as wavepackets or using box normalization, since we understand the nature of these continuum normalized eigenfunctions we will, with appropriate care, use them directly.

1.3.8. Boundary Conditions on the Wavefunction

By Postulate 2, the probability density $\rho = |\psi(\vec{r},t)|^2$ is observable, hence it must be everywhere finite and continuous. $|\psi|^2$ is finite if and only if the wavefunction $\psi(\vec{r},t)$ is finite everywhere. Further it is a sufficient condition for $|\psi|^2$ to be continuous that $\psi(\vec{r},t)$ is continuous. Using the principle of superposition it can also be shown to be necessary. Assume ψ_1 is continuous and, by superposition, that $\psi = \psi_1 + \lambda\psi_2$ is a solution to the Schrödinger equation with ψ_1, ψ_2 solutions and $\lambda \in \mathbb{C}$. We can show that ψ_2 is continuous by considering $|\psi_1|^2$, $|\psi_2|^2$ and $|\psi|^2 = |\psi_1 + \lambda\psi_2|^2$, all of which are continuous. Since $|\psi|^2 = |\psi_1|^2 + |\lambda|^2|\psi_2|^2 + \lambda\psi_1^*\psi_2 + \lambda^*\psi_1\psi_2^*$ we have that

$$\lambda\psi_1^*\psi_2 + \lambda^*\psi_1\psi_2^* \text{ is continuous.}$$

Choosing $\lambda = \lambda^* \Rightarrow \psi_1^* \psi_2 + \psi_1 \psi_2^*$ is continuous
Choosing $\lambda = -\lambda^* \Rightarrow \psi_1^* \psi_2 - \psi_1 \psi_2^*$ is continuous

Thus it follows that $\psi_1^* \psi_2$ must be continuous. So since ψ_1 is continuous this implies ψ_2 must be i.e (Note: we exclude pathological ψ_1 with zeros at x by assumption)

$$\lim_{\epsilon \to 0} \left(\psi_1^*(x+\epsilon) \psi_2(x+\epsilon) - \psi_1^*(x) \psi_2(x) \right) = 0$$

$$= \lim_{\epsilon \to 0} \psi_1^*(x) \left(\psi_2(x+\epsilon) - \psi_2(x) \right)$$

$$\Rightarrow \lim_{\epsilon \to 0} \left(\psi_2(x+\epsilon) - \psi_2(x) \right) = 0 .$$

Thus continuity of $|\psi|^2$ combined with the principle of superposition implies ψ is continuous.

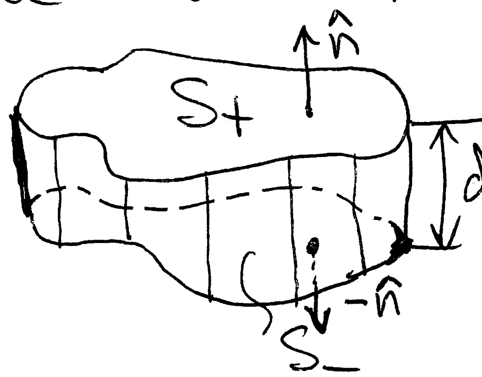
Proceeding further, consider integrating the Schrödinger equation, $\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi = E \psi$, over volume Ω

$$\int_\Omega d^3r \, \nabla^2 \psi = \frac{2m}{\hbar^2} \int_\Omega d^3r \, V \psi - \frac{2mE}{\hbar^2} \int_\Omega d^3r \, \psi$$

Using Gauss' theorem on the LHS implies

$$\oint_{\Sigma} d\vec{S} \cdot \vec{\nabla} \psi = \frac{2m}{\hbar^2} \int_\Omega d^3r \, V \psi - \frac{2mE}{\hbar^2} \int_\Omega d^3r \, \psi ,$$

where Σ_1 is the surface bounding volume Ω. Consider a volume with infinitesimal height as below



The surface integral over the sides is infinitesimal and so negligible, thus

$$\oint_{\Sigma_1} d\vec{S}\cdot\vec{\nabla}\psi = \int_{S_+} d\vec{S}\cdot\vec{\nabla}\psi + \int_{S_-} d\vec{S}\cdot\vec{\nabla}\psi .$$

The volume integral of ψ is also negligible since ψ is continuous and the volume is infinitesimal.
So we obtain

$$\int_{S_+} da\,\hat{n}\cdot\vec{\nabla}\psi - \int_{S_-} da\,\hat{n}\cdot\vec{\nabla}\psi$$
$$= \frac{2m}{\hbar^2}\int_{\Omega} d^3r\, V\psi ,$$

where $d\vec{S} = \hat{n}\,da$ on S_+ and $d\vec{S} = -\hat{n}\,da$ on S_-.

If the potential V is non-singular in Ω, then $\int_\Omega d^3r\, V\psi$ is negligible

hence

$$\int_{S_+} da\,\hat{n}\cdot\vec{\nabla}\psi = \int_{S_-} da\,\hat{n}\cdot\vec{\nabla}\psi ,$$

This implies that $\hat{n}\cdot\vec{\nabla}\psi\Big|_{S_+} = \hat{n}\cdot\vec{\nabla}\psi\Big|_{S_-}$,

the gradient is continuous across the volume. Since the volume was arbitrarily chosen we conclude that

$\vec{\nabla}\psi$ is continuous wherever the potential V is non-singular.

In the case of singular potentials such as Dirac δ-function potentials the correct boundary condition for the gradiant of ψ can be obtained directly from integrating the Schrödinger equation as above for the case at hand along with the continuity of the wave function. Alternatively, one can approximate the singular potential with a sequence of regular potentials for which the gradiant of the wavefunction is continuous & then take the limit to obtain the correct wavefunction.

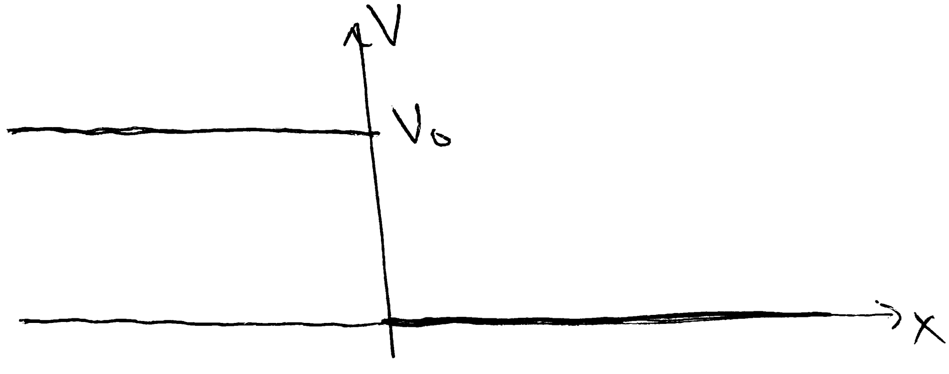
In short then, the boundary conditions for the wavefunction are

1) ψ is everywhere finite
2) ψ is everywhere continuous
3) for a non-singular potential, $\vec{\nabla}\psi$ is continuous.

As an aside, the boundary condition on $\vec{\nabla}\psi$ can be obtained by demanding continuity of the probability current along with the principle of superposition.

<u>Example</u>: Consider a particle of mass m and energy $E>0$ in one dimension moving in the potential

$$V(x) = \begin{cases} V_0 > 0 & \text{if } x<0 \\ 0 & \text{if } x>0 \end{cases}$$



The Schrödinger equation in the 2 regions is given by

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)+V_0\psi(x)=E\psi(x) \quad ; \; x<0$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)=E\psi(x) \quad ; \; x>0.$$

Defining $k\equiv\sqrt{\frac{2mE}{\hbar^2}}>0 \quad (E>0)$

and $v_0\equiv\frac{2mV_0}{\hbar^2}=\text{constant}>0$,

the Schrödinger equation takes the form,

$$\frac{d^2\psi}{dx^2}+(k^2-v_0)\psi=0 \quad , \; x<0$$

$$\frac{d^2\psi}{dx^2}+k^2\psi=0 \quad , \; x>0.$$

Considering the case where $0<E<V_0$, we have that $0<k^2<v_0$, thus with the definition of $\kappa\equiv\sqrt{v_0-k^2}>0$, the Schrödinger equation reduces to

$$\frac{d^2}{dx^2}\psi-\kappa^2\psi=0 \quad , \; x<0$$

$$\frac{d^2}{dx^2}\psi+k^2\psi=0 \quad , \; x>0.$$

The solution is

$$\psi(x) = \begin{cases} A_< e^{\kappa x} + B_< e^{-\kappa x} & , x<0 \\ A_> \cos kx + B_> \sin kx & , x>0. \end{cases}$$

We next impose the boundary conditions on $\psi(x)$

1) ψ is finite everywhere: in particular

$$\psi(-\infty) \text{ is finite} \Rightarrow \boxed{B_< = 0.}$$

2) ψ is continuous everywhere: in particular ψ is continuous at $x=0$

$$\lim_{\epsilon \to 0} \left(\psi(-\epsilon) = \psi(+\epsilon) \right)$$

$$\Rightarrow \boxed{A_< = A_>}$$

3) V is non-singular hence $\frac{d}{dx}\psi$ is continuous everywhere: in particular at $x=0$

$$\lim_{x \to 0^-} \frac{d}{dx}\psi(x) = \lim_{x \to 0^+} \frac{d}{dx}\psi(x)$$

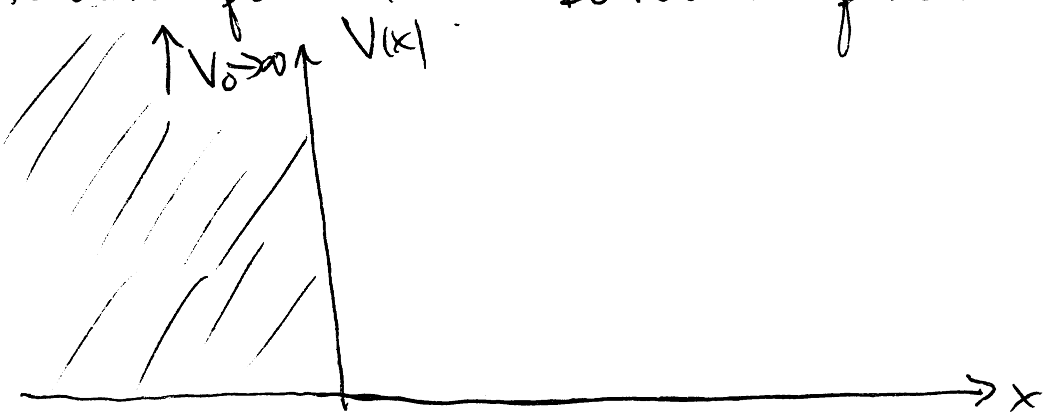
$$\Rightarrow \boxed{\kappa A_< = k B_>}$$

Thus, calling $B_> \equiv N$, we have

$$\psi(x) = \begin{cases} N \frac{k}{\kappa} e^{\kappa x} & , \text{if } x<0 \\ N\left(\sin kx + \frac{k}{\kappa}\cos kx\right), & \text{if } x>0. \end{cases}$$

This satisfies the Schrödinger equation and is everywhere continuous and finite, with its derivative also continuous everywhere.

We can take the limit $V_0 \to \infty$, to determine the solution to the infinite potential barrier problem



For $V_0 \to \infty \Rightarrow \nu_0 = \frac{2mV_0}{\hbar^2} \to \infty$

and hence $\kappa = \sqrt{\nu_0 - k^2} \to \infty$.

Thus the solution becomes

$$\psi(x) = \begin{cases} 0 , & \text{if } x<0 \\ N \sin kx , & \text{if } x>0 . \end{cases}$$

Thus in the region where the potential $V(x)$ diverges, the wave function vanishes, $\psi(x) = 0$ for $x<0$. Further $\psi(x)$ is still finite and continuous everywhere, but the derivative of the wave function is no longer continuous where the potential has the infinite discontinuity, at $x=0$.

$$\lim_{x\to 0^-} \frac{d}{dx}\psi(x) = 0 , \quad \text{but}$$

$$\lim_{x\to 0^+} \frac{d}{dx}\psi(x) = kN \neq 0 .$$