

Brief Notes on Quantum Mechanics in Physical Biochemistry

Matthew Holland
matthew.holland@cmd.ox.ac.uk

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1 Introduction

The concept of wave-particle duality is a fundamental one in quantum mechanics, which states that particulate matter (for example electrons or photons) can behave as both waves and particles. This has been demonstrated experimentally by firing a beam of electrons through a very fine double slit (analogous to Thomas Young's experiment with light in 1801). They are shown to create a diffraction pattern on a screen behind the slits (as light would), thus suggesting that electrons are waves. However, placing a detector by one of the slits results in the pattern on the screen changing, and instead of a diffraction pattern you see two 'piles' of electrons, as if they were now behaving as particles. This has revealed two items of weirdness:

1. Electrons can behave as both waves and particles.^a
2. This behaviour changes when they are observed directly.

This is strange, and the more one tries to consider it the weirder it becomes, but it has been shown to match reality by many experiments to a great degree of precision, so it is currently the best theory we have. A very thorough understanding of why and how this quantum strangeness occurs is outside of the scope of this course (indeed senior physicists spend their careers arguing about it), but some of the consequences of this theory are very important for understanding the chemical processes that govern life, so it is worth taking time to appreciate (albeit at a relatively superficial level) these results.

2 Particle in a Box

Another key result from quantum mechanics is that the energy levels available to particles are quantized; in other words their energies are restricted to certain values. Again this has been very well shown experimentally, but it seems strange in our macroscopic world. To understand how this quantization comes about, consider taking a particle (for example an electron) and trapping it in a very small box of length L with solid walls, so that it cannot escape. We know from the wave-particle duality illustrated above that this electron behaves as both a particle and a wave, so it is convenient (and valid) to consider it as a wave when thinking about the energy it is allowed to have. It is a postulate^b of quantum mechanics that the square of the wavefunction at a certain position is related to the probability of finding a particle at that position. We have said that the particle can exist inside the box, but cannot ever leave this box, thus the probability of finding it outside the box is 0. We have said that the square of the wavefunction at a point is related to the probability of finding the particle at that point, thus as the particle cannot exist outside of the box, the value of the wavefunction at all points outside of the box and at each wall of the box^c must be 0. This is illustrated in Figure 1a.

These are called *boundary conditions*, and are the key to the quantization of the energy levels.

^aThe analogy extends to other particles - indeed this experiment has been repeated with buckyballs!

^bPostulates are fundamental to quantum mechanics, and are assumptions or principles that are accepted without formal proof (the 'proof' is that the theories we derive having assumed them can be experimentally shown to be true to a high degree of accuracy - *the proof is in the pudding*)

^cIt turns out that waves in quantum mechanics must be *continuous*; this means that they can never suddenly drop to a different value, but must gradually approach that value smoothly. This means that the value of the wavefunction at the very edge of the box must be 0 too, otherwise a situation would arise where the wavefunction had a non-zero value at the very edge of the box, and then must immediately drop to 0, which would give a vertical line with an infinite gradient, which is not allowed!

Value of Wavefunction at $x = 0$ is 0
Value of Wavefunction at $x = L$ is 0

These boundary conditions mean that not all waves are allowed to exist in the box; a wave that was not 0^d at the edge of the box would imply that the particle could exist outside of the box, which we have already said is not possible.

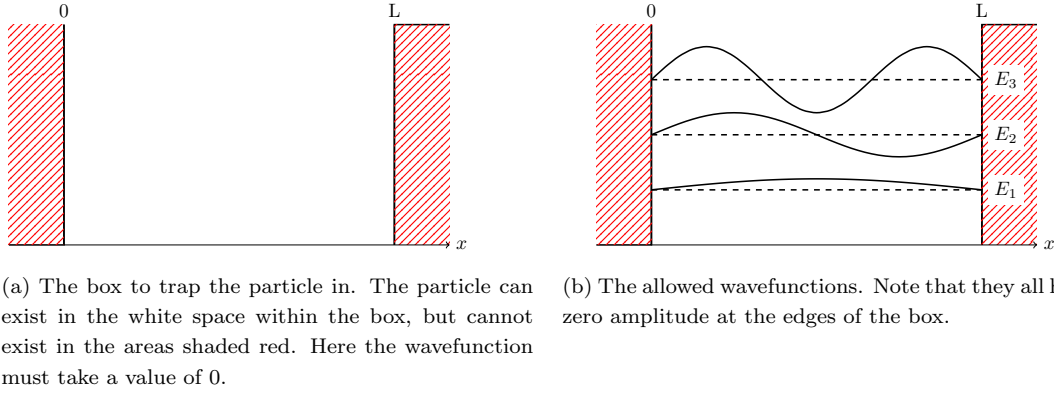


Figure 1. The Particle in a box.

To determine the energies of the allowed waves, first consider the allowed wavelengths. In order for the boundary conditions to be satisfied (the amplitude of the wave must be 0 at $x = 0$ and $x = L$), the wave must have completed either half an oscillation (see Figure 2, where it is clear that after half a wavelength the amplitude of the wavefunction is 0; this situation is demonstrated for the particle in a box in Figure 1b E_1 where half of a complete oscillation spans the length of the box, thus in this situation $\frac{\lambda}{2} = L$) or a full oscillation (The situation illustrated in Figure 1b E_2 , where one complete oscillation of the wave spans the length of the box, thus $\lambda = L$). Figure 2 shows that the amplitude of the wave is also 0 at $\frac{3\lambda}{2}$, 2λ , and generally at $\frac{n\lambda}{2}$, so if these multiples of the wavelength are equal to the length of the box, these are also valid wavefunctions for the particle in a box. Mathematically this is stated as $\frac{n\lambda}{2} = L$, or more helpfully

$$\lambda = \frac{2L}{n} \quad (1)$$

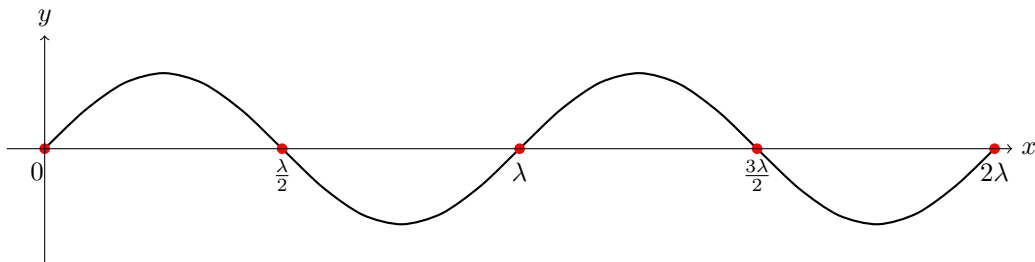


Figure 2. The wavelength of a sinusoidal wave. One wavelength (λ) is a complete oscillation of the wave (the amplitude and direction of the wave at $x = \lambda$ is the same as at $x = 0$). All the points on the wave where the amplitude is 0 are marked by red dots.

These are the allowed wavelengths for the particle in a box that meet the boundary conditions of the wave having 0 amplitude at each end. To calculate the energies of these allowed wavelengths, first consider the de Broglie relation $\lambda = \frac{h}{p}$, which helpfully relates the wavelength of a wave to its momentum. Knowing that the kinetic energy of a particle is given by $\frac{1}{2}mv^2$, putting this in terms of momentum ($p = mv$) then allows the substitution of the de Broglie relation, which we can use to find the energies of the allowed wavelengths.

$$\text{Kinetic Energy} = \frac{1}{2}m \cdot v^2 = \frac{p^2}{2m}$$

^dFormally has non-zero amplitude

$$\text{K.E.} = \frac{p^2}{2m} = \frac{(\frac{h}{\lambda})^2}{2m} = \frac{h^2}{2m \cdot \lambda^2} \quad (2)$$

Now, using the expression for the allowed wavelengths in Equation 1, it is possible to derive the expression for the energies of the allowed wavelengths.

$$\begin{aligned} \text{K.E.} &= \frac{h^2}{2m \cdot (\frac{2L}{n})^2} \\ E_n &= \frac{n^2 \cdot h^2}{8m \cdot L^2} \end{aligned} \quad (3)$$

There are a few interesting points to note about this expression:

1. As n can only be an integer, the energies available to this particle can only take certain values, thus we say it is *quantized*.
2. The energies are inversely proportional to L , so a smaller box gives particles with higher energy levels.
3. The energy levels are proportional to n^2 , so the gaps between energy levels increases as n increases, thus the gap from $n = 1 \rightarrow 2$ is much smaller than the gap from $n = 2 \rightarrow 3$, and so on.

It might seem that this is quite an abstract model, after all why would one trap a particle in a box at all? However, this is almost directly analogous to the behaviour of electrons in atoms. In an atom, the negatively charged electron is attracted to the positively charged nucleus by the Coulomb force (the electrostatic attraction between opposing charges). It turns out that the potential energy as a result of this attraction is equivalent to ‘trapping’ the particle in a box (albeit this time a 3-dimensional box), where the boundary conditions are set by the required behaviour of the electron at $x = \infty$ and as the electron approaches the nucleus. The allowed waves that satisfy these boundary conditions are found in a very similar manner to that illustrated above, and the wavefunctions that result are the *atomic orbitals* that you have met in chemistry (for example the 2s orbital is simply the name of a wavefunction with $n = 2$ - the same n as in the example above).

3 Particle on a Ring

A very similar situation is that for the particle confined on a ring. Again the boundary conditions that are imposed determine the quantization of the energy levels, but now the boundary conditions are subtly different. Whereas for the particle in a box the boundary conditions were that the amplitude of the wave must be 0 at both $x = 0$ and $x = L$, for the particle in a ring the wave must have completed a full oscillation (that is a complete wavelength) after one full circumference of the ring. This is because not only does the amplitude of the wave need to be the same after a full circumference, but the direction of the wave (the *phase*) must also be the same. This means that, as illustrated in Figure 3, allowed wavelengths must correspond to one whole circumference, thus the boundary conditions in this case are $l\lambda = 2\pi r$

Calculating the energy levels for these allowed waves is now exactly the same as the for the particle in a 1-dimensional box; simply substitute the expression for the allowed wavelengths on a ring into Equation 3.

$$\begin{aligned} \lambda &= \frac{2\pi r}{l} \\ \text{K.E.} &= \frac{h^2}{2m \cdot \lambda^2} \\ &= \frac{h^2}{2m \cdot (\frac{2\pi r}{l})^2} \\ &= \frac{l^2 \cdot h^2}{2m(2\pi)^2 r^2} \end{aligned} \quad (4)$$

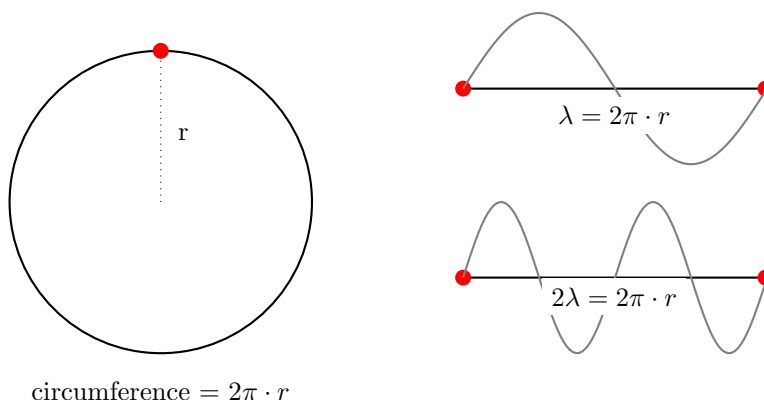


Figure 3. The relation between the circumference of the ring, and the allowed wavelengths. As the wave must have completed a full oscillation after a circumference of the ring, only integer multiples of the wavelength that equal the circumference are allowed.

This is a correct expression for the energy levels of the particle in a ring, however it is possible to make this look more beautiful by including the reduced Planck's constant $\hbar = \frac{h}{2\pi}$. This gives the final equation for the energy levels of a particle confined to a ring:

$$E_l = \frac{l^2 \cdot \hbar^2}{2mr^2} \quad (5)$$

Just as for the particle in a box, these levels are quantized - only integer values of l are permitted. As the energy levels again depend on l^2 , the separation between adjacent energy levels increases significantly with l .

Important Aside: n vs l

The key difference will be discussed later on in the course, but it is important that you have an idea of the differences between the quantum numbers n and l .

In the particle in a box derivation, we used n , which is analogous to the *principal quantum number* that you will come across when atomic orbitals are covered. This takes integer values from $n = 1, 2, 3, \dots, \infty$. Crucially, the lowest energy level for the particle in a box is $n = 1$.

For the particle on a ring, l is used as the quantum number, which is analogous to the *orbital angular momentum quantum number* that will arise when atomic orbitals are covered. This takes integer values from $l = 0$ to $l = n - 1$ in integer steps.^a This means that the lowest energy level for the particle in a ring corresponds to $l = 0$, which has an energy of 0.^b

The precise reasons why $n \neq 0$ but l can be is a little complex, so do not worry about this.^c It is sufficient for this course just to learn the below summary:

$$\begin{aligned} n &= 1, 2, 3, \dots, \infty \\ l &= 0, 1, 2, \dots, n - 1 \end{aligned}$$

^aThis is exactly the same as s, p, d, and f orbitals that you have covered in chemistry. When a 2p orbital is discussed, this really means that $n = 2$ and $l = 1$. This also explains why d orbitals only appear in the third row of the periodic table where $n = 3$, therefore it is possible for $l = 2$, which corresponds to a d orbital.

^bThe reason this does not violate the uncertainty principle is because the particle, according to relativity, has energy mc^2 on account of its mass, thus the total energy is not 0.

^cFor those that are interested, this is because the boundary conditions for the particle in a box insist that the value of the wavefunction must be 0 at either end of the box. If $n = 0$, the only way this could be satisfied is if the wavefunction is 0 everywhere, which would imply that the particle does not exist at all, but we have said that it does within the box. A contradiction! For the particle on a ring there is no requirement that the wavefunction is 0 after a full circumference, just that it has the same value and phase. When we set $l = 0$, this actually implies that the wavefunction is constant around the ring, not 0, implying that the particle is equally likely to be found at any position along the ring.