

Lecture 1

Classical versus Quantum Mechanics

Suggested books:

- Physical Chemistry, by P. Atkins and J. de Paula
- Physical Chemistry, by I. N. Levine
- Physical Chemistry; A Molecular Approach, by D. A. McQuarrie and J. D. Simon
- Solve more numerical and analytical problems from the reference books

Energy of a classical particle can vary continuously.

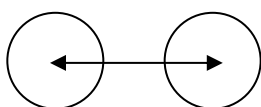
- Newton's laws describe motion of everyday objects:
Forces cause acceleration; hence they change velocity and momentum:

$$\vec{F} = m\vec{a} = m \frac{d\vec{v}}{dt} = \frac{d\vec{p}}{dt}$$

Examples: Electromagnetic force between charges q_1 and q_2 . Gravitational force between masses m_1 and m_2 .

Force results in acceleration due to the change in velocity and momentum.

Both forces point directly along the line between the two particles. Masses and opposite charges attract; like charges repel.



$$F(r) = \frac{q_1 q_2}{(4\pi\epsilon_0 r^2)}; F(r) = -\frac{Gm_1 m_2}{r^2}$$

NOTE: For a net force to act the velocity must change—change of speed is not important. Velocity is a vector quantity (it has both magnitude and direction). For example, the force of gravity holds the Earth in a near-circular orbit around the Sun. If the orbit were perfectly circular, the Earth's speed would be constant, although the direction (hence the velocity vector) is always changing.

- Total Momentum is conserved in a Closed System
 - For Example: Space shuttle moves up and the exhaust gases move down (to conserve total momentum).

$$\vec{F}_{total} = \frac{d\vec{p}_{total}}{dt} = 0 \quad \text{From Newton's 3rd Law}$$

- Energy can be interconverted between different forms
 - When the spring is fully extended, the balls are not moving (they have no kinetic energy). Energy is stored in the spring.
 - In exothermic reactions, stored chemical energy is converted into heat.
 - Energy conservation is subtler than the momentum conservation.

- Energy Storage can be motivated by defining Potential Energy

$$\vec{F}(x) = \frac{-dU(x)}{dx} \text{ defines potential energy } U(x) \text{ (to within a constant).}$$

- Compressing or extending a spring requires work; energy stored as potential energy.
- Release stretched spring: force accelerates mass

Sum of kinetic energy $K = \frac{mv^2}{2}$ and potential energy U is conserved (ignoring friction)

At the turn of the 20th century, many experiments showed that usual classical mechanics approach to microscopic mass, length, time scales was not appropriate.

- Discrete spectra of the atomic lines.
"Classical" theories simply cannot explain the atomic and subatomic level. For example, if Newtonian mechanics governed the workings of an atom, electrons would rapidly travel towards and collide with the nucleus. In the natural world the electron normally remains in a stable orbit around a nucleus. Old Quantum Mechanics (Neils Bohr) was initially developed to explain the atom—the electron staying in discrete orbits around the nucleus.
- Bohr's model (1913) could explain H-atom emission spectrum by considering that energies that an electron can possess in the hydrogen atom are given by

$$E_n = \frac{\text{constant}}{n^2}, \quad n = 1, 2, \dots$$

Quantum \Leftrightarrow Discrete

And, quantization of energy was required to explain several experiments.

- Max Plank assumed that blackbody radiation was caused by the oscillations of electrons (1900). He could then explain the blackbody radiation by considering that the energy of the oscillator is quantized as $E = nh\nu$, where n is an integer, h is the Plank's constant, with $h = 6.626 \times 10^{-34}$ J s, and ν is the frequency of the electromagnetic wave.
- Einstein could explain the photoelectric effect considering that light is composed of particle like entities (called photons), with each photon having an energy $E = h\nu$ (1905).

Only photons of a high-enough frequency, (above a certain threshold value) could knock an electron free. For example, photons of blue light, but not photons of red light, have sufficient energy to free an electron from the metal. More intense light above the threshold frequency could release more electrons, but no amount of light below the threshold frequency could release an electron. Thus, light seems to exhibit dual nature: wave-like and particle-like.

Thus, quantum mechanics incorporates three classes of phenomena that classical physics cannot account for: (i) the quantization (discretization) of certain physical quantities, (ii) wave-particle duality, & (iii) the uncertainty principle.

de Broglie's Postulate (1924): Wave-Particle Duality

Bohr's theory couldn't answer why the energy of hydrogen electron is quantized. Atomic spectrum shows discrete frequencies, i.e. only certain energies of motion are allowed. It is difficult to explain such quantization within classical description, but quantization is possible in wave motion; for e.g. fundamental and overtone frequencies of a violin string. This lead deBroglie to arrive at the conclusion that electrons might have some wave nature. Also, in many experiments, light shows wave like character (for e.g. dispersion of white light into its spectrum) but in many other experiments, light behaved like a stream of

photons (for e.g. photoelectric effect). de Broglie argued that if light displays dual nature, matter also should ("Wave-Particle Duality"). He deduced this connection based on the Einstein–Planck expression for the energy of an electromagnetic wave and classical result for the momentum of waves.

$$E = h\nu = h\frac{c}{\lambda}$$

Now, $p = \frac{E}{c}$ By substitution: $p = \frac{hc}{c\lambda} = \frac{h}{\lambda}$, which is then true for any particle, so we have: $\lambda = \frac{h}{p} = \frac{h}{mv}$.

Thus, any particle with momentum p possess wavelike properties characterized by the wavelength λ (called the de Broglie's wavelength). This was later confirmed by experiments by Davisson and Germer in 1927, and by Thomson in 1928. In their experiments, they observed diffraction of electrons. Later, same effects were also seen for helium atoms and hydrogen molecules (Stern, 1932) confirming this to be a universal law.

For an electron (electronic mass = 9.11×10^{-31} kg) traveling at 1% of the speed of light (3.0×10^8 m/s) has a de Broglie wavelength $\lambda = 2.43 \times 10^{-10}$ m = 2.43 Å. This is not a negligible number for the length-scale while dealing with electrons or atoms. On the other hand, de Broglie wavelength associated with a ball that weighs 150 g and traveling at a velocity of 100 km/h is 1.59×10^{-34} m. This is so small that it cannot be detected and has no significance when dealing with the motion of ball. Hence value of the Planck's constant sets the length-scales at which wave-character of a particle is significant.

de Broglie proposed that electron bound to a nucleus behaves like a standing wave. He argued that, the length of the wave must fit to the circumference of the orbit exactly. If not, the wave would partially cancel itself on each successive orbit, eventually reducing their amplitudes to zero.

The Heisenberg Uncertainty Principle (1927)

To describe the classical motion of a particle we require position and momentum of particles. However, wave–particle duality has serious effect while we measure the position and momentum of microscopic particles such as electrons! The act of measurement introduces uncontrollable disturbance in the system being measured, resulting in uncertainties in momentum/position measurement. Heisenberg proposed a principle that uncertainties in the simultaneous measurement of momentum (Δp) and position (Δx) of a particle are multiplied together, the product is approximately equal to Planck's constant divided by 4π . In other words, if we compute the uncertainty Δx of the position measurements and the standard deviation Δp of the momentum measurements, then

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$

where \hbar is the reduced Planck's constant (Planck's constant divided by 2π).

Dirac's constant: $\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34}$ Js.

Components of angular momentum operator also follow the uncertainty relationship as they are complementary operators. A pair of conjugate variables is often Fourier transform duals of one-another. The duality relations lead naturally to an uncertainty relation between them.

How to define uncertainty as Δx and Δp ?

For a set of positions: $x_1, x_2, x_3, \dots, x_N$, average \bar{x} : $\bar{x} = \frac{1}{N}(x_1 + x_2 + \dots + x_N)$

$$\overline{x^2} = \frac{1}{N}(x_1^2 + x_2^2 + \dots + x_N^2)$$

Standard deviation, i.e., RMS deviation: $\sqrt{\langle \overline{x^2} \rangle - \langle \bar{x} \rangle^2} \equiv \Delta x$

We can understand the origin of relationship between the two uncertainties considering the example of an electron. If we would like to measure the position of an electron to an accuracy Δx , we need to use a light whose wavelength $\lambda \leq \Delta x$. When light collide with electrons, part of the photon's momentum ($p = h/\lambda$) will be transferred to electron. Thus, such a measurement will affect the momentum of the electron, resulting in uncertainty in its momentum by Δp . Smaller the wavelength of the light, higher is the momentum of photons, resulting in higher uncertainty in the momentum of electrons. This is not the result of poor measurement or experimental limitation, rather, a fundamental property.

For macroscopic systems, like a cricket ball, the uncertainties in momentum is negligible as we do not try to measure their position to very high accuracy; thanks to the fact that Planck's constant is a "very small" number. However, when dealing with systems at atomic scale, uncertainty principle becomes relevant.

Thus, Quantum \Rightarrow size of system of interest $\sim \Delta x \ll$ size of system of interest \Rightarrow Classical

In 1927, Paul Dirac gave the mathematical formulation of quantum mechanics which unifies and generalizes the two earliest formulations of quantum mechanics, matrix mechanics (invented by Werner Heisenberg) and wave mechanics (invented by Erwin Schrödinger).

In this formulation, the instantaneous state of a quantum system encodes the probabilities of its measurable properties, or "observables". Examples of observables include energy, position, momentum, and angular momentum. Observables can be either continuous (e.g., the position of a particle) or discrete (e.g., the energy of an electron bound to a hydrogen atom).

We can also express Heisenberg uncertainty principle in terms of energy and time, as

$$\text{momentum} = \text{mass} \times \text{velocity} = \text{mass} \times \frac{\text{velocity}}{\text{time}} \times \text{time} = \text{force} \times \text{time}$$

Now,

$$\text{momentum} \times \text{distance} = \text{force} \times \text{distance} \times \text{time} = \text{energy} \times \text{time}$$

Thus:
$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

Bohr's theory (old quantum mechanics) is inconsistent with the Uncertainty Principle, since a specific circular path is assigned for electronic motion. Soon we will discuss a theory which is consistent with the Uncertainty Principle and is applicable to all the atoms and molecules (thus define a theoretical/mathematical framework for chemistry!). Please note that the uncertainty principle implies that we have to abandon the classical notion of a trajectory, i.e., $[x(t), p_x(t)]$.