Expectation values

If we know $\Psi(x, t)$ (a solution of the TDSE), then knowledge of $\Psi^*\Psi\, dx$ allows the *average* position (or any other observable) to be calculated:

$$\langle x \rangle \equiv \sum_i x_i p(x_i) \delta x$$

In the limit that $\delta x \rightarrow 0$, the summation becomes:

$$\langle x(t) \rangle = \int_{-\infty}^{\infty} x p(x) dx = \int_{-\infty}^{\infty} x \Psi^*(x, t) \Psi(\mathrm{x}, \mathrm{t}) dx$$

The average is also know as the *expectation value* and is very important in quantum mechanics because in many cases precise values cannot, even in principle, be determined.

Expectation values

The expectation value is not limited to *x*, for example:

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 p(x) dx = \int_{-\infty}^{\infty} x^2 \Psi^*(x,t) \Psi(\mathrm{x},\mathrm{t}) dx$$

Stationary States

We saw that even when the potential is independent of time the wavefunction still oscillates in time. The Solution to the full TDSE is:

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

But the corresponding probability distribution is *static*:

$$p(x,t) = |\Psi(x,t)|^2 = \psi^*(x)e^{i\frac{E}{\hbar}t}\psi(x)e^{-i\frac{E}{\hbar}t} = |\psi(x)|^2$$

Therefore, a solution of the TISE which consists of a single eigenstate of the Hamiltonian (with specific energy) is known as a Stationary state.

What other information can you get from ψ? (and how!)

We have seen how we can use the probability density function, $\psi^*\psi$, to calculate the average position of a particle. What happens if we want to calculate the *average energy* or *momentum ?*

These observables are represented by the following differential operators:

$$\hat{H} = \frac{\hat{\vec{p}}^{\,2}}{2m} + V(x) \quad \text{and} \quad \hat{\vec{p}} = -i\hbar\nabla \quad \text{with} \quad \nabla \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial x}\right)$$

Do the operators work on $\psi^*\psi$, or on ψ, or on ψ^* alone?

What other information can you get from ψ? (and how!)

Take TISE for an eigenfunction of the Hamiltonian, multiply from the left by ψ^* and integrate (ψ is normalized).

$$\hat{H}\psi_n = E_n\psi_n$$

$$\int_{-\infty}^{\infty} \psi_n^* \hat{H}\psi_n dx = \int_{-\infty}^{\infty} \psi_n^* E_n \psi_n dx = E_n$$

This suggests that in order to calculate the *average value* of the physical quantity associated with a QM operator we carry out the following integration:

$$\langle \hat{q} \rangle = \int_{-\infty}^{\infty} \psi^* \, \hat{q}\psi dx$$

Note that sometimes the limits of the integration are not specified and it implies that the integration is from $-\infty$ to ∞.

Momentum and energy expectation values

The expectation value of *momentum* involves the representation of momentum as a quantum mechanical operator:

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\hat{p}_x \Psi(x,t)dx = \int_{-\infty}^{\infty} \Psi^*(x,t)\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t)dx \quad where\ we\ used \quad \hat{p}_x \equiv \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$\hat{p}_x$ is the operator for the *x* component of the momentum.

Example: Derive an expression for the average energy of a free particle.

$$E = \frac{p^2}{2m} \Longrightarrow \langle E \rangle = \frac{\langle p^2 \rangle}{2m}$$

Since $V = 0$ the expectation value for energy for a particle moving in one dimension is

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\Psi(x,t)dx$$

Our definition of the expectation value is one of the postulates of QM.

The Heisenberg Uncertainty Principle

We saw earlier that the energy of a free particle with momentum p_0 can be written as

$$E_0 = \frac{p_0^2}{2m} = \frac{\hbar^2 k_0^2}{2m} = \hbar\omega(k_0)$$

And its wavefunction can be written as $\psi(x,t) = A_0 e^{i(k_0 x - \omega(k_0)t)}$

Considering the fact that we interpret the square of the wavefunction as the probability density we find

$$p(x,t) = |\psi(x,t)|^2 = A_0^2$$

Namely, the probability density is independent of the position. We have the same probability to find the particle at any location! which implies we have no knowledge about the position. However, the momentum is precisely defined.

The Heisenberg Uncertainty Principle

The Heisenberg uncertainty principle states that, in any **simultaneous measurement** of the position and the momentum of a particle,

$$\Delta x \cdot \Delta p \geq \hbar/2$$

where Δx is the uncertainty in the measurement of a particular coordinate x, and Δp is the uncertainty in the measurement of the corresponding momentum.

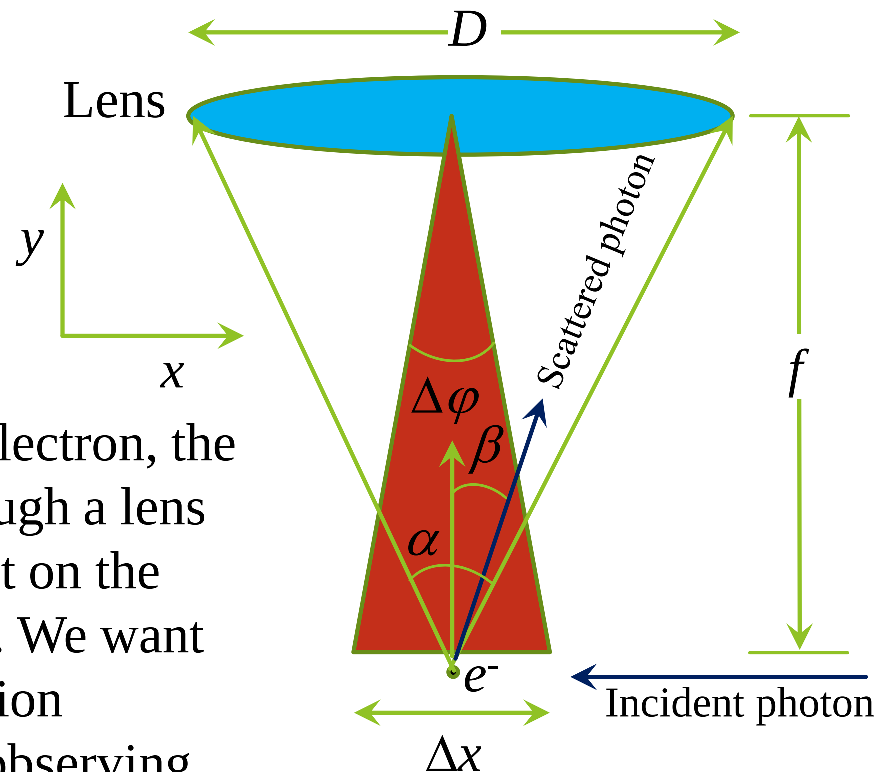
Since 1927, there have been many attempts to invent methods by which this principle could be violated, but none has succeeded. Let us examine a simple thought experiment to see how these uncertainties actually occur.

Heisenberg Microscope

Imagine that we are able to use a microscope to measure the position of an electron, and that we can detect a single photon scattered from the electron.

Photographic plate or CCD

From the geometry, $\tan(\alpha/2) = D/(2f)$



Electron position (Δx)

After striking the electron, the photon passes through a lens and produces a spot on the photographic plate. We want to deduce the position of the electron by observing the position of the spot on the plate.

Conservation of momentum yields

$$\vec{p}_{photon} = \frac{h}{\lambda}(\sin\beta\,\hat{x} + \cos\beta\,\hat{y})$$

(scattered photon)

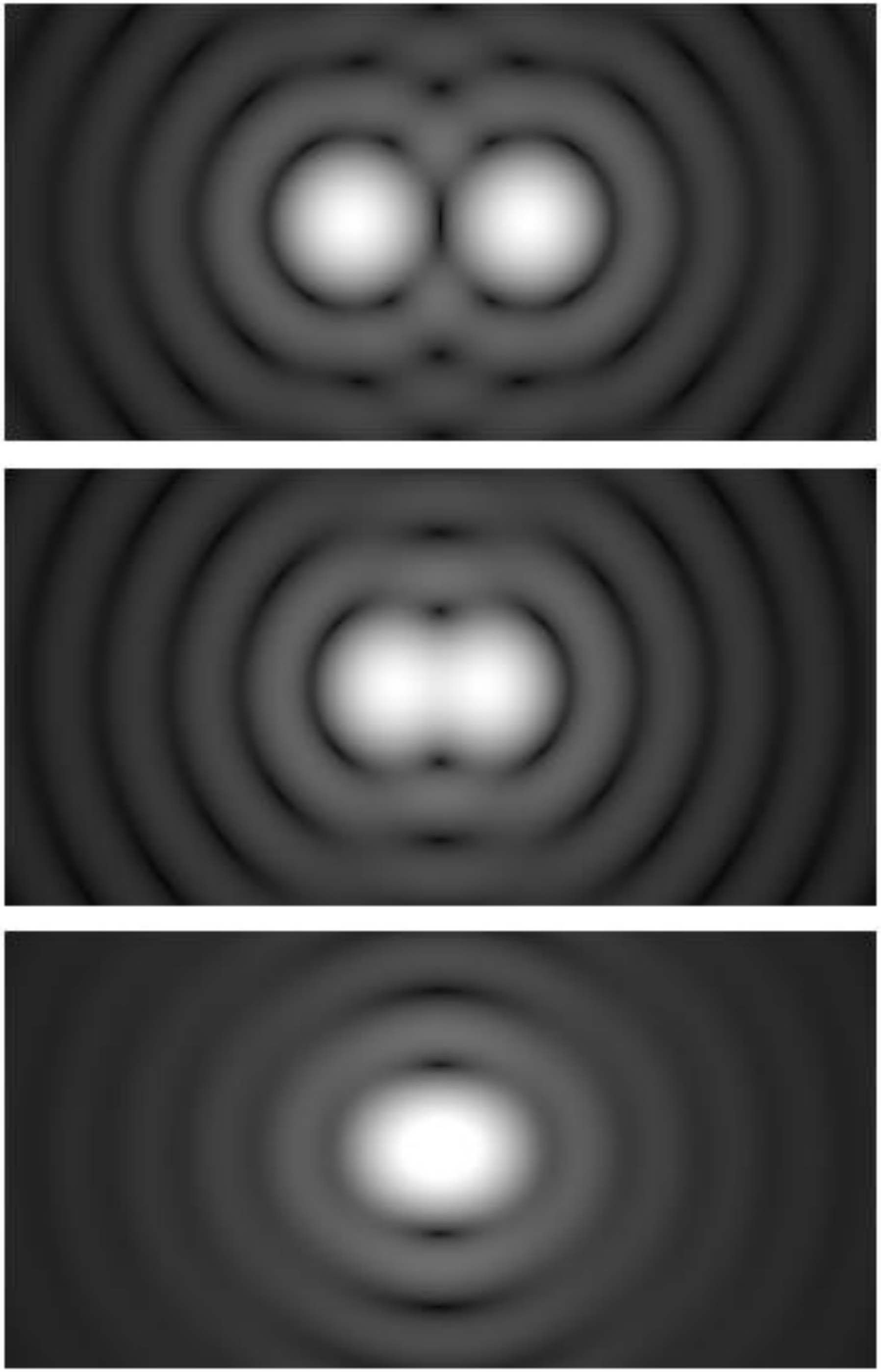
From optics, the minimum angular resolving power is

$$\Delta\varphi \approx \frac{\lambda}{D}$$

then $\Delta x \approx f\,\Delta\varphi \approx \dfrac{f\lambda}{D}$,

which is the uncertainty in the position of the electron.

Airy diffraction patterns generated by light from two point sources passing through a circular aperture, such as the pupil of the eye. Points far apart (top) or meeting the Rayleigh criterion (middle) can be distinguished. Points closer than the Rayleigh criterion (bottom) are difficult to distinguish.



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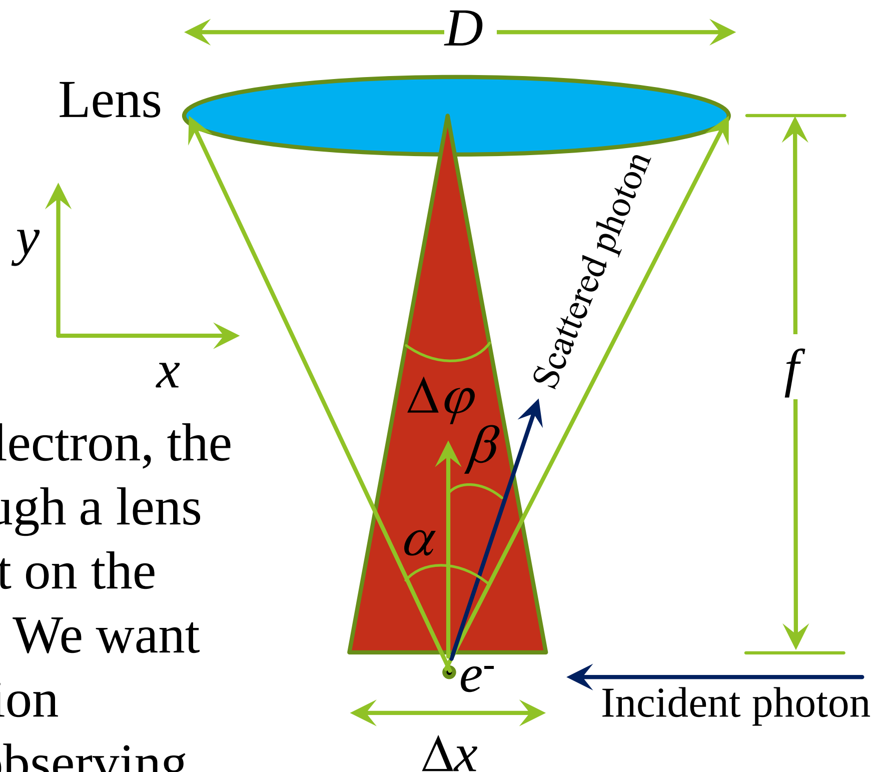

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After striking the electron, the photon passes through a lens and produces a spot on the photographic plate. We want to deduce the position of the electron by observing the position of the spot on the plate.

The Heisenberg Uncertainty Principle

From the geometry, $\tan\left(\frac{\alpha}{2}\right) = \frac{D}{2f}$, assuming that the angle α is small we can write $\alpha \approx D/f$.

For the scattered photon, the momentum is given by

$$\vec{p}_{photon} = p_x\,\hat{x} + p_y\,\hat{y} = \frac{h}{\lambda}(sin\beta\hat{x} + cos\beta\,\hat{y})$$

with p_x lying in the range:

$$-\frac{h}{\lambda}\sin\left(\frac{\alpha}{2}\right) \leq p_x \leq \frac{h}{\lambda}\sin\left(\frac{\alpha}{2}\right) \qquad since\ \beta \leq \alpha/2$$

Using the small angle approximation

$$-\frac{h}{\lambda}\frac{\alpha}{2} \leq p_x \leq \frac{h}{\lambda}\frac{\alpha}{2} \qquad or\ -\frac{h}{\lambda}\frac{D}{2f} \leq p_x \leq \frac{h}{\lambda}\frac{D}{2f}$$

The Heisenberg Uncertainty Principle

Consequently, $\Delta p_x = hD/(f\lambda)$ and $\Delta x \approx f\lambda/D$ which results in

$$\Delta p_x \cdot \Delta x \approx h$$

which is independent of the size (D) and focal length (f) of the lens and wavelength of the photon (λ).

Notice that a small (large) wavelength leads to a large (small) Δp_x and small (large) Δx.

The exact expression that we use for the Heisenberg uncertainty principle is $\Delta x \cdot \Delta p \geq \hbar/2$ and it can be derived using straightforward methods in quantum mechanics.

Wave packet

One way to get a localized particle is to consider a wave packet. As we saw earlier the Shcrödinger equation is linear and any linear combination of solutions is also a solution.

$$\psi(x,t) = \int_{-\infty}^{\infty} \frac{1}{2\pi}\, e^{ikx}\tilde{\psi}(k,t)dk$$

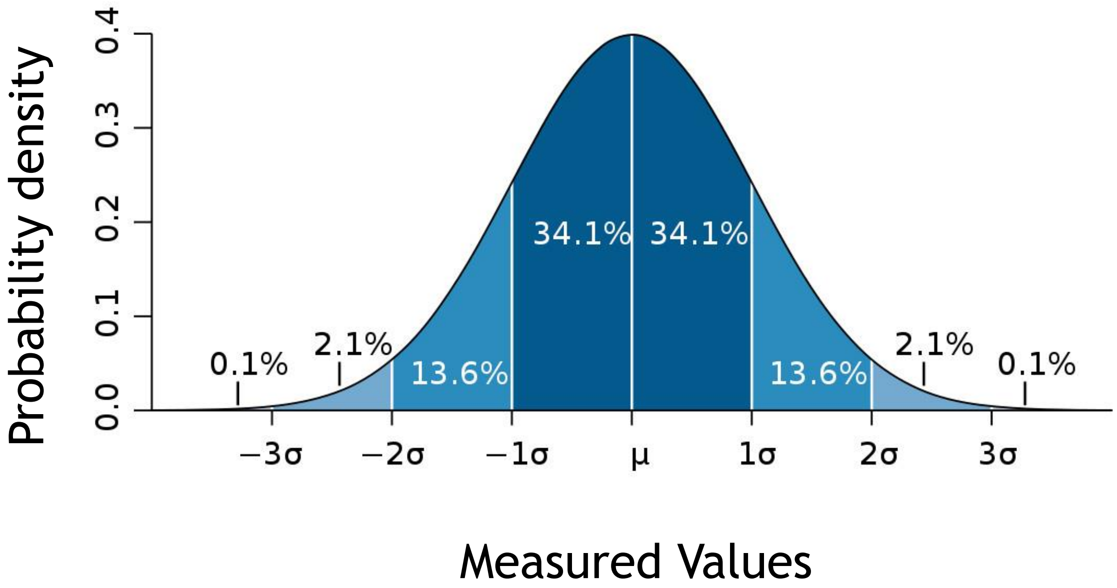
The wave packet is a linear combination of waves.

Many things closely follow a Normal or Gaussian Distribution in Nature:

For example:

- Heights of people
- Weights of elephants
- Marks (grades) on a test
- Random errors in many types of measurements in nature

We say the data is "normally distributed" when there are random variations about a mean, average, or expectation value (μ). σ is the standard deviation. σ^2 is the variance.



$$P(x) = \frac{\exp\left[-(x-\mu)^2 / 2\sigma^2\right]}{\sigma\sqrt{2\pi}}$$

$$\int_{-\infty}^{\infty} P(x)dx = 1$$

The Heisenberg Uncertainty Principle using Gaussian wave packets

We consider a Gaussian wave packet

$$\tilde{\psi}(k) = \left(2\pi a^2\right)^{1/4} e^{-\frac{a^2}{4}(k-k_0)^2}$$

We can use Parseval's theorem to check for normalization

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} \left|\tilde{\psi}(k)\right|^2 dk = \int_{-\infty}^{\infty} |\psi(x)|^2 dx \qquad Parseval's\ theorem$$

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} \left|\left(2\pi a^2\right)^{\frac{1}{4}} e^{-\frac{a^2}{4}(k-k_0)^2}\right|^2 dk = \frac{1}{2\pi}\int_{-\infty}^{\infty} \left(2\pi a^2\right)^{\frac{1}{2}} e^{-\frac{a^2}{2}(k-k_0)^2} dk$$

$$= 1$$

By inverting the Fourier transform of the wavefunction we find

$$\psi(x) = \left(\frac{2}{\pi a^2}\right)^{\frac{1}{4}} e^{ik_0 x} e^{-\frac{x^2}{a^2}}$$

The Heisenberg Uncertainty Principle using Gaussian wave packets

$$Var(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left|\tilde{\psi}(k)\right|^2 \Delta k^2 dk = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left(2\pi a^2\right)^{\frac{1}{2}} e^{-\frac{a^2}{2}(\Delta k)^2}\Delta k^2 dk = \frac{1}{a^2}$$

$$Var(x) \ = \int_{-\infty}^{\infty}|\psi(x)|^2 \Delta x^2 dx = \int_{-\infty}^{\infty}\left(\frac{2}{\pi a^2}\right)^{\frac{1}{2}} e^{-\frac{x^2}{a^2}} x^2 dx = \frac{a^2}{4}$$

$$\Delta k = \sqrt{Var(k)} = \frac{1}{a}; \Delta x = \sqrt{Var(x)} = a/2$$

$$p = \hbar k \rightarrow \Delta p = \hbar \Delta k = \hbar/a$$

$$\Delta p \Delta x = \frac{\hbar}{2}$$

which agrees with the Heisenberg uncertainty principle $\Delta x \cdot \Delta p \geq \hbar/2$.

The Heisenberg Uncertainty Principle using Gaussian wave packets

An alternative derivation of the momentum uncertainty is by considering the momentum operator.

$$Var(p) = \langle p^2 \rangle - \langle p \rangle^2$$

$$\psi(x) = \left(\frac{2}{\pi a^2}\right)^{\frac{1}{4}} e^{ik_0 x} e^{-\frac{x^2}{a^2}} \rightarrow \frac{\partial}{\partial x}\psi(x) = \left(ik_0 - \frac{2x}{a^2}\right)\psi(x)$$

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x) \frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x)dx = \hbar k_0$$

$$\langle p^2 \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 \psi(x)dx = \hbar^2 k_0^2 - \frac{4\hbar^2}{a^4}\langle x^2 \rangle + \frac{2\hbar^2}{a^2} = \hbar^2 k_0^2 + \frac{\hbar^2}{a^2}$$

$$\psi(x) = \left(\frac{2}{\pi a^2}\right)^{\frac{1}{4}} e^{ik_0 x} e^{-\frac{x^2}{a^2}} \rightarrow \frac{\partial^2}{\partial x^2}\psi(x) = \left(-k_0^2 - \frac{2x}{a^2}\left(ik_0 - \frac{2x}{a^2}\right) - \frac{2}{a^2}\right)\psi(x)$$

$$Var(p) = \langle p^2 \rangle - \langle p \rangle^2 = \frac{\hbar^2}{a^2} \rightarrow \Delta p = \frac{\hbar}{a}$$

Commutation Relations

If two observables, A and B, have linear operators associated with them, the commutator is defined by,

$$\left[\hat{A},\hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

The commutator is a composite operator and must be treated as such when operating on any function.

$$\left[\hat{A},\hat{B}\right]\psi \equiv \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right)\psi = \hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi$$

If ψ is an eigenfunction, with eigenvalues *a* and *b* for observables *A* and *B* respectively, it implies that the operators commute

$$\hat{A}\psi = a\psi \quad and \qquad \hat{B}\psi = b\psi$$

Therefore,

$$\left[\hat{A},\hat{B}\right]\psi = \hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi = \hat{A}b\psi - \hat{B}a\psi = ab\psi - ba\psi = 0$$

In this case, the observables A and B can be measured simultaneously with infinite precision, i.e., uncertainties $\Delta A = 0$ and $\Delta B = 0$, simultaneously. ψ is then said to be the simultaneous eigenfunction of A and B.

When observables commute, measurements of A and B do not cause any change of state (i.e., initial and final states are the same before and after the measurement).

Suppose we measure A to get value a. We then measure B to get the value b. We measure A again and still get the same value a. Clearly the state (ψ) of the system is not destroyed and so we are able to measure A and B simultaneously with infinite precision. However, if

$$[\hat{A}, \hat{B}] \neq 0$$

Namely, the operators do not commute and the two observables cannot be measured simultaneously, resulting in an uncertainty principle relation.

The most relevant example is for momentum and position:

$$[\hat{x},\hat{p}_x]\psi = (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\psi = x\frac{\hbar}{i}\frac{\partial}{\partial x}\psi - \frac{\hbar}{i}\frac{\partial}{\partial x}(x\psi)$$
$$= x\frac{\hbar}{i}\frac{\partial}{\partial x}\psi - \frac{\hbar}{i}\left(x\frac{\partial}{\partial x}\psi + \psi\frac{\partial}{\partial x}x\right) = i\hbar\psi$$
$$\Longrightarrow [\hat{x},\hat{p}_x] = i\hbar$$

which is consistent with the Heisenberg uncertainty principle.

The uncertainty relation can be generalized as follows for any two observables A and B (*Robertson uncertainty relation*) :

$$\text{If} \quad [\hat{A},\hat{B}] = i\hat{C} \qquad \text{then} \qquad \Delta A\cdot\Delta B \geq \frac{1}{2}\left|\langle\hat{C}\rangle\right| = \frac{1}{2}\left|\langle[\hat{A},\hat{B}]\rangle\right|$$

Example: $\Delta x\cdot\Delta p \geq \frac{1}{2}\left|\langle[\hat{x},\hat{p}]\rangle\right| = \frac{1}{2}\left|\langle i\hbar\rangle\right| \quad \Rightarrow \quad \Delta x\cdot\Delta p \geq \frac{\hbar}{2}$

More generally, $\left[\hat{r}_i,\hat{p}_j\right] = i\hbar\delta_{ij}$ where the Kronecker delta is $\delta_{ij} = \begin{cases}1 & i=j\\ 0 & i\neq j\end{cases}$

Summary

TDSE:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}+V(x,t)\Psi=i\hbar\frac{\partial\Psi}{\partial t}$$

Born interpretation:

$$\Psi^*(x,t)\Psi(x,t)dx=\left|\Psi(x,t)\right|^2 dx=P(x,t)dx$$

Normalization:

$$\int_{-\infty}^{\infty}P(x)dx=\int_{-\infty}^{\infty}\left|\Psi(x,t)\right|^2 dx=1$$

TISE:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+V(x)\psi=E\psi \quad \text{or} \quad \hat{H}\psi=E\psi$$

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

Conditions on ψ: single-valued, continuous, normalizable, continuous first derivative.

Expectation value of operator Ω:

$$\int_{-\infty}^{\infty}\Psi^*(x,t)\hat{\Omega}\Psi(x,t)dx$$

The Heisenberg uncertainty principle: $\Delta x\cdot\Delta p\geq\hbar/2$

Additional References

1. *The Quantum Theory of Atoms and Molecules*, Grant Ritchie, University of Oxford
2. *Introduction to Modern Physics*, John D. McGervey
3. The lecture notes linked on the course webpage.

Solving fundamental problems in quantum mechanics

Solutions of the Schrödinger Equation for

- Quantum wells with infinite and finite potential barriers
- Tunneling and scattering of electron waves incident on barriers and step potentials
- The Harmonic Oscillator Potential

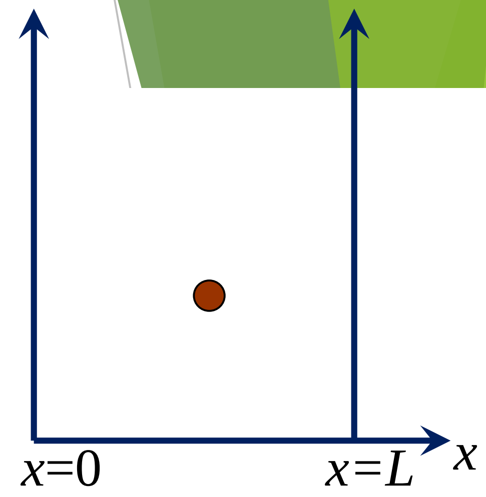
Solving fundamental problems in quantum mechanics

We are now in a position to see in detail how quantized energy levels are predicted by the Schrödinger equation.

- In quantum theory, we must determine the behavior of the particle by solving the Schrödinger equation.
- We wish to find the wavefunction $\psi(x)$ for a state of energy $E = \hbar\omega$.
- Let us solve somewhat artificial examples whose simplicity allows us to concentrate on the fundamentals.
- Again, we limit ourselves to one dimension. We can easily generalize to two and three dimensions once the formalism is fully developed.

Particle in a box (Square-Well Potential)

The simplest such system is that of a particle confined in a box with infinitely hard walls that the particle cannot penetrate.



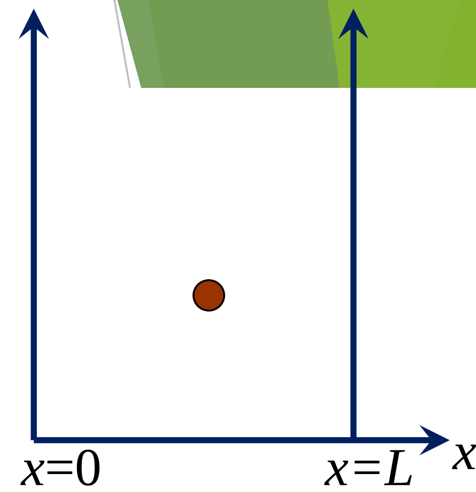
This potential is called a square well potential and is given by:

$$V(x) = \begin{cases} \infty & x \le 0, x \ge L \\ 0 & 0 < x < L \end{cases}$$

Clearly the wave function must be zero where the potential is infinite.

Boundary conditions: $\psi(x) = 0 \quad for \quad x \le 0, x \ge L$

Particle in a box (Square-Well Potential)



Where the potential $V(x)$ is zero (inside the box),

the time-independent Schrödinger equation becomes:

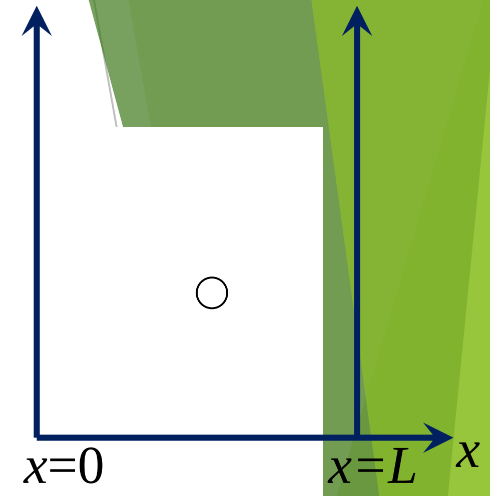
$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}=E\psi(x) \quad or \quad \hat{H}\psi(x)=E\psi$$

$$\Rightarrow \frac{\partial^2\psi(x)}{\partial x^2}=-\frac{2mE}{\hbar^2}\psi(x)=-k^2\psi(x) \quad where \quad k=\sqrt{\frac{2mE}{\hbar^2}}$$

The general solution is: $\psi(x)=Asin(kx)+Bcos(kx)$

From the left boundary condition, $\psi(x)|_{x=0}=0$, we find $B=0$.

Quantization of allowed states



The right boundary condition, $\psi(x)|_{x=L} = 0$, yields $k = \frac{n\pi}{L}$

This yields valid solutions for integer values of *n*.

The wave function is:

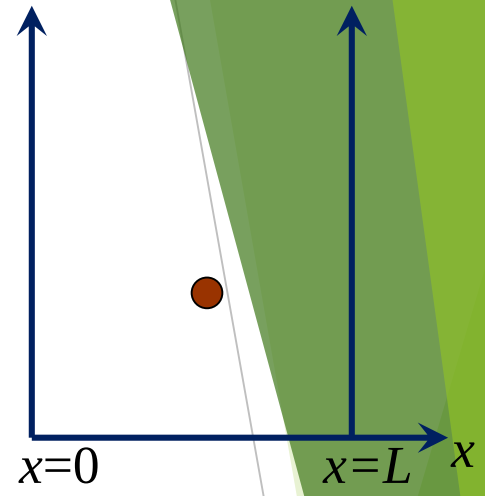
$$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right)$$

We normalize the wave function:

$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)dx = 1$$

$$\Rightarrow \quad A^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx = A^2\frac{1}{2}\int_0^L \left(1 - \cos\left(\frac{2n\pi x}{L}\right)\right)dx$$

Quantization of allowed states



$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)dx = A^2\frac{L}{2} \quad \Rightarrow A = \sqrt{\frac{2}{L}}$$

The normalized wavefunction is:

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

These functions are identical to those obtained for the fluctuations in a vibrating string with fixed ends.

Quantized Energy Levels

The quantized wave number now becomes:

$$k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}}$$

Solving for the energy yields:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = n^2 \frac{\pi^2 \hbar^2}{2mL^2} \qquad (n = 1,2,3 \ldots)\; n \in Positive\ integers$$

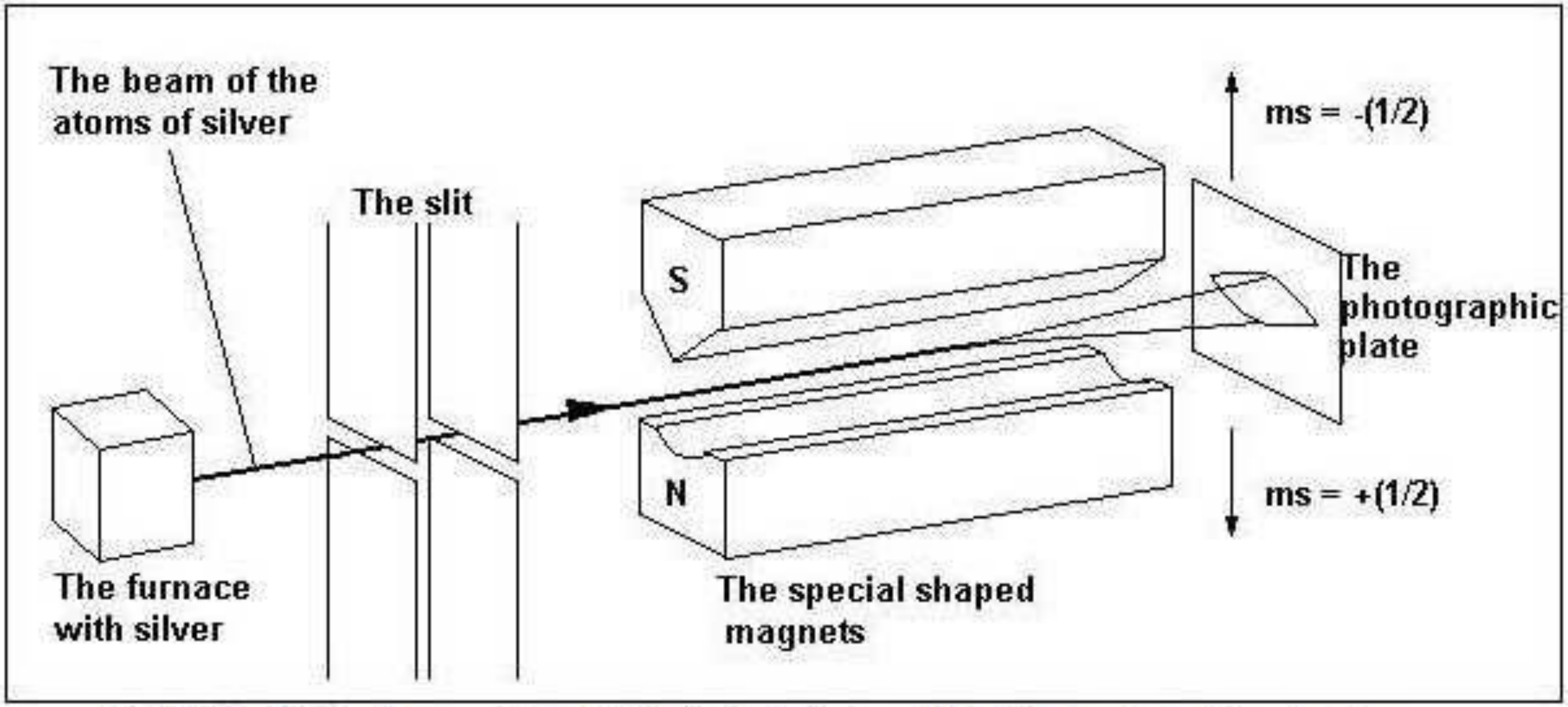
Note that the energy depends on integer values of *n*. Hence the energy is quantized and nonzero.

The special case of $n = 1$ is called the ground state.

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$$

The Stern-Gerlach experiment and Spin

Experiments in the early 1920s discovered a new aspect of nature, and at the same time found the simplest quantum system in existence. In the Stern-Gerlach experiment, a beam of hot atoms is passed through a nonuniform magnetic field. This field would interact with the magnetic dipole moment of the atom, if any, and deflect it.

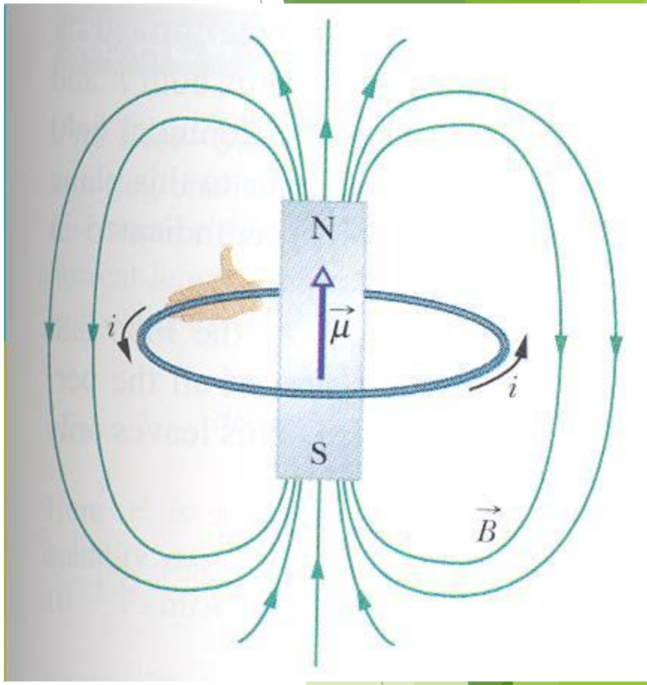


The Stern-Gerlach experiment. On the photographic plate are two clear tracks.

The Stern-Gerlach experiment and Spin

The experiment revealed that atoms (specifically, the unpaired outer electrons) have a magnetic dipole moment. In addition to possessing a charge, electrons acted like tiny bar magnets.

They also have a tiny intrinsic amount of spin angular momentum (s_z), equal to $\hbar$ /2. (This quantity is called spin, and all known elementary particles have nonzero spin except for Higgs boson.) Electrons are called spin-1/2 particles.



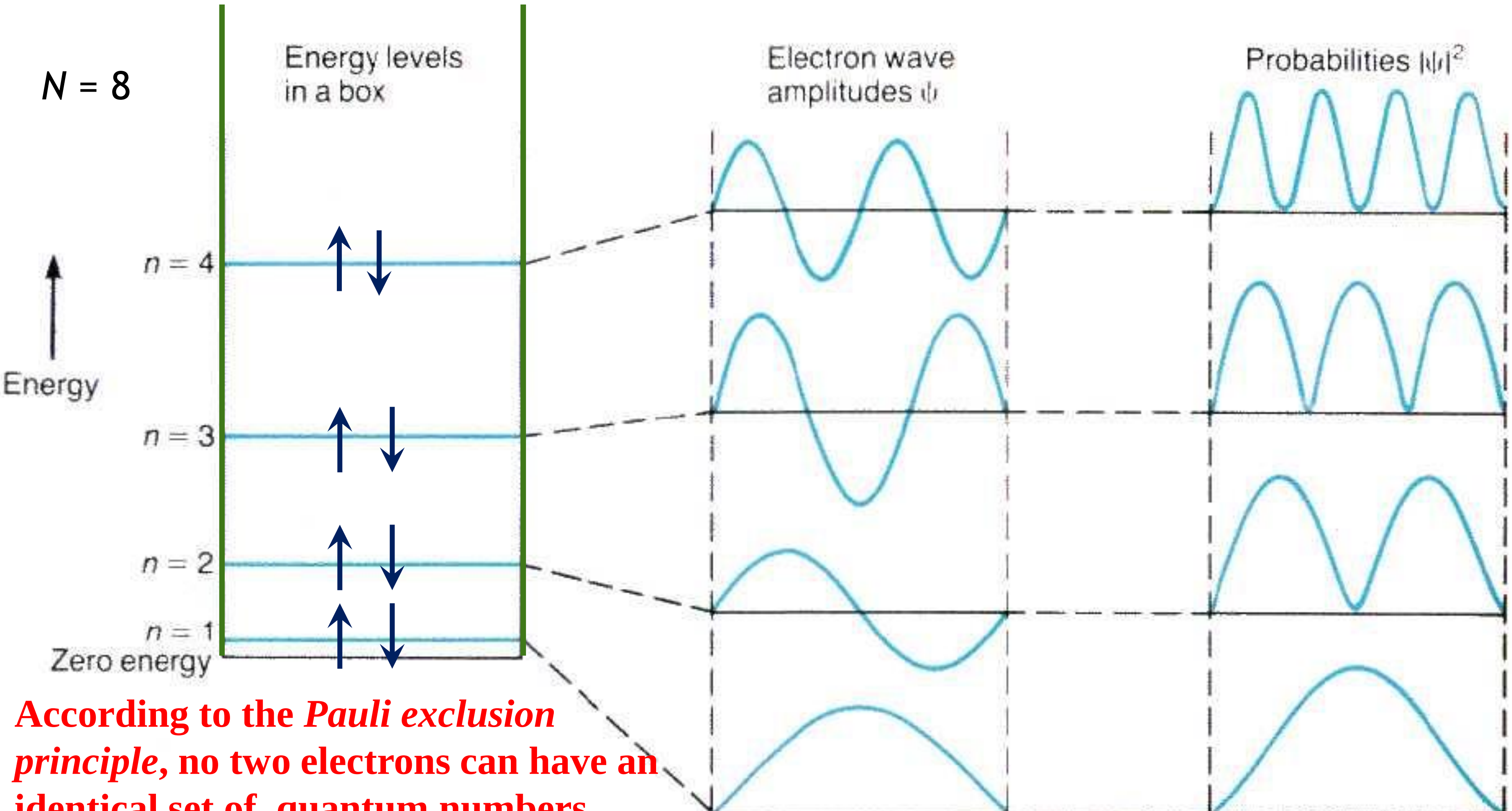
$$\vec{\mu}_z = -g_S \mu_B m_S \hat{z} \qquad where \quad \mu_B = \frac{e\hbar}{2m_e}, \quad m_S = \pm\frac{1}{2}, \qquad s_z = m_S \hbar$$

μ_B is called the Bohr magneton.

g_S is called the electron spin g-factor which has the value $g_S \approx 2$.

Filling quantum wells with *N non-interacting* electrons

First introduction of the spin quantum number: $m_s = \pm ½$. Electrons fill energy states from lowest to highest (i.e., from n small to large), forming pairs of electrons described by spin up / spin down quantum numbers m_s.



According to the *Pauli exclusion principle*, no two electrons can have an identical set of quantum numbers.