Section 3:  
Particle in a Box and Harmonic Oscillator  
Solutions

Here is a summary of the most important points from the recent lectures, relevant for either solving homework problems, or for your general education. This material is covered in the first part of Chapter 2 of [1].

Let us consider the Schrödinger equation for a point particle of mass $m$ where the potential energy $V$ is time-independent. Then, we solve the equation as follows. First, we find all normalizable solutions of the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi. \quad (1)$$

Denote the normalized solutions of this equation with $\psi_n(x)$, and the corresponding energies with $E_n$. Then the solution of the time-dependent Schrödinger equation as

$$\Psi(x,t) = \sum_n c_n \psi_n(x)e^{-iE_n t/\hbar}, \quad (2)$$

where

$$c_n \equiv \int_{-\infty}^{\infty} dx \, \psi_n^*(x)\Psi(x,0). \quad (3)$$

The states $\psi_n$ obey an orthogonality relation if $n \neq m$ (in one dimension, this also implies $E_n \neq E_m$):

$$\int_{-\infty}^{\infty} dx \, \psi_n^*(x)\psi_m(x) = \delta_{mn} \equiv \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}. \quad (4)$$

An example of this is the particle in a box, where

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & \text{otherwise} \end{cases}. \quad (5)$$

There is a discrete set of stationary states $\psi_n$ labeled by $n = 1, 2, 3, \ldots$:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}, \quad (6)$$

with energies

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2}. \quad (7)$$
It is often helpful to think of position as an operator $\hat{x}$, and momentum as an operator $\hat{p}$, with the properties that

$$\hat{x}\Psi(x,t) = x\Psi(x,t), \quad (8a)$$
$$\hat{p}\Psi(x,t) = -i\hbar\frac{\partial\Psi(x,t)}{\partial x}. \quad (8b)$$

We define the commutator of two operators to be$^1$

$$[A,B] = AB - BA. \quad (9)$$

An important example is

$$[\hat{x},\hat{p}] = i\hbar. \quad (10)$$

An important problem in quantum mechanics is the simple harmonic oscillator, with

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2. \quad (11)$$

It is useful because it is a good approximation to the “near ground state” behavior of many physical systems, such as the vibrations atoms in molecules or solids. Quantize this as follows: we define

$$a = \frac{m\omega\hat{x} + i\hat{p}}{\sqrt{2\hbar m\omega}}, \quad (12a)$$
$$a^\dagger = \frac{m\omega\hat{x} - i\hat{p}}{\sqrt{2\hbar m\omega}}. \quad (12b)$$

Note that

$$[a,a^\dagger] = 1. \quad (13)$$

Some formal manipulations with these operators lead us to conclude that there is a discrete set of stationary states $\psi_n$, $n = 0,1,2,\ldots$, with

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right). \quad (14)$$

And

$$a\psi_n = \sqrt{n}\psi_{n-1}, \quad (15a)$$
$$a^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}. \quad (15b)$$

Physically, we can interpret that the wave function $\psi_n$ has $n$ “quanta of energy”, each $\hbar\omega$. The operator $a^\dagger$ adds a quantum of energy, and $a$ takes one away. Remarkably, this simple interpretation becomes physical in the quantization of light, and other quantum fields!

Here are some problems to practice the physics on the problem set, and also to get you some practice with understanding the length and energy scales associated with experimental realizations of the two quantum systems we’ve now solved.

$^1$Unfortunately the way Griffiths has ordered topics makes a discussion of this seem rather obsolete. The emphasis here will make a lot more sense after Chapter 3.
**Problem 1:** Sometimes there can be subtleties in trying to take classical limits in quantum mechanics.

(a) Suppose we had a free classical particle of mass $m$ in a box of width $a$, at energy $E$. Describe the motion as a function of time. If we wait for a very long time, what is the limiting probability distribution for where we will find the particle?

**Solution:** A free classical particle of mass $m$ at energy $E$, in the infinite square well, has no potential energy, so the kinetic energy (which is then conserved) is

$$E = \frac{mv^2}{2}.$$ 

The particle will travel at constant speed back and forth between the two walls, bouncing forever. The speed at which it travels is given by $v = \sqrt{2E/m}$. So if we wait for a very long time, the probability density that it is found in any given spot in the well has to be constant; the time it spends in any given region of the well is linearly proportional to the size of that region. We conclude

$$\rho_{cl}(x) = \frac{1}{a}.$$ 

Note that this probability density is normalized, as

$$\int_0^a dx \rho_{cl}(x) = \frac{a}{a} = 1.$$ 

(b) Now suppose we have a quantum particle in a box. Choose $\Psi(x,0)$ to be a real-valued quantum wave function with the same probability density as in part (a). Be sure to normalize $\Psi(x,0)$. Compute $c_n(0)$, the overlap of $\Psi$ with the $n^{th}$ stationary state at $t = 0$. Conclude by stating $\Psi(x,t)$.

**Solution:** Remember that $|\Psi|^2$ is the probability density of finding the quantum particle at position $x$ if we make a measurement. And so if we take $\Psi$ to be real, that forces us to take

$$\Psi(x,0) = \frac{1}{\sqrt{a}},$$

in the region $0 < x < a$. Of course for all $t$, and $x$ outside of this range, $\Psi = 0$. $\Psi(x,0)$ is normalized since $\rho_{cl}$ was normalized. And now we compute

$$c_n(0) = \int_0^a dx \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \times \frac{1}{\sqrt{a}} = \sqrt{\frac{2}{a}} \cdot \frac{a}{n\pi} \left[ - \cos \frac{n\pi x}{a} \right]_0^a = \sqrt{\frac{2}{n\pi}} (1 - (-1)^n) = \sqrt{\frac{8}{n\pi}} \times \left\{ \begin{array}{ll} 1 & n \text{ odd} \\
0 & n \text{ even} \end{array} \right\}.$$ 

One can check (if you remember some tricks about sums of integers from high school math competitions, or wherever...) that

$$1 = \sum_{n=1}^{\infty} |c_n|^2 = \frac{8}{\pi^2} \sum_{n=1,3,5,...} \frac{1}{n^2}.$$ 

In any case, we know that the solution to the Schrödinger equation is therefore

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n(0)e^{-i\frac{n\pi x^2}{2ma^2}} \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}.$$ 

3
(c) What is $\langle H \rangle$ – the expected energy we observe on measurement. Explain the result you find.

Solution: We find

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n(0)|^2 E_n = \sum_{n=1,3,5,...}^{\infty} \frac{8 \hbar^2 n^2 \pi^2}{\pi^2 n^2 2ma^2} = \sum_{n=1,3,5,...}^{\infty} \frac{4\hbar^2}{ma^2} = \infty.$$ 

So this state has infinite energy – unlike the classical state we constructed above! Why is that? Well, the wave function jumps from being $\Psi = 1/\sqrt{a}$ at $x = 0^+$ to $\Psi = 0$ at $x = 0^-$. When we evaluate $\langle H \rangle$, we're evaluating

$$\int_{-\infty}^{\infty} dx \Psi^* \left( -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \right) + \cdots = \int_{-\infty}^{\infty} dx \frac{\hbar^2}{2m} \frac{\partial \Psi}{\partial x} \frac{\partial \Psi^*}{\partial x} + \cdots,$$

and that rapid jump in $\Psi(x,0)$ turns out to have “infinite derivative squared”, which gives you $\infty$. This will make a bit more sense later, when we discuss $\delta$ functions.

(d) Consider a particle in stationary state $\psi_n$. Sketch the probability distribution of where it is most likely to be found if $n = 1$. What about $n \gg 1$? Compare to the classical case. Does the probability distribution limit to the classical one as $n \to \infty$? There are various mathematics answers here – what about physically?

Solution: The probability of being found at point $x$ in the well is given by

$$\rho_n(x) = |\psi_n(x)|^2 = \frac{2}{a} \sin^2 \frac{n\pi x}{a}.$$ 

This is not so difficult to sketch, but I’ll just show you the actual plot of these functions:

Let’s compare to what we found classically. When $n = 1$, the probability distribution is (substantially) peaked in the center of the well. We’d easily measure that this is quite different from $\rho_{cl}$ in the lab. However, if we have $n$ very large, and our measuring device can only see in “blocks” of size $\gg a/n$, then we won’t be able to resolve the fine structure in $\rho_n$ – to us, the distribution will basically look uniform! Mathematically, $\rho_n$ does not converge pointwise to the uniform distribution since it is a rapidly varying function. However, in a distributional sense $\rho_n$ does converge to $\rho$.

Problem 2 (Quantum Dots): One of the practical uses of the particle in the box in the laboratory is to serve as a mobile, robust and precise emitter of light. A very important use for this technology is as follows: a nanoscale semiconductor arrangement called a quantum dot, consisting of various layers of
semiconducting materials, is attached to a molecule with a “flag” on the end. This flag will consist of a molecular group that is heavily attracted to certain receptors on proteins – for example, a toxin or other unwanted substance. By releasing these quantum dot flags into a cell, we can track down and image (in real time) where all the bad proteins are, by observing the photons emitted from the quantum dots \[2\]. A cartoon of this setup is below.

We can model this system as a particle in the box (with some complications) of length \(a \approx 5\) nm. When a photon of the right frequency hits this dot, it excites an electron out of the filled energy levels of the metal – this costs an energy \(\Delta \approx 2.5 \times 10^{-19}\) J. This electron becomes confined in the inner part of the semiconductor, and behaves as though it is a particle in a box. Unfortunately, the hole left behind (the absence of an electron in the filled band of the metal) behaves as a positively charged particle, and so we’ll approximately have to double the required energy of the photon necessary to excite our electron, to account for the quantum behavior of this hole as well.

(a) How much energy does the photon need to kick both the electron and the hole into the ground state of the box? Does \(\Delta\) or the ground state energy of the particle in the box dominate this energy requirement?

Solution: Let’s compute the energy it takes to kick the electron into the ground state of the infinite square well:

\[
E_{el} = \Delta + E_1 = \Delta + \frac{\hbar^2 \pi^2}{2ma^2}.
\]

We have to excite a hole too. So we find

\[
E_{tot} = 2E_{el} = 2\Delta + \frac{\hbar^2 \pi^2}{ma^2} = \left[ 5 \times 10^{-19} + \frac{10^{-68} \pi^2}{10^{-30} \times 25 \times 10^{-18}} \right] J \approx \left[ 5 \times 10^{-19} + 4 \times 10^{-21} \right] J.
\]

The \(\Delta\) contribution dominates, so \(E_{tot} \approx 5 \times 10^{-19}\) J.

(b) Suppose that we re-emitted a photon at about the same wavelength at which we absorbed a photon. What would the wavelength \(\lambda\) of these photons be? In the lab, you would easily be able to detect light being strongly emitted by the dot at wavelengths of about \(\lambda\).

Solution: We know that \(h\nu\) is the energy carried by the photon that gets absorbed. Using that \(\lambda \nu = c\), we find

\[
\lambda = \frac{hc}{E} = \frac{6 \times 10^{-34} \times 3 \times 10^8}{5 \times 10^{-19}} \approx 3 \times 10^{-7}\ m.
\]

This is in the visible range of light, but it is also easily detected by a machine.

(c) How should we change the width of the quantum dot \(a\) if we want to make the emitted photon redder? Bluer?

Solution: Recall that red photons have lower energy, and blue photons have higher energy. Now, from part (a), we know that the contribution to \(E_{tot}\) from the ground state of the particle in the box increases as \(a\) shrinks. We conclude that bluer photons come from decreasing \(a\), and redder photons come from increasing \(a\).
**Problem 3 (Carbon Dioxide):** One of the concerns with greenhouse gas emissions – primarily CO\(_2\), carbon dioxide – is that they can lead to global warming via the greenhouse effect. A physical cartoon of this is as follows. Imagine that you have a CO\(_2\) molecule in the atmosphere, and a photon comes up from the Earth’s surface, carrying away energy. If the molecule can absorb this photon, it will re-emit it towards space half the time, but half the time emit it back down to Earth, where it gets reabsorbed. This process repeats many times until the photon escapes, but more energy is trapped on Earth while this process occurs, and this leads to a rise in temperature. In this problem we will ask whether this process is likely to occur frequently, based on microscopic estimates.

(a) The energy scale associated with a chemical bond is about \(10^{-18}\) J, and the length of a chemical bond is about \(10^{-10}\) m. Estimate from dimensional analysis what the spring constant \(k\) should be for a typical chemical bond.

**Solution:** By dimensional analysis:

\[
[k] = \frac{[\text{force}]}{[\text{length}]} = \frac{[\text{energy}]}{[\text{length}]^2},
\]

so we estimate

\[
k \sim \frac{10^{-18} \text{ J}}{(10^{-10} \text{ m})^2} \sim 10^2 \frac{\text{N}}{\text{m}}.
\]

(b) Using your estimate of \(k\) from above, and the mass of hydrogen at \(m \approx 2 \times 10^{-27}\) kg, estimate the angular frequencies of photons which the harmonic oscillator(s) associated with vibrations of the CO\(_2\) molecule will effectively absorb (and emit).

**Solution:** The mass scale associated with the carbon and oxygen atoms is going to be about 20 times larger than the hydrogen mass: \(M \sim 4 \times 10^{-26}\) kg. We estimate

\[
\omega \sim \sqrt{\frac{k}{M}} \sim 5 \times 10^{13} \text{ s}^{-1}.
\]

Now, the energy difference between energy levels of the harmonic oscillator is

\[
\Delta E_{nm} = \left( n + \frac{1}{2} \right) \hbar \omega - \left( m + \frac{1}{2} \right) \hbar \omega = (n - m) \hbar \omega.
\]

So photons will get absorbed by the harmonic oscillator with angular frequencies given in positive integer multiples of \(\omega\); and \(\omega\) is a reasonable estimate for the scale of photons that are optimally absorbed by CO\(_2\).

(c) Estimate the angular frequency of the “typical” photon emitted from Earth’s surface, and compare to the result in part (b).

**Solution:** Approximating the Earth as a blackbody, we estimate that the typical photon emitted has angular frequency

\[
\omega \sim \frac{k_B T}{\hbar} \sim \frac{4 \times 10^{-21}}{10^{-34}} \text{ s}^{-1} = 4 \times 10^{13} \text{ s}^{-1},
\]

which is very close to the scale of frequencies of photons that CO\(_2\) absorbs well.

The absorption spectrum of real gases is far more complicated [3], of course – some molecules absorb lots of photons, and others don’t. But this gives you a sense that the numbers make the greenhouse effect possible.
Problem 4 (Bogoliubov Quasiparticles): Let $a$ and $a\dagger$ be the annihilation and creation operators for a harmonic oscillator in one dimension, and let $\psi_n$ denote the stationary states associated with the $n^{th}$ energy state of the harmonic oscillator. Consider the Hamiltonian

$$H = \epsilon a\dagger a + \eta \left( aa + a\dagger a\dagger \right).$$

$\epsilon$ and $\eta$ are real parameters. More complicated Hamiltonians – but with the essential feature of $\eta$-like terms – arise in the Hamiltonians describing superfluids and superconductors.

(a) Show that $\psi_n$ is not a stationary state of $H$ for any $n$.

Solution: We act on $\psi_n$ with $H$. If $\psi_n$ is a stationary state, then we will get an answer proportional to $\psi_n$ alone:

$$H\psi_n = \epsilon a\dagger \sqrt{n}\psi_{n-1} + \eta a\dagger \sqrt{n+1}\psi_{n+1} = \epsilon n\psi_n + \eta \sqrt{n(n-1)}\psi_{n-2} + \eta \sqrt{(n+1)(n+2)}\psi_{n+2}. $$

(In the above equation, if $n < 2$, then the terms with $\psi_{-1,-2}$ vanish because of the factor of 0 sitting in front, and should be ignored.) Since $H\psi_n$ always has a term proportional to $\psi_{n+2}$, we conclude that no $\psi_n$ is a stationary state of $H$.

(b) Consider the Bogoliubov creation and annihilation operators given by

$$b = a \cosh \theta + a\dagger \sinh \theta, \quad b\dagger = a\dagger \cosh \theta + a \sinh \theta.$$ 

Show that $[b, b] = [b\dagger, b\dagger] = 0$, and that $[b, b\dagger] = 1$.

Solution: Note that $[A + B, C] = (A + B)C - C(A + B) = AC - CA + BC - CB = [A, C] + [B, C]$. We find

$$[b, b\dagger] = [a \cosh \theta + a\dagger \sinh \theta, a\dagger \cosh \theta + a \sinh \theta] = [a, a\dagger] \cosh^2 \theta + [a\dagger, a] \sinh^2 \theta = \cosh^2 \theta - \sinh^2 \theta = 1.$$ 

Since $bb - bb\dagger = 0$ for any operator $b$, $[b, b] = [b\dagger, b\dagger] = 0$ is trivial.

(c) Find the value of $\theta$ such that

$$H = \zeta b\dagger b + E_0,$$

for constants $\zeta$ and $E_0$; also determine $\zeta$ and $E_0$. Conclude by determining the energy spectrum of the Hamiltonian.

Solution: This is just a bit of algebra. First, we need to express $a$ and $a\dagger$ in terms of $b$ and $b\dagger$. First we note that

$$b \cosh \theta - b\dagger \sinh \theta = a(\cosh^2 \theta - \sinh^2 \theta) + a\dagger \sinh \theta \cosh \theta (1 - 1) = a,$$

and similarly $b\dagger \cosh \theta - b \sinh \theta = a\dagger$. So now we find that, after expanding all of this out:

$$H = \left(b\dagger b + bb\dagger\right) \left(\eta \cosh^2 \theta + \eta \sinh^2 \theta - \epsilon \cosh \theta \sinh \theta\right)$$

$$+ \left(b\dagger b - \eta \sinh \theta \cosh \theta\right) + \left(\eta \cosh^2 \theta - 2\eta \sinh \theta \cosh \theta\right) + \left(\epsilon \cosh^2 \theta - 2\eta \cosh \theta \sinh \theta\right)$$

Now, we choose $\theta$ so that the term in the first line cancels out. We find using hyperbolic trig identities that

$$0 = \eta \cosh(2\theta) - \epsilon \frac{\sinh(2\theta)}{2},$$

7
or
\[\tanh(2\theta) = \frac{2\eta}{\epsilon}.\]

Now we study the terms on the second line, using \(b b^\dagger = b^\dagger b + 1:\)
\[H = b^\dagger b (\epsilon \cosh(2\theta) - 2\eta \sinh(2\theta)) + \epsilon \sinh^2 \theta - \eta \sinh(2\theta).\]

We conclude using more hyperbolic trig identities:
\[\tanh(2\theta) = \frac{\sinh(2\theta)}{\sqrt{1 + \sinh^2(2\theta)}} \implies \sinh(2\theta) = \frac{2\eta}{\sqrt{\epsilon^2 - 4\eta^2}}.\]
\[\zeta = \sqrt{\epsilon^2 - 4\eta^2},\]
\[E_0 = \frac{\epsilon}{2} \left( \frac{\epsilon}{\sqrt{\epsilon^2 - 4\eta^2}} - 1 \right) - \frac{2\eta^2}{\sqrt{\epsilon^2 - 4\eta^2}} = \frac{\sqrt{\epsilon^2 - 4\eta^2} - \epsilon}{2}\]

But of course, \(H\) written in terms of \(b\) has similar eigenvalues to the simple harmonic oscillator:
\[E_n = E_0 + n\zeta, \quad n = 0, 1, 2, \ldots\]

(d) Discuss the nature of the stationary states of \(H\) – though you do not need to give exact expressions for all of them, at least show clearly how to compute them. In particular, comment physically on what has happened by writing the ground state in terms of the wave functions \(\psi_n\) – the stationary states of the original oscillator when \(\eta = 0\).

Solution: The ground state is the state \(\phi_0\) that is killed by the \(b\) operator. We construct excited states \(\phi_n\) as
\[\phi_n \equiv \frac{1}{\sqrt{n!}} b^n \phi_0.\]

Let
\[\phi_0 = \sum c_n \psi_n.\]

Then
\[0 = b\phi_0 = \sum_n c_n \left( \sqrt{n} \cosh \theta \psi_{n-1} - \sqrt{n+1} \sinh \theta \psi_{n+1} \right) = \sum \psi_n \left( \sqrt{n+1} c_{n+1} \cosh \theta - \sqrt{n} c_{n-1} \sinh \theta \right),\]
so we conclude that
\[c_{n+2} = c_n \sqrt{\frac{n+1}{n+2}} \tanh \theta.\]

The coefficients of all even \(n\) are related to \(c_0\); the coefficients of all odd \(n\) are related to \(c_1\). But if \(c_1 \neq 0\), then in the sum above, we get an equation we cannot satisfy: the coefficient of \(\psi_0\) in \(b\phi_0\) vanishes only if \(c_1 = 0\). So we conclude that the ground state consists of all even occupancy states, with relative weights given above. Most importantly, the operator \(a^\dagger a\) – which counts the number of quanta of “original” particles, has a non-vanishing expectation value in the true ground state.

This is the idea of the superfluid state (or, with some complications, the superconductor). The true ground state consists of a condensation of many of the microscopic particles (the electrons, etc.). There is an effective description of the superfluid in terms of the \(b\) operators, or so called “quasiparticles”. When you think about the quasiparticles as the fundamental degrees of freedom of the system, then it behaves just like ordinary particles.
