History of Pre-Quantum Mechanics con't

[Note: The following history is again only a pale approximation of what actually happened. It is at times an-historic, explaining the past in terms of the present.]

Specific Heat

There were a number of other developments during the period before 1925. In the next year after he had published his paper on the photo-electric effect, Einstein applied the same reasoning to another puzzle. In particular, the specific heat of materials behaved strangely at low temperatures. It fell. The specific heat is the amount of energy required to raise the temperature of a material by one degree. Ie, if E is the internal energy of a substance (usually per unit volume), then $C = \frac{\partial E}{\partial T}$. It was found that the specific heat fell at low temperatures– for many materials, especially insulators, it drops as T^3. However, one could apply that same arguments as Raleigh applied to the electromagnetic field to argue that each mode of motion within the material should have kT of energy. Since the number of modes should not change as the temperature is lowered, the energy should just be equal to the number of modes times kT, and the specific heat should be constant– just equal to the k times the number of modes.

However, as Planck had shown for black-body radiation, the energy in the material is not simply equal to kT per mode. In particular Einstein argued that the energy should be very similar to that given by Planck's formula. In particular, instead of the modes having energy of $kT/2$ per mode, the energy in a mode should be more like

$$\epsilon = \frac{h\nu}{(e^{\frac{h\nu}{kT}} - 1)} \tag{1}$$

What this means is that, for modes whose "energy" $h\nu$ is much less than kT, the energy per mode is just $kT/2$. However, for higher frequencies, the contribution to the energy dies off exponentially. Ie, modes whose frequency is higher than the temperature (using h and k to convert frequencies to temperatures) are frozen out. They do not get excited, or have any energy. Again, for low enough temperatures, the number of modes in "sound waves"– modes of vibration of the material– is just the same as for electromagnetic radiation in a box. Ie, the total energy density goes as T^4 and the specific heat would then go as T^3.

For higher temperatures, kT/h would become higher than the maximum frequency of vibration of the modes in the material. In this case all of the modes of the material will now have a specific heat of $kT/2$ and the specific heat will become a constant. Ie, by measuring the specific heat of a material as a function of temperature, one was also measuring how many modes of vibration

in the material there are. Ie, the specific heat is just a measure of the number of modes which are "active" (ie have a low enough frequency.)

Spin

In doing more investigation of the spectra of atoms, confusion arose higher and higher. By placing a magnetic field on the material, one found that what originally looked like a single line, a single transition from energy state to the other, once magnetic fields were applied, the lines split into a number of lines. Ie, under Bohr's theory, what looked like single states with energy proportional to $1/n^2$, one now had energies which depended on the strength of the magnetic field. Calculations using the the Bohr Sommerfeld theory indicated a possible source for this. In particular, there were some extra conserved quantum numbers associated with the angular momentum of the electrons in orbit around the nucleus. There are two aspect– the total angular momentum and the direction that the angular momentum points in. The circulating electron acts like a current running in a wire, and has a magnetic moment (like a small magnet). Just a wire in a magnetic field tries to orient itself with respect to the field, the magnetic moment of the circulating electron changes the energy of the atom. (The principle quantum number, the n in Bohr's formula, corresponds to the major axis of the elliptical orbit orbit of the electron about the atom, while the angular momentum quantum number corresponds to the minor axis. Finally, one has the component of the angular momentum in the direction of the magnetic field, the third quantum number associated with an electron orbit). However, it seemed that for some atoms there seemed to be yet another quantum number which could take on two values.

First Kronig (dissuaded by Pauli and others, by the necessity of having the surface of the electron rotate faster than light, and by apparent disagreement with experiment from publishing), and then Uhlenbeck and Goudsmit suggested that perhaps this was due to the electron itself having a quantum number, a sort of spin. It was as though the electron itself were spinning and that rotating electric current gave the electron a tiny magnetic moment. The idea seemed silly, and when they suggested to Ehrenfest that their paper should not be published, Ehrenfest said:"I have already sent your paper off. You are both young enough that you will be forgiven one stupidity." Uhlenbeck and Goudsmit won the Nobel prize for this suggestion.

The most surprising result was found by Stern and Gerlach. They sent silver atoms through a highly inhomogeneous magnetic field. Such a field will exert a force on a small magnetic dipole (the force of one magnet on the other is due to the inhomogeneity of the field of the first magnet at the second. If the field is uniform, than the magnet will not move, it will simply try to align itself with the field.) The expectation was that the direction of the small magnetic dipole in the silver atom would exert a force on the atom, and deflect the atom, depending on the direction the small internal magnet pointed to with respect to the magnetic field. Since that little magnet could point in many directions, one would expect that one should get a continuous range of deflections, from
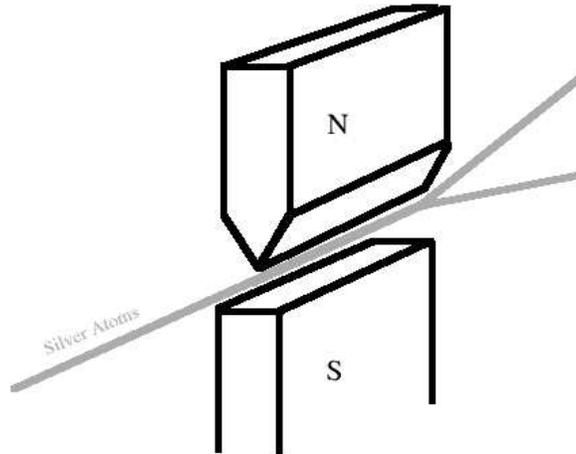
Figure 1: The deflection of the silver atoms by an inhomogeneous magnetic field. There are only two deflections as though the magnetic moment could only have two values.

maximum in one direction if the little magnet was aligned with the field in one direction, to maximum in the other if the alignment was in the opposite direction, to deflections in between.

Instead they found only two deflections, as though the little magnet could have only two orientations with respect to the field. Why would there be only two values to the orientation of the field?

Although they did not do so, one could also run say the upper bean through another magnet oriented in the same direction, and now you would only see one deflected beam again in the up direction.

On the other hand, if you place a magnet oriented in an orthogonal direction, one again saw two beams. Ie, it was as though when one measured the magnet, it would grab some orientation, which it would then keep if you tried to measure the same component. However if you measured it in the orthogonal direction, suddenly you would get two components again.

Exclusion Principle Bohr had already suggested that the various stationary levels of the atom were steadily occupied by electrons as one looked at atoms with more and more atoms. But the puzzle was why the extra electrons
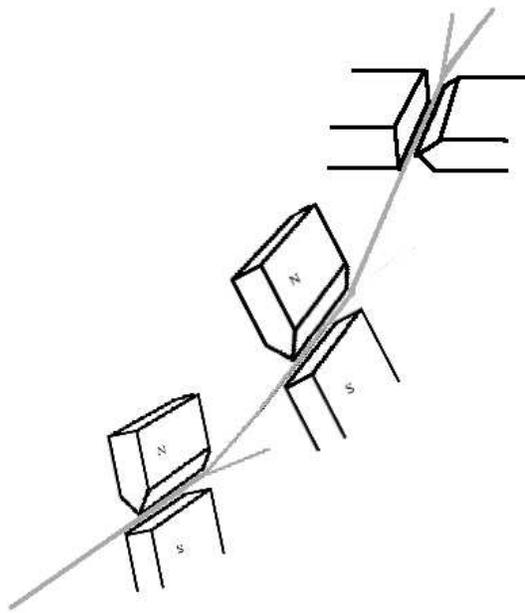
Figure 2: Multiple deflections of the silver atom beam. If the atoms are put through in the same direction, the up-deflected beam is still up-deflected. However, if the beam is sent through a sideways magnet, it would again split into two.

did not all fall down into the lowest energy level. One electron in Hydrogen does progressivly loose energy to end up in the lowest (n=1) level. Why don't all electrons. It was Pauli who suggested that perhaps there was some sort of exclusion principle, that no two electrons could ever occupy the same state together.

Using Bohr's and Pauli's ideas one finally had a reasonable model for the structure of the atom– with successive electrons occupying higher and higher energy levels. The outer, least bound of the electrons would correspond to those electrons which would participate most readily with other atoms, and thus determine the chemical properties of the atoms. In fact by steadily filling up the various energy levels, one could group the atoms into families, and explain why successive elements (eg, the noble gases, He, Ne, Ar, Kr– numbers 2,10, 18, 36,54, 86) corresponded to the filling of various orbital groups. Similarly the Actinides (Li,Na, K, Rb,Cs) had one extra electron above the filled shells of the noble gases, that lone electron being highly likely to interact with other atoms making them very reactive. Similarly, the Halides (F,Cl, Br,I)with one too few electrons are also highly reactive, wanting to steal an electron from other atomes. Ie, on the basis of the wild hypothesis, many of the characteristics of atoms and molecules became "explained", explained by a theory with no logically consistant structure, A theory cobbled together on the basis of classical physics, together with ad-hoc rules outlawing most classical solutions, a theory in which "transitions" played a role in the emission of radiation, but where those transitions had not classical model describing them. It was an unholy mess, redeemed only by the brilliant, astonishing explanation of a huge raft of exerimental facts.