

Modern Physics (PHY 3305) Lecture Notes

Bound States (Ch. 5.3-5.5)

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Review

tags:
lecture

- We discussed the meaning of the SWE and considered the simplest solutions to it: free particles (free meaning no external forces)
- We then discussed the implication for knowledge, specifically the Uncertainty Principle
- We started considering "bound states" - problems of particles under the influence of constraints/forces

Stationary States Revisited: Separation of Variables

Our first step is to separate the space and time parts of the wave into separate functions, multiplied times one another:

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

This is an assumption, but making it allows us to try to simplify the problem and test our solutions. It does reduce the generality of our solutions, but its advantage is a practical one: these special solutions are often of great interest (and utility!).

We can now re-write the SWE:

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

and then re-order the terms to achieve separation:

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

What does separating the variables mean? It means that we assume that x is not affected by t and t is not affected by x . That means that if time changes, the left-hand side of the SWE above DOES NOT. If that side of the equation is constant, then the right side MUST be constant. Thus:

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

C is the "separation constant". Can we constrain this constant?

Yes: Let us now consider each part of the equation separately.

Stationary States: the temporal part, $\phi(t)$

This is:

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

or

$$\frac{d\phi(t)}{dt} = -\frac{iC}{\hbar} \phi(t)$$

NOTA BENE: Eqn. 5-6 in Harris is MISSING the minus sign!

A solution to this equation is:

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

What does all this mean? Write the solution in terms of the Euler Equation:

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

We see that C/\hbar represents a pure frequency (e.g. $2\pi f$). That means $C = 2\pi\hbar f = \hbar\omega = E$.

This means that when we separate variables, we are in fact FOCUSING ON STATES WITH *WELL-DEFINED* ENERGIES. The separation constant IS that energy.

According to the separation of our original wave function, we can now write:

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

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

DISCUSSION: what is the probability density of this wave function?

Answer:

$$\Psi^*(x, t)\Psi(x, t) = \left(\psi^*(x)e^{i(E/\hbar)t}\right) \left(\psi(x)e^{-i(E/\hbar)t}\right) = \psi^*(x)\psi(x)$$

- Is there time dependence in the probability?
 - No - it disappears under the case we can separate space and time components of the wave function
 - The properties of such objects do not change in time - they are "stationary states"
- What are the implications for, say, electrons in an atom?
 - The electron is bound by the coulomb force to the atom. That potential is time independent. Classically, as it whizzes around the nucleus it should be losing energy. But quantum mechanics says that's not the case: it tells us that the electron can appear in many places around the atom ($\psi(x)$), but its energy is constant and well-defined. The electron is not orbiting, in the classical sense, but rather in a probability cloud around the nucleus. If the probability density is constant, the charge density is constant, and if the charge density is constant, EM tells us it radiates no energy.

Wild stuff, a beautiful description of exactly what is observed about atoms.

Stationary States: the spatial part, $\psi(x)$

We cannot say anything too specific about $\psi(x)$ without $U(x)$, so that is where we shall go next. Based on our work with the temporal part of the SWE, we can write a useful form for the SWE that contains only the spatial part.

If we now identify the constant $C = E$, the total energy of the matter wave, and we multiply both sides of the SWE by $\psi(x)$, we obtain the

TIME-INDEPENDENT SWE:

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

This equation will be the basis of our next discussion: bound states.

Bound States

These are states which are not free of forces, but act under their influence. These forces only have a spatial component, and can be described by adding a space-dependent POTENTIAL, $U(x)$, to the SWE as follows:

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

This equation resulted from hypothesizing that the spatial and temporal dependence of the wave function can be separated:

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

and when we did this we found that the SWE is equal to a constant. We learned that the probability of finding the particle depends only on space

and not time. In order to make progress on $\psi(x)$, we need to know the exact nature of the potential, $U(x)$. Before we do that, we have some more things to discuss regarding wave functions and the SWE.

Physical Conditions: *Well-Behaved* Functions

Physicality of elements of a problem are of prime concern in physics. By this, I mean how "realistic" or "natural" an assumption is. While such notions - "realism" and "naturalism" - are constantly put to the test by science, within what we know we usually have to impose these notions to make progress in solving a problem.

Two such physicality requirements that we will routinely impose on wave functions are *Normalization* and *Smoothness*

Normalization

This simply means that the total probability of finding the particle anywhere in space or time is 100%, or 1.0.

If the wave function describes a PROBABILITY DENSITY, or probability per unit length, then we should expect that multiplying it by a very tiny piece of length (dx) and summing over all such pieces, we get 100% probability of finding the particle:

$$\int \Psi(x, t) dx = 1$$

This is a naturalness requirement - we don't expect probabilities to exceed 100% in the natural world. That would be "getting something for nothing".

Smoothness

This is simply a requirement that the wave function and its first derivative are continuous. By this, I mean there are no places where the wave function itself has a discontinuity, or where the derivative of the wave function has a discontinuity (is infinite, for instance).

Why? Think about what discontinuities in curvature would mean - they would signal a wave with a place of infinite kinetic energy, which is not very realistic. The wave function can NEVER be discontinuous. Abrupt jumps act like short wavelengths (high frequencies), which mean huge

energies.

What about the first derivative. If the first derivative is discontinuous, it means that the second derivative is a sequence of opposing sign contributions from infinity - not very natural or descriptive. We cannot make sense of such a pathological function.

There is an exception to the latter requirement. The first derivative can be discontinuous if we require the potential energy to be infinite at some point in space. By infinite, we can mean "so large as to completely oppose any motion of the particle" - this can be useful when we need to introduce boundaries into problems, places where the particle is opposed in further motion. These are very common situations.

So in the case of walls (infinite potentials), we don't expect the wave function's first derivative to be continuous.

Classical Bound States

Before proceeding with a discussion of quantum bound states, let's review the components of classical bound states. They will provide a useful language from which to start and a use juxtaposition to some of the results of quantum bound states.

In the presence of only CONSERVATIVE FORCES, the total mechanical energy is:

$$E = KE + U$$

where KE is the kinetic and U the potential energy. This total is conserved. Plots of energy vs. position show this clearly (see slides).

DISCUSSION: Classical oscillatory motion under conservative forces, turning points in the motion, and classically forbidden regions of the energy plot.

Another example of a bound state is two atoms. (See slides)

DISCUSSION: Again, illustrate the existence of bound states in the plot, classically forbidden regions, and the "unbound" region where KE is great enough that the second atom can move freely from the first (only a single

turning point, in that case).

Quantum Mechanical Bound States - Qualitative

Let's take a qualitative peek at quantum bound states. We have requirements to impose:

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

As a result of all this, we should expect that 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 situations. We'll see this mathematically next.

The quirky part of this, in juxtaposition to the classical analog, is that the boundaries of the wave function are not necessarily where the potential energy equals the kinetic energy. Since the position and momentum of the particle are not both well-defined quantities, there is a chance that the particle can be found in what is the "classically forbidden" region. The wave nature of matter predicts that the boundaries of bound states are not simply described as they are for particles.

Case 1: Particle in a Box - the infinite well

The first case we will consider is the one in which the confining potential, $U(x)$, leads to the simplest solutions to the SWE when such potentials are included.

- The Particle in a Box or "Infinite Well": the particle is confined in x by a potential which represents infinitely steep, insurmountable "walls"

DISCUSSION: what do we expect a classical particle to do?

To frame this problem, let us consider an electron of charge $q = -e$ to be trapped between two "walls" of electrostatic potential energy. See slides for an image of this "experiment"

- Capacitors with little holes in them form the "walls" on either side. Inside the plates there is a strong electric field, and in this region the motion of the electron is opposed by a force $\vec{F} = -e\vec{E}$.
- Everywhere else, the electron is free of forces and will move at constant speed (and thus has constant kinetic energy).
- Everywhere but between the capacitors, the electrostatic potential is constant.

This is a practical example of how you can generate such a bound state. It's practical, but as we'll see later it's very hard to solve.

To make this problem more approachable for now, let's idealize it by imagining that

- the plates are infinitesimally close together, making the distance between them negligible compared to the dimension of the space between the capacitors
- we can crank the voltage on the plates so high as to essentially make the electric field insurmountable by a non-relativistic particle.

For our purposes, this is as good as making an "infinite well" - a potential of infinite magnitude. The wave function cannot extend beyond the walls of an infinitely steep potential. That means we arrive at our first constraint on the wave function:

- **The wave function in the infinite potential-well problem must be ZERO outside the "walls" - $\psi(x) = 0$ when $x \leq 0$ or $x \geq L$. In this region, we also have the constraint on the potential that $U(x) = \infty$.**

If this is the case, then our problem reduces to finding the solutions to the SWE *BETWEEN* the walls - that is, for $0 < x < L$. We then only need to insure that the overall wave function is continuous.

Between the walls, the *Time-Independent* SWE becomes:

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

because here $U(x) = 0$.

We can rearrange this:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

What is $2mE/\hbar$ equal to? Does this look familiar (ala Homework 004)?
Remembering that $E = p^2/2m$, the answer is k^2 :

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x)$$

We now have to solve this second-order differential equation. What kind of solution is the equation begging for?

- Whatever the form of the solution, taking the derivative twice must return $\psi(x)$, multiplied by no more than a constant (since all the space dependence on the right-hand side is contained in $\psi(x)$).
- A good candidate for this solution is a sine or cosine function. Either one will satisfy this equation

$$\psi(x) = A \sin(kx)$$

or

$$\psi(x) = A \cos(kx)$$

But which is it?

DISCUSSION: what physical conditions haven't we applied yet in solving this problem?

ANSWER: the requirement that the wave function vanish at $x = 0$ and $x = L$

forces us to pick sine, since that naturally is zero at $x = 0$.

$$\psi(x) = A \sin(kx)$$

But what about the other constraint - that the wave function vanish at $x = L$ as well?

To meet that constraint, we need to work on this function a little bit more. Let's write down the constraint and see what we can learn:

$$A \sin(kL) = 0$$

DISCUSSION: When will this be satisfied?

ANSWER: when $kL = \sqrt{2mE/\hbar^2}L = n\pi$, where n is an integer. Any integer will work.

This requirement then can be rewritten as a constraint on the ENERGY of the wave:

$$E = n^2 \pi^2 \hbar^2 / (2mL^2)$$

DISCUSSION: what does this equation tell us?

ANSWER: the matter wave's energy CANNOT BE ARBITRARY - it is discrete, and the only values allowed by the constraints on the matter wave are given above. They are simply multiples of a FUNDAMENTAL or *GROUND-STATE* energy, $n = 1$.

Our wave function now takes its final form:

$$\psi_n(x) = A \sin(n\pi x/L) \quad (0 < x < L)$$

These solutions are STANDING WAVES, just like those for sound in an organ pipe or on a guitar string.

To complete our solution, we must impose our final requirement: the wave

function must be normalized.

$$1 = \int_{-\infty}^{\infty} |\psi(x)|^2 dx = \int_0^L A^2 \sin^2(2\pi x/L) dx$$

The integral $\int_0^L \sin^2(2\pi x/L) dx = L/2$ independent of n , so that

$$A^2 L/2 = 1 \rightarrow A = \sqrt{2/L}$$

Thus we have NORMALIZED, CONTINUOUS WAVE FUNCTIONS representing the allowed states of a particle bound in an infinite well. We also have the corresponding ENERGIES for each state.

$$\psi_n(x) = \sqrt{2/L} \sin(n\pi x/L)$$

for $0 < x < L$ and

$$\psi_n(x) = 0$$

otherwise. The energy of each state is:

$$E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

What do we learn from these solutions:

1. The matter wave can only exist in a STANDING WAVE configuration in the box
2. The probability densities, $|\psi(x)|^2$, have nodes, so there are places where the particle is MORE LIKELY to be found - the particle is not equally likely to be anywhere in the well. But how is it that a particle has a chance of NEVER being found in certain places? That answer is unique

to quantum mechanics, and in fact is a prediction of the theory: particles are not classical particles - they are WAVES of probability, and there are places you'll never observe them to be. You cannot demand a quantum particle behave like a classical one. CONSIDER TWO CASES: where the well becomes very, very wide or where the quantum universe was more at the scale of everyday life)

3. We can't "watch" the particle in the box continuously, and thus establish its location - to do that means introducing photons, for instance, and when you do that you need to add new potentials to the problem, $U(x)$, which then changes the problem. The quantum world requires careful thought before thinking it's weird or strange - just remember what it means to "observe" something.
4. The wave function has a minimum energy, below which the only allowed energy is zero. This is the GROUND STATE, and it's nonzero. This means that a matter wave in a box like this is ALWAYS in motion - if it's in there, it's moving. It cannot stand still, because if that happens it doesn't exist and, thus, there is no particle in the box.
5. In the ground state, the particle is most likely to be found in the middle of the well.
6. For large n , you recover the "classical limit" where the particle is equally likely to be found everywhere - just like a classical bound state.

DISCUSSION: how do you determine the probability of finding the particle in a certain region inside the well?

ANSWER: integrate the probability density in the region of interest.

NEXT LECTURE

- A more realistic case: the finite well
- Another realistic and practical case: the simple harmonic oscillator
- We'll begin to discuss UNBOUND states