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. At this point, we will take the mathematical rules of QM as a **hypothesis** that 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 called 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.

1. Hilbert Space Operators Correspond to Observables

The first rule of QM is: all observables are associated with **operators** in Hilbert Space. We have already encountered this rule, we just didn't know the operators lived in Hilbert space. Now, for most intents and purposes, Hilbert Space 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 quantum effect we discovered in the experiments: **non-commuting observations**. Also, note that **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 Vector

In Hilbert Space, the system is represented by a **state**. Again, we already knew this, but the fact that the states live in Hilbert space lets us know some new facts. First, we note that there are three simple

operations one can execute on a state. First, one can multiply it by a constant to obtain a new state:

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

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:

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

As we have seen before, $|\psi\rangle$ is a **superposition** of the two states $|\psi_1\rangle$ and $|\psi_2\rangle$. Finally, there is one new operation we need to introduce, called **Hermitian conjugation**. By definition, the Hermitian conjugate (dentoed by '†') is given by:

$$\left(c_1|\psi_1\rangle + c_2|\psi_2\rangle\right)^\dagger = \langle\psi_1|c_1^* + \langle\psi_2|c_2^*$$

$$\left(\langle\psi_1|c_1 + \langle\psi_2|c_2\right)^\dagger = c_1^*|\psi_1\rangle + c_2^*|\psi_2\rangle$$

Where '*' denotes complex conjugation. Further, Thus, the Hermitian conjugate takes kets to bras (and vice versa) and takes the complex conjugate of any constant. Hermitian conjugation in Hilbert space is analogous to the transpose in a traditional vector space. Thus:

$$|\psi\rangle = \langle\psi|^\dagger \Leftrightarrow \begin{pmatrix} \\ \\ \end{pmatrix} = \begin{pmatrix} & & \end{pmatrix}^T$$

To be precise, we will ultimately find that Hermitian conjugation is the same as taking the transpose and complex conjugate simultaneously. Finally, we note one important fact about a Hilbert space. There always exists a **basis** of states, $\{|\phi_\alpha\rangle\}$, such that any other state can be written as a linear combination of the basis states:

$$|\psi\rangle = \sum_\alpha c_\alpha |\phi_\alpha\rangle$$

We have as yet said nothing about the *number* of these states. In general, the basis for a Hilbert space involves an *infinite* number of states. The definition above assumes they are denumerable (i.e. we can assign them numbers i=1,2,3,4…) In some situations, the basis will be *continuous*. In these situations, we can replace the sum by an integral:

$$|\psi\rangle = \int c(\alpha)|\phi_\alpha\rangle d\alpha\,.$$

3. Bra-Ket Gives Probability

Now, in order to make predictions, we need to understand a few properties of the bra-ket product. To be mathematically precise, bar and ket states are dual to one another. 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**. We can also define the norm of a state by:

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

One of the properties of the bracket product in Hilbert space is that the norm of a state is always greater than or equal to zero and it can only be zero for the trivial state that corresponds to the origin. 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**.

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 allows us to define the Hermitian Conjugate (HC) of an operator 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.

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.

We are now in a position to restate the third rule of QM: <u>for a system in the sate $|\psi\rangle$,the expectation value of an observable, O , is given by</u>:

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

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

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

4. Operators and Eigenvalues

One important fact is that operators in Hilbert Space 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_{α}, and eigenstates, $|\psi_{\alpha}\rangle$, with any linear operator, $\hat{O}$, by finding all of the solutions of the eigenvalue equation:

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

This allows us to state the final two rules of QM: 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. And, finally, after O has been observed and found to have a value o_α then the wavefunction of the system collapses into the eigenstate $|\psi_\alpha\rangle$.

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:

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

As we have seen in the polarization experiments, 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:

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

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) and the form a basis (any state $|\psi\rangle$ can be written as a linear combination of these states). We can write the orthonormality condition 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 first important results we will prove 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, note that up to now we have 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.

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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_α 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 α and the bra equation for α'

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

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:

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

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

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

Thus, either:

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

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:

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

This turns out to be difficult to prove, and so we simply defer to our math colleagues and assert that it *can* be proven ☺

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.