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Comunicazioni docente → studente: e-mail, MOODLE (password: chim-comput)

Comunicazioni studente → docente: e-mail, telefono, in studio

Ricevimento: su appuntamento (anche al volo)

SCOPO DEL CORSO

1) Acquisire conoscenze sulle basi teoriche della chimica ed in particolare sulla chimica quantistica. Capire i fondamenti della natura atomica e molecolare della materia e dei concetti cardine di funzione d'onda, legame chimico e quantizzazione delle osservabili fisiche.
2) Acquisire conoscenze e capacità per risolvere semplici problemi di chimica quantistica.

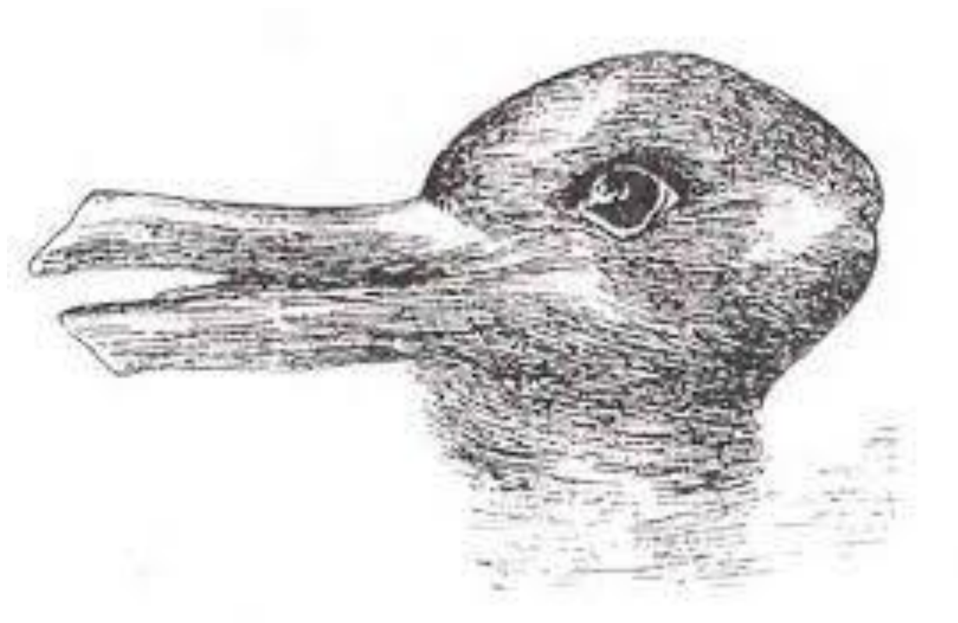
MATERIALE DIDATTICO

1) I. N. Levine, Quantum Chemistry (testo di riferimento) 5 ed. 2000, Prentice-Hall International, Inc. (OK anche 4 ed.)
2) P. Atkins e J. De Paula, Chimica Fisica, Qunta Edizione Italiana 2012, Zanichelli Editore
3) Diapositive lezioni (MOODLE). Usare come guida allo studio

Conoscenze di base

1. **Algebra elementare**
2. **Derivate, integrali** (semplici e multipli)
3. **Sommatorie, serie**
4. **Numeri complessi** (richiami in classe)
5. **Equazioni differenziali** (richiami in classe)
6. **Vettori** (richiami in classe)
7. **Concetti di fisica classica**: Es. quantità di moto, momento della quantità di moto, energia cinetica, energia elettrostatica. (richiami in classe)
8. **Concetti di chimica di base** (protone, elettrone, atomo, molecola, configurazioni elettroniche di atomi, orbitali)

LA MECCANICA QUANTISTICA



FUNDAMENTAL STEPS **(wave nature of light)**

1801. Thomas Young gave convincing experimental evidence for the wave nature of light by observing diffraction and interference when light goes through two adjacent pinholes

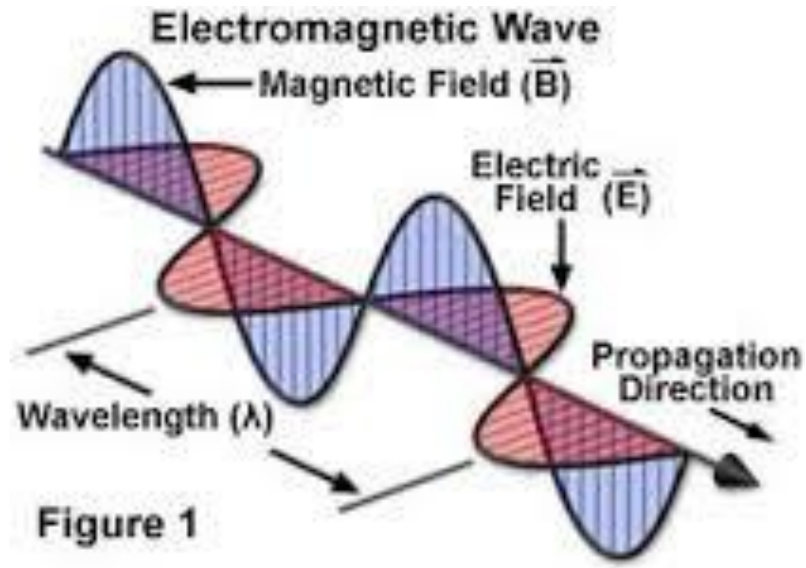
Diffraction is the bending of a wave around an obstacle.
Interference is the combining of two waves to give a wave whose intensity at each point in space is the vector sum of the intensities at that point resulting from each interfering wave

FUNDAMENTAL STEPS (wave nature of light)

1860. James C. Maxwell developed four equations, known as Maxwell's equations, which unify the laws of electrostatics and magnetism. Maxwell concluded that light is an electromagnetic wave

ELECTROMAGNETIC WAVES

All electromagnetic waves travel at speed of light c (dependent on medium). In vacuum, c = 2.998 10^8 m/s. Frequency ν, period T and wavelength λ of an electromagnetic wave are related by



$$\lambda = cT \qquad \lambda\nu = c$$

Radiation type	Frequency	Wavelength
Radio-waves	< 300 MHz	>1 m
Micro-waves	300 MHz - 300 GHz	1 m - 1 mm
Infrared	300 GHz - 428 THz	1 mm - 700 nm
Visible	428 THz - 749 THz	700 nm - 400 nm
UV	749 THz - 30 PHz	400 nm - 10 nm
X-rays	30 PHz - 300 EHz	10 nm - 1 pm
Γ-rays	>300 EHz	<1 pm

ENERGY EMITTED BY ATOMS IS QUANTIZED

1900. Planck discovered that the atoms of a blackbody could emit light energy only in amounts given by (blackbody = object that absorbs all light falling on it. A good approximation to a blackbody is a cavity with a tiny hole)

$$\boxed{E = h\nu}$$

where ν is the radiation's frequency and h is a proportionality constant, called Planck's constant

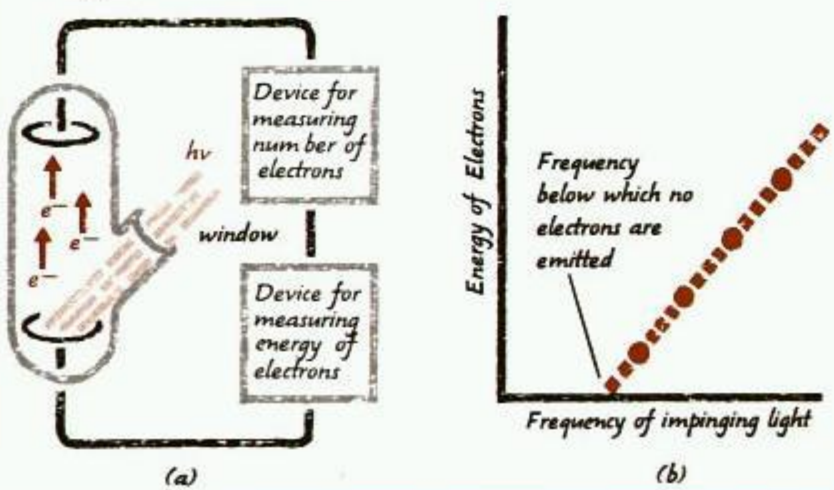
$$h = 6.6\ 10^{-34}\ \text{J s}$$

FUNDAMENTAL STEPS (particle-like nature of light)

1905. Albert Einstein discovered the photoelectric effect. In the photoelectric effect, light shining on a metal causes emission of electrons. The kinetic energy of an emitted electron is independent of the light's intensity, but increases as the light's frequency increases

Figura 9 L'effetto fotoelettrico

a) Schema dell'apparecchio utilizzato per lo studio dell'effetto fotoelettrico
b) La frequenza della luce deve superare un valore di soglia affinche' avvenga l'emissione fotoelettrica



Observations could be explained by regarding light as composed of particle-like entities (called photons), with each photon having an energy

$$E = h\nu$$

FUNDAMENTAL STEPS **(atomic nature of matter)**

1904. Thomson proposed the "raisin bread" model for atoms. In this model, the atomic volume is made by a continuous distribution of positive charge, where negative charged particles, the electrons, get around with chaotic motion

1909. Rutherford carried out a series of experiments in which a beam of α particles passed through a thin metal foil and observed the deflections of the particles. α particles are (positively charged) helium nuclei. Most of the α particles passed through the foil essentially undeflected, but a few underwent large deflections, some being deflected backward. Conclusion: <u>the atom is basically empty space with positive charge being concentrated in a tiny, heavy nucleus</u>

FUNDAMENTAL STEPS (atomic nature of matter)

Atom: An atom contains a tiny (10^{-13} to 10^{-12} cm radius), heavy nucleus consisting of neutrons and Z protons, where Z is the atomic number. Outside the nucleus there are Z electrons. The charged constituents of atoms interact according to Coulomb's law. The nucleons are held together in the nucleus by strong, short-range nuclear forces. The radius of an atom is about one angstroem (symbol $\text{Å} = 10^{-10}$ m). Molecules have more than one nucleus

1911. Rutherford proposed a planetary model of the atom in which the electrons revolved about the nucleus in various orbits. According to classical electromagnetic theory, an accelerated charged particle radiates energy in the form of electromagnetic waves. Hence the electrons should continually lose energy and therefore would collapse toward the nucleus

FUNDAMENTAL STEPS **(atomic nature of matter)**

1913. Bohr assumed that the energy of the electron in a hydrogen atom is quantized, with the electron constrained to move only on one of a number of allowed circles (orbits). When an electron makes a transition from one orbit to another, a photon of light whose frequency ν satisfies

$$E_{upper} - E_{lower} = h\nu$$

is absorbed or emitted, where E_{upper} and E_{lower} are the energies of the upper and lower states (conservation of energy). Bohr theory is in agreement with the observed hydrogen spectrum

However, attempts to fit the helium spectrum failed. Moreover, the theory could not account for chemical bonds in molecules

FUNDAMENTAL STEPS (wave nature of matter)

1927. De Broglie suggested that the motion of electrons might have a wave aspect; that an electron of mass m and speed v would have a wavelength

$$\boxed{\lambda = \frac{h}{mv} = \frac{h}{p}}$$

associated with it, where p is the linear momentum. De Broglie arrived at his conclusion by reasoning in analogy with photons

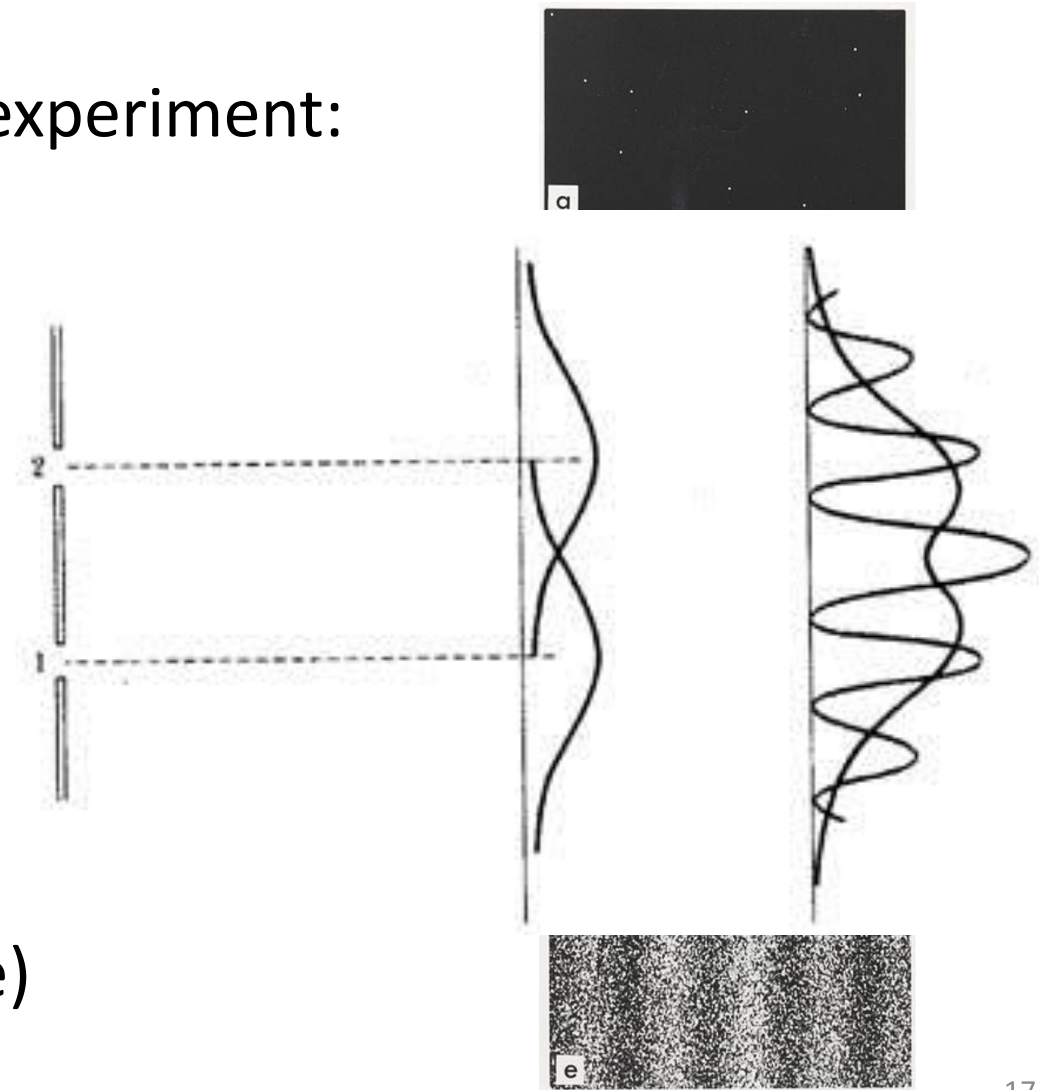
WAVE-PARTICLE DUALISM OF MATTER

The particles forming the matter (electrons, protons, atoms, molecules) show a wave-particle dual behavior

The appearance of the wave or particle behavior of matter depends on how the system interacts with the experimental device

WAVE-PARTICLE DUALISM OF MATTER

Electron diffraction experiment:



Sorgente
luce, elettroni,
atomi, molecole,
palle da tennis,
animali (non vivi),
automobili (non nuove)

FUNDAMENTAL STEPS

(uncertainty principle by Heisenberg)

1927. The wave-particle duality of microscopic "particles" imposes a limit on our ability to measure simultaneously the position and momentum of such particles. The more precisely we determine the position, the less accurate is our determination of momentum

$$\Delta x \, \Delta p_x \cong h$$

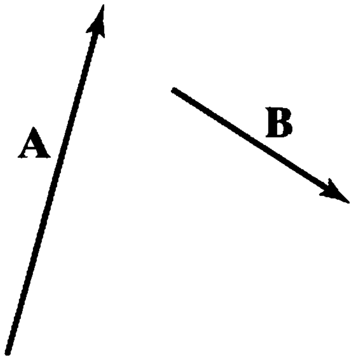
This limitation is the <u>uncertainty principle</u>. Because of the wave-particle duality, the act of measurement introduces an uncontrollable disturbance in the system being measured. The measurement changes the state of a system

VECTORS

Physical properties (for example, mass, length, energy) that are completely specified by their magnitude are called **scalars**

Physical properties (for example, force, velocity, momentum) that require specification of both magnitude and direction are called **vectors**. A vector is represented by a directed line segment whose length and direction give the magnitude and direction of the property

The point of application of a vector does not matter



VECTORS

The **sum** of two vectors **A** and **B** is defined as follows: Slide the first vector so that its head touches the tail of the second vector, keeping the direction of the first vector fixed. Then draw a new vector from the tail of the first vector to the head of the second vector

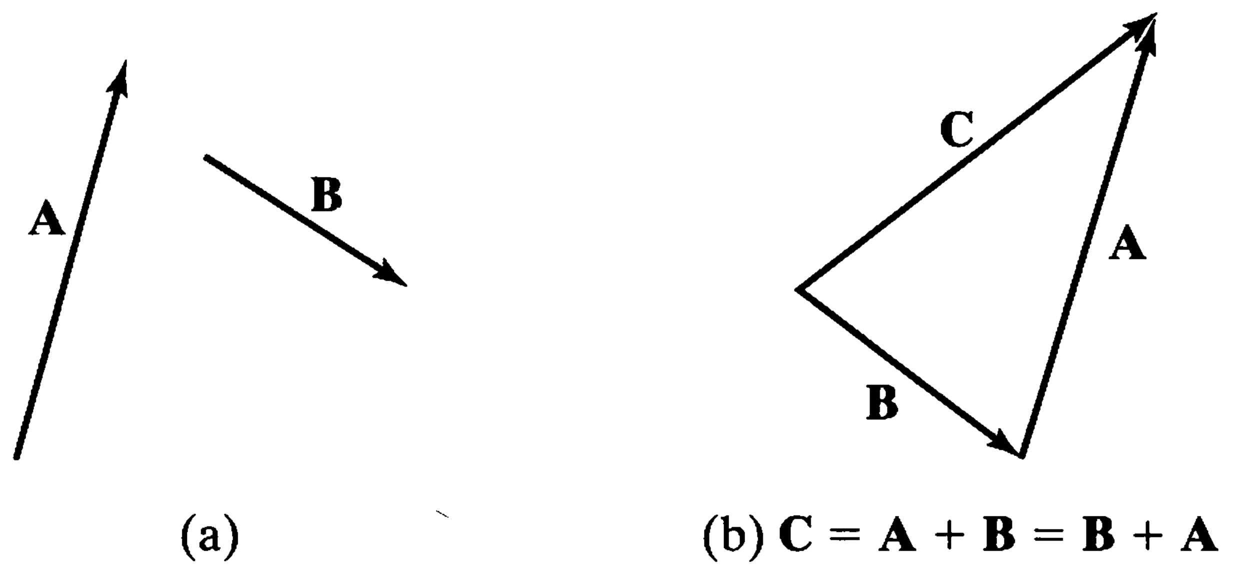


FIGURE 5.1 Addition of two vectors.

The **product of a vector and a scalar**, *c***A**, is defined as a vector of length *c* times the length of **A** with the same direction as **A** if *c* is positive, or the opposite direction to **A** if *c* is negative

VECTORS

Representation in algebraic form of a vector

$$\mathbf{A} = A_x\mathbf{i} + A_y\mathbf{j} + A_z\mathbf{k}$$

Magnitude of a vector

$$|\mathbf{A}| = (A_x^2 + A_y^2 + A_z^2)^{1/2}$$

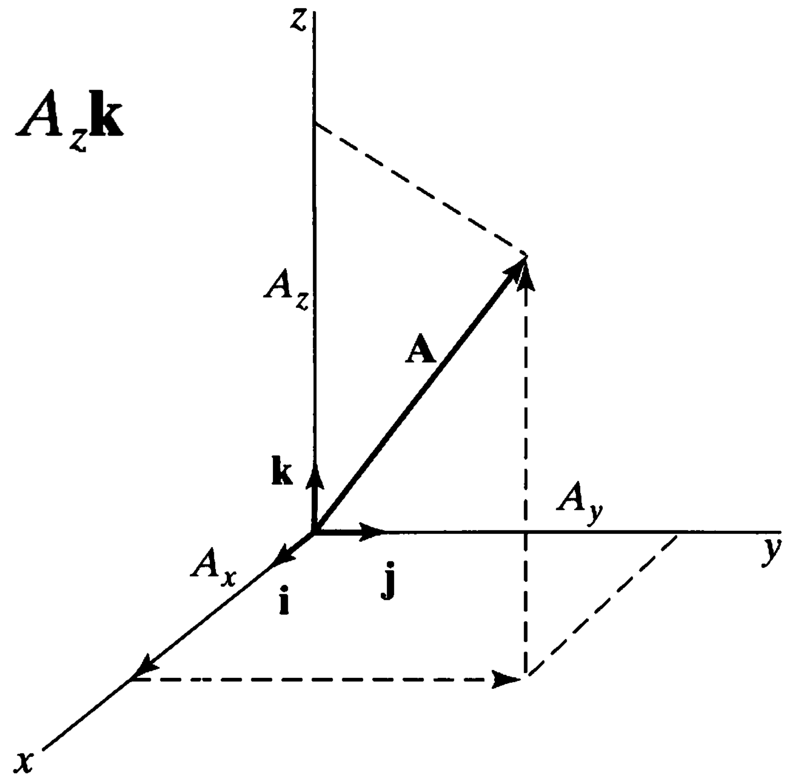


FIGURE 5.2 Unit vectors **i**, **j**, **k**, and components of **A**.

VECTORS

Operations in algebraic form

$$\mathbf{A} + \mathbf{B} = (A_x + B_x)\mathbf{i} + (A_y + B_y)\mathbf{j} + (A_z + B_z)\mathbf{k}$$

$$c\mathbf{A} = cA_x\mathbf{i} + cA_y\mathbf{j} + cA_z\mathbf{k}$$

The **dot product** or **scalar product** **A • B** of two vectors

$$\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}|\,|\mathbf{B}| \cos\theta = \mathbf{B} \cdot \mathbf{A}$$

where θ is the angle formed by the vectors. The dot product, being the product of three scalars, is a scalar

VECTORS

Since the three unit vectors **i**, **j**, and **k** are each of unit length and are mutually perpendicular, we have

$$\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = \mathbf{k} \cdot \mathbf{k} = \cos 0 = 1$$

$$\mathbf{i} \cdot \mathbf{j} = \mathbf{j} \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{i} = \cos (\pi/2) = 0$$

Using the distributive law, we have

$$\mathbf{A} \cdot \mathbf{B} = (A_x\mathbf{i} + A_y\mathbf{j} + A_z\mathbf{k}) \cdot (B_x\mathbf{i} + B_y\mathbf{j} + B_z\mathbf{k})$$

$$\mathbf{A} \cdot \mathbf{B} = A_xB_x + A_yB_y + A_zB_z$$

VECTORS

The **cross product** or **vector product** $\mathbf{A} \times \mathbf{B}$ is a vector whose magnitude is

$$|\mathbf{A} \times \mathbf{B}| = |\mathbf{A}|\,|\mathbf{B}| \sin\theta$$

whose line segment is perpendicular to the plane defined by **A** and **B**, and whose direction is such that **A**, **B**, and $\mathbf{A} \times \mathbf{B}$ form a right-handed system (just as the x, y, and z axes form a right-handed system)

From the definition

$$\mathbf{B} \times \mathbf{A} = -\,\mathbf{A} \times \mathbf{B}$$

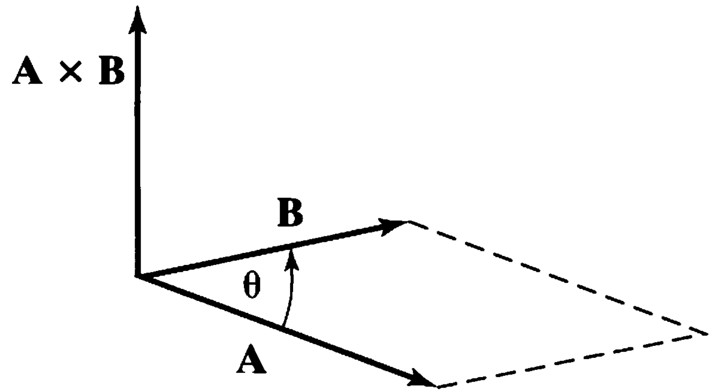


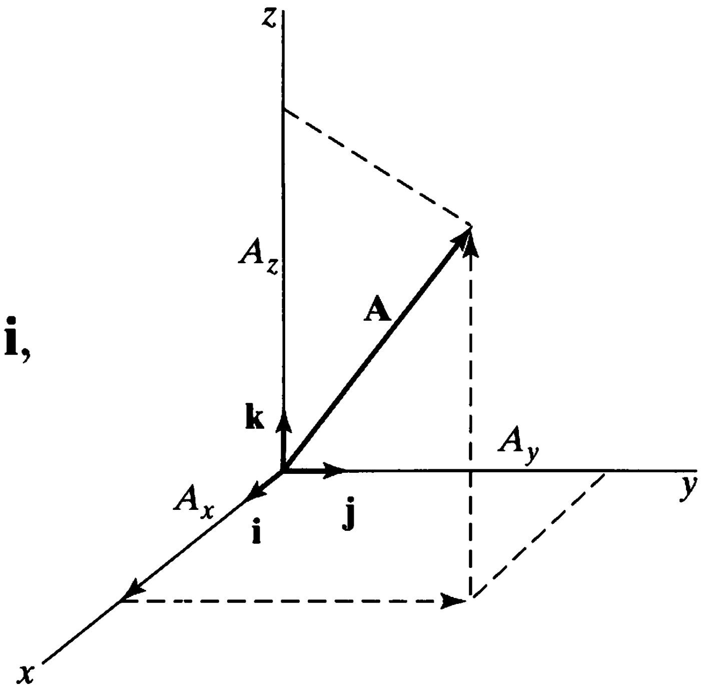
FIGURE 5.3 Cross product of two vectors.

VECTORS

Vector product

$$\mathbf{i} \times \mathbf{i} = \mathbf{j} \times \mathbf{j} = \mathbf{k} \times \mathbf{k} = \sin 0 = 0$$

$$\mathbf{i} \times \mathbf{j} = \mathbf{k}, \qquad \mathbf{j} \times \mathbf{i} = -\mathbf{k}, \qquad \mathbf{j} \times \mathbf{k} = \mathbf{i},$$



$$\mathbf{A} \times \mathbf{B} = (A_x\mathbf{i} + A_y\mathbf{j} + A_z\mathbf{k}) \times (B_x\mathbf{i} + B_y\mathbf{j} + B_z\mathbf{k})$$

$$\mathbf{A} \times \mathbf{B} = (A_yB_z - A_zB_y)\mathbf{i} + (A_zB_x - A_xB_z)\mathbf{j} + (A_xB_y - A_yB_x)\mathbf{k}$$

COMPLEX NUMBERS (The wave function can be complex)

A complex number z is a number of the form

$z = x + iy$ where $i = \sqrt{-1}$ $i^2 = -1$

Imaginary unit

and x and y are real numbers:

Real part of z: $x = \mathrm{Re}(z)$
Imaginary part of z: $y = \mathrm{Im}(z)$

If $x \neq 0$ and $y = 0$ then z is a **real** number
If $x = 0$ and $y \neq 0$ then z is a **pure imaginary** number
If $x \neq 0$ and $y \neq 0$ then z is an **imaginary** number

COMPLEX NUMBERS

A convenient representation of the complex number *z* is as a point in the complex plane, where the real part of *z* is plotted on the horizontal axis and the imaginary part on the vertical axis

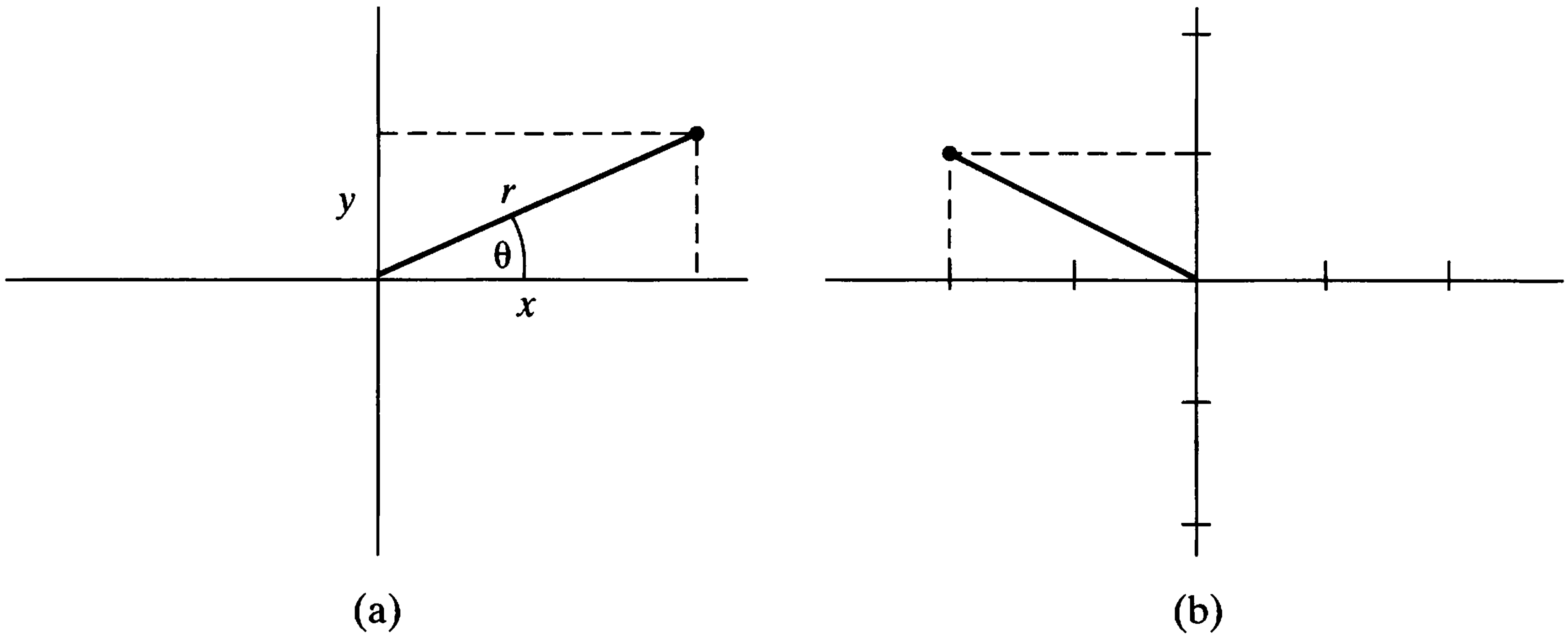


FIGURE 1.3 (a) Plot of a complex number $z = x + iy$. (b) Plot of the number $-2 + i$.

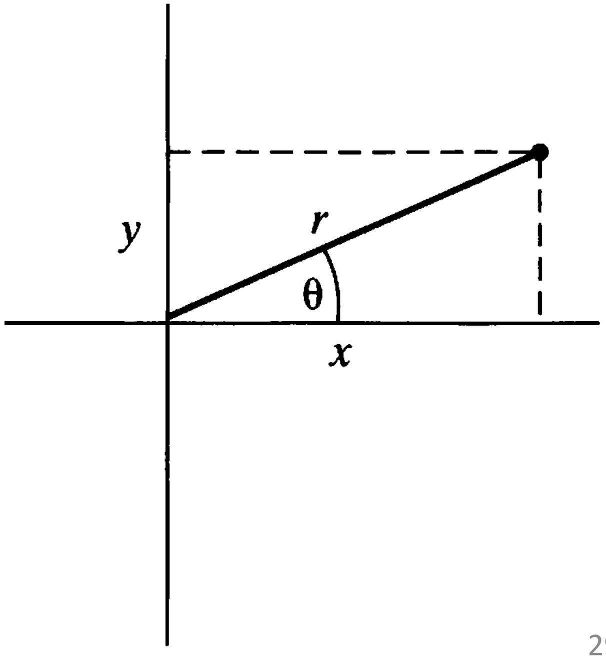
COMPLEX NUMBERS

The distance *r* of the point *z* from the origin is called the **absolute value** or **modulus** of *z* and is denoted by |*z*|

The angle θ (in radiants) that the radius vector to the point *z* makes with the positive horizontal axis is called the **phase** or **argument** of *z*

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

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



We can write

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

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

COMPLEX NUMBERS

If $z = x + iy$, the ***complex conjugate*** z^* of the complex number z is defined as

$$z^* \equiv x - iy = re^{-i\theta} \qquad \textbf{(1.29)*}$$

If z is a real number, its imaginary part is zero. Thus z is real if and only if $z = z^*$. Taking the complex conjugate twice, we get z back again, $(z^*)^* = z$. Forming the product of z and its complex conjugate and using $i^2 = -1$, we have

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

$$zz^* = x^2 + y^2 = r^2 = |z|^2 \qquad \textbf{(1.30)*}$$

COMPLEX NUMBERS

For the product and quotient of two complex numbers $z_1 = r_1 e^{i\theta_1}$ and $z_2 = r_2 e^{i\theta_2}$, we have

$$z_1 z_2 = r_1 r_2 e^{i(\theta_1 + \theta_2)}, \qquad \frac{z_1}{z_2} = \frac{r_1}{r_2} e^{i(\theta_1 - \theta_2)} \tag{1.31}$$

It is easy to prove, either directly from the definition of complex conjugate or from (1.31), that

$$(z_1 z_2)^* = z_1^* z_2^* \qquad \textbf{(1.32)*}$$

Likewise,

$$\left(\frac{z_1}{z_2}\right)^* = \frac{z_1^*}{z_2^*}, \qquad (z_1 + z_2)^* = z_1^* + z_2^*, \qquad (z_1 - z_2)^* = z_1^* - z_2^* \tag{1.33}$$

For the absolute values of products and quotients, it follows from (1.31) that

$$|z_1 z_2| = |z_1||z_2|, \qquad \left|\frac{z_1}{z_2}\right| = \frac{|z_1|}{|z_2|} \tag{1.34}$$

Therefore, if ψ is a complex wave function, we have

$$|\psi|^2 = \psi^* \psi \tag{1.35}$$

STATE of a SYSTEM (in classical mechanics)

The word **state** in **classical mechanics** means a specification of the position and velocity of each particle of the system at some instant of time, plus specification of the forces acting on the particles. According to Newton's second law, given the state of a system at a time, its future (past) states and motions are exactly determined

STATE of a SYSTEM (in quantum mechanics $\equiv$ QM)

To describe the state of a system in QM, we **postulate** the existence of a **function of the particles' coordinates** called the **wave function** or **state function** Ψ. Since the state will, in general, change with time, Ψ is also a **function of time**

Examples:

1 particle, 1 dimension: $\Psi(x, t)$

2 particles, 3 dimensions: $\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)$

The wave function contains all possible information about a system, so instead of speaking of "the state described by the wave function Ψ", we simply say "the state Ψ"

How to predict the time evolution of a QM state?

Time-dependent Schrödinger equation (postulate)

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

where $\hbar = \frac{h}{2\pi}$ $\quad i = \sqrt{-1}$

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

For a particle of mass m moving along one dimension, say x

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

Hamiltonian operator $\quad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)$

PROBABILITY

1) If an experiment has n equally probable outcomes, m of which are favorable to the occurrence of a certain outcome *A*, then the probability that *A* occurs is

$$P_A = \frac{m}{n}$$

2) Suppose that we perform the experiment N times and that in M of these trials the event *A* occurs. The probability of *A* occurring is then defined as

$$P_A = \lim_{N \to \infty} \frac{M}{N}$$

PROBABILITY in QUANTUM-MECHANICS

In QM we must deal with probabilities involving continuous variables, for example, the particle coordinates. It does not make much sense to talk about the probability of a particle being found at a particular point such as $x = 0.523$, since there are an infinite number of points on the x axis, and for any finite number of measurements we make, the probability of getting exactly 0.523 is vanishingly small

PROBABILITY in QUANTUM-MECHANICS

In QM, instead, we talk of the probability of finding the particle in a small interval of the x axis lying between x and $x + \mathrm{d}x$, $\mathrm{d}x$ being an infinitesimal element of length. This probability is proportional to $\mathrm{d}x$ and will vary for different regions of the x axis

Hence the probability that the particle will be found between x and $x + \mathrm{d}x$ is equal to $g(x)\mathrm{d}x$, where $g(x)$ is some function that tells how the probability varies over the *x* axis. The function $g(x)$ is called the probability density, since it is a probability per unit length

The wave function $\Psi(x,t)$ gives us information about the result of a measurement of the x coordinate of the particle at time t

$\Psi(x,t)$ **does not provide the exact position** of the particle. Max Born **postulated** that

$$|\Psi(x,t)|^2 \mathrm{d}x$$

gives the **probability that at time t the particle is found in the region of the x axis lying between x and $x + \mathrm{d}x$.** The bars denote the absolute value and $\mathrm{d}x$ is an infinitesimal length on the x axis. The function $|\Psi(x,t)|^2$ **is the probability density** for finding the particle at various places on the *x* axis

Example: $\Psi(x,t) = a \exp(-b(x^2 - c\, t)) \exp(ix)$

TIME-INDEPENDENT SCHRÖDINGER EQUATION

As the potential energy of the system does not depend on time, i.e.

$$V(x,t) \equiv V(x)$$

the time-dependent Schrödinger equation is written as follows

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

The solutions are expressed as the product of a function of t and a function of x (separation-variable method)

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

(Levine p. 12-13)

Linear homogeneous second-order differential equations with constant coefficients

General form

$$y'' = \frac{d^2y(x)}{dx^2}$$

$$a\,y'' + b\,y' + c\,y = 0$$

$$y' = \frac{dy(x)}{dx}$$

The generic solution is of the form

$$y(x) = A\,e^{s_1 x} + B\,e^{s_2 x}$$

where s_1 and s_2 are the solutions of the auxiliary equation

$$a\,s^2 + b\,s + c = 0$$

A and B are obtained from boundary conditions

Example: $y'' + 6\,y' - 7\,y = 0$

TIME-INDEPENDENT SCHRÖDINGER EQUATION

The solution is (see Levine p. 12-13)

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

We postulate that E is the energy of the system (real number). The quantity of interest is

$$|\Psi(x,t)|^2 = \Psi^*(x,t)\,\Psi(x,t) = \psi^*(x)\,\psi(x) = |\psi(x)|^2$$

The probability density of the state does not depend on time. The state is called **stationary state**

TIME-INDEPENDENT SCHRÖDINGER EQUATION

The wave function $\psi(x)$ satisfies the **time-independent Schrödinger equation**

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

the unknowns being E and $\psi(x)$. To solve for two unknowns, we need to impose additional conditions on ψ (called boundary conditions)

In general $$\boxed{\hat{H}\psi(x)=E\,\psi(x)}$$ **Schrödinger Equation**

PROBABILITY in QUANTUM-MECHANICS

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

We must sum up the probabilities $|\Psi(x,t)|^2 \mathrm{d}x$ of finding the particle in all the infinitesimal regions lying between a and b. This is just the definition of the definite integral

$$P(a \leq x \leq b, t) = \int_a^b |\Psi(x,t)|^2 \mathrm{d}x$$

A probability of 1 represents certainty. Since it is certain that the particle is somewhere on the *x* axis, we have the requirement

Normalization condition

$$\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \mathrm{d}x = 1$$

1) A wave function which satisfies the above equation is said to be normalized. This condition implies that $\Psi(x,t)$ must be **quadratically integrable**

2) Since $|\Psi(x,t)|^2 \mathrm{d}x$ is a probability $\Psi(x,t)$ must also be **single-valued**

3) **Continuity** of $\Psi(x,t)$ is also required

A function which satisfies the above conditions is said **well-behaved**

POSTULATE

The state of a system is described by a function Ψ of the coordinates and the time. This function, called the state function or wave function, contains all the information that can be determined about the system. We further postulate that Ψ is single-valued, continuous, and quadratically integrable (well-behaved function)

POSTULATE

The time evolution of the state of a QM system is given by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

where $\hat{H}$ is the Hamiltonian (i.e. the energy) operator of the system