Quantum mechanics. Introduction.

What is quantum mechanics?
Quantum mechanics (aka wave mechanics) is the study of matter and radiation at an atomic level.

Why was quantum mechanics developed?
In the early 20-th century some experiments produced results which could not be explained by classical physics. For instance, it was well known that electrons orbited the nucleus of an atom. However, if they did so in a manner which resembled the planets orbiting the sun, classical physics predicted that the electrons would spiral in and crash into the nucleus within a fraction of a second. Obviously that doesn't happen, or life as we know it would not exist. That incorrect prediction, along with some other experiments that classical physics could not explain, showed scientists that something new was needed to explain science at the atomic level.
If classical physics is wrong, why do we still use it?
For everyday things, which are much larger than atoms and much slower than the speed of light, classical physics does an excellent job. Plus, it is much easier to use than either quantum mechanics or relativity (each of which require an extensive amount of math).

What is the importance of quantum mechanics?
The following are among the most important things which quantum mechanics can describe while classical physics cannot:

- Discreteness of energy
- The wave-particle duality of light and matter
- Quantum tunneling
- The Heisenberg uncertainty principle
- Spin of a particle
Wave-Particle Duality
Electrons exhibit weave-like behavior. Every particle has a wavelength (de Broglie) given by $\lambda = \frac{h}{p}$.

**Question:** Why don’t we see particle waves (i.e., diffraction and interference) in day-to-day life?

**Answer:** Macroscopic objects have *wavelengths too small* to interact with slits, but atomic-sized objects do appear to behave like waves!

**Example:** *Macroscopic Object* – ping pong ball

$$\lambda (\text{ping pong ball}) = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(2 \times 10^{-3} \text{ kg})(5 \text{ m/s})} = 6.6 \times 10^{-32} \text{ m}$$

Immeasurably small!

**Example:** *Microscopic Object* – “slow electron” (1% speed of light)

$$\lambda (\text{electron}) = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(9.1 \times 10^{-31} \text{ kg})(10^6 \text{ m/s})} = 7.3 \times 10^{-10} \text{ m}$$

Atomic Dimensions
2.4. Quantum mechanics

**Probability and the Uncertainty Principle**

It is impossible to describe with absolute precision events involving individual particles on the atomic scale.

Instead, we must speak of the *average values* (expectation values) of position, momentum, and energy of a particle such as an electron.

The theory describes the *probabilistic nature* of events involving small particles (atoms, electrons, elementary particles). The fact is that such quantities as the position and momentum of an electron do not exist apart from a particular uncertainty.
Heisenberg uncertainty principle

The magnitude of uncertainty to determine physical quantities (position, momentum, energy) is described by the *Heisenberg uncertainty principle* (also known as the principle of indeterminacy)

In any measurement of the position and momentum of a particle, the uncertainties in the two measured quantities will be related by

\[
(\Delta x) \cdot (\Delta p_x) \geq \hbar
\]
Heisenberg uncertainty principle – 2

Similarly,

The uncertainties in an energy measurement will be related to the uncertainty in the time at which the measurement was made by:

\[(\Delta E) \cdot (\Delta t) \geq \hbar\]
Heisenberg uncertainty principle – 3

Example:
What is the *uncertainty* in velocity for an electron in a 1 Å radius orbital in which the positional uncertainty is 1% of the radius?

\[ \Delta x = 1 \times 10^{-10} \text{ (m)} \times 0.01 = 1 \times 10^{-12} \text{ (m)} \]

\[ \Delta p = \frac{h}{2\pi \Delta x} = \frac{6.626 \times 10^{-34} \text{ (J \cdot s)}}{2\pi \times 1 \times 10^{-12} \text{ (m)}} = 1.05 \times 10^{-22} \text{ (kg \cdot m/s)} \]

\[ \Delta v = \frac{\Delta p}{m} = \frac{1.05 \times 10^{-22} \text{ (kg \cdot m/s)}}{9.11 \times 10^{-31} \text{ (kg)}} = 1.2 \times 10^8 \text{ (m/s)} \]

Huge!
Heisenberg uncertainty principle – 4

Example:
What is the uncertainty in position for a 80 kg student walking across campus at 1.3 m/s with an uncertainty in velocity of 1%.

\[ \Delta p = m \times \Delta v = 80(\text{kg}) \times 0.013(\text{m/s}) = 1.04 \ (\text{kg} \cdot \text{m/s}) \]

\[ \Delta x = \frac{h}{4\pi\Delta p} = \frac{6.626 \times 10^{-34} (\text{J} \cdot \text{s})}{4\pi \times 1.04(\text{kg} \cdot \text{m/s})} = 5.07 \times 10^{-35} \ (\text{m}) \]

Uncertainty in position of a student is very small – we know where you are!
The uncertainty principle brings us to an idea that we cannot properly speak of the position of an electron, but must look for the *probability* of finding an electron at a certain position.

Thus one of the important results of quantum mechanics is that a *probability density function* can be obtained for a particle in a certain environment, and this function can be used to find the expectation value of important quantities such as position, momentum, and energy.

For this purpose, it is common to define:

A *probability density function* $P(x)$ describes the *probability of finding a particle within a certain volume*. 
Probability – 2

The **probability** of finding the particle in a range from \(x\) to \((x + dx)\) is \(P(x)dx\).

Since the particle will be somewhere, the **probability to find it in some point within region** \((-\infty, \infty)\) must be 1:

\[
\int_{-\infty}^{\infty} P(x)\,dx = 1
\]

if the function \(P(x)\) is properly chosen – normalized.

To find the **average value** of a function of \(x\) \((f(x))\), we need only multiply the value of that function in each increment \(dx\) by the probability \((P(x))\) of finding the particle in that \(dx\) and sum over all range of \(x\):

**Average value of \(f(x)\):**

\[
\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)P(x)\,dx
\]

where \(P(x)\) is **normalized**.
The Schrödinger wave equation - 1

Basic postulates:

Postulate 1.

Each particle in a physical system is described by a wave function \( \Psi(r,t) = \Psi(x,y,z,t) \).

This function and its partial space derivative \( \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi}{\partial y} + \frac{\partial \Psi}{\partial z} \) are continuous, finite, and single valued.

Wave function can be interpreted as probability amplitude
The Schrödinger wave equation - 2

Postulate 2.

In dealing with classical quantities such as energy $E$ and momentum $p$, we must relate these quantities with abstract quantum mechanical operators defined in the following way (one-dimensional case).

<table>
<thead>
<tr>
<th>Classical variable</th>
<th>Quantum operator</th>
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<tbody>
<tr>
<td>$x$</td>
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<tr>
<td>$f(x)$</td>
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<td>$p(x)$</td>
<td>$\frac{\hbar}{j} \frac{\partial}{\partial x}$</td>
</tr>
<tr>
<td>$E$</td>
<td>$\frac{\hbar}{j} \frac{\partial}{\partial t}$</td>
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</table>
The Schrödinger wave equation - 3

Postulate 3.

The *probability* of finding a particle with wave function $\Psi$ in the volume $(dx \times dy \times dz)$ is $(\Psi^* \Psi) \, dx \times dy \times dz$.

$(\Psi^*$ is the complex conjugate of $\Psi$, obtained by reversing the sign of each $j$. Thus, $(e^{ij})^* = e^{-ij}$).

The product $\Psi^* \Psi$ is *normalized* so that $\int_{-\infty}^{\infty} \Psi^* \Psi \, dx \, dy \, dz = 1$

and the *average value* $\langle Q \rangle$ of any variable $Q$ is calculated from the wave function by using the *quantum operator* $Q_{\text{op}}$ defined in postulate 2:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \Psi^* Q_{\text{op}} \Psi \, dx \, dy \, dz = 1$$
The Schrödinger wave equation - 4

The classical equation for the energy of a particle: \( E_{\text{kin}} + E_{\text{pot}} = E_{\text{tot}} \)

**Kinetic energy** \( E_{\text{kin}} \):  \[ E_{\text{kin}} = \frac{mV^2}{2} = \frac{p^2}{2m} \]

**Potential energy** \( E_{\text{pot}} \):  \[ E_{\text{pot}} = U(\vec{r}) \quad (U - \text{potential energy}) \]

\[ \frac{p^2}{2m} + U = E_{\text{tot}} \]
The Schrödinger wave equation - 5

\[
\frac{p^2}{2m} + U = E_{\text{tot}}
\]

In quantum mechanics we have to use the operator form for variables momentum \( p \) and energy \( E \) (postulate 2); the operators are allowed to operate on the wave function \( \Psi \).

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</tr>
<tr>
<td>( E )</td>
<td>( \frac{\hbar}{j} \frac{\partial}{\partial t} )</td>
</tr>
</tbody>
</table>

\[
\frac{p^2}{2m} + U = E_{\text{tot}} \quad \Rightarrow \quad -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(\vec{r},t)}{\partial \vec{r}^2} + U(\vec{r})\Psi(\vec{r},t) = -\frac{\hbar}{j} \frac{\partial \Psi(\vec{r},t)}{\partial t}
\]
The Schrödinger wave equation - 6

We can rewrite the equation using conventional notation:

\[ \nabla^2 \Psi = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \]

\[ -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(\vec{r},t)}{\partial \vec{r}^2} + U(\vec{r})\Psi(\vec{r},t) = -\frac{\hbar}{j} \frac{\partial \Psi(\vec{r},t)}{\partial t} \]

\[ \downarrow \]

\[ -\frac{\hbar^2}{2m} \nabla^2 \Psi + U \Psi = -\frac{\hbar}{j} \frac{\partial \Psi}{\partial t} \]

\[ \text{– the Schrödinger wave equation.} \]

Note: the wave function \( \Psi \) in the Schrödinger wave equation includes both space and time dependencies.
The Schrödinger wave equation - 7

\[
\frac{-\hbar^2}{2m} \nabla^2 \Psi + U \Psi = -\frac{\hbar}{j} \frac{\partial \Psi}{\partial t}
\]

where \( \Psi(r,t)=\Psi(x,y,z,t) \) is a function of space coordinates and time (!);

\( U(r) \) – potential energy (field). (It may have very complex form)

Wave functions are solutions to the Schrodinger wave equation. The wave function, \( \Psi(x, t) \) describes physical state of the particle, such as its momentum, energy etc. and also where the particle is (in terms of probability ).

This is quite complex differential equation – typically it is very difficult to solve it and find \( \Psi(r,t) \).

In many cases, it is possible to solve the wave equation by breaking it into two equations by the technique of separation of space coordinates and time variables.

Let \( \Psi(x,t) \) be represented by the product \( \psi(x) \times \phi(t) \)
The Schrödinger wave equation - 8

Let $\Psi(x,t)$ be represented by the product $\psi(x) \times \phi(t)$:

$$\Psi(x,t) = \psi(x) \times \phi(t)$$

Substituting this product in the Schrödinger wave equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t) = -\frac{\hbar}{j} \frac{\partial \Psi(x,t)}{\partial t}$$

we have:

$$-\frac{\hbar^2}{2m} \phi(t) \frac{\partial^2 \psi(x)}{\partial x^2} + U(x)\psi(x)\phi(t) = -\frac{\hbar}{j} \psi(x) \frac{\partial \phi(t)}{\partial t}$$

Now the variables can be *separated*!
The Schrödinger wave equation - 9

Separation of variables allows us to derive two independent equations:

(1) **the time-dependent Schrödinger equation** in one dimension:

\[
\frac{\partial \phi(t)}{\partial t} + \frac{jE}{\hbar} \phi(t) = 0
\]

[We are not going to discuss the time-dependent Schrödinger wave equation in this course]

(2) **the time-independent Schrödinger equation.**

To derive time-independent Schrödinger equation, we have to recall quantum operator to determine energy:

\[
-\hbar \frac{\partial}{j \partial t}
\]
The Schrödinger wave equation - 10

\[-\frac{\hbar^2}{2m} \phi(t) \frac{\partial^2 \psi(x)}{\partial x^2} + U(x)\psi(x)\phi(t) = -\frac{\hbar}{j} \psi(x) \frac{\partial \phi(t)}{\partial t}\]

Using quantum energy operator:

\[-\frac{\hbar}{j} \frac{\partial}{\partial t}\]

Thus, eliminating time dependent function \(\phi(t)\) we have:

\[-\frac{\hbar^2}{2m} \phi(t) \frac{\partial^2 \psi(x)}{\partial x^2} + U(x)\psi(x)\phi(t) = \psi(x)E\phi(t)\]

or

\[\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} \left[E - U(x)\right] \psi(x) = 0\]
The Schrödinger wave equation - 11

**The time-independent (stationary) Schrödinger equation:**

\[
\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} [E - U(x)] \psi(x) = 0
\]

Solution of this equation, wave function \( \psi(x) \), describes a particle in stationary state.

Constant \( E \) corresponds to the energy of the particle when particular solutions are obtained, such that a wave function \( \psi_n \) corresponds to a particle energy \( E_n \).

This equation is the basis of wave mechanics. From it we can determine the wave functions for particles in various simple systems.

For calculations involving electrons, the potential term \( U(x) \) usually represents electrostatic or magnetic field.
Particle in potential well – 1
(“particle in a box”)

\[ \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} [E - U(x)] \psi(x) = 0 \]

It is quite difficult to find solutions to the Schrödinger wave equation for most realistic potential fields \( U(x) \).

“1-D”: \( U(x) = -\frac{q^2}{x} \)

“2-D”:

The simplest problem is the potential energy well with infinite boundaries - “particle in a box”
Particle in potential well – 2

For free particle (electron) of mass $m$ inside one-dimensional potential well ($U(x) = 0$) Schrödinger time-independent (stationary) equation:

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} [E - U(x)] \psi(x) = 0$$

for $0 < x < L$
Particle in potential well – 3

This Schrödinger equation for free particle (electron) of mass \( m \) inside one-dimensional well \((U(x) = 0)\)

\[
\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E\psi(x) = 0 \quad \text{for } 0 < x < L
\]

has general solution: \( \psi(x) = Ae^{jkx} + Be^{-jkx} \)

Shape of the potential well dictates the **boundary conditions**: the solution \((\psi(x))\) must have **zero** values at the walls of the well \((x = 0 \text{ and } x = L)\). This is due to the fact that probability to find particle outside the well must be zero: \(|\psi(x)|^2 = 0\) for any \(x < 0\) and \(x > L\).

Thus, the **boundary conditions**: \( \psi(0) = 0 ; \quad \psi(L) = 0 \)
Particle in potential well – 4

General solution of the equation
\[ \psi(x) = ae^{jkx} + be^{-jkx} \]
can be given in more simple form:
\[ \psi(x) = A \sin(kx) + B \cos(kx) \]

We must examine boundary conditions to choose a solution:

Solution should satisfy boundary condition: \( \psi(x=0) = 0 \)
At \( x = 0 \) we have: (1) \( A \sin(k0) = 0 \); (2) \( B \cos(k0) \neq 0 \)

\[ \downarrow \]
\[ \psi(x) = A \sin(kx) \] satisfies boundary condition \( \psi(0) = 0 \)
and \( \psi(x) = B \cos(kx) \) – does not.

The solution of the equation is \( \psi(x) = A \sin(kx) \)
Particle in potential well – 5

Thus, the solution of the Schrödinger equation for free particle inside one-dimensional potential well is \( \psi(x) = A \sin(kx) \)

Parameter \( k \) can be found by substituting solution \( \psi(x) = A \sin(kx) \) into equation

\[
\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E\psi(x) = 0 \quad \text{for } 0 < x < L
\]

\[
\frac{\partial^2 A \sin(kx)}{\partial x^2} + \frac{2m}{\hbar^2} EA \sin(kx) = 0
\]

\[
-Ak^2 \sin(kx) + \frac{2m}{\hbar^2} EA \sin(kx) = 0
\]

\[
-k^2 + \frac{2mE}{\hbar^2} = 0 \quad \Rightarrow \quad k = \sqrt{\frac{2mE}{\hbar^2}}
\]
On the other hand, according to the boundary conditions $\psi(x)$ has to be zero at $x = 0$ and $x = L$.

$k$ must then be some integer multiple of $\pi/L$:

$$k = \frac{n\pi}{L} \quad \text{where } n = 1, 2, 3, \ldots$$

This formula shows what values of energy the particle in the potential well may have.

The energy is quantized !!!

The integer $n$ is called a quantum number.

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \]
Particle in potential well – 7

In order to find amplitude \( A \) of the wave function \( \psi(x) = A \sin(kx) \), – the solution of the Schrödinger equation, – we have to use Postulate 3 stating that probability to find particle anywhere from \(-\infty\) to \(\infty\) is 1. Actually, the probability to find particle in the region from 0 to \(L\) is 1:

\[
\int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,dx = \int_{0}^{L} \psi^*(x)\psi(x)\,dx = 1
\]

[Using formula from table of integrals: \( \int (\sin x)^2 \,dx = \frac{1}{2}x - \frac{1}{4}\sin 2x + C \) ]

\[
\int_{-\infty}^{\infty} \psi^*\psi\,dx = \int_{0}^{L} A^2 \left[ \sin\left(\frac{n\pi}{L}x\right) \right]^2\,dx = A^2 \frac{L}{n\pi} \int_{0}^{L} \left[ \sin\left(\frac{n\pi}{L}x\right) \right]^2 \,d\left(\frac{n\pi}{L}x\right) = \\
= \frac{A^2L}{n\pi} \left[ \frac{1}{2} \left(\frac{n\pi}{L}x\right) - \frac{1}{4}\sin\left(2\frac{n\pi}{L}x\right) \right]_{0}^{L} = \frac{A^2L}{n\pi} \left[ \frac{1}{2} \left(\frac{n\pi}{L}L\right) \right] = \frac{A^2L}{2}
\]
Particle in potential well – 8

Based on Postulate 3: \[ \int_{-\infty}^{\infty} \psi^*(x)\psi(x)\,dx = 1 \]

\[ \frac{A^2 L}{2} = 1 \quad \Rightarrow \quad A = \sqrt{\frac{2}{L}} \]

**Conclusion:**

Free particle of mass \( m \) in one-dimensional potential well \( (U(x) = 0) \) is described by Schrödinger time-independent (stationary) equation:

\[ \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E\psi(x) = 0 \quad \text{with solution} \quad \psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \]
Summary

Free particle of mass $m$ in one-dimensional potential well ($U(x) = 0$) is described by wave functions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \left(\frac{n\pi}{L} x\right)$$

For each allowable value of $n$ the particle may have only certain value of energy given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

This formula describes energy spectrum of the particle in the potential well.

- The energy of a particle in potential well is quantized.
- The integer $n$ is called a quantum number.
- The particular wave function $\psi_n(x)$ and corresponding to it energy $E_n$ describe the quantum state of the particle.
Particle in potential well – 10

\[ U(x), \; E_n \]

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \]

\[ E_1 = \frac{\hbar^2 \pi^2}{2mL^2} \]

\[ E_2 = \frac{4 \hbar^2 \pi^2}{2mL^2} \]

\[ E_3 = \frac{9 \hbar^2 \pi^2}{2mL^2} \]

\[ U(x) = \begin{cases} 
\infty & \text{for } x < 0 \\
0 & \text{for } 0 \leq x \leq L \\
\infty & \text{for } x > L
\end{cases} \]
Particle in potential well – 11

\[ \psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi}{L} x \right) \]
Wave function $\psi_n(x)$.

Probability of finding a particle at a position $x$ inside the well is proportional to $|\psi_n(x)|^2$
Probability to find electron in the interval from $x = 2$ to $x = 3$ is

$$
\int_{2}^{3} |\Psi(x)|^2 \, dx = 0.194 \approx 20\%
$$

Probability to find electron in the interval from $x = 4.5$ to $x = 5.5$ is

$$
\int_{4.5}^{5.5} |\Psi(x)|^2 \, dx = 0.0000065 \approx 0.00065\%
$$
Tunneling – 1

The wave functions are relatively easy to obtain for the potential well with infinite walls, since the boundary conditions force wave function $\psi_n$ to be zero at the walls. Such shape of potential well models quite unrealistic situation.

A finite potential well is more appropriate model of cases existing in real world.

In this case, process of quantum mechanical tunneling of an electron through a barrier of finite height and thickness may take place.
Solution $\psi_n(x)$ of corresponding Schrödinger equation has nonzero value inside the barrier and beyond it.

Exponential decrease of probability inside barrier

$|\psi_n(x)|^2 \neq 0$ beyond barrier
Tunneling – 3

\[ \psi(x) \]

\[ V \]

\[ E \]

\[ 0 \]

\[ a \]
Tunneling – 4

When the barrier width and height is not infinite, the boundary conditions do not force $\psi$ to zero at the barrier. Instead, we must use the condition that $\psi$ and its slope $d\psi/dx$ are continuous at each boundary of the barrier (postulate 1).

Thus $\psi$ must have a nonzero value within the barrier and also on the other side.

Since $\psi$ has a value to the right of the barrier, $\psi^*\psi$ exists there also, implying that there is some none-zero probability of finding the particle beyond the barrier.

The particle does not go over the barrier! – particle’s total energy is less than the barrier height $U_0$.

The mechanism by which the particle "penetrates" the barrier is called tunneling.

It is impossible to explain effect of tunneling using classical concept. Quantum mechanical tunneling is bound to the uncertainty principle.

Tunneling is important only over very small dimensions, but it can be of great importance in the conduction of electrons in solid-state devices: p-n junctions, field-effect transistors.