Physics 200-04

Quantum Prehistory

The theory of relativity arose out of the wresting with what the meaning of the waves that were electromagnetism actually were. Waves were changes in some medium, but the properties of that medium seemed experimentally invisible. Einstein's brilliance was to see that the problem could be resolved by making two simple but far reaching postulates. Out of these, by an almost straightforward logical progression came all of the consequences of Special Relativity.

Quantum mechanics was a far more messy affair historically, and had a much messier formulation. Here there were no natural postulates which led ineluctable to all of the consequences of the theory. Instead what developed was a view of nature and of matter which is still not fully understood in the deepest of senses. It is a far more mysterious field that is Special Relativity– mysterious not only in that the relationship between the mathematical formalism and the real world is far less intuitive than in Special relativity, but in that it seems to beggar the imagination which tries to visualize what the world must be like in order to be described by Quantum theory.

But the prehistory of quantum mechanics (ie before 1925) seemed much more chaotic. Again there were violations of the models one had of physical world, but violations which seemed to be not intractable. But each "solution" led into a deeper and deeper mystery.

Black Body Radiation

If we heat up a body until it is white hot, it radiates light. Exactly how much it radiates depends on many of the details of the body– how reflective it is at various colours, etc. But, if we enclose the light inside a box, one would eventually expect the radiation in the box to come into equilibrium with the hot walls of the box– one would have a system of radiation at the same temperature as the walls, and there would after a long time be no detectable changes inside the box.

What would you expect to see if you went into the box, or rather, and more practically, what would happen if you put a tiny hole into the box, so small that the energy coming out of the hole made only a trivial difference to the state of the radiation inside the box? This was the question which was asked and experiments carried out on in the latter parts of the 19th century.

The results of the experiment were completely unexpected. radiation came out, and how much depended on the temperature. Stephan measured and Boltzmann "explained" that the amount of radiation which exited a hole of area A was equal to some constant σ, now called the Stephan Boltzmann constant, times the area times the temperature to the fourth power. Furthermore if one looked in detail at the frequencies of the radiation coming out, one found that at low frequencies, little radiation came out. The energy coming out increased as the frequency increased, until one reached a maximum at some frequency. Thereafter the amount of energy coming out decreased rapidly. Wien discovered that the frequency at which the amount of energy coming out (per unit frequency) reached a maximum was directly proportional to the Temperature. Figure 1 is a rough plot of the spectrum (total energy per unit frequency, vs frequency). This relation between maximum temperature and frequency was called Wien's law.

This corresponds to the fact that as something gets hotter and hotter its colour changes, the colour corresponding roughly to the frequency at the maximum. Thus as you heat a piece of steel, the colour starts off as almost black. As it gets hotter and hotter the bar begins to glow, first a dark dark red, then a brighter red, then orange, then yellow. If it were to get hot enough (it never does– it would melt first) it would eventually get bluer and bluer. The surface of white dwarf stars does get up to the temperature where the light becomes blue.

None of this was at all surprising. What was surprising was the total inability of physicists to explain it.

Raleigh Jeans With Maxwell and Boltzmann and others, the 1870s saw the growth of the field of physics we now call Statistical Mechanics. This was and is the field which attempts to explain the behaviour of hot bodies in terms of the behaviour of the constituent parts of the body (atoms, molecules). One of the key consequences of Maxwell and Boltzmann's results was that if there was a way in which a constituent could move, if there was a mode of motion of that constituent, then each of those modes would, if the body eventually reached equilibrium, have on average $\frac{1}{2}kT$ of energy, where T is the temperature, and k is a universal constant called Boltzmann's constant. Ie, an atom, which has three ways of moving– in the x, y, and z directions, then each of these ways of moving for the atom should contain on average $\frac{1}{2}kT$ of energy. Thus the total energy of an atom should be $\frac{3}{2}kT$ of energy.

This calculation was fine for atoms and molecules (well, now that we know that atoms and molecules are not fundamental particles, but have constituents parts– electrons, nuclei, protons, neutrons, quarks,.... one can ask if each constituent has $\frac{1}{2}kT$ of energy) but what about light? We know that hot bodies radiate, and place part of their energy into electromagnetic radiation. How does the electromagnetic radiation participate in the process of coming into equilibrium?

The first attempt to answer this came up with a very definite answer– the radiation should contain an infinite amount of energy– definite but also clearly wrong. The argument went that light, being a field, did not have some fixed number of particles between which the energy could be shared. Instead it had modes of vibration. Just as the top of a drum can vibrate all as one, or with a node in the center, or with two nodes crossing, or with a circular node, or...., so the electromagnetic radiation within the body can vibrate in the equivalent types of vibration– some where the electric field has a node (ie is always zero) across the middle of the box, some with two crossed nodes, etc. Each of these modes of vibration should act as a separate degree of freedom for the electromagnetic field. Each of these nodes should then have $\frac{1}{2}kT$ of energy when the system was in equilibrium. Unfortunately, unlike atoms where there are a definite number of atoms within the material, there are an infinite number of modes inside the box. One can imagine the drumhead vibrating with more and more nodes. These vibrations will have higher and higher frequency of vibration, and larger and larger energy for any amplitude of vibration. Furthermore for higher frequencies there will be more and more modes for any given frequency of vibration. If each of these modes has $\frac{1}{2}kT$ of energy, the amount of energy within the box will be infinite (or at least very very very large). Furthermore, since the number of modes who have approximately a given frequency increases, (as the frequency squared in three dimensions) one would expect to have more and more energy the higher the frequency becomes. There would be no maximum– the spectrum would continue growing without bound with frequency.

Well, that would have been the end of a beautiful theory, if it had not been for a problem. The problem was the theory actually worked, up to a point. If one looked at the low frequency part of the spectrum, at the region well below the frequency of the maximum, one did see that the spectrum did increase. Moreover it increased in **exactly** the way this theory predicted. Exactly not just qualitatively, but quantitatively. Ie, if one asked how much

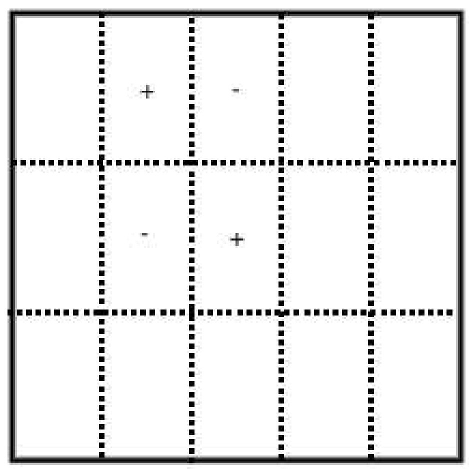

Figure 1: One of the modes of a drumhead with the dotted lines being the nodes (places where the drum does not vibrate). On opposite sides of a nodeline the vibration is in opposite directions. The frequency of vibration of this mode is the same as that of a drum the size of one of the little plaquets– and increases as the size decreases(it is proportional to $\sqrt{\frac{1}{\Delta x^2}+\frac{1}{\Delta y^2}}$ where Δx and δy are the size of each little plaquet.) Thus at high frequencies there are more modes with approximately the same frequency. the number of modes within a frequency band $\Delta\nu$ increases in this two dimensional case proportional to the frequency. In three dimensions it increases proportional to the frequency squared.

energy came out between a frequency ν and $\nu + \Delta\nu$ where both were much less than the frequency at the maximum of the spectrum, then the agreement between theory and experiment was essentially perfect.

Ie, it was as if the low frequency the modes really each had $\frac{1}{2}kT$ of energy, but that for some weird reason the high frequency modes did not.

One could understand this if for some reason the high frequency modes simply did not exist, but then the turnover should occur at the same frequency at all temperatures. It does not. It increases with temperature.

Wien had also suggested a theory in analogy with Maxwell's theory of gasses, in which at high frequencies the energy fell off exponentially with frequency. This had little justification except via the analogy, but at least was not infinite. However, at low frequencies it did not agree with experiment, though it did at high.

Planck Max Planck, one of Germany's most respected older scientists published a paper in 1900 in which he suggested a way around this disaster. He was concerned with the tiny charged oscillators in the walls of the cavity which produces and absorbed the light. Maybe, instead of being able to produce arbitrary frequencies of radiation, these little oscillators had a finite amount of energy distributed as chunks of energy. The idea was nuts, as there was no evidence for this at all. However, IF he assumed that these chunks were such that the energy ϵ of each chunk was related to the frequency of the oscillator ν by the relation

$$h\nu = \epsilon \tag{1}$$

Then he obtained an expression which did have a maximum, which did act like the Rayleigh Jeans law at low frequencies, did have a maximum which depended linearly on frequency just as Wien had found, and did produce just the Stephan Boltzmann law (with the right coefficient). Furthermore, the curve fit the experiments to within experimental accuracy. But his reasoning was both weird and suspect. He himself regarded it only as a fudge, and that that silly hypothesis of the discreteness of the energy would on deeper analysis go away. He however had the good sense to publish his paper in the same issue of the *Annalen der Physik* as a young student at the ETH who was just finishing his first degree and publishing his first paper. Thus Planck ensured (he was editor of the journal) that at least this student would read his paper. (Thanks to Jim Carolan for pointing this out)

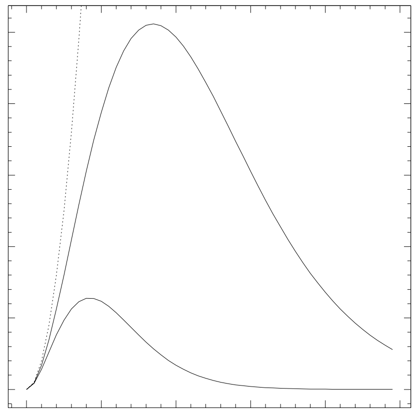

Figure 2: The Plack spectrum of energy emitted by a blackbody divided by the temperature, plotted against frequency for two different temperatures, one twice as big as the other. The dotted curve is the prediction of Raleigh. All three agree at low frequencies. Note that the frequency at which the maximum occurs has shifted to twice the frequency of the other curve.

Einstein That student was Albert Einstein. He was a student at the ETH in Zurich, who had graduated in 1900, second last in his class. The world of science was not exactly falling over themselves to offer him jobs, so his friend, Grossman persuaded his father to help get Einstein a job in the Swiss patent office. There he spent his time deciding whether various devices, based on physical principles, were worth granting patents to. While working on this job, Einstein kept notepaper in his desk on which wrote down his thoughts on various subjects which had interested him as a student. One was a paper on "The Electrodynamics of Moving Bodies", in which the principles of what we now call Special Relativity were laid out. One was a paper on the weird phenomenon of Brownian motion– in which tiny spheres of lycopodium powder (spores of a fungus) in water kept moving it seemed eternally. He explained it by showing that if the powder were bombarded by atoms, the powder particles were small enough that statistically, sometimes they would be hit on one side by more atoms than on the other, causing them to move. It was the first proof of the existence of atoms, and he calculated Avegadro's number (the number of atoms in a "mole" (grams=atomic weight) of material). In addition to two other "lesser" papers (including his doctorate from U Zurich), he also tackled another problem using ideas he had gotten from Planck's paper.

Electrons had been discovered in the 1897s, and a variety of experiments had shown how they could be easily created. One experiment was to shine light onto some of the alkali metals (Li, Na) in vacuum, which would emit electrons when the light shone on them. It was found that they behaved strangely as the intensity of the light was decreased. Since a decrease in the intensity of light delivered less energy to the surface of the metal, one would expect that these expelled electrons would come out with lower and lower energies themselves–less energy in–¿ less energy out. But instead all that happened was that fewer electrons came out, but with the same energies as in a stronger light. It is like going to the seaside in a storm and seeing trees ripped out of the banks and thrown up into the air, and later going to the seaside on a quiet day, and instead of seeing the trees perhaps move a bit as the waves hit, one still saw trees flung up exactly as in the storm, only fewer of them.

Einstein grabbed Planck's idea, that energy was perhaps lumped into packets, but instead of applying it to the oscillators in the walls of a blackbody, he applied it to light itself. Perhaps light, instead of behaving like a wave, which 100 years of experiments had demonstrated conclusively that it was and Maxwell's theory had enthroned, light actually was like a particle, where each particle carried an energy of $h\nu$ where ν was the frequency of the light, and h was the constant that Planck had introduced. Then the electrons squirting out of the metals were just what one might expect as the detritus of the surface of the metal being hit by these bullets of light. Then it would not be surprising that intense or weak light would produce the same effect. Each bullet would produce the same effect, just that when the light was intense, there were more bullets. (To take the beach analogy, the observation of trees flung up would not be surprising if the beach were bombarded with shells. You would expect to see the same trees flung up if there was only an occasional shell coming in, as if there was a huge barrage, only fewer of them).

Furthermore if one increased the frequency of the light, the energy of the ejected electrons should increase– more energy in the incoming bullet, more energy in the ejecta. A plot of the maximum ejected energy vs frequency of the light gave a linear plot, with slope just equal to that same constant

$h = 6.626\ 10^{-34} J - sec$ that Planck had used. (that the electrons did not come out with the total energy in the light particle could be ascibed due to the fact that some energy was needed to tear the electrons out of the metal itself. This work function was found to be a property of the metal, and the only reasons all metals did not exhibit this so called photo-electric effect was because most metal's work function is too large. (Einstein won the Nobel prize in 1920 for this work, and not for Special Relativity, because the Nobel committee did not believe Special Relativity was right).

Thus, in some instances, light was behaving as if it were a particle, shooting electrons out of materials, and in others (all of optics and diffraction) it behaved like a wave.

Rutherford As mentioned above, electrons had been discovered in the 1897 by JJ Thompson. All attempts to measure their properties showed that they carried a charge (they were accelerated by electric fields and deflected by magnetic) and seemed to behave like particles (no diffraction, sharp edges to shadows). As such they must be some sort of a constituent of matter. The problem was how did they live inside matter. There must also be positive charges in matter, which was neutral. But if the positive matter and the electrons were separated inside the atoms, then the positive would attract the electrons, which would move and created electromagnetic radiation. Thus one would expect all positive charges and electrons to fall together. this led Thompson to his model of an atom with the electrons being like the raisins in the positive matter dough of a plum pudding (or raisin bread). Electrons came out of metals easily (by heating or by shining light onto certain metals) but positive charges did not. A few materials emitted positive particles, of large mass, naturally, but heating or shining light on materials did not produce positive charges. Thus the positive dough was probably somewhat sticky. Besides estimates of the mass of the electrons showed them to be much much lighter than the estimated mass of an atom.

It was into this atmosphere that Rutherford (a New Zealander, who had briefly spent time in Canada at McGill before getting a far more prestigious position at Cambridge), got some of his students to chase up some weird results some people had reported when trying to look at the behaviour of alpha rays given off for example by radium and some other radioactive materials. While shining them past edges to see if they were waves of particles, some people had noticed that the edges though sharp, sometimes seemed a bit fuzzier than they perhaps should be. He persuaded Geiger and Marsden to look at the behaviour of these alpha rays as they passed through very thin sheets of gold. While he expected occasional small defections as the alpha particle traversed the plum pudding, what his students saw instead (spending months staring at zinc fluoride screens which would emit a flash or light when the alpha particles hit them) was typically very little deflection but with occasional huge deflections– by up to 90 degrees, or when they looked behind the gold foil, sometimes by almost 180 degrees. The plumb pudding seemed to have rocks in it!

By 1911 he had an explanation– instead of the positive charges being more or less uniformly spread out like the dough in a pudding, they were concentrated into incredibly small chunks. The positively charged alpha particles would occasionally come very close to this center and be scattered through a large angle. Detailed calculations showed that the number of particles deflected through an angle θ were just what would be expected if the positively charged alpha particle scattered off a point positive charge. Ie, the dough was all rocks– occupying almost none of the matter.

But how then were the electrons distributed? They could not be stuck in the positive charges– the energy required to tear them free would have been far far far greater than that supplied by the light, or than could be supplied by simply heating the material. Besides, the experiments showed that the positive charges were not neutralized by negative charges, but seemed to be sitting there in splendid isolation.

Rutherford's model, instead of being inspired by Christmas feasts, was rather inspired by the walks in the clear nights afterwards– namely the solar system. He saw the positive charges as being like the sun, sitting in the center. Around this fixed point the negative electrons circled like the planets circled the sum. The size of the atoms would then be determined by the size of these electron orbits about the center.

Stability Unfortunately this theory was nonsense for exactly the reason Thompson had foreseen. It was not stable. With the electrons circling the central sum, the electrons were an oscillating charge. Such an oscillating charge produces electromagnetic radiation which would take energy away from the solar system, causing the electrons to gradually (well in 10^{-8} sec or so) sink toward the central "sun". The matter would collapse.

Bohr Niels Bohr, a Danish young physicist, had become a post doc of Rutherford's in Cambridge in 1911. He grabbed Rutherford's idea, together with Einstein's idea. Into this weird brew he mixed results from the atomic spectroscopy of hydrogen. Balmer, in 1885, had used the results of øAngstöm and others on frequencies emitted by very hot hydrogen to derive a formula. Hydrogen, like all other materials, when a dilute gas, did not give of a continuous range of frequencies, like a black body did. Rather it gave of very sharp lines, with virtually nothing at other frequencies. He managed to use the four lines which had been very carefully measured to derive a formula

$$\frac{1}{\lambda} = \frac{\nu}{c} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{2}$$

where $R = 1.047 \times 10^7 m^{-1}$ is now called the Rydberg constant. (Balmer's formula was actually for λ, and Rydberg rewrote it for $1/\lambda$ or ν) with n taking values of 3,4,5,6 for the four measured lines. It agreed to better than one part in 10^3. This formula had absolutely no theoretical basis– it was purely a phenomenological expression, but amazingly simple.

Bohr used Einstein's hypothesis to say that the light emitted by these hydrogen atoms came in clumps of energy of amount $h\nu$. Thus the light emitted in each of the lines carried a definite amount of energy out of the atom. The above formula could therefor therefor becomes naturally interpreted as saying that the hydrogen atom existed in definite energies, given by

$$E_n = -hcR\left(\frac{1}{n^2}\right) \tag{3}$$

(negative because of the binding energy between the electron and the central charge) and that the Balmer formula represented the conversion of the hydrogen atom from one of the energy states to the energy state with n=2. But this would imply that for some entirely unknown reason, hydrogen has only certain energies. It would be as if in the solar system, the orbits of the planets all could only occur with certain fixed energies.

Thus, there seemed to be a new law of nature that stated that electrons could only orbit around the nucleus with fixed energies. Over the next few years, he and Sommerfeld formalized these new rules into definite predictions about how electrons should behave around nuclei. In particular, the "action", the integral of the momentum dotted into the velocity over one orbit should always be equal to some whole number times h. Pythagoras seemed to be returning with a vengeance.

Over the next 10 years, these largely incoherent strands were applied to more and more atomic systems, and proved amazingly fruitful, though sometimes they disagreed in detail with the experiments. But all of these separate almost incoherent strands finally culminated in 1925-26 with the publication of two series of papers, one by Heisenberg and one by Schrödinger put forward a totally new theory of dynamics, and as would become clear, of the state of the world.. I am not going to follow the historical thread any further, not least because it is too mathematically sophisticated. Instead I will jump ahead many many years, to present the simplest of quantum system, and to describe, rather than try to derive the results. As can be seen, quantum theory has not come about, as special relativity did, via some fundamental principles from which one can derive most of the rest of the theory. Rather it has been a series of gropings, of confusion, etc. And as I said, it is still a theory which is not well understood, even though it is probably one of the most successful theories in the history of all of physics.