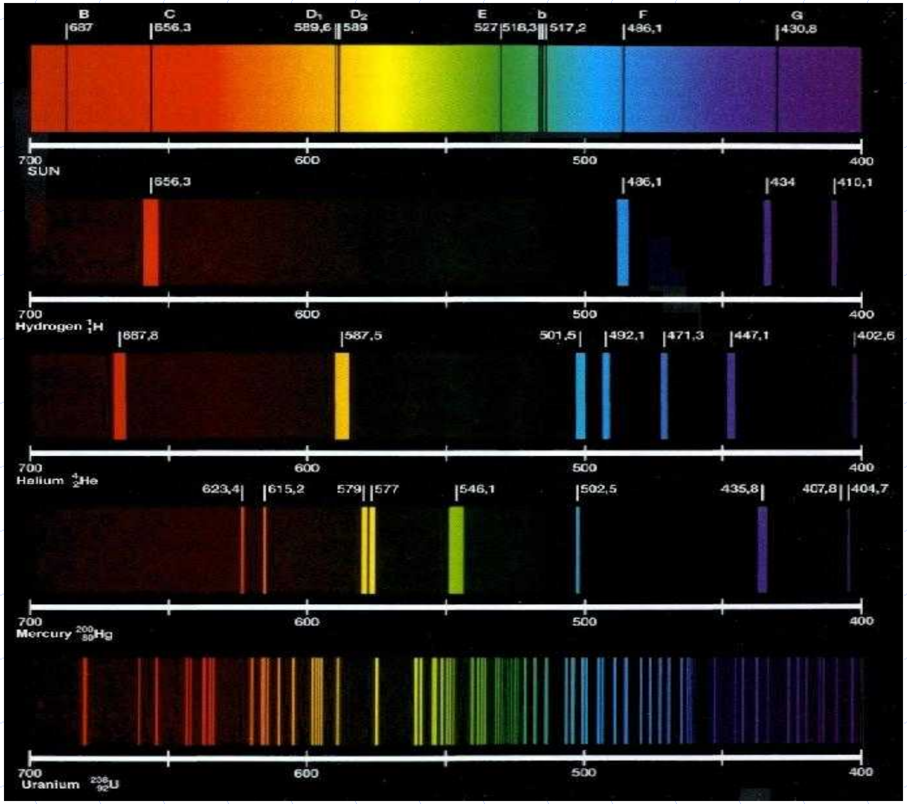
Physical Chemistry

Lecture 9

Introduction to Quantum Mechanics

The energy "problem"

- Early experiments
  - Observed only certain emission frequencies
  - Spectra of atoms
    - H and other atoms
  - Colors of mineral solutions
- Scientists involved have very familiar names
    - Angstrom
    - Balmer
    - Bunsen
    - Fraunhofer
    - Kirchoff
    - Rydberg



Other "problems"

- Planck's theory of blackbody radiation
  - Inferred quantization of modes of a cavity
- Bohr's theory of the H atom
  - Rejected classical electrodynamics to interpret Rydberg's observation
  - Quantization of energy
- DeBroglie's hypothesis
  - Quantized electron momentum to explain a variety of effects

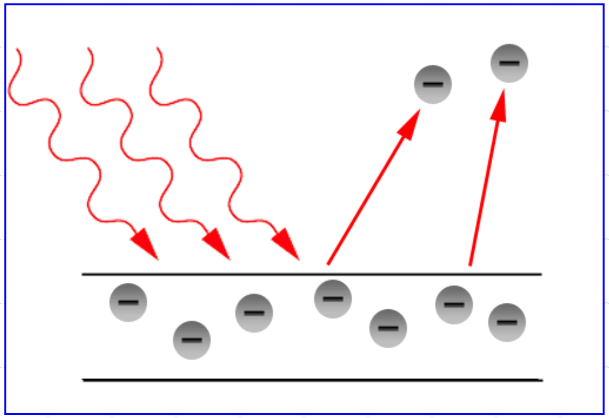
$$E = h\nu$$

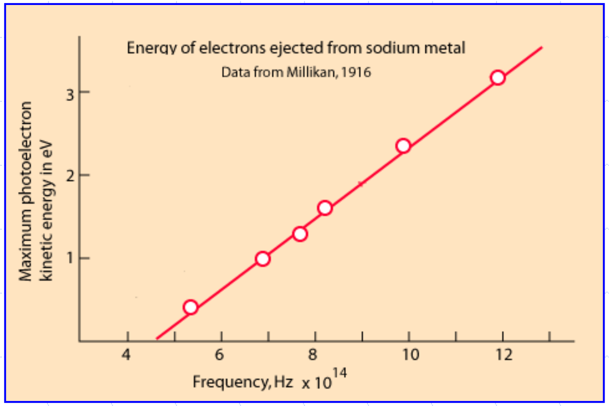
$$\nu = \Re\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$p = N\hbar$$

Photoelectric effect

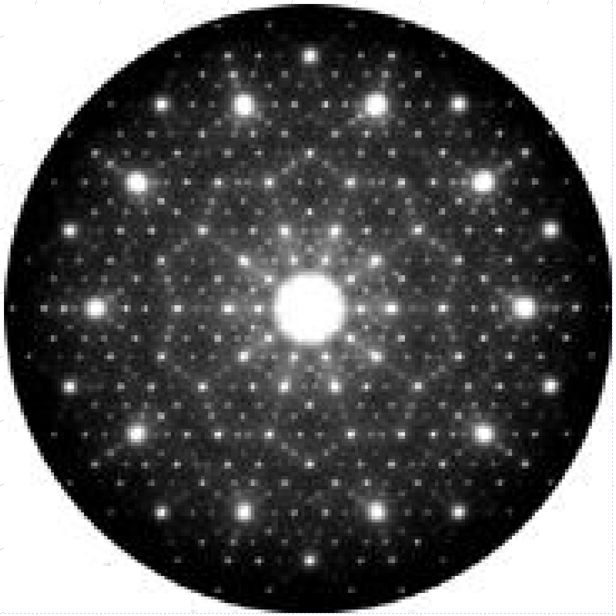
- Light ejects electrons from a metal plate
  - No emission below a minimum frequency
  - Number of electrons emitted is proportional to the intensity
- Electron kinetic energy
  - Does not depend on light intensity
  - Depends linearly on the frequency above the threshold frequency
  - Slope of line gives Planck's constant





Diffraction by particles

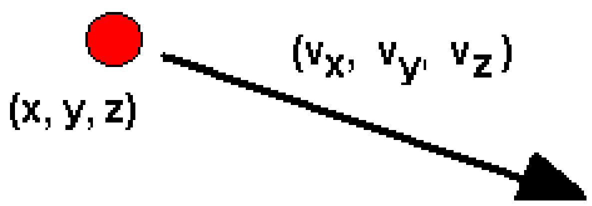
- Diffraction is a property of waves
- Davisson and Germer demonstrated that electrons (particles) interacting with matter act as if they diffract like waves
- Further example of wave-particle duality



Diffraction pattern from electrons interacting with crystalline cobalt

Classical mechanics and states

- In mechanics, one describes precisely
  - Where particles are
  - Where particles are going subject to forces
- The system's state is completely defined by the positions and momenta of all particles -- trajectories
- Everything is absolutely determined by forces and initial conditions

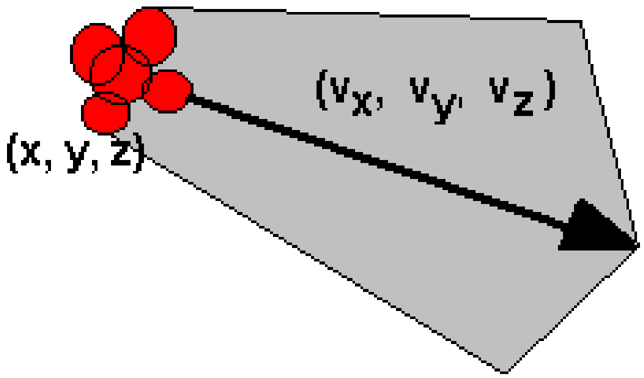


$$v(t) = v(0) + \frac{1}{m}\int_0^t F(t')dt'$$

$$r(t) = r(0) + \int_0^t v(t')dt'$$

Heisenberg's uncertainty principle

- There is no way to measure simultaneously with infinite precision the position and the conjugate momentum of a particle
  - Cannot know trajectories exactly
  - Cannot describe a system as precisely as with classical mechanics
- Inherent property of all systems
- Theory must reflect this property



Quantum mechanical state

- Heisenberg's principle eliminates the correspondence of position and momentum to "state" inherent to classical physics
- Obvious that one needs a definition of state of a quantum system
  - The "state" of a system is given by a function of the positions of particles, but it is not the trajectory under definite forces
  - Function gives all possible information on a system
  - Properties found by operation
  - Definition builds in the restriction of limited information, consistent with Heisenberg's observation
- Born's idea: State is related to the probability of a particular condition, since we cannot know positions and momenta precisely.

Schroedinger's equation

- Chemists primarily interested in systems with constant energy
- Need a means (like Newton's equations for classical mechanics) to determine the state of constant energy
- Functions corresponding to constant qualities found from eigenvalue equations

$$H\Psi = E\Psi$$

Summary

- Early experiments showed that many systems, particularly small systems, could only have certain energies
- Agreement with observation achieved by “violating” classical mechanics
- Uncertainty principle recognizes the wave nature of particles and the inability to use deterministic mechanics
- Totally new theory required
  - Definition of state
  - Operators for properties
  - Eigenvalue equations for property values