QUANTUM-MECHANICAL DESCRIPTION OF MENDELEEV PERIODIC TABLE

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Contents

Summary

The quantum mechanical description of the periodic table is given. We mention also some of the historical notes on the development of the classification of the chemical elements. We review the basic concepts of the hydrogen atom model, which is the basis for the periodic table construction. The block structure of the periodic table is discussed in detail. We discuss also some important chemical labels.

1. Introduction

One of the major achievements in the history of chemistry is the recognition of the existence of the different chemical elements and that they can be organized according to their chemical properties. This organization was based on the concept of atom and its electrons and was fitted in a periodic table of elements. A brief historical account is given below.

The scientific basis for the classification of the various elements was given at the beginning of the twentieth century, with the development of quantum mechanics and by the solution of the Schrödinger equation of the hydrogen atom. Although heavier, multielectronic atoms, are described by a much more complicated equation, the quantum numbers obtained for the hydrogen atom give a good estimate for atoms with small atomic mass.

Not all the elements of the periodic table exist in nature. Some of the heaviest elements have been produced artificially under special conditions by scientists.

2. Historical Notes

The concept of atom was first mentioned by Democritus 25 centuries ago. He was a pre-Socratic philosopher, born in Abdera ca. 460 BC. Democritus had the belief that all kind of matter was made of various indivisible elementary units and declared that one can divide a sample many times, but at the end of a finite number of divisions, one would find the elementary unit called *atomon*. He also mentioned that the different forms of matter found in nature were combinations of a set of basic elements. Although he did not know those elements, he believed that they had a particular size, shape, and weight and the other physical properties like color are the result of complex interactions between the atoms of the observer and the sample under examination. In Figure 1 we show a banknote of 100 Greek Drachma as homage to Democritus.

Figure 1. The 100 Greek drachma banknote with Democritus on one side.

Moreover, Democritus was also the first thinker to develop the difficult concept of void, but the existence of empty space was not accepted by the philosophers of that time.

Some years before, in 490 BC, another philosopher, Empedocles, was born at Agrigentum in Sicily. He had a very different concept of the components of matter. He put forward a cosmogonic theory in which fire, air, water, and soil are the four basic elements of which any type of substance is composed. This theory became dominant over the centuries. The reason was that the latter idea was accepted by Aristotle who amended it by introducing the ether as a supplementary element. In addition to the five-element 'table' of which any substance is formed, Aristotle claimed that the elements could change from one to another and this idea led to alchemy (the art of transformation, in Arabic), a pseudoscience with the main purpose of producing gold, starting with any other elements. The alchemy dominated chemistry up to the times of Boyle (1661) and Lavoisier (1780).

It was only in the 18th and 19th centuries that the majority of chemical elements have been discovered. The idea of atoms has been revived by J. Dalton, who established that the atoms of different elements have different weights. In 1808 Dalton published his theory of matter based on the following postulates:

1. Each element is made up of tiny particles called atoms.
2. The atoms of a given element are identical; the atoms of different elements are different in some fundamental ways.
3. Chemical compounds are formed when atoms combine with each other. A given compound always has the same relative numbers and types of atoms.
4. Chemical reactions involve changes in the way they are bound together. The atoms themselves are not changed in a chemical reaction.

He also calculated atomic weights from percentage compositions of compounds, using an arbitrary system to determine the likely atomic structure of each compound. Dalton was the first to publish a small atomic table of about 20 elements that were known at his time. Although, later this table was proved to be wrong because of Dalton's incorrect assumption about the formulas of given compounds, the construction of the table was an important step forward.

DALTON'S ELEMENTS	
Hydrogen=1	Strontian=46
Azote=5	Barytes=60
Carbon=5.4	Iron=50
Oxygen=7	Zinc=56
Phosphorus=9	Copper=56
Sulphur=18	Lead=90
Magnesia=20	Silver=190
Lime=24	Gold=190
Soda=28	Platina=190
Potash=42	Mercury=167

Table 1. The first table of chemical elements published by J. Dalton. On the right of each element is the weight that he estimated in units of the one of H. Azote was the name used for nitrogen.

Nowadays the concept of atomic weight is changed for atomic mass, since weight is the force exerted by the earth. The atomic mass unit (amu) is used at the present time to measure the relative mass of atoms and molecules. It is equal to one-twelfth of the mass of a carbon-12 atom, which is approximately the mass of a proton or $1.66 \cdot 10^{-27}$ kg. The relative atomic mass of an atom has no units; thus oxygen-16 has an atomic mass of 16 Daltons but a relative atomic mass of 16.

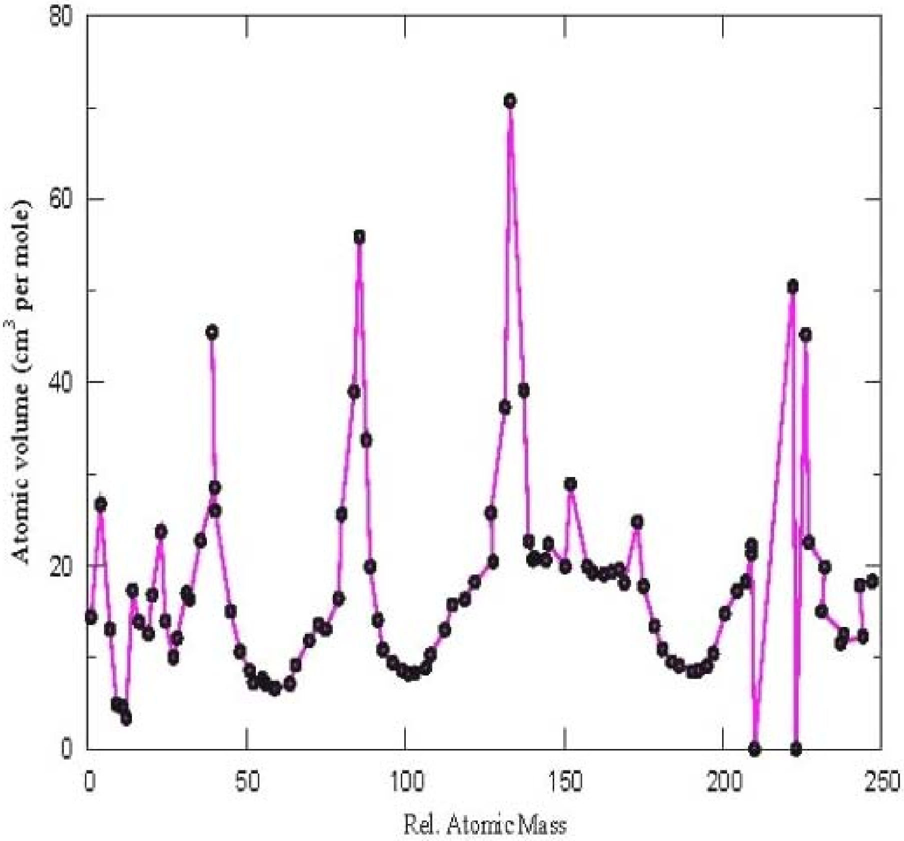

Figure 2. The periodicity revealed by Meyer’s method of atomic volume, which is the ratio between the atomic weight and density. The plot with 96 points is a modern version of the Meyer graphics which contained only 28 points. The Astatine (Relative atomic mass =210) and Francium (Rel. atomic mass = 223) atomic volumes are set equal to zero because their density is unknown.

At the First International Congress of Chemistry in 1860, organized in Karlsruhe, Germany, the determination of the atomic weight of all 58 elements known at that time has been recognized as a first priority. Among the attendants two young chemist were present: Julius Lothar Meyer and Dmitri Ivanovich Mendeleev.

The two were challenged for the developing of the periodic table and returned to their institutions to work on it. In a publication that appeared in 1864, Meyer used the atomic weights to arrange 28 elements into 6 families that bore similar chemical and physical characteristics.

The introduction of the concept of chemical valence was his main contribution. Meyer discovered some chemical periodicity by using the variation of atomic volumes with the atomic masses but missed shortly to predict more elements.

This is shown in Figure 2.
Some precursor ideas in favor of the concept of chemical periodicity can be encountered in the works of J.W. Döbereiner (law of triads, 1810), Alexander É. Beguyer de Charcourtois and John A.R. Newlands (law of octaves or eight-fold periodicity) [1]. The order of this valence periodic table is given by the increasing order of the atomic weight and by the similarity of the physical and chemical properties.

Although the electron was not known at that time, the empirical accumulation of knowledge allowed inferring the periodic regularities of the set of known elements which has been used to predict the existence of other elements that were lately discovered.

Mendeleev was appointed chair of Chemistry at the University of St. Petersburg and published some papers in 1869 about his version of the periodic table in which he used also the key concept of valence that helped him to claim the existence of four new elements:

A	B	C	D	E	F
			Ti=50	Zr=90	?=180
			V=51	Nb=94	Tl=182
			Cr=52	Mo=96	W=186
			Mn=55	Rh=104.4	Pt=197.4
			Fe=56	Ru=104.4	Ir=198
			Ni=Co=59	Pl=106.6	Os=199
H=1			Cu=63.4	Ag=108	Hg=200
	Be=9.4	Mg=24	Zn=65.2	Cd=112	
	B=11	Al=27.4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210
	O=16	S=32	Se=79.4	Te=128?	
	F=19	Cl=35.5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85.4	Cs=133	Tl=204
		Ca=40	Sr=87.6	Ba=137	Pb=207
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75.6	Th=118?		

Table 2. Mendeleev’s table based on the concept of *chemical* valence, which later was identified with *electron* valence.

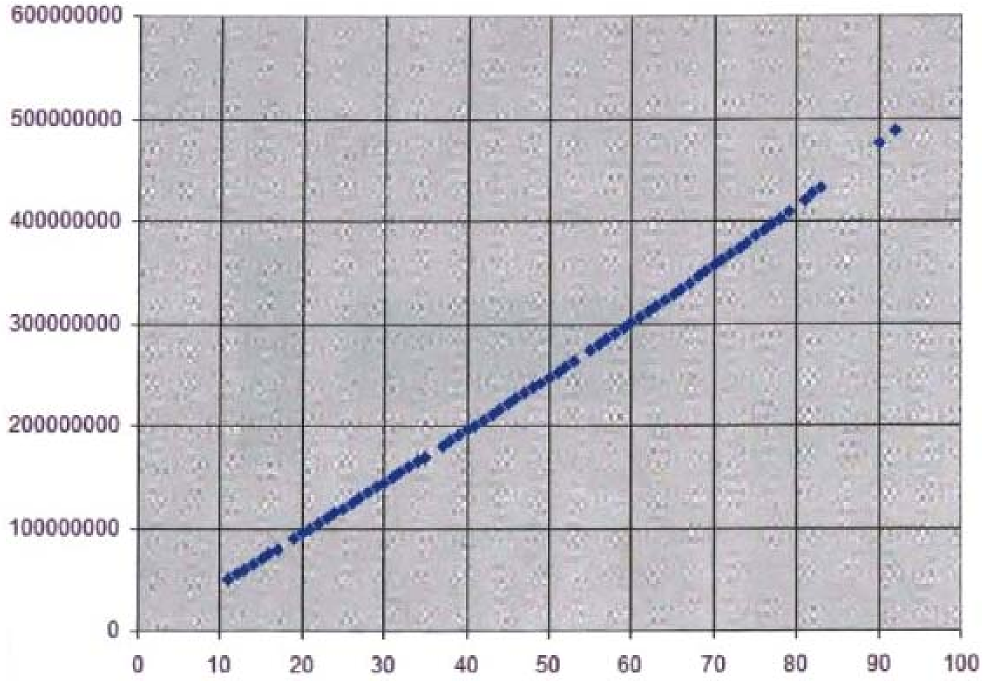

Figure 3. The Moseley scaling.

eka-silicon (Germanium), *eka-aluminium* (Gallium), *eka-boron* (Scandium), and *eka-manganese* (Technetium) that were indeed discovered later (see Table 2). *Eka*, meaning 'one' in Sanskrit, was used in the sense of chemically similar by Mendeleev.

It was also essential to use the atomic number dependence instead of the atomic weight in tracking the chemical periodicity. This is because atomic masses are far more difficult to measure than atomic numbers that can be determined with precision by the Moseley scaling of atomic X rays [2]. Moseley found that the square root of the frequency f of the most intense X-ray line, K_α, of a particular element was directly proportional to the atomic number Z of the element (see Fig. 3)

$$\sqrt{f} = 4.96 \times 10^7 (Z-1)\,\mathrm{Hz}^{\frac{1}{2}}. \tag{1}$$

Now we know that there are 92 natural elements on our planet and a handful of other ones have been produced by artificial means.

3. The Atomic Models

On the basis of the work of Dalton, Meyer, Mendeleev, and others, the concept of atom was well supported. Inevitably, scientists began to wonder about the nature of the atom. What is an atom made of, and how do the atoms of the various recognized elements differ?

The first important experiments that lead to the understanding of the atom were performed in the period 1898 to 1903 by J.J. Thomson (1856-1940), who studied electrical discharges in cathode-ray tubes. He found that when high voltage was applied to the tube electrodes, a ray that he called cathode-ray, was produced. He identified that the ray was a stream of negatively charged particles, now called electrons. Furthermore, from his experiments he could estimate the charge-to-mass ratio of the electron:

$$\frac{e}{m} = -1.76 \times 10^{8}\ \mathrm{C/g}. \qquad (2)$$

Here, e is the electron charge in Coulombs and m is its mass in grams.

Since this kind of negative particles could be produced from electrodes made of various types of metals, he concluded that all atoms must contain electrons. Furthermore, he postulated that an atom consisted of a positive charged cloud, whose extent was determined by the atomic radius, with the electrons embedded in it. In order to prove this model, Ernest Rutherford, accelerated α-particles and made them collide with a metallic gold film. If the model was correct, the massive α-particles (their mass is 7300 times that of the electron), would go through the film with minor deflections in their paths. The result was that many particles went just through but some particles were deflected at large angles [3]. Then he concluded that the atom must have a small nucleus carrying the positive charge and most of the atomic mass.

In the light of his experiments Rutherford proposed a kind of planetary model for the atom, in which the electrons would be moving around a positive nucleus, at distances much larger than the nuclear radius. Although Rutherford's planetary atomic model explained qualitatively well the deflection of α-particles, it had two major deficiencies.

First, according to electrodynamics, an electron moving around the atom in circular paths, is under a constant acceleration and must radiate energy. This fact would lead to a situation in which the electron would lose energy continuously and would collapse onto the nucleus.

The second major problem, is that the model could not account for the spectra of radiation from atoms, which was not continuous but discrete (see *Molecules Atoms and Nuclei*). The data obtained from the emission of light by excited atoms had very characteristic frequencies and was unique for each atom. These spectroscopic observations were put in a systematic form in 1908 through the so-called Rydeberg-Ritz combination principle [5]. Their principle says that the frequency of a spectral emission or absorption line can be expressed as a sum or difference between the members of a set of well defined frequency terms. Rutherford's model could not explain this discrete spectroscopy.

It was the great merit of Niels Bohr, a Danish physicist, to formulate in 1913 the hypotheses, or postulates, that could allow the explanation of the atomic spectral lines based on the planetary atomic structure. Although Bohr's postulates were rather strange because they were not completely classical the simplicity of getting the experimental spectroscopic results turned them into the preferred explanation and understanding of atoms for more than a decade.

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Biographical Sketches

Haret C. Rosu was born in Bucharest, Romania, in 1952. He studied physics at the University of Bucharest and obtained the PhD degree in nuclear physics in 1987 during his period as researcher in the campus Magurele-Bucharest, where the main National Physics Laboratory of Romania is located. He stayed there for the decade 1980-1990. Between 1990–1993 he was visiting professor at the Abdus Salam International Centre for Theoretical Physics in Italy. Starting March 1993 he worked for eight years as Associate Professor at the Institute of Physics of the University of Guanajuato (IFUG), in Leon, Mexico, and since January 2002 he is a Full Professor in the Institute for Scientific and Technological Research in San Luis Potosi, Mexico (IPICyT). For his academic achievements he was awarded the Potosí Prize 2006 by IPICyT. Dr. Rosu published 120 research papers, most of them since he came to Mexico, and is known as an expert in supersymmetric quantum mechanics as well as other areas of theoretical physics and applied sciences. He also published 4 book chapters and has many contributed papers in proceedings of workshops. Some of his graduate courses on quantum and classical mechanics are freely available in the Internet at the arXiv and other sites. He supervised three PhD students who now are on academic positions in Mexican universities.

J.L. Morán-López was born in Charcas, San Luis Potosí, Mexico in 1950. He got his M.Sc. from the Center for Research and Advanced Studies, Mexico City (1974) and the Doctor Rerum Naturalium Degree from the Freie Universitaet Berlin, Germany (1977). Later, he spent two years as a Posdoc at University of California, Berkeley, USA. He was the Founder General Director of the Institute for Scientific and Technological Research in San Luis Potosi, Mexico, 2000-2005. He was also the academic coordinator of the National Supercomputer Center (IPICYT) from 2006 to 2008. Now he is Professor at the Polytechnic University of San Luis Potosi, Mexico.

He was John Simon Guggenheim Fellow (USA) during 1984-1985. Then he got a fellowship at the International Centre for Theoretical Physics, Trieste, Italy, 1985-1991, and was appointed as Senior

Associate for the period 1992-1997. He received the C. V. Raman Award, given by the International Centre for Theoretical Physics, Trieste, Italy in 1990. He was Alexander von Humboldt Fellow (Germany) in 1992-1993. In 1993 he was distinguish as a Fellow by the American Physical Society. He is member of the Academy of Sciences for the Developing World (TWAS) since 1991. His contributions for science were recognized by the Mexican Government by awarding him the National Prize on Sciences and Arts in the area of Exact and Natural Sciences in 1995. He acted as Editor of the Mexican Journal of Physics during the period 1996-2000. In 1999 he was elected as Vice-president of the Union of Pure and Applied Physics for the period 1999-2002. The last academic recognition to his scientific achievements was the TWAS Medal Lecture in 2004. Now he acts as he Treasurer of the TWAS.

His main scientific interests are the physicochemical properties of nanostructures materials. Other interests are phase transitions in low dimensional and confined systems, quasicrystals, and magnetic properties of binary and ternary alloys.