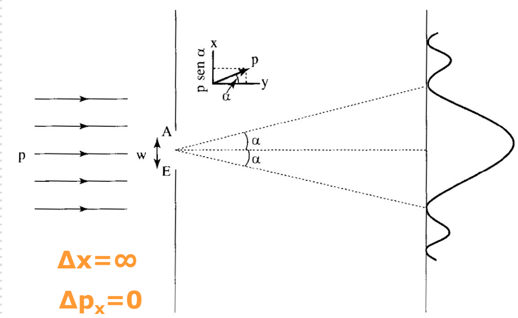
Ira N. Levine, Quantum Chemistry,

Heisenberg Uncertainty Principle

a beam of particles with momentum p, traveling in the y direction, and fall on a narrow slit (w)

uncertainty in the coordinate at the time of going through the slit = Δx

Diffraction and interference



$\Delta x=\infty$

$\Delta p_x=0$

$\Delta x=w$

$\Delta p_x = p\sin\alpha$

photographic plate

Heisenberg Uncertainty Principle

For a particle deflected upward by an angle α:

$$p_x = p\sin\alpha$$

For a particle deflected downward by an angle α:

$$p_x = -p\sin\alpha$$

most of the particles undergo deflections in the range $-\alpha$ to $+\alpha$, where α is the angle to the first minimum in the diffraction pattern

$$\Delta p_x = p\sin\alpha$$

$$\Delta x\Delta p_x = pw\sin\alpha$$

Heisenberg Uncertainty Principle

$\Delta x \Delta p_x = pw\sin\alpha$ $W\sin\alpha = \lambda$

$\Delta x \Delta p_x = p\lambda$ $\lambda = h/p$

$\Delta x \Delta p_x = h$

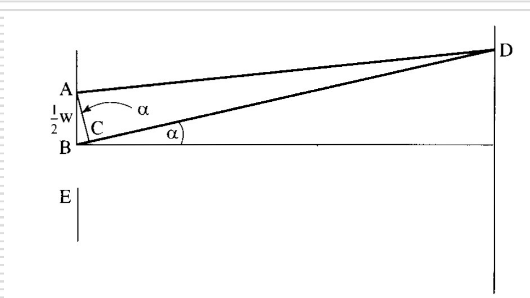
$\Delta x \Delta p_x \approx h$

$\Delta x \Delta p_x \geq h/4\pi$ Uncertainty Principle

Heisenberg Uncertainty Principle

Exercises:

Drive: $W\sin\alpha = \lambda$



Time-dependent Schrödinger equation

- The word (state) in classical mechanics means a specification of the position and velocity of each particle at some instant time, plus specification of the forces acting on the particles.
- To describe the state in quantum mechanics, we postulate the existence of a function of the coordinates called the wave function (State function), Ψ. For one particle, one-dimensional system:

$$\Psi = \Psi(x,t)$$

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

$\hbar = \frac{h}{2\pi}$ **m = particle mass, V(x,t) = potential energy. i = $\sqrt{-1}$**

Time-dependent Schrödinger equation.

Time-dependent Schrödinger equation

Born Postulate

$$|\Psi(x,t)|^2 \, dx$$

The probability at time t of finding the particle in the region of the x axis lying between x and x = dx

$|\Psi(x,t)|^2$ **Probability density**

Time-independent Schrödinger equation

Special case where the potential energy is independent of time but depends only on x

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

Schrödinger equation can be solved by the technique called separation of variables:

$$\Psi(x,t) = \psi(x)f(t)$$

the partial derivatives of this equation:

$$\frac{\partial\Psi(x,t)}{\partial t} = \frac{df(t)}{dt}\psi(x) \ , \ \frac{\partial^2\Psi(x,t)}{\partial x^2} = \frac{d^2\psi(x)}{dx^2}f(t)$$

Time-independent Schrödinger equation

Making the substitution in equation 2:

$$\frac{-}{i}\frac{df(t)}{dt}\psi(x) = \frac{-h^2}{2m}\frac{d^2\psi(x)}{dx^2}f(t) + V(x)\psi(x)f(t)$$

Dividing by

$$\psi(x)f(t)$$

$$\frac{-h}{i}\frac{1}{f(t)}\frac{df(t)}{dt} = \frac{-h^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = \mathbf{E}$$

$$\frac{-\hbar}{i}\frac{1}{f(t)}\frac{df(t)}{dt}=\frac{-\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+V(x)=E$$

$$\frac{df(t)}{f(t)}=\frac{-iE}{\hbar}dt \qquad\qquad \frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)$$

Time-independent Schrödinger equation

Taking the left side of equation:

$$\frac{df(t)}{f(t)}=\frac{-iE}{\hbar}dt$$

integration:

$$\downarrow$$

$$\ln f(t)=\frac{-iEt}{\hbar}+C \qquad \text{integration constant}$$

$$\downarrow$$

$$f(t)=e^{c}e^{-iEt/\hbar}$$

$$f(t)=Ae^{-iEt/\hbar}$$

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

ψ contains an imaginary quantity, So, it has no physical meaning.

Time-independent Schrödinger equation

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

or

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

time-independent Schrödinger equation for a single particle of mass m moving in one dimension.

The constant E has the dimension of energy.

It is postulated that E is the energy of the system.

Probability Density

Wave function is a complex, i.e.

$$|\Psi|^2=\psi\psi^*$$

ψ^* is a complex conjugate of ψ

$$|\Psi(x,t)|^2=\left[\psi(x)e^{-iEt/\hbar}\right]\left[\psi(x)e^{-iEt/\hbar}\right]^* \quad \text{for stationary state}$$

$$=e^0\psi^*(x)\psi(x)=\psi(x)\psi^*(x)=|\psi(x)|^2$$

is called the Probability Density (Time-independent wave function).

What ψ (x) means?

- ψ is sometimes a complex function, not measurable, imaginary value.
- ψψ* is a function, which may be real, and positive.
- ψ has no physical meaning but ψψ* is the probability density

The probability

What is the probability that the particle lies in some finite region of space $a \le x \le b$.

$$\int_a^b |\Psi|^2\,dx = \Pr(a \leqslant x \leqslant b)$$

The probability of a certainty

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

If we have two different wave functions, ψ_1 and ψ_2

$$\left.\begin{aligned}\int_{-\infty}^{+\infty} \psi_1(x)\psi_1^*(x)dx = 1\\ \int_{-\infty}^{+\infty} \psi_2(x)\psi^*{}_2(x)dx = 1\end{aligned}\right\} \quad \textbf{\textit{Normalized}}\text{ function}$$

The probability

$$\int_{-\infty}^{+\infty} \psi_1(x)\psi^*{}_2(x)dx = 0$$

$$\int_{-\infty}^{+\infty} \psi_2(x)\psi^*{}_1(x)dx = 0$$

Orthogonal functions

$$\int_{-\infty}^{+\infty} \psi_i(x)\psi^*{}_j(x)dx = \delta_{ij}$$

Orthonormalized functions

δ_{ij}(called Kronecker Delta) = $\begin{cases} = 0 & i \neq j \\ = 1 & i = j \end{cases}$

The probability

EXAMPLE : A one-particle, one-dimensional system has $\Psi = a^{-1/2}e^{-|x|/a}$ at t = 0, where a = 1.0000 nm (1 nm = 10^{-9}m). At t = 0,the particle's position is measured, (a) Find the probability that the measured value lies between x = 1.5000 nm and x = 1.5001 nm. (b) Find the probability that the measured value is between x = 0 and x = 2 nm. (c) Verify that Ψ is normalized.

a) $|\Psi|^2\,dx = a^{-1}e^{-2|x|/a}\,dx = (1\text{ nm})^{-1}e^{-2(1.5\text{ nm})/(1\text{ nm})}(0.0001\text{ nm}) = 4.979 \times 10^{-6}$

b)
$$\Pr(0 \leqslant x \leqslant 2\text{ nm}) = \int_0^{2\text{ nm}} |\Psi|^2\,dx = a^{-1}\int_0^{2\text{ nm}} e^{-2x/a}\,dx$$
$$= -\tfrac{1}{2}e^{-2x/a}\Big|_0^{2\text{ nm}} = -\tfrac{1}{2}(e^{-4} - 1) = 0.4908$$

c)
$$\int_{-\infty}^{\infty} |\Psi|^2\,dx = a^{-1}\int_{-\infty}^{0} e^{2x/a}\,dx + a^{-1}\int_0^{\infty} e^{-2x/a}\,dx$$
$$= a^{-1}(\tfrac{1}{2}ae^{2x/a}\Big|_{-\infty}^{0}) + a^{-1}(-\tfrac{1}{2}ae^{-2x/a}\Big|_0^{\infty}) = \tfrac{1}{2} + \tfrac{1}{2} = 1$$

Homeworks:
1) What is a complex number?
2) Two different systems of units are cgs Gaussian and SI.
State units of length, mass, force and charge in these systems.
3) Solve problems 1-29

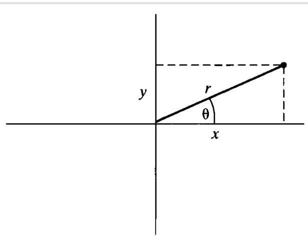
COMPLEX NUMBERS

$z = x + iy$ $\qquad$ $i \equiv \sqrt{-1}$

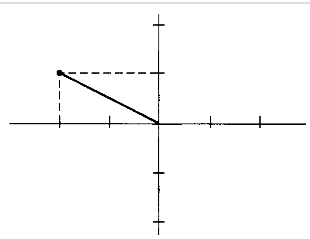
x and y (real and imaginary parts of z) are real numbers

x= Re(z); y = Im(z).

A convenient representation:



z = x + iy



-2 + i

the complex conjugate z* $z^* \equiv x - iy = re^{-i\theta}$

$$zz^* = (x+iy)(x-iy) = x^2 + iyx - iyx - i^2y^2$$

$$zz^* = x^2 + y^2 = r^2 = |z|^2$$

$$|z| = r = (x^2+y^2)^{1/2}, \qquad \tan\theta = y/x$$

$$z = x + iy$$

$$x = r\cos\theta, \qquad y = r\sin\theta$$

$$z = r\cos\theta + ir\sin\theta = re^{i\theta} \qquad e^{i\theta} = \cos\theta + i\sin\theta$$

- ✓ z is real if and only if z = z*.
- ✓ (z*)* = z
- ✓ $i^2 = -1$

$$\left.\begin{aligned} z_1 &= r_1 e^{i\theta_1} \\ z_2 &= r_2 e^{i\theta_2} \end{aligned}\right\} z_1 z_2 = r_1 r_2 e^{i(\theta_1+\theta_2)}, \qquad \frac{z_1}{z_2} = \frac{r_1}{r_2} e^{i(\theta_1-\theta_2)}$$

$$(z_1 z_2)^* = z_1^* z_2^*$$

$$\left(\frac{z_1}{z_2}\right)^* = \frac{z_1^*}{z_2^*}, \qquad (z_1+z_2)^* = z_1^* + z_2^*, \qquad (z_1-z_2)^* = z_1^* - z_2^*$$

$$|z_1 z_2| = |z_1||z_2|, \qquad \left|\frac{z_1}{z_2}\right| = \frac{|z_1|}{|z_2|}$$

UNITS

the cgs Gaussian system:
- ✓ Length → centimeter (cm)
- ✓ Mass → gram (g)
- ✓ Time → second (s)
- ✓ Force → dynes (dyn)
- ✓ energy → ergs

Coulomb's law $F = Q'_1 Q'_2 / r^2$ statcoulombs (statC)

International System (SI):
- ✓ Length → meter (m)
- ✓ Mass → kilogram (kg)
- ✓ Time → second (s)
- ✓ Force → newtons (N)
- ✓ energy → joules (J)

Coulomb's law $F = Q_1 Q_2 / 4\pi\varepsilon_0 r^2$

$Q' = Q/(4\pi\varepsilon_0)^{1/2}$

Calculus

- c, n, and b are constants and f and g are functions of x,

$$\frac{dc}{dx} = 0, \quad \frac{d(cf)}{dx} = c\frac{df}{dx}, \quad \frac{dx^n}{dx} = nx^{n-1} \quad \frac{de^{cx}}{dx} = ce^{cx}$$

$$\frac{d(\sin cx)}{dx} = c\cos cx, \quad \frac{d(\cos cx)}{dx} = -c\sin cx, \quad \frac{d\ln cx}{dx} = \frac{1}{x}$$

$$\frac{d(f+g)}{dx} = \frac{df}{dx} + \frac{dg}{dx}, \quad \frac{d(fg)}{dx} = f\frac{dg}{dx} + g\frac{df}{dx}$$

$$\frac{d(f/g)}{dx} = \frac{d(fg^{-1})}{dx} = -fg^{-2}\frac{dg}{dx} + g^{-1}\frac{df}{dx}$$

$$\frac{d}{dx}f(g(x)) = \frac{df}{dg}\frac{dg}{dx}$$

An example of the last formula is $d[\sin(cx^2)]/dx = 2cx\cos(cx^2)$. Here, $g(x) = cx^2$ and $f = \sin$.

$$\int cf(x)\,dx = c\int f(x)\,dx, \quad \int [f(x) + g(x)]\,dx = \int f(x)\,dx + \int g(x)\,dx$$

$$\int dx = x, \quad \int x^n\,dx = \frac{x^{n+1}}{n+1} \text{ for } n \neq -1, \quad \int \frac{1}{x}dx = \ln x$$

$$\int e^{cx}\,dx = \frac{e^{cx}}{c}, \quad \int \sin cx\,dx = -\frac{\cos cx}{c}, \quad \int \cos cx\,dx = \frac{\sin cx}{c}$$

$$\int_b^c f(x)\,dx = g(c) - g(b) \quad \text{where } \frac{dg}{dx} = f(x)$$