The Development of the Concept of Atoms and Molecules

Dalton and Beyond

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The concept that all matter is made up of atoms was suggested by Dalton in 1803. It was a very useful concept, which could explain many of the experimental observations, but people were sceptical and considered atoms to be hypothetical objects until the beginning of the 20th century. By the end of the 20th century, advances in science and technology led to imaging of atoms and molecules. Now we are in a position to actually 'see' them using the scanning probe microscopies.

Keywords
Dalton, atomic theory, STM, AFM.

1. Introduction

The idea that any piece of matter is made of tiny indivisible units, all identical to one another, which if further divided will lose the characteristics of that substance, had existed for thousands of years. One finds the idea in ancient Indian writings, and in Greek philosophy. The idea was the result of abstract, philosophical thinking, and not a result of attempts to explain some experimental observations. The Hindu sage and philosopher, Kanada (2nd century BC), was among the first to propose such an idea. This was later developed into a more detailed theory of how atoms combine to form more complex objects. In fact, the word 'kanam' (meaning particle, or small object in Sanskrit) is said to have origins in the name of Kanada. In Greek philosophy, the idea of an indivisible atom was introduced by Democritus. According to him all matter was made of atoms. The material content of all atoms is the same, but atoms of different substances were different in their shapes and

sizes. The properties of the substance are determined by the shape and size of its atom. Thus, sweet substances are made of atoms which are smooth, while bitter things are made of sharp atoms!

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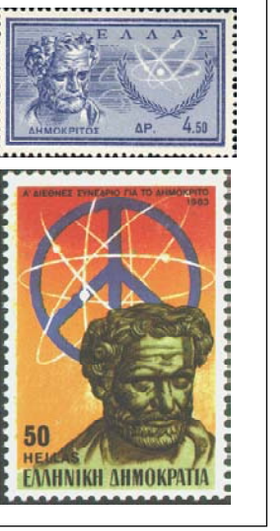
Dalton in 1803 put forward the idea of atoms in a very clear and scientific manner. His aim was to explain experimental results. He made the observation that water, ice and water vapor must contain the same kind of tiny particles, which must all be identical to one another. Further, he logically reasoned that if this is true of water, then it must be true of other materials, for there is nothing special about water. He thus concluded that all matter is made of tiny particles which are all identical to one another. Dalton's article, which is reproduced in this issue of *Resonance* is truly a classic, which stands out for its clear and logical arguments in support of the atomic theory.



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2. Further Developments

The ideas of Dalton started a new era, that of understanding the properties matter in terms of the atomic theory. Dalton himself proposed that the indivisible units of compounds are molecules; and that molecules are made of atoms combining in definite proportions.

The idea that atoms/molecules would be moving about either in a gas or a liquid was important and very useful. It was argued that gases consist of a large number of molecules moving in random directions, and colliding with each other and with the surface of the container. Their impact on a surface causes the gas pressure. What we feel as heat was ascribed to the kinetic energy of their motion. This idea was taken up by A K Krönig (1856) and independently by R Clausius (1857) who developed the kinetic theory of gases. After reading the paper of Cluasius, J C Maxwell, in 1859, formulated the Maxwell distribution law of molecular velocities, which quantitatively described 'randomness' of molecular velocities,

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and made the calculation of macroscopic properties of the gas possible. In 1871, Boltzmann generalized this work and proposed the Maxwell–Boltzmann distribution. Further, he made a very important suggestion – the connection embodied by his famous relationship between entropy and probability. This was an extremely important idea having far-reaching implications. Entropy, which was a rather mysterious quantity, developed and used in thermodynamics, was given a simple physical interpretation as a measure of the amount of 'molecular disorder' that the material has because of the randomness in the position and movement of its molecules.

See *Resonance,* Vol.5, Nos.3 and 4, 2000.

In spite of all these very interesting developments, even at the beginning of the twentieth century, many physicists still thought of atoms as purely hypothetical constructs. An important turning point, which convinced many of the real existence of atoms was Einstein's (1905) paper on Brownian motion, which succeeded in making definite and accurate quantitative predictions based on the idea of atoms in incessant motion [1], which could be experimentally verified. In 1897, Thomson did experiments on 'cathode rays' and concluded that these rays are streams of negatively charged particles much smaller than atoms. He suggested that they might make up all of the matter in atoms. This was a startling suggestion, as most people had thought of the atom as indivisible. In 1911, Rutherford, in order to explain his experiments on scattering of alpha particles from matter, suggested the now accepted nuclear model for the atom – all the positive charge in an atom is located in a nucleus, which occupies a very tiny fraction of the whole volume of an atom. The electrons were thought of as moving around the nucleus in orbits resembling those of planets around the Sun – the force of attraction between them and the nucleus arising from the charges, and thus the importance of electromagnetic interactions, in description of

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the atom was realized. However, this immediately lead to a serious problem. The model predicted that the atom would not be stable – for example, the electron in a hydrogen atom would radiate energy and collapse into the nucleus within about 10^{-8} seconds!

An understanding of how the atom could be stable had to await the formulation of wave mechanics by Schrödinger (1926) and the equivalent matrix mechanics of Heisenberg (1925). According to wave mechanics, all microscopic particles have a wave nature. In the atom, the electron exists as a standing wave that is held onto the nucleus by the attractive interaction between the two. States of an atom, which correspond to such standing waves, form what are known as stationary states, which can be studied using spectroscopic techniques. Similar states would exist in molecules, the only difference being that the waves would encompass all the nuclei in it. The electron density ρ at any point in the molecule is determined by the square of the wave function ψ, which quantifies the strength of the wave at that point. The fact that the waves extend over all the nuclei causes their charge density to be distributed such that the molecule is stable. The electron density distribution for a hydrogen atom as well as for the simplest molecular ion H_2^+ obtained by solving the Schrödinger equation are shown in *Figures* 1 and 2.

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3. Seeing Atoms and Molecules

The radius of an atom is of the order of 0.5−2 Angstroms, ruling out the possibility of seeing them under an optical microscope. However, in the 1980s, it became possible to image and manipulate atoms using the then developed scanning tunneling microscope (STM) (for more details, see: http://www.physics.leidenuniv.nl/sections/cm/ ip/ group/Principle_of_SPM.htm). The STM can be used to image atoms on the surface of a metal. The technique uses a sharp metallic tip, believed to be having only one

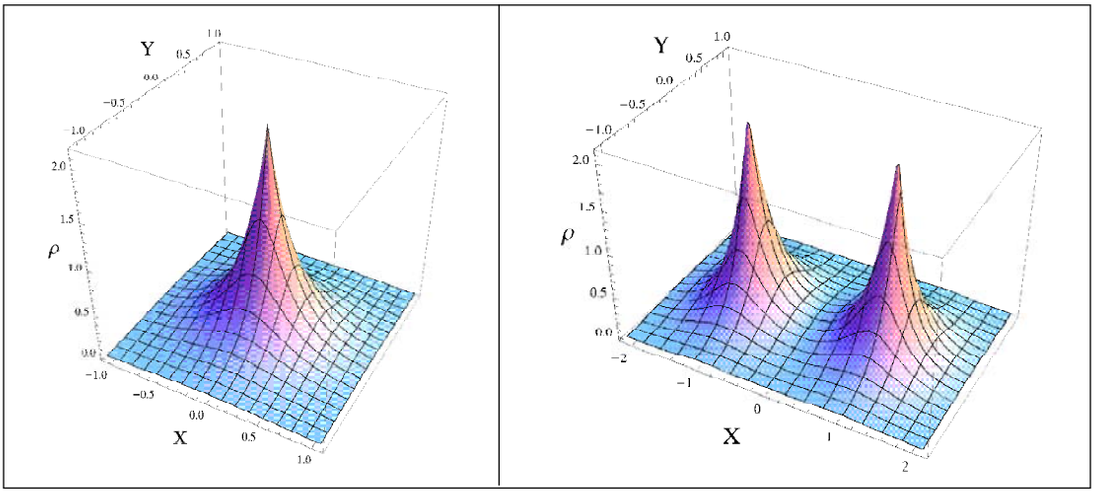


Figure 1 (left). Plot of the electron density (ρ) of hydrogen atom. Imagine that one puts the H atom at the origin of an XYZ coordinate system and measures its electron density at each point in the XY-plane and then plots it in the Z-direction – the result would be this figure. In the figure, distances in the X- and Y-directions are measured in Angstroms. The peak is at the position where the nucleus is in the XY-plane.

Figure 2 (right). Plot similar to Figure 1 but for the molecular ion H_2^+. The two nuclei are imagined to be stationary at the equilibrium internuclear distance (=1.05 Å) of the ion. Distances in the X- and Y-directions are measured in Å. The two peaks occur at the two nuclei.

atom at its end, brought near the surface of the sample that is to be scanned (see *Figure* 3). Within the tip or the sample, the potential energy of the electrons is low, due to their interaction with the positively charged nuclei. But in the gap between the two, their potential energy is high, as there are no nuclei there (see *Figure* 4). Hence there exists a barrier for the motion of the electron from the tip to the sample.

Application of a potential difference V between the substrate and the tip, shifts the energies of occupied states in the sample with respect to that in the tip. Thus the energies of the highest occupied states in the sample and tip are different (see *Figure* 4). This causes the electrons to jump from the occupied states (shown with light red color) of the tip, to the unoccupied states of

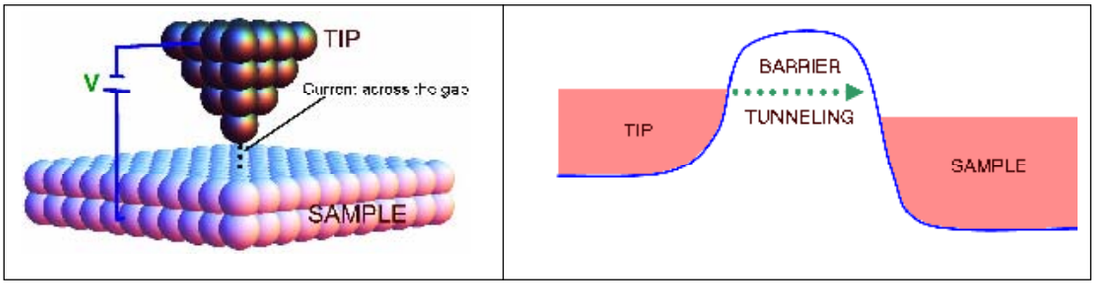


Figure 3 (left). Schematic representation of the principle of STM. A tip is brought within a few Angstroms of the sample. A potential difference V is applied between the two. This causes the electrons to jump across the gap, resulting in a tunneling current. This current is $I \propto e^{-d\kappa}$***, where*** κ ***is a constant and d is the distance between the sample and the tip. Hence this current is a sensitive measure of the distance. As one moves the tip across the sample, using a piezoelectric device, the current varies, and from this variation, an image of the corrugation of the surface at an atomic level can be obtained.***

Figure 4 (right). Within the tip and the sample, the electrons feel the charges of their nuclei, lowering the potential energy of the electrons in them. In the gap, there are no nuclei and hence the potential energy of the electrons is higher, resulting in the barrier. The variation of the potential energy in the direction perpendicular to the surface of the sample is shown by the blue curve.

the sample. This motion across the gap is a result of the wave nature of the electrons and is a typical quantum mechanical phenomenon, referred to as tunneling. The magnitude of the current that results is exponentially dependent on the distance d between the two and hence very sensitive to the size of the gap between the tip and the sample. Thus, if the tip is right on top of an atom on the surface, then the current would be more, while positioning it at regions between two atoms would give a smaller current. As one moves the tip across the sample, the current would vary, thus effectively leading to imaging of the electron density variation across the surface of the sample. The STM has also been used to manipulate atoms and molecules on surfaces. At close proximity there is attractive interaction between the tip and an atom sitting on the surface. So the tip can be used to move a Xe atom sitting on the surface of Ni, and position it at a new location. Thus we can literally drag an atom along the surface and place it anywhere

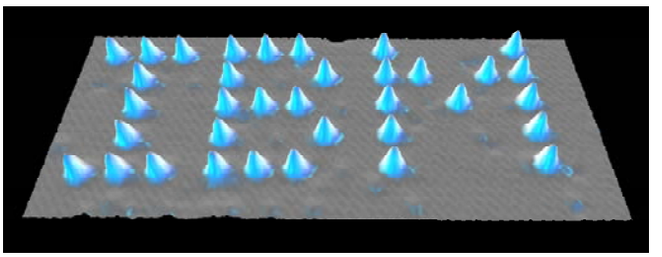


Figure 5. IBM written with Xe atoms [2,3]. Each small peak is one Xe atom. Notice the similarity between the experimentally seen peaks and peaks in the electron density in the hydrogen atom/molecule ion in Figures 1 and 2.
Courtesy: Image originally created by IBM Corporation.

we want! Researchers at IBM have been particularly good at this [2,3]. The first thing that they did with this technique was to write the letters 'IBM' using Xe atoms on a Nickel surface (see *Figure* 5 and [2]). They have also written the Japanese Kanji character seen in *Figure* 6, which stands for 'atom' in Japanese, and wrote a variety of other things (see [3]).

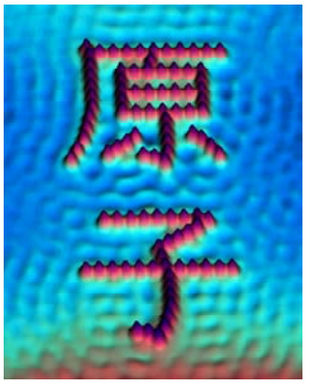
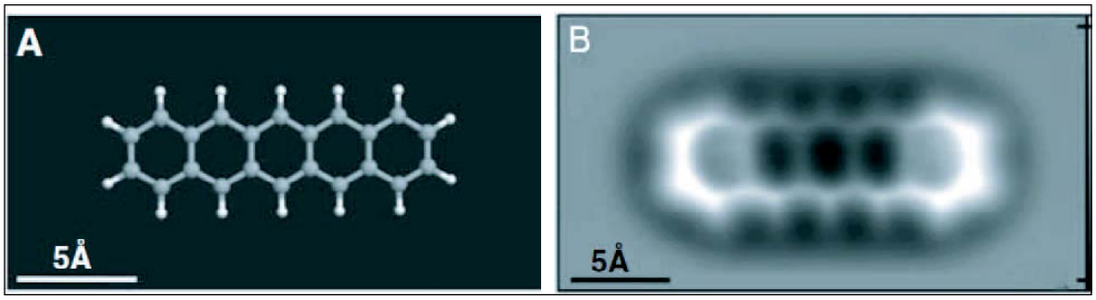


Figure 6. The Japanese Kanji character for 'atom' written with atoms [3] (each small peak is one atom).
Courtesy: Image originally created by IBM Corporation.

Nowadays, imaging surfaces using STM has become a routine technique. A related technique is atomic force microscopy (AFM), which measures the force between a tip and atoms on the surface, and thus images the surface. This too has been used to image nanosized systems. A very interesting image of the molecule 'pentacene' (a hydrocarbon containing five benzene rings fused together to form $C_{22}H_{14}$), made using AFM has attracted a lot of attention recently, because one can 'see' the molecule, as well as the atoms of which it is made of (see *Figure* 7 and [4]).

Figure 7. AFM image of pentacene on Cu(111). (A) Ball-and-stick model of the pentacene molecule. (B) AFM image of pentacene. Notice that AFM is able to show atoms in the molecule. Adapted from the paper by Gross et al [4].



Thus the concept of the atom originated as a figment of imagination of Kanada and Democritus. It was later proposed by Dalton to explain experimental observations and developed further by others. Even in the beginning of the 20th century many physicists considered them hypothetical, until Einstein argued for the possibility of observing their effects indirectly, by studying Brownian motion. Finally, towards the end of the 20th century atoms could be seen and manipulated, thanks to the intense intellectual efforts of a large number of scientists.

Suggested Reading

[1] **Sriram Ramaswamy, *Resonance*, Vol.5, No.3, pp.16–34, 2000.**

[2] **D Eigler and E Schweizer, *Nature*, Vol.344, p.524, 1990.**

[3] **http://www.almaden.ibm.com/vis/stm/atomo.html**

[4] **L Gross, F Mohn, N Moll, P Liljeroth and G Meyer, *Science*, Vol.325, p.1110, 2009.**

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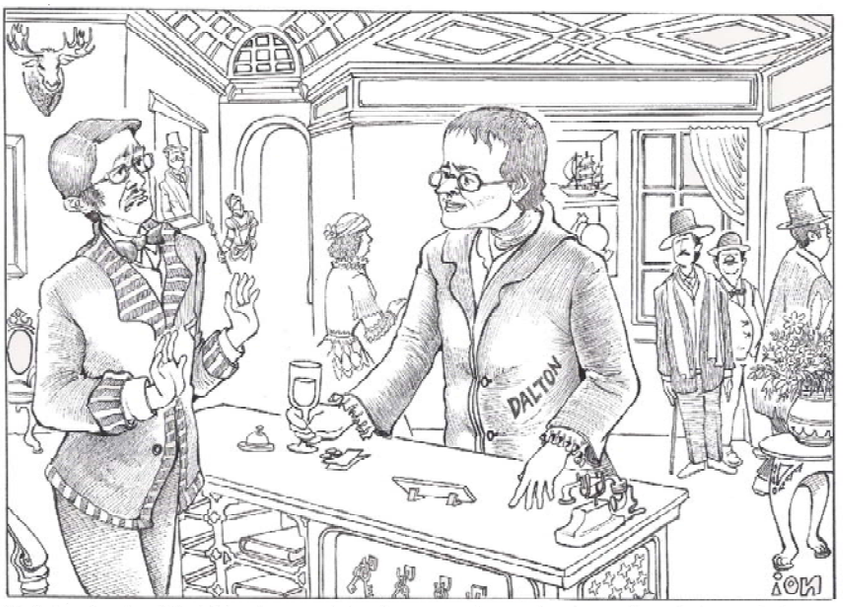

"You may say that water and ice are made of the same stuff, Mr. Dalton; however, can you prove that when ice melts to give you water, God does not put his spirit into ice and convert it to water?"