

Lecture 3.

Heisenberg uncertainty principle.

One of the consequences of the particle-wave dualism in quantum mechanics is the inability to determine the momentum ($p_x = \frac{h}{\lambda}$) and the position (x) simultaneously.

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

Later in the course we will derive a more general form of the uncertainty principle. For now let us see how the uncertainty principle works for the hydrogen atom:

$$E \sim \frac{\Delta p^2}{2m} - \frac{e^2}{\Delta r}$$

Using $\Delta r \sim \frac{\hbar}{\Delta p}$ we get $E = \frac{\Delta p^2}{2m} - \frac{e^2 \Delta p}{\hbar}$

Let us minimize the latter expression:

$$\text{min } E : \frac{\partial E}{\partial \Delta p} = 0 = \frac{\Delta p}{m} - \frac{e^2}{\hbar}$$

$$\Delta p = \frac{me^2}{\hbar} \quad \Delta r = \frac{\hbar}{\Delta p} = \frac{\hbar^2}{me^2} \quad - \text{Bohr radius!}$$

$$E = \frac{1}{2m} \left(\frac{me^2}{\hbar} \right)^2 - \frac{e^2 me^2}{\hbar^2} = -\frac{1}{2} \frac{me^4}{\hbar^2} \quad - \text{exactly}$$

the energy of the first Bohr orbit

Now we can see why no energy lower than $E_1 = -\frac{1}{2} \frac{me^4}{\hbar^2}$ (approximately) is possible.

The energy can be lowered by decreasing p or decreasing r in

$$E = \frac{p^2}{2m} - \frac{e^2}{r}$$

However, the uncertainty principle $\Delta p \Delta r \approx \hbar$ prevents such a scenario.

Stationary states

The solution of the Schrödinger equation is greatly simplified when the potential does not explicitly depend on time, i.e. $V = V(x)$ [not $V(x,t)$]. We can employ the method of separation of variables, in which we first look for solutions in the form

$$\Psi(x,t) = \psi(x)\varphi(t)$$

By plugging this into the SE, which has the form $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi$, we obtain

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

Now let us divide everything by $\psi(x)\varphi(t)$:

$$i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V$$

Each side must be a constant (as t and x are independent variables). Let us call this constant E

$$i\hbar \frac{1}{\varphi} \frac{d\varphi}{dt} = E \quad \text{or} \quad \frac{d\varphi}{dt} = -\frac{iE}{\hbar} \varphi$$

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V = E \quad \text{or} \quad -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

$$\varphi(t) = A e^{-\frac{iEt}{\hbar}}$$

$$\Psi(x,t) = \psi(x) e^{-\frac{iEt}{\hbar}}$$

Note that with such a form of $\Psi(x,t)$ any operator's expectation value remains constant in time (as long as the operator is not explicitly dependent on time):

$$\langle Q \rangle = \int \psi^* Q(\hat{x}, \hat{p}) \psi dx \neq f(t)$$

and

$$|\Psi(x,t)|^2 = |\psi(x)|^2$$

$\Psi(x,t) = \psi(x) e^{-\frac{iEt}{\hbar}}$ are called stationary solutions to the SE. They are states of definite energy, because they are eigenfunctions of the Hamiltonian: $H(p,x) = \frac{p^2}{2m} + V(x)$

(recall that $p = -i\hbar \frac{\partial}{\partial x}$)

Hence

$$H\psi = E\psi$$

and

$$\langle H \rangle = \int \psi^* H\psi dx = E \int |\psi|^2 dx = E \int |\Psi(x,t)|^2 dx = E$$

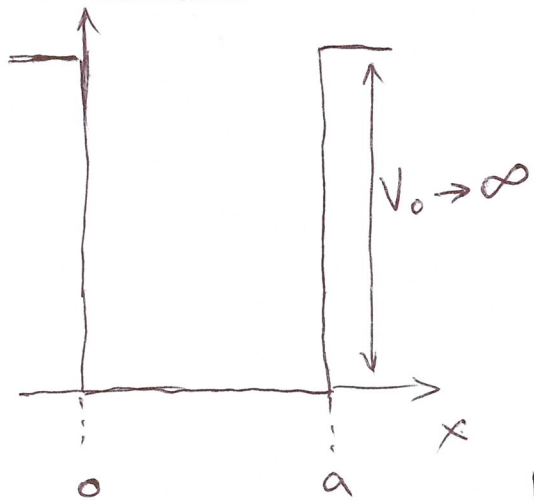
$$\text{Similarly, } \langle H^2 \rangle = E^2 \quad \text{and} \quad \sigma_H = \sqrt{\langle H^2 \rangle - \langle H \rangle^2} = 0$$

The general solution in the method of separation of variables is sought as a linear combination of $\psi_{E_i}(x) \varphi_{E_i}(t)$ where E_i are the allowed values of E (which must be determined by solving $H\psi_{E_i} = E_i \psi_{E_i}$)

$$\Psi(x,t) = \sum_k c_k \psi_k(x) e^{-\frac{iE_k t}{\hbar}}$$

Note that c_k is constant (i.e. independent of time)

Infinite square well (particle in 1D box)



$$V(x) = \begin{cases} V_0 & , 0 \leq x \leq a \\ 0 & , \text{otherwise} \end{cases}$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

When $V_0 \rightarrow \infty$ $\psi(x)$ must vanish.

Hence we have to require that $\psi(0) = \psi(a) = 0$

In the interval $[0, a]$ the SE has the following simple form:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

This is a well known harmonic oscillator equation, which can be rewritten as

$$\psi'' + k^2\psi = 0 \quad \text{where } k = \sqrt{\frac{2mE}{\hbar^2}}$$

The solution of this equation is:

$$\psi(x) = F e^{ikx} + G e^{-ikx} = C \cos(kx + \alpha) = A \sin kx + B \cos kx$$

Since $\psi(0) = 0$ B must be zero

$$\psi(a) = A \sin ka = 0 \quad \Rightarrow \quad ka = n\pi \quad n = 0, 1, 2, \dots$$

If $n=0$ then we get a trivial solution $\psi=0$

$$k = \frac{n\pi}{a}$$

Because only certain values of k satisfy the condition $\psi(0) = \psi(a) = 0$ and they can be "indexed", we will use a subscript, k_n

$$k_n = \frac{n\pi}{a} \quad n = 1, 2, 3, \dots$$

If only certain k_n values are allowed then the energy is also "quantized":

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

← important expression worth memorizing

Now let us turn to the wave function:

$$\psi_n(x) = A_n \sin\left(\frac{n\pi}{a}x\right)$$

To find A_n we will normalize ψ_n :

$$1 = \int_{-\infty}^{+\infty} |\psi(x)|^2 dx = \int_0^a |A_n|^2 \sin^2(k_n x) dx =$$

$$= \int_0^a |A_n|^2 \left(\frac{1 - \cos(2k_n x)}{2}\right) dx = |A_n|^2 \frac{a}{2}$$

$$A_n = \sqrt{\frac{2}{a}} \quad \leftarrow \text{independent of } n!$$

There are important properties of ψ_n , some are general for any form of $V(x)$

1) $\psi_n(x)$ are either even or odd. This is a result of the symmetry of the potential, $V(x)$

2) ψ_{n+1} has one more node than ψ_n . This is actually related to the property in 3)

3) Functions ψ_n and ψ_m are orthogonal when $n \neq m$

$$\int_a^a \psi_m^*(x) \psi_n(x) dx = \frac{2}{a} \int_0^a \sin\left(\frac{m\pi}{a}x\right) \sin\left(\frac{n\pi}{a}x\right) dx$$

$$= \frac{2}{a} \int_0^a \frac{1}{2} \left[\cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right) \right] dx =$$

$$= \left[\frac{1}{(m-n)\pi} \sin\left(\frac{m-n}{a}\pi x\right) - \frac{1}{(m+n)\pi} \sin\left(\frac{m+n}{a}\pi x\right) \right] \Big|_0^a = 0 \text{ if } m \neq n$$

For $m = n$ we get 1. Therefore,

$$\int_a^a \psi_m^*(x) \psi_n(x) dx = \delta_{mn}$$

4) Set of functions ψ_n is called complete, because any function (at least those that have relevance to describing a physical system in QM) can be expanded as a linear combination in terms of ψ_n :

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right)$$

It turns out that for this particular case of ψ_n we basically get a Fourier series.

Coefficients c_n are found as follows:

$$c_n = \int_a^a \psi_n^*(x) f(x) dx$$

If we need to represent an arbitrary time-dependent ~~function~~ solution to the SE we must specify the initial state, $\Psi(x, t=0)$:

Then $c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \psi(x,0) dx$

5) $\sum_{n=1}^{\infty} |c_n|^2 = 1$

$$\begin{aligned} 1 &= \int |\psi(x,0)|^2 dx = \int \left(\sum_{m=1}^{\infty} c_m^* \psi_m^*(x) \right) \left(\sum_{n=1}^{\infty} c_n \psi_n(x) \right) dx = \\ &= \sum_{m,n=1}^{\infty} c_m^* c_n \int \psi_m^*(x) \psi_n(x) dx = \sum_{m,n=1}^{\infty} c_m^* c_n \delta_{mn} = \sum_{n=1}^{\infty} |c_n|^2 \end{aligned}$$