Functional Conditions on Acceptable QM Wavefcns ψ.

1) For simplicity, we work in 1D and with time-independent potentials $V = V(x)$. Generalization to 3D is not hard (one coordinate at a time), and our claims are OK when $V \to V(x,t)$ so long as the t-variation does not radically alter the shape of V (e.g. by making V vanish). So, the working version of Schrödinger's Eqtn we use is

$$\underline{\underline{\psi''(x) + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0}}, \quad E = \text{cnst system energy}, \quad \psi' = d\psi/dx,\ \psi'' = d^2\psi/dx^2. \tag{1}$$

This is a 2nd order ODE (ordinary differential eqtn), and it requires two arbitrary cnsts in its solution -- we need two "initial conditions" on ψ in order to specify a particular solution. Usually, these "initial conditions" are values of $\psi(x_0)$ & $\psi'(x_0)$ at a given point.*

Although we cannot assign precise values of $\psi(x_0)$ & $\psi'(x_0)$ before $V(x)$ is given explicitly, we can discuss the general behavior of the ψ & ψ' that we deem "acceptable" in our QM theory. We require that -- for all finite P.E.'s V -- both ψ & ψ' be finite and continuous everywhere. Reasoning is:

1. ψ is finite everywhere, so that the probability $|\psi|^2 dx$ is finite.
2. And, since the energies E & V are finite (for all physical problems), then// $\psi''(x) = \frac{2m}{\hbar^2}[V(x) - E]\psi(x) \to$ finite everywhere. This implies that $\psi'(x)$ is everywhere continuous.
3. ψ' is finite everywhere, so that momentum changes $dp = \psi^*\left\{\frac{\hbar}{i}\frac{d}{dx}\right\}\psi\, dx$ are finite. This implies $\psi(x)$ is everywhere continuous.

SO: for finite $V(x)$, $\psi(x)$ & $\psi'(x)$ are finite & continuous for all x. (2)

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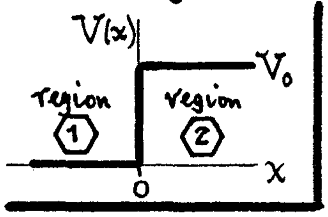
* The counterpart in solving Newton II, i.e. $m\ddot{x}(t) = F(t)$, is to specify m's position $x(t_0)$ and velocity $\dot{x}(t_0)$ at a given time t_0.

2) For some problems, the potential $V \to$ large, or -- as an idealization -- we imagine $V \to \infty$. We thus consider the case of a step-fcn potential...



$$V(x) = \begin{cases} 0, \text{ for } x<0 \text{ (region ①)}; \\ V_0, \text{ cnst, for } x>0 \text{ (region ②)}. \text{ Later, } V_0 \to \infty. \end{cases} \quad (3)$$

NOTE: $F(0) = -(dV/dx)_0 \to (-)\infty \Rightarrow \infty$ repulsive force @ $x=0$.

When $V_0 \to \infty$, this potential represents a perfectly rigid reflecting wall at $x=0$. With $V_0 =$ cnst, we can easily solve Schrödinger's Eqtn...

In region ①: $\psi''(x) + \alpha^2 \psi(x) = 0$, w/ $\alpha = [2mE/\hbar^2]^{1/2}$;

so// $\psi(x) = A \sin \alpha x + B \cos \alpha x$, A & B = cnsts. (4A)

In region ②: $\psi''(x) - \beta^2 \psi(x) = 0$, w/ $\beta = [2m(V_0 - E)/\hbar^2]^{1/2}$;

so// $\psi(x) = C e^{-\beta x} + D e^{+\beta x}$, C & D = cnsts. (4B)

These are general solutions. Fix the cnsts A, ..., D by imposing on these ψ's the "smoothness" conditions of Eq. (2), viz.

ψ finite as $x \to +\infty \Rightarrow D \equiv 0$;

ψ continuous as $x \to 0 \Rightarrow C = B$;

ψ' continuous as $x \to 0 \Rightarrow \alpha A = -\beta C$.

so// $\psi(x<0) = A[\sin \alpha x - \frac{\alpha}{\beta} \cos \alpha x]$,

$\psi(x>0) = -(\alpha/\beta) A e^{-\beta x}$. (4C)

Now, as the step becomes large, i.e. $V_0 \to \infty$, the parameter $\beta \to \infty$. Both A & α remain finite (so that ψ and the energy E remain finite); from the 3rd of Eqs. (4C), we see then that $\beta C = -\alpha A =$ finite, so when $\beta \to \infty$ we have $C \to 0$ in such a way that $\beta C =$ cnst. The ψ solutions in (4C) become:

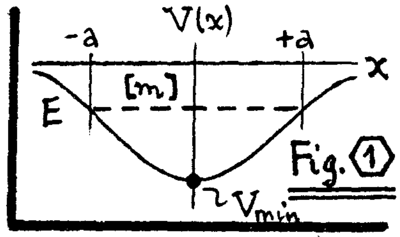
for $V_0 \to \infty$ $\begin{cases} \psi(x<0) = A \sin \alpha x, \text{ w/ } \psi'(0-) = \alpha A = \text{cnst} \neq 0; \\ \psi(x>0) \equiv 0, \text{ w/ } \psi'(0+) \equiv 0. \text{ (m not found in region ②)}. \end{cases}$ (4D)

SO: when $V \to \infty$, $\psi \equiv 0$ and ψ' is discontinuous. The discontinuity in ψ' (related to $p = (\hbar/i)\, d/dx$) is connected with the total reflection of m.

Implications of ψ & ψ' continuous for 1D bound state problem.

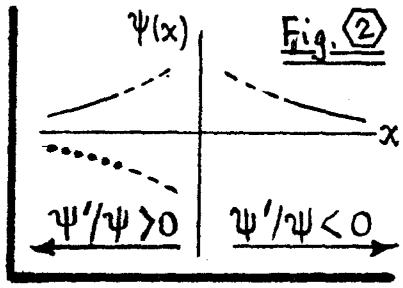
3) The "smoothness conditions" on ψ & ψ' are -- by themselves -- enough to ensure <u>discrete</u> values of m's energy E in a bound-state problem (i.e. a problem where V(x) confines or binds m to a ~finite region of space).

Consider V(x) = a <u>potential</u> <u>well</u> of the generic form shown in Fig. ①, and a bound state at energy E...



$$\left[\begin{array}{l} \text{bound state}: 0 > E > V_{min} \;(m \text{ confined to } |x| \lesssim a). \\ V(x) \to 0 \text{ as } |x| \to \infty \Rightarrow \psi(x) \propto e^{-\alpha|x|},\; \text{w/}\; \alpha = [2mE/\hbar^2]^{1/2}. \end{array}\right. \quad (5)$$

The wavefcn at large |x| thus starts out <u>exponentially</u>, as indicated in Fig. ②; at $x<0$, we show both choices of sign for ψ. Notice that $\psi'/\psi \gtrless 0$ for $x \lessgtr 0$. Now ψ can be extended in toward $x=0$ by using the wave lgth plus continuity. We have...

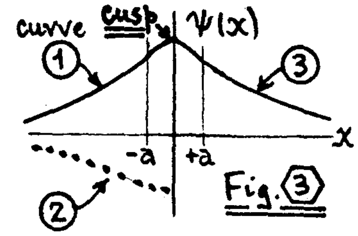


$$\left[\begin{array}{l} \text{At large } |x|,\ V(x) > E, \text{ so: } \frac{1}{\psi}\psi''(x) = \frac{2m}{\hbar^2}[V(x)-E] > 0. \\ \text{This} \Rightarrow \psi \text{ is } \underline{\underline{\text{convex}}} \text{ toward } x\text{-axis, and justifies } \psi'/\psi \gtrless 0 \;@\; x \lessgtr 0. \end{array}\right. \quad (6)$$

As we move in toward $x=0$, the <u>sign</u> of the curvature changes, since...

$$\left[\begin{array}{l} \text{At small } |x| \text{ (i.e. } |x|<a),\ V(x) < E, \text{ and: } \frac{1}{\psi}\psi''(x) < 0. \\ \text{This} \Rightarrow \psi \text{ becomes } \underline{\underline{\text{concave}}} \text{ toward } x\text{-axis.} \end{array}\right. \quad (7)$$

Now, depending on the <u>size</u> of the energy |E|, there are 3 possible ways to extend ψ in to $x=0$ from |x| = large (where $\psi \sim e^{-\alpha|x|}$ as above)...



$$\left[\begin{array}{l} |E| \sim \text{"large"} \Rightarrow \text{region } (|x|<a) \text{ w/ } \psi \text{ concave is "small".} \\ \text{Curves ① \& ③} \Rightarrow \psi \text{ is continuous @ } x=0, \text{ but } \underline{\text{not}}\ \psi'. \\ \text{Curves ② \& ③} \Rightarrow \psi' \text{ is continuous @ } x=0, \text{ but } \underline{\text{not}}\ \psi. \end{array}\right. \quad (8A)$$

So |E| ~ large must be ruled out, since we cannot make <u>both</u> ψ & ψ' continuous at $x=0$. Thus we try |E| ~ small, to expand the $\psi \to$ concave region:

Location of discrete bound states via continuity arguments.

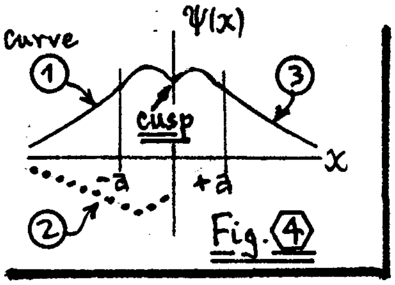


Fig. ④

$|E|$ ~ "small" ⇒ region ($|x|<a$) w/ ψ concave is "large."
Curves ① & ③ ⇒ ψ is continuous @ $x=0$, but not ψ'!
Curves ② & ③ ⇒ ψ' is continuous @ $x=0$, but not ψ. (8B)

Thus $|E|$ ~ small is also ruled out because ψ & ψ' cannot both be continuous. We have to pick $|E|$ just right to satisfy continuity, i.e.

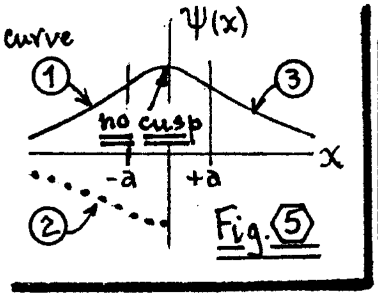


Fig. ⑤

Adjust $|E|$ to E_1, so region $|x|<a$ w/ ψ concave is "just right."
Curves ① & ③ ⇒ both ψ & ψ' are continuous @ $x=0$.
Curves ② & ③ ⇒ ψ' is continuous @ $x=0$, but not ψ. (8C)

Then $E=(-)E_1$ is the first discrete bound energy of the system. E_1 is discrete because it is bounded from above (Fig. ③) and below (Fig. ④) by the requirement that both ψ & ψ' be continuous.

If the potential well is deep enough, we get a second bound state @ $E=(-)E_2$...

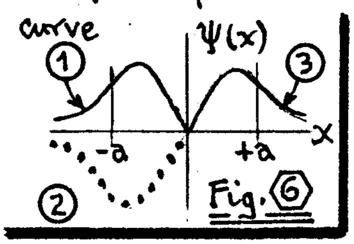
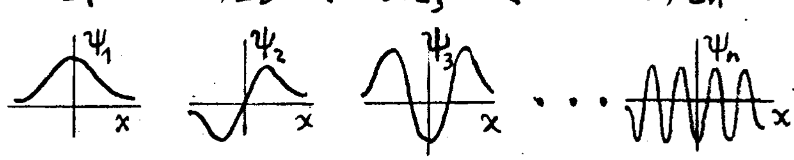


Fig. ⑥

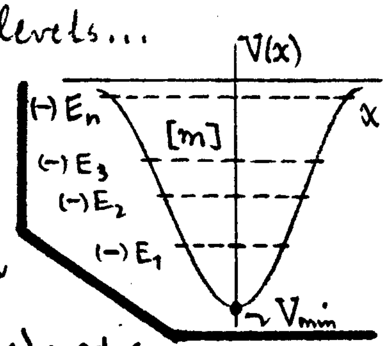
$|E|=E_2<E_1$ "just right" so curves ② & ③ join up smoothly.
Curves ① & ③ ⇒ ψ is continuous @ $x=0$, but not ψ'!
Curves ② & ③ ⇒ both ψ & ψ' are continuous @ $x=0$. (9)

In general, we can get a series of discrete bound energy levels...

$$V_{min} < (-)E_1 < (-)E_2 < (-)E_3 < \cdots (-)E_n < 0.$$



(10)



NOTE: the wavefcn ψ_n for energy E_n ($n=1,2,3,\ldots$) has $(n-1)$ nodes.
The number of bound states depends on the depth V_{min} of the well; as $|V_{min}|\to\infty$, we can get an ∞ number of bound energies. Note also in this 1D problem that each energy level is non-degenerate, since there is a unique ψ_n (with a unique # of nodes) for each E_n.