New Topic:

rounding out classical physics:
thermal equilibrium

The experimental basis of quantum mechanics
The black body problem - Planck's quantization postulate
The photoelectric effect - Quantization of EM radiation
The Compton effect - Light is a particle
The atomic spectrum and the stability of the atom - Bohr

Electron diffraction - Electrons are waves

Any retrospective comments
on old philosophical issues?

The 2ⁿᵈ law of Thermodynamics

- There are various equivalent early forms, e.g.:
  - An isolated system approaches thermal equilibrium, in which all its component objects have the same temperature.
  - One cannot separate a system into hot and cold parts without putting in energy. Your refrigerator has to be plugged in.

- There are limits on how much mechanical energy can be obtained from thermal energy.
  - As Sadi Carnot obtained from "caloric" theory.
- There are not limits the other way.
  - The <u>First law is a conservation law, and thus completely reversible in time</u>,
  - the Second law (however stated) is completely IRREVERSIBLE.

- <u>A typical example</u>:
  - A locomotive can accelerate, burning coal and heating up.
  - Don't hold your breath waiting to see one go backwards, come to rest, while cooling down, sucking CO_2 and H_2O from the atmosphere, emitting O_2 and dumping newly made coal into the hopper.

From Thermodynamics to Statistical Mechanics

<u>The connection between thermal energy and other forms?</u>

- In the late 19th century Boltzmann, Maxwell, Gibbs et al. showed that <u>thermal energy is just potential and kinetic energy of the microscopic parts</u> of objects (molecules, etc.), moving in "random" directions.
  - What does "random" mean?
- In an isolated system, the energy gradually leaves large-scale organized forms (mechanical motions) and goes into small-scale, disorganized thermal forms.
  - What does "organized" mean?
  - What's the line between "large-scale" and "small-scale"?

- "Entropy" can increase but never decrease in an isolated system. <u>Entropy is a measure of how many ways the system could be arranged microscopically while keeping the same macroscopic appearance</u>.
  - For example, the overall behavior of a box of gas will not be noticeably different if each individual molecule happens to go a different direction, so long as they are spread out fairly uniformly and have very little net momentum. That leaves <u>a lot</u> of different possibilities for how the molecules might be placed and how they might be moving.
  - Entropy had appeared in pre-statistical thermal physics, but with a Byzantine definition.
 - But how close is "the same"?

two peculiarities

- The 2cd law is still completely irreversible in time, even though it describes phenomena consisting of microscopic events which are reversible in time.
    - Stay tuned!
- The law at this point involves some form of distinction between "macroscopic" and "microscopic", or equivalently between "organized" and "random".
- Aren't these fuzzy, subjective distinctions?

- Billiard balls may quickly come to look "random", but a person with reasonably quick hands could harness their energy to compress springs, and use that stored energy to do any sort of work.
  What's more "random' about the motions of air molecules, in principle?
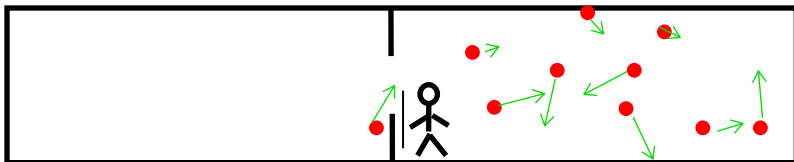
Maxwell's Demon

It seemed that one ought to be able to cheat the second law.

- Consider "Maxwell's demon," a hypothetical entity who performs impossible feats. For example, he stands at the door between two rooms and only lets molecules through one way. This process would *reduce entropy*, since there's more ways to place the molecules if they can go on either side than if they're confined to one side.

- Then you get high pressure on one side, low pressure on the other. You could then use that pressure difference to drive a piston. Is this possible?

- ## Before:
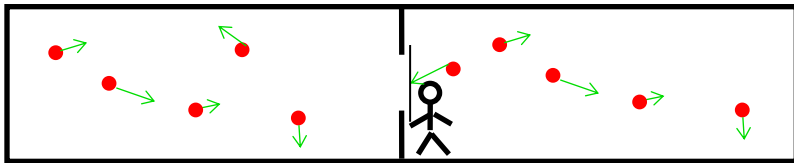
- ## After:

Classical physics has no account of why this Maxwell demon procedure is impossible, although it obviously wouldn't be easy. Classically, this is *in principle* not different from trapping all the billiard balls on one side of a table. So there's a bit of a paradox about classical thermodynamics.
That paradox will be ~removed by quantum mechanics. We won't worry about it yet.

Classical Ideal Gas

- https://www.youtube.com/watch?v=YgGik5q1JSA
- We can predict the average force from pressure on any wall if we know
  - the average kinetic energy of each particle
  - that the directions of the motions are "random"
- How do we know they're random?

Classical Equipartition

- In "random" collisions between big and little particles, energy is transferred.
  - On the average, after many collisions, the kinetic energy $mv^2/2$ will be the same for all particles, even if they have different m's.
  - The same energy will go into any spring potential $kx^2/2$.
  - And into *any* "quadratic" mode, i.e. where the energy goes as the square of some number (x, v_x, ...) where the density of microstates should be independent of the number.
    - Rotations, vibrations, ...
- Heat capacity is a measure of how much energy must be added per degree change of T.
Equipartition gives
  - ~ the right heat capacity of most solids at room temperature,
  - ~ right heat capacity of gases at room temperature.
  - Are the deviations important?

Something's Missing

There were two types of problems with classical physics.

- First, there was something very major missing, since there was no explanation of any chemical properties, mechanical properties, phase transitions, colors, etc. of materials- or even an explanation of why the atom wouldn't collapse. So it looked like some whole new set of force laws or something was needed to describe the world at the scale of atoms and molecules. It might seem that filling in these huge missing pieces, where unknown ingredients were needed to make predictions, was a giant task, but one that could be performed within the confines of classical physics.

- Second, and much more serious, there were a small set of problems for which classical physics made predictions that were wrong. We'll follow the track of these problems, because historically it was these sharper problems which led to the new physics.

We'll explore these problems and their initial fixes.
Then we'll shift out of historical mode. because
too many presentations of quantum mechanics give incorrect historical patches as if they were currently used.
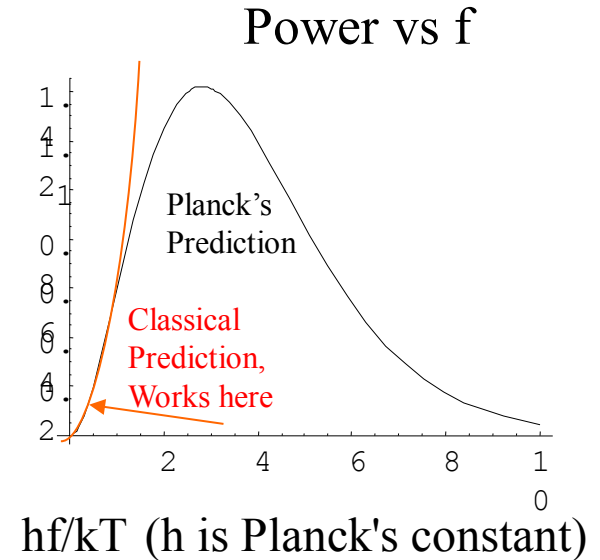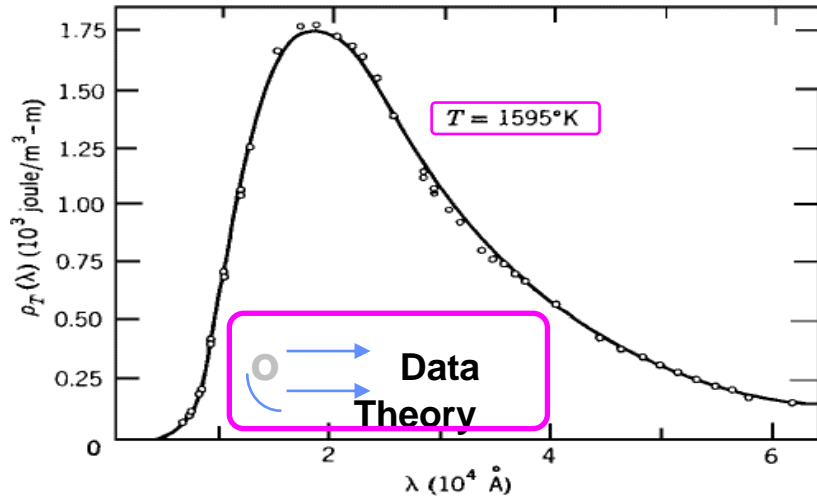We need to get beyond them.

The black body problem

- Equipartition of energy. In thermal equilibrium, the average amount of energy in each "mode" of motion is kT/2. (k is Boltzman's constant, T is absolute temperature)
  - A mode of motion is an independent motion. For example, motion of each molecule along x, y, and z are three modes. Rotation and vibration also, depending on molecular structure.
- What about the thermodynamics of waves (*e.g.*, light)? We know that hot objects emit light. How much? What colors?
- Consider waves on a string (or light in a mirrored box). The modes consist of the various standing waves:
  How many?
- There are an infinite number of modes at very short wavelengths (high frequency). Then equipartition would imply that there should be infinite energy in the EM radiation at any finite T. We would all be glowing infinitely brightly!
  - This is called the ultraviolet catastrophe, because the infinite amount of energy appears in the high-frequency (ultraviolet and higher) modes.

Limits to Equipartition for Light

- Equipartition worked up to some frequency (which depends on T) but not at higher frequencies

$T = 1595°K$

$\rho_T(\lambda)$ (10^3 joule/m^3–m)

λ (10^4 Å)

Data
Theory

Power vs f

Planck's Prediction

Classical Prediction, Works here

hf/kT (h is Planck's constant)

Planck proposed, in 1900, to modify the law of the interaction of radiation with matter., saying energy can only be emitted or absorbed in integral multiples of hf. That is, 0, hf, 2hf, 3hf, *etc.* are allowed, but not 0.5hf.

The same laws of stat. mech. that gave equipartition if continuous values of the energy are possible then imply an exponential suppression of the probability of the excited states.

Planck's hypothesis gave the right answer, but had no physical motivation. Is the phenomenon a property of the light, the atoms, or of the interaction between them? Is this an epicycle? It breaks the seamless description of motion and energy just as an epicycle would break a crystal sphere.

Photoelectric effect

- Hertz 1887): shining UV light on metal electrodes can induce sparks across a voltage gap. Even intense, red light doesn't.

- Einstein (1905): proposed extending Planck's solution to the BB spectrum problem to explain this effect. He suggested that the quantization of the EM energy was not in the interactions with matter, but a property of the radiation itself. That is, light waves come in little packages, or quanta (photons), each of which has a specific amount of energy, hf.

- This photon hypothesis led to several predictions about the behavior of the photoelectric effect. If the electrons in a metal are bound to it by a certain amount of energy (call it E_o), then:

  - If $hf < E_o$, the photons don't have enough energy to knock electrons out.

  - If $hf > E_o$, then electrons will come out, with energy $hf - E_o$.
    In a typical metal, E_o ~ hf for yellow light.

  - Increasing the *intensity* of the light increases the *rate* of electron ejection (the current) but not the individual energies.

- In the classical wave picture of light, the only important quantity is the rate at which energy is put into the metal, so one expects no significant frequency dependence, only an intensity dependence.
  Predictions were verified by Millikan in 1914.

- How can waves behave like particles?

Compton effect

- Classically, If one shines a light wave on a free electron, the electron will oscillate in response to the electric field, emitting radiation with the same frequency as the incident light. As the electron accelerates, the radiation picks up a Doppler shift.

-

Before: After: $E'=hf'$

$E=hf$

-

- What actually happens? The emitted radiation has a frequency corresponding to the energy light would have if it were a particle of E = hf=pc colliding with the electron.

- The energy of the scattered particle (frequency of the light) depends on the angle. This effect is only sizable when hf ~ mc^2, so the "light" needs to be gamma rays. This is due to SR momentum-energy relations, not any special property of light.

- This effect was first observed in 1923 and confirmed the view that in some circumstances light behaves more like a classical particle.

Heat Capacity of Solids

- The heat capacities of solids at temperatures of around room temperature or higher are usually in ~agreement with equipartition, but at lower T the heat capacities become very small.

- Debye (1912), following a cruder idea of Einstein (1907), showed that this behavior would result if:

  - the energy were stored in sound waves (a sensible classical idea) and

  - the energy in the sound wave at frequency f comes in lumps of size hf!

  The data points here
  are for silver.

 Same h as for light!
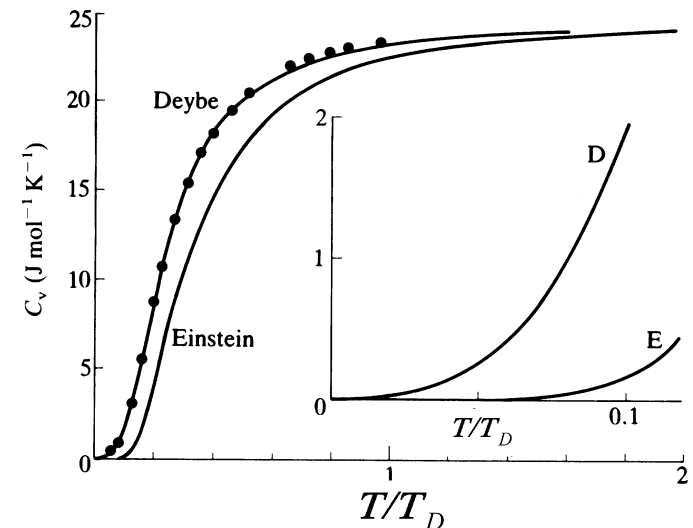
Atomic spectra

- Atoms and molecules emit specific wavelengths of light. One can identify atoms and molecules by looking at the spectra. This phenomenon cannot be understood easily in classical E&M. The frequency of emitted radiation depends on the frequency of motion of the electric charges, and it is hard to see why the motion should be restricted like that.
- In hydrogen, the frequency spectrum follows a simple pattern:
- $f = const * (1/n^2 - 1/m^2)$ (Ritz)
  - where n and m are integers.
- With the discovery of the electron by Thomson in 1897, the question became, what is the structure of the atom?
- In 1910, Rutherford showed that the atom's positive charge is very heavy and also very small. Are the electrons orbiting the nucleus like the planets orbit the Sun?
  - This appealing picture has a fatal flaw. As the electrons orbit, they should emit radiation and lose energy. They will spiral into the nucleus in about a nanosecond. This not how atoms behave.
- The planetary atom also does not explain the discrete spectrum, since orbits can have any frequency.

# The Bohr atom:
a suggestive temporary ad-hoc fix

In 1913, Niels Bohr postulated that quantization applies not only to photon energy, but also to the orbital angular momentum of electrons in atoms, which could only take on discrete values, integral multiples of Planck's constant divided by 2π. $L = nh/2\pi$
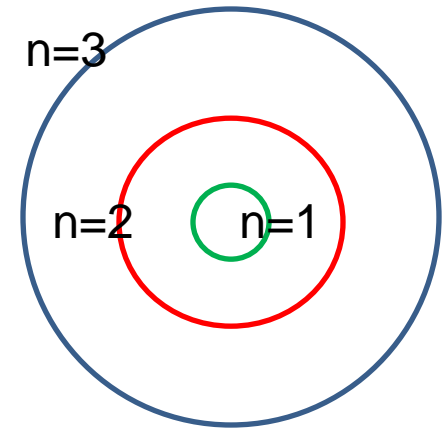
- This proposal "solved" both of the problems.
  - The atom becomes stable, because the orbit with lowest angular momentum also is the orbit with lowest energy. It is forbidden (*by special fiat*!) for the electron to spiral in.
  - The energies of the orbits are proportional to $1/n^2$, so the Ritz formula is automatically satisfied.   The right frequency photon is emitted when the electron "jumps" between orbits.
- Bohr leaves much unexplained. E.g. if only certain orbits are allowed, how does the electron get from one to another? Also, why is the angular momentum quantized? How is that connected with the quantization of light?
- Planck's constant describes both electrons and light (as well as sound) so it seems to play some very general role. Although the Bohr model was wrong in all of its essentials, it was extremely important for demonstrating that Planck's constant had *something* important to do with atomic structure, not just with light and sound.

Electron diffraction

- Davisson scattered electrons from crystals and showed that they tended to bounce in particular directions. (1921-7) These directions were exactly those which one would expect if electrons are waves of wavelength *l = h/p*.
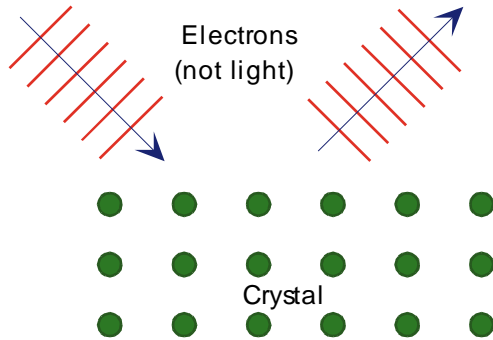
This is the same diffraction behavior that X-rays show, and was the evidence that had been used 30 years before to show that X-rays are waves (part of the EM spectrum).

How can particles behave like waves?

Light, which usually seems to be a wave, exhibits particle properties. Electrons, which usually seem to be particles, exhibits wave properties. Both phenomena involve Planck's constant. $E = hf$ and $p = h/\lambda$ are just two manifestations of the same 4-D SR relationship. Remember, energy and time are related in the same way as momentum and space. Otherwise, the Lorentz transformation would fail. The relation $p = h/\lambda$ was first proposed on this theoretical basis by A. C. Lunn (U. Chicago) in 1921, and subsequently by L. deBroglie (1923). Lunn's paper was not accepted by the Physical Review, so $p = h/\lambda$ is known as the deBroglie relation. (Davisson had been a student of Lunn, who urged his students to explore the "wave properties of beta radiation".)

2-Slit diffraction of electrons, etc.

Let's revisit this gedanken experiment (done briefly in the first lecture). The electrons start at a source (a hot cathode, as in your TV) and strike a scintillating screen. Each electron always produces a spot of light, like a particle, not a spread-out glow, like a wave. The screen registers whole electron charges, not fractions.
Now, put an absorber between the cathode and the screen. The absorber has two holes (slits) in it.

Electron source

scintillating screen

A

B

absorber with two holes

Look at what happens when we open and close the holes in various combinations. The curves indicate the rate at which electrons hit the various parts of the screen. First, open only slit A. We will see a distribution of flashes something like the lower left curve. If only slit B is open, we see the lower right curve. Opening hole B shouldn't affect the passage of the electron through hole A, and *vice versa*. So, the natural prediction is that the rate with both A and B open is the sum of the two curves, the bigger central peak.
What do we actually see?
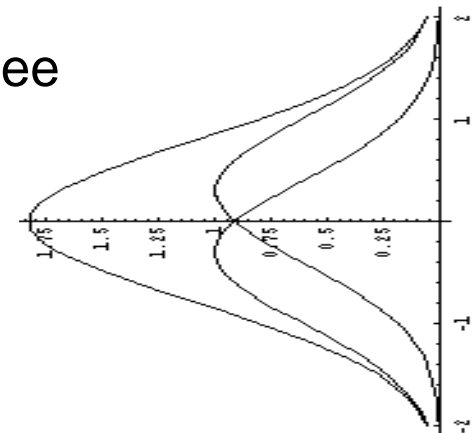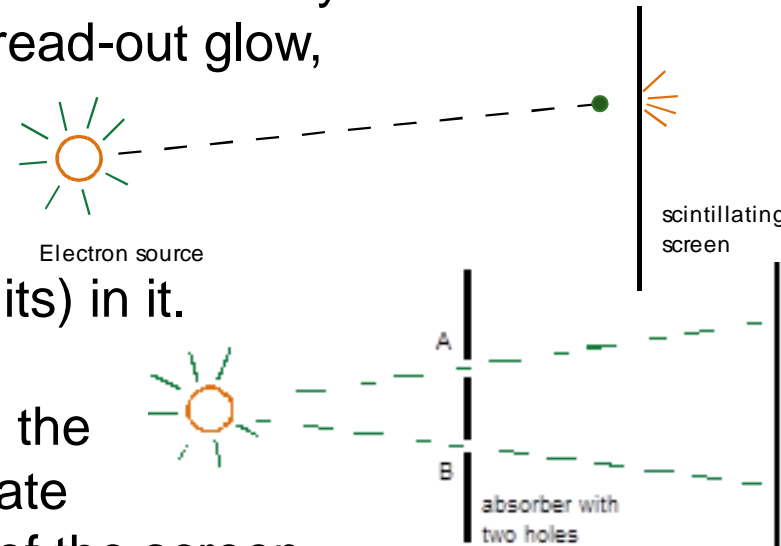
2-slit results

- Instead, we observe an interference pattern. Not only do the two distributions not add, but there are places on the screen where opening the second hole actually *decreases* the electron arrival rate!

- Experiments like this have actually been done, not only with electrons but also with neutrons, atoms and even buckyballs.

- We see, in a single apparatus, both the wave and particle aspects of elementary objects.

- How is this possible?

- One obvious possibility is that electrons etc. act like particles individually, but collectively they exhibit wave behavior. This is not correct. One can decrease the intensity of the source in the 2-slit experiment until there is usually just zero or one electron in the apparatus at any time. The interference pattern is still observed. So, whatever the waviness is, it is a property of *individual* electrons, C60's….
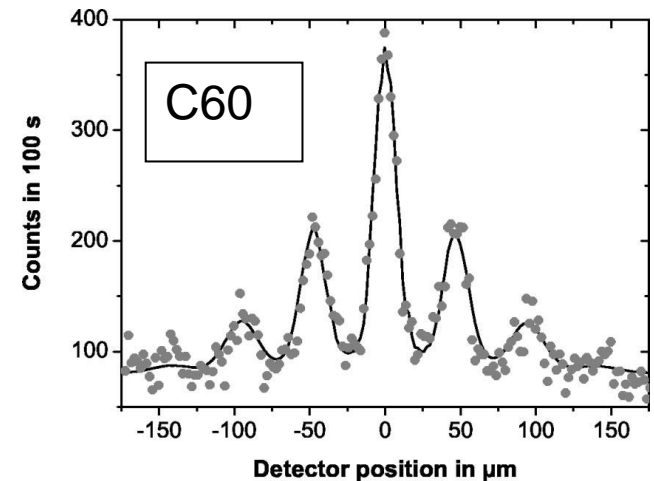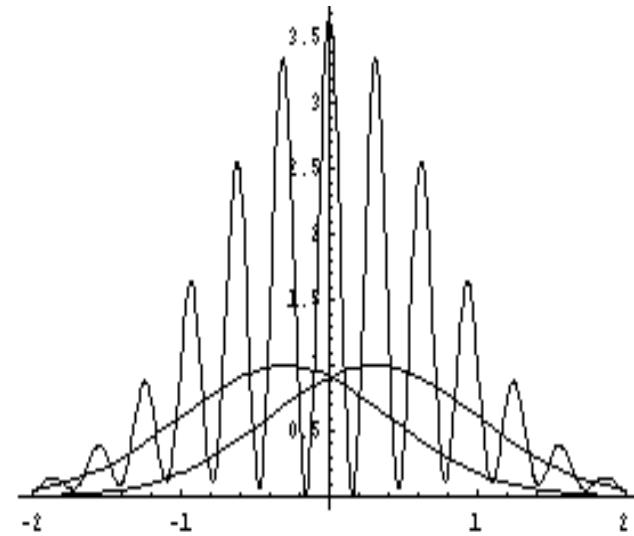
Particle Waves

- Light
  - is a wave. It exhibits interference (Young, 1814).
  - now it is seen to have some particle properties: photoelectric effect & Compton scattering
- Electrons
  - Appear at fluorescent screen (CRT) at ~a point, like particles.
  - Have wave properties: Interference (Davisson, ~1922).
- <u>Our old particles</u> have frequency, wavelength…
- <u>Our old waves</u> have discrete lumps of energy, momentum….
- The old dualism (world consists of particles interacting by continuous fields) is gone- everything consists of quantum objects which have both wave-like and particle-like aspects, which become relevant in different situations.
- The common claim that these objects are *both* waves and particles is false- they're just something else, with a resemblance to both classical waves and classical particles, but also with properties of *neither*.
- We *seem* to be saying something very incoherent. A wave cannot have a wavelength, even approximately, unless it is spread out over distances large compared with the wavelength. A particle is supposed to have a particular position. How can we say "the momentum of the particle is given by its wavelength?"

De Broglie's hypothesis (Lunn, 1921)

- De Broglie proposed that every particle has an associated wave (called a pilot wave), and every wave has an associated particle. The relationship between the two is always the same:

- $E = hf$ and $p = h/\lambda$ (or vector version, $\mathbf{p}=(h/2\psi)\mathbf{k}$
  - This doesn't yet explain atoms, but there's a suggestive relation: if there were an integer number of DeBroglie wavelengths around a circular orbit, Bohr quantization would result! (Again, this is NOT the way it really works- almost everything about the Bohr model was wrong.)

- The full solution requires understanding what persistent wave patterns can exist in the atom, which requires finding the wave equation. The waves will be genuine 3-D waves, not waves on an imaginary 1-D orbit.

- The electron is described by a wave function, $\psi(\mathbf{r},t)$, which obeys a differential equation. The non-relativistic version is called Schrödinger's equation. (also first due to Lunn)

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = i\hbar\frac{\partial\psi}{\partial t}$$

  - First term, (squared momentum), depends on how ψ wiggles in space.
  - Second term, (potential energy), due to various neighbors (whose positions are presumed fixed in our reference frame).
  - Third term (total energy) is how fast ψ changes in time.