Matter Waves: Quantization of Bound Systems

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Bohr's atomic model is covered in the course presentation and the text reference books.

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DeBroglie's matter waves

Found solution to the Bohr puzzle (1924): Electrons also have wave-like properties. The experiment by Davisson and Germer proved that electrons scattered back from a crystal lattice show wave-like interference patterns.

So, let's try to construct a wave function for electrons by adapting the information known for photons to massive electrons.

Wavelength for photons $\lambda = \dfrac{c}{\nu} = \dfrac{hc}{h\nu} = \dfrac{hc}{E} = \dfrac{h}{E/c} = \dfrac{h}{p}$

since $E = \sqrt{(pc)^2 + (mc^2)^2} = pc$ *for* $m=0$

What if massive particles also have a wavelength given by the same relation to the momentum,

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad ?$$

Question: Is the concept compatible with previous experience or does classical experience contradict this wave property?
Consider as an example a macro-object, a ball. Would we have seen the wave-like pattern if it existed?

Tennis ball (m= $6 \cdot 10^{-2}$ kg, v = 140 mph or 62m/s). One calculates

$$\lambda = \frac{h}{mv} = \frac{6.6 \cdot 10^{-34} \, Js}{6 \cdot 10^{-2} kg \cdot 62 ms^{-1}} = 1.8 \cdot 10^{-34} m$$

This is a very small wavelength, smaller than the size of an atom. Therefore, such wave-like behavior cannot be detected.

So, no contradiction between classical experience and quantal behavior.

On the other hand: An electron moving with the same speed (v = 62 m/s) has a wavelength of

$$\lambda = \frac{h}{mv} = \frac{6.6 \cdot 10^{-34} \, Js}{9.1 \cdot 10^{-31} kg \cdot 62 ms^{-1}} = 1.2 \cdot 10^{-5} m$$

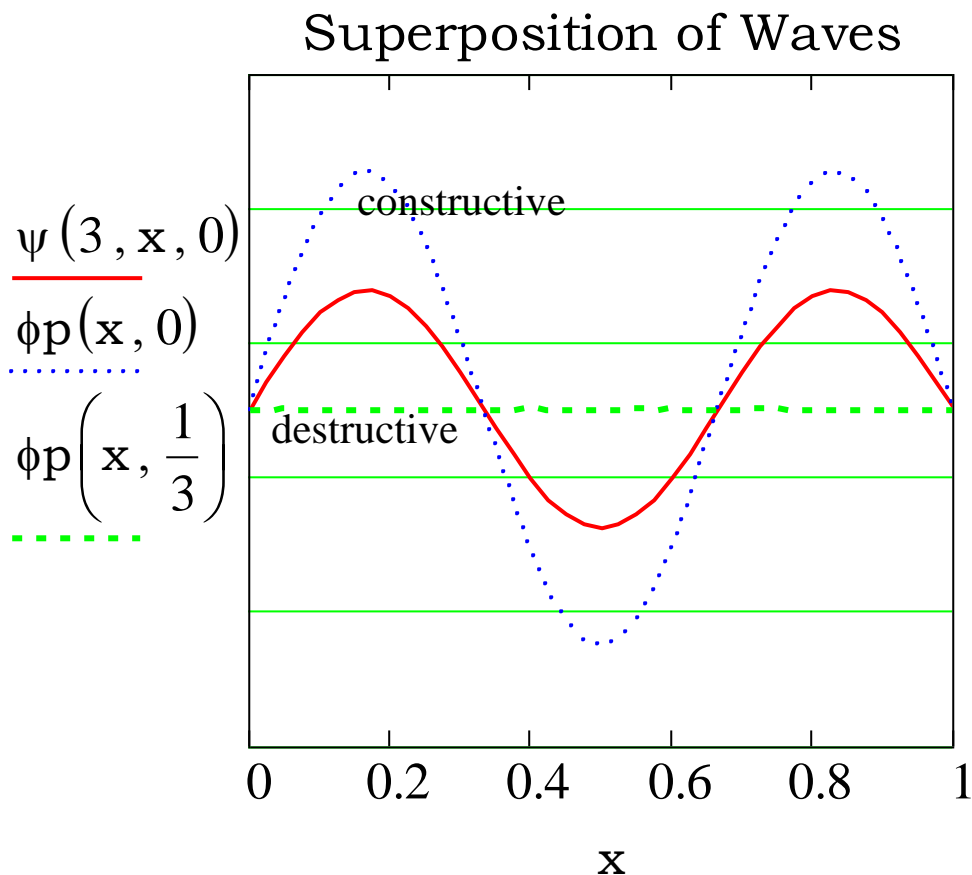This is a wavelength in the infrared, hence, detectable like in   Davisson's and Germer's experiments.

Possible scenario: free particles → traveling waves
bound particles → standing waves

The wave function has to look something like this:

$$\psi(x) = A \cdot \sin(2\pi \frac{x}{\lambda})$$

where *A* is the wave amplitude (the height of the crest). It has to have positive and negative parts, such that a superposition can cancel (destructive interference) some parts of another wave function and enhance (constructive interference) others, as it is known for light

particles (photons). The figure shows as a solid red curve the sample wave with a wave length of $\lambda = 2/3$ and the sum

Superposition of Waves

$\psi(3, \mathrm{x}, 0)$

$\phi\mathrm{p}(\mathrm{x}, 0)$

$\phi\mathrm{p}\left(\mathrm{x}, \dfrac{1}{3}\right)$

constructive

destructive

0   0.2   0.4   0.6   0.8   1

x

$$\phi_p(x, \Delta x) = A \cdot \left[\sin(2\pi \frac{x}{2/3}) + \sin(2\pi \frac{x + \Delta x}{2/3}) \right]$$

of two such waves shifted by *Δx*. Adding two of the same wave functions (*Δx=0*) yields the dotted blue curve. It has the same wavelength but twice the amplitude as either of the two waves, which add up in ***constructive interference.*** However, adding one wave to a similar wave function, but shifted by half a wave length (*Δx=λ/2*), yields ***destructive interference.*** Wave crests and valleys of the two waves just meet and cancel each other in this situation.

What is the information on the particle carried by the wave function? Again, in analogy of experience made with light waves, one conjectures that *the wave function indicates where the particle is located*. According to Bohr's interpretation, the *intensity of the wave*

$$I(x) = \psi^2(x) = A^2 \sin^2(2\pi \frac{x}{\lambda})$$

gives the likely positions of the particle as some kind of a probability. The particle is not localized as suggested by classical theory. The figure shows a sine-wave (solid red curve) with an amplitude of $A = 2$. The associated intensity, the square of the wave function is shown as dotted blue curve. It is always *non-negative*. The particle is found most likely at the positions of maximum intensity (*crest or valley*) and is absent at zero intensity. But it is not confined to a single point within the box.


$\psi(3, x, t_i)$

$(\psi(3, x, t_i))^2$
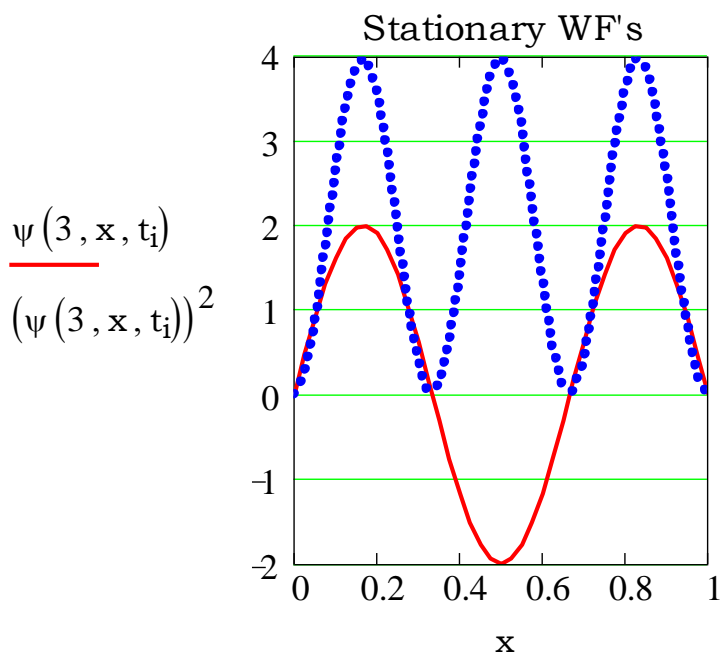
Take a simple, one-dimensional case. A box of length *a* with perfectly reflecting walls, corresponding to an infinitely high potential wall,

$$V = \begin{cases} 0 & 0 < x < a \\ \infty & x = 0, a \end{cases}$$

What kind of standing waves can one have in such a box?

If it is supposed to be a standing wave, then the wavelength of the particle has to fit exactly into the width of the box. At least half of the wavelength has to fit, in order to have zeros (nodes) on both ends. The wave needs to be held fixed at both ends of the box (boundary conditions). This would be the ground state pictured as a solid red curve in the sketch. Since $p = h/\lambda$, the largest wavelength corresponds to the lowest energy and lowest frequency. The shorter wavelengths of the dotted (blue) and dashed (green) curves indicate higher energies for the corresponding states of the particle in a box.

$\psi\left(1, x, t_i\right)$
⎯⎯⎯

$\psi\left(2, x, t_i\right)$
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$\psi\left(3, x, t_i\right)$
▬ ▬ ▬ ▬ ▬
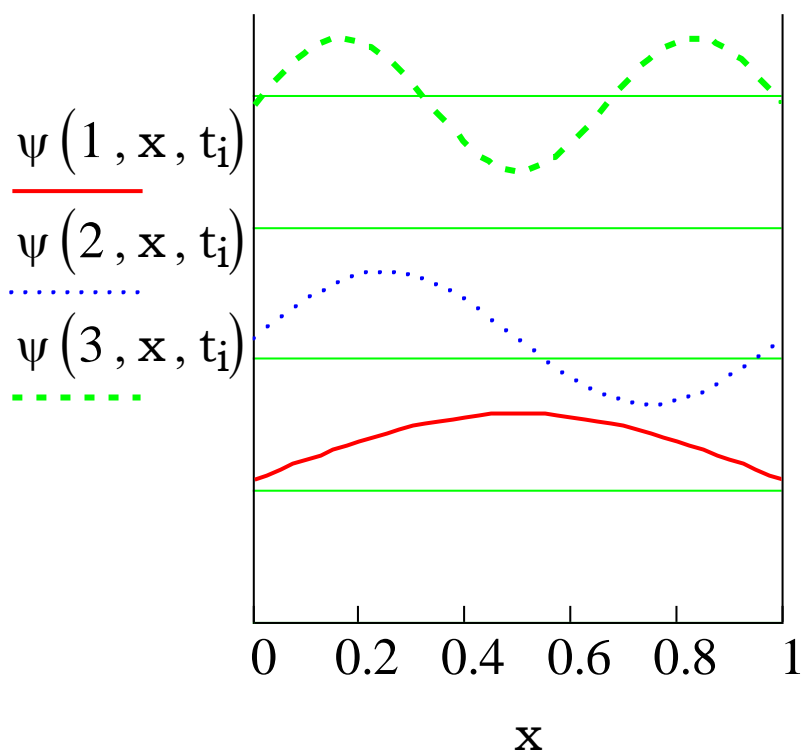
So, if one-half of the wavelength (λ) fits into the box an integer number of times, the system has a stable (stationary) state and a standing wave develops. These conditions already determine the discrete (quantized) energy states of the

0   0.2   0.4   0.6   0.8   1

x

$$n \cdot \frac{\lambda_n}{2} = n \cdot \frac{1}{2}\left(\frac{h}{p_n}\right) = a \quad \text{with } n=1,2,3....$$

n-1 is the number of nodes of the corresponding wave function, disregarding the two trivial zeros at the two boundaries. ***There is no state for n = 0***. And consequently,

$$p_n = \left(\frac{h}{2a}\right)n$$

This momentum corresponds to a particle energy of

$$\varepsilon = \frac{(p_n)^2}{2m} = \frac{1}{2m}\left(\frac{h}{2a}\right)^2 n^2 = \frac{h^2}{8ma^2}\cdot n^2$$

where m is the mass of the particle. This is the kinetic energy, but also the total particle energy, because the potential energy V is zero inside the box. No potential has been assumed inside the box. *One sees that the energy increases with the square of the* so-called *quantum number n*, or with the square of the number (+1) of nodes of the wave function, since *the wavefunction ψ_n has (n-1) nodes*.

Then, the various wave functions (*n =1,2,3,…..*)

$$\psi_n(x) = A\cdot\sin(n\pi\frac{x}{a})$$

with energies

$$\varepsilon_n = \frac{h^2}{8ma^2}\cdot n^2$$

should describe the particle in the box completely, i.e., all the physical properties associated with its motion in x direction. The ***probability to find the particle at a position x is given by I(x), the square of the wave function***,

$$I_n(x) = \left[\psi_n(x)\right]^2 = A^2\cdot\sin^2(n\pi\frac{x}{a})$$

There is still one undetermined parameter in the wave function, its amplitude A. This parameter can now be determined by requiring that the particle must be somewhere within the box. Therefore, ***the integrated probability must be unity (a 100%)***:

$$\int_0^a dx I_n(x) = \int_0^a dx \left[\psi_n(x)\right]^2 = A^2 \cdot \int_0^a dx \sin^2(n\pi \frac{x}{a}) = 1$$

One can look up the above integral in the tables and finds,

$$\int_0^a dx \sin^2(n\pi \frac{x}{a}) = \frac{a}{n\pi} \int_0^{n\pi} dz \sin^2(z) = \frac{a}{n\pi} \cdot \left(\frac{n\pi}{2}\right) = \frac{a}{2}$$

Therefore, choosing $A^2 = a/2$ will ensure the condition for the integrated probability. This implies also that the complete wave functions can now be written as,

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

The integral

$$\int_0^a dx I_n(x) = \int_0^a dx \, \psi_n(x) \cdot \psi_n(x) = A^2 \cdot \int_0^a dx \sin^2(n\pi \frac{x}{a}) = 1$$

is an example of an ***overlap integral***, here of the wave function $\psi_n(x)$ with itself. More generally, one defines the overlap integral for two different wave functions $\psi_n(x)$ and $\psi_m(x)$ with $m \neq n$ as,

$$I_{nm} = \int_{-\infty}^{+\infty} dx \, \psi_n(x) \cdot \psi_m(x)$$

The integration limits go formally from minus infinity to plus infinity. However, practically the integration is carried out only over the region in *x* where both functions, i.e., the integrand, are defined and non-zero. ***Wave functions for stationary states at different energies have vanishing overlap integrals***. For example, for the particle-in-a-box problem, all overlap integrals of two different functions are zero,

$$I_{n \neq m} = \int_0^a dx\, \psi_n(x) \cdot \psi_m(x) = \frac{2}{a} \int_0^a dx\, \sin(n\pi \frac{x}{a}) \cdot \sin(m\pi \frac{x}{a}) = 0$$

while all overlap integrals of the same two functions are unity. These two properties are written in a combined form as

$$I_{nm} = \int_0^a dx\, \psi_n(x) \cdot \psi_m(x) = \frac{2}{a} \int_0^a dx\, \sin(n\pi \frac{x}{a}) \cdot \sin(m\pi \frac{x}{a}) = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}$$

With the information on intensity and overlap integral, it is easy to calculate some properties of the particle in a box. For example, it is straightforward to calculate ***the average position of the particle*** in the box, while in state *n*, from a ***weighted average***:

$$\langle x \rangle_n = \int_0^a dx\, x \cdot \psi_n^2(x) = \frac{2}{a} \int_0^a dx\, x \cdot \sin^2(n\pi \frac{x}{a}) = \frac{a}{2}$$

This expectation value is independent of the particular state, as it should, since there is physically no place inside the box different from any other.

Similarly, one can calculate the ***spread in the position*** of the particle in the box by calculating the ***variance*** (mean square deviation from the average):

$$\left(\sigma_x^2\right)_n = \left\langle\left(x - \langle x\rangle\right)^2\right\rangle_n = \int_0^a dx\left(x - \langle x\rangle\right)^2 \cdot \psi_n^2(x)$$

$$= \frac{2}{a}\int_0^a dx\left(x - \langle x\rangle\right)^2 \cdot \sin^2(n\pi\frac{x}{a}) = \left(\frac{a}{2\pi n}\right)^2\left(\frac{\pi^2 n^2}{3} - 2\right)$$

For the lowest state, **n = 1**, the spread is equal to $\left(\sigma_x^2\right)_{n=1} = 0.03$, corresponding to standard deviation of $\left(\sigma_x\right)_{n=1} = 0.18$. This result implies that, in the ground state, the particle is localized fairly well in the middle of the box. With increasing quantum number **n**, the particle becomes less and less localized and appears to be "smeared" all over the box. This latter behavior is expected for a classical particle bouncing back and forth between the walls of the box and spending about an equal time anywhere inside the box. This behavior is an example of a more general principle:
In the limit of large quantum numbers, a quantal particle behaves classically.

    In order to check whether this theory (a particle enclosed in a box with perfectly reflecting walls) makes practical sense, one should look for a microscopic object in nature that has a very elongated shape and contains some freely moving electrons, such that the particle-in-a-box scheme can be tested. Fortunately, there are a number of long chain molecules, for which the picture appears appropriate. One such example is β–carotene, a 29-Å long, linear polyene with 40 carbon atoms. The molecule plays an important role in the vision process. β–carotene has 11 conjugated double bonds and, therefore, 22 π electrons. These electrons can roam nearly the full length of the molecule, about 18.3 Å.

The actual energy spectrum of electrons in β−carotene has simi-larities to that of a particle in a 18.3- Å long, one-dimensional box. For example, the molecule absorbs light of wavelength $\lambda = 480\ nm.$ This wavelength is thought to be associated with the $n =10 \rightarrow n =11$, which is the longest wavelength in the absorption spectrum. It arises naturally from the transition of one electron from its lowest level to the first free level.

The next obvious problem is that of another independent degree of freedom, say *y*, in addition to *x*. It is reasonable to adopt a simi-lar wave function for *y:*

$$\varphi_m(y) = \sqrt{\frac{2}{a}} \cdot \sin(m\pi \frac{y}{a})$$

if the box has the same length *a* in the *y* direction. The probability of finding the particle at coordinate *y* is given by the corresponding intensity,

$$I_m(y) = \frac{2}{a} \cdot \sin^2(m\pi \frac{y}{a})$$

which is similar to the probability to find it at a position *x*. The prob-ability to find the particle ***simultaneously at coordinate x and at coordinate y is the product of the individual probabilities,***

$$I_{nm}(x, y) = I_n(x)I_m(y) = \left(\frac{2}{a}\right)^2 \cdot \sin^2(n\pi \frac{x}{a}) \cdot \sin^2(m\pi \frac{y}{a})$$

Therefore, it is consistent to require that ***the wave function in two independent degrees of freedom (x,y) is the product of the two in-dividual wave functions***:

$$\Psi(x, y) = \psi_n(x) \cdot \varphi_m(y) = \frac{2}{a} \cdot \sin(n\pi \frac{x}{a}) \cdot \sin(m\pi \frac{y}{a})$$

And for three dimensions,

$$\Psi_{nml}(x, y, z) = \psi_n(x) \cdot \varphi_m(y) \cdot \chi_l(z)$$

$$= \sqrt{\frac{2}{a}}^3 \cdot \sin(n\pi \frac{x}{a}) \cdot \sin(m\pi \frac{y}{a}) \cdot \sin(l\pi \frac{z}{a})$$

This is a general principle whose validity is required from simple considerations of probability: *Probabilities are multiplicative and so are the component wave functions for independent degrees of freedom.*
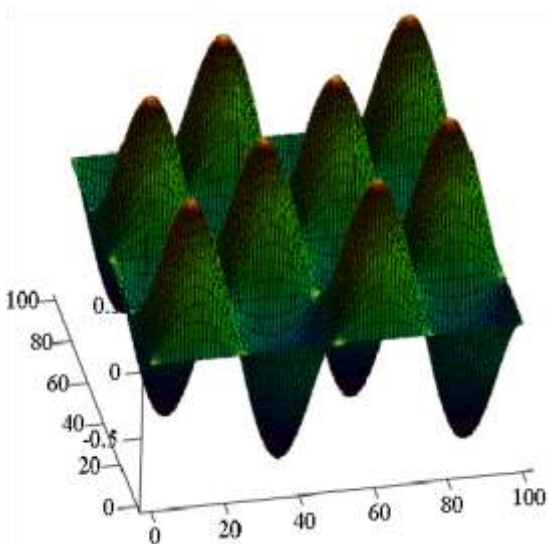
The figure illustrates an example of a 2-dimensional wave function of an electron in a square box. In each dimension, there are 4 half-waves fitting into the box of length $a = 100$ (in some units). Therefore, the figure pictures the wave function $\Psi_{44}(x, y)$.

These one- or two-dimensional sine waves are *standing-wave vibrational patterns* that are observable also with macroscopic one- or two-dimensional objects such as ropes (1-dim) or metal sheets (2-dim), when they are fixed in position at the ends. The symmetry of the standing-wave pattern reflects the shape of the object. For example, the waves for a rectangular sheet (box) are perpendicular to each other, as illustrated in the figure above. The standing-wave pattern of a circular disk held fixed at

its periphery is expected to have a regular circular, radial, and angular pattern.

Since the **x, y**, and **z** coordinates represent independent degrees of freedom, the associated energies should add up to the total energy. For example, the total energy associated with the wave function $\Psi_{nml}(x, y, z)$ is the sum of the individual energies,

$$\varepsilon_{nml} = \varepsilon_n(x) + \varepsilon_m(y) + \varepsilon_l(z) = \frac{h^2}{8ma^2} \cdot \left(n^2 + m^2 + l^2\right)$$

Since the total energy is the sum of three individual terms, each representing the same energy spectrum, there is the possibility that several different wave functions have the same energy. Since the box is spatially symmetric, it does not matter for the total energy, whether the wave is excited in *x, y,* or *z* direction. This is called **degeneracy**. For example, the energies

$$\varepsilon_{n_x n_y n_z} = \varepsilon_{211} = \varepsilon_{121} = \varepsilon_{112} = 2 \cdot \varepsilon_{111}$$

are the same (degenerate). Similarly, the energies

$$\varepsilon_{n_x n_y n_z} = \varepsilon_{321} = \varepsilon_{312} = \varepsilon_{231} = \varepsilon_{123} = \varepsilon_{132} = \varepsilon_{213} = \frac{14}{3} \cdot \varepsilon_{111}$$
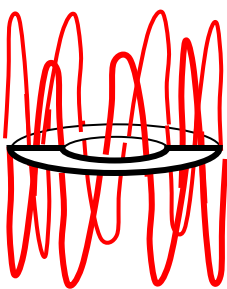
coincide with each other.

A variation of the particle-in-a-box model is that of the particle-on-a-ring model, which is useful for π electrons in large aromatic molecules such as porphyrins, heme, chlorophyll, etc. Here, the potential is zero everywhere on the ring structure. A standing electron wave corresponds to an
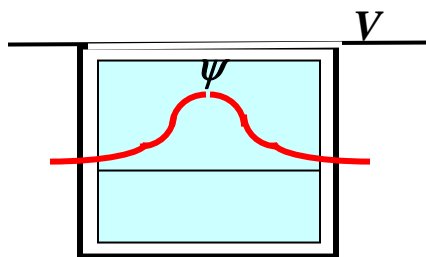
"endless" wave function, one where the beginning matches the end perfectly smoothly.

The most stringent assumption made in the particle-in-a-box model is that of infinitely high potential walls at both ends, requiring the electronic wave function to have a zero at either end of the box. In reality, such infinitely high potential energies do not exist. The box is defined by a finite "well depth". Consequently, the wave function does not exactly vanish at either end; it can "leak out" of the box somewhat. This leads to the important "tunnel effect" in quantum mechanics. Such tunneling is of interest for the semi-conductor industry building fast electronic switches, but also for biological and biochemical systems. For example, tunneling electrons are important for respiration and photosynthesis processes and also for protons, in their transfer through membranes driven by molecular pumps.
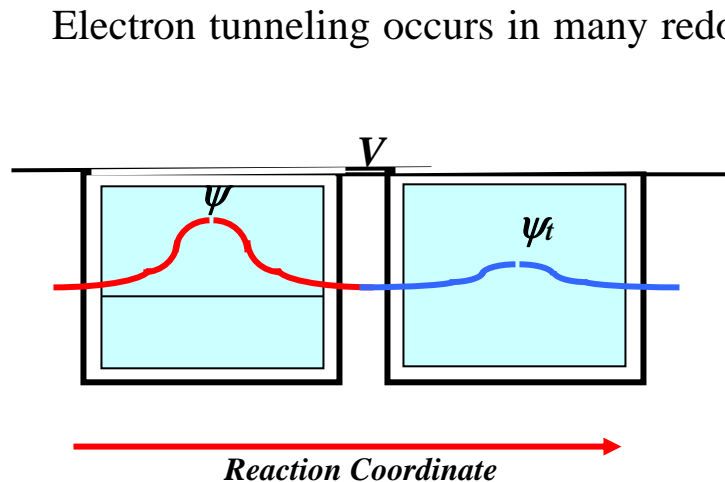
Electron tunneling occurs in many redox reactions catalyzed by enzymes. Proton transfer through tunneling can also occur in such processes. This is the case in the oxidation of ethanol by a liver enzyme alcohol dehydrogenase, which forms acetaldehyde:

Reaction Coordinate

$$CH_3CH_2OH + NAD^+ \rightarrow CH_3HC = O + NADH + H^+$$

Here, NAD^+ stands for ***nicotineamid adenine dinucleotide***. Classically, the reactants need a certain amount of energy to overcome the barrier, for the reaction to take place. However, it takes place even for less energy, albeit with a relatively lower rate, through the tunnel effect.

There is one interesting observation yet to be made from the particle-in-a-box model. The lowest energy is not zero but finite,

$$\varepsilon_1 = \frac{h^2}{8ma^2}$$

It is also called the ***zero-point energy***. It corresponds to the minimum particle momentum in the box,

$$p_1 = \sqrt{2m\varepsilon_1} = \sqrt{2m\frac{h^2}{8ma^2}} = \frac{h}{2a}$$

Furthermore, the smaller the box, i.e., better the particle is localized, the larger its momentum. For any state of the particle in the box, one has the condition

$$p \cdot a \geq \frac{h}{2}$$

Therefore, the uncertainty $\Delta p \lambda p$ in momentum of the particle and the uncertainty in its position, $\Delta x \lambda a$, are related via the ***Heisenberg Uncertainty Relation***,

$$\Delta p \cdot \Delta x \geq \frac{h}{2}$$

In other words, it is impossible to measure momentum and position of a particle simultaneously with arbitrary accuracy. If the

momentum is measured well, then the position is rather uncertain. If one measures the particle position very accurately, i.e., if one confines a particle to a narrow region in space, one does so at the expense of a large uncertainty in the particle momentum. Similar uncertainty relations exist for all pairs of "conjugated" variables, such as position and momentum, angle and angular momentum, energy and time, etc.

The deBroglie matter wave functions describing the physical properties of particles should have properties like ordinary electromagnetic or mechanical waves. In particular, one postulates that a valid wave function must

- *be a well-defined, single-valued function,*
- *must vary in a continuous fashion, differentiable at any point,*
- *must be finite at any point, and*
- *its square (intensity) must be normalizable.*