La Chimica nella Scuola

n. 4 anno **2021**

- > Metodologie didattiche e percorsi laboratoriali anche in contesti non formali
- > Pagine di storia: non solo personaggi
- > Il ricordo di un amico scomparso, ma anche buone notizie

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Integrating the history and philosophy of science and restoring the centrality of the periodic table into a college general chemistry course

ABSTRACT The article proposes the enhancement of college level general chemistry courses by integrating various historical and philosophical aspects of chemistry. This goal is explained in some detail in the case of selected main topics in a typical general chemistry curriculum. A second goal of the article is to restore the centrality of the periodic table (PT) into teaching general chemistry. This includes a brief account of how the PT developed without initially mentioning atomic structure and atomic orbitals. After these latter topics are introduced one can return to the PT in order to show the extent to which quantum mechanics explains this central motif of the field of chemistry. Chemical bonding is likewise introduced in a classical fashion according to Lewis structures and VSEPR model followed by the more comprehensive explanations provided by quantum theories of bonding. As in the case of the periodic table the aim is to show students the limitations of the classical approaches and the motivation for and advantages of adopting a quantum description.

RIASSUNTO *Questo articolo propone il rafforzamento* di corsi universitari di chimica generale mediante l'integrazione di aspetti storico-filosofici. Questo obiettivo è discusso in dettaglio per alcuni argomenti selezionati entro un tipico programma di chimica generale. Una seconda finalità dell'articolo consiste nel ristabilire la centralità della Tavola Periodica (TP) nell'insegnamento della chimica. Ciò prevede una introduzione a come la TP sia stata originariamente elaborate senza alcun riferimento alla struttura atomica e agli orbitali. Dopo aver presentato questi aspetti, è possibile tornare sulla TP per discutere come la meccanica quantistica è in grado di spiegare questo tema centrale della chimica. Allo stesso modo, il legame chimico è introdotto secondo un approccio classico fondato sulle strutture di Lewis e il modello VSEPR, sequiti dalla interpretazione più completa fornita dalle teorie quantistiche. Come nel caso della

TP, lo scopo è mostrare agli studenti i limiti degli approcci classici e la motivazione ed i vantaggi dell'adozione di una descrizione quantistica.

Introduction

O ne frequently hears it said that chemical education can benefit from the inclusion of some history and philosophy of science. However, such vague suggestions do not amount to very much unless they can be accompanied by more specific recommendations as to what should be done. As somebody who has taught general chemistry courses for about 40 years, and has done so in a historical and philosophical manner, I would like to share some suggestions in this area. I should emphasize that the following article refers to the teaching of undergraduate, rather than high school, students at a leading US research university, namely the University of California Los Angeles (UCLA).

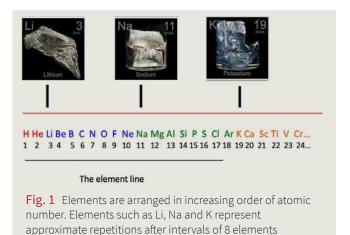
The second goal of this article is to propose that the periodic table which is the single most important unifying motif and icon of chemistry should be exploited to a far greater extent in teaching general chemistry [1]. As things stand at present the periodic table is regarded as a useful tool for looking up atomic weights and perhaps for discussing such trends as ionization energies or atomic radii. However, the unifying role that the table plays seems to be overlooked, especially in general chemistry courses that concentrate on fundamental principles drawn mainly from physical chemistry. Rather than waiting until more advanced courses in inorganic chemistry, it is my sincere belief that the periodic table's central role in the history of chemistry, as well as in its present state, should be highlighted from the outset of any chemistry course.

Before moving onto some detailed points, I should also stress that I do not merely advocate the addition of historical and philosophical content into an already crowded chemistry curriculum. What I am suggesting instead, is that history and philosophy should be deployed in and implicit way in order to provide greater unity and continuity to the material that general chemistry courses need to convey to students.

Having said that, my first two lectures are the only ones in which HPS is openly an explicitly addressed while starting to explore the scientific method. It is a guite remarkable, and rather depressing fact, that chemistry textbooks, in the US at least, invariably include a section claiming to discuss the scientific method but do so in a completely outdated fashion [2]. The typical account of the scientific method that one finds is nothing short of the view of logical positivism, according to which science is primarily based on the facts and observations. Flow-chart are often included to argue that science proceeds linearly from observation to hypotheses, moving to further observations and then branching off, either towards the establishment of theories or cycling back to revise the hypotheses, if the evidence is not supportive of the initial hypothesis. While this serves a good purpose in a broad sense, it places too much emphasis on observation as the primary driving force of the scientific method.

Even more worryingly, it implies that a sharp distinction exists between observations and theories. Modern philosophy of science, which can be dated to the 1960s and 1970s has been a reaction against the central notions of this view of science termed logical positivism. Karl Popper and Thomas Kuhn were among the most prominent critics of logical positivism, although for different reasons [3]. While Popper reacted to the notion that theories could be verified, Kuhn highlighted the importance of the historical dimension, rather than focusing on logical and formal aspects. For all the well-known differences between the views of these two giants in the field, they both stressed the impossibility of sharply separating observations from theories, due to the theory laden nature of observations.

If one accepts this point, it becomes clear that observation does not necessarily precede the proposal of a hypothesis. In fact, Popper makes this point explicitly, through his well-known slogan of "conjecture and refutation" or in other words, first comes a conjecture, theory or idea and then come attempts to refute them by means of observations. And yet not one single textbook of chemistry, that I know of, so much as even mentions the contributions of Popper or Kuhn while perpetuating the view of a scientific method with no apparent theoretical preconceptions. Needless to say, the logical positivist notion of science was also meant to reinforce the



myth that science is completely objective and that it does not allow preconceptions to enter the picture, both of which features have turned out to be unattainable.

The Periodic Table

My course then presents the development of the periodic table in a historical manner starting with the discovery of triads of elements. By focusing on this development, one can begin to convey the notion that there are groups of elements such as Li, Na and K that behave similarly to each other and the fact that there are some numerical regularities that connect these elements together.

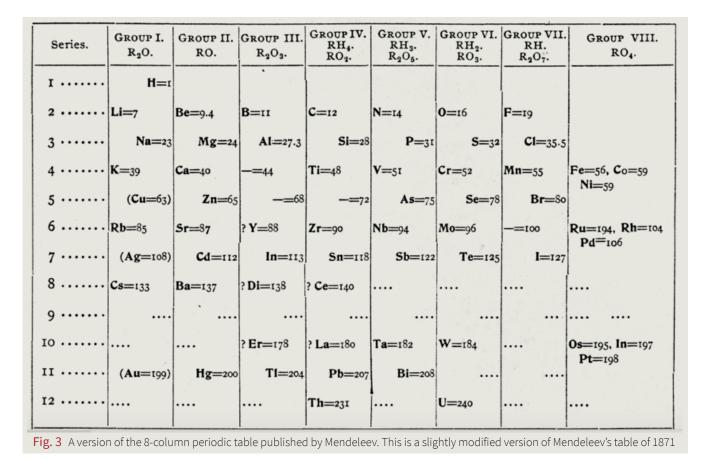
We then move on to the central notion of chemical periodicity. If the elements are arranged in order of increasing atomic weight, or atomic number in modern times, there is an approximate repetition in their chemical and physical properties after certain intervals (Figure 1).

I make it a point to present the original 8-column table of Mendeleev and other pioneer discoverers since this format displays periodicity in its clearest and simplest manner. I like to explain how this process succeeds very well until the element manganese is reached. The following element, iron, is not a noble gas however and so cannot be placed in the eighth column of such a table (Figure 2).

The manner in which Mendeleev solved this problem was to 'exclude' iron from the main body of the table while placing it into a miscellaneous group, a move which he also applied to the subsequent ele-

H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca Sc Ti V Cr Mn Fe?

Fig. 2 The elements in the number line are presented as a series of rows such as to reflect chemical periodicity in each column



ments cobalt and nickel (Figure 3). After that, things resume as before in that copper and zinc are placed in groups 1 and 2 respectively since they commonly display valences of 1 and 2 respectively. I also take the opportunity of stating that there is little that is 'wrong' with such tables since they do collect together elements which share a common valence such as Be, Mg, Ca, Zn, Sr, Ba etc. all of which display valences of 2.

Nevertheless, the modern periodic table (Figure 4) solves the problem of Fe, Co and Ni by creating what are effectively a set of new vertical groups in the periodic table. In fact, a total of 10 new groups are created in what we now call the d-block of the

, i																	² He
3 Li	4 Be											5 B	6 C	7 N	8 0	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 CI	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 TI	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 FI	115 Mc	116 Lv	117 Ts	118 Og
Fig. 4 The modern 18-	-	/	57	58	59	60	61	62	63	64	65	66	67	68	69	70	
column periodic table,			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	
features an apparently disconnected set of 28 elements, the f-block			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	

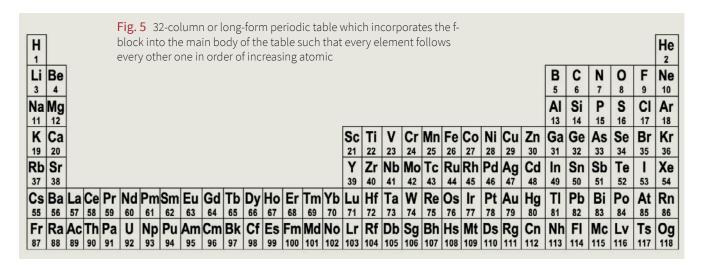


table. It is pointed out that this format, which is almost ubiquitous these days, appears to commit an analogous act of excluding some elements and indeed to a greater degree since as many as 28 elements are relegated to a footnote known as the fblock elements that lie below the foot of the main table.

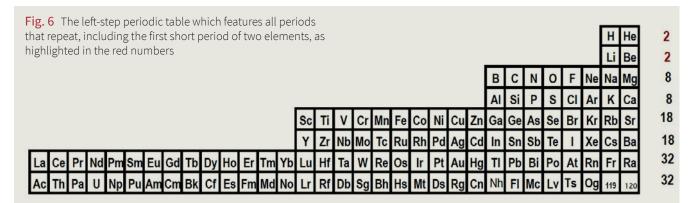
This provides a perfect opening for presenting the 32-column presentation of the periodic table (Figure 5), which very naturally incorporates all of these 'excluded elements' into the main body of the table and which some textbooks are starting to display as what is perhaps a more coherent periodic table. I carry out this section while trying very hard not to mention electrons, since they had not yet been discovered when the first periodic tables were published in the 1860s. Secondly, I delay presenting the underlying explanation of the periodic table until we have covered quantum theory, quantum numbers, the aufbau etc. Too many modern chemistry courses "put the cart before the horse" by first explaining the structure of atoms and then leaping straight into the explanation for the periodic table in terms of electronic configurations [4]. Taking such an approach completely misrepresents the historical sequence and in my view is educationally unsound [5].

Before completing this introduction to the periodic table, it is desirable to present some of the most recent thinking about this topic in case the student might be of the impression that the periodic table is a finished subject or a 'closed book'. This can be carried out by introducing the left-step periodic table. As some readers of this journal may be aware this representation involves moving the element helium to the top of group 2 of the table and then relocating this now modified s-block of elements to the right edge of the table (Figure 6) [6].

The advantage of this table, apart from its far more regular appearance compared with the conventional 18 and 32-column tables, is that each period, including the very first one is seen to be repeated in terms of its length. Needless to say the field of chemistry is full of anomalies, although the proponents of this left-step table do not believe that the existence of just one period length that does not repeat may be one such genuine anomaly.

Laws of chemical combination and Dalton's atomic theory

My third section consists of an examination of the laws of chemical combination and how they were explained by Dalton's atomic theory. By following this approach students are rendered aware of the



historical dimension of chemistry, including how Dalton developed his fruitful atomic theory and how it provided explanations for the laws of chemical combination such as the law of constant proportion and how he was led to predict the law of multiple proportions.

Simple atomic structure including early models of Thomson and Rutherford

We then proceed to briefly discuss early views of the structure of the atom including those of J.J. Thomson and Rutherford, and the limitation of each of these models. In a few words, Thomson could not explain the scattering of alpha particles off a piece of gold foil. The successor model, proposed by Rutherford, was an improvement but was also faced with problems such as the lack of collapse of electrons onto the nuclei of all atoms, as well as an inability to explain the existence of discrete atomic spectra. At this point one can begin to discuss atomic mass, the existence of isotopes of elements and so on.

Stoichiometry

Next, we cover the topic of stoichiometric calculations, which is based on the atomic weights of each of the elements as well as the law of the conservation of mass. I make it a point of mentioning that stoichiometric calculations are rather paradoxically almost exclusively based on the nucleus of the atoms, whereas almost all of the rest of chemistry is dependent on electrons, including group membership in the periodic table, acid-base behavior, redox reactions and so forth.

The course progresses on to the obligatory, and to my mind tedious exercises, on how much product is obtained, in principle, from how much reactant. In addition, there is the equally tedious but admittedly useful calculations of empirical formulas, yields etc.

The nature of light and the early quantum theory of Planck, Einstein and Bohr

One is now ready to move into some more interesting and less formal parts of chemistry, as well as the underlying physical principles. This is the point at which we begin to discuss the quantum theory, by first reviewing the properties of wave diffraction and interference. The invention of quantum theory by Planck is mentioned and his conclusion that E =hv is announced, without entering into too much detail, since this is almost entirely a physics topic. As I see it, the attempts by textbooks to show how Planck derived this law always leave the students stranded and more confused than before. The full derivation is surely best left to graduate level physics courses. It is better to just state the result, rather than to invite questions that cannot be addressed in general chemistry if mention is made of oscillators or Wien's, Stefan's or Rayleigh's laws. In any case, as is well-known, Planck was not convinced by the usefulness of his own law, and it fell to Einstein to make the first significant application of the notion of quantization to the photo-electric effect.

Here I feel it useful to enter into some of the details. One can mention the confusion that existed before Einstein, when it was mysterious why raising the intensity of the incident light had no effect on the kinetic energy of the ejected electrons. Moreover, the kinetic energy appears to depend on frequency, but only if a threshold frequency is exceeded.

Here is how I try to explain the importance of bringing quantum into the photo electric effect. The classical equation for the photo-electric effect, before Einstein's entry into the discussion, was simply

$E = \Phi + K.E.$

where E stands for the energy of the incident light, Φ is the work function and K.E. the kinetic energy of ejected electrons.

According to Einstein, the equation can now be rewritten to take account of the quantum nature of light, as,

$hv = \Phi + K.E.$

Since h and Φ are constants, it follows immediately that the kinetic energy is proportional to frequency as observed. Next, we address the question of how Einstein interpreted the threshold frequency and the Φ term. The answer is by writing,

$hv = hv_{o} + K.E.$

Since v_o is a constant for any metal, one needs a minimum energy to dislodge electrons, and only if the incident light delivers this energy do the electrons acquire kinetic energy. In addition, the discrete nature of hv_o for any metal suggested to Einstein that light was made of packets, or indeed particles, of light that would later be called 'photons' by the chemist G. N. Lewis.

We now move on historically by about eight years, to Bohr's importing of quantum theory into the structure of the atom in 1913. Whereas electrons were assumed to orbit the nucleus randomly in Rutherford's model, in Bohr's model they orbit the nucleus in specific shells or energy levels. This provides an elegant way to explain how spectral lines result from transitions between energy levels.

However, the fact that electrons don't collapse into the nucleus is not at all well explained by the Bohr model, a fact that seems to be glossed over in most textbook accounts. It's all very well for Bohr to claim that energy is only lost when an electron moves from a less to a more stable level, but it does not explain why an electron in the lowest level does not lose energy. Perhaps one is supposed to accept that this happens simply because there is no lower energy level but this is obviously an ad hoc argument. Bohr's model simply does not overcome the collapse issue.

De Broglie, Schrödinger and the wave nature of electrons

Next, we discuss the De Broglie's perfectly reasonable suggestion that if light behaves as particles, as Einstein had shown, then perhaps the opposite is also true, namely that particles, such as electrons, might behave as waves. This provides an opportunity to look back to the earlier talk of wave diffraction interference as the sine gua non of wave behavior. De Broglie's hypothesis could therefore be tested by firing a beam of electrons at a target whose dimension was of the same order as the magnitude as the wavelength of the electron, which De Broglie's formula could conveniently provide. As we know, such experiments by Davisson and Germer and others did indeed reveal diffraction and interference patterns obtained from a beam of electrons. With this fact established, experts in wave mechanics, such as Erwin Schrödinger, could get to work in writing and solving the wave equation for the hydrogen atom. And as the saying goes the rest is history.

The solutions to the Schrödinger equation are characterized by three so-called quantum numbers and the relationship among these values can also be rigorously derived. Then came Pauli's idea that a fourth quantum number, later dubbed spin, was also required. Now it immediately follows that successive electron shells can contain 2, 8,18, 32 and so on electrons. As a result, an important feature of the periodic table is explained from first principles. Who says that chemistry does not reduce the quantum mechanics? But the capacity of shells is not the full story of the periodic table because it features successive periods of 2, 8, 8, 18, 18 etc. electrons. This is the well-known 'doubling' of all but the very first short period of two elements. It so happens that a derivation of period doubling, which is embodied in the Madelung or n + l rule has not yet been obtained. I firmly believe that students should be made aware of the limitations of such claims to the full reduction of the periodic table, rather than being given the impression that physics has been completely triumphant over chemistry.

Some problems for VSEPR method

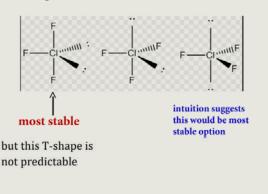


Fig. 7 The VSEPR method cannot predict the precise shape of the ClF₃ molecule

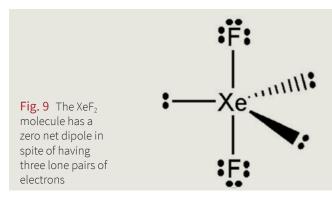
Representing orbitals and electronic configurations

The next topics involve various ways to represent orbitals, and of course the writing of electronic configurations by making use of the aufbau principle. An interesting side-issue occurs in the configurations of transition metals. Textbooks almost invariably claim with the configuration of scandium involves the occupation of the 4s orbital followed by 3d. This is factually and logically inconsistent, but entering into the details would entail too much of a detour in the present article [7].

Classical bonding theories including Lewis structures, resonance, VSRPR and dipole moments.

At this point in the course the eager student, who may be starting to tire of so much physics in what is supposed to be a chemistry course, finally encounters molecules. The way I present chemical bonding is to begin with the classical approaches such as Lewis structures and VSEPR model before moving to quantum bonding theories. It not only makes sense historically but also serves as a motivation for the need for quantum theory in chemistry.

-	More Serious Prob	lems for VSEPR
	NH ₃	OH ₂
Fig. 8 Four molecules whose experimental bond angles differ very significantly	107º	104.5°
	PH ₃ 93	SH ₂ 92
from what one might predict on the basis of VSEPR theory	AsH3 91	SeH2 91



Next, I cover the obligatory rules and exercises for writing Lewis structures, resonance structures, formal charges and so on. These exercises seem to take on an ahistorical and timeless status. Students become convinced that there exists one real and actual Lewis structure for any given molecule. No amount of telling them that Lewis structures are useful figment ever seems to dissuade them from thinking that there exists one real Lewis structure for any given molecule.

Similarly, the classical bonding theory of VSEPR nicely builds on Lewis structures by moving onto how the electron pairs around the central atom produce the 3-D shape or structure of the molecule. What I like to stress, in addition to trotting out all the typical shapes for molecules in the categories *AXn*, *AXnEm*, and *AXnYm*, are the many cases in which VSEPR fails to accommodate the observed structure of some molecules.

For example, in the case of the SF_4 one can deduce that there are four bonded pairs and one lone pair in the Lewis structure. It follows the molecule has a trigonal bipyramidal electronic geometry. But VSEPR alone cannot settle the question of whether the lone pair is located in an axial or an equatorial position. Similar issues arise with ClF_3 with a placement

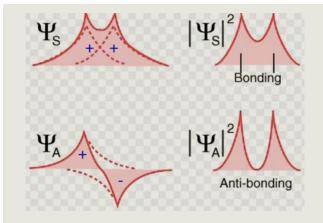


Fig. 10 Bonding and anti-bonding molecular orbitals arising from constructive and destructive interference respectively, from electron waves centered on adjacent atoms

of two lone pairs is not determined by VESPR reasoning (Figure 7).

I also like to present more serious problems for VSEPR in the form of the PH₃, SbH₃, H₂S and H₂Se molecules (Figure 8). The first of these two molecules should have bond angles close to 107° since, electronically speaking, they are analogous to the ammonia molecule. Meanwhile H₂S H₂Se should have angles close to the angle of 104.5 as in the case of the water molecule. The observed facts tell a drastically different story. The VSEPR model is completely incapable of accounting for these unexpected bond angles.

Cases like these serves to motivate the need to import quantum mechanics into explaining molecular structure. While still within the classical approach to bonding I like to proceed to determining whether a molecule has a net dipole, something which follows logically on from VSEPR theory. If a molecule is of the type AX_n it implies that it has a zero net dipole. The converse does not hold however. If a molecule has a zero net dipole it does not follow that it must have be of the class of AXn molecules. Counter-examples would be such molecules is XeF_2 which has three lone pairs and yet also has a zero, net dipole (Figure 9).

Molecular orbital theory and hybridization

Before starting to draw the M.O. diagrams for homonuclear diatomic molecules I believe it is a good strategy to teach the physical basis for this approach. This can be done by returning to the topic of constructive and destructive interference of waves. This time one considers the electron waves surrounding to atoms as they are brought closer to each other to produce constructive interference, which leads to stabilization or a lowering of energy relative to the contributing atomic orbital energies. In addition, there is an accompanying purely quantum mechanical effect due to destructive interference between the waves around each atom, which causes there to be a destabilization and therefore a raising of energy relative to the contributing atomic orbital energies. While constructive interference produces bonding molecular orbitals, destructive interference results in the formation of anti-bonding orbitals (Figure 10).

The remaining parts of this topic essentially involve going through the mechanical motion of building up the M.O. diagram for each case by applying the aufbau, Pauli and Hund principles that were introduced earlier in the course when discussing the configurations of atoms. Of course, one needs to mention the crossing of energy levels that takes place after the N_2 molecule as one moves across the 2^{nd} period diatomic molecules.

The advantages of using M.O. theory as compared with the classical approaches to bonding can now be given, such as the case of the O_2 molecule whose Lewis structure consists only of pairs of electrons and therefore gives no hint of its being paramagnetic. The M.O. diagram for this molecule, on the other hand, clearly shows the presence of two unpaired electrons [8].

One way to emphasize the difference between Lewis structures and the M.O. approach is by saying that the former considers the existence of 'real chemical bonds' between atoms whereas the M.O. model considers the existence of 'bonding' which is the overall result of contributions from bonding electrons as well as some highly non-intuitive anti-bonding electrons.

As is well-known, the valence bond and associated hybridization approach is far more 'chemical' in that it maintains the view the bonds that are directional in nature. This alternative approach is also required since molecular orbital theory fails to deliver structural information, at least at this most elementary and qualitative level of the theory. One should also stress that hybridization does not truly predict the shape of molecules but only accommodates it.

Conclusions

Following a historical thread serves to bring together what might otherwise be a series of disconnected formal exercises, like the writing of Lewis structures of working out the shape of molecules and so on. Secondly the approach of asking just how much each model or theory explains, serves to develop essential critical skills among students.

I hope I've managed to give at least some of the reasons why smuggling some historical and perhaps even philosophical background into general chemistry can be intellectually rewarding for instructors and students alike. Of course, basic techniques and factual aspects also matter but in the final analysis I suggest the big picture matters just as much in the study of chemistry.

In this brief article I have not attempted to discuss all topics that one would normally cover in a general chemistry course. For example, I have said nothing of discussion of periodic trends in quantities such as atomic radii, ionization energies or electron affinities. Nor have I discussed the topic of electronegativity and its periodic trends which help us in determining the occurrence of molecular dipoles. Entire topics such as thermodynamics, acid-base chemistry, equilibrium theory, kinetics and transition metal complexes have all been omitted from my discussion. But I hope to have given at least the flavor of how a general chemistry course can benefit from the injection of more historical, critical and philosophical approaches. A similar discussion of the remaining topics that were mentioned will be provided in a later article.

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- [5] In truth there is an element of Whiggism at play here. It is only in modern times that all the f-block elements have been discovered and that the need for a 32column display becomes more pressing.
- [6] The motivation for wanting to move helium into group 2 of the periodic table is the fact that its atoms have two electrons while the members of group 2 have two outer-electrons. But such talk of electrons was supposed to be excluded from this brief introduction to the periodic table, which aims to put chemistry and qualitative similarities among the elements to the fore. However, there is little doubt that beginning undergraduate chemistry students are already well aware of the fundamental explanation for the periodic table in terms of outer-shell electrons, even if the college course being presented here aims to provide a deeper understanding of this explanation.
- [7] For a detailed discussion of the 4s-3d conundrum see my YouTube workshop on this subject, https://www.youtube.com/watch?v=5cfKot3nBFA
- [8] Strictly speaking Lewis and also Pauling, neither of whom used M.O. theories of bonding, were fully aware of the need to include Lewis structures with unpaired electrons. It is just the most obvious Lewis structure that is taught to beginning chemistry students that lacks any such unpaired electrons.