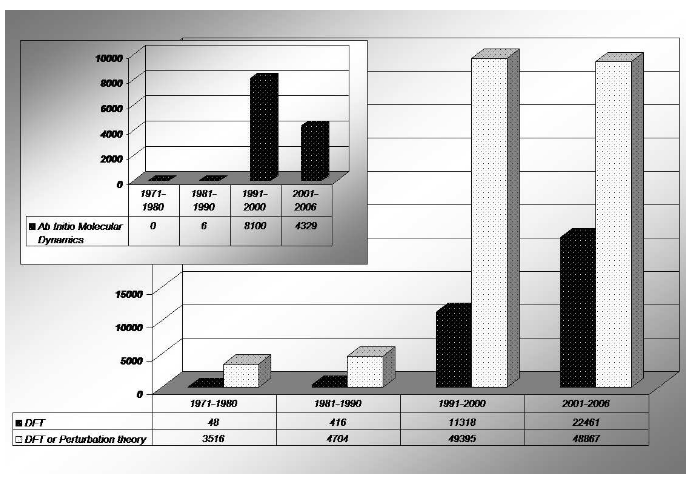
1 Now, Why do we want to learn Quantum Mechanics

- Quantum mechanics is a mathematical theory that can be used to *predict* chemical properties.
- **But this fact has been known since the 1920s, so what's new?**
- Today with *better computational methods and faster computers*, one is able to study systems of interest to chemistry.
- With accurate quantum mechanical calculations, one can calculate properties for systems that are *difficult* to isolate experimentally. This may result in a quantitative understanding of transition states, prediction alternate reaction pathways, and *sometimes prediction of new chemical concepts*!!
- A brief search on web of science shows an exponential growth in the number of articles that pertain to the utilization and development of quantum chemical tools:



- Quantum chemistry is well on its way towards becoming an established chemical analysis and predictive tool.

2 The Stern-Gerlach experiments

1. To learn quantum mechanics, we could choose one of two options:
   (a) A historical perspective: experimental findings between 1905 to 1922. In this approach there are some key experiments such as black body radiation, photo-electric effect, etc.
   (b) The other option is to concentrate on one of these experiments to convey the need for a "new physics"
2. In this course we do the latter. During the first week of classes we study the Stern-Gerlach experiments, which in my opinion, fully illustrate the need for a quantum mechanical theory.
3. However, in the process of studying the results from the Stern-Gerlach experiments, we will note that these can be understood by constructing an analogy to polarized light. Furthermore, we will also see that polarized light can be treated using vector algebra. Hence we find it necessary to use vectors to understand quantum mechanics. As a result, your will need to complete the linear algebra and complex variables handouts before proceeding further.
4. Silver atoms are heated in an oven that has a small hole through which some atoms escape.

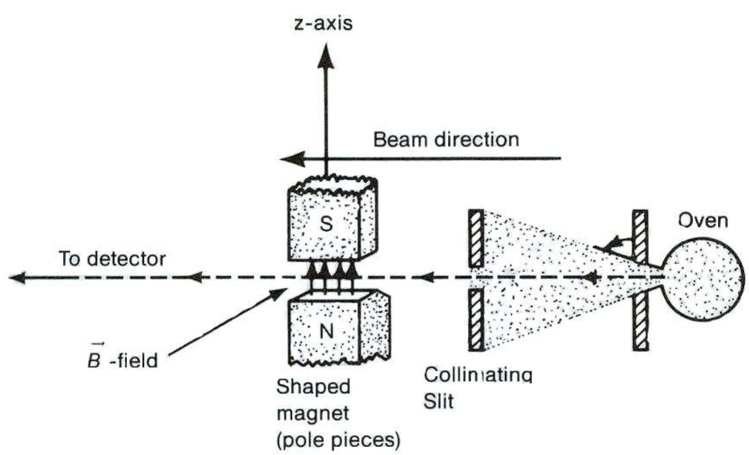


Figure 1: The Stern-Gerlach experimental setup.

5. The atoms go through a region that contains a magnetic field as seen in the figure. What happens?

6. To understand what happens let us analyze the silver atoms.
   - The atomic number for silver is 47.
   - So it has 46 electrons that are paired (*i.e.* upspin-downspin partners) and there is one electron that is unpaired.
   - Classical theory of magnetism : a "spinning electron" behaves as a magnet and the heavy silver atom has a magnetic moment due to the one extra (unpaired) 47th electron. *So each silver atom is like a tiny magnet due to that extra, unpaired electron.*
   - Any magnet that is placed in a magnetic field, experiences a force due to the magnetic field which bends its path.
   - Hence each silver atom that escapes from the oven into the region of the magnetic field experiences a force that bends its path.
7. Which way do the paths bend for a given silver atom?

8. To explain this, a little understanding of magnetism helps:

   - Force on the silver atom that drags it along the direction of the magnetic field is proportional to the magnetic moment of the silver atom.

   $$F_z = \frac{\partial}{\partial z} (\mu \cdot B) = \mu_z \frac{\partial B_z}{\partial z} \tag{2.1}$$

   - The equation above implies there is a force on the silver atom due to its magnetic moment.
   - This force is along z (the direction of the magnetic field). and proportional to the component of the magnetic moment along the direction of the magnetic field (μ_z).
   - The magnetic moment of the silver atom is proportional to the spin of the extra electron

   $$\mu \propto \mathbf{S} \tag{2.2}$$

   - Hence the force on each silver atom (which drags the silver atom and bends its path) is proportional to the spin component of the extra electron along the z-axis direction.

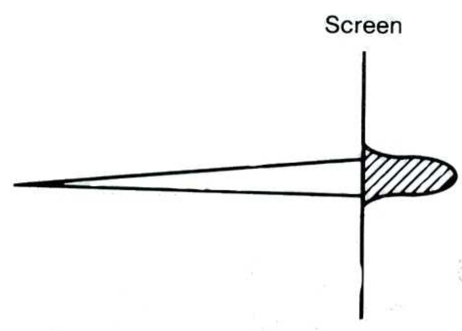
   $$F_z \propto \mathbf{S_z}, \tag{2.3}$$

   $$F_z = C\mathbf{S_z} \tag{2.4}$$

   where C is some constant.

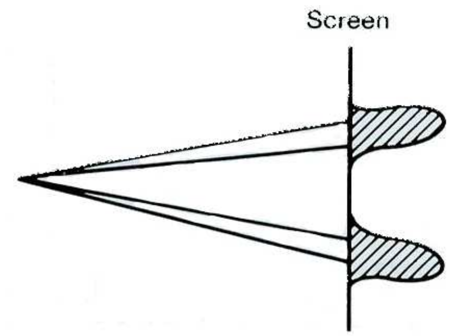
9. Thus, the z-component of the spin of the extra electron on the silver atom determines the force on the silver atoms

10. But the silver atoms are rolling and tumbling around freely inside the oven.
11. Does this mean their spins can be aligned along any direction as they tumble and roll? Perhaps so. (*We certainly do not know otherwise at this point.*)
12. If the spin can be aligned along any direction the spin component along the z-axis can be *any number* between +**S** and -**S**.
13. Hence the force acting along the z-direction on the silver atom can have any value between +C**S** and -C**S**.
14. Which means the silver atoms can bend on either sides up to some maximum value. The amount it bends is proportional to the force acting on it.
15. We already saw earlier that we expect the spins to be oriented randomly as the silver atoms roll and tumble.
16. *Hence on the detector there should be a continuous distribution of silver atoms as shown in the figure*



17. **Is this what Stern and Gerlach really observed? No !!!!!!** What did they see?

18. They saw just two spots like what we have in the figure below.



19. Whats wrong? Why did they see just two spots.

20. Something has got to be wrong in the "classical" thinking that we exhibited above.

21. How can we reconcile two spots on the detector, instead of one continuous spot?

22. The spin of the silver atoms, along the z-direction, cannot be random. This is the only possible explanation for what Stern and Gerlach saw.

23. Empirically, $\mathbf{S_z}$ has to be quantized and not continuous and can have only two values:

$$\mathbf{S_z} = \pm\hbar/2 \tag{2.5}$$

where h is a constant number derived by Planck and known as the Planck's constant. $\hbar$ is a simplified notation of $h/2\pi$. We call these up-spin and down-spin but realize that we have used a z-magnetic field. This will be important later.

This was quite a surprising result at the time when classical mechanics and classical theory of electro-magnetics were considered complete. However, this was not the only experiment that exposed the limitation of the classical style of thinking. There were others: Planck's black body radiation and the Einstein-debye theory of specific heats to name a couple. We have chosen to concentrate here only on the Stern-Gerlach so as to quickly expose the short-comings. What we have arrived at above is known as **spin quantization**, a very important concept in quantum mechanics. *Spin is quantized not continuous.*

24. As to why exactly spin has to be quantized we will see further down when we construct an analogy between the Stern-Gerlach experiments and polarized light. But, for now, lets proceed further to other even more surprising facts.

2.1 Sequential Stern-Gerlach experiments

The sequence of experiments that I consider here can be performed computationally using the java applet at:
http://www.indiana.edu/%7Essiweb/C561/spins.jar. You should try this yourself and we will have some homework problems based on this applet. If you have difficulties, please see us.

1. The experiments thus far can be summarized using the following figure.

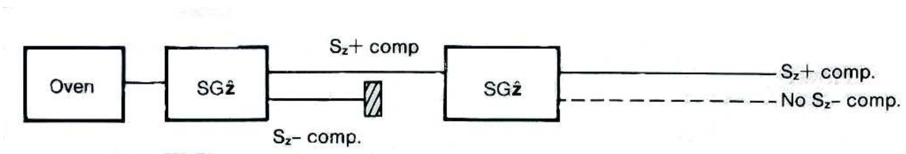


Figure 2: SG$\hat{z}$ represents a Stern-Gerlach experiment with z-magnetic field. Clearly, the incoming beam of silver atoms is split as we have seen before. We depict the state of the silver atoms having spin $+\hbar/2$ as S_z+, etc.

2. What happens if we choose to pass S_z^+ through a magnetic field oriented along the x-direction?

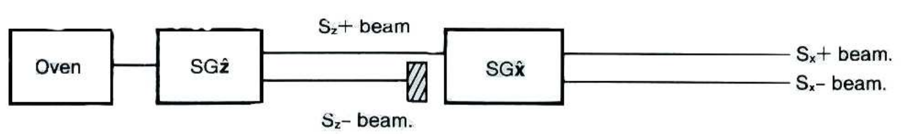


Figure 3:

3. Experimentally we find the states S_x^+ and S_x^-.
4. This makes sense. Although S_z^+ has a non-zero spin component along the positive z-axis, there is no definite information here regarding what the component along x-axis might be.
5. What happens when we block S_x^- and let S_x^+ go through another magnetic field oriented along the z-direction
6. A completely different story. *We are in for a shock.*

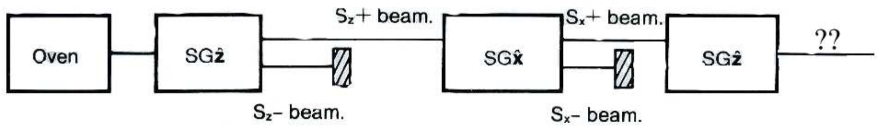


Figure 4:

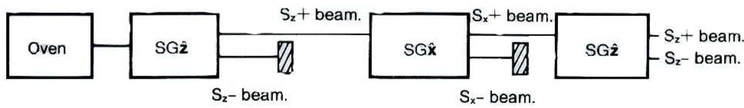


Figure 5:

7. We find that both $\mathbf{S_z^+}$ and $\mathbf{S_z^-}$ are present in the result.
8. **How can this make any sense? We blocked off $\mathbf{S_z^-}$ before it entered into the x-directed magnetic field. Yet it makes its appearance after passing through the z-directed magnetic field. Whats going on?**
9. This last part *most drastically* illustrates the peculiarities of quantum mechanics. And it is an observed fact and a complete surprise !!
10. How is it possible that $\mathbf{S_z^-}$ which we completely eliminated initially has resurfaced? It almost seems as if when we passed the $\mathbf{S_z^+}$ state through the x-magnetic field, it forgot that it was passed through the z-magnetic field before that. Weird!
11. Is there an explanation? Yes. And we will get into that in a little bit. But it is to be clearly understood that this problem encountered between $\mathbf{S_z}$ and $\mathbf{S_x}$ is not due to incompetence in the experiment and cannot be done away with by improving the quality of the experiment or such. There is a very fundamental concept here that we will get into next.

