# II. The Machinery of Quantum Mechanics

Based on the results of the experiments described in the previous section, we recognize that real experiments do not behave quite as we expect. This section presents a *mathematical framework* that reproduces all of the above experimental observations. I am not going to go into detail about how this framework was developed. Historically, the mathematical development of QM was somewhat awkward; it was only years after the initial work that a truly rigorous (but also truly esoteric) foundation was put forth by Von Neumann. In this section, we will instead take the mathematical rules of QM as a **hypothesis** and proceed to show that this hypothesis is consistent with all the experimental results we have encountered.

Now, there is no physics or chemistry in what we are about to discuss; the physics always arises from the experiments. However, just as Shakespeare had to learn proper spelling and grammar before he could write Hamlet, so we must understand the mathematics of QM before we can really start using it to make interesting predictions. This is both the beauty and the burden of physical chemistry; the beauty because once you understand these tools you can answer **any** experimental question without having to ask a more experienced colleague; the burden because the questions are **very hard** to answer.

## A. Measurements Happen in Hilbert Space

All the math of QM takes place in an abstract space that we call Hilbert Space. The important point to realize is that Hilbert Space has no connection with the ordinary three dimensional space that we live in. For example, a Hilbert Space can (and usually does) have an **infinite number of dimensions**. These dimensions do not correspond in any way to the length, width and height we are used to. However, QM gives us a set of rules that connect operations in Hilbert Space to **measurements** in real space. Given a particular experiment, one constructs the appropriate Hilbert Space, and then uses the rules of QM within that space to make predictions. In what follows, we will introduce what is called ‘Dirac notation’ for Hilbert Space. We will use this notation throughout the semester.

## 1. Operators Correspond to Observables

As a short hand, we will call anything that can be measured in an experiment an *observable*. The first rule of QM is: all observables are associated with **operators** in Hilbert Space. Generically, operators are things that *do something* to the system, and we will place a hat (e.g. $\hat{x}$) over operators to differentiate them from simple variables. We have already encountered some operators; in the light polarization experiment, we represented the different filters by $\hat{P}_x$, $\hat{P}_y$, etc. $\hat{P}_x$ and $\hat{P}_y$ are the operators that represent measurements of the polarization in the $x$ and $y$ directions.

Now, for most intents and purposes, operators behave like variables: you can add them, subtract them, multiply them, etc. and many of the familiar rules of algebra hold, for example ($\hat{X}, \hat{Y}, \hat{Z}$ are arbitrary operators):

*Addition Commutes:* $\hat{X} + \hat{Y} = \hat{Y} + \hat{X}$

*Addition is Associative:* $\left(\hat{X} + \hat{Y}\right) + \hat{Z} = \hat{X} + \left(\hat{Y} + \hat{Z}\right)$

*Multiplication is Associative:* $\left(\hat{X}\hat{Y}\right)\hat{Z} = \hat{X}\left(\hat{Y}\hat{Z}\right)$

However, the multiplication of operators **does not commute**:

*Multiplication does not commute:* $\hat{X}\hat{Y} \neq \hat{Y}\hat{X}$

We already knew that this was true; in the case of the polarization operators we showed that $\hat{P}_x$ and $\hat{P}_{x'}$ do not commute:

$$\hat{P}_y \hat{P}_{x'} \neq \hat{P}_{x'} \hat{P}_y$$

Thus, the association of observables with operators allows us to describe the first two quantum effects we discovered in the experiments: **non-commuting observations** and **uncertainty**. Recall that the uncertainty comes solely from the fact that the order of measurements matters; hence we can't know the result of both measurements simultaneously.

Now, deciding that operators have all the above features (e.g. associative multiplication, commutative addition) may seem rather arbitrary at first. For example, why does operator multiplication need to be associative? The deep result that motivates this is a theorem that asserts that if a set of operators satisfies the above relations (together with a few other benign conditions) guarantees that

***operators in Hilbert space can always be represented by matrices***. Hence a better way to remember how to multiply and add operators is to remember that they work just like matrices; any relation that is true for two arbitrary matrices is also true for two arbitrary operators.

### 2. The System is Described by a State

Experiments are always performed on a physical system. In Hilbert Space, the system is represented by a **state**. In order to differentiate a wavefunction from operators and variables, we will enclose it in brackets, $|\ \rangle$, and call it a 'ket' state. In between the brackets, we will write a label to tell us necessary information about the ket state. For example, an $x$-polarized photon would be in a state $|y\rangle$, while an electron that passed through the upper slit in the two-slit experiment might be in the state $|U\rangle$. The ket state corresponds to a particular means of representing the wavefunction of the system, and we will use the two terms interchangeably. The important point is that *the state contains all the information that can be known about the system*. Thus, if one knows the state of the system, one can predict the outcome of any experiment on the system (within the bounds of the uncertainty principle).

Now, there are two simple operations one can execute on a state. First, one can multiply it by a constant:

$$c|\psi\rangle = |\psi\rangle c$$

In general, this constant can be *complex*. It does not matter which side the constant appears on. The second thing one can do is to add two states together to make a new state:

$$|\psi\rangle = |\psi_1\rangle + |\psi_2\rangle$$

What is the meaning of this new state? We interpret $|\psi\rangle$ as a **superposition** of the two states $|\psi_1\rangle$ and $|\psi_2\rangle$. We encountered this in the case of the two slit experiment outlined in the previous section; when there were no detectors to tell us which slit the particle went through, the system existed in the superposition of two states that went through the upper and lower slits:

$$|\psi\rangle = |U\rangle + |L\rangle .$$

### 3. Measurements Always Give Eigenvalues

Now, as we mentioned above, operators are associated with things that can be observed by performing an experiment on the system. It is therefore not surprising that **operators act on states**, which we will write as:

$$\hat{O}|\psi\rangle$$

An operator acting on a ket state just gives another ket state. Further, observable operators are always **linear**, which means:

$$\hat{O}\left(|\psi_1\rangle + |\psi_2\rangle\right) = \hat{O}|\psi_1\rangle + \hat{O}|\psi_2\rangle$$

This is another one of the traits that allows operators to be represented in terms of a matrix algebra (they call it *linear* algebra for a reason).

Now, one can associate a set of eigenvalues, $o_\alpha$, and eigenstates, $|\psi_\alpha\rangle$, with each operator, $\hat{O}$, by finding all of the solutions of the eigenvalue equation:

$$\hat{O}|\psi_\alpha\rangle = o_\alpha|\psi_\alpha\rangle$$

The next fundamental rule of QM is that when measuring the value of the observable $O$, the **only possible** outcomes are the eigenvalues of $\hat{O}$. If the spectrum of eigenvalues of $\hat{O}$ is discrete, this immediately implies that the resulting experimental results will be **quantized**, as we know is quite often the case. If the spectrum of eigenvalues of $\hat{O}$ is continuous, then this rule gives us little information.

Now, after $O$ has been observed and found to have a value $o_\alpha$ then the wavefunction of the system collapses into the eigenstate $|\psi_\alpha\rangle$. In a rigorous justification of QM, this has to be taken as an independent rule. It is perhaps the most disturbing of the basic principles of QM: how can an observation (especially a very delicate one) have such a drastic effect on the system? However, in most applications, the collapse of the wavefunction after a measurement follows naturally, based on some assumptions about what it is we mean by 'measurement' and 'observation'. Hence, we will almost never need to refer to this postulate in practice. However, at least at first, it is conceptually simpler to take this as a basic rule.

### 4. Bra-Ket Gives Probability

As mentioned above, operators can be associated with matrices. It is therefore natural to associate an operator acting on a ket state with a matrix-vector product:

$$\hat{O}|\psi\rangle \Leftrightarrow \begin{pmatrix} & \\ & \end{pmatrix} \times \begin{pmatrix} \\ \end{pmatrix}$$

This qualitative association is actually rigorous as we will show shortly. For the moment, however, we only want to use this illustration to motivate the definition of **bra states**. Note that when performing (matrix)x(vector), the vector must be a *column vector*. If one has a *row vector*, the operation is reversed: (vector)x(matrix). Just as we can place ket states in correspondence with column vectors, we propose that there are also states ('bra' states) that correspond to row vectors:

$$|\psi\rangle \Leftrightarrow \begin{pmatrix} \\ \end{pmatrix} \qquad \langle\psi| \Leftrightarrow \begin{pmatrix} & \end{pmatrix}$$

and for which the operator should be placed on the right:

$$\langle\psi|\hat{O} \Leftrightarrow \begin{pmatrix} & \end{pmatrix} \times \begin{pmatrix} & \\ & \end{pmatrix}.$$

To be mathematically precise, bra and ket states are *dual* to one another. By defining the bra states we are really postulating the existence of a dual space. The illustration in terms of vectors is invaluable in understanding what this means, because column vectors and row vectors are also dual to one another. Thus, essentially all the properties of row and column vectors can be transferred over to bra and ket states. Most notably, one can define an overlap (or inner product) analogous to the dot product for ordinary vectors.

$$\langle\chi|\psi\rangle \Leftrightarrow \begin{pmatrix} & \end{pmatrix} \cdot \begin{pmatrix} \\ \end{pmatrix}$$

The overlap between a bra and a ket has all the same intuitive content as the dot product: it tells you how similar the two states are.

If the overlap is zero, the two states are **orthogonal**. The overlap between bra and ket has the ubiquitous “bra-ket”, or bracket, structure. I assume this is what passed for humor in the early days of QM.

It is important to notice that the order of operations is crucial at this point. Operators will **always** appear to the left of a ket state and to the right of a bra state. The expressions

$$\hat{O}\langle\psi| \quad and \quad |\psi\rangle\hat{O}$$

are not incorrect; they are simply useless in describing reality. This might be clearer if we write the associated matrix expressions:

$$\begin{pmatrix} \\ \\ \end{pmatrix}\begin{pmatrix} \end{pmatrix} \quad and \quad \begin{pmatrix} \\ \\ \end{pmatrix}\begin{pmatrix} \end{pmatrix}$$

One can give meaning to these expressions (in terms of a tensor product) but the result is not useful.

Another key aspect of row and column vectors is that they can be placed in one-to-one correspondence with one another. Each column vector is clearly associated with a unique row vector – its transpose. There is an analogous operation that takes each ket to a corresponding bra and vice versa – this operation is called **Hermitian conjugation** and is denoted by a superscript ‘†’ (a ‘dagger’). Each ket is then associated with a unique bra via Hermitian conjugation:

$$\left(|\psi\rangle\right)^{\dagger} \equiv \langle\psi| \qquad \left(\langle\psi|\right)^{\dagger} \equiv |\psi\rangle$$

We can also define the Hermitian conjugate (HC) of an operator in the logical way, by forcing the HC $\hat{O}|\psi\rangle$ to be the HC of $|\psi\rangle$ times the HC of $\hat{O}$:

$$\left(\hat{O}|\psi\rangle\right)^{\dagger} \equiv \langle\psi|\hat{O}^{\dagger}$$

This defines $\hat{O}^{\dagger}$, the HC of $\hat{O}$. This is also called the **adjoint** of the operator $\hat{O}$. If an operator is equal to its adjoint, it is **hermitian**. This is analogous to a symmetric matrix. If we multiply the state by a constant, then we find that the adjoint becomes:

$$\left(c|\psi\rangle\right)^{\dagger} \equiv \langle\psi|c^{*}$$

where $c^{*}$ is the **complex conjugate** of $c$.

The inner product together with the HC relationship allows us to define the norm of a state:

$$|\psi|^2 = \langle\psi|\psi\rangle$$

It turns out that the norm of the state has no physical relevance; any value between 0 and ∞ gives the same physical answer. In practice it is often easiest to multiply the wavefunction by a *normalization constant,* $c = \langle\psi|\psi\rangle^{-1/2}$, that makes the norm 1. This does not affect our predictions but often makes the expressions simpler. If two states are both orthogonal to one another and normalized, they are said to be **orthonormal**.

Now, we have already established that it is not generally possible to predict the precise outcome of an experiment in QM. We can, however, predict what the average outcome of an experiment would be if we performed it many, many times and summed the results. This is called an *expectation value* and according to the rules of QM, for a system in the sate $|\psi\rangle$,the expectation value of an observable, $O$, is given by:

$$\langle\hat{O}\rangle = \frac{\langle\psi|\hat{O}|\psi\rangle}{\langle\psi|\psi\rangle}.$$

Note that this equation simplifies if $|\psi\rangle$ is normalized, in which case

$$\langle\hat{O}\rangle = \langle\psi|\hat{O}|\psi\rangle.$$

This final rule is the key result that allows one to make predictions about the outcome of experiments in QM.

### 5. Some Interesting Facts

Before moving on to describe the experiments from the previous section in terms of our newly proposed rules, it is useful to define a few concepts. The first is the idea of an outer product. Just as we can write the inner product as (bra)x(ket), we can write the outer product as (ket)x(bra). This is in strict analogy to the case of vectors where the outer product is a column vector times a row vector:

$$|\chi\rangle\langle\psi| \quad \Leftrightarrow \quad \begin{pmatrix} \\ \\ \end{pmatrix} \begin{pmatrix} \end{pmatrix}$$

Notice that the outer product is an operator; if we act on a state with it, we get another state back:

$$\left(|\chi\rangle\langle\psi|\right)|\phi\rangle = |\chi\rangle\langle\psi|\phi\rangle = c|\chi\rangle \qquad \left(c \equiv \langle\psi|\phi\rangle\right)$$

This is, again, in direct analogy with vector algebra, where the outer product of two vectors is a matrix. One interesting operator is the outer product of a ket with its own bra, which is called the **density operator**:

$$\hat{P}_\psi = |\psi\rangle\langle\psi|$$

If $|\psi\rangle$ is normalized, this operator happens to be equal to its own square:

$$\hat{P}_\psi \hat{P}_\psi = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi| = \hat{P}_\psi$$

$$\langle\psi|\psi\rangle = 1$$

This property is called **idempotency**. Hence, we see that the density operator for any quantum state is idempotent. Further, we see that $\hat{P}_\psi$ acting on any state gives back the state $|\psi\rangle$ times a constant:

$$\left(|\psi\rangle\langle\psi|\right)|\phi\rangle = |\psi\rangle\langle\psi|\phi\rangle = c|\psi\rangle \qquad \left(c \equiv \langle\psi|\phi\rangle\right)$$

By this token, density operators are also called **projection operators**, because they project out the part of a given wavefunction that is proportional to $|\psi\rangle$.

One very important fact about Hilbert space is that there is always a **complete orthonormal basis**, $\{|\phi_i\rangle\}$, of ket states. As the name implies, these states are orthonormal: the overlap between different states is zero and each state is normalized. We can write this in shorthand as

$$\langle\phi_i|\phi_j\rangle = \delta_{ij}$$

Where we have defined the **Kroenecker delta**- a symbol that is one if *i=j* and zero otherwise. The fact that these kets form a complete basis means that one can write *any state*, $|\psi\rangle$,in Hilbert space as a *linear combination* of the $|\phi_i\rangle$:

$$|\psi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle + c_3|\phi_3\rangle + \ldots = \sum_i c_i|\phi_i\rangle$$

Finally, it is also useful to define the **commutator** of two operators:

$$\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

If two operators commute, then the order in which they appear does not matter and the commutator vanishes. Meanwhile, if the operators

do not commute, then the commutator measures “how much” the order matters.

## B. Description of Model Experiments

Both to familiarize ourselves with Dirac notation and to prove that the rules of QM actually do describe the weird effects seen in experiments, we proceed to re-formulate the three experiments discussed in the introductory lectures in terms of operations in Hilbert Space.

### 1. Polarization of Light

We have already seen that the polarization filters in this experiment can be represented by operators: $\hat{P}_x$, $\hat{P}_y$, etc. But how do they act on the states? And what are the states, anyway? These two questions arise any time one treats a new class of systems, and the solution to this dilemma is properly considered an additional rule of QM. Indeed, many of the early difficulties in the field came not in the definition of the basic principles but in the practical association of real observables with appropriate operators. In the end, once again, the correctness of our association of operators with observables must be verified by testing the agreement with experimental observations.

Defining the state space is fairly straightforward. The set of all possible polarizations for the photon is just the set of all unit vectors perpendicular to the direction the photon is traveling (recall that light is a transverse wave). Hence, we will denote the photon’s state by $|\vec{u}\rangle$, where $\vec{u}$ is the unit vector pointing in the direction of the photon’s polarization. Then, it makes sense to define the overlap between two polarization states to be the same as the dot product of their polarization vectors:

$$\langle \vec{u} | \vec{v} \rangle \equiv \vec{u} \cdot \vec{v}$$

This agrees with our idea that if the polarizations point in orthogonal directions, there is no overlap between the states. Notice that, in general:

$$a|\vec{u}\rangle + b|\vec{v}\rangle \neq |a\vec{u} + b\vec{v}\rangle$$

The state on the right corresponds to a photon with polarization in the *direction* $a\vec{u} + b\vec{v}$; the state on the left corresponds to a photon in a

*superposition* of the two states $|\vec{u}\rangle$ and $|\vec{v}\rangle$. As an example of the inequality of these two states, consider the superposition:

$$\tfrac{1}{\sqrt{2}}|\vec{x}\rangle + \tfrac{i}{\sqrt{2}}|\vec{y}\rangle$$

clearly this cannot be equivalent to $\left|\tfrac{1}{\sqrt{2}}\vec{x} + \tfrac{i}{\sqrt{2}}\vec{y}\right\rangle$, since a complex polarization direction has no meaning. Indeed, the above state *cannot* be assigned a definite polarization direction; as it turns out, $\tfrac{1}{\sqrt{2}}|\vec{x}\rangle + \tfrac{i}{\sqrt{2}}|\vec{y}\rangle$ corresponds to *circularly* polarized light, and our basis states correspond to the various possible *linear* photon polarizations.

What about the reverse statement? Well, if $|\vec{u}\rangle$ and $|\vec{v}\rangle$ are independent vectors, they form a complete basis. As a result, we can always write:

$$|a\vec{u} + b\vec{v}\rangle = c_1|\vec{u}\rangle + c_2|\vec{v}\rangle$$

for some constants, $c_1$ and $c_2$. Our task is to determine these constants. First, note that for the state on the left to be admissible, $a$ and $b$ must be real. Given this, we determine the to constants by taking the inner product of the above equation with $|\vec{u}\rangle$ and $|\vec{v}\rangle$:

$$\langle\vec{u}|a\vec{u} + b\vec{v}\rangle = c_1\langle\vec{u}|\vec{u}\rangle + c_2\langle\vec{u}|\vec{v}\rangle = c_1 + c_2\langle\vec{u}|\vec{v}\rangle$$
$$\langle\vec{v}|a\vec{u} + b\vec{v}\rangle = c_1\langle\vec{v}|\vec{u}\rangle + c_2\langle\vec{v}|\vec{v}\rangle = c_1\langle\vec{v}|\vec{u}\rangle + c_2$$

Simplifying the left hand side:

$$\Rightarrow a + b\vec{u}\cdot\vec{v} = c_1 + c_2\langle\vec{u}|\vec{v}\rangle$$
$$\Rightarrow a\vec{v}\cdot\vec{u} + b = c_1\langle\vec{v}|\vec{u}\rangle + c_2$$

This is a set of two equations for two unknowns, and by inspection we see that $c_1 = a$ and $c_2 = b$. Thus, for real $a$ and $b$:

$$|a\vec{u} + b\vec{v}\rangle = a|\vec{u}\rangle + b|\vec{v}\rangle.$$

The important point is that *every state can be written as a superposition*, but *not every superposition has a definite polarization*.

Now, given that we know what the states are, we come to the difficult part of determining what the operators $\hat{P}_x$ and $\hat{P}_y$ are. We are given a hint by the fact that, experimentally, we know that given any initial state, we always end up with an $\vec{x}$-polarized photon after we act with $\hat{P}_x$ and a $\vec{y}$-polarized photon after we act with $\hat{P}_y$. Thus the filters must be represented by projection operators and it is easily guessed that the correct forms are:

$$\hat{P}_x = |\vec{x}\rangle\langle\vec{x}| \qquad \hat{P}_y = |\vec{y}\rangle\langle\vec{y}|\text{, etc.}$$

Again, these operators are to be associated with the observable "how much of the light passes through the filter".

To verify our guess, we proceed to 'predict' the results of the polarization experiments we already discussed.

Experiment 0: In this case, we begin with initially unpolarized light and pass it through an $\vec{x}$-filter. This immediately poses a difficulty because we haven't defined what "initially unpolarized light" means, and for good reason. By saying the light is 'unpolarized', we essentially mean we don't know what the state of the system is'. How then do we make a prediction? First, we must recognize that the beam of light consists of many, many photons, each of which must have a definite polarization – we just don't know what each polarization is. However, since we are only asked to predict the *average* outcome, this does not pose a problem; we merely assume an arbitrary polarization direction for the photon and then average over this direction. So, our arbitrary polarization direction will be:

$$|\vec{u}\rangle = |\cos\theta\vec{x} + \sin\theta\vec{y}\rangle$$

Then, using the rules of QM, we predict that the probability that a photon in this state will make it through the $\vec{x}$-filter is:

$$\langle\vec{u}|\hat{P}_x|\vec{u}\rangle = \langle\vec{u}|\vec{x}\rangle\langle\vec{x}|\vec{u}\rangle = \langle\cos\theta\vec{x} + \sin\theta\vec{y}|\vec{x}\rangle\langle\vec{x}|\cos\theta\vec{x} + \sin\theta\vec{y}\rangle = \cos^2\theta$$

The effect of measuring the polarization of many, many photons in different states is to *average* over the value of $\theta$. So the fraction of the light that passes through the filter will be:

$$\int\langle\vec{u}|\hat{P}_x|\vec{u}\rangle = \tfrac{1}{\pi}\int_0^{\pi}\cos^2\theta d\theta = \tfrac{1}{2}.$$

And hence, our rules predict (correctly) that half the initially unpolarized light will pass through the –filter, assuming that unpolarized light is made up of many randomly polarized photons.

Experiment 1: In this case, we are making two successive measurements: an $\vec{x}$-filter followed by a $\vec{y}$-filter. We have already determined that half of the unpolarized light passes through the first filter. After the first measurement, the state of the system is given by:

$$|\vec{u}'\rangle = \hat{P}_x|\vec{u}\rangle = |\vec{x}\rangle\langle\vec{x}|\vec{u}\rangle = |\vec{x}\rangle\langle\vec{x}|\cos\theta\vec{x} + \sin\theta\vec{y}\rangle = \cos\theta|\vec{x}\rangle$$

Note that, because of our definition of the $\hat{P}_x$ operators, the polarization automatically *collapses* to $|\vec{x}\rangle$ after the measurement has been made (recall that the norm of the state is unimportant). Hence, our task is now to figure out how much of the $\vec{x}$-polarized light that comes out of the first filter passes through the second filter. According to the rules:

$$\langle \vec{x}|\hat{P}_y|\vec{x}\rangle = \langle \vec{x}|\vec{y}\rangle\langle \vec{y}|\vec{x}\rangle = 0$$

Thus, none of the light makes it through the second filter.

Experiment 2: In this case, we again make two measurements: $\vec{x}$ first and then $\vec{x}' = \frac{1}{\sqrt{2}}(\vec{x}+\vec{y})$. As before, half the light passes through the first filter, ending up with $\vec{x}$-polarization. For the second filter:

$$\langle \vec{x}|\hat{P}_{x'}|\vec{x}\rangle = \langle \vec{x}|\vec{x}'\rangle\langle \vec{x}'|\vec{x}\rangle = \left\langle \vec{x}\middle|\tfrac{1}{\sqrt{2}}(\vec{x}+\vec{y})\right\rangle\left\langle \tfrac{1}{\sqrt{2}}(\vec{x}+\vec{y})\middle|\vec{x}\right\rangle = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) = \frac{1}{2}$$

Thus, half the $\vec{x}$-polarized light passes through the second filter, and on quarter of the total intensity is transmitted.

Experiment 3: Here, we perform three measurements: first $\vec{x}$, then $\vec{x}' = \frac{1}{\sqrt{2}}(\vec{x}+\vec{y})$, then $\vec{y}$. The results of the first two measurements were already computed in Expts. 0 and 2. Hence, we only need to predict the effect of the final polarization filter. The light coming out of the $\vec{x}'$-filter is $\vec{x}'$-polarized since:

$$|\vec{u}'\rangle = \hat{P}_{x'}\hat{P}_x|\vec{u}\rangle = |\vec{x}'\rangle\langle \vec{x}'|\vec{x}\rangle\langle \vec{x}|\vec{u}\rangle = |\vec{x}'\rangle\left(\tfrac{1}{\sqrt{2}}\right)(\cos\theta) \propto |\vec{x}'\rangle$$

Hence, the outcome of the third measurement is:

$$\langle \vec{x}'|\hat{P}_y|\vec{x}'\rangle = \langle \vec{x}'|\vec{y}\rangle\langle \vec{y}|\vec{x}'\rangle = \left\langle \tfrac{1}{\sqrt{2}}(\vec{x}+\vec{y})\middle|\vec{y}\right\rangle\left\langle \vec{y}\middle|\tfrac{1}{\sqrt{2}}(\vec{x}+\vec{y})\right\rangle = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right) = \frac{1}{2}$$

So, we loose half the intensity of the light by passing it through the third filter. Thus, 1/8 of the total initial intensity makes it through.

So, to recap, once we correctly identified the possible states of the system ($|\vec{x}\rangle, |\vec{y}\rangle$,etc.) and made an *ansatz* for the operators ($\hat{P}_x = |\vec{x}\rangle\langle\vec{x}|, \hat{P}_y = |\vec{y}\rangle\langle\vec{y}|$,etc) we were able to correctly predict the results of all the polarization experiments using the rules of QM. Score one for Dirac notation.

## 2. Single Molecule Fluorescence

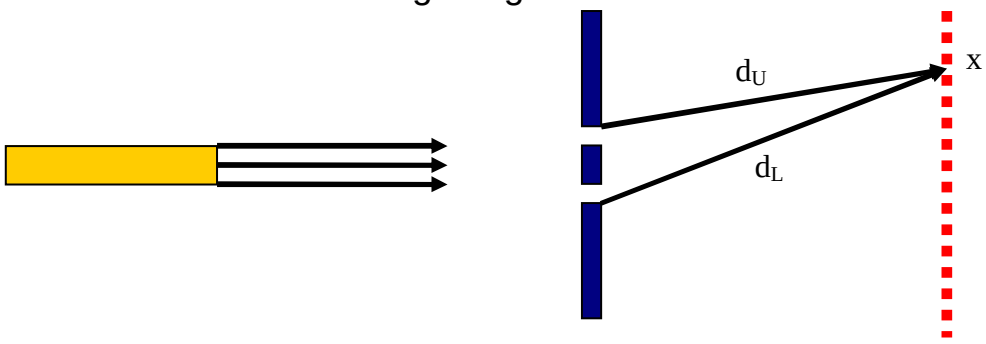
There really isn't anything for QM to predict here. The main thrust of this experiment was to prove that observations are probabilistic; however, QM only predicts *probabilities* and so there can be no contradiction here.

## 3. Nanoscale Electrical Conduction

These experiments illustrated several important physical principles: interference, superposition and the influence of measurement. The new facet here is that we must deal with the *evolution* of the electrons between the measurements. In the polarization experiments, the light propagates essentially undisturbed between the filters. In the conduction case, the electrons take different paths and the *difference between the paths matters*. We will not be able to make quantitative predictions, since there is too much we do not know about the structure of the semiconductor, width of the slits, etc. However, we will focus on isolating the qualitative effects.

<u>Interference Between Two Slits:</u>

Just as before, we need to define the possible states of the system. For the states, it is most convenient here to work in terms of the *paths* that the system can take. Then, if we ignore all the electrons that get reflected by the barrier, there are only two physically reasonable paths for the electron to take getting to our detector:




For simplicity we will denote the paths from the upper and lower slits to the arbitrary point, $x$, as $|U;x\rangle$ and $|L;x\rangle$, respectively. Now, it is physically clear that these states form a complete basis; because of the set-up of our experiment, there are no other reasonable paths that allow the electron to reach the detector. Therefore, since any state can be written as a linear combination of the basis states, the state of our system when it reaches the detector can be written:

$$|\psi; x\rangle = c_U |U; x\rangle + c_L |L; x\rangle$$

Now, we need an ansatz that lets us determine the coefficients. As far as the basic rules of QM go, we have complete freedom in defining these coefficients. The only guideline we have is, again, that our answer should agree with the experiment. One hint that guides us is that the particles display an *interference pattern*, which is characteristic of **wave** propagation. We might therefore guess that $c_U$ and $c_L$ are solutions of the wave equation:

$$\frac{\partial^2}{\partial d^2} c(d) = -k^2 c(d)$$

where $d$ measures the distance the wave has traveled from the slit. This turns out to be a special case of the *Schrödinger wave equation* that describes the wavefunction of a particle in real space. The solutions to the wave equation are well known: they are **plane waves**

$$c(d) = e^{\pm ikd}$$

Here, the speed of propagation of the wave is determined by its wavevector, $k$, and the sign of $k$ determines the direction the wave is moving. We will be interested in waves that travel toward the right, which corresponds to positive $k$. This is the first example of why it is necessary to allow complex coefficients in Hilbert space; if we forced $c_U(d)$ and $c_L(d)$ to be real, we could never obtain a solution to the wave equation that moved in a particular direction.

Now, notice that an electron that passes through the upper slit will traverse a distance ($d_U$) that is different than the electron passing through the lower slit ($d_L$). We therefore guess that the correct form for the wavefunction as it arrives at $x$ is:

$$|\psi; x\rangle \approx e^{ikd_U} |U; x\rangle + e^{ikd_L} |L; x\rangle$$

[Aside: I will use the "≈" symbol quite often. Roughly translated, it means "I threw away some terms that are not important".]

With this wavefunction, we wish to predict the outcome of the measurement. If we use $\hat{P}_x$ to denote the operator associated with detecting the particle at $x$, the probability of observing an electron at $x$ is:

$$\langle \psi; x|\hat{P}_x|\psi; x\rangle \approx \left(\langle U; x|e^{-ikd_U} + \langle L; x|e^{-ikd_L}\right)\hat{P}_x\left(e^{ikd_U}|U; x\rangle + e^{ikd_L}|L; x\rangle\right)$$

$$\approx \begin{pmatrix} \langle U; x|\hat{P}_x|U; x\rangle + e^{-ik(d_L-d_U)}\langle L; x|\hat{P}_x|U; x\rangle \\ + e^{ik(d_L-d_U)}\langle U; x|\hat{P}_x|L; x\rangle + \langle U; x|\hat{P}_x|U; x\rangle \end{pmatrix}$$

Complex Conjugates!

Now, once the electron arrives at the detector, there is no way for us to tell whether it went through the upper slit or the lower slit. The two states are **indistinguishable**. The result of this is that all measurements of $\hat{P}_x$ must give the same result,

$$\langle U; x|\hat{P}_x|U; x\rangle = \langle L; x|\hat{P}_x|U; x\rangle = \langle U; x|\hat{P}_x|L; x\rangle = \langle U; x|\hat{P}_x|U; x\rangle = \alpha$$

If the measurements on, say, $|U; x\rangle$ gave a different answer than for $|L; x\rangle$, we would be able to tell the difference between the two states by this measurement – contradicting our assertion that they were indistinguishable. Using this we can finally write the probability of detecting the particle at $x$:

$$\langle \psi; x|\hat{P}_x|\psi; x\rangle \approx \alpha + e^{-ik(d_L-d_U)}\alpha + e^{ik(d_L-d_U)}\alpha + \alpha$$

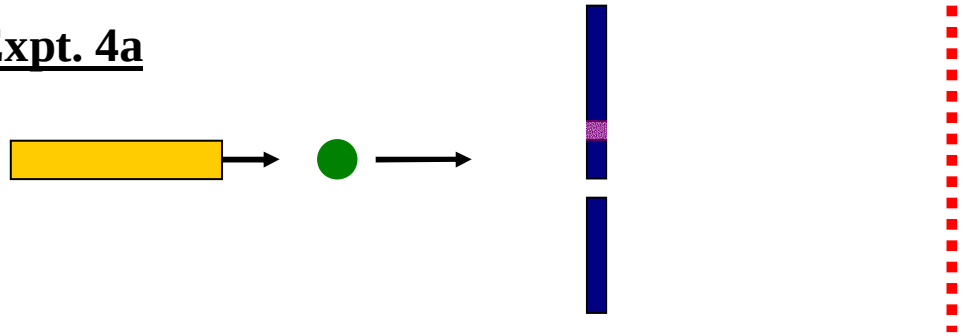
$$\approx 1 + \cos(k(d_L - d_U)).$$

Hence, we see that we do, in fact, get an interference pattern; if $d_U - d_L \approx 2\pi n$ we will get *constructive* interference, while if $d_U - d_L \approx \pi n$ we will get *destructive* interference.

Measurement and Collapse:

Perhaps the most shocking aspect of the two slit experiment is the fact that *observing* which slit the particle took (without deflecting the particle in any way) destroys the interference pattern. Describing this effect is quite challenging, but the key realization is that we cannot consider a 'system' that consists of the electron by itself; we must consider the detector as part of the quantum mechanical system, as well. To this end, consider the following set up:

## Expt. 4a



Thus, we have a two-slit experiment, but there is a detector that turns "on" if the electron passes through the upper slit and is "off" otherwise (I like to think of it as a light bulb). Again, we will only consider electrons that actually make it to the screen. Then, there are really four possible states for the electron+detector system:

$$|U;off\rangle, |U;on\rangle, |L;off\rangle, |L,on\rangle$$

If we assume our detector is 100% efficient, the first state will only be important before the electron passes through the slit, and the last state will never appear. Consider the initial state:

$$c_U|U;off\rangle + c_L|L;off\rangle$$

This describes an arbitrary superposition of electronic paths that will (eventually) pass through the upper and lower slits, and where the detector has yet to register a count. The result of the measurement is:

$$c_U|U;off\rangle + c_L|L;off\rangle \xrightarrow{measure} c_U|U;on\rangle + c_L|L;off\rangle$$

That is, the state of the electron is not disturbed, but the detector turns on if the particle went through the upper slit. This is the result of the measurement process. Our task is now to try to deduce what this state means.

The first point is that after it has passed through the detector, *we cannot think about the 'state' of the electron by itself*. To illustrate this, assume we could ignore the detector and describe the electron by its own wavefunction:

$$|\phi\rangle = c_U|U\rangle + c_L|L\rangle$$

[Note: $c_U$ and $c_L$ are *arbitrary*.] Now, consider the three operators:

$$\hat{X} \equiv |U\rangle\langle L| + |L\rangle\langle U| \qquad \hat{Y} \equiv i\left(|U\rangle\langle L| - |L\rangle\langle U|\right) \qquad \hat{Z} \equiv |U\rangle\langle U| - |L\rangle\langle L|$$

the actions of these operators on $|\phi\rangle$ are:

$$\hat{X}|\phi\rangle = \left(|U\rangle\langle L| + |L\rangle\langle U|\right)\left(c_U|U\rangle + c_L|L\rangle\right)$$
$$= |U\rangle c_U \underbrace{\langle L|U\rangle}_{0} + |L\rangle c_U \underbrace{\langle U|U\rangle}_{1} + |U\rangle c_L \underbrace{\langle L|L\rangle}_{1} + |L\rangle c_L \underbrace{\langle U|L\rangle}_{0} = c_U|L\rangle + c_L|U\rangle$$

$$\hat{Y}|\phi\rangle = i\left(|U\rangle\langle L| - |L\rangle\langle U|\right)\left(c_U|U\rangle + c_L|L\rangle\right)$$
$$= |U\rangle ic_U \underbrace{\langle L|U\rangle}_{0} - |L\rangle ic_U \underbrace{\langle U|U\rangle}_{1} + |U\rangle ic_L \underbrace{\langle L|L\rangle}_{1} - |L\rangle ic_L \underbrace{\langle U|L\rangle}_{0} = -ic_U|L\rangle + ic_L|U\rangle$$

$$\hat{Z}|\phi\rangle = \left(|U\rangle\langle U| - |L\rangle\langle L|\right)\left(c_U|U\rangle + c_L|L\rangle\right)$$
$$= |U\rangle c_U \underbrace{\langle U|U\rangle}_{1} - |L\rangle c_U \underbrace{\langle L|U\rangle}_{0} + |U\rangle c_L \underbrace{\langle U|L\rangle}_{0} - |L\rangle c_L \underbrace{\langle L|L\rangle}_{1} = c_U|U\rangle - c_L|L\rangle$$

Thus, the average values of these observables are:

$$\boxed{\begin{aligned}
\langle\phi|\hat{X}|\phi\rangle &= \left(\langle U|c_U^* + \langle L|c_L^*\right)\left(c_U|L\rangle + c_L|U\rangle\right) = c_U^* c_L + c_L^* c_U = 2\,\mathrm{Re}\,c_L^* c_U \\
\langle\phi|\hat{Y}|\phi\rangle &= \left(\langle U|c_U^* + \langle L|c_L^*\right)\left(-ic_U|L\rangle + ic_L|U\rangle\right) = ic_U^* c_L - ic_L^* c_U = 2\,\mathrm{Im}\,c_L^* c_U \\
\langle\phi|\hat{Z}|\phi\rangle &= \left(\langle U|c_U^* + \langle L|c_L^*\right)\left(c_U|U\rangle - c_L|L\rangle\right) = c_U^* c_U - c_L^* c_L = |c_U|^2 - |c_L|^2
\end{aligned}}$$

These equations summarize the possible results we can get from measuring $\hat{X}, \hat{Y}$ and $\hat{Z}$ on *any purely electronic state*. For now, it does not matter what these observations correspond to; simply that they can be made, and would have the boxed values.

Now, we need to define how these operators act on the true state of the electron+detector system, $|\psi\rangle \equiv c_U|U;on\rangle + c_L|L;off\rangle$. To do so, notice that $\hat{X}, \hat{Y}$ and $\hat{Z}$ only affect the electron and not the detector; we therefore define the actions of $\hat{X}, \hat{Y}$ and $\hat{Z}$ to give the same result as above when acting on $|\psi\rangle$, ignoring entirely the state of the detector. Thus,

$$\hat{X}\left(c_U|U\rangle + c_L|L\rangle\right) = c_U|L\rangle + c_L|U\rangle \Rightarrow \hat{X}\left(c_U|U;on\rangle + c_L|L;off\rangle\right) = c_U|L;on\rangle + c_L|U;off\rangle$$
$$\hat{Y}\left(c_U|U\rangle + c_L|L\rangle\right) = -ic_U|L\rangle + ic_L|U\rangle \Rightarrow \hat{Y}\left(c_U|U;on\rangle + c_L|L;off\rangle\right) = -ic_U|L;on\rangle + ic_L|U;off\rangle$$
$$\hat{Z}\left(c_U|U\rangle + c_L|L\rangle\right) = c_U|U\rangle - c_L|L\rangle \Rightarrow \hat{Z}\left(c_U|U;on\rangle + c_L|L;off\rangle\right) = c_U|U;on\rangle - c_L|L;off\rangle$$

Further, note that now the states $|U;on\rangle$ and $|U;off\rangle$ are orthogonal:

$$\langle U;on|U;off\rangle = \langle L;on|L;off\rangle = 0$$

This is because I can clearly **distinguish** between the two states by checking if the light in the detector is on or off. With these definitions, we can now compute the average values of $\hat{X}, \hat{Y}$ and $\hat{Z}$ for the true state of the system+detector:

$$\boxed{\begin{aligned}
\langle\psi|\hat{X}|\psi\rangle &= \left(\langle U;on|c_U^* + \langle L;off|c_L^*\right)\left(c_U|L;on\rangle + c_L|U;off\rangle\right) = 0 \\
\langle\psi|\hat{Y}|\psi\rangle &= \left(\langle U;on|c_U^* + \langle L;off|c_L^*\right)\left(ic_U|L;on\rangle - ic_L|U;off\rangle\right) = 0 \\
\langle\psi|\hat{Z}|\psi\rangle &= \left(\langle U;on|c_U^* + \langle L;off|c_L^*\right)\left(c_U|U;on\rangle - c_L|L;off\rangle\right) = |c_U|^2 - |c_L|^2
\end{aligned}}$$

It is immediately clear that these average values cannot be reproduced by any choice of $|\phi\rangle = c_U|U\rangle + c_L|L\rangle$, even if we adjust the coefficients to (i.e. $c_U \to c_U', c_L \to c_L'$) . We therefore conclude that *it is impossible to consider the state of the electron apart from the state of the detector after the measurement is made*. The state of the electron and the state of the detector are said to be **entangled**.

But if we cannot describe the electron by a quantum state, how are we to describe it? Observe that while the three average values are not possible if the electron has a single state, they are completely consistent with a *statistical mixture* of states. That is, assume that the electron "collapses" to either $|U\rangle$ (with probability $|c_U|^2$)or $|L\rangle$(with probability $|c_L|^2$). Then, when the system is in $|U\rangle$, we find the average values

$$\begin{aligned}
\langle U|\hat{X}|U\rangle &= \langle U|\left(|U\rangle\langle L| + |L\rangle\langle U|\right)|U\rangle = 0 \\
\langle U|\hat{Y}|U\rangle &= i\langle U|\left(|U\rangle\langle L| - |L\rangle\langle U|\right)|U\rangle = 0 \\
\langle U|\hat{Z}|U\rangle &= \langle U|\left(|U\rangle\langle U| - |L\rangle\langle L|\right)|U\rangle = 1
\end{aligned}$$

and when it is in $|L\rangle$ we find

$$\begin{aligned}
\langle L|\hat{X}|L\rangle &= \langle L|\left(|U\rangle\langle L| + |L\rangle\langle U|\right)|L\rangle = 0 \\
\langle L|\hat{Y}|L\rangle &= i\langle L|\left(|U\rangle\langle L| - |L\rangle\langle U|\right)|L\rangle = 0 \\
\langle L|\hat{Z}|L\rangle &= \langle L|\left(|U\rangle\langle U| - |L\rangle\langle L|\right)|L\rangle = -1
\end{aligned}$$

If we add the two results with the appropriate probabilities, we get

$$\begin{aligned}
|c_U|^2\langle U|\hat{X}|U\rangle + |c_L|^2\langle L|\hat{X}|L\rangle &= 0 \\
|c_U|^2\langle U|\hat{Y}|U\rangle + |c_L|^2\langle L|\hat{Y}|L\rangle &= 0 \\
|c_U|^2\langle U|\hat{Z}|U\rangle + |c_L|^2\langle L|\hat{Z}|L\rangle &= |c_U|^2 - |c_L|^2
\end{aligned}$$

Hence, *the result of making many measurements on the entangled state of the electron+detector is entirely equivalent to making repeated measurements on an electron that randomly "collapses" to either* $|U\rangle$ *or* $|L\rangle$. In practice, it is simply easier to assume the system

collapses than to worry about the entangled state, and this is what is done. Note that there is *no way to tell the difference* between the entangled state and the collapsed state simply by looking at the electron; the experimental predictions made by both models are identical. Hence, we can choose to describe the situation using whichever picture we deem more "physical".

Now, for the two slit experiment, we are interested in the average number of electrons that strike the detector at a given point $\langle\psi|\hat{P}_x|\psi\rangle$. This calculation would be more involved than the ones above, since we have to worry about the wavelike propagation between the slit and the screen, etc. However, the basic principle would be the same: the average value for the entangled state would be identical to an experiment where electron passes either through one slit or the other, in which case there is no interference. Hence, the most perplexing aspect of this experiment is explained.

## C. Matrix Mechanics

We now turn to the a pragmatic aspect of QM: given a particular problem, how can we translate the Dirac notation into a form that might be interpretable by a computer? As hinted at previously, we do this by mapping Dirac notation onto a *complex vector space*. The operations in Hilbert space then reduce to linear algebra that can easily be done on a computer. This formalism is completely equivalent to the Dirac notation we've already covered; in different contexts, one will prove more useful than the other.

### 1. States can be represented by vectors

First, we will begin with an arbitrary complete orthonormal basis of states $\{|\phi_i\rangle\}$. Then, we know that we can write any other state as:

$$|\psi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle + c_3|\phi_3\rangle + ... = \sum_i c_i|\phi_i\rangle$$

How are these coefficient determined? Here, we follow a common trick and take the inner product with the $j^{th}$ state:

$$(\langle\phi_j|)|\psi\rangle = (\langle\phi_j|)\sum_i c_i|\phi_i\rangle = \sum_i c_i(\langle\phi_j|)|\phi_i\rangle = \sum_i c_i\delta_{ij}$$

Since the Kronecker delta is only non-zero when i=j, the sum collapses to one term:

$$\langle\phi_j|\psi\rangle = c_j$$

The simple conclusion of these equations is that *knowing the coefficients is equivalent to knowing the wavefunction*. If we know $|\psi\rangle$, we can determine the coefficients through the second relation. Vice versa, If we know the coefficients, we can reconstruct $|\psi\rangle$ by performing the sum $\sum_i c_i|\phi_i\rangle$. Thus, if we fix this arbitrary basis, we can throw away all the basis state and just keep track of the *coefficients* of the ket state:

$$\boxed{|\psi\rangle \rightarrow \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \dots \end{pmatrix}_\phi}$$

In harmony with the intuitive arguments made in Section A, here we associate the ket states with column vectors. Notice the small subscript "$\phi$", which reminds us that this vector of coefficients represents $|\psi\rangle$ in the $\{|\phi_i\rangle\}$ basis. If we were really careful, we would keep this subscript at all times; however, in practice we will typically know what basis we are working in, and the subscript will be dropped.

How to we represent the corresponding bra state $\langle\psi|$ as a vector? Well, we know that

$$\langle\psi| = (|\psi\rangle)^\dagger = \left(\sum_i c_i|\phi_i\rangle\right)^\dagger = \sum_i \langle\phi_i|c_i^* .$$

Now, as noted in Section A, we expect to associate bra states with row vectors, and the above relation shows us that the elements of this row vector should be the *complex conjugates* of the column vector:

$$\boxed{\langle\psi| \rightarrow \begin{pmatrix} c_1^* & c_2^* & c_3^* & \dots \end{pmatrix}_\phi}$$

Noting that bra states and ket states were defined to be Hermitian conjugates of one another, we see that *Hermitian conjugation in state space corresponds to taking the complex conjugate transpose of the coefficient vector.*

Now, the vector notation is totally equivalent to Dirac notation; thus, anything we compute in one representation should be exactly the same if computed in the other. As one illustration of this point, it is

useful to check that this association of states with vectors preserves the inner product:

$$\langle\psi|\psi'\rangle = \left(\sum_i \langle\phi_i|c_i^*\right)\left(\sum_j c_j'|\phi_j\rangle\right) = \sum_{ij} c_i^* c_j' \langle\phi_i|\phi_j\rangle = \sum_{ij} c_i^* c_j' \delta_{ij} = \sum_i c_i^* c_i'$$

$$\begin{pmatrix} c_1^* & c_2^* & c_3^* & \ldots \end{pmatrix}_\phi \cdot \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \ldots \end{pmatrix}_\phi = \sum_i c_i^* c_i'$$

So, the two ways of writing the inner product give identical results, and overlaps between the vectors have the same quantitative (and qualitative) meaning as their bra-ket counterparts.

### 2. Operators Become Matrices

In order to complete our transition to linear algebra we need to determine how operators act on the coefficient vectors described in the previous section. Before we do this, we need to consider the operator:

$$\hat{O} = \sum_i |\phi_i\rangle\langle\phi_i|$$

Acting this operator on an arbitrary state:

$$\hat{O}|\psi\rangle = \sum_i |\phi_i\rangle\langle\phi_i|\psi\rangle$$

However, we showed above that $\langle\phi_j|\psi\rangle = c_j$, the coefficients of the state $|\psi\rangle$. Thus,

$$\hat{O}|\psi\rangle = \sum_i |\phi_i\rangle\langle\phi_i|\psi\rangle = \sum_i |\phi_i\rangle c_i = |\psi\rangle$$

Thus, $\hat{O}$ acting on any state gives the same state back. The operator that accomplishes this is the identity operator, $\hat{1}$, and so we write:

$$\hat{1} = \sum_i |\phi_i\rangle\langle\phi_i|$$

and say that this is a *resolution of the identity*.

With this in hand, we manipulate the expression for the bra-ket sandwich of and arbitrary operator $\hat{A}$:

$$\langle\psi| \quad \hat{A} \quad |\psi'\rangle$$

$$\hat{1} = \sum_i |\phi_i\rangle\langle\phi_i| \qquad \hat{1} = \sum_j |\phi_j\rangle\langle\phi_j|$$

$$\Rightarrow \sum_{ij} \langle\psi|\phi_i\rangle\langle\phi_i|\hat{A}|\phi_j\rangle\langle\phi_j|\psi'\rangle$$

$$\Rightarrow \sum_{ij} c_i^* \langle\phi_i|\hat{A}|\phi_j\rangle c_j'$$

We can re-write this last line as a standard (row)x(matrix)x(column) multiplication if we define the matrix $\mathbf{A}$, whose elements are $A_{ij} = \langle\phi_i|\hat{A}|\phi_j\rangle$. This association is so common, in fact, that even in Dirac notation, these objects are typically referred to as "matrix elements". So, to summarize, we can write:

$$\hat{A} \rightarrow \begin{pmatrix} \langle\phi_1|\hat{A}|\phi_1\rangle & \langle\phi_1|\hat{A}|\phi_2\rangle & \langle\phi_1|\hat{A}|\phi_3\rangle & \ldots \\ \langle\phi_2|\hat{A}|\phi_1\rangle & \langle\phi_2|\hat{A}|\phi_2\rangle & \ldots & \\ \langle\phi_3|\hat{A}|\phi_1\rangle & \ldots & & \\ \ldots & & & \end{pmatrix}_\phi \equiv \mathbf{A}$$

This matrix has all the same action on row and column vectors that the operator $\hat{A}$ has on bras and kets:

$$\hat{A}|\psi\rangle \leftrightarrow \mathbf{A}\cdot\mathbf{c} \qquad \langle\psi|\hat{A} \leftrightarrow \mathbf{c}^\dagger \cdot \mathbf{A}$$

It is also easy to show that the product of two operators is correctly represented by the product of their matrix representations. Further, similar to the case of vectors, the adjoint of $\hat{A}$ is the complex conjugate transpose of $\mathbf{A}$. Using the above associations, we can write every operation in Hilbert space in terms of matrix-vector multiplications, which are easily handled by a computer.

### 3. Some Interesting Matrix Properties

We are now going to prove a number of interesting things about particular classes of matrices which will prove useful later. These same identities can be proven for the raw operators, but the results are somewhat more familiar when one has the matrix formulation in hand.

The first two results concern Hermitian operators. Given a Hermitian operator, $\hat{H}$, it turns out that 1) the eigenvalues of $\hat{H}$ are always real, and 2) the eigenstates can be made to form a complete orthonormal basis. Both these facts are extremely important. First, recall that we know experimental results (which correspond to eigenvalues) are

always real numbers; thus, it is not surprising that every observable we deal with in this course will be associated with a Hermitian operator. Also, recall that in defining matrix mechanics, we appealed to the existence of an orthonormal basis, but gave no hints about how such a basis was to be constructed. We now see that every Hermitian operator associated with an observation naturally defines its own orthonormal basis!

As with nearly all theorems in chemistry, the most important part of this is the *result* and not how it is obtained. However, we will outline the proof of this theorem, mostly to get a little more practice with ins and outs of Dirac notation.

---

1) Consider the eigenvalue equation and its Hermitian conjugate:

$$\hat{H}|\psi_\alpha\rangle = h_\alpha|\psi_\alpha\rangle \xrightarrow{\text{Hermitian Conjugate}} \langle\psi_\alpha|\hat{H} = \langle\psi_\alpha|h_\alpha^*$$

Now we apply one of our tricks and take the inner product of the left equation with $\langle\psi_\alpha|$ and the inner product of the right equation with $|\psi_\alpha\rangle$:

$$\Rightarrow \langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle = h_\alpha\langle\psi_\alpha|\psi_\alpha\rangle \qquad \langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle = h_\alpha^*\langle\psi_\alpha|\psi_\alpha\rangle$$

We see that the left hand sides (l.h.s.) of both equations are the same, so we subtract them to obtain:

$$\Rightarrow 0 = \left(h_\alpha - h_\alpha^*\right)\langle\psi_\alpha|\psi_\alpha\rangle .$$

In order to have the right hand side (r.h.s) be zero, either:

$$0 = \left(h_\alpha - h_\alpha^*\right) \quad \text{or} \quad 0 = \langle\psi_\alpha|\psi_\alpha\rangle$$

Since we defined our states so that their norms were *not zero*, we conclude that

$$0 = \left(h_\alpha - h_\alpha^*\right)$$

Which implies that $h_\alpha$ is real ☺

2) Here, we need to prove that the eigenstates are a) normalized, b) orthogonal and c) form a complete basis. We will take these points in turn.

a) The eigenstates can be trivially normalized, since if $|\psi_\alpha\rangle$ is an eigenstate of $\hat{H}$, then so is $c|\psi_\alpha\rangle$:

$$\hat{H}\left(c|\psi_\alpha\rangle\right) = \hat{H}c|\psi_\alpha\rangle = c\hat{H}|\psi_\alpha\rangle = ch_\alpha|\psi_\alpha\rangle = h_\alpha\left(c|\psi_\alpha\rangle\right)$$

So given an unnormalized eigenstate, we can always normalize it without affecting the eigenvalue ☺

b) Consider the ket eigenvalue equation for one value of $\alpha$ and the bra equation for $\alpha'$

$$\hat{H}|\psi_\alpha\rangle = h_\alpha|\psi_\alpha\rangle \qquad\qquad \langle\psi_{\alpha'}|\hat{H} = \langle\psi_{\alpha'}|h_{\alpha'}$$

where we have already made use of the fact that $h_{\alpha'} = h_{\alpha'}^*$.
Now, take the inner product of the first equation with $\langle\psi_{\alpha'}|$ and the second with $|\psi_\alpha\rangle$. Then:

$$\Rightarrow \langle\psi_{\alpha'}|\hat{H}|\psi_\alpha\rangle = h_\alpha\langle\psi_{\alpha'}|\psi_\alpha\rangle \qquad\qquad \langle\psi_{\alpha'}|\hat{H}|\psi_\alpha\rangle = h_{\alpha'}\langle\psi_{\alpha'}|\psi_\alpha\rangle$$

Once again, the l.h.s. of the equations are equal and subtracting gives:

$$\Rightarrow 0 = (h_\alpha - h_{\alpha'})\langle\psi_{\alpha'}|\psi_\alpha\rangle$$

Thus, either:

$$0 = (h_\alpha - h_{\alpha'}) \quad \text{or} \quad 0 = \langle\psi_{\alpha'}|\psi_\alpha\rangle$$

Now, recall that we are dealing with two different eigenstates (i.e. $\alpha \neq \alpha'$). If the eigenvalules are not **degenerate** (i.e. $h_\alpha \neq h_{\alpha'}$), then the first equation cannot be satisfied and the eigenvectors must be orthogonal. In the case of degeneracy, however, we appear to be out of luck; the first equality is satisfied and we can draw no conclusions about the orthogonality of the eigenvectors. What is going on? Notice that, if $h_\alpha = h_{\alpha'} \equiv h$, then *any linear combination of the two degenerate eigenstates, $a|\psi_\alpha\rangle + b|\psi_{\alpha'}\rangle$, is also an eigenstate with the same eigenvalue*:

$$\hat{H}\left(a|\psi_\alpha\rangle + b|\psi_{\alpha'}\rangle\right) = a\hat{H}|\psi_\alpha\rangle + b\hat{H}|\psi_{\alpha'}\rangle = ah|\psi_\alpha\rangle + bh|\psi_{\alpha'}\rangle = h\left(a|\psi_\alpha\rangle + b|\psi_{\alpha'}\rangle\right)$$

So, when we have a degenerate eigenvalue, the definition of the eigenstates that correspond to that eigenvalue are not unique, and not all of these combinations are orthogonal to one another. However, there is a theorem due to Gram and Schmidt – which we will not prove – that asserts that *at least one of the possible choices forms an orthonormal set*. The difficult part in proving this is that there may be two, three, four… different degenerate states. So, for non-degenerate eigenvalues, the states must be orthogonal, while for a

degenerate eigenvalue, the states are not necessarily orthogonal, we are free to choose them to be orthogonal ☺

c) The final thing we need to prove is that the eigenstates form a complete basis. Abstractly, this means that we can write any other state as a linear combination of the eigenstates:

$$|\chi\rangle = \sum_\alpha c_\alpha |\psi_\alpha\rangle$$

In matrix language, this is equivalent to asserting that the *number of eigenstates* is the same as the *number of columns* in the matrix $\mathbf{H}$; both of these are equal to the **dimension** of the vector space. This turns out to be difficult to prove, and so we simply defer to our math colleagues and assert that it *can* be proven ☺

---

Now, since each Hermitian operator defines its own orthonormal basis, we often be interested in making a change of basis from the eigenbasis of one Hermitian operator, $\hat{A}$, to that of another, $\hat{B}$. Denote the eigenbasis of $\hat{A}$ by $\{|\varphi_\alpha\rangle\}$ and the eigenbasis of $\hat{B}$ by $\{|\chi_\alpha\rangle\}$. Then according to the result above $\{|\varphi_\alpha\rangle\}$ and $\{|\chi_\alpha\rangle\}$ are both orthonormal bases. Thus, we can write any state as

$$|\psi\rangle = \sum_\alpha a_\alpha |\varphi_\alpha\rangle \quad \text{or} \quad |\psi\rangle = \sum_\alpha b_\alpha |\chi_\alpha\rangle$$

Our task is to get $\{a_\alpha\}$ from $\{b_\alpha\}$ (or vice versa). This is accomplished using our favorite trick; take the inner product of each equation with $|\chi_\beta\rangle$:

$$\langle\chi_\beta|\psi\rangle = \sum_\alpha a_\alpha \langle\chi_\beta|\varphi_\alpha\rangle \quad \text{or} \quad \langle\chi_\beta|\psi\rangle = \sum_\alpha b_\alpha \langle\chi_\beta|\chi_\alpha\rangle$$

Equating the r.h.s. and making use of the orthonormality of the $\{|\chi_\alpha\rangle\}$ gives:

$$\sum_\alpha a_\alpha \langle\chi_\beta|\varphi_\alpha\rangle = \sum_\alpha b_\alpha \langle\chi_\beta|\chi_\alpha\rangle = \sum_\alpha b_\alpha \delta_{\alpha\beta} = b_\beta$$

$$\Rightarrow \sum_\alpha a_\alpha \langle\chi_\beta|\varphi_\alpha\rangle = b_\beta$$

This leads to the definition of the **Transformation matrix**:

$$\mathbf{T} \equiv \begin{pmatrix} \langle \chi_1 | \varphi_1 \rangle & \langle \chi_1 | \varphi_2 \rangle & \langle \chi_1 | \varphi_3 \rangle & \cdots \\ \langle \chi_2 | \varphi_1 \rangle & \langle \chi_2 | \varphi_2 \rangle & \cdots & \cdots \\ \langle \chi_3 | \varphi_1 \rangle & \cdots & \cdots & \\ \cdots & \cdots & & \end{pmatrix}$$

The columns of this matrix are the coefficients of the "new" basis states ($\{|\chi_\alpha\rangle\}$) in terms of "old" ones ($\{|\varphi_\alpha\rangle\}$) and it allows us to transform from one basis to another using simple matrix algebra:

$$\boxed{\mathbf{b} = \mathbf{T}\mathbf{a}}$$

Now, what about the reverse transformation (i.e. $\mathbf{b}$ to $\mathbf{a}$)? Well, our designation of the "old" ($\{|\varphi_\alpha\rangle\}$) and "new" ($\{|\chi_\alpha\rangle\}$) bases was completely arbitrary; we can change the direction of the transformation by simply switching the roles of $\{|\chi_\alpha\rangle\}$ and $\{|\varphi_\alpha\rangle\}$. For example, we can obtain the $\mathbf{b}$ to $\mathbf{a}$ transformation matrix by simply swapping the letters $\varphi$ and $\chi$ in our definition of $\mathbf{T}$

$$\mathbf{S} \equiv \begin{pmatrix} \langle \varphi_1 | \chi_1 \rangle & \langle \varphi_1 | \chi_2 \rangle & \langle \varphi_1 | \chi_3 \rangle & \cdots \\ \langle \varphi_2 | \chi_1 \rangle & \langle \varphi_2 | \chi_2 \rangle & \cdots & \cdots \\ \langle \varphi_3 | \chi_1 \rangle & \cdots & \cdots & \\ \cdots & \cdots & & \end{pmatrix}$$

This matrix satisfies:

$$\mathbf{a} = \mathbf{S}\mathbf{b}.$$

However, looking at our definition of $\mathbf{S}$, we see that it is just the Hermitian conjugate of $\mathbf{T}$! This leads to an important result:

$$\mathbf{a} = \mathbf{S}\mathbf{b} = \mathbf{T}^\dagger\mathbf{b} = \mathbf{T}^\dagger(\mathbf{T}\mathbf{a}) = \mathbf{T}^\dagger\mathbf{T}\mathbf{a}$$

Reading from right to left, this shows that $\mathbf{T}^\dagger\mathbf{T}$ acting on any vector $\mathbf{a}$ *gives back the same vector*. Thus, we conclude that:

$$\mathbf{T}^\dagger\mathbf{T} = \mathbf{1}$$

Matrices that satisfy this special property are called **unitary** matrices. Any property we are interested in will be *invariant to unitary transformations*. From a physical perspective, this is because unitary transforms correspond to a change of basis and we know that the basis we choose to represent things is arbitrary and should not matter. From a mathematical point of view, this results from the fact that unitary matrices will always occur in Hermitian conjugate pairs in our results (because of the bra-ket structure of the inner product) and $\mathbf{T}^\dagger\mathbf{T}$ is the identity.

The transformation matrix also allows us to change the basis for an operator. Denote the matrix representation of $\hat{H}$ in the eigenbasis of $\hat{A}$ by:

$$\begin{pmatrix} \langle\varphi_1|\hat{H}|\varphi_1\rangle & \langle\varphi_1|\hat{H}|\varphi_2\rangle & \langle\varphi_1|\hat{H}|\varphi_3\rangle & \dots \\ \langle\varphi_2|\hat{H}|\varphi_1\rangle & \langle\varphi_2|\hat{H}|\varphi_2\rangle & \dots & \\ \langle\varphi_3|\hat{H}|\varphi_1\rangle & \dots & & \\ \dots & & & \end{pmatrix} \equiv \mathbf{H}_A$$

Then we have that a matrix element of $\hat{H}$ can be represented in the $\hat{A}$ basis by:

$$\langle\psi|\hat{H}|\psi'\rangle = \mathbf{a}^\dagger \mathbf{H}_A \mathbf{a}'$$

and in the $\hat{B}$ basis by:

$$\langle\psi|\hat{H}|\psi'\rangle = \mathbf{b}^\dagger \mathbf{H}_B \mathbf{b}'$$

Now, using the fact that $\mathbf{a}' = \mathbf{T}^\dagger \mathbf{b}'$ (and the Hermitian conjugate relation $\mathbf{a}^\dagger = \mathbf{b}^\dagger \mathbf{T}$),

$$\Rightarrow \langle\psi|\hat{H}|\psi'\rangle = \mathbf{a}^\dagger \mathbf{H}_A \mathbf{a}' = \mathbf{b}^\dagger \mathbf{T} \mathbf{H}_A \mathbf{T}^\dagger \mathbf{b}'$$

Comparing this last equation with the definition of $\mathbf{H}_B$ leads to the conclusion that under a change of basis from $\hat{A}$ to $\hat{B}$, an arbitrary matrix transforms as:

$$\mathbf{H}_B = \mathbf{T} \mathbf{H}_A \mathbf{T}^\dagger$$

One important special case of this relation is when $\hat{H} = \hat{A}$. Then, we know the matrix elements:

$$\begin{pmatrix} \langle\varphi_1|\hat{A}|\varphi_1\rangle & \langle\varphi_1|\hat{A}|\varphi_2\rangle & \langle\varphi_1|\hat{A}|\varphi_3\rangle & \dots \\ \langle\varphi_2|\hat{A}|\varphi_1\rangle & \langle\varphi_2|\hat{A}|\varphi_2\rangle & \dots & \\ \langle\varphi_{31}|\hat{A}|\varphi_1\rangle & \dots & & \\ \dots & & & \end{pmatrix} = \begin{pmatrix} a_1 & 0 & 0 & 0 \\ 0 & a_2 & 0 & \dots \\ 0 & 0 & a_3 & \dots \\ 0 & \dots & \dots & \dots \end{pmatrix} = \mathbf{A}_A$$

That is, the matrix that represents $\hat{A}$ *is diagonal in the eigenbasis of* $\hat{A}$. This allows us to very easily represent $\hat{A}$ in any other eigenbasis:

$$\mathbf{A}_B = \mathbf{T} \mathbf{A}_A \mathbf{T}^\dagger$$

Where we recall that $\mathbf{A}_A$ is just a diagonal matrix. In practice, we will very often want to work with a matrix in its eigenbasis and only use the transformation rules to move to other bases when necessary.

As an example, consider a **function of a matrix**. This is defined by the power series expansion of the function:

$$f(\mathbf{A}) \equiv \mathbf{1} + f'(0)\mathbf{A} + \frac{f''(0)}{2!}\mathbf{AA} + \frac{f'''(0)}{3!}\mathbf{AAA} + \ldots$$

One important example of this is the **exponential** of a matrix, which we will use quite frequently:

$$e^{\mathbf{A}} \equiv \mathbf{1} + \mathbf{A} + \frac{\mathbf{AA}}{2!} + \frac{\mathbf{AAA}}{3!} + \ldots$$

If we transform from whatever arbitrary basis we are in into the eigenbasis, we can write $\mathbf{A}$ in diagonal form ($\mathbf{A} = \mathbf{T}\mathbf{A}_A\mathbf{T}^\dagger$) and the function becomes:

$$f(\mathbf{A}) = \mathbf{1} + f'(0)\mathbf{T}\mathbf{A}_A\mathbf{T}^\dagger + \frac{f''(0)}{2!}\mathbf{T}\mathbf{A}_A\cancel{\mathbf{T}^\dagger}\cancel{\mathbf{T}}\mathbf{A}_A\mathbf{T}^\dagger + \frac{f'''(0)}{3!}\mathbf{T}\mathbf{A}_A\cancel{\mathbf{T}^\dagger}\cancel{\mathbf{T}}\mathbf{A}_A\cancel{\mathbf{T}^\dagger}\cancel{\mathbf{T}}\mathbf{A}_A\mathbf{T}^\dagger + \ldots$$

$$\Rightarrow f(\mathbf{A}) = \mathbf{1} + f'(0)\mathbf{T}\mathbf{A}_A\mathbf{T}^\dagger + \frac{f''(0)}{2!}\mathbf{T}\mathbf{A}_A\mathbf{A}_A\mathbf{T}^\dagger + \frac{f'''(0)}{3!}\mathbf{T}\mathbf{A}_A\mathbf{A}_A\mathbf{A}_A\mathbf{T}^\dagger + \ldots$$

and noting that $\mathbf{1} = \mathbf{T}\mathbf{T}^\dagger$ and that the coefficients (which are *numbers*) commute with the transformation matrix:

$$\Rightarrow f(\mathbf{A}) = \mathbf{T}\mathbf{T}^\dagger + \mathbf{T}f'(0)\mathbf{A}_A\mathbf{T}^\dagger + \mathbf{T}\frac{f''(0)}{2!}\mathbf{A}_A\mathbf{A}_A\mathbf{T}^\dagger + \mathbf{T}\frac{f'''(0)}{3!}\mathbf{A}_A\mathbf{A}_A\mathbf{A}_A\mathbf{T}^\dagger + \ldots$$

$$\Rightarrow f(\mathbf{A}) = \mathbf{T}\left(\mathbf{1} + f'(0)\mathbf{A}_A + \frac{f''(0)}{2!}\mathbf{A}_A\mathbf{A}_A + \frac{f'''(0)}{3!}\mathbf{A}_A\mathbf{A}_A\mathbf{A}_A + \ldots\right)\mathbf{T}^\dagger$$

$$\Rightarrow f(\mathbf{A}) = \mathbf{T}f(\mathbf{A}_A)\mathbf{T}^\dagger$$

Thus, *functions of matrices transform just like matrices* when we change basis. Why is this important? In its eigenbasis, we know that $\hat{A}$ is represented by a diagonal matrix, and it is trivial to apply a function to a diagonal matrix; the result is a diagonal matrix, with the diagonal elements given by $f(x)$ evaluated at each of the eigenvalues:

$$f(\mathbf{A}_A) = f\begin{pmatrix} e_1 & 0 & 0 & 0 \\ 0 & e_2 & 0 & 0 \\ 0 & 0 & e_3 & 0 \\ 0 & 0 & 0 & \ldots \end{pmatrix} = \begin{pmatrix} f(e_1) & 0 & 0 & 0 \\ 0 & f(e_2) & 0 & 0 \\ 0 & 0 & f(e_3) & 0 \\ 0 & 0 & 0 & \ldots \end{pmatrix}$$

Thus, we can apply a function to a matrix in three steps: 1) Change basis to the eigenbasis of $\hat{A}$ ($\mathbf{A} = \mathbf{T}\mathbf{A}_A\mathbf{T}^\dagger$) 2) Apply $f(x)$ to the

diagonal elements of $\mathbf{A}_A$ to obtain $f(\mathbf{A}_A)$ 3) Transform back to the original basis ( $f(\mathbf{A}) = \mathbf{T} f(\mathbf{A}_A) \mathbf{T}^{\dagger}$ )