

Chapter 1. The Schrödinger Equation

1. What is QM?

Mathematical model that describes the behavior of small (atomic and subatomic) particles

2. Why QM doesn't make sense?

Things that make sense are part of our everyday experience. For example, if I drop a book, it will land on the floor. This makes sense to me, because it has happened many times before. Small particles are not a part of our everyday experience.

3. What are the main differences between QM and CM?

- QM works for all objects. CM is QM in a limit of large objects.
- In QM, particle can be at many places at the same time (superposition of states).
- In QM, particle cannot have any energy or speed, only quantized values
- In QM, we cannot determine the location and velocity of the particle in the future. We can only determine the probability that location and velocity will have a certain value. (Heisenberg uncertainty principle).
- In QM, we can have tunneling (particle can penetrate the potential energy barrier).
- wave-particle duality in QM

4. Why did we have to invent QM? Historical overview.

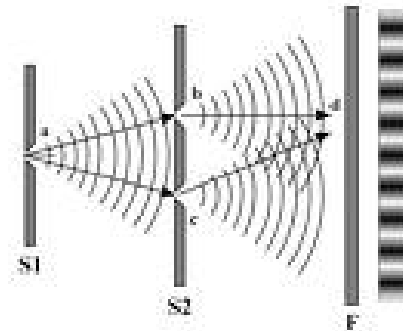
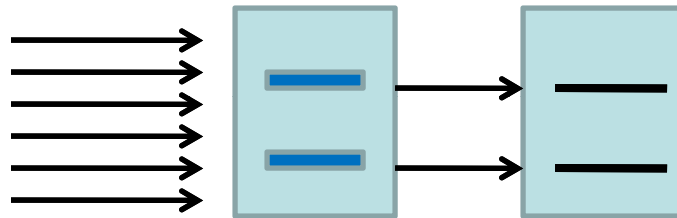
4. Why did we have to invent QM? Historical overview, LIGHT:

LIGHT: wave and a particle

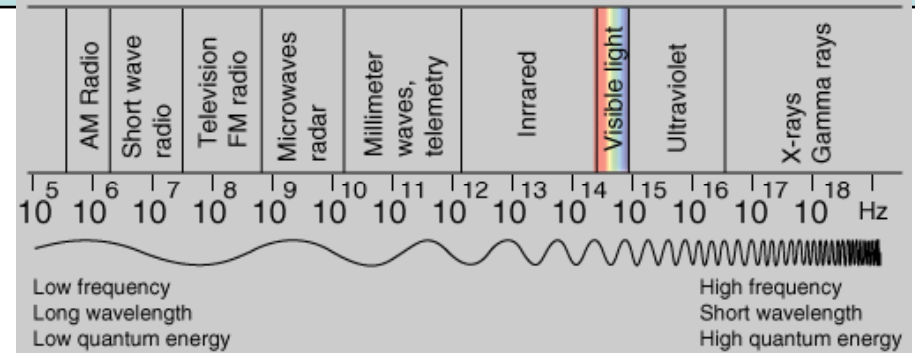
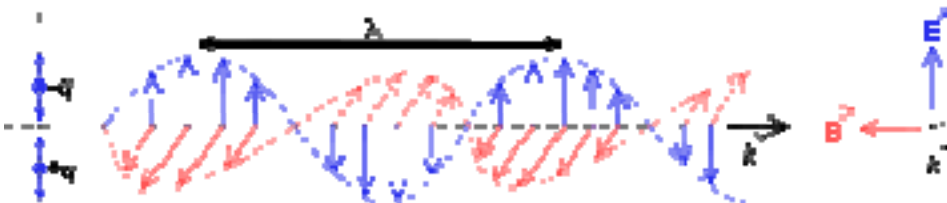
Thomas Young (1801)
 Confirms the wave nature of light (observed diffraction and interference)

Double slit experiment:  Waves show pattern like this:

Particles show pattern like this:



James Clerk Maxwell (1860)
 Developed equations that unite electricity and magnetism (described light as an electromagnetic wave). His predicted speed of light coincided with measured c . So, he concluded that light as an el.-mag. wave: $\lambda \cdot \nu = c$



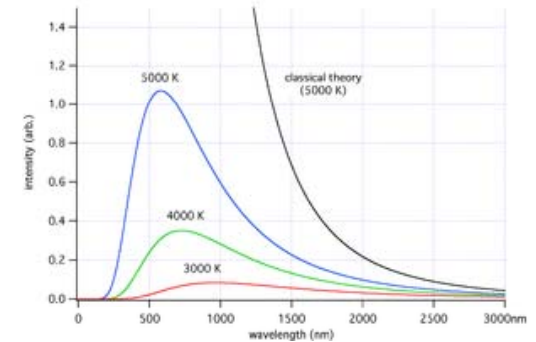
Max Planck (1900)

Explained blackbody radiation. Emission of light from a heated blackbody (absorbs all light, nothing passes through or is reflected). Emission does not obey classical physics. Planck explained it by assuming that the energy of oscillators was quantized.

Blackbody: can be modeled by an oven with a pinhole: light comes in, but nothing comes out; when heated, it emits light whose spectrum depends on temperature, but not on the material.

$$\text{Wien's displacement law: } \lambda_{MAX} = \frac{b}{T}$$

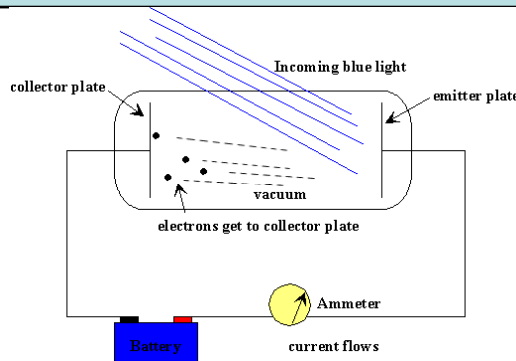
$$\text{Stefan-Boltzman law: } I_{TOT} = \sigma \cdot T^4$$



Albert Einstein (1905)

Explained photoelectric effect (light shining on metal causes emission of electrons). According to classical: E_k of electron should be proportional to light intensity. Instead, it was found proportional to frequency). Einstein explained this by assuming that light is a particle.

$E_{\text{photon}} = h\nu = \Phi + E_K$ (Φ : energy required to remove electron, metal's work function).



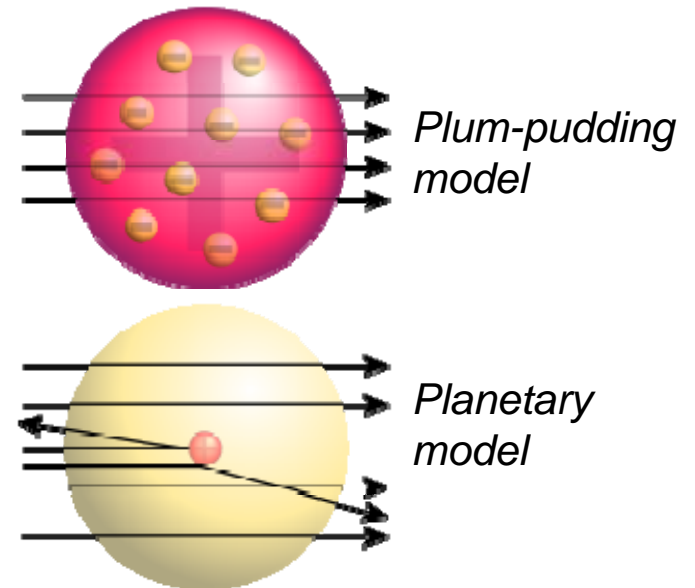
4. Why did we have to invent QM? Historical overview, MATTER:

Rutherford (1911)

Proposed a planetary model of the atom. Problem with this model: classical physics predicts that accelerated charges will emit EM radiation. So, electron circling round nucleus would emit energy and finally collapse into the nucleus.

Before Rutherford's findings, people believed in a plum-pudding model of the atom: electrons (plums) surrounded by a soup of positive charge (pudding).

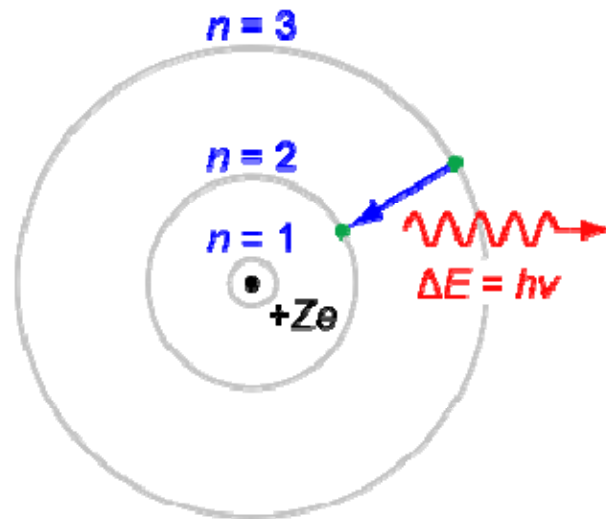
Rutherford's experiment: send α -particles (He^{2+} : 2 p & 2 n) through a gold foil). According to plum-pudding model: all particles should have been deflected by a few degree. Observed: small percent of particles deflected by 90° . Rutherford explained this findings by proposing a planetary model of the atom in which nucleus contained a large density of positive charge.



Niels Bohr (1913)

Found a solution to the Rutherford model by assuming that the electron energies are quantized. When electron makes a transition from one state to another, energy is absorbed or emitted: $E_{\text{upper}} - E_{\text{lower}} = h\nu$

His model worked for hydrogen, but failed for larger atoms. Problem: he was using classical mechanics to describe electronic motion



De Broglie (1923)

Electrons can behave like waves. The wavelength of the electron would be:

$$\lambda = h/p = h/mv$$

Later, experiments confirmed it: diffraction of electrons, helium atoms and hydrogen molecules.

The Uncertainty Principle

“There is a limit to the fineness of our powers of observation and the smallness of the accompanying disturbance- a limit which is inherent in the nature of things and can never be surpassed by improved technique or increased skill on the part of the observer.”

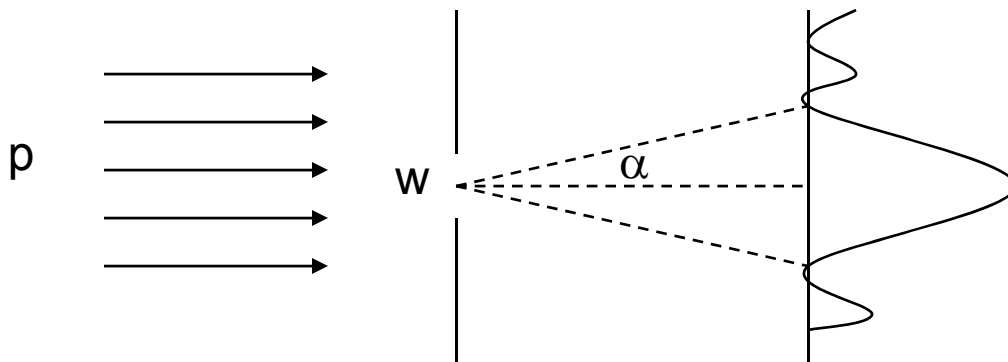
Dirac

Our measurement introduces an uncontrollable disturbance in the system being measured.

The wave-particle duality of subatomic particles imposes a limit on our ability to measure simultaneously the position and the momentum of particle. The more precisely we determine the position, the less accurate is our determination of the momentum.

$$\Delta x \Delta p = h$$
$$\Delta E \Delta t = h$$

Example: diffraction of particles



The uncertainty in x position is determined by width w of a slit:

$$\Delta x = w$$

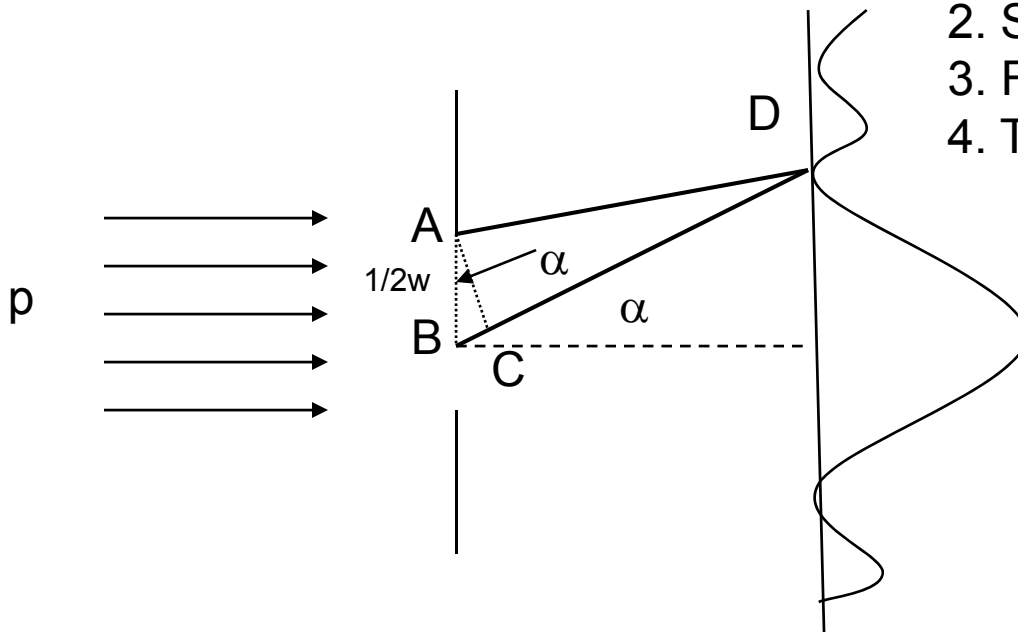
When particles diffract (because they have wave properties), their momentum changes. The x component of momentum becomes $p \sin \alpha$ or $-p \sin \alpha$ (depending on the direction). So, total uncertainty in momentum will be $\Delta p = p \sin \alpha$

$$\text{So, } \Delta p \Delta x = p w \sin \alpha$$

The Uncertainty Principle

-How to calculate α :

1. First minimum occurs when $BD-AD=\lambda/2$
2. Draw AC so that $AD=CD$. So, $BC= \lambda/2$
3. Since AD and BD are nearly parallel, so $BAC= \alpha$
4. $BC=1/2w\sin\alpha$
5. $\lambda/2=1/2w\sin \alpha$...so $\sin \alpha= \lambda/w$



To get uncertainty:

1. The uncertainty: $\Delta p \Delta x = p w \sin \alpha$
2. Substituting for α : $\Delta p \Delta x = p \lambda$
3. From de Broglie: $\lambda = h/p$
4. The uncertainty is: $\Delta p \Delta x = h$

So, the product of the uncertainties is of the order of magnitude of Planck constant

The Time Dependent Schrodinger Equation

We define a wave function Ψ . This is a state function that describes our particles position. For 1D system:

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

To find the future state of the system, we need to know how the equation changes with time - Schrodinger equation:

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

Example: A certain one-particle, one dimensional system has a wave function:

$$\Psi = a e^{-ibt} e^{-bmx^2 / \hbar}$$

Find the potential energy function V for this system.

$$\frac{d\Psi}{dt} = ae^{-bmx^2/\hbar} (-ib)e^{-ibt} = -ib\Psi$$

$$\frac{d\Psi}{dx} = a(-2bmx/\hbar)e^{-bmx^2/\hbar} e^{-ibt} = -2bmx/\hbar\Psi$$

$$\frac{d^2\Psi}{dx^2} = (-(2bm/\hbar)e^{-bmx^2/\hbar} - 2(bmx/\hbar)(-2(bmx/\hbar)e^{-bmx^2/\hbar}))ae^{-ibt}$$

$$\frac{d^2\Psi}{dx^2} = -2bm/\hbar\Psi + 4b^2m^2x^2/\hbar^2\Psi$$

Substituting into Schrodinger equation: $V=2b^2mx^2$

The Time-Independent Schrodinger Equation

-It's simpler than time-dependent equation.

-We restrict ourselves to looking for those solutions of time-dependent Schrodinger equation that can be written as the product of a function of time and a function of x . In general, such expression would not be correct. But, it turns out that we can express general solution to S.E. as the sum of such special, separable solutions.

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

-Taking partial derivatives:

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

-Substitution into time-dependent equation gives:

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

-Dividing by ψ :

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

The Time-Independent Schrodinger Equation

-The right-hand side does not depend on t, the left-hand side does not depend on x. So, the function that both of these sides equal must also be independent of t and x. We'll call it constant E. The left side is then:

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

-Integrating both sides gives:

$$\ln f(t) = -\frac{iEt}{\hbar} + C \longrightarrow f(t) = e^C e^{-\frac{iEt}{\hbar}} = Ae^{-\frac{iEt}{\hbar}} \xrightarrow{\text{A can be omitted}} f(t) = e^{-\frac{iEt}{\hbar}}$$

-The right side is then:

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

This is time-independent Schrodinger equation. It gives us important info about the system. E is the energy of the system.

Finding solutions to time-independent S.E. will generate the components we need for building time-dependent solutions.

Probability

If an experiment has n possible outcomes, m of which favor the occurrence of outcome A , then the probability that A occurs is m/n .

Example: Frank and Ana have two children, one of which is a girl. What is the probability that the other child is a girl?

GG BG GB 33% chance

Bob and Barbara have two children. The older child is a girl. What is a probability that the younger child is a girl?

BG GG 50 % chance

In QM, we find the probability of finding a particle in a certain region of space, by summing up the probabilities in that space:

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

Example: At a certain instant of time, a one-particle, 1D system has:

$$\Psi = \left(\frac{2}{b^3} \right)^{\frac{1}{2}} x e^{-\frac{|x|}{b}}$$

Where $b=3$ nm. If a measurement of x is made at this time in the system, find the probability that the result lies between 0 and 2 nm.

First we get the square value:

$$|\Psi|^2 = \left(\frac{2}{b^3} \right) x^2 e^{-\frac{2|x|}{b}}$$

Then, we integrate:

$$\int_0^{2nm} |\Psi|^2 dx = \frac{2}{b^3} \int_0^2 x^2 e^{-\frac{2|x|}{b}} dx$$

$$u = x^2$$

-We use integration by parts:

$$dv = e^{-\frac{2x}{b}} dx$$

$$du = 2x dx$$

$$v = \int e^{-\frac{2x}{b}} dx = -\frac{b}{2} e^{-\frac{2x}{b}}$$

$$\int_0^{2nm} |\Psi|^2 dx = \frac{2}{b^3} \left(x^2 \left(-\frac{b}{2} e^{-\frac{2x}{b}} \right) + \frac{b}{2} \int e^{-\frac{2x}{b}} 2x dx \right)$$

Need to do another integration by parts:

$$A = \int e^{-\frac{2x}{b}} 2x dx$$

$$u = x$$

$$dv = e^{-\frac{2x}{b}} dx$$

$$du = dx$$

$$v = \int e^{-\frac{2x}{b}} dx = -\frac{b}{2} e^{-\frac{2x}{b}}$$

$$A = x \left(-\frac{b}{2} e^{-\frac{2x}{b}} \right) + \frac{b}{2} \int e^{-\frac{2x}{b}} dx = -\frac{bx}{2} e^{-\frac{2x}{b}} - \frac{b^2}{4} e^{-\frac{2x}{b}}$$

Finally:

$$\int_0^{2nm} |\Psi|^2 dx = \frac{2}{b^3} e^{-\frac{2x}{b}} \left(-\frac{x^2 b}{2} - \frac{b^2 x}{2} - \frac{b^3}{4} \right) \Bigg|_0^{2nm} = -e^{-\frac{2x}{b}} \left(\frac{x^2}{b^2} + \frac{x}{b} + \frac{1}{2} \right) \Bigg|_0^{2nm}$$

$$\int_0^{2nm} |\Psi|^2 dx = -e^{-\frac{4}{3}} \left(\frac{4}{9} + \frac{2}{3} + \frac{1}{2} \right) + \frac{1}{2} = 0.0753$$

Probability

Since it is certain that the particle is somewhere on the x-axis, we have the requirement:

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$$

When ψ satisfies this condition, it is said to be normalized.

Example: Verify that ψ from the previous example is normalized.

$$\Psi = \left(\frac{2}{b^3}\right)^{\frac{1}{2}} x e^{-\frac{|x|}{b}} \quad |\Psi|^2 = \left(\frac{2}{b^3}\right) x^2 e^{-\frac{2|x|}{b}} \quad \int_{-\infty}^{\infty} |\Psi|^2 dx = \frac{2}{b^3} \int_{-\infty}^{\infty} x^2 e^{-\frac{2|x|}{b}} dx = 1$$

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = \frac{2}{b^3} \int_{-\infty}^{\infty} x^2 e^{-\frac{2|x|}{b}} dx = 1$$

$$\frac{2}{b^3} \int_{-\infty}^{\infty} x^2 e^{-\frac{2|x|}{b}} dx = \frac{2}{b^3} \int_{-\infty}^0 x^2 e^{\frac{2x}{b}} dx + \frac{2}{b^3} \int_0^{\infty} x^2 e^{-\frac{2x}{b}} dx$$

-Let $w=-x$ for the first integral:

$$\int_{-\infty}^0 x^2 e^{-\frac{2x}{b}} dx = \int_{\infty}^0 w^2 e^{-\frac{2w}{b}} (-dw) = \int_0^{\infty} w^2 e^{-\frac{2w}{b}} dw$$

-The two integrals are the same:

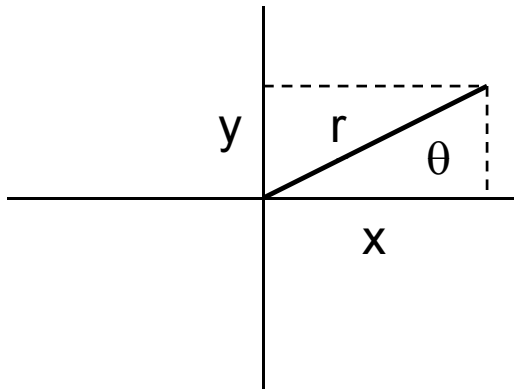
$$\frac{2}{b^3} \int_{-\infty}^{\infty} x^2 e^{-\frac{2|x|}{b}} dx = 2 \frac{2}{b^3} \int_0^{\infty} x^2 e^{-\frac{2x}{b}} dx = \frac{4}{b^3} \frac{2!}{\left(\frac{2}{b}\right)^3} = 1$$

Complex Numbers

Since wave function can be complex, we'll review complex numbers.
Two ways to represent complex numbers:

$$z = x + iy$$

$$z = re^{i\theta}$$



Absolute value: $|z| = r = \sqrt{x^2 + y^2}$

Phase (in radians): $\tan \theta = \frac{y}{x}$

1radian=180/ π degrees ~57.3 degrees
--

$$x = r \cos \theta$$

$$y = r \sin \theta$$

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

since

$e^{i\theta} = \cos \theta + i \sin \theta$

Example: Find the absolute value and a phase of: $1-2i$

$$r = \sqrt{1^2 + (-2)^2} = \sqrt{5} \quad \tan \theta = \frac{-2}{1} = -2$$

$$\theta = -63.4^\circ = 296.6^\circ = 5.176 \text{ radians}$$

$$z = \sqrt{5}e^{5.176i}$$

Complex Numbers

Complex conjugate of $z=x+iy$: $z^*=x-iy$;

$$z=re^{i\theta}; z^*=re^{-i\theta}$$

Product of z and its complex conjugate gives: $zz^*=r^2$

Operations:

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

$$\left(\frac{z_1}{z_2}\right)^* = \frac{z_1^*}{z_2^*}$$

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

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

Complex Numbers

For the absolute values:

$$|z_1 z_2|^* = |z_1|^* |z_2|^*$$

$$\frac{|z_1|^*}{|z_2|^*} = \frac{|z_1|^*}{|z_2|^*}$$

So, if ψ is a complex wave function:

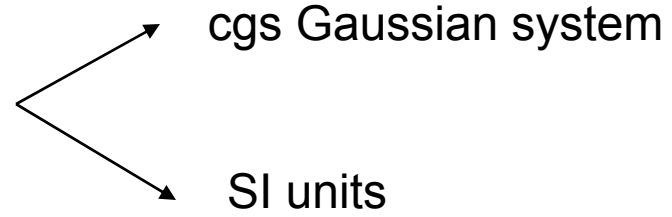
$$|\psi^2| = |\psi|^2 = \psi^* \psi$$

Example: Find the complex conjugate of: a) -4; b) -2i; c) $2e^{-i\pi/5}$

- a) -4
- b) 2i
- b) $2e^{i\pi/5}$

Units

Two different systems of units are used:



	Gaussian	SI
length	cm	m
mass	g	kg
time	s	s
force	dyn	N
energy	ergs	joules

Units

Coulomb law:

-In Gaussian units: $F=Q_1'Q_2'/r^2$ (charge expressed in statcoulombs)

-In SI units: $F=Q_1'Q_2'/4\pi\epsilon_0r^2$ (charge is expressed in coulombs)

Example: Calculate the force of an α particle passing a gold atomic nucleus at a distance of 0.003 Å. Do the calculation twice, once using SI units and once using Gaussian units.

- α particle is a helium nucleus.

SI units: atomic number of Helium is 2, of Au is 79:

$$F = \frac{Q_1 Q_2}{4\pi\epsilon_0 r^2} = \frac{2(1.6 \cdot 10^{-19} \text{ C})79(1.6 \cdot 10^{-19} \text{ C})}{4\pi(8.854 \cdot 10^{-12} \text{ C}^2 / \text{Nm}^2)(3 \cdot 10^{-13} \text{ m})^2} = 0.405 \text{ N}$$

Gaussian units: proton charge in statC, radius in cm, no need to use $4\pi\epsilon_0$ term:

$$F = \frac{Q_1 Q_2}{r^2} = \frac{2(4.8 \cdot 10^{-10} \text{ statC})79(4.8 \cdot 10^{-10} \text{ statC})}{(3 \cdot 10^{-11} \text{ cm})^2} = 40500 \text{ dyn}$$