Historical Approach to Quantum Mechanics

REMINDER: TERM PAPER TOPICS

Today: 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

Coming Up:
De Broglie's wave-particle hypothesis (1924)
Born's probability interpretation
The indeterminacy ("uncertainty") principle
What is happening?
The Copenhagen interpretation
Why people remain unsatisfied

Something's Missing

There were two types of problems with classical physics.

- 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.

- 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.

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:
- 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.

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.

- But it doesn't always work!

Limits to Equipartition for Light

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

- 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.
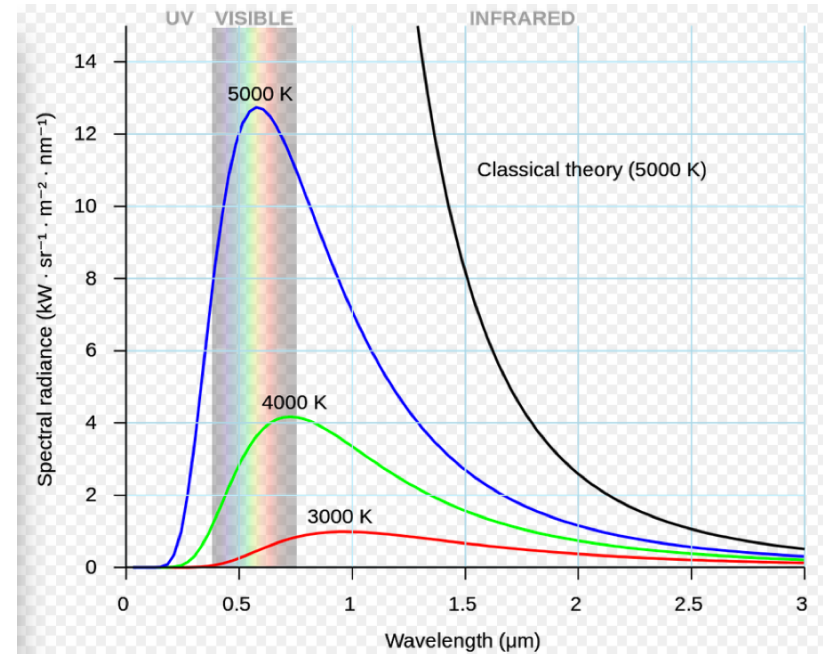
- With this assumption, statistical mechanics implies an exponential suppression of the probability of the excited states.

- 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 changes the 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. But even intense red light never does.

- Einstein (1905): proposed extending Planck's solution to explain this effect. He suggested that the <u>quantization</u> 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, (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, $E_o \sim hf$ 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. <u>Predictions were verified by Millikan in 1914.</u>

- How can waves behave like particles?

Compton effect (1923)

- 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: $E=hf$ After: $E'=hf'$

- 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 $hf \sim mc^2$, so the "light" needs to be gamma rays. This is just due to relativistic 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!
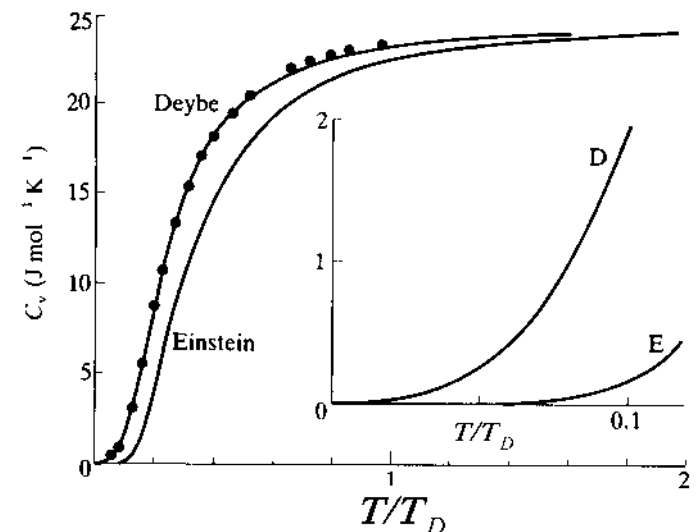
Atomic spectra

- 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 (1897), the question became, what is the structure of the atom?
- Rutherford (1910) 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 temporary ad-hoc fix

Niels Bohr (1913) 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. $L = nh/2\pi$
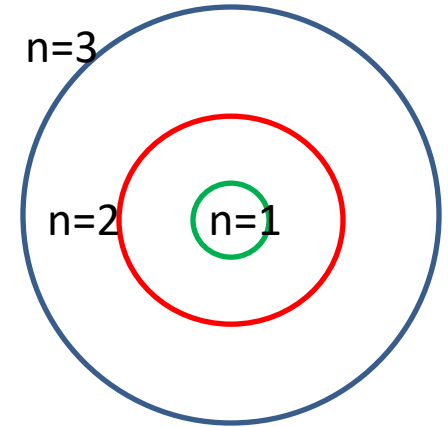
- This proposal "solved" both of the problems.
  - The atom becomes stable, because the orbit with lowest angular momentum also is the orbit with lowest energy. It is forbidden (*by special fiat*!) for the electron to spiral in.
  - The energies of the orbits are proportional to $1/n^2$, so the Ritz formula is automatically satisfied. The right frequency photon is emitted when the electron "jumps" between orbits.
- But if only certain orbits are allowed, how does the electron get from one to another? 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 λ= h/p.

Electrons (not light)

Crystal
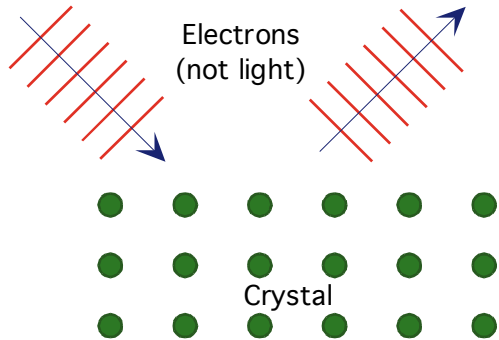
This is the same diffraction behavior that X-rays show, and was the evidence that had been used 30 years before to show that X-rays are waves (part of the EM spectrum).

How can particles behave like waves?

- Light, which usually seems to be a wave, seems to exhibit particle properties.
- Electrons, which usually seem to be particles, sometimes exhibit wave properties.
- Planck's constant is the common connection between the phenomena.
- E = hf and p = h /λ 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 / λ was first proposed on this theoretical basis by A. C. Lunn (U. Chicago) in 1921, and subsequently by L. deBroglie (1923).

2-Slit diffraction of electrons

Let's revisit this gedanken experiment (see the first lecture). The electrons start at a source (a hot cathode, as in old TVs) 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

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.

A

B

absorber with two holes
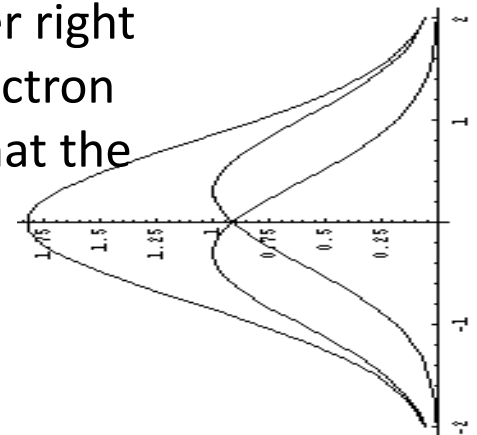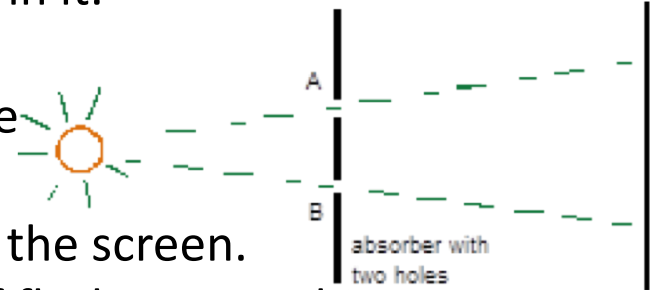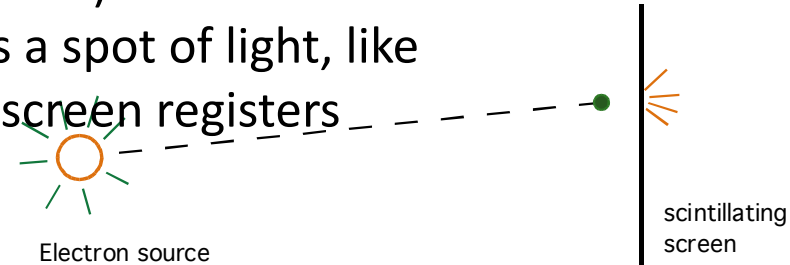
What do we actually see?

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 (C_{60} molecules).

- We see, in a single apparatus, both the wave and particle aspects of elementary objects.
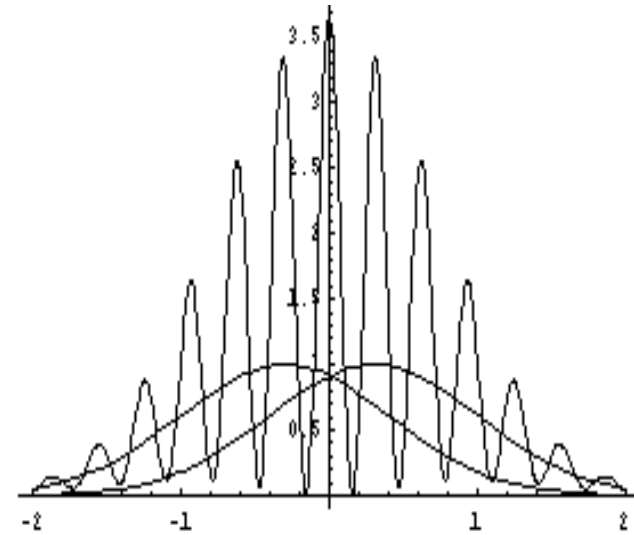
How is this possible?

- One obvious possibility is that electrons act like particles individually, but collectively they exhibit wave behavior. **This is wrong**. 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, C_{60}'s....
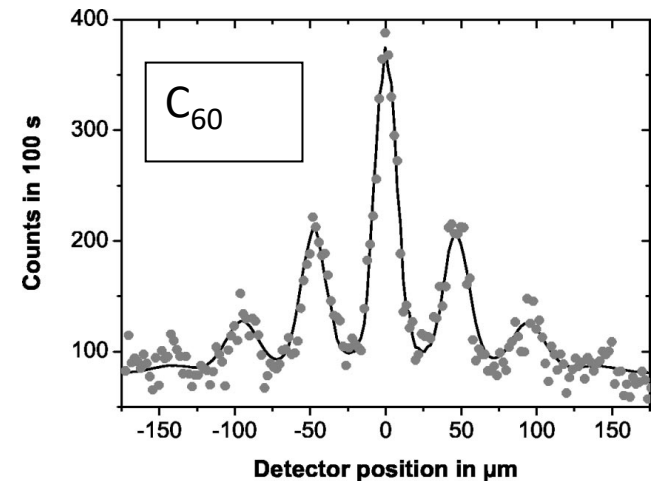
Particle Waves

- 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 simplified- they're really something new, 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/λ (or vector version, **p**=(h/2π)**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.)

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

- The electron is described by a wave function, ψ(**r**,t), which obeys a differential equation. The non-relativistic version is called <u>Schrödinger's</u> equation. (also first due to Lunn)

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

  - 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.

Superposition

- A crucial feature of this equation is that it is linear, implying <u>superposition</u>:
  - <u>Adding any two solutions produces another solution</u>.
- The "stable orbits" are replaced by wave patterns which have a fixed distribution of ψ_ν (standing waves).
  - These are ones with a well-defined value of the energy (E_n).
- Superposing different ψ_n's with different energies make interference patterns that change in time, so the places where ψ is big or small move around.
- The common statement that ψ must have a particular value of energy is <u>false</u>. Only stationary states, where nothing is really changing, have specific values of energy. Most states have a distribution of different values of energy (and f), just as they have distributions of values for position and velocity.
- The electron does not orbit the atom in Keplerian elliptical orbits. A more accurate image of the electron is a fuzzy blob (but a classical blob would remain blob-like even if you probe it with a pin, but the electron blob can "collapse" to a smaller blob if probed with a small, high-energy particle).