# I. Experimental Evidence for Quantum Mechanics

Quantum mechanics (QM) is a *tool* that was invented to *explain* experimental results. It is nothing more and nothing less than that. The utility of QM is therefore based entirely upon its ability to predict and explain experimental results, and by this measure it is a phenomenal success. There has yet to be an experiment of any type that violates the basic principles of QM. Thus, to begin with, we should discuss some of the experimental results that illustrate key principles of QM. Since this is a chemistry course, we will slant our perspective towards *chemically relevant* experiments, but similar effects can be found in any situation where the systems are small enough and the temperature is low enough.
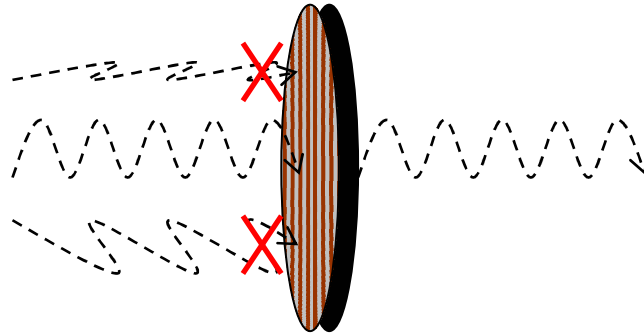
a. Polarization of Light

Light waves can be polarized in any direction perpendicular to the direction of motion of the wave. So, for example, if we have a laser propagating in the $\bar{z}$ direction, the light beam can be polarized either along $\bar{x}$ or $\bar{y}$. In this sense, light can be thought of as a transverse wave (i.e. one whose oscillations are perpendicular to the direction of propagation) and the two polarization directions can be thought of as:
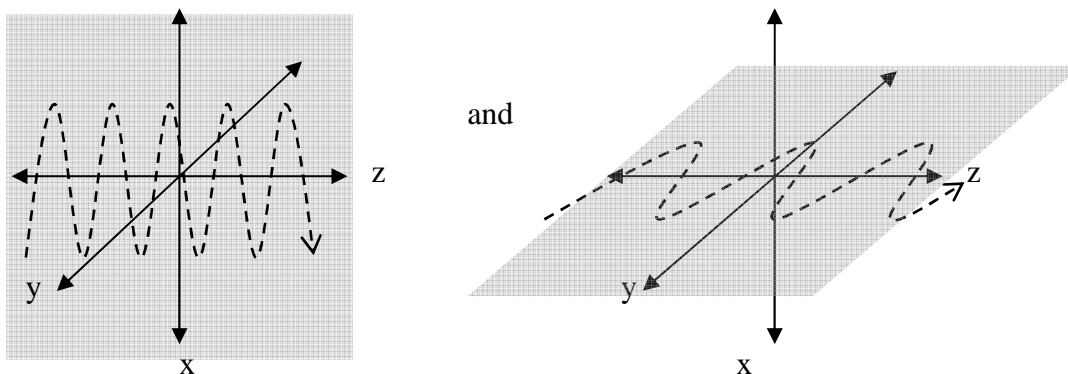
These two polarization components can be separated using a *polarization filter*. Typically, the filter consists of a crystal composed of rows of aligned molecules. Then, light whose polarization is not aligned with these rows will not pass through the crystal; meanwhile, light whose polarization is aligned with the crystal axis will be able to pass through the gaps between the rows.

Light from typical sources (such as a lamp or the sun) is not polarized; if you pass it though a polarization filter, some of the light passes though, and some does not. We will depict this simple experiment by:

Where the round circle represents a polarization filter, and the vertical lines indicate that it is a polarization filter in the $\bar{x}$ direction. The polarization filter performs a simple **measurement**; it tells us how much of the light is polarized in a given direction.

This measurement is, however, very boring. It gets interesting when we start to consider multiple polarization measurements being applied to one laser beam. For example, if the first filter is $\bar{x}$ while the second filter is $\bar{y}$, we get no light transmitted:

**Expt. 1**

y   x
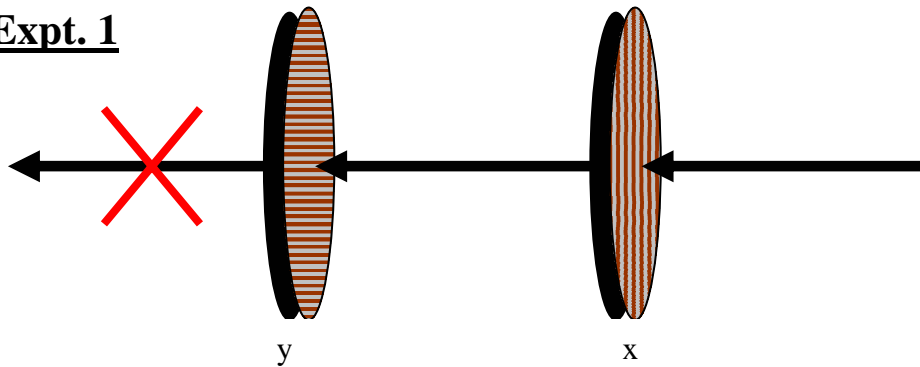
To put it another way, the first filter *measures* the polarization of the light and tells us that a certain part of the wave is $\bar{x}$-polarized. Then, the second filter *measures* how much of the resulting $\bar{x}$-polarized beam is actually $\bar{y}$-polarized. The obvious result of this experiment is that **none** of the $\bar{x}$-polarized light is simultaneously $\bar{y}$-polarized. This makes sense from a physical perspective (none of the $\bar{x}$-polarized waves would fit between the $\bar{y}$-oriented slits) and also from

a logical point of view (it is impossible to have the light polarized in two mutually exclusive directions).

On the other hand, if we perform an experiment where the first filter is $\bar{x}$ while the second filter is aligned at a 45^0 angle to $\bar{x}$ (along a direction $\bar{x}'$) we do get some transmission:

Expt. 2

x'   x
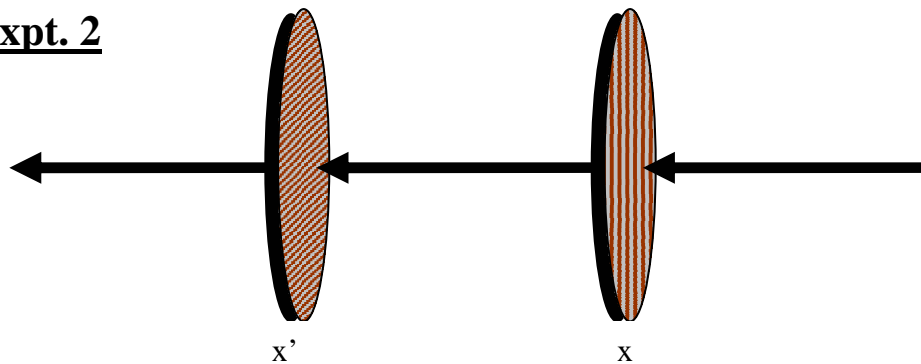
In fact, if we have very good filters, we can get 50% of the $\bar{x}$-polarized light to pass through the $\bar{x}'$ filter. We can rationalize this, as well, because $\bar{x}'$ is half-way between $\bar{x}$ and $\bar{y}$, so having half of the $\bar{x}$-polarized beam pass through the $\bar{x}'$ filter makes sense.

Now, we come to the key experiment. Let's take the beam of light produced in Expt. 2 and measure its polarization in the $\bar{y}$ direction:

Expt. 3

?

y   x'   x
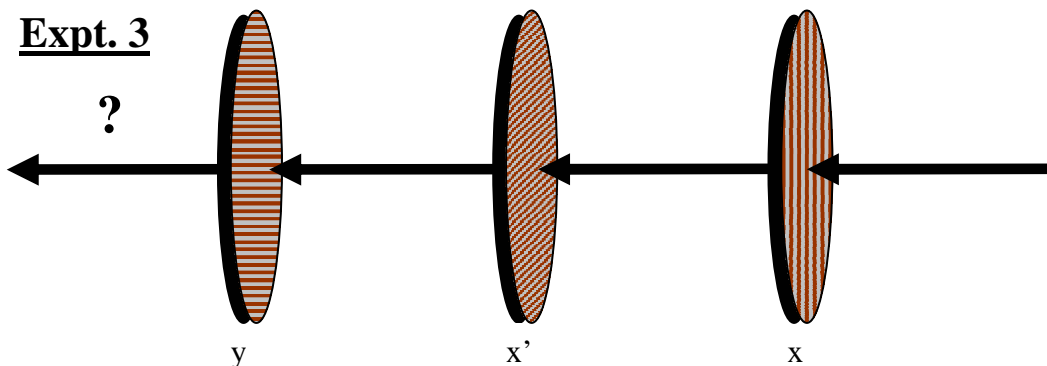
We find again that 50% of the light passes through the final filter. This may seem benign, but notice that if we remove the $\bar{x}'$ filter, we recover Expt. 1, where **none** of the light passed through the final filter. So, basically, the $\bar{x}'$ filter takes in a beam of light that is 0% polarized in the $\bar{y}$ direction, **removes** some of the light, and the resulting beam is then 50% $\bar{y}$-polarized! What is going on here?

How Do We Expain This Result?

There is one obvious explanation of these experiments: perhaps the polarization filters do not *filter* the light, but instead *rotate* the direction of the polarization. This is actually the explanation given in most freshman physics texts. However, we should note two things that would make this a very strange interpretation. First, different polarizations of light are rotated in *different directions*. For example, if we pass $\bar{x}$-polarized light through the $\bar{x}'$ filter, the light polarization is 'rotated' +45⁰ to $\bar{x}'$. On the other hand if we pass $\bar{y}$-polarized light through the same filter, it again comes out $\bar{x}'$, a net rotation of -45⁰. If we want to denote this with a picture, we might note that a normal rotation acts on the two independent polarizations like this:
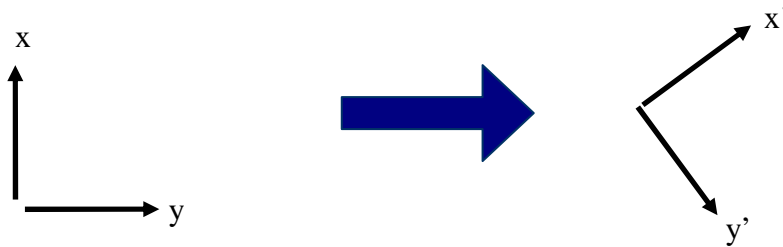
while the 'rotation' of polarizations looks quite different:
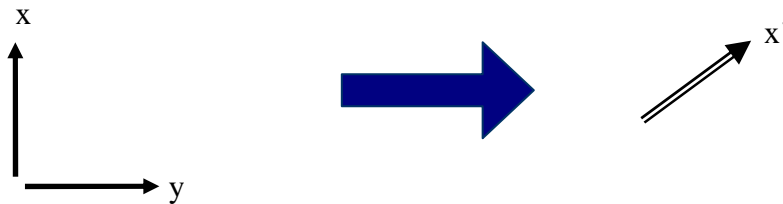
where the double arrow on the right indicates that the two independent polarizations on the left get 'collapsed' into one polarization on the right. The second weird feature of this 'rotation' is that we always get *less* light out after the rotation than we put in, and often the difference is significant. This contradicts our notion that with perfect optics we should be able to get perfect rotation. These two facts combined make it very difficult to think of this as a rotation.

Another interpretation is to assume that the $\bar{x}'$ filter sometimes lets light through that isn't exactly polarized in the $\bar{x}'$ direction. This, however, is inconsistent with the fact that, if we apply an $\bar{x}'$ filter once and then apply another $\bar{x}'$ filter to the resulting beam, we get 100%

transmission through the second filter (in the limit of perfect optics). If the filter sometimes admits light that is not $\bar{x}'$ polarized, then applying the filter again should remove some of those photons on the second pass. So the data seem to indicate that we are getting definite polarizations out of the filters.

Quantum Interpretation of Polarization Experiments

This experiment illustrates several key concepts of quantum mechanics. The first is the idea that the order in which we perform experiments matters. Consider the following set-up:

Expt. 3a

x'   y   x
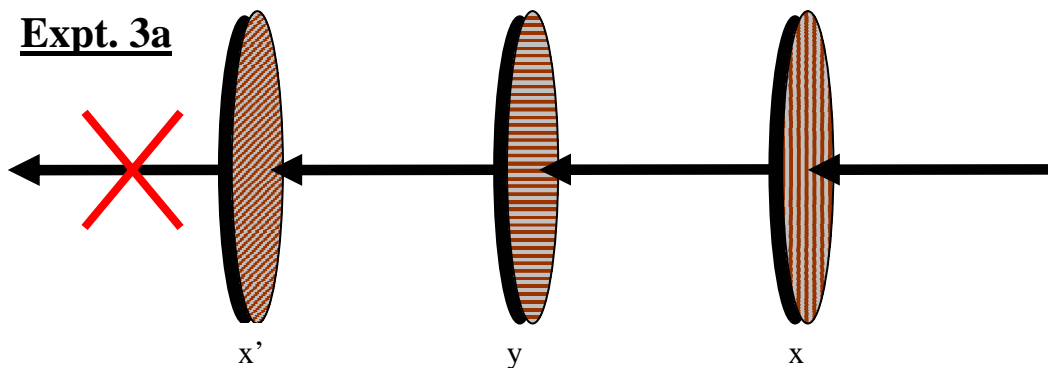
This differs from Expt. 3 only in the order in which the filters are applied (i.e. $\bar{y}\,\bar{x}'\,\bar{x}$ versus $\bar{x}'\,\bar{y}\,\bar{x}$), but in the one case, we get light transmittance and the other we do not. If the order of two experimental observations does not change the result, the two observations are said to **commute**. The surprise that QM brings is that, in general, experimental observations **do not commute** with one another. In this case, for example, the action of applying the $\bar{y}$ filter does not commute with the use of an $\bar{x}'$ filter. AS we discussed in class, another way of saying this is to say that the $\bar{x}'$ filter **disturbs** the system while it measures the polarization. This is not because we have a bad filter; we could use any number of different experimental set-ups to perform analogous polarization measurements and we would find that every single one of them disturbs the system in exactly the same way.

Naturally, we want some manner of quantifying these results. In order to do this, we require mathematical shorthand to describe these experiments concisely, and this shorthand is Quantum Mechanics

(QM). The experiments give us several guidelines as to what is (and is not) permissible if we want QM to reproduce the experiments.

1. Observables Are Represented by Operators

As a short hand, we will call anything that can be measured in an experiment an *observable*. The first rule of QM is: <u>all observables are associated with **operators**</u>. 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. In the polarization experiments, one observable is "how much of the light is $\bar{x}$ polarized?", which is answered by applying the polarization filter in the $\bar{x}$ direction. We associate an operator, $\hat{P}_x$, with this observable and similarly define $\hat{P}_{x'}$ and $\hat{P}_y$. By declaration, the multiplication of operators is interpreted as a sequence of measurements, by convention read from right to left. Thus

$$\hat{P}_{x'}\hat{P}_x$$

translates into "first apply an $\bar{x}$-filter and then apply an $\bar{x}'$ filter". Using this shorthand, we can denote the inequivalence of Expts. 3 and 3a by the symbolic equation:

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

or, if we strip off the leading factor of $\hat{P}_x$ on both sides:

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

We thus arrive at the important point that the multiplication of operators **does not commute**:

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

At this point, we have a nice shorthand for the polarization filters. Next, we need to create something to represent the photons.

2. The System is Described by a State

<u>The physical system that is being observed is represented by a **state**</u>. We will also sometimes call states "wavefunctions". In order to differentiate a state from an operator or variable, we will enclose it with "$|\ \rangle$" and call it a 'ket' state. In between the "$|\ \rangle$", we will write a label to tell us necessary information about the ket state. For example, a $\bar{y}$-polarized photon would be in a state $|y\rangle$. 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. 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:

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

For example, applying a $\vec{y}$-polarized filter to an $\vec{x}$ polarized photon would be written:

$$\hat{P}_y|x\rangle$$

An operator acting on a ket state just gives another ket state. The resulting ket represents **the state of the system after the measurement has been performed**. Note that, because we know the filters disturb the system, the state of the system after the measurement will, in general, be different than it was before the measurement.

3. Bra-Ket Gives Probability

Finally, we need some method of getting hard numbers out of operators and states. For this purpose, we create a set of states ('bra' states) that are complementary to ket states. Like kets, bra states also carry all the information that can be known about the system. We will enclose the bra states in "$\langle\ |$" to differentiate bra states from ket states. The key property of bra states is that when we multiply bra times ket we will get a number:

$$\langle\psi|\chi\rangle = \textit{a number.}$$

Here, ψ and χ are two different possible states for the system. This may seem a little odd. Why do we need these bra states, anyway? We'll get into this a little bit more later on, but we note that a very similar thing happens if we talk about vectors; there are two kinds of vectors (row and column) and we can only get a number out of a pair of vectors if we make the dot product (row)x(column). Hence, ket states are analogous to column vectors and bra states are analogous to row vectors, while the bra-ket (or 'bracket') product is analogous to a dot product. The bra-ket notation is due to Dirac and is named in

his honor. We will make this analogy between Dirac's states and vectors more concrete later on.

We can associate a physical meaning with this number if we adopt what is called the Copenhagen interpretation, which associates the bracket with an average (or expectation) value of a measurement. That is to say, the bracket allows us to predict what the average outcome of an experiment would be if we performed it many, many times and summed the results. The third rule we will adopt is that <u>for a system in the sate $|\psi\rangle$,the expectation value of an observable, O, is given by</u>:

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

First we recall that $\hat{O}|\psi\rangle$ is also a ket vector. Thus, the numerator is a bra-ket (a number) and so is the denominator, so we are, indeed, getting a number out. Unlike the first two rules, which could have been guessed relatively easily, the third rule seems a bit arbitrary. The only justification we can give is that *it works* – all the experimental results ever obtained fit are correctly predicted by this principle. In order to convince ourselves of this, let's return to the polarization experiments and see QM in action.

4. Explaining the Polarization Experiments

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.

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,

$$\hat{P}_x | \vec{u} \rangle = c_x | \vec{x} \rangle \qquad\qquad \hat{P}_y | \vec{u} \rangle = c_y | \vec{y} \rangle$$

where c is an undetermined constant. At this point, we have just inserted c because we suspect it will be useful; the rules of QM that we have set up so far don't tell us what multiplying a state by a constant *means*. To fix the constant, we recall that applying two identical filters gives the same answer as applying one:

$$\hat{P}_x \hat{P}_x | \vec{u} \rangle = \hat{P}_x | \vec{u} \rangle = c_x | \vec{x} \rangle \qquad \hat{P}_y \hat{P}_y | \vec{u} \rangle = \hat{P}_y | \vec{u} \rangle = c_y | \vec{y} \rangle$$

this property is called **idempotency** and idempotent operators are also called projection operators. It is easy to verify that the equations above are satisfied if

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

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

$$\hat{P}_x | \vec{u} \rangle = \left(| \vec{x} \rangle \langle \vec{x} | \right) | \vec{u} \rangle = | \vec{x} \rangle \langle \vec{x} | \vec{u} \rangle = c_x | \vec{x} \rangle \qquad \left(c_x \equiv \vec{x} \cdot \vec{u} \right)$$
$$\hat{P}_y | \vec{u} \rangle = \left(| \vec{y} \rangle \langle \vec{y} | \right) | \vec{u} \rangle = | \vec{y} \rangle \langle \vec{y} | \vec{u} \rangle = c_y | \vec{y} \rangle \qquad \left(c_y \equiv \vec{y} \cdot \vec{u} \right)$$

While applying the $\vec{x}$ filter twice gives:

$$\hat{P}_x \hat{P}_x | \vec{u} \rangle = \hat{P}_x c_x | \vec{x} \rangle = c_x \hat{P}_x | \vec{x} \rangle = c_x \left(| \vec{x} \rangle \langle \vec{x} | \right) | \vec{x} \rangle = c_x | \vec{x} \rangle \langle \vec{x} | \vec{x} \rangle = c_x | \vec{x} \rangle$$

where, in the first step we have used the result of the single-filter experiment, in the second step we have used the (assumed) fact that numbers commute with everything and in the final step we have used the fact that $\vec{x}$ is a unit vector so that $\langle \vec{x} | \vec{x} \rangle = \vec{x} \cdot \vec{x} = 1$. A strictly analogous result holds if we apply the $\vec{y}$ filter twice. Hence, this way

of associating operators with the filters is at least a plausible guess. To fully 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 $\bar{x}$-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 $\bar{x}$-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 θ. 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 $\bar{x}$-filter followed by a $\bar{y}$-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 $\bar{x}$-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:

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

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:

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

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.

b. Single Molecule Fluorescence

Suppose we want to measure the properties of individual sodium atoms. To do this, we can begin with sodium vapor at high pressure, and allow the gas to expand through a small nozzle to an area of lower pressure (supersonic expansion). The expanding gas can be

Low Pressure

High Pressure

Beam of Atoms
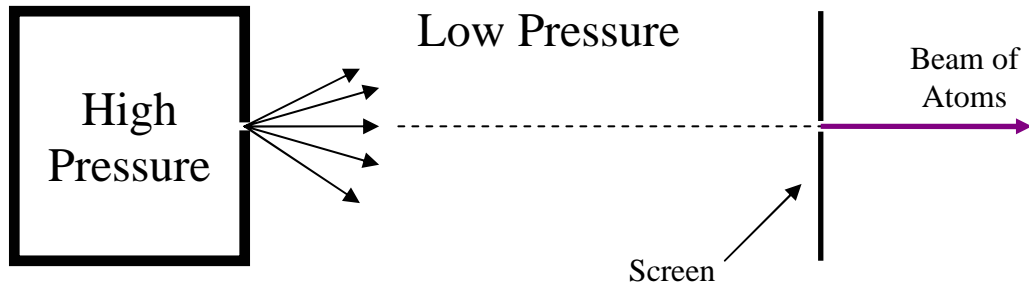
Screen

collimated by placing a sceen a distance away from the nozzle. This results in a very cold, very dilute beam of atoms.

Now, sodium has an important excited state (the 'D line' state) and we are interested in measuring its **lifetime**. That is, we are interested in determining how long it takes an excited sodium atom to emit a photon:

$$Na^* \rightarrow Na + photon$$
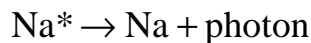
We know from experience that fluorescence typically occurs on the nanosecond time scale, so our measurements need to be **fast**. In order to accomplish this task, a team of graduate students working round the clock for three years designs a tuneable ultrafast laser that operates in the region of spectral interest (in this case, about **589** nm) with picosecond time resolution. They also design a very accurate detector with similar time resolution in the same spectral range. Using these two devices, we can measure the lifetime of the sodium 'D line' state by hitting the molecular beam with a laser pulse at one point along the beamline at time t_1 and placing a detector further down the line to register any sodium fluorescence at a later time t_2:

Detector

Na   Na   Na   Na   Na*   Na*   Na*   Na*   Na   Na

laser t_1 t_2
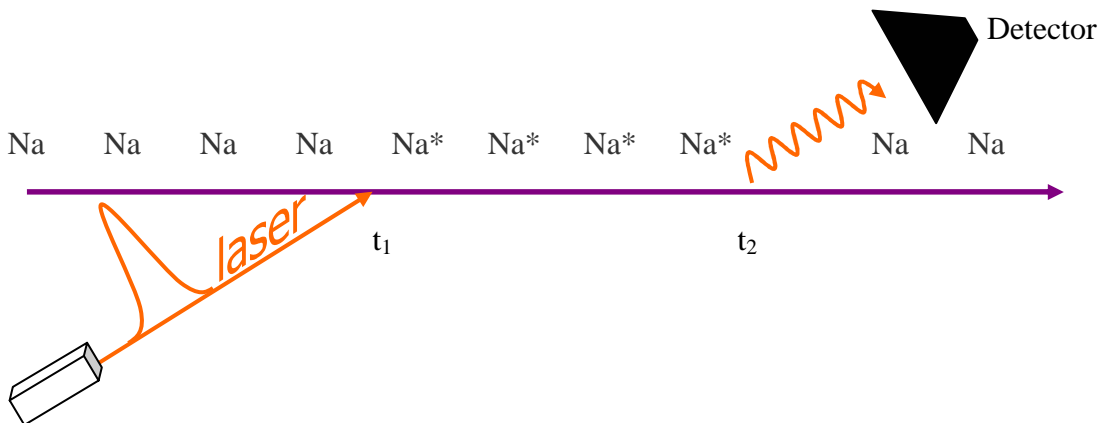
The lifetime is then determined by the time delay between excitation and emission (t_2-t_1). Now, even a very accurate detector misses many photons; further, very often, the pulse will not succeed in

exciting a sodium atom, because sometimes there won't be any atoms in the path of the laser beam (recall that the molecular beam is very dilute). Hence, we will have to try this many, many times before we get a successful result. But when we do, we can be very confident that the count came from the fluorescence decay (assuming we are careful to isolate our experiment from outside light sources).

So, we do this experiment several thousand times (we can fire the laser every microsecond, so this doesn't take as long as you might think) and eventually we register a successful count at the detector, and determine that the lifetime is 12.554(2) ns, where the uncertainty results from our picosecond time resolution in the excitation and detection. Just to check our results, we run the experiment again. This time we register a lifetime of 8.492(2) ns. If we run the experiment a third time, we register a lifetime of 22.100(2) ns. Again, we have been very careful to ensure that we have ps time resolution, and the initial states of the sodium atoms are **absolutely identical** in the repeated experiments. What could be going on here?

One interpretation of these experiments is in terms of the energy-time uncertainty relation. To review, if we want to have a short pulse, then, pictorially, we need to have higher frequency oscillations to make this happen:

Long Pulse

Short Pulse

High Frequency

High Frequency
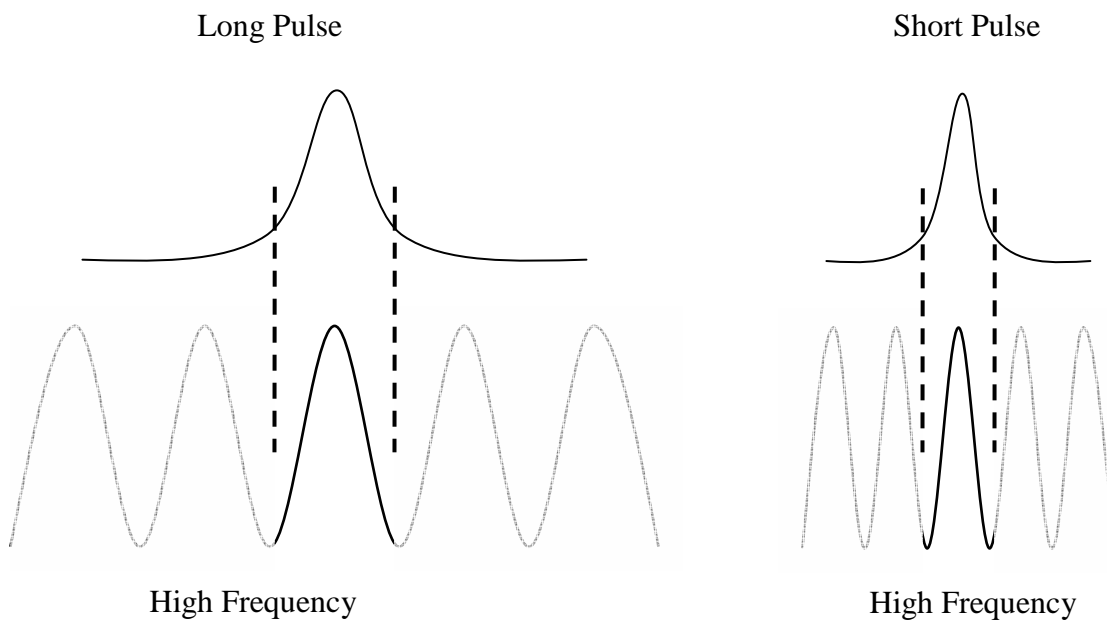
We can put mathematical heft to this if we think of the electric field of the emitted light as being a sum of different waves:

$$E(t) = \sum_i c_i \cos(\omega_i t)$$

Then, we define the width of the pulse:

$$\Delta t^2 = \left\langle t^2 \right\rangle - \left\langle t \right\rangle^2 = \int t^2 E(t) dt - \left(\int t \; E(t) dt \right)^2$$

and the variance of the frequencies

$$\Delta \omega^2 = \sum_i c_i \omega_i^2 - \left(\sum_i c_i \omega_i \right)^2$$

then it can be shown that, for any pulse

$$\Delta \omega \, \Delta t \geq 1.$$

We will prove this relation later in the course, but for now, let's take it as given. The uncertainty relation definitely would explain the spread in arrival times; for a given frequency resolution, the arrival time cannot be determined any more precisely than to within $\Delta t \geq 1/\Delta \omega$. Hence, it appears that there is some (very small) variance to the frequencies that is causing a very broad distribution of emission times. Indeed, if we measure the frequency of the emitted photon (rather than its arrival time) then in a series of runs we might find ω=589.59 nm, 589.58 nm, 589.61 nm … so it does appear that the large uncertainty in time is related to a small uncertainty in energy.

However, there are two perplexing things about this interpretation. First off, what is the origin of $\Delta \omega$? We can easily verify that it does not arise from our laser or from our detector; we can vary the frequency bandwidth of both and Δt does not change. Hence $\Delta \omega$ **must be a property of the molecule**. This is actually one of the first observations that lead to the development of QM, namely that atoms and molecules have discrete, fairly well defined energy states rather than the continuous spectrum associated with energies in classical mechanics. Our QM formalism will have to confront the existence of these "special" states.

The second perplexing issue is as follows: the uncertainty in time relates to the time difference t_1-t_2, but for times *between* t_1 and t_2 there are **no photons in the system**, there is only the sodium atom. How, then, does the sodium atom know to wait (on average) a time interval Δt before emitting the photon? To put it another way, how

does the sodium atom know about the energy-time uncertainty relation? This conundrum frustrated physicists for many years. On the one hand, we know atoms are particles, but under these circumstances the sodium atom is behaving like a wave (because the energy-time uncertainty relation is a property of waves). This **particle-wave duality** is another aspect of QM.

Before moving on to show how QM deals with these experiments, we return to the point we started with: can we do better than simply predicting the average outcome of an experiment? These experiments show that the answer, in general, is no; all observations are by their nature **probabilistic**: one cannot in general *predict* the precise outcome of an experiment. The best one can do is predict the *probability* that one outcome will be observed as compared to another. In fluorescence experiments above, we found that decay times around 10-20 ns are very common, while a decay time of, say 2 hours is very uncommon. If we repeat the experiment many, many times and make a histogram plot of the number of counts that appear after a given elapsed time (t_2-t_1), we obtain a probability distribution that looks like:
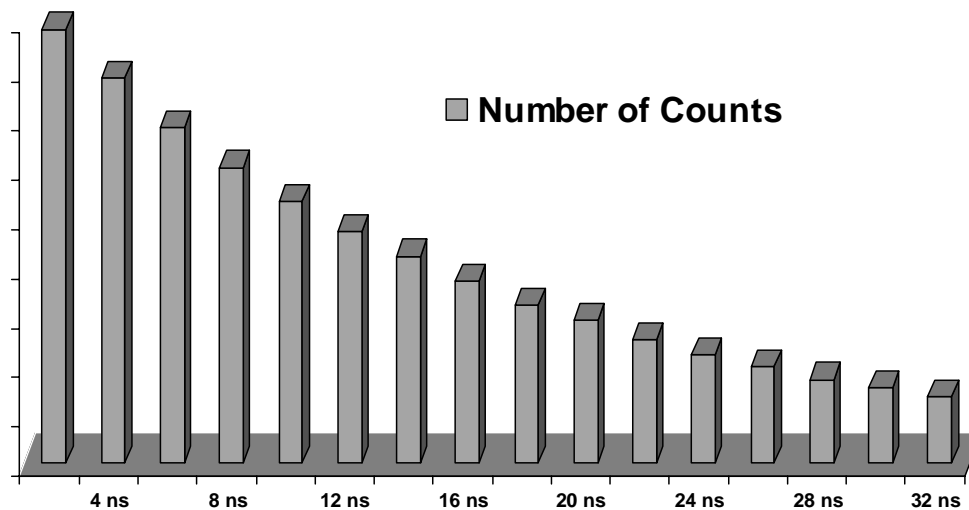
This tells us how likely it is that the molecule will fluoresce within a given period of time. The shocking thing is that this is absolutely the best one can do in terms of predicting the fluorescence time accurately. This effect is not due to some weakness of our experiment, nor to any inhomogeneity of our sample. Instead, it arises from a very deep limitation on what we can know about a quantum system. If we are interested in knowing whether the system

is in a given **state**, α, the best one can hope for is a way to predict the probability, P_α, that we will find the system in that state. If we perform the measurement of (t_2-t_1) once, we cannot predict the result; but if we perform the experiment many, many times and keep track of the individual times, we will **always** obtain the distribution above. In this sense our experiments are reproducible.

Quantum Interpretation of Polarization Experiments

In order to explain the very narrow distribution of energies of the sodium atom we need another rule. One can associate a set of eigenvalues, o_α, 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 fourth fundamental rule of QM is that <u>when measuring the value of the observable O, the **only possible** outcomes are the eigenvalues of $\hat{O}$</u>. If the spectrum of eigenvalues of $\hat{O}$ is discrete, this immediately implies that the resulting experimental results will be **quantized**. This immediately explains the narrow range of energies observed in the flourescence experiments. By detecting the frequency of the emitted photon, we immediately know the energy of the emitted photon (since $E = \hbar\omega = h\nu$). Further, we can measure the energy of the sodium atoms after emission. Then, by conservation of energy (which we certainly hope holds in this strange new world of QM!) we can determine the energy of the excited sodium atom:

$$E(Na^*) - E(Na) = \hbar\omega_{emit}$$

if there is only one possible eigenenergy of the system, then we expect a very narrow distribution of final energies, as is observed. Of course, concomitantly we expect a broad distribution of emission **times**.

In order to properly account for the wave-particle duality, we need to define the concept of a **superposition** of two states. Say that $|Na\rangle$ represents the sodium atom in the ground state and $|Na^*\rangle$ represents the excited state. In general, what does it mean for the system to be in the state $a|Na\rangle + b|Na^*\rangle$? Does this have any meaning at all? In QM, this superposition of states is interpreted to mean that the system has two physically accessible states and that no

measurement has been made to tell us which one is actually realized. When a measurement is made, the **superposition** collapses to one or the other of the observable states. Thus, between absorption and detection of the emitted photon, the sodium is said to be in a **superposition** of two states; it is simultaneously both excited and not excited. The two states can interfere with one another, and this gives rise to the (wave-like) uncertainty principle. We destroy the superposition by making a measurement that detects the photon (or does not). The measurement always gives us one of the two superposed states, but never both. After the **superposition** collapses to one state, the interference between states is destroyed.

This is popularly recounted in the Schrödinger's cat paradox. Suppose you have a sick cat and you put it in a box for a long time, and do not look at for a long time. Then according to quantum mechanics, it exists in a **superposition** of two states: "cat is dead" and "cat is alive". Once you open the box, however, it will either be dead or alive – the **superposition** will have collapsed to a single state. This is a bit of an unrealistic experiment, but it does illustrate one key point: Schrödinger did not like cats. This also illustrates the point that QM assumes no knowledge of anything that is not experimentally observable, because observation has the potential to change the outcome of later experiments. In between experiments our uncertainty about how the system evolves factors very heavily in how we make predictions about future experiments.

This leads to the fifth (and final) rule of QM: <u>after O has been observed and found to have a value o_α then the wavefunction of the system collapses into the eigenstate $|\psi_\alpha\rangle$</u>. This is perhaps the most unsatisfying of the postulates of QM, because the collapse is completely probabilistic – we can't predict the outcome no matter how hard we try. Indeed, there is a small but vocal faction of physicists that maintain that this postulate is, in fact, wrong. You may have heard Einstein's famous quote that "God does not play dice." This was Einstein's justification for rejecting the fifth postulate. The alternatives are called "hidden variable" theories. Basically one assumes that there is some variable that is not accessible to us experimentally that determines which state the wavefunction ultimately collapses to. Whether or not a hidden variable theory can

work (and the majority of physicists agree that no hidden variable theory will be able to match all the experimental data) the fact remains that the fifth postulate of QM is consistent with **all the experimental data ever collected**. Hence, while we may not like it on a philosophical level, we are not philosophers. From a scientific perspective, the fifth postulate is perfect.

We are now in a position to describe the fluorescence experiments. After getting hit by the initial laser pulse, the sodium atom is in the superposition state:

$$a|Na;\omega_i\rangle + b|Na*;0\rangle$$

where the first state means "no absorption, atom remains in ground state" and the second mean "absorption, atom excited" and (as we saw in the polarization experiments) the constants relate to the probability of the system being in each state. We will assume these states are orthogonal:

$$\langle Na;\omega_i|Na*;0\rangle = 0$$

which simply reflects the fact that the two states are mutually exclusive. Now, after a certain amount of time (*dt*), the atom will evolve to a new superposition

$$|\psi\rangle = a|Na;\omega_i\rangle + b|Na*;0\rangle + c|Na;\omega_i;\omega_f\rangle$$
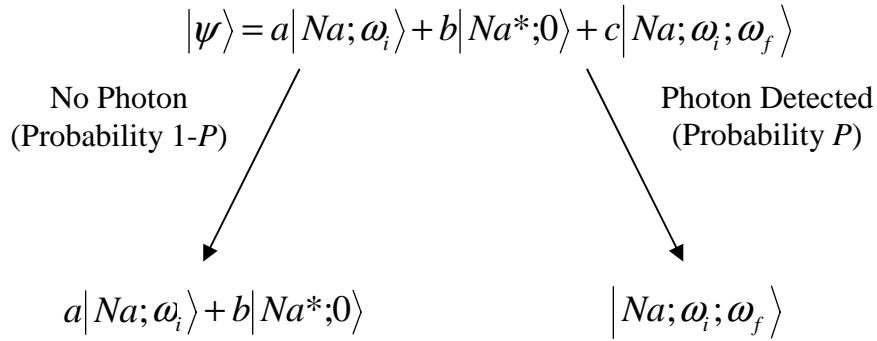
where the third state means "absorption, then emission, sodium returns to ground state". By turning on our detector, we **make a measurement** of the probability of finding this third state. Following our definitions from the polarization experiments, we could define the detector operator:

$$\hat{D} \equiv |Na;\omega_i;\omega_f\rangle\langle Na;\omega_i;\omega_f|$$

which will certainly tell us if there is a photon emitted or not. We find that the probability of detecting the photon is

$$P = \frac{\langle\psi|\hat{D}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{c^2}{a^2 + b^2 + c^2}.$$

After the measurement, the state collapses to either $a|Na;\omega_i\rangle + b|Na*;0\rangle$ (if no photon is detected) or $|Na;\omega_i;\omega_f\rangle$ (if the photon is detected). Thus, between time 0 and time *dt* we have something that looks like:

$$|\psi\rangle = a|Na;\omega_i\rangle + b|Na^*;0\rangle + c|Na;\omega_i;\omega_f\rangle$$

No Photon
(Probability 1-*P*)

Photon Detected
(Probability *P*)

$$a|Na;\omega_i\rangle + b|Na^*;0\rangle$$

$$|Na;\omega_i;\omega_f\rangle$$

Now, because we could detect the photon at any time, this same process repeats itself every *dt*. Hence, if we are interested in the number of atoms still exicited (*N*), we see that

$$dN = -P\,dt$$

$$\Rightarrow \frac{dN}{dt} = -P$$

$$\Rightarrow N(t) = -e^{-Pt}$$

Thus, we should see exponential decay. This is characteristic of probabilistic decay and is completely consistent with our experimental observations.