Quantum mechanics notes

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DISCLAIMER: These notes are formed from notes for PHYS2941 at a more rigorous level than the course itself, as well as for PHYS3040, and are subject to errors and typos. They are also not complete, particularly the sections on matrix mechanics, angular momentum, and the applications of the Schrödinger equation to physical systems.

1 The Stern-Gerlach device

A Stern-Gerlach (SG) device is comprised of a magnetic field which can be oriented along any direction, through which a beam of particles can be sent. At the end of the SG device we can place a screen that the particles in the original beam can hit after passing through the magnetic field.

Suppose we send a beam of electrons through the SG device when the magnetic field is oriented along the z-axis. We will call such a device an SGz device to denote the direction of the magnetic. Elementary particles like electrons are endowed with an intrinsic form of angular momentum called spin, which can be affected a magnetic field. Classically, the angular momentum of a particle can take on any value and so we expect that if the spin of an electron were analogous to classical angular momentum that the electrons in the beam would have a random range of spins, and that when they pass through the magnetic field, they are deflected by a continuum of values. If we were to place a screen at the end of the SGz device, we would expect to see the electrons land along a line, corresponding to the continuum of values for the spins of the particles. However, when we do this experiment in practice, the electrons land only in two places, symmetrically about the axis of the beam, in what we will call either 'up' or 'down'. For individual particles that we spontaneously create, we find experimentally that the particles have a 50% of landing either up or down. Furthermore, we find that if we were to take the particle that landed either up or down and send them back through the SGz device and have them land again on a detector screen, they always end up landing in the same spot. As such, the particles have a distinct state in relation to the SGz device and the subsequent measurement. We will call these states

$$\text{'Up'} \equiv |+z\rangle \quad \text{and} \quad \text{'Down'} \equiv |-z\rangle. \tag{1.1}$$

If we were now to send through a beam of particles, and allow only those to be measured in the state $|+z\rangle$ to pass through the device, and then to pass through an SGx device, with its magnetic field oriented along the x-axis, we would find something very strange. Instead of the particles all landing either spin 'up' or spin 'down' along this axis, we find that 50% land spin up and 50% land spin down. We will call these states $|+x\rangle$ and $|-x\rangle$ respectively. Clearly, for a particle the state $|+z\rangle$, there is no preference for it to be in either the $|+x\rangle$ or the $|-x\rangle$ state.

Now, suppose that we take this beam of particles that exit from the SGx device and then send them through an SGz device again, we find not that they all are in the state $|+z\rangle$, as they were before passing through the SGz device, but rather that 50% are in the state $|+z\rangle$ and the other half are in the state $|-z\rangle$.

2 States as vectors

Clearly, when the particles emerge from the SGx device, they are in some sense in a superposition of the spin up and spin down states along the z-axis magnetic field. In this sense, we can think of the particles emerging from the SGx device as being in a superposition of the states $|+z\rangle$ and $|-z\rangle$. We can represent this by

$$|+x\rangle = a|+z\rangle + b|-z\rangle. \tag{2.1}$$

We denote this form of a state as a 'ket' vector, every one of which has a corresponding 'bra' vector. For every bra vector $|\psi\rangle$ the bra vector is denoted by $\langle\psi|$. If we wish to find the coefficients, a and b, we take the inner product of the ket with the bra, basis vectors. That is

$$\langle+z|\psi\rangle = a \quad \text{and} \quad \langle-z|\psi\rangle = b. \tag{2.2}$$

In this sense, we say that the basis states $|+z\rangle$ and $|-z\rangle$ are mutually orthogonal and are both normalised. That is,

$$\langle+z|-z\rangle = \langle-z|+z\rangle = 0 \tag{2.3}$$
$$\langle+z|+z\rangle = \langle-z|-z\rangle = 1. \tag{2.4}$$

In this way they form an orthonormal basis. Thus, we can expand the inner product, $\langle+z|\psi\rangle$ as

$$\langle+z|\psi\rangle = \langle+z|(a|+z\rangle + b|-z\rangle) \tag{2.5}$$
$$= \langle+z|a|+z\rangle + \langle+z|b|-z\rangle. \tag{2.6}$$

We thus see that inner products are linear in constants. That is

$$\langle\varphi|(c|\psi\rangle) = c\langle\varphi|\psi\rangle. \tag{2.7}$$

Then our inner product above becomes

$$\langle+z|\psi\rangle = a\langle+z|+z\rangle + b\langle+z|-z\rangle \tag{2.8}$$
$$= a \tag{2.9}$$

taking advantage of the orthonormality of our basis. If we have two states $|\varphi\rangle$ and $|\psi\rangle$, then the inner product

$$\langle\varphi|\psi\rangle \tag{2.10}$$

gives the probability for a particle in the $|\psi\rangle$ state to be measured to be in the $|\varphi\rangle$ state.

As above, we can find the values of the constants a and b above by taking the inner products

$$a = \langle+z|\psi\rangle \quad \text{and} \quad b = \langle-z|\psi\rangle. \tag{2.11}$$

More generally, if we have an orthonormal basis $\{|e_1\rangle, |e_2\rangle, \ldots, |e_n\rangle\}$, then we can express any vector $|\psi\rangle$ in the form

$$|\psi\rangle = k_1|e_1\rangle + k_2|e_2\rangle + \cdots + k_n|e_n\rangle \tag{2.12}$$

where any constant k_j can be complex. To find any constant, k_i, we take the inner product of $|\psi\rangle$ with the corresponding basis vector

$$\langle e_j|\psi\rangle = \langle e_j| \sum_{i=1}^{n} k_i |e_i\rangle. \tag{2.13}$$

Since the basis is orthonormal, the only surviving term is

$$\langle e_j|\psi\rangle = k_j \langle e_j|e_j\rangle \tag{2.14}$$
$$= k_j. \tag{2.15}$$

Therefore

$$|\psi\rangle = \sum_{i=1}^{n} \langle e_i|\psi\rangle |e_i\rangle \tag{2.16}$$
$$= \sum_{i=1}^{n} |e_i\rangle\langle e_i|\psi\rangle. \tag{2.17}$$

We write the actual vector before the coefficient so that when we take the inner product with a bra, we don't have to move the constant later. It's simply a visual preference that allows for ease of reading later on. Just remember that the bra-ket is the coefficient and the lone ket is the vector.

Similarly, for the corresponding bra vector $\langle\psi|$, since it belongs to a different vector space, we write it as a linear combination of the bra vectors of the basis. That is

$$\langle\psi| = \sum_{i=1}^{n} c_i \langle e_i| \tag{2.18}$$
$$\langle\psi|e_j\rangle = c_j \langle e_j|e_j\rangle \tag{2.19}$$
$$c_j = \langle\psi|e_j\rangle \tag{2.20}$$
$$\langle\psi| = \sum_{i=1}^{n} \langle\psi|e_i\rangle\langle e_i|. \tag{2.21}$$

We can now construct the inner product between a ket $|\psi\rangle$ and a bra $\langle\phi|$ by using Eqs. (2.17) and (2.21),

$$\langle\phi|\psi\rangle = \left(\sum_{i=1} \langle\phi|e_i\rangle\langle e_i|\right)\left(\sum_{j=1} |e_j\rangle\langle e_j|\psi\rangle\right) \tag{2.22}$$
$$= \sum_{i=1}\sum_{j=1} (\langle\phi|e_i\rangle\langle e_i|)(|e_j\rangle\langle e_j|\psi\rangle). \tag{2.23}$$

Here, we have removed the upper limits on the summations, since in general we may have an infinite basis (to be discussed later). In order to carry out the remaining double sum, we can expand the brackets exactly how you would expect, and the inner basis vectors turn into a braket (inner product), leaving us with

$$\langle\phi|\psi\rangle = \sum_{i=1}\sum_{j=1} \langle\phi|e_i\rangle \underbrace{\langle e_i|e_j\rangle}_{=\delta_{ij}} \langle e_j|\psi\rangle \tag{2.24}$$

$$= \sum_{i=1} \langle \phi | e_i \rangle \langle e_i | \psi \rangle. \tag{2.25}$$

Therefore, by expanding any two arbitrary states $|\psi\rangle$ and $|\phi\rangle$ in terms of some complete orthonormal basis, we can construct their inner product using just the expansion coefficients of each vector in terms of the basis; for $|\psi\rangle$ these are just the $\langle e_i|\psi\rangle$ while for $\langle\phi|$ these are the $\langle\phi|e_i\rangle$. This may be familiar to you from what we do generally in linear algebra, where we will often take dot products between vectors by representing the vectors as column vectors, where the coefficients of this column vector correspond to the expansion coefficient of that vector in terms of the basis vectors (usually $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$ if we are working in rectangular coordinates). As we will see later, any **ket** state $|\psi\rangle$ can be represented as column vectors in the exact same way, where the corresponding entries in each row of the column vector is given by the corresponding expansion coefficient ($\langle e_i|\psi\rangle$ if we have an orthonormal basis), while any bra state $\langle\phi|$ can be represented as a **row** vector where the corresponding entries are the expansion coefficients ($\langle\phi|e_i\rangle$, again if we have an orthonormal basis). In other words, we can make the identification

$$|\psi\rangle \xrightarrow[\{|e_n\rangle\} \text{ basis}]{} \begin{pmatrix} \langle e_1|\psi\rangle \\ \langle e_2|\psi\rangle \\ \vdots \end{pmatrix} \tag{2.26}$$

$$\langle\phi| \xrightarrow[\{|e_n\rangle\} \text{ basis}]{} \begin{pmatrix} \langle\phi|e_1\rangle & \langle\phi|e_2\rangle & \dots \end{pmatrix}, \tag{2.27}$$

in which case the inner product between $|\psi\rangle$ and $\langle\phi|$ is given by Eq. (2.25), which is exactly just given by the matrix product of the row and column vectors above, i.e.

$$\langle\phi|\psi\rangle = \begin{pmatrix} \langle\phi|e_1\rangle & \langle\phi|e_2\rangle & \dots \end{pmatrix} \begin{pmatrix} \langle e_1|\psi\rangle \\ \langle e_2|\psi\rangle \\ \vdots \end{pmatrix} \tag{2.28}$$

$$= \langle\phi|e_1\rangle\langle e_1|\psi\rangle + \langle\phi|e_2\rangle\langle e_2|\psi\rangle + \dots \tag{2.29}$$

$$= \sum_{i=1} \langle\phi|e_i\rangle\langle e_i|\psi\rangle. \tag{2.30}$$

This is a hint that instead of dealing with the abstract state vector $|\psi\rangle$ when calculating inner products, we can just use the expansion coefficients (which are just numbers!) with respect to a particular basis instead. Indeed, we will see that not only inner products, but any calculation that you can do in quantum mechanics can be done by representing the state vector as a column vector of its expansion coefficients in a particular basis. This is a formalism of quantum mechanics known as matrix mechanics, and is actually the original form in which a full theory of quantum mechanics was expressed. This will be discussed in more detail in Section 5.

3 The quantum state vector

In quantum mechanics, the state of a system is described by a mathematical vector that lives in a Hilbert space $\mathcal{H}$ of dimension N over the complex numbers $\mathbb{C}$. Note that this vector space is complex, and so we have slightly different axioms to those of real inner product spaces you would be familiar with from MATH2001. These vectors are acted on by linear operators, usually denoted by capital letters with a hat above them (e.g. $\hat{A}$), that transform vectors in the Hilbert space into other vectors in the Hilbert space (or the same vector if the operator is the identity, $\hat{\mathbb{I}}$). For two

vectors $|\psi\rangle, |\phi\rangle \in \mathcal{H}$ (two vectors in the Hilbert space) and complex constants α and β, an operator, $\hat{A}$, is linear if it obeys

$$\hat{A}(\alpha|\psi\rangle + \beta|\phi\rangle) = \alpha\hat{A}|\psi\rangle + \beta\hat{A}|\phi\rangle. \tag{3.1}$$

That is to say, constants multiplying vectors can be pulled through the operator and the operator acting on the sum of two vectors equals the sum of the operator acting on the two vectors separately. To each ket, $|\psi\rangle$, there is the notion of its bra vector $\langle\psi|$, which can be put together with the ket to form an inner product $\langle\psi|\psi\rangle$.

Suppose we have an operator $\hat{A}$ acting on a ket $|\psi\rangle \in \mathcal{H}$ to form a new vector $|\phi\rangle = \hat{A}|\psi\rangle$. If we wish to find the bra corresponding to $|\phi\rangle$, we can take the **Hermitian conjugate** of $|\phi\rangle$ in the following way

$$|\phi\rangle^\dagger = (\hat{A}|\psi\rangle)^\dagger \tag{3.2}$$

$$= \langle\psi|\hat{A}^\dagger. \tag{3.3}$$

That is, you turn any bras into kets and any operators into their Hermitian conjugates. Similarly, if we wish to find the bra vector corresponding to $c|\phi\rangle$, where c is some arbitrary complex number, we can do this by

$$(c|\phi\rangle)^\dagger = \langle\phi|c^* \tag{3.4}$$

where we turn kets into bras and complex numbers into their conjugates. Note that the corresponding notation in the lecture notes and Griffiths is

$$\langle\psi|\hat{A}^\dagger = \langle\hat{A}\psi| \tag{3.5}$$

but all this means is that you act $\hat{A}$ on $|\psi\rangle$ and then turn the corresponding vector that you get into the bra. I don't really like this but whatever.

Suppose now that we want to take the inner product between the two vectors $\hat{A}|\psi\rangle$ and $\hat{B}|\phi\rangle$, with the former being the ket. Then, following the procedure from before, we can write this as

$$\Big(\langle\psi|\hat{A}^\dagger\Big)\Big(\hat{B}|\phi\rangle\Big) = \langle\psi|\hat{A}^\dagger\hat{B}|\phi\rangle. \tag{3.6}$$

But note that we can now also write this as

$$\langle\psi|\Big(\hat{A}^\dagger\hat{B}|\phi\rangle\Big) \tag{3.7}$$

in which we first act $\hat{B}$ on $|\phi\rangle$ and then act $\hat{A}^\dagger$ on the resulting vector, and then finally take the inner product between this vector and the bra $\langle\psi|$. Or we could also write this as

$$\Big(\langle\psi|\hat{A}^\dagger\hat{B}\Big)|\phi\rangle \tag{3.8}$$

where we first act $\hat{A}^\dagger$ on $\langle\psi|$, then act $\hat{B}$ on the resulting bra, and then take the inner product between the resulting bra vector and the ket $|\phi\rangle$. That's why I like this approach and notation better than Griffith's. I just think it's cleaner and I think you can do more with it.

Finally, we turn our attention to basis vectors. A set of basis vectors $\{e_n\}$ is *complete* and *orthonormal* if any arbitrary vector $|\psi\rangle$ in the Hilbert space can be written as a linear combination of them, and the inner products between the basis vectors is given by

$$\langle e_i|e_j\rangle = \delta_{ij} = \begin{cases} 0, & i \neq j \\ 1, & i = j \end{cases} \tag{3.9}$$

Suppose a set of vectors, $\{|e_n\rangle\}$, is orthonormal. Then, some arbitrary vector, $|\psi\rangle$, can be written as a superposition of these basis states

$$|\psi\rangle = c_1|e_1\rangle + c_2|e_2\rangle + c_3|e_3\rangle + \dots \tag{3.10}$$

$$= \sum_n c_n|e_n\rangle \tag{3.11}$$

where $\{c_n\}$ are constants to be determined. To determine c_n, we can take the inner product on both sides of this equation with the basis vector $|e_m\rangle$. This gives

$$\langle e_m|\psi\rangle = \langle e_m|\left(\sum_n c_n|e_n\rangle\right) \tag{3.12}$$

$$= \sum_n c_n\langle e_m|e_n\rangle \tag{3.13}$$

$$= \sum_n c_n\delta_{mn} \tag{3.14}$$

$$= c_m. \tag{3.15}$$

Therefore, inserting this expression for c_m into our expression for $|\psi\rangle$ as the linear superposition of basis states gives

$$|\psi\rangle = \sum_n \langle e_n|\psi\rangle|e_n\rangle$$

$$= \sum_n |e_n\rangle\langle e_n|\psi\rangle \tag{3.16}$$

where we have just moved the constants $\langle e_n|\psi\rangle$ in the summation for convenience. Similarly, for the bra vector $\langle\psi|$, we have

$$\langle\psi| = \sum_n \langle\psi|e_n\rangle\langle e_n|. \tag{3.17}$$

With these two expressions, we can now introduce the identity operator for a discrete spectrum

$$\hat{\mathbb{I}} = \sum_n |e_n\rangle\langle e_n| \tag{3.18}$$

which when applied to any ket gives

$$\hat{\mathbb{I}}|\psi\rangle = \sum_n |e_n\rangle\langle e_n|\psi\rangle = |\psi\rangle \tag{3.19}$$

as we'd expect from above. When applied to a bra, and using the fact that $\hat{\mathbb{I}}^\dagger = \hat{\mathbb{I}}$, we have

$$\langle\psi|\hat{\mathbb{I}}^\dagger = \langle\psi|\hat{\mathbb{I}} = \sum_n \langle\psi|e_n\rangle\langle e_n| = \langle\psi| \tag{3.20}$$

which also gives the correct result.

3.1 Hermitian operators

We now introduce a **very** important class of linear operators in quantum mechanics. This is the notion of a Hermitian or self-adjoint operator, which obeys the rule

$$\hat{A}^\dagger = \hat{A}. \tag{3.21}$$

In quantum mechanics, these operators play a very important role, in that they correspond to *observables*. By observables we mean things that you can measure. This is one of the postulates of quantum mechanics

Postulate 1. *Observables in quantum mechanics correspond to Hermitian operators. Measuring an observable in quantum mechanics results in the quantum state collapsing to one of the* ***eigenstates*** *of the corresponding Hermitian operator, with the measurement outcome you obtain being given by the* ***eigenvalue*** *of that eigenstate.*

Things are made easier here by the fact that you prove that the eigenvectors of Hermitian operators form a complete orthonormal basis for your Hilbert space, meaning that any vector in the Hilbert space can be written as a linear combination of the vectors in the Hilbert space, as in Eq. (3.16). So, if you measure the observable corresponding to a Hermitian operator, you have the possibility of collapsing the state to potentially any of its eigenstates.

One way to perhaps motivate this rather unjustified seeming postulate are the following two theorems:

Theorem 1. *The eigenvectors of a Hermitian operator form a complete basis for the Hilbert space* $\mathcal{H}$*.*

Since the eigenstates of a Hermitian operator form a basis for the Hilbert space, any physical system represented by a vector in that Hilbert space can be written as a linear superposition of these eigenstates. Hence, if we were to measure the observable associated with this Hermitian operator, we would always be guaranteed to measure the system to be in **one** of the eigenstates. The second theorem that provides us a sort of vanity check for Postulate 1 is

Theorem 2. *The eigenvalues of* $\hat{A}$ *are all real and the eigenvectors of a Hermitian operator* $\hat{A}$ *belonging to distinct eigenspaces (that is, they have different eigenvalues) are orthogonal.*

Proof. We will begin by proving that the eigenvalues of a Hermitian operator are all real. To do so, suppose our Hermitian operator $\hat{A}$ has eigenstates $|\alpha\rangle$ and $|\beta\rangle$ with corresponding eigenvalues a and b such that $a \neq b$. Then, we have the following two eigenvalue equations

$$\hat{A}|\alpha\rangle = a|\alpha\rangle \text{ and } \hat{A}|\beta\rangle = b|\beta\rangle. \tag{3.22}$$

To prove the result

$$\hat{A}|\alpha\rangle = a|\alpha\rangle \tag{3.23}$$

$$\langle\beta|\hat{A}|\alpha\rangle = \langle\beta|a|\alpha\rangle \tag{3.24}$$

$$(\langle\beta|\hat{A})|\alpha\rangle = a\langle\beta|\alpha\rangle. \tag{3.25}$$

Using the fact that $\hat{A}$ is Hermitian so that $\hat{A}^\dagger = \hat{A}$ we have

$$(\langle\beta|\hat{A}^\dagger)|\alpha\rangle = a\langle\beta|\alpha\rangle \tag{3.26}$$

$$(\langle\beta|b^*)|\alpha\rangle = a\langle\beta|\alpha\rangle \tag{3.27}$$
$$b^*\langle\beta|\alpha\rangle = a\langle\beta|\alpha\rangle. \tag{3.28}$$

Similarly, we have

$$\hat{A}|\beta\rangle = b|\beta\rangle \tag{3.29}$$
$$\langle\alpha|\hat{A}|\beta\rangle = \langle\alpha|b|\beta\rangle \tag{3.30}$$

3.2 Compatible observables

The notion of measurement in quantum mechanics being so closely linked to Hermitian operators gives us a powerful tool for determining the absolute limits of our knowledge in measuring certain features of a system. Suppose we have two Hermitian operators $\hat{A}$ and $\hat{B}$ with the following eigenvalue equations

$$\hat{A}|a_i\rangle = a_i|a_i\rangle \quad \text{and} \quad \hat{B}|b_j\rangle = b_j|b_j\rangle \tag{3.31}$$

where $i, j \in \{1, 2, \ldots, N\}$, N is the dimensionality of the Hilbert space, and $a_i, b_j \in \mathbb{C}$. Suppose now that we measure the observable corresponding to the Hermitian operator $\hat{A}$ and obtain (according to Postulate 1) the measurement outcome a_n. The state of the system has now collapsed to the corresponding eigenstate $|a_n\rangle$ and any repeated measurement of the observable corresponding to $\hat{A}$ will also yield the outcome a_n. Suppose we now wish to measure the observable corresponding to the operator $\hat{B}$. Recalling Postulate 1, if this state, $|a_n\rangle$, is an eigenstate of $\hat{B}$ then the measurement outcome of the observable corresponding to $\hat{B}$ will result in the same measurement outcome in each trial where a system is prepared in an identical way. If $|a_i\rangle$ is not an eigenstate of $\hat{B}$ then we do not know the measurement outcome of the observable corresponding to the operator $\hat{B}$ with 100% certainty. Thus, we would say that $\hat{A}$ and $\hat{B}$ correspond to **compatible observables**, since we can know their measurement outcomes at the same time with absolute certainty (since they share the same set of eigenstates). To see how this compatibility occurs mathematically, suppose that $\hat{A}$ has two eigenstates $|a_n\rangle$ and $|a_m\rangle$, corresponding to distinct eigenvalues $a_n \neq a_m$, in which case

$$\langle a_m|[\hat{A}, \hat{B}]|a_n\rangle = \langle a_m|\Big(\hat{A}\hat{B} - \hat{B}\hat{A}\Big)|a_n\rangle \tag{3.32}$$
$$= \langle a_m|\Big(a_m^*\hat{B} - \hat{B}a_n\Big)|a_n\rangle \tag{3.33}$$
$$= (a_m^* - a_n)\langle a_m|\hat{B}|a_n\rangle. \tag{3.34}$$

If we are supposing that $\hat{A}$ and $\hat{B}$ are two commuting, Hermitian operators, a_n and a_m are real, and so $a_m^* - a_n = a_m - a_n$. Furthermore, since we assumed that $a_m \neq a_n$, we must have that the term in parentheses on the right-hand side is nonzero, while the left-hand side is zero since $[\hat{A}, \hat{B}] = 0$. Therefore, in order for the right-hand side to be zero, we require $\langle a_m|\hat{B}|a_n\rangle = 0$, which means that the eigenstates of $\hat{A}$, $\{|a_i\rangle\}$, must also diagonalise $\hat{B}$. Therefore, any two commuting Hermitian operators must share a complete set of (nondegenerate) eigenstates.

Since any two commuting Hermitian operators $\hat{A}$ and $\hat{B}$ share the same set of eigenstates, each eigenstate will have an eigenvalue with respect to $\hat{A}$ and a generally different eigenvalue with respect to $\hat{B}$. It is therefore common to label their common eigenstates according to the respective eigenvalue of each operator, i.e., the common eigenstate $|a, b\rangle$ is understood to satisfy the eigenvalue equations,

$$\hat{A}|a, b\rangle = a|a, b\rangle \quad \text{and} \quad \hat{B}|a, b\rangle = b|a, b\rangle. \tag{3.35}$$

3.3 Normalisation and probability

An essential feature of quantum mechanics is the notion of probability. Classically, the state of a system can always be measured with an arbitrarily high precision, with the intrinsic state of the system being unaffected in theory by our measurement. In quantum mechanics, probability in the measurement process is a fundamental. Since we can only ever measure the state to be in one of the eigenstates of the Hermitian operator associated with the observable of interest, measurements cannot take on a continuum of outcomes (for Hermitian operators with a discrete spectrum). This leads to a central postulate of quantum mechanics

Postulate 2. *Given a system prepared in some arbitrary state $|\Psi\rangle$, the probability of measuring an observable of the system to be the eigenvalue, λ_n, with corresponding eigenvector $|e_n\rangle$ of the Hermitian operator corresponding to said observable is given by $|\langle e_n|\Psi\rangle|^2 = |\langle\Psi|e_n\rangle|^2$.*

This also tells us that the inner product between a state and itself must be equal to 1 since if we have prepared a physical system in a state $|\psi\rangle$, the probability of finding it in that state is 100%. Another way to see why this must be the case, we will express the state as a superposition of the eigenstates $\{|e_n\rangle\}$ of some arbitrary linear operator

$$\begin{aligned}
|\Psi\rangle &= \sum_n |e_n\rangle\langle e_n|\Psi\rangle \\
\langle\Psi| &= \sum_m \langle\Psi|e_m\rangle\langle e_m|. \\
\implies \langle\Psi|\Psi\rangle &= \left(\sum_m \langle\Psi|e_m\rangle\langle e_m|\right)\left(\sum_n |e_n\rangle\langle e_n|\Psi\rangle\right) \\
&= \sum_m\sum_n \langle\Psi|e_m\rangle\langle e_m|e_n\rangle\langle e_n|\Psi\rangle \\
&= \sum_m\sum_n \langle\Psi|e_m\rangle\delta_{mn}\langle e_n|\Psi\rangle \\
&= \sum_n \langle\Psi|e_n\rangle\langle e_n|\Psi\rangle \\
&= \sum_n |\langle e_n|\Psi\rangle|^2 \\
&= \sum_n |c_n|^2. \qquad (3.36)
\end{aligned}$$

But these are just the sums of the probability of measuring the particle to be in each eigenstate upon measurement. And since we can *only* measure the quantum state to be one of these states, these probabilities *must* add to 1 since we must obtain one of these eigenvalues upon measurement. Hence, for a state to correspond to a physical system, we require

$$\langle\Psi|\Psi\rangle = 1. \qquad (3.37)$$

3.4 The uncertainty principle

4 The Schrödinger equation

4.1 Unitary operators

Another important class of linear operators in quantum mechanics are unitary operators. These are operators which act together with their Hermitian conjugate to give the identity matrix

$$\hat{U}^\dagger \hat{U} = \hat{U}\hat{U}^\dagger = \hat{\mathbb{I}} \tag{4.1}$$

where $\hat{\mathbb{I}}$ is the identity operator.

4.2 The time evolution operator

The most important unitary operator for PHYS2941/2041 and also PHYS3040 (I think??) is the time-evolution operator $\hat{U}(t)$. This operator, when applied to quantum states at some arbitrary time t, evolves them forward in time such that

$$\hat{U}(a)|\psi(t)\rangle = |\psi(t+a)\rangle. \tag{4.2}$$

The time-evolution operator is defined in terms of another operator, $\hat{H}$, which we'll see corresponds to the Hamiltonian operator, $\hat{H}$. We say that the operator $\hat{H}$ is the *generator of time translations*, since, as we'll see, exponentiating it gives the time evolution operator. The unitary time evolution operator is defined in terms of $\hat{H}$ by

$$\hat{U}(dt) = \hat{\mathbb{I}} - \frac{i}{\hbar}\hat{H}dt. \tag{4.3}$$

Suppose we have a state that is normalised at time $t = 0$ so that $\langle\psi(0)|\psi(0)\rangle$. Then, we expect that evolving these states forward in time will not alter this normalisation in any way so that

$$\begin{aligned} 1 = \langle\psi(0)|\psi(0)\rangle &= \langle\psi(t)|\psi(t)\rangle && (4.4)\\ &= \Big(\langle\psi(0)|\hat{U}(t)^\dagger\Big)\Big(\hat{U}(t)|\psi(0)\rangle\Big) && (4.5)\\ &= \langle\psi(0)|\hat{U}(t)^\dagger\hat{U}(t)|\psi(0)\rangle. && (4.6) \end{aligned}$$

Comparing the LHS and RHS, we see that indeed this operator is unitary since

$$\begin{aligned} \langle\psi(0)|\psi(0)\rangle &= \langle\psi(0)|\hat{U}(t)^\dagger\hat{U}(t)|\psi(0)\rangle. && (4.7)\\ \therefore\ \hat{U}(t)^\dagger\hat{U}(t) &= \hat{\mathbb{I}}. && (4.8) \end{aligned}$$

This condition that $\hat{U}(t)$ (and in turn, $\hat{U}(dt)$) is unitary implies that $\hat{H}$ needs to be Hermitian since

$$\begin{aligned} \hat{U}(dt) &= \hat{\mathbb{I}} - \frac{i}{\hbar}\hat{H}dt && (4.9)\\ \hat{U}^\dagger(dt) &= \hat{\mathbb{I}}^\dagger + \frac{i}{\hbar}\hat{H}^\dagger dt && (4.10)\\ &= \hat{\mathbb{I}} + \frac{i}{\hbar}\hat{H}^\dagger dt. && (4.11) \end{aligned}$$

Therefore

$$\hat{U}^\dagger(dt)\hat{U}(dt) = \hat{\mathbb{I}} \tag{4.12}$$

$$\hat{\mathbb{I}} = \left(\hat{\mathbb{I}} + \frac{i}{\hbar}\hat{H}^\dagger dt\right)\left(\hat{\mathbb{I}} - \frac{i}{\hbar}\hat{H}dt\right) \tag{4.13}$$

$$= \hat{\mathbb{I}} - \frac{i}{\hbar}\hat{H}dt + \frac{i}{\hbar}\hat{H}^\dagger dt + \frac{1}{\hbar^2}\hat{H}^2 dt^2. \tag{4.14}$$

We will ignore any terms that are higher order than linear in dt assuming it is sufficiently small so we get

$$\hat{U}^\dagger(dt)\hat{U}(dt) = \hat{\mathbb{I}} = \hat{\mathbb{I}} - \frac{i}{\hbar}\hat{H}dt + \frac{i}{\hbar}\hat{H}^\dagger dt \tag{4.15}$$

$$0 = -\frac{i}{\hbar}\hat{H}dt + \frac{i}{\hbar}\hat{H}^\dagger dt \tag{4.16}$$

$$\hat{H}^\dagger = \hat{H}. \tag{4.17}$$

Hence, the generator of time translations is Hermitian and so corresponds to an observable. We also see it has units of energy and so we conclude that it is the operator which corresponds to the energy of a system, i.e. the Hamiltonian.

If we wish to evolve the system forward in time by a finite amount, we need to apply the time-evolution operator an "infinite" number of times by rewriting

$$dt = \lim_{N\to\infty}\frac{t}{N} \tag{4.18}$$

Therefore

$$\hat{U}(t) = \lim_{N\to\infty}\hat{U}(dt)^N \tag{4.19}$$

$$= \lim_{N\to\infty}\left[\hat{\mathbb{I}} - \frac{i}{\hbar}\hat{H}\left(\frac{t}{N}\right)\right]^N. \tag{4.20}$$

We note that this is just the definition of the exponential function but with the argument $-i\hat{H}t/\hbar$. Therefore

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar}. \tag{4.21}$$

Thus, $\hat{U}(t)$ is actually defined in terms of the Taylor series for the exponential function and *this* is what it means to exponentiate an operator (in this case that operator is the Hamiltonian, but it turns out that any unitary operator is "generated" by a corresponding Hermitian operator). Using this result, we now know that to evolve any state forward in time, we simply apply the time evolution operator to it

$$|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle \tag{4.22}$$

$$= e^{-i\hat{H}t/\hbar}|\psi(0)\rangle. \tag{4.23}$$

We note that if $|\psi(0)\rangle$ happens to be an eigenstate of $\hat{H}$ with eigenvalue E (the energy), which we will denote by $|E\rangle$, then in our Taylor series definition of $\hat{U}(t)$, each instance of $\hat{H}$ becomes E

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar} \tag{4.24}$$

$$= \sum_{n=0}^{\infty}\left(\frac{-i\hat{H}t}{\hbar}\right)^n\frac{1}{n!} \tag{4.25}$$

$$= \left(\frac{-i\hat{H}t}{\hbar}\right)^0 \frac{1}{0!} + \left(\frac{-i\hat{H}t}{\hbar}\right)^1 \frac{1}{1!} + \left(\frac{-i\hat{H}t}{\hbar}\right)^2 \frac{1}{2!} + \dots \tag{4.26}$$

$$= \hat{\mathbb{I}} - \frac{i\hat{H}t}{\hbar} - \frac{\hat{H}^2t^2}{2\hbar^2} + \dots . \tag{4.27}$$

$$\therefore\ \hat{U}(t)|E\rangle = \left(\hat{\mathbb{I}} - \frac{i\hat{H}t}{\hbar} - \frac{\hat{H}^2t^2}{2\hbar^2} + \dots\right)|E\rangle \tag{4.28}$$

$$= \hat{\mathbb{I}}|E\rangle - \frac{it}{\hbar}(\hat{H}|E\rangle) - \frac{t^2}{2\hbar^2}(\hat{H}^2|E\rangle) + \dots \tag{4.29}$$

$$= |E\rangle - \frac{it}{\hbar}(E|E\rangle) - \frac{t^2}{2\hbar^2}(E^2|E\rangle) + \dots \tag{4.30}$$

$$= \left[\sum_{n=0}^{\infty}\left(\frac{-iEt}{\hbar}\right)^n \frac{1}{n!}\right]|E\rangle \tag{4.31}$$

$$= e^{-iEt/\hbar}|E\rangle \tag{4.32}$$

which is just the usual result for the time evolution of a stationary state of the Hamiltonian. Therefore, in order to time-evolve some arbitrary state vector $|\psi(0)\rangle$ we wish to express it as a linear superposition of the eigenstates of the Hamiltonian, denoted by the set $\{|E_n\rangle\}$ with corresponding eigenvalues $\{E_n\}$

$$|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle \tag{4.33}$$

$$= e^{-i\hat{H}t/\hbar}\sum_n |E_n\rangle\langle E_n|\psi(0)\rangle \tag{4.34}$$

$$= \sum_n e^{-i\hat{H}t/\hbar}|E_n\rangle\langle E_n|\psi(0)\rangle \tag{4.35}$$

$$= e^{-i\hat{H}t/\hbar}|E_1\rangle\langle E_1|\psi(0)\rangle + e^{-i\hat{H}t/\hbar}|E_2\rangle\langle E_2|\psi(0)\rangle + e^{-i\hat{H}t/\hbar}|E_3\rangle\langle E_3|\psi(0)\rangle + \dots \tag{4.36}$$

$$= e^{-iE_1t/\hbar}|E_1\rangle\langle E_1|\psi(0)\rangle + e^{-iE_2t/\hbar}|E_2\rangle\langle E_2|\psi(0)\rangle + e^{-iE_3t/\hbar}|E_3\rangle\langle E_3|\psi(0)\rangle + \dots \tag{4.37}$$

$$= \sum_n e^{-iE_nt/\hbar}|E_n\rangle\langle E_n|\psi(0)\rangle \tag{4.38}$$

$$= \sum_n c_n e^{-iE_nt/\hbar}|E_n\rangle \tag{4.39}$$

using the usual definition of c_n with respect to the orthonormal basis $\{|E_n\rangle\}$ given by $c_n = \langle E_n|\psi(0)\rangle$.

4.3 Deriving the Schrödinger equation

From the unitary time-evolution operator, we can now derive the Schrödinger equation from (somewhat) first principles. To do so, we evolve the quantum state vector $|\Psi(t)\rangle$ in time infinitesimally

$$\hat{U}(dt)|\Psi(t)\rangle = |\Psi(t+dt)\rangle \tag{4.40}$$

$$= \left(\hat{\mathbb{I}} - \frac{i}{\hbar}\hat{H}dt\right)|\Psi(t)\rangle \tag{4.41}$$

$$|\Psi(t+dt)\rangle = |\Psi(t)\rangle - \frac{i}{\hbar}\hat{H}|\Psi(t)\rangle dt \tag{4.42}$$

$$|\Psi(t+dt)\rangle - |\Psi(t)\rangle = -\frac{i}{\hbar}\hat{H}|\Psi(t)\rangle dt \tag{4.43}$$

$$\frac{|\Psi(t+dt)\rangle - |\Psi(t)\rangle}{dt} = -\frac{i}{\hbar}\hat{H}|\Psi(t)\rangle. \tag{4.44}$$

On the left-hand side, we just have the time derivative of $|\Psi(t)\rangle$ in the limit that $dt \to 0$ and so this equation becomes

$$\frac{d|\Psi(t)\rangle}{dt} = -\frac{i}{\hbar}\hat{H}|\Psi(t)\rangle \tag{4.45}$$

$$i\hbar\frac{d|\Psi(t)\rangle}{dt} = \hat{H}|\Psi(t)\rangle \tag{4.46}$$

which is just the time-dependent Schrödinger equation.

4.4 Deriving the TISE

To derive the time-independent Schrödinger equation, we note that if we solve for the eigenstates of the Hamiltonian, these will satisfy the equation

$$\hat{H}|\Psi(0)\rangle = E|\Psi(0)\rangle \tag{4.47}$$

where we have used E for the eigenvalue since the eigenvalues correspond to what you measure when you measure the observable associated with the Hamiltonian, i.e. the energy of the system. This is just the time-independent Schrödinger equation, but in its most general form. For a particle in some potential $V(|\hat{\mathbf{r}}|)$, the Hamiltonian takes on the familiar form

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(|\hat{\mathbf{r}}|). \tag{4.48}$$

5 Matrix mechanics

There are two main formalisms in quantum mechanics. Although wave mechanics is the more well-known, a year earlier before the Schrödinger equation dropped on the scene, Werner Heisenberg developed the first theory of quantum mechanics called matrix mechanics. Although linear algebra existed by this point, its use in physics was not common and Heisenberg actually independently developed a lot of the machinery himself when he developed matrix mechanics since he didn't know any linear algebra.

5.1 Vector representation of kets

In QM, we can choose to represent a ket $|\psi\rangle$ in terms of some orthonormal basis vectors $\{|e_n\rangle\}$ in the expansion

$$|e_n\rangle = \sum_n |e_n\rangle\langle e_n|\psi\rangle. \tag{5.1}$$

But writing this over and over again when performing inner products and transforming vectors under linear operators can get quite tedious. Indeed, if we all agree beforehand on what set of basis vectors to represent our vectors in beforehand, we don't need to explicitly write out the summation above. Instead, we can just list the coefficients $\langle e_n|\psi\rangle$ of each basis vector in order in a matrix like so

$$|\psi\rangle \xrightarrow[\{|e_n\rangle\}\text{ basis}]{} \begin{pmatrix} \langle e_1|\psi\rangle \\ \langle e_2|\psi\rangle \\ \vdots \end{pmatrix}. \tag{5.2}$$

Note that there is an important distinction here between the ket $|\psi\rangle$ which is the actual **state** of the system, which lives in some abstract mathematical vector space, and the column vector in Eq. (5.2), which is just the **representation** of this state with respect to some basis. They are definitely **not** the same, although they are isomorphic.

5.2 Matrix representations of operators

Given that we now have a way to express kets in vector form, we now turn our attention to how linear operators are represented in a particular basis. To figure out how to do this, suppose we have some arbitrary operator $\hat{A}$ and a ket $|\phi\rangle$ related to $|\psi\rangle$ and $\hat{A}$ by the linear operation

$$|\phi\rangle = \hat{A}|\psi\rangle. \tag{5.3}$$

Suppose we wish to find ith vector element of $|\phi\rangle$ with respect to the same basis as we used for $|\psi\rangle$ in the previous section. Then, this is given by

$$\begin{aligned} \phi_i &= \langle e_i|\phi\rangle \\ &= \langle e_i|\hat{A}|\psi\rangle. \end{aligned} \tag{5.4}$$

In the first line here, ϕ_i represents the ith entry in the vector representation of the vector $|\phi\rangle$. In the second line, we have just used the fact that $|\phi\rangle = \hat{A}|\psi\rangle$, which is how we defined $|\phi\rangle$. Although Eq. (5.4) is technically correct, it doesn't really tell us anything useful. We can see that the ket $|\phi\rangle$ is related to $|\psi\rangle$ through some linear operation given by $\hat{A}$, so we imagine that so too should the *vector representation* of $|\phi\rangle$ be related to the *vector representation* of $|\psi\rangle$ through some linear operation, i.e. matrix multiplication for vectors. To see how this arises, we can insert the identity operator between $\hat{A}$ and $|\psi\rangle$ in Eq. (5.4) to get

$$\phi_i = \langle e_i|\hat{A}\left(\sum_j |e_j\rangle\langle e_j|\right)|\psi\rangle \tag{5.5}$$

$$= \sum_j \langle e_i|\hat{A}|e_j\rangle\langle e_j|\psi\rangle. \tag{5.6}$$

We realise that $\langle e_j|\psi\rangle$ is just the jth entry in the column vector of the representation of $|\psi\rangle$, so we will call this ψ_j. Therefore, we get

$$\phi_i = \sum_j \langle e_i|\hat{A}|e_j\rangle\psi_j \tag{5.7}$$

which we see takes on the form of a matrix multiplication if we identify

$$A_{ij} \equiv \langle e_i|\hat{A}|e_j\rangle \tag{5.8}$$

as being the matrix elements of the operator $\hat{A}$ with respect to the $\{|e_n\rangle\}$ basis. Therefore, we find

$$\phi_i = \sum_j A_{ij}\psi_j \tag{5.9}$$

which is exactly the equation for matrix multiplication written in index notation.

5.3 Example: Spin 1/2

Now that we know how to work with quantum systems in different bases, we can revisit our old friend, the Stern-Gerlach experiment. Recall that when measuring the spin of a spin-1/2 particle along the z-axis that the only results were $+\hbar/2$ or $-\hbar/2$ for the intrinsic angular momentum, or "spin", of the particle. Since this is a measurable feature of the system there is a Hermitian operator corresponding to the spin of the particle in the z-direction, which we will denote by $\hat{S}_z$. Since we only have two possible measurement outcomes it follows from Postulate 1 that there are two eigenstates of $\hat{S}_z$, which we denoted previously by $|+z\rangle$ and $|-z\rangle$ but which we will now denote by

$$|-z\rangle \equiv \left|-\frac{\hbar}{2}, \frac{\hbar}{2}\right\rangle \text{ and } |+z\rangle \equiv \left|\frac{\hbar}{2}, \frac{\hbar}{2}\right\rangle \tag{5.10}$$

for reasons that will become clear shortly. Note that we can equally measure the spin along the x- or y-axes (corresponding to $\hat{S}_x$ and $\hat{S}_y$, respectively) and we would also find only $-\hbar/2$ or $\hbar/2$ for the spin along these directions, but their eigenstates are not necessarily the same states as the one listed above. Indeed, because measuring in a different direction leads to an indeterminate measurement outcome, it follows from the section above on commutation relations that that these three operators each mutually don't commute since they cannot be measured simultaneously. Thus, we expect that the three spin operators will obey the commutation relations

$$[\hat{S}_i, \hat{S}_j] = \begin{cases} 0, & i = j \\ \text{not } 0, & i \neq j \end{cases} \tag{5.11}$$

where the indices i and j run through $1, 2, 3$ and denote the three different spin operators.

These commutation relations can be worked out from the fact that spin is an intrinsic form of **angular momentum**. In classical mechanics, the orbital angular momentum $\mathbf{L}$ of a particle with position vector $\mathbf{r} = x\hat{\mathbf{i}} + y\hat{\mathbf{j}} + z\hat{\mathbf{k}}$ and linear momentum vector $\mathbf{p} = p_x\hat{\mathbf{i}} + p_y\hat{\mathbf{j}} + p_z\hat{\mathbf{k}}$ about some point is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{5.12}$$

$$= (yp_z - zp_y)\hat{\mathbf{i}} + (zp_x - xp_z)\hat{\mathbf{j}} + (xp_y - yp_x)\hat{\mathbf{k}} \tag{5.13}$$

or, matching components,

$$L_x = yp_z - zp_y \tag{5.14}$$

$$L_y = zp_x - xp_z \tag{5.15}$$

$$L_z = xp_y - yp_x. \tag{5.16}$$

But the quantities in the equations above are all classical quantities. But to develop a quantum mechanical theory, we must start with the classical theory and **quantise** it (there are other ways to develop quantum mechanical theories but this is the most common and the only one I know). In this case, we promote all of these quantities to operators. That is,

$$x \xrightarrow[\text{quantise}]{} \hat{x} \quad \text{and} \quad p_x \xrightarrow[\text{quantise}]{} \hat{p}_x \tag{5.17}$$

$$y \xrightarrow[\text{quantise}]{} \hat{y} \quad \text{and} \quad p_y \xrightarrow[\text{quantise}]{} \hat{p}_y \tag{5.18}$$

$$z \xrightarrow[\text{quantise}]{} \hat{z} \quad \text{and} \quad p_z \xrightarrow[\text{quantise}]{} \hat{p}_z. \tag{5.19}$$

In this case, we have the three orbital angular momentum operators

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \tag{5.20}$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \tag{5.21}$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x. \tag{5.22}$$

In order to work out the commutation relations between these three operators, we need to work out the commutation relations between the position and momentum operators they are defined in terms of. One way to do this is in terms of the classical Poisson brackets between generalised position and its conjugate momentum in the classical Hamiltonian theory of point particles, but that is beyond the scope of these notes (see Chapter 1.6 of Sakurai for more information), and so we will simply take the following so-called **canonical commutation relations** to be true:

$$[\hat{x}_i, \hat{p}_i] = i\hbar\hat{\mathbb{I}},\ [\hat{p}_i, \hat{p}_j] = 0,\ [\hat{x}_i, \hat{x}_j] = 0,\ \forall\, i, j \text{ and } [\hat{p}_i, \hat{x}_j] = 0,\ i \neq j. \tag{5.23}$$

In this case, we can work out the commutation relations between the three angular momentum operators

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \tag{5.24}$$

which can be expanded out using the linearity of commutators and the commutation relations listed above to yield

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z. \tag{5.25}$$

We could work out the other commutation relations in the same way or by simply performing a cyclic substitution of coordinates

$$[\hat{L}_i, \hat{L}_j] = i\hbar \sum_{k=1}^{3} \varepsilon_{ijk}\hat{L}_k \tag{5.26}$$

where ε_{ijk} is the Levi-Cevita tensor defined as

$$\varepsilon_{ijk} = \begin{cases} 1, & ijk = 123, 231, 312 \\ -1, & ijk = 321, 213, 132 \\ 0, & \text{any two or more indices repeat} \end{cases} \tag{5.27}$$

Although these commutation relations have been worked out from the orbital angular momentum operators, it turns out that these exact same commutation relations also apply to the spin angular momentum operators[1], so that,

$$[\hat{S}_i, \hat{S}_j] = i\hbar \sum_{k=1}^{3} \varepsilon_{ijk}\hat{S}_k. \tag{5.28}$$

[1] In fact, there is no classical analogue of spin in classical mechanics, so one cannot "quantise" spin from some classical theory. However, it is borne out by experiment that the exact same properties of orbital angular momentum are present for spin angular momentum, and so the quantum mechanical theory of spin takes on the exact same structure as that of orbital angular momentum.

We also define the operator $\hat{\mathbf{S}}^2$ as the square of the total spin of the system

$$\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 \tag{5.29}$$

and we note that it commutes with all the individual spin operators

$$[\hat{\mathbf{S}}^2, \hat{S}_x] = [\hat{\mathbf{S}}^2, \hat{S}_y] = [\hat{\mathbf{S}}^2, \hat{S}_z] = 0. \tag{5.30}$$

Since $\hat{S}_z$ and $\hat{\mathbf{S}}^2$ commute, we can construct a basis of eigenstates common to both of these Hermitian operators. Note that we could choose a shared basis between $\hat{S}_x$ or $\hat{S}_y$ and $\hat{\mathbf{S}}^2$, but we choose the z-direction as a matter of convention. Note also that since $\hat{S}_z$ doesn't commute with the spin operators along the other directions, these eigenstates are not in general also going to be eigenstates of $\hat{S}_x$ and $\hat{S}_y$. We denote these eigenstates by $|s, m\rangle$ and they obey the eigenvalue equations

$$\hat{S}_z|s, m\rangle = m\hbar|s, m\rangle \tag{5.31}$$

$$\hat{\mathbf{S}}^2|s, m\rangle = \hbar^2 s(s+1)|s, m\rangle \tag{5.32}$$

for reasons that will be clear shortly. The label inside the ket could in theory be anything – we just choose a label for notational convenience, all that matters is how it acts mathematically – but the label s is in place to help make clear the eigenvalue with respect to $\hat{\mathbf{S}}^2$ while the label m is in place to help make clear the eigenvalue with respect to $\hat{S}_z$ (cf. Section 3.2).

In order to determine the actual eigenvalues, it is useful to construct two more non-Hermitian operators, which are defined as

$$\hat{S}_+ = \hat{S}_x - i\hat{S}_y \tag{5.33}$$

$$\hat{S}_- = \hat{S}_x + i\hat{S}_y. \tag{5.34}$$

To determine what these operators do, we have

$$\hat{S}_+|s, m\rangle = (\hat{S}_x - i\hat{S}_y)|s, m\rangle \tag{5.35}$$

$$\hat{S}_z(\hat{S}_+|s, m\rangle) = \hat{S}_z(\hat{S}_x - i\hat{S}_y)|s, m\rangle \tag{5.36}$$

$$= (\hat{S}_z\hat{S}_x - i\hat{S}_z\hat{S}_y)|s, m\rangle. \tag{5.37}$$

We can rewrite the products $\hat{S}_z\hat{S}_x$ and $\hat{S}_z\hat{S}_y$ using the commutation relations between the angular momentum operators.

$$[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y \tag{5.38}$$

$$i\hbar\hat{S}_y = \hat{S}_z\hat{S}_x - \hat{S}_x\hat{S}_z \tag{5.39}$$

$$\hat{S}_z\hat{S}_x = i\hbar\hat{S}_y + \hat{S}_x\hat{S}_z. \tag{5.40}$$

To determine what these eigenvalues actually are we note that the eigenvalue $m\hbar$ is the measurement outcome for the spin of a particle along the z-direction while the eigenvalue $\hbar^2 s(s+1)$ is the measurement outcome for the total spin squared of a particle.

6 Position basis

We now consider the particular basis that is most often used in PHYS2041, the coordinate basis. In this basis, our eigenstates are the kets $|x\rangle$, which correspond to the eigenstates of the Hermitian position operator $\hat{x}$ such that

$$\hat{x}|x\rangle = x|x\rangle. \tag{6.1}$$

But since we could in theory measure the particle to be at any location, these basis states are not discrete. Therefore, instead of representing the identity operator as a sum, we represent the identity as an integral of these states

$$\hat{\mathbb{I}} = \int_{-\infty}^{\infty} |x\rangle\langle x| dx. \tag{6.2}$$

Thus, we can insert this inbetween the inner product $\langle\Psi|\Psi\rangle$ to yield

$$\begin{aligned}
\langle\Psi|\Psi\rangle &= \langle\Psi|\hat{\mathbb{I}}|\Psi\rangle && (6.3)\\
&= \langle\Psi|\left(\int_{-\infty}^{\infty} |x\rangle\langle x| dx\right)|\Psi\rangle && (6.4)\\
&= \int_{-\infty}^{\infty} \langle\Psi|x\rangle\langle x|\Psi\rangle dx && (6.5)\\
&= \int_{-\infty}^{\infty} |\langle x|\Psi\rangle|^2 dx. && (6.6)
\end{aligned}$$

Just as we identify $|c_n|^2$ in the summation in Eq. (3.36) as the probability of measuring the particle to be in the state $|e_n\rangle$, so too can we identify

$$|\langle x|\Psi\rangle|^2 dx \tag{6.7}$$

as being the probability of measuring the particle's position to be between x and $x+dx$. Therefore, we call $\langle x|\Psi\rangle$ the wave function of the particle

$$\Psi(x) \equiv \langle x|\Psi\rangle. \tag{6.8}$$

Therefore, to solve the Schrödinger equation in position space, we project the Schrödinger equation onto position space

$$\begin{aligned}
\left[\frac{\hat{p}^2}{2m} + V(\hat{x})\right]|\psi\rangle &= E|\psi\rangle && (6.9)\\
\langle x|\left[\frac{\hat{p}^2}{2m} + V(\hat{x})\right]|\psi\rangle &= \langle x|E|\psi\rangle && (6.10)\\
\frac{1}{2m}\langle x|\hat{p}^2|\psi\rangle + \langle x|V(\hat{x})|\psi\rangle &= E\langle x|\psi\rangle. && (6.11)
\end{aligned}$$

We now make use of the results

$$\begin{aligned}
\langle x|\hat{p}|\psi\rangle &= -i\hbar\frac{\partial}{\partial x}\langle x|\psi\rangle && (6.12)\\
&= -i\hbar\frac{\partial\psi(x)}{\partial x} && (6.13)
\end{aligned}$$

$$\langle x|V(\hat{x})|\psi\rangle = V(x)\langle x|\psi\rangle \tag{6.14}$$
$$= V(x)\psi(x) \tag{6.15}$$

which gives

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x). \tag{6.16}$$

7 The quantum harmonic oscillator

We now turn our attention to solving the Schrodinger equation for the quadratic, time-independent potential, $V(x) = kx^2$. This leads to the Hamiltonian of the form

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2. \tag{7.1}$$

We then wish to know the eigenvalues of the Hamiltonian in the time-independent Schrodinger equation so that the solutions may be known:

$$\hat{H}|\psi\rangle = E|\psi\rangle \tag{7.2}$$
$$\boxed{\left(\frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2\right)|\psi\rangle = E|\psi\rangle.} \tag{7.3}$$

This method can be solved primarily in two ways. The first method that will be outlined here will be to use the method of ladder operators which is entirely algebraic, using operators, eigenvalues, and commutation relations. The second method will be by projecting Eq. (7.3) onto position space and then solving the resulting differential equation directly using the power series method.

7.1 Algebraic ladder operator method

In order to determine the eigenvalues and eigenvectors of the Hamiltonian algebraically, we introduce the two non-Hermitian operators,

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{p}_x\right) \tag{7.4}$$
$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}_x\right). \tag{7.5}$$

Their usefulness derives from their commutator

$$[\hat{a}, \hat{a}^\dagger] = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} \tag{7.6}$$
$$= -\frac{i}{\hbar}[\hat{x}, \hat{p}_x]. \tag{7.7}$$

If we now use the canonical commutation relation between $\hat{x}$ and $\hat{p}_x$,

$$[\hat{x}, \hat{p}_x] = i\hbar$$
$$\therefore\ [\hat{a}, \hat{a}^\dagger] = -\frac{i}{\hbar}\cdot i\hbar$$
$$[\hat{a}, \hat{a}^\dagger] = 1 = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}. \tag{7.8}$$

We now wish to rewrite $\hat{x}$ and $\hat{p}_x$ in terms of $\hat{a}$ and $\hat{a}^\dagger$. If we add $\hat{a}$ and $\hat{a}^\dagger$, we have

$$\hat{a} + \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{i}{m\omega}\hat{x} + \hat{x} - \frac{i}{m\omega}\hat{x}\right)$$
$$\therefore\ \hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a} + \hat{a}^\dagger\right). \tag{7.9}$$

Similarly, if we subtract $\hat{a}$ and $\hat{a}^\dagger$, we get

$$\hat{a}^\dagger - \hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{x} + \hat{x} - \frac{i}{m\omega}\hat{x}\right)$$
$$\therefore\ \hat{p}_x = i\sqrt{\frac{m\hbar\omega}{2}}\left(\hat{a}^\dagger - \hat{a}\right). \tag{7.10}$$

If we now substitute these expressions for $\hat{x}$ and $\hat{p}_x$ in terms of $\hat{a}$ and $\hat{a}^\dagger$ into the Hamiltonian in Eq. (7.1), we get

$$\hat{H} = -\frac{1}{2m}\frac{m\hbar\omega}{2}\left(\hat{a}^\dagger - \hat{a}\right)^2 + \frac{1}{2}\frac{\hbar}{2m\omega}m\omega^2\left(\hat{a} + \hat{a}^\dagger\right)^2 \tag{7.11}$$
$$= \frac{\hbar\omega}{2}\left(\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\right). \tag{7.12}$$

We can now use the commutation relation in Eq. (7.8) to rewrite the Hamiltonian purely in terms of the operator $\hat{a}^\dagger\hat{a}$.

$$\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1$$
$$\hat{a}\hat{a}^\dagger = \hat{a}^\dagger\hat{a} + 1.$$
$$\therefore\ \hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right). \tag{7.13}$$

Hence, any eigenvalues of the operator $\hat{a}^\dagger\hat{a}$ are also eigenvalues of the Hamiltonian. We call the operator, $\hat{a}^\dagger\hat{a}$, the number operator, $\hat{N}$,

$$\hat{N} \equiv \hat{a}^\dagger\hat{a}. \tag{7.14}$$

The reason for this name will become clear as we look for its eigenvalues, and because the Hamiltonian is just a linear function of $\hat{N}$, we can look for eigenvalues of $\hat{N}$ to indirectly find the energy eigenvalues of $\hat{H}$. This can also be done by noting that $[\hat{H}, \hat{N}] = 0$ and that $\hat{N}$ is Hermitian, meaning that the number operator is a Hermitian operator which commutes with the Hamiltonian, and so it shares a common eigenbasis with the Hamiltonian.

To begin with, we note that if $|\lambda\rangle$ is an arbitrary eigenvector of $\hat{N}$ with eigenvalue λ then we have

$$\hat{N}|\lambda\rangle = \lambda|\lambda\rangle \tag{7.15}$$
$$\hat{a}^\dagger\hat{a}|\lambda\rangle = \lambda|\lambda\rangle. \tag{7.16}$$

If we take the inner product on both sides with λ, this yields

$$\langle\lambda|\hat{a}^\dagger\hat{a}|\lambda\rangle = \langle\lambda|\lambda|\lambda\rangle \tag{7.17}$$

$$(\langle\lambda|\hat{a}^\dagger)(\hat{a}|\lambda\rangle) = \lambda\langle\lambda|\lambda\rangle. \tag{7.18}$$

If we call the vector $\hat{a}|\lambda\rangle = |\varphi\rangle$, then we have

$$\langle\varphi|\varphi\rangle = \lambda\langle\lambda|\lambda\rangle. \tag{7.19}$$

On the left-hand side, we have the self inner product, $\langle\varphi|\varphi\rangle \geq 0$, and on the right-hand side, $\langle\lambda|\lambda\rangle \geq 0$. To maintain the equality we must therefore have

$$\lambda \geq 0. \tag{7.20}$$

Thus, we have an absolute lower limit on the eigenvalues of $\hat{N}$.

To reveal the action of the operators $\hat{a}^\dagger$ and $\hat{a}$ on the eigenvectors of $\hat{N}$, suppose that $|\lambda\rangle$ is an eigenvalue of $\hat{N}$ with eigenvalue λ. Then

$$\hat{N}|\lambda\rangle = \lambda|\lambda\rangle \tag{7.21}$$
$$\hat{a}^\dagger\hat{N}|\lambda\rangle = \hat{a}^\dagger\lambda|\lambda\rangle \tag{7.22}$$
$$\hat{a}^\dagger(\hat{a}^\dagger\hat{a})|\lambda\rangle = \lambda(\hat{a}^\dagger|\lambda\rangle). \tag{7.23}$$

Using the commutation relation in Eq. (7.8) to rewrite the left-hand side in terms of $\hat{a}\hat{a}^\dagger$ yields

$$\hat{a}^\dagger(\hat{a}\hat{a}^\dagger - 1)|\lambda\rangle = \lambda(\hat{a}^\dagger|\lambda\rangle) \tag{7.24}$$
$$\hat{a}^\dagger\hat{a}\hat{a}^\dagger|\lambda\rangle = \lambda(\hat{a}^\dagger|\lambda\rangle) + \hat{a}^\dagger|\lambda\rangle \tag{7.25}$$
$$\hat{N}(\hat{a}^\dagger|\lambda\rangle) = (\lambda+1)(\hat{a}^\dagger|\lambda\rangle). \tag{7.26}$$

Hence, we see that the ket $\hat{a}^\dagger|\lambda\rangle$ is an eigenvector of $\hat{N}$, with an eigenvalue one greater than the eigenvector $|\lambda\rangle$. Hence, the action of $\hat{a}^\dagger$ on an eigenvector of $\hat{N}$ is to change it into an eigenvector with an eigenvalue raised by 1. Hence, we see that $\hat{a}^\dagger$ is a raising operator, whose action on an eigenvector of $\hat{N}$ is

$$\hat{a}^\dagger|\lambda\rangle = c_+|\lambda+1\rangle. \tag{7.27}$$

Similarly, for $\hat{a}$, we can perform a similar procedure using the commutator identity

$$\hat{a}\hat{N}|\lambda\rangle = \lambda\hat{a}|\lambda\rangle \tag{7.28}$$
$$\hat{a}\hat{a}^\dagger(\hat{a}|\lambda\rangle) = \lambda(\hat{a}|\lambda\rangle) \tag{7.29}$$
$$(\hat{N}+1)(\hat{a}|\lambda\rangle) = \lambda(\hat{a}|\lambda\rangle) \tag{7.30}$$
$$\hat{N}(\hat{a}|\lambda\rangle) = (\lambda-1)(\hat{a}|\lambda\rangle). \tag{7.31}$$

Therefore, $\hat{a}$ is a lowering operator

$$\hat{a}|\lambda\rangle = c_-|\lambda-1\rangle. \tag{7.32}$$

We can now determine the lower limit on the eigenvalues of the number operator. Suppose that $|\lambda_0\rangle$ is the eigenstate of $\hat{N}$ with the lowest eigenvalue, λ_0, satisfying $\lambda \geq 0$. Then, applying the lowering operator to this eigenstate gives zero back. Thus

$$\hat{N}|\lambda_0\rangle = \lambda_0|\lambda_0\rangle \tag{7.33}$$

$$\hat{a}^\dagger(\hat{a}|\lambda_0\rangle) = \lambda_0|\lambda_0\rangle \tag{7.34}$$
$$0 = \lambda_0|\lambda_0\rangle \tag{7.35}$$
$$\therefore\ \lambda = 0. \tag{7.36}$$

Thus, we see that the eigenvalues of $\hat{N}$ are quantised, only being able to take on integer values, starting from 0. Denoting the eigenstates and their respective eigenvalues by $|n\rangle$ and n, we have

$$\hat{N}|n\rangle = n|n\rangle, \quad n = 0, 1, 2, \ldots \tag{7.37}$$

We have thus found the eigenvalues of the Hamiltonian for the harmonic oscillator:

$$\hat{H}|n\rangle = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)|n\rangle \tag{7.38}$$
$$\implies\ \hat{H}|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle, \quad n = 0, 1, 2, \ldots \tag{7.39}$$

Hence, the eigenvalues give the energies of the corresponding eigenstates of the Hamiltonian with the harmonic oscillator.

We now wish to find the coefficients, c_+ and c_-. To do so, we have

$$\hat{a}|n\rangle = c_-|n-1\rangle \tag{7.40}$$
$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle = c_-c_-^*\langle n-1|n-1\rangle \tag{7.41}$$
$$\langle n|\hat{N}|n\rangle = |c_-|^2\langle n-1|n-1\rangle \tag{7.42}$$
$$n\langle n|n\rangle = |c_-|^2\langle n-1|n-1\rangle. \tag{7.43}$$

Imposing the orthonormality of the basis eigenstates we have

$$|c_-|^2 = n \tag{7.44}$$
$$c_- = \sqrt{n}. \tag{7.45}$$

Similarly, for c_+,

$$\langle n|\hat{a}\hat{a}^\dagger|n\rangle = |c_+|^2\langle n+1|n+1\rangle \tag{7.46}$$
$$\langle n|(\hat{a}^\dagger\hat{a} + 1)|n\rangle = |c_+|^2 \tag{7.47}$$
$$c_+ = \sqrt{n+1}. \tag{7.48}$$

Hence, the actions of the raising and lowering operators on the eigenstates of the Hamiltonian are

$$\boxed{\begin{aligned}\hat{a}|n\rangle &= \sqrt{n}|n-1\rangle \\ \hat{a}^\dagger|n\rangle &= \sqrt{n+1}|n+1\rangle\end{aligned}} \tag{7.49, 7.50}$$

We can also explicitly work out the representation of any of these eigenstates in position space. To do so, we note that to get to any eigenstate, we can start with the state $|0\rangle$, and then apply the raising operator n times to reach the state $|n\rangle$. In general then

$$(\hat{a}^\dagger)^n|0\rangle = \sqrt{n}\sqrt{n-1}\sqrt{n-2}\cdots\sqrt{1}|n\rangle \tag{7.51}$$
$$= \sqrt{n!}|n\rangle \tag{7.52}$$

$$\therefore \ |n\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^n|0\rangle. \tag{7.53}$$

To find the corresponding wave function, we take the inner product with an arbitrary position state $|x\rangle$ to get

$$\langle x|n\rangle = \langle x|\frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^n|0\rangle \tag{7.54}$$

$$= \frac{1}{\sqrt{n!}}\langle x|\left[\sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{i}{m\omega}\hat{p}_x\right)\right]^n|0\rangle. \tag{7.55}$$

Using the relationships

$$\hat{x}|x\rangle = x|x\rangle \tag{7.56}$$

$$\langle x|\hat{p}_x|\psi\rangle = -i\hbar\frac{\partial}{\partial x}\langle x|\psi\rangle \tag{7.57}$$

we get

$$\langle x|n\rangle = \psi_n(x) = \left(\frac{m\omega}{2\hbar(n!)}\right)^{n/2}\left(x - \frac{\hbar}{m\omega}\frac{d}{dx}\right)^n\langle x|0\rangle. \tag{7.58}$$

We just need to find the projection of $|0\rangle$ onto position space. To do so, we note that applying the lowering operator to $|0\rangle$ gives back 0. Therefore

$$\langle x|\hat{a}|0\rangle = 0 \tag{7.59}$$

$$\left(x + \frac{\hbar}{m\omega}\frac{d}{dx}\right)\langle x|0\rangle = 0 \tag{7.60}$$

$$\frac{d}{dx}\psi_0(x) = -\frac{m\omega}{\hbar}x\psi_0(x), \tag{7.61}$$

where in the last line I have just switched to the more familiar notation of $\psi_0(x) = \langle x|0\rangle$. This is a separable ODE in ψ_0 and x with the straightforward solution

$$\psi_0(x) = Ae^{-m\omega x^2/2\hbar}. \tag{7.62}$$

To determine the constant A we impose normalisation on the ground state $|0\rangle$. Thus, in position space,

$$\langle 0|0\rangle = 1 = \int_{-\infty}^{\infty}|\psi_0(x)|^2\,dx \tag{7.63}$$

$$1 = \int_{-\infty}^{\infty}A^2e^{-m\omega x^2/\hbar}\,dx. \tag{7.64}$$

Evaluating this Gaussian integral and taking A to be real and non-negative, we find

$$A = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}. \tag{7.65}$$

Therefore, the nth eigenfunction of the Hamiltonian in position space is given by

$$\boxed{\langle x|n\rangle = \psi_n(x) = \left[\frac{m\omega}{2\hbar(n!)}\right]^{n/2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\left(x - \frac{\hbar}{m\omega}\frac{d}{dx}\right)^n e^{-m\omega x^2/2\hbar}.} \tag{7.66}$$