

UNIT 9: QUANTUM HARMONIC OSCILLATOR

After this unit, you should be able to

- Compute what frequency of light can be emitted and absorbed, given a set of allowed energies for a quantum system.
- Use the allowed energies for a system to explain whether it is more likely that the system is described by a harmonic oscillator or infinite square well potential.
- Determine the potential that led to a given measured spectrum.

A more realistic potential

While there are some artificially created systems that we can model as something close to an infinite square well, most potential energy functions (force laws) are somewhat different. In this chapter, we will consider the quantum equivalent of a mass on a spring, which you studied in introductory classical mechanics.

One aspect of quantum mechanics is that it is much *harder* to solve for the dynamics of a system than in classical mechanics. For all but some very simple systems, the solution is done numerically using a computer, or we simply learn about quantum systems by observing them experimentally. While this is highly technical, there are some useful things that we can learn about quantum systems by understanding the output of the experiments or numerical calculations. For the remainder of the course, we will just provide you with the energy eigenstates for a given potential, and discuss what they mean.

Photon emission/absorption

A hydrogen atom has the following energy levels: -13.6 eV, -3.4 eV, and -1.5 eV. Suppose that it starts in the ground (lowest energy) state. It can absorb light with photon energy either $(-3.4 - (-13.6)) = 10.2$ eV, or $(-1.5 - (-13.6)) = 12.1$ eV. We can solve for the frequency of that light by using $hf = E$, and therefore $f = E/h$. Here it is useful to use h in terms of electron volts (eV) to get:

$$f_1 = \frac{10.2 \text{ eV}}{4.135667 \times 10^{-15} \text{ eV} \cdot \text{s}} = 2.466 \times 10^{15} \text{ s}^{-1} \quad (1)$$

and similarly for f_2 . Those are the frequencies of light that can be absorbed by a hydrogen atom in the ground state.¹ If the hydrogen atom absorbs light of frequency f_1 , then it is now in the state with energy -3.4 eV.

On the other hand, suppose that the hydrogen atom is in the first excited state (the one at -3.4 eV). It may be in that state because it absorbed light as in the previous paragraph, or we can induce an excitation using an electric field or temperature. In this case, it can absorb light of energy (-1.5

¹In reality, this is broadened a little bit by temperature effects.

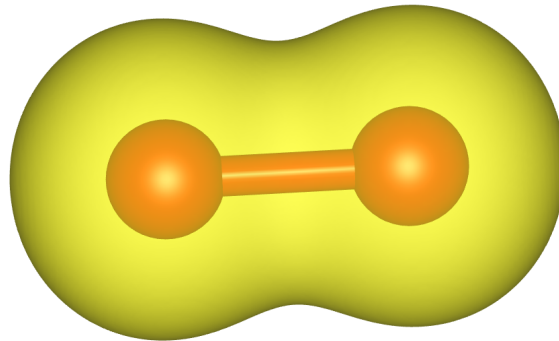


Figure 1: An O_2 molecule, which is present in the air. The electrons (in yellow, this is an averaged view of the electronic wave function) bind the nuclei (in red) together. The nuclei act as if they are connected by a spring, which gives rise to evenly spaced quantized energy levels that can be observed as absorption of infrared light.

- (-3.4) = 1.9 eV to go to the level at -1.5 eV, or it can emit light of energy 10.2 eV to go back to the ground state. This is the origin of the emission lines of atoms.

Harmonic oscillator: verifying the ground state

In the previous section, we considered only a very simple and idealized potential, $U(x)$. This choice was to make the math relatively tractable. In reality, $U(x)$ can be more complicated and can require advanced techniques to find the energy eigenstates from the Schrödinger equation. Solving the Schrödinger equation for the general case of many particles is an area of active research in physics, so in this course we will not cover explicit solution of the equation. However, it is much easier to *check* whether a given wave function is an energy eigenstate for a given $U(x)$.

Let's go through this for a harmonic oscillator potential. The Schrödinger equation is given by:

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

In contrast to the infinite square well, there are no boundary conditions on this; the wave function can be non-zero everywhere in space.

Let's try a guess wave function: $\Psi(x) = A \sin(bx)$, where we use b because k is already taken

for the spring constant. Then plugging that into the equation, we get

$$\frac{\hbar^2 b^2}{2m} A \sin(bx) + \frac{1}{2} k x^2 A \sin(bx) = E A \sin(bx) \quad (3)$$

$$\frac{\hbar^2 b^2}{2m} + \frac{1}{2} k x^2 = E \quad (4)$$

$$(5)$$

This is **NOT** an energy eigenstate, since there is no way to set A , k , and E such that this equation is satisfied at all values of x .

Let's try a better guess²: $\Psi(x) = Ae^{-\alpha x^2}$. We take the derivative on the left-hand side and find:

$$-\frac{\hbar^2}{2m} A(4\alpha^2 x^2 - 2\alpha)e^{-\alpha x^2} + \frac{1}{2} k x^2 A e^{-\alpha x^2} = E A e^{-\alpha x^2} \quad (6)$$

$$x^2 \left(\frac{1}{2} k - \frac{4\hbar^2 \alpha^2}{2m} \right) + \left(\frac{\hbar^2 \alpha}{m} - E \right) = 0 \quad (7)$$

The parts in the parentheses must each equal zero for this equation to be true for all values of x . This means that

$$\alpha = \frac{1}{2\hbar} \sqrt{mk} \quad (8)$$

$$E = \frac{\hbar^2 \alpha}{m} = \frac{\hbar}{2m} \sqrt{mk}. \quad (9)$$

To simplify the equation for energy, often this is written in terms of ω , where $k = m\omega^2$, so that $E = \frac{\hbar}{2}\omega$. Note that when we solved for α , we could have chosen the negative value. That would not have worked because e^{x^2} diverges as x goes to infinity, so α must be positive for the wave function to be normalizable.

Harmonic oscillator: spectrum

It turns out that just like the infinite square well, there are an infinite number of discrete solutions to the Schrödinger equation for the harmonic oscillator. The functions are a bit complicated and don't offer a lot of physical intuition, so we will not list them here. However the spectrum is very simple: $E_n = (n + \frac{1}{2}) \hbar\omega$, where $n = 0, 1, 2, \dots$. Note here that n can be zero, unlike the infinite square well.

Contrast the harmonic oscillator result with the result for the infinite square well: $E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$, with $n = 1, 2, \dots$. The harmonic oscillator has evenly spaced energies, called energy levels, while the infinite square well has energies that get farther apart as n increases. The difference between these two is the potential energy term, $U(x)$. This means that by looking at the spectrum; that is, what light is emitted and absorbed by the object, we can tell something about the potential energy in the quantum system! If for example we see evenly spaced levels, then it may be that the potential energy looks like a harmonic oscillator. By measuring the spacing between the levels we can tell what the value of k is for that oscillator.

²The guess and check method is a long-standing and useful tool in physics!

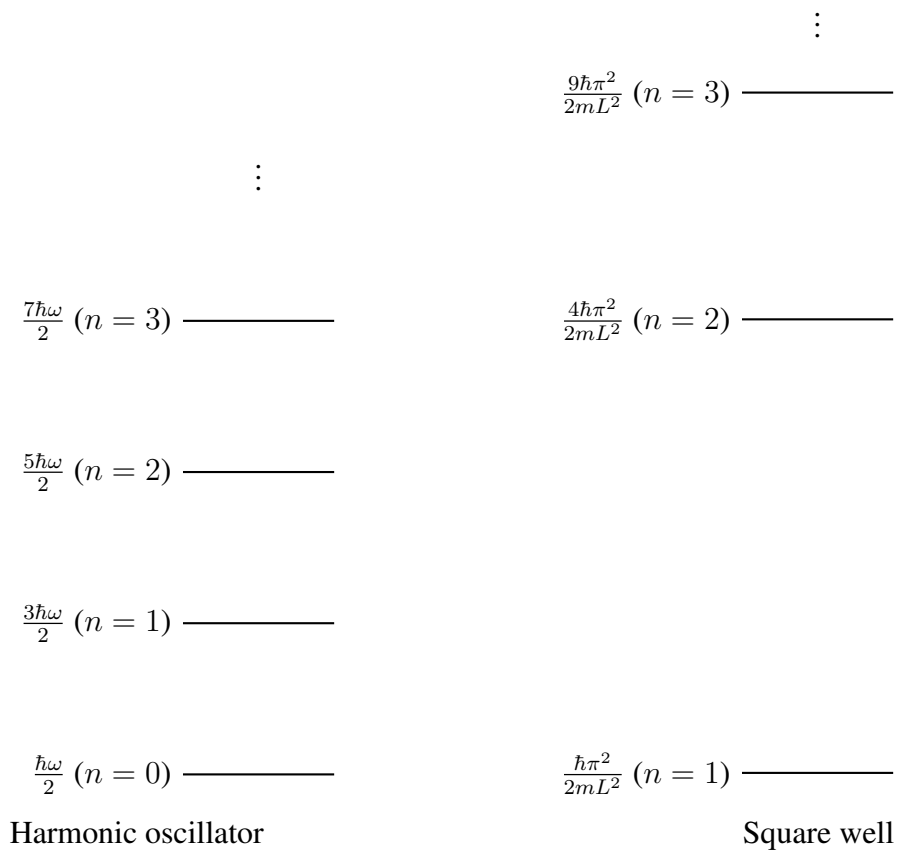


Figure 2: Energy level diagrams for the harmonic oscillator and infinite square well. The energy levels are spaced differently. Light can only be absorbed and emitted in units equal to the difference between the energy levels.

Energy level diagrams

For the rest of the class, we will be using energy level diagrams to understand the "allowed" energies for a quantum system. In Fig 2, we show diagrams for two different potentials: a harmonic oscillator and square well. The *differences* between the energy levels tell us what frequencies of light can be absorbed by the system.

Using energy levels to determine the potential

A common way of understanding the vibrations in molecules is to send infrared light through a gas, and measure what frequencies are absorbed by the vibrations of atoms. These vibrations are often well-described as harmonic oscillators. Each type of vibration has its own effective mass and spring constant.

As an example, when infrared light is passed through the atmosphere, which is filled with water, some frequencies are absorbed by the water. By reading off the frequency of light, we can

Spectrum of Solar Radiation (Earth)

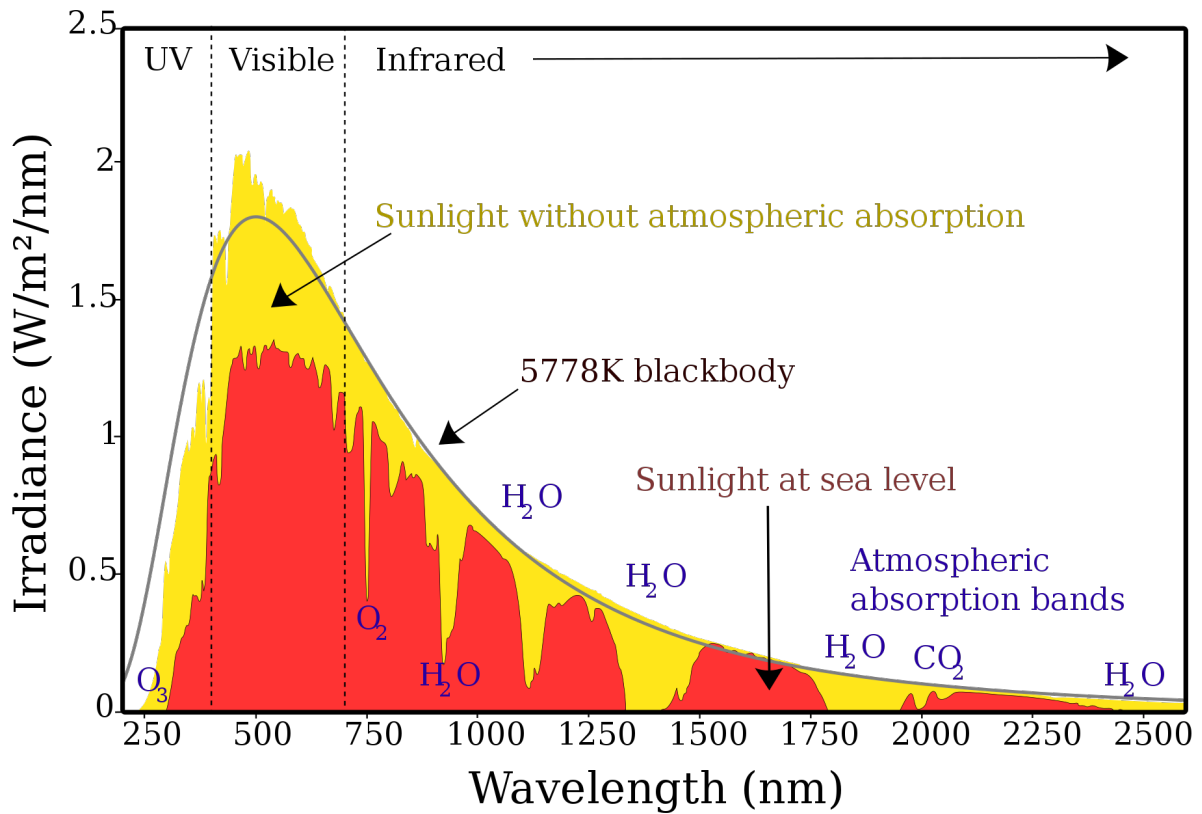


Figure 3: Solar irradiation at the Earth's surface, filtered by frequency. Image credit. By Nick84 - File:Solar_spectrum_ita.svg, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=24648395>

tell ω by using

$$E_{\text{photon}} = hf \quad (10)$$

$$E_{\text{photon}} = \frac{3}{2}\hbar\omega - \frac{1}{2}\hbar\omega = \hbar\omega, \quad (11)$$

since the photon will only be absorbed if it matches the difference in energy levels of the vibrational system. This shows up as dips in the amount of light from the sun that we observe on earth (Fig 3). Each dip is due to a harmonic oscillator of the characteristic frequency.