

2. An Overview of Physics at Nanoscale

In previous chapter we have seen that we use different physical theories to model the physics at different length scales of the nature. Here, we will see how the wave nature of matter becomes significant at relevant length scales. In this chapter we will take a look at the basics of quantum mechanics. Using the principles from quantum mechanics we will construct a model for solids. We will also review basics of the electromagnetic theory that is relevant to nanotechnology.

2.1 New Physics Towards "Nano"

"After dinner, the weather being warm, we went into the garden and drank tea, under the shade of some apple trees...he told me, he was just in the same situation, as when formerly, the notion of gravitation came into his mind. It was occasion'd by the fall of an apple, as he sat in contemplative mood. Why should that apple always descend perpendicularly to the ground, thought he to himself..."

This excerpt is taken from William Stukeley's *Memoirs of Sir Isaac Newton's Life* book on the famous apple story. A falling apple had inspired Newton to think about a set of rules that keep the moon up in the orbit of the Earth while that makes an apple fall from a tree. How far can we stretch this thinking? Would it be possible to apply the Newtonian physics to galaxies or atoms? Interestingly enough the Newtonian mechanics can explain many of the observed phenomena in nature very well. Yet, when we start investigating phenomena that directly arise from the atomistic properties of matter we will start seeing the quantum effects. Indeed, at the end of 19th century, in a speech Lord Kelvin had given, he stated that there are two significant problems of physics which one of them was relevant to the quantum mechanics while the other was to the theory of relativity before these theories were around.

Figure 2.1 gives the visible spectrum of the light that reaches to the Earth surface from the Sun. There are missing lines in the spectrum due to absorption of the elements in the atmosphere of the Sun as well as the Earth. More interestingly these missing lines come in discrete form. They have a very specific wavelength as well as width. Indeed, this is one of the first hints towards the

quantum nature of the atomistic physics. The observation of the spectral lines dates back to early 19th century.

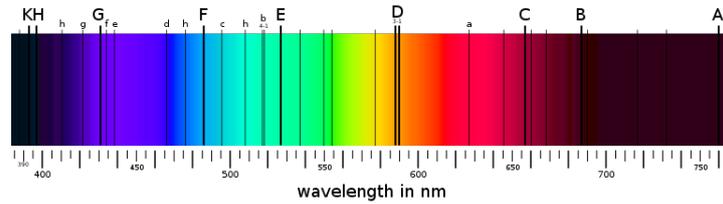


Figure 2.1: Chart shows the solar spectrum also known as the Fraunhofer spectrum. The missing lines correspond to the discrete energy levels of the elements absorbing the light at specific energies. (Courtesy of Wikipedia)

Another significant mystery in the Newtonian physics was the spectrum emitted by a heated black body. A black body is an hypothetical object that absorbs all the incident radiation, thus it heats up and re-emits radiation at a different wavelength. The problem was, when the problem solved taking energy as a continuous parameter, emitted power increases exponentially towards shorter wavelengths. The solution came in 1900 by Max Planck, a German physicist. He first found the formula that explains the observed spectrum. With the agreeing formula in hand, he realized that the energy needs to be "quantized". This quantization, resulted in the correct explanation for the black body radiation and also for the first time the Planck's constant appeared in a formula to spark the beginning of the quantum mechanics. Five years later, another significant contribution to

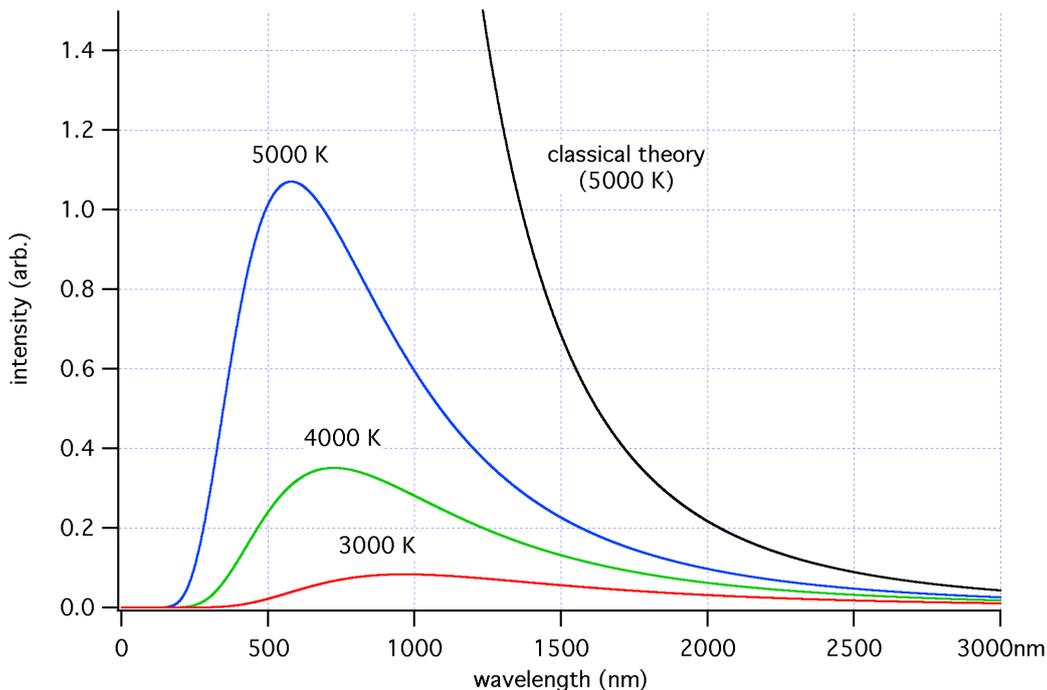


Figure 2.2: Blackbody radiation at various temperature compared to the prediction of the classical theory (Courtesy of Wikipedia).

the quantum theory came from Albert Einstein in 1905. After Maxwell's equations (1860's) there was no doubt that the light was an electromagnetic wave from a theoretical stand point. However, when the wave picture applied to the photoelectric effect, the momentum delivered to the metal

surface was simply not enough to knock out any electrons. Einstein, explained this problem by quantizing the light, this time. This is the first glimpse of the wave-particle duality! Under certain conditions it seems like the light behaves like a wave and in some others it behaves like a particle!

2.1.1 Wave Nature of Matter

Now we will fast forward in the history of quantum mechanics by about a 20 years to understand the wave nature of matter. An experiment performed by Davisson and Germer demonstrated that electrons behave as a wave.

de Broglie Relation and Davisson-Germer Experiment

An old PhD student Lois de Broglie, came up with an hypothesis that applies Planck's and Einstein's ideas to matter. He claimed that matter just like light, may have a wave nature and its wavelength can be written as

$$\lambda = \frac{h}{mv} \quad (2.1)$$

where h is the Planck's constant, m is the mass and v is the velocity of the matter. This relation, as we will see later on, is consistent with Bohr's atomic model and explains a major assumption in that model. Around similar dates Davisson and Germer was working on electron scattering from a nickel surface and in a meeting they realized that the data they get can be explained by the de Broglie's hypothesis. From the diffraction data they extracted that for their 54 eV electrons the Bragg's law give 0.165 nm while the de Broglie wavelength is 0.167 nm, in close agreement.

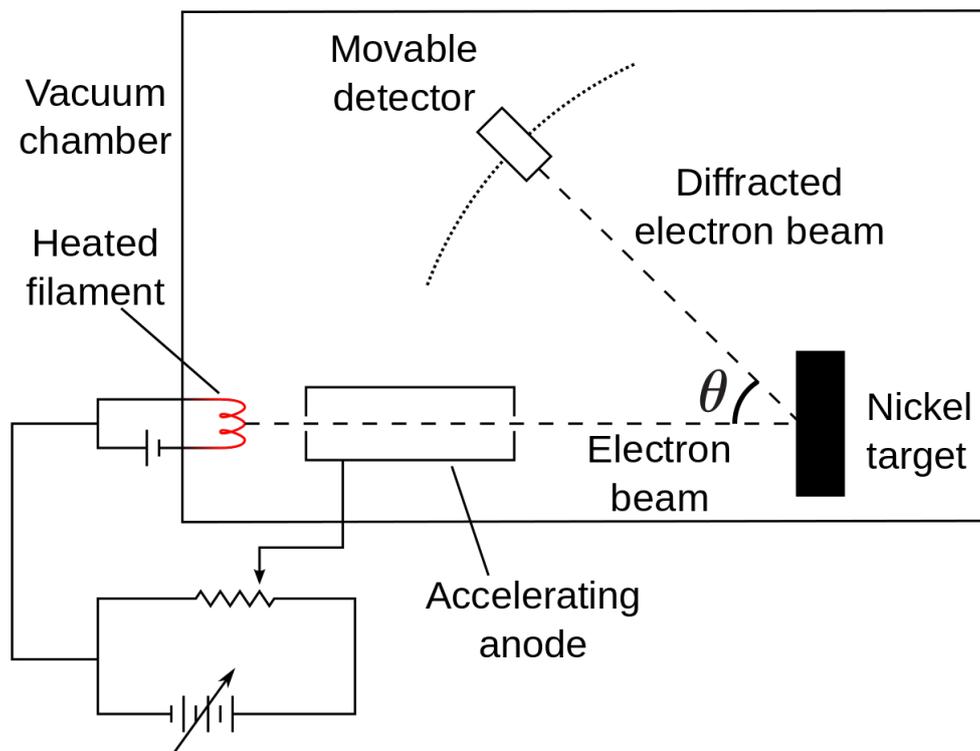


Figure 2.3: Schematic of the Davisson-Germer Experiment (Courtesy of Wikipedia).

Yet it is difficult to comprehend what this wave-like nature of matter is as in our classical world it has no counterpart. It is important to understand that this wave behavior is not a property

in ordinary three-dimensional space, but is in an abstract configuration space. There are real consequences to it though! To be able to comprehend it further, we need to take a deeper look in the the mathematical structure of the quantum theory.

2.1.2 Probability Density

In physical systems, dynamics are determined by the relevant energies and time evolution of the system under these energies. It turns out that in quantum mechanics a quantity called the **wave function** evolves with the energy of the system and **wave function**² gives the probability density. The wave function gives a description of the quantum system.

Notation 2.1. Wave Function

1. Let's denote the wave function with $\Psi(x, t)$;
2. Thus the probability density will be $|\Psi(x, t)|^2$.

Probability density is a function of spatial position and time and by integrating this density over relevant quantities we can find the probability of finding the value of the parameter that we are interested in a given range of values. At this point I am aware that this explanation might sound a little too abstract to the reader. Here, I will give a classical example to elucidate the concept of probability density a bit more.

■ **Example 2.1** Let's assume we drop a pebble from an height of h . Assuming that the gravitational acceleration g is constant throughout h , find the probability density of position of the pebble.

Solution Time dependent position of the pebble will be given by $x(t) = h - \frac{1}{2}gt^2$ and the speed is $v(t) = \frac{dx}{dt} = gt$. When the pebble hits the ground, the total time of $T = \sqrt{\frac{2h}{g}}$ will be passed. At any infinitesimal time section dt probability of finding the pebble is $\frac{dt}{T}$ will be equal to the probability density of position of the pebble $\rho(x)$ times the infinitesimal position segment dx . Thus, $\frac{dt}{T} = \rho(x)dx$. We would like to manipulate the equation so that we get a time independent $\rho(x)$. $\frac{dx}{dt} = (T\rho(x))^{-1}$ and we can write $gt = (T\rho(x))^{-1}$. Instead of T we can use the above expression, $\rho(x) = \sqrt{\frac{g}{2h}}/gt$ and $\rho(x) = \sqrt{\frac{1}{2hgt^2}}$. Here we can replace gt^2 with $2x$ and we will have $\rho(x) = \sqrt{\frac{1}{4hx}}$. If we plot this probability density with respect to position we will see that towards the ground probability of finding the pebble decreases. One other parameter we can find using the probability density is the average position of the particle, $\langle x \rangle$. We simply integrate all possibilities from 0 to h ,

$$\langle x \rangle = \int_0^h x\rho(x)dx \quad (2.2)$$

which will give the expected value of $h/3$ as the average. Also if you check the total probability of finding the pebble you will get 1! ■

Definition 2.1.1 — the Schrödinger equation. There is no derivation of the Schrödinger equation. However its form uses the concept of conservation of energy. It is a linear partial differential equation.

(Kinetic Energy Term + Potential Energy Term) $\Psi(x,t) =$ Total Energy Term $\Psi(x,t)$

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right]\Psi(x,t) = -i\hbar \frac{d}{dt}\Psi(x,t) \quad (2.3)$$

For any given system if you solve the Schrödinger equation, you will find out how the wave function (thus the probability density) evolves in time and space. However, we will see shortly that this is easier said than done. The complexity of the equation makes it impossible to solve it analytically even for very simple systems. The difficulty mainly arises from the difficulty of solving many body interactions.

2.2 Basic Concepts in Statistical Models

When we talk about statistics, and probabilistic models there are two major quantities we are interested in the most:

1. Average
2. Standard deviation

As you will see shortly, average is referred as the "expectation value" and standard deviation is referred as the "uncertainty" in quantum mechanics.

2.2.1 Average - Expectation Value

Lets consider this very simple example. Imagine there is a class of 12 people and after a test, scores are distributed as 3 students got 40, 5 students got 45, 1 student got 50 and 3 got 55. The average of the test can be calculated as follows:

$$\langle av \rangle = \frac{3 \times 40 + 5 \times 45 + 1 \times 50 + 3 \times 55}{12} \approx 46.7 \quad (2.4)$$

As you can see, from this very simple example that the average is not the most probable value. If you were asked to pick a student randomly from the class, most probably you will choose someone that got 45, as 45 is the most probable grade.

We can generalize this example to a more general case where there are N people in the class and there J are the grades. If there $n(J)$ people who got J from the test, then the average will be

$$\langle av \rangle = \frac{\sum Jn(J)}{N} \quad (2.5)$$

Thus probability of randomly choosing a person with grade J is $P(J) = n(J)/N$. Using this we can write the above average equation simply as

$$\langle av \rangle = \sum JP(J) \quad (2.6)$$

When we deal with a continuous example, then we can express the probability along certain values in terms of probability density $\rho(J)$ and an interval dJ . In the limit as dJ goes to 0, the summation in equation (2.6) becomes an integration:

$$\langle av \rangle = \int J\rho(J)dj \quad (2.7)$$

We will use this form of the average expression extensively in finding quantum mechanical expectation value.

2.2.2 Standard Deviation - Uncertainty

In statistics, the standard deviation quantifies the amount of variation of a set of data points. A small standard deviation means that the values are cluttered around the mean while a large standard deviation means a spread of values over a wider range around the mean. We are after a positive number that will give a measure of deviation of each grade from the average. So we look at square root of the average of the square of $J - \langle J \rangle$ which is $\sigma = \sqrt{\langle (J - \langle J \rangle)^2 \rangle}$.

Lets go back to the example of class with 12 students in previous subsection.

$$(40 - 46.7)^2 = (-6.7)^2 = 44.89 \quad (45 - 46.7)^2 = (-1.7)^2 = 2.89 \quad (2.8)$$

$$(50 - 46.7)^2 = (3.3)^2 = 10.89 \quad (55 - 46.7)^2 = 8.3^2 = 68.89 \quad (2.9)$$

If we take the average of these values then, we get

$$\sigma^2 = \frac{3 \times 44.89 + 5 \times 2.89 + 1 \times 10.89 + 3 \times 68.89}{12} \approx 1.58 \quad (2.10)$$

$$\sigma = 1.26 \quad (2.11)$$

This value shows, on average by how much the grades are away from the average value.

In the context of quantum mechanics this quantity will give us the uncertainty. If we had all the students to get the same grade, the standard deviation would be zero, thus we would be certain about the grade of any randomly chosen student. However, when there are multiples of vales, our certainty on the outcome of any measurement will be lowered by the amount of spread of the values. To have more generalized definition of the uncertainty lets massage $\sigma = \sqrt{\langle (J - \langle J \rangle)^2 \rangle}$. a little.

$$\sigma^2 = \langle (J - \langle J \rangle)^2 \rangle \quad (2.12)$$

$$= \sum (J - \langle J \rangle)^2 P(J) \quad (2.13)$$

$$= \sum J^2 P(J) - \sum \langle J \rangle^2 P(J) \quad (2.14)$$

$$= \langle J^2 \rangle - \langle J \rangle^2 \sum P(J) \quad (2.15)$$

$$= \langle J^2 \rangle - \langle J \rangle^2 \quad (2.16)$$

2.2.3 The Expectation Value and the Uncertainty in Quantum Mechanics

As we have seen in the continuous case where x is not a discrete parameter anymore, we deal with probability density rather than probabilities to calculate the average and the standard deviation. By the statistical interpretation in subsection 2.1.2 $|\Psi(x, t)|^2$ is the probability density. Thus for instance to find the expectation value of the position we will calculate

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi(x, t)|^2 dx \quad (2.17)$$

This expression can be generalized to any quantum mechanical observable as

$$\langle O \rangle = \int_{-\infty}^{+\infty} \Psi(x, t)^* O \Psi(x, t) dx = \langle \Psi | O | \Psi \rangle \quad (2.18)$$

Similarly for the average of square of an observable can be calculated as

$$\langle O^2 \rangle = \int_{-\infty}^{+\infty} \Psi(x, t)^* O^2 \Psi(x, t) dx = \langle \Psi | O^2 | \Psi \rangle \quad (2.19)$$

R Here I would like to introduce the Dirac notation. In Dirac notation rather than wave function we use bras($\langle\Psi|$) and kets($|\Psi\rangle$) (bra-c-kets) to represent quantum states. In the following sections we will utilize and introduce this notation more extensively.

The expectation value in quantum mechanics is the average of the many measurements on the exact copy of a system. It is not outcome of a single measurement or it may not be the most probable outcome of a measurement.

The uncertainty is a measure of how much the possible attainable values spread from the expectation value. Larger spread of values mean larger uncertainty in the observable.

2.3 Heisenberg's Uncertainty Principle

Let's imagine that we have an electron inside a box and we have an imaginary microscope to measure the position and the momentum of the electron. This microscope uses photons (light) to perform the measurements. To measure the position of the electron with high precision the experimenter needs to use short wavelength, thus high energy photons. However, this means that upon collision with the electron, photon will transfer large and uncertain amount of momentum to the electron, thus making electron scatter in a random direction. If the experimenter tunes the photon energy to a lower value, than the scattered photon will not reveal the position of the electron.

This thought experiment, indeed summarizes the Heisenberg's uncertainty principle. Although, the Heisenberg's microscope example overestimates the loss of precision, and it is misleading in the sense that it takes the uncertainty principle as an observer effect, it provides a more comprehensible picture of the Heisenberg uncertainty principle. It should be noted however that the uncertainty principle in quantum mechanics is an inherent property of the theory. It arises in all wave-like systems and roots down to the fact that quantum matter behaves like a wave. We will visit the Heisenberg's Uncertainty Principle after studying an exemplary systems.

2.3.1 The Stern-Gerlach Experiment

Perhaps one of the most striking experiments in the history of quantum mechanics is the Stern-Gerlach experiment. This simple experiment truly demonstrates many intricate aspects of quantum mechanics.

R To understand the Stern-Gerlach experiment, notion of "spin" has to be introduced. Spin is an intrinsic property of elementary particles like the mass. We will come back to notion of spin in the following chapters.

Experimental Details

Experimental setup consists of an oven that heats silver atoms to form a silver vapor. This vapor is sent through a collimator and then it passes through an inhomogeneous magnetic field. Silver 47 has 1 unpaired electron in its 5s orbital. Spin of this 47th electron dictates the overall magnetic moment of the silver atom. In other words we can say that silver atoms behave as tiny magnets where the magnetic moment of this magnet μ is proportional to the electron spin \mathbf{S} . Now, as these silver atoms pass through the inhomogeneous magnetic field pointing in one direction they experience a force that is proportional to the alignment of silver magnetic moment with the applied magnetic field.

When the silver atoms leave the furnace they have no preferred orientation of magnetic moment. They can be in any direction and classically we would expect to see silver atoms to be uniformly diverted by the magnetic field. However, the result shows that the atoms come out of the magnetic

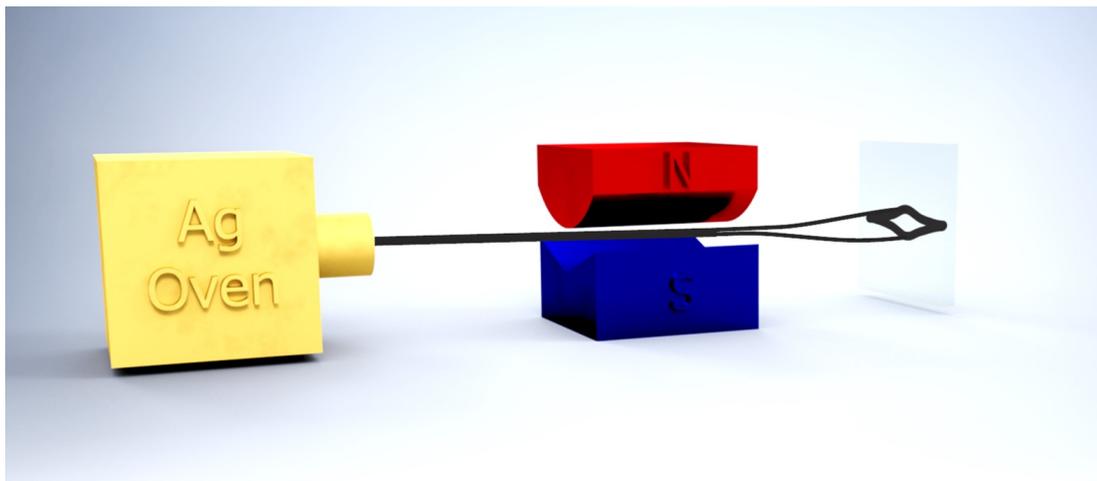


Figure 2.4: Schematic of the Stern-Gerlach Experiment. Silver atoms emitted from the oven goes through an inhomogeneous magnetic field. On the screen atoms split into two distinct bunches. Classical expectation would be a uniform distribution of atoms on the screen as the atoms have random orientation.

field in two distinct bunches. This separation indicates that the electron spin is quantized and can be in two distinct values.

A careful reader will ask these questions, what is so particular about the chosen direction? What will happen if we rotate the inhomogeneous magnetic field by 90 degrees? The answer is simply there is nothing particular about the choice of the direction and a rotation will only change the axis atoms will spread.

Consecutive Measurements

What will happen if I place two consecutive inhomogeneous magnetic fields perpendicular to each other in the path of the silver atom beam? In other words, one outcome of the first magnetic stage will be directed to another magnetic stage at a 90 degree orientation to the first one. One naively expects that the beam will split into two again, in the perpendicular direction to the first stage. This expectation would be correct. Now, lets take an output of the second stage and one more time lets pass it through the same orientation as the first stage. What will be the outcome? Again, naively it is tempting to think that since the beam was composed of one particular choice of atoms, another selection after the second stage, which was in a different direction anyways, would have no effect on the result. Thus, the sole outcome would be the selection after the first stage. However, this is where another interesting result of the Stern-Gerlach experiment emerges. The result is just like the first stage we observe two distinct beam bunches. A schematic of consecutive measurements is given in Figure 2.5.

The reason for this bizarre outcome lies in the heart of the quantum mechanics. To explain it better, I will introduce a notation of expressing the electronic spin. Let's say we take an orthogonal set of spins along x, y and z directions. As we know from the outcome of the Stern-Gerlach experiment for each spin direction we have two possible states, up and down¹. Using the Dirac notation we can denote up state along the z direction as $|S_z, \uparrow\rangle$ and down state $|S_z, \downarrow\rangle$. This notation can be extended to x, y directions as well. Now, again from the Stern-Gerlach experiment we know that a measurement along x must have both $|S_z, \uparrow\rangle$ and $|S_z, \downarrow\rangle$ in equal parts. So we can

¹Indeed you can name it + and - or this and that, what matters is you need something to set them apart.

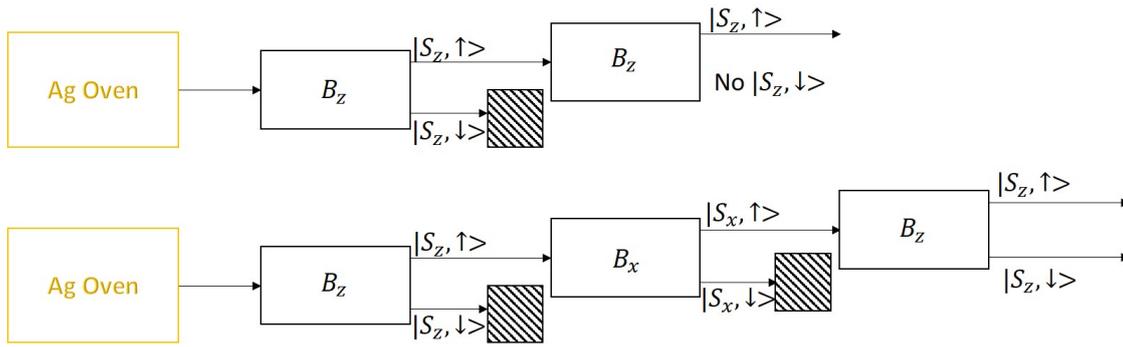


Figure 2.5: Schematic of consecutive Stern-Gerlach Experiment. Top experiment shows two consecutive measurements along the z direction. After the second measurement there is no down component. In the second case, when we measure x after z we get splitting along the x direction. Another measurement along z on any of the outputs of the x measurement again yields both up and down.

write $|S_x, \uparrow\rangle$ as:

$$|S_x, \uparrow\rangle = \frac{1}{\sqrt{2}}|S_z, \uparrow\rangle + \frac{1}{\sqrt{2}}|S_z, \downarrow\rangle \quad (2.20)$$

Similarly $|S_x, \downarrow\rangle$ as:

$$|S_x, \downarrow\rangle = \frac{1}{\sqrt{2}}|S_z, \uparrow\rangle - \frac{1}{\sqrt{2}}|S_z, \downarrow\rangle \quad (2.21)$$

The convention why $-$ sign is used in $|S_x, \downarrow\rangle$ comes from the orthogonality condition and its discussion is beyond the scope of this text. These two expressions can explain how we can have up and down results after consecutive measurements along x and z . Using the notation introduced earlier lets say we measure z followed by x

$$\langle S_x, \uparrow | S_z, \uparrow \rangle = \frac{1}{\sqrt{2}} \langle S_z, \uparrow | S_z, \uparrow \rangle + \frac{1}{\sqrt{2}} \langle S_z, \downarrow | S_z, \uparrow \rangle = \frac{1}{\sqrt{2}} \quad (2.22)$$

$$\langle S_x, \downarrow | S_z, \uparrow \rangle = \frac{1}{\sqrt{2}} \langle S_z, \uparrow | S_z, \uparrow \rangle - \frac{1}{\sqrt{2}} \langle S_z, \downarrow | S_z, \uparrow \rangle = -\frac{1}{\sqrt{2}} \quad (2.23)$$

So the probability of having up and down states after taking the up spin from z measurement is $|\langle S_x, \uparrow; \downarrow | S_z, \uparrow \rangle|^2 = 1/2$.

This interesting result actually is an indicator of the Heisenberg Uncertainty principle. When we measure one state, we lose the information on the other. Yet, this time our variables are not position and momentum but rather spin along different axes. When, there is such a relation among the pairs of measurable quantities we call them **incompatible**. Likewise, if two measurable quantities can be measured simultaneously they are called **compatible**. An example to compatible observables would be the square of the total spin and spin along any axis.

2.3.2 The Uncertainty Principle

Now we can introduce the Heisenberg's Uncertainty Principle in firmer grounds.