**General approach to solving Schrödinger's equation for a periodic potential:**

The general approach to solving the TISE in an infinitely repeating periodic potential involves the use of a powerful theorem called Bloch's theorem. The essence is that the solutions to the problem are modulated plane waves, and the modulation is determined by the shape of the potential that is repeated periodically. Thus the important thing is to be able to determine the solutions for a single element of the potential.

Our example will be the mathematically tractable finite square well. The main features of the periodic system are easily seen, and the exact nature of the well is not terribly important for our purposes. This example is found in many quantum mechanics textbooks, including Liboff. Griffiths treats the "Dirac Comb", an infinitely repeated delta function potential, which is rather cute.

**SOLUTION TO SCHROEDINGER’S EQUATION FOR A FINITE SQUARE WELL**

This is a classic textbook problem, found in every QM text. I repeat it here because usually texts have the bottom of the well at negative energy. I have it at zero – there is no difference in the physics. You will have seen it in PH 424 before.
\[
x < -a \quad \text{REGION 1}
\]

\[
-V \quad \begin{array}{ccc}
\text{Region 1} & \text{Region 2} & \text{Region 3}
\end{array} \quad V
\]

\[
\begin{equation}
-x=a
\end{equation}
\]

\[
\begin{equation}
V_0
\end{equation}
\]

\[
E
\]

\[
\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_1(x) + V_0 \psi_1(x) = E \psi_1(x) \quad \text{implies} \quad \frac{d^2}{dx^2} \psi_1(x) = -\frac{2m(E - V_0)}{\hbar^2} \psi_1(x)
\]

\[
\psi_1(x) = C' e^{i \frac{2m(E-V_0)}{\hbar^2} x} + C e^{-i \frac{2m(E-V_0)}{\hbar^2} x}
\]

Now we assume \( E < V_0 \)

but \( C' = 0 \) otherwise \( \psi_1(x \to -\infty) = C' e^{i \frac{2m(E-V_0)}{\hbar^2} (-\infty)} = C' e^{2 \frac{m(E-V_0)}{\hbar^2}} \to \infty \)

\[
\psi_1(x) = Ce^{-i \frac{2mE}{\hbar^2} x} \quad E < V_0 \quad \to \quad Ce^{\frac{2m(E-V_0)}{\hbar^2} x} \quad \to \quad Ce^{\beta x} \quad \beta = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}
\]

(Goswami's \( \beta \) is \( \sqrt{\frac{2mE}{\hbar^2}} \), because of the different zero; Liboff uses \( \kappa \))
\( x > a \) \hspace{1cm} \text{REGION 3}

For general \( E \)

\[
-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_3(x) + V_0 \psi_3(x) = E \psi_3(x) \quad \text{implies} \quad \frac{d^2}{dx^2} \psi_3(x) = -\frac{2m(E-V_0)}{\hbar^2} \psi_3(x)
\]

\[
\psi_3(x) = De^{-\frac{2m(E-V_0)}{\hbar^2}x} + De^{\frac{2m(E-V_0)}{\hbar^2}x}
\]

For \( E < V_0 \)

\[
D' = 0 \quad \text{otherwise} \quad \psi_3(x \to +\infty) = De^{-i\frac{2m(E-V_0)}{\hbar^2}(+\infty)} = De^{-\frac{2m(E-V_0)}{\hbar^2}(+\infty)} \to \infty
\]

\[
\psi_3(x) = De^{-\frac{2m(E-V_0)}{\hbar^2}x} \quad E < V_0 \quad \to \quad De^{-\frac{2mE}{\hbar^2}x} \quad \to \quad De^{-\beta x}
\]

\( -a < x < a \) \hspace{1cm} \text{REGION 2}
\[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_2(x) + V(x)\psi_2(x) = E\psi_2(x)\]

\[\frac{d^2}{dx^2} \psi_2(x) = -\frac{2mE}{\hbar^2} \psi_2(x)\]

\[\psi_2(x) = A e^{i\sqrt{\frac{2mE}{\hbar^2}} x} + B e^{-i\sqrt{\frac{2mE}{\hbar^2}} x},\]

which we can also write as \( \psi_2(x) = A e^{ik'x} + B e^{-ik'x} \)

with \( k' = \sqrt{\frac{2mE}{\hbar^2}} \).

Notice \( E > 0 \) so solutions are oscillatory.

Goswami’s \( k' \) is \( \sqrt{\frac{2mE - V_0}{\hbar^2}} \), because of the different zero; Liboff uses \( k \). Liboff leaves the solution in this form, and sets up boundary conditions; Goswami instead chooses to write the solution in region 2 in terms of sines and cosines, and then sets up boundary conditions.

Also \( A' = \pm B' \) because of symmetry (general argument can be proved rigorously, but seems clear here because there is nothing in the potential to distinguish \(+x\) from \(-x\)).

**Either (EVEN SOLUTION)**

\[\psi_2(x) = A \left( e^{i\sqrt{\frac{2mE}{\hbar^2}} x} + e^{-i\sqrt{\frac{2mE}{\hbar^2}} x} \right) = A \cos \left( \sqrt{\frac{2mE}{\hbar^2}} x \right)\]
Notice that the cosine is not necessarily zero at the boundaries of region 2.

**Or (ODD SOLUTION)**

\[
\psi_2(x) = A \left( e^{i \frac{2mE}{\hbar^2} x} - e^{-i \frac{2mE}{\hbar^2} x} \right) = B \sin \left( \sqrt{\frac{2mE}{\hbar^2}} x \right)
\]

Again, the sine functions are not necessarily zero at the boundaries of region 2.

We can also write

\[
\psi_2(x) = A \cos \left( \sqrt{\frac{2mE}{\hbar^2}} x \right) + B \sin \left( \sqrt{\frac{2mE}{\hbar^2}} x \right)
\]

expecting that when \( A \neq 0 \) then \( B = 0 \) and when \( B \neq 0 \) then \( A = 0 \). Actually, we don’t need to invoke the symmetry argument, but simply let the matching of the boundary conditions bring out the sines and cosines for us, but it’s nicer this way.
BOUNDARY CONDITIONS

Wave function continuous at $x = -a$

$$\psi_2(-a) - \psi_1(-a) = 0$$

$$A \cos \left( -\frac{2mE}{\hbar^2}a \right) - B \sin \left( \frac{2mE}{\hbar^2}a \right) - Ce^{-\beta a} = 0$$

Wave function derivative continuous at $x = -a$

$$\left. \frac{d\psi_2(x)}{dx} \right|_{x=-a} - \left. \frac{d\psi_1(x)}{dx} \right|_{x=-a} = 0$$

$$A \sqrt{\frac{2mE}{\hbar^2}} \sin \left( \frac{2mE}{\hbar^2}a \right) + B \sqrt{\frac{2mE}{\hbar^2}} \cos \left( \frac{2mE}{\hbar^2}a \right) - \beta Ce^{-\beta a} = 0$$

Wave function continuous at $x = a$

$$\psi_2(a) - \psi_3(a) = 0$$

$$A \cos \left( \frac{2mE}{\hbar^2}a \right) + B \sin \left( \frac{2mE}{\hbar^2}a \right) - De^{-\beta a} = 0$$

Wave function derivative continuous at $x = a$

$$\left. \frac{d\psi_2(x)}{dx} \right|_{x=a} - \left. \frac{d\psi_3(x)}{dx} \right|_{x=a} = 0$$

$$-A \sqrt{\frac{2mE}{\hbar^2}} \sin \left( \frac{2mE}{\hbar^2}a \right) + B \sqrt{\frac{2mE}{\hbar^2}} \cos \left( \frac{2mE}{\hbar^2}a \right) + \beta De^{-\beta a} = 0$$

Write these in matrix form:
\[
\begin{pmatrix}
\cos(k'a) & -\sin(k'a) & -e^{-\beta a} & 0 \\
k' \sin(k'a) & k' \cos(k'a) & -\beta e^{-\beta a} & 0 \\
\cos(k'a) & \sin(k'a) & 0 & -e^{-\beta a} \\
-k' \sin(k'a) & k' \cos(k'a) & 0 & \beta e^{-\beta a}
\end{pmatrix} = 0
\]

where \( k' = \sqrt{\frac{2mE}{\hbar^2}} \)

A solution exists for \( A, B, C, D \) if the determinant vanishes:

\[
\begin{vmatrix}
\cos(k'a) & -\sin(k'a) & -e^{-\beta a} & 0 \\
k' \sin(k'a) & k' \cos(k'a) & -\beta e^{-\beta a} & 0 \\
\cos(k'a) & \sin(k'a) & 0 & -e^{-\beta a} \\
-k' \sin(k'a) & k' \cos(k'a) & 0 & \beta e^{-\beta a}
\end{vmatrix} = 0
\]

which leads to

\[
\left( \tan(k'a) - \frac{\beta}{k'} \right) \left( \tan(k'a) + \frac{k'}{\beta} \right) = 0
\]

Cannot have both brackets zero at same time, so we are led to two sets of solutions, which correspond to the previously mentioned condition that when \( A \neq 0 \) then \( B = 0 \) and when \( B \neq 0 \) then \( A = 0 \). It’s not possible to find values for \( E \) (recall both \( k' \) and \( \beta \) depend on \( E \)) analytically - we have to resort to a graphical method, nicely outlined in Goswami or Liboff.

If \( \tan(k'a) = \frac{\beta}{k'} \), this corresponds to even solutions, and the values of \( E \) (buried in \( k' \) and \( k \)) that solve this "transcendental equation") are the required eigenvalues. Let's manipulate the equation a bit …
\[
\tan(k' a) = \frac{\beta a}{k' a} \\
\tan(k' a) = \frac{\sqrt{2 m(V_0 - E) a^2}}{\hbar k' a} \\
\tan(k' a) = \frac{\sqrt{\lambda^2 - (k' a)^2}}{k' a} \text{ where } \lambda^2 = \frac{2 m V_0 a^2}{\hbar^2}
\]

The graphical solution to this equation is in Goswami Fig 4.5, where he plots the LHS and the RHS as functions of \(k' a\). In Liboff’s Fig 8.2, it looks a bit different, but only because he has recast the equation as

\[k' a \tan(k' a) = \beta a,\] and notes that \((k' a)^2 + (\beta a)^2 = \lambda^2\) where \(\lambda^2 = \frac{2 m V_0 a^2}{\hbar^2}\), and he plots both equations on a \(k'a\) vs. \(\beta a\) plot.

In both cases the solutions are discrete, and decrease in number as the parameter \(\lambda\) becomes smaller (this corresponds to decreasing the width or the height of the well.

There is another set of solutions (the odd ones) – read up on these – that follows a similar pattern, only it is possible to have NO solutions if the well becomes narrow or shallow.

Here are the graphical solutions to these equations – the even solutions (top) and odd (bottom). The points of intersection on the graphs determine the allowed energies of the system. The blue, red and green lines correspond to different well parameters, and any given set of parameters corresponds to one color.
WAVE FUNCTIONS FOR BOUND STATES OF A FINITE WELL:

The quantities $V_0, a, m, h$ are known. The bottom of the well is at $V = 0$, and the top at $V = V_0$. The well extends from $x = -a$ to $x = a$.

**EVEN SOLUTIONS ($n = 1, 3, 5, ...$)**

$$\varphi_n(x) = A \cos \left[ \frac{\sqrt{2mE_n}}{\hbar} x \right] e^{\frac{\sqrt{2mV_0 - E_n}}{\hbar^2} (x - a)} \quad \text{for } x > a$$

$$\varphi_n(x) = A \cos \left[ \frac{\sqrt{2mE_n}}{\hbar} x \right] e^{\frac{\sqrt{2mV_0 - E_n}}{\hbar^2} (x + a)} \quad \text{for } x < -a$$

$$\varphi_n(x) = A \cos \left[ \frac{\sqrt{2mE_n}}{\hbar} x \right] e^{\frac{\sqrt{2mV_0 - E_n}}{\hbar^2} (x - a)} \quad \text{for } -a < x < a$$

with the energy $E_n$ determined by

$$\frac{\sqrt{2m(V_0 - E_n)a^2 / \hbar^2}}{\sqrt{2mE_n a^2 / \hbar^2}} = \tan \left[ \frac{\sqrt{2mE_n a^2 / \hbar^2}}{2} \right]$$

and the coefficient $A$ determined by

$$\int_{-\infty}^{\infty} |\varphi_n|^2 \, dx = 1$$

**ODD SOLUTIONS ($n = 2, 4, 6, 8 ...$)**

$$\varphi_n(x) = -B \sin \left[ \frac{\sqrt{2mE_n}}{\hbar} x \right] e^{\frac{\sqrt{2mV_0 - E_n}}{\hbar^2} (x + a)} \quad \text{for } x > -a$$

$$\varphi_n(x) = B \sin \left[ \frac{\sqrt{2mE_n}}{\hbar} x \right] \quad \text{for } -a < x < a$$
\[ \varphi_n(x) = B \sin \left( \frac{\sqrt{2mE_n}}{\hbar} x \right) e^{-\frac{\sqrt{2m(V_0-E_n)}/a}{\hbar}} \] for \( x > a \)

with the energy \( E_n \) determined by

\[
\frac{\sqrt{2m(V_0-E_n)/a^2}}{\hbar^2} = -\cot \left( \frac{\sqrt{2mE_n/a^2}}{\hbar^2} \right)
\]

and the coefficient \( B \) determined by

\[ \int_{-\infty}^{\infty} |\varphi_n|^2 \, dx = 1 \]

The INFINITE WELL corresponds to the limit \( V_0 \to \infty \) where \( E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2m(2a)^2} \) and

\[ \varphi_n(x) = \sqrt{\frac{2}{(2a)}} \cos \left( \frac{\sqrt{2mE_n}}{\hbar} x \right) \] (\( n \) odd) and \( \varphi_n(x) = \sqrt{\frac{2}{(2a)}} \sin \left( \frac{\sqrt{2mE_n}}{\hbar} x \right) \) (\( n \) even).

If the well extends from \( x = 0 \) to \( x = L \), a completely equivalent form is \( \varphi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi}{L} x \right) \)

and \( E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \).

Here are the first three functions for a well with 3 bound states. The dashed line indicates the well boundaries. Note the symmetry of the wave functions, the exponential decay beyond the boundaries, and the decay lengths increasing for larger energies.