Lecture #19

Energy quantization

Consider a particle moving in 1D in a potential $V(x)$.

Then $\Psi_E(x,t) = \underbrace{\psi_E(x)}_{\text{energy eigenfunctions}} e^{-\frac{i}{\hbar}Et}$

$\Rightarrow$

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

$\Downarrow$

$$\frac{d^2\psi_E(x)}{dx^2} = \frac{2m}{\hbar^2}\left[V(x) - E\right]\psi_E(x)$$

$\Downarrow$

Let's analyze this equation:

2nd order diff. eq. $\Rightarrow$ has two linearly independent solutions for any E

If $V(x)$ is finite everywhere $\Rightarrow$ $\psi_E''(x)$ is finite $\Rightarrow$ $\psi_E'(x)$ and $\psi_E(x)$ are continuous

Out of all mathematical solutions, we have to choose those that are *physical* $\Rightarrow$ $\Psi(x)$ must be finite and single-valued everywhere.

need to eliminate unphysical solutions

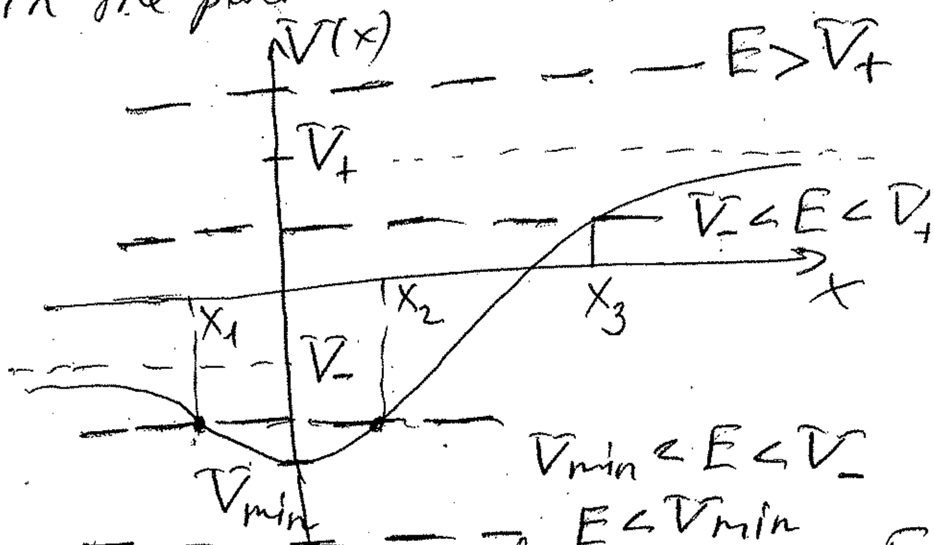
Example

Consider a particle in the potential $V(x)$

$V \to V_+$ at $x \to +\infty$

$V \to V_-$ at $x \to -\infty$

$V = V_{min}$ at $x = 0$



Four cases can be distinguished, depending on the value of energy E

Case 1 $\quad E < V_{min}$

$$\frac{d^2\Psi_E(x)}{dx^2} = \frac{2m}{\hbar^2}\underbrace{(V(x)-E)}_{>0 \text{ at all } x\text{'s}}\Psi_E(x) \Rightarrow \Psi_E'' \text{ and } \Psi_E \text{ are always of the same sign!}$$

if $\Psi_E > 0 \Rightarrow \Psi_E'' > 0$

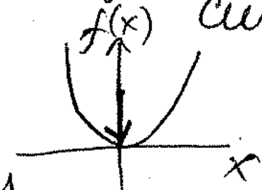
$\Psi_E < 0 \Rightarrow \Psi_E'' < 0$

Recall from functional analysis $\Rightarrow$ a sign of the 2nd derivative shows (determines) the sign of the curvature

Example $f = x^2$; $f'' = 2 > 0$

$\Downarrow$

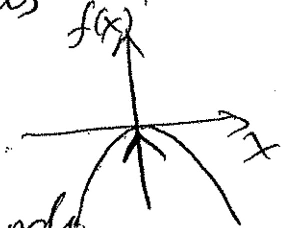
concave upwards



$f = -x^2$; $f'' = -2 < 0$

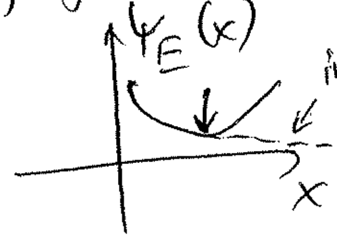
$\Downarrow$

concave downwards



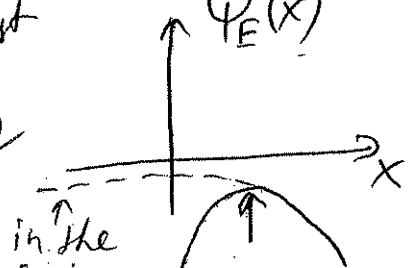
Back to our Case 1

If for all x's ψ_E'' is either > 0 or < 0 $\Rightarrow$



$\psi_E, \psi_E'' > 0$

or



$\psi_E, \psi_E'' < 0$

$\Rightarrow$ in both cases $\psi_E(x)$ blows up either at $x \to \infty$, or at $x \to -\infty$ or both!

$\Downarrow$

no physical solution in this case!

Also note that

if $V(x) - E > 0$ $\Rightarrow$ kinetic energy is negative ~~at~~ all x's!

$\uparrow$

$T + V$

(classically – no motion is possible)

Case 2 $\quad V_{min} < E < V_-$

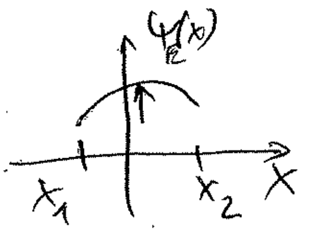
At $x = x_1$ and $x = x_2$ $\Rightarrow$ $E = V(x)$ $\Leftarrow$ these are the classical turning points $\Leftarrow$ limits of the motion of a classical particle of energy E

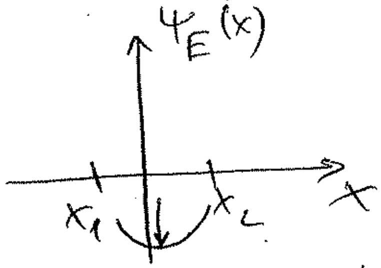
So, classically, the motion is confined to $x_1 \le x \le x_2$ (at $x < x_1$ and $x > x_2$ the kinetic energy becomes negative)

What about quantum-mechanically?

Consider three regions: $x < x_1$, $x_1 \le x \le x_2$, $x > x_2$

In the region $x_1 \le x \le x_2 \Rightarrow V(x) - E < 0 \Rightarrow$





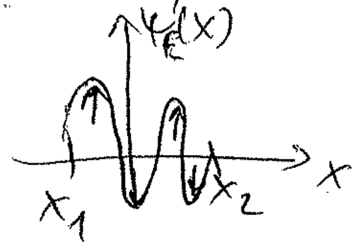
$\Leftarrow$ ψ_E'' is of opposite sign to ψ_E

$\psi_E > 0$, $\psi_E'' < 0$ $\qquad$ $\psi_E < 0$, $\psi_E'' > 0$

$\Downarrow$

oscillatory behavior (once ψ_E reaches 0 its curvature flips) $\Rightarrow$

(two linearly independent oscillatory solutions)

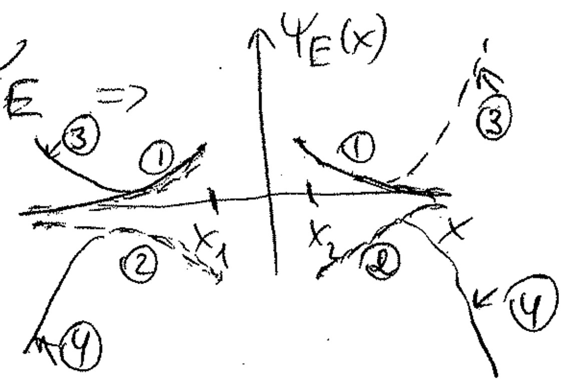


In the regions $\left[\begin{array}{l} x > x_2 \\ x < x_1 \end{array}\right. \Rightarrow$

ψ_E'' is of the same sign as $\psi_E \Rightarrow$

solutions like ① or ② are physical ($\psi_E \to 0$ at $x \to \pm\infty$)

③ & ④ are unphysical



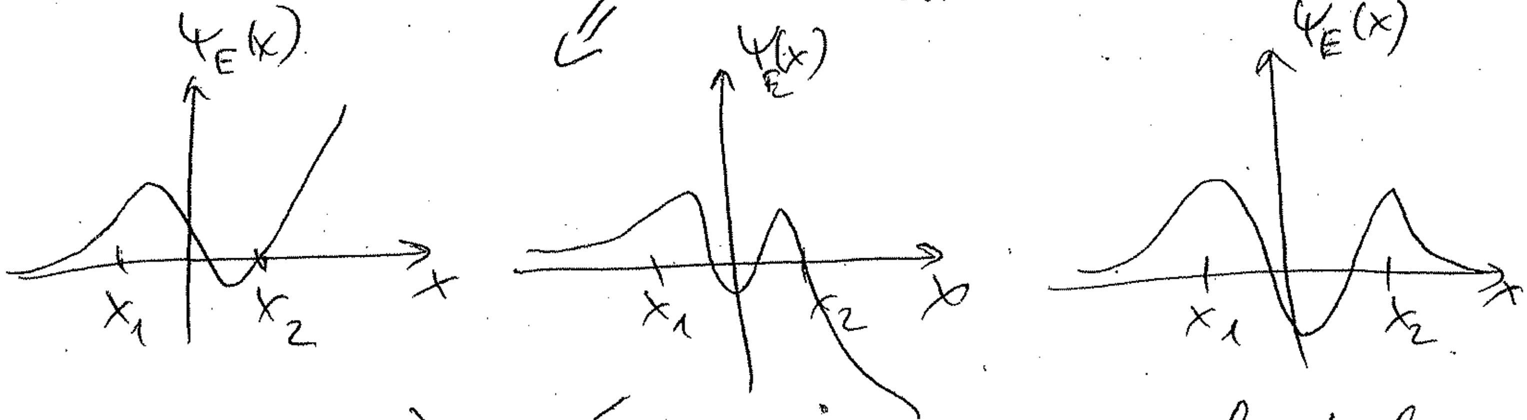
Example: $\psi_E'' - k^2 \psi_E = 0 \Rightarrow \psi_E(x) = C_1 e^{kx} + C_2 e^{-kx}$

If consider $x > x_2 \Rightarrow$ have to have $C_1 = 0$
$x < x_1 \Rightarrow C_2 = 0$
$\Big\}$ to keep $\psi_E(x)$ finite at $x \to \pm\infty$

So, when joining the three regions, we need to ensure that:

1) $\psi_E(x)$ is finite at $x \to \pm\infty$
2) $\psi_E(x)$ is continuous
3) if $V(x)$ is finite everywhere, then $\frac{d\psi_E(x)}{dx}$ is continuous

Note: if $V(x) = C\delta(x-x_0)$ $\Rightarrow$ then it's not the case



physically inadmissible

physical

Since $\psi_E(x) \to 0$ Beyond $x_1 \leq x \leq x_2$ (and the probability density $|\psi_E(x)|^2$) $\Rightarrow$ these eigenfunctions represent bound states. The spectrum of the bound states is discrete $\Rightarrow$ quantization of energy $\to E_n$

The number of the discrete energy levels depends on $V(x)$ $\Rightarrow$ can be finite or infinite.

In 1D the bound-state (discrete) energy eigenvalues are non-degenerate (not true for 2D or 3D)

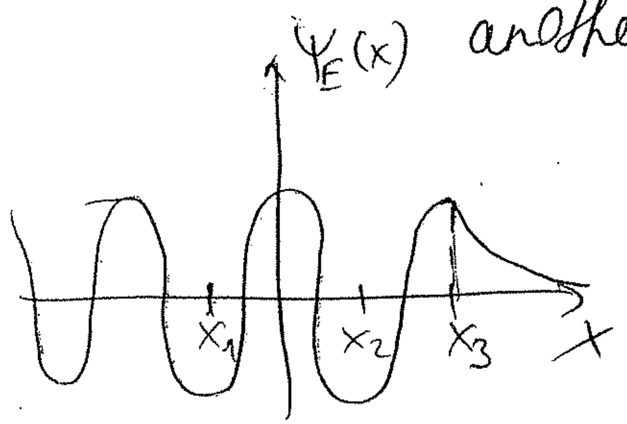
Case 3 $\quad V_- < E < V_+$

At this energy interval, there is only one classical turning point at $x = x_3$ (no classical motion is allowed at $x > x_3$). Classically the particle is unbound (since it can move in an infinite region of the x-axis). The particle moving to the right would be reflected

At $x < x_3 \Rightarrow$ get oscillatory solutions $\psi_E(x)$

At $x > x_3 \Rightarrow$ get one $\psi_E(x) \to 0$ as $x \to \infty$ and another one $\psi_E(x) \to \infty$ as $x \to \infty$

unphysical



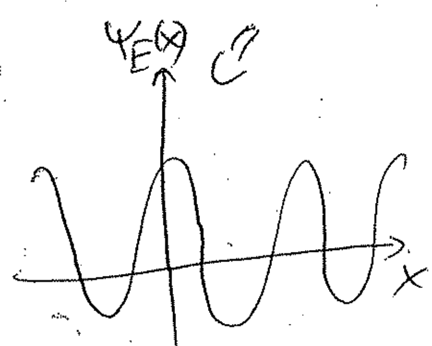
In this case, "smooth matching" of $\psi_E(x)$ and $\psi_E'(x)$ at $x = x_3$ can be made at all energies $V_- < E < V_+ \Rightarrow$ allowed energies form a continuum and are non-degenerate

Wave functions $\psi_E(x)$ which are non-zero and finite at infinity (in this case at $-\infty$) correspond to unbound (or scattering) states.

Case 4 $E > V_+$

$E - V(x) > 0$ for all x's $\Rightarrow$

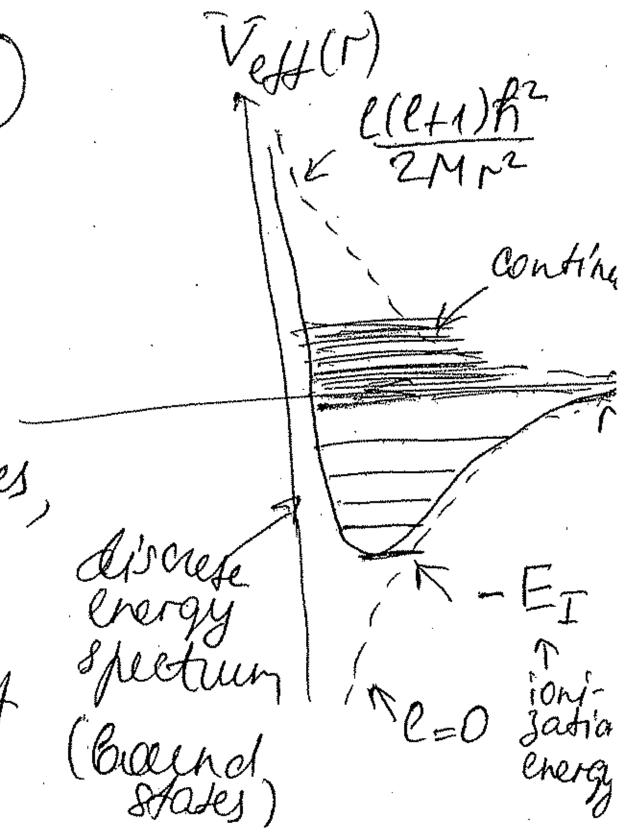
$\psi_E''(x)$ is opposite in sign to $\psi_E(x)$ for all x $\Rightarrow$ two oscillatory solutions which are physically admissible for every energy. So at $E > V_+$, the energy eigenvalues form a continuum and are doubly degenerate (because of the two independent states of motion $\rightleftarrows$). The eigenfunctions $\psi_E(x)$ describe unbound states



Example Hydrogen atom (H)

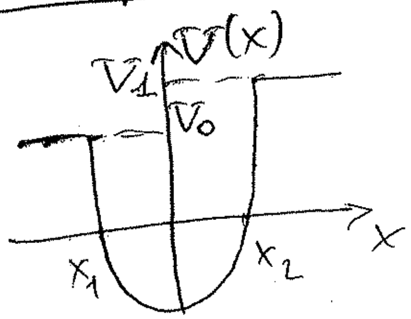
$$V_{eff}(r) = \underset{\substack{\uparrow \\ \text{Coulomb} \\ -\frac{e^2}{r}}}{V(r)} + \underbrace{\frac{l(l+1)\hbar^2}{2Mr^2}}_{\substack{\text{centrifugal} \\ \text{potential}}}$$

Normally we care about bound states, since unbound states here represent the electron after ionization of (H) i.e. free electron $\Leftarrow$ this is of interest in particle collision / scattering though

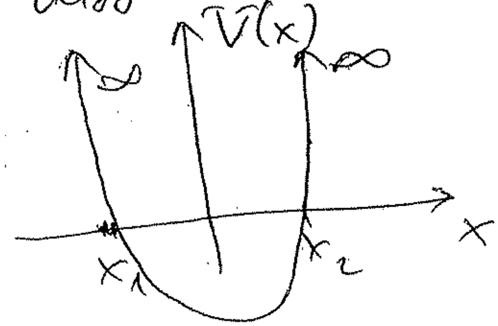


Until now we've considered finite $V(x)$.
What if $V=\infty$? $\Rightarrow$ because a particle cannot have an infinite energy, it cannot penetrate in a region where $V=\infty \Rightarrow \psi_E = 0$ in that region.

Example How are the energy spectra of these two systems different?



$\Longleftrightarrow$?



(1)

$\Downarrow$

$E < V_0 \Rightarrow$ discrete spectrum

$E > V_0 \Rightarrow$ continuum

(2)

$\Downarrow$

For all E's $\Rightarrow$ discrete, allowed energy level determined by boundary conditions $\psi(x_1) = \psi(x_2) = 0$