Welcome back
to PHY 3305

Today's Lecture:

Schrödinger Equation

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1887-1961

Revisit SWE:

$$-\frac{\hbar^2}{2m}\frac{\partial\Psi(x,t)}{\partial x^2} = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

We discussed the plane wave solution -

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

What do we get if we substitute this into SWE?

$$-\frac{\hbar^2}{2m}(ik)^2 Ae^{i(kx-\omega t)} = i\hbar(-i\omega)Ae^{i(kx-\omega t)}$$

$$\frac{\hbar^2 k^2}{2m}\Psi(x,t) = \hbar\omega\Psi(x,t)$$

$$\frac{\hbar^2 k^2}{2m}\Psi(x,t) = \hbar\omega\Psi(x,t)$$

What is the quantity $\frac{\hbar^2 k^2}{2m}$?

$$p = \hbar k$$

$$\frac{p^2}{2m} = \frac{1}{2}mv^2$$

kinetic energy of a particle

What is the quantity $\hbar\omega$?

total energy of a particle

This suggests ....

$$(KE)\Psi(x,t) = (E)\Psi(x,t)$$

SWE has something to do with classical energy accounting.

How could we extend SWE to include forces?

We could add a potential energy term to the equation.

$$(KE + U(x))\Psi(x,t) = (E)\Psi(x,t)$$

Note: This only works for CONSERVATIVE FORCES such as the electrostatic force.

Time-Dependent Schroedinger Equation

$$\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}}$$

$$-\frac{h^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+U(x)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

In classical physics, how do we determine the outcome of motion?

Given knowledge of the external force, solve the force equation for r.

$$\vec{F}=m\frac{d^2\vec{r}}{dt^2}$$

For the SWE, we must solve $\Psi(x,t)$ given knowledge of U(x)

$$-\frac{h^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+U(x)\Psi(x,t)=i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

Stationary States: Separation of Variables

Step 1: Separate the space and time parts of the wave equation into separate functions.

$$\Psi(x,t)=\psi(x)\phi(t)$$

Note: This reduces the generality of our solutions, but the special solutions are often of greatest interest.

Step 2: Re-write SWE

$$-\frac{\hbar^2}{2m}\phi(t)\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)\phi(t)=i\hbar\psi(x)\frac{d\phi(t)}{dt}$$

$$-\frac{\hbar^2}{2m}\phi(t)\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)\phi(t)=i\hbar\psi(x)\frac{d\phi(t)}{dt}$$

Step 3: Re-order the terms to achieve separation.

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}$$

Say that our equation holds when $(x,t) = (x_1,t_1)$. What happens when $(x,t) = (x_1,t_2)$?

The LHS does not change, so the RHS can not change.

Step 4: Set our equation equal to a separation constant.

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}=C$$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}=C$$

Notes:

1. If the potential energy is a function of time, this technique would fail. We could not separate the variables.
2. In the case that U is time-independent, we have 2 ODEs connected by the constant C.

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = C$$

The Temporal Part, φ(t):

$$i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = C \longrightarrow \boxed{\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = -\frac{iC}{\hbar}}$$

Note: Error in eqn 5-6 of your text.

$$\frac{1}{i} = (\frac{1}{i})(\frac{i}{i}) = -i$$

The solution to this equation is

$$\phi(t) = e^{-i(\frac{C}{\hbar})t}$$

Appendix K in your textbook discusses the method for solving this differential equation.

What does this mean?

$$\phi(t) = e^{-i(\frac{C}{\hbar})t}$$

Write solution in terms of the Euler Equation:

$$e^{-i(\frac{C}{\hbar})t} = \cos\left(\frac{C}{\hbar}t\right) - i\sin\left(\frac{C}{\hbar}\right)t$$

=ω

Thus,

$$\omega = \frac{C}{\hbar} \longrightarrow C = \hbar\omega = E$$

When we separate variables, we are focusing on states with well defined energies. The separation constant **IS** that energy.

Remember, we started by assuming our wave function could be written as

$$\Psi(x,t) = \psi(x)\phi(t)$$

That means our total wave function can be written as

$$\Psi(x,t) = \psi(x)e^{-i(\frac{E}{\hbar})t}$$

Note: We haven't considered interactions with the potential yet, so $\psi(x)$ is still *general* and unsolved for.

$$\Psi(x,t) = \psi(x)e^{-i(\frac{E}{\hbar})t}$$

What is the probability density for this wave function?

$$\Psi^*(x,t)\Psi(x,t) = [\psi^*(x)e^{i\frac{E}{\hbar}t}][\psi(x)e^{-i\frac{E}{\hbar}t}]$$

$$\Psi^*(x,t)\Psi(x,t) = \psi^*(x)\psi(x)$$

Is there a time dependence in the probability?

1. No, it disappears under the case we can separate space and time components of the wave function.
2. The properties do not change in time - **"stationary states"**

What are the implications for electrons in an atom?

The electron is bound by the Coulomb force to the atom. The potential is time-independent. Classically, as it whizzes around the nucleus it should be losing energy.

Quantum mechanics says that this is NOT the case. It tells us the electron can appear in many places around the atom ($\psi(x)$), but its energy is constant and well-defined.

The electron does not orbit in the classical sense, but rather in a probability cloud around the nucleus.

The probability density is constant. Thus, the charge density is constant and if charge density is constant, EM tells us it radiates no energy.

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}=C$$

The Spacial Part, ψ(x):

We can not say anything too specific w/o U(x).

Time-Independent SWE

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

Physical Conditions:

- Each case we will consider will have it’s own wave function ψ(x) to describe the particle.
- Certain physical conditions must be met.
    - The total probability of finding the particle must be one. (**Normalization**)
    - The particle must have a definite charge with a strict value.
    - The wave function must be **smooth**.

To be physically acceptable, a wave function must be normalizable.

The total probability of finding the particle anywhere in space is 100%.

The wave function describes a PROBABILITY DENSITY. Thus, to get 100% probability for finding the particle -

$$\boxed{\int |\Psi(x,t)|^2 dx = 1}$$

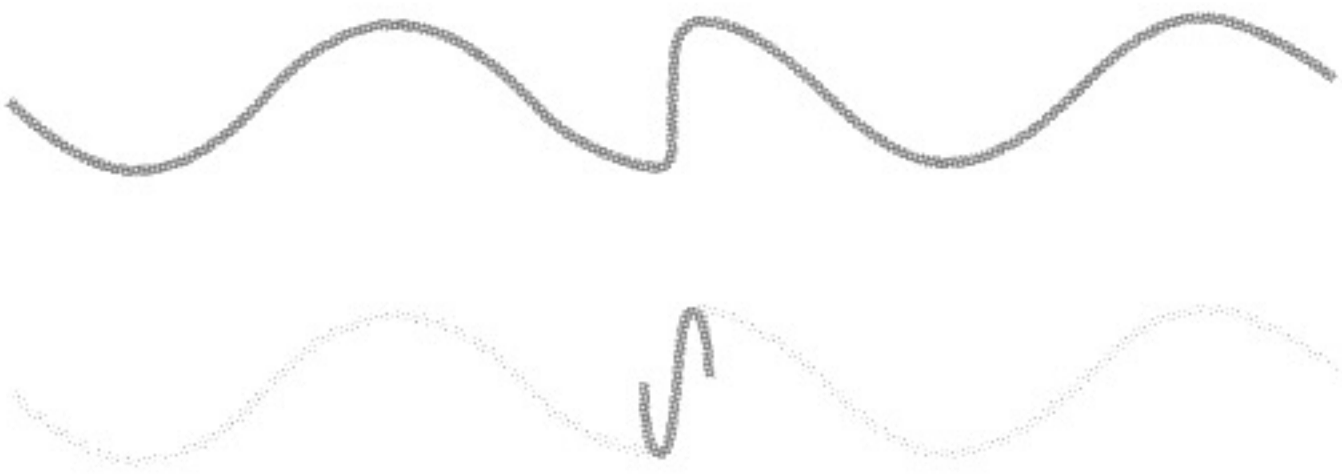
This is often referred to as a "naturalness" requirement. We don't expect probabilities greater than 100%.

To be physically acceptable, a wave function must be smooth.

The wave function and it's first derivative must be continuous.

Why must the wave function be continuous?

Say that the wave function has a point where it is infinite. This would signal a wave with a place of infinite kinetic energy - not realistic.



Abrupt jumps act like short wavelengths (high frequencies) which mean huge energies.

$$E = hf = \hbar\omega$$

Why must the first derivative be continuous?

- The first derivative is the slope of the wave function.
- If the first derivative is continuous, the second derivative (slope of the first derivative) is finite. Thus the kinetic energy is finite. This must be true for the Schrodinger equation to hold (since U(x) and E_{total} are finite.

$$(KE + U(x))\Psi(x,t) = (E)\Psi(x,t)$$

Note: There is an exception. The first derivative can be discontinuous if we require the potential energy to be infinite at some point in space. infinite = so large as to completely oppose any motion of the particle

What is a bound state?

Cases where a particle's motion is restricted by a force. The motion is restricted to a finite region.

- States that are NOT free of forces. They are states that act under the influence of forces.
- These forces have only a spacial component. They can be described by adding a space-dependent potential, U(x), to the SWE.

Examples of bound states:

- Mass on a spring (Hook's law)
- Gas in a box
- ball rolling between two hills.

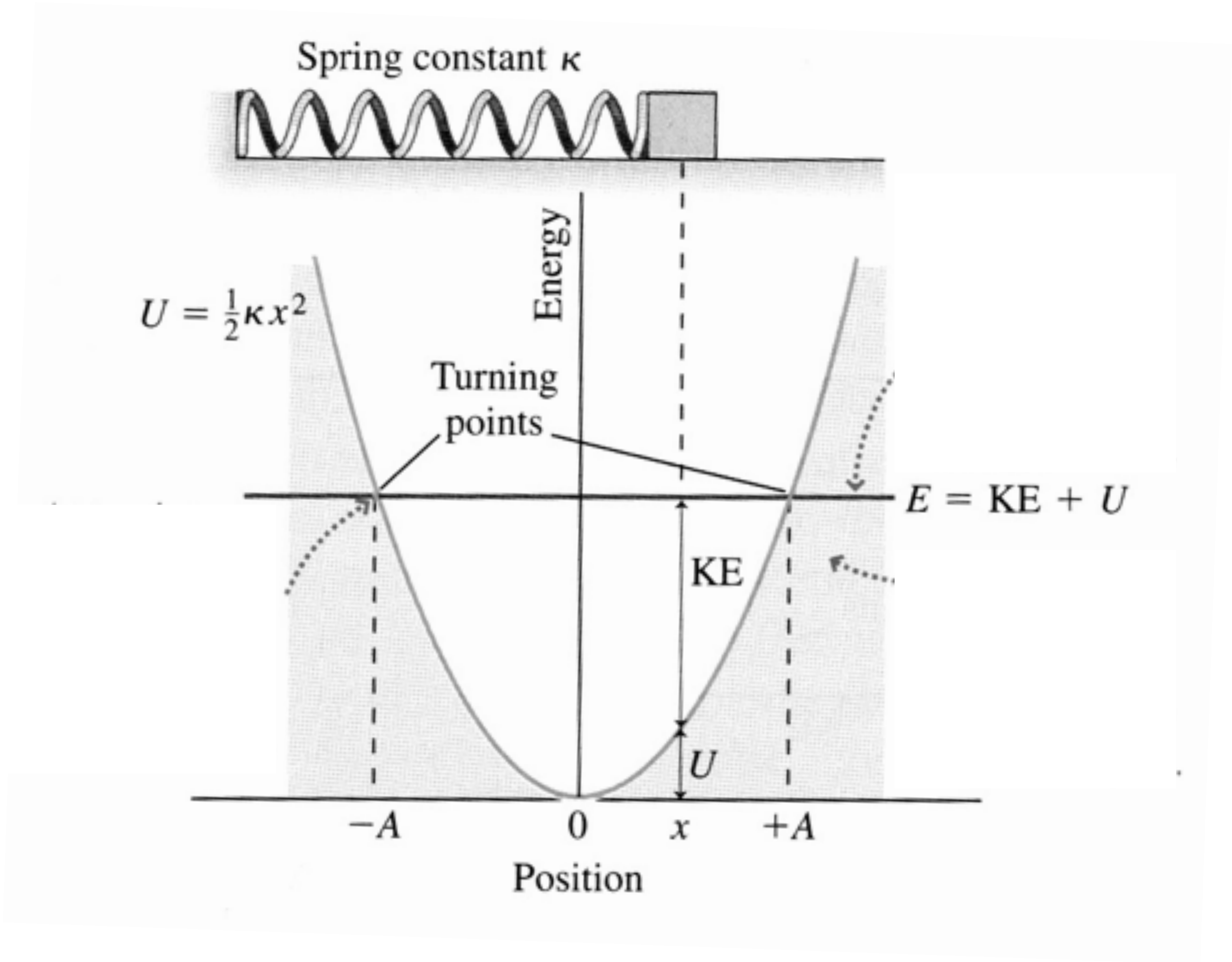
In order to understand the "hopelessly complicated" we will use seemingly over-simple problems involving objects bound under various conditions.

REVIEW: CLASSICAL BOUND STATES

In the presence of only conservative forces, the total mechanical energy is conserved.

$$E = KE + U$$

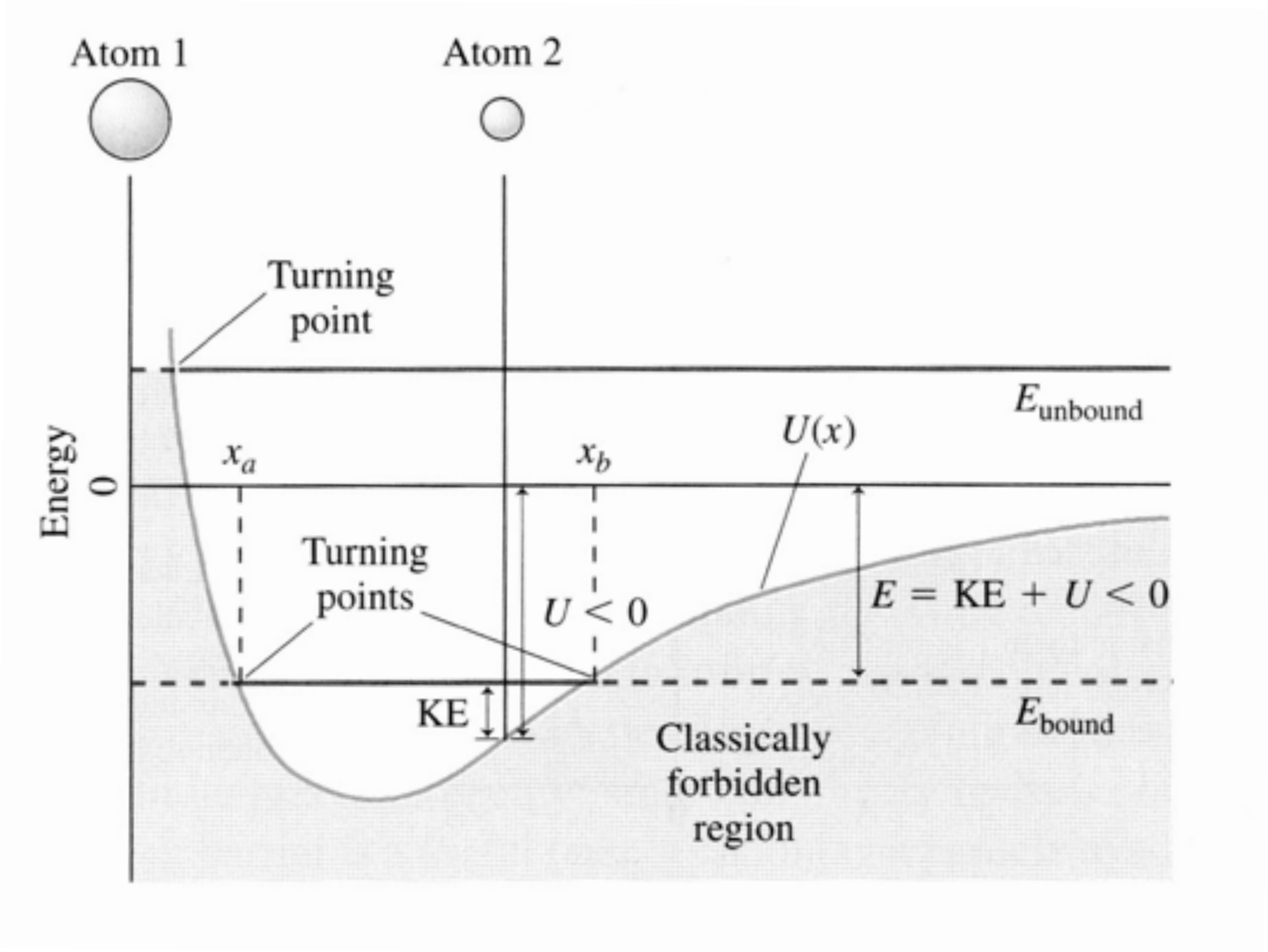
Bound State: Spring



1. The total mechanical energy is constant.
2. At the turning points, U is max, KE is zero.
3. At position zero, the U is zero, KE is maximum.
4. Area outside the potential area curve is the classically forbidden area.

Bound State: Two Atoms

Atom 1 is fixed and atom 2 moves in response to their shared electrostatic interaction.



1. U is positive and strong for small interatomic spacing.
2. U has a minimum value that is negative, then approaches 0 as x approaches infinity.
3. Atom 2 is repelled at small distances ($F = -dU/dx > 0$) and attracted ($-dU/dx < 0$) at large distances.

- If E_{tot} is negative, atom 2 is bound - oscillates between x_a & x_b.
- If E_{tot} is positive, atom 2 is unbound (only 1 turning point). It can move freely from atom 1.

How does this relate to Quantum Mechanically Bound States?

Recall our requirements:

- The player(s) are described as quantum waves of probability density.
- The waves must be continuous.
- The first derivatives of the waves (in space) will nearly always be continuous.

The quantum bound states of a particle under the influence of a potential will be STANDING WAVES. There are only discrete states allowed for particles in such bound states. (think wave on a string, bound at two ends)

Quirk: Wave functions can exist in the "classically forbidden" area. i.e. You can find the particle where, classically, it can not be.

THE END
(FOR TODAY)