Quantum Mechanics and Atomic Physics

Lecture 6: Potential Wells: Part II

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Prof. Eva Halkiadakis
Last Time

- We solved S.E. for the Infinite Potential Well

\[ \Psi(x, t) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \cdot e^{-iE_n t/\hbar} \]

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad n = 1, 2, 3, \ldots \]

Next: we consider the Finite Potential Well
The Finite Square Well

- **Mass m in a potential well of finite depth**
  - This is a more realistic case than infinite square well: e.g. electron trapped in surface of metal which needs a few eV to escape (as in photoelectric effect)

- **V=0 for \(-L \leq x \leq L\)**
  - Inside the well

- **V= \(V_0\) for \(|x| > L\)**
  - Outside the well

- For \(E < V_0\) we are seeking **bound energy states** (bottom of the well is at \(V=0\))
Solutions inside and outside the well

- In regions 1 and 2:  \( V(x) = V_0 \)

\[-\frac{\hbar^2}{2m} \frac{d^2 \psi_{\text{out}}}{dx^2} = (E - V_0) \psi_{\text{out}} \]

- In region 3:  \( V(x) = 0 \)

\[-\frac{\hbar^2}{2m} \frac{d^2 \psi_{\text{in}}}{dx^2} = E \psi_{\text{in}} \quad \text{(like infinite square well)} \]

Let's rewrite:

\[ \frac{d^2 \psi_{\text{out}}}{dx^2} = k_1^2 \psi_{\text{out}} \quad k_1 = \frac{2m}{\hbar^2} (V_0 - E) \]

\[ \frac{d^2 \psi_{\text{in}}}{dx^2} = k_2^2 \psi_{\text{in}} \quad k_2 = \frac{2mE}{\hbar^2} \]

\( k_1, k_2 \) are positive and real.
Inside and outside the well

In region 2 (in):

\[ \Psi_2 = A e^{ik_2 x} + Be^{-ik_2 x} \quad (-L \leq x \leq L) \]

In regions 0 \& \frac{1}{3}:

\[ \Psi_1 = C e^{k_1 x} + D e^{-k_1 x} \quad (x \leq -L) \]
\[ \Psi_3 = G e^{k_1 x} + F e^{-k_1 x} \quad (x \geq L) \]
Boundary Conditions

\[ \psi_1 = \psi_2 \quad \text{at} \quad x = -L \]
\[ \psi_2 = \psi_3 \quad \text{at} \quad x = +L \]

\[ \left. \frac{d\psi_1}{dx} \right|_{x=-L} = \left. \frac{d\psi_2}{dx} \right|_{x=-L} \quad \text{and} \quad \left. \frac{d\psi_2}{dx} \right|_{x=L} = \left. \frac{d\psi_3}{dx} \right|_{x=L} \]

and

\[ \int_{-\infty}^{-L} \psi_1^* \psi_1 \, dx + \int_{-L}^{L} \psi_2^* \psi_2 \, dx + \int_{L}^{\infty} \psi_3^* \psi_3 \, dx = 1 \]
Finiteness of Wavefunctions

- But, are the wavefunctions finite?
  - \( \Psi_1 \to \infty \) as \( x \to -\infty \) and \( \Psi_3 \to \infty \) as \( x \to \infty \)

- Therefore finiteness requires that \( D=0 \) and \( G=0 \)

- That leaves four constants: \( A, B, C \) and \( F \)

- But we have five constraints!
  - The four boundary conditions plus normalization

  - Are we over-determined? Yes, we have an over-deternined system of five conditions and four constants.
Boundary Conditions, con’t

In region 2:

\[ \Psi_2 = A e^{i\kappa_2 x} + B e^{-i\kappa_2 x} \]

but more convenient to write as:

\[ \Psi_2 = A \sin\kappa_2 x + B \cos\kappa_2 x \]

- \( \Psi \) at \( x = -L \):
  \[ C e^{-\kappa_2 L} = -A \sin\kappa_2 L + B \cos\kappa_2 L \]

- \( \frac{d\Psi}{dx} \) at \( x = -L \):
  \[ \kappa_2 C e^{-\kappa_2 L} = \kappa_2 A \cos\kappa_2 L + \kappa_2 B \sin\kappa_2 L \]

- \( \Psi \) at \( x = +L \):
  \[ F e^{-\kappa_2 L} = A \sin\kappa_2 L + B \cos\kappa_2 L \]

- \( \frac{d\Psi}{dx} \) at \( x = +L \):
  \[ -\kappa_2 F e^{-\kappa_2 L} = \kappa_2 A \cos\kappa_2 L - \kappa_2 B \sin\kappa_2 L \]
Let's define two new constants:

\[ n = \kappa_1 L = \sqrt{\frac{2m (V_0 - E)}{\hbar^2}} L \]

\[ \zeta = \kappa_2 L = \sqrt{\frac{2mE}{\hbar^2}} L \]

\[
\begin{align*}
C e^{-n} &= -A \sin \zeta + B \cos \zeta & (1) \\
\left(\frac{n}{\xi}\right) C e^{-n} &= A \cos \zeta + B \sin \zeta & (2) \\
F e^{-n} &= A \sin \zeta + B \cos \zeta & (3) \\
\left(-\frac{n}{\xi}\right) F e^{-n} &= A \cos \zeta - B \sin \zeta & (4)
\end{align*}
\]

Four equations
\[ \zeta \]
Four unknowns.
Divide:

\[ \frac{\text{3}}{\text{1}} \Rightarrow \frac{F}{C} = \frac{(A \sin \xi + B \cos \xi)}{(-A \sin \xi + B \cos \xi)} \]

\[ \frac{\text{4}}{\text{2}} \Rightarrow \frac{E}{C} = \frac{-(A \cos \xi - B \sin \xi)}{A \cos \xi + B \sin \xi} \]

Set equal & cross multiply:

\[ A^2 \sin^2 \xi \cos^2 \xi + B^2 \sin^3 \cos \xi + AB = A^2 \sin^2 \xi \cos^2 \xi + B^2 \sin^3 \cos \xi - AB \]

\[ \Rightarrow AB = -AB \Rightarrow 2AB = 0 \Rightarrow \boxed{AB = 0} \]

Square eqn (1):

\[ (Ce^{-n})^2 = A^2 \sin^2 \xi + B^2 \cos^2 \xi - 2AB \sin^3 \cos \xi \]

Square eqn (3)

\[ (Fe^{-n})^2 = A^2 \sin^2 \xi + B^2 \cos^2 \xi + 2AB \sin^3 \cos \xi \]

Use \( AB = -AB \) or \( AB = 0 \)

\[ \Rightarrow \boxed{F^2 = c^2} \]

So, \( F = \pm C \)
Two classes of solutions!

- **Even Parity solutions:**
  
  - If $A=0$:
    
    \[
    C e^{-\frac{k_1}{2}L} = B \cos k_2 L \\
    F e^{-\frac{k_1}{2}L} = B \cos k_2 L \\
    \Rightarrow C = F
    \]
    
    And $\Psi_2 = B \cos k_2 x$
    
    Even parity: $\Psi_2(x) = \Psi_2(-x)$

- **Odd Parity solutions:**
  
  - If $B=0$:
    
    \[
    C e^{-\frac{k_1}{2}L} = -A \sin k_2 L \\
    F e^{-\frac{k_1}{2}L} = A \sin k_2 L \\
    \Rightarrow C = -F
    \]
    
    And $\Psi_2 = A \sin k_2 x$
    
    Odd parity: $\Psi_2(x) = -\Psi_2(-x)$

- **Not all of the boundary conditions can be satisfied simultaneously!**
The Strength Parameter

\[ \xi^2 + \eta^2 = \frac{2m V_0 L^2}{\hbar^2} = K^2 = \text{constant} \]

- For a given K, only certain values of \( \xi \) will satisfy the boundary conditions
- From our definitions of \( \eta \) and \( \xi \), these will correspond to particular values of the energy of the particle.
- The energy levels are given by:

\[ E_n = \xi_n^2 \frac{\hbar^2}{2mL^2} \]
Finite Square Well: Even Solutions

\[ A = 0; \quad C = F \]

\[ \Psi_1 = Ce^{k_1 x} \quad (x \leq -L) \]
\[ \Psi_2 = B \cos k_2 x \quad (-L \leq x \leq L) \]
\[ \Psi_3 = Ce^{-k_1 x} \quad (x > L) \]

\[ C = B \cos k_2 L \]
\[ = B \cos \xi \]
\[ = B \cos \xi \quad e^k \]

So,

\[ \Psi_1 = B \cos \xi \quad e^n \quad e^{k_1 x} \quad (x \leq -L) \]
\[ \Psi_2 = B \cos k_2 x \quad (-L \leq x \leq L) \]
\[ \Psi_3 = B \cos \xi \quad e^n \quad e^{-k_1 x} \quad (x > L) \]
Dividing eqns (2) \( \frac{(2)}{(1)} \):

\[
\left( \frac{\cos \theta}{\sin \theta} \right) = \frac{A \cos \theta + B \sin \theta}{-A \sin \theta + B \cos \theta}
\]

and with \( A = 0 \)

\[
\left( \frac{\sin \theta}{\cos \theta} \right) = \tan \theta
\]

This gives us the energy equation:

\[
\tan \theta = \frac{\sin \theta}{\cos \theta} = \sqrt{\frac{V_0 - E}{E}} \Rightarrow \tan \frac{k_2 L}{\hbar} = \sqrt{\frac{V_0 - E}{E}}
\]

\[
\tan \left( L \sqrt{\frac{2mE}{\hbar^2}} \right) = \sqrt{\frac{V_0 - E}{E}}
\]

This is what gives us energy quantization!
Energy Quantization

\[
\tan \left( L \sqrt{\frac{2mE}{\hbar^2}} \right) = \sqrt{\frac{V_0 - E}{E}}
\]

- This expression cannot be solved analytically.
- Let’s plot both the left hand side and right hand side on the same graph

**Note:**
- The right hand side = \( \infty \) for \( E=0 \)
- The right hand side = 0 for \( E=V_0 \)
Graphical Solution

\[ \tan(L \sqrt{\frac{2mE}{\hbar^2}}) = \sqrt{\frac{V_0 - E}{E}} \]

\[ \xi = L \sqrt{\frac{2mE}{\hbar^2}} \]

- Red: Left hand side
- Blue: Right hand side
  - expressed as functions of \( \xi = L \sqrt{\frac{2mE}{\hbar^2}} \)
- For three different values of \( V_0 \)
Graphical Solution, con’t

- We get quantized energy eigenvalues.
- At least one solution must exist, no matter how small $V_0$ is (remember that $E < V_0$).
- Total number of solutions is finite, no matter how large $V_0$ is.

\[ \tan(L \sqrt{\frac{2mE}{\hbar^2}}) = \sqrt{\frac{V_0 - E}{E}} \]

\[ \xi = L \sqrt{\frac{2mE}{\hbar^2}} \]
Two possible eigenfunctions are shown (n=1 and n=3)

- \( \Psi \) is symmetric in \( x \): \( \Psi(-x) = \Psi(x) \)
  - Since cosine is symmetric
  - We have even parity

Note: we get penetration into the classically forbidden regions (1) and (3)

For the case \( E>V_0 \) we get oscillatory solutions in all three regions. No bound states: continuum of energies is possible.
Normalization

- We can get B from the normalization condition

\[
\text{Normalization:} \quad \int_{-L}^{L} \psi_1 \psi_1 \, dx + \int_{-L}^{L} \psi_2 \psi_2 \, dx + \int_{-\infty}^{\infty} \psi_3 \psi_3 \, dx = 1
\]

\[
\int_{-\infty}^{\infty} \psi_1 \psi_1 \, dx = \int_{-\infty}^{\infty} \psi_3 \psi_3 \, dx = C^2 \int_{-\infty}^{\infty} e^{-2\kappa_1 x} \, dx
\]

\[
= \frac{C^2}{-2\kappa_1} \left[ 0 - e^{-2\kappa_1 L} \right] = \frac{C^2}{2\kappa_1} e^{-2\kappa_1 L}
\]

So this term enters twice in the normalization.
\[
\int_{-L}^{L} \psi_1^* \psi_2 \, dx = B^2 \int_{-L}^{L} \cos^2 \frac{x_2}{L} \, dx
\]
\[
= B^2 \left[ \frac{x}{2} + \frac{\sin(2x_2 \xi)}{4x_2} \right]_{-L}^{L}
\]
\[
= B^2 \left[ \frac{\sin 2\xi}{2x_2} + L \right]
\]
\[
2 \times \frac{C^2}{2 \xi_1} e^{-\frac{2a}{C}} + B^2 \left[ \frac{\sin 2\xi}{2x_2} + L \right] = 1
\]

Substitute \( C = B \cos \xi e^a \)

\[
2 \times \frac{B^2 \cos^2 \frac{2\xi}{2x_2}}{2 \xi_1} + B^2 \left[ \frac{\sin 2\xi}{2x_2} + L \right] = 1 \quad \text{Multiply by} \frac{1}{L}
\]
\[
2 \times \frac{B^2 \cos^2 \frac{2\xi}{2x_2}}{2 \lambda} + \frac{B^2 \sin 2\xi}{2 \xi} + B^2 = \frac{1}{L}
\]
Once a given energy state $\xi_n$ is specified, the $B$ (and therefore $C$) can be computed.

Unlike the infinite well, here the normalization constants depend on the energy eigenvalue involved!

Exercise you can try on your own: determine the probability of finding the particle outside the well (cross check with eqn. 3.4.11 in your book). It is independent of $B$ and $C$, and depend only on the energy eigenvalue.

Also see your HW problems this week (for the odd-parity solutions)!
Finite Square Well: Odd Solutions

\[ B = 0, \quad C = -F \]

\[ \Psi_1 = Ce^{x_1x} \quad (x < -L) \]
\[ \Psi_2 = A\sin k_2x \quad (-L \leq x \leq L) \]
\[ \Psi_3 = -Ce^{-x_1x} \quad (x > L) \]

\[ C = -A\sin k_2L e^{x_1L} = -A\sin \xi e^n \]

So,

\[ \Psi_1 = -A\sin \xi e^n e^{x_1x} \quad (x < -L) \]
\[ \Psi_2 = A\sin k_2x \quad (-L \leq x \leq L) \]
\[ \Psi_3 = A\sin \xi e^n e^{-x_1x} \quad (x > L) \]
Dividing \( \frac{(2)}{(1)} \):

\[
\left( \frac{\frac{A}{\xi}}{\frac{B}{\xi}} \right) = \frac{A \cos \xi + B \sin \xi}{-A \sin \xi + B \cos \xi}
\]

and \( A \omega / B = 0 \)

\[
\frac{\frac{A}{\xi}}{\frac{B}{\xi}} = \frac{-\cos \xi}{\sin \xi} = -\cot \xi
\]

\[-\cot \xi = \frac{\frac{A}{\xi}}{\frac{B}{\xi}} = \sqrt{\frac{V_0 - E}{E}}
\]

But \(-\cot \xi = \tan (\xi + \frac{\pi}{2})\)
Odd Solution Eigenfunctions

- Again, two possible eigenfunctions are shown (n=2 and n=4)
- This time $\Psi$ is anti-symmetric in x: $\Psi(-x) = -\Psi(x)$
  - Since sine is anti-symmetric
  - We have odd parity

- Whenever the potential is symmetric, $V(-x) = V(x)$, eigenfunctions must have definite parity, i.e. $\Psi(-x) = \pm \Psi(x)$
  - Symmetric V implies symmetric probabilities
    $P(-x) = P(x)$ but $P(x) = |\Psi(x)|^2$
    so $\Psi(-x) = \pm \Psi(x)$
So the graphical solution is the same as for the even parity solutions, except that the tangent curves are displaced by \( \pi/2 \)!

This time if \( V_0 \) is small enough, we may get no solutions!

- As \( V_0 \) increases we get more solutions, but always a finite number
- In general, for a given \( V_0 \), the particle will have a mixture of both classes even and odd parity (\( A=0 \) and \( B=0 \)).
Summary/Announcements

- The Finite Potential Well

- Next time:
  - Potential Barriers and Scattering

- Next homework due on Monday Oct 2