Orthogonality of solution of Schrodinger equation The orthogonality of solution of Schrodinger equation follows from properties of linear differential equation.

Consider a 1-D problem

$$H\psi(x) = E\psi(x)$$

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

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x) \text{ , where } k^2 = \frac{2m(E-V)}{\hbar^2}$$

Consider two independent solutions,$\psi_1(x) and \psi_2(x)$ then

$$\frac{d^2\psi_1(x)}{dx^2} = -k_1^2\psi_1(x) \text{ ——- } (1)$$

$$\frac{d^2\psi_2(x)}{dx^2} = -k_2^2\psi_2(x) \text{ —— } (2)$$

Take complex conjugate of eqn (1),multiply from right by $\psi_2(x)$; and mulitply eqn (2) from left by $\psi_1^*(x)$

$$\psi_2\frac{d^2\psi_1^*(x)}{dx^2} = -k_1^2\psi_1^*\psi_2 \text{ —-}(3)$$

$$\psi_1^*\frac{d^2\psi_2(x)}{dx^2} = -k_2^2\psi_1^*\psi_2 \text{ ——}(4)$$

Subtract eqn(3) from (4) and integrate
$\int_{-\infty}^{+\infty}(\psi_1^*\psi_2" - \psi_1^{*"}\psi_2)dx = -(k_2^2 - k_1^2)\int_{-\infty}^{+\infty}\psi_1^*\psi_2 dx$
Integrating by parts

$$\psi_1^*\psi_2'|_{-\infty}^{\infty} - \int_{-\infty}^{+\infty}(\psi_1^{*\prime}\psi_2' dx) - \psi_1^{*\prime}\psi_2|_{-\infty}^{\infty} + \int_{-\infty}^{\infty}(\psi_1^{*\prime}\psi_2')dx = (k_1^2 - k_2^2)\int_{-\infty}^{\infty}\psi_1^*\psi_2 dx$$

Since ψ_1 and ψ_2 are both zero at $x = \pm\infty$, the first and the third term on LHS disappear. The second and fourth term cancel each other out. Therefore,

$$\int_{-\infty}^{\infty}\psi_1^*\psi_2 dx = 0$$