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The Periodic Table. The Power of Systematization. The Importance of Precision

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ABSTRACT

One hundred and fifty years ago the first important systematization in the realm of chemistry was done, ordering the elements in terms of its atomic mass. This first attempt was crucial even though not totally correct. A better knowledge of the atomic structure improved this initial systematization in terms of the atomic number; but a real understanding of the periodicity in the atomic properties was possible only when the mathematical functions describing the electrons within an atom were obtained. The use of the variational principle looking for the minimal energy of an atomic or molecular system was the engine behind this understanding, though soon it became also clear that, in some specific cases, second order properties could be not adequately described even if the precision got for the energy was large. Magnetic properties are a good example, or the singularity of the elements of the first row of the periodic table with respect to the others within the same group. Some of these questions will be analyzed in our presentation.

INTRODUCTION

The Periodic Table, as it is illustrated in Figure 1 was born 150 years ago, when in 1869 Dmitri Mendeleev propose to order the known chemical elements according to their atomic mass. This was a first rationalization attempt of the known bricks forming the universe, but what we want to emphasize here is that the Periodic Table is still a living object with many surprises yet to come.

The revolution of Mendeleev Table was the systematization this table introduced in our knowledge of the universe around us. To use the atomic mass as the criterion to order the known elements was pure empiricism but the elements appeared grouped in families with common chemical properties, even though the explanation of this evidence was completely unknown at that moment. On the other hand, it was also observed that the ordering was not completely satisfactory, and for instance tellurium--iodine, argon-potassium and cobalt-nickel couples should be located in the reversed order. Nevertheless, and in spite of this small inconsistencies, the value of the systematization was huge, and the best proved of that was that the predictions made of the properties of several elements still unknown, Eka-Boron, Eka-Aluminum, Eka-Manganesse, and Eka-silicon turned out to be totally correct when the corresponding elements, that would be named Scandium (Sc), Gallium (Ga), Technetium (Tc) and Germanium (Ge) were isolated and characterized.

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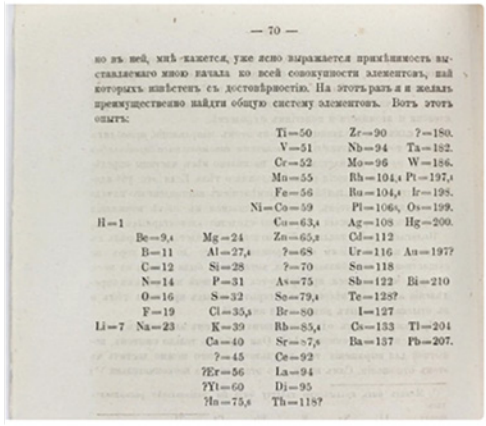

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но въ ней, имѣ-кажется, уже ясно выражается примѣнимость вы-
ставляемаго мною начала ко всей совокупности элементовъ, най
которыхъ извѣстенъ съ достовѣрностію. На этотъ разъ я и желалъ
преимущественно найдти общую систему элементовъ. Вотъ этотъ
опытъ:

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=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,	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?		

Figure 1
Dmitri Mendeleev and his hand-written and printed versions of the first Periodic Table.

The crucial next step in the systematization of our knowledge as far as the ordering of the elements was concerned was a direct consequence of the periodic law presented by the British Henry Moseley at the beginning of the 20th century. Indeed, Moseley found a rather simple and systematic relationship between the frequency of the X-rays produced by different elements and their atomic numbers (see Figure 2).[1] Although it was not clear yet what was the physical origin of this relationship, it was immediately evident that when the elements were ordered according to their atomic number no inversions, as the one observed when the masses were used, appeared. The researchers started to be familiar with a new way of representing the Periodic Table, which is essentially the one we still used nowadays.

$$\sqrt{\nu} = k_1 + k_2 \cdot Z$$

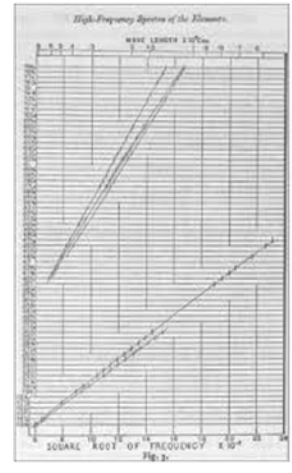

Figure 2
Henry Moseley and the law that related the frequency of the radiation emitted by an element and the number of protons in its nucleus, the atomic number, Z.

Moseley's law was a very important step forward because, for the first time a mathematical equation provided a way to ordered the elements as a function of a very simple variable as it was the atomic number; but still the main question remained, why the elements when ordered according to the atomic number they appeared grouped in families with very specific properties? To answer this question, it was necessary the contribution of mathematics to solve the equation that represents the interactions that stabilize the simplest atom we can think of, the hydrogen atom.

The Schrödinger equation for one-electron systems

A crucial step in our progress to understand the electronic structure of the atoms and the rules they follow to form molecules was done in 1925 when Erwin Schrödinger (See Figure 3) deduced and solved the equation that describe the system formed by a proton and an electron in the framework of wave mechanics.[2]

$$\left\{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{Ze^2}{r}\right]\right\}\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

Figure 3.
Erwin Schrödinger and its equation that describes a one-electron atom with nuclear charge Z usually called hydrogenlike system.

The equation in Figure 3 could be solved exactly because it is separable in the three coordinates, r, θ and φ, so that:

$$\psi(r,\theta,\phi)=R_{n,l}(r)\Theta_{l,m}(\theta)\Phi_m(\phi)$$

where

$$R_{nl}(r)=\sqrt{\left(\frac{2Z}{na_\mu}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]}}e^{-Zr/na_\mu}\left(\frac{2Zr}{na_\mu}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_\mu}\right)$$

$$\Theta_{l,m}=\frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)(l-|m|!)}{2(l+|m|)!}}sin^{|m|}\theta\frac{d^{l+|m|}sin^{2l}\theta}{d(cos\theta)^{l+|m|}}$$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

The total energy being:

$$E(n) = -\frac{1}{n^2}\frac{Z^2 e^2}{2a_0}$$

The expression obtained for the energy was of a fundamental importance because in it, an integer number n appears quantizing the energy. This means that when the atom is described as a system in which the electron is characterized by a wave that fulfils the Schrödinger equation in Figure 3, the quantization of the system appears automatically in the equation's solutions, and it is not necessary to impose it a priori as in the Bohr model.[3] On top of that, the solution of the Schrödinger equation provided the energy not only for the ground state, *1s*, but also for the excites states of the system (See Figure 4a), and therefore the transitions between the different energetic levels allowed to exactly calculate the frequencies of the lines observed in the emission spectra of hydrogenlike systems

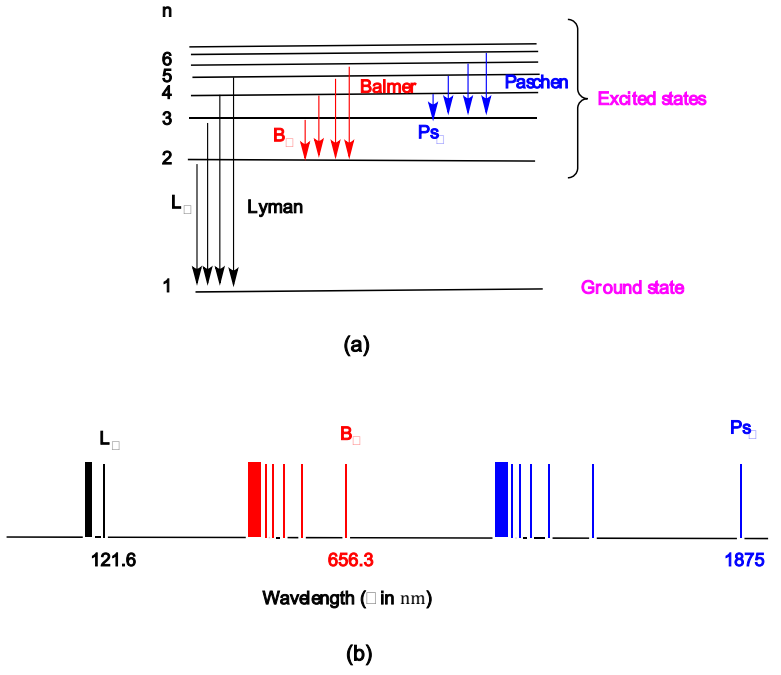

Figure 4.
(a) Energy levels for the hydrogen atom obtained by solving the corresponding Schrödinger equation; (b) emission spectrum of the hydrogen atom indicating the position of the α-lines of the different spectral series: Lyman, Balmer, Paschen….

The bad news is that the Schrödinger equation cannot be solved when we go from hydrogen to helium. The presence of two electrons in the system leads to an equation which is no longer separable in the coordinates of the two particles, because the electrons repel each other as a function of the distance and the distance depends on the coordinates of the two. If one assumes that the electrons do not repel

each other, which is known as the *independent particle approximation* then the solution is just given by the product of the functions that describe each electron, and that is why we say that whereas the electronic configuration of hydrogen is $1s$, that of He is $1s^2$, the one of Li is $1s^22s$, etc. The success of this model was such that even today, many people believe that the true and correct electronic configuration of He is $1s^2$, but this is an approximation, very good, because it accounts for more than 90% of the total energy of the system, but still an approximation.

THE IMPORTANCE OF PRECISION.

Some ambiguities

The electronic distribution in the different elements was the necessary motif that explained the periodicity of the Table, for instance, the alkaline metals were in the same group, sharing common properties because all of them are characterized by having an unpaired electron in one *s* orbital; but 150 years after the formulation of the first periodic table, the actual one is not free of ambiguities starting from the very first element.[4] In the conventional Periodic Table H is on top of the group al the alkaline metals, and one may think this is consistent with the fact that in compounds like hydrogen fluoride (FH) the hydrogen atom bears a rather positive charge, as the alkaline metals do, but H can also form hydrides, like LiH, in which the H atom bears a rather high negative charge, like fluorine in LiF, so it could be equally situated at the top of the halogen elements!

A similar ambiguity affects the position of He.[5] The IUPAC decided to situate He in the group zero together with Ne, Ar, Xn, Rn, and not above Be, because He does not form molecules. However, the related question, does Be form molecules? Is neither trivial nor evident. Indeed, the first theoretical studies in the sixties and seventies, concluded that Be_2 molecule was less stable than 2 Be atoms.[6,7] At the end of the seventies more precise calculations concluded that Be_2 was a very weakly bound system[8]. Little later, the first full CI calculations published in 1983 by Harrison et al.[9] concluded that Be_2 presented a $^1\Sigma_g^+$ ground state with an equilibrium distance of 2.513 Å and a dissociation energy of 650.5 cm^{-1}. However, Be_2 would not be detected experimentally until 2009.[10]

The first reliable electronic configuration, able to reproduce the most accurate experimental values (R_e = 2.445(5) Å and D_e = 934.9(0.4) cm^{-1}, would be published in 2014,[11] providing an electronic configuration (see Figure 5) totally coherent with the very weak bond of the dimer.

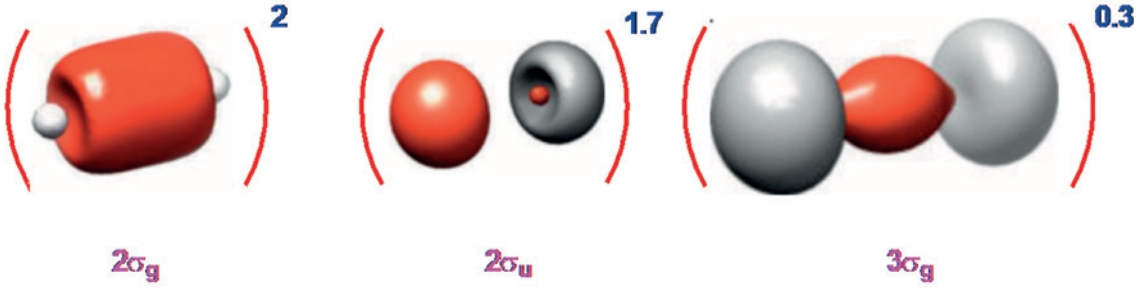

Figure 5.
Occupied molecular orbitals of Be_2 showing that the bonding in this dimer is the consequence of a partial occupation of the $3\sigma_g$ bonding orbital.

Relativistic effects

The 20s witnessed the first revolution that led to the development of quantum mechanics, the 70s would witness a second revolution, the incorporation of relativistic effects.[12,13] These effects are very small for light elements and were usually neglected in the first quantum chemical calculations, but its role is fundamental to understand some specificities of the Periodic Table that without those effects cannot be rationalized.[14] In the relativistic hamiltonian the two-electron term:

$$h_{ij} = h_C + h_R$$

includes besides the coulomb repulsion, h_C, the relativistic term, h_R, which is given by:

$$h_R = -\frac{1}{2r_{ij}}\left[\alpha_i \cdot \alpha_j + \left(\alpha_i \cdot r_{ij}\right)\left(\alpha_j \cdot r_{ij}\right)/r_{ij}^2\right]$$

To account for the interaction between the magnetic moments of the two electrons. The important question is that relativistic effects may imply huge changes in the properties of the systems. Gold is a paradigmatic example, whose Ionization Energy (IE) and Electron Affinity (EA) change dramatically, as shown in Table 1 when relativistic effects are included,[14] explaining for instance why gold is a noble metal practically inert and why is yellow. In fact, relativistic effects are behind the strong peculiarities of all the elements of the sixth period (Cs-Rn) of the Periodic Table.

Table 1. Ionization energy (IE) and electron affinity (EA) of gold. Values in eV.

Property	Nonrelativistic	Relativistic	Experimental
IE	7.057	9.197	9.22554(2)
EA	1.283	2.295	2.20861(3)

But the precision of our mathematical tools has increased a lot in the last decades, and nowadays it is possible to give an answer to questions like: what happens when we have a molecule of Au_2 instead of millions and millions of gold atoms in a three-dimensional arrangement? What does the electrostatic potential look like around a single molecule of gold? The answer to these questions is clear in the pictures shown in Figure 6 in which we compare the characteristics of the electrostatic potential of a highly reactive molecule, such as Cl_2, with a Au_2 molecule.[15] It is apparent the strong similarity between both representations, characterized by the presence of σ-holes that render them strongly reactive with respect to any base. The conclusion is obviously unexpected, gold is in the bulk unreactive, but gold molecules might be even more reactive than chlorine molecules.

But, as shown in Figure 6, the picture does not change significantly when the cluster size increases. As Tore Brink et al. showed in 2017,[15] although gold metal is inert, gold clusters from two to hundreds of atoms are highly reactive and there is a rich chemistry associated with this phenomenon.

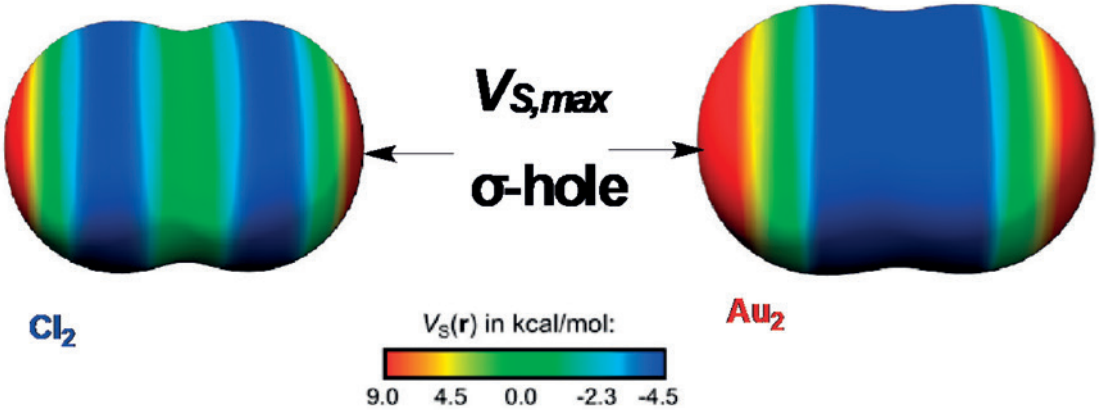

Figure 6.
Molecular electrostatic potential around the Cl_2 and the Au_2 molecules. The red areas correspond to areas of very positive potentials usually known as σ-holes. It is evident from the picture that this feature is clearly more intense in gold than in chlorine molecule.

Effects on molecular bonding

The precision is important also for molecules. Theories like Valence Bond (VB) and Molecular Orbitals (MO) give very good energies for simple molecules like O_2, but the description of other properties such as magnetism is a different matter. VB organized the electrons in pairs, whereas MO has no such restriction. As it is illustrated in Figure 7, in the MO theory electrons, which are fermions, are distributed in pairs, except in the highest orbitals, because the two highest orbitals are strictly degenerate (identical energy), and accordingly the last two electrons accommodate one in each orbital, to decrease their mutual repulsion and with the same spin because the magnetic interaction is more stabilizing. The immediate consequence is that O_2 in its $^3\Sigma_g^-$ ground state is paramagnetic, i.e., it is a magnet with a permanent magnetic moment.

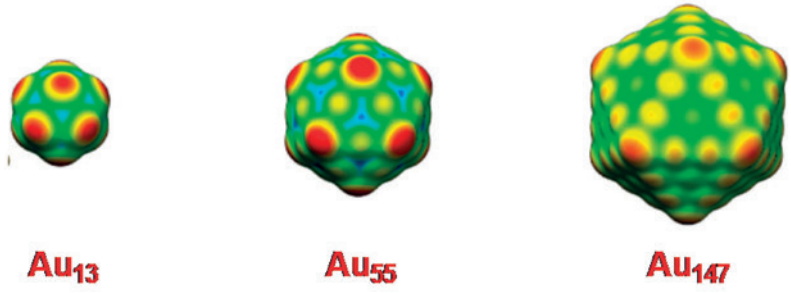

Figure 7.
Molecular electrostatic potential around the icosahedral Au_{13}, Au_{55} and Au_{147} clusters. Color conventions as in Figure 6.

This prediction of the MO theory is fully confirmed by the experimental evidence. As illustrated in Figure 9, when one pours liquid oxygen between the poles of a magnet the liquid is retained between these poles confirming that it has a permanent magnetic moment, situation which is not observed when pouring liquid nitrogen.

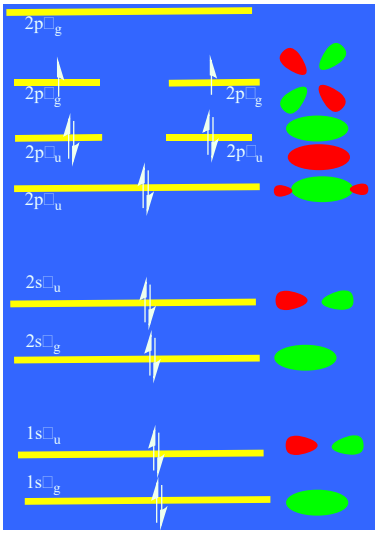

Figure 8.
Schematic MO diagram for the O_2 molecule in its ground $^3\Sigma_g^-$ state

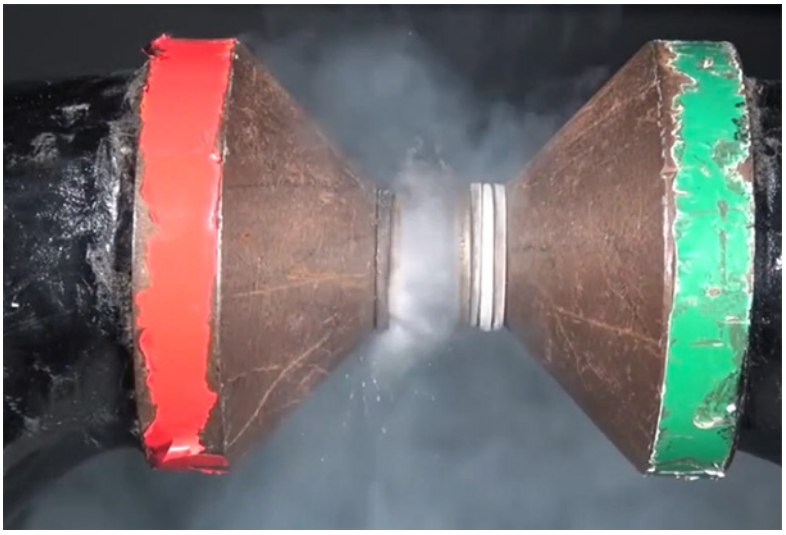

Figure 9.
After pouring liquid O_2 between the poles of a magnet (marked in red and green) the liquid remains trapped, confirming that the O_2 molecule in its ground $^3\Sigma_g^-$ state is a magnet.

At this point it should be emphasized that the electronic configuration of O_2 with all the electrons forming pairs leads to a singlet excited state, close in energy to the ground state, but which is far more reactive. More importantly, as it is shown schematically in Figure 10, it is used in photodynamics therapy to selectively destroy cancer tumors. The procedure requires to have a photosynthesizer that activated by the light liberates singlet O_2 that will kill the tumor cells.[16,17]

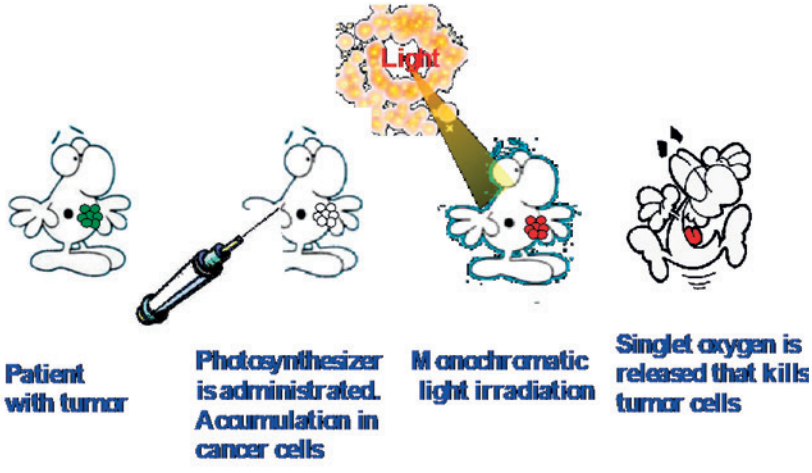

Figure 10.
Photodynamics therapy consist in administrating to a patient with a cancer tumor a photosynthezizer that accumulates in the cancer cells. The action of light of the appropriate frequency liberates singlet O_2 from the photosynthezizer that will kill the cancer cells.

The singularity of the first row of the Periodic Table

Precision is also behind some other singularities of the Periodic Table. For instance, why water is liquid at room temperature? All the other hydrides of the first row of the Periodic Table are gases at room temperature. Also going down in the same group, SH_2 is a gas at room temperature in spite of being heavier than H_2O. Another important characteristic of water is that macroscopically it is neither acidic nor basic, it is the paradigm of neutrality. Perhaps from this fact one could deduce that the basicity of a water molecule should be identical to its acidity. Is this true? Since the seventies it was possible to measure with precision these intrinsic properties of many molecules, and the most precise measurements for water indicate that its basicity, measured as its proton affinity, is $PA(H_2O) = 690.8 \pm 1.3$ kJ/mol.[18] Quite surprisingly its gas-phase acidity is rather different!: 1630 kJ/mol. [19] Then, the obvious question is, if the basicity and the acidity of a single water molecule are very different, how to explain that liquid water is strictly neutral? Do become water molecules different when they interact with each other? The answer to this question is "yes". When two water molecules interact to form a dimer, the interaction energy is very weak, and that is why precision becomes an issue to describe the water dimer, but when high-level calculations are carried out one finds that, as shown in Figure 11, one of the water molecules behaves as a proton donor with respect to the other one, which in turn behaves as a proton acceptor.

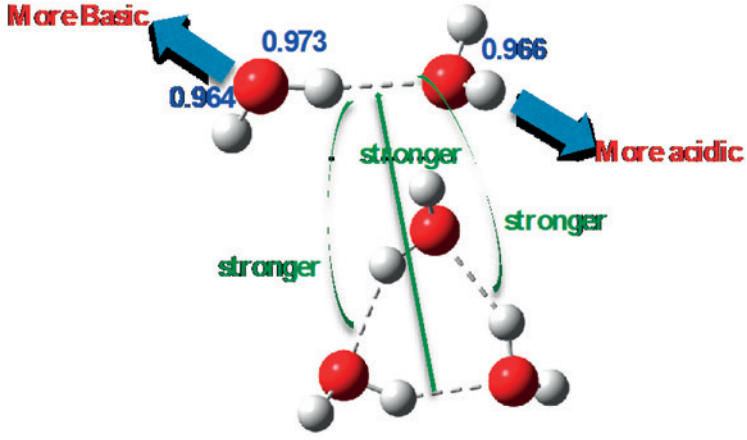

Figure 11.
Structure of the water dimer and water trimer. The latter is a cyclic structure due to cooperativity effects that reinforce the three hydrogen bonds that stabilize it.

The immediate consequence is that the OH bonds of the proton donor molecule, that initially were identical, become different in the dimer, because one of the H atoms is now attracted by the second water molecule and the corresponding O–H bond becomes longer. We say that a hydrogen bond between the two molecules has been formed. This obviously implies that the proton donor molecule becomes more basic (a better proton acceptor), whereas the molecule that behaves as a proton acceptor becomes more acidic (a better proton donor). This situation has two important consequences. One is that in the dimer the basicity and the acidity of the two molecules become closer, and the other one is that the structure of the trimer should be, and it is, a three-membered ring,[20] because being cyclic the three hydrogen bonds formed are necessarily stronger than the hydrogen bond in the dimer.

This situation appears also in the larger water clusters. As shown in Figure 12a, the most stable conformation of the pentamer, the octamer and the decamer, to give three different examples are also cyclic.

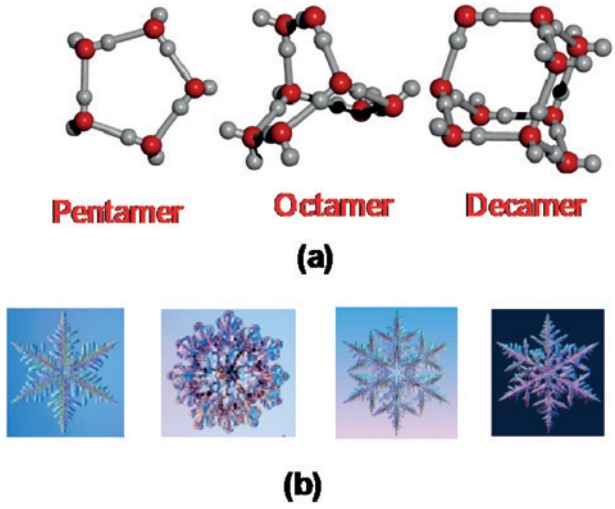

Figure 12.
(a) The most stable structures for the water pentamer, octamer and decamer **(b)** different structures of ice crystals.

Figure 12 also shows how the ability of water molecules to bind with each other through hydrogen bonds leads to the formation of beautiful crystals in the solid phase (see Figure 12b). The fact that these hydrogen-bonded clusters are predominant in the solid phase explains why ice is less dense than liquid water, a fundamental feature for the development of life in lakes, rivers and oceans.

But not only H_2O differs significantly from the other hydrides of the first row and from SH_2, C and Si are also in the same group, but the chemistry of C is very different from the chemistry of Si. A very simple derivative permits to illustrate the previous assertion. It is very well established, both from the experimental and the theoretical viewpoints, that acetylene is a non-polar hydrocarbon which exhibits a linear structure as illustrated in Figure 13, the CC bond being a triple bond, however the equivalent linear structure for Si does not exist as a local minimum of the potential energy surface. A theoretical searching of the possible structure of the Si_2H_2 molecule shows that it can adopt the three conformations shown in the second row of Figure 13,[21] but this only illustrates one of the many differences that can be found between the chemistry of Silicon with respect to the chemistry of Carbon.

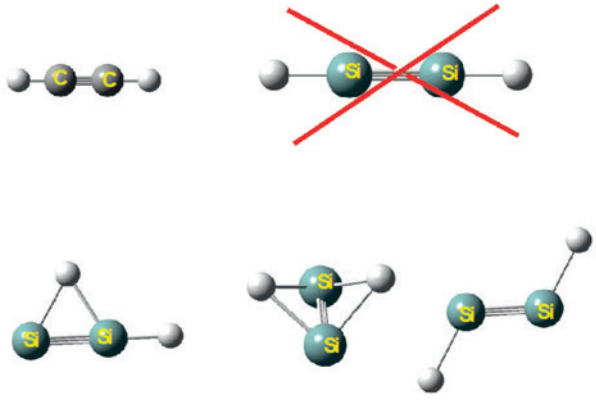

Figure 13.
Whereas the linear structure of acetylene (C_2H_2) is well established both experimentally and theoretically, the same structure for the corresponding Si derivative (Si_2H_2) does not exist. Theoretical calculations predict for Si_2H_2 the three structures shown in the second line of the figure.

This finding together with the characteristics of water and with many other examples that for the sake of conciseness will not be describe here led in the last decades of the XX century to conclude that in some manner the first row of the Periodic Table is a singularity!

CONCLUDING REMARKS

As we have already mentioned at the beginning of this paper, the Periodic Table is a living object that may change still further when new atomic and molecular properties will be explored. Its importance was initially related to the systematization of our knowledge concerning the bricks that form our universe, but after this first systematization, the scientists realized little by little that a much richer information beyond the pure systematization is contained in it, though in not few cases such information can only be obtained when the precision of our experimental setups or our calculations is high enough. This paper tried to show a few examples, but perhaps we can singularized, as an important conclusion, that many results seem to indicate that within the Periodic Table the first row is somehow a singularity.

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