Chapter 28

Quantum Mechanics of Atoms

“Your theory is crazy, but it's not crazy enough to be true”

N. Bohr to W. Pauli

Limitations of the Bohr Model

- The model was a great break-through, but there were issues:
  - the nature of angular momentum quantization was not clear, and L being multiples of $h/2\pi$ looked like a coincidence
  - the model did not describe atoms with ≥2 electrons
- The theory was not crazy enough to be true
  - more radical departures from classical concepts were needed

Particles as Waves

- Light, which everybody thought was waves, also behaves like particles
- How about particles? Maybe they can also behave like waves?
  - Searching for symmetries in nature is extremely fruitful!

De Broglie: electron can behave like a wave, and its wavelength is $\lambda = h/p$

same as photon

Electron Diffraction

- Davisson & Germer (1927): a beam of electrons is diffracted on a crystal, much like the X-rays
  - they were able to measure the electron wavelength from the diffraction pattern, and knowing the electron speed, confirm that

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

* It was later confirmed for other particles (e.g. α-particles)
* Macroscopic objects do not exhibit wave properties –the *h* value is small

Uncertainty Principle

- If you want to measure the object position, you will need to touch it. Any touch will change its momentum!
- Even if you just look at an object, if you see it, it means that photons stroke the object and got reflected into your eye. The strike changed the object's momentum!

Uncertainty Principle

- To see an object, we need wavelengths less than its size
  - can't see atoms with eyes! Why?
  - distance ~10^{-10} m, λ=(3-7)×10^{-7} m
- We can only determine distances with accuracy $\Delta x \sim \lambda$
- Suppose we are looking at objects using single photons
  - when the photon strikes an object, it changes its momentum by a value of order of its own momentum:

$$\Delta p \sim p_\gamma = \frac{h}{\lambda} \qquad\qquad \Delta p\,\Delta x \sim h$$

Particles as Waves and Uncertainty Principle

$$\psi = \sin(kx - \omega t) \qquad k = \frac{2\pi}{\lambda} = \frac{p}{\hbar}$$

- If we know wave number *k* (and momentum *p*) precisely, we have no clue where the particle is
- If we don't know the wave number well, the particle looks like a mixture of waves with different *k*
  – this is what is called a wave packet
- The wider is the *k* spread, the narrower is the wave packet

Uncertainty Principle

- If a particle is also a wave, then it doesn't have a definite trajectory. If we know well its direction, then we don't know well its position and vice versa.

Heisenberg uncertainty principle(s):

$$\Delta x \, \Delta p_x \geq \hbar \qquad \qquad \Delta t \, \Delta E \geq \hbar$$

Probability vs Determinism

- Classical view: if the initial conditions (positions and velocities) and the forces are known, the motion is determined (always the same).
- Quantum world: particles released in the same way will not all end in the same place!
  - double slit experiment with single photons or electrons
- Probability in QM is not a limitation of our tools – it's inherent.
- Space-time description of atoms and electrons is not possible. They are spread over time/space.

Particles and Waves

- Light is EM waves, what is oscillating is electric and magnetic fields
- When we are talking about other particles, what is oscillating?
  - Probability.

$$\psi(x, y, z, t)$$

wave function = probability amplitude

$|\psi|^2$ is the probability to find a particle at *x*, *y*, *z*, at time *t*

Quantum Mechanics and Atoms

- Electrons do not follow orbits – they form "clouds"
- The ground state in hydrogen is spherically symmetric (not a circle!)

Atom: Quantum Numbers

- Principal quantum number *n*: like Bohr said

$$E_n = -\frac{13.6\ \text{eV}}{n^2}$$

- *n* can have any integer value (1, 2, …)
- It determines the total energy of a state in the hydrogen atom

Atom: Quantum Numbers

- Orbital quantum number l: yes, the angular momentum is quantized
- l can be an integer from 0 to (n-1)

larger than $l\hbar$

$$L = \sqrt{l(l+1)}\hbar$$

- Magnetic quantum number m_l: determines the momentum direction
- m_l can be an integer between $-l$ and l

$$L_z = m_l \hbar$$

nothing known about L_x, L_y

Spin

- Each spectral line of hydrogen actually consists of two very close lines ("fine structure")
- The splitting is ~$(Z\alpha)^2$, where $$\alpha = \frac{ke^2}{\hbar c} \approx \frac{1}{137}$$
  - Hypothesis: this is due to angular momentum associated with spinning of the electron (planetary model)
  - Can't be true (electrons are point-like), however electrons do have some intrinsic property which looks like an angular momentum
- m_s can be +1/2 or −1/2

$$S_z = m_s\hbar$$

Pauli Exclusion Principle

- No two electrons in an atom can occupy the same quantum state
- Closely related to spin: refer to particles with half-integer spin (electrons, protons), but not to particles with integer spin (photons)