Advanced QM I: 251a

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Contents

Chapter 1

Quantum Mechanics: basic formalism

A standard QM course usually takes a historical route showing how a series of unexplained experimental results lead scientists in the early 20th century to abandon many of the classical notions leading to the formulation of quantum mechanics as a fully fledged theory. In this course, we are going to take a different route. Imagine we have a late 19th century physicist time-travel to us nowadays and we want to convince them of quantum mechanic using a single experiment that most embodies quantum mechanics and would most easily illustrate the structure of theory. What would this experiment be? This experiment is the Stern-Gerlach experiment performed by Stern and Gerlach in Frankfurt in 1922.

1.1 The Stern-Gerlach experiment

In the Stern-Gerlach experiment, silver atoms are heated in a furnace that has a hole in it. A collimator is then used to generate a beam of silver atoms. This beam is then subjected to an **inhomogenous** magnetic field that can be produced using a magnet shaped as shown in Fig. 1.1. We now suppose that the silver atoms has some magnetic moment $\boldsymbol{\mu}$. At this point, we are assuming we do not really know anything about about quantum mechanics, spin, or the atomic number of silver. We are just assuming that there is a quantity called magnetic moment that couples to magnetic field such that an object with magnetic moment $\boldsymbol{\mu}$ has an energy $\boldsymbol{\mu} \cdot \boldsymbol{B}$ in a magnetic field. A particle with magnetic moment $\boldsymbol{\mu}$ placed in an inhomogenuous magnetic field will feel a force given by

$$F_a = \partial_a[\boldsymbol{\mu} \cdot \boldsymbol{B}(\boldsymbol{r})] = \boldsymbol{\mu} \cdot \partial_a \boldsymbol{B}(\boldsymbol{r}) \tag{1.1}$$

Assuming the field points in the z-direction, $\boldsymbol{B} = B\hat{z}$ and it only changes along the z-direction as well, we find the force in the z-direction to be

$$F_z = \mu_z \partial_z B(z) \tag{1.2}$$

We then have a screen at some distance that detects the silver atoms. If we make the reasonable assumption that the magnetic moments of silver atoms all have the same magnitude $\boldsymbol{\mu} = \mu_0$ [1] and come out of the oven with random orientation, then we expect μ_z to have all possible values between $-\mu_0$ and $+\mu_0$ leading to a continuous bundle of beams which leaves a continuous line on the screen as shown in Fig. 1.1 .

Rather remarkably, this is not what is seen in experiment. Instead, the beam splits into only two beams, leaving two spots on the screen as shown in Fig. 1.1. This means that the atoms in the beam seem to have only two possible values of their magnetic moment $\boldsymbol{\mu} = \pm\mu_0\hat{z}$. First, let us try to find some plausible classical explanation for this observation. After thinking for a bit, we can see that the only possibility is that somehow the magnetic moments of the silver atoms are pointing in the z-direction with an equal probability to be pointing up or down. To check whether this is really the case, we can simply rotate the device. If the moments are pointing in the $\pm$ z-direction, then using a device rotated by an angle θ relative to the z-axis, let's say in the $x - z$ plane, we should see two spots corresponding to the projection of the z-magnetic

[1] This assumption is not really needed. See Problem 1 in the first problem set.

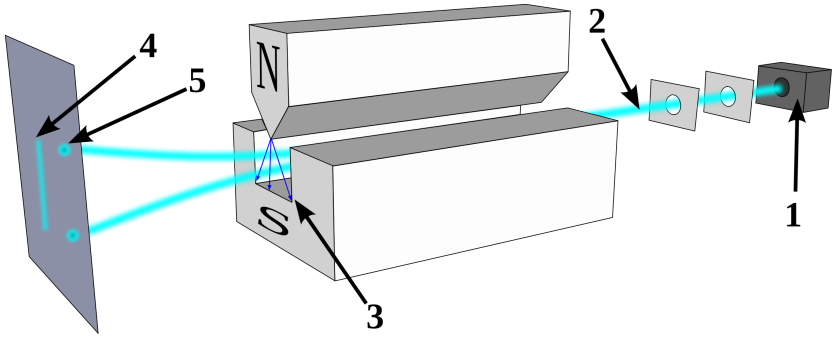

Figure 1.1: Stern–Gerlach experiment: Silver atoms travelling through an inhomogeneous magnetic field, and being deflected up or down depending on their spin; (1) furnace, (2) beam of silver atoms, (3) inhomogeneous magnetic field, (4) classically expected result, (5) observed result

moment along the axis of the device. This yields $\boldsymbol{\mu} = \pm\mu_0 \cos\theta$. In particular, if we rotate the device by $\pi/2$, we expect to get no splitting at all. This corresponds to the rather obvious statement that a classical vector pointing in some direction has zero projection in a perpendicular direction.

The main surprise here is that this very reasonable expectation is false. No matter how we rotate the Stern-Gerlach device, we always find the beam split into two corresponding to magnetic moment $\pm\mu_0$ in the direction of the splitting. To make the discussion more quantitative, I will introduce the notation SG$\hat{n}$ to denote a Stern-Gerlach device which splits the beam according to the magnetic moment in the $\hat{n}$ direction. For example, the device that splits the beam in the z direction is denoted SGz. We also introduce the notation SG$\hat{n}\pm$ to denote an SG$\hat{n}$ device followed by a filter that only lets the $\pm$ beam through. Let us now consider the following cascaded SG setup where we first let the beam pass through SGz+ then let the output beam of that device go through SG$\hat{n}_\theta^{xz}$ where n_θ is the unit vector in the xz-plane rotated by an angle θ relative to the z-axis. If $\theta = 0$, this is basically placing an SGz after an SG$z+$ and since we have filtered out the $-z$ component, we get only one beam corresponding to $\mu_z = +\mu_0$ (see top panel of Fig. 1.2). Once we start rotating the second SG so that $\theta \neq 0$, we immediately find that the beam is split in two corresponding to magnetic moments $\mu_{\hat{n}} = \pm\mu_0$. However, we should still expect the information about the rotation angle to be encoded somehow in the result of the experiment (otherwise, the limit $\theta \to 0$ will be discontinuous). The only other experimental variable where this info can be encoded is the intensity of the two beams. Assuming the original beam had an intensity I_0, the $\pm$ beams will have intensities $I_\pm(\theta)$ which satisfy

$$I_+(\theta) + I_-(\theta) = I_0 \tag{1.3}$$

For $\theta = 0$, we should have $I_+(0) = I_0$ and $I_-(0) = 0$. We also note that rotating the SG device by π leaves it unchanged which means that $I_\pm(\theta + \pi) = I_\mp(\theta)$. The simplest positive functions satisfying these properties are $I_+ = \cos^2(\theta/2)$ and $I_- = \sin^2(\theta/2)$ which turns out to be the right answer. This particularly means that for a device rotated by $\theta = \pi/2$, i.e. a device which splits the beam along the x-axis, we get two beams of equal intensity equal to half the original beam intensity. Thus, the beam whose magnetic moment is aligned in the $+z$ direction can be decomposed into an equal mix of beams whose magnetic moments are

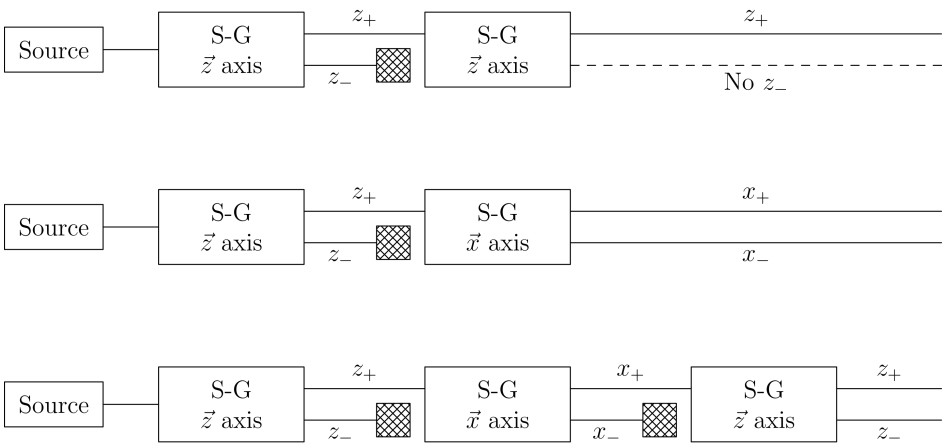

Figure 1.2: Different configurations for cascaded Stern-Gerlach device.

along $\pm x$ direction. By now, it is clear that this behavior is incompatible with any classical vector aligned with the z axis.

Let us consider one final setup where where we have a succession of SG$z+$ and SG$+x$ devices followed by SGz (bottom panel of Fig. 1.2). Here, we find that we get an equal amount of $\mu_z = \pm\mu_0$. Thus, although the original beam had only $+z$ component, after passing through SG$x+$, the electrons forgot they were polarized in the $+z$ direction and they again split into two beams.

Although this is a very counter-intuitive result, it has classical analogs which are realized when we have a device that decomposes a vector into parallel and perpendicular components and filters out one of them. One very cool example is how sail boats manage to sail perpendicular to or even into the wind although they only use the force generated by the wind to move. The main part of a sailboat is the sail. If the sail is parallel to the wind, it feels no force. This means that for a general angle between the sail and the wind, the sail decomposes the wind into a parallel and perpendicular components and only picks out the perpendicular one. The next important part in a sailboat is something called the keel. It's the bottommost longitudinal part that prevents the boat from moving sideways. This part picks out the component of the force that is parallel to the body of the boat. If the sail is at an angle of 45^o relative to the wind direction and the keel is an angle 45^o relative to the sail, we can successfully convert the wind force from pointing along the y-direction to the x-direction as shown in Fig. 1.3c. By using different angles, we can even manage to have a force component against the wind direction as shown in Fig. 1.3d. As an exercise, try to identify the ingredients of the Stern-Gerlach setup in the sailing example above.

The sailing example above hints towards the mathematical structure needed to describe the Stern-Gerlach experiment. An SG device defines a coordinate system in some abstract space of possible quantum states with two basis vectors. The SG device decomposes any given entering beam into a parallel and a perpendicular component, which can be identified by the $\pm$ values of the magnetic moment. An SG$\hat{n}\pm$ device acts by projecting out one component, i.e. projecting the input on the direction on one of the two basis vectors. Finally, rotating the SG apparatus amounts to rotating coordinate frame or basis vectors. However, there is an important subtlety. If we identify the $\pm z$ magnetic moments with the x and y directions in some abstract space, we see that the angle in this abstract space between two vectors is *half* the physical angle between the directions of the magnetic moment. As a consequence, physically rotating the SG device by an angle θ corresponds to a rotation by $\theta/2$ in the abstract space describing the state. With all these observations, we can write out some expressions to capture what we discussed. We denote the "quantum state" of a beam that gets deflected in the $\pm$ direction by an SG$\hat{n}$ device by $|\pm, \hat{n}\rangle$, where the notion of quantum state will be defined precisely later. The results of the SG experiment can be summarized by the relation

$$\begin{aligned} |+, \hat{n}_\theta^{xz}\rangle &= \cos(\theta/2)|+, z\rangle + \sin(\theta/2)|-, z\rangle \\ |-, \hat{n}_\theta^{xz}\rangle &= -\sin(\theta/2)|+, z\rangle + \cos(\theta/2)|-, z\rangle \end{aligned} \tag{1.4}$$

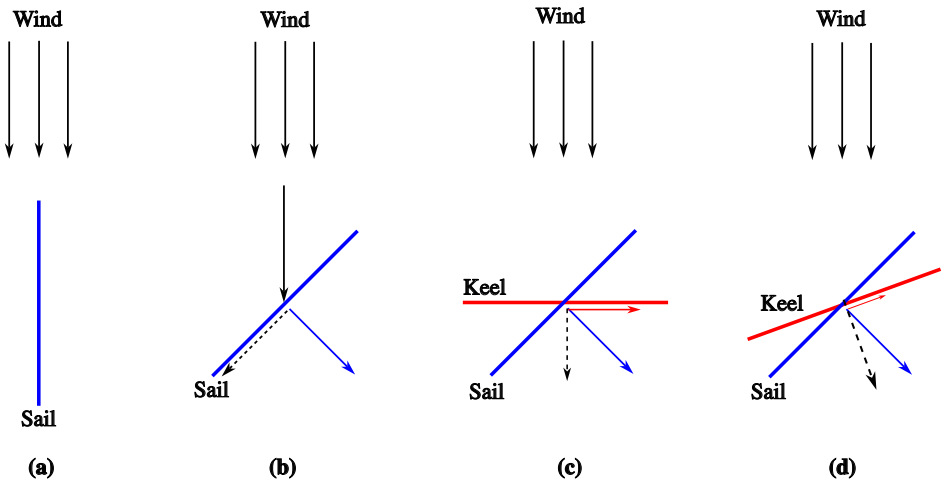

Figure 1.3: Illustration of how a sailboat transforms wind force: (a) when the sail is parallel to the wind, it feels no force. (b) when the sail is at an angle (45^o here), it feels only the component of the force perpendicular to the sail. (c) A horizontal keel ensures the boat only picks up the x-component of force (the one parallel to the boat). (d) a different angle for the keel allowing the boat to sail against the wind.

Furthermore, we can see that the intensities $I_{\pm}(\theta)$ can be identified with the coefficients of these expansions. For example, the intensity of the $+$ beam coming out of a cascade of of an SGx whose input is polarized in the $+z$ direction is given by the square of the $|+,x\rangle$ coefficient of the expansion of the $|+,z\rangle$ in terms of the basis vectors $|\pm,x\rangle$.

While the theory we have right now seems to capture all aspects of the SG experiment, there is one crucial missing ingredient: how can we describe rotations in the third (y) direction? We can surely rotate our SG apparatus also in the yz plane and we expect the same results as we got for xz. However, using the same basis decomposition for yz as for xz (Eqs. 1.4) will mean that $|+,x\rangle$ and $|+,y\rangle$ are identical. However, clearly having a cascade of SGx and SGy will yield identical behavior to that of SGz and SGx we considered before.

To identify this last remaining ingredient, we invoke another classical analog. This is again something that our late 19th century physicist will be familiar with. From a classical perspective, light is an electromagnetic wave consisting of oscillating electric and magnetic fields (we are not discussing photons at all here). An electromagnetic wave is characterized by a quantity called polarization specifying the direction of the electric field vector. If that direction is a constant, we say the light is linear polarized. For example, a linear polarized light in the x-direction, propagating along the z-axis is described by the electric field

$$\boldsymbol{E} = E_0\hat{x}\cos(kz - \omega t) \tag{1.5}$$

A device called polarizer can select a specific direction of linear polarization. Its simplest implementation is a series of parallel metallic rods which absorbs the electric field parallel to the rods but lets the field perpendicular to the rods through. For example, for the x-polarized light above, a polarizer in the y-direction lets it pass through whereas a polarizer in the x-direction completely blocks it. Thus, a general linear polarizer picks up the component of $\boldsymbol{E}$ perpendicular to the direction of the polarizer. It is easy to see that the linear polarizer works exactly as an SG device followed by a filter which selects one of the two beams. In fact, we can realize the same results we got from the cascade of SGs with a cascade of linear polarizers. For example, an x-polarizer followed by a y-polarizer will let no light through. This acts the same way as cascaded SG setup consisting of SG$z+$ followed by SG$z-$ which also has no output. The setup discussed in the bottom panel of Fig. 1.2 where an SG$x+$ is placed between SG$z+$ and SG$z-$ is the same as placing a linear polarizer at an angle of 45^o between the x and y polarizers.

So far, the polarization example has reproduced what we understood about the SG setup. We have still not answered the question about including the third direction. To answer this, we recall that linear polar-

ization is not the only possibility for an electromagnetic wave. There is also circular polarization and more generally elliptic polarization. These more general patterns of polarization arise if the two perpendicular components of an electromagnetic wave have a phase shift

$$\boldsymbol{E} = E_x\hat{x}\cos(kz - \omega t) + E_y\hat{y}\cos(kz - \omega t + \phi) \tag{1.6}$$

In general, this field will trace an ellipse in the x-y plane as the light propagatres that reduces to a line if $\phi = 0$ and to a circle if $\phi = \pm\pi/2$ (the two signs correspond to right and left circular polarization). Any EM wave can be decomposed into a circularly polarized wave and a linearly polarized wave which in turn can be decomposed into x and y components. Thus, the phase shift allows us to describe one more degree of freedom. Introducing a vector notation for the x and y components, we can write any EM wave as

$$\boldsymbol{E} = \mathrm{Re}\{e^{i(kz-\omega t)}\boldsymbol{P}\}, \qquad \boldsymbol{P} = \begin{pmatrix} E_x \\ E_y e^{i\phi} \end{pmatrix} \tag{1.7}$$

This means that by allowing the polarization vector to be *complex*, we can describe an arbitrary polarization state with the special cases of x and y-linearly polarized light given respectively by $\boldsymbol{P}_x = (1,0)^T$ and $\boldsymbol{P}_y = (0,1)^T$ wheres circularly polarized light given by $\boldsymbol{P}_{\mathrm{circ}} = (1,\pm i)^T$ (Here, T denotes vector transposition that maps a row vector to a column vector). This provides us with the missing ingredient to understand the SG experiment if we identify the rotation into the y-direction by a relative phase shift between the two basis vectors and think of our abstract space as a complex rather than real vector space.

To do this explicitly, we can simply write

$$|+,y\rangle = \frac{1}{\sqrt{2}}(|+,z\rangle + i|-,z\rangle) \tag{1.8}$$

$$|-,y\rangle = \frac{1}{\sqrt{2}}(|+,z\rangle - i|-,z\rangle) \tag{1.9}$$

If we identify the intensities by the square absolute value of these complex coefficients, we see that the results of a cascaded SG experiment where SG$z+$ is followed by SGx or by SGy is identical. On the other hand, if we have SG$x+$ followed by SGy, we see the beam splits as expected.

Thus, if the only experiment our 19-th century physicist physicist learned about is the Stern-Gerlach experiment, they will be lead to two main conclusions. First, the magnetic moment of a silver atom and, in general, a microscopic object cannot be described by a classical vector in 3D space. Instead, the different directions should correspond to basis vectors in an abstract finite dimensional *complex* vector space. In addition, we need a notion of length of the projection of a vector on another one to extract the measured intensities out of these abstract vectors i.e. we need a notion of an inner product. In the next lecture, we will see how we can build the quantum theory formalism from the example of the Stern-Gerlach experiment. This example makes it clear that the proper mathematical structure is that of a complex vector space with an inner product associated with it. Such a space is called a Hilbert space.

1.2 Quantum mechanics in finite-dimensional Hilbert spaces

In the last section, we discussed the Stern-Gerlach experiment which demonstrated the need to use a complex linear vector space to describe quantum state. This means that the main formalism needed to describe quantum mechanics is linear algebra. We will now discuss the correspondence between the main concepts we encounter in linear algebra and their physical interpretation in the quantum theory. We will use the bra-ket notation developed by Dirac which is particularly suited for calculations in the quantum theory.

In the SG experiment, we needed two basis vectors to described the outcome of any given experiment which means that the vector space was two-dimensional. In the following, we will focus on the case where the vector space is finite-dimensional which means that we need a finite number of basis vectors to describe any given state. The more subtle case of infinite dimensional space will be discussed next week.

1.2.1 Bras and Kets

The basic objects in a linear vector space are vectors. In the Dirac notation, vectors are called kets and denoted by $|u\rangle$. Quantum states correspond to *rays* in the vector space which means that the two kets $|u\rangle$ and $\alpha|u\rangle$, with α being a non-zero complex number $\alpha! = 0$, describe the same physical state. This means that the Hilbert space description of quantum mechanics has a redundancy i.e. a given ket defines a unique state but a given state can be described by several kets. Such situations are quite common in physics with the most prominent example being electromagnetism where the gauge potential (consisting of the scalar and vector potentials) uniquely determines the physical electric field and the magnetic flux through any region, but a physical electric and magnetic field configuration corresponds to many gauge potentials. This is called a gauge ambiguity and it leads to some subtle effects that we will discuss later. For $\alpha = 0$, $\alpha|v\rangle$ for any v is called the null-vector. We can form linear superposition of states as $\alpha|u\rangle + \beta|v\rangle$ where α and β are complex scalars. An example from the SG setup was how we wrote the beam polarized in the $+x$ direction as a superposition of the $+z$ and $-z$ beams: $|+x\rangle = \frac{1}{\sqrt{2}}(|+z\rangle + |-z\rangle)$.

Vectors in a Hilbert space are equipped with an inner product. The inner product is the analog of the scalar product of two vectors which gives the components of a vector u in the direction of another vector v scaled by the length of v. The inner product satisfies the following properties

1. Positive definiteness: $\langle u|u\rangle > 0$ unless $|u\rangle$ is the null ket.
2. Linearity in the second argument: $\langle u|\alpha v_1 + \beta v_2\rangle = \alpha\langle u|v_1\rangle + \beta\langle u|v_2\rangle$
3. Conjugate symmetry $\langle u|v\rangle = \langle v|u\rangle^*$.

The first property is the obvious generalization of the fact that the length of a non-zero real vector is positive. The positive number $\|u\| = \sqrt{\langle u|u\rangle}$ is known as the norm of $|u\rangle$. For any ket $|u\rangle$, we can define a normalized ket $|\tilde{u}\rangle$:

$$|\tilde{u}\rangle = \frac{|u\rangle}{\|u\|} \tag{1.10}$$

Since the physical state does not change under multiplication by a scalar, we can always define our states to be normalized (notice that the phase ambiguity still remains). The second property has also an obvious analog for real vectors where the projection of a sum of vectors is the sum of projections and the projection of a scaled vector is the scaled projection. The last property is the analog of the fact that scalar product is symmetric. For complex inner products, we need conjugate symmetry instead to guarantees that the norm

$$\|u+v\|^2 = \langle u+v|u+v\rangle = \|u\|^2 + \|v\|^2 + \langle u|v\rangle + \langle v|u\rangle \tag{1.11}$$

is real. [2]. The conjugate symmetry also implies $\langle \alpha u_1 + \beta u_2|v\rangle = \alpha^*\langle u_1|v\rangle + \beta^*\langle u_2|v\rangle$.

A vector in an N-dimensional vector space can always be expanded in a set of basis which we denote by $|a\rangle$, $a = 1, \ldots, N$. For example, in the SG device, we can describe any beam as a linear superposition of $|+z\rangle$ and $|-z\rangle$. Tor a general ket $|u\rangle$, this means we can write

$$|u\rangle = \sum_a u_a|a\rangle \tag{1.12}$$

We can always choose these basis vectors to be orthonormal which means that

$$\langle a|a'\rangle = \begin{cases} 1 & a = a' \\ 0 & a \neq a' \end{cases} \tag{1.13}$$

If we now take the inner product of the vector $|u\rangle$ with the basis vectors $|a\rangle$, we find that the components of $|u\rangle$ in the $|a\rangle$ basis are $u_a = \langle a|u\rangle$.

[2] It suffices to assume $\mathrm{Re}\langle u|v\rangle = \mathrm{Re}\langle v|u\rangle$ which together with positive definiteness implies $\langle u|v\rangle = \langle v|u\rangle^*$ due to Eq. 1.11

It is very useful to think about the left part of the inner product $\langle v|u\rangle$ as an independent object called a bra $\langle v|$ that acts on the ket vector $|u\rangle$ to give us the inner product. In other words, the bra (dual vector) defines a linear map from the kets (vectors) to the complex numbers $f_v(|u\rangle) = \langle v|u\rangle$. To satisfy the property $\langle \alpha v|u\rangle = \alpha^*\langle v|u\rangle$, the bras satisfy $\langle \alpha v| = \alpha^*\langle v|$. If we use the basis expansion (1.12), we see that $f_v(|u\rangle) = \sum_a u_a f_v(|a\rangle) = \sum_a u_a\langle v|a\rangle = \sum_a u_a v_a^*$. This gives us the analog for the scalar product formula in terms of components for complex vectors and implies that the components of a bra in a given basis are given by the complex conjugate of the components of the corresponding ket.

1.2.2 Operators

An operator in a vector space maps vectors to vectors. In the bra-ket notation, operators act on a ket from the left $A|u\rangle$ and on a bra from the right $\langle u|A$ (always next to the vertical line). We will sometimes use the notation $|Au\rangle := A|u\rangle$. The bra dual to the ket $A|u\rangle$ is defined to be $\langle u|A^\dagger$ where $A^\dagger$ is called the adjoint of A. From the definition of a dual vector $f_{|Av\rangle}(|u\rangle) = \langle Av|u\rangle = \langle v|A^\dagger|u\rangle = \langle v|A^\dagger u\rangle$.

To preserve the linear structure of the vector space, we consider linear operators satisfying

$$A(\alpha|u\rangle + \beta|v\rangle) = \alpha A|u\rangle + \beta A|v\rangle \tag{1.14}$$

However, it turns out that in the quantum theory, since we do not care about the overall phase of the wave-function, we can also have *anti-linear* operators satisfying

$$A(\alpha|u\rangle + \beta|v\rangle) = \alpha^* A|u\rangle + \beta^* A|v\rangle \tag{1.15}$$

We will discuss such operators later in the course. For the time-being, we are going to restrict ourselves to linear operators.

You can think of the example of an SG device when thinking about quantum operators. For example, SG$z+$ can be represented by an operator that selects the $|+z\rangle$ component of an incoming beam. Using this example, we can deduce the properties of operators in quantum mechanics. For example, two SG devices are considered identical, if they give exactly the same output given the same input for any input. The corresponding statement is that two operators A and B are equal if $A|u\rangle = B|u\rangle$ for any $|u\rangle$. Next, consider what happens when we cascade SG devices. Let us take an input beam described by a ket $|u\rangle$ and have it go through a cascade of two SG devices described by operators B and A. The output of B is $B|u\rangle$ is the input of A. Thus, the final output is $AB|u\rangle$. This means that we can identify the operator AB as the operator representation of the cascaded device. Let us try to understand its properties. First, consider a cascade of three SG devices C, B, and A. We can first think of the output of the C device, being fed into the cascade of B and A, which is described by the operator AB, or we can first combine C and B, described by BC, then consider this as an input to A. Since these are two descriptions for the same physical setup, the operator multiplication has to be associative

$$(AB)C = A(BC) \tag{1.16}$$

Finally, let us consider the setup from last lecture where we had SG$z+$ (let's call it C), followed by SG$x+$ (let's call it B), followed by SG$z-$ (let's call it A). We found that this configuration generally has a non-zero output since the $+x$ beams coming from the middle SG has forgotten it was originally in the $|+z\rangle$ state. On the other hand, if we do the cascade SG$z+$, SG$z-$, SG$x+$ (described by the operator BAC), we find that the output is zero. From this we conclude that $ABC \neq BAC$ which implies that, in general, for any two operators

$$AB \neq BA \tag{1.17}$$

This property is responsible for many of the counter-intuitive aspects of quantum mechanics.

The power of the bra-ket notation comes from the fact that we can always place a bra to the left of a ket to obtain a meaningful object. For example, we said that we can understand the bra $\langle u|$ as a linear map that acts on a ket $|v\rangle$ to give the complex number $\langle u|v\rangle$. Using the same reasoning, we can define the object

$|u\rangle\langle v|$ which acts on a ket $|w\rangle$ to give us $|u\rangle\langle v|w\rangle$. Since $\langle v|w\rangle$ is a complex number, the whole object $|u\rangle\langle v|w\rangle$ is a ket. Thus $|u\rangle\langle v|$ acts as an operator. It is easy to see from the linearity of the inner product that this will be a linear operator.

Let us now define the identity operator $\mathbb{1}$ as the operator that leaves every vector invariant: $\mathbb{1}|u\rangle = |u\rangle$ for any $|u\rangle$. Given an arbitrary ket $|u\rangle$, we can write the basis expansion (1.12) with $u_a = \langle a|u\rangle$. This means that

$$|u\rangle = \sum_a |a\rangle\langle a|u\rangle = \left(\sum_a |a\rangle\langle a|\right)|u\rangle \tag{1.18}$$

Since this identity holds for every $|u\rangle$, it implies

$$\sum_a |a\rangle\langle a| = \mathbb{1} \tag{1.19}$$

This relation is called resolution of unity and it is one of the most important relations in quantum mechanics. It tells us that if we take the projection on a vector relative to each basis vector, multiply it by that basis vector, then add all these components, we can reconstruct the full vector.

To demonstrate the usefulness of this identity, let us consider an operator A. Since the identity operator does nothing, we can insert it anywhere in an expression

$$A = \mathbb{1}A\mathbb{1} = \left(\sum_a |a\rangle\langle a|\right) A \left(\sum_b |b\rangle\langle b|\right) = \sum_{a,b} |a\rangle\langle a|A|b\rangle\langle b| = \sum_{a,b} A_{ab}|a\rangle\langle b| \tag{1.20}$$

where $A_{ab} = \langle a|A|b\rangle$ are the matrix elements of the operator A which specify the decomposition of $A|a\rangle$ in the $|a\rangle$ basis

$$A|a\rangle = \sum_b A_{ba}|b\rangle \tag{1.21}$$

For an N-dimensional space, A_{ab} describes an $N \times N$ matrix. The operator product AB can be written as

$$AB = \sum_{a,b,c} |a\rangle\langle a|A|b\rangle\langle b|B|c\rangle\langle c| = \sum_{a,c} |a\rangle\langle c| \sum_b A_{ab}B_{bc} = \sum_{a,c} (AB)_{ac}|a\rangle\langle c| \tag{1.22}$$

We see that the matrix elements of the operator AB are given by the matrix product of the matrix elements of the operators A and B. This means that, for the case of finite-dimensional Hilbert spaces, we can always think of the operators as matrices. However, it is important to distinguish the abstract operator A which describes a physical device or observable from its matrix elements A_{ab} which require us to specify a basis and is thus basis-dependent.

The identification of operators in the quantum theory with matrices (for finite-dimensional Hilbert space) allows us to deduce a lot of their properties from what we know about matrices. For instance, we can define eigenkets of an operator as $A|u\rangle = \lambda|u\rangle$ where λ is a complex number called the eigenvalue. We also see that we can identify the matrix elements of the hermitian adjoint of an operator $A^\dagger$ with the hermitian matrix adjoint obtained by transposing and complex conjugating the matrix elements $(A^\dagger)_{ab} = A^*_{ba}$.

There are three classes of operators that play a special role in quantum mechanics

1. Hermitian operators ($A = A^\dagger$): these operators have the very important property that their eigenvalues are real. To see this consider an eigenket $|u\rangle$ with eigenvalue λ:

   $$A|u\rangle = \lambda|u\rangle \tag{1.23}$$

   Taking the dual of both sides, we get

   $$\langle u|A^\dagger = \lambda^*\langle u| \tag{1.24}$$

   If we now take the inner product of (1.23) with $\langle u|$ and of (1.24) with $|u\rangle$, we get

   $$\lambda\langle u|u\rangle = \langle u|A|u\rangle = \langle u|A^\dagger|u\rangle = \lambda^*\langle u|u\rangle \tag{1.25}$$

which implies $\lambda = \lambda^*$. Another important property of Hermitian operators is that their eigenkets provide a complete basis of the vector space that can be chosen to be orthonormal. This implies that an operator is diagonal when expressed in its own eigenbasis. If we denote the eigenkets and eigenvalues of an operator A by $|a\rangle$ and λ_a [3]

$$A = \sum_a \lambda_a |a\rangle\langle a| \tag{1.26}$$

Notice the absence of off-diagonal terms $|a\rangle\langle b|$ with $a \neq b$.

2. Unitary operators ($UU^\dagger = U^\dagger U = \mathbb{1}$): Unitary operators correspond to norm-preserving maps since the norm of $|v\rangle = U|u\rangle$ is $\|v\| = \sqrt{\langle v|v\rangle} = \sqrt{\langle u|U^\dagger U|u\rangle} = \sqrt{\langle v|v\rangle} = \|u\|$. Thus, they map normalized kets to normalized kets. They usually describe basis transformations in the quantum theory.

3. Projection operators ($P^2 = P = P^\dagger$): these are Hermitian operators which square to themselves. For example, the SG device which filters one polariztion, e.g. SG$z+$, is described by a projector since passing its output by an identical device SG$z+$ does not change the result. Recall that cascading SG devices corresponds to operator multiplication, we see that i.e. $P^2 = P$.

1.2.3 Observables

In the quantum theory, physical observables are represented by hermitian operators and the possible values of a given observable correspond to the eigenvalues of this operator. Since the eigenvalues of a Hermitian operator are real, this guarantees that the allowed values of a physical observable are real. Since the eigenkets of a hermitian operator provide a complete basis, we can expand any ket in terms of the eigenbasis of a given hermitian operator.

Let us take our SGz device as an example. This device measures the magnetic moment in the z direction. It has two possible outcomes $\mu_z = \pm\mu_0$. As an aside, we have so far been discussing the magnetic moment without specifying its value μ_0. To understand this value, we invoke a classical analogy where we consider a charged spinning classical particle. For such a particle, the magnetic moment is proportional to the spin angular momentum $\boldsymbol{S}$, $\boldsymbol{\mu} = \gamma \boldsymbol{S}$, where the proportionality constant is called gyromagnetic ratio. If we assign a value for the spin angular momentum corresponding to the measured magnetic moment in the SG device, we find it corresponds to $S_z = \pm\hbar/2$ where $\hbar$ is the Planck's constant. From now onwards, we will refer to the different results of the SG device in terms of the values of spin rather than magnetic moment. This means that this device should be described by a Hermitian operator, which we call S_z acting on a two dimensional Hilbert space whose eigenkets are $|\pm z\rangle$ with corresponding eigenvalues $\pm\hbar/2$. Using Eq. 1.26, we can write

$$S_z = \frac{\hbar}{2}(|+z\rangle\langle +z| - |-z\rangle\langle -z|) \tag{1.27}$$

If we use a vector notation where

$$|+z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |-z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{1.28}$$

we see that S_z is the diagonal matrix

$$S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{1.29}$$

The operators describing S_x has the same form in the $|\pm x\rangle$ basis

$$S_x = \frac{\hbar}{2}(|+x\rangle\langle +x| - |-x\rangle\langle -x|) \tag{1.30}$$

[3] Here, we are assuming all eigenvalues are distinct

To write the same operator in the $|\pm z\rangle$ basis, we use

$$|\pm x\rangle = \frac{1}{\sqrt{2}}(|+z\rangle \pm |-z\rangle) \tag{1.31}$$

Substituting in (1.30), we find

$$S_x = \frac{\hbar}{2}(|+z\rangle\langle -z| + |-z\rangle\langle +z|) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{1.32}$$

Performing a similar calculation for S_y, we find

$$S_y = \frac{i\hbar}{2}(-|+z\rangle\langle -z| + |-z\rangle\langle +z|) = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{1.33}$$

Thus, the three components have the matrix representation $S_i = \frac{\hbar}{2}\sigma_i$ where σ_i are called the Pauli matrices and play a central role in the theory of spin.

1.3 Measurement in quantum mechanics

In the previous section, we have started building a dictionary between the abstract formalism of Hilbert spaces and the different physical objects in the quantum theory. We have identified the state of a quantum system with rays in the Hilbert space. We have also identified physical observables with hermitian operators. The real eigenvalues of a Hermitian operators correspond to the possible measurement outcomes. For example, $S_x = \pm\hbar/2$ in the Stern-Gerlach experiment. The eigenkets of the Hermitian operator correspond to the possible states associated with the different measurement outcomes. The fact that the eigenkets of a Hermitian operator form a complete basis is necessary for this interpretation.

However, we have not answered the very important question: what determines which measurement outcome is realized in a given experiment? Let us for concreteness consider again a cascaded Stern-Gerlach setup of SG$z+$, which yields a beam polarized in the $+z$ direction, followed by SGx. As we discussed in Lecture 1, the intensity of the beam is split equally between the two possible outcomes representing $+x$ and $-x$ polarization. Now we ask the question: what would happen if the input $+z$ polarized beam has only one atom? Since quantum mechanics is a fundamental theory of microscopic objects (rather than an emergent theory where concepts only make sense at a certain scale), we should be able to write a ket to describe the state of a single atom. However, a single atom cannot split into two with $\pm x$ polarization. Instead, the atom 'picks' one of the two outcomes with equal probability of 0.5 each. This means that are two very unusual aspects of the quantum theory. First, although the input state was a definite state without built-in uncertainty, the output of the experiment can only be determined probabilistically in the quantum theory. Second, the measurement device seems to play an active rule, forcing the atom that was living happily in a superposition of $|+x\rangle$ and $|-x\rangle$ to make up its mind and choose of of the two alternatives.

If we accept these two pecularities of the quantum world, we can incorporate them in the formalism by introducing the notion of a measurement. To every measurement device, we associate an observable which is a Hermitian operator and we define the measurement as a process which forces the input state into one of the eigenkets of the corresponding operator. The probability of obtaining a certain measurement outcome associated with the eigenvalue λ_a and an eigenket $|a\rangle$ starting from a general normalized ket $|u\rangle$ is given by $|\langle a|u\rangle|^2$. This is known as the Born rule. Let us first make sure that such rule makes sense i.e. the numbers $p_a(u) = |\langle a|u\rangle|^2$ can be interpreted as probabilities. For a set of numbers p_a to represent probabilities, they need to be non-negative and sum to 1. This can seen using the resolution of the unity

$$\langle u|u\rangle = 1 = \sum_a \langle u|a\rangle\langle a|u\rangle = \sum_a |\langle u|a\rangle|^2 = \sum_a p_a(u) \tag{1.34}$$

An important class of measurement is called selective measurements or filtrations. These are measurements which selects only one of the eigenkets of the measurement device. In the Stern-Gerlach setup, these

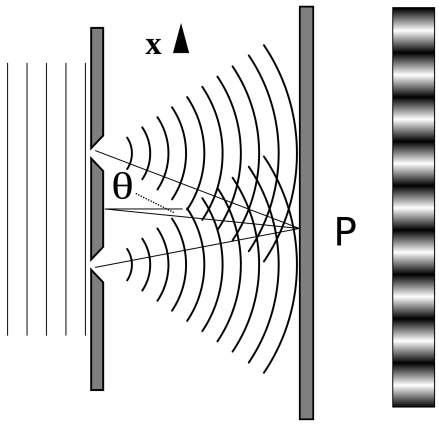

Figure 1.4: Schematic illustration of the double slit experiment

were the devices SG$\hat{n}\pm$ which only let one of the beams through. A selective measurement which selects the outcome a is described by the operator $\Lambda_a = |a\rangle\langle a|$. This operator satisfies the important property that it is equal to its square

$$\Lambda_a^2 = |a\rangle\langle a|a\rangle\langle a| = |a\rangle\langle a| = \Lambda_a \tag{1.35}$$

Physically, this reflects the fact that applying a filtration device Λ_a to the output of an identical filtration device Λ_a does nothing. Operators satisfying (1.35) are called projection operators [4].

Although the final measurement outcome is obtained through a probability distribution, there is a very important distinction between the quantum theory and standard probability theory. Let us illustrate this with an example. Imagine we have a cascade of three filteration devices (which we can think of as some SG devices with some relative angles), so that the first device $A = \Lambda_a$ selects some outcome $|a\rangle$, the second $B = \Lambda_b$ selects some outcome b and the third $C = \Lambda_c$ selects some outcome c. Assuming the beam coming out of a is normalized, the probability of getting an output in B (the intensity of the B beam) is $|\langle a|b\rangle|^2$. The probability of getting an output in C is $|\langle c|b\rangle|^2|\langle b|a\rangle|^2$ since probabilities are multiplicative. If we repeat the experiment each time filtering a different output of b, the total probability will be

$$\sum_b |\langle c|b\rangle|^2|\langle b|a\rangle|^2 = \sum_b \langle c|b\rangle\langle b|a\rangle\langle a|b\rangle\langle b|c\rangle \tag{1.36}$$

Remarkably, this turns out to be different from the probability we get if we remove the B device altogether which is given by

$$|\langle c|a\rangle|^2 = \Big|\sum_b \langle c|b\rangle\langle b|a\rangle\Big|^2 = \sum_{b,b'} \langle c|b\rangle\langle b|a\rangle\langle a|b'\rangle\langle b'|c\rangle \tag{1.37}$$

This means that although we have allowed for all possible intermediate values of B, the fact that we have measured it (and we can record it) makes this different from removing the B device altogether. The reason for the distinction is that in quantum mechanics, if we do not perform a measurement, the intermediate state is a ket that can be in a superposition. Another way to see this is that, unlike probability theory where we add the probabilities of mutually exclusive intermediate steps, in the quantum theory, we add the complex coefficients of basis expansion of a certain ket $\langle a|u\rangle$ whose absolute value squares is the probability (these complex coefficients are called probability amplitudes).

[4]Note that a projection operator is more general since any operator of the form $P = \sum_a |a\rangle\langle a|$ satisfying $P^2 = P$ where the sum goes over any subset of eigenstates

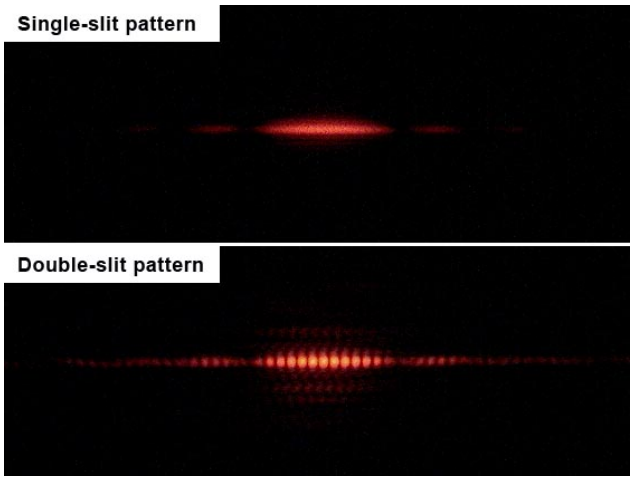

Figure 1.5: Comparison of the output of a single slit and double slit with the latter displaying clear interference pattern

1.3.1 The double-slit experiment

A very dramatic illustration of this effect is realized in the double-slit experiment, shown in Fig. 1.4. The double slit experiment is a very old experiment to illustrate the wave nature of light. Its setup involves letting a monochromatic light through a screen with two narrow slits in it. A screen is then placed behind the slits to observe the light. The main observation in this experiment is that the light exhibits an interference pattern of dark and light spots. This pattern is not a simple sum of the output of each individual slit (see Fig. 1.5). Instead it features interference where waves which are in phase add and those which are out of phase subtract. The phase difference arises because the light travels a different distance between the two slits to the screen.

When performing the double slit experiment with electrons instead of light, the same interference pattern is observed. Although the electrons are registered on the screen as individual spots, their distribution follows the same interference pattern as the light waves. The interference pattern is compatible with the rules we have discussed where the probability amplitudes for the two paths are first added, then we take the absolute value squared of the result, leading to an interference pattern. The setup we discussed with the filtration device would correspond to blocking one of the slits and then the others and adding the outputs. Clearly, the resulting output will not show any interference pattern. In fact, even if we let both slits open, but we have some way to measure which slit the electron goes through, for example by shining light on the slits, this will disturb the electrons enough to destroy the interference pattern. This illustrates a fundamental aspects of quantum mechanics where the measurement is not a passive operation *even if we allow for all intermediate measurement outcomes*.

1.3.2 Expectation value and variance

The born rule means that a given state, $|u\rangle$ defines a probability distribution over the space of possible measurement outcomes with the probability $p_a(u) = |\langle a|u\rangle|^2$ associated with the measurement outcome λ_a. Two important quantities for any probability distribution are the mean or expectation value and the variance. The expectation value of an operator A is defined as $\langle u|A|u\rangle$. It can be written in the familiar form of the mean value for a probability distribution using the resolution of unity:

$$\langle u|A|u\rangle = \sum_{a,b}\langle u|a\rangle\langle a|A|b\rangle\langle b|u\rangle = \sum_a \lambda_a|\langle u|a\rangle|^2 = \sum_a \lambda_a p_a(u) \tag{1.38}$$

It is important to note that although the allowed values of an observable are discrete, e.g. $S_z = \pm\hbar/2$, the expectation value $\langle S_z\rangle$ can take any value between $-\hbar/2$ and $+\hbar/2$. This is similar to saying that the

average number of students per class at Harvard is let's say 12.3 although the allowed numbers can only be positive integers. Another important quantity for a given probability distribution is the variance

$$\langle(\Delta A)^2\rangle = \langle(A - \langle A\rangle)^2\rangle = \langle A^2\rangle - \langle A\rangle^2 = \sum_a (\lambda_a - \langle A\rangle)^2 p_a(u) \tag{1.39}$$

Clearly, the variance is a non-negative real number $\langle(\Delta A)^2\rangle \geq 0$. The variance of an operator A in a state $|u\rangle$ is zero if and only if $|u\rangle$ is an eigenket of A. To see this, note that the last expression in (1.39) is a sum of non-negative numbers so for the sum to vanish, each term has to vanish which implies $\lambda_a = \langle A\rangle$ or $p_a(u) = 0$ for each a. To satisfy normalization, at least one p_a has to be non-zero. If the eigenvalues λ_a are all distinct, then there can only be one $\lambda_a = \langle A\rangle$. Thus, $p_a(u) = \delta_{a,b}$ for some b i.e. $|u\rangle$ is an eigenket of A. Even if the eigenvalues of A has some degeneracy, we can still deduce from the above argument that all non-zero values for p_a correspond to the same eigenvalue $\lambda_a = \langle A\rangle$ which means that $|u\rangle$ is in one of the eigenspaces of A.

1.3.3 Compatible and incompatible observables

As we have seen in the Stern-Gerlach device, there is a big distinction between cascading devices which have the same set of eigenkets, for example SGz, SG$z+$ and SG$z-$, and cascaded devices with different eigenkets e.g. SGz and SGx. This distinction is formalized through the notion of compatible and incompatible observables. Compatible observables are described by operators A and B which commute with each other

$$[A, B] = AB - BA = 0 \tag{1.40}$$

As a result, they have a common set of eigenkets (but not eigenvalues). In linear algebra, this corresponds to the statement that commuting matrices can be diagonalized simultaneously. Let us see how this is realized in the language of the quantum theory. Let us first consider the non-degenerate case where all the eigenvalues of A are distinct. Then we can write

$$0 = \langle a|[A, B]|b\rangle = \langle a|AB|b\rangle - \langle a|BA|b\rangle = (\lambda_a - \lambda_b)\langle a|B|b\rangle \tag{1.41}$$

For $a \neq b$, this implies $\langle a|B|b\rangle = 0$. This means that the off-diagonal matrix elements of B vanish in the eigenket basis of A. In other words, B is diagonal in that basis and has the same eigenkets.

Let us now consider the case where the eigenvalues are degenerate. For example, there are two linearly independent eigenkets $|a, 1\rangle$ and $|a, 2\rangle$ with the same eigenvalues λ_a. Clearly, any linear combination of these two kets is also an eigenket. This means that the eigenkets corresponding to λ_a form a two dimensional subspace. Eq. 1.41 implies that the matrix elements connecting any state in this space with a state with different eigenvalues λ_b vanish but it does not restrict the form of B in this subspace which will be some 2×2 Hermitian matrix. We can diagonalize this 2×2 Hermitian matrix and label the common eigenstates of A and B in this subspace by $|a, b\rangle$. This example reveals the general matrix structure of commuting operators. In the A eigenbasis, B decomposes into a Block-diagonal form with each Block corresponding to a degenerate subspace of A eigenkets with the same eigenvalue. We can choose special linear combinations of these eigenkets to be eigenkets of B. If some degeneracies are still let, we can have a third commuting operator C and repeat the procedure.

Operators which do not satisfy (1.40) are called incompatible. Incompatible observables do not have a complete set of common eigenkets since if $A|a, b\rangle = \lambda_a|a, b\rangle$ and $B|a, b\rangle = \lambda_b|a, b\rangle$ for all $|a, b\rangle$ then

$$AB|a, b\rangle = \lambda_b A|a, b\rangle = \lambda_a \lambda b|a, b\rangle = B(\lambda_a|a, b\rangle) = BA|a, b\rangle \tag{1.42}$$

which implies $AB = BA$. Is there a way to quantify how incompatible two observables are? clearly, some pairs of observables can be almost compatible, in the sense that they deviate from the relation (1.40) by a small amount (think of an SGz device followed by one rotated by a small angle θ relative to the z axis) while some can be maximally incompatible.

Operator incompatibility has important physical consequences. It is the reason why a beam polarized in $|+z\rangle$ retains this information when it goes through the device SGz but completely forgets it when it goes through SGx. This can be quantified through uncertainty relations which places constraints on the variance of different observables in the same state. Recall, the variance of an operator in a given state measures how close this state is to being an eigenstate of this operator. For incompatible observables, reducing the variance of one observables would increase the variance of the other due to the absence of a common eigenstate. To derive the uncertainty principle, we use the Cauchy-Schwarz inequality

$$|\langle u|v\rangle|^2 \leq \|u\|^2\|v\|^2 \tag{1.43}$$

The intuitive meaning of the Cauchy-Schwarz inequality is that the projection of a vector onto another cannot be longer than the vector itself. We now take $|u\rangle = \Delta A|w\rangle$ and $|v\rangle = \Delta B|w\rangle$ leading to

$$\|u\|^2\|v\|^2 = \langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq |\langle\Delta A\Delta B\rangle|^2 \tag{1.44}$$

We now use the relation $AB = \frac{1}{2}([A,B] + \{A,B\})$ where $\{A,B\}$ is the anticommutator defined as $\{A,B\} = AB + BA$. Due to the relation $(AB)^\dagger = B^\dagger A^\dagger$, the commutator of two hermitian operators is anti-hermitian $[A,B]^\dagger = -[A^\dagger, B^\dagger] = -[A,B]$ whereas the anticommutator is hermitian $\{A,B\}^\dagger = \{A^\dagger, B^\dagger\} = \{A,B\}$. Since the expectation value of a hermitian operator is real and that of an anti-hermitian operator is imaginary, we have

$$|\langle\Delta A\Delta B\rangle|^2 = \frac{1}{4}|\langle[\Delta A, \Delta B]\rangle|^2 + \frac{1}{4}|\langle\{\Delta A, \Delta B\}\rangle|^2 \tag{1.45}$$

This implies

$$\langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq |\langle[\Delta A, \Delta B]\rangle|^2 = |\langle[A,B]\rangle|^2 \tag{1.46}$$

In the last inequality we used the fact that the commutator of a constant with any operator vanishes. This means we can drop out the constant $\langle A\rangle$ in ΔA. Eq. 1.46 is the uncertainty relation between general observables A and B. When taking A and B to represent position and momentum, this reduces to the famous Heisenberg uncertainty which will be discussed in the next lectures.

1.3.4 Basis transformations

So far we have been discussing hermitian operators which correspond to physical observables in the quantum theory. There is another class of important operators of the quantum theory; those corresponding to basis transformations. These can be understood as analogs of rotating the $x-y$ coordinates by some angle in a real vector space. Equivalently, we can also think of active transformations where we rotate all vectors while keeping the $x-y$ axes fixed. In both cases, such transformation keeps the lengths of vectors as well as the angles between them fixed. This means that the transformation $|u\rangle \mapsto U|u\rangle$ satisfies $\langle u|U^\dagger U|v\rangle = \langle u|v\rangle$ for every u and v. This is only possible if $U^\dagger U$ is the identity operator:

$$U^\dagger U = \mathbb{1} \tag{1.47}$$

which means that U is unitary. Any pair of orthonormal complete bases are related by a unitary transformation. To see this, let us call the two bases vectors $|a_l\rangle$ and $|b_l\rangle$ where $l = 1, \ldots, N$ (note that here a and b do not label eigenvalues). Then the matrix $U = \sum_l |b_l\rangle\langle a_l|$ provides a basis transformation since $U|a_l\rangle = |b_l\rangle$ and $U^\dagger U = \sum_{l,m} |a_l\rangle\langle b_l|b_m\rangle\langle a_m| = \sum_l |a_l\rangle\langle a_l| = \mathbb{1}$. Two operators related via $B = UAU^\dagger$ are called unitary equivalent. Unitary equivalent operators have the same eigenvalues since for

$$A|u_a\rangle = \lambda_a|u_a\rangle \tag{1.48}$$

we can construct $|\tilde{u}_a\rangle = U|u_a\rangle$ with

$$B|\tilde{u}_a\rangle = UAU^\dagger U|u_a\rangle = UA|u_a\rangle = \lambda_a U|u_a\rangle = \lambda_a|\tilde{u}_a\rangle \tag{1.49}$$

Useful unitary invariants are the determinant and the trace of the operator which are expressed purely in terms of eigenvalues. For the trace, this follows from the cyclic property $\mathrm{tr}XY = \mathrm{tr}YX$ which implies $\mathrm{tr}U^\dagger AU = \mathrm{tr}A$. A hermitian matrix can always be diagonalized through a unitary basis transformation.

1.4 Quantum mechanics in infinite-dimensional Hilbert spaces

So far, we have restricted our attention to the quantum mechanics in finite-dimensional Hilbert spaces. We now consider the case of infinite-dimensional Hilbert spaces. On going from finite dimensional to (uncountably) infinite-dimensional spaces, we are immediately confronted by questions of continuity and convergence of integrals that we didn't have to deal with in the finite-dimensional case. These would require rigorous mathematical treatments that are beyond the scope of our course. Here, we will instead consider the case of infinite-dimensional Hilbert spaces as a special limit for the finite-dimensional case and we will point out the main subtleties involved in taking this limit.

1.4.1 Position eigenbasis

The infinite-dimensional Hilbert space is best illustrated by considering a particle in one spatial dimension. Classically, the position of the particle is specified by a real number. We now want to construct a quantum mechanical description of the position of a particle. Recall in our previous lectures, we replaced a classical observable, the magnetic moment, which was described by a classical vector of fixed length by a vector in a Hilbert space whose basis span all possible values of this observable. Such basis corresponds to the eigenbasis of this observable. The analogy for the position is to consider an operator, which we denote by $\hat{x}$, whose eigenvalues are all possible positions of the particle and whose eigenkets correspond to the particle being localized at any of these positions. This is written as

$$\hat{x}|x_0\rangle = x_0|x_0\rangle \tag{1.50}$$

To make this more concrete, we consider a course graining of the system where the position can only be determined up to an error Δx. In other words, we think of a measurement device that measures the position of a particle but that can only detect it within a region of width Δx. We denote the state where an electron is in the interval $(x - \Delta x/2, x + \Delta x/2)$ by $|x; \Delta x\rangle$. If we also take the system size to be finite L, then everything reduces to the case of finite dimensional Hilbert space we considered earlier [5]. For a general state $|\psi\rangle$, we can write the expansion in the position basis as

$$|\psi\rangle = \sum_x |x; \Delta x\rangle\langle x; \Delta x|u\rangle \tag{1.51}$$

where $|\langle x; \Delta x|\psi\rangle|^2$ gives the probability of finding the particle in the interval $(x - \Delta x/2, x + \Delta x/2)$ and they satisfy the relation $\sum_x |\langle x; \Delta x|u\rangle|^2 = 1$ necessary for the probabilistic interpretation. Now for a generic state where the particle is not infinitely localized, as we make Δx smaller and smaller, we expect that $|\langle x; \Delta x|\psi\rangle|^2$ would also become smaller and go as $\sim \Delta x$. Thus, we can write $|\langle x; \Delta x|\psi\rangle|^2 = p_\psi(x)\Delta x$ where $p_\psi(x)$ defines a continuous probability distribution satisfying

$$\sum_x \Delta x\, p_\psi(x) \overset{\Delta x\to 0}{=} \int dx\, p_\psi(x) = 1 \tag{1.52}$$

Now if $|\psi\rangle$ describes a particle infinitely localized at $x = x_0$, then we have $|\langle x; \Delta x|u\rangle|^2 = \delta_{x,x_0}$ which implies that $p_u(x) = \frac{\delta_{x,x_0}}{\Delta x} \to \delta(x - x_0)$ where $\delta(x)$ is the Dirac Delta function defined by the conditions

$$\delta(x) = 0 \quad \text{for} \quad x \neq 0, \qquad \int dx\delta(x) = 1 \tag{1.53}$$

Note that this equation implies that $\delta(x)$ has dimension of inverse length.

[5] As we will see later, this is not something we can generally do, but it will be useful for the current purpose. We can always think that our analysis is restricted to wavefunctions which vanish outside a finite region such that $\langle x; \Delta x|\psi\rangle = 0$ for $x < 0$ or $x > L$. This will only be problematic when we consider the translation operator.

Let us now define the continuous position eigenbasis as

$$|x\rangle = \lim_{\Delta x \to 0} \frac{1}{\sqrt{\Delta x}} |x; \Delta x\rangle \tag{1.54}$$

We then can interpret $|\langle x|u\rangle|^2 = p_\psi(x)$ as a continuous probability distribution. Recall that in wave mechanics, the norm squred of the wavefunction $|\psi(x)|^2$ played the same role as $p_\psi(x)$. Thus, we can make the identification $\psi(x) = \langle x|\psi\rangle$. With this identification, we can use the same equations we used before for the finite-dimensional case provided that we replace every sum over a complete basis by an integral and every Kronecker delta function by a Dirac delta function. Thus, our recipe to move from the finite-dimensional case to the infinite dimensional one is

	Finite dimensional	Infinite dimensional
Orthonormality	$\langle \alpha \vert \alpha' \rangle = \delta_{\alpha,\alpha'}$	$\langle x \vert x' \rangle = \delta(x - x')$
Resolution of unity	$\sum_\alpha \vert\alpha\rangle\langle\alpha\vert = \mathbb{1}$	$\int dx \vert x\rangle\langle x\vert = \mathbb{1}$
Wavefunction normalization	$\sum_\alpha \vert\langle\psi\vert\alpha\rangle\vert^2 = 1$	$\int dx \vert\langle\psi\vert x\rangle\vert^2 = \int dx \vert\psi(x)\vert^2 = 1$

1.4.2 Translation operator and momentum

Given a position basis, one very important operator we can define in addition to the position operator is the translation operator. A translation operator T_a is defined as an operator which shifts a position eigenstate localized at $x = x_0$ to a position eigenstate localized at $x = x_0 + a$. This means that it satisfies

$$\hat{x}T_a - T_a\hat{x} = aT_a \tag{1.55}$$

To see this, we act on the position eigenstate $|x\rangle$

$$\hat{x}T_a|x\rangle = T_a\hat{x}|x\rangle + aT_a|x\rangle = (x + a)T_a|x\rangle \tag{1.56}$$

This means that $T_a|x\rangle$ is an eigenstate of $\hat{x}$ with eigenvalues $|x + a\rangle$ i.e. $T_a|x\rangle = |x + a\rangle$ up to a phase. We can take this phase to be zero by simply fixing some state $|0\rangle$ and defining $|x\rangle := T_x|0\rangle$ [6]. Thus, we can simply write

$$T_a|x\rangle = |x + a\rangle \tag{1.57}$$

We would now like to construct an explicit representation of the translation operator based on its properties. First, we see that T_a has to preserve the norm since $1 = \langle x + a|x + a\rangle = \langle x|T_a^\dagger T_a|x\rangle$ for every $|x\rangle$ and a which means that

$$T_a^\dagger T_a = \mathbb{1} \tag{1.58}$$

Second, translating by a then b is the same as translating by $a + b$:

$$T_aT_b = T_bT_a = T_{a+b} \tag{1.59}$$

Third, the translation by $a = 0$ is the identity $T_0 = \mathbb{1}$. This implies that we can reverse any translation $T_aT_{-a} = T_{a-a} = \mathbb{1}$ which implies

$$T_{-a} = T_a^{-1} = T_a^\dagger \tag{1.60}$$

These relations imply that translations form an Abelian group.

These properties have a particularly simple form for infinitesmal translations $a = dx$. Let us write the expansion

$$T_{dx} = \mathbb{1} - idx\,\hat{k} \tag{1.61}$$

[6] Recall that multiplication by a phase yields a different ket that describes the same physical state. This means that we can choose the ket which makes the representation of certain operators as easy as possible. This is usually referred to as a gauge choice.

where $\hat{k}$ is some operator which has dimension of inverse length whose properties we will derive below. This operator is called the infinitesmal generator of translation. To satisfy (1.60), we write

$$\mathbb{1} + idx\,\hat{k} = \mathbb{1} + idx\,\hat{k}^\dagger \tag{1.62}$$

which implies that $\hat{k}$ is hermitian. Using the commutation relation (1.55), we find

$$\hat{x}\hat{k} - \hat{k}\hat{x} = [\hat{x}, \hat{k}] = i \tag{1.63}$$

To interpret the operator $\hat{k}$, let us introduce wavevector eigenbasis $|k\rangle$ related to $|x\rangle$ via the Fourier transform

$$|x\rangle = \int \frac{dk}{2\pi} e^{-ikx}|k\rangle \tag{1.64}$$

Acting with T_a, we get

$$T_a|x\rangle = \int \frac{dk}{2\pi} e^{-ikx} T_a|k\rangle = |x+a\rangle = \int \frac{dk}{2\pi} e^{-ikx} e^{-ika}|k\rangle \tag{1.65}$$

From which we deduce

$$T_a|k\rangle = e^{-ika}|k\rangle \tag{1.66}$$

Thus, $|k\rangle$ are eigenvectors of the translation operator. Taking the infinitesmal limit, $a = \Delta x$, we find

$$\hat{k}|k\rangle = k|k\rangle \tag{1.67}$$

Thus, the operator $\hat{k}$ which is the generator of translation is the wavevector operator. To make the connection with momentum, we have to invoke another relation which relates the momentum of a quantum particle to the wavelength of the associated wave. This is called the De-Broglie wavelength and is given by $\lambda = h/p$. Writing this as a wavenumber $k = 2\pi/\lambda$, we get the relation $p = \hbar k$. Thus, we can identify the quantum mechanical momentum operator by the generator of infinitesmal translation times $\hbar$. Substituting in (1.63), we get the famous Heisenberg commutation relations

$$[\hat{x}, \hat{p}] = i\hbar \tag{1.68}$$

Using the general uncertainty relation derived last lecture, we can derive the Heisenberg uncertainty relation

$$\langle(\Delta x)^2\rangle\langle(\Delta p)^2\rangle \geq \frac{\hbar^2}{4} \tag{1.69}$$

We note something very peculiar about the commutation relation (1.68). Unlike the commutation relation for spin components which had a non-trivial operator on the right-hand-side. Here, the right-hand-side is proportional to the identity. To see why this is strange, let us imagine, we can represent $\hat{x}$ and $\hat{p}$ with matrices in a course grained description and take the trace of both sides. The trace of a commutation always vanishes since $\mathrm{tr}AB = \mathrm{tr}BA$, thus the trace of the left-hand-side is zero. The trace of the right-hand-side on the other hand is equal to the dimension of the space. This tells us that the relation (1.68) can only be realized by operators on an infinite dimensional space. In particular, $\hat{x}$ and $\hat{p}$ both have an unbounded spectrum from above and below. This means that truncating the system will introduce large error.

From the previous discussion, we see that we can write the momentum operator as

$$\hat{p} = i\hbar \lim_{\Delta x \to 0} \frac{T_{\Delta x} - \mathbb{1}}{\Delta x} \tag{1.70}$$

To connect with the familiar expression from wave mechanics, note that

$$\begin{aligned} T_{\Delta x}|\psi\rangle &= T_{\Delta x} \int dx|x\rangle\langle x|\psi\rangle = \int dx|x+\Delta x\rangle\psi(x) = \int dx|x\rangle\psi(x-\Delta x) \\ &= \int dx|x\rangle\psi(x) - \Delta x \int dx|x\rangle \frac{d}{dx}\psi(x) \end{aligned} \tag{1.71}$$

This yields the expression

$$\hat{p}|\psi\rangle = \int dx|x\rangle \left(-i\hbar\frac{d}{dx}\right)\psi(x) \tag{1.72}$$

which is the expression we get in wave mechanics. Notice that this is a Hermitian operator since

$$\langle\phi|\hat{p}\psi\rangle = -i\hbar\int dx\phi^*(x)\frac{d}{dx}\psi(x) = i\hbar\int dx(\frac{d}{dx}\phi^*(x))\psi(x) = \int dx(-i\hbar\frac{d}{dx}\phi(x))^*\psi(x) = \langle\hat{p}\phi|\psi\rangle \tag{1.73}$$

Here, we have integrated by parts and assumed that the function $\phi(x)$ and $\psi(x)$ vanish at infinity (which is always the case for normalized wavefunctions).

The generalization for multi-spatial dimensions is straightforwards since, unlike the different components of spin, the operators associated with the different spatial components, x, y, and z, commute with each other [7]. Thus, we can choose simultaneous eigenbasis for $\hat{x}$, $\hat{y}$, and $\hat{z}$:

$$\hat{x}|x_0, y_0, z_0\rangle = x_0|x_0, y_0, z_0\rangle, \qquad \hat{y}|x_0, y_0, z_0\rangle = y_0|x_0, y_0, z_0\rangle, \qquad \hat{z}|x_0, y_0, z_0\rangle = z_0|x_0, y_0, z_0\rangle \tag{1.74}$$

Similarly, the generators for translations in the x, y, and z commute with each other. Also, the generators of translations along one direction, let's say x, commute with the position operator along a perpendicular direction, let's say y or z. This leads to the more general commutation relation

$$[x_i, x_j] = [p_i, p_j] = 0, \qquad [x_i, p_j] = i\hbar\delta_{i,j} \tag{1.75}$$

The action of the momentum operator on the wavefunction $\psi(\vec{x})$ becomes $-i\hbar\vec{\nabla}\psi(\vec{x})$.

[7] Ultimately, this is due to the fact the different translations and boosts (translations in momentum) commute with each other but different rotations do not

Chapter 2

Quantum dynamics and time evolution

2.1 Time evolution operator

In the previous chapter, we have discussed the formalism for the quantum theory in terms of states and observables. However, we have not discussed how such states or observables change with time. Note that unlike position which is promoted in the quantum theory to an operator, time remains a parameter. Nevertheless, we will see that there are several similarities between the way we introduced translation operator which translates states in space and time-evolution operator which translates them in time. We define the time evolution operator $\mathcal{U}(t, t_0)$ as the operator which takes an initial state $|\alpha, t_0\rangle$ at time t_0 to a final state $|\alpha, t_0; t\rangle$ at time t:

$$|\alpha, t_0; t\rangle = \mathcal{U}(t, t_0)|\alpha, t_0\rangle \tag{2.1}$$

Similar to our discussion of spatial translation operator, we can deduce some general properties of the time evolution operator that are system- and basis-independent.

First, the time evolution should conserve the probability, which means that it should map normalized states to normalized states. As we have seen before, operators which preserve norm are unitary. Thus, time-evolution needs to be unitary

$$\mathcal{U}(t, t_0)\mathcal{U}^\dagger(t, t_0) = \mathbb{1} \tag{2.2}$$

The second important property of time-evolution is that we can build time evolution over a long interval by combining time-evolution over shorter intervals. That is, the time evolution operator from t_0 to t is equal to the product of the time evolution operator from t_0 to t_1 and the evolution from t_1 to t. Since the operator on the **right** acts first on the state, this is written as

$$\mathcal{U}(t, t_0) = \mathcal{U}(t, t_1)\mathcal{U}(t_1, t_0), \qquad t_0 < t_1 < t \tag{2.3}$$

The final property is that time evolution should approach the identity as t approaches t_0

$$\lim_{t \to t_0} \mathcal{U}(t, t_0) = \mathbb{1} \tag{2.4}$$

Similar to our previous discussion for the translation operator, we can consider infitesmal time evolution $t = t_0 + dt$ and expand $\mathcal{U}$ to first order in dt:

$$\mathcal{U}(t_0 + dt, t_0) = \mathbb{1} - i\Omega dt \tag{2.5}$$

The unitarity of $\mathcal{U}$ implies that the generator of time-translation Ω is a Hermitian operator $\Omega^\dagger = \Omega$. The operator Ω has units of frequency or inverse time. Now, recall that one of the very first steps in the development of the quantum theory by Planck and Einstein was to assign to vibrational modes with frequency ω an energy $E = \hbar\omega$. This is similar to the identification of the momentum with the wavevector we discussed in the previous lecture. This means that we can identify the operator $\hbar\Omega$ with the energy operator. Such

operator is called the Hamiltonian after the classical Hamiltonian which gives the energy as a functional on configuration space. Substituting in (2.5), we get

$$\mathcal{U}(t_0 + dt, t_0) = \mathbb{1} - i\frac{\mathcal{H}}{\hbar}dt \tag{2.6}$$

We can now derive one of the most fundamental relations in the quantum theory, which relates the Hamiltonian to the time-evolution operator *for arbitrary time separations* $t - t_0$. Use the relation (2.3), we write

$$\mathcal{U}(t + dt, t_0) = \mathcal{U}(t + dt, t)\mathcal{U}(t, t_0) = \mathcal{U}(t, t_0) - i\frac{dt}{\hbar}\mathcal{H}\mathcal{U}(t, t_0) \tag{2.7}$$

which yields

$$i\hbar\frac{\partial}{\partial t}\mathcal{U}(t, t_0) = \mathcal{H}\mathcal{U}(t, t_0) \tag{2.8}$$

If we act with both sides on an initial state ket $|\alpha, t_0\rangle$ (which is time-independent), we get the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle = \mathcal{H}\,|\alpha, t_0; t\rangle \tag{2.9}$$

Note that the Hamiltonian operator itself can depend on time.

We would now like to solve Eq. 2.8 to write the time evolution operator as a function of the Hamiltonian. It turns out that the solution depends on whether the Hamiltonian depends on time or not. To see this, recall the solution to first order differential equations. For the DE

$$\frac{d}{dt}f(t) = \alpha f(t) \tag{2.10}$$

the solution is given simply by $f(t) = Ce^{\alpha}$ where C is determined by the initial conditions $f(0) = f_0$. On the other hand, if α is time-dependent, we write $\frac{df}{f} = \alpha(t)dt$ which is solved by

$$f(t) = Ce^{\int_0^t dt' f(t')} \tag{2.11}$$

To solve for the time-evolution operator, we do something very similar. To make our notation as simple as possible, we will assume $t_0 = 0$ and write $\mathcal{U}(t, t_0) = \mathcal{U}(t)$. If $\mathcal{H}$ is time-independent, the solution have exactly the same form as in the scalar case

$$\mathcal{U}(t) = e^{-\frac{i}{\hbar}\mathcal{H}t} \tag{2.12}$$

We can verify that this is indeed a solution to Eq. 2.8, by direct substitution and using the series expansion.

$$i\hbar\frac{\partial}{\partial t}\mathcal{U} = i\hbar\frac{\partial}{\partial t}\sum_n \frac{t^n}{n!}\left(\frac{\mathcal{H}}{i\hbar}\right)^n = \mathcal{H}\sum_n \frac{nt^{n-1}}{n!}\left(\frac{\mathcal{H}}{i\hbar}\right)^{n-1} = \mathcal{H}\sum_n \frac{t^{n-1}}{(n-1)!}\left(\frac{\mathcal{H}}{i\hbar}\right)^{n-1} = \mathcal{H}\mathcal{U} \tag{2.13}$$

Now if $\mathcal{H}$ is time-dependent, we can write an equation similar to (2.11):

$$\mathcal{U}(t) = e^{-\frac{i}{\hbar}\int_0^t dt'\mathcal{H}(t')} \tag{2.14}$$

Let us see if this satisfies Eq. 2.8. We can again use the series expansion of the exponential

$$i\hbar\frac{\partial}{\partial t}\mathcal{U} = i\hbar\frac{\partial}{\partial t}\sum_n \frac{1}{n!}\left(-\frac{i}{\hbar}\right)^n\left(\int_0^t dt'\mathcal{H}(t')\right)^n \tag{2.15}$$

However, we now encounter a problem. The action of the derivative on an operator to the n-th power $\frac{\partial}{\partial t}A^n$ is *not* equal to $n(\frac{\partial}{\partial t}A)A^{n-1}$ in general. The reason is that the operators A and $(\frac{\partial}{\partial t}A)$ do not necessarily commute. This means that, in general, Eq. 2.14 does not provide a solution to the time evolution equation.

However, it will be a solution provided that the operators $\int_0^t dt' \mathcal{H}(t')$ and $\frac{\partial}{\partial t}\int_0^t dt' \mathcal{H}(t') = \mathcal{H}(t)$ commute. This is only possible if $\mathcal{H}(t)$ commute at different times, i.e. $[\mathcal{H}(t), \mathcal{H}(t')] = 0$ for all t and t'.

So what happens if $\mathcal{H}(t)$'s at different times do not commute. In this case, the general solution is given by the so-called Dyson series

$$\mathcal{U}(t) = \mathbb{1} + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n A_n(t, \mathcal{H}), \quad A_n(t, \mathcal{H}) = \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \mathcal{H}(t_1)\mathcal{H}(t_2)\ldots\mathcal{H}(t_n) \tag{2.16}$$

Notice that t only enters in the integration limit for the first integral, so that action of the t derivative only pulls out the first $\mathcal{H}$:

$$\frac{\partial}{\partial t} A_n(t) = \mathcal{H}(t) \int_0^t dt_2 \cdots \int_0^{t_{n-1}} dt_n \mathcal{H}(t_2)\ldots\mathcal{H}(t_n) = \mathcal{H}(t) A_{n-1}(t) \tag{2.17}$$

This is also the reason there is no $n!$ in the denominator. To convince yourself that this expression reduces to Eq. 2.14 when $\mathcal{H}(t)$'s commute with each other, consider $A_2(t)$ and recall the heaviside theta function

$$\theta(x) = \begin{cases} 1 & : x \geq 0 \\ 0 & : x < 0 \end{cases} \tag{2.18}$$

Then we can write

$$\begin{aligned} A_2(t) &= \int_0^t dt_1 \int_0^{t_1} dt_2 \mathcal{H}(t_1)\mathcal{H}(t_2) = \int_0^t dt_1 \int_0^t dt_2 \theta(t_1 - t_2)\mathcal{H}(t_1)\mathcal{H}(t_2) \\ &= \frac{1}{2}\int_0^t dt_1 \int_0^t dt_2 \left\{\theta(t_1 - t_2)\mathcal{H}(t_1)\mathcal{H}(t_2) + \theta(t_2 - t_1)\mathcal{H}(t_2)\mathcal{H}(t_1)\right\} \\ &= \frac{1}{2}\int_0^t dt_1 \int_0^t dt_2 \mathcal{H}(t_1)\mathcal{H}(t_2)\left\{\theta(t_1 - t_2) + \theta(t_2 - t_1)\right\} \\ &= \frac{1}{2}\int_0^t dt_1 \int_0^t dt_2 \mathcal{H}(t_1)\mathcal{H}(t_2) = \frac{1}{2}\left(\int_0^t dt_1 \mathcal{H}(t_1)\right)^2 \end{aligned} \tag{2.19}$$

In the second line, we have added to the integral an identical term by exchanging the dummy variables $t_1 \leftrightarrow t_2$. In the third line, we used the assumption that $[\mathcal{H}(t_1), \mathcal{H}(t_2)] = 0$ and in the fourth lines, we used $\theta(x) + \theta(-x) = 1$. The same analysis can be done for $A_n(t)$ leading to $A_n(t) = \frac{1}{n!}\left(\int_0^t dt_1 \mathcal{H}(t_1)\right)^n$ if $[\mathcal{H}(t), \mathcal{H}(t')] = 0$ for all t, t'.

2.1.1 Energy eigenkets

While the Dyson series represents the most general case for time-evolution, for most of our applications, we will consider time-independent Hamiltonians where the time-evolution operator has the significantly simpler form (2.12). For a time-independent Hamiltonian $\mathcal{H}$, we can introduce the energy eigenkets

$$\mathcal{H}|a\rangle = E_a|a\rangle \tag{2.20}$$

If the eigenvalues are non-degenerate, we have a one-to-one corresponence between the label a and the energy eigenvalues. For the degenerate case, we can follow the same procedure described last lecture where we find a set of operators which commute with the Hamiltonian and use their eigenvalues to label the eigenstates. In the following, I will assume the label a already combines all these eigenvalue labels such that different a's could correspond to the same energy eigenvalue. Energy eigenkets are stationary states for the time evolution since they only change by a phase

$$e^{-\frac{i}{\hbar}\mathcal{H}t}|a\rangle = e^{-\frac{i}{\hbar}E_a t}|a\rangle \tag{2.21}$$

For a more general state $|u\rangle = \sum_a c_a|a\rangle$, with $c_a = \langle a|u\rangle$, we have

$$e^{-\frac{i}{\hbar}\mathcal{H}t}|u\rangle = \sum_a e^{-\frac{i}{\hbar}\mathcal{H}t}|a\rangle\langle a|u\rangle = \sum_a e^{-\frac{i}{\hbar}E_a t}|a\rangle\langle a|u\rangle = \sum_a c_a(t)|a\rangle, \qquad c_a(t) = c_a e^{-\frac{i}{\hbar}E_a t} \tag{2.22}$$

Thus, the change of a general state is not just by an overall phase but by the relative phase between the different basis vectors. Changing the relative phase produces physically distinct states. For example, the difference between $|+x\rangle$ and $|+y\rangle$ was in the relative phase between the basis vectors: $|x+\rangle = \frac{1}{\sqrt{2}}(|z+\rangle + |z-\rangle)$ whereas $|x+\rangle = \frac{1}{\sqrt{2}}(|z+\rangle + i|z-\rangle)$. The time-evolution operator can be written in the energy eigenbasis as

$$e^{-\frac{i}{\hbar}\mathcal{H}t} = \sum_a e^{-\frac{i}{\hbar}E_a t}|a\rangle\langle a| \tag{2.23}$$

A simple example which illustrates the different aspects of the formalism above is that of spin precession. Consider a spin $1/2$ electron under the effect of magnetic field $\boldsymbol{B}$. The Hamiltonian is given by

$$\mathcal{H} = -\gamma \boldsymbol{S}\cdot\boldsymbol{B} \tag{2.24}$$

where $\gamma = \frac{e}{mc}$. If we take $\boldsymbol{B}$ to be in the z-direction, the Hamiltonian takes the form

$$\mathcal{H} = \omega S_z, \qquad \omega = \gamma B = \frac{|e|B}{mc} \tag{2.25}$$

Since $\mathcal{H}$ is proportional to S_z, they commute and the eigenkets of the Hamiltonian are given by $|\pm z\rangle$ which we will denote for simplicity by

$$|+z\rangle := |\uparrow\rangle, \qquad |-z\rangle := |\downarrow\rangle \tag{2.26}$$

Both $|\uparrow\rangle$ and $|\downarrow\rangle$ are stationary states since

$$e^{-\frac{i}{\hbar}\mathcal{H}t}|\uparrow\rangle = e^{-\frac{i}{2}\omega t}|\uparrow\rangle, \qquad e^{-\frac{i}{\hbar}\mathcal{H}t}|\downarrow\rangle = e^{\frac{i}{2}\omega t}|\downarrow\rangle \tag{2.27}$$

On the other hand, let us consider the state $|+x\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle)$. Under time evolution, this state evolves as

$$|+x;t\rangle = e^{-\frac{i}{\hbar}\mathcal{H}t}|+x\rangle = \frac{1}{\sqrt{2}}(e^{-\frac{i}{2}\omega t}|\uparrow\rangle + e^{\frac{i}{2}\omega t}|\downarrow\rangle) \tag{2.28}$$

This state rotates in the x-y place as can be seen from the fact that the relative phase of the two terms takes arbitrary values. We can see this more directly by computing the expectation values

$$\langle S_x\rangle = \frac{\hbar}{4}((e^{\frac{i}{2}\omega t}\langle\uparrow| + e^{-\frac{i}{2}\omega t}\langle\downarrow|)(|\downarrow\rangle\langle\uparrow| + |\uparrow\rangle\langle\downarrow|)(e^{-\frac{i}{2}\omega t}|\uparrow\rangle + e^{\frac{i}{2}\omega t}|\downarrow\rangle) = \frac{\hbar}{2}\cos\omega t \tag{2.29}$$

$$\langle S_y\rangle = \frac{i\hbar}{4}((e^{\frac{i}{2}\omega t}\langle\uparrow| + e^{-\frac{i}{2}\omega t}\langle\downarrow|)(|\downarrow\rangle\langle\uparrow| - |\uparrow\rangle\langle\downarrow|)(e^{-\frac{i}{2}\omega t}|\uparrow\rangle + e^{\frac{i}{2}\omega t}|\downarrow\rangle) = \frac{\hbar}{2}\sin\omega t \tag{2.30}$$

Thus, the spin does precess in the x-y plane with frequency ω.

An important property of time-evolution is that non-stationary states lose their memory of the initial state after a certain characteristic time. This can be seen by considering the overlap between a non-stationary state and its time-evolved version

$$C(t) = \langle u|e^{-\frac{i}{\hbar}\mathcal{H}t}|u\rangle = \sum_a |c_a|^2 e^{-\frac{i}{\hbar}E_a t} \tag{2.31}$$

Now let us say that the dominant contribution to the sum above comes from a set of eigenkets within a certain energy interval $(E_0 - \Delta E, E_0 + \Delta E)$ such that $|c_a|^2$ is neglegible for E_a outside this range. We can then write

$$C(t) = e^{-\frac{i}{\hbar}E_0 t}\sum_a |c_a|^2 e^{-\frac{i}{\hbar}\Delta E_a t}, \qquad \Delta E_a = E_a - E_0 \tag{2.32}$$

We notice that for $t \ll \hbar/\Delta E$, the phase factors are all close to one so the sum over a is close to 1 which means that the time-evolved state is close to the initial state. However, once t is comparable to $\hbar/\Delta E$, then the sum above contains many oscillating terms that cancel out leading to a very small value. Thus, after a characteristic time $t \sim \frac{\hbar}{\Delta E}$, a non-stationary state loses its memory about where it started [1]. This is sometimes called energy-time uncertainty principle. However, we should bear in mind that, due to the asymmetry between position (which is an operator) and time (which is a parameter), the energy-time uncertainty does not have the same meaning as the position momentum uncertainty relation which is a precise statement about operator expectation values.

2.1.2 Schrodinger and Heisenberg pictures

So far, we have taken the point of view that the operators, such as the spin, are time-independent whereas the states, represented by kets, change in time according to the time-evolution operator [2]. However, the states themselves are not directly observable in the quantum theory. The observables in the quantum theory are overlaps of diffent kets $\langle\alpha|\beta\rangle$, operator eigenvalues, and operator expectation values $\langle\alpha|A|\beta\rangle$. The first two are invariant under unitary transformations which means that they remain unchanged under unitary evolution. This leaves operator expectation values which encode the information about time-evolution through:

$$\langle\alpha, t|A|\beta, t\rangle = \langle\alpha|\mathcal{U}(t)^\dagger A\mathcal{U}(t)|\beta\rangle \tag{2.33}$$

Now notice that we will get the exact same result for operator expectation value if we assume that the operators evolve in time according to $A(t) = \mathcal{U}(t)^\dagger A\mathcal{U}(t)$ whereas the state kets are time-independent. This yields a completely equivalent formulation of the theory that gives the same physical results. The formulation we have discussed so far where states evolve in time is called the Schrödinger picture, whereas the formulation where operators change in time is called the Heisenberg picture. The two are related by

$$A^H(t) = \mathcal{U}^\dagger(t)A^S\mathcal{U}(t), \qquad |\alpha^S, t\rangle = \mathcal{U}(t)|\alpha^H\rangle \tag{2.34}$$

where we assume the operators and states in both pictures are equal at $t = 0$.

The time-evolution for operators in the Heisenberg picture can be derived from Eq. 2.8 via

$$\begin{aligned} i\hbar\frac{d}{dt}A^H(t) &= i\hbar[\frac{d}{dt}\mathcal{U}^\dagger(t)]A^S\mathcal{U}(t) + \mathcal{U}^\dagger(t)A^S\frac{d}{dt}\mathcal{U}(t)] = [-\mathcal{U}^\dagger(t)\mathcal{H}^S A^S\mathcal{U}(t) + \mathcal{U}^\dagger(t)A^S\mathcal{H}^S\mathcal{U}(t)] \\ &= [A^H(t), \mathcal{H}^H(t)] = [A^H(t), \mathcal{H}] \end{aligned} \tag{2.35}$$

In the last equality, we assumed that the Hamiltonian in the Schrödinger picture does not depend explicitly on time so that $\mathcal{H}^H(t) = \mathcal{U}^\dagger(t)\mathcal{H}^S\mathcal{U}(t) = \mathcal{H}^S = \mathcal{H}$. The equation of motion for operators in the Heisenberg picture is called the Heisenberg equation of motion.

2.2 Harmonic oscillator

Last section, we have introduced the time-evolution operator whose generator was identified with the Hamiltonian operator. We saw how the time evolution operator can be used to understand how the states change in time in the Schrödinger picture or how operators change in time in the Heisenberg picture. We also saw that the eigenkets of the Hamiltonian, whose eigenvalues are the energies, play an important role in the theory, being the stationary states that only change by a phase under time evolution.

[1] Note that if the sum over a contains only finitely many terms and the ratio of the oscillating frequencies are all rational, there will be a time where the initial state is recovered. If the ratios are irrational, there will be times where $C(t)$ get very close to 1, corresponding to rational approximants for the different oscillating terms. As the number of terms increase, the recurrence time goes to infinity and the system loses its memory of the initial state

[2] Notice that this does not include explicit time-dependence of operators such as externally changing the Hamiltonian of a system

2.2.1 Creation and annihilation operators

We are now ready to apply this formalism to one of the most central problems in the quantum theory: the harmonic oscillator. In typical treatments of quantum mechanics, one introduces the Schrödinger equation for the wavefunction in position representation, then proceeds to find its solution for several specific potentials including the harmonic oscillators. We will present such treatment later. We will now instead present a different algebraic approach to the harmonic oscillator, originally due to Dirac, that does not rely on the position basis and instead relies on the commutation relations. The Hamiltonian for the one-dimensional Harmonic oscillator is given by

$$\mathcal{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \tag{2.36}$$

Here, m is the mass of the particle and ω has units of inverse time or frequency. The crucial observation here is that the Hamiltonian is a sum of two squares $\hat{A}^2 + \hat{B}^2$ so we can use the identity $(\hat{A} + i\hat{B})(\hat{A} - i\hat{B}) = \hat{A}^2 + \hat{B}^2 + i[\hat{B}, \hat{A}]$ to express it in terms of the commutator $[\hat{A}, \hat{B}]$ and the **non-Hermitian** operators $\mathcal{D} = \hat{A} + i\hat{B}$ and $\mathcal{D}^\dagger = \hat{A} - i\hat{B}$. Identifying $\hat{A} = \frac{\hat{p}}{\sqrt{2m}}$ and $\hat{B} = \omega\hat{x}\sqrt{\frac{m}{2}}$, we can write

$$\mathcal{H} = -\frac{i}{2}\omega[\hat{x}, \hat{p}] + (\frac{\hat{p}}{\sqrt{2m}} + i\omega\hat{x}\sqrt{\frac{m}{2}})(\frac{\hat{p}}{\sqrt{2m}} - i\omega\hat{x}\sqrt{\frac{m}{2}}) = \hbar\omega\left[a^\dagger a + \frac{1}{2}\right] \tag{2.37}$$

where we defined the operators $a^\dagger$ and a, called the creation and annihilation operators, as

$$a = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} + \frac{i}{m\omega}\hat{p}), \qquad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} - \frac{i}{m\omega}\hat{p}) \tag{2.38}$$

The operators a and $a^\dagger$ satisfy the simple commutation relations

$$[a, a^\dagger] = \frac{m\omega}{2\hbar}\frac{1}{m\omega}(-2i)[\hat{x}, \hat{p}] = \frac{1}{i\hbar}[\hat{x}, \hat{p}] = 1 \tag{2.39}$$

It is generally always a good idea to identify certain combinations of variables that appear together in a problem and identify what these might mean. In the definition of the creation and annihilation operators for the Harmonic oscillator, we see that $\hat{x}$ and $\frac{\hat{p}}{m\omega}$ has to have the same units. Recall that $\hat{p} = \hbar\hat{k}$ which means that $\hat{p}$ has units of action divided by length. This means that we can define a length scale $l^2 = \frac{\hbar}{m\omega}$. Then, we have

$$a = \frac{1}{\sqrt{2}l}(\hat{x} + i\frac{l^2}{\hbar}\hat{p}), \qquad a^\dagger = \frac{1}{\sqrt{2}l}(\hat{x} - i\frac{l^2}{\hbar}\hat{p}) \tag{2.40}$$

This also makes it clear that a is dimensionless.

It is very useful to introduce the hermitian number operator $\hat{N} = a^\dagger a$. First, notice that the Hamiltonian has the simple form $\mathcal{H} = \hbar\omega[\hat{N} + \frac{1}{2}]$ which means that $[\mathcal{H}, \hat{N}] = 0$. Thus, we can construct the energy eigenstates by constructing the eigenstates of $\hat{N}$ which we will has a simple form due to the simple commutation relation (2.39). First, note that for any state $|u\rangle$, the expectation value $\langle u|\hat{N}|u\rangle = \langle u|a^\dagger a|u\rangle = \|au\|^2$. This means that the eigenvalues of $\hat{N}$ are non-negative[3]. Thus, the energy expectation value satisfies $E = \langle u|\mathcal{H}|u\rangle \geq \frac{1}{2}\hbar\omega$.

Notice that the number operator $\hat{N}$ has simple commutation relations with the operators a and $a^\dagger$. We can see this using the relation we proved in problem set one: $\mathrm{ad}_A BC := [A, BC] = (\mathrm{ad}_A B)C + B\mathrm{ad}_A C$:

$$[\hat{N}, a] = -\mathrm{ad}_a a^\dagger a = -a, \qquad [\hat{N}, a^\dagger] = -\mathrm{ad}_{a^\dagger} a^\dagger a = a^\dagger \tag{2.41}$$

These relations should remind you of something. Recall the commutation relations for the translation operator with the position operator

$$\hat{x}T_\alpha - T_\alpha\hat{x} = \alpha T_\alpha \tag{2.42}$$

[3]This is true for any operator with the form $\hat{A} = \sum_i \mathcal{D}_i^\dagger \mathcal{D}_i$.

This relation meant that T_a acting on an eigenstate of $\hat{x}$ shifts its eigenvalue by a. To see how this relates to the commutation relations above, we identify $\hat{N}$ with the position operator. We then see that the first relation implies that, acting on an eigenstate of $\hat{N}$, a lowers the eigenvalue by 1 whereas $a^\dagger$ raises its eigenvalue by 1. Explicitly, we write

$$\hat{N}|q\rangle = q|q\rangle, \qquad \langle q|q'\rangle = \delta_{q,q'} \tag{2.43}$$

Acting with Eqs. 2.41 on $|q\rangle$, we get

$$\hat{N}(a|q\rangle) = (q-1)(a|q\rangle), \qquad \hat{N}(a^\dagger|q\rangle) = (q+1)(a^\dagger|q\rangle) \tag{2.44}$$

These relations mean that

$$a|q\rangle = C_q|q-1\rangle, \qquad a^\dagger|q\rangle = K_q|q+1\rangle \tag{2.45}$$

where C_q and K_q are constants. In the case of translations, we argued that we could choose the constant to be one since T_a is unitary: $\langle x|T_a^\dagger T_a|x\rangle = \langle x|x\rangle$. This means we only needed to fix an overall phase that can be chosen to be 1. Here, the situation is different since a is not a unitary operator $a^\dagger a \neq \mathbb{1}$. This implies that

$$|C_q|^2\langle q-1|q-1\rangle = \langle q|a^\dagger a|q\rangle = \langle q|\hat{N}|q\rangle = q\langle q|q\rangle, \qquad |C_q| = \sqrt{q} \tag{2.46}$$

where we used the normalization condition. Similarly, we find

$$|K_q|^2\langle q+1|q+1\rangle = \langle q|aa^\dagger|q\rangle = \langle q|(\hat{N}+1)|q\rangle = (q+1)\langle q|q\rangle, \qquad |K_q| = \sqrt{q+1} \tag{2.47}$$

Choosing the phase of C_q and K_q to be 1, we get

$$a|q\rangle = \sqrt{q}|q-1\rangle, \qquad a^\dagger|q\rangle = \sqrt{q+1}|q+1\rangle \tag{2.48}$$

So far, we only know that the spectrum of $\hat{N}$ is non-negative but we do not know whether it is continuous or discrete. To see that it should be the latter, we notice that we can iterate Eq. 2.48 to lower the eigenvalue q by any integer

$$a^n|q\rangle = \sqrt{q(q-1)(q-2)\dots(q-n+1)}|q-n\rangle \tag{2.49}$$

If q can take any value, then we can choose a large enough n such that $q-n$ is negative contradicting the non-negativity of the spectrum we just established. The only resolution is that for $q<1$, $a|q\rangle = 0$. This implies that for $q<1$, $\hat{N}|q\rangle = q|q\rangle = a^\dagger a|q\rangle = 0$ which implies that the only valid $q<1$ is $q=0$. Applying the raising operator $a^\dagger$, we see that the spectrum of $\hat{N}$ is given by non-negative integers $n \geq 0$

$$|n\rangle = \frac{a^\dagger}{\sqrt{n}}|n-1\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle, \qquad a|0\rangle = 0 \tag{2.50}$$

Thus, we can find the full spectrum of $\hat{N}$ once we know $|0\rangle$. The explicit form of $|0\rangle$ in the position representation can be obtained by writing

$$a|0\rangle = a\sum_x |x\rangle\langle x|0\rangle = \frac{1}{\sqrt{2}l}(\hat{x} + \frac{i}{m\omega}\hat{p})\sum_x |x\rangle\psi_0(x) = \frac{1}{\sqrt{2}l}\sum_x |x\rangle(x + l^2\partial_x)\psi_0(x) \tag{2.51}$$

To satisfy $a|0\rangle = 0$, we need

$$(x + l^2\partial_x)\psi_0(x) = 0 \tag{2.52}$$

which implies $\psi_0(x) = Ce^{-\frac{1}{2l^2}x^2}$ for some constant C which is fixed by the normalization to be $C = \frac{1}{\pi^{1/4}\sqrt{l}}$.

2.2.2 Coherent states

We have some far discussed many operators. This includes hermitian operators such that the position $\hat{x}$, momentum $\hat{p}$, and Hamiltonian $\hat{H}$ operators. These operators have real spectrum and eigenstates which form a complete orthonormal basis. We have also encountered unitary operators such as translation and time-evolution which can be written as the exponentials of Hermitian generators and thus also have a complete set of orthonormal basis. How about the creation and annihilation operators? It turns out that their eigenstates have very interesting properties that differ significantly from what we discussed so far.

First, let us focus our attention to eigenkets. The eigenbras of a ($a^\dagger$) are simply the duals of the eigenkets of $a^\dagger$ (a). The first thing to notice is that $a^\dagger$ has no eigenkets. We can see this by expanding a general ket into the $|n\rangle$ eigenbasis:

$$|u\rangle = \sum_{n=0}^{\infty} u_n |n\rangle \tag{2.53}$$

Now denote the smallest integer n such that u_n is non-zero by $N_{\min}$. This means that $\langle N_{\min}|u\rangle = u_{N_{\min}} \neq 0$. On the other hand,

$$\langle N_{\min}|a^\dagger|u\rangle = \sum_{n=N_{\min}}^{\infty} u_n \sqrt{n+1}\langle N_{\min}|n+1\rangle = 0 \tag{2.54}$$

Thus, it is impossible to satisfy the relation $a^\dagger|u\rangle = \lambda|u\rangle$ for $\lambda \neq 0$ i.e. $a^\dagger$ has no non-zero eigenkets. It is also impossible to have $a^\dagger|u\rangle = 0$ since this implies $0 = \langle u|aa^\dagger|u\rangle = \langle u|\hat{N}|u\rangle + 1$ which is impossible since $\langle u|\hat{N}|u\rangle \geq 0$. Visually, we can understand the absence of eigenkets of $a^\dagger$ by visualizing the states $|n\rangle$ as a semi-infinite lattice starting at zero and extending to $+\infty$ to the right. Acting with $a^\dagger$ shifts any state to the right by one site which can never leave any state invariant.

On the other hand, this picture suggests it is plausible that a has some non-trivial eigenkets. To find these, we write

$$|\alpha\rangle = \sum_{n=0}^{\infty} \alpha_n |n\rangle \tag{2.55}$$

Substituting in the eigenvalue equation $a|\alpha\rangle = \alpha|\alpha\rangle$, we get

$$a|\alpha\rangle = \sum_{n=1}^{\infty} \alpha_n \sqrt{n}|n-1\rangle = \sum_{n=0}^{\infty} \alpha_{n+1}\sqrt{n+1}|n\rangle = \alpha \sum_{n=0}^{\infty} \alpha_n |n\rangle \tag{2.56}$$

Taking the inner product of both sides with $\langle n|$, we get the relation

$$\alpha_{n+1} = \alpha \frac{\alpha_n}{\sqrt{n+1}} \tag{2.57}$$

which we can iterate to get

$$\alpha_n = \frac{\alpha^n}{\sqrt{n!}}\alpha_0 \tag{2.58}$$

Using $|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle$, we get

$$|\alpha\rangle = \alpha_0 \sum_{n=0}^{\infty} \frac{(\alpha a^\dagger)^n}{n!}|0\rangle = \alpha_0 e^{\alpha a^\dagger}|0\rangle = \alpha_0 e^{\alpha a^\dagger} e^{-\alpha^* a}|0\rangle \tag{2.59}$$

In the last equality, we used the fact that $a|0\rangle = 0$ so $e^{\beta a}|0\rangle = |0\rangle$ for any β. To compute the normalization, we write

$$\langle\alpha|\alpha\rangle = |\alpha_0|^2 \langle 0|e^{-\alpha a^\dagger} e^{\alpha^* a} e^{\alpha a^\dagger} e^{-\alpha^* a}|0\rangle = 1 \tag{2.60}$$

To simplify the last equation, let us recall the Baker-Campbell-Hausdorff (BCH) formula

$$e^A B e^{-A} = e^{\mathrm{ad}A} B, \qquad e^{\mathrm{ad}A} = \sum_n \frac{1}{n!} \mathrm{ad}_A^n \tag{2.61}$$

The relation above also implies

$$e^{\mathrm{ad}_A} B^n = e^A B e^{-A} e^A B e^{-A} \cdots = (e^{\mathrm{ad}A} B)^n, \quad \implies \quad e^{\mathrm{ad}_A} f(B) = f(e^{\mathrm{ad}_A} B) \tag{2.62}$$

Using the BCH formula, we write

$$e^{\alpha^* a} e^{\alpha a^\dagger} e^{-\alpha^* a} = e^{\alpha^* \mathrm{ad}_a} e^{\alpha a^\dagger} = e^{\alpha e^{\alpha^* \mathrm{ad}_a} a^\dagger} = e^{\alpha a^\dagger + |\alpha|^2 \mathrm{ad}_a a^\dagger} = e^{\alpha a^\dagger + |\alpha|^2} \tag{2.63}$$

This implies the relation

$$e^{-\alpha a^\dagger} e^{\alpha^* a} e^{\alpha a^\dagger} e^{-\alpha^* a} = e^{|\alpha|^2} \tag{2.64}$$

Substituting in (2.60), we get

$$|\alpha_0|^2 e^{|\alpha|^2} = 1, \quad \implies \quad |\alpha_0| = e^{-\frac{1}{2}|\alpha|^2} \tag{2.65}$$

which gives the normalized coherent states

$$|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} e^{\alpha a^\dagger} e^{-\alpha^* a} |0\rangle \tag{2.66}$$

We see that unlike the operator $\hat{N}$ whose eigenvalues were discrete and real, the eigenvalues of a, given α span all the complex numbers. Thus a has complex and continuous spectrum. Another property of the states $|\alpha\rangle$ that makes them very distinct from the eigenkets of hermitian operators is that they are not orthogonal. Instead, they satisfy

$$\begin{aligned} \langle\alpha|\beta\rangle &= e^{-\frac{1}{2}(|\alpha|^2+|\beta|^2)} \langle 0| e^{\beta^* a} e^{\alpha a^\dagger} |0\rangle = e^{-\frac{1}{2}(|\alpha|^2+|\beta|^2)} \langle 0| e^{\beta^* a} e^{\alpha a^\dagger} e^{-\beta^* a} |0\rangle \\ &= e^{-\frac{1}{2}(|\alpha|^2+|\beta|^2-2\alpha\beta^*)} \langle 0| e^{\alpha a^\dagger} |0\rangle = e^{-\frac{1}{2}(|\alpha|^2+|\beta|^2-2\alpha\beta^*)} \end{aligned} \tag{2.67}$$

In the last equality, we used the relation $\langle 0| = (|0\rangle)^\dagger = (e^{\alpha^* a}|0\rangle)^\dagger = \langle 0| e^{\alpha a^\dagger}$. Although the coherent states are not orthogonal, they still form a complete basis in the sense that any state can be expanded in terms of them i.e. we can write a resolution of unity in terms of coherent states:

$$\frac{1}{\pi} \int d^2\alpha |\alpha\rangle\langle\alpha| = \sum_{n,m} \frac{(a^\dagger)^n}{n!} |0\rangle\langle 0| \frac{(a)^m}{m!} \int d^2\alpha e^{-|\alpha|^2} \alpha^n (\alpha^*)^m \tag{2.68}$$

Here, we define the integration measure $d^2\alpha = d\alpha_r \, d\alpha_i$ where α_r and α_i are the real and imaginary parts of α. The integral over α can be evaluated by going to polar coordinates $\alpha = re^{i\phi}$

$$\int d^2\alpha e^{-|\alpha|^2} \alpha^n (\alpha^*)^m = \int_0^\infty r dr \int_0^{2\pi} d\phi r^{n+m} e^{i(n-m)\phi} e^{-r^2} = \pi n! \delta_{n,m} \tag{2.69}$$

Substituting in (2.68) gives

$$\frac{1}{\pi} \int d^2\alpha |\alpha\rangle\langle\alpha| = \sum_n \frac{(a^\dagger)^n}{\sqrt{n!}} |0\rangle\langle 0| \frac{(a)^n}{\sqrt{n!}} = \sum_n |n\rangle\langle n| = \mathbb{1} \tag{2.70}$$

A basis that is complete (satisfies resolution of identity) but not orthogonal is called overcomplete. The coherent states had to be overcomplete by state counting since they are labelled by a continuous parameter α while at the same time spanning the same space as $|n\rangle$ which are labelled by a discrete parameter. The coherent states play a crucial role in the development of path integrals as we will see later. They replace a

complete discrete set of states describing the system by an *overcomplete continuous* set of states. Since they are labelled by a continuous parameter, they are the states that mostly resemble classical states and appear prominently in path integral approaches to quantum mechanics and semiclassical approximations as we will see later.

Another property of the coherent states is that they are minimum uncertainty states. This is compatible with their interpretation as the most classical states. In fact, below we will show a stronger statement: a state $|\alpha\rangle$ is a minimum uncertainty state in $\hat{x}$ and $\hat{p}$ if and only if there exists an a such that $a|\alpha\rangle = \alpha|\alpha\rangle$ or alternatively $a|\alpha\rangle = 0$. To prove this statement, we need to recall a few important steps in the proof for the uncertainty relation. The first step was writing $|u\rangle = (\hat{x} - \langle x\rangle)|w\rangle$ and $|v\rangle = (\hat{p} - \langle p\rangle)|w\rangle$ and using the Cauchy-Schwarz inequality

$$\|u\|^2\|v\|^2 \geq |\langle u|v\rangle|^2 \tag{2.71}$$

which is saturated if and only if $|u\rangle = \lambda|v\rangle$ for some λ [4]. This means that

$$\Delta x|u\rangle = \lambda\Delta p|u\rangle = \eta\frac{l^2}{\hbar}\Delta p|u\rangle \tag{2.72}$$

Here we have introduced the dimensionless parameter η which we can choose such that $|\eta| = 1$ and the parameter l with units of length. Assuming the inequality is saturated, we have

$$|\langle\Delta x\rangle|^2|\langle\Delta p\rangle|^2 = |\langle\Delta x\Delta p\rangle|^2 = \frac{1}{4}|\langle[x,p]\rangle|^2 + \frac{1}{4}|\langle\{\Delta x, \Delta p\}\rangle|^2 \tag{2.73}$$

To satisfy the minimum uncertainty $|\langle\Delta x\rangle||\langle\Delta p\rangle| = \frac{\hbar}{2}$, we need $\langle\{\Delta x, \Delta p\}\rangle = 0$. Using Eq. 2.72, we find

$$0 = \langle\Delta x\Delta p + \Delta p\Delta x\rangle = \frac{2l^2}{\hbar}\mathrm{Re}[\eta]\langle(\Delta p)^2\rangle \tag{2.74}$$

which implies $\eta = \pm i$ [5]. Thus $a_\pm|u\rangle = \alpha|u\rangle$ where $\alpha = \frac{1}{\sqrt{2}l}(\langle x\rangle \pm i\frac{l^2}{\hbar}\langle p\rangle)$ and $a_\pm = \frac{1}{\sqrt{2}l}(\hat{x} \pm i\frac{l^2}{\hbar}\hat{p})$. However, only the $+$ solution is valid since $[a_\pm, a_\pm^\dagger] = \pm 1$ which means that a_+ is an annihilation operator whereas a_- is a creation operator which does not have any eigenfunctions.

2.2.3 Time dynamics of the harmonic oscillator

One final aspect we want to study for the Harmonic oscillator is the time dynamics. This illustrates the formalism we introduced last week. In particular, it demonstrates the usefulness of the Heisenberg picture which allows us directly to evaluate the time dependence of the variables x and p whose physical meaning is transpart instead of the less physically transparent eigenkets $|n\rangle$. The easiest way to evaluate the time dependence of $\hat{x}$ and $\hat{p}$ in the Heisenberg picture is to write them in terms of the creation and annihilation operators by inverting Eq. 3 from last lecture:

$$\hat{x} = \frac{l}{\sqrt{2}}(a + a^\dagger), \qquad \hat{p} = i\frac{\hbar}{\sqrt{2}l}(a^\dagger - a) \tag{2.75}$$

The Heisenberg equation of motion for a and $a^\dagger$ has a particularly simple form

$$\frac{da}{dt} = \frac{1}{i\hbar}[a, \mathcal{H}] = -i\omega[a, \hat{N}] = -i\omega a, \qquad \frac{da^\dagger}{dt} = \frac{1}{i\hbar}[a^\dagger, \mathcal{H}] = -i\omega[a^\dagger, \hat{N}] = i\omega a \tag{2.76}$$

The solution to these equations is

$$a(t) = a(0)e^{-i\omega t}, \qquad a(t)^\dagger = a(0)^\dagger e^{i\omega t} \tag{2.77}$$

[4] To see this note that $\frac{1}{\|v\|^2}\|\|v\|^2|u\rangle - \langle u|v\rangle|v\rangle\|^2 = \|u\|^2\|v\|^2 - |\langle u|v\rangle|^2$

[5] This implication holds unless $|u\rangle$ is a momentum eigenstate. If that is the case, we can do the same argument replacing Δp with Δx

Substituting in (2.75) yields

$$\hat{x}(t) = \frac{l}{\sqrt{2}}[(a(0) + a(0)^\dagger)\cos\omega t + i(a(0)^\dagger - a(0))\sin\omega t] = x(0)\cos\omega t + \frac{l^2}{\hbar}p(0)\sin\omega t \tag{2.78}$$

$$\hat{p}(t) = -\frac{\hbar}{l^2}x(0)\sin\omega t + p(0)\cos\omega t \tag{2.79}$$

These are the same as the equations for the classical phase space trajectory of the classical harmonic oscillator where the position and momentum variables oscillate out of phase.

It is instructive to evaluate $\hat{x}(t)$ directly by acting with the time evolution operator $x(t) = \mathcal{U}(t)^\dagger x(0)\mathcal{U}(t)$:

$$\hat{x}(t) = e^{\frac{i}{\hbar}\mathcal{H}t}\hat{x}e^{-\frac{i}{\hbar}\mathcal{H}t} \tag{2.80}$$

Thus, we can write

$$\hat{x}(t) = e^{\frac{i}{\hbar}t\,\mathrm{ad}_\mathcal{H}}\hat{x} \tag{2.81}$$

We now use

$$\mathrm{ad}_\mathcal{H}\hat{x} = \frac{1}{2m}\mathrm{ad}_{\hat{p}^2}\hat{x} = -i\frac{\hbar}{m}\hat{p} \tag{2.82}$$

$$\mathrm{ad}^2_\mathcal{H}\hat{x} = -i\frac{\hbar}{m}\mathrm{ad}_\mathcal{H}\hat{p} = -i\frac{\hbar\omega^2}{2}\mathrm{ad}_{\hat{x}^2}\hat{p} = \hbar^2\omega^2\hat{x} \tag{2.83}$$

From the second equation we see that $\mathrm{ad}^2_\mathcal{H}$ on $\hat{x}$ by multiplying by $(\hbar\omega)^2$. This means that

$$\mathrm{ad}^{2n}_\mathcal{H}\hat{x} = (\hbar\omega)^{2n}\,\hat{x}, \qquad \mathrm{ad}^{2n+1}_\mathcal{H}\hat{x} = (\hbar\omega)^{2n}\,\mathrm{ad}_\mathcal{H}\hat{x} = -i\frac{\hbar}{m}\,(\hbar\omega)^{2n}\,\hat{p} \tag{2.84}$$

Substituting in (2.81), we get

$$\begin{aligned}\hat{x}(t) &= \sum_n \frac{1}{n!}\left(\frac{it}{\hbar}\right)^n \mathrm{ad}^n_\mathcal{H}\hat{x} = \sum_l \frac{1}{(2l)!}\left(\frac{it}{\hbar}\right)^{2l}\mathrm{ad}^{2l}_\mathcal{H}\hat{x} + \sum_l \frac{1}{(2l+1)!}\left(\frac{it}{\hbar}\right)^{2l+1}\mathrm{ad}^{2l+1}_\mathcal{H}\hat{x} \\ &= \hat{x}\sum_l \frac{(-1)^l}{(2l)!}\,(\omega t)^{2l} + \frac{1}{m\omega}\hat{p}\sum_l \frac{(-1)^l}{(2l+1)!}\,(\omega t)^{2l+1} = \hat{x}\cos\omega t + \frac{1}{m\omega}\hat{p}\sin\omega t\end{aligned} \tag{2.85}$$

2.3 Wave mechanics

Although the more abstract approach we used for the harmonic oscillator has many advantages, it is not generalizable for more general potentials where there is not simple algebraic structure that allows us to solve the problem without specifying a basis. In particular, for the problem of a particle subject to a general potential $\hat{V}$ which is diagonal in position space and depends only on position $\langle x'|\hat{V}|x\rangle = \delta(x - x')V(x)$, it is convenient to work explicitly in the position basis. Starting from the general Schrödinger equation for state kets, we can write

$$i\hbar\langle x|\frac{d}{dt}|\psi, t\rangle = \langle x|\frac{\hat{p}^2}{2m} + \hat{V}|\psi, t\rangle \tag{2.86}$$

Recall that the position basis $|x\rangle$ is defined via $\hat{x}|x\rangle = x|x\rangle$. Since operators are time-independent in the Schrödinger picture, the basis kets $|x\rangle$ are also time-independent. Thus, $\langle x|\frac{d}{dt}|\psi, t\rangle = \frac{d}{dt}\langle x|\psi, t\rangle = \frac{d}{dt}\psi(x, t)$. We can also simplify the action of $\hat{p}$ and $\hat{V}$ using $\langle x|\hat{p} = i\hbar\frac{d}{dx}\langle x|$ and $\langle x|\hat{V} = V(x)\langle x|$ leading to the celebrated time-dependent Schrödinger wave equation

$$i\hbar\frac{d}{dt}\psi(x, t) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x, t) \tag{2.87}$$

We note that in many approaches introducing quantum mechanics, the Schrödinger wave equation is introduced as the fundamental object. However, in our approach it appears as a special case for the more general basis-independent Schrödinger equation for the time evolution operator.

For a stationary state with $\psi(x,t) = \psi(x)e^{-\frac{i}{\hbar}Et}$, we get the time-independent Schrödinger wave equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \tag{2.88}$$

In most cases, the potential $V(x)$ is taken to grow at infinity, e.g. for the harmonic oscillator $V(x) \sim x^2$. This serves to confine the particle in a finite region. For $E < \lim_{x\to\pm\infty} V(x)$, we have the condition $\lim_{x\to\infty}\psi(x) = 0$. This boundary condition leads to the quantization of energy eigenvalues E similar to the case of a vibrating string. In the next lecture, we will discuss cases where this assumption does not hold leading to a continuous rather than discrete spectrum.

2.3.1 Harmonic Oscillator in wave mechanics

Let us now revisit the harmonic oscillator from the point of view of wave mechanics. In the context of a particle in a potential $V(x)$, the harmonic oscillator plays a fundamental role since the expansion of the potential around any local minimum has the form $V(x) = V_0 + \frac{1}{2}V''(x_0)(x-x_0)^2$. Thus, the harmonic oscillator forms the basis of approximating the solution to any potential close to its minima. The time-independent Schrödinger equation for the harmonic oscillator has the form

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right]\psi(x) = E\psi(x) \tag{2.89}$$

First, we notice that for every solution of this equation $\psi(x)$, $\psi(-x)$ is also a solution. This arises from the inversion or parity symmetry of the potential $V(x) = V(-x)$. Note that this does **not** imply the spectrum is doubly degenerate since $\psi(-x)$ may be proportional to $\psi(x)$. If that is the case, then we have $\psi(-x) = \lambda\psi(x)$ which implies $\psi(x) = \lambda\psi(-x) = \lambda^2\psi(x)$ yielding $\lambda = \pm 1$. In fact, from the algebraic treatment, we saw that the eigenstates of the harmonic oscillator were labelled by an integer $|n\rangle$ with eigenvalues $\hbar\omega(n+1/2)$ which means that the spectrum is non-degenerate. In the next lecture, we will show that this is a general property of the discrete spectrum of the Schrödinger equation in one dimension.

Whether the eigenfunctions are degenerate or not, the fact that $\psi(x)$ and $\psi(-x)$ are eigenfunctions of the same energy, means we can form the linear combinations

$$\psi_\pm(x) = \frac{1}{2}(\psi(x) \pm \psi(-x)) \tag{2.90}$$

which satisfy $\psi_\pm(-x) = \pm\psi(x)$. This means we can solve the Schrödinger equation once for even parity states $\psi_+(-x) = \psi_+(x)$ and once for odd parity states $\psi_-(-x) = -\psi_-(x)$. This usually simplifies the solution.

Second, we can again define $l = \sqrt{\frac{\hbar}{m\omega}}$ and introduce the dimensionless quantities

$$r = \frac{x}{l}, \qquad \epsilon = \frac{2E}{\hbar\omega} \tag{2.91}$$

Eq. 2.89 then simplifies to

$$\psi''(r) + [\epsilon - r^2]\psi(r) = 0 \tag{2.92}$$

In the limit $r \to \pm\infty$ for fixed ϵ, we can ignore the term $\epsilon\psi(r)$ and find $\psi(r) \sim r^n e^{-\frac{1}{2}r^2}$, where the $\sim$ sign here indicates that we are keeping only the leading power of r in the pre-exponent. This motivates the ansatz

$$\psi(r) = f(r)e^{-\frac{1}{2}r^2} \tag{2.93}$$

Substituting in (2.92), we get

$$f''(r) - 2rf' + \lambda f = 0, \qquad \lambda = \epsilon - 1 \tag{2.94}$$

To solve this equation, we write a power series in r. We can separately consider solutions of even or odd parity. For even parity, we have

$$f_+(r) = \sum_n f_n r^{2n} \tag{2.95}$$

Substituting in (2.94) and matching the coefficients for each power of r, we get

$$f_{n+1} = \frac{4n - \lambda}{(2n+1)(2n+2)} f_n \tag{2.96}$$

If the series does not terminate, we see that $f_+(r)$ behaves as e^{r^2} for large r since $\frac{f_{n+1}}{f_n} = \frac{1}{n}$. This would lead to a non-normalizable state. Thus, we conclude that the series has to terminate which is only possible if $\lambda = 4n$ for some n. This leads to the energy

$$\epsilon = 4n + 1 = 2(2n) + 1, \quad \implies \quad E = \hbar\omega(2n + 1/2) \tag{2.97}$$

A similar analysis for the odd parity gives $\lambda = 4n + 2$ leading to the energies

$$\epsilon = 4n + 3, \quad \implies \quad E = \hbar\omega(2n + 1 + 1/2) \tag{2.98}$$

These are the same eigenvalues we obtained from the algebraic solution with even n corresponding to even parity states and odd n corresponding to odd parity states. This is something we could have guessed from the form $|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle$ by noticing that $|0\rangle$ was a simple Gaussian and thus have even parity. $\langle x|0\rangle = \langle -x|0\rangle$ and also noting that the action of the creation operator $a^\dagger$ flips parity since it is odd in both $\hat{x}$ and $\hat{p}$. We can combine both results by writing $\lambda = 2n$ for some integer n.

We can construct the wavefunctions explicitly from the series solution, but there is a more clever way. Let us denote the unnormalized eigenfunction corresponding to the eigenvalue $\lambda = 2n$ by $H_n(r)$ and consider the series

$$g(r,t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} H_n(r) \tag{2.99}$$

Such function is called the generating function for the series $H_n(r)$. First, we can choose the normalization of H_n such that $H_{2n}(0) = (-1)^n \frac{(2n)!}{n!}$ which gives $g(0,t) = e^{-t^2}$. We now notice that

$$\left[\frac{d^2}{dr^2} - 2r\frac{d}{dr}\right] g(r,t) = -2\sum_{n=0}^{\infty} n\frac{t^n}{n!} H_n(r) = -2t\frac{d}{dt} g(r,t) \tag{2.100}$$

It is easy to see that this equation with the boundary condition $g(0,t) = e^{-t^2}$ is solved by choosing $g(r,t) = e^{-t^2+2rt}$. The functions $H_n(r)$ which are called the Hermite polynomials can be extracted from $g(r,t)$ via

$$H_n(r) = \frac{d^n}{dt^n} g(r,t)|_{t=0} = \frac{d^n}{dt^n} e^{r^2-(t-r)^2}|_{t=0} = (-1)^n e^{r^2} \frac{d^n}{dr^n} e^{-r^2} \tag{2.101}$$

The final normalized wavefunctions have the form

$$\psi_n(r) = C_n H_n(r) e^{-\frac{r^2}{2}} = C_n e^{-\frac{r^2}{2}} \frac{d^n}{dt^n} e^{-t^2+rt}|_{t=0} \tag{2.102}$$

The normalization can be evaluated using

$$\int_{-\infty}^{\infty} \psi_n^*(r)\psi_m(r) = \frac{d^n}{dt^n}\frac{d^m}{dt'^m} e^{-t^2-t'^2} \int dr e^{-r^2+2r(t+t')} = \sqrt{\pi}\frac{d^n}{dt^n}\frac{d^m}{dt'^m} e^{2tt'} = 2^m\sqrt{\pi}\frac{d^n}{dt^n} t^m = 2^n n!\sqrt{\pi}\delta_{n,m} \tag{2.103}$$

2.3.2 Free particle in 3D

In the previous lecture, we considered the case of harmonic oscillator where the potential grows quadratically at infinity giving rise to a discrete spectrum of states that decay as Gaussians at larger distances. We will now consider a different case where the spectrum and wavefunctions have a very different character.

Consider the case of a free particle in 3D where $V(\boldsymbol{x}) = 0$. We can solve the time-independent Schrödinger equation in two ways. First, we can use the separation of variables ansatz $\psi(x, y, z) = \psi_x(x)\psi_y(y)\psi_z(z)$ and introduce the variables $k_{x,y,z}$ such that $E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$ (notice that at this point, we do not assume $k_{x,y,z}$ are real). Then, we find that we can solve the Schrödinger equation using separation of variables by dividing both sides by $\psi(x, y, z)$

$$\left[\frac{1}{\psi_x(x)}\frac{d^2\psi_x(x)}{dx^2} + k_x^2\right] + \left[\frac{1}{\psi_y(y)}\frac{d^2\psi_y(y)}{dy^2} + k_y^2\right] + \left[\frac{1}{\psi_z(z)}\frac{d^2\psi_z(z)}{dz^2} + k_z^2\right] = 0 \tag{2.104}$$

This leads to the solution $\psi(x, y, z) = Ce^{i(k_x x + k_y y + k_z z)}$ where $k_{x,y,z}$ has to be real otherwise, ψ will blow up in some direction at ∞. We notice that there are at least six degenerate solutions corresponding to $\pm k_x$, $\pm k_y$ and $\pm k_z$. This can be incorporated by assuming $k_{x,y,z}$ can take positive or negative real values. Note that, we could have found the eigenstates by just noting that the Hamiltonian only depends on $\hat{\boldsymbol{p}} = \hbar\hat{\boldsymbol{k}}$, thus its eigenstates are the momentum or wavevector eigenstates $|\boldsymbol{k}\rangle$ introduced in Lecture 4. We have seen that $|\boldsymbol{k}\rangle$ are related to the $|\boldsymbol{x}\rangle$ by Fourier transform

$$|\boldsymbol{k}\rangle = C\int \frac{d^2\boldsymbol{x}}{(2\pi)^2} e^{i\boldsymbol{k}\cdot\boldsymbol{x}}|\boldsymbol{x}\rangle \tag{2.105}$$

which implies

$$\psi_{\boldsymbol{k}}(\boldsymbol{x}) = C\langle\boldsymbol{x}|\boldsymbol{k}\rangle = Ce^{i\boldsymbol{k}\cdot\boldsymbol{x}} \tag{2.106}$$

To normalize the wavefunctions, we need to put the system in a box of dimensions $L_x \times L_y \times L_z$ and impose periodic boundary conditions $\psi(x_i + L) = \psi(x_i)$. This leads to the quantization of $k_{x,y,z}$ via

$$k_i = \frac{2\pi n_i}{L_i}, \tag{2.107}$$

The normalization can then be computed as $C = \frac{1}{\sqrt{L_x L_y L_z}}$. The energy eigenvalues are

$$E = \frac{2\pi^2\hbar^2}{m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] \tag{2.108}$$

Notice that unlike the case of the Harmonic oscillator, the eigenfunctions $\psi_{\boldsymbol{k}}(\boldsymbol{x})$ do not decay at infinity in the limit $L_i \to \infty$. In addition, the spectrum becomes contineous in this limit such that any energy window ΔE around a positive energy E contains infinitely many states.

2.3.3 Square well

We have seen two distinct behaviors in the two examples we considered. For the free particle, we had a continuous spectrum with the corresponding wavefunctions being extended states that do not decay at infinity and are only normalizable by placing the system in a big box. For the harmonic oscillator, we had a discrete spectrum associated with wavefunctions that are bound (or localized) states which decay at infinity. The distinction between the two cases lie in the asymptotic behavior of the potential at infinity with the former case approaching a constant whereas the latter growing at infinity. We will now consider the case of the square well potential which, as we will see, has both extended and bound states.

The potential is given by

$$V(x) = \begin{cases} 0 & : |x| > a \\ -V_0 & : |x| < a \end{cases} \tag{2.109}$$

where $V_0 > 0$. First, note that in general the energy expectation value of any state can never be smaller than the minimum value of the potential since

$$\langle\psi|\mathcal{H}|\psi\rangle = \langle\psi|\frac{\hat{p}^2}{2m}|\psi\rangle + \langle\psi|\hat{V}|\psi\rangle \geq \int dx|\psi(x)|^2 V(x) \geq V_{\min}\int dx|\psi(x)|^2 = V_{\min} \tag{2.110}$$

Here, we used the fact that $\hat{p}$ is a Hermitian operator whose eigenvalues are real which means that its square has non-negative eigenvalues and as a result a non-negative expectation value in any state. For the square well potential, this implies $E \geq -V_0$.

Second, notice that although the potential is discontinuous, both ψ and ψ' are continuous as long as V is finite. To see this, consider the vicinity of the discontinuity point at $x = a$ and integrate the Schrödinger equation between $x = a - \epsilon$ and $x = a + \epsilon$. Then we get

$$-\frac{\hbar^2}{2m}\int_{a-\epsilon}^{a+\epsilon} dx\psi''(x) = -\frac{\hbar^2}{2m}[\psi'(a+\epsilon) - \psi'(a-\epsilon)] = \int_{a-\epsilon}^{a+\epsilon} dx[E-V]\psi(x) \xrightarrow{\epsilon\to 0} 0 \tag{2.111}$$

Thus, ψ' is continuous which implies ψ is continuous. Notice that this argument implies that ψ' would be discontinuous if the potential is infinite, as in the case of a δ potential.

Thus, the strategy to solve the Schrödinger equation in the potential V is to write the solution in each region and match at the point $x = \pm a$. We will focus on the case of $-V_0 < E < 0$. The case of $E > 0$ yields extended states and will be discussed in detail in the section. First, let us recall the discussion of the parity symmetry from last lecture. Since the potential has the symmetry $V(-x) = V(x)$, the wavefunctions can be taken to be even or odd under parity. This means that we can focus on $x > 0$ and do the matching only at $x = a$. For $x > a$, the Schrödinger equation takes the simple form $\psi'' = \kappa^2\psi$ where κ is the **real** parameter defined as $\kappa = \sqrt{-\frac{2mE}{\hbar^2}}$ (recall $E < 0$). The general solution in this region is then $\psi_> = Ae^{-\kappa x} + Be^{+\kappa x}$. The requirement that the wavefunction decays at $x \to +\infty$ implies that $B = 0$. For $x < a$, the Schrödinger equation takes the form $\psi'' = -k^2\psi$ where $k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}}$ whose general solution is $\psi_< = C\cos kx + D\sin kx$. For even parity, we should select $D = 0$ whereas for odd parity, we have $C = 0$. Let us first consider even parity. The matching conditions $\psi_<(a) = \psi_>(a)$ and $\psi'_<(a) = \psi'_>(a)$ implies

$$A\cos ka = Ce^{-\kappa a}, \qquad Ak\sin ka = C\kappa e^{-\kappa a} \tag{2.112}$$

which lead to the condition

$$k\tan ka = \kappa \tag{2.113}$$

Note that κ and k are not independent but are both defined in terms of E leading to the condition

$$E = -\frac{\hbar^2}{2m}\kappa^2 = \frac{\hbar^2}{2m}k^2 - V_0 \tag{2.114}$$

which implies that k and κ lie on a circle

$$k^2 + \kappa^2 = \frac{2mV_0}{\hbar^2} \tag{2.115}$$

The two equations (2.113) and (2.115) can be solved numerically to obtain the spectrum. To simplify the solution, we notice that both k and κ has units of inverse length, so we can define the dimensionless parameters $k' = ka$ and $\kappa' = \kappa a$, leading to

$$k'^2 + \kappa'^2 = \lambda^2, \qquad k'\tan k' = \kappa' \tag{2.116}$$

We see that the solution depends only on the dimensionless parameter $\lambda^2 = \frac{2mV_0a^2}{\hbar^2}$. Plotting $\kappa' = \sqrt{\lambda^2 - k'^2}$ and $\kappa' = k\tan k$ on the same plot, we can identify the intersection of the two curves with solutions to these equations. We see that for $\lambda < \pi$, this equation has only one solution. For $\pi < \lambda < 2\pi$, it

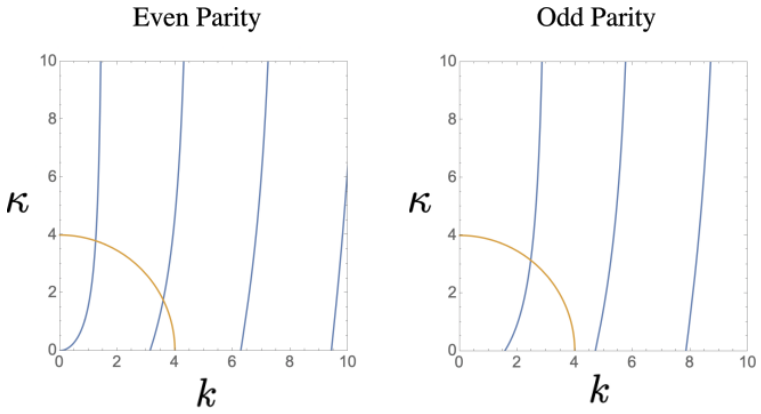

Figure 2.1: Illustration of the graphical solution for the equations (2.116) for even parity (left) and odd parity (right) for $\lambda = 4$.

has two solutions and in general we find $n+1$ even parity solutions for $n\pi < \lambda < (n+1)\pi$. We can do the same for odd parity solutions. The final equations are similar to (2.116) with the second equation replaced by $k' \cot k' = -\kappa$. We can clearly see that the energy eigenvalues alternate between even and odd parity with the lowest one (the ground state) having even parity.

We notice we have more bound state as the potential well becomes deeper or wider as we may intuitively expect. However, we always have at least one state no matter how narrow or shallow the potential is. In particular, we can consider the limit of a δ potential which corresponds to taking $V_0 = v_0/a$ and $a \to 0$. In this limit, we have $\lambda^2 \propto a \to 0$. Thus, we always have a single bound state no matter how large v_0 is.

2.3.4 Properties of bound states

The bound states we found for the square well and the harmonic oscillator seemed to have several features in common. In both cases, we could use the parity eigenvalues to classify the eigenfunctions. We found that the eigenfunctions had alternating parity when ordered by energy with the lowest eigenfunction having even parity. Also, all boundstate eigenvalues were non-degenerate. It turns out many of these are general features as we will show now.

First, we will show that bound states are non-degenerate i.e. if two eigenfunctions ϕ and ψ correspond to the same eigenvalue E, then they are proportional $\phi = \lambda\psi$ which means that they describe the same state. To see this, let us consider the following quantity

$$W(x) = \phi(x)\psi'(x) - \phi'(x)\psi(x) \tag{2.117}$$

This quantity is called the Wronskian and it plays an important role in the theory of second order differential equations. Assuming ϕ and ψ are eigenfunctions with the same eigenvalue, we find

$$W'(x) = \phi(x)\psi''(x) - \phi''(x)\psi(x) = -\frac{2m}{\hbar^2}[(E-V)\phi(x)\psi(x) - (E-V)\psi(x)\phi(x)] = 0 \tag{2.118}$$

This means that the Wronksian is a constant. Since ϕ and ψ describe bound states, they vanish at infinity, which implies W also vanishes at infinity, but since it is a constant, it has to be zero everywhere. Thus,

$$\frac{\phi'(x)}{\phi(x)} = \frac{\psi'(x)}{\psi(x)}, \implies \frac{d}{dx}\ln\phi(x) = \frac{d}{dx}\ln\psi(x) \implies \ln\phi(x) = \ln\psi(x) + C \implies \phi(x) = \lambda\psi(x) \tag{2.119}$$

which means that ϕ and ψ describe the same state. Notice that our proof relies crucially on the vanishing of the states at infinity. For extended plane wave states, this does not hold as we have seen for the free particle which has two degenerate eigenstates $e^{\pm ikx}$.

A consequence of the result above is that the bound state eigenfunctions can be chosen to be real. To see this, notice that whenever $\psi(x)$ is an energy eigenstate $\psi^*(x)$ is also an eigenstate. The above argument then implies that $\psi^*(x) = e^{i\chi}\psi(x)$ for some real phase χ. However, since the phase of ψ is arbitrary, we can define $\tilde{\psi} = e^{i\chi/2}\psi$ such that $\tilde{\psi}^* = \tilde{\psi}$.

Another important property of the bound states in one dimension is that it does not have any zeros. To see this, assume that $\psi(x)$ has some zeros. Let us write the energy expectation value

$$\begin{aligned} E = \langle\psi|\mathcal{H}|\psi\rangle &= \int dx \left\{ -\frac{\hbar^2}{2m}\psi^*(x)\psi''(x) + V(x)|\psi(x)|^2 \right\} \\ &= \int dx \left\{ \frac{\hbar^2}{2m}|\psi'(x)|^2 + V(x)|\psi(x)|^2 \right\} \end{aligned} \tag{2.120}$$

Here, we have integrated by parts and used the fact that ψ vanishes at infinity. As we discussed above, we can assume ψ to be real. Now notice that if we replace $\psi(x)$ by $|\psi(x)|$, the potential energy term is unchanged. The kinetic energy term is also unchanged apart away the zeros. At the zeros of $|\psi(x)|$, the derivative $\frac{d}{dx}|\psi(x)|$ has a kink (rather than a divergence) and thus does not contribute the integral since the zeros form a set of measure 0. Thus, $|\psi|$ have the same energy expectation value as ψ. Now replace $|\psi|$ by a constant in the vicinity of each zero. For example, let us consider for simplicity the case of a single zero at $x = 0$. Then consider the state

$$\tilde{\psi}(x) = C \begin{cases} |\psi(x)| & : |x| > \epsilon \\ |\psi(\epsilon)| & : |x| < \epsilon \end{cases} \tag{2.121}$$

where C is a normalization constant. Intuitively, $\tilde{\psi}$ removes the zero in $|\psi|$ by smoothing its value around the zero. The replacement $|\psi(x)| \mapsto \tilde{\psi}(x)$ changes the kinetic energy and the potential energy around zero as well as the overall normalization. Let us first consider the normalization. Assume ψ was normalized and assume $\psi(x) \approx cx$ close to 0. Then we can write

$$1 = I_{|x|>\epsilon} + \frac{2}{3}|c|^2\epsilon^3, \quad \implies \quad I_{|x|>\epsilon} = \int_{|x|>\epsilon} dx|\psi(x)|^2 = 1 - \frac{2}{3}|c|^2\epsilon^3 \tag{2.122}$$

The normalization constant C is then given by

$$C = \frac{1}{\sqrt{I_{|x|>\epsilon} + |c|^2\epsilon^2 \int_{-\epsilon}^{\epsilon} dx}} = \frac{1}{\sqrt{1 - \frac{2}{3}|c|^2\epsilon^3 + 2|c|^2\epsilon^2}} = \frac{1}{\sqrt{1 + \frac{4}{3}|c|^2\epsilon^3}} \approx 1 - \frac{2}{3}|c|^2\epsilon^3 \tag{2.123}$$

The change in kinetic energy is

$$\frac{2m}{\hbar^2}[E_{\text{kin}}(\tilde{\psi}) - E_{\text{kin}}(\psi)] = (|C|^2 - 1)\int_{|x|>\epsilon} dx|\psi'|^2 - |c|^2 \int_{-\epsilon}^{\epsilon} dx \approx -2|c|^2\epsilon \tag{2.124}$$

The potential energy difference is

$$E_{\text{pot}}(\tilde{\psi}) - E_{\text{pot}}(\psi) = (|C|^2 - 1)\int_{|x|>\epsilon} dxV(x)|\psi(x)|^2 + \frac{4}{3}|c|^2\epsilon^3 V(0) \sim O(\epsilon^3) \tag{2.125}$$

Thus, the change $\psi \mapsto \tilde{\psi}$ always reduces the energy which means that ψ could not have been the ground state.

For excited state, we can generally have zeros of the wavefunction. However, there are still restrictions about these zeros. First, it is not possible for any wavefunction to have a double zero since $\psi(0) = \psi'(0) = 0$ implies $\psi''(0) = \psi'''(0) = \cdots = 0$ which means that $\psi(x) = 0$ for all x. Second, it turns out that the n-th excited state has exactly n zeros. We will not show this proof in detail, but one way to convince yourself this is true is by considering the Wronksian between the first excited state and the ground state

$$W_{10}(x) = \psi_1'(x)\psi_0(x) - \psi_1(x)\psi_0'(x) \tag{2.126}$$

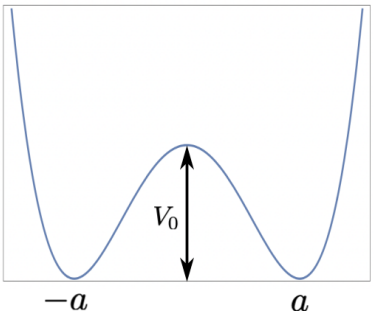

Figure 2.2: Schematic illustration of the double well potential with minima at $x = \pm a$

Its derivative is

$$W'_{10}(x) \propto -(E_1 - E_0)\psi_1(x)\psi_0(x) \tag{2.127}$$

Since both ψ_0 and ψ_1 vanish at infinity, W_{10} should vanish at $x = \pm\infty$. But since $\psi_0(x)$ does not change sign (it has no zeroes), $\psi_1(x)$ has to change sign at least ones. Otherwise, the derivative of W_{10} does not change sign so W_{10} is always increasing or decreasing which is inconsistent with it vanishing at infinity. This argument tells us that ψ_1 has at least one zero. From the discussion above, it makes sense that we would like to have as few zeros as possible to minimize the energy, so that ψ_1 has one zero, ψ_2 has two zeros, etc.

2.3.5 Double well potential

One final example we would like to discuss is that of a double well potential shown in Fig. 2.2. Although this potential does not have a simple analytical solution, it helps illustrate several important concepts. First, we note that if we are interested in energies smaller than the barrier V_0, we can expand the potential around one of the minima $V_R(x) = \frac{1}{2}V''(a)(x-a)^2$. This yields a harmonic oscillator whose center is shifted to $x = a$. As a result, we expect the low energy eigenstates of a harmonic oscillator centered at $x = a$ to provide a good approximation for the low energy eigenstates of the square well potential. We can also do the same in the left well. Although these solutions will approach the actual eigenstates of the system as the two wells get more separated, for any finite separation these cannot be exact eigenstates. Otherwise, we will get a double degeneracy of the eigenstates which we have shown is impossible. Furthermore, the eigenstates localized within the left/right well are not invariant under parity although the potential is parity symmetric $V(-x) = V(x)$. Thus a natural ansatz for the approximate eigenstates of the double well is to take the $\pm$ linear combinations of the state from the two double well. In particular, the lowest two energy eigenfunctions can be approximated as $\psi_{0,\pm}(x) = \psi_{0,L}(x) \pm \psi_{0,R}(x)$. Since $\psi_{0,L}(0) = \psi_{0,R}(0)$, $\psi_{0,-}$ has a zero at $x = 0$ so it cannot be the ground state. Thus, $\psi_{0,+}$ is a good approximation for the ground state. The energy splitting between the two states is proportional to the matrix elements $\Delta E \sim \langle\psi_{0,L}|\mathcal{H}|\psi_{0,R}\rangle$ which is exponentially small. This can be seen from the fact that the overlap of $\psi_{0,L}$ and $\psi_{0,R}$ is exponentially small in a [6].

This leads to a very interesting consequence. If we start with a particle localized in one of the wells, whose energy is significantly lower that the barrier, there is a finite probability of finding the particle in the other well after some time. This is because $\psi_{0,L}$ and $\psi_{0,R}$ are not stationary states. For a particle whose initial state $|\psi(t=0)\rangle = |\psi_{0,L}\rangle = \frac{1}{2}(|\psi_+\rangle + |\psi_-\rangle)$ with $E_\pm = E_0 \pm \Delta E$, the time evolution gives

$$|\psi(t)\rangle = e^{\frac{i}{\hbar}\mathcal{H}t}|\psi(0)\rangle = \frac{1}{2}e^{\frac{i}{\hbar}\mathcal{H}t}(|\psi_+\rangle + |\psi_-\rangle) = \frac{e^{\frac{i}{\hbar}E_0 t}}{2}(e^{\frac{i}{\hbar}\Delta E t}|\psi_+\rangle + e^{-\frac{i}{\hbar}\Delta E t}|\psi_-\rangle) \tag{2.128}$$

[6] To see this, notice that the shifted ground states of the harmonic oscillator are just the coherent states we discussed earlier. The overlap between the left and right eigenfunctions is $\langle a|-a\rangle = e^{-2a^2}$

Thus, after a time $t \sim \frac{\hbar}{\Delta E}$ an initial particle at $\psi_{0,L}$ will have a sizable overlap with $\psi_{0,R}$ i.e. will have a high probability of being in the right well. This is a reflection of the energy time uncertainty.

2.4 Path integrals

So far, we have employed the so-called operator formalism of the quantum theory centered on operators acting on vectors on a Hilbert space. One feature of the operator formalism of the quantum theory, which you can see either as a feature or as a bug, is that it is in some sense maximally different from the classical theory and it is generally hard to take the classical limit. In problem set 3, we have discussed Ehrenfest theory which showed that the expectation values of quantum operators satisfy the classical equations of motion, but there was no simple way to take the classical limit by taking some parameter (this parameter turns out to be $\hbar$) to zero and reproducing classical mechanics [7]

I would also like to emphasize that although we tried to motivate several elements of the formalism we introduced, we have not really 'derived' any of the fundamental laws. Instead, we used some minimal experimentally motivated assumptions to postulate the formalism and derive its consequences. Today I will discuss another formulation of the quantum theory that can be similarly motivated using some minimal experimentally motivated assumptions. Although this formulation is equivalent to the operator formalism, it connects more naturally to the classical limit and is thus very convenient for semiclassical approximations.

2.4.1 Introducing path integrals

Similar to how we used the Stern-Gerlach experiment to motivate the Hilbert space or operator formulation of the quantum theory, I will now use a simple experiment to motivate the path integral formulation. I would like to think again of having a 19th century physicist teleported to the present day and showing them this one experiment and trying to use it to deduce the formalism of the quantum theory. That experiment is the double slit experiment we considered earlier. In the double slit experiment (see Fig. 2.3a), we found that the wave-like interference pattern on the wall can only be understood by summing together two wavelike contributions coming from the two slits. The intensity measured on the screen is itself independent on the overall phase of the wave but it depends strongly on the **relative** phase of the waves coming from the two slits leading to constructive (destructive) interference when the waves are in-phase (out-of-phase). To describe this interference phenomenon, it is known from classical waves that it is very convenient to use complex numbers. So we assign a complex number to each of the two paths the electron can go through. This complex number is nothing but the probability amplitude we discussed earlier. The final intensity on the screen, or the probability of a particle hitting the screen, is given by summing these complex number from the two different parths then taking the absolute value squared. Now since the probability is the square of the amplitude, it follows that the amplitude for the composition of two events, e.g. a particle travelling from A to B and then B to C is the product of the amplitudes of the two events. We will see now how using these two assumption plus a third assumption motivated from the correspondence to classical physics will be all we need to write the path integral formulation.

Let us first see what these assumptions lead us when we consider more complicated variants of the double slit experiment (similar to what we did with the Stern-Gerlach device). First, let us consider adding a third hole to the screen, then clearly we are adding three amplitudes for the particle to go through any of the three holes as shown in Fig. 2.3b. Generization to n-holes is straightforward, we have to add the ampltiudes from all the holes. Next let us consider adding another screen with a bunch of holes. Then the rules above tell us that the total amplitude is obtained by summing the amplitude of the electron going through every pair of holes from the first and second screens with every amplitude formed as the product of the amplitude of going from the screen to the first hole, from the first hole to the second hole, then from the second hold to the detector. This is pictorially illustrated in Fig. 2.3c. Since a screen with infinitely many holes is just equivalent to removing the screen altogether, in the limit of infinitely many screens with

[7] Compare this to special relativity which reproduces Newtonian mechanics in the limit $c \to \infty$.

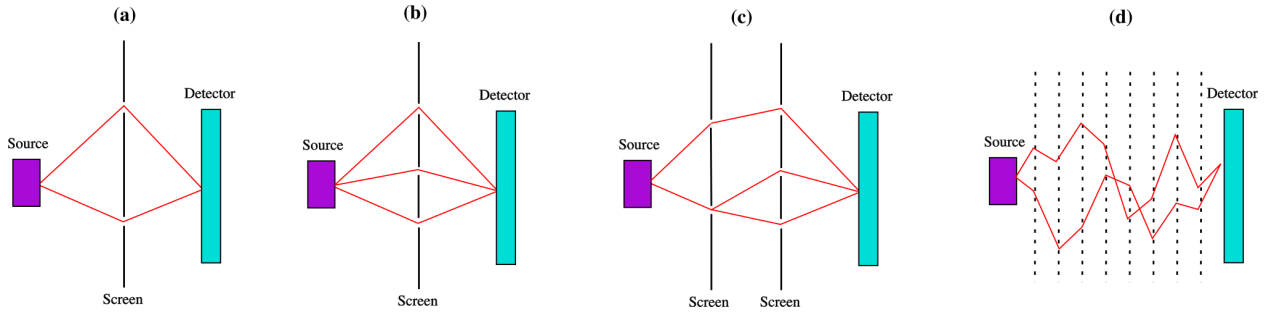

Figure 2.3: Schematic illustration of the (a) double slit experiment, (b) a similar setup where the screen has three holes allowing for three distinct trajectories, (c) a cascaded setup with two screens with different number of holes (d) the path integral limit of infinite number of screens with infinite number of holes

infinitely many holes, we basically end up with a sum over all possible paths/trajectories to go from the source to the detector (See Fig. 2.3d). The amplitude for every path is obtained by breaking up the path into small pieces and taking the product of these pieces.

Let us introduce some notation to facilitate discussing these amplitudes. We denote the probability amplitude of a particle to travel from a point x_i at time t_i to a point x_f at time t_f by $\langle x_f, t_f | x_i, t_i \rangle$. Our discussion above is equivalent to the statement that we break up the time interval $T = t_f - t_i$ into $N \to \infty$ intervals with width $\Delta t = \frac{T}{N}$. Denoting $t_n = t_i + n\Delta t$ such that $t_0 = t_i$ and $t_N = t_f$ we can write the probability amplitude $\langle x_f, t_f | x_i, t_i \rangle$ as

$$\langle x_f, t_f | x_i, t_i \rangle = \int dx_1 \dots dx_{N-1} \langle x_f, t_f | x_{N-1}, t_{N-1} \rangle \langle x_{N-1}, t_{N-1} | x_{N-2}, t_{N-2} \rangle \dots \times \langle x_2, t_2 | x_1, t_1 \rangle \langle x_1, t_1 | x_i, t_i \rangle \quad (2.129)$$

We have now reduced the problem of calculating the probability amplitude over a finite time interval T to that of an infinitesmal time-interval $\langle x', t+\Delta t | x, t \rangle$. The latter should satisfy the condition that it approaches a delta function $\delta(x - x')$ as Δt approaches 0. We can also assume it only depends on the interval Δt but not the absolute time t. This alone is not sufficient to fix its form and we need additional assumption. If we are deriving the path integral from the operator formalism, we can simply write $\langle x', t + \Delta t | x, t \rangle = \langle x' | e^{-\frac{i}{\hbar}\mathcal{H}\Delta t} | x \rangle$ and evaluate this expression. We will discuss this later. Instead, we will now try to guess the answer based on some physical assumptions similar to what a 19th century physicist not exposed to quantum mechanics will do. Using the representation of the delta function $\delta(x) = \lim_{\epsilon \to 0} \sqrt{\frac{1}{2\pi\epsilon}} e^{-\frac{x^2}{2\epsilon}}$, a reasonable ansatz for $\langle x', t + \Delta t | x, t \rangle$ is

$$\langle x', t+\Delta t | x, t \rangle = \sqrt{\frac{\alpha m}{2\pi\hbar\Delta t}} e^{\alpha \frac{m(x-x')^2}{2\hbar\Delta t}} [1 + f(x)\Delta t + O((\Delta t)^2)] \approx \sqrt{\frac{\alpha m}{2\pi\hbar\Delta t}} e^{\frac{\alpha}{\hbar}[\frac{m(x-x')^2}{2\Delta t} + F(x)\Delta t]} \quad (2.130)$$

Here, we have included the factors $\hbar$ and m to make the factor in the exponential dimensionless as it should be and we included the dimensionless parameter α. The function F will in principle depend on x and x' but the exponential factor forces x and x' to be close such that $x' - x \sim \sqrt{\Delta t}$ so we can effectively replace x' to x if we do not care about higher order terms in Δt. Substituting in (2.130), we get the expression

$$\langle x_f, t_f | x_i, t_i \rangle = \int_{x(t_i)=x_i}^{x(t_f)=x_f} \mathcal{D}x(t)\, e^{\frac{\alpha}{\hbar}\int_0^T dt[\frac{m}{2}\dot{x}^2 + F(x)]}, \qquad \mathcal{D}x(t) = \left(\sqrt{\frac{\alpha m}{2\pi\hbar\Delta t}}\right)^{N-1} \prod_{n=1}^{N-1} dx_n \quad (2.131)$$

where we defined $\dot{x}(t) = \frac{x(t+\Delta t) - x(t)}{\Delta t}$. This expression has the form of an infinite-dimensional integral over all paths. It turns out that to get a unitary theory we have to choose α to be imaginary and $F(x)$ to be real.

This is expected since our probability amplitudes where introduced to explain interference so they should be described as a phase.

To proceed further, we make the requirement that our theory reduces to classical mechanics in the limit $\hbar \to 0$. Here, let me digress a bit to review some basic concepts in classical mechanics. When we are introduced to classical mechanics in high school, we are introduced to Newton's laws whose central concept is that of force and how it causes acceleration. Newton's second law $F = m\ddot{x}$ relates the force to the second derivative of position so we need to specify both position and velocity (its first derivative) at an initial time to solve for a particles motion. In the 19th century, new formulations of classical mechanics that center the concepts of momentum and energy were introduced. In Hamilton's formulation, we define a Hamiltonian function of coordinate x and momentum p given by the sum of kinetic and potential energies $H(p,x) = \frac{p^2}{2m} + V(x)$. The relation between p and x as well as Newton's second law are derived from Hamilton's equations of motion

$$\dot{p} = -\frac{\partial H}{\partial x}, \qquad \dot{x} = \frac{\partial H}{\partial p} \tag{2.132}$$

Several elements of Hamiltonian mechanics carry over to the operator formalism of the quantum theory where the Hamiltonian, p and x are promoted to operators. Here we also consider time evolution given some initial values of x and p.

Another formulation of classical mechanics is centered on the concept of Lagrangian which depends on position x and velocity $\dot{x}$. It can be obtained from the Hamiltonian through a so-called Legendre transformation that gets rid of the momentum in favor of the velocity $\dot{x}$

$$L(x,\dot{x}) = p\dot{x} - H(x,p) = \frac{1}{2}m\dot{x}^2 - V(x) \tag{2.133}$$

The Lagrangian is the difference between the kinetic and potential energies. The time integral of the Lagrangian along some classical path is called the action

$$S = \int_0^T dt L(x(t), \dot{x}(t)) \tag{2.134}$$

A central concept in the Lagrangian formulation of classical mechanics is the stationary action principle. This means that the system will take the trajectory $x_0(t)$ for which the variation of the action δS vanishes. This means that if we write $x(t) = x_0(t) + \delta x(t)$ and expand the action above in $\delta x(t)$, the leading term vanishes. This is equivalent to the Euler-Lagrange equations

$$\frac{\partial}{\partial x}L - \frac{d}{dt}\frac{\partial}{\partial \dot{x}}L = 0 \tag{2.135}$$

The least action principle is an unusual way to formulate classical mechanics in terms of a global or integral condition rather than a local (differential) condition. One of its intuitive applications is Fermat's principle in optics which states that light chooses the path of least time to travel between a pair of points A and B. This for example explains snell's law of diffraction where light chooses to travel longer in the medium where its speed is faster. It is also related to a popular riddle asking for the path you should take to save a drowning person if your speed on land v_{land} is higher than your speed in water v_{water}.

One final fact we need to review is the saddle point approximation. This is the statement that the integral

$$\int dx\, e^{i\lambda f(x)} \tag{2.136}$$

for large λ is dominated by the stationary points or extrema of $f(x)$, where $f'(x) = 0$, in the limit of large λ. The reason is that for large λ, any interval of width Δx will contain several terms with different phases differing by $\lambda f'(x)\Delta x$ which generally cancel out whenever $\lambda f'(x)\Delta x \sim 1$. Around stationary points, however, the phase oscillates much slowly and there is no cancellation. This is illustrated in Fig. 2.4 which

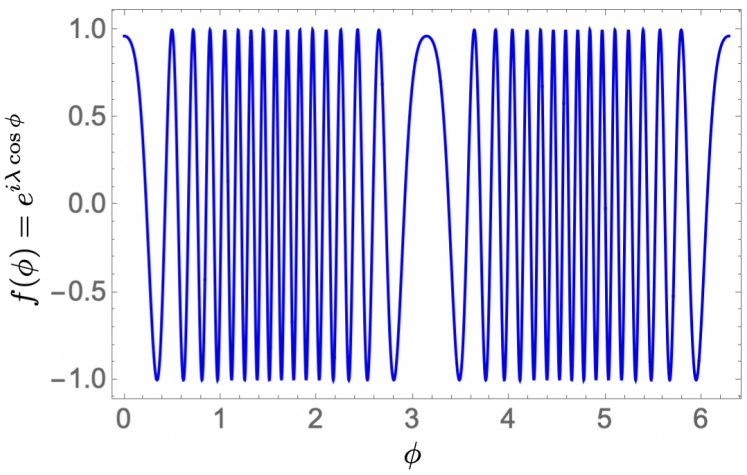

Figure 2.4: Plot of the function $f(\phi) = e^{i\lambda\cos\phi}$ for $\lambda = 50$.

plots the real part of $e^{i\lambda\cos\phi}$ for $\lambda = 50$. We see that the function changes slowly at the minimum and the maximum of the cosine function at π and 0, respectively.

With this background in mind, we see that the path integral in (2.131) will be dominated by the paths where the quantity $\int_0^T dt[\frac{m}{2}\dot{x}^2 + F(x)]$ in the exponential is stationary. Comparing to the stationary action principle of classical mechanics leads to the identification of this quantity with the classical action, i.e. $F(x) = -V(x)$. It remains to fix the magnitude of α which is not specified by anything we discussed so far. In fact, the magnitude of α can be absorped in the definition of $\hbar$. This has to be taken as input by comparing to some experimental results which define the value of $\hbar$. Recall that we did a similar thing when identifying the generator for time-evolution operator with the Hamiltonian. The correct answer turns out to be $|\alpha| = 1$ which leads to the path integral representation of the probability amplitude

$$\langle x_f, t_f | x_i, t_i \rangle = \int_{x(t_i)=x_i}^{x(t_f)=x_f} \mathcal{D}x(t)\, e^{\frac{i}{\hbar}\int_0^T dt L[x,\dot{x}]} = \int_{x(t_i)=x_i}^{x(t_f)=x_f} \mathcal{D}x(t)\, e^{\frac{i}{\hbar}S} \tag{2.137}$$

The path integral formalism allows us to formulate the quantum theory in terms of purely classical variables; $x(t)$ here is a classical trajectory not an operator. The price we have to pay is that we have to sum over all possible classical trajectories with some complex phases. It also gives us a measure of how quantum mechanical a problem is by comparing the magnitude of the action to $\hbar$. Interestingly, path integral provides some intuition for the classical stationary action principle. One can ask: how does the system know which path leads to stationary action? the answer in the path integral formalism is that the system really probes all possible trajectories and that is how it can decide which one gives the stationary action.

2.4.2 Derivation of the path integral from operator formalism

We have so far presented the path integral as an alternative way to formulate quantum mechanics that can be derived from reasonable physical assumptions. We will now show that it is equivalent to the operator formulation. We will do this by first deriving it from the operator formalism, then using it to derive the Schrödinger equation. In the operator formalism, the probability amplitude $\langle x_f, t_f | x_i, t_i \rangle$ is given by:

$$\langle x_f, t_f | x_i, t_i \rangle = \langle x_f | e^{-\frac{i}{\hbar}\mathcal{H}(t_f - t_i)} | x_i \rangle \tag{2.138}$$

This object is usually called the propagator which tells us what is the overlap of a state initially localized at x_i with a state localized at x_f after it is allowed to evolve for time $t_f - t_i$. We now divide the time-interval $T = t_f - t_i$ into N intervals with width $\Delta t = T/N$ and insert the resolution of unity

$$\int dx |x\rangle\langle x| = \mathbb{1} \tag{2.139}$$

$N-1$ times to get

$$\langle x_f,t_f|x_i,t_i\rangle = \int dx_1\dots dx_{N-1}\langle x_f|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|x_{N-1}\rangle\langle x_{N-1}|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|x_{N-2}\rangle\dots \\ \times\langle x_2|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|x_1,\rangle\langle x_1|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|x_i\rangle \quad (2.140)$$

This is the same as Eq. 2.129 with the infinitesmal propagator $\langle x',t+\Delta t|x,t\rangle$ replaced by $\langle x'|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|x\rangle$. We now consider the Hamiltonian $\mathcal{H}=\frac{\hat{p}^2}{2m}+V(\hat{x})$. The action of the potential energy operator $V(\hat{x})$ in the position basis is simple but not the kinetic energy operator. To simplify this expression, we use the Baker-Campbell-Haussdorff formula $e^{(X+Y)\Delta t}=e^{X\Delta t}e^{Y\Delta t}e^{-\frac{1}{2}[X,Y])\Delta t)^2}\dots$ where the dots contain exponential with higher powers of Δt. Since the Hamiltonian is multiplied by Δt and we are interested in the $\Delta t\to 0$ limit, we can write $e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}=e^{-\frac{i}{\hbar}\frac{\hat{p}^2}{2m}\Delta t}e^{-\frac{i}{\hbar}V(\hat{x})\Delta t}$. This leads to the simplification

$$\langle x'|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|x\rangle=\langle x'|e^{-\frac{i}{\hbar}\frac{\hat{p}^2}{2m}\Delta t}e^{-\frac{i}{\hbar}V(x)\Delta t}|x\rangle=\langle x'|e^{-\frac{i}{\hbar}\frac{\hat{p}^2}{2m}\Delta t}|x\rangle e^{-\frac{i}{\hbar}V(x)\Delta t} \quad (2.141)$$

To simplify further, we insert another resolution of unity but using the momentum basis

$$\int dp|p\rangle\langle p| = \mathbb{1} \quad (2.142)$$

leading to

$$\langle x'|e^{-\frac{i}{\hbar}\frac{\hat{p}^2}{2m}\Delta t}|x\rangle=\int dp\langle x'|e^{-\frac{i}{\hbar}\frac{\hat{p}^2}{2m}\Delta t}|p\rangle\langle p|x\rangle=\int dp\langle x'|p\rangle\langle p|x\rangle e^{-\frac{i}{\hbar}\frac{p^2}{2m}\Delta t} \quad (2.143)$$

Using $\langle p|x\rangle=\frac{1}{\sqrt{2\pi\hbar}}e^{-\frac{i}{\hbar}px}$, we finally get

$$\langle x'|e^{-\frac{i}{\hbar}\frac{\hat{p}^2}{2m}\Delta t}|x\rangle=\frac{1}{2\pi\hbar}\int dp\, e^{-\frac{i\Delta t}{2m\hbar}[p^2+\frac{2mp}{\Delta t}(x'-x)]}=\frac{1}{2\pi\hbar}\int dp\, e^{-\frac{i\Delta t}{2m\hbar}[p+\frac{m}{\Delta t}(x'-x)]^2+i\frac{m}{2\hbar\Delta t}(x-x')^2} \\ =\sqrt{\frac{im}{2\pi\hbar\Delta t}}e^{i\frac{m}{2\hbar\Delta t}(x-x')^2} \quad (2.144)$$

This leads to

$$\langle x'|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|x\rangle=\sqrt{\frac{im}{2\pi\hbar\Delta t}}e^{\frac{i}{\hbar}\Delta t[\frac{m(x-x')^2}{2(\Delta t)^2}-V(x)]} \quad (2.145)$$

Substituting in (2.145) yields the path integral expression (2.140).

Having derived the path integral from the operator formalism, we will now show that the Schrödinger equation can be derived from it. However, before doing that we would like to emphasize some important conceptual distinctions between the path integral and operator formalisms. In the path integral formalism, the fundamental object in the path integral is the probability amplitude $\langle x_f,t_f|x_i,t_i\rangle$ which is usually called the propagator (since it gives us the probability of a particle to propagate from an initial position x_i at time t_i to a final position x_f at time t_f). Although the notation we use for propagators is inspired by the Dirac bra-ket notation, we did not really need to introduce a Hilbert space or the notion of state bras and kets to define the propagator. Instead, we are thinking of an experiment where the initial and final state can be characterized by classical variables and considering all possible trajectories between them.

2.4.3 Propagators and the Schrödinger equation

To make the connection to the operator formalism, we need to connect the wavefunction to the propagator defined above. This is straightforward since the wavefunction $\psi(x,t)$ is generally obtained by acting with the time evolution operator on some initial state $\psi(x,t_0)=\langle x|\psi,t_0\rangle$. This means that we can write the wavefunction in terms of the propagator $\langle x_f,t_f|x_i,t_i\rangle$ via

$$\psi(x,t)=\langle x|\psi,t\rangle=\langle x|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|\psi,t_0\rangle=\int dx_0\langle x|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|x_0\rangle\psi(x_0,t_0)=\int dx_0\langle x,t|x_0,t_0\rangle\psi(x_0,t_0) \quad (2.146)$$

This means that the propagator can be interpreted as an integration Kernel that generates the action of the time evolution. Notice that the dependence on the Hamiltonian is fully contained in the propagator $\langle x,t|x_0,t_0\rangle$. This means that the propagator satisfies the Schrödinger equation

$$i\hbar\frac{d}{dt}\langle x,t|x_0,t_0\rangle = \mathcal{H}(x)\langle x,t|x_0,t_0\rangle \tag{2.147}$$

If the energy eigenstates $|n\rangle$ and eigenvalues E_n are known for a given Hamiltonian, the propagator can be written as

$$\langle x,t|x_0,t_0\rangle = \langle x|e^{-\frac{i}{\hbar}\mathcal{H}(t-t_0)}|x_0\rangle = \sum_n e^{-\frac{i}{\hbar}E_n(t-t_0)}\langle x|n\rangle\langle n|x_0\rangle = \sum_n e^{-\frac{i}{\hbar}E_n(t-t_0)}\psi_n(x)\psi_n^*(x_0) \tag{2.148}$$

We will now show that the propagator defined through the path integral from the previous lectures satisfies the Schrödinger equation. Let us write

$$\langle x,t|x_0,t_0\rangle = \sqrt{\frac{im}{2\pi\hbar\Delta t}}\int dx_{N-1}e^{\frac{i}{\hbar}\Delta t[\frac{m(x-x_{N-1})^2}{2(\Delta t)^2}-V(x)]}\langle x_{N-1},t-\Delta t|x_0,t_0\rangle \tag{2.149}$$

Defining the variable $\xi = x_{N-1} - x$, we can rewrite this as

$$\langle x,t|x_0,t_0\rangle = \sqrt{\frac{im}{2\pi\hbar\Delta t}}\int d\xi e^{\frac{i}{\hbar}\Delta t[\frac{m\xi^2}{2(\Delta t)^2}-V(x)]}\langle x+\xi,t-\Delta t|x_0,t_0\rangle \tag{2.150}$$

The factor $e^{\frac{i}{\hbar}\frac{m\xi^2}{\Delta t}}$ cause the integral over ξ to be strongly peaked around $\xi = 0$ with width $\sqrt{\Delta t}$ so we can expand the integrand in power of ξ and Δt (noting that the $\xi^2 \sim \Delta t$)

$$\langle x,t|x_0,t_0\rangle = \sqrt{\frac{im}{2\pi\hbar\Delta t}}\int d\xi e^{\frac{i}{\hbar}\frac{m\xi^2}{2\Delta t}}[1-\frac{i}{\hbar}V(x)\Delta t][1-\Delta t\frac{d}{dt}+\xi\frac{d}{dx}+\frac{\xi^2}{2}\frac{d^2}{dx^2}]\langle x,t|x_0,t_0\rangle \tag{2.151}$$

Now we use the relations

$$\sqrt{\frac{\beta}{2\pi}}\int d\xi e^{-\frac{\beta}{2}\xi^2} = 1 \tag{2.152}$$

$$\sqrt{\frac{\beta}{2\pi}}\int d\xi\xi e^{-\frac{\beta}{2}\xi^2} = 0 \tag{2.153}$$

$$\sqrt{\frac{\beta}{2\pi}}\int d\xi\xi^2 e^{-\frac{\beta}{2}\xi^2} = \frac{1}{\beta} \tag{2.154}$$

Substituting in (2.151) yields

$$\langle x,t|x_0,t_0\rangle = [1-\frac{i}{\hbar}V(x)\Delta t-\Delta t\frac{d}{dt}+\frac{i\hbar\Delta t}{2m}\frac{d^2}{dx^2}]\langle x,t|x_0,t_0\rangle \tag{2.155}$$

Setting the terms of order Δt on the right hand side to zero leads to

$$[-i\hbar\frac{d}{dt}+V(x)-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}]\langle x,t|x_0,t_0\rangle = 0 \tag{2.156}$$

which is the Schrödinger wave equation.

2.4.4 Path integral for free particle and Harmonic oscillator

I would like now to consider some examples of computing the propagators for some of the quantum mechanical problems we considered before and show that the path integral can reproduce these results. These calculations will help illustrate the mathematical structure of the path integral and show how it can be convenient to understand the quantum dynamics in the semiclassical limit. First consider the free particle example whose energy eigenstates are the momentum eigenstates $\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}px}$ and eigenvalues are $\frac{p^2}{2m}$. Substituting in (2.148), we get

$$\langle x_f, T|x_0, 0\rangle = \frac{1}{2\pi\hbar}\int dp\, e^{-\frac{i}{\hbar}[\frac{p^2}{2m}T - p(x_i - x_f)]} = \sqrt{\frac{m}{2\pi i\hbar T}} e^{\frac{im}{2\hbar}\frac{(x_f-x_i)^2}{T}} \tag{2.157}$$

Let us check if this expression satisfies all the properties we expect. First, in the limit of $T \to 0$, this expression approaches a delta function $\delta(x_f - x_i)$. This is expected since at the initial time, the particle was at x_i. As the time increases, we see that this expression is dominated by $x_f - x_i \sim \sqrt{T}$ [8] This is very similar to the behavior of a diffusing particle and can be understood in terms of a random walk where the particle turns left or right at each step at random. It is known that after n steps, the particle explores a region of size $\sqrt{n}$ around the starting position. The reason the propagator resembles a random walk is that it contains an equal superposition of left moving states with $p < 0$ and right moving states with $p > 0$. The normalization factor $\frac{1}{\sqrt{T}}$ precisely accounts for the fact that the probability is now spread over an 'area' proportional to $\sqrt{T}$.

The same expression can be computed in the path integral as follows. First, we write any trajectory connecting x_i to x_f as $x(t) = x_{\rm cl}(t) + y(t)$ where $x_{\rm cl}(t)$ is the classical trajectory which satisfies the classical equations of motion and the boundary condition $x(0) = x_i$ and $x(T) = x_f$. For a free particle, the classical equations of motion take the simple form $\ddot{x} = 0$. Thus, $x_{\rm cl}(t) = x_i + \frac{t}{T}(x_f - x_i)$. The action $S = \frac{m}{2}\int dt \dot{x}^2$ can be expended in terms of $x_{\rm cl}$ and y leading to

$$S = \frac{m}{2}\int_0^T dt\, \dot{x}_{\rm cl}^2 + \frac{m}{2}\int_0^T dt\, \dot{y}^2 + m\int_0^T dt\, \dot{x}_{\rm cl}\dot{y} \tag{2.158}$$

The last term vanishes after integrating by parts since $\ddot{x} = 0$ and $y(0) = y(T) = 0$. We note that this is a general feature that holds beyond the simple free particle problem. The linear term in $x_{\rm cl}$ always vanishes since $x_{\rm cl}$ satisfies the classical equations of motion. The first term is the classical action given by

$$S_{\rm cl} = \frac{m(x_f - x_i)^2}{2T} \tag{2.159}$$

This gives us the propagator

$$\langle x_f, T|x_i, 0\rangle = C(T) e^{\frac{im}{2\hbar}\frac{(x_f-x_i)^2}{T}}, \qquad C(T) = \int_{y(0)=0}^{y(T)=0} \mathcal{D}y\, e^{\frac{im}{2\hbar}\int_0^T dt\, \dot{y}^2} \tag{2.160}$$

The constant $C(T)$ is independent of the initial and final positions and only depends on T. The computation of such factors will be discussed in future problem sets and sections. However, for the time being let me emphasize that the dependence of the propagator on the variables x_f and x_i is more manifest in the path integral where the exponential is just given by the action of the classical path.

The same analysis can be performed for the harmonic oscillator. Here, we can also write $x(t) = x_{\rm cl}(t) + y(t)$. The classical trajectory satisfy $\ddot{x}_{\rm cl} = -\omega^2 x_{\rm cl}$ whose general solution is $x_{\rm cl} = A\cos\omega t + B\sin\omega t$.

[8] The magnitude of the exponential is always one but its phase oscillates rapidly as the term in the exponential increases. Since we mainly use the propagator as an integration Kernel to generate time evolution (cf. Eq. 2.146), such rapidly oscillating phase leads to a neglegible contribution when integrating against any sufficiently smooth function.

The boundary conditions $x(0) = x_i$ and $x(T) = x_f$ fix the coefficients to be $A = x_i$ and $B = \frac{x_f - x_i \cos \omega T}{\sin \omega T}$. After some tedious algebra, we get

$$S_{\rm cl} = \int_0^T dt[\frac{m}{2}\dot{x}_{\rm cl}^2 - \frac{m}{2}\omega^2 x_{\rm cl}^2] = \frac{m\omega}{2\sin\omega T}[(x_f^2 + x_i^2)\cos\omega T - 2x_f x_i] \tag{2.161}$$

Here, again the action decomposes into $S[x] = S[x_{\rm cl}] + S[y]$ so the propagator takes the form

$$\langle x_f, T|x_i, 0\rangle = C_{\rm HO}(T) e^{\frac{i}{\hbar}S_{\rm cl}} \tag{2.162}$$

where $C_{\rm HO}(T)$ is some normalization constant. I would like to emphasize here two things. First, computing the propagator by summing over all harmonic oscillator eigenstates, while doable, is more tedious than the above approach which only involved solving the classical equation of motion. Second notice that the action above reduces to the free particle classical action $\frac{m(x_i - x_f)^2}{2T}m$ in the limit of small T. This is in fact a general feature that holds for any potential $V(x)$. It can be seen from the observation that at short times T, the contribution of the kinetic term to the action goes as $1/T$ whereas the contribution from the potential term goes as T. Since the total kinetic term at short times will be at least equal to $\frac{m(x_i - x_f)^2}{2T}$, we can also employ the saddle point approximation whenever this value is large compared to $\hbar$. Thus, the propagator for any potential reduces to the free particle propagator at short times.

I would like to emphasize that in general, the propagator does not have the simple form of the exponent of the classical action times a factor that only depends on the time interval T. This was a particular simplification for the harmonic oscillator (the free particle can be thought as a harmonic oscillator with $\omega \to 0$). In general, the propagator will have the form $\langle x_f, T|x_i, 0\rangle = C(T, x_i, x_f)e^{\frac{i}{\hbar}S_{\rm cl}}$.

2.4.5 Path integral for spin

We started our course by discussing the minimal quantum system, that of a spin 1/2. We found that this example is the one that best captures the formalism of kets and operators without all the complications of the continuous coordinates and infinite dimensional Hilbert spaces. For the path integral, on the other hand, we face the opposite problem. Since the formulation is rooted in continuous classical trajectories, we anticipate that the description of spin will be more subtle. In other words, since the spin 1/2 problem is the most quantum mechanical system, it is the hardest one to come up with a classical analog for. This is one of the reasons why it took a long time between the initial development of path integrals in the late 40s to the final development of the path integral for spins in the 80s. With hindsight, there is nothing really complicated about the path integral for spins, just a novel conceptual ingredient that ensures the pecularities of the finite dimensional Hilbert space is accounted for.

For definiteness, let us consider the Hamiltonian

$$\mathcal{H} = \gamma \boldsymbol{B} \cdot \boldsymbol{S} \tag{2.163}$$

where γ is the gyromagnetic ratio $\gamma = \frac{|e|}{mc}$ and we are assuming a particle with charge $-e$. How will we go about formulating a path integral to this problem? We would like to construct the most classical representation possible for spin states. We have seen before that the ket for a spin 1/2 state whose spin is pointing in a general direction $\hat{n}$ is described

$$|\hat{n}\rangle = \cos\frac{\theta}{2}|+\rangle + \sin\frac{\theta}{2}e^{i\phi}|-\rangle \tag{2.164}$$

which can describe any spin orientation. For example, if $|+\rangle$ and $|-\rangle$ describes spin polarization in the z-direction, then $\theta = 0, \pi$ describes the $|\pm z\rangle$ state, $\theta = \pi/2$, $\phi = 0, \pi$ describe $|\pm x\rangle$ and $\theta = \pi/2$, $\phi = \pm\pi/2$ describe $|\pm y\rangle$. This state is the closest to a classical spin vector we can write and it satisfies the expected relation

$$\langle\hat{n}|\boldsymbol{S}|\hat{n}\rangle = \frac{\hbar}{2}\hat{n} \tag{2.165}$$

We now want to derive a path integral representation for the propagator $\langle \hat{n}_f, T|\hat{n}_i, 0\rangle = \langle \hat{n}_f|e^{-\frac{i}{\hbar}\mathcal{H}T}|\hat{n}_i\rangle$. We can now divide the time interval T into N intervals with width $\Delta t = T/N$. Recall that the crucial step in our derivation was inserting the resolution of the identity. Now our basis states $|\pm\rangle$ do provide a resolution of unity

$$\sum_{\sigma=\pm} |\sigma\rangle\langle\sigma| = \mathbb{1} \tag{2.166}$$

However, attempting to derive the path integral by inserting the above identity will not lead to a continuous family of classical paths. Instead, the paths will have to jump between $|+\rangle$ and $|-\rangle$ which will not yield a continuous limit when the intervals get very short. The problem arises from the fact that, to derive path integrals, we need a resolution of unity in terms of a set of states that **varies continuously in space**. For the position and momentum basis, this happened also to be the natural basis of the problem but for spin states, this is not the case. To resolve this issue, recall that we did not require that the resolution of unity used an orthonormal basis. Instead, it suffices to have a complete basis. We have seen from our discussion of coherent states that we can have complete sets of states that provide a resolution of unity without being orthogonal. In fact, we will see now that the states (2.164) are overcomplete and thus provide a resolution of unit. First, it is clear that $|\hat{n}\rangle$ and $|\hat{n}'\rangle$ are generally non-orthogonal since

$$\langle \hat{n}|\hat{n}'\rangle = \left(\frac{1+\hat{n}\cdot\hat{n}'}{2}\right)^{1/2} \tag{2.167}$$

Second note that we can write a resolution of unity using

$$\int d\hat{n}|\hat{n}\rangle\langle\hat{n}| = \frac{1}{\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta |\hat{n}\rangle\langle\hat{n}| = |+\rangle\langle+| + |-\rangle\langle-| = \mathbb{1} \tag{2.168}$$

We can now write the expression for the propagator with the resolution of unity inserted $n-1$ times and define $\hat{n}_0 = \hat{n}_i$ and $\hat{n}_N = \hat{n}_f$

$$\langle \hat{n}_f, T|\hat{n}_i, 0\rangle = \int \prod_{i=1}^{N-1} d\hat{n}_i \prod_{l=1}^{N} \langle \hat{n}_l|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|\hat{n}_{l-1}\rangle \tag{2.169}$$

Similar to out discussion last lecture, we can simplify the time evolution over a very short time segment as

$$\begin{aligned}
\langle \hat{n}_l|e^{-\frac{i}{\hbar}\mathcal{H}\Delta t}|\hat{n}_{l-1}\rangle &= \langle \hat{n}_l|\hat{n}_{l-1}\rangle - \gamma\frac{i}{2}\Delta t\boldsymbol{B}\cdot\hat{n}\langle\hat{n}_l|\hat{n}_l\rangle \\
&= 1 + [\langle \hat{n}_l|\hat{n}_{l-1}\rangle - \langle\hat{n}_l|\hat{n}_l\rangle] - \gamma\frac{i}{2}\Delta t\boldsymbol{B}\cdot\hat{n} \\
&= 1 + \Delta t[-\langle\hat{n}_l|\partial_t\hat{n}_l\rangle - \gamma\frac{i}{2}\boldsymbol{B}\cdot\hat{n}] = e^{-\Delta t[\langle\hat{n}_l|\partial_t\hat{n}_l\rangle + \frac{i}{2}\gamma\boldsymbol{B}\cdot\hat{n}]}
\end{aligned} \tag{2.170}$$

Here, we have assumed that $\hat{n}$ does not change much over an infinitesmal interval Δt. Substituting in (2.169) gives

$$\langle \hat{n}_f, T|\hat{n}_i, 0\rangle = \int \mathcal{D}\hat{n}(t) e^{\frac{i}{\hbar}S[\hat{n}(t)]}, \qquad \mathcal{D}\hat{n}(t) = \prod_{i=1}^{N-1} d\hat{n}_i, \qquad S[\hat{n}(t)] = \hbar\int_0^T dt[i\langle n|\partial_t n\rangle - \frac{\gamma}{2}\boldsymbol{B}\cdot\hat{n}] \tag{2.171}$$

The second term above is the term we expect from the Hamiltonian by thinking of $\boldsymbol{B}\cdot\boldsymbol{S}$ as a potential energy. The first term is the unexpected term that crucially captures the essense of the quantum mechanical nature of the spin. It can be understood as the analog of the classical $p\dot{x}$ term that is used in the Legendre transform to construct the Lagrangian from the Hamiltonian. Before discussing the properties of this term, let me briefly mention that for more general spins, we can define some different kets $|\hat{n}\rangle$ that still satisfy the relation [9]

$$\langle\hat{n}|\boldsymbol{S}|\hat{n}\rangle = \hbar s\hat{n} \tag{2.172}$$

[9] We will discuss the formalism for higher spins in detail in the next weeks

in addition to the resolution of unity (2.168). Following the same steps, we get the path integral (2.171) with the action changed to

$$S[\hat{n}(t)] = 2s\hbar \int_0^T dt[i\langle \hat{n}|\partial_t \hat{n}\rangle - \frac{\gamma}{2}\boldsymbol{B}\cdot\hat{n}] \tag{2.173}$$

Notice that nothing in our analysis explicitly referred to the fact that the spin is integer or half-integer. We only required the two relations (2.172) and (2.168). As it turns out, the action (2.173) already knows about the quantization of spin as we will see now. Let us focus on the second term of the action

$$S_B[\hat{n}(t)] = 2i\hbar s \int_0^T dt\langle \hat{n}|\partial_t \hat{n}\rangle \tag{2.174}$$

We first note that this term is real since $\langle \partial_t \hat{n}|\hat{n}\rangle^* = \langle \hat{n}|\partial_t\hat{n}\rangle = -\langle \partial_t\hat{n}|\hat{n}\rangle + \partial_t\langle \hat{n}|\hat{n}\rangle = -\langle \partial_t\hat{n}|\hat{n}\rangle$. Second notice that this term only depends on the path $\hat{n}$ takes but not how fast it does it. This can be seen by rescaling $t \mapsto \lambda t$ (with $\hat{n}(\lambda T) = \hat{n}_f$) which does not change the value of the expression. These terms are called geometric terms (in contrast to dynamical terms). To understand the behavior of this term more, let us write it explicitly

$$S_B[\hat{n}(t)] = -\hbar s \int_0^T dt\dot{\phi}(1-\cos\theta) \tag{2.175}$$

The geometric meaning of this term can be made more obvious by noting that the velocity of a point moving on a sphere described by the unit vector $\hat{n}$ is $\dot{\hat{n}} = \dot{\phi}\sin\theta\hat{e}_\phi + \dot{\theta}\hat{e}_\theta$. This leads to the expression

$$S_B[\hat{n}(t)] = -\hbar s \int_0^T dt\,\dot{\hat{n}}\cdot\boldsymbol{A}[\hat{n}] = -\hbar s\int_{\hat{n}_i}^{\hat{n}_f} d\hat{n}\cdot\boldsymbol{A}[\hat{n}], \qquad \boldsymbol{A}[\hat{n}] = \frac{1-\cos\theta}{\sin\theta}\hat{e}_\phi \tag{2.176}$$

Notice that the potential $\boldsymbol{A}$ is singular at the south pole $\theta = \pi$. The form (2.176) makes it clear that S_B only depends on the trajectory taken by $\hat{n}$ but not how fast or slow it is traversed. Let us now consider the special case of $\hat{n}_f = \hat{n}_i$. Our theory should be valid for any initial and final values including when they are equal. In this case, we can rewrite the line integral in (2.176) using Stokes theorem as an integral over area enclosed by the path

$$S_B[\hat{n}(t)] = -\hbar s\int d\boldsymbol{S}\cdot\tilde{\boldsymbol{B}}, \qquad \tilde{\boldsymbol{B}} = \nabla\times\boldsymbol{A} = \hat{e}_r \tag{2.177}$$

Notice however that there is an ambiguity in the expression above: a closed path on the circle divides it into two areas (See Fig. 2.5). Each can be said to be 'enclosed' by it [10]. In order for the theory to be consistent, these two alternatives should be equivalent. Since the area needs to be taken with opposite sign for the two regions, the different between the two choices is

$$S_{B,2}-S_{B,1} = \hbar s\int_{\text{region},1} d\boldsymbol{S}\cdot\tilde{\boldsymbol{B}} + \hbar s\int_{\text{region},2} d\boldsymbol{S}\cdot\tilde{\boldsymbol{B}} = S_{B,1}-S_{B,2} = \hbar s\int_{\text{sphere}} d\boldsymbol{S}\cdot\tilde{\boldsymbol{B}} = 4\pi\hbar s \tag{2.178}$$

Although the difference is non-zero, we note that the action only affects the physics through the exponential factor $e^{\frac{i}{\hbar}S}$ which means that changes in the action by an integer multiple of $2\pi\hbar$ do not change the physics. This imposes the condition

$$4\pi\hbar s = 2\pi m\hbar, \quad \Longrightarrow \quad s = \frac{m}{2} \tag{2.179}$$

for m an arbitrary integer. Remarkably, we have derived the quantization of spin from the requirement that the path integral we derived is consistent!

There are a lot of deep and interesting physics hidden inside the term S_B above. Beside the fact that it enforces a quantization condition and that it is geometric, it also have the singular behavior at $\theta = \pi$. In addition, you can convince yourself it is not gauge invariant; For example, under the transformation $|\hat{n}\rangle \mapsto$

[10] Recall the proof of Stokes theorem which divides the area into small regions and show the cancellation of the curl between them

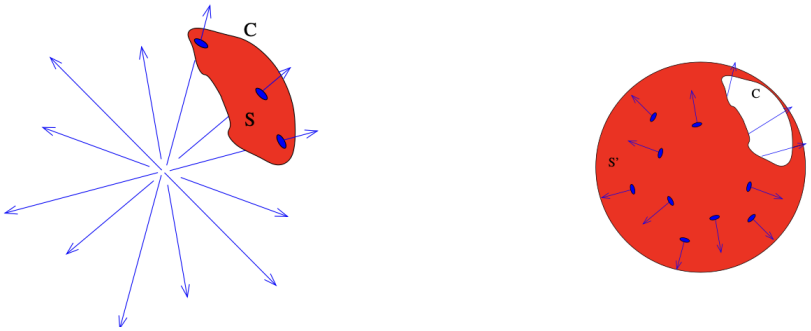

Figure 2.5: Illustration of the two possible choices of area on the unit sphere to compute the magnetic flux enclosed by a closed curve [Figure adapted from David Tong's lecture notes on Gauge theory]

$e^{-i\phi}|\hat{n}\rangle$ which does not alter the relations (2.172) and (2.168), this term changes to $\hbar s \int_0^T dt\dot{\phi}(1+\cos\theta)$. We see that the singularity is now at the north pole rather than the south pole. The difference between this new term and the original one for loops $n_i = n_f$ turns out to again given a factor of $4\pi\hbar sm$ that drops out from the path integral. For more general phases, it changes the action by a boundary term which yields an unimportant overall phase for the propagator.

Let me summarize the properties of the term S_B below:

1. It depends on the path $\hat{n}(t)$ but not how fast it is traversed. We say such a term is geometric.
2. Its prefactor should be quantized to have a consistent theory
3. It is not gauge invariant in general. For paths starting and ending at the same point it changes by a multiple of $4\pi\hbar s$ which drops out of the amplitude for integer or half-integer s.
4. It describes the motion of a particle in a singular vector potential.

Each of these properties turn out to have far-reaching consequences beyond the specific example of the spin path integral that we will discuss during this and the next lecture. However, before doing that, let us see how the spin path integral above reproduces some of the results about spin $1/2$ systems we know obtained previously using the operator formalism.

Let us first see what kind of classical equations of motion we would get from the action (2.175). Without loss of generality, we can choose the field B to point in the z direction, $\boldsymbol{B} = B\hat{z}$. Then the action takes the form

$$S[\theta,\phi] = -\frac{\hbar}{2}\int_0^T dt[\dot{\phi}(1-\cos\theta) + \gamma B\cos\theta] \tag{2.180}$$

The classical equations of motion are derived by replacing $\theta \mapsto \theta + \delta\theta$ and $\phi \mapsto \phi + \delta\phi$ and setting the linear terms in $\delta\theta$ and $\delta\phi$ to zero. This leads to

$$\delta S = -\frac{\hbar}{2}\int_0^T dt[\delta\phi\frac{d}{dt}\cos\theta + (\dot{\phi}-\gamma B)\sin\theta\delta\theta] \tag{2.181}$$

Setting the terms proportional to $\delta\theta$ and $\delta\phi$ to zero gives the equations

$$\theta(t) = \text{const.} = \theta(0), \qquad \dot{\phi}(t) = \gamma B = \omega \tag{2.182}$$

This describes spin precession around the z axis where the z-component $n_z = \cos\theta$ remains unchanged as a function of time while the x and y components rotate with frequency ω, $n_x = \sin\theta\cos\phi = \sin\theta\cos\omega t$ and $n_y = \sin\theta\sin\phi = \sin\theta\sin\omega t$. Thus, the classical equations of motion reproduce the physics of spin precession we obtained from the operator formalism. Note that the first term in the action was crucial to obtain this result. Without it, we would have obtained the wrong equation of motion $\sin\theta = 0$.

I want to briefly mention a very intriguing connection between the path integral for the propagator $\langle f|e^{-\frac{i}{\hbar}\mathcal{H}T}|i\rangle$ and the partition function of statistical mechanical systems at inverse temperature β (recall that inverse temperature is $\frac{1}{k_B T}$ where k_B is the Boltzmann constant and T is temperature) given by $\mathcal{Z} = \sum_\alpha \langle\alpha|e^{-\beta\mathcal{H}}|\alpha\rangle = \mathrm{tr}e^{-\beta\mathcal{H}}$. Formally, these two expressions seem related by the replacement $T = -i\hbar\beta$ i.e. a system at finite temperature looks like a dynamical quantum system propagating in imaginary time. This correspondence can be implemented in a transparent in the path integral formalism. The reason is that for integrals, we can always deform the integration contour as long as we do not encounter any singularity. Thus, in many cases we can actually deform the contour in a path integral to relate a quantum mechanical propagator to a statistical partition function in imaginary time. Such deformation to imaginary time is called Wick rotation $t \mapsto -i\hbar\tau$. It changes the action into

$$\frac{i}{\hbar}S = -\int_0^\beta d\tau \left\{\frac{1}{2}m\dot{x}^2 + V(x)\right\} \tag{2.183}$$

Importantly, the relative sign between kinetic and potential term is now positive and we get the total energy integrated over time in the exponential instead of the action. Beside its usefulness in relating quantum mechanical models to statistical mechanical models, Wick rotation can also be useful in evaluating quantum mechanical path integrals, particularly for problems where the classical equations of motion has no solution for real time which usually happens for tunneling problems. Such problems usually have some stationary (or saddle point) solutions in imaginary time.

One final aspect we want to illustrate about the spin path integral is how the finite dimensional Hilbert space is reproduced in this formalism which again can be traced to the term S_B. For such calculation, it is very convenient to use imaginary time and think of the partition function of the spin $1/2$ system which can be written simply in operator language

$$\mathcal{Z} = \sum_{\sigma=\pm} e^{-\beta B\frac{\hbar\gamma}{2}\sigma} = 2\cosh\frac{\hbar\gamma\beta B}{2} \tag{2.184}$$

To derive the same result in path integral, we rewrite S_B as (note that S_B has the same form in real and imaginary time)

$$\begin{aligned} S_B[\theta,\phi] &= -\frac{\hbar}{2}\int_0^\beta d\tau\dot{\phi}(1-\cos\theta) = -\frac{\hbar}{2}\int_0^\beta d\tau\phi\frac{d}{d\tau}\cos\theta - \frac{\hbar}{2}\phi(\tau)[1-\cos\theta(\tau)]|_{\tau=0}^{\tau=\beta} \\ &= -\frac{\hbar}{2}\int_0^\beta d\tau\phi\frac{d}{d\tau}\cos\theta - \frac{\hbar}{2}2\pi k[1-\cos\theta(0)] \end{aligned} \tag{2.185}$$

In the first line, we used integration by parts. In the second line, we used the boundary conditions, $\cos\theta(\beta) = \cos\theta(0)$ and $\phi(\beta) = \phi(0) + 2\pi k$. Thus, the full action has the form

$$S[\theta,\phi] = -\frac{\hbar}{2}\int_0^\beta d\tau\phi\frac{d}{d\tau}\cos\theta - \frac{i}{2}\int_0^\beta d\tau\gamma B\cos\theta - \hbar\pi k[1-\cos\theta(0)] \tag{2.186}$$

Notice that the dependence on ϕ is only contained in the first term. The path integral over ϕ can be evaluated explicitly by noting that

$$\int \mathcal{D}\phi(t)e^{-\frac{i}{2}\int_0^\beta d\tau\phi\frac{d}{d\tau}\cos\theta} = \int\prod_{l=1}^{N-1} d\phi_l e^{-\frac{i}{2}\phi_l(\cos\theta_l - \cos\theta_{l-1})} = \prod_{l=1}^{N-1}\delta(\cos\theta_l - \cos\theta_{l-1}) \tag{2.187}$$

This means that $\cos\theta(t)$ is a constant and the action reduces to

$$S[\theta] = \frac{i\hbar^2}{2}\beta\gamma B\cos\theta(0) - \hbar\pi k[1-\cos\theta(0)] \tag{2.188}$$

The full result for the partition function is obtained by integrating over the initial value $\theta(0)$ and performing the summation over the integer k leading to

$$\mathcal{Z} = \sum_{k=-\infty}^{\infty} \int_0^{\pi} d\theta \sin\theta \, e^{-i\pi k[1-\cos\theta] - \frac{\hbar}{2}\beta\gamma B\cos\theta} = \sum_{k=-\infty}^{\infty} \int_{-1}^{1} dx \, e^{-i\pi k[1-x] - \frac{\hbar}{2}\beta\gamma Bx}$$
$$\propto \sum_{m=-\infty}^{\infty} \int_{-1}^{1} dx \, \delta(1-x-2m) \, e^{-\frac{\hbar}{2}\beta\gamma Bx} = 2\cosh\frac{\hbar\beta\gamma B}{2} \tag{2.189}$$

2.5 The adiabatic approximation and Berry phase

Let us now get back to the first term in the action (2.175). This term turns out to represent a very important effect in quantum mechanics called the Berry phase. To understand how the Berry phase appears in a more general context, consider a Hamiltonian that changes in time. For sufficiently slow changes, we can apply a result called the adiabatic theorem to significantly simplify the analysis of the problem. The adiabatic theorem is the statement that for suffficiently slow changes in the Hamiltonian, a state that was the eigenstate of the initial Hamiltonian at time $t = 0$, remains an instantaneous eigenstate at finite time t. The statement makes intuitive sense. For example, consider the spin Hamiltonian $\mathcal{H} = \gamma \boldsymbol{B} \cdot \boldsymbol{S}$. If we take $\boldsymbol{B}$ to be time-dependent and start with $\boldsymbol{B}(t=0) = B\hat{z}$ then slowly rotate $\boldsymbol{B}$ away from the z-plane, we expect a system initially in the ground state $|\alpha, t=0\rangle = |z+\rangle$ to slowly rotate to follow the direction of $\boldsymbol{B}$.

2.5.1 Berry phase definition

Now consider for simplicitly a Hamiltonian that changes in time such that $\mathcal{H}(T) = \mathcal{H}(0)$ and assume the change is sufficiently slow such that the adiabatic theorem is valid (this will be made more precise below). The adiabatic theorem tells us that if we start in the ground state at $t = 0$, we end up at the ground state at $t = T$. However, remember that a state in quantum mechanics is specified by a ray in the Hilbert space. This means that going back to the same state means that

$$|\psi, T\rangle = e^{i\gamma}|\psi, 0\rangle \tag{2.190}$$

For a long time, it was thought that the phase factor γ is unimportant and can be dropped. However, it turned out that it is physically measurable. The reason is that this is really a phase difference. To see this, imagine taking an electron that could take to possible paths, one involving the slowly changing Hamiltonian and one that doesn't. The interference pattern between these paths will be sensitive to the phase γ. This is precisely what happens in the Aharonov-Bohm effect which will be discussed in the next lecture.

To derive the explicit form of the phase γ and clarify what we mean by slow changes in the Hamiltonian, let us introduce the simultaneous eigenkets and eigenvalues of a Hamiltonian $\mathcal{H}(t)$ as

$$\mathcal{H}(t)|\psi_n(t)\rangle = E_n(t)|\psi_n(t)\rangle \tag{2.191}$$

We emphasize here that $|\psi_n(t)\rangle$ does not correspond to any unitary time evolution associated with the Hamiltonian. Instead, it represents the eigenbasis of the Hamiltonian $\mathcal{H}(t)$. Now consider the time-dependent Schrödinger equation for a general ket $|\alpha, t\rangle$:

$$i\hbar\frac{d}{dt}|\alpha, t\rangle = \mathcal{H}(t)|\alpha, t\rangle \tag{2.192}$$

Since $|\psi_n(t)\rangle$ is a complete basis, we can expand any state in terms of it:

$$|\alpha, t\rangle = \sum_n c_n(t)|\psi_n(t)\rangle \tag{2.193}$$

It s important to note here that both the coefficients $c_n(t)$ and the basis states $|\psi_n(t)\rangle$ depend on t. The first through the time evolution governed by the Schrödinger equation and the second through the fact that the Hamiltonian itself is time-dependent. Substituting in the Schrödinger equation, we get

$$i\hbar \sum_n [\dot{c}_n(t)|\psi_n(t)\rangle + c_n(t)\frac{d}{dt}|\psi_n(t)\rangle] = \sum_n c_n(t)E_n(t)|\psi_n(t)\rangle \tag{2.194}$$

Multiplying both sides by $\langle\psi_m(t)|$ and using the orthonormality of the eigenkets: $\langle\psi_m(t)|\psi_n(t)\rangle = \delta_{nm}$, we get

$$\dot{c}_m(t) = -\frac{i}{\hbar}E_m(t)c_m(t) - \sum_n c_n(t)\langle\psi_m(t)|\frac{d}{dt}\psi_n(t)\rangle \tag{2.195}$$

Note that the second term vanishes if the Hamiltonian is time-independent. To simplify the second term on the right hand side, we take the time derivative of Eq. 2.191:

$$\dot{\mathcal{H}}(t)|\psi_n(t)\rangle + \mathcal{H}(t)\frac{d}{dt}|\psi_n(t)\rangle = \dot{E}_n(t)|\psi_n(t)\rangle + E_n(t)\frac{d}{dt}|\psi_n(t)\rangle \tag{2.196}$$

Again acting with $\langle\psi_m(t)|$ on both sides, we get

$$\langle\psi_m(t)|\dot{\mathcal{H}}(t)|\psi_n(t)\rangle = \dot{E}_n(t)\delta_{nm} + [E_n(t) - E_m(t)]\langle\psi_m(t)|\frac{d}{dt}|\psi_n(t)\rangle \tag{2.197}$$

Thus, for $n \neq m$, we get

$$\langle\psi_m(t)|\frac{d}{dt}\psi_n(t)\rangle = \frac{\langle\psi_m(t)|\dot{\mathcal{H}}(t)|\psi_n(t)\rangle}{E_n(t) - E_m(t)} \tag{2.198}$$

Substituting in (2.195) and separating the terms $n = m$ and $n \neq m$, we get

$$\dot{c}_m(t) = -[\frac{i}{\hbar}E_m(t) + \langle\psi_m(t)|\frac{d}{dt}\psi_n(t)\rangle]c_m(t) - \sum_{n\neq m} c_n(t)\frac{\langle\psi_m(t)|\dot{\mathcal{H}}(t)|\psi_n(t)\rangle}{E_n(t) - E_m(t)} \tag{2.199}$$

The adiabatic approximation corresponds to neglecting the last term in the expression above. This is justified if the Hamiltonian changes slowly which means that its matrix elements $\langle\psi_m(t)|\dot{\mathcal{H}}(t)|\psi_n(t)\rangle$ for $n \neq m$ are small compared to the gap $E_n(t) - E_m(t)$ [11]. Once we ignore this term, we see that if $c_m(0) = 0$, then $c_m(t) = 0$ which means that if we start at an eigenstate at $t = 0$, we always remain in that eigenstate for all time t.

For a given m, we can solve Eq. 2.199 to get

$$c_m(t) = e^{i\gamma_n(t) - \frac{i}{\hbar}\int_0^t dt' E_m(t)}c_m(0) \tag{2.200}$$

The second term in the exponent is the expected dynamical phase which simply generalizex the factor $e^{-\frac{i}{\hbar}E_m T}$ to the time-dependent case. The first term, however, is different. It is explicitly given by

$$\gamma_n(t) = i\int_0^t dt' \langle\psi_n(t)|\frac{d}{dt}\psi_n(t)\rangle \tag{2.201}$$

This term is called the Berry phase. Notice that this term has the same form as the first term that appears in the path integral action for the spin problem with $|\psi_n(t)\rangle$ replaced by $|\hat{n}(t)\rangle$. The Berry phase is manifestly real since

$$\langle\psi_n(t)|\frac{d}{dt}\psi_n(t)\rangle = \frac{d}{dt}\langle\psi_n(t)|\psi_n(t)\rangle - \langle\frac{d}{dt}\psi_n(t)|\psi_n(t)\rangle = -\langle\psi_n(t)|\frac{d}{dt}\psi_n(t)\rangle^* \tag{2.202}$$

which means that $\langle\psi_n(t)|\frac{d}{dt}\psi_n(t)\rangle$ is purely imaginary.

[11] The quantitiy $\frac{\langle\psi_m(t)|\dot{\mathcal{H}}(t)|\psi_n(t)\rangle}{E_n(t)-E_m(t)} \sim \frac{1}{\tau}$ has units of inverse time. To neglect it, τ needs to be long compared to the characteristic time scale of the state of interest given by the inverse of the first term on the right hand side in (2.199)

2.5.2 Berry curvature

The Berry phase features prominently in problems where the Hamiltonian depends on a set of continuous parameters R^a and we consider a trajetory in parameter space R^a as a function of time. For instance, we can think of the Hamiltonian for a 3D particle in a potential which confines the particle in a box (the potential is infinite outside the box). We can then move this box as a function of time which effectively implements moving the confining potential of the electron slowly in space. Another application is in band theory. Here, we have a Hamiltonian with discrete translation symmetry whose eigenstates are labelled by an analog of momentum called crystal momentum, that is defined modulo $2\pi/a$ (a is the lattice constat) in each direction. This means that crystal momentum parametrizes a torus. We can consider state at momentum at crystal momentum $k^a(t)$ which depends on time.

If the Hamiltonian only depends on time through the parameters $R^a(t)$, the same will be the case for $|\psi_n(t)\rangle$. We will denote by $\boldsymbol{R}$, the vector whose components are the parameters R^a such that

$$\mathcal{H}(\boldsymbol{R})|\psi_n(\boldsymbol{R})\rangle = E_n(\boldsymbol{R})|\psi_n(\boldsymbol{R})\rangle \tag{2.203}$$

Then we can write the Berry phase as

$$\gamma = i\int_0^t dt' \dot{R}^a \langle\psi_n(\boldsymbol{R})|\frac{\partial}{\partial R^a}|\psi_n(\boldsymbol{R})\rangle = i\int_{\boldsymbol{R}=\boldsymbol{R}(0)}^{\boldsymbol{R}=\boldsymbol{R}(t)} dR^a \langle\psi_n(\boldsymbol{R})|\frac{\partial}{\partial R^a}|\psi_n(\boldsymbol{R})\rangle = \int_{\boldsymbol{R}=\boldsymbol{R}(0)}^{\boldsymbol{R}=\boldsymbol{R}(t)} d\boldsymbol{R}\cdot\mathcal{A}(\boldsymbol{R}) \tag{2.204}$$

Here, we used the convention where repeated upper/lower indices are summed over. This illustrates that the Berry phase is in general a geometric phase that depends on the path in parameter not on how fast it is traversed. The quantity $\mathcal{A}$ is called the Berry connection:

$$\mathcal{A}_a(\boldsymbol{R}) = i\langle\psi_n(\boldsymbol{R})|\frac{\partial}{\partial R^a}|\psi_n(\boldsymbol{R})\rangle \tag{2.205}$$

The quantity $\mathcal{A}_a$ shares several features with the more familiar electromagnetic vector potential. First, note that Eq. 2.203 which defines the instantaneous eigenstates does not fix the overall phase of the wavefunction $|\psi_n(\boldsymbol{R})\rangle$ [12]. This means that we have the freedom to multiply the ket $|\psi_n(\boldsymbol{R})\rangle$ by any **$\boldsymbol{R}$-dependent phase** $e^{-i\varphi(\boldsymbol{R})}$. Under such transformation, the Berry connection changes as

$$\mathcal{A}_a(\boldsymbol{R}) \mapsto \mathcal{A}_a(\boldsymbol{R}) + \partial_a\varphi(\boldsymbol{R}) \tag{2.206}$$

which is precisely how the electromagnetic vector potential changes under gauge transformation. This suggests defining the gauge invariant quantity

$$\mathcal{F}_{ab} = \partial_a\mathcal{A}_b - \partial_b\mathcal{A}_a \tag{2.207}$$

which is called the Berry curvature. If the parameter space spanned by $\boldsymbol{R}$ is two-dimensional, the Berry curvature has a simple form since it reduces to a scalar $F_{ab}(\boldsymbol{R}) = \epsilon_{ab}\Omega(\boldsymbol{R})$ (here ϵ_{ab} is the antisymmetric tensor).

The Berry phase associated with any close path $\mathcal{C}$ can be written in terms of the flux of the Berry curvature across any 2D surface $\mathcal{S}$ enclosing this path

$$\gamma = i\oint_{\mathcal{C}} dR^a\mathcal{A}_a = i\int_{\mathcal{S}} d\mathcal{S}^{ab}\mathcal{F}_{ab} \tag{2.208}$$

We emphasize here that the Berry phase is obtained by a one-dimensional line integral of the Berry connection or a two-dimensional surface integral of the Berry curvature **irrespective of the dimension of the parameter space**. Another way to say this is that the Berry connection is a one-form and the Berry curvature is a two-form.

[12] this is always the case for wavefunctions defined as the eigenfunctions of some operator

This leads naturally to the question: can there be sources for the Berry curvature? the answer turns out to be yes. Sources of the Berry curvature are points in the parameter space where the energy eigenvalues become degenerate such that the adiabatic approximation becomes invalid and the Berry curvature becomes singular. However, similar to the argument we employed last time, the Berry curvature associated with such sources has to be constrained to yield a well-defined theory. To see this, consider any closed 2D surface $\mathcal{M}$ and consider the Berry phase along any closed path $\mathcal{C}$. Similar to what we did last lecture, we can write this as the surface integral of Berry curvature in two possible ways corresponding to the two surfaces on $\mathcal{M}$ whose boundary is $\mathcal{C}$. These two choices should give the same phase up to integer multiples of 2π. This means that the integral of the Berry curvature across all $\mathcal{M}$ should be quantized

$$\int_{\mathcal{M}} d\mathcal{S}^{ij}\mathcal{F}_{ij} = 2\pi C \tag{2.209}$$

The integer C is called the Chern number. This means that sources of the Berry curvature has to have integer charge.

One of the most prominent application of these ideas is in topological band theory. For example, in two spatial dimensions, the crystal momentum lives on the two-dimensional torus. The Berry curvature is simply a scalar on this torus whose integral over the entire torus is quantized in integer multiples of 2π. The Chern number in this case has very clear physical manifestation. It yields the Hall conductance of the system measured in units e^2/h and is responsible for the perfect quantization plateaus observed in the quantum Hall effect.

2.5.3 Examples of Berry phase

The discussion of Berry phase has so far been very general and abstract. We will now illustrate all these concepts using a simple example. Let us again consider the Hamiltonian

$$\mathcal{H}(\boldsymbol{B}) = \frac{\hbar\gamma}{2}\boldsymbol{B}\cdot\boldsymbol{\sigma} \tag{2.210}$$

where we will now think of the magnetic field $\boldsymbol{B}$ as an external parameter that we are changing. Remember $\boldsymbol{\sigma}$ are the Pauli matrices defined as

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.211}$$

Writing $\boldsymbol{B} = B(\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta)$, we can write the Hamiltonian as

$$\mathcal{H}(\boldsymbol{B}) = \frac{\hbar\gamma}{2}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} = \frac{\hbar\gamma B}{2}\begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix} \tag{2.212}$$

The ground state of this Hamiltonian is $|-,\boldsymbol{B}\rangle = \begin{pmatrix} \sin\frac{\theta}{2} \\ -e^{i\phi}\cos\frac{\theta}{2} \end{pmatrix}$ [13]. This gives the Berry connection

$$\mathcal{A}_\theta = i\langle -,\boldsymbol{B}|\partial_\theta|-,\boldsymbol{B}\rangle = 0, \qquad \mathcal{A}_\phi = i\langle -,\boldsymbol{B}|\partial_\phi|-,\boldsymbol{B}\rangle = \cos^2\frac{\theta}{2} = \frac{1+\cos\theta}{2} \tag{2.213}$$

This gives the Berry curvature

$$\mathcal{F}_{\theta\phi} = -\frac{1}{2}\sin\theta \tag{2.214}$$

[13] A quick way to see this is to notice that the Hamiltonian has the form $\mathcal{H}(\boldsymbol{B}) = \frac{\hbar\gamma}{2}U^\dagger\sigma_z U$ with $U = e^{\frac{i}{2}\theta\sigma_y}e^{\frac{i}{2}\phi\sigma_z}$. Thus, its ground state is $|-,\boldsymbol{B}\rangle = U^\dagger\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} -e^{-\frac{i}{2}\phi}\sin\frac{\theta}{2} \\ e^{\frac{i}{2}\phi}\cos\frac{\theta}{2} \end{pmatrix}$ which is related to the expression in the main text by multiplication by a simple phase.

with all other components vanishing. The Berry curvature has a more transparent form in Cartesian coordinates given by [14]

$$\mathcal{F}_{ij} = -\epsilon_{ijk}\frac{B^k}{2|B|^3} \tag{2.215}$$

We can define a magnetic field in the parameter space (which is parametrized by the real magnetic field $\boldsymbol{B}$). Recall that the magnetic field is related to the field tensor via

$$\mathcal{B}_i(\boldsymbol{B}) = -\frac{1}{2}\epsilon_{ijk}F^{jk} = -\frac{B_i}{2|B|^3} \tag{2.216}$$

Notice that this field is singular at the origin. This is the point where the two eigenstates of the Hamiltonian are degenerate and the adiabatic approximation fails. This point acts as a source for Berry curvature. Integrating this field over a sphere in the $\boldsymbol{B}$ space gives -2π consistent with our discussion of quantized Chern number.

2.6 Electromagnetism in quantum mechanics

2.6.1 Electromagnetic gauge fields and the Schrödinger equation

We have already been discussing several examples that behave like the electromagnetic gauge field. Now we are going to discuss how the actual electromagnetic field behaves in the quantum theory. Recall that in Maxwell theory, the electromagnetic scalar and vector potentials are defined via

$$\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}, \qquad \boldsymbol{E} = -\boldsymbol{\nabla}\phi - \frac{\partial}{\partial t}\boldsymbol{A} \tag{2.217}$$

The first equation follows from the Maxwell equation $\boldsymbol{\nabla}\cdot\boldsymbol{B} = 0$ which forbids the existence of magnetic monopole. We will get back to this later and see that there is actually a loop hole that allows for the existence of monopoles despite Eq. 2.217 (provided that the vector potential $\boldsymbol{A}$ is not globally defined). The second equation ensures the Maxwell equation $\boldsymbol{\nabla}\times\boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}$. Importantly, the scalar and vector potentials yield a redundant description for the physics since the gauge transformation

$$\boldsymbol{A} \mapsto \boldsymbol{A} + \boldsymbol{\nabla}\Lambda, \qquad \varphi \mapsto \varphi - \frac{\partial}{\partial t}\Lambda \tag{2.218}$$

leaves the $\boldsymbol{E}$ and $\boldsymbol{B}$ fields invariant. For this reason, the gauge potentials are usually thought in the classical context as a convenient tool to introduce electromagnetism in the Hamiltonian and Lagrangian formalisms but not as an essential ingredient of the physics. The latter only depends on the physical fields $\boldsymbol{E}$ and $\boldsymbol{B}$. As we will see, the situation is different in the quantum theory where there is a sense in which gauge fields are fundamental objects.

In the Hamiltonian formulation of classical physics, the gauge fields $\boldsymbol{A}$ and V enter the Hamiltonian for a particle with charge q through

$$H = \frac{1}{2m}(\boldsymbol{p} - q\boldsymbol{A})^2 + q\varphi \tag{2.219}$$

This ensures that the Hamilton's equations of motion yields correct law for the force exerted on a charged particle (the Lorentz force)

$$\dot{\boldsymbol{x}} = \frac{1}{m}(\boldsymbol{p} - q\boldsymbol{A}), \qquad \dot{\boldsymbol{p}} = -\boldsymbol{\nabla}H = q(\boldsymbol{E} + \dot{\boldsymbol{x}}\times\boldsymbol{B}) \tag{2.220}$$

In the Lagrangian formulation, this corresponds to the Lagrangian

$$L = \boldsymbol{p}\cdot\dot{\boldsymbol{x}} - H = \frac{1}{2}m\dot{\boldsymbol{x}}^2 + q\boldsymbol{A}\cdot\dot{\boldsymbol{x}} - q\varphi \tag{2.221}$$

[14] To derive this form, use the coordinate transformation rule for tensors $\tilde{\mathcal{F}}_{\mu\nu} = T^\lambda_\mu T^\rho_\nu \mathcal{F}_{\lambda\rho}$ where $T^\mu_\nu = \frac{\partial x^\mu}{\partial x^\nu}$

In the quantum theory, $\boldsymbol{p}$ and $\boldsymbol{A}$ are promoted to operators which, in general, do not commute (since $\boldsymbol{A}$ generally depends on position), but the Hamiltonian retains the same form

$$\mathcal{H} = \frac{1}{2m}(\hat{\boldsymbol{p}} - q\boldsymbol{A}(\hat{\boldsymbol{x}}))^2 + q\varphi(\hat{\boldsymbol{x}}) = \frac{1}{2m}\hat{\boldsymbol{\Pi}}^2 + q\varphi(\hat{\boldsymbol{x}}) \tag{2.222}$$

Here, we have introduced the so-called mechanical momentum operator $\hat{\boldsymbol{\Pi}} = \hat{\boldsymbol{p}} - q\hat{\boldsymbol{A}}$. We should now be careful on the definition of the different objects, their commutation relations and their behavior under gauge transformations. First, we note that the canonical momentum components $\hat{p}_i$ are defined as the generators of translation. Thus, they satisfy the commutation relations

$$[\hat{p}_i, \hat{p}_j] = 0, \qquad [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \tag{2.223}$$

In contrast, the mechanical momentum $\hat{\boldsymbol{\Pi}}$ satisfy the commutation relations

$$[\hat{\Pi}_i, \hat{\Pi}_j] = iq\hbar\epsilon_{ijk}B_k, \qquad [\hat{x}_i, \hat{\Pi}_j] = i\hbar\delta_{ij} \tag{2.224}$$

The Heisenberg EOM for the position operator is

$$\frac{d\hat{x}_i}{dt} = \frac{1}{i\hbar}[\hat{x}_i, \mathcal{H}] = \frac{\hat{\Pi}_i}{m} \tag{2.225}$$

Since the position operator is a physical observable, it should not depends on the gauge. This means that $\hat{\boldsymbol{\Pi}}$ should also be gauge invariant. This means that the canonical momentum $\hat{\boldsymbol{p}}$, defined as the generator of translation and satisfying the Heisenberg commutation relations is **not** gauge invariant. This is consistent with the discussion you had in the section and some of the earlier problem sets where the translation operator acquires some gauge dependent phase factors in the presence of a magnetic field.

2.6.2 Solenoid flux and Aharonov-Bohm effect

The behavior of the Hamiltonian under gauge transformations enforces a corresponding change in the wavefunctions. In particular, consider a solution for the Schrödinger equation

$$i\hbar\frac{d}{dt}|\psi, t\rangle = \mathcal{H}|\psi, t\rangle \tag{2.226}$$

Under the gauge transformation (2.218), the Hamiltonian transforms as

$$\mathcal{H} \mapsto \tilde{\mathcal{H}} = \frac{1}{2m}(-i\hbar\boldsymbol{\nabla} - q\boldsymbol{A} - q\boldsymbol{\nabla}\Lambda)^2 + q(\varphi + \frac{\partial}{\partial t}\Lambda) \tag{2.227}$$

It is straightforward to verify that the wavefunction

$$|\tilde{\psi}, t\rangle = e^{\frac{iq}{\hbar}\Lambda}|\psi, t\rangle \tag{2.228}$$

satisfies the Schrödinger equation with $\mathcal{H}$ replaced by $\tilde{\mathcal{H}}$.

The way the vector potential enters the Hamiltonian in quantum mechanics has far-reaching consequences. Consider the following simple problem. Take an infinitely long solenoid with a total magnetic flux Φ. Although the field outside the solenoid is zero, the vector potential cannot be made zero since the flux piercing any closed loop that contains the solenoid is Φ. This means

$$\Phi = \int d\boldsymbol{S}\cdot\boldsymbol{B} = \int d\boldsymbol{l}\cdot\boldsymbol{A} \tag{2.229}$$

This, we can choose $\boldsymbol{A}$ in cylindrical polar coordinates to be

$$A_\phi = \frac{\Phi}{2\pi r} \tag{2.230}$$

outside the solenoid which guarantees (2.229) is satisfied. Now consider a particle confined to a ring of radius R that encloses the solenoid. It is straightforward to write the Schrodinger equation

$$\frac{1}{2m}(-i\frac{\hbar}{r}\frac{\partial}{\partial\phi}-q\frac{\Phi}{2\pi r})^2\psi_n(\phi)=E_n\psi_n(\phi) \tag{2.231}$$

whose solutions are

$$\psi_n(\phi)=e^{in\phi},\qquad E_n=\frac{1}{2mr^2}(\hbar n-\frac{q\Phi}{2\pi})^2 \tag{2.232}$$

Remarkably, we find that the energy spectrum knows about the magnetic flux Φ although the particle only moves in a region where the magnetic field vanishes. This illustrates the crucial importance of the electromagnetic gauge potential in quantum mechanics. Although the gauge invariant and thus physical quantity is the $\boldsymbol{B}$ fields (or more generally the flux of the $\boldsymbol{B}$ field through different surfaces) a quantum mechanical particle depends **non-locally** on the physical fields/fluxes. If we insist that the state and energy of a quantum mechanical particle only depends on local fields it experiences, we have to use the gauge dependent vector potential $\boldsymbol{A}$ instead. This indicates the fundamental role of the vector potential $\boldsymbol{A}$ in the quantum theory.

A dramatic manifestation of this phenomenon is realized in the so-called Aharonov-Bohm effect. This effect is most clearly illustrated in the path integral language. Assuming the scalar potential φ vanishes, we see that the gauge potential enters the action as

$$S[\boldsymbol{A}]=S[\boldsymbol{A}=0]+q\int_0^T dt\dot{\boldsymbol{x}}\cdot\boldsymbol{A}=S[\boldsymbol{A}=0]+q\int_{\boldsymbol{x}_i}^{\boldsymbol{x}_f}d\boldsymbol{x}\cdot\boldsymbol{A} \tag{2.233}$$

We note that the dependence on the field is contained in the last term which is geometric, i.e. only depends on the path. As a result, the probability amplitude for a particle to go through a loop that encloses a solenoid flux Φ is modified due to the flux as $\langle x,T|x,0\rangle\mapsto\langle x,T|x,0\rangle e^{i\gamma}$ where

$$e^{i\gamma}=e^{\frac{iq}{\hbar}\oint_C d\boldsymbol{x}\cdot\boldsymbol{A}}=e^{\frac{iq}{\hbar}\Phi} \tag{2.234}$$

Crucially, this phase does not depend on the details of the loop as long as it winds around the solenoid only once (for a path that winds n times, we get the phase $e^{in\gamma}$). The phase γ can be identified with the Berry phase we introduced last lecture if we think of slowly deforming the Hamiltonian to change the location of the particle so that it traces a loop. For example, we can take a confining potential which confines the particle in the vicinity of a point x_0 that is taken to change slowly in time to trace a loop enclosing the solenoid. An observable consequence of the Aharonov-Bohm effect is realized if we consider a setup where an electron is forced to take one of two paths that enclose the solenoid flux Φ. This can be realized in a modified double slit experiment where the flux is introduced somewhere behind the two-slit screen or in a metallic ring that encloses some flux. At $\Phi=0$ and at any given point, there will be some probability (or intensity) that depends on the relative phase of the amplitude from the two slits/paths. As we change Φ, we are effectively changing the relative phase leading to a periodic pattern of constuctive/destructive interference with period $2\pi\hbar/q$.

2.6.3 Monopole quantization

Let me now discuss another important implication of the way the electromagnetic field affects quantum mechanical probability amplitudes. It is related to some of the properties for the spin Berry phase discussed earlier that seemed mysterious. First, the spin Berry phase could be phrased as the flux of a particle moving in the field of a magnetic monopole. Second, the corresponding gauge field always seemed to have a singularity. These two properties turned out to be tied.

Let us first try to understand the first property. Let us assume that we somehow have a magnetic monopole. Can we deduce anything about its properties? a brilliant argument by Dirac which we have already presented in a different context shows that indeed there is an important restriction on any monopole

we could have. The field of a magnetic monopole of strength g is $\boldsymbol{B} = g\frac{\hat{r}}{4\pi \boldsymbol{r}^2}$ which represents a field pointing radially outwards and decaying as $1/r^2$. A particle with charge q moving on a closed loop on a circle of radius R acquires the Aharonov-Bohm phase $e^{\frac{iq}{\hbar}\int_{\mathcal{S}} d\boldsymbol{S}\cdot\boldsymbol{B}}$ where $\mathcal{S}$ is any area enclosing the loop. Following our previous discussions, we see that we have two possible areas which should give us the same phase which means that the integral $\frac{iq}{\hbar}\int d\boldsymbol{S}\cdot\boldsymbol{B}$ over a sphere of radius R has to be quantized leading to

$$qg = 2n\pi\hbar \tag{2.235}$$

This is a remarkable result! It tells us that if a monopole exists, its charge has to be quantized. Furthermore, repeating this argument for other particles with charge q', we deduce that all charges in the universe has to be quantized in terms of an elementary charge e, $q = ne$, such that the minimal monopole charge is $g = \frac{2\pi\hbar}{e}$.

In the argument above, we have avoided discussing the gauge potential. In fact, when trying to think of the gauge potential of a monopole, we immediately encounter an issue: a magnetic field constructed from a vector potential via $\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}$ cannot have a monopole i.e. a source of the magnetic field, since the divergence of a curl is always zero. This something we know from electromagnetism where the magnetic field lines always form closed loops and a magnet always have two poles. So how would we ever get a magnetic monopole? the loophole in this argument is that it assumes the field $\boldsymbol{A}$ is non-singular. For singular $\boldsymbol{A}$ fields, it turns out to be possible to describe a magnetic monopole as we have seen earlier. Let me now present a simpler calculation to illustrate this effect. Consider the magnetic vector potential defined in the 2D plane by

$$\boldsymbol{A} = \Phi\boldsymbol{\nabla}\arg(x+iy) = -i\Phi\boldsymbol{\nabla}\ln\frac{x+iy}{\sqrt{x^2+y^2}} = \frac{(-y,x)}{x^2+y^2} \tag{2.236}$$

This field is singular at $x = y = 0$ and non-singular everywhere else. Consider the field $\boldsymbol{B}$ defined as $B\hat{z} = \boldsymbol{\nabla}\times\boldsymbol{A}$. Naively substituting (2.236), we get zero field which is not surprising since the curl of a gradient is zero. On the other hand, the flux through a circle of radius r surrounding 0 is given by

$$\oint d\boldsymbol{l}\cdot\boldsymbol{A} = \Phi\oint d\phi = 2\pi\Phi \tag{2.237}$$

This shows that we should be careful when dealing with singular gauge fields.

The singularity of the gauge field can be understood as follows. Imagine we only have particles whose charge is a multiple of a certain fundamental charge e, $q = ne$. A consequence of the Aharonov-Bohm effect is that a flux of $2\pi\hbar/e$ is undetectable. This means that if we consider an infinitely thin solenoid enclosing a flux of $2\pi\hbar/e$, it will be undetectable unless a particle intersect with it. Now, the end points of such solenoid will looks like a source and sink of magnetic flux, i.e. a magnetic monopole and anti-monopole. If we send the anti-monopole to infinity, we basically have a description for a magnetic monopole. The invisible solenoid connecting the monopole to infinity is called the Dirac string and it coincides with.

While we may be able to get away with this notion of a singular gauge field, it is mathematically problematic. Furthermore, this singularity is unphysical since the magnetic field itself is only singular at the origin not at a line extending from the origin to infinity. To resolve this isse and find a more mathematically sound way to define the gauge field of a monopole, recall another example of an unnecessary singularity: the polar coordinates on the sphere. The polar coordinates are not well-defined at the north and the south pole of the sphere since at $\theta = 0, \pi$, ϕ is undefined. On the other hand, there is nothing special about the north or the south pole and we should be able to define coordinates there without the problem. The caveat is that we need to define two different coordinate patches, rather than a single global coordinate chart. The resolution to our monopole gauge potential is very similar. Let us define the vector potential

$$A^N_\phi = \frac{g}{4\pi r}\frac{1-\cos\theta}{\sin\theta} \tag{2.238}$$

This potential is well-defined away from the south pole and it gives us the monopole field since

$$\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}^N = \frac{1}{r\sin\theta}\frac{d}{d\theta}(A^N_\phi\sin\theta)\hat{r} - \frac{1}{r}\frac{\partial}{\partial r}(rA^N_\phi)\hat{\theta} = g\frac{\hat{r}}{4\pi r^2} \tag{2.239}$$

We now define another gauge potential

$$A_\phi^S = -\frac{g}{4\pi r}\frac{1+\cos\theta}{\sin\theta} \tag{2.240}$$

which is singular at the north pole but not at the south pole and also yields the same magnetic field. The trick now is to define two patches: one covering the northern hemisphere and extending a bit in the southern hemisphere (but avoiding the south pole) where we take A_ϕ to be A_ϕ^N and the other covering the southern hemisphere and extending a bit in the northern hemisphere (while avoiding the north pole) where we take A_ϕ to be A_ϕ^S. We are free to do as long as we can define a gauge transformation connecting the two gauge field on the region where they overlap. It is straightforward to see that the two vector potentials are related by

$$A_\phi^N = A_\phi^S + \frac{1}{r\sin\theta}\partial_\phi\omega, \qquad \omega = \frac{g\phi}{2\pi} \tag{2.241}$$

However, we see there is a problem. The function ω is not really single valued on the equator (where the two patches are overlapping) since its value at $\phi = 0$ and $\phi = 2\pi$ is different. It seems we have moved the singularity somewhere else! However, remember that a gauge transformation acts on the wavefunctions via $e^{\frac{iq\omega}{\hbar}}$ (Eq. 2.228), thus it suffices that this phase is single-valued on the sphere. This is satisfies if

$$qg = 2\pi\hbar n \tag{2.242}$$

leading to the monopole quantization condition. In summary, we can define two patches with two associated gauge fields which are non-singular on the patch they are defined on. The non-trivial element of the construction is to ensure that the two patches are related by a valid (i.e. single-valued) gauge transformation where they overlap. This yields a consistency condition that imply the quantization of monopole charge. Some of you may recognize this as the construction of a non-trivial $\mathrm{U}(1)$-bundle on the sphere.

Chapter 3

Angular momentum in quantum mechanics

In this chapter, we will discuss the formalism of angular momentum in quantum mechanics. We have already introduced the notion of spin that was necessary to explain the results of the Stern-Gerlach experiment. Spin seems to be related to classical angular momentum but it also has some very unusual features that emphasize its quantum nature. Our approach will follow the logic we have been employing in our course so far where we identify some symmetry operator whose generator is related to angular momentum. Similar to how we identified momentum with generators of translation, Energy with the generator of time-translation, we will find that angular momentum is identified with the generators of rotation.

3.1 Rotations and angular momentum

3.1.1 Properties of rotation in 3D

Rotations act on 3D real vectors via $v \mapsto Rv$ where R is a 3×3 real matrix. Since rotations preserve scalar product, we get

$$u \cdot v = u^T v = u^T R^T R v \tag{3.1}$$

which holds for arbitrary vectors u and v. This implies that

$$R^T R = \mathbb{1} \tag{3.2}$$

which means that R is an orthogonal matrix. 3×3 Orthogonal matrices form a group called $\mathrm{O}(3)$. To see this, note that for $R_{1,2} \in \mathrm{O}(3)$, $(R_1 R_2)^T R_1 R_2 = R_2^T R_1^T R_1 R_2 = \mathbb{1}$ which implies that $R_1 R_2 \in \mathrm{O}(3)$ (the existence of an inverse and an identity are obvious). Note, however, that not any orthogonal matrix represents a rotation since condition (3.2) is also satisfied by mirror reflections. For example, $M_z = \mathrm{diag}(1, 1, -1)$ represents a reflection about the $x - y$ plane. To distinguish the two, we note that Eq. 3.2 implies that $\det R = \pm 1$ (since $\det R^T = \det R$). Reflections always have $\det R = -1$ whereas pure rotations always have $\det R = +1$. Thus, we can split the orthogonal group into elements with $\det R = +1$, which represent pure rotations, and elements with $\det R = -1$ which represent combinations of a reflection and a rotation. Note that only the first set of elements forms a group since the product of two matrices with determinant -1 yields a matrix with determinant $+1$. The group of orthogonal matrices with determinant $+1$ is called the special orthogonal group, denoted by $\mathrm{SO}(3)$.

A rotation in 3D space is specified by a rotation axis $\hat{n}$, that is left invariant under the rotation, and a rotation angle φ. We will denote such rotation by $R_{\hat{n}}(\varphi)$ and use the convention that φ is positive for counterclockwise rotations. This means that a rotation is specified by three real parameters since $\hat{n}$ specifies a point on the two-dimensional sphere. We can see that this is also the count we get from Eq. 3.2 whose right hand side RR^T is a symmetric matrix specified by 6 real parameters which represents 6 constraints leading to $9 - 6 = 3$ free parameters. Given an element R of $\mathrm{SO}(3)$, we can find the rotation axis $\hat{n}$ as the

unit vector left invariant by R [1]. The rotation angle can be found by considering any unit vector $\hat{n}_\perp$ in the plane perpendicular to $\hat{n}$ and taking its dot product with its rotated version

$$\hat{n}_\perp.(R_{\hat{n}}(\varphi)\hat{n}_\perp) = \cos\varphi, \tag{3.3}$$

This fixes φ up to a sign. The latter can be fixed by the relation

$$\hat{n}\cdot[\hat{n}_\perp \times (R_{\hat{n}}(\varphi)\hat{n}_\perp)] = \sin\varphi \tag{3.4}$$

It is a known fact the rotations about different axes in 3D space do not commute. This is something you can see easily by considering some simple examples. For instance, $\pi/2$ rotation about the z-axis followed by $\pi/2$ rotation about the x-axis is not the same as doing the x-rotation before the z-rotation. For instance, the first sequence, which we can denote by $R_x(\pi/2)R_z(\pi/2)$ maps the north pole on the sphere to the point $(0,-1,0)$ whereas the second sequence $R_z(\pi/2)R_x(\pi/2)$ maps it to $(1,0,0)$.

To specify the commutation relations for general rotation operators, we notice that the operator

$$Q_{\hat{n},\hat{m}}(\theta,\varphi) = R_{\hat{m}}(\theta)^T R_{\hat{n}}(\varphi)R_{\hat{m}}(\theta) \tag{3.5}$$

leaves $R^T_{\hat{m}}(\theta)\hat{n}$ invariant and satisfies

$$\hat{n}_\perp^T R_{\hat{m}}(\theta)Q_{\hat{n},\hat{m}}(\theta,\varphi)R^T_{\hat{m}}(\theta)\hat{n}_\perp = \cos\varphi, \tag{3.6}$$

which implies that $Q_{\hat{n},\hat{m}}(\theta,\varphi) = R_{R^T_{\hat{m}}(\theta)}(\varphi)$ [2]. As a result, we have the relation

$$R_{\hat{m}}(\theta)^T R_{\hat{n}}(\varphi)R_{\hat{m}}(\theta) = R_{R^T_{\hat{m}}(\theta)\hat{n}}(\varphi) \tag{3.7}$$

which holds for arbitrary unit vectors $\hat{n}$ and $\hat{m}$ and arbitrary angles θ and φ. You can verify that this relation holds in some simple cases. For example, if $\hat{n} = \hat{m}$, the two rotations commute and the RHS reduces to $R_{\hat{n}}(\varphi)$. The LHS also reduces to $R_{\hat{n}}(\varphi)$ since $R^T_{\hat{m}}(\theta)\hat{n} = \hat{n}$. A less trivial example is taking $\hat{m} = \hat{z}$, $\hat{n} = \hat{x}$ and $\theta = \varphi = \pi/2$. The LHS gives rotation around the y-axis by $\pi/2$. It is easy to verify this is the same we get by rotating by $\pi/2$ around $\hat{z}$, then by $\pi/2$ around $\hat{x}$, and then by $-\pi/2$ around $\hat{z}$.

Similar to our approach with different symmetry operations, we can gain a lot of insights by considering infinitesmal rotations $R_{\hat{n}}(d\varphi)$

$$R_{\hat{n}}(d\varphi) = \mathbb{1} + \Gamma_{\hat{n}}d\varphi \tag{3.8}$$

Substituting in Eq. 3.2, we find that

$$\Gamma^T_{\hat{n}} = -\Gamma_{\hat{n}} \tag{3.9}$$

An arbitrary real antisymmetric matrix can be expanded in terms of the three real antisymmetric matrices

$$\gamma_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \qquad \gamma_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \qquad \gamma_3 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{3.10}$$

Thus, we can write $\Gamma_{\hat{n}} = \sum_{i=1}^3 \alpha^i_{\hat{n}}\gamma_i$. In the following, we will not write the summation explicitly and always assume that repeated indices are summed over. The condition $R_{\hat{n}}(\varphi) = \hat{n}$ for any φ implies

$$\Gamma_{\hat{n}}\hat{n} = 0 = \alpha^i_{\hat{n}}\gamma_i\hat{n} = \boldsymbol{\alpha}_{\hat{n}} \times \hat{n} \tag{3.11}$$

where $\boldsymbol{\alpha}$ is the vector whose components are α_i. The equation above means that $\boldsymbol{\alpha}_{\hat{n}}$ is parallel to $\hat{n}$, i.e. $\alpha^i_{\hat{n}} = \alpha\hat{n}^i$ for some constant α Since this constant is universal (independent of both $\hat{n}$ and φ), we can fix

[1] Any non-trivial element R of SO(3) has only one eigenvalues equal to 1

[2] This condition fixes this form up to a sign $\pm\varphi$. You can check that Eq. (3.4) fixes this sign to be the positive one

it by considering the rotation matrix for some simple rotation. For example, rotation around the z-axis is given by

$$R_z(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3.12}$$

Expanding to leading order in φ gives

$$\Gamma_{\hat{z}} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \gamma_3 \tag{3.13}$$

This means that the constant $\alpha = 1$ and we can write

$$\Gamma_{\hat{n}} = \sum_{i=1}^{3} \hat{n}_i \gamma_i = \begin{pmatrix} 0 & -n_z & n_y \\ n_z & 0 & -n_x \\ -n_y & n_x & 0 \end{pmatrix} \tag{3.14}$$

Substituting in (3.8), we get

$$R_{\hat{n}}(d\varphi) = \mathbb{1} + d\varphi \hat{n}^i \gamma_i \tag{3.15}$$

The generators for the 3D rotation γ_i satisfying

$$[\gamma_i, \gamma_j] = \epsilon_{ijk}\gamma_k \tag{3.16}$$

We can then write a finite rotation by exponentiating the generator using

$$R_{\hat{n}}(\varphi) = \lim_{N\to\infty} (\mathbb{1} + \frac{\varphi}{N}\hat{n}^i\gamma_i)^N = e^{\varphi \hat{n}^i \gamma_i} \tag{3.17}$$

3.1.2 Representations of rotation

To describe the action of rotations on a quantum state specified by a ket $|\alpha\rangle$, we need to find a unitary operator that 'represents' the rotation in the sense that

$$|u\rangle_R = D(R)|u\rangle \tag{3.18}$$

We see that $D(R)$ has to satisfy several consistency conditions. First, for $R = R_1R_2$, we have $|u\rangle_R = |u\rangle_{R_1R_2}$ which implies $D(R) = D(R_1R_2) = D(R_1)D(R_2)$. We also see that $D(\mathbb{1}) = \mathbb{1}$ and $\mathbb{1} = D(RR^T) = D(R)D(R^T)$ which implies $D(R^T) = D(R)^{-1} = D(R)^\dagger$. This means that D defines a unitary representation of $\mathrm{SO}(3)$. It is important to emphasize the distinction between R which is a 3×3 real orthogonal matrix and $D(R)$ which is a unitary matrix whose dimension is the Hilbert space dimension and can be arbitrary. For example, for spin-$1/2$, $D(R)$ will be two-dimensional. Note also that when defining the properties of $D(R)$, we could have allowed for some arbitrary phases since $|u\rangle$ is defined up to a phase. These phases need to satisfy some consistency conditions. Such representations are called projective representations. For our current analysis, where we focus on infinitesmal rotations, we can restrict ourselves to the projective case since such phases drop.

We now introduce the infinitesmal generator for $D(R)$

$$D(R_{\hat{n}}(d\varphi)) = \mathbb{1} - iG_{\hat{n}}d\varphi = D(\mathbb{1} + d\varphi\hat{n}^i\gamma_i) = \mathbb{1} + d\varphi\hat{n}^i\frac{d}{d\epsilon}D(\mathbb{1}+\epsilon\gamma_i)|_{\epsilon=0} \tag{3.19}$$

This implies that $G_{\hat{n}}$ has the form

$$G_{\hat{n}} = J_i\hat{n}^i, \qquad J_i = i\frac{d}{d\epsilon}D(\mathbb{1}+\epsilon\gamma_i)|_{\epsilon=0} \tag{3.20}$$

Previously, we have identified the generator of translation with momentum and the generator of time-translation with energy (the Hamiltonian). Both identification can be motivated by classical considerations. In classical mechanics, angular momentum is associated with the generators of rotation. This motivates us to identify J_i with angular momentum measured in units of $\hbar$.

Similar to what we did for R, we can construct the elements $D(R)$ corresponding to finite rotation by exponentiating the generator

$$D(R_{\hat{n}}(\varphi)) = e^{-i\varphi J_i \hat{n}^i} = D(e^{\varphi\gamma_i\hat{n}^i}) \tag{3.21}$$

We are now ready to derive the very important angular momentum commutation relations in quantum mechanics. To do this, we write

$$e^{-i\epsilon_1 J_j}e^{-i\epsilon_1 J_i}e^{-i\epsilon_2 J_j}e^{i\epsilon_1 J_i} = e^{-i\epsilon_1 J_i}e^{-i\epsilon_1 \mathrm{ad}_{J_i}}e^{-i\epsilon_2 J_j} = D(e^{\epsilon_1\gamma_j}e^{\epsilon_1\gamma=i}e^{\epsilon_2\gamma-j}e^{-\epsilon_1\gamma-i}) = D(e^{-\epsilon_2\gamma_j}e^{\epsilon_1\mathrm{ad}_{\gamma_i}}e^{\epsilon_2\gamma_j}) \tag{3.22}$$

and expand in ϵ_1 and ϵ_2 to get

$$\mathbb{1} - \epsilon_1\epsilon_2[J_i, J_j] = D(\mathbb{1} + \epsilon_1\epsilon_2[\gamma_i, \gamma_j]) = D(\mathbb{1} + \epsilon_1\epsilon_2\epsilon_{ijk}\gamma_k) = \mathbb{1} - i\epsilon_1\epsilon_2\epsilon_{ijk}J_k \tag{3.23}$$

This leads to the angular momentum commutation relation

$$[J_i, J_j] = i\epsilon_{ijk}J_k \tag{3.24}$$

If we use the physical angular momentum $J_i\hbar$, then we get an extra factor of $\hbar$ on the RHS.

We see that unlike the different components of momentum which commute with each other, the different components of angular momentum do not commute. This is something we have already seen when studying the Stern-Gerlach device for spin $1/2$ where the devices rotated relative to each other measured incompatible observables.

Since the different components of angular momentum do not commute with each other, we cannot simultaneously diagonalize them. However, in addition to the three angular momentum components, we can also define the total angular momentum

$$\boldsymbol{J}^2 = \sum_i (J_i)^2 \tag{3.25}$$

It is easy to see that this operator commutes with all three angular momentum components J_i since $\mathrm{ad}_{\boldsymbol{J}^2}J_i = \sum_l\{J_l, \mathrm{ad}_{J_l}J_i\} = i\sum_{l,k}\epsilon_{lik}\{J_l, J_k\}$ which vanishes since the Levi-civita symbol is antisymmetric in l and k whereas the anticommutator is symmetric. This means that we can take $\boldsymbol{J}^2$ and one of the angular momentum components and use them to label the different angular momentum eigenstates. The convention is to choose J_z.

Let us consider a simultaneous eigenstate of $\boldsymbol{J}^2$ and J_z denoted by $|a, b\rangle$ such that

$$\boldsymbol{J}^2|a, b\rangle = |a, b\rangle, \qquad J_z|a, b\rangle = b|a, b\rangle \tag{3.26}$$

Notice that since $\boldsymbol{J}^2$ is a sum of non-negative operators, $a \geq 0$. It is useful to define the non-hermitian 'ladder' operators

$$J_\pm = J_x \pm iJ_y \tag{3.27}$$

which satisfy the commutation relations

$$[\boldsymbol{J}^2, J_\pm] = 0, \qquad [J_z, J_\pm] = \pm J_\pm, \qquad [J_+, J_-] = 2J_z \tag{3.28}$$

These relations should remind you of some commutation relations we discussed earlier. First, when we discussed translation operators, we had the relation

$$[\hat{x}, T_{\pm a}] = \pm aT_{\pm a} \tag{3.29}$$

The meaning of this relation is that the operator $T_{\pm a}$, acting on an eigenstate of $\hat{x}$, raises or lowers its eigenvalue by a. We also had similar relations for the harmonic oscillator algebra

$$[\hat{N}, a] = -a, \qquad [\hat{N}, a^\dagger] = a^\dagger \tag{3.30}$$

Here, again the interpretation is that $a^\dagger$ (a) increases (decreases) the eigenvalue of $\hat{N}$ by 1. The interpretation of the ladder operators $J_\pm$ is exactly the same. This means that

$$J_\pm|a, b\rangle = c_\pm|a, b \pm 1\rangle \tag{3.31}$$

Although the second equation in (3.28) is similar to the ladder operator algebra we encountered for translations and for the harmonic oscillator, the last equation is different and makes the properties of the angular momentum eigenstates quite distinct from these two other cases. To see this, let us recall what would be the analog of that relation in these two cases. For translation, the analog is $[T_a, T_{-a}] = 0$ since all translations commute. This does not impose any restrictions of the eigenvalues of the position operator (it is unbounded from above and below). For the harmonic oscillator, the anolagous relation is $[a, a^\dagger] = 1$. We saw that this relation had important implications on the spectrum of $\hat{N} = a^\dagger a$ which we found was bounded from below by 0 but unbounded from above. For the angular momentum algebra, we will see that the spectrum is bounded from both sides. First, we note that for any state $|u\rangle$

$$\langle u|\boldsymbol{J}^2 - J_z^2|u\rangle = \langle u|J_x^2 + J_y^2|u\rangle \geq 0 \tag{3.32}$$

This means that for a given fixed a, the eigenvalue of J_z^2, can never exceed a. In other words, there is a maximum value $b_{\max}$ such that

$$b \leq b_{\max} \leq \sqrt{a} \tag{3.33}$$

Since we cannot raise the eigenvalue of J_z beyond $b_{\max}$, J_+ has to annihilate $|a, b_{\max}\rangle$. This allows us to write

$$\boldsymbol{J}^2|a, b_{\max}\rangle = a|a, b_{\max}\rangle = [J_z^2 + \frac{1}{2}J_+J_- + \frac{1}{2}J_-J_+]|a, b_{\max}\rangle = b_{\max}[b_{\max} + 1]|a, b_{\max}\rangle \tag{3.34}$$

which implies

$$a = b_{\max}[b_{\max} + 1] \tag{3.35}$$

Now we can run the same argument for the minimum value $-\sqrt{a} \leq b_{\min} \leq b$ to get

$$a = b_{\min}[b_{\min} - 1] \tag{3.36}$$

Comparing with (3.35), we see that $b_{\min} = -b_{\max}$. Now starting from $b_{\min}$, we should be able to reach $b_{\max}$ by applying the raising operator a finite number of times. This yields

$$b_{\max} - b_{\min} = n, \qquad b_{\max} = \frac{n}{2} \tag{3.37}$$

Thus, the eigenvalues of J_z are only allowed to be integer or half-integer. It is customary to use the notation where $b_{\max} = j$ and $b = m$ and define

$$\boldsymbol{J}^2|j, m\rangle = j(j + 1)|j, m\rangle, \qquad J^z|j, m\rangle = m|j, m\rangle \tag{3.38}$$

The states $|j, m\rangle$ also satisfy

$$J_\pm|a, b\rangle = c_\pm|a, b \pm 1\rangle \tag{3.39}$$

The constants $c_\pm$ can be fixed by the normalization. For c_+, we have

$$|c_+|^2 = \langle j, m|(J^+)^\dagger J^+|j, m\rangle = \langle j, m|\boldsymbol{J}^2 - (J^z)^2 - J^z|j, m\rangle = [j(j+1) - m(m+1)] = (j-m)(j+m+1) \tag{3.40}$$

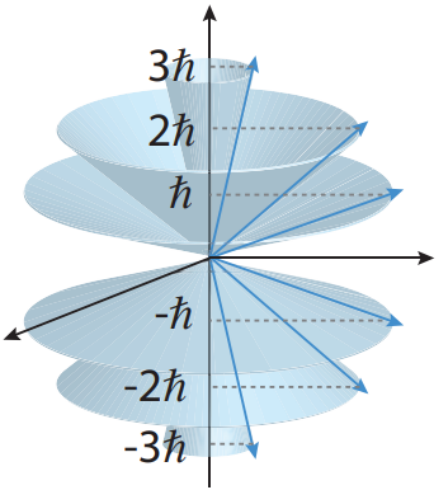

Figure 3.1: Illustration of the z component of angular momentum for $l = 3$. Note that the maximum value of J_z is smaller than the total angular momentum $\sqrt{12}\hbar \approx 3.46\hbar$.

We can do a very similar calculation for c_- to get

$$c_{\pm,j,m} = \sqrt{(j \mp m)(j \pm m + 1)} \tag{3.41}$$

Pictorially, the components of angular momentum in quantum mechanics are quantized into $2j + 1$ equally spaced values whose maximum is **not** equal to the magnitude of the angular momentum as shown in Fig. 3.1. This counter-intuitive property follows from the last commutation relation in (3.28) which implies that $J_x^2 + J_y^2 = J_- J_+ + J_z$. Thus for the maximum value of $m = j$, $(J_x^2 + J_y^2)|j, j\rangle = j|j, j\rangle$ which means that the maximum possible value for any component of the angular momentum is always strictly smaller than the total angular momentum.

It is instructive to see what happens in the limit of large j. To make this discussion clear, let us restore the factor of $\hbar$ and think of the actual angular momentum rather than the dimensionless one measured in units of $\hbar$. In this case, the total angular momentum corresponding to j is $\hbar\sqrt{j(j+1)}$. For large j, the spacing between different values of J_z remains the same ($= \hbar$) but the size of the spacing relative to the total angular momentum, which we denote by Δ, decreases since $\Delta = \frac{1}{\sqrt{j(j+1)}}$. Furthermore, the ratio of the maximal value of J_z to the total angular momentum $\sqrt{\boldsymbol{J}^2}$ approaches 1 since $\frac{j(j+1)}{j^2} = 1 + \frac{1}{j} \approx 1$. This means that the limit of large j reproduces the expectation for a classical vector. We also note that when we did the path integral for spin, we had the factor s, which corresponds to our j here, multiplying the whole action. In the limit of large s, we can perform the saddle point approximation on the action and find that we recover the classical equations of motion for a classical unit vector.

Despite the unusual quantum mechanical nature of the angular momentum operators J_i, we still expect its components to transform like a vector under rotation. For instance, consider the rotated ket $|\alpha\rangle_R = e^{-i\varphi J_z}|\alpha\rangle$. The expectation value of J_x in the rotated ket are related to their expectation value in the unrotated ket via

$${}_R\langle\alpha|J_x|\alpha\rangle_R = \langle\alpha|e^{i\varphi J_z} J_x e^{-i\varphi J_z}|\alpha\rangle = \langle\alpha|e^{i\varphi \mathrm{ad}_{J_z}} J_x|\alpha\rangle \tag{3.42}$$

Using the commutation relations (3.24), we find

$$\mathrm{ad}_{J_z} J_x = iJ_y, \quad \mathrm{ad}_{J_z}^2 J_x = i\mathrm{ad}_{J_z} J_y = J_x \tag{3.43}$$

which implies $\mathrm{ad}_{J_z}^{2n} J_x = J_x$. Substituting in (3.42), we get

$${}_R\langle\alpha|J_x|\alpha\rangle_R = \langle\alpha|J_x \sum_{n \text{ even}} \frac{(i\varphi)^n}{n!} + iJ_y \sum_{n \text{ odd}} \frac{(i\varphi)^n}{n!}|\alpha\rangle = \cos\varphi\langle\alpha|J_x|\alpha\rangle - \sin\varphi\langle\alpha|J_y|\alpha\rangle \tag{3.44}$$

A similar calculation for J_y yields

$$ {}_R\langle\alpha|J_y|\alpha\rangle_R = \sin\varphi\langle\alpha|J_x|\alpha\rangle + \cos\varphi\langle\alpha|J_y|\alpha\rangle \tag{3.45} $$

More generally, the components of angular momentum transform as a vector under R

$$ {}_R\langle\alpha|J_i|\alpha\rangle_R = \sum_l R_{il}\langle\alpha|J_l|\alpha\rangle \tag{3.46} $$

Although the expectation value of J_i behaves like a classical vector, when we consider the effect of J_i on kets, we will find a very surprising and counter intuitive result. Consider the case of spin-$\frac{1}{2}$ with $j = 1/2$. The Hilbert space is spanned by the two kets $|\pm\rangle$ satisfying

$$ J_z|\pm\rangle = \pm\frac{1}{2}|\pm\rangle, \qquad J_+|+\rangle = J_-|-\rangle = 0 \tag{3.47} $$

If we introduce the vector notation

$$ |+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{3.48} $$

we can write the J operators in terms of the Pauli matrices as $J_i = \frac{1}{2}\sigma_i$. Let us now consider the action of rotation by angle φ around the z-axis on a general ket $|\alpha\rangle$

$$ R_z(\varphi)|\alpha\rangle = e^{-i\varphi J_z}(|+\rangle\langle+|\alpha\rangle + |-\rangle\langle-|\alpha\rangle) = e^{-\frac{i}{2}\varphi}|+\rangle\langle+|\alpha\rangle + e^{\frac{i}{2}\varphi}|-\rangle\langle-|\alpha\rangle \tag{3.49} $$

The appearance of the factor of $\frac{1}{2}$ here has a very important implication: the action of rotation with $\varphi = 2\pi$ is non-trivial!

$$ R_z(2\pi)|\alpha\rangle = -|\alpha\rangle \tag{3.50} $$

More generally, for angular momentum j we have

$$ R_z(2\pi)|\alpha\rangle = e^{-2\pi i J_z}\sum_{m=-j}^{j}|j,m\rangle\langle m,j|\alpha\rangle = \sum_{m=-j}^{j} e^{-2\pi i m}|j,m\rangle\langle m,j|\alpha\rangle = (-1)^{2j}|\alpha\rangle \tag{3.51} $$

Thus, for half-integer j, the action of 2π rotation gives a $-$ sign. Although the ket $-|\alpha\rangle$ represents the same state, we have seen in the discussion of Berry phase that such overall factor has physical consequences. For instance, if we have interference between two trajectories one involving the particle undergoing a 2π rotation and the other does not, we will get a destructive interference due to the extra minus sign if j is half-integer but a constructive interference if j is integer. This has implications for example when we consider electrical transport in solids where the momentum direction and spin are locked to each other. A trajectory where the momentum have rotated by 2π will be associated with an extra negative sign leading to some interesting quantum interference effects.

3.1.3 Orbital angular momentum and spherical harmonics

Our discussion of angular momentum so far has focused on the perspective that angular momentum is a fundamental quantity not derived from other quantities. This is indeed the case for spin which is an intrinsic property of the quantum system that cannot be derived from other properties. However, the notion of angular momentum we know from classical physics is the orbital angular momentum. This is not fundamental and is derived from the position and momentum variables via

$$ \boldsymbol{L} = \boldsymbol{x} \times \boldsymbol{p} \tag{3.52} $$

However, since orbital angular momentum is also an angular momentum, it should satisfy the commutation relations (3.24). We can verify that the definition (3.52) together with the position-momentum commutation

relations indeed yield the correct commutation relations for orbital angular momentum. We can verify this explicitly for L_x and L_y by writing

$$[L_x, L_y] = [yp_z - zp_y, zp_x - xp_z] = [yp_z, zp_x] + [zp_y, xp_z] = i\hbar(-yp_x + xp_y) = i\hbar L_z \tag{3.53}$$

The relation for other components can be derived in a similar fashion. It is instructive to compare the discussion here to the discussion of the creation and annihilation operators in the harmonic oscillator. The way we introduce the operators was by building them out of x and p and showing that they satisfy the harmonic oscillator algebra. Alternatively, we could have introduced them as fundamental objects defined by the commutation relations $[a, a^\dagger] = 1$.

Drawing further parallels with the harmonic oscillator, recall that we have presented an algebraic construction of the harmonic oscillator spectrum that only used the commutation relations to construct the spectrum and the wavefunctions. This is similar to the construction of the eigenfunctions $|j, m\rangle$ for the angular momentum operators. However, we have also shown that we can solve the harmonic oscillator in the position basis using the representation of the creation/annihilation operators in terms of x and p. This is what we would want to do now. Our goal is to find the representation of orbital angular momentum in the position basis. Similar to how we constructed the representation of linear momentum through the action of infinitesmal translation. First, let us consider the action of infinitesmal rotation on the positin eigenket $|x, y, z\rangle$

$$(\mathbb{1} - \frac{i}{\hbar}d\varphi L_z)|x, y, z\rangle = (\mathbb{1} - \frac{i}{\hbar}d\varphi[xp_y - yp_x])|x, y, z\rangle = T^y_{xd\varphi}T^x_{-yd\varphi}|x, y, z\rangle = |x - yd\varphi, y + xd\varphi, z\rangle \tag{3.54}$$

From this, we can derive the action of L_z on the wavefunction $\psi(x, y, z) = \langle x, y, z|\psi\rangle$ using

$$(\mathbb{1}-\frac{i}{\hbar}d\varphi L_z)|\psi\rangle = \int dxdydz|x-yd\varphi, y+xd\varphi, z\rangle\langle x, y, z|\psi\rangle = \int dxdydz|x, y, z\rangle\langle x+yd\varphi, y-xd\varphi, z|\psi\rangle \tag{3.55}$$

which means that L_z acts on the wavefunction as

$$L_z\psi(x, y, z) = -i\hbar[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}]\psi(x, y, z) \tag{3.56}$$

Notice that we could have already guess this from the expression (3.52). This action is a lot simpler in spherical coordinates, where rotation by around the z axis just shifts the azimuthal angle φ leading to

$$L_z\psi(r, \theta, \varphi) = -i\hbar\frac{\partial}{\partial\varphi}\psi(r, \theta, \varphi) \tag{3.57}$$

Similarly, we can construct the action of L_x and L_y as

$$L_x\psi(x, y, z) = -i\hbar[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}]\psi(x, y, z), \quad L_x\psi(r, \theta, \varphi) = -i\hbar(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\varphi\frac{\partial}{\partial\varphi})\psi(r, \theta, \varphi) \tag{3.58}$$

$$L_y\psi(x, y, z) = -i\hbar[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}]\psi(x, y, z), \quad L_y\psi(r, \theta, \varphi) = -i\hbar(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi})\psi(r, \theta, \varphi) \tag{3.59}$$

This leads to the slightly simpler expression for $L_\pm$ as

$$L_\pm\psi(x, y, z) = -i\hbar e^{\pm i\varphi}[\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}]\psi(x, y, z) \tag{3.60}$$

Finally, the expression for $\boldsymbol{L}^2$ is

$$\boldsymbol{L}^2\psi(x, y, z) = -\hbar^2[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}]\psi(x, y, z) \tag{3.61}$$

This coincides with the angular part of the Laplacian in spherical coordinates.

Our goal now is to construct the wavefunctions $\langle r, \theta, \varphi | l, m\rangle$. These are usually called spherical harmonics and denoted by $Y_l^m(\theta, \varphi)$. Note that the spherical harmonics do not depend on the radial coordinate since the orbital angular momentum operators L_i do not depend on r. We can also use the notation $Y_l^m(\hat{n})$ where $\hat{n}$ is a unit vector. Spherical harmonics satisfy

$$L_z Y_l^m(\theta, \varphi) = m\hbar Y_l^m(\theta, \varphi), \qquad \boldsymbol{L}^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) Y_l^m(\theta, \varphi) \tag{3.62}$$

with L_z and $\boldsymbol{L}^2$ given by (3.57) and (3.61). The first equation is easily solved by $e^{im\varphi}$ which means we can write $Y_m^l(\theta, \varphi) = e^{im\varphi}\tilde{Y}_m^l(\theta)$. To solve for $\tilde{Y}$, we note that $L_+ Y_l^l = 0$ which implies

$$0 = [+i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}]Y_l^l(\theta, \varphi) = [\frac{\partial}{\partial\theta} - m\cot\theta]\tilde{Y}_l^l(\theta) \tag{3.63}$$

whose solution is $\tilde{Y}_m^l(\theta) = \sin^l\theta$ up to some normalization factor. To construct the other spherical harmonics, we simply apply the lowering operator to Y_l^l. The unnormalized spherical harmonics wavefunctions are thus given by

$$Y_m^l(\theta, \varphi) \propto J_-^{l-m} Y_l^l(\theta, \varphi) \propto e^{-i(l-m)\varphi}[-i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}]^{l-m} e^{il\varphi}\sin^l\theta = (-i)^{l-m} e^{im\varphi}[\frac{\partial}{\partial\theta} + l\cot\theta]^{l-m}\sin^l\theta \tag{3.64}$$

The normalization of the spherical functions is given by

$$\int d\varphi d\theta \sin\theta Y_m^l(\theta, \varphi) Y_{m'}^{l'}(\theta, \varphi) = \delta_{ll'}\delta_{mm'} \tag{3.65}$$

The spherical harmonics at $m = 0$ are given by Legendre polynomials

$$Y_0^l(\theta, \varphi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta) \tag{3.66}$$

An important property of the spherical harmonics is that they correspond to angular momentum which is quantized to integers not half-integers. We can see this from the angular dependence of the wavefunction which has the form $e^{im\varphi}$ which is only single-valued for integer m. In fact, we can see directly from the definition of orbital angular momentum $\boldsymbol{L} = \boldsymbol{x} \times \boldsymbol{p}$ that a rotation by 2π will give the identity since

$$\begin{aligned} R_z(2\pi)|\psi\rangle &= e^{-\frac{2\pi i}{\hbar}(xp_y - yp_x)} \int dxdydz|x, y, z\rangle\psi(x, y, z) \\ &= \int dxdydz|x\cos 2\pi - y\sin 2\pi, y\cos 2\pi + x\sin 2\pi, z\rangle\psi(x, y, z) = \psi(x, y, z) \end{aligned} \tag{3.67}$$

This tells us that half-integer spin cannot be realized as orbital angular momentum.

3.2 Schrödinger equation for central potential

3.2.1 General formalism

A spherically symmetric or central potential is a potential that only depends on the radial distance from the origin $r = \sqrt{x^2 + y^2 + z^2}$. The Hamiltonian for a central potential has the form

$$\mathcal{H} = -\frac{\hbar^2\nabla^2}{2m} + V(r) \tag{3.68}$$

Recall the form of the Laplacian in spherical coordinates:

$$\begin{aligned}\nabla^2\psi(r,\theta,\varphi) &= \frac{1}{r}\frac{\partial^2}{\partial r^2}r\psi(r,\theta,\varphi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\psi(r,\theta,\varphi) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\psi(r,\theta,\varphi)\\ &= [\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{1}{r^2\hbar^2}\boldsymbol{L}^2]\psi(r,\theta,\varphi)\end{aligned} \tag{3.69}$$

Substituting in the Hamiltonian, we get

$$\mathcal{H} = -\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}r + \frac{1}{2mr^2}\boldsymbol{L}^2 + V(r) = \mathcal{H}(r) + \frac{1}{2mr^2}\boldsymbol{L}^2 \tag{3.70}$$

Notice several things about this equation. First, it is clear that the Hamiltonian commutes with $\boldsymbol{L}^2$ and L_z since both only depend on θ and φ while ?$\mathcal{H}(r)$ only depends on r. Second notice the appearance of the term proportional to $\boldsymbol{L}^2$ which represents an effective repulsive "centrifugal" potential. This can be made more transparent by separating the radial and angular dependence of the eigenfunctions of the Hamiltonian. Since the Hamiltonian commutes with both L_z and $\boldsymbol{L}^2$, we can simultaneoulsy diagonalize H, L_z and $\boldsymbol{L}^2$. As a result, we can label the wavefunction with the eigenvalues of the three operators as follows

$$H|E,l,m\rangle = E|E,l,m\rangle, \qquad \boldsymbol{L}^2|E,l,m\rangle = \hbar^2 l(l+1)|E,l,m\rangle, \qquad L_z|E,l,m\rangle = \hbar m|E,l,m\rangle \tag{3.71}$$

Since we have already constructed the eigenfunctions of L_z and $\boldsymbol{L}^2$ given by the spherical harmonics in Eq. 3.62, we can write the wavefunctions in spherical coordinates as

$$\psi_{E,l,m}(r,\theta,\varphi) = \langle r,\theta,\varphi|E,l,m\rangle = Y_m^l(\theta,\varphi)R_{E,l}(r) \tag{3.72}$$

with $R_{E,l}(r)$ satisfying the equation

$$\mathcal{H}R_{R,l}(r) = [-\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}r + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)]R_{E,l}(r) = ER_{E,l}(r) \tag{3.73}$$

We see the appearance of an extra repulsive potential that is non-vanishing for $l > 0$ and is singular at $r = 0$. This implies that for $l > 0$, the electrons face an infinite potential barrier to be at the origin. The normalization of the wavefunction is given by

$$1 = \int_0^\infty dr r^2 \int_0^\pi d\theta\sin\theta\int_0^{2\pi} d\varphi|\psi_{E,l,m}(r,\theta,\varphi)|^2 = \int_0^\infty dr r^2|R_{E,l}(r)|^2\int_0^\pi d\theta\sin\theta\int_0^{2\pi} d\varphi|Y_m^l(\theta,\varphi)|^2 \tag{3.74}$$

Since the spherical harmonics are assumed to be normalized on the unit sphere ($r = 1$), this means that the normalization for $R_{E,l}(r)$ is

$$\int_0^\infty dr r^2|R_{E,l}(r)|^2 = 1 \tag{3.75}$$

This suggests defining the function $u_{E,l}(r) = rR_{E,l}(r)$ such that

$$\int_0^\infty dr|u_{E,l}(r)|^2 = 1 \tag{3.76}$$

which is a normalized wavefunction describing an electron living on the one-dimensional semi-infinite line $r > 0$. Substituting $R_{E,l}(r) = \frac{u_{E,l}(r)}{r}$ in the Schrödinger equation (3.73), we get

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u_{E,l}(r) + [\frac{\hbar^2 l(l+1)}{2mr^2} + V(r)]u_{E,l}(r) = Eu_{E,l}(r) \tag{3.77}$$

This describes a 1D particle living in the region $r > 0$ and experiencing the potential $V_l(r) = \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)$.

To understand the general structure of this equation, let us first consider the limit $r \to 0$. Let us also assume that the potential is not very singular at $r = 0$, i.e. $\lim_{r\to 0} r^2 V(r) = 0$. Since the wavefunction itself cannot be singular in the limit $r \to 0$ (otherwise it will not be normalizable) then in the limit $r \to 0$ and for $l > 0$, we have

$$\frac{d^2}{dr^2} u_{E,l}(r) = \frac{l(l+1)}{r^2} u_{E,l}(r) \tag{3.78}$$

The general solution to this equation is

$$u_{E,l}(r) = Ar^{l+1} + B\frac{1}{r^l} \tag{3.79}$$

Normalizability of the wavefunctions implies $B = 0$. Thus $u_{E,l}(r) \sim r^{l+1}$ for $r \to 0$. This result makes sense since the centrifugal potential barrier at $r = 0$ for $l > 0$ implies the vanishing of the wavefunction at $r = 0$. As the strength of this barrier is increased, the power by which the function vanishes also increases.

For $l = 0$, we can consider a general expansion

$$u_{E,0}(r) = \sum_{n=0}^{\infty} a_n r^n \tag{3.80}$$

at small r. Let us assume that the constant term is non-vanishing. Then $u_{E,0}(r) \sim 1$ for small r which implies $R_{E,0}(r) \sim \frac{1}{r}$ and $\psi_{E,0,0}(r, \theta, \varphi) \sim \frac{1}{r}$. However, since $\nabla^2 \frac{1}{r} = -4\pi\delta(\boldsymbol{r})$, we can only get this result for a fine-tuned delta potential. For any other potential, the expansion (3.80) generically starts at $u_{E,0} \sim r$.

3.2.2 Isotropic harmonic oscillator

Consider the isotropic harmonic oscillator where $V(r) = \frac{1}{2}m\omega^2 r^2$. Substituting in Eq. 3.77, we get

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} u_{E,l}(r) + [\frac{\hbar^2 l(l+1)}{2mr^2} + \frac{1}{2}m\omega^2 r^2] u_{E,l}(r) = E u_{E,l}(r) \tag{3.81}$$

This equation can be simplified by introducing the dimensionless variables λ and ρ via

$$E = \frac{1}{2}\hbar\omega\lambda, \qquad r = \sqrt{\frac{\hbar}{m\omega}}\rho \tag{3.82}$$

Substituting in (3.81), we get

$$u''(\rho) - \frac{l(l+1)}{\rho^2} u(\rho) + (\lambda - \rho^2) u(\rho) = 0 \tag{3.83}$$

We have already seen from our earlier discussion that for $\rho \to 0$, $u(\rho) \sim \rho^{l+1}$. We would also like to extract the asymptotics at $\rho \mapsto \infty$ where the above equation reduces to

$$u''(\rho) - \rho^2 u(\rho) = 0 \tag{3.84}$$

whose solution is $u(\rho) \sim e^{-\frac{\rho^2}{2}}$. Similar to what we did when we solved the harmonic oscillator, it is usually convenient to extract the asymptotic dependence of the wavefunction. In this case, we can extract the asymptotics both at small and large ρ, leading to

$$u(\rho) = \rho^{l+1} e^{-\frac{\rho^2}{2}} f(\rho) \tag{3.85}$$

Substituting in (3.83), we get the differential equation for $f(\rho)$

$$\rho f''(\rho) + 2[(l+1) - \rho^2] f'(\rho) + [\lambda - (2l+3)]\rho f(\rho) = 0 \tag{3.86}$$

We can solve this equation by assuming the series expansion

$$f(\rho) = \sum_{n=0}^{\infty} a_n \rho^n \tag{3.87}$$

Substituting in (3.86), we get

$$\begin{aligned} 0 &= \sum_{n=0}^{\infty} a_n \left\{ n(n-1)\rho^{n-1} + 2(l+1)n\rho^{n-1} - 2n\rho^{n+1} + [\lambda - (2l+3)]\rho^{n+1} \right\} \\ &= \sum_{n=0}^{\infty} \rho^n \left\{ n(n+1)a_{n+1} + 2(l+1)(n+1)a_{n+1} - 2(n-1)a_{n-1} + [\lambda - (2l+3)]a_{n-1} \right\} \end{aligned} \tag{3.88}$$

For $n = 0$, the only surviving term is $2(l+1)a_1 = 0$ which implies $a_1 = 0$. Otherwise, we have the relation

$$a_{n+2} = \frac{2n + 2l + 3 - \lambda}{(n+2)(n+2l+3)} a_n \tag{3.89}$$

since $a_1 = 0$, this equation implies $a_{2r+1} = 0$ for any r, i.e. only even terms contribute to the series. Similar to our discussion for the harmonic oscillator, we can find the asymptotic value of a_{n+2}/a_n for large n

$$\frac{a_{n+2}}{a_n} \to \frac{2}{n}, \qquad n \to \infty \tag{3.90}$$

Thus, a_{2r} behaves asymptotically as $a_{2r} \sim \frac{1}{r!}$ giving $f(\rho) \sim \sum_r \frac{1}{r!}(\rho^2)^r \sim e^{\rho^2}$. This yields a non-normalizable function unless the series terminates which is realized if

$$\lambda = 2n + 2l + 3 = 4r + 2l + 3 \tag{3.91}$$

This gives the energy eigenvalues

$$E = \hbar\omega(2r + l + \frac{3}{2}) = \hbar\omega(N + \frac{3}{2}), \qquad N = 2r + l \tag{3.92}$$

where r and l are non-negative integers. The factor of $3/2$ is what we expect since we have three independent harmonic oscillator. The degeneracy of the energy level labelled by integer N is given by

$$g_N = \sum_{l \le N, l = N \mod 2} (2l+1) \tag{3.93}$$

For $N = 0$, the sum only contains $l = 0$ which gives $g_0 = 1$, for $N = 1$, the sum only contains $l = 1$ which gives $g_1 = 3$. The first few degeneracies are $\{1, 3, 6, 10, 15, 21, \ldots, \}$.

3.2.3 Hydrogen atom

One of the most famous and iconic example for the success of quantum mechanics was the explanation of the spectral lines of the hydrogen atom by Schrödinger in 1926. With our developed formalism, we can finally discuss the hydrogen atom which is given by the central potential $V(r) = -\frac{e^2}{r}$. We note that since the potential is produced by the proton, the proper quantum mechanical treatment of the problem involves writing a wavefunciton describing the coordinates of both the electron and the proton. However, since the proton mass is almost 2000 times larger than the electron mass, we can assume that the proton is not really affected by the potential of the electron and just provides a static potential [3]. A more principled way of doing

[3] this is similar to the case when we consider the effect of earth's gravity on a small everyday object. Although the object and the earth affect each other with the same force, the earth moves very little as a result of this force and it is a very good approximation to think of the earth as being fixed

this is to introduce the relative and center of mass coordinates. In the center of mass frame, the Schrodinger equation reduces to that of a particle with reduced mass $\mu = \frac{m_e m_p}{m_e+m_p}$. Since $m_e \ll m_p$, this reduces to $\mu \approx m_e$ and the relative coordinates basically becomes the electron coordinates. Thus, we can think of the electron moving in a central potential generated by the proton.

The analysis of the Coulomb potential is very similar to the isotropic 3D harmonic oscillator. The first step is to identify the asymptotic behavior of the wavefunction at large r. Unlike the harmonic oscillator potential which grows at infinity, the Coulomb potential decays at infinity. This means that we can have both bound and propagating states like the square well potential. We will now focus on the bound states with $E < 0$. At large r, the radial Schrödinger equation (3.77) becomes

$$u''(r) = \kappa^2 u(r), \qquad \kappa^2 = -\frac{2mE}{\hbar^2} > 0 \tag{3.94}$$

The only normalizable solution is $u(r) \propto e^{-\kappa r}$. Defining $\rho = \kappa r$, we can separate the asymptotic behavior at small and large ρ by writing

$$u_{E,l}(\rho) = \rho^{l+1} e^{-\rho} f(\rho) \tag{3.95}$$

We further define

$$\rho_0 = \sqrt{\frac{2m}{-E}} \frac{e^2}{\hbar} \tag{3.96}$$

$f(\rho)$ satisfies the equation

$$\rho f''(\rho) + 2(l+1-\rho) f'(\rho) + [\rho_0 - 2(l+1)] f(\rho) = 0 \tag{3.97}$$

Substituting a series solution of the form (3.87), we get

$$\begin{aligned} 0 &= \sum_{r=0}^{\infty} a_n \left\{ n(n-1)\rho^{n-1} + 2(l+1)n\rho^{n-1} - 2n\rho^n + [\rho_0 - 2(l+1)]\rho^n \right\} \\ &= \sum_{n=0}^{\infty} \rho^n \left\{ n(n+1)a_{n+1} + 2(l+1)(n+1)a_{n+1} - 2na_n + [\rho_0 - 2(l+1)]a_n \right\} \end{aligned} \tag{3.98}$$

which gives

$$a_{r+1} = \frac{-\rho_0 + 2(r+l+1)}{(r+1)(r+2(l+1))} a_r \tag{3.99}$$

For large r, we have $\frac{a_{r+1}}{a_r} \to \frac{2}{r}$ which implies $a_r \sim \frac{2^r}{r!}$. This gives $f(\rho) \sim e^{2\rho}$ which is unnormalizable. Thus, we require the series to terminate which implies

$$\rho_0 = 2(r+l+1) = 2n \tag{3.100}$$

where we defined the principal quantum number $n = r + l + 1 = 1, 2, 3, \ldots$. The energy is

$$E = -\frac{me^4}{2\hbar^2 n^2} = -\frac{1}{2} mc^2 \frac{\alpha^2}{n^2} \tag{3.101}$$

where $\alpha = e^2/\hbar c \approx 1/137$ is the fine structure constant. The energy scale $\frac{1}{2}mc^2\alpha^2 \approx 13.6$ eV is called a Rydberg. For a nucleas with atomic number Z, it is straightforward to see that E will be modified as

$$E_Z = E_{Z=1} Z^2 \tag{3.102}$$

We see that the energy eigenvalues only depend on the principle quantum number n. For $n = 1$, we have $r = l = 0$. For $n = 2$, we have $r = 0$, $l = 1$ or $r = 1$, $l = 0$. In general, the degeneracy of the n-the level is

$$g_n = \sum_{l=0}^{n-1} (2l+1) = n^2 \tag{3.103}$$

Notice that this degeneracy is larger than what we would have expected on symmetry ground only. Symmetry will tell us that for a given l, all $2l+1$ states with different values of $m = -l, \ldots, l$ are degenerate but there is no reason for different values of l to give rise to degenerate energy eigenvalues. It turns out that the Coulomb potential has an extra symmetry that explains this accidental degeneracy. We will discuss this symmetry later.

We note that in realistic systems, there are corrections beyond the $1/r$ correction, e.g. relativistic corrections that split this degeneracy. Furthermore, in crystals, even the degeneracy associated with different values of m is lifted since the crystal breaks continuous rotation symmetry.

We also note that the Coulomb problem has a build-in length scale

$$\frac{1}{\kappa} = a_0 \frac{n}{Z} \tag{3.104}$$

where a_0 is called the Bohr radius

$$a_0 = \frac{\hbar^2}{me^2} \tag{3.105}$$

The bohr radius gives the characteristic size of the bound state. In the energy level labelled by the principle quantum number n, the size of the bound state is roughly given by $n^2 a_0$.

3.3 Addition of angular momenta

So far, we have discussed two types of angular momentum. There is intrinsic or spin angular momentum. This angular momentum can be thought of as a fundamental property of quantum objects that cannot be reduced to simpler properties. It satisfies the angular momentum algebra $[S_i, S_j] = i\hbar\epsilon_{ijk}S_k$ and its representations are generally labelled by non-negative half-integers s. We also discussed orbital angular momentum $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ which is constructed from position and momentum operators and whose representations, the spherical harmonics, are labelled by non-negative integers l.

In general, a particle has both spin and orbital angular momentum and we will now discuss how to combine them together. This applies more generally to the addition of any pair of angular momentum operators as we will see. The first thing we want to consider when thinking of combining spin and orbital angular momenta is the structure of the Hilbert space. We have so far either focused on the spin component. For example, for spin $1/2$, we labelled the Hilbert space by the ket vectors $|+\rangle$ and $|-\rangle$. On the other hand, when considering the orbital or spatial dependence of the states, we ignored the spin part and expanded the kets in terms of eigenkets of the position operator $\hat{\boldsymbol{x}}$, $|\boldsymbol{x}\rangle$. However, since the position operator and the spin operator commute, we can construct basis labelled by both spin and position operators $|\pm, \boldsymbol{x}\rangle$ and write the wavefunction $\psi_\pm(\boldsymbol{x}) = \langle \pm, \boldsymbol{x}|\psi\rangle$ which can be written in the vector notation

$$\psi(\boldsymbol{x}) = \begin{pmatrix} \psi_+(\boldsymbol{x}) \\ \psi_-(\boldsymbol{x}) \end{pmatrix}, \qquad \int d^3\boldsymbol{x}\, \psi^\dagger(\boldsymbol{x})\psi(\boldsymbol{x}) = 1 = \int d^3\boldsymbol{x}\, [|\psi_+(\boldsymbol{x})|^2 + |\psi_-(\boldsymbol{x})|^2] \tag{3.106}$$

The basis $|\pm, \boldsymbol{x}\rangle$ can be understood as a tensor product $|\pm\rangle \otimes |\boldsymbol{x}\rangle$. A tensor product of two Hilbert spaces V_1 and V_2 with basis vectors $\boldsymbol{e}^{(1)}_l$, $l = 1, \ldots, N_1$ and $\boldsymbol{e}^{(2)}_m$, $m = 1, \ldots, N_2$ is the $N_1 \times N_2$-dimensional Hilbert space whose basis vectors can be constructed by combining the basis vectors $\boldsymbol{e}^{(1)}$ and $\boldsymbol{e}^{(2)}$.

The total angular momentum operator is the sum of spin and orbital angular momenta $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$. Since $\boldsymbol{L}$ only acts on the orbital part and $\boldsymbol{S}$ only acts on the spin part, the proper way to write this as an operator acting on the full Hilbert space is

$$\boldsymbol{J} = \mathbb{1} \otimes \boldsymbol{L} + \boldsymbol{S} \otimes \mathbb{1} \tag{3.107}$$

This makes it clear that the operators $\boldsymbol{L}$ and $\boldsymbol{S}$ commute with each other. However, for simplicity, it is common to use the simpler but more sloppy notation where an operator $\mathbb{1} \otimes \mathcal{O}$ is just written as $\mathcal{O}$ with the understanding that the operator acts as the identity in the parts of the Hilbert space where its action is

not defined. Since $[L_i, S_j] = 0$, the total angular momentum $\boldsymbol{J}$ satisfies the angular momentum algebra as expected.

Another example for the addition of angular momenta is if we take two spin $1/2$ particles. The Hilbert space for the two spins is 4-dimensional and is spanned by $|\sigma_1\rangle \otimes |\sigma_2\rangle$, $\sigma_{1,2} = \pm$. The total spin operator is given by

$$\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2 = \boldsymbol{S} \otimes \mathbb{1} + \mathbb{1} \otimes \boldsymbol{S} \tag{3.108}$$

More generally, we would like to consider two angular momentum operators $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$ and define the total angular momentum as $\boldsymbol{J} = \boldsymbol{J}_1 \otimes \mathbb{1} + \mathbb{1} \otimes \boldsymbol{J}_2$. The individual components of $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$ commute with each other $[J_{1i}, J_{2j}] = 0$ which immediatley implies

$$[J_i, J_j] = [J_{1i} + J_{2i}, J_{1j} + J_{2j}] = [J_{1i}, J_{1j}] + [J_{2i}, J_{2j}] = i\hbar\epsilon_{ijk}(J_{1k} + J_{2k}) = i\hbar\epsilon_{ijk}J_k \tag{3.109}$$

Thus, the total angular momentum satisfies the angular momentum commutation relations as expected. The action of a finite rotation by an angle φ around an axis $\hat{n}$ is given by

$$D[R_{\hat{n}}(\varphi)] = D_1[R_{\hat{n}}(\varphi)] \otimes D_2[R_{\hat{n}}(\varphi)] = e^{-i\varphi\frac{\boldsymbol{J}_1\cdot\hat{n}}{\hbar}} \otimes e^{-i\varphi\frac{\boldsymbol{J}_2\cdot\hat{n}}{\hbar}} \tag{3.110}$$

For infinitesmal φ, we can write $D[R_{\hat{n}}(\varphi)] = \mathbb{1} - i\frac{\varphi}{\hbar}\hat{n} \cdot [\boldsymbol{J}_1 \otimes \mathbb{1} + \mathbb{1} \otimes \boldsymbol{J}_2]$. This means that $\boldsymbol{J} = \boldsymbol{J}_1 \otimes \mathbb{1} + \mathbb{1} \otimes \boldsymbol{J}_2$ is the generator for a total rotation $D[R_{\hat{n}}(\varphi)]$ as expected. Our goal is to understand how the eigenfunctions of the total angular momentum are related to the eigenfunctions of the individual angular momentum operators.

Recall that, in general, we need to find a (maximal) set of commuting operators to label the basis of the Hilbert space. For the angular momentum algebra, we found that a natural choice of such commuting set of operators is given by the total angular momentum and any given component (taken to be the z-component by convention). However, for the case of addition of two angular momentum operators $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$, it turns out there are two natural choices. One is just to take $\boldsymbol{J}_1^2$, J_{1z}, $\boldsymbol{J}_2^2$ and J_{2z}. On the other hand, many physical contexts requires labelling the state with the total angular momentum, which is usually the quantity that couples to external physical probes, instead of individual components. In this case, it makes sense to use the total angular momentum $\boldsymbol{J}^2$ and its z-component J_z to label the states. Now since $\boldsymbol{J}^2 = \boldsymbol{J}_1^2 + \boldsymbol{J}_2^2 + 2\boldsymbol{J}_1 \cdot \boldsymbol{J}_2 = \boldsymbol{J}_1^2 + \boldsymbol{J}_2^2 + 2J_{1z}J_{2z} + J_{1+}J_{2-} + J_{2+}J_{1-}$. This means that $\boldsymbol{J}^2$ commutes with $\boldsymbol{J}_1^2$ and $\boldsymbol{J}_2^2$ but not J_{1z} or J_{2z}. Thus, the second possible choice for commuting operators is $\boldsymbol{J}^2$, J_z, $\boldsymbol{J}_1^2$ and $\boldsymbol{J}_2^2$. The eigenfunctions for the first choice are given by $|j_1 j_2; m_1 m_2\rangle$

$$\boldsymbol{J}_1^2|j_1 j_2; m_1 m_2\rangle = \hbar^2 j_1(j_1+1)|j_1 j_2; m_1 m_2\rangle, \qquad J_{1z}|j_1 j_2; m_1 m_2\rangle = \hbar m_1|j_1 j_2; m_1 m_2\rangle \tag{3.111}$$

$$\boldsymbol{J}_2^2|j_1 j_2; m_1 m_2\rangle = \hbar^2 j_2(j_2+1)|j_1 j_2; m_1 m_2\rangle, \qquad J_{2z}|j_1 j_2; m_1 m_2\rangle = \hbar m_2|j_1 j_2; m_1 m_2\rangle \tag{3.112}$$

The eigenfunctions for the second choice are given by $|j_1 j_2; jm\rangle$

$$\boldsymbol{J}_1^2|j_1 j_2; jm\rangle = \hbar^2 j_1(j_1+1)|j_1 j_2; jm\rangle, \qquad \boldsymbol{J}_2^2|j_1 j_2; jm\rangle = \hbar^2 j_2(j_2+1)|j_1 j_2; jm\rangle \tag{3.113}$$

$$\boldsymbol{J}^2|j_1 j_2; jm\rangle = \hbar^2 j(j+1)|j_1 j_2; jm\rangle, \qquad J_z|j_1 j_2; jm\rangle = \hbar m|j_1 j_2; jm\rangle \tag{3.114}$$

3.3.1 The Clebsch-Gordan coefficients

Using the resolution of unity, we can expland one of these bases into the other

$$|j_1 j_2; jm\rangle = \sum_{m_1, m_2} |j_1 j_2; m_1 m_2\rangle\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle \tag{3.115}$$

The coefficients $\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle$ are known as the Clebsch-Gordan coefficients.

The Clebsch-Gordan coefficients have several important properties. First since $J_z - J_{1z} - J_{2z} = 0$, we can derive the relation

$$0 = \langle j_1 j_2; m_1 m_2|J_z - J_{1z} - J_{2z}|j_1 j_2; jm\rangle = \hbar(m - m_1 - m_2)\langle j_1 j_2; m_1 m_2|j_1 j_2; jm\rangle \tag{3.116}$$

Thus, the Clebsch-Gordan coefficient $\langle j_1 j_2; m_1 m_2 | j_1 j_2; jm\rangle$ vanishes unless $m = m_1 + m_2$. This makes sense since a state with total z-component of angular momentum m can only be decomposed into states whose z-component adds up to m.

A second relation is that

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \tag{3.117}$$

This relation makes intuitive sense since the length of a sum of two vectors cannot exceed the sum of their lengths (which is realized if they are parallel) and cannot be smaller than the difference between their lengths (which is realized if they are anti-parallel). This relation implies that the dimension of the Hilbert space labelled by $|j_1 j_2; jm\rangle$ and $|j_1 j_2; m_1 m_2\rangle$ match. To see this, note that in the $|j_1 j_2; m_1 m_2\rangle$ basis, $-j_1 \leq m_1 \leq j_1$ and $-j_2 \leq m_2 \leq j_2$ leading to a total Hilbert space dimension of $(2j_1 + 1)(2j_2 + 1)$. On the other hand, counting the dimension of the $|j_1 j_2; jm\rangle$ gives $\sum_j (2j + 1)$. Without loss of generality, we can assume $j_1 > j_2$ which implies that the sum over j goes from $j_1 - j_2$ to $j_1 + j_2$ yielding

$$\sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) = (j_1+j_2)(j_1+j_2+1) - (j_1-j_2-1)(j_1-j_2) + 2j_1 + 1 = (2j_1+1)(2j_2+1) \tag{3.118}$$

Thus, the Clebsch-Gordan coefficients $\langle j_1 j_2; m_1 m_2 | j_1 j_2; jm\rangle$ form a square matrix whose linear dimension is $(2j_1 + 1)(2j_2 + 1)$. It is relatively easy to see that this matrix is unitary since it relates to orthonormal basese to each other. As we will see later, the Clebsch-Gordan coefficients can also be chosen to be real which means that the matrix they form is an orthogonal matrix.

Before discussing the general procedure to construct the Clebsch-Gordan coefficients, it is useful to consider some simple examples. The first one is the addition of two spin $1/2$ particles. Here, $j_1 = j_2 = 1/2$ and we can drop the j_1 and j_2 indices from the basis kets for simplicitly. The first basis choice corresponds to labelling a state with the S_z component of each of the two particles yielding four states $|++\rangle$, $|+-\rangle$, $|-+\rangle$, and $|--\rangle$. The second basis is labelled by the total spin $j = s$ whose possible values are $s = 0, 1$. For $s = 0$, $m_s = 0$ whereas for $s = 1$, $m_s = 0, \pm 1$. These are called singlet ($s = 0$) and triplet ($s = 1$) representations. To expand the singlet state $|0, 0\rangle$ in terms of the state $|\pm, \pm\rangle$, we use the fact that $m = 0 = m_1 + m_2$ which means that only $|+, -\rangle$ and $|-, +\rangle$ will contribute to the expansion. Thus,

$$|0, 0\rangle = \alpha|+-\rangle + \beta|-+\rangle \tag{3.119}$$

Applying $J_+ = J_{1+} + J_{2+}$ to both sides, we get the condition $0 = (\alpha + \beta)|++\rangle$ which implies $\alpha = -\beta$. The normalization fixes the total magnitude of $|\alpha| = \frac{1}{\sqrt{2}}$ while the overall phase can be chosen arbitrarily. This gives the singlet state

$$|0, 0\rangle = \frac{1}{\sqrt{2}}[|+-\rangle - |-+\rangle] \tag{3.120}$$

For the triplet states, we can perform a similar analysis. Due to the constraint, $m = m_1 + m_2$, the state $|1, 1\rangle$ can only receive contribution from $|++\rangle$ which implies $|1, 1\rangle = |++\rangle$. Similarly, $|1, -1\rangle$ only receives contribution from $|--\rangle$ which implies $|1, -1\rangle = |--\rangle$. Finally, $|1, 0\rangle$ can be expanded in terms of $|+, -\rangle$ and $|-, +\rangle$. The requirement that this state is orthogonal to $|0, 0\rangle$ immediately yields

$$|1, 0\rangle = \frac{1}{\sqrt{2}}[|+-\rangle + |-+\rangle] \tag{3.121}$$

In summary

$$|0,0\rangle = \frac{1}{\sqrt{2}}[|+-\rangle - |-+\rangle], \quad |1,1\rangle = |++\rangle, \quad |1,-1\rangle = |--\rangle, \quad |1,0\rangle = \frac{1}{\sqrt{2}}[|+-\rangle + |-+\rangle] \tag{3.122}$$

In general, we can derive recursion relations for the Clebsch-Gordan coefficients by acting with the raising/lowering operators as follows

$$J_\pm |j_1 j_2; jm\rangle = (J_{1,\pm} + J_{2,\pm}) \sum_{m_1, m_2} |j_1 j_2; m_1 m_2\rangle \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm\rangle \tag{3.123}$$

Using the relation

$$J_\pm|j,m\rangle = \sqrt{(j\mp m)(j\pm m+1)}|j,m\pm 1\rangle \tag{3.124}$$

we get

$$\begin{aligned}\sqrt{(j\mp m)(j\pm m+1)}&|j_1j_2;j,m\pm 1\rangle \\ &= \sum_{m_1,m_2}\sqrt{(j_1\mp m_1)(j_1\pm m_1+1)}|j_1j_2;m_1\pm 1,m_2\rangle\langle j_1j_2;m_1m_2|j_1j_2;jm\rangle \\ &\quad+\sum_{m_1,m_2}\sqrt{(j_2\mp m_2)(j_2\pm m_2+1)}|j_1j_2;m_1,m_2\pm 1\rangle\langle j_1j_2;m_1m_2|j_1j_2;jm\rangle\end{aligned} \tag{3.125}$$

Multiplying both sides by $\langle j_1,j_2;m_1,m_2|$ and using orhtonormality, yields

$$\begin{aligned}\sqrt{(j\mp m)(j\pm m+1)}&\langle j_1,j_2;m_1,m_2|j_1j_2;j,m\pm 1\rangle \\ &= \sqrt{(j_1\mp m_1+1)(j_1\pm m_1)}\langle j_1j_2;m_1\mp 1m_2|j_1j_2;jm\rangle \\ &\quad+\sqrt{(j_2\mp m_2+1)(j_2\pm m_2)}\langle j_1j_2;m_1m_2\mp 1|j_1j_2;jm\rangle\end{aligned} \tag{3.126}$$

Using this relation together with normalization, we can determine the Clebsch-Gordan coefficients in general up to an overall phase that can be chosen by convention so that all coefficients are real.

3.3.2 Transformation under rotations

We have so far considered many vector quantities that are promoted in the quantum theory to operators such as $\boldsymbol{x}$, $\boldsymbol{p}$ and $\boldsymbol{L}$. However, we have not yet discussed systematically the requirement of compatibility between how a general vector operator is expected to transform under rotation and how rotation is represented on kets. More specifically, let us consider some vector $\boldsymbol{V}$ with components V_i. The expectation value of $\boldsymbol{V}$ in any ket should transform as a vector under rotation as

$$\langle\alpha|V_i|\alpha\rangle \mapsto R_{ij}\langle\alpha|V_j|\alpha\rangle = R_{ij}\langle\alpha|V_j|\alpha\rangle \tag{3.127}$$

On the other hand, the ket itself transforms under rotation as $|\alpha\rangle \mapsto D(R)|\alpha\rangle$. This means that

$$R_{ij}\langle\alpha|V_j|\alpha\rangle = \langle\alpha|D(R)^\dagger V_i D(R)|\alpha\rangle \tag{3.128}$$

Since this should apply for any ket $|\alpha\rangle$, it implies the operator identity

$$D(R)^\dagger V_i D(R) = R_{ij}V_j \tag{3.129}$$

Taking R to be an infinitesmal rotation implies

$$[J_l,V_i] = -i\hbar[\gamma_l]_{ij}V_j \tag{3.130}$$

where γ_l are the infinitesmal generators of 3D rotations given by

$$\gamma_1 = \begin{pmatrix}0&0&0\\0&0&-1\\0&1&0\end{pmatrix},\qquad \gamma_2 = \begin{pmatrix}0&0&1\\0&0&0\\-1&0&0\end{pmatrix},\qquad \gamma_3 = \begin{pmatrix}0&-1&0\\1&0&0\\0&0&0\end{pmatrix} \tag{3.131}$$

It is not hard to see that $[\gamma_l]_{ij} = -\epsilon_{lij}$ which implies

$$[J_i,V_k] = i\hbar\epsilon_{ijk}V_k \tag{3.132}$$

which is a property of any objects that transforms as a vector in the quantum theory.

Chapter 4

Symmetries in Quantum Mechanics

We have already seen a few examples of symmetries in quantum mechanics. For instance, we have seen that the Schrödinger equation with a spherically symmetric potential commutes with the angular momentum operator. We have also seen that the free particle Schrödinger equation commutes with the translation operator which means that its eigenstates are also momentum eigenstates. These two are examples of continuous symmetries in quantum mechanics. We have also earlier discussed the parity operation when studying the harmonic oscillator and double well problems. Parity is an example of a discrete symmetry operation. In this and the following lectures, we will have a more systematic discussion of symmetries in quantum mechanics.

4.1 General Formalism

The connection between symmetries and conservation laws has already been well understood in classical mechanics. For instance, if the classical Hamiltonian of a system is independent of the position variable $\boldsymbol{x}$, i.e. the Hamiltonian is symmetric under translation $\boldsymbol{x} \mapsto \boldsymbol{x} + \boldsymbol{a}$, the Hamilton equations of motion imply $\dot{\boldsymbol{p}} = 0$ which means that $\boldsymbol{p}$ is a constant of motion. In the quantum theory, symmetries are described by unitary operators that leave the Hamiltonian invariant

$$\mathcal{S}\mathcal{H}\mathcal{S}^\dagger = \mathcal{H} \tag{4.1}$$

If $\mathcal{S}$ is a continuous symmetry labelled by some set of parameters λ^a, then we can define its infinitesimal generator G_a, as we have done for translation and rotation, via

$$\mathcal{S}(\lambda^a) = \mathbb{1} - \frac{i}{\hbar}\lambda^a G_a + O(\lambda^2) \tag{4.2}$$

where G_a are Hermitian operators $G_a^\dagger = G_a$.

The invariance of the Hamiltonian under the action of $\mathcal{S}$ implies

$$[G_a, \mathcal{H}] = 0 \tag{4.3}$$

That is, the infinitesimal symmetry generators commute with the Hamiltonian. An important consequence of this relation is that operators G_a are time independent in the Heisenberg picture since

$$i\hbar\frac{dG_a}{dt} = [G_a, \mathcal{H}] = 0 \tag{4.4}$$

This means that the operators G_a are constants of motion. This is the quantum version of the classical statement that a symmetry implies a conserved quantity or a constant of motion. In the Schrödinger picture where the time-dependent is in the states not the operators, the commutation relation (4.3) also has an important consequence. Consider an eigenket of a symmetry operator G at time $t = 0$

$$G|\lambda\rangle = \lambda|\lambda\rangle \tag{4.5}$$

Under time-evolution, $|\lambda\rangle$ will generally evolve to a different state (note that we are not assuming here that $|\lambda\rangle$ is a stationary state)

$$|\lambda, t_0; t\rangle = \mathcal{U}(t, t_0)|\lambda\rangle \tag{4.6}$$

Now recall that $\mathcal{U}(t, t_0)$ only depends on the Hamiltonian [1]. Thus, $[G_a, \mathcal{H}] = 0$ implies $[G_a, \mathcal{U}(t, t_0)] = 0$ which leads to

$$G|\lambda, t_0; t\rangle = G\mathcal{U}(t, t_0)|\lambda\rangle = \mathcal{U}(t, t_0)G|\lambda\rangle = \lambda\mathcal{U}(t, t_0)|\lambda\rangle = \lambda|\lambda, t_0; t\rangle \tag{4.7}$$

Thus, $|\lambda, t_0; t\rangle$ remains an eigenstate of G with eigenvalue λ at all times. Notice that this does not mean $|\lambda, t_0; t\rangle$ is a stationary state. For instance, let us consider a non-stationary state described by an even wavefunction $\psi(-x) = \psi(x)$ in the 1D harmonic oscillator. Such state will in general be described by a linear combination of even parity harmonic oscillator eigenstates. Under time evolution, the coefficients of such linear combination will change and the wavefunction itself will change but it will remain an even parity wavefunction. We will never introduce non-vanishing coefficients in the odd parity wavefunctions.

Symmetry has an important consequence for the spectrum of the Hamiltonian. Consider an eigenket of the Hamiltonian $|n\rangle$ with eigenvalue E_n, then the state $G|n\rangle$ is also an eigenket with the same eigenvalue since

$$\mathcal{H}G|n\rangle = G\mathcal{H}|n\rangle = E_n G|n\rangle \tag{4.8}$$

Then we have two possibilities:

1. $G|n\rangle = \lambda|n\rangle$ for some constant λ: this implies that $|n\rangle$ is also an eigenstate of G.
2. $G|n\rangle \neq \lambda|n\rangle$ for any λ: this means that $G|n\rangle$ and $|n\rangle$ represent different states i.e. the spectrum of the Hamiltonian $\mathcal{H}$ is degenerate.

We have already seen this with rotation symmetry which implies that the orbital angular momentum components commute with the Hamiltonian $[L_a, \mathcal{H}] = 0$. We have chosen to label the orbital angular momentum eigenspaces by the eigenvalues of $\boldsymbol{L}^2$ and L_z, denoted by $|l, m\rangle$. For the case of L_z, we have the first case above where $L_z|l, m\rangle \propto |l, m\rangle$. However for $L_{x,y}$, or more conveniently $L_\pm$, we have $L_\pm|l, m\rangle \propto |l, m \pm 1\rangle \neq \lambda|l, m\rangle$ for any λ. This represents the second case and implies that $|l, m\rangle$ and $|l, m \pm 1\rangle$ are degenerate energy eigenstates. This gives a $2l + 1$ degenerate space of eigenstates for a given l.

4.2 Parity symmetry

Parity or space-inversion is an operation that flips all spatial components sending a vector $\boldsymbol{x}$ to $-\boldsymbol{x}$. It is an example of the norm preserving operators we discussed in Lecture 13 which are described by an orthogonal matrix $RR^T = 1$ with $\det R = -1$ (it is not part of the special orthogonal group). Explicitly, the parity action on a 3D vector is described by the matrix

$$P = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{4.9}$$

Our goal now is to define a unitary operator π which represents the action of parity on kets in the same way $D(R)$ represented the action of rotation. The operator π should be distinguished from P in that it acts on kets that can be of arbitrary dimension. Similar to what we did with rotations, we require π to satisfy

$$\langle\alpha|\pi^\dagger x_i \pi|\alpha\rangle = \sum_j P_{ij}\langle\alpha|x_j|\alpha\rangle = -\langle\alpha|x_i|\alpha\rangle \tag{4.10}$$

[1] In the simplest cases it is just given by $e^{-\frac{i}{\hbar}\mathcal{H}(t-t_0)}$ but even in complicated cases where it is given by the Dyson series (Eq. 16 in Lecture 5), it only depends on $\mathcal{H}(t)$.

Since $|\alpha\rangle$ is an arbitrary ket, this implies

$$\pi^\dagger \boldsymbol{x} \pi = -\boldsymbol{x}, \tag{4.11}$$

or equivalently, $\{\pi, \boldsymbol{x}\} = 0$.

The anticommutation of the parity operator and the position operator implies that the ket $\pi|\boldsymbol{x}\rangle$ satisfies

$$\boldsymbol{x}\pi|\boldsymbol{x}_0\rangle = -\pi\boldsymbol{x}|\boldsymbol{x}_0\rangle = -\boldsymbol{x}_0\pi|\boldsymbol{x}_0\rangle \tag{4.12}$$

Thus, the ket $\pi|\boldsymbol{x}_0\rangle$ is also a position eigenket with eigenvalue $-\boldsymbol{x}_0$ which means that $\pi|\boldsymbol{x}_0\rangle = e^{i\chi(\boldsymbol{x}_0)}|-\boldsymbol{x}_0\rangle$. The phase χ can be removed by an appropriate choice of gauge for the position eigenkets [2]. This implies that acting with π twice yields the same state $\pi^2|\boldsymbol{x}_0\rangle = |\boldsymbol{x}_0\rangle$, i.e. $\pi^2 = 1$. A unitary operator that squares to 1 is also hermitian since

$$\pi^\dagger = \pi^\dagger\pi^2 = (\pi^\dagger\pi)\pi = \pi \tag{4.13}$$

This also implies that the eigenvalues of the parity operator are ± 1.

The action of parity on momentum can be understood as follows. In the position basis, the momentum is represented as $\boldsymbol{p} = -i\hbar\nabla_{\boldsymbol{x}}$ which suggests that $\boldsymbol{p}$ is also odd under parity. We can understand this from a more general basis-independent perspective by noting that translation and space inversion satisfy

$$Pt_{\boldsymbol{a}} = t_{-\boldsymbol{a}}P \tag{4.14}$$

which is the statement that translating a vector by $\boldsymbol{a}$ then applying inversion is the same as translating the inverted vector by $-\boldsymbol{a}$. The same relation should apply for the operators $T_{\boldsymbol{a}}$ and π representing the action of translation and inversion on kets, respectively, i.e. $\pi T_{\boldsymbol{a}} = T_{-\boldsymbol{a}}\pi$. Taking $\boldsymbol{a}$ to be infinitesimal and using the fact that momentum is the generator of translation $T_{\boldsymbol{a}} = \mathbb{1} - \frac{i}{\hbar}\boldsymbol{a}\cdot\boldsymbol{p}$ yields

$$\pi\boldsymbol{p} = -\boldsymbol{p}\pi \tag{4.15}$$

Thus, parity also anti-commutes with the momentum operator.

Finally, we want to understand the behavior of angular momentum under parity. As discussed previously, there is two types of angular momentum: (i) orbital angular momentum $\boldsymbol{L} = \boldsymbol{x}\times\boldsymbol{p}$ and (ii) intrinsic angular momentum which is defined more abstractly as the generator of rotation. The fact that parity anticommutes with both $\boldsymbol{x}$ and $\boldsymbol{p}$ means that it commutes with the orbital angular momentum. For more general angular momenta that cannot be written in terms of $\boldsymbol{x}$ and $\boldsymbol{p}$, we need to use the definition of angular momentum as generator of rotation and note that parity commutes with a general 3D rotation, $PR = RP$, which implies that it commutes with the infinitesimal generator of rotation

$$[\pi, \boldsymbol{J}] = 0 \tag{4.16}$$

This relation is a little strange. We generally expect a vector quantity to behave as a vector under rotation $V_i \mapsto R_{ij}V_j$ and to flip its sign under inversion $V_i \mapsto -V_i$. Although this is true for $\boldsymbol{x}$ and $\boldsymbol{p}$, it is not true for $\boldsymbol{J}$ which remains invariant under inversion. Such vector quantities which are invariant under inversion are called Axial or pseudovectors. We note that if we take the inner product of two vectors or pseudovectors, e.g. $\boldsymbol{x}\cdot\boldsymbol{p}$, the resulting quantity is a scalar that is invariant under both rotation and inversion. On the other hand, the inner product of a vector and a pseudovector yields a quantity that is odd under inversion. Such quantities are called pseudoscalars.

To understand how electromagnetic fields transform under parity, let us see what we expect classically. The equation for the classical Lorentz force is

$$\boldsymbol{F}_{\text{Lorentz}} = q(\boldsymbol{E} + \boldsymbol{v}\times\boldsymbol{B}) \tag{4.17}$$

Since $\boldsymbol{F} = m\ddot{\boldsymbol{x}}$, we expect $\boldsymbol{F}$ to be odd under parity, i.e. to transform as a vector rather than a pseudovector. Since electric charge q is clearly a scalar, then the electric field should also be a vector, i.e. odd under

[2] For example, in 1D, we can define $|-x\rangle = \pi|x\rangle$ for $x > 0$.

parity. On the other hand, since the velocity $\boldsymbol{v}$ is odd under parity, $\boldsymbol{B}$ has to be even under parity i.e. $\boldsymbol{B}$ is a pseudovector. We can also verify that Maxwell equations are invariant under

$$\boldsymbol{x} \mapsto -\boldsymbol{x}, \qquad \boldsymbol{J} \mapsto -\boldsymbol{J}, \qquad \boldsymbol{E} \mapsto -\boldsymbol{E}, \qquad \boldsymbol{B} \mapsto \boldsymbol{B} \tag{4.18}$$

Thus, in the quantum theory, we expect the addition of an electromagnetic potential to a Hamiltonian to preserve parity i.e. $\pi\mathcal{H}(\boldsymbol{A},\varphi)\pi = \mathcal{H}(\boldsymbol{A},\varphi)$. This implies

$$\pi\mathcal{H}(\boldsymbol{A},\phi)\pi = \frac{1}{2m}(\boldsymbol{p} + q\pi\boldsymbol{A}\pi)^2 + q\pi\varphi\pi = \frac{1}{2m}(\boldsymbol{p} - q\boldsymbol{A})^2 + q\varphi \tag{4.19}$$

which implies

$$\pi\varphi\pi = \varphi, \qquad \pi\boldsymbol{A}\pi = -\boldsymbol{A} \tag{4.20}$$

up to a gauge transformation. This immediately gives

$$\pi\boldsymbol{E}\pi = \pi(-\nabla\varphi - \partial_t\boldsymbol{A})\pi = \nabla\varphi + \partial_t\boldsymbol{A} = -\boldsymbol{E}, \qquad \pi\boldsymbol{B}\pi = \pi(\boldsymbol{\nabla}\times\boldsymbol{A})\pi = \boldsymbol{\nabla}\times\boldsymbol{A} = \boldsymbol{B} \tag{4.21}$$

The behavior of the wavefunctions $\psi(\boldsymbol{x}) = \langle\boldsymbol{x}|\psi\rangle$ under inversion can be understood as follows. The wavefunction corresponding to the ket $\pi|\psi\rangle$ can be easily obtained as

$$\psi_\pi(\boldsymbol{x}) = \langle\boldsymbol{x}|\pi|\psi\rangle = \langle -\boldsymbol{x}|\psi\rangle = \psi(-\boldsymbol{x}) \tag{4.22}$$

If $|\psi_\pm\rangle$ is an parity eigenket with eigenvalue $\pm$, then we have

$$\langle\boldsymbol{x}|\pi|\psi_\pm\rangle = \pm\langle\boldsymbol{x}|\psi_\pm\rangle = \pm\psi_\pm(\boldsymbol{x}) \tag{4.23}$$

Equations (4.22) and (4.23) imply

$$\psi_\pm(-\boldsymbol{x}) = \pm\psi_\pm(\boldsymbol{x}) \tag{4.24}$$

This means that $+$ parity eigenvalues correspond to even wavefunctions and $-$ parity eigenvalues correspond to odd wavefunctions, as we discussed earlier.

If the Hamiltonian commutes with the parity operator $[\mathcal{H},\pi] = 0$, then every non-degenerate eigenket of the Hamiltonian is also a parity eigenket. Degenerate eigenkets are generally not parity eigenvalues but we can choose particular linear combinations that are even or odd under parity. If $\mathcal{H}$ describes the motion of a particle in some potential $V(\boldsymbol{x})$, then the condition $[\mathcal{H},\pi] = 0$ is equivalent to $V(-\boldsymbol{x}) = V(\boldsymbol{x})$. Let us now consider some simple cases of potentials satisfying this condition. For simplicity, we will restrict ourselves now to the 1D limit. The simplest case we can think of is that of a free particle where $V(x) = 0$. The eigenfunctions of the Hamiltonian are plane waves $\psi_k(x) = e^{ikx}$. These are not parity eigenfunctions since $\pi\psi_k(x) = e^{-ikx} = \psi_{-k}(x)$. This is consistent with the theorem above since the states $\psi_k(x)$ and $\psi_{-k}(x)$ are degenerate with the same energy $\frac{\hbar^2k^2}{2m}$. Instead of the plane waves, we can choose to write the eigenfunctiosn of the Hamiltonian in terms of sin and cosine, $\psi_{\pm,k}(x) = e^{ikx} \pm e^{-ikx}$ which is proportional to $\cos kx$ for $+$ and $\sin kx$ for $-$ [3] Another example is the harmonic oscillator. Recall that the ground state of the 1D Harmonic oscillator was a Gaussian, which is even under parity. Now since the raising operator is a linear function of x and p, it is odd under parity

$$\{\pi, a\} = 0 = \{\pi, a^\dagger\} \tag{4.25}$$

This means that the n-th eigenstates of the harmonic oscillator $|n\rangle \propto (a^\dagger)^n|0\rangle$ has parity $(-1)^n$. This is consistent with the fact that the eigenstates of the 1D harmonic oscillator are bound states which are always non-degenerate, thus they have to be parity eigenstates.

[3] Note here that we should restrict ourselves to $k > 0$ since $\psi_{\pm,-k}(x) = \pm\psi_{\pm,k}(x)$. The special case of $k = 0$ has only the $+$ state since the $-$ state vanishes.

One important physical consequence of parity symmetry is the following. Consider two parity eigenstates $|\sigma\rangle$ and $|\epsilon\rangle$ such that $\pi|\sigma\rangle = \sigma|\sigma\rangle$ and $\pi|\epsilon\rangle = \epsilon|\epsilon\rangle$, where $\sigma, \epsilon = \pm$. Now imagine an operator that commutes or anticommutes with parity

$$\pi^\dagger \hat{O}_\alpha \pi = \alpha \hat{O}_\alpha, \qquad \alpha = \pm \tag{4.26}$$

Then the matrix elements of such operator between the states $|\sigma\rangle$ and $|\epsilon\rangle$ vanish unless $\alpha\sigma\epsilon = 1$. To see this, consider

$$\langle\sigma|\hat{O}_\alpha|\epsilon\rangle = \langle\sigma|(\pi^\dagger)^2\hat{O}_\alpha\pi^2|\epsilon\rangle = \langle\sigma|\pi^\dagger(\pi^\dagger\hat{O}_\alpha\pi)\pi|\epsilon\rangle = \sigma\epsilon\alpha\langle\sigma|\hat{O}_\alpha|\epsilon\rangle \tag{4.27}$$

Thus, $\sigma\epsilon\alpha = -1$ implies $\langle\sigma|\hat{O}_\alpha|\epsilon\rangle = 0$.

This is an example of something called selection rules that plays an important role in understanding radiative transitions between different atomic states. A particular example is when the operator $\hat{O}$ is taken to be the position operator $\hat{\boldsymbol{x}}$. The selection rule above implies that only states with opposite parity can be connected by $\boldsymbol{x}$. An important consequence of this rule is that for a parity symmetric Hamiltonian with non-degenerate eigenstates $|n\rangle$, the dipole moment of any energy eigenstate, which is proportional to $\boldsymbol{x}$, vanishes since $\langle n|\boldsymbol{x}|n\rangle = 0$.

4.3 Coulomb potential revisited: Lenz vector

Another example where a symmetry has important spectral consequences is related to something we already encountered for the Coulomb potential where we found that the degeneracy was larger than what we expected based on angular momentum conservation alone. Such 'accidental degeneracy' turns out not to be an accident at all. It turns out there is a hidden symmetry of the Coulomb potential that is responsible for this degeneracy. Below, I will briefly outline, how this symmetry works and how it affects the spectrum. For those interested, you can check Sec. 4.1.4 for more details.

It is known that the Coulomb problem in the classical theory had an extra constant of motion in addition to angular momentum known as the Lenz vector given by $\boldsymbol{M} = \frac{\boldsymbol{p}\times\boldsymbol{L}}{m} - \frac{e^2}{r}\boldsymbol{x}$. The quantum version of this vector is given by the operator

$$\boldsymbol{M} = \frac{1}{2m}(\boldsymbol{p}\times\boldsymbol{L} - \boldsymbol{L}\times\boldsymbol{p}) - \frac{e^2}{r}\boldsymbol{x} \tag{4.28}$$

It is tedious but straightforward to verify that $\boldsymbol{M}$ commutes with the Coulomb Hamiltonian

$$\mathcal{H} = \frac{\boldsymbol{p}^2}{2m} - \frac{e^2}{r} \tag{4.29}$$

Furthermore, the commutation relations for the different components of $\boldsymbol{M}$ with the components of angular momentum and with each other are given by

$$[M_i, L_j] = i\epsilon_{ijk}\hbar M_k, \qquad [M_i, M_j] = -i\hbar\epsilon_{ijk}L_k\frac{\mathcal{H}}{2m} \tag{4.30}$$

The occurence of the Hamiltonian in the last relation implies that $\boldsymbol{L}$ and $\boldsymbol{M}$ do not generally form a closed algebra under commutations. This means that the successive application of commutator of different operators L_i and M_i cannot be written as a linear combination of the operators L_i and M_i alone. This implies that if we define the symmetry operator $R_{\alpha,\beta} = e^{-\frac{i}{\hbar}(\alpha^i L_i + \beta^j M_j)}$, the product of two such $R's$ cannot be written again in the same form i.e. these operators will not form a group which is a fundamental requirement for a physical symmetry. This discussion tells us that M_i's do not generate a symmetry action for the Hamiltonian in general. However, if we restrict ourselves to the space of bound states of a given energy $E < 0$, we can define the operator

$$\boldsymbol{N} = \sqrt{-\frac{m}{2E}}\boldsymbol{M} \tag{4.31}$$

we get the algebra

$$[L_i, L_j] = i\epsilon_{ijk}L_k, \qquad [N_i, L_j] = i\epsilon_{ijk}N_k, \qquad [N_i, N_j] = i\epsilon_{ijk}L_k \tag{4.32}$$

which is a higher-dimensional version of the angular momentum algebra where we have 6 generators instead of 3. Can we identify what group this belongs to? We are looking for a group that includes $\mathrm{SO}(3)$ as a subgroup and has 6 generators. The obvious choice which turns out to be the correct one is $\mathrm{SO}(4)$, the group of rotations in 4D. An easier way to understand this algebra is to define $\boldsymbol{I} = \frac{\boldsymbol{L}+\boldsymbol{N}}{2}$ and $\boldsymbol{K} = \frac{\boldsymbol{L}-\boldsymbol{N}}{2}$ which turn out to satisfy the algebra

$$[I_i, I_j] = i\epsilon_{ijk}I_k, \qquad [K_i, K_j] = i\epsilon_{ijk}K_k, \qquad [I_i, K_j] = 0 \tag{4.33}$$

This means that the algebra above is equivalent to two copies of the $\mathrm{SO}(3)$ algebra. The two operators $\boldsymbol{I}$ and $\boldsymbol{K}$ each satisfies the angular momentum algebra so the eigenstates can be labelled by the total angular momenta $\hbar^2 i(i+1)$ and $\hbar^2 k(k+1)$ where i and k are arbitrary half-integers. However, note that $\boldsymbol{I}^2 - \boldsymbol{K}^2 = \boldsymbol{L}\cdot\boldsymbol{N} = 0$ which implies that $i = k$. Thus, the degeneracy of a given eigenstate defined by $i = k$ is $(2i+1)(2k+1) = (2k+1)^2 = 1, 4, 9, \ldots$ (remember that k is half-integer). This is the same degeneracy we found in the Coulomb problem if we identify the principal quantum number n with $2k+1$. Thus, the extra hidden symmetry explains the accidental degeneracy of the Coulomb Hamiltonian.

4.4 Time-reversal symmetry

Time-reversal symmetry in the classical theory is the statement that, in the absence of dissipative forces, if $\boldsymbol{x}(t)$ is a solution to the classical equations of motion in a potential $V(\boldsymbol{x})$, then $\boldsymbol{x}(-t)$ is also a solution since the classical equation of motion $m\ddot{x} = -\boldsymbol{\nabla}V(\boldsymbol{x})$ is invariant under the replacement $t \mapsto -t$. Another way to say this is that if we have a movie for a particle or a collection of particles experiencing a potential and interacting with each other in the absence of dissipative forces, we cannot tell the difference between the movie playing forward or backward. In classical physics, we expect velocity to be odd under time reversal which implies that momentum and current are also odd. Again considering the expression for the Lorentz force, we can deduce that, under time-reversal, $\boldsymbol{E}$ is even while $\boldsymbol{B}$ is odd. We can explicitly verify that the Maxwell equations are invariant under

$$\boldsymbol{x} \mapsto \boldsymbol{x}, \qquad t \mapsto -t, \qquad \boldsymbol{J} \mapsto -\boldsymbol{J}, \qquad \boldsymbol{E} \mapsto \boldsymbol{E}, \qquad \boldsymbol{B} \mapsto -\boldsymbol{B} \tag{4.34}$$

The fact that $\boldsymbol{B}$ is odd under time-reversal makes intuitive sense since $\boldsymbol{B}$ is usually generated microscopically by some circulating currents which would switch direction under time-reversal. It is important to emphasize the following. If we study a system subject to a fixed external magnetic field, the system will appear to break time-reversal symmetry. This means that if we look at the time-reversed versions of trajectories of the system *keeping the external field fixed* we can tell the difference between a forward moving and a backward moving trajectory. Our goal now is to understand how time-reversal manifests in the quantum theory.

Let us start by considering the Schrödinger equation

$$i\hbar\frac{d}{dt}\psi(\boldsymbol{x}, t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{x})\right)\psi(\boldsymbol{x}, t) \tag{4.35}$$

Since this equation is linear rather than quadratic in time-derivatives, we see that for a solution $\psi(\boldsymbol{x}, t)$, $\psi(\boldsymbol{x}, -t)$ is not necessarily a solution. Does this mean time-reversal is broken in the quantum theory? This would be very surprising. One hint of how time-reversal should act in the quantum theory is the fact that time always appears in the quantum theory combined with a factor of i suggesting that the correct implementation of time-reversal symmetry should also involve complex conjugation. Indeed, if we can verify that whenever $\psi(\boldsymbol{x}, t)$ is a solution to the Schrödinger equation, $\psi(\boldsymbol{x}, -t)^*$ is also a solution.

But what does it mean to say that time-reversal action involves complex conjugation? In the operator formalism of the quantum theory, we have seen that symmetry transformations are implemented by unitary operators. However, the transformation that maps ψ to ψ^* is clearly non-unitary. The simplest way to see this is that $\langle\psi|\chi\rangle = \int d\boldsymbol{x}\psi^*(\boldsymbol{x})\chi(\boldsymbol{x}) \mapsto \int d\boldsymbol{x}\psi(\boldsymbol{x})\chi^*(\boldsymbol{x}) = \langle\psi|\chi\rangle^*$ i.e. the inner product of two kets is not invariant under complex conjugation. Does this mean that time-reversal is an invalid symmetry operation in the quantum theory?

The answer turns out to be no. We have just been using a restricted definition of symmetry operators. It is something we have already touched upon very briefly in one of the earlier lectures, but we can address more systematically now. The only measurable in the quantum theory is the absolute value of the overlap of two kets $|\langle\alpha|\beta\rangle|$ whose square gives the probability for the state $|\alpha\rangle$ to be measured in the state $|\beta\rangle$. This means that a symmetry operator $|\alpha\rangle \mapsto S|\alpha\rangle$ should satisfy the requirement

$$|\langle\alpha|\beta\rangle| \mapsto |\langle S\alpha|S\beta\rangle| = |\langle\alpha|\beta\rangle| \tag{4.36}$$

This is clearly satisfied by any unitary transformation $|\alpha\rangle \mapsto U|\alpha\rangle$ since $|\langle U\alpha|U\beta\rangle| = |\langle\alpha|U^\dagger U\beta\rangle| = |\langle\alpha|\beta\rangle|$. However, it is also satisfies with the complex conjugation operator $\psi \mapsto \psi^*$ defined above which maps $\langle\alpha|\beta\rangle$ to $|\langle\alpha|\beta\rangle^*$ which still preserves the absolute value of the overlap. Complex conjugation belongs more generally to a class of symmetry operators called anti-unitary. An anti-unitary operator is defined by $|\alpha\rangle \mapsto \Theta|\alpha\rangle$

$$\langle\Theta\alpha|\Theta\beta\rangle = \langle\alpha|\beta\rangle^*, \qquad \Theta(c_1|\alpha\rangle + c_2|\beta\rangle) = c_1^*\Theta|\alpha\rangle + c_2^*\Theta|\beta\rangle \tag{4.37}$$

It is easy to see that the product of two anti-unitary operators is unitary which means that anti-unitary operators do not form a group by themselves. Instead, we can construct a group consisting of unitary and anti-unitary operators which contains unitary operators as a subgroup.

We have already seen an example of an anti-unitary operator which is the complex conjugation operator that we denote by $\mathcal{K}$. Consider for example the spin operators for a spin $1/2$ particle given by $S_i = \frac{\hbar}{2}\sigma_i$ where σ_i are the Pauli matrices given by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.38}$$

We emphasize that these matrices are expressed in the basis $|z,\pm\rangle$. For example, $S_y = \frac{i\hbar}{2}(|z,-\rangle\langle z,+| - |z,+\rangle\langle z,-|)$. Since $\sigma_{x,z}$ are real while σ_y is imaginary, we have

$$\mathcal{K}S_{x,z}\mathcal{K} = S_{x,z}, \qquad \mathcal{K}S_y\mathcal{K} = -S_y \tag{4.39}$$

However, it is important to note that the representation of the complex conjugation operator is basis-dependent. For example, in the y-basis, $|y,\pm\rangle$, $S_y = \frac{\hbar}{2}(|y,+\rangle\langle y,+| - |y,-\rangle\langle y,-|)$. The action of complex conjugation in this basis is just $\mathcal{K}S_y\mathcal{K} = S_y$ which seems to contradict Eq. 4.39. To resolve this apparent contradiction, we note that like any other operator, $\mathcal{K}$ is not basis-independent. Instead, under a change of basis, it changes as $\mathcal{K} \mapsto \sum_{ab}|a\rangle\langle a|\mathcal{K}|b\rangle\langle b|$. For the example above, the transformation from the z basis to the y basis is implemented by a $\pi/2$ rotation around the x-axis, given by the unitary $U = e^{-\frac{i\pi}{2\hbar}S_x} = e^{-\frac{i\pi}{4}\sigma_x}$. Under this transformation, $\mathcal{K}$ maps to $U^\dagger\mathcal{K}U = U^\dagger U^*\mathcal{K} = e^{\frac{i\pi}{2}\sigma_x}\mathcal{K} = i\sigma_x\mathcal{K}$. We can verify that the operator $i\sigma_x\mathcal{K}$ anticommutes with S_y expressed in the new basis. This example illustrates that a complex conjugation operator in one basis maps to a more general anti-unitary operator in a different basis.

So what is the most general anti-unitary operator? Since the product of any two anti-unitary operators is unitary, for any unitary operator, we can construct the combination $\Theta\mathcal{K}$ which is a unitary operator U. Noting that $\mathcal{K}^2 = 1$, we see that $\Theta = U\mathcal{K}$. Thus, any anti-unitary operator can be written as the product of a unitary operator times complex conjugation. We can now ask the question: are there any symmetry operators satisfying (4.36) that are not unitary or anti-unitary (up to unphysical phase factors)? The answer turns out to be no. A theorem by Wegner, whose proof is beyond the scope of this course, have shown that symmetries in the quantum theory can only be unitary or anti-unitary.

With our understanding of anti-unitary symmetries, we now revisit the question of time-reversal symmetry which as we argued before requires the introduction of complex conjugation. Time-reversal operator can be defined through its relation to the time evolution operator via

$$\mathcal{T}\mathcal{U}(t) = \mathcal{U}(-t)\mathcal{T} \tag{4.40}$$

This relation means that evolving a state by the time t then applying time-reversal is the same as applying time-reversal then evolving in the reverse time direction. Using the fact that the Hamiltonian is the generator of time-evolution $\mathcal{U}(dt) = \mathbb{1} - \frac{i}{\hbar}\mathcal{H}dt$, we find that

$$\mathcal{T}i\mathcal{H} = -i\mathcal{H}\mathcal{T} \tag{4.41}$$

Here, we kept the factor of i to account for the possibility that $\mathcal{T}$ is anti-unitary. According to Wegner theorem, we have two possibilities: either $\mathcal{T}$ is unitary which means that $\mathcal{T}i = i\mathcal{T}$ which implies $\mathcal{T}\mathcal{H} = -\mathcal{H}\mathcal{T}$. This equation implies that for any non-zero energy eigenvalue E of $\mathcal{H}$, there is a corresponding energy eigenvalues $-E$. This does not make sense physically which can be seen by considering simple examples such as the free particle Hamiltonian which we expect to be time-reversal symmetric but whose spectrum satisfies $E \geq 0$ and is unbounded from above. The other possibility is that $\mathcal{T}$ is anti-unitary

$$[\mathcal{T}, \mathcal{H}] = 0, \qquad \mathcal{T}^{-1}i\mathcal{T} = -i \tag{4.42}$$

The anti-unitarity of $\mathcal{T}$ has an important consequence. Physically, we expect that applying time-reversal twice to a state yields the same state. But recall that in the quantum theory, physical states correspond to rays in the Hilbert space rather than unique ket vectors. This means that for any ket $|\psi\rangle$, $\mathcal{T}^2|\psi\rangle = e^{i\theta}|\psi\rangle$ where θ is independent of $|\psi\rangle$ [4]. Thus, we can write $\mathcal{T} = e^{i\theta}\mathbb{1}$ which implies $U_{\mathcal{T}}U^*_{\mathcal{T}} = e^{i\theta}$ or equivalently $U_{\mathcal{T}} = e^{i\theta}U^T_{\mathcal{T}}$. Transposing both sides gives $U^T_{\mathcal{T}} = e^{i\theta}T_{\mathcal{T}} = e^{2i\theta}U^T_{\mathcal{T}}$ which implies $e^{2i\theta} = 1$. Thus, $\theta = 0$ or π which implies $\mathcal{T}^2 = \pm 1$. As we will see later, these two possibilities are realized for integer $(+)$ and half-integer $(-)$ spin.

The action of time-reversal on different physical observables can be understood based on simple physical considerations. First, we expect time-reversal to leave position eigenkets invariant $\mathcal{T}|x\rangle \propto |x\rangle$ which means that

$$\mathcal{T}\boldsymbol{x}\mathcal{T}^{-1} = \boldsymbol{x} \tag{4.43}$$

We also expect time-reversal to commute with the translation operator $T_{\boldsymbol{x}}$. Now since momentum is the generator of translation, we get

$$\mathcal{T}(i\boldsymbol{p})\mathcal{T}^{-1} = i\boldsymbol{p}, \quad \Longrightarrow \quad \mathcal{T}\boldsymbol{p}\mathcal{T}^{-1} = -\boldsymbol{p} \tag{4.44}$$

Thus, momentum is odd under time-reversal as expected. This is what we would have obtained also from the position representation of the momentum operator $p_l = -i\hbar\frac{\partial}{\partial x_l}$. In fact, we can show a more general statement where any unitary operator must either commute with both $\boldsymbol{x}$ and $\boldsymbol{p}$ or anticommute with both $\boldsymbol{x}$ and $\boldsymbol{p}$ whereas an anti-unitary operator has to commute with one and anticommute with the other [5]. We can see this by acting with an arbitrary symmetry operator S on the Heisenberg commutation relation. Let us for simplicity consider the 1D case

$$S[x, p]S^{-1} = Si\hbar S^{-1} = [SxS^{-1}, SpS^{-1}] = SiS^{-1}\hbar \tag{4.45}$$

For unitary S, $SiS^{-1} = i$ which implies that S should commute with both x and p or anticommute with both x and p whereas for anti-unitary S, $SiS^{-1} = -i$ which implies that S should commute with one of x and p and anticommute with the other. An example of an operator that anticommute with both x and p is

[4] To see that this has to be the case, consider two different kets $|\psi_{1,2}\rangle$ and assume $\mathcal{T}^2|\psi_{1,2}\rangle = e^{i\theta_{1,2}}|\psi_{1,2}\rangle$. If $\theta_1 \neq \theta_2$, then the state $|\psi_1\rangle + |\psi_2\rangle$ will map to a different state $|\psi_1\rangle + e^{i(\theta_2-\theta_1)}|\psi_2\rangle$ under the action of $\mathcal{T}^2$.

[5] Here, we are not considering operators that mix $\boldsymbol{x}$ and $\boldsymbol{p}$

the parity operator π we studied last lecture. Time-reversal $\mathcal{T}$ is an example of an operator which commutes with x but anticommutes with p. Finally, we can consider the anti-unitary operator $\pi\mathcal{T}$ which anticommutes with x and commutes with p.

Finally, we expect time-reversal to commute with spatial rotations which implies

$$\mathcal{T}(iJ_a)\mathcal{T}^{-1} = iJ_a, \quad \implies \quad \mathcal{T}J_a\mathcal{T}^{-1} = -J_a \tag{4.46}$$

This is again the result we expect at least for the case of orbital angular momentum $\boldsymbol{L} = \boldsymbol{x} \times \boldsymbol{p}$. Note that the an operator that anticommutes with all angular momentum components have to to be antiunitary to respect the angular momentum commutation relations.

To understand the action of time-reversal symmetry on a system characterized by an arbitrary angular momentum labelled by a half-integer j, let us first consider the case of a spin $1/2$ particle ($j = 1/2$). As we discussed earlier, the spin operators can be represented in terms of the Pauli matrices $S_i = \frac{\hbar}{2}\sigma_i$. Notice that the Pauli matrices σ_x and σ_z are real whereas the Pauli matrix σ_y is imaginary. This means that if we write $\mathcal{T} = \mathcal{U}_\mathcal{T}\mathcal{K}$ we have

$$\mathcal{U}_\mathcal{T}\sigma_x\mathcal{U}_\mathcal{T}^\dagger = -\sigma_x, \qquad \mathcal{U}_\mathcal{T}\sigma_y\mathcal{U}_\mathcal{T}^\dagger = \sigma_y, \qquad \mathcal{U}_\mathcal{T}\sigma_z\mathcal{U}_\mathcal{T}^\dagger = -\sigma_z \tag{4.47}$$

Thus, in the space defined by the three component vector $(\sigma_x, \sigma_y, \sigma_z)$, $\mathcal{U}_\mathcal{T}$ acts as a rotation around the y-axis by an angle π. Such rotation is represented by $\mathcal{U}_\mathcal{T} = e^{-\frac{i}{\hbar}\pi S_y} = e^{-\frac{i\pi}{2}\sigma_y} = i\sigma_y$. We now see that $\mathcal{T}^2 = \mathcal{U}_\mathcal{T}U_\mathcal{T}^* = e^{-i\pi\sigma_y} = -1$. Thus, the action of time-reversal on a spin $1/2$ particle satisfies $\mathcal{T}^2 = -1$. We can anticipate the action on higher spins by recalling the formalism for addition of angular momentum we discussed in Lecture 16. There we found that combining an even number of spin $1/2$ particles can generally be expanded in terms of states whose total spin is integer while an odd number of spin $1/2$ particles can be expanded in terms of states whose total spin is half-integer. This suggests that the action of time-reversal on a state with n spin $1/2$ particles, defined via the tensor product $\mathcal{T}_n = \mathcal{T} \otimes \mathcal{T} \otimes \mathcal{T} \ldots$, satisfines $\mathcal{T}_n^2 = \mathcal{T}^2 \otimes \mathcal{T}^2 \otimes \mathcal{T}^2 \cdots = (-1)^n$.

We can see this more generally by considering some arbitrary angular momentum algebra $[J_i, J_j] = i\epsilon_{ijk}\hbar J_k$. We can always choose two of the components to be real and one to be imaginary which is chosen to be J_y by convention. This means that

$$\mathcal{K}J_{x,z}\mathcal{K} = J_{x,z}, \qquad \mathcal{K}J_y\mathcal{K} = -J_y \tag{4.48}$$

This can be done explicitly by considering a specific representation $|j, m\rangle$. J_z is diagonal and real in this representation. $J_\pm$ can also be chosen to be real which means that $J_x = \frac{J_+ + J_-}{2}$ is real while $J_y = \frac{J_+ - J_-}{2i}$ is imaginary. Using Eq. 4.48 and the relation $\mathcal{T}J_a\mathcal{T}^{-1} = -J_a$ yields

$$\mathcal{U}_\mathcal{T}J_{x,z}\mathcal{U}_\mathcal{T}^\dagger = -J_{x,z}, \qquad \mathcal{U}_\mathcal{T}J_y\mathcal{U}_\mathcal{T}^\dagger = J_y, \tag{4.49}$$

which means that $\mathcal{U}_\mathcal{T} = e^{-\frac{i\pi}{\hbar}J_y}$ up to a phase. This gives $\mathcal{T}^2 = U_\mathcal{T}U_\mathcal{T}^* = e^{-\frac{2i\pi}{\hbar}J_y} = (-1)^{2j}$ where we used the fact that rotation by 2π around any axis gives $(-1)^{2j}$.

The last aspect of time-reversal symmetry we would like to discuss are its spectral consequences. First, let us note that time-reversal acts on wavefunctions by complex conjugation since $\mathcal{T}|x\rangle = |x\rangle$ which means that $\mathcal{T}$ maps $\psi(x) = \langle x|\psi\rangle$ to $\langle x|\mathcal{T}\psi\rangle = \langle \mathcal{T}^{-1}x|\mathcal{T}^{-1}\mathcal{T}\psi\rangle^* = \langle \mathcal{T}^{-1}x|\psi\rangle^* = \psi(x)^*$. We would now like to discuss the implication of time-reversal symmetry on the spectrum. For a unitary symmetry, we found a non-degenerate energy eigenstate is also an eigenstate of the symmetry operator. Below, we will see that we can derive a very similar result for time-reversal. Consider an eigenstate $|n\rangle$ with energy eigenvalue E_n for a time-reversal symmetric Hamiltonian $[\mathcal{T}, \mathcal{H}] = 0$. Then

$$\mathcal{H}\mathcal{T}|n\rangle = \mathcal{T}\mathcal{H}|n\rangle = E_n\mathcal{T}|n\rangle \tag{4.50}$$

which means that $\mathcal{T}|n\rangle$ is an eigenstate with the same eigenvalue. Then we have two possibilities: If $|n\rangle$ is non-degenerate, then $\mathcal{T}|n\rangle$ is equal to $|n\rangle$ up to a phase that we can choose to be 1. The statement

$\mathcal{T}|n\rangle = |n\rangle$ implies that the corresponding wavefunction $\psi_n(x) = \langle x|n\rangle$ is real. On the other hand, if $\mathcal{T}|n\rangle$ represents a different state compared to $|n\rangle$, then we deduce the spectrum has to be degenerate. At this point, the discussion completely parallels the one for unitary symmetry. There is however one consequence that is unique for anti-unitary operators that satisfy $\mathcal{T}^2 = -1$ known as Kramers' degeneracy. Consider the overlap

$$\langle\psi|\mathcal{T}\psi\rangle = -\langle\mathcal{T}^2\psi|\mathcal{T}\psi\rangle = -\langle\mathcal{T}\psi|\psi\rangle^* = -\langle\psi|\mathcal{T}\psi\rangle \tag{4.51}$$

Thus the overlap of $|\psi\rangle$ and $\mathcal{T}|\psi\rangle$ vanishes identically whenever $\mathcal{T}^2 = -1$. As a result, $|\psi\rangle$ and $\mathcal{T}|\psi\rangle$ cannot describe the same state. For a time-reversal symmetric Hamiltonian, this implies that every energy eigenvalue is doubly degenerate.

4.5 Lattice translation symmetry

The last important symmetry we are going to consider is lattice translation symmetry. Earlier in the course, we considered continuous translation symmetry discribed by the unitary operator $T_{\boldsymbol{a}}$ which satisfies

$$T_{\boldsymbol{a}}\boldsymbol{x}T_{\boldsymbol{a}}^{-1} = \boldsymbol{x} + \boldsymbol{a} \tag{4.52}$$

The different translation operators commute $T_{\boldsymbol{a}}T_{\boldsymbol{a}'} = T_{\boldsymbol{a}'}T_{\boldsymbol{a}}$ and the the generator for infinitesmal translations can be identified with momentum. For a single particle, continuous translation symmetry is very restrictive. It is only realized if the potential $V(\boldsymbol{x})$ is a constant. However, in a lot of contexts, we want instead to think of an electron living in a periodic potential. This usually occurs when we consider the movement of an electron subject to the potential generated by a lattice of positive ions. Due to the much heavier mass of the ions compared an electron, we can ignore their movement to a very good approximation and think of them as providing some background periodic potential $V(\boldsymbol{x} + \boldsymbol{a}) = V(\boldsymbol{x})$.

In the following, we will focus for simplicity on the 1D case $V(x + a) = V(x)$ since translations along different directions commute and we can easily generalize our analysis to the multi-dimensional case. Similar to our discussion of the free electron case, it is very useful to place our system on a large box and consider periodic boundary conditions $\psi(x + L) = \psi(x)$. However, to be compatible with translation, L has to be an integer multiple of the lattice constant a, $L = Na$. Since the kinetic energy $\frac{p^2}{2m}$ commutes with any translation operator, the condition $V(x + a) = V(a)$ implies that $T_a\mathcal{H}(x)T_a^{-1} = \mathcal{H}(x + a) = \frac{p^2}{2m} + V(x + a) = \frac{p^2}{2m} + V(x) = \mathcal{H}(x)$. This means that $[T_a, \mathcal{H}] = 0$ and since $T_{na} = T_a^n$, it also implies $[T_{na}, \mathcal{H}] = [T_a^n, \mathcal{H}] = 0$. Thus, we can simultaneously diagonalize $\mathcal{H}$ and T_a and use the eigenvalues of T_a to label the energy eigenstates. The periodic boundary conditions can be expressed as

$$T_a^N|\psi\rangle = |\psi\rangle \tag{4.53}$$

Denoting an eigenstate of T_a by $|k\rangle$ such that $T_a|k\rangle = \lambda_k|k\rangle$, the boundary condition implies that $\lambda_k^N = 1$. This means that λ_k is an N-th root of unity

$$\lambda_k = e^{\frac{2\pi i}{N}n_k}, \qquad n = 0, \ldots, N-1 \tag{4.54}$$

Notice that the states labelled by n_k and $n_k + mN$ for any integer m are equivalent. Defining $k = \frac{2\pi}{Na}n_k$ such that $\lambda_k = e^{ika}$, we see that the discrete translation eigenstates are labelled by a wavevector k, but unlike continuous translation, the eigenstates corresponding to k and $k + \frac{2\pi}{a}m$ label the same state for any integer m.

So what is the most general eigenstate of discrete translation $|k\rangle$. An obvious choice is $\psi_k(x) = \langle x|k\rangle = e^{ikx}$. However, this cannot be the only possibility. One way to convince yourself of this is to take the limit of $V(x) \mapsto 0$. In this case, we should recover the free particle case where the eigenstates are labelled by $|k\rangle$ where the wavevector k is unrestricted, i.e. goes from $-\infty$ to $+\infty$, while for the periodic case k goes from 0 to $2\pi/a$. Clearly the number of eigenstates of the Hamiltonian cannot abruptly change as we switch on a small periodic potential. Another way to convince yourself is to look at the matrix elements of the

Hamiltonian in the plane wave basis. To make our notation more transparent, we denote the plane waves in the continuum by $|q\rangle$, where $q \in (-\infty, \infty)$ and reserve $|k\rangle$ for the case where $k \in [0, \frac{2\pi}{a})$

$$\langle q'|\mathcal{H}|q\rangle = -\frac{\hbar^2 q^2}{2m}\delta_{q,q'} + \langle q'|V(x)|q\rangle \tag{4.55}$$

The matrix elements of the potential are simply the Fourier components

$$\langle q'|V|q\rangle = \int dx\, e^{i(q-q')x} V(x) \tag{4.56}$$

Since the potential is a periodic function with period a, its Fourier components are only non-vanishing for a discrete set given by $q - q' = \frac{2\pi}{a}n$. This means that the Hamiltonian is not diagonal in the continuum plane wave basis. Instead, it connects plane wave states whose momenta differ by $\frac{2\pi}{a}n$. A general eigenstate of such Hamiltonian can be written as

$$\psi_k(x) = \sum_n e^{i(k+\frac{2\pi}{a}n)x} a_n(k) = e^{ikx} u_k(x), \quad u_k(x) = \sum_n e^{i\frac{2\pi}{a}nx} a_n(k) \tag{4.57}$$

where $u_k(x)$ is a periodic function $u_k(x+a) = u_k(x)$. In general, an eigenfunction of discrete translation satisfies $\psi_k(x+a) = e^{ika}\psi_k(x)$ which implies that it can be written as

$$\psi_k(x) = e^{ikx} u_k(x) \tag{4.58}$$

for some periodic function $u_k(x)$.

The Hamiltonian will have many eigenstates of the form (4.58) for any given k which we can label as usual by some integer n. Thus, the common eigenstates of translation and the Hamiltonian are labelled by $k \in [0, \frac{2\pi}{a})$ and an integer n, $|n, k\rangle$ such that

$$T_a|n,k\rangle = e^{ika}|n,k\rangle, \qquad \mathcal{H}|n,k\rangle = E_{n,k}|n,k\rangle \tag{4.59}$$

where the wavefunctions $\psi_{n,k}(x) = \langle x|n,k\rangle$ have the form

$$\psi_{n,k}(x) = e^{ikx} u_{n,k}(x), \qquad u_{n,k}(x+a) = u_{n,k}(x) \tag{4.60}$$

This is the statement of the Bloch theorem. $\psi_{n,k}(x)$ are called Bloch states whereas $u_{n,k}(x)$ are called cell-periodic states. k is usually called the crystal momentum. It differs from actual momentum in that it is only conserved up to terms of the form $\frac{2\pi}{a}m$ for integer m. Such momenta are called reciprocal lattice momenta.

In the thermodynamic limit $N \to \infty$, we can think of k as a continuous parameter since the spacing between different consecutive values of k is $\Delta k = \frac{2\pi}{Na}$ goes to 0. It is important to emphasize that the range of k is given by the interval $[0, \frac{2\pi}{a})$ which is independent on the system size and only depends on the lattice constant a. The contintuum limit is obtained by taking $a \to 0$ where we recover continuous lattice translations and the range of k can be taken to be $[0, \infty)$ [6].

It is important to emphasize that while the Bloch states are orthonormal since the are the eigenfunctions of a Hermitian (or unitary) operator with different eigenvalues, the cell-periodic states at different momenta are not generally orthogonal.

The generalization to higher-dimensions is straightforward. In d dimensions, k is promoted to a d-dimensional vector with d components satisfying $0 \le k_i < \frac{2\pi}{a_i}$ where a_i is the lattice constant in the i-th direction. This means that the vector $\boldsymbol{k}$ lives on the d-dimensional torus. Such torus is called the Brillouin zone.

[6] we can also make a more symmetric choice and choose $k \in (-\frac{\pi}{a}, \frac{\pi}{a}]$ which becomes $k \in (-\infty, +\infty)$ in the continuum limit

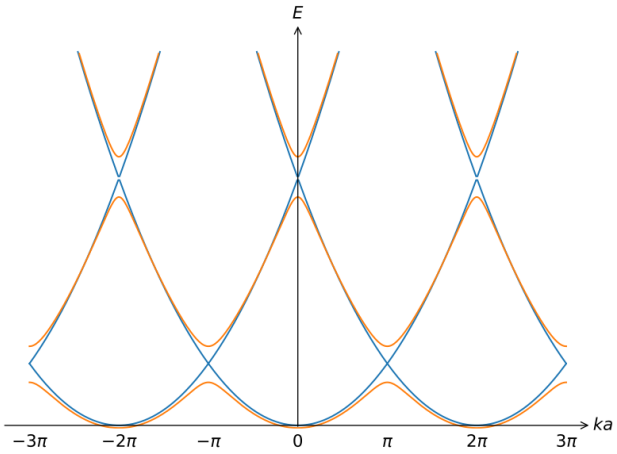

Figure 4.1: Illustration of the nearly free electron model.

4.5.1 Nearly free electron

We will now consider a few cases to illustrate the Bloch theorem. First, consider the limit of very weak potential. Since the case of zero potential corresponds to plane waves $|q\rangle$, it makes sense to express the Hamiltonian in this basis as in Eq. 4.55. Since the Hamiltonian only connects states with $q - q' = \frac{2\pi}{a}n$, we can write $q = k + \frac{2\pi}{a}n$ where k is inside the Brillouin zone and define

$$H_{n',n}(k) = \langle k+n'|\mathcal{H}|k+n\rangle = \frac{\hbar^2(k+\frac{2\pi}{a}n)^2}{2m}\delta_{n,n'} + V_{n'n}, \quad V_{n',n} = \langle k+n'|V|k+n\rangle = \int dx e^{i(n-n')x}V(x) \tag{4.61}$$

We see that for $V = 0$, this Hamiltonian is diagonal n. It corresponds to a rewriting of the free particle Hamiltonian, which is diagonal in a single unrestricted momentum q, in terms of one Brillouin zone momentum k and one integer index n. Pictorially, this corresponds to 'folding' the quadratic band dispersion to lie in the Brillouin zone and labelling the different branches with an integer n.

When V is small and non-zero, we will get some mixing between different branches at the same Brillouin zone momentum k. To understand the effect of this mixing, let us consider the following simple example. Take the following 2×2 matrix

$$A = \begin{pmatrix} E_1 & V \\ V^* & E_2 \end{pmatrix} \tag{4.62}$$

Its eigenvalues can be computed in a straightforward manner to be $\frac{E_1+E_2}{2} \pm \sqrt{\left(\frac{E_1-E_2}{2}\right)^2 + |V|^2}$. If $|V| \ll |E_1 - E_2|$, its effect will be negligible and the eigenvalues of this matrix will be simply given by its diagonal entries E_1 and E_2. On the other hand, if $|V| \gg |E_1 - E_2|$, we can basically replace $E_1 \approx E_2 \approx E_0$ and find that the eigenvalues are $E_0 \pm |V|$ i.e. the splitting between the eigenvalues is given by $2|V|$. When we add a small potential V to the folded free electron dispersion, its effect is to connect different branches of the dispersion at the same crystal momentum k. This can be represented by a large matrix whose diagonal entries are the energies $\epsilon_{n,k} = \frac{\hbar^2(k+\frac{2\pi}{a}n)^2}{2m}$ and the off-diagonal entries are $V_{nn'}$. For small V, we can neglect the term $V_{nn'}$ unless $|V_{nn'}| \gtrsim |\epsilon_{nk} - \epsilon_{n'k}|$ which only happens at the center or edge of the Brillouin zone when $k \approx 0, \pm\frac{\pi}{a}$ as shown in Fig. 4.1. This opens up gaps of the order $|V_{nn'}|$ at the edge of the Brillouin zone leading to the emergence of separated energy bands.

4.5.2 Tight-binding model

There is an alternative way to understand the emergence of energy bands that starts from the opposite limit of very strong periodic potential. Let us start with a periodic potential consisting of potential wells

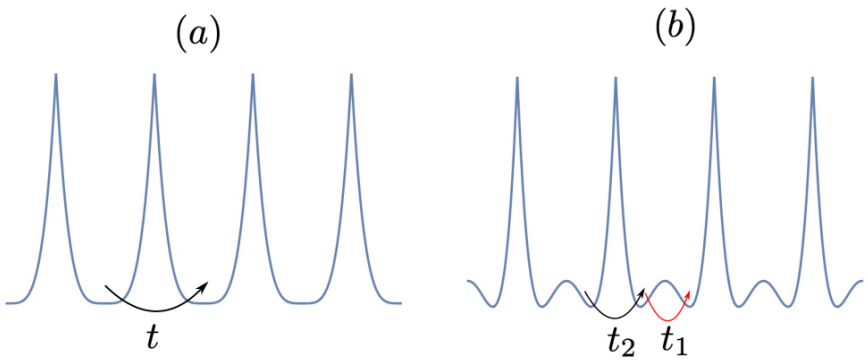

Figure 4.2: (a) Periodic potential well with tunneling t between neighboring well. (b) Periodic double potential well with tunneling t_1 between left and right states within each double well and t_2 between adjacent wells.

at $x = na$ separated by infinite potential barriers. This is a generalization of the double well potential we studied earlier. There, we found that in the limit where the potential barrier is infinite, the wells get effectively disconnected and we can find the spectrum in each well separately. Denoting the lowest energy state localized at the l-th well by $|l\rangle$, we see that $|l\rangle$ are all degenerate energy eigenstates with an energy eigenvalues that we denote by E_0. The states $|l\rangle$ are not translation eigenstates. Instead, they satisfy $T_a|l\rangle = |l+1\rangle$.

Since the energy eigenvalues are degenerate, we can choose any linear combination of these eigenstates which will also be energy eigenvalues with the same energy. Following our discussion of the Bloch theorem, it makes sense to look for eigenstates of the translation operator T_a. It is straightforward to verify that the state

$$|k\rangle = \sum_l e^{-ikla}|l\rangle \tag{4.63}$$

is an eigenstate of the translation operator with eigenvalue e^{ika}. Notice that since we are keeping only one state per well, we have only one state for every Brillouin zone momentum k. We can verify this by comparing the dimension of the Hilbert spaces of the states $|l\rangle$ and $|k\rangle$. For a system with N unit cells, such that $T_a^N = 1$, the basis $|l\rangle$ spans a Hilbert space of dimension N. On the other hand, the basis $|k\rangle$ spans a Hilbert space parametrized by $k = \frac{2\pi}{Na}n$ where $n = 0, \ldots, N-1$ which also contains N points.

Once we make the potential barrier finite, we expect the states $|l\rangle$ to no longer be eigenstates similar to the case of potential well where the eigenstates are instead the $\pm$ linear combinations of the states from the left and right well. However, the states $|k\rangle$ remain eigenstates since they are eigenstates of the translation operator. If the barrier is still reasonably high, we expect the mixing between the states localized in different wells to be small and also expect the mixing between non-adjacent wells to be neglegible. This, we can approximate the Hamiltonian by

$$\mathcal{H} = \sum_l \{E_0|l\rangle\langle l| + t|l\rangle\langle l+1| + t^*|l+1\rangle\langle l|\}, \qquad t = \langle l|\mathcal{H}|l+1\rangle \tag{4.64}$$

For simplicity, we will assume t is real in what follows. Acting on the states $|k\rangle$, we get

$$\mathcal{H}|k\rangle = (E_0 + 2t\cos ka)|k\rangle \tag{4.65}$$

This gives the energy dispersion $E_k = E_0 + 2t\cos ka$.

The tight-binding model can be easily generalized to include multiple states per well. For instance, imagine each well is itself a double well potential with a potential barrier as shown in Fig. 4.2b. Then we can focus on the two lowest energy eigenstates that can be expressed in terms of eigenstates localized in the left or the right parts denoted by $|l, \sigma\rangle$ where $\sigma = L/R$. If we again consider tunneling between nearest

neighboring wells only, then we can focus on tunneling between the left and right wells within each double well, denoted by t_1, or tunneling from the right part to the left part of two adjacent wells denoted by t_2. The Hamiltonian is then given by (we will drop the constant term E_0 in what follows)

$$\mathcal{H} = \sum_l \{t_1(|l,L\rangle\langle l,R| + |l,R\rangle\langle l,L|) + t_2(|l,R\rangle\langle l+1,L| + |l+1,L\rangle\langle l,R|)\} \tag{4.66}$$

Defining the states

$$|k,\sigma\rangle = \sum_l e^{-ikla}|l,\sigma\rangle \tag{4.67}$$

we can write the Hamiltonian

$$\mathcal{H} = \sum_k \left\{(t_1 + t_2e^{ika})|k,L\rangle\langle k,R| + (t_1 + t_2e^{ika})|k,R\rangle\langle k,L|\right\} \tag{4.68}$$

We see that the Hamiltonian is diagonal in k and can be written as

$$\langle k,\sigma|\mathcal{H}|k',\sigma'\rangle = \delta_{kk'}H_{\sigma,\sigma'}(k), \qquad H(k) = \begin{pmatrix} 0 & t_1 + t_2e^{ika} \\ t_1 + t_2e^{-ika} & 0 \end{pmatrix} \tag{4.69}$$

The energy spectrum of this Hamiltonian is given by $\pm|t_1 + t_2e^{ika}| = \pm\sqrt{(t_1 + t_2\cos ka)^2 + (t_2\sin ka)^2}$. This Hamiltonian describes the so-called Su-Schrieffer-Heeger (SSH) model which is the simplest model for a topological insulator in 1D.

We see that the main advantange of tight-binding models is that they allows us to focus on a few relevant states within each well (usually called orbitals) and writing a matrix Hamiltonian for each crystal momentum k that depends on k and a few model parameters. The last thing I want to discuss is how symmetries are represented in the tight-binding picture. For a unitary symmetry that leaves momentum invariant, we have $\mathcal{S}|k,\alpha\rangle = \sum_\beta S_{\beta,\alpha}(k)|k,\beta\rangle$. If the symmetry S leaves the Hamiltonian invariant, $S^\dagger\mathcal{H}S = \mathcal{H}$, then the tight-binding Hamiltonian satisfies

$$H_{\alpha,\beta}(k) = \langle k,\alpha|\mathcal{H}|k,\beta\rangle = \langle k,\alpha|\mathcal{S}^\dagger\mathcal{H}\mathcal{S}|k,\beta\rangle = \sum_{\gamma,\delta} S^*_{\gamma,\alpha}S_{\delta,\beta}\langle k,\gamma|\mathcal{H}|k,\delta\rangle = \sum_{\gamma,\delta} S^*_{\gamma,\alpha}S_{\delta,\beta}H_{\gamma,\delta}(k) \tag{4.70}$$

which means that as a matrix $H(k) = S^\dagger(k)H(k)S(k)$. For k-flipping unitary symmetries such as parity, we have $\mathcal{S}|k,\alpha\rangle = \sum_\beta S_{\beta,\alpha}(k)|-k,\beta\rangle$ which yields

$$H_{\alpha,\beta}(k) = \langle k,\alpha|\mathcal{H}|k,\beta\rangle = \langle k,\alpha|\mathcal{S}^\dagger\mathcal{H}\mathcal{S}|k,\beta\rangle = \sum_{\gamma,\delta} S^*_{\gamma,\alpha}S_{\delta,\beta}\langle -k,\gamma|\mathcal{H}|-k,\delta\rangle = \sum_{\gamma,\delta} S^*_{\gamma,\alpha}S_{\delta,\beta}H_{\gamma,\delta}(-k) \tag{4.71}$$

which means that as a matrix $H(k) = S^\dagger(k)H(-k)S(k)$. Finally, for a k-flipping anti-unitary symmetry such as time-reversal, we have $\mathcal{T}|k,\alpha\rangle = \sum_\beta T_{\beta,\alpha}(k)\mathcal{K}|-k,\beta\rangle$

$$H_{\alpha,\beta}(k) = \langle k,\alpha|\mathcal{H}|k,\beta\rangle = \langle k,\alpha|\mathcal{T}^{-1}\mathcal{H}\mathcal{T}|k,\beta\rangle = \sum_{\gamma,\delta} T^*_{\gamma,\alpha}T_{\delta,\beta}\langle -k,\gamma|\mathcal{H}|-k,\delta\rangle^* = \sum_{\gamma,\delta} S^*_{\gamma,\alpha}S_{\delta,\beta}H^*_{\gamma,\delta}(-k) \tag{4.72}$$

which implies $H(k) = T(k)^\dagger H(-k)^*T(k)$.

The fact that parity and time-reversal relate the tight-binding Hamiltonian means that they do not impose a local symmetry constraint at every k point. However, they impose a symmetry constraint for momenta which satisfy $-k = k + G$ where G is a reciprocal lattice vector since $H(k+G) = H(k)$. In 1D, these are just the momenta $k = 0$ and $k = \frac{\pi}{a}$ within the Brillouin zone. All our conclusions about the symmetries is thus valid at these points. In particular, for parity symmetric Hamiltonians, we can label non-degenerate eigenstates at momenta $k = 0, \pi/a$ by their parity eigenvalues if the Hamiltonian is parity symmetric. For time-reversal symmetric Hamiltonians with $\mathcal{T}^2 = -1$, we have Kramers degeneracy at $k = 0, \pi/a$ but not at a generic point in the Brillouin zone. These considerations play an important role in the theory of topological insulators which is beyond the scope of this course.

Chapter 5

Approximation Methods

5.1 Time-independent perturbation theory

5.1.1 Non-degenerate perturbation theory

In this chapter, we will begin our study of approximation methods. We will begin with "perturbation theory," which begins from an exactly solvable starting point and systematically computes corrections in a Taylor series like form. In particular we begin with a Hamiltonian of the form

$$H = H_0 + \lambda V \tag{5.1}$$

where H_0 is exactly solvable; we know all of its eigenstates $|n^{(0)}\rangle$ and eigenenergies $E_n^{(0)}$, such that $H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$. We have introduced a perturbation operator V, as well as a perturbation strength λ. One could absorb λ into V, or define V so that $\lambda = 1$, but it is convenient to retain λ as a free parameter while deriving the perturbation series as it is a convenient way to effectively count powers of V. Indeed, any physical quantity computed from (5.1) that has d powers of λ will necessarily have d powers of V.

We will compute $|n\rangle = |n(\lambda)\rangle$ and $E_n = E_n(\lambda)$ such that

$$H |n\rangle = E_n |n\rangle . \tag{5.2}$$

We assume that there is no degeneracy; there is a single state $|n\rangle$ with energy E_n. In the next lecture we will address the case of degeneracy. Note that since $H = H_0 + \lambda V$ is a function of λ, so are $|n\rangle$ and E, though we will often leave this dependence implicit. The computation of $|n\rangle$ and E will be done order-by-order in λ (and thus V). In particular we consider expanding

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \lambda^3 |n^{(3)}\rangle + \cdots \\ E &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \cdots \end{aligned} \tag{5.3}$$

so that $|n^{(d)}\rangle$ and $E^{(d)}$ are order d in V, but don't have λ dependence. We will systematically calculate these corrections order by order. We pause to comment that we do not include $1/n!$ factors that would enable us to associate $E^{(d)}$ with the n-th order derivative of E with respect to λ evaluated at $\lambda = 0$, as is typical in Taylor series. This is essentially a convention choice in how $E^{(d)}$ is defined and the choice we make here will be slightly more convenient for our purposes.

There is another subtlety that we will have to address which is gauge redundacies associated with $|n\rangle$ as a function of λ. As an example, for $V = 0$, where all corrections should be trivial, we could imagine the "perturbed" state $|n(\lambda)\rangle = e^{i\alpha(\lambda)} |n^{(0)}\rangle$; the exponential could then be expanded to generate a series with $|n^{(d)}\rangle \propto |n^{(0)}\rangle$. These corrections that are proportional to $|n^{(0)}\rangle$ do not change the state physically, they simply change its unphysical coefficient. In order to derive a canonical expression for $|n\rangle$ we will need

to remove this gauge redundancy. To do this, we simply imagine deleting the part of $|n^{(d)}\rangle$ that lies along $|n^{(0)}\rangle$ and therefore impose

$$\langle n^{(0)}|n^{(d)}\rangle = 0, \qquad \text{for } d \geq 1. \tag{5.4}$$

That is, all corrections are required to change the unperturbed *state* rather than adjust its coefficient. We pause to comment that the set up we have outlined typically results in states that are not normalized, since the leading order part $|n^{(0)}\rangle$ has a fixed coefficient of 1 in (5.3), but the state can always be renormalized after it is computed to the desired order.

Expanding out the eigenequation (5.2), and writing $\Delta_n = E_n - E_n^{(0)}$ for the energy shift, we have

$$(E_n^{(0)} - H_0)\,|n\rangle = (\lambda V - \Delta_n)\,|n\rangle\,. \tag{5.5}$$

This rewritten eigenequation will be the starting point for our expansion. The reason is that it relates the order D correction to $|n\rangle$ to orders $d < D$ on the right hand side, as both λV and Δ_n contain at least one power of λ.We begin by acting with $|n^{(0)}\rangle$ on the left. Since $H_0\,|n^{(0)}\rangle = E_n^{(0)}\,|n^{(0)}\rangle$ (likewise for the dual "bra" version because H_0 is Hermitian), the left hand side vanishes and we obtain

$$\langle n^{(0)}|\,(\lambda V - \Delta_n)\,|n\rangle = 0 \tag{5.6}$$

which says that $(\lambda V - \Delta_n)\,|n\rangle$ is orthogonal to $|n^{(0)}\rangle$

$$\Delta_n = \langle n^{(0)}|\,\lambda V\,|n\rangle \implies E^{(d)} = \langle n^{(0)}|\,V\,|n^{(d-1)}\rangle \tag{5.7}$$

so that we can compute the order d energy in terms of the order $d-1$ state. Next we invert (5.5):

$$|n\rangle = |n^{(0)}\rangle + \frac{1}{E_n^{(0)} - H_0}(\lambda V - \Delta_n)\,|n\rangle \tag{5.8}$$

The above equation requires some explanation. The operator $(E_n^{(0)} - H_0)$ is not invertible; it has exactly one zero mode, $|n^{(0)}\rangle$, and exactly one state not in its image, also $|n^{(0)}\rangle$. Thus, in the Hilbert subspace of states orthogonal to $|n^{(0)}\rangle$ we *can* invert $(E_n^{(0)} - H_0)$. This is what the second term in (5.7) corresponds to: the state $(\lambda V - \Delta_n)\,|n\rangle$ is orthogonal to $|n^{(0)}\rangle$, so it lies within the desired Hilbert subspace. The resulting state $\frac{1}{E_n^{(0)} - H_0}(\lambda V - \Delta_n)\,|n\rangle$ then yields the part of $|n\rangle$ that is orthogonal to $|n^0\rangle$. We can then add anything proportional to $|n^{(0)}\rangle$ to $|n\rangle$ while still satisfying (5.5); the specific addition of $|n^{(0)}\rangle$ is obtained through consistency with (5.3) and (5.4).

We can obtain another form of (5.8) by using the energy basis to diagonalize $(E_n^{(0)} - H_0)^{-1}$ (though sometimes other bases or techniques for this inversion can be useful). We insert a complete set of states, the eigenstates of H_0, as

$$(\lambda V - \Delta_n)\,|n\rangle = \sum_k |k^{(0)}\rangle\,\langle k^{(0)}|\,(\lambda V - \Delta_n)\,|n\rangle = \sum_{k\neq n} |k^{(0)}\rangle\,\langle k^{(0)}|\,(\lambda V - \Delta_n)\,|n\rangle$$

where we used again the orthognality (5.6) to restrict to $k \neq n$. We then use $(E_n^{(0)} - H_0)^{-1}\,|k^{(0)}\rangle = (E_n^{(0)} - E_k^{(0)})^{-1}\,|k^{(0)}\rangle$ to obtain

$$|n\rangle = |n^{(0)}\rangle + \sum_{k\neq n} \frac{1}{E_n^{(0)} - E_k^{(0)}}\,\langle k^{(0)}|\,(\lambda V - \Delta_n)\,|n\rangle\,|k^{(0)}\rangle\,. \tag{5.9}$$

We could have also obtained the above expression by acting from the left with $\langle k^{(0)}|$ on (5.5) to obtain an expression for $\langle k^{(0)}|n\rangle$ and then using the basis expansion $|n\rangle = |n^{(0)}\rangle + \sum_{k\neq n}\langle k^{(0)}|n\rangle\,|k^{(0)}\rangle$.

Thus, starting from E and $|n\rangle$ up through order $d-1$, we can compute $E^{(d)}$ from (5.7) and then $|n^{(d)}\rangle$ from (5.9). We will now obtain explicit expressions to first and second order, which are the orders most often used. First, from (5.7) we have

$$E^{(1)} = \langle n^{(0)}|\,V\,|n^{(0)}\rangle \tag{5.10}$$

which amounts to just taking the expectation value of V in the unperturbed state. We note that this is the only correction that appears in perturbation theory if $[H_0, V] = 0$; indeed, in this case the perturbation may be simultaneously diagonalized with the Hamiltonian such that the unperturbed states $|n^{(0)}\rangle$ are exact. Then, the only correction is (5.10). All higher order corrections result from $[H_0, V] \neq 0$ and resulting corrections to the eigenstates $|n\rangle \neq |n^{(0)}\rangle$.

The first eigenstate correction is

$$|n^{(1)}\rangle = \sum_{k \neq n} \frac{\langle k^{(0)}| V |n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle , \tag{5.11}$$

where we have used that we can replace $|n\rangle$ with $|n^{(0)}\rangle$ on the right hand side of (5.9) in computing $|n^{(1)}\rangle$ because λV is already first order in λ. We have also used that the term $\langle k^{(0)}| \Delta_n |n^{(0)}\rangle = 0$ because $\Delta_n = E_n - E_n^{(0)}$ is a number and $k \neq n$.

We can now plug (5.11) into (5.7) to obtain

$$E_n^{(2)} = \sum_{n \neq k} \frac{\left|\langle k^{(0)}| V |n^{(0)}\rangle\right|^2}{E_n^{(0)} - E_k^{(0)}}. \tag{5.12}$$

There are a few remarks to make on this form of the second order energy correction.

1. The correction only depends on the difference between unperturbed energies.

2. Eigenvalues that are very far away from the one of interest have very little influence on perturbed state and thus very little influence on the second order energy correction.

3. The sign of the correction is such that eigenvalues are "repelled" with an equal and opposite "force." Indeed, the expression for $E_k^{(2)}$ has the same form but with the opposite sign, and the above expression is positive if $E_n^{(0)} > E_k^{(0)}$ and negative otherwise.

4. The second order correction and repulsion strength diverges as two eigenvalues approach each other. This indicates that our assumption of non-degeneracy above was not innocuous; as we approach degeneracy, the perturbation theory we have developed here degenerates. Said another way, the perturbation must be much smaller than the spacing between eigenvalues in order to trust the perturbation theory developed here.

We note that the second order correction diverges as two energy levels approach each other leading to breakdown of the formalism. Perturbation theory with degeneracy then requires a change of goals and formalism, nondegeneracy is not a mere simplifying assumption.

Before jumping into non-degenerate perturbation theory, we will study a simple example. This simple example will allow us to practice applying non-degenerate perturbation theory, but it will also point us in the correct direction for developing degenerate perturbation theory.

The example is simply a two band Hamiltonian with

$$H_0 = \omega_0 + \omega\sigma_z, \qquad V = \varepsilon\sigma_x. \tag{5.13}$$

The unperturbed states are $|\pm\rangle = |\pm z\rangle$, and the first order energy correction vanishes:

$$E_\pm^{(1)} = \langle \pm| \varepsilon\sigma_x |\pm\rangle = 0. \tag{5.14}$$

The second order correction however is nonzero. Picking the negative state leads to

$$E_-^{(2)} = \frac{|\langle +| V |-\rangle|^2}{-\omega - (\omega)} = -\frac{\varepsilon^2}{2\omega}. \tag{5.15}$$

Let us compare to the exact solution. We will set $\lambda = 1$ for simplicity here since we already have ε to characterize the strength of the perturbation. Then the exact spectrum of $H = H_0 + \varepsilon V$ is

$$E_\pm = \omega_0 \pm \sqrt{\omega^2 + \varepsilon^2} \tag{5.16}$$

The above can be derived by brute force, analogy to a spin problem, or by squaring $H - \omega_0$ and obtaining $\omega^2 + \varepsilon^2$ and taking the square root, noting that there has to be a positive and negative branch since tr $(H - \omega_0) = 0$. In any case, for $\omega \gg \varepsilon$ we can expand the square root in small ε to obtain

$$E_\pm = E_\pm^{(0)} \pm \frac{\varepsilon^2}{2\omega} \tag{5.17}$$

which precisely matches the perturbation theory calculation.

However, in the degenerate limit $\omega \to 0$ we instead obtain

$$E_\pm = \omega_0 \pm \varepsilon \tag{5.18}$$

such that now there is a *first order* correction to the energies, despite the fact that the first order standard perturbation theory result (5.14) is zero. One way to view the origin of this issue is that, when there is degeneracy, there is no preferred basis for the eigenstates of H_0. If, instead, we choose the $|\pm x\rangle$ basis, for $\omega = 0$ the states would still be eigenstates of H_0 but we would recover the first order correction $\langle \pm x| V |\pm x\rangle = \pm\varepsilon$. These nonzero matrix elements in the $|\pm x\rangle$ basis can also manifest as off diagonal matrix elements in the $|\pm z\rangle$ basis, i.e.

$$\langle \pm z| V |\mp z\rangle = \varepsilon. \tag{5.19}$$

The conclusion is that, in degenerate perturbation theory, off-diagonal matrix elements of the perturbation within the degenerate subspace must be taken into account entirely.

5.1.2 Degenerate perturbation theory

Indeed, the problem must be solved essentially exactly within the degenerate subspace; there is no perturbative simplification to the energies (5.16) for generic ω, ε. But if the degenerate subspace is a small, isolated part of the entire spectrum of H_0, we don't want to solve the entire Hamiltonian H exactly. We should be able to perturbatively take into account the influence of remote energy levels on the degenerate subspace.

Our goal will then be to derive an effective Hamiltonian that only acts within a suitably perturbed degenerate subspace. The leading corrections to this effective Hamiltonian will be that of H_0 and the projected perturbation, and the subleading corrections will involve the influence of energy levels outside the degenerate subspace. This effective Hamiltonian can then be diagonalized afterwards.

We will begin by labeling eigenstates of the unperturbed degenerate eigenspace as $|n^{(0)}, l\rangle$, where n labels the degenerate eigenspace of interest and l labels the states within the eigenspace such that $H_0 |n^{(0)}, l\rangle = E_{n,l}^{(0)} |n^{(0)}, l\rangle$ where $E_{n,l}^{(0)}$ are not necessarily distinct for different l — we are allowing for degeneracy after all! We have, for simplicity, chosen a basis where H_0 acts diagonally, but this is not necessary and in general may not be the most natural basis. However, the basis of the degnerate subspace can also be changed after deriving the effective Hamiltonian. States that are outside the degenerate subspace we will continue to label as $|k^{(0)}\rangle$ with energes $E_k^{(0)}$; degeneracies amongst these states are unimportant for our purposes here, k simply indexes all of the states outside of the degenerate subspace of interest.

The effective Hamiltonian and perturbed degenerate states are defined by demanding that the action of H on $|n, l\rangle$ keeps the state within the degenerate subspace:

$$H |n, l\rangle = h_{n,ll'} |n, l'\rangle \tag{5.20}$$

Here h is a matrix in the l, l' indices that implicitly depends on λ because H does. We are using the repeated index summation convention, where the repeated l' above implies that the above equation should

be interpreted with a sum over l'. We then expand

$$\begin{aligned} h_n &= h_n^{(0)} + \lambda h_n^{(1)} + \lambda^2 h_n^{(2)} + \cdots \\ |n,l\rangle &= |n^{(0)},l\rangle + \lambda\,|n^{(1)},l\rangle + \lambda^2\,|n^{(2)},l\rangle \cdots \end{aligned} \tag{5.21}$$

as before. Our gauge fixing condition is generalized to

$$\langle n^{(0)},l|n^{(d)},l'\rangle = 0, \qquad \text{for } d \geq 1. \tag{5.22}$$

so that every correction changes the makeup of the degenerate subspace, and doesn't have a part that rotates one basis state into another, for example. With this set up we can more or less directly generalize the non-degenerate perturbation theory to the degenerate case.

Expanding out the eigenequation (5.20), and writing $\Delta_{n,ll'} = h_{n,ll'} - E_n^{(0)}\delta_{ll'}$, we can manipulate the eigenequation as before to obtain

$$(E_{nl}^{(0)} - H_0)\,|n,l\rangle = (\lambda V\delta_{ll'} - \Delta_{nll'})\,|n,l'\rangle\,. \tag{5.23}$$

We have introduced $\delta_{ll'}$ factors on the Hilbert space operators, like λV, that do not directly act on the l index of the state, in order to consistently have $|n,l'\rangle$ on the right hand side of the above equation and $|n,l\rangle$ on the left hand side. Acting with $\langle n^{(0)},l''|$ from the left, the left hand side simplifies to

$$\langle n^{(0)},l''|\,(E_{nl}^{(0)} - H_0)\,|n,l\rangle = (E_{nl}^{(0)} - E_{nl''})\,\langle n^{(0)},l''|n,l\rangle = (E_{nl}^{(0)} - E_{nl''})\delta_{l,l''} = 0 \tag{5.24}$$

where we used (5.22) in the second to final equality above. We then arive at

$$\langle n^{(0)},l''|\,(\lambda V\delta_{ll'} - \Delta_{n,ll'})\,|n,l'\rangle = 0 \tag{5.25}$$

which says that the state $(\lambda V\delta_{ll'} - \Delta_{n,ll'})\,|n,l'\rangle$ is orthogonal to $|n^{(0)},l''\rangle$ for all l''; that is, it is orthogonal to the unperturbed degenerate subspace. Again using $\langle n^{(0)},l''|n,l'\rangle = \delta_{l',l''}$, we have

$$\Delta_{nll'} = \langle n^{(0)},l|\,\lambda V\,|n,l'\rangle \implies h_{l,l'}^{(d)} = \langle n^{(0)},l|\,V\,|n^{(d-1)},l'\rangle \tag{5.26}$$

so that we can compute the order d effective Hamiltonian in terms of the order $d-1$ states.

Next we act with $\langle k^{(0)}|$ on (5.23); i.e. we are acting with an eigenstate outside the degenerate subspace. We then obtain

$$\langle k^{(0)}|n,l\rangle = \frac{1}{E_{nl}^{(0)} - E_k^{(0)}}\,\langle k^{(0)}|\,(\lambda V\delta_{ll'} + \Delta_{n,ll'})\,|n,l'\rangle \tag{5.27}$$

so that the basis expansion $|n,l\rangle = |n^{(0)},l\rangle + \sum_{k\neq n}\langle k^{(0)}|n,l\rangle\,|k^{(0)}\rangle$ yields

$$|n,l\rangle = |n^{(0)},l\rangle + \sum_{k\neq n}\frac{1}{E_{nl}^{(0)} - E_k^{(0)}}\,\langle k^{(0)}|\,(\lambda V\delta_{ll'} + \Delta_{n,ll'})\,|n,l'\rangle\,|k^{(0)}\rangle\,. \tag{5.28}$$

The equations (5.26) and (5.28) again play the role of enabling us to calculate higher order terms in the expansion from lower order ones. Let us compute the first few corrections. The first order correction to the effective Hamiltonian is

$$h_{n,ll'}^{(1)} = \langle n^{(0)},l'|\,V\,|n^{(0)},l\rangle\,. \tag{5.29}$$

We see that the effective Hamiltonian takes into account the projection of V on the degenerate subspace entirely. For the two dimensional example above, this would represent no simplification at all, but if the degenerate subspace is small relative to the entire Hilbert space then (5.29) can be very helpful. Diagonalizing $h_{n,ll'}^{(1)}$ can range from easy to extremely difficult or impossible depending on the size and complexity of the degenerate space.

At higher order we arrive at corrections that change the makeup of the degenerate subspace through (5.28). At leading order, as before, we can replace $|n,l\rangle \to |n^{(0)},l\rangle$ on the right hand side so that the $\Delta_{n,ll'}$ term drops by orthogonality. We then obtain

$$|n^{(1)},l\rangle = \sum_{k\neq n} \frac{\langle k^{(0)}|\, V\, |n,l\rangle}{E^{(0)}_{nl} - E^{(0)}_k}\, |k^{(0)}\rangle\,, \tag{5.30}$$

and the associated second order correction to the effective Hamiltonian

$$h^2_{n,ll'} = \sum_k \frac{\langle n,l|\, V\, |k^{(0)}\rangle\, \langle k^{(0)}|\, V\, |n,l'\rangle}{E^{(0)}_{nl} - E^{(0)}_k}. \tag{5.31}$$

There is a nice way to think about (5.31); the perturbation kicks one out of the degenerate subspace, leading to the matrix element from $\langle k^{(0)}|\, V\, |n,l\rangle$ and then brings one back to the degenerate subspace, though not necessarily in the same state, leading to the matrix element $\langle n,l|\, V\, |k^{(0)}\rangle$. Because of the "intermediate" high energy state $|k^{(0)}\rangle$, this process is divided by $(E^{(0)}_{nl} - E^{(0)}_k)^{-1}$ which suppresses the process if the intermediate state is very far away in energy.

5.1.3 Applications of perturbation theory

In this section, we consider some applications of perturbation theory following the formalism developed in the previous two sections. Before considering specific examples, let me first point out that although the expression for the second order perturbation theory is rather complicated and requires the knowledge of all eigenstates and eigenenergies of the non-perturbed Hamiltonian, in many cases, we can derive an upper bound on the value of this term that provides a reasonable estimate for the value of this perturbative correction. Consider the correction to the ground state energy $n = 0$ for a perturbation V such that the first order correction vanishes $E^{(1)}_0 = \langle n^{(0)}|V|n^{(0)}\rangle = 0$. Then the leading correction to the ground state energy is given by

$$E^{(2)}_0 = -|E^{(2)}_0|, \qquad |E^{(2)}_0| = \sum_{k\neq 0} \frac{|\langle k^{(0)}|V|0^{(0)}\rangle|^2}{E^{(0)}_k - E^{(0)}_0} \tag{5.32}$$

Using the fact that

$$E^{(0)}_k - E^{(0)}_0 \geq E^{(0)}_1 - E^{(0)}_0 = \Delta E_{\min} \tag{5.33}$$

We can simplify $|E^{(2)}_0|$ as

$$|E^{(2)}_0| \leq \frac{1}{\Delta E_{\min}} \sum_{k\neq 0} |\langle k^{(0)}|V|0^{(0)}\rangle|^2 = \frac{1}{\Delta E_{\min}} \sum_k \langle 0^{(0)}|V|k^{(0)}\rangle\langle k^{(0)}|V|0^{(0)}\rangle = \frac{\langle 0^{(0)}|V^2|0^{(0)}\rangle}{\Delta E_{\min}} \tag{5.34}$$

Historically, the earliest and most prominent application of perturbation theory was to understand the fine features of the atomic spectra with the simplest example being the Hydrogen atom. For an energy level with principal quantum number n, we have found earlier that the degeneracy of the energy levels is n^2 (ignoring spin). This means that for $n > 1$, understanding the effect of any perturbation requires the use of non-degenerate perturbation theory. On the other hand, for $n = 1$ and for spin-independent perturbations, we can use the non-degenerate perturbation theory described above. A simple and illustrative example is the (quadratic) Stark effect.

Quadratic Stark effect

The Stark effect corresponds to the shift in the energy levels in the presence of an electric field. It is obtained by considering the Hamiltonian (5.1) with

$$H_0 = H_{\text{Hydrogen}}, \qquad V = -eEz, \qquad e < 0 \tag{5.35}$$

Here, we assumed the magnetic field is in the z direction, $\boldsymbol{E} = E\hat{z}$. We will consider the limit of small E so that the perturbation V can be considered small [1].

The effect of the perturbation V on the energy of the lowest energy state $n = 1$ in the Hydrogen atom, labelled $|1, 0, 0\rangle$ ($n = 1$, $l = 0$, $m = 0$) can be understood as follows. First, we notice that the first order contribution to the energy vanishes since $\langle 1, 0, 0|z|1, 0, 0\rangle = 0$. This can be understood by recalling that the spherical harmonic $Y_{m=0}^{l=0}$ is spherically symmetric (it is independent of the angles θ and φ), so the angular integral $\int d\theta \sin\theta \cos\theta |Y_0^0|$ vanishes. Another way to see this is using the parity selection rule we discussed earlier. Since H_0 is parity symmetric, a non-degenerate eigenstate has to be a parity eigenvalue, but since V is odd under parity, then its expectation value in any parity eigenstate has to vanish since $\langle 1, 0, 0|V|1, 0, 0\rangle = \langle 1, 0, 0|\pi V \pi|1, 0, 0\rangle = -\langle 1, 0, 0|V|1, 0, 0\rangle = 0$.

This means that the leading contribution to the energy of the $n = 1$ state is quadratic in E. It is given by

$$E_0^{(2)} = -\frac{1}{2}\alpha E^2, \qquad \alpha = 2e^2 \sum_{k\neq(1,0,0)} \frac{|\langle k|z|1, 0, 0\rangle|^2}{E_k - E_{1,0,0}} \tag{5.36}$$

Notice here that the sum does not only include the bound states of the Hydrogen atom but also the extended (scattering) states that we have not discussed. Evaluating this expression is quite tedious but can be done analytically yielding the result $\alpha = 4.5a_0^3$. Here, instead, we will use the simplification discussed in Eq. 5.34 to derive an upper bound on α which will turn out to be not very far off from the exact result. Using (5.34), and noting that $\Delta E_{\min} = \frac{e^2}{2a_0}[1 - \frac{1}{4}] = \frac{3e^2}{8a_0}$, we get

$$\alpha \leq \frac{16a_0}{3}\langle z^2\rangle \tag{5.37}$$

where we used the shorthand $\langle z^2\rangle$ for $\langle 1, 0, 0|z^2|1, 0, 0\rangle$. Due to the full rotation symmetry of the $n = 1$ state, $\langle z^2\rangle = \langle x^2\rangle = \langle y^2\rangle = \frac{1}{3}\langle r^2\rangle$. Recalling that the radial part of the Hydrogen atom wavefunction goes as e^{-r/a_0}, we find

$$\langle r^2\rangle = \frac{\int_0^\infty dr r^4 e^{-2r/a_0}}{\int_0^\infty dr r^2 e^{-2r/a_0}} = 3a_0^2 \tag{5.38}$$

which implies $\langle z^2\rangle = a_0^2$. Substituting in (5.37) gives

$$\alpha \leq \frac{16a_0^3}{3} = 5.3a_0^3 \tag{5.39}$$

We see that this upper bound is not so far off the actual value. The reason for this is the following. Since the energy goes as $1/n^2$ for the bound states, the recplacement of the denominator by ΔE only introduces a small error for $n > 2$. For the extended states, this replacement may introduce large errors since the denominator is unbounded but the matrix elements $|\langle k|z|1, 0, 0\rangle|$ are expected to be small since they include the overlap between a bound state whose probability is concentrated over a small region in space and a plane wave whose probability to be in this region is very small.

Linear Stark effect

To understand the effect of electric field on higher energy levels, we need to employ degenerate perturbation theory. As we discussed last time, in degenerate perturbation theory we consider certain subspaces labelled by $|n^{(0)}, l\rangle$ where l labels the states within each subspace. Each subspace is characterized by small energy separation between the states when the energy is evaluated using the unperturbed Hamiltonian H_0. In degenerate perturbation theory, the action of the perturbation is assumed to modify the degenerate subspaces

[1] An important subtlety here is that since the potential V is unbounded from below (it goes to $-\infty$ at $z \to -\infty$), perturbation theory is strictly speaking not applicable. In particular, bound states can now escape. However, for small V, the lifetimes of such bound states will be long so that it still makes sense to talk about the energies of the states as long lived metastable states.

labelled by n only perturbatively, whereas its effect on the individual states within each subspace could be large. This is captured by writing an effective Hamiltonian

$$H|n,l\rangle = h_{n,ll'}|n,l'\rangle \tag{5.40}$$

where $|n,l\rangle$ and $h_{n,ll'}$ have the perturbative expansions

$$h_n = \sum_d \lambda^d h_n^{(d)}, \qquad |n,l\rangle = \sum_d \lambda^d |n^{(d)},l\rangle \tag{5.41}$$

where the first and second order terms in λ are given by

$$h^{(1)}_{n,ll'} = \langle n^{(0)},l'|V|n^{(0)},l\rangle, \qquad h^{(2)}_{n,ll'} = \sum_{k\neq n} \frac{\langle n,l|V|k^{(0)}\rangle\langle k^{(0)}|V|n,l'\rangle}{E^{(0)}_{nl} - E^{(0)}_k} \tag{5.42}$$

We would now like to use this formalism to understand the effect of electric field, Eq. 5.35, on the energy levels of the Hydrogen atom for $n > 1$. For simplicity, let us consider the case $n = 2$. Here, we have 4 degenerate eigenstates corresponding to $l = 0, m = 0$ (2s orbital) and $l = 1$, $m = 0, \pm 1$ (2p orbitals). We begin by noting that the electric field along the z-direction breaks full rotation symmetry but still retains a 2D subgroup corresponding to rotations around the z-axis. This means that $[V, \boldsymbol{L}^2] \neq 0$ but $[V, L_z] = 0$. As a result, the matrix elements of V between states with different m should still vanish since

$$0 = \langle l,m|[L_z,V]|l',m'\rangle = \hbar(m-m')\langle l,m|V|l',m'\rangle \tag{5.43}$$

Thus, for $m \neq m'$, $\langle l,m|V|l',m'\rangle$ has to vanish. This means that we can only have non-vanishing matrix elements between the states $|0,0\rangle$ and $|1,0\rangle$. Furthermore, since the $|l,m\rangle$ states are parity eigenstates, the diagonal matrix elements $\langle l,m|V|l,m\rangle$ are also zero. This means that the matrix h has the form

$$h = \begin{pmatrix} 0 & \langle 0,0|V|1,0\rangle & 0 & 0 \\ \langle 1,0|V|0,0\rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{5.44}$$

where the basis states are $|0,0\rangle$, $|1,0\rangle$, $|1,1\rangle$, and $|1,-1\rangle$. The matrix element $\langle 0,0|V|1,0\rangle$ can be directly evaluated as $3ea_0E$. Thus, the first order correction to the energy

$$\Delta^{(1)}_{\pm} = \pm 3ea_0E \tag{5.45}$$

The corresponding energy eigenstates are

$$|\pm\rangle = \frac{1}{\sqrt{2}}(|0,0\rangle \pm |1,0\rangle) \tag{5.46}$$

Notice that the effect of electric field in degenerate perturbation theory is linear rather than quadratic. This can be understood by noting that, in the absence of degeneracy, all eigenstates are parity eigenstates so the eigenstates can have no dipole moment which leads to the vanishing of the linear term in perturbation theory. The only response to electric field is then obtained through the quadratic (polarizability term) which can be understood as a field-induced dipole moment. On the other hand, in the degenerate case, we can choose linear combinations of the states which have a dipole moment and such combinations acquire linear energy corrections proportional to their dipole moment in the presence of field.

Spin-orbit coupling

The final effect we would like to discuss is the spin-orbit coupling. Spin-orbit coupling is ultimatlely a relativistic effect so its proper treatment should wait until we introduce the proper relativistic generalization of quantum mechanics, the Dirac equation. Here, I will instead present a crude intuitive argument that turns out to reproduce the correct expression up to a factor of 2. The idea is that an electron moving in any potential feels an electric field given by

$$\boldsymbol{E} = -\frac{1}{e}\nabla V \tag{5.47}$$

For the particular case where the potential only depends on the radial coordinate, we get an electric field pointing in the radial direction given by

$$\boldsymbol{E} = -\frac{1}{e}\frac{\boldsymbol{r}}{r}\frac{d}{dr}V(r) \tag{5.48}$$

Now, although in the rest frame of the nucleus, there is no magnetic field, in the rest frame of the electron it feels an effective magnetic field since it sees the nucleous moving with velocity $-\boldsymbol{v}$ [2]. The effective magnetic field is given by

$$\boldsymbol{B}_{\text{eff}} = -\frac{1}{c}\boldsymbol{v}\times\boldsymbol{E} = -\frac{1}{mc}\boldsymbol{p}\times\boldsymbol{E} \tag{5.49}$$

Substituting (5.48) in (5.49) yields

$$\boldsymbol{B}_{\text{eff}} = -\frac{1}{mcer}\frac{d}{dr}V(r)\boldsymbol{L} \tag{5.50}$$

Thus, there is an effective magnetic field that is proportional to the orbital angular momentum. On the other hand, since the electron has a magnetic moment proportional to its spin, its energy in the presence of a field is changed by

$$\Delta H_{\boldsymbol{B}} = -\boldsymbol{\mu}\cdot\boldsymbol{B}, \qquad \boldsymbol{\mu} = \frac{e\boldsymbol{S}}{mc} \tag{5.51}$$

Thus, there is a correction to the Hamiltonian due to the effective magnetic field given by

$$\Delta H_{LS} = \frac{1}{m^2c^2r}\frac{d}{dr}V(r)\boldsymbol{L}\cdot\boldsymbol{S} \tag{5.52}$$

The actual correct answer turns out to be smaller by a factor of 2

$$\Delta H_{LS} = \frac{1}{2m^2c^2r}\frac{d}{dr}V(r)\boldsymbol{L}\cdot\boldsymbol{S} \tag{5.53}$$

Applying degenerate perturbation theory we see that this term can lead to linear corrections to the energies within the $2n^2$ degenerate subspace for a given principal quantum number n. This degenerate subspace is labelled by the the eigenvalues of $\boldsymbol{L}^2$, L_z, $\boldsymbol{S}^2$, S_z corresponding to the quantum numbers l, m, $s = 1/2$, and $m_s = \pm 1/2$. The spin orbit coupling term commutes with $\boldsymbol{S}^2$ and $\boldsymbol{L}^2$ but not with L_z and S_z. We can compute the matrix elements of ΔH_{LS} between states with different m and m_s, but a much more convenient approach is to use the formalism for the addition of angular momentum we developed earlier. We can introduce the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ and notice that $2\boldsymbol{L}\cdot\boldsymbol{S} = \boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2$ which implies that $\boldsymbol{L}\cdot\boldsymbol{S}$ commutes with both $\boldsymbol{J}^2$ and J_z. This means that we can label the states with the quantum numbers l, s, j and m_j instead of l, s, m, and m_s. In the new basis, ΔH_{LS} is diagonal and we only need to compute the diagonal matrix elements. The transformation between the two basis is performed via the Clebsch-Gordan coefficients we discussed earlier.

We now notice that the action of $\boldsymbol{L}\cdot\boldsymbol{S}$ is simple in the new basis since

$$\boldsymbol{L}\cdot\boldsymbol{S}|l,s,j,m_j\rangle = \frac{1}{2}(\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2)|l,s,j,m_j\rangle = \frac{\hbar^2}{2}(j(j+1) - l(l+1) - s(s+1))|l,s,j,m_j\rangle \tag{5.54}$$

[2] We are here neglecting for the moment that this is not an inertial frame

We can substitute $s = 1/2$ above. The first order energy correction is diagonal in the new basis and given by

$$\Delta_{l,j,m_j} = \langle \frac{1}{2m^2c^2r}\frac{d}{dr}V(r)\rangle_{n,l,j,m_j}\frac{\hbar^2}{2}(j(j+1) - l(l+1) - \frac{3}{4}) \tag{5.55}$$

For Coulomb potential with atomic number Z, we have $V(r) = -\frac{Ze^2}{r}$. Thus, we need to evaluate the expectation value $\langle \frac{Ze^2}{r^3}\rangle_{n,l,j,m_j}$. While we can try doing this by brute force, there is a nice trick we can use. First, we notice that since the states $|n, l, j, m_j\rangle$ are eigenstates of the Hamiltonian, the expectation value of the commutator $\langle [H_0, A]\rangle_{n,l,j,m_j}$ vanishes for any operator A where $H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{r}$ is the radial Hamiltonian. Now choosing $A = \frac{d}{dr}$, we get the identity

$$\langle \frac{1}{r^3}\rangle_{n,l,j,m_j} = \frac{2Ze^2m^2}{l(l+1)\hbar^4}\langle \frac{\hbar^2}{2mr^2}\rangle_{n,l,j,m_j} \tag{5.56}$$

The term $\frac{\epsilon\hbar^2}{2mr^2}$ effectively modifies the centrifugal term by sending $l \mapsto l + \frac{\epsilon}{2l+1}$, which correspond to a correction to the energy $\Delta E_n = E_{n+\frac{\epsilon}{2l+1}} - E_n = \frac{1}{2}mc^2\frac{Z^2\alpha^2}{n^3}\frac{\epsilon}{l+1/2} = -\frac{1}{n(l+1/2)}E_n$. This gives

$$\langle \frac{Ze^2}{r^3}\rangle = -\frac{2Z^2e^4m^2}{nl(l+1)(l+1/2)\hbar^4}E_n = -\frac{2Z^2\alpha^2m^2c^2}{nl(l+1)(l+1/2)\hbar^2}E_n \tag{5.57}$$

Substituting in the energy expression gives

$$\Delta_{n,l,j,m_j} = -\frac{Z^2\alpha^2}{nl(l+1)(l+1/2)}E_n(j(j+1) - l(l+1) - \frac{3}{4}) \tag{5.58}$$

The correction is proportional to the energy eigenvalue E_n times the dimensionless number $Z^2\alpha^2$ where α is the fine structure constant $\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$. The smallness of the fine structure constant justifies the perturbative treatment. An important observation is that the spin-orbit coupling scales as the square of the atomic number so it becomes more important for heavier elements.

5.2 Variational Method

In perturbation theory, we found that we can find approximate solutions to quantum mechanical problems which are sufficiently close to an exactly solvable limit. However, this is not always possible. In many cases, we want to solve a problem that is not close to a solvable limit or where perturbation theory is known to fail. In this case, another approximation approach, known as the variational method, is very helpful.

The variational method is mainly used to estimate the energy and the wavefunction for the ground state of a given Hamiltonian. It can be adapted in some cases to determine excitations but we will not consider such cases here. The variational principle relies on the simple observation that since the ground state is the lowest energy eigenstate of the Hamiltonian and since we can expand an arbitrary state in terms of eigenstates of the Hamiltonian (since they form a complete basis), then the expectation value of the Hamiltonian in *any* state has to be larger than or equal that in the ground state. To see this explicitly, consider a Hamiltonian H with eigenstates $|n\rangle$ and eigenenergies E_n, $n = 0, 1, \ldots$ with $E_0 \leq E_1 \leq E_2 \ldots$. For an arbitrary state $|\psi\rangle$, the energy expectation value is given by

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \tag{5.59}$$

Here, we have taken into account that $|\psi\rangle$ is not necessarily normalized. We can expand $|\psi\rangle$ in terms of the complete basis $|n\rangle$

$$|\psi\rangle = \sum_n c_n|n\rangle, \qquad c_n = \langle n|\psi\rangle \tag{5.60}$$

Substituting in (5.59), we get

$$E = \sum_n \frac{|c_n|^2 E_n}{\sum_m |c_m|^2} = \sum_n \frac{|c_n|^2 (E_n - E_0 + E_0)}{\sum_m |c_m|^2} = E_0 + \sum_n \frac{|c_n|^2 (E_n - E_0)}{\sum_m |c_m|^2} \geq E_0 \tag{5.61}$$

Thus, the energy expectation value of $|\psi\rangle$ provides an upper bound on the ground state energy. Furthermore, this bound is saturated if and only if $|c_n|^2(E_n - E_0) = 0$ which means that $|\psi\rangle$ is a ground state, $H|\psi\rangle = E_0|\psi\rangle$.

5.2.1 One-dimensional Schrödinger equation

While the variational method does not provide us with a control to how close we are to the actual ground state, we can use our physical intuition about the problem to come up with some good guess for the ground state. Variational methods are particularly powerful if we can come up with a family of wavefunctions $|\psi_{\{\xi\}}\rangle$ parametrized by a family of parameters $\{\xi\}$ that we expect provides a good approximation for the ground state. We can then compute the variational energy as a function of $\{\xi\}$ and find the minimum of $E_{\{\xi\}}$. We expect that, at least within this family, this minimum value provides the best approximation of the ground state and if this family of states is chosen properly we usually get a good approximation for the ground state and its energy.

Let us now consider some examples. If we want to find the ground state for the 1D Schrödinger equation for a potential that grows at infinity or at least is sufficiently large such that we have a bound state, then we know the ground state does not have any zeros and that it has to decay at infinity. We can also impose further symmetry requirements. For instance, for parity-symmetric potentials, the ground state should have even parity. These considerations suggest using a Gaussian variational ansatz $\psi_\xi(x) = e^{-\frac{x^2}{2\xi^2}}$ labelled by a single positive real number ξ is a good starting point to estimate the ground state for a general potential that grows at $\pm\infty$. Let us first consider the Harmonic oscillator whose Hamiltonian is given by

$$H = \frac{1}{2}\hbar\omega \left[-\frac{d^2}{dx^2} + x^2 \right] \tag{5.62}$$

Here, we are measuring x in terms of $l = \sqrt{\hbar/m\omega}$. The variational energy is given by

$$E_\xi = \frac{1}{2}\hbar\omega\epsilon_\xi, \qquad \epsilon_\xi = \frac{\int_{-\infty}^{\infty} dx \psi_\xi(x) H \psi_\xi(x)}{\int_{-\infty}^{\infty} dx \psi_\xi(x)\psi_\xi(x)} = \frac{1}{2\xi^2} + \frac{1}{2}\xi^2 \tag{5.63}$$

This expression grows at $\xi \to 0$ and $\xi \to \infty$ so it should have a minimum somewhere in between. To find the minimum, we simply set $0 = \frac{d\epsilon_\xi}{d\xi} = -\xi^{-3} + \xi$ which implies $\xi^4 = 1$ whose only real solution is $\xi = 1$. The corresponding dimensionless energy is $\epsilon_\xi = 1$. In the original dimensionful units, this corresponds to $\xi = l$ and $E = \frac{1}{2}\hbar\omega$. This is the same as the exact answer since the family of states ψ_ξ does contain the harmonic oscillator ground state.

Let us now consider another example. Consider the linear potential $V(x) = k|x|$. The Hamiltonian can be written in terms of a dimensionless position variable x measured in units of $x_0 = (\hbar^2/mk)^{1/3}$ and the energy scale $\varepsilon_0 = kx_0$ as

$$H = \varepsilon_0 \left[-\frac{1}{2}\frac{d^2}{dx^2} + |x| \right] \tag{5.64}$$

We can now use the same variational state and write

$$E_\xi = \varepsilon_0\epsilon_\xi, \qquad \epsilon_\xi = \frac{\int_{-\infty}^{\infty} dx \psi_\xi(x) H \psi_\xi(x)}{\int_{-\infty}^{\infty} dx \psi_\xi(x)\psi_\xi(x)} = \frac{1}{4\xi^2} + \frac{1}{\sqrt{\pi}}\xi \tag{5.65}$$

This expression also grows at 0 and infinity and has a minimum between given by $0 = \frac{d\epsilon_\xi}{d\xi} = -\frac{1}{2}\xi^{-3} + \frac{1}{\sqrt{\pi}}$ whose only real solution is $\xi = (\sqrt{\pi}/2)^{1/3}$. The corresponding dimensionless energy is $\epsilon_{\min} = \frac{3}{2(2\pi)^{1/3}} \approx$

0.813. This potential can be exactly solved with wavefunctions that can be written in terms of Airy functions. The exact ground state energy $\epsilon \approx 0.809$. We see that the variational method provides an excellent approximation for the ground state energy since the difference between the variational and exact energies is $\approx 0.004E_0$ where E_0 is the natural energy scale of the problem.

Let us consider a third example with a quartic potential

$$H = \varepsilon_0 \left[-\frac{1}{2}\frac{d^2}{dx^2} + x^4 \right] \tag{5.66}$$

This is a potential for which no analytical solution exists. However, we can still solve this equation numerically to find that the ground state energy is $\approx 0.668E_0$. Using the Gaussian variational ansatz, we find

$$\epsilon_\xi = \frac{1}{4\xi^2} + \frac{3}{4}\xi^4 \tag{5.67}$$

Again this expression has at least one minimum for positive ξ obtained by solving $0 = \frac{d\epsilon_\xi}{d\xi} = -\frac{1}{2}\xi^{-3} + 3\xi^3$ leading to $\xi = 1/6^{1/6}$. The corresponding energy is $\epsilon_{\min} = \left(\frac{3}{4}\right)^{4/3} \approx 0.681$. We see again that the difference between the variational and exact solutions is very small $0.013E_0$.

5.2.2 Ground state wavefunction

In all the examples we considered we found that the Gaussian ansatz provided a good approximation for the ground state energy. How about the ground state wavefunction? In general, a state which provides a good approximation to the ground state energy could have very little overlap with the actual ground state if it happened that there is another eigenstate of the Hamiltonian whose energy is close to the ground state [3] On the other hand, in many cases, we can place a lower bound on the gap between the ground state energy and that of excited states. If we know the gap to the first excited state is at least Δ, then we can use Eq. 5.61 to write (here for simplicity, we will assume $|\psi\rangle$ is normalized)

$$E - E_0 = \sum_n |c_n|^2 (E_n - E_0) \geq \Delta \sum_{n=1} |c_n|^2 = \Delta(1 - |c_0|^2) \tag{5.68}$$

This implies that the deviation of the wavefunction overlap from 1 cannot exceed $\frac{E-E_0}{\Delta}$ or equivalently

$$|\langle\psi|0\rangle| \geq \sqrt{1 - \frac{E - E_0}{\Delta}} \approx 1 - \frac{E - E_0}{2\Delta} \tag{5.69}$$

In all the 1D cases we considered, since we have a confining potential, we expect the spacing between eigenstates to be of order E_0 where E_0 is the typical energy scale of the problem. Thus, since the difference $E - E_0$ was at most 1%, we expect a very large overlap $> 99\%$ with the actual ground state wavefunction.

5.2.3 Helium atom

As a final example for the variational method, we consider the problem of the ground state of the Helium atom. Here, we have two electrons and two protons. The Hamiltonian takes the form

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{5.70}$$

Without the last term, this Hamiltonian simply decomposes into a sum of Hamiltonians for the first and the second electrons whose ground state can be obtained by separation of variables to be the product of

[3] An extreme case would be if the first excited state has energy very close to the ground state and our variational ansatz happens to be exactly equal to that state. In this case, the ansatz will have zero overlap with the ground state due to the orthogonality of different wavefunctions.

ground states of each Hamiltonian separately $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2)$. However, the last term makes it impossible to perform a separation of variables. Note that there is no sense in which the last term is a small perturbation to the problem since it is of the same order as the interaction between each of the electrons and the nucleus, so we do not expect perturbation theory to be applicable.

So How do we proceed? we can begin by deriving a crude bound where we simply use the state

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_{100}(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_2) = e^{-2(r_1+r_2)/a_0} \tag{5.71}$$

as an ansatz. Recall that the ground state energy of a single-particle in the Coulomb potential $V(r) = -\frac{Ze^2}{r}$ is $-Z^2 R_y$ where $R_y = 13.6$ eV. Thus, the energy expectation value for the two electrons excluding the last (electron-electron interaction) term is $-8R_y \approx -109$ eV. The expectation value of the last term can be evaluated as $5R_y/2 \approx 34$ eV, leading to the variational energy estimate -75 eV. The actual energy measured experimentally or determined using more sophisticated methods is -78.96 eV which means that our variational estimate is off by 3.96eV which is around 5% error. Is there a way to do a better variational estimate? it turns out there is. This comes from the observation that for each electron, the presence of the other electrons means that on average it sees a reduced nuclear charge. This can be implemented by assuming the wavefunction is again a product of two separate ground state wavefunctions for a Coulomb potential but with a reduced value of Z. Such ansatz can be written explicitly as

$$\psi_Z(\boldsymbol{r}_1, \boldsymbol{r}_2) = e^{-Z(r_1+r_2)/a_0} \tag{5.72}$$

The variational energy is then given by

$$E_Z = R_y \left[2Z^2 - \frac{27}{4} Z \right] \tag{5.73}$$

This expression has a minimum at $Z = 27/16 \approx 1.69$ with minimum energy $E = -77.5$ eV. We see that this gives a better estimate of the total energy since the energy difference is now 1.46 which is within 2% of the actual value. The value of $Z \approx 1.69$ can be physically interpreted as each electron seeing an effective nuclear charge reduced by roughly $0.3e$ due to the other electron.

This example is an illustration of a powerful set of methods known as mean-field or Hartree-Fock methods where we write a variational ansatz for the ground state of many-interacting electrons in terms of a product of single-particle states that depends on some physically motivated variational parameters. More sophisticated variational methods employing more complicated wavefunctions are also used (e.g. Density matrix renormalization group which uses variational states called tensor networks or matrix product states) and is an active area of research.