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History of the idea of atom

Auguste Laurent, Methode de chimie, Paris 1854

En effet, pour nous donner une idée de la composition d'un corps réel, on est dans l'habitude d'imaginer deux ou trois corps hypothétiques, auxquels on assigne de nouveaux noms et une composition particulière, de sorte que l'étude de la chimie a non-seulement pour objet les propriétés, la composition et les noms de milliers de corps réels, mais encore les propriétés, la composition et les noms d'un plus grand nombre d'êtres purement fictifs.

C'est l'introduction dans la science, de cette foule d'êtres hypothétiques, qui m'a fait dire, il y a quelque temps, que la chimie d'aujourd'hui est devenue la science des corps qui n'existent pas.

As a matter of facts in order to supply an idea of the composition of a real body we are used to imagine two or three hypothetical bodies to whom we assign new names and a particular composition such that the study of chemistry has not only as an object the composition, the properties and the names of thousands of real bodies, but also the composition, the properties and the names of a larger number of purely fictive entities.

The introduction in the science of this crowd of hypothetical bodies has driven me to write, since some time, that today's chemistry is the science of the non existing bodies.

Non existing bodies: the atoms

The existence of atoms, discussed for more than 2000 years mostly by the natural philosophers, became part of physics and chemistry only in the 19th Century. As we shall see, great physicists and chemists (Lord Kelvin, Helmoltz, Lavoisier) had difficulties in accepting the atom's concept.

The structure of matter in the Greek philosophy

Meditation on the composition and structure of matter originated in western civilization in Greece but several ideas developed by the Greek philosophers had their roots in the ancient Far East civilizations, i.e. in the Sumerian, Babylonian, Egyptian and far East cultures. However, the Greek philosophers were the first to ask logical questions about natural sciences and to seek rational explanations of the physical phenomena.

The Pre-Socratic philosophers thought that there was a single underlying primitive substance that incorporated the principles of change. This underlying substance and its inherent principles could become anything.

In the original Greek cosmology this primordial substance was actually a kind of emptiness, referred to as either the Void or the Chaos, *the dark, silent abyss from which all things came into existence.* What came next must have sprung from this *first* thing.

Greek philosophy started to develop in the Ionia, today part of Turkey, closer to Asia Minor and more exposed to the influences of the Babylonian and Egyptian cultures that followed the caravan routes of commerce. Ionian philosophers rejected mythological explanations for the physical phenomena in favor of more rational explanations. The Ionic philosophers were all educated, in Egypt to a mathematical and overall geometrical vision of nature.

Classical Geometry requires the definition of an empty space in which geometrical objects are inserted. This space is a three-dimensional continuum i.e., an arrangement of all possible point locations to which Euclidean postulates apply and can be divided ad infinitum as can be done for each element of the geometrical representation. To such a spatial manifold, Cartesian coordinates seem most naturally adapted.

The endless divisibility of matter was thus a basic principle of the first Ionian philosophers and underlined their representation of the world.

In ancient philosophies, in particular in those born in India, the concept of infinite was essentially a geometrical one. Infinity is endless and can be represented in an endless number of ways. The Endless (*apeiron*) is at the origin of all what exists.
In the Isha Upanishad (about 4th century b.C.) is written that if from an infinity one extracts part of it, what is left is always infinite:

Pūrṇam adaḥ pūrṇam idam	the Whole is a whole
Pūrṇāt pūrṇam udacyate,	from the Whole the whole originates
Pūrṇasya pūrṇam ādāya,	when a whole is extracted from the Whole
Pūrṇam evāvasiṣyate,	what is left is always the Whole

The concept of atom very probably reached Greece from India where it was developed in the framework of the Vaisheshika philosophy.

Vaisheshika, one of the six Hindu schools of philosophy (Vedic systems) of India is closely associated with the Nyaya Hindu school of logic. The Vaisheshika philosophy adopts a form of atomism and contends that all objects in the universe are reducible to a finite number of atoms. The concept of *paramāṇu*s (atoms) was originally proposed by the wise man Kanada, Kana-bhuk, (atom-eater) about. the 6th century B.C.

The Kanada syllogism intends to prove that all objects i.e. the four bhūtas, *pṛthvī* (earth), *ap* (water), *tejas* (fire) and *vāyu* (air) are made of indivisible *paramāṇu*s (atoms):

Assume that the matter is not made of indivisible atoms, and that it is continuous. Take a stone. One can divide this up into infinitely many pieces. Now, the Himalayan mountain chain also has infinitely many pieces, so one may build another Himalayan mountain chain with these infinite number of pieces. One begins with a stone and ends up with the Himalayas, which is obviously ridiculous - so that the original assumption that matter is continuous must be wrong, and all objects must be made up of a finite number of *paramāṇu*s (atoms).

The Ionic School

Between the 6th and the 5th century B.C. the Ionian philosophers started investigating the nature of matter and its transformation into the myriad of things of which the universe is made. They maintained that a unique basic and incorruptible principle existed, the *arché* (αρχή), from which everything was generated and in which everything was dissolved by death.

Thales of Miletus (ca. 624 BC–ca. 546 BC) arché: water

↓

Anaximander of Miletus (c. 610 B.C.– c. 546 B.C.) arché: unlimited entity (*Ἄπειρον*)

↓

Anaximenes of Lampsacus (c. 585 BC–c. 525 BC) arché: air

↓

Anaxagoras of Clazomenae (c. 500-428 BC). All things existed in infinitesimally small fragments, endless and inextricably mixed.

Greek atomism

The term ἆτομος ws first used by Leucippus from Miletus, but his pupil Democritus (ca. 460-360 a.C.) from Abdera made if famous

Empedocles (490-435 a.C.) from Agrigento gave final form to the four basic elements, arir, fire, water and earth, made of minute parts, idea that anticipated that of the atom.

For more than 2000 years Democritus ideas found the hostility of the ruling religions since it denied the creative process due to God’s will. In the Middle Ages Democritus theory became for the Scholastic philosophers a blasphemous and sinful manifestation of atheism, considered heretical since it denied the cosmic order and the perfection of the Creation due to God’s will, believing in caos and disorder, as described by Dante

quivi vid' ïo *Socrate* e *Platone*,
che 'nnanzi a li altri più presso li stanno;
Democrito che 'l mondo a caso pone,
Dïogenès, *Anassagora* e *Tale*
Empedoclès, *Eraclito* e *Zenone*

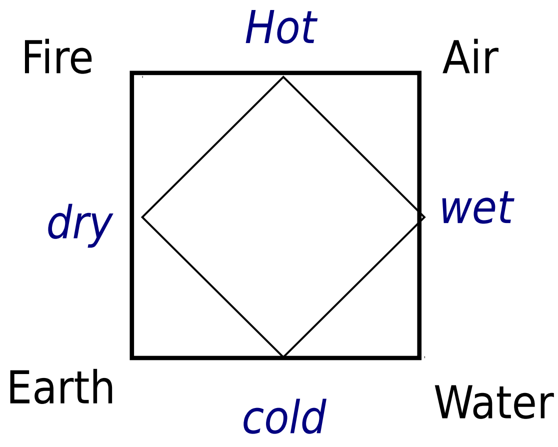
there I beheld both Socrates and Plato,
closest to him, in front of all the rest;
Democritus, who ascribes the world to chance,
Diogenes, Empedocles, and Zeno,
and Thales, Anaxagoras, Heraclitus;

Aristotle (384-323 a.C.)

Plato considered philosophy as an unicum in which different items were interconnected and not separable. Aristotle instead devided philosophy into separate branches, metaphysics, physics, logic, esthetics, ethics and politics, a division universally accepted and still used today.

Aristotle trasformed logics into a true science, codifying is principles and specifying its operational structures, categories and propositions. Dialectics became with him the dominant deductive and syllogistic procedure up to the development of mathematical logic in the 19th Century.

Aristotle believed in the existence of an original primordial matter (πρώτη ὕλη), from which the four Empedocle's elements originated, earth, water, air and fire, arranged on Earth according to their weight, down the heavier as earth and water and up the lighter, air and fire. To these he added a fifth one, πέμπτον στοιχεῖον, called ether that in the Medioeval tradiction became the *quinta essentia*. Ether was pure and unchangeable, without weight and endowed of circular motion.



The existence of four elements on Earth, could not easily explain the huge number of different objects occurring in Nature. To overcame this difficulty Aristotle considered the elements as combination of four qualities, warm, cold, dry and wet, in variable proportions. Fire had the qualities of dry and hot, water of cold and wet, earth of dry and cold and air of hot and wet

For Aristotle the speed of a body was a function of his weight and of the resistance of the medium. Therefore in the void a body would have infinite velocity, a fact against common sense. the void thus could not exist. Matter had to be continuous and thus the atoms could not exist, since between two atoms there would be void. Matter was thus endless divisible. Division, however, led to parts of matter smaller and smaller up to the point that if further divided, they would loose the properties of the initial substance. Qualities, i.e. physical properties of a chemical compound were thus due to his extension. Beyond a given dimension, the properties were lost, and the initial substance became a new one. The mixing of two liquids, κράσις, or that of two solids, μϊξις, led to a new substance with properties different from those of the initial substances.

The Aristotle's conception of the potential infinity

It is always possible to think of a number greater than a given one since the number of times a quantity can be divided into two part is infinite. The number of parts that can be subtracted from a whole is always greater than any number. — *Physica 207 b8*

In his potential infinity it is always possible to find a number of entities greater than a given number even if these entities do not exist. In other words "for each integer n exists always another integer m such that m > n".

Potential infinity was clearly defined in the Middle Ages by *William of Ockham*

***Sed omne continuum est actualiter existens. Igitur quaelibet pars sua est vere existens in rerum natura. Sed partes continui sunt infinitae quia non tot quin plures, igitur partes infinitae sunt actualiter existentes*.**

but every continuum is actually existing. Therefore each of his parts is really existing in nature. However the parts of a continuum are infinite since these are never too many so that more parts cannot exist and therefore the infinite parts are really existing.

Muslim theories of the structure of matter

The ideas elaborated by the Greek philosopher on the structure of matter and on the number of elements reached the Muslim world through the study of the Greek texts, essentially of those of Aristotle.

For the Muslim alchemists the true promoter of their science was the omàyyade prince *Khalid ibn Yazid ibn Mu‘awiyya* (665-704), followed by the Shi'a imam Ja’far al-Sadiq (699-765), descendant from Mohammad son-in-low, who was the master of the most famous arab alchemist Giabir ibn Hayyàn, known in the West as Geber or Giabir.

Giabir accepted the four elements theory fire, air, water and earth with the four Aristotle’s qualities heat, cold, dryness and humidity that for him, were properties of the matter and became elements only when connected to a material substance

The most original contribution of Giabir to alchemical thoughts concerns the origin of metals, formed in the bowels of the earth under the influence of the planets by union of two opposite, Sulphur and Mercury. The first supplied the *natures* of the hot and dry, the second those of the cold and wet. Metals were a combination of two of these *natures*, that could be either internal to the metal, i.e. hidden, or external i.e. manifest. For instance gold had as external properties those of the hot and wet and as hidden properties those of the cold and dry. In lead instead cold and dry were external properties and wet and hot internal ones. Therefore to transform lead in gold it was sufficient to extract from lead the internal qualities of wet and hot allowing the external ones of cold and dry to migrate in the interior of the metal.

In the Middle Ages the sulphur-mercury theory of Giabir was widely accepted. For instance Paracelsus, Philippus Aureolus Theophrastus Bombastus von Hohenheim (1493-1541) extended Giabir’s theory to the whole mineral, animal and vegetable matter. According to him, matter was always made of the four aristotelian elements, but to the properties of sulphur and mercury he added a third one, the salt.

These three elements, sulphur, mercury and salt, formed the *tria prima*, i.e. the three primary factors of the Cosmos. The tria prima should not be considered as true elements but rather as abstraction of properties: Salt represented constancy and incombustibility, mercury fusibility and volatility and sulphur inflammability and combustibility.

Heinrich Cornelius Agrippa von Nettesheim, (1486-1535) pushed the faith in the four Aristotelian elements up to maintain that they existed in extolling form in the Paradise in the stars, in the angels, and even in God.

For the Aristotelians chemical substances could be endless devided only conceptually. Divisione led to the *minima naturalia,* particles that, if further divided, were not anymore part of the initial substance. The physical properties of a chemical compound were thus bound to his “extension“; when the dimensions went below those of the *minima*, the initial properties were lost and the substance changed his nature.

The theory was further developed by the Scholastics assuming that the *minima* existed independently from the division procedure and that chemical reactions were the result of the combination of *minima* of the reacting substances to form minima of the products.

Aristotle works were extensively translated into Arabic. During the Middle Ages the greatest interpreter od Aristotle’s philosophy was the Arab philosopher Abū'l-Walīd Muhammad ibn Ahmad ibn Rushd, better known in the West as Averroè (1126–1198), who developed the *minima naturalia* theory to eliminate the difficulties created by Aristotle’s endless divisibility.

The “minima naturalia”

The atomic concept as basic stone of matter stayed practically ignored for the whole Middle Ages, obscured by Aristotle’s continuum theory and only at the beginning of the 16th century started to reappear in the philosophical discussion. Two forms of atomism, a mechanical one inherited from the Greek empiricists, the other derived from the idea of endless divisibility of matter of Aristotle, opposed each other for about two centuries, finally converging on the atomic theory of modern chemistry.

1. Mechanical atomism was essentially a cosmological theory of the physical world based on the existence of very small particles in motion in the void. The atoms of the mechanical philosophers were characterized by few properties, shape, dimension and motion, were unchangeable and indivisible and had no internal structure from which their properties could depend.

2. A different atomic conception, called of the “minima naturalia”, Latin version of the Greek word ***elachista*** (*elachista*), had his roots in the Aristotelian’s thoughts and become a theory applied essentially to chemical transformations. The“*minima naturalia*” were the smallest part of a subtance still keeping its properties

Averroé's ideas of the minima naturalia were picked up by the Calabrian Agostino Nifo (1473-1538) who maintained that the minima were true physical entities, and that they played a substantial role in chemical processes.

Also Giulio Cesare della Scala (1484–1558), asserted that the minima naturalia had different dimensions depending upon the substance. He evalued also the dimensions of the minima of the four Aristotelian elements. For instance, according to him the minimum of earth was about 100 times larger than that of fire del minimo del fuoco and that of air was in between.

Reviving the idea of *minima naturalia* the German Daniel Sennert (1572-1637) maintained that they possessed physical reality and were not different from Democritus' atoms. He classified the minima as "first and second order elements". First order elements were not further divisible whereas the second order ones were true compouds.

In the same period even the Italian Angelo Sala (1576–1637) practised in Germany ideas similar to those of Sennert.

The minima naturalia gained a closer correspondence to the atoms in Giordano Bruno (1548-1600) cosmology.

His stormy relationships with the Roman Inquisition compelled him in 1576 to escape to Switzerland, to France and finally in 1583 to England, where he wrote in 1584 the cosmological Italian dialogues, *la cena delle ceneri*, *De la Causa, Principio et Uno* and *De l'Infinito Universo et Mondi*. After a short return to Paris in 1585, he moved to Germany, to Marburg, to Wittenberg, Prague, Helmstedt, and finally to Frankfurt, where in 1591 he published the Latin trilogy *De Magia, De triplici minimo et mensura* and *De Vinculis in Genere*. Back to Italy in 1592, he was denounced to the Inquisition, arrested and transferred to Rome where, after a seven years trial, was burnt alive in Campo dei fiori on February 17th 1600.

The minima naturalia were transformed in a form of atomism in the transition from the Italian dialogues of London to the Latin trilogy of Frankfurt. In the dialogues the atomism is still a virtual concept, a simple corollary to the cosmology. In the trilogy instead the atoms assumed a true reality, characterized by a strong form of animism to distinguish among different atoms. Physically they had all the same spherical shape and dimension, but were distinguished by the type of force that controlled their motion.

René Descartes (1596–1650)

Atomism growth in the following centuries was bound not only to the minima naturalia theory but also to the development of the mechanistic theories that found in France ad England a fertile humus to their diffusion.

For Descartes (Cartesio) the fundamental property of matter was the extension, from which all other properties derived. He had no difficulty in accepting the existence of particles like the atoms, but denied Democritus' model of indivisible atoms in motion in the void. The denial of the void, the *horror vacui*, was actually the cornerstone of his cosmology, inherited from the Aristotelian theory of motion.

According to Descartes, each physical object exists only because it fills a space: all what exists is a "*res extensa*", a substance with a space-dimension. The void is thus impossible. If a void existed, different parts of matter would not be in contact and one had to assume the existence of an action at a distance, i.e. of an immaterial action propagating in the void. The action at a distance will become with Newton the basis of the universal attraction. For a mechanistic philosopher of the Seventeenth century it was, however, impossible to accept its existence, since this would involve the existence of a metaphysical entity of the same nature of the vital spirits that he denied.

In the Seventeenth century atomism started to occupy a significant position in the philosophical discussion, thanks to the empiristic positions of the French philosopher Pierre Gassendi (1592-1655) and to the diffusion of Epicurus' ideas through his writings

In contrast to Descartes Gassendi considered space as an absolute and infinite void, *vacuum separatum*, existing independently from the objects. God furnishes the empty space with atoms and with their combinations, giving origin to a world of finite dimensions. This vision of space anticipates the Newtonian idea of absolute space and time. He believed in the existence of a *vacuum disseminatum*, an ensemble of small voids distributed among the atoms. Aristotle's theory of the continuum and of an infinite divisibility had a meaning only in mathematics and geometry, but not in the real world.

Gassendi's ideas had a strong influence not only on minor thinkers of the Century but also on important figures of the science of the 17th and 18th century such as Boyle, Locke, Hume and even Newton.

Robert Boyle (1627-1691)

The first chemist who really succeeded to impose the corpuscular theories against those of Aristotle and Paracelsus was Robert Boyle.

In order to prove the absurdity of Aristotle and Paracelsus theory and to furnish a corpuscular ground to the new chemical theory, Boyle published is famous book, *The sceptical Chymist*.

Boyle criticism of the typical Scholastics example of the bourning wood giving rise to the four elements fire, air, earth and water, is one of the masterpiece of chemical literature.

> *It may likewise be granted, that those distinct Substances, which Concretes generally either afford or are made up of, may without very much Inconvenience be call'd the Elements or Principles of them.*
>
> *Robert Boyle,The sceptical Chymist, First part pg. 46*

Boyle's atoms "corpuscles", were all made of the same primordial matter, although with different shapes, dimensions and motion. Chemical reactions were due to a change in the organization of matter, caused by the rearrangement of the relative position of the corpuscles, by their fusion or separation.

Boyle’s corpuscles possessed two basic properties as ancestors of the atoms: shape and motion. To these the reciprocal attraction based on the gravitational theory was added by Isaac Newton (1643–1727) Newton, following the ideas of his masterIsaac Barrow (1630-1677), believed in absolute space and time and maintained that time exist independently from motion and that even existed before God had created the universe.

According to Newton, matter was made of primordial particles of first, second and higher complexity. Those of first complexity, hard, indivisible and impenetrable, joining together thanks to the attraction, gave rise to particles of second complexity that in turn associated to form particles of higher complexity, eventually up to chemical compounds. The structures of highest complexity had pores in which solvents or reagents could enter. For example mercury could penetrate the pores of gold merging in an amalgam.

Isaac Newton (1643–1727)

The action at a distance. Importance of the ether. Absolute space and time

The action at a distance was unacceptable even for firmly convinced atomists, since it seemed impossible that an inanimate object could exert an action in a place different from that where it was located. The existence of an action at a distance lead to suppose that the motion was controlled by a magic or even diabolic spirit. Even Galileo and Leibnitz did not believe in it at the point that they refused Kepler theory that the tides were due to the action of the moon. Bacon as well as great physicists like Faraday and Huyghens, joined this position. The same Newton had difficulties in justifying the action at a distance. The *force* of *gravity* collided with the common sense since it occurred among bodies at large distance and not among close lying objects. To avoid speculations on the interpretation of the gravitational interaction Newton maintained that the interaction was transmitted through the ether, that filled the whole space and acted as a support to his propagation.

Newton was not only an exceptional mathematician and physicist but also a convinced alchemist who studied with enthusiasm alchemic text from 1668 until to his death. In the spirit of the magic tradition Newton was convinced that the alchemical knowledge should be reserved to few elected scholars, since its diffusion could be a true danger for persons not prepared to this kind of magic wisdom. For instance he wrote a letter to Boyle asking him to preserve the secret on this argument and to avoid discussing the alchemical principle in public. At his death the Royal Society decided to keep secret his alchemical works to not deteriorate his public image.

Newton's manuscripts were dispersed between the USA, Europe and Israel. in 1936 a good deal of them went back to England as consequence of a famous auction held by Sotheby at London in which 329 lots of manuscripts were offered on sale. The manuscripts were bought by John Maynard Keynes one of the key personalities in the history of economics. Keynes, in his article *Newton, the Man*, read by his brother Geoffrey Keynes at the meeting organized by the Royal Society on July 1946 for the celebration of the three-centenary of Newton wrote:

John Maynard *Keynes*

Newton was not the first of the age of reason. He was the last of the magicians, the last of the Babylonians and Sumerians, the last great mind which looked out on the visible and intellectual world with the same eyes as those who began to build our intellectual inheritance rather less than 10,000 years ago. Isaac Newton, a posthumous child bom with no father on Christmas Day, 1642, was the last wonderchild to whom the Magi could do sincere and appropriate homage. Newton opened a door to our world, sure. But he belonged to the world we have left behind.

Roger Joseph Boscovich (1711-1787)

Important changes to the interaction at a distance were proposed by the Dalmatian mathematician and astronomer from Dubrovnik, the Jesuit Roger Joseph *Boscovich* (1711-1787), who suggested that matter was made of punctiform and indivisible particles interacting at large distance with an attractive and at short distance with a repulsive force, with a swinging behavior as a function of distance. At a given distance it was equal to zero then it became repulsive then again zero, then again attractive and soon, until it became strongly repulsive at very short distance to avoid that the atoms could be in direct contact.

Boscovich believed that the matter was made of punctiform and indivisible particles among which an attractive force was acting at large distances. This force decreased at shorter distances, reached zero and then became repulsive, then again zero, then again attractive and so on, until at very short distances was strongly repulsive preventing the contact among the particles. The equilibrium between attractive and repulsive forces explained the existence of non infinitesimal bodies.

an important step toward the acceptance of the concept of atom as a basic stone of matter was made by the French Louis-Joseph Proust (1754-1826), the discoverer of the principle of definite proportions who realized that the chemical compounds had all a fixed composition. This law is a banal consequence of the fact that matter is made of atoms but this idea did not interest chemists and physicists but only philosophers used to complex cosmological theories. For the chemist and the physicist it was largely sufficient to have the elements at their disposal to build up their theories. Even Lavoisier, a man of a fine culture and a subtle thinker considered the discussion on the number and nature of the atoms as a pure metaphysical one.

Tout ce qu'on peut dire sur le nombre & sur la nature des éléments se borne suivant moi à des discussions purement métaphysiques: ce sont des problèmes indéterminés qu'on se propose de résoudre, qui sont susceptibles d'une infinité de solutions, mais dont il est très-probable qu'aucune en particulier n'est d'accord avec la nature.

The true father of modern atomism was John Dalton (1766-1844), the first to introduce in the theory the concept of atomic weight and to publish a table of atomic weights.

Dalton's atomic theory

1. The elements are made of atoms;
2. All atoms of a given elements are identical;
3. The atoms of a given element are different from those of another element;
4. The atoms of one element combine with the atoms of other elements to form compounds. A compound will always be made of the same number of atoms of different species;
5. Atoms cannot be created nor destroyed. In a chemical reaction all what happens is the rearrangement of the atoms among the components.

Dalton's atomism introduced a completely different conception of the chemical mass, based on the concept of atomic weight. The weight of a composed atom (molecule) was obtained as sum of the atomic weights of the component atoms. For the first time atoms and molecules were weighted.

In the first half of the 19th century Dalton’s theory found great praise but also great oppositions as always happens for revolutionary ideas.

The opposition to the atomic theory arose from the fact that the chemists could not realize why the atomic theory needed to use atomic weights instead of the experimentally measured weights of combination and volumetric

Furthermore it was not easy to accept Dalton’s theory in a cultural milieu dominated by the continuum theory in electricity and magnetism and used to believe in the existence of a single species of atoms. Dalton’s hypothesis that so many types of atoms as elements could exist brought to about 50 the basic stones of matter with whom God had built the world. This absence of a project simplicity seemed to many chemists less probable and appeared as a manifestation of wasting and inefficiency of Mother Nature.

The final test of Dalton’s theory was due to a series of highly precise experiments made at the beginning of the 19th century by the French chemist Joseph Louis **Gay-Lussac** (1778–1850)

On December 31st 1808 Gay-Lussac presented to the *Societé Philomatique* of Paris his experiments on the volumes of gases under the title *Mèmoire sur la combinaison des substances gazeuses, les unes avec les autres*. From these data Gay Lussac deduced his famous law that establishes that gases combine together in simple volumetric ratios expressed by integer numbers.

Dalton was always skeptical about Gay Lussac’s data that he considered wrong. The person who instead credited Gay Lussac’s experiments was **Lorenzo Romano Amedeo Carlo Avogadro** (1776-1856), count of Quaregna and Cerreto, with his famous principle that equal volumes of gas contain the same number of molecules. A direct consequence of Avogadro’s hypothesis was that the ratio between the molecular weight of a given gas and that of a reference gas is equal to the ratio of the corresponding densities.

Avogadro's principle was, however, not easily accepted by the scientific community. Avogadro was actually internationally well known for his researches on electricity but was practically ignored by the natural philosophers. Furthermore even in Italy Avogadro had difficult relationships with his colleagues of the vTurin Academy who continued to refuse his articles normally well accepted in French journals.

M. Gay-Lussac a fait voir que les combinaisons des gaz entre eux se font toujours selon des rapports très-simples en volume, et que lorsque le résultat de la combinaison est gazeux, son volume est aussi en rapport très-simple avec celui de ses composants; Il faut donc admettre qu'il y a aussi des rapports très-simples entre les volumes des substances gazeuses, et le nombre des molécules simples ou composées qui les forme. L'hypothèse qui se présente la première à cet égard, et qui parait même la seule admissible, est de supposer que le nombre des molécules intégrantes dans-les gaz quelconques, est toujours le même à volume égal, ou est toujours proportionnel aux volumes.

A further complication arose in 1814 owing to a letter of the French mathematician **André-Marie Ampère** in which this latter claimed to have reached the same conclusions of Avogadro. Avogadro soon asked for priority but his request had no effect for about 50 years until another Italian, Stanislao Cannizzaro (1826-1910), did not resume the problem at a famous meeting held in Karlsruhe from September3 to 5 1860.

Cannizzaro and the Karlsruhe Congress

The idea to organize an international meeting of chemistry was suggested by Kekulé who in 1859 contacted Weltzien and Wurtz to explore the possibility to organize it.

"Si propone di adottare concetti diversi per molecola e atomo, considerando molecola la quantità più piccola di sostanza che entra in reazione e che ne conserva le caratteristiche fisiche, e intendendo per atomo la più piccola quantità di un corpo che entra nella molecola dei suoi composti"

In the 19th century chemists and physicists had a completely different image of electricity.. The chemists, in contact with a discontinuous and discrete world made of atoms and molecules that they handled and combined together at will in their laboratories, conceived the electricity as made of charges indissolubly bound to matter and responsible of the affinities binding together the atoms in the molecules. .

The proposition that electricity could consist of particles did instead look as a heresy to the physicists, used to discuss the phenomena of electrical conduction in terms of a continuous fluid and to master abstract concepts as waves, fields and potentials. At the end of the century the idea of the corpuscular nature of electricity had, however, already entered the physics world through the study of electrical discharges in rarefied gases at low pressure, a phenomenon known since some time and normally presented to show the prodigies of electricity in elegant soirées to ladies and gentleman’s. This physical effect was discovered in 1838 by Michael Faraday who found that a flux of electrical current is observed by applying a potential difference of thousands of volt to the metallic electrodes of a void glass tube.

A model of the atom had been already proposed in 1867, before the discovery of the electron, by Lord Kelvin (William Thomson) resuming an old paper of Helmholtz on the dynamics of vortices

Helmholtz’s idea was that filaments of an ideal incompressible and non viscous fluid, rolled up in the form of rings in vortex motion would be stable and last to infinity. Of course in air and water that are non ideal fluids, the vortices are rapidly dissolved. Ether, however, was considered a true ideal fluid and therefore vortices in the ether could possess an infinite life..

Lord Kelvin started to be interested in vortices after having assisted to a lecture of his friend Peter Tait. Peter Guthrie Tait (1831-1901), professor of physics at the university of Edinburgh, was a mathematical physicist who in addition to develop the quaternion physics had worked for long time on the vortex theory (Tait, 1877, 1884, 1885). In order to prove experimentally the validity of Helmholtz’s vortex theory, he even built a machine made of two receivers, each equipped with a rubber diaphragm that once compressed produced beautiful smoke rings in vortex rotation in air. These rings behave as made of rubber: colliding one with the other they would bounce without breaking and if one tried to break them with a knife they simply would roll up around the blade. Lord Kelvin was enthused of the idea of the vortices and in the period 1867-1900 published a series of papers on the argument. Since he had always been an adversary of the atoms as material objects, he ventured with great enthusiasm in the attempt to represent them as vortices in the ether

The vortices theory of the atom had a short life but the fact that a scientist of the level of Lord Kelvin had adopted it and that also Maxwell, even without believing it too much, had considered it as a "a marvellous example of creative interaction between mathematics and physics, excited the interest of several mathematicians especially in England leading to important developments of the hydrodynamic theory. In 1902 Lord Kelvin, however, completely abandoned the idea of the vortices and proposed a new model that regarded the atom as made of a positive charge balanced by a negative one. In this model Lord Kelvin resumed the ideas developed more than hundred years before by Franz Maria Ulrich Theodosius Aepinus (1724-1802), a German physicist and astronomer at the court of Catherine the great in Russia, who in a treatise of 1759 had been the first to connect electricity and magnetism, developing a theory of the electrical fluid made of very small immaterial particles filling the space.

In 1897 Joseph John Thomson (1856-1940), professor at Cambridge, restarted the study of the mysterious cathodic beams studied by several physicists, including Julius Plucker**,** Johann Crookes and Jean-Baptiste Perrin who proved that these were particles with a negative charge and measuring the deviation in magnetic and electric fields succeeded in computing the ratio e/m between the charge and the mass of the particles that he called "corpuscles", showing that the mass was about 1/1000 of the mass of the hydrogen atom.

On April 30 1897, at the Royal Institution theater in London, J.J. Thomson told to a selected audience of dames and gentlemen’s that he had discovered a particle 1000 times smaller than an atom. In 1881 George Johnstone Stoney (1826-1911) suggested for these negatively charged particles the name *electron* that was soon accepted (Stoney, 1881). From that moment the electron overbearingly entered the scientific world as the first known elementary particle and as basic constituent of matter.

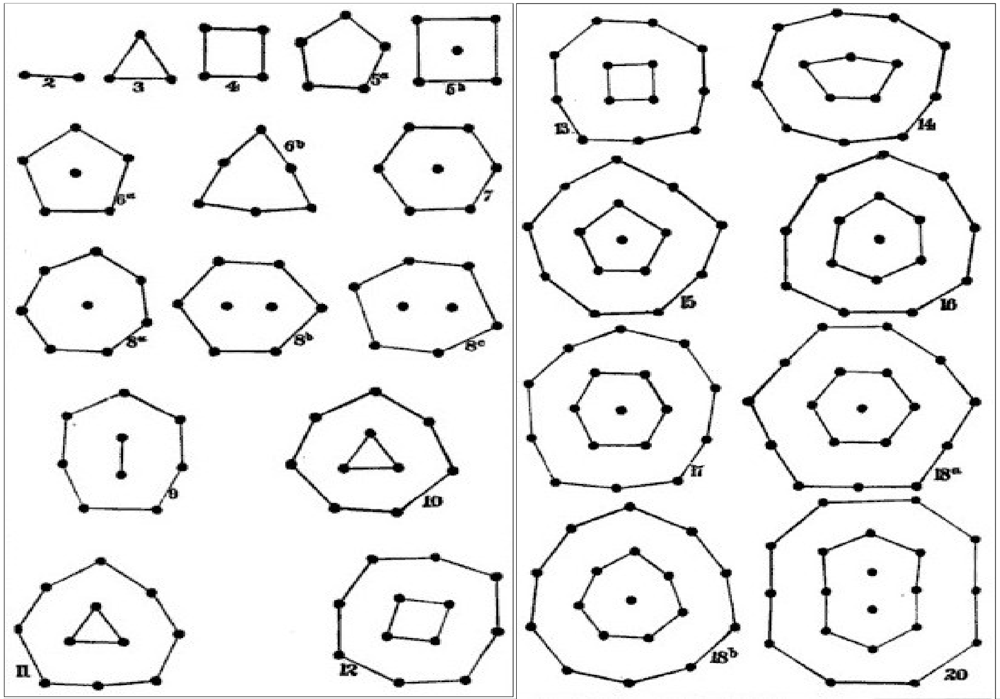
The discovery of the electron represented a fundamental step in the development of the structure of matter. The indivisible atom of the Greek philosophers, whose existence had given rise to so many discussions and controversies during the XIX century, resulted now made of particles of dimension smaller than that of the atom and in addition electrically charged. Electricity, long considered as a continuous fluid, acquired now a particle structure and the interaction between opposite charges became the basic interaction in the interpretation of the atomic structure.

Lord Kelvin’s idea of atoms balancing positive and negative charges was resumed by J. J. Thomson (Thomson J, 1904). Thomson’s model was made of a sphere of uniform positive charge of the dimension of the atom in which the electrons were inserted as seeds in a watermelon or as raisins in the *plum-pudding*, the typical English Christmas cake. The electrons occupied equilibrium positions stabilized by the balance between their repulsion and by the attractive interaction with the part of positive charge internal to their position.

Up to a given number, the electrons were disposed on a plane and for greater numbers on ring structures. In this pudding of positive charge the electrons would oscillate with fixed frequencies around their equilibrium positions, emitting or absorbing the spectral lines characteristic of the atoms Thomson concluded on the basis of complex calculations that few electrons would form triangular, tetrahedral etc. structures, whereas after eight electrons concentric structures would be formed.

In 1878 the American Alfred Marshall Mayer (1836-1897) of the university of Maryland, in the attempt to prove how atoms were organized in the molecules, had the idea of immerging in a water receiver a series of magnetized needles mounted upon corks, with their south poles upward. Hanging at the center of the receiver a powerful steel magnet with his north pole oriented toward them he discovered that the needles were arranged on concentric circles forming regular structures. Three magnets would form a triangle and four would arrange themselves at the corners of a square. five may either formed a square with one magnet in the center, or set themselves into a pentagon. Six would form a pentagon with one in the center, or arrange themselves three on a side in the form of an equilateral triangle. Seven magnets would form an hexagon with a magnet at the centre and eight magnets would be arranged either in the form of an hexagon with two magnets at the centre or alternatively of an heptagon with a centered magnet.

For higher combinations made of nine or more needles represented in the figure above, Mayer discovered that the configurations of the floating magnets could be divided into primary, secondary, tertiary, etc., classes, and that the stable configurations of a lower class form the basis of the succeeding ones. When there are two or more forms of arrangement, some are more stable than others, and only the most stable would survive in higher classes.



Mayer’s picture of the arrangement of the magnetized needles

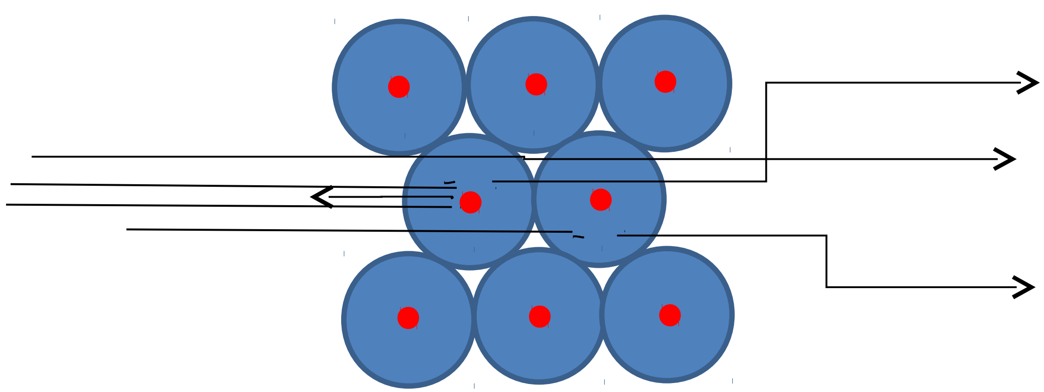
J.J. Thomson considered Mayer picture very appealing, pointing out the close resemblance with the periodic table of the elements and used Mayer's organization of magnets to build his atomic model

In the same year 1904 the Japanese Hantaro Nagaoka (1865–1961), professor of physics at the university of Tokyo, developed a planetary model of the atom of the type of the Saturn planet, namely a structure made of a heavy central nucleus of positive charge surrounded by a ring of electrons orbiting around it.
The model predicted that the electron ring should be stabilized by the relatively large mass of the nucleus. This prediction, although supported by lord Rutherford was soon recognized to be physically incorrect since a ring of negative charges would be very unstable due to the disruptive repulsion of the electrons and was in fact abandoned by Nagaoka himself in 1908.

Also Thomson's atomic model had a short life. It was not well considered by the chemistry community of the time that could not easily accept the idea that such a huge dissymmetry could occur between the negative charge condensed in very small particles, the electrons, and the positive charge uniformly spread in a volume many orders of magnitude larger.

It was just a pupil of Thomson, Ernest Rutherford, the one who invented the crucial experiment that marked the end of the *plum-pudding* model and paved the route to the modern theory of the atom.

In 1907 Ernest Rutherford professor of physics at Manchester started a collaboration with the German physicist, Johannes Wilhelm Geiger, who, studying the diffusion of beams of alfa particles through thin metallic foils with a young student, Ernest Marsden, discovered that some were so strongly deviated from a straight path to even go back. Rutherford, thought it through for two years, until he grasped the right solution that he presented to the 7 March 1911 meeting of the *Literary and Philosophical Society of Manchester* in the form of a short note in which he concluded that the only possible explanation for the Geiger and Marsden results was to assume that both the positive charge and the atomic mass were localized in a volume much smaller than the total volume of the atom, volume that he named atomic nucleus.



The "old" quantum theory

On the basis of these results Rutherford proposed in 1911 a new atomic model consisting of a positive central nucleus aroung which the negatively charged electrons rotated as the planets around the Sun .

an atomic model with a positive central nucleus around which the electrons rotated on stationary orbits was undoubtedly fascinating and presented a nice parallelism between the infinitely big and the infinitely small worlds, between electrons and planets both forced to move on fixed orbits by the deterministic laws of classical dynamics. This model, although highly appealing, presented, however, an insurmountable difficulty, being in strong contrast with Maxwell's electromagnetic theory, that imposes that an electric charge in motion on an orbit, being subjected to an acceleration, must continuously radiate energy. The atom then, loosing energy would be unstable and after an extremely short time the electron would fall on the nucleus.

Rutherford who was aware of the limits of the planetary model for electrically charged particles, had actually avoided in his 1911 paper to speak of orbits, specifying that in his model the atom consisted of a positively charged nucleus surrounded by an uniform distribution of negative charges.

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The problem of assigning the electron to specific orbits was instead tackled by Niels Bohr in a famous series of three papers making a brilliant attempt to save the determinism of classical mechanics, bound to the concept of orbit, by conciliating the electron dynamics with the electromagnetism on the basis of an hypothesis made by Max Planck in 1900 assuming that the radiation could not be emitted or absorbed in a continuous process but only by discrete amounts that he named light quanta giving thus rise to the theory known today as the old quantum theory.

In Bohr's model the electrons preserved their classical motion on circular orbits but their energy possessed only discrete values, defined by two conditions known as the quantization conditions.
The first of these conditions, radically changed the mechanism of classical electromagnetism at the microscopic level, imposing that the energy difference between two orbits was equal to a multiple of the quantity $h\nu$, where h is a constant introduced by Planck and ν the frequency of the radiation emitted or absorbed in the transition between two discrete orbits.

Bohr defined this first quantization condition on the basis of a discussion with his friend and former classmate, the spectroscopist Hans Marius Hansen (1886-1956), who told him the existence of the Balmer equation that Bohr ignored.

$$\nu = R_H \left[\frac{1}{4} - \frac{1}{n^2} \right]$$

where n = 3, 4, 5, etc. and RH is the so called Rydberg constant (RH = 109,737 cm-1).

The second condition "quantized" the angular momentum of the electron imposing that it should be a multiple of *hν/c* where c is the speed of light. This condition was suggested to Bohr by the papers of John William Nicholson (1881-1955), a mathematical physicist of Cambridge who had attempted to interpret the complex emission spectrum of the solar corona with an atomic model in which rings of electrons orbited around the nucleus (Nicholson, 1912). According to Nicholson the electron oscillations in these rings gave rise to the spectrum. Even if incorrect, this theory involved an important idea that was included in Bohr's theory. Nicholson wanted to incorporate Planck's ideas in his model and knowing that the Planck *h* constant had the right dimension, decided to use it as an unit of angular momentum, imposing that the atom could lose or gain angular momentum only in definite amounts, multiple of *h*. According to him, the angular momentum quantization was more correct and important then the energy quantization.

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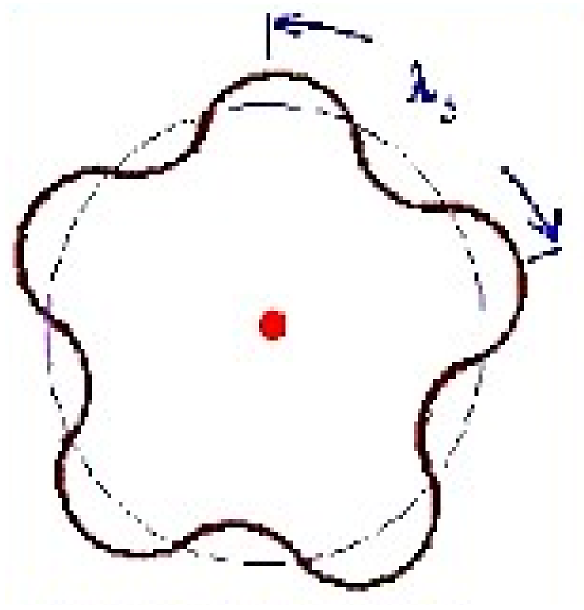
The quantization of the angular momentum corresponded to consider the electron not only as a particle but also as a wave. Actually an orbit that satisfies the de Broglie principle, in order to be stable must correspond to a stationary wave and therefore the closed path followed must be an integer multiple of the wavelength. As a consequence only special values of the radius of the circumference are allowed.



Bohr’s genial ideas were from one side to couple the energy and the angular momentum quantization, reducing in this way the number of possible circular electron orbits only to the stationary ones.
Bohr succeeded in this way in obtaining a stupefying agreement between his theory and the empirical relationships found by several authors, in particular by Balmer and Rydberg, for the visible frequencies of the hydrogen atom

The extension of Bohr’s theory to many electron systems, presented in the second and third papers of 1913 was not very satisfactory for the interpretation of their emission spectra. An important improvement of the theory was developed by Arnold Sommerfeld (1868-1951) introducing elliptical orbits in addition to the circular ones in Bohr’s theory (Sommerfeld 1916) and defining more general quantization conditions than those of Bohr.

With Sommerfeld help and taking into account Abegg’s and Kossel’s ideas, Bohr developed in a series of papers from 1921 to 1923 the *Aufbau* (building) principle that established how distribute the electrons in the atomic orbits of the elements of the periodic system

The Aufbau principle started from the hypothetical possibility of constructing the electronic structure of an atom of the periodic system adding one electron to the electronic distribution of the previous atom and applying the concept of quantization of the orbits. Starting from the hydrogen atom with only one electron the energy levels of the following atoms were one at a time filled with electrons starting from the lowest energy levels up, on the basis of essentially empirical rules.
The electronic orbits were thus distributed in the atoms in shells or "barks" that contained the nucleus as onion layers.

The original form of the Aufbau principle, developed in the period 1921-1923, did soon show its limitations when Bohr tried to extend its idea of filling the electronic orbits of many-electron atoms. In 1924 a new and more efficient version was proposed separately by two English scientists, the chemist John David Main-Smith of the university of Birmingham and the physicist Edmund Clifton Stoner who worked at the Cavendish Laboratory of Cambridge.

THE ELECTRON SPIN

In 1920 Sommerfeld proposed the existence of an internal quantum number associated to an “hidden” rotation (Sommerfeld, 1920) to describe the anomalous reaction of many electron atoms to an external magnetic field (anomalous Zeeman effect). In 1925 Pauli published his *Ausschliessungsprinzip,* exclusion principle (Pauli, 1925) that proposed the existence of a fourth quantum number.

Rydberg had noticed that the number series 2, 8, 18, 32, ..., defining the length of the periods of the periodic system, was the series 2n2. Pauli realized that this factor 2 recurring in Rydberg formula as well as in Bohr’s and in Langmuir’s theory, had no theoretical justification and derived from a not jet discovered condition.

Pauli exclusion principle imposes that two electrons cannot have the same set of four quantum numbers. When an electron occupies an energy state defined by four values of the quantum numbers, that state is filled and cannot host another electron. This rule is actually valid only for particles like the electrons obeying the Fermi-Dirac statistic (fermions).

The first to suggest that a fourth quantum number could be connected to a spinning motion of the electron was a young American student of physics, Ralph de Laer Kronig (1904-1995),. The idea that the electron could spin like a whipping top did not please Heisenberg nor Pauli who suggested him to give up insisting on this funny idea that he qualified as deprived of any physical reality. Kronig, discouraged by these criticisms gave up and decided not to publish his ideas.

In 1926 the Swedish physicists George Eugene Uhlenbeck (1900-1988) and Samuel Abraham Goudsmit (1902-1978), working at Leyden in Holland under the supervision of Ehrenfest, read the just published Pauli's paper where he mentioned a fourth quantum degree of freedom. The two friends published right away the spin theory in papers in which the electron was assimilated to a small sphere of negative electricity rotating around the nucleus and spinning like a small whip top. Being an electric charge in rotation on an orbit it had to be associated to an intrinsic magnetic moment. The two Dutch imposed then to the rotation of the electron the condition that the spin angular momentum could only have the value $(\frac{1}{2})h/2\pi$ and that the magnetic moment could be oriented in a magnetic field only in two ways, parallel or anti-parallel to the direction of the field

LA MECCANICA QUANTISTICA

The black body emission

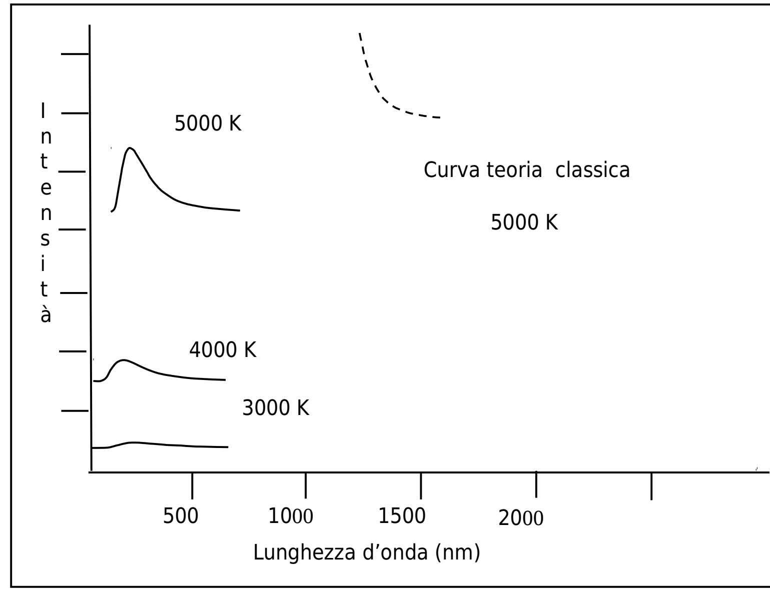
The black body expression was coined by Gustav Kirchoff

1. Gustav Kirchoff.
2. Wilhelm Wien.
3. Jožef Stefan.

Wien: $$\rho(\upsilon,T)=\alpha\upsilon^{3}\varepsilon^{-\beta\upsilon/T}$$

Lord Rayleigh:
James Jeans $$\rho(\nu,T)=\frac{2\nu^{2}KT}{c^{2}}$$

Paul Ehrenfest : ultraviolet cathastrophy



Max Planck $$\rho(\nu,T)=\frac{8\pi h\nu^{3}}{c^{3}}\frac{1}{e^{h\nu/KT}-1}$$

Planck was persuaded that the second principle of thermodynamics was an absolute truth and would not accept the probabilistic interpretation of Boltzmann that the increase of entropy in the spontaneous evolution of physical systems is justified by the fact that it is by far more probable than a decrease. The possibility of an entropy decrease in a physical process was a war-horse in the debate between Boltzmann and Poincaré.

If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations — then so much the worse for Maxwell's equations. If it is found to be contradicted by observation — well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

Arthur Eddington, The Nature of the Physical World

The mathematician Henry Poincaré (1854–1912) demonstrated in 1890 a famous theorem, the recurrence paradox (Poincaré, 1889) that asserted that any physical system evolving from a given state, unavoidably returns to visit that state if one waits long enough. The German mathematician Ernst Zermelo (1871-1953) used in 1896 (Zermelo, 1896 a,b) Poincaré result to attack the mechanistic approach, arguing that any theory inconsistent with the second law of thermodynamics must be false. .

Boltzmann showed, however, that the recurrence theorem was consistent with the statistical viewpoint, and that physical processes leading to negative entropy variations are not in principle forbidden, but only highly improbable .

In particular the waiting time for a physical system to go back to the initial state was found to be superior to the duration of the existence of the universe.

The idea that the energy could be emitted or absorbed in discrete quantities was too new and strange to be easily accepted in the scheme of classical physics. Even more difficult to digest was the appearance of a new universal constant, the h Planck's constant, that defined the energy as a function of frequency. It was only thanks to the talent of Albert Einstein that the quantum theory finally prevailed. In the period 1905-1907. Einstein, in order to explain the specific heat of solids, suggested a quantum nature also for the photoelectric effect, introducing the concept of a light quantum, the photon, associated to a quantized impulse $h\nu/c$

In 1922 the French physicist Louis de Broglie (1892–1987), carrying Einstein's hypothesis to extremes in his thesis entitled *Recherches sur la théorie des quanta*, concluded that if the radiation had a double nature of wave and particle, also an electron could have the same dualistic behaviour:

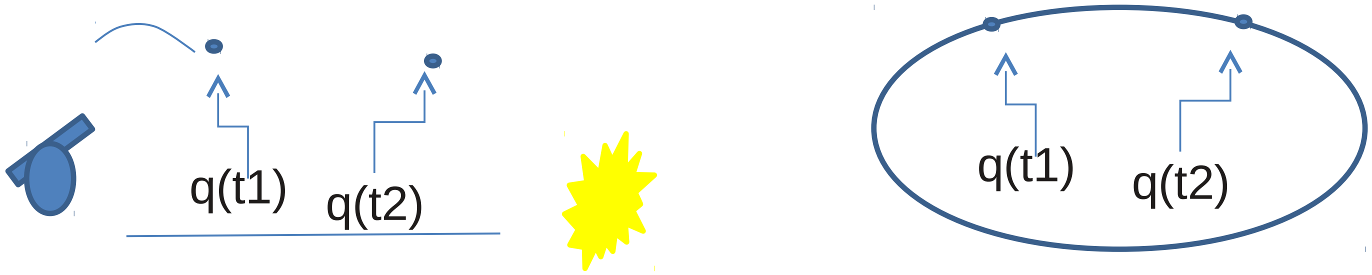
L'atome de lumière équivalent en raison de son énergie totale à une radiation de fréquence ν est le siège d'un phénomène périodique interne qui, vu par l'observateur fixe, a en chaque point de l'espace même phase qu'une onde de fréquence ν se propageant dans la même direction avec une vitesse sensiblement égale (quoique très légèrement supérieure) à la constante dite vitesse de la lumière.

When the idea that both the electromagnetic radiation and the electrons possessed a double nature of wave and particle started to spread out, another pillar of classical physics started to waver: the concept of orbit.

In 1924 there were two important centres of theoretical physics in Europe: the Niels Bohr institute at Copenhagen and that of Max Born at Göttingen. In these laboratories the suspicion that the concept of orbit was the true responsible of the difficulty of extending classical mechanics to the world of the electrons was already going around. Among the physicists involved in the discussion of this problem, the young Werner Heisenberg (1901-1976) was the one who, at the age of only 23 years, started to put into effect the elimination of orbits from particles dynamics.

In classical dynamics the orbits are determined by Newton equations and by the initial conditions. He realized that this deterministic description was correct for objects of the macroscopic world where the orbits are directly observable, but was not easily transferable to the microscopic world, arbitrarily assuming that electrons move as planets or satellites.

Classically an orbit is described by time dependent coordinates q(t) and momenta p(t), continuously varying as a function of time. The classical solutions of the dynamics of an object such as an electron are obtained by solving the equations of motion where the potential energy is normally written as a function of the squares of the coordinate's q and the kinetic energy as a function of the squares of the moment's p. In this way, however, one unavoidably arrives to a description of the motion of the object in terms of trajectories or orbits, just because coordinates and moments are continuous variables.



Heisenberg decided to define discrete quantum coordinates qnn(t) to describe the electron in a stationary energy level n and coordinates qnm(t) to describe the electron in the transition from an energy level n to an energy level m. In the same way he defined a discrete momentum pnn(t) of the electron in the n level and a momentum pnm(t) of the electron in the transition n→m.

To calculate the energies En of the quantum levels, Heisenberg used the classical theory of computing the total energy H = V + T, where V is the potential and T the kinetic energy. In order to calculate V and T he needed the squares of the coordinates and moments and had thus to face the difficulty of squaring quantities with a double index, problem never encountered before. After a long struggle, Heisenberg used the expressions

$$q_{nm}^2(t) = \sum_k q_{mk}(t) \cdot q_{kn}(t) \qquad p_{nm}^2(t) = \sum_k p_{mk}(t) \cdot p_{kn}(t)$$

and wrote the product between two different quantities q(t) and p(t) in the form

$$\left[q(t) \cdot p(t)\right]_{mn} = \sum_k q_{mk}(t) \cdot p_{kn}(t) \qquad \left[p(t) \cdot q(t)\right]_{mn} = \sum_k p_{mk}(t) \cdot q_{kn}(t)$$

Born, Jordan: Matrix Algebra

While Heisenberg, Born e Jordan had improved the matrix formulation of quantum mechanics and Dirac supplied a more elegant interpretation in terms of quantum operators, a formally completely different theory, the wave mechanics, came in the limelight thanks to the work of a Viennese physicist, Erwin Schrödinger, supporter of the physics of the continuum against that of the discrete.

Schrödinger, inspired by the ideas of De Broglie on the wave nature of matter, tried to develop, in opposition to the quantum theory of the discrete of the German school, a quantum theory of the continuum. Owing to his theoretical background, he knew well that for a continuum medium the solutions of the wave equation for simple systems, such as a vibrating cord fixed at the extremities, led always to a discrete number of waves, the fundamental ψ_1 of frequency ν and the overtones ψ_2, ψ_3,…ψ_n, with frequencies 2ν ,3ν,…,$n\nu$, etc., as well as to all their possible combinations

$$\psi(q.t) = \sum_n c_n \psi_n(q.t)$$

$$H\psi_n = E_n\psi_n \qquad H = \left(-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right)$$

At quite uncertain times and places,
the atoms left their heavenly path,
and by fortuitous embraces,
engendered all that being hath.
And though they seem to cling together,
and form "associations" here,
yet, soon or late, they burst their tether,
and through the depths of space career.
James Clerk Maxwell