2(k_0^2 - \gamma^2)}{2m} - 2i\frac{\hbar^2 \gamma k_0}{2m} \\ &\equiv E_0 - \frac{i\Gamma}{2} \end{aligned} \tag{7.36}$$

which gives us complex energies! What does this mean? If we plug this into an energy eigenstate with time-dependence, we get:

$$\begin{aligned}\Psi(x,t) &\sim e^{-iEt/\hbar}\psi(x) \\ &= e^{-iE_0t/\hbar}e^{-\Gamma t/2\hbar}\psi(x)\end{aligned} \tag{7.37}$$

which has some exponentially decaying portion. If $\psi(x)$ is the free-particle solution e^{ikx}, then we get:

$$\Psi(x,t) \sim e^{ik_0x}e^{-iE_0t/\hbar}e^{\gamma x - \frac{\Gamma t}{2\hbar}} \tag{7.38}$$

This physically corresponds to having a 2-camel-hump potential with bound states between the humps. These however are not actual bound states since over time, these state would tunnel out and will have behaviour like that solution above. The imaginary part of these complex wave-vectors $k = k_0 - i\gamma$ are actually the *transmission resonances* we saw in the square-well potential, whereas the real parts correspond to the bound state energies. To see why this is, we look at the transmission coefficient at $E = E_0 - i\Gamma/2$. So we have:

$$\begin{aligned}t(E) &\approx \frac{Z}{E - E_0 + i\Gamma/2} \\ \Rightarrow \quad T &\approx \frac{|Z|^2}{(E-E_0)^2 + \Gamma^2/4}\end{aligned} \tag{7.39}$$

where Z is some complex number and that point is that $t(E)$ will be dominated by the pole (denominator). This is a *Lorentzian distribution* (appeared when we were doing magnetic resonance) where Γ is the full-width-half-max value of the distribution.

Example:

Consider again the potential step:

$$V(x) = \begin{cases} V_0, & |x| < a \\ 0, & |x| > a \end{cases} \tag{7.40}$$

as seen earlier, we will have 2 wave-numbers:

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad k' = \sqrt{\frac{2m(E-V_0)}{\hbar^2}} \tag{7.41}$$

$$\Rightarrow \quad T = \frac{4kk'e^{2i(k-k')a}}{e^{4ik'a}(k-k')^2 - (k+k')^2} \tag{7.42}$$

The poles of this system exists where the denominator vanishes, which give the solutions:

$$k = k'\left(\frac{e^{2ik'a}-1}{e^{2ik'a}+1}\right) \quad \text{or} \quad k = k'\left(\frac{e^{2ik'a}+1}{e^{2ik'a}-1}\right) \tag{7.43}$$

We can now consider 2 regimes of k':

1. $\underline{k' \in \mathbb{R}\ (E > V_0)}$:
   This gives us:
   $$k = ik' \tan(k'a) \tag{7.44}$$
   If $E > 0$, we get no solutions, but if $E < 0$, then we get poles and hence bound states. This is exactly what we found before.
2. $\underline{k' \in \mathbb{C}\ (E < V_0)}$:
   Let us define $k' = i\kappa$, which gives us:
   $$k = -\kappa \tanh(\kappa a) \tag{7.45}$$
   These give unphysical solutions since they will either produce solutions on the negative k-axis or positive imaginary axis.
3. $\underline{k \in \mathbb{C}}$:

§7.2.1 Linear Potentials

Consider a potential:

$$V(x) = \begin{cases} kx, & x > 0 \\ -kx, & x < 0 \end{cases} \tag{7.46}$$

So the Schrödinger's equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}u_E(x) + k|x|u_E(x) = Eu_E(x) \tag{7.47}$$

So since $V(x)$ is an even function, we must have that the wavefunctiosn are either even or odd functions. First let us pick some unit of length for this system, which we will define as x_0. Then we will do a change of variable from $x \to x/(kx_0)$ to get:

$$-\frac{\hbar^2}{2mkx_0}u_E'' + \frac{|x|}{x_0}u_E = \frac{E}{kx_0}u_E(x) \tag{7.48}$$

and we will also define a new variable $y \equiv x/x_0$. So we have:

$$-\frac{\hbar^2}{2mkx_0^3}\frac{d^2u_E(y)}{dy^2} + yu_E = \frac{E}{kx_0}u_E(x) \tag{7.49}$$

and also defining $x_0 \equiv (\hbar^2/mk)$ and $\epsilon \equiv E/kx_0$, we have:

$$\frac{d^2u_E}{dy^2} - 2(y - \epsilon)u_E = 0 \tag{7.50}$$

final;y defining $z \equiv 2^{1/3}(y - \epsilon)$:

$$\frac{d^2u_E}{dz^2} - z \cdot u_E = 0 \tag{7.51}$$

This equation above is known as *Airy's equation*, and the solutions are *Airy functions* $(A_i(z), B_i(z))$. Note that $z = 0$ is the classical turning point, so we should expect that these solutions should look like an oscillating functions with some envelope that either exponentially decays or grows at the tail. The one that decays happens to be $A_i(x)$ and since we want to look for normalizable wavefunctions, we drop the $B_i(x)$ solution. However, the Airy function is **not** symmetric. So at $x = 0$ $(z = z_0 = -2^{1/3}\epsilon)$, the Airy function $(A_i(z = z_0) = 0)$ or its derivative $(A_i'(z = z_0) = 0)$ must vanish (even or odd solutions). So physically realizable solutions must coincide with one these conditions. To do this, we need to pick a special value of E to make this condition hold, and this once again quantizes the energy.

Note: Some actual system with linear potentials are systems with constant gravitation fields (mgh) and approximations of the strong nuclear force (QCD, linear quark potential).

§7.3 The WKB Approximation

We've been talking about wavefunction solutions to the SChrödinger equation in particular potentials, ending (up to this point) with the linear potential. We will now be looking at a semi-classical approximation which utilizes the linear potential. The motivation for this is as follows. We had the standard 1D schrödinger equation as:

$$\frac{d^2\psi_E}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi_E = 0 \tag{7.52}$$

Defining $k(x) \equiv \sqrt{2m[E - V(x)]/\hbar^2}$, this grants us:

$$\begin{aligned} & \psi_E''(x) - k^2(x)\psi_E(x) = 0 \\ \Rightarrow \quad & \psi_E(x) = e^{\frac{iW(x)}{\hbar}} \end{aligned} \tag{7.53}$$

Plugging this into the Schrödinger's equation, we get:

$$i\hbar\frac{d^2W(x)}{dx^2} - \left(\frac{dW(x)}{dx}\right)^2 + p^2(x) = 0 \tag{7.54}$$

where we have defined $p(x) \equiv \hbar k(x)$. Now consider the limit where $\hbar$ is small (that is some physical regime where such scales are relatively small and negligible). This give us that:

$$\hbar\left|\frac{d^2W(x)}{dx^2}\right| \ll \left|\frac{dW(x)}{dx}\right|^2 \tag{7.55}$$

We can write an ansatz:

$$W(x) = W_0(x) + \hbar W_1(x) + \hbar^2 W_2(x) + \dots \tag{7.56}$$

which in the small $\hbar$ regime, we can drop the higher order terms in the expansion. Plugging this ansatz into the differential equation in $W(x)$, we get:

$$\left[-W_0'(x)^2 + p(x)^2\right]\hbar^0 + \left[iW_0''(x) - 2W_0'(x)W_1'(x)\right]\hbar + \mathcal{O}(\hbar^2) = 0 \tag{7.57}$$

We then assert that each power of $\hbar$ vanishes separately, which grants us:

$$\begin{aligned} & W_0'(x) = \pm p(x) \quad \Rightarrow \quad W_0''(x) = \pm p'(x) \\ \text{and} \quad & -2iW_1'(x) = \frac{W_0''(x)}{W_0'(x)} = \frac{p'(x)}{p(x)} \end{aligned} \tag{7.58}$$

This is simply a first order differential equation, which we can solve as:

$$\begin{aligned} & -2iW_1(x) = \ln p(x) + C \\ \Rightarrow \quad & W_1(x) = i \ln \sqrt{p(x)} + C' \\ \Rightarrow \quad & \boxed{\psi_E(x) = \frac{A}{\sqrt{p(x)}} \exp\left\{ \pm \frac{i}{\hbar} \int_{x_0}^{x} p(x')dx' \right\}} \end{aligned} \tag{7.59}$$

So this approximation scheme "generalizes" the plane-wave solution where the potential varies in space in the regime that $\hbar \to 0$ and $E > V(x)$ locally. Let us check if this solution is valid. That is, we check if we indeed have:

$$\begin{aligned} & \hbar W_1(x) \ll W_0(x) \\ \Rightarrow \quad & i\hbar \ln \sqrt{p(x)} \ll \int_{x_0}^{x} p(x')dx' \\ \Rightarrow \quad & \frac{i\hbar}{2} \int_{x_0}^{x} \frac{p'(x')}{p(x')} dx' \ll \int_{x_0}^{x} p(x')dx' \\ \Rightarrow \quad & |k'(x)| \ll |k(x)|^2 \end{aligned} \tag{7.60}$$

Now defining $\lambda(x) = 2\pi/k(x)$, which gives us:

$$\begin{aligned} & \lambda'(x) = -\frac{2\pi k'(x)}{k(x)^2} \\ \Rightarrow \quad & \boxed{\left| \frac{d\lambda(x)}{dx} \right| \ll 1} \end{aligned} \tag{7.61}$$

So this tells us that for the WKB approximation to work, we need that the potential is essentially slowly varying so that the wavelength does not vary quickly through space. To see this explicitly, we can rearrange the equations above to get:

$$\lambda(x) \left| \frac{dV(x))}{dx} \right| \ll \frac{p(x)^2}{m} \tag{7.62}$$

This implies that the WKB approximation definitely breaks down at **classical turning points** ($E - V(x) \to 0$). So far, we have assumed that $E > V(x)$, we could also consider the case where $E < V(x)$ (classically forbidden region). In this case, we define:

$$\begin{aligned} & \kappa = \sqrt{\frac{2m}{\hbar^2}[V(x) - E]} \\ \Rightarrow \quad & \boxed{\psi_E(x) = \frac{B}{\sqrt{\kappa(x)}} \exp\left\{ \pm \int_{x_0}^{x} \kappa(x')dx' \right\}} \end{aligned} \tag{7.63}$$

This approximation looks at local regions of the wavefunction, but we can in fact patch WKB solutions across classical turning points to get a more global picture. Let's consider a classical turning at $x = a$ across a approximately linear potential with positive slope. Near this point, we can write that $V(x) - E \approx (x - a)$ (linear approximation). We will thus have 3 parts of the solution at $(x < a)$, $(x \approx a)$ and $(x > a)$. The outer 2 solutions would be WKB solutions and the one around a would be the Airy-function solutions we saw earlier for linear potentials. All we have to do now is match the coefficients to stitch them together. We note that for $z \to \infty$, the Airy functions are approximated by:

$$\begin{aligned} A_i(z \to \infty) &\to \frac{1}{2\sqrt{\pi}} z^{-1/4} \exp\left\{-\frac{2}{3} z^{3/2}\right\} \\ A_i(z \to -\infty) &\to \frac{1}{\sqrt{\pi}} |z|^{-1/4} \cos\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right) \end{aligned} \tag{7.64}$$

We can actually use these approximations in the WKB approximation scheme because in the first place for WKB, we had $|k'(x)| \ll \left|k^2(x)\right|$. We were also working in the linear regime where $V(x) - E = g \cdot (x - a)$ where $g > 0$ which indeed gives us Airy functions, but so this grants us that $k^2 \propto -z$ so $|z| \gg 1$. This is essentially saying that the linear region is large enough compared to length scales in the Airy function such that we can simply take the long-range approximations of the Airy function as solutions. The detailed version of this argument is in Merzbacher 7.2. This grants us the connection formulas:

$\underline{x > a}$:

$$\frac{A}{\sqrt{\kappa(x)}} \exp\left[-\int_a^x dx' \kappa\left(x'\right)\right] + \frac{B}{\sqrt{\kappa(x)}} \exp\left[\int_a^x dx' \kappa\left(x'\right)\right] \tag{7.65}$$

$\underline{x < a}$:

$$\frac{2A}{\sqrt{k(x)}} \cos\left[\int_x^a dx' k\left(x'\right) - \frac{\pi}{4}\right] - \frac{B}{\sqrt{k(x)}} \sin\left[\int_x^a dx' k\left(x'\right) - \frac{\pi}{4}\right] \tag{7.66}$$

§7.4 Applications of the WKB Approximation

§7.4.1 WKB Bound States

Consider an inverted-Gaussian potential well and a particle with energy $E < 0$. We split this into 3 regions, one (1) where $x < -\sigma$, the second (2) within $-\sigma < x < \sigma$ and the last (3) being $x > \sigma$ where σ is the standard deviation of the Gaussian.

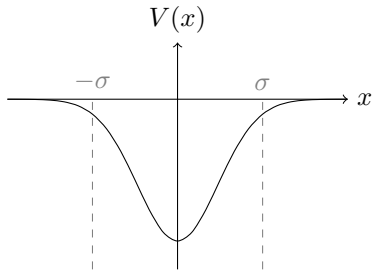


Figure 7.4: Inverted Gaussian Potential

The respective solutions in the WKB approximation scheme would then be:

$$\psi_1(x) \approx \frac{A}{\sqrt{\kappa(x)}} \exp\left\{ -\int_x^b dx' \kappa(x') \right\} \tag{7.67}$$

We now use the connection formulas but now, since we are working with a downward linear slope, we will have to flip the integration limits on them and set a to b. As such, the connection would give us:

$$\psi_2(x) \approx \frac{2A}{\sqrt{k(x)}} \cos\left(\int_b^x dx' k(x') - \frac{\pi}{4} \right) \tag{7.68}$$

To get useful results, we are going to rewrite the above equation as:

$$\begin{aligned}
\psi_2(x) &\approx \frac{2A}{\sqrt{k(x)}} \cos\left(\int_b^a dx' k(x') - \int_a^x dx' k(x') - \frac{\pi}{4} \right) \\
&= \frac{2A}{\sqrt{k(x)}} \left[\cos\left(\int_b^a dx' k(x') \right) \cos\left(\int_a^x dx' k(x') + \frac{\pi}{4} \right) + \sin\left(\int_b^a dx' k(x') \right) \sin\left(\int_a^x dx' k(x') + \frac{\pi}{4} \right) \right] \\
&= \frac{2A}{\sqrt{k(x)}} \left[\sin\left(\int_b^a dx' k(x') \right) \cos\left(\int_a^x dx' k(x') - \frac{\pi}{4} \right) - \cos\left(\int_b^a dx' k(x') \right) \sin\left(\int_a^x dx' k(x') - \frac{\pi}{4} \right) \right]
\end{aligned} \tag{7.69}$$

Now looking at the third region, we have:

$$\psi_3(x) \approx \frac{A'}{\sqrt{\kappa(x)}} \exp\left\{ -\int_x^a dx' \kappa(x') \right\} \tag{7.70}$$

To now match $\psi_3(x)$ to $\psi_2(x)$, we get quantization:

$$\begin{aligned}
& \cos\left(\int_b^a dx' k(x') \right) = 0 \\
\Rightarrow \quad & \int_b^a dx' k(x') = \pi \left(n + \frac{1}{2} \right) \\
\Rightarrow \quad & \int_b^a dx' \sqrt{2m[E - V(x')]} = \pi\hbar \left(n + \frac{1}{2} \right) \\
\Rightarrow \quad & \int_b^a dx' p(x') = \pi\hbar \left(n + \frac{1}{2} \right)
\end{aligned} \tag{7.71}$$

which is what we would expect for a bound state. We see that if this were a classical system, there would be an orbit (in phase-space) between the 2 classical turning points, which could motivate us quantum mechanically to write:

$$\boxed{\oint p(x) dx = h \left(n + \frac{1}{2} \right)} \tag{7.72}$$

This relation is known as the *Bohr-Sommerfeld quantization relation*, where the closed integral goes over the closed phase-space orbit.

§7.4.2 WKB Tunneling

Consider some potential barrier that has a finite $V_{\max}$. The scattering relation matrix (**not** the S-matrix) is given by:

$$\begin{bmatrix} A \\ B \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 2\theta + 1/(2\theta) & i(2\theta - 1/(2\theta)) \\ -i(2\theta - 1/(2\theta)) & 2\theta + 1/(2\theta) \end{bmatrix} \begin{bmatrix} F \\ G \end{bmatrix} \tag{7.73}$$

where $\theta = \exp\left\{\int_a^b \kappa(x')dx'\right\}$. So we have tunneling entirely parameterized by one parameter θ. The transmission coefficient would then be:

$$T = \frac{|F|^2}{|A|^2} = \frac{4}{(2\theta + 1/2\theta)^2} \tag{7.74}$$

In the limit where θ is large, that is when the barrier is very wide, we have the approximate solution:

$$T \approx \frac{1}{\theta^2} = \exp\left\{-\frac{2}{\hbar}\int_a^b \sqrt{2m[V(x) - E]}\right\} \tag{7.75}$$

Example:

We are going to look at α-decay now. We can model the potential as:

$$V(r) = \begin{cases} 0, & 0 < r < R \\ \frac{2Ze^2}{r}, & r > R \end{cases} \tag{7.76}$$

where Z is the charge of the daughter nucleus and R is the nuclear radius. Note that this potential badly breaks the assumption of the WKB approximation at the left edge, but we can ignore that and still get a very useful result. It works out that the transmission coefficient follows the relation:

$$-\frac{1}{2}\ln T = \int_R^\rho dr'(r')^2\kappa(r') = \sqrt{\frac{2m}{\hbar}}\int_R^\rho dr'(r')^2\sqrt{\frac{2Ze^2}{r} - E} \tag{7.77}$$

where $(r')^2$ pops in because this is in fact a 3D integral over 3D real-space. Using the escape energy as a proxy for the energy, we have:

$$E = \frac{1}{2}mv^2 = \frac{2Ze^2}{\rho} \tag{7.78}$$

Now, we take the limit as $R \to 0$ because this is a good approximation to the actual physical system, we get:

$$-\frac{1}{2}\ln T \approx \frac{2\pi Ze^2}{\hbar v} \tag{7.79}$$

$$\Rightarrow \quad T \approx \exp\left\{-\frac{4\pi Ze^2}{\hbar v}\right\} \tag{7.80}$$

This could allow us to then compute a decay rate as follows:

$$\Gamma = Tf = T\left(\frac{v}{2R}\right) \tag{7.81}$$

Chapter 8

Symmetries

Symmetries in nature lead to profound facts about the physical system we are dealing with. In physics, symmetries refer to operators that when applied to a physical system, leave an associated quantity invariant. Symmetries fall under 2 broad categories, discrete and continuous symmetries. We will be touching on both of these in this chapter and see the amazing things that pop out of such systems.

§8.1 Periodic Potentials

To start off, we are going to analyze systems with *discrete symmetries*. More specifically, we will be looking at potentials that have a periodic discrete symmetry (a.k.a finite/lattice translation symmetry):

$$V(x) = V(x \pm a) \tag{8.1}$$

Real physical systems that have such symmetries are crystals, optical lattices and many others. Consider the *translation operator* defined by:

$$\begin{aligned} & \hat{\tau}(L)\,|x\rangle = |x + L\rangle \\ \Rightarrow \quad & \hat{\tau}^\dagger(L)\hat{x}\hat{\tau}(L) = x + L \end{aligned} \tag{8.2}$$

These must then also obey the property that:

$$\begin{aligned} & \hat{\tau}^{-1}(L) = \hat{\tau}(-L) \\ \Rightarrow \quad & \hat{\tau}^\dagger(-L)\hat{x}\hat{\tau}(-L) = x - L \\ \Rightarrow \quad & \hat{\tau}^\dagger(L)\left[\hat{\tau}^\dagger(-L)\hat{x}\hat{\tau}(-L)\right]\hat{\tau}(L) = \hat{x} - L\left(\mathbb{I} - \hat{\tau}^\dagger(L)\hat{\tau}(L)\right) = \hat{x} \\ \Rightarrow \quad & \hat{\tau}^\dagger(L)\hat{\tau}(L) = \mathbb{I} \end{aligned} \tag{8.3}$$

So the translation operator **must** be unitary. Now consider the momentum operator. If we apply

the translation operator on this, we should get that nothing happens:

$$\begin{aligned}\langle x'|\,\hat{\tau}^\dagger(L)\hat{p}\hat{\tau}(L)\,|x\rangle &= \langle x'+L|\,\hat{p}\,|x+L\rangle \\ &\sim \delta[(x+L)-(x+L')]\frac{\hbar}{i}\frac{\partial}{\partial x} \\ &= \langle x'|\,\hat{p}\,|x\rangle\end{aligned} \tag{8.4}$$

Now looking at the Hamiltonian, applying the translation operator:

$$\begin{aligned}\hat{\tau}^\dagger(L)\hat{H}\hat{\tau}(L) &= \hat{\tau}^\dagger(L)V(\hat{x})\hat{\tau}(L) \\ &= V(\hat{x}+a)\end{aligned} \tag{8.5}$$

So if we indeed have a periodic potential by a, then:

$$\hat{\tau}^\dagger(L)\hat{H}\hat{\tau}(L) = V(\hat{x}) \tag{8.6}$$

So the translation operator commutes with the Hamiltonian and they can be simultaneously diagonalized (possible to find simultaneous eigenstates)! So let's try to work with this by looking at an example.

§8.1.1 The Tight Binding Approximation

Consider periodic potential wells that are separated by asymptotes (of distances between each asymptote a) and let's try solving for one of these potentials (generalization of the Ammonia system to N wells). With this system, we would expect to find simultaneous eigenstates between the Hamiltonian and the translation operator. The translation operator would take some state $|n, E\rangle$ and transform it as follows:

$$\hat{\tau}(a)\,|n,E\rangle = |n+1,E\rangle \tag{8.7}$$

The translation eigenstates would have to be some infinite sum:

$$\begin{aligned}|\theta,E\rangle &= \sum_{n=-\infty}^{\infty} e^{in\theta}\,|n,E\rangle \\ \Rightarrow\quad \hat{\tau}(a)\,|\theta,E\rangle &= \sum_{n=-\infty}^{\infty} e^{in\theta}\,|n+1,E\rangle = e^{-i\theta}\,|\theta,E\rangle\end{aligned} \tag{8.8}$$

where n is the periodicity index. So the eigenvalue is simply a phase (which is expected since these are unitary operators), which dictates that the physical states must have $\theta \in [-\pi, \pi]$ since all other states would be equivalent. Now let's see what happens when we lower the barriers. Picking some energy E_0 and assume that the barriers are still high enough such that there is negligible overlap of the wavefunctions 2 wells apart. Rigorously, we have:

$$\begin{aligned}&\langle n|\,\hat{H}\,|n\rangle = E_0 \\ \Rightarrow\quad &\langle n'|\,\hat{H}\,|n\rangle = -\Delta\delta_{n',n\pm1}\end{aligned} \tag{8.9}$$

where Δ is some small (relative to the perfectly-separated bound state spectrum) value of energy (does **not** have to be positive). This is known as the *tight-binding approximation*. With this, we have:

$$\begin{aligned} \hat{H}\left|n\right\rangle &= E_0\left|n\right\rangle - \Delta\left|n+1\right\rangle - \Delta\left|n-1\right\rangle \\ \Rightarrow \quad \hat{H}\left|\theta\right\rangle &= E_0\left|\theta\right\rangle - \Delta\sum_{n=-\infty}^{\infty}\left(e^{in\theta}\left|n+1\right\rangle + e^{in\theta}\left|n-1\right\rangle\right) \\ &= E_0\left|\theta\right\rangle - \Delta\left(e^{-in\theta} + e^{in\theta}\right)\left|\theta\right\rangle \\ &= \left(E_0 - 2\Delta\cos\theta\right)\left|\theta\right\rangle \end{aligned} \tag{8.10}$$

So we see that this causes an energy splitting of E_0 which contains a continuous spectrum of energies parameterized by θ. This gives us a dispersion relation:

$$\boxed{E(k) = E_0 - 2\Delta\cos(ka)} \tag{8.11}$$

This is illustrated in figure 8.1 below. The wavefunction is found by:

$$\begin{aligned} \left\langle x|\theta\right\rangle &= \left\langle x\right|\hat{\tau}^\dagger(L)\hat{\tau}(L)\left|\theta\right\rangle \\ &= e^{-i\theta}\left\langle x+a|\theta\right\rangle \end{aligned} \tag{8.12}$$

So we see that up to a phase, the x-space representation is periodic. This would tell us that we can write the θ-eigenstates in the x-basis as:

$$\boxed{\left\langle x|\theta\right\rangle = u_k(x)e^{-i\frac{\theta x}{a}}} \tag{8.13}$$

where we have that $u_k(x) = u_k(x+a)$ with the wave-number being $k \equiv \theta/a$. This is known as *Bloch's theorem*. So we have that:

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a} \tag{8.14}$$

where this is known as the *Brillouin zone*. Physically, this means that the momentum of a particle in a periodic potential will have to be restricted to this range.

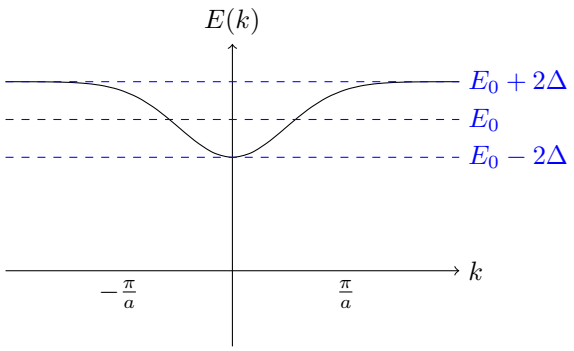


Figure 8.1: Dispersion Relation Plot

In a finite chain of potential wells with periodic boundary conditions however, we would have:

$$\begin{aligned} & \hat{\tau}(a)\,|N\rangle = |1\rangle \\ \Rightarrow \quad & \langle x|\,\hat{\tau}^N(a)\,|\theta\rangle = \langle x|\theta\rangle \\ & \langle x - Na|\,|\theta\rangle = \langle x|\theta\rangle\, e^{iN\theta} \\ \Rightarrow \quad & \theta = \frac{2\pi j}{N} \end{aligned} \tag{8.15}$$

where $j \in [-N/2, N/2]$. Let's now consider a specific example of this approximation.

Example (Periodic Delta-Function Potential):

Consider the potential:

$$V(x) = \sum_{n=-\infty}^{\infty} V_0 \delta(x - an), \quad V_0 > 0 \tag{8.16}$$

We know from Bloch's theorem that:

$$\psi(x) = e^{ikx} u_k(x) \tag{8.17}$$

However, we also know that between the delta-functions, we have:

$$\psi(x) = Ae^{iqx} + Be^{-iqx} \tag{8.18}$$

since the potential is zero between the delta-functions. Comparing this to the Bloch theorem result, we get:

$$u_k(x) = Ae^{i(q-k)x} + Be^{-i(q-k)x}, \quad u_k(x) = u_k(x + a) \tag{8.19}$$

Using anyone one of the boundary conditions (say $x = 0$), we get:

$$\begin{aligned} A + B &= Ae^{i(q-k)a} + Be^{-i(q-k)a} \\ \psi'(\varepsilon) - \psi'(-\varepsilon) &= \frac{2mV_0}{\hbar^2}(A + B) \end{aligned} \tag{8.20}$$

To get the left-hand side of the discontinuity equation, we note that:

$$\begin{aligned} & \psi'(\varepsilon) = \psi'(a + \varepsilon)e^{ika} \\ \Rightarrow \quad & iq\left[A\left(1 - e^{i(q-k)a}\right) + B\left(1 - e^{-i(q-k)a}\right)\right] = \frac{2mV_0}{\hbar^2}(A + B) \end{aligned} \tag{8.21}$$

Combining the boundary conditions, these finally grants us:

$$\boxed{\cos(ka) = \cos(qa) + \frac{mV_0}{\hbar^2}\frac{\sin(qa)}{qa}} \tag{8.22}$$

which is also a transcendental equation. This dispersion relation tells us the relationship between the momentum (corresponding to k) and energy (corresponding to q). Taking the limit as $q \to \infty$ (energy of the particle is very large), we get:

$$\cos(ka) \to \cos(qa) \tag{8.23}$$

which grants us that we recover the free-particle solutions. If we now plot the right-hand side as a function of qa, it will obey a periodic (sinusoidal) function which does not in general have to be bounded by -1 and $+1$. So the regions where the right-hand side exceed these bounds would be unphysical regions (since the left-hand side **is** bounded by -1 and $+1$). These grant us what are known as energy *band-gaps*.

§8.2 Continuous Symmetries in Quantum Mechanics

We begin with a theorem which generalizes what we have seen in the discrete case.

Theorem 8.2.1. *Symmetry operators $\hat{T}$ are unitary or anti-unitary operators.*

Proof. This is going to be a quick sketch of a proof that will be sufficient for our purposes.

1. *It is a transformation that acts on all states of the Hilbert space.*
2. *$\hat{T}$ leaves all physics unchanged.*
3. *$\hat{T}$ obeys Born's rule which implies*:

$$\begin{aligned} & |\langle x|\psi\rangle|^2 = \left|\langle x|\,\hat{T}^\dagger\hat{T}\,|\psi\rangle\right|^2 \\ \Rightarrow \quad & \hat{T}^\dagger\hat{T} = \mathbb{I} \end{aligned} \tag{8.24}$$

For the Born's rule, we actually could have that $\left|\langle x|\,\hat{T}^\dagger\hat{T}\,|\psi\rangle\right|^2 = |\langle\psi|s\rangle|^2$, which is known as *anti-unitarity*. □

We now also list a fact about Hermitian operators, that is if $\hat{Q}$ is a Hermitian operator, then we can always find:

$$\hat{U}(a) = \exp\left\{-\frac{i\hat{Q}a}{\hbar}\right\} \tag{8.25}$$

being a unitary operator where $a \in \mathbb{R}$.

Note: The converse that any unitary has corresponding Hermitian operator to generate it via the exponential map is **not** always true.

With this, consider the translation operator over very small translations $L \to \varepsilon$:

$$\langle x|\,\hat{\tau}(\varepsilon)\,|\psi\rangle = \psi(x-\varepsilon) \tag{8.26}$$

Then writing the translation operator as generated by some Hermitian operator:

$$\begin{aligned}
& \hat{\tau}(L) = \exp\left\{-\frac{i\hat{G}L}{\hbar}\right\} \\
\Rightarrow \quad & \hat{\tau}(\varepsilon) \approx \mathbb{I} - \frac{i\hat{G}}{\hbar}\varepsilon + \dots \\
\Rightarrow \quad & \langle x|\psi\rangle - \frac{i\varepsilon}{\hbar}\langle x|\hat{G}|\psi\rangle = \psi(x) - \varepsilon\frac{d\psi}{dx} \\
\Rightarrow \quad & \hat{G} = \hat{p} \\
\Rightarrow \quad & \boxed{\hat{\tau}(x) = \exp\left\{-\frac{i\hat{p}x}{\hbar}\right\}}
\end{aligned} \tag{8.27}$$

The above implications are not rigorous but they can be shown rigorously by taking limits on powers. When such Hermitian operators exist to create unitary operators via the *exponential map*, they are called *generators*. A nice property of this is that if we have a genrator $\hat{Q}$ of the unitary $\hat{U}_Q$, then:

$$\left[\hat{A}, \hat{U}_Q\right] = 0 \quad \Rightarrow \quad \left[\hat{A}, \hat{Q}\right] = 0 \tag{8.28}$$

So if we have a symmetry (unitary operator) that commutes with the Hamiltonian, then it implies that there is a conserved quantity (known as a *Noether charge*) that is conserved. This is the *Neother's theorem* which we write formally as:

Theorem 8.2.2. Noether's Theorem *Every continuous symmetry of the Hamiltonian implies a conserved Neother charge. That is, for a continous symmetry $\hat{C}_a$ parameterized by the continous parameter a which satisfies the properties*

1. $\hat{C}_a\hat{C}_b = \hat{C}_{a+b}$
2. $\hat{C}_0 = \mathbb{I}$
3. $\hat{C}_a^{-1} = \hat{C}_{-a} = \hat{C}_a^\dagger$

then we can always find a Hermitian operator that generates (there exists a smooth connection to $\mathbb{I}$) this continuous symmetry which corresponds to a conserved quantity (the symmetry has a Lie group structure).

So going back to the translation operator, we have that translational invariance of a system implies conservation of momentum. Symmetry is going to be very important for this class and in fact all of physics. For the rest of the class, we will be looking at *gauge symmetries* and *rotational symmetries*. Let's start with gauge symmetries.

§8.3 Propagators

To understand gauge symmetries, we first need to know the concept of propagators in quantum mechanics. Suppose that we find $\hat{A}$ such that it commutes with the Hamiltonian ($\left[\hat{A}, \hat{H}\right] = 0$), then both this operator and the Hamiltonian will have simultaneous eigenstates $|a\rangle$. As such, we

can write:

$$\begin{aligned}
|\psi(t)\rangle &= \exp\left\{-\frac{i\hat{H}(t-t_0)}{\hbar}\right\}|\psi(0)\rangle \\
&= \sum_a |a\rangle\langle a|\psi(0)\rangle \exp\left\{-\frac{iE_a(t-t_0)}{\hbar}\right\} \\
\Rightarrow \quad \langle x|\psi(t)\rangle &= \sum_a \langle x|a\rangle\langle a|\psi(0)\rangle \exp\left\{-\frac{iE_a(t-t_0)}{\hbar}\right\} \\
&= \sum_a \langle x|a\rangle \int d^3x' \langle a|x'\rangle\langle x'|\psi(0)\rangle \exp\left\{-\frac{iE_a(t-t_0)}{\hbar}\right\} \\
\Rightarrow \quad \psi(x,t) &\equiv \int d^3x' K(x',t;x,t_0)\psi(x,t_0)
\end{aligned} \tag{8.29}$$

where we defined:

$$\boxed{K(x',t;x,t_0) \equiv \sum_a \langle x'|a\rangle\langle a|x\rangle \exp\left\{-\frac{iE_a(t-t_0)}{\hbar}\right\}} \tag{8.30}$$

This is known as the *propagator*, which takes an initial state $\psi(0)$ and propagates it in time from t_0 to t. More generally in 3D, we can replace x with $\vec{x}$ which grants us:

$$\boxed{K(\vec{x}',t;\vec{x},t_0) \equiv \sum_a \langle \vec{x}'|a\rangle\langle a|\vec{x}\rangle \exp\left\{-\frac{iE_a(t-t_0)}{\hbar}\right\}} \tag{8.31}$$

Notice that if we take away the completeness relation, we can rewrite this as:

$$K(\vec{x}',t;\vec{x},t_0) = \langle \vec{x}'|\exp\left\{-\frac{i\hat{H}(t-t_0)}{\hbar}\right\}|\vec{x}\rangle \tag{8.32}$$

So we get that:

$$\lim_{t\to t_0} K(\vec{x}',t;\vec{x},t_0) = \delta^3(\vec{x}-\vec{x}') \tag{8.33}$$

So K represents the wavefunction perfectly localized at $\vec{x}$, for which plugging this into the Schrödinger's equation, we get:

$$\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\vec{x}) - i\hbar\frac{\partial}{\partial t}\right] K(\vec{x}',t;\vec{x},t_0) = -i\hbar\delta^3(\vec{x}-\vec{x}')\delta(t-t_0) \tag{8.34}$$

which tells us that $K(\vec{x}',t;\vec{x},t_0)$ is in fact the *Green's function* with $K(\vec{x}',t;\vec{x},t_0) = 0$ if $t < t_0$.

Example:

Consider a free-particle in 1D, which has the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} \tag{8.35}$$

So the momentum commutes with the Hamiltonian and we can write:

$$\begin{aligned} K(x', t; x, t_0) &= \int dp \, \langle x'|p\rangle \, \langle p|x\rangle \, e^{-\frac{ip^2 t}{2m\hbar}} \\ &= \frac{1}{2\pi\hbar} \int dp \exp\left\{ \frac{ip(x'-x)}{\hbar} - \frac{ip^2(t-t_0)}{2m\hbar} \right\} \\ &= \sqrt{\frac{m}{2\pi i\hbar(t-t_0)}} \exp\left\{ \frac{im(x'-x)^2}{2\hbar(t-t_0)} \right\} \Theta(t-t_0) \end{aligned} \tag{8.36}$$

where Θ is the unit-step function.

It is useful now to look at some properties of propagators.

1. **Propagator composition**:

$$\begin{aligned} K(x', t; x, t_0) &= \int d^3x'' \, \langle x'| \, e^{-\frac{i\hat{H}(t-t')}{\hbar}} \, |x''\rangle \, \langle x'| \, e^{-\frac{i\hat{H}(t'-t_0)}{\hbar}} \, |x\rangle \\ &= \int d^3x'' \, [K(x', t; x'', t') \times K(x'', t'; x, t_0)] \end{aligned} \tag{8.37}$$

2. **Quantum partition function**:

   Getting rid of the spatial portions by setting $x = x'$ and integrating over x:

$$\begin{aligned} G(t) &\equiv \int d^3x K(x', t; x, t_0) \\ &= \int d^3x \sum_a \langle x|a\rangle \, \langle a|x\rangle \, e^{-iE_a t\hbar} \\ &= \sum_a \int d^3x \, \langle a|x\rangle \, \langle x|a\rangle \, e^{-iE_a t\hbar} \\ &= \sum_a e^{-iE_a t\hbar} \end{aligned} \tag{8.38}$$

   which is very much like the parition function in statistical mechanics, but where in our case, we have $\beta = -it/\hbar$ instead of $\beta = 1/(k_B T)$ like in statistical mechanics.

3. **Complex pole energy eigenvalues**:

$$\begin{aligned}\tilde{G}(E) &= -\frac{i}{\hbar}\int_0^\infty dt G(t) e^{iEt\hbar} \\ &= -\frac{i}{\hbar}\int_0^\infty dt \sum_a e^{-iE_a t\hbar} e^{-iEt\hbar}\end{aligned} \tag{8.39}$$

This integral does **not** converge as it is oscillatory unless we allow for complex energies which would give us:

$$\boxed{\tilde{G}(E) = \sum_a \frac{1}{E - E_a + i\varepsilon}} \tag{8.40}$$

which gives us the all the energy eigenvalues as the complex poles.

4. **Heisenberg picture**:

$$\begin{aligned}K(x', t; x, t_0) &= \sum_a \langle x'|a\rangle \langle a|x\rangle e^{-\frac{iE_a(t-t_0)}{\hbar}} \\ &= \sum_a \langle x'| e^{-\frac{i\hat{H}t}{\hbar}} |a\rangle \langle a| e^{\frac{i\hat{H}t_0}{\hbar}} |x\rangle \\ &= \langle x', t|x, t_0\rangle\end{aligned} \tag{8.41}$$

which grants us a transition amplitude, so we can take the absolute square of this quantity to find the probability of a transition of the particle at x at time t_0 to x' at time t.

Example (the Moshinsky quantum race):

Consider a particle with mass m with energy E incoming from the left. It then is incident on a shutter at $x = 0$ which is closed until $t = 0$, after which it is open and we have a detector at the end of some distance away from the shutter. Initially, we have:

$$\psi(x, 0) = e^{ikx}\Theta(-x) \tag{8.42}$$

where the heaviside function is to ensure that the incoming plane wave is only on the left side of the shutter at $t = 0$. So we have:

$$\begin{aligned}\psi(x, t) &= \int_{-\infty}^{\infty} d^3x' K_{free}(x', t; x, t_0)\psi(x', 0) \\ &= \sqrt{\frac{m}{2\pi i\hbar t}}\int_{-\infty}^{0} \exp\left\{\frac{i}{\hbar}\left(\frac{m(x-x')^2}{2t} + kx'\right)\right\} \\ &= \frac{1}{2}\exp\{ikx - ik^2\tau\}\mathrm{erfc}\left(\frac{x - k\tau}{\sqrt{2i\tau}}\right), \quad \tau \equiv \frac{\hbar t}{m}\end{aligned} \tag{8.43}$$

where $k = \sqrt{2mE}/\hbar$. So we see that the wavefunction is some oscillatory function past the shutter but before the detector, and once it hits the detector, it rapidly decays past the step-function drop.

Example:

Consider the electron double-slit experiment with the apertures labelled O_1 and O_2. At the screen, we have the propagator written as:

$$\langle B,t|A,0\rangle \tag{8.44}$$

where A indicates the source position and B the detector screen position. There will be a decomposition of the propagator into 2 parts, from the source to the barrier, and from the barrier to the screen:

$$\langle B,t|A,0\rangle = \int_0^{t_1} dt\, \langle B,t|O_1,t_1\rangle \langle O_1,t_1|A,0\rangle + \int_0^{t_1} dt\, \langle B,t|O_2,t_1\rangle \langle O_2,t_1|A,0\rangle \tag{8.45}$$

where there are 2 integrals because we noticed that there are 2 paths the electrons could take (O_1 or O_2). Everywhere but the barriers and screen, we have free propagation of the wavefunction so we get free-particle propagators:

$$\langle O_1,t_1|A,0\rangle = \frac{m}{2\pi i\hbar t_1}\exp\left\{\frac{ima_1^2}{2\hbar t_1}\right\} \tag{8.46}$$

where a_1 is the distance from A to O_1. We then have:

$$\langle B,t|O_1,t_1\rangle \langle O_1,t_1|A,0\rangle = \frac{m}{4\pi^2\hbar^2(t-t_1)}\exp\left\{\frac{im}{2\hbar}\left(\frac{a_1^2}{t_1}-\frac{b_1^2}{t-t_1}\right)\right\} \tag{8.47}$$

where b_1 is the distance from O_1 to B. If we plot this against path-length a_1 and b_1, we notice that this is an oscillatory function with period decreasing with increasing path-lengths. So we get a very small contribution from the fast oscillating regions and only get a significant contribution where $x \approx 0$. So we get to make the approximation ($t \approx t_1$):

$$\begin{aligned} \langle B,t|O_1,t_1\rangle \langle O_1,t_1|A,0\rangle &\approx \frac{m}{4\pi^2\hbar^2t^2}\exp\left\{\frac{im}{2\hbar t_1}(a_1-b_1)(a_1+b_1)\right\} \\ \Rightarrow \quad |\langle B,t|A,0\rangle|^2 &\propto 1+(l_1-l_2)\cos\left(\frac{m(l_1+l_2)}{2\hbar t}\right) \end{aligned} \tag{8.48}$$

where $l_j = a_j + b_j$ for $j \in \{1,2\}$.

The examples above don't seem much more useful than usual time evolution we have seen thus far, but the usefulness of the propagator comes in when we have an arbitrary number of barriers, each with arbitrary number of slits. Then the propagator becomes extremely useful because the answer would just be the sum over propagators describing all possible paths. What's interesting now is that if we take the limit of an infinite number of barriers with an infinite number of slits, this physically corresponds to free-space propagation! This was Feynman's insight and the key insight which leads to the *path-integral formulation* of quantum mechanics. Let's try to work through this.

Subdividing the time into steps starting with initial time t_1 and final time t_N:

$$t_j - t_{j-1} = \frac{t_N - t_1}{N-1} \tag{8.49}$$

We can also subdivide positions from initial position x_1 to final position x_N to get:

$$\langle x_N, t_N | x_1, t_1 \rangle = \int dx_{N-1} \int dx_{N-2} \ldots \int dx_2 \, \langle x_N, t_N | x_{N-1}, t_{N-1} \rangle \ldots \langle x_2, t_2 | x_1, t_1 \rangle \tag{8.50}$$

Each of these terms can be written as:

$$\begin{aligned}
\langle x_j, t_j | x_{j-1}, t_{j-1} \rangle &= \langle x_j | \exp\left\{ -\frac{i\hat{H}\Delta t}{\hbar} \right\} | x_{j-1} \rangle \\
&\approx \langle x_j | \exp\left\{ -\frac{i\hat{p}^2 \Delta t}{2m\hbar} \right\} \exp\left\{ -\frac{iV(\hat{x})\Delta t}{\hbar} \right\} | x_{j-1} \rangle + \mathcal{O}(\Delta t^2) \\
\Rightarrow \quad \langle x_j, t_j | x_{j-1}, t_{j-1} \rangle &\approx \int dx' \, \langle x_j | \exp\left\{ -\frac{i\hat{p}^2 \Delta t}{2m\hbar} \right\} | x' \rangle \, \langle x' | \exp\left\{ -\frac{iV(\hat{x})\Delta t}{\hbar} \right\} | x_{j-1} \rangle \\
&= \int dx' \, \langle x_j | \exp\left\{ -\frac{i\hat{p}^2 \Delta t}{2m\hbar} \right\} | x' \rangle \, e^{-\frac{iV(x_{j-1})\Delta t}{\hbar}} \delta(x' - x_{j-1}) \\
&= \sqrt{\frac{m}{2\pi i\hbar \Delta t}} \int_{-\infty}^{0} \exp\left\{ \frac{i\Delta t}{\hbar} \left(\frac{m(x_j - x_{j-1})^2}{2(\Delta t)^2} - V(x_j) \right) \right\}
\end{aligned} \tag{8.51}$$

So multiplying these together, we get:

$$\begin{aligned}
\langle x_N, t_N | x_1, t_1 \rangle = \left(\frac{m}{2\pi i\hbar \Delta t} \right)^{(N-1)/2} & \int dx_{N-1} \int dx_{N-2} \ldots \int dx_2 \\
& \times \exp\left\{ \frac{i\Delta t}{\hbar} \sum_{j=1}^{N-2} \left(\frac{m(x_j - x_{j-1})^2}{2(\Delta t)^2} - V(x_j) \right) \right\}
\end{aligned} \tag{8.52}$$

Taking the limit as $\Delta t \to \infty$, we get:

$$\begin{aligned}
\langle x_N, t_N | x_1, t_1 \rangle &= \int_{x_1}^{x_N} D[x(t)] \exp\left\{ \frac{i}{\hbar} \int_{t_0}^{t} dt \left[\frac{1}{2} m\dot{x}(t) - V(x(t)) \right] \right\} \\
&= \int_{x_1}^{x_N} D[x(t)] \exp\left\{ \frac{i}{\hbar} \int_{t_0}^{t} dt \mathscr{L}(x, \dot{x}) \right\} \\
&= \int_{x_1}^{x_N} D[x(t)] \exp\left\{ \frac{i}{\hbar} S(x, \dot{x}) \right\}
\end{aligned} \tag{8.53}$$

where $\mathscr{L}(x, \dot{x})$ is the *Lagrangian*, $S(x, \dot{x})$ is the *action* from classical mechanics and we defined:

$$\int_{x_1}^{x_N} D[x(t)] = \lim_{N \to \infty} \left(\frac{m}{2\pi i\hbar \Delta t} \right)^{(N-1)/2} \int dx_{N-1} \int dx_{N-2} \ldots \int dx_2 \tag{8.54}$$

The above result is known as the *Feynman path integral*. Recall that in classical mechanics, we get the classical equations of motion by taking the variation of the action to zero (extremizing the action). Now in the quantum picture, comparing 2 paths S_0 and $S_0 + \delta S$, the propagator becomes:

$$\text{propagator} \sim \exp\left\{ \frac{iS_0}{\hbar} \right\} + \exp\left\{ \frac{i(S_0 + \delta S)}{\hbar} \right\} = \exp\left\{ \frac{iS_0}{\hbar} \right\} (1 + \exp\{i\delta S/\hbar\}) \tag{8.55}$$

So we get this 1 plus rapidly oscillating term (if $\delta S \gg \hbar$), so we get the recovery of classical mechanics since we integrate over all the paths, and classical mechanics would allow us to minimize the action "up to $\hbar$".

Sadly in practice, it is difficult to solve the Feynman path integral analytically for most quantum systems (the integral is intractable), albeit possible numerically via Monte-Carlo methods. However, this formulation does come in useful for revealing some very interesting properties for symmetries which is not obvious from the other formalisms we have come across (Schrödinger and Heisenberg picture). This leads us into *gauge symmetries*.

§8.4 Gauge Symmetries

Given a potential $V(x)$, we can transform it to $\tilde{V}(x) = V(x) + V_0$, which is known as a *gauge transformation*. This is easily done classically since the constant does not affect the Lagrangian and hence the physics). The question then is, is this effect also true in quantum mechanics? Well, looking at the Schrödinger's equation, we see that taking $V(x) \to \tilde{V}(x)$ does affect time-evolution:

$$\begin{aligned} \left|\tilde{\psi}(t)\right\rangle &= \exp\left\{-\frac{i}{\hbar}\left[\frac{\hat{p}^2}{2m} + V(\hat{x}) + V_0\right] t\right\} |\psi(0)\rangle \\ &= \exp\left\{-i\frac{V_0 t}{\hbar}\right\} |\psi(t)\rangle \end{aligned} \tag{8.56}$$

If we consider these states $|\psi\rangle$ energy eigenstates, we get:

$$e^{-i\frac{V_0 t}{\hbar}} |\psi(t)\rangle = e^{-i\frac{(E+V_0)t}{\hbar}} |\psi\rangle = \left|\tilde{\psi}(t)\right\rangle \tag{8.57}$$

So we simply replaced $E \to E + V_0$, which is just a shifting for the energy and has no actual physical effect we well!

Note: This always holds true because we can always expand any arbitrary state into energy eigenstates.

Example:

Consider sending a beam of electrons in which we split the beam into 2 beams, such that each beam passes through conducting cages with constant potentials V_1 and V_2. After exiting these cages, they exit and are recombined. Further notes, there is no electric field inside and outside the capacitors since we take the potentials as uniform within the cages. If we measure the intensity of electrons after they have been recombined to be:

$$I \sim \cos\left(\frac{1}{\hbar}\int dt\,[V_2(t) - V_1(t)]\right) \tag{8.58}$$

We see that this is a quantum mechanical result since there is an $\hbar$, which in the classical limit of small $\hbar$, we have the oscillation occurring extremely rapidly which would then be averaged over. So there is something more interesting going on even with constant

potentials, and in quantum mechanics the potential is more fundamental than we expect.

Example (Gravity Interferometry):

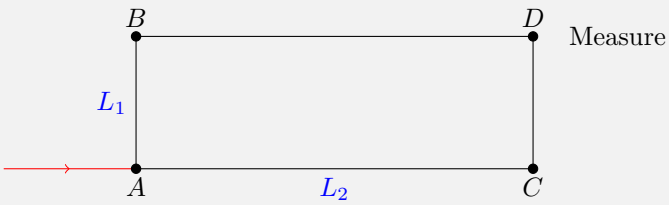


Figure 8.2: Gravity interferometer set-up.

Consider that we are close to the surface of the Earth, so classically we would have the equation of motion as $\ddot{z} = -g$. Quantum mechanically, we have:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + m\Phi_g\right]\psi(z,t) = i\hbar\frac{\partial}{\partial t}\psi(z,t) \tag{8.59}$$

Unlike the classical case, we cannot cancel the m's out anymore, but write $\Phi_g = gz$ so that we can have:

$$\left[-\frac{\hbar^2}{2m^2}\frac{d^2}{dz^2} + \Phi_g\right]\psi(z,t) = i\frac{\hbar}{m}\frac{\partial}{\partial t}\psi(z,t) \tag{8.60}$$

Now consider sending neutrons into an interferometry set-up with a rectangular configuration with lengths $L_2 > L_1$ (L_2 is the width and L_1 is the height) illustrated in figure 8.2. If this experiment lies on the plane surface of the Earth, we would so see effects due to gravity. But if we rotate the experiment by an angle δ such that one arm of length L_2 is higher than the other, we have:

$$\Delta\Phi = m_n g L_2 \sin\delta \tag{8.61}$$

where m_n is the mass of the neutrons. It is then not too hard to show that the change in phase between the 2 paths would be:

$$\Delta\phi = \exp\left\{-i\frac{m_n g L_2 \sin\delta}{\hbar}T\right\} \tag{8.62}$$

where T is the time-of-flight of the horizontal paths. This experiment was actually done in 1975 using a table top set-up and worked out that the scales allowed non-trivial results.

Example (Electromagnetic Potential):

Consider the gauge transformation of the scalar and vector potentials:

$$\phi \to \phi + \lambda(\vec{x}) \tag{8.63}$$

$$\vec{A} \to \vec{A} + \boldsymbol{\nabla}\Lambda(\vec{x}) \tag{8.64}$$

We will use the Hamiltonian formalism since we use that in quantum mechanics. The classical Hamiltonian would be:

$$H = \frac{1}{2m}\left[\vec{p} - \frac{e}{c}\vec{A}(\vec{x})\right]^2 + e\phi(\vec{x}) \tag{8.65}$$

where e is the electronic charge and c is the speed of light. Converting this into quantum mechanics, there are in fact different ways to write the Hamiltonian since operators now do not commute, but the key is that as long we we keep things Hermitian, it will suffice. So we choose:

$$\left[\vec{p} - \frac{e}{c}\vec{A}(\vec{x})\right]^2 \to \hat{\vec{p}}^2 + \frac{e^2}{c^2}\hat{\vec{A}}^2 - \frac{e}{c}\left(\hat{\vec{p}}\cdot\hat{\vec{A}} + \hat{\vec{A}}\cdot\hat{\vec{p}}\right) \tag{8.66}$$

where we are also treating $\vec{A}$ as an operator here (this is going to be important and we will explore this in a bit). In the Heisenberg picture, we have:

$$\frac{d}{dt}\hat{x}_i = \frac{1}{i\hbar}\left[\hat{x}_i, \hat{H}\right] = \frac{1}{m}\left(\hat{p}_i - \frac{e}{c}\hat{A}_i\right) \tag{8.67}$$

We now define a quantity known as the *kinematical momentum*:

$$\hat{\vec{\Pi}} = m\frac{d}{dt}\hat{\vec{x}} = \hat{p}_i - \frac{e}{c}\hat{A}_i \tag{8.68}$$

where $\hat{\vec{p}}$ is the *canonical momentum* which satisfies all the commutation relations we are familiar with and the kinematical. In fact, the kinematical momentum doesn't even commute with itself!

$$\left[\hat{\Pi}_i, \hat{\Pi}_j\right] = \left(\frac{i\hbar e}{c}\right)\varepsilon_{ijk}\hat{B}_k \tag{8.69}$$

However, it works out that:

$$m\frac{d^2}{dt^2}\hat{\vec{x}} = \frac{d}{dt}\hat{\vec{\Pi}} \tag{8.70}$$

$$= e\left[\hat{\vec{E}} + \frac{1}{2c}\left(\frac{d}{dt}\hat{\vec{x}}\times\hat{\vec{B}} - \hat{\vec{B}}\times\frac{d}{dt}\hat{\vec{x}}\right)\right] \tag{8.71}$$

which is the Lorentz force law. The continuity equation we get from this Hamiltonian in this gauge would the be:

$$\vec{j} = \frac{\hbar}{m}\,\mathrm{Im}\{\psi^*\boldsymbol{\nabla}\psi\} - \frac{e}{mc}|\psi|^2\vec{A}(\vec{x}) \tag{8.72}$$

Example (Particle in a Magnetic Field):

Consider an external magnetic field $\vec{B} = B\hat{z}$ for which we can choose the vector potential as:

$$\vec{A} = \begin{bmatrix} -yB \\ 0 \\ 0 \end{bmatrix} \tag{8.73}$$

So this would give us the Hamiltonian:

$$\hat{H} = \frac{1}{2m}\left[\left(\hat{p}_x + \frac{e}{c}B\hat{y}\right) + \hat{p}_y^2 + \hat{p}_z^2\right] \tag{8.74}$$

From the form above, we can tell that the Hamiltonian commutes with $\hat{p}_x$ and $\hat{p}_z$, which means we can find simultaneous eigenstates $|E, p_x, p_z\rangle$. This allows us to write:

$$\hat{H}\,|E, p_x, p_z\rangle = \left[\frac{\hat{p}_y^2}{2m} + \frac{\hat{p}_z^2}{2m} + \frac{1}{2m}\left(p_x + \frac{e}{c}B\hat{y}\right)^2\right]|E, p_x, p_z\rangle \tag{8.75}$$

This is in fact the harmonic oscillator potential, which we can clearly see when we rewrite this as:

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega_c^2(\hat{y} - y_0)^2 + \frac{\hat{p}_z^2}{2m} \tag{8.76}$$

where $\omega_c = eB/(mc)$. So this grants us the energy eigenstates:

$$E_n(p_z) = \hbar\omega_c\left(n + \frac{1}{2}\right) + \frac{p_z^2}{2m} \tag{8.77}$$

So now, if we had instead chosen the gauge:

$$\vec{A} = \begin{bmatrix} -\frac{yB}{2} \\ \frac{xB}{2} \\ 0 \end{bmatrix} \tag{8.78}$$

This would result in the Hamiltonian:

$$\hat{H} = \frac{1}{2m}\left[\left(\hat{p}_x + \frac{eB}{2c}\hat{y}\right)^2 + \left(\hat{p}_y - \frac{eB}{2c}\hat{x}\right)^2 + \hat{p}_z^2\right] \tag{8.79}$$

where we have:

$$\begin{aligned} \hat{\Pi}_x &= \hat{p}_x + \frac{eB}{2c}\hat{y} \\ \hat{\Pi}_y &= \hat{p}_y - \frac{eB}{2c}\hat{x} \\ \Rightarrow \quad \left[\hat{\Pi}_x, \hat{\Pi}_y\right] &= \frac{i\hbar e}{c}B_z = i\hbar m\omega_c \end{aligned} \tag{8.80}$$

which looks very much like the canonical position and momentum commutation relation! In fact, if we define:

$$\begin{aligned} \hat{Q} &\equiv -\frac{\hat{\Pi}_y}{\hbar\omega_c} \\ \Rightarrow \quad \left[\hat{Q}, \hat{\Pi}_x\right] &= i\hbar \end{aligned} \tag{8.81}$$

Rewriting the Hamiltonian in terms of these operators we have defined, we get:

$$\hat{H} = \frac{\hat{p}_z^2}{2m} + \frac{\hat{\Pi}_x}{2m} + \frac{1}{2}m\omega_c\hat{Q}^2 \tag{8.82}$$

which we again see is very much like the harmonic oscillator and we will indeed retrieve the same energy eigenvalues! However, we find that $\langle \hat{p}_x \rangle$ is not the same in the 2 cases, which tells us that $\hat{p}$ is **not** gauge invariant, **but** $\hat{\Pi}$ is. Now if there is a local gauge transformation of the form:

$$\phi \to \phi \tag{8.83}$$

$$\vec{A} \to \vec{A} + \boldsymbol{\nabla}\Lambda(\vec{x}) \tag{8.84}$$

we claim that this results in a transformation of the state:

$$\psi(x,t) \to \tilde{\psi}(x,t) = e^{i\theta(x)}\psi(x,t) \tag{8.85}$$

which we know would result in the same probabilities. However, this gets a little more subtle when we discuss quantum dynamics:

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \left[\frac{\hat{p}^2}{2m} + V(\hat{x})\right] e^{i\theta(x)}\psi(x,t) \tag{8.86}$$

Notice how the momentum operator acts on this new state:

$$\begin{aligned} \hat{p}\left[e^{i\theta(x)}\psi(x,t)\right] &= -i\hbar\frac{\partial}{\partial x}\left[e^{i\theta(x)}\psi(x,t)\right] \\ &= e^{i\theta(x)}\left[-i\hbar\frac{\partial}{\partial x}\psi(x,t) + \hbar\frac{\partial\theta(x)}{\partial x}\psi(x,t)\right] \end{aligned} \tag{8.87}$$

This results in a phase shift which in no way had we specified it to be the same initially, so this results in a strange variation in the wavefunction. To fix this, we introduce the *comparator* $\hat{U}(x_1, x_2)$, which satisfies that under gauge transformation:

$$\hat{U}(x_1,x_2) \to e^{i\theta(x)}\hat{U}(x_1,x_2)e^{-i\theta(x)} \tag{8.88}$$

which allows $U(x_1, x_2)\psi(x_2)$ to keep the same phase as $\psi(x_1)$ (this is analogous to the parallel transport operation in general relativity). We require that this transformation satisfy $\hat{U}(x_1, x_2) = \hat{U}(x_2, x_1)$ which implies also that it is unitary, which allows us to build the *covariant derivative* operator:

$$\hat{D}_x\psi(x) \equiv \lim_{\varepsilon\to 0}\frac{1}{\varepsilon}\left[\psi(x+\varepsilon) - U(x+\varepsilon,x)\psi(x)\right] \tag{8.89}$$

Notice that when we Taylor expand this comparator:

$$\hat{U}(x_1,x_2) \approx \mathbb{I} + i\frac{e}{\hbar c}\varepsilon\hat{A}_x(x) + \mathcal{O}(\varepsilon^2) \tag{8.90}$$

where we call $\hat{A}_x(x)$ the *connection*. This gives us:

$$\begin{aligned} U(x+\varepsilon,x) &\to e^{i\theta(x+\varepsilon)}U(x+\varepsilon,x)e^{-i\theta(x)} \\ &\approx e^{i\theta(x+\varepsilon)}\left[\mathbb{I} + i\frac{e}{\hbar c}\varepsilon\hat{A}_x(x) + \mathcal{O}(\varepsilon^2)\right]e^{-i\theta(x)} \\ &\approx \mathbb{I} + i\frac{e}{\hbar c}\varepsilon\hat{A}_x(x) + \varepsilon\theta'(x) + \dots \end{aligned} \tag{8.91}$$

So from this, we see that we have:

$$\hat{A}_x(x) \to \hat{A}_x(x) + \frac{\hbar c}{e}\theta'(x)\mathbb{I} \tag{8.92}$$

which in turn allows us to formally define the covariant derivative as:

$$\begin{aligned} \hat{D}_x\psi(x) &= \left[\frac{\partial}{\partial x} - i\frac{e}{\hbar c}\hat{A}_x(x)\right]\psi(x) \\ \Rightarrow \quad -i\hbar\hat{D}_x\psi(x) &= \hat{\Pi}_x\psi(x) \end{aligned} \tag{8.93}$$

In general, we have:

$$\boxed{-i\hbar\hat{D}_j = \hat{\Pi}_j} \tag{8.94}$$

So the punch line is that the local gauge invariance (invariance under $\psi(x) \to e^{i\theta(x)}\psi(x)$) implies electromagnetism. In fact, the strong and weak nuclear forces also arise from a local (non-abelian) gauge invariance (where the comparator depends on the path from x_1 to x_2).

§8.4.1 The Aharonov-Bohm Effect

This is an experimental demonstration that the potential is the fundamental object in quantum mechanics and not the $\vec{E}$ and $\vec{B}$ fields. The set-up is as follows.

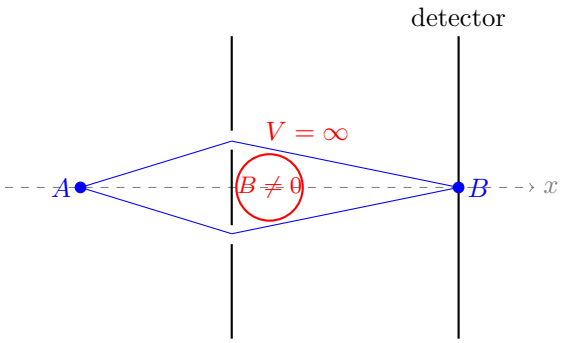


Figure 8.3: The Aharonov-Bohm effect set-up.

Consider a double-slit experiment, but pass the double slit, there is a cylinder that runs into the plane of the page such that there is only a non-trivial magnetic field **within** the cylinder, asserting the potential on the surface is infinite (illustrated in figure 8.3). We use the path integral formulation, so we write the classical Lagrangian for this being:

$$\mathscr{L} = \frac{1}{2}m\dot{\vec{x}}^2 + \frac{e}{c}\dot{\vec{x}}\cdot\vec{A} \tag{8.95}$$

where this form comes from the need to derive the Lorentz force law from this. Along a line segment $(\vec{x}_{n-1}, t_{n-1}) \to (\vec{x}_n, t_n)$, we have the action being:

$$\begin{aligned} S &= \int_{t_{n-1}}^{t_n} dt \mathscr{L} \\ &= S_0 + \int_{t_{n-1}}^{t_n} dt \frac{e}{c} \dot{\vec{x}} \cdot \vec{A} \\ &= S_0 + \frac{e}{c} \int_{\vec{x}_{n-1}}^{\vec{x}_n} \vec{A} \cdot d\vec{s} \\ \Rightarrow \quad e^{\frac{i}{\hbar}S} &= e^{\frac{i}{\hbar}S_0} \exp\left\{ \frac{ie}{\hbar c} \int_{\vec{x}_{n-1}}^{\vec{x}_n} \vec{A} \cdot d\vec{s} \right\} \end{aligned} \tag{8.96}$$

To perform this integral, we need to remember Stoke's theorem, which grants us:

$$\oint \vec{A} \cdot d\vec{s} = \Phi_B^{(inside)} \tag{8.97}$$

The integral we currently have is not closed, but if we consider the path that goes back and forth (that is $\vec{x}_1 \to \vec{x}_N$ plus $\vec{x}_N \to \vec{x}_1$), then this path is closed. Furthermore, we note that any closed path that does **not** enclose the solenoid would be zero:

$$\int_{\vec{x}_1}^{\vec{x}_N} \vec{A} \cdot d\vec{s}_1 - \int_{\vec{x}_1}^{\vec{x}_N} \vec{A} \cdot d\vec{s}_2 = 0 \tag{8.98}$$

But if the closed path does enclose the solenoid, we get:

$$\frac{e}{\hbar c} \left[\int_{\vec{x}_1}^{\vec{x}_N} \vec{A} \cdot d\vec{s}_1 - \int_{\vec{x}_1}^{\vec{x}_N} \vec{A} \cdot d\vec{s}_2 \right] = \frac{e}{\hbar c} \Phi_B \tag{8.99}$$

where we took path 1 to be above path 2. The intensity of this would then be given by:

$$\begin{aligned} I &\sim \left| \int [dx]_1 e^{-\frac{i}{\hbar}S} \right|^2 + \left| \int [dx]_2 e^{-\frac{i}{\hbar}S} \right|^2 + 2\,\mathrm{Re}\left\{ \int [dx]_1 e^{-\frac{i}{\hbar}S} \int [dx]_2 e^{-\frac{i}{\hbar}S} \right\} \\ &\sim \cos\left(\frac{e\Phi_B}{\hbar c} \right) \end{aligned} \tag{8.100}$$

So we indeed get that what effects the experimentally measurable quantities is only the flux which is given by the vector potential and **not** the magnetic field, since we only consider paths enclosing the cylinder which would not experience a magnetic field (but a vector potential).

§8.4.2 Magnetic Monopoles (?)

As we know from classical electromagnetic theory, Maxwell's equations are symmetric in $\vec{E}$ and $\vec{B}$, except for that the electric field is sourced by charges. If we tried to make it more symmetric, we could frivolously write:

$$\boldsymbol{\nabla} \cdot \vec{B} = 4\pi \rho_M \tag{8.101}$$

where ρ_M are defined as the *magnetic monopole charge density*. Suppose we have a point magnetic monopole of charge e_M at the origin, then:

$$\begin{aligned} & \vec{B} = \frac{e_M}{r^2}\hat{r} \\ \Rightarrow \quad & \boldsymbol{\nabla} \times \vec{A} = \hat{r}\left[\frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(A_\phi \sin\theta) - \frac{\partial}{\partial\phi}A_\theta\right] + \dots \\ \Rightarrow \quad & \vec{A} = \left[\frac{e_M(1-\cos\theta)}{r\sin\theta}\right]\hat{\phi} \end{aligned} \tag{8.102}$$

We realize this is **not** well behaved at $\theta = \pi$ ($\vec{A} \to \infty$). One way to resolve this is to find another solution and add them together:

$$\begin{aligned} \vec{A}^{(I)} &= \left[\frac{e_M(1-\cos\theta)}{r\sin\theta}\right]\hat{\phi}, \quad (\theta < \pi) \\ \vec{A}^{(II)} &= -\left[\frac{e_M(1+\cos\theta)}{r\sin\theta}\right]\hat{\phi}, \quad (\theta > 0) \end{aligned} \tag{8.103}$$

Since these both are valid solutions (both give the same $\vec{B}$ field), they must be related by a gauge transformation. Notice that:

$$\begin{aligned} & \vec{A}^{(II)} - \vec{A}^{(I)} = -\left(\frac{2e_M}{r\sin\theta}\right)\hat{\phi} \\ \Rightarrow \quad & \boxed{\Lambda = -2e_M\phi} \end{aligned} \tag{8.104}$$

We know that for such a gauge transformation, the wavefunctions are simply related by a coordinate dependent phase which gives us:

$$\begin{aligned} \psi^{(II)} &= e^{\frac{ie\Lambda}{\hbar c}}\psi^{(I)} \\ &= \exp\left\{-\frac{2iee_M\phi}{\hbar c}\right\}\psi^{(I)} \end{aligned} \tag{8.105}$$

We know that wavefunctions must be single-valued, we assert that:

$$\begin{aligned} & \psi(\phi = 0) = \psi(\phi = 2\pi) \\ \Rightarrow \quad & \frac{2ee_M}{\hbar c} = \pm n \\ \Rightarrow \quad & \boxed{e_M = \pm n\left(\frac{\hbar c}{2e}\right), \quad \text{or} \quad e = \pm n\left(\frac{\hbar c}{2e_M}\right)} \end{aligned} \tag{8.106}$$

So we get that either electric charge or the magnetic charge is quantized! So we would have a quantization of the electric charge with the existence of magnetic monopoles (which could perhaps explain why the electron and proton have exactly the same charge, but nobody knows this).

Chapter 9

Rotations and Angular Momentum

Rotations are a very important concept in general and also in quantum mechanics. Furthermore, the algebra of rotations also show up in many places that do not directly correspond to physical rotations, but nonetheless grant us powerful tools to solve relevant systems described by the same algebra.

§9.1 Introduction

Classically, we can treat rotations as 3×3 matrices that are orthogonal $R^T R = \mathbb{I}$ and preserve the norm of vectors ($\|R\vec{v}\| = \|\vec{v}\|$). Rotations are **not commutative**. Furthermore, we have that the determinant of these rotation matrices are always ± 1 as seen from:

$$\begin{aligned} & \det\{R^T R\} = \det(R^T) det(R) = \det(R)^2 = 1 \\ \Rightarrow \quad & \det\{R\} = \pm 1 \end{aligned} \tag{9.1}$$

Rotation matrices can be written in terms of sines and cosines in the entries and any rotation in 3-d space can be fully parameterized by 3 parameters which are often referred to as the *Euler angles*. In quantum mechanics, we are concerned with generators of some unitary transformation via the exponential map. The way we derive this is through infinitesimal translations from these unitaries, so let's consider an infinitesimal rotation by angle ε around the z-axis (without loss of generality):

$$R_z(\varepsilon) = \begin{bmatrix} 1 - \varepsilon^2/1 & -\varepsilon & 0 \\ \varepsilon & 1 - \varepsilon^2/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{9.2}$$

Considering the commutator of $R_z(\varepsilon)$ and $R_y(\varepsilon)$, we get:

$$\begin{aligned}[R_z(\varepsilon), R_y(\varepsilon)] &= \begin{bmatrix} 0 & -\varepsilon^2 & 0 \\ \varepsilon^2 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\ &= R_z(\varepsilon) - \mathbb{I} + \mathcal{O}(\varepsilon^4)\end{aligned} \tag{9.3}$$

As for quantum mechanics, supposed $R(\vec{n}, \theta)$ is now some unitary operator $\hat{U}[R(\vec{n}, \theta)]$ which allows us to rotate states:

$$|\psi\rangle_R = \hat{U}[R(\vec{n}, \theta)]\,|\psi\rangle \tag{9.4}$$

Expanding this operator out by Taylor expansion, we get:

$$\hat{U}(\vec{n}, d\theta) = \mathbb{I} - \frac{i}{\hbar}\hat{O}_{\vec{n}} d\theta + \dots \tag{9.5}$$

where $\hat{O}_{\vec{n}}$ is some operator that tells us about the axis of rotation. We claim that this operator can be written as a vector of operators that act on each axis whivh let's us write:

$$\begin{aligned}&\hat{U}(\vec{n}, d\theta) = \mathbb{I} - \frac{i}{\hbar}(\hat{\vec{J}} \cdot \hat{\vec{n}}) d\theta + \dots \\ \Rightarrow \quad &\hat{U}(\vec{n}, d\theta) = \exp\left\{-\frac{i\hat{\vec{J}} \cdot \hat{\vec{n}}}{\hbar}\right\}\end{aligned} \tag{9.6}$$

We want that the commutators of these unitaries acting in each axis not to vanish, so we try with x and y:

$$\begin{aligned}&\left[\hat{U}(\hat{\ },\hat{x}), \hat{U}(\hat{\ },\hat{y})\right] = \hat{U}(\hat{\ },\hat{z}) - \mathbb{I} + \dots \\ \Rightarrow \quad &\left[\mathbb{I} - \frac{i}{\hbar}\hat{J}_x\varepsilon - \frac{1}{2\hbar^2}\hat{J}_x^2\varepsilon^2, \mathbb{I} - \frac{i}{\hbar}\hat{J}_y\varepsilon - \frac{1}{2\hbar^2}\hat{J}_y^2\varepsilon^2\right] = -\frac{i}{\hbar}\hat{J}_y\varepsilon^2 \\ \Rightarrow \quad &\left[-\frac{i}{\hbar}\hat{J}_x\varepsilon, -\frac{i}{\hbar}\hat{J}_y\varepsilon\right] = -\frac{i}{\hbar}\hat{J}_y\varepsilon^2 \\ \Rightarrow \quad &\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z\end{aligned} \tag{9.7}$$

or more generally,

$$\boxed{\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\varepsilon_{ijk}\hat{J}_k} \tag{9.8}$$

These $\hat{J}$ operators are in fact angular momentum, because just like how the momentum operator were the generators of translation in position, these the angular momentum operators are the generators of rotations. A useful property of these operators are that $\left[\hat{\vec{J}}^2, \hat{J}_j\right] = 0$, which means that we can simultaneously diagonalize these operators. To do so, we define a new set of operators:

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \tag{9.9}$$

which are called the *angular momentum ladder operators*. These are analogous to the ladder operators we saw in the quantum harmonic oscillator and are also **not** Hermitian. Some properties of these operators are listed below.

1. $\left[\hat{J}_+, \hat{J}_-\right] = 2\hbar\hat{J}_z$
2. $\left[\hat{J}_z, \hat{J}_\pm\right] = \pm\hbar\hat{J}_\pm$
3. $\left[\hat{\vec{J}}^2, \hat{J}_\pm\right] = 0$

Now to find the simultaneous eigenstates of $\hat{\vec{J}}^2$ and $\hat{J}_z$. To do so, we write:

$$\begin{aligned} \hat{\vec{J}}\,|a,b\rangle &= a\,|a,b\rangle \\ \hat{J}_z\,|a,b\rangle &= b\,|a,b\rangle \end{aligned} \tag{9.10}$$

Now consider the action of the ladder operators we have just constructed on these states as follows:

$$\begin{aligned} \hat{J}_z\left(\hat{J}_\pm\,|a,b\rangle\right) &= \left(\left[\hat{J}_z, \hat{J}_\pm\right] + \hat{J}_\pm\hat{J}_z\right)|a,b\rangle \\ &= \left(\pm\hbar\hat{J}_\pm + b\hat{J}_\pm\right)|a,b\rangle \\ &= (b \pm \hbar)\hat{J}_\pm\,|a,b\rangle \end{aligned} \tag{9.11}$$

So we see that $\hat{J}_\pm\,|a,b\rangle$ are $\hat{J}_z$ eigenstates and the action of these ladder operators simply raise and lower the eigenvalue of $\hat{J}_z$ by $\hbar$ (which is why they get they're name). If we work it out, we also find that:

$$\hat{\vec{J}}^2(\hat{J}_\pm\,|a,b\rangle) = a(\hat{J}_\pm\,|a,b\rangle) \tag{9.12}$$

We now state a claim.

Claim: *We cannot apply the ladder operators indefinitely without destroying the state. That is, there is a finite number of $|a,b\rangle$ eigenstates.*

Proof. To show this, we consider the operator:

$$\begin{aligned} \hat{\vec{J}}^2 - \hat{J}_z^2 &= \frac{1}{2}(\hat{J}_+\hat{J}_- - \hat{J}_-\hat{J}_+) \\ &= \frac{1}{2}(\hat{J}_+\hat{J}_+^\dagger - \hat{J}_+^\dagger\hat{J}_+) \end{aligned} \tag{9.13}$$

So the right-hand side would grant us:

$$\langle a,b|\,\hat{J}_+^\dagger\hat{J}_+\,|a,b\rangle \propto \langle a, b+\hbar|a,b+\hbar\rangle \geq 0 \tag{9.14}$$

whereas the left-hand side gives us:

$$\langle a,b|\,(\hat{\vec{J}}^2 - \hat{J}_z^2)\,|a,b\rangle = a - b^2 \tag{9.15}$$

so we get that:

$$\boxed{a - b^2 \geq 0} \tag{9.16}$$

So this grants us that there must be some $b_{\max}$ such that:

$$\begin{aligned} & \hat{J}_+ |a, b_{\max}\rangle = 0 \\ \Rightarrow \quad & \hat{J}_- \hat{J}_+ |a, b_{\max}\rangle = (\hat{\vec{J}}^2 - \hat{J}_z^2 - \hbar \hat{J}_z) |a, b_{\max}\rangle = 0 \\ \Rightarrow \quad & a - b_{\max}^2 - \hbar b_{\max} = 0 \\ \Rightarrow \quad & \boxed{a = b_{\max}(b_{\max} + \hbar)} \end{aligned} \tag{9.17}$$

A similar computation can be done for $b_{\min}$, which would grant us:

$$\boxed{a = b_{\min}(b_{\min} - \hbar)} \tag{9.18}$$

So we have 2 equations in terms of $b_{\min}$ and $b_{\max}$, for which equating them grants us:

$$b_{\max} = -b_{\min} \tag{9.19}$$

For which self-consistency dictates that we should be able to get from $|a, b_{\min}\rangle$ to $|a, b_{\max}\rangle$ using ladder operators. That implies that they are related by an integer number of $\hbar$ terms:

$$\begin{aligned} & b_{\max} = b_{\min} + h\hbar \\ \Rightarrow \quad & b_{\max} = \frac{n\hbar}{2} \end{aligned} \tag{9.20}$$

□

From the result above, we further see that this gives us a quantization of b and thus a quantization of a:

$$a = \frac{\hbar^2}{4} n(n+2) \tag{9.21}$$

In the more commonly adopted notation in physics, we define the quantities j and m that are:

$$\begin{aligned} & j \equiv \frac{n}{2}, \quad m = \frac{b}{\hbar} \\ \Rightarrow \quad & \boxed{\begin{array}{c} \hat{J}_z |j, m\rangle = m\hbar |j, m\rangle \\ \hat{\vec{J}}^2 |j, m\rangle = \hbar^2 j(j+1) |j, m\rangle \end{array}} \end{aligned} \tag{9.22}$$

where we have that $m \in [-j, j]$ and we will soon see that j can **only** take on integer or half-integer

values. First, recall the operator we introduced in one of the steps earlier:

$$\begin{aligned} & \hat{J}_- \hat{J}_+ = (\hat{\vec{J}}^2 - \hat{J}_z^2 - \hbar \hat{J}_z) \\ \Rightarrow \quad & \langle j,m| \hat{J}_- \hat{J}_+ |j,m\rangle = \langle j,m| (\hat{\vec{J}}^2 - \hat{J}_z^2 - \hbar \hat{J}_z) |j,m\rangle \\ \Rightarrow \quad & \langle j,m| \hat{J}_- \hat{J}_+ |j,m\rangle = \hbar^2 j(j+1) - \hbar^2 m(m+1) \end{aligned} \tag{9.23}$$

To evaluate the left-hand side, we look at the action of the ladder operators on these eigenstates:

$$\begin{aligned} & \hat{J}_+ |j,m\rangle = c_{j,m} |j,m+1\rangle , \quad \langle j,m| \hat{J}_- = \langle j,m+1| c_{j,m}^* \\ \Rightarrow \quad & \hbar^2 j(j+1) - \hbar^2 m(m+1) = |c_{j,m}|^2 \\ \Rightarrow \quad & c_{ij} = \hbar \sqrt{j(j+1) - m(m+1)} = \hbar \sqrt{(j-m)(j+m+1)} \\ \Rightarrow \quad & \hat{J}_+ |j,m\rangle = \hbar \sqrt{j(j+1) - m(m+1)} \, |j,m+1\rangle = \hbar \sqrt{(j-m)(j+m+1)} \, |j,m+1\rangle \end{aligned} \tag{9.24}$$

where we rewrote the equation within the square-root for convenience as we will soon see. From these results, we can write the matrix elements of the ladder operators in the j,m eigen-basis as:

$$\boxed{\langle j',m'| \hat{J}_\pm |j,m\rangle = \hbar \delta_{j,j'} \delta_{m',m\pm1} \sqrt{(j \mp m)(j \pm m + 1)}} \tag{9.25}$$

There are several things from these matrix elements. First, it is that setting $j = 0$ gives us the state $|0,0\rangle$ which is annihilated not just by the ladder operators, but also $\hat{J}$ and $\hat{\vec{J}}^2$ (trivial state). The other thing we can see is that the lowest non-trivial value of j is $j = 1/2$, which gives us that $m = -1/2, 1/2$. This is in fact a 2-level system in m which when we work out the matrix elements, is exactly the quantum mechanical spin-$\frac{1}{2}$ states we have seen from before:

$$\hat{J}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \hat{J}_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \hat{J}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \tag{9.26}$$

$$\hat{J}_- = \frac{\hbar}{2} \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}, \quad \hat{J}_+ = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \tag{9.27}$$

Let's consider the case where $j = 1$, so we have $m = -1, 0, 1$ which is a 3-level system in m. The matrix representation of the $\hat{J}$ operators work out to be:

$$|1,-1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad |1,0\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad |1,1\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \tag{9.28}$$

$$\begin{aligned} \Rightarrow \quad & \hat{J}_- = \hbar \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}, \quad \hat{J}_+ = \hbar \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{bmatrix} \\ & \hat{J}_z = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \end{aligned} \tag{9.29}$$

And we can keep increasing the value of j by $1/2$ to get larger and larger Hilbert spaces.

§9.2 Orbital Angular

In classical mechanics, we know that orbital angular momentum is given by:

$$\vec{L} = \vec{r} \times \vec{p} \tag{9.30}$$

So in quantum mechanics, we can try this but with operators instead, which gives us:

$$\hat{\vec{L}} = \hat{\vec{r}} \times \hat{\vec{p}} \tag{9.31}$$

This operator works out to satisfy the commutation relation:

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\varepsilon_{ijk}\hat{L}_k \tag{9.32}$$

which is exactly the algebra (commutation relation) of the generators of rotation (angular momentum operators $\hat{J}$). Now consider the operator:

$$\mathbb{I} - i\frac{\delta\phi}{\hbar}\hat{L}_z \tag{9.33}$$

where $\delta\phi$ is some small real number. To find the action of this operator on a state in the coordinate space representation, we take:

$$\begin{aligned}\langle x,y,z|\left[\mathbb{I} - i\frac{\delta\phi}{\hbar}\hat{L}_z\right]|\psi\rangle &= \langle x,y,z|\left[\mathbb{I} - i\frac{\delta\phi}{\hbar}\left(\hat{p}_y\hat{x} - \hat{p}_x\hat{y}\right)\right]|\psi\rangle \\ &= \psi(\vec{x}) - \delta\phi x\frac{\partial}{\partial y}\psi(\vec{x}) + \delta\phi y\frac{\partial}{\partial x}\psi(\vec{x}) \\ &\approx \psi(x + y\delta\phi, y - x\delta\phi, z)\end{aligned} \tag{9.34}$$

which looks like a rotation about the z-axis by a small angle $\delta\phi$. So as expected, we have that these orbital angular momentum operators are indeed the generators of rotation. If we then work out what the operator $\hat{L}_z$ in spherical coordinates, we get:

$$\boxed{\begin{array}{c}\hat{L}_x = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\ \hat{L}_y = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\ \hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}\end{array}} \tag{9.35}$$

The operators for $\hat{L}_{x,y}$ are a little messy, so we usually write them in terms of the ladder operators which have nice forms in coordinates space:

$$\langle x,y,z|\hat{L}_\pm|\psi\rangle = -i\hbar e^{\pm i\phi}\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)\langle x,y,z|\psi\rangle \tag{9.36}$$

and we also have:

$$\begin{aligned}\langle x,y,z|\hat{\vec{L}}^2|\psi\rangle &= \langle x,y,z|\hat{L}_z^2 + \frac{1}{2}\left(\hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+\right)|\psi\rangle \\ &= -\hbar^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]\langle x,y,z|\psi\rangle\end{aligned} \tag{9.37}$$

which is in fact the radial portion of the Laplacian operator! As such, we can write:

$$\boxed{\frac{\hat{\vec{p}}^2}{2m} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 = -\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{\vec{L}}^2}{2mr^2}} \tag{9.38}$$

§9.2.1 Complete Set of Commuting Observables

Now we take an aside to understand the concept of a *complete set of commuting observables (CSCO)*. The idea is that if we find a set of observables that all commute with each other, then measuring these observables allows us to collapse the system to a definite state of eigenvalues $\{a, b, c, \ldots\}$, $|a, b, c, \ldots\rangle$. The set of $\{a, b, c, \ldots\}$ eigenvalues for a CSCO are known as *quantum numbers*. It is nice but not necessary that the Hamiltonian is in the CSCO we find. This is possible because the CSCO is **not** unique.

For instance, in a 2-level system we can have the CSCO's as $\{\hat{S}_x, \hat{S}_y\}$, $\{\hat{S}_z\}$ or $\{\hat{\vec{S}}^2, \hat{S}_z\}$. While for the quantum harmonic oscillator, we could have $\{|n\rangle\langle n|\}$ (which is an infinite set). We can then ask the question, how do we know a given set of commuting observables is in fact complete? Well, we can look at degeneracies. By degeneracoes, we mean that making a measurement on each of the operators must produce a unique state with regards to their entire spectrum.

Example:

Consider a spin-$\frac{1}{2}$ particle in a simple harmonic oscillator. To do this, we need to introduce the *direct product* $\otimes$, which is defined as a binary operation on Hilbert spaces:

$$\otimes : \mathcal{H}_1 \times \mathcal{H}_2 \to \mathcal{H}_1 \times \mathcal{H}_2 \tag{9.39}$$

$$|\alpha\rangle \otimes |\beta\rangle \mapsto |\alpha, \beta\rangle \tag{9.40}$$

where we have the short-hand notation of combining ket states on direct product Hilbert spaces into one ket with 2 labels. A property of this direct product is that $\dim\{\mathcal{H}_1 \otimes \mathcal{H}_2\} = \dim\{\mathcal{H}_1\}\dim\{\mathcal{H}_2\}$. Back to the physical system, we supposed we don't know about the spin state but prepare it such that:

$$|\psi\rangle = \left(\frac{3}{5}|0\rangle + \frac{4}{5}|-\rangle\right) \otimes (\alpha|+\rangle + \beta|-\rangle) \tag{9.41}$$

$$= \frac{3}{5}\alpha|0,+\rangle + \frac{3}{5}\beta|0,-\rangle + \frac{4}{5}\alpha|1,+\rangle + \frac{4}{5}\beta|1,-\rangle \tag{9.42}$$

If we then compute the probability of getting an energy with quantum number $n = 0$, this works out to be:

$$\mathbb{P}\left(E = \frac{\hbar\omega}{2}\right) = |\langle 0,+|\psi\rangle|^2 = \frac{9}{25}(|\alpha|^2 + |\beta|^2) = \frac{9}{25} \tag{9.43}$$

Which is exactly the same probability we would get with the individual system of the QHO without spin. So this tells us that we need a measurement sensitive to the spin as well to indeed have all the information we require. So determining a CSCO becomes an experimental endeavour.

§9.3 3-d Schrödinger's Equation

Now back to rotations, we will use our new knowledge of CSCO's to study quantum systems in 3-dimensions. First, we assume that the system we are dealing with is spherically symmetric ($V(\vec{r}) = V(r)$). In a spherically symmetric system, knowing the form of the angular momentum operators tells us that we will have the commutator relations:

$$\left[\hat{\vec{L}}^2, \hat{H}\right] = 0, \quad \left[\hat{L}_j, \hat{H}\right] = 0, \quad \left[\hat{\vec{L}}^2, \hat{L}_j\right] = 0 \tag{9.44}$$

$$\Rightarrow \quad \text{CSCO} : \{\hat{H}, \hat{\vec{L}}^2, \hat{L}_z\} \quad \rightarrow \quad \text{simultaneous eigenstates} : |E, l, m\rangle \tag{9.45}$$

The angular momentum operators acting on these states $|E, l, m\rangle$ would pull out the eigenvalues we have already seen earlier ($\hbar m$ and $\hbar^2 l(l+1)$. In the coordinate space representation, the equation we have is:

$$\begin{aligned} &-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{\vec{L}}^2}{2mr^2}\psi_{E,l,m}(\theta,\phi) = [E - V(r)]\,\psi_{E,l,m}(\theta,\phi) \\ \Rightarrow \quad &\boxed{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l(l+1)}{r^2} + V(r)\right]\psi_{E,l,m}(r,\theta,\phi) = E\psi_{E,l,m}(r,\theta,\phi)} \end{aligned} \tag{9.46}$$

This is the 3-*d spherically symmetric Schröinger's equation.* We now try to find separable solutions to this equation, which take the form:

$$\psi_{E,l,m}(\theta,\phi) = R_{E,l}(r)Y_{l,m}(\theta,\phi) \tag{9.47}$$

where of course $Y_{l,m} = \langle\theta,\phi|l,m\rangle$ are the famed *spherical harmonics* that satisfy:

$$-i\hbar\frac{\partial}{\partial\phi}Y_{l,m}(\theta,\phi) = \hbar m Y_{l,m}(\theta,\phi) \tag{9.48}$$

Furthermore, the completeness relation follows from the orthogonality of the $|l,m\rangle$ states ($\langle l',m'|l,m\rangle = \delta_{l,l'}\delta_{m,m'}$):

$$\begin{aligned} \langle\theta',\phi'|\theta,\phi\rangle &= \delta(\phi-\phi')\delta(\theta-\theta') \\ &= \sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_{l,m}(\theta',\phi')Y^*_{l,m}(\theta,\phi) \end{aligned} \tag{9.49}$$

If we do another separation of variables for these spherical harmonics, we find that the ϕ dependence is simply a phase given by:

$$Y_{l,m}(\theta,\phi) = T(\theta)\rho(\phi) = T(\theta)e^{im\phi} \tag{9.50}$$

where m has to take on integer values since the wavefunction has to be single-valued ($\rho(\phi+2\pi) = \rho(\phi)$). From the spherical harmonics, we also have the *associated Legendre polynomials* $P_l(\cos\theta)$ defined as:

$$\boxed{Y_{l,0}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}}P_l(\cos\theta)} \tag{9.51}$$

Lastly on these, the spherical harmonics satisfy a nice property in the parity of m:

$$Y_{l,-m}(\theta,\phi) = (-1)^m Y^*_{l,m}(\theta,\phi) \tag{9.52}$$

In spectroscopy, the l labels are also referred to with letter labels $\{0,1,2,3,4,\ldots\} \to \{s,p,d,f,g,\ldots\}$.

§9.3.1 Parity of Spherical Harmonics

The first thing to ask here is what does parity look like in 3-d? Well, it is simply:

$$\hat{P}\,|x,y,z\rangle \to |-x,-y,-z\rangle \tag{9.53}$$

$$\Rightarrow \quad \hat{P}\,|r,\theta,\phi\rangle \to |r,\pi-\theta,\phi+\pi\rangle \tag{9.54}$$

So we have that the parity operator acting on the spherical harmonics is given by:

$$\begin{aligned} & \hat{P}Y_{l,m}(\theta,\phi) = \hat{P}P_l^m(\cos\theta)e^{im\phi} \\ \Rightarrow \quad & \hat{P}Y_{l,m}(\theta,\phi) = (-1)^{l-|m|}P_l^m(\cos\theta)e^{im\phi}(-1)^m e^{im\phi} \\ \Rightarrow \quad & \boxed{\hat{P}Y_{l,m}(\theta,\phi) = (-1)^l Y_{l,m}(\theta,\phi)} \end{aligned} \tag{9.55}$$

§9.4 3-d Wave Mechanics

We will now be looking at the radial portion of the 3-d wavefunction. For this, it is useful to know some special functions. Several online resources for this are https://dlmf.nist.gov/ and http://functions.wolfram.com/. Recall that the 3-d Schrödinger's equation for a spherically symmetry potential is given by:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l(l+1)}{r^2} + V(r)\right]\psi_{E,l,m}(\theta,\phi) = E\psi_{E,l,m}(\theta,\phi) \tag{9.56}$$

So the radial portion for separable solutions is given by:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l(l+1)}{r^2} + (V(r)-E)\right]R_{El}(r) = 0 \tag{9.57}$$

Defining $\rho \equiv kr$ where $k^2 = 2m(E-V)/\hbar^2$, we have:

$$R''(\rho) + \frac{2}{\rho}R'(\rho) + \left[1 - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0 \tag{9.58}$$

for which the solutions to this equation is given by spherical *Bessel* and *Neuman functions*:

$$j_l(\rho) = (-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{\sin\rho}{\rho} \tag{9.59}$$

$$n_l(\rho) = (-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{\cos\rho}{\rho} \tag{9.60}$$

In the limit as $\rho \to 0$, we have the asymptotic versions of these special functions tend to:

$$\lim_{\rho\to 0} j_l(\rho) \approx \frac{\rho^l}{(2l+1)!!} \tag{9.61}$$

$$\lim_{\rho\to 0} n_l(\rho) \approx -\frac{(2l+1)!!}{\rho^{l+1}} \tag{9.62}$$

and in the limit where $\rho \to \infty$, we have:

$$\lim_{\rho\to \infty} j_l(\rho) \approx \frac{1}{\rho}\sin\left(\rho - \frac{l\pi}{2}\right) \tag{9.63}$$

$$\lim_{\rho\to \infty} n_l(\rho) \approx -\frac{1}{\rho}\cos\left(\rho - \frac{l\pi}{2}\right) \tag{9.64}$$

Notice that the Bessel functions j_l re regular at the origin whereas the Neuman functions n_l are regular at infinity.

Example:

$$V(r) = \begin{cases} 0, & r \leq R \\ \infty, & r > R \end{cases} \tag{9.65}$$

Since we have for this potential, that the boundary condition is that the wavefunction must be finite at $r = 0$, we have:

$$R_{El}(\rho) = A_l j_l(\rho) \tag{9.66}$$

while the other boundary condition is that $R_{El}(\rho) = 0$ at $r = R$, this grants us the solution:

$$\begin{aligned} & j_l(kR) = 0 \\ \Rightarrow \quad & \frac{\sin(kR)}{kR} = 0, \quad (l = 0) \\ \Rightarrow \quad & kR = n\pi, \quad n \geq 1 \\ \Rightarrow \quad & E_{n,l=0} = \frac{\hbar^2 n^2 \pi^2}{2mR^2} \end{aligned} \tag{9.67}$$

For other values of l we need to find these solutions numerically. With this, we have the general solution to the time-independent 3-d Schrödinger's equation to be:

$$\psi_{n,l,m} = A_{n,l} j_l(k_n r) Y_{l,m}(\Omega) \tag{9.68}$$

where the $A_{n,l}$ coefficients are determined by normalization.

Example:

Consider the finite square-well:

$$V(r) = \begin{cases} 0, & r \leq R \\ V_0, & r > R \end{cases} \tag{9.69}$$

We are looking for bound-states $0 < E < V_0$, where we now define $\kappa^2 = 2m(V - E)/\hbar^2$. In the far-field limit ($r \to \infty$), if we naively choose the solution the same way we did for the infinite square-well, we would have:

$$\begin{aligned} j_l(i\kappa r) &\to -\frac{i}{\kappa r}\sin\left(i\kappa r = \frac{l\pi}{2}\right) \\ &= \frac{1}{\kappa r}\left[\cos\left(\frac{l\pi}{2}\right)\sinh(\kappa r) + i\sin\left(\frac{l\pi}{2}\right)\cosh(\kappa r)\right] \end{aligned} \tag{9.70}$$

But we see that both sinh and cosh blow up at infinity! So we instead use a linear combination of the Bessel and Neuman functions to get:

$$h_l^{(1)}(\rho) = j_l(\rho) + in_l(\rho) \tag{9.71}$$

$$h_l^{(2)}(\rho) = j_l(\rho) - in_l(\rho) \tag{9.72}$$

These are known as *spherical Hankel functions*. These functions in the asymptotic $r \to \infty$ limit will grant us:

$$h_l^{(1)}(\rho) \to -\frac{i^{-l}}{\kappa r}e^{-\kappa r} \tag{9.73}$$

$$h_l^{(2)}(\rho) \to \frac{i^{l}}{\kappa r}e^{\kappa r} \tag{9.74}$$

for which the only physical solutions will be the first Hankel functions.

§9.4.1 Recasting to 1-d

We are going to use a trick now we have used in classical mechanics for the 2-body problem, and we can use the mechanics we have found in the 1-d situation. The first thing we do is to replace the radial function to take the form:

$$R_{El}(r) = \frac{u_{El}(r)}{r} \tag{9.75}$$

This grants us the equation:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{2mr^2}\right]u_{El}(r) = Eu_{El}(r) \tag{9.76}$$

where if we define:

$$\begin{aligned} & V_{eff}(r) \equiv V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \\ \Rightarrow \quad & \left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V_{eff}(r)\right]u_{El}(r) = Eu_{El}(r) \end{aligned} \tag{9.77}$$

which gives us exactly the 1-d Schrödinger's equation we have been working with. However, note that these $u_{El}(r)$ functions satisfy the normalization:

$$\int dr|u_{El}(r)|^2 = \int dr|R_{El}(r)|^2 r^2 = 1 \tag{9.78}$$

Now, if we have the case where $\lim_{r\to 0} r^2 V(r) = 0$ (the centrifugal term is dominant near the origin), then we have:

$$\begin{aligned} & \frac{d^2}{dr^2}u_{El}(r) \approx \frac{l(l+1)}{r^2}u_{El}(r) \\ \Rightarrow \quad & u_{El}(r) = Ar^{l+1} + \frac{B}{r^l} \end{aligned} \tag{9.79}$$

Very close to the origin, we have $B \to 0$ to keep the wavefunction regular, so we have $R_{El}(r) \sim r^l$. There are some real physical potentials that have such a behaviour such as the Coulomb potential, which for $r \ll a_0$, the probability to find the electron $\sim (r/a_0)^{2l}$.

In the Bohr model, the energy scales like $E_n = 13.6/n^2$ eV (works as a good approximation for Hydrogen). Alkali metals also have effectively a single electron due to its electronic configuration, however the spectrum is not nicely approximated by the Bohr model especially the electrons within the outermost shell.

Example:

Consider a potential that vanishes as $r \to \infty$. In this case, the centrifugal term vanishes as well at long distances so we have:

$$\begin{aligned} & \frac{d^2}{dr^2}u_E(r) = -\frac{2mE}{\hbar^2}u_E(r) \\ \Rightarrow \quad & u_E \sim e^{-\kappa r} \end{aligned} \tag{9.80}$$

if $E < 0$, or some exponential dependence in general. In general for such potential, we can remove the asymptotics by having the function:

$$\boxed{w_{El}(\rho) = \rho^{-(l+1)}e^{\rho}u_{El}(\rho)} \tag{9.81}$$

Example:

Consider the 3-d isotropic harmonic oscillator:

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + \frac{1}{2}m\omega^2\hat{r}^2 \tag{9.82}$$

For convenience, we define $E \equiv \hbar\omega\lambda/2$ and $r \equiv \rho\sqrt{\hbar/(m\omega)}$. This grants us:

$$\begin{aligned} & \frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u + (\lambda - \rho^2)u = 0 \\ \Rightarrow \quad & u(\rho) = \rho^{l+1}e^{-\rho^2/2}f(\rho) \end{aligned} \tag{9.83}$$

With the differential equation in ρ, we can plug in the ansatz above to get a differential equation for $f(\rho)$:

$$\begin{aligned} & \rho\frac{d^2}{d\rho^2}f(\rho) + 2\left[(l+1)-\rho^2\right]\frac{d}{d\rho}f(\rho) + \left[\lambda-(2l+1)\right]\rho f(\rho) = 0 \\ \Rightarrow \quad & f(\rho) = \sum_{n=0}^{\infty} a_n \rho^n \end{aligned} \tag{9.84}$$

Plugging in this ansatz, we get:

$$\sum_n n(n-1)a_n\rho^{n-1} + 2\sum_n n a_n\left[(l+1)\rho^{n-1}-\rho^{n+1}\right] + \left[\lambda-(2l+3)\right]\sum_n a_n\rho^{n+1} = 0 \tag{9.85}$$

which in fact produces the recursion relation for the coefficients (where we had that we can treat each term in n to vanishes because the equation must hold for any value of ρ):

$$\boxed{a_{n+2} = \frac{2n+2l+3-\lambda}{(n+1)(n+2l+3)}a_n} \tag{9.86}$$

We notice that we only have even coefficients left because of the form above, and produces the asymptotic ($\rho \ll 1$ implying large n) behaviour:

$$\lim_{n\to\infty}\frac{a_{n+2}}{a_n} = \frac{2}{n} \equiv \frac{1}{q}, \quad q \in \mathbb{Z} \tag{9.87}$$

Using this new definition of integers q, we have that in this asymptotic limit, the function $f(\rho)$ becomes:

$$f(\rho) \to \sum_q \frac{1}{q!}(\rho^2)^q \sim e^{\rho^2} \tag{9.88}$$

showing that the solutions blow up at infinity, which is disastrous (we know that the wavefunction should decay at infinity)! However physically, we are looking for bound-states which implies a quantization condition. As such, this signals to us that the sum should in fact be truncated (terminates at some q) allowing for a well-behaved wavefunction instead. To find at what q the sum terminates, we look back at the recursion relation and have that the numerator vanishes:

$$\begin{aligned} & 2n+2l+3-\lambda = 0 \\ \Rightarrow \quad & \lambda = 2n+2l+3 \\ \Rightarrow \quad & E_{q,l} = \left(2q+1+\frac{3}{2}\right)\hbar\omega \equiv \left(N+\frac{3}{2}\right)\hbar\omega \end{aligned} \tag{9.89}$$

which indeed grants us the harmonic oscillator energies if we define $N \equiv 2q+l$. This energy relation however results in a high degree of degeneracy in q and l (there are additionally also the m states). Another way to view these degeneracies is writing this isotropic harmonic oscillator as:

$$\begin{aligned} & V(\vec{r}) = \frac{1}{2}m\omega^2(\hat{x}^2+\hat{y}^2+\hat{z}^2) \\ \Rightarrow \quad & E_{n_j} = \left(n_x+n_y+n_z+\frac{1}{2}\right)\hbar\omega \equiv \left(N+\frac{1}{2}\right)\hbar\omega \end{aligned} \tag{9.90}$$

This degeneracy is often referred to as an *accidental symmetry* where q and l contribute similarly to E, but is in fact due to a symmetry in the *Runge-Lenz vector*. This also occurs in the Hydrogen atom where that system as energies:

$$E_{q,l} = \frac{1}{2}mc^2\frac{\alpha^2}{(q+l+1)^2} \tag{9.91}$$

§9.5 Spin-1/2 Revisited

To start, if we think back about orbital angular momentum, only integer values of l are allowed. However, for the general solution of angular momentum operators (eigenvalues), we have that l could be both integers **and** half-integers with the condition that $|m| \leq l$ ($2l+1$ dimensional Hilbert space). Let us think about the Hilbert spaces for several values of l and classical correspondence.

1. $\underline{l=0}$: 1-d Hilbert space (trivial) $\rightarrow$ behaves like scalars in classical physics.
2. $\underline{l=1}$: 3-d Hilbert space $\rightarrow$ behaves like spatial vectors.

However above, we skipped one of them which is $l = 1/2$, which grants us a 2-d Hilbert space. When we try to think about these with a classical correspondence, this is very strange because its somewhere in between a scalar and a vector. So we can ask now, how does a spin-1/2 system actually transform under finite rotation? Specifically, we pick rotations around the z-axis (ϕ rotations). We know that the spin operators generate rotations, we can write:

$$|\psi_R\rangle = \hat{U}(\phi)\,|\psi\rangle = \exp\left\{-i\frac{\hat{S}_z}{\hbar}\phi\right\}|\psi\rangle \tag{9.92}$$

Let's first check if this actually undergoes rotations:

$$\begin{aligned}
\langle\hat{S}_x\rangle \rightarrow &= \langle\psi_R|\,\hat{S}_x\,|\psi_R\rangle \\
&= \langle\psi|\exp\left\{i\frac{\hat{S}_z}{\hbar}\phi\right\}\hat{S}_x\exp\left\{-i\frac{\hat{S}_z}{\hbar}\phi\right\}|\psi\rangle \\
&= \frac{\hbar}{2}\langle\psi|\exp\left\{i\frac{\hat{S}_z}{\hbar}\phi\right\}\Big[\,|+\rangle\langle-| + |-\rangle\langle+|\,\Big]\exp\left\{-i\frac{\hat{S}_z}{\hbar}\phi\right\}|\psi\rangle \\
&= \frac{\hbar}{2}\langle\psi|\left[e^{i\phi}\,|+\rangle\langle-| + e^{-i\phi}\,|-\rangle\langle+|\right]|\psi\rangle \\
&= \langle\hat{S}_x\rangle\cos\phi - \langle\hat{S}_y\rangle\sin\phi
\end{aligned} \tag{9.93}$$

which shows that this is indeed a rotation around the z-axis. In fact in general, we can work out that:

$$\langle\hat{S}_k\rangle \rightarrow R_{kl}\langle\hat{S}_l\rangle \tag{9.94}$$

where Einstein sum notation is adopted above and the arrow above is the application of a rotation. Let's now instead consider an arbitrary state, and rotations generated by the spin-1/2 operators applied to it. This can be done by an expansion into the eigenstates:

$$\exp\left\{-i\frac{\hat{S}_z}{\hbar}\phi\right\}|\psi\rangle = e^{-i\phi/2}|+\rangle\langle+|\psi\rangle + e^{i\phi/2}|-\rangle\langle-|\psi\rangle \tag{9.95}$$

We notice a strange artifact, that now, the state is 4π periodic since applied rotations rotate the state by $\phi/2$ instead of ϕ. We actually have seen this before when we considered a particle in a magnetic field $\vec{B}$, which gives us the Hamiltonian:

$$\hat{H} = \hat{\vec{\mu}}\cdot\vec{B} = -\frac{e}{m_e c}\hat{\vec{S}}\cdot\vec{B} \tag{9.96}$$

We saw before that applying a magnetic field would cause spin particles to precess. For instance, if $\vec{B} = B\hat{z}$, we had that:

$$\begin{aligned}\langle\hat{S}_x\rangle &= \langle\hat{S}_x\rangle\cos(\omega t) - \langle\hat{S}_y\rangle\sin(\omega t)\\ |\psi(t)\rangle &= e^{-i\omega t/2}|+\rangle\langle+|\psi\rangle + e^{i\omega t/2}|-\rangle\langle-|\psi\rangle\end{aligned} \tag{9.97}$$

with $\omega = |e|B/(m_e c)$. So the spin system is indeed 4π periodic! This has to do with the way we represent spins, which is a 2-component vector-like quantity but not quite a vector under rotations.

§9.5.1 Scattering in Spin Systems

Consider a scattering process, we we have a beam of incoming particles incident on a spherically symmetric scattering center A.

> **Note**: The arguments we are about to make also work for non-spherically symmetric scattering centers but for our purposes, it would be easier to consider spherically symmetric ones.

It works out that geometrically, the only parameter that matters is the angle between the scattered beam and the axis of the incident θ_1. If we now take the scattered beam and scatter it off another scattering center B, then we need 3 angles θ_1, θ_2 and ϕ to characterize this, where ϕ is the angle between the planes that make each scattering occurrence effective 2-d.

If we instead scattered light, the scattering off scattering center B would result in some amplitude $I = I(\theta_2)\cos^2\phi$ and polarization. Now if we did this for quantum spin-$\frac{1}{2}$ particles, we find that the intensity off scattering center B follows the relation:

$$I = I(\theta_2)|\cos\phi| \tag{9.98}$$

This weird behaviour arises because these spin objects transform uniquely and are known as *spinors*.

§9.6 Addition of Angular Momentum

We have seen that there is a distinction between spin and orbital angular momentum operators, but they are **both** generators of rotation. However, the orbital angular momentum operator generates rotations in real-coordinate space, whereas the spin angular momentum operators generate rotations in spin-space. in general, we can describe both these spaces as a tensor product:

$$|\vec{x}\rangle \otimes |s\rangle \in \mathcal{H} \tag{9.99}$$

So rotations on this Hilbert space is given by:

$$\mathscr{D}(R) = \exp\left\{-i\frac{\hat{\vec{L}}\cdot\vec{n}}{\hbar}\phi\right\} \otimes \exp\left\{-i\frac{\hat{\vec{S}}\cdot\vec{n}}{\hbar}\phi\right\} \tag{9.100}$$

where we have that $\vec{n}$ and ϕ is the same, implying one single rotation in this expanded Hilbert space. As such, we can write that the total angular momentum $\hat{\vec{J}}$, which we define as:

$$\hat{\vec{J}} \equiv \hat{\vec{L}} \otimes \mathbb{I} + \mathbb{I} \otimes \hat{\vec{S}} \tag{9.101}$$

This is usually written in the short hand notation:

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}} \tag{9.102}$$

There are many instances where it is more convenient to work in terms of $\hat{\vec{J}}$, especially for system with total angular momentum being conserved (e.g. the Hydrogen atom). Let's now develop a little formalism. To generalize, suppose we have $\hat{\vec{J}}_1, \hat{\vec{J}}_2$ acting on separate subspaces. We know that individually, each of these satisfy the usual commutator relations:

$$\left[\hat{J}_{1,i}, \hat{J}_{1,j}\right] = i\hbar\varepsilon_{ijk}\hat{J}_{1,k} \tag{9.103}$$

$$\left[\hat{J}_1, \hat{J}_2\right] = 0 \tag{9.104}$$

So we can then define $\hat{\vec{J}} \equiv \hat{\vec{J}}_1 + \hat{\vec{J}}_2$. It is then easy to show that:

$$\left[\hat{J}_i, \hat{J}_j\right] = i\hbar\varepsilon_{ijk}\hat{J}_k \tag{9.105}$$

Now let us try to diagonalize this operator (that is also to ask what is the CSCO of this observable). One of them would be $\{\hat{\vec{J}}_1^2, \hat{J}_{1,z}, \hat{\vec{J}}_2^2, \hat{J}_{2,z}\}$, which allows us to write the eigenstates as $|j_1, j_2; m_1, m_2\rangle$.

Note (State Labels): In addition of angular momentum problems, the labels of the eigenstates are formatted such that the labels to the left of the semicolon specify the angular momenta of the system, and the labels to the right specify the basis being used. For instance, in the state $|j_1, j_2; m_1, m_2\rangle$, the labels $\{j_1, j_2\}$ indicate the angular momentum numbers present in the system, whereas $\{m_1, m_2\}$ denotes the specific eigenstate of the current basis. Sometimes, the labels on the left are dropped for lighter notation when the system in question has been specified.

A problem arises in this because the Hamiltonian will not always be in this CSCO we have chosen, because if we have couplings between these 2 subspaces, this information is not included in an obvious way. So let's consider another list of operators $\{\hat{\vec{J}}^2, \hat{J}_z, \hat{\vec{J}}_1^2, \hat{\vec{J}}_2^2, \hat{\vec{J}}_1 \cdot \hat{\vec{J}}_2\}$. These are a lot of operators, so let's narrow this down a little. First, we note that:

$$\hat{\vec{J}}^2 = \hat{\vec{J}}_1^2 + \hat{\vec{J}}_2^2 + 2(\hat{\vec{J}}_1 \cdot \hat{\vec{J}}_2) \tag{9.106}$$

This means that we can drop one of these since it is redundant (the dot product operator). As such, we pick our CSCO to be $\{\hat{\vec{J}}^2, \hat{J}_z, \hat{\vec{J}}_1^2, \hat{\vec{J}}_2^2\}$. The eigenstates here would thus be written as $|j_1, j_2; j, m\rangle$. First, we are going back to use the ladder operators to see that we can write the dot product term as:

$$\boxed{\hat{\vec{J}}_1 \cdot \hat{\vec{J}}_2 = \hat{J}_{1,z}\hat{J}_{2,z} + \frac{1}{2}\left(\hat{J}_{1,+}\hat{J}_{2,-} + \hat{J}_{1,-}\hat{J}_{2,+}\right) = \frac{1}{2}\left(\hat{\vec{J}}^2 - \hat{\vec{J}}_1^2 - \hat{\vec{J}}_2^2\right)} \tag{9.107}$$

So this tells us the second basis grants a much nicer way to consider the couplings between the 2 subspaces. This is a very useful identity because note than in the direct sum basis, we get:

$$\boxed{\frac{1}{2}\left(\hat{\vec{J}}^2 - \hat{\vec{J}}_1^2 - \hat{\vec{J}}_2^2\right)|j_1, j_2; j, m\rangle = \frac{\hbar^2}{2}\left[j(j+1) - j_1(j_1+1) - j_2(j_2+1)\right]|j_1, j_2; j, m\rangle} \tag{9.108}$$

§9.6.1 Clebsch-Gordan Coefficients

To move between the 2 bases we had above, we can write with the completeness relation:

$$|j_1, j_2; j, m\rangle = \sum_{m_1, m_2} |j_1, j_2; m_1, m_2\rangle \langle j_1, j_2; m_1, m_2 | j_1, j_2; j, m\rangle \tag{9.109}$$

where $\langle j_1, j_2; m_1, m_2 | j_1, j_2; j, m\rangle$ are known as the *Clebsch-Gordan coefficients*. Why these are given a fancy name is because they are widely used and have interesting properties. One of which, can be seen from the following derivation:

$$\begin{aligned} & (\hat{J}_z - \hat{J}_{1,z} - \hat{J}_{2,z})|j_1, j_2; j, m\rangle = 0 \\ \Rightarrow \quad & \langle j_1, j_2; m_1, m_2|\,(\hat{J}_z - \hat{J}_{1,z} - \hat{J}_{2,z})|j_1, j_2; j, m\rangle = 0 \\ \Rightarrow \quad & \hbar(m - m_1 - m_2)\langle j_1, j_2; m_1, m_2 | j_1, j_2; j, m\rangle = 0 \\ \Rightarrow \quad & \boxed{m = m_1 + m_2} \end{aligned} \tag{9.110}$$

This is known as a *selection rule* since it selects only specific Clebsch-Gordan coefficients that can be non-zero:

$$\boxed{\langle j_1, j_2; m_1, m_2 | j_1, j_2; j, m\rangle \neq 0 \quad \text{if} \quad m = m_1 + m_2} \tag{9.111}$$

We can also see with some algebra that:

$$\boxed{|j_1 - j_2| \leq j \leq j_1 + j_2} \tag{9.112}$$

which is often referred to as the *triangle selection rule*.

Note: The triangle selection rule can also be derived by the counting of the eigenstates.

§9.6.2 2p Hydrogen

We will now look at an actual physical system, Hydrogen. We have that the electron has the observables $\{\hat{\vec{L}}, \hat{\vec{S}}\}$ (corresponding to orbital and spin angular momenta), where $l = 1$ and $s = 1/2$. It turns out that the Hamiltonian of only the spin-orbit states is given by:

$$\begin{aligned} \hat{H}_{SO} &= f(r)\hat{\vec{S}} \cdot \hat{\vec{L}} \\ &= f(r)(\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2) \end{aligned} \tag{9.113}$$

where $f(r)$ is some function of r that we will get back to later. Counting the number of eigenstates, we have 6 of these written either as $|l, s; m, m_s\rangle$ or $|l, s; j, m\rangle$ (where $j = 1/2, 3/2$ from the inequality we had above). So this splits the second basis into 2 sets of states:

$$\left|1, \frac{1}{2}; \frac{3}{2}, m\right\rangle, \quad \left|1, \frac{1}{2}; \frac{1}{2}, m\right\rangle \tag{9.114}$$

where the leftmost set has 4 states and that on the right has 2. The Hamiltonian acting on these states then will be:

$$\hat{H}_{SO} |j, m\rangle = \frac{\hbar^2}{2} f(r) \left[j(j+1) - l(l+1) - s(s+1)\right] |j, m\rangle \tag{9.115}$$

$$\Rightarrow \quad \hat{H}_{SO} \left|\frac{1}{2}, m\right\rangle = -\hbar^2 f(r) \left|\frac{1}{2}, m\right\rangle, \quad \hat{H}_{SO} \left|\frac{3}{2}, m\right\rangle = \frac{\hbar^2}{2} f(r) \left|\frac{3}{2}, m\right\rangle \tag{9.116}$$

The energies can then be found by taking the expectation value:

$$E_{SO} = \langle j, m| \hat{H}_{SO} |j, m\rangle \tag{9.117}$$

$$\Rightarrow \quad E_{SO,j} = \int_0^\infty dr |R_{n,l}(r)|^2 r^2 f(r) \langle j, m| \hat{\vec{S}} \cdot \hat{\vec{L}} |j, m\rangle \tag{9.118}$$

which gives us a value of $\sim 5 \times 10^{-5}$ eV, which indicates an energy splitting of the energy eigenstates of Hydrogen due to the spin-orbit coupling.

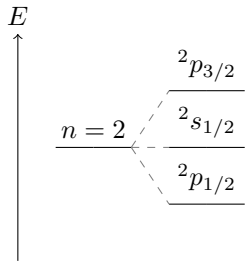


Figure 9.1: Energy splitting from spin orbit coupling in Hydrogen.

It turns out that is true but for the "wrong reasons" because notice that we haven't used Clebsch-Gordan coefficients at all (it just worked out because of a happy convenience). If now we turn on an external magnetic field B which adds the Hamiltonian term:

$$\hat{H}_B = \mu_B B(\hat{L}_z + 2\hat{S}_z) \tag{9.119}$$

this no longer allows us to treat nicely the energy eigenstates from the basis we have been working in. So looking back at our Hydrogen system where we have the angular momentum $(l = 1, s = 1/2)$ as:

$$m = m_l + m_s \quad \Rightarrow \quad -\frac{3}{2} \leq m \leq \frac{3}{2} \tag{9.120}$$

$$\text{and} \quad \left|1 - \frac{1}{2}\right| \leq j \leq 1 + \frac{1}{2} \quad \Rightarrow \quad \frac{1}{2} \leq j \leq \frac{3}{2} \tag{9.121}$$

$$\Rightarrow \quad \begin{cases} \left|\frac{3}{2}; \frac{3}{2}\right\rangle, & \left|\frac{3}{2}; \frac{1}{2}\right\rangle, \quad \left|\frac{3}{2}; -\frac{1}{2}\right\rangle, \quad \left|\frac{3}{2}; -\frac{3}{2}\right\rangle \\ \left|\frac{1}{2}; \frac{1}{2}\right\rangle, & \left|\frac{1}{2}; -\frac{1}{2}\right\rangle \end{cases} \tag{9.122}$$

Then to change into the basis where we can look at j, m, we use the Clebsch-Gordan coefficients to get:

$$\begin{aligned} |j_1, j_2; j, m\rangle &= \sum_{m_1, m_2} |j_1, j_2; m_1, m_2\rangle \langle j_1, j_2; m_1, m_2 | j_1, j_2; j, m\rangle \\ \Rightarrow \quad |j, m\rangle &= \sum_{m_1, m_2} |j_1, j_2; m_1, m_2\rangle \langle j_1, j_2; m_1, m_2 | j, m\rangle \end{aligned} \tag{9.123}$$

since j_1 and j_2 are constant specified, allowing us to drop those labels. For the top state, we only have one non-trivial term in the sum:

$$\begin{aligned} \left|\frac{3}{2}, \frac{3}{2}\right\rangle &= \left|1, \frac{1}{2}; 1, \frac{1}{2}\right\rangle \left\langle 1, \frac{1}{2}; 1, \frac{1}{2} \middle| \frac{3}{2}, \frac{3}{2}\right\rangle \\ &= \left|1, \frac{1}{2}; 1, \frac{1}{2}\right\rangle \end{aligned} \tag{9.124}$$

As for the state $\left|\frac{3}{2}, \frac{1}{2}\right\rangle$, we will have contributions from $m_l = 1, m_s = -1/2$ and $m_l = 0, m_s = 1/2$. So this is a little more tedious to find the coefficients. However, we can use the ladder operators to help us:

$$\hat{J}_\pm |j, m\rangle = \hbar\sqrt{(j \pm m)(j \pm m + 1)}\, |j, , m \pm 1\rangle \tag{9.125}$$

So we can find the necessary states:

$$\begin{aligned} \hat{J}_- \left|\frac{3}{2}, \frac{3}{2}\right\rangle &= \hbar\sqrt{3} \left|\frac{3}{2}, \frac{1}{2}\right\rangle \\ =(\hat{L}_- + \hat{S}_-) \left|1, \frac{1}{2}; 1, \frac{1}{2}\right\rangle &= \hbar\sqrt{2} \left|1, \frac{1}{2}; 0, \frac{1}{2}\right\rangle + \hbar \left|1, \frac{1}{2}; 1, -\frac{1}{2}\right\rangle \\ \Rightarrow \quad \left|\frac{3}{2}, \frac{1}{2}\right\rangle &= \sqrt{\frac{2}{3}} \left|1, \frac{1}{2}; 0, \frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}} \left|1, \frac{1}{2}; 1, -\frac{1}{2}\right\rangle \end{aligned} \tag{9.126}$$

The same procedure can be done for $\left|\frac{3}{2}, -\frac{1}{2}\right\rangle$ and $\left|\frac{3}{2}, -\frac{3}{2}\right\rangle$. As for the states with $j = 1/2$, there are a few ways to do this. One of them is by orthogonality, but the other more general technique

is again by using the ladder operators as follows:

$$\begin{aligned}
&\hat{J}_+ \left|\frac{1}{2},\frac{1}{2}\right\rangle = 0 \\
\Rightarrow\quad &(\hat{l}_+ + \hat{S}_+)\left(\alpha\left|1,\frac{1}{2};0,\frac{1}{2}\right\rangle + \beta\left|1,\frac{1}{2};1,-\frac{1}{2}\right\rangle\right) = \hbar\alpha\left|1,\frac{1}{2};0,\frac{1}{2}\right\rangle + \hbar\beta\sqrt{2}\left|1,\frac{1}{2};1,-\frac{1}{2}\right\rangle = 0 \\
\Rightarrow\quad &\alpha + \beta\sqrt{2} = 0 \quad \text{and} \quad |\alpha|^2 + |\beta|^2 = 1 \\
\Rightarrow\quad &\left|\frac{1}{2},\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\left|1,\frac{1}{2};0,\frac{1}{2}\right\rangle - \sqrt{\frac{1}{3}}\left|1,\frac{1}{2};1,-\frac{1}{2}\right\rangle
\end{aligned} \tag{9.127}$$

However, there is an ambiguity in what we have been doing because the state we found above is true up to a sign. In general, we choose the convention where $\beta > 0$, and that the overlap between the maximal $\hat{J}_z$ and maximal $\hat{J}_{1,z}$ to be positive (same for the minimal states). For instance, with the system we are working with we want:

$$\left\langle\frac{3}{2},\frac{3}{2}\middle|1,\frac{1}{2};1,\frac{1}{2}\right\rangle > 0, \quad \left\langle\frac{1}{2},\frac{1}{2}\middle|1,\frac{1}{2};1,-\frac{1}{2}\right\rangle > 0 \tag{9.128}$$

The use of ladder operators to find Clebsch-Gordan coefficients can also be used to derive a recursion relation between them, this is:

$$\boxed{\langle j_1, j_2; m_1 - 1, m_2 | j, j\rangle = -\sqrt{\frac{(j_2 + m_2)(j_2 - m_2 + 1)}{(j_1 + m_1)(j_1 - m_1 + 1)}}\,\langle j_1, j_2; m_1, m_2 - 1 | j, j\rangle} \tag{9.129}$$

where all these coefficients are real. These come in handy every once in awhile and is good to keep at the back of your mind. Going back to the physics of the Hydrogen system, let's first summarize what we have so far:

$$\left|\frac{3}{2},\frac{3}{2}\right\rangle = \left|1,\frac{1}{2};1\frac{1}{2}\right\rangle \tag{9.130}$$

$$\left|\frac{3}{2},\frac{1}{2}\right\rangle = \sqrt{\frac{2}{2}}\left|1,\frac{1}{2};0,\frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\left|1,\frac{1}{2};1,-\frac{1}{2}\right\rangle \tag{9.131}$$

$$\left|\frac{1}{2},\frac{1}{2}\right\rangle = \sqrt{\frac{2}{3}}\left|1,\frac{1}{2};0,\frac{1}{2}\right\rangle - \sqrt{\frac{1}{3}}\left|1,\frac{1}{2};1,-\frac{1}{2}\right\rangle \tag{9.132}$$

$$\left|\frac{3}{2},-\frac{1}{2}\right\rangle = \sqrt{\frac{1}{3}}\left|1,\frac{1}{2};0,\frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\left|1,\frac{1}{2};0,-\frac{1}{2}\right\rangle \tag{9.133}$$

From these, we can compute the energy by first invoking a result from perturbation theory that we haven't yet seen but will just take for true for now:

$$E_{B,j,m} \approx \langle j, m|\,\mu_B B(\hat{L}_z + 2\hat{S}_z)\,|j, m\rangle \tag{9.134}$$

So for each of our states, we have:

$$E_{B,\frac{3}{2},\frac{3}{2}} = 2\hbar\mu_B B, \quad E_{B,\frac{3}{2},\frac{1}{2}} = \frac{2}{3}\hbar\mu_B B \tag{9.135}$$

Doing this for the other eigenstates, we finally find that there is a nice closed form energy relation in this perturbative regime:

$$\boxed{E_{B,j,m} = \frac{m}{3}(2j+1)\hbar\mu_B B} \tag{9.136}$$

So this implies a further energy splitting of the ${}^2p$ states of Hydrogen as illustrated in figure 9.2 below.

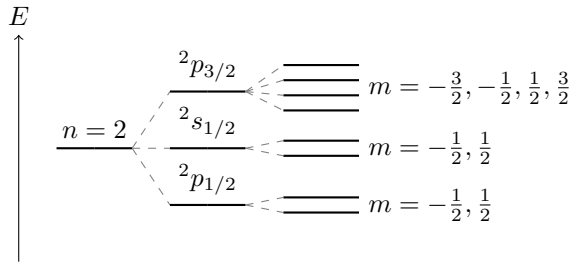


Figure 9.2: Energy splitting from spin orbit coupling in Hydrogen.

§9.7 Angular Momentum and Reducible Representations

We just saw that we can change the basis of angular momentum we are working in:

$$|l, s; m_l, m_s\rangle \to |j, m\rangle \tag{9.137}$$

This corresponds to the representations that we can write as:

$$\begin{aligned} & l \otimes s = j \oplus m \\ \Rightarrow \quad & 1 \otimes \frac{1}{2} = \frac{3}{2} \oplus \frac{1}{2} \end{aligned} \tag{9.138}$$

where the numbers denote the angular momentum quantum numbers relevant to that basis. In general, if we have 2 angular momentum operators $\hat{\vec{J}}_1 + \hat{\vec{J}}_2$, then the Hilbert space $\mathcal{H}$ decomposes as:

$$j_1 \otimes j_2 = |j_1 - j_2| \oplus (|j_1 - j_2| + 1) \oplus \ldots \oplus (j_1 + j_2) \tag{9.139}$$

To understand this notation better, we will look a little into representation theory and define what the Direct product and sum are formally.

§9.7.1 Direct Sums and Products

Suppose we have 2 vector spaces V_A and V_B where by their dimensions are m and n which basis vectors $\{\hat{e}_1, \ldots \hat{e}_m\}$ and $\{\hat{f}_1, \ldots \hat{f}_n\}$ respectively. There are 2 ways to "combine" these vector spaces into a larger one, one of which is the *direct sum* denoted as $V_A \oplus V_B$ (with dimensions

$m+n$). The vectors in this new space are then written as $v \oplus w \in V_A \oplus V_B$. In matrix representation, direct sum of vectors just stack them, for example ($m=2, n=3$):

$$\vec{v} = \begin{bmatrix} v_1 \\ v_2 \end{bmatrix}, \quad \vec{w} = \begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix} \tag{9.140}$$

$$\Rightarrow \quad \vec{v} \oplus \vec{w} = \begin{bmatrix} v_1 & v_2 & w_1 & w_2 & w_3 \end{bmatrix}^T \tag{9.141}$$

The direct sum of operators on the direct summed vector space would act on direct sum vectors as follows:

$$(\hat{A} \oplus \hat{B})(v \oplus w) = (\hat{A}v \oplus \hat{B}w) \tag{9.142}$$

As such, the matrix representation of these operators are **block diagonal** matrices, where the diagonal blocks are the matrix representations of the individual operators:

$$\begin{aligned} \hat{A} &= \begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & & \ddots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{bmatrix}, \quad \hat{B} = \begin{bmatrix} b_{11} & b_{12} & \dots & b_{1nm} \\ b_{21} & b_{22} & \dots & b_{2m} \\ \vdots & & \ddots & \vdots \\ b_{m1} & b_{m2} & \dots & b_{mm} \end{bmatrix} \\ \Rightarrow \quad \hat{A} \oplus \hat{B} &= \begin{bmatrix} \hat{A} & \hat{0} \\ \hat{0} & \hat{B} \end{bmatrix} \end{aligned} \tag{9.143}$$

Alternatively, the other way to expand the vector space is via the direct product (a.k.a. the tensor product) denoted as $V_A \otimes V_B$ (with dimensions $m \times n$). So back to the example we had earlier with $m=2, n=3$, the matrix representation of direct product of vectors $v \otimes w \in V_A \otimes V_B$ will be:

$$\vec{v} \oplus \vec{w} = \begin{bmatrix} v_1 w_1 & v_1 w_2 & v_1 w_3 & v_2 w_1 & v_2 w_2 & v_2 w_3 \end{bmatrix}^T \tag{9.144}$$

The operators on a direct product space will generally have dense matrix representations, since their construction would be:

$$\begin{aligned} \hat{A} &= \begin{bmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \vdots & & \ddots & \vdots \\ a_{n1} & a_{n2} & \dots & a_{nn} \end{bmatrix}, \quad \hat{B} = \begin{bmatrix} b_{11} & b_{12} & \dots & b_{1nm} \\ b_{21} & b_{22} & \dots & b_{2m} \\ \vdots & & \ddots & \vdots \\ b_{m1} & b_{m2} & \dots & b_{mm} \end{bmatrix} \\ \Rightarrow \quad \hat{A} \otimes \hat{B} &= \begin{bmatrix} a_{11}\hat{B} & a_{12}\hat{B} & \dots & a_{1n}\hat{B} \\ a_{21}\hat{B} & a_{22}\hat{B} & \dots & a_{2n}\hat{B} \\ \vdots & & \ddots & \vdots \\ a_{n1}\hat{B} & a_{n2}\hat{B} & \dots & a_{nn}\hat{B} \end{bmatrix} \end{aligned} \tag{9.145}$$

Note: Tensor products written as a matrix operation are referred to as *Kronecker products*.

§9.7.2 Groups and Representation Theory

We begin by stating the definition of a group.

Definition 9.7.1. Groups *A group G is a set of elements and a binary operation "$\bullet$" which satisfies the following.*

1. *Closure*: $a \bullet b \in G$
2. *Associativity*: $(a \bullet b) \bullet c = a \bullet (b \bullet c)$
3. *Identity*: $\exists \mathbb{I}$ s.t. $\mathbb{I} \bullet a = a \bullet \mathbb{I} = a$
4. *Inverses*: $\exists a^{-1}$ s.t. $a^{-1} \bullet a = a \bullet a^{-1} = \mathbb{I}$

An example of a group is $GL(N, \mathbb{C})$ which is the called the *general linear group* (the group of invertible $N \times N$ complex matrices). In fact, we can represent any arbitrary group by mapping group elements into matrices. To be concrete, we can define a *representation*.

Definition 9.7.2. Representations: *A representation is a map*:

$$R : G \to GL(N, \mathbb{C}) \tag{9.146}$$

which preserves the group, meaning that the group binary operation is maintained by the map:

$$a \bullet b = c \quad \Rightarrow \quad R(a)R(b) = R(c) \tag{9.147}$$

The dimension of R is then $\dim\{R\} = N$.

A trivial example is the map $R(g) = 1$ for all $g \in G$. This is valid but not a *faithful representation* where a faithful representation is a *bijective* map. Representations in general are **not** unique. To see this, consider the group $\mathbb{Z}_2 = \{1, a\}$ where we must have $a \bullet a = 1$. A faithful representation would be:

$$R(1) \to \mathbb{I}_{N\times N} \tag{9.148}$$

$$R(a) \to \hat{A}_{N\times N} \tag{9.149}$$

such that $A^2 = \mathbb{I}$. But we see there are actually an infinite number of possible representations then, since first of all, we can map each of these into $N \times N$ matrices where N is an arbitrary size.

Why however, should we as physicists care about representation theory? In physics, we do encounter many groups, mostly commonly the group of symmetries. The reason we care about these is because we want to understand their action on physical objects. So indeed, the states we act in would correspond to a specific representation of these groups by construction, and that's why we care.

Example:

Consider the rotation group $SO(3)$ which has elements R that satisfy $\det\{R\} = 1$ and $R^T R = \mathbb{I}$ in 3-dimensions (as per the definition of $SO(3)$). In classical mechanics, we can think of several types of physical quantities and how they transform under rotation. These quantities would be *vectors* (e.g. coordinates of position $\vec{r}$):

$$\vec{r} \to R\vec{r} \tag{9.150}$$

tensors, such as the inertia tensor:

$$I \to RIR^T \tag{9.151}$$

and *scalars* such as energy:

$$E \to E \tag{9.152}$$

where the arrows indicate how they transform under the rotation group elements. The way we represent how vectors transform under these rotations is known as the *fundamental representation* of the group (scalars transform as the trivial representation). As for tensor of rank-2, they could be transformed by 9×9 matrix (9-dimensional representation). Consider again the inertia tensor from classical mechanics. Recall that it is commonly denoted as:

$$I_{ij} = \int dV \rho(\vec{r})(r^2\delta_{ij} - r_i r_j) \tag{9.153}$$

which is known as a *dyadic tensor* (2 vectors stuck together). So this would be a direct product of 2 3-vectors $3 \otimes 3$. The hope, is that we can decompose this into having a block diagonal structure of smaller elements that we can direct sum instead. In fact this is possible from representation theory by the decomposition:

$$3 \otimes 3 = 5 \oplus 3 \oplus 1 \tag{9.154}$$

which is exactly what we have seen with angular momentum in quantum mechanics!

Any representation of a direct product space that can be decompose into a direct sum of smaller (dimesionality) representations is known as a *reducible representation*. It is *irreducible* otherwise. The general problem of finding all such decompositions and irreducible representations for a given group is known as *plethysm*. Now back to quantum mechanics and angular momentum, we consider what is known as the *Wigner D-Matrix*, whose elements are defined as:

$$\boxed{\mathscr{D}^{(j)}_{m',m}(R) = \langle j, m' | \exp\left\{-i\frac{\hat{\vec{J}}\cdot\hat{n}}{\hbar}\phi\right\} | j, m\rangle} \tag{9.155}$$

These are in fact the matrix elements of the rotation matrix in the $\{j, m\}$ basis. Notice that there

is no j', but this is because $\left[\hat{\vec{J}}^2, \hat{\vec{J}}\right] = 0$, so sticking in a $\hat{\vec{J}}^2$ operator inside the bracket:

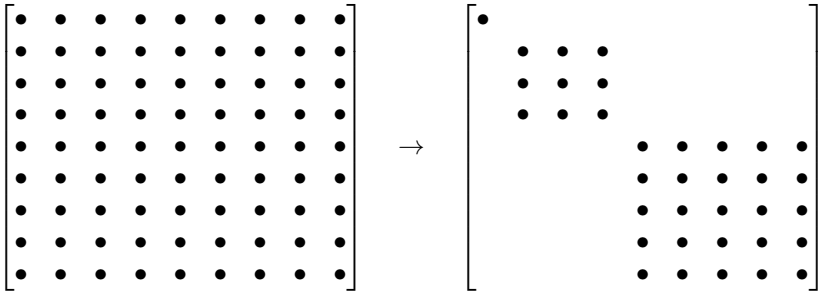
$$\begin{aligned}\langle j', m'| \exp\left\{\frac{-i(\hat{\vec{J}}\cdot\vec{n})\phi}{\hbar}\right\}\hat{\vec{J}}^2 |j, m\rangle &= \hbar^2 j(j+1)\langle j', m'| \exp\left\{\frac{-i(\hat{\vec{J}}\cdot\vec{n})\phi}{\hbar}\right\}|j, m\rangle \\ &= \hbar^2 j'(j'+1)\langle j', m'| \exp\left\{\frac{-i(\hat{\vec{J}}\cdot\vec{n})\phi}{\hbar}\right\}|j, m\rangle\end{aligned} \tag{9.156}$$

we see that it just pulls out a number and doesn't "affect" the unitary rotation operator. Cancelling out the Wigner D-matrix elements on both sides, we are left with:

$$\hbar^2 j(j+1) = \hbar^2 j'(j'+1) \quad \Rightarrow \quad j = j' \tag{9.157}$$

So indeed we get that if we had j', it would simply equate to j. Then if we had the angular momentum operator $\hat{\vec{J}}_1 + \hat{\vec{J}}_2$ with $j_1 = j_2 = 1$ (each j having 3 m states), this would grant us a 9×9 Wigner D-matrix for which is in fact reducible in the way exactly done for the inertia tensor in classical mechanics in the example above. The resulting Wigner D-matrix of a direct sum of irreducible representations would then be a block diagonal matrix of 1×1, 3×3 and 5×5 ($j = 0, j = 1, j = 2$ where $j = j_1 + j_2$) blocks:

Tensor Product Representation → Direct Sum Decomposition



(9.158)

where the • indicates a non-trivial entry and all zeros in the matrix are excluded for clarity.

§9.8 Vector Operators

Let's start by a motivation for what we are about to do. If we are interested in matrix elements, tensor products of matrices generally have a huge number of matrix elements, but if we find rotational symmetries, we can work with much fewer matrix entries and their symmetry relations. To do this in quantum mechanics, this may get a little confusing as we would have matrix representations of the operator observables, and also the group elements. However, we will be careful to make things explicit as we go along.

Since observables are promoted to operators in quantum mechanics, we now want to think about multi-index operator objects. Let's start with *vector operators*. A vector operator is simply appending operators into an array/list just as you would with classical variables (e.g. $\hat{\vec{x}} = \{\hat{x}, \hat{y}, \hat{z}\}$). It would be good from now on to adopt index notation (including Einstein sum

notation unless otherwise specified). We can then ask if a quantum vector operator has the same transformation properties as classical vectors. Recall that rotations of quantum states can be written as:

$$\begin{aligned} & |\alpha\rangle \to \hat{\mathscr{D}}(R)\,|\alpha\rangle \\ \Rightarrow \quad & \langle \hat{O}\rangle = \langle\alpha|\,\hat{O}\,|\alpha\rangle \to \langle\alpha|\,\hat{D}^{\dagger}(R)\hat{O}\hat{\mathscr{D}}(R)\,|\alpha\rangle \end{aligned} \tag{9.159}$$

where once again, we have that $\hat{\mathscr{D}}(R)$ is the Wigner D-matrix. However, we want that in the appropriate limit, we retrieve classical mechanics from quantum mechanics. Classically, we would have:

$$\langle V_i\rangle \to R_{ij}\langle V_j\rangle \tag{9.160}$$

Since we require the above relation to hold for any state $|\alpha\rangle$, we arrive at the operator identity:

$$\hat{\mathscr{D}}^{\dagger}(R)\hat{V}_i\hat{\mathscr{D}}(R) \to R_{ij}\hat{V}_j \tag{9.161}$$

Now consider an infinitesimal rotation, we have:

$$\begin{aligned} & \hat{\mathscr{D}}(R) = \mathbb{I} - \frac{i\varepsilon}{\hbar}(\hat{\vec{J}}\cdot\hat{n}) \\ \Rightarrow \quad & \hat{V}_i - \frac{i\varepsilon}{\hbar}\Big[\hat{V}_i, \hat{\vec{J}}\cdot\hat{n}\Big] = R_{ij}\hat{V}_j \end{aligned} \tag{9.162}$$

where $\varepsilon \ll 1$. If we then consider the case where $\hat{n} = \hat{z}$, use the result of the classical rotation matrix for infinitesimal rotations to get:

$$\begin{aligned} & R(\hat{z},\varepsilon) = \delta_{ij} - \varepsilon\epsilon_{ijz} \\ \Rightarrow \quad & \hat{V}_i - \frac{i\varepsilon}{\hbar}\Big[\hat{V}_i, \hat{J}_k\Big] = (\delta_{ij} - \varepsilon\epsilon_{ijk})\hat{V}_j \\ \Rightarrow \quad & \boxed{\Big[\hat{V}_i, \hat{J}_k\Big] = i\hbar\epsilon_{ijk}\hat{V}_j} \end{aligned} \tag{9.163}$$

which is the usual relation for angular momentum operators. This commutation relation can be taken as a definition for a vector operator. As for scalar operators, since we would have for a scalar operator $\hat{K}$:

$$\begin{aligned} & \langle\hat{K}\rangle \to \langle\hat{K}\rangle \\ \Rightarrow \quad & \hat{\mathscr{D}}^{\dagger}(R)\hat{K}\hat{\mathscr{D}}(R) \to \hat{K} \\ \Rightarrow \quad & \boxed{\Big[\hat{K}, \hat{J}_i\Big] = 0} \end{aligned} \tag{9.164}$$

Note: In quantum mechanics, $\hat{\vec{U}}\cdot\hat{\vec{V}}$ is a scalar operator **but** we have that in general, $\hat{\vec{U}}\cdot\hat{\vec{V}} \neq \hat{\vec{V}}\cdot\hat{\vec{U}}$, since operators do not always commute.

Now generalizing the idea we have just gone through, we consider a rank-3 tensor (rank indicating the number of indices) operator $\hat{T}_{ijk}$. This would classically transform as:

$$T_{ijk} \to R_{i,i'} R_{j,j'} R_{k,k'} T_{i'j'k'} \tag{9.165}$$

We call such a tensor written as above a *Cartesian tensor*, since we use Cartesian coordinates to label its components. Although a Cartesian tensor may be familiar to work with (since they are just generalizing Cartesian vectors), it is often hard to work with regarding rotations. It turns out that rotations of Cartesian tensors are reducible (can be decomposed it into different smaller objects which each rotate differently). To see this, consider a simple example of the *dyadic tensor*.

§9.8.1 The Dyadic Tensor and the Spherical Basis

Consider what is known as the *dyadic tensor* $\hat{T}_{ij} = \hat{U}_i \hat{V}_j$, which is basically 2 vectors put together. We now want to ask how this transform under rotations:

$$\hat{\mathscr{D}}^\dagger(R) \hat{T}_{ij} \hat{\mathscr{D}}(R) \quad \to \quad ? \tag{9.166}$$

First, we write out the dyadic tensor explicitly:

$$\hat{U}_i \hat{V}_j = \frac{1}{3}(\hat{\vec{U}} \cdot \hat{\vec{V}})\delta_{ij} + \frac{1}{2}(\hat{U}_i \hat{V}_j - \hat{U}_j \hat{V}_i) + \left(\frac{\hat{U}_i \hat{V}_j + \hat{U}_j \hat{V}_i}{2} - \frac{1}{3}(\hat{\vec{U}} \cdot \hat{\vec{V}})\delta_{ij} \right) \tag{9.167}$$

where this form is obtained from considering the symmetry properties of each object. Now if we look at the transformation properties of each of these terms, the first term transforms like a scalar, the second like a vector (result of a cross product), and the last like traceless-symmetric tensor. Knowing that, the dyadic tensor looks suspiciously like the sum of angular momentum, where we again have the decomposition:

$$1 \otimes 1 = 0 \oplus 1 \oplus 2 \tag{9.168}$$

This allows us to employ the machinery we have already developed in angular momentum to isolate the components with a specific j ($|j_1, j_2; m_1, m_2\rangle \to |j_1, j_2; j, m\rangle$). What would be the change of basis for operators then? Consider the basis known as the *spherical basis* defined by the unit basis vectors:

$$\hat{e}_1 = -\frac{\hat{x} + i\hat{y}}{\sqrt{2}}, \quad \hat{e}_0 = \hat{z}, \quad \hat{e}_{-1} = \frac{\hat{x} - i\hat{y}}{\sqrt{2}} \tag{9.169}$$

(These might look familiar as they are actually the polarization basis vectors for light propagation). These obey orthonormality relation $\hat{e}_a^* \cdot \hat{e}_{a'} = \delta_{a,a'}$. Vectors in general can then be written as:

$$\vec{x} = \hat{e}_q^* x_q \tag{9.170}$$

where the expansion coefficients are defined as $x_q = \hat{e}_q \cdot \vec{x}$.

Note: The hats on the spherical basis elements denote unit vectors, **not** operators. This notation may by confusing since spherical tensors are not strictly defined for quantum operators, but also used in classical mechanics. However, the rest of these notes will only be using hats for operators unless otherwise specified.

The spherical basis greatly simplifies the mathematical treatment of certain problems. To see this, consider the example of radiative transition below.

Example:

Consider now a radiative transitions in Hydrogenic atoms. We will ignore the spin in this system for now which gives the eigenbasis $|n, l, m\rangle$. Although these quantum numbers are conserved for the system in isolation, the electron can undergo radiative transitions (photon emission which changes the state of the electron). Photon emissions can be treated via a multipole expansion. The dipole transition matrix element (probability amplitude for a dipole transition) is proportional to:

$$\langle n', l', m'| \hat{\vec{r}} |n, l, m\rangle \tag{9.171}$$

Suppose we look at the transition from the $3d$ state to the $2p$ state. This grants 45 total possible transitions since the $3d$ states have $2l + 1 = 5$ levels and the $2p$ has $2l + 1 = 3$, while there are 3 coordinates $\{x, y, z\}$ which gives us $5 \times 3 \times 3 = 45$. These are a lot of matrix elements, so let's instead consider the expansion in the spherical basis which will greatly reduce the number of non-trivial matrix elements:

$$r_a = \hat{e}_a \cdot \vec{r} \tag{9.172}$$

a being an index $a \in \{-1, 0, 1\}$. Now looking at each coordinate of the spherical basis, we have:

$$\begin{aligned} r_1 &= -\frac{x + iy}{\sqrt{2}} \\ &= -r\frac{\sin\theta e^{i\phi}}{\sqrt{2}} \\ &= \sqrt{\frac{4\pi}{3}} r Y_1^1(\theta, \phi) \end{aligned} \tag{9.173}$$

where $r = \sqrt{x^2 + y^2 + z^2}$. Repeating this manipulation for r_0 and r_{-1}, we find that:

$$r_a = r Y_1^a(\theta, \phi)\sqrt{\frac{4\pi}{3}} \tag{9.174}$$

which tells us that this basis has components proportional to spherical harmonics! So in this basis, we have:

$$\begin{aligned} \langle n', l', m'| \hat{r}_a |n, l, m\rangle = &\int_0^\infty r^3 R^*_{n',l'}(r) R_{n,l}(\theta, \phi) dr \\ &\times \sqrt{\frac{4\pi}{3}} \int Y^*_{l',m'}(\Omega) Y_{1,a}(\Omega) Y_{l,m}(\Omega) d\Omega \end{aligned} \tag{9.175}$$

where we have inserted a complete set of position eigenstates $\int |r\rangle \langle r| \, d^3r$ to get this relation. In our context, the integral over 3 spherical harmonics is written as:

$$\int Y^*_{l',m,'}(\Omega) Y_{1,a}(\Omega) Y_{l,m}(\Omega) d\Omega = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}} \times \langle l', m'|1, l; a, m\rangle \langle 1, l; 0, 0|l, 0\rangle \tag{9.176}$$

Using this, it turns out as alluded to earlier that a lot of these 45 terms are trivial due to implicit selection rules coming from the dependence on Clebsch-Gordan coefficients. Specifically, this is due to the selection rule that $m' = m + a$. This will be done more rigorously in the next section.

So what we have seen from the example above is that in the position space representation (kets contracted with $\langle r, \theta, \phi|$), the spherical basis coordinates transform under rotations like spherical harmonic functions! In general, the triple spherical harmonics angular integral shows up often in atomic physics and satisfies a nice relation:

$$\boxed{\int Y^*_{l_3,m_3}(\Omega) Y_{l_2,m_2}(\Omega) Y_{l_1,m_1}(\Omega) d\Omega = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)}} \langle l_3, m_3|l_1, l_2; m_1, m_2\rangle \langle l_1, l_2; 0, 0|l_3, 0\rangle} \tag{9.177}$$

§9.8.2 Rotations and Spherical Harmonics

Now let's see the selection rules in the example of radiative transition above at play explicitly. We will then generalize this to selection rules of general spherical tensors. From the example above, we now know that:

$$\begin{aligned} & Y_l^m(\theta, \phi) = \langle \theta, \phi|n, l, m\rangle = \langle \hat{n}|n, l, m\rangle \\ \text{and} \quad & |\hat{n}\rangle = \hat{\mathscr{D}}(\theta, \phi) \, |\hat{z}\rangle = \sum_{l',m'} \hat{\mathscr{D}}(\theta, \phi) \, |l', m'\rangle \langle l', m'|\hat{z}\rangle \\ \Rightarrow \quad & \langle l, m|\hat{n}\rangle = \sum_{l',m'} \langle l, m| \, \hat{\mathscr{D}}(\theta, \phi) \, |l', m'\rangle \langle l', m'|\hat{z}\rangle \end{aligned} \tag{9.178}$$

where $\hat{n}$ can be thought of in terms of its spherical coordinate definition (vector function of $\{\theta, \phi\}$). The inner product furthest to the right in the last expression above is in fact a specific spherical harmonic, as we can see from:

$$\begin{aligned} \langle l', m'| \, \hat{L}_z \, |\hat{z}\rangle &= m' \langle l', m'|\hat{z}\rangle \\ &= \langle l', m'| \, (\hat{x}\hat{p}_x - \hat{y}\hat{p}_y) \, |\hat{z}\rangle = 0 \\ \Rightarrow \quad m' &= 0 \\ \Rightarrow \quad \langle l', m'|\hat{z}\rangle &= Y_l^0(0, \phi) \end{aligned} \tag{9.179}$$

where we let $\hat{L}_z$ act on the bra and then the ket states it was sandwiched in to get the result

above since it is Hermitian. This, with some algebra grants us:

$$\boxed{\mathscr{D}^{(l)}_{m,0}(\theta,\phi) = \sqrt{\frac{4\pi}{2l+1}} Y^m_l(\theta,\phi)^*} \tag{9.180}$$

Now consider again the joint eigenstates under rotation $\hat{\vec{J}}_1, \hat{\vec{J}}_2$ in the separable basis:

$$\begin{aligned}\langle j_1, j_2; m_1', m_2'| \hat{\mathscr{D}}(R) |j_1, j_2; m_1, m_2\rangle &= \langle j_1; m_1'| \hat{\mathscr{D}}_1(R) |j_1; m_1\rangle \langle j_2; m_2'| \hat{\mathscr{D}}_2(R) |j_2; m_2\rangle \\ &= \mathscr{D}^{(j_1)}_{m_1',m_1}(R) \mathscr{D}^{(j_2)}_{m_2',m_2}(R)\end{aligned} \tag{9.181}$$

This however still produces a dense matrix since the operator representations here are Kronecker products. So we want now to change our basis into irreducible representations as we have been doing. The way to do this in practice is of course by utilizing the Clebsch-Gordan coefficients:

$$\langle j_1, j_2; m_1', m_2'| \hat{\mathscr{D}}(R) |j_1, j_2; m_1, m_2\rangle = \sum_{j,m,m'} C^{j,m'}_{m_1',m_2'} \langle j_1, j_2; j, m'| \hat{\mathscr{D}}(R) |j_1, j_2; j, m\rangle C^{j,m}_{m_1,m_2} \tag{9.182}$$

where $C^{j,m}_{m_1,m_2} = \langle j_1, j_2; m_1, m_2 | j_1, j_2; j_1, j_2; j, m\rangle$ are the Clebsch-Gordan coefficients. Now consider the case where we are looking at orbital angular momentum such that $j_{1,2} = l_{1,2}$ and we pick $m_1 = m_2 = 0$. We just saw that when we have the m value being 0, the Wigner D-matrix elements are just spherical harmonics:

$$\begin{aligned}\mathscr{D}^{(l_1)}_{m_1',0}(R) \mathscr{D}^{(l_2)}_{m_2',0}(R) &= \frac{4\pi}{\sqrt{(2l_1+1)(2l_2+1)}} \left(Y^{m_1'}_{l_1}(\theta,\phi) Y^{m_2'}_{l_2}(\theta,\phi)\right)^* \\ &= \sum_{l',m'} C^{l',m'}_{m_1',m_2'} C^{l',0}_{0,0} \sqrt{\frac{4\pi}{2l'+1}} Y^{m'}_{l'}(\theta,\phi)^*\end{aligned} \tag{9.183}$$

So we get an identity that relates the Wigner D-matrices as a sum over spherical harmonics with Clebsch-Gordan coefficients. We will now employ the orthogonality of spherical harmonics:

$$\int d\Omega (Y^{m'}_{l'})^* Y^m_l = \delta_{m,m'} \delta_{l,l'} \tag{9.184}$$

to get another specific triple spherical harmonic integral identity:

$$\int d\Omega (Y^{m'}_{l'})^* Y^{m_1}_{l_1} Y^{m_2}_{l_2} = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}} \langle l_1, l_2; 0, 0 | l_1, l_2, l, 0\rangle \langle l_1, l_2; m_1, m_2 | l_1, l_2, l, m\rangle \tag{9.185}$$

So now, we going back to the physical system we were working with in the example of Hydrogenic photon transitions above, to get the relations:

$$\begin{aligned}\langle n', l', m'| \hat{r}_a |n, l, m\rangle &\sim \int d\Omega (Y^{m'}_{l'})^* Y^{m_1}_{l_1} Y^{m_2}_{l_2} \\ &\sim \langle l, 1; m, a | l, 1; l', m'\rangle\end{aligned} \tag{9.186}$$

So this grants us *selection rules*:

$$\boxed{|l-1| \leq l' \leq l+1, \quad m' = a+m} \tag{9.187}$$

So for the $3d \to 2p$ transition, we have $l' = 1, l = 2$ so that $1 \leq (l'=1) \leq 3$ which gives us only 9 matrix elements compared to the 45 we saw earlier!

§9.8.3 Spherical Tensors

Spherical tensors are another set of objects that resemble tensors, but have nice transformation properties under rotation. Specifically, these are irreducible tensor operators of order/rank k as a set of $2k+1$ operators $\hat{T}_q^{(k)}$ with $q \in \{-k, -k+1, \ldots, k-1, k\}$. It is also useful to know that any tensor can be decomposed into the direct sum of spherical tensors. Spherical tensors are the generalization of spherical vectors $\hat{\vec{r}}$ (which happen to just be vectors), which as we saw earlier transforms just as Y_1^m would under rotation ($l = 1$). Now consider a totally general rotation:

$$|\hat{n}'\rangle = \hat{\mathscr{D}}(R)\,|\hat{n}\rangle \tag{9.188}$$

which differs from what we saw earlier ($\hat{z}$ rotation to some vector $\hat{n}$). The spherical harmonic here would then be:

$$\begin{aligned} Y_l^m(\hat{n}') &= \langle \hat{n}|l,m\rangle \\ &= \langle \hat{n}|\,\hat{\mathscr{D}}(R)^{-1}\,|l,m\rangle \\ &= \sum_{l',m'} \langle \hat{n}|l',m'\rangle\,\langle l',m'|\,\hat{\mathscr{D}}(R)^{-1}\,|l,m\rangle \\ &= \sum_{m'} Y_l^{m'}(\hat{n})\mathscr{D}^{(l)}_{m,m'}(R)^* \end{aligned} \tag{9.189}$$

where we had that $\hat{\mathscr{D}}(R)^{-1} = \exp\left\{i\hat{\vec{J}}\cdot\hat{n}/\hbar\right\}$. Now generalizing this to tensors (rank-k), we want to rotate these as follows:

$$\boxed{\hat{\mathscr{D}}(R)^\dagger \hat{T}_q^{(k)} \hat{\mathscr{D}}(R) = \sum_{q'=-k}^{k} \mathscr{D}^{(k)}_{q,q'}(R)^* \hat{T}_{q'}^{(k)}} \tag{9.190}$$

where q replaces the index a we had on spherical vectors earlier, and k is a new index which aids in the generalization. That is, these spherical tensors transform $(2k+1)$-dimensional irreducible representations of the rotation group. These are slightly different from the usual tensors we have encountered, where here the rank is specified by this superscript k and defined how they transform under rotations. Now considering infinitesimal rotations, we get that spherical tensors follow the commutation relations:

$$\boxed{\left[\hat{J}_z, \hat{T}_q^{(k)}\right] = \hbar q \hat{T}_q^{(k)}, \qquad \left[\hat{J}_\pm, \hat{T}_q^{(k)}\right] = \hbar\sqrt{(k\pm q)(k\pm q\pm 1)}\hat{T}_{q\pm 1}^{(k)}} \tag{9.191}$$

These give rise to the selection rules from $\langle \alpha', j', m' | \hat{T}_q^{(k)} | \alpha, j, m \rangle$, which satisfy:

$$\boxed{|j-k| \leq j' \leq j+k, \quad m' = q+m} \tag{9.192}$$

similar to what we saw before. Spherical tensors transform just as Y_l^m as well but with $l = k$ and $m = q$. To better grasp what these objects are, let us look at an example that will hopefully make things clearer. We start with a claim.

Claim: $\hat{\vec{U}} \cdot \hat{\vec{V}}$ *is a rank-0 spherical tensor.*

This is shown be proving $\left[\hat{J}_z, \hat{\vec{U}} \cdot \hat{\vec{V}}\right] = 0$ since we know that rank-0 spherical tensors do not transform under rotations at all ($\hat{\mathscr{D}}^{(0)} = \mathbb{I}$). It turns out that rank-1 spherical tensors $\hat{V}_i$ are simply vectors, which follow the commutation relations:

$$\left[\hat{V}_i, \hat{J}_j\right] = i\hbar \epsilon_{ijk} \hat{V}_k \tag{9.193}$$

However, this is not the commutation relation that we had for spherical tensors, so we need an appropriate transformation to get those relations. Consider then a linear combination of the vectors:

$$\hat{V}_{-1} = \frac{\hat{V}_x - i\hat{V}_y}{\sqrt{2}}, \quad \hat{V}_0 = \hat{V}_z, \quad \hat{V}_1 = -\frac{\hat{V}_x + i\hat{V}_y}{\sqrt{2}} \tag{9.194}$$

analogous to what we saw for defining coordinates of the spherical basis (here, $\hat{V}_q = \hat{T}_q^{(k=1)}$). The commutator of this with $\hat{J}_z$ will give:

$$\left[\hat{J}_z, \hat{V}_z\right] = 0, \quad \left[\hat{J}_z, \mp\frac{\hat{V}_x \pm i\hat{V}_y}{\sqrt{2}}\right] = \mp\hbar \left(\frac{\hat{V}_x \pm i\hat{V}_y}{\sqrt{2}}\right) \tag{9.195}$$

which now does indeed satisfy the first spherical tensor relation. If we hadn't added the appropriate signs and the $1/\sqrt{2}$ normalization, we would get:

$$\left[\hat{J}_\pm, \hat{V}_z\right] = \mp\hbar \left(\hat{V}_x \pm i\hat{V}_y\right) \tag{9.196}$$

which is indeed almost what we want but with a missing minus sign and square-root of 2 (compared to the second spherical tensor relation with $q = 0$). So this grants us that the spherical basis definition fixes the normalization that grants us the definition of vectors as rank-1 spherical tensors:

$$\boxed{\hat{V}_{-1} = \frac{\hat{V}_x - i\hat{V}_y}{\sqrt{2}}, \quad \hat{V}_0 = \hat{V}_z, \quad \hat{V}_1 = -\frac{\hat{V}_x + i\hat{V}_y}{\sqrt{2}}} \tag{9.197}$$

rewritten for clarity. As for rank-2 spherical tensors, we first claim that any 2-index Cartesian tensor can be written as:

$$\hat{T}_{ij} = E\delta_{ij} + \hat{A}_{ij} + \hat{S}_{ij} \tag{9.198}$$

where $\hat{A}_{ij}$ is anti-symmetric and $\hat{S}_{ij}$ is a traceless-symmetric tensor ($\sum_i S_{ii} = 0$). Writing this grants us several nice properties of the components.

1. $E = \frac{1}{3}\sum_i T_{ii}$
2. $A_{ij} = \frac{1}{2}(T_{ij} - T_{ji})$
3. $S_{ij} = \frac{1}{2}(T_{ij} + T_{ji}) - E\delta_{ij}$

Now consider how each of these terms transform under classical rotations.

$$
\begin{aligned}
E\delta ij &\rightarrow R_{im}R_{jn}E\delta_{mn} = [R^T R]_{ij}E = E && (9.199)\\
A_{ij} &\quad \text{transforms as a rank-1 spherical tensor} && (9.200)\\
S_{ij} &\rightarrow R_{im}R_{jn}S_{mn}(\text{remains symmetric}) && (9.201)\\
S_{ii} &\rightarrow R_{im}R_{jn}S_{mn} = \delta_{mn}S_{mn} = S_{mm} = 0 && (9.201)
\end{aligned}
$$

For the first few components in the subscript q, we have:

$$
\begin{aligned}
T_0^{(0)} &= E\\
T_0^{(1)} &= A_{xy}, \quad \hat{T}_{\pm 1}^{(1)} = \mp\frac{1}{\sqrt{2}}\left(A_{yz} \pm iA_{zx}\right)\\
T_0^{(2)} &= \sqrt{\frac{3}{2}}S_{zz}, \quad \hat{T}_{\pm 1}^{(2)} = \mp\left(S_{zx} \pm iS_{zy}\right)\\
T_{\pm 1}^{(2)} &= \mp\left(S_{zx} + iS_{zy}\right)\\
T_{\pm 2}^{(2)} &= \frac{1}{2}\left(S_{xx} - S_{yy} \pm 2iS_{xy}\right)
\end{aligned}
\qquad (9.202)
$$

where we dropped the hats here since these statements hold for general tensors even for non-operator classical observables. In the case of dyadic rank-2 spherical tensors $U_i V_j$ (refer back to equation 9.167), the above relations become:

$$
\begin{aligned}
T_0^{(0)} &= -\frac{\vec{U}\cdot\vec{V}}{3} = \frac{U_1V_{-1} + U_{-1}V_1 - U_0V_0}{3}\\
T_q^{(1)} &= \frac{\left(\vec{U}\times\vec{V}\right)_q}{i\sqrt{2}}, \quad q = -1, 0, 1\\
T_0^{(2)} &= \frac{U_1V_{-1} + U_{-1}V_1 + 2U_0V_0}{\sqrt{6}}\\
T_{\pm 1}^{(2)} &= \frac{U_0V_{\pm 1} + U_{\pm 1}V_0}{\sqrt{2}}\\
T_{\pm 2}^{(2)} &= U_{\pm 1}V_{\pm 1}
\end{aligned}
\qquad (9.203)
$$

In the case where both of the spherical vectors in a dyadic rank-2 spherical tensors are Cartesian coordinate vectors in the spherical basis (9.169), these would give rise to the rank-2 spherical tensors as $l = 2$ spherical harmonics written as:

$$
\boxed{T_q^{(2)} = r^2\sqrt{\frac{8\pi}{15}}Y_2^q(\theta,\phi)} \qquad (9.204)
$$

where the conversion from Cartesian to spherical coordinates was done to produce this. Now consider the following example to see how this expression above could be applied.

Example:

Consider the potential where we have:

$$\hat{V}(x,y,z) = V_0 \hat{T}_{xy} = V_0 \hat{x}\hat{y} \tag{9.205}$$

We can see that this is a rank-2 tensor since it is a dyadic tensor (2 vectors put together). Decomposing this, we can see that:

$$E = \frac{1}{3}\sum_i \hat{r}_i \hat{r}_i = \frac{1}{3}\hat{r}^2 \tag{9.206}$$

$$A_{ij} = 0 \tag{9.207}$$

$$S_{ij} = \hat{r}_i \hat{r}_j - \frac{1}{3}\delta_{ij}\hat{r}^2 \tag{9.208}$$

If we write all these out, we get that:

$$\boxed{\langle r,\theta,\phi|\, \hat{T}^{(2)}_q \,|\psi\rangle = r^2 \sqrt{\frac{8\pi}{15}} Y^q_2(\theta,\phi)\, \langle r,\theta,\phi|\psi\rangle} \tag{9.209}$$

which is the quantum mechanical operator analog to what we have for classical spherical tensors above. So this grants us:

$$\hat{V}(x,y,z) = V_0 \frac{i}{2}\left(\hat{T}^{(2)}_{-2} - \hat{T}^{(2)}_2\right) \tag{9.210}$$

The selection rules then tell us that $|l-2| \leq l' \leq l+2$ or another way to write this is $|\Delta l| \leq 2$. Furthermore, we have $m' = m \pm 2$ (or $\Delta m = \pm 2$). There is one more selection rule due to parity symmetry of this system, since $\hat{x}\hat{y} = (-\hat{x})(-\hat{y})$. Since we have the parity operator acts as:

$$\begin{aligned} & \hat{P} Y^m_l(\theta,\phi) = (-1)^l Y^m_l(\theta,\phi) \\ \Rightarrow \quad & \Delta l = \text{even} \\ \Rightarrow \quad & |\Delta l| = 0, 2 \end{aligned} \tag{9.211}$$

where $\Delta = l' - l$.

§9.8.4 Combinations of Spherical Tensors

We want to now know how to combine spherical tensors to get a new spherical tensor. In fact, for an object like the dyadic tensor where we're combining two rank-1 spherical tensors, it's a straightforward way to derive the components in terms of $\hat{U}_i$ and $\hat{V}_i$. This process turns out to just be once again the addition of angular momentum. That is, given 2 spherical tensors

$X_{q_1}^{(k_1)}, Z_{q_2}^{(k_2)}$, then:

$$\boxed{T_q^{(k)} = \sum_{q_1,q_2} \langle k_1, k_2; q_1, q_2 | k_1, k_2; k, q \rangle \, X_{q_1}^{(k_1)} Z_{q_2}^{(k_2)}} \tag{9.212}$$

where $\langle k_1, k_2; q_1, q_2 | k_1, k_2; k, q \rangle$ are the Clebsh-Gordan coefficients following the selection rules:

$$|k_1 - k_2| \leq k \leq k_1 + k_2, \quad m = m_1 + m_2 \tag{9.213}$$

Also, the inverse of this is then:

$$\boxed{X_{q_1}^{(k_1)} Z_{q_2}^{(k_2)} = \sum_{q_1,q_2} \langle k_1, k_2; k, q | k_1, k_2; q_1, q_2 \rangle \, T_q^{(k)}} \tag{9.214}$$

§9.8.5 The Wigner-Eckart Theorem

We start of by simply stating the theorem.

Theorem 9.8.1. Wigner-Eckart Theorem: *Given a spherical tensor operator $\hat{T}_q^{(k)}$ in the basis $\{|\alpha, j, m\rangle\}$, the Wigner-Ekhert theorem states that these can be computed via the relation*:

$$\langle \alpha', j', m' | \, \hat{T}_q^{(k)} \, | \alpha, j, m \rangle = \langle j, k; m, q | j, k; j', m' \rangle \, \frac{\langle \alpha', j' | \, | \hat{T}^{(k)} | \, | \alpha, j \rangle}{\sqrt{2j'+1}} \tag{9.215}$$

where α is just a place holder for any other quantum number that does not have to do with angular momentum. The double line $\langle \ldots | \, | \ldots | \, | \ldots \rangle$ indicates a "reduced matrix element".

In the theorem above, $j' = j + k$ and in the language of angular momentum, we have m' as the magnetic quantum number associated to j', m to j and q to k. These reduced matrix elements introduced in the theorem are actually defined by the statement of the theorem itself.

What this statement means, is that $|j, m\rangle$ and $|j, m'\rangle$ are related by rotations, and the dependence on the magnetic quantum numbers $\{m, m', q\}$ are fully captured in terms of Clebsch-Gordan coefficients, $\langle j, k; m, q | j, k; j', m' \rangle$. The power of this theorem is that it greatly reduces the number of entries required to explicitly compute. This theorem also immediately implies the selection rules as a corollary:

$$|j - k| \leq j' \leq j + k, \quad m' = m + q \tag{9.216}$$

Now we prove the Wigner-Eckart theorem as follows. We remember that $\langle \alpha', j' | \, | \hat{T}^{(k)} | \, | \alpha, j \rangle$ is a reduced matrix element (as denoted by the double lines).

Proof. First recall the identity:

$$\langle \alpha', j', m' | \left[\hat{J}_\pm, \hat{T}_q^{(k)} \right] | \alpha, j, m \rangle = \langle \alpha', j', m' | \, \hbar \sqrt{(k \pm q)(k \pm q \pm 1)} \hat{T}_{q\pm1}^{(k)} \, | \alpha, j, m \rangle \tag{9.217}$$

Acting with the raising and lowering operators to the right and left states, we get:

$$\begin{aligned}&\sqrt{(j' \pm m')(j' \mp m' + 1)}\, \langle \alpha', j', m' \mp 1 | \hat{T}^{(k)}_q | \alpha, j, m \rangle \\ &= \sqrt{(j \mp m)(j \pm m + 1)}\, \langle \alpha', j', m' | \hat{T}^{(k)}_q | \alpha, j, m \pm 1 \rangle \\ &+ \sqrt{(k \mp q)(k \pm q + 1)}\, \langle \alpha', j', m' | \hat{T}^{(k)}_{q\pm 1} | \alpha, j, m \rangle\end{aligned} \tag{9.218}$$

This rewriting is in fact the Clebsch-Gordan recurrence relation. That is, the matrix elements $\langle \alpha', j', m' | \hat{T}^{(k)}_q | \alpha, j, m \rangle$ satisfy the Clebsch-Gordan recurrence relation and is proportional to the Clebsch-Gordan coefficients (for addition $j + k \to j'$). Explictly, we have:

$$\langle \alpha', j', m' | \hat{T}^{(k)}_q | \alpha, j, m \rangle = c(\alpha, \alpha', j, j', k)\, \langle j, k; m, q | j, k; j', m' \rangle \tag{9.219}$$

where $c(\alpha, \alpha', j, j', k)$ is the constant of proportionality. The expression above is close to the formula in the theorem. It works out that the factor $1/\sqrt{2j'+1}$ in the theorem is a normalization factor (varies in different texts), such that:

$$\left| \langle \alpha', j' | \hat{T}^{(k)} | \alpha, j \rangle \right|^2 = \sum_{m,m',q} \left| \langle \alpha', j', m' | \hat{T}^{(k)}_q | \alpha, j, m \rangle \right|^2 \tag{9.220}$$

□

Example:

Consider the spherical components of the operator $\hat{\vec{J}}$, where we have:

$$\hat{J}^{(1)}_{\pm 1} = \mp \frac{1}{\sqrt{2}} \hat{J}_{\pm} \tag{9.221}$$

$$\hat{J}^{(1)}_0 = \hat{J}_z \tag{9.222}$$

To find $\langle j | \, | \hat{J}^{(1)} | \, | j \rangle$ (only has diagonal entries), we first pick $q = 0$ and apply the Wigner-Ekhert theorem to get:

$$\langle j, m' | \hat{J}^{(1)}_0 | j, m \rangle = \langle j, m' | \hat{J}_z | j, m \rangle = \hbar m \delta_{m,m'} \tag{9.223}$$

$$= \langle j, 1; m, 0 | j, 1; j, m \rangle \frac{\langle j | \, | \hat{J}^{(1)} | \, | j \rangle}{\sqrt{2j+1}} \tag{9.224}$$

Since j is arbitrary, we cannot look this coefficient up in a table, but so we introduce the *Wigner 3j-symbol* $\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{bmatrix}$ defined as:

$$\boxed{\langle j_1, j_2; m_1, m_2 | j_1, j_2; j, m \rangle = (-1)^{j_1 - j_2 + m} \sqrt{2j+1} \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{bmatrix}} \tag{9.225}$$

These have the properties that

1. they are invariant under cyclic permutation of columns;

2. any other column permutation gives a factor of $(-1)^{j_1+j_2+j}$;
3. $\begin{bmatrix} j_1 & j_2 & j \\ -m_1 & -m_2 & -m \end{bmatrix} = (-1)^{j_1+j_2+j} \begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix}$;
4. they satisfy the *Racah formula*.

Apart from a phase factor, Racah's W-coefficients are equal to Wigner's $6j$-symbols which in general, is very messy. However, in specific cases like the current example, the Racah formula simplifies the Clebsch-Gordan coefficient that we need to something nice:

$$\begin{aligned} \begin{bmatrix} j & 1 & j \\ m & 0 & -m \end{bmatrix} &= (-1)^{1-j-m} \frac{m}{\sqrt{j(j+1)(2j+1)}} \\ \Rightarrow \quad \langle j | \, | \hat{J}^{(1)} | \, | j \rangle &= \hbar(2j+1)\sqrt{j(j+1)} \end{aligned} \tag{9.226}$$

Another very useful theorem in practice is known as the *replacement theorem*, and its stated below.

Theorem 9.8.2. Replacement Theorem: *Given the matrix elements of some spherical tensor* $\langle \alpha', j', m' | \, \hat{X}^{(k)})_q \, | \alpha, j, m \rangle$ *and we wanted to write this in terms of the matrix elements of another spherical tensor of the same rank* $\langle \beta', j', m' | \, \hat{Z}^{(k)})_q \, | \beta, j, m \rangle$*, then we have the relation*:

$$\langle \alpha', j', m' | \, \hat{X}^{(k)}_q \, | \alpha, j, m \rangle = \left(\frac{\langle \alpha', j' | \, | \hat{X}^{(k)} | \, | \alpha, j \rangle}{\langle \beta', j' | \, | \hat{Z}^{(k)} | \, | \beta, j \rangle} \right) \langle \beta', j', m' | \, \hat{Z}^{(k)})_q \, | \beta, j, m \rangle \tag{9.227}$$

as long as the angular momentum quantum numbers j *and* m *are the same.*

This relation is always true, but not always useful (sometimes ends up being trivial). For instance, consider if we choose $\hat{Z}^{(k)}_q$ as the operator $\hat{\vec{J}}$, this operator only connects $j' = j$ making the relation for other cases trivial. However, given some vector operator $\hat{\vec{V}}$ and try to relate it with $\hat{\vec{J}}$. This gives:

$$\langle \alpha', j', m' | \, \hat{V}^{(1)}_q \, | \alpha, j, m \rangle = \left(\frac{\langle \alpha', j' | \, | \hat{V}^{(1)} | \, | \alpha, j \rangle}{\langle \beta, j | \, | \hat{J}^{(1)} | \, | \beta, j \rangle} \right) \langle \beta, j, m' | \, \hat{J}^{(1)})_q \, | \beta, j, m \rangle \tag{9.228}$$

where $\beta' = \beta$ and $j' = j$ now for the $\hat{J}$ operator since all other entries would be trivial. We now use the identity:

$$\hat{\vec{U}} \cdot \hat{\vec{V}} = \hat{U}^{(1)}_0 \hat{V}^{(1)}_0 - \hat{U}^{(1)}_1 \hat{V}^{(1)}_{-1} - \hat{U}^{(1)}_{-1} \hat{V}^{(1)}_1 \tag{9.229}$$

This grants us:

$$\begin{aligned} \langle \alpha', j', m' | \, \hat{\vec{J}} \cdot \hat{\vec{V}} \, | \alpha, j, m \rangle &= \langle \alpha', j', m' | \left[\hat{J}^{(1)}_0 \hat{V}^{(1)}_0 - \hat{J}^{(1)}_1 \hat{V}^{(1)}_{-1} - \hat{J}^{(1)}_{-1} \hat{V}^{(1)}_1 \right] | \alpha, j, m \rangle \\ &= c_{j,m} \, \langle \alpha', j | \, | \hat{V}^{(1)} | \, | \alpha, j \rangle \end{aligned} \tag{9.230}$$

where the last line results from the Wigner-Ekhert theorem and $c_{j,m}$ is some relational constant

dependent on j and m. If we then pick $\hat{\vec{V}} = \hat{\vec{J}}$, we get:

$$\begin{aligned}\langle \alpha', j', m' | \, \hat{\vec{J}}^2 \, | \alpha, j, m \rangle &= \langle \alpha, j, m | \, \hat{\vec{J}}^2 \, | \alpha, j, m \rangle \\ &= c_j \, \langle \alpha, j | \, | \hat{\vec{J}}^{(1)} | \, | \alpha, j \rangle\end{aligned} \tag{9.231}$$

But we know that $\langle \alpha, j, m | \, \hat{\vec{J}}^2 \, | \alpha, j, m \rangle = \hbar^2 j(j+1)$, which grants us:

$$\boxed{\langle \alpha', j', m' | \, \hat{V}_q^{(1)} \, | \alpha, j, m \rangle = \left(\frac{\langle \alpha', j', m' | \, \hat{\vec{J}} \cdot \hat{\vec{V}} \, | \alpha, j, m \rangle}{\hbar^2 j(j+1)} \right) \langle j, m' | \, | \hat{J}_q^{(1)} | \, | j, m \rangle} \tag{9.232}$$

This result is known as the *projection theorem.*

Example:

Let's us study the Landé g-factor. Consider the Hydrogen atom in an external magnetic field $\vec{B} = B\hat{z}$. This gives a contribution to the Hamiltonian:

$$\hat{H}_1 = \frac{eB}{2m_e c} \left(\hat{L}_z + 2\hat{S}_z \right) \tag{9.233}$$

implying to the spin and orbital angular momentum of the atom. Assuming B is small such that we can adopt $|j, m\rangle$ as eigenstates (perturbation theory), we then now want to compute expectations of this Hamiltonian. If we take the dot product:

$$\begin{aligned}\hat{\vec{L}} \cdot \hat{\vec{J}} &= \hat{\vec{L}} \cdot (\hat{\vec{L}} + \hat{\vec{S}}) \\ &= \hat{\vec{L}}^2 + \frac{1}{2} \left(\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2 \right)\end{aligned} \tag{9.234}$$

And similar:

$$\hat{\vec{S}} \cdot \hat{\vec{J}} = \hat{\vec{S}}^2 + \frac{1}{2} \left(\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2 \right) \tag{9.235}$$

Then the matrix elements would simply be:

$$\langle j, m | \, \hat{\vec{L}} \cdot \hat{\vec{J}} \, | j, m \rangle = \frac{\hbar^2}{2} \left[j(j+1) + l(l+1) - s(s+1) \right] \tag{9.236}$$

$$\langle j, m | \, \hat{\vec{S}} \cdot \hat{\vec{J}} \, | j, m \rangle = \frac{\hbar^2}{2} \left[j(j+1) + s(s+1) - l(l+1) \right] \tag{9.237}$$

Then if we want to know $\langle j, m | \, \hat{L}_z \, | j, m \rangle$, we use the projection theorem to get:

$$\begin{aligned}\langle j, m | \, \hat{L}_0^{(1)} \, | j, m \rangle &= \left(\frac{\langle j, m | \, \hat{\vec{L}} \cdot \hat{\vec{J}} \, | j, m \rangle}{\hbar^2 j(j+1)} \right) \langle j, m | \, \hat{J}_0^{(1)} \, | j, m \rangle \\ &= \frac{\hbar m}{j(j+1)} \left[j(j+1) + l(l+1) - s(s+1) \right]\end{aligned} \tag{9.238}$$

We can do a similar procedure for $\langle j,m|\,\hat{S}_0^{(1)}\,|j,m\rangle$, and plug the results in to get the energy correction which is the expectation value of $\hat{H}_1$:

$$E_1 = \langle \hat{H}_1 \rangle = g_J \frac{eB}{2m_e c}\hbar m \tag{9.239}$$

$$\text{where } g_J = \frac{3}{2} + \frac{s(s+1)-l(l+1)}{2j(j+1)} \tag{9.240}$$

where g_J is the Landé g-factor.

§9.8.6 Electric Multipole Expansions

Consider the expansion of the potential analogous to mutlipole expansions done in classical mechanics ($V(\vec{r}) = qU(\vec{r}) = q\sum_l \sum_m f_{l,m}(r)Y_{l,m}(\Omega)$), assuming an external electric/magnetic field (no sources leading to Laplace's equation):

$$\frac{1}{r}\frac{d^2}{dr^2}\left(r f_{l,m}(r)\right) - \frac{l(l+1)}{r^2} f_{l,m}(r) = 0 \tag{9.241}$$

$$\Rightarrow \quad f_{l,m}(r) = \sqrt{\frac{4\pi}{2l+1}} c_{l,m} r^l \tag{9.242}$$

where we dropped the $r^{-(l+1)}$ dependence as we want a solution well-behaved near the origin. We then define:

$$V(\hat{\vec{r}}) \equiv \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{l,m} \hat{Q}_m^{(l)} \tag{9.243}$$

where $\hat{Q}_l^m$ is the electric mutlipole operator which is in fact a spherical tensor of rank (l). The matrix elements of these tensors are given by:

$$\boxed{\langle \vec{r}'|\,\hat{Q}_l^m\,|\vec{r}\rangle = q\sqrt{\frac{4\pi}{2l+1}} r^l Y_l^m(\theta,\phi)\delta(\vec{r}-\vec{r}')} \tag{9.244}$$

The multipoles are thus given by:

$$\hat{Q}_0^{(0)} = q, \quad \hat{\vec{Q}}_1 = q\hat{\vec{r}}, \quad \hat{Q}_2^{(2)} = \frac{q}{2}(3\hat{z}^2 - \hat{\vec{r}}^2), \quad \ldots \tag{9.245}$$

For N particle systems, these multipole operators can be expressed as a collective multipole moment which is simply the sum of the individuals ones:

$$\left\langle \hat{\vec{r}}'_1,\ldots,\hat{\vec{r}}'_N \right| \hat{Q}_l^m \left| \hat{\vec{r}}_1,\ldots,\hat{\vec{r}}_N \right\rangle = \sqrt{\frac{4\pi}{2l+1}} \sum_{n=1}^{N} q_n r_n^l Y_l^m(\theta_n,\phi_n)\delta(\vec{r}_n - \vec{r}'_n) \tag{9.246}$$

Since these are spherical tensors, we can apply the Wigner-Ekert theorem on them to get:

$$\langle \alpha', l_2, m_2 | \hat{Q}^{(l)}_m | \alpha, l_1, m_2 \rangle = \langle l_1, l; m_1, m | l_1, l; l_2, m_2 \rangle \frac{\langle \alpha', l_2 | |\hat{Q}^{(l)}| | \alpha, l_1 \rangle}{\sqrt{2l_2+1}} \tag{9.247}$$

$$\text{where } \langle \alpha', l_2 | |\hat{Q}^{(l)}| | \alpha, l_1 \rangle = q\sqrt{2l_1+1}\, \langle l_1, l; 0, 0 | l_1, l; l_2, 0 \rangle \int_0^\infty r^{l+2} R^*_{\alpha', l_2}(r) R_{\alpha, l_1}(r) \tag{9.248}$$

These result in the selection rules:

$$\langle l_1, l; 0, 0 | l_1, l; l_2, l \rangle = 0 \text{ if } l_1 + l_2 - l = \text{ odd} \tag{9.249}$$

$$|l_1 - l_2| \leq l \leq l_1 + l_2 \tag{9.250}$$

If we consider the case where $l_1 = l_2$, then we have:

$$0 \leq l \leq 2l_1 \quad \text{and} \quad \langle l_1, l; 0, 0 | l_1, l; l_1, l \rangle = 0 \text{ if } 2l_1 - l = \text{ odd} \tag{9.251}$$

$$\Rightarrow \quad \boxed{\langle l_1 | |\hat{Q}^{(l)}| | l_1 \rangle = 0 \quad \text{unless } l = 0, 2, \ldots, 2l_1} \tag{9.252}$$

Let's look at a few examples of what this tells us.

1. For the Hydrogen groundstate ($n = 1, l = 0$), we have that there are only $l = 0$ multipoles.
2. For any orbital angular momentum eigenstate has **no** electric dipole moment.
3. Deuteron has been experimentally observed to have a quadrupole moment, which implies $l \neq 0$.

Chapter 10

The Fine Structure of Hydrogen

As a closing chapter to this semester, we will be continuing our analysis on Hydrogen. Specifically, we will be looking into a more realistic treatment of its spectrum by including several physical corrections to the simplified model we have been working with. To do so, we employ a powerful tool known as perturbation theory. To address the fine structure that arises in Hydrogen, it turns out that we only need knowledge of first-order, time-independent, non-degenerate perturbation theory. This is far from the most general means of perturbation theory, but will already grant us interesting insights to a very real and extensively studied physical system. More perturbation theory will indeed be covered in the next semester of graduate quantum mechanics.

§10.1 First-Order Time-Indepedent Perturbation Theory

We start by assuming a Hamiltonian which is of the form:

$$\hat{H} = \hat{H}^{(0)} + \lambda\delta\hat{H} \tag{10.1}$$

for which we have that $\hat{H}^{(0)}$ is a Hamiltonian that is exactly solvable (e.g. the quantum harmonic oscillator), λ is a small continuous parameter and $\delta\hat{H}$ is the perturbation Hamiltonian. What we want to find then is:

$$\left(\hat{H}^{(0)} + \lambda\delta\hat{H}\right)|n\rangle = E_n\,|n\rangle \tag{10.2}$$

To solve this, we expand in the small parameter λ, that is:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \mathcal{O}(\lambda^2) + \dots \tag{10.3}$$

$$|n\rangle = \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \mathcal{O}(\lambda^2) + \dots \tag{10.4}$$

$$\Rightarrow \quad \left(\hat{H}^{(0)} + \lambda\delta\hat{H}\right)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \dots\right) = \left(E_n^{(0)} + \lambda E_n^{(1)} + \dots\right)\left(\left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \dots\right) \tag{10.5}$$

For which if we compare the first order terms in λ, we get:

$$\boxed{E_n^{(1)} = \left\langle n^{(0)} \middle| \delta\hat{H} \middle| n^{(0)} \right\rangle} \tag{10.6}$$

Note: This only holds for non-degenerate spectrums or if we have degenerate states that we can still uniquely label (a CSCO that includes $\delta\hat{H}$).

We will now apply this to Hydrogen (Hydrogenic atoms, where the nuclear charge is arbitrary and called Z), which although has a huge amount of degeneracy, does have a CSCO we know with $\delta\hat{H} = \hat{J}_z$ in it. This system as:

$$V(r) = -\frac{Ze^2}{r}, \quad \psi(r,\theta,\phi) = R_{n,l}(r)Y_l^m(\theta,\phi) \tag{10.7}$$

for which the wavefunctions are analytically solvable with associated *Laguerre polynomials* $L_p^q(\rho)$ or the *confluent hypergeometric functions* $F(a,c,p)$:

$$R_{n,l}(r) \sim F_1\left(-n+l+1, 2l+2, \frac{2zr}{na_0}\right) e^{-zr/(na_0)} \tag{10.8}$$

where $a_0 = \hbar^2/(m_e e^2)$ is the Bohr radius. It works out that te energy eigenvalues work out to be:

$$E_n = -\frac{1}{2}mc^2\frac{Z^2\alpha^2}{n^2} = -\frac{Z^2}{n^2}R_y \tag{10.9}$$

where $\alpha = e^2/(\hbar c)$ is known as the *fine structure constant* and $R_y = e^2/(2a_0)$ is known as the Rydberg atom radius. These energy are degenerate with a degeneracy n^2 that comes from $\sum_l(2l+1)$ since only n is specified. However, this is an idealized model and there are indeed corrections to the energy spectrum if we wanted to be precise. Some of these are

1. relativistic corrections;
   (a) magnetic coupling;
   (b) Lamb shift;
   (c) relativistic Kinetic term;
   (d) Darwin term;
2. finite size nucleus correction;
3. nuclear spin coupling (hyperfine correction).

We are going to start with the finite nuclear size correction.

§10.1.1 Finite Nuclear Size Corrections

We are going to model the nucleus here as a sphere of radius r_0, with constant charge density. This gives us the potential:

$$V(r) = \begin{cases} -\frac{Ze^2}{r}, & r \geq r_0; \\ \frac{Ze^2}{2r_0}\left[\left(\frac{r}{r_0}\right)^2 - 3\right], & r < r_0 \end{cases} \tag{10.10}$$

So, it would be appropriate to treat the perturbation to the Hamiltonian as:

$$\delta\hat{H} = \begin{cases} 0, & r \geq r_0; \\ \frac{Ze^2}{2r_0}\left[\left(\frac{r}{r_0}\right)^2 - 3 + \frac{2r_0}{r}\right], & r < r_0 \end{cases} \tag{10.11}$$

Starting with the ground state of the unperturbed Hamiltonian $|n,l,m\rangle = |1,0,0\rangle$, the wavefunction can be written down as:

$$\psi_{1,0,0}(r,\theta,\phi) = 2\sqrt{\frac{Z^3}{4\pi a_0^3}}e^{-Zr/a_0} \tag{10.12}$$

So the first order correction to the energy would be given as:

$$\begin{aligned} E^{(1)}_{1,0,0} &= \langle 1,0,0|\,\delta\hat{H}\,|1,0,0\rangle \\ &= \int_0^{r_0} r^2 \frac{2Z^4e^2}{r_0^2 a_0^3}\left[\left(\frac{r}{r_0}\right)^2 - 3 + \frac{2r_0}{r}\right]e^{-2Zr/a_0}dr \\ &\approx \frac{4}{5}\frac{Z^4 r_0^2}{a_0^2}\left(\frac{e^2}{2a_0}\right) \\ &= \frac{4}{5}Z^2 E^{(0)}_{1,0,0}\left(\frac{r_0}{a_0}\right)^2 \end{aligned} \tag{10.13}$$

which turns out to be an extremely small correction since $a_0 \sim 10^{-10}$m and $r_0 \sim 10^{-15}$m. Now, let us move on to the relativistic correction.

§10.1.2 Relativistic Corrections and the Feynman-Hellmann Theorem

In order to account for the correction, we need to change the kinetic energy term in the Hamiltonian to:

$$\hat{T} = c\sqrt{\hat{p}^2 + m^2c^2} - mc^2 \tag{10.14}$$

We have that the electron speed is about $v/c \sim \alpha$, and so we do a series expansion around this to get:

$$\hat{T} \approx \frac{\hat{p}^2}{2m_e} - \frac{\hat{p}^4}{8m_e^2c^2} \tag{10.15}$$

which grants us that the perturbation Hamiltonian is given as:

$$\delta\hat{H}_{rel} = -\frac{\hat{p}^4}{8m_e^2c^2} \tag{10.16}$$

$$\Rightarrow \quad E^{(1)}_{n,l} = -\frac{\langle\hat{p}^4\rangle}{8m_e^2c^2} \tag{10.17}$$

To solve this, are are going to do a mathematical rewriting trick as follows:

$$\begin{aligned}\left\langle \delta\hat{H}_{rel} \right\rangle &= -\frac{1}{2m_e c^2}\left\langle \left(\frac{\hat{p}^2}{2m_e}\right)^2 \right\rangle \\ &= -\frac{1}{2m_e c^2}\left\langle \left(\hat{H}^{(0)} + \frac{Ze^2}{r}\right)^2 \right\rangle \\ &= -\frac{1}{2m_e c^2}\left[(E_n^{(0)})^2 + 2E_n^{(0)} Ze^2 \left\langle \frac{1}{r} \right\rangle + Z^2 e^4 \left\langle \frac{1}{r^2} \right\rangle \right]\end{aligned} \tag{10.18}$$

to get the $1/r$ expectation, we can exploit the Virial theorem $2\langle T\rangle = -\langle V\rangle$ to give us:

$$\left\langle \frac{1}{r} \right\rangle = -\frac{2}{Ze^2} E_n^{(0)} \tag{10.19}$$

As for the $1/r^2$ term, we use the *Feynman-Hellmann* theorem which is stated as follows.

Theorem 10.1.1. Feynman-Hellmann Theorem: *Given a Hamiltonian dependent on a continuous parameter λ, we have that*:

$$\frac{dE_\lambda}{d\lambda} = \langle E_\lambda | \frac{d}{d\lambda}\hat{H} | E_\lambda \rangle \tag{10.20}$$

Proof. Starting from the expectation value:

$$E_\lambda = \langle E_\lambda | \hat{H} | E_\lambda \rangle \tag{10.21}$$

We take the derivative with respect to λ and collect terms to get:

$$\frac{dE_\lambda}{d\lambda} = \langle E_\lambda | \frac{d\hat{H}}{d\lambda} | E_\lambda \rangle + E_\lambda \frac{d}{d\lambda}\big(\langle E_\lambda | E_\lambda \rangle \big) \tag{10.22}$$

Since $\langle E_\lambda | E_\lambda \rangle = 1$ is just a constant, its derivative vanishes leaving us with:

$$\frac{dE_\lambda}{d\lambda} = \langle E_\lambda | \frac{d\hat{H}}{d\lambda} | E_\lambda \rangle \tag{10.23}$$

□

This theorem is purely a mathematical theorem, so λ can be taken to be any continuous parameter in the Hamiltonian that is convenient. This then allows us to apply this theorem to our Hamiltonian, by first considering the Hamiltonian in position space:

$$\langle \vec{r} | \hat{H} | n, l, m \rangle = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) - \frac{l(l+1)}{r^2} \right] \psi_{n,l,m}(r) - \frac{Ze^2}{r}\psi_{n,l,m}(r) \tag{10.24}$$

for which if we take the derivative with respect to $\lambda = l$, this gives us:

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{a_0^2 n^2 (l + 1/2)} \tag{10.25}$$

where $n = q + l + 1$. So in total, we get that the expectation of the perturbative Hamiltonian is given by:

$$\langle \delta \hat{H}_{rel} \rangle = \frac{Z^4 e^2}{m_e c^2 n^3 a_0} \left(\frac{3}{4n} - \frac{1}{l + \frac{1}{2}} \right) R_y = \frac{Z^4}{n^3} \alpha^2 \tag{10.26}$$

which again is indeed a very small correction to the Hamiltonian.

§10.1.3 The Fine Structure of Hydrogen

From here on out, we will actually be working with Hydrogen and working out all the first-order corrections to its spectrum, which means us setting $Z = 1$ and including the electron spin, giving us the eigenstates $|n, l, m, m_s\rangle$. We will assert that all the necessary corrections to the spherically symmetric Hamiltonian can be written as:

$$\hat{H}_{fine} = \hat{H}^{(0)} + \delta \hat{H}_{rel} + \delta \hat{H}_{SO} + \delta \hat{H}_D \tag{10.27}$$

where $\delta \hat{H}_{SO}$ is the perturbation due to spin-orbit coupling and $\delta \hat{H}_D$ is the Darwin correction term. Starting with the spin-orbit term, we have:

$$\delta \hat{H}_{SO} = \frac{e^2}{2 m_e^2 c^2 r^3} \hat{\vec{L}} \cdot \hat{\vec{S}} \tag{10.28}$$

This can be nicely solved in the $|n, l, s; j, m_{l,s}\rangle$ basis with the rewriting of the perturbation Hamiltonian into $\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2$ where $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$ which we are now familiar with doing. This works out to also give a correction of order α^2.

Finally for the Darwin term, we actually need to know the full relativistic Hamiltonian which produces a phenomenon known as *zitterbewegung* (i.e. trembling motion) that affects the motion of the particles with spin. However, we will simply state the Hamiltonian here as:

$$\delta \hat{H}_D = -\frac{\pi e^2 \hbar^2}{2 m_e^2 c^2} \delta(\vec{r}) \tag{10.29}$$

$$\Rightarrow \quad \langle \delta \hat{H}_D \rangle = \frac{\pi e^2 \hbar^2}{2 m_e^2 c^2} |\psi(0)|^2 \tag{10.30}$$

which is indeed 0 unless $l = 0$ (s-orbitals). This works out to give us a order of magnitude correction of the size $m_e c^2 \alpha^4$. To deeper explore the fine structure, we consider the specific energy spectrum where $n = 2$. Starting with the $2s$ state ($n = 2, l = 0$), we get:

$$\langle \delta \hat{H}_{rel} \rangle = -\frac{13}{64} \alpha^2 R_y \tag{10.31}$$

$$\langle \delta \hat{H}_D \rangle = \frac{1}{8} \alpha^2 R_y \tag{10.32}$$

$$\langle \delta \hat{H}_{SO} \rangle = 0 \tag{10.33}$$

As for the $2p$ state ($n = 2, l = 1$), we get:

$$\langle \delta \hat{H}_{rel} \rangle = -\frac{7}{192}\alpha^2 R_y \tag{10.34}$$

$$\langle \delta \hat{H}_D \rangle = 0 \tag{10.35}$$

$$\langle \delta \hat{H}_{SO} \rangle = \begin{cases} -\frac{1}{24}\alpha^2 R_y, & j = \frac{1}{2} \\ -\frac{1}{48}\alpha^2 R_y, & j = \frac{3}{2} \end{cases} \tag{10.36}$$

Getting the spin-orbit for this state required finding the term $\langle 1/r^3 \rangle$ by using *Kramer's relations*, which is not particularly enlightening so is not presented here. Combining all these corrections, we get:

$$\Delta E_{2s} = -\frac{5}{64}\alpha^2 R_y \tag{10.37}$$

$$\Delta E_{2p,j=1/2} = -\frac{5}{64}\alpha^2 R_y \tag{10.38}$$

$$\Delta E_{2p,j=3/2} = -\frac{1}{64}\alpha^2 R_y \tag{10.39}$$

The first 2 corrections work out to be the same which is only by coincidence and known as an *accidental degeneracy*. Although, such accidental symmetries barely are accidental in theoretical physics, but full relativistic quantum mechanics utilizing the Dirac equation has to be done in order to get these relations out explicitly. In reality however, the degeneracies do not show up because we are missing something known as the *Lamb shit* which is actually a perturbation of order $\mathcal{O}(\alpha^3)$, however this cannot be dealt with without knowing relativistic quantum mechanics, so it will not be covered here. It is a very small correction ($\sim$ 1GHz, with the standard energy splitting in Hydrogen being $\sim$ 2000 THz). We can however, do a hyperfine correction due to the proton spin.

§10.1.4 Hyperfine Corrections

The proton magnetic moment is given by:

$$\hat{\mu}_I = \frac{g_p \mu_n}{\hbar}\hat{\vec{I}} \tag{10.40}$$

where g_p is the g-factor for the proton (≈ 5.6) and μ_n is the nuclear magneton where $\mu_n = e\hbar/(2m_p)$ which is much smaller than the Bohr magneton. This magnetic moment adds 3 corrections to the Hamiltonian:

$$\hat{\vec{\mu_I}} \cdot \hat{\vec{L}}, \quad \hat{\vec{\mu_I}} \cdot \hat{\vec{S}}, \quad \frac{8\pi g_p e^2}{3m_e m_p c^2}\delta(\vec{r})\hat{\vec{I}} \cdot \hat{\vec{S}} \tag{10.41}$$

where the last correction term is called the *contact term* (refer to *Cohen-Tannoudji* for more information on this). For this analysis, we will be looking at $n = 1$ Hydrogen, which have the fine structure corrections:

$$\begin{aligned} \langle \delta \hat{H}_{rel} \rangle &= -\frac{5}{8}\alpha^2 R_y \\ \langle \delta \hat{H}_D \rangle &= \frac{1}{2}\alpha^2 R_y \end{aligned} \tag{10.42}$$

Consider the electron-nucleon spin coupling, which admit the states $|i, s; m_i, m_s\rangle$ (4 of these states). For the $1s$ state, we get that the nuclear spin-orbit coupling term and the nuclear-electron spin coupling terms vanish. This leaves us with the contact term, which we can take the expectation to get:

$$\langle \delta \hat{H}_{hf,c} \rangle = \left[\frac{2}{3\hbar^2} \frac{g_p m_e}{m_p} \left(1 + \frac{m_e}{m_p} \right)^{-3} \alpha^2 R_y \right] \langle \hat{\vec{I}} \cdot \hat{\vec{S}} \rangle \equiv A \langle \hat{\vec{I}} \cdot \hat{\vec{S}} \rangle \tag{10.43}$$

where the "hf, c" subscript denote the hyperfine, contact perturbation Hamiltonian. Defining the operator $\hat{\vec{F}} = \hat{\vec{I}} + \hat{\vec{S}}$, we can do the standard change of basis into the irreducible basis to get:

$$\hat{\vec{I}} \cdot \hat{\vec{S}} = \frac{1}{2} \left(\hat{\vec{F}}^2 - \hat{\vec{I}}^2 - \hat{\vec{S}}^2 \right) \tag{10.44}$$

$$\Rightarrow \quad \langle \delta \hat{H}_{hf,c} \rangle = \begin{cases} \frac{A\hbar^2}{4}, & f = 1 \\ -\frac{3A\hbar^2}{4}, & f = 0 \end{cases} \tag{10.45}$$

where A is the complicated constant defined in the expectation value formula above. This correction is actually very useful for astronomy and astrophysics.

§10.2 Relativistic Quantum Mechanics (Motivations)

To some extent, we can deal with relativistic quantum mechanics by amending the Schrödinger equation into something that is more "relativity friendly". Some of these equations include the *Klein-Gordon equation* and the *Dirac equation*. The full answer however, is the formalism of *quantum field theory* (QFT). To understand this, we need to know about fields.

Definition 10.2.1. Field: *A field $F = F(\vec{x}, t)$ is a function of space and time that takes on values everywhere. This is as opposed to particles that are localized objects that are fixed in space.*

To say that a particle is fixed in time implies the measured quantity of position, not the wave-function. The question that brings us to quantum field theory is how to quantize classical fields? To summarize these ideas in a table (by Sid Coleman), we have

	Single-Particle	Many-Particle
Classical	Classical Mechanics	Continuum Mechanics
Quantum	Quantum Mechanics	Quantum Field Theory
	$N \quad \rightarrow \quad \infty$	

Table 10.1: N-body extension to quantum and classical mechanics.

There is also another classification that we want to think about and that is adding relativity to our theories.

	Non-Relativistic	Relativistic
Classical	Classical Mechanics	Spatial Relativity
Quantum	Quantum Mechanics	Quantum Field Theory
	$v/c \quad \to \quad 1$	

Table 10.2: Relativistic extension to quantum and classical mechanics.

To see the necessity for relativitic quantum mehcanics, we consider the equations $E = mc^2$ and $\Delta x \Delta p \geq \hbar/2$. Imagine trapping a particle within Δx and using $E \approx pc$, we get:

$$\Delta E \Delta x \geq \hbar c \tag{10.46}$$

So if $\Delta E \geq mc^2$, new particles can in fact be created in this trap! This has only been resolved in the formalism of QFT, and it is in fact the most accurate scientific theory in human history. There is of course limits on the creation or annihilation of particles, because we cannot violate conservation laws. To fix this, QFT asserts that particle creation comes in *particle-antiparticle pairs* (e.g. creation of electron-positron (e^- and e^+) pair). To more rigorously see the need for a relativistic quantum theory, consider the propagation with the free particle Hamiltonian:

$$\begin{aligned} U(\vec{x}, t) &= \langle \vec{x} | \, e^{i\hat{H}t} \, | \vec{x} = 0 \rangle \\ &= \int \frac{d^3p}{(2\pi)^3} \langle \vec{x} | \, e^{i\hat{H}t} \, | \vec{p} \rangle \langle \vec{p} | \, | \vec{x} = 0 \rangle = \Big(\frac{m}{2\pi i t} \Big)^{3/2} e^{\frac{im\vec{x}}{2t}} \end{aligned} \tag{10.47}$$

This is non-zero for space-like propagation, which fails in the theory of relativity! What if we instead change the Hamiltonian to:

$$\begin{aligned} & \hat{H} = \sqrt{\hat{\vec{p}}^2 + m^2c^2} \\ \Rightarrow \quad & U(\vec{x}, t) = \int \frac{d^3p}{(2\pi)^3} \exp\Big\{ -ict\sqrt{p^2 + m^2c^2} \Big\} \exp\{ i\vec{p} \cdot \vec{x} \} \\ \Rightarrow \quad & U(\vec{x}, t) \sim \exp\{ -m|x| \} \end{aligned} \tag{10.48}$$

which is better since it is exponentially suppressed, but not completely resolved! How QFT comes in to fix this, is insisting on causality by considering the order of measurements which immediately dictates the need for particle creation. As such, we see that QFT is absolutely necessary to resolve the difference between special relativity and quantum mechanics. In fact, QFT is the most accurate physical theory of our universe we have to date!

Appendices

Appendix A

Gaussian Integrals

The best way to go about solving Gaussian integrals is to define a function of α:

$$I(\alpha) = \int dx \exp\bigl(-\alpha x^2\bigr) = \sqrt{\frac{\pi}{\alpha}} \tag{A.1}$$

Then to get more Gaussian integrals with polynomial factors, we can take derivatives:

$$\frac{d}{d\alpha} I(\alpha) = -\int dx x^2 \exp\bigl(-\alpha x^2\bigr) = \sqrt{\frac{\pi}{\alpha}} = -\frac{\sqrt{\pi}}{2\alpha^{3/2}} \tag{A.2}$$

And more generally, we have:

$$\int dx x^n \exp\bigl(-\alpha x^2\bigr) = \frac{(n+1)!!\sqrt{\pi}}{2^{n/2}\alpha^{(n+1)/2}} \tag{A.3}$$