NanoEnergy
ECE 597/697 Special Topics: Energy Transport and Conversion at the Nanoscale
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Meeting time and place: MWF 12:20 in Elab 306
*Office Hours*: Tue 10:30am, Wed/Fri after class?
“Review”: Waves and Quantum Mechanics

• Goal: remind ourselves of the main consequences of the particle—wave duality

• Travelling wave: \[ \Psi(x,t) = A \sin\left(2\pi ft - \frac{2\pi}{\lambda_x} x\right) \hat{y} \]
  \[= A \sin\left(\omega t - k_x x\right) \hat{y} \]

• Notation: A—amplitude
  \[ k_x = \frac{2\pi}{\lambda_x} \] \( \omega \)—angular frequency=2\( \pi \)f
  k—wavevector: counts the number of wave nodes per unit distance along the direction of propagation;

• Waves in complex representation: \[ \Psi(x,t) = Ae^{i(\omega t - k_x x)} \hat{y} \]
Phase velocity and standing waves

• Constant phase plane given by $\omega t - k_x x = \text{const.}$
• Propagates at a velocity called “phase velocity”, given by $v_p = \frac{dx}{dt} = \frac{\omega}{k_x} = \lambda_x f$
• If velocity is constant “c” (e.g. light, sound) $\omega = ck_x$ so $v_p = c$
• Standing wave: superposition of two waves with equal phase speed in opposite directions:
  
  $$
  \Psi(x, t) = A \left[ \sin(\omega t - k_x x) + \sin(\omega t + k_x x) \right] \hat{y}
  $$
  
  $$
  \Psi(x, t) = -2A \cos(\omega t) \sin(k_x x) \hat{y}
  $$

• Positions where $\Psi(x, t) = 0$ are fixed in space: $\sin(k_x D) = 0$
• $D = ?$
Schrödinger Equation

• Let’s start with our wave in complex representation

$$\Psi(x, t) = Ae^{i(k_x x - \omega t)}$$

• Apply the wave-particle duality expressions for energy and momentum: $E=\hbar \omega$ and $p_x=\hbar k_x$ to obtain:

$$\Psi(x, t) = Ae^{i(p_x x - Et)/\hbar}$$

• In 3D we can call the position coordinate “r” and write:

$$\Psi(\vec{r}, t) = Ae^{i(\vec{p} \cdot \vec{r} - Et)/\hbar}$$

• Now let’s take some derivatives and see what we get:

$$\nabla_{\vec{r}} \Psi(\vec{r}, t) = \frac{i}{\hbar} \vec{p} Ae^{i(\vec{p} \cdot \vec{r} - Et)/\hbar} = \frac{i}{\hbar} \vec{p} \Psi(\vec{r}, t)$$

$$\frac{\partial}{\partial t} \Psi(\vec{r}, t) = -\frac{i}{\hbar} EAe^{i(\vec{p} \cdot \vec{r} - Et)/\hbar} = -\frac{i}{\hbar} E \Psi(\vec{r}, t)$$
Schrödinger Equation, cont.

- Based on these two equations, we can “define” the momentum operator $p$ as:

$$\nabla_{\vec{r}} \Psi(\vec{r}, t) = \frac{i}{\hbar} \hat{p} \Psi(\vec{r}, t) \Rightarrow \hat{p} = \frac{\hbar}{i} \nabla_{\vec{r}}$$

- And the energy operator $E$ as:

$$\frac{\partial}{\partial t} \Psi(\vec{r}, t) = -\frac{i}{\hbar} E \Psi(\vec{r}, t) \Rightarrow E = -\frac{\hbar}{i} \frac{\partial}{\partial t}$$

- Now we can write total energy as kinetic+potential:

$$E = \frac{1}{2} m v^2 + V(\vec{r}) = \frac{\hat{p} \cdot \hat{p}}{2m} + V(\vec{r})$$

- Substituting our new operators for $p$ and $E$, we get:

$$\frac{\hat{p} \cdot \hat{p}}{2m} \Psi(\vec{r}, t) + V(\vec{r}) \Psi(\vec{r}, t) = E \Psi(\vec{r}, t)$$

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}) \Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t)$$

Hamiltonian operator $H$
Schrödinger Equation, cont.

• Time-independent (steady-state) version:

\[ H \Psi(\vec{r}, t) = E \Psi(\vec{r}, t) \]

\[ -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + (V(\vec{r}) - E) \Psi(\vec{r}, t) = 0 \]

• The SE defines the wavefunction \( \Psi \) up to a constant. This is called normalization and is needed to uniquely define it:

• 1D:

\[ \int_{-\infty}^{\infty} \Psi^* \Psi \, dx = 1 \]

• 3D:

\[ \iiint \Psi^* \Psi \, d\vec{r} = 1 \]

• Expectation of an operator \( \langle H \rangle \):

\[ \langle H \rangle = \iiint \Psi^* H \Psi \, d\vec{r} \]

• Standard deviation/Variance?
1D particle in a box

• Let’s start with a simple example which has all the key features. In 1D the time-independent Schroedinger Eqn is:

\[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) + (V(x) - E) \Psi(x) = 0\]

• Imagine a 1-dimensional land where the potential is zero inside the region between x=0 and x=L and infinite elsewhere

\[V(x) = \begin{cases} 0 & \text{if } 0 < x < L \\ \infty & \text{otherwise} \end{cases}\]

\[\frac{d^2}{dx^2} \Psi(x) + \frac{2mE}{\hbar^2} \Psi(x) = 0\]
1D particle in a box, cont.

- The solution has to be zero outside 0<x<L since \( V(x) \) is infinite.
- At the walls, the boundary conditions require the wavefunction to go to zero.
- Inside the walls, we need a function whose second derivative is twice the function itself.
- Solution: guess a form which has the right properties:

\[
\Psi(x) = Ae^{ik_n x} + Be^{-ik_n x}
\]

\[
k_n^2 = \frac{2mE_n}{\hbar^2}
\]

- then apply the BCs: at \( x=0 \), we have \( A+B=0 \) so \( A=-B \), which allows us to combine the two parts and simplify:

\[
\Psi(x) = A \sin(k_n x)
\]

\[
\Psi(L) = A \sin(k_n L) = 0
\]

Apply BC at \( x=L \):

\[
k_n L = n\pi \Rightarrow k_n = \frac{n\pi}{L}
\]

\[
E_n = \frac{\hbar^2 k_n^2}{2m}
\]
1D particle in a box, cont.

• Finally, we can find $A$ from the normalization condition:

$$\int_0^L \Psi^*(x)\Psi(x) = A^2 \int_0^L \sin^2(k_n x) = 1$$

$$A^2 = \frac{2}{L} \Rightarrow \Psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

• Question: what happens if the walls are not infinite?

![Graphical representation of a 1D particle in a box with potential energy $V(x) = V_0$ and $V(x) = 0$ at different positions.](image-url)
2D particle in a box

- Same problem, only in 2D:

\[ V(x, y) = \begin{cases} \infty & \text{if } 0 < x, y < L \\ \infty & \text{otherwise} \end{cases} \]

\[ \Psi(x, y) = \begin{cases} 0 & \text{if } x = 0, y = 0 \\ \infty & \text{if } x = L, y = L \end{cases} \]

- Try separation of variables: assume the wavefunction can be written as a product of two functions, one in \( x \) and other in \( y \):

\[ \Psi(x, y) = X(x)Y(y) \]

\[ Y(y) \frac{d^2 X(x)}{dx^2} + X(x) \frac{d^2 Y(y)}{dy^2} + \frac{2mE}{\hbar^2} X(x)Y(y) = 0 \]

\[ \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2 Y(y)}{dy^2} + \frac{2mE}{\hbar^2} = 0 \]
2D particle in a box, cont.

- **Rearranging:**
  \[
  \frac{1}{X(x)} \frac{d^2X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} + \frac{2mE}{\hbar^2} = 0
  \]

- Notice that \(2mE/\hbar\) is a positive constant so we can separate the solutions into a function of \(x\) and function of \(y\):
  \[
  \frac{1}{X(x)} \frac{d^2X(x)}{dx^2} + k_n^2 = 0 \implies \frac{d^2X(x)}{dx^2} + k_n^2 X(x) = 0
  \]
  \[
  \frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} + k_m^2 = 0 \implies \frac{d^2Y(y)}{dy^2} + k_m^2 Y(y) = 0
  \]

- Boundary conditions as \(X(0) = X(L) = 0\) and \(Y(0) = Y(L) = 0\)
- Didn’t we just solve a problem like this? Use our 1D solution:
  \[
  X(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right) \quad Y(y) = \sqrt{\frac{2}{L}} \sin \left( \frac{m\pi y}{L} \right)
  \]
Combine them into one complete solution:

$$\Psi(x, y) = X(x)Y(y) = \frac{2}{L} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right)$$

The total energy is now a sum of two terms, one in “n” and the other in “m”:

$$\frac{2mE_{n,m}}{\hbar^2} = k_n^2 + k_m^2 \Rightarrow E_{n,m} = \frac{\hbar^2 \pi^2 \left(n^2 + m^2\right)}{2mL^2}$$

Notice that we can now have two solutions with different wavefunctions but same energy: $E_{n,m} = E_{m,n}$ while $\Psi_{n,m} \neq \Psi_{m,n}$

This is called “degeneracy” when different solutions have the same energy

The term “degeneracy” is borrowed from linear algebra where it is used to denote when different eigenvectors have the same eigenvalue
Harmonic Oscillator

• The 3rd example we will consider is a harmonic oscillator

• Harmonic usually refers to second order behavior so \( V(x) = Kx^2/2 \) so the 1D Schroedinger equation is:

\[
\frac{d^2}{dx^2} \Psi(x) + \frac{2m}{\hbar^2} \left( \frac{Kx^2}{2} - E \right) \Psi(x) = 0
\]

• Such a quadratic potential represents a classical mass+spring

• The potential \( V(x) \) keeps increasing forever so the BCs are:

\[
\Psi(x \to \infty) = 0 \quad \text{and} \quad \Psi(x \to -\infty) = 0
\]

• The solutions are related to so-called Hermite polynomials:

\[
\Psi(x) = \left( \frac{1}{2^n n! \sqrt{\pi \hbar}} \right)^{1/2} H_n \left[ \sqrt{\frac{m\omega x^2}{\hbar}} \right] \exp \left( - \frac{m\omega x^2}{2\hbar} \right) \quad E_n = \left( n + \frac{1}{2} \right) \hbar \omega
\]
Periodic Potentials

- Most of the materials we will study have “crystal structure”
- The arrangements of atoms is periodic with constant spacing “a” between neighbor atoms:

\[
V(x) \text{ is periodic with } V(x+a) = V(x)
\]

- Each atom has associated with it a potential \( V(r) \) due to the Coulomb charge-charge interactions between electrons and protons in the atomic core
- Consequently, \( V(x) \) is periodic with \( V(x+a) = V(x) \)
Kronig-Penney Model

- This classic model dating back to 1930 is as bare-bones as they come.
- Assume 1-d periodic potential which is zero for $0 < x < a$ and $V_0$ for $-b < x < 0$:

$$V(x) = \begin{cases} 
0 & \text{if } 0 < x \leq a \\
V_0 & \text{if } -b < x \leq 0
\end{cases}$$

$V(x + a + b) = V(x)$

- Solve the Schrödinger eqn. for this potential

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) + (V(x) - E)\Psi(x) = 0$$
Kronig-Penney Model, cont.

• We will assume the same form of the solution as before, only there are two separate segments:

\[ \Psi(x) = Ae^{i\alpha x} + Be^{-i\alpha x} \quad (0 < x < a) \]
\[ \Psi(x) = Ce^{\beta x} + De^{-\beta x} \quad (-b < x < 0) \]

\[ \alpha^2 = \frac{2mE}{\hbar^2} \]
\[ \beta^2 = \frac{2m}{\hbar^2}(V_0 - E) \]

• The boundary condition at x=0 gives us: A+B=C+D

• Continuity of the derivative at x=0 gives: \( i\alpha(A-B) = \beta(C-D) \)

• However, we have 4 unknowns so we need two more BCs!

• Use the periodicity: observables are periodic so:

\[ \Psi^*(x+a+b)\Psi(x+a+b) = \Psi^*(x)\Psi(x) \]
\[ \Psi(x+a+b) = \Psi(x)\exp\left[ik(a+b)\right] \]
Kronig-Penney Model, cont.

• Now the BCs can be applied at $x=a$:
  $$\Psi(a) = Ae^{i\alpha a} + Be^{-i\alpha a}$$
  $$\Psi(a) = (Ce^{-\beta b} + De^{\beta b}) \exp[ik(a+b)]$$

• And for the first derivative:
  $$\Psi'(a) = i\alpha(Ae^{i\alpha a} - Be^{-i\alpha a})$$
  $$\Psi'(a) = \beta(Ce^{-\beta b} - De^{\beta b}) \exp[ik(a+b)]$$

• This is a set of 4 linear equations in unknowns A, B, C, and D
  $$\begin{pmatrix}
  1 & 1 & -1 & -1 \\
  i\alpha & -i\alpha & -\beta & \beta \\
  e^{i\alpha a} & e^{-i\alpha a} & -e^{-\beta b + ik(a+b)} & -e^{\beta b + ik(a+b)} \\
  i\alpha e^{i\alpha a} & -i\alpha e^{-i\alpha a} & -\beta e^{-\beta b + ik(a+b)} & \beta e^{\beta b + ik(a+b)}
  \end{pmatrix}
  \begin{pmatrix}
  A \\
  B \\
  C \\
  D
  \end{pmatrix} = 0$$
Kronig-Penney Model, cont.

• The equality is satisfied when the determinant of the matrix is zero, which gives us:

\[
\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh(\beta b) \sin(\alpha a) + \cosh(\beta b) \cos(\alpha a) = \cos\left[ k \left( a + b \right) \right]
\]

• For a given wavevector “k” this equation allows us to determine the energy E; this relationship E(k) is called “dispersion” or “electronic structure”

• Adding 2\pi/(a+b) to k does not change the solution—it is periodic

• The RHS cannot be larger than 1, so there are ranges of E for which no solution is possible gives rise to energy gaps!
• We can simplify the problem in the limit where \( b \to 0 \) and \( V_0 \) becomes infinite (delta function).

• Keeping \( \beta ba / 2 = P \) constant allows us to approximate:

\[
\sinh(\beta b) \approx \beta b \\
\cosh(\beta b) \approx 1
\]

• To get a much simpler:

\[
\frac{P}{\alpha a} \sin(\alpha a) + \cos(\alpha a) = \cos(ka)
\]

• This can be solved graphically by equating \( k = \alpha \) (as it would be in the free electron case):

• Note that as the 1\(^{st}\) term on LHS \((P\sin(c(\alpha a)))\) decays, we recover \( k = \alpha \)!