17: Quantum Mechanics

17.1 Weird Issues with Classical Physics

At the end of the 19th century, there was a widespread feeling in the physics community that most all the big ideas were nailed down, and that the world was understood about as completely as it could be. In retrospect this seems incredibly naive given how little they knew about how things like solid matter and chemistry worked, but physics wasn't thought of as all-encompassing the way it is now. Today, chemistry can be viewed as an applied subfield of quantum physics. That is a very modern perspective, however, and at the time there was no reason not to view the two as independent fields.

In any event, physicists were in for a rude surprise when a couple of the "loose ends" they were trying to nail down turned out to have a truly bizarre implication: quantum mechanics.

17.1.1 Blackbody Radiation and Energy Quantization

The first problem was the radiation of hot objects. It was understood that accelerating charges produced electromagnetic waves of various wavelengths and that this was the reason that things like campfires glow. The problem came in when physicists tried to develop a statistical model to explain the exact distribution of emitted radiation. By assuming that material was composed at some level of charges (they knew about electricity and all that obviously, so something had to be in the material carrying charge, even if they didn't t know about protons and electrons exactly), they were able to predict statistically that at different temperatures, different accelerations would be more prevalent than others and so some wavelengths of light would be brighter at different temperatures than others. This part was correct and satisfying. The problem was that nobody could come up with a theory that predicted the *right* distribution of wavelengths. By making different, contradictory assumptions, two models emerged as the best efforts of the time:

Wien's model and the Rayleigh-Jeans model. However, while each of these models was able to get certain aspects of the "Blackbody Spectrum" (as this distribution of radiation was called) correct, both failed miserably in other ways.

It was at this stage that Max Planck, essentially in desperation, made a 3rd assumption which was, by the understanding of the day, manifestly incorrect: he assumed that energy could only be broken up in pieces that were a certain size, and no smaller.

$E = nhf$ $\qquad$ $n = 1, 2, 3...$ $\qquad$ $h =$ Planck's constant

The statistics change dramatically if you assume this sort of *quantization*, and mathematically Planck's idea bore fruit by predicting the blackbody spectrum with extremely good accuracy and precision. At this stage, however, it was treated as mathematical trick that must be hiding some cleverness of structure that no-one had figured out yet. Perhaps, for whatever reason, it just happened that energy got split up this way because of a complicated feature of material structure or heating.

17.1.2 Photoelectric Effect

Another mystery was what is known as the photoelectric effect. The photoelectric effect, as its name suggests, relates light and electricity. Not a big surprise after our study of electromagnetism, but the details were peculiar. The specific observed phenomenon we call the photoelectric effect is the following. A potential difference is built up between two electrodes (metal surfaces) but kept small enough that arcing doesn't occur. Then, a light is shone on the negative electrode (which we expect to have an excess of electrons based on our study of circuits earlier). While the light is turned on, a current may be observed to flow through the circuit as electrons dump from the negative to positive electrode.

So far this isn't surprising: it is known that it takes a certain amount of energy to get an electron to leave its electrode and jump to the other, otherwise a potential difference wouldn't build up at all. It is also known that light carries energy. So, if we build up a strong-but-not-strong-enough potential difference, and then give the electrons a little bit of extra energy, it makes sense that they would make the jump.

The thing that didn't make sense was, again, the details. Our study of EM waves told us that the energy stored in a wave is proportional to the square of the strengths of the fields. This corresponds to the intensity, or brightness, of the light. So from this, it seems that the energy received by electrons in the electrode would be proportional to the intensity of the light applied. As such, electromagnetic theory predicted essentially a slow, continuous ramping-up of current in the circuit as the light was cranked up. Instead, it was found that this was in fact true for certain *wavelengths* of light, but that for others, the current simply refused to flow no matter how bright the light was. Above a certain wavelength, there simply was not a current. What's more, the wavelength was different for electrodes of different material.

The obvious implication is that wavelength is somehow relevant to the energy content of a wave, despite not appearing in our earlier derivation. This would have been interesting but not horribly earth-shattering. Such a discovery would have amounted to a refinement of the existing theory of electromagnetic waves, and Planck had already related energy and frequency to explain the blackbody spectrum. However, there was no assumption resting purely on this idea of frequency dependence that could explain the sharp nature of the cutoff. If the energy content of the light depended on wavelength as well as intensity, one would expect a smooth turn-on of current as the two were varied, and that for longer wavelengths perhaps more intensity would be needed for the same current, but that one could still produce a current with long wavelengths. Experiment refused to conform.

The answer was once again to consider energy coming in discrete packets. In this case, Einstein proposed that light was in fact composed of particles, photons, which carried energy of the quantity that appeared in Planck's theory, $E = hf$.

This idea is bizarre. Einstein has apparently proposed a self contradiction: a particle whose energy depends on its frequency, which is a property of waves. Had I been teaching physics at the time and a student made such a blatant error in understanding of the essential difference of waves and particles... Well, they wouldn't have gotten a good score. Earlier that year, Einstein had published his theory of Special Relativity, which wasn't exactly a traditional idea either.

17.1.3 Resolution: Wave-Particle Duality

Einstein's contradiction was an acceptance of the fact that nature doesn't always follow our neat categorization of things. If nature wants light to have both wave properties and particle properties, it is futile to try and describe it as one or the other: use both and move on. The idea that something can be both a wave and a particle is known as wave-particle duality. This just means that some experiments will be sensitive to wave properties and give results consistent with that, while others will be sensitive to particle properties and give results consistent with that.

Despite the emergence of wave-particle duality, there is still such a thing as a pure wave. There is no such thing, for instance, as a particle associated with the waves one sets up in a slinky waving it around in the air. That being said, there are fewer exceptions than you might at first think. There is a common and effective concept in the study of solids called a "phonon" which is essentially a particle of sound. Phonons are in no way physical objects, but there are phenomena which can be best described in terms of a mathematical construct equivalent to the quantization of sound. I still think that's weird.

17.2 Running with the idea: Matter

If waves can have particle properties, it only seems fair for particles to have wave properties. And in fact, this was found to be the case.

17.2.1 de Broglie Wavelength

Louis de Broglie proposed exactly this idea, and by analogy with the result for a photon which relates momentum and wavelength,

$p = \frac{h}{\lambda}$

he predicted that solid objects would have wavelengths given by

$\lambda = \frac{h}{p} = \frac{h}{mv}$

You may think this is preposterous. I've played basketball, and the ball doesn't diffract through the hoop when you make a basket! I don't spread out in a series of wavefronts when I walk through the door of the classroom, even tho that is essentially a single slit in a barrier, and Huygens' principle would suggest I should diffract.

Well, it turns out, the basketball and I *do* diffract according to Huygen's principle. However, notice the presence of $\frac{1}{m}$ in the equation above. I never gave you the numeric value of h, but it is

$h = 6.6 \times 10^{-34} J \cdot s$

If I divide this by a typical mass and velocity for a ball, I get something like

$\lambda = 1 \times 10^{-34} m$

OK! Not big! Remember that diffraction of light wasn't noticed early on because the wavelength of visible light is around $10^{-7}m$. Good luck seeing something 10^{27} times smaller.

Note that the velocity appears in the denominator of the de Broglie equation for wavelength. What happens when an object is at or near rest? A very small velocity should result in a large wavelength, but even an inert chunk of metal sitting on a table doesn't start to spread as a wave would. The answer is essentially that while the block as a whole is at rest, it is composed of particles in motion relative to each other, and as a result the calculation of a wavelength for the block as a whole is a bit complex. It is possible to cool collections of atoms to near absolute zero temperature and observe collective wavelength effects. Its called a Bose-Einstein condensate and they make them in the basement.

17.2.2 Electron Diffraction/Microscopes

While the wavelength of a macroscopic object like a basketball or a person might be utterly preposterous, things get a bit more interesting when we talk about single particles, especially relatively light ones like an electron. There is no set wavelength of an electron since there is a velocity dependence, but if we pick a velocity typical of an electron in a circuit, we get things like

$1 \times 10^{-10} m$. Note that it is extremely hard to slow electrons down very far because of thermal effects, so the wavelengths won't get much smaller than this.

Remember that a nanometer is $10^{-9} m$, so this electron wavelength isn't much shorter than that of blue light. This suggests that its wave nature can be observed, and in fact it is. Shining electrons through materials with a regular crystal structure functions like a double-slit (or many slit) experiment, and it is possible to see an interference pattern. This is in fact a primary method used to measure the crystal structure of some materials, as it is possible to accelerate electrons to a shorter wavelength than available EM waves, meaning that smaller crystal separations can be measured effectively.

We didn't discuss this feature of optics, but one of the most important limits of optical imaging or magnification is the diffraction limit. It is impossible to see details smaller than the wavelength of light being used to make the image, because the light will diffract around the detail and wash it out. This is just like when light spreads out from a small hole in a barrier: its hard to tell what shape the hole was when the light spreads out all over the place. As a result, there is a fundamental limit on how much magnification one can squeeze out of an optical microscope, no matter how perfect your lenses or clever your microscope. This is the primary motivation behind the use of *electron microscopes*. Because electrons can be easily accelerated to have much smaller wavelengths than light, and are easily detected and recorded with great precision and accuracy, they can be used to image details far smaller than can be accomplished with optics.

Of course, blasting a sample with high energy electrons can have detrimental effects, so there are certain limits on what we can take such images of. Nevertheless, such images have greatly expanded our understanding of the very small.

17.2.3 Early Attempts at Atomic Models

Greek

The Greeks' originated the idea that all matter was composed of indivisible constituents, or at least that's where we get the word. They believed in an atomic structure of matter on philosophical grounds, while later arguments were based on more concrete observation. Despite, their arguments were good and have obviously been borne out since.

Plum Pudding

The plum pudding model simply stated that atoms were composed of some uniform sphere of positive charge that carried the majority of the atoms mass and had electrons embedded inside. This theory predicted dramatically different scattering results than those found by Rutherford, a British physicist credited with discovering the nucleus through said scattering experiments.

Planetary

Once it was realized that the mass and positive charge of an atom were concentrated heavily in the center of an atom, the next most obvious picture was that of an atom as a sort of miniature solar system, with electrons orbiting the nucleus like planets around the sun. The main problem with this idea is than orbiting electrons are accelerating charges and should thus radiate EM waves, lose energy, and spiral into the nucleus in a flash of light. This doesn't happen, and it turns out to be because of the quantization of energy (as well as the fact that the planetary model is horribly misleading, despite being used in many textbooks still today). We will look at this issue more carefully shortly when we consider the hydrogen from a modern quantum mechanical perspective.

Bohr/de Broglie

This is similar to the Planetary Model, but takes advantage of some quantum ideas. It was essentially proposed that electrons can only exist in orbits whose circumference is an integer number of de Broglie wavelengths. This is a largely unmotivated assumption which proves to have some (minimal) real meaning in hindsight. In any case, it gives some (but not all) correct results. This was a huge step up from previous models, which consistently failed to get much of anything quantitative right.