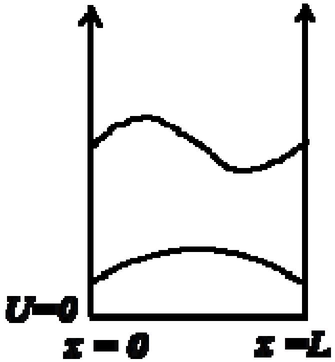
Physics 48 February 1, 2008
Happy Ground Hog Day (a day early)!

- A few remarks about solutions to the SE.
  - Complete orthonormal sets
  - Expectation values
  - Uncertainty
- The "Swarthmore solution" to the Semi-infinite square well.
- Some sample review problems you will work as a team for Monday.

Particle in a Box

With $U(x) = 0$ if $0 \le x \le L$

and $U(x) = \infty$ if $x < 0$ or if $x > L$



<u>Inside the box we have</u>

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) \quad \text{or} \quad \frac{\partial^2\psi(x)}{\partial x^2} = -\frac{2m}{\hbar^2}E\psi(x) \equiv -k^2\psi(x)$$

The equation is that of a harmonic oscillator with solutions

$$\psi(x) = A\sin(kx) + B\cos(kx).$$

We match these solutions within the well to the Boundary Condition that the wavefunction must vanish a 0 and at L. These imply that B=0 and that the constant $k = {}^{n\pi}\!/_{L}$, with n an integer.

Thus $k_n = n\pi / L = \sqrt{2mE_n} / \hbar$ with n = 1, 2, 3, ..

Applying the normalization condition on the solutions yields the eigenstates:

$$\psi_n(x) = \sqrt{2/L}\,\sin\left(\frac{n\pi\,x}{L}\right) \quad \text{where n = 1, 2, 3, ...}$$

And the corresponding energies are $E_n = \dfrac{k^2\hbar^2}{2m} = \dfrac{n^2\pi^2\hbar^2}{2mL^2}$.

It can be easily shown that the ψ_n form a complete orthonormal set of functions on the interval between $x = 0$ and L (Fourier's theorem).

i.e. $$\int \psi_m(x)^* \psi_n(x)\,dx = \delta_{mn} \qquad \text{(Orthonormal)}$$

Any arbitrary function can be written as a linear combination of these eigenfunctions.

$$f\left(x\right) = \sum_{n} c_n \psi_n\left(x\right) \qquad \text{(Complete)}$$

One may use Fourier's trick to determine the coefficients.

$$\int \psi_m(x)^* f(x)dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)dx$$

$$= \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m$$

Once the coefficients are determined (usually from the initial conditions) the general solution of the TDSE is known.

$$\boxed{\Psi\left(x,t\right) = \sum_{n} c_n \psi_n\left(x\right) e^{-iE_n t/\hbar}}$$

The normalization condition $$\int_{-\infty}^{\infty}\left|\Psi(x,t)\right|^2 dx = 1$$

$$\int\left|\sum_n c_n\psi_n(x)e^{-iE_nt/\hbar}\right|^2 dx = \int(\sum_m c_m{}^*\psi_m{}^*(x)e^{iE_mt/\hbar})(\sum_n c_n\psi_n(x)e^{-iE_nt/\hbar})dx$$

$$= \sum_m c_m{}^* e^{iE_mt/\hbar}\sum_n c_n e^{-iE_nt/\hbar}\int\psi_m{}^*(x)\psi_n(x)dx$$

$$= \sum_m c_m{}^* e^{iE_mt/\hbar}\sum_n c_n e^{-iE_nt/\hbar}\delta_{mn}$$

$$= \sum_n\left|c_n\right|^2$$

So $$\boxed{\sum_n\left|c_n\right|^2 = 1}$$

Once we have the wave function we may calculate the “expectation” value of any function of x.

$$\langle g(x) \rangle = \int_{-\infty}^{\infty} P(x,t)\, g(x)\, dx = \int_{-\infty}^{\infty} \left|\Psi(x,t)\right|^2 g(x)\, dx$$

e.g. < x >, < U(x) > etc.

Notice that even though the operators are **time independent**. The expectation value can be **time dependent**. In the Schrödinger picture the time dependence is carried by the wave functions and is usually not explicit in the operators.

Note: In fact we can calculate the expectation value of any operator $\hat{O}$ in the Schrodinger picture:

$$\langle \hat{O} \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\hat{O}\Psi(x,t)dx$$

Here it is understood the operator $\hat{O}$ acts on the wave function to the right. e.g. consider the momentum operator that has a d/dx in it! We will explore this further when we lay out the fundamental postulates of Quantum Mechanics.

e.g. The expectation value of the energy operator is

$$
\begin{aligned}
\langle H \rangle &= \int_{-\infty}^{\infty} \Psi^*(x,t) H \Psi(x,t) dx \\
&= \int \Big(\sum_m c_m^{\ *} \psi_m^{\ *}(x) e^{iE_m t/\hbar}\Big) i\hbar \frac{\partial}{\partial t} \Big(\sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}\Big) dx \\
&= i\hbar \sum_m c_m^{\ *} e^{iE_m t/\hbar} \sum_n c_n \tfrac{\partial}{\partial t}\big(e^{-iE_n t/\hbar}\big) \int \psi_m^{\ *}(x) \psi_n(x) dx \\
&= \sum_m c_m^{\ *} e^{iE_m t/\hbar} \sum_n c_n E_n e^{-iE_n t/\hbar} \delta_{mn} \\
&= \sum_n |c_n|^2 E_n
\end{aligned}
$$

$$\boxed{\langle H \rangle = \sum_n |c_n|^2 E_n}$$

This is like a weighted average of the eigenenergies. $|c_n|^2$ is the probability of finding the particle with an energy E_n.

If you measure the energy, what will you find?

Note that the expectation value of the energy does not vary with time.

This is not really surprising since we only allowed conservative forces (forces with potentials) into our analysis.

Using the above formalism we can show that the Schrodinger equation produces solutions that are compatible with the uncertainty principle.

With

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$

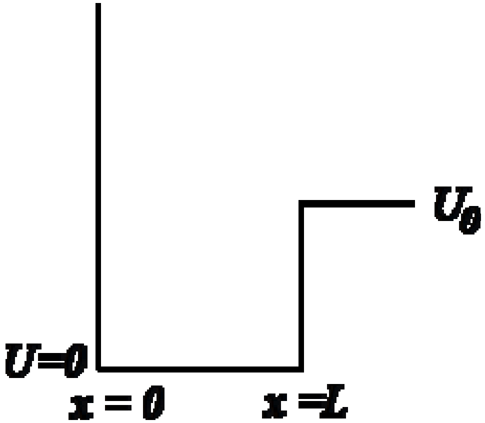
We find that $\Delta x \cdot \Delta p \geq \hbar / 2$.

The semi-infinite square well

With $U(x) = 0$ if $0 \le x \le L$

and $U(x) = \infty$ if $x < 0$

$U(x) = U_0$ if $x > L$



The Schrodinger Equation and solutions **inside** the well are as before

$$\psi(x) = A\sin(kx) + B\cos(kx), \text{ with } k = \sqrt{2mE}/\hbar$$

For $x < 0$ we require that the wave function vanish. Hence $B = 0$.

$$\psi(x) = A\sin(kx), \text{ with } k = \sqrt{2mE}/\hbar$$

For $x > L$

The SE becomes $$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+U_0\psi(x)=E\psi(x)$$

Rearranging => $$\frac{d^2\psi(x)}{dx^2}=\frac{2m}{\hbar^2}(U_0-E)\psi(x)\equiv k'^2\,\psi(x)$$

Where $k'=\sqrt{2m(U_0-E)}/\hbar$

With $E<U_0$ the solutions are rising and decaying exponentials

$$\psi_+(x)=Ce^{-k'x}+De^{k'x}\ \text{ for } x>L$$

We require that the wave function vanish at ∞. This implies that D is zero.

Boundary condition at L

Matching the wave function and its derivative at $x = L$ yields

$$A\sin(kL) = Ce^{-k'L}$$

and

$$Ak\cos(kL) = -Ck'e^{-k'L}$$

Take the ratio

$$\boxed{k\cot(kL) = -k'}$$

This is a transcendental equation. It has no analytic solution.
There are many possible ways to approach it.
We will do a graphic solution.

The “Swarthmore Solution“

$$k\cot(kL) = -k'$$

Square $$k^2\cot^2(kL) = k'^2$$

Note $$\cot^2(kL) = \frac{\cos^2(kL)}{\sin^2(kL)} = \frac{1-\sin^2(kL)}{\sin^2(kL)} = \frac{1}{\sin^2(kL)} - 1$$

Thus $$\frac{k^2}{\sin^2(kL)} - k^2 = k'^2$$

So $$\sin^2(kL) = \frac{k^2}{k^2+k'^2} = \frac{k^2}{2m(U_0-E)/\hbar^2 + 2mE/\hbar^2} = \frac{\hbar^2 k^2}{2mU_0}$$

$$\sin^2(kL) = \frac{\hbar^2 k^2}{2mU_0}$$

And thus

$$\boxed{\sin(kL) = \pm\sqrt{\hbar^2 / 2mU_0}\; k}$$

Note $k\cot(kL) = -k'$ implies that $\cot(kL) < 0$.

So $\boxed{\frac{(2n-1)\pi}{2L} \le k \le \frac{n\pi}{L} \quad \text{for n = 1, 2, 3,...}}$

These solutions can be found either numerically or graphically.

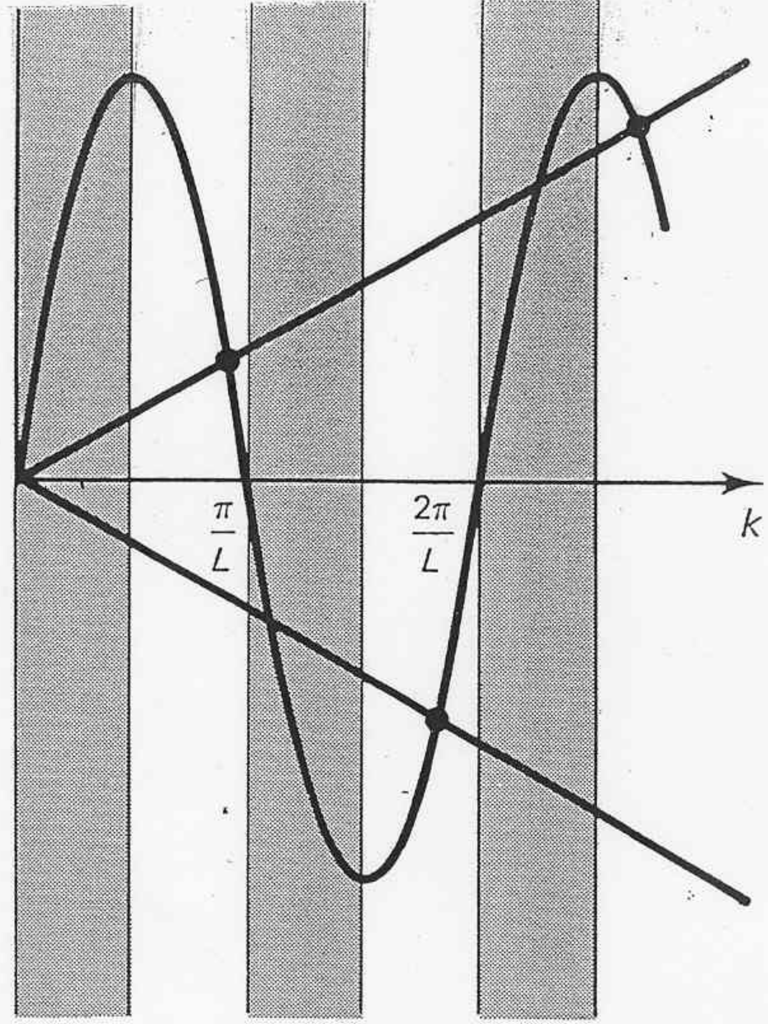


Fig. 6.6 Plots of $\sin kL$ vs. k and of $\pm\sqrt{\hbar^2/(2mU_0)}\,k$ vs. k. The intersections of these two plots give solutions of Eq. (49). The intersections in the shaded intervals must be excluded.

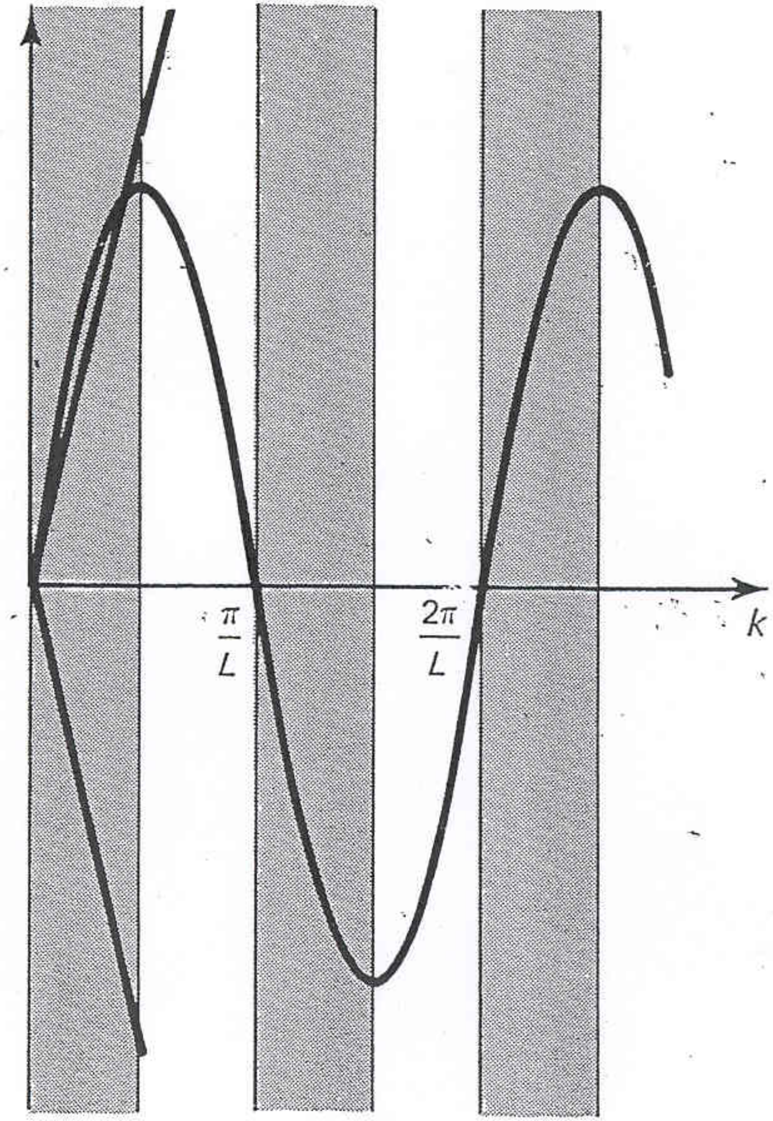


Fig. 6.7 If U_0 is small, there are no valid intersections

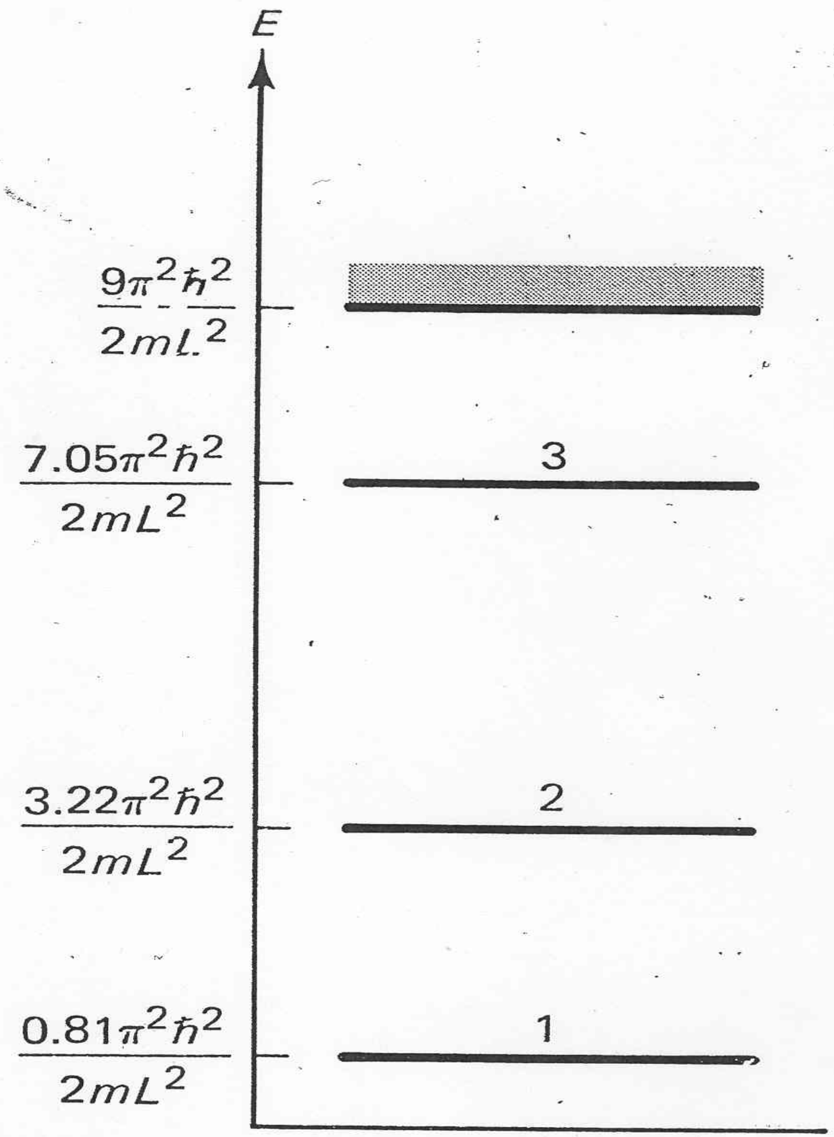


Fig. 6.8 Energy-level diagram for a finite well with $U_0 = 9\pi^2\hbar^2/(2mL^2)$. This well has three energy levels.

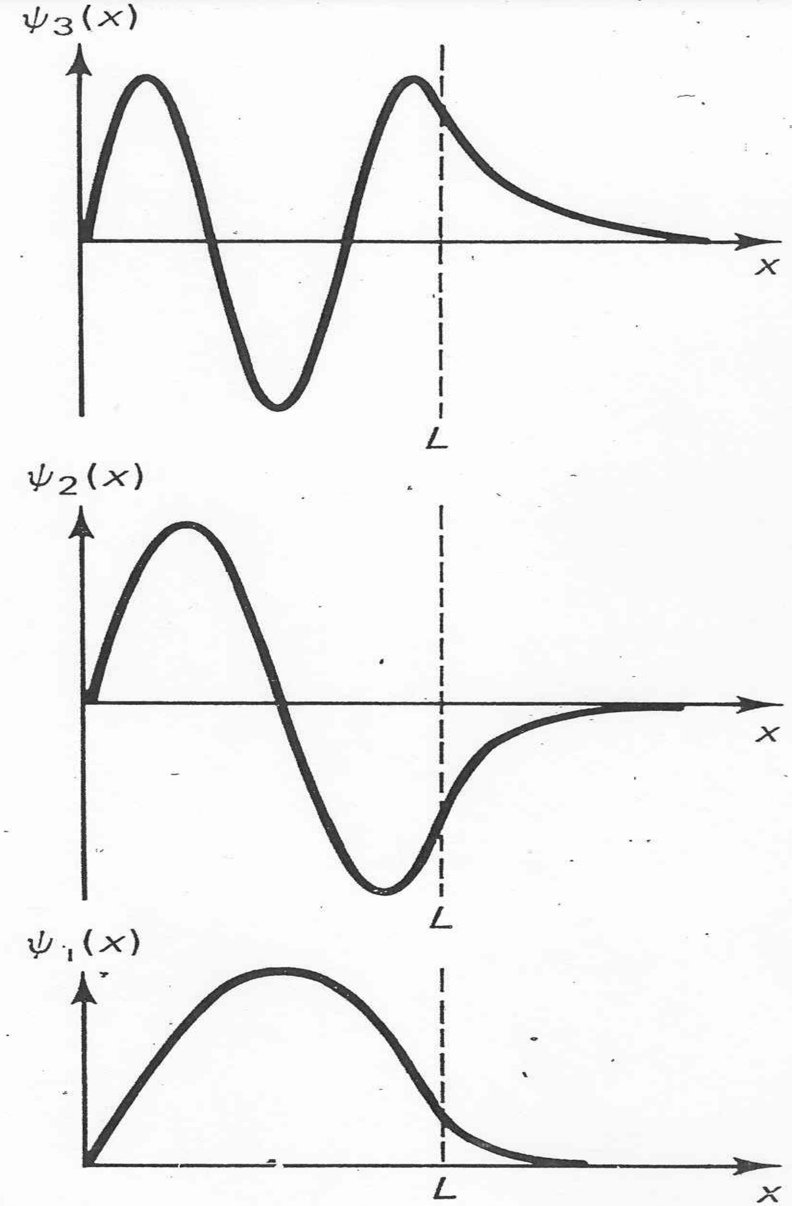


Fig. 6.9 Space dependence of the wavefunctions for the finite well with $U_0 = 9\pi^2\hbar^2/(2mL^2)$.

Completion of our P25 review

- 3 problems have been chosen, you will be randomly picked to work on one of these problems.
- One member of your group will be randomly picked to do a presentation of your solution to this problem on Monday.
- Please try to make your presentations thorough, but tidy. Aim for 15 minutes.